METHOD 6800

ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method consists of two approaches: (1) isotope dilution mass spectrometry (IDMS) for the determination of total metals, elements and (2) speciated isotope dilution mass spectrometry (SIDMS) for the determination of elemental and molecular species. This method is applicable to the determination of total metals, metal species and molecular species at µg/g and sub µg/L levels in water samples, solid samples or in extracts or digests. In general, elements and molecules that have more than one available stable isotope can be analyzed by IDMS. SIDMS may require more isotopes of an element or molecule, depending on the number of interconvertible species. The analyses of the following elements are applicable by this method:

Element		CASRN[a]
Antimony	(Sb)	7440-36-0
Boron	(B)	7440-42-8
Barium	(Ba)	7440-39-3
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2

Zinc	(Zn)	7440-66-6

[a] Chemical Abstract Service Registry Number

Other elements, molecules and species may be analyzed by this method if appropriate performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 9.0).

1.2 Isotope dilution is based on the addition of a known amount of enriched isotope to a sample. Equilibration of the spike isotope with the natural element/molecule/species in the sample alters the isotope ratio that is measured. With the known isotopic abundance of both spike and sample, the amount of the spike added to the known amount of sample, concentration of the spike added, and the altered isotope ratio, the concentration of the element/molecule/species in the sample can be calculated.

1.3 IDMS has proven to be a technique of high accuracy for the determination of total metals in various matrices (Refs. 1, 9 and 10). IDMS has several advantages over conventional calibration methodologies. Partial loss of the analyte after equilibration of the spike and the sample will not influence the accuracy of the determination. Fewer physical and chemical interferences influence the determination as they have similar effects on each isotope of the same element. The isotope ratio to be measured for quantification in IDMS can be measured with very high precision, typically RSD $\leq$0.25%. Quantification is a direct mathematical calculation from determined isotopic ratios and known constants and does not depend on a calibration curve or sample recovery.

1.4 SIDMS takes a unique approach to speciated analysis that differs from traditional methods. Traditional speciation methods attempt to hold each species static while making the measurement. Unfortunately, speciation extraction and analysis methods inherently measure the species after species conversions have occurred. SIDMS has been developed to address the correction for the species conversions. In SIDMS, each species is “labeled” with a different isotope-enriched spike in the corresponding species form. Thus, the interconversions that occur after spiking are traceable and can be corrected. While SIDMS maintains the advantages of IDMS, it is capable of correcting for the degradation of the species or the interconversion between the species (Refs. 2, 3, 5 through 8, and 11 through 23). SIDMS is also a diagnostic tool that permits the evaluation of species-altering procedures and permits evaluation and validation of other more traditional speciation analysis methods. SIDMS is applicable to be used in conjunction with other methods when knowledge of species concentration, conversion and stability is necessary.

1.5 Both IDMS and SIDMS require the equilibration of the spike isotope(s) and the natural isotopes. For IDMS, the spike and sample can be in different chemical forms; only total elemental concentrations will result. In general, IDMS equilibration of the spike and sample isotopes occurs as a result of decomposition, which also destroys all species-specific information when the isotopes of an element are all oxidized or reduced to the same oxidation state. For SIDMS, spikes and samples must be in the same speciated form. This requires the chemical conversion of the elements in spikes to be in the same molecular form as those in the sample.

For solution or liquid samples, spiking and equilibration procedures can be as simple as mixing the known amount of the sample and the spikes prior to analysis. Efforts are taken to keep the species in their original species forms after spiking. Aqueous samples such as drinking water, ground water, and other aqueous samples may be directly spiked and analyzed. Solid samples such as soils, sludges, sediments, industrial materials, biological tissues,

botanicals, lysed cells, foods, mixed samples, blood, and urine and other samples containing solid matrices require spiking before or after extraction or digestion prior to analysis to solubilize and equilibrate the species prior to introduction to the mass spectrometer. This method has also been and can be used to certify reference materials and for environmental forensic analysis such as water, soil, air and other samples for detecting chemical and biological agents for homeland defense and homeland security purposes.

1.6 Sensitivity and optimum ranges of the elements will vary with the matrix, separation method, and isotope ratio measurement methods. With the popularity of chromatography and ICP-MS, it is convenient to separate elemental species and to measure the isotope ratios. Although this method is not restricted to chromatography as the separation method of the species and the ICP-MS as the isotope ratio measurement method, this method will use these two techniques as examples in describing the procedures. Other species separation methods, such as extraction, precipitation, and solid phase chelation, and other isotope ratio measurement techniques, such as thermal ionization mass spectrometry (TIMS), electrospray ionization mass spectrometry (ESI-MS) and matrix assisted laser desorption ionization mass spectrometry (MALDI) and other mass spectrometers such as time-of-flight mass spectrometers (TOF-MS) can also be used.

1.7 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.8 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 IDMS method

2.1.1 Samples may require a variety of sample preparation procedures, depending on sample matrices and the isotope ratio measurement methods. One primary purpose of sample preparation is to solubilize the analyte of interest and equilibrate the spike isotopes with sample isotopes. Solids, slurries, and suspended material must be subjected to digestion after spiking using appropriate sample preparation methods (such as Method 3052). Water samples may not require digestion when ICP-MS is used as a detection method because ICP can destroy elemental species and thus many species are indistinguishable for ICP-MS.

2.1.2 A representative measured sample is thoroughly mixed with a measured amount of the isotopic spike. If a digestion procedure is required, the spiked sample is then digested to equilibrate the spikes and samples. The sample solutions are then measured with mass spectrometry such as ICP-MS to obtain the altered isotope ratios. Method 6020 can be used as a reference method for ICP-MS detection. In addition to Method 6020, dead time correction and mass bias correction must be included in the measurement protocol. The equations described in Sec. 12.1 are used to calculate the concentrations.

Figure 2 shows an example of an IDMS determination of vanadium in crude oil (Ref. 1). IDMS determination of the restricted elements Cd, Cr, Pb and Hg in electrical components are demonstrated in Table 11 (Ref. 26).

2.2 SIDMS method

2.2.1 Speciated samples generally require sample preparation specific to the sample matrices, species, and the isotope ratio measurement method. The purpose of sample preparation is to solubilize the species of interest and to equilibrate the natural and spiked species, creating a homogeneous solution. Solids, slurries, and suspended material must be subjected to extraction before or after spiking, using appropriate sample preparation methods (such as Method 3060A for the determination of Cr(VI) in soils). Water samples may not need extraction. In contrast to total element analysis, efforts must be taken to avoid the destruction of the species in SIDMS.

2.2.2 Although SIDMS is a general method applicable to many elements in various species forms, such environmental samples as water samples or soil extracts, containing chromium species, Cr(III) and Cr(VI), will be used for demonstration purposes. Two isotopic spikes are prepared and characterized as follows: ^{50}Cr(III) spike enriched in ^{50}Cr and ^{53}Cr(VI) enriched in ^{53}Cr. The dominant natural isotope for Cr is ^{52}Cr, at 83.79% (^{50}Cr, 4.35%; ^{53}Cr, 9.50%; ^{54}Cr, 2.36%). A measured amount of a representative aqueous sample is mixed well with an appropriate amount of ^{50}Cr(III) and ^{53}Cr(VI) spike solutions. The spiked sample is then separated into Cr(III) and Cr(VI) using chromatography or other separation method (Figure 3). Four isotope ratios are measured: ^{50}Cr(III)/^{52}Cr(III), ^{53}Cr(III)/^{52}Cr(III), ^{50}Cr(VI)/^{52}Cr(VI), and ^{53}Cr(VI)/^{52}Cr(VI). The concentrations of the species are determined from speciated isotope dilution calculations.

Figures 4 and 5 show an example of the SIDMS for the determination of chromium species in an aqueous sample. Any transformation from Cr(VI) to Cr(III) or from Cr(III) to Cr(VI) is mathematically corrected, as described in Sec. 12.2.

3.0 DEFINITIONS

See the "Glossary" at the end of this method for definitions of applicable terms. Also refer to Chapters One and Three and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware.

4.2 Sample preparation

4.2.1 Because this method requires the equilibration of the spike isotope(s) and the natural isotopes, the solid samples must be digested, dissolved or extracted into a solution. If the analyte of interest does not completely dissolve, if the spike or sample isotopes are selectively lost before equilibration, or if contamination occurs in the sample preparation process, the measured isotope ratio will not reflect the accurate ratio of added spike atoms to sample atoms for that element or species (Ref. 1).

4.2.2 In general, SIDMS incorporates the assumption that all the converted species can be found in other species that are monitored. As an example, in the interconversion between Cr(III) and Cr(VI), the lost Cr in one species must be found in the other species. Thus, efforts should be made to keep all species in solution.

4.2.3 Preservation of the species is required in SIDMS since the interconversion degrades the precision of the determination. The complete conversion of the species will disable the deconvolution of the species concentration. Thus, digestion methods used for total metals are inappropriate for SIDMS. However, the altered isotope ratios will indicate the conversion that has occurred and will not lead to an incorrect answer, but to a situation where the concentration cannot be determined. Approaches that have been developed to maintain the species are applicable to SIDMS.

4.3 Isotope ratio measurement

4.3.1 Discussions about isobaric interference, doubly-charged ion interference, and memory interference in Method 6020 are applicable to this method. The discussion about the physical interference, suggesting the addition of an internal standard, does not apply. The internal standard is unnecessary because the isotope ratio measurement is free from physical interferences. (General considerations for isotope ratio measurement can be found in the document of Sec. 13.5.1.)

4.3.2 Dead time measurement must be performed daily. At high count rates, two effects cause pulse counting systems to count less events than actually occur (Sec. 13.5.2 and 13.5.3). The first is dead time (τ), the interval during which the detector and its associated counting electronics are unable to resolve successive pulses. If the true rate, n, is much less than $1/\tau$, then:

$$m \approx n(1 - m\tau)$$

where m is the observed rate. The second effect is the loss of gain at high rates caused by the inability of the multiplier's dynode string to supply enough current to maintain constant dynode voltage drops. This effect is indicated by a sharp increase in apparent

dead time at high count rates. Both effects cause the measured isotope ratios to diverge from the true isotope ratios with increasing count rate. While the dead time can be mathematically corrected, the gain loss cannot.

A series of solutions with different concentrations can be prepared from isotopically certified standards for the determination of dead time. The concentrations may not be accurate, but the concentrations should spread out evenly, covering the blank to the highest count rate that may be used in measurements. The isotope pairs that are monitored should have large differences between their isotopic abundances, since the major isotopes suffer dead time effects much more seriously than minor isotopes; this makes the dead time correction significant. The sum of the dead-time-corrected counts is used for calculating the isotope ratios after background subtraction.

$$R_m = \frac{{}^{Isotope1}S_{sample/standard} - {}^{Isotope1}S_{background}}{{}^{Isotope2}S_{sample/standard} - {}^{Isotope2}S_{background}}$$

_ R_m is the dead-time-corrected isotope ratio;

_ ${}^{Isotope1}S_{sample/standard}$ and ${}^{Isotope2}S_{sample/standard}$ are the integrated dead-time-corrected-counts for the sample or standard of Isotope1 and Isotope2, respectively;

_ ${}^{Isotope1}S_{background}$ and ${}^{Isotope2}S_{background}$ are the integrated dead-time-corrected-counts for the background of Isotope1 and Isotope2, respectively.

As shown in Figure 1, which displays the ${}^{50}Cr/{}^{52}Cr$ ratios for SRM 979 ($Cr(NO_3)_3 \bullet 9H_2O$) as a function of the count rate, the isotope ratios are highly dependent on the number used for dead time correction. When the dead time is set to 43.5 ns, the isotope ratios are approximately constant up to the count rate of 5.8×10^5. At higher count rates, gain loss will occur and cannot be mathematically corrected. Therefore, the solutions must be diluted in the case where the count rate is higher than this value.

NOTE: Dead time correction is performed before mass bias correction, so the dead-time-corrected isotope ratios may be different from the certified isotope ratios. Although it is unnecessary to use isotopically certified material for the determination of dead time, the certified material is still required for the measurement of mass bias factors. Thus, it is convenient to use the same certified material for both dead time and mass bias factor measurement.

NOTE: It has been observed that using different isotope pairs for dead time measurement may obtain different dead times. Thus, it is required to do the dead time measurement for each isotope pair that will be used. The dead time must be determined daily.

4.3.3 Instrumental discrimination/fraction effects are changes induced in the "true" isotope ratios from the ionization process or from differential transmission/detection

by the mass spectrometer. This effect can bias the ratios either positively or negatively. To correct for the mass bias, mass bias factors should be determined with isotopically certified materials.

$$\text{mass bias factor} = R_t / R_m$$

where:

_ R_t and R_m are the certified isotope ratio and the measured dead-time-corrected-isotope-ratios of the standard material, respectively.

The dead-time-corrected isotope ratios of the samples can be corrected using:

$$R_c = \text{mass bias factor} \times R_m$$

where:

_ R_c and R_m are the corrected isotope ratio and the measured dead-time-corrected-isotope-ratios of the sample, respectively.

Mass discrimination is a time-dependent instrumental effect, so the mass bias factors must be determined periodically during the measurement of the samples. Samples are run with the assumption that mass bias factors remain constant. In general, the mass bias factors are stable over several hours for ICP-MS measurements. However, the measurement interval for determining mass bias factors should generally not exceed four hours.

NOTE: Some previous work observed the following relationship between the measured and the true isotope ratios for ICP-MS: $R_m=R_t(1+an)$, where *a* is the bias per mass unit, *n* is the mass difference between isotopes. This enables the calculation of the mass bias factors of other isotope pairs based on the measurement of one pair of isotopes. However, this must be verified experimentally. Otherwise, the mass bias factor for each isotope pair must be determined.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Refer to Chapter Three for a discussion on safety-related references and issues.

5.3 Many chromium compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of hexavalent chromium reagents. Hexavalent chromium reagents should only be handled by analysts who are knowledgeable of their risks and of safe handling procedures.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

6.1 Inductively coupled plasma-mass spectrometer (ICP-MS) or other mass spectrometer systems capable of base line (at least 1 amu) resolution are required. The data system should allow for corrections of isobaric interferences, dead time and mass bias, or the raw data may be exported to a computer for further processing. For quadrupole mass spectrometers, the dwell time should be adjustable since proper settings of dwell time can significantly improve the precision of the isotope ratio measurement. Both scan mode and peak jump mode can be used, depending on the instrumentation. The use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended. When chromatography is coupled to ICP-MS for on-line detection, the ICP-MS data system must be capable of correcting interferences, dead time and mass bias, and calculating the isotope ratios in time resolved analysis mode (TRA), or the raw data can be exported for off-line processing. Other mass spectrometers may also be used, providing a precision of 0.5% or better can be obtained for the isotope ratio measurement. Examples of other ionization and mass spectrometers would be electrospray and/or MALDI and/or microwave induced plasma (MIP) ionization coupled to quadrupole, time-of-flight and/or ion-trap mass spectrometers. Appropriate correction protocols for these mass spectrometers should be applied.

6.2 Chromatography or other separation methods are used to isolate species prior to isotope ratio measurement. Chromatography, such as ion exchange chromatography, may be used to separate the species on-line in SIDMS (Figure 3). Chromatography components should be chemically inert based on the specific reagents and analytes. The eluent components and the flow rate of the chromatography system must be compatible with ICP-MS. An interface between the chromatography and ICP-MS may be required for compatibility reasons. Alternatively, any appropriate separation methods, including extraction, chelation, and precipitation, can be used after validation.

7.0 REAGENTS AND STANDARDS

7.1 All reagents should be of appropriate purity to minimize the blank levels due to contamination. Whenever possible, acids should be sub-boiling distilled. All references to water in the method refer to high purity reagent water. Other reagent grades may be used if it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurity.

7.2 For higher precision, solutions may be prepared by weight. For IDMS, standard stock solutions with natural isotopic abundance may be purchased or prepared from ultra-high purity grade chemicals or metals. See Method 6020 for instructions on preparing standard solutions from solids. Generally, the same procedures are applicable to isotope-enriched materials. However, when a limited amount of the isotope-enriched material is used (usually due to cost considerations) to prepare the stock solutions, the solutions require calibration with inverse isotope dilution (see Sec. 7.4.1). Isotope-enriched materials with known enrichment can be purchased from several suppliers, such as the Oak Ridge National Laboratory Electromagnetic Isotope Enrichment Facility (ORNL-EMIEF).

7.3 Currently, few standard stock solutions made for speciation analysis are commercially available. Thus, in addition to the dissolution of the standard solid, the chemical conversion of the element into the desired species is usually required for SIDMS. The preparation of Cr(VI) and Cr(III) stock standards for SIDMS will be illustrated as an example. For other elements and species, procedures must be specifically developed. One supplier of stable isotope standards for SIDMS and IDMS includes Applied Isotope Technologies (AIT), Inc. These standards may be covered by patents. AIT, Inc. is located at 851 Stella Court, Sunnyvale, CA 94087, info@sidms.com, http://www.sidms.com.

7.3.1 There are five standards to be prepared for the simultaneous analysis of Cr(VI) and Cr(III), including ^{nat}Cr(VI) and ^{nat}Cr(III) with natural abundance, ^{53}Cr(VI) enriched in ^{53}Cr, ^{50}Cr(III) enriched in ^{50}Cr, and isotopic-abundance-certified Cr standard solution.

7.3.2 1 mg/mL Cr(VI) and Cr(III) standards are commercially available. ^{nat}Cr(VI) and ^{nat}Cr(III) can also be prepared from $K_2Cr_2O_7$ and Cr metal, respectively.

7.3.2.1 ^{nat}Cr(VI) standard solution, stock, 1 g = 1 mg Cr: Dissolve 0.2829 g of $K_2Cr_2O_7$ in about 80 mL of reagent water and dilute to 100 g with reagent water.

7.3.2.2 ^{nat}Cr(III) standard solution, stock, 1 g = 1 mg Cr: Dissolve 0.1 g of Cr metal (accurately to at least 4 significant figures) in a minimum amount of 6M HCl and dilute the solution with 1% HNO_3 to 100 g.

7.3.3 ^{53}Cr(VI) standard solution, 1 g $\approx$ 10 μg Cr: The following procedure describes chromium oxide as the source material. A 150-mL glass or quartz beaker is used for the dissolution. Weigh 5.8 mg of ^{53}Cr-enriched oxide (the exact amount should be calculated based on the content of Cr in the material) into the beaker and add 8 mL of concentrated $HClO_4$. Slowly heat the beaker on a hot plate until bubbles form on the bottom; the solution should not boil. Keep heating the solution for up to 6 hrs until all solids are dissolved and only 1 to 2 mL of the solution remains. Turn off the hot plate and wait until the beaker cools down. Rinse the beaker and watch glass with 10 mL of reagent water; the solution should turn intense yellow. Add 50 μL of 30% H_2O_2 and 4.5 mL of concentrated NH_4OH. Slowly heat the vessel until the solution gently boils to oxidize all Cr to Cr(VI). Allow the solution to boil for at least 15 minutes to remove the excessive H_2O_2. Transfer the solution to a 500-mL polymeric (e.g., polytetrafluoroethylene [PTFE], polyethylene, polypropylene, etc.) bottle and dilute the solution to 400 g. The exact concentration of the ^{53}Cr(VI) spike must be calibrated with ^{nat}Cr(VI) standard as described in Sec. 7.4.

NOTE: The procedure may be simpler when the isotope-enriched materials are available in other forms. For example, when $K_2Cr_2O_7$ enriched in ^{53}Cr is

available, the solid can be dissolved in reagent water without further conversion; when Cr metal is available, the metal can be dissolved in 6M HCl as described in Sec. 7.3.2.2, followed by the addition of H_2O_2 and NH_4OH to oxidize Cr(III) to Cr(VI) as described above.

WARNING: Concentrated $HClO_4$ is a very strong oxidizer. Safety protocols require this reagent only be used in a perchloric acid hood or equivalent solution and vapor handling system.

7.3.4 ^{50}Cr(III) standard solution, 1 g $\approx$ 10 μg Cr: The following procedure describes chromium metal as the source material. Weigh 4 mg of the metal into a 30-mL PTFE vessel. Add 4 mL of 6M HCl and gently heat the solution but do not boil it until the solid is dissolved. Continue to heat the solution until only 1 to 2 mL of the solution remains. The solution is then cooled and transferred to a 500-mL polymeric bottle. Dilute the solution with 1% HNO_3 to 400 grams. The exact concentration of the ^{50}Cr(III) spike must be calibrated with ^{nat}Cr standard as described in Sec. 7.4.

NOTE: The procedure depends on the form of the material. For example, when $K_2Cr_2O_7$ enriched in ^{50}Cr is available, the solid can be dissolved in 1% HNO_3, followed by the addition of H_2O_2 to reduce Cr(VI) to Cr(III). The excessive H_2O_2 can be removed by boiling the solution.

7.3.5 Isotopic-abundance-certified standard solution, stock, 1 g $\approx$ 10 μg Cr: Weigh 31 mg of $Cr(NO_3)_3 \cdot 9H_2O$ (SRM 979) into a 500-mL polymeric container. Dissolve the solid and dilute it with 1% HNO_3 to 400 g.

7.4 The isotope-enriched spikes require characterization since a limited amount of material is usually weighed, complex treatment is involved, or the purity of the source material is limited (usually <99%). For the SIDMS method, in addition to the total concentration of the standard, the distribution of the species must be determined before it can be used (see Section 12.2.2, 2nd NOTE). Inverse IDMS and inverse SIDMS measurement is used to calibrate the isotope-enriched spike and to determine the species distribution. The characterization of ^{53}Cr(VI) spike solution will be illustrated as an example.

7.4.1 Calibration of total concentration of spike solution with natural material: Weigh the proper amount (W_X) of 10 μg/g ($C_{Standard}$) ^{nat}Cr standard and the proper amount (W_S) of the ^{53}Cr(VI) spike (nominal concentration is 10 μg/g) into a polymeric container, and dilute the mixture with 1% HNO_3 to a concentration suitable for isotope ratio measurement. Use direct aspiration mode to determine the isotope ratio of ^{53}Cr/^{52}Cr ($R_{53/52}$). The concentration of the spike, C_{Spike} , can be calculated using the following equations:

$$C_{Spike} = C_S \, M_S$$

$$C_S = \frac{C_X \, W_X}{W_S} \left(\frac{{}^{53}A_X - R_{53/52} \; {}^{52}A_X}{R_{53/52} \; {}^{52}A_S - {}^{53}A_S} \right)$$

$$C_X = C_{Standard} / M_X$$

where C_S and C_X are the concentrations of the isotope-enriched spike and the standard with natural isotopic abundance in μmole/g, respectively. M_S and M_X are the average atomic weights of the spike and the standard in g/mole, respectively. $^{53}A_S$ and $^{53}A_X$ are the atomic fractions of ^{53}Cr for the spike and standard, respectively. $^{52}A_S$ and $^{52}A_X$ are the atomic fractions of ^{52}Cr for the spike and standard, respectively.

NOTE: The same procedure is applicable to the calibration of the isotope-enriched spike solutions in IDMS. The same procedure is also applicable to the calibration of $^{50}Cr(III)$ by changing isotope ^{53}Cr to ^{50}Cr.

NOTE: Average atomic weight = Σ(atomic weight of the isotope x atomic fraction)

7.4.2 Calibration of the concentration of the Cr(VI) in the $^{53}Cr(VI)$ spike with $^{nat}Cr(VI)$: Weigh the proper amount (W_X) of 10 μg/g ($C^{VI}_{standard}$)$^{nat}Cr(VI)$ standard and the proper amount (W_S) of the $^{53}Cr(VI)$ spike (nominal concentration is 10 μg/g) into a polymeric container, and dilute the mixture with reagent water to a concentration suitable for measurement. Acidify the solution to pH 1.7 - 2.0 with concentrated HNO_3. Separate the Cr(VI) with chromatography or other separation methods and measure the isotope ratio of $^{53}Cr/^{52}Cr$ in Cr(VI) species ($R^{VI}_{53/52}$). The concentration of Cr(VI) in the spike, C^{VI}_{Spike}, can be calculated using the following equations:

$$C^{VI}_{Spike} = C^{VI}_S M_S$$

$$C^{VI}_S = \frac{C^{VI}_X W_X}{W_S} \left(\frac{^{53}A_X - R^{VI}_{53/52}\ ^{52}A_X}{R^{VI}_{53/52}\ ^{52}A_S - ^{53}A_S} \right)$$

$$C^{VI}_X = C^{VI}_{Standard} / M_X$$

where C^{VI}_S and C^{VI}_X are the concentrations of Cr(VI) in the isotope-enriched spike and standard with natural isotopic abundance in μmole/g, respectively. M_S and M_X are the average atomic weights of the spike and the standard in g/mole, respectively. $^{53}A_S$ and $^{53}A_X$ are the atomic fractions of ^{53}Cr for the spike and standard, respectively. $^{52}A_S$ and $^{52}A_X$ are the atomic fractions of ^{52}Cr for the spike and standard, respectively.

NOTE: This set of equations is similar to those used in the determination of total Cr in $^{53}Cr(VI)$ standard (Sec. 7.4.1). The general equations for inverse SIDMS are not so simple. However, for speciation of Cr(VI) and Cr(III) in standard solutions, because the matrix is so simplified, only the reduction of Cr(VI) to Cr(III) is observed at low pH. Thus, the existence of Cr(III) species will not

influence the isotope ratio of Cr(VI), and the complex equations can be simplified to the equations shown above (Ref. 3).

7.4.3 The distribution of Cr(III) and Cr(VI) in $^{53}Cr(VI)$ spike can be calculated as:

$$\text{percentage of Cr(VI)} = \frac{C_{Spike}^{VI}}{C_{Spike}} \text{ x } 100\%$$

$$\text{percentage of Cr(III)} = \left(1 - \frac{C_{Spike}^{VI}}{C_{Spike}}\right) \text{ x } 100\%$$

NOTE: No determination of the species distribution in $^{50}Cr(III)$ spike is required because only Cr(III) is present in this solution.

7.5 Blank samples -- Three types of blank samples are required for the analysis; namely, a background blank for subtracting background in isotope ratio measurement, a preparation blank for monitoring possible contamination resulting from the sample preparation procedures, and a rinse blank for flushing the system between all samples and standards.

7.5.1 The background blank consists of the same concentration(s) of the acid(s) used to prepare the final dilution of the sample solution (often 1% HNO_3 (v/v) in reagent water).

7.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

7.5.3 The rinse blank consists of 1 to 2 % HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. Refer to Method 6020 regarding the interference check solution.

7.6 Refer to Method 6020 for preparing mass spectrometer tuning solution.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 Due to the possible degradation or interconversion of the species, samples collected for speciation analysis must be isotopically spiked as soon as possible. The measurement, however, can be carried out later provided that less than 80% degradation or interconversion occurs. The holding time prior to measurement depends on the preservation of the species.

8.3 Proper methods to retard the chemical activity of the species are applicable to SIDMS.

8.4 All sample containers must be prewashed with detergents, acids, and water. Polymeric containers should be used. See Chapter Three for further information on clean chemistry procedures to reduce blank effects in these measurements.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with the appropriate sample preparation and the isotope ratio measurement methods by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. Method 8000 provides information on how to accomplish a demonstration of proficiency for standard methods. This method, using SIDMS, has unique proficiency requirements as concentrations are determined by direct calculation based on isotopic properties of the target analyte and the enriched isotopic species spike without the use of calibration curves as described in Method 8000. During SIDMS analysis by Method 6800, analyte transformations may occur to some extent in some matrices and can be corrected by using its protocol. Proficiency is established for each species such as Cr(VI), methylmercury, tributyltin, and any polyisotopic species and each matrix such as water, soil, tissue and others. These proficiencies are to be determined using appropriate standards prepared to test proficiency of spiking, extraction, species separation, mass spectrometric operation and calculation which together constitute this method's SIDMS protocol. A suite of proficiency testing materials, as well as guidelines, for the implementation of the proficiency testing is available from Applied Isotope Technologies (info@sidms.com). Determination of total element using this method's IDMS protocol is similar to more traditional methods that are spiked with elements as the matrix spike. However, in this method, concentration of the species of interest is calculated directly from the isotopic element spike and not from calibration curves.

9.3 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity, species conversion). At a minimum, this should include the analysis of QC samples including background blank, preparation blank, rinse blank, matrix spike, duplicate, and laboratory control sample (LCS) and/or proficiency samples if available and were applicable for each analytical batch. A sample of known concentration, such as Standard Reference Material, an appropriate reference

material or a suitable set of proficiency materials can be used as LCS. Any blank, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.3.1 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample processed through the entire sample preparation and analytical procedure. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, water, tissue, etc.). If statistical compilations are desired, a sufficient number of duplicate samples should be analyzed to produce the desired statistical results.

9.3.2 Spiked samples and/or standard reference materials and/or reference materials or proficiency materials (if available) should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed and proficiency should be established for each sample matrix. For SIDMS, because the species may degrade or convert to other species when they are spiked into samples, low recovery may be observed. Thus, the low recovery does not immediately invalidate this method. For example, if Cr(III) is spiked into a basic solution, due to the hydrolysis of Cr(III) and the limited solubility of chromium hydroxide, low recovery of Cr(III) may be obtained. Low recovery may indicate an unfavorable matrix for preserving the corresponding species (Ref. 4). The conversion of one species to another should be calculated and recorded with the final corrected concentration. If equilibration is reached prior to species-loss, an isotopic ratio may still be measurable and will result in an acceptable species measurement. In most cases, conversion can be quantified and corrected. If a sample, isotopic spike of one species is completely converted into another species, then the matrix and/or the sample preparation procedure may be responsible for species conversion. This will indicate that this specific matrix can support the stability of only select species. The results of concentration and conversion should be recorded as an acceptable set of data. Species concentration and species conversion should be measured and recorded in the laboratory report. Speciation under this method is a relatively new field and additional equations and other QC, proficiency support, and reference materials are updated through Ref. 27.

9.3.3 Blank samples should be prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples. Also see Sec. 7.5 for more information regarding blank samples.

10.0 CALIBRATION AND STANDARDIZATION

10.1 IDMS calibration

10.1.1 Follow the appropriate sections in Method 6020 to set up and tune the ICP-MS. The determination is performed in direct aspiration mode. The following procedure is illustrated with the measurement of $^{50}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ isotope ratios.

10.1.2 Determine the dead time (Sec. 4.3.2). Solutions prepared from reference material SRM 979 ($Cr(NO_3)_3 \bullet 9H_2O$) are used in this determination. A range of solutions of different concentrations should be prepared, but do not need to be accurately known. Masses 50, 52 and 53, as well as masses which could affect data quality, should be

monitored. The raw count rates for each solution are measured and integrated. Assume a dead time and use the equation described in Sec. 4.3.2 to correct the integrated counts. The dead-time-corrected counts are then used for calculating the isotope ratios after background subtraction. By trial and error, the dead time is determined to bring the isotope ratios obtained from solutions of different concentrations to a constant (the relative standard deviation of the isotope ratios reaches the minimum). The isotope ratios obtained from high counts may be excluded as gain loss may occur.

NOTE: The concentration range of the solutions may be adjusted depending on the sensitivity and dynamic range of the instrument.

NOTE: For direct aspiration mode, the dead time correction can be done either before or after the integration of the raw data. However, it is simpler to do the dead time correction after the integration.

10.1.3 Determine the mass bias factor (Sec. 4.3.3). The mean of isotope ratios obtained in Sec. 10.1.2 is used for calculating the mass bias factor. The equation is provided in Sec. 4.3.3. The measurement of the mass bias factor must be done periodically between sample measurements. The interval between these measurements depends on the mass bias stability of the instrument. The relative difference between two consecutive mass bias factors should not exceed 1%.

10.2 SIDMS calibration

10.2.1 Follow the appropriate sections in Method 6020 to set up and tune the ICP-MS. Follow Sec. 10.1.2 to measure the dead time. If the calibration of the isotope-enriched spikes is required, the mass bias factors for direct aspiration mode and the altered isotope ratios for the spiked standards are measured at this step. The measured isotope ratios obtained at this step are used in the calibration of total concentrations.

10.2.2 Determine the mass bias factor (Sec. 4.3.3). Connect the chromatography outlet to the nebulizer of the ICP-MS. Stabilize the entire system. Background blank and an isotopic abundance certified standard are used for the measurement of the mass bias factors for TRA mode. The raw data at each point are corrected for dead time using the equation described in Sec. 4.3.2 and then integrated by summing the data across each peak. The intervals between two consecutive injections must be long enough for the signal to return to baseline. The integrated counts are then used to calculate the isotope ratios with the equation shown in Sec. 4.3.2. Apply the equation in Sec. 4.3.3 to the calculation of the mass bias factors for each isotope pair by comparing the measured isotope ratios to the certified isotope ratios.

NOTE: For the TRA mode, the dead time correction must be done at each data point before the data integration.

NOTE: For other ionization and mass spectrometer types such as electrospray and/or MALDI and/or microwave induced plasma (MIP) ionization coupled to quadrupole, time-of-flight and/or ion-trap mass spectrometers, appropriate correction protocols for these mass spectrometers should be utilized.

11.0 PROCEDURE

11.1 IDMS

11.1.1 Closed-vessel microwave digestion is used as an example method to decompose, solubilize, equilibrate and stabilize the elements of interest. The following procedure is applicable to samples specified in Method 3052. Refer to Method 3052 for specification of the microwave apparatus.

11.1.2 Prepare the isotope-enriched spike and calibrate it with the inverse isotope dilution mass spectrometry procedure described in Secs. 7.3 and 7.4.1. Isotope enriched spikes are available as commercial products from Applied Isotope Technologies, Inc. (e-mail: info@sidms.com; http://www.sidms.com).

11.1.3 Weigh a representative sample to the nearest 0.001 g into an appropriate microwave digestion vessel equipped with a pressure relief mechanism. Spike the sample with the calibrated isotope-enriched spike. The concentration of the spike should be high enough so that only a small volume of the solution is used. At least three significant figures should be maintained for the mass of the spike.

11.1.4 Digest the sample according to the procedure described in Method 3052.

NOTE: For filtered and acidified aqueous samples, digestion may not be required. Sample solutions can be directly analyzed with ICP-MS after spiking and equilibration.

11.1.5 Measurement of the isotope ratios can be carried out using ICP-MS or other appropriate mass spectrometers.

11.1.5.1 Determine the mass bias factor periodically as described in Sec. 10.1.3.

11.1.5.2 Measure the isotope ratio of each sample. Flush the system with the rinse blank. The ideal isotope ratio is 1:1. Isotope ratios must be within the range from 0.1:1 to 10:1, except for blanks and samples with extremely low concentrations. Samples may be respiked to achieve an isotope ratio close to 1:1. Samples must be diluted if too high of a count rate is observed to avoid gain loss of the detector.

NOTE: For elements such as lithium, lead, and uranium, the unspiked solution is used to measure the isotopic abundance of all the isotopes because the isotopic abundances of these elements are not invariant in nature.

11.2 SIDMS

11.2.1 SIDMS is currently applicable to the quantification of elemental species in various samples. Solid samples require isolation and separation to solubilize the elemental species before analysis. Procedures for such extraction of the species from different matrices must be specifically designed. Extraction procedures for tissue and hair and bacteria are found in references (Refs. 20 through 22 respectively). The following procedure is an illustration of the simultaneous determination of Cr(III) and Cr(VI) in water samples or soil or sediment extracts. Solids are extracted for Cr(VI) using Method 3060A.

11.2.2 Prepare the isotope-enriched spikes in species forms and calibrate them with inverse isotope dilution mass spectrometry described in Sec. 7.4. Isotope enriched spikes in species form are available as commercial products from Applied Isotope Technologies, Inc (e-mail: info@sidms.com; http://www.sidms.com).

11.2.3 Weigh a proper amount of water sample, solid or semi-solid sample, or extract to the nearest 0.0001 g into a polymeric container. Spike the sample with 10 µg/g of ^{53}Cr(VI) spike to a concentration so that the isotope ratio of $^{53}Cr/^{52}Cr$ in Cr(VI) will be approximately 1:1. Spike the sample with ^{50}Cr(III) spike to a concentration so that the isotope ratios of $^{50}Cr/^{52}Cr$ in Cr(III) will also be approximately 1:1 and the species concentrations are suitable for measurement. Thoroughly mix the spike and the sample. The isotope ratios $^{53}Cr/^{52}Cr$ for samples must be within the range of 0.1:1 to 10:1, except for blanks or samples with extremely low concentrations. Determined ratios outside these example ratios indicate sample that should be respiked and reanalyzed.

NOTE: If only the Cr(VI) is of interest, the sample can be single spiked with ^{53}Cr(VI) instead of double-spiking with both ^{50}Cr(III) and ^{53}Cr(VI). However, this is based on the assumption that only unidirectional conversion, the reduction of Cr(VI) to Cr(III), can occur after spiking. This is usually true if the sample is acidified to a low pH after spiking, especially for matrices containing reducing agents.

11.2.4 Extract the species from the samples such as soils and sludges. Method 3060A can be used to extract Cr(VI) from soils and other samples and Method 3200 can be used to extract methylmercury from many sample types for example.

NOTE: For aqueous samples, extraction may not be required. Sample solutions can be directly analyzed with ICP-MS, ESI-TOF-MS and other appropriate ionization MS methods after spiking and equilibration. Extremely concentrated samples may also need to be adjusted in spike to sample ratio and may be pushed to a lighter spike ratio to conserve spike or sub-sampled.

11.2.5 If the solution is strongly basic, neutralize the sample with concentrated HNO_3 to avoid the hydrolysis of Cr(III).

11.2.6 Acidify the spiked samples to pH 1.7 to 2.0; under these conditions Cr is usually retained in the solutions (although there might be interconversion between Cr(III) and Cr(VI)). The spiked samples can be stored at ≤6 °C to retard the interconversion of the species. Other methods that can retard the transformation of the species are applicable as long as no interference with the isotope ratio measurement is introduced. For example, some soil extracts contain large concentrations of reducing agents that reduce Cr(VI) rapidly after acidification. To slow down the reduction, stoichiometric amounts of $KMnO_4$ can be added to the sample to compete with Cr(VI) in the oxidation of reducing matrices.

NOTE: Studies have shown that the lower the interconversion, the more precise the determination (Ref. 3). Thus, efforts should be made to prevent interconversion between the species.

11.2.7 The measurement of the isotope ratios in each species can be carried out using ICP-MS or other equivalent mass spectrometers following the separation of the

species using chromatography or other separation methods. An ion-exchange chromatograph coupled with ICP-MS will be illustrated as an example in the measurement of $^{50}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ isotope ratios in both Cr(III) and Cr(VI) species in samples.

11.2.7.1 Determine the mass bias factors periodically as described in Sec. 10.2.2.

11.2.7.2 Measure the isotope ratios of each sample. Flush the system with the eluent until the signal returns to the baseline. The ideal isotope ratios for $^{50}Cr/^{52}Cr$ in Cr(III) and $^{53}Cr/^{52}Cr$ in Cr(VI) are 1:1. Ratios between 0.1:1 to 10:1 are also appropriate. Samples may be respiked to achieve an isotope ratio close to 1:1. Samples must be diluted if excessively high count rates are observed to avoid gain loss of the detector.

NOTE: For elements such as lithium, lead, and uranium, the unspiked solution is used to measure the isotopic abundance of all the isotopes because the isotopic abundances are not invariant in nature.

NOTE: For the simultaneous determination of three species with correction following the SIDMS protocol, a new equation and example are required. This example for three mercury species can be found in Ref. 24 along with a version of the equation developed for three species. Equations for two and three species are in this reference and in formats constructed to simplify these calculations for the user. New and determinative equations will be published in the literature and updated references will be made available through the SIDMS.com website (Ref. 27).

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 IDMS calculations

The quantitative values must be reported in appropriate units, such as micrograms per liter (μg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions are performed, the appropriate corrections must be applied to the sample values.

12.1.1 Calculate the isotope ratios. Calculations should include appropriate interference corrections (see Sec. 4.3 for data integration, dead time correction, and mass bias correction).

12.1.2 The following equations are applied to the calculation of the concentration of the element, C_{Sample}(μg/g), in the final sample solutions:

$$C_{Sample} = C_X\, M_x$$

$$C_S = C_{Spike} / M_S$$

$$C_X = \frac{C_S\, W_S}{W_X}\left(\frac{{}^{53}A_S - R_{53/52}\ {}^{52}A_S}{R_{53/52}\ {}^{52}A_X - {}^{53}A_X}\right)$$

where, C_S and C_X are the concentrations of the isotope-enriched spike and the sample in µmole/g, respectively. M_S and M_X are the average atomic weights of the isotope-enriched spike and the sample in g/mole, respectively. $^{53}A_S$ and $^{53}A_X$ are the atomic fractions of ^{53}Cr for the isotope-enriched spike and sample, respectively. $^{52}A_S$ and $^{52}A_X$ are the atomic fractions of ^{52}Cr for the isotope-enriched spike and sample, respectively. C_{spike} is the concentration of the isotope-enriched spike in µg/g. A general guideline for IDMS calculations can be found in the documents of Section 13.5.4.

NOTE: When isotope ^{50}Cr is used, substitute 53 with 50 in the above equations.

12.1.3 If appropriate or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.
(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C_{Sample}}{S}$$

where, C_{Sample} = Concentration based on the wet sample (µg/g)

$$S = \frac{\%\,\text{Solids}}{100}$$

12.2 SIDMS calculations

The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions are performed, the appropriate corrections must be applied to the sample values.

12.2.1 Calculate the isotope ratios. Calculations should include appropriate interference corrections, dead time correction, and mass bias correction (Sec. 4.3).

12.2.2 The following equations are used to deconvolute the concentrations of the species at the time of spiking, as well as the conversion of the species after spiking:

$$R^{III}_{50/52} = \frac{\left({}^{50}A_X C_X^{III} W_X + {}^{50}A_S^{III} C_S^{III} W_S^{III}\right)(1-\alpha) + \left({}^{50}A_X C_X^{VI} W_X + {}^{50}A_S^{VI} C_S^{VI} W_S^{VI}\right)\beta}{\left({}^{52}A_X C_X^{III} W_X + {}^{52}A_S^{III} C_S^{III} W_S^{III}\right)(1-\alpha) + \left({}^{52}A_X C_X^{VI} W_X + {}^{52}A_S^{VI} C_S^{VI} W_S^{VI}\right)\beta}$$

$$R^{III}_{53/52} = \frac{\left({}^{53}A_X C^{III}_X W_X + {}^{53}A^{III}_S C^{III}_S W^{III}_S\right)(1-\alpha) + \left({}^{53}A_X C^{VI}_X W_X + {}^{53}A^{VI}_S C^{VI}_S W^{VI}_S\right)\beta}{\left({}^{52}A_X C^{III}_X W_X + {}^{52}A^{III}_S C^{III}_S W^{III}_S\right)(1-\alpha) + \left({}^{52}A_X C^{VI}_X W_X + {}^{52}A^{VI}_S C^{VI}_S W^{VI}_S\right)\beta}$$

$$R^{VI}_{50/52} = \frac{\left({}^{50}A_X C^{III}_X W_X + {}^{50}A^{III}_S C^{III}_S W^{III}_S\right)\alpha + \left({}^{50}A_X C^{VI}_X W_X + {}^{50}A^{VI}_S C^{VI}_S W^{VI}_S\right)(1-\beta)}{\left({}^{52}A_X C^{III}_X W_X + {}^{52}A^{III}_S C^{III}_S W^{III}_S\right)\alpha + \left({}^{52}A_X C^{VI}_X W_X + {}^{52}A^{VI}_S C^{VI}_S W^{VI}_S\right)(1-\beta)}$$

$$R^{VI}_{53/52} = \frac{\left({}^{53}A_X C^{III}_X W_X + {}^{53}A^{III}_S C^{III}_S W^{III}_S\right)\alpha + \left({}^{53}A_X C^{VI}_X W_X + {}^{53}A^{VI}_S C^{VI}_S W^{VI}_S\right)(1-\beta)}{\left({}^{52}A_X C^{III}_X W_X + {}^{52}A^{III}_S C^{III}_S W^{III}_S\right)\alpha + \left({}^{52}A_X C^{VI}_X W_X + {}^{52}A^{VI}_S C^{VI}_S W^{VI}_S\right)(1-\beta)}$$

where,

$R^{III}_{50/52}$ is the measured isotope ratio of ^{50}Cr to ^{52}Cr of Cr(III) in the spiked sample

$^{50}A_X$ is the atomic fraction of ^{50}Cr in the sample (usually a constant in nature)

C^{III}_X is the concentration of Cr(III) in the sample (μmole/g, unknown)

W_X is the weight of the sample (g)

$^{50}A^{III}_S$ is the atomic fraction of ^{50}Cr in the $^{50}Cr(III)$ spike

C^{III}_S is the concentration of Cr(III) in the $^{50}Cr(III)$ spike (μmole/g)

W^{III}_S is the weight of the $^{50}Cr(III)$ spike (g)

C^{VI}_X is the concentration of Cr(VI) in the sample (μmole/g, unknown)

α is the percentage of Cr(III) oxidized to Cr(VI) after spiking (unknown)

β is the percentage of Cr(VI) reduced to Cr(III) after spiking (unknown)

NOTE: The unit of the concentrations shown above is μmole/g. The conversion factor from μmole/g to μg/g is: M, where M is the average atomic weight of the element in μg/μmole (Sec. 7.4.1). The following equation can be used to convert the unit of the concentration. Be aware that samples with different isotopic abundance have different average atomic weights.

Concentration (μmole/g) x M = Concentration (μg/g)

NOTE: Although the species distribution of the isotopic spike is determined (Sec. 7.4), the above equations assume that each isotope-enriched spike is only in one species form to simplify the equations. This has been validated for $^{50}Cr(III)$ and $^{53}Cr(VI)$ spikes prepared using the procedures described in Sec. 7.3. For other speciation analysis, this assumption must be verified experimentally, or the distribution of the species in the isotope-enriched spikes must be taken into account.

NOTE: For the quantification of the single-spiked samples, the following equations are used:

$$C_{Sample}^{VI} = C_X^{VI} M_X$$

$$C_S^{VI} = C_{Spike}^{VI} / M_S^{VI}$$

$$C_x^{VI} = \frac{C_s^{VI} W_s}{W_x} \left(\frac{{}^{53}A_S^{VI} - R_{53/52}^{VI}\ {}^{52}A_S^{VI}}{R_{53/52}^{VI} - {}^{52}A_X\ {}^{53}A_X} \right)$$

where C_S^{VI} and C_X^{VI} are the concentrations of the isotope-enriched spike and the sample in μmole/g, respectively. M_S^{VI} and M_X are the average atomic weight of the isotope-enriched spike and the sample in g/mole, respectively. ${}^{53}A_S^{VI}$ and ${}^{53}A_X$ are the atomic fraction of ^{53}Cr for the isotope-enriched spike and sample, respectively. ${}^{52}A_S^{VI}$ and ${}^{52}A_X$ are the atomic fractions of ^{52}Cr for the isotope-enriched spike and sample, respectively. C_{spike}^{VI} is the concentration of the isotope-enriched spike in μg/g.

NOTE: When isotope ^{50}Cr is used, substitute 53 with 50 in the above equations.

12.2.3 A computer program such as a spreadsheet can be developed to solve this set of second power, four variable equations. Solutions of the values for, C_X^{III}, C_X^{VI}, α and β are required. The following mathematics is a way to solve the equations iteratively. To assist the analyst a spreadsheet file with these preprogrammed equations has been placed on the internet (Ref. 11). Additional discussion and alternate equations are also available.

To make the expression simpler, assume

$$C_X^{III} W_X = N_X^{III},\ C_X^{VI} W_X = N_X^{VI},\ C_S^{III} W_S^{III} = N_S^{III},\ C_S^{VI} W_S^{VI} = N_S^{VI}$$

At the beginning of the iteration, arbitrary values can be assigned to N_X^{VI} and α. For example, both of them are assigned as 0s. Now we need to know the expression of N_X^{III} and β. After careful derivation, we can get the following equations:

$$\begin{cases} (1-\alpha)\left(R_{50/52}^{III}\ {}^{52}A_X - {}^{50}A_X\right)N_X^{III} + \left[R_{50/52}^{III}\left({}^{52}A_X\ N_X^{VI} + {}^{52}A_S^{VI}\ N_S^{VI}\right) - \left({}^{50}A_X\ N_X^{VI} + {}^{50}A_S^{VI}\ N_S^{VI}\right)\right]\beta \\ = \left(-R_{50/52}^{III}\ {}^{52}A_S^{III} + {}^{50}A_S^{III}\right)N_S^{III}\left(1-\alpha\right) \\ (1-\alpha)\left(R_{53/52}^{III}\ {}^{52}A_X - {}^{53}A_X\right)N_X^{III} + \left[R_{53/52}^{III}\left({}^{52}A_X\ N_X^{VI} + {}^{52}A_S^{VI}\ N_S^{VI}\right) - \left({}^{53}A_X\ N_X^{VI} + {}^{53}A_S^{VI}\ N_S^{VI}\right)\right]\beta \\ = \left(-R_{53/52}^{III}\ {}^{52}A_S^{III} + {}^{53}A_S^{III}\right)N_S^{III}\left(1-\alpha\right) \end{cases}$$

These equations can be rewritten as:

$$\begin{cases} A_1 N_X^{III} + B_1\beta = C_1 \\ A_2 N_X^{III} + B_2\beta = C_2 \end{cases}$$

The solutions are:

$$\beta = \frac{\begin{vmatrix} A_1 & C_1 \\ A_2 & C_2 \end{vmatrix}}{\begin{vmatrix} A_1 & B_1 \\ A_2 & B_2 \end{vmatrix}} \quad \text{and} \quad N_X^{III} = \frac{\begin{vmatrix} C_1 & B_1 \\ C_2 & B_2 \end{vmatrix}}{\begin{vmatrix} A_1 & B_1 \\ A_2 & B_2 \end{vmatrix}}$$

Use these two values in the following equations to solve N_X^{VI} and α

$$\begin{cases} (1-\beta)\left(R_{50/52}^{VI}\ {}^{52}A_X - {}^{50}A_X\right)N_X^{VI} + \left[R_{50/52}^{VI}\left({}^{52}A_X\ N_X^{III} + {}^{52}A_S^{III}\ N_S^{III}\right) - \left({}^{50}A_X\ N_X^{III} + {}^{50}A_S^{III}\ N_S^{III}\right)\right]\alpha \\ = \left(-R_{50/52}^{VI}\ {}^{52}A_S^{VI} + {}^{50}A_S^{VI}\right)N_S^{VI}\left(1-\beta\right) \\ (1-\beta)\left(R_{50/52}^{VI}\ {}^{52}A_X - {}^{53}A_X\right)N_X^{VI} + \left[R_{53/52}^{VI}\left({}^{52}A_X\ N_X^{III} + {}^{52}A_S^{III}\ N_S^{III}\right) - \left({}^{53}A_X\ N_X^{III} + {}^{53}A_S^{III}\ N_S^{III}\right)\right]\alpha \\ = \left(-R_{53/52}^{VI}\ {}^{52}A_S^{VI} + {}^{53}A_S^{VI}\right)N_S^{VI}\left(1-\beta\right) \end{cases}$$

Rewrite the equation as:

$$\begin{cases} A_3 N_X^{VI} + B_3\alpha = C_3 \\ A_4 N_X^{VI} + B_4\alpha = C_4 \end{cases}$$

again:

$$\alpha = \frac{\begin{vmatrix} A_3 & C_3 \\ A_4 & C_4 \end{vmatrix}}{\begin{vmatrix} A_3 & B_3 \\ A_4 & B_4 \end{vmatrix}} \quad \text{and} \quad N_X^{VI} = \frac{\begin{vmatrix} C_3 & B_3 \\ C_4 & B_4 \end{vmatrix}}{\begin{vmatrix} A_3 & B_3 \\ A_3 & B_3 \end{vmatrix}}$$

Repeating the calculation, the variables N_X^{III}, N_X^{VI}, α and β will converge to constant values, and these values are the solution of the equations.

12.2.4 If conversion is complete from one species to another, then the starting samples may be respiked with the isotope-enriched spikes and analyzed, with a particular attention to retard the conversion of the species, if possible. As long as the isotope ratio can be determined the SIDMS protocol will correct for the conversion even if extensive conversion has occurred. If 100% conversion occurs, this is the result of an active matrix. This indicates that the species converted is highly unstable in that matrix and under the extraction procedure chosen.

12.2.5 If appropriate or required, calculate results for solids on a dry-weight basis as described in Sec. 12.1.3.

12.3 Examples, calculation aids, and help documents for SIDMS are available as referenced in the web (Ref. 11).

12.4 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Performance and use of IDMS as a definitive method in standard reference material certification has been well established in practice and in the literature. Review and discussion articles are referenced for performance criteria of this highly accurate method (Refs. 1, 9, and 10).

13.3 Accuracy, precision, and use of SIDMS/6800 in quantifying and correcting species interconversion are shown in Tables 1 through 11. Table 2(A) and Table 2(B) compare data against Method 7196 analysis for Cr(VI) in chromium ore process residues (COPR) and soil extracts. Table 1 demonstrates the ability of this method to correct for transformations of both Cr(VI) and Cr(III) in aqueous samples. Table 1 also displays the magnitude of errors that may be expected when using other methods unable to track and determine the conversion of these species. Table 2(A) indicates a sample type where double spikes were added into the same extract (spiked after extraction with Method 3060A) used for determination of Cr(VI) with Method 7196 and then analyzed with Method 6800. In this case, both the traditional 3060A/7196 methods and 3060A/6800 methods produced statistically similar data indicating that transformation had already occurred and confirmation between these two analytical methods was observed (Refs. 8 and 12). Whereas Table 2(B) indicates a situation where one set of samples were extracted with Method 3060A and analyzed with Method 7196 and another set of sub-samples of the same samples were double spiked before extraction with Method 3060A and then analyzed with Method 6800. In this case, statistically significant different results were obtained from both the traditional 3060A/7196 and 3060A/6800 methods (Refs. 3 and 12). Method 6800 provided the ability to correct for the transformation of Cr(III) to Cr(VI) using the mathematical protocol described in Sec.12.2.3. This is also an example of how Method 6800 can be used as a diagnostic tool to isolate the origin of species-shifts in sample handling, and in analytical preparation steps of methods.

The SIDMS analysis technique, applied to difficult environmental sample matrices, demonstrates the advantages of having the capability to identify and understand the transformations and method perturbations of dynamic species (Refs. 13 and14). The study described in Table 3 demonstrates how Method 6800 can be used to field-spike reactive samples that would have degraded by the time they reached the analytical laboratory. Table 3 analytically evaluates and validates the field application of a chemical spiking at the sampling site and permits evaluation of the process involving ferrous iron and chromate in the treatment or remediation of hexavalent chromium runoff by using another waste by-product, acid mine drainage (AMD) (Ref. 14). Figure 6 demonstrates the analysis of the isolated flyash runoff and the waste stream mixed with the second waste stream of AMD. These data in Table 3 and Figure 6 as cited in the literature (Ref. 14) demonstrate the accuracy and precision of both a stable and a less stable sets of samples.

Tables 4(A) and 4(B) demonstrate how Method 6800 can be used as a diagnostic tool to observe whether chromium species transformation occurs during or after extraction steps. It is reported in the literature that there is a possibility of precipitation of Pb as $PbCrO_4$ during acidification. In order to determine if there is a bias introduced for Cr(VI) during acidification, the extracts were analyzed directly after acidification, without filtration and after filtration. From

Table 4(A), it is observed that the results obtained for the same extract aliquots after performing filtration completely agree with those obtained from direct analysis of unfiltered samples after neutralization (Ref. 13). In Method 6800, loss of some portion of an already equilibrated sample does not cause an error as the ratio does not depend on recovery of the analyte but only on the isotopic ratio (Refs. 13 and 18). Standard calibration is effected by the loss of analyte however the SIDMS is not effected by loss of analyte after isotopic species equilibration. From Table 4(B), after extraction it is observed that the determination of Cr(VI) is the same for three different instrumental calibrations. In most cases, similar results were obtained by analyzing the same extract using external calibration, IDMS (single spike after extraction) or SIDMS (double spike after extraction). This is because the equilibration chemistry, including species transformation, has usually taken place during extraction of the sample. It can be observed from Table 4(A) and 4(B) that substantial transformation of Cr(III) to Cr(VI) can occur during extraction of the sample, and transformations generally occur nominally during post-extraction manipulation

Table 5 demonstrates the correction necessary in some soil samples where the sample matrix causes a bias in more traditional methods. These bias corrections demonstrate the ability of Method 6800 to identify and correct for the degradation and transformation of species during the measurement process. Traditional methods such as Methods 7196, 7196A and 7199 are not able to correct for Cr(VI) transformations which may increase or decrease during Method 3060A extraction. Transformations occurring in transportation, storage, extraction, and sample preparation that have changed the species are not accounted for and all errors add to create biases that are undetectable. Method 6800 corrects for transformations occurring during extraction and other targeted steps when the enriched isotopic spike(s) are added to include those step including in the field at collection.

The SIDMS approach in Method 6800 was applied in the simultaneous determination of chromium species in food supplement, in this case biological samples, by an independent laboratory (Ref. 22). The Institute of National Measurement Standards, National Research Council of Canada has independently validated Method 6800 on brewers' yeast where they found Cr(VI) converting to Cr(III) and Cr(III) converting to Cr(VI), and concluded that the SIDSM method enabled the accurate determination of both Cr(VI) and Cr(III) under these conditions. This work is summarized in Table 6 which was abstracted with permission from that author in Ref. 22. This study concluded that despite the presence of significant bidirectional transformation of species during sample preparation, an accurate simultaneous determination of both chromium species in yeast was made possible through the application of the SIDMS method (Table 6).

13.4 The SIDMS analysis technique has successfully been applied for the determination of other species. For example, methylmercury and inorganic mercury have been successfully determined in biological tissues, human tissue and other tissues, and soils. Table 7 demonstrates concentration measurements in soil samples (Refs. 15 and 16). Method 6800 has also been applied as a diagnostic tool to determine the concentration and to identify analytical biases caused by species transformations using the Microwave-Assisted Extraction methods such as Method 3200, used in mercury species extraction. The SIDMS protocol of Method 6800 provides the ability to measure the concentration of species and to evaluate if species transformations have occurred. In Table 7, the sample was spiked, both pre- and post-extraction. One set of samples was double-spiked before extraction and another aliquot of the same sample was double-spiked after extraction. It was observed that this extraction method did not alter the species or permit them to transform in this matrix, using this extraction protocol. The deconvoluted concentrations for each species (Table 7) obtained from both sets of extractions overlap at the 95% CI and are statistically indistinguishable (Ref. 15).

In a separate study, the SIDMS protocol was used as a diagnostic tool for the evaluation of different mercury speciation methods published in the literature and in Method 3200 (Refs. 16 and 17). From this study, it was observed that two of the five literature methods were highly prone to form inorganic mercury from methylmercury during extraction. These two published methods converted approximately ~100% of the methylmercury to inorganic mercury, including the spiked isotope enriched methylmercury. In another literature method, as much as 45% of methylmercury was converted into inorganic mercury during extraction. Two methods, Method 3200 and one sonication-based method induced very little or no methylmercury to inorganic mercury conversion during extraction (Table 8) (Ref. 17). Method 6800 has also been used to validate other speciation method. For example, if used in conjunction with Method 3200, Method 6800 corrects for matrix-induced and method-induced transformations of species if they occur, thus permitting the evaluation of this and other speciation methods. Method 6800 also was used as a method of evaluating other methods of speciation analysis in the literature (Refs. 15, 17, 20 and 21).

The SIDMS protocol of Method 6800 along with Method 3200 was applied for the determination of mercury species in tissue samples (Ref. 20) (Table 9). After analyzing a fish tissue reference material (BCR-464) with a 20% precision, approximately 20% of the inorganic mercury was converted to methylmercury during analysis. Here, the creation of the species of interest from inorganic mercury would be undetected without the ability of Method 6800 to evaluate and correct for the species-conversions in these speciated measurements.

The SIDMS method was applied as a diagnostic tool to evaluate eight published literature methods for mercury speciation in human hair (IAEA-085) (Ref. 21). From this study, it is observed that most of the methods induced minor or no statistically significant species transformation from this human tissue matrix during extraction. However, two of the eight methods induced larger amounts of species transformation from methylmercury to inorganic mercury. One method transformed approximately 90% and the other transformed almost 20% of methylmercury to inorganic mercury during extraction (Table 10). Because an IAEA reference material was used in this study, the reference value was available for validation of all methods. The inorganic and methylmercury concentrations were obtained by method SIDMS/6800 as were the amount of inorganic mercury converted into methylmercury. The correction for interconvertion of methylmercury and inorganic mercury was also determined. The total mercury was determined mathematically by adding inorganic and methylmercury. Without correction for conversion, the correct concentration can not be assured.

The SIDMS protocol can also be used successfully to determine the concentration of one or more analytes from samples where species conversion, or degradation and/or incomplete separation take place before or during analysis (Refs. 2, 3, 5 through 8 and 11 through 27). The determination of three simultaneous species requires additional equations and mathematical manipulation that has been developed and published. For mathematical solutions to three simultaneous species equations, tutorials and calculation aids you are referred to the references, referenced web sites and related publications cited (Refs. 24 and 27).

The IDMS protocol can be used to determine simultaneously elemental concentrations for materials as totals elemental concentrations in conjunction with decomposition methods such as Method 3052. An example of such IDMS analysis is demonstrated for grounded and pulverized electronic components and circuit boards. The European environmental regulations referred to as RoHS, WEEE and REACH (Reduction of Hazardous Substances, Waste, Electrical and Electronic Equipment, Registration, Evaluation, Authorization and Restriction of Chemicals, respectively) require total and speciated analyses. Table 11 demonstrates total elemental analysis by IDMS in conjunction with 3052 microwave-enhanced total decomposition where the isotopes of Cd-112, Cr-50, Pb-206 and Hg-199 were added during Method 3052 decomposition.

IDMS analysis was accomplished on a commercial ICP-MS and total elemental content reported in Table 11 (Ref. 26). Chromium species can be accomplished as described in this method and demonstrated in Sec. 13.3 to complete the analysis requirements under the European RoHS regulations.

13.5 The following documents may provide additional guidance and insight on the isotope ratio measurement using ICP-MS:

13.5.1 K. E. Jarvis, A. L. Gray and R. S. Houk, *Handbook of Inductively Coupled Plasma Mass Spectrometry*; Blackie Academic & Professional: London, U.K. 1992, p-315.

13.5.2 G. P. Russ III, J. M. Bazan, *Spectrochim. Acta, Part B* 1987, 42B, 49- 62.

13.5.3 H. E. Taylor, *Inductively Coupled Plasma Mass Spectrometry: Practice and Techniques*, Academic Press: San Diego, CA, USA, 2001, p-48.

13.5.4 M. Sargent, R. Harte and C. Harrington, *Guidelines for Achieving High Accuracy in Isotope Dilution Mass Spectrometry*, The Royal Society of Chemistry: Cambridge, UK, 2002.

13.5.5 The web sites http://www.epa.gov/epaoswer/hazwaste/test/new-meth.htm contains Method 6800 and www.sampleprep.duq.edu and www.sidms.com, contain SIDMS/Method 6800 analysis aids, tutorials and update information and applications (Ref. 27).

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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6. D. Huo, H. M. Kingston and B. Larget, “Application of Isotope Dilution in Elemental Speciation: Speciated Isotope Dilution Mass Spectrometry (SIDMS),” In: *Comprehensive Analytical Chemistry,* J. A. Caruso, K. L. Sutton and K. L. Ackley (eds.), Vol. 33 (Elemental Speciation: New Approaches for Trace Element Analysis), Elsevier, New York, USA, 2000, p-277-313.

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method. The pages also contain two flow diagrams (one each for IDMS and SIDMS). A glossary follows these materials.

TABLE 1

ANALYSIS OF AN ARTIFICIALLY SYNTHESIZED WATER SAMPLE
(Refs. 6 and 7)

		Concentration (ng/g)		Conversion (%)	
Aliquot	Days after spiking	Cr(III)	Cr(VI)	Cr(III) to Cr(VI)	Cr(VI) to Cr(III)
1	1	69.8 ± 0.3	68.8 ± 0.3	4.87 ± 0.22	3.57 ± 0.03
	4	69.2 ± 0.6	69.4 ± 0.3	3.47 ± 0.11	11.9 ± 0.5
	13	70.5 ± 0.9	68.5 ± 0.4	2.80 ± 0.13	22.4 ± 0.2
2	1	69.6 ± 0.2	68.8 ± 0.4	17.6 ± 0.1	2.95 ± 0.02
	4	69.3 ± 0.7	69.6 ± 0.6	14.6 ± 1.3	11.4 ± 0.7
	13	70.7 ± 0.4	68.8 ± 0.3	12.8 ± 0.1	22.1 ± 0.3
3	1	69.8 ± 0.6	69.0 ± 0.2	23.8 ± 0.3	2.76 ± 0.08
	4	69.0 ± 0.8	69.6 ± 0.3	21.6 ± 0.2	10.2 ± 0.1
	13	70.4 ± 0.5	68.9 ± 0.8	17.6 ± 0.3	22.1 ± 0.1
True		69.67	68.63		

mean ± 95% confidence interval

Aliquots 1, 2 and 3 were from the same isotopically-spiked synthesized sample. These aliquots were treated in different ways to permit different degrees of interconversion between Cr(III) and Cr(VI). Measurements were done on different days to check the stability of the species during storage. Despite the different degrees of interconversion, the deconvoluted concentrations for both Cr(III) and Cr(VI) were always corrected successfully within experimental error to the true concentrations.

TABLE 2 (A)

CONCENTRATIONS OF Cr(VI) IN COPR SAMPLES DETERMINED WITH METHOD 7196 AND SIDMS (SPIKED AFTER EXTRACTION)
(Refs. 8 and 12)

sample	Method 7196		SIDMS	
	Conc. of Cr(VI) (μg/g)	Average (mean ±std)	Conc. of Cr(VI) (μg/g)	Average (mean ±std)
COPR1	1330	1410 ± 85	1373	1445 ± 70
	1410		1449	
	1500		1512	
COPR3	91.2	85.3 ± 5.2	93.9	88.8 ± 6.1
	81.5		82.1	
	83.1		90.4	
COPR4	408.9	407.8 ± 7.2	419.8	418.0 ± 9.2
	414.4		426.1	
	400.2		408.0	

COPR: chromite ore processing residue.
Method 3060A was used for Cr(VI) extraction.
Results obtained from SIDMS and Method 7196 are comparable for COPR samples.

TABLE 2(B)

OXIDATION OF Cr(III) TO Cr(VI) DURING EXTRACTION WITH METHOD 3060A FROM THREE COPR SAMPLES AND DETERMINED WITH METHOD 7196 AND SIDMS (SPIKED BEFORE EXTRACTION)
(Refs. 3 and 12)

	Total Cr	Cr(VI) ($\mu g\ g^{-1}$)		*RE*[e]
	($mg\ g^{-1}$)	SIDMS Corrected for Cr(III) to Cr(VI) conversion	Method 7196 Uncorrected for Cr(III) to Cr(VI) conversion	(%)
COPR 1	10.4[a]	2573 ± 35[d]	2671 ± 17	3.8
COPR 3	1.97[a]	161 ± 6	351 ± 8	118
COPR 4	4.60[a]	614 ± 13	877 ± 21	43
Fresh Fly Ash	0.0475[b]	8.3 ± 0.3	10.0 ± 0.4	21
Fly Ash (at 41 ft.)	0.0582[b]	3.3 ± 0.3	4.1 ± 0.1	24
SRM 1645 (River sediment)	29.6[c]	1045 ± 46	2753 ± 31	163

[a] provided by Environmental Standards, Inc.

[b] determined with EPA method 3052

[c] certified values

[d] mean ± 95% confidence interval

[e] Relative error

TABLE 3

ANALYSIS OF Cr(VI) IN LEACHATE FROM COAL FLYASH AND ACID MINE DRAINAGE (AMD) COMBINATION SAMPLES
(Ref. 14)

Sample mixture	Aliquot	Cr(VI) calculated/ $ng\ g^{-1}$ [b]	Cr(VI) measured/ $ng\ g^{-1}$
1:1 F	Aliquot 1	704	46.6 ± 8.6
1:1 L	Aliquot 2	704	17.5 ± 4.2
5:1 F	Aliquot 1	1172	963 ± 53
5:1 L	Aliquot 2	1172	25.5 ± 3.5

[a]Uncertainties are at 95% confidence interval, n = 3
[b]Only dilution of the leachate is considered
L – spiked in laboratory
F – spiked in filed

TABLE 4(A)

HEXAVALENT CHROMIUM RESULTS OBTAINED FROM INDUSTRIAL MATERIALS EXTRACTED WITH METHOD 3060A AND ANALYZED WITH METHOD 6800 (DOUBLE SPIKED BEFORE EXTRACTION)
(Ref. 13)

Sample Matrix	Sample ID	EPA Method 6800 (diagnostic SIDMS)			
		Cr^{6+} before filtration	Cr^{6+} after filtration	Cr^{3+} to Cr^{6+} before filtration	Cr^{3+} to Cr^{6+} after filtration
		($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	(%)	(%)
SRM	SRM 2704	7 ± 3	8 ± 1	50 ± 2	45 ± 4
	SRM 2711	N/A	N/A	N/A	N/A
Sediments	Sediment-1	ND	N/A	N/A	N/A
	sediment-2	1.77 ± 0.34	N/A	N/A	N/A
Aggregate Material	Aggregate-1	308 ± 44	314 ± 28	56 ± 3	57 ± 2
	Aggregate-2	341 ± 29	334 ± 36	46 ± 1	47 ± 1
	Aggregate-3	206 ± 9	205 ± 16	48 ± 6	49 ± 7
	Aggregate-4	141 ± 6	141 ± 14	33 ± 3	33 ± 2
	Aggregate-5	223 ± 28	216 ± 17	41 ± 2	41 ± 1
	Aggregate-6	289 ± 27	291 ± 22	19 ± 3	19 ± 3
	Aggregate-7	278 ± 32	306 ± 29	20 ± 1	20 ± 1

Uncertainties are at 95% CI, n = 3

ND = not detectable (lowest measurable chromium = 0.5 ng mL^{-1} and this corresponds to 12.5 ng g^{-1} in soil or sediment sample)

NA = not applicable

TABLE 4(B)

HEXAVALENT CHROMIUM RESULTS OBTAINED FROM INDUSTRIAL MATERIALS EXTRACTED WITH METHOD 3060A AND ANALYZED WITH IC-ICP-MS (EXTERNAL CALIBRATION) AND METHOD 6800 (IDMS & SIDMS) (SINGLE & DOUBLE SPIKED AFTER EXTRACTION)
(Ref. 13)

Sample	External calibration	IDMS[a]	EPA method 6800[b]	
	(μg g^{-1})	(μg g^{-1})	(μg g^{-1})	Cr^{3+} converted to Cr^{6+} (%)
SRM 2704	7 ± 2	12 ± 1	14 ± 2	10 ± 1
SRM 2711	7 ± 1	1.5 ± 0.1	12 ± 4	9 ± 4
Aggregate-1	342 ± 19	367 ± 25	342 ± 26	12 ± 3
Aggregate-2	440 ± 6	448 ± 17	409 ± 11	5 ± 2
Aggregate-3	245 ± 17	259 ± 12	242 ± 16	4 ± 1
Aggregate-4	164 ± 8	171 ± 7	184 ± 11	10 ± 2
Aggregate-5	199 ± 22	215 ± 17	214 ± 23	9 ± 2
Aggregate-6	277 ± 22	295 ± 15	319 ± 23	10 ± 2
Aggregate-7	291 ± 22	298 ± 18	328 ± 24	17 ± 4

Uncertainties are at 95% CI, n = 3

[a]Extracts were spiked with $^{53}Cr^{6+}$ spike after extraction

[b]Extracts were double spiked with $^{iso\text{-}50}Cr^{3+}$ and $^{53}Cr^{6+}$ after extraction

TABLE 5

RECOVERY OF Cr(VI) SPIKED INTO SOIL EXTRACTS
(Ref. 8)

Sample	Mass of Soil (g)	Spiked ^{nat}Cr(VI)	Recovery (%)	
		(μg/g)	Method 7196	SIDMS
1	0	2.997	101 ± 0.4	100 ± 1.3
2	1.53	3.033	91.8 ± 1.7	100 ± 0.3
3	3.06	2.993	81.9 ± 1.1	101 ± 0.3
4	3.12	1.587	71.6 ± 2.5	99.3 ± 0.3

Results obtained from SIDMS and Method 7196 are incomparable for soil extracts due to the serious matrix effects resulting from the coexisting reducing agents in soil. Method 7196 is incapable of correcting conversion of Cr(VI) leading to low recoveries. Results are based on N = 3 with uncertainties expressed in standard deviation.

TABLE 6

RESULTS FOR SPECIATION OF Cr IN YEAST
(Ref. 22)

Sample	^{Nat}Cr(III) added, (mg/kg)	^{Nat}Cr(VI) added, (mg/kg)	Measured Cr(III), (mg/kg)	Measured Cr(VI), (mg/kg)	^{Nat}Cr(III) Recovery (%)	^{Nat}Cr(VI) Recovery (%)	Measured Cr(III) + Cr(VI) (mg/kg)	Measured Total Cr (mg/kg)
Yeast	0	0	1952 ± 103	76 ± 48	NA	NA	2028 ± 57	2014 ± 16
Spiked Yeast	1784	2398	3749 ± 43	2466 ± 40	101 ± 2	100 ± 2	NA	NA

NA – not applicable
Uncertainties are at 95% confidence interval, n = 3.

TABLE 7

THE DECONVOLUTED CONCENTRATION AND TRASFORMATION OF MERCURY SPECIES IN REFERENCE SOIL (MATERIAL-1) USING SIDMS CALCULATIONS.
(Ref. 15)

	Deconvoluted Concentration		Interconversion	
	Hg^{2+} (µg/g)	CH_3Hg^+ (µg/g)	Hg^{2+} to CH_3Hg^+ (%)	CH_3Hg^+ to Hg^{2+} (%)
DSBE	3.05 ± 0.12	2.69 ± 0.10	1.3 ± 1.5	0.1 ± 1.4
DSAE	2.94 ± 0.07	2.62 ± 0.09	0.8 ± 1.5	0.7 ± 0.6

DSBE = double spiked before extraction; DSAE = double spiked after extraction.

Uncertainties are expressed at 95% CL with n = 3.

Material-1: 100% processed topsoil containing both inorganic mercury and methylmercury.

TABLE 8
EVALUATION OF DIFFERENT LITERATURE METHODS FOR MERCURY SPECIATION IN SOILS AND SEDIMENTS USING METHOD 6800.
(Ref. 16)

Sample	Extraction Method	Deconvoluted Concentration (μg/g)		% Recovery		Interconversion (%)	
		Hg^{2+}	CH_3Hg^+	Hg^{2+}	CH_3Hg^+	Hg^{2+} to CH_3Hg^+	CH_3Hg^+ to Hg^{2+}
Material-1	M-3200	2.68 ± 0.34	2.20 ± 0.29	89 ± 12	73 ± 10	0 ± 3	0 ± 9
	SONI-1	2.49 ± 0.16	1.83 ± 0.13	83 ± 5	61 ± 4	5 ± 1	45 ± 4
	SONI-2	1.88 ± 0.20	1.96 ± 0.24	63 ± 7	65 ± 8	2 ± 3	10 ± 5
	MAE	1.99 ± 0.14	2.01 ± 0.16	66 ± 8	67 ± 5	0 ± 3	7 ± 3
	CAE	NA	NA	NA	NA	NA	~ 100
Material-2	M-3200	4.09 ± 0.93	2.79 ± 0.29	91 ± 21	62 ± 6	2 ± 2	6 ± 5
	SONI-1	3.67 ± 0.16	2.65 ± 0.09	81 ± 3	59 ± 2	2 ± 1	44 ± 4
	SONI-2	3.09 ± 0.23	2.29 ± 0.20	67 ± 5	51 ± 5	1 ± 1	2 ± 2
	MAE	3.09 ± 0.24	2.26 ± 0.13	69 ± 5	50 ± 3	2 ± 1	4 ± 3
	CAE	NA	NA	NA	NA	NA	~ 100

Uncertainties are expressed at 95% CL, n = 9.

NA – analyzed but could not perform SIDMS calculations.

TABLE 9

SIDMS ANALYSIS OF FISH TISSUE (TUNA FISH) (BCR-464) AFTER EXTRACTION WITH METHOD 3200 (MICROWAVE-ASSISTED EXTRACTION)
(Ref. 20)

	Methylmercury (as Hg) (µg/g)	Total Mercury (µg/g)	Hg^{2+} to CH_3Hg^+ (%)	CH_3Hg^+ to Hg^{2+} (%)
Certified Value	5.12 ± 0.16	5.24 ± 0.10		
Method 6800	5.60 ± 0.30	5.71 ± 0.42	18.07 ± 4.14	0.84 ± 0.62

Uncertainties are at 95% CI, n = 4.

TABLE 10

EVALUATION OF DIFFERENT LITERATURE METHODS FOR MERCURY SPECIATION IN HUMAN HAIR (IAEA-085) USING METHOD 6800
(Ref. 21)

Extraction Method	**Hg^{2+} (µg/g)**	**$MeHg^+$ (µg/g)**	**Total Mercury (µg/g)**	**Hg^{2+} to $MeHg^+$ (%)**	**$MeHg^+$ to Hg^{2+} (%)**
Certified value	0.3	22.9 ± 1.4	23.2 ± 0.8	------	------
Akagi *et. al.*	1.96 ± 0.59	23.81 ± 0.67	25.77 ± 0.89	< 0	< 0
Diez *et. al.*	1.36 ± 0.39	24.82 ± 1.59	26.18 ± 1.64	< 0	4 ± 1
Bermejo *et. al.*	1.32 ± 0.16	22.39 ± 0.49	23.71 ± 0.52	4 ± 1	2 ± 1
Feng *et. al.*	1.15 ± 0.40	23.49 ± 0.49	24.64 ± 0.63	4 ± 2	3 ± 1
Chai *et. al.*	1.00 ± 0.56	23.62 ± 0.57	24.62 ± 0.80	2 ± 2	5 ± 2
Montuori *et. al.*	1.15 ± 0.42	25.17 ± 0.96	26.32 ± 1.05	14 ± 2	22 ± 1
Morton *et. al.*	1.09 ± 0.23	23.50 ± 1.21	24.59 ± 1.23	< 0	90 ± 5
Method 3200 (MAE)	0.59 ± 0.22	23.65 ± 1.42	24.24 ± 1.44	4 ± 2	6 ± 1
Method 3200 (UAE)	1.13 ± 0.25	19.80 ± 1.25	20.93 ± 1.28	9 ± 3	0 ± 1

Uncertainties are at 95% CL, n = 12.

MAE – Microwave-assisted extraction; UAE – Ultrasound-assisted extraction.

TABLE 11

ANALYSIS OF RoHS GROUND AND PULVERIZED CIRCUIT BOARDS FOR ALL REGULATED METALS SIMULTANEOUSLY USING IDMS
(Ref. 26)

Sample ID	Cadmium (µg/g)	Chromium (µg/g)	Lead (µg/g)	Mercury (µg/g)
2811	1.916 ± 0.054	23.829 ± 0.866	19,806 ± 973	4.134 ± 1.059
Compaq #1	2.087 ± 0.107	13.462 ± 1.252	15,257 ± 917	6.316 ± 1.709
Dell Optiplex #5	2.081 ± 0.049	20.624 ± 1.010	23,496 ± 1,354	3.838 ± 0.871
Dell Optiplex #3	2.013 ± 0.086	38.512 ± 3.113	21,634 ± 972	N/A
AVVA	2.017 ± 0.115	35.399 ± 1.045	23,883 ± 1,243	N/A

Uncertainties are at 95% CI with n = 3

N/A – not analyzed.

FIGURE 1

THE INFLUENCE OF THE DEAD TIME CORRECTION ON THE ISOTOPE RATIOS MEASURED WITH ICP-MS EQUIPPED WITH A CONTINUOUS DYNODE MULTIPLIER
(Ref. 12)
Gain loss occurs when the count rate exceeds $5.8x10^5$.

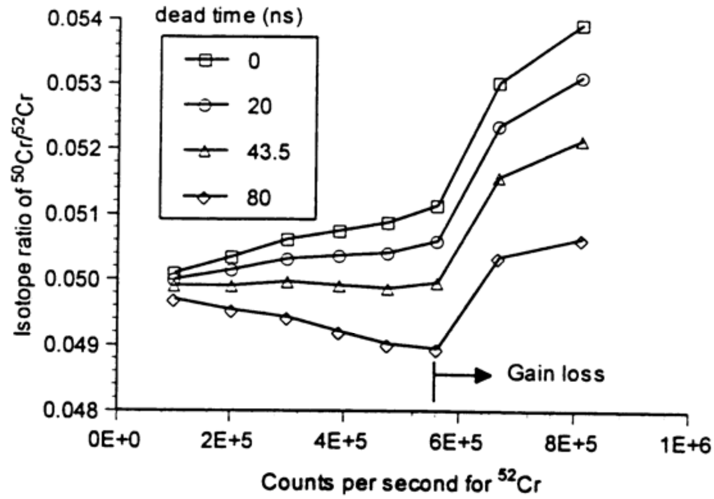


FIGURE 2

IDMS DETERMINATION OF VANADIUM IN CRUDE OIL. NUMBERS SHOWN ABOVE THE BARS ARE THE ATOMIC FRACTION
(Revised from Ref. 1)

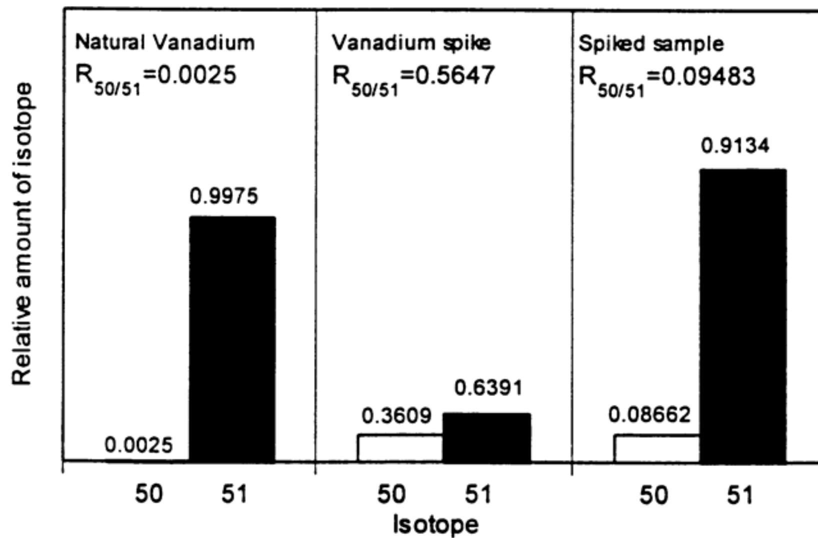


FIGURE 3

SEPARATION AND DETECTION OF Cr(III) AND Cr(VI) WITH ION-EXCHANGE CHROMATOGRAPHY COUPLED WITH AN ICP-MS
(Ref. 5)

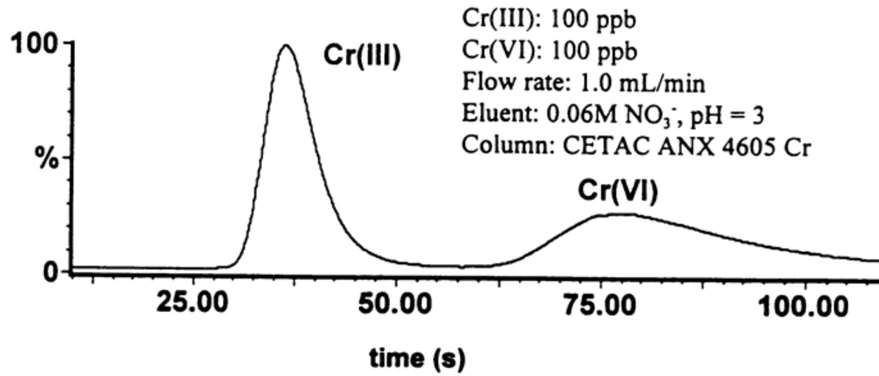


FIGURE 4

SEPARATION OF THE UNSPIKED SAMPLE AND ISOTOPICALLY SPIKED SAMPLE
(Ref. 6)

(a): Chromatograms of a solution containing Cr(III) and Cr(VI) with natural isotopic abundance.

(b): Chromatograms of the same solution spiked with isotope-enriched spikes ^{50}Cr(III) and ^{53}Cr(VI) .

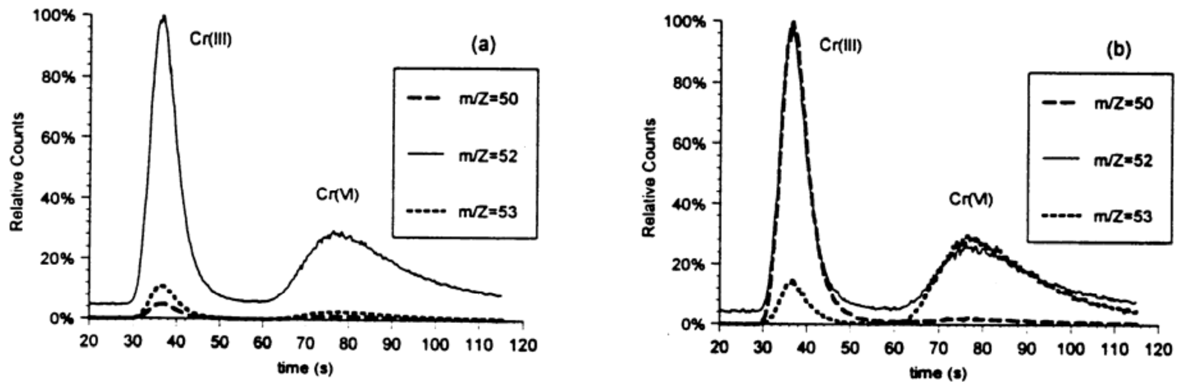
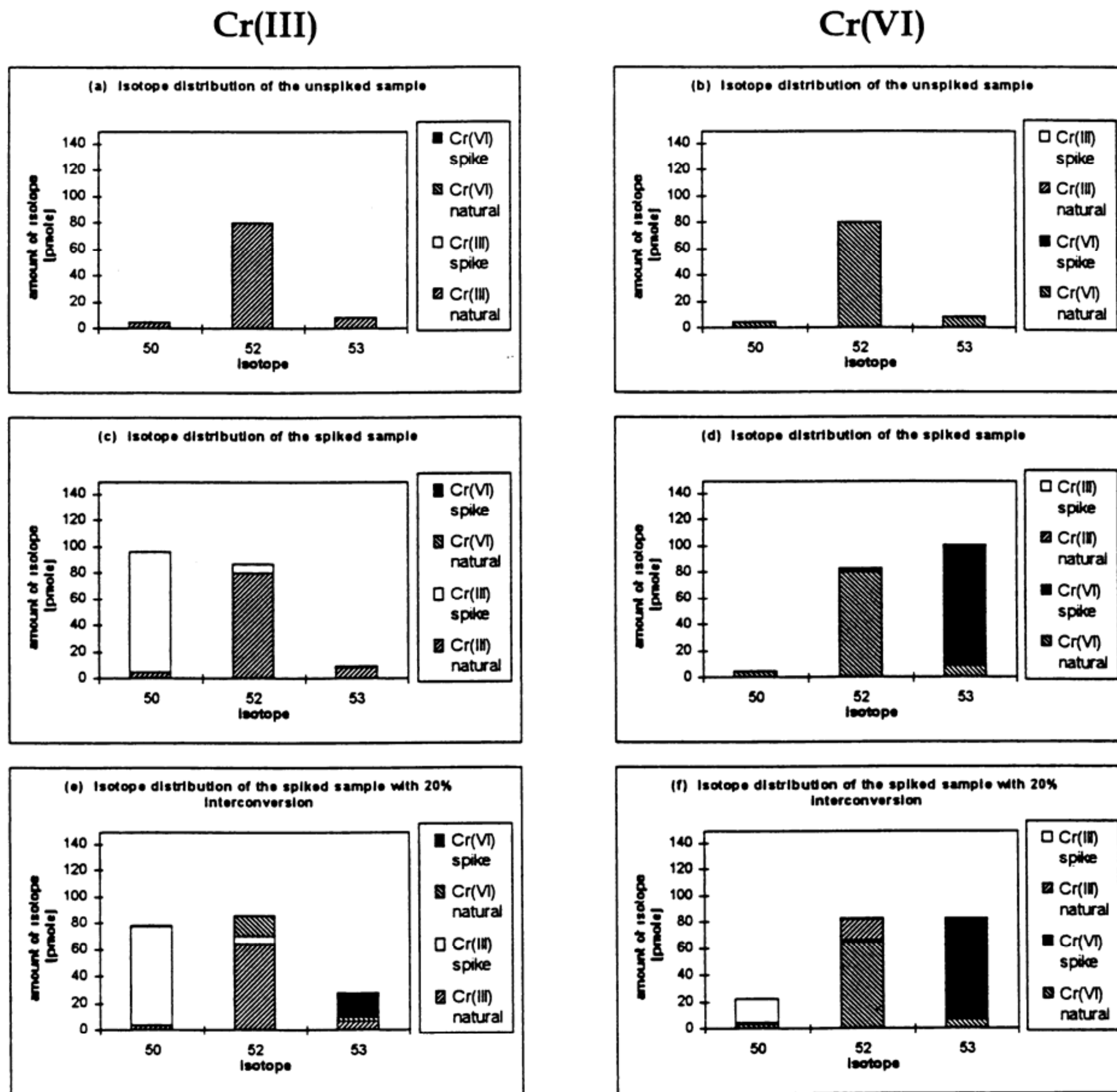


FIGURE 5

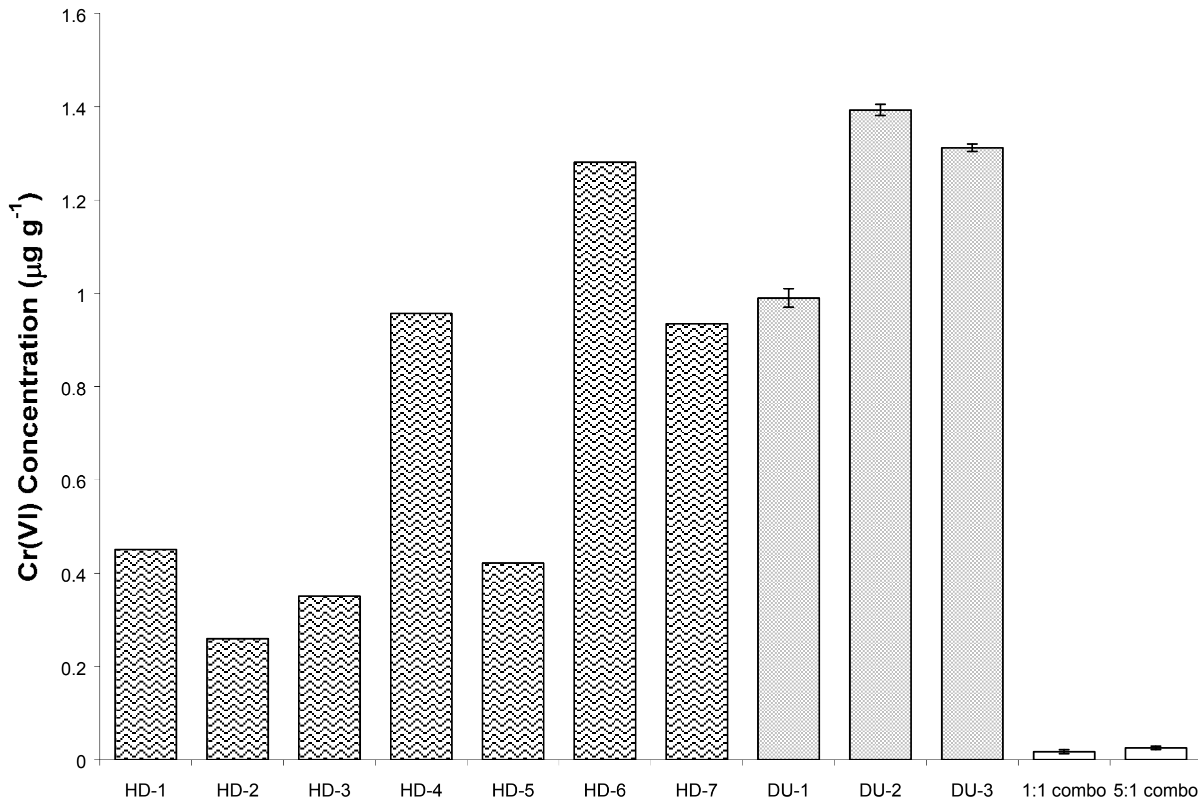
GRAPHIC CALCULATED ILLUSTRATION OF THE APPLICATION OF SIDMS TO THE SIMULTANEOUS DETERMINATION OF Cr(III) AND Cr(VI) (Ref. 6)



(a) and (b) show the initial natural isotopic abundance of species Cr(III) and Cr(VI) in a 50_l 200 ppb Cr solution in which the concentrations of both Cr(III) and Cr(VI) are 100 ppb. In (c) and (d), the sample is spiked with 100 ppb ^{50}Cr(III) (in which ^{50}Cr is enriched) and 100 ppb ^{53}Cr(VI) (in which ^{53}Cr is enriched), there is no interconversion between Cr(III) and Cr(VI). In (e) and (f), 20% of Cr(III) is converted to Cr(VI), and 20% of Cr(VI) is converted to Cr(III). Different degrees of interconversion results in different isotopic abundances, so the change of the relative isotopic abundance can be applied to the determination of the species and the degree of the interconversion.

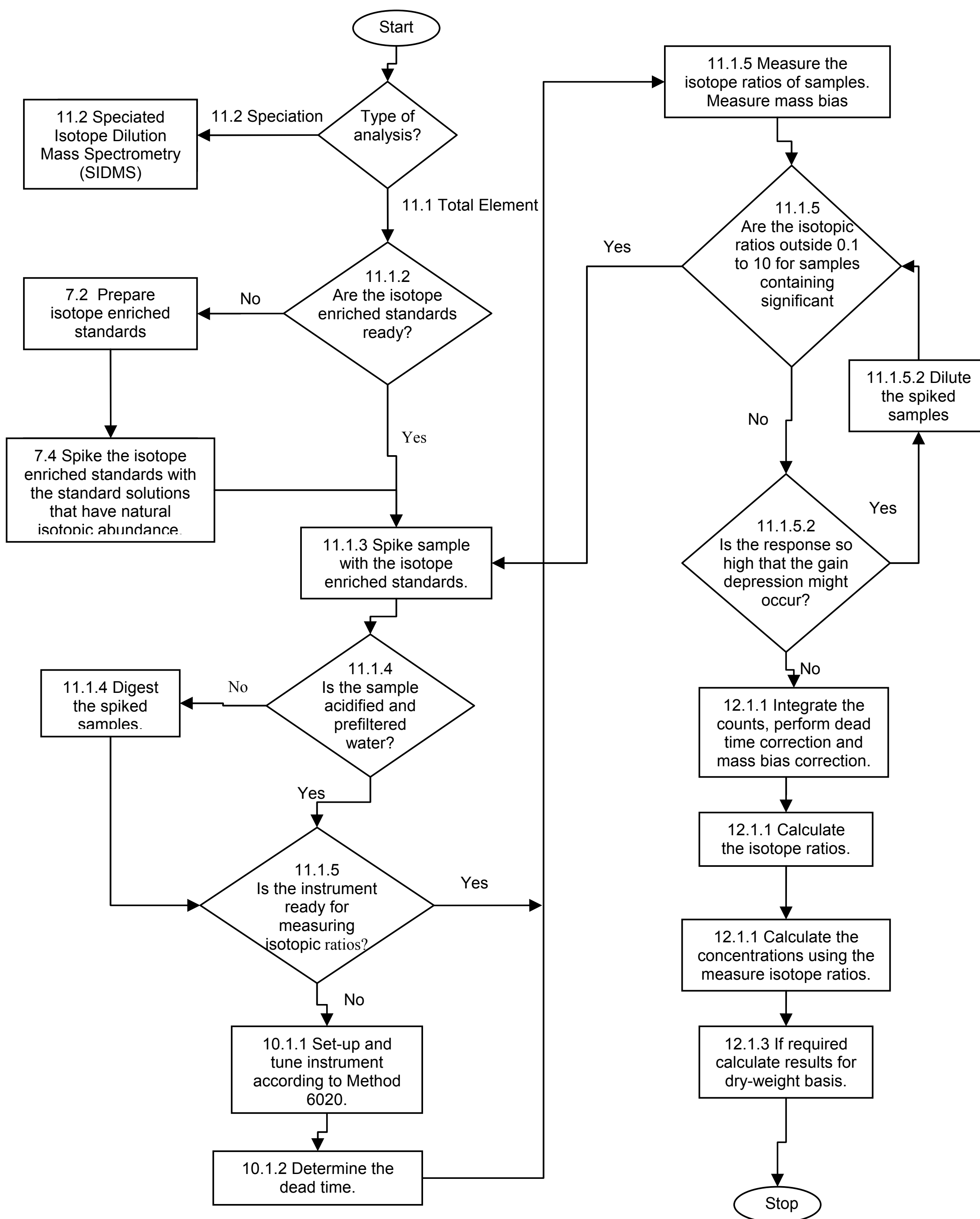
FIGURE 6

HEXAVALENT CHROMIUM CONCENTRATIONS IN FLY ASH LEACHATE OBTAINED FROM HISTORICAL DATA (HD), STUDY WITH SIDMS (DU); AND BEFORE AND AFTER COMBINATION WITH ACID MINE DRAINAGE (AMD)
(Ref. 14)

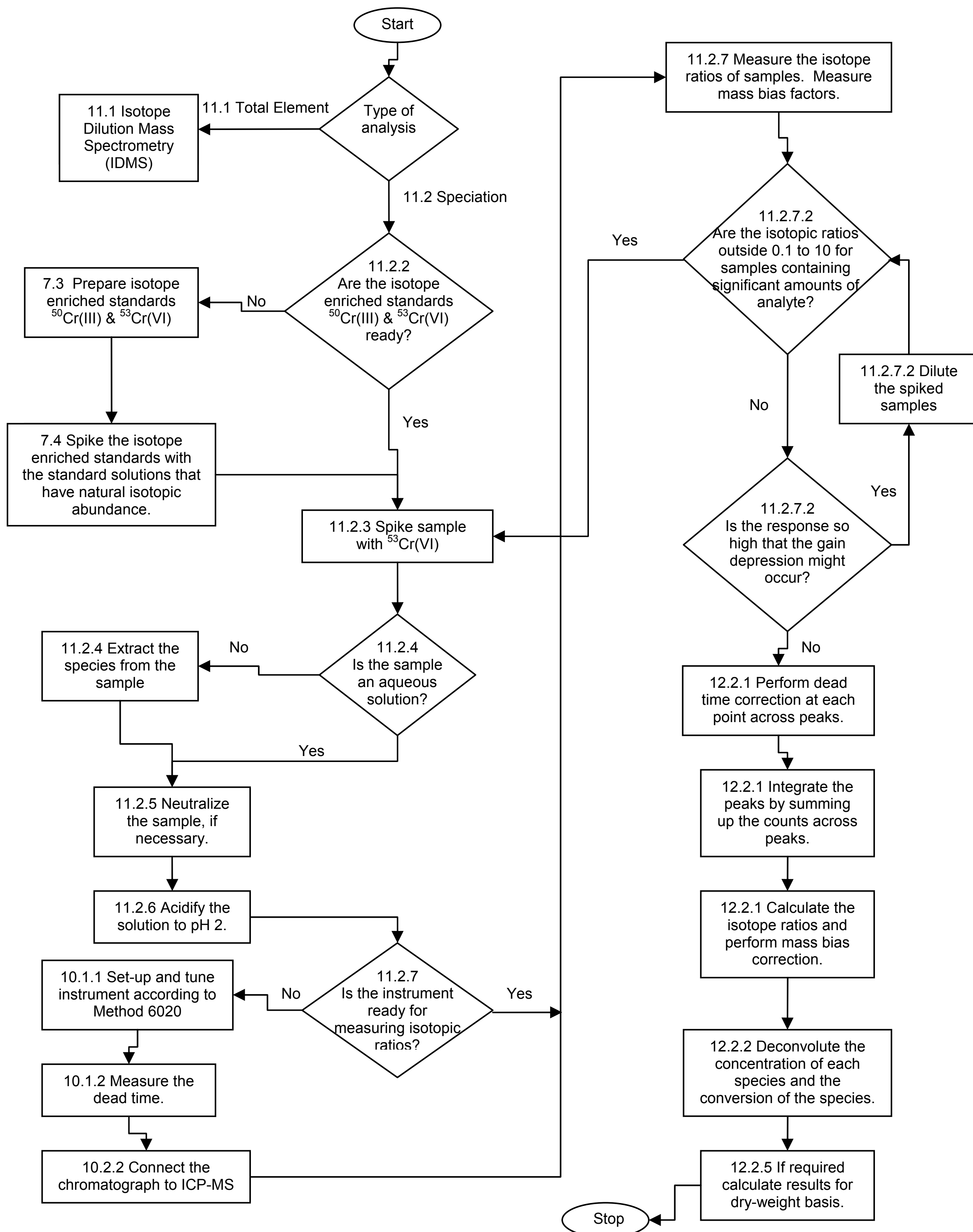


Cr(VI) concentration in leachate before and after combination with AMD, which illustrate the dramatic and statistically significant decrease in Cr(VI) concentrations in the fly ash leachate as a result of treating with AMD. Observations from HD-1 to HD-7 (dark gray bars) were historical data obtained from the power plant. Observations from DU-1 to DU-3 (light gray bars) were obtained from the SIDMS analysis at Duquesne University during current study, and observations '1:1 combo' and '5:1 combo' were obtained by mixing leachate and AMD with the ratios of 1:1 and 5:1 (leachate to AMD), respectively. Error bars are shown at 95% confidence intervals with n = 3.

ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY: ISOTOPE DILUTION MASS SPECTROMETRY (IDMS)



METHOD 6800
ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY: SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY (SIDMS)



GLOSSARY

Isotope dilution mass spectrometry (IDMS) -- A quantitative method for total concentration of an analyte based on the measurement of the isotope ratio of a nuclide using mass spectrometry after isotope dilution.

Isotope dilution -- Mixing of a given nuclide with one or more of its isotopes. The isotope usually has an enriched isotopic abundance different from that occurring naturally.

Speciated isotope dilution mass spectrometry (SIDMS) -- A quantitative method for determining elemental species based on the measurement of isotope ratio(s) in each species of a nuclide using mass spectrometry after speciated isotope dilution. Samples are mixed with one or more isotopic spikes which have different isotopic abundance and are artificially converted to chemical forms corresponding to the species to be analyzed. The spiked samples are then subjected to the separation of the species and the measurement of the altered isotope ratios in each species. Both species concentrations and species conversions can be mathematically deconvoluted.

Isotopic abundance -- The relative number of atoms of a particular isotope in a mixture of the isotopes of an element, expressed as a fraction of all the atoms of the element.

Isotopes -- Nuclides having the same atomic number but different mass numbers.

Species -- Chemical forms in which an element exists.

Natural isotopic abundance -- Isotopic abundance of elements from natural sources. Most elements (except lithium, lead and uranium) found in nature have a constant isotope abundance.

Isotope ratio -- Ratio of the isotopic abundances of two isotopes.

Speciation (or speciated) analysis -- Quantification of elements in specific chemical forms.

Isotope-enriched material -- Material containing elements artificially enriched in minor isotopes.

Isotopic spike (Isotope-enriched spike) -- Standards prepared from isotope-enriched materials.

Dead time -- The interval during which the detector and its associated counting electronics are unable to resolve successive pulses. The measured counts are lower than the true counts if no correction is performed.

Gain loss -- The loss of gain in detector caused by the inability of the multiplier's dynode string to supply enough current to maintain constant dynode voltage drops. The measured counts are lower than the true counts, and cannot be mathematically corrected if gain loss occurs.

Mass bias -- The deviation of the measured isotope ratio from the true value caused by the differential sensitivity of the instrument to mass. This effect may occur in the ionization process or from differential transmission/detection by the mass spectrometer.

Mass bias factor -- A number used to correct for the mass bias of the measured isotope ratios. Mass bias factor is measured by employing an isotopically certified standard.

Isotopic-abundance-certified standard (Isotopically certified standard) -- Standard material with certified isotopic abundance.
Inverse isotope dilution -- Analysis method to determine the concentrations of isotopic spikes. A known quantity and isotopic abundance of an isotopic spike is mixed with a known amount and isotopic abundance (usually tabulated natural isotopic abundance or certified isotopic abundance) of standard(s) and the altered isotope ratio(s) is (are) measured and used in the calculation to find the concentration of the isotopic spike. Usually, a natural material is used to calibrate and determine the concentration of the separated isotopic spike solution using this method. Only in the case of such elements as uranium, lead, and lithium are the natural isotopic abundances not constant in terrestrial materials.

Single spiking -- Addition of one isotopic spike to the sample.

Double spiking -- Addition of two isotopic spikes to the sample. The two isotopic spikes are enriched in different isotopes, and are prepared in different chemical forms, each of which corresponds to a species form.

Unidirectional conversion -- One directional transformation occurring between two species. One species can convert to the other; the reverse transformation does not occur.

Interconversion -- Bi-directional transformation occurring between two species. Species convert back and forth between the two chemical forms.

Time resolved analysis (TRA) -- A data collection mode in which the data can be acquired at designated intervals for a continuously aspirated sample, over a user-defined period of time.