



Project Summary

Evaluation of Spark Source Mass Spectrometry and Plasma Emission Spectroscopy for Comprehensive Elemental Analysis of Environmental Samples

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This report presents the results of an extensive literature review and evaluation of spark source mass spectrometry, inductively coupled plasma emission spectrometry, and direct current plasma emission spectrometry. The goal of this study was to determine if these techniques are capable of providing comprehensive elemental screening of environmental samples and, if so, the limitations to be expected.

Sample preparation, introduction, identification, and quantitation procedures were evaluated to gain understanding of the elemental coverage and data quality to be expected using each technique.

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

The complete and cost-effective elemental characterization of environmental samples may become a requirement rather than a goal as quality control and environmental monitoring requirements

become stricter. To meet this need, techniques are needed that can provide comprehensive elemental analysis in a timely manner.

The Air and Energy Engineering Research Laboratory (AEERL) of the U.S. Environmental Protection Agency (EPA), Research Triangle Park, North Carolina, for many years has recognized the need for such techniques and, until recently, has advocated the use of spark source mass spectrometry (SSMS) to perform comprehensive elemental analyses in its Level 1 environmental assessment studies.

Until recently, no candidate technique was available to challenge SSMS in terms of cost per analysis, comprehensive elemental analysis capability, and data quality (accuracy, precision, detection limits). However, the recent development of commercially available inductively coupled plasma (ICP) and direct current plasma (DCP) emission spectrometers, the interest shown by other Agency laboratories in proposing plasma techniques as the chief elemental analysis techniques for environmental analyses, and the reported excellent accuracy and short-/long-term precision of these techniques have prompted AEERL to reassess the role SSMS should play in analytical support work for the laboratory in Level 1 and related analysis activities.

The objectives of this study were to compare SSMS and the plasma techniques for the following characteristics:

- Elemental coverage or survey capability
- Ease of sample preparation
- Analysis time
- Interferences
- Accuracy
- Precision
- Detection limit
- Applicability to routine environmental analyses
- Availability of validated protocols
- Commercial availability.

The information generated from this assessment should prove useful in determining the future roles of SSMS and plasma techniques in AEERL sponsored programs.

Approach

A truly effective comparison of the capabilities of SSMS and plasma techniques necessarily would involve analyses of the same samples by both techniques. Because very little comparison data of this nature exists, a number of other characteristics that individually and collectively determine overall data quality must be evaluated.

The ability of a technique to determine many elements in a simultaneous or nearly simultaneous fashion in the same sample is defined here as its potential for comprehensive coverage. This coverage capability can provide qualitative, semi-quantitative, or quantitative data. Each of these levels of specification is evaluated.

The ease with which field samples can be processed prior to analysis is often a limiting factor as to (1) how long it will take to obtain the analytical result, (2) what fraction of the original matrix can be analyzed, and (3) what elements can be determined. Very complex matrices containing refractory forms of some elements often require elaborate sample dissolution/extraction steps that are time consuming and restrictive as to the final number of determinable elements. These factors were evaluated for both plasma spectroscopy and SSMS. Because no single sample preparation procedure exists, several of the most common are evaluated.

Sample analysis, the part of analyte determination that begins with sample introduction into the measurement device and ends with data acquisition by a computer or other recording device, were

evaluated with respect to spectral interferences and sample transport. The advantages and disadvantages of various detector systems are discussed.

Data processing is defined here as the handling of spectral data generated by the detector systems and recording devices.

Data quality was evaluated by comparing plasma techniques and SSMS with respect to three common measures of method performance: accuracy, precision, and detection limit. Analyses of environmental samples of known composition form the basis for the accuracy assessment. Precision is assessed by comparing results obtained on repeat analyses of the same sample or on aliquots of the same sample taken through a sample preparation procedure. Detection limits seldom were reported for environmental matrices. Assessment of method detection limits was limited to a comparison of the instrument manufacturer's claims supplemented with available environmental data.

The applicability of plasma and SSMS techniques to routine environmental analyses was assessed by examining the availability of commercial instrumentation and analysis protocols as well as the relative and absolute costs of sample analysis on a per-element and per-sample basis.

Results and Discussion

ICP-Atomic Emission Spectroscopy (AES) and SSMS techniques generally required a vastly different set of sample preparation and introduction methods that depended primarily on the type of matrix and to a certain extent on the element(s) of interest.

The SSMS technique is superior to the ICP-AES, with regard to sample preparation and introduction, for inorganic powders and other solid materials with less than 50 percent organic content amenable to grinding and fabrication of homogeneous electrodes. Thus, most geological type samples (e.g., coal, soil, silicate rocks, fly ash, air particulates, and stream sediments) were transported more easily from the raw sample to the detector system in SSMS than in ICP-AES. Samples that were primarily organic in composition (e.g., plant materials, other biota, animal tissue, oils, other liquid fuels, and aqueous samples) in general were better suited to sample preparation and introduction into the ICP-AES.

The data presented in this study suggest that neither SSMS nor ICP-AES is entirely suitable for the comprehensive, precise, and accurate determination of all elements, in all types of matrices, and at all levels. No single technique offers this capability. When appropriate steps are included to increase the elements present at below-instrumental detection limits and to permit the introduction of elements present in matrices incompatible with the instrument sample introduction/excitation systems, the number of elements that can be determined by each technique can be extended to a maximum of around 100 elements. However, this cannot take place in a single sample or without putting forth an unacceptable amount of effort for the return that is expected.

The accuracy and precision of SSMS were much poorer than for ICP-AES, even when comparing the analyses for matrices that are easily compatible with the SSMS. To achieve better accuracy and precision with SSMS would require that the number of elements to be determined be reduced to only a handful.

The most significant conclusion to be drawn from this study is that SSMS and ICP-AES are complementary techniques that together provide much greater coverage and detection capability than either technique alone when many different matrices are considered.

The applicability of any measurement technique to routine environmental analysis is highly dependent on the availability to users of documented protocols. Ideally, the protocols should be validated prior to dissemination for general use and should be compatible with commercially available instrumentation. Several recommended and required test methods for SSMS and plasma techniques have been prepared by the American Society for Testing and Materials (ASTM) and EPA in the last seven years. Some of these protocols are quite detailed and can almost serve as "stand-alone" documents for analysis of certain types of samples. Others are, at best, guidelines for conducting analyses by these techniques and presume considerable prior knowledge on the part of the analyst.

Additional guidance is available in the operating and applications handbooks that accompany the instrumentation and in the open literature. However, with the exception of the EPA ICP-AES method for water and wastes, there are no satisfactory comprehensive standard operating procedures (SOPs) for SSMS or plasma techniques. The EPA method is directly

applicable only to dilute aqueous samples and thus does not address the analysis of solids or nonaqueous liquids. Until such comprehensive SOPs are available, analysts will have to depend on the open literature and their own specific needs to develop methods of analysis for these types of samples.

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The complete report, entitled "Evaluation of Spark Source Mass Spectrometry and Plasma Emission Spectroscopy for Comprehensive Elemental Analysis of Environmental Samples," (Order No. PB 87-145 686/AS; Cost. \$24.95, subject to change) will be available only from:

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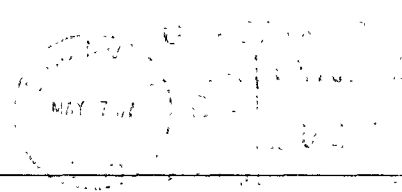
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