MM100[a]

Inductively Coupled Plasma-Mass Spectrometry for Radionuclide Analyses

Note: **This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.**

1.0 Scope and Application

Inductively coupled plasma-mass spectrometry (ICP-MS) is an experimental technique generally used for trace analysis (µg/L) of elemental species in aqueous solutions. Instrument detection limits (IDLs) are typically in the pG/L to µg/L range, depending on elemental sensitivity and potential matrix effects. Sample preparation, such as acid or microwave digestions, can be performed to accommodate analysis of nonaqueous sample matrices, such as soils, oils, sludges, glasses, and sediments. The ICP-MS technique is not conducive to concentrations of dissolved solids that exceed 0.2%, as these solids can saturate the detector and produce solid deposition on the system sampling interface components, thereby reducing instrument performance.

The intention of this method is to serve as a guidance document for generating laboratory specific ICP-MS standard operating procedures (SOPs). For some procedures, additional documentation, such as data quality objectives (DQOs) and statements of work (SOWs) may be required. Each laboratory SOP should be specific to site requirements and regulations and instrument types. Primarily, this method is intended to provide analytical protocols for environmental regulatory support. Secondarily, because of the large potential analytical capability of ICP-MS, this method provides the latitude necessary for research and development projects.

This method supplements the U.S. Environmental Protection Agency (EPA) SW-846 Method 6020 (EPA 1992), and addresses the application of ICP-MS to radioactive elements that are not covered in 6020. Method 6020 should be used as the basis for this method. Table 1 provides a list of potential radionuclides for analysis.

(a) Method was submitted by Steven B. Wyrick (Science Applications International Corporation, Gaithersburg, Maryland), Gary M. Mong and Eric J. Wyse (Pacific Northwest Laboratory, Richland, Washington).

Determination of radionuclides by ICP-MS is a complementary technique to radiochemical counting. The major considerations when selecting ICP-MS versus radiochemical counting techniques are the limiting factors of detection. Generally, ICP-MS performs better for lower activity isotopes, as radiochemical counting methods may require several days to complete, while radiochemical counting methods are more accurate for higher activity isotopes. For samples with intermediate activities, the method of choice may depend on factors such as interferences or radiation handling requirements. Potentially, both methods could be used to complement and corroborate results.

2.0 Summary of Method

The aqueous sample is aspirated into an argon plasma to atomize, ionize, and entrain sample constituents in an argon gas stream. The ionized elements then pass through a sampling interface to reduce the pressure from 760 torr to 1 X 10^{-5} torr and then into a quadrupole mass spectrometer. The ionized elements are then separated, detected, and quantified according to their respective mass-to-charge ratios. The raw data are examined to correct for potential interference and matrix effects before characterizing the sample components.

This method is meant to be very basic; it will analyze low activity aqueous samples, using the basic instrument configuration (i.e., no instrument upgrades or any special sample preparation, separation or preconcentration). Also, this method is limited to low radioactivity levels, so that minimal special shielding is required. Any instrument upgrades or requirements beyond the scope of this method should be written as separate, element-specific procedures.

3.0 Interferences

Table 1 gives some potential interferences for radioisotopes to be analyzed. In addition, some isobaric interferences are described and accounted for in Method 6020. However, some of the equations used in Method 6020 for corrected interferences assume natural abundance for elemental isotopics; one must consider that samples covered in this method may not always have natural isotopic ratios.

Method 6020, Table 2 (EPA 1992) defines an interference check sample (ICS) to determine potential isobaric interferences. The high concentrations of the components seem to cause some concern to ICP-MS users as to the deleterious effect they may have on instrument performance[(a)]. Thus, an appropriate level of ICS material is to be determined by the instrumentation. In addition to the components listed in 6020, Ru should be added as a check for its potential contribution to ^{99}Tc. See Table 1 of this procedure for additional interferent information.

(a) R. Henry, personal written communication, Fisons Instrument (1993).

Certain techniques, such as dilution, preconcentration, and chemical and physical separation, are occasionally used to reduce or eliminate potential interferences. But the same techniques that minimize interference effects may inadvertently degrade the method detection limit and dilution-corrected concentration accuracy. Any sample modification should be fully described in a separate element-specific procedure.

4.0 Safety

Department of Energy wastes submitted for analysis by ICP-MS may contain various fission products in addition to the long-lived analytes to be determined by the technique. Laboratory protocols for radioactivity screening, handling radioactive samples, and surface decontamination should be in place before sample analysis. Two possible methods for screening are liquid scintillation counting and hand-held radiation monitor counting.

Laboratory and/or site radiation safety procedures should be closely followed. Additionally, laboratory and vendor manual safety procedures, involving the operation of the ICP-MS instrument should be used.

5.0 Apparatus and Materials

Some applications might require specialized modifications to the conventional ICP-MS instrument. These variations can improve sample input efficiency (and thus reduce the total amount of sample required), separate or preconcentrate sample analytes, reduce memory effects, and/or allow for analysis of solid or organic samples. These procedural changes should be covered in element-specific procedures. Some sample system variations are

- dynamic range enhancement
- ultrasonic nebulizer
- direct injection nebulizer
- chromatographic column
- electro-thermal vaporization
- laser ablation
- flow injection analysis.

6.0 Reagents

Isotopic standards must have elemental isotopic abundance well documented and traceable to appropriate national standards. One should not assume natural abundances for elemental isotopics (e.g., the natural abundance of ^{235}U is approximately 0.7%, but some U used for reference standards is depleted, and the ^{235}U isotopic abundance is closer to 0.3%). Calibration standards and quality control standards requirements, as they apply to DQOs should be addressed in appropriate SOPs, if required.

7.0 Sample Collection, Preservation, and Handling

7.1 Sample Collection. The initial sample collection and handling should be addressed in the SOP or in a project SOW, if applicable.

7.2 Sample Dissolution. The kind of dissolution required will depend on what type of analysis is required. Leachable analytes may be required for some applications, while total analytes may be required for other applications. If the samples to be analyzed were received as a solid, sludge, or slurry, they must be dissolved for conventional ICP-MS analysis. Dissolution procedures vary greatly between sample types, but the chosen procedure should be fully described in a separate element-specific procedure. Some dissolution methods are

- microwave digestion
- hot acid digestion
- cold acid digestion
- alkali fusion
- sodium fusion

7.3 Sample Dilution. If the elements of concern are of sufficiently high concentration (≥500 µg/L) sample dilution is usually necessary. Dilutions are usually made by volume (rather than by weight) with calibrated pipets. The solvent used for dilution is usually a dilute acid.

7.4 Sample Preconcentration. Sample preconcentration may be necessary if the concentration of an analyte is below the IDL, or if a separation is required, as described in section 3.0. Any sample preconcentration should be fully described in a separate element-specific procedure.

8.0 Procedure

8.1 **Methods**. Several types of methods (with associated calibration protocols) are used to obtain various types of information, with each having its own level of uncertainty. Some of the more commonly used methods are quantitative (QA), semi-quantitative (SQA), standard addition (SA), isotope ratio (IR) and isotope dilution (ID) (Adams et al. 1988).

A qualitative or semi-quantitative scan can be run before other methods to gain a better understanding of the sample composition. These preliminary scans can be useful to determine if radioactive, hazardous, or undesirable analytes, which may produce significant memory or interference effects to the instrument, exist in the sample. If these analytes are not present, or if high accuracy is not required, then these elemental standards do not need to be introduced into the system.

Any prescreening methods should be included in the SOP, element-specific procedure, or project SOW, when required.

8.2 **System Parameters**. Commercial ICP-MS instruments are provided with software that can automate data acquisition, calibration, and quantification. To take advantage of these capabilities, the analyst must specify the elements and isotopes to be determined, the mode of data acquisition, the calibration technique, standard concentrations, and the sequence in which samples and standards are to be measured. Analysts should refer directly to their instrument manuals for specific instructions on how to enter these parameters.

8.3 **Data Acquisition**. The three methods of sample acquisition generally available are scanning, peakjumping, and single ion monitoring (Jarvis et al. 1992).

8.4 **Tuning**. Instrument tuning should be specific to the laboratory SOP, but should meet, as a minimum, the requirements set in Method 6020. Tuning should be specific to the mass range to be analyzed. If specific shorter mass ranges are to be tuned for high resolution, then the associated tuning method should be addressed in the element-specific procedure or project SOW.

9.0 Calculations

Results are ordinarily calculated by the vendor supplied software; however, with some date, the results must be calculated manually or on a spreadsheet because the elemental isotopic abundances are not natural (e.g., samples that contain fission products). If the unnatural isotopic abundances are known, some vendors' software allows the user to modify the isotopic abundances.

For the radioisotopes, activity levels should be reported in addition to concentrations. Given the concentration, atomic weight, and half-life of a radioisotope, the activity can be determined as follows:

$$\frac{(X_i)(\ln 2)(N_o)\left(10^{12}\ \mathrm{pCi/Ci}\right)}{(AW)\left(t_{1/2}\right)\left(3.7 \times 10^{10}\right)} = A_i$$

where

A_i	=	the activity of species i in pCi/L
X_i	=	the concentration of species i in g/L
N_o	=	Avogardo's number (6.02×10^{23} atoms per mole)
$t_{1/2}$	=	half life of species i
AW	=	atomic weight of species i
ln2	=	natural log of 2

Note: 3.7×10^{10} is the conversion factor for atomic disintegrations per sec to curies; other values are conversion factors to get desired activity units.

For example, if the concentration of ^{235}U were measured to be 0.28 µg/L, and given the half-life and atomic weight of ^{235}U are 7.1 X 108 years and 235 g/mole, respectively, the corresponding activity, A_i, in pCi/L would be calculated as follows:

$$\frac{0.28\ \mu g/L \cdot 10^{-6}\ g/\mu g \cdot 0.693 \cdot 6.02 \times 10^{23}\ \text{atoms/mole} \cdot 10^{12}\ \text{pCi/Ci}}{235\text{g/mole} \cdot 7.1 \times 10^{8}\ \text{yr} \cdot 3.1536 \times 10^{7}\ \text{sec/yr} \cdot 3.7 \times 10^{10}\ \text{atoms/sec/Ci}} = 0.60\ \text{pCi/L}$$

10.0 Quality Control

10.1 Instrument Detection Limit. Although Method 6020 defines the IDL, it is not being used consistently among ICP-MS users. The IDL defined below may be used; it differs from Method 6020, in principle, but retains the same intent. However, the user may still use the IDL method in Method 6020. The method used should be well documented in the SOP or project work plan.

On three nonconsecutive days, the analyst should calibrate the instrument with standards prepared per Method 6020. The analyst shall determine the concentration equivalent of the blank intensity for each analyte on each day. The standard deviations of the blank equivalent concentrations shall be pooled (Miller and Miller 1993) and multiplied by three; this number shall be defined as the instrument detection limit. In general, this figure of merit, once established, need not be re-evaluated unless: 1) a significant change in instrument sensitivity occurs, of 2) a significant change in instrument background occurs.

10.2 Control Charts

Long-term instrument stability should be monitored to maintain assurance the instrument is functioning properly, or to detect early signs of performance deterioration. Control charting is becoming a popular indicator of instrument performance. Control limits for the control charts should be stated in the SOP, according to the requirements set forth in relevant SOPs and DQOs. One possible plan for control charging is as follows:

Data for the control chart are obtained through a specific analysis on the control standard only; however, it an independent check standard containing the elements of interest is analyzed on a regular sample analysis, these data may also be used. A standard counting the appropriate elements {preferably a multi-element standard reference material (SRM), e.g., National Institute for Standards and Technology (NIST)1643c} is analyzed against prepared calibration standards that originate from a different stock than does the control standard. Results obtained for each element are plotted against time on the control chart. At a minimum, the chart should display historic data from the current month, as well as the entire previous month. Data for the control chart should be obtained no less frequently than once a week, when the instrument is performing analyses, and no less than once a month, when the instrument is assumed to be functioning properly, but is not processing samples.

11.0 References

Adams, F., et al., eds. 1988. *Inorganic Mass Spectrometry*. Ch. 6 and 7. J. Wiley and Sons, New York.

Jarvis, K. E., A. L. Gray, and R. S . Houk. 1992. *Handbook of Inductively Coupled Plasma Mass Spectrometry*. Chapman and Hall, New York.

Miller, J. C., and J. N. Miller. 1993. *Statistics in Analytical Chemistry: Third Edition*. P. 55, Ellis Horwood PTR, Prentice Hall, Chichester, United Kingdom.

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U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Wastes. Physical/Chemical Methods*, 3rd Edition, Proposed Update II, SW-846. Office of Solid Waste and Emergency Response. Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Table 1. Potential Elements and Characteristics

Element	Isotope	Internal Standard	Interferant	Sample Prep	Analysis Method[a]	Comments
Tc	97	^{115}In	^{97}Mo	TRU•Spec®	IR, ID	Sample
	99	^{115}In	^{99}R	Ion Exchange	QA, ID	preconcentration
I	127	^{115}In			QA	Memory effects
	129	^{115}In	^{129}Xe	IC[b]	IR, ID	Preconcentration
Ra	226	^{232}Th			SQA	Use ^{238}U
	228	^{232}Th			SQA	
Th	230	^{232}Th			IR, ID	
	232	^{209}Bi			QA	
U	233	^{232}Th			IR	Use ^{238}U
	234	^{232}Th			IR	Use ^{238}U
	235	^{232}Th			IR	Use ^{238}U
	236	^{232}Th			IR	Use ^{238}U
	238	^{232}Th	^{238}Pu	TRU•Spec®	QA	
Np	237	^{232}Th			SQA	Use ^{238}U
Pu	239	^{232}Th	UH	TRU•Spec®	SQA	Use ^{238}U
	240	^{232}Th			SQA	Use ^{238}U
	241	^{232}Th			SQA	Use ^{238}U
	242	^{232}Th			SQA	Use ^{238}U
Am	243	^{232}Th			SQA	Use ^{238}U

(a) Analysis methods are defined in section 8.1.
(b) Ion chromatography