



## Project Summary

# Multielemental Analytical Techniques for Hazardous Waste Analysis: The State-of-the-Art

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Based on a comprehensive review of the literature, the multielemental techniques of inductively coupled plasma optical emission spectroscopy (ICP), x-ray fluorescence spectroscopy (XRF) and instrumental neutron activation analysis (INAA) have been compared for the determination of antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc in hazardous waste matrices. These particular elements were chosen because they are on the list for classifying a waste as hazardous and/or on the U.S. Environmental Protection Agency's (EPA's) Priority Pollutant list. Each technique is discussed with respect to theory, anticipated interferences and correction techniques, observed precision and accuracy for simple and complex matrices, detection limits, and cost.

The literature review revealed that there has not been sufficient analytical work on complex matrices to fully compare these three techniques for many of the priority pollutant elements. For those elements with a sufficient database to compare precision and accuracy by the three techniques (arsenic, barium, chromium, lead, nickel and zinc) ICP offers an advantage in detection limits and precision, whereas XRF may be very useful as a preliminary screening technique due to its ability to provide rapid, semi-quantitative data even at trace levels. XRF and ICP have significant cost advantages

over INAA, requiring much less capital expenditure and lower labor costs.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, 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

Information on the pollutant content of wastes is required to properly assess the hazard and the need for waste management or for remedial action. Multielemental analytical techniques are attractive as the means to obtain inorganic content information on wastes rapidly and/or economically. Although multielemental techniques are widely used, complex wastes and contaminated soil present the potential for interferences not normally encountered. The elements antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl) and zinc (Zn) are identified in federal publications as pollutants of special concern.

The present work is a literature evaluation of currently available multielemental techniques in order to compare the advantages and limitations for the analysis of the specified elements in hazardous wastes or in contaminated soils. The currently available multielemental techniques for trace element

determinations are isotope dilution mass spectrometry, spark source mass spectrometry, multielemental atomic absorption spectroscopy, voltammetry, inductively coupled plasma optical emission spectroscopy, instrumental neutron activation analysis, and x-ray fluorescence spectroscopy. Each technique was evaluated in terms of accuracy, precision, detection limits, severity of matrix interferences and economic factors.

## Procedure

A preliminary evaluation was conducted to select the most promising techniques for an extensive literature search and a survey of users. A thorough literature search was accomplished with the assistance of the Lockheed computer system DIALOG which enables the user to search selected abstract files. The files searched included Chemical Abstracts, National Technical Information Service (NTIS), Compendex (collection of engineering journals), Agricola (collection of agricultural journals), Foundation Grants Index, Dissertation Abstracts, Enviroline (collection of environmentally oriented journals), Scisearch, Pollution Abstracts, SSIE Current Research, and Conference Papers Index. More than 50 different journals and abstracts were searched. Any publication which provided information on detection limits, precision or accuracy for any of the selected elements was included in the data set. This was accomplished with the aid of the computer system Datatrieve on the VAX 11/780 computer. In addition, a questionnaire was sent out to users of the various techniques to solicit the most recent information.

Finally, an assessment and comparison of the most promising techniques for analyzing hazardous wastes was conducted with respect to analytical capabilities and limitations, detection limits, precision, accuracy, complexity of sample preparation, availability of commercial services and cost.

## Results and Discussion

Table 1 summarizes the advantages and disadvantages of each of the potential analytical techniques. Isotope dilution mass spectrometry and spark source mass spectrometry possess unacceptable economic factors of large capital cost, expensive labor costs, and lengthy analysis time. Multielemental atomic absorption spectroscopy is not currently available commercially, and has not been fully investigated. Voltammetry lacks sufficient selectivity to be developed as a

**Table 1.** Comparison Summary of Multielemental Techniques (+ = advantage, - = disadvantage)

Property	Technique							
	MAAS	AAS	ICP	XRF	INAA	IDMS	SSMS	VM
Minimal Operator Skill Required	+	+	-	-	-	-	-	-
Cost	-	+	+	+	-	-	-	+
Detection Limits	+	+	+	-	+	+	+	+
Freedom from Interferences	+	+	+	-	+	-	+	-
Precision	+	+	+	+	+	+	-	+
Availability	-	+	+	+	-	-	-	+
Working Range	-	-	+	+	+	-	+	-
Large Number of Elements	+	-	+	+	+	-	+	-
Analysis Time	+	-	+	+	-	-	-	-

MAAS = Multielemental Atomic Absorption Spectroscopy.

AAS = Atomic Absorption Spectroscopy.

ICP = Inductively Coupled Plasma Optical Emission Spectroscopy.

XRF = X-Ray Fluorescence Spectroscopy.

INAA = Instrumental Neutron Activation Analysis.

IDMS = Isotope Dilution Mass Spectrometry.

SSMS = Spark Source Mass Spectrometry.

VM = Voltammetry.

method for routine multielemental analyses of complicated matrices. ICP, INAA and XRF were judged to be the most promising multielemental methods for the determination of the specified elements in hazardous wastes.

The numerical results of the literature search are summarized by element and technique in Table 2. A minimal amount of data was found for x-ray fluorescence determination of Ag, Cd, Sb, Hg, Se and Tl. XRF has traditionally been used for determining major elements and this explains the paucity of data for these elements, which typically occur at fairly low concentrations in environmental samples. For neutron activation there is a minimal amount of data available on Be, Pb and Tl because these elements do not possess isotopes with adequate reaction cross-sections to form sufficient gamma-emitting radio-nuclides. For ICP, little data are available for Hg or Tl because these elements can be determined to lower

concentrations using cold-vapor AAS and furnace AAS, respectively; and few standard reference materials have these elements present at concentrations measurable by ICP. Information entries on the specified elements number 1220 for ICP, 521 for XRF and 305 for INAA.

## Inductively Coupled Plasma Optical Emission Spectroscopy (ICP)

Inductively coupled plasma is a form of optical emission spectroscopy that utilizes an argon plasma as the excitation source. Optical emission spectroscopy is a technique that involves heating a sample in a flame, electric arc, electric spark or plasma to produce a population of excited atoms and ions that return to the ground state by emitting radiation. Each element emits light of a characteristic wavelength, and signal response is proportional to concentration level.

Accuracy is affected by a number of potential sources of error. Analytical errors in ICP are caused by direct spectral and background interferences due to matrix elements, sample interaction with the plasma, variable physical characteristics of different matrices and instrumental drift. Accuracy is assessed by examining percent recoveries for analytes added to samples or by agreement with certified values for reference materials, such as Standard Reference Materials (SRMs) from the National Bureau of Standards. For 12 of the 14 elements there are sufficient data available to make some assessments for determinations by ICP. For Hg and Tl there are no available data on precision and accuracy. This is principally because

**Table 2.** Number of Records in the Literature by Element and Technique

Element	Technique			Total
	ICP	INAA	XRF	
Ag	34	10	1	45
As	50	18	11	79
Ba	87	53	82	222
Be	55	1	0	56
Cd	110	15	7	132
Cr	137	54	96	287
Cu	198	12	66	276
Hg	9	18	4	31
Ni	149	34	116	299
Pb	166	6	56	228
Sb	27	31	1	59
Se	27	18	3	48
Tl	7	0	0	7
Zn	164	35	78	277

Hg and Tl are usually determined with far greater sensitivity using cold-vapor AAS and furnace AAS, respectively. In addition, there are no SRMs with certified values for Hg or Tl at levels measurable by ICP.

The ICP instrumental analysis rate is typically 30-100 samples per day. The rate-limiting step for analysis of solid samples is the required preliminary digestion to provide a liquid for introduction into the instrument. Although the digestion can be set up for batches of 50-100 samples, the overall digestion time for these samples is several hours. Many laboratories offer ICP analysis at rates ranging from \$20-\$100/sample, depending on the number of elements being analyzed and the complexity of the sample preparation.

#### Capital Investment (ICP)

- \$50K (Basic ICP) Add \$10K for sampler and printer
- \$100K (ICP/AAS full system - Monochromator or 20 channel Simultaneous ICP)
- \$175K (Top-of-the-Line Simultaneous ICP with scanning capacity and 40 channels).

### **Instrumental Neutron Activation Analysis (INAA)**

Instrumental neutron activation analysis is a nuclear technique in which the sample is exposed to a neutron flux and the induced radioactivity is determined using gamma ray spectrometry. Characterization and measurement of the energy of the emitted gamma rays yields qualitative and quantitative analysis of the sample. The advantages of this technique are its nondestructive nature, minimum sample manipulation requirements and low detection limits. The main limitations are matrix interferences, required access to a neutron source (with associated high capital costs), the fact that not all elements are amenable to this type of analysis, and the possibility that the small solid specimen which is analyzed may not be homogeneous and representative of the bulk sample.

In multielemental analysis by INAA, detection limits must be sacrificed sometimes in order to avoid serious interferences with the other elements being determined and the major matrix constituents. Beryllium cannot be analyzed by INAA because it forms no gamma-emitting radionuclide. Only one gamma-emitting nuclide exists for Pb and for Tl, and the very low reaction cross-section for these nuclides implies poor detection limits for Pb and Tl by INAA.

Analytical errors in INAA occur when factors affecting the formation of the radioactive isotope or detection of the emitted radiation differ significantly between the sample and the standard. Formation of the radioactive isotope is dependent on the neutron flux density, the number of target nuclei, and the reaction cross-section. The number of target nuclei and the reaction cross-section are intrinsic properties of the sample, and variations in the flux density hitting samples and standards are trivial due to constant rotation of the specimens within the reactor. The detection of the emitted gamma-rays is primarily a potential source of error. The accuracy of the total photopeak count must be corrected for systematic errors arising from spectral interferences, peak-broadening errors, absorption errors, and instrument dead-time losses. Random errors result from counting statistics and procedural uncertainties.

Using several irradiations for different periods and counting after different decay periods eliminate many potential sources of error. Different irradiation times allow the analyst to obtain data for short-lived isotopes without generating high specific activity from longer lived isotopes (with a potential for large dead-time corrections). Alternate decay periods make it easy to resolve peaks of similar energy but different half-lives. Sophisticated computer software is essential for performing these corrections.

Precision improves with increasing concentration for INAA while the accuracy is excellent for the high levels but poor for some of the elements at low levels (<10  $\mu\text{g/g}$ ). No INAA data were reported for Ag, possibly because its INAA detection limit near 1  $\mu\text{g/g}$  is comparable to, or larger than, the level in most terrestrial materials used as SRMs. The precision exceeds 20% for As at 10  $\mu\text{g/g}$ , for Ba at 100  $\mu\text{g/g}$ , for Cr at 10  $\mu\text{g/g}$ , for Ni at 100  $\mu\text{g/g}$ , and for Sb at <1  $\mu\text{g/g}$ . The poor Ni precision probably reflects measurements with reactors having few fast neutrons, while Ba suffers from Fe interference. The accuracy exceeds the arbitrary acceptance criterion of  $100 \pm 20\%$  recovery at, and below, a level of 10  $\mu\text{g/g}$  for Cd, 10  $\mu\text{g/g}$  for Cr, <1  $\mu\text{g/g}$  for Hg, 10  $\mu\text{g/g}$  for Ni, and 10  $\mu\text{g/g}$  for Sb.

INAA involves no elaborate sample preparation procedures. Solids are ground, and a representative aliquot is mixed with cellulose and pressed into a standard size pill. Dissolved material in liquids can be analyzed after freeze drying and pelletizing the resulting powder. Chromium contamination at the level of

0.5  $\mu\text{g/g}$  sometimes results from the tool-steel dies used to prepare the pellets.

The rate limiting step is the time required before interfering radiation has decayed sufficiently to allow long-lived isotopes to be counted. This can be as long as 30 days for the analysis of long half-life isotopes such as  $\text{Cr}^{51}$ . Throughput can also depend on the cross-sections of matrix interferences as well as the half-life of the element of interest. If matrix elements become highly radioactive, it may be difficult to detect the small amount of radiation emitted by a trace element. In this case, provided the interferences have shorter half-lives than the elements of interest, it is necessary to wait until the interfering radiation has decayed away before counting the sample.

Typical cost for single-sample multielemental analysis is \$400 with delivery times of 5-6 weeks after receipt of sample. Availability of commercial services is quite limited because of the difficulties in acquiring access to a nuclear reactor. Services which use university reactors are available, but typically only on a research basis and not for routine analyses. It is possible to perform INAA using a radioactive element as a neutron source (such as  $\text{Cf}^{254}$ ), but the flux obtained from such a source is typically not adequate for trace level work.

#### Capital Investment (INAA)

\$500K (requires permit)	Nuclear Reactor (or access to irradiation source)
\$135K and up depending on required length of irradiation, sample size, and neutron flux	Commercial Irradiation Cost (for short-lived isotopes, the detector must be at the irradiation site)
\$30K and up	Gamma-Ray Spectrometer and Detector

### **X-ray Fluorescence**

X-ray fluorescence is a form of spectroscopy in which a sample is bombarded with x-rays and inner-orbital electrons are ejected from atoms within the sample. The resulting excited atoms dissipate energy by filling these vacancies with electrons from higher energy levels and emitting characteristic x-ray photons. This secondary emission of x-rays is referred to as fluorescence and, because only certain emissions occur, the x-ray spectral lines are indicative of the elements present. Element concentrations are deduced from the x-ray count

rate of a characteristic line. The advantages of this technique are basically the same as those of neutron activation analysis. XRF is nondestructive, allows for direct analysis of solid samples, and exhibits useful detection limits. Disadvantages of this technique are the severity of matrix effects, difficulty in analyzing liquid samples directly, and the fact that elements with atomic numbers less than 10 cannot be determined with conventional instrumentation.

In XRF a significant portion of the secondary and primary x-rays is absorbed by the major constituents comprising the sample matrix. The key to obtaining reliable x-ray fluorescence data is proper sample preparation. The sample must be prepared in a manner which will minimize matrix absorption problems and also ensure homogeneity (which is important because incident x-rays do not penetrate far into the sample). Conversion of x-ray count rate to element concentration will not be accurate unless the sample mass absorption effects can be compensated for or eliminated. Interferences which can occur in addition to matrix absorption are direct spectral interferences, background radiation interferences, and self-absorption of fluorescent radiation.

XRF precision does not often drop below the arbitrary acceptance value of 20% for the relative standard deviation until the concentration is greater than 10 µg/g and, in some cases (Ba, Cr, Ni), not until the concentration is greater than 100 µg/g. Barium and chromium, along with Pb, are also the elements that exhibit poor accuracy at lower concentrations.

Commercial analysis costs range \$5-\$100 per sample depending upon the quantity of samples and the complexity of the analyses. No commercial services offer analysis for the 13 listed elements (excluding Be) that are measurable; by conventional XRF instruments. The availability of commercial XRF services is much more limited than for ICP.

### Capital Investment (XRF)

- \$75-85K (Energy Dispersive) add \$15-20K for sampler
- \$95K (Wavelength Dispersive, sequential)
- \$125K (Wavelength Dispersive - more intensity)
- \$350K (Wavelength Dispersive, Simultaneous, Deluxe)

### Comparison of ICP, INAA and XRF Techniques

ICP is the only technique, among the three, capable of analyzing all of the 14

specified pollutant elements. Beryllium cannot be determined by INAA (because its radionuclide emits no gammas) nor by conventional XRF (because the long wavelengths of the emitted x-rays cannot be dispersed). Pb and Tl are too weakly activated to be successfully determined by INAA, except at very high concentrations. The lack of a substantial database for XRF analysis of trace elements reflects the trend for it to be used most frequently as a major element technique. Table 3 ranks these three techniques for eight characteristics. Table 4 shows the median detection limit for each element as a function of instrumental technique.

A comparison of the accuracy and precision for the three techniques was obtained by using data for rock, sediment, soil, sludge, coal, oil, steel, and pottery. The comparison was made by calculating the percentage of sample data where recovery (accuracy) exceeded an arbitrary criterion of 100 ± 20% and where the relative standard deviation (precision) exceeded an arbitrary criterion of 20%. The results of these calculations are shown in Tables 5 and 6.

For some of the elements, insufficient data were available for all three techniques, and a valid comparison could not be made. This is the case for the precision data on Ag, Be, Cd, Hg, Pb, Sb, Se, and Tl. In terms of precision, ICP appears to yield the best results for almost all the remaining elements. For Zn the precision differences among the three techniques are insignificant. Cu has insufficient data by INAA to allow a comparison. For XRF and INAA, there are only sufficient data for comparison of As, Ba, Cr, Ni, and Zn. Table 6 shows that these two techniques give approximately the same criterion percentages for As, Ba, Cr and Zn while Ni results are better by XRF than by INAA.

Inspection of the accuracy data indicates insufficient information for Ag, Be, Hg, Sb, Se, and Tl. Of the eight remaining elements, ICP gives the best results for Cd, Cr, Cu and Ni. For XRF and INAA there are insufficient data for comparison of As. INAA gives better results for Ba, and XRF

**Table 4.** Comparison of Median Detection Limits (µg/g) for the Selected Elements as a Function of Instrumental Technique

Element	Technique		
	ICP*	XRF	INAA
Ag	0.3	—	1
As	3	0.9	0.2
Ba	0.05	10	53
Be	0.05	—	—
Cd	0.2	5	15
Cr	0.3	1	2
Cu	0.2	1	6
Hg	3	2	0.3
Ni	0.8	1	160**
Pb	2	2	—
Sb	3	—	0.08
Se	2	13	0.3
Tl	2	—	—
Zn	2	3	5

\*Assuming digestion of 100 mg of solid sample with 10 ml of acid.

\*\*Result for Ni is probably biased by unoptimized procedure.

**Table 5.** Percentage of Sample Data Where Accuracy (Recovery) Exceeds Arbitrary 100 ± 20% Criterion

Element	Technique		
	ICP	XRF	INAA
Ag	31%(16)*	NA†	NA
As	15%(13)	0%(2)	0%(2)
Ba	11%(36)	20%(71)	0%(16)
Be	47%(15)	NA	NA
Cd	39%(26)	75%(4)	50%(4)
Cr	33%(54)	35%(79)	44%(18)
Cu	5%(76)	41%(39)	100%(1)
Hg	NA	NA	20%(5)
Ni	19%(47)	21%(90)	62%(13)
Pb	44%(63)	29%(34)	25%(4)
Sb	NA	NA	86%(7)
Se	NA	0%(1)	0%(1)
Tl	NA	NA	NA
Zn	19%(43)	2%(49)	12%(17)

\*Numbers in parentheses indicate the quantity of data records for a technique.

†"NA" indicates information Not Available.

gives better results for Zn. The case of Pb is somewhat misleading for it appears that INAA gives comparable results to XRF. This observation would be disturbing since INAA is known to be a poor trace

**Table 3.** Comparison of ICP, INAA and XRF Characteristics

Characteristic	Relative Ranking (Best to Worst)
1 Rapid Analysis	XRF>ICP>INAA
2 Detection Limits	ICP, INAA>XRF
3 Precision and Accuracy	INAA>ICP, XRF
4 Ease of Error Corrections	INAA, ICP>XRF
5 Low Cost	ICP>XRF>>INAA
6 Flexibility	ICP, INAA>XRF
7 Availability	ICP>XRF>INAA
8 Ease of Sample Preparation	INAA>XRF>ICP

**Table 6.** *Percentage of Sample Data Where the Relative Standard Deviation Exceeds Arbitrary 20% Criterion*

Element	Technique		
	ICP	XRF	INAA
Ag	20%(5)*	NA†	NA
As	14%(7)	40%(5)	45%(11)
Ba	0%(12)	8(12)	6%(35)
Be	0%(7)	NA	NA
Cd	4%(27)	100%(1)	NA
Cr	0%(28)	21%(34)	19%(26)
Cu	12%(49)	29%(17)	0%(1)
Hg	NA	NA	NA
Ni	16%(43)	18%(38)	53%(15)
Pb	3%(30)	18%(11)	NA
Sb	0%(2)	NA	46%(13)
Se	NA	0%(1)	0%(2)
Tl	NA	NA	NA
Zn	2%(40)	0%(20)	8%(12)

\*Numbers in parentheses indicate the quantity of data records for a technique.

†"NA" indicates information Not Available.

technique for Pb. Closer inspection revealed that the INAA Pb results are based on only four samples with extremely high levels of Pb.

The relative importance of the various sources of analytical error for the three techniques is shown in Table 7. For both INAA and XRF, the counting errors are the least significant error and never amount to more than 1%. For XRF, sample preparation is the most important source of error because it is directly related to the nonspectral errors which are a major problem in XRF. Unless sample preparation is adequate, satisfactory data will never be generated no matter how elaborate the nonspectral correction procedures. Nonspectral errors rank second in importance followed by spectral interference errors and then instrumental errors. The different types of spectral interferences are well documented and can usually be anticipated and corrected. Adequate correction for spectral and nonspectral errors is completely dependent on the operator's skill and experience. Instrumental error results in a small residual background. This error can be corrected by plotting the spectral background as a function of the Compton scattered radiation and discern-

ing the value of the y-intercept. For INAA, both instrument and sample preparation errors are minimal. The major source of INAA error is spectral interference, and the major requirement for adequate correction is an experienced operator skilled in making confirmative isotope measurements for an element. The major source of error for ICP is sample preparation because of the potential for contamination or loss of analyte during this step. Spectral interference is the next most important source of error in ICP because correction is dependent on the skill and experience of the operator in recognizing these errors. Instrumental drift is usually not a serious ICP problem, if re-calibration is performed periodically.

XRF is far superior to ICP and INAA in its ability to generate a rapid semi-quantitative analysis scan of a sample in less than 5 minutes. The sample preparation time for ICP takes well over an hour while INAA requires weeks to allow sample activity decay for certain elements. XRF could, therefore, have utility as a preliminary screening technique for hazardous waste samples of totally unknown composition.

ICP is the least costly of the three methods in terms of both capital investment and operating costs. In addition, commercial services for ICP are low in cost compared to XRF or INAA. The cost of operating an XRF system is comparable to ICP although more extensive computer facilities are required. The expense of operating an INAA system is on the order of 5 to 10 times that of ICP or XRF, and even commercial service fees are 5 to 10 times higher.

## Conclusions

After considering detection limits, precision, accuracy, errors and correction procedures, expense, flexibility, availability and sample preparation, ICP appears to be the multielemental technique most amenable to analysis of hazardous waste samples; XRF may be most useful as a preliminary of hazardous waste samples; and XRF may be most useful as

a preliminary screening technique. Any literature review suffers from:

- A lack of comparable databases for individual techniques with respect to sample types, definition of detection limits, and elements.
- An inherent bias that published data are typically the best available and not indicative of what may be observed in routine applications.

A laboratory comparison of identical samples by all three techniques is necessary before a more comprehensive comparison can be made for determining these elements in wastes that are potentially hazardous.

**Table 7.** *Ranking the Importance of Error Sources for ICP, INAA and XRF*

Technique	Error Categories				
	Sample Prep	Instrumental	Counting	Non-Spectral	Spectral
ICP	1	3	-	4	2
INAA	3	4	5	2	1
XRF	1	4-5	5	2	3

1 = High (very important).

5 = Low (Trivial).

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*The complete report, entitled "Multielemental Analytical Techniques for Hazardous Waste Analysis: The State-of-the-Art," (Order No. PB 84-178 425;*

*Cost: \$13.00, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

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*The EPA Project Officer can be contacted at:*

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