

PROCESS MEASUREMENTS REVIEW



INDUSTRIAL
ENVIRONMENTAL
RESEARCH
LABORATORY

Volume 1, Number 2

Research Triangle Park, N.C. 27711

Second Quarter, 1978

WHAT IS THE *PROCESS* *MEASUREMENTS* *REVIEW*?

The *Process Measurements Review* (PMR), the new publication of the Process Measurements Branch (PMB) of EPA's Industrial Environmental Research Laboratory (IERL-RTP), has received widespread attention among those interested in environmental assessment and control technology measurement programs. The first issue, published last quarter, enjoyed a circulation of well over 1,800 copies. But for those of you receiving the PMR for the first time, it may be appropriate to review its basic objectives.

The *Process Measurements Review* reports on items of interest in the development, assessment, and application of measurement techniques applicable to IERL-RTP energy and industrial process research and development programs. Articles describing advances in sampling, analysis, quality assurance, and on-line process control are featured regularly. The first few issues are primarily based on PMB-sponsored work. However, it is intended that future issues feature articles submitted by other organizations. In this context, comments and suggestions for future topics are actively solicited by the IERL-RTP Task Officer and the Editor.

The *Process Measurements Review* is available to anyone involved or interested in measurement techniques applicable to the characterization and evaluation of energy and industrial processes and control equipment. If you are not currently receiving the *Process Measurements Review* and would like to be on the mailing list, complete and return the request form contained in this issue.

SULFUR OXIDE MEASUREMENT WORKSHOP

The "Workshop on Measurement Technology and Characterization of Primary Sulfur Oxides Emissions from Combustion Sources" was held at Southern Pines, N.C., April 24-26, 1978. It was sponsored by EPA's Environmental Sciences Research Laboratory (ESRL). Twenty-eight papers were presented that dealt with the sampling and analysis of particulate sulfate, sulfuric acid mist, and sulfur dioxide. Also discussed were the effects of process operating parameters on the emission levels and on the measurement of these sulfur oxide species. Accurate discrimination between particulate sulfates and sulfuric acid was identified as a major problem in the characterization of the emissions. The controlled condensation technique is the most accurate method presently available for this differentiation. However, even this technique may suffer losses of 20 percent of the sulfur trioxide. A series of recommendations for research programs in sulfur oxide measurements was developed by the workshop attendees. Proceedings of the workshop will be available soon. Information is available from the ESRL Project Officer, John Nader (919-541-3085).

The views expressed in the *Process Measurements Review* do not necessarily reflect the views and policies of the Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by EPA.

FIELD EVALUATION OF THE SOURCE ASSESSMENT SAMPLING SYSTEM AND LEVEL 1 PROCEDURES

For Level 1 environmental assessment procedures to be effective, the precision and accuracy of both the sample collection and sample analysis schemes must satisfy Level 1 data quality requirements. The primary procedure for characterizing process streams containing particulate matter and vapors is the Source Assessment Sampling System (SASS) for sample collection and specified analytical methods for subsequent sample analysis. An experimental program designed to evaluate the SASS and the associated Level 1 analytical procedures has been completed. The experimental program was coordinated by Research Triangle Institute (RTI) in conjunction with Arthur D. Little, Inc. (ADL), Southern Research Institute (SoRI), TRW Systems, and Radian Corporation.

The project was conducted in two phases. Phase I consisted of a field evaluation of the SASS on a preselected, stable source characterized by high organics and high particulate loadings. Simultaneous samples were collected with two SASS trains and a Method-5 train. Three complete sample runs were made. The relative positions of the trains were fixed with the probes of the two SASS trains positioned at a point of average duct velocity and within a few inches of each other. The Method-5 train was downstream from the SASS trains and operated according to the *Federal Register* method; i.e., the duct was traversed, and isokinetic sampling conditions were maintained. To ensure consistency, all analytical work for Phase I was done by one organization. Results from Phase I were used to estimate within- and between-train precisions for particulate and to estimate the biases of the SASS trains with respect to Method 5 for total particulate determinations. In addition, the results were used for comparisons between SASS trains for organic and inorganic sampling.

Phase II of the program consisted of interlaboratory evaluation of the analytical methods involving the analysis of split samples by participating laboratories. Three aliquots of each of three sample types were supplied to each of the three participating organizations for analysis by current Level 1 procedures. The three sample types were:

- A known, artificial, liquid sample containing 16 components.
- A real particulate sample obtained from a source significantly different from the one selected for Phase I sampling.

- The combined XAD-2 extracts from the SASS runs in Phase I.

A full Level 1 analysis was performed on one aliquot of each of three sample types; the remaining aliquots were analyzed using a reduced Level 1 scheme.

PHASE I RESULTS

Particulate Loading and Sizing

Results of the particulate loading and sizing comparisons showed the following:

- Particle size distributions compared very well between SASS trains for all three runs. Typical results are shown in Figure 1.
- Particulate matter concentrations determined by the SASS trains compared very well with Method 5. The largest difference was within 20 percent (Table 1).
- The estimated precision between trains, given as a standard deviation, is 36 mg/m^3 (10 percent on a relative basis).

Collected Organics

A complete Level 1 organics analysis was carried out on one set of SASS runs. For this set, the organic material collected by the SASS trains agreed well in quantity and composition (i.e., volatile (TCO), nonvolatile (Grav), and organic compound categories) and was collected proportionally in corresponding SASS components. The results of volatile and nonvolatile analyses are given in Table 2.

Collected Inorganics

For one set of SASS runs, mercury, arsenic, and antimony were determined by atomic absorption on the combined second and third impinger solutions. For these limited analyses, the data for each element agreed within a factor of 2.

Table 1. Particulate Matter Concentration, mg/m^3

Run	SASS-1	SASS-2	Method 5
1	408	337	342
2	399	349	322
3	353	315	371

$\sigma = 28 \text{ mg/m}^3$ (8%) within train precision, including source variation
 $(\sigma^2 + \sigma_t^2)^{1/2} = 36 \text{ mg/m}^3$ (10%) between train precision

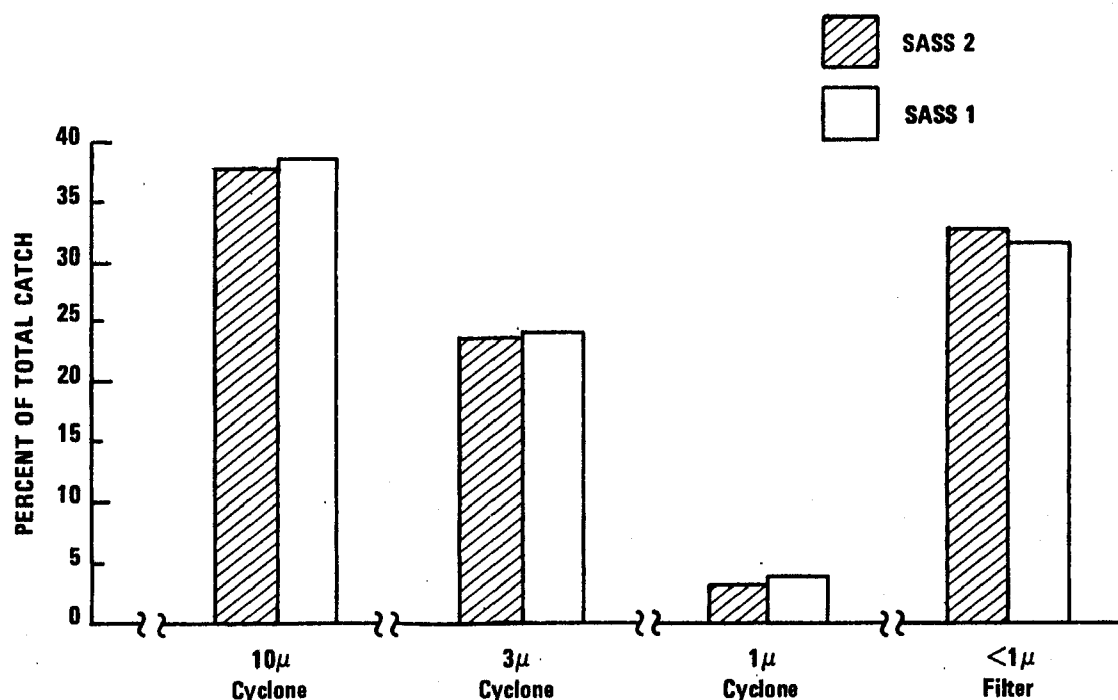


Figure 1. Comparison of particle size fractionation of two SASS trains.

Table 2. Organic Extractables, mg/m³

	Cyclone		XAD-2 (Extract)		XAD-2 (Module)	
	SASS-1	SASS-2	SASS-1	SASS-2	SASS-1	SASS-2
TCO	0.03	0.01	3.41	3.58	(Rinse)	
Grav	1.65	1.58	10.2	8.99	69	81
Total	1.7	1.6	13.6	12.6	69	81

PHASE II RESULTS

Certain methods employed in the organic analysis scheme are still being refined, and interpretation of the organic data from complex sources can be an involved process requiring great attention

to detail. However, from this preliminary analysis of Phase II data, it appears that the organic analysis scheme can yield results of adequate quality to satisfy Level 1 requirements.

Results of the inorganic sample preparation and Spark Source Mass Spectrometer (SSMS) analysis scheme indicate that variability in the values for some elements may be exceeding the allowable factor of 2 to 3 in the Level 1 procedures. The cause of the variability cannot be isolated with the data available. Further studies will be initiated to examine potential solutions to the problem.

A report on the evaluation, in draft form, is being reviewed by EPA with publication expected shortly. Also, a paper describing the evaluation was presented at the EPA process measurements symposium in Atlanta in February. The proceedings of the symposium, including this paper, are scheduled to be available soon. The IERL-RTP Project Officer for the SASS evaluation is Bill Kuykendal (919-541-2557).

(See page 6 for articles on ion chromatography and analysis of sulfur in coal.)

**REVISIONS TO "IERL-RTP PROCEDURES MANUAL:
LEVEL 1 ENVIRONMENTAL ASSESSMENT," EPA-600/2-76-160a**

(Changes 1-5 were reported in the Volume 1, Number 1 issue of the PMR.)

Change 6 - "Cleaning XAD-2 with Methylene Chloride, Drying"
Appendix D, Page 130
Date Accepted: April 6, 1978

To remove contaminants from manufacturer-supplied XAD-2 resin, the original procedure required cleaning of the resin by extraction with water, methanol, diethyl ether, and pentane. Ether and pentane are hazardous to store, difficult to contain in the extraction equipment, and present greater flammability and explosion hazards than other acceptable solvents. The new cleaning procedure substitutes methylene chloride for the ether and pentane. The old procedure remains acceptable, but is no longer recommended for Level 1. In addition, the original procedure fails to specify a drying procedure for the cleaned resin. The new procedure specifies a fluidized-bed technique using pure nitrogen for drying.

Change 7- "Total Chromatographable Organic Analysis (TCO)"
Chapter VIII, Pages 82, 90, 93, and 102
Date Accepted: April 14, 1978

The original procedures specified analysis of C_1 - C_6 hydrocarbon compounds by gas chromatography in the field. C_7 - C_{12} compounds were analyzed in the laboratory from solvent extraction solutions. Higher molecular weight hydrocarbons were classified by liquid chromatography from dried extract. Data have shown that significant amounts of the more volatile compounds are lost in this analytical scheme. Therefore, the field analysis is expanded to include the C_7 compounds and the laboratory solvent extraction analyses are expanded to include C_8 - C_{16} compounds. The nonvolatile compounds are characterized in the original manner after exchange to cyclopentane solvent.

Change 8- "Use of SASS Cyclones Without Vortex Breakers"
Chapter III, Page 29
Date Accepted: April 13, 1978

Originally, vortex breakers were specified for use in the three SASS cyclones. However, rigorous calibrations of the cyclone set have shown that the cut points for the two larger cyclones (10 and 3 micrometers) are more nearly achieved without vortex breakers. Accordingly, the procedure has been changed to specify that the 10- and 3-micrometer cyclones are to be operated without the vortex breakers.

Change 9- "IR Sample Preparation and Analysis"
Chapter VIII, Page 102
Date Accepted: May 22, 1978

The original procedure for preparation of samples for infrared analysis specified the use of a single NaCl plate. However, single plate preparations are subject to sample evaporation and other adverse thermal effects. Therefore, the procedure has been modified to require analysis of the sample between two NaCl plates or mixture of the sample material with KBr and formation of a pellet.

NOTE: Revisions appear in condensed form. For complete change notices, contact Ann Turner at RTI (919-541-6893).

RECENT EPA PUBLICATIONS OF INTEREST

D. E. Blake.

Source Assessment Sampling System: Design and Development, EPA-600/7-78-018, PB 279757/AS (2/78).

This document chronologically describes the design and development of the Source Assessment Sampling System (SASS). The SASS train is the principal sampling element for ducted sources when performing EPA's Level 1 environmental assessment studies. As such, it samples process streams and separates the samples into filterable particulate (four size fractions), organic vapors, and inorganic vapors. The design concept and philosophy are discussed, as well as the evolutionary development of the system. Developmental testing, problem areas, and subsequent system changes are described in detail. The document also includes a complete description of the calibration procedures used to determine the size cut points of the particulate fractionating cyclones.

J. C. Harris and P. L. Levins.

EPA/IERL-RTP Interim Procedures for Level 2 Sampling and Analysis of Organic Materials, EPA-600/7-78-016, PB 279212/AS (2/78).

This document is an interim report representing concepts and guidelines to be utilized in considering procedures for sampling and analysis of organic compounds during Level 2 environmental assessments. The guidelines are general in nature, but suggestions for specific procedures are also presented. Please note that this is an interim document that will be replaced eventually by a Level 2 Organics Procedure Manual. That manual will contain more developed concepts and procedures specified for a wide range of conditions.

This document is intended for use by experienced research chemists who are thoroughly familiar with environmental sampling and analysis, Level 1 procedures, and the objectives of the phased approach. It does not attempt to teach details of EPA's Environmental Assessment Program. Rather, it relies heavily on reports previously published by IERL-RTP and its contractors.

J. W. Adams, T. E. Doerfler, and C. H. Summers.

Effect of Handling Procedures on Sample Quality, EPA-600/7-78-017, PB 279910/AS (2/78).

This report presents results of an evaluation of the effects of typical shipping and storage procedures on organic materials collected in Level 1 environmental assessment studies. Parameters reviewed included sample container composition, head space composition, temperature, lighting, and catalytic species content. Three sample sets representing fractions obtained during a Level 1 environmental assessment were used for the evaluation. Each contained six model organic compounds. A simulated 3-week shipping and storage cycle represented elapsed time between sample collection and analysis. All three experiments were conducted in accordance with statistical principles appropriate for factorial experiments. Experimental results were analyzed using analysis of variance to assess the relative effect of each shipping/storage condition studied.

L. N. Davidson, W. J. Lyman, D. Shooter, and J. R. Valentine.

Technical Manual for the Analysis of Fuels, EPA-600/7-77-143, PB 279196/AS (12/77).

This manual is intended as a guide in research projects concerned with fuel combustion. It discusses standard methods of sampling and analysis for a variety of hydrocarbon fuels. The analyses covered are those of prime concern to the combustion engineer. For each fuel covered, the manual indicates the analyses that are likely to be required, the preferred method of analysis, and available sampling procedures. For each method of analysis listed, the manual summarizes the method, discusses its applicability, and describes its precision. Gaseous fuels, liquid petroleum fuels, waste lubricating oil, shale oil, coal liquids, methyl fuel, coal, coke, refuse-derived solid fuels, and peat are included. The appendixes give the availability of Standard Reference Materials for fuel-related analyses, laboratory directories, typical values (or ranges) of parameters specified for each fuel, and results of fuel analyses conducted by the contractor.

P. P. Leo and J. Rossoff.

Controlling SO₂ Emissions From Coal-Fired, Steam-Electric Generators: Solid Waste Impact (Volumes 1 and 2), EPA-600/7-78-044a and -044b, PB 281099/AS and 281100/AS (3/78).

R. L. Sugarek and T. G. Sipes.

Controlling SO₂ Emissions From Coal-Fired, Steam-Electric Generators: Water Pollution Impact (Volumes 1 and 2), EPA-600/7-78-045a and -045b, PB 279635/AS and 279636/AS (3/78).

J. R. Koscianowski, L. Koscianowska, and M. Szablewicz.

Tests of Fabric Filtration Materials, EPA-600/7-78-056, PB 279637/AS (3/78).

J. A. Cavallaro, G. A. Gibbon, and A. W. Deurbrouck.

A Washability and Analytical Evaluation of Potential Pollution From Trace Elements in Coal, EPA-600/7-78-038, PB 280759/AS (3/78).

Copies of these publications are available at cost from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151.

ION CHROMATOGRAPHY

Ion exchange chromatography has long been known as a powerful tool for the separation of ions in solution. Until recently though, its applicability has been somewhat limited by the lack of a universal ion detection technique. One technique responsive to all ions, conductimetric detection, was considered impractical because of the presence of the high concentration of electrolytic eluent normally used in the separation. A novel technique, developed by H. Small, T. S. Stevens, and H. C. Bauman, and reported in a 1975 issue of *Analytical Chemistry*, reduces this background to a minimum and makes possible the use of a conductimetric detector. The key to the technique is a second eluent neutralization column in series with the separator column. The combination of these two columns and a conductimetric detector has resulted in a new analytical methodology known as ion chromatography.

Ion chromatography allows the separation and detection of several anions as low as 10 ppb in a single analysis. Analysis time is less than 30 minutes and precision (replicability) is better than ± 3 percent. Numerous applications of the technique have begun to appear in the literature. Mulik, et al. reported in a 1976 issue of *Analytical Letters* the use of ion chromatography to determine sulfate and nitrate in ambient aerosols. Recently, Steiber and Statnick demonstrated the applicability of this technique in the measurement of sulfite and sulfate in flue gas desulfurization systems. The paper has been published by Ann Arbor Science Publishers, Inc. in a book entitled "Ion Chromatographic Analyses of Environmental Pollutants." Applicability of the technique in the study of wet limestone and dual alkali scrubbers has also been demonstrated in work conducted at TRW Systems, Redondo Beach, California, for EPA. Finally, S. A. Bouyoucos stated in an article in *Analytical Chemistry* that ion chromatography has been used for the determination of certain organic compounds.

Because ion chromatography is a rapid, sensitive, and selective method for the analysis of a large variety of ions, it is now being considered as a technique for the laboratory-based analyses of all simple and complex anions and select cations (e.g.,

NH_4^+) in the Level 1 environmental assessment program. The anions to be analyzed would include NO_2^- , NO_3^- , $\text{SO}_3^{=}$, $\text{SO}_4^{=}$, $\text{PO}_4^{=}$, F^- , and Cl^- . From an analytical point of view, ion chromatography is much more efficient than using a variety of individual analysis techniques, including classical colorimetric techniques and ion selective electrodes. Indeed, one can safely predict that ion chromatography will replace such techniques in many other laboratories in addition to those involved in the Level 1 program.

For further information on how ion chromatography is being utilized in the environmental assessment program, contact Ray Merrill, IERL-RTP (919-541-2557).

ANALYSIS OF SULFUR IN COAL

An improved technique for the analysis of sulfur forms (pyritic, organic, and inorganic) in coal has been developed by TRW Systems and Energy, Redondo Beach, California, under an EPA program. The procedure uses low temperature plasma ashing to remove organic sulfur from the sample, leaving the pyritic and inorganic sulfur free of interferences from the organic matrix. To evaluate the procedure, sulfate sulfur and pyritic sulfur were determined on a series of nine plasma ashed coals in triplicate and the results compared to analyses of the same coals using standard ASTM procedures. Three of the samples were Eastern interior coals expected to contain significant amounts of sulfur occurring as finely divided, homogenous particles. Six were Appalachian coals expected to have the sulfur occurring in large particle nodes.

The sulfate sulfur values determined for Eastern interior coal by plasma ashing were 40 percent higher than those determined by ASTM methods. They were 14 percent higher for Appalachian coals. Pyritic sulfur values by plasma ashing were 8 percent higher for Eastern interior coals and 8 percent lower for Appalachian coals than the ASTM values. The plasma ashing procedure gave total inorganic sulfur results which were 24 percent higher than ASTM procedures for Eastern

interior coals and 1.4 percent lower for Appalachian coals. Results from a single sample of coal tailings showed differences in the total inorganic sulfur values that were similar to those for Eastern interior coals; i.e., the ashing results were 22 percent higher than the ASTM procedure values. These results indicate that the plasma ashing procedure is more effective for analyzing coals containing finely divided sulfur than the ASTM procedures and is equally as effective as the ASTM procedures for other coals.

The TRW program will also investigate extension of the plasma ashing technique to the direct measurement of organic sulfur. This will be accomplished by trapping the sulfur dioxide liberated during the ashing process. Successful completion of this project will provide a technique which directly analyzes all three sulfur forms in a single sample of coal. The IERL-RTP Project Officer is Frank Briden (919-541-2557).

FUGITIVE EMISSIONS SYMPOSIUM

The "Third Symposium on Fugitive Emissions: Measurement and Control," sponsored by EPA's Industrial Environmental Research Laboratory-RTP, will be held October 23-25 at the Jack Tar Hotel, San Francisco, California. The symposium will provide a forum for the exchange of information on the impact, measurement, and control of airborne and waterborne fugitive emissions from industrial sources. Twenty-five speakers from industrial, academic, and governmental organizations will discuss the current status of research, development, and applications studies. If you are interested in attending the Symposium, contact Hank Kolnsberg or Joanne King, TRC, Wethersfield, Connecticut (203-563-1431).

Request for the *Process Measurements Review*

Name _____ Position or Title _____

Company _____

Address _____
(Street)

(City)

(State)

(Zip Code)

(Phone)

Return to: **Ann Turner**
Research Triangle Institute
P.O. Box 12194, Building 6
Research Triangle Park, N.C. 27709
(919)541-6893

Check if applicable:

☐

Incorrect address

☐

Discontinue

The *Process Measurements Review* is prepared by the Research Triangle Institute, P. O. Box 12194, Research Triangle Park, N.C. 27709, for the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Process Measurements Branch, Research Triangle Park, N.C. 27711, under EPA Contract No. 68-02-2156. The EPA Task Officer is James A. Dorsey (919-541-2557) and the RTI Editor is Raymond M. Michie, Jr. (919-541-6492). Comments on this issue and suggestions for future topics are welcome and may be addressed to either the Task Officer or the Editor.

United States
Environmental Protection
Agency

Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, N.C. 27711

Official Business
Penalty for Private Use
\$300

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335



US EPA
Headquarters and Chemical Libraries
EPA West Bldg Room 3340
Mailcode 3404T
1301 Constitution Ave NW
Washington DC 20004
202-566-0556

U.S. Environmental Protection
Agency, Region V, Library
230 South Dearborn Street
Room 1455-A
Chicago, Illinois 60604

If your address is incorrect or you do not wish to continue receiving the *Process Measurements Review*, please fill out the **Request Form** on page 7, check the appropriate box, and return it to the designated address.