

1 PCB-Analysis

AMERICAN CHEMICAL SOCIETY DIVISION OF
WATER, AIR, AND WASTE CHEMISTRY

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R. S. Baker, Chairman
J. L. Tinsley, Secretary

1. RELATIVE RATES OF PURGING OF ORGANIC COMPOUNDS FROM AQUEOUS SOLUTIONS. Walter D. Smith, and John W. Swinnerton, U.S. Naval Research Laboratory, Code 8330, Washington, D. C. 20390.

One ml of water, previously equilibrated with an organic compound, was injected into a purging chamber, filled with a fixed volume of distilled water (9 ml). Helium at a constant rate of 80 ml/min was passed through a frit in the bottom of the chamber. The gaseous effluent flowed directly to a flame ionization detector via a short length of heated tubing. The rise and fall in the signal was followed on a recorder, the time required for the signal to fall to one-half a given value was taken to be the "purging half-time". The ratio of the "purging half-time" of a given organic to that of $n-C_6$, an arbitrary reference, was expressed as the "relative purging half-time". A plot of the logarithm of the "relative purging half-time" vs the molar volume gave a linear relationship for each type of organic studied. Paraffins, olefins, cycloolefins, cycloparaffins and branched-chain paraffins gave straight lines with positive slopes. For a given molar volume the "relative purging half-times" were 1.0, 0.9, 0.9, 0.9 and 0.1 respectively. Aromatics, methyl ketones and alcohols gave similar plots save with negative slopes. The "relative purging half-times" for the 6 C-atom compounds of these types were 1.5, 47.0 and 130.0 respectively. Purging was practical and effective in the removal of hydrocarbons, $C_3 - C_{10}$ from solution, but was of little or no value in the removal of the more water soluble organics.

2. RAPID OIL-IN-WATER ANALYSIS BY CAPILLARY TEST BOTTLE: A FIELD EVALUATION. Lerna Engberg Heern, Fram Corporation/Industrial Division, P. O. Box 50096, Tulsa, Oklahoma 74150.

A rapid procedure for determining trace quantities (5 to 2000 ppm) of oily substances in water has been developed and widely field-tested. The method is based on sample emulsification followed by transfer to a specially designed trace oil analysis bottle and subsequent demulsification. The released oil is concentrated by centrifugation and then forced into the capillary neck of the bottle by further addition of demulsifier to the aqueous phase. The height of the oil column thus formed is measured and converted to concentration using a calibration curve. The emulsifier is composed of a blend of anionic and non-ionic surfactants. A 0.82 Molar solution of sodium citrate is the principal demulsifier. The effects of additional water contaminants on the test is discussed, as is modification of the procedure to accommodate soluble and volatile oils. A comprehensive summary of the results obtained by different workers with widely varying oily-water systems, both in the laboratory and in the field, is presented together with evaluation of these results.

3. AN IMPROVED METHOD FOR REMOVAL OF ORGANIC POLLUTANTS FROM WATER. J. A. Vinson, Department of Chemistry, Washington and Jefferson College, Washington, Pennsylvania 15301.

Organic pollutants are commonly removed from waste or potable water by solvent extraction or activated carbon adsorption. These methods suffer from limitations due to the lack of quantitative removal of the pollutants, especially at trace levels. This work describes a new method of extraction using macroroteticular polymeric adsorbents. Aromatic hydrocarbons, carboxylic acids, amines, phenols, pesticides, herbicides, monomers, polymers and plasticizers are quantitatively removed by passage of the water through a short column of the resin. The organics may be quantitatively eluted with an organic solvent and analyzed by any convenient means. Separations are accomplished by making use of the resins.

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preference for non-ionized molecules. Possible applications of the resins for industrial waste water and municipal water treatment is discussed.

4. COMPUTER-CONTROLLED MASS SPECTRAL CHARACTERIZATIONS OF INDUSTRIAL ORGANIC POLLUTANTS. L. H. Keith and J. M. McGuire, Environmental Protection Agency, Southeast Water Laboratory, Athens, Georgia 30601.

A computer-controlled quadrupole mass spectrometer tentatively identified about 25 compounds on re-examination of a treated petrochemical waste effluent. About 500 spectra can be automatically collected on magnetic tape (a 40 minute GC run) and then transferred to an auxiliary disc for rapid manipulations. Limited mass reconstructed gas chromatograms using select mass ranges indicative of various molecular fragments revealed much about the compounds in this sample even before the mass spectra were analyzed. The computer subtracted background or interfering peaks from the spectra of interest and matched these spectra with a library of over 11,000 mass spectra. Plotting a typical mass spectrum takes only 3-4 minutes and spectral matching is completed within 2 minutes. Spectra of pesticides and other compounds being found in the environment are added to the computer library of mass spectra to enhance chemical characterization of environmental samples.

5. SPECTROSCOPIC CHARACTERIZATION OF HUMIC ACID FRACTIONS IN AQUEOUS MEDIA by Alan R. Monahan and Allen F. DeLuca, Xerox Rochester Research Center, Rochester, New York 14603, and Robert L. Mershaw, U.S. Geological Survey, Denver, Colorado 80225.

Analyses of the electronic absorption spectra of a series of fractionated sodium humate samples in aqueous media (pH=9) demonstrated the presence of monomer-dimer equilibria in the 10^{-7} - 10^{-4} M concentration range. The sodium humate samples in this study were extracted from a North Carolina soil and fractionated on a Sephadex G-50 chromatographic column. The dimerization constants, $k_{eq} = [D]/[M]^2$, were found to have a range of 10^4 to 10^{10} depending on the sample fraction. The absorption spectra of the pure monomer and the aggregate were measured for each fraction by a spectroscopic-computer procedure. The aggregates were characterized by broad absorption maxima at ~200mμ and structureless absorption into the green region of the visible. The resolved monomer spectra were found to have at least one absorption band in the ultraviolet viz. 210, 270, 320 and/or 380mμ. The number of bands appearing in the resolved monomer spectra and their relative intensities were dependent on the sample fraction. Confirmation of the absorption measurements were obtained by fluorescence emission and excitation spectra as a function of sodium humate concentration.

- 1 R. L. Mershaw, S. J. Heller and D. J. Pinckney, Advan. X-Ray Anal., **13**, 609 (1970).
- 2 A. R. Monahan and D. F. Blossley, J. Phys. Chem., **74**, 4014 (1970).

6. ORGANIC COMPOUNDS IN CHARLES RIVER BASIN (BOSTON). Ronald A. Hites and K. Niemann, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

The major lipophilic organic compounds present in the water of the Charles River Basin (Boston) have been identified by gas chromatography-mass spectrometry and by high pressure liquid chromatography. They are alkanes (C₁₅ to C₃₁), alkyl benzenes, alkyl naphthalenes, alkyl anthracenes or phenanthrenes, pyrene, fluoranthene, dibutyl phthalate, and di-(2-ethyl-hexyl) phthalate. Quantification of the aromatic hydrocarbons was carried out by liquid-solid chromatography on Porasil T with heptane as the eluent. On a weekly basis, there is a high correlation between the naphthalene concentration and the effective storm-water runoff content of the river. (The effective runoff, R_n , of week n is defined as:

$$R_n = \sum_{i=0}^n \frac{1}{2^{i-1}} R_{n-i}$$

where R_{n-i} is the precipitation in inches of week $n-i$.) This indicates that the aromatic hydrocarbons are being washed off of the streets and buildings by rainfall and finally into the river. The types of these compounds found in the river are very similar to those found in auto exhaust. This, therefore, would seem to be their ultimate source.

MONDAY AFTERNOON - GENERAL - C. R. O'Melia, Presiding

7. PROCESS CHANGES IN AN ORGANIC CHEMICALS PRODUCTION PLANT TO IMPROVE YIELDS AND DECREASE BYPRODUCTS. Robert E. Bailey, Thomas L. Kennedy, Richard T. Keller, R. A. Gaske, The Dow Chemical Company, Midland, Michigan 48640.

The production of crofonate, the common name for 4-t-butyl-2-chlorophenyl methyl methylphosphoromate, is accompanied by the formation of sizeable amounts of byproducts. In addition to tars, a large aqueous stream containing organics and NaCl had to be treated and disposed of. Intensive laboratory work has led to the planned implementation of a hydrolysis step in which the tars and aqueous wastes are hydrolyzed and converted to the starting feed compound, 4-t-butyl-2-chlorophenol. Instead of experiencing only a 55% yield, the process will now enjoy close to a 90% yield and avoid difficult waste disposal problems. The recovery and recycle of byproducts is an economically attractive venture. Startup of the process additions was completed in March 1972 with excellent results.

8. FLOCCULATION OF RAW SEWAGE WITH POLYELECTROLYTES. V. Srekantham, Donald L. Sussman, Department of Civil & Environmental Engineering, University of Rhode Island, Kingston, Rhode Island 02881.

In the physical-chemical treatment of raw sewage, the initial step is a clarification by using a precipitating agent with a flocculant. This study was concerned with the use of a flocculant to remove turbidity and nutrients from raw sewage. The flocculants used were anionic, cationic and nonionic polyelectrolytes that are commercially available. These polyelectrolytes were used alone, and in the case of anionic polyelectrolytes, ion binding and complexing cations were added to note the effect on the flocculation process. Raw sewage was obtained at the University of Rhode Island sewage treatment plant at times corresponding to peak loads. This sewage was characterized by the COD, organic N, NH₃, total P, turbidity and hardness. This study was defined in terms of the rate of flocculation, the final turbidity and removal of nutrients from the sewage.

9. FLOCCULATION OF METAL PLATING WASTES WITH POLYELECTROLYTES, Edward C. Weng, and Donald L. Sussman, Department of Civil and Environmental Engineering, University of Rhode Island, Kingston, Rhode Island 02881.

This presentation describes the studies on the flocculation of metal plating wastes with cationic, anionic, and nonionic polyelectrolytes. Model wastes were prepared with CrO₇²⁻, Ni²⁺, Cu²⁺, and clay as a source of turbidity. Actual waste samples also were used. These were taken as untreated effluents from metal plating and finishing plants. The efficiency of the treatment of these wastes with polyelectrolytes was defined in terms of the flocculation kinetics. The parameters of interest were the initial decrease in turbidity, dt/dt and the turbidity after 1 hour. Other parameters that were evaluated in order to follow the flocculation process were the final particle size and the settled sludge resistivity to flow. The treatment of metal plating wastes by polyelectrolyte flocculation is compared to the treatment by reduction and precipitation methods.

10. CARBON ISOTOPE RATIOS AS REFLECTIONS OF CHANGES IN THE CARBON CYCLE John A. Calder and David J. Shultz, Dept. Oceanography, FSU, Tallahassee, Florida 32306.

The various natural reservoirs of carbon have a definite and often distinct range of C-13/C-12 values. In instances where modern civilization has altered the natural cycle of carbon, changes can often be observed in the C-13/C-12 ratio. Pulp mill wastes present an interesting situation to the geochemist, in that the isotope ratio of these wastes is identical to normal terrestrial organic matter. Particulate organic carbon from pulp mills is detectable in marine sediments up to 3 to 4 miles from shore. Domestic sewage wastes contain inorganic carbon generated by oxidative processes during waste treatment which is about

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12 per mil enriched in C-12 compared to normal marine inorganic carbon. Petrochemical operations release wastes which are enriched in C-12. Both of these types of waste can be traced in the marine environment by using C-13/C-12 measurements. The extent of organic waste clean-up operations can be determined by monitoring the C-13/C-12 ratio of the remaining organic matter in the final effluent.

11. INHIBITION OF OXIDATION OF SULFUR DIOXIDE DURING ALKALINE SCRUBBING.
Paul Counterman and Elmer R. Altwick, Bio-Environmental Engineering Division, Rensselaer Polytechnic Institute, Troy, New York 12181.

The inhibition of the oxidation of sulfur dioxide during alkaline scrubbing is desirable from the standpoint of pollution control and economics. The aim of this research is to study the oxidation in a system that may permit translation of the data to industrial absorption systems such as packed columns. The experimental system used consisted of a continuously stirred batch reactor into which gas stream consisting of 88.9% nitrogen, 9.8% oxygen and 1.3% sulfur dioxide was continuously diffused. Sulfite and sulfate concentrations and SO₂ removal efficiency were measured as a function of time. The system parameters studied were: inhibitor-type, inhibitor concentration, catalyst, pH, and time. Benzyl alcohol (2%), phenol (.005%), and hydroquinone (.001%) were all found to be effective inhibitors for contact times as long as 30 minutes. Evidence would indicate that the inhibitor is consumed during oxidation.

TUESDAY MORNING - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - Joint with Division of Pesticide Chemistry - C. G. Gustafson, Presiding

PCB'S I - EVIDENCE FOR UBIQUITY

12. POLYCHLORINATED BIPHENYL (PCB) IDENTIFICATION IN MARINE ARCTIC AND SUBARCTIC FOOD CHAINS. OWEN M. BOWEN (1) and Charles J. Jonkel (2).
(1) Toxic Chemicals Section, Canadian Wildlife Service, 6 Beechwood Ave., Ottawa, Ontario; (2) Canadian Wildlife Service, Eastern Region, 2721 Highway 31, Ottawa, Ontario, Canada.

Analysis of biological samples from Arctic and Subarctic marine food chains revealed gas chromatographic patterns similar to those of the polychlorinated biphenyls (PCB). Samples were taken from polar bears, seals and fish. Zooplankton, and possibly phytoplankton, analyses also will be reported. Geographical locations represented by the data extend across North America from Alaska to Baffin Island, and down into Hudson Bay. Tissues analysed included brain, liver, meat, and fat. Samples were extracted with hexane after having been ground with sodium sulfate or digested in glacial acetic-perchloric acid. Column material employed for extract clean-up included both Florisil, deactivated 101, and Celite-fuming sulfuric acid. Quantitation was done on 5% SP-2401 (fluorosilicone) on 100-120 mesh Supelcoport. Confirmatory techniques included use of the GC alkaline pre-column, conversion of PCB to decachlorobiphenyl, and silica gel column separation of the PCB and chlorinated pesticides. Electron-capture GC indicates the PCB concentration in polar bears to be greater than the combined DDT and DDE. A striking feature is that the GC PCB pattern in bears from all geographical locations sampled to date, is similar.

13. INSECTICIDES, POLYCHLORINATED BIPHENYLS AND MERCURY IN WILD CORMORANTS, PELICANS, THEIR EGGS, FOOD AND ENVIRONMENT. Yvonne A. Greichus, Algridas Greichus, Royce J. Zherick, Experiment Station Biochemistry Department and Entomology-Zoology Department, South Dakota State University, Brookings, South Dakota 57006.

A study of the levels and distribution of organochlorine insecticides, polychlorinated biphenyls (PCB's) and mercury in water, bottom sediments, fish and fish-eating birds from the Lake Poinsett, South Dakota ecosystem was conducted during the summers of 1970 and 1971. Levels of all three compounds increased in higher trophic levels with insecticides concentrating most rapidly and mercury least rapidly. Average levels in bodies of Double-crested Cormorants were 10.0, 4.6 and .64 parts per million and in bodies of White Pelicans were 12.3, 2.3 and .29 ppm for insecticides, PCB's and mercury respectively. Other tissues examined for these compounds included brain, muscle, kidney, liver, fat and eggs.

Procedures used in the purification, identification and quantitation of insecticides and PCB's included column, gas-liquid and thin-layer chromatography and saponification and oxidation of samples. The presence of PCB's in pelicans, cormorants and their eggs was confirmed with mass-spectrometry. A procedure for the removal of all insecticides from the PCB's was employed prior to the mass-spectrometry analysis.

14. MOVEMENT OF PCB'S THROUGH THE CHESTER RIVER ESTUARY. J. D. Tasler and T. O. Munson, Westinghouse Ocean Research Laboratory, P.O. Box 1771, Annapolis, Maryland 21404.

As part of a multi-disciplinary study (jointly funded by the State of Maryland and the Westinghouse Electric Corporation) of the Chester River Estuary (part of Upper Chesapeake Bay), the authors analyzed bottom sediments, suspended sediments, water and biological tissues for PCB's and "hard" chlorinated pesticide residues. The levels of pesticides observed were relatively low for most of the year although some "contaminant" peaks were observed which could easily be mistaken for pesticides or PCB's. The PCB contamination (of the Aroclor 1232-42 type) was low compared to the part-per-million levels observed by others in the lower Chesapeake Bay but was high enough to indicate inputs other than general atmospheric fallout. Information from the hydrological, meteorological, and geological parts of the program was used to estimate the possible rates and routes of the chlorinated hydrocarbons through the system.

15. PCB CONTAMINATION OF THE AQUATIC ENVIRONMENT IN ONTARIO. D.W. Berg, P.L. D'Geady and G.A.V. Rees, Ministry of the Environment, Laboratory Branch, Box 213, Rexdale, Ontario, Canada.

Sporadic analyses of samples from the aquatic environment have shown that PCB's are universal pollutants. Almost without exception the contaminant was of the Aroclor 1254 type. The approximate levels were as follows: effluents from sewage treatment plants-0.001-0.1 ppm, river sediments-up to 0.6 ppm, fish-up to 20 ppm and seagulls-up to 1500 ppm in oil.

In order to gain more systematic type of information, a large scale survey was undertaken. Four different types of aqueous systems were studied: 1. industrialized "impounded system", 2. industrialized "dynamic system", 3. natural "impounded system" - a clean lake receiving no waste and 4. natural "dynamic system". Data concerned with the analysis of water, bottom sediments and fish are presented and discussed.

The analytical techniques - separation of PCB's from other chlorinated materials and the determination of PCB's in terms of the fully chlorinated derivatives-decachloro biphenyl are discussed as well.

16. DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE AQUATIC ENVIRONMENT. Marvin L. Yates, Herman R. Feltz, and Hans J. Crump-Welener, U.S. Geological Survey, Water Resources Division, Washington, D.C. 20242.

Data gathered from limited monitoring activities and project studies in several States indicate the ubiquitous occurrence and distribution of polychlorinated biphenyls in the aquatic environment. Residues have been detected in samples collected in several States, including Connecticut, New York, Pennsylvania, Virginia, South Carolina, Florida, Mississippi, Texas, Arkansas, and California. Data indicate concentrations ranging from 0.1 µg/l to 4 µg/l in unfiltered water samples and 0.5 µg/kg to 3200 µg/kg in bottom material. Some PCB residues were found in fish and aquatic plants. Samples were prepared by the same techniques used for general chlorinated insecticide detection, with special attention to clean-up and separation of PCB's from other compounds. Basic identification and quantification were made by dual-column electron-capture gas chromatography. Confirmation was accomplished by gas chromatography-mass spectrometry whenever possible. The sampling program is expected to be broadened geographically in 1973, and increased in successive years in order to more adequately assess the presence of PCB residues in major drainage basins of the contiguous United States, Hawaii, and Puerto Rico.

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17. COMPOSITIONAL CHANGES OF CHLOROBIPHENYL MIXTURES IN ANAEROBIC LAKE SEDIMENTS. Richard B. Flisard and CLYDE W. TAYLOR, Water Chemistry Program, University of Wisconsin, Madison, Wisconsin 53706.

The compositional changes of chlorobiphenyl mixtures in anaerobic sediments have been investigated by incubating Aroclor 1254 in littoral sediments from Lake Michigan - Green Bay. Replicate samples of 25 ml wet sediment (10% dry weight) containing 100 ug of Aroclor 1254 were sealed and incubated at 40° C. Duplicate samples were analyzed periodically. The analysis of chlorobiphenyls in sediments has been evaluated using exhaustive solvent extraction and steam distillation methods. Because steam distillation removes chlorobiphenyls from sediments more rapidly than does solvent extraction and eliminates the need for liquid chromatographic cleanup procedures, a modified Dean-Stark apparatus has been developed for the sediment analysis. Refluxing acidified sediments for four hours results in the transfer of approximately 85 percent of Aroclor 1254 from the sediments to the cold hexane trap. The extract is dried with anhydrous MgSO_4 , refluxed over clean, powdered copper to remove elemental sulfur, and analyzed by electron capture gas chromatography. This paper will discuss the changes in the chlorobiphenyl concentrations during the four-month incubation period.

18. POLYCHLORINATED BIPHENYL LEVELS IN HUMANS. A. R. Yobs, State Services Branch, Div. of Pesticide Community Studies, Off. of Pesticides Programs, EPA, Chamblee, Ga. 30341.

Polychlorinated biphenyls (PCBs) have been reported in many different parts of the environment. Previous reports of PCBs in humans have been few in number and have generally been concerned primarily with analytical procedures, reporting findings in only a few individuals. This report presents results from a human monitoring program in which samples have been routinely analyzed for these materials since April 1971. Case reports are presented in selected instances.

TUESDAY AFTERNOON - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - (Continued) - Joint with Division of Pesticide Chemistry - C. G. Gustafson, Presiding

PCB'S II - ANALYSIS AND DEGRADATION

19. ANALYTICAL ASPECTS OF POLYCHLORINATED BIPHENYL DETERMINATIONS IN HUMAN AND ANIMAL ADIPOSE TISSUE. F. J. Biles, M. P. Bous, A. C. Walker, and J. F. Thompson, EPA, Perrine Private Lab., P.O. Box 490, Perrine, Fla. 33157. A. R. Yobs, EPA, Div. of Pestic. Community Studies, Off. of Pesticides Programs, Chamblee, Ga. 30341.

An analytical evaluation and comparative study have been performed to establish and improve the efficacy of a method employed routinely for semi-quantitative determination of polychlorinated biphenyls (PCBs) in tissue samples by thin layer chromatography (TLC). (Mulhern, B. et. al, Abstr. 84th ann. meeting, AOAC, Oct. 1970). Quantitative results obtained at various stages of the TLC procedures to eliminate interferences from organochlorine pesticide residues, have been compared with those obtained by total area measurements of gas-liquid chromatograms of the same tissue samples. These evaluations have resulted in modifications of the original procedure and recommendations concerning the choice of Aroclor standard used in the semi-quantitative estimation of sample PCB concentration. Additional studies have been performed to establish quantitative PCB levels in human and animal tissue samples which would (a) escape detection, and (b) be expected to lead to ambiguities in the estimation of levels of certain organochlorine pesticide residues including DDT and its isomers, analogs, and metabolites concurrent in the sample. A total of 140 general population adipose tissue samples have been subjected to analysis by combined gas chromatography-mass spectrometry to confirm and identify PCB components stored in human adipose tissue. Levels of total PCB ranged from 0.4 to 3.5 ppm. Representative chromatographic and mass spectral data will be presented in addition to identification of common PCB components encountered.

20. IDENTIFICATION OF PCB'S IN THE PRESENCE OF DDT-TYPE COMPOUNDS USING LOW TEMPERATURE LUMINESCENCE. J. T. Brownrigg, J. Gulliflye, and A. W. Hornig, Baird-Atomic, Inc., 125 Middlesex Tpk., Bedford, Mass. 01730.

Polychlorinated biphenyls (PCB's) interfere with gas chromatographic analyses of DDT and related compounds, necessitating a simple independent method for PCB and

DDT determination. The purpose of the present study was to determine the applicability of low temperature (77°K) luminescence methods to this problem. Basic studies included documentation of excitation/emission spectra of 6 pesticides (p,p'- and o,p'-DDE, DDD and DDT), 7 PCB isomers, and 5 PCB mixtures (Aroclors). Although phosphorescence spectra of the DDD and DDT compounds are very similar, possible differences in lifetime and polarization measurements may aid in differentiation. Emission from DDE is at least 100X less intense than that of DDD or DDT, and is therefore more difficult to determine with adequate sensitivity. Spectral differences among various Aroclors are sufficient to allow those studied to be differentiated. In our work, emission from solvent impurities limited detection sensitivities to about 1.0 ppm for DDT/DDD and about 0.01 ppm for Aroclors. By removing interference, detection sensitivities should be improved by two orders of magnitude. Low temperature luminescence studies in various binary mixtures of Aroclor 1254 and p,p'-DDT indicate Aroclor 1254 may be identified and quantitated in the presence of DDT concentrations 100X greater. (Work supported by EPA Contract No. 68-01-0082)

21. QUANTITATIVE PCB STANDARDS FOR ELECTRON CAPTURE GAS CHROMATOGRAPHY.
Ronald G. Webb, Ann C. McCall, Southeast Water Laboratory, College
Station Road, Athens, Georgia 30601.

Solutions of Aroclors 1221 through 1260 have been prepared in which the weight of PCB present in each GC peak is known. These materials will be proposed as quantitative PCB standards. Their composition was determined by elemental analysis, gas chromatography with a Coulson conductivity detector, GC-MS, and EC in both the pulsed and D. C. modes. They can be used for PCB analysis of water, sediments, fish, and other environmental samples.

22. A COMPUTER ASSISTED GC-MS EXAMINATION OF FISH EXTRACTS FOR PCB AND PESTICIDE RESIDUES IN SILICIC ACID COLUMN FRACTIONS. David L. Stalling, Fish-Pesticide Research Laboratory, Route 1, Columbia, Missouri 65201.

Extracts of 20.0 g of fish from selected areas in the environment were prepared for mass spectrometry using a combination of gel permeation (GPC) and column adsorption chromatography. Extracts after GPC (using cyclohexane-BioGrade S-X2) were separated into 6 and 151 diethyl ether-pet ether fractions using Florisil[®]. The 6X fraction was resolved by GLC and concentrated prior to GC-MS examination. Reverse-phase TLC was also employed to examine the PCB fraction. The GC-MS computer system was a PDP-12 LDP computer interfaced to a Perkin Elmer 270-3 GC-mass spectrometer. The MASH (Mass Spectrometer Handler) software system was used for data acquisition and preparation of mass fragmentograms. Spectra were acquired every 6-8 seconds for up to 33 minutes (up to 250 scans). A mass range of 14-555 was scanned and each spectrum was stored on magnetic tape. Mass searches for up to five combined masses were made on each set of spectra. The distribution and incidence of parent ions of the PCB homologues were indicative of PCB residues and mass fragmentograms greatly facilitate location of spectra for confirmation. Mixtures of PCB formulations as residues in fish are clearly indicated. The occurrence of Halowaxes[®] or chlorinated terphenyls have not yet been detected. The GC-MS computer system is one of the few available techniques for identification of these contaminants.

23. PHOTOCHEMICAL DEGRADATION OF ISOMERICALLY PURE Di-, Tetra-, Hexa-, Octa- AND DECAChlorobiphenyls. O. Hutzinger, W. D. Swenson, S. Safe, National Research Council of Canada, Atlantic Regional Laboratory, Halifax, N. S., and V. Zitko, Environment Canada, Fisheries Service Biological Station, St. Andrew's, N. B., CANADA.

The photoinitiated degradation of 4,4-di-, 2,2',5,5'-tetra-, 3,3',4,4'-tetra-, 2,2',4,4',5,5'-hexa-, 2,2',3,3',4,4',5,5'-octa- and decachlorobiphenyls was investigated under natural and simulated natural (avoiding organic solvents, wavelength of irradiation >300 nm) conditions. In most experiments, thin films of sample were photolyzed in the presence of H₂O. From the abovementioned chlorobiphenyls, major products were those resulting from dechlorination and/or polymerization as well as polar compounds which had retained little or no chlorine. Qualitative analyses

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of products were by usual techniques such as GLC-mass spectrometry as well as by high resolution mass spectrometry using photoplate detection. Structures of degradation products will be discussed as will be conditions for their formation.

24. DEGRADATION OF PCB'S AS STUDIED BY OXIDATIVE ELECTROCHEMISTRY. James D. Stuart, Richard R. Keenan, Robert J. Fenn, Department of Chemistry, and Robert G. Jansen, Walter J. Pudelekiewicz, Pesticide Research Laboratory, University of Connecticut, Storrs, Connecticut 06268.

Although very resistant to oxidation, PCB's are oxidized at very high anodic potentials in moderately-dried acetonitrile solvent. The anodic voltammetry at a glassy carbon and shiny platinum microelectrode of Aroclor samples yielded an irreversible peak in the region of +1.2 Volts vs. (aqueous) SCE. A series of pure 2,5-chloro-substituted biphenyls, with increasing numbers of chlorine atoms ranging from one to ten, was studied by fast sweep electrochemical techniques. Voltammetric data showed that their anodic pathways involved the irreversible removal of one or more electrons followed by rapid chemical reactions whose unstable products were, in turn, further oxidized. Macro-scale electrolyses, keeping the anode at a constant potential with a carbon felt or platinum mesh electrode, were used to produce sufficient amounts of the oxidative products. Coulometry indicated a large irreproducible electron count. After the initial removal of electrons from the π -aromatic system, the intermediate and final products suggest pathways that involve (a) hydrolysis through hydroxy compounds that in turn suffer further oxidation, (b) solvolysis of the cationic species, (c) intra-molecular oxidative coupling, (d) inter-molecular dimerization. Fast follow-up chemical reactions between the unstable cationic species with traces of water, inevitably present as impurities in the acetonitrile solvent or between other nucleophiles added to the solution will be discussed lending support to the anodic pathways suggested.

25. DETERMINATION OF PCB AND PCT IN PAPERBOARD SAMPLES. G.H. Thomas and L.M. Reynolds, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

PCBs are now recognised as possible contaminants in paperboards, particularly those containing recycled material. During the course of analysing paper and board samples for PCBs, analytical problems were encountered due to the presence of components with very long retention times under GLC conditions that were used for the PCB analysis. This paper will describe our methods for PCB analysis in pulp samples, how the contaminants other than PCB were identified as polychloroterphenyls (PCTs), methods of analysis for PCTs, and how PCTs are now routinely analysed in the presence of PCBs. The procedures involved positive extraction of the paperboard sample with hexane, followed by cleanup and separation using Florisil column chromatography. PCTs are quantitated using electron capture (N^3) and/or (N^{63}) gas chromatography. Recovery data substantiating the reliability of the method will be presented. Some discussion will relate to methods of confirmation involving GC-MS and perchlorination.

- WEDNESDAY MORNING - SECTION A - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - (Continued) - Joint with Division of Pesticide Chemistry - J. I. Tassley, Presiding

PCB'S III - TOXICOLOGY AND PHYSIOLOGICAL ACTIVITY

26. PCB'S IN LAYING HENS. Helene C. Cecil, Joel Bitman, George F. Frigs, L. W. Smith, and R. J. Little. Animal Science Research Division, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland 20705.

Polychlorinated biphenyls (Aroclors 1221, 1232, 1242, 1248, 1254, 1268), a polychlorinated triphenyl (PCT-Aroclor 5442) and a polybrominated biphenyl (PBB) were administered to 12 groups of 35 laying white Leghorn chickens at a dietary level of 2 or 20 ppm. Egg production, eggshell characteristics, body weight, feed consumption, mortality, fertility, hatchability, and progeny performance were measured. The transfer of dietary PCB, PCT and PBB into eggs and carcass tissue of hens was determined. Rates of depletion (decontamination) of PCB residues in tissues were studied following withdrawal of dietary PCB. The patterns and rates of PCB, PCT, and PBB excretion were followed in feces of hens fed these materials. In addition, the fate of these polyhalogenated bi- and triphenyl compounds was studied during processing and recycling to rats and cows.

27. EVALUATION OF RESIDUES OF AROCHLOR 1254 IN POULTRY PRODUCTS - R. H. Teske; B. W. Ambrecht, Bldg. 339-D, Agricultural Research Center, Beltsville, Md. 20705; and H. J. Paulin, Bionetics Research Laboratories, Inc., Falls Church, Va. 22046.

PCB residues occurring in tissues and eggs from White Leghorn chickens following feeding of Arochlor 1254 at graded dietary concentrations are reported.

Broiler Phase: Chicks were initiated on an 8-week feeding study employing diets containing Arochlor 1254 at graded concentrations up to 10 mg PCB/kg of feed. Tissue samples for PCB analysis were collected from birds sacrificed at termination of the feeding period (no withdrawal period) and tissue residue depletion was followed for 3 weeks following termination of the feeding period.

Layer Phase: Chicks (Group A) were initiated on diets containing graded concentrations of Arochlor 1254 and maintained until onset of egg production. A parallel group of birds (Group B) were maintained on control diet until onset of egg production at which time feeding of test diets was initiated. Eggs from both PCB analysis and hatchability determinations were collected periodically. PCB residues and egg hatchability for Groups A and B were compared.

28. TOXICODYNAMICS OF AROCHLOR(R) 1254 IN THE MALE RAT. D. L. Grant, C. A. Moodie, and W. E. J. Phillips, Research Laboratories, Health Protection Branch, Department of National Health and Welfare, Ottawa, Canada.

Male Wistar rats, 30 days old, were placed on a ground cube diet containing one of four levels (0, 2, 20 or 100 ppm) of Arochlor(R) 1254, a polychlorinated biphenyl (PCB), for 8 months and then on the basal diet containing no PCB's for a further 6 months. Five rats were killed from each group after 2, 4, 6 and 8 months to study accumulation of residues as well as biochemical, physiological and pathological changes. Rats were also killed at 10, 12 and 14 months to determine the reversibility of the changes. The blood, brain, heart, liver and fat were analysed for residues of PCB's and were found to be dose related. Consistently, the 20 ppm diet significantly ($P < 0.05$) decreased the vitamin A stored in the liver and increased the hepatic aniline hydroxylase activity. This microsomal enzyme activity was also significantly increased by the 2 ppm diet after 4 and 6 months. Liver weight was significantly increased by the 100 ppm diet after 2, 4, 6 and 8 months and by the 2 and 20 ppm diet after 2 months. Rats ingesting the 2 ppm diet for 2 and 4 months were significantly heavier, while rats receiving the 100 ppm diet were lighter. Results of the pathological examination of the liver and kidney, the rate of depletion of body burdens of the PCB and reversibility of the physiological and pathological changes will be presented.

29. INDUCTION OF RAT LIVER MONOOXYGENASE ACTIVITY BY SELECTED PCB ISOMERS. J. C. Strickland, R. D. Geer², F. W. Orr¹, P. A. Balend², and S. E. Blau¹. ¹Department of Animal Science, Division of Biochemistry, Utah State University, Logan, Utah 84321. ²Department of Chemistry, Montana State University, Bozeman, Montana 59715.

Previous study in this laboratory established the range of liver monooxygenase activity induced by the Arochlor® PCB products. Such enzyme induction was shown to be a direct function of the percentage chlorine in these products and was highly correlated with their mean partition coefficients (determined as R_m values in reversed phase TLC). We now report the enzyme induction obtained with a series of PCB isomers administered in the diet of female rats for 15 days. Liver enlargement was minimal (1X) with the 2,3,2',5'-tetrachlorobiphenyl, fed at either 50 or 100 ppm in the diet. Hepatic enzyme activity gradually increased to a maximum of 14 and 20X (respectively for these dosages) through the series 2,4,6,2',4',6'-hexachloro-, 2,5,2',4',5'-pentachloro-, 3,3,3',3'-tetrachloro-, decachloro-, and 2,4,5,2',4',5'-hexachlorobiphenyl.

Monooxygenase activities measured in the 10,000 x g supernatant of liver homogenates using EPN, p-nitroanisole, and aniline as substrates followed the same progression as the liver enlargement. The 2,5,2',5'-isomer increased these activities slightly but only at the 100-ppm dietary level (120, 106, 118% of control for the three substrates, respectively) while the most active isomer, 2,4,5,2',4',5'-hexachlorobiphenyl, led to values of 413, 358, and 247% of control at the 50-ppm dietary level. These activities were found to be inconsistent with the R_m values of the compounds. Similar investigation with asymmetric PCB isomers (only one ring chlorinated) will be reported.

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30. ENZYMIC CHANGES IN THE LIVER OF RATS FED CHLORINATED BIPHENYLS, TRIPHENYLS AND DDT. James R. Allen and Lois J. Abrahamson, Department of Pathology, University of Wisconsin, Madison, Wisconsin 53706.

Similar morphological and biochemical changes occurred in the liver of rats receiving chlorinated biphenyls, triphenyls and DDT in the diet with the major variation being in the time required for changes to develop. The most obvious gross alteration was hypertrophy of the liver which developed within the initial 24 hours and persisted throughout the 30 day examination period. This increase in size was attributed primarily to proliferation of the smooth endoplasmic reticulum (SER) and to the formation of numerous large cytoplasmic concentric membrane arrays (CMA) within the hepatic cells. Homogenates prepared from these livers had increased levels of protein and RNA and decreased concentrations of DNA. The microsomal fractions of the hepatocytes had a decided increase in N-demethylase and nitroreductase while esterase levels were not altered appreciably. There were reduced levels of glucose-6-phosphatase and aromatic hydroxylase when expressed as a ratio to microsomal protein. These enzymatic changes were obvious within the initial 24 hours reaching a maximum deviation from the controls during the first week and leveling off thereafter. Animals that survived for 4 months showed a reduction in rate of gain, decreased hepatic SER, reduced numbers of CMA and decreased enzyme activities of the liver.

31. PHOSPHOLIPID SELECTIVITY IN REVERSAL OF BEEF BRAIN (Na^+K^+) ATPase INHIBITION BY POLYCHLORINATED BIPHENYLS AND DDT. C. W. Sharp and M. E. Wilson, Anal. Syn. Chemistry Branch, NIEHS, P. O. Box 12233, Research Triangle Park, N. C. 27709.

Since membrane (Na^+K^+) ATPases may play several important physiological roles, we have tried to ascertain the mode of action of polychlorinated biphenyls (PCBs) and DDT as inhibitors of the brain microsomal enzyme. In addition to chlorinated hydrocarbons (CHs), we investigated enzyme responsiveness to oleate, dodecyl sulfate and deoxycholate (DOC). At inhibitory concentrations, the CHs and detergents form oil-in-water dispersions or micelles; thus, limiting conditions were determined for reversal of and protection against enzyme inhibition by the CHs and the detergents. (Na^+K^+) ATPase responsiveness to the detergents exhibits a thermal dependence which is not observed for CHs. Albumin or the phospholipids can protect against or reverse inhibition by oleate or dodecyl sulfate. (Na^+K^+) ATPase responsiveness to phosphatidyl serine (PS) and, to a lesser extent, to phosphatidyl inositol (PI) contrasts with that to phosphatidyl choline or to phosphatidyl ethanolamine in two respects: (1) PS and PI can reverse enzyme inhibition by DDT and by PCBs. (2) PS and PI can protect the enzyme from severe inhibition by DOC. PS and/or PI are also effective as activators of phospholipase-treated (K. Taniguchi and Y. Tomomura, *J. Biochem.*, 69, 543, 1971) or DOC-solubilized (K. P. Wheeler and R. Whitten, *J. Physiol.*, 207, 303, 1970) preparations of brain (Na^+K^+) ATPase. Should each of the various observations of phospholipid selectivity have a common significance, it could be hypothesized that DDT and the PCBs may effect their inhibitory action by interfering with normal phospholipid stabilization of the brain (Na^+K^+) ATPase.

32. DYNAMICS AND METABOLISM OF POLYCHLORINATED BIPHENYLS (PCBs) IN COLD EXPOSED PIGEONS. A. B. W. deFuria, R. J. Norstrom, National Research Council of Canada, Ottawa K1A 0R6; O. Hutzinger, NRCC, Halifax, Nova Scotia, Canada.

Metabolism of PCBs in cold exposed White Carneau pigeons occurred most rapidly immediately after dosing, slowing down to a much lower rate after storage of the PCBs was complete. The relative rate of this initial metabolism of the various component peaks appeared to be similar over a fifty fold range in total dose. Movement from adipose tissue to muscle, brain and liver tissues occurred during starvation-induced utilization of half their lipid reserves. On subsequent refeeding the PCB content of these tissues returned to normal values. Similar studies with DDT have shown the same effect. The enzyme systems involved in PCB metabolism are probably linked to glycolysis as a preferred energy source, since their metabolism was more pronounced during refeeding than during starvation-induced movement from adipose tissue. Essentially no metabolism of the hexachloro components was observed. However, preferential mobilization and/or metabolism of other Aroclor 1254 components suggested that the position of the chlorine atoms, as well as the degree of chlorination has an influence.

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WEDNESDAY MORNING - SECTION B - GENERAL - J. L. Monkman, Presiding

33. PARTICLE-BORNE STRONG ACID: OCCURRENCE, EFFECTS AND REMEDIATION METHODS. Cyrill Irgensell, Swedish Water & Air Research Laboratory, S-400 40 Gothenburg, Sweden.

Studies on the formation of strong acid on particles have shown that this process is dependent upon the time of suspension of a particle in different air spaces as well as of SO_2 -concentration and humidity of these air spaces. Particle-borne strong acid, but also that formed as a result of the impact of SO_2 on different surfaces could be associated with two very severe effects. Firstly, the acidification of lakes and of the ground. Secondly, the harmful effect on human health arising when sulphuric acid is deposited in the lower respiratory tracts. As already pointed out by Larsen (MCA, 1970), this could be interpreted as a synergistic effect of SO_2 and particles. It is therefore of importance that continuous measurements of strong acid in respirable dust are made in connection with close surveillance of mortality and morbidity as related to air pollution. Three major problems are associated with satisfactory measurement methods: 1) Adequate sampling; 2) Suitable filters for collection of particles and 3) Determination of strong acid in the neutral sample. We are approaching the solution to 1) and 2), whereas 3) can now be regarded as solved.

34. THE APPLICATION OF SCALE FACTORS TO EMISSION STANDARDS. Mr. Robert B. Coleman and Professor Arthur C. Stern, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, North Carolina, 27514.

A linear programming model which produces a rational basis for determining the rate of change of allowable emission with change of source size, capacity or throughput is derived. It is designed to minimize cost of control to achieve air quality standards subject to the constraints of available technology. It provides a viable alternative to standards based solely on available technology, such as process weight standards, which do not directly consider cost or air quality considerations.

35. A CASE STUDY IN THE DEVELOPMENT OF AIR QUALITY MANAGEMENT STANDARDS-HYDROGEN CHLORIDE. Dr. Giuseppe Fumagalli and Professor Arthur C. Stern, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, North Carolina, 27514.

Historically, hydrogen chloride was one of the first industrial pollutants regulated. Development of air quality management standards for it presents an illuminating case study of the problem of the interpretations of data on air pollution effects and on control technology. Of particular current interest is the evaluation of sensory and reactivity data from diverse sources.

36. THE RELATION BETWEEN CONCENTRATIONS OF SULFATE AND AMMONIUM IN AIR SAMPLES. L. Dubois, L. Egan, T. Teichman, and J. L. Monkman. Air Pollution Control Div., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

Sulfate, a ubiquitous contaminant in a suspended particulate matter, has received some attention on account of the relatively high concentration. There is also a suspicion that sulfates may be partly responsible for the irritating properties of smog. With the present availability of specific ion electrodes for the ammonium ion, it became possible to study the ammonium to sulfate relationship on a large number of samples. At the same time, it has become feasible to monitor the genesis of ammonium sulfate in polluted air. Analytical comparison has also been made with ammonium ion levels obtained using other methods.

37. THE PHOTO-OXIDATION OF ISOPRENE IN THE PRESENCE OF NITROGEN DIOXIDE, CARBON MONOXIDE AND WATER VAPOR, by Daniel Lillian and Mark Antell, Dept. of Environmental Sciences, College of Agriculture & Environmental Science, Rutgers, the State University, New Brunswick, N.J. 08903.

Isoprene is a biologically generated atmospheric constituent suggested by theory and some experimental observations of undergoing tropospheric photo-oxidation similar to smog forming olefins.

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As such, it may play an important role in the formation of naturally occurring organic aerosol and the behavior of other atmospheric trace constituents such as ozone, NO_x , and CO.

A study was undertaken in our laboratory of the effects of simulated solar irradiation on mixtures of isoprene, NO_2 , ozone, and other selected atmospheric constituents. The results of this study will be presented.

Based on the kinetics data obtained during the controlled irradiation, possible mechanisms for the photo-oxidation of isoprene will be discussed.

38. AEROSOL FORMATION FROM THE PHOTO-OXIDATION OF NON-LEADED FUELS

Daniel Lillian and David Hansen, Dept. of Environmental Sciences, College of Agriculture & Environmental Science, Rutgers, the State University, New Brunswick, N.J. 08903.

A study to characterize the formation of light scattering aerosol and condensation of non-leaded highly aromatic fuels is now in progress.

Gaseous mixtures of nitrogen dioxide and fuel, or its individual constituents, are contained in 200 liter teflon bags. The bags are placed in a controlled temperature chamber and irradiated by a 10kw linear xenon lamp with suitable filtering for tropospheric solar simulation.

Variables measured as a function of time during the two irradiations include: condensation, nuclei, ozone, light scattering aerosol, oxidants, NO_x , and hydrocarbons. The effect of aromatic fuel content on these variables will be presented and the mechanistic implications will be discussed.

WEDNESDAY AFTERNOON - SECTION A - SYMPOSIUM ON PCB'S - STILL PREVALENT - STILL PERSISTENT - (Concluded) - Joint with Division of Pesticide Chemistry - C. G. Gustafson, Presiding

PCB'S IV - TOXICOLOGY AND PHYSIOLOGICAL ACTIVITY

39. METABOLISM OF ISOMERICALLY PURE MONO-, DI-, TETRA- AND HEXACHLORO-BIPHENYLS BY MAMMAL, BIRD AND FISH. O. Hutzinger, D. Nash, S. Safe, National Research Council of Canada, Atlantic Regional Laboratory, Halifax, N. S., A. S. W. DeFreitas, R. J. Norstrom, National Research Council of Canada, Division of Biology, Ottawa, D. J. Wildish and V. Zitko, Environment Canada, Fisheries Service Biological Station, St. Andrew's, N. B. CANADA.

Commercial polychlorobiphenyl preparations, because of their complex isomer composition are unsuitable for a study of the metabolic change of these important environmental pollutants. Several unlabelled, chemically defined chlorobiphenyls have been administered to rats (50 mg/kg for 3 days) and comparative data for pigeons and brook trout are being obtained for 4-chloro-, 4,4'-dichloro-, 2,2',5,5'-tetrachloro- and 2,2',4,4',5,5'-hexachlorobiphenyl. Excreta were hydrolyzed, to liberate phenolic compounds from the glucuronic and sulfate forms, and feces and urine from treated animals compared to controls by thin-layer and gas chromatography. Mass spectrometry established that the main metabolite, in most cases, is a hydroxychlorobiphenyl which is formed by hydroxylation without replacement (loss) of chlorine. In each instance, the majority of the administered chlorobiphenyl appears unchanged in the feces. Attempts at establishing the structures of the metabolites by synthesis and 220 MHz NMR will be discussed.

40. ELIMINATION PATTERN OF AROCLOR 1254 COMMONLY IN THE BOBWHITE. George S. Bagley, EPA, Pesticide Regulation Division, So. Agriculture Bldg., Rm 1159, 14th and Independence Ave., S. W., Washington, D. C. 20250; Eugene Cromartie, Patuxent Wildlife Research Center, Laurel, Maryland 20810.

The elimination pattern of the components of Aroclor 1254 in the bobwhite quail (*Colinus virginianus*) was studied under laboratory conditions. Aroclor 1254 was administered

as a dietary component at the rate of 300 ppm for a period of 14 days. Birds were then placed on untreated food and sacrificed at 14 or 42 days thereafter. At the end of test, three birds from the control group were each given an oral capsule dose of Aroclor 1254 in corn oil equivalent to 500 mg/kg body weight and were sacrificed after 1 hour. Analysis by combined gas chromatography - mass spectrometry was accomplished on several samples from each group of test birds. Chromatograms of the treated and untreated birds are presented. The chromatograms show that a dynamic system is at work, slowly removing certain components while increasing others. The GC profile for Aroclor 1254 did not maintain its integrity in bobwhite quail fed Aroclor 1254 for 14 days and clean food 14 or 42 days thereafter. Absorption of all components occurred at essentially the same rate, as shown by analysis of birds sacrificed an hour after a single oral dose of Aroclor. Significant alterations of certain PCB isomers appeared to take place. Dechlorination was clearly apparent and isomeric transformation was suggested.

41. EFFECT OF DIETARY POLYCHLORINATED BIPHENYLS ON GROWTH AND REPRODUCTION OF MINK.
R. K. Ringer, R. J. Aulrich and M. Zabik, Departments of Poultry Science and Entomology, Michigan State University, East Lansing, Michigan 48823.

Reproductive failure or total early kit mortality has occurred in mink receiving diets that contain Lake Michigan coho salmon. Research indicates that an environmental pollutant of industrial origin such as the chlorinated hydrocarbons may be responsible. Feeding known dietary levels of DDT, its isomers and dieldrin (a) in excess of that found in coho salmon failed to duplicate the results. Adult mink were divided into three groups (12 females and 3 males) and fed either a basal ration, basal ration except for the substitution of 30% coho salmon for 30% ocean fish, or the basal ration supplemented with 30 ppm PCB's (10 ppm each of Aroclors[®] 1242, 1248 and 1254). All mink receiving PCB's died within 121 days. Six mink fed the coho salmon died in this same period. Histopathological examination and PCB residue analysis were conducted. PCB content of brain, liver, kidney, spleen, lung, muscle and heart of mink that died when fed coho salmon or PCB supplementation was extremely similar. Brain content of PCB was about twice that of other tissues measured. Organ weights, expressed as percent of brain weight, were not significantly different. Feeding 10 ppm Aroclor 1254 significantly reduced body weight gains during the growing period. Combinations of Aroclor 1254 with either 0.5 ppm dieldrin or 10 ppm DDT further reduced body weight gains. Data on effect of continuous low-level feeding of Aroclor 1254 alone and in combination with DDT and/or dieldrin on mortality and reproduction will be presented.

42. TOXICITY AND PHYSIOLOGICAL ACTIVITY OF AROCLOR 1254 TO SEVERAL ESTUARINE ORGANISMS.
D. R. Himm, D. J. Hansen, J. A. Couch, N.R. Cooley, and P. R. Parrish, Environmental Protection Agency, Gulf Breeze Laboratory, Sabine Island, Gulf Breeze, Florida 32561.

The polychlorinated biphenyl, Aroclor 1254, was detected in oysters from Escambia Bay, Florida, for the first time in April 1969. The latest survey, 26 Oct. 1971, illustrates the extent of contamination: residues in biota ranged from non-detectable in plants to 10.0 parts per million (whole body) in fish (*Menidia beryllina*). Since 1969, much of our effort has been to study the effects of this chemical on species, populations, and ecosystems.

Population density of test tube cultures of the ciliate *Tetrahymena pyriformis* W at 96 hours was reduced significantly by 1.0 part per billion.

Chronic toxicities of Aroclor to seven species of estuarine organisms were determined in flowing-water bioassays. The minimum concentration that killed shrimp was 0.9 parts per billion. Fishes were killed and oyster growth was reduced at slightly higher concentrations. Residues in organs of shrimp (*Penaeus duorarum*) were greatest in the hepatopancreas, least in the abdominal muscle or exoskeleton. Grass shrimp (*Palaemonetes pugio*) accumulated Aroclor 1254 from water that contained concentrations less than 40 parts per trillion.

Tissue alterations were found in oysters, shrimp, and fish after chronic laboratory exposures to the chemical. Shrimp had the least detectable histological change—nuclear damage in hepatopancreatic cells. Oysters had more generalized tissue responses with heavy infiltration of leukocytes and atrophy of digestive diverticula. Fish had extreme vacuolization and necrosis of the liver.

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43. SOURCES, LEVELS, AND TOXICOLOGICAL SIGNIFICANCE OF PCB IN HATCHERY-REARED ATLANTIC SALMON. V. Zitzke and O. Nutzinger, Biological Station, St. Andrews, N.B., Canada, and Atlantic Regional Laboratory, National Research Council of Canada, Halifax, N.S., Canada.

PCB residues found in hatchery-reared juvenile Atlantic salmon (1.2-3.7 $\mu\text{g/g}$ wet weight, whole fish) originate from an antifouling paint, containing 6.5% of Aroclor[®] 1254. Fish food (PCB level 0.3-0.5 $\mu\text{g/g}$) is a minor source of PCB, leading to an equilibrium PCB level of 0.19 $\mu\text{g/g}$ in fish never exposed to other PCB sources, and to a decrease from 1.97 to 0.78 $\mu\text{g/g}$ in 120 days in fish removed from tanks painted with the antifouling paint. No buildup of PCB residues occurred in fish fed dry food containing 1.0 $\mu\text{g/g}$ of Aroclor[®] 1254. An equilibrium level of 3.5 $\mu\text{g/g}$ was reached in fish fed dry food with PCB level of 10.3 $\mu\text{g/g}$. Feeding food with PCB at 100 $\mu\text{g/g}$ results in significant PCB accumulation (28 $\mu\text{g/g}$ in 120 days). "Normal" mortality of fish could not be related to their PCB levels. A study of the toxicological significance of found PCB residues is under way. The PCB concentration in the antifouling paint decreases 50% on irradiation in air and changes only slightly on irradiation under water. Possible formation of chlorinated dibenzofurans under these conditions is investigated.

44. RESIDUE DYNAMICS AND BIOLOGICAL EFFECTS OF POLYCHLORINATED BIPHENYLS IN AQUATIC ORGANISMS. F. L. Mayer, Jr., P. M. Mehre, R. H. O. Sanders. Fish-Pesticide Research Laboratory, Route 1, Columbia, Missouri 65201.

Toxicity residue dynamics and biological effects of polychlorinated biphenyls (PCBs) were investigated in several freshwater fishes and invertebrates. Acute toxicity (96-hr LC_{50}) of PCBs to fish ranged from 278 to 30,000 $\mu\text{g/l}$ while those for aquatic invertebrates were 3.2 to 2,400 $\mu\text{g/l}$. The LC_{50} values for fish continuously exposed for 25 to 30 days varied from 3.4 to 433 $\mu\text{g/l}$ and 3- to 10-day exposures of invertebrates resulted in LC_{50} values of 0.6 to 80 $\mu\text{g/l}$. Biological magnification of Aroclors 1248 and 1254 by bluegill was 26,300 to 71,400 times the levels in water after 60 days. Invertebrates exposed to Aroclor 1254 showed a residue magnification up to 47,000 times greater than in water. Dietary doses from 1.45 to 14,500 μg Aroclor 1254/kg body wt. per day to coho salmon had no effect on growth, nor produced observable toxicosis until death occurred in the highest dosage group after 260 days. Thyroid activity, as measured by 72-hr thyroidal ^{125}I uptake, was increased significantly. Stimulated thyroid activity occurred in salmon dosed with 1/1000th of that causing mortality. Dietary doses of Aroclors 1222, 1248, 1254, and 1260 to channel catfish at concentrations of 48 and 480 $\mu\text{g/g}$ caused no mortality nor had any effect on growth. Thyroid activity was altered only by Aroclor 1254. The low dose increased thyroid activity by 56%, whereas a 91% increase was induced by the high dose. Implications concerning PCBs in the aquatic environment are discussed.

45. EXTENDING TOXICOLOGICAL INVESTIGATIONS. Joseph C. Street, Department of Animal Science, Division of Biochemistry, Utah State University, Logan, Utah 84321.

Discussion on the future of toxicological studies for the PCB's with both terrestrial and aquatic organisms.

46. PROSPECTS FOR THE FUTURE: FDA REGULATIONS AND TOLERANCE LIMITS. A. C. Colbye, Jr., U. S. Food and Drug Administration, Washington, D.C. 20000.

The Food and Drug Administration's regulations and tolerance limits for the PCB's will be discussed as well as the prospects regarding future PCB tolerance limits.

WEDNESDAY AFTERNOON - SECTION B - GENERAL - J. L. Monkman, Presiding

47. THE ORGANIC CONTENT OF STANDARD REFERENCE SAMPLES OF ASBESTOS. A. Zdrzejewski, J. Rithorn, L. Dubois, and J. L. Monkman. Air Pollution Control Div., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

Some studies on the total organic and polycyclic hydrocarbon content of asbestos have been made under conditions which could have led to significant losses. Indeed, in some of the methods used complete evaporation of the solvent was made after extraction of the organic compounds.

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With low boiling compounds such as the C-9 etc. aliphatics and some aromatics, complete elimination of the solvent should be avoided. Four standard asbestos samples, provided by the International Union against Cancer, have been extracted with a low boiling solvent and the organic content measured by ultraviolet spectrophotometry and gas chromatography *inter alia*.

48. AN INTERIM REPORT ON ANALYTICAL METHODS USED IN A COKE OVEN EFFLUENT STUDY, Donald J. Larsen and John V. Creble, U.S. DHV-PHS-NIOSH-National Institute for Occupational Safety and Health, 1014 Broadway, Cincinnati, Ohio 45202.

NIOSH is evaluating the applicability and efficiencies of sampling procedures and analytical methods in determining the potential hazards associated with coking and roofing operations. This is an interim report discussing analyses obtained from seven analytical methods that were applied to samples collected in a coke oven effluent study. The analytical methods included: (1) benzene soluble extract; (2) the gas chromatographic separation method for fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(e)pyrene, benz(c)acridine, benz(a)anthrone, benzo(b)fluoranthene, benzo(g,h,i)perylene; (3) thin-layer chromatography for benzo(a)pyrene; (4) the liquid column chromatographic separation for pyrene, fluoranthene, chrysene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(k)fluoranthene, perylene, benzo(g,h,i)perylene, and anthanthrene; (5) fluorimetric index; (6) atomic absorption techniques for nickel, cobalt, chromium, manganese, copper, and zinc; (7) gas chromatographic procedures for samples of solvent vapors on charcoal tubes for benzene, toluene, xylene, and naphthalene.

49. INSTRUMENTATION. L. Dubois, R. S. Thomas, and J. L. Monkman, Air Pollution Control Div., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

An enhanced public awareness about the environment has broadened the scope and diversity of ambient air quality measurements. Increasing demands are being placed on control agencies to provide data on both long term trend and transient pollution levels. As concentrations of permitted pollutants are lowered by legislation, the onus falls on the analyst and instrument manufacturers to provide techniques and instruments which will produce data comparable and interrelatable from city to city and country to country. While new techniques are becoming available, much of the data published in the literature suffers from inconsistencies related to sampling problems, sample preparation, calibration standards, chemical interferences and non-reliable monitoring instrumentation. As the emphasis toward network monitoring grows, an increasing reliance will be placed on field or remote sensors feeding data to a central processing centre. A number of failures and pitfalls are discussed and some solutions are offered in problem areas.

50. MONITORING REACTIVE AND NON-REACTIVE HYDROCARBONS IN AIR USING SELECTIVE ADSORPTION. Bernard E. Saltzman, William R. Burg, John E. Cuddeback, Kotterling Laboratory, University of Cincinnati, Cincinnati, Ohio 45219.

A convenient air monitoring system capable of assessing concentrations of hydrocarbons with the potential for producing photochemical smog is reported. A pump with appropriate flow controls continuously forces sample air through an empty column and an absorbent column arranged in parallel. The air flow from each column is directed alternately by a switching valve to a flame ionization detector. Quantitative measurements of the concentrations of total hydrocarbons and of unreactive hydrocarbons are made directly. The concentration of reactive hydrocarbons removed in the packed column is obtained by difference. Solid absorbents and the factors affecting their ability to absorb various classes of hydrocarbons were studied. Column dimensions, flow rates and the temperature were adjusted so that a maximum of the hydrocarbons participating in atmospheric photochemical reactions was absorbed, while allowing all remaining hydrocarbons to pass through the column unaltered. Monitoring data for Cincinnati is reported using this technique.

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51. THE APPLICATION OF GAS-PHASE TITRATION IN THE SIMULTANEOUS CALIBRATION OF NO, NO₂, NO_x, AND O₃ ATMOSPHERIC MONITORS. K. A. Reine, R. F. Martin, and J. J. Wozniak. Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, N. C. 27711.

The fast reaction between nitric oxide and ozone has been used to compare independent methods for calibrating NO, NO₂, NO_x, and O₃ monitors, and to provide a routine calibration procedure for NO, NO₂, NO_x, and O₃ at a common manifold. A constant flow of air containing NO at concentrations of 0 to 1 ppm is established in a flow reactor. Upstream of the reactor, the air passes through an ozonizer capable of producing ozone concentrations of 0 to 1 ppm. Ozone is added to the air stream in concentrations up to 50 percent of the initial NO concentration. The concentration of NO₂ produced is equivalent to the concentration of O₃ added, whereas the NO_x concentration remains the same. The decrease in NO, or the appearance of NO₂ can be monitored by means of specific indicators (e.g., chemiluminescence) and related to the ozone added. The experimental apparatus and the titration conditions will be described. This system permits routine calibration of monitors of oxides of nitrogen and ozone at a common manifold, using a primary standard for only one of the gases. The primary standard can be known concentrations of NO₂, NO or O₃, as determined by use of permeation tubes, precalibrated cylinders, or wet chemical methods. Absolute relations among these standards, as determined by gas-phase titration, will be presented.

52. A COMPARISON OF SULFUR COMPOUNDS (H₂SO₄, F.S.S. AND T.S.S.) FOUND IN THE ATMOSPHERE OF MEXICO CITY, MEXICO, MONTREAL AND OTTAWA, CANADA. H. Bravo A., Instituto de Geofísica, Universidad Nacional de México, México, 20, D.F., México, L. Monkman, Department of the Environmental Air Pollution Control Division, Ottawa, Ontario, Canada, A. Lowe, Instituto de Geofísica, Universidad Nacional de México, México, 20, D.F., México.

Sulfur compounds are found in urban atmospheres as gases and particulate matter such as mecaptans, hydrogen sulfides, sulfur dioxide and sulfates of calcium or ammonium. One of the constituents of sulfur compounds found in the atmosphere is sulfuric acid.

In our sampling we used a High Volume Air Sampler with fiberglass free sulfate filter) which collected all the sulfur compounds discriminating the gaseous sulfur compounds. The sulfuric acid determination was carried on by the micro diffusion method described by Monkman. The polarographic method of Mayer with some modification was used to measure the sulfates. Samples from Mexico City 1968-1969, Montreal and Ottawa are compared and are reported in this paper.

The near values of sulfuric acid in Mexico City were to three times higher than that found in Ottawa's air. The percentage of sulfuric or T.S.S. is higher than usual in Mexico. The values in Montreal during the winter are near the value for sulfuric acid in Mexico City. The correlation coefficients found in Mexico City and Montreal among particulate matter in relation to sulfuric acid and F.S.S. and T.S.S.^B, ranged from 0.86 to 0.97.

53. THE MEASUREMENT OF MERCURY IN AMBIENT AIR. G. L. Corte, J. L. Monkman, R. S. Thomas, and L. Dubois. Air Pollution Control Directorate, Environmental Health Centre, Tunney's Pasture, Ottawa, Ontario. KIA 0H3, Canada.

An air sampling device for air borne mercury was developed and evaluated. The trapping element is silver in the form of gauze which is able to quantitatively absorb, retain and quantitatively desorb up to 100 nanograms of elemental mercury from air. Air is drawn through the absorber by means of a modified "personal" air sampler, which is operated by a 4.8 volt rechargeable nickel cadmium battery. The sampling time can be selected manually, by means of clock-work timers and by remote radio control. By varying sampling times and flow rates, one can measure a range of 5 to 100,000 nanograms of mercury per cubic metre of air sampled. The mercury collected is desorbed into a modified DuPont 400 mercury analyzer and measured by ultraviolet absorption. A strip chart recorder and a Hewlett Packard G.C. integrator provide total output measurement. The analyzer was calibrated by liberating mercury from standard aqueous solutions by injecting known volumes of saturated mercury vapor and by means of a mercury permeation tube.

A multipurpose sampling manifold was constructed with provision for the continuous measurement of mercury in air, in compressed gases, in rock and ore samples, and in liquids. Some applications of the method to organic mercurial compounds are given.

54. THE VOLATILITY OF POLYCYCLIC AROMATIC HYDROCARBONS AND RELATED PROBLEMS IN AIR POLLUTANT ANALYSIS. L. Dubois, A. Albagli, J. L. Monkman and A. Zdrojewski, Air Pollution Control Div., Environmental Health Centre, Tunney's Pasture, Ottawa, KIA 0H3, Canada.

It has been observed in the paper chromatography of polycyclic aromatic hydrocarbons that most of an anthracene spot (as an example) would disappear from the paper in a few days. Knowing the volatility of the two and three ring polycyclics it seems appropriate to find out if some of the higher numbered ring hydrocarbons are also volatile in the conditions usually encountered during the measurement of these compounds. In evaluating this property, it was found that the adsorption of the compounds on the surface of beakers and glass fibre sheets is much more important if the solvent is completely evaporated.

From these results, it is indicated that in any method for the measurement of such compounds, all steps involving the complete evaporation of the solvent should be eliminated and other methods of sampling and extraction should also be investigated.

THURSDAY MORNING - SECTION A - SYMPOSIUM ON THE TRACE METAL INTERACTIONS WITH SEDIMENTS - J. O. Leckie, Presiding

55. MODELS FOR THE FATE OF HEAVY METALS IN SEDIMENT. Teh Fu Yen and Kenneth Y. Chen, Environmental Engineering Programs, Univ. of Southern Calif., Los Angeles, Calif. 90007.

Sorption, redox reactions, precipitation and complex formation co-determine the fate of heavy metals in natural waters and sediments. Heavy metals are concentrated by metal oxides and hydroxides, e.g. MnO_2 , $Fe(OH)_3$, Al_2O_3 , up to several thousand times of solution concentrations and coprecipitate in sediment. Supersaturation with respect to metal carbonates could also lead to precipitation and accumulation in sediment. An example is the precipitation of $CaCO_3$ observed in some parts of Southern California coastal waters. In sediments, reducing conditions can lead to the dissolution of metal oxides and hydroxides with subsequent release of heavy metals. However, under this condition, metal sulfides are usually formed and further reduce the availability of heavy metals to overlying waters.

Availability of heavy metals can be increased through complex formation. Many of the metal complexes and chelates found in sediment were actually present via template reactions. Organic ligands from biological debris and synthetic organic materials bind tightly to metal ions in covalent linkages. Frequently organic ligands, which appear as functional groups of hydroxyl, carbonyl, aldehyde, amino, amide, mercaptan, etc., are part of natural macromolecular systems. In this manner, micelle formation, association and disassociation, characteristics of water-sediment interface and other colloidal behavior can be explained.

Experimental results and evidence using electron spin resonance, mass spectrometry, infrared spectrometry, and atomic absorption methods will be discussed to substantiate these models.

56. THE EXTRACTION OF BIO-DIAGENETICALLY AVAILABLE TRACE ELEMENTS FROM SEDIMENTS AND SOILS. E. A. Jenne and J. W. Ball, U. S. Geological Survey, Water Resources Division, 345 Middlefield Road, Menlo Park, California 94025.

The important short-range trace-element sinks in sediments and soils are organic, hydrous oxides of iron and manganese, and carbonates. The trace elements in these sediment fractions may be released to the biosphere under the combined action of biological and chemical diagenetic processes. A method has been developed for the extraction of trace elements from earth materials at 80°C by the serial addition of reagents using a single container. Carbonates which may be present are dissolved with hydrogen-sodium citrate (pH 3), then hydrogen peroxide in dilute nitric acid is added to decompose readily oxidizable organics and allowed to react overnight. Finally sodium dithionite is added to reduce iron and manganese oxides. Following centrifugation and decantation the trace elements in this extract are analyzed directly by atomic absorption or following solvent concentration as appropriate. The trace elements presently analyzed for include Ag, Be, Cd, Co, Cu, Mo, Ni, Pb, and Zn.

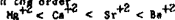
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57. TRACE METAL INTERACTIONS AT THE MANGANESE DIOXIDE - SOLUTION INTERFACE. J.W. Murray, Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543.

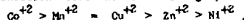
Manganese Dioxide has long been known to be an efficient scavenger of trace metals. The two factors that are responsible for this phenomenon (the surface charge and specific adsorption) have been studied in detail.

Electrophoresis, Na^+ and K^+ adsorption, and alkalimetric titration experiments have been used to locate the pH (ZPC) of a suspension of MnO_2 at approximately 2.25. As for other metal oxides, H^+ and OH^- have been found to be potential determining ions; however, below pH 3 the reduction of MnO_2 by H_2O releases Mn^{2+} and it is possible that this ion must also be considered to be potential determining. Because of the low pH (ZPC) the surface charge in the pH range of natural waters can reach values up to $100 \mu\text{Coul/cm}^2$.

In addition to the high surface charge, specific adsorption is an important factor in considering the adsorption of some trace metals. Alkalimetric experiments have been combined with direct measurements of adsorption and desorption for several metal ions. The results of these experiments indicate that the alkali earths adsorb reversibly on the MnO_2 surface in the order:



and that the transition metals adsorb in a highly irreversible manner in the order



58. KINETICS OF SOME SILICATE REACTIONS IN SEDIMENTS. R. Siever and J. B. Heynard, Department of Geological Sciences, Harvard University, Cambridge, Mass. 02138.

Dissolution of magnesium silicates and of potassium feldspar have been reported to follow parabolic kinetics. We have found that the dissolution of plagioclase feldspars also obeys this rate law as does a silicate reconstitution or "reverse weathering" type reaction, that of kaolinite sorption of H_2SiO_4 and K^+ from solution. We find rate constants for the aluminosilicate reactions of about 10^{-13} moles/cm 2 sec $^{1/2}$ at 25 $^\circ\text{C}$, in agreement with the K-feldspar data but somewhat slower than the 10^{-11} reported for magnesium silicates. Except for a very rapid initial portion of the reaction that seems to be essentially a surface phenomenon, the rates are largely independent of solution composition so long as the stability field of the reactant mineral is not entered or at least closely approached. These observations indicate that the reaction is limited by diffusion within the solid either through a kind of some distinct product phase or along a continuous gradient of variable composition of the phase produced by alteration of the original structure and composition. These rates are sufficiently rapid for equilibration of silicates with any surrounding waters over geological time scales as low as thousands of years. This may indeed be the case for sea water, at least at siliceous concentrations found in the pore spaces of many recent sediments. The persistence of detrital feldspars of sand grain size for 10^3 years may imply long term equilibrium with ground water and clays.

59. THE ADSORPTION OF HYDROLYZABLE METAL IONS AT THE OXIDE-WATER INTERFACE. R. O. JAMES, Department of Applied Earth Sciences, Stanford University, Stanford, California 94305.

The adsorption behavior of hydrolyzable metal ions at the solid-water interface is strongly pH dependent and is characterized by a general agreement between the hydrolysis of the aqueous metal ions and their enhanced adsorption, charge reversal and coagulant properties. Models which are used to describe the phenomena, including the ion exchange and specific adsorption of certain species are compared to a recent model proposed by James and Healy. In this model all the species of hydrolyzable metal ion are considered as potential adsorbates, but only the lower charged, less strongly hydrated hydrolyzable complexes have favorable free energies for the adsorption process.

THURSDAY MORNING - SECTION B - GENERAL - J. L. Monkman, Presiding

60. PHOTOFRAGMENT DETECTION OF NO_2 AT REDUCED PRESSURE. W. A. McClenny, J. P. Bell, and J. A. Hodgeson. ENVIRONMENTAL PROTECTION AGENCY, National Environmental Research Center, Research Triangle Park, N. C. 27711.

A low-pressure system for the separate detection of nitrogen dioxide (NO_2) and ozone (O_3) at ambient concentrations is described. A sample air stream containing NO_2 and O_3 is passed through an irradiation chamber in which NO_2 is photolyzed to form oxygen atoms (O) and nitric oxide (NO). After passing through a double hood's horn

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light trap, the air stream enters a reaction chamber into which pure NO is also introduced. Chemiluminescence occurs from the reactions:



The light signal is viewed by a photomultiplier tube and filter combination, and is recorded continuously. Ozone is determined separately by turning off the irradiation source and recording only the signal from reaction (2). This signal is subtracted from the total signal of reactions (1) and (2) to give that due to NO₂ alone. The sensitivity of this system depends upon several factors, which include: (1) light source, (2) reaction-chamber pressure, (3) pumping speed, and (4) nitric oxide flow rates. With a nitric oxide flow rate, of 10 ml/min., a 200 watt Xe-Hg arc source, a pumping speed of 4 liters/min., and a reaction chamber pressure of 8 Torr, the sensitivity of the system is greater than 0.05 na/ppb. Data showing signal dependence upon the different factors are given, and interferences are discussed.

61. AN ANALYTICAL TECHNIQUE FOR CARCINOGENIC POLLUTANTS BASED ON PHOTOLYSIS AND DETECTION OF PRIMARY FRAGMENTS. J. A. Hodgeson and W. A. McClenny. ENVIRONMENTAL PROTECTION AGENCY, National Environmental Research Center, Research Triangle Park, N. C. 27711.

A new technique is proposed for the detection of a class of toxic air pollutants which have the common property that each undergoes photolysis in the solar region or the near-ultraviolet. This class includes pollutants such as nitrogen dioxide, ozone, formaldehyde, halogens, hydrogen halides, hydrogen peroxide, and organic peroxides. These molecules yield, upon photolysis, reactive atomic and molecular fragments, which may be important in atmospheric chemical processes. By a spectroscopic detection of the fragment, the photolysis property may be used in the measurement scheme for the primary pollutant. The fragment will inherently possess more intense emission and absorption spectra than the primary molecule. Detection schemes proposed include applications of chemiluminescence and resonance fluorescence. The primary fragments of interest are the oxygen atom, hydrogen atom, halogen atoms, and the hydroxyl radical. Related work on detection of these species are reviewed. The experimental methods being employed in both chemiluminescence and fluorescence detection schemes are described.

62. DETECTION OF NITRIC OXIDE BY CHEMILUMINESCENCE AT ATMOSPHERIC PRESSURE. B. E. Martin, J. A. Hodgeson, and R. K. Stevens, Environmental Protection Agency, Environmental Research Center, Research Triangle Park, N. C. 27711.

A system for detecting ambient concentrations of nitric oxide (NO) is described. This system is similar to other chemiluminescence systems, except that it is operated at atmospheric pressure. The system consists of a detector cell, a photomultiplier, a cut off filter, a sampling pump, and two low-pressure, mercury lamps. The detector cell is similar in design to the Netherbragt ozone-ethylene detector cell. A visible cut off filter is added in front of the photomultiplier to make the system specific for NO. A small pump pulls the sample through the detector cell where it is mixed with an excess of ozone. The total flow into this system is 1600 cc/min., which includes 75 cc/min. of oxidized oxygen. The light emitted from the reaction between ozone and NO is monitored by a closely coupled, thermoelectrically cooled photomultiplier. With the current system, 0.006 ppm of NO can be detected with a 2:1 signal-to-noise ratio when the response time is 10 seconds. Data are given for signal versus concentration of NO for various sample and ozone flow rates. Operating conditions for achieving optimum sensitivity and linearity will be given. Data will be shown for real-time ambient measurement. A list of compounds that produce chemiluminescence when reacted with ozone will be given. Also given will be data obtained with and without the cut off filter, which was added to reduce the interference from such compounds.

63. APPLICATION OF SOLID ABSORBENTS IN AIR POLLUTION SAMPLING AND ANALYSIS. Bernard E. Saltzman, J. F. Cuddeback, and William R. Burg, Department of Environmental Health, University of Cincinnati, Cincinnati, Ohio 45219.

The use of solid absorbents for the sampling and analysis of NO_x has been studied. Several absorbents have been found suitable for use with highly sensitive detectors such as the Coulson conductivity detector and the microcoulometric detector. The absorbents provide a versatile easily

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handled system for taking samples at a remote location with subsequent desorption and analysis done in the laboratory. Efficiency data, sampling rates, capacity and other data will be presented for a copper based absorbing system as well as the analytical procedure for quantitation of NO_x. The system is not subject to interferences from the commonly occurring air pollutants.

64. DEPOSITION OF DUST ON A BODY IN A FLOW STREAM. G. F. Morr and R. L. Sog, Department of Mechanical and Industrial Engineering, University of Illinois, Urbana, Illinois 61801.

Deposition of dust on a body in the form of an ellipsoid of revolution was studied to determine the ways of enhancing or reducing deposition of dust particles. In flow velocities up to 66 feet per second in a wind tunnel, deposition of 10 micron magnesia dust on an ellipsoid made of brass was measured. The dust particles were charged as in the case of particles in nature; the influence of electric potential on the ellipsoid was also studied. Deposition patterns showed effects of flow regimes over the body.

65. MEASUREMENT OF STATIONARY SOURCE GAS EMISSIONS: EXTRACTIVE MONITORING TECHNIQUES. John S. Nader, Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711.

The extractive method of measuring gas emissions is presented as the approach utilized more extensively than the newer approaches under development. The whole measurement system is treated and includes both sampling and analysis. Systems for sample transport and sample pretreatment, which vary, are described. Mechanical dilution and diffusion techniques are discussed. Analytical methods of both on-going systems and those under development or evaluation are presented. The techniques are reviewed in terms of physical and/or analytical principles that are categorized as electrical, nuclear, thermal, electromagnetic, chemi-electromagnetic, and magnetic. A summary is given of the status of development of extractive monitoring systems that includes commercial systems, prototype systems, research instruments, and feasibility studies.

66. MORTALITY EXPERIENCES OF U. S. ROOFING WORKERS EXPOSED TO POLYCYCLIC HYDROCARBONS. Irving J. Selikoff, Mount Sinai School of Medicine of the City University of New York, Fifth Avenue and 100 Street, New York, N. Y. 10029.

We have been following, prospectively, the mortality experience of all 18,000 members of the Roofers' Union in the U. S. and Canada on the Union's lists as of Jan. 1, 1959. More than 2,500 deaths occurred by Dec. 31, 1971. Age, year and specific expected death rates have been calculated and will be compared with the numbers observed, by specific cause. We have also measured the exposure of such workers to benzo(a)pyrene and other polycyclic hydrocarbons at job sites, using personal (mask) samplers. Comparison of expected and observed deaths will thus provide information concerning cancer risk associated with occupational polycyclic hydrocarbon exposure derived from coal tar pitch and asphalt.

67. PREDICTION OF HEAVY METALS IN SETTLEABLE PARTICULATES. Ross F. McQuady and Harold J. Paulue, School of Public Health, University of Minnesota, Minneapolis, Minnesota 55455.

Dustfall samples have been collected for a one year period in Sydney, Nova Scotia, Canada. The main industry in this city consists of an integrated iron and steel manufacturing complex consisting of coke ovens, two blast furnaces, a sintering plant and five open hearth furnaces. The dustfall samples were analyzed by the classical gravimetric procedure. The iron, manganese, and zinc contents of each of the samples were determined using a Beckman Atomic Absorption Spectrophotometer.

Analysis of variance, linear and multiple regression techniques were applied to the data. Seasonal trends appeared to be absent. The dustfall residue showed a high degree of correlation with the dustfall ash. Similarly, the iron, manganese and zinc were found to be significantly correlated with the dustfall residue or ash. A working probability model for prediction of heavy metals in dustfall was estimated.

Several important results can be drawn from this study. By knowing the statistical distribution of air pollution variables, a prediction model may be implemented to estimate with accuracy the concentration of certain air pollutants, with a limited amount of information. Secondly, to avoid complicated or tedious laboratory analysis, the most easily determined constituent can be analyzed and other constituents predicted. The man hours and money saved could be projected in extending useful areas.

THURSDAY AFTERNOON - SECTION A - SYMPOSIUM ON PHOSPHATE INTERACTIONS WITH SEDIMENTS - J. O. Leckie, Presiding

68. PHOSPHATES IN THE SEDIMENTS OF THE PAMlico ESTUARY. Joseph R. Upchurch, James K. Edmond, Charles R. O'Neill, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, N. C. 27514.

The amount of "available" P extracted from sediment samples along the 30 mile length of the Pamlico estuary was observed to decrease from 1.8 mg P/g sediment in fresh water to 0.3 mg P/g in water with a salinity of 18 ppt. Wet-sieve analyses indicated that silt and clay-sized materials comprised 90 percent by weight of these sediments. X-ray diffraction measurements indicated that the clay minerals were primarily kaolinite, illite, chlorite, and a chlorite-like intergrade clay. The "available" P was measured by modification of the $\text{HCl-H}_2\text{SO}_4$ (pH 1.1) acid extraction procedure of Olsen and Dean (Olsen, S.R., Dean, L.A., *Methods of Soil Analysis*, Part 2, C.A. Black, Ed., pp. 1035-40, Amer. Soc. Agron., Madison, Wis., 1953). A high degree of correlation ($r = 0.99$) between available-extractable P and "available" P was found in the upper reach of the estuary (salinity < 1 ppt). Correlation between Fe and P has also been reported in fresh waters for sediments collected from Wisconsin lakes (Williams, et al., *Environ. Sci. & Technol.*, 1: 1113-20, (1971)). In the lower part of the estuary (salinity > 1 ppt) this Fe - P correlation decreased ($r = 0.86$). The decrease in the "available" P content of the sediments and the reduction in the Fe - P correlation along the length of the estuary are consistent with the suggestion that P is held to suspended clays and sediments by some type of Fe-inorganic P complex of limited stability. Clays entering the estuary in the freshwater inflow would then lose P as they are transported through waters of increasing salinity to the mouth of the estuary.

69. KINETIC STUDY OF PHOSPHATE REACTION WITH ALUMINUM OXIDE AND KAOLINITE. Y.S. Chen, J. N. Butler, W. Stumm, Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass. 02138.

The kinetics of phosphate reaction with Al_2O_3 and kaolinite involves two steps (1) an initial rapid step, (2) a following slower step (after 24 hours). In the rapid step, phosphate quickly adsorbs on Al-OH surface sites or is precipitated by available positively charged aluminum ions. In the slow step, phosphate reacts with the aluminum which dissolves from aluminum oxide or kaolinite and forms a new aluminum phosphate solid phase. The formation of hexagonal crystals of a new solid phase was verified by electron microscopy. The x-ray diffraction pattern showed lines which are probably due to an aluminum phosphate.

The heterogeneous reactions of phosphate with Al_2O_3 and kaolinite in acid solution after the initial rapid removal step can be described by the first order form

$$-d[P]/dt = K_{obs}[P]$$

where $[P]$ is the total soluble phosphate and t is time. The observed specific rate constant (K_{obs}) is higher for lower pH, higher surface areas and higher temperatures. At high pH (approx. pH 7-8) there is adsorption but essentially no aluminum phosphate precipitation. The slow step reaction rate for a second phosphate addition was higher than for the first phosphate additions. For the Al_2O_3 system, a fluoride ion concentration of 1×10^{-4} M decreases the degree of phosphate removal in the initial rapid step, but does not decrease the rate in the following slower step.

Successive additions of phosphate to the Al_2O_3 -phosphate and kaolinite-phosphate systems show that the amount of phosphate removal in the initial rapid step decreases with each addition of phosphate. This indicates the degree of surface saturation by phosphate and the relative scarcity of exchangeable aluminum in solution.

70. SPECIFIC ADSORPTION OF PHOSPHATE AND SILICATE AT HYDROUS ALUMINUM OXIDE/ELECTROLYTE (0.1M NaCl) INTERFACE. Chin-pao Huang, (Department of Civil Engineering, Wayne State University, Detroit, Michigan 48202) and Werner Stumm (ZAWAG-ETH, Zurich, Switzerland).

The adsorption characteristics of ortho-phosphate and mono-silicate species on hydrous $\gamma\text{-Al}_2\text{O}_3$ surface from dilute aqueous solutions (10^{-4} M to 10^{-6} M) at constant ionic

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strength (0.1M NaCl) is reported. Phosphate and silicate ions are strongly adsorbed onto either positively or negatively charged hydrous aluminum oxide surfaces, resulting in a release of protons. The amount adsorbed is apparently pH dependent with a maximum at 4.5 for phosphate and 9.0 for silicate. In general, the rate of adsorption is a function of suspension pH, total solute concentrations, and total solid surface; the addition of divalent cations (Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+}) has little effect on modifying the extent of adsorption at 1:10 level, but enhanced adsorption is observed with increase cation concentration (1:1). The mechanism of adsorption can be primarily described by the Grahame-Stern model of ionic double layer.

71. THE MECHANISM OF CRYSTAL GROWTH OF CALCIUM PHOSPHATES. G.H. Nancollas and J.S. Mefel; Chemistry Department, State University of New York at Buffalo, Buffalo, New York, 14214.

The precipitation and dissolution of calcium phosphates frequently pose important problems in natural water systems. Their solution depends upon an understanding of the mechanisms of these processes and the ways in which they can be controlled. Most previous studies have been concerned with spontaneous precipitation experiments which are complicated by the fact that nucleation and crystal growth occur simultaneously. In our work, we have studied the kinetics of crystal growth of both dicalcium phosphate dihydrate (DCPD) and hydroxyapatite (HAP) under reproducible conditions of seeded crystal growth. The growth kinetics of DCPD has revealed a second order dependence of rate upon relative supersaturation whereas dissolution is first order with respect to subsaturation. The remarkable growth inhibiting effects of adsorbed additives such as pyrophosphate ions can be interpreted in terms of a simple Langmuir type adsorption isotherm as an effective blocking, by adsorption, of the active growth sites at the crystal surface. The growth of HAP takes place through the formation of one or more precursors having a calcium:phosphate mole ratio appreciably lower than that required for the final crystalline product. The effects of additives such as phosphonate, magnesium and other metal ions upon the crystal growth will be discussed.

72. THE EFFECT OF PHOSPHATES AND PHOSPHONATES ON NUCLEATION AND CRYSTAL GROWTH OF CALCIUM CARBONATE. N.M. Reddy and G.H. Nancollas; Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214.

Characterization of the rates and mechanism of calcium carbonate crystal growth have been performed using a highly reproducible seeded growth technique. Results of these investigations indicate that the rate determining step in the growth of calcium carbonate, a common sediment in natural water systems, is a surface controlled reaction. Precipitation of calcium carbonate in the presence of certain phosphates and phosphonates may play a role in phosphorus exchange between natural waters and sediments. Seeded crystal growth experiments have been carried out in solutions with phosphorus containing ions. Results of these experiments show that both the nucleation and crystal growth rates of calcium carbonate are markedly reduced by low concentrations (10ppm) of several phosphonate or phosphate ions. In addition, striking changes in calcite crystal morphology have been observed during spontaneous precipitation of calcium carbonate in the presence of these ions. These results have been interpreted in terms of an adsorption process involving blockage of crystal growth sites on the calcite surface by phosphonate and phosphate ions. This adsorption mechanism may be responsible for both (1) the decreased rates of nucleation and crystal growth of calcium carbonate and (2) the removal of phosphorus containing ions, in natural waters supersaturated with calcium carbonate.

THURSDAY AFTERNOON - SECTION B - GENERAL - J. L. Monkman, Presiding

73. AN AUTOMATED INSTRUMENT FOR THE SPECIFIC DETERMINATION OF AMBIENT H_2SO_4 AEROSOL. S. C. Barton, R. G. McAuley, Department of Physical Chemistry, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

A sensitive and selective method for the automated measurement of ambient H_2SO_4 aerosol levels over one-hour intervals with a detection limit of ~0.02 ppb is described. H_2SO_4 aerosol is collected, together with other particulates, on an inert Nuclepore polycarbonate membrane filter, then selectively eluted with 1-propanol for analysis by the barium chloranilate method. After color development occurs in a stirred reactor, the excess reagent is removed by filtration and the absorbance is measured with a double-beam UV photometer. Experiments have shown a collection efficiency of ~95% in the ppb range for a synthetic H_2SO_4 aerosol with mass median dia-

metry of 0.7%. Oxidation of SO_2 on the filter is not a problem, nor are other gaseous pollutants retained by the filter. Interference from other particulate material is eliminated by selective elution of the H_2SO_4 from the total particulate sample and buffering of the colorimetric system. Buffon with i -propanol has been shown to remove H_2SO_4 selectively from filters containing sulphate salts in amounts several times greater than amounts reported in typical atmospheric particulate samples. Four months of field operation in downtown Toronto have proven the basic concept of the method and the design of the prototype instrument. Average H_2SO_4 aerosol concentrations measured were significantly lower than those reported from other North American cities. The measured H_2SO_4 aerosol concentrations show a significant correlation of concurrent SO_2 concentrations, but do not bear any fixed relationship to the total sulphate content of high-volume suspended particulate samples.

74. REACTIVITIES OF COMPLEX MIXTURES OF HYDROCARBONS AND NO . S. L. Kopiczynski and E. L. Kunze, EPA, NERC, BCP, Research Triangle Park, North Carolina, 27711.

Because of interactions between pollutants, results from photochemical studies of mixes of individual hydrocarbons with NO may not be generally valid for predicting reactivities of complex mixtures. In order to better predict the effects of various hydrocarbon and NO emission controls in the real atmosphere, photochemical studies were carried out using a simulated atmospheric hydrocarbon mix.

The hydrocarbon mixes consisted of acetylene, 5 paraffins, 6 olefins, and 5 aromatics in proportions found in the Los Angeles atmosphere.

The complex mixtures of hydrocarbons and NO in air were reacted for 5 1/2 hours in a large irradiation chamber using ultraviolet fluorescent lamps. The hydrocarbons were reacted at concentrations of 5, 10, and 20 ppmC in mixes containing 1/2 or 1 ppm NO . Rate of oxidation of nitric oxide, nitrogen dioxide dosage, hydrocarbon consumption, eye irritation, and yields of peroxyacetyl nitrate, formaldehyde, and oxidant were measured.

The effects of changes in hydrocarbon composition and hydrocarbon concentration on the various measures of photochemical reactivity were evaluated.

75. X-RAY FLUORESCENCE ANALYSIS OF AIR POLLUTION PARTICULATES.

J. V. Gilfrich, P. C. Burkhalter, L. S. Birks, Naval Research Laboratory, Washington, D. C. 20390 and J. Wagman, Environmental Protection Agency, Research Triangle Park, N. C. 27711.

X-ray fluorescence analysis is a very rapid and efficient tool for analysing the particulate matter filtered out of ambient air or from the effluent gases of pollution sources. The sample collected on filter paper can be used directly as the x-ray specimen because its mass is small and therefore the contribution to background by the scattered primary radiation is minimized. Because the particulate sample is thin matrix effects are negligible, at least to a first approximation.

Measurements have been made to establish sensitivity and detection limits for x-ray tube excitation and crystal spectrometer measurement, as well as for energy dispersion analysis using x-ray tubes, first fluorescers, radioisotopes, and ions (protons and alpha-particles) to excite the samples. Detection limits were the best for proton excitation - one to a few ng/cm^2 in 100 secs - but required that the specimen be deposited on a thin nitrocellulose or carbon film which is not practical for routine analysis. Detection limit for x-ray tube excitation is a few tens of ng/cm^2 in 100 secs, using either a crystal spectrometer or a solid state detector, making the technique suitable for analysis of a wide variety of sample types and elements of interest.

76. EFFECT OF pH ON THE STOICHIOMETRY OF THE IODOMETRIC DETERMINATION OF OZONE. Russell M. Diele, Jacob Frazzansky, and James D. Smith, Brookhaven National Laboratory, Department of Applied Science, Upton, New York 11973.

The reference technique for the determination of oxidants in the air is the neutral buffered potassium iodide procedure assuming a 1:1 stoichiometry. A spectrophotometric analyzer, which measured the absorbance

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due to ozone in the ultraviolet at 254 nm, was calibrated absolutely by measuring the increase in pressure resulting from decomposition of 1 to 3% ozone in oxygen mixtures; the ratio of spectrophotometrically measured O_3 to absolute determination was 1.00 ± 0.03 . The analyzer was then used to determine the stoichiometry of the ozonide reaction using 1 and 2% KI buffered solutions at pH from 4 to 14 for ozone concentrations ranging from 50 to 600 ppm. The stoichiometry (ratio of spectrophotometric to KI determined ozone) at various pH were: 0.80 ± 0.10 at 14.0; 0.93 ± 0.05 at 12.0; 1.00 ± 0.02 at 9.18; 1.04 ± 0.01 at 6.86; and 1.07 ± 0.05 at 4.01. Using a midjet impinger, a calibrated colorimetric procedure based upon measurement of the iodine-starch color at 440 nm, and air containing 0.1 ppm O_3 collected at 2.5 liters/minute, the stoichiometry was confirmed to be 1:1 for neutral buffered KI determination of ambient ozone.

77. AN ALIPHATIC ALDEHYDE COLORIMETRIC DETECTOR FOR GAS CHROMATOGRAPHY. John M. Gray and Paul Urrue, Environmental Engineering, University of Florida, Gainesville Florida 32601.

A flowing colorimetric detector for aliphatic aldehydes has been built using the 3-methyl-2-benzothiazolone method of Hauser & Cummins (Hauser, T. R., Cummins, R. L., *ANAL. CHEM.* 36, 679 (1964)) and Sawicki et al. (Sawicki, E., Hauser, T. R., Stanley, T. W., Elbert, W., *ANAL. CHEM.* 33, 93 (1961)). This detector has been coupled to a dual-channel gas chromatograph with a flame ionization detector. Using this system it has been possible to simultaneously analyze aliphatic aldehydes in the presence of other oxygenated compounds and hydrocarbons without the need for previous derivatization or extensive flow switching mechanisms. The flowing liquid colorimetric detector has been studied at various operating conditions and in various configurations to determine the optimum response, sensitivity and detection limit. Sensitivity is in the microgram range with extension to submicrogram quantities being possible. The combined gas chromatograph-flowing liquid colorimetric detector has been used to study some reactions of aldehydes and hydrocarbons with mixtures of NO and SO in air. Attempts have been made to determine rates of reaction for aldehydes in air and to correlate these with other studies.

78. MAINTAINING AIR QUALITY IN THE VICINITY OF THE SMELTER. F. Francis, INCO, Toronto-Dominion Centre, P. O. Box 46, Toronto 111, Ontario, Canada.

Three smelters in the Sudbury area, two owned by INCO, produce 60% of the free world's nickel. The smelters treat sulfide ore, releasing sulfur dioxide to the atmosphere. In 1956, a network of 10 SO_2 monitors was established within a 40 mile radius of Sudbury. This network has later expanded to include three fixed and one mobile station in Sudbury. Again later, INCO designed a warning system to detect deteriorating air conditions. In creating the API, which is based on SO_2 and suspended particulate matter, the Ontario Government assumed similar air systems affected London, U.K., New York, Osaka, Detroit and the industrial cities of Ontario. At API of 50, the Government may request a production cut-back. To hasten cut-back, time can be saved only in stack-to-detection, and this by eliminating from API the COH factor. Cut-back does not correspondingly reduce ground-level SO_2 concentration, since a cooler gas and lower plume rise is produced. Heating of stack gas is required. Incorporating this feature, INCO in March, 1971, inaugurated a warning system, and the record of Sudbury's air quality is now better than that of Toronto or Hamilton.

79. THE UTILIZATION OF AN URBAN AIR POLLUTION MODEL IN AIR MANAGEMENT. L. Shenfeld, A. E. Boyer, Ontario Ministry of the Environment, Air Quality Branch, 880 Bay Street, Toronto, Ontario, Canada.

A mathematical simulation model has been completed for the urban atmosphere of Metropolitan Toronto and has been in usage by Ontario Ministry of the Environment, Air Quality Branch, for the past year. Emission data of five pollutants - sulphur dioxide, carbon monoxide, hydrocarbons, nitrogen oxides and suspended particulate matter - have been treated for three types of sources - point sources, area sources and line sources.

A point source is a major source in terms of quantity of emission, normally a large combustion or industrial processing plant. The area source sums a large number of small emissions, such as from home heating. Line sources are used to model emissions from major expressways. The output of the model is a prediction of air quality. Normally, this output is in the form of a contour map with the isopleths joining points of equal concentrations for a specific time of day. A number of these predictions will be presented and discussed. This paper will discuss the usage of the atmospheric simulation model as a planning tool in an air management programme. Planning strategies to best insure air quality goals include consideration of variable land usage, urban development, industrial expansions, abatement programmes for point and mobile sources, locations of such sources as airports, traffic arteries, incinerators, power stations, and degrees of control on the sulphur content of fuels.

80. FLUX FORCE SCRUBBERS - AN ENGINEERING ANALYSIS. Jhuda Goldshmid, David Loith - APT Inc., P. O. Box 71, Riverside, Ca. 92502 and Seymour Calvert, University of California, Riverside, Ca. 92507.

Collection efficiency of particles in wet scrubbers reaches a minimum for the range 0.1- μ m in diameter. Particles in this size range are too small to be collected efficiently by inertial forces, and too large to be collected efficiently by Brownian diffusion forces. One way to increase collection efficiency of particles in this range is to supplement inertia by additional forces which do not approach zero at the 0.1- μ m particle size range. Among such forces are the diffusio-phoretic and thermophoretic forces, which are part of the group called flux forces. The magnitude of these forces is directly proportional to the condensing vapor concentration and to the temperature gradient, respectively. Thus a detailed analysis of the magnitude of flux forces in scrubbers and their variation with residence time, requires the knowledge of change of temperature and vapor concentration gradients with time and position inside the scrubber.

The collection efficiency for basic geometrical configurations (such as bubbles, drops, or liquid sheets) was calculated for combinations of inertial, diffusion and flux forces. Predictions were made for the increase in collection efficiency of various scrubbers using bubbles, drops or liquid sheets. The effect of the system physical properties on collection due to flux forces was also shown.

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81. GAS CONTENT OF AIRBORNE PARTICULATE MATTER. R. C. Leo, R. S. Thomas and L. Dubois. Air Pollution Control Div., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

Air pollutants emitted to the atmosphere can react with other pollutants or with normal constituents of the atmosphere. Consequently, their effect as polluting agents can be completely different from what could be expected as originally emitted. Since particulate matter can act as a catalyst for some of these reactions, it seems appropriate to identify the presence of gases adsorbed and absorbed on the dust. Experimentally, four different samples of dust were placed in a high vacuum system and the gases were desorbed at four temperatures, room temperature, 50° C, 150° C and 250° C. The desorbed gases were collected in liquid nitrogen traps and analyzed by mass spectrometry.

82. SAMPLE TREATMENT AND PREPARATION IN THE ACCURATE MEASUREMENT OF METALS IN THE ANALYSIS OF AIR POLLUTANTS. L. Ruhoff, J. C. Hilborn, and J. L. Monahan, Air Pollution Control Div., Environmental Health Centre, Tunney's Pasture, Ottawa, Canada.

Since the quantities of metals in airborne pollutants may be low, it can be difficult to obtain an accurate measurement. When shorter than usual sampling times are used, proportionately less material may be captured, putting an additional strain on the analytical sensitivity. An example might be the change from 24 hour sampling by high volume instrument to a 2 hour sample taken on paper tape. As the sample available decreases in amount, the care or lack of care taken in sample preparation becomes increasingly important as does the filter and/or reagent blank. The analyst must be assured that the metal is in a form which can be extracted or made available for measurement. The impurities present in the sampling medium and in the reagents must be under control at all times. Illustrations are given of the large scale accurate analysis of such airborne metals using atomic absorption and polarography. The sensitivity, accuracy and precision of such measurements are discussed.

WATER

83. AN EFFICIENT SEPARATION OF BENZO(a)PYRENE FROM BENZO(k)FLUORANTHENE AND THEIR FLUOROMETRIC DETERMINATION IN AIR SAMPLES. E.G. Adamk, Government of Ontario, Dept. of the Environment, 880 Bay St., Toronto, Ont. Canada.

The suitability of various organic solvents as extractants for polynuclear hydrocarbons from particulate air samples was investigated by determining extraction efficiencies and effects on fluorescence by these solvents. For the fluorometric determination of Bap in air sample extracts, its isolation from compounds of similar fluorescence is necessary, but difficulties are invariably caused by the presence of BkF. Separation of BkF from Bap was only possible by elaborate and time-consuming procedures which are unsuitable for large-scale analytical surveys. However, by a fluorometric approximation technique, the interference from the presence of BkF can be minimized, provided that Bap does not greatly exceed the amount of BkF. A generally more applicable method of determining Bap is now reported. A chromatographic procedure has been developed by which Bap and BkF can be separated from each other in a one-step operation directly from the sample extracts. Subsequent or simultaneous fluorometric analysis of these two compounds can be done without mutual interference. After surveying these compounds in the air of eight urban communities in Ontario, attempts have been made to correlate differences and changes in their levels with a number of environmental conditions, such as sampling location, wind direction, amount of dust, seasonal variations, and others.

84. A DILUTION DEVICE FOR COUPLING MONITORS TO SOURCE EMISSIONS. James B. Homolya & Robert J. Griffin, Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, N. C., 27711.

The coupling of continuous gaseous source monitors to stacks or ducts usually requires some degree of sample conditioning. Conventional techniques involve extracting a stack gas sample via a probe and transporting the sample to analyzers through heated inert tubing to prevent moisture condensation and loss of sample. The tubing must be either steam-traced or electrically heated. Particulate matter is usually filtered at the probe inlet and moisture present in the sample line (often 10-12% H₂O) is removed at the monitor by condensation. Such methods are costly and still suffer from varying degrees of sample losses. A novel device has been designed and constructed to eliminate the problem of moisture condensation and particulate entrainment by diluting the gas sample immediately within the stack environment. A rotating perforated-disc placed in the stack gas atmosphere is used to extract a small volume of gas which is mixed with a metered stream of diluent. The mixture can then be analyzed directly by ambient air or source-level monitors without the need of heated sample lines, particulate filters or refrigerated driers. A prototype of the disc-dilutor has been designed to encompass a range of dilution ratios of from 10:1 through 1500:1. The device can be readily inserted through any standard 3" sample port and requires minimal maintenance. The choice in using an ambient or source level monitor and the appropriate diluting ratio is dependent on the initial pollutant concentration as well as the moisture and particulate levels. Laboratory and field studies have been carried out using both ambient and source level SO₂ monitors.

85. AN IMPROVED METHOD FOR THE CONTINUOUS ANALYSIS OF ATMOSPHERIC ALIPHATIC ALDEHYDES. S. C. Barton, E. N. Turner, Department of Physical Chemistry, Ontario Research Foundation, Sheridan Park, Ontario, Canada.

Aldehydes and ketones, although major and detrimental products of photochemical air pollution processes, have not been studied extensively. There are no satisfactory continuous measurement methods for either total carbonyls or individual aldehydes or ketones. A continuous adaptation of the 3-methyl-2-benzothiazole hydrazone (MBTH) method, the most widely used and recommended reference method for total carbonyls, is described. Air is sampled continuously through a submerged jet into a spherical, spray-type scrubber which provides essentially 100% collection efficiency. Long color development time, bubble formation and solution turbidity were the major problems encountered in using the static MBTH method. In the continuous method, the use of increased temperature results in the formaldehyde-MBTH reaction and subsequent color development being completed in approximately 3 minutes. Bubble formation and turbidity have been eliminated by replacing the usual oxidizing solution, ferric chloride, with an acidic ceric ammonium sulphate solution. This also provides a self-cleaning action which eliminates solid deposition in the spectrophotometer cells. A small multiple-

channel penstatic pump is used to meter the reagents and to maintain a smooth and constant liquid flow through the system. With an air sampling rate of 2 l. min^{-1} and an air/liquid contact ratio of 1000:1, the detection limit of the method is $5 \mu\text{g. m}^{-3}$ (as formaldehyde), compared with reported average concentrations of $50 \mu\text{g. m}^{-3}$ in urban areas.

86. MONITORING CARBON MONOXIDE IN AMBIENT AIR. Robert S. Ajemian, Great Lakes Steel Ecorse, Detroit, Michigan, 48229.

Interest in ambient carbon monoxide levels resulted from the concern over the establishment of air quality standards. Due to this interest, a method was developed utilizing equipment available in most laboratories engaged in an air sampling program. The method does not require the purchase of infrared detection systems, will yield reliable data, and uses a sequential air sampler and plastic bags.

Samples were collected in the plastic bags over a twenty-four hour period and returned to the laboratory for analysis. The concentration of carbon monoxide in the sampling bags was determined by the catalytic conversion to methane and analyzed using a gas chromatograph with a flame ionization detector. A comparison of ambient carbon monoxide levels obtained using this sampling technique and the infrared analyzer will yield comparable results. Although the carbon monoxide concentration was determined by gas chromatography, the analysis could be made with infrared equipment if available.

87. COMPARISON OF ANALYTICAL METHODS TO MEASURE AMBIENT CONCENTRATIONS OF NITROGEN DIOXIDE AND NITRIC OXIDES. R. K. Stevens, T. A. Clark, R. Baumgardner, and J. A. Hodgson. ENVIRONMENTAL PROTECTION AGENCY, National Environmental Research Center, Research Triangle Park, N. C. 27711.

Recently, the Environmental Protection Agency has developed two chemiluminescent procedures that are capable of measuring sub-part-per-million concentrations of nitrogen dioxide (NO_2) and nitric oxide (NO). Both procedures are based on the chemiluminescent reaction of NO with ozone (O_3), supported by the conversion of NO_2 to NO . One technique is designed to operate at 1 to 5 Torr pressure, whereas the second method measures the luminescent reaction of NO and O_3 at about 300 Torr. These two procedures are compared with the classic colorimetric Saltzman and Jacob-Hochheiser methods. Other principles evaluated during this study were based upon second-derivative spectroscopy in the visible region, (4480 Å) and upon microcoulometry.

Correlation of measurements between instruments, in addition to a detailed study of maintenance requirements, calibration stability, and typical response patterns, will be presented.

88. STANDARD REFERENCE MATERIALS FOR AIR POLLUTION AND GAS ANALYSIS. Ernest E. Hughes and John K. Taylor, Microchemical Analysis Section, Analytical Chemistry Division, National Bureau of Standards, Washington, D. C. 20234.

The increasing importance of the analytical chemistry of the atmosphere and its natural and unnatural components has emphasized a critical shortage of gaseous standard reference materials. The National Bureau of Standards is engaged in a program to produce such reference materials for a number of major constituents and pollutants. A number of materials are currently being investigated and a smaller number have already been made available as NBS Standard Reference Materials. Oxides of nitrogen, high concentrations of sulfur dioxide, carbon monoxide in air and propane in air are nearing completion while atmosphere concentration of oxygen and carbon dioxide, and methane in air are already available. Sulfur dioxide permeation tubes are also available. The lack of extensive data concerning the stability of gas mixtures and the need for development of methods of sufficient accuracy for primary certification and methods of sufficient speed and precision for final certification are among the factors which results in a long delay between recognition of the need for such standards and the final distribution. In some cases special containers and devices are required to produce satisfactory standards. An important part of the development of standards of this type is long term stability. The history of gas mixtures up to five years of age have been compiled.

WATH

89. EVALUATION OF NEW OZONE MONITORING INSTRUMENTS FOR MEASUREMENTS IN NONURBAN ATMOSPHERES. T. A. Clark, R. Baumgardner, K. Krost, and J. K. Stevens. ENVIRONMENTAL PROTECTION AGENCY, National Environmental Research Center, Research Triangle Park, N. C. 27711.

The chemiluminescent reaction between ozone and ethylene is the reference method cited in the April 30, 1971, Federal Register for the measurement of ambient concentrations of ozone. Three new analytical procedures capable of measuring sub-part-per-million concentrations of ozone have recently become commercially available and are being considered as alternate methods. The measurement principles are based on: (1) measuring the second derivative of the absorbance of ozone with respect to wavelength at 2635 Å; (2) direct measurement of the attenuation of the 2567 Å band ascribable to ozone; and (3) the decomposition of ozone on an aluminum surface, which produces light energy proportional to the ozone concentration. This report describes the general performance characteristics of each of these new monitoring procedures and correlates their response to ambient concentrations of ozone to that of the reference method. Descriptions of calibration procedures and stability as well as typical response patterns of the several monitoring principles are presented.

90. FINE PARTICLE EMISSIONS FROM AUTOMOTIVE EMISSIONS CONTROL CATALYSTS - PRELIMINARY INVESTIGATION - William D. Balgord, Research & Development Unit, New York State Department of Environmental Conservation, Albany, New York 12201.

High number concentrations ($>10^6$ particles/cc) of condensation nuclei have been induced from stabilized catalysts containing chromium, copper, and nickel under conditions similar to that of automobile exhaust. Small samples of commercial formulations previously evaluated for NO_x reduction, as well as catalysts prepared in the New York State D.E.C. laboratory, have been investigated and found to emit fine particles under a range of controlled conditions: 150 to 600°C, in 3% CO in N_2 and in synthetic automobile exhaust (pulsed flame combustor product stream) at flow rates of approximately 500 cc/minute. It is postulated that metal carbonyl formation may occur at the lower temperature ranges. Metal carbonyls, being unstable at moderately elevated temperatures, decompose leaving finely divided metal or metal oxide particles depending on the prevailing oxygen partial pressure. The fine particles are detected with a condensation nuclei detector which counts all submicron sized particles larger than about 30Å diameter. Subsequent experiments with GE Research and Development Center using surface ionization interfaced with magnetic sector mass spectrometry demonstrated conclusively the emission of the fine chromium containing particles from a commercial copper chromite and corroborated our initial observations suggesting potentially hazardous particle emissions from certain catalysts being considered for use in automotive emissions control systems.

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