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Project Summary

Effects of Residual Organic Matter on Elemental Analyses by Spark Source Mass Spectrography (SSMS)

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A research program was designed and conducted to define the effect of organics in SSMS and to evaluate several sample preparation methods for their removal. Samples of known organic content were fabricated by diluting NBS SRM 1633 fly ash with a mixture of organic compounds. The SRM 1633 fly ash was spiked with several trace elements prior to this mixing. Samples containing 0, 10, 50, and 90 percent organic material were developed. These fabricated samples and NBS SRM 1632 coal were analyzed by three laboratories using SSMS without prior pretreatment (neat) and after processing by several preparation procedures. The effects of organic material on neat SSMS analysis were assessed for the various concentration levels. Samples containing ≤ 50 percent organic material could be successfully analyzed by SSMS without pretreatment. Difficulties were encountered with 90 percent organics. Four preparation procedures (Parr oxygen bomb, HF bomb, low temperature ashing, and mineral acid extraction) were evaluated for removal of organic interference and maintenance of sample integrity for SSMS, AAS (primarily Hg), and ICP analyses. Conclusions were drawn regarding their suitability for use in the Level 1 and/or Level 2 analysis schemes and the benefits of further research.

This Project Summary was developed by EPA's Air and Energy Engineering 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).

Introduction

A three-phased approach to the environmental assessment of stationary sources of pollution has been developed by EPA's Air and Energy Engineering Research Laboratory at Research Triangle Park (AEERL-RTP). The first phase, Level 1, is devoted to comprehensiveness and employs broad survey techniques to define the hazard potential of source emissions and to identify possible control needs. Level 2 seeks more specific elemental composition and compound identification information, while Level 3 uses process and control monitoring to define temporal variation of source emissions. Although the Level 1 sampling and analytical scheme has been used for several years by the EPA and its contractors, questions still exist regarding the performance of the techniques in meeting Level 1 criteria of precision and accuracy. Of particular concern is the multielement analytical technique, spark source mass spectrography (SSMS), used for Level 1 elemental surveys. SSMS can determine 70 elements simultaneously with an accuracy (combined with sampling accuracy) of a factor of 2 or 3, a criterion set for Level 1 environmental assessment measurements. In conducting Level 1 studies, however, questions arose as to whether such limits could be achieved for

all of the elements measured in all of the sample matrices encountered in stationary source assessments. The effect of organic matter on SSMS analyses and if interference of such organic matter could be eliminated by various sample preparation techniques were unknown, but adverse effects were suspected.

A research program was designed and conducted to define the effect of organics on SSMS and to evaluate several sample preparation methods for their removal. Major work elements required to accomplish this were:

1. Fabrication of test samples from National Bureau of Standards (NBS) Standard Reference Material (SRM) 1633 (fly ash), additionally spiked with nine metals and an organic mixture of L-ascorbic acid, benzoic acid, and graphite.

2. Preparation of samples for SSMS analysis by three techniques (Parr oxygen bomb, low temperature ashing, and hydrofluoric acid bombs) and for inductively coupled argon plasma (ICP) and atomic absorption (AA) analysis by Level 1 acid extraction.

3. Elemental analysis of neat and prepared samples by SSMS at three laboratories, and in-house analysis of the acid extracted material by ICP and AA.

4. Evaluation of quantitative data for Level 1 and 2 applications and assessment of SSMS photoplate quality.

Experimental Procedures

Fabrication of Test Samples

The fabricated test samples were prepared from spiked NBS SRM 1633 fly ash and an organic mixture of 80 percent L-ascorbic acid (Fisher Scientific Co.), 10 percent benzoic acid (Fisher Scientific Co.), and 10 percent spectral grade graphite (National brand-Union Carbide). The NBS fly ash was chosen because it represents a well characterized sample. Prior to mixing with the organics, it was spiked with nine elements (U, Pb, Ce, I, Ag, Se, As, Sc, and Cl) to disguise its identity and to obtain information on the recoverability of these elements. The organic mixture was chosen because it contributed only oxygen, hydrogen, and carbon to the test samples. Also, it formed an abundance of molecular spectral lines on the ion sensitive photoplates which were typical of those that might be caused by residual organic material in environmental samples.

The test samples were fabricated from the spiked NBS fly ash and the organic mixture. Four representative dilutions of the fly ash were produced: 100 percent spiked NBS fly ash/0 percent organic mixture, 90 percent spiked NBS fly ash/10 percent organic mixture, 50 percent spiked NBS fly ash/50 percent organic mixture, and 10 percent spiked NBS fly ash/90 percent organic mixture. These classes of test samples will be referred to throughout the remainder of this Summary as 0, 10, 50, and 90 percent organic matter, respectively. (The NBS fly ash organic contributions were considered to be negligible with respect to the final organic content of the test samples.)

Sample Preparation

Most of the aliquots from the four classes of test samples were analyzed neat (i.e., no preparation prior to making into electrodes). The remaining aliquots were subjected to three preparation techniques: Parr oxygen bomb (PB), low temperature ashing (LTA), and hydrofluoric acid bomb (HFB).

The Parr bomb was modified for trace metal analysis by replacing the standard electrodes with electrodes of 97 percent platinum and 3 percent rhodium and by fitting the bomb with a quartz liner including a cover. Level 1 procedures were followed. The LTA method used the LFE Model 302 LTA. A preweighed sample, placed in a quartz dish, was ashed for several hours. It was then reweighed and agitated to expose fresh surface. Ashing was continued until a constant weight was obtained. The HFB method called for digestion in a mixture of aqua regia and HF. Digestion was accomplished by sealing the bomb and heating in an oven at 100°C for 1 to 2 hours. All sample preparations were conducted in-house, and extracts were submitted to other laboratories for SSMS analysis.

An acid extraction (AE) procedure was performed on selected samples according to the Level 1 acid extraction method for solid samples and particulate filter samples to be subjected to cold vapor mercury analysis. This procedure specifies a 6-hour extraction with a 4:1 mixture of HNO_3 and HCl, respectively. These extracts were analyzed only in-house.

Analytical Methods

The laboratories used for SSMS elemental analysis represented a cross-section of instrument types and procedural details. SSMS analyses were performed on SRM 1633/organic mixtures and on NBS SRM 1632 coal samples after preparation by the PB and the LTA techniques. Additional samples were selected and prepared by these techniques, and the extracts were then submitted to the participating laboratories for analysis. Table 1 gives the number of analyses done by each laboratory on the four classes of samples. The electrode preparation, SSMS operation, and photoplate analysis procedures used by each laboratory are similar in theory and follow the basic guidelines of the Level 1 manual.

All AA spectrophotometry (AAS) analyses were performed in-house on a Perkin Elmer Model 460 equipped for both flame and flameless methods. The cold vapor technique described in the Level 1 manual was used for all mercury determinations. Other elemental determinations by AAS employed either standard flame or graphite furnace (Model HGA 2100) techniques.

Selected elemental determinations were also made by ICP spectroscopy. A Jarrell-Ash Model 1160 Plasma Atom-Comp™, equipped with 24 fixed wavelength channels and a Mark V N+1 channel, was used for all ICP analyses.

Results

Most of the neat samples were analyzed by SSMS with relatively few problems. The 90 percent organic samples could not, however, be analyzed in a neat form by two of the participating laboratories because sample electrodes burned too quickly to be analyzed in their instruments. The third laboratory was able to analyze the 90 percent neat sample because of a different instrument design, but experienced increased pressure in the ion source and greater difficulty in operating the SSMS because of a slower charge accumulation. No such problems were encountered with 0, 10, or 50 percent samples.

The accuracy of data from neat analyses was analyzed for elements with known NBS or spiked values. The 0 percent sample was used as the baseline for all effects considered. Data reported for the 0, 10, and 50 percent samples indicate that there is little difference in the results for these three samples.

Several preparation methods were evaluated with respect to their effects on SSMS determinations. Three of the methods (PB, LTA, and HFB) effectively eliminated most of the interfering molecular spectra. The neat sample plates exhibited

Table 1. Summary of SSMS Data Collection

Laboratory	% Organic	Number of analyses			
		Neat	PB	LTA	HFB
A	0	2	1	--	--
	10	2	1	--	--
	50	2[a]	1	--	--
	90	2[a]	1	--	--
B	0	1	--	--	--
	10	1	--	--	--
	50	1	--	--	--
	90	--[b]	--	1[b]	--
C	0	3	1	--	--
	10	3	1	--	--
	50	3	1	1	1
	90	--[c]	1	1	--

[a]Lab A needed to dilute one run each of 50% and 90% neat samples by 10 times. They were able to give analyses for the other high percentage samples that were duplicated.
[b]Lab B could not run the 90% organic sample neat, and used LTA instead.
[c]When 90% neat sample was tried by Lab C, the electrodes eroded much too rapidly to obtain an analysis.

multiple molecular spectra throughout and caused suspected interferences with Hf, Lu, Ho, Dy, Gd, Du, Br, and Zn determinations. They were tedious to analyze and require greater qualitative data reduction time.

The Level 1 acid extraction procedure extracted substantial quantities of most elements. With some exceptions, quantitites sufficient to meet Level 1 requirements were extracted. However, the data clearly show a negative bias owing to incomplete dissolution.

Accuracy analyses were also conducted for neat and prepared samples for comparison to Level 1 and 2 acceptance limits. These data revealed that many more inaccurate determinations are lower than the expected values. In fact, only 12 percent of the inaccurate determinations were higher than expected. Therefore, contamination due to the preparation methods appears to be minimal. However, a number of elemental losses are specific to certain preparation methods. The largest contributor to the elemental loss category was the PB method.

This high PB error can be attributed to the fact that incomplete sample combustion occurs frequently. When the residue (left after the PB preparation) was retained and combined with the solution prior to SSMS analysis, better results were obtained.

An alternative approach to the accuracy analysis indicates that the general problem element determinations for all laboratories occur with Ta, I, Ag, Cl, Si, and Be. These elements are consistently listed outside of the precision range of SSMS.

Other problem elements that appear to be specific to each laboratory are: Laboratory A—RB, Fe, and Al; Laboratory B—W, Cd, Br, and Cr; and Laboratory C—Sc.

Conclusions

Several conclusions were drawn from the organic effects study:

● Organic components of a sample can adversely affect, and in some cases preclude, SSMS data collection.

● Organic molecular spectra can hinder qualitative interpretation of the elemental spectra.

● Molecular spectra produced by organic constituents are readily discernible by SSMS analysts.

● Interference from the coincidence of organic and elemental spectra was not a problem.

● For the test organic matrix used, 50 percent organic content was tolerable.

It is clear from the data obtained that, in some cases, preparation prior to SSMS analysis is necessary. In addition, the delineation of sample preparation methods suitable for Level 2 elemental analyses is highly desired.

Several conclusions were also drawn from the sample preparation study:

● The Parr Oxygen Bomb (PB) eliminates organic constituents adequately for SSMS analysis. Although this procedure can result in a mixed phase sample, it appears to be the most comprehensive SSMS preparation technique when all residues can be collected and analyzed. While the method is inadequate for the dissolution of many elements, it is an excellent preparation method for cold vapor mercury analysis. In terms of Level 1 elemental analysis, the only significant drawback to this method is the limited sample size that can be accommodated by the standard apparatus.

● Low Temperature Plasma Ashing (LTA) is superior to any technique studied for the elimination of organic matter. However, when nominally volatile elements are of interest, the method is questionable; halogen losses represent a fundamental problem with the method. A major advantage of the method is its ability to accommodate large sample sizes. Disadvantages include its vulnerability to ambient environmental contamination and the long ashing times required for some samples.

● The Modified Hydrofluoric Acid Digestion Bomb (HFB) is the most comprehensive dissolution technique studied. With the addition of a fuming nitric acid step, organics can also be removed. Concentration steps achieved by solution evaporation will result in the loss of silicon; halogen losses also occur. While the boric acid step aids sample dissolution, the resulting matrix interferes with graphite furnace AAS measurements.

● Level 1 Acid Extraction (AE) is adequate for the preparation of particulate samples for cold vapor mercury analysis. Some other elements can also be successfully extracted by this method; however, it has limited application potential for Level 2 analysis.

Recommendations

In summary, the Level 1 elemental analysis scheme was found to be reliable and to provide the kind of information desired from the Level 1 study. Problems, noted with some SSMS determinations, could be eliminated by additional work in this area. The preparation of particulate filter samples for SSMS analysis by the AE procedure may bias the resulting data. The HFB method shows great promise as a Level 2 preparation procedure for analytical techniques requiring solution samples. Additional work in this area would, no doubt, be beneficial.

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The complete report, entitled "Effects of Residual Organic Matter on Elemental
*   Analyses by Spark Source Mass Spectrography (SSMS)," (Order No. PB 86-119*
*   575/AS; Cost: $22.95, subject to change) will be available only from:*
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            5285 Port Royal Road
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