Radiolysis Products in Gamma-Irradiated Plastics by Thermal Desorption–Gas Chromatography–Mass Spectrometry

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Additional papers are being prepared, but have not yet been submitted for publication.

Abstract

Low-molecular-weight ('volatile') radiolysis products of polymers were investigated by **thermal desorption–gas chromatography–mass spectrometry** (TDS–GC–MS), a technique comparable to dynamic headspace analysis. The experiments have a two-fold background, namely, radiation sterilization of medical products and packaging in food irradiation; the main objectives were (1) to allow a better assessment of the risks potentially associated with these techniques (safety evaluation), and (2) to evaluate whether thermal desorption allows to distinguish between irradiated and non-irradiated materials (irradiation detection).

The volatiles were analyzed with commercially availabe equipment that uses a cooled injection system (CIS; a PTV-type split/splitless injector) to interface the TDS-unit with the GC column. After a qualitative screening of six medical polymers aimed at identifying the volatiles produced by a sterilizing dose of ca. 25 kGy, and a digression into LDPE and polypropylene films (inspired by some rather unexpected results), it was decided to focus the investigation on polystyrene (PS), and—as a third major objective—to quantify the major radiolysis products of PS.

All the **medical polymers—PS, MABS, PA-6, PVC, PE, and PP—**produce detectable amounts of volatiles which remain trapped in the polymer matrix for considerable times; the products and their concentrations are characteristic for each plastic. The main products of PS are acetophenone, benzaldehyde, phenol, 1-phenylethanol, and phenylacetaldehyde; their concentrations are ca. one order of magnitude below the residual styrene/styrene dimer levels. Some trace components are formed with still lower yields—with the exception of benzene these are also oxidized aromatic structures. The same compounds are observed in MABS, which additionally gives some aliphatic radiolysis products. PA-6 yields pentanamide as the main product, plus traces of some homologous amides. The main products of PVC and of PP are fragments of additives, i. e., of organotin stabilizers and of phenol-type antioxidants, respectively. The medical PE produces only traces of hydrocarbons, aldehydes, ketones, and carboxylic acids, which largely disappear within weeks. The effects of irradiation on non-processed polymer pellets and on parts injection-molded from these granulates are comparable.

Turning—half by accident—to **LDPE and polypropylene films**, it was found that, contrary to previous reports, low-MW radiolysis products are retained in LDPE films for considerable times, and in PP films much longer than expected. The films produce fingerprint chromatograms with highly characteristic patterns of groups of radiation-induced peaks; these are mainly hydrocarbons, aldehydes, ketones, and carboxylic acids with concentrations (after 25 kGy) ca. one order of magnitude below that of the residual hydrocarbons (oligomers). PP additionally produces very substantial amounts of three degradation products of phenol-type antioxidants. Besides product identification, the following topics were addressed in these series of measurements: Effects of the absorbed dose and the desorption temperature; comparison of several commercial (proprietary) films; high-temperature thermal desorption; the question whether TDS analyzes radiation-induced artifacts rather than genuine products; the possible existence of cyclic radiolysis products; the possibility of identifying an LDPE film as irradiated after a dose of only 1 kGy; and atypical trace fragments of antioxidants.

Quantitation is based on the assumption that—under dynamic (continuous) extraction conditions—volatile compounds can be desorbed quantitatively from polymer matrices at temperatures above the polymer's glass transition temperature, T_g. Total desorption conditions (TDS-temperature and time) were established for the main radiolysis products of PS, and calibration was achieved by injecting external standards into the CIS.

After sterilizing doses of ca. 25 kGy ^{60}Co-gamma-radiation, the concentrations of **1-phenylethanol (1-Pet) and acetophenone (Acp)** were determined as ca. 6-8 ppm (mg/kg) and ca.

30-40 ppm, respectively; their radiation-chemical yields (G-values) are in the range of 2.5 to 3.5 nmol/J (1-Pet; G ≈ 0.03) and 10 to 15 nmol/J (Acp; G ≈ 0.13). The levels of the other main products, benzaldehyde, phenol, phenylacetaldehyde, and benzoic acid, are of the same order of magnitude. The concentrations of the radiolysis products apparently do not change with time, and the results with some commercial polystyrenes and irradiated 'real-life' samples (Petri dishes and culture flasks) indicate that it is indeed possible to identify radiation-sterilized products made from PS.

A comprehensive parallel test program, consisting of system sensitivity, analyte recovery, and TDS performance tests was developed to monitor the analytical system. A new desorption technique was successfully tested, namely, **thermal desorption of polymer solutions with solvent evaporation** (initially called the 'DSC-Method'), which requires almost no sample pre-treatment; and it is suggested to directly inject polymer solutions into the CIS (i. e., to use a PTV-type injector for thermal desorption).

One of several minor projects was the identification of **trace products;** experiments with relatively high sample loads yielded another potential 'marker' for irradiation detection. Finally, a GC-method was developed that allows the splitless-injection of parts-per-million standards of benzene. The method was used to quantify **benzene** in some high dose-irradiated PS samples, and benzene concentrations at sterilizing doses can be expected to be in the range of 1 to 2 ppm.

The overall findings are briefly examined from an analytical point of view, and their implications for irradiation detection, and for the safety of medical devices and packaging materials are discussed.

There is no such thing as *a* scientific method for ensuring objectivity. There are methods—approximately one for each scientist. ... It has been very common to train young people to believe in a *scientific method*. ... In fact, no one works that way in science.

Stanley Goldberg: Understanding Relativity. Origin and Impact of a Scientific Revolution. Birkhäuser, Boston, 1984

Preface

The experimental work underlying this thesis was performed at the *Institute for Social Medicine and Epidemiology* of the Federal Health Office (BGA) and at the BGA-successor institution *Federal Institute for Health Protection of Consumers and Veterinary Medicine* (BgVV) in Berlin.

In 1990/1991 Professor Klaus Werner Bögl, presently head of the BgVV's Fachbereich 2, recognized the need to update an earlier literature review by Jutta Fielitz and Klaus Stockhausen on the effects of ionizing radiation on polymers.[#] At about that time, the medical device industry planned to file a petition to exempt implants made of UHMWPE (ultra-high molecular-weight polyethylene) from a regulatory approval procedure (the so-called approval with respect to radiation treatment) claiming that „irradiation has no effect what-so-ever" on medical polymers. At the same time, various bodies, e. g., the *Kunststoffkommission* advising the Federal Ministry of Health, or the ICGFI (the *International Consultative Group on Food Irradiation* of the FAO, IAEA, and WHO), were interested in the effects of radiation on plastic food packaging materials.

I was engaged to update the review mentioned above, and the task turned out to be more complex than I had ever imagined. As a junior scientist, having just received my approbation as a pharmacist, I was overwhelmed by the 'feedback' that I received from the international irradiation 'community', and by their interest in my work. In fact, this response strongly influenced my decision to publish these data compilations in English[##]. In the course of this literature research, I noticed that there was very little information on **one** aspect: the formation of low-molecular-weight ('volatile') radiolysis products (cf. Chapter 2). The 'thesis project', the analysis of volatile products in medical polymers by thermal desorption, was jointly devised with my co-authors, Mr. Christian Boess, currently head of the BgVV's Fachgebiet 212, and Professor Klaus Werner Bögl.

As I already mentioned, Professor Bögl had foreseen that 'polymer irradiation' is a „timely topic" (to paraphrase an anonymous reviewer of the Journal of Food Protection). I would like to thank him, not for 'proposing a thesis project' (which he didn't), and not merely for 'support' and 'discussions' (though I had his full support and we shared many discussions). I would like to thank him for leaving major decisions to a junior scientist, for letting me work quite independently, and, overall, for a co-operative style of working and of leadership, which, I'm afraid, is still too rare in German academia (and, maybe, beyond). I would also like to thank Christian, for going out of his way to support the project, for continuous discussions, and for his endless attention to detail (e. g., when proofreading my manuscripts). Without you, this project would have been impossible, and it has been a pleasure to work with you !

Of course, this work would not have been possible without the cooperation and advice of colleagues from the BgVV, the industry, and the scientific community. I would like to thank for technical assistance during the various 'Phases' of this work: Mrs. Gabriela Gebhardt, Mr. Andreas Stock, Mr. Peter Fritz, and, especially, Mrs. Antje Völkel, who did an excellent job during her two months with us. I would like to thank the Braun AG (Melsungen) for kindly providing the medical-grade polymers, especially Mr. Till Krapp and Mrs. Neumann-Ebel, who irradiated and shipped the samples; Dr. Harms, Mrs. Siegel, Mr. Ulrich Brethauer, Dr. Heinrich Koch, and Dr. Fleckenstein (Braun AG), who participated in early discussions of

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[#] Fielitz, J., Stockhausen, K., and Bögl, K. W. 1979. Strahlenbehandlung von medizinischen Artikeln und Verpackungsmaterialien. Teil 1. Literaturübersicht. Teil 2. Strahlen-induzierte chemische und physikalische Veränderungen. STH-Berichte 18/1979 and 19/1979, Institut für Strahlenhygiene des Bundesgesundheitsamtes, Berlin.

[##] Buchalla et al., 1992, 1993a, b, c, 1995.

the project; Professor Otto Piringer (Fraunhofer-Institut für Lebensmitteltechnologie und Verpackung, München), who visited us to discuss the Phase I-results and provided an experimental PP-film; Dr. Wanner and Dr. Sandor Zarka (4P Folie, Forchheim), and Dr. Weiß and Dr. Klerner (BASF AG, Ludwigshafen), who provided the Lupolen and Novolen films; Dr. H.-J. Lengert and Dr. W. Zerweck (Willy Rüsch AG; Waiblingen), who performed an 'extra'-irradiation; Mrs. Ali Spiegelberg and Dr. Grit Schulzki (BgVV), who shared their laboratory facilities and their GC-MS-experience with us; Mr. Werner Blaas Sr. (BgVV) for help and discussions; Dr. Jack Hamilton (The Agriculture and Food Science Centre, Belfast) for an early briefing on MS operation and spectra interpretation; Dr. Andreas Hoffmann (Gerstel GmbH, Mülheim/Ruhr) for TDS- and CIS-operating hints; Dr. Bernd Pfeffer (J & W Scientific) for advice on column selection; Professor Wolfram Schnabel (Hahn-Meitner-Institut, Berlin) for advice and discussions; Mrs. Q. Q. Zhu (HMI), who prepared and irradiated the film samples I used for benzene quantitation; and Professor Walter Jennings (J & W Scientific / Univ. of California, Davis, CA) and Dr. Koni Grob (Kantonales Labor, Zürich, CH), whose seminars on gas chromatography and large-volume injection, respectively, conveyed a sense of how exciting analytical GC can be.

Thanks are also due to many others, particularly of the analytical and irradiation 'communities', for answering specific questions, for discussions, comments, and for encouragement; and I would finally like to thank *for moral and material support* during the writing of this thesis: my parents, Gerda and Manfred (special thanks to the former for shipping her famous chocolate cakes all the way to Berlin, and special thanks to the latter for providing the stainless-steel sieves used in 'Phase II'), and, last but not least, my friends for their continued association—special thanks to Annette for keeping up our 'Jour fixe' !.

Berlin, December 1999

Rainer Buchalla

Contents in Brief

Contents

1. Introduction

1.1 General Introduction and Objectives of the Investigation

Medical devices (or: medical products) play an important role in modern medicine. These devices—ranging from 'simple' single-use *syringes* to extracorporal *dialysis units* or *implants* (e. g., artificial hip joints)—are often made (partly or entirely) from synthetic polymers, and they are increasingly sterilized with ionizing radiation (see Section 2.1). Plastic *packaging materials* can also be exposed to ionizing radiation: in (medical) radiation sterilization, of course, but also in food irradiation (Section 2.2) or when they are sterilized for aseptic filling procedures.

At present, little is known on an aspect of radiation sterilization one is probably most concerned about from a toxicological point of view,[#] namely, the formation of low-molecular weight ('volatile') radiolysis products; some data have been published on packaging films (mainly LDPE and polypropylene), but virtually nothing on medical polymers (Section 2.3). It is generally expected that in the future „a much greater emphasis [will be] placed on the *chemical basis* for biocompatibility, including a *complete characterization* of materials, *identification and quantification of extractable chemicals* from [medical] devices ... including the study of degradation products produced by device materials" (Wallin, 1995).

During a recent FDA (Food and Drug Administration) meeting in the United States, packaging issues have been described „as the 'Achilles heel' of food irradiation" (Pargas, 1998); at the same time the (German) Federal Department of Health (BMG) has funded another investigation of radiation's effects on food packaging materials (Welle and Franz, 1998, 1999; Demertzis et al., 1999); and thermal desorption-GC-MS studies similar to the present investigation are currently being undertaken at the (U. S.) National Center for Food Safety and Technology (Sadler, 1999).

Accordingly, the **first** major objective of the present experimental work could be described as contribution to a 'chemical characterization' of irradiated plastics: to **identify** radiolysis products in medical polymers (and in packaging materials) in order to allow a better assessment of the risks potentially associated with radiation sterilization (and food irradiation).

The **second** major objective was to evaluate whether thermal desorption (TDS) allows to distinguish between irradiated and non-irradiated materials. To explain this emphasis on **'irradiation detection'** it should be said that the BgVV has been involved for many years in establishing detection methods for irradiated food items (Section 2.5).

Thus, the initial 'working hypotheses' could be summarized, very briefly, as follows:

– volatile radiolysis products are not only formed in LDPE and PP, but also in polymers such as *polystyrene, polyamide, poly(vinyl chloride), etc.*,
– volatiles are not just 'released' during irradiation into the 'headspace' of a closed sampling vial; rather, they *remain trapped in the polymer matrix* for some time, much like the residual monomer(s),
– there might exist volatiles that could be used as *markers* to differentiate analytically between irradiated and non-irradiated materials,
– there might exist *cyclic radiolysis products* (see Section 2.3), possibly analogous to the *cyclobutanones* used as markers in the detection of irradiated food.

[#] Of course, the potential toxicity of low-MW radiolysis products is only one aspect of *product safety*; other areas of concern might include *mechanical failure* because of polymer chain scission and/or post-irradiation 'ageing'; *increased wear* of UHMWPE implants; *adverse effects on surface properties / blood compatibility* (Buchalla et al., 1992, 1993a, b, c, 1994, 1995).

Initially, a **quantitative analysis** of volatiles by thermal desorption appeared not to be an option. *Static* headspace techniques are routinely used to quantify residual monomers in polymers; the inherently more sensitive *dynamic* techniques[#] are widely used in environmental applications, but much less work performed with polymers has been described in the scientific literature (see Sections 2.6–2.8).

The fact that these methods are relatively new and that their potential has not yet been fully realized is reflected, for example, in the title of a recent article: *Toward an Optimized Dynamic Headspace Method for the Study of Volatiles in LDPE* (Hodgson et al., 1998). Similarly (and surprisingly), the dynamic techniques are mentioned only very briefly in *Hyphenated Techniques in Polymer Characterization*, a monograph published in the ACS Symposium Series (Provder et al., 1994); and Hachenberg and Beringer (1996), for example, devote only a small part of their book to the dynamic technique.

It became clear very early during the initial screening program (Chapter 4) that the concentrations of the radiolysis products are considerably lower than those of the residual monomers / oligomers already present in the resins.[##] Nevertheless, quantitation appeared to be highly desirable as quantitative *dose-response relationships* are central to toxicology (SOLA DOSIS FACIT VENENUM, in the immortal words of Paracelsus—see Section 13.4).

When quantitation finally appeared to become a real option (Chapter 6), it was decided to focus the investigation on polystyrene, and—as a **third** major objective—to **quantify the major radiolysis products of PS** (Chapters 6 through 11). A comprehensive review of the literature revealed that a few authors already have expressed similar ideas (Section 2.7); some of them have demonstrated (more or less convincingly) that it is in fact possible to quantify volatiles in polymers using dynamic (gas-solid) extraction techniques, e. g., residual styrene in PS, or BHT in some packaging materials (see Section 2.7). However, this is, to my best knowledge, the first time that volatiles *in the low ppm-range* have been quantitatively determined with a dynamic technique.

1.2 A Brief Survey

The previous Section (1.1) has already outlined Chapter 2, or the *Background* of this work; at this point, I would like to give a brief survey over Chapters 4 through 11 (the '*Results-and-Discussion*-Chapters'), and to comment on the structure of the thesis.

The focus of the present investigation was very much on *method development* and *method optimization*, and I believe that the best way to organize the material is to present and to discuss the results almost (though not entirely) in the sequence in which the experiments were conducted. Overall, the analyses were performed **in five different 'Phases'**—influenced by the gradual and 'non-linear' analytical progress; some questions (e. g., the identification of trace products) were addressed parallel to the 'main projects.'

[#] Thermal desorption, dynamic headspace analysis, purge-and-trap methods: As these techniques rely on the same principle, the terms are increasingly used as synonyms (another one is *gas-solid extraction*), cf. Section 2.6. Whether authors describe their work as *thermal desorption*, *dynamic headspace*, or *purge-and-trap* investigation appears to depend very much on the equipment used and on personal preferences.

[##] An exception being the degradation products of (phenol-type) antioxidants in *polypropylene* (see Sections 4.6 and 5.7); their heavily overloaded peaks dominate the fingerprint chromatograms of irradiated PP.

In order not to confuse the reader I have made every effort to make cross-references to *Chapters* and not to *Phases* (or, parallel, to Chapters *and* Phases); however, as the five Phases reflect different sets of experimental conditions, it was impossible to avoid the term, especially so in the quantitative Chapters. **The following synopsis indicates the relationship between Phases I to V and Chapters 4 to 11:**

Synopsis

Phase		Chapter
I	Screening of Six Medical Polymers	**4**
II	Polyethylene and Polypropylene Films	**5**
III	Preliminary Quantitation of Radiolysis Products in PS:	
	– The Way to Quantitation	**6**
	– Initial Quantitative Results	**7**
IV	Confirmation of the Quantitative Results	**8**
III / IV	Thermal Desorption of PS Solutions with Solvent Evaporation (The 'DSC-Method')	**9**
I – IV	Identification of Trace Radiolysis Products	**10**
V	Quantitation of Benzene in PS	**11**

Phase I

Chapter 4 summarizes the initial **Screening of Six Medical Polymers.** While some of these qualitative results—obtained during an early period of method development—may be unsatisfactory from today's point of view, the findings are certainly interesting enough to deserve further investigation. As there are no reports in the scientific literature on volatile radiolysis products of *medical polymers*, the results for PS, MABS, and PA-6, and—to some extent—for PVC, PE and PP are considered to be novel.

Phase II

The experiments with **Polyethylene and Polypropylene Films (Chapter 5)** were, in some sense, a deviation from the original research program. The finding that 'volatile' radiolysis products are formed *in* (or: *by*) PE and PP films is not entirely new (see Section 2.3)—if we neglect, for the moment, that previous work has largely been done with *electron-beam* irradiation. The results obtained, however, touch a number of questions that have not been addressed in sufficient depth so far, for example, the effect of the desorption temperature, the retention of radiolysis products in polymer films, the relationship between dynamic headspace and thermal desorption techniques, and the extent to which these techniques analyze (radiation-induced) artifacts rather than genuine volatile products. Also discussed in Chapter 5 are trace degradation products of (phenol-) antioxidants with atypical structures, possible cyclic radiolysis products, and the prospects for irradiation detection. Finally, there is a brief comment on the *design* (geometry) and *efficiency* of the thermal desorption system.

Phase III

Chapter 6, entitled **The Way to Quantitation,** describes how the initial perception of thermal desorption as a qualitative technique changed and how 'total desorption' or 'quantitative extraction' conditions were gradually established.

The promising results of a first series of quantitative TDS-analyses are reported in **Chapter 7, Initial Quantitative Results,** followed by a description of analytical problems at the end of Phase III, of the resulting strategy for future investigations, and of the TDS-Performance-Test developed as part of a more comprehensive parallel test program for characterizing system performance in future investigations (i. e., Phases IV and V).

Phase IV

The main objectives of Phase IV were to reproduce the quantitative results, to confirm the apparent absence of concentration changes with time, and to analyze some 'real-life' sterilized PS samples **(Chapter 8, Confirmation of the Quantitative Results).** The analyses were performed with a different column, system performance was closely monitored with various tests, and TDS-parameters had to be adjusted (as an unexpected consequence of a software-update).

Chapter 9, Thermal Desorption of PS Solutions with Solvent Evaporation (The 'DSC-Method'), describes a new desorption technique; preliminary experiments with this technique were performed in Phase III and a 'full-scale' trial in Phase IV. The experiments ultimately led to the suggestion to directly inject the polymer solution (*'Thermal Desorption with the CIS'*). The concentrations determined with the DSC-Method have been used to calculate radiation-chemical yields, and the results of a dissolution-precipitation experiment are also included in Chapter 9.

The topic of **Chapter 10** is the **Identification of Trace Radiolysis Products** in polystyrene; experiments with relatively high sample loads were performed with various columns in Phase I, 'pre-Phase III,' and in Phases III and IV.

Phase V

Chapter 11, Quantitation of Benzene in PS, describes a newly developed method for the *splitless*-injection of benzene standards and the quantitative results obtained for benzene in irradiated polystyrene.

Summary and Conclusions

While the **Summary (Chapter 12)** can, of course, be read indepently of Chapters 4 to 11, direct references are made to some Figures to facilitate the exploration of important subjects in more depth. The summary ends with a special discussion of the recurrent question *whether the radiolysis products are genuine or artifacts of thermal desorption.*

The implications of the results for radiation sterilization and food irradiation are discussed in **Chapter 13 (Conclusions)** with little or no reference to analytical details; it is divided into four sections: *Analytical* Considerations, *Radiation-Chemical* Considerations, Implications for *Irradiation Detection*, and *Safety Aspects.*

Appendices

Material that has been relegated to **Appendices** includes the original data of the quantitative series of measurements (calibration data, calibration curves, PS data), data characterizing system performance, MS Identification Tables for the trace products, etc.

2. Background

2.1 Radiation Sterilization of Medical Products

General

Radiation sterilization is according to Charlesby (1991) one of the two *most successful practical applications to date of radiation chemistry* (the other being irradiation of polymers to improve their physical properties). Besides ethylene oxide (gas) sterilization, gamma irradiation is the second most important *terminal cold sterilization process* used by the medical industry. The technique has been characterized as having „a certain elegance," (Woolston, 1990) mainly because only a single process parameter, the absorbed dose or irradiation time, has to be controlled (cf. parametric release, below).

The Importance of Radiation Sterilization

The number of gamma-irradiation plants in operation throughout the world rose from 54 plants in 1977, employing ca. 47.8 MCi (Mega Curie) of Cobalt 60, to 143 facilities by the end of 1989, employing ca. 135 MCi of Cobalt 60, and offering a potential sterilization capability of some 3.3 million m^3 per year (Artandi, 1977; Woolston, 1990). Brinston (1990) estimated that a total of ca. 10 million m^3 of disposable medical products and related health care items were being sterilized around the world in 1988; she estimated the market shares of the various cold sterilization processes to be 70% for ethylene oxide, 27% for gamma-irradiation, and 3% for electron-irradiation, and expected these values to become 55% for EtO and 42% for gamma-sterilization in 1993. On a local basis, a source quoted by Woolston (1990) suggests that 40 to 50% of medical disposables are processed by irradiation in the U.S.A., approximately 35% in Europe and 50% in Australia.

While some authors (Brinston, 1990; Brinston and Wilson, 1993; Woolston, 1990) expect this trend to continue—with gamma-sterilization becoming the method of choice for the 1990s — the surveys of Pearson (1993a, 1994) indicate „that EtO sterilization is as popular as ever, and has not been overtaken by radiation technologies." According to Peacock (1993), present and future developments in the areas of residue reduction, biological indicators, and emission control are likely to ensure the place of EtO sterilization „as the principle method of sterilization for the twenty first century."

Use of Plastics in Medical Applications

As already noted by Szycher (1991) and Pearson (1993b) there is a certain lack of information on the medical use of plastics. According to Lantos (1988), the medical market has become the fourth largest area of applications for plastic materials; he estimates that 2% of all plastics or a total of ca. 800,000 tons (1986 in the U.S.A.) find use in this market.

Lantos (1988) and Szycher (1991) have estimated the use of various plastics in medical applications (Table 2.1). Both authors observe that the *volume polymers* (PVC, PS, PE and PP) find the greatest usage as the most cost effective materials; however, a significant fraction of all medical plastics are of the *high performance variety* that replace stainless steel, glass, and other traditional materials by virtue of offering outstanding mechanical properties, chemical resistance, sterilizability or biocompatibilty (Lantos, 1988; Szycher, 1991).

The data in Table 2.2 for the *volumes of plastics radiation-sterilized* in the U.S. are „private industry estimates“ reported by Ellis (1991). Comparison with the *total volumes* listed in Table 2.1 indicates some major shifts in the relative importance of the materials (e. g., PVC, LDPE, Polyesters, ABS); this probably reflects differing areas of applications as well as differing radiation stabilities.

The Advantages of Radiation Sterilization

Cold sterilization processes are required for plastic materials that cannot withstand thermal (i. e., steam or dry heat) sterilization, because their softening points are too low, or because manufacturing-induced internal stresses cause distortions at the temperatures applied (Plester, 1967; Handlos, 1981).

Table 2.1 **Use of plastics in medical applications** in the U.S.A. (in tons).
Estimates by Lantos (1988) and Szycher (1991).

Year	1986	1989
Poly(vinyl chloride) (PVC)	213,000	218,000
Polystyrene (PS)	150,000	154,000
LD Polyethylene (LDPE)	141,000	145,000
HD Polyethylene (HDPE)	109,000	114,000
Polypropylene (PP)	77,000	79,000
Polycarbonate (PC)	23,000	27,000
Thermoplastic Polyesters	18,000	20,000
Acrylics	16,000	18,000
Silicones	9,000	11,000
Nylon	9,000	9,000
ABS	7,000	7,000
Thermoplastic Urethanes (TPU)	11,000	5,000
All others	23,000	23,000
Total	806,000	831,000

Table 2.2 **Plastics radiation-sterilized for healthcare use** in the U.S.A. in 1988 (in tons).
Estimates by Ellis (1991).

Polystyrene (PS)	40,800
Polypropylene (PP)	23,600
HD Polyethylene (HDPE)	22,700
Thermoplastic Polyesters	12,700
ABS	6,800
Poly(vinyl chloride) (PVC)	6,400
LD Polyethylene (LDPE)	5,900
Polycarbonate (PC)	5,500
Acrylics	1,800
Others	1,400
Total	127,000

Compared to EtO sterilization, the advantages of radiation processes are:

– simple process control (only one parameter, the absorbed dose, must be controlled);
– dosimetric (or: 'parametric') release (no need for degassing activities, biological indicators, or quarantine);
– complete penetration (less restrictions in product design and packaging);
– the problems associated with EtO-toxicity are avoided (no EtO residues in the products, no EtO emissions that have to meet working safety or environmental regulations).

These topics are discussed to varying extents by Woolston (1990), Brinston (1990, 1991), Koppensteiner (1988), Chin (1980), Dempsey and Thirucote (1989), Frohnsdorff (1981), and Landfield (1983).

Sterilizing Doses

While most European countries recommend or require an absorbed dose of 25 kGy as minimum dose, the probabilistic concept of sterility would allow reduced doses—depending on the actual bioburdens. Reducing the dose levels has been discussed in the U.S.; doses < 25 kGy are accepted in the U. S., and, partially, in Europe; Scandinavian countries require minimum doses of 32 - 50 kGy arguing that there exist microorganisms of high radiation-resistance. Dorpema (1990), Woolston (1990), Frohnsdorff (1981), Koppensteiner (1981), and the U. K. Panel (1987) comment on these differing regulatory viewpoints.

Finally, it should be mentioned that the development of radiation sterilization has exerted a considerable influence on modern concepts of sterility control, i. e., on the development of the probabilistic concept of sterility—see Artandi (1977) and Dorpema (1990).

2.2 Packaging in Food Irradiation

Food Irradiation

In food irradiation the emphasis has so far been on relatively low (sub-sterilizing) doses (see the following paragraph); however, as the *Joint FAO/IAEA/WHO Study Group* has just published a report on the wholesomeness of high-dose (>10 kGy) irradiated food (WHO, 1999), it is likely that *sterilization* of food by ionizing radiation will also become an important application (cf. below).

Food can be treated with ionizing radiation to reduce microbial contamination, to inhibit sprouting or ripening, or to control insect infestation. In 1980 the *Joint FAO/IAEA/WHO Expert Committee on the Wholesomeness of Irradiated Food* "concluded that the irradiation of any food commodity up to an overall average dose of 10 kGy presents no toxicological hazard" and "introduces no special nutritional or microbiological problems" (WHO, 1981). Since then, irradiated food has been given access to markets, where it previously had been prohibited (e. g. in the United Kingdom), other countries, e. g. the United States, who had considered food irradiation an additive, have changed their regulations to control irradiation treatment as a food process instead (Chuaqui-Offermanns, 1989), and new approvals for the irradiation of certain foods have been made. The European Union (EU) so far has not arrived at common regulations.

In its new report, the *Joint FAO/IAEA/WHO Study Group* concludes that „food irradiated at any dose ... is both safe to consume and nutritionally adequate" and that irradiation „does not result in any toxicological hazard" (WHO, 1999: p. 161). Current applications of doses

> 10 kGy include the development of shelf-stable foods for general use and for specific target groups, such as immunosuppressed patients. The radiation sterilization of hospital diets is permitted, for example, in the Netherlands (with up to 75 kGy) and in the U. K. (no dose limit specified); South Africa has permitted the marketing of meat products irradiated to a minimum dose of 45 kGy (WHO, 1999).

The Role of Packaging

Plastic packaging materials in the form of single- or multi-layered films, or of trays, play an important role in the irradiation processing of foods, since, in order to prevent recontamination, the products are usually irradiated in their final packages. For example, a large fraction of the items presently processed in the EU or in South Africa, namely fruits, vegetables (dried or cut), poultry, venison, shrimps, shell-fish, frog legs, herbs, spices and ingredients, is irradiated in pre-packaged form; the quantities treated in selected countries amount—according to the International Atomic Energy Agency—to about 10,000 tons annually in Belgium and about 20,000 tons each in France, the Netherlands and South Africa, and are expected to increase globally. No consumer packages are commonly used in large-scale irradiations for disinfestation (of e. g. cereals) or inhibition of sprouting (of onions and potatoes).

As already pointed out by Gilbert and Shepherd (1981) it is „notoriously difficult“ to obtain information on which plastics are used with what foods, because of commercial secrecy, because of the constantly changing pattern of usage for economic reasons, and also because of the fragmented nature of the industries involved. Overall, the most important materials in food packaging appear to be[#] polypropylene (PP), polystyrene (PS), polyethylene (PE), polyamide (PA) and polyethylene terephthalate (PET); multilayer-materials, i. e., combinations of the above [plus a few others, such as ethenyl-vinylalcohol (EVOH) or poly(vinylidene chloride) (PVDC)] play a very important role in modern packaging, as they combine the barrier and mechanical properties of the individual compounds. However, from an analytical point of view, it obviously makes sense to begin any investigation of radiation's effects with single ('pure') materials, and even the most recent studies of Demertzis et al. (1999) or Riganakos et al. (1999) have largely concentrated on single (mono-layer) films (cf. Section 2.3).

Finally, it should be said that packaging materials are increasingly sterilized by ionizing radiation for use in *aseptic* processing lines—in the food, pharmaceutical and cosmetic industry (Ley, 1976; Tacker et al., 1999; Walter, 1988).

[#] This rather general assessment is based on numerous articles and books (e.g., Piringer, 1993; Piringer and Baner, 1999) un-related to irradiation. There is almost no information on which packaging materials are actually used in food irradiation, and even contract irradiators and industry associations are unable (or unwilling) to provide useful data. Packaging materials formally approved for irradiation in various countries have been listed repeatedly in the literature; the most up-to-date compilation is probably that by the *Joint FAO/IAEA/WHO Study Group* (WHO, 1999; p. 148). In its recent study, the *Fraunhofer-Institut für Verfahrenstechnik und Verpackung*, an institution that obviously has the expertise in this area, has also concentrated on 'the usual suspects,' i. e., PE, PP, PVC, PET, PA, and PS (Welle and Franz, 1998, 1999; Demertzis et al., 1999).

2.3 Low-Molecular Weight ('Volatile') Radiolysis Products of Polymers

Low molecular-weight radiolysis products of some **polymer films** have been investigated by combined gas chromatography-mass spectrometry (GC-MS) in connection with various dynamic headspace and / or thermal desorption-concentration techniques. In a few cases, indirect evidence has been obtained for the existence of low-MW radiolysis products, or products have been determined by other techniques.

Identification of Radiolysis Products

In an earlier review, Killoran (1972) reports some results from the research programs of the U. S. Army, Atomic Energy Commission and their contractors, which in the mid-Sixties led to the FDA-approval of various food packaging materials for use in food irradiation (U. S. Food and Drug Administration, 1989). The polymer films—**LDPE, HDPE, polyamide-6 (PA-6), and a vinylidene chloride-vinyl chloride copolymer (PVDC-VC)**—were electron-irradiated *under vacuum*; the volatiles were collected with a „low-temperature high-vacuum technique" and analyzed by GC-MS. The two PEs and PA-6 produced various aliphatic hydrocarbons, whereas the PVDC-VC produced chlorinated hydrocarbons with two to ten C-atoms. In the case of LDPE, for example, ninety different hydrocarbons were found, ranging in molecular weight from 16 (methane) to 184 (tridecane); their total amount increased with the absorbed dose from 56 µg/g of film after 10 kGy to 191 µg/g after 60 kGy, and to 339 µg/g after 120 kGy. The films also produced some hydrogen, methane (except PA-6), carbon dioxide, and hydrogen chloride (PVDC-VC only). Similar results have been reported by Bersch et al. (1959) and Tripp (1959).

More recently, low-MW radiolysis products of polymer films have been investigated by Japanese and French groups using dynamic headspace and/or thermal desorption techniques combined with GC-MS: Azuma et al. (1983) have detected more than one hundred volatile compounds in the **headspace** of **LDPE** films electron-irradiated in air with 20 kGy; 50 of the compounds could be identified by mass spectrometry. Rojas de Gante and Pascat (1990) have obtained similar results: electron-irradiation in air with 10 and 25 kGy produced 100 volatiles in **LDPE** and 58 in oriented **polypropylene** (OPP) films. The compounds identified are predominantly hydrocarbons, alcohols, aldehydes, ketones and carboxylic acids. The total amounts of volatiles formed were greater for polypropylene than for LDPE, the polypropylene gave more branched isomers, while LDPE gave mainly linear products.

Deschênes et al. (1995) have found a similar spectrum of volatiles in a (gamma- and EB; 10 kGy-) irradiated barrier film, which consisted of **Nylon, PVDC, and an EVA copolymer** (and was analyzed with a dynamic headspace-GC-MS technique); whereas Kim-Kang and Gilbert (1991a, b), who analyzed Soxleth extracts of a **PETG/PVDC/PE laminate** by GC-MS, found only three 'major new compounds' after a sterilizing dose of gamma-radiation. The Fraunhofer-Institut's recent study (Welle and Franz, 1998, 1999; Demertzis et al., 1999) concentrated on the analysis of extracts by GC-MS and on (static) headspace-GC-FID. While they may not have found many 'new' radiolysis products, it is remarkable that they were able to identify several products in the extracts of irradiated **PE, PP, and PVC films;** the amounts of solvent extractable compounds in **PET, PA and PS** did not change significantly. Riganakos et al. (1999) have again used a dynamic headspace-GC-MS technique to investigate **LDPE, ethylene vinyl acetate (EVAc)** and a **PET / PE / EVOH / PE multilayer film.** Overall, the results confirm those of Azuma et al. (1983, 1984a, b) and Rojas de Gante and Pascat (1990): the films produce up to one hundred volatiles, and the spectrum of products is quite similar for the three (polyolefin !) films.

In a sensory test designed to be highly critical of packaging material performance, **PVC** and —to a lesser extent—**high-impact polystyrene (HIPS)** were found to carry a risk of tainting food on gamma-irradiation with 2.6 - 3.9 kGy (Kilcast, 1990). This indicated that even *styrene-based polymers* produce—at least trace amounts of—low-MW radiolysis products, though they generally exhibit superior radiation resistance, e. g., in terms of gas yields or mechanical strength retention. Shintani (1992, 1995, 1996) and Shintani and Nakamura (1989) have reported that a carcinogen, 4,4'-methylenedianiline (MDA), is formed in thermosetting **polyurethane** for medical devices. While the MDA levels determined (< 1 ppm at 25 kGy) were not considered a significant risk, serum extracts from the irradiated material contained additional unidentified mutagens, which are thought to be toxicologically more important and require further investigation (Shintani, 1996).

Cyclic Radiolysis Products

Among the radiolysis products identified in the headspace of irradiated LDPE and PP films by Rojas de Gante and Pascat (1990) there are a total of nine *cyclic compounds*, for example, *oxetane-2,2-dimethyl* (observed in LDPE after 10 and 25 kGy), *cyclobutane-1,2-diethyl (cis)* (in LDPE/25 kGy), or *cyclobutane* (in PP/25 kGy). While the authors did not specifically comment on these products, I found this observation quite intriguing, because various *cyclobutanones* are used in the detection of irradiated food (Boyd et al., 1991; Schreiber et al., 1993; Stevenson et al., 1990; see also Section 2.5). Together with alkanes and alkenes, these cyclobutanones are radiation-induced degradation products of triglycerides.

Film Variety and Irradiation Conditions

Azuma et al. (1984a) have investigated nine **different LDPE films:** the amounts of carboxylic acids produced were found to depend on the processing history of the films and on the presence of additives, the antioxidant butylhydroxytoluene (BHT) reducing very effectively the formation of carboxylic acids. Rojas de Gante and Pascat (1990) have also observed an influence of formulation and processing methods on the amount of volatiles, but give no further details.

To determine the effects of **absorbed dose** and **oxygen concentration,** the relative peak areas of the carboxylic acids have been compared: they increased with the absorbed dose (Rojas de Gante & Pascat, 1990) and with increasing concentration of oxygen in the atmosphere (Azuma et al. 1984b, Rojas de Gante & Pascat, 1990). The effect of (electron beam) irradiation conditions has been studied by Azuma et al. (1984b): the amounts of the carboxylic acids increased with increasing **temperature** and **radiation energy** (= acceleration voltage), and with decreasing **beam current.** Electron-irradiation was found to produce smaller amounts of volatiles than gamma-irradiation, which is considered to be a **dose-rate effect.**

Quantitative Data

Quantitative data have been obtained (Azuma et al., 1984a) for the aliphatic carboxylic acids with two to five C-atoms in low-density polyethylene: the total concentrations of the four acids, which account for ca. 18% of the total peak area of a gas chromatogram with some 50 identified peaks (Azuma et al., 1983), were ca. 2 to 16 ppm (µg per gram of film) after a dose of 20 kGy.

Retention of Radiolysis Products in the Films

El Makhzoumi (1994) has investigated volatile radiolysis products of three commercial food packaging films (LDPE, a polyester, and a polypropylene copolymer) after electron-irradiation with 5 kGy. A dynamic desorption-concentration technique was used in connection with GC-MS to analyze (a) the headspace of samples irradiated in glass vials, and (b) the volatiles that remain trapped in the polymer matrix when samples are irradiated in open air.

Numerous volatile compounds—several methylketones, hydrocarbons and degradation products of antioxidants—were formed by the polypropylene copolymer after 5 kGy; 24 compounds were identified in the headspace analyses, and **13 volatiles were found to be retained in the polymer matrix.** LDPE irradiated with 5 kGy produced some 20 volatile radiolysis products; the compounds could be detected in the headspace of the glass vials, but apparently *were not retained in the LDPE matrix*. Only very small amounts of three volatile products were found with the polyester, one of them was identified as acetone.

The effect of the absorbed dose (5 to 50 kGy) has been studied for the polypropylene copolymer by monitoring several keto-compounds and three aromatic degradation products of antioxidants—namely *1,3-bis-(1,1-dimethylethyl)-benzene*, the phenol *2,4-bis-(1,1-dimethylethyl)-phenol*, and the quinone *2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione*. In most cases the amounts of the products increased with the absorbed dose, but some volatiles also went through or reached a maximum at certain doses. Their quantities ranged —for the closed-vial experiments after 5 kGy—from 0.1 to 20 ppm for the ketones, and from 0.1 to 3 ppm for the aromatic compounds.

According to El Makhzoumi (1991), the amounts of volatile products also increased with the quantity of oxygen present during irradiation, and with the presence of food simulants (water, alcoholic and acidic solution); a kinetic study showed the volatiles **to remain trapped in the polypropylene for three months.** El Makhzoumi (1994) concluded that the degradation products might possibly migrate into food, and that the resulting toxicological and sensory risks should be evaluated.

Sensory Changes (Off Odors and Taint Transfer)

Many of the authors quoted so far have pointed out that these volatiles may cause *sensory changes* in (or: *taint transfer* to) packed products; as mentioned above, Kilcast (1990) has actually identified PVC and HIPS as carrying a risk of tainting food on irradiation; and similar problems have been mentioned earlier by Grünewald and Berger (1961), Feazel et al. (1960), Keay (1969), and Tripp (1959). As recommended by Kilcast (1990), manufacturers should take these risks very seriously, but they have not been a primary concern in the present investigation.

2.4 Radiolysis Products of Additives

It had not been intended initially to study the degradation of additives; however, since degradation products of phenol-type antioxidants are the major radiolysis products in PP films (and the medical PP under investigation), the relevant literature on the subject is briefly reviewed in this section. Data are available for some widely-used antioxidants, namely:

Irgafos 168 = Tris-(2,4-di-t-butylphenyl)-phosphite
Irganox 1010 = Pentaerythrityl tetrakis-3-(-3',5'-di-t-butyl-4'-hydroxy-phenyl)-propanoate
Irganox 1330 = 1,3,5-Tri-methyl-2,4,6-tris-(3',5'-di-t-butyl-4'-hydroxybenzyl)-benzene
Irganox 1076 = Octadecyl-3-(-3',5'-di-t-butyl-4'-hydroxyphenyl)-propanoate

Degradation of Antioxidants

Sterically hindered phenol and phosphite antioxidants are gradually destroyed with increasing absorbed dose, the extent of degradation depending on the nature of both the antioxidant and the polymer, and possibly on the processing history of the sample **(Allen et al., 1987a, 1988a, 1991a).** The phosphite antioxidant Irgafos 168 incorporated into polypropylene is destroyed far more rapidly than the hindered phenols, the rate of destruction seeming to be even greater in the presence of the phenol Irganox 1010 **(Allen et al., 1987b, 1988a, 1990a).**

Similar results have been obtained by other workers: **Bourges et al. (1992a)** reported 50–65% degradation for the hindered phenols Irganox 1010 and Irganox 1076 present in LDPE and two different polypropylene films after electron-irradiation with 10 kGy; 85–90% and 50% of the phosphite Irgafos 168 were degraded in polypropylene and LDPE, respectively. **Horng and Klemchuk (1984)** have investigated the degradation of four different stabilizers in gamma-irradiated polypropylene and its effect on some properties of the polymer. After 25 kGy, Irganox 1076 (initial concentration 0.47%) and Irgafos 168 (0.34%) were degraded 65% and 80%, respectively; the level of the hindered amine 2,2,6,6-tetramethyl-4-piperidyl sebacate (0.52%) was 37% reduced, while that of the thioester distearyl thiodipropanoate (0.4%) had fallen below the detection limit.

The degradation of the stabilizers was reflected by changes in the molecular weight distribution and breaking angle of the samples: only the hindered amine and the phenol (Irganox 1076) reduced the shift to low molecular weights in GPC curves and prevented a decrease in breaking angle. A further slight decrease in the stabilizer concentrations was observed after six months of ambient storage (Horng and Klemchuk, 1984).

The effects of ^{60}Co-gamma- and electron-irradiation (1 to 50 kGy) on the degradation of phenol and phosphite antioxidants present in polypropylene and/or LDPE were found to be comparable in magnitude **(Allen et al. 1990b).**

Covalent Binding of Antioxidants on Irradiation

Phenol antioxidants incorporated into polyolefins seem to become—at least to some extent—covalently bound to the polymer on irradiation. The total (chloroform-) extractable ^{14}C-activity of polypropylene and HDPE samples containing a ^{14}C-labelled phenol antioxidant (Irganox 1076) was found to decline progressively with increasing absorbed dose. At the same time, the residual activity of the extracted samples increased, "indicating the probable binding of at least 20% of the total available ^{14}C-activity to the polymer" after 50 kGy. Dissolution of the polypropylene in hot tetralin followed by precipitation with hexane indicated a polymer-binding of at least 12.4% and the true figure is estimated to be significantly higher **(Allen et al. 1990a, 1991a).**

Covalent binding has also been proposed as a mechanism that would explain a reduction in residual monomer (acrylonitrile) concentrations in styrene acrylonitrile (SAN) resins electron-irradiated with 0.5 to 2 kGy **(Derbyshire, 1979),** and a reduced taint transfer from polyethylene- and polypropylene-based films into food simulants after absorbed doses of 2.6 to 3.9 kGy of gamma-irradiation **(Kilcast, 1990).**

Degradation Products of Antioxidants

By HPLC, ^{31}P-NMR-spectroscopy, and mass spectrometry **Allen et al. (1987b, 1988a)** have identified an oxidation product of the phosphite antioxidant Irgafos 168, that was detected in extracts of irradiated polypropylene samples, as the corresponding triaryl phosphate tris-(2,4-di-t-butylphenol)-phosphate.

Bourges et al. (1992a), who also observed the phosphate as degradation product of Irgafos 168, have identified two degradation products of the phenol antioxidants Irganox 1010 and Irganox 1076 by UV spectroscopy, mass spectrometry and comparison with authentic samples, namely 2,4-bis-(1,1-dimethylethyl)-phenol [*bis-DME-P*] and 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione [*quinone*]. Their concentrations were 70 ppm (*bis-DME-P*) and 7 ppm (*quinone*) in the two polypropylenes, and 30 ppm (*bis-DME-P*) and 4 ppm (*quinone*) in LDPE. These values were consistent with the observed degradation of the antioxidants, the polypropylene being thought to be more subject to oxidation than the polyethylene, due to the presence of tertiary carbon atoms.

Besides of the *phenol* and the *quinone*, **El Makhzoumi (1994)** has investigated a third degradation product, namely *1,3-bis-(1,1-dimethylethyl)-benzene* (see Retention of Radiolysis Products ... in Section 2.3).

In a kinetic study **Bourges et al. (1992b)** have identified two additional degradation products, namely 3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzaldehyde and a *quinone methide*, 3'-(4-oxo-3,5-bis-(1,1-dimethylethyl)-cyclohexa-2,5-dien-ylidene)-propanoic acid. The products are formed in post-irradiation reactions, their concentrations gradually increase during storage coinciding with a decrease in Irganox 1010 concentration.

Radiation-Specific / De-Alkylated Structures

Allen et al. (1993a) have characterized degradation products of three antioxidants present in polypropylene by combined high performance liquid chromatography–mass spectrometry (HPLC–MS). The polymer samples containing either Irganox 1010, Irganox 1076, or Irganox 1330 at 0.1 to 0.25% (w/w) were gamma- or electron-irradiated with 50 kGy and extracted with chloroform.

Both gamma- and electron-irradiation led to the formation of a range of transformation products of Irganox 1010, *none of which were detected after thermal oxidation*. With the antioxidants Irganox 1076 and 1330 the structure of the transformation products was largely the same for irradiation and thermal oxidation, with the exception that irradiation led to *de-alkylated structures* that have lost t-butyl groups.

For Irganox 1010, the authors suggest—based on the MS data—four structures, that represent the progressive reductive cleavage of two *3,5-bis-(1,1-dimethylethyl)-4-hydroxyphenyl-propanoic acid* moieties from the parent antioxidant. The resulting structures—tris- and bis-esters of the acid with pentaerythritol or its reduced analogues—still retain hindered phenol functionality, while the unit cleaved is ultimately oxidized to the *quinone* 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione.

Further evidence that the proposed structures are not oxidized, was obtained from UV data (from diode array detection) and from ^{1}H-NMR-spectra. Synthetic samples of two of the compounds gave identical chromatographic and spectroscopic data.

Thermal oxidation (under conditions that reduced the concentration of Irganox 1010 to a similar extent) produced a number of compounds that were *different* to those observed in the irradiated samples. The compounds are thought to have cinnamate and/or quinoid structure, and no cleavage of 3,5-bis-(1,1-dimethylethyl)-4-hydroxyphenyl-propanoic acid moieties was detected.

In the case of Irganox 1076, the *de-butylated analogue* of the antioxidant, and a range of oxidized structures, ranging from the corresponding cinnamate ester to dimeric systems, was observed.

Two *de-butylated transformation products* have been characterized for Irganox 1330, and oxidation of individual hindered phenol moieties as well as oxidative cleavage of one moiety (which is converted to the *quinone*) was observed with both, the original antioxidant and its de-butylated analogues. Results for Irganox 1330 are also discussed — in more detail, and illustrated with chromatograms, mass spectra and UV spectra — by **Allen et al. (1993b).**

According to an earlier meeting abstract, where the detection of a range of extractable degradation products of Irganox 1076 and 1010 was announced **(Allen et al., 1991b),** some of these products "are significant migrants after a dose of 10 kGy."

Migration of Antioxidant Degradation Products

Bourges et al. (1993) have studied the relationship between the degradation of antioxidants in polypropylene and the migration (10 days at 40°C) of their degradation products into aqueous food simulants. A bi-oriented film stabilized with the hindered phenol Irganox 1010 and the phosphite Irgafos 168 was electron-irradiated with 2, 5, and 10 kGy while being in contact with either distilled water, 3% acetic acid, or 15% ethanol.

HPLC analyses of polypropylene extracts revealed a progressive destruction of the antioxidants and formation of tris-(2,4-di-t-butylphenol)-phosphate, the main oxidation product of Irgafos 168 (which is already 90% destroyed after 2 kGy). The presence of any of the three food simulants had no effect on the concentration of the antioxidants or the phosphate (in the polymer), and neither the two antioxidants nor the tris-(2,4-di-t-butylphenol)-phosphate were detected as migrants in the food simulants after 10 kGy.

Different effects were observed with four degradation products of Irganox 1010, namely 2,4-bis-(1,1-dimethylethyl)-phenol, the *quinone* 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione, the *quinone methide* 3'-(4-oxo-3,5-bis-(1,1-dimethylethyl)-cyclohexa-2,5-dienylidene)-propanoic acid, and 3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzaldehyde. Their concentrations in the polymer matrix generally increased with the absorbed dose, but were also dependent on the presence and the type of the food simulants. The concentrations of the four compounds (in the polymer) were lower in the presence of the food simulants (lowest with 15% ethanol); at the same time, the compounds were found as migrants in the food simulants, where their amounts increased with increasing absorbed dose.

Since the quantities lost by the polypropylene were higher than those recovered in the food simulants, Bourges et al. (1993) concluded that after migration the compounds possibly had *decomposed to some unknown products*. Degradation products of antioxidants have also been noted by **Allen et al. (1991b)** as "significant migrants after a dose of 10 kGy."

2.5 Irradiation Detection

Detection of Irradiated Food

Detection methods have been established in recent years for many types of irradiated *food items*; the main methods being used are ESR spectrometry, thermoluminescence (TL) and gas chromatography (typically GC-MS)—see the monograph edited by McMurray et al. (1996) for the current status of irradiation detection. Detection methods for irradiated food have also been reviewed by Chuaqui-Offermanns (1992), and Schreiber et al. (1993), and, more recently, by Haire et al. (1997), Delincée (1998), and Raffi (1998).

The GC-MS-techniques use hydrocarbons (and cyclobutanones) produced by the radiolysis of lipids as *radiation markers*; today's standardized (and codified) methods are based on the pioneering work of Nawar[#] in the early Seventies and are the result of years of coordinated world-wide research efforts including EU-funded interlaboratory trials and support by the ICGFI[##]; for some types of food, methods have been validated that even allow an estimation of the absorbed dose. In comparison, the present study was a small-scale investigation and we are only at the beginning of a possible future detection method for irradiated plastics.

Detection of Irradiated Plastics

Detection methods for irradiated plastics would be of interest for an *indirect identification* of irradiated food items that (as yet) cannot be identified directly, for *screening procedures* (which should be reasonably fast), or to obtain *additional evidence* that a product is irradiated. In medical product sterilization, they would permit to check correct *labelling* of products, and to identify components that have undergone *multiple* sterilization cycles.

There are presently no established methods to unequivocally identify a plastic item as irradiated with ionizing radiation. There are, of course, various radiation-induced changes in polymers that are proportional to the absorbed dose, but these changes are generally not sufficiently radiation-specific and do not permit to decide whether an *unknown* sample has undergone some radiation treatment. This situation is probably best illustrated by the undyed polymers, such as polymethylmethacrylate (PMMA) or cellulose tri-acetate (CTA), that are used as routine dosimeters in radiation processes (Barret, 1982; McLaughlin, 1990; Sharpe, 1990): The response of these systems depends on factors such as temperature, humidity, fading, and the dose rate (electron beam- vs. gamma-irradiation), which have to be controlled carefully. PVC film dosimeters have „many drawbacks" and „cannot be recommended for anything but rough dose estimation" (Sharpe; 1990).

So far, only a few authors have commented briefly on possible detection methods for irradiated plastics, and no one seems to have given the subject a great deal of attention. Marqué et al. (1994) mention the possibility to use the ESR signal of stable NO-radicals deriving from amine stabilizers to identify polypropylene as irradiated with ionizing radiation. Bourges (1991) has proposed to use *1,3-bis-(1,1-dimethylethyl)-benzene*, a degradation product of phenol-type antioxidants, as an analytical marker for irradiated polypropylene. Allen et al. (1989, 1990a) observed that the triazine antioxidant Irganox 565, used as an internal HPLC standard, is destroyed in contact with certain irradiated plastics; they concluded that it might be possible to develop a chemical test for irradiated plastics based on „this unexpected chemistry."

[#] For references to the work of Nawar & colleagues see Schulzki (1996), or McMurray et al. (1996).

[##] ICGFI, the International Consultative Group on Food Irradiation of the FAO, IAEA, and WHO.

The present investigation's emphasis on irradiation detection was inspired by the apparent observation of *cyclic radiolysis products* in LDPE and polypropylene films by Rojas de Gante and Pascat (1990) (see Sections 2.3 and 5.8), which captured the author's imagination as his colleagues at the BgVV were using cyclobutanones (and hydrocarbons) as chemical markers to identify irradiated food items by GC-MS (and LC-GC)—see, for example, Spiegelberg et al. (1994), Schulzki (1996), and Schulzki et al. (1995a, b, 1996, 1997).

2.6 Polymer Characterization by Thermal Desorption / Dynamic Headspace Techniques

Thermal desorption, dynamic HSA, purge-and-trap, and similar techniques are, of course, widely used in other areas, especially to monitor trace levels of volatile organic compounds **in environmental air and water analysis.** There are numerous other applications as well, for example: Characterization of geological samples (e. g., van Lieshout, 1997), determination of volatiles in strawberry foliage (Hamilton-Kemp et al., 1993) or in virgin olive oil (Morales et al., 1994), detection of traces of gasoline in arson cases (e. g., Kärkkäinen, 1993), analysis of chemical warfare samples (e. g., Black et al., 1993), or quantitation of triazolam in a tablet (Hida et al., 1997)—to list but a few. Some of this research is absolutely fascinating, many of the related papers are very interesting from an analytical point of view, but they are not directly relevant in this context and cannot be reviewed here.

The decision to investigate low-MW radiolysis products was a direct consequence of earlier literature reviews (Buchalla et al., 1992, 1993a, b, c, 1994, 1995), which had revealed a lack of information on this important subject. The picture of the research that had been done in this area appeared to be fairly complete (cf. Section 2.3). It was apparent that **static headspace analysis** was widely used to determine volatiles, especially residual monomers, in polymers (see, for example, Hachenberg, 1975; Hachenberg and Beringer, 1996; Kolb et al., 1981a, b, c; Kretzschmar, 1987; Lattimer and Pausch, 1980) but the **method of choice** for identifying trace radiolysis products was clearly the more sensitive **dynamic technique** (dynamic headspace analysis or thermal desorption[#]).

Apart from a few application notes (cf. below), there appeared to be little information on volatiles in polymers, and it was assumed that probably neither radiation nor polymer chemists had been very much interested in analyzing trace volatiles. This assumption, however, turned out to be wrong when the scientific literature was searched for 'volatiles' and 'polymers' (omitting any reference to 'radiation'). The search led to a number of quite interesting papers that will be reviewed in some detail in Section 2.7, because they confirmed the author's view of thermal desorption, and, especially, the premises underlying quantitation.

In practical terms, the starting point for setting TDS-, CIS-, and GC-parameters had been three confidential chromatograms from Gerstel, obtained with (non-irradiated) plastic films—one of these, a fingerprint of a microwave food wrap, has meanwhile been published (Hoffmann and Bremer, 1994). The work of Azuma et al. (1983, 1984a, b), and of Rojas de Gante and Pascat (1990) had provided additional guidance, e. g., on column selection. The application notes mentioned above were a three-page „sample handling bulletin" featuring fingerprints of PE, styrene-butadiene, polysulfon, and PP (Anonymous, 1991), and two notes with fingerprints of polycarbonate and „a butadiene-based polymer" (Anonymous, 1989a, b).

[#] The principles underlying these techniques are, in fact, so similar that the terms **dynamic headspace analysis** and **thermal desorption** are increasingly used as synonyms, for example by Venema (1986), who gives yet another synonym, **gas-solid extraction.** In practice, TDS instruments usually permit higher desorption temperatures, while dynamic headspace equipment offers the possibility to irradiate polymers in closed vials, i. e., to analyze the volatiles that have been released into the headspace during irradiation.

2.7 Quantitative Aspects of Thermal Desorption

In this section, several papers on thermal desorption (and related techniques) are reviewed that are, in my opinion, quite important and also quite instructive; Table 2.3 gives a first impression of their content. It can be seen that many of the authors experimented with *specially designed* desorption equipment, and that—with the efficiency of today's *capillary columns* being vastly superior to those of packed columns—the work of four is now clearly out-dated with respect to the GC-separation that could be achieved. Nevertheless, these papers represent a period of method development with authors discussing the potential and the quantitative aspects of the technique, and this is precisely what still makes them interesting reading.

The method of **Meyer (1974)** involves an integrated *vacuum-distillation-GC* system that looks quite complex, but it is a dynamic method entirely comparable to thermal desorption. Results are presented for some rather light-weight volatiles: Hexane and hydrocarbon volatiles in HDPE, H_2O and hexane in PP, and n-butanol in HDPE. The chromatograms were recorded with an FID, an MS, or a TCD (for water). The topics discussed include the determination of suitable sample sizes, distillation temperatures and times, *quantitation* with external standards using a solvent-flush injection technique (!), and experiments demonstrating the *recovery* of volatiles. The method was routinely used for water and hexane in PP at levels ranging from 5 ppm to 5%; n-butanol could be monitored down to 0.1 ppm.

The work of **Ligon and George (1978)** is probably best characterized in the words of Myers (cf. below), who says it is „excellent"—but adds that „their equipment is complicated and not easily made." The chromatograms presented include fingerprints of high-impact polystyrene

Table 2.3 A quick look at some of the papers under review (see text for details).

Reference	Dev.	GC	Qu.	Key Words
Meyer, 1974	–	–	+	V*acuum distillation*-GC method; hydrocarbons in HDPE
Ligon and George, 1978	–	–	+	TDS-GC-MS; High-impact PS (HIPS), PMMA, PC, etc. excellent discussion of quantitative aspects
Shen, 1977	–	–	–	TDS-GC-MS; solvents in flame retarding polystyrenes
Myers, 1982	–	–	+	TDS-GC; *solvent exposure history* of polymers
Venema, 1986	+	+	+	Dynamic HSA-GC (overview); MMA monomer in PMMA
Venema, 1988	+	+	+	Residual styrene in polystyrene
Watanabe et al., 1991	–	+	+	New pyrolyzer for TDS and/or Pyrolysis-GC; Plasticizers in acrylonitrile-butadiene rubbers
van Lieshout et al., 1996	+	+	+	*Multi-step* thermal desorption–pyrolysis technique using a high-temperature PTV-injector
Hagman & Jacobsson, 1988, 1989	–	+	+	Theoretical model; *multiple dynamic headspace extraction* (MDHE); antioxidants in PE and PP
Hodgson et al., 1998	–	+	+	Toward an optimized dynamic headspace method for the study of volatiles in LDPE

Legend: TDS **Dev**ice: author's design (–) / commercially availabe instrument (+);
GC Column: packed (–) / capillary (+);
Quantitative aspects are discussed: yes (+) / no (–).

(HIPS), PMMA, polycarbonate, and Nylon-6,6, which were desorbed at temperatures ranging from 175°C (HIPS) to 300°C (PMMA, PC). The authors observe that „even relatively polar, high-MW 'volatiles' can be successfully desorbed," they propose various applications for the technique (e. g., confirmation of polymer identification), and comment on the necessity to avoid „areas of lower temperature [cold spots] between the desorption device and the GC." They estimate that, with 300 mg-samples, detection limits are in the range of 30 ppb to 30 ppm,—and down to 3 ppt when the MS is operated in SIM-mode; they also consider, in this context, the dangers of loosing GC resolution or of contaminating the MS-ion source due to sample overload.

Futhermore, Ligon and George give an *'operational definition'* of the term 'volatile' („some material with a vapor pressure so high that it can be vaporized by heating at a temperature lower than the thermal decomposition point of the polymer"), and discuss the factors influencing the *efficiency* and *rate of desorption*. (In this context, they assume that „the polymer substrate is not fundamentally different from a GC-liquid phase.") They conclude that an efficient extraction of volatiles requires „a *temperature* above the polymer's glass transition and below its decomposition temperature, a *continuous flow design*, and preferably a substrate configuration with *minimal particle cross section"* [emphasis added]. The authors finally anticipate *that a quantitative mode of analysis is possible, if desorption temperature, time, and particle size are optimized* for a given combination of polymer and volatile(s).

In a closely related paper, Ligon and Johnson (1976) describe an earlier version of their TDS-device; they provide a description of its design and an evaluation of its performance; the transfer of material was found to be of „reasonable efficiency" and „acceptably reproducible." The upper MW-limit for effective transfer was determined with a crude oil distillate (desorbed at 300°C and with Tenax GC as adsorbent): A reduced transfer efficiency was observed to start around C-22 ($C_{22}H_{46}$).

Shen (1977) does *not* consider quantitative aspects, he directly desorbes whole polymer pellets (as done in 'Phase I' of the present investigation—cf. Chapter 4). Shen's „in-situ sampling system" permits to heat samples for a certain period of time in air (!) or in a controlled atmosphere, and then to transfer the volatiles to the GC. The materials under investigation are several commercial flame-retarding *polystyrene* resins, and the focus is on *thermal degradation* of PS at processing temperatures. Heating in air produced various aromatics (benzene, xylene, etc.), aldehydes (acetaldehyde, acrolein, benzaldehyde), and olefines (ethylene, butene, butadiene, etc.) indicating a certain extent of thermal degradation of the resin. Heating under helium atmosphere produced less volatiles and both acetaldehyde and acrolein were not observed. Various halogenated compounds (di- and tetrachloroethane, etc.) were also found; they were quite characteristic for the different PS resins and had been used as solvents for the flame-retarding agents.

The focus of **Myers (1982)** is on „*trapped solvents in polymers*" as a possible cause for mechanical failure or discoloration of plastic parts; TDS is used to examine the „*solvent exposure history*" of a polymer. After an introduction and a description of his apparatus (both still worth reading), he presents three examples how the method was successfully applied to engineering problems: In one case, a significant correlation could be established between the presence (ca. 0.1%) of entrapped solvents and *mechanical failure* of some PE parts. High concentrations of dimethylformamide (DMF; at ca. 460 ppm, as quantified by using an external standard) were found to be responsible for a delamination problem occuring with epoxy circuit boards. And trichloroethane could be identified as the cause for severe discoloration of some parts made of polypropyleneoxide.

The paper of **Venema (1986)** is based on a presentation made at a GC-symposium, it contains a *very concise* description of the principles underlying quantitation, which is highly recommended reading. The results presented were obtained with two commercially available dynamic HSA instruments, and with modern capillary GC columns. The examples include a determination of MMA monomer in PMMA (at ca. 120-130 ppm) showing that the desorption temperature should be above the glass transition point (T_g) of the polymer: The T_g of PMMA

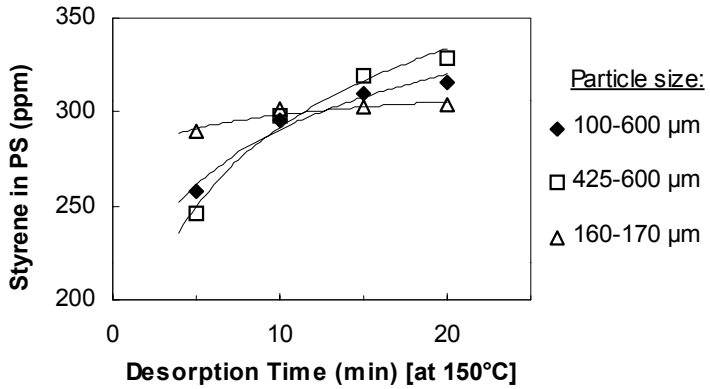


Figure 2.1 **Effect of particle size on the rate of styrene release from polystyrene.** In the case of the fine (160-170 ppm) particles, it appears that 99% of the residual styrene is desorbed after 10 min (and already >95% after only 5 min). Graph by the author based on data from **Venema (1988);** desorption temperature 150°C; gas flow (nitrogen): 10 ml/min, cryogenic trap: -100°C; detector: FID.

is 110°C, MMA concentrations sharply increase at a TDS temperature of 120°C (for 10 min) and then appear to reach a plateau at ca. 130°C. The author concludes that „for analyzing solid samples the dynamic headspace technique is to be preferred to the static method“ and that quantitation „can be performed simply and reliably by the external standard method.“

Venema (1988) has determined residual styrene in polystyrene by dynamic headspace-GC at levels of ca. 300 ppm; he demonstrates that the size of the polymer particles influences the desorption time needed for a complete removal of styrene (Figure 2.1), and that the mathematical treatment used by Kolb and Pospisil (1977) in multiple [static] headspace extraction (MHE) will fail in this situation. Interestingly, the conditions used by Venema for styrene (150°C for 5 to 20 min) are quite similar to the conditions established in the present study for acetophenone and 1-phenylethanol: 160°C and 200°C for 10 min (in Phases III and IV, respectively), the higher temperatures reflecting the higher boiling points of these polar analytes (ca. 200°C vs. 145°C for styrene).[#] Venema also presents some *qualitative* comparisons, showing, for example, the effect of an antioxidant on the thermal stability of a PETP/PE mixture, the detection of an impurity in a polyaramide, and of additives in PETP samples.

Watanabe et al. (1991) describe a specially designed pyrolyzer for either (single-step) pyrolysis at temperatures up to 800°C, or (two-step) thermal desorption followed by pyrolysis; the volatiles and/or pyrolysis products are analyzed by capillary GC with FID- or MS-detection. Optimum desorption conditions (temperature, time) were determined for three plasticizers incorporated at ca. 4% in an acrylonitrile-butadiene rubber. Thermal desorption at 300°C for 10 min „resulted in almost quantitative recoveries ... and excellent reproducibility.“

Moncur et al. (1981) describe a *two-step* dynamic headspace/pyrolysis-GC-MS technique with focused cryogenic trapping; they demonstrate how they used the technique to „troubleshoot complex industrial polymer products,“ e. g., a multilayer (electronic) circuit board. A *multi-step* thermal desorption/pyrolysis technique has been described by **van Lieshout et al. (1996):** samples are desorbed and subsequently pyrolyzed in a high-temperature PTV-injector (programmable temperature vaporization-injector), and the analytes are refocused in the capillary column by cryogenic trapping. The authors conclude that the „method has interesting potentials for the characterization of polymer compositions,“ that the system's

[#] For the effect of desorption time see Figures 6.2, 6.3, and 8.10 (Sections 6.2 and 8.8).

geometry reduces the risk of losing higher-MW compounds, and that reproducibility is „acceptable“ but has to be improved for quantitative analysis.

Volatiles from high-temparature polymers (polyimides) have been analyzed by **Long et al. (1988)**; their (semi-quantitative) work focused on the *relative* amounts of residual solvents left under varying process conditions.

Hagman and Jacobsson (1989) have developed a theoretical model for the quantitative determination of volatiles in polymers by *multiple dynamic headspace extraction* (MDHE). While some component parameters could only be estimated roughly, the authors note a „very good correlation“ between calculated and experimental results. They also studied the effects of some process parameters and conclude that for less volatile compounds the *desorption temperature* should be as high as possible (but lower than the melt index for the polymer), and that the best solution is generally to have a small *film thickness* and as high a *contact area* as possible. Finally they observe that the optimum *gas flow* depends on the geometry of the system, the type of extraction gas, and the efficiency of the cold trap. An application of the theoretical model to the analysis of volatiles in *polyethylene and polypropylene* has also been published **(Hagman and Jacobsson, 1988):** the authors observe that the concentrations measured for some additives were close to the values specified by the resin supplier; they conclude that the dynamic headspace technique is „a powerful method“ for analyzing solid samples, and that it gives reliable quantitative results.

The potential and limitations of a quantitative method for dynamic headspace analysis using *multiple runs* have also been discussed briefly by **Westendorf (1985)**; the method is analogous to multiple [static] headspace extraction (MHE) and does not work under certain conditions [e. g., when analyte recovery is very high—as Venema (1988) observed in the case of PS]. Westendorf (1985) gives one example of a quantitative analysis of a polymer: N-nitrosodimethylaniline was determined at ca. 37 ppm in a *rubber* baby-bottle nipple.

Manura (1993) has quantified butylhydroxytoluene (BHT) in food and food packaging materials. The emphasis is very much on various food items; the polymers are poorly identified (two „plastic wraps“ and two „chip bags“); and it is not entirely clear how quantitative desorption conditions were established. Calibration was achieved with what the author calls „spiked internal standards“ (ISTDs)—standard solutions of deuterated BHT injected into the TDS tube. As Manura himself notes that errors may „occur in weighing the solids, but also when injecting the ... ISTD,“ it would probably be more appropriate to speak of an external standard (or of some sort of ‘recovery standard’). A similar method has been used by **Panceram and Pernak (1996)** to quantify volatiles in polyurethane foams; the method is based on a test protocol of the Landesgewerbeanstalt Nürnberg (Germany) (Paul Pernak; personal communication), and again the reader is somewhat misled by the term ‘ISTD.’

Hodgson et al. (1998) have recently published a paper concerned with *optimizing* dynamic headspace conditions for the study of volatiles in LDPE. They are interested in a *complete* extraction of volatiles not to quantify individual compounds, but to characterize potential off-odours from PE. Comparing the design and efficiency of their experimental system with those of others, they introduce a parameter ε, characterizing the extent to which a given system is purged. This very interesting discussion has inspired me to apply the mathematical analysis of Hodgson et al. (1998) to the thermal desorption system I have used, and in **Section 5.11,** at the end of Chapter 5, I would like to comment, briefly, on the **Geometry and Efficiency of the TDS-CIS-System.**

2.8 Other Applications of Thermal Desorption

> The remaining papers are certainly of interest in their own right, though none of them is concerned with *quantitatively* assaying the *total concentrations* of volatile products in a polymer. [The authors of three articles on microwace susceptor packagings (cf. below) attempted to determine the *amounts released* under conditions of use.]

Before proceeding with more recent research, one last paper from the era of packed columns should be mentioned: **Mlejnek's (1972)** „Analysis of volatiles in polymers by GC." After a brief survey of related sampling techniques, the author describes his TDS device, a „microreactor" that can be loaded with sealed glass ampoules containing the polymer. One of the examples Mlejnek presents is a chromatogram obtained with a butadiene-styrene paper-based laminate; among the volatiles identified are ethanol, toluene, styrene monomer, and acetophenone.

The following studies on microwave packagings do *not* use *dynamic* HSA; they have been included because their background is very similar to that of this work (i. e., concerns about the safety of a new technical process). Volatiles released from so-called *microwave susceptor* food packagings have been investigated by the U. S. Food and Drug Administration (FDA) and by the industry. **McNeal and Hollifield (1993)** describe the FDA's test protocol: Test strips cut from the susceptors are placed in headspace vials, heated in a microwave oven and analyzed by (static) HSA and gas chromatography. Qualitative analyses are performed with GC-MS, quantitation with GC-FID and a *standard additions* technique. The difficulties of accurately quantifying the amounts of specific chemicals are discussed, and a survey of 11 commercial susceptors illustrates the type of data obtained with this protocol. 44 volatiles have been identified from the 11 susceptors; 10 peaks with concentrations > 0.5 µg/in^2 (≈ 7.8 µg/dm^2) and many more with concentrations ≤ 0.5 µg/in^2 remained unidentified.

A less detailed account of these experiments is given in an earlier paper, **(Hollifield, 1991),** that additionally summarizes some related migration/extraction and temperature measurement studies. In response to FDA requests, industry associations have also developed test protocols; **Rose (1991)** describes a method very similar to the above, involving microwave heating, static headspace sampling, and GC-FID & GC-MS. His report summarizes methodological details, method validation (calibration, recovery studies), and qualitative and quantitative results for 42 different samples from 15 companies.

Sturaro et al. (1991) have identified „low-boiling products in the polystyrene matrix" by thermal desorption-GC-MS; PS pellets were directly desorbed (as done in the initial stages of this work) at a temperature of 200°C. The compounds identified represent four different groups: Solvents (toluene, tetrachloroethene), additives [2,4-di(tert-butyl)-phenol, bis(2-ethylhexyl)-phthalate], the monomer (styrene) and its byproducts (various alkylbenzenes), and the dimer with its isomers. The emphasis is on identifying the *dimer isomers* by spectra interpretation, comparison with known / published spectra, and comparison with spectra of authentic compounds.

Gilburt et al. (1991) of the London Metropolitan Police have examined the potential of TDS for establishing links between control and recovered materials in forensic investigations. Thirty-seven *clingfilms* made of PE, PVDC, and PVC were analyzed with an automated TDS-instrument and GC-FID. All 37 samples could be distinguished „by inspection of the overall pattern of peaks." Since exposure to light or contact with wrapped material caused major changes in the chromatograms, the authors concluded that TDS „is less useful for linking samples of ... differing histories," but that there is still „considerable evidential value in being able to link samples that have shared the same environmental history."

Tayler et al. (1989) have used a combination of TDS-GC-MS with computerized pattern analysis to differentiate between nine commercial polypropylene samples. The PP was investigated in the form of pellets which were directly desorbed at 150°C. All individual mass spectra of a chromatogram were added to obtain a *composite mass spectrum*, which was then analyzed with a PC-based *pattern recognition* software. The authors conclude that TDS-GC-MS pattern recognition is „a valid method for the differentiation of commercial PP samples" and, since the analysis of pyrolysis-MS data was less successful, that „the residual volatiles and additives ... are more important to the differentiation."

A basically similar approach (dynamic headspace-GC & pattern recognition analysis) has been used by **Hagman et al. (1988)** to differentiate between batches of a polypropylene/-polyethylene copolymer; in contrast to the method of Tayler et al. (1989), the multivariate data analysis of Hagman et al. (1988) is based on randomly chosen *GC-peaks* that are converted to a set of variables.

There are another three articles by this Swedish group: **Jacobsson (1984)** has identified volatiles in two types of pharmaceutical packaging materials by dynamic headspace-GC-MS; for example, 2-ethylhexanol, bis(2-ethylhexyl)phthalate, and 1,2,3-propanetriole in plasticized PVC, and aliphatic hydrocarbons and BHT in PP/PE copolymers. **Hagman and Jacobsson (1987)** describe a *multidimensional* dynamic headspace-GC-MS-system that uses a „cold trap–re-injection interface" to transfer a fraction of the volatiles to a second analytical column; the technique was used to identify volatiles in a PP/PE copolymer, and the authors demonstrate convincingly that the system's increased resolving power can help to solve complex separation problems. **Schmidt et al. (1988)** have coupled dynamic headspace-GC with an FTIR detector (Fourier transform infrared spectroscopy); they show some chromatograms and IR spectra obtained with PVC, polybutylene terephthalate, and with a toner for a laser printer (referred to as „polyacrylate").

Jansen et al. (1988) use TDS-GC with a *parallel* FTIR- and MS-*detector configuration*, with the MS being equipped for both electron impact (EI) and chemical ionization (CI). In one example (out of three) the authors demonstrate how the combination of IR spectrum, and EI- and CI-mass spectra helped to identify, in polycarbonate (PC), a p-alkylphenol used as chain regulator during polymerization. Volatiles from PC have also been studied by **McIntyre et al. (1994)** with TDS-GC-MS at relatively low temperatures (150, 75, and 50°C). The paper is mainly of interest because of its background, i. e., contamination of Si wafer surfaces (during semiconductor manufacturing) by VOCs released from polymeric materials.

The article „Headspace analysis of volatile impurities in polymers" by **Bureiko and Ioffe (1991)** is a brief review comparing *discrete* [static] against *continuous* [dynamic] headspace extraction, and discussing the kinetics of outgassing processes. The applications of static and dynamic headspace analysis have also been reviewed by **McNally and Grob (1985a, b);** in Part Two of the review, subtitled *non-environmental applications* (McNally and Grob, 1985b), 19 references are made to the analysis of polymers: 17 to the static, and 2 to the dynamic technique.

Finally, a special (though essentially static) headspace technique should be mentioned, i.e., the matrix-independent *full-evaporation technique*, which addresses „the problems associated with ... unpredictably changing sample matrices" **(Markelow and Guzowski, 1993).** The authors explain in detail the theory underlying the *full-evaporation* technique (the term refers to the evaporation of the *analytes* and *not necessarily* to the matrix), and they discuss some experimental results verifying the concept. It would be very interesting to see whether this method would work with the (relatively high-boiling) main radiolysis products of PS.

3. Experimental Section

3.1 The Experimental Program (Overview)

Screening of Six Medical Polymers (Chapter 4)

For an initial screening ('Phase I'), six different plastics were selected that are representative for the most commonly used polymers in medical device manufacturing. By coincidence, they also cover some important materials for food packaging. Since the objective was to search for unknown products, and since there was little guidance on experimental conditions, different GC columns were tried and instrumental parameters were continuously varied; in other words, the entire screening program was intertwined with initial efforts at **method optimization.** The chromatograms shown are the 'best' from a period of method development stretching over several weeks / months (cf. Section 3.6); no concentration changes could be observed during that time (except for PE), and no conclusions on diffusion processes could / can be drawn.

Polyethylene and Polypropylene Films (Chapter 5)

The experiments performed in 'Phase II' were, in some sense, a deviation from the original research program concerned with medical polymers. When the initial screening program had reached what appeared to be a 'dead end' (see Section 4.8 *Analytical Resumée*), I turned—half by accident—to the polyolefin films: During some pre-tests with packaging films that had been irradiated several months earlier two totally unexpected results were obtained—firstly, that radiolysis products **are retained in LDPE** (in contrast to the results reported by El Makhzoumi, 1994), and that they are retained **for considerable times,** and, secondly, that they are retained in polypropylene (PP) films **much longer than expected** (see Chapter 5).

Quantiative Analysis of Radiolysis Products in Polystyrene (Chapters 6–11)

When quantitation finally became possible (see Chapter 6), I decided to concentrate on PS, because (i) unlike LDPE and PP (see Section 2.3), polystyrene had not been investigated before; (ii) besides PE, PP, and PVC, polystyrene is the most important material for both food packaging and medical products (see Sections 2.1 and 2.2); and (iii) I was intrigued by the fact that this polymer—which otherwise is so resistant to ionizing radiation—produces detectable amounts of volatiles.

There were additional factors, as well: I expected that the results might also be of interest for other styrene-based polymers, such as SAN or MABS; the fingerprint chromatograms of PS were relatively 'clean' (in contrast to, e. g., those of MABS); and there were no such problems as, for example, the *caprolactam* memory effect observed with PA-6 (see Section 4.3). In the case of PP and PVC, I felt that the emphasis in a future investigation should be on the *stabilizers*, and that this complex matter should be addressed in a separate research project. A further argument against PVC was that there are attempts to ban, or at least to reduce, for environmental reasons, the use of chlorine-containing polymers.

3.2 Instrumentation

The TDS-GC-MS consists of a *Gerstel* thermal desorption-unit (TDS 1) that uses the *Gerstel* CIS 3, a cooled-injection system or PTV-type split/splitless-injector as interface to the GC column (Gerstel GmbH, 45473 Mülheim/Ruhr, Germany). The gas chromatograph, a *Hewlett Packard* HP 5890 Series II model, is connected to a mass spectrometer, a *Hewlett Packard* HP 5971A MSD (mass selective detector).

A schematic drawing of the TDS-unit is shown Figure 3.1, the entire system has also been described by Hoffmann and Bremer (1994). See Section 3.3 *Instrumental Modifications*, for more information on the TDS; the CIS's principle of operation is illustrated in Figure 3.2; and a temperature-time-diagram for the TDS, CIS and GC is shown in Figure 3.3 (see Section 3.6 *Experimental Conditions*).

The CIS is essentially a PTV (programmable-temperature vaporizer) or split-splitless injector that can be cooled down to –150°C using liquid nitrogen. The CIS serves as the interface betweeen the TDS-unit and the GC column: the volatiles are trapped at room or sub-ambient temperature in the injector liner (usually packed with an adsorbent, e. g., Tenax TA) and subsequently transferred to the GC column by rapidly heating the injection block—usually in splitless-mode (cf. Figure 3.2).

The CIS glass liner (or: *injector liner*; with an outer diameter of 2 mm) was filled with ca. 1.5 cm of the adsorbent Tenax TA (35 - 60 mesh; *Chrompack*, Lot. No. A 35). Tenax is a porous polymer based on 2,6-diphenyl-p-phenylene oxide (Anonymous, 1982).

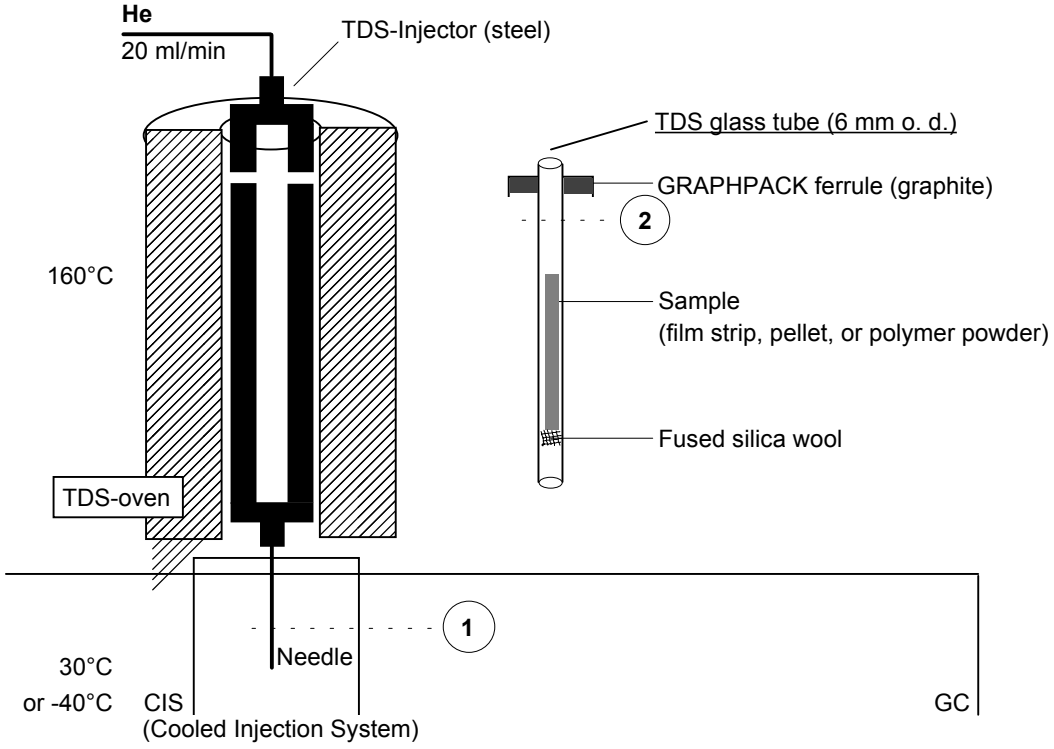


Figure 3.1 **The TDS-injector** (1, 2 = instrumental modifications, see text for explanation)

(1) The needle of the TDS-injector is shortened by 20 mm to minimize condensation of higher-boiling volatiles at the 'cold spot' where the needle protrudes into the CIS; and

(2) the TDS glass-liner is cut below the ferrule and the lower part replaced with single-use standard-laboratory glass tubing.

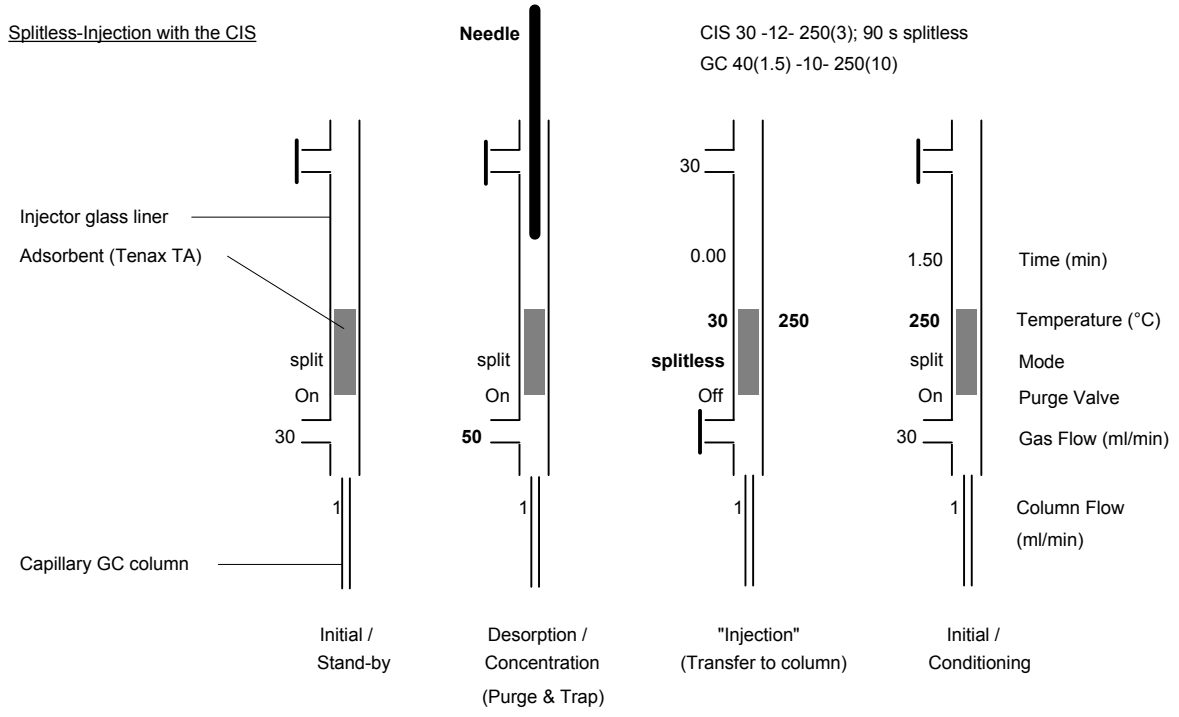


Figure 3.2 Schematic drawing of the **Cooled Injection System (CIS)**—essentially a temperature-programmable split-splitless injector (or: PTV = programmable-temperature vaporizer) that operates as the interface between the TDS-unit and the GC-column. The *volatiles* desorbed in the TDS are trapped in the CIS and transferred (usually in splitless-mode) to the analytical column (see text for further details; cf. also Figure 3.3).

3.3 Instrumental Modifications

The TDS-injector is originally designed to desorb adsorbent-filled sampling tubes from environmental air analyses. The volatiles in these tubes are quantitatively removed either in the desorption step or later at somewhat higher temperatures (*baking out* the adsorbent). When it was decided that it would be desirable to go beyond the melting temperatures of the polymers, a serious *cleaning problem* arose, since the graphite fitting (Graphpack ferrule) on top of the desorption tube (cf. Figure 3.1) should be protected from solvents (if one does not want a huge solvent peak in the chromatogram), and since it can be removed only a limited number of times (without starting to leak).

The best solution turned out to be cutting the glass tube ca. 1 cm below the fitting and replacing the lower part with carefully cleaned ‘single-use’ pieces that were cut from standard laboratory glass tubing (see Figure 3.1). This may result in a slight (and usually acceptable) increase in background peaks and / or may require that the (metal) TDS-injector is cleaned.

Another problem that could not be totally resolved is partial condensation of higher-boiling components in the cool section of the needle protruding into the injector. Acceptable results could be obtained either by *not totally inserting* the TDS-injector (less recommended) or by *reducing the needle length* as much as possible (the better way; cut ca. 20 mm from the needle’s tip—see Figure 3.1). This *cold spot* (not an uncommon problem in thermal-desorp-

tion–cryo-focussing techniques) can force the analyst to concentrate *either* on the highly volatile *or* on the higher-boiling components (or to run each analysis in duplicate).

Another 'instrumental modification' is (in some sense) the '*Stainless-Steel Sieve Sandwich* Technique' for measuring polymer films—it is described in Section 5.5 (Figure 5.5).

3.4 Other Equipment

Analytical Mill

A piece of equipment central to quantitation in Phases III and IV was the **analytical mill,** which allowed to ground the PS pellets and parts into a fine powder (see Chapter 6 for the principles underlying quantitation).

A *Janke & Kunkel* laboratory mill (Janke and Kunkel GmbH & Co KG, 79219 Staufen, Germany) was used to produce fine PS powders; it could be described as a 'somewhat-more-sophisticated coffee mill' revolving at 10,000 rev./min. (In fact, initial attempts to mill polystyrene with a standard coffee mill had failed because its plastic cap had started to fragment under the impact of the PS particles). The analytical mill comes with a *full-metal* milling chamber which can externally be cooled with water, and with a rotor having two relatively blunt blades. For light-weight analytes, the manufacturer recommends the use of a special *sharp-edged four-blade rotor* ('star-rotor'), and of a *disc that reduces the size of the milling chamber* (by sealing off the dead volume in the mill's cap).

Operating the Mill and the Problem of Particle Size

With these two special pieces of equipment (the 'star-rotor' and the disc), standard PS can be pulverized quite easily with, or even without, water cooling. **0.5 to 1 g PS at a time** were usually milled by operating the mill for exactly **one minute.** The particle size or particle size distribution of the powders was not analyzed. The problem was considered several times in the course of this work, but I was not convinced that a better definition of particle size would significantly improve the results (cf. the data of Venema (1988) discussed in Section 2.7). Of course, a standardization of particle size would be better laboratory praxis, and an easy way to achieve it in future investigations (e. g., interlaboratory trials) would be to analyze only a certain *sieve fraction*.

Polymers that are less brittle (MABS and others) require the addition of small quantities of liquid nitrogen as a coolant. Another interesting concept is to add water to the polymer, to freeze the mixture by adding liquid nitrogen, to mill the ice-covered polymer particles, and then to dry the powder under vacuum. The theory is that ice of –196°C has a much higher capacity to absorb the heat generated by milling than liquid nitrogen alone. This procedure was used only for a few samples milled *before* irradiation; the drying step does apparently not affect any 'precursors' of the radiolysis products, since their concentrations were not diminished. It was not investigated whether this method would result in a loss of radiolysis products (or other low-MW compounds), if it were applied after irradiation.

Analytical Balances

For quantitation, 5 or 10 mg PS powder (see Table 3.2) was directly weighed into the desorption glass tubes. This was done in Phase III with a 'standard' analytical balance with a scale division (d) of 0.1 mg, and in Phases IV and V with a *Sartorius* 'Research RC 210 P' model with d = 0.01 mg.

3.5 GC-Columns

The Columns Used

The following **synopsis** shows which columns were used in the various 'Phases' of this work; for the rationale behind these choices (or, sometimes, trials) see the following two Sections entitled *A Comment on Column Selection* and *Columns for Quantitation*. The columns' technical data are listed in Table 3.1, and in later Chapters they are referrred to only as „the DB-5," the „DB-1701" etc.

Phase	Chapter(s)	'Project'	Column
I	4	Screening ...	Supelcowax 10, DB-5, DB-1701, SP 2330
II	5	PE & PP Films	DB-1701, Rtx-1701
III	6, 7	Initial Quantitation	DB-5
IV	8, 9	Confirmation	Supelcowax 10
V	11	Benzene	DB-5

With PS, some qualitative comparisons were also performed 'pre-Phase III' with the Rtx-1701 (Chapter 6), and 'post-Phase III' with an Rtx-200 (50%-trifluoropropyl-50%-methylpolysiloxane; 30 m; 0.25 µm; Restek). Experiments to identify trace products in PS (Chapter 10) were performed in Phases I, III, IV, and 'post-Phase III' with the DB-5, the Supelcowax 10, and the Rtx-200.

Table 3.1 List of columns used (wall-coated open tubular (WCOT) fused silica types; all with an inner diameter of 0.25 mm).

	Stationary Phase	L ; f. t. [a]	Manufacturer
Supelcowax 10	Poly(ethylene glycol)	30 ; 0.25	Supelco
DB-5	5%-Phenyl-95%-methylpolysiloxane	30 ; 0.25	J & W Scientific
DB-1701	14%-Cyanopropylphenyl-86%-methylpolysiloxane	60 ; 1.0	J & W Scientific
Rtx-1701	14%-Cyanopropylphenyl-86%-methylpolysiloxane	60 ; 1.0	Restek
SP 2330	50%-Cyanopropylphenyl-50%-methylpolysiloxane	60 ; 0.25	Supelco

[a] Dimensions: Length (m) ; film thickness (µm)

A Comment on Column Selection

There is, of course, ample advice on proper column selection in the scientific literature and in the catalogues of column manufacturers, however, if you do not know what you are looking for and what your separation problem might be, it is best to try different columns, and that is what I did initially. With an MS as detector, column *diameter* is restricted by the pumping capacity of the vacuum system. The use of a 60 m-length column in the case of the DB-1701 was pure chance, since, after trying our standard 30 m (and 0.25 µm f. t.) DB-5 and Supelcowax columns, I asked a colleague for a column with a *medium-polarity* phase and did not want to cut it. This column, with its somewhat thicker film (1 µm), was particularly suited for the more volatile compounds in the PE and PP films; however, when

quantitation became possible (Chapter 6), I soon got tired of having to wait longer—with no apparent benefit—for the high-boiling compounds to elute, and so I switched to the DB-5. In Phase IV, I finally went back to the Supelcowax 10 to achieve a detection limit below 10 ppb (10 pg) for the alcohol 1-phenylethanol. However, as long as it does not show adsorption in the relevant concentration range(s), a DB-5, or, depending on the compounds you are interested in, any other column, may also be perfectly suited for PS.

In summary, it is highly recommended to try different columns, because the polymer *fingerprint* chromatograms are so highly complex that there always will be coeluting peaks (and, even with an MS, one needs at least *some* separation to be able to do *meaningful* 'calculations,' such as spectra subtraction etc.).

As far as column *film thickness* is concerned, there exists an inherent dilemma in this type of analysis, caused by the extremely differing concentrations of the compounds desorbed. *With thin films*, the sensitivity for trace compounds increases, while the peaks of the main components become more and more overloaded, thus obscuring ever greater segments of the chromatogram. *Conversely, increasing film thickness* (column capacity) reduces overloading and sensitivity simultaneously—in other words, a trace compound that formerly may have been hidden in the fronting flank of a (severly overloaded) peak may now be below the detection limit.

Columns for (Polystyrene-) Quantitation

For quantifying the *main radiolysis products* of polystyrene, a DB-5 column was used in Phase III, and a Supelcowax 10 column (polyethylene glycol) in Phase IV—the reasons for this switch have been mentioned briefly in the previous section and are further detailed in Sections 7.8, 7.9 and 8.2. Selecting the DB-5 for *benzene* analysis was part of the related method development—in fact, no suitable solvents were found that would allow a splitless-injecton of benzene standards with either the Rtx-1701 or the polyethylene glycol column: see Chapter 11.

To summarize: I would presently recommend a polyethylene glycol phase for the main products (especially when using the 'DSC-Method,' see Chapter 9), while a DB-5-type phase *must be* used for benzene.

3.6 Experimental Conditions and Methods

Desorption (TDS) temperature and time; *injector*-temperatures (i. e., trapping *and* 'injection' temperatures) and *splitless-time*; *column* phase, length and film thickness; and the *MS* conditions have to be optimized for a given polymer, the radiolysis product(s) of interest, and their concentrations. In the later (quantitative) stages of the present work, for example, two different columns and two sets of injector conditions were used—one for benzene, and one for the main radiolysis products of polystyrene. This is partially a consequence of the TDS-CIS design (see 'the cold spot problem' in Section 3.3 *Instrumental Modifications*), but mainly due to the very different chromatographic behaviour of benzene and 1-phenylethanol (see Chapter 11.3).

Phases I and II: Qualitative Analyses (Chapters 4 and 5)

Initially, the sole guidance on experimental conditions had been the work of Azuma et al., and Rojas de Gante and Pascat (see Section 2.3), plus three confidential chromatograms from *Gerstel*, obtained with (non-irradiated) plastic films—one of these, a fingerprint of a microwave food wrap, has meanwhile been published (Hoffmann and Bremer, 1994).

As mentioned in Section 3.5, columns were frequently switched and instrumental parameters were continously varied. *Key experimental parameters* (TDS-, CIS-, and GC-settings) deviating from those established later for PS quantitation (Phases III and IV) *are indicated in Chapters 4 and 5 using the* **abbreviated notation** *explained below.*

Polymer granulates (usually 3 to 5 pellets), fragments of injection-molded parts, or film samples were directly desorbed without any pre-treatment. The samples were analyzed one day, and up to several weeks / months, after irradiation.

For the polymer films, a special technique, the '*Stainless-Steel Sieve Sandwich* Technique,' was developed to prevent the collapse of the films' surface at higher desorption temperatures; it is described in Section 5.5 (Figure 5.5).

Phases III and IV: Quantitative Analysis of the Main Products in PS (Chapters 6 to 10)

The principles of TDS-quantitation and the establishment of 'total desorption' conditions are the subject of Chapter 6. The rationale underlying the 'DSC-Method' is explained in Chapter 9; for technical details see Figure 9.1 and the related text.

Fine PS powders were obtained with an analytical mill as described in Section 3.4; 5 or 10 mg PS powder (see Table 3.2) was directly weighed into the desorption glass tubes (cf. the subsection *Analytical Balances* in 3.4). Calibration was achieved with external standards (cf. Chapter 6, Section 3.8, and the Appendices containing the original data).

The following *sets of experimental conditions were used for quantitation*; key experimental parameters are summarized in Table 3.2:

TDS	TDS temperatures and times see Table 3.2; TDS flow: 20 ml/min (helium).
CIS	X°C –12°C/s– 250°C (3 min); 90 s splitless; X is the initial hold (= trapping) temperature, i. e., –40°C or + 30°C according to Table 3.2.
Carrier gas	Helium with a 'total' flow of 30 ml/min; CHP = 0.6 or 0.8 bar (Table 3.2); the resulting linear velocities and volumetric flows are plotted in Figure A-2.1 of Appendix 2; analyses with the 60 m Rtx-1701 column were performed with a CHP of 1.5 bar.
GC	Temperature programs see Table 3.2.
Columns	See Tables 3.2 (and 3.1).
MS	Transfer line temperature: 280°C; Electron impact (EI) ionization at 70 eV; Scan range: 33-300 (2.6 scans / second); Scan treshold: 500; Electron multiplier voltage (EMV) = Tune value (ca. 2000 V).
SIM	MS SIM parameters see Tables 3.3 and 3.4.

Phase V: Quantitative Analysis of Benzene in PS (Chapter 11)

The development of a quantitative TDS-method for benzene is the subject of Chapter 11; the experimental conditions developed in this process are given in Section 11.4.

Table 3.2 Experimental conditions: Main differences between Phases III and IV.

	Phase III	Phase IV	Phase IV — DSC
Sample	5 mg // 10 mg [a]	5 mg	10 µl of 1% PS in CH_2Cl_2 (≡ 0.1 mg PS)
TDS	160°C (10 min)	160°C (10 min) and 200°C (10 min)	200°C (10 min)
CIS	–40°C	+30°C	+30°C
	split // splitless 90 sec [a]	splitless 90 sec	splitless 90 sec
GC	CHP: 0.6 bar	CHP: 0.8 bar	CHP: 0.8 bar
	CIS-Injection: 40(1.5) -10- 250(5) [b] TDS-Analysis: 40(11.5) -10- 250(5) [b]	40(1.5) -10- 210(8.5)	50(1.5) -20- 220(6)
Column	DB-5	Supelcowax 10	Supelcowax 10
MS	Scan 33-300 // SIM [a]	Scan 33-300	SIM

[a] **Three** series of measurements were performed in Phase III: (1) split-scan-5 mg, (2) splitless-scan-5 mg, and (3) splitless-SIM-10 mg.

[b] As explained in the text (see: *An Important Note: System Times vs. Real Retention Times*), the old version of the software started its time count **with** thermal desorption. The newer version used in Phase IV started when the desorption step was over; therefore, there is **no** difference between TDS-analyses and CIS-injections.

Table 3.3 MS SIM parameters in Phase III (splitless-SIM-analyses).

Group ID	Start Time (min)	m/z	
Phe + Paa	x6.7 [a]	94.1	91.1
1-Pet + Acp	x8.1 [a]	79.1	120.1

Dwell time = 30 ms, Low mass resolution = ON;
MS switched OFF at x8.5 min; [a]
EMV = Tune value *plus* 200 V.

a x = 0 for CIS-injections,
x = 1 for TDS-analyses.

Table 3.4 MS SIM parameters in Phase IV (DSC-method).

Group ID	Start Time (min)	m/z	
Sty	4.5	78.05	104.00
Acp	7.5	76.95	120.00
1-Pet	8.2	79.00	107.05
BHT	9.0	205.10	220.15
Phe	9.5	66.00	94.00

Dwell time = 30 ms, Low mass resolution = ON; MS switched OFF at 5.00 min, ON at 7.50 min, and OFF at 10.10 min.

Abbreviated Notation

As mentioned, TDS-, CIS-, and GC-conditions in Phases I and II may be quite different from those used for PS quantitation, and an **abbreviated notation** is used to indicate the respective parameters. In this notation, the conditions from the first column in Table 3.2 would be written as follows:

TDS 160(10); CIS –40; GC 40(11.5 #) –10– 250(5)

with *normal-type figures* representing hold temperatures in °C, *parentheses* indicating hold times (in minutes), and *hyphens* indicating temperature rates –in °C/min–; for the CIS, only the 'initial hold' (= trapping) temperature is given. Figure 3.3 shows a temperature-time-diagram for TDS, CIS and GC.

 # An Important Note: System Times vs. Real Retention Times

With the software version used initially (in Phases I to III), data aquisition started with the beginning of thermal desorption (*System Time* as indicated in Figure 3.3)—please note that the GC-run (or: *chromatography proper*) starts at time 10.00 min ! The updated software version used in Phases IV and V starts its time count with the *injection* (= *after* thermal desorption is completed).

Consequently, whereas the chromatograms in Chapters 4 through 7 allow a direct reading of retention times (system time = retention time), one has to subtract the TDS-time (usually 10 min) from most of the chromatograms presented in Chapters 8 through 11 to obtain real retention times.

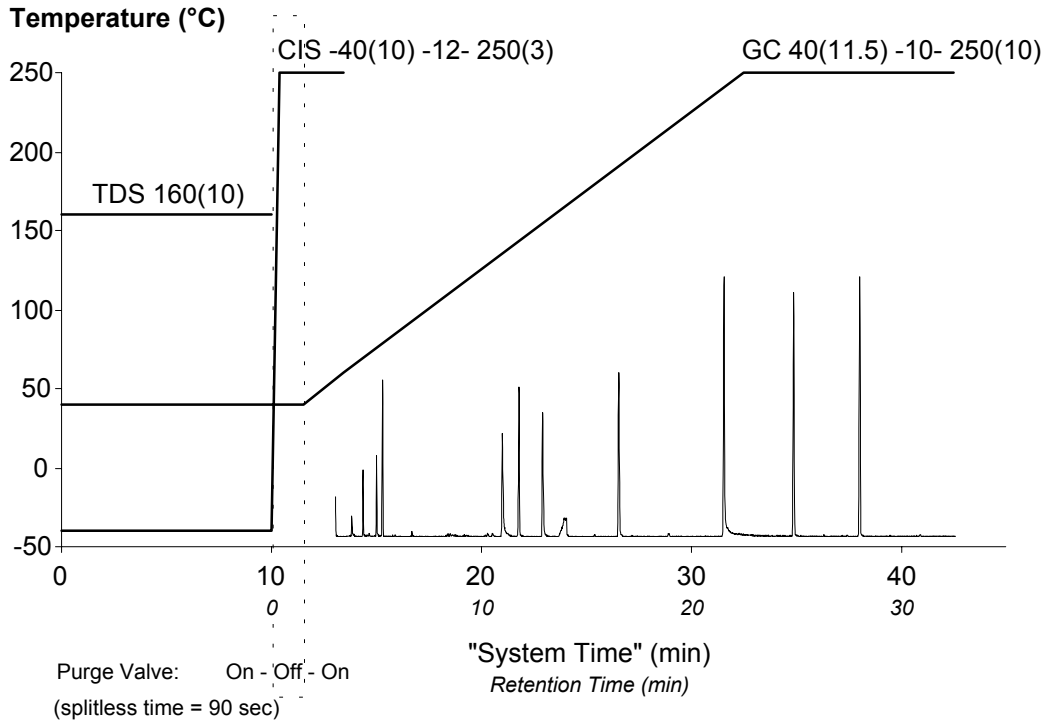


Figure 1.3 Temperature diagram (TDS-, CIS-, and GC-temperatures) for typical experimental conditions. **System Time** versus **real retention time** see text.
The abbreviated notation used in this diagram (e. g. TDS 160(10)) is also explained in the text.

3.7 Polymers under Investigation & Irradiation Conditions

Phase I: Medical Polymers (Chapter 4)

All six plastics under investigation (Table 3.5) meet the requirements of various European and/or U. S. Pharmacopoeia monographs or tests (e. g., USP class VI); all manufacturers are ready to supply more detailed information and/or certificates.

Table 3.5 Sample description—medical polymers.

Polymer		Type	Manufacturer	Lot No.
Polystyrene	PS	Polystyrol 168 N	BASF AG [c]	65-204-3 18H0984
Methyl methacrylate-Acrylonitrile-Butadiene-Styrene	MABS	Terlux 2802 TR trans-parent	BASF AG [c]	22895901
Polyamide-6	PA-6	Ultramid B3S ungefärbt [un-dyed]	BASF AG [c]	03-206-5 275 19H8852
Poly(vinyl chloride)	PVC	Hyvin VQ 130 clear 116 [a]	Hydro Polymers Ltd. [d]	F9937.F7
High-Density Polyethylene	HDPE	Lupolen 5031 L	BASF AG / Elenac GmbH [e]	134 304022
Polypropylene	PP	Neste VC 1064 K [b]	Neste Chemicals B. V. [f]	2399B

[a] The PVC formulation is not gamma-stable and contains an organotin stabilizer.

[b] A gamma-stable homopolymer containing Irgafos 168 [= tris-(2,4-di-t-butylphenyl)-phosphite] and three other additives.

[c] BASF AG, 67056 Ludwigshafen, Germany.

[d] Hydro Polymers Ltd., Newton Aycliffe, Co. Durham, DL5 6EA England, U. K.

[e] BASF AG, now available from Elenac GmbH, 77694 Kehl, Germany.

[f] Neste Chemicals B. V., now available as 'Borealis HD800P' from Borealis A. B., 44486 Stenungsund, Sweden.

To detect pure radiation effects (if any) it was decided to study a system as simple as possible, namely the pellets as received (i. e., as they are received by the medical device manufacturer from the resin supplier), and, in a second step, to investigate possible effects of processing (injection-molding), which usually involves high temperatures and pressures.

The six medical polymers—pellets and the injection-molded parts made from them—were kindly supplied and irradiated by the Braun AG, a medical device manufacturer based in Melsungen, Germany. The samples were irradiated with absorbed doses of ca. 25 kGy in the company's in-house sterilization facility, a batch-type ^{60}Co-gamma-irradiator, at an average dose rate of ca. 1 kGy/h; they were packed in sealed LDPE/polyamide bags. Some lower-dose irradiations were done with the experimental ^{60}Co-source of the Hahn-Meitner-Institut (HMI), Berlin. Dosimetry was performed with *Red Perspex Type 4034 BX*[#] dosimeters, the reported absorbed dose values are **accurate to ± 10%.**

[#] For information on dosimetry with Red Perspex (= dyed polymethylmethacrylate, PMMA) see Sharpe (1990), and, especially, Barret (1982).

Phase II: PE and PP Films (Chapter 5)

Initial experiments were performed with some poorly defined 'commercial' LDPE films (e. g., cut from a 1.5 liter-milk bag), and with polypropylene film „A", which contained as major anti-oxidants: 0.040% Irgafos 168, 0.035% oxidized Irgafos, 0.002% Irganox 1076, and 0.021% Irganox 1010. The film was kindly provided by Prof. Otto Piringer, Fraunhofer-Institut für Lebensmitteltechnologie und Verpackung, München.

The investigation was then extended to some LDPE Lupolen types (see Figure 5.3), and to three PP Novolen types (3225 MCX, 1325 L, and 1125 L). Lupolen and Novolen are trademarks of the BASF AG (Ludwigshafen). The Lupolen films typically did not contain additives, except 2003 H (contains an antiblocking agent) and 2424 H (lubricants & antiblocking agents); 2441 D contained 1% n-BA as co-monomer. The Novolen films were described as homo-polymer (1125 N), homo-polymer with a higher atactic fraction (1325 L), and as random co-polymer (3225 MCX). The BASF Lupolen and Novolen types were kindly provided by the BASF AG (Ludwigshafen), with the exception of Lupolen 2410 F (film and pellets) and Lupolen 3020 K, which were kindly provided by 4P Folie (Forchheim).

Most of the PE and PP film samples were again irradiated by the Braun AG with absorbed doses of ca. 25 kGy; they were packed in LDPE bags. Some lower-dose (1, 3, and 10 kGy) and one 20 kGy-irradiation were done with the experimental ^{60}Co-source of the HMI (cf. the previous section).

Phases III and IV: Polystyrene Quantitation (Chapters 6 to 10)

The initial ('Phase III') quantitation was performed with the 'old' PS samples that were at hand; to confirm the results, the samples were again analyzed in Phase IV together with newly irradiated polystyrenes and with some 'real-life samples.'

The materials under investigation are listed in Tables 3.6 and 3.7 (Phase III) and Table 3.8 (Phase IV); the Tables show the absorbed doses, the time elapsed after irradiation, and the **codes** used in later Chapters to identify the samples. The 'new' samples were again kindly provided and/or irradiated by the Braun AG.

Table 3.6 Materials analyzed in Phase III **— polystyrene (PS):** BASF *Polystyrol 168 N* granulate (Lot No. 65-204-3 18H0984), and injection-molded parts made from this resin:

Sample	Dose (kGy)	Time p. I. [a]	Code [b]	Code [b]
Granulate	0	---	G, C	0 Gy
Granulate	25.5	18 months	G, I	25.5 kGy
Injection-molded Parts	0	---	P, C	----
Injection-molded Parts	24.7	15 months	P, I	----
Granulate	1, 3, and 10	2 months	----	1, 3, and 10 kGy

[a] Time elapsed since irradiation

[b] Code: The PS powder samples are identified *either by a two-letter code*, where **G = Granulate**, **P =** Injection-Molded **Part, C =** Non-Irradiated **Control** (0 Gy), **I = Irradiated** (sterilizing doses only) *or by the absorbed dose*. In the case of polystyrene, **G, C / P, C / G, I** and **P, I** were prepared **four months** before Phase III-quantitation for qualitative comparisons, while the other powders were prepared some **days** before the analyses.

Table 3.7 Materials analyzed in Phase III **— methyl methacrylate-acrylonitrile-butadiene-styrene (MABS):** BASF *Terlux 2802 TR transparent* granulate (Lot No. 22895901), and injection-molded parts made from this resin:

Sample	Dose (kGy)	Time p. I. [a]	Code [b]
Granulate	24.4	17 months	G, I
Injection-molded Parts	24.9	15 months	P, I

[a] Time elapsed since irradiation

[b] In contrast to PS, the coded MABS powders **G, C / P, C / G, I** and **P, I** were prepared some **days** before the analyses.

Other Samples in Phase III:

— **Petri Dish x kGy**: a Becton Dickinson *tissue culture dish* from our laboratory shelf labelled as „sterile/gamma irradiated," made of PS.

— Yoghurt Tray: a tray from a local market labelled with a PS-recycling symbol, probably made of some PS-copolymer.

Phase V: Quantitation of Benzene in PS (Chapter 11)

Benzene was quantified in a polystyrene *molecular-weight* standard with an average molecular weight M_W of 170,000 g/mol (Arro Laboratories, Joliett, Ill., USA).

Film samples were obtained by solvent-casting; the films were irradiated *under vacuum* or *in oxygen* with the experimental ^{60}Co-gamma source of the Hahn-Meitner-Institut (HMI), Berlin.

Absorbed Doses:

437, 946, and 1460 kGy (under vaccum)

127 and 276 kGy (in oxygen)

> **Note**
>
> These 'high dose'-irradiations were part of an entirely separate project (the 'LET-Project' mentioned in Section 11.5); the quantitative experiments were performed with these samples, since they had been irradiated most recently when the benzene method was established (cf. Sections 11.3 and 11.4), and the expected higher yield was a welcome side-effect.

Table 3.8 Materials Analyzed in Phase IV.

Non-irradiated controls are not listed in this Table. In later chapters, specimens will be identified by a **Code** consisting of the designation plus the absorbed dose, e. g., **186N 0 Gy** (= non-irradiated), **XY 23.5 kGy**, or **Petri Dish x + 23.5 kGy.**

Designation	Dose (kGy)	Time p. I. [a]	T. [b]	Annotations	
168 N	23.5			c	
168 N diss.-prec.	23.5		TDS	c, d	Pre-treated
168 N t.ds. 160(60)	23.5			c, e	Pre-treated
168 N	25.5	ca. 2.5 years		c	
168 N	22.5	ca. 2.5 years	DSC	c	
168 N Parts	24.7	ca. 2.25 years	DSC		Injection-molded parts
168 N	10	ca. 1.25 years	DSC	c	
XY	23.5			f	
1x-Glass	23.5				One-way (party) 'glass', PS
Petri Dish	x	Unknown		g, j	RLS ('real-life-sample')
Petri Dish	x + 23.5			g	RLS, re-irradiated
Culture Flask	x	Unknown		h, j	RLS
Culture Flask	x + 23.5			h	RLS, re-irradiated
N. Cult. Flask	> 15 kGy	ca. 9.25 years (!)	DSC	i	RLS
Yoghurt Tray	23.5			k	Copolymer
Tray 'WM'	23.5		TDS	k	Copolymer
Tray 'F'	23.5		TDS	k	Copolymer
MABS	23.5		TDS	l	

[a] Time elapsed since irradiation. No time is given for the newly irradiated 23.5 kGy specimens, which were analyzed ca. 8 days after irradiation (ca. 4 weeks p. I. by the DSC-method).

[b] Technique: Indicates whether a specimen was analyzed, in Phase IV, with only *one* technique:
TDS = 'conventional' TDS-analyses (desorption of powder) only
DSC = DSC-method only
(No entry = *both* techniques).

c BASF Polystyrol 168 N granulate.

d Dissolved in dichloromethane and precipitated with methanol (prior to irradiation, to reduce low-molecular weight fraction).

e Thermally desorbed at 160°C (60 min) under a 20 ml/min flow of Helium (prior to irradiation, to reduce low-molecular weight fraction).

f Polystyrene XY: A *new* medical-grade polystyrene granulate supplied by the Braun AG.

g A Becton Dickinson tissue culture dish labelled as „sterile/gamma irradiated".

h A culture flask from our laboratory shelf with label: „5102 LUX, Tissue Culture Ambitube™, 16 x 110 mm, 10 Tubes, Sterile, Polystyrene, Lot No. 142158, Lab-Tek Division, Miles Laboratories."

i A Nunclon culture flask with label: „Sterilized by Gammairradiation at Nuncatom Co-60 irradiation plant, Min. dose 1.5 megarad, Date of irradiation and ref. no. 15. Jan 86 044360 ... ."

j Absorbed doses and irradiation dates are unknown.

k Commercial trays with „PS" recycling symbol but apparently not made of standard polystyrene.

l Methyl methacrylate-acrylonitrile-butadiene-styrene: BASF Terlux 2802 TR transparent.

3.8 Standards and Solvents

The standards and solvents used are listed in Table 3.9.

In most cases, n-hexane was used as the solvent. Stock solutions of 1-phenylethanol, acetophenone, phenol, phenylacetaldehyde, and styrene were prepared by dissolving ca. 100.0 mg of the standards, accurately weighed, to 100.0 ml. Calibration standards were prepared by diluting the stock solutions; concentrations of the standards were typically in the range of 1 to 100 ppm for quantitation of 'normal', splitless TDS-analyses, and in the range of 0.1 to 10 ppm for the DSC-Method (see the Tables containing the original data in the related Appendices).

In the case of benzene, dichloromethane (CH_2Cl_2) had to be used as solvent (see Ch. 11).

Table 3.9 Standards and solvents.

	Quality	Supplier / Art. No.
1-Phenyl-1,2-ethanediol	for synthesis	Merck 807007
1-Phenylethanol	98% GC	Aldrich P1380-0
Acetophenone	for synth., > 98% GC	Merck 800028
Benzaldehyde	puriss., DAB 6	Merck
Benzene	rückstandsfrei	Merck
BHT (2,6-Di-tert.-butyl-p-kresol)	purum	Fluka 34750
Dichloromethane	Uvasol® / for spectroscopy	Merck 6048
Grob-Mix [a]	-----	Fluka 86501
Hexane	„Baker analyzed" ®	Baker 9262-54
Phenol	p. a.	Merck 100206
Phenylacetaldehyde	50% in DEP	Fluka 77800
Styrene	for synth., >99%	Merck 807679

[a] „Test mixture 2 for capillary columns according to Grob," cf. Section 7.10.

3.9 On Product Identification by Mass Spectrometry

In the scientific literature one may occasionally find the statement that „compounds have been identified," accompanied by listings that may look like the following:

- Pentane-, 2-hydroxy-, 2-methyl-
- Cyclobutane-, 1,1-dimethyl-
- (etc. pp.)

Considering this *inversed* nomenclature, one is tempted to suspect that this might be the result of an automated library search, and wonders whether the authors have thought much about the plausibility of these proposals (or tried to confirm the identity of the more obscure of the proposed compounds).

One may also read that „compounds have been *tentatively* identified," which clearly indicates that the results have been obtained solely by interpreting the mass spectra (interpreting, of course, would include library searching),—and that no authentic samples have been analyzed for confirmation. With some exceptions (most notably the main radiolysis products of PS, *plus* benzene) the identifications in this study are also tentative, often con-

taining elements of an *informed guess*, or supported by additional *circumstantial information*. All compound identifications reported are considered to be highly probable; whenever I felt not entirely convinced, I preferred to label a compounds as *Unknown / Unidentified*, or, at least, to make my reservations explicit in some way.

The following considerations may help the reader, who is not familiar with mass spectrometry, to understand the underlying concepts.

The library searches performed with the HP ChemStation *Data Analysis*-software use a probability-based-matching (PBM) algorithm that finds the best matches in a library of recorded spectra and returns them with a match probability (or 'quality') factor. These match qualities depend—for pure GC-peaks—on the quality of both spectra (that under investigation and that in the library !) that is, ultimately, on various MS operating parameters, and they are influenced by the setting of some search algorithm variables.

Generally, a match quality of 90 is considered, in everyday language, as *almost 100% sure*. However, you do not always get a quality of 90, even if you inject pure standards of compounds that yield higly characteristic mass spectra; you may not get 90 when trying to match a spectrum that you recorded ten minutes earlier with your own instrument and then copied into the library; you may get several wrong proposals for a known injected standard that have better match qualities than the true spectrum; and, finally, you may get several fits better than 90—this is often the case with isomers.

It may appear then that library searches are not of much use and that tentative identifications are not very reliable, however, this is where circumstantial evidence comes in, and, of course, experience and a basic understanding of mass spectrometry. You will not be surprised to find residual monomers and oligomers in polymers, so there is no reason to be much worried about the spectra of styrene and its dimer in PS, of ε-caprolactam in polyamide-6, or of alkanes in PE. In the case of PE, one usually finds the almost complete homologous series of the alkanes, which makes it virtually impossible to assign them incorrectly—one being identified everything else 'falls in place.' (Besides, styrene *was* injected as were various hydrocarbons that were on the shelf... .) Or, consider polypropylene: you get 1,3-bis-(1,1-dimethylethyl)-benzene with a match quality of 92. Knowing that the compound has already been identified as radiolysis product of sterically hindered phenol antioxidants, and knowing that PP is practically never processed without antioxidants, you will be very confident about its true identity.

Another example are the carboxylic acids: None of them has been injected as a standard, and match qualities were usually far below 90. However, the spectra are highly characteristic and there is additional chromatographic information: the peak shape—tailing or fronting depending on the column used (which is clearly unsatisfactory from a chromatographer's point of view...)—indicates compounds with 'extreme' properties (here: acidity and / or polarity), thus supporting the library proposal. Unfortunately, the spectra of many aliphatic compounds are much less characteristic than those of most aromatic compounds, and therefore, more difficult to interprete or to match with library spectra. This is reflected, for example, in Figure 4.8 (PVC), Table 5.1(LDPE film), or Figure 5.8 (PP film).

3.10 On Data Analysis with 'Extracted Ion Chromatograms'

Chromatographers, of course, have occasionally complained about a tendency 'from separating to calculating' (Günther, 1995), arguing that achieving a (perfect) baseline-separation is what chromatography is all about, rather than 'sorting things out' with sophisticated detectors. While I basically share this view, I felt justified to do some 'calculations,' since the fingerprint (!)-chromatograms are usually so complex that it is virtually impossible to separate *all* compounds in a single run.

The main reason for calculating the areas of extracted 'ion tracks' (EIC-Peak Areas) is to reduce the error introduced by possibly co-eluting compounds, which contribute to the total ion chromatogram (TIC), but much less likely to properly selected exctracted ion chromatograms (EICs). Usually, when running a series of calibration standards in (full) scan-mode, you may obtain two calibration curves (i. e., concentration vs. EIC- and concentration vs. TIC-peak areas, respectively) that yield almost identical quantitative results—for pure samples and complete separation. However, with decreasing concentrations resulting in decreasing peak sizes, EICs become less reliable (as do, finally, the TICs themselves), and at this point you will switch to a selected ion monitoring (SIM) method, scanning, for example, the characteristic m/z ratios you formerly used to extract from the TICs.

What is important, however, for some results presented in this study, is to bear in mind **that ratios of peak areas do not necessarily reflect ratios of concentrations,** and this is especially so with EICs and with 'real' SIM-chromatograms. Consider the following chromatograms (Figure 3.4) of an 1-phenylethanol (1-Pet) / acetophenone (Acp) standard (10 ng each). As it happens—by chance, or rather due to their similar chemical structures—the response factors in the MS and, therefore, the TIC-peak areas are almost equal; however, if you extract the characteristic ions m/z 79 and 120 for 1-Pet and Acp, respectively, the ratio will become ca. 2 : 1 (for ions x and y it may become 1 : 3, or anything). So, if you see a diagram such as the following (Figure 3.4: *EIC-peak areas* in three consecutive runs), you should **not** conclude that the **concentration** of compound A is three times that of compound B (the real factor might be 6, or 0.1, or anything); you can only conclude that the concentrations are apparently independent of the other parameter (in this case the No. of runs). You may also conclude that, as explained above, I possibly wanted to exclude errors due to coeluting peaks, or—in Phases III to V—that, for some reason, I did not 'absolutely' quantitate this particular series of measurements or these particular compounds.

3.11 Obtaining Clean Blanks and The Problem of Adsorptive Activity

Obtaining **clean blanks** has been a major problem that often interfered with the analyses. Of course, 'clean' is a *relative* concept, and *acceptable* levels of contamination (memory effects) may vary widely depending on the concentration of a radiolysis product, the absorbed dose, and the type of analysis (i. e., 'normal' TDS-analysis vs. a DSC-analysis—see Chapter 9).

In the TDS-analysis of polymers, 'clean blanks' should be considered as a means to an end, not as an end in itself. It is highly recommend to compare any background peaks in a blank

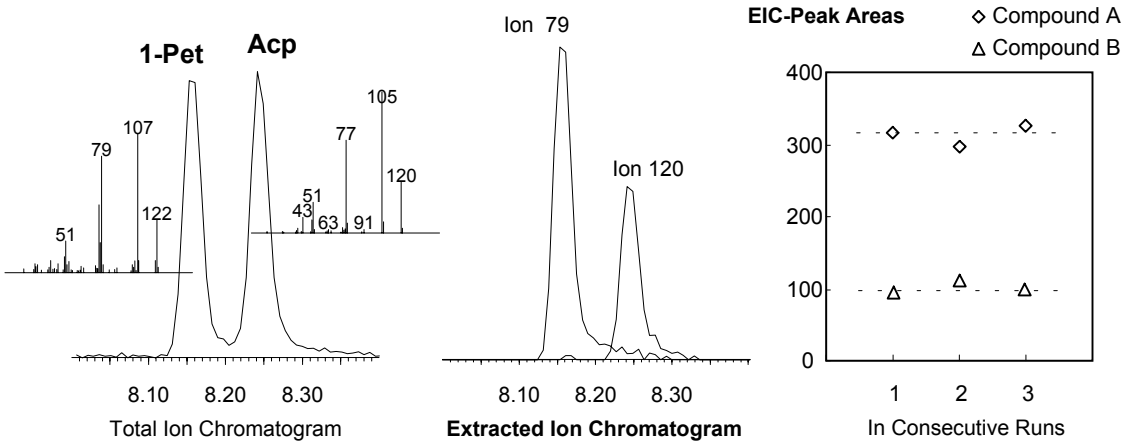


Figure 3.4 **Extracted** vs. **Total** Ion Chromatograms (see text).

against standards of known concentrations (e. g., calibration standards or the Grob-Mix, see Section 7.10), and then to assess their potential effect on quantitation. [It is a good idea to inject a standard, e. g., the Grob-Mix, when recording a blank, i. e., effectively performing a TDS-Performance-Test (see Section 7.10). Unfortunately, this is not always possible, for example, if one is interested in volatile compounds that co-elute with the solvent(s).]

For the single-use TDS glass tubes (cf. Section 3.3) three different cleaning procedures were used, which all led to acceptable results: One method, used in Phase III, consisted of *ultrasonic cleansing* in (1) hot water with an added detergent, (2) methanol, and (3) dichloromethane, followed by drying under vacuum. Another method, used in Phase IV, consisted of boiling in conc. HNO_3, rinsing with double-distilled water and drying in an oven at 450°C (the theory being that all organic matter is oxidized to CO_2 and H_2O at that temperature). Finally, in Phases IV and V, the glass tubes were simply boiled in an Extran (Merck) solution, rinsed with distilled water, and dried in the oven at 450°C.

Contamination of the TDS-needle is a problem that cannot be avoided in the TDS-analysis of polymers, since, especially at higher desorption temperatures, relatively high-boiling material (e. g., in PS, styrene dimers and trimers) will condense in the cold tip of the needle. This problem is largely absent in environmental *air* analysis, where it therefore makes sense to go to some length to prepare very clean and 'artifact-free' sampling tubes—see, for example, Helmig (1996).

We have, in intervals, rinsed the TDS-needle by pipetting small volumes (ca. 0.5 ml) of various organic solvents (cyclohexanone, hexane, dichloromethane, acetone) into the TDS-injector, and then connecting it to the TDS-gas line to press the solvent(s) through the needle. The injector was then dried overnight in the TDS-oven with a small flow of helium passing through it. It should be noted that this procedure produces memory effects of its own: The solvent(s) will be present as (a) major peak(s) in the following analyses.

A problem that was not sufficiently addressed is the presence of **active sites** in the TDS—mainly on the surface of the glass liner, but probably also in the (stainless steel) needle of the TDS-injector. Recovery of the analytes in both, *recovery tests* (with the standards) and *TDS-Performance-Tests* (with the Grob-Mix) appeared to be consistently somewhat lower than 100% (see, e. g., Figure 6.5 and Figure A-15.5 in Appendix 15) — especially for the more polar compounds, such as 1-phenylethanol (1-Pet) or 1-octanol (ol).

Reproducibility of manual injections into the cold injector (CIS) is relatively good (Figure 6.5), and so the effect is probably genuine. However, since one can perform only a limited number of test injections, the extent of the problem was initially under-estimated. I did not introduce any correction factors into the quantitative equations (= the formulae used to calculate concentrations), because the situation may be different for the desorption of powders: For polar analytes the chances of getting adsorbed to 'active sites' may be relatively low when they are desorbed from the polymer surface and then carried away by the carrier gas. In contrast, their chances of getting adsorbed are probably higher when they are injected as a solution, left behind on the glass surface by the evaporating solvent, and then have to be desorbed into the gas stream.

In any case, it might be a good idea to make further attempts to desactivate any *active sites* that are present on the surface of the glass liners. Besides 'conventional' desactivation, e. g., *silylation*, an interesting alternative might be *polyimide coating* as described by Biedermann et al. (1997). To reduce any background peaks I would also suggest to develop some conditioning process (e. g., heating the glass tubes under a flow of He or N_2), and to store these desactivated and conditioned tubes under an inert atmosphere.

Ultimately, it would certainly be worth the effort to attempt some *engineering re-design* of the TDS/CIS-interface in order to reduce the length of, or possibly eliminate, the 'cold spot' at the tip of the TDS-needle.

4. Screening of Six Medical Polymers

4.1 Polystyrene (PS)

Magnitude of the Radiation-Induced Changes

The results obtained with PS are quite typical insofar as the concentrations of the radiolysis products after ca. 25 kGy are *ca. one order of magnitude* lower than those of the monomers / oligomers / low-MW compounds already present in the non-irradiated polymers (see Figure 4.1). There was one remarkable exception to this general rule, namely, PP (cf. Section 4.6), where an aromatic degradation product of an antioxidant became the dominant peak in the fingerprint chromatograms. The results were also somewhat unexpected, because PS is one of the most radiation-resistant polymers, and it was quite surprising to find that several radiolysis products can be detected in PS quite easily.

Figure 4.1 shows a fingerprint chromatogram of PS, irradiated with 25.5 kGy, to illustrate the magnitude of the radiation-induced changes in comparison to the residual styrene and dimer levels. Drawn to the same scale, the chromatogram of the non-irradiated control would look practically identical with respect to styrene, the dimer and its cyclic analogue (cD), toluene (T), ethylbenzene (E), and 1,1'-(1,3-propanediyl)-bis-benzene (Pbb); in other words, there is no detectable change in the peak areas of these compounds.

The Main Radiolysis Products

The main radiolysis products of PS are shown in Figure 4.2, which is a detail view of Figure 4.1 (t_R 16–19 min) compared against the non-irradiated control. The products are benzaldehyde (with an increase in peak area of ca. 73%), phenol, phenylacetaldehyde [1-phenylethanal], 1-phenylethanol (below detection limit in the control; in scan mode), and acetophenone [1-phenylethanone]. The identity of the five compounds was *confirmed by comparison with authentic samples* (splitless-injection of 10 ppm-solutions of the compounds under identical CIS and GC conditions); their structural formula are given in Figure 4.3. (The ab-

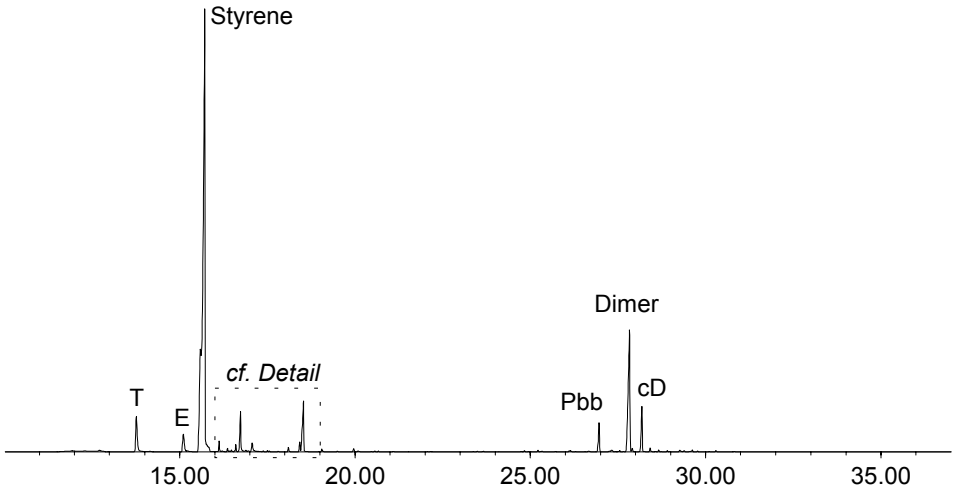


Figure 4.1 **Fingerprint chromatogram** of polystyrene, irradiated with 25.5 kGy.
T = Toluene Pbb = 1,1'-(1,3-Propanediyl)-bis-benzene
E = Ethylbenzene cD = Diphenylcyclobutane ('cyclo-dimer').
Experimental Conditions: Sample: BASF Polystyrol 168 N (5 pellets), six weeks after irradiation with 25.5 kGy; TDS 150(10); CIS 30; GC 40(11) -10- 250(5); column: DB-5.

breviations in Figures 4.2 and 4.3 are introduced here, since they will be used in the quantitative Chapters.)

As you may have noticed, the chromatograms in Figure 4.2 were recorded six weeks after irradiation. The sole reason for not showing one of the earlier chromatograms is that separation of 1-phenylethanol from acetophenone (Acp) was very bad initially. While an acceptable separation could be achieved by optimizing column flow and the GC temperature-program (please note that the Acp-peak shows *fronting* due to overloading), there was apparently *no change* in the concentration of the radiolysis products during these six weeks; there was, in other words, no decrease with time that could be detected with the TDS-methods still being in the early stages of development.

Irradiation Detection vs. Material Balances

In Table 4.1 some of the products are characterized in terms of their *relative vs. absolute increases* in peak areas. According to their absolute yields the products might be classified as major (benzaldehyde, acetophenone) minor (1-phenylethanol), or trace products (2-phenylpropenal), whereas the relative increase indicates the potential of a compound as *radiation marker* (cf. also Figure 4.2). Clearly, compounds such as 1-phenylethanol [1-Pet] will be more promising candidates for an attempt to distinguish irradiated from non-irradiated materials, whereas radiation chemists, interested in establishing a material balance, may not want to neglect compounds such as benzaldehyde. An ideal radiation marker would (1) be produced in a 'radiation-specific' reaction (though this is a somewhat problematic statement), and (2) be below detection limit in the non-irradiated control. Supposed the sensitivity of one's method is not an issue, one will not be much interested in its absolute yield (or amount produced). Initially, 1-Pet seemed to be a radiation-specific product (Figure 4.2); later measurements, however, clearly established its presence as a trace impurity in non-irradiated PS (cf. Chapters 7, 8, and 9).

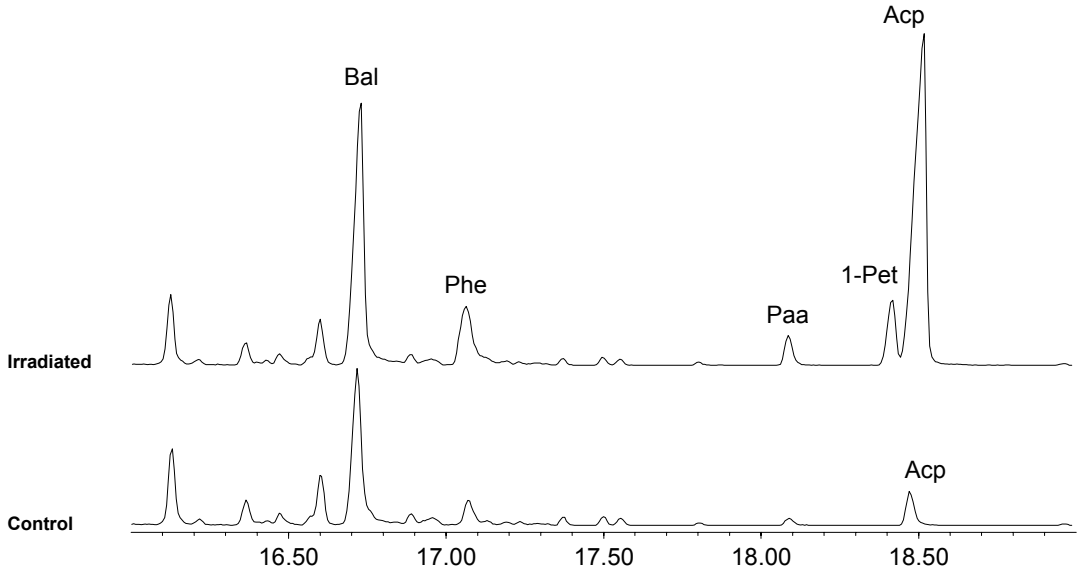


Figure 4.2 The **main radiolysis products of PS**: Detail (t_R 16–19 min) of Figure 4.1 — irradiated (25.5 kGy; top) vs. the non-irradiated control (bottom).
Bal = Benzaldehyde Paa = Phenylacetaldehyde Acp = Acetophenone
Phe = Phenol 1-Pet = 1-Phenylethanol

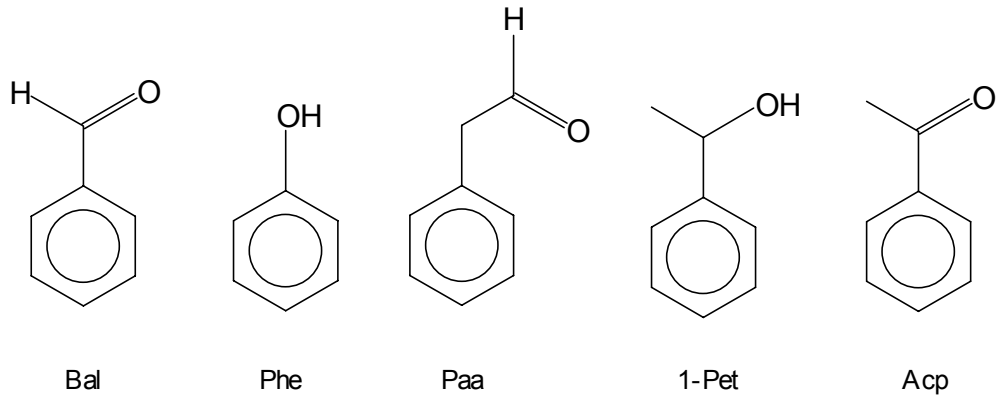


Figure 4.3 Formula of the main radiolysis products of PS (cf. Figure 4.2): Bal = Benzaldehyde, Phe = Phenol, Paa = Phenylacetaldehyde (Benzeneacetaldehyde), 1-Pet = 1-Phenylethanol, Acp = Acetophenone (1-Phenylethanone).

These considerations are, of course, somewhat simplistic and linked to existing product concentrations in the non-irradiated controls. Also, the term 'absolute yield' should not be confused with 'radiation-chemical yield' (expressed in nmol/J, or, in an older non-SI-unit, as G-values (= molecules per 100 eV of absorbed energy)). 'Real' radiation-chemical yields for radiolysis products of PS are presented in Sections 7.4 and 9.7.

Trace Products

There are additional minor radiolysis products with concentrations approximately one order of magnitude below that of the main products: the concentration of 2-phenylpropenal, for example, is at least ten times lower than that of acetophenone (cf. Table 4.1). These trace products were investigated in more detail at a later stage (see Chapter 10).

Table 4.1 Peak areas (arbitrary units) for some radiolysis products of PS (cf. Figure 4.2; see text for explanation).

	Non-irradiated Control (C)	Irradiated with 25.5 kGy (I)	**Relative Increase**	**'Absolute' Yield**
Compound	A [C]	A [I]	Quotient A[I] / A[C]	Difference A[I] – A[C]
Benzaldehyde	16,831	29,080	x 1.7	12,249
Acetophenone	3,091	42,263	x 13.7	39,172
1-Phenylethanol	---	4,985	---	4,985
2-Phenylpropenal [a]	312	2,035	x 6.5	1,723

[a] Not visible in Figure 4.2 (t_R = 19.96 min).

Benzene in PS

Evidence of benzene formation in gamma-irradiated PS is presented in Figure 4.4. Initially, the small benzene peak had been overlooked; only in Phase III, when quantitation of the main products had revealed the true sensitivity of the TDS-technique, the question imposed itself: Shouldn't there be some 'side-chain scission' in PS resulting in the formation of—at least trace amounts of—benzene? And should the technique not be sensitive enough to detect these traces? Consequently, those of the earlier chromatograms were re-examined that had been obtained under conditions most favorable for a compound as volatile as benzene, i. e., those obtained with a CIS-temperature of –40°C and with the 'thick film' (1 µm) DB-1701 column (Figure 4.4). Benzene was also found in a series of quantitative analyses of the main products (see Figure 11.1).

Since benzene is toxic and a carcinogen, and since the MS response factors of analytes may vary to some degree, it was very desirable to quantify the compound. Clearly, it is not a major problem to analyze higher concentrations of benzene, e. g., in gasoline, by gas chromatography with *split*-injection, and it is also not a problem to analyze traces of benzene in, e. g., environmental water samples, by GC with *purge & trap-injection* (applications for both types of analyses are described in the catalogues of most column suppliers). The difficulties arise from the need to quantitate *trace amounts of a volatile compound in a polymer matrix*. Good peak shapes with relatively volatile compounds, such as benzene, are obtained with thicker-film columns, as often used in purge & trap-analyses (and as demonstrated in Figure 4.4). However, in contrast to, e. g., spiking water with benzene, it is clearly impossible to distribute exactly known ppm-amounts of benzene in a polymer matrix, in order to produce (external) calibration standards for TDS-analyses. The alternative was quantitation by *splitless*-injection of benzene solutions (as already practiced with the main products); it required finding a combination of *solvent*, *column* (phase), and *splitless time* that produced sufficient reconcentration of benzene (solvent effect) without interference of benzene with the 'solvent tail.' The benzene method and the results obtained are presented in Chapter 11.

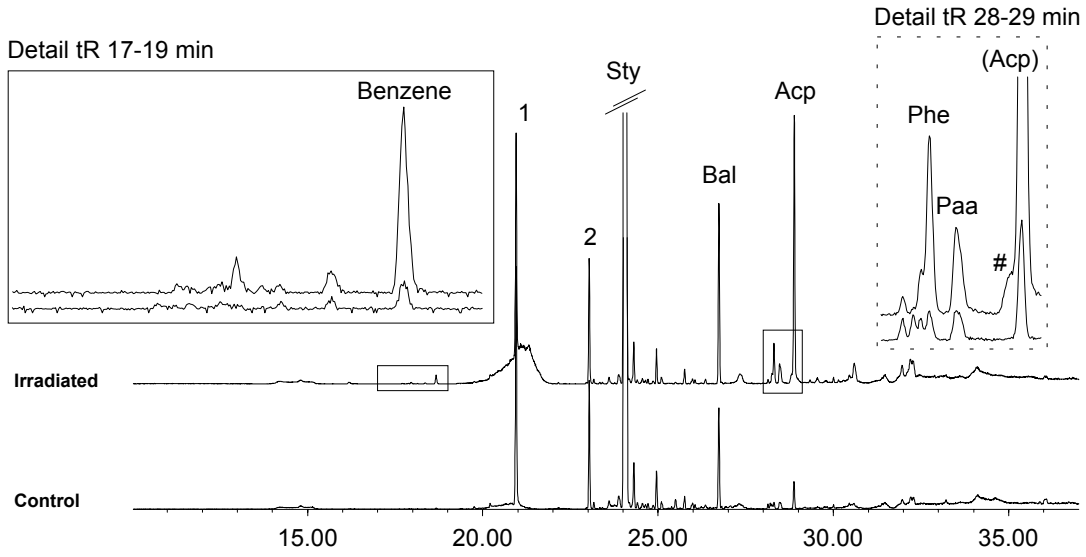


Figure 4.4 **Benzene formation** in PS irradiated with 25.5 kGy (top) vs. non-irradiated control (bottom); the details giving an impression of the magnitude of benzene formation vs. the main products.
1 = Toluene # = 1-Phenylethanol (as shoulder on Acp)
2 = Ethyl- or Dimethylbenzene Other symbols as in Figure 4.2.
Exp. Condit.: As in Fig. 4.1, but recorded 2 months after irradiation with the DB-1701 column.

4.2 Methyl methacrylate-Acrylonitrile-Butadiene-Styrene (MABS)

General

As one would expect, the fingerprint chromatograms of the *methyl methacrylate-acrylonitrile-butadiene-styrene* polymer (MABS) are quite complex (not shown). Three of the *main* peaks, namely, methyl acrylate, and the residual monomers methyl methacrylate and styrene, are clearly *decreased* by irradiation; the 'trace monomer' acrylonitrile disappears almost completely. The disappearance of unsaturated monomers is well known (e. g., Derbyshire, 1979; Ludwig et al., 1988); it is ascribed to covalent binding to the polymer molecules. Incidentally, covalent binding has also been demonstrated for antioxidants by Allen et al. (1990a, 1991a), see Section 2.4. A similar effect is seen with the 1-alkenes in HDPE (cf. Figure 4.9), but, as mentioned, no reduction of styrene levels could be observed in PS.

The Aromatic Radiolysis Products

I was mainly interested in the aromatic degradation products already known from PS, namely benzaldehyde, acetophenone, phenol, 1-phenylethanol and 1-phenyl-1-propanone. As with PS, acetophenone is the main aromatic product, and formation of benzaldehyde is somewhat obscured by its small relative increase, in other words, by the presence of relatively large amounts in the non-irradiated control. *Minor* and *trace* aromatic products may be overlooked quite easily in chromatograms as complex as the MABS-fingerprints. This is demonstrated in Figure 4.5 (left chromatograms) for phenol, phenylacetaldehyde, and 1-phenylethanol. To document the formation of these products in MABS, SIM-analyses were performed monitoring only the ions characteristic for the three compounds (plus acetophenone)—see Figure 4.5 (right chromatograms). Please note that the four chromatograms have been recorded 7.5 months after irradiation without any sample (pre-) treatment, i. e., by di-

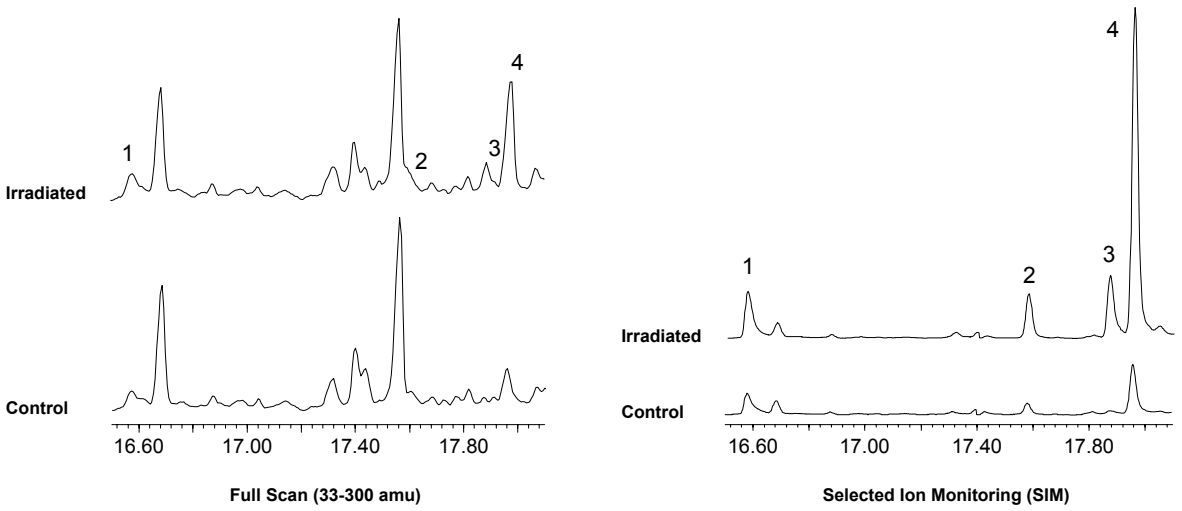


Figure 4.5 **Main aromatic radiolysis products of MABS:** Details (t_R 16.55–17.95 min) of 24.4 kGy-sample (top) vs. non-irradiated control (bottom) — full scan (left) vs. SIM data acquisition (right chromatograms).
1 = Phenol 3 = 1-Phenylethanol
2 = Phenylacetaldehyde 4 = Acetophenone.
Experimental Conditions: Sample: BASF Terlux 2802 TR transparent (3 pellets), 7.5 months after irradiation; TDS 150(10); CIS 30; GC 40(11) -10- 250(5); column: DB-5.
Ions monitored in the SIM runs: m/z 39, 66.1, and 97 for Phe; m/z 65, 91, and 120.1 for Paa; m/z 79, 107, and 122.1 for 1-Pet; and m/z 77, 105, and 120 for Acp.

rectly measuring the pellets. The aromatic radiolysis products of MABS were re-examined in Phase III (PS quantitation; see Section 7.7).

In addition to the aromatic compounds with their characteristic mass spectra, there are many aliphatic, often oxidized radiolysis products, e. g., 1-dodecene (?), hexanal, or acetic acid. Generally, their mass spectra are much less characteristic, and often quite demanding to interprete; most of these compounds are probably alkenes or oxidized hydrocarbons (aldehydes, ketones, and alcohols—with and without olefinic double bounds).

Benzene in MABS

With MABS yielding all the major products already observed in PS, it was only logical to extend the search for *benzene* to MABS. Clearly, the absolute levels of benzene are very low, but they were definitely and consistently increased in the 24.4 kGy-samples up to (at least) 4 weeks after irradiation (Figure 4.6).

Suggestions for Future Investigations

Irrespective of the types (aromatic vs. non-aromatic) of radiolysis products one might be concerned about, it certainly would be worth the effort to re-examine MABS, and possibly *other styrene-based polymers* as well, using the somewhat more sophisticated techniques that were developed during PS-quantitation.

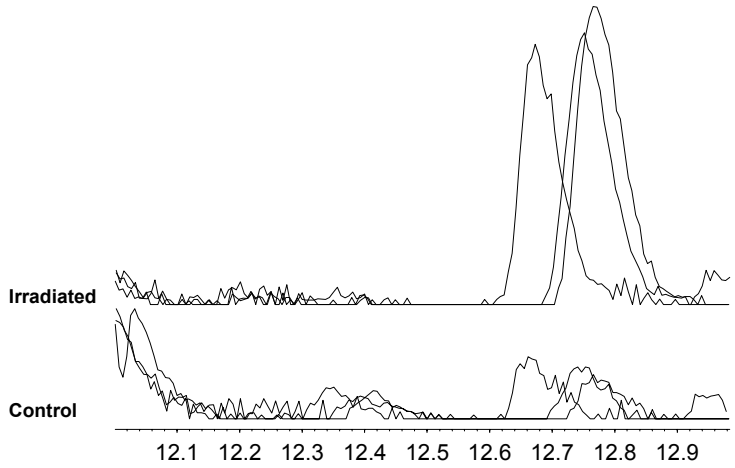


Figure 4.6 **Increase of benzene** (t_R = 12.75 min) **in MABS** irradiated with 24.4 kGy — three irradiated samples on days 2, 7, and 28 after irradiation vs. the corresponding non-irradiated controls; presented as *added* **extracted ion chromatograms** (for m/z 50 + 51 + 52 + 78).
Exp. Condit.: 3 pellets; TDS 160(10); CIS -40; GC 40(11) -5- 170 -20- 250(5); column: DB-5.

4.3 Polyamide-6 (PA-6)

Amide Formation

The main radiolysis product of PA-6 (poly-ε-caprolactam) is *pentanamide*; traces of hexanamide and of the homologous amides with one to four C-atoms (formamide to butanamide) are also formed. In chromatograms obtained with the Supelcowax 10 three weeks after irradiation, the peak area of pentanamide was ca. one third (0.31) that of of the residual monomer ε-caprolactam. Separation of the first three amides was very bad on this column; acetamide and formamide (eluting in this order) showed severe tailing, with the propanamide peak sitting on the right flank of the latter.

Figure 4.7 is a detail of chromatograms obtained with the DB-1701, it shows *extracted ion chromatograms* for the amides, which elute in the order of increasing number of C-atoms, and with good peak shapes, from this medium polarity phase. It is suggested to use a thinner film of this (or a similar) phase for further investigations. (On the DB-5 all the important peaks were distorted—the amides showing severe tailing, caprolactam showing equally severe fronting.) Of course, from today's point of view, there are additional means to increase sensitivity, especially increasing the *surface* for desorption by milling the samples and increasing the *desorption* (TDS-) *temperature*.

It is quite interesting that, in contrast to the sytrene-based polymers (PS and MABS) and the polyolefines (PE and PP), there appear to be no low-MW radiolysis products that are the products of oxidation in the narrow sense of 'incorporation-of-oxygen' — in other words, there appear to exist *no* (low-MW) radiation-induced *oxidation products* in PA-6.

Analytical Problems with Caprolactam

One problem that prevented a more thorough investigation of PA-6 in 'Phase I' was the severe contamination of the TDS-injector (probably mainly the needle) *and* of the CIS [!] by the residual monomer ε-caprolactam (memory effect). Apparently, caprolactam has a very high affinity for Tenax TA, the adsorbent used in the CIS. The contamination of the CIS could be

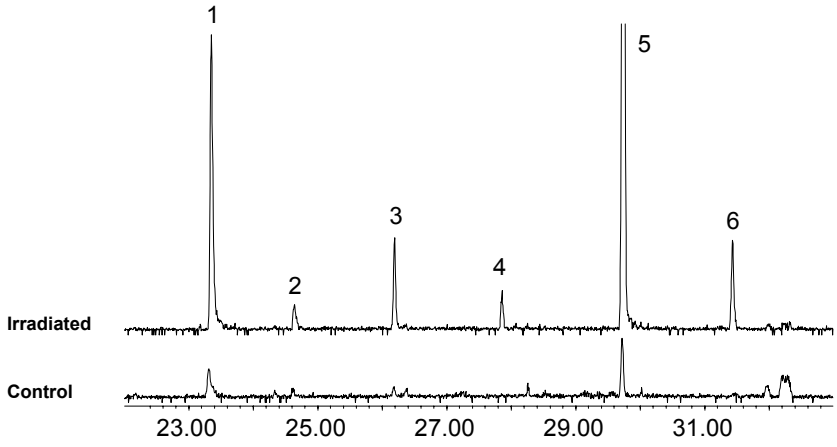


Figure 4.7 **Polyamide-6** seven weeks after irradiation with 24.7 kGy — irradiated (top) vs. non-irradiated control (bottom); detail (22–33 min) of fingerprints presented as *added extracted ion chromatograms* for m/z (44 + 45 + 59).
1 = Formamide 3 = Propanamide 5 = Pentanamide
2 = Acetamide 4 = Butanamide 6 = Hexanamide
Experiment. Condit.: 1 pellet; TDS 160(10); CIS 30; GC 40(11) -10- 250(5); column: DB-1701.

reduced by adding an additional temperature ramp to the CIS program, whereas effective cleaning procedures for the TDS-injector could be developed only at a later time.

Suggestions for Future Investigations

Future investigations of polyamides should include (1) a screening of different commercially available PA-6 resins, (2) quantitation of the amide levels, and (3) an attempt to better understand the mechanism of amide formation (it seems unlikely that pentanamide is exclusively produced by ε-caprolactam, since the radiation-chemical yield of this reaction would be atypically high). It also would be extremely interesting to investigate polyamides that are synthesized from other monomers, e. g. polyamide-11 or polyamide-66, or copolymers, such as polyamide-6/66 or polyamide-6/12.

4.4 Poly(vinyl chloride) (PVC)

General

As in the case of PP, considerable efforts have been made to develop gamma-stable PVC formulations. In contrast to PP, the main problem is not degradation of mechanical properties, but severe discoloration caused by conjugated polyene systems that result from the elimination of hydrogen chloride. See, for example, Beenen (1990), Housel (1985), and Rakita and Fouré (1984).

Main Radiolysis Products

Figure 4.8 shows the main products of the *Hyvin* PVC plus some minor volatiles; the chromatograms were recorded *two months* after irradiation (and many of the products could still be detected 14 months after irradiation with 24 kGy). 2-Ethyl-1-hexanol (the peak labeled with an asterisk) is *not* added deliberately; its presence is obviously associated with the organotin stabilizer (cf. below); and its concentration is probably anywhere between 100 and 1000 ppm.

None of the volatiles contains chlorine, and they are probably degradation products of additives (though elimination of HCl from PVC-degradation products might also yield chlorine-free products). The four major products that could be identified—octane, 1-octene, acetic acid 2-ethylhexylester and 1-octanol—are thought to result from the degradation of the stabilizer(s). I assumed that *acetic acid 2-ethylhexylester* can only be formed by an organotin stabilizer, such as dibutyltin bis-(*2-ethylhexylthioglycollate*) (cf. below), and *Hydro Polymers Ltd.* was so kind to confirm that the stabilizer has in fact a thioglycollate substituent.

Thus, the TDS-results appear to complement the finding of Allen et al. (1987c), who investigated the *tin-containing (non-volatile)* radiolysis products of two stabilizers, and found that they are ultimately converted to $SnCl_4$. One would expect that Allen's stabilizers—dibutyltin bis-(2-ethylhexylthio*glycollate*) and the corresponding *maleate*—yield similar volatile products, such as 2-ethylhexane, 2-ethylhexanol, etc., *plus* the (2-ethylhexylester) esters of *acetic acid* and *propenoic acid*, respectively.

HCl and Vinylchloride ?

During this initial screening program the TDS-technique was not validated for gaseous hydrogen chloride (HCl) or for the highly volatile monomer. The elimination of HCl from PVC is well documented (Hill et al., 1989), and various stabilizers are added to adsorb the gas (cf.

above). Therefore, the presence of significant amounts of free HCl is unlikely; furthermore, it is questionable whether thermal desorption would measure *true* HCl concentrations or reproduce HCl as an analytical artifact. Formation of vinyl chloride (VC) is very unlikely and has not been reported (Hegazy et al., 1981, Hill et al., 1989); it can be expected, though, that radiation-chemists did not look for *trace* products. In any case, it would be worth the effort to validate a TDS-method for VC, because, irrespective of the sterilization technique, there are some legal restrictions in this area, and TDS appears to be the method of choice for low levels of VC in PVC.

Suggestions for Future Investigations

In principle, an identification of irradiated PVC items seems to be not impossible, since PVC always contains various additives, which should yield detectable amounts of radiolysis products. If the degradation products of common additives were studied in more detail, it should not be too difficult to establish a detection method for radiation-*sterilized* PVC. It is suggested to analyze various known plasticizers (phthalate & others) and stabilizers (organotin & others).

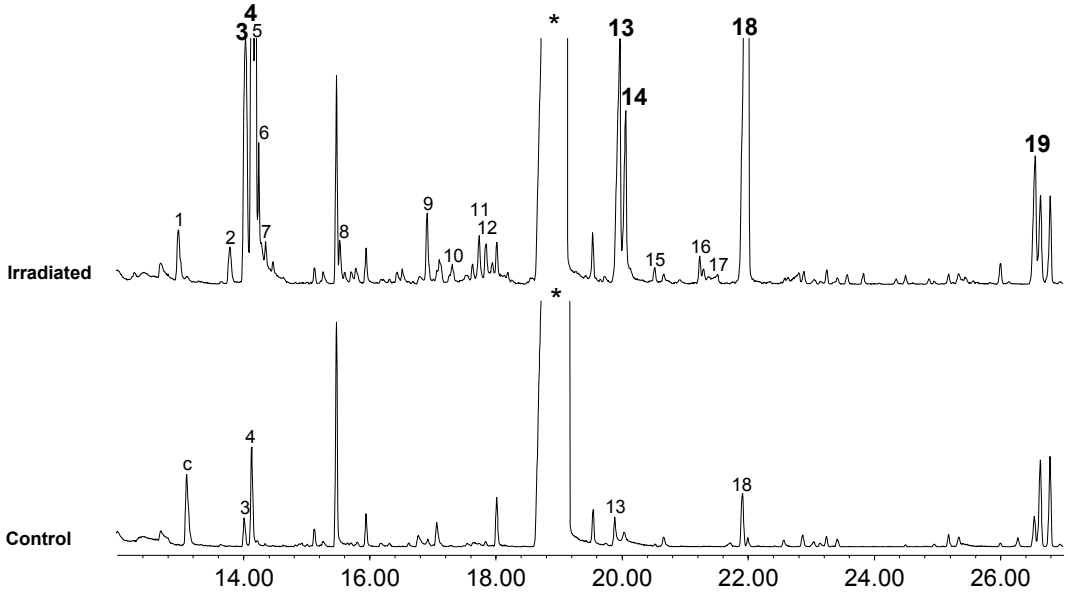


Figure 4.8 **Radiolysis products of poly(vinyl chloride)** two months after irradiation with 22.5 kGy (top) vs. non-irradiated control (bottom):

1 = Heptane
c = Unidentified
2 = 3-Methylheptane
3 = 1-Octene or isomer(s)
4 = Octane
5 = Octane-isomer (?)
6 = 2-Octene
7 = 4-Octene
8 = 3-Heptanone
9 = 2-Ethylhexanal
10 = 4-Octanone or isomer
11 = 6-Methyl-2-heptanone
12 = Benzene derivative
[* = 2-Ethyl-1-hexanol]
13 = 1-Octanol
14 = Unidentified
15 = Undecane
16 = Pentylcyclopropane (?)
17 = 2-Ethylhexanoic acid
18 = Acetic acid 2-ethylhexylester
19 = Unidentified.

Experimental Conditions: Sample: Hydro Polymers Hyvin VQ 130 clear 116 (3 pellets); TDS 120(10); CIS -40; GC 40(11) -10- 70 -5- 200 -30- 250(5); column: DB-5.

4.5 High-Density Polyethylene (HDPE)

General

The fingerprint chromatograms of the HDPE pellets (and injection-molded parts) are quite different from those of the LDPE pellets (and films) measured later. Whereas LDPE—irradiated or not—shows a more or less uniform distribution of alkanes up to C18 (octadecane) or C20 (eicosane), regardless of their number of C-atoms, the hydrocarbons with an *even* number of C-atoms (decane, dodecane, etc.) clearly dominate the fingerprints of HDPE (Figure 4.9), with the odd-C-atom hydrocarbons (e. g., undecane, tridecane) being present only in trace quantities. Irradiation produces a similar spectrum of volatiles in both HDPE and LDPE, but in the case of HDPE one could literally watch how some of the volatiles disappeared within days (cf. below), while they could be observed for months in LDPE.

Effects on Hydrocarbons / Ethylene-Oligomers

The major peaks in the fingerprint of HDPE (Figure 4.9) are heavily overloaded, and there is apparently no change in the concentration of these 'ethylene-oligomers'—with the possible exception of octadecane (C18) and eicosane (C20), which appear to increase. In contrast,

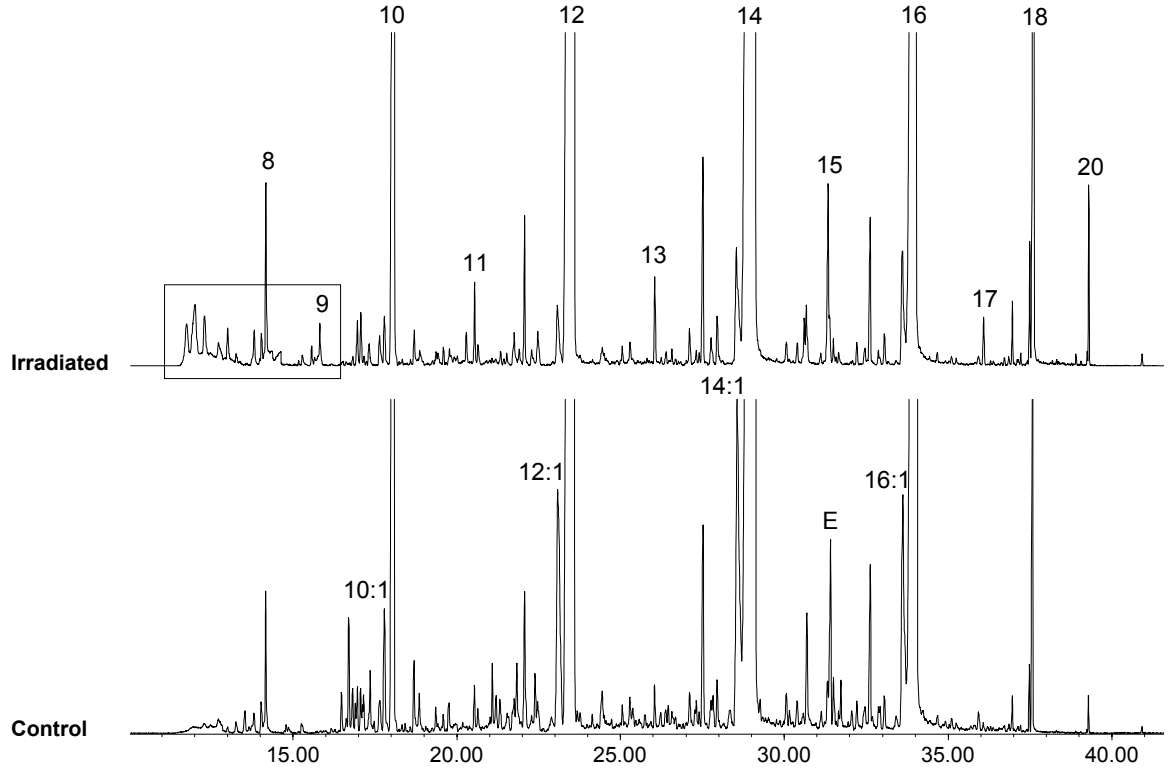


Figure 4.9 **Polyethylene fingerprint chromatograms** one day after irradiation with 23.6 kGy — irradiated (top) vs. non-irradiated control (bottom).
Peak identification:
8 to 20 = linear alkanes by number of C-atoms (octane through eicosane)
10:1, 12:1 etc. = the corresponding 1-alkenes (decreased by irradiation)
E = 1,4-[or 1,3-] Benzenedicarboxylic acid dimethyl ester (decrease)
The box (t_R 11–16 min) highlights a group of more volatile radiolysis products, including butane through nonane, 2-methyl-2-propanol, 3-heptanone, butanoic, 2,2-dimethyl-propanoic, and pentanoic acid. Experimental Conditions: Sample: BASF Lupolen 5031 L (5 pellets); TDS 120(10); CIS -40; GC 40(11) -10- 70 -5- 200 -30- 250(5); column: DB-5.

the levels of the hydrocarbons with an *odd* number of C-atoms clearly increase, while those of some 1-alkenes appear to decrease. The alkanes probably result from side-chain cleavage and/or 'terminal' main chain scission, whereas the alkenes may undergo radiation-induced oxidation and/or covalent binding. Alkanes are also formed in LDPE; however, only with the HDPE pellets the overall picture was this clear. Radiation-induced hydrocarbons in polyethylenes have also been found by Bersch et al. (1959), Killoran (1972), Azuma et al. (1983), and Rojas de Gante and Pascat (1990); cf. Section 2.3. The ester E in Figure 4.9, a trace additive or (thermal ?) degradation product of an additive, is largely destroyed.

Low-MW Oxidized Products

Some more volatile products elute from 11–16 min as highlighted by the *box* in Figure 4.9. They include several hydrocarbons, carboxylic acids, and the ketone *3-heptanone*, which was also observed as a very characteristic product in LDPE. In contrast to the other five medical polymers, one could observe a quite dramatic loss of volatiles from HDPE *within several days*. Chromatograms obtained with the (1 µm f. t.) DB-1701 column, which later turned out to be best for LDPE, revealed increased trace levels of volatiles, such as 2-methyl-2-propanol, butanal, 2-butanone, heptane etc.; the compounds could still be detected after *six weeks* (not shown). The presence of various carboxylic acids (acetic to heptanoic) is only partially visible in the fingerprint (total ion) chromatograms, but can be seen nicely in 'extracted ion chromatograms' (EICs) for m/z 45, 60, and 73.

Degradation Products of Antioxidants

Also produced by the HDPE were *traces of the quinone* 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione, while the 'trace antioxidant' *butylhydroxytoluene* was destroyed. Increased levels of the quinone could still be detected after four weeks; traces of *1,3-bis-(1,1-dimethylethyl)-benzene*, another degradation product of phenol-type antioxidants (cf. Section 4.6 *Polypropylene*), were found in later measurements, but disappeared within several days.

Suggestions for Future Investigations

The following measures are suggested to increase sensitivity in future investigations of PE: Increase the surface available for desorption by milling the samples; increase the desorption- and optimize the trapping- (CIS-) temperature; and use a relatively thick film of a medium-polarity phase. It would be quite interesting to analyze different PE types; besides various 'normal' PEs, such as LDPE, linear LDPE (LLDPE), and HDPE, it would be especially interesting to investigate UHMWPE, the polymer used for orthopedic implants and the subject of an earlier literature study (Buchalla et al. 1993c, 1995).

4.6 Polypropylene (PP)

General

On irradiation, PP suffers severe main chain scission, oxidation, and degradation of mechanical properties; antioxidants added to reduce these effects often may lead to unacceptable color changes (yellowing). The main problem, however, is post-irradiation degradation (ageing) caused by trapped free radicals; this requires careful validation of long-term product stability, since a PP article that is acceptable after irradiation may fail to pass basic mechanical testing after some week's storage. Therefore, PP has long been classified as a borderline material, and considerable efforts have been made to develop gamma-stable (radiation-grade) polypropylenes. See, for example, Horng and Klemchuk (1984), Plester (1967), and Yousefi and Katbab (1994).

The Main Product: 1,3-(1,1-Dimethylethyl)-benzene

An absorbed dose of only 3 kGy, applied for preliminary tests, produced a peak in the PP-fingerprint that could not be overlooked. It was already larger than many of the hydrocarbon peaks present in the non-irradiated PP, and it became a dominating (and heavily overloaded) peak after one sterilization cycle. The compound, 1,3-bis-(1,1-dimethylethyl)-benzene, a radiolysis product of the antioxidant Irgafos 168 [tris-(2,4-di-t-butylphenyl)-phosphite], has already been identified in irradiated PP films (Loriot et al., 1991; El Makhzoumi 1991, 1994); its concentration in the non-irradiated controls was below the detection limit, and it was still the main peak in the PP-chromatograms after *15 months*.

Trace Aromatic Products

In the *Neste* PP, the (trace) antioxidant butylhydroxytoluene (BHT) was almost completely destroyed on irradiation, and traces of three aromatic degradation products were formed (which are not necessarily radiolysis products of BHT). While pre-irradiation BHT levels are relatively low compared to those in the PP films investigated later, both, BHT and one of the trace products are already visible 'to the naked eye,' i. e., in total ion chromatograms, whereas the two others can only be seen when extracting suitable ions.

Two of the trace compounds are characterized by base peaks at 189 amu and a molecular ion (M+) of 204 amu; they might be degradation products of (a) phenol-type antioxidant(s) and were also observed in the PP films; one of them is possibly 1,3-bis-(1,1-dimethylethyl)-*5-methyl*-benzene. The third compound, with m/z 123, 138 (M+), may be *4-ethyl-1,3-benzenediol* or *1,4-dimethoxybenzene* and was also found in the PP films. The search for *trace* aromatic degradation products was inspired both by own observations (some of them simply cannot be overlooked) and by the identification of radiation-specific and/or de-butylated degradation products of antioxidants by Allen et al. (1993a, b). This subject will be discussed further in connection with the PP-films (see Section 5.10).

Non-Aromatic 'Volatiles'

Some low-MW non-aromatic products could be best observed on the 60 m DB-1701 with its thicker (1 µm) film (Figure 4.10). Please note that these chromatograms were recorded six weeks after irradiation, and that some of the compounds present (e. g., butene, pentane) are really quite 'volatile'. Besides some saturated and unsaturated hydrocarbons, they are mainly oxidized products, such as aldehydes, ketones and carboxylic acids; they are—by and large—the same that were later observed in the PP *films*. As one would expect from

PP, many of them are branched-chain isomers. It was not examined why 2,4-pentanedione, eluting from t_R 22–23 min, gives such a strange peak shape, actually a kind of 'mountain' consisting of several peaks, on this column.

Suggestions for Future Investigations

It would be very interesting to study the degradation of various additives / antioxidants used in PP; unfortunately, though understandably, suppliers of *gamma-stable* PPs are reluctant to disclose their formulations. It might also be fascinating—based on radiation-chemical considerations—to postulate possible structures of atypical / radiation-specific (?) *trace* products, and then to search for them in a 'target-analysis'. Another project—and a more down-to-earth one—would be *quantitation* of 1,3-bis-(1,1-dimethylethyl)-benzene and of the volatiles from Figure 4.10.

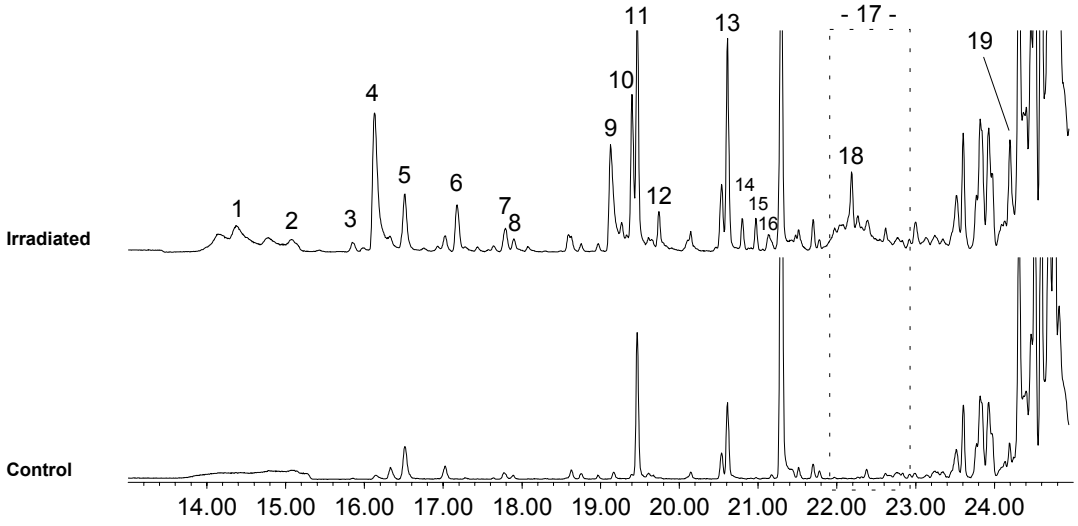


Figure 4.10 Low-MW radiolysis products in **polypropylene** — detail (t_R 13–25 min) of fingerprints recorded six weeks after irradiation with 24.4 kGy — irradiated (top) vs. non-irradiated control (bottom):

1 = (Butene / isomers ?)
2 = (Pentane ?)
3 = 2-Methylpentane
4 = 2-Propanone (Acetone)
5 = 2-Methyl-2-propanol (increase)
6 = 2-Methyl-2-propenal
7 = Unknown
8 = 2-Butanone (increase)
9 = Acetic acid
10 = 3-Methyl-2-cyclopenten-1-one
11 = 4-Methylheptane (increase)
12 = 2-Pentanone
13 = 2,4-Dimethylheptane (increase)
14 = 2-Hexanone
15 = 2-Methyl-2-hepten-4-one (?)
16 = Propanoic acid
17 = 2,4-Pentanedione (peak shape ?)
18 = 4-Methyl-3-penten-2-one (?)
19 = 4-Hydroxy-4-methyl-2-pentanone (?)

Experimental Conditions: Sample: Neste Chemicals N. V.–Neste VC1064K (1 pellet); TDS 140(10); CIS -40; GC 40(11) -10- 250(5); column: DB-1701.

4.7 Granulates (Polymer Pellets) vs. Injection-Molded Parts

It had been anticipated that irradiation would affect non-processed polymer granulates and injection-molded parts differently; however, to study the additional effects (if any) of processing turned out to be more difficult than had been expected. In the absence of a suitable technique to standardize the sample's surface-to-volume ratio, one could only compare a certain number of pellets with an equal mass of fragments of the processed parts.

Qualitatively, the effects of irradiation appear *not* to depend on whether the polymers are processed or not, in other words, the thermo-mechanical stress associated with injection-molding *neither appears to induce* the formation of additional ('new') radiolysis products, *nor does it suppress* the formation of volatiles. Quantitatively, processing also does *not* appear to induce dramatic changes; concentrations in the injection-molded parts are generally comparable to those in the granulates. Consequently, the more interesting question turned out to be: Does processing alone already produce significant amounts of the volatiles that were considered to be promising 'markers' for irradiation detection?

It was concluded that *1-phenylethanol* is a promising marker for PS and MABS, since there appears to be no significant 1-Pet formation during injection-molding. With PS, residual toluene levels were tentatively used as an 'internal standard' to demonstrate that processing produces significant amounts of benzaldehyde, and enough acetophenone to limit its use as radiation marker. Processing of PA-6 and PVC appears to induce the formation of at least *some* pentanamide and acetic acid 2-ethylhexylester, respectively. In HDPE, injection-molding apparently does not produce significant amounts of radiolysis products such as butanal, 2-butanone, acetic or propanoic acid; and in PP, no, or only traces of, 1,3-bis-(1,1-dimethylethyl)-benzene are formed.

4.8 Analytical Resumée

On the one hand, these initial results had greatly exceeded all expectations: There were *marked differences* between control and irradiated specimens for all samples but PE, where they were smaller and obviously diminished with time. Some of the products appeared to be radiation-specific, thus possibly permitting the development of methods to detect irradiated plastics (cf. Section 13.3). Additionally, almost no *sample (pre-) treatment* was needed and, in hindsight at least, not much *optimization* of TDS, CIS, GC, and MS parameters.

On the other hand, the situation was clearly unsatisfactory: It was not possible to compare *pellets* and injection-molded *parts* in a straightforward way; there was no chance for a meaningful *quantitation*; there seemed (with the exception of PE) to be no post-irradiation changes in product concentrations—*but it was impossible to prove this*; and all these problems were in some way related to the ill-defined, or rather non-defined, *surface-to-volume ratio* of the relatively bulky samples, which could not be 'totally desorbed' or 'quantitatively extracted.' Initial efforts to ground the pellets to a fine powder had failed—due, mainly, to poor equipment.

As mentioned in Section 3.1, it was at this point that I turned—half by accident—to the polyethylene and polypropylene films (see Chapter 5).

5. Polyethylene and Polypropylene Films

5.1 Retention of Radiolysis Products in LDPE Films

Figure 5.1 shows fingerprint chromatograms of a commercial LDPE film—irradiated with 20 kGy (top) vs. the non-irradiated control (bottom). This film, cut from a 1.5-liter milk bag, had been irradiated 7.5 months earlier for some test analyses that never were carried out. It is interesting to note that in contrast to the high-density polyethylene investigated earlier (i. e., Lupolen 5031 L; see Section 4.5), there is a more or less homogeneous distribution of alkanes—irrespective of their number (even vs. odd) of C-atoms.

The *main* radiolysis products elute from t_R ca. 17 to 26 min as detailed in Figure 5.2. Table 5.1 contains some additional information on these major and on several minor radiolysis products (retention time and characteristic ions). I do not want to discuss these products in more detail, because, as indicated in Table 5.1, most of the compounds have already been identified in dynamic headspace analyses.

What was totally unexpected—and considered quite intriguing—was not the spectrum of the radiolysis products present, but the fact *that they were still present after 7.5 months*. El Makhzoumi (1994) had reported that—in contrast to PP—volatile radiolysis products were *not* retained in the matrix of LDPE films. Rojas de Gante and Pascat (1990) have also used a „DCI-technique“ (cf. below) in addition to dynamic HSA, but they are not totally explicit about that.

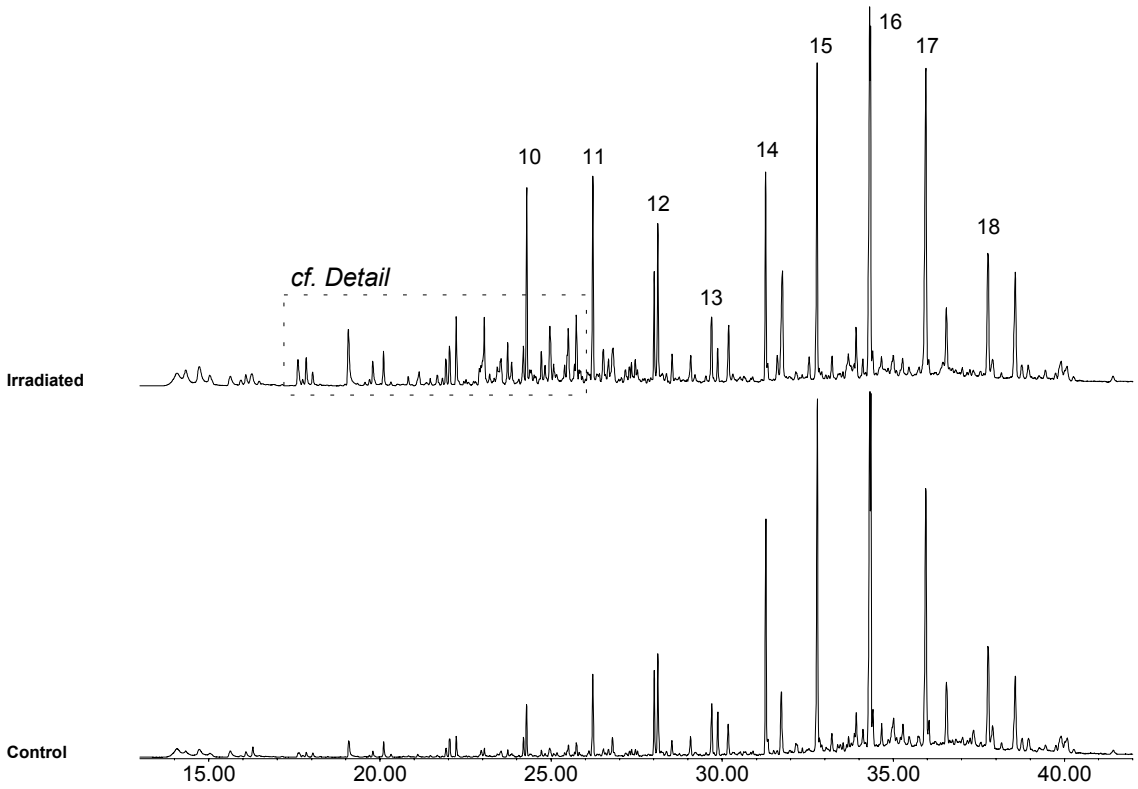


Figure 5.1 **Fingerprint chromatogram of a commercial LDPE film** 7.5 months after irradiation with 20 kGy — irradiated (top) vs. non-irradiated control (bottom). 10 to 18 = the linear hydrocarbons from decane to octadecane. The main radiolysis products are detailed in Figure 5.2.
Experimental Conditions: Sample: 3 x (3 x 100 mm^2) = 9 cm^2 of film;TDS 140(10); CIS -40; GC 40(11) -10- 250(10); column: DB-1701.

The following desorption temperatures were used in previous investigations:

El-Makhzoumi (1994)..... 100°C (DCI)
Rojas de Gante & Pascat (1990) .....25°C (HSA)
.....90°C (DCI)
Azuma et al. (1983) .....80°C (HSA)
(DCI = desorption-concentration-introduction
HSA = dynamic headspace analysis)

Rojas de Gante & Pascat (1990) describe their DCI-conditions (direct desorption of irradiated films), and *their* Figure 6, for example, shows PP chromatograms obtained with the DCI-technique; however, they do not comment on the time elapsed after irradiation or on a possible *retention* of products in the films.

In these first experiments, there is certainly a contribution of the higher absorbed dose of ca. 20 kGy vs. the 5 kGy applied by El Makhzoumi (1994). However, it must be concluded from the subsequent 1, 3, and 10 kGy measurements that the considerably *higher desorption temperatures* permitted by the TDS are a key factor (cf. Figure 5.4, below). One implication of this may be that TDS possibly analyzes additional thermal degradation products of *radiation-induced precursors* as discussed in connection with Figure 5.6. Higher desorption temperatures (and, possibly, the geometry of the analytical system) are probably also responsible for the impression that the fingerprint chromatograms obtained in this investigation appear to look quite different from those obtained by Azuma et al. (1983, 1984a, b), Rojas de Gante & Pascat (1990) or El Makhzoumi (1994).

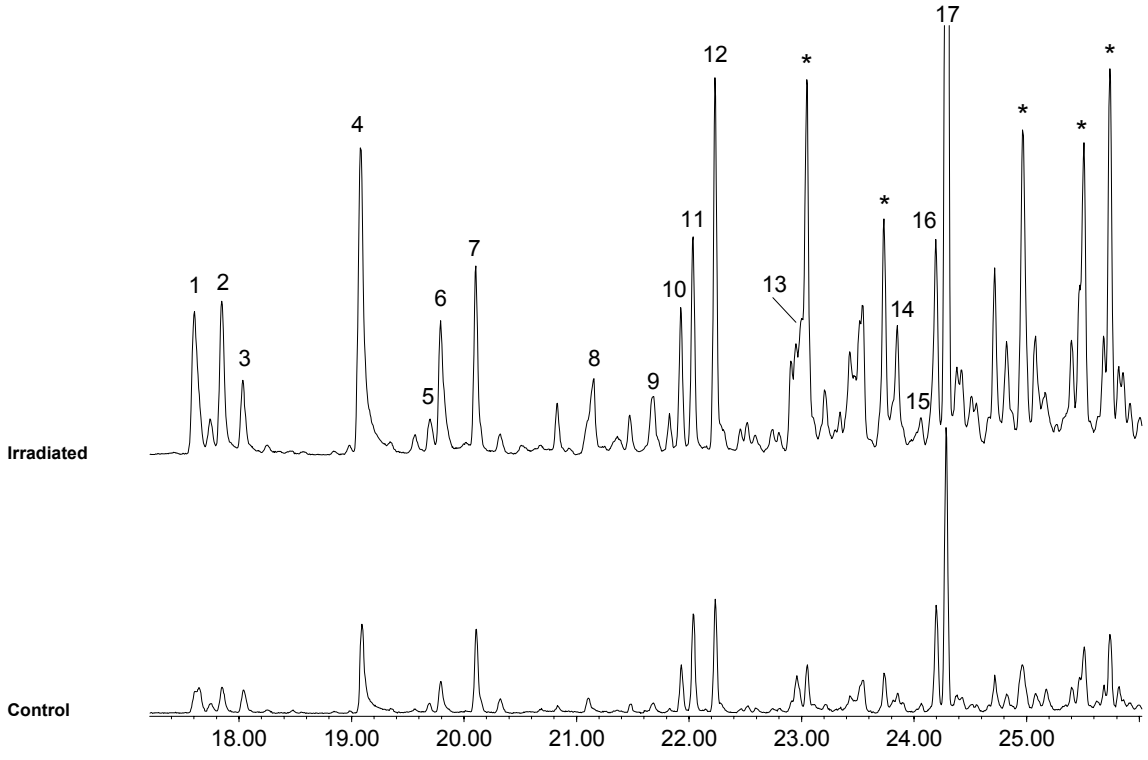


Figure 5.2 **Detail** (t_R 17–26 min) **of Figure 5.1,** peak identification see Table 5.1.
Peaks marked with an asterisk (*) are alkylbenzenes (m/z 91, 106 and 105, 120), a contamination possibly caused by printing inks on the film; the effect was not observed in other analyses of this sample.

Table 5.1 Major radiolysis products / radiation-induced degradation products in the commercial LDPE film (see Figures 5.1 and 5.2). The dotted lines separate the characteristic groups in the fingerprint chromatogram.

No.[a]	t_R	Characteristic Ions	Compound	Id. in HSA[b]
	14.33	44, 58 m+	Butane	A / R&P
	14.72	44 m+	Acetaldehyde	A / R&P
	15.03	43, 75, 72 m+	Pentane	A / R&P
	15.63	45, 46	Ethanol ?	A
	15.94	45, 58 m+	Propanal ?	A / R&P
	16.08	43, 58 m+	2-Propanone / Acetone	R&P
	16.26	43, 57, 86	Unknown	
	16.28	(86)	Hexane	
	16.47	59, 84	Unknown	
1	17.61	41, 44, 72 m+	Butanal	A / R&P
2	17.85	43, 72 m+	2-Butanone	A / R&P
3	18.04	(100)	Heptane	A / R&P
4	19.08	45, 60 m+	Acetic acid	A / R&P
5	19.70	43, 55, 71, 86 m+	2-Pentanone	R&P
6	19.79	41, 44, 58, 86 m+	Pentanal	A / R&P
7	20.11	(114)	Octane	A / R&P
8	21.15	45, 73, 74 m+	Propan. acid	A / R&P
9	21.68	43, 57, 71, 100 m+	3-Hexanone (coelut.?)	A
	21.83	43, 56, 61, 73 (101, 116 m+)	Ac. acid butylester	
10	21.93	43, 58, 71, 85, 100 m+	2-Hexanone	A / R&P
11	22.04	41, 44, 56, 67, 72, 82, 100 m+	Hexanal	R&P
12	22.23	(128)	Nonane	A / R&P
13	22.99	60, 73, 88m+	Butan. acid	A / R&P
14	23.85	57, 72, 85, 114 m+	3-Heptanone	A / R&P
15	24.06	43, 58, 71, 85, 114 m+	2-Heptanone	
16	24.19	41, 44, 55, 70, 81, 96 114 m+	Heptanal (coelut.)	
17	24.29	(142)	Decane	A / R&P
	24.94	60, 73, 87 (no 102)	Pentan. acid (coelut.)	A
	26.22	(156)	Undecane	R&P
	26.87	60, 73, 87, 88 (no 116)	Hexan. acid (coelut.)	
	29.08	73, 88, 101, 116, no 144	2-Ethyl-hexan. acid	
	31.62	43, 45, 56	3-Meth.-2,4-pentane-diol?	
	32.54	dto.	dto.	

a Peak number in Figure 5.2.

b Compound has earlier been identified in *dynamic headspace* analyses (LDPE films irradiated *in closed vials*): A = Azuma et al. (1983), R&P = Rojas de Gante and Pascat (1990).

5.2 LDPE Films vs. LDPE Pellets

These surprising results were considered to be significant enough to deserve further investigation. A first step consisted in analyzing a better-defined LDPE film (i. e., BASF Lupolen 2410 F), and the corresponding granulate (pellets) from which this film is made—with the intention to find out whether the striking difference to the medical HDPE pellets was caused by the sample dimensions/surface-to-volume ratios (*film* vs. *pellets*) or by the different PE types (*resins*). (During the initial screening of six medical polymers, HDPE had been an exception: the levels of the radiolysis products had been quite low, and one could literally 'watch' how some of them disappeared within several days—see Section 4.5.)

A comparison of the Lupolen 2410 F *film* and the commercial LDPE film from Figure 4.2 reveales that there exists a highly characteristic *pattern* of groups of radiation-induced peaks that is almost identical for the two films, in other words, that they *qualitatively* yield the same radiolysis products. (The relative peak sizes of individual compounds vary to some extent; cf. Figure 4.3). The same can be said of the Lupolen 2410 F *pellets*, allowing the conclusion that the differing behaviour of the medical HDPE is a function of resin type rather than of surface-to-volume ratio or thermal stress suffered during processing. (A quantitative, or even semi-quantitative, comparison between 2410 F *films* and *pellets* was beyond the analytical capabilities at that time.) Most of these characteristic radiation-induced peaks were still present in the 'commercial' LDPE film-sample more than one year (13 months) after irradiation with 20 kGy.

5.3 Comparison of Ten Different LDPE-Films

The logical next step (with *irradiation detection* in mind) was to extend the investigation to a number of different LDPE films to see whether this good correlation between a random commercial sample and Lupolen 2410 F was a chance observation, or whether it reflects some property of LDPE itself. More LDPE-chromatograms cannot be shown for reasons of

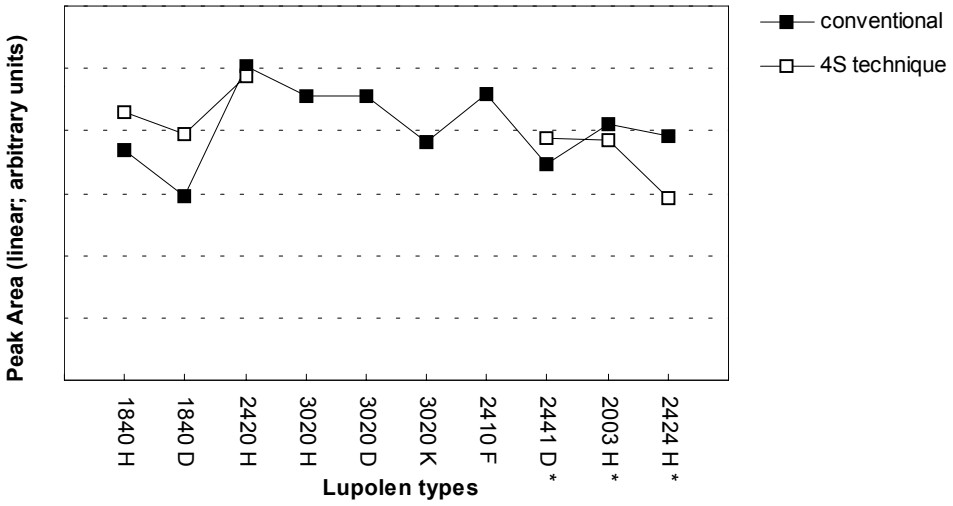


Figure 5.3 Peak area of 3-heptanone in **ten different Lupolen (LDPE) films** after 24.1 kGy using either the 'conventional' or the 'stainless-steel sieve sandwich' (4S) technique at a TDS-temperature of 140°C. Films marked with an asterisk (*) contain a co-monomer or an additive(s); cf. Section 3.7.
Experimental Conditions: Sample: 1 strip of film (3 mm x 70 mm); TDS 140(10); CIS -40; GC 40(11) -10- 250(10), column: Rtx-1701.

space, but all irradiated samples exhibited the already familiar *pattern* of radiation-induced, or at least radiation-increased, peaks, e. g., the highly characteristic *butanal / 2-butanone*-group, the tailing peak of *acetic acid* with *pentanal* eluting on its right flank, the *3-hexanone / 2-hexanone / hexanal* cluster, etc. A graph comparing the peak areas of *3-heptanone* in *all ten* irradiated films is presented in Figure 5.3.

For six films parallel runs were performed with the *stainless-steel sieve sandwich* technique (cf. below); please note that in this series only *one* film strip (3 x 70 mm^2) was used with both techniques, which greatly reduces the geometry effect (cf. below) that had been observed *at 140°C* with three strips. The results of the two techniques agree quite well, and, overall, the variation between the films is relatively small—given the fact that the sample load is small (ca. 5 mg) and that the peak areas are from (full scan) total ion chromatograms (TICs).

5.4 The Effect of Desorption Temperature

Figure 5.4 shows the effect of desorption temperatures from 90°C to 140°C on the peak areas of some LDPE radiolysis products after 26.5 kGy—the right graph is a detail view (80°C to 130°C) of the left. The apparent plateau between 100°C and 110°C is probably related to some property of the LDPE film, such as its softening point or crystallinity; however, it presently cannot be excluded with certainty that the plateau is an artifact due to data scatter, since, in the context of this work, the phenomenon appeared to be not relevant enough to deserve further investigation. What appeared to be much more interesting is the dramatic increase in peak area that is taking place above 120°C, because it is obviously accompanied by an equally dramatic increase in sensitivity. This increase is caused by melting of the films, which, at 140°C, visibly lose their shape, and shrink to *threads* that extend in a zigzag-like fashion through the TDS-glass tube, clinging partially to its inner wall.

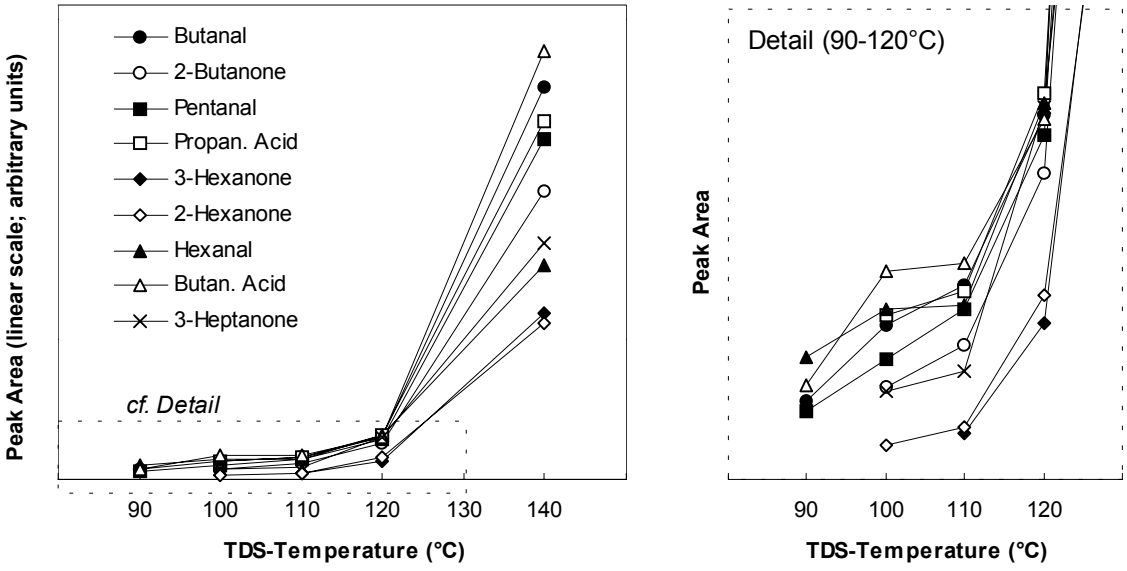


Figure 5.4 **Effect of the TDS-temperature** on some radiolysis products of LDPE (BASF Lupolen 2410 F; 26.5 kGy). There is a dramatic increase above 120°C, and there appears to be a plateau between 100 and 110°C, probably related to some property of the film (softening point ?).
Experimental Conditions: Sample: 3 strips of film (3 x (3 x 100 mm^2)); CIS -40; GC 40(11) -10-250(10); column: DB-1701.

Already at 120°C, softening of the films causes them to stick slightly together without losing their shape. To answer the question whether this effect impaired the desorption of the volatiles by reducing the available surface, a series of measurements was performed with stacks of one, two, and three strips of films, 3 mm x 100 mm in size. It was concluded from the observed linear increase in peak area that there is *no* geometry effect and that the initial three-strip configuration (9 cm^2 of film) could safely be used *at 120°C*. The same overall picture was obtained in parallel runs of control and 5 kGy-films (in the case of the non-irradiated controls, the *hydrocarbon* peaks were integrated).

5.5 High-Temperature Thermal Desorption

Figure 5.5 illustrates the principle of the *stainless-steel sieve sandwich* (4S-) technique. It was developed to prevent the collapse of the film surface at higher temperatures, and to prevent contamination of the TDS-glass tube by the melting polymer. (The tube's graphite ferrule interfered with several conceivable cleaning procedures, and we ultimately resorted to single-use glass tubes combined with a small piece of original tubing bearing the ferrule—see Section 3.3.) The steel sieves, which were cut into small strips, are produced for papermills and were kindly provided by *Oberndorfer* (Heidenheim/ Brenz, Germany). Similar sieves or *metal cloths* may be obtained from some lab-ware suppliers. The steel sieves do not prevent a certain shrinkage of the films, but generally do preserve a very large surface for desorption.

To evaluate the technique the peak areas of some typical compounds have been have monitored in two series of consecutive runs at a TDS-temperature of 140°C—one using the 'conventional' technique (in this case a 'stack' of 3 films, 3 x 70 mm in size), the other using the 4S-technique. The analysis of these data showed that, despite a threefold sample load, the conventional desorption technique yielded, on average, only ca. twice the amount of butanal (radiolysis product), and almost as little pentadecane as the 4S-technique. Additionally, the standard deviation with the 4S-technique was much smaller for both analytes.

The 4S-technique allowed to increase the TDS-temperature considerably; Figure 5.6 shows the results of a *high-temperature thermal desorption* study. There is clearly a difference between the radiolysis products and the hydrocarbons: While the peak areas of the former increase more or less linearly with temperature, there is almost no effect on C14 and C15, whereas C16, C17, and C18 appear to reach maxima somewhere between 180 and 200°C.

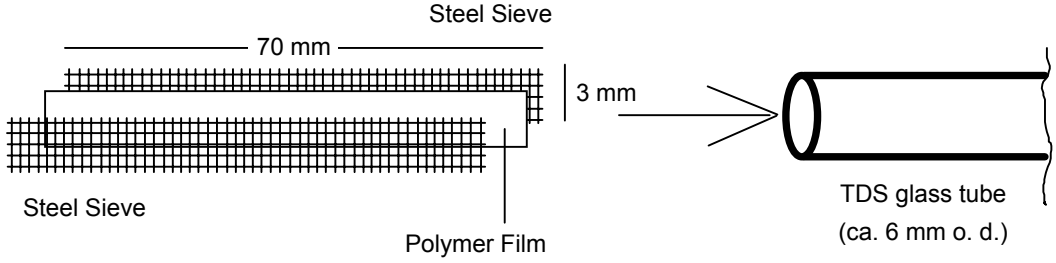


Figure 5.5 Principle of the *stainless-steel sieve sandwich* (4S) technique.

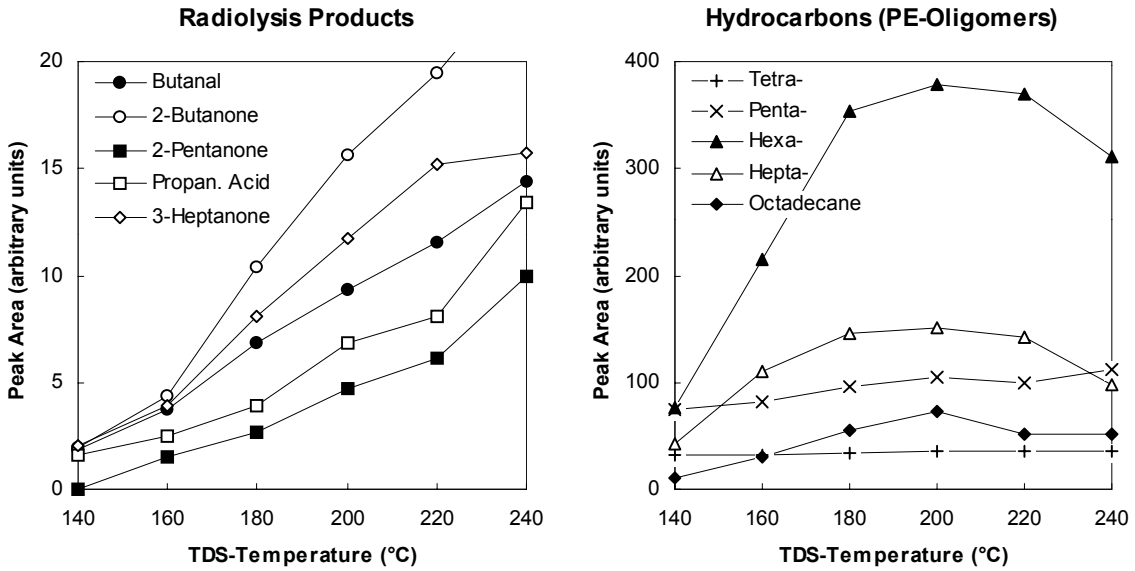


Figure 5.6 **High-temperature thermal desorption** of an LDPE film irradiated with 26.5 kGy using the 'stainless-steel sieve sandwich' technique — effect of temperature on the peak areas of some radiolysis products (left), and of some hydrocarbons (oligomer or low-MW fraction; right plot).
Experimental Conditions: Sample: Lupolen 2410 F; CIS -40; GC 40(11) -10- 250(10); column: Rtx-1701.

5.6 Radiation-Induced Artifacts ?

One possible explanation for this phenomenon might be that—under these conditions—the 'radiolysis products' (or: a significant fraction of them) are formed as thermal degradation products of some radiation-induced precursors, e. g., peroxides or hydroperoxides. If this interpretation were correct, then the radiolysis products would appear to be artifacts, and quantitation of these compounds by thermal desorption would probably be meaningless —with respect to migration, at least.

Hydroperoxides are considered to be the main (or primary) oxidation products of polyolefines. Lacoste et al. (1996) have used IR spectrometry to monitor their concentration during gamma-irradiation, as well as the concentrations of their degradation products, such as alcohols, ketones and acids. It appears that hydroperoxides are simultaneously formed *and* decomposed by ionizing radiation, and one would expect that these unstable intermediates will also gradually decompose under ambient-storage conditions ('post-irradiation oxidation'). Thus a determination of volatile oxidation products by (high-temperature) thermal desorption might provide a worst-case estimate of the amount of products that ultimately will be formed.

In any case, analysis by thermal desorption might be a valuable tool in the study of radiation-induced oxidation processes. And it should finally be mentioned that the main radiolysis products of *polystyrene* behaved very differently at similar TDS-temperatures (their concentrations did not increase as shown in Sections 6.2 and 8.8).

5.7 Polypropylene Films

As summarized in Chapter 2, both the (non-aromatic) radiolysis products of polypropylene and the degradation products of some phenol-type antioxidants commonly used in PP have already been analyzed by others. Therefore, the results shall not be discussed in too much detail.

Figure 5.7 shows fingerprint chromatograms of PP film „A“ recorded six days after irradiation with 26.6 kGy vs. the corresponding non-irradiated control. The (heavily-overloaded) peaks of three aromatic degradation products of antioxidants dominate the chromatogram, while the butylhydroxytoluene (BHT) peak disappears completely upon irradiation. Besides from 1,3-bis-(1,1-dimethylethyl)-benzene, irradiation produces

– an analogous *phenol*, 2,4- [or: 2,6-] bis-(1,1-dimethylethyl)-phenol,
– and the *quinone* 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione.

The compounds were also observed by Allen et al. (1993a–quinone), Bourges et al. (1992a, b–phenol & quinone), and by El Makhzoumi (1994–all three compounds).

The evidence that benzoic acid (symbol „Ac“ in Figure 5.7) is also a radiolysis product is ambiguous: In the pairs of runs performed on Day 6 (Figure 5.7) and Day 7 it looks like a perfect radiolysis product, whereas one day later (Day 8) in a pair of LDPE analyses it seems to be a TDS contaminant. It was not found three months later, when the three main degradation products were still present.

Figure 5.8 shows a detail view of the more volatile non-aromatic radiolysis products; there is obviously a considerable number of products that could not be identified (co-eluting compounds and/or non-convincing library matches). The detail is from another run with a GC rate of 5°C/min so that the retention times differ from those in Figure 5.7. A similar spectrum

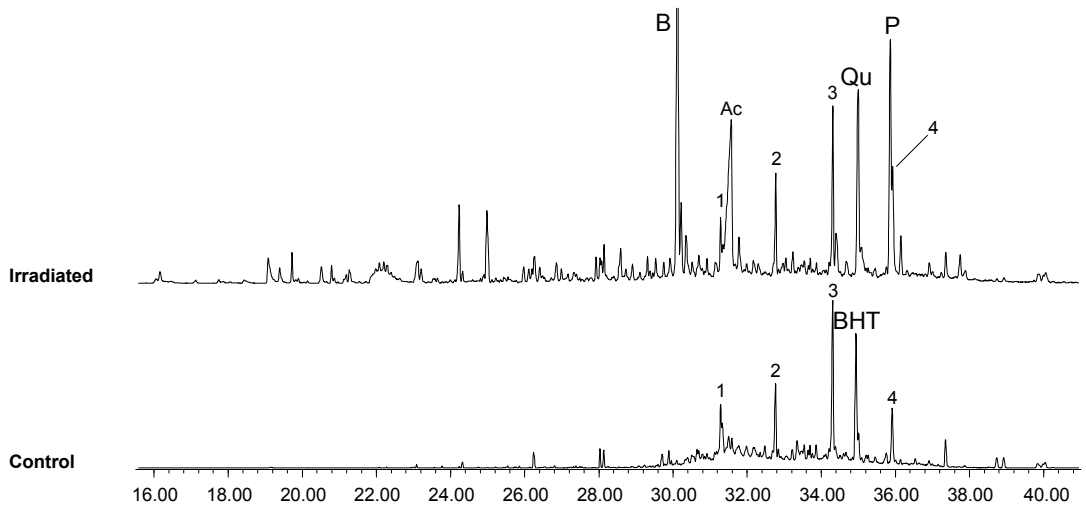


Figure 5.7 Fingerprint chromatograms of **polypropylene film „A“** six days after irradiation with 26.6 kGy — irradiated (top) vs. non-irradiated control (bottom) showing the three main radiolysis products (i. e., degradation products of phenol antioxidants):
B = 1,3-Bis-(1,1-dimethylethyl)-benzene,
Qu = 2,6-Bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione,
P = 2,4-Bis-(1,1-dimethylethyl)-phenol.
BHT (butylhydroxytoluene) is completely destroyed on irradiation; Ac (benzoic acid) may be a contaminant (see text); the hydrocarbon peaks 1, 2, 3, and 4 (tetra-, penta-, hexa-, and heptadecane) do not change on irradiation. See Figure 5.8 for the early-eluting non-aromatic radiolysis products. Experimental Conditions: Sample 9 cm^2 of film; TDS 140(10); CIS 30; GC 40(11) -10- 250(10); column: DB-1701.

of volatile compounds—aldehydes, ketones, alcohols, and carboxylic acids—has been observed by Rojas de Gante and Pascat (1990) in the *headspace* of irradiated PP films; by El Makhzoumi (1994), who found that they were retained in the PP matrix for three months (after an absorbed dose of 5 kGy); —and in the medical (radiation-grade) polypropylene (cf. Section 4.6). As one would expect from PP, many of these products are branched-chain isomers.

The peaks of the three aromatic degradation products still dominate the fingerprint of PP film „A“ *one year* after irradiation. A comparison of their *relative* intensities (peak areas) indicates that there must have been a massive loss of 1,3-bis-(1,1-dimethylethyl)-*benzene* to the ‘environment’ during storage. It may be expected that a fraction (theoretically 50%) of the missing compound(s) will contaminate any product that is packed into such a film. Unfortunately, no standard solutions were injected at the time of these measurements; therefore, a comparison of the absolute peak areas of the bis-(1,1-dimethylethyl)-*phenol* does not make much sense (because of instrumental drift, etc.). However, it may be assumed that there is also some loss of the phenol, since migration of these compounds into food simulating solvents has actually been observed (Bourges et al., 1993). Many of the low-molecular weight (non-aromatic) radiolysis products—such as 2-propanone, 2-methyl-2-propenal, formic and acetic acid, 2-pentanone, etc.—are also still present *one year* after irradiation with 26.6 kGy.

Very similar results were obtained with three BASF Novolen polypropylene types (Novolen 3225 MCX, 1325 L, and 1125 L). Samples analyzed two days after irradiation with 10 kGy

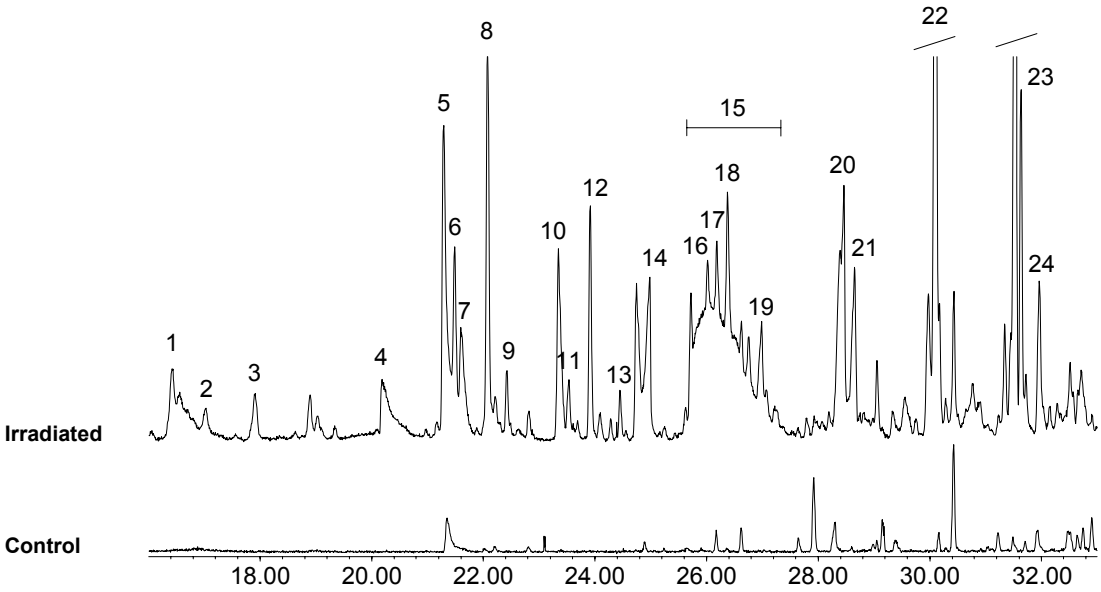


Figure 5.8 Detail (t_R 16–33 min) of fingerprints obtained with **PP film „A“** six days after irradiation with 26.6 kGy — irradiated (top) vs. non-irradiated control (bottom).

1 = 2-Propanone (Acetone)
2 = 2-Methyl-2-propanol
3 = 2-Methyl-2-propenal
4 = Formic acid
5 = Acetic acid
6 = 3-Methyl-2-cyclopenten-1-one
7 = 2-Methyl-2-propen-1-ol
8 = 2-Pentanone
9 = 2,3-Pentanedione ?
10 = 1-Hydroxy-2-propanone
11 = 2-Methyl-2-pentanol
12 = 2-Hexanone ? (coelut. with toluene?), cf. #16
13 = 2-Methylpentenal
14 = Propanoic acid
15 = 2,4-Pentanedione
16 = 2-Hexanone ?, cf. #12
17 = Hexanal
18 = 4-Methyl-3-penten-2-one
19 = Di-methyl-propanedioic acid
20 = Butanoic & 2,2-Dimethylpropan. acid
21 = 2-Methyl-2-propenoic acid
22 = 4-OH-4-meth.-2-pentanone
23 = 4-Methyl-2-heptanone
24 = Pentanoic acid, coeluting with ?

Experimental Conditions: GC programmed with 5°C/min, MS scan range 15-300 amu; other conditions as in Figure 5.7.

again show a massive formation of the already familiar aromatic degradation products and an almost complete destruction of BHT. If we assume similar desorption characteristics and MS response factors for BHT and the three degradation products, then the BHT present in the non-irradiated controls cannot account for the total amounts of radiolysis products. The peak areas of BHT and of the three main degradation products of antioxidants have been monitored in all three films after 1, 3 and 10 kGy. Overall the picture is quite complex (the phenol, for example, appears to be an intermediate product that is destroyed at higher doses), and probably cannot be explained without real quantitative data and without information on the additional higher-MW antioxidants, which are not accessible to TDS-analysis, but must be assumed to be present.

In any case, significant amounts of these antioxidant-degradation products are already formed at the low absorbed doses used in food irradiation, and most of the low-MW radiolysis products that have been observed in PP film „A“ were also found in the three Novolen films after 10 kGy.

5.8 Cyclic Radiolysis Products ?

The cyclic products listed by Rojas de Gante and Pascat (1990) [see Section 2.3] were *not* found—indeed, no cyclic compounds at all were found in the LDPE and PP film samples under investigation; the phenomenon, however, is considered to be interesting enough to deserve further investigation.

Since it was obviously possible to detect compounds as volatile as butane or acetaldehyde (see Table 5.1), one can be quite confident that it should have been possible to detect compounds such as cyclobutane or diethylcyclobutane. According to Rojas de Gante (1988) there was a clear difference between the ('semi-dynamic' GC-MS-) chromatograms obtained by analyzing the *headspace* and those obtained by *directly desorbing* the films: with the latter, she observed a 'very strong diminution' of very low-MW compounds and a much higher quantity of heavier products. (It still seems improbable, however, that *no* cyclic products should be retained in the polymer matrix.) She also notes that the large amounts of CO_2 present in the headspace analyses resulted in poor peak resolution and interfered with spectra interpretation. Thus, it might be a good idea to repeat the headspace analyses to try and confirm the initial observation. On the other hand, since the cyclobutanones used as markers in irradiated food items are quite well-defined products resulting from the radiolysis of triacylglycerides, and since similar structures are absent in polyolefines, it is likely that no cyclobutanones are formed (and it is conceivable that no—or only ultra-traces of—other cyclic compounds are formed).

5.9 SIM-Analyses of Low-Dose Irradiated LDPE

The initial experiments with Lupolen 2410 F had been performed after sterilizing doses (i. e., ca. 25 kGy), and in a first attempt to reduce the absorbed dose to the range relevant for food irradiation (≤ 10 kGy), a 5 kGy-sample was analyzed. Of course, one would like to have more data points between 0 and 25 kGy, but it appears that there is a linear relationship between product yield (peak area) and the absorbed dose, eg., for butanal, butanone, pentanal, propanoic acid or 3-hexanone. Similar observations have been made by El Makhzoumi (1994) and by Rojas de Gante and Pascat (1990).

It is obvious that the analysis of low-dose irradiated samples would greatly profit from the inherently greater sensitivity of SIM data acquisition (SIM = selected ion monitoring). One would also quantitate these compounds in SIM-mode, since it provides considerably more accurate peak areas when the peaks are small. The objective of these preliminary SIM-ana-

lyses (Figure 5.9a) was not quantitation, but to see whether it would be possible *to detect* an increase in concentration of the previously identified radiolysis products after 1 kGy.

Figure 5.9a shows the *butanal / 2-butanone*-group after 1 kGy vs. the non-irradiated control. Clearly, there is a detectable increase in butanal and 2-butanone after irradiation with 1 kGy; unfortunately however, the TDS-blanks obtainable at that time (dotted line in Figure 5.9a) were too bad to allow a decision, whether traces of the two compounds were already present in the non-irradiated control, or whether the peaks were 'background' resulting from contamination of the TDS-injector. A similar picture was obtained with 3-hexanone, 2-hexanone, and 3-heptanone (not shown); the peaks were markedly increased on irradiation, and the presence of the compounds in the non-irradiated control may, partially at least, have been attributable to contamination of the TDS.

A closer look at the chromatogram in Figure 5.2 leads to the question: Are the products, e. g., *butanal / 2-butanone*, radiation-specific, and/or is the gap between irradiated and control samples wide enough for *irradiation detection* ? This will depend on the absorbed dose one is interested in, and, as suggested by Figure 5.2 (obtained 7.5 months after irradiation), *ageing* (autoxidation) of the films *may increase* the levels of some potential radiation markers.

It may, however, be concluded from Figure 5.9b that the project *irradiation detection* should not yet be abandoned. Figure 5.9b shows the *butanal / 2-butanone*-group of the commercial LDPE film almost *one year* after irradiation: 20 kGy vs. *3 kGy* vs. the non-irradiated control (this is the same film as in Figure 5.2). This film was more than two times thicker than the other LDPE films, which resulted in higher sample loads and may have retarded the loss of radiolysis products during storage.

In any case, it would be quite an interesting project to re-examine low-dose irradiated LDPE (or PP) films to see whether improved cleaning procedures and advanced concepts of increasing sensitivity would permit an identification of irradiated packaging materials. Besides

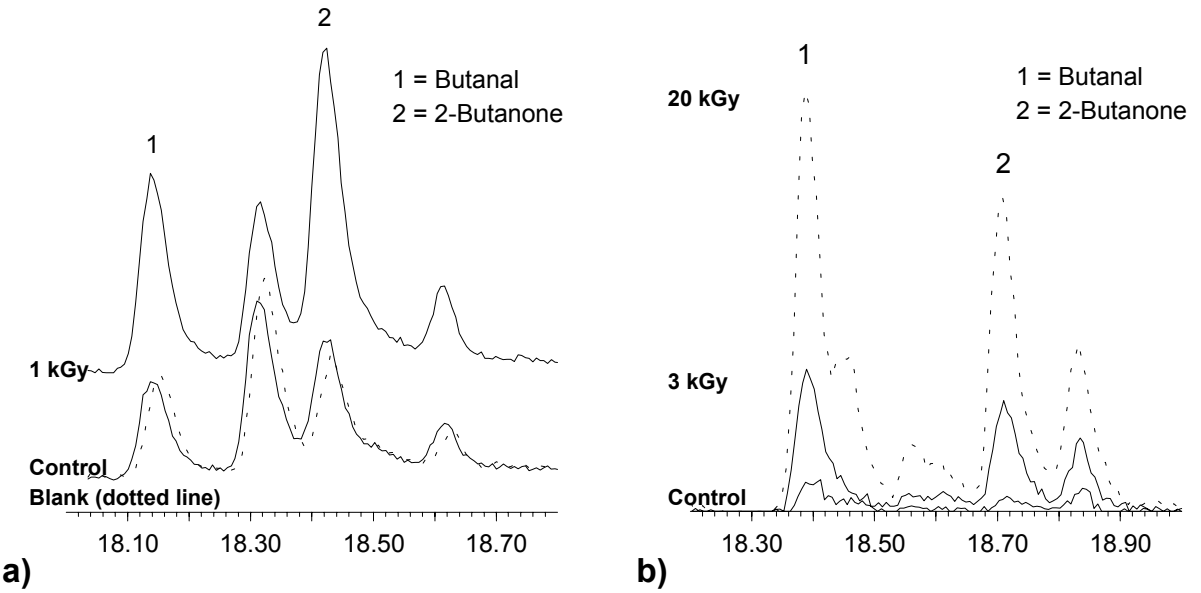


Figure 5.9 a) Detail (18–18.8 min) of **SIM (selected ion monitoring) chromatograms** of LDPE (Lupolen 2420 H) irradiated with 1 kGy (top) *vs.* non-irradiated control *vs.* TDS-blank.

Figure 5.9 b) Detail (18.2–19.1 min) of TIC (total ion) chromatograms of a commercial LDPE film: 20 kGy vs. 3 kGy vs. non-irradiated control (see text).

Experimental Conditions: CIS -40; GC 40(11.5) -10- 250(15); column: Rtx-1701.
(a): TDS 200(10) two days after irradiation; the 'ions' monitored were m/z 72.0, 86.0 and 100.0; EMV + 200 V. (b): TDS 140(10) 11.5 months after irradiation.

from such strategies as increasing TDS-temperature and TDS-time, or using a 'sandwich' of three films separated by two steel sieves to increase sample load, it might also be a good idea to re-consider, and possibly to *optimize* the *CIS- and GC-parameters* (splitless time; column phase, film thickness, and length; GC initial temperature) *for* some *specific compounds*. It should be contemplated, whether a 1 µm film is really optimum for, e. g., butanal / 2-butanone; the dilemma is that a thick film is needed for the more volatile compounds to reconcentrate them after splitless-transfer to the column, while reducing film thickness would increase sensitivity (less peak broadening, increased peak heights). A strategy for somewhat higher-boiling components might be to inject one microliter of a suitable solvent into the cold injector to achieve reconcentration by a *solvent effect* (as it was finally done with benzene in PS).

5.10 Trace Aromatic Degradation Products

The search for *trace* aromatic degradation products in polyolefin films was inspired both by own observations (some of the products simply cannot be overlooked), and by the identification of radiation-specific and/or de-butylated degradation products of antioxidants by Allen et al. (1993a, b). Consequently, a search was undertaken for aromatic compounds —and for possible de-butylated / de-methylated analogues of the three main antioxidant degradation products—by *extracting* suitable ions from the total ion chromatograms (TICs) obtained with various irradiated films. Figure 5.10 shows exemplarily the results of one such data analysis: for polypropylene film „A."

The first two trace compounds—the *unidentified* product #1 and product #2 [1,3-bis-(1,1-dimethylethyl)-*5-methyl*-benzene]—have already been observed in the medical polypropylene (see Section 4.6). The structure of product #1 must be closely related to 1,3-bis-(1,1-di-

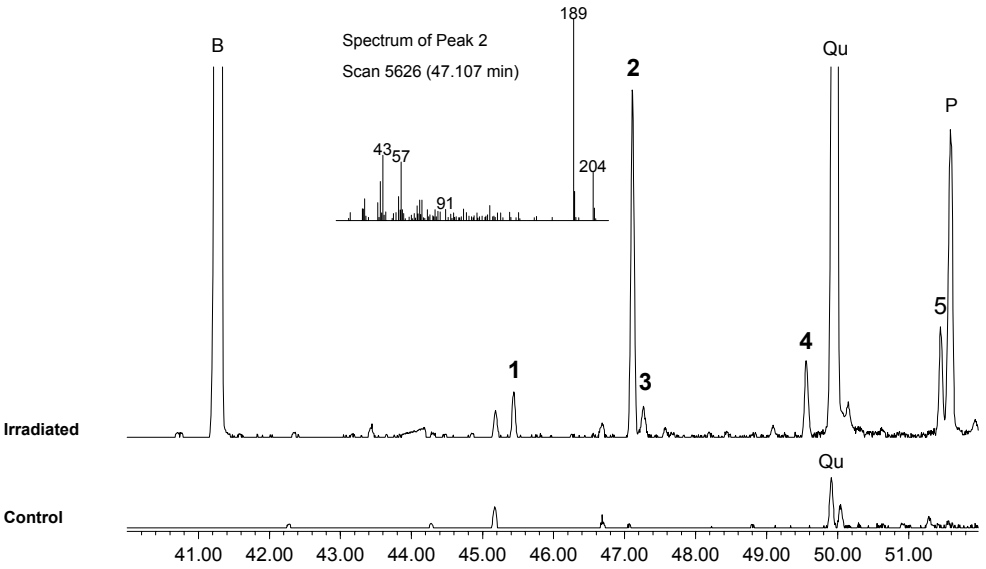


Figure 5.10 **Trace aromatic degradation products** in PP film „A" seven days after irradiation with 26.6 kGy — irradiated (top) vs. non-irradiated control (bottom).
1 = Unidentified (m/z 189.1, 204.2)
2 = 1,3-Bis-(1,1-dimethylethyl)-5-methylbenzene
3 = (1,1-Dimethylethyl)-phenol isomer ? (m/z 107, 135, 150.1)
4 = Unidentified (m/z 163, 177.1, 205.1, 220.1)
5 = Undecylphenol ? (m/z 107, 248)
B, Qu., and P are the main antioxidant degradation products (see Figure 5.7).
The Figure shows *added* extracted ion chromatograms [added EICs for m/z (190.2 + 189.1 + 204.2 + 135.1 + 220.1 + 107); t_R 40–52 min]—please note that the peak areas of EICs do not necessarily reflect 'true' or total ion chromatogram peak areas ! Exp. Condit. as in Figure 5.8.

methylethyl)-5-methylbenzene (#2), because their spectra are quite similar, with m/z 204.2 probably being the molecular ion (M+). Product #3 [a (1,1-dimethylethyl)-phenol isomer ?] might be a de-butylated analogue of the main degradation product *bis-(1,1-dimethylethyl)-phenol* (P), whereas the *unidentified* product #4 is probably an isomer of the quinone *2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione* (Qu), because it yields the same characteristic ions (m/z 163, 177.1, 205.1, 220.1), though with different intensities.

The radiation-induced formation of trace degradation products of antioxidants, especially the possible formation of atypical / de-butylated / de-methylated (?) and/or radiation-specific degradation products should be investigated in more detail, because this might be a promising approach for irradiation detection. The increased sensitivity available with appropriately optimized SIM data-acquisition methods should more than compensate for the anticipated lower product yield at food irradiation doses. To identify the products one would perform full-scan analyses and try to enhance their sensitivity by conventional means, such as increasing sample load, TDS-temperature (and -time) etc. Initially, one might also want to use absorbed doses higher than 25 kGy to increase product yields. An interesting strategy might also be to *postulate* atypical structures, and then to look for these compounds with suitable SIM-methods, e. g., scanning the molecular ion M+ —ideally, together with the major anticipated fragment ions.

5.11 Geometry and Efficiency of the TDS-CIS-System

The TDS-injector is originally designed to desorb adsorbent-filled sampling tubes from environmental air analyses, and PTV-injection, in general, has become the subject of some *critical remarks* by Grob (1993). However, the TDS appears to be quite an efficient desorption device for polymers, and the concept of using a PTV injector (the CIS) as interface to the GC column—or, to put it differently: the concept of trapping volatiles directly in a split/splitless-injector—appears to be very elegant. (Since I neither designed the system, nor envisaged its 'abuse' for polymer analysis, and since I shall also note its disadvantages, this should not be considered an unfair statement.)

Hodgson et al. (1998) have recently proposed to characterize the extent to which a given system is purged with a parameter ε, defined as

$$\varepsilon = V / (V_h \, m)$$

where V is the volume of purge gas, V_h is the vapor volume in the sampling vessel (= the headspace), and *m* is the sample mass.

ε-Values for two different LDPE film-samples (and sizes) have been tentatively calculated (see Table 5.2), assuming that V_h is the cylindrical space inside the ca. 4 mm i. d. desorption tube occupied by the film strips. Clearly, these ε-values are much higher than that of Hodgson et al. (ε = 53.1 g^{-1}), and they are also higher than ε = 159 g^{-1}, the value they calculated for a *complete* extraction (of LDPE *pellets* at room temperature, and with N_2 as

Table 5.2 Values of the parameter ε calculated for various LDPE film samples.

Sample Configuration	LDPE film	mass (g)	V_h (ml)	ε (g^{-1})
3 x (3 mm x 100 mm)	Commercial (see Fig. 5.1)	0.075	1.26	2116
	Standard 25 µm	0.021	1.26	7559
3 mm x 70 mm	Commercial	0.018	0.88	12987
	Standard 25 µm	0.005	0.88	46382

The volume of the films was neglected in calculating V_h; and ε was calculated with V = 200 ml.

purge gas). Of course, ε does not take into account the geometry of the sample (or the kinetics of the actual desorption process), and it is clearly not possible to desorb polymer *pellets* quantitatively during 10 minutes even at high ε-values.

However, while this has not yet been tested experimentally, it should be possible to quantitatively desorb PE *films* with the Gerstel TDS-system—even at room temperature (which may be preferable for the characterization of odorous volatiles). Ligon and George (1978) have already suggested that it is possible to desorb polymers quantitatively at temperatures above their glass transition temperature, T_g, where they are in liquid-like state comparable to that of a GC liquid-phase—incidentally, this is the premise on which the quantitative method for PS is based (cf. Section 6.2)—and the T_g of LDPE is ca. -100°C.

The desorption of the Tenax 'trap' inside the CIS is also a *dynamic* process: during the 90 seconds of splitless transfer to the GC column, the space occupied by the Tenax is 'purged' with ca. 1.5 ml He (at an estimated column flow of 1 ml/min). For a Tenax 'column' (cylinder) of 15 mm length, ca. 0.5 mm radius, and a mass of ca. 6 mg, ε would be > 20,000 (or even higher, if the volume of the adsorbent were subtracted from V_h).

In contrast, Hodgson et al. (1998) desorb their Tenax trap with a *static* technique: it appears that they desorb 'only' ca. 22% of the total volatiles (during a desorption period of 150 s at 200°C), and transfer 'only' 5 ml of a total headspace of 20 ml (via a sampling loop and transfer line) to the GC column. (I would like to repeat, at this point, that I am only comparing system geometries, and that I found the data analysis of Hodgson et al. (1998) very inspiring indeed.)

Based on present experiences with the TDS-CIS-system, it can be said that it is relatively easy to identify volatiles present at 10 ppm in a 5 mg polymer sample (they will yield '50 ng-peaks'—if desorption, transfer to the CIS, and finally to the GC-column are complete); if we assume that we can correctly assign the mass spectrum of a '10 ng-peak', which is admittedly easier with aromatic compounds, then we could identify volatiles present at 0.1 ppm in a 100 mg sample (etc.). Of course, the system described by Hodgson et al. (1998) does permit higher sample loads and therefore should be more sensitive 'in the last analysis'.

Clearly, the TDS has its disadvantages, too: Most obviously, since desorption takes place in an *on-line*-mode, the entire GC-MS is 'blockaded' during that time, and one would not want to use long desorption times, for example, to 'extract' whole polymer pellets. It also has a limited sample capacity, and will not accomodate more than ca. 25 spherical pellets, 3–4 mm in diameter. Problems that may occur mainly, but not exclusively, at higher temperatures are: Contamination of the desorption tube by melting polymers; condensation of higher-MW volatiles in the needle of the TDS-injector; and difficulties to obtain 'clean' blanks. On the other hand, these 'memory effects', problems with 'cold spots', clean blanks, and possibly adsorptive activity (loss of analytes) are by no means an uncommon experience in thermal desorption / dynamic HSA, and solutions may be found depending on the analytes one is interested in and the scope of the investigation.

6. The Way to Quantitation

Initially, thermal desorption—while being an extremely sensitive technique to detect and to identify traces of volatile compounds in polymer matrices—had been perceived as an essentially **qualitative** technique. In this Chapter, it is described how the experimental results gradually changed this attitude, and how **'total desorption'** or **'quantitative extraction' conditions** were established.

6.1 Qualitative Comparisons

During the initial screening of six medical polymers (see Chapter 4) quantitation had not appeared to be an option. No attempts to quantify **trace** compounds in polymers using thermal desorption or dynamic headspace techniques were known. Quantitation by **static** headspace analysis (HSA), as, for example, described for styrene in PS by Hempel and Rüdt (1988), was clearly not sensitive enough for the radiolysis products. It was obvious that volatiles could not be **quantitatively** desorbed from the relatively bulky pellets or from fragments of the (injection-molded) parts.

Initial attempts to produce fine polymer powders with a standard coffee mill had failed. Additionally, since I was somewhat pre-occupied with the **concept of equilibrium** underlying

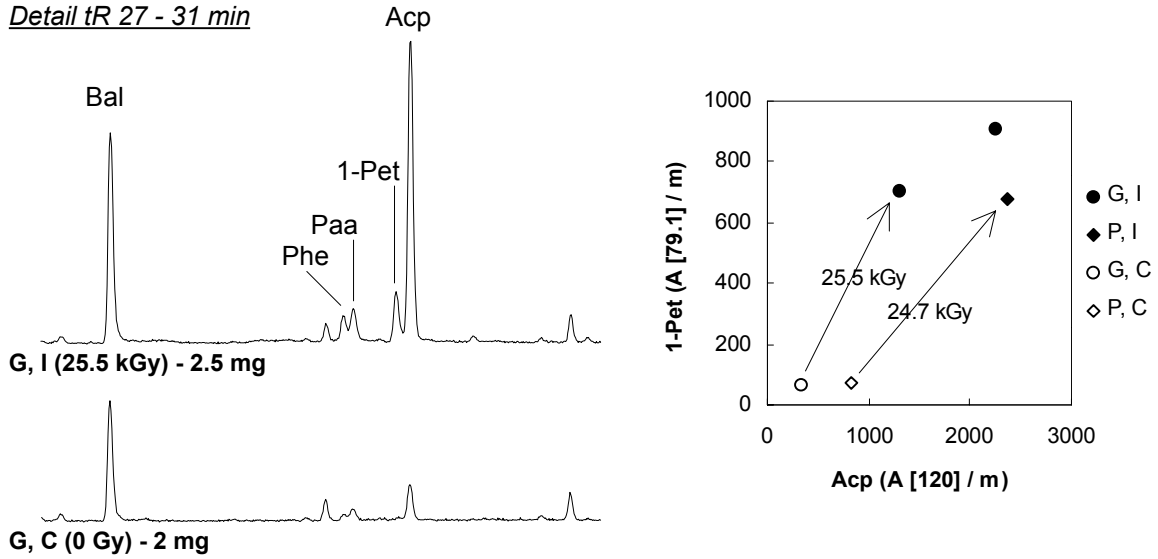


Figure 6.1 **Qualitative comparison of PS granulate and injection-molded parts: Detail t_R 27–31 min** of irradiated (25.5 kGy; top) vs. non-irradiated PS (bottom) and **2D-plot of 1-phenylethanol vs. acetophenone** (peak areas divided by sample mass). Concentration estimates (in ppm or µg/g of polymer) for 1-Pet and Acp in these analyses are presented in **Appendix 10.**

G, C = granulate control G, I = granulate, irradiated (25.5 kGy)
P, C = inj.-molded parts, control P, I = parts, irradiated (24.7 kGy)

Experimental Condit.: Sample: BASF Polystyrol 168 N, 2 mg of powder (obtained by milling the granulate at 10,000 rev./min for one min); TDS 80 -40- 160(8); CIS 30; GC 40(11.5) -10-250(10); column: Rtx-1701. Parameters in the 2D-plot are **extracted ion chromatogram** (EIC) **peak areas** normalized on sample masses – A [79.1] / m, and A [120] / m for 1-Pet and Acp, respectively. The samples were analyzed two days after milling; 13 and 10 months after irradiation (G, I and P, I, respectively).

static headspace quantitation (cf. below), I was not very convinced that a fine powder would actually allow meaningful quantitative analyses. In any case, the problem of determining radiolysis product concentrations was postponed.

A first step towards quantitation was undertaken based on the idea that if it was impossible to determine **concentrations**, then one could at least attempt to determine **the amounts** of products **desorbed** from the pellets under a set of defined experimental conditions. This might allow to estimate the amounts potentially released from a medical product with a given surface area. The 'values' obtained in these pseudo-quantitative experiments are of little significance today, but during this series of measurements the **first external standard (ESTD) injections** and tentative **TDS recovery tests** were performed.

Another idea was to determine **residual styrene levels** in PS by established **static** headspace procedures, and then to **estimate** the concentrations of the radiolysis products by comparing their peak areas in a TDS-fingerprint chromatogram with that of styrene. However, it appeared that **improvising** a static headspace method with inadequate equipment would not necessarily provide meaningful results, and so the project was postponed several times and finally abandoned. It would certainly be interesting to compare styrene levels determined by the TDS-technique with those obtained by state-of-the-art static HSA; however, this has not been an option, and ultimately it was thought that it was not absolutely necessary.

For a while, it appeared to be easier to quantitatively desorb the thin **polymer films** (Chapter 5), and in this context the **'stainless steel sieve sandwich'**-technique was developed (cf. Figure 5.5). However, the different TDS-temperature effects on radiolysis products vs. residual hydrocarbons in LDPE (see Figure 5.6) suggested that the observed products might be thermal degradation products of some radiation-induced precursors (cf. Section 5.6), and so it was decided to address other problems first.

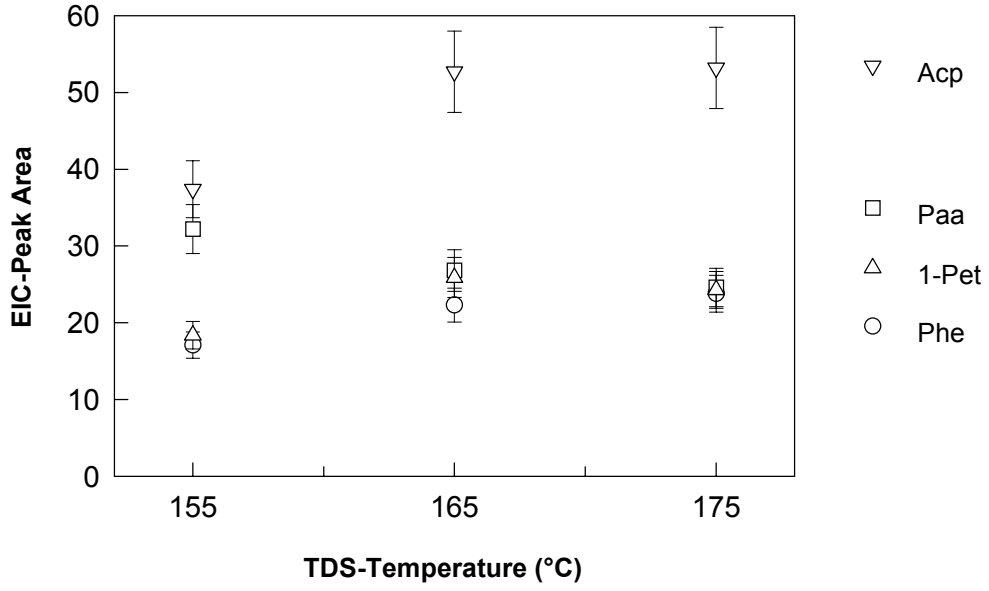


Figure 6.2 Radiolysis products from PS **powder** as a function of **TDS-temperature.**
Peak areas (arbitrary units) for extracted ions m/z 120 (acetophenone), 91.1 (phenylacetaldehyde), 79.1 (1-phenylethanol), and 94.1 (phenol). Error bars indicate ± 10%.
Experimental Conditions: Sample: BASF Polystyrol 168 N, 25.5 kGy, **20 to 25 mg** of the G, I - powder (= granulate, irradiated – 14 months after irradiation, 4 weeks after milling); TDS X°C (10 min); CIS 30, **split;** GC 40(11.5) -40- 180 -10- 250(13); column: Rtx-1701.

Thus, there was quite an impasse as far as quantitation is concerned, which gradually began to dissolve after the **analytical mill** described in Section 3.4 became available. It allowed to produce very fine powders from the polymer pellets and injection-molded parts —in the case of PS even without the addition of liquid nitrogen as a coolant.

The immediate objective was a **qualitative comparison** of pellets vs. injection-molded parts, which previously had not been possible in a satisfactory way (cf. Sections 4.7 and 4.8). **Figure 6.1** shows the results of the first analyses of PS powders, performed with the 60 m, thick film (1.0 µm) Rtx-1701 column. The Figure shows details of fingerprint chromatograms with the main radiolysis products—benzaldehyde, phenol, phenylacetaldehyde, 1 phenylethanol, and acetophenone—eluting from 27 to 31 min.

Figure 6.1 also contains a **2-dimensional plot** of 1-phenylethanol vs. acetophenone levels in the four specimens under investigation, i. e., non-irradiated and irradiated granulates (G, C and G, I) and injection-molded parts (P, C and P, I); the values plotted are EIC-peak areas divided by sample mass. One can see that a sterilizing dose of ca. 25 kGy shifts the data points towards higher 1-Pet and Acp levels, and that it does so in a similar way with both pellets and processed parts. Additionally, it appears that injection-molding induces some formation of Acp, but not of 1-Pet: the data points of the *parts* (P, C and P, I) are shifted horizontally towards higher Acp levels. The idea underlying this and similar 2D-plots will be discussed in Chapter 7 (Section 7.5), as will be the retrospective ('ex-post') concentration estimates in Appendix 10 (Section 7.8).

I was not totally satisfied with the results of these first five measurements, mainly because of the low sample masses: when a first trial with ca. 12 mg of the „G, I"-powder had yielded severely overloaded peaks, the complete series of all four specimens was analyzed with only 2–3 mg polystyrene powder. There also may have been a problem with the analytical balance, which had to be repaired a few days after these measurements. Therefore, the next two series of measurements were performed with 20 to 30 mg PS in **split-mode**, which

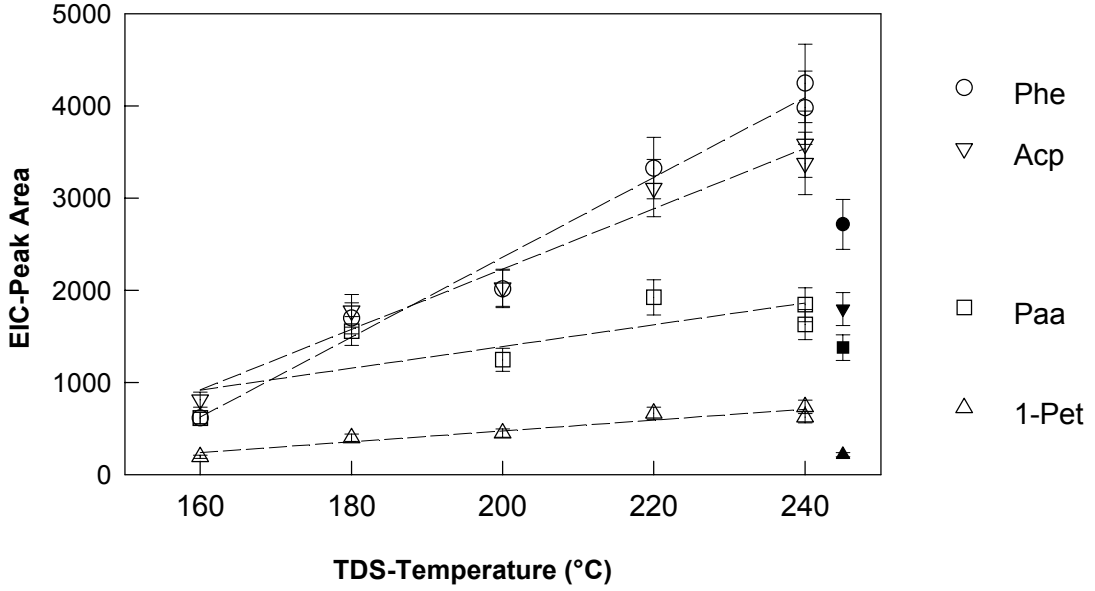


Figure 6.3 Radiolysis products from PS **granulate** (pellets) vs. **TDS-temperature.**
Black Symbols = Non-irradiated control samples (at 240°C !)
Peak areas (arbitrary units) for extracted ions m/z 94.1 (phenol), 120 (acetophenone), 91.1 (phenylacetaldehyde), and 79.1 (1-phenylethanol). Error bars indicate ± 10%.
Exp. Conditions: Sample: BASF Polystyrol 168 N, **1 kGy,** 5 pellets, 10 days after irradiation; TDS X°C (10 min); CIS -40, GC 40(11.5) -40- 180 -10- 250(13); column: Rtx-1701.

means that after trapping the volatiles in the CIS a huge fraction (more than 95% at an estimated split ratio of 1 : 30) is deliberately vented through the split valve—certainly a somewhat unusual practice in *trace* analysis.

The first of these series was a failed attempt to repeat the comparison of the four PS specimens with additionally injecting a 'recovery-standard' to test the system's performance. While the standard did not work for some reason (the TDS-temperature was probably too low), a data analysis of the PS fingerprints gives a 2D-plot very similar to that in Figure 6.1 —see Appendix 1: Figure A-1.1. The second series in split-mode was a 'quick look' at the effect of desorption temperature **(Figure 6.2);** the first series (Figure A-1.1) had already covered TDS-temperatures of 150°C and 170°C besides the 'standard' 160°C. (160°C had been used in Phase I as the highest temperature with PS.)

All these measurements were performed as 'minor projects' parallel to the investigation of polyolefin films; together with the films, a sample of PS granulate had been irradiated with absorbed doses of 1, 3, and 10 kGy. These specimens were analyzed using the 'old' technique of directly desorbing whole pellets. There appeared to be a linear relationship between product yield and absorbed dose, and there appeared to be a detectable difference between the non-irradiated control and the 1 kGy specimen (Appendix 1: Figures A-1.2 and A-1.3, respectively). Direct desorption of the pellets also indicated a linear increase of peak areas with the TDS-temperature up to 240°C (**Figure 6.3** as opposed to Figure 6.2).

6.2 Establishing 'Total Desorption' or 'Quantitative Extraction' Conditions

The Principles of Quantitation

At some point during these experiments my perception of thermal desorption changed and quantitation appeared to become possible. In static headspace analysis, the volatile analytes, e. g., the residual monomers, reach an equilibrium distribution between the headspace and an added higher-boiling solvent, and this equilibrium allows quantitation and the use of internal standards for calibration (for literature on static HSA, see Section 2.6).

It was thought that in thermal desorption it might be precisely the absence of equilibrium conditions that might permit quantitation. Under these **non-equilibrium conditions** ('dynamic extraction' or 'sink conditions') the ongoing loss of volatiles into the headspace, from which they are constantly removed, would create a concentration gradient in the polymer. This gradient would drive the *diffusion of volatiles* to the surface, and thus it might be possible to completely 'extract' a polymer. The time required for this process would depend on the size of the polymer particles and on the diffusion velocity of the analytes, which in turn would depend on the temperature. This overall concept is supported by several authors who have argued along similar lines, but said that they had „not rigorously investigated" the quantitative aspects, e. g., Ligon and George (1978), Myers (1982), and Venema (1986), see Section 2.7.

The desorption temperature for volatiles should be above the polymer's **glass transition temperature,** T_g, where polymers are in a *liquid-like* state comparable to a GC-liquid phase. The diffusion of „organic vapors" [volatiles] above T_g has been discussed by Fujita (1968): At temperatures well above T_g, the diffusion kinetics of small molecules are „rather simple", obeying *Fick's laws of diffusion*, while they are „exceedingly complex", exhibiting non-Fickian

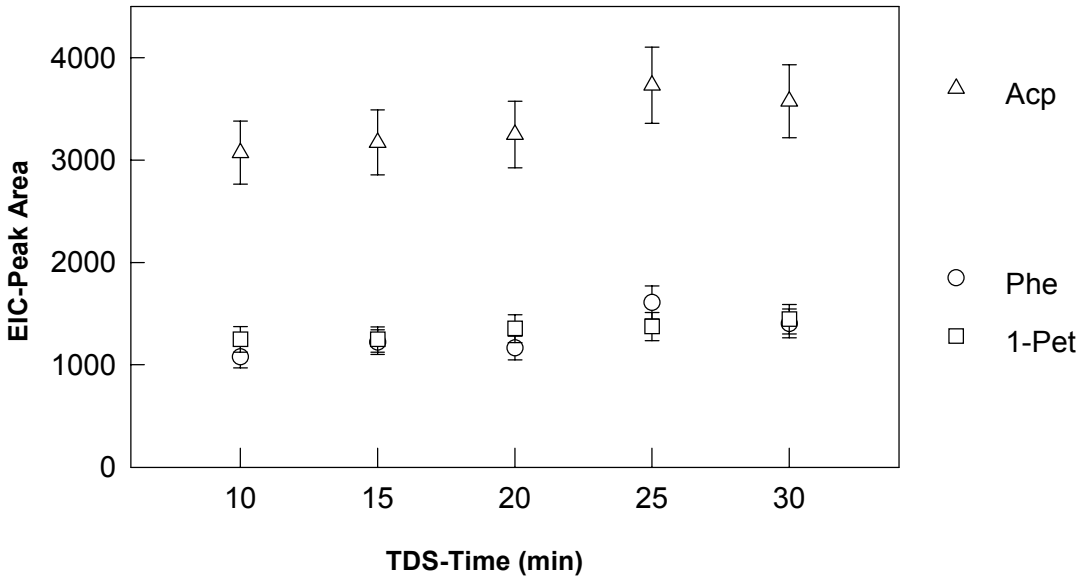


Figure 6.4 Radiolysis products from **PS powder** as a function of **TDS-time.**
Peak areas (arbitrary units) for extracted ions m/z 120 (acetophenone), 94.1 (phenol), and 79.1 (1-phenylethanol). Error bars indicate ± 10%.
Experimental Conditions: Sample: BASF Polystyrol 168 N, 25.5 kGy, **5 mg** of the G, I -powder (= granulate, irradiated – 17 months after irradiation, 4 months after milling); TDS 160(x min); CIS -40; GC 40(11.5) -5- 80 -2- 100 -40- 210(5); column: DB-5.

anomalies, below and in the vicinity of T_g. These features are unique to polymer systems and reflect the *molecular mechanisms* underlying the diffusion of molecules comparable with, or larger than, the monomer unit (as opposed to gas molecules, such as H_2, Ar, N_2, CO_2, etc.). The glass transition temperature of polystyrene is 100°C; the figure is quoted from Woo et al. (1991).

Desorption Temperature and Time

The **TDS-temperature** studies, though somewhat limited, suggested that a plateau is reached at 160°C, above which there is no further increase in peak areas (Figure 6.2, and Figure A-1.1 in Appendix 1). To confirm this assumption, an additional series of quantitative analyses was later performed at a TDS-temperature of 240°C (see Section 7.6).

To confirm that a **TDS-time** of 10 min was sufficient, the desorption time was increased in intervals of 5 minutes (**Figure 6.4**). As mentioned in Section 3.5, the Rtx-1701 was replaced by the DB-5 column to reduce GC runtime during quantitation (and the TDS-time series in Figure 6.4 was already recorded with the DB-5).

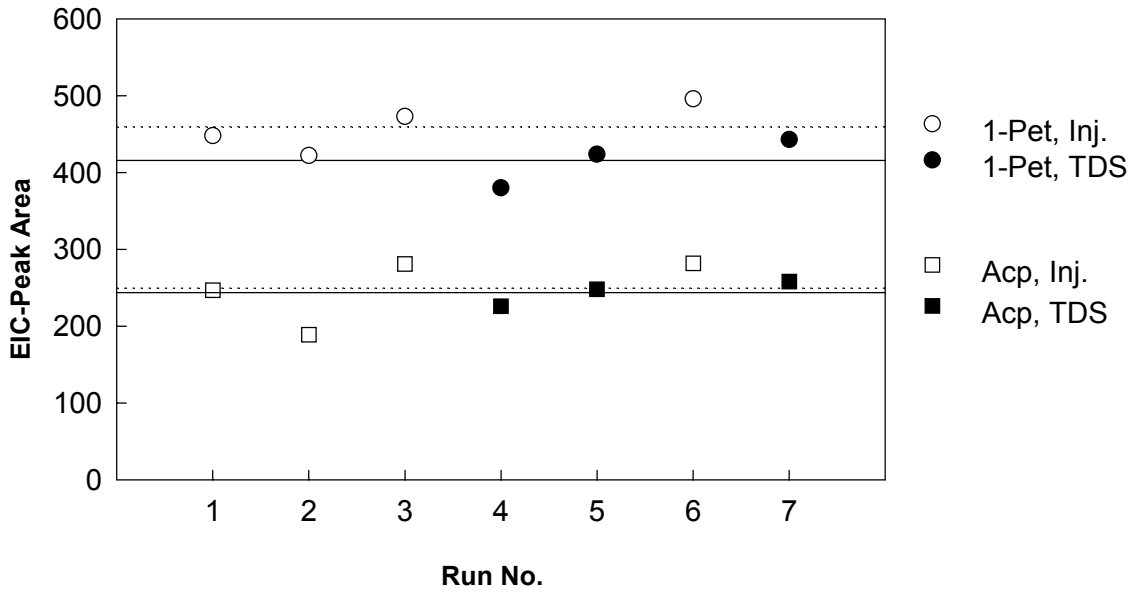


Figure 6.5 Comparison of direct (splitless) injections into the CIS and TDS-analyses (**TDS recovery test**) — indicating correct system performance (complete sample transfer) and showing the high reproducibility of manual injections into the cold injector (CIS).
Peak areas (arbitrary units) for extracted ions m/z 79.1 (1-phenylethanol; top) and 120 (acetophenone; bottom) in seven consecutive analyses; ○, □ = direct injection, ●, ■ = TDS-injection. The small losses (< 10%) of 1-phenylethanol are thought to result from irreversible adsorption on the TDS glass liner surface. Exp. Conditions: Injection of 1.0 µl of a 10 ppm standard solution (≡ 10 ng). TDS 160(10); CIS 30; GC 40(11.5) -10- 250(5); column: DB-5.

Test Injections and Calibration

To prove that the system works correctly and that the analytes are transferred completely from the TDS-unit to the CIS, a series of **test injections** into the CIS and TDS was made (**Figure 6.5**). Recovery from the TDS is almost 100% for acetophenone and > 90% for 1-phenylethanol, probably because of irreversible adsorption of the alcohol onto the surface of the TDS glass liner. The graph also illustrates the high reproducibility of manual (!) liquid injections into the *cold* injector.

Since exact ppm-amounts of volatiles cannot be incorporated into polymers in a reliable manner (Kolb and Pospisil, 1977; Westendorf, 1985), quantitation must be achieved with external standard calibration (ESTD). This requires that known aliquots of the standard solutions, usually 1 µl, are injected as exactly as possible. To this end the so-called **solvent-flush-technique** was chosen; it is explained in Figure 6.6.

The solvent-flush-technique was compared on several occasions against the 'standard' injection technique, in which the syringe is completely filled with the analyte solution only. Two of these comparisons are shown in Appendix 1—Figure A-1.4 (two operators) and Figure A-1.5 (one operator). It can be seen that the reproducibility of the solvent-flush-technique is much better than that of the 'standard' technique, and that there is a general trend towards

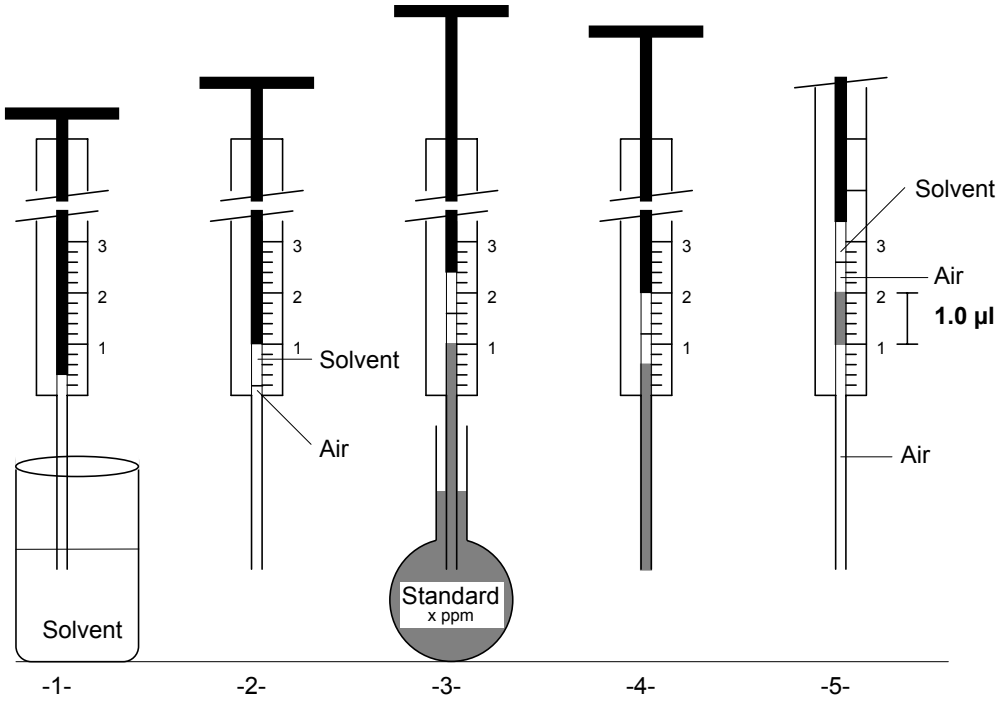


Figure 6.6 Using the **solvent-flush-technique** to inject external standard solutions into the cold injector (schematic drawing).

-1- Fill the syringe with 0.2 to 0.4 µl of pure solvent (in the same way as you would fill it for a 'normal' injection).
-2- Draw back the plunger positioning it **exactly** at the 1.0 µl-mark.
-3- Draw back the plunger **beyond** the 2.0 µl-mark filling the syringe with **more than** 1 µl of the analyte solution.
-4- Move the plunger gently forward positioning it **exactly** at the 2.0 µl-mark, and wipe excess solution from the needle.
-5- Visual Control: Draw back the plunger to check the volume.
-6- Inject.

Steps 2, 4, and 5 may be conveniently carried out holding the syringe in a horizontal position.

increased peak areas with the latter. Obviously, the ‘standard’ technique delivers the nominal volume (e. g., 1 µl) *plus* an unknown and varying fraction of the solution present in the syringe’s needle. While this is irrelevant for internal standard (ISTD) quantitation, it is not acceptable in the external standard (ESTD) quantitation of thermal desorption.

Appendix 2 contains some *GC background-data* that characterize the analytical system during the initial series of quantitative ananlyses (= Phase III); these include linear velocities and volumetric flows of the carrier gas (Figure A-2.1), separation numbers for 1-phenylethanol and acetophenone (Figures A-2.2 and A-2.3), the effect of the GC temperature program on the retention times and peak areas of 1-Pet and Acp (Figure A-2.4), and a comparison of splitless- and split-injection (Figure A-2.5 and Table A-2.1).

7. Initial Quantitative Results ('Phase III')

7.1 General

The radiolysis product concentrations reported in this Chapter rest on the premise that, for the experimental conditions used, the following assumptions are true:

— **extraction** of the analytes during dynamic thermal desorption is complete (cf. Chapter 6),

— **transfer** of the analytes from the **TDS-unit** to the **CIS** (recovery) is complete (cf. Figure 6.5), and

— **transfer** from the **CIS** to the capillary **GC column** during splitless-injection is complete (for both TDS-analyses and external standard injections).

The last assumption, complete sample transfer during splitless injection, was checked under '*conditions of forced sample transfer*' (Grob, 1993): the peak areas obtained at *increased* carrier gas flow rates (= increased column head pressures) and *extended* splitless periods were found to be equal to those obtained under 'standard' conditions. [Without an on-column-injector, a more comprehensive check would have been 'on-column injection into a detached column inlet' as described by Grob (1993).] For the split-series (cf. below) it is assumed that the vaporizing solvent in a standard injection does not significantly alter the split ratio, in other words, that the split ratios are identical in TDS-analyses (where no solvent is present) and in CIS-injections of standard solutions.

After 'total desorption' conditions had been established, it was decided to analyze the PS (and MABS) specimens that were at hand, i. e., the granulates and injection-molded parts irradiated 15 to 18 months earlier with ca. 25 kGy, and the granulates irradiated more recently with 1, 3, and 10 kGy (see Section 3.7 *Polymers under Investigation*). In a future investigation, the concentrations of the radiolysis products should be determined immediately after irradiation, and possible concentration changes-with-time should be monitored (see 'Phase IV': Chapter 8).

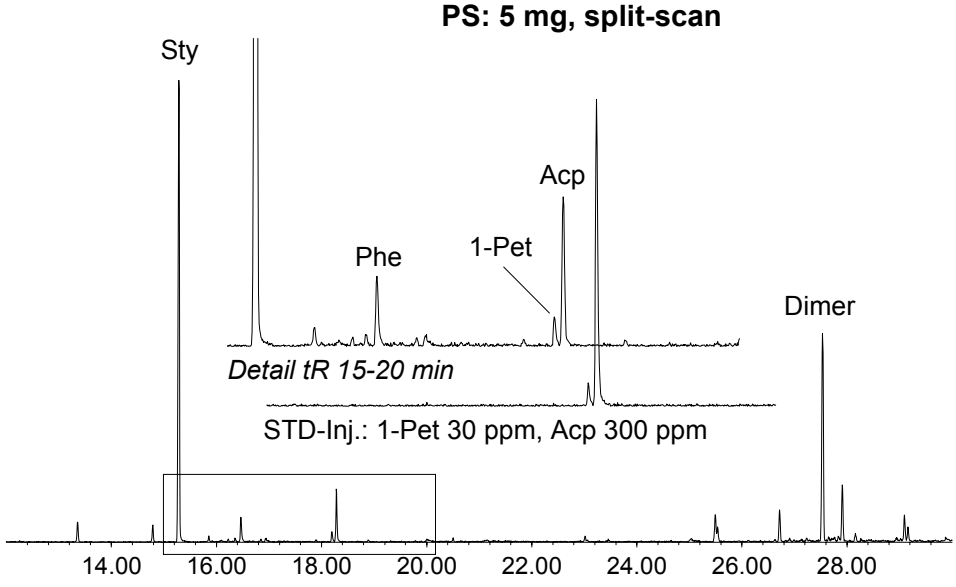


Figure 7.1 **Split-scan analysis:** 5 mg PS 168 N, fingerprint of 25.5 kGy-irradiated sample *plus* detail t_R 15–20 min vs. standard injection.
Exp. Conditions: TDS 160(10); CIS -40, **split;** GC 40(11.5) -10- 250(5); column: DB-5.

7.2 The Three Series of Measurements

Based on previous experiences with sample masses and peak areas, it was decided to try three different procedures, resulting in **three independent series** of measurements, namely, in order of increasing sensitivity:

(1) a **split-scan series** with 5 mg PS, split-injection, and data acquisition in scan mode,

(2) a **splitless-scan series** with 5 mg PS, splitless-injection, and data acquisition in scan mode, and

(3) a **splitless-SIM series** with 10 mg PS, splitless-injection, and data acquisition in SIM mode (selected ion monitoring).

Each series consists of PS-analyses (by thermal desorption), and of a number of injections of external standards; the concentrations of the radiolysis products in the PS specimens are calculated with the calibration relationships established by the ESTD-injections. The split-scan series was primarily designed for the 25 kGy-specimens, the splitless-SIM series for the non-irradiated controls and low-dose (1 and 3 kGy) irradiated specimens.

Figure 7.1 shows a fingerprint chromatogram from the split-scan series (PS irradiated with 25.5 kGy), a detail view of t_R 15 to 20 min, plus the corresponding detail of a standard injection (1-phenylethanol and acetophenone). The original data, i. e., the calibration data, calibration curves, and the polystyrene data of the split-scan series are presented in Appendix 3; chromatograms and the quantitation data for the splitless-scan and splitless-SIM series are presented in Appendices 4 and 5, respectively.

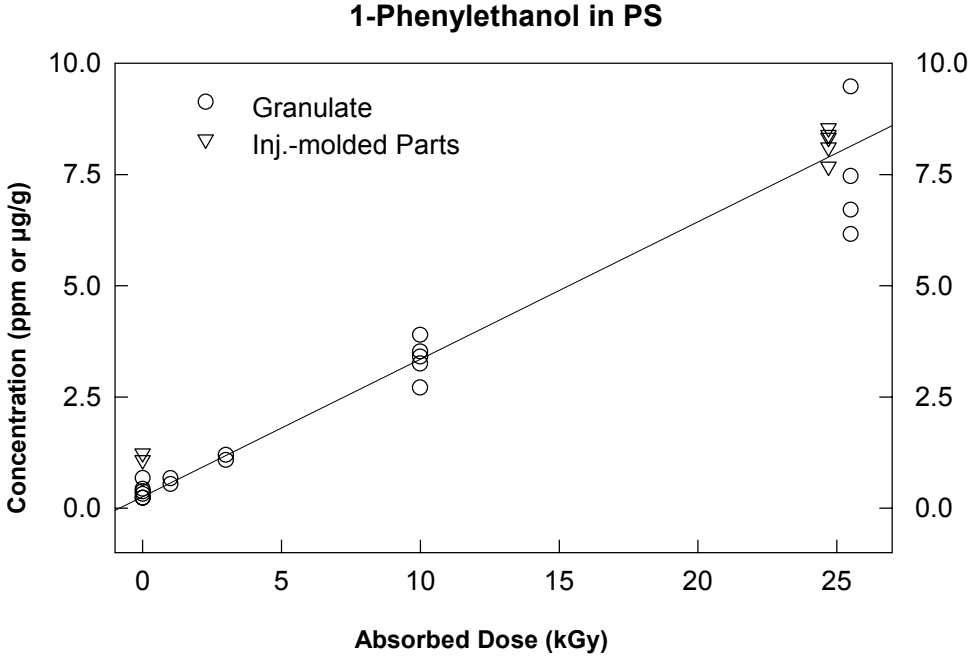


Figure 7.2 **1-Phenylethanol concentrations in PS 168 N vs. the absorbed dose.** The plot summarizes the results of the three series of measurements performed at TDS 160(10), i. e. split-scan, splitless-scan, and splitless-SIM (see Appendices 3 to 5). Please note that only the 1, 3, and 10 kGy-values have been used to calculate the linear regression.
The time elapsed after irradiation is 1.5 years for the 25.5 kGy-irradiated granulate, 15 months for the injection-molded parts (24.7 kGy), and 2 months for the 1, 3, and 10 kGy-irradiated granulates. Experimental Conditions: See Section 3.6.

7.3 Product Concentrations vs. the Absorbed Dose

The results obtained in the three series agree quite well (most specimens were analyzed in at least two of the series—see Appendices 3 to 5); therefore, the split-scan, splitless-scan, and splitless-SIM data are plotted collectively against the absorbed dose in **Figure 7.2** (1-phenylethanol) and **Figure 7.3** (acetophenone concentrations). The good agreement between the three series was not entirely unexpected, because they rest on the same principles and—apart from requiring independent calibration—differ mainly in sensitivity.

1-Phenylethanol concentrations (Figure 7.2) are below 1 ppm in the non-irradiated granulate, and in the range of 6 to 8 ppm in the 25.5 kGy-irradiated granulate (if we consider the 9.5 ppm data point as out-of-range value). The levels of 1-Pet appear to be slightly higher in the injection-molded parts, for both the non-irradiated controls and the 24.7 kGy-specimens. **Acetophenone** concentrations (Figure 7.3) are in the range of 5 to 15 ppm in the non-irradiated granulate, and ca. 25 to 35 ppm in the 25.5 kGy-granulate; the levels are significantly higher in the processed parts (ca. 25 ppm non-irradiated, ca. 50 to 60 ppm after 24.7 kGy), which is in agreement with the earlier qualitative results (see Figure 6.1).

An interesting feature in both, Figures 7.2 and 7.3, is the **linear relationship** between product concentration and the absorbed dose, especially so because only the 1, 3 and 10 kGy data points have been used to calculate the regressions. The data points of the 25.5 kGy-irradiated granulates lie almost perfectly on these regressions, despite the fact that they had been irradiated more than one year earlier. This had already been observed in a qualitative experiment with whole pellets (see Figure A-1.2), and it suggests that there is practically no loss of these relatively high-boiling compounds during storage (or, alternatively, that they might be thermal degradation products of some radiation-induced non-volatile precursors —see Section 12.8). As far as irradiation detection is concerned, Figure 7.2 suggests that 1-phenylethanol could be used as **radiation marker** down to an absorbed dose of 3 kGy, if it should be possible to differentiate between granulates and processed parts.

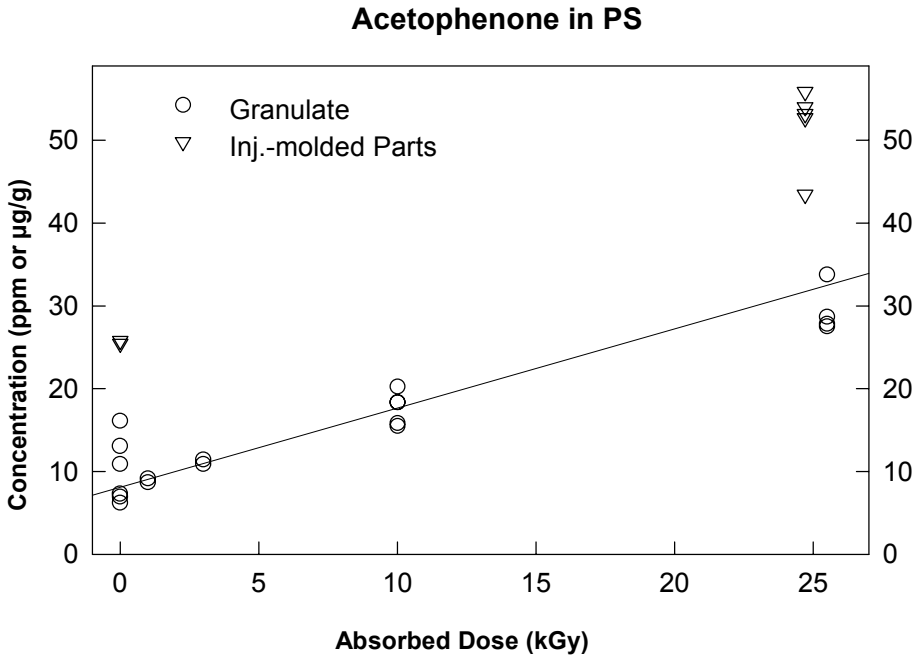


Figure 7.3 **Acetophenone concentrations in PS 168 N vs. the absorbed dose.** See Figure 7.2 (1-phenylethanol) for more information.

7.4 Radiation-Chemical Yields (see also Section 9.7)

In radiation chemistry, a special quantity is used to characterize reactions, namely the *radiation-chemical yield* which is defined as the *number of molecules formed* divided by the *energy absorbed* by the irradiated matter (see also Section 9.7). From a plot of concentration (mg/kg) vs. the absorbed dose (kGy or kJ/kg), one can directly read the quotient *product mass* per *energy absorbed* (mg/kJ) and convert it to the radiation-chemical yield (mmol/J). (An older, non-SI unit still widely used is the G-Value or 100 eV-yield, a figure that indicates the number of molecules formed per 100 eV of absorbed energy.) The slope of the regression line in Figure 7.2 is 0.31 mg/kJ, the radiation-chemical yield of 1-phenylethanol is accordingly 2.5 nmol/J (nanomol/Joule) or G = 0.025. With 8 nmol/J (or G = 0.08) the radiation-chemical yield of acetophenone, as determined from Figure 7.3, is ca. three times higher. These values agree reasonably well with those obtained in the DSC-series (cf. Section 9.7 and Appendix 19).

7.5 2-D-Plot of 1-Phenylethanol vs. Acetophenone Concentrations

Figure 7.4 is a **two-dimensional plot** of 1-phenylethanol vs. acetophenone concentrations for the PS specimens of the splitless-scan and splitless-SIM series. The concept underlying this type of plot is to use a combination of two (or more) radiolysis products as radiation markers, as practiced in the detection of irradiated food, where, in certain cases, combinations of radiation-induced hydrocarbons and / or cyclobutanones are used (McMurray et al., 1996). The multiple-concentration plots are intended to visualize this concept: In a space of three (or even more) dimensions, irradiated and non-irradiated specimens might be located in distinctly different regions of such a three- or n-dimensional space, which would allow to identify an irradiated specimen more reliably and, possibly, with higher sensitivity (i. e., after lower absorbed doses) than when considering a single radiolysis product alone.

Unfortunately, the available computer graphic programs did not permit to create satisfactory 3D-plots; therefore, I experimented with a set of 2D-plots (1-Pet vs. Acp, phenol vs. Acp, and phenol vs. 1-Pet), which can be considered as right-angle projections of the 3D-data points onto the three planes defining the 3D-space. [**Phenol** concentrations were determined in the splitless-SIM series only (Appendix 6), and the peak shapes of phenol on the DB-5 column were relatively bad at low concentrations; therefore, no phenol-vs.-dose graph or 2D-plot with phenol is presented here. See Appendix 6 for the Phase III-results with phenol, and Figure 8.5 for a 2D-plot of phenol vs. acetophenone from Phase IV.]

Irradiated and non-irradiated specimens in Figure 7.4 are arranged along two different lines that intersect somewhere near the „0 Gy"-granulate specimens. In contrast to Figures 7.2 and 7.3, we differentiate between two granulate specimens coded „0 Gy" and „G, C", depending on when the pellets have been milled (some days vs. four months earlier, respectively; cf. Section 3.7 *Polymers under Investigation*).

The linear regressions in Figure 7.4 are for the 1, 3, and 10 kGy-specimens and for the non-irradiated „G, C"-specimens, respectively; and it is interesting to note that the former extends into the region of the 25 kGy-irradiated specimens, while the latter intersects with the non-irradiated parts „P, C" (the intersection near 0 Gy has already been mentioned). Thus, it appears that ageing of the polystyrene powder („G, C" vs. „0 Gy") and processing („P, C" vs. „G, C") induce oxidation along a similar 'direction', with Acp concentrations increasing much stronger than those of 1-Pet. As far as irradiation detection is concerned, it appears that—while the 1 kGy-specimens are still poorly 'resolved' from the non-irradiated granulates—the chances to positively identify a 3 kGy-specimen as irradiated have improved.

Also included in Figure 7.4 is the **Petri dish** analyzed during the MABS series (cf. below). This 'real-life' specimen, sterilized with an unknown dose, is located exactly on the line representing the irradiated specimens. [The values for the Petri dish are probably underestimated because of incomplete desorption (see Appendix 8), and it is thought that the real concentrations would shift the data point towards „G, I" and „P, I".]

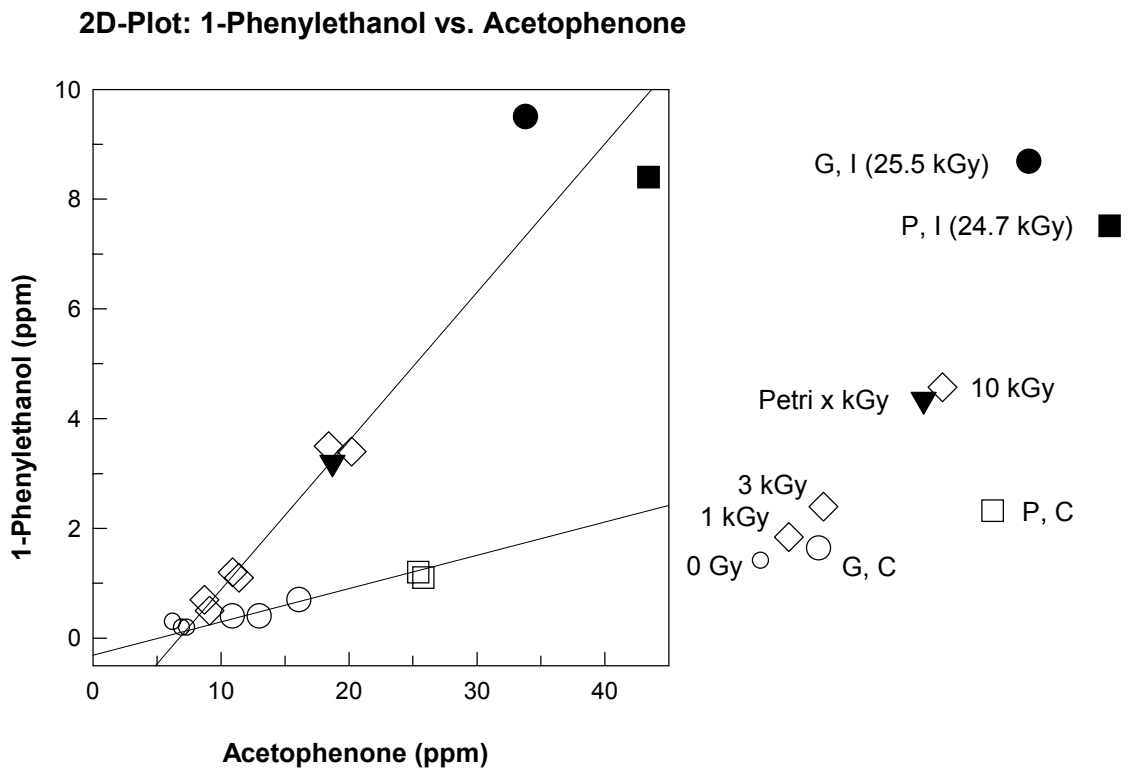


Figure 7.4 **Two-dimensional plot of 1-phenylethanol vs. acetophenone concentrations in polystyrene.** Irradiated and non-irradiated specimens are arranged along two different lines (though there is little distinction in the low-dose range). Ageing of the milled powder (*G, C* vs. *0 Gy*) and processing (*P, C* vs. *G, C*) also appear to induce oxidation—with Acp concentrations increasing much stronger than those of 1-Pet.

The plot combines the results of the two splitless-series of measurements (splitless-scan and splitless-SIM; see Appendices 4 and 5) plus the Petri dish analyzed in the MABS-series (Appendix 8). The linear regressions are for the 1, 3, and 10 kGy-granulates, and for the non-irradiated granulate *G, C* which had been milled 4 months earlier. True values for the Petri dish are assumed to be higher (Appendix 8) which would shift the data point towards *G, I* and *P, I*.

7.6 Re-Evaluating the Desorption Temperature

In the light of these interesting and promising results, it was felt that the claim to have established 'total extraction' conditions rested on somewhat insufficient experimental data with respect to **desorption temperature** (see Figures 6.2 and A-1.1). Therefore, a series of measurements with a TDS-temperature of **240°C** was performed to confirm that the 160°C used so far had been sufficient. Various non-irradiated, as well as 1 and 3 kGy-specimens were analyzed in splitless-SIM-mode; the results (black symbols) are compared against the previous splitless-SIM series (open symbols) in **Figure 7.5.** The 240°C-series almost exactly reproduced the 160°C-results indicating that 160°C is really in the plateau region, in other words, that it allows a complete desorption of the PS powders.

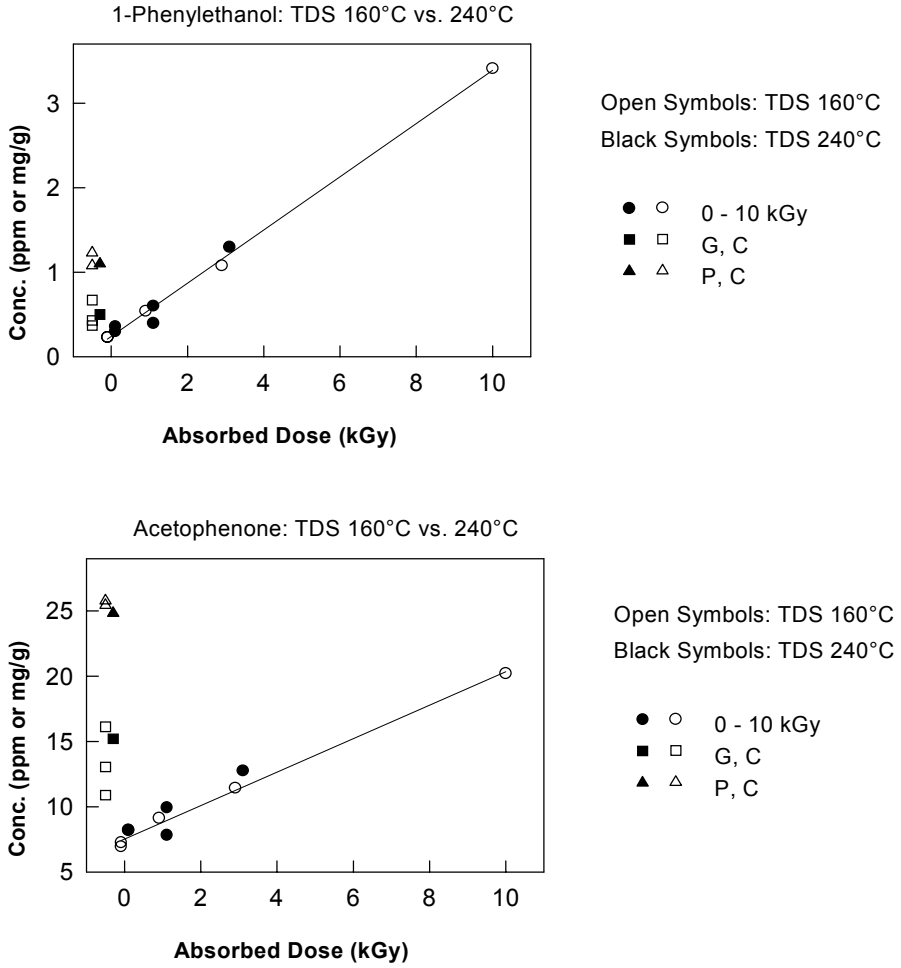


Figure 7.5 **1-Phenylethanol (top) and acetophenone (bottom) in polystyrene vs. the absorbed dose: TDS 240(10) vs. 160(10).**
To ascertain that 10 min thermal desorption at 160°C were sufficient to completely extract the PS powders (and to supplement the earlier TDS-temperature study—Figure 6.2) a limited number of runs was performed at TDS 240°C (10 min).
The plot compares the results obtained at 240°C (black symbols) with the corresponding 160°C-results of the splitless-SIM series (open symbols). **Please note:** Only the 0 - 10 kGy values obtained at TDS 160 have been used to calculate the regression, and, for reasons of clarity, data points have been **shifted slightly along the x-** (absorbed dose) **axis.** The data of the TDS 240°C-series may be found in Appendix 7.

7.7 Methyl methacrylate-Acrylonitrile-Butadiene-Styrene (MABS)

Figure 7.6 shows some **MABS data** presented as a two-dimensional plot of 1-Pet vs. Acp concentrations. The results should be considered as semi-quantitative or as minimum concentrations, because, unfortunately, a different rotor was used to mill most of these specimens (see Appendix 8 for more information and for the original data). The higher concentrations found in „G, I (20)“ vs. „G, I“ (i. e., after 20 min desorption vs. the normal 10 min) suggest a generally incomplete desorption of possibly all the MABS specimens under investigation. While these MABS powders may have caused a relatively high data scatter, the overall picture seems to be comparable to the one obtained with PS: Irradiation increases 1-Pet and Acp concentrations in a very similar way in both pellets and processed parts, whereas processing mainly increases Acp levels (the data points, e. g., „P, I“ vs. „G, I“, are shifted parallel to the Acp-axis). While the values in Figure 7.6 are certainly underestimated, it is very likely that the true concentrations of these products are actually lower in MABS than in polystyrene.

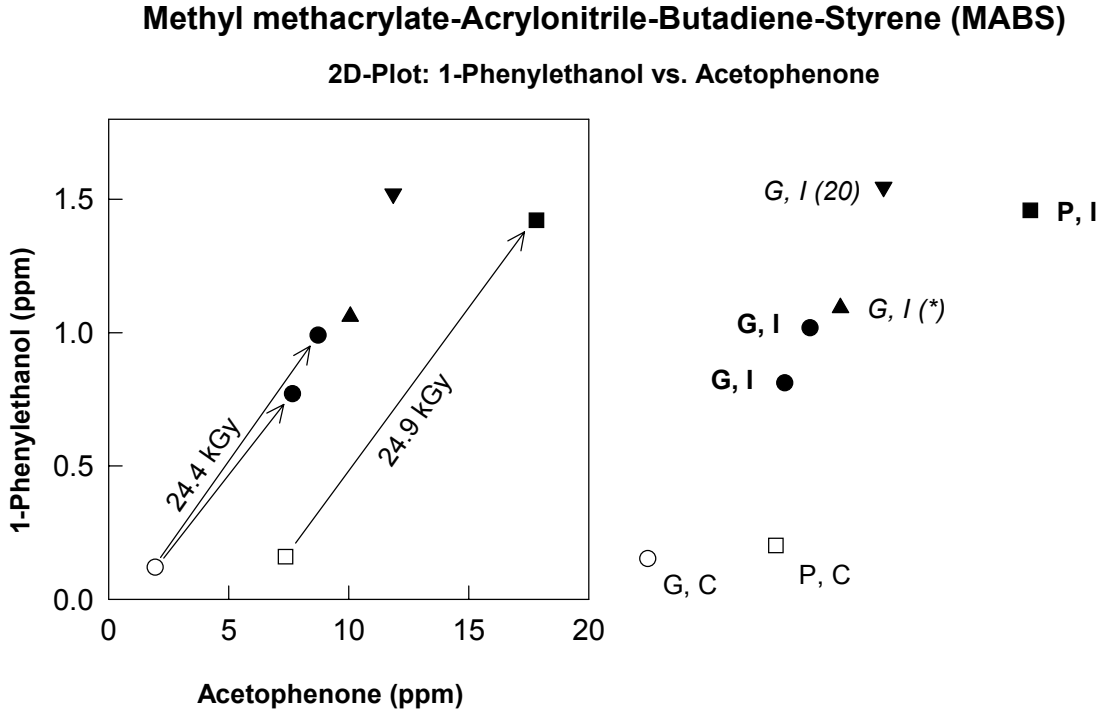


Figure 7.6 Two-dimensional plot of **1-phenylethanol vs. acetophenone concentrations in MABS** (methyl methacrylate-acrylonitrile-butadiene-styrene). As explained in connection with the original data (Appendix 8), these values should be considered as **minimum concentrations.**
All MABS-samples, except G, I (*), were milled with a relatively blunt *two-blade rotor*.
G, I (20) = 20 min desorption time
G, I (*) = Milled with the sharp-edged *four-blade rotor* (‘star-rotor’ – cf. Appendix 8)
Experimental Conditions were those of the PS splitless-SIM series.

7.8 Analytical Problems at the End of 'Phase III'

Approximately seven weeks into Phase III, several problems occured and the quantitative program, that had been so successfull initially, came to a halt. During an effort to further optimize CIS- and GC-conditions for some preliminary migration and 'DSC-Method' tests (see Section 9.3) that required a higher sensitivity, it was noticed that the *detection limit for 1-phenylethanol* was not nearly as good as that for acetophenone (**Figure 7.7**). A slight tailing of 1-Pet had already been observed ten days earlier during routine 10 ppm-test injections (**Figure 7.8:** the chromatogram of May 31); however, this had not interfered with the last TDS-quantitation, i. e., the MABS-series analyzed on May 31. Now, the detection-limit series (Figure 7.7) revealed that at a concentration of 0.05 ppm the height of the 1-Pet 'peak' was reduced to ca. one fifth of the Acp-peak and that it exhibited *severe tailing*. This loss of sensitivity for 1-Pet interfered with quantitation of the initial 'DSC' experiments described in Section 9.3. Seven days later, the tailing was visibly increased in the 10 ppm-test injections (Figure 7.8: the chromatogram of June 17), the degradation of the column accelerated, and, within another week (June 24), the tailing was so severe that quantitation of 1-Pet became practically impossible.

A more disturbing observation was *'The Mystery of the Lost Dimer'* (**Figure 7.9**): Seven weeks after the split-scan series, the dimer peak had disappeared from the chromatogram of the 25 kGy PS-powder. A genuine loss appeared to be highly improbable, because the dimer clearly had not disappeared from the corresponding „G, I"-powder during the *four months* before quantitation. (All the main series of quantitative analysis had been performed before the missing dimer was noticed, and all the available evidence indicated that they had not been affected by any deterioration of system performance.)

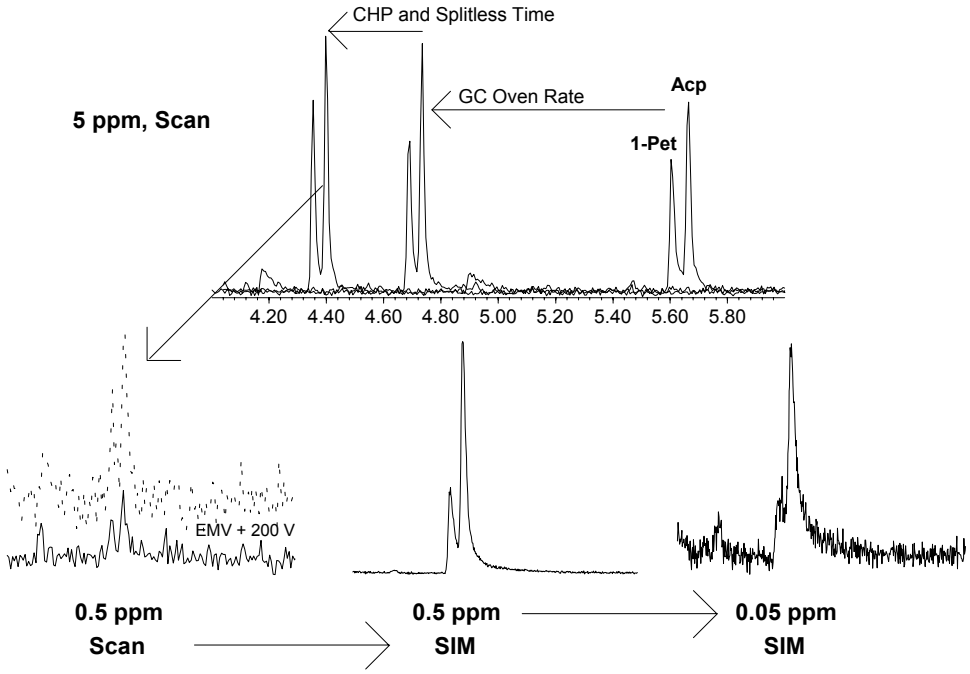


Figure 7.7 **Detection limits of 1-phenylethanol and acetophenone** on the DB-5 column six weeks into Phase III. The loss of 1-Pet at low concentrations (beginning column degradation ?) interfered with quantitation of the compound during initial tests of the 'DSC-Method' (see Section 9.3).
After optimizing injector and GC parameters and diluting the 5 ppm-standard, the MS was switched to SIM data acquisition. Exp. Condit. & peak height data for 1-Pet see Appendix 9.

To confirm the impression that there were no dramatic changes with time it was attempted to obtain concentration estimates for some earlier *qualitative* analyses. For example, the experimental conditions of the first qualitative PS-powder measurements (see Figure 6.1) had already been close to those established later for quantitative desorption, and a number of standards had been injected parallel to these analyses as part of a 'GC training program' with a technician. When the puzzle created by two operators using different injection techniques *plus* an MS-tune was finally solved (see Appendix 10), the data suggested that the concentrations of the radiolysis products had not changed during these four months (Appendix 10). Concentration estimates for the TDS-time series, which was performed some *days* before the quantitative measurements, were based on 10 ppm-test injections (one-point calibration); the results (Appendix 11) agree quite well with those of the ensuing 'full-scale' quantitation.

In any case, the loss of the dimer was thought to be caused by a *degrading* '*TDS-performance*.' It was suspected that higher-boiling volatiles might condense in the cold tip of the TDS-needle, gradually creating a film, which would act as a stationary phase retaining the dimer (and possibly other analytes as well). Whatever the true cause of the actual problem would turn out to be, it was concluded that additional tests would be highly desirable to better characterize the overall performance of the system. With such tests it would be possible to recognize (and to differentiate between) real changes in the fingerprint chromatograms, a degrading system performance, and normal instrumental drift.

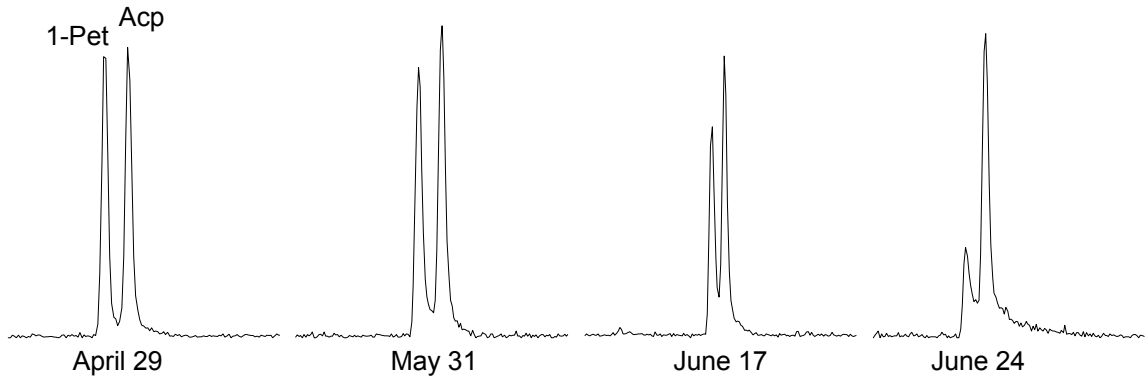


Figure 7.8 **Column degradation** at the end of Phase III revealed by test injections of a 10 ppm standard (1-Pet & Acp in hexane). All TDS-quantitations were performed in May, all series (except one) of DSC- and migration-measurements before June 17. The detection-limit series (Figure 7.7) was measured on June 10, the *lost dimer* (Figure 7.9) was noted on June 17.
Remark: The scale of the y-(abundance)-axes of the four chromatograms are not necessarily identical; t_R is ca. 8 min (parameters such as CHP or oven rate were sometimes varied during test injections). Exp. Conditions: CIS 30, splitless 90 s; GC 40(1.5) -10- 250(x); column: DB-5.

7.9 A Strategy for Future Investigations

It was decided that the top priority was now to establish such a 'TDS-Performance-Test.' Then the quantitative analyses would be repeated *to see whether the results could be reproduced*, and, equally important, *newly irradiated specimens* would be analyzed. A new column would be selected with a liquid phase offering *maximum sensitivity* for 1-phenylethanol, the most promising radiation marker (sensitivity would be especially important for further experiments with the DSC-Method). The performance of the column would be regularly monitored with a 'System Sensitivity Test' indicating any column degradation before it affected quantitation. The sensitivity test would be composed of the main analytes with concentrations near the detection limit. Overall system performance and substance transfer from the TDS to the CIS would be monitored regularly with the general 'TDS-Performance-Test,' and, as already practiced, with injections of standard solutions of the analytes being determined.

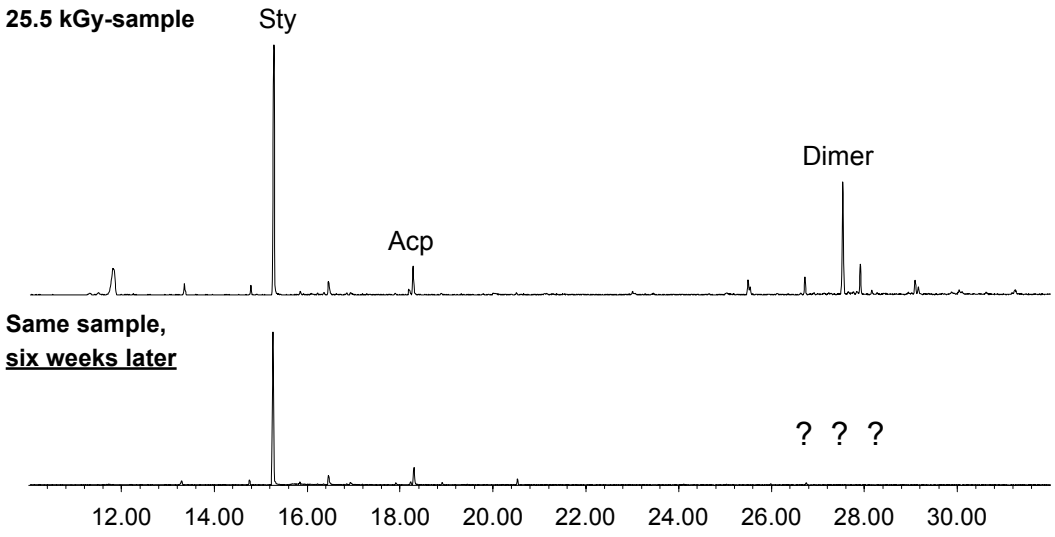


Figure 7.9 **The Mystery of the Lost Dimer:** Seven weeks into Phase III, it was noted that the dimer peak had disappeared from the fingerprint chromatogram of the 25.5 kGy-powder. A genuine loss of the dimer appeared to be highly improbable, because the phenomenon had not been observed with „G, I" in the four months (!) before quantitation (and also because styrene was still present). It was concluded that to differentiate between the effects of real **concentration changes-with-time**, degrading **system performance**, and normal **instrumental drift,** additional test strategies and a better overall characterization of the analytical system would be desirable.
The first chromatogram is from the **split-scan**-series, the second was obtained with identical parameter settings (but obviously not under identical conditions).

7.10 The TDS-Performance-Test

The solution (!) that nearly suggested itself for a *recovery test* was the „test mixture 2 for capillary columns“ according to Grob. The procedure for testing columns is described by Grob et al. (1978, 1981); the test, a polarity mixture, yields information on „four basic aspects of column quality, namely, *adsorptive activity, acidity/basicity*, separation efficiency and film thickness“ (Grob et al., 1981); a quantitative interpretation of test results is possible when the chromatograms are recorded with an FID (flame ionization detector). The mixture is composed of a set of substances with a relatively broad range of volatilities (see **Figure 7.10**); there are two alkanes [labelled 10 & 12] and three methyl esters of carboxylic acids [E10 to E 12], which all are *not* adsorbed on columns of reasonable quality. The polar compounds are a (neutral) aliphatic alcohol [ol] and a diol [D], a (weakly acidic) hindered phenol [P], a free carboxylic acid [S], and (in sequence of increasing basicity) a hindered aromatic [A] and an aliphatic amine [am]—cf. Figure 7.10. The peak shapes (and FID-peak heights) of the polar compounds, compared to the ‘100%-line’ established by the alkanes and esters, provide qualitative (and quantitative) information on adsorptive activity and acidity / basicity of the column.

Some technical regulations concerning laboratory safety did not allow to operate an FID and consequently no quantitative test results could be obtained. While this was clearly unsatisfactory, *column quality* was not our primary concern; as mentioned above column performance was to be monitored with a special *sensitivity test*. I was interested in a *TDS-recovery test*, and obviously the Grob-Mix fitted perfectly my needs: If I compared an injection into the TDS with a ‘direct’ injection into the CIS, I would get a quite comprehensive picture of TDS-performance: The various polar compounds would indicate partial or complete losses of specific classes of compounds (e. g., of amines; cf. Figure 7.10), while the high-boiling

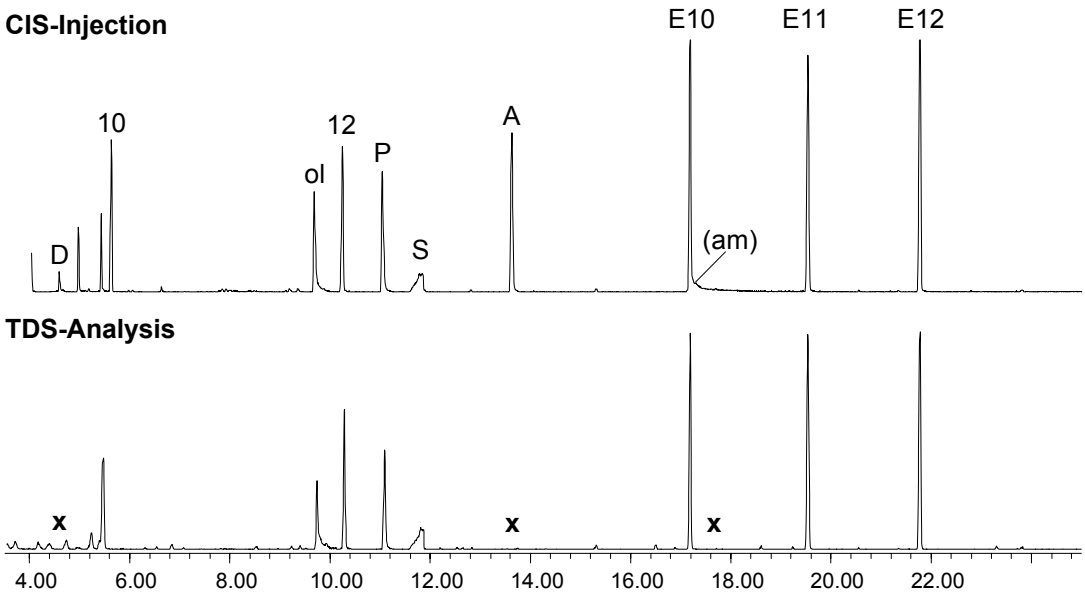


Figure 7.10 TDS-Performance-Test using the Grob-Mix (2 µl 1:5 solut.; ca. 20 ng) at TDS 250 / CIS 30 (the column is an Rtx-200).

D	= 2,3-Butanediol	A	= 2,6-Dimethylaniline
10	= n-Decane	am	= Dicyclohexylamine (as shoulder on E10)
ol	= 1-Octanol	E10	= Methyldecanoate
12	= n-Dodecane	E11	= Methylundecanoate
P	= 2,6-Dimethylphenol	E12	= Methyldodecanoate
S	= 2-Ethylhexanoic acid	**x**	**= Peaks missing in the TDS Analysis**

Exp. Conditions: TDS 50 -20- 250(5); CIS 30; GC 40(1.5) -5- 180(5); column: Rtx-200.

esters would alert me to problems unrelated to activity, e.g., a gradual contamination of the needle resulting in the loss of higher-boiling analytes (via condensation / trapping / retention at the 'cold spot;'—cf. the lost dimer in Figure 7.9).

The concentration of the Grob-Mix is adjusted for column testing in *split*-mode; since the quantitative TDS-analyes were usually performed with the CIS in *splitless*-mode, a 1:5 dilution in n-hexane of the original solution was used for the TDS-performance tests. **Figure 7.10** shows an early test with the Rtx-200 column, Figure A-12.1 (Appendix 12) a combined performance / recovery test with 1 µl of the diluted Grob-Mix *plus* 1 µl of a 10 ppm acetophenone / 1-phenylethanol standard. A representative test from Phase IV with the polyethylene glycol column is presented in Appendix 15: Figure A-15.4 (chromatograms) and A-15.5 (relative recoveries).

It is probably not necessary, in an analytical context, to stress how important it is *to know the potential and the* **limitations** *of one's technique(s)*. It is very clear that (at the time the chromatograms in Figure 7.10 were recorded) there was little chance to detect amines in a TDS-analysis, because they were obviously lost during transfer (or: adsorbed to the TDS glass liner upon injection). In a later test performed in Phase IV, recovery of the aromatic amine [A] was quite good, while the more strongly basic aliphatic amine [am] was still completely missing (Appendix 15: Figure A-15.4). Also absent from the TDS-chromatogram in Figure 7.10 is the polar diol [D].

These observations have serious implications for the characterization, by thermal desorption, of low-molecular-weight radiolysis products. A *comprehensive* description ideally would *list the products positively identified*, and it would additionally *state which classes of compounds* (or: chemical structures) *were not accessible to analysis*—as far as this makes sense, at least. [It is reasonable to assume that irradiation of PS does not produce amines, and that there are no radiation-induced reactions with atmospheric nitrogen that lead to stable products—but amines may clearly be formed by additives, e. g., by hindered amine stabilizers (in polypropylene), or, possibly, by some 'exotic' polymers.] More relevant for PS is the conclusion that diols are 'problematic' compounds in that they are prone to adsorption; this may explain why the trace product *1-phenyl-1,2-ethanediol* could be observed only once (i. e., in two analyses performed post-Phase III; see Section 10.2).

7.11 Recovery of C_{18}- to C_{24}-Hydrocarbons

Also documented in Appendix 12 is another experiment that characterizes thermal desorption, though it originally had another purpose. We can see (Figures A-12.2, A-12.3, and Table A-12.1) that for a given TDS-temperature (160°C) there is a constant recovery—probably even a complete recovery, but here I was not interested in that—up to a certain molecular weight ($C_{19}H_{40}$ or $C_{20}H_{42}$), and beyond that there is an *exponential drop*. The data explain why one can readily observe styrene dimer(s) ($C_{16}H_{32}$), but has to search for the trimer(s) ($C_{24}H_{48}$), which can be found only in trace quantities.

[The initial intention had been to incorporate traces of styrene into a 'model-PS' to see whether styrene was a precursor of the radiolysis products. Based on the hydrocarbon-recovery experiments in Appendix 12 it was decided to try tetracosane ($C_{24}H_{50}$), assuming that we could tolerate a 0.4% desorption of the tetracosane matrix (see Table A-12.1). This was probably a mistake; the experiment did not work and I am inclined to think that tetracosane causes major problems by condensing in the TDS-needle. I did not try to find another model-polymer or matrix—see also Section 9.7, where the likely role of styrene is discussed in connection with *Radiation-Chemical Yields*.]

8. Confirmation of the Quantitative Results ('Phase IV')

As already mentioned the main objectives of **Phase IV** were:

– to reproduce the earlier quantitative results,

– to determine whether the concentrations of the products changed over time, and

– to assess the potential of the DSC-Method (see Chapter 9).

An additional project was the analysis of some 'real-life samples' from the laboratory shelf to assess the true potential of thermal desorption for *irradiation detection*. Finally, the analysis of some 'experimental' pre-treated specimens was intended as a *first step* towards an elucidation of the *mechanism* of the underlying radiation-chemical reactions.

8.1 Qualitative ('Pre-Phase IV') Results

In the meantime ('Pre-Phase IV'), I had been occupied with the TDS-Performance-Test, the identification of trace radiolysis products (see Chapter 10), the re-location of the laboratory to a new place, endless troubles with GC columns, and various experiments leading nowhere.

Two results from that time (Post-Phase III or Pre-Phase IV) are reported in Appendix 14: In an attempt to accelerate the analytical procedure the TDS-temperature was increased to 250°C and the TDS-time reduced to 5 min. This led to decreased peak areas compared to the standard conditions of 160°C for 10 min, indicating that desorption was incomplete (Figure A-14.1). A more successfull experiment indicated *qualitatively* that there was no detectable loss of radiolysis products from the PS powders during storage (Figure A-14.2); this series of measurements also gives an impression of the relatively *high reproducibility* of the TDS-technique.

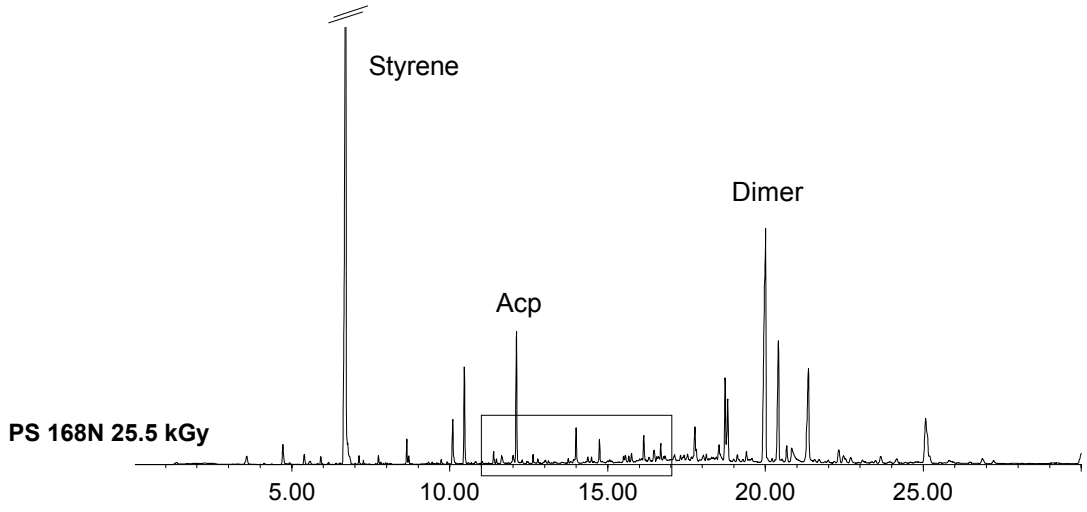


Figure 8.1 **Fingerprint chromatogram** of PS 168 N irradiated with 25.5 kGy on the Supelcowax 10 column—the **detail t_R 11–17 min** is shown in **Figure 8.2** vs. the corresponding non-irradiated control.
Experimental Conditions: 5 mg PS powder; TDS 160(10); CIS 30; GC 40(1.5) -10- 210(5); column: Supelcowax 10.

8.2 Column Selection, Column and System Testing

Based on the general principles of column selection (see GC-textbooks: e. g., Jennings, 1987) it was decided to use a *polyethylene glycol* column in Phase IV to achieve maximum sensitivity for 1-phenylethanol. It is of some irony that this was the type of liquid phase that had already been used at the very beginning of Phase I, in anticipation of the presence of polar oxygen-containing radiolysis products. Thus, a closer look at those old qualitative chromatograms indicated that this choice was probably right (Appendix 14).

A first test chromatogram of the new column obtained with the Grob-Mix was almost perfect: The peak of the alcohol *1-octanol (ol)* was in very good shape with no visible tailing, and even traces of the diol *2,3-butanediol (D)* were present (Appendix 15: Figure A-15.1). Finally, a sensitivity test (Figure A-15.2) indicated that 1-phenylethanol (plus acetophenone and phenol) could be detected at a level of 5 ppb (0.005 ppm), i. e., 5 pg (0.005 ng) for a 1 µl-injection; clearly enough for a quantitative determination of 1-Pet with the 'DSC-Method' (see Chapter 9), even of *traces of 1-Pet* in non-irradiated PS.

The column was then monitored continuously with sensitivity tests, i. e., with 0.01 ppm injections of a standard mix (Appendix 15: Figure A-15.3); the performance of the TDS was checked in intervals by injecting the Grob-Mix, first into the CIS and then into the TDS (TDS-Performance-Test),—see Figures A-15.4 and A-15.5.

8.3 Concentrations Are Under-Estimated after Desorption at 160°C

The PS specimens were analyzed under the desorption conditions established in Phase III, i. e., 160°C for 10 min: **Figure 8.1** shows a fingerprint chromatogram of the 'old' PS irradiated with 25.5 kGy, **Figure 8.2** shows a detail view of t_R 11–17 min with the three compounds assayed, namely acetophenone, 1-phenylethanol, and phenol.

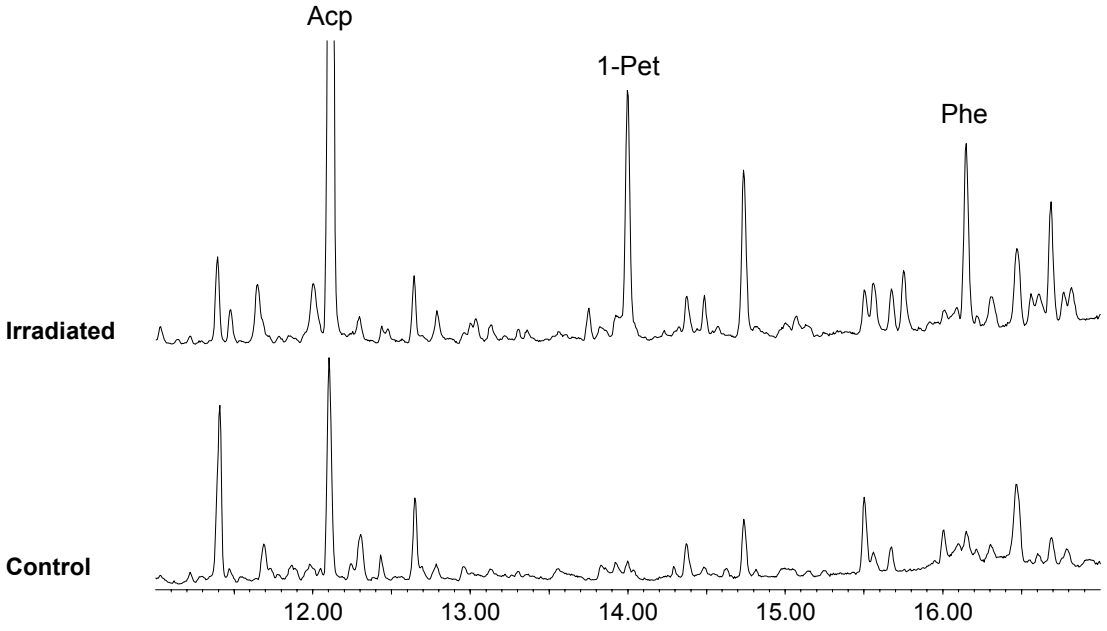


Figure 8.2 **Detail t_R 11–17 min** of Figure 8.1, PS 168 N 25.5 kGy, (top) vs. the non-irradiated control (bottom)—showing the three radiolysis products assayed in Phase IV.

To my considerable surprise, the 'new' concentrations were consistently lower than those obtained in Phase III; the 25 kGy-granulate specimens reached only some 50 to 60 percent of the 'original' levels (**Figure 8.3**), and a similar ratio appeared to exist for the non-irradiated controls. It was reasonable to assume that the new values were correct, because of the parallel test program that was much more elaborate and comprehensive than the occasional test injections during Phase III. On the other hand, it was hard to believe that the results obtained in Phase III should have been *that wrong*. A first hypothesis was that there might be something wrong with the calibration standards, but this was clearly not the case, as newly prepared standards gave nearly identical results (Appendix 16: Figure A-16.2). It still seemed inconceivable that a major mistake should have been made in Phase III, leading to concentrations over-estimated by a factor of almost 2. Overall, this was really puzzling, the measurements were continued, and, at some point, it was decided to see what would happen if the desorption temperature was increased.

Five measurements were performed at a TDS-temperature of 200°C, and their results (**Figure 8.9**) agreed almost exactly with those obtained in Phase III. The question was then: Why do we now need 200°C, when 160°C had been sufficient earlier ? — It took me some time to figure this out, and before presenting the solution I would like to discuss the 160°C-results, which can be viewed as semi-quantitative in a very verbal meaning of the expression, i. e., yielding roughly *one half* of the true concentrations. Since the entire series of measurements was not repeated at 200°C, some qualitative relationships would get lost, if the 160°C-results we omitted from the discussion. The original data of the experiments (calibration data, calibration curves, and PS data) may be found in Appendix 16.

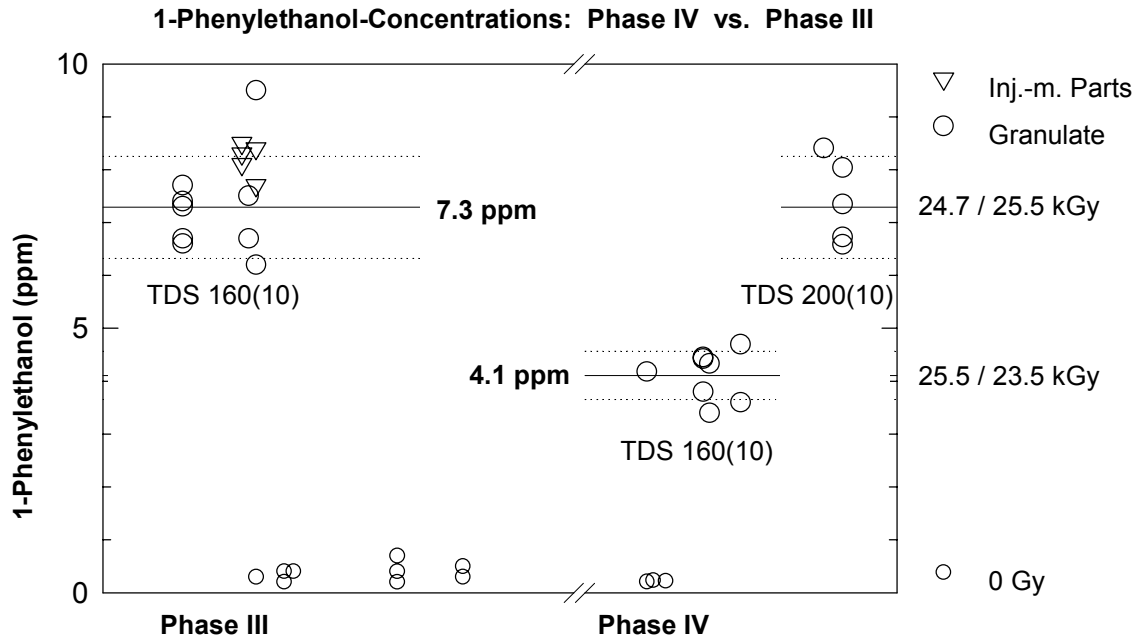


Figure 8.3 1-Phenylethanol concentrations: Phase IV vs. Phase III-results. Unexpectedly, **the TDS-temperature had to be raised above 160°C** (for 10 min) to reproduce the earlier results—see text for explanation. The effect could later be attributed to the use of a newer software version in Phase IV (cf. Figures 8.9 to 8.11).
The graph compares the 1-Pet concentrations of **all PS 168 N** granulate (25.5 kGy) and injection-molded part (24.7 kGy) **samples analyzed in Phase III,** including the concentration estimates for the TDS-time series, **with all PS 168 N and PS XY samples** (25.5 kGy or 23.5 kGy) **of Phase IV.** The reference lines indicate the respective **mean values** and **standard deviations** (granulate samples only).

8.4 Qualitative Relationships within the 160°C-Data

Figure 8.4 is a 2-dimensional plot of 1-phenylethanol vs. acetophenone concentrations (cf. Figure 7.4 in Chapter 7). We find the non-irradiated controls in the lower left corner of the graph with ca. 0.2 ppm 1-Pet and ca. 4 to 7 ppm Acp. (The three data points are for PS 168 N, PS XY, and the PS one-way 'glass.') Most specimens irradiated with 25.5 or 23.5 kGy are situated in a 'central region' defined by Acp levels of ca. 18 to 25 ppm and 1-Pet levels between 3 and 5 ppm; these include most of the 'standard' polystyrenes 168 N and XY plus the irradiated one-way glass made of PS. There is no satisfying explanation for the three standard polystyrenes with Acp levels between 10 and 15 ppm (see also Figure 8.6, where PS XY and 168 N specimens are further differentiated).

Very close to the central region are the Petri dish and the culture flask both sterilized with unknown absorbed doses; re-irradiation with 23.5 kGy shifts their data points to higher 1-Pet and Acp concentrations as indicated by the arrows. Two PS 168 N specimens have been irradiated after pre-treatments designed to remove the (or some of the) low-molecular-weight material, and consisting either of dissolution in dichloromethane followed by precipitation in methanol, or of thermal desorption at 160°C for 60 min under a flow of helium. After irradiation, 1-Pet and Acp levels of the former (Code: „diss.-prec.") are almost as low as those of the 'normal' non-irradiated controls, while the data point of the latter (Code: „t.ds. 160(60)") is found at ca. one third the distance between the non-irradiated controls and the central region. This strongly suggests that in PS the low-MW fraction plays a major role in the formation of volatile radiolysis products.

Figure 8.5, the corresponding 2D-plot of *phenol* vs. acetophenone concentrations, gives a very similar picture; there are possibly two more out-of-range values, the non-irradiated control with ca. 5 ppm phenol, and the irradiated PS XY with ca. 10 ppm, but it is also con-

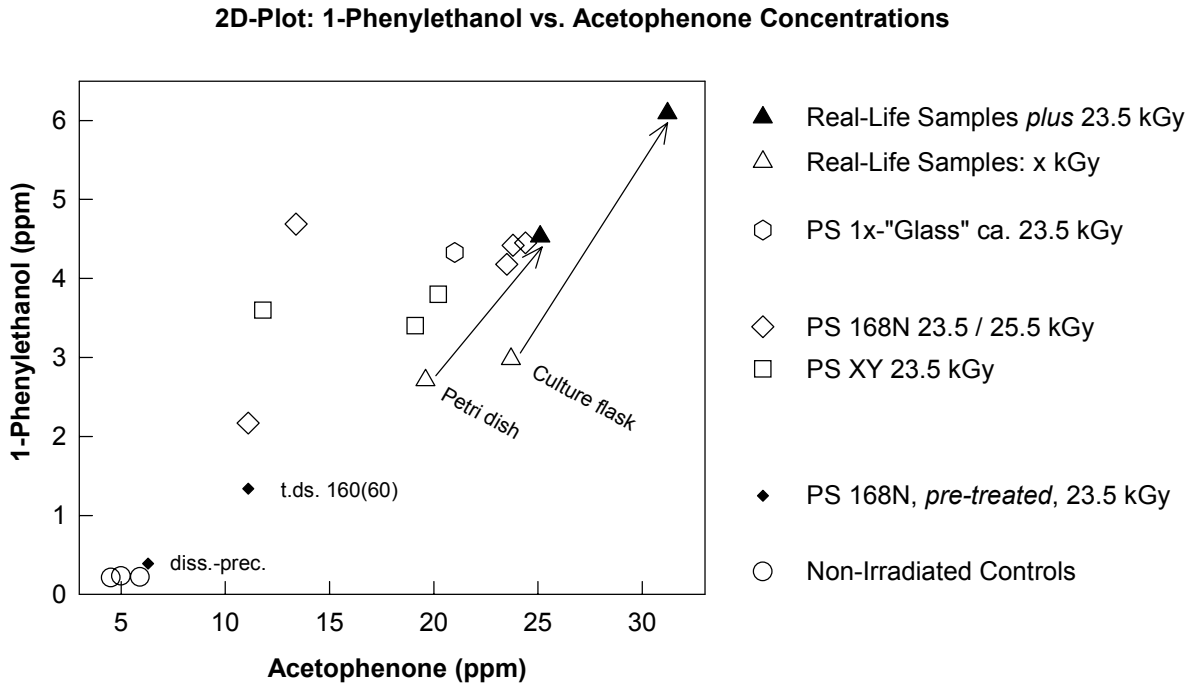


Figure 8.4 Summary of Phase IV-results obtained at **TDS 160°C** (10 min): **2D-Plot: 1-Phenylethanol vs. acetophenone concentrations**—see text for discussion. The results for PS 168 N and PS XY are further differentiated in Figure 8.6. Original data see Appendix 16.

ceivable that phenol levels are genuinely higher in PS XY (the control with 5 ppm phenol is also PS XY, and thus all three PS XY-data points are arranged along a single straight line).

Taken together, the two 2D-plots define a 3D-space of phenol *vs.* 1-Pet *vs.* Acp concentrations, and if we neglect the three out-of-range values and the experimental pre-treated polystyrenes, then the spatial distance between the specimens irradiated with sterilizing doses and the non-irradiated controls is so impressive that it appears to be possible to correctly identify medical products made of standard PS as *radiation-sterilized*.

8.5 The Various PS 168 N and PS XY Specimens

Figure 8.6 differentiates further between the various specimens of the two standard polystyrenes PS 168 N and PS XY. 1-Phenylethanol and acetophenone levels are almost identical in PS 168 N newly irradiated with 23.5 kGy and PS 168 N irradiated 2.5 years earlier with 25.5 kGy (when *irradiated as granulates* and milled prior to thermal desorption). This indicates again that there are no concentration changes-with-time. (The absorbed dose values determined by Red Perspex dosimetry are accurate to ±10%, and quantitation by TDS is probably even less accurate.)

As far as the out-of-range data points are concerned, it appeared to be a good explanation to assume that the PS 168 N *irradiated as powder* had not been milled fine enough for complete desorption. It was therefore re-milled and analyzed again, but it is not clear why this substantially increased 1-Pet, while having almost no effect on Acp. It is also not clear why the PS XY *granulate* specimen is associated with the 168 N *powder* specimens, and conversely, why the XY *powders* are closer to the 168 N *granulates*. Ultimately, there remain —after re-milling—two data points that are in a strange way (or: partly) out-of-range, i. e., out-of-range with respect to acetophenone, but quite well in-range with respect to 1-phenyl-

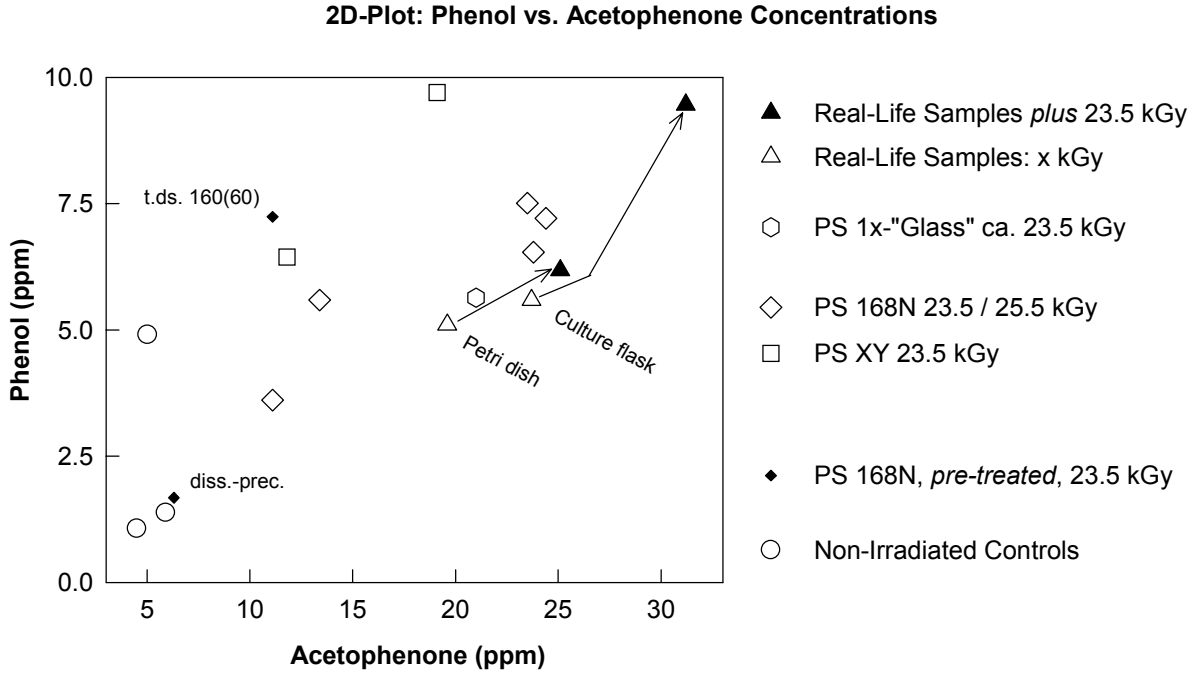


Figure 8.5 Summary of Phase IV-results obtained at **TDS 160°C** (10 min): **2D-Plot: Phenol** vs. acetophenone **concentrations**—see text for discussion.
Original data see Appendix 16.

ethanol. There is probably no difference between specimens irradiated as granulate and specimens irradiated as powder, because the average dose rate in gamma-sterilization (ca. 1 kGy per hour) is so low that the oxygen diffusion rate is not a limiting factor and the geometry of a sample does not play a role.

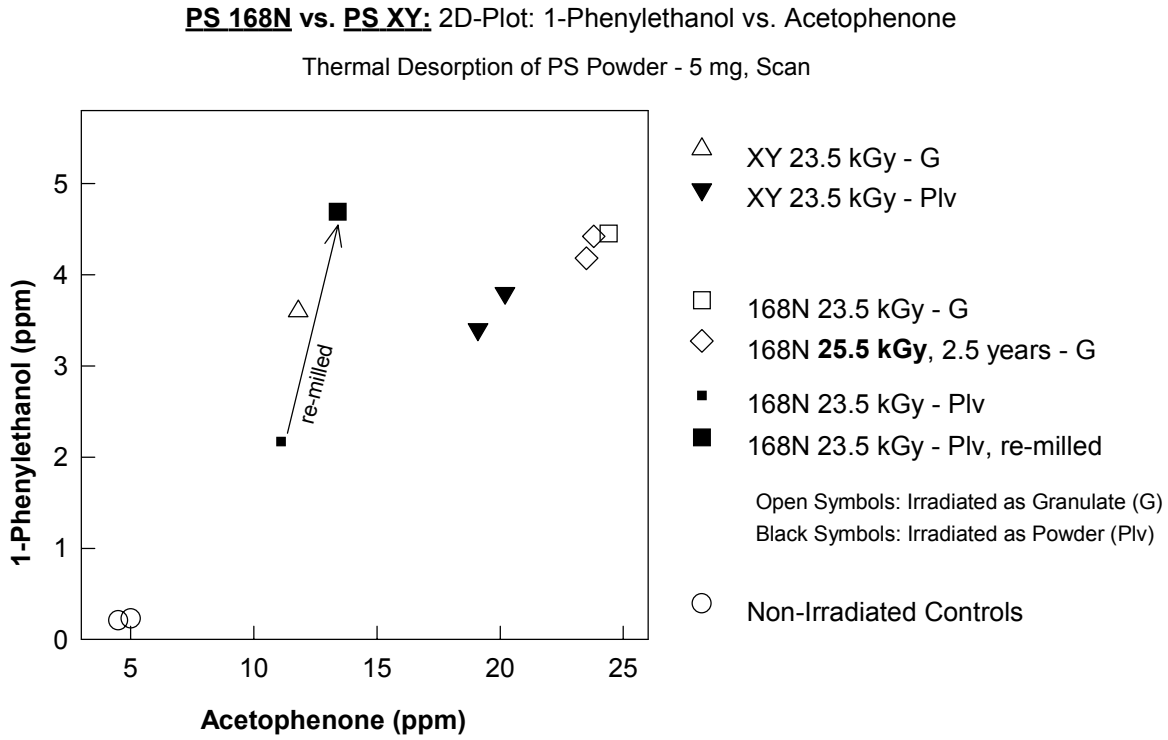


Figure 8.6 2D-Plot: 1-Phenylethanol vs. acetophenone concentrations: **Results for polystyrenes 168 N and XY** obtained at **TDS 160°C** (10 min)—the graph differentiates the PS 168 N and PS XY-data from Figure 8.4.

8.6 Styrene-Copolymers

In addition to the standard polystyrenes (168 N and XY), the real-life samples (Petri dish and culture flask), and the one-way 'glass' which obviously consisted of some standard PS, the following samples were analyzed: a newly irradiated MABS specimen (BASF Terlux 2802 TR transparent); and three commercial trays, namely, a yoghurt tray and two fruit trays („F" and „WM") from local markets.

All three were labelled with a „PS" recycling symbol, but apparently had been made from some styrene-copolymers. The results for the four samples—ca. 8 ppm Acp and ca. 0.4 to 2 ppm 1-Pet after 23.5 kGy (see Appendix 16: Table A-16.2)— have not been included into Figure 8.4 because they clearly do not fit into the 2D-plot. Of course, there is no excuse for simply omitting data that do not 'fit into the picture,' and so I was looking for criteria that

would indicate whether a particular „PS“ sample should (or should not) be included into a polystyrene-2D-plot designed for *irradiation detection*.

I tentatively propose the following set of criteria (which might be supplemented by more sophisticated techniques like IR-spectrometry), namely:

– *fingerprint* chromatogram,
– mechanical flexibility, and
– transparency.

A sample may then be included (i. e., irradiation detection might be possible), if the fingerprint resembles the typical standard-PS chromatogram, i. e., a relatively ‘clean’ chromatogram dominated by the residual monomer styrene and its dimer(s)—see, for example, Figure 8.1—and if it has glass-like rigidness / brittleness and transparency. The following synopsis shows how the samples under investigation did (or did not) meet these criteria:

		PS Fingerprint	Brittleness	Transparency		
Petri Dish	(*)	+	+	+	⇒	PS
Culture Flask		+	+	+	⇒	PS
1x-Glass		+	+	+	⇒	PS
Yoghurt Tray	(*)	(+)	--	--	⇒	Copolymer (?)
Tray „F“	(*)	--	--	+	⇒	Copolymer
Tray „WM“	(*)	--	--	+	⇒	Copolymer

Chromatograms of the four samples labelled with an asterisk (*) are shown in **Figure 8.7.** The chromatogram of the Petri dish is *clearly* a standard-PS fingerprint; it is virtually identical to that of PS 168 N in Figure 8.1, and so are the chromatograms of the culture flask and the 1x-glass. The chromatograms of the two trays „F“ and „WM“ are *obviously not* PS fingerprints—the former resembles-chromatograms of the MABS analyzed earlier (Section 4.2) though the material is probably not an MABS resin, while the latter has a very strange appearance that was not observed before.

The most interesting and, possibly, disturbing chromatogram is that of the yoghurt tray, a non-transparent (white) and relatively flexible tray: It appears to be a fingerprint of a ‘pure’ standard PS (Figure 8.7) with an added peak of the antioxidant butylhydroxytoluene (BHT), which is partly destroyed on irradiation (ca. 50% reduction in peak area) and may explain the low levels of radiolysis products. [The yoghurt tray was also analyzed during the ‘DSC’-series (see Chapter 9), its dichloromethane-solution had an opaque / milky appearance, and the concentrations of 1-phenylethanol and acetophenone (ca. 3 ppm 1-Pet, and ca. 24 ppm Acp after 23.5 kGy, see Appendix 18: Table A-18.2) again did not reach the levels observed in the standard polystyrenes.]

Clearly, the situation is not totally satisfactory, and additional work will be needed, if one intends to establish a detection method for *irradiated* styrene-based resins. One would ultimately have to elucidate the *mechanism* of radiolysis product formation, or, at least, be able to demonstrate how product concentrations (radiation-chemical yields) depend on the (co-) polymer structure and on any antioxidants that might be present. It is likely that thermal desorption as a detection method will have to rely on additional data characterizing the material under investigation. This may be acceptable if it means recording an infrared-spectrum, but if it means that additives have to be determined by some combination of extraction (e. g., SFE) and chromatography (HPLC, LC-MS), then the whole procedure will certainly no longer qualify as a simple and fast screening method.

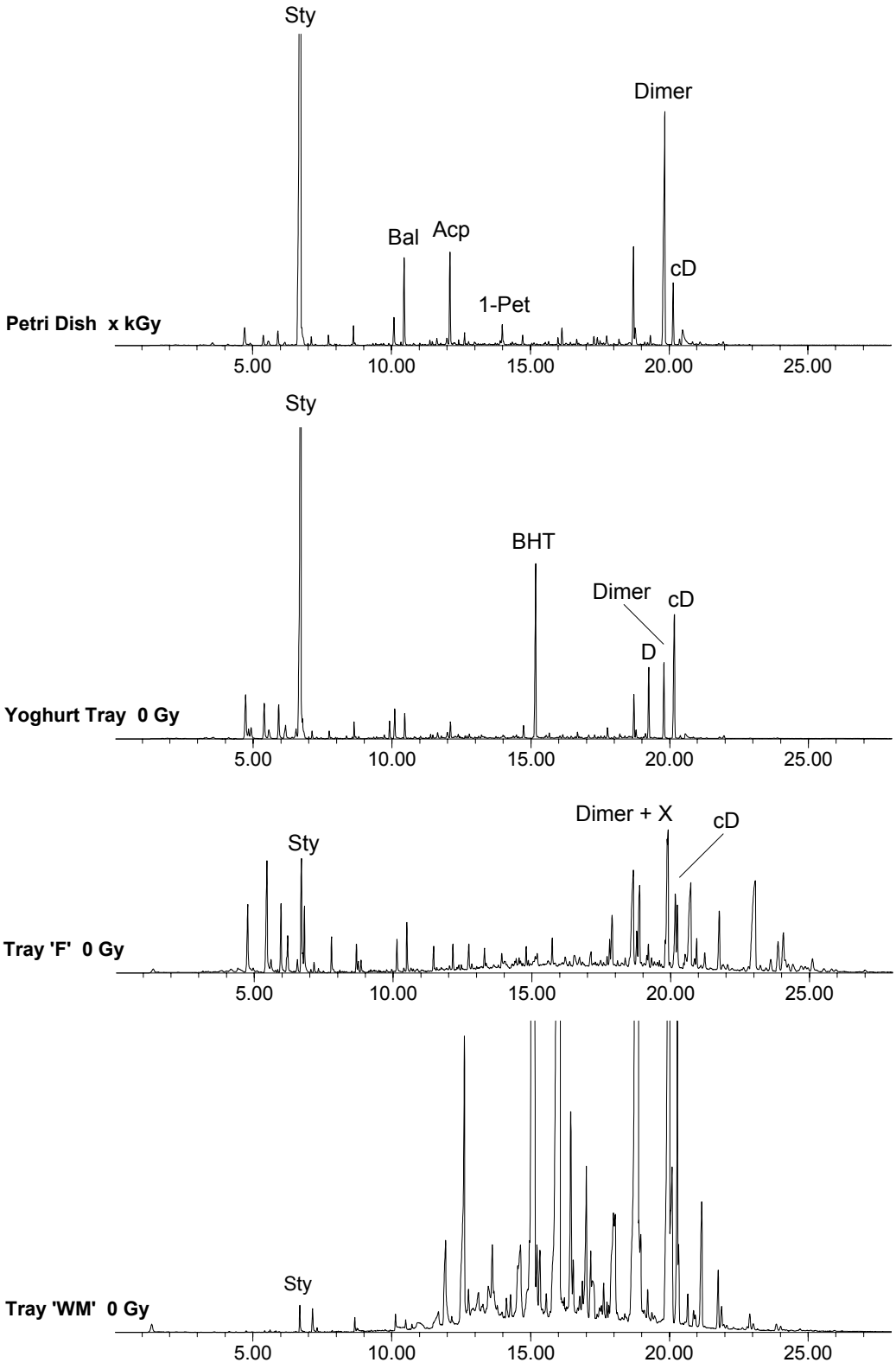


Figure 8.7 **Fingerprint chromatograms of the copolymer samples** vs. the Petri dish. The Petri dish ('standard' PS) fingerprint is almost identical to that of PS 168 N in Figure 8.1. The antioxidant BHT (butylhydroxytoluene) in the yoghurt tray is partly destroyed on irradiation (ca. 50% reduction in peak area). It is also interesting to note the different 'dimer pattern' in this sample.
The scale of the y-(abundance)-axis is identical in all four fingerprints and full peak heighs are not shown in #1, #2 and #4. cD = 'cyclo-Dimer' [cis- and/or trans-isomer(s) of 1,1'-(1,2-cyclo-butanediyl)-bis-benzene], D = some other isomer of styrene dimer, X = a coeluting compound.

8.7 The Data Obtained at 200°C Confirm the Earlier ('Phase III') Quantitative Results

When it was finally recognized that the desorption temperature had to be increased, only a limited number of measurements was performed at 200°C (**Figure 8.9**). The data (mean concentrations of ca. 7.5 ppm for 1-Pet, and of ca. 38 ppm for Acp) agree almost exactly with those obtained in Phase III. The difference between the CIS temperatures is not considered significant. [A CIS temperature of -40°C had been used in Phase III, +30°C were used in Phase IV. The CIS temperature was varied in this experiment *to prove* that this change in parameters was not responsible for the initially under-estimated concentrations. This had been inferred from some limited Phase III-results and had also been considered unlikely for theoretical reasons: In splitless GC analyses, a temperature difference of 150°C between a compound's boiling point and the initial column temperature is considered sufficient for *cold trapping*; thus, it was reasonable to assume that the analytes (with boiling points near 200°C) would be completely trapped at 30°C in the adsorbent-filled injector.]

8.8 The Cause of the TDS-Temperature Problem

Parallel to the 200°C-series, the experiments with the 'DSC-Method' were resumed (see Section 9.4) and the first results were so impressive that the 'normal' TDS-quantitation was not continued, and the desorption temperature-problem was no longer considered *that important*. The solution was actually found several weeks later; it is presented now somewhat out-of-sequence before describing, in Chapter 9, the DSC-results.

In a first step, another desorption temperature curve was recorded—this time covering the whole temperature range from 160°C to 240°C (**Figure 8.10:** Peak areas vs. TDS-temperature). We can see that there is a distinct increase between 160°C and 180°C and that the

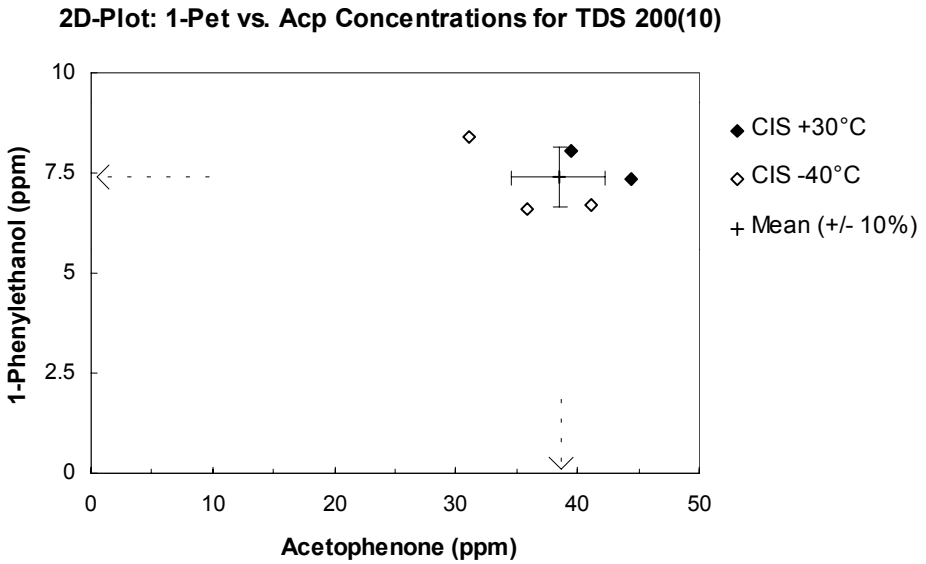


Figure 8.9 2D-Plot: 1-Phenylethanol vs. acetophenone concentrations at a **desorption temperature of 200°C** (10 min). This series of measurements was performed to see whether a higher TDS-temperature would confirme the earlier (Phase III) results, and whether there was an effect of trapping (CIS) temperature (-40°C vs. + 30°C).
Sample: PS 168 N 25.5 kGy; original data see Appendix 16: Table A-16.3.

'plateau' probably begins somewhere between 180°C and 200°C. The increase is most obvious for acetophenone and for the relatively high-boiling dimer (which was not quantitatively determined); it is much less pronounced for 1-phenylethanol than one would expect from Figure 8.3 and I do not have an explanation for this. It is equally difficult to explain the curves of styrene and phenol—the GC conditions were certainly not optimum for styrene (the polar column, the long splitless-time in the absence of a solvent), and the weakly acidic phenol is a 'problematic' analyte that will suffer first from any adsorptive activity. It should be stated again that this was a 'post-Phase IV' experiment performed weeks after the DSC-series (Sections 9.4–9.6), at a time when system performance was less closely monitored than during the main quantitative series. In any case, there appeared to be no further increase in peak areas above 200°C and the question remained: Why did we need a TDS-temperature of 200°C (for 10 min) in Phase IV when 160°C for 10 min had been sufficient in Phase III ?

The sole remaining explanation was that it might be associated with an *updated version of the software* controlling the TDS (and the CIS), which had been installed between Phases III and IV. The TDS can be *programmed*, for example, to go with a *rate* of 20°C/min from a *start temperature* of 60°C to a *final temperature* of 160°C, and to hold the latter for 5 min (*hold time*). This had been done initially in Phase I, but it appeared to make not much sense, and to save time the procedure had been abandoned in favour of 'isothermal' desorption, e. g., 160°C for 10 min. It had always been clear that this was only nominally isothermal (or: 'pseudo-isothermal'), since the samples need some time to reach the desorption temperature, and since there is an initial drop in oven-temperature when the massive metal TDS-injector is inserted.
Since the new version of the software allowed to program the TDS with a *maximum rate* of

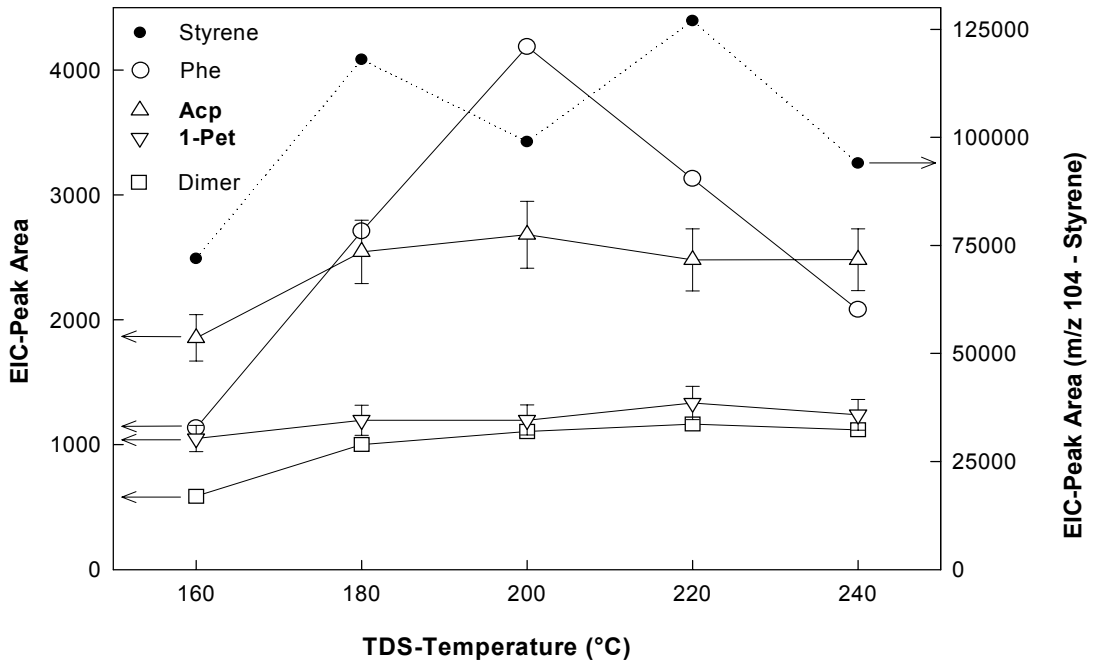


Figure 8.10 Effect of **desorption (TDS-) temperature.** This series of measurements was performed to confirm that 200°C for 10 min (with the new software) is in the 'plateau region' for complete desorption.
Error bars for 1-Pet and Acp **indicate ± 10%.** Peak areas (arbitrary units) for extracted ions m/z 120 (acetophenone), m/z 79.1 (1-phenylethanol), m/z 94 (phenol), m/z 104 (styrene), and m/z 208 (diphenylcyclobutane = 'cyclo-dimer'). Experimental Conditions: PS 168 N 10 kGy, ca. 5 mg; TDS X°C (10 min); CIS 30; GC 50(1.5) -20- 220(11); column: Supelcowax 10.

20°C/min, whereas the old version had permitted rates of up to 40°C/min, it was suspected that it now took the TDS-oven longer to regain the preset temperature level, in other words, *that the actual desorption time at the intended temperature was reduced*. Since this software update had also required the exchange of a hardware component (an EPROM), the original version could not re-installed to ultimately prove this hypothesis. Instead, the magnitude of the effect has been assessed by estimating the actual *temperature-time-courses in the samples* for both Phase IV- and Phase III-conditions (**see Figure 8.11**).

To this end, the nominal TDS-temperature, read from the TDS/CIS-remote control, was monitored during the initial temperature drop. In Figure 8.11, the readings from two runs are plotted against time, and we can see that—with the new software (at a rate of 20°C/min)—the oven needs ca. 3 min to regain the preset 200°C. For extrapolating the sample temperature it is assumed that, being located inside the massive TDS-injector, it lags behind ca. one minute, reaching its final temperature after ca. 4 min (the hairline curve in Figure 8.11). It is further assumed that with the old software (i. e., at a rate of 40°C/min) the TDS-temperature was re-adjusted much more quickly (that therefore the initial drop in oven temperature was less pronounced and less extended), and that the sample temperature, again lagging behind one minute, reached 200°C within ca. 2 min (the dotted-line curve in Figure 8.11). Thus, the actual desorption time at the nominal TDS-temperature may have been reduced from ca. 8 min in Phase III to ca. 6 min in Phase IV (i. e., by ca. 25%), and increasing the TDS-temperature compensated for the reduction in time.

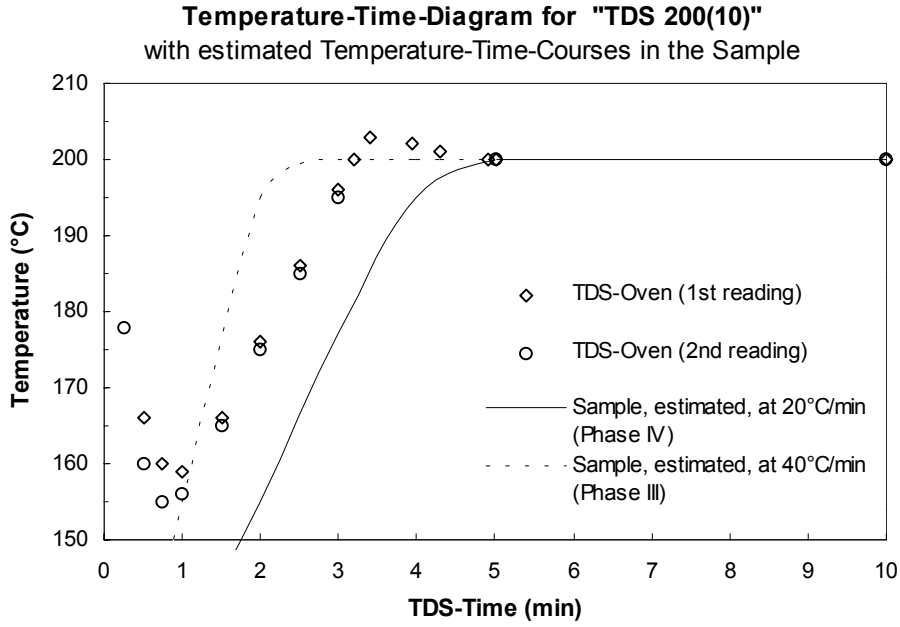


Figure 8.11 **Temperature-time-diagram for a nominally 'isothermal' desorption.** The TDS-oven temperature was read from the remote control during two analyses (at TDS 200°C, 10 min) performed with the new software.
When the cold TDS-injector is inserted, there is a sharp temperature drop to ca. 155°C and the oven needs almost 3 minutes to regain the pre-set 200°C. It is assumed that the temperature of the sample inside the massive metal TDS-injector (see Figure 3.1) lags ca. one minute behind the oven temperature.
Since the software version used in Phase III allowed to program the oven temperature with 40°C instead of 20°C / min, it is assumed that the temperature drop was both *less pronounced* and *less extended*, and it is estimated that the samples reached their final temperatures two minutes earlier (dotted line). Thus, the real desorption time at the nominal TDS-temperature may have been ca. 33% longer in Phase III (8 min vs. 6 min), which might explain the lower values initially obtained under seemingly identical conditions.

Why was the problem not recognized with the Grob-Mix test injections ? — Unfortunately, the experiments with these *TDS Performance Tests* were taken up at about the same time the new software was installed (there was, at best, one successfull injection before the update). Additionally, the tests were considered to be totally *independent* of the quantitative PS analyses; it appeared to be no contradiction to first run a test at 200°C (e. g., Figure A-15.4 in Appendix 15) and then to quantitate PS at 160°C. (And I still believe that fundamental system tests *may be* performed under conditions different from those of actual analyses.)

It is of some irony that the problem could have been recognized at one point *before* Phase IV, namely during the *qualitative* comparisons presented in Appendix 13 (they have already been mentioned at the beginning of this Chapter). If we compare the *160°C-10 min*-results in Figure A-13.1 (the white bars) with the results in Figure A-13.2, we can see that the peak areas in the latter are higher: ca. 1.1 vs. 0.8 million units for 1-Pet, and ca. 2.2 vs. 1.4 million units for Acp. The PS powders in Figure A-13.2 were desorbed with a temperature program (TDS 50°C –20°C/min– 250°C(5 min) ≡ 15 min desorption time), and the increased peak areas indicate that 160°C for 10 min was no longer sufficient for complete desorption. At the time of the measurements the data had not been examined very closely—possibly because those of Figure A-13.1 were disappointing while those of Figure A-13.2 simply met the expectations—and so the difference went unnoticed.

In any case, the idea that *'isothermal TDS at 160(10)'* changes its meaning in such a subtle way is certainly not the first thing that crosses one's mind; the whole event is probably one of those one cannot be prepared for in a complex experimental design.

8.9 Resumée

Overall, two major objectives of Phase IV had been met:

– the earlier ('Phase III') quantitative data had been reproduced, and

– the apparent absence of concentration changes with time had been confirmed.

The results with some 'real-life samples' indicate that the prospects for *irradiation detection* are promising—at least for standard polystyrenes irradiated with sterilizing doses. Analyses of two pre-treated specimens suggest that the low-MW fraction plays a major role in the formation of volatile radiolysis products. And unexpectedly, the TDS-temperature for quantitative desorption had to be increased from 160°C to 200°C (which was ultimately recognized as the subtle side-effect of a software-update).

9. Thermal Desorption of PS Solutions with Solvent Evaporation (The 'DSC-Method')

9.1 Introductory Remarks

Thermal Desorption of Polymer Solutions with Solvent Evaporation (the DSC-Method) is essentially a *new* technique; to my knowledge, no one has ever proposed a similar approach to the analysis of polymers. The technique is inherently less sensitive than direct thermal desorption of a polymer powder, and it is certainly not the method of choice to identify unknown radiolysis products; however, it can clearly be used to monitor known volatiles in polymers (e. g., to detect *radiation-sterilized* PS samples), and the technique can probably be adapted for other polymers that are soluble in suitable (relatively low-boiling) solvents.

Initial experiments in 'Phase III' were promising (Section 9.3), but had to be abandoned since sensitivity for 1-phenylethanol with the DB-5 column was no longer sufficient. The immediate objectives in Phase IV (Sections 9.4–9.6) were to assess the method's potential for **quantitation** and for **irradiation detection** under optimized and carefully controlled conditions. The results were so impressive that 'normal' TDS-quantitation was not continued, and as a consequence of this, some important measurements, eg., of 'real-life' samples, were performed only with the new technique (cf. Sections 9.4–9.6).

9.2 Principle of the Technique

The technique was inspired by the work of a colleague investigating the photo-(UV)-degradation of phthalate plasticizers in PVC, who visited us to identify some degradation products by GC-MS. The technique he used to prepare his films, *solvent-casting*, inspired an adaptation of this procedure for TDS-analysis. The idea was to **dissolve** the polymer, to inject the solution into the TDS glass liner, to wait for the solvent to evaporate, and then to desorb the **solvent-cast** polymer. Initially, the procedure was called 'DSC-Method' for *Dissolution*-(followed by)-*Solvent-Casting*.

The aim was to produce very thin films with a maximum surface for quantitative desorption; in fact, the polymer solution is virtually *sprayed* into the TDS glass liner by a rapid injection, and the resulting 'structure' is possibly described more accurately as an *ultra-fine distribution of traces of PS* on the inner surface of the glass liner and on the plug of fused-silica wool near its front end.

An initial question was whether there would be a significant loss of analytes during evaporation of the solvent. It was later found that this is not a problem with polystyrene dissolved in dichloromethane: At a CIS temperature of +30°C this highly volatile solvent is not retained on the adsorbent (Tenax TA) in the CIS. This can be easily demonstrated by so-called wet-needle injections in split-mode at different CIS-temperatures; or by injecting CH_2Cl_2, waiting several minutes with the purge valve open, and then heating the CIS in splitless-mode, i. e., with the purge valve closed.

Consequently, specimens can be analyzed immediately after injection: The solvent is vented through the split-valve during desorption and the radiolysis products are trapped on the adsorbent. Alternatively, and more accurately, the method may therefore be described as **Thermal Desorption of Polymer Solutions with Solvent Evaporation.** The principle of the method is detailed in the schematic drawing in **Figure 9.1.**

A logical next step was to *directly* dissolve pellets or fragments of parts, i. e., without producing a powder first. This eliminates the milling step that had always been suspected to be associated with a loss of analytes, and leads to an analytical procedure requiring almost *no sample pre-treatment*. (It must be admitted, however, that the pellets or fragments dissolve very slowly; therefore, prolonged vigorous shaking of the vials, as well as patience, are required). In Figures 9.5 and 9.6 (Sections 9.5 and 9.6) specimens are differentiated according to whether they were obtained by direct dissolution or by dissolving PS powders.

9.3 Initial Experiments (Phase III)

From the quantitative data obtained by *direct* thermal desorption it was concluded that 10 µl of a 1% solution of 25 kGy-irradiated PS (i. e., 0.1 mg PS) would be sufficient to produce detectable peaks. Because of the beginning column degradation and its effect on 1-phenylethanol, this turned out to be true for acetophenone only. It was not investigated whether it is possible to use *somewhat* higher concentrations, but a 10% solution of PS in dichloromethane was too viscous to be handled with a 50 µl (HPLC-) syringe.

Figure 9.2 shows a chromatogram of 25.5 kGy-irradiated PS vs. two 5 ppm standards injected into the CIS and TDS, respectively; the concentration of Acp (in PS) was estimated as

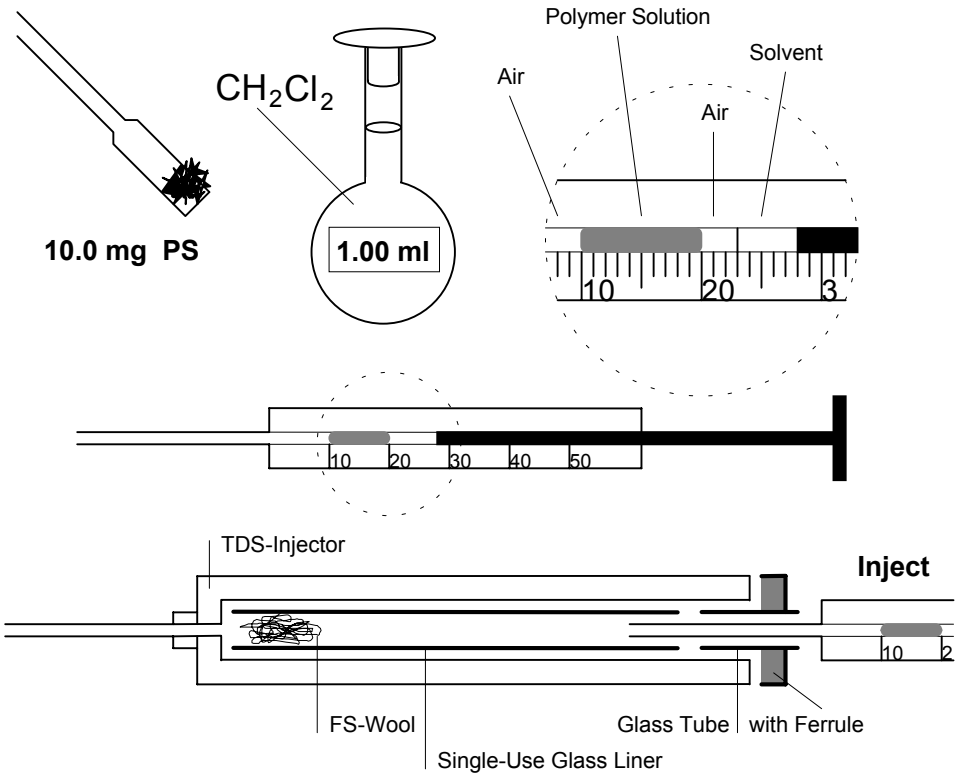


Figure 9.1 **Thermal Desorption of Polymer Solutions with Solvent Evaporation** (the DSC-Method): **Principle of the technique.**
Dissolve ca. 10 mg of PS, accurately weighed, in dichloromethane to 1.00 ml. Draw ca. 10 µl of the solution into a 50 µl HPLC-syringe (*solvent-flush*-technique ! — cf. Figure 6.6), inject into the TDS-injector, **immediately** connect to the TDS-gas line, insert into the TDS-oven and start the run.
Since it is almost impossible to draw 10.0 µl of CH_2Cl_2 into the syringe, read the volume as accurately as possible (the exact amount of PS desorbed in a run is calculated from the concentration of the polymer solution and the volume injected). Inject by **rapidly** pushing the plunger.

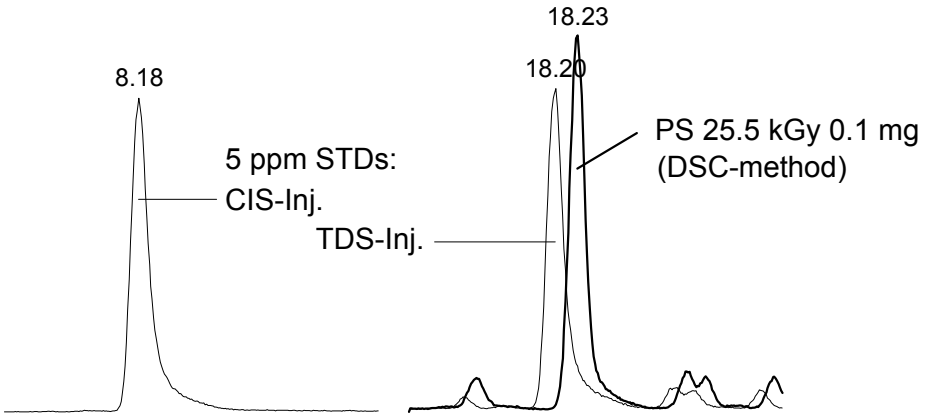


Figure 9.2 Testing the DSC-Method: **Acetophenone** in irradiated PS (BASF Polystyrol 186 N, 25.5 kGy) — data recorded in SIM-mode.
Experimental conditions, integration data and concentration estimates see Appendix 17.

< 52 ppm. This and the following values should be considered as very *rough estimates*; they are based on very limited numbers of standard injections (one-point calibration) and are calculated for an injected volume of 10 µl.

Figure 9.3 shows the acetophenone peak in a series of five consecutive analyses, i. e., three analyses of PS specimens and two TDS-blanks. Acetophenone concentrations are estimated as < 9 ppm for the non-irradiated control, and as < 43 ppm and < 36 ppm for the 25.5 kGy-irradiated PS and the Petri dish, respectively.

Despite the inherent limitations of these experiments two interesting observations could be made: Firstly, the acetophenone concentrations obtained with the technique seemed to be in the same range as those determined with 'normal' TDS-quantitation, and, secondly, the Petri dish sterilized with an unknown dose appeared to be much closer to the 25.5 kGy-specimen now than in the earlier 2D-plot (Figure 7.4), where desorption was assumed to have been incomplete for the Petri dish-*powder*.

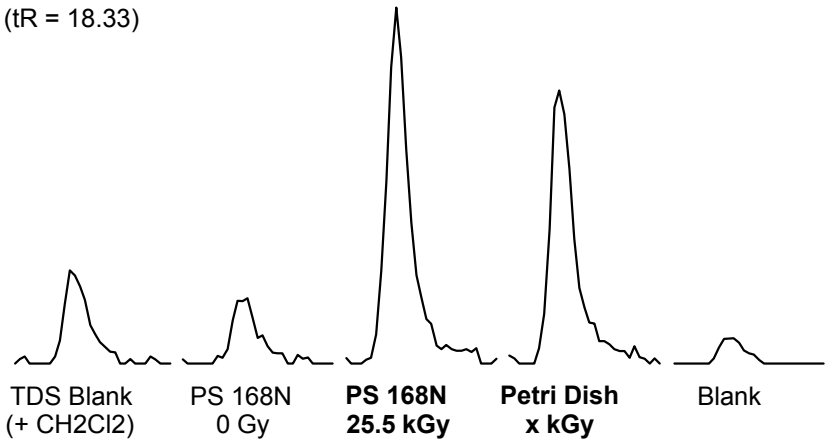


Figure 9.3 Testing the DSC-Method: **Acetophenone** in different PS samples and in TDS-blanks — data recorded in scan-mode, the graph showing extracted ion chromatograms for m/z (77 + 105 + 120).
Experimental conditions, integration data and concentration estimates see Appendix 17.

9.4 The Quantitative Series of Measurements (Phase IV)

Chromatograms (from Phase IV) of an irradiated and a non-irradiated PS specimen are presented in **Figure 9.4,** as is a chromatogram of a 0.1 ppm-standard injection—with the abundance-(y)-axis magnified by a factor of 10; the chromatograms were recorded in SIM-mode with the parameters given in Section 3.6. Overall, a series of 139 measurements was performed—these included CIS-injections of external standards, TDS-blanks, standard injections into the TDS (= recovery tests), and 42 PS-analyses, *plus* additional TDS-Performance-Tests with the Grob-Mix. The original data of the series are presented in Appendix 18; some technical details and the way the concentrations were calculated will be discussed below (see Section 9.10).

9.5 Reproducibility for 1-Phenylethanol

Figure 9.5 illustrates the **reproducibility** of the technique for 1-phenylethanol; it contains the data of *all irradiated* specimens that have been analyzed *more than once*. We differentiate between specimens obtained by *direct dissolution* and specimens obtained by *dissolving PS powders* as explained above. With two exceptions, reproducibility appears to be very good. The (large) open circles are for a *single* CH_2Cl_2 solution of PS 168 N (irradiated with 25.5 kGy) measured on four different days. The data points of PS XY (open rhombs) are for *three* different CH_2Cl_2 solutions analyzed on one day; these four analyses were

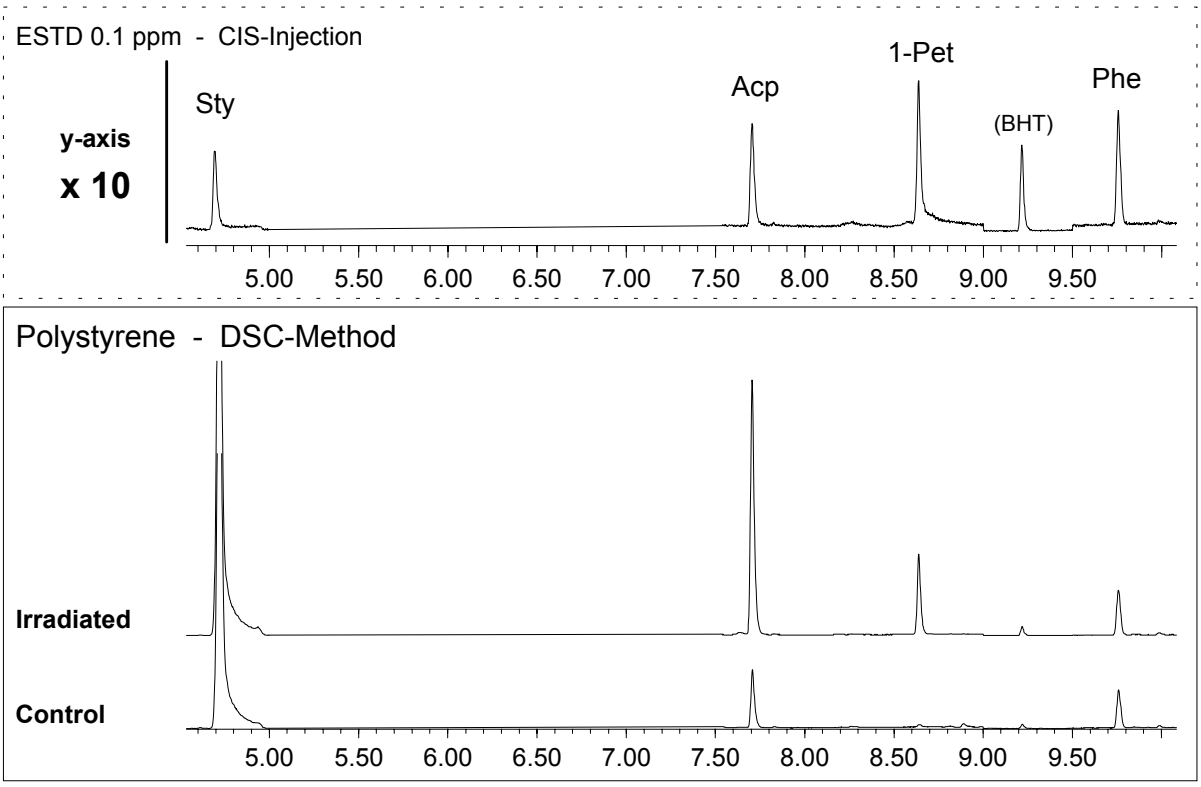


Figure 9.4 **Thermal Desorption of Polymer Solutions with Solvent Evaporation** (the DSC-Method): External standard, 0.1 ppm, injected into the CIS, and **solutions of PS (1% in dichloromethane),** injected into the TDS: **PS 168 N irradiated with 25.5 kGy (top)** vs. non-irradiated control (bottom).
Data acquisition in SIM-mode (selected ion monitoring). Exp. Conditions: See Section 3.6.

made to assess the overall error associated with preparation of the solutions. When the two polystyrenes (168 N and XY) were analyzed after *directly* dissolving one pellet, the levels of 1-Pet were almost identical (black symbols). This indicates that there are no, or only insignificant, losses of 1-Pet when the specimens are milled.

Reproducibility is also excellent for the Petri dish, and for the >15 kGy-culture flask in repeated injections of single solutions. Compared to the results described so far, there is a major difference between the two values obtained for the 24.7 kGy-injection-molded parts (one after dissolution of the powder, the other after direct dissolution); and some of the 10 kGy-data obtained with two CH_2Cl_2 solutions appear to be out-of-range (see Appendix 18: Table A-18.2 for the sequence of injections). While some potential sources of errors will be discussed in connection with Figure 9.6, there are no very convincing explanations for these aberrations.

9.6 Relationships between Various PS-Samples (2D-Plot)

Figure 9.6, a 2-dimensional plot of 1-phenylethanol vs. acetophenone concentrations, **summarizes the results** obtained with the DSC-Method.

Most of the specimens irradiated with absorbed doses of ca. 25 kGy are situated in a 'central region' (marked by the circle) with 1-Pet concentrations of 8 to 12 ppm and Acp concentrations of 30 to 50 ppm. Between this central region and the non-irradiated controls in the lower left corner of the plot we find the 10 kGy-specimens, the >15 kGy-irradiated culture flask (a 'real life sample'), and the experimental „PS 168 N t.ds. 23.5 kGy," which had been thermally desorbed for 60 min at 160°C *prior* to irradiation to reduce its low-MW fraction. The two 'real-life samples' sterilized with unknown absorbed doses (a Petri dish and another culture flask) are also situated in, or near, the central region; re-irradiation with 23.5 kGy shifts their data points towards the upper right corner of the plot as indicated by the arrows.

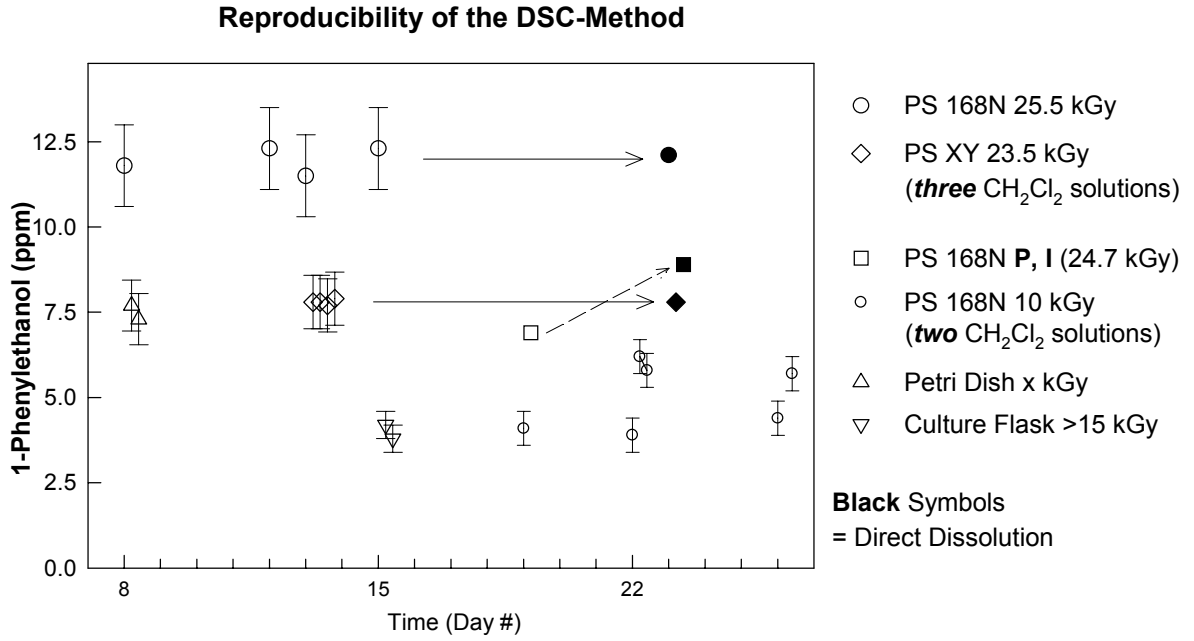


Figure 9.5 **Reproducibility** of the DSC-Method: **1-Phenylethanol concentrations.** Black symbols indicate direct dissolution (cf. Figure 9.6); Error bars indicate +/- 10% of mean values.

Overall, the picture is quite straightforward and consistent with the earlier 2D-plots (e. g., Figures 7.4, 8.4, and 8.6). Unfortunately, a closer look at some details evokes a number of questions that are hard to answer—even if we assume an added *relative* error of 20%. The results for the three PS XY-solutions suggest that the added relative errors of weighing and of determining the volumes injected are far below that figure. Memory effects and loss of analytes (due to irreversible adsorption in the TDS) may have led to over- and under-estimated peak areas, respectively; the additional relative errors introduced by these effects are estimated to be in the range of 10 to 20% depending on the analyte (see Section 9.10 *Technical Details*).

None of these errors appears to offer a sufficient explanation for the following observations. One disturbing feature is the apparent increase of Acp in the 25.5 kGy-*PS 168 N* specimen after dissolution: The data points of the 2nd, 3rd, and 4th measurement are shifted to higher Acp-levels parallel to the x-axis; in other words, the concentration of 1-Pet remained constant. A proportional increase for both (all) analytes could be explained by a loss (evaporation) of the highly volatile solvent CH_2Cl_2. The unilateral increase in Acp may have been

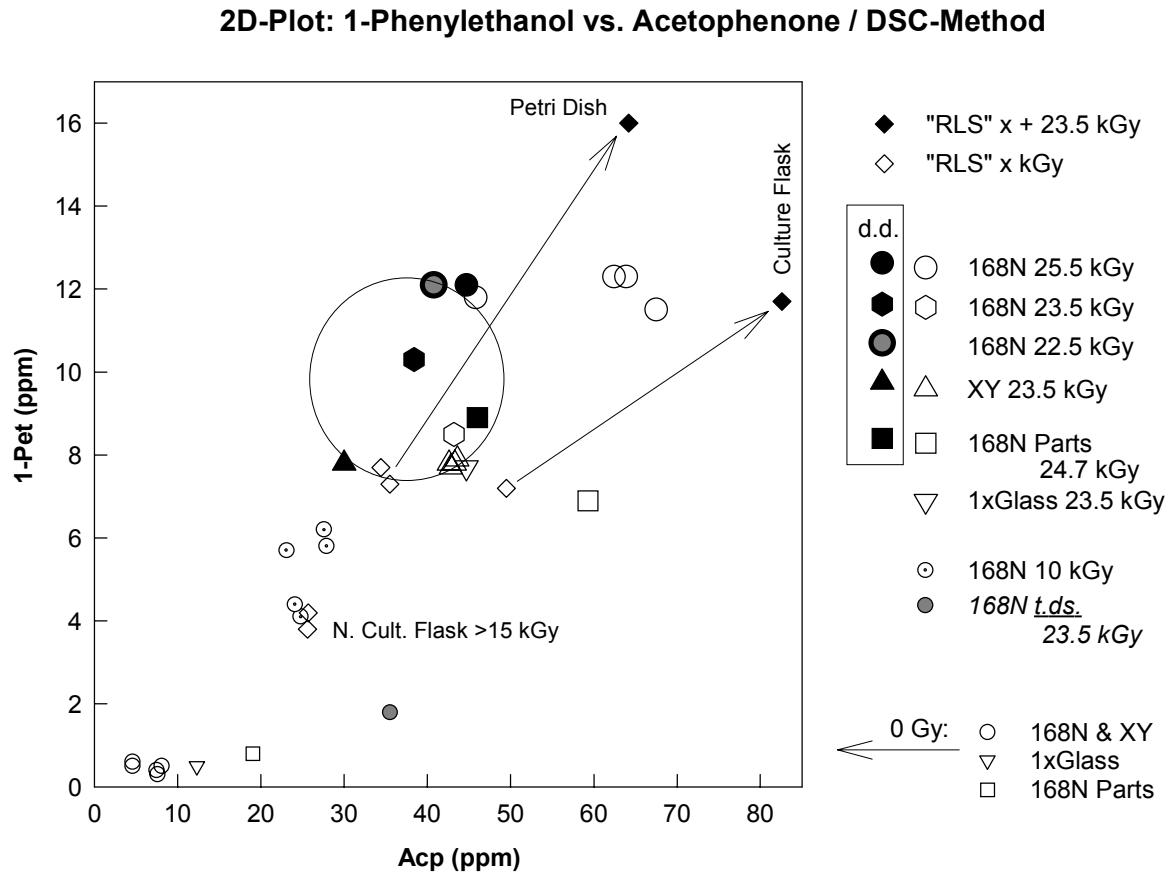


Figure 9.6 Summary of the results obtained with the DSC-Method: **2D-Plot: 1-Phenylethanol vs. acetophenone.** „d. d." stands for direct dissolution; these solutions were obtained without any pre-treatment by 'directly' dissolving whole pellets or fragments of parts, the others by dissolving PS *powders*.
Most of the samples irradiated with ca. 25 kGy are situated in a 'central region' (marked by the circle) with 1-Pet concentrations of ca. 8 to 12 ppm and Acp concentrations of 30 to 50 ppm. Between this central region and the non-irradiated controls in the lower left corner we find the 10 kGy-samples, the >15 kGy-irradiated culture flask ('real-life sample'), and the experimental „*PS 168 N t. ds. 23.5 kGy*" (see text). The two 'real-life samples' with unknown irradiation doses are also in (or: near) the central region; re-irradiation with a sterilizing dose shifts their data points towards the upper right corner.

caused by post-dissolution oxidation of the polymer, but a similar effect was *not* observed with the two 10 kGy-solutions. (These are the only CH_2Cl_2-solutions that have been analyzed on several consecutive days; the general strategy had been to analyze freshly prepared solutions. The sequence of repeated injections is indicated in Appendix 18: Table A-18.2)

If we neglect the three 168 N-25.5 kGy-data points with increased Acp-levels, there remain three major questions. These concern (1) the relationship between the PS 168 N and PS XY specimens, (2) the relationship between the 168 N specimens irradiated with 25.5 kGy, 22.5 kGy, and 23.5 kGy in three different sterilization cycles, and (3) the relationship between the DSC-results and the results of the earlier thermal desorption of powders (cf. Chapters 7 and 8).

(1) It was initially concluded from the 2-dimensional plot of 'semi-quantitative' results in Figures 8.4 and 8.6 that 1-Pet and Acp levels are identical in PS 168 N and PS XY. (Interestingly, this was not stated explicitly in Chapter 8, it is implicit in the description of a 'central region' and I probably *did not look for* potential differences.) With the DSC-Method (Figure 9.6) it appears that there is a general trend towards higher 1-Pet levels in PS 168 N. This is already visible in the two 23.5 kGy specimens that have undergone the same irradiation cycle (the two *hexagons*), and it is still more pronounced in the 22.5 and 25.5 kGy specimens (*circles*) irradiated 2.5 years earlier. With ca. 12 ppm vs. 8 ppm, the concentration of 1-Pet seems to be some 50% higher in these (22.5 and 25.5 kGy) specimens than in PS XY. It is assumed that there is a minor structural difference between the two polystyrenes, for example, a higher concentration in PS 168 N of some pre-cursor(s) responsible for 1-Pet formation on irradiation. This would explain the difference—on average some 10%—between the *23.5 kGy*-specimens of PS XY and PS 168 N in both Figures 8.6 and 9.6.

(2) The difference between the three 168 N granulates irradiated at different dose levels may be explained by the uncertainty of the absorbed dose values, and possibly by a slight post-irradiation oxidation (the 'old' 22.5 and 25.5 kGy data vs. the 'new' 23.5 kGy data). As already mentioned in Section 8.5, the dose levels determined by Red Perspex dosimetry are accurate to ±10%. Unfortunately, we have only two independent data points for the 24.7 kGy-*injection-molded parts*—one obtained with a directly dissolved fragment, the other with dissolved powder (the black and open *squares*, respectively). For the parts *dissolved-as-powders* (24.7 kGy and 0 Gy), there appears to be an elevated Acp-level as observed earlier in Phase III (Figure 7.3). The concentration of Acp appears to be lower in the directly dissolved part (and there is a similar situation with the PS XY granulate specimens), but these data are too limited to allow a conclusion.

(3) Ultimately, a comparison of the two techniques (DSC-Method vs. desorption of powders) indicates that the DSC-Method may yield 1-Pet concentrations that are as much as 50% higher, while Acp concentrations are comparable to those obtained with thermal desorption of powders (Figure 9.6 vs. Figure 8.9). Unfortunately, the comparison is based on a very limited number of data obtained with the 25.5 kGy-irradiated PS 168 N: the five analyses in Figure 8.9, and two independent data points in Figure 9.6 (we consider only the *first* analysis of the dissolved *powder* series, and neglect the three data points with increased Acp-levels). At the moment, there is no convincing explanation why dissolution of PS in CH_2Cl_2 should increase the apparent 1-Pet levels by 50%. On the other hand, there is little evidence that the high concentrations obtained with the DSC-Method are out-of-range values, in other words, the difference appears to be genuine. Of course, this difference is of little significance from a toxicological point of view, and it is clear that a future comparison of the two techniques—be it performed with a radiation-chemical or with an analytical focus—has to be based on larger series of measurements.

9.7 Radiation-Chemical Yields

Radiation-chemical yields have been calculated for 1-phenylethanol (**Figure 9.7**) and acetophenone from the product concentrations determined with the DSC-Method. The *radiation-chemical yield* is defined as the *number of molecules* formed (or consumed) in a radiation-chemical reaction divided by the *energy absorbed* by the irradiated matter. The quotient *product mass* per *energy absorbed* (mg/kJ) can be directly read from a plot of concentration (mg/kg) vs. the absorbed dose (kGy or kJ/kg)—see Appendix 19; dividing this quotient by the molecular mass (g/mol) of the product gives the radiation-chemical yield (mmol/J). The yield is usually expressed in µmol/J, or, in this case, in nmol/J (nanomol per Joule); an older, non-SI, unit is the G-value or 100 eV-yield, a figure that indicates the number of molecules formed per 100 eV of absorbed energy (cf. Appendix 19: Table A-19.1).

The data presented in Figure 9.7 are average values that have been calculated separately for each specimen (and for each irradiation level). Of course, the regressions underlying the calculation of a radiation-chemical yield (Appendix 19: Figure A-19.1) should be defined by more data points; ideally, the specimens should have been irradiated at the same time with dose levels of, e. g., 10, 20 and 30 kGy. On the other hand, the sum total of earlier results, especially Figures 7.2 and 7.3, appears to justify this approach—in fact, calculating radiation-chemical yields from Figures 7.2 and 7.3 gives almost identical results (Section 7.4).

In any case, the main objective had been to determine the *order of magnitude* of the radiation-chemical yields, and to see whether they were comparable for the various polystyrenes under investigation. It can be seen from Figure 9.7 that the radiation-chemical yields for **1-phenylethanol** are in the range of 3 nmol/J (G = 0.03); with the exception of the experimental PS 168 N t.ds. (thermally desorbed *prior to* irradiation) and the re-irradiated culture flask, all the values are in, or near, the range of 2.5 to 3.5 nmol/J.

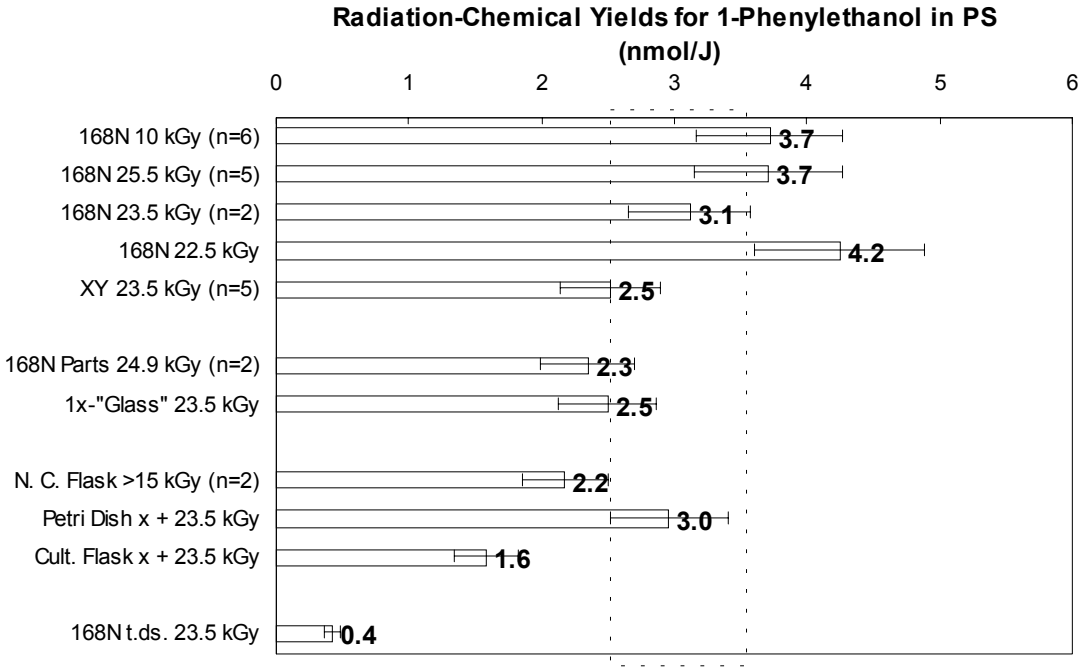


Figure 9.7 **Radiation-chemical yields (nmol/J) for 1-phenylethanol.** With two exceptions (the re-irradiated culture flask and the experimental *PS 168 N t. ds.*) the radiation-chemical yields are in, or near, the range of 2.5 to 3.5 nmol/J.
The values were calculated as described in Appendix 19. Divide by 100 to obtain G-values (e. g., 3 nmol/J corresponds to G = 0.03). Error bars indicate +/- 10%.

Radiation-chemical yields for **acetophenone** are some 3 to 5 times higher—with values between 10 and 15 nmol/J. The value most obviously out-of-range is 18.5 nmol/J obtained in the 2nd to 4th analysis of the PS 168 N 25.5 kGy solution. The value calculated for the 1st analysis of this solution is 12.3 nmol/J, and, as already mentioned in connection with Figure 9.6, there is no convincing explanation for this phenomenon. The radiation-chemical yields for Acp have been calculated in the same way as described for 1-Pet; however, the values were calculated separately for the samples analyzed on Days 22 to 26 to see whether the subtraction of increased Acp background levels (see Section 9.10 *Technical Details*) had caused any major deviations. Apparently, this was not the case; the results obtained before and after the background 'crisis' agree quite well.

The order of magnitude of the radiation-chemical yields has an important implication for the *mechanism* underlying the radiation-chemical reaction(s), in which 1-Pet, Acp, and the other major radiolysis products are formed. It provides a strong argument for the hypothesis that the residual monomer *styrene* is **not** (or only to an insignificant extent) involved in the formation of these products. It has not been possible—even in the earlier qualitative comparisons—to detect any changes on irradiation in the concentration of styrene. It was thought that, since the styrene peak is heavily overloaded, it was simply not possible to notice a radiation-induced decrease by, for example, 10 percent. On the other hand, it had always been suspected that the concentrations of the major products are too high to be explained as radiolysis products of styrene (the GC-peaks are simply too big).

The values obtained for the radiation-chemical yields appear to support this view. The styrene concentrations in the polystyrenes as determined by the DSC-Method are commonly in the range of 100 to 300 ppm (Appendix 18: Table A-18.2), which would be in agreement with the ca. 200 ppm that are considered 'state-of-the-art' in PS. According to Dunkel (1993), 50 ppm can be achieved, while 200 ppm are state-of-the-art in PS intended for food contact. Gilbert and Startin (1983) have determined styrene levels of ca. 100-500 ppm in PS samples, Hempel and Rüdt (1988) of ca. 400 ppm, and Venema (1988) of ca. 300 ppm.

Let us consider a hypothetical PS containing 200 ppm of residual styrene, and with radiation-chemical yields of 3 and 12 nmol/J for 1-Pet and Acp, respectively. When the products are solely formed by (radiation-induced) oxidation of *styrene*, we can calculate *another* radiation-chemical yield taking into account only *that* fraction of energy that is absorbed by the residual monomer. If we assume that there is no energy transfer from the polymer molecules to the styrene molecules, then the residual styrene absorbs only 200 per 1,000,000 (200 ppm or one fivethousandth) of the energy absorbed by the PS sample. Consequently, radiation-chemical yields would be increased by a factor of 5000, i. e., with our hypothetical model-PS we would obtain 15,000 nmol/J (G = 150) for 1-Pet, and 60,000 nmol/J (G = 600) for Acp. Compared to the radiation-chemical yields (G-values) that have been determined for gases and other small organic molecules (Hill et al., 1989) these values are exceptionally high; therefore, it appears that the radiolysis products could originate from styrene only if we assumed a very substantial / near total transfer of energy from the polymer chains to the residual monomer molecules.

Unfortunately, it is very difficult to directly determine the yield of the radiation-chemical oxidation of styrene to acetophenone or 1-phenylethanol (if there *is* such an oxidation). Irradiation of pure styrene results, of course, in polymerization. It was attempted to incorporate traces of styrene into a 'matrix' of tetracosane ($C_{24}H_{50}$ – cf. Section 7.11 and Appendix 12), but for reasons that are not entirely clear, it was not even possible to retrieve the styrene analytically *before* irradiating the 'spiked' tetracosane. Either a major mistake in preparing this 'model polymer' has been made, or it is not possible to uniformly distribute several hundred ppms of styrene in tetracosane (though it is not clear why this should be so), or, most likely, tetracosane causes severe problems during thermal desorption (e. g., by condensing in the needle of the TDS-injector). The experiments have not been repeated, and it was not attempted to find another, possibly more suitable 'model polymer.' One would like to have some matrix that is inert during irradiation, but it is not clear what this could be, and how a known (trace) amount of styrene could be dispersed in it.

9.8 Direct Injection / Thermal Desorption with the CIS

It has been said earlier that, after establishing the DSC-Method, one logical step had been to directly dissolve the PS specimens, thus eliminating the risk of loosing some of the volatiles during milling. In the course of this work it occured to the author that there is another logical step, a *final* step that eliminates thermal desorption, or rather, shifts the place where desorption occurs—namely, into the cooled injection system (or injector). What appears, at first glance, to be a chromatographer's worst nightmare—injecting a polymer solution 'into the GC'—may be a very interesting concept from a practical point of view. Of course, to reduce any conceivable risks, the idea was put to a test only after the DSC-series had been completed, at a time when the 'sensitivity test' indicated that the CIS glass liner had to be replaced anyway (cf. Appendix 15: Figure A-15.3).

If we take into account that this was another 'quick-and-dirty' experiment (consisting of two injections only), and that two factors greatly reduced the sensitivity of the analyses—(1) the injection volume being only *one tenth* of that used for the DSC-experiments, and (2) the slightly contaminated injector liner scheduled for replacement—, then the results for 1-phenylethanol and acetophenone (**Table 9.1**) agree quite well with the earlier DSC-results.

Table 9.1 **Direct Injection / Thermal Desorption with the CIS** — concentrations (ppm or mg/kg) relative to the polymer mass.

V inj. [a]	m PS [b]	**Styrene**	**Aceto-phenone**	**1-Phenyl-ethanol**	**Phenol**
(µl)	(mg)	(ppm)	(ppm)	(ppm)	(ppm)
0.8	0.006	458	55.6	8.9	17
0.9	0.007	486	56.3	8.8	12

[a] Volume injected
[b] Mass of polystyrene in this volume

Ca. 1 µl of PS dissolved in dichloromethane were injected into the CIS. The sample was **PS 168 N, 22.5 kGy**, the concentration of the solution was 7.9 mg/ml — obtained by directly dissolving one pellet.

Experimental Conditions: CIS 30; GC 50(1.5) -20- 220(x); column: Supelcowax 10; MS: SIM.

Since the CIS is heated only a few minutes during the injection of a sample, there is almost no degradation of the polymer remaining in the injector. From the experiences with the DSC-Method (cf. Section 9.10 *Technical Details*) it can be predicted that it will be possible to perform a reasonable number of analyses (let us say, 10 to 20 injections) before degradation of the accumulating polymer will interfere with quantitation. Thus, the concept of thermal desorption with the CIS (or with another PTV) requires only that one can afford (and is willing) to replace the injector glass liner whenever the background level becomes inacceptable.

Potential **benefits** of the technique are:

– no need to invest in a TDS-unit,
– no risk of loosing analytes at the TDS/CIS-interface,
– reduction of analysis time,
– it may be possible to use an autosampler, [#]
– it may be possible to perform large-volume injections with an autosampler [#] (to increase the sensitivity of the technique).

[#] This will depend on the viscosities of the polymer solutions.

It is clear that 'normal' thermal desorption remains the method of choice for identifying trace radiolysis products, and that its sensitivity will usually be much higher—the masses of PS in our direct injections were 6 and 7 µg compared to 5 mg in the 'standard' TDS-analysis of a PS powder. Nevertheless, the concept of direct injection may be of interest for large-scale screenings, routine analyses, or interlaboratory trials, and the possibility to perform large-volume injections with an autosampler certainly deserves further investigation.

9.9 Dissolution-Precipitation

Table 9.2 presents the results of a preliminary dissolution-precipitation experiment designed as another first step towards an elucidation of the mechanism of the underlying radiation-chemical reactions. The PS specimen was dissolved in dichloromethane and precipitated with methanol *after* irradiation. The precipitate was analyzed by 'normal' thermal desorption, i. e., by directly desorbing 20 mg; MS data were acquired in SIM-mode; concentrations were therefore calculated with the (SIM-) calibration curves of the DSC-series.

Originally, it had been intended to re-concentrate and analyze the solution in order to assess the fraction of radiolysis products *genuinely present* in the polymer—as opposed to the fraction suspected to result from a *thermal breakdown* of radiation-induced precursors. Unfortunately, an inadequate reconcentration procedure and technical problems rendered the results for the solutions meaningless; therefore, we can only draw some limited conclusions from the *complementary results* obtained with the precipitate in TDS-analyses. The dissolution-precipitation procedure has apparently reduced the styrene level from an estimated 200 ppm (cf. Table A-18.2) to ca. 35 ppm (Table 9.2) — but this 'residual' level must be to a considerable extent the result of thermal degradation (pyrolysis), since the monomer is almost completely removed in the procedure.

The data for the radiolysis products (Table 9.2) suggest that some 25 to 30% of the *acetophenone*, and ca. 5% of the *1-phenylethanol* are in fact **thermal degradation products** of some macromolecular radiation-induced precursors, e. g., of peroxides or hydroperoxides. (Interestingly, similar fractions of Acp and 1-Pet in the non-irradiated control also appear to be formed by thermal degradation of macromolecular precursors.) *Phenol* concentrations in normal (non-precipitated) PS are estimated to be in the range of 10 ppm (cf. Tables A-16.3 and A-18.2); consequently, some 20% of the phenol would also result from thermal breakdown of some precursor(s). The remainder, i. e., 70–75% of the Acp, 95% of the 1-Pet, and probably 80% of the phenol, is either genuinely present after irradiation—or formed by thermal degradation of **low-molecular-weight (!)** radiation-induced **precursors.**

Table 9.2 Thermal desorption of PS after **dissolution** in dichloromethane and **precipitation** with methanol – concentrations (ppm) relative to the polymer mass.

	Styrene (ppm)	Acetophenone (ppm)	1-Phenylethanol (ppm)	Phenol (ppm)
0 Gy	36	1.9	0.07	0
23.5 kGy	35	**12.6**	**0.32**	**2**

Dissolution and precipitation were performed **after** irradiation. The samples were **PS XY**, ca. 20 mg.
Exp. Condit.: TDS 200(10); CIS 30; GC 50(1.5) -20- 220(6); col.: Supelcowax 10; MS: SIM.

It was concluded that simple dissolution-precipitation experiments could not differentiate between these two possibilities—even if one succeeded in concentrating and analyzing the solution, because it would still contain both the genuine products and the potential low-mol-

ecular-weigth precursors. In any case, the results of the experiment confirm the important role of the low-MW fraction.

As far as product safety is concerned, it is probably better to calculate a worst-case-scenario based on the (apparent) concentrations determined by thermal desorption, and, if necessary, to conduct additional migration studies. If one is interested in elucidating the mechanism of the radiation-chemical reactions involved, one would possibly proceed to the analysis of polystyrenes with well-defined molecular weights, and of oligomers / very-low molecular-weight polystyrenes specifically synthesized (and / or isolated) for that purpose.

9.10 On Some Technical Details of, and Problems Associated with, the DSC-Method

> The following discussion of technical details, of the way the concentrations were calculated, and of some problems associated with the technique is related to the material presented in **Appendix 18;** it is *not* essential for a general understanding of the method and of the results presented in this Chapter. It has been mentioned earlier that the DSC-Method is essentially a *new* technique; to my knowledge, no one has ever proposed a similar approach to the analysis of polymers. In order to obtain any results at all it has been necessary to find ways to deal with conditions that were —despite all efforts at optimization and despite a comprehensive parallel test program—not totally satisfactory.

As already mentioned (in Section 3.3), the TDS is originally designed for environmental air analysis, and using the system to thermally desorb polymers may result in problems caused by contamination (memory effects) and in difficulties to obtain clean blanks. While reducing the amount of polymer desorbed in a single run *may* reduce contamination of the TDS-unit, it is clear that the increased sensitivity needed for these analyses aggravates the difficulty to obtain *acceptable* blanks. Obviously, a blank that is perfectly clean for a 'conventional' TDS-analysis of 5 mg PS (with data acquisition in scan *or* in SIM-mode) may turn out to be inacceptable for the desorption of 0.1 mg PS dissolved in CH_2Cl_2 (in SIM-mode).

For these reasons, the measurements of the DSC-series were performed exclusively with a *new* (second) TDS-injector, while the conventional analyses of powders were continued with the first injector. Despite the use of carefully cleaned TDS glass liners (the cleaning procedure consisted of boiling in conc. HNO_3, rinsing with double-distilled water, and drying at 450°C) which yielded very good blanks in scan-mode, there were still increased background levels of 1-Pet, Acp, phenol, and styrene in the TDS-blanks recorded in SIM-mode.

The reasons for this are still not totally clear—there appear to be three possible sources for the increased background levels: (1) the inner metal surface of the TDS-injector and the glass liner might be contaminated by ambient (laboratory) air each time the injector is opened for a new analysis. (2) New glass liners might adsorb contaminants when they are allowed to cool down after the drying step. (3) The Graphpack ferrule connecting the TDS-injector to the TDS gas supply-line might adsorb, and then release, volatiles and / or it might be subject to some degradation.

The average levels of contamination were clearly less than 0.05 ng for 1-Pet, less than 0.3 ng for Acp, and slightly more than 1 ng for styrene. This appears to be not very much in relation to the quite extended surface areas that are exposed to ambient air each time a new sample is injected, but it results in peaks that are comparable in size to those obtained with the lower-concentration calibration standards.

In the absence of viable means to reduce these levels of contamination, there was no choice but to accept this situation and to see whether it was still possible to obtain meaningful results. Since **1-phenylethanol** was considered the most interesting product, it was decided

to proceed with the analyses of PS-solutions whenever the 1-Pet background level was below 0.1 ng (i. e., whenever the 1-Pet peak was smaller than in the 0.1 ppm external standard); this would lead to an over-estimation of 1-Pet concentrations in the radiation-sterilized (25 kGy) specimens of, in the worst case, roughly 10%. The average background level of 1-Pet turned out to be less than 0.05 ng, and, in fact, the 1-Pet peak in the blanks were often below the integration treshold (i. e., nominally zero—see Appendix 18: Figure A-18.4). No background subtraction was performed for 1-Pet, which means that the concentrations of 1-Pet in PS may be slightly over-estimated in some cases, and, of course, more so for the *non-irradiated controls* than for the irradiated specimens. No limits were defined for the background levels of Acp, styrene, and phenol (Figures A-18.3, A-18.5, and A-18.6, respectively); instead, the respective average background levels were subtracted from the peak areas obtained in the PS analyses.

Before discussing these background subtractions in more detail, a brief comment should be made on the subject of *repeated injections* using a single TDS glass liner, and on the *background 'crisis'* of Day 21. Surprisingly, it was not absolutely necessary to replace the TDS glass liner after each analysis; on the contrary, recording a blank after a PS analysis without exchanging the liner usually resulted in *lower* background levels than when using a *new* glass liner. (Obviously, there is no significant degradation of the PS accumulated in the liner, which appears to be plausible, because it cools down to room temperature immediately after desorption and is protected against oxidation by the constant flow of helium through the TDS-injector. This is the experience on which the proposal is based—in context with Table 9.1—to *repeatedly inject* polymer solutions *directly* into the CIS. Additionally, this observation appears to confirm the hypothesis that airborne contaminations are, at least partly, responsible for the increased background levels.)

Thus, after obtaining an acceptable blank with a new glass liner, this liner was used repeatedly as long as it met the criterion that the 1-Pet background be below 0.1 ng. To reduce contamination as far as possible the metal TDS-injector was kept overnight at 200°C in the TDS-oven—with a small flow of helium going through it, without being connected to the CIS, and *without the glass liner*. On Day 21 the glass liner was accidentally not taken out, which resulted in a visible discoloration (to yellow-brown) of the traces of PS present, and in a contamination 'crisis' with increased background levels (see Appendix 18: Figure A-18.3).

In the case of **acetophenone**, a constant background of 25 area units is subtracted initially, then on Day 22 three analyses are omitted because of excessive background levels, and, for the last three days, a declining background subtraction is used that starts each day at 100 units and drops by 10 units in each consecutive analysis on that day (see Appendix 18: Figure A-18.3 and Table A-18.2; this declining background subtraction is based on experiences with multiple *consecutive* blanks performed during the DSC-series). Of course, this is not very elegant, but there was no other choice. To assess whether the procedure has introduced major errors the *radiation-chemical yields* before and after the blank 'crisis' have been compared, indicating no major difference in radiation-chemical yields, or in the underlying Acp-concentrations. It should also be said that the initial background subtraction of 25 units induces an error, if any, of *less than* 10% for the irradiated specimens.

In the case of **styrene**, the data (Appendix 18: Figure A-18.5) appeared to justify a constant subtraction of 200 area units. It should be mentioned at this point that the PEG column, the relatively long splitless-time, and the fact that most of the solvent is vented during desorption (i. e., there is hardly a solvent effect for reconcentrating styrene), are certainly not optimum conditions for a GC-analysis of styrene.

The sole rationale for 'quantifying' styrene under these conditions was to get a general and approximate impression of the styrene concentrations in the specimens under investigation. As already mentioned in context with the radiation-chemical yields, styrene levels are typically between 100 and 300 ppm; the scatter of the data is relatively high (Appendix 18: Table A-18.2), and, limited though they are, the data suggest that there is no significant change of styrene levels on irradiation.

In the case of **phenol**, background levels are relatively higher than for the analytes discussed so far, and they did not return to acceptable levels after Day 21 (see Appendix 18: Figure A-18.6); it was decided to perform no background subtraction before Day 21 and to omit the values thereafter—the phenol concentrations tabulated in Table A-18.2 should therefore be considered as *maximum* concentrations.

There is no convincing explanation for the differing behaviour of the various compounds, for example, why 1-Pet and styrene contaminations returned to 'normal' quite readily, whereas Acp went back much slower, and phenol persisted at high levels. This is all the more puzzling, since one would expect, for example, phenol and the alcohol to behave similarly, or styrene to behave distinctly different from the three polar oxygen-containing compounds.

I would like to close this Section with a few remarks on the *calibration curves* and on potential **operator effects**. All data of the DSC-series (calibration and PS data) were recorded by two operators in very close collaboration; each of them (identified in Appendix 18 as operators #1 and #2) performed roughly one half of the injections. At the end of the series some standards were injected that were prepared from *new stock solutions* and contained only 1-Pet and Acp; this was done to confirm that the standard solutions had remained stable. The new solutions are labelled with an 'N' in Table A-18.1, and there is no difference between old and new standards. After omitting a few values that are apparently out-of-range —it appears that operator #1 had a 'bad day' at the end of the series, see Figures A-18.7 and A-18.8—we obtain two independent calibration curves that agree perfectly well (Figure A-18.1). In a similar way (not shown), the PS data in Table A-18.2 were analyzed for any signs of an operator bias. Of course, the picture is much more complex here, but there is again no evidence for any operator-related systematic error.

A final comment must be made on Figure A-18.7 (Appendix 18), which plots the results of the 1 ppm-standard injections. We can see that four out of five TDS-injections (recovery tests) reach only some 80% of the average peak area of the CIS-injections. It can be concluded from parallel recovery tests with 0.1 and 10 ppm standards, and from the results for 1-octanol with the 'TDS-Performance-Test' (see Appendix 15: Figure A-15.5) that there may be a real loss of these alcohols in the order of magnitude of 10 to 20%. It also appears that these losses are proportional to the quantities injected rather than being a constant.

At the time of the measurements, the true extent of this problem was not fully recognized, and during data analysis it was thought that not too many correction factors should be introduced into the calculations; in any case, it cannot be excluded that the 1-Pet concentrations determined in this first major trial of the DSC-Method are under-estimated by 10 to 20%. The same is *not* true for acetophenone as can be seen from Figure A-18.8 (Appendix 18).

To avoid such losses, which are thought to be caused by irreversible adsorption of the polar alcohols to some 'active sites,' it might be a good idea to experiment with various *specially desactivated* glass liners in future DSC-investigations of 1-Pet in PS. Overall, it must be concluded that thermal desorption of polymers as an analytical technique would greatly profit from any technical improvements that *prevented contaminations* and *excluded losses* of the analytes *more reliably* (cf. the related comments in Section 3.11).

9.11 Analytical Resumée

While the emphasis in this Chapter was very much on the problems associated with the technique, it appeared that the method worked reasonably well, and the whole project was considered a relative success. The DSC-Method, or Thermal Desorption of Polymer Solutions with Solvent Evaporation, can clearly be used to monitor volatiles in polymers (e. g., to detect *radiation-sterilized* PS samples), and the technique can probably be adapted for other polymers that are soluble in suitable (relatively low-boiling) solvents. The concept of directly injecting polymer solutions into a PTV-type injector also deserves some attention.

10. Identification of Trace Radiolysis Products

10.1 Desorption of PS Pellets

It was apparent very early that additional *minor* radiolysis products are formed in polystyrene with concentrations approximately one order of magnitude below that of the main products. A first attempt to identify these trace products was made during the initial screening program (Phase I).

To enhance sensitivity the number of pellets analyzed in a single run was increased from the usual 5 (cf. Figure 4.2) to 12 and ultimately to 24. To prevent filament damage with such high sample load the MS was turned off during the elution of styrene. (It can be expected that the styrene peak would be comparable in size to that of the solvent in a 'conventional' GC-analysis.) The peaks of the main radiolysis products also become heavily overloaded.

Figure 10.1 shows a detail view of two chromatograms recorded with 12 pellets; compound identification is based on the mass spectra obtained in a third run (not shown) with 24 irradiated pellets—the maximum number that fits into the desorption glass tubes. The concentration of 2-phenylpropenal (peak No. 3) is at least ten times lower than that of acetophenone (cf. Figure 4.2 and Table 4.1 in Section 4.1).

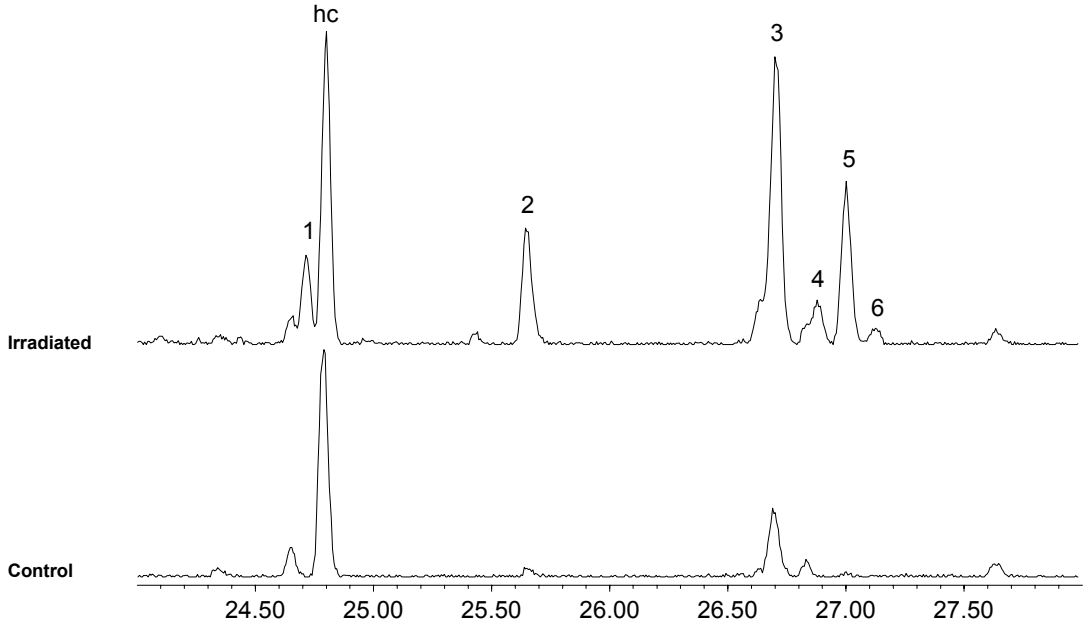


Figure 10.1 **Trace radiolysis products in polystyrene** eight days after irradiation with 22.5 kGy. The concentration of Peak # 3 (2-phenylpropenal) is at least ten times lower than that of acetophenone (cf. Figure 4.2).

1 = α-Methylbenzeneactaldehyde
2 = 1-Phenyl-2-propanone
3 = 2-Phenylpropenal
4 = 1-(4-Hydroxyphenyl)-ethanone, or 1-(2-Hydroxyphenyl)-ethanone
5 = 1-Phenyl-1-propanone
6 = 1-Phenyl-1,2-propanedione
hc = an unidentified hydrocarbon, or hc-derivative; not a radiolysis product.

Experimental Conditions: Sample: BASF Polystyrol 168 N, 12 or 24 pellets (cf. text); TDS 160(10); CIS -40; GC 40(11) -4- 250(x); column: DB-5.

10.2 Desorption of PS Powders

Objectives

With the analytical mill it became possible to produce fine polymer powders, resulting in a dramatic increase in the surface available for desorption which was expected to be accompanied by an equally dramatic increase in sensitivity. One objective of these experiments was to take full advantage of this effect and to identify potential 'new' radiolysis products that might be useful as markers in irradiation detection.

An additional motivation was to get an impression of how sensitive the technique really is, in other words 'to push the systems to its limits.' The concentrations of the main products (Chapters 7–9) had turned out to be relatively high—in an analytical sense, i. e., in the low ppm-rather than somewhere in the ppb-range. Ligon and George (1978) have estimated that, with 300 mg-samples, detection limits are in the range of 30 ppb to 30 ppm—and down to 3 ppt when the MS is operated in SIM-mode (which, of course, is possible only if one knows *which* ions to monitor).

Product Identification

Several analyses were performed in Phase III with the DB-5 column, post-Phase III with the Rtx-200, and in Phase IV with the Supelcowax 10 column. Appendix 20 contains an 'MS Identification Table for Figure 10.2 (Table A-20.1) and for the other runs performed with the

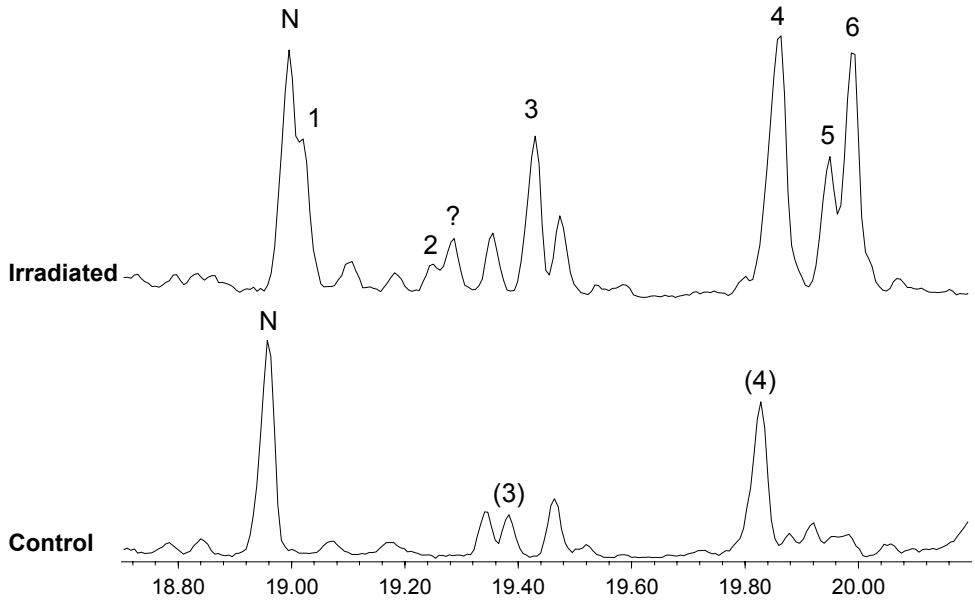


Figure 10.2 **Trace radiolysis products** in polystyrene (desorption of **50 mg** PS powder) —detail (18.7–20.2 min) of fingerprint chromatograms obtained with the DB-5 column. The concentrations of the compounds are estimated to be in the 0.1 to 1 ppm-range.

1 = 2-Phenylpropanal
2 = Benzeneethanol
? = Unidentified
3 = 1-Phenyl-2-propanone
4 = 2-Phenylpropenal
5 = 1-(4-Hydroxyphenyl)-ethanone, or 1-(2-Hydroxyphenyl)-ethanone
6 = 1-Phenyl-1-propanone

See also Table A-20.1 (Appendix 20).
Experimental Conditions: PS 168 N, **50 mg** powder, ca. 1.5 years after irradiation (25.5 kGy) of the pellets; TDS 160(10); CIS 30; GC 40(1.5) -10- 250(5); column: DB-5.

Rtx-200 and Supelcowax 10 columns (Tables A-20.2 through A-20.5). For each trace product, they tabulate its retention time, the characteristic ions of the mass spectrum, a rough estimate of its *relative increase* on irradiation, data related to identification (library match qualities and whether scans were averaged and/or background subtracted), and other information (e. g., peak shapes, coeluting peaks, etc.).

Thus, the structures of the trace products proposed in Tables A-20.1 to A-20.5 (and in Figures 10.1 through 10.6) are the results of a *qualified* and thorough interpretation of library search proposals, and the author is quite confident to have identified the compounds correctly. Compounds are labeled as 'Unidentified' or 'Unknown', whenever there was some doubt about their true identity (cf. Section 3.9). In the case of the trace products no authentic samples were injected for confirmation—only the identity of benzoic acid and of 1-phenyl-1,2-ethanediol was subsequently confirmed (during some experiments with high-dose irradiated PS).

The following synopsis shows the differences between the five pairs of measurements:

Column	Sample	Dose	m PS	Misc.	see Table ...
DB-5	168 N	25.5 kGy	50 mg		A-20.1
Rtx-200	168 N	25.5 kGy	50 mg	10°C/min *	A-20.2
	168 N	25.5 kGy	50 mg	5°C/min *	A-20.3
Supelcowax 10	XY	23.5 kGy	50 mg		A-20.4
	168 N	10 kGy	300 mg		A-20.5

* Rate of GC temperature program.

Chromatograms and Concentration Estimates

Figure 10.2 shows details of two chromatograms from Phase III obtained with the DB-5 column; the mass of PS powder desorbed was 50 mg, i. e., 10 times the mass used for quantitation of the main products. The peaks in the chromatogram of the irradiated PS (*top*) are shifted slightly toward higher retention times, probably because of the huge and severely overloaded peak of acetophenone, which elutes from 18 to 18.5 min (the MS was switched off during that time). The concentration of the *'major trace products'*, compounds # 1, 3, 4, and 6, are estimated to lie in the range of 0.1 to 1 ppm in the irradiated PS; the estimates are based on a comparison with injected 1-Pet and Acp calibration standards.

Figure 10.3 shows the *structural formula* of the trace products, they are generally *oxidized* aromatic structures, usually derivatives of phenylethane and phenylpropane. As mentioned in Section 4.1 irradiation produces an additional non-oxygen-containing trace product, *benzene* (see Chapter 11 for quantitative data).

The concentration estimates of 0.1 to 1 ppm from Figure 10.2 were confirmed in the subsequent analyses; thus the level of the trace products *is one to two orders of magnitude below* that of the main products. Benzoic acid concentrations are difficult to estimate because of poor peak shapes on all three columns used; the levels of benzoic acid may be distinctly higher than 1 ppm (up to 10 ppm ?), which would place the compound on the borderline between *main* and *trace products*. (It must be admitted that the terms main products and trace products are used in a rather casual way; since there is obviously a continuum of radiolysis product concentrations, any exact definition would be quite arbitrary.)

Trace Products as Radiation Markers ?

In terms of *relative increase* (difference between irradiated and control sample), the more interesting trace products are:
– 2-Phenylpropanal,
– 1-Phenyl-1-propanone,
– 2-Hydroxy-1-phenyl-ethanone, and possibly
– 1-Phenyl-1,2-ethanediol (cf. Figure 10.6)
(these are highlighted in **boldface** in Tables A-20.1 to A-20.5).

One of the trace products, **1-phenyl-1-propanone**, is tentatively used as **radiation marker** in **Figure 10.4.** The Figure combines detail views of the 1-phenyl-1- (and 1-phenyl-2-) propanone peaks of *five* different PS specimens, namely PS 168 N, PS XY, and the PS 1x-glass (non-irradiated controls vs. ca. 25 kGy), plus two 'real-life samples', i. e., the Petri dish and a culture flask, sterilized with unknown doses (x kGy) vs. re-irradiated (x + 23.5 kGy). To eliminate the background the peaks are presented as *added* extracted ion chromatograms (added EICs). Figure 10.4 is the result of an ex-post (or: retrospective) data analysis of chromatograms obtained in Phase IV at TDS 160°C(10 min); TDS- and GC-conditions have not been otimized specifically for the two trace compounds.

We can see that the levels of 1-phenyl-1-propanone are very low in the three non-irradiated controls, and that they increase markedly on irradiation. The concentrations in the x kGy-*sterilized* 'real-life samples' are comparable to those in the two granulates and in the PS 1x-glass after absorbed doses of ≈ 25 kGy. Re-irradiation of the real-life samples with 23.5 kGy

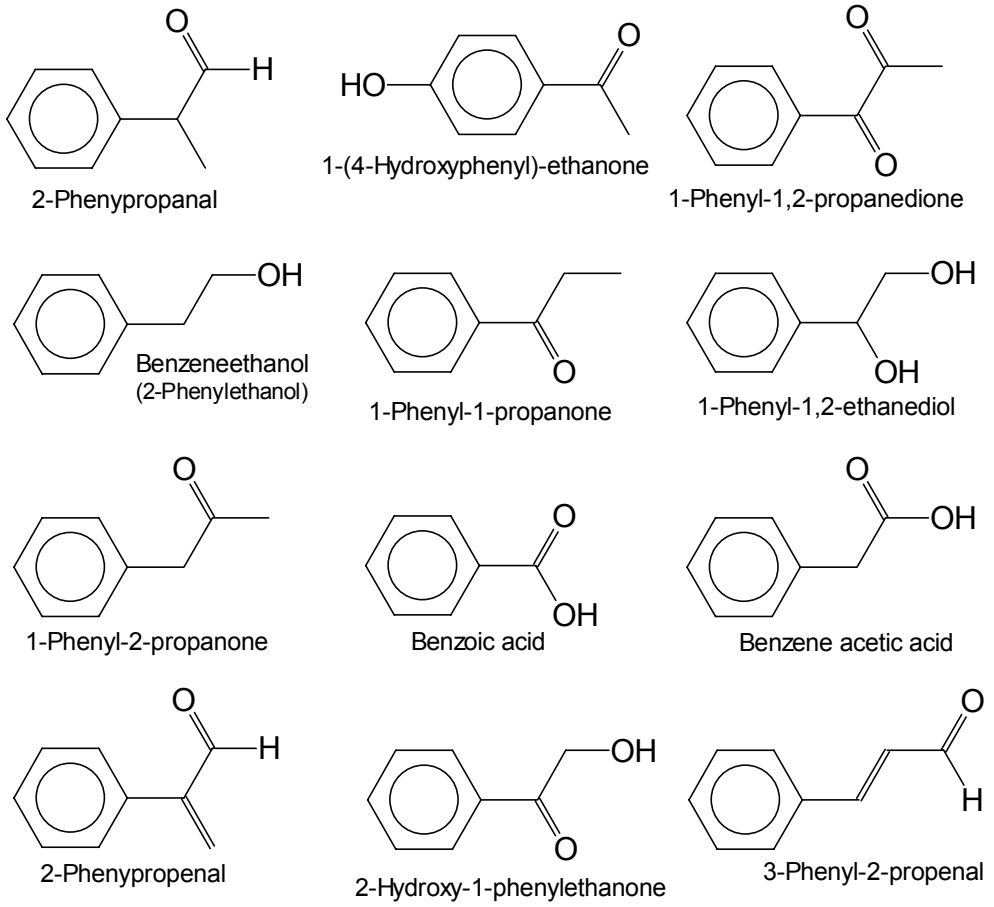


Figure 10.3 Structural formula of some **trace radiolysis products** identified in PS.

leads to a further increase in 1-phenyl-1-propanone concentrations, which appears to be more pronounced in the culture flask. Overall, a comparison of irradiated and non-irradiated samples indicates that it may be possible to use the trace product *1-phenyl-1-propanone* as a marker for the identification of radiation-*sterilized* polystyrene. Of course, one would establish a suitable SIM-(data acquisition)-method for that purpose.

Results for two other trace products are presented in Figures 10.5 and 10.6. **Figure 10.5** shows the mass spectrum of the **unidentified 'ultra-trace' product** labelled with a question mark in Figure 10.2, *plus* the extracted ion chromatograms (EICs) for its major ions. From the EICs one might conclude that this is not a pure peak, but the slight distortions may also be the consequence of its extremely small size (cf. Figure 10.2). This second interpretation is supported by the fact that the peak could also be observed with the two other columns (cf. Appendix 20). In any case, the library proposal *2-phenyl-propanoic acid* is not totally convincing.

Figure 10.6 shows the sole evidence obtained for the presence of **1-phenyl-1,2-ethanediol**, possibly a 'radiation-specific' trace product. The compound was observed with the Rtx-200 column and in the irradiated samples only (Tables A-20.2 and A-20.3). Because of the peak's slight tailing it may have been impossible to detect traces of the diol in the non-irradi-

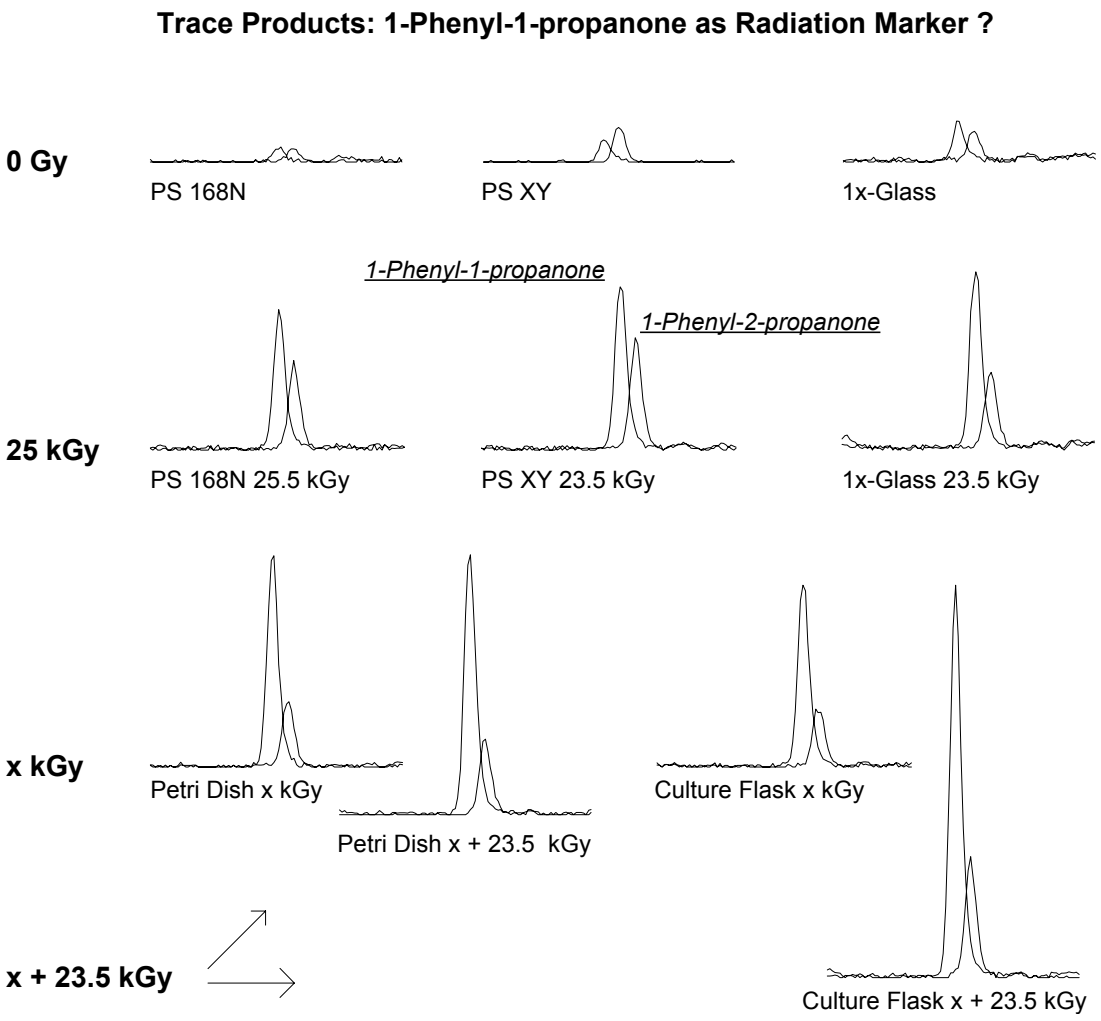


Figure 10.4 **1-Phenyl-1-propanone as radiation marker ?**
Detail (t_R 12.7–13.3 min) of fingerprint chromatograms presented as (added) extracted ion chromatograms — m/z (77 + 105) for 1-phenyl-1-propanone, and m/z (65 + 91) for 1 phenyl-2-propanone.
Experimental Conditions: See Phase IV-quantitation [5 mg; TDS 160(10); Scan].

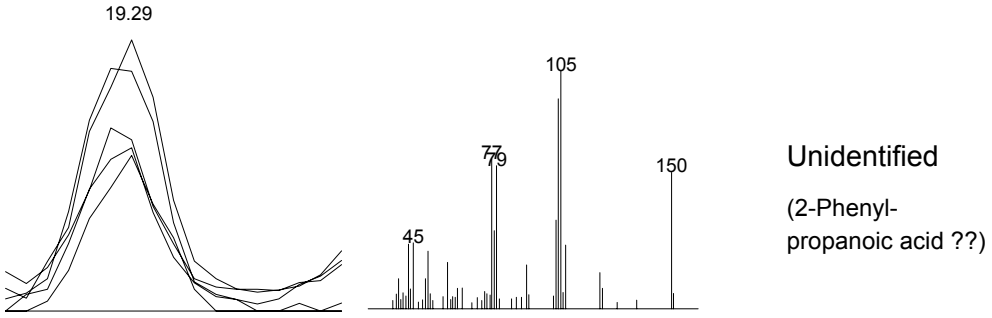


Figure 10.5 The unidentified trace compound „?“ from Figure 10.2 — extracted ion chromatograms (EICs) and mass spectrum. Experimental Conditions: See Figure 10.2.

ated controls. *1-Phenyl-1,2-ethanediol* could not be observed with the DB-5 and Supelcowax 10 columns, possibly because of some column activity. Thus, the magnitude of the radiation-induced formation of this diol, and whether it is really a radiation-specific product, remains to be determined.

It should finally be said that the last (300 mg) analysis (Table A-20.5) was erronously performed with the 10 kGy-specimen. It was, of course, scheduled for one of the more recently irradiated *23.5 kGy*-specimens, which, at least theoretically (cf. below), should have resulted in a six-fold increase in sensitivity compared to the previous 50 mg-analyses.

Resumée

In retrospect, the search for *trace products* appears to have been less successfull than had been expected initially. Compared to what was already known from the ‘primitive’ Phase I-experiment (Figure 10.1), the addition of another ‘handful’ of new trace products is not very impressive. (In relation to the time spent with data analysis, the results might well be called frustrating.) One reason for this may be that higher sample masses result in a simultaneous increase of both, the amounts of trace products and the ‘non-specific’ chemical background interfering with them—in other words, that the *real* increase in sensitivity is less ‘dramatic’ than expected from the ratio of the sample masses. Another reason may be that PS simply yields a limited number of *trace* products, and that most of them have been found.

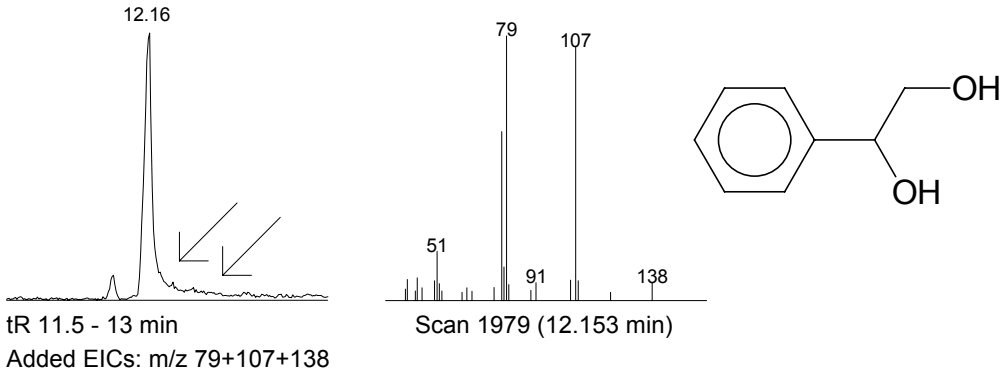


Figure 10.6 **1-Phenyl-1,2-ethanediol** — a radiation-specific trace product ?: (Added) extracted ion chromatograms (EICs) and mass spectrum. Experimental Conditions: See Appendix 20: Table A-20.2.

11. Quantitation of Benzene

11.1 Qualitative Results

As mentioned in Section 4.1, benzene was discovered 'retrospectively' in qualitative analyses performed with the thick-film (1 µm) DB-1701 (see Figure 4.4), and also in chromatograms recorded with the DB-5 to quantitate the main products (see **Figure 11.1;** these chromatograms are from the 'Phase III-*splitless-scan* series'—cf. Chapter 7). There is clearly an increase in benzene concentration in all irradiated samples; since the two 25 kGy-samples had been irradiated ca. one year before the 3 and 10 kGy-samples, it may be concluded from the peak areas observed that a considerable loss of benzene to the atmosphere has occured during this time.

11.2 Reasons for Quantifying Benzene

The formation of benzene during gamma-irradiation caused some concern as the chemical is „very toxic" (Klaassen, 1985a), a proven carcinogen, and a mutagen. Most chemists probably know that it is replaced in laboratories by less toxic solvents whenever possible, and even the general public should have heard about its role in air pollution (with gasoline being one of its major sources).

These concerns grew, when I learned that the U. S. Food and Drug Administration (FDA) had used a fairly complex protocol—involving dissolution in hexadecane at 150°C, purge-and-trap enrichment with He as purge gas and methanol as trapping solvent, and analysis

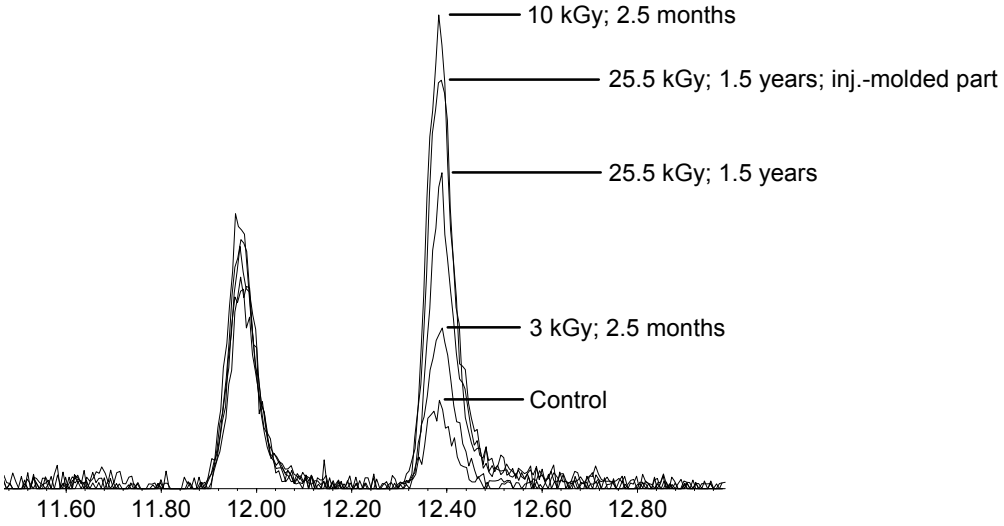


Figure 11.1 **Benzene (t_R 12.40) in polystyrene** — detail; presented as **extracted ion chromatograms** (for m/z 50 + 51 + 52 + 78). The tailing of the peak results from insufficient reconcentration of benzene on the 0.25 µm f. t. DB-5 column: there is no *cold trapping* (initial GC-temperature = 40°C) and no *solvent effect* (TDS-analysis). The peak labels indicate the absorbed dose and the time elapsed after irradiation.
Experimental Conditions: Sample: BASF Polystyrol 168 N, 5 mg PS powder, obtained from *pellets* and, in one case, from a *part* injection-molded from this resin; TDS 160(10); CIS -40; GC 40(11.5) -10- 250(5); column: DB-5 (= Conditions of 'Phase III-Quantitation').

by static headspace-GC—to determine low parts-per-billion (µg/kg) concentrations of benzene in *polypropylene* food packaging materials and food-contact *paraffin waxes* (Varner et al., 1991). Benzene was also found in *microwave susceptor* food packagings; it was present in eight of the susceptors analyzed by the FDA, and in five of the samples analyzed on behalf of the industry, and the formulation of these plastics was subsequently changed to eliminate benzene (McNeal and Hollifield, 1993; Rose, 1991;—cf. Section 2.8).

The qualitative chromatograms (Figure 4.4) had indicated that benzene is probably only a minor product, but it was felt that this should be confirmed quantitatively with benzene standards of known concentrations, since *MS response factors* for different analytes may vary (up to a factor of 10 in extreme cases, but usually much less). The development of a quantitative TDS-method for benzene (see below) was the last project of this research program, and it was by no means clear initially, whether a splitless-injection of benzene standards would be possible at all (cf. below).

11.3 The Difficulties Associated with Quantifying Benzene in PS

The difficulties with benzene arise (again) from the need to quantitate *trace amounts of a volatile compound in a polymer matrix*. It is not a major problem to analyze higher concentrations, e. g., in gasoline, by gas chromatography with *split*-injection, and it is also not a problem to analyze traces of benzene in, e. g., environmental water samples, by GC with *purge & trap-injection* (applications for both types of analyses are described in the catalogues of most column suppliers). Good peak shapes with relatively volatile compounds, such as benzene, are obtained with thicker-film columns, as often used in purge & trap-analyses (and as demonstrated in Figure 4.4).

However, in contrast to, e. g., spiking water with benzene, it is clearly impossible to distribute exactly known ppm-amounts of benzene in a polymer matrix, in order to produce (external) calibration standards for TDS-analyses. Thus, the prerequisite for quantitatively determining benzene in PS was *to develop a method permitting* the *splitless-injection* of liquid (external) standards containing ppm-amounts of benzene (as already practiced with the—relatively high-boiling—main products).

The challenge with an analyte (solute) as volatile as benzene was to find a combination of *solvent, stationary phase, initial column temperature,* and *splitless-time* that

– sufficiently *reconcentrates* benzene at the column entrance via a *solvent effect*, and,
– at the same time, *resolves* the benzene peak from the *solvent tail*.

To produce a *solvent effect*, i. e., to temporarily retain and to reconcentrate the analyte(s) in a splitless-analysis, the solvent

– must be more volatile than the analyte(s),
– must *wet* the surface of the film (stationary phase) inside the column, and
– must condense at the initial GC temperature (i. e., it must not be too volatile !).

Additionally, solvent peaks in splitless-injections become severely tailed and may interfere with closely eluting analytes, which will usually be the case when the difference in volatility is small. The length of the *solvent tail* depends on the time the split valve is kept closed (the splitless-time), and this can only be reduced to the *minimum time* required for complete sample transfer.

It is obvious that with increasingly volatile analytes the choice of solvents becomes more and more limited, and there remains little ‘manoeuvring room’ for separating the solute molecules from the solvent (especially if one cannot, or does not want to, cool the GC to sub-ambient temperatures).

The benzene method was developed in several series of (partially overlapping) steps involving

– so-called *wet-needle injections* in split-(!)-mode of 1:1 mixtures of benzene with various possible solvents to determine their separation in the absence of splitless-effects,
– splitless-injections of ca. 10 ppm-standards to assess the *solvent effect* achieved (benzene peak shape !),
– optimization of splitless-time (benzene peak area),
– 'challenging' the optimized method with injections of ca. 0.1 ppm-standards, and
– TDS-recovery tests (CIS / trapping temperature).

A few chromatograms from these series of measurements are presented in Appendix 21.

11.4 The Benzene Method

The GC is held isothermally at an *initial temperature* of 26°C until benzene elutes. Without subambient cooling facilities, the GC's door was left open during the first three minutes of the run; this can result in slight variations of retention times (see Figures 11.2 and A-21.3) though this is not a problem with MS detection.

After experimenting with the Supelcowax 10, Rtx-1701, and DB-5 columns and with the solvents hexane, pentane, diethylether, and dichloromethane, the following conditions were established:

CIS: -40°C –12°C/s– 250°C (3 min); **60 s splitless**,
GC : 26°C (3 min) –20°C/min– 220°C (10 min),
with **dichloromethane** (CH_2Cl_2) as solvent,
and a 5%-phenyl-95%-methylpolysiloxane (DB-5) column.

> Please note that CH_2Cl_2 is not only the solvent for the benzene standards; the method also *requires the presence of (1 µl) CH_2Cl_2 in a PS-analysis* (without solvent, there would be no solvent effect and no reconcentration). Depending on the CIS-temperature the solvent can be injected into the TDS or—after desorption and before the run is started—directly into the CIS.

11.5 Quantitative Results for Benzene

Benzene concentrations were determined with a polystyrene *molecular-weight* standard after relatively high absorbed doses (see Section 3.7 for details). These samples had been irradiated most recently when the method was finally established, and the expected higher yield was a welcome side-effect.

In fact, the samples had been irradiated for a separate (and experimental) project with a purely theoretical background: A comparison of (low-LET) gamma-radiation with so-called high-LET radiation, in this case a 200 MeV $^{129}Xenon^{14+}$ *ion-beam* from a cyclotron (where LET means *linear energy transfer*). The project is totally irrelevant for radiation sterilization and therefore not part of this thesis. However, it may be interesting to note, that the participating radiation chemists regarded these 'high' dose levels as quite 'normal', whereas the colleagues from the food irradiation laboratory found them 'absurd'.

Chromatograms for the samples irradiated under vacuum (vs. a non-irradiated control) are shown in **Figure 11.2;** benzene *concentrations* vs. the absorbed dose are plotted in **Figure 11.3** (for irradiation under vacuum and in oxygen). Benzene levels at sterilization or food

irradiation doses have been calculated as explained below, and their implications for the safety of irradiated PS are discussed in Section 13.4.

The very high concentration in the third (1460 kGy) vacuum-sample was ascribed to the presence of large amounts of benzophenone, which was obviously a contaminant (it gave a huge peak in the fingerprint of the 1460 kGy-sample and was virtually absent in the others); the data point was omitted in calculating the radiation-chemical yield.

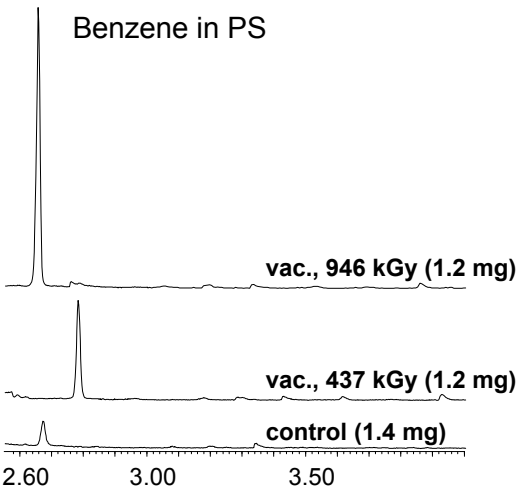


Figure 11.2 **Benzene in polystyrene**—two samples irradiated under vacuum vs. a non-irradiated control.
The differing retention times are caused by the instability of the GC-temperature during the initial low-temperature isothermal hold, i. e. 26°C (3 min), with the GC oven's door left open.

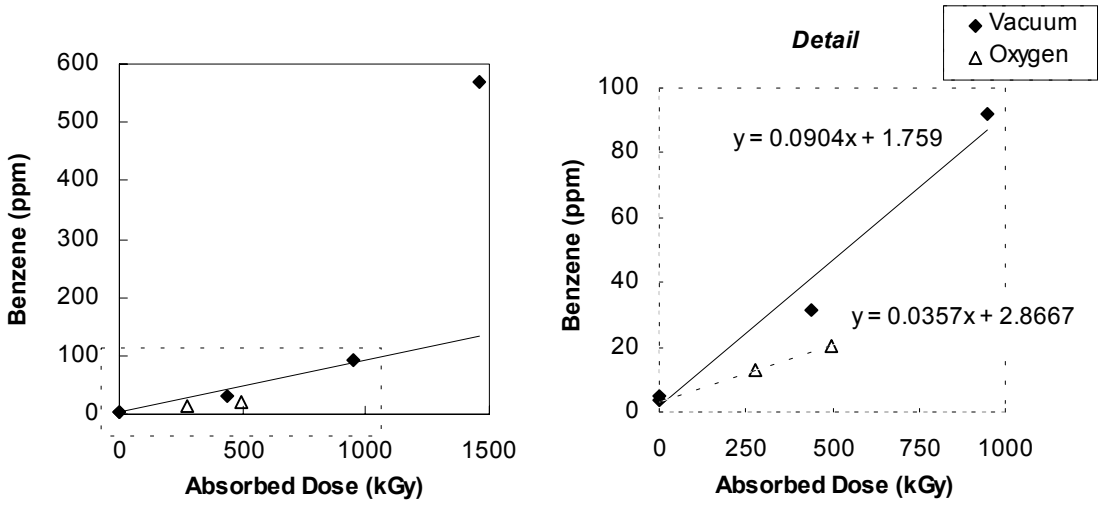


Figure 11.3 **Benzene concentrations** vs. the absorbed dose.
The 1460 kGy-vacuum sample was contaminated with benzophenone (cf. text). Only the values displayed in the detail were used to calculate the linear regressions.

Benzene levels increase linearly with the absorbed dose; concentrations after ca. 500 kGy are in the range of 50 ppm (vacuum) and 20 ppm (O_2). The following G-values (radiation-chemical yields[#]) have been calculated from the linear regressions in Figure 11.3:

	G	nmol/J
Benzene; vacuum	0.011	1.16
Benzene; O_2	0.004	0.46

As benzene levels (and yields) are ca. 2.5 times higher under vacuum, it appears that O_2 does interfere, in some way, with the underlying radiation-chemical reaction.

11.6 Extrapolated Concentrations at Sterilizing Doses

If we assume that benzene is formed by some radiation-induced *elimination* of a phenyl group (and a hydrogen atom) from the polymer chain, and if we further assume that each phenyl group is equally likely to undergo such an elimination, then benzene formation would be independent of the polymer's molecular-weight distribution, in other words, it would be equal for the PS-molecular weight-standards under investigation and for commercial polystyrenes. The radiation-chemical yields determined in these experiments could then be used to calculate benzene levels for a sterilizing dose of 25 kGy, or for a 'typical' food irradiation dose of, e. g., 3 kGy:

Benzene in PS (ppm)

calculated for	Oxygen	Vacuum
25 kGy	0.9	2.3
3 kGy	0.1	0.27

Benzene levels of 1 to 2 ppm after 25 kGy would be consistent with the size of the benzene peak in the qualitative chromatograms obtained with the medical PS (see Figure 4.4).

Real benzene concentrations for irradiation in air are probably somewhere between the O_2- and the vacuum-data, and it is proposed to use the latter as a worst-case scenario in safety evaluation / risk assessment (see Section 13.4).

[#] The *number of molecules* formed divided by the *energy absorbed* by the irradiated matter (cf. Sections 7.4 and 9.7).

12. Summary

12.1 Qualitative Results with the Six Medical Polymers

In the six medical polymers under investigation a single sterilizing dose of ca. 25 kGy suffices to produce *detectable amounts* of low-MW radiolysis products which *remain trapped* in the polymer matrix for considerable spaces of time. The products and their concentrations are very characteristic for each plastic: Their structure is related to the polymer type (backbone) and/or to the additive(s) present; compared to the levels of the low-MW constituents already present in the non-irradiated materials their quantities range from '*marginal'* to '*very substantial*.'

Radiolysis Products

The main products of **polystyrene (PS)** are *acetophenone, benzaldehyde, phenol, 1-phenylethanol*, and *phenylacetaldehyde*; their concentrations are ca. one order of magnitude below the residual styrene / styrene dimer levels. Some trace products are formed with still lower yields—with the exception of *benzene* (Section 12.7) these are also *oxidized aromatic structures* (cf. Section 12.6).

The *aromatic products* observed in PS (including traces of *benzene*) are also formed in the **methyl methacrylate-acrylonitrile-butadiene-styrene (MABS)** resin under investigation. Overall, the MABS fingerprint chromatograms are quite complex compared to those of PS, and additional *aliphatic radiolysis products* such as hexanal or acetic acid can be observed. It is suggested that different MABS resins as well as other styrene-based copolymers, such as styrene-acrylonitrile (SAN) or styrene-butadiene (SB), be studied in more detail.

The main product of **polyamide-6 (PA-6;** poly-ε-caprolactam) is *pentanamide*; its concentration after 25 kGy may be in the range of *one third* that of the residual monomer caprolactam. Also formed are traces of the homologous amides *formamide, acetamide, propanamide, butanamide,* and *hexanamide*. It would be very interesting to analyze different PA-6 resins, to quantify the resulting pentanamide levels, and also to study the radiolysis products of other polyamides, such as polyamide-11 or polyamide-6/66.

The main products of the **poly(vinyl chloride) (PVC)** under investigation—*octane, 1-octene, acetic acid 2-ethylhexylester*, and *1-octanol*—are degradation products of additives. *Acetic acid 2-ethylhexylester* is thought to be formed by an organotin stabilizer containing (at least) one *2-ethylhexylthioglycollate* substituent. No chlorine-containing degradation products were observed—the various radiation-induced *trace products* also originate from additives. The presence of free HCl in irradiated PVC is very unlikely and probably cannot be established by thermal desorption. While formation of vinyl chloride (VC) is also considered unlikely, VC levels should be monitored in future investigations. It is also suggested to investigate the radiation-induced degradation of PVC formulations containing *known* additives. These should include various common stabilizers (organotin & others) and plasticizers (phthalate & others).

The fingerprint chromatograms of the medical **high-density polyethylene (HDPE)** are quite different from those of the LDPE films investigated in Phase II, and so are the effects of irradiation. Compared to the levels of the hydrocarbons ('ethylene-oligomers') already present, the concentrations of the radiolysis products are very small; they include various *hydrocarbons, aldehydes, ketones, and carboxylic acids*. The PE was the only polymer where some radiolysis products could literally be watched to disappear within *days*. Increased levels of the carboxylic acids could still be detected six weeks after irradiation. Future inves-

tigations should be extended to other relevant PEs such as LLDPE or UHMWPE, and to ethylene copolymers.

The main radiolysis product of the **polypropylene (PP)** under investigation is *1,3-bis-(1,1-dimethylethyl)-benzene*, a degradation product of (a) phenol-type antioxidant(s). After only 3 kGy its peak is already larger than many of the residual-hydrocarbon peaks; after a sterilizing dose of ca. 25 kGy it is heavily overloaded and dominates the fingerprint chromatograms. Another interesting features is also related to antioxidant degradation: the formation of *trace aromatic degradation products* (see also Section 12.2). Various other low-MW products are thought to result from radiation-induced oxidation of the polymer molecules themselves; these include *hydrocarbons, aldehydes, ketones, and carboxylic acids*. It is suggested to investigate different *radiation-grade* polypropylenes and to quantitate 1,3-bis-(1,1-dimethylethyl)-benzene. It might also be an interesting project to investigate the trace aromatic degradation products in more detail, and to search for possible atypical / radiation-specific aromatic structures.

Granulates vs. Injection-Molded Parts

The effects of irradiation on non-processed polymer pellets and on parts injection-molded from them are *qualitatively and quantitatively comparable*. Processing neither induces formation of additional ('new') products nor suppresses formation of the products known from the irradiated granulates; it also does not lead to dramatically altered product concentrations. The more interesting question turned out to be, to what extent some potential *radiation markers* were already formed during processing.

It may be concluded from the results obtained that *1-phenylethanol* is a promising marker for **PS** and **MABS,** i. e., there appears to be no significant 1-phenylethanol formation during injection-molding (cf. Sections 12.4 and 12.5). Processing of **PA-6** and **PVC** appears to induce the formation of at least *some* pentanamide and acetic acid 2-ethylhexylester, respectively. In the **PE** under investigation, processing alone apparently does not produce significant amounts of products such as butanal, 2-butanone, acetic or propanoic acid. In the medical **PP,** no, or only traces of, 1,3-bis-(1,1-dimethylethyl)-benzene is formed during injection-molding. Of course, to establish any of these compounds as marker for a radiation-sterilized plastic will require additional work.

12.2 Qualitative Results with LDPE and Polypropylene Films

Retention of Radiolysis Products in LDPE and Polypropylene

The most important result of these experiments is that—contrary to previous reports—low-MW radiolysis products are also retained for considerable times in LDPE films, and that they are retained in polypropylene (PP) films much longer than had been expected.

All the polyolefin films produced various hydrocarbons, aldehydes, ketones, and carboxylic acids; their concentrations after 25 kGy are in the range of *one tenth* that of the residual hydrocarbons ('ethylene-oligomers'). The PP films additionally produced quite significant amounts of three degradation products of phenol-type antioxidants; the peaks of these compounds—1,3-bis-(1,1-dimethylethyl)-benzene, 2,4-bis-(1,1-dimethylethyl)-phenol, and 2,6-bis-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione—dominate the fingerprint chromatograms of the irradiated films.

Most of the low-MW products have previously been identified in the *headspace* of irradiated LDPE and PP films; some of them, plus the antioxidant degradation products, have been found to be retained in PP films. The fact that these products could still be detected *more*

than one year after irradiation in both LDPE and PP may be partly ascribed to the higher absorbed doses applied, but mainly to the considerably higher *desorption temperatures* permitted by the TDS-unit.

The Effect of Desorption Temperature

The effect of TDS-temperature was studied in some detail with LDPE. Above 120°C there is a dramatic increase in the peak areas of the radiolysis products; it is accompanied by an equally dramatic increase in sensitivity. To prevent the 'collapse' of the film's surface a special technique, the '*stainless-steel sieve sandwich* technique,' was developed, which allowed to increase the temperature up to 240°C. The results of these 'high-temperature' measurements suggest that the radiolysis products (or a significant fraction of them) may be formed as thermal degradation products of some radiation-induced precursors, e.g., of peroxides or hydroperoxides.

Irradiation of LDPE produces a highly characteristic *pattern* of groups of radiation-induced peaks, e.g., *butanal / 2-butanone*, *acetic acid / pentanal*, or *3-hexanone / 2-hexanone / hexanal*. These characteristic groups were very similar in several 'no-name' films, in ten proprietary LDPE films, and in one LDPE granulate. An attempt to *detect* increased product levels after only 1 kGy (see Section 5.9) suggests that there may be a remote possibility to develop a detection method for low-dose irradiated films. (As the subsequent quantitative experiments with PS have clearly led to a better understanding of the TDS-technique, it would probably be worth the effort to re-address the problem, and to determine whether 'pushing the system to its limits' would 'do the job'... .)

PP films produce another characteristic pattern of radiation-induced peaks, which was quite similar in one experimental and three proprietary PP films. Quantitatively, the formation of antioxidant degradation products is far more important in PP. Besides the three main products mentioned above, there appear to exist some *trace aromatic products*; since one could imagine a detection method based on atypical / radiation-specific aromatic structures, it would be quite interesting to study them in more detail.

Cyclic Radiolysis Products ?

As mentioned in Chapter 2, the potential formation of *cyclic* products in LDPE and PP films was considered to be quite intriguing, as various *cyclobutanones* are used in the detection of irradiated food items. None of the cyclic compounds listed by Rojas de Gante and Pascat (1990)—and, indeed, no cyclic compound at all—was found to be retained in the LDPE and PP films under investigation. Since the cyclobutanones are quite well-defined products resulting from the radiolysis of triacylglycerides, and since similar structures are absent in polyolefines, it is likely that no cyclobutanones are formed (and it is conceivable that no—or only ultra-traces of—other cyclic compounds are formed). Nevertheless, the phenomenon is considered to be interesting enough to deserve further investigation, or, at least, an attempt to confirm the initial observation.

Geometry and Efficiency of the TDS-CIS-System

In Section 5.11, the analytical system is compared with that used by Hodgson et al. (1998); it is concluded that the TDS-CIS-system is purged much more effectively in terms of a parameter ε, and that the concept of trapping volatiles directly in a split / splitless injector (i. e., the CIS) is a very elegant one.

12.3 Establishing Quantitative Desorption Conditions

Thermal desorption was initially perceived as an essentially *qualitative* technique, and this notion changed only during some experiments performed parallel to the analysis of the PE and PP films. Quantitation is based on the central assumption that thermal desorption is a dynamic (non-equilibrium) process, in which the constant removal of volatiles creates a concentration gradient in the polymer matrix. This concentration gradient is the driving force behind a diffusion process that can be used to completely desorb / extract the polymer. The time required for this process depends on the distance the volatiles have to travel and on their diffusion coefficient, i. e., ultimately on the sample dimensions and on the desorption temperature.

TDS-conditions for a quantitative desorption of *fine PS powders* were established as **160°C for 10 min.** Quantitation is further based on a *complete transfer* of analytes from the TDS to the CIS, which was confirmed in a series of test injections, and a complete transfer from the CIS to the capillary column during injection. Since 'true' internal standard (ISTD) quantitation would require distributing known ppm-amounts of a volatile ISTD in the polymer matrix (which is considered highly impractical, if not impossible), *external standards* (ESTDs) were injected into the CIS to obtain calibration curves. The standards were injected using a special injection technique that allows an exact injection of known volumes, namely, the so-called *solvent-flush*-technique.

12.4 Quantitation by 'Direct' Thermal Desorption

Quantitative Results

In a first step, the 'old' ca. 25 kGy-samples were analyzed—plus some 1, 3, and 10 kGy-samples irradiated more recently. On the basis of previous experiences with sample masses and peak areas, a program of three parallel series of measurements was designed: a *split*-scan, a *splitless*-scan, and a splitless-*SIM* series with sample masses of 5 and 10 mg, respectively. The three procedures—which rest on the same principles, but differ in sensitivity and require independent calibration—yielded practically identical results.

The concentrations of 1-phenylethanol (1-Pet) and acetophenone (Acp) *increase linearly* with the absorbed dose (Figures 7.2 and 7.3), and, remarkably, the regressions for the 1, 3, and 10 kGy-samples extend to the 25 kGy samples, despite the fact that these had been irradiated more than one year earlier. Concentrations after 25 kGy are in the range of 6 to 8 ppm (mg/kg) for 1-Pet and ca. 25 to 35 ppm for Acp in the PS *granulate*; in *parts* injection-molded from this granulate the level of 1-Pet is slightly and that of Acp *markedly* higher (50 to 60 ppm)—an observation that is consistent with earlier qualitative results.

From the slope of the regression lines in Figures 7.2 and 7.3, *radiation-chemical yields* have been calculated for 1-phenylethanol and acetophenone. The values—2.5 nmol/J (nanomol/Joule) for 1-Pet and 8 nmol/J for Acp—agree reasonably well with those determined later (cf. Section 12.5 *Thermal Desorption of Polymer Solutions* ...).

Phenol concentrations were determined in the splitless-SIM series, i. e., with the low-dose specimens only; peak shapes were relatively bad at low concentrations (because of column activity), but phenol levels (Appendix 6) are clearly, and in agreement with earlier qualitative analyses, comparable to that of 1-Pet. No calibration curves were recorded for *benzaldehyde* (Bal) and *phenylacetaldehyde* (Paa), but it can be inferred from the fingerprint chromatograms that their radiation-chemical *yields* are in the same order of magnitude: the resulting concentration of Bal is comparable to that of Acp, while Paa is probably less important than 1-Pet. *Benzoic acid* may be another 'major' product (see Section 12.6).

Irradiation Detection

Two-dimensional plots of 1-Pet and Acp concentrations have been drawn in an attempt to *visualize* the idea of using two (or more) radiolysis products as possible markers for **irradiation detection** (Figure 7.4). It can be seen that irradiated and non-irradiated specimens are arranged along two different lines that intersect in the low-dose range. Irradiation with 1, 3 and 10 kGy shifts the data points, proportionally to the absorbed dose, along a regression line extending to the 25 kGy-samples, whereas ageing of the non-irradiated PS *powders* appears to shift data points along another regression towards the non-irradiated injection-molded parts. A qualitatively similar picture was obtained with the MABS resin (Figure 7.6).

A 'real-life' Petri dish sterilized with an unknown dose was found exactly on the line indicating irradiation (Figure 7.4); the 3 kGy-samples are clearly better resolved from the non-irradiated controls than in 'one-dimensional' concentration-dose plots, and it is conceivable that three (or: n) radiolysis products establishing a three- (or: n-) dimensional space might improve the chances to positively identify a PS specimen as irradiated. Additional products (or 'dimensions' in a plot) might increase the reliability and/or sensitivity of a TDS-based detection method.

Characterizing System Performance

When serious troubles—a declining column performance and a mysteriously degraded 'TDS-performance'—began to interfere with the measurements, it was decided to switch to a polar polyethylene glycol column offering maximum sensitivity for the oxidized products, especially for 1-Pet, and to monitor the overall system performance with a much more elaborate parallel test program of '*system sensitivity'*, *analyte recovery*, and special '*TDS-performance'*-tests. For the latter, the *Grob-Mix* was used, a polarity mixture originally designed for column testing—comparing TDS-analyses of this solution with 'direct' CIS-injections provides comprehensive information on the behaviour of a variety of compounds during thermal desorption, thus *characterizing* the 'TDS-performance'. It was concluded that such a general test is particularly important when searching for unknown radiolysis products, because it indicates whether one is in danger of 'missing' whole classes of compounds, e. g., amines.

Confirmation of the Initial Quantitative Results

The main objectives of 'Phase IV' were to reproduce the earlier quantitative results, to see whether there were concentration changes-with-time, and to investigate some 'real-life' sterilized PS samples, styrene-copolymers, and experimental (pre-treated) PS samples. Surprisingly, the 'new' concentrations were initially consistently lower—with 1-Pet concentrations reaching only some 50 to 60% of the 'original' levels. It was then realized that a TDS-temperature of 160°C for 10 min was no longer sufficient for complete desorption, and this was ultimately attributed to a software-update concerning the so-called TDS-/CIS-*Controller*.

Mean concentrations of ca. 7.5 ppm 1-phenylethanol (1-Pet) and ca. 38 ppm acetophenone (Acp) were finally obtained at increased TDS-temperatures (200°C for 10 min); these values agree almost exactly with the earlier results (cf. above). While only a few samples were re-analyzed under the new conditions, some interesting conclusions can be drawn from 2D-plots based on the 160°C-results (which could be described as 'semi-quantitative' in a very verbal meaning of the expression, i. e., giving only some 50% of the true concentrations).

The 'real-life' samples that had been sterilized with unknown doses fit very well into these 2D-plots; re-irradiation with 23.5 kGy shifts their data points towards higher 1-Pet and Acp levels. Product levels in two 'experimental' polystyrenes were much lower, indicating that the

low-MW fraction in PS does probably play a major role in the formation of volatile radiolysis products. The data obtained with a few styrene copolymers (which produce distinctly different fingerprints) do not fit into the picture; it is concluded that to establish a *detection method* for copolymers more information is needed on the underlying radiation chemistry, or on the relationship between product yield and *polymer structure*.

Overall, it was concluded that

– the experiments had confirmed the validity of thermal desorption as a *quantitative method*,
– it is possible to correctly *identify* items made from pure standard polystyrene *as radiation-sterilized*, i. e., as irradiated with doses of ca. 25 kGy, and
– the *concentrations* of the main radiolysis products *do not change with time*.

12.5 Thermal Desorption of Polymer Solutions with Solvent Evaporation and Related Results

Thermal Desorption of Polymer Solutions with Solvent Evaporation

Thermal Desorption of Polymer Solutions with Solvent Evaporation (or: the DSC-Method) is essentially a new and experimental desorption technique that, to my knowledge, has not been described in the scientific literature: The polymer is dissolved, a certain volume of the solution is injected into the TDS-unit, and the highly volatile solvent is *vented* through the split valve while the analytes are trapped on the adsorbent in the CIS. The initial idea had been to create a maximum surface area for desorption. It was then realized that PS fragments can be dissolved directly (to eliminate the milling step), and a final step was to eliminate the desorption step, or, more accurately, to shift the place where desorption occurs into the injector (See *Direct Injection / Thermal Desorption with the CIS*, below).

Generally, the technique appears to yield highly reproducible results, and the overall picture agrees quite well with that obtained by ‘normal’ desorption of PS powders. The results are summarized in a two-dimensional plot of 1-phenylethanol vs. acetophenone-concentrations (Figure 9.6), which is fully consistent with the plots obtained earlier. Some specimens were analyzed with the new technique only; one of these, a ‘real-life’ culture flask, deserves special mentioning, since—having been irradiated more than 9 years previously (!)—it fits remarkably well into the plot.

1-Pet concentrations appear to be higher with the DSC-Method (up to 50% ?), and while the comparison is based on a very limited number of data the difference may be genuine. There is no immediate explanation for this (see Section 9.6). A major problem of the technique is that sample masses are extremely small (≈ 0.1 mg PS compared to 5 to 10 mg in a ‘normal’ desorption)—and the overall demands on the analytical system are correspondingly high: Contamination levels (memory effects) should be *extremely* low, and any loss of analytes (due to adsorption or to the ‘cold spot’) should be minimal. These requirements were not totally met; certain background levels had to be accepted, and recovery was less than 100% for 1-Pet.

Radiation-Chemical Yields

Radiation-chemical yields for 1-Pet and Acp have been calculated from the concentrations determined with the DSC-Method. The values for the various polystyrenes agree quite well, with few exceptions they are in the range of 2.5 to 3.5 nmol/J for 1-Pet, and in the range of 10 to 15 nmol/J for Acp. As mentioned, similar results had been obtained during earlier ex-

periments (Section 12.4 *Quantitation by 'Direct' Thermal Desorption*). The order of magnitude of the radiation-chemical yields supports the hypothesis that the products are *not* (or only to an insignificant extent) formed by the residual monomer styrene.

Direct Injection / Thermal Desorption with the CIS

With the DSC-Method established, the logical next step was to directly inject the PS-solution into the injector, in other words, to use the CIS for thermal desorption. Initial results were encouraging, and it can be predicted that it will be possible to perform a reasonable number of analyses before degradation of the accumulating polymer will interfere with quantitation and make a replacement of the (CIS-) glass liner necessary. The technique has several advantages: All problems associated with the TDS (contamination) and with the transfer to the CIS (loss of analytes) are eliminated, analysis time is reduced, and it may be possible to use an autosampler, even to perform large-volume injections (to increase sensitivity). 'Normal' thermal desorption clearly remains the method of choice for product *identification*, but in interlaboratory trials or routine analyses *known* radiolysis products might be monitored using the CIS (or another PTV) as thermal desorption-unit.

Interestingly, the concept of directly using a PTV for thermal desorption has recently been proposed by others: Van Lieshout et al. (1997) have characterized oil and kerogen in geological rock and coal samples by combined *thermal desorption-pyrolysis* and GC with atomic emission detection. Sample amounts of 1 to 10 mg were directly weighed into the (3.4 mm i. d.) liner of a PTV injector. It is certainly possible to adopt this technique for polymer *powders* and the CIS, though the inner diameter of its liner is considerably smaller. It might also be helpful to re-design the CIS in some way in order to facilitate a frequent exchange of the glass liner.

Dissolution-Precipitation

A dissolution-precipitation experiment indicated that certain fractions of the radiolysis products, ca. 25 to 30% of the acetophenone and ca. 5% of the 1-phenylethanol, are formed as thermal degradation products of some macromolecular radiation-induced precursors. The remainder, i. e., 70 to 75% of the Acp and 95% of the 1-Pet, is either genuinely present after irradiation—or an 'artifact' produced by the low-MW fraction. These data confirm the observation that the products, be they genuine or not, are associated to a considerable extent with the low-MW fraction.

12.6 Identification of Trace Radiolysis Products

Experiments with increased sample masses (usually 50 mg) were performed on several occasions with three different columns. It appears that the resulting increase in sensitivity was somewhat smaller than had been expected, probably because there is an equal increase in the 'non-specific' chemical background that obscures very small peaks and makes an identification of (ultra-) trace compounds more difficult.

It was possible to confirm the presence of some trace products that had been observed first in a 'primitive' Phase-I experiment (performed with whole pellets), e. g., 2-phenylpropanal and 1-phenyl-1-propanone. A few 'new' products were also found, e. g., 2-hydroxy-1-phenylethanone and 1-phenyl-1,2-ethanediol. All the products are oxidized aromatic compounds and their concentrations are estimated to be in the range of 0.1 to 1 ppm. (A non-oxidized trace product is benzene, see below). 1-Phenyl-1-propanone might be used as an additional *marker* for irradiation detection. 1-Phenyl-1,2-ethanediol may be a radiation-specific trace

product, but its absence in non-irradiated PS has to be confirmed in future investigations. Benzoic acid should probably be classified as 'major' product; its concentration may be as high as 10 ppm (estimated) after 25 kGy.

12.7 Benzene Quantitation

Benzene levels were quantitatively determined in polystyrene *molecular-weight standards,* which had been irradiated most recently (with relatively high doses under vacuum and in oxygen) when the benzene method was finally established. Benzene concentrations are ca. 2.5 times higher under vacuum than in oxygen, indicating that O_2 does in some way interfere with benzene formation; radiation-chemical yields for ^{60}Co-gamma-radiation are ca. 1.16 nmol/J under vacuum and ca. 0.46 nmol/J in oxygen.

Based on the assumption that benzene is formed in some *elimination* reaction that is independent of the polymer's molecular-weight distribution, benzene levels have been tentatively *calculated* as **ca. 0.9 ppm (in O_2) and ca. 2.3 ppm (under vacuum)** for medical polystyrenes after a sterilizing (gamma-) dose of 25 kGy. This would be consistent with the size of the benzene peak in the qualitative chromatograms obtained with the medical PS, and it is proposed to use the vacuum-data as a worst-case scenario in the safety evaluation of irradiated devices or packaging materials (cf. Section 13.4 *Safety Aspects*).

12.8 Genuine Products or Artifacts of Thermal Desorption ?

The possibility that the products analyzed are *thermal degradation products of some radiation-induced macromolecular precursors*, such as peroxides or hydroperoxides, has been stated repeatedly (e. g., in context with Figures 7.2 and 7.3, or Table 9.2). Such a 'low-temperature' pyrolysis was suspected for the first time during the temperature study with LDPE (Sections 5.5 and 5.6), when the oxidized PE radiolysis products increased linearly with temperature while the residual hydrocarbons (oligomers) did not. In contrast, the fact that the radiolysis products of PS reach a plateau (like styrene or the dimer) was initially interpreted as an argument for the genuine presence of these products.

The different temperature effects in LDPE and PS certainly have some cause(s), but they clearly do not *prove* anything, and it may well be possible that *all* low-MW *radiolysis products* are formed in a (relatively low-temperature) pyrolysis process. All radiolysis products would include not only those determined by thermal desorption, but equally those determined by dynamic headspace analyses, a basically similar technique—in other words, the products identified by Azuma et al. (1983, 1984a, b), Rojas de Gante and Pascat (1990), etc. might be artifacts as well.

On the other hand, it clearly cannot be excluded that the products are genuine and there are several observations that appear to support such a view:

(1) *Gaseous* radiolysis products (H_2, CH_4, CO, CO_2, etc.) of polymers are well investigated[#] and no one has ever proposed—and there is little reason to suspect—that they are artifacts of the analytical techniques used. It might then be argued: If radiation-induced oxidation (ionizing radiation in the presence of oxygen) produces 'genuine' CO and CO_2, why should it not also produce 'genuine' low-molecular-weight alcohols, aldehydes, ketones, etc. ? Oxidation may start with peroxides, but it certainly proceedes via alcohols

[#] See Hill et al. (1989) for a comprehensive compilation of G-values; or the work of Killoran (1972), Bersch et al. (1959), and Tripp (1959), which is directly related to food packaging.

to aldehydes / ketones and finally to carboxylic acids, and *these* are probably the precursors of CO and CO_2—so why should they not be genuine themselves ?

(2) There have been repeatedly reports of *off-odours and taint transfer* associated with irradiation of plastics (e. g., Kilcast, 1990; Azuma et al., 1984b; Tripp, 1959); these sensory changes must have a molecular basis and it can be assumed that they are caused by exactly the types of compounds that are analyzed by TDS, namely, small and more-or-less volatile organic molecules. There exist volatiles with extremely low odour-thresholds, and it may be interesting to note that Koszinowski and Piringer (1983) have used the human nose as a GC detector to characterize volatiles released from packaging materials.

(3) It also appears that the (or, at least, some of the) radiolysis products of *phenol-type antioxidants* are genuine (see Section 2.4): They have been observed in TDS / dynamic HSA analyses, they have been specifically investigated by HPLC-MS and a variety of other techniques, and they have been found as migrants in migration studies. Overall, the evidence for the genuine existence of these degradation products is compelling, and the same can be said about radiolysis products of organotin stabilizers in PVC (Allen et al., 1987c, Haesen et al., 1983).

Implications ...

... for the Analysis of Radiolysis Products ...

Ultimately, one could even postulate that all radiolysis products found in migration / extraction experiments are formed via some *solvent-induced* breakdown of radiation-induced macromolecular precursors (a process that, with water as extraction medium, would be called 'hydrolysis'). This would imply that there is no way to determine whether a radiolysis product is genuine or not, and that the only sensible thing to do is to perform migration / extraction tests under conditions as close as possible to those of actual use.

... and for the Status of Thermal Desorption as an Analytical Technique

Thermal desorption should be considered as a *complementary* technique for the chemical characterization of materials, a technique that cannot replace migration / extraction studies or the toxicity testing of medical products. It is therefore recommended:

(1) to take advantage of the high sensitivity of TDS *to identify and to quantitate* the low-MW radiolysis products—be they genuine or not,

(2) to perform *model calculations* that provide worst-case scenarios for the intended area of use, and then

— **if** these models indicate exposure levels to toxic substances that appear to be inacceptable —

(3) to perform *migration / extraction studies* under conditions of actual use.

When migration / extraction experiments are considered necessary, or have to be performed in the context of a 'chemical characterization', it is strongly suggested to consider the use of relatively new analytical techniques, such as large-volume on-column injection (LOCI) or on-line coupled LC-GC (see Appendix 22 *Research Proposal*...).

13. Conclusions

As mentioned in Section 1.1, there has been little information on an aspect of radiation sterilization one is probably most concerned about from a *toxicological* point of view, namely, **the formation of low-molecular-weight ('volatile') radiolysis products** (see Section 2.3).

While there are still some unanswered questions, **we now have a much more comprehensive picture.** This picture has been *qualitative*, and/or *semi-quantitative* in Phases I and II (for various medical-grade polymers, and for PE & PP films—see Chapters 4 and 5), and, for polystyrene, the experiments of Phases III to V (Chapters 6 to 11) have added **a quantitative dimension.** Before discussing *safety aspects*, I would like to comment briefly on *analytical aspects*, *radiation-chemical* questions, and the prospects for *irradiation detection*.

13.1 Analytical Considerations

Manufacturers must confirm that their medical devices and packaging are compatible with the sterilization methods used (ISO 11607: Packaging for Terminally Sterilized Medical Devices). To achieve this, medical device and packaging materials must be evaluated with validated chemical (and physical) test methods. In the course of this work, *the validity of thermal desorption as a method for the chemical characterization of medical plastics has been demonstrated.* 'Total desorption' conditions for the main radiolysis products of *polystyrene* have been established*,* and a quantitative method for traces of *benzene* in PS has been developed.

Additionally, a new desorption technique requiring almost no sample pre-treatment has been successfully tested, namely, *Thermal Desorption of Polymer Solutions with Solvent Evaporation* (the DSC-Method), and the potential of directly injecting polymer solutions into the CIS (i. e., using a PTV for thermal desorption) has been indicated. While 'classic' TDS (or dynamic HSA) will clearly remain the method of choice for *identifying* volatiles, the desorption (with solvent evaporation), or direct injection, of polymer solutions are attractive alternatives for *monitoring* known volatiles, e. g., in a future irradiation-detection method.

Volatile / low-MW radiolysis products of polymers apparently have been largely neglected during decades of radiation-chemical research (which is, to some extent, understandable, since dynamic HSA and TDS are *relatively* new). Quantitative techniques to determine these volatiles might help to solve some fundamental problems in polymer radiation chemistry (see, for example, Schnabel et al., 1991).

Overall, the technique is highly sensitive but, at the same time, quite demanding; it has been demonstrated that *comprehensive parallel test programs* have to be performed, particularly during quantitative series of measurements. Further attempts should be made to reduce memory effects (the 'cold spot' problem) and adsorptive activity in the TDS. For various reasons—related to external standard (ESTD) quantitation, memory effects, adsorptive activity in the TDS, the question of radiation-induced artifacts, etc.—the quantitative results obtained by thermal desorption may not be as 'true' or as 'correct' as one might possibly wish. However, I am convinced that these quantitative data are the best that presently can be achieved.

13.2 Radiation-Chemical Considerations

We presently do not know the *molecular mechanism(s)* underlying the formation of volatile products. We also do not know exactly *to what extent* these products are genuine (see Section 12.8 *Genuine Products or Artifacts of Thermal Desorption ?*). There is some evidence that in PS the *low-molecular-weight fraction* plays a major role in radiolysis product formation; on the other hand, it appears that the products are *not*, or only to an insignificant extent, formed by oxidation of the residual monomer *styrene*.

Overall, the vast majority of radiolysis products in all polymers under investigation are *oxidized* compounds—one exception being benzene in PS. The effects of ionizing radiation in the presence of air (oxygen) are probably best characterized as effects of a **radiation-induced oxidation:** The reaction of oxygen with organic polymer (or additive) molecules—while favored *by thermodynamics*—is inhibited by *reaction kinetics*, and ionizing radiation simply provides the *activation energy* for a variety of oxidation reactions. For thermodynamical reasons, one can expect that radiolysis products in the presence of O_2 will always be *degradation* or *fragmentation products* of existing structures; there will be no 'synthesis' of more complex structures or of entirely new compounds.

13.3 Implications for Irradiation Detection

In comparison with the efforts that have been undertaken to establish detection methods for irradiated food items (see Section 2.5), this was a small-scale investigation and we are only at the beginning of a possible future detection method for irradiated plastics.

The results obtained with medical 'standard' polystyrenes, and with some commercial and 'real-life' samples, do indicate **that thermal desorption can be used to correctly identify items made from standard polystyrenes as radiation-sterilized**, i. e., as irradiated with doses in the range of 25 kGy. They also indicate that simultaneously monitoring two or more radiolysis products will probably increase the reliability and / or sensitivity of the detection method, and that it therefore may be possible to optimize the method for the lower doses commonly applied in food irradiation.

More information will clearly be needed to extend this approach to **styrene copolymers**—this will require a better understanding of the underlying radiation-chemical reactions, or of the relationship between (co-) polymer structure and product concentrations. It is also likely that additional techniques, e. g., IR spectrometry, will have to be used to provide additional information on the resins under investigation.

The results obtained during the initial screening program suggest that it should be possible to develop detection methods for radiation-sterilized **polypropylene, poly(vinyl chloride),** and, possibly, **polyamides**, while the situation with polyethylenes is less clear. In the case of **PP and PVC,** an identification would be based on the degradation products of additives (antioxidants, stabilizers), which are always present in radiation-grade types of these polymers. In the case of phenol-type antioxidants there appear to exist trace products with a-typical / radiation-specific structures (Sections 4.6 and 5.10), and it is conceivable that other additives also yield atypical trace fragments. In the case of **PA-6,** an identification might be based on an assay of pentanamide, or, maybe, even on the 'trace amides'.

While it appears to be relatively easy to decide whether PS has been radiation-sterilized or not, irradiation detection will certainly be much more difficult at lower absorbed doses, since (1) a 'radiation-specific' product that is definitely absent in non-irradiated PS has not been found so far, and (2) the yield of the products may vary to some degree with the type of the resin, and it may be influenced by the same environmental factors that affect dosimeter response (see Section 2.5).

A promising approach towards irradiation detection might be **multivariate data analysis** or **pattern recognition analysis** of mass spectral data. Tayler et al. (1989) have successfully used such a technique (principal components analysis, PCA) to discriminate various (non-irradiated) polypropylene resins from their *TDS-GC* mass spectra (cf. Section 2.8). Related methods, employing **artificial neural networks** (ANNs) capable of 'supervised learning,' have been applied to the analysis of *pyrolysis* mass spectra. Goodacre et al. (1992), for example, have demonstrated the ability of Py-MS combined with ANN-analysis to differentiate between virgin and adulterated olive oils.

13.4 Safety Aspects

General / Qualitative Considerations

Medical Products

If one looks at the fingerprint chromatograms of the medical polymers, it appears that—with the possible exception of PP—the *concentrations* of the radiolysis products may be insignificant compared to the levels of the residual monomers/oligomers, or, in the case of PVC, of 2-ethyl-1-hexanol. One might also argue that the *oxidized* products of, e.g., PS or PE, should regularly be less toxic than styrene and the hydrocarbons, respectively. One might however be somewhat concerned about trace levels of *benzene* in PS (cf. below), and about the relatively large amounts of *1,3-bis-(1,1-dimethylethyl)-benzene* in PP.

As long as we accept that plastic formulations *of undisclosed composition* may qualify as 'biomaterials' by complying with certain test protocols, we would impose a double standard by requiring from polymers *containing unknown radiolysis products* that they comply with more than that 'black box-toxicology.' On the other hand, the results of the initial screening program (Chapter 4) prove very impressively

- that ionizing radiation *does have an effect* on (medical) plastics;
- that it *may* produce significant amounts of 'volatiles' which are not formed during processing;
- that it is *absolutely necessary to perform a qualified product validation after the final processing step*, be it radiation sterilization or some other procedure;
- and, finally, *that the results obtained for one sterilization method do not necessarily have to be valid for another*.

Whether the radiolysis products identified by thermal desorption are really significant in a toxicological sense, i. e., whether they might constitute a potential health hazard, cannot, of course, be assessed by TDS-analyses alone. It should also be kept in mind that irradiation may produce higher-MW analogues of these products. While being non-volatile under TDS-conditions, these compounds might be mobile enough to be released from devices or packaging materials.

Food Packaging Materials

A *preliminary* safety assessment of irradiated food packaging materials would look practically identical: Most of the radiolysis products may be expected to be less toxic than the low-molecular weight constituents already present, and their concentrations may appear to be marginal. Again, benzene in PS and the antioxidant degradation products in PP would raise some concern.

Non-irradiated food packaging materials must comply with *global migration* and, where applicable, *specific migration* tests. Current global migration limits in the EU are 10 mg/dm^2 or

60 mg/kg (relative to the contact area or to the amount of solvent); specific migration limits exist for, e. g., vinyl chloride (0.01 mg/kg), or caprolactam (15 mg/kg).

Obviously, the sole problem with irradiation is: *Do we accept irradiated materials that comply with these tests, even if they release compounds that are not normally encountered in food packaging (for example, because they are 'radiation-specific') ?* Can we assume that a (gravimetric) global migration test is sensitive enough for every conceivable radiolysis product ? Or, to put it differently, if we need specific migration limits for vinyl chloride or caprolactam, can we exclude that we need a limit for, e. g., 1,3-bis-(1,1-dimethylethyl)-benzene ?

Quantitative Considerations (With Emphasis on Polystyrene)

Quantitative *dose-response relationships* are central to toxicology and for this reason considerable efforts were made to determine the concentrations of the radiolysis products. The importance of dose-response relationships has been recognized more than four centuries ago by Paracelsus (1493–1541), and—while modern toxicology is no longer exclusively dealing with 'poisons' and 'remedies' (drugs)—his famous SOLA DOSIS FACIT VENENUM is still quoted in leading textbooks (Klaassen, 1985b):

> „All substances are poisons; there is none which is not a poison. *The right dose differentiates a poison and a remedy*."

With the quantitative data obtained, we can now calculate *worst-case scenarios* for the release of radiolysis products from irradiated plastics that might occur in a packaging or medical application. In a packaging context such a model calculation might look as follows:

We assume a complete transfer of low-molecular-weight compounds from a plastic bag into its liquid content. We suppose the bag has the shape of a cube with an edge of 10 cm, its volume is accordingly 1000 cm^3 (and its surface 600 cm^2). The thickness of the film be 25 µm (which is quite typical); the density of both, the plastic film and the bag's liquid content be 1 g/cm^3; the total mass of the film is then 1.5 g, that of its content is 1 kg.[#]

The model can easily be extended to other situations, such as substance transfer from a tray, an infusion container, or a blood bag; if the contact medium is an aqueous one, we will still be on the safe side assuming that the interaction occurs only with a surface layer of 25 or 50 µm (see below). It is now possible to calculate the product concentrations resulting from a complete transfer into the contact medium – see Table 13.1.

It must be emphasized that this model evokes **a worst-case scenario** deliberately overestimating the resulting concentrations, since

– there will be no total transfer, certainly not with aqueous contact media,[##]
– the products may be, to some extent, artifacts of thermal desorption, and
– varying amounts of them are already present in the non-irradiated controls.

[#] A geometrically similar concept is underlying the 60 mg/kg *global migration* limit of EC-Directive 90/128/EEC of 23 February 1990 (relating to plastic materials and articles intended to come into contact with foodstuffs).

[##] Aqueous media interact only with the surface of a lipophilic packaging material and migration is „in most cases exceptionally small" (Figge, 1996). Lipophilic contact media (fats, oils) penetrate the plastic and form a structurally loosened and continuously expanding *mixed phase* which releases larger amounts of low-MW material. The two cases have been described as, on the one hand, a „multicomponent two-phase system with a ... constant phase boundary," and, on the other hand, a „multicomponent ... multiphase system with moving phase boundaries" (Figge, 1996).

Table 13.1 **Worst-case scenario** for the total transfer of PS radiolysis products into a contact medium: see text for details (styrene levels are for comparison only).

Concentrations in the	Polymer (**ppm** or mg/kg)	Contact Medium (**ppb** or µg/kg)	Comments
Styrene (residual monomer)	100 - 300	150 - 450	
Acetophenone	30 - 40	45 - 60	
1-Phenylethanol	6 - 8	9 - 12	
Phenol	< 8	< 12	
Phenylacetaldehyde	< 8	< 12	
Benzaldehyde	30 - 40	45 - 60	
Various Trace Products	< 1	1.5	
Benzoic acid	10 (?)	15	
Benzene	1 - 2	1.5 - 3	Very toxic, carcinogen

It must also be said that this model calculation only serves to illustrate **the order of magnitude** of a possible release of low-MW material and has little direct relevance, because standard polystyrene is not typically used for flexible packaging films, or blood bags.

As already observed during the initial screening program (Section 4.1), the levels of the radiolysis products are at least one order of magnitude below those of the residual monomer styrene. Overall, the resulting product concentrations in our hypothetical contact medium are in the low ppb-(µg/kg)-range, which is probably well below levels of concern. Whether we want to accept these levels of 'contamination' will depend on the anticipated exposure to the substances in question, i. e., ultimately, on the intended use of a product or packaging material.

In medical applications we will be prepared to accept higher risks, certainly so with life-saving devices; generally, an assessment of the benefits vs. the risks associated with a medical device will be quite similar to that for a pharmaceutical drug.

With respect to **food packaging,** I would like to neglect, for the moment, the potential benefits of food irradiation, and concentrate instead on the potential risks associated with radiolysis products. Presently, there are no specific migration limits for the compounds that have been identified as radiolysis products of PS (in fact, specific migration limits do exist only for vinyl chloride and caprolactam). The main question is still: If an irradiated polymer passes the official global migration tests (< 10 mg/dm^2 or 60 mg/kg), can we be sure that we do not need a limit for the (or some of the) radiolysis products ? After all, some of the products are virtually absent in normal, non-irradiated materials, and probably have not been considered when the limits were established.

A final comment should be made on **benzene**, the radiolysis product one is probably most concerned about, because it is „very toxic" (Klaassen, 1985a), a proven carcinogen, and a mutagen. Please note that benzene has also been detected in irradiated MABS (Section 4.2), which indicates that it may be produced *by all styrene-based polymers*.

The levels of benzene in our model calculation are within the range of the current EPA limit of 5 ppb for *benzene in drinking water* (EPA is the U. S. Environmental Protection Agency). Of course, actual benzene levels will be significantly lower in aqueous contact media. One can also expect that irradiated styrene-based packaging is overall a less important source of exposure to benzene than environmental sources, like tobacco smoke or gasoline. On the other hand, one probably does not want to have a carcinogen in a yoghurt tray that has been pre-sterilized for aseptic filling, and many scientists believe *that there is no safe level of exposure to a carcinogen*.

14. Zusammenfassung

14.1 Hintergrund und Problemstellung

Medikalprodukte (oder: 'Medizinprodukte') spielen eine wichtige Rolle in der modernen Medizin. Diese Produkte—deren Spektrum von 'einfachen' Einmalspritzen bis hin zu Dialysegeräten oder Implantaten (z. B. künstlichen Hüftgelenken) reicht—bestehen oft ganz oder teilweise aus synthetischen Polymeren und sie werden zunehmend mit Hilfe ionisierender Strahlung sterilisiert (Kapitel 2.1). Auch *Verpackungsmaterialien* aus Kunststoffen können ionisierenden Strahlen ausgesetzt sein: Bei der (medizinischen) Strahlensterilisation natürlich, aber auch bei der Lebensmittel-Bestrahlung (Kapitel 2.2) oder wenn Verpackungsmaterialien für eine spätere aseptische Befüllung sterilisiert werden.

Wenig ist gegenwärtig bekannnt über **eine** Wirkung ionisierender Strahlung auf Kunststoffe: die Entstehung niedermolekularer (flüchtiger) Verbindungen (= Radiolyseprodukte), ein Aspekt, der für die toxikologische Bewertung der Strahlensterilisation (Unbedenklichkeit ?) von zentraler Bedeutung ist.[#] Über Verpackungsfolien (hauptsächlich aus LDPE und Polypropylen) sind bereits einige Daten veröffentlicht worden, nicht jedoch über medizinisch verwendete Kunststoffe (Kapitel 2.3). Es wird allgemein erwartet, daß „die chemische Basis von Biokompatibilität in Zukunft eine viel stärkere Beachtung finden wird, einschließlich einer kompletten Charakterisierung der Materialien, der Identifizierung und Quantifizierung von aus Medikalprodukten extrahierbaren Chemikalien ... und der Untersuchung von Abbauprodukten der verwendeten Materialien" (Wallin, 1995).

Während eines Seminars der amerikanischen FDA[§] wurde unlängst die Verpackung als mögliche „Achillesferse der Lebensmittel-Bestrahlung" bezeichnet (Pargas, 1998). Ungefähr zur gleichen Zeit wurde im Auftrag des Bundesgesundheitsministeriums eine weitere Studie über den Einfluß ionisierender Strahlen auf Verpackungsmaterialien durchgeführt; im Zentrum dieses vom Fraunhofer-Institut für Verfahrenstechnik und Verpackung durchgeführten Projektes standen Extraktions- und Migrations-Versuche (Welle und Franz, 1998, 1999; Demertzis et al., 1999). Untersuchungen mit einer Thermodesorptions-Technik (vergleichbar der in dieser Arbeit verwendeten) werden zur Zeit am amerikanischen NCFST[§§] durchgeführt (Sadler, 1999).

Das **erste** wichtige Ziel dieser Arbeit könnte folglich als Beitrag zu einer besseren 'chemischen Charakterisierung' von bestrahlten Kunststoffen beschrieben werden: Die **Identifizierung** flüchtiger Radiolyseprodukte in medizinischen Polymeren (und Verpackungsmaterialien), um eine bessere Einschätzung der möglicherweise mit der Strahlensterilisation (und mit der Lebensmittel-Bestrahlung) verbundenen Risiken zu ermöglichen.

Das **zweite** wichtige Ziel war herauszufinden, ob mit der Thermodesorption-GC-MS eine analytische Unterscheidung zwischen bestrahlten und unbestrahlten Materialien möglich ist. Dieser Schwerpunkt **'Nachweis einer Bestrahlung ?'** wurde dadurch inspiriert und beeinflußt, daß das BGA / BgVV[+] über viele Jahre maßgeblich an der Entwicklung von Nachweisverfahren für bestrahlte Lebensmittel beteiligt war (Kapitel 2.5).

[#] Was die Sicherheit von Medikalprodukten angeht ist die mögliche Toxizität niedermolekularer Radiolyseprodukte natürlich nur ein Aspekt; weitere mögliche Problemfelder sind z. B. *mechanisches Versagen* aufgrund von Polymer-Kettenspaltung und/oder 'Alterung' nach der Bestrahlung, *erhöhter Verschleiß* von UHMWPE-Implantaten oder eine *Verschlechterung der Oberflächen-Eigenschaften / Blutkompatibilität* (Buchalla et al., 1992, 1993a, b, c, 1994, 1995).

[§] FDA = Food and Drug Administration

[§§] NCFST = National Center for Food Safety and Technology

[+] Das Bundesgesundheitsamt (BGA) bzw. Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin (BgVV), an dem diese Arbeit durchgeführt wurde.

Die ursprünglichen ‘Arbeitshypothesen’ lassen sich wie folgt zusammenfassen:

– Flüchtige Radiolyseprodukte entstehen nicht nur in LDPE und Polypropylen, sondern auch in Polymeren wie *Polystyrol, Polyamid, Polyvinylchlorid, etc.*,
– Die flüchtigen Verbindungen werden nicht nur während der Bestrahlung in den ‘Headspace’ eines geschlossenen Behälters ‘freigesetzt’; *sie bleiben* vielmehr für längere Zeit *in der polymeren Matrix eingeschlossen* (wie etwa die Restmonomere),
– Es existieren möglicherweise Radiolyseprodukte, die sich als *‘Marker’* für eine analytische Differenzierung zwischen bestrahlten und unbestrahlten Materialien eignen;
– Es existieren möglicherweise *zyklische Radiolyseprodukte* (Kapitel 2.3) analog zu den Cyclobutanonen, die beim Bestrahlungsnachweis von (bestimmten) Lebensmitteln als Marker verwendet werden.

Eine **quantitative Analyse** flüchtiger Verbindungen mit Hilfe der Thermodesorption erschien anfänglich nicht möglich. *Statische* Headspace-Techniken werden routinemäßig zur Quantifizierung von Restmonomeren in Kunststoffen eingesetzt; die empfindlicheren *dynamischen* Techniken[#] werden zwar verbreitet in der Umweltanalytik eingesetzt, doch sind nur vergleichsweise wenige Untersuchungen von Polymeren in der Literatur beschrieben (siehe Kapitel 2.6–2.8).

Die Tatsache, daß diese Techniken vergleichsweise neu und ihre Möglichkeiten noch nicht vollständig ausgeschöpft sind, zeigt sich z. B. im Titel einer kürzlich erschienen Arbeit von Hodgson et al. (1998): *Toward an Optimized Dynamic Headspace Method for the Study of Volatiles in LDPE*. Auch in in dem Band *Hyphenated Techniques in Polymer Characterization*, einer Monographie der ACS Symposium Series (Provder et al., 1994), werden die dynamischen Techniken nur ganz kurz erwähnt; und Hachenberg und Beringer (1996) widmen nur einen kleinen Teil ihres Buches der dynamischen Methode.

Schon sehr früh während des (qualitativen) Screenings medizinisch verwendeter Kunststoffe (Kapitel 4) wurde deutlich, daß die Konzentrationen der Radiolyseprodukte beträchtlich niedriger sind als die der bereits in den Polymeren vorhandenen Restmonomere und Oligomere.[##] Dennoch erschien eine quantitative Analyse höchst wünschenswert, da quantitative Dosis-Wirkungs-Beziehungen eine zentrale Rolle in der Toxikologie spielen (SOLA DOSIS FACIT VENENUM, mit den berühmten Worten von Paracelsus—vgl. Kapitel 15.4).

Als eine Quantifizierung schließlich möglich zu werden schien (Kapitel 6), wurde beschlossen, die weiteren Untersuchungen auf Polystyrol (PS) zu konzentrieren und—als **drittes** wichtiges Ziel—**die Haupt-Radiolyseprodukte von PS quantitativ zu bestimmen** (Kapitel 6–11). Eine umfassende Literaturauswertung ergab, daß die Prinzipien einer quantitativen Analyse schon von anderen Autoren diskutiert worden sind (Kapitel 2.7); einige von ihnen haben auch—mehr oder weniger überzeugend—gezeigt, daß es tatsächlich möglich ist, flüchtige Verbindungen in Kunststoffen mit dynamischen (‘gas-solid’) Extraktionstechniken zu bestimmen, z. B. Styrol in PS oder BHT in Verpackungsmaterialien (siehe Kapitel 2.7). Meines Wissens wurden im Rahmen der vorliegenden Arbeit jedoch zum ersten Mal flüchtige Verbindungen *im unteren ppm-Bereich* mit Hilfe einer dynamischen Methode quantitativ bestimmt.

[#] Thermodesorption, dynamische Headspace-Analyse, Purge-and-Trap-Methoden: Da diese Techniken alle auf demselben Prinzip beruhen, werden die Begriffe zunehmend als Synonyme verwendet (ein weiteres ist ‘gas-solid-extraction’). Ob Autoren ihre Arbeit als Thermodesorptions-, dynamische Headspace-, oder als Purge-and-Trap-Untersuchung beschreiben, scheint vor allem von der verwendeten Ausrüstung (‘Hardware’) und von persönlichen Vorlieben abzuhängen.

[##] Eine Ausnahme bilden jedoch die Abbauprodukte von (Phenol-) Antioxidantien in Polypropylen (PP) (vgl. Kapitel 4.6 und 5.7), deren stark überladene Peaks die Fingerprint-Chromatogramme von bestrahltem PP dominieren.

14.2 Screening von sechs medizinisch verwendeten Kunststoffen

Eine Sterilisationsdosis von ca. 25 kGy reicht aus, um in den sechs untersuchten Kunststoffen *nachweisbare Mengen* von niedermolekularen Radiolyseprodukten zu erzeugen, die für beträchtliche Zeit in der polymeren Matrix *eingeschlossen bleiben*. Die Produkte und ihre Konzentrationen sind sehr charakteristisch für die einzelnen Kunststoffe; ihre Struktur hängt zusammen mit dem Polymertyp und/oder den vorhandenen Additiven; verglichen mit dem 'Level' der niedermolekularen Verbindungen, die sich bereits im unbestrahlten Material finden, können ihre Mengen teilweise als '*marginal*,' teilweise aber auch als '*recht beträchtlich*' beschrieben werden.

Identifizierung von Radiolyseprodukten

Die Hauptprodukte von **Polystyrol (PS)** sind *Acetophenon, Benzaldehyd, Phenol, 1-Phenylethanol* und *Phenylacetaldehyd*; ihre Konzentrationen liegen etwa eine Größenordnung unter denen des Reststyrols und Styrol-Dimers. Einige Spurenprodukte werden mit noch geringeren Ausbeuten gebildet; mit Ausnahme von *Benzol* (Kapitel 14.8) handelt es sich dabei ebenfalls um *oxidierte aromatische Strukturen* (vgl. Kapitel 14.7).

Dieselben *aromatischen Produkte* werden auch im untersuchten **MABS,** einem **Methylmethacrylat-Acrylonitril-Butadien-Styrol-**Copolymeren, gebildet. Verglichen mit denen von PS sind die Fingerprint-Chromatogramme von MABS recht komplex und zusätzlich werden *aliphatische Produkte* wie Hexanal oder Essigsäure beobachtet.

Das Hauptprodukt von **Polyamid-6 (PA-6;** Poly-ε-caprolactam) ist *Pentanamid*; seine Konzentration könnte etwa bei einem Drittel von der des Restmonomers ε-Caprolactam liegen. Außerdem werden Spuren der homologen Amide *Formamid, Acetamid, Propanamid, Butanamid* und *Hexanamid* gebildet.

Die Hauptprodukte des untersuchten **Polyvinylchlorids (PVC)**—*Octan, 1-Octen, Essigsäure-2-ethylhexylester und 1-Octanol*—sind Abbauprodukte von Additiven. Der Essigsäure-2-ethylhexylester wird sehr wahrscheinlich von einem Organozinn-Stabilisator gebildet, der (mindestens) einen *Thioglycolsäure-2-ethylhexylester*-Substituenten (Liganden) enthält. Es wurden keine chlorhaltigen Abbauprodukte beobachtet (die verschiedenen Spurenprodukte entstehen ebenfalls aus den Additiven). Die Gegenwart von freiem Chlorwasserstoff (HCl) in bestrahltem PVC ist unwahrscheinlich und kann wahrscheinlich nicht mittels Thermodesorption festgestellt werden.

Die Fingerprint-Chromatogramme des medizinischen **High-Density Polyethylens (HDPE)** unterscheiden sich recht deutlich von denen der LDPE-Folien (Kapitel 5) und dasselbe gilt für die Wirkung der Bestrahlung. Verglichen mit den Konzentrationen der bereits vorhandenen Kohlenwasserstoffe ('Ethylen-Oligomere') sind die der Radiolyseprodukte sehr klein; zu ihnen gehören verschiedene *Kohlenwasserstoffe, Aldehyde, Ketone und Carbonsäuren*. Das HDPE war das einzige Polymer bei dem buchstäblich 'zugesehen' werden konnte, wie einige Radiolyseprodukte binnen weniger Tage verschwanden. Erhöhte Konzentrationen der Carbonsäuren konnten noch nach sechs Wochen nachgewiesen werden.

Das Haupt-Radiolyseprodukt im untersuchten **Polypropylen (PP)** ist *1,3-bis-(1,1-Dimethylethyl)-benzol*, ein Abbauprodukt eines Antioxidants vom Typ der sterisch gehinderten Phenole. Nach einer Dosis von nur 3 kGy ist sein Peak bereits größer als viele der Rest-Kohlenwasserstoff-Peaks; nach einer Sterilisationsdosis von ca. 25 kGy ist er stark überladen und dominiert die Fingerprint-Chromatogramme. Im Zusammenhang mit dem Abbau von Antioxidantien steht auch die Bildung *aromatischer Spurenprodukte* (vgl. Kapitel 14.3). Von den anderen niedermolekularen Produkten wird angenommen, daß sie bei der strahlen-indu-

zierten Oxidation der Polymermoleküle selbst entstehen; zu ihnen gehören wieder verschiedene *Kohlenwasserstoffe, Aldehyde, Ketone und Carbonsäuren*.

Granulate vs. Spritzgußteile

Die Wirkung der Bestrahlung auf das nicht-verarbeitete Kunststoff-Granulat (Pellets) und auf die daraus hergestellten Spritzgußteile ist *qualitativ und quantitativ vergleichbar*. Das Spritzgießen induziert weder die Bildung zusätzlicher ('neuer') Produkte, noch unterdrückt es die Entstehung der von den Granulaten her bekannten Produkte und es führt auch nicht zu dramatisch veränderten Produkt-Konzentrationen. Als interessanter stellte sich deshalb die Frage heraus: In welchem Ausmaß entstehen potentielle *Bestrahlungs-'Marker'* bereits während der Verarbeitung ?

Die Ergebnisse zeigen, daß *1-Phenylethanol* ein vielversprechender Marker für **PS** und **MABS** ist, d. h. während des Spritzgießens scheinen keine nennenswerten Mengen von 1-Phenylethanol zu entstehen (vgl. Kapitel 14.5 und 14.6). Der Verarbeitungsschritt scheint beim **PA-6** und beim **PVC** die Bildung von kleineren Mengen Pentanamid bzw. Essigsäure-2-ethylhexylester zu induzieren. Im untersuchten **PE** erzeugt die Verarbeitung alleine offensichtlich keine signifikanten Mengen von Produkten wie Butanal, 2-Butanon, Essigsäure oder Propansäure. Im medizinischen **PP** wird 1,3-bis-(1,1-Dimethylethyl)-benzol während des Spritzgießens nicht oder höchstens in Spuren gebildet. Zur Etablierung dieser Substanzen als Marker für den Nachweis einer Strahlenbehandlung sind natürlich weitere Untersuchungen notwendig.

14.3 Qualitative Ergebnisse mit LDPE- und Polypropylen-Folien

Retention 'flüchtiger' Radiolyseprodukte in LDPE und PP-Folien

Das wichtigste Ergebnis der mit LDPE und Polypropylen-Folien durchgeführten Versuche ist, daß—anders als in früheren Arbeiten (Rojas de Gante und Pascat, 1990; El Makhzoumi, 1994) berichtet—niedermolekulare Radiolyseprodukte *auch in LDPE-Folien* für längere Zeit nachweisbar sind, und daß sie in PP-Folien viel länger zurückgehalten werden als erwartet.

In allen Polyolefin-Folien werden verschiedene Kohlenwasserstoffe, Aldehyde, Ketone und Carbonsäuren gefunden; ihre Konzentrationen liegen nach einer Dosis von 25 kGy bei ungefähr *einem Zehntel* derjenigen der Rest-Kohlenwasserstoffe ('Ethylen-Oligomere'). In den PP-Folien finden sich außerdem in recht beträchtlichen Mengen drei Abbauprodukte von Antioxidantien vom Typ der sterisch gehinderten Phenole, die Peaks dieser Verbindungen —1,3-bis-(1,1-Dimethylethyl)-benzol, 2,4-bis-(1,1-Dimethylethyl)-phenol, und 2,6-bis-(1,1-Dimethylethyl)-2,5-cyclohexadien-1,4-dion—beherrschen die Fingerprint-Chromatogramme der bestrahlten Folien.

Die meisten dieser flüchtigen Produkte sind bereits früher im *Headspace* über bestrahlten LDPE- und PP-Folien identifiziert worden, und es wurde auch bereits beschrieben, daß einige von ihnen (wie auch die Abbauprodukte der Phenol-Antioxidantien) in PP-Folien zurückgehalten werden. Die Tatsache, daß diese Produkte noch *mehr als ein Jahr* nach der Bestrahlung sowohl in LDPE als auch in PP nachgewiesen werden konnten, kann wohl zum Teil auf die höheren Strahlendosen zurückgeführt werden, die (anfänglich) in der vorliegenden Untersuchung verwendet wurden, hauptsächlich jedoch auf die mit dem Thermodesorptions-System möglichen wesentlich höheren *Desorptions-Temperaturen*.

Der Einfluß der Desorptionstemperatur

Der Einfluß der Desorptions-Temperatur wurde mit **LDPE** näher untersucht. Oberhalb von 120°C steigen die Peakflächen der Radiolyseprodukte (und damit die Empfindlichkeit des Verfahrens) dramatisch an. Um den 'Kollaps' der für die Desorption zur Verfügung stehenden Oberfläche zu verhindern, wurde eine spezielle Technik, die '*Stainless-Steel Sieve Sandwich*-Technik' entwickelt, die es erlaubte die Desorptionstemperatur auf bis zu 240°C zu erhöhen. Die Ergebnisse dieser 'Hochtemperatur-Messungen' legen die Vermutung nahe, daß die Radiolyseprodukte (oder wenigstens ein beträchtlicher Anteil derselben) als thermische Abbauprodukte von strahlen-induzierten Vorstufen entstehen, wie z. B. von Peroxiden oder Hydroperoxiden.

Die Bestrahlung von LDPE erzeugt ein sehr charakteristisches Muster von Gruppen strahlen-induzierter Peaks, z. B. *Butanal / 2-Butanon*, *Essigsäure / Pentanal* oder *3-Hexanon / 2-Hexanon / Hexanal*. Diese charakteristischen Gruppen waren sehr ähnlich in mehreren zufällig ausgewählten Folien, in zehn verschiedenen LDPE *Lupolen* Folientypen (BASF AG) und in einem *Lupolen* Granulat. Ein Versuch erhöhte Produktkonzentrationen nach einer Dosis von nur 1 kGy *nachzuweisen* zeigte, daß mindestens die entfernte Möglichkeit besteht, ein Nachweisverfahren auch für niedrigbestrahlte Folien zu entwickeln (siehe Kapitel 5.9).

Die **Polypropylen-Folien** erzeugen ebenfalls ein charakteristisches Muster von strahlen-induzierten Peaks, das in einer experimentellen Folie und in drei Novolen-Folientypen (BASF AG) sehr ähnlich war. Quantitativ ist jedoch die Bildung von Abbauprodukten von Antioxidantien von weit gößerer Bedeutung. Neben den erwähnten drei Hauptprodukten scheinen verschiedene **aromatische Spurenprodukte** zu existieren, und da ein Bestrahlungsnachweis vorstellbar ist, der auf der Analyse atypischer / strahlen-spezifischer aromatischer Strukturen beruht, wäre es recht interessant diese Verbindungen eingehender zu untersuchen.

Zyklische Radiolyseprodukte ?

Wie in Kapitel 14.1 erwähnt, weckte die mögliche Entstehung zyklischer Produkte in LDPE- und PP-Folien das Interesse des Autors, da verschiedene Cyclobutanone beim Bestrahlungsnachweis von Lebensmitteln als 'Marker' verwendet werden können. In den untersuchten LDPE- und PP-Folien wurden jedoch keine zyklischen Verbindungen gefunden—weder die von Rojas de Gante und Pascat (1990) aufgeführten noch irgendwelche anderen. Da die Cyclobutanone auf definierte Weise bei der Radiolyse von *Triacylglyeriden* entstehen und vergleichbare Strukturen in Polyolefinen fehlen, ist es wahrscheinlich, daß bei der Bestrahlung von PE oder PP *keine* Cyclobutanone entstehen, und es ist vorstellbar, daß auch keine (oder höchstens Ultra-Spuren von) anderen zyklischen Verbindungen gebildet werden. Dennoch scheint das Phänomen interessant genug zu sein, weitere Untersuchungen zu rechtfertigen oder zumindest einen Versuch, die ursprüngliche Beobachtung zu bestätigen.

Geometrie und Effizienz des TDS-CIS-Systems

In Kapitel 5.11 wird das analytische System mit dem von Hodgson et al. (1998) verwendeten verglichen. Dabei zeigt sich, daß—ausgedrückt durch einen von Hodgson et al. vorgeschlagenen Parameter ε —das TDS-CIS-System wesentlich effizienter vom Gasfluß durchspült ('ge-purgt') wird, und daß das Konzept, flüchtige Verbindungen direkt in einem split / splitless-Injektor (dem CIS) zu 'trappen' ein sehr elegantes ist.

14.4 Quantitative Desorptionsbedingungen

Die Thermodesorption wurde zu Anfang als eine zwar hochempfindliche, jedoch prinzipiell qualitative Technik wahrgenommen und dieser Eindruck änderte sich erst während einiger Experimente, die parallel zu den Analysen der PE- und PP-Folien durchgeführt wurden (Kapitel 6). Die Quantifizierung basiert auf der zentralen Annahme, daß die thermische Desorption ein dynamischer (Nicht-Gleichgewichts-) Prozeß ist, bei dem die ständige Entfernung der flüchtigen Verbindungen einen Konzentrationsgradienten in der Polymer-Matrix erzeugt. Dieser Konzentrationsgradient ist die treibende Kraft eines Diffusionsprozesses, mit dessen Hilfe das Polymer vollständig desorbiert bzw. extrahiert werden kann. Die für diesen Prozeß erforderliche Zeit hängt ab von der Distanz, die die Analyten überwinden müssen, und von ihrem Diffusionskoeffizienten, d. h. letztlich von den Dimensionen der Probe und der Desorptionstemperatur.

Als TDS-Bedingungen für die quantitative Desorption von feinem Polystyrol-Pulver wurden **160°C für 10 min** etabliert. Die Quantifizierung basiert außerdem auf einem vollständigen Transfer der Analyten von der TDS-Einheit zum Injektor (CIS), der in einer Serie von Test-Injektionen bestätigt wurde, und auf einem vollständigen Transfer vom CIS zur Kapillarsäule. Die Quantifizierung mittels 'echter' interner Standards (ISTDs) scheitert daran, daß es praktisch unmöglich ist, exakte ppm-Mengen von flüchtigen ISTDS reproduzierbar in einer polymeren Matrix zu verteilen (Kolb und Pospisil, 1977; Westendorf, 1985); deshalb wurden zur Kalibrierung *externe Standards* (ESTDs) in das Kaltaufgabesystem (CIS) injiziert. Die Injektion erfolgte mit Hilfe einer speziellen Technik, der sogenannten *Solvent-Flush*-Technik, die die exakte Dosierung eines bestimmten Volumens erlaubt.

14.5 Quantifizierung mittels 'direkter' Thermodesorption

Quantitative Ergebnisse (Phase III)

In einem ersten Schritt wurden die bereits früher mit 25 kGy bestrahlten Proben analysiert, sowie einige 'neuere' 1, 3 und 10 kGy-Proben. Basierend auf früheren Erfahrungen mit Probenmassen und Peakflächen wurden drei parallele Meßreihen durchgeführt: eine *split-scan*, eine *splitless-scan-* und eine *splitless-SIM*-Meßreihe mit Einwaagen von ca. 5 bzw. 10 mg. Die drei Meßreihen—die zwar auf demselben Prinzip beruhen, sich aber in ihrer Empfindlichkeit unterscheiden und jeweils unabhängig kalibriert werden müssen—lieferten praktisch identische Ergebnisse (Kapitel 7).

Die Konzentrationen von 1-Phenylethanol (1-Pet) und Acetophenon (Acp) steigen linear mit der absorbierten Dosis an, und die Datenpunkte der 25 kGy-Proben liegen ziemlich genau auf einer Ausgleichsgeraden, die durch die Datenpunkte der 1, 3 und 10 kGy-Proben führt (Abbildungen 7.2 und 7.3). Dies ist deshalb bemerkenswert, weil die 25 kGy-Proben bereits etwas mehr als ein Jahr zuvor bestrahlt worden waren. Die Konzentrationen nach 25 kGy liegen bei ca. 6-8 ppm (mg/kg) für 1-Pet und ca. 25-35 ppm für Acp im Polystyrol-Granulat; in den daraus hergestellten Spritzgußteilen ist die Konzentration von 1-Pet etwas und die von Acp deutlich höher (mit 50-60 ppm)—eine Beobachtung die mit früheren qualitativen Ergebnissen übereinstimmt.

Mit Hilfe der Ausgleichsgeraden in Abb. 7.2 und 7.3 wurden für 1-Phenylethanol und Acetophenon *strahlenchemische Ausbeuten (G-Werte)* berechnet. Die Werte—2.5 nmol/J (nanomol/ Joule) für 1-Pet (G = 0.025) und 8 nmol/J für Acp (G = 0.08)—stimmen relativ gut mit denen überein, die später mit der DSC-Methode bestimmt wurden (vgl. Kapitel 14.6).

Die Konzentration von *Phenol* wurde nur in der splitless-SIM-Meßreihe bestimmt, d. h. nur mit den niedrigbestrahlten Proben; die Peakform war bei den geringen Konzentrationen

relativ schlecht (aufgrund von adsorptiver ‘Aktivität’ der GC-Säule), aber die Mengen an Phenol (Anhang 6) sind eindeutig—und in Übereinstimmung mit früheren qualitativen Analysen—denen von 1-Pet vergleichbar. Für *Benzaldehyd* und *Phenylacetaldehyd* wurden keine Eichkurven aufgenommen, aus den Fingerprint-Chromatogrammen kann jedoch abgeleitet werden, daß ihre strahlenchemische Ausbeute von gleicher Größenordnung ist: Die Konzentration von Benzaldehyd ist der von Acp vergleichbar, während Phenylacetaldehyd wahrscheinlich weniger wichtig ist als 1-Pet. Benzoesäure muß möglicherweise ebenfalls zu den ‘Haupt-Radiolyseprodukten’ von PS gezählt werden (vgl. Kapitel 14.7).

Bestrahlungsnachweis

Das Konzept *zwei* (oder auch mehr) Radiolyseprodukte als Marker für einen **Bestrahlungnachweis** zu verwenden, wird veranschaulicht mit Hilfe einer **zwei-dimensionalen Auftragung** der 1-Phenylethanol gegen die Acetophenon-Konzentration (Abbildung 7.4). Dabei zeigt sich, daß die bestrahlten und unbestrahlten Polystyrol-Proben auf zwei verschiedenen Linien angeordnet sind, die sich im Bereich niedriger Dosen schneiden. Bestrahlung mit 1, 3 und 10 kGy verschiebt die Datenpunkte, proportional zur absorbierten Dosis, entlang *einer* Regressionsgerade, die sich weiter bis zu den 25 kGy-Proben erstreckt, während die ‘Alterung’ des unbestrahlten Polystyrols die Datenpunkte entlang einer *anderen* Regressionsgerade in Richtung der unbestrahlten Spritzgußteile verschiebt. Ein qualitativ ähnliches Bild wird mit dem untersuchten MABS erhalten (Abb. 7.6).

Der Datenpunkt einer mit unbekannter Dosis sterilisierten Petrischale, also einer ‘realen’ Probe, findet sich exakt auf der Geraden, die eine Bestrahlung anzeigt (Abbildung 7.4); die 3 kGy-Proben sind eindeutig besser von den unbestrahlten Kontrollen zu unterscheiden als in einer ‘ein-dimensionalen’ Auftragung der Konzentration gegen die Dosis, und es ist vorstellbar, daß drei (oder: n) Radiolyseprodukte, die einen drei- (oder: n-) dimensionalen Raum aufspannen, die Chance verbessern könnten, eine PS-Probe als bestrahlt zu identifizieren. Diese zusätzlichen Produkte (oder: ‘Dimensionen’) könnten die Verläßlichkeit und/oder Empfindlichkeit eines TDS-basierten Nachweisverfahrens vergrößern.

Charakterisierung des analytischen Systems (der System-’Performance’)

Die quantitativen Messungen wurden nach einigen Wochen beeinträchtigt durch ein Nachlassen der Säulenleistung und insbesondere durch eine unerklärliche Verschlechterung der ‘TDS-Performance’. Es wurde deshalb beschlossen, für weitere Analysen eine polare Polyethylenglycol-Säule zu verwenden, die die höchste Empfindlichkeit für die oxidierten Produkte (besonders für 1-Pet) bietet, und außerdem das gesamte analytische System mit einem wesentlich umfangreicheren parallelen Test-Programm—bestehend aus *Empfindlichkeits-, Wiederfindungs- und speziellen ‘TDS-Performance’-Tests*—zu überwachen.

Für Letztere wurde der **Grob-Mix** verwendet, eine ursprünglich für den Test von Kapillarsäulen konzipierte Lösung von Substanzen unterschiedlicher Polarität (‘polarity mix’). Ein Vergleich von TDS-Analysen dieser Testlösung mit ‘direkten’ Injektionen in das CIS liefert umfassende Informationen über das Verhalten eines breiten Spektrums von Verbindungen während der Thermodesorption und ermöglicht so eine Charakterisierung der TDS-Performance. Die Ergebnisse mit dem Grob-Mix unterstreichen, daß solch ein allgemeiner Test besonders dann sehr wichtig ist, wenn man unbekannte Radiolyseprodukte sucht, da er anzeigt, ob man Gefahr läuft ganze Verbindungsklassen (z. B. Amine) zu ‘übersehen.’

Bestätigung der quantitativen Ergebnisse (Phase IV)

Die Experimente der 'Phase IV' wurden vor allem mit dem Ziel durchgeführt, die früheren quantitativen Ergebnisse (Phase III) zu reproduzieren und herauszufinden, ob sich die Konzentrationen der Radiolyseprodukte im Laufe der Zeit verändern (Kapitel 8). Daneben sollten einige 'reale' Proben (strahlensterilisierte Medikalprodukte aus PS), Styrol-Copolymere und 'experimentelle' (vorbehandelte) PS-Proben untersucht werden. Überraschenderweise waren die 'neuen' Konzentrationen anfänglich konsistent niedriger als in Phase III, z. B. erreichte 1-Pet nur ungefähr 50-60% des ursprünglichen Niveaus. Es stellte sich heraus, daß eine TDS-Temperatur von 160°C für 10 min für eine vollständige Desorption nicht mehr ausreichend war; die Ursache für diesen Effekt war ein zwischenzeitlich erfolgtes Software-Update, das über eine Verringerung der TDS-Heizrate indirekt zu einer Verkürzung der Desorptionszeit geführt hatte (Kapitel 8.8).

Bei einer höheren TDS-Temperatur (200°C für 10 min) wurden schließlich mittlere Konzentrationen von ca. 7.5 ppm 1-Phenylethanol (1-Pet) und ca. 38 ppm Acetophenon (Acp) erhalten (Kapitel 8.7); diese Werte stimmen beinahe exakt mit den früheren Ergebnissen überein (s. o.). Unter den neuen Analysenbedingungen wurden nur einige wenige Proben nachgemessen; die auf den buchstäblich 'halb-quantitativen' 160°C-Messungen basierenden 2D-Diagramme erlauben jedoch einige interessante Schlußfolgerungen (Kapitel 8.4).

Die mit unbekannten Dosen bestrahlten 'realen' Proben passen sehr gut in diese 2D-Diagramme und eine Nachbestrahlung mit 23.5 kGy verschiebt ihre Datenpunkte zu noch höheren 1-Pet und Acp-Niveaus. Die Konzentrationen in zwei 'experimentellen' PS-Proben sind viel niedriger und zeigen, daß die niedermolekulare Fraktion in PS wahrscheinlich eine sehr wichtige Rolle bei der Entstehung flüchtiger Radiolyseprodukte spielt. Die Styrol-Copolymere liefern völlig andere Fingerprint-Chromatogramme und die quantitativen Daten passen nicht in das für 'Standard'-Polystyrole erhaltene Bild. Ein Bestrahlungsnachweis an Copolymeren erfordert also weitere Informationen über die zugrunde liegenden strahlenchemischen Reaktionen oder über den Zusammenhang zwischen Produktausbeute und Struktur des Polymeren.

Insgesamt lassen sich die 'konventionellen' Messungen (= direkte Desorption von PS) in Phase IV wie folgt bilanzieren:

– die Experimente bestätigen das Potential der Thermodesorption als *quantitativer Methode*;
– es ist möglich, Gegenstände aus reinem Standard-Polystyrol zutreffend *als strahlensterilisiert zu identifizieren*, d. h. als bestrahlt mit Dosen von ca. 25 kGy;
– die Konzentrationen der Haupt-Radiolyseprodukte *verändern sich* über längere Zeiträume *nicht*.

14.6 Thermodesorption von Polymerlösungen mit Lösungsmittelausblendung und 'verwandte' Versuche

Thermodesorption von Polymerlösungen mit Lösungsmittelausblendung

Die TDS von Polymerlösungen mit Lösungsmittelausblendung (oder: DSC-Methode für 'Dissolution-Solvent-Casting'; Kapitel 9) ist eine neue und experimentelle Desorptionstechnik, die meines Wissens in der Literatur noch nicht beschrieben ist: Das Polymer wird gelöst, ein bestimmtes Volumen der Lösung wird in die TDS injiziert, und das leichtflüchtige Lösungsmittel wird durch das Splitventil 'ausgeblendet', während die Analyten auf dem Adsorbent im CIS getrappt werden. Die ursprüngliche Idee war, auf diese Weise eine maximale Oberfläche für die Desorption zu erzeugen. In einem nächsten Schritt wurden größere PS-Frag-

mente direkt gelöst (um das Vermahlen der Proben zu umgehen), und in einem letzten Schritt wurde dann die Thermodesorption selbst eliminiert, oder genauer gesagt, die Desorption wurde in den Injektor verlegt (siehe *Direktinjektion / Thermodesorption mit dem CIS*, weiter unten).

Generell scheint die 'DSC-Methode' in hohem Maße reproduzierbare Ergebnisse zu liefern, und das Gesamtbild stimmt recht gut mit dem überein, das bei der 'normalen' Desorption von PS-Pulvern erhalten wurde. Die Ergebnisse sind in einem 2D-Diagramm von 1-Phenylethanol- vs. Acetophenon-Konzentrationen zusammengefaßt (Abbildung 9.6), das mit den früheren 2D-Auftragungen konsistent ist. Einige Proben wurden nur mit der neuen Technik analysiert, erwähnenswert ist besonders eine der 'realen' Proben, eine Kulturflasche, die mehr als 9 Jahre zuvor sterilisiert worden war und deren Datenpunkt bemerkenswert gut in das Diagramm 'paßt.'

Die Konzentrationen von 1-Pet scheinen mit der DSC-Methode höher zu sein (bis 50% ?), und obwohl dieser Vergleich nur auf einer sehr geringen Anzahl von (direkt vergleichbaren) Daten beruht, ist der Unterschied möglicherweise real. Für dieses Phänomen gibt es keine unmittelbar einleuchtende Erklärung (siehe Kapitel 9.6). Das größte Problem der Technik ist, daß die Probenmassen extrem gering sind (ca. 0.1 mg PS verglichen mit 5 bis 10 mg bei der 'normalen' Desorption)—und die Anforderungen an das analytische System sind entsprechend hoch: Kontaminationen ('Memory-Effekte') sollten extrem niedrig sein, und jeglicher Verlust von Analyten (aufgrund von Adsorption oder wegen des 'cold spots') sollten minimal sein. Diese Forderungen konnten nicht vollständig erfüllt werden; gewisse 'Hintergrund'-Kontaminationen mußten hingenommen werden und die Wiederfindung für 1-Pet war etwas geringer als 100%.

Strahlenchemische Ausbeuten

Strahlenchemische Ausbeuten für 1-Pet und Acp wurden aus den mit der DSC-Methode bestimmten Konzentrationen errechnet. Die Werte für die verschiedenen Polystrol-Proben stimmen recht gut überein und liegen mit wenigen Ausnahmen im Bereich von 2.5 bis 3.5 nmol/J (nanomol pro Joule) für 1-Pet und im Bereich von 10 bis 15 nmol/J für Acp. Wie bereits bemerkt lassen sich ähnliche Werte aus den quantitativen Daten der früheren Experimente berechnen ('direkte' Desorption von PS-Pulver; vgl. Kapitel 14.5). Die Größenordnung der strahlenchemischen Ausbeuten unterstützt die Hypothese, daß die Produkte *nicht* (oder nur in unbedeutendem Ausmaß) aus dem Restmonomer Styrol entstehen.

Direktinjektion / Thermodesorption mit dem CIS

Nachdem die DSC-Methode so gut funktionierte, war der nächste logische Schritt, die PS-Lösungen direkt in den Injektor zu injizieren, mit anderen Worten, das CIS zur thermischen Desorption zu verwenden. Erste Ergebnisse waren ermutigend und es kann vorhergesagt werden, daß es möglich ist, eine ausreichende Zahl von Analysen durchzuführen bevor die Zersetzung des sich akkumulierenden Polymers die Quantifizierung beeinträchtigen und einen Ersatz des (CIS-) Glasliners erforderlich machen wird. Die Technik hat eine Reihe von Vorteilen: Alle mit der TDS (Kontamination) und mit dem Transfer zum CIS (Verlust von Analyten) verbundenen Probleme werden eliminiert, die Analysenzeit wird verringert, es könnte möglich sein, einen Autosampler zu verwenden oder sogar Large-Volume Injektionen durchzuführen, um die Empfindlichkeit zu vergrößern. Die 'normale' Thermodesorption bleibt natürlich die Methode der Wahl für die Produkt*identifizierung*, aber in Ringversuchen oder Routineanalysen könnten *bekannte* Radiolyseprodukte gemessen werden, indem das CIS (oder ein anderer PTV-Injektor) als Thermodesorptionseinheit verwendet wird.

Die ‘direkte’ Thermodesorption mit einem PTV-Injektor wurde kürzlich auch von van Lieshout et al. (1997) zur Charakterisierung geologischer Gesteins- und Kohleproben eingesetzt, dabei wurden Probenmengen von 1 bis 10 mg direkt in den Glasliner des PTV-Injektors eingewogen. Diese Technik kann sicherlich auch mit Polymerpulvern und dem CIS verwendet werden, obwohl der Glasliner des CIS wesentlich dünner ist als der des erwähnten PTV-Injektors (1 mm vs. 3.4 mm innerer Durchmesser). Hilfreich wäre auch eine konstruktive Veränderung des CIS, um ein häufiges Auswechseln des Glasliners zu erleichtern.

Auflösung-Ausfällung

Ein Auflösungs-Ausfällungs-Experiment zeigte, daß eine bestimmte Fraktion der Radiolyseprodukte—ca. 25-30% des Acetophenons und ca. 5% des 1-Phenylethanols—wahrscheinlich als thermische Abbauprodukte von makromolekularen, strahlen-induzierten Vorstufen (Precursoren) entsteht. Der Rest, d. h. 70-75% des Acp und 95% des 1-Pet, ist entweder wirklich nach der Bestrahlung vorhanden—oder ein Artefakt, das aus der niedermolekularen Fraktion entsteht. Die Daten bestätigen die Beobachtung, daß die Produkte (seien sie real vorhanden oder nicht) in beträchtlichem Ausmaß mit der niedermolekularen Fraktion assoziiert sind.

14.7 Identifizierung von Spuren-Radiolyseprodukten

Experimente mit höheren Einwaagen (i. d. R. 50 mg) wurden bei verschiedenen Gelegenheiten und mit drei verschiedenen Säulen durchgeführt. Es scheint, daß die resultierende Zunahme der Empfindlichkeit etwas geringer ist als erwartet, möglicherweise weil der ‘unspezifische’ chemische Hintergrund gleichzeitig zunimmt, der sehr kleine Peaks verdeckt und eine Identifizierung von (Ultra-) Spurenverbindungen schwieriger macht.

Die Gegenwart einiger Spurenprodukte, die zuerst in einem ‘primitiven’ Phase I-Experiment (direkte Desorption von Pellets) beobachtet worden waren, konnte bestätigt werden, z. B. von 2-Phenylpropenal und 1-Phenyl-1-propanon. Einige ‘neue’ Produkte wurden ebenfalls gefunden, z. B. 2-Hydroxy-1-phenylethanon und 1-Phenyl-1,2-ethandiol. All diese Produkte sind oxidierte aromatische Verbindungen und ihre Konzentrationen werden auf ca. 0.1 bis 1 ppm geschätzt. (Ein nicht-oxidiertes Spuren-Produkt ist Benzol, siehe weiter unten.) 1-Phenyl-1-propanon kann möglicherweise als ein weiterer *Marker* für den Bestrahlungsnachweis verwendet werden. 1-Phenyl-1,2-ethandiol ist möglicherweise ein strahlen-spezifisches Produkt, aber seine Abwesenheit in unbestrahltem PS muß in künftigen Untersuchungen noch bestätigt werden. Benzoesäure sollte wahrscheinlich zu den ‘Hauptprodukten’ gezählt werden; ihre Konzentration nach 25 kGy könnte bis zu 10 ppm betragen (Schätzung).

14.8 Quantifizierung von Benzol

Die Konzentration von Benzol wurde in Polystyrol-Molekulargewichts-Standards bestimmt, die gerade mit relativ hohen Dosen unter Vakuum und in Sauerstoff bestrahlt worden waren als die Entwicklung der Benzol-Methode abgeschlossen war. Die Konzentrationen von Benzol sind ca. 2.5-mal höher unter Vakuum als in Sauerstoff, was darauf hindeutet, daß O_2 in irgendeiner Weise mit der Benzol-Abspaltung interferiert; die strahlenchemischen Ausbeuten sind ca. 1.16 nmol/J unter Vakuum und ca. 0.46 nmol/J in Sauerstoff.

Basierend auf der Annahme, daß Benzol in einer *Eliminations*-Reaktion entsteht, die unabhängig von der Molekülmassen-Verteilung des Polymers ist, wurden die Benzol-Konzentrationen für medizinisch verwendetes Polystyrol extrapoliert: Nach einer Sterilisationsdosis von 25 kGy enstehen demnach ca. 0.9 ppm (in O_2) und ca. 2.3 ppm (unter Vakuum). Diese

Werte sind konsistent mit der Größe des Benzol-Peaks in früheren qualitativen Chromatogrammen, und es wird vorgeschlagen, die Vakuum-Daten als 'Worst-Case-Scenario' für die Sicherheitsbewertung bestrahlter Produkte bzw. Packmittel zu verwenden (vgl. Kapitel 15.4 *Sicherheitsaspekte*).

14.9 Reale Produkte oder Artefakte der Thermodesorption ?

Die Möglichkeit, daß die analysierten Verbindungen thermische Abbauprodukte von strahlen-induzierten, makromolekularen Vorstufen wie z. B. Peroxiden oder Hydroperoxiden sind, ist mehrfach erwähnt worden (z. B. in Verbindung mit den Abbildungen 7.2 und 7.3 oder mit Tabelle 9.2). Der Verdacht auf eine solche 'Niedrigtemperatur-Pyrolyse' drängte sich zum ersten Mal bei der Temperatur-Meßreihe mit LDPE auf (Kapitel 5.5 und 5.6), als die oxidierten Radiolyseprodukte des PE linear mit der Desorptions-Temperatur anstiegen, während die Rest-Kohlenwasserstoffe (Oligomere) dies nicht taten. Demgegenüber wurde die Tatsache, daß die Radiolyseprodukte von PS ein Plateau erreichen (wie Styrol oder das Styrol-Dimer), anfänglich als Argument für die reale Existenz dieser Produkte interpretiert.

Die unterschiedlichen Temperatur-Effekte in LDPE und PS haben mit Sicherheit irgendwelche Gründe, aber sie beweisen natürlich überhaupt nichts, und es könnte gut möglich sein, daß *alle* niedermolekularen Radiolyseprodukte in einem Pyrolyseprozeß bei (relativ) niedrigen Temperaturen entstehen. Alle Radiolyseprodukte würde nicht nur die durch Thermodesorption, sondern auch die durch Dynamische Headspace-Analyse bestimmten einschließen —mit anderen Worten, die von Azuma et al. (1983, 1984a, b), Rojas de Gante und Pascat (1990) etc. identifizierten Produkte könnten ebenfalls Artefakte sein.

Andererseits kann nicht ausgeschlossen werden, daß die Produkte real sind und es existieren verschiedene Beobachtungen, die diese Interpretation zu stützen scheinen:

(1) Die gasförmigen Radiolyseprodukte von Polymeren (H_2, CH_4, CO, CO_2, etc.) sind vergleichsweise gut untersucht,[#] und niemand hat jemals vorgeschlagen (und es gibt wenig Grund zu der Annahme), daß sie Artefakte der verwendeten Analysentechniken sind. Man könnte also argumentieren: Wenn strahlen-induzierte Oxidation (ionisierende Strahlung in Gegenwart von Sauerstoff) 'reales' CO und CO_2 erzeugt, warum sollte sie nicht auch 'reale' niedermolekulare Alkohole, Aldehyde, Ketone etc. erzeugen ? Die Oxidation beginnt vielleicht mit Peroxiden, aber sie verläuft mit Sicherheit über Alkohole zu Aldehyden/Ketonen und schließlich zu Carbonsäuren, und diese sind wahrscheinlich die Vorstufen von CO und CO_2—warum sollten sie also nicht auch selbst real vorhanden sein ?

(2) Fehlgerüche ('off odours' und 'taint transfer') bei der Bestrahlung von Kunststoffen wurden schon mehrfach beschrieben (Kilcast, 1990; Azuma et al., 1984b; Tripp, 1959); diese sensorischen Veränderungen müssen eine molekulare Basis haben, und die Annahme liegt nahe, daß sie exakt von solchen Verbindungen verursacht werden, die mit der TDS analysiert werden, d. h. von kleinen und mehr-oder-weniger flüchtigen organischen Verbindungen. Es existieren flüchtige Verbindungen mit extrem niedrigen Geruchsschwellen und Koszinowski und Piringer (1983) haben sogar die menschliche Nase als GC-Detektor eingesetzt, um flüchtige Verbindungen in Lebensmittelverpakkungen zu charakterisieren.

(3) Es scheint außerdem so zu sein, daß die (oder wenigstens einige der) Radiolyseprodukte von Phenol-Antioxidantien 'real' sind (vgl. Kapitel 2.4): Sie wurden in TDS / Dynamischen Headspace-Analysen beobachtet, sie wurden speziell mittels HPLC-MS und

[#] Siehe Hill et al. (1989) für eine umfassende Zusammenstellung von G-Werten; oder die Arbeiten von Killoran (1972), Bersch et al. (1959) und Tripp (1959), die sich direkt auf Lebensmittel-Verpackungen beziehen.

einer Reihe weiterer Techniken untersucht und sie wurden nach Migrationsversuchen in den Kontakt-Lösemitteln gefunden. Insgesamt sind die Beweise für die reale Existenz dieser Abbauprodukte überwältigend, und dasselbe gilt für die Radiolyseprodukte von Organozinn-Stabilisatoren in PVC (Allen et al., 1987c; Haesen et al., 1983).

Implikationen ...

... für die Analyse von Radiolyseprodukten ...

Letztlich könnte man sogar postulieren, daß auch die Radiolyseprodukte, die man bei Migrations- / Extraktionsversuchen findet, durch irgendeinen lösungsmittel-induzierten Abbau strahleninduzierter makromolekularer Vorstufen entstehen (also in einem Prozeß, den man mit Wasser als Extraktionsmedium ‘Hydrolyse’ nennen würde). Dies würde implizieren, daß es keine Möglichkeit gibt herauszufinden, ob ein Radiolyseprodukt real ist oder nicht, und daß die einzig sinnvolle Strategie wäre, Migrations- / Extraktionsversuche durchzuführen unter Bedingungen, die denen des tatsächlichen Gebrauchs möglichst nahe kommen.

... und für den Status der Thermodesorption als analytischer Technik

Die Thermodesorption sollte als eine komplementäre Technik für die chemische Charakterisierung von Materialien betrachtet werden, als eine Technik die Migrations- / Extraktionsversuche oder Toxizitätsprüfungen von Medikalprodukten nicht ersetzen kann. Es wird deshalb empfohlen:

(1) Die hohe Empfindlichkeit der Thermodesorption zur Identifizierung und Quantifizierung niedermolekularer Radiolyseprodukte—seien sie nun real oder nicht—zu nutzen,

(2) Modellrechnungen durchzuführen, die ein ‘Worst-Case-Scenario’ für das geplante Einsatzgebiet liefern, und dann

—**wenn** solch ein Modell anzeigt, daß es zu einer inakzeptablen Exposition gegenüber toxischen Substanzen kommen könnte—

(3) Migrations- / Extraktionsversuche unter Bedingungen des tatsächlichen Gebrauchs durchzuführen.

Für solche Versuche wird vorgeschlagen, die relativ neuen Techniken der Large-Volume On-Column Injection (LOCI) oder der on-line gekoppelten LC-GC zu verwenden (siehe Anhang 22 *Research Proposal*...).

15. Schlußfolgerungen

Wie in Kapitel 14.1 bemerkt, ist wenig bekannt über einen Aspekt der Strahlensterilisation, der für deren toxikologische Bewertung von zentraler Bedeutung ist, nämlich **die Enstehung niedermolekularer ('flüchtiger') Radiolyseprodukte** (Kapitel 2.3).

Obwohl es immer noch einige ungeklärte Fragen gibt, **zeigt sich uns nun ein viel umfassenderes Bild.** Dieses Bild war *qualitativ* und/oder *semi-quantitativ* in den 'Phasen' I und II (für verschiedene medizinisch verwendete Kunststoffe, und für PE- und PP-Folien—siehe Kapitel 4 und 5), und für Polystyrol haben die Experimente von Phase III bis V dem Bild eine **quantitative Dimension** hinzugefügt (Kapitel 6 bis 11). Bevor ich zur *Sicherheit / Unbedenklichkeit* des Verfahrens komme, möchte ich kurz *analytische Aspekte, strahlenchemische Fragen* und die Aussichten für einen *Bestrahlungsnachweis* diskutieren.

15.1 Analytische Betrachtungen

Die Hersteller von Medikalprodukten müssen bestätigen, daß ihre Produkte und Packmittel mit dem verwendeten Sterilisationsverfahren kompatibel sind (ISO 11607: Packaging for Terminally Sterilized Medical Devices). Dazu müssen die Produkte und Packmittel mit validierten chemischen (und physikalischen) Prüfmethoden evaluiert werden. Im Rahmen der vorliegenden Arbeit wurde *das Potential der Thermodesorption als Methode für die chemische Charakterisierung medizinischer Kunststoffe demonstriert*. Quantitative Desorptionsbedingungen wurden etabliert für die Haupt-Radiolyseprodukte von *Polystyrol*, und eine quantitative Methode zur Bestimmung von Spuren von *Benzol* in PS wurde entwickelt.

Außerdem wurde eine neue Desorptionstechnik, die fast keine Probenvorbereitung benötigt, erfolgreich getestet, nämlich die *Thermodesorption von Polymerlösungen mit Lösungsmittelausblendung* (oder: DSC-Methode); und die Möglichkeit, Polymerlösungen direkt in das CIS zu injizieren (d. h. einen PTV-Injektor für die thermische Desorption zu verwenden), wurde aufgezeigt. Während die 'klassische' Thermodesorption (oder dynamische Headspace-Analyse) eindeutig die Methode der Wahl für die *Identifizierung* flüchtiger Verbindungen bleiben wird, sind die Desorption (mit Lösungsmittelausblendung) oder die direkte Injektion von *Polymerlösungen* interessante Alternativen zur Bestimmung *bekannter* Produkte, z. B. in einer zukünftigen Nachweismethode.

Die flüchtigen / niedermolekularen Radiolyseprodukte von Polymeren sind über mehrere Jahrzehnte strahlenchemischer Forschung hinweg weitgehend mißachtet worden (was insofern teilweise verständlich ist als die Dynamische Headspace-Analyse bzw. Thermodesorption eine *relativ* neue Technik ist). Eine quantitative Bestimmung dieser flüchtigen Produkte könnte helfen, einige grundlegende Probleme der Strahlenchemie von Polymeren aufzuklären (vgl. Schnabel et al., 1991).

Generell ist die Technik äußerst empfindlich, aber gleichzeitig auch recht anspruchsvoll; es wurde gezeigt, daß umfangreiche parallele Test-Programme durchgeführt werden müssen, insbesondere während quantitativer Meßreihen. Weitere Anstrengungen sollten unternommen werden, um Memory-Effekte (durch den 'cold spot') und adsorptive Aktivität im TDS-Injektor zu reduzieren. Aus verschiedenen Gründen—die zusammenhängen mit der externen Standard-(ESTD)-Methode, Memory-Effekten, adsorptiver Aktivität in der TDS, der Frage der strahleninduzierten Artefakte, etc.—sind die mit der Thermodesorption erhaltenen quantitativen Ergebnisse möglicherweise nicht so 'richtig' oder 'wahr' wie man es vielleicht gerne hätte. Dennoch bin ich davon überzeugt, daß bessere quantitative Daten derzeit nicht realisierbar sind.

15.2 Strahlenchemische Betrachtungen

Wir wissen gegenwärtig nichts über die molekularen Mechanismen, die der Entstehung flüchtiger Radiolyseprodukte zugrunde liegen. Wir wissen auch nicht in welchem Ausmaß diese Produkte real sind (siehe Kapitel 14.9 *Reale Produkte oder Artefakte der Thermodesorption ?*). Es gibt einige Hinweise darauf, daß in Polystyrol die *niedermolekulare Fraktion* eine wichtige Rolle bei der Enstehung der Produkte spielt, andererseits scheint es, daß die flüchtigen Verbindungen nicht, oder nur in unbedeutendem Ausmaß, durch Oxidation des Restmonomers *Styrol* gebildet werden.

Die große Mehrheit der Radiolyseprodukte in allen untersuchten Polymeren sind *oxidierte* Verbindungen—eine Ausnahme ist z. B. Benzol in PS. Die Wirkungen von ionisierender Strahlung in Gegenwart von Luft (Sauerstoff) lassen sich wahrscheinlich am besten als Effekte einer **strahlen-induzierten Oxidation** beschreiben: Die Reaktion von Sauerstoff mit organischen Polymer- (oder Additiv-) Molekülen ist—obwohl *thermodynamisch* begünstigt—*kinetisch* gehemmt, und die ionisierende Strahlung liefert einfach die *Aktivierungsenergie* für eine Vielzahl von Oxidationsreaktionen. Aus thermodynamischen Gründen kann man erwarten, daß in Gegenwart von Sauerstoff die Radiolyseprodukte immer *Abbau- oder Fragmentierungs*produkte existierender Strukturen sein werden, und daß es nicht zu einer 'Synthese' von komplexeren Strukturen oder völlig neuen Verbindungen kommen wird.

15.3 Implikationen für einen Bestrahlungsnachweis

Im Vergleich zu den Anstrengungen die unternommen worden sind, um Nachweisverfahren für bestrahlte Lebensmittel zu entwickeln (s. Kapitel 2.5), war die vorliegende Untersuchung nur ein kleines Projekt und wir stehen erst am Anfang einer möglichen zukünftigen Nachweismethode für bestrahlte Kunststoffe.

Die Ergebnise mit den medizinisch verwendeten 'Standard'-Polystyrolen sowie mit einigen kommerziellen und 'realen' Proben zeigen, **daß die Thermodesorption dazu verwendet werden kann, Artikel aus Standard-Polystyrol zutreffend als strahlensterilisiert zu identifizieren,** d. h. als bestrahlt mit Dosen im Bereich von 25 kGy. Sie zeigen außerdem, daß die gleichzeitige Bestimmung von zwei oder mehr Radiolyseprodukten wahrscheinlich die Zuverlässigkeit und/oder Empfindlichkeit des Nachweisverfahrens erhöht, und daß es deshalb möglich sein könnte, die Methode für die niedrigeren Dosen zu optimieren, die gewöhnlich bei der Lebensmittelbestrahlung eingesetzt werden.

Weitere experimentelle Daten sind eindeutig notwendig, um diesen Ansatz auf **Styrol-Copolymere** zu übertragen; dies wird ein besseres Verständnis der zugrunde liegenden strahlenchemischen Reaktionen erfordern (oder wenigstens der Beziehung zwischen Polymerstruktur und den resultierenden Poduktkonzentrationen). Vermutlich müssen auch weitere Techniken, wie z. B. IR-Spektrometrie, eingesetzt werden, um zusätzliche Informationen über die jeweils untersuchten Copolymere zu erhalten.

Die Daten, die während des anfänglichen Screening-Programms (Kapitel 4) erhalten wurden, erlauben die Vermutung, daß es möglich sein sollte, Nachweisverfahren für strahlensterilisiertes **Polypropylen, Polyvinylchlorid** und eventuell für **Polyamide** zu entwickeln, während eine solche Einschätzung für High-Density Polyethylen weniger eindeutig ist. Im Falle von **PP und PVC** würde die Nachweismethode auf den Abbauprodukten von Additiven (Antioxidantien, Stabilisatoren) beruhen, die in strahlenstabilen Typen dieser Polymere immer enthalten sind. Im Falle der Phenol-Antioxidantien scheinen Spurenprodukte mit atypischen / strahlenspezifischen Strukturen zu existieren (Kapitel 4.6 und 5.10), und es ist vorstellbar, daß andere Additive ebenfalls Spurenmengen atypischer Fragmente liefern. Beim **PA-6** könnte der Nachweis auf der Bestimmung von Pentanamid oder eventuell sogar der 'Spurenamide' basieren.

Obwohl es relativ einfach erscheint zu entscheiden, ob PS strahlen*sterilisiert* wurde oder nicht, wird der Nachweis einer Bestrahlung bei niedrigeren Dosen sicherlich sehr viel schwieriger sein, denn (1) ein 'strahlenspezifisches' Produkt, das in unbestrahltem PS definitiv nicht vorhanden ist, wurde bis jetzt nicht gefunden, und (2) die Produktausbeute variiert möglicherweise in gewissem Ausmaß mit der untersuchten Polystyrol-Type und/oder sie wird beeinflußt von denselben Umgebungsfaktoren, die sich auf die Response von Dosimetern auswirken (siehe Kapitel 2.5).

Ein vielversprechender Ansatz für ein Nachweisverfahren könnte die **multivariate Datenanalyse** oder **Pattern-Recognition-Analyse** der massenspektrometrischen Daten sein. Tayler at al. (1989) haben eine solche Technik (principal components analysis, PCA) erfolgreich eingesetzt, um verschiedene (unbestrahlte) Polypropylen-Typen anhand ihrer *TDS-GC*-Massenspektren zu unterscheiden (vgl. Kapitel 2.8). Verwandte Techniken, die neuronale Netze (**artificial neural networks;** ANNs) verwenden, sind zur Auswertung von *Pyrolyse*-Massenspektren verwendet worden; z. B. haben Goodacre et al. (1992) gezeigt, daß Pyrolyse-MS kombiniert mit einem ANN eine Unterscheidung zwischen reinen und verfälschten Olivenölen erlaubt.

15.4 Sicherheitsaspekte (Unbedenklichkeit der Strahlensterilisation)

Allgemeine / qualitative Betrachtungen

Medikalprodukte

Wenn man die Fingerprint-Chromatogramme der medizinisch verwendeten Polymere betrachtet, scheint es, daß—mit Ausnahme von PP—die *Konzentrationen* der Radiolyseprodukte unbedeutend sind verglichen mit den Konzentrationen der Restmonomere/-oligomere (oder, im Falle von PVC, verglichen mit der Konzentration von 2-Ethyl-1-hexanol). Man könnte außerdem argumentieren, daß die oxidierten Produkte, z. B. von PS oder PE, in der Regel weniger toxisch sein sollten als Styrol bzw. die Kohlenwasserstoffe. Anlaß zu Besorgnis könnten eventuell die Spuren von *Benzol* in PS sein (vgl. dazu weiter unten) sowie die relativ großen Mengen von *1,3-bis-(1,1-Dimethylethyl)-benzol* in PP.

Solange wir akzeptieren, daß Kunststoff-Formulierungen, deren genaue Zusammensetzung Firmengeheimnis ist, als 'Biomaterialien' qualifiziert werden, wenn sie den Anforderungen bestimmter Prüfprotokolle entsprechen, solange dürfte es schwierig sein, von Polymeren die unbekannte Radiolyseprodukte enthalten, mehr zu verlangen als den Anforderungen einer solchen 'Black-Box-Toxikologie' zu entsprechen. Auf der anderen Seite zeigen die Ergebnisse des anfänglichen Screening-Programms (Kapitel 4) sehr eindrücklich

- daß ionisierende Strahlung in der Tat eine Wirkung auf (medizinische) Kunststoffe hat;
- daß sie bedeutende Mengen von 'flüchtigen' Verbindungen erzeugen kann, die bei einer 'normalen' Verarbeitung nicht entstehen;
- daß es unumgänglich ist, eine qualifizierte Produkt-Validierung *nach dem* letzten Verarbeitungsschritt durchzuführen, sei dies die Strahlensterilisation oder irgendein anderes Verfahren;
- und, schließlich, daß die für *eine* Sterilisationsmethode erhaltenen Ergebnisse nicht notwendigerweise auch für eine *andere* gelten.

Ob die mit der Thermodesorption identifizierten Radiolyseprodukte wirklich signifikant im toxikologischen Sinne sind, d. h. ob sie ein potentielles Gesundheitsrisiko darstellen, kann natürlich nicht mit TDS-Analysen alleine abgeschätzt werden. Es sollte außerdem bedacht werden, daß die Bestrahlung möglicherweise auch höhermolekulare Analoge dieser Produkte erzeugt. Diese könnten, obwohl unter den Bedingungen der Thermodesorption nicht

flüchtig, mobil genug sein, um von Medikalprodukten oder Verpackungsmaterialien freigesetzt zu werden.

Verpackungen für Lebensmittel

Eine vorläufige Sicherheitseinschätzung für bestrahlte Lebensmittelverpackungen würde sehr ähnlich aussehen: Von den meisten Radiolyseprodukten kann angenommen werden, daß sie weniger toxisch sind als das bereits vorhandene niedermolekulare Material, und ihre Konzentrationen scheinen marginal zu sein. Wiederum könnten Benzol in PS und die Abbauprodukte von Antioxidantien in PP Anlaß zu Besorgnis sein.

Unbestrahlte Verpackungsmaterialien müssen die Anforderungen von *globalen* (und teilweise auch *spezifischen*) *Migrationstests* erfüllen. In der Europäischen Union gelten gegenwärtig globale Migrationsgrenzwerte von 10 mg/dm^2 oder 60 mg/kg (bezogen auf die Kontaktfläche bzw. die Lösungsmittelmenge); spezifische Grenzwerte existieren z. B. für Vinylchlorid (0.01 mg/kg), oder Caprolactam (15 mg/kg).

Das einzige Problem mit der Bestrahlung ist folglich: *Wollen wir bestrahlte Materialien akzeptieren, die die Anforderungen dieser Tests erfüllen—auch wenn sie Verbindungen freisetzen, die man normalerweise nicht in Lebensmittelverpackungen findet (z. B., weil sie 'strahlenspezifisch' sind) ?* Können wir annehmen, daß ein (gravimetrischer) Migrationstest empfindlich genug für jedes denkbare Radiolyseprodukt ist ? Oder, um es anders auszudrücken, wenn wir spezifische Migrationslimits für Vinylchlorid oder Caprolactam brauchen, können wir *ausschließen*, daß wir einen Grenzwert z. B. für 1,3-bis-(1,1-Dimethylethyl)-benzol brauchen ?

Quantitative Betrachtungen (mit Betonung auf Polystyrol)

Das Konzept quantitativer *Dosis-Wirkungs-Beziehungen* spielt eine zentrale Rolle in der Toxikologie, und deshalb wurden beträchtliche Anstrengungen unternommen, quantitative Ergebnisse zu erhalten, d. h. die tatsächlichen Konzentrationen der Radiolyseprodukte zu bestimmen. Die Bedeutung dieses Konzepts wurde bereits vor mehr als vierhundert Jahren von Paracelsus (1493–1541) erkannt, und obwohl sich die moderne Toxikologie nicht mehr ausschließlich mit 'Giften' und 'Arzneien' beschäftigt, wird sein berühmter Satz „SOLA DOSIS FACIT VENENUM" noch heute in führenden Lehrbüchern zitiert (Klaassen, 1985b):

> „Alle Substanzen sind Gifte; es gibt keine die kein Gift ist. *Die richtige Dosis unterscheidet die Arznei vom Gift.*"

Mit den für Polystyrol erhaltenen quantitativen Daten können wir nun *Worst-Case-Scenarios* für die Freisetzung von Radiolyseprodukten aus bestrahlten Kunststoffen berechnen, die bei einer Verwendung als Verpackungsmaterial oder in einem Medikalprodukt auftreten könnten. Für eine Verpackung könnte eine solche Modellrechnung wie folgt aussehen:

Wir nehmen einem vollständigen Transfer niedermolekularer Verbindungen aus einem Kunststoffbeutel in dessen flüssigen Inhalt an. Der Beutel habe die Form eines Würfels von 10 cm Kantenlänge, sein Volumen ist folglich 1000 cm^3 (und seine Oberfläche 600 cm^2). Die Dicke der Folie sei 25 µm (eine recht typische Größe); die Dichte, sowohl der Kunststofffolie als auch des flüssigen Inhalts sei 1 g/cm^3; die Masse der Folie ist also 1.5 g, die des Inhalts 1 kg.[#]

[#] Ein geometrisch ähnliches Konzept liegt dem 60 mg/kg-Grenzwert für die Globalmigration der EC-Direktive 90/128/EEC vom 23. Februar 1990 zugrunde, die sich auf Kunststoffmaterialien und -artikel bezieht, „die dazu bestimmt sind mit Lebensmitteln in Kontakt gebracht zu werden."

Dieses Modell kann sehr leicht auf andere Anwendungen übertragen werden, wie z. B. den Substanztransfer aus einer Schale ('Tray'), aus einem Infusionsbehälter oder einem Blutbeutel; wenn das Kontaktmedium eine wässrige Lösung ist, werden wir immer noch auf der sicheren Seite sein, wenn wir annehmnen, daß die Interaktion nur mit einer Oberflächenschicht von 25 oder 50 µm erfolgt (vgl. dazu weiter unten).

Wir können nun die Konzentrationen berechnen, die aus dem vollständigen Transfer eines Produkts in das Kontaktmedium resultieren—siehe Tabelle 13.1 in Kapitel 13.4.

Es sei nochmals darauf hingewiesen, daß diese Modellrechnung **ein Worst-Case-Scenario** liefert, das die resultierenden Konzentrationen absichtlich überschätzt,

– weil in der Wirklichkeit kein vollständiger Substanztransfer stattfinden wird, jedenfalls nicht mit wässrigen Kontaktmedien,[#]
– weil die Produkte zu einem gewissen Anteil Artefakte der Thermodesorption sein könnten, und
– weil sie in unterschiedlichem Ausmaß bereits in den unbestrahlten Vergleichsproben enthalten sind.

Es muß außerdem noch angemerkt werden, daß diese Modellrechnung nur dazu dient, die **Größenordnung** einer möglichen Freisetzung von niedermolekularem Material zu veranschaulichen und wenig praktische Relevanz hat, da Standard-Polystyrol typischerweise nicht für flexible Verpackungen oder Blutbeutel verwendet wird.

Wie bereits während des anfänglichen Screening-Programms (vgl. Kapitel 4.1) festgestellt, liegen die Konzentrationen der Radiolyseprodukte mindestens um eine Größenordnung unter der des Restmonomers Styrol. Insgesamt liegen die Produktkonzentrationen in unserem hypothetischen Kontaktmedium im unteren ppb (µg/kg)-Bereich (s. Tabelle 13.1), und damit vermutlich weit unter einem Level, das Anlaß zu Besorgnis geben könnte. Ob wir eine 'Kontamination' dieser Größenordnung akzeptieren wollen, wird von der zu erwartenden Exposition gegenüber den fraglichen Substanzen abhängen, d. h. letztlich von der geplanten Verwendung eines Produkts oder Verpackungsmaterials.

Im **medizinischen Bereich** werden wir bereit sein höhere Risiken zu akzeptieren, insbesondere bei lebensrettenden Anwendungen; generell wird die Nutzen-Risiko-Abschätzung für ein Medikalprodukt ähnlich aussehen wie die für ein Arzneimittel.

Was die **Lebensmittelverpackung** angeht, so möchte ich im Moment nicht auf die potentiellen Vorteile der Lebensmittelbestrahlung eingehen, sondern nur auf die potentiell mit den Radiolyseprodukten verbundenen Risiken.

Zur Zeit gibt es keine Grenzwerte für die spezifische Migration der Verbindungen, die in dieser Untersuchung als Radiolyseprodukte von PS identifiziert wurden (de facto existieren solche Grenzwerte nur für Vinylchlorid und Caprolactam). Die Frage bleibt deshalb offen: Wenn ein bestrahlter Kunststoff die Anforderungen eines Globalen Migrationstests (< 10 mg/dm^2 oder 60 mg/kg) erfüllt, können wir sicher sein, daß wir nicht ein spezifisches Limit für die (oder einige der) Radiolyseprodukte brauchen ? Immerhin sind einige der Produkte in den unbestrahlten Materialien praktisch nicht vorhanden und wurden wahrscheinlich bei der Festlegung der Grenzwerte nicht berücksichtigt.

[#] Wässrige Medien treten nur mit der Oberfläche lipophiler Verpackungsmaterialien in Wechselwirkung, und die Migration ist „in den meisten Fällen außerordentlich klein" (Figge, 1996). Lipophile Kontaktmedien (Fette, Öle) dringen in den Kunststoff ein und führen zur Entstehung einer strukturell gelockerten und kontinuierlich expandierenden Mischphase, die größere Mengen an niedermolekularem Material freisetzt. Die beiden Fälle sind beschrieben worden als „Multikomponenten-Zwei-Phasen-System mit einer ... konstanten Phasengrenze" bzw. als „Multikomponenten-Multi-Phasen-System mit sich bewegenden Phasengrenzen" (Figge, 1996).

Abschließend soll noch kurz auf **Benzol** eingegangen werden, das Radiolyseprodukt das vielleicht am meisten Grund zu Besorgnis gibt, da es hochtoxisch ist (Klaassen, 1985a), als nachgewiesenes Carcinogen gilt, und als Mutagen. Da Benzol auch im bestrahlten MABS (Kapitel 4.2) nachgewiesen wurde, muß außerdem damit gerechnet werden, daß es möglicherweise in allen Styrol-basierten Polymeren entsteht.

Die Benzol-Konzentrationen in unserer Modellrechnung liegen noch unterhalb des derzeit geltenden Grenzwertes der U. S. EPA (Environmental Protection Agency) von 5 ppb *für Trinkwasser*. In wässrigen Kontaktmedien werden die tatsächlichen Benzol-Konzentrationen natürlich noch deutlich geringer sein. Außerdem ist zu erwarten, daß bestrahlte Styrol-basierte Verpackungen insgesamt zu einer geringeren Benzol-Belastung führen als 'Umwelt'-Quellen, wie z. B. Tabakrauch oder Benzin. Andererseits möchte man wahrscheinlich nicht unbedingt ein Carcinogen in einem Joghurtbecher haben, der für eine aseptische Befüllung sterilisiert worden ist, und viele Wissenschaftler glauben, *daß es für die Exposition gegenüber einem Carcinogen keinen sicheren Grenzwert gibt*.

Appendices

List of Appendices

Appendix 1

Pre-Phase III: The Way to Quantitation

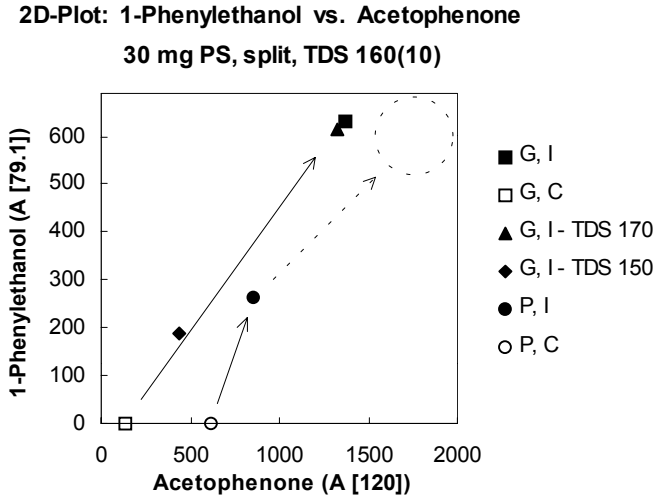


Figure A-1.1 **Qualitative comparison** of PS specimens analyzed as powder: 2D-Plot: 1-Phenylethanol vs. acetophenone.
G, C = granulate control G, I = granulate, irradiated (25.5 kGy)
P, C = inj.-molded parts, control P, I = parts, irradiated (24.7 kGy)
To reduce weighing errors **30 mg powder** were desorbed and analyzed in **split-mode.** The P, I data (black circle) appear to be somewhat out-of-range — one would expect P, I in the upper right corner of the plot (compare the 2D-plot in Figure 6.1 and the later quantitative results). Since increasing the TDS-temperature above 160°C appeared to have no effect, only a limited number of experiments were performed in the subsequent TDS-temperature study (namely, 155°C, 165°C and 175°C — see Figure 6.2.)
Exp. Condit.: TDS X°C (10 min); CIS -40; GC 40(11.5) -40- 180 -10- 250(13); col.: Rtx-1701.

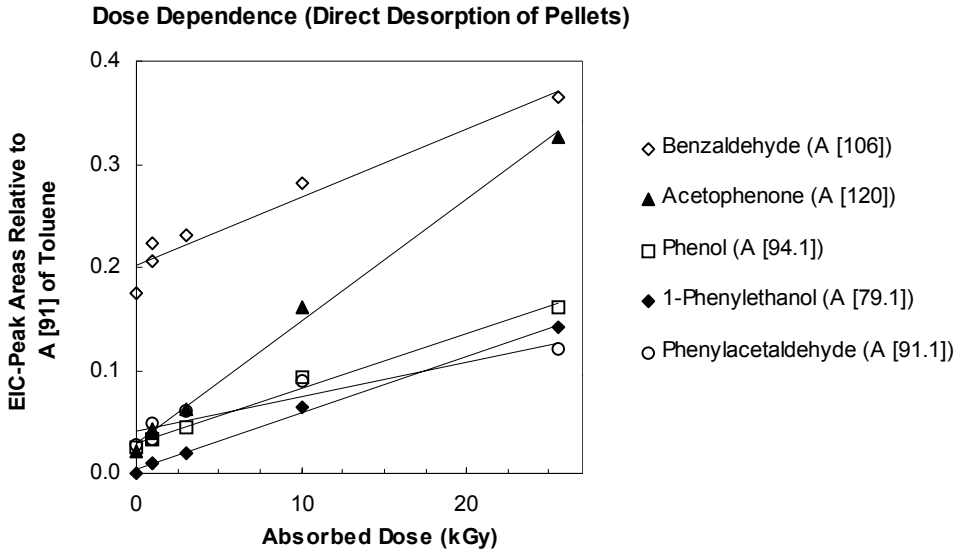


Figure A-1.2 **Relative peak areas** of radiolysis products **vs. the absorbed dose** — direct desorption of PS granulate (PS 168 N).
Exp. Conditions: **5 pellets**, **eight days** after irradiation with 1, 3, and 10 kGy, and 15 months after 25.5 kGy; TDS 160(10); CIS -40; GC 40(11.5) -40- 180 -10- 250(13); col.: Rtx-1701.

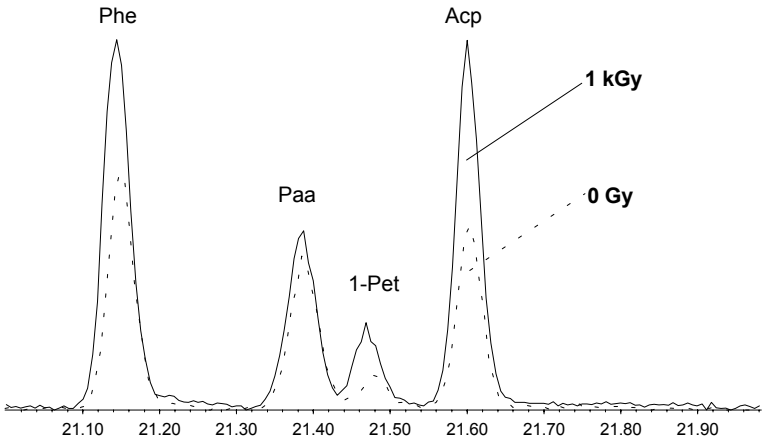


Figure A-1.3 **PS pellets 1 kGy** vs. non-irradiated control at **TDS 240°C** — detail t_R 21 to 22 min of fingerprint chromatograms obtained two weeks after irradiation; **direct desorption of the granulate** (PS 168 N).
The two runs at 240°C were performed as a supplement to the dose series in Figure A-1.2, to confirm that there was an observable effect of an absorbed dose of only 1 kGy. Exp. Conditions: **5 pellets;** TDS 240(10); CIS -40; GC 40(11.5) -40- 180 -10- 250(13); col.: Rtx-1701.

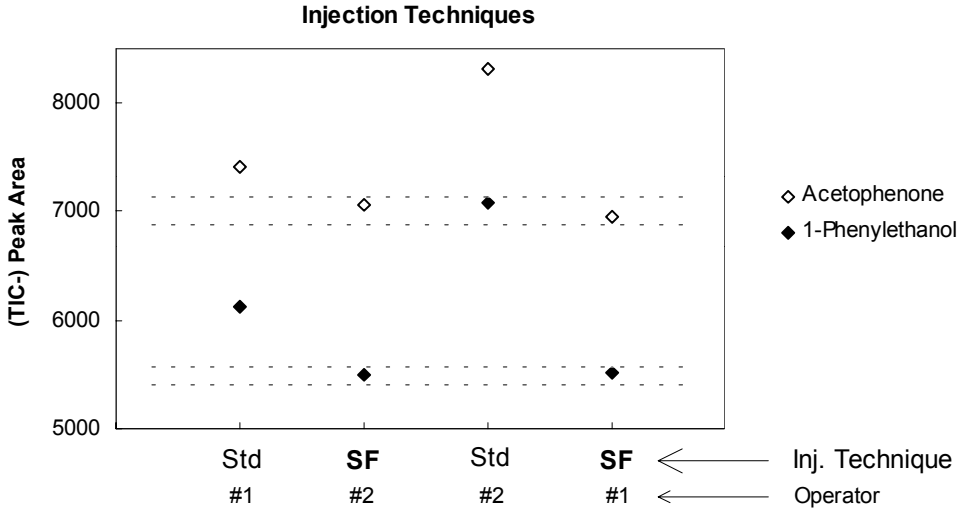


Figure A-1.4. Comparison of standard (Std) and **solvent-flush** (SF) injection techniques: Peak areas of 1-phenylethanol and acetophenone in four consecutive injections of a 10 ppm solution (in hexane) performed by two operators.
Experimental Conditions: CIS 30; GC 40(1.5) -40- 250(x); column: Rtx-1701.

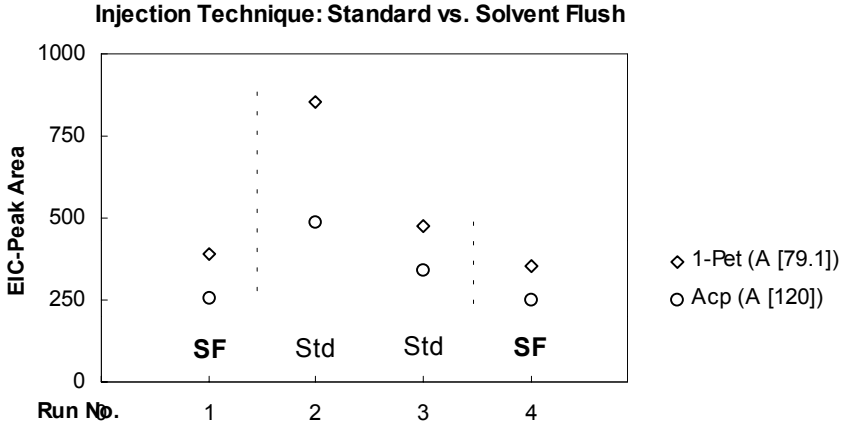


Figure A-1.5 **Solvent-flush** (SF) vs. standard (Std) injection technique: (EIC-) peak areas of 1-phenylethanol and acetophenone in four consecutive injections.
Exp. Condit.: 1 µl 5 ppm STD; CIS 30; GC 40(1.5) -10- 100 -20- 250(5); col.: DB-5; MS: SIM.

Appendix 2

System Characterization for Phase III

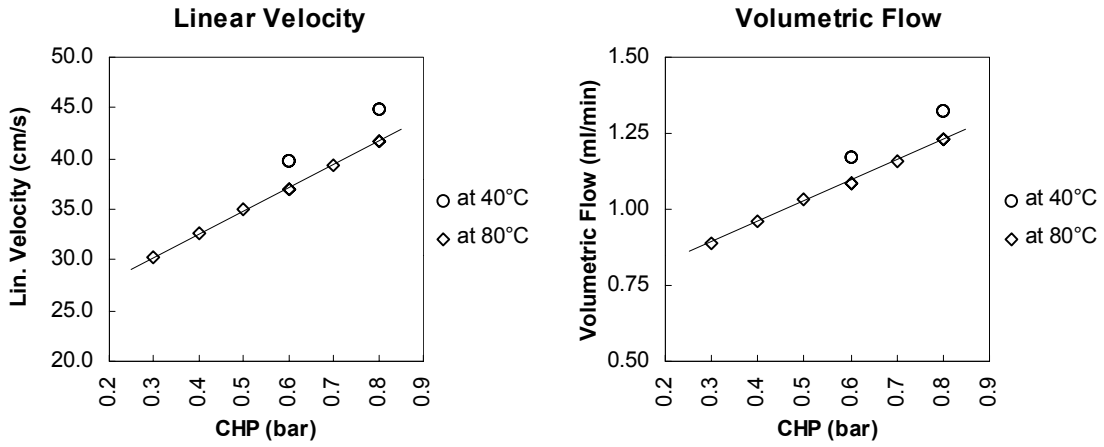


Figure A-2.1 **Linear velocity** (cm/s) & **volumetric flow** (ml/min) vs. column head pressure.
Values determined at 40°C and 80°C by injecting small volumes of air in **split-**mode. CIS: 30°C [80°C], split; GC: 40°C [80°C]; column: DB-5, 30 m, 0.25 mm i. d., 0.25 µm f. t.; MS: Scan 15-100. Calculated with an assumed *actual* length of 25 m (vs. the original 30 m).

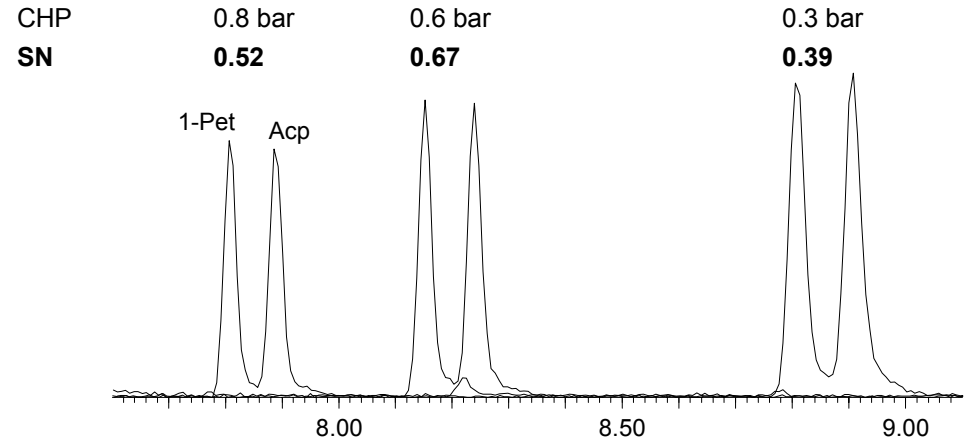


Figure A-2.2 **Separation number (SN)** for 1-phenylethanol and acetophenone at different column head pressures (CHP): Differences are marginal on the DB-5 column.
Exp. Conditions: 1 µl 10 ppm STD; CIS 30; GC 40(1.5) -10- 250(5); column: DB-5.

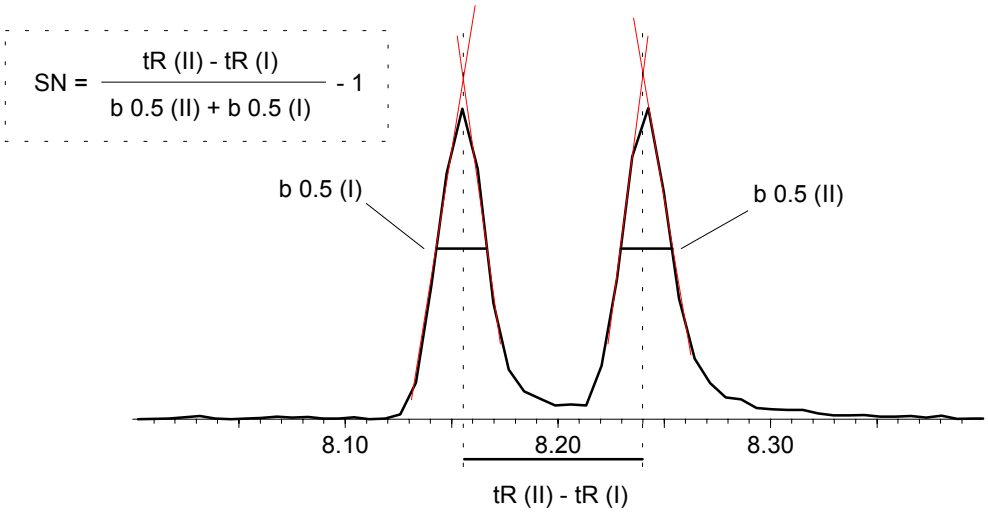


Figure A-2.3 Determining the separation number (SN).
Detail of another chromatogram recorded at a CHP of 0.6 bar; the resulting SN is now 0.58 (compared to 0.67 at 0.6 bar in Figure A-2.2). Overall, the two Figures indicate that the carrier gas velocity (which is a function of column head pressure) has only a negligible effect on the separation of 1-Pet and Acp *on the apolar DB-5 column*.
Exp. Conditions as in Figure A-2.2 (CHP = 0.6 bar)

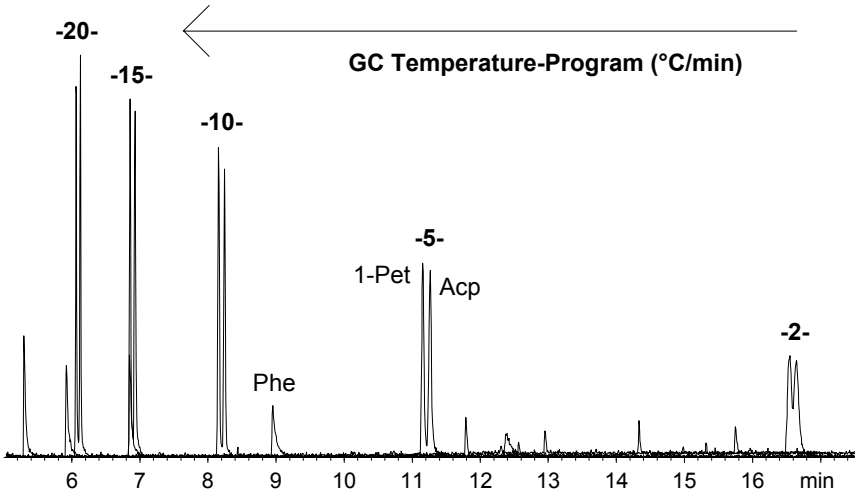


Figure A-2.4 Retention times and peak shapes of phenol, 1-phenylethanol, and acetophenone with different **GC temperature-programs.**
Exp. Conditions: 1 µl 10 ppm Standard, CIS 30, splitless 90 sec; GC 40 (1.5) **-X-** 250(5); column: DB-5.

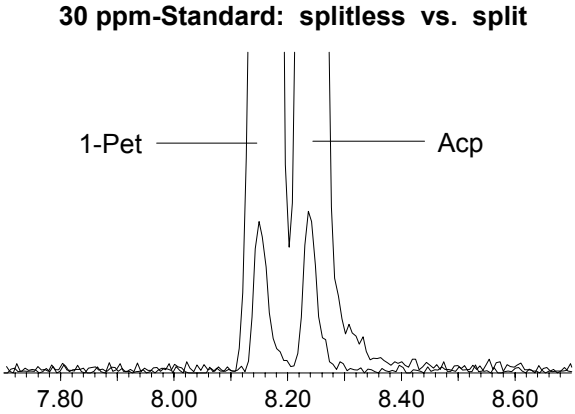


Figure A-2.5 Comparing splitless and split-injections (cf. Table A-2.1, below).

Table A-2.1 **Peak areas** (arbitrary units) for Figure A-2.5 (split / splitless-injections).

	A split	A splitless	**Ratio** split / splitless
1-Phenylethanol	413	9765	0.04
Acetophenone	414	9901	0.04
Calculated Split Ratio [a]	----	------	0.03

[a] Calculated for a 'total' flow of 30 ml/min and an estimated column flow of 1 ml/min.

Exp. Conditions: 1 µl of a 30 ppm standard (1-Pet, Acp in hexane); CIS 30, splitless 90 s or split; GC 40(1.5) -10- 250(5); column: DB-5.

Appendix 3

Phase III: TDS-Quantitation: The SPLIT-Scan Series

A chromatogram of the split-scan-series (PS 168 N 25.5 kGy; 5 mg) is shown in Figure 7.1 (Chapter 7) vs. an injected 1-Pet:Acp-standard (30:300 ppm).

Table A-3.1 Calibration data.

File	c Pet (ppm)	c Acp (ppm)	A [79.1]	A [120]
503-04	20.8	202	38	232
-05	20.8	202	33	239
-06	10.4	101	---	125
-07	31.2	303	51	320
-08	52.0	505	96	601
-09	31.2	303	68	428

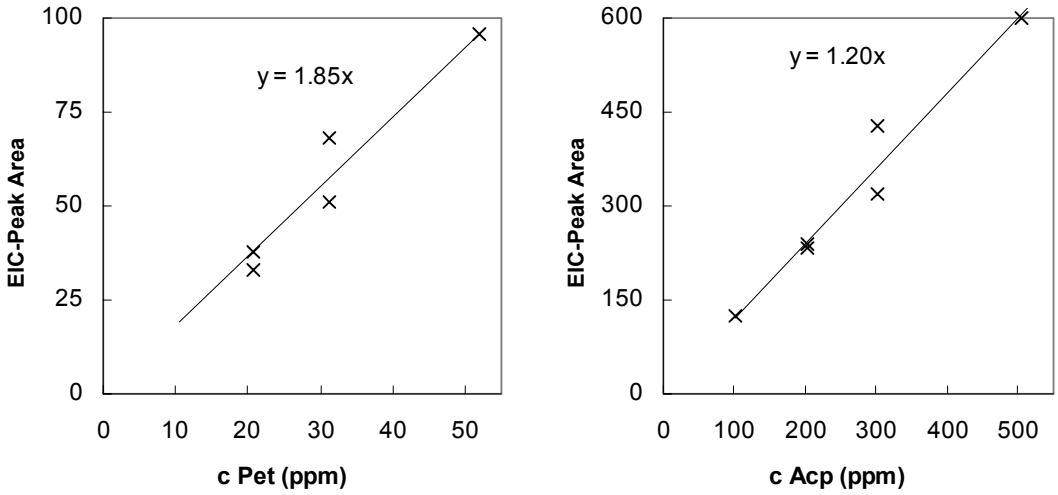


Figure A-3.1 Calibration curves.

Table A-3.2 Polystyrene data.

File	Code	Dose (kGy)	A [79.1]	A [120]	**1-Pet** (ppm)	**Acp** (ppm)
503 03	P, I	24.7	77	335	8.3	55.8
10	P, I	24.7	75	324	8.1	54.0
11	P, I	24.7	79	319	8.5	53.2
504 04	1 kGy	1.0	---	38	----	6.3
05	3 kGy	3.0	---	48	----	8.0
06	10 kGy	10.0	30	110	3.2	18.3
07	25.5 kGy	25.5	62	165	6.7	27.5
08	10 kGy	10.0	25	93	2.7	15.5
09	0 Gy	0.0	---	27	----	4.5
10	25.5 kGy	25.5	69	167	7.5	27.8
505 01	10 kGy	10.0	36	95	3.9	15.8
02	G, I	25.5	57	172	6.2	28.7
03	P, I	24.7	71	316	7.7	52.7

1-Pet and Acp concentrations are calculated as
c 1-Pet = (A [79.1] / 1.85 ng^{-1}) / 5 mg, and
c Acp = (A [120] / 1.20 ng^{-1}) / 5 mg.

Appendix 4

Phase III: TDS-Quantitation: The SPLITLESS-Scan Series

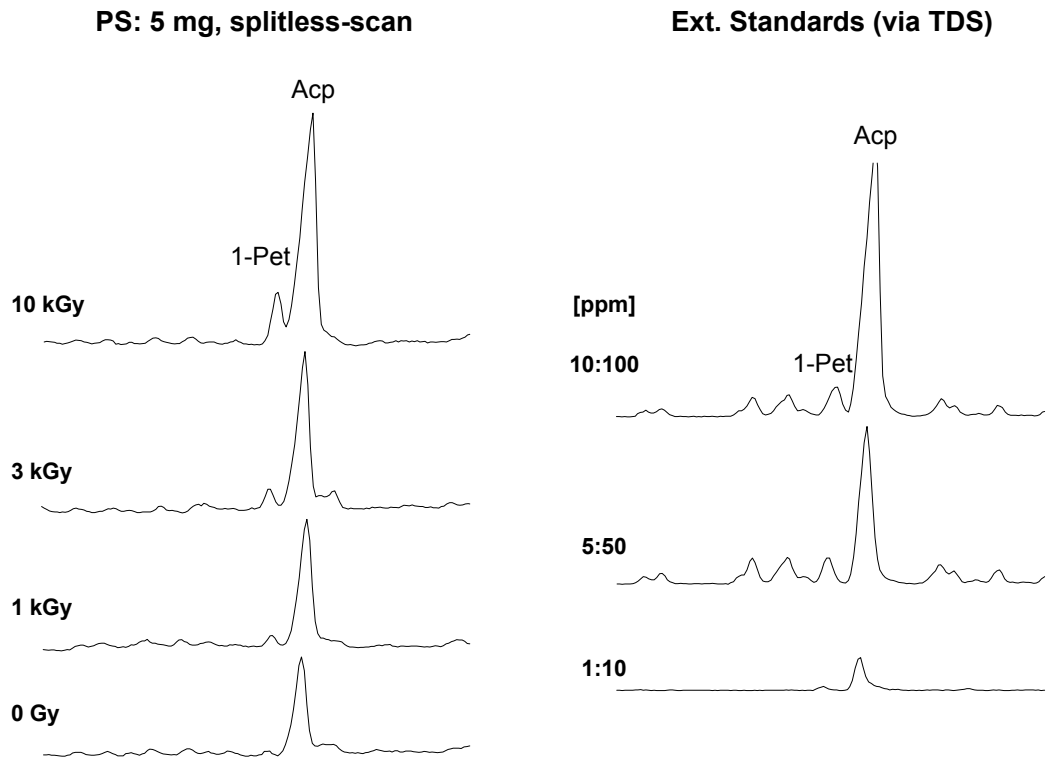


Figure A-4.1 Splitless-scan analyses: 5 mg PS 168 N (0–10 kGy) vs. standard injections — detail t_R 17.7–18.7 min.
In the splitless-scan series, standards were injected into the TDS.
Exp. Condit.: TDS 160(10); CIS -40, splitless 90 sec; GC 40(11.5) -10- 250(5); col.: DB-5.

Table A-4.1 Calibration data.

File	c Pet nom. (ppm)	**c Pet corr. (ppm)**	c Acp nom. (ppm)	**c Acp corr. (ppm)**	**A [79.1]**	**A [120]**
506-02	1.04	0.96	10.1	9.9	44	200
-03	5.20	4.78	50.5	49.5	192	867
-04	10.40	9.57	101.0	99.0	320	1925

Nomimal concentrations (c nom.) were multiplied by correction factors (see below) to give corrected concentrations (c corr.).

Table A-4.2 Mean peak areas for 10 ppm 1-Pet and Acp in TDS- and CIS-injections, and correction factors for standard injections into the TDS.

	TDS	CIS	f = TDS / CIS
Mean 1-Pet (A [79.1])	415.67	459.75	0.90
Mean Acp (A [120])	244	249.75	0.98

(Mean values of the 4 CIS- and the 3 TDS-analyses in Figure 6.5.)

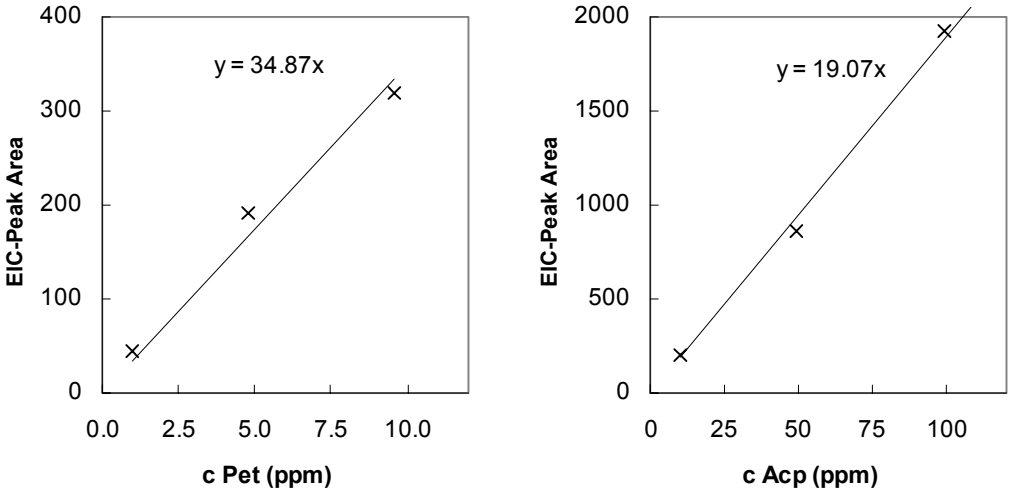


Figure A-4.2 Calibration curves.

Table A-4.3 Polystyrene data.

File	Code	Dose (kGy)	A [79.1]	A [120]	**c Pet** (ppm)	**c Acp** (ppm)
505-04	1 kGy	1.0	116	828	0.7	8.7
-05	G, I	25.5	1652	3219	9.5	33.8
-06	P, I	24.7	1463	4137	8.4	43.4
-07	10 kGy	10.0	613	1750	3.5	18.4
-08	3 kGy	3.0	209	1036	1.2	10.9
-09	0 Gy	0.0	56	590	0.3	6.2

1-Pet and Acp concentrations are calculated as
c 1-Pet = (A [79.1] / 34.87 ng^{-1}) / 5 mg, and
c Acp = (A [120] / 19.07 ng^{-1}) / 5 mg.

Appendix 5

Phase III: TDS-Quantitation: The Splitless-SIM Series

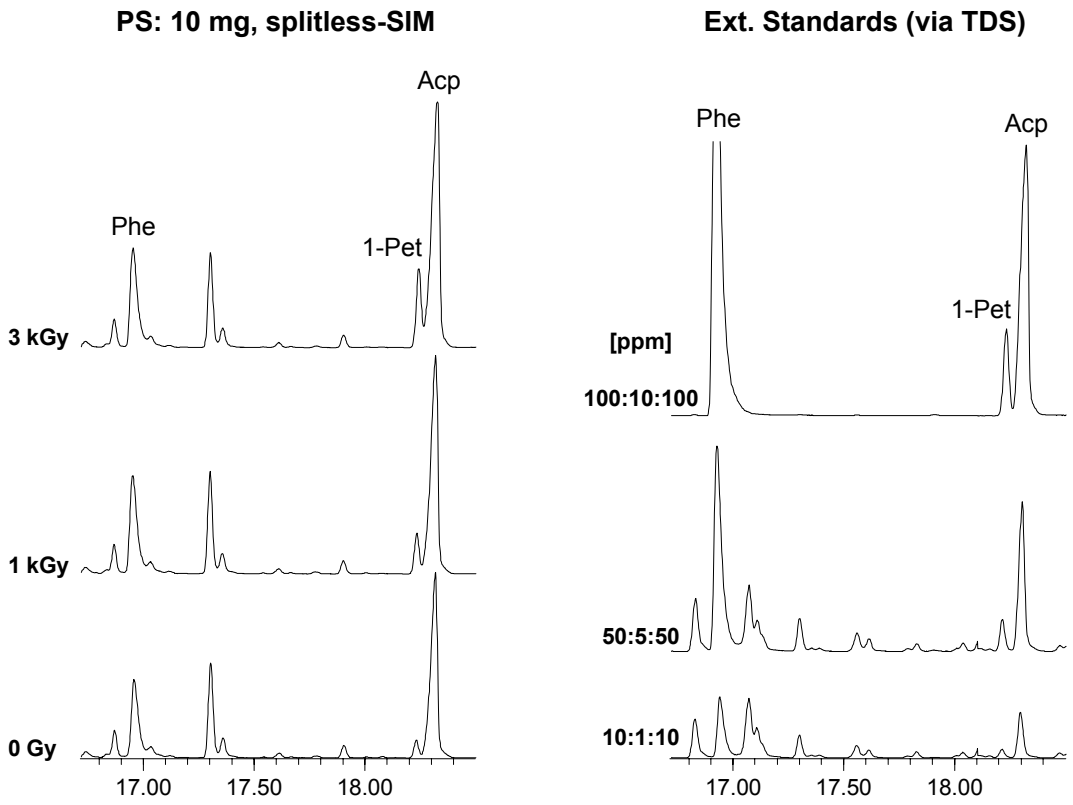


Figure A-5.1 Splitless-**SIM** analyses: 10 mg PS 168 N (0–3 kGy) vs. standard injections — detail t_R 16.7–18.5 min.
Standards were injected into the TDS, and, in another series of measurements, into the CIS. Exp. Cond.: TDS 160(10); CIS -40, splitless 90 sec; GC 40(11.5) -10- 250(5); column: DB-5; Ions monitored: 94.1, 91.1 (from 16.7 to 18.1 min), and 79.1, 120.0 (from 18.1 to 18.5 min).

Table A-5.1 Calibration data.

c Pet (ppm)	c Acp (ppm)	File TDS	A [79.1]	A [120]	File CIS	A [79.1]	A [120]
1.04	10.1	510-02	144	781	531-01	18	529
5.20	50.5	-04	570	3011	-02	628	4355
10.40	101.0	-05	1616	7459	-03	1176	6809
20.80	202.0	-06	2578	11460	-04	2605	12812

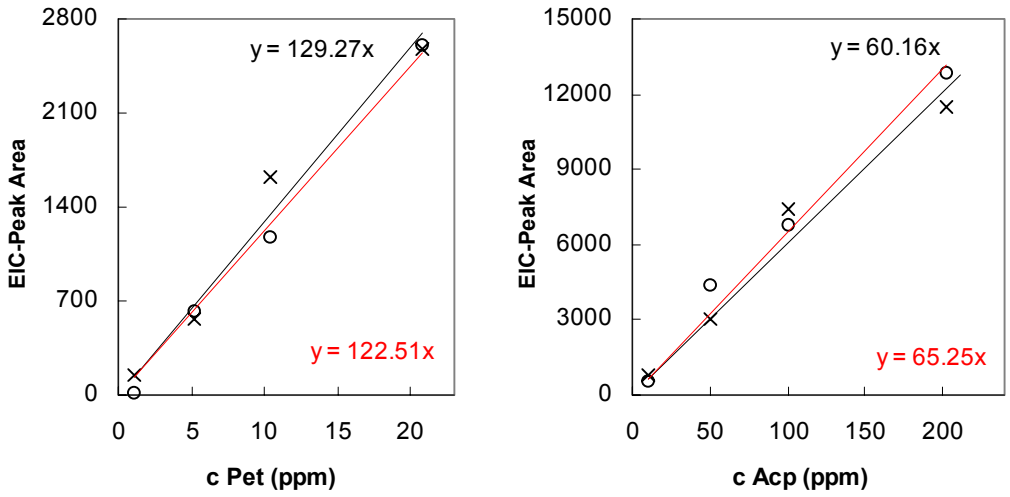


Figure A-5.2 Calibration curves.

Table A-5.2 Polystyrene data.

File	Code	Dose (kGy)	A [79.1]	A [120]	**c Pet** (ppm)	**c Acp** (ppm)
509-02	G, C	0	561	7836	0.4	13.0
-03	0 Gy	0	302	4377	0.2	7.3
-04	P, C	0	1393	15509	1.1	25.8
-05	1 kGy	1	701	5498	0.5	9.1
-06	3 kGy	3	1401	6874	1.1	11.4
510-09	10 kGy	10	4403	12171	3.4	20.2
525-01	0 Gy	0	301	4175	0.2	6.9
-02	G, C	0	870	9700	0.7	16.1
-03	G, C	0	480	6553	0.4	10.9
-04	P, C	0	1593	15304	1.2	25.4

1-Pet and Acp concentrations are calculated as
c 1-Pet = (A [79.1] / 129.27 ng^{-1}) / 10 mg, and
c Acp = (A [120] / 60.16 ng^{-1}) / 10 mg.

Appendix 6

Phase III: Quantitative Results for Phenol (Splitless-SIM)

Table A-6.1 Calibration data.

c Phe (ppm)	File	A [94.1]	File	A [94.1]
10.2	510-02	1566	531-01	728
51.0	-04	5768	-02	7198
102.0	-05	14372	-03	11562
204.0	-06	25156	-04	25155

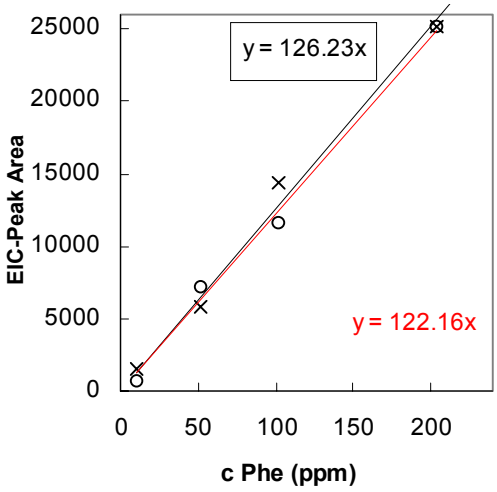


Figure A-6.1 Calibration curve.

Table A-6.2 Polystyrene data.

File	Code		A [94.1]	**Phe (ppm)**
509-02	G, C	0	3247	2.6
-03	0 Gy	0	1992	1.6
-04	P, C	0	6786	5.4
-05	1 kGy	1	2594	2.1
-06	3 kGy	3	2607	2.1
510-09	10 kGy	10	5259	4.2
525-01	0 Gy	0	1849	1.5
-02	G, C	0	4650	3.7
-03	G, C	0	2925	2.3
-04	P, C	0	5192	4.1

Phenol concentrations are calculated as
c Phe = (A [94.1] / 126.23 ng^{-1}) / 10 mg.

Appendix 7

Phase III: The TDS 240°C Series

Table A-7.1 Polystyrene data (PS 168 N; splitless-SIM).

File	Code	Dose (kGy)	A [94.1]	A [79.1]	A [120]	**c Phe** (ppm)	**c 1-Pet** (ppm)	**c Acp** (ppm)	
531-05	0 Gy	0	3404	457	4931	2.7	0.4	8.2	
-06	1 kGy	1	2929	510	4712	2.3	0.4	7.8	
-08	3 kGy	3	5563	3584	13372	(4.4)	(2.8)	(22.2)	[a]
601-01	G, C	0	4451	609	9140	3.5	0.5	15.2	
-02	P, C	0	6270	1346	14934	5.0	1.0	24.8	
-03	0 Gy	0	3309	352	4953	2.6	0.3	8.2	
-04	1 kGy	1	3427	785	5987	2.7	0.6	10.0	
-05	3 kGy	3	3986	1683	7669	3.2	1.3	12.7	

[a] Values are not included in Figure 7.5, because something went wrong in the previous run (531-07; 3 kGy); 531-08 might actually be an analysis of two thermal desorptions.

Phe, 1-Pet, and Acp concentrations are calculated with the *splitless-SIM* calibration relationships, i. e., as c Phe = (A [94.1] / 126.23 ng^{-1}) / 10 mg, c 1-Pet = (A [79.1] / 129.27 ng^{-1}) / 10 mg, and c Acp = (A [120] / 60.16 ng^{-1}) / 10 mg.

Appendix 8

Phase III: The MABS - Series

Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene (MABS): Terlux 2802 TR transparent

Splitless-scan analyses

Table A-8.1 MABS-data (scan).

File	Code	Dose (kGy)	A [94.1]	A [79.1]	A [120]	**c 1-Pet** (ppm)	**c Acp** (ppm)
525-05	MABS G, C	0	277	0	379	0	2.0
525-06	MABS G, I	24.4	1074	874	1657	2.5	8.7

Concentrations are calculated — using the *splitless-scan* calibration curves recorded for PS — as c 1-Pet = (A [79.1] / 34.87 ng^{-1}) / 10 mg, and c Acp = (A [120] / 19.07 ng^{-1}) / 10 mg.
Phenol calibration standards (A [94.1]) have not been injected in the splitless-scan-series.

Splitless-SIM analyses

In contrast to the other PS specimens, those of the MABS-series [except *MABS G, I (*)*] were milled with a different **rotor,** having only two (relatively blunt) blades. The powders obtained with this rotor were visibly coarser — of course, those of the MABS specimens (as one would expect from the high impact resistance of this polymer), but also that of the relatively brittle (standard PS-) Petri dish. As can be concluded from the results with *G, I (*)* and *G, I (20)* (= 20 min TDS), thermal desorption of these powders is **incomplete;** therefore, the values in this Table should be considered as **minimum concentrations.**

Table A-8.2 MABS-data (SIM).

File	Code	Dose (kGy)	A [94.1]	A [79.1]	A [120]	**c Phe** (ppm)	**c 1-Pet** (ppm)	**c Acp** (ppm)	
526-01	MABS G, I	24.4	2048	992	4610	1.6	0.8	7.7	G, I
-02	MABS G, C	0	709	149	1167	0.6	0.1	1.9	
-03	MABS P, C	0	1134	212	4425	0.9	0.2	7.4	
-04	MABS P, I	24.9	4505	1830	10721	3.6	1.4	17.8	
-05	Yogh. Tray [a]	0	690	148	2053	0.5	0.1	3.4	
-06	MABS G, I (*) [b]	24.4	3198	1367	6059	2.5	1.1	10.1	G, I (*)
-07	**PS Petri Dish**	**x**	3377	4135	11241	**2.7**	**3.2**	**18.7**	**PS !**
-08	MABS G, I	24.4	2187	1275	5252	1.7	1.0	8.7	G, I
-09	MABS G, I (20) [c]	24.4	3272	1968	7136	2.6	1.5	11.9	G, I (20)

[a] PS-Copolymer

[b] Milled with the sharp-edged *four-blade rotor* ('star-rotor') used for PS, and consequently a finer powder than „MABS G, I."

[c] Desorbed 20 min instead of 10.

The concentrations are calculated with the *splitless-SIM* calibration relationships, i. e., as c Phe = (A [94.1] / 126.23 ng^{-1}) / 10 mg, c 1-Pet = (A [79.1] / 129.27 ng^{-1}) / 10 mg, and c Acp = (A [120] / 60.16 ng^{-1}) / 10 mg.

Appendix 9

Phase III: Detection Limit 1-Phenylethanol / Acetophenone

These data are related to the chromatograms in Figure 7.7.

Table A-9.1 **Experimental conditions** and **optimization effect** on 1-phenyl-ethanol peak height

Column: DB-5; 30 m, 0.25 mm i. d., 0.25 µm f. t.
CHP: 0.8 bar / 0.9 bar
CIS: 40 -12- 250(90), splitless 60 s / 45 s
GC: 35 / 40 (1 / 0.75) -20- / -30- 250(5.25) / 200(8.5)
MS: solvent delay: 4 min
EMV: 2129 V (= Tune value + 200 V)
scan range: 33 - 300
scan treshold: 200

Parameters varied in runs -07 through -13:

Run No. →	-07	-08	-09	-10	-11	-12	-13
Std. Concentration [a] (ppm)	5	5	5	**0.5**	0.5	0.5	**0.05**
MS Data Acquisition	Scan	Scan	Scan	Scan	Scan [b]	**SIM**	SIM
CHP (bar)	0.8	0.8	**0.9**	0.9	0.9	0.9	0.9
splitless (sec)	60	60	**45**	45	45	45	45
GC rate (°C/min)	20	**30**	30	30	30	30	30
Data Analysis:							
Peak Area 1-Pet (A [79.1])	326	327	332				
Peak Area Acp (A [120])	173	174	174				
Peak Height 1-Pet	**19,500**		**29,900**	**1300 (!)**			

[a] 1-Pet and Acp in n-hexane.
[b] EMV 400 V above tune value.

The combined effect of increasing column head pressure, accelerating GC temperature program, and reducing splitless time is a ca. 50% increase in peak height (run -09 vs. -08). A 1:10-dilution of the standard yields less than half the expected peak height (1300 instead of the theoretical ≈ 3000; run -10 vs. -09). The missing 1-Pet is thought to be irreversibly adsorbed to active sites in the chromatographic system (column and / or injector).

Appendix 10

Retrospective Concentration Estimate

Table A-10.1 Peak areas and **concentration estimates** for Figure 6.1.

File	Code	Dose (kGy)	m PS (mg)	A [79.1]	A [120]	**c 1-Pet** (ppm)	**c Acp** (ppm)
1227-10	**G, I**	25.5	11.8	8311	15264	**8.6**	**35.0**
1229-07	G, C	0	2	136	673	0.8	9.1
1229-08	P, C	0	3	215	2486	0.9	22.4
1229-09	**G, I**	25.5	2.5	2268	5611	**11.1**	**60.7**
1229-10	**P, I**	24.7	2.8	1906	6611	**8.3**	**63.8**

1-Pet and Acp concentrations are calculated as c 1-Pet = (A [79.1] / 82 ng^{-1}) / m PS, and c Acp = (A [120] / 37 ng^{-1}) / m PS.

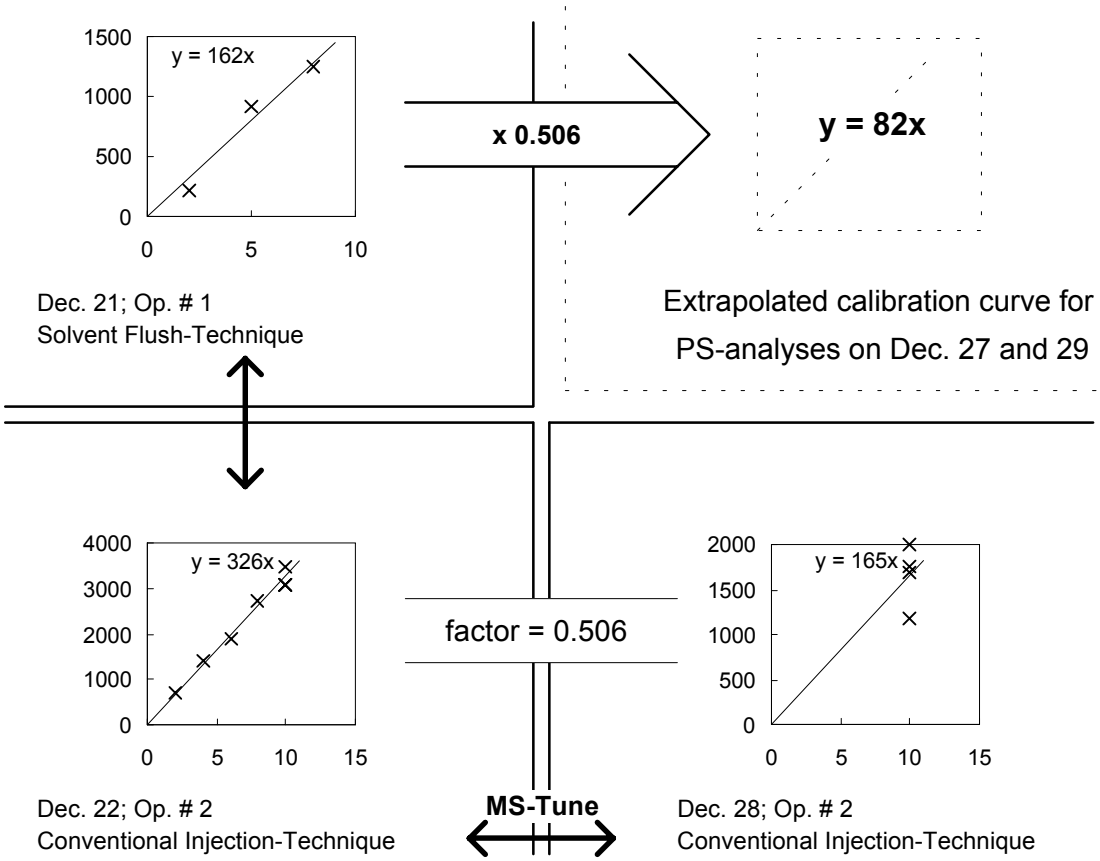


Figure A-10.1 **Extrapolating** a calibration curve to estimate radiolysis product concentrations in the first TDS-analyses of PS-*powder*. The three plots of (EIC-) peak areas vs. 1-phenylethanol masses (in ng) could not be used directly because of an MS-tune on Dec. 27 and / or a 'wrong' injection technique by operator # 2. In a similar way, an extrapolated relationship was obtained for *acetophenone*. As already mentioned, the resulting concentrations of 1-Pet and Acp in PS (Table A-10.1) should be considered as very rough estimates.

Appendix 11

Concentration Estimates for the TDS-Time-Series

These data are related to Figure 6.4.

Table A-11.1 Calibration data (one-point calibration).

File	c Pet (ng)	c Acp (ng)	c Phe (ng)	A [79]	A [120]	A [94]
428-09	10.4	10.1	10.2	367	197	338
429-01	10.4	10.1	10.2	411	205	290
429-02	10.4	10.1	10.2	376	207	395

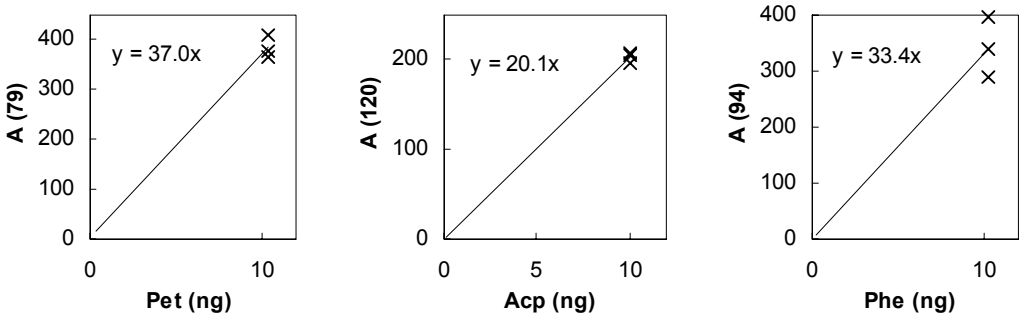


Figure A-11.1 Calibration relationships.

Table A-11.2 Polystyrene data.

File	TDS-Time (min)	A [79]	A [120]	A [94]	1-Pet (ppm)	Acp (ppm)	Phe (ppm)
42804	10	1230	2310	990	6.6	23	5.9
42805	15	1240	3170	1110	6.7	32	6.6
42806	20	1350	3250	1140	7.3	32	6.8
42807	25	1370	3730	1410	7.4	37	8.4
42808	30	1430	3570	1360	7.7	36	8.1

The concentrations are calculated as c 1-Pet = (A [79.1] / 37.0 ng^{-1}) / 5 mg,
c Acp = (A [120] / 20.1 ng^{-1}) / 5 mg, and c Phe = (A [94.1] / 33.4 ng^{-1}) / 5 mg,

Appendix 12

TDS-Performance Test: Characterizing Analyte Recovery

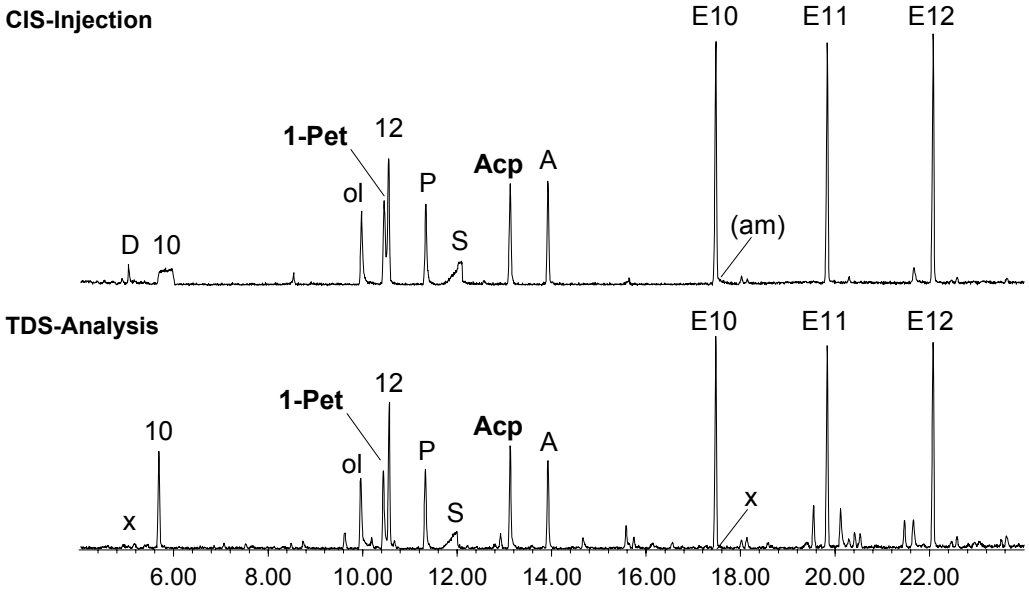


Figure A-12.1 **TDS-Performance- (or: Recovery-) Test:** Test Injection = **1 µl Grob-Mix** (1:5 dilution) **plus 1 µl 1-Pet / Acp standard** (10 ppm) at TDS 250 / CIS 30.

D	= 2,3-Butanediol (traces ?)	A	= 2,6-Dimethylaniline
10	= n-Decane	am	= Dicyclohexylamine (as shoulder on E10)
ol	= 1-Octanol	E10	= Methyldecanoate
12	= n-Dodecane	E11	= Methylundecanoate
P	= 2,6-Dimethylphenol	E12	= Methyldodecanoate
S	= 2-Ethylhexanoic acid	**x**	**= Peaks missing in the TDS analysis** (D & am).

Experimental Condit.: TDS 50 -20- 250; CIS 30; GC 40(1.5) -5- 200(5.5); column: **Rtx-200.**

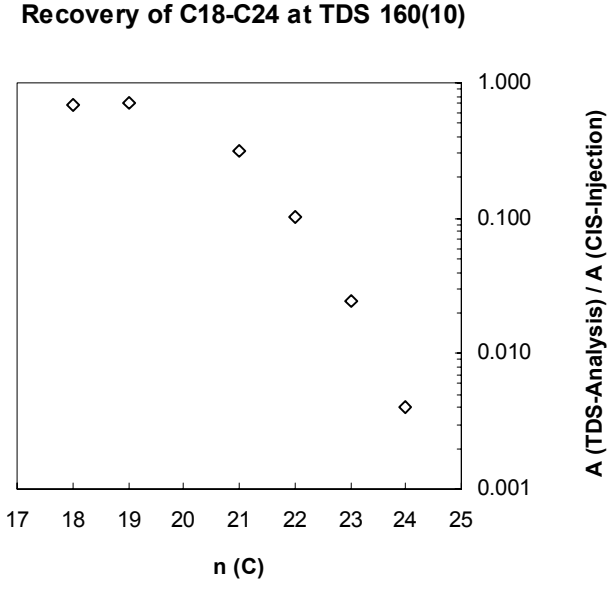


Figure A-12.2 **Recovery of linear hydrocarbons at TDS 160(10):** Relative peak areas (log scale) vs. number of C-atoms. Cf. Figure A-12.3 and Table A-12.1.

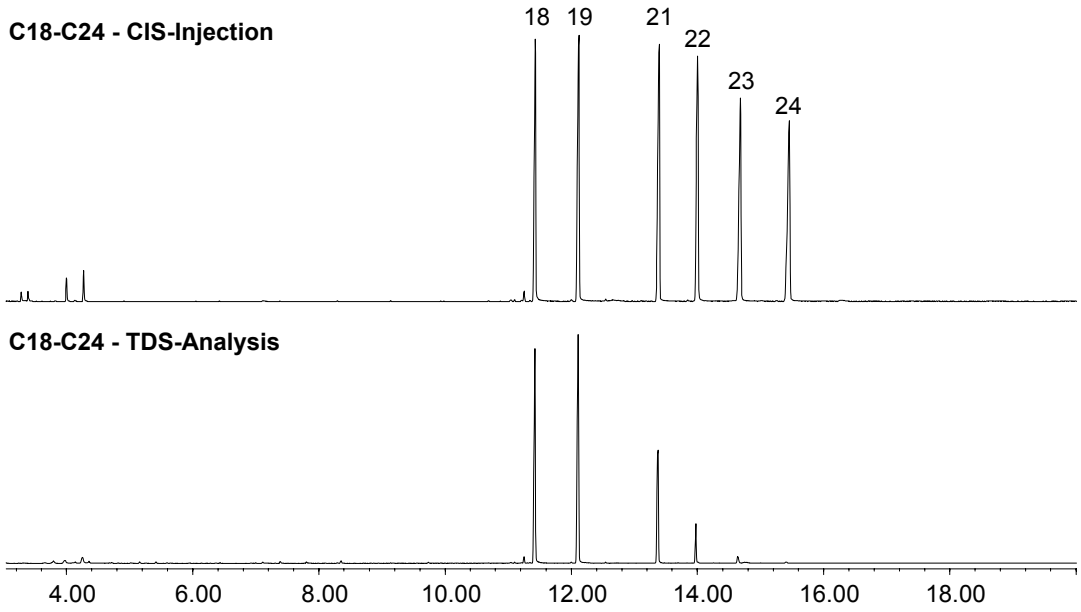


Figure A-12.3 **C18-C24 hydrocarbons as 'model-PS' ?**
C18 = Octadecane
.....
C24 = Tetracosane
The concentration of each hydrocarbon in the test mix was ca. 10 ppm. Please note that there is **no loss** of C22, C23, and C24 during **CIS-injection** — the **peak areas** are equal (cf. Table A-12.1); increased peak widths and diminished peak heights are caused by the GC temperature program. Experimental Conditions: TDS 160(10); CIS 30;
GC 40(1.5) -15- 220(6.5); col.: Rtx-200.

Table A-12.1 Peak Areas (arbitrary units) of C18-C24 — CIS-Injection vs. TDS-Analysis (cf. Figure A-12.3).

	CIS-Injection	TDS-Analysis	Quotient
C18	23.9	16.7	0.7
C19	26	18.2	0.7
C21	25.6	8	0.31
C22	26	2.7	0.1
C23	24.2	0.6	0.025
C24	24.9	0.1	0.004

Appendix 13

Special Projects / Pre-Phase IV Results

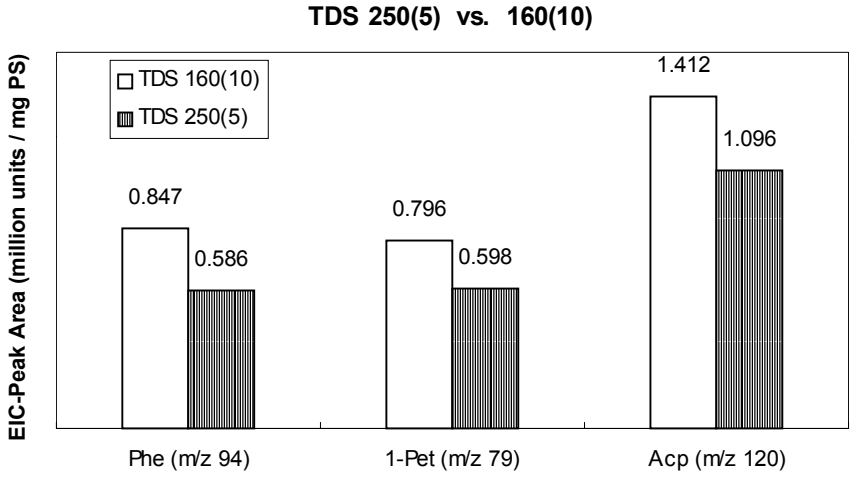


Figure A-13.1 **TDS 250°C (5 min) vs. 160°C (10 min).** With the intention to accelerate the analytical procedure, it was checked whether an elevated TDS-temperature would allow to reduce desorption time. Obviously, 5 min at 250°C yield lower peak areas than 10 min at 160°C. In these nominally *isothermal* desorptions, the TDS-oven and the sample inside the massive TDS-injector need several minutes to regain the preset temperature level — **see Figure 8.11.**
Exp. Conditions: Sample: PS 168 N, 25.5 kGy, two years after irradiation, ca. 5 mg powder; CIS 30; GC 40(1.5) -5- 180(5); column: Rtx-200.

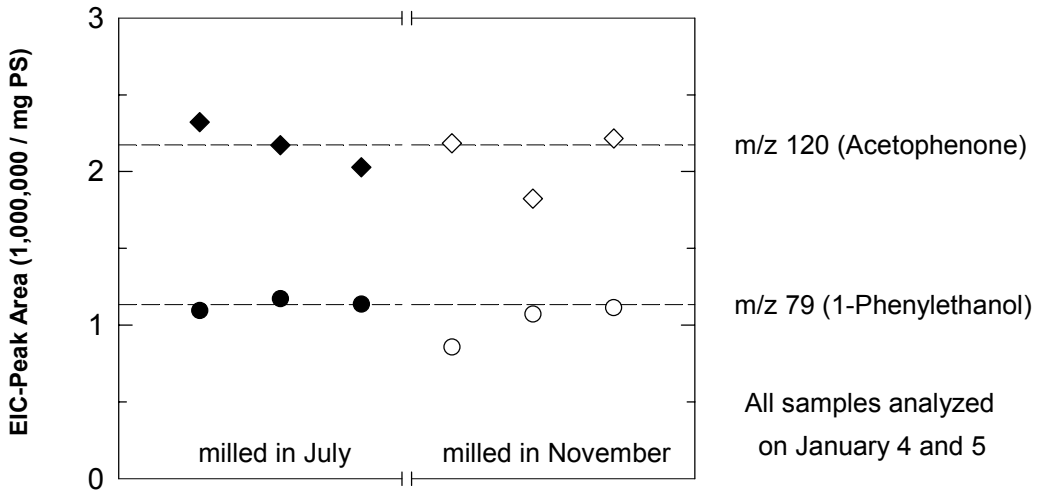


Figure A-13.2 To confirm the observation that there appeared to be no **loss of radiolysis products from the PS powder during storage** (see Phase III quantitation: *G, I* vs. *25.5 kGy,* and *G, C* vs. *0 Gy* samples), two additional powder specimens were analyzed: the first had been milled 6 months, the second 5 weeks (November 29) before the analyses, which were performed in triplicate on two consecutive days. The mean lines are for the 'milled-in-July' samples. The graph also gives an impression of the **relatively high reproducibility** of the TDS-technique.
Experimental Conditions: As in Figure A-13.1, with TDS 50 -20- 250(5).

Appendix 14

Column Selection for Phase IV

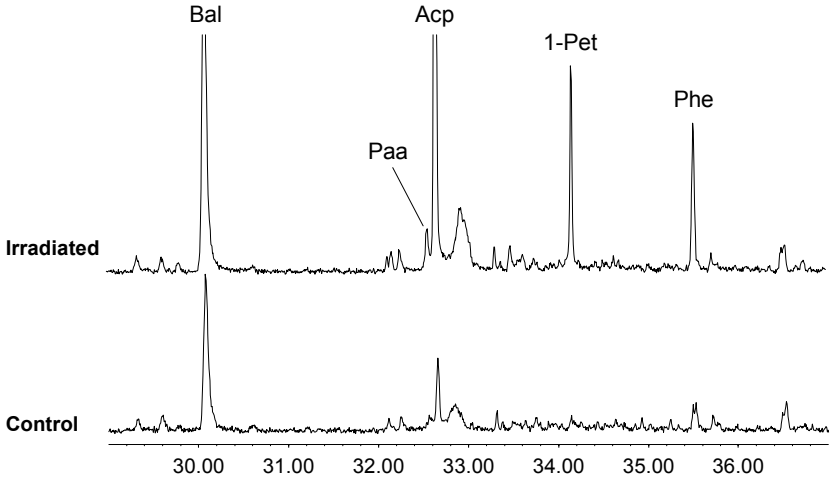


Figure A-14.1 Qualitative analyses on a **poly(ethylene glycol) column** (Phase I) — 3 weeks after irradiation with 22.5 kGy (top) vs. non-irradiated control.
Experimental Conditions: Direct desorption of PS granulate: PS 168 N, 2 pellets; TDS x:160; CIS 30; GC 40(11) -3- 70 -5- 120 -30- 210(5); column: Supelcowax 10.

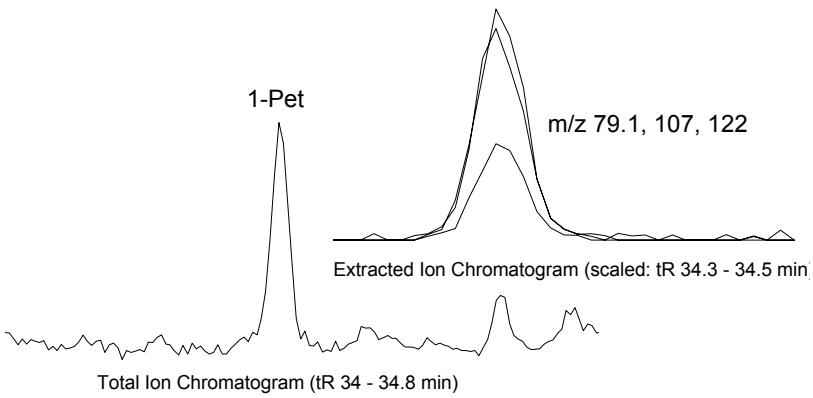


Figure A-14.2 **1-Phenylethanol** in another run of 22.5 kGy-irradiated polystyrene on the **poly(ethylene glycol) column.** Though the peak is very small, there appears to be no tailing.
Experimental Conditions: Sample: PS 168 N, 1 pellet, 2 days after irradiation; TDS 40:160; CIS 30; GC 40(11) -3- 70 - 5- 120 -30- 210(5); column: Supelcowax 10. This was actually the first analysis, in Phase I, of irradiated polystyrene.

Appendix 15

System Characterization for Phase IV

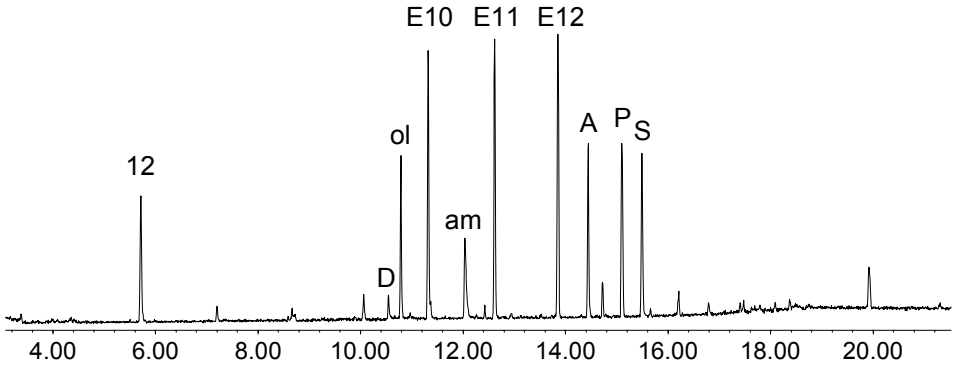


Figure A-15.1 **Grob-Mix** at the beginning of Phase IV on the poly(ethylene glycol) column.

12	=	n-Dodecane	E11	=	Methylundecanoate
D	=	2,3-Butanediol	E12	=	Methyldodecanoate
ol	=	1-Octanol	A	=	2,6-Dimethylaniline
E10	=	Methyldecanoate	P	=	2,6-Dimethylphenol
am	=	Dicyclohexylamine	S	=	2-Ethylhexanoic acid

n-Decane (10) elutes before the MS is switched on (solvent delay).
Experimental Conditions: 1 µl of the 1:5 diluted Grob-Mix; CIS 30; GC 40(1.5) -10- 210 (5); column: Supelcowax 10.

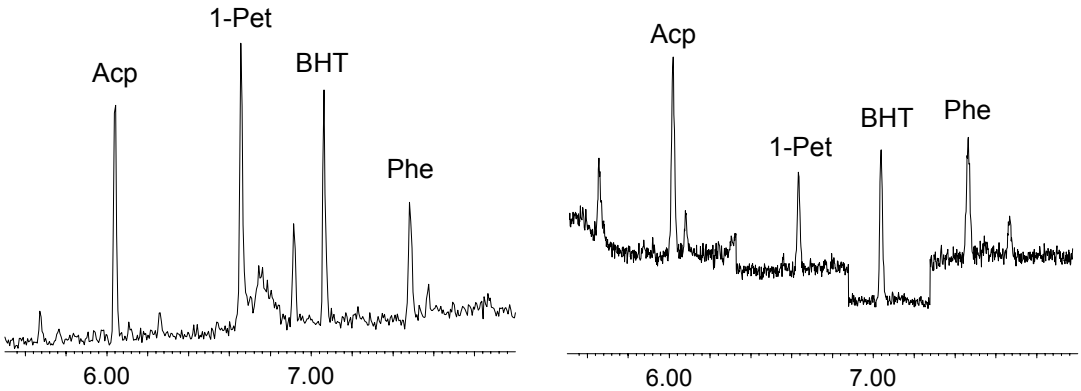


Figure A-15.2 **System Sensitivity Test** at the beginning of Phase IV.
Experimental Conditions: Standard: acetophenone, 1-phenylethanol, butylhydroxytoluene, and phenol in n-hexane; CHP = **1.0 bar**; CIS 30, splitless **60 sec**; GC 40(**1**) **-30-** 210(5); column: Supelcowax 10. Ions monitored in the SIM groups: See Section 3.6.

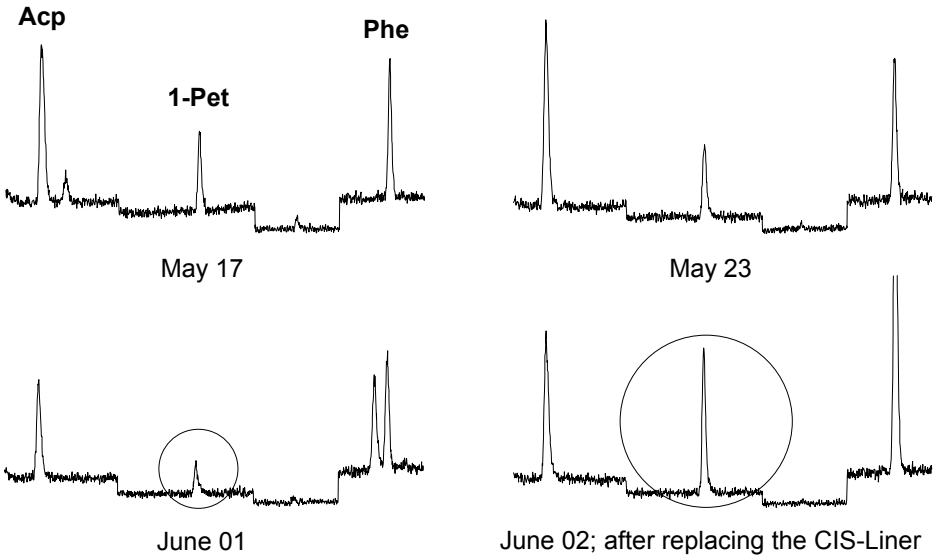


Figure A-15.3 **System Sensitivity Tests** in SIM-mode (t_R 7.5 to 10 min) **with a 0.01 ppm standard** (chromatograms from Phase IV).
A degrading overall performance is recognized before it affects quantitation at higher concentrations. In this case, the gradual build-up of residues in the injector-(CIS)-liner had created 'active sites' for the alcohol 1-phenylethanol; the normally white adsorbent (Tenax TA) had become dark grey. Experimental Conditions: CIS 30; GC 40(1.5) -20- 220(6); column: Supelcowax 10. Ions monitored in the SIM groups: See Section 3.6.

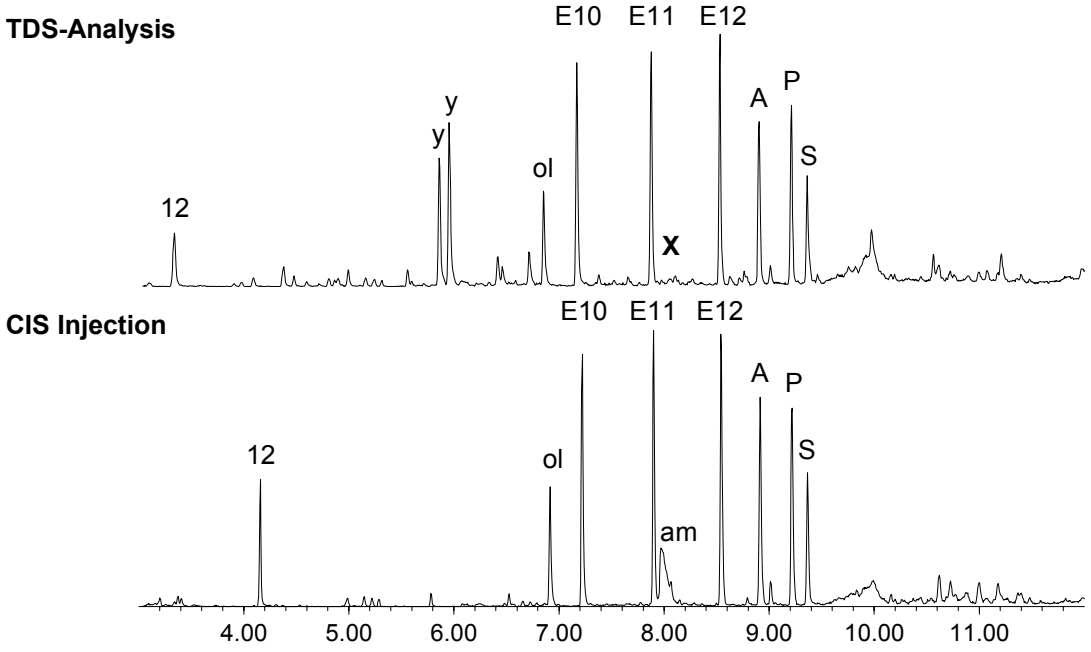


Figure A-15.4 **TDS-Recovery-Test from Phase IV** with the **Grob-Mix** (1 µl 1:5 dilution).
This test was performed on Day 8 of the **DSC-series** after the first five PS-analyses. The background in the TDS-analysis is remarkably low; it would be an excellent **blank** for normal analyses of PS-*powders*, (i. e., thermal desorption of several milligrams of PS).

12	=	n-Dodecane	A	=	2,6-Dimethylaniline
ol	=	1-Octanol	P	=	2,6-Dimethylphenol
E10	=	Methyldecanoate	S	=	2-Ethylhexanoic acid
am	=	Dicyclohexylamine	X	=	Peak missing in the TDS-analysis
E11	=	Methylundecanoate	y	=	contamination (alkylbenzenes)
E12	=	Methyldodecanoate	**Relative recoveries see Figure A-15.5.**		

Exp. Cond.: TDS: 200(10); CIS 30; GC 50(1.5) -20- 220(6); MS: Scan; col.: Supelcowax 10.

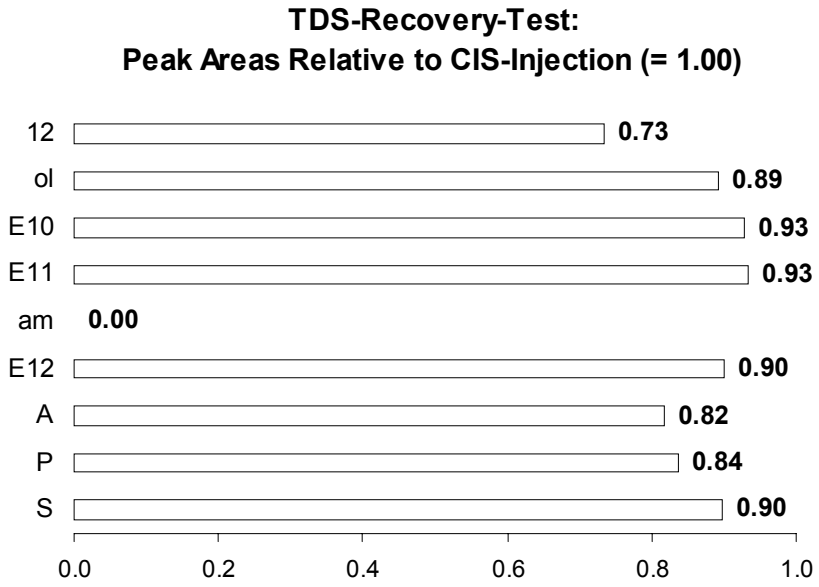


Figure A-15.5 **Relative recoveries** for Figure A-15.4 (Peak areas in the TDS-analysis relative to those in the CIS-injection).

12 = n-Dodecane
ol = 1-Octanol
E10 = Methyldecanoate
E11 = Methylundecanoate
am = Dicyclohexylamine
E12 = Methyldodecanoate
A = 2,6-Dimethylaniline
P = 2,6-Dimethylphenol
S = 2-Ethylhexanoic acid.

Appendix 16

Quantitation by Direct Thermal Desorption (Phase IV)

Table A-16.1 Calibration data.

File		c Acp (ppm)	c 1-Pet (ppm)	c Phe (ppm)	A [120]	A [79.1]	A [94.1]
412-05	--	10.10	1.04	1.02	540	82	68
-06	--	10.10	1.04	1.02	530	83	52
-07	--	10.10	10.40	10.20	500	1130	1280
418-07	--	10.10	10.40	10.20	500	1100	1120
421-06	--	10.10	10.40	10.20	540	1170	1240
-07	--	10.10	10.40	10.20	590	1180	1270
-08	--	10.10	10.40	10.20	500	1080	1050
424-01	--	10.10	10.40	10.20	440	1270	1130
425-06	--	10.10	10.40	10.20	390	990	990
426-01	--	10.10	10.40	10.20	500	1240	1160
-02	--	10.10	10.40	10.20	450	1090	1020
-03	--	10.10	10.40	10.20	500	1190	1140
-04	n	10.10	10.40	10.20	550	1120	1210
-05	n	10.10	10.40	10.20	490	1030	1090
-06	n	1.01	1.04	1.02	49	110	120
502-02	n	1.01	1.04	1.02	45	96	83
-03	n	1.01	1.04	1.02	52	105	109
505-01	n	1.01	1.04	1.02	62	126	126
-06	n	1.01	1.04	1.02	58	121	126
508-01	n	10.10	10.40	10.20	561	1422	1251
-04	n	10.10	10.40	10.20	432	1004	1025
-05	--	10.10	10.40	10.20	654	1635	1532
-06	n	10.10	10.40	10.20	606	1288	1431
-09	--	10.10	10.40	10.20	535	1400	1198
-10	n	10.10	10.40	10.20	629	1255	1342
-11	n	1.01	1.04	1.02	66	124	114
-12	n	101.00	104.00	102.00	4104	12177	9654

n = newly prepared standard solutions.

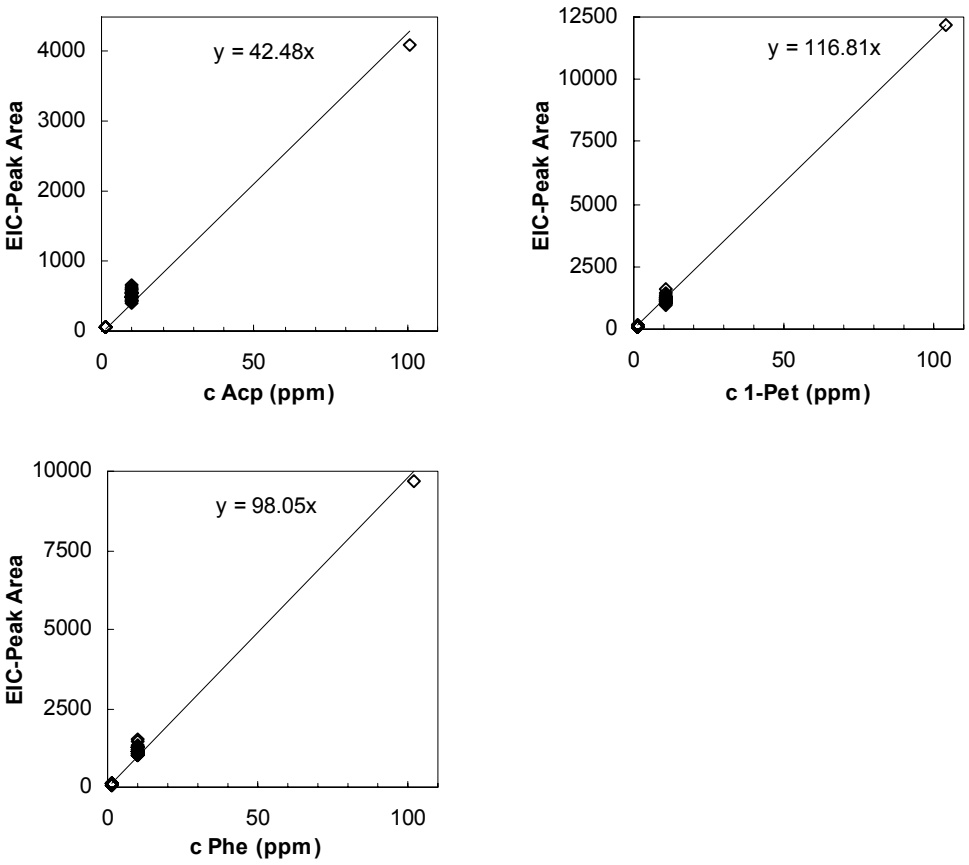


Figure A-16.1 Calibration curves.

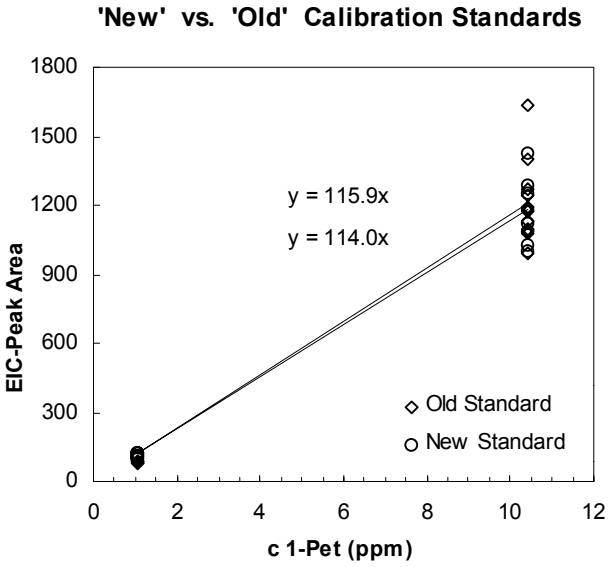


Figure A-16.2 Comparison of new and old standard solutions (1-phenylethanol): The nearly identical calibration relationships indicated that the standards could not be responsible for the low 1-Pet concentrations initially observed in Phase IV.

Table A-16.2 Polystyrene Data — **TDS 160(10)**

File	Code	Rem. [a]	m PS (mg)	A [120]	A [79.1]	A [94.1]	**c Acp** (ppm)	**c 1-Pet** (ppm)	**c Phe** (ppm)
410-06	168N 0 Gy		4.57	880	110	480	4.5	0.21	1.1
-07	168N **25.5 kGy**		4.59	4590	2240	3380	23.5	4.18	7.5
411-03	XY 0 Gy		5.59	1190	150	2690	5.0	0.23	4.9
412-02	Petri Dish **x kGy**	RLS	5.56	4620	1760	2780	19.6	2.71	5.1
-03	Yoghurt Tray 0 Gy	Co-p.	6.23	660	150	570	2.5	0.21	0.9
413-02	PS 1x-'Glass' 0 Gy		5.37	1350	140	730	5.9	0.22	1.4
418-03	Tray „WM" 0 Gy	Co-p.	5.09	340	100	380	1.6	0.17	0.8
-04	Culture Flask **x kGy**	RLS	4.71	4740	1640	2580	23.7	2.98	5.6
-05	Tray „F" 0 Gy	Co-p.	4.69	1120	99	680	5.6	0.18	1.5
419-02	168N **25.5 kGy**		4.65	4710	2400	2980	23.8	4.42	6.5
-03	168N **23.5 kGy** - G		5.42	5610	2820	3830	24.4	4.45	7.2
-04	168N **23.5 kGy** - Plv		5.65	2670	1430	2000	11.1	2.17	3.6
-05	XY **23.5 kGy** - Plv		5.49	4700	2440	---- [b]	20.2	3.80	----
420-02	XY **23.5 kGy** - Plv		5.11	4140	2030	4860	19.1	3.40	9.7
-03	PS 1x-'Glass' **23.5 kGy**		5.3	4730	2680	2930	21.0	4.33	5.6
-04	Petri Dish **x + 23.5 kGy**	RLS	5.1	5440	2700	3090	25.1	4.53	6.2
-05	Culture Flask **x + 23.5 kGy**	RLS	5.1	6750	3630	4730	31.2	6.09	9.5
421-03	Tray „WM" 23.5 kGy	Co-p.	5.5	1980	230	460	8.5	0.36	0.9
-04	Tray „F" 23.5 kGy	Co-p.	5.4	1920	480	840	8.4	0.76	1.6
424-03	Yoghurt Tray 23.5 kGy	Co-p.	5	1690	780	860	8.0	1.34	1.8
-04	168N diss.-prec. **23.5 kGy**	pre-tr.	5.9	1590	270	970	6.3	0.39	1.7
425-02	MABS 23.5 kGy - Plv	MABS	5.6	1980	1240	2410	8.3	1.90	4.4
-03	XY **23.5 kGy** - G		7.3	3660	3070	4610	11.8	3.60	6.4
-04	168N **23.5 kGy** - Plv, re-milled		6.3	3590	3450	3450	13.4	4.69	5.6
-05	168N t.ds. 160(60) **23.5 kGy**	pre-tr.	4.1	1940	640	2910	11.1	1.34	7.2

[a] Remarks: RLS = 'Real-Life Sample'
Co-p. = Co-polymer
pre-tr. = pre-treated
MABS = Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene (BASF Terlux 2802 TR transparent)

[b] Data acquisition was stopped before the elution of phenol.

Concentrations were calculated as c Acp = (A [120] / 42.48 ng^{-1}) / m PS,
c 1-Pet = (A [79.1] / 116.81 ng^{-1}) / m PS, and c Phe = (A [94] / 98.05 ng^{-1}) / m PS.

Table A-16.3 Polystyrene Data — **TDS 200(10)**

File	Code	m PS (mg)	CIS (°C)	Plv.	A [120]	A [79.1]	A [94.1]	**Acp** (ppm)	**1-Pet** (ppm)	**Phe** (ppm)
505-04	168N 25.5 kGy	7.3	-40	?	9638	7163	4966	31.1	8.40	6.9
508-02	168N 25.5 kGy	5.1	30	old	9636	4372	5450	44.5	7.34	10.9
-03	168N 25.5 kGy	5.2	-40	old	9099	4082	4776	41.2	6.72	9.4
-07	168N 25.5 kGy	5.2	30	new	8723	4879	4857	39.5	8.03	9.5
-08	168N 25.5 kGy	5.4	-40	new	8236	4150	4644	35.9	6.58	8.8

Concentrations were calculated as above [TDS 160(10)].

Appendix 17

Thermal Desorption of Polymer Solutions (Phase III-Tests)

Thermal Desorption of PS Dissolved in CH_2Cl_2 (10 mg / 1 ml)

Data from three series of pre-tests performed in Phase III. Injection volume: 10 µl polymer solution (≡ 0.1 mg PS). Acetophenone concentrations are based on the standards injected in each series and should be considered as **rough estimates** (one-point calibration).

Table A-17.1 First Series.

File	Sample Description	A [Acp] [a]	**Acp in PS (ppm)**	
607-08	0.5 ppm Standard (CIS)	26		
-10	5 ppm Standard (TDS)	310		
-11	**PS 25.5 kGy**	**328**	**< 52**	**see Figure 9.2.**
-12	5 ppm Standard (CIS)	313		

[a] EIC-Peak Area: m/z 120 for acetophenone.
Exp. Conditions: TDS 160(10); CIS 30, GC 40(11.5) -10- 100 -20- 250(5); col.: DB-5; **MS: SIM.**

Table A-17.2 Second Series.

File	Sample Description	A [Acp] [a]	**Acp in PS (ppm)**
615-01	5 ppm Standard (CIS)	841	
-02	**PS 25.5 kGy**	**761**	**45**

[a] EIC-Peak Area: m/z (77 + 105 + 120) for acetophenone.
Experimental Conditions: TDS 160(10); CIS 30, GC 40(11.5) -10- 250(x);
column: DB-5; **MS: EMV + 100 V; Scan 33-300.**

Table A-17.3 Third Series.

File	Sample Description	A [Acp] [a]	**Acp in PS (ppm)**	
616-04	10 µl CH_2Cl_2 (TDS)	143		
-05	PS Control (0 Gy)	108	< 9	
-06	**PS 25.5 kGy**	**514**	**< 43**	**see Figure 9.3.**
-07	**Petri Dish x kGy**	**426**	**< 36**	
-08	TDS-Blank	40		
-09	10 ppm Standard (CIS)	1101		
617-11	dto.	1320		
-12	dto.	1321		

[a] EIC-Peak Area: m/z (77 + 105 + 120) for acetophenone.
Exp. Conditions: TDS 160(10); CIS 30, GC 40(11.5) -10- 250(x); column: DB-5; **MS: Scan 33-300.**

Concentrations were calculated assuming a peak area of 1200 for 10 ng actophenone, and neglecting the apparent Acp-background in the TDS-analyses (see 616-04 and -08). Run 616-04 was originally intended as a solvent blank, but the high Acp-level probably results from contamination of the TDS-injector. Of course, the polymers should have been analyzed only after obtaining clean (or: acceptable) blanks; checking solvent purity was probably unnecessary and / or could have been performed with the CIS (e. g., with multiple injections / solvent evaporation).

Appendix 18 — Thermal Desorption of Polymer Solutions (Phase IV)

Table A-18.1 Calibration data.

File	a	b	c	c (Sty) (ppm)	c (Acp) (ppm)	c (1-Pet) (ppm)	c (Phe) (ppm)	A [104]	A [120]	A [79]	A [94]
426-08	2			0.1056	0.101	0.104	0.102	19	10	16	18
427-02	1			0.1056	0.101	0.104	0.102	14	9	16	22
427-03	1			0.1056	0.101	0.104	0.102	16	11	18	22
427-04	1			1.056	1.01	1.04	1.02	149	80	154	161
728-03	1			0.1056	0.101	0.104	0.102	14	9	16	19
502-05	1			0.1056	0.101	0.104	0.102	14	10	14	22
503-02	1			1.056	1.01	1.04	1.02	142	79	154	177
503-03	1			0.1056	0.101	0.104	0.102	15	9	15	22
504-02	1		o.	0.1056	0.101	0.104	0.102	11	7	13	16
508-16	2			1.056	1.01	1.04	1.02	168	87	170	183
509-01	1			1.056	1.01	1.04	1.02	158	89	172	191
509-02	1			1.056	1.01	1.04	1.02	182	103	199	247
509-03	1			0.1056	0.101	0.104	0.102	16	11	16	21
509-04	1			10.56	10.1	10.4	10.2	1606	828	1669	1835
511-01	1			1.056	1.01	1.04	1.02	117	73	138	167
211-07	2			0.1056	0.101	0.104	0.102	13	8	14	15
512-01	1			1.056	1.01	1.04	1.02	142	84	172	206
512-02	1			1.056	1.01	1.04	1.02	135	76	144	170
512-03	1			0.1056	0.101	0.104	0.102	16	10	16	19
512-04	1		o.	10.56	10.1	10.4	10.2	1198	641	1290	1313
515-01	1			1.056	1.01	1.04	1.02	112	73	141	158
515-10	2			0.1056	0.101	0.104	0.102	14	10	17	18
516-01	1			1.056	1.01	1.04	1.02	156	82	153	173
517-01	1			1.056	1.01	1.04	1.02	170	100	184	219
517-02	1			0.1056	0.101	0.104	0.102	13	9	14	17
517-04	2			0.1056	0.101	0.104	0.102	15	22	15	25
517-05	2			0.1056	0.101	0.104	0.102	13	11	15	18
518-07	2			1.056	1.01	1.04	1.02	144	79	158	168
519-01	2			0.1056	0.101	0.104	0.102	19	11	16	33
519-02	2			0.1056	0.101	0.104	0.102	13	9	16	17
519-03	2			1.056	1.01	1.04	1.02	160	87	173	183
522-01	1		o.	1.056	1.01	1.04	1.02	102	63	130	145
522-04	2			0.1056	0.101	0.104	0.102	11	8	15	16
522-07	2			0.1056	0.101	0.104	0.102	16	10	17	17
522-10	2			0.1056	0.101	0.104	0.102	20	9	17	17
523-01	1		o.	1.056	1.01	1.04	1.02	120	63	124	128
523-02	1	N	o.	-	-	1	-		-	103	-
523-03	1	N	o.	-	-	1	-	-	-	69	-
523-04	1	N	o.	-	1.0016	1	-	-	76	134	-
523-05	1	N	o.	-	0.10016	0.1	-	-	8.5	13	-
523-06	1	N	o.	-	1.0016	1	-	-	65	113	-
523-07	1	N	o.	-	10.016	10	-	-	675	1277	-
523-11	2	N		-	1.0016	1	-	-	92	158	-
523-12	2			1.056	1.01	1.04	1.02	172	97	181	179
523-13	2	N		-	0.10016	0.1	-	-	13	16	-
523-14	2			0.1056	0.101	0.104	0.102	19	13	17	17
524-01	2			1.056	1.01	1.04	1.02	155	94	170	164
524-02	2			0.1056	0.101	0.104	0.102	20	12	18	18

[a] Operator #1 or #2;
[b] N = standards prepared from new stock solutions;
[c] o. = out-of-range values (ignored in establishing calibration relationships).

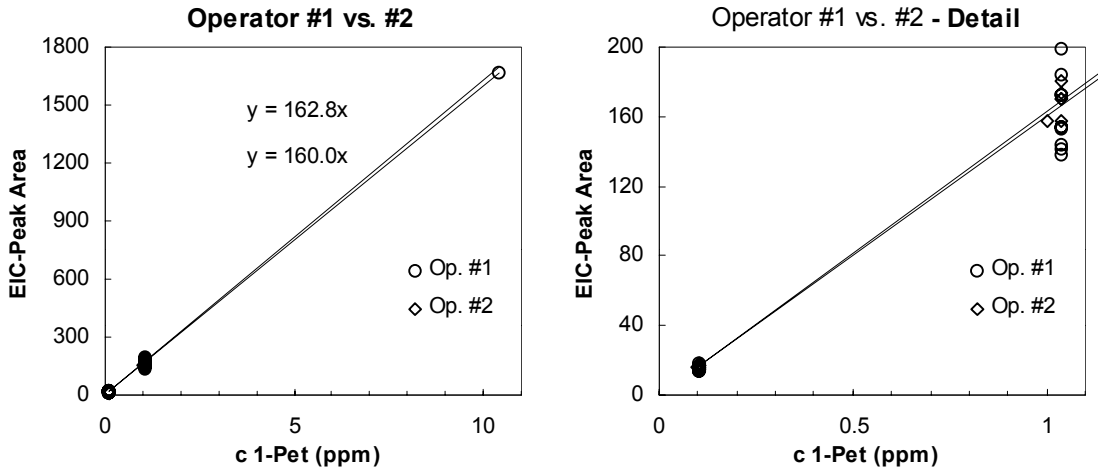


Figure A-18.1 Comparison of manual standard injections by two GC operators: Calibration relationships for 1-phenylethanol (see also Figure A-18.2).

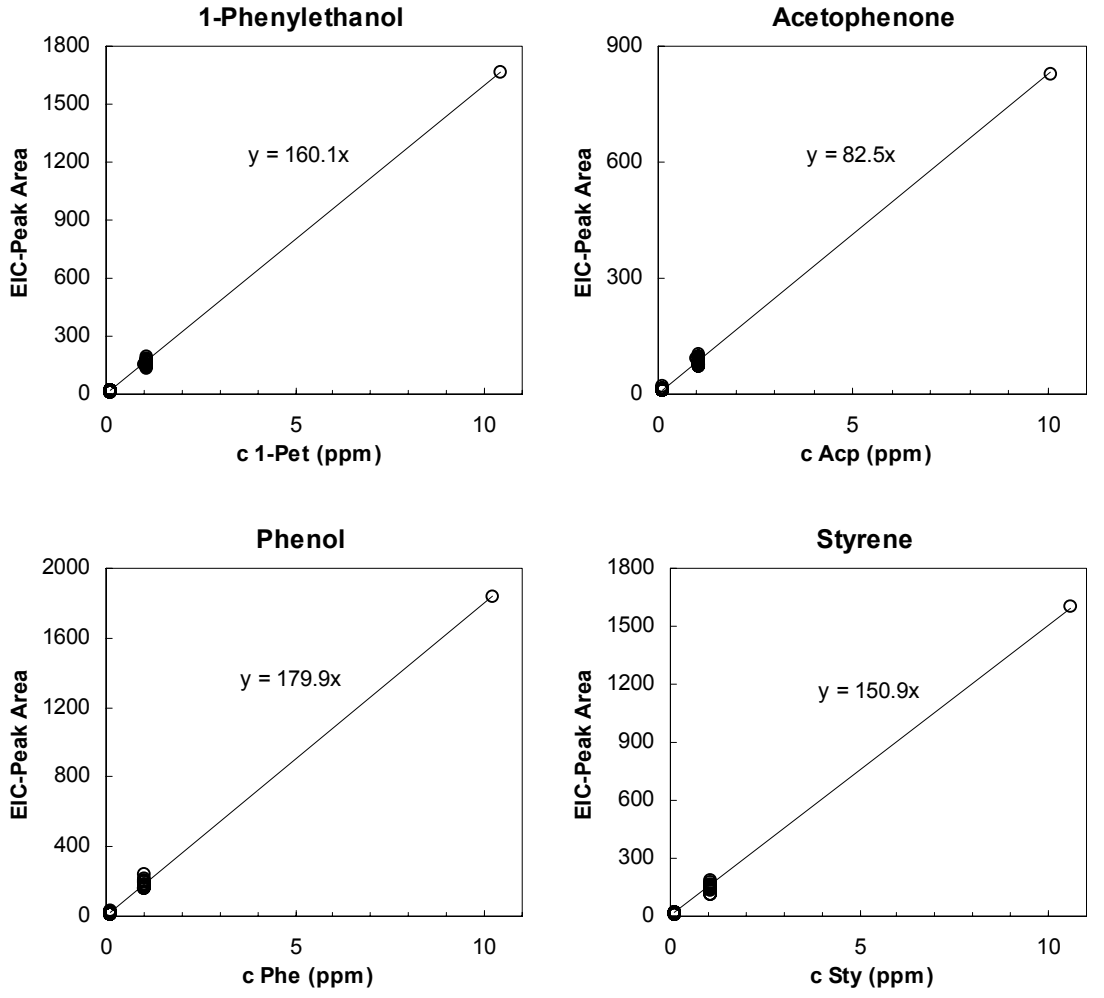


Figure A-18.2 Calibration curves for the DSC-Method.

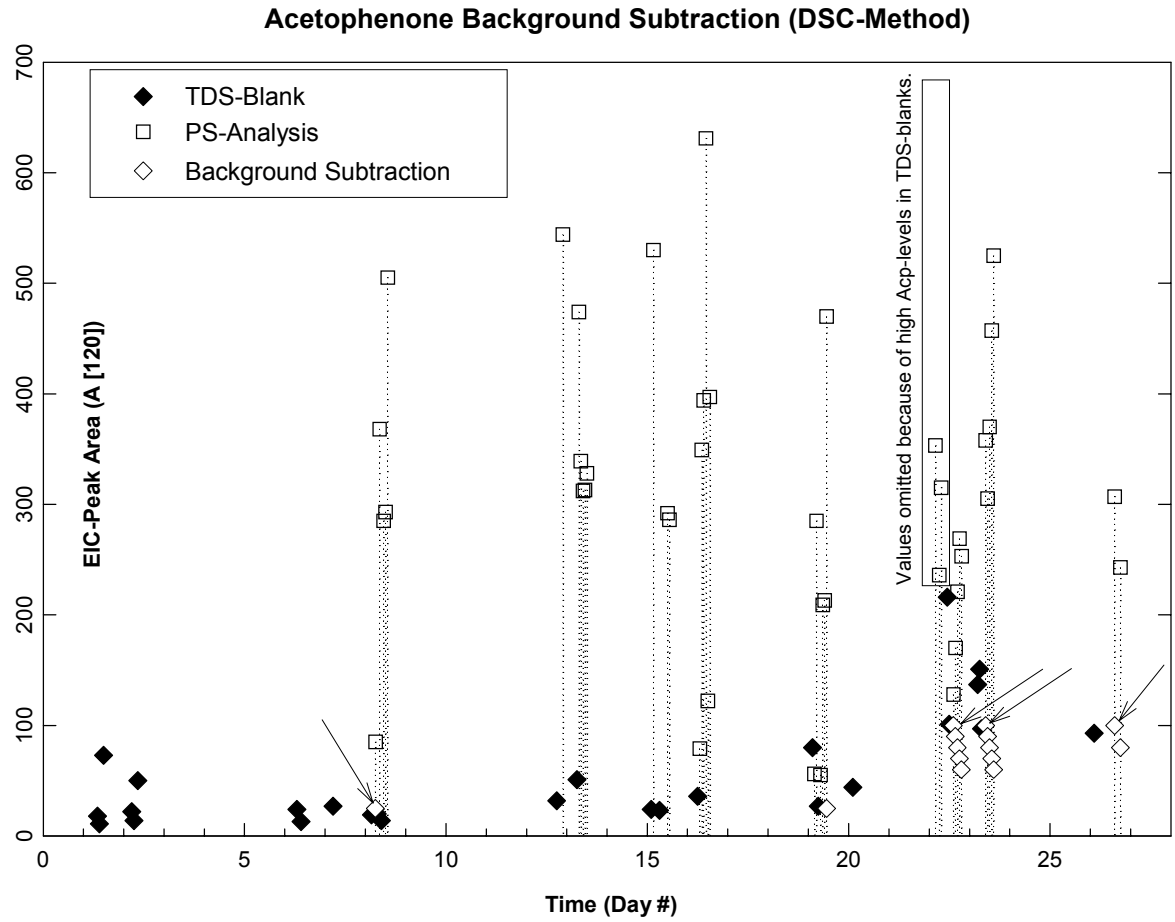


Figure A-18.3 **Background subtraction for acetophenone** (DSC-Method). The graph shows the peak areas of acetophenone in all PS-analyses and TDS-blanks performed as part of the DSC-series.
Based on this plot it was decided **to subtract a constant value of 25** from Day 8 through Day 19, whereas on Days 22, 23, and 26 **background subtraction starts with 100 and is reduced by 10 in each consecutive analysis** as indicated by the white rhombs (cf. also the Table A-18.2 *Polystrene Data*, below). Acetophenone concentrations were **not** calculated for the first three runs on Day 22 because of excessive Acp-levels in a preceding blank (with A [120] = 1047).
A Technical Note: The x-data (Time) were obtained by dividing the file (or: run) numbers by 2 and adding the result as decimal places to the Day Number; for example, the five PS analyses on Day 8 with run numbers 05, 07, 09, 10, and 11 (cf. Table *Polystrene Data*) are plotted with x-values of 8.25, 8.35, 8.45, 8.5 and 8.55.

Next Page:

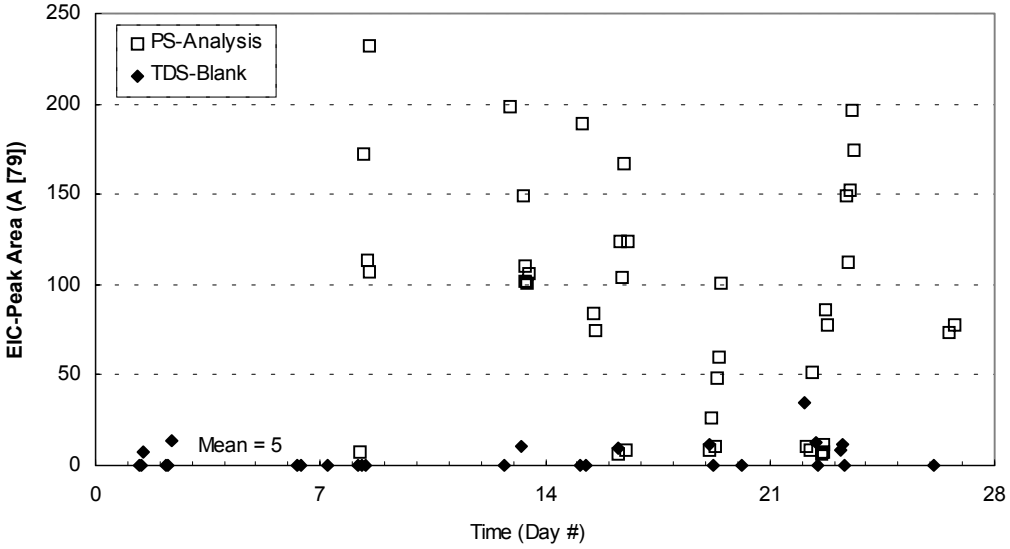
(from top to bottom)

Figure A-18.4 **1-Phenylethanol** background.

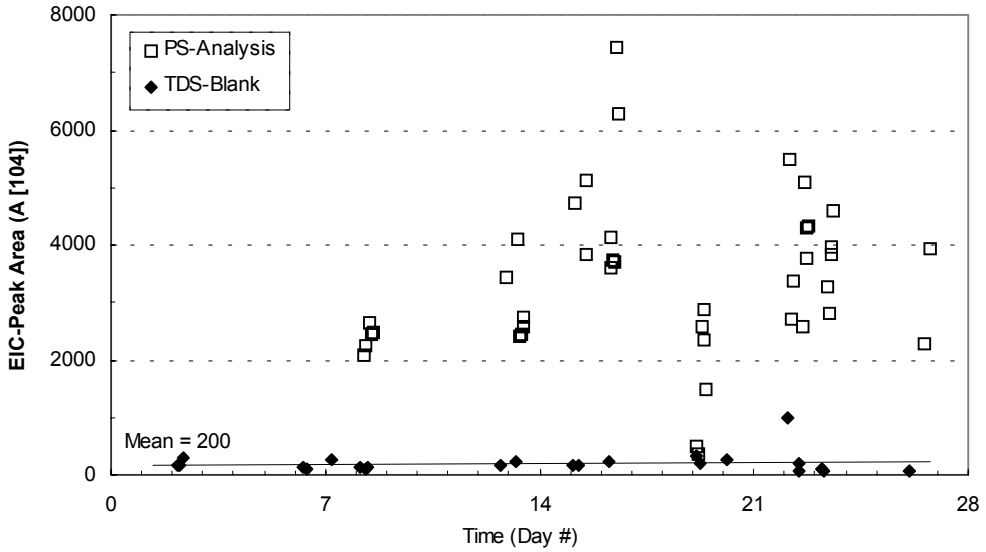
Figure A-18.5 **Styrene** background.

Figure A-18.6 **Phenol** background.

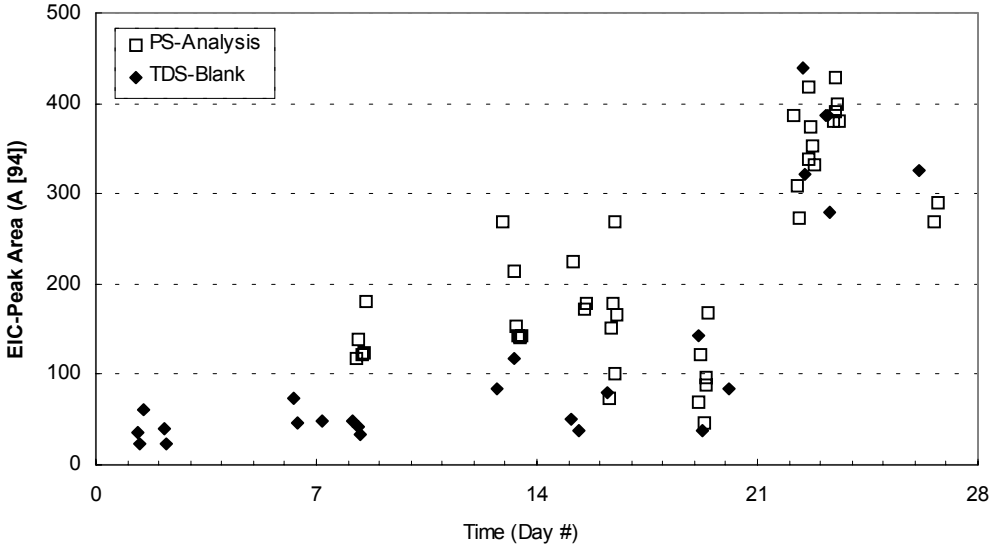
1-Phenylethanol in TDS-Blanks vs. PS-Analyses (DSC-Method)



Styrene in TDS-Blanks vs. PS-Analyses (DSC-Method)



Phenol in TDS-Blanks vs. PS-Analyses (DSC-Method)



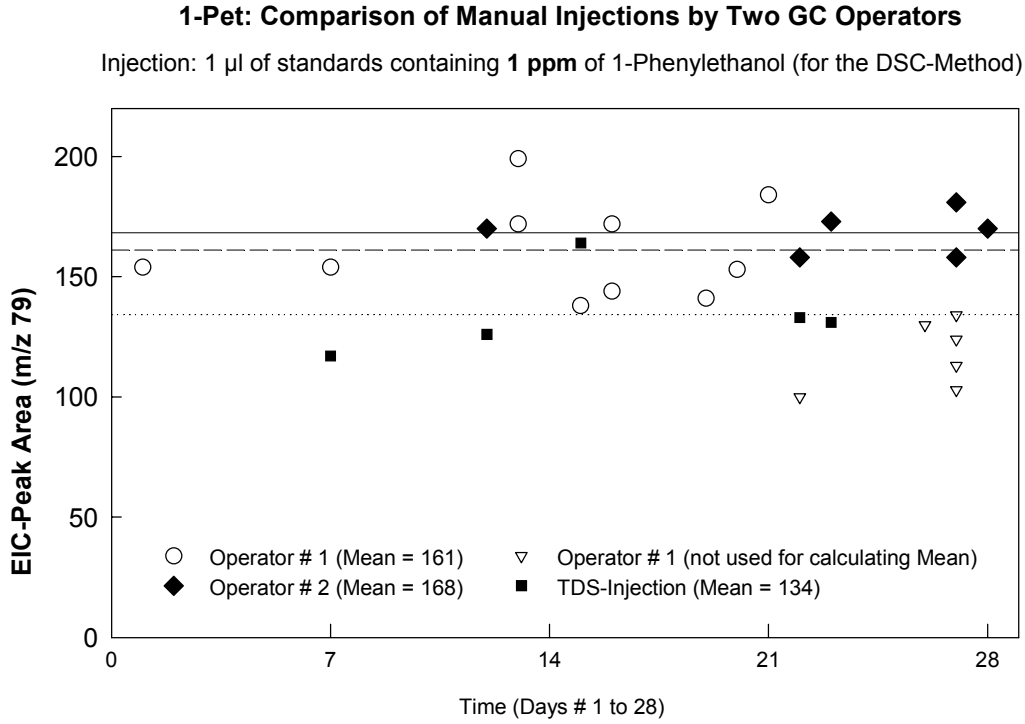


Figure A-18.7 Comparison of manual injections by two operators — **1-penylethanol.**
In contrast to Figure A-18.1, this analysis includes only the 1 ppm-standards.

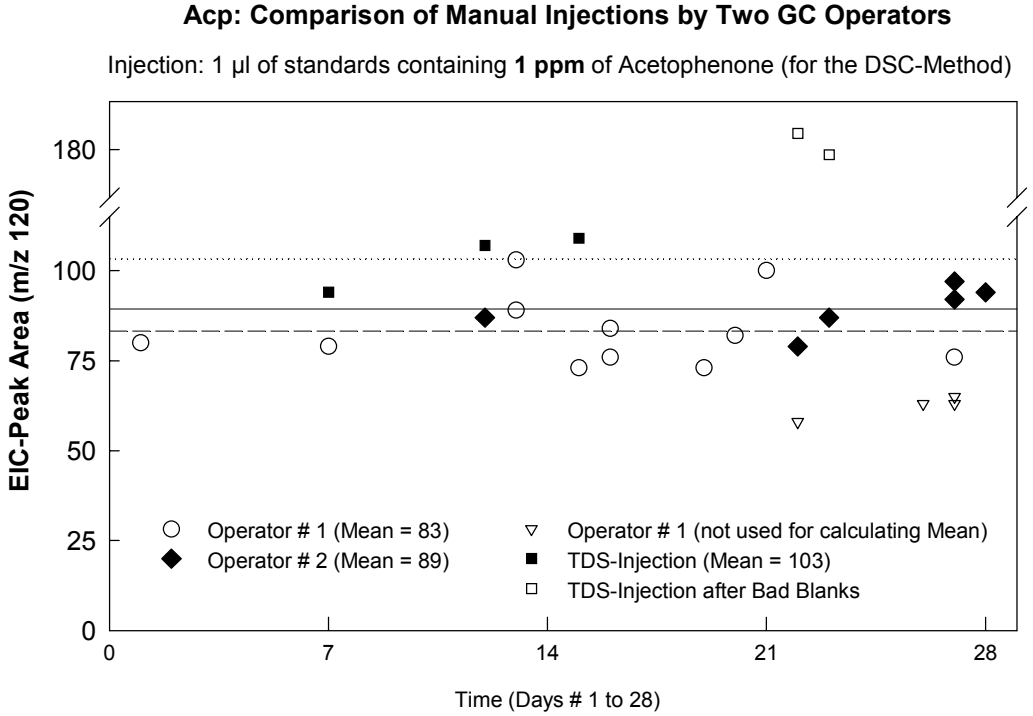


Figure A-18.8 Comparison of manual injections by two operators — **acetophenone.**
In contrast to Figure A-18.1, this analysis includes only the 1 ppm-standards.

Table A-18.2 Polystyrene data. *continued on next page →*

Day	File	Code	V inj. (µl)	c PS (mg/ml)	**m PS** (mg)	A [104]	A [120]	bg [a] [120]	A [79]	A [94]
08	504-05	168N 0 Gy	9.0	10.03	0.090	2070	85	*25*	7	118
	-07	168N **25.5 kGy**	9.0	10.08	0.091	2250	368	*25*	172	138
	-09	P. Dish **x kGy**	9.0	10.18	0.092	2645	285	*25*	113	121
	-10	P. Dish **x kGy**	9.0	10.18	0.092	2437	293	*25*	107	124
	-11	P. Dish **x + 23.5 kGy**	9.0	10.07	0.091	2494	505	*25*	232	180
12	508-18	168N **25.5 kGy**	10.0	10.08	0.101	3433	544	*25*	199	268
13	509-06	168N **25.5 kGy**	8.0	10.08	0.081	4110	474	*25*	149	214
	-07	XY **23.5 kGy**	8.7	10.10	0.088	2400	339	*25*	110	154
	-08	XY **23.5 kGy**	8.0	10.20	0.082	2444	312	*25*	102	142
	-09	XY **23.5 kGy**	8.0	10.20	0.082	2582	313	*25*	101	140
	-10	XY **23.5 kGy**	8.3	10.14	0.084	2752	328	*25*	107	142
15	511-03	168N **25.5 kGy**	9.5	10.08	0.096	4736	530	*25*	189	224
	-10	N. Cult. Flask **>15 kGy**	9.7	13.00	0.126	5108	292	*25*	84	173
	-11	N. Cult. Flask **>15 kGy**	9.5	13.00	0.124	3820	286	*25*	75	179
16	512-06	XY 0 Gy	8.5	10.20	0.087	3603	79	*25*	6	73
	-07	168N **23.5 kGy**	9.0	10.10	0.091	4143	349	*25*	124	152
	-08	Cult. Flask **x kGy**	8.9	10.15	0.090	3741	394	*25*	104	179
	-09	Cult. Fl. **x + 23.5 kGy**	8.8	10.10	0.089	3687	631	*25*	167	269
	-10	1x-'Glass' 0 Gy	9.5	10.10	0.096	7424	122	*25*	8	101
	-11	1x-'Glass' **23.5 Gy**	9.8	10.30	0.101	6285	397	*25*	124	166
19	515-03	168N t.ds. 0 Gy	8.0	10.20	0.082	480	56	*25*	8	70
	-04	168N t.ds. **23.5 kGy**	8.8	10.10	0.089	378	285	*25*	26	122
	-06	Yogh. Tray 0 Gy	9.4	10.00	0.094	2564	55	*25*	10	47
	-07	Yogh. Tray **23.5 kGy**	9.1	10.10	0.092	2347	209	*25*	48	97
	-08	168N **10 kGy**	9.0	10.20	0.092	2876	213	*25*	60	88
	-09	168N Parts **24.7 kGy**	9.0	10.10	0.091	1498	470	*25*	101	169
22	518-03	168N 0 Gy	8.0	13.50	0.108	5475	353	-	11	387
	-05	XY 0 Gy	7.0	7.85	0.055	2724	236	-	8	309
	-06	168N **10 kGy**	9.0	9.00	0.081	3359	315	-	51	273
	-12	XY 0 Gy	9.5	7.85	0.075	2593	128	*100*	6	338
	-13	168N 0 Gy	9.5	13.50	0.128	5078	170	*90*	7	418
	-14	168N Parts 0 Gy	9.0	9.98	0.090	3785	221	*80*	12	373
	-15	168N **10 kGy**	9.7	9.00	0.087	4291	269	*70*	86	352
	-16	168N **10 kGy**	9.3	9.00	0.084	4327	253	*60*	78	332
23	519-08	168N **22.5 kGy**	9.7	7.90	0.077	3272	358	*100*	149	380
	-09	168N **23.5 kGy**	9.7	7.00	0.068	2820	305	*90*	112	428
	-10	168N **25.5 kGy**	9.7	8.10	0.079	3837	370	*80*	152	390
	-11	XY **23.5 kGy**	6.8	23.00	0.156	3973	457	*70*	196	399
	-12	168N Parts **24.7 kGy**	9.8	12.50	0.123	4588	525	*60*	174	381
26	522-12	168N **10 kGy**	10.2	10.20	0.104	2269	307	*100*	74	269
	-14	168N **10 kGy**	9.8	9.00	0.088	-	-	-	-	-
	-15	168N **10 kGy**	9.5	9.00	0.086	3938	243	*80*	78	290

[a] bg [120] = Acetophenone background subtraction.

Table A-18.2 Polystyrene Data, *continued*.

File	No.	Code	↓↓↓ [a]			**Sty** (ppm)	**Acp** (ppm)	**1-Pet** (ppm)	**Phe** (ppm)	Remarks
504-05	01	168N 0 Gy				137	8.1	0.5	< 7	
-07	02	168N **25.5 kGy**	1			150	45.8	11.8	< 8	
-09	03	P. Dish **x kGy**		1		177	34.4	7.7	< 7	
-10	04	P. Dish **x kGy**		2		162	35.5	7.3	< 8	
-11	05	P. Dish **x + 23.5 kGy**				168	64.2	16.0	< 11	
508-18	06	168N **25.5 kGy**	2			213	62.4	12.3	< 15	
509-06	07	168N **25.5 kGy**	3			321	67.5	11.5	< 15	
-07	08	XY **23.5 kGy**				166	43.3	7.8	< 10	three
-08	09	XY **23.5 kGy**		1		182	42.6	7.8	< 10	CH_2Cl_2 -
-09	10	XY **23.5 kGy**		2		193	42.8	7.7	< 10	solutions
-10	11	XY **23.5 kGy**				201	43.6	7.9	< 9	
511-03	12	168N **25.5 kGy**	4			314	63.9	12.3	< 13	
-10	13	N. Cult. Flask **>15 kGy**		1		258	25.7	4.2	< 8	
-11	14	N. Cult. Flask **>15 kGy**		2		194	25.6	3.8	< 8	
512-06	15	XY 0 Gy				260	7.5	0.4	< 5	
-07	16	168N **23.5 kGy**				287	43.2	8.5	< 9	
-08	17	Cult. Flask **x kGy**				260	49.5	7.2	< 11	
-09	18	Cult. Fl. **x + 23.5 kGy**				260	82.6	11.7	< 17	
-10	19	1x-'Glass' 0 Gy				499	12.3	0.5	< 6	
-11	20	1x-'Glass' **23.5 Gy**				399	44.7	7.7	< 9	
515-03	21	168N t.ds. 0 Gy				23	4.6	0.6	< 5	
-04	22	168N t.ds. **23.5 kGy**				13	35.5	1.8	< 8	
-06	23	Yogh. Tray 0 Gy				167	3.9	0.7	< 3	Copolymer
-07	24	Yogh. Tray **23.5 kGy**				155	24.3	3.3	< 6	
-08	25	168N **10 kGy**	1			193	24.8	4.1	< 5	
-09	26	168N Parts **24.7 kGy**				95	59.3	6.9	< 10	
518-03	27	168N 0 Gy			1	324	-	0.6	-	
-05	28	XY 0 Gy		1		304	-	0.9	-	
-06	29	168N **10 kGy**	1			258	-	3.9	-	
-12	30	XY 0 Gy		2		213	4.6	0.5	-	
-13	31	168N 0 Gy			2	252	7.6	0.3	-	
-14	32	168N Parts 0 Gy				265	19.0	0.8	-	
-15	33	168N **10 kGy**	2			311	27.6	6.2	-	
-16	34	168N **10 kGy**	3			327	27.9	5.8	-	
519-08	35	168N **22.5 kGy**				266	40.8	12.1	-	direct
-09	36	168N **23.5 kGy**				256	38.4	10.3	-	dissolution
-10	37	168N **25.5 kGy**				307	44.7	12.1	-	
-11	38	XY **23.5 kGy**				160	30.0	7.8	-	
-12	39	168N Parts **24.7 kGy**				237	46.0	8.9	-	
522-12	40	168N **10 kGy**	2			132	24.1	4.4	-	
-14	41	168N **10 kGy**				-	-	-	-	GC Error
-15	42	168N **10 kGy**		4		290	23.1	5.7	-	

[a] Numbers indicate repeated analyses of the same solutions (cf. column *c PS* on previous page).

Concentrations are calculated as c Sty = ((A [104] **- 200**) / 150.9 ng^{-1}) / m PS,
c Acp = ((A [120] **- bg [120]**) / 82.5 ng^{-1}) / m PS, **c 1-Pet = (A [79] / 160.1 ng^{-1}) / m PS**, and
c Phe = (A [94] / 179.9 ng^{-1}) / m PS.

Appendix 19

Calculating Radiation-Chemical Yields

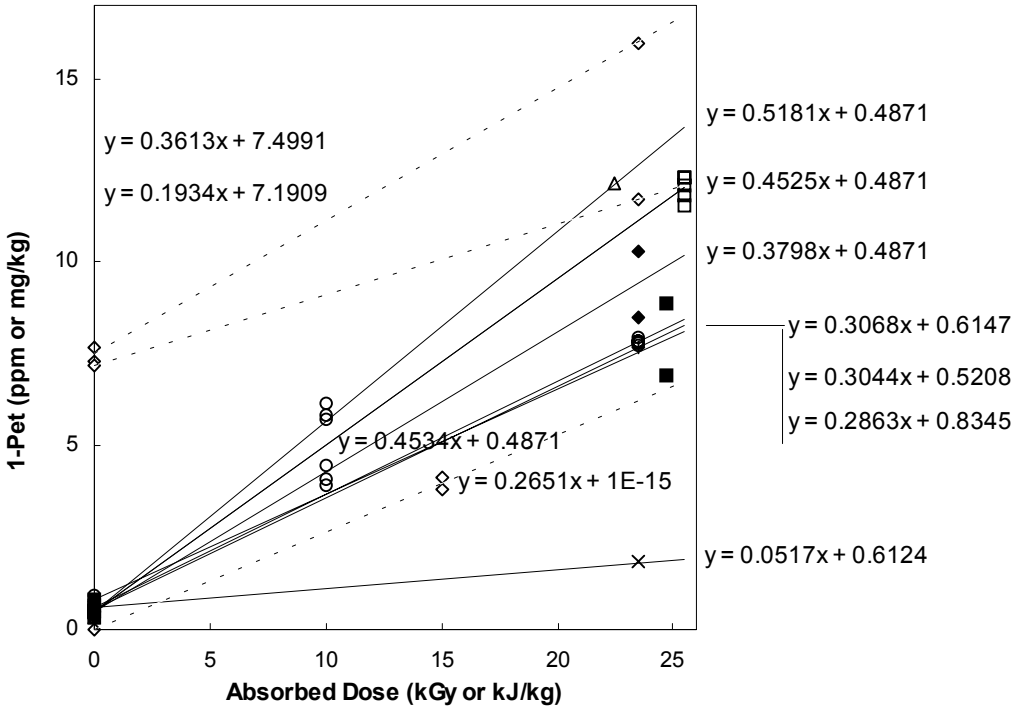


Figure A-19.1 Plot of **1-phenylethanol <u>concentrations</u> vs. the absorbed dose.**
The slopes of the curves give the radiation-chemical yields for the sample(s) in **mg/kJ** [(mg/kg) / (kJ/kg)], which may be converted to **nmol/J** or to a **G-value** (molecules per 100 eV of absorbed energy). The analysis is for the results obtained with the DSC-Method.

Table A-19.1 **<u>Radiation-chemical yields</u>** for **1-phenylethanol** calculated from the slope of the linear regressions in the concentration-dose plot (data for Figure 9.7).

	Code	mg/kJ	mmol/kJ or µmol/J	**nmol/J**	G [a]
Granulates	168N **10 kGy** (n=6)	0.4534	0.0037	**3.7**	0.037
	168N **25.5 kGy** (n=5)	0.4525	0.0037	**3.7**	0.037
	168N **23.5 kGy** (n=2)	0.3798	0.0031	**3.1**	0.031
	168N **22.5 kGy**	0.5181	0.0042	**4.2**	0.042
	XY **23.5 kGy** (n=5)	0.3068	0.0025	**2.5**	0.025
Inj.-Molded Parts	168N Parts **24.9 kGy** (n=2)	0.2863	0.0023	**2.3**	0.023
	1x-'Glass' **23.5 kGy**	0.3044	0.0025	**2.5**	0.025
'Real-Life Samples'	N. C. Flask **>15 kGy** (n=2) [b]	0.2651	0.0022	**2.2**	0.022
	Petri Dish x **+ 23.5 kGy** [c]	0.3613	0.0030	**3.0**	0.030
	Cult. Flask x **+ 23.5 kGy** [c]	0.1934	0.0016	**1.6**	0.016
Special	168N t.ds. **23.5 kGy**	0.0517	0.0004	**0.4**	0.004

[a] G-Value: **Molecules per 100 eV** of absorbed energy.
[b] Calculated for 15.0 kGy and assuming that c (1-Pet) was zero before irradiation.
[c] Calculated for the second (re-) irradiation with 23.3 kGy.

Appendix 20

MS Identification Tables for Trace Radiolysis Products

Legend for Tables A-20.1 to A-20.5:

t_R	Retention time in minutes.
m/z	Major ions including (or: plus) the molecular ion; the base peak is underlined.
I/C	(Irradiated vs. Control) = **Relative increase after irradiation;** these are **rough estimates** based on *peak height* comparisons of *extracted ion chromatograms* (EICs) like those in Figures 10.4 to 10.6.
Misc. Info	– Match quality of library fits (%): av indicates averaged scans, (-) indicates background subtraction – Observations on peak shapes / concentrations

Table A-20.1 **Trace radiolysis products** in polystyrene with the **DB-5** column (PS 168 N, 25.5 kGy, **50 mg**).

t_S [a]	m/z	#	Compound	I/C	Misc. Info
19.02	77,105,134	1	**2-Phenylpropanal**	10	87% av
19.25	91,92,122	2	Benzeneethanol	?	81% av (-)
19.29	77,79,104,105,150		Unidentified	?	---
19.43	65,91,134	3	1-Phenyl-2-propanone	4	72% av
19.86	77,103,104,132	4	2-Phenylpropenal	<2	80% scan 199
19.96	121,136	5	1-(4-Hydroxyphenyl)-ethanone or 1-(2-Hydroxyphenyl)-ethanone	7	91% scan 213
19.99	77,105,134	6	**1-Phenyl-1-propanone**	>10	parametric retrieval
20.50	77,105,122	7	Benzoic acid	?	94% av
21.20	77,105,136	8	2-Hydroxy-1-phenyl-ethanone	2	87% scan 414 coeluting with next
21.20	77,105,148	9	1-Phenyl-1,2-propanedione	?	86% av
23.43	69,105,147,162	10	1-Phenyl-1,3-butanedione	5	83% av

[a] „System Time“ — these runs were performed with the old version of the software; chromatography starts at „t_S“ 10.00 min (cf. Section 3.6).

Exp. Conditions: PS 168 N, **50 mg** powder, ca. 1.5 years after irradiation (25.5 kGy) of the pellets; TDS 160(10); CIS 30; GC 40(1.5) -10- 250(5); column: DB-5.

Table A-20.2 **Trace products** (PS 168 N, 25.5 kGy; column: **Rtx-200;** GC: **10°C/min**).

t_R	m/z	#	Compound	I/C	Misc. Info
9.10	91,92,122	2	Benzeneethanol	3-4	87% scan 1467
9.53	77,105,134	1	**2-Phenylpropanal**	10	72% scan 1539 (-) coeluting with Acp
9.54	77,79,104,105,150		Unidentified	?	coeluting with previous
10.44	77,105,134	6	**1-Phenyl-1-propanone**	10	86% scan 1692 coelut. with benzoic acid
10.52	65,91,134	3	1-Phenyl-2-propanone	3-4	coelut. with benzoic acid
10.54	121,136	5	1-(4-Hydroxyphenyl)-ethanone or 1-(2- Hydroxyph.)-ethanone	4	coelut. with benzoic acid and 2-Phenylpropenal
10.55	77,103,104,132	4	2-Phenylpropenal	2	72% av (-) coelut. with b. acid
9.8-10.8	77,105,122	7	Benzoic acid	?	93% scan 1742 **severe fronting**
10.95	77,105,148	9	1-Phenyl-1,2-propanedione	5	94% scan 1777 (-)
11.49	91,136		Benzene acetic acid	?	90% scan 1869 (-) fronting
11.98	43,91,105,148		*4-Phenyl-2-butanone ?*	?	coeluting with next; *ultra-trace*
12.00	77,105,136	8	2-Hydroxy-1-phenyl-ethanone	2-3	87% scan 1954 (-)
12.16	77,79,107,138		**1-Phenyl-1,2-ethanediol**	?	91% scan 1979
12.76	77,103,131,132		*3-Phenyl-2-propenal*	2	91% scan 2081; *ultra-trace*
13.86	69,105,147,162	10	1-Phenyl-1,3-butanedione	?	peak shape

Exp. Conditions: PS 168 N, **50 mg** powder, ca. 2 years after irradiation (25.5 kGy) of the pellets; TDS 50 -20- 250(5); CIS 30; GC 40(1.5) **-10-** 180(5); column: Rtx-200.

Table A-20.3 **Trace products** (PS 168 N, 25.5 kGy; column: **Rtx-200;** GC: **5°C/min**).

t_R	m/z	#	Compound	I/C	Misc. Info
12.89	91,92,122	2	Benzeneethanol	?	83% scan 2083
13.67	77,105,134	1	**2-Phenylpropanal**	10	87% scan 2216
13.76	77,79,104,105,150		Unidentified	?	---
15.42	77,105,134	6	**1-Phenyl-1-propanone**	10	72% av (-); coelut. with benzoic acid
15.56	121,136	5	1-(4-Hydroxyphenyl)-ethanone or 1-(2- Hydroxyphenyl)-ethanone	5	coelut. with benzoic acid
15.59	65,91,134	3	1-Phenyl-2-propanone	<4	coelut. with benzoic acid
15.64	77,103,104,132	4	2-Phenylpropenal	>2	87% scan 2547 (-); coelut. with benzoic acid
14.30-16.30	77,105,122	7	Benzoic acid	?	**severe fronting**
16.40	77,105,148	9	1-Phenyl-1,2-propanedione	5	94% scan 2674
17.55	91,136		Benzene acetic acid	?	fronting
18.35	77,105,136	8	**2-Hydroxy-1-phenyl-ethanone**	10	90% scan 3002
18.39	43,91,105,148		*4-Phenyl-2-butanone ?*	?	coeluting with previous *ultra-trace*
18.76	77,79,107,138		**1-Phenyl-1,2-ethanediol**	?	90% av
19.83	77,103,131,132		*3-Phenyl-2-propenal*	-	98% av *ultra-trace*
21.95	69,105,147,162	10	1-Phenyl-1,3-butanedione	?	peak shape

Exp. Conditions: PS 168 N, **50 mg** powder, ca. 2 years after irradiation (25.5 kGy) of the pellets; TDS 50 -20- 250(5); CIS 30; GC 40(1.5) **-5-** 180(5); column: Rtx-200.

Table A-20.4 **Trace products (PS XY, 23.5 kGy;** column: **Supelcowax 10).**

t_R	m/z	#	Compound	I/C	Misc. Info
10.95	77,105,134	1	2-Phenylpropanal	4	coeluting with Paa
11.45	77,79,104,105,150		Unidentified	?	---
12.00	77,105,134	6	**1-Phenyl-1-propanone**	6	coeluting with next
12.04	65,91,134	3	1-Phenyl-2-propanone	4	87% av (-)
12.93	77,103,104,132	4	2-Phenylpropenal	<2	72% scan 1668
12.96	121,136	5	1-(4-Hydroxyphenyl)-ethanone or 1-(2- Hydroxyphenyl)-ethanone	4	91% scan 1673 (-)
13.58	91,105,148		*3-Phenyl-2-butanone*	?	93% av (-) *ultra-trace*
16.72	69,105,147,162	10	1-Phenyl-1,3-butanedione	5	coelut. with ?
19.35	77,105,122	7	Benzoic acid	>2	coeluting with cD
20.79	91,136		Benzene acetic acid	?	91% scan 2979

Exp. Conditions: PS XY, **50 mg** powder, ca. 6 weeks after irradiation (23.5 kGy) of the pellets; TDS 200(10); CIS 30; GC 50(1.5) -10- 220(6); column: Supelcowax 10.

Table A-20.5 **Trace products** (PS 168 N, **10 kGy, 300 mg;** column: Supelcowax 10).

t_R	m/z	#	Compound	I/C	Misc. Info
7.66	77,105,134	1	2-Phenylpropanal	2-3	coeluting with Paa
7.87	77,79,104,105,150		Unidentified	?	---
8.20	77,105,134	6	**1-Phenyl-1-propanone**	4	coeluting with next
8.22	65,91,134	3	1-Phenyl-2-propanone	2	---
8.68	77,103,104,132	4	2-Phenylpropenal	2	coeluting with 1-Pet
8.73	77,105,148	9	1-Phenyl-1,2-propanedione	<2	coeluting with next
8.73	121,136	5	1-(4-Hydroxyphenyl)-ethanone or 1-(2- Hydroxyphenyl)-ethanone	<3	---
9.02	91,105,148		*3-Phenyl-2-butanone*	<2	*ultra-trace*
10.75	69,105,147,162	10	1-Phenyl-1,3-butanedione	?	---
12.63	77,105,122	7	Benzoic acid	2-3	---
13.95	91,136		Benzene acetic acid	?	---

Exp. Conditions: PS 168 N, **300 mg** powder, ca. 1.5 years after irradiation (**10 kGy**) of the pellets; TDS 200(10); CIS 30; GC 40(1.5) -20- 220(11); column: Supelcowax 10.

Appendix 21

Method Development for Benzene Quantitation

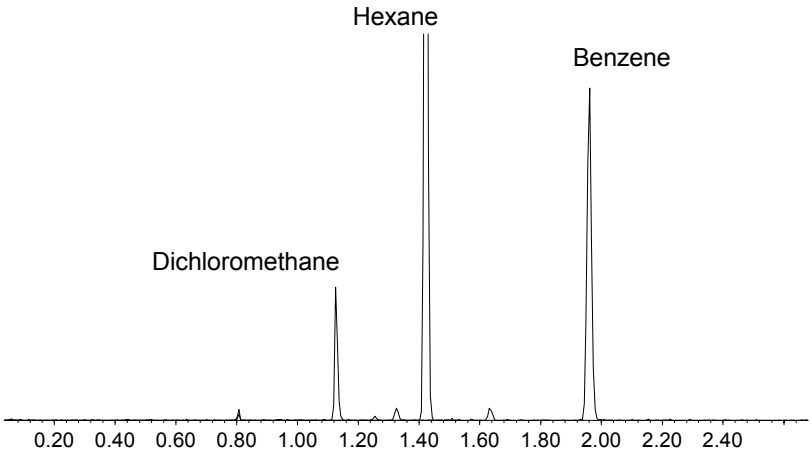


Figure A-21.1 Wet-needle injections of benzene and two potential solvents, dichloromethane, and hexane.
Conditions: CIS 150°C, **split;** GC isothermal 25°C; column: DB-5.

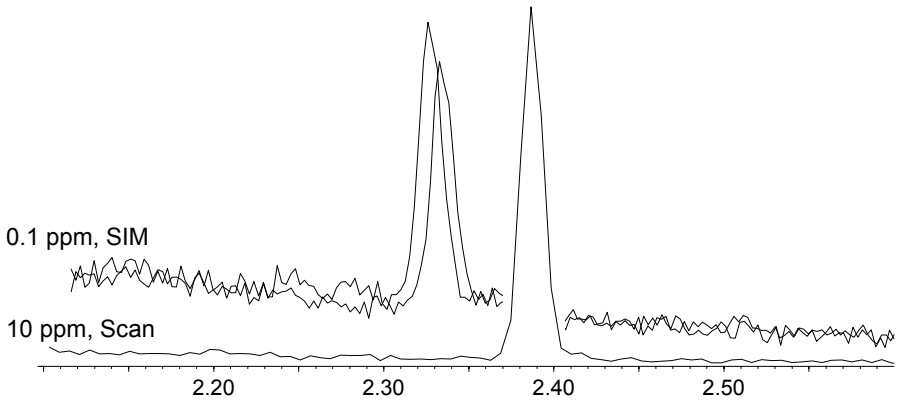


Figure A-21.2 **Splitless-**injections of benzene standards in dichloromethane: an early version of the method is 'challenged' with 0.1 ppm injections.
Conditions: CIS 30 -12°C/s- 150 (1), 0.33 s splitless; GC isothermal 25°C; column: DB-5; MS Scan (10 ppm) or SIM (0.1 ppm). The abundance-(y)-axes are, of course, not identical.

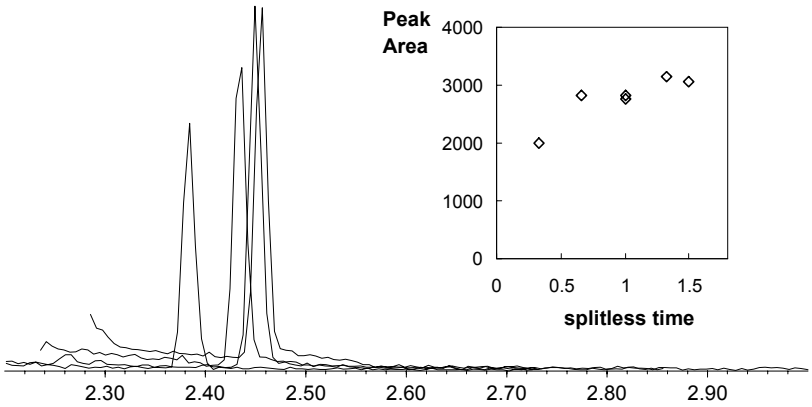


Figure A-21.3 Optimization of **splitless-time.**
Exp. Conditions: CIS 30 –12°C/s– 150 (1); GC isothermal 25°C; column: DB-5.

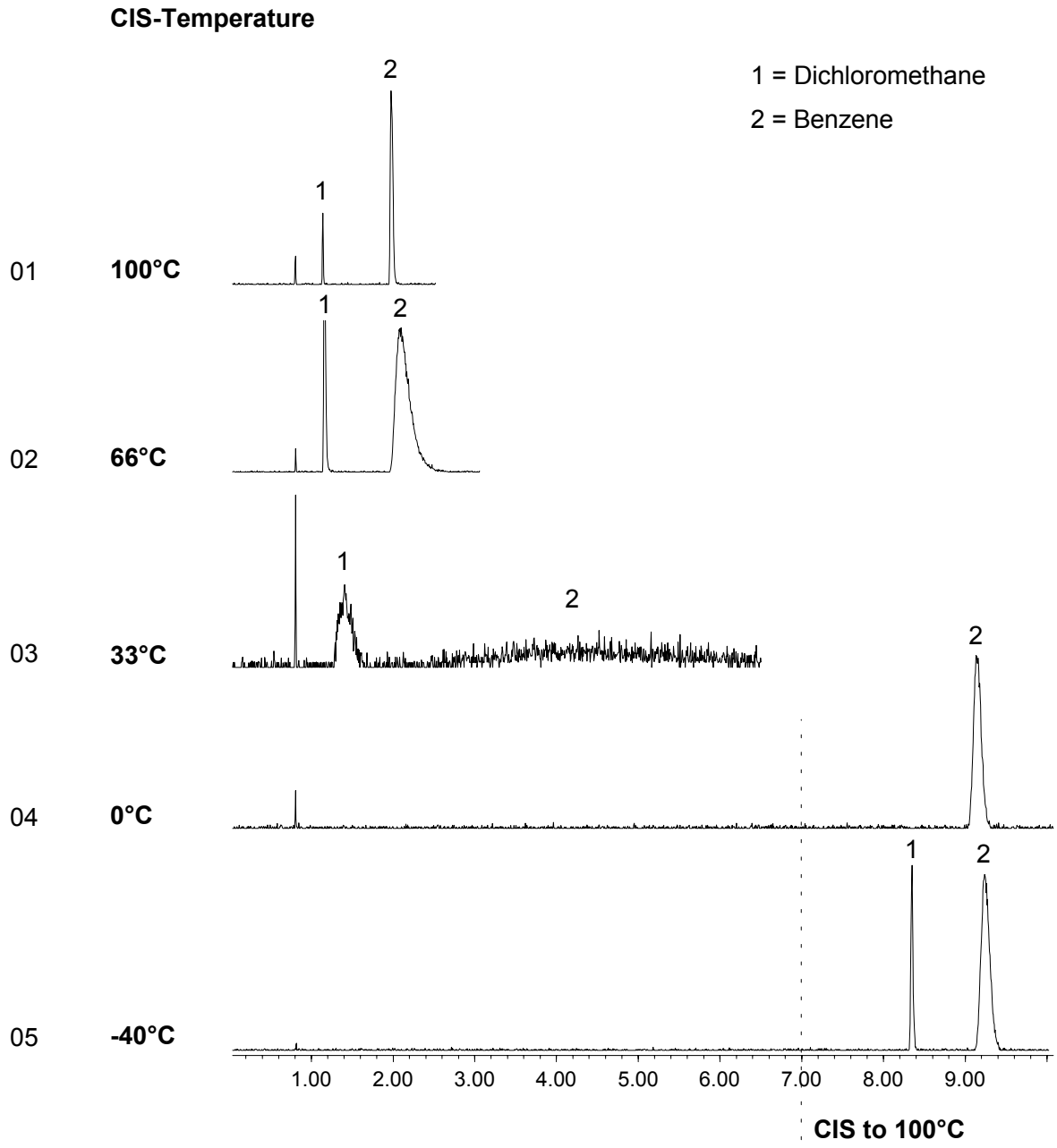


Figure A-21.4 **Retention of dichloromethane and benzene in the CIS** (filled with 1.5 cm Tenax TA) **at various temperatures.**

01: Both analytes are not retained;
02: Benzene starts to interact with the Tenax-'column' in the CIS-liner;
03: Benzene is somewhat retained and reaches the detector from ca. 3 to 6 min, we can observe its 'breakthrough' through the Tenax trap;
04: Benzene is completely trapped, and then released when the CIS is programmed to 100°C; dichloromethane still breaks through;
05: Both analytes are trapped at -40°C.

Conditions: wet-needle injections of a 1:1 mixture; CIS: split, (and in runs 04 and 05 programmed with 12°C/s to 100°C at 7.00 min); GC isothermal at 25°C; the abundance-(y)-axes are not identical (wet-needle injections !); the peak at ca. 1.15 min is a contaminant.

Appendix 22

Research Proposal: Migration Studies with Large-Volume On-Column Injection (LOCI)

Background

Some preliminary migration / extraction tests were performed (in 'Phase III') to see whether there was any transfer of radiolysis products into a solvent, and whether one could see anything in very simple tests (with n-hexane as solvent[#]).

The beginning column degradation (see Section 7.8) with its resulting loss in sensitivity for 1-phenylethanol forced us to abandon these projects prematurely. Despite the limitations of these measurements, there was clearly an overall trend towards increased acetophenone concentrations (in hexane) after irradiation, and there also appeared to be a proportionality with the absorbed dose. The problem of migration / extraction was not not re-addressed in the course of this work, because it was felt that qualified migration studies should be part of an entirely new research project.

It is proposed to use **large-volume on-column injection (LOCI),** combined with a pre-concentration step, in a future migration study with irradiated plastics.

Large-Volume On-Column Injection (LOCI)

The concept of combining a pre-concentration step with LOCI was inspired by K. Grob, who, in a seminar on LOCI, explained how VOCs (volatile organic compounds) in drinking water are analyzed in his laboratory, namely by extraction with hexane or pentane followed by LOCI. The technique could be applied to the analysis of migration into aqueous solutions, and one could imagine different migration variants, e. g., plastic films are first irradiated 'alone' and then kept in contact with water, or sealed pouches filled with water are irradiated (which would be closer to 'real-life' conditions). In any case, the aqueous solutions would be extracted with pentane or hexane, and the extracts analyzed by GC-MS with LOCI. Other extraction media (food simulating liquids) such as octane would be analyzed with LOCI alone, i. e., without the preconcentration step.

The CIS can also be used to 'introduce' large volumes 'into a GC', however, the approach is somewhat different, as the solvent is evaporated in the CIS (and vented through the split vent). An important (and inherent) advantage of the LOCI technique is the fact that, with appropriate optimization, a loss of highly volatile solutes can be largely avoided. This is possible because the solvent film in the pre-column acts as a temporary stationary phase *trapping and reconcentrating the volatiles* during solvent evaporation, and it is ultimately a geometry effect.

A good introduction to LOCI is the paper of Munari et al. (1995) featuring a commercially available instrument with software-controlled optimization of conditions. Key terms and concepts (early vapour exit, partially concurrent solvent evaporation, etc.) are explained and a schematic drawing beautifully illustrates the *reconcentration* of volatile analytes. Further references to the literature are made below.

[#] While non-polar low-MW solvents tend to yield migration values that are considerably higher than those obtained with more realistic food-simulating liquids (e. g., olive oil or synthetic triglycerides), they are used for reasons of time and analytical convenience, and/or to obtain a worst-case scenario. Migration from irradiated plastics into iso-octane has been determined by Allen et al. (1988b, 1990a), and into heptane by Haesen et al. (1983). The results obtained Allen et al. (1988b, 1990a) provide „some justification for the use of iso-octane as a convenient indicator simulant," but generally the idea of using analytically simple organic liquids should be „treat[ed] with caution" (Figge 1996), because of their distinctly different interaction with plastics and the difficulty to find the 'right' test conditions.

If a GC-autosampler for on-column injection is not available, an alternative concept is to use an improvised 'large-volume injector' consisting of a HPLC sample loop, a HPLC pump, and two six-port valves. The aim, of course, is to transfer a defined volume of solvent with a defined velocity into the pre-column of the LOCI-system, where the solvent is evaporated and vented through the 'early vapor exit'. The idea to use a HPLC pump was inspired by the on-line coupled LC-GC of our colleagues (cf. Schulzki, 1996; Schulzki et al., 1995b, 1996, 1997), and can be considered as an **'LC-GC without analytical LC column.'** Similar 'loop-type interfaces' have been used by other authors (e. g., Hankemeier et al., 1996).

Large-Volume Techniques for Aqueous Samples

With the proposed *migration system water / hexane*, it is not totally clear to what extent non-polar compounds would migrate into an aqueous solution in the first place, or to what extent polar compounds would finally 'make it' into the organic solvent. The latter problem could obviously be circumvented by directly injecting water or aqueous solutions, an option that is particularly interesting, since distilled water and 15% ethanol are 'official' food simulants of the EU Global Migration test (EC-Directive 90/128/EEC), and 95% ethanol is being used as an alternative fatty food simulant.[#]

Since water attacks stationary phases and desactivated surfaces by hydrolyzing siloxane bonds, chromatographers are reluctant to inject aqueous samples, and initially I did not consider the option to perform large-volume injections with H_2O -containing samples. It appears however that the damage is caused by *condensed* water rather than water vapour (Grob and Biedermann, 1996; Biedermann et al., 1997), and that large volumes of aqueous samples can be injected with special *packed vaporising chambers*. Packing materials such as Tenax are resistant to water, and the vapour is vented through an 'early vapour exit' without allowing it to condense in the (retaining) precolumn.

Grob and Biedermann (1996) describe such a *packed vaporising chamber–precolumm solvent split–gas discharge system*, they demonstrate its robustness towards 'dirty' samples and present some test chromatograms obtained with up to 500 µl of water and methanol-water (1:1) solutions. Polyimide coating has been suggested to deactivate the vaporising chamber (Biedermann et al., 1997). Techniques to directly inject large volumes of water are also discussed in a review by Mol et al. (1995).

> In any case, **large-volume injection** appears to be the **method of choice** for migration studies, and it would be most interesting to compare it with standard analytical procedures.
>
> For more information on large-volume injection techniques, and for further references, see the *reviews* of Grob and Biedermann (1996) and Mol et al. (1995), the papers of Munari et al. (1995), Hagman and Roeraade (1993), Hiller et al. (1993), Hankemeier et al. (1996), and Bosboom et al. (1996).

[#] Ethanol 95% has been used in tests leading to the 1986 FDA-authorization of ethylene-vinylacetate copolymer for use in food irradiation. Other investigations have been reviewed by Figge (1996), who discusses alternative simulants in some detail and warns that their „practical application ... should still be treated with great caution."

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Abbreviations

1-Pet	1-Phenylethanol
2D-	Two-dimensional (in: 2D-plot)
A [ ]	Peak area, e. g., A [1-Pet], the peak area of 1-phenylethanol A [79.1], the peak area for m/z 79.1 in an EIC
Acp	Acetophenone (1-Phenylethanone)
Bal	Benzaldehyde
BHT	Butylhydroxytoluene, 2,6-bis-(1,1-dimethylethyl)-4-methylphenol
c	Concentration, e. g., c Acp = acetophenone concentration
cD	„Cyclodimer“ (diphenylcyclobutane [or: (cyclobutanediyl)-bis-benzene] isomers)
CHP	Column head pressure
CIS	Cooled injection system / CIS conditions
DSC	Dissolution-solvent-casting (the DSC-Method, ‘working title’ for Thermal Desorption of Polymer Solutions with Solvent Evaporation)
EIC	Extracted ion chromatogram
EMV	Electron multiplier voltage
ESTD	External standard
f. t.	Film thickness
G	G-Value, radiation-chemical yield (molecules per 100 eV of absorbed energy)
G, C	Granulate, Control (= non-irradiated)
G, I	Granulate, Irradiated (sterilizing dose)
GC	Gas chromatography / GC conditions
HPLC	High-performance liquid chromatography
HSA	Headspace analysis
i. d.	Inner diameter
I/C	Irradiated-to-control ratio (in: MS Identification Tables)
ISTD	Internal standard
LC	Liquid chromatography
LOCI	Large-volume on-column injection
m	Mass, sample mass
m/z	Mass-to-charge ratio (the „ion“ in a mass spectrum)
MABS	Methyl methacrylat-Acrylonitrile-Butadiene-Styrene
MS	Mass spectrometry / mass spectrum / MS parameters
MW	Molecular weight (molecular mass)
o. d.	Outer diameter
P, C	Part, injection-molded, Control (= non-irradiated)
P, I	Part, injection-molded, Irradiated (sterilizing dose)
Paa	Phenylacetaldehyde (Benzeneacetaldehyde, Phenylethanal)
Phe	Phenol
ppb	Parts per billion (µg/kg)
ppm	Parts per million (mg/kg)
PS	Polystyrene
PTV	Programmable-temperature vaporizer
SIM	Selected ion monitoring
Sty	Styrene (Ethenylbenzene, Phenylethene)
TDS	Thermal desorption / TDS parameters
TIC	Total ion chromatogram
t_R	Retention time
V	Volume (V inj. = the volume injected in a ‘DSC’-analysis)