Introduction

This publication is devoted to discussion of the analysis of hazardous materials by plasma emission spectroscopy. Thirteen contributions from laboratories in both the United States and Europe describe successful engineering and chemical strategies that allow the use of plasma spectroscopic sources for the study of hazardous materials without endangering the health of the analyst or the general public. A substantial fraction of the papers deals with the analysis of radioactive materials, but the techniques cataloged here are also appropriate for the analysis of hazardous nonradioactive materials. That this technology was initially developed to support activities in the nuclear community is not surprising: the nuclear industry is required to abide by strict release limits for radionuclides, which can be monitored by extraordinarily sensitive radiation monitors, such as the proportional counter. As monitors for toxic nonradioactive materials, such as beryllium, mercury, lead, selenium, and organic toxins, increase in sensitivity, it is likely that measures advocated in this volume will be increasingly applied for plasma emission studies of those materials.

During analysis by plasma spectroscopy, sample solutes are converted to finely divided particulates by a nebulizer, entrained in a flow of argon gas, and then introduced into a plasma torch. The torch heats the sample to a temperature between 6000 to 10 000 K, which atomizes and eventually ionizes most of the sample constituents. The ions and any atoms remaining are then raised to an electronically excited state and eventually relax to their ground electronic state by emitting photons of a characteristic energy (or wavelength). The resulting spectrum of emitted light can then be analyzed to determine the solution composition.

The analysis of the spectrum of light emitted by a plasma source is the most common route to the determination of the solution composition. However, the ions produced by the plasma source also can be mass analyzed [inductively coupled plasma/mass spectroscopy (ICP-MS)] to determine the initial solution composition. Even though no papers were presented at the symposium that discussed the use of ICP-MS for the analysis of hazardous materials, there was active interest in and discussion of this allied technique. The unavoidable problem of eventual contamination of the mass spectrometer system and detectors by entrapped radioactive species will determine the extent and manner of future applications of ICP-MS to radioactive materials.

The toxicity of most materials (for example, plutonium, uranium, and mercury) is greatest when those materials are inhaled in a finely divided form, which is the form that the plasma source requires for efficient utilization. Hence, the plasma source tends to exacerbate the ordinary safety problems associated with the handling of hazardous materials. All installations described in this volume utilize high-efficiency particulate air (HEPA) filters to remove hazardous particulates from the plasma exhaust stream. On-line testing of these filters indicates that a serial combination of

1. "Environmental Protection, Safety, and Health Protection Program for DOE Operations," DOE Order No. 5480.1, U.S. Department of Energy, Washington, DC, 4 March 1981.
2. "Standards for Protection Against Radiation," Code of Federal Regulations—Energy, Part 20, Title 10, U.S. Nuclear Regulatory Commission, Washington, DC, 31 Jan. 1986, Chapter 1.
3. Houk, R. S., Fassel, V. A., Fiesch, G. D., Svec, H. J., Gray, A. L., and Taylor, C. E., "Inductively Coupled Argon Plasma as an Ion Source for Mass Spectrometric Determination of Trace Elements," Analytical Chemistry, Vol. 52, 1980, pp. 2283–2289.
4. Palmieri, M. D., Fritz, J. S., Thompson, J. J., and Houk, R. S., "Separation of Trace Rare Earths and Other Metals from Uranium by Liquid-Liquid Extraction with Quantitation by Inductively Coupled Plasma Mass Spectrometry," Analytica Chimica Acta, Vol. 184, 1986, pp. 187–196.
5. Blair, P. D., "The Application of Inductively Coupled Mass Spectrometry in the Nuclear Industry," TrAC, Vol. 5, 1986, pp. 220–223.
two to three such filters will effectively cleanse the exhaust stream so that it can be safely
discharged into the atmosphere.\textsuperscript{6,7} It is also reported by many workers (McMillan, Hiller, and
Lawry, Edelson and DeKalb, Mainka et al., and others) that the particulates in the plasma exhaust
tend to "plate out" on cold surfaces in the exhaust ducting prior to coming in contact with a
HEPA filter, thus providing a prefilter that can prolong the effective lifetime of the exhaust HEPA
filters. (Mainka et al. report that they have successfully utilized one HEPA filter for longer than
four years.) It is conceivable that the safe use of plasma sources for the analysis of gamma-emitting
materials could require more frequent HEPA filter changes to reduce operator exposure to radiation
from trapped particulates, before reductions in the HEPA filter air flow rate dictate filter replacement.
The safety of an enclosed plasma facility is therefore strongly dependent on the operating
performance of the HEPA filters utilized. Since the performance of HEPA filters is temperature
dependent, and the exhaust gases from plasma instruments are at elevated temperatures, it is
prudent to provide exhaust gas cooling (Mainka et al.) or exhaust gas temperature monitoring
(Edelson and DeKalb) to ensure that the HEPA filters are being used within their designed range of
operation.

The systems described in this volume range in cost (that is, total installation costs) from about
$20,000 to well over $1,000,000. These costs reflect the capabilities of the instruments selected
and the complexity of the installation, which includes such design features as plasma source
isolation and radiation shielding. The simplest designs are the "open" installations; this term
refers to plasma source units installed in radiological hoods. These hoods permit hands-on operation
of certain plasma source components, while the plasma source is enclosed within a negative
pressure environment and the plasma exhaust gases are passed through high-efficiency particulate
air filters. The "hot cell" installations, which have plasma source units installed in fully shielded
enclosures, where many plasma source components are accessible only by the use of remote
manipulators, are quite complex and more costly to build and operate.

Four papers (Matsuzaki and Hara, Apel et al., Stone and Dykes, and Mainka et al.) describe
the use of radiation shielding to avoid operator exposure to penetrating radiation. Such shielding
is required for samples containing high-gamma-emitting components, such as might occur in work
with nuclear waste and spent nuclear fuels. Generally in those cases, containment is also essential,
and source shielding is an additional requirement imposed on the containment system.

The authors of the symposium papers had been requested to emphasize the engineering and
operational characteristics of their instrumentation rather than the results obtained with the
instruments, in keeping with the philosophy that led to the publication of this volume. In some
instances, illustrative experimental results have been provided.

The editors hope that this volume will serve its intended purpose, which is to provide guidance
for those who are interested in safely utilizing plasma spectroscopy for the analysis of hazardous
materials and, specifically, to assist readers in establishing the optimum facilities for their
requirements.

\textbf{Martin C. Edelson}

Ames Laboratory, Iowa State University, Ames, IA
50011; symposium chairman and editor.

\textbf{J. Leland Daniel}

Pacific Northwest Laboratory, Richland, WA 99352;
coeditor.

\textsuperscript{6} Macleod, K. C., Hendrie, R. W., and Berry, T., "Applications of ICP/OES to Measurement of Impurities
in Uranium and Plutonium," Karlsruhe International Conference on Analytical Chemistry in Nuclear Technology,
Karlsruhe, Federal Republic of Germany, 3–6 June 1985.

\textsuperscript{7} Davies, J. A. and Jefferyes, A. C., "Size Distribution of Particulate Matter in Exhaust Gases in Inductively
Coupled Plasma Atomic Emission Spectrometry," \textit{Analyst.} Vol. 111, 1986, pp. 221–223.