PROGRAM

Fifth Annual Symposium
on
Recent Advances
in the
Analytical Chemistry
of Pollutants

May 19-21, 1975







Aquarama Convention Center
Jekyll Island, Georgia, U.S.A.

MONS 214215

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MONS 214216

Monday, May 19

Morning Session—8:30-12:00
Chairman, William T Donaldson

8:30 Plenary Lecture: Thomas W. Carmody, Vice President—Safety, Health and Affairs Related to the Environment, Union Carbide Corporation, New York, New York

9:30 (1) **Simultaneous Multielement Determinations—Meeting the Needs in Environmental Analytical Chemistry**
Charles H. Anderson, Southeast Environmental Research Laboratory, Athens, Georgia

10:10 Break

10:40 (2) **Activation Analysis with Radiochemical Separation in Pollution Control**
W. Haerdi, C. Bergerioux and J P Blanc, University of Geneva, Geneva, Switzerland

11:20 (3) **Application of X-Ray Photoelectron Spectroscopy to the Chemical Characterization of Air Pollution Aerosol Particles**
Ticha Novakov, Lawrence Berkeley Laboratory, Berkeley, California

12:00 Lunch

Afternoon Session—1:30-5:20
Chairman, Gary Hieftje

1:30 (4) **Inductively Coupled Plasma—Optical Emission Spectroscopy**
Richard N Kniseley, Ames Laboratory ERDA, Ames, Iowa

2:10 (5) **Application of Enzymes to the Determination of Contaminants in Water**
Leon N. Klatt, Oak Ridge National Laboratory, Oak Ridge, Tennessee, and David R Senn and Peter W. Carr, University of Georgia, Athens, Georgia

2:50 (6) **Heavy-atom Effects in the Luminescence Analysis of Aromatic Systems**
H. Dreeskamp, Max-Planck Institute, Mulheim-Ruhr, Germany, and M Zander, Rutgerswerke AG, Castrop-Rauxel, and Technische Universitat, Clausthal, Germany

3:30 Break

4:00 (7) **Polarography and Voltammetry in Organic Environmental Analysis**

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EXL Petr Zuman, Clarkson College of Technology, Potsdam, New York

4 40 **High Resolution Mass Spectrometry in Environmental Organic Studies**
(8) A. L. Burlingame, University of California, Berkeley, California
UBD

Tuesday, May 20

Morning Session—8:30-9 30
Chairman, Roland Frei

8 30 Planary Lecture. Gordon G. Robeck, Director, Water Supply Research Laboratory, National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio

9:30 **Integrated Dust Analysis by Physical Methods**
NOT (9) H. Malissa, E. Pell, and H. May, Institute of Technology, Vienna, Austria

10:10 Break

10:40 **Chlorinated Dibenzofurans: Recent Analytical Studies**
(10) Irwin H. Pomerantz, Terry J. Farrell and John A. G. Roach, Food and Drug Administration, Washington, D.C.
BS

11:20 **Speciation of Ambient Levels of Mercury**
(11) Robert S. Braman, University of South Florida, Tampa, Florida
IMT

12.00 Lunch

Evening Session—7 00-10·00
Chairman, Ernest Merian

7:00 **X-Ray Fluorescence Techniques for Multi-Element Pollutent Analysis**
(12) David C. Camp, Lawrence Livermore Laboratory, Livermore, California
505

7.30 **Analysis and Importance of Chelating Agents—Key Determinants in Heavy Metals Pollution**
(13) Stanley E. Manahan, University of Missouri, Columbia, Missouri
GOOD

8:20 Break

8:40 **Analytical UV-Photoelectron Spectroscopy**
GOOD (14) Jack Betteridge, University College of Swansea, Swansea, United Kingdom

9:20 **GC-IR System with Sub-Microgram Sensitivity**
?? (15) Leo Azarraga, Southeast Environmental Research Laboratory, Athens, Georgia

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Wednesday, May 21

Morning Session—8 30-12 00
Chairman, Otto Hutzinger

8:30 Plenary Lecture: Robert H. White-Stevens, Chairman, Bureau of Conservation and Environmental Science, Rutgers University, New Brunswick, New Jersey

9 30 (16) **Improved Detection, Identification, and Quantitation in Liquid Chromatography**
L. S. Rogers, University of Georgia, Athens, Georgia

10:10 Break

10:40 (17) **A Contribution to the Problem of Strong Acid Determination in Air**
Dieter Klockov and Helmut Denzinger, Universitat Freiburg, Freiburg, Germany and Gerhard Ronicke, Aerosolmeßstelle Schauinsland, Schallstadt-Wolfenweiler, Germany

11:20 (18) **The Application of ESCA to Surface Analysis**
David M. Hercules, University of Georgia, Athens, Georgia

12.00 Lunch

Afternoon Session—1:30-3:30
Chairman, Francis Karasek

1:30 (19) **Analysis of a Carcinogen Conglomerate in the Environment and in Tissue**
Eugene Sawicki, Environmental Protection Agency, Research Triangle Park, North Carolina

2:10 (20) **Recent Developments in Spark Source Mass Spectrometry**
Willard W. Harrison, University of Virginia, Charlottesville, Virginia

2:50 (21) **Ion-Selective Electrodes**
E. Pungor, K. Toth and G. Nagy, Technical University, Budapest, Hungary

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(1) SIMULTANEOUS MULTIELEMENT DETERMINATIONS–MEETING THE NEEDS IN ENVIRONMENTAL ANALYTICAL CHEMISTRY Charles H Anderson, Environmental Protection Agency, Southeast Environmental Research Laboratory Athens, Georgia 30601

The need for the determination of trace levels of twenty of more elements in a single sample has increased significantly over the past several years Environmentally related studies have contributed to this demand and have resulted in an unreasonable work load for analytical facilities Instrumental techniques that can determine a broad range of elements in a relatively short time must be used to process samples more efficiently and keep costs at a minimum

In terms of accuracy precision, selectivity, sensitivity, cost analysis time, and operator skill required no one technique is optimum for all problems Each has both strengths and weaknesses in its application to environmental analytical problems Compared with the conventional methods of determining elements one at a time substantial savings can be achieved through the multielement approach

(2) ACTIVATION ANALYSIS WITH RADIOCHEMICAL SEPARATION IN POLLUTION CONTROL W Haerdi, C Bergerioux and J P Blanc Institute for Analytical Chemistry, University of Geneva, Geneva Switzerland

Because of its inherent sensitivity Neutron Activation Analysis (NAA) is one of the prime techniques for qualitative and quantitative determination of traces and ultra traces of inorganic pollutants in environment samples Detection limits are between 10^{-9} and 10^{-12} g depending on the element Since the metal of metals of interest may be present in concentrations of 10^{-3} to 10^{-10} M, a purely instrumental Neutron Activation Analysis (INAA) is often impossible to apply The same problem arises when the matrix itself may become highly radioactive and obscures the activity of the trace metals present, limiting the exploitation of the maximum sensitivity (in foodstuffs, biological or other natural systems like seawater samples)

One solution to the former case is to make a preconcentration before activation, however, great care is necessary to avoid introducing impurities during the procedure In the latter case, we must proceed to a post irradiation separation and isolate one or a group of trace metals from the bulk matrix, in this case contamination and blank problems are greatly eliminated The so called chemical spectrum stripping method can be applied Radiochemical procedures with high chemical recoveries are of course essential to reach this goal and must clearly adapt the development of instrumentation irradiation conditions and radiation detections

Some specific preconcentration and separation techniques (activity groups or single activities) will be presented and discussed (coprecipitation and adsorption on organic or inorganic supports, ion exchange, redox exchange) These techniques, when coupled with either gamma or x-ray spectrometry, offer advantages such as operative simplicity, rapidity and selectivity

(3) APPLICATION OF X RAY PHOTOELECTRON SPECTROSCOPY TO THE CHEMICAL CHARACTERIZATION OF AIR POLLUTION AEROSOL PARTICLES T Novakov, Energy and Environment Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

This paper deals with the application of x ray photoelectron spectroscopy (also known as ESCA or XPS) to the chemical characterization of air pollution aerosol particles, with particular emphasis on the determination of concentrations and chemical forms of suspended carbon, nitrogen and sulfur species For completeness, a short summary on the application of the method to the study of some gas-particle reactions relevant to the formation of such nitrogen and sulfur species, will be presented Detailed x ray photoelectron spectroscopic study of urban air pollution particles shows that 1) nitrate is usually a relatively minor constituent of aerosol particles; 2) ammonium, which may account for about one half of the total particulate nitrogen, is not necessarily in the form of common salts such as ammonium-nitrate or ammonium sulfate but it is found instead in a previously unsuspected form characterized by its relatively high volatility 3) occuring in concentrations similar to the "volatile" ammonium is a group of reduced nitrogen species which are identified as amine, amide and nitrile 4) sulfate which has been found to exist as essentially sulfuric acid adsorbed on particles, is the principal chemical form of particulate sulfur, 5) in addition to sulfate, sulfide is sometimes observed in concentrations comparable to the sulfate and 6) most of the particulate carbon appears in a neutral chemical state compatible with either condensed hydrocarbons or primary combustion generated carbonaceous particles or both Laboratory experiments, performed with the aid of x-ray photoelectron spectroscopy, demonstrates that surface chemical and catalytic reactions of NO and SO_2 with combustion generated carbonaceous (soot) particles result in the formation of suspended nitrogen and sulfur species identical to those observed in the polluted air For example surface ammonium complexes are produced in NO soot reaction in air (in the presence of moisture) at ambient temperatures, however, produce amine, amide and nitrile complexes associated with soot particles Soot particles are also efficient catalysts for SO_2 oxidation to sulfate at temperatures below 150°C

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(4) INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP OES) Richard N Kniseley Ames Laboratory ERDA Iowa State University, Ames, Iowa 50010

Extensive studies on argon supported inductively coupled plasmas (ICP) have clearly shown that these excitation sources offer great promise for the determination of metals and metalloids at ultratrace levels When this source is coupled with a multichannel direct reading spectrometer simultaneous multielement determinations can be achieved This paper presents a critical assessment of the ICP OES system for the determination of major minor and ultratrace constituents in samples of environmental interest The data collected in this study show that (a) the powers of detection achievable with the ICP OES are generally equal to or superior to those obtained by other atomic emission or absorption techniques (b) the ICP OES possesses virtually ideal characteristics for simultaneous multielement determinations because one set of experimental parameters provides essentially optimal conditions for all of the metals and metalloids interelement effects are non existent or reduced to a tolerable level for the systems studied thus far, and most samples can be handled with minimal or no preparation prior to analyses These characteristics make the ICP OES an ideal rapid quantitative survey instrument for a variety of sample types

(5) APPLICATION OF ENZYMES TO THE DETERMINATION OF CONTAMINANTS IN WATER Leon N Klatt, Analytical Chemistry Division Oak Ridge National Laboratory Oak Ridge, Tennessee and David R Senn and Peter W Carr Department of Chemistry, University of Georgia, Athens Georgia 30602

During the past decade enzymes have become more widely accepted by analytical chemists as valuable reagents particularly in the area of clinical chemistry and more recently in the measurement of water contaminants With the availability of enzymes from a number of commercial houses and an increased understanding of how enzymes can be efficiently immobilized the economical use of enzymes is quite feasible We will discuss the use of enzymes in water analysis and emphasize the improvement of a classical nitrate method by use of nitrate reductase Possible future uses of immobilized enzymes will be presented The most sensitive nitrate determination presently available (1 d = 50 ppb of nitrate) involves reduction of NO_3^- to NO_2^- with a copper-cadmium reductor followed by diazotization of sulfanilamide and formation of an azo dye by coupling to Marshall's reagent (N-1 napthyl ethylenediamine dihyrochloride) The product has a λmax = 543 nm and a molar extinction coefficient of 50 000 (cm^2)/mole The cadmium reductor can be replaced by substituting an enzymatic reduction step The radical cation methyl viologen (mv^+), which is generated by sodium dithionite acting on methylviologen (mv), will reduce nitrate in the presence of nitrate reductase (NaR)

$$mv + S_2O_4^{-2} \rightarrow mv^+ + HSO_3^- \quad (1)$$

$$mv^+ + NO_3^- \xrightarrow{NaR} mv + NO_2^- \quad (2)$$

The color development procedure is identical with that described above A detection limit of 10 ppb NO_3^- using a 1 cm cell in a continuous flow analyzer has been achieved We noted that the major contributor to the noise is derived from the flow system when a stabilized photometer is employed The detection limit using a non flow system should be about 1 ppb NO_3^- using a 1 cm cell The enzyme can quantitatively reduce nitrate and is therefore relatively free of errors due to activators and can tolerate reasonable levels of inhibitors Sample concentrations in the range 10 ppb NO_3^- to 7 ppm can be measured with a precision of approximately 1 0% at 0 2 ppm if steady state flow conditions are used A variety of real samples were determined, correlation with the method was generally acceptable

We have found that several sulfur oxyanions interfere in the color development step The problem was minimized by adding formaldehyde subsequent to reduction and increasing the acidity to approximately 1 25 M in strong acid Linear calibration curves from 50 ppb to 5 0 ppm (A=1 5) have been obtained

(6) HEAVY-ATOM EFFECTS IN THE LUMINESCENCE ANLYSIS OF AROMATIC SYSTEMS H Dreeskamp, Institut for Strahlenchemie im Max Planck Institut fur Kohlenforschung Mulheim Ruhr, und Universitat Stuttgart Germany and M. Zander, Rutgerswerke AG Castrop-Rauxel, und Technische Universitat Clausthal, Germany

Important luminescence Parameters of π electronic systems e g quantum yield, lifetime and vibrational structure of emission spectra are altered under the influence of atoms of high nuclear charge either as substituent or part of the solvens (internal and external heavy atom effect) Increasingly these effects are used to enhance the sensitivity and selectivity of fluorescence and phosphorescence analytical methods Our recent work attempts to improve the understanding of these effects Predictions as to the luminescence behavior of π electronic systems influenced by heavy atoms are extended

This talk gives a summary of the experimental and theoretical basis of heavy atom effects and their analytical applications

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(7) POLAROGRAPHY AND VOLTAMMETRY IN ORGANIC ENVIRONMENTAL ANALYSIS Petr Zuman, Dept of Chemistry Clarkson College of Technology Potsdam, New York 13676

Comparison of the three most important electroanalytical methods namely d c. polarography differential pulse polarography and linear sweep voltammetry, from the point of view of their practical applications will be given The limits of applications of the individual techniques with respect to classes of compounds, presence and mutual position of electroactive groups and substituents and sensitivity will be discussed

Specific cases to be discussed will include determination of carbon disulfide in the atmosphere after conversion into dithiocarbamate determination of nitro compounds in the atmosphere and of nitrosamines in various materials determination of insecticides residues and of phenolic materials

(8) HIGH RESOLUTION MASS SPECTROMETRY IN ENVIRONMENTAL ORGANIC STUDIES A L Burlingame Space Sciences Laboratory University of California, Berkeley California 94720

The development of real time gas chromatography high resolution mass spectrometry (GC/HRMS) – producing accurate mass measurements of all peaks in each spectrum – provides elemental compositions which significantly aid in structure and compound identification This information is especially useful for the characterization of complex organic mixtures from environmental sources such as waste waters, sediments and biological tissues which have been polluted with petroleum and synthetic organics

The performance of the instrumentation will be discussed as well as examples of work currently in progress in the environmental field

Acknowledgement of financial support Environmental Protection Agency Grant R803019-01 and National Institutes of Health Grant RR 719-02

(9) DUST ANALYSIS BY PHYSICAL METHODS H Malissa, E Pail and H May, Institute for Analytical Chemistry and Microchemistry, Technical Institute, Vienna, Austria

In order to gain proper informations about the harm of dust the exact single element determination only will never lead to the right conclusions even if the best methods are used

Therefore we must have methods and schemes for

a) the accurate and sensitive determination of single elements,
b) the proper correlation of chemical elements in dust samples,
c) obtaining information about the chemical or physical bonding of dust components, and
d) measuring particle size and gaining morphological information

It is absolutely essential to balance the chemical results and to show the completeness of analysis Here we are already confronted with a very great difficulty because in practice we have mostly only a few milligrams of a sample and very often trace elements are the most essential ones Therefore we need micromethods in the trace range and should be able to determine up to 20 elements

The chemical and physical bonding dictates also the solubility and transportation (and furthermore the reaction) of the elements in human bodies Particle size and morphology have a great influence on the biological effect of dust

The investigations of these phenomena can be done most successfully by use of physical analytical methods like EMPA IMMA, IR GC, SEM and others

In order to obtain meaningful results with these methods the proper sampling techniques have to be applied which is still the greatest problem in dust analysis

(10) CHLORINATED DIBENZOFURANS: RECENT ANALYTICAL STUDIES Irwin H Pomerantz, Terryl J Ferrell and John A G. Roach, Division of Chemical Technology, Bureau of Foods, Food and Drug Administration Washington, D C

Chlorinated dibenzofurans of a wide range of chlorine content have been reported as contaminants of several types of widely used industrial chemicals Available toxicity information on chlorinated dibenzofurans, as well as toxicity data on the related chlorinated dibenzo-p-dioxins, suggests potentially hazardous chlorinated dibenzofurans may be reaching the environment along with the commercially used chemicals in which they are contaminants

Evidence will be presented for the presence of chlorinated dibenzofurans in several commercial chlorinated biphenyl (PCB) mixtures of U S manufacture and one made in Japan. The chlorinated dibenzofurans were separated from the bulk of the biphenyls by column chromatography and analyzed using gas chromatography-mass spectrometry The degree of chlorination in the dibenzofurans found and approximate levels of dibenzofurans in the PCB mixtures will be discussed

Using available chlorinated dibenzofurans of known structure, relative retention times were determined on 4 non-polar and several polar GLC liquid phases The resulting data show the superior separation capabilities of the polar liquid phases, particularly for resolution of peaks of isomeric chlorinated dibenzofurans

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(11) SPECIATION OF AMBIENT LEVELS OF MERCURY Robert S Braman Department of Chemistry University of South Florida Tampa Florida 33620

Particulate mercury, elemental mercury methylmercury (II) type compounds non-particulate inorganic mercury compounds and dimethylmercury may be determined down to the 0.1 - 1 ng m^{-3} range by means of specific absorption tubes and a dc discharge emission spectroscopy method Analyses of ambient air indicate that elemental mercury is the major form present in an urban area but significant amounts of methylmercury (II) and volatile inorganic mercury type compounds also are found Over open ocean areas mercury (II) type compounds and elemental mercury are the major forms present but in low concentrations Air indoors is generally much higher in mercury than ambient outdoor air (over 100 ng m^{-3}, elemental mercury is the major form Mercuric chloride is rapidly biomethylated by soil biota Except in cases of extreme chemical conditions mercury in natural waters may be limited to inorganic mercury compounds and complexes and methylmercury (II) type compounds Dissolved oxygen rapidly oxidizes elemental mercury; dimethylmercury reacts with mercury (II) type compounds

GC discharge detection techniques have been developed for speciation of mercury in water into elemental mercury, dimethylmercury methylmercury (II) type compounds and inorganic mercury compounds at the sub-ppb range Inorganic mercury appears to be the major form in natural waters

A variety of GC methods have been extensively employed for speciation in biological samples but lack sufficient sensitivity for many natural water analyses applications

(12) X RAY FLUORESCENCE TECHNIQUES FOR MULTI ELEMENT POLLUTANT ANALYSIS David C Camp, Lawrence Livermore Laboratory Livermore, CA 94550

Energy and wavelength dispersive x ray fluorescence spectrometry (EDXES and WDXRF) are being applied to the analysis of environmental samples These methods can yield quantitative information in relatively short time periods with minimum to no sample preparation They are non-destructive and can be adapted to automated sample analyses in laboratories with environmental monitoring responsibilities

Wavelength dispersive spectrometry is an older well known and accepted technique, while energy dispersive is relatively new and not as well accepted. After briefly presenting the principles of both techniques with emphasis on the latter, examples of the spectra and analyses of environmental samples using photon, filtered x-ray tube, secondary target and accelerator particle excitation methods will be presented Their relative advantages will be summarized.

Results from a recent intercomparison involving 22 investigators who used 8 different analytical techniques will be summarized The objective was to evaluate EDXES's viability for the multi-element analyses of real aerosol samples Techniques in addition to EDXES and WDXRF included were atomic absorption spectrophotometry, emission spectroscopy and neutron activation analysis The study showed that EDXES provided superior convenience and speed of analysis, and accuracies of about ± 10% for all elements above potassium (Z = 19), with somewhat larger errors for elements down to aluminum (Z = 13)

(13) ANALYSIS AND IMPORTANCE OF CHELATING AGENTS KEY DETERMINANTS IN HEAVY METALS POLLUTION Stanley E Manahan Department of Chemistry University of Missouri, Columbia, 123 Chemistry Building, Columbia, Missouri 65201

Despite the well-deserved attention given to contamination of water by heavy metals, little consideration has been given to chelating agents of both natural and synthetic origin, which play a strong role in heavy metal transport Chelating agents in water may originate from decay of vegetable matter (fulvic acid) and from industrial or residential pollution sources For example EDTA is used in the treatment of water for some industrial applications food processing, and as a chemical reagent Some of this product is discharged with waste water Replacement of detergent phosphates with NTA in the United States would result in the discharge of large quantities of this chelating agent to sewage treatment facilities where, in some cases only partial degradation would occur Clearly consideration of chelating agents should have a high priority in water quality research and monitoring

Much of the dearth of knowledge about chelating agents in water is a result of a lack of analytical techniques applicable to chelating agents Several approaches are described in this paper One method based on the solubilization of copper from a slightly soluble copper containing precipitate, yields a value of total strong heavy metal chelating capacity, an important water quality parameter A similar approach is used in which the copper-containing solid phase is a cation exchanger in the copper form Approaches to species specific chelating agent analysis based upon liquid chromatographic separation and ion exchange-atomic absorption detection are discussed

MONS 214223

(14) ANALYTICAL UV PHOTOELECTRON SPECTROSCOPY D Betteridge Chemistry Department, University College of Swansea, Singleton Park Swansea SA2 8PP United Kingdom

UV photoelectron spectroscopy (UPS) is a technique for measuring the binding energies of the electron in the valence shell orbitals of molecules This paper describes and discusses recent developments in experimental technique, methods of interpretation of spectra and analytical applications

Sample throughput and sensitivity have been improved by the construction of an easily built, robust photoelectron spectrometer Spectra have been obtained from solid samples, with m pts of up to 250°C Vapour phase samples may be introduced via a needle tube (for head-space sampling) or a GLC Spectra on 10µg samples can be obtained in less than 1 min, although usually 0 1mg and 7 mins respectively are taken

A GLC has been coupled directly to the spectrometer The GLC can serve as a heated inlet system which allows a measured amount of sample to be let into the spectrometer and simultaneously checks its purity Alternatively the spectrometer can monitor the effluent of the chromatograph It is possible to identify by the complete spectrum, two components being eluted as one It is also possible to fix the spectrometer at a predetermined characteristic IP and to use it as a selective GLC detector

The GLC and computer analysis have been used for quantitative analysis All round improvements have been brought about by the use of a microprocessor for data handling Spectra are obtained with 0 1s scans and accumulated Programs of integration and spectrum stripping are available and are suitable for quantitative analysis.

Simplified methods and semi empirical molecular orbital calculations have been applied to the interpretation spectra, and it has been found that rule of thumb" procedures are satisfactory for many purposes

These developments will be exemplified and critically discussed by reference to the spectra of pesticides, nitrosamines, fluorinated anaesthetics flavours and polymer degradation products

(15) GC-IR SYSTEM WITH SUB MICROGRAM SENSITIVITY Leo Azzarega, Environmental Protection Agency, Southeast Environmental Research Laboratory, Athens, Georgia 30601

Identifiable spectra of 1 6 to 0 8 µg of hydrocarbons and 0 8 to 0 4 µg of oxygen-containing organic compounds were obtained on-the-fly with a Fourier transform infrared spectrophotometer equipped with a Mercury-Cadmium-Telluride detector and a 100 8 cm long x 2 mm diameter light pipe

The practicality of FTIR as an analytical tool was demonstrated by its application to the analysis of a New Orleans drinking water sample Identifiable IR spectra were obtained for GC peaks, even when they were superimposed on a relatively complex background

(16) IMPROVED DETECTION, IDENTIFICATION AND QUANTITATION IN LIQUID CHROMATOGRAPHY L B Rogers, Chemistry Department, University of Georgia, Athens, Georgia 30602

Analyses at the trace level place much higher demands upon the chemist, the chemical systems, and the instruments than those at higher concentrations Basically, this can be viewed as placing the ultimate demand upon signal-to noise ratio and stability of the overall chromatographic system In addition, there may be heavy demands placed upon the information content as well as the sensitivity provided by the detector

The purpose of this presentation is to translate the basic requirements for good, sensitive, selectivity measurements from liquid chromatographic systems into specific experimental factors For example, although much of the emphasis with respect to new packing materials has been on the better resolution they afford, they can also result in higher sensitivities Likewise, new detection systems have also been directed toward those affording higher sensitivity However, there has also been a trend toward the use of detectors that will provide more structural information, a matter that becomes extremely important when trying to identify components of a complex mixture Several recently proposed detection system for liquid chromatography will be examined in the light of those requirements

Finally, better control of chromatographic variables such as temperature, flow rate of the eluent, and sample injections will be discussed Most chromatographers have accepted too casually the usual level of control of these variables Without adding much cost or difficulty of operation, significant reductions in background variability should be possible

(17) A CONTRIBUTION TO THE PROBLEM OF STRONG ACID DETERMINATION IN AIR Dieter Klockow, Helmut Denzinger, Chemisches Laboratorium der Universität, Lehrstuhl fur Analyt Chemie D 78 Freiburg, Albertstr 21 and Gerhard Ronicke, Aerosolmeßstelle Scheuernsland D-7801 Schallstadt Wolfenweiler

The main indicator for acidic substances in the atmosphere is, now as before, the pH of rainwater Factors influencing the acidity of precipitation are discussed, using results of air monitoring stations in Germany

MONS 214224

It is generally believed, that mainly sulphuric acid is responsible for the increase in atmospheric acidity, but only little information exists on the concentration of sulphuric acid and other strong acids (HCl, HNO_3) in air. A few attempts have been made to solve this analytical problem, and the present situation in this field is briefly reviewed.

Finally a simple radiochemical thermodiffusion-procedure for the selective determination of strong acids is presented. Experimental details of this new method are described as well as its application to the analysis of precipitation and airborne particulate matter. The combination of the thermodiffusion technique with a selective extraction[1] and a new sensitive sulphate-specific method[2] makes possible the analysis of air samples for strong acids in total and for sulphuric acid separately.

1) S. C. Barton, H. G. Mc Adie, Proceedings of the 2nd International Clean Air Congress of the IUAPPA, Washington, D. C., December 1970

2) D. Klockow, H. Denzinger, G. Roricke, Chemie-Ingenieur-Technik 46, 831 (1974)

(18) THE APPLICATIONS OF ESCA TO SURFACE ANALYSIS. David M. Hercules, Dept. of Chemistry, University of Georgia, Athens, Georgia 30602.

There are several characteristics of ESCA which make it useful for chemical analysis. First, it is sensitive to nearly all elements in the periodic table. Second, chemical shifts give some indication of the nature of a species present. Third, ESCA is capable of examining surfaces and surface reactions. Fourth, it has high absolute sensitivity. The present paper summarizes work from our laboratory indicating types of analytical problems which can be studied by ESCA. We have studied adhesion of polymer films to clean aluminum surfaces and have determined that cohesive failure occurs within the polymer layer when it is stripped from the aluminum. ESCA has been applied to studies of dental enamel and the fluoridation of dental enamel by sodium fluoride and stannous fluoride solutions. We have investigated the applicability of ESCA to quantitative analysis for bulk constituents, in terms of parameters which are important for establishing calibration curves. We have also investigated the application of ESCA to trace metal analysis by combining the inherent sensitivity of ESCA with the ability of chelating glasses to scavenge metals from solution.

(19) ANALYSIS OF A CARCINOGEN CONGLOMERATE IN THE ENVIRONMENT AND IN TISSUE. Eugene Sawicki, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

When people talk about environmental carcinogens, the questions invariably asked are what do we measure for a meaningful study, what numbers do we collect in a minimal study and what do we collect in a thorough study of a particular environment. The answers are shaped by the state of our knowledge. In this presentation some tentative answers are given and discussed.

A variety of analytical methods are discussed critically. The materials of interest to be discussed will include precarcinogens, irritants, cofactors, anti-carcinogenic factors, metabolites, enzyme systems, toxic syntheses, lethal syntheses, bioassay systems, the Devil's book of genesis, etc.

(20) RECENT DEVELOPMENTS IN SPARK SOURCE MASS SPECTROMETRY. W. W. Harrison, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22903.

Spark source mass spectrometry (SSMS) was characterized by a period of intense interest and development in the 1960's. After a subsequent leveling off in activity, renewed interest has surfaced recently, particularly with regard to "energy" problems. The capabilities of SSMS for qualitative elemental analysis are outstanding. The entire periodic table of elements can be surveyed in an 8 minute scan to sub-ppm sensitivities. SSMS quantitative capabilities have been more modest, 20-30% in the multielement survey mode, 5-10% by peak switch integration. In recent years, attention has been directed to the study of factors affecting precision and the means by which these parameters may be controlled. These studies have included, among others, feedback control of ion flux, control of spark gap and shielding, and signal averaging by repetitive scans. With careful attention (and experience), it is today possible to obtain good quantitative results; the degree of precision and accuracy attained may be determined by the amount of effort and control which can be justified (i.e., what accuracy is "good enough"?). Multielement isotopic dilution analysis by SSMS exemplifies a more time consuming method justified for those samples requiring high analytical accuracy. These various developments in SSMS are advantageously applied today to many sample types, such as energy, biological and environmental.

(21) ION-SELECTIVE ELECTRODES. E. Pungor, K. Toth, G. Nagy, Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary.

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A brief discussion of the theory of electrodes is given, first of all in connection with the dynamic characteristics of the various electrodes. Application of the electrodes for environmental analysis is presented in connection with gaseous materials (fluoride etc.) and with aqueous pollutants (cyanide etc.).

The calibration technique in dynamic measuring circumstances is discussed using the multi-additional technique and the triangle coulometric signal.

A view of the application possibilities is also the subject of the paper.

MONS 214226