

ENVIRONMENTAL AND FUEL MATERIALS ANALYSES BY  
MULTI-ELEMENT ISOTOPE DILUTION SPARK-SOURCE MASS SPECTROMETRY\*

J. A. Carter, D. L. Donohue, J. C. Franklin and  
R. W. Stelzner

Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830

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ABSTRACT

The isotope dilution method of analysis has been expanded to allow the addition of twenty or more enriched stable isotopes to a single sample. The method combines the survey capability of spark-source mass spectrometry with the accuracy and precision of isotope dilution techniques. The limit on the precision of analysis may well be the variability in response of the Ilford QII emulsion. The method has been studied using National Bureau of Standards reference materials in order to determine the accuracy and precision of the method. The method has been used to measure impurities in a variety of environmental samples at several concentration ranges. A microphotometer has been interfaced with a mini-computer to permit rapid collection of data and subsequent concentration determinations. The data system and its operation will be discussed briefly.

MASTER

INTRODUCTION

The method of isotope dilution analysis for trace elements has been described by Webster (1). A known amount of "spike" (tracer) element with non-normal isotopic abundance is added to the sample. The altered isotopic ratio is measured mass spectrometrically, and the concentration of the element calculated from the spike concentration and isotope ratios.

Usually isotope dilution is used to determine one or two elements with a thermal emission mass spectrometer. Leipziger (2) used spark-source mass spectrometry isotope dilution (IDSSMS) to determine Cu and Sb in standard samples. Multi-element analyses for up to six elements have been previously reported (3-6).

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Isotope dilution adds dimensions of precision and accuracy to spark-source mass spectrometry that are not usually obtained by SSMS. The combination of accuracy with the broad elemental range and the sensitivity of SSMS provides a new capability in trace metals analysis.

Twenty-four stable enriched isotopes have been added to gasoline and water samples at the 20 ng/ml to 1 µg/ml levels. In addition to being used as spike isotopes, these enriched isotopes may be used as internal standards for other elements. Thirty elements have been determined by the combination of methods.

If the sample element or elements are available in quantities of  $10^{-9}$  g, the element can be determined with a precision of 5% and an accuracy of about 10 percent.

#### MATERIALS AND METHODS

The analyses were performed with Mattauch-Herzog double-focusing mass spectrometers, either the AEI-MS-7 or the MS-702. All data were collected on Ilford QII photographic plates.

##### Sample Preparation

Water Samples. The water samples were prepared for analysis by adding from two to four micrograms of enriched stable isotopes (acid solution) to 100 ml of the water sample. The sample was evaporated to a volume of a few ml; 2-10 µl of this solution was evaporated on high purity graphite electrodes.

Gasoline Samples. The isotope spike solutions were prepared by diluting the aqueous stock solutions of the isotopes with acetone. The solutions were 90% acetone, 10% water. The concentrations of the isotopes in the acetone spike solutions were from 0.2 to 0.4 µg/ml of solution.

Four methods of equilibration of the spike and sample were used.

1. Bromine oxidation was the first method of equilibration. The samples were spiked, oxidized with bromine in  $\text{CCl}_4$ . The oxidized sample was freeze dried and the resulting tar carburized in vacuum at 60°C. The carbon was then pressed and sparked with standard spark-source procedures.
2. Direct ignitions. The gasoline samples were spiked with the stable isotopes in acetone. The resulting solution was burned in open dishes. The tar remaining after ignition was leached in aqua regia. The acid leachate was dried on graphite, baked for five minutes at 400°C and sparked by the usual spark-source procedure.

3. Burner oxidation. The samples were spiked as above. The equilibrated samples are burned in a lamp using a fiber glass-graphite wick. The chimney of the lamp was connected to an aspirator so that air flow forced the sooty flame up the chimney. The soot and the chimney walls were leached with nitric acid. This acid solution was dried on graphite and sparked directly.
4. A stable isotope spike solution was made in distilled HCl to contain 1 µg/ml of the following isotopes:  $^{25}\text{Mg}$ ,  $^{43}\text{Ca}$ ,  $^{53}\text{Cr}$ ,  $^{57}\text{Fe}$ ,  $^{61}\text{Ni}$ ,  $^{65}\text{Cu}$ ,  $^{67}\text{Zn}$ ,  $^{77}\text{Se}$ ,  $^{87}\text{Sr}$ ,  $^{97}\text{Mo}$ ,  $^{106}\text{Cd}$ ,  $^{113}\text{In}$ ,  $^{135}\text{Ba}$ ,  $^{203}\text{Tl}$ , and isotopically normal Er. 1.0 ml of this spiked acid was refluxed with 10.0 ml of gasoline for a period of four hours. During this time, the gasoline partially decomposed as evidenced by the appearance of brown-black solid material.

The aqueous layer was then drawn off, concentrated, and the entire aliquot deposited on the tips of machined graphite electrodes. The electrodes were placed in an oven at 300°C for 15 minutes to drive off any organic residue. The electrodes were sparked in the spark-source mass spectrometer to produce a graduated set of exposures from 10 to  $1 \times 10^{-2}$  C.

The data, regardless of sample preparation, were collected on Ilford QII photographic plates. The plates were developed for three minutes in Kodak D-19, short stopped in dilute acetic acid and fixed with Kodak rapid fixer.

The density of the lines of the photoplate and the elemental concentrations were calculated with a computerized plate reader. The microphotometer was converted into a single beam instrument, and the output of the photomultiplier was amplified and digitized. The digitized data were stored in a PDP-8E computer as percent transmittance and element identification data. When data collection was complete, the transmittance of the lines was converted to density or intensity by the Churchill method, using previously stored emulsion calibration curves.

Concentration of the individual elements was calculated by use of the altered isotope ratios according to:

$$CS = CK * \left( \frac{MW_{\text{SAMPLE}}}{MW_{\text{SPIKE}}} \right) * \left( \frac{VK}{VS} \right) * \frac{[(KX/SX) * SK - KK]}{[-(KX/SX) * SS + KS]}$$

where

CS = concentration of sample solution,  
CK = concentration of spike solution,  
MW = atomic weight,  
VK = volume of spike solution.  
VS = volume of sample solution  
KX = relative ion-beam intensity, spike isotope,  
SX = relative ion-beam intensity, sample isotope,  
KS = % abundance (atom %), spike isotope in sample solution,  
SS = % abundance (atom %), sample isotope in sample solution,  
KK = % abundance (atom %), spike isotope in spike solution,  
SK = % abundance (atom %), sample isotope in spike solution.

The operation of the system and details of construction have been described by Stelzner, Sites, and McKown (7).

#### Isotope Spike Solutions

The isotope spike solutions were prepared using enriched stable isotopes obtained from the Isotopes Division of Oak Ridge Holifield National Laboratory. Whenever possible, the isotopes had an isotopic abundance greater than 90% and chemical purity of 99%. The compounds or elements were dissolved in the appropriate acid or solvent and diluted to stock solutions containing 100 µg/ml of the spike element.

The isotope of choice, isotopic abundance and chemical form of the spike elements, are summarized in Table 1. In addition to the stock solutions of the individual isotopes, four different solutions of combined isotopes were prepared for specialized needs. These four solutions, described in Table 2, have proved satisfactory for water, biological, and fuel samples.

Synthetic gasoline samples were prepared in two different forms. Metal-gasoline solutions were prepared by dissolving NBS organo-metallic standards in a mixed solvent of xylene, ethyl alcohol, and hexanes. The SRM solution was diluted with ordinary regular gasoline so that the added concentration of each of the metals was 10 µg/ml in the stock solution. The SRM samples used to prepare the standard solutions are summarized in Table 3.

Table 1. Enriched Stable Isotopes Used in IDSSMS

<u>Isotope</u>	<u>Spike Abundance</u>	<u>Normal Abundance</u>	<u>Chemical Form</u>
$^{204}\text{Pb}$	94.3	1.37	Pb
$^{203}\text{Tl}$	94.96	29.52	$\text{Tl}_2\text{O}_3$
$^{194}\text{Pt}$	54.85	32.8	Pt
$^{196}\text{Hg}$	47.5	0.16	HgO
$^{183}\text{W}$	83%	14.28	$\text{WO}_3$
$^{135}\text{Ba}$	93.6	6.56	$\text{Ba}(\text{NO}_3)_2$
$^{125}\text{Te}$	91.23	7.03	Te
$^{113}\text{In}$	96.3	4.16	In
$^{106}\text{Cd}$	88.4	1.22	CdO
$^{102}\text{Pd}$	75.45	0.8	Pd
$^{98}\text{Ru}$	89.0	2.2	Ru
$^{97}\text{Mo}$	94.25	9.6	Mo
$^{91}\text{Zr}$	86.6	11.23	$\text{ZrO}_2$
$^{87}\text{Sr}$	93.29	6.96	$\text{Sr}(\text{NO}_3)_2$
$^{77}\text{Se}$	87.24	7.50	Se
$^{73}\text{Ge}$	86.1	7.77	$\text{GeO}_2$
$^{71}\text{Ga}$	99.8	40	$\text{Ga}_2\text{O}_3$
$^{67}\text{Zn}$	89.55	4.12	ZnO
$^{65}\text{Cu}$	99.5	30.91	CuO
$^{61}\text{Ni}$	99.54	1.2	Ni
$^{57}\text{Fe}$	90.42	2.2	$\text{Fe}_2\text{O}_3$
$^{53}\text{Cr}$	96.4	9.54	$\text{Cr}_2\text{O}_3$
$^{43}\text{Ca}$	81.1	0.13	$\text{CaCO}_3$
$^{25}\text{Mg}$	99.2	10.1	MgO

Table 2. Enriched Isotope Solutions for IDSSMS

<u>Solution 1</u>	<u>Solution 2</u>	<u>Solution 3</u>		<u>Solution 4</u>	
$^{25}\text{Mg}$	$^{204}\text{Pb}$	$^{204}\text{Pb}$	$^{77}\text{Se}$	$^{204}\text{Pb}$	$^{91}\text{Zr}$
$^{57}\text{Fe}$	$^{106}\text{Cd}$	$^{203}\text{Tl}$	$^{67}\text{Zn}$	$^{201}\text{Hg}$	$^{87}\text{Sr}$
	$^{65}\text{Cu}$	Normal <sub>Er</sub>	$^{65}\text{Cu}$	$^{180}\text{W}$	$^{77}\text{Se}$
	$^{67}\text{Zn}$	$^{135}\text{Ba}$	$^{61}\text{Ni}$	$^{150}\text{Nd}$	$^{73}\text{Ge}$
		$^{113}\text{In}$	$^{57}\text{Fe}$	$^{135}\text{Ba}$	$^{67}\text{Zn}$
		$^{106}\text{Cd}$	$^{53}\text{Cr}$	$^{125}\text{Te}$	$^{61}\text{Ni}$
		$^{97}\text{Mo}$	$^{43}\text{Ca}$	$^{106}\text{Cd}$	$^{57}\text{Fe}$
		$^{87}\text{Sr}$	$^{25}\text{Mg}$	$^{97}\text{Mo}$	$^{53}\text{Cr}$

Table 3. NBS SRM-1050-1075 Compounds for Standard Gasoline Samples

<u>Element</u>	<u>Compound</u>
Si	Octaphenylcyclotetrasiloxane
V	Bis(1-phenyl-1,3-butanediono)oxovanadium(IV)
Fe	Tris(1-phenyl-1,3-butanediono)iron(III)
Zn	Zinc cyclohexanebutyrate
Cu	Bis(1-phenyl-1,3-butanediono)copper(II)
Cd	Cadmium cyclohexanebutyrate
Sn	Dibutyltin bis(2-ethylhexanoate)
Cr	Tris(1-phenyl-1,3-butanediono)chromium(III)
Ni	Nickel cyclohexanebutyrate
P	Triphenyl phosphate

A second set of synthetic sample solutions in gasoline was prepared by dilution of a metal sulfonate mix, CONOSTAN D-20 (Continental Oil Company CONOSTAN, Ponca City, Oklahoma). This mixture as purchased contained 20 metallic elements at a concentration of 100  $\mu\text{g/g}$  of the mixture. The CONOSTAN solution was diluted with regular gasoline to provide a gasoline stock solution with one  $\mu\text{g/ml}$  of the twenty elements.

## RESULTS

Water samples have been limited to demineralized water, distilled water, and a few samples of process water. The data in Table 4 summarizes the elements sought in the various water samples. The detection limits reported are calculated on the basis of the most abundant isotope of the normal element. The total sample volume for all data here was 100 ml.

A second type of data was obtained from the demineralized water samples. The samples were high purity, and the added elements were in an isotopically enriched state so that several elements were added at masses and concentrations such that interferences were highly improbable. Relative sensitivity factors (RSF) are obtained from this data that are useful in other general survey-type analyses. The RSF data are compared in Table 5 with previously determined or estimated RSF values.

The impurity content of the gasoline samples depends on the source of the gasoline, type of gasoline, lead content, and unknown factors. Table 6 is a summary of certain elements found in gasoline samples, along with the concentration ranges that have been measured.

## DISCUSSION

The first requirement of IDSSMS is that the isotope spikes must stay in solution along with the sample elements. Equilibration is not feasible if the sample or the spike is not soluble. The second desirable requirement is that the spike isotope be present in the normal element at a low abundance. A third requirement is that the spike isotope be free of interference or be available as a multiply charged ion (odd mass).

Table 4. Selected Metallic Impurities in Water Samples

<u>Element</u>	<u>Water Analysis, ng/ml</u>		
	<u>Distilled</u>	<u>Demineralized</u>	<u>Process</u>
As	<.1	<.1	1.0
Be	<.01	<.01	<.01
Cr	<0.1	0.2	6
Cu	3	5	16
Fe	2	3	20
Mo	<0.5	<0.5	1
Ni	1	1	5
Pb	<1	<1	2
Se	<0.5	<0.5	1
Sr	<0.1	<0.1	100
V	<.01	<.01	<.01
Zn	<0.2	<0.2	250

Table 5. Relative Sensitivity Factors Determined by Addition of Stable Isotopes at 20 to 40 Nanogram/ml Concentration

<u>Element</u>	<u>RSF<sup>(a)</sup></u>	<u>Previous RSF</u>
Tl	1.54	2
In	0.70	0.5
Cd	1.92	0.5
Mo	0.73	1
Se	0.95	0.7
Cu	0.54	0.5
Ni	0.62	0.5
Fe	0.46	0.5
Cr	0.48	0.5
Ca	0.52	0.5

(a) Assuming that RSF for Er = 1.



IDSSMS provides a second type of analysis that is not traditional isotope dilution, but a modified internal standard method. It is practical to use an enriched isotope of one element as the internal standard for a second element. We have determined Sb with a  $^{123}\text{Te}$  spike, As with a  $^{77}\text{Se}$  spike and Bi with a  $^{204}\text{Pb}$  spike. The analysis of these solutions has been duplicated using standard solutions, and the accuracy seems to be about 10%.

The analysis of water samples by IDSSMS has detection limits for some elements in the range of  $1 \times 10^{-12}$  g/ml for a 100-ml sample. In addition, the precision of the analysis is generally from 5 to 10%; photographic plates as ion detectors limits the precision to  $\pm 5\%$ . The water analysis can be complicated by the presence of high levels of Ca, Mg and K because of oxide and chloride polymers. Organic compounds present in the water must be removed by heating at  $400^\circ\text{C}$  for a few minutes. If not removed, the organic compounds may produce poor sensitivity for metallic elements.

The analysis of the gasoline samples is complicated by the fact that the metallic elements except for Pb are present as unknown organic compounds. For the measurement of the other three metals, the spike isotopes were prepared in aqueous solution, since the cost of synthesis of appropriate organo-metallic compounds with enriched stable isotopes would be prohibitive. The fact that the metals in gasoline are organo-metallics and are not equilibrated even after 50 hrs with isotope spikes is demonstrated by the data in Table 7. The elements were added to the gasoline as the NBS organo-metallic compounds at about 0.5  $\mu\text{g/ml}$  concentration range and the sample equilibrated with the isotope spike dissolved in 90% acetone and 10% aqueous acid solutions. In some cases, extra acetone was added to the gasoline-acetone-spike mix to insure single phase solutions. These data demonstrate the failure to equilibrate between added organo-metallic elements and the appropriate spike. These data were obtained from analysis of the residue that remained when the gasoline and spike mixture was burned. Examination of the soot indicated that the normal metallic elements associated with organic ligand and was primarily concentrated in the soot which was collected on a cold surface. The  $^{106}\text{Cd}$  spike remained in the residue, but the normal cadmium from the organo-metallic compound was found in the soot. Sn, Cr and other elements behaved in a similar manner.

Table 6. Impurity Concentrations in Gasolines

<u>Element</u>	<u>Concentration Range, µg/ml</u>
Bi	0.001 - 0.1
Ba	0.005 - 0.5
Sn	0.05 - 0.3
Cd	0.001 - 0.05
Mo	<0.001 - 0.05
Sr	0.002 - 0.01
Se	0.001 - 0.02
Zn	0.01 - 2.0
Ca	0.05 - 0.2
Co	0.005 - 0.1
Ni	0.005 - 0.1
Fe	0.05 - 2
Cr	0.01 - 0.5
V	0.0005 - 0.002
Cu	0.01 - 0.2

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Table 7. Non-Equilibrated Metals in Gasoline

<u>Element</u>	<u>Found (µg/ml)</u>	<u>Added (µg/ml)</u>
Cd	0.05	0.48
Sn	0.05	0.47
Ni	0.1	0.35
Cr	0.1	0.25
P	0.3	0.61

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The reflux procedure was then adopted as the method of choice to equilibrate the isotope spikes with the samples. The results obtained from this reflux procedure showed that the technique essentially assures complete equilibration between the enriched isotope spike and the trace organo-metallic constituents.

#### CONCLUSION

Isotope dilution spark-source mass spectrometry has been shown to be a valuable multi-element method of analysis for water and fuel samples. The analysis requires an unequivocal method of equilibration of sample and spike isotopes. The data for the poorly equilibrated gasolines demonstrate that recovery of the spike isotope can lead to the conclusion that an accurate analysis has been made when the sample element has, in fact, been almost completely lost.

The analysis of water samples requires a large (100 ml) sample and the presence of large amounts of Ca, Mg, K and organics in the water may lead to incorrect concentrations for some elements if careful preparation of the samples is not used.

In general, the detection limit for metallic impurities in water is in the range of  $5 \times 10^{-11}$  g/ml in a 100-ml sample, and the accuracy is in the 5-10% range. The detection limits in gasoline are in the  $10^{-10}$  g/ml range for 10 ml samples with a precision and accuracy comparable to that in the water samples.

We have developed a method of refluxing the gasoline with an HCl solution spiked with isotopically enriched spike elements. This method of spiking the gasoline samples permits a quantitative analysis with an accuracy of 10% at the one  $\mu\text{g/ml}$  level.

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