

Technical University of Denmark



## Annual Report 1984. Chemistry Department

Funck, Jytte; Larsen, Elfinn; Nielsen, Ole John

*Publication date:*  
1985

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Funck, J., Larsen, E. (Ed.), & Nielsen, O. J. (1985). Annual Report 1984. Chemistry Department. Roskilde: Risø National Laboratory. (Risø-M; No. 2497).

## DTU Library

Technical Information Center of Denmark

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

RISØ-M-2497

**ANNUAL REPORT 1984  
CHEMISTRY DEPARTMENT**

**Edited by Jytte Funck, Elfinn Larsen, and Ole John Nielsen**

**Abstract.** This report contains a brief survey of the main activities in the Chemistry Department. All articles and reports published and lectures given in 1984 are presented. The facilities and equipment are mentioned briefly. The activities are divided into the following groups: radioisotope chemistry, analytical- and organic chemistry, environmental chemistry, polymer chemistry, geochemistry and waste disposal, radical chemistry, positron annihilation, mineral processing, and general.

**INIS Descriptors:** ATMOSPHERIC CHEMISTRY; BIBLIOGRAPHIES; CHEMICAL ANALYSIS; CHEMICAL REACTION KINETICS; GEOCHEMISTRY; NEUTRON ACTIVATION ANALYSIS; ORE PROCESSING; PHOTOCHEMISTRY; POLYMERS; POSITRONS; RAMAN SPECTRA; RESONANCE SCATTERING; RISØE NATIONAL LABORATORY; URANIUM ORES; WASTE MANAGEMENT

**UDC 543.53 : 621.039.7 : 622.7**

**March 1985**

**Risø National Laboratory, DK-4000 Roskilde, Denmark**

**ISBN 87-550-1101-2**

**ISSN 0418-6435**

**Risø Reprø 1985**

**CONTENTS**

	<b>page</b>
<b>1. Introduction</b> .....	<b>4</b>
<b>2. Publications</b> .....	<b>23</b>
<b>3. Lectures</b> .....	<b>48</b>

This report contains a brief survey of the main activities in the Chemistry Department. All articles and reports published and lectures given in 1984 are presented. The facilities and equipment are mentioned briefly.

The activities are divided into nine groups:

1. radioisotope chemistry
2. analytical- and organic chemistry
3. environmental chemistry
4. polymer chemistry
5. geochemistry and waste disposal
6. radical chemistry
7. positron annihilation
8. mineral processing
9. general

## 1. Radioisotope Chemistry

A two-volume monograph about neutron activation analysis determinations of trace elements in clinical chemistry has been published by CRC Press of USA. The interest in trace element research in relation to human diseases has been continued.

A post-graduate study of the counting of rapidly decaying radioactive indicators has begun in co-operation with the Technical University.

A part of the work is often performed in collaboration with researchers in the medical, geological, and archaeological fields from universities and hospitals. Certification work for EEC Community Bureau of Reference continues to be a major effort.

Industrial irradiation of silicon continues to be an activity of major concern, and a new irradiation facility is being designed. A description of facilities in operation has been published.

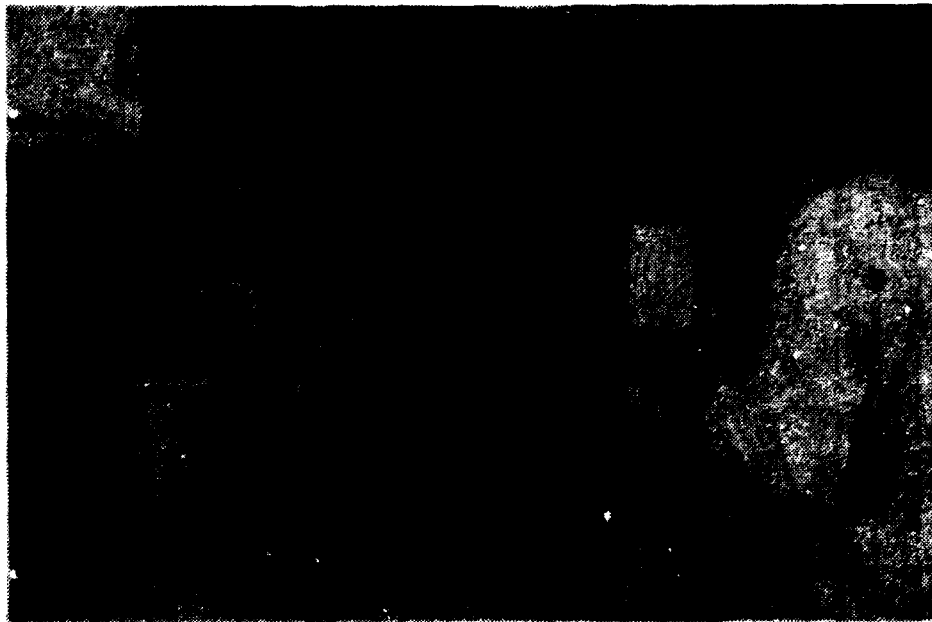


Fig. 1.1. Measurement of radioactivity.

Scientific Staff: K. Heydorn, Kirsten Andresen, L. Højslet Christensen, Else Damsgaard, Ulf Jacobsen, Jesper Jørgensen, Johnny Olesen Schmidt, Henrik Kalfod Nielsen.

Technical Staff: Erna Christensen, Ib Funck-Hansen, Henning G. Jacobsen, Jytte Jacobsen, Jytte Fritsche, Børge Valentiner, Sv.E. Kerchhoff, Kirsten Madsen, Gitte Rasmussen, Ulrik W. Hansen, Bente Jacobsson, Mette Thomson, Lene Birch, Jette Iversen, Gert Rahbek Kastel.

Guest Scientists: Galal El-Shaboury, Cairo.  
András Simonits, Budapest.  
Franz de Corte, Gent.  
A. de Wispelaere, Gent.

## 2. Analytical- and Organic Chemistry

In addition to further investigations in trace elemental analysis, the analytical activities followed the changing demands in accordance with the projects received by groups and sections, e.g. determination of Au and Ag in studies of mineral processing, I<sub>2</sub> in plate-out experiments in the ventilation system of the Hot-Cell facility, and H<sub>2</sub>O-content in materials for waste disposal.

The high-vacuum system of the analyzer of the old mass spectrometer has been updated by the installation of two turbomolecular pumps. As expected, the isotopic and quantitative analyses were improved mainly due to the lower background level of the instrument and reduced memory effect from previous samples.

The synthesis group has prepared widely different organic compounds including deuterium-,  $^{13}\text{C}$ -, and radioactive-labelled compounds for several research groups at Risø, as well as for groups outside the establishment. *p*-Iodo-*N*-isopropylamphetamine prepared to a Dutch Company and cyano-pararoseaniline prepared in collaboration with the Accelerator Department can be mentioned as examples.

The research within organic chemistry was centred on mass spectrometry. The studies on unimolecular gas phase pyrolysis of organic molecules were continued, and the equipment has been further improved (Fig. 2.1). Studies on the applicability of the system to gas kinetic investigations have been carried out. The gas phase pyrolytical studies have been presented in a series of lectures. In collaboration with the Free University in Brussel the Cu (I) assisted radioiodine labelling of *p*-Iodo-*N*-isopropylamphetamine is currently studied.

A laboratory for hydrocarbon characterization has been established to undertake detailed analysis of crude oils and gases. These data together with conventional PVT-data are to be used to predict phase behaviour for compositional reservoir simulators and processing equipment.

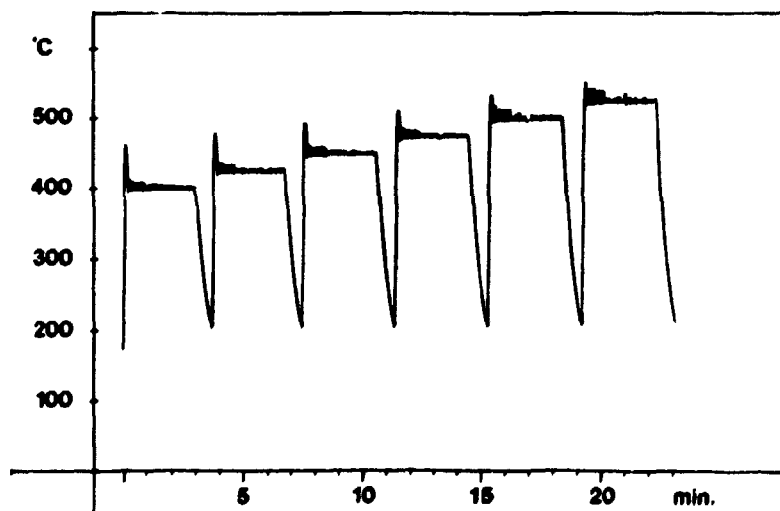


Fig. 2.1. Pulse pyrolysis sequence for kinetic studies.





Fig. 2.2. Withdrawing of a gas sample in Tønder.

The group has assisted DONG (Dansk Olie og Natur-Gas) with gas analyses on a commercial basis in autumn 1984.

DONG carried out a testing programme for evaluating the dispersion characteristics of a natural nitrogen gas reservoir in Tønder with the potential of natural gas storage. The reservoir is located in a tight sandstone formation approximately 1600 m below sea level between claystones. It contains large quantities of dry nitrogen gas with minor amounts of argon, helium, and methane.

The test was based on the injection of nitrogen gas mixed with a tracer gas, argon, in the concentration of 0.5 % by volume followed by a production period. During seven days 450 000 m<sup>3</sup> (STP) nitrogen was expected to be injected into the reservoir at a constant rate and constant concentration of argon. The

injection period was terminated by a one-day injection of nitrogen only. Then a production period with constant rate equal to the injection rate should continue until the concentration of argon approached the initial level of the reservoir. The entire experiment was planned to last four weeks. The large quantities of liquid nitrogen and argon were supplied by AGA A/S, whereas the Halliburton Company (the Netherlands) carried out the gas-mixing and the injection as well. Risø was responsible for the on-site measurements of argon and helium in the injected and produced gases. Additional gas samples were withdrawn every four hours (Fig. 2.2) for independent analysis at Risø.

We installed our Hewlett-Packard Gas Chromatograph-Mass Spectrometer Instrument (GC-MS) in a shed located near to the well (Fig. 2.3). A gas line was established from the well site to the computer-controlled inlet manifold of the GC-MS system. The gas analyses were carried out sequentially, three samples followed by a reference sample. The results were recorded on line. With the exception of the power-up period and some closing calibration experiments the analyses were performed entirely

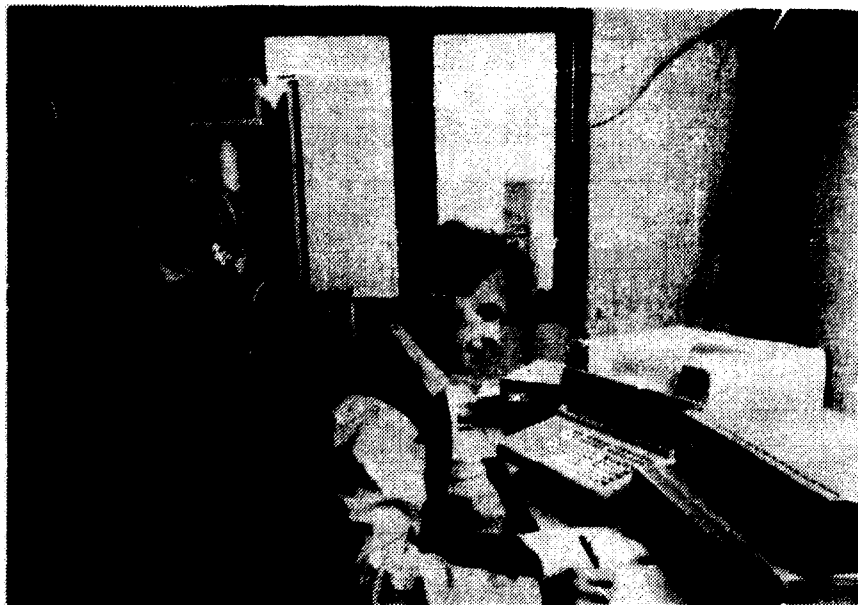


Fig. 2.3. The gas chromatograph-mass spectrometer system installed in the shed in Tønder.

under computer control with only brief inspections to ensure the supply of carrier gas, paper, etc. The instrument had been operating continuously 24 hours per day during four weeks except for few short-term interruptions due to power failures and to replacement of a valve in the inlet manifold. Close to 3000 analyses were performed without the need of maintenance of the GC-MS system.

The frequent analysis of a reference gas was necessary since the absolute sensitivity changed with time. However, longterm stability was also attained, e.g. from 66 measurements (equal to a period of 48 hours) on the reference gas the relative standard deviations for argon and helium were 2.8 and 2.5 %, respectively.

The samples taken every four hours were transported to Risø for mass spectrometric measurements of the concentration of argon, helium and nitrogen. The content of methane was measured by gas chromatography.

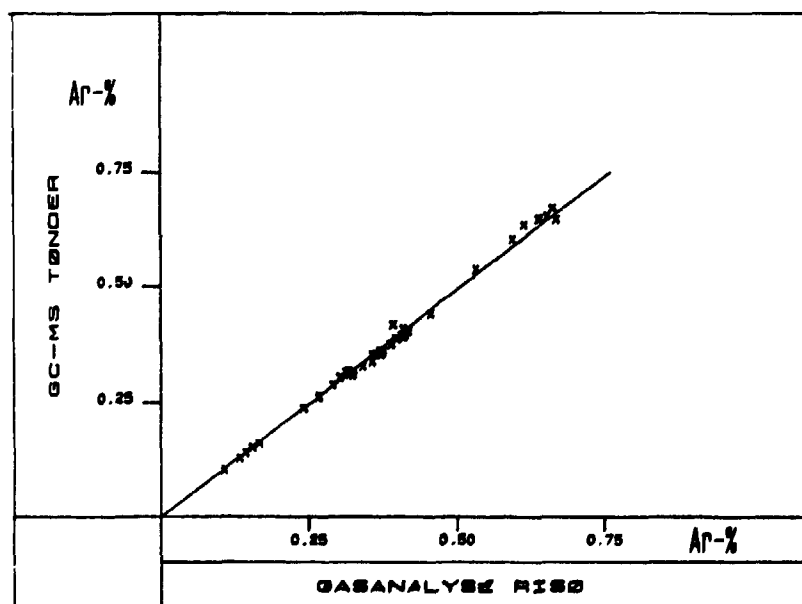


Fig. 2.4. The GC-MS measurement in Tønder versus the MS measurement in the laboratory at the equivalent "four-hour" sample.

The on-site GC-MS measurements were in excellent agreement with the analysis performed in the laboratory at Risø on the "four-hour" samples. Figure 2.4 shows the results of argon.

The argon, helium and methane results from the production period are shown in Fig. 2.5. The pronounced maximum at the argon curve

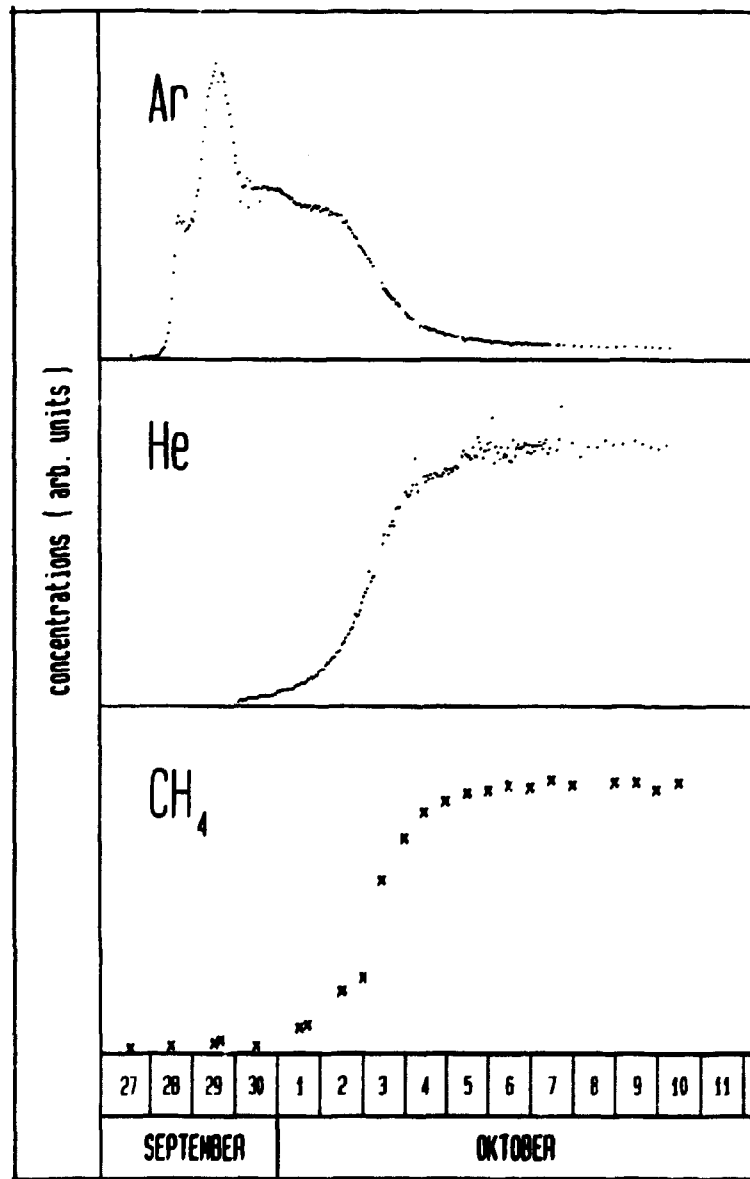


Fig. 2.5. The content of argon, helium and methane in the nitrogen gas from the production period.

can be related to a transient but high argon concentration in the injection period. The dispersion characteristics may be derived from the front and end profiles of the tracer concentrations.

We have many years of experience performing gas analyses in the laboratory. DONG's gas mixing test gave us the opportunity to test a mass spectrometer over a longer period in the field.

In conclusion, the application of a computerized GC-MS system turned out to be a most reliable technique for the on-site gas analysis. Its principal advantage is its large analytical capacity combined with a high specificity and accuracy.

Scientific Staff: Lars Carlsen, Asger Baltzer Hansen, Elfinn Larsen, Per Solgaard

Technical Staff: Karen Lis Christensen, Helge Egsgaard, Jytte Funck-Hansen, Ole Jørgensen, Lis Vinther Kristensen, Dorte Platz, Suzanne Petersen, Niels Vinther

Guest Scientist: Susanne Elbel, Inst. für Anorganische und Angewandte Chemie, University of Hamburg.

### 3. Environmental Chemistry

The main research field within environmental chemistry lies with atmospheric chemistry. One of two major research projects is concerned with the contribution from combustion of coal to the presence of polycyclic organic matter and their further reactions in the atmosphere. These experiments include model experiments in the laboratory as well as field measurements. In the second project reactivity of the OH radical with ethane and a series of Cl- and F-substituted methanes in the temperature

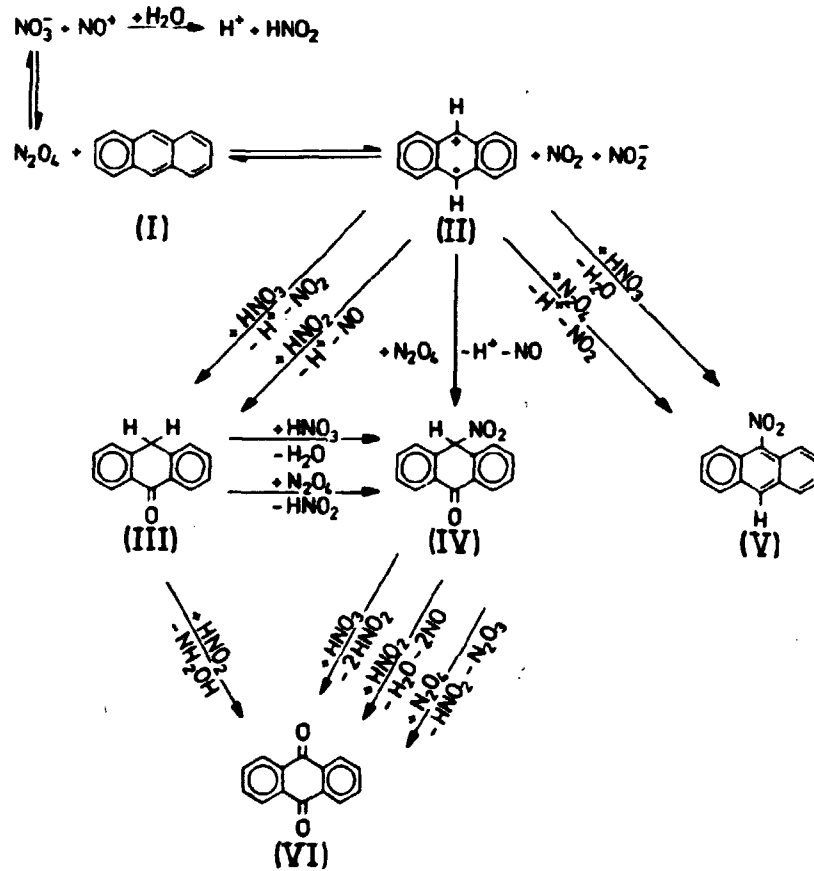


Fig. 3.1. Reaction mechanism for nitration of anthracene using  $\text{N}_2\text{O}_4$  in solution.

range 300-400 K was investigated. This work is related to the current debate on potential depletion of stratospheric ozone.

Scientific Staff: Torben Nielsen, Ole John Nielsen, Palle Pagsberg.

Technical Staff: Bente Christensen, Jette Munk, Preben Genske.

#### 4. Polymer Chemistry

Studies of relaxation processes in amorphous polymers were continued. Small-angle neutron scattering measurements on hydrogenated and deuterated 1,2-polybutadienes with high molar masses and narrow molar mass distributions were started. These experiments are designed to test the presence of theoretically predicted relaxation mechanisms in real polymeric materials.

A new method for a non-destructive and fast determination of the degree of crosslinking in polyethylene has been evaluated.

In the development of new production methods for soft contact lenses, liquid chromatography techniques (HPLC) and mechanical

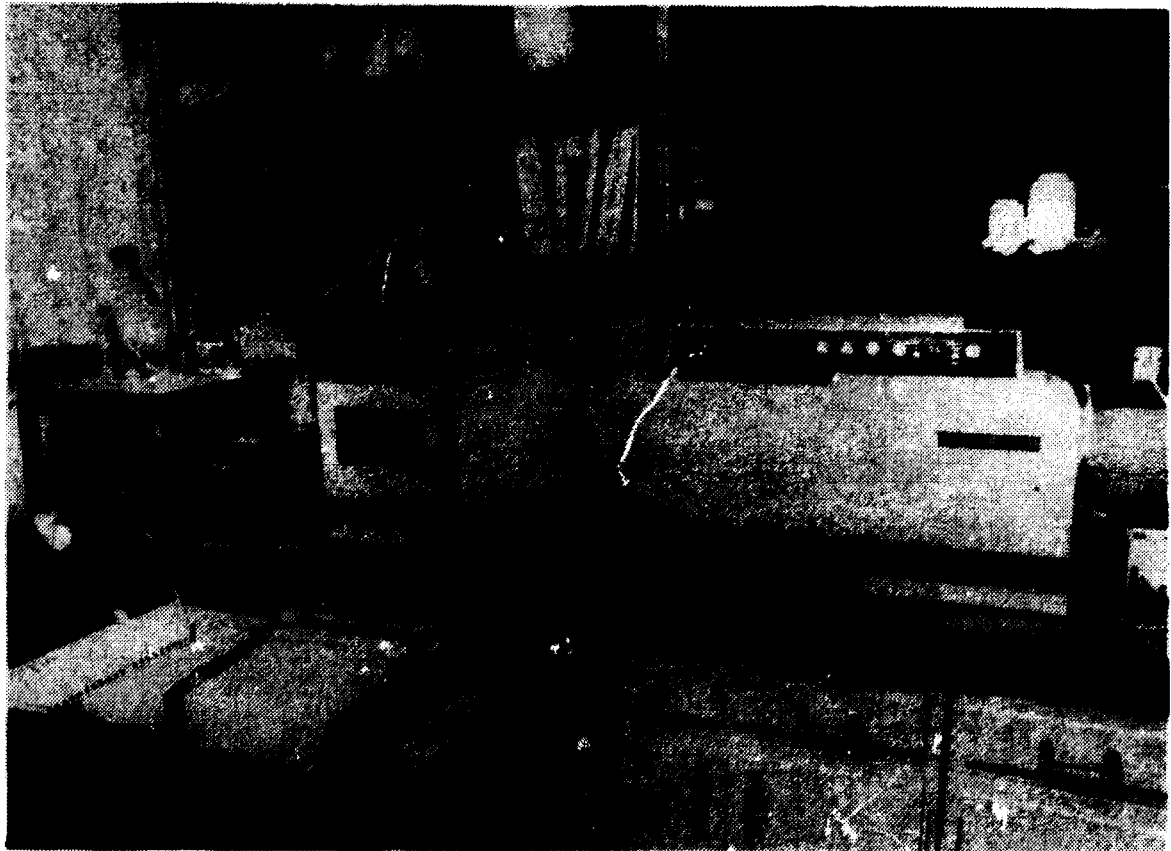


Fig. 4.1. Laser light-scattering instrument, the only one of its kind in Denmark. The instrument is used for polymer characterisation and to monitor polymer associations.

measurements on highly swollen hydrogels have contributed significantly to a better understanding of the polymerisation process.

In the practical application of size-exclusion chromatography (SEC) the main effort has been given to studies of aggregation processes in insulin solutions and the characterisation of polymers with extremely high molar masses. The laser light-scattering instrument has been used extensively in the insulin project as well as for the characterisation of other water soluble polymers.

In the field of sterilization technology studies have been carried out on the diffusion of ethylene oxide in different plastic materials. The influence of ionizing radiation on different plastic materials, irradiated with sterilization doses, has further been investigated using HPLC-, SEC- and ESR-measurements.

Guidance has been given to local authorities concerning the use of ethylene oxide for industrial sterilization. The work has resulted in a general regulation for emission of ethylene oxide to the environment.

Scientific Staff: Walther Batsberg Pedersen, Vagn Neerup Handlos, Ole Kramer, Asger B. Hansen

Technical Staff: Lisbeth Halby

## 5. Geochemistry and Waste Disposal

In geochemistry theoretical as well as experimental studies have been performed for several years. The migration of radionuclides related to possible geological disposal of nuclear waste has specially been investigated. Also studies on the possible transport of organic pollutants with ground-water have



been initiated. The interaction between rock-salt and radio-nuclides has been investigated with emphasis on the ability of salt to act as a natural barrier against radionuclide migration.

A new approach for geochemical modelling of polyphase systems is under development. The results obtained with the programme so far are very promising with regard to speed and versatility although its use demands qualified interaction from the user.

THIS IS TEST CASE NO.3E

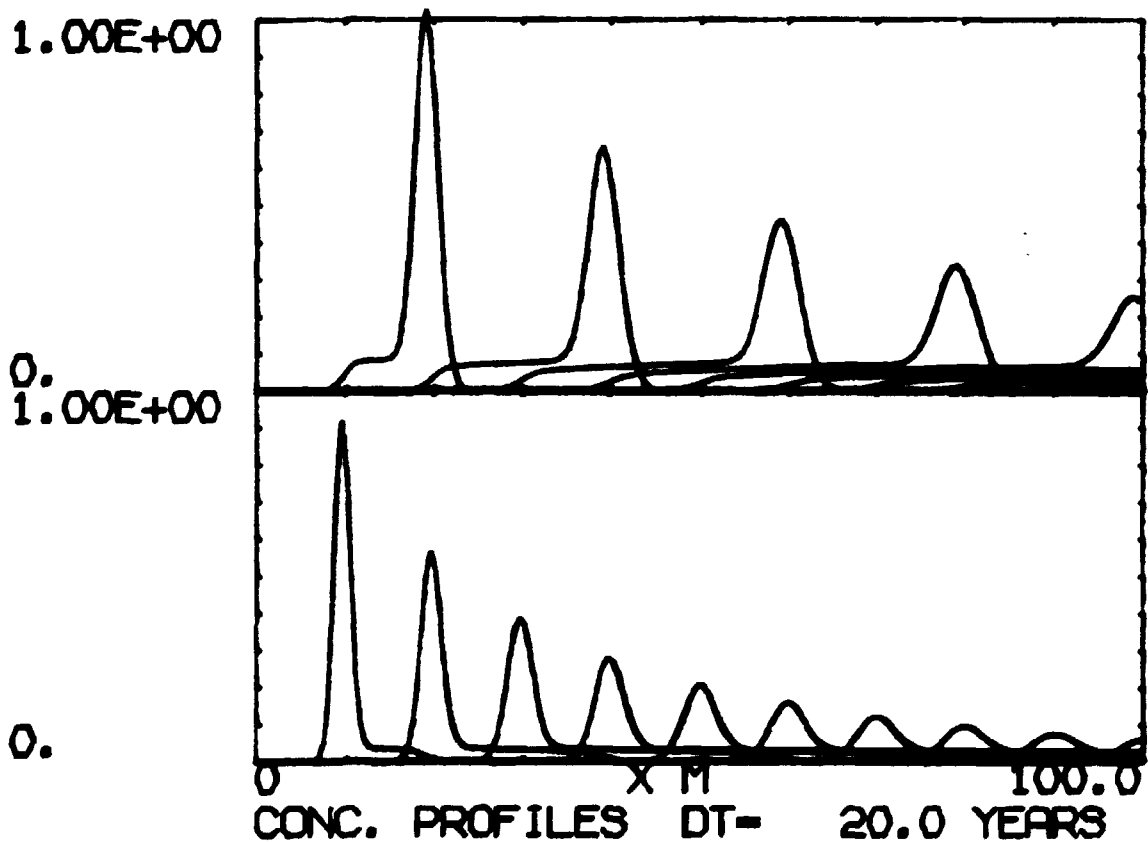


Fig. 5.1. Plotted output of concentration profiles for two components reacting with each other - calculated using the new COLUMN2 computer program for simulation of migration.

The problem of multi-element interaction in sorption processes is under study and useful equations applying to strongly acidic ion-exchangers have been derived and tested.

Studies of test methods for characterising bituminized or cemented low- and medium level waste materials are made under contract with the CEC as well as supported by the Nordic Council of Ministers.

The use of concrete as a barrier material around waste containers is under investigation. Densit, a special type of concrete containing silica fume as an additive, shows promising properties.

Scientific Staff: Bror Skytte Jensen, Ole John Nielsen, Knud Brodersen, Bodil Mose Pedersen, Arne Vinther, Lars Carlsen, Peter Bo, Vagn Voldbro Larsen, Karen Nilsson.

Technical Staff: Hanne Jensen, Dorte Platz, Lene Hubert, Gitte Larsen.

Guest Scientist: Kirk Nordstrom, U.S. Geological Survey, Menlo Park, California, USA.

## 6. Radical Chemistry

The main activities of the radical chemistry group can be divided into two main areas: studies of gas phase kinetics and time-resolved resonance Raman spectroscopy investigations of photochemical and radiation chemical processes in solution. In the gas phase studies rate constants for reactions involving radicals of environmental interest have been determined using pulse radiolysis combined with kinetic spectroscopy. The main subject of the gas phase studies has been spectroscopy and kine-

tics of free radicals involved in atmospheric chemistry and combustion processes. In pulse radiolysis of  $H_2/O_2$  mixtures at 298 K we observed chain reactions carried by  $H$ ,  $HO_2$  and  $OH$  radicals. The predominant termination reaction was found to be  $OH+HO_2 \rightarrow H_2O+O_2$  which is also an important sink for  $HO_x$  species in the stratosphere. UV-spectra of the alkyl radicals  $C_2H_5$  and  $i-C_3H_7$  and of the corresponding peroxy radicals  $C_2H_5O_2$  and  $i-C_3H_7O_2$  have been recorded and rate constants for the respective formation and decay reactions have been determined. The alkylperoxy radicals play an important role in the oxidation of hydrocarbons.

Time-resolved resonance Raman spectroscopy in connection with flash photolysis and pulse radiolysis has been used for stu-



Fig, 6.1. Studies of biological processes using time-resolved resonance Raman spectroscopy in connection with pulse radiolysis.

dying excited states of biological polyenes and processes of relevance for an understanding of photosynthesis and vision. An excimer laser, funded by the Natural Science Research Council, has been installed in collaboration with the Accelerator Department and is used for flash photolysis studies in addition to the existing pulse radiolysis facility.

Scientific Staff: Palle Pagsberg, Robert Wilbrandt, Niels-Henrik Jensen, Ole John Nielsen, Frans W. Langkilde, Alfred Sillesen.

Technical Staff: Jette Munk, Preben Genske.

Guest Scientists: Emil Ratajczak, Wroclaw University, Poland.  
Gösta Nilsson, Studsvik, Sweden.  
G. Britton, Liverpool, England.  
R. Bensasson, Paris, France.

### 7. Positron Annihilation

The positron annihilation technique at Risø is used mainly for studying vacancy-type defects in molecular crystals and metals, positronium and positron chemical reactions, and radiation chemistry problems. In 1985 the group will move to the Metallurgy and Physics Departments.

Scientific Staff: Morten Eldrup, Finn Medard Jacobsen, Ole Mogensen, Kjeld Jensen.

Technical Staff: Niels Jørgen Pedersen.

Guest Scientists: O.A. Anisimov, Inst.f. Chemical Kinetics and Combustion, Novosibirsk, USSR.  
J.H. Evans, Harwell, UK.  
G.M. Hood, Chalk River, Canada.  
J. Warman, Delft, Holland.  
M. Charlton and M. Drinkwater, University College London, UK.



Fig. 7.1. Morten Eldrup acting as opponent at a disputation in Helsinki (Feb. 1984).

## 8. Mineral Processing

The section works in areas of extraction of elements from ores, conditioning of tailings and other waste materials, synthesis of silicates, and in general processing involving the use of high-temperature autoclaves. Chemistry, engineering and environmental science are integrated in this section. Current projects include gold extraction, oil sludge treatment and extraction of metals from sea sediments.

Scientific Staff: Jørgen Jensen, Emil Sørensen, Torkild Lundgaard, Bertel Bukholt, Jette Paulsen, Susanne Koefoed, Kim Pilegaard, Peter Bo.

Technical Staff: Helle Krogh, Jette Posskov, Anne Nielsen, Sv. Kr. Olsen, Thomas Fernqvist.



Fig. 8.1. Precipitated gold from the thiourea process.

## 9. General

The Department accomplishes chemical analysis and services for other departments at Risø and on a commercial basis for customers outside Risø. The Isotope Laboratory has continued to fulfill its commitment as the sole producer of neutron-irradiated materials for technical and scientific purposes in Denmark. The production of radiopharmaceuticals for medical diagnostics in collaboration with the Isotope Pharmacy has proceeded, as well as of radioisotopes mainly for scientific research. The supply of  $\alpha$ ,  $\beta$ , and  $\gamma$  demonstration sources for educational purposes to the Nordic countries continues, and as a supplement a Radium-226 source for continuous cloud chambers has been developed. The handling and disposal of radioactive wastes from Risø and other users of radioactive isotopes are taken care of at The Waste Treatment Plant.

A numerous technical staff takes care of typing, workshop, laundry, radioactive cleaning, etc.: Aase Neve Larsen, Kirsten B. Christensen, Ingrid M. Petersen, Annie C. S. Andersen, Jytte Green, Ellen M. Jensen, Inger Jacobsen, Fini Lindskou, Knud Larsen, Erling Christensen, Bent Willumsen, Elsebeth G. Jensen, O. Sølling-Hansen, Bent Nielsen, Jørgen Larsen, Sven Jensen, Børge Rasmussen, Signe Hansen, Birthe Sonne Hansen, Birthe I. Hansen, Birthe N. Andersen, Peter Slott Nielsen, V. Munch Jacobsen, Nina Thomsen.

Risø's Chemistry Department includes four geographically separated sections: The Chemical Laboratory, The Radioisotope Laboratory, The Waste Treatment Plant, and The Mineral Processing Plant.

The staff of The Department consists of 31 employees with an academic degree, 3 Ph.D. students and 55 technicians.

## NEUTRON ACTIVATION ANALYSIS FOR CLINICAL TRACE ELEMENT RESEARCH

K. Heydorn.

Vol 1-2, CRC Press, Boca Raton, USA (1984)

The application of scientific methods to the study of health and disease has a long history, and progress in analytical chemistry has always stimulated clinical research. The interface between these two subjects is the sampling process, which, however, has attracted very little attention until recent years.

Trace element analysis is carried out routinely by a variety of methods, but the present-day challenge is the reliable determination of elements at the ultratrace level, where neutron activation analysis is superior to all other methods for many elements.

Only within the last decade have the unique advantages of NAA been fully utilized to control sampling problems and improve the quality of clinical trace element data.

This monograph is intended as a reference for prospective or existing research groups engaged in the study of elements at the ultratrace level in clinical samples. In such an interdisciplinary cooperation there is a need to bridge the gap between the analytical and the clinical scientist with information on the possibilities and the problems associated with the use of neutron activation analysis. This book is not a textbook to convert a medical doctor into an analyst or the reverse, and many subjects are only briefly introduced before being discussed, but it is to be hoped that the exchange of ideas across the interdisciplinary boundary will be stimulated.

Quality assurance of clinical trace element research cannot usually be based on the routine methods of the clinical laboratory. The small number of results characterizing the clinical research work must instead be produced by methods with few and well-known sources of variation. NAA is particularly applicable to these requirements and has been shown to be capable of yielding results in statistical control. In this book this property of NAA is the basic condition for using the Analysis of Precision to detect and identify other sources of random or systematic errors.

Only by exact control of the sampling procedure can results in statistical control be ascertained, and an entire chapter is devoted to this subject. The next chapters discuss in some detail all sources of variation associated with NAA, and it is shown that all those of importance for biological samples may be brought in statistical control, even at the ultratrace level of concentration. Neither *in vivo* activation analysis nor analysis by prompt gamma-ray emission are capable of producing results at such low levels, and in addition their technical sources of variation are quite different from reactor neutron activation analysis.

Sample homogeneity is taken into account as a special source of variation, separate from analytical precision, and in this way the Analysis of Precision may be used to detect and identify systematic errors and eliminate unreliable data. This methodology is developed in Chapter 5 and used in Chapter 6 to ascertain reliable data for normal levels of a number of trace elements in human tissue and blood. The identification of significant sources of variation in healthy individuals is discussed in the next chapter together with a method of detecting abnormal distributions of trace elements in the human body by multi-dimensional data analysis. The final chapter gives examples of associations between such abnormal trace element levels and various diseases.

Recent progress in this field has shown that many previous assertions were based on inadequately controlled data, and the present book is therefore almost exclusively based on the literature published in the last decade. No attempt has been made to quote all relevant papers, but to select material best suited to illustrate the main line of thought and to emphasize aspects less thoroughly covered in other monographs.



INTERNAL QUALITY ASSURANCE IN BIOMEDICAL NEUTRON ACTIVATION ANALYSIS.

K. Heydorn.

IAEA-TECDOC-323, 179-190 (1984)

In neutron activation analysis standard deviations of individual results are estimated from a priori precision and counting statistics, and sample heterogeneity is taken into account by a sampling constant. Statistical control means agreement between observed and estimated variability; additional sources of variation, including contamination during sampling, are detected by stepwise application of the Analysis of Precision.

AN AUTOMATIC CONTROLLED, HEAVY WATER COOLED FACILITY FOR IRRADIATION OF SILICON CRYSTALS IN THE DR 3 REACTOR AT RISØ NATIONAL LABORATORY, DENMARK.

K.Hansen, K.Stendal, K.Andresen and K.Heydorn.

in Neutron Transmutation Doping of Semiconductor Materials, Plenum Press, New York, 91-120 (1984).

Neutron transmutation doping of silicon crystals with phosphorus has been carried out in the DR 3 reactor since 1975.

The irradiation capacity has been enlarged concurrently with the growing demand for neutron transmutation doped crystals.

This report describes a recently developed facility for the irradiation of 4 inches silicon crystals. The irradiation rig is placed in one of the vertical experimental tubes in the heavy water moderator of the reactor.

The rig is filled with heavy water, and the nuclear heat absorbed in the crystals during irradiation is removed by convection.

During the irradiation the crystals are placed in round aluminum containers. Transport of the containers from the irradiation zone to the top of the rig is made by heavy water flow. The irradiation cycle is controlled automatically by instrumentation.

**ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY: A VERSATILE ANALYTICAL TECHNIQUE FOR DETERMINATION OF MAJOR AND MINOR ELEMENTS IN PAINT.**

Leif Højslet Christensen and Iver Drabæk.

Schweizerische Vereinigung der Lack-und Farben-Chemiker  
Proc. XVII Fatipecc-Congress, Lugano, I: 327 23-28/9-1984

We have recently introduced a new energy-dispersive x-ray fluorescence method for the direct, non-destructive, and simultaneous determination of major and minor elements in various types of paint. Since the introduction of the method we have improved its capabilities and extended the range of determined elements down to Al. Furthermore, the method has been applied to a variety of coating products. Theory and instrumentation as well as results demonstrating some of the performance characteristics of the method, i.e., versatility, precision, and accuracy, are presented.

**KVALITATIV OG KVANTITATIV ANALYSE VED EN KREDS AF MEDARBEJDERE.**

**Isotoplaboratoriet 1959-1984**

**Risø - M - 2410**

Abstract. En kortfattet beskrivelse af laboratoriets bestræbelser gennem 25 år på at konvertere de flest mulige reaktor-neutroner til samfundsnyttige produkter. Indeholder et fototek omfattende 71 nuværende eller tidligere medarbejdere, samt en liste med 116 fremmedsprogede publikationer.

**DIRECT DETERMINATION OF  $^{18}\text{O}$  ENRICHMENT IN  $\text{KClO}_3$  AND  $\text{KBrO}_3$   
BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY.**

**Elfinn Larsen , Helge Egsgaard and Nis Bjerre**

**J. Trace and Microprobe Techniques, 1 (4) 387-397 (1983)**

Curie-point pyrolysis-gas chromatography-mass spectrometry has been used for the determination of the isotopic composition of oxygen in  $\text{KClO}_3$  and  $\text{KBrO}_3$ . The linearity of the method has been investigated in the natural to 97%  $^{18}\text{O}$  range. For sample sizes of 0.2 micromole a standard deviation less than 1% was obtained on samples containing 50%  $^{18}\text{O}$ .

**PREPARATIVE HPLC PURIFICATION, A KEY TO PURE  $^{123}\text{I}$ IMP SHOWING  
HIGH BRAIN UPTAKE.**

**J.Mertens, W.Vanryckeghem, A.Bossuyt and L.Carlsen.**

**Nuclear Medicine Communications 5, 705-710, (1984)**

**Summary**

$^{123}\text{I}$ IMP has been advocated as a promising radiotracer for assessing regional cerebral perfusion. A major drawback of this radiopharmaceutical is a rather poor brain to lung activity ratio. When applying an efficient HPLC separation, based on a complex blend of ACN, MeOH,  $\text{H}_2\text{O}$ , TMA and HAC, to reaction mixtures obtained with previously described labelling methods, the chromatograms show several cold and labelled side products. The latter are less lipophilic than IMP. They may at least in part be responsible for a decreased uptake of activity in the brain due to preferential receptor-mediated lung uptake. The use of a Cu(I)-Sn(II) couple in the reaction mixture allows a yield of more than 95% to be obtained and the side products to be reduced to negligible amounts.

GAS-PHASE PYROLYSIS OF METHYL DITHIOACETATE. THE ABSENCE OF A 1,3-METHYL GROUP MIGRATION.

Lars Carlsen and Helge Egsgaard.

J. Chem. Research (S), 340-341 (1984)

The flash vacuum pyrolysis of methyl dithioacetate (1) was studied by application of the gas-phase-Curie-point-pyrolysis technique. To obtain mechanistic information specific sulfur-34 labelling was used. Application of a D<sub>2</sub>O saturated pyrolysis system revealed evidence for the intermediacy of an enethiolized tautomer of 1.

INTERCOMPARISON OF 11 MASS SPECTROMETERS APPLIED FOR QUANTITATIVE ORGANIC ANALYSIS IN DENMARK.

Helga Flachs, Elfinn Larsen and Gustav Schroll

Biomedical Mass Spectrometry, Vol.11 No.10 545-548 1984

Eleven mass spectrometers all connected with a gas chromatograph were used for quantitative determination by the isotopic dilution technique. The purpose of the investigation was to compare the virtual performances of the instruments rather than the routines of the individual laboratories. Therefore, calibration compounds and samples were distributed to the participants. A satisfactory linearity but poor reproducibility was found.

TECHNIQUES IN GAS-PHASE THERMOLYSES

PART 5. CONTINUOUS-FLOW INLET SYSTEMS FOR LOW PRESSURE  
CURIE-POINT PYROLYSIS. INTRODUCTION OF PULSE-PYROLYSIS.

Helge Egsgaard and Lars Carlsen.

Journal of Analytical and Applied Pyrolysis, 7, 1-13 (1984)

With emphasis on a constant reactant flow, a series of inlet systems for gas-phase Curie-point pyrolysis-mass spectrometry experiments have been studied. Inlet systems for the handling of gaseous, liquid and oligomeric (solid) samples have been designed and their performances evaluated. The principle of pulse-pyrolysis is introduced and its applicability to kinetic studies outlined.

3-MERCAPTOPROPANAL.

Lars Carlsen, Helge Egsgaard, Flemming S. Jørgensen and M. Nicolaisen.

J. Chem. Soc. Perkin Trans. II 609-613 (1984)

Gaseous 3-mercaptopropanal, generated by thermal decomposition of the corresponding oligomer, has been characterized by i.r. and photoelectron spectroscopy, and mass spectrometry. The possibility of a 3-mercaptopropanal-thietan-2-ol equilibrium is discussed, as is the mechanism of unimolecular thermal decomposition.

THERMAL DECOMPOSITION OF 1,2-OXATHIOLANE IN THE GAS PHASE.

Lars Carlsen and Helge Egsgaard.

Chem. Ber. 117, 1393-1399 (1984)

The cyclic sulfenic ester 1,2-oxathiolane (1) decomposes thermally (400-450 K) exclusively to give acrolein (3) via 3-mercaptopropanal (2) by loss of hydrogen sulfide. Isotopic labelling experiments reveal the presence of a 1,2-oxathiolane-thietane 1-oxide equilibrium (1  $\rightleftharpoons$  4).

**GAS PHASE CURIE POINT PYROLYSIS.**

Lars Carlsen.

in "Analytical Pyrolysis. Techniques and Applications".  
K. Voorhees, ed.-Butterworth, New York, 69-94, (1984)

Abstract. Curie point pyrolysis appears, in combination with field ionization- and collision activation mass spectrometry, as an excellent tool for 'real-time-analysis' of unimolecular gas phase pyrolytic reactions. The Flash Vacuum Pyrolysis/Field Ionization Mass Spectrometry (FVP/FIMS) technique, which is based on a direct connection between the pyrolysis unit and a double focusing mass spectrometer is described, the applicability being illustrated by recent investigations on the gas phase pyrolyses of acetic acid esters, including the mono- and dithio derivatives, and the cyclic sulfenic acid ester 1,2-oxathiolane. The possible involvement of surface catalytic reactions is discussed.

**AN AB INITIO CASSCF STUDY OF THE PHOTOLYTICAL FORMATION AND DECOMPOSITION OF OXATHIIRANE.**

Gunnar Karlström, Björn O. Roos and Lars Carlsen.

The Journal of the American Chemical Society, Vol.106 nr.6  
1557-1561, (1984)

Abstract: Ab initio calculations on the  $H_2CSO$  system have been carried out by the CASSCF method. It appears that photolysis of thioformaldehyde *S*-oxide most probably affords rearrangement into the three-membered ring oxathiirane via an excited singlet state. Further photolysis of oxathiirane apparently leads to a weakened S-O bond, the product being best described as a biradical, whereas no evidence for a possible ring opening to the corresponding formaldehyde *O*-sulfide was obtained. The wave function of the latter compound seems to be best described as a complex between a distorted sulfur atom and a formaldehyde molecule. On the basis of the calculations the previously reported photolyses of diarylthione *S*-oxides and the corresponding diaryloxathiiranes are discussed.

**IDENTIFICATION OF ONONITOL AND O-METHYL-SCYLLO-INOSITOL  
IN PEA ROOT NODULES.**

**Leif Skøt and Helge Egsgaard**

**Planta 161 32-36 (1984)**

**Abstract.** Ononitol (4-O-methyl-*myo*-inositol) and O-methyl-*scyllo*-inositol were identified in pea (*Pisum sativum* L.) root nodules formed by two *Rhizobium leguminosarum* strains. Ononitol was the major soluble carbohydrate in nodules formed by strain 1045 while O-methyl-*scyllo*-inositol and two unidentified components were dominant in the carbohydrate pattern of the nodules formed by strain 1a. The cyclitols were also present in the denodulated roots, but to a much smaller extent; in the above-ground plant parts only traces were found. The identification of ononitol and O-methyl-*scyllo*-inositol was established by gas chromatography and gas chromatography-mass spectrometry utilizing trimethylsilyl- and acetyl-derivatives.

**ONONITOL AND O-METHYL-SCYLLO-INOSITOL IN PEA ROOT NODULES.**

**Leif Skøt and Helge Egsgaard.**

**in Advances in Nitrogen Fixation Research.  
Proceedings of the 5th International Symposium on Nitrogen  
Fixation, Noordwijkerhout, The Netherlands,  
Aug.28 - Sept.3, 524, (1983)**

Cyclitols (hexahydroxycyclohexanes) and their methyl ethers occur in legumes (1). In soybean root nodules a correlation between Depnitol (3-O-methyl-*chiro*-inositol) and nitrogen fixation has been observed suggesting a role for pinitol in  $N_2$  fixation (2). Here we report on ononitol (4-O-methyl-*myo*-inositol) and O-methyl-*scyllo*-inositol as major components of the soluble carbohydrates in pea root nodules and that the cyclitol pattern depends on the *Rhizobium* strain inhabiting the nodules.

**PULSE RADIOLYSIS OF GASES H ATOM YIELDS, OH REACTIONS, AND KINETICS OF H<sub>2</sub>S SYSTEMS**

Ole John Nielsen.

R-480            Risø National Laboratory, April (1984)

**Abstract (shorten)**

The pulse radiolysis equipment and technique are described and its relevance to atmospheric chemistry is discussed.

Pulse radiolysis of a number of different chemical systems have been described and computer simulations have been used to check the validity of the proposed mechanisms.

**KARAKTERISERING AF POLYCYCLISK ORGANISK MATERIALE ( POM ) I RØGGASSER FRA KULFYREDE FORBRÆNDINGSANLÆG I ATMOSFÆREN OG UNDERSØGELSER AF DERES OMDANNELSE I ATMOSFÆREN.**

Torben Nielsen.

M-2420    Forsøgsanlæg Risø. Marts (1984)

Abstrakt. Dette arbejde omhandler undersøgelse af forekomsten af polycykliske aromatiske kulbrinter (PAH), nitro-PAH og basiske azaarener i atmosfæren, afklaring af forskellige kilders betydning (specielt kulfyrede kraftværker) for forekomsten af PAH i atmosfæren og afklaring af PAH's atmosfærekemi, specielt deres reaktioner med nitrogendioxid/dinitrogentetraoxid og salpetersyre.



KINETICS OF THE REACTION OF OH WITH ETHANE AND A SERIES OF Cl- AND F-SUBSTITUTED METHANES AT 300-400 K, STUDIED BY PULSE RADIOLYSIS COMBINED WITH KINETIC SPECTROSCOPY.

O.J.Nielsen, P.Pagsberg and A.Sillesen

551.5 European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants, 3, 283-292  
10-12 April Varese (1984)

Gas phase reactions of OH with ethane and a series of Cl- and F-substituted methanes were studied in the temperature range 300-400 K. In contrast to most previous experimental work our experiments were carried out at atmospheric pressure. OH was produced by pulse radiolysis of water vapour and the decay rate was studied by monitoring the transient light absorption at 3090 Å. Arrhenius parameters ( $A, E_a$ ) for the reaction  $RH + OH \rightarrow R + H_2O$  were obtained for reactants  $RH = C_2H_6, CH_3Cl, CH_2Cl_2, CH_2FCl_2$  :

$$\begin{aligned}k(OH+C_2H_6) &= 8.1 \times 10^{12} \times \exp(-2160/RT) \text{ cm}^3\text{mole}^{-1}\text{s}^{-1} \\k(OH+CH_3Cl) &= 3.2 \times 10^{12} \times \exp(-2510/RT) \text{ cm}^3\text{mole}^{-1}\text{s}^{-1} \\k(OH+CH_2Cl_2) &= 4.1 \times 10^{12} \times \exp(-2220/RT) \text{ cm}^3\text{mole}^{-1}\text{s}^{-1} \\k(OH+CH_2FCl_2) &= 1.1 \times 10^{12} \times \exp(-3550/RT) \text{ cm}^3\text{mole}^{-1}\text{s}^{-1}\end{aligned}$$

$CF_2Cl_2$  which contains no C-H bonds was found to be inert toward attack by OH.

A LITERATURE REVIEW ON WET DEPOSITION.

Frits Heikel Vinther and Ole John Nielsen.

M-2475 Forsøgsanlæg Risø, December 1984

Abstract. The literature on wet deposition or precipitation scavenging have been reviewed with special reference to predicting the radiological consequences of accidental contamination. The work was part of the EEC Radiation Protection Programme and done under a subcontract with Association Euratom-C.E.A. No. SC-014-BIAF-423-DK(SD).

OCCURRENCE OF NITRO-PAH IN THE ATMOSPHERE IN A RURAL AREA.

Torben Nielsen, Bernhard Seitz and Thomas Randahl.

Atmospheric Environment Vol. 18, 10, 2159-2165 (1984)

**Abstract**—By means of gas chromatography with nitrogen sensitive detection and negative ion chemical ionization mass spectrometric detection 7 mononitro-PAH, 9-nitroanthracene, x-nitro-4,5-methylene-phenanthrene, 3-nitrofluoranthene, 1- and 2-nitropyrene, 10-nitrobenzo(a)anthracene and 6-nitrobenzo(a)pyrene have been identified in samples of airborne particulate matter. Furthermore, 8-nitrofluoranthene has been tentatively identified. The amounts of mononitro-PAH are one to two orders of magnitude lower than the most common carcinogenic PAH, as e.g. benzo(a)pyrene. Filter effects have been studied. 9-nitroanthracene can be transformed during sampling at low atmospheric concentrations of NO<sub>2</sub> and photochemical oxidants to 9,10-dinitroanthracene and 10-nitroanthrone.

WATER CHEMISTRY IN SOIL SYSTEMS.

Knud Brodersen.

M-2445 Risø National Laboratory, September 1984

**Abstract.** The theoretical basis for the development of a model describing hydrology and water chemistry in top soil layers is described. The purpose of the model is to simulate the effect of acid rain or the deposition of polluting materials such as cadmium. The soil layers are treated as completely mixed compartments. A set of equations is presented taking into account the permanent and variable cation exchange capacity of the soil as well as the anion exchange which may occur in special soil types. The lime potential concept is used in modelling permanent ion exchange. The carbon dioxide equilibria as well as precipitation or dissolution of chalk or gypsum in soil are also included. Some general considerations on complex chemistry of aluminium are given and a framework for later inclusion of slow weathering of silicate minerals is set up.

**FURTHER STUDIES OF PLUTONIUM AND AMERICIUM AT THULE, GREENLAND.**

**Asker Aarkrog Henning Dahlgaard, Karen Nilsson and Elis Holm.**

**Health Physics Vol.46, no 1 29-44 (1984)**

**Abstract**—Eleven years after the accidental loss of nuclear weapons in 1968, the fourth scientific expedition to Thule occurred. The estimated inventory of 1 TBq  $^{239,240}\text{Pu}$  in the marine sediments was unchanged when compared with the estimate based on the 1974 data. Plutonium from the accident had moved further away from the impact point and at some locations the vertical distribution indicated a downward displacement of Pu in the sediment column since 1974. Seawater and seaplants showed no evidence of the presence of Pu from sources other than fallout; but Pu in benthos varied nearly proportionally with the levels in sediments. From the measurements of  $^{239,240}\text{Pu}$  in the *Macoma* community since 1970, the transfer factor to this community was estimated at 0.01 Bq a per Bq released to the sediments. The inventory of  $^{241}\text{Am}$  was 0.1 TBq. The vertical distribution of Am in sediments did not differ from that of Pu, but in benthos  $^{241}\text{Am}/^{239,240}\text{Pu}$  were two times higher than in sediments. Seaplants showed the same value of Am/Pu as seawater. There was no indication of any biomagnification of Pu or Am through the marine food chains at Thule.

**APPLICATION OF A METHOD FOR RAPID  $^{226}\text{Ra}$  DETERMINATION IN URANIUM TAILINGS USING ALPHA SPECTROMETRY.**

**Karen Nilsson, Kim Pilegaard and Emil Sørensen.**

**Nuclear Instruments and Methods in Physics Research 223, 582-584 North-Holland, Amsterdam. (1984)**

A method for rapid determination of  $^{226}\text{Ra}$  was employed on tailings from a pilot plant project involving Greenland uranium deposits. Attempts to measure  $^{226}\text{Ra}$  by alpha spectrometry directly were not successful due to poorly resolved spectra, and it proved necessary to make use of conventional techniques. The results suggest different behavior of  $^{226}\text{Ac}$  and  $^{226}\text{Pa}$  during the uranium extraction process. The  $^{226}\text{Ra}$  released during processing is immediately concentrated in a material, which may to a minor extent coat the tailings. However, in that form the  $^{226}\text{Ra}$  is and remains completely insoluble.

**RADIONUCLIDE-HUMIC ACID INTERACTIONS STUDIED BY DIALYSIS.**

**Lars Carlsen, Peter Bo and Gitte Larsen.**

**American Chemical Society. 167-178 (1984)  
Geochemical Behavior of Radioactive Waste.**

Dialysis has been used to study the interaction between radionuclides and humic acid. The technique gives information on 1) the complexing capacity of the humic acid samples, i.e. the concentration of complexing sites, and 2) the radionuclide - humic acid complexes by a) its stoichiometry (i.e. metal ion/ligand ratio), and b) interaction constants. The applicability of the technique is illustrated by studies on the interaction between a humic acid and  $^{134}\text{Cs}^+$ ,  $^{85}\text{Sr}^{2+}$ ,  $^{60}\text{Co}^{2+}$ , and  $^{154}\text{Eu}^{3+}$ .

**A-APFALD KAN GEMMES I UNDERJORDISK KALK.**

**Lars Carlsen.**

**Ingeniøren nr.38 Side 12 21 September (1984)**

Det må antages, at kalkfor-  
mationer er særdeles effek-  
tive som naturlige barrierer  
mod spredning af radioak-  
tivt materiale opløst i grund-  
vandet. Dette er konklusio-  
nen på et projekt udført af  
kemiafdelingen på Risø. Med  
projektets målemetoder er  
det også muligt at under-  
søge, hvordan nedgravede  
kemikalier eller tungmetal-  
ler forurener grundvandet.

BASIC GEOCHEMICAL RESEARCH FOR MIGRATION STUDIES

-----  
COMPLEX FORMATION OF SELECTED RADIONUCLIDES WITH LIGANDS  
COMMONLY FOUND IN GROUND WATERS.

Bror Skytte Jensen and Hanne Jensen.

Contract No. 194-81-6 WASDK

A general approach to the analysis of potentiometric data on complex formation between cations and polybasic amphoteric acids is described. The method is used for the characterisation of complex formation between  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{La}^{3+}$ , and  $\text{Eu}^{3+}$  with the  $\alpha$ -hydroxy acids, tartaric acid and citric acid, and with the  $\alpha$ -amino acids, aspartic acid and L-cysteine. The cations have been chosen as typical components of reactor waste, and the acids because they are often found as products of microbial activity in pits or wherever organic material decays.

**RESONANCE RAMAN SPECTRA OF THE TRANSIENT  $\text{Cl}_2^-$  AND  $\text{Br}_2^-$  RADICAL ANIONS.**

**Robert Wilbrandt, Niels-Henrik Jensen, Alfred H. Sillesen and Knud B. Hansen**

**Chemical Physics Letters Vol.106, no.6 503-507 11 may (1984)**

The resonance Raman spectra of the short-lived radical anions  $\text{Cl}_2^-$  and  $\text{Br}_2^-$  in aqueous solution are reported. The observed wavenumbers of  $279 \text{ cm}^{-1}$  for  $\text{Cl}_2^-$  and  $177 \text{ cm}^{-1}$  for  $\text{Br}_2^-$  are about 10% higher than those published for the corresponding species isolated in solid argon matrices. Under the assumption of a Morse potential, harmonic frequencies and anharmonicity constants are calculated to be  $286.4$  and  $3.83 \text{ cm}^{-1}$  for  $\text{Cl}_2^-$  and  $187.2$  and  $5.17 \text{ cm}^{-1}$  for  $\text{Br}_2^-$ . These values lead to extrapolated dissociation energies of  $0.66$  and  $0.21 \text{ eV}$ , respectively. These results are compared with those from matrix-isolation studies at low temperatures and work in the gas phase.

**TIME-RESOLVED RESONANCE RAMAN SPECTRUM OF ALL-TRANS-DIPHENYL-BUTADIENE IN THE LOWEST EXCITED SINGLET STATE.**

**Robert Wilbrandt, Niels Henrik Jensen and Frans W. Langkilde.**

**Chemical Physics Letters. Vol.111, 123-127 (1984)**

The resonance Raman spectrum of all-trans-diphenylbutadiene in its lowest excited  $S_1$  state excited in resonance with the  $S_1 \rightarrow S_n$  absorption band at  $650 \text{ nm}$  in non-polar solvents is reported. Three vibrational bands at  $1572$ ,  $1481$  and  $1165 \text{ cm}^{-1}$  are observed. A possible assignment of the the  $1481 \text{ cm}^{-1}$  band to the C=C double-bond stretching mode may support the lowest  $S_1$  state being of  $^1A_g^-$  symmetry.

EXCITED TRIPLET STATES OF HEXATRIENES.

F.W.Langkilde, R.Wilbrandt and N.-H.Jensen

Poster.

X th Iupac Symposium on Photochemistry, Interlagen, Schweiz.  
22-27 July (1984)

In the photoisomerization of polyenes, triplet intermediates are considered to be of importance. In several studies, longer polyenes like retinal and  $\beta$ -carotene have been investigated.<sup>1-7</sup> The study of the structure of the intermediates in the photoisomerization of these compounds is made difficult by the size or complicated substitution pattern of the mentioned molecules. We have therefore chosen to study the triplet states of simpler polyenes. For a simple model polyene we have chosen all-trans 1,3,5-heptatriene. Two types of experimental techniques have been used: i) Pulse radiolysis combined with time-resolved absorption spectroscopy and ii) laser flash photolysis combined with time-resolved resonance Raman (RR) spectroscopy.

**TIME-RESOLVED ABSORPTION AND RESONANCE RAMAN SPECTRA OF THE  
LOWEST EXCITED TRIPLET STATE OF ALL-TRANS-1,3,5-HEPTATRIENE.**

Frans W.Langkilde, Robert Wilbrandt and Niels-Henrik Jensen.

Chemical Physics Letters. Vol.111, 372-378 (1984)

The lowest excited triplet state of all-trans-1,3,5-heptatriene has been studied by time-resolved absorption and resonance Raman spectroscopy. The difference absorption spectrum of the triplet state has a maximum around 315 nm, and the triplet state decays by first-order kinetics with  $k = (3.4 \pm 0.3) \times 10^6 \text{ s}^{-1}$ . Time-resolved resonance Raman spectra of the heptatriene triplet excited at 317.5 nm showed bands at 1574, 1298, 1275, 1252, 1209, and 1132  $\text{cm}^{-1}$ .

**TRIPLET-STATE RESONANCE RAMAN SPECTRUM OF all-trans-DIPHENYL-  
BUTADIENE.**

R.Wilbrandt, W.E.L.Grossman P.M.Killough J.E.Bennett and  
R.E.Hester.

The Journal of Physical Chemistry, Vol.88 5964-5971  
(1984)

The preresonance Raman spectrum of *all-trans*-diphenylbutadiene (DPB) in its ground state and the resonance Raman spectrum (RRS) of DPB in its short-lived electronically excited triplet state are reported. Transient spectra were obtained by a pump-probe technique using two pulsed lasers. The preresonance spectrum of the ground state is not significantly changed from that of the nonresonance spectrum. In the resonance spectrum of the triplet state the double-bond stretching mode of the butadiene part is shifted by 43  $\text{cm}^{-1}$  downward to 1582  $\text{cm}^{-1}$ , whereas the single-bond stretching mode is essentially unchanged. A transient band at 1556  $\text{cm}^{-1}$  is tentatively assigned to the 8a ring mode shifted downward by 39  $\text{cm}^{-1}$ . These results are discussed in detail.



**RESONANCE RAMAN SPECTROSCOPY OF FREE RADICALS PRODUCED  
BY IONIZING RADIATION.**

Robert Wilbrandt.

Faraday Discuss.Chem.Soc. 80 1-9 (1984)

Applications of time-resolved resonance Raman spectroscopy to the study of short-lived free radicals produced by ionizing radiation are briefly reviewed. Potential advantages and limitations of this technique are discussed in the light of given examples. The reduction of *p*-nitrobenzylchloride and subsequent formation of the *p*-nitrobenzyl radical and the reaction of *p*-nitrotoluene with  $O^{\cdot -}$  are studied by resonance Raman and optical absorption spectroscopy.

**TRIPLET STATE RESONANCE RAMAN SPECTRUM OF ALL-TRANS-DIPHENYL-  
BUTADIENE.**

R.Wilbrandt, W.E.L.Grossman, P.M.Killough, J.E.Bennett and  
R.E.Hester.

Proceedings of the IXth International Conference on  
Raman Spectroscopy. Tokio, Japan. 27 Aug.- 1 Sept. (1984)

Time-resolved resonance Raman spectroscopy has been applied to the study of excited states for the first time in 1978<sup>(1)</sup>. In the present paper the preresonance Raman spectrum of all-trans-diphenylbutadiene (DPB) in its ground state and the resonance Raman spectrum of DPR in its short-lived electronically excited triplet state sensitized by biphenyl (BP) are reported<sup>(2)</sup>. Transient spectra were obtained by a pump-probe technique using two pulsed lasers at 248 and 396 nm, the first one being an excimer laser and the second an excimer pumped dye laser. The preresonance spectrum of the ground state is not significantly changed from that of the nonresonance spectrum. In the resonance spectrum of the triplet state the double-bond stretching mode of the butadiene part is shifted by 43  $cm^{-1}$  downwards to 1582  $cm^{-1}$ , whereas the single-bond stretching mode is essentially unchanged. A transient band at 1556  $cm^{-1}$  is tentatively assigned to the 8a ring mode shifted downwards by 39  $cm^{-1}$ . Time-resolved resonance Raman spectra are seen in Fig. 1.

**EXCITED STATES OF BIOLOGICAL POLYENES: ISOMERIZATION AND STRUCTURE OF RETINALS IN THE TRIPLET STATE.**

N.-H.Jensen, R.Wilbrandt, C.Houée-Levin and R.Bensasson.

Proceedings of the Xth Iupac Symposium on Photochemistry.  
CCC-Interlagen, Switzerland, 595-596 22-27 July, 1984

The triplet states of biological polyenes (carotenoids and retinals) have been the subject of numerous investigations. Undoubtedly, these investigations have been prompted partly by the well documented importance of carotenoid triplet states in the protective reactions which inhibit photodestruction of the living organisms and partly by the qualitative similarity between the photochemical reactions of free retinal and of retinals bound in the intact biological chromophores. We have recently presented results which suggest that carotenoids undergo conformational relaxation in the triplet state by torsion around one or more of the formal C=C double bonds<sup>1-3</sup>. Upon intersystem crossing back to the ground state these conformational changes eventually lead to complete isomerization. Contrary to the existing literature, we were able to demonstrate<sup>4</sup> that sensitized photoisomerization (sensitizer chlorophyll a) of all-trans-β-carotene occurs with considerable efficiency.

**TIME-RESOLVED RESONANCE RAMAN AND ABSORPTION SPECTRA OF 9-CIS-, 11-CIS-, 13-CIS- AND ALL-TRANS-RETINAL IN THEIR LOWEST EXCITED TRIPLET STATES.**

R.Wilbrandt, N.-H.Jensen and C.Houée-Levin.

Proceedings of the IXth International Conference on  
Raman Spectroscopy. Tokio, Japan. 27 Aug.- 1 Sept. (1984)

The triplet-triplet absorption spectra of 9-cis-, 13-cis- and all-trans-retinal as well as the time-resolved resonance Raman spectra of the lowest electronically excited triplet states of 9-cis-, 11-cis-, 13-cis- and all-trans-retinal in aromatic solvents at room temperature have been obtained under conditions ensuring the isomeric purity of the starting materials. The triplet states were produced by triplet energy transfer from a sensitizer in pulse-radiolysis experiments. The overall results suggest that the isomeric retinals form either different relaxed triplet species or different mixtures of relaxed triplet species. The consequences for the energy barriers separating the various triplet species are discussed. The resonance Raman spectra obtained by using either anthracene ( $E_T = 177.7 \text{ kJ mol}^{-1}$ ) or naphthalene ( $E_T = 254.8 \text{ kJ mol}^{-1}$ ) as sensitizers were virtually identical for the triplet states from each of the isomers 11-cis-, 13-cis- and all-trans-retinal, suggesting that the relaxed triplet species or the mixture of relaxed triplet species formed from each isomer is independent of the energy of the sensitizer.

REVERSIBLE TRIPLET ENERGY TRANSFER BETWEEN NEO-ALLOOCIMENE  
AND ANTHRACENE.

A.A.Gorman, I.Hamblat and N.-H.Jensen.

Chemical Physics Letters. Vol.111 293-296 (1984)

The rate constants for triplet energy transfer between neo-alloocimene and anthracene have been redetermined by a combination of pulsed laser photolysis and computer simulation of previously reported pulse radiolysis data. The true rate constants are 4-6 times larger than previously reported. Variable temperature experiments confirm that neo-alloocimene is a vertical acceptor of triplet energy from anthracene although, presumably as a consequence of fast subsequent relaxation within the encounter complex, the rate constant is faster than predicted by the Sandros equation. If the rate constants for forward and back transfer of triplet energy exhibit approximately the same pre-exponential factors, the relaxed triplet energy of neo-alloocimene is placed at  $\approx 168 \text{ kJ mol}^{-1}$  above the ground-state surface,  $\approx 29 \text{ kJ mol}^{-1}$  less than the corresponding value for the spectroscopic triplet.

NYT LASERUDSTYR TIL KEMISK FORSKNING.

Robert Wilbrandt and Knud Sehested.

Risø Nyt. September 1984

I en årrække har Kemi- og Acceleratorafdelingen udført forskning inden for radikal kemi og hurtige kemiske reaktionsmekanismer i gas- og væske-fase. Forskningen er udført ved hjælp af stråling fra elektronacceleratorer og det dertil knyttede avancerede udstyr til pulsradiolyse og tidsopløst Raman spektroskopi. Man har med disse metoder først og fremmest studeret fundamentale kemiske processer, specielt i vandig fase, idet et grundlæggende kendskab til disse er forudsætningen for at forstå de mere indviklede processer, der foregår i naturen, hvor vand optræder overalt i levende organismer. Forståelse og kendskab til de kemiske mekanismer, der foregår i tidsrum fra  $0,000000001 - 0,000001$  sek. er af afgørende vigtighed for studiet af bl.a. atmosfære-kemiske og biologiske processer og for forståelsen af bl.a. fotosyntesen, for en gang i fremtiden bedre at kunne udnytte solenergien.

Respond to  
COMMENT ON "POSITRONIUM FORMATION AND DIFFUSION IN A MOLECULAR  
SOLID STUDIED WITH VARIABLE-ENERGY POSITRONS".

M.Eldrup, A.Vehanen, P.J.Schultz and K.G.Lynn

Physical Review Letters. Vol.53 953-954 (1984)

The Comment by Van House, Rich, and Zitkewitz<sup>1</sup> is interesting in that their calculation semiquantitatively is able to reproduce the low-energy part of our experimental results (Fig. 1 of Eldrup *et al.*<sup>3</sup>), in agreement with the main points of our qualitative interpretation<sup>2</sup> for this low-energy region.

POSITIVE-ION SCAVENGING IN THE POSITRON SPUR.  
ORTHO-Ps YIELDS IN CYCLOPROPANE AND AMMONIA SOLUTIONS OF  
CYCLOHEXANE AND TRANS-DECALIN.

Göran Wikander, Niels J.Pedersen and Ole E.Mogensen.

Chemical Physics 86 213-225, Amsterdam. (1984)

Positron annihilation lifetime spectra were obtained for mixtures of the two positive-hole scavengers cyclopropane and NH<sub>3</sub>, and two solvents, cyclohexane and trans-decalin, in which the holes are rapidly moving. A scavenging of the hole in the positron spur is expected to enhance the Ps yield provided the product of the scavenging has a lower reactivity towards the excess electron than that of the initial positive ions. Previously, it was shown that the hole scavengers pyridine, DMA, TMPD and TPA increased the Ps yield in the solvents with fast holes but not in other non-polar solvents. Naturally, this was attributed to fast-hole scavenging. However, *c*-C<sub>3</sub>H<sub>6</sub> gave no strong Ps increase at concentrations where a large fraction of the holes is trapped. Trans-decalin and adamantane in *c*-C<sub>6</sub>H<sub>12</sub> and adamantane in trans-decalin gave no Ps enhancement either. On the other hand, NH<sub>3</sub> enhanced the Ps yield to the same degree in *c*-C<sub>6</sub>H<sub>12</sub> and *t*-C<sub>10</sub>H<sub>18</sub> although the rate constant for hole trapping is five times larger in *c*-C<sub>6</sub>H<sub>12</sub> than in *t*-C<sub>10</sub>H<sub>18</sub>. Nine different models and processes for the explanation of the data are put forward and tested. For example, the Ps enhancement cannot be caused directly by the large mobility of the hole, as *c*-C<sub>3</sub>H<sub>6</sub> traps the fast hole but gives no Ps enhancement. Apparently, our results can best be explained in terms of an initially very fast hole in cyclohexane and trans-decalin combined with a field-assisted detrapping of the hole from the hydrocarbon hole scavengers.

**THE TEMPERATURE DEPENDENCE OF THE POSITRONIUM BUBBLE STATE.  
AN ANGULAR CORRELATION AND DOPPLER BROADENING STUDY OF A  
PHENYL ETHER.**

O.E.Mogensen, N.J.Pedersen, B.D.Malhotra and R.A.Pethrick.

Chemical Physics 87 139-148, Amsterdam. (1984)

Positron annihilation angular correlation and Doppler broadening measurements are reported as a function of temperature for the supercooling liquid bis(*m*-(*m*-phenoxyphenoxy)phenyl)ether (6PO). A comparison of these observations with predictions based on lifetime measurements is presented and indicates limitations of particular experiments in characterising the annihilation processes. The ratio  $I_3/I_1$ , where  $I_3$  is the ortho-Ps yield and  $I_1$  the narrow-peak intensity, was observed to be 4-6 instead of its "ideal" value of 3 in the glassy state. This is interpreted as evidence for a Ps center-of-mass wavefunction consisting of a component strongly localized on the Ps trap and a broader, "spilled over" component. Only the latter gives rise to a narrow peak of intensity  $I_1$ . The variation of  $I_3/I_1$  with temperature depends on the Ps state and hence, provides evidence for the effect of the initial size of the Ps trap and the molecular motion within the Ps lifetime.

**TEMPERATURE DEPENDENCE OF THE INHIBITION OF POSITRONIUM  
BY CHLORINE-SUBSTITUTED HYDROCARBONS IN NON-POLAR LIQUIDS.**

Göran Wikander, Ole E.Mogensen and Niels J.Pedersen.

Chemical Physics 87 149-161, Amsterdam. (1984)

Positron annihilation lifetime spectra were measured for solutions of 1,2,3,5- $C_6H_2Cl_4$  in hexane, toluene, *m*-xylene and mesitylene,  $CCl_4$  in hexane and toluene, and  $C_2HCl_3$  in *n*-hexane for concentrations below 1 M and at various temperatures between  $-30^\circ C$  and  $67^\circ C$ . The Ps inhibition by  $C_6H_2Cl_4$  was roughly 14 times stronger at  $-30^\circ C$  than at  $67^\circ C$  in toluene, *m*-xylene, and mesitylene, while that of  $CCl_4$  displayed hardly any temperature dependence in hexane and toluene. Previously, the Ps inhibition by  $C_6H_2Cl_4$  in various liquids at  $20^\circ C$  was explained by a competition between electron pick off by the positron from  $C_6H_2Cl_4^-$  formed by electron scavenging in the positron spur, and dehalogenation of the same anion at picosecond times after the spur formation. Three effects might reasonably explain the strong temperature dependence of the Ps inhibition of  $C_6H_2Cl_4$ : (1) The dechlorination time of  $C_6H_2Cl_4^-$  might be much shorter at low than at high temperatures. (2) The positron mobility might decrease very strongly with decreasing temperature. (3) Positrons possibly trapped on  $C_6H_2Cl_4$  might thermally detach at high but not at low temperatures.

**POSITRONIUM FORMATION IN GASES AND LIQUIDS.**

Finn M.Jacobsen.

In Positron Scattering in Gases.  
Edited by J.W.Humbertson and M.R.C.McDowell. 85-97  
( Plenum, London 1984 )

Generally, most discussions of the yields of positronium, Ps, in gases and liquids have been constrained to the framework of either the Ore or spur model of Ps formation. In this paper, we shall demonstrate that by a slight extension of the frames of these models it is possible to formulate a single model of Ps formation in gases and liquids. Furthermore, we shall give a semi-quantitative discussion of the thermalization properties of positrons in gases. These results will be used in a discussion of the density behaviour of Ps yields in gases.

**A SLOW-POSITRON STUDY OF POSITRONIUM FORMATION AND DIFFUSION  
IN CRYSTALLINE AND AMORPHOUS ICE.**

M.Eldrup, A.Vehanen, P.J.Schultz and K.G.Lynn.

In Proceedings of the International Workshop "Slow Positrons in Surface Science". Ed. A.Vehanen. Helsinki University of Technology, Lab.of Physics, Report 135, (1984)

**HELIUM BUBBLES IN 600 MEV PROTON IRRADIATED ALUMINIUM  
STUDIED BY POSITRON ANNIHILATION.**

**K.O.Jensen, B.N.Singh, M.Eldrup, M.Victoria and W.V.Green.**

**In Proceedings of the 5th Risø International Symposium on  
Metallurgi and Materials Science. Ed. N.Hessel Andersen et al.  
333, Risø. 3-7 September 1984**

Aluminium samples containing He-bubbles produced by 600 MeV proton irradiation at 120, 140, and 430°C were investigated by Positron Annihilation Technique (PAT); both lifetime and angular correlation measurements were made. In the low temperature irradiated samples, changes in the lifetime of trapped positrons with dose and temperature are correlated with the bubble size. From the lifetime the He-density in the bubbles is estimated to be  $7 \pm 4 \times 10^{22} \text{ cm}^{-3}$ . The 430°C irradiated samples exhibit an unusually narrow angular correlation curve component associated with positronium formation in the bubbles, probably a result of transmutation produced Na segregating at the bubble surfaces.

**MICROSTRUCTURAL CHARACTERIZATION OF MATERIALS BY  
NON-MICROSCOPICAL TECHNIQUES.**

**Editors:**

**N.Hessel Andersen, M.Eldrup, N.Hansen, D.Juul Jensen,  
T.Leffers, H.Lilholt, O.B.Pedersen and B.N.Singh.**

**Proceedings of the 5th Risø International Symposium on  
Metallurgi and Materials Science. Risø, Denmark.  
3-7 September 1984**

HEAVY METAL UPTAKE FROM AIR AND SOIL BY TRANSPLANTED PLANTS  
OF *ACHILLEA MILLEFOLIUM* AND *HORDEUM VULGARE*.

K.Pilegaard and I.Johnsen.

Ecological Bulletins 36, 97-102, Stockholm (1984)

The amount of metal taken up by *Achillea millefolium* and *Hordeum vulgare* through leaves and roots was studied by growing the plants in six different soils, one of which was artificially enriched with Cd, Cu, Ni, and Pb at five different concentrations. Plants were grown in pots placed at five sites with varying aerial deposition of heavy metals.

For Cu and Pb there was a significant correlation between the concentrations in plants and the rate of aerial deposition, while metal concentrations in plants and soils were unrelated.

Nickel and Cd concentrations in plants were correlated with the rate of aerial deposition and soil concentrations. It was therefore concluded that *A. millefolium* and *H. vulgare* can be used to monitor aerial deposition of Cu and Pb, but their use to monitor Ni and Cd requires that chemical properties of the soil are constant throughout the monitored area.

POTENTIAL POLLUTANTS FROM A PROPOSED URANIUM MINE IN GREENLAND.

Kim Pilegaard.

Environmental Contamination. International Conference,  
London. 753-756, July 1984

The sources of pollution from a proposed uranium mining and milling complex in South Greenland have been evaluated. The open pit, waste dump and tailings impoundment will be the most important sources of pollution. The mobility of non-radioactive elements was lower in the tailings than in the ore, whereas the reverse was true for radioactive elements.

The potential pollutants include: Be, F, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Nb, Zr, Mo, Cd, Sb, REE, Hg, Pb, Th, U, Ra-226, Pb-210 and Po-210. This list was based on abundance and mobility in ore and tailings and general toxicity of the elements. Fluorine is the most mobile of the elements in ore and tailings. The concentration in ore and tailings may be up to 1% and in combination with its high toxicity, F can then be regarded as the most serious pollutant.



Lectures

- 1.1 K. Heydorn: "Quality assurance in neutron activation analysis". 5th International Conference on Nuclear Methods in Environmental and Energy Research, Mayaguez, Puerto Rico, 5th April 1984.
- 1.2 Johnny O. Schmidt: "Determination of Li, B and F by rapid instrumental neutron activation analysis using beta-particle counting". 5th International Conference on Nuclear Methods in Environmental and Energy Research, Mayaguez, Puerto Rico, 5th April 1984.
- 1.3 K. Heydorn: "The accuracy of precision". University of California, Irvine, 16th April 1984.
- 1.4 K. Heydorn: "Biological and environmental applications of nuclear chemistry". Lawrence Livermore National Laboratory, California, 19th April 1984.
- 1.5 K. Heydorn: "Equalization of axial neutron flux density for the transmutation doping of silicon in a heavy water reactor". 5th International Conference on Neutron Transmutation Doping, San Jose, 9th February 1984.
- 1.6 K. Heydorn: "Neutron transmutation doping of silicon". Tun Ismail Atomic Research Centre, Selangor, Malaysia, 21st February 1984.
- 1.7 Leif Højslet Christensen: "Certification of reference materials by energy-dispersive X-ray fluorescence spectrometry". Denver, August 1984.
- 1.8 Leif Højslet Christensen: "EDXRF determination of major and minor elements in compound fertilizers". 33rd Conference on X-Ray analysis. Denver, August 1984.

- 1.9 Leif Højslet Christensen: "Energy-dispersive X-ray fluorescence spectrometry: A versatile analytical technique for determination of major and minor elements in paint". 17th Fatipec Kongress. Lugano, September 1984.
- 2.1 Elfinn Larsen: "Massespektrometri". Den Kgl. Veterinær- og Landbohøjskole, 7th March 1984.
- 2.2 Helge Egsgaard, Peter Bo and Lars Carlsen: "Intramolecular isotope distribution derived directly from the ion pattern". EUCHEM Conference on New Techniques in Organic Mass Spectrometry, Stockholm, 1st - 5th July 1984.
- 2.3 Lars Carlsen: "On the migration behaviour of radionuclides in salt formations". Institut für Tieflagerung (Gesellschaft für Strahlen und Umweltforschung), Braunschweig, May 1984.
- 2.4 Lars Carlsen: "On the migration behaviour of radionuclides in salt formations". Hahn-Meitner Institut, Berlin, May 1984.
- 2.5 Lars Carlsen, Helge Egsgaard and Flemming S. Jørgensen: "Enols/enethiols in the gas phase pyrolysis of mono- and dithioacetates". XIth International Symposium on Organic Sulphur Chemistry, Lindau, September 1984.
- 2.6 Lars Carlsen and Helge Egsgaard: "Pulse pyrolysis". 6th International Symposium on Analytical and Applied Pyrolysis, Wiesbaden, September 1984.
- 2.7 Lars Carlsen and Dorte Platz: "The retention of radionuclides in salt". International Symposium on Nuclear and Radiochemistry, Lindau, October 1984.
- 3.1 Ole John Nielsen: "Study of OH reactions with ethane and some substituted methanes at 300 - 400 K, using pulse radiolysis and kinetic spectroscopy". Working Party 2 Orleans, 30th - 31st October 1984.

- 3.2 Palle Pagsberg: "Atmosferisk grundforskning med relation til sur regn". Roskilde Universitetscenter, 7th November 1984.
- 5.1 Knud Brodersen: "How to integrate waste package characteristics and engineered barriers interactions into characterisation and long term behaviour programs". International Seminar on: Leaching release mechanisms in low and medium level waste packages under actual disposal conditions, Cadarache, 13th - 15th November 1984.
- 6.1 Robert Wilbrandt: "Time-resolved resonance Raman spectroscopy of excited molecules and free radicals", (invited paper). Annual Meeting of the Italian Group of Photochemistry, Assisi, Italy, 28th September 1984.
- 6.2 Robert Wilbrandt: "Time-resolved resonance Raman spectroscopy of excited states and free radicals", (invited paper). Gordon Conf. Radiation Chemistry, Wolfboro, USA, 23rd June 1984.
- 6.3 Robert Wilbrandt: "Time-resolved resonance Raman spectroscopy", (invited paper). N.A.T.O. Advanced Study Institute on "Primary Photoprocesses in Biology and Medicine", Bressanone, Italy, 18th September 1984.
- 6.4 R. Wilbrandt, "Time-resolved resonance Raman spectroscopy of excited states of polyenes", (invited paper). IX Int. Conf. Raman Spectrosc., Tokyo, Japan, 28th August 1985.
- 6.5 R. Wilbrandt, "Resonance Raman spectroscopy of free radicals", (invited paper). Faraday Discussions on Radicals in Condensed Phases, Leicester, England, 5th September 1985.
- 6.6 Niels-Henrik Jensen: "Excited states of biological polyenes: Isomerization and structure of retinals in the triplet state". Xth IUPAC Symposium on Photochemistry, Interlaken, Schweiz, 22nd - 27th July 1984.

- 6.7 Niels-Henrik Jensen: "Photochemistry and spectroscopy of retinals in the triplet state". 7th International Symposium on Carotenoids, Munich, Western Germany, 27th - 31st August 1984.
- 6.8 Niels-Henrik Jensen: "Isomerization and structure of retinals in the triplet state". Primary Photo-Processes in Biology and Medicine. N.A.T.O. Advanced Study Institute, Bressanone, Italy, 16th - 28th September 1984.
- 6.9 Niels-Henrik Jensen: "Excited triplet states of biological polyenes". Centre d'Etudes Nucléaires de Saclay, France, 19th November 1984.
- 6.10 Ole John Nielsen: "On the detection of interstellar ions, radicals and molecules and theories for their formation". H.C. Ørsted Institute, University of Copenhagen, 1st February 1984.
- 7.1 Morten Eldrup, A. Vehanen, P.J. Schultz and K.G. Lynn: "A slow-positron study of positronium formation and diffusion in crystalline and amorphous ice". International Workshop on "Slow Positrons in Surface Science", Pajulahti, Finland, 25th - 29th June 1984.
- 7.2. Morten Eldrup: "Molecular crystals". Meeting on "Matière Condensée et Positrons", Saclay, France, 9th November 1984.
- 7.3 Morten Eldrup, K.O. Jensen, B.N. Singh, H. Victoria and W.V. Green: "Helium bubbles in 600 MeV proton irradiated aluminium studied by positron annihilation". 5th Int. Symposium on Metallurgy and Materials Science, Risø, September 1984.
- 7.4 Morten Eldrup: "Positrons in molecular substances". Helsinki University of Technology, 8th Februar 1984.

- 8.1 Kim Pilegaard: "Potential pollutants from a proposed uranium mine in Greenland". Environmental Contamination - International Conference, London, July 1984.
  
- 8.2 Emil Sorensen: "Proceskemisektionens aktiviteter indenfor metaludvinding". ATV-Meeting at Risø, 13th November 1984.

Risø - M - 2497

<p>Title and author(s)</p> <p>Annual Report 1984 Chemistry Department</p> <p>Edited by Jytte Funck, Elfinn Larsen and Ole John Nielsen</p>	<p>Date March 1985</p>
<p>52 pages + tables + illustrations</p>	<p>Department or group</p> <p>Chemistry Department</p>
<p>Abstract</p> <p>This report contains a brief survey of the main activities in the Chemistry Department. All articles and reports published and lectures given in 1984 are presented. The facilities and equipment are mentioned briefly. The activities are divided into the following groups: radioisotope chemistry, analytical- and organic chemistry, environmental chemistry, polymer chemistry, geochemistry and waste disposal, radical chemistry, positron annihilation, mineral processing, and general.</p> <p>Available on request from Risø Library, Risø National Laboratory (Risø Bibliotek), Forsøgsanlæg Risø), DK-4000 Roskilde, Denmark Telephone: (03) 37 12 12, ext. 2262. Telex: 43116</p>	<p>Group's own registration number(s)</p> <p>Copies to</p>