



Project Summary

**Proceedings:
Second Symposium on
Process Measurements for
Environmental Assessment
February 25-27, 1980**

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Philip L. Levins, Judith C. Harris, and Karen D. Drewitz

This report is a summary of the proceedings of the Second Symposium on Process Measurements for Environmental Assessment held in Atlanta, GA, February 25-27, 1980.

The symposium focused on the state-of-the-art of sampling and analysis techniques that are appropriate for process measurements in the context of an environmental assessment program. It included methods for qualitative and quantitative chemical characterization of organic and inorganic species in process and discharge streams and biological assays of environmental samples. The symposium represents a continuing effort on the part of the Process Measurements Branch of the EPA's Industrial Environmental Research Laboratory at Research Triangle Park, NC, to share recently developed methodology and encourage the interchange of ideas among researchers in government, industry and academia. Topics included:

- Use of sorbents for sampling.
- Sampling of reactive species.
- Sampling and analysis methodology for coal conversion processes.
- Advanced inorganic analysis techniques.
- Advanced organic analysis techniques.

- Application of bioassay methods to complex samples.

The interchange of information was accomplished through the presentation of 22 papers and through a poster session. The poster session was an experiment at this symposium that proved very successful. Twelve research groups were provided space during one evening session to display posters outlining their research programs. Leaders involved in the 12 programs manned the exhibits and responded to questions by attendees on an informal basis.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Summaries of the speakers' remarks follow:

M. R. Guerin, Analytical Chemistry Division, Oak Ridge National Laboratory

Guerin discussed disciplinary approaches to program objectives, emphasizing the integrated approach to chem-

ical/biological analysis. He stated that, while environmental and health assessments are increasingly dependent on the results of biological testing, biological testing, in turn, is becoming increasingly dependent on physical and chemical assistance to achieve reliable and interpretable results. Examples of ongoing programs related to environmental assessments were presented by Guerin to indicate the nature of the products generated at various levels of interaction. He identified the three approaches to program objectives as the independent, the interactive, and the integrated approaches. Guerin explained that the most effective approach to an integrated chemical/biological program requires that each level of interaction be present and that the collaborating groups give the programmatic objective as much attention as is given to disciplinary concerns.

A. R. Kolber, Research Triangle Institute

Kolber described results of a study of the toxic potential of coal gasification byproducts and effluents. He also recommended future bioassay study needs in support of a major synfuels industry. Kolber explained that the study indicates that simple bioassay of crude complex mixtures, such as effluent tar and oils, may not provide an accurate estimation of potential health risk when these mixtures contain highly bioactive minor substituents, or when antagonistic reactions within the mixture mask actual mutagenicity and/or toxicity.

Kolber summarized recent progress in sampling, chemical analysis, and bioassay methodology development for synthetic fuel process effluents (complex mixtures). He characterized the various streams and effluents of environmental significance regarding potentially hazardous substances, and he specified bioassay tests for various types of samples.

J. C. Harris, Arthur D. Little, Inc.

Harris gave results of a systematic laboratory investigation of the applicability of macroreticular resins for general and compound-specific sampling of organics from water, based on small-scale chromatographic experiments. She explained that the objective was to develop screening procedures and a data base that would allow selection of the resin(s) best suited to a particular sampling application and selection of a sampling module size/configuration

that gives quantitative collection of contaminant(s) from the aqueous stream of interest. Harris described the experimental approach which involved quantitative characterization of sorbent/sorbate systems by frontal chromatographic analysis of breakthrough and measurement of recovery. Effects of sample flow rate, sorbent type, organic compound type, and (to a limited extent) sample matrix have been considered and were also described.

Harris concluded by reporting that a mixed resin cartridge, incorporating XAD-2 for collection of non-polar organics and XE-347 for collection of polar organics, has been tested and appears promising for full-scale sampling applications.

W. F. Gutknecht, Systems and Measurements Division, Research Triangle Institute

Gutknecht detailed the approaches to measurement and interpretation of infrared (IR) and low resolution mass spectra (LRMS) taken by four EPA contractors following the guidelines of the Level 1 Environmental Assessment Program. He also discussed the mechanism of evaluation which involved supplying each contractor with test spectra and samples for analysis and interpretation. Using IR, the contractors identified 55 to 85 percent of the structural moieties present in the various samples, and, using LRMS, the contractors identified 50 to 90 percent of the compound classes represented.

The sources of error in IR and LRMS measurement and interpretation were identified, and Gutknecht suggested methods to improve data quality and interpretation. He stressed that thoroughness of interpretation is most important for accuracy of the IR analyses. Recommendations to improve LRMS data quality include using the reference series *Eight Peak Index of Mass Spectra*, setting intensity and mass/charge range criteria to simplify spectra, using the LC fraction data with caution, and analyzing IR and LRMS data independently to avoid bias.

K. W. Lee, Radian Corporation

Lee described characterization of coal gasification by-products and ambient air samples taken from a Lurgi gasification facility in the Kosovo Region of Yugoslavia. Primary by-products, organic vapors, and particulate-borne organics were analyzed for sulfur- and nitrogen-containing organic compounds

using selective-detector gas chromatography. The main problem was correlating the emissions from the gasification plant with the components found in the ambient air samples.

Lee discussed the phased analytical approach that was developed to solve the correlation problem. The methods verifications, and quality controls were discussed and the application of these methods to the Lurgi gasification facility was outlined. According to Lee, selective detection revealed a positive correlation between sulfur- and nitrogen-containing compounds in the primary by-products and the ambient air samples. Relative quantification and tentative identification of the major sulfur- and nitrogen-containing compounds was established by comparison with standards and by peak enrichment techniques. These identifications were confirmed by GC/MS.

Bruce W. Farnum, Grand Forks Energy Technology Center, U.S. Department of Energy

Farnum discussed the characterization of process streams from the liquefaction of low-rank coal with synthesis gas (1:1 CO:H₂). He identified the process streams obtained and described the methods of analysis chosen for each stream. Reaction conditions were also specified. The characterizations of the water effluent, the light oils, and the heavy oils were described in detail by Farnum.

J. M. Giddings, Environmental Sciences Division, Oak Ridge National Laboratory

Giddings described the 4-hour photo synthesis test which is a rapid bioassay to measure the effects of coal-derived materials on algal photosynthesis. Researchers at Oak Ridge National Laboratory developed the test as part of an overall program to assess the potential environmental hazards of coal conversion technologies.

Giddings explained that algal culture or natural algal communities are exposed to the test materials for 4 hours. Photosynthesis is determined by the ¹⁴C-bicarbonate method during the final 2 hours of exposure and compared with controls for a measure to toxicity. In bioassays with individual aromatic compounds, quinones and aromatic amines were found to be particularly toxic to algae; azarenes and thiophene were the least toxic classes tested.

Experiments with the water soluble fractions (WSFs) of more than 20 natural and synthetic oils showed that coal liquefaction products are considerably more toxic than petroleum products; shale oils are intermediate in toxicity. Further studies with particular subfractions of several WSFs have identified ether-soluble bases as the major contributors to the toxicity of coal-derived oils.

Giddings also reported on and explained the advantages that the 4-hour photosynthesis test has over the Algal Assay Bottle Test for measuring the toxicity of complex materials.

V. A. Fassel, Ames Laboratory (U.S. Department of Energy) and the Department of Chemistry (Iowa State University)

Fassel described the direct determination of benz(a)pyrene and other polynuclear aromatic hydrocarbons (PAHs) in SRC II, a coal liquid and a sample of shale oil by the utilization of laser-excited Shpol'skii effect spectroscopy (LESS). This is a simple and less elaborate approach than the existing methodologies which require that individual compounds or a small group of compounds be isolated by utilizing high performance liquid chromatography, capillary column gas chromatography, or thin layer chromatography. Detection and quantitation of the isolated PAH compounds is usually performed by mass spectrometry or luminescence spectrometry. In contrast, LESS allows the determinations to be accomplished without prior isolation of the compounds.

Fassel explained that less of PAHs in n-octane, frozen to a solid at 15 K, has been utilized to achieve: (1) site selected luminescence of a PAH compound, (2) selectively excited luminescence of any individual alkylated benz(a)anthracene present in a mixture of multialkylated benz(a)anthracenes, and (3) quantitate selected PAHs including benz(a)pyrene in diluted samples of SRC II and shale oil.

T. Vo-Dinh, Health and Safety Research Division, Oak Ridge National Laboratory

Vo-Dinh reported on a study to gauge how well certain rapid, easy-to-use, and cost-effective luminescence techniques can be employed for the analysis of polynuclear aromatic (PNA) compounds. Two luminescence techniques were considered; synchronous luminescence (SL) spectroscopy of solutions at room

temperature and room temperature phosphorimetry (RTP).

Vo-Dinh described the analysis carried out on 13 polynuclear components in a liquid chromatography fractionated XAD-2 extract from Source Assessment Sampling System runs. This same sample was used in an interlaboratory evaluation of current Environmental Protection Agency Level 1 organic analysis procedures. Comparative results show that SL and RTP provide data that are of more than adequate quality for Level 1. These techniques should also be seriously considered in the development of Level 2 organic analysis procedures.

Vo-Dinh also gave an example of the use of luminescence for rapid screening of an unfractionated coal liquefaction product for a major PNA component.

D.L. Stalling, Columbia National Fisheries Research Laboratory, U.S. Fish and Wildlife Service

Stalling summarized the application of a series of modular chromatographic enrichment procedures designed to be integrated into an automated sequential system, controlled by a microprocessor, for fractionation of complex residues extracted from environmental samples. Stalling reported that complex multiclass residues are usually encountered in the analysis of environmental samples for organic contaminants. Analyses of this type can be facilitated by a comprehensive approach, including fractionation of contaminants by class. He described the three modular chromatographic procedures developed and tested in an effort to provide such a procedure: gel permeation chromatography (GPC), cesium silicate chromatography (CsSC), and dispersed-carbon chromatography. These procedures have enabled detection of chlorinated dibenzofurans, terpenes, naphthalenes, and phenolics in addition to the common organochlorine pollutants in fish samples by electron capture gas chromatography (EC-GC), negative ion mass spectrometry (NI-MS), and conventional GC/MS.

D.C. Tigwell, Illinois Environmental Protection Agency

Tigwell described the design and construction of a multichannel, remote-controlled, Teflon-and-glass positive-displacement apparatus and its use for the simultaneous sampling of trace organic compounds on XAD and granular activated carbon. He explained the

sampling theory which led to the conclusion that the type of information which will be most useful for assessing the environmental impact of trace levels of organic compounds is loading data obtained from constant-volume (time-proportioned) composite samples. The theoretical results define the sampling requirements of the composite which consequently specify the operational requirements of the composite sampling device. Tigwell showed how the sampling and operational requirements are met by the new composite sampler.

Tigwell also cited several applications of this apparatus. It has been used to collect samples of raw and finished drinking water, samples from the Illinois River, and from municipal and industrial effluents, including an untreated coal conversion process wastewater. Four radio-controlled units are being used in a nationwide EPA-funded study of the movement of organics through municipal treatment plants.

K.T. Menzies, Arthur D. Little, Inc.

Menzies discussed two ion chromatographic techniques developed to quantify formic and acetic acid in both diesel engine exhaust and mine air subjected to diesel emissions. A commonly reported anion separation system (utilizing a weak borate eluent) adequately separated the acids of interest in diesel exhaust. It was, however, affected by the presence of strong acids during subsequent consecutive analyses.

Menzies explained that, in order to preclude this problem and the necessary frequent regeneration of the anion system's suppressor column, an ion chromatography exclusion scheme was utilized. Samples collected in a mine environment were reliably concentrated by freeze-drying and then analyzed on an ICE system with dilute hydrochloric acid eluent. The precision of the ICE method was experimentally determined to be $\pm 2.5\%$. The accuracy was not independently determined but good precision and recovery yield confidence that measured values are within $\pm 5\%$ of the true value. No interferences were observed in the ICE system due to strong acids, carbonic acid, or other water soluble species present in mine air subject to diesel emissions.

R.P. Baldwin, Department of Chemistry, University of Louisville

Baldwin described and tentatively evaluated a new electroanalytical ap-

proach using chemically modified electrodes for the determination of specific classes of organic compounds. In particular, Baldwin considered a model analytical system applicable specifically for the determination of dissolved aldehydes and ketones.

The method detailed by Baldwin proposes the use of recently developed chemically modified electrodes (CMEs): first to pre-concentrate a specific organic analyte at the electrode surface via a selective chemical reaction; and then to quantitate the subsequent surface-bound reaction product via conventional voltammetric techniques. Baldwin examined the chemical reactivity of the surface-modifying functional groups toward specific classes of organics with respect to the sensitivity enhancement and the gross chemical selectivity that can be imparted by means of the pre-concentration step.

In the example described by Baldwin, for the model analyte ferrocene carboxaldehyde, a detection limit of 10^{-7} M was observed using a pre-concentration time of only 5 minutes. No major interference was observed when the analysis was carried out in the presence of a hundredfold excess of ferrocene.

J. Cairns, Jr., University Center for Environmental Studies and Biology Department, Virginia Polytechnic Institute and State University.

Cairns discussed a computer-interfaced toxicity testing system for simulating variable effluent loading. Mini- and microcomputer interfacing with a toxicity testing system provides a means of systematically varying the concentration of a test chemical or chemicals in a continuous-flow system. The same computer can also be used for the data acquisition system to store the voluminous time-series biological response data necessary for cross correlations with variable chemical concentrations.

Cairns described the instrumentation making such tests feasible and gave an example of a toxicity test on fish using this method. According to Cairns, the apparatus and the results of the test provide compelling evidence that sufficient promise exists for resolving some or all of the problems encountered in simulating "real world" conditions in toxicity testing and for justifying continued research and development of the apparatus.

M. Auyong, Lawrence Livermore Laboratory

Auyong discussed the design and operational experience of the on-line wastewater monitoring system at the Lawrence Livermore Laboratory. This system was developed to monitor the sewage effluent on a continuous basis as a check on control procedures. The monitoring system is designed to detect elevated radiation, metal concentration, and pH levels.

The detection assembly was described by Auyong as consisting of an x-ray fluorescence unit which detects high levels of metals, sodium iodide crystal detectors that scan the sewage for the presence of elevated levels of radiation, and an industrial probe for pH monitoring. With the aid of a microprocessor, the data collected are reduced and analyzed to determine whether levels are approaching established environmental limits. If these levels are exceeded, a sample of the suspect sewage is automatically collected for further analysis, and an alarm is sounded to alert personnel.

Auyong gave examples of instances when the monitoring system has helped to avert treatment plant problems when a spill has occurred.

D.E. Bause, GCA/Technology Division

Bause gave results of an evaluation of four leachate procedures, ASTM Method A, ASTM Method B, EPA/OSW Extraction (EP), and Carbonic Acid Extraction (CAE). They were examined for their general applicability, reproducibility, Environmental Assessment methods compatibility, and leaching power.

Bause explained that the leachates generated by these methods were analyzed for nine metals by atomic absorption methods and for F^- , Cl^- , and SO_4^{2-} by ion chromatography. Seven energy process wastes (including oil shale, FBC waste, fly ash, boiler slag, scrubber sludge, and hopper ash) were extracted to evaluate the general applicability of the leachate tests.

Results described by Bause indicated that the ASTM methods had the best reproducibility, while the EP had the poorest precision. The EP and CAE procedures leached the largest quantities of trace metals from the wastes. However, based on the total metal concentration in the sample, the leachate methods generally extracted $< 1\%$. The EP and ASTM-B methods caused some difficulty with flameless AA analyses.

Based on the Resource Conservation and Recovery Act (RCRA) criteria, five of the energy wastes would be classified as hazardous by at least one of the leachate procedures. Selenium usually exceeded the threshold value for the leachate.

Bause concluded by recommending improvements to the leachate test.

D.J. Brusick, Director of the Department of Genetics and Cell Biology, Litton Bionetics, Inc.

Brusick reviewed sample collection, storage, and pretest handling procedures, and illustrated how the application of these techniques to the specific health effects and ecological tests proposed for Level 1 biological assessment will affect the test responses and ultimately the goals of this program. Level 1 Environmental Assessment Bioassays should permit an accurate ranking of emissions from stationary site sources with respect to their potential hazard. Moreover, the ranking must ensure that the potential hazard is likely to be derived from the emissions as released into the environment and that pretest processing should be kept to a minimum and applied uniformly across all Level 1 bioassays if performed.

Brusick stressed the importance of the sample history in the final interpretations of the test results. He also stressed that Level 1 assessment should include the environmental fate and rate of release of the emission along with the chemical and bioassay toxicity determinations.

D.F.A. Natusch, Colorado State University

Manuscript not available.

G.L. Fisher, Battelle Columbus Laboratories

Fisher described the application of bioassays including bacterial mutagenesis, mammalian lung cell function, and mammalian hematopoietic cell maturation to the study of the biological significant physical and chemical properties of coal fly ash. He discussed the effects of sample collection, particle size, solvent extraction, temperature treatment, and irradiation.

He reported that the results of the study demonstrate the extreme complexity of coal fly ash in terms of matrix composition, morphological appearance, surface trace element, and organic chemical composition. Acute inhalation studies have demonstrated that coal fly

ash may be equally as toxic as alpha-quartz to the pulmonary alveolar macrophage. The feasibility of application of sophisticated cloning techniques for the evaluation of potential lymphohematopoietic effects from complex mixtures has been demonstrated. Mutagens in coal fly ash appear to be absorbed to fly ash surfaces and hence may exist in the environment for relatively long periods of time. Fisher also described new techniques which are being developed to evaluate the carcinogenic potential of coal fly ash and to measure the potential immunotoxicity of fly ash.

K.T. McGregor, GCA/Technology Division

McGregor summarized part of a recent series of studies to evaluate several areas of the Level 1 elemental analysis scheme. The effects of organic matter on elemental determinations by spark source mass spectrography (SSMS), the primary Level 1 elemental analysis technique, were investigated. In addition, several sample preparation techniques were evaluated in terms of efficacious elimination of organic matter without resultant elemental losses or contamination. The utility of the methods as preparation techniques for atomic absorption spectrometry (AAS) measurements (principally Hg) was also assessed.

McGregor reported the Level 1 elemental analysis scheme to be reliable and to provide the kind of information desired from the Level 1 study. Problems were noted with some SSMS determinations and additional work in this area is recommended. The preparation of particulate filter samples for SSMS analysis by the Level 1 Acid Extraction procedure may bias the resulting data. The Modified Hydrofluoric Acid Digestion Bomb method shows great promise as a Level 2 preparation procedure for analytical techniques requiring solution samples.

R.F. Maddalone, TRW DSSG

Maddalone described the application of several inorganic sampling and analysis methods to particulate samples from oil- and coal-fired boilers equipped with FGD systems. As a result of these analyses, data was obtained on such topics as SMSS accuracy, trace element enrichment across an FGD, particle size and elemental distribution, surface composition, and compound identification using Fourier Transform Infrared (FTIR) instruments.

Maddalone discussed the results that showed that certain elements (As, Cr, Mn, Ni, Sb, Se, V, and Zn) exhibit a concentration increase in the particulate matter emitted from one examined FGD system compared to the material entering a FGD under both oil- and coal-firings. This enrichment is due to the preferential emission of small particles ($<3 \mu\text{m}$) which contain increased concentrations of these trace elements. Surface analysis using Electron Spectroscopy for Chemical Analysis (ESCA) showed that particles emitted from the La Cygne FaD system were coated with sulfur and carbon. The materials emitted from an FGD can be identified using FTIR. Sensitivities on the order of $0.1 \mu\text{g}/\text{cm}^2$ can be expected for FTIR.

R.L. Barbour, Battelle Columbus Laboratories

Barbour discussed the application of Fourier Transform Infrared Spectroscopy (FTIR) to environmental assessment programs and various sample handling methods. Also discussed, in relation to their potential contributions to the field of environmental assessment, were inorganic compound speciation and on-the-fly GC/FTIR.

Barbour explained that FTIR is a versatile tool in the field of environmental assessment because it is the only method by which both organic and inorganic compounds can be analyzed. Information concerning both inorganics and organics can range from simple class determination to compound-by-compound characterization of the sample. Methods currently being developed such as the computer-assisted spectral interpretation program and GC/FTIR, promise rapid expansion of application of FTIR to the field of environmental assessment.

Philip L. Levins, Judith C. Harris, and Karen D. Drewitz are with Arthur D. Little, Inc., Cambridge, MA 02140.

Larry D. Johnson is the EPA Project Officer (see below).

The complete report, entitled "Proceedings: Second Symposium on Process Measurements for Environmental Assessment, February 25-27, 1980," (Order No. PB 82-211 574; Cost: \$27.00, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Industrial Environmental Research Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

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