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A SINGLE-LABORATORY EVALUATION OF OSMIUM ANALYTICAL METHODS

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The results of a single-laboratory study of osmium analytical methods are described. The methods studied include direct-aspiration atomic absorption spectroscopy (EPA Method 7550), furnace atomic absorption spectroscopy and inductively coupled plasma atomic emission spectroscopy using (a) direct nebulization (heated and unheated) (b) continuous nebulization and (c) volatilization (batch and heated continuous). Also presented are the results of several methods of sample preparation. The stability of osmium concentrations in digests over a three-week period are also presented. Method performance data including detection limits, optium concentration ranges (linearity), spike recoveries, interferences, precision, accuracy, and recommended operating parameters are presented and discussed.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) with direct nebulization offers an instrumental detection limit that is 1000-fold lower than the 0.3-mg/L value obtained for AAS Method 7550. The minimum instrumental detection limit achieved (0.03 ug/L for 1 mL) was obtained by batch volatilization of osmium concentrations above 1 mg/L, conventional ICP-AES for osmium concentrations above 1 ug/L, and batch-volatilization ICP-AES for osmium concentrations below 1 ug/L.

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ABSTRACT

The results of a single-laboratory study of osmium analytical methods are described. The methods studied include direct aspiration atomic absorption spectroscopy (EPA Method 7550), furnace atomic absorption spectroscopy and inductively coupled plasma atomic emission spectroscopy using (a) direct nebulization (heated and unheated), (b) continuous nebulization, and (c) volatilization (batch and heated continuous). The results of several methods of sample preparation are presented along with the results of osmium concentration stability over a three-week period. Method performance data including detection limits, optimum concentration ranges (linearity), spike recoveries, interferences, precision, accuracy, and recommended operating parameters are presented and discussed.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AAS	-- atomic absorption spectroscopy
EPA	-- Environmental Protection Agency
g	-- gram
GFAAS	-- graphite furnace atomic absorption spectroscopy
ICP	-- inductively coupled plasma
ICP-AES	-- inductively coupled plasma-atomic emission spectroscopy
IDL	-- instrument detection limit
kg	-- kilogram
L	-- liter
mL	-- milliliter
MDL	-- method detection limit
mg	-- milligram
ng	-- nanogram
nm	-- nanometers
NBS-SRM	-- U.S. National Bureau of Standards (now National Institute of Standards and Technology) Standard Reference Material
pg	-- picogram
RSD	-- relative standard deviation
ug	-- microgram
v/v	-- volume/volume
w/v	-- weight/volume

SYMBOLS

Al	-- aluminum
Ca	-- calcium
Ce	-- cerium
Co	-- cobalt
Cr	-- chromium
Cu	-- copper
Fe	-- iron
HCl	-- hydrochloric acid
HNO_3	-- nitric acid
H_2SO_4	-- sulfuric acid
Os	-- osmium
OsO_4	-- osmium tetroxide (or tetraoxide)
V	-- vanadium

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SECTION 1

INTRODUCTION

Osmium tetroxide is listed among Hazardous Constituents in Appendix VIII (Federal Register) and has the lowest Threshold Limit Value in air (at 0.0006 ppm) of any compound listed by the American Conference of Governmental Industrial Hygienists (ACGIH). Methods of known precision and accuracy are needed for the U.S. EPA to accomplish its mission. This study was conducted to provide the needed information for atomic absorption osmium Method 7550 and for other methods which seemed to offer improved detection limits. Since there was uncertainty in the scientific community on the loss of osmium using furnace atomic absorption, this issue as well as any digestion losses were resolved using radioactive ^{185}osmium. Based on evidence that ICP-AES offers a lower detection limit than flame AAS, this technique was included in the study to provide the performance data needed to add osmium to the list of elements approved for determination by ICP-AES. Variations in sample introduction for ICP-AES were investigated to evaluate improvements possible in the osmium detection limit. Since osmium tetroxide produces a stronger measurement signal than other forms of osmium as a result of its high volatility, oxidative treatment of a digest could provide evidence that osmium was (or was not) already present in the digest as the tetroxide.

A single-laboratory study was undertaken to evaluate SW-846 Method 7550, Osmium (Atomic Absorption, Direct Aspiration) and to investigate the use of graphite furnace atomic absorption spectroscopy (GFAAS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the determination of osmium. The purpose of this study was to obtain method-performance data. The study included a comparison of five methods of sample introduction for ICP-AES: direct nebulization, heated direct nebulization, continuous nebulization, heated continuous volatilization, and batch volatilization. This report also describes a study of four sample-preparation methods and a sample-digest stability study.

There are reports in the literature of elements whose presence in solution interfere with the determination of osmium by flame AAS (4, 5, 6) and ICP-AES (7, 8); however, most of these elements are not likely to be present at significant levels in environmental samples. Because of the relative lack of data regarding interference from the more common environmental elements, several of these elements were investigated in this study. For Method 7550, the elements investigated are: Al, Ca, Cr, Fe, Mg, Na, and V. For the ICP-AES methods, Al, Ca, Ce, Cr, Fe, Mg, and Na were tested. Hydrochloric acid has been used in sample preparation methods (3) and in the preparation of osmium standard solutions (8). The effect of various concentrations of hydrochloric acid on the osmium signal during a determination was also examined.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results of this single-laboratory study show that AAS Method 7550 (excluding the sample preparation procedure) is precise and accurate for determining osmium in extracts and digests of a variety of liquid and solid sample types. Conventional ICP-AES (with direct nebulization) offers an instrumental detection limit that is 1000-fold lower than the 0.3-mg/L value obtained for AAS Method 7550. The minimum instrumental detection limit achieved (0.03 µg/L for 1 mL) was obtained by batch volatilization of osmium (as the tetroxide) into the ICP-AES instrument. Method 7550 is recommended for osmium concentrations above 1 mg/L, conventional ICP-AES for osmium concentrations above 1 µg/L, and batch-volatilization ICP-AES for osmium concentrations below 1 µg/L.

Recovery studies, including the use of radioactive ^{185}osmium, revealed that furnace atomic absorption spectroscopy and several digestion procedures cannot be recommended for osmium determinations. The digestion procedures in Method 7550 and in Method 3050 should be avoided for osmium. The pressure-bomb digestion procedure, with osmium recoveries in the range of 84 to 98 percent, is recommended. The Appendix to this report contains the detailed changes recommended for AAS Method 7550.

The 228.2-nm wavelength is recommended for direct nebulization ICP-AES determinations to avoid the chromium and iron spectral interferences observed at 225.5 nm. The batch-volatilization technique is recommended as a means to avoid even minor spectral interferents because these non-volatile components do not reach the plasma with this technique.

SECTION 3

EXPERIMENTAL PROCEDURES

GENERAL PROCEDURES

The primary objective of this single-laboratory study was to determine the method-performance parameters for the determination of osmium in solution by acetylene-nitrous oxide flame AAS for inclusion into SW-846. Secondary objectives included investigation of alternate methods of instrumental determination, sample preparation, and a study of sample-digest stability. The two alternate instrumental methods of osmium determination examined were furnace AAS and ICP-AES. The method-performance parameters studied include:

1. Detection Limits,
2. Optimum Concentration Ranges (Linearity),
3. Spike Recoveries,
4. Interferences,
5. Precision,
6. Accuracy, and
7. Ruggedness Testing

All data were generated according to the procedures described in "Guidelines for Selection and Validation of U.S. EPA Measurement Methods" (1) and "Test Methods for Evaluating Solid Wastes," SW-846 (2).

The instrumental methods of analysis addressed in this report all require sample digestion. Method 7550 contains an aqueous sample preparation method and cites Method 3050 for the preparation of solid samples. The two other sample preparation methods investigated were a sodium peroxide fusion method [an adaptation of (3)], and a pressure bomb digestion method (PARR Instrument Manufacturing Company). The procedure used for the pressure-bomb digestion was that recommended by the manufacturer.

The instrument detection limits and the optimum concentration ranges were determined in aqueous standards that were free of interferences. For the Method 7550 evaluation, the method detection limit, spike recoveries, precision, and accuracy were determined in digests of each of the nine samples. The stability of osmium in the sample digests was monitored twice a week for a period of 3 weeks.

A thorough literature search revealed no mention of osmium reference materials. Nine samples were chosen for this study. Of the nine materials, two were U.S. National Bureau of Standards - Standard Reference Materials (NBS-SRM); two were certified materials from the U.S. EPA; one material was from a U.S. EPA hazardous waste site; one was a certified reference material

from the National Research Council of Canada. These materials are well-characterized reference matrices, but not reference materials with certified values for osmium.

All aqueous and solid waste samples were digested prior to analysis by the methods under study. Four liquid and five solid samples were chosen to evaluate the performance of Method 7550. These samples were also used to investigate several sample preparation methods. A study of the stability of osmium concentrations in digests of these sample matrices was also conducted. To ensure consistency, all standards and dissolved-osmium spikes were prepared from one lot of 1000-mg/L osmium (as the tetrachloride) stock standard (Spectrum Chemical Manufacturing Corp.). All acids used in the study were Ultrex Spectrograde (J.T. Baker brand) unless otherwise stated.

Liquids

All aqueous samples were digested by the procedure described in Method 7550 using HNO_3 and H_2SO_4. The four aqueous samples used in this study were:

1. A standard solution of osmium (as the tetrachloride) prepared from the osmium stock standard by serial dilution with a solution containing 1 percent each (v/v) of HNO_3 and H_2SO_4;

2. NBS-SRM No. 1643b, Trace Elements in Water;

3. A "synthetic interference solution" containing osmium (as the tetrachloride) and 500 mg/L concentrations of Al, Ca, Fe, and Mg in a solution containing 1 percent each (v/v) of HNO_3 and H_2SO_4;

4. A TCLP extract of soil from a U.S. EPA hazardous waste site.

Solids

The solid samples were digested using several different sample preparation methods, which are described in the Sample Preparation Methods portion of this section. The five solid samples used in this study were:

1. NBS-SRM No. 1633a, Coal Fly Ash;

2. U.S. EPA Municipal Digested Sludge #0319;

3. UNLV-QAL/EPA - CLP Reference Materials - Solid Laboratory Control Sample (0387);

4. Certified Reference Material No. MESS-1, Marine Sediment (National Research Council, Canada); and

5. Soil from a U.S. EPA hazardous waste site.

A sixth solid was used as a solid spiking material to evaluate sample preparation methods: Spectromel No. 2 Standard Powder Mixture, containing 12.5 percent osmium metal (Johnson Matthey Chemicals Limited, England).

METHOD 7550

This method is intended to provide the information needed to determine osmium by acetylene-nitrous oxide flame AAS.

Instrumentation

A Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer, fitted with an acetylene-nitrous oxide burner head was used to obtain data for Method 7550. Deuterium background correction was used for all determinations.

Optimization of Instrument Variables

Prior to the collection of data for the method parameters, several instrument variables were adjusted in order to optimize osmium absorbance in the acetylene-nitrous oxide flame. These variables include the following:

Burner Height--
Burner height was measured in millimeters from the burner surface to the center of the light beam from the hollow-cathode lamp. Changing the burner height dramatically affects absorbance measurements as the zone containing the highest concentration of osmium atoms is moved. Prior to this exercise, the burner slot was aligned with the light beam by means of the burner controls that adjust the in/out and rotational orientation of the burner assembly.

Fuel-to-Oxidant Ratio--
The recommended acetylene-nitrous oxide flame is a rich, red reducing flame. Once the burner position was optimized, the fuel-to-oxidant ratio was varied in order to achieve the conditions that yielded the highest absorbance from a 20-mg/L solution of osmium in an aqueous matrix containing 1 percent each (v/v) HNO_3 and H_2SO_4. Under the proper reducing conditions, the population of atomic osmium is maximized.

Sample Flow Rate--
Changing the sample flow rate (aspiration rate) changes the absorbance by increasing or decreasing the number of atoms in the light path.

Results from this optimization of burner height, fuel-to-oxidant ratio, and sample flow rate for Method 7550 are reported in Section 4 of this report.

Detection Limits

Instrument Detection Limit (IDL)--
The IDL of a given analyte is the concentration that corresponds to three times the standard deviation of seven replicate measurements of a blank solution, according to the definition on page "THREE-2" in SW-846 (2). The IDL for osmium was determined while aspirating an aqueous solution of 1 percent each (v/v) HNO_3 and H_2SO_4 into the flame.

Method Detection Limit (MDL)--
The MDL takes into account that some sample-digest matrices can enhance the absorbance of osmium and thereby increase the apparent sensitivity.

Likewise, the matrix can also depress the absorbance and thereby decrease the apparent sensitivity. Therefore, the digests of the 12 liquid and solid samples were subjected to standard additions of osmium in order to produce a calibration line for each matrix, according to the procedure on page "ONE-15" in SW-846 (2). IDL and MDL values for Method 7550 are reported in Section 4.

Optimum Concentration Range

The absorbance values of a set of osmium standards prepared in an aqueous matrix containing 1 percent each (v/v) HNO_3 and H_2SO_4 (free of interferences), ranging from a blank solution to 100 mg/L, were measured.

Spike Recoveries

Three portions of each of the liquid and solid samples were spiked to bring the concentration of osmium to 10 mg/L above the endogenous levels.

Interferences

Three different matrices were tested to determine the effect they would have on the determination of osmium at the analytical wavelength of 290.9 nm. These matrices were:

1. An aqueous solution containing 1 percent each (v/v) HNO_3 and H_2SO_4 (as described in Method 7550),

2. An aqueous solution containing 4 percent each (v/v) HNO_3 and H_2SO_4 (the acid composition after pressure-bomb digestion), and

3. 6-molar HCl.

Each matrix was tested alone and with 20 mg/L osmium.

Seven elements, Al, Ca, Cr, Fe, Mg, Na, and V, were tested individually to determine whether they interfere with the determination of osmium at the 290.9-nm analytical wavelength. First, a 20-mg/L solution of osmium containing 1000 mg/L of the element in question was measured, and the absorbance was compared to that from a 20-mg/L, interference-free osmium standard. When an interference was observed for a particular element (5 percent suppression or enhancement of the osmium signal), its concentration was varied from 100 mg/L to 5000 mg/L to determine the extent of the interference.

A 1000-mg/L solution of each element containing no osmium was also analyzed at 290.9 nm to evaluate spectral interferences. When a spectral interference was observed, the concentration of the interfering element was varied from 100 mg/L to 5000 mg/L, and the measured absorbance was compared to that from a blank solution. All solutions used for interference studies were prepared in an aqueous matrix containing 1 percent each (v/v) HNO_3 and H_2SO_4.

Precision

Each concentration or absorbance measurement reported in this study was the average of five consecutive four-second readings. These five readings were used to calculate the RSD. Precision data are presented in Section 4.

Stability Studies

All solutions were reanalyzed twice a week over a three-week period to determine the stability of osmium in the sample digests.

FURNACE AAS METHOD

The furnace AAS method for the determination of osmium was studied alone and in combination with radiochemical techniques in order to determine the fate of osmium during analysis.

Instrumentation

A Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer, fitted with a Model HGA-500 Graphite Furnace/Programmer, an AS-40 Auto Sampler, and a Data System 10, was utilized to obtain data for osmium determination using furnace AAS alone. Standard graphite tubes and pyrolytically coated platforms were used.

For the radiochemical studies of furnace AAS, a Varian Model 1275 AAS with a GTA 95 Temperature Program Controller, pyrolytically coated graphite tubes (without platforms) was used. The radioactivity counts were obtained using a 3-inch sodium iodide scintillation crystal with a 1-inch well (gamma detector) coupled to a Nuclear Data Model 62 pulse-height analyzer. The radiochemical studies were performed at the Scripps Institute of Oceanography.

^{185}Os Tracer (15)

A carrier-free ^{185}Os (half-life of 93.6 days) was produced using a cyclotron at McGill University, Montreal, Canada. An ultra-pure rhenium foil target (0.025 mm thick, Alfa Products #00279) was bombarded with protons for 20 hours (20 MeV tandem, ca. 4 microcuries/ua hr.) which produced about 76 microcuries as of April 6, 1987.

After delivery to the Scripps Institute of Oceanography, the irradiated part of the rhenium foil was cut into multiple small pieces (ca. 1.5 mm) and used as required. Each rhenium piece was placed into a 50-mL distillation flask and dissolved with 250 uL of concentrated HNO_3, followed by distillation of the ^{185}Os as OsO_4. Ceric sulfate was used as the oxidant in a solution of H_2SO_4 (ca. 15 percent H_2O). The ^{185}Os was collected into a mixture of ethanol:9 M HCl (1:2) and transferred into a teflon digestion vessel upon verification of the ^{185}Os activity.

The OsO_4 was heated in a drying oven at 120° C for 2 hours to reduce the Os^{+8} to Os^{+4}, followed by evaporation of the solution to dryness at low heat.

The ^{185}Os was dissolved in 6 M HCl, diluted to the desired concentration, and transferred into a glass liquid scintillation vial. The gamma peaks at 646 KeV and 875 KeV were used to determine the yields for all samples.

Optimization of Instrument Variables

The following parameters were varied in an attempt to optimize the osmium signal:

Drying Temperature--
The drying temperature was varied from 80° C to 200° C. The time for the drying step was varied from 10 seconds to 60 seconds.

Ashing Temperature--
The ashing temperature was varied from 200° C to 1500° C. The time for the ashing step was varied from 1 second to 30 seconds.

Atomization Temperature--
The atomization temperature was varied from 2700° C to 3000° C. The time for the atomization step was varied from 4 seconds to 10 seconds.

At successive stages of the furnace temperature program cycle, the program was halted and the radioactivity was determined for both the furnace and the pyrolytically coated graphite tube. The results of this study are presented in Section 4.

ICP-AES METHODS

Five different methods of sample introduction were investigated in order to determine the feasibility of using ICP for osmium determination. The first method uses unmodified direct nebulization. The other four methods involve some modification of the sample introduction hardware. The torch, spectrometer, and computer hardware were not altered for any of the methods. However, different analytical wavelengths and integration times have been used. The five sample introduction methods are:

1. Direct nebulization,

2. Heated direct nebulization,

3. Continuous nebulization,

4. Heated continuous volatilization, and

5. Batch volatilization.

Each of these methods was studied in detail to determine relative sensitivity, detection limits, and measurement precision for osmium determination. The continuous direct-nebulization sample introduction method was included to show osmium standard volatility during nebulization relative to a standard composed of non-volatile copper ions. Heat was applied in

three of the methods to exploit the volatile nature of OsO_4 (8,16). Each of these sample introduction methods will be explained separately.

Instrumentation

An Applied Research Laboratories Model 35000 sequential ICP-AES spectrometer with a spectral bandpass of 0.27 nm, equipped with a Tylan mass-flow controller and a Digital PDP 11/23 computer was used to obtain data for the evaluation of the ICP-AES methods. The ICP-AES was operated with a standard extended torch at an applied power of 1200 watts.

Direct Nebulization--

The ICP-AES sampling train was fitted with a Gilman peristaltic pump and a Meinhard concentric nebulizer for the direct nebulization method of sample introduction (Figure 1).

Heated Direct Nebulization--

The sampling train is the same as that for the direct nebulization method above, except that a cylindrical heating rod (0.5-inch diameter, maximum 70 watts power) is placed in front of the nebulizer. The heater is surrounded by a 10-turn glass coil (1.2 mm i.d., Technicon part no. 157-0226-01) through which the sample flows (Figure 2).

Continuous Nebulization--

The sampling train is the same as that for the direct nebulization method, except that the liquid drained from the nebulization chamber is recycled to the peristaltic pump so that the sample stream is continuously fed to the nebulizer in a closed loop (Figure 3).

Heated Continuous Volatilization--

The sample stream is fed through a 10-turn glass coil (1.2 mm i.d., Technicon part no. 157-0226-01) surrounding a cylindrical heating rod (0.5-inch diameter, maximum 70 watts power). The heated sample stream flows into a glass phase separator (Varian VGA-76, part no. 20-100559) at which point the vapor enters the ICP torch through a tygon tube 10 cm long and 5 mm i.d. The liquid phase is drained into a waste container (Figure 4). This apparatus is a simplified version of that designed by Bazan (16), and it is based on the same principles.

Batch Volatilization--

This sample introduction apparatus utilizes an 80-mL purging cell containing 22 mL H_2SO_4 and 0.3 g ceric ammonium nitrate (ACS grade), which is placed in a 1-L beaker filled with boiling water (Figure 5). Also investigated was a 500-mL purging cell containing 100-mL of 10 percent H_2SO_4 with 20 g/L potassium dichromate (ACS grade). A liquid sample is injected through a septum into the purging cell. Argon is used as the carrier gas. Vapor from the purging cell, containing volatile OsO_4, enters a glass condenser tube 20 cm long and 15 mm i.d. which is cooled with water flowing through close-wound tygon tubing. The sample vapor then continues through a U-shaped glass drying tube (Ace 14/35) 40 cm long and 20 mm i.d. This tube was used with and without magnesium perchlorate (ACS grade, screened to remove

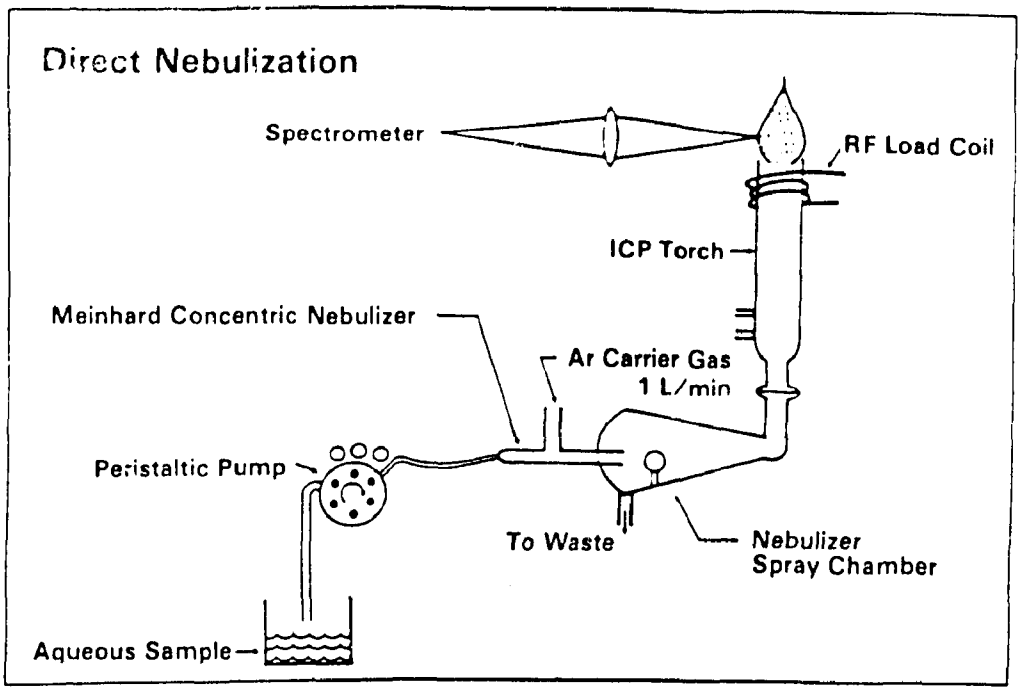

Figure 1. Apparatus for direct-nebulization ICP-AES.

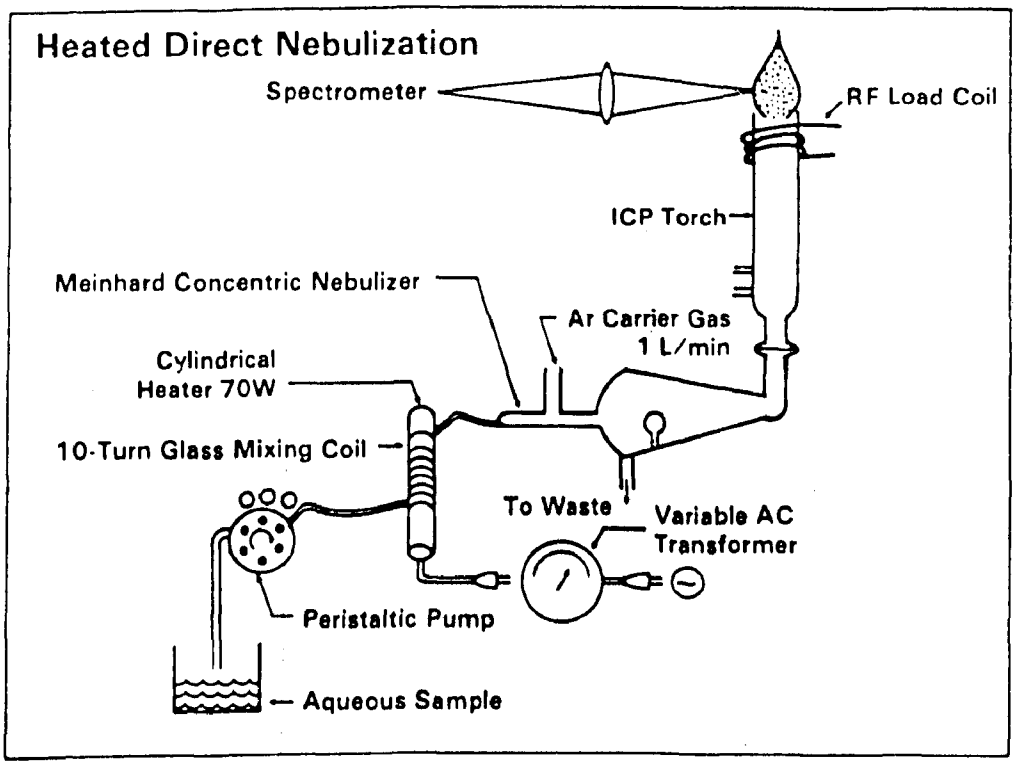

Figure 2. Apparatus for heated direct-nebulization ICP-AES.

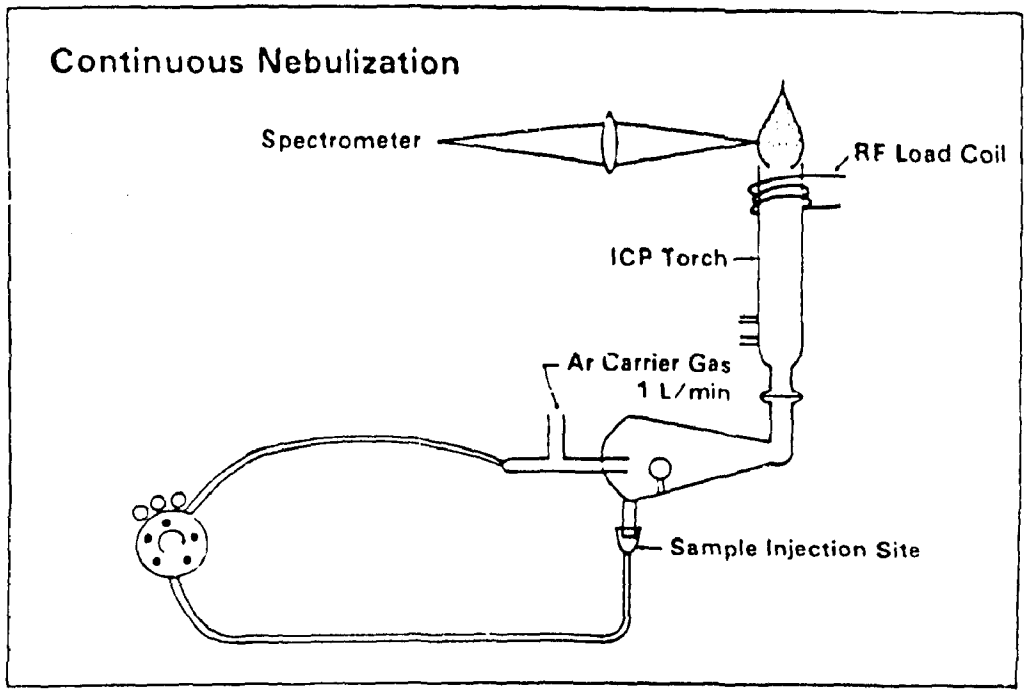

Figure 3. Apparatus for continuous-nebulization ICP-AES.

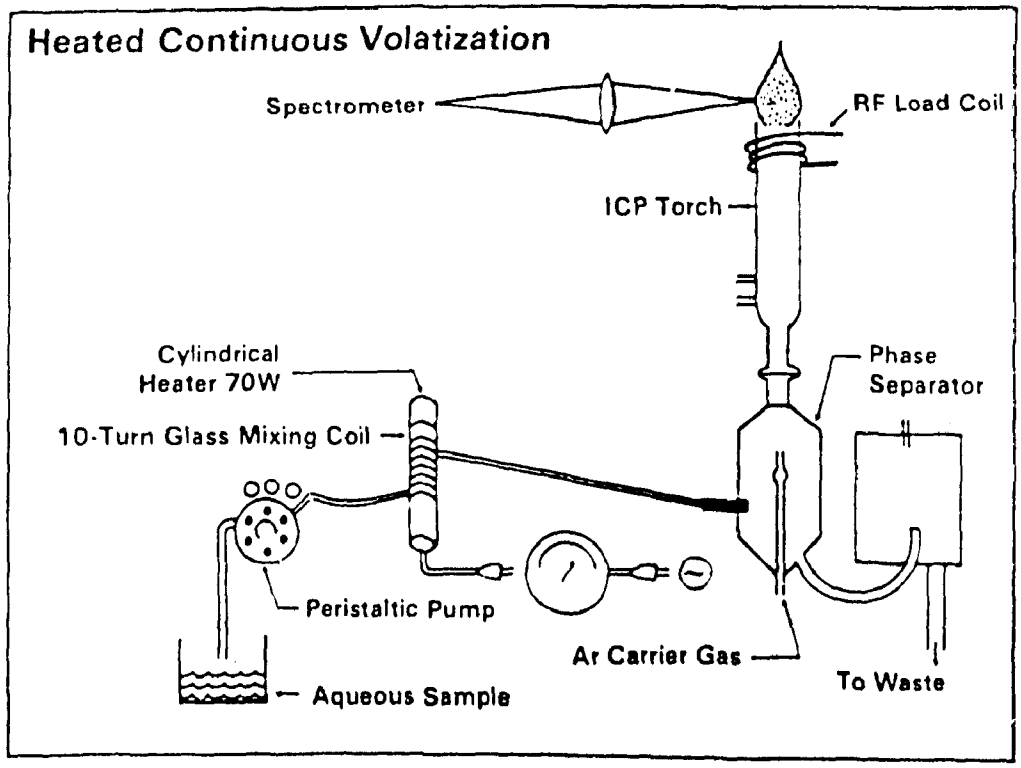

Figure 4. Apparatus for heated continuous-volatilization ICP-AES.

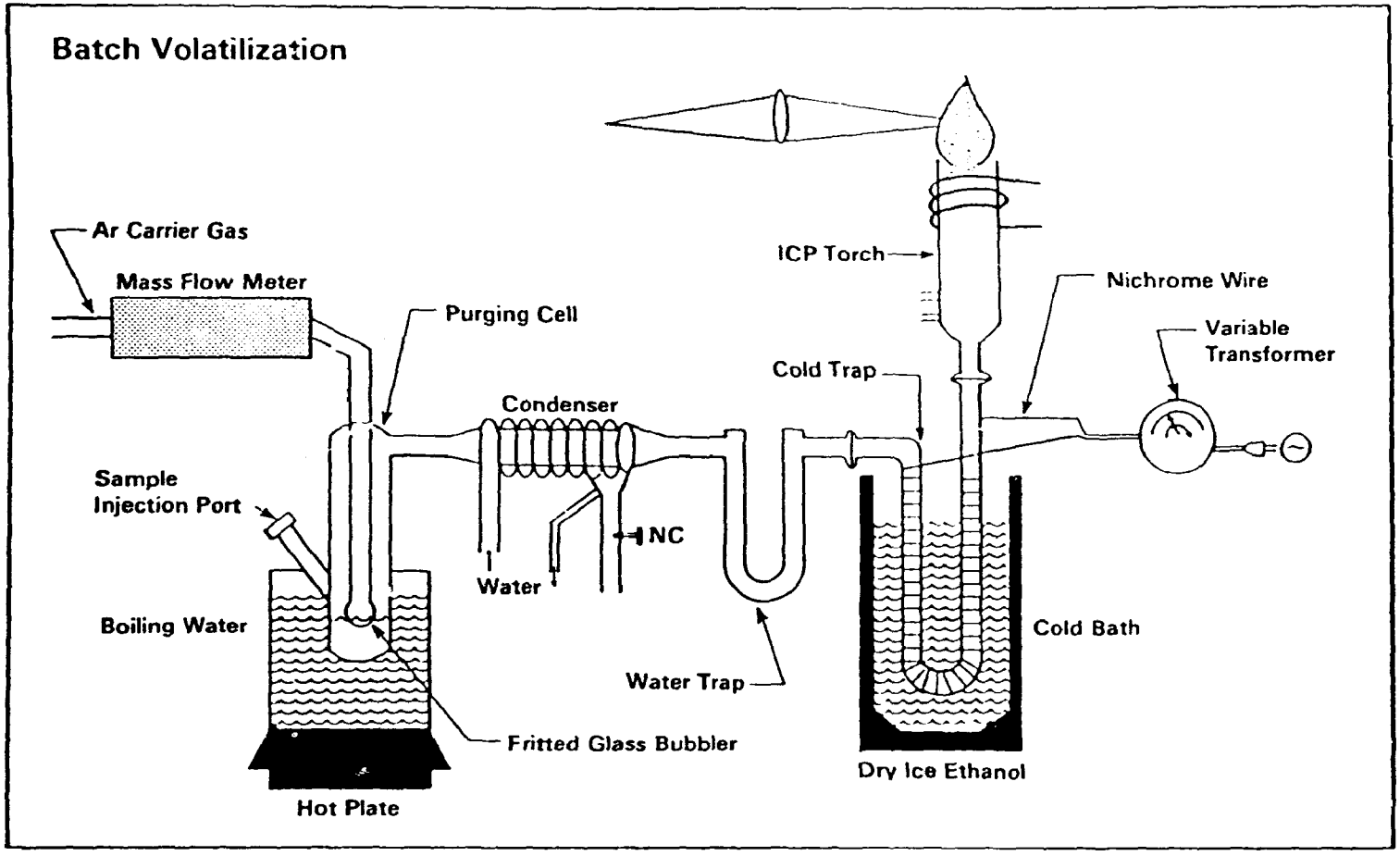

Figure 5. Apparatus for batch-volatilization ICP-AES.

particles smaller than 1 mm). This apparatus is loosely based on one described by Tao et al. (8).

The vapor proceeds through a U-shaped glass tube 70 cm long and 5 mm i.d., which is filled with crushed borosilicate glass screened to ca. 1-mm size. The tube rests in a vacuum Dewar flask, containing a dry ice/ethanol slurry, to trap the OsO_4. The cold bath is raised and lowered about the stationary apparatus.

Nichrome wire is wound around the cold trap tube and connected to a variable transformer (Variac 0-120 volt) to facilitate heating. Once the OsO_4 has been collected in the trap, the cold bath is lowered, and voltage is applied to the Nichrome wire heater. The OsO_4 is thereby re-volatilized and introduced directly into the torch.

Optimization of Instrument Variables

For the majority of data collected, the sequential spectrometer stepper motor was commanded to the peak position of osmium emission, derived by direct nebulization of a 1-mg/L osmium standard. The position of maximum signal intensity was located by integrating at the stepper motor positions around, and including, the expected position for maximum intensity.

Instrument variables were optimized prior to the collection of data for the method parameters. Several adjustments were made in order to maximize the osmium signal. These instrument variables are addressed separately for each type of sample introduction.

Direct Nebulization--

Optimization consisted of routine adjustment of torch height and peristaltic pump flow rate to achieve minimum detection limit for the instrumental tuning element manganese, at the analytical wavelenth 257.6 nm, with 1200 watts of applied RF power to the ICP-AES load coil. Argon carrier gas flow rate was 1.0 L/minute. The peristaltic pump was adjusted to a sample flow rate of 1 mL/minute.

Heated Direct Nebulization--

In addition to the routine optimization procedure above, the temperature of the sample stream was varied using a variable transformer (Variac, 1-120 volts) to control the voltage to the heating rod.

Continuous Nebulization--

The optimization procedure was the same as that for direct nebulization.

Heated Continuous Volatilization--

Parameter optimization consisted of varying the temperature of the sample stream using a variable transformer to control the voltage to the heating rod. In order to maximize the osmium signal, the argon carrier gas flow rate was varied using a mass-flow controller. The results of this study are presented in Section 3.

Batch Volatilization--

Parameter optimization involved, in addition to that for direct nebulization, the investigation of two purging cell solutions:

1. 10-percent (v/v) H_2SO_4 with 20 g/L potassium dichromate, and

2. concentrated H_2SO_4 with 15 percent added water (to reduce surface tension) and 12 mg/mL ceric ammonium nitrate.

The drying tube was used with and without magnesium perchlorate. Three different packing materials were used in the cold trap: borosilicate glass wool, 3-mm borosilicate glass beads, and crushed borosilicate glass (screened to ca. 1 mm).

The length of time for cold trapping was also optimized by monitoring the osmium vapor signal with the cold trap in the heated condition and noting the amount of time required for complete volatilization of osmium tetroxide from the purging cell. The signal integration time was also varied. The argon carrier gas flow rate (and therefore the purging rate during the cold trapping cycle) was varied using a mass flow controller. The injection volume was held constant at 1 mL for each determination.

Detection Limits

Detection limits were calculated using the method outlined in SW-846. The detection limit is defined as three times the standard deviation of seven integrated signals from a blank solution at the wavelength of interest. The detection limit was determined for each of the sample introduction methods. Using the direct-nebulization sample introduction method, the detection limits were determined using the two most sensitive analytical wavelengths for osmium, 225.5 nm and 228.2 nm (17).

Optimum Concentration Range

The linear range was determined for the direct nebulization sample introduction method at two analytical wavelengths, 225.5 and 228.2 nm. The linearity of signal response versus osmium concentration was investigated using a set of interference-free osmium standards ranging from a blank solution to 20 mg/L osmium. These standards were prepared in an aqueous matrix containing 1 percent each (v/v) of HNO_3 and H_2SO_4.

Spike Recoveries

Reference materials (determined to be free of osmium) were spiked with 10 ng/mL osmium. All osmium spiking solutions were prepared from one lot of 1000-mg/L osmium tetrachloride stock standard (Spectrum Chemical Manufacturing Corporation). Spike recoveries were evaluated using the direct-nebulization and batch-volatilization sample introduction methods.

Interferences

Osmium-free solutions containing known concentrations of Al, Ca, Ce, Cr, Fe, Mg, and Na were analyzed using direct nebulization to check for possible spectral interference at two osmium analytical wavelengths, 225.5 nm and 228.2 nm. Solutions of the individual elements were prepared at concentrations of either 500 mg/L or 1000 mg/L by serial dilution from stock standards (Spex Industries, Inc.).

Since osmium is sometimes determined in solutions of hydrochloric acid (3), an experiment was conducted to study the effects of varying concentrations of hydrochloric acid in osmium-free and osmium standard solutions that had been prepared in 1 percent each (v/v) HNO_3 and H_2SO_4. The hydrochloric acid concentrations examined were 0 percent (v/v), 1 percent (v/v), 3 molar, and 6 molar.

Precision

Since samples and standards were all measured in triplicate, precision data are available for each of the sample introduction methods, and are presented in Section 3.

Accuracy

Spike recoveries were used to assess the method accuracy (sample preparation in combination with instrumental determination).

SAMPLE PREPARATION METHODS

The samples were prepared using three different methods. Preparation of liquid samples was performed according to SW-846 Method 7550 for osmium and according to a pressure-bomb procedure (Parr Instrument Company). The preparation of solids was performed according to SW-846 Method 3050 (as prescribed by Method 7550), a sodium peroxide fusion method (3), and the pressure-bomb procedure.

Method 7550 Aqueous Sample Preparation

Liquid samples were spiked at appropriate levels and digested according to the procedure given in Method 7550, using HNO_3 and H_2SO_4. Borosilicate glassware and Spectro grade acids were used.

A test was performed to determine whether the Method 7550 digestion procedure would release osmium from a water sample containing ascorbic acid (ACS grade, Fisher Scientific). It was thought that ascorbic acid would serve to reduce osmium to a non-volatile oxide (14). An aqueous solution containing 0.2 gram/L ascorbic acid was spiked with 1 mg/L osmium and was digested using the procedure outlined in Method 7550. Thirty percent hydrogen peroxide (ACS grade), ceric ammonium nitrate (8), and ammonium peroxydisulfate (ACS grade) were used to reoxidize the reduced osmium. The results of this experiment are presented in Section 3.

Method 3050 Solid Sample Preparation

As specified in Method 7550, the Method 3050 digestion procedure was used to prepare solid samples. Borosilicate glassware, Spectrograde HNO_3 and HCl, and ACS grade H_2O_2 were used.

In order to quantitate osmium losses occurring during the Method 3050 digestion, and to determine at which point during the procedure the losses were occurring, samples were spiked with radioactive ^{185}Os. At progressive stages of the digestion procedure, the total radioactivity was counted; percent loss of ^{185}Os corresponds to the percentage loss of total osmium.

Sodium Peroxide Fusion Method for Solid Samples

Solid samples were prepared by sodium peroxide fusion in 30-mL zirconium crucibles. A 0.5-gram solid sample was mixed with 5 grams of sodium peroxide (ACS grade). The mixture was brought to red heat (about 550° C) over a Bunsen burner for 10 minutes with constant swirling. After cooling, 15 mL of water were slowly added to the reaction mixture. After further cooling, the crucible contents were transferred to a 50-mL beaker. Then slowly, with stirring, 13 mL conc. HCl and 3 mL conc. HNO_3 were added. (All osmium spikes were added prior to fusion.) Several solid samples were prepared in this manner and results from the analyses are tabulated in Section 3.

Pressure-Bomb Method

Samples were prepared using 23 mL teflon-lined acid digestion bombs (Parr Instrument Company No. 4745). The quantities of samples and HNO_3 were those recommended by the manufacturer. Several solid and liquid samples were prepared using this method. Results from the analyses of the digests are presented in Section 5.

Liquid Samples--

Ten mL sample and 2 mL concentrated HNO_3 were placed in the pressure bomb and heated at 150° C for 2 hours. After cooling, 2 mL concentrated H_2SO_4 were added and the digest was then diluted to 50 mL with Type II water. The resultant acid composition was 4 percent each of HNO_3 and H_2SO_4.

Solid Samples--

A 0.1-gram sample and 2 mL concentrated HNO_3 were placed in the pressure bomb and heated at 150° C for 4 hours. After cooling, 2 mL concentrated H_2SO_4 were added and the digest was diluted to 50 mL with Type II water. The resultant acid composition was 4 percent each of HNO_3 and H_2SO_4.

Osmium Concentration Stability

In order to determine whether osmium is stable in sample digests for extended periods of time, each of the target samples was digested using the pressure-bomb digestion method and analyzed twice weekly over a period of 3 weeks by Method 7550. The four liquid and five solid samples (listed under General Procedures) were digested in triplicate; they had been spiked such that they contained 10 mg/L osmium in the final volume of 50 mL.

QUALITY ASSURANCE/QUALITY CONTROL

Accuracy

Since no reference materials are available with certified values for osmium, homogeneous materials were the next acceptable alternative. To ensure consistency, all osmium standards and osmium spiking solutions were prepared from one lot of 1000 mg/L osmium tetrachloride stock standard (Spectrum Chemical Manufacturing Corporation). Spectromel No. 2 Standard Powder Mixture, containing 12.5 percent osmium metal (Johnson Matthey Chemicals Limited, England) was used as a solid spiking material in experiments involving the sodium peroxide fusion method.

Preparation Blank Analysis

For each set of sample digests, at least one preparation vessel served as a blank and received all of the reagents used in the sample preparation procedure. Preparation blanks were analyzed along with the rest of the samples in the set.

Precision

Samples to be analyzed by flame AAS were prepared in triplicate; those to be analyzed by ICP-AES were prepared in duplicate.

Continuing Calibration Verification

A solution of known osmium concentration was used to check for drift after every set of not more than 10 samples. When more than a 5-percent drift was observed, the instrument was recalibrated, and the samples were analyzed again.

SECTION 4

RESULTS AND DISCUSSION

This section will first present results for the determination of osmium in the nine matrices by flame AAS Method 7550. The method-performance and experimental results for furnace AAS and ICP-AES methods are then examined, followed by examination of the results of the sample preparation and the concentration-stability study.

METHOD 7550

The method-performance parameters and experimental results include:

1. Optimum Conditions and Ruggedness Testing,
2. IDL,
3. MDL,
4. Optimum Concentration Range (Linearity),
5. Spike Recovery,
6. Interferences, and
7. Stability Studies.

All analytical results are reported in units of mg/L or ug/L for the solutions. The standard deviation values are reported to two significant figures following the guidance of the Association of Official Analytical Chemists (17). All of the data reported (except burner height) were obtained by employing automatic spectral-background correction (deuterium lamp) and with the optimum measurement conditions discussed below.

Optimum Conditions

In the initial instrument set-up, a solution of known concentration is aspirated into the flame, and the analyst attempts to adjust the instrument in order to maximize the absorbance signal from the test solution. In the optimization of flame AAS, the analyst normally adjusts the burner position, gas flow rates, and sample flow rates. The extent to which these parameters can be varied without significantly decreasing the absorbance is a measure of the ruggedness of the method.

In the current study, before data were collected for any of the method-performance parameters, the absorbance signal was optimized by varying the burner height, acetylene-nitrous oxide flow rate, and sample aspiration rate.

Burner Height--

The results for the adjustment of burner height are shown in Figure 6. The observed absorbance from a 20-mg/L solution of osmium in 1 percent (v/v)

each of HNO_3 and H_2SO_4 varied from 0.006 to 0.134 absorbance units as the burner surface to center-of-beam distance was increased from 2 mm to 4 mm. A distance of 3.6 mm was chosen, because it gave the highest absorbance reading.

Fuel-to-Oxidant Ratio--

It is known that an acetylene-rich flame is necessary for the best osmium sensitivity. As shown in Figure 7, a ratio of acetylene-to-nitrous oxide of 1.4 yields the highest absorbance for a 20-mg/L solution of osmium.

Sample Flow Rate--

It can be seen from Figure 8 that the absorbance from a 20-mg/L solution of osmium can vary by a factor of five in response to changes in the aspiration rate. The maximum absorbance value was observed at 4.8 mL/min. However, at this point, any small change in sample flow rate, possibly due to a change in sample viscosity, will result in a large decrease in absorbance and thus an apparent decrease in osmium concentration.

Summary of Optimization Procedure

The following initial set-up procedure by which analysts should seek the optimum absorbance conditions for their particular instruments is recommended:

1. Place the burner surface approximately 3.6 mm below the center of the hollow-cathode light beam.

2. Set the acetylene-to-nitrous oxide gas flow ratio at approximately 1.4.

3. Set the sample flow rate to approximately 4.8 mL/min, using an aqueous solution.

4. Adjust all three variables while aspirating a 20 mg/L solution of osmium until the optimum absorbance signal is obtained.

Instrument Detection Limit (IDL)

The IDL is defined in SW-846 as three times the standard deviation of seven consecutive measurements of a reagent blank's signal, or,

$$IDL = KS_B$$

where: $K = 3$
S_B = the standard deviation of the average instrument noise.

For this study, a solution containing 1 percent (v/v) HNO_3 and 1 percent (v/v) H_2SO_4, free of interferents, was used as the reagent blank.

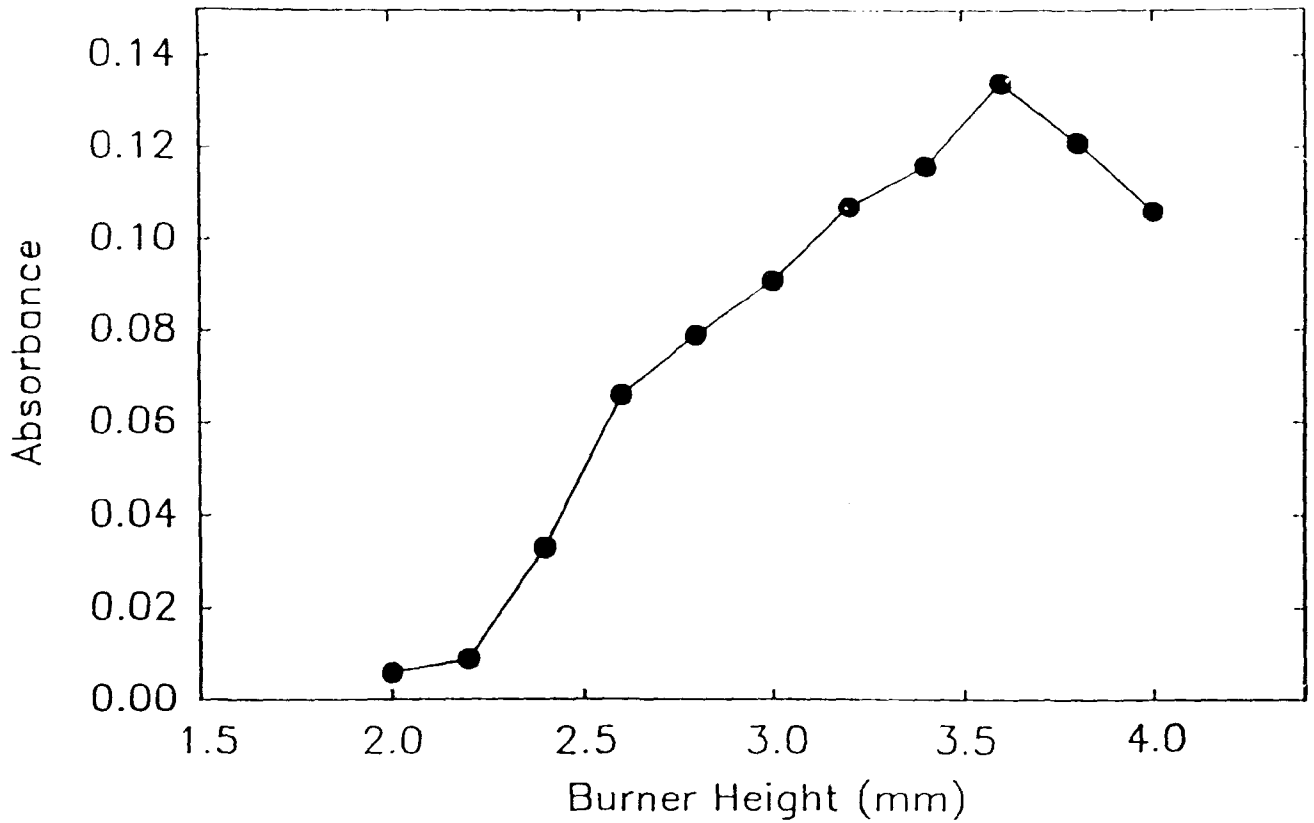

Figure 6. Relationship between absorbance and distance of burner surface from center-of-light beam for flame AAS determination of 20 mg/L osmium.

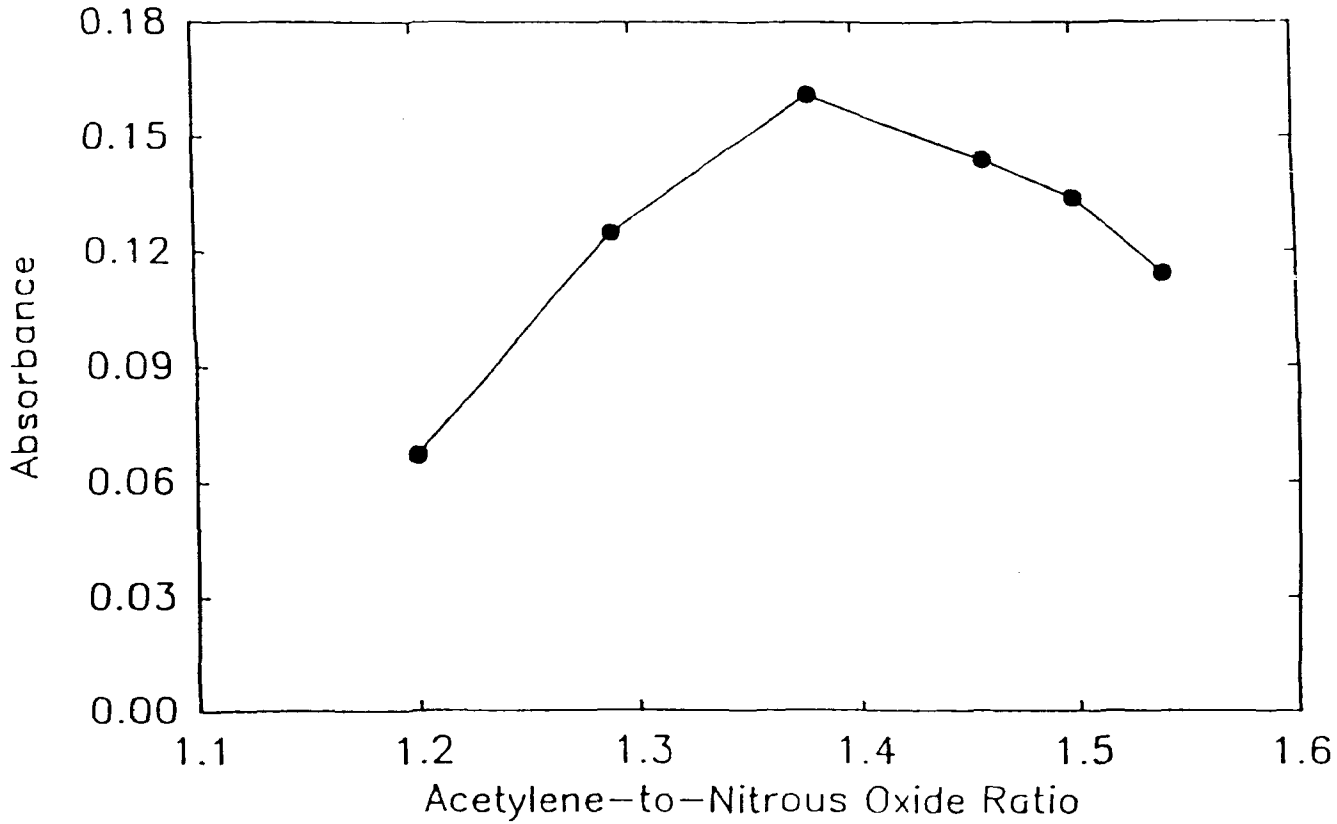

Figure 7. Relationship between absorbance and acetylene-to-nitrous oxide ratio for flame AAS determination of 20 mg/L osmium.

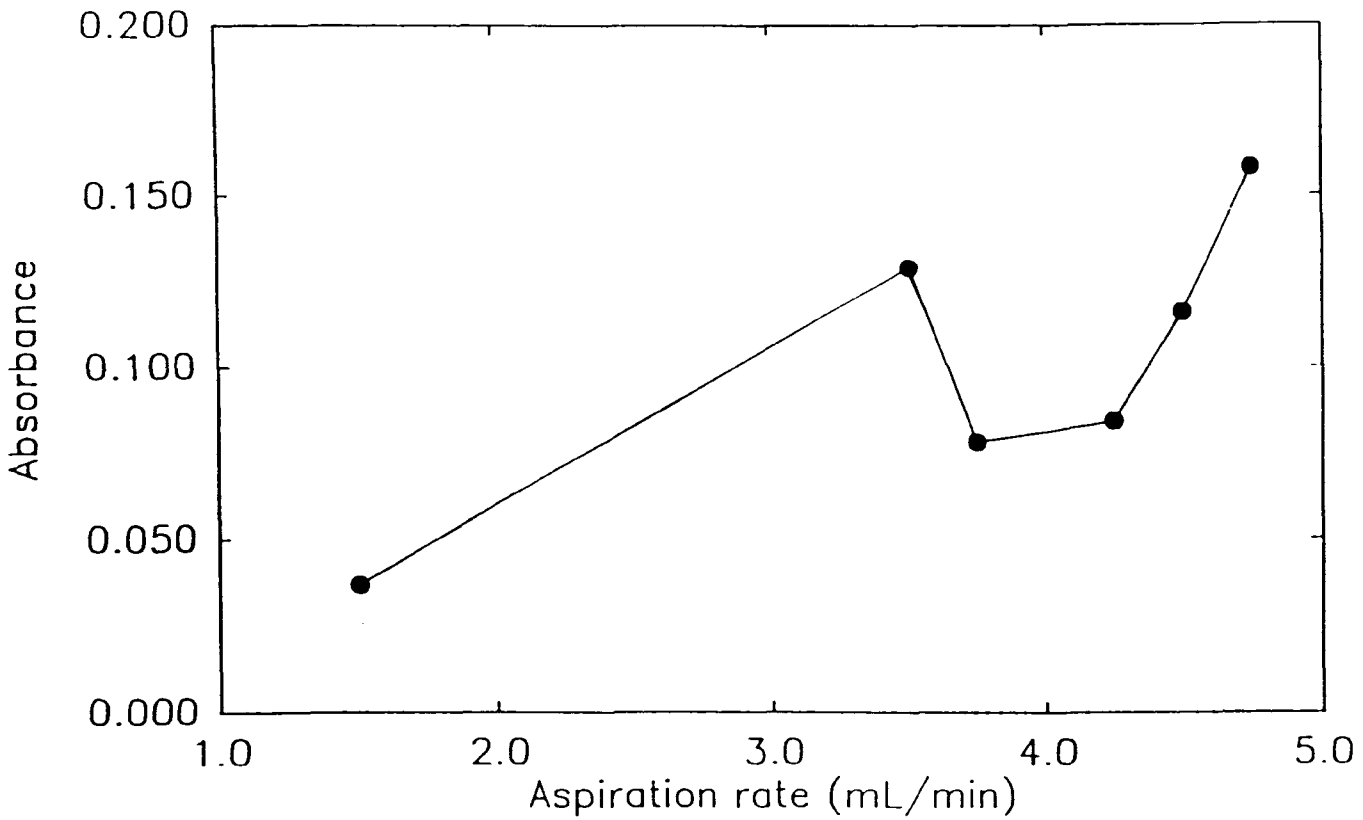

Figure 8. Relationship between absorbance and sample aspiration rate for the flame AAS determination of 20 mg/L osmium.

Results for the determination of the IDL by absorbance readings on non-consecutive days are listed in Table 1. The IDL determined from the absorbance readings is 0.28-mg/L. This agrees with the value given in Method 7550, 0.30 mg/L.

TABLE 1. INSTRUMENT DETECTION LIMIT FOR THE DETERMINATION OF OSMIUM BY FLAME ATOMIC ABSORPTION SPECTROSCOPY METHOD 7550

Date		IDL (mg/L)
09-21-88		0.36
09-23-88		0.27
09-28-88		0.21
	Average	0.28

Method Detection Limit (MDL)

The MDL is defined in SW-846 as the minimum concentration of an analyte that can be measured in a sample which has been processed through the preparative procedure. The MDL for this study was determined for the nine sample digests by the following relationship:

$$MDL = KS_B/m$$

where: KS_B = the IDL
m = the slope of the calibraton line in the sample digest.

Portions of each digest were spiked to contain osmium at three concentrations. The results from this procedure produced a calibration line for each of the nine samples. The MDLs of the nine matrices were used to calculate an average MDL of 0.30 mg/L (Table 2).

Optimum Concentration Range

The optimum concentration range is the range over which there is a linear relationship between absorbance and concentration. This method parameter was determined by preparing several osmium standard solutions ranging from blank to 100 mg/L. The solutions were prepared in 1 percent (v/v) each HNO_3 and H_2SO_4, which was free from interfering elements. The test for deviation from linearity was defined as that point on the curve where the predicted absorbance differed by more than 5 percent from the calculated absorbance value. This value was obtained from a linear regression of the absorbance versus concentration at the blank level, 2.0 mg/L, and 5.0 mg/L. The results of this test are presented in Table 3. Although the predicted absorbance did not differ by more than 5 percent from the calculated absorbance value, it was

TABLE 2. METHOD DETECTION LIMIT FOR THE DETERMINATION OF OSMIUM BY FLAME ATOMIC ABSORPTION SPECTROSCOPY METHOD 7550

Matrix	Slope	MDL (mg/L)[a]
Trace Elements in Water	0.83	0.34
Osmium Spectrometric Solution	0.85	0.33
Synthetic Interference Solution	0.99	0.28
TCLP Extract of Hazardous Waste	0.83	0.34
Coal Fly Ash	1.11	0.25
Municipal Digested Sludge	0.98	0.29
Marine Sediment	0.96	0.29
Laboratory Control Sample	0.96	0.29
Hazardous Waste Site Soil	0.99	0.28
Average	0.94	0.30

[a]The method detection limit is defined by MDL = 3 S_B/m where S_B is the standard deviation of the instrument background signal and m is the slope of the calibration line in the sample matrix.

TABLE 3. OPTIMUM CONCENTRATION RANGE (LINEARITY) FOR THE DETERMINATION OF OSMIUM BY FLAME ATOMIC ABSORPTION SPECTROSCOPY, METHOD 7550

Os Added (mg/L)	Absorbance		Percent[a] Error
	Observed	Calculated	
0.00	0.001	0.001	
2.00	0.009	0.011	-19
5.00	0.027	0.027	0.5
10.0	0.051	0.053	-4.1
20.0	0.103	0.106	-2.7
30.0	0.153	0.158	-3.4
40.0	0.202	0.211	-4.3
50.0	0.253	0.264	-4.1
60.0	0.301	0.316	-4.8
70.0	0.355	0.369	-3.8
80.0	0.407	0.422	-3.5
90.0	0.468	0.474	-1.3
100.	0.508	0.527	-3.6

[a]Percent Error = [(observed absorbance - calculated absorbance)/calculated absorbance] x 100.

decided not to increase the osmium concentration above 100 mg/L; it is unlikely that environmental samples would contain osmium at such high levels.

Spike Recoveries

Each of the nine samples was digested by the pressure-bomb method (Section 3). No osmium could be detected in the samples. So, three portions of each of the nine samples were spiked prior to digestion with 10 mg/L of osmium as the tetrachloride. Table 4 shows the spike recovery data. Greater than 94 percent recovery was obtained from the liquid samples. Spike recoveries for the soils were all in the 80-percent range, except for Coal Fly Ash which is at 94 percent. An average of 91 percent recovery was obtained for all of the samples digested. The lower-than-100-percent recovery is likely due to physical losses of osmium during the digestion procedure, or due to interfering elements.

TABLE 4. RECOVERY AND PRECISION OF OSMIUM DETERMINED BY FLAME ATOMIC ABSORPTION SPECTROSCOPY METHOD 7550

Matrix	Os Added (mg/L)	Percent[a] Recovery
Trace Elements in Water	10.0	96
Osmium Standard Solution	10.0	94
Synthetic Interference Solution	10.0	98
TCLP Extract of Hazardous Waste	10.0	96
Coal Fly Ash	10.0	94
Municipal Digested Sludge	10.0	84
Marine Sediment	10.0	88
Laboratory Control Sample	10.0	85
Hazardous Waste Site Soil	10.0	86
Average		91

[a]Average of three digestions.

Interferences

Three different matrices were evaluated to determine whether they interfere with the detection of osmium. The 1 percent (v/v) each HNO_3 and H_2SO_4 solution and the 4 percent (v/v) each HNO_3 and H_2SO_4 solution (the resultant matrix of the digestion procedures) gave the same absorbance reading for a 20-mg/L solution of osmium. The 6-M HCl matrix gave a significantly lower absorbance reading, and thus was not used for any of the analyses.

Seven elements, Al, Ca, Cr, Fe, Mg, Na, and V, were tested to determine whether or not they interfere with the quantification of osmium. Interference data are presented in Table 5. Al, Fe, Mg, and Na did not interfere with the

TABLE 5. EFFECT OF Al, Ca, Cr, Fe, Mg, Na, AND V ON THE OBSERVED CONCENTRATION FOR 20-mg/L SOLUTIONS OF Os BY FLAME ATOMIC ABSORPTION SPECTROSCOPY METHOD 7550

Interfering Element	Interfering Element Concentration (mg/L)			
	100	500	1000	5000
Al	a	a	20.0	a
Ca	19.4	19.3	19.0	17.9
Cr	20.7	21.3	22.9	34.3
Fe	a	a	19.9	a
Mg	a	a	20.0	a
Na	a	a	19.9	a
V	19.4	19.2	19.0	18.3

[a]Not tested at these concentrations because no interference was detectable when the interfering element was at a concentration of 1,000 mg/L.

detection of osmium when their concentrations were 1000 mg/L or lower and were not investigated further. Ca and V both suppressed the osmium signal slightly; this is probably due to viscosity and surface tension effects rather than a chemical interference, but this was not experimentally verified. Chromium caused a large increase in the apparent osmium signal. This is because chromium has an absorption line very close to that of osmium; a solution containing 1000 mg/L of chromium alone gave an apparent osmium concentration reading of 3 mg/L, while 5000 mg/L chromium gave a signal corresponding to 15 mg/L osmium. These effects were reproducible in the presence of 20 mg/L osmium, as shown in Table 5, which suggests a spectral, rather than a physical interference.

Precision

Measurement precision was determined from five repetitive concentration readings for each sample. The relative standard deviation (RSD) was used as an estimate of precision. Table 6 shows the RSD for each of the nine sample digests. The RSDs for osmium at about the 10-mg/L level are excellent. All RSDs are better than 2.6 percent with an average of 1.5 percent.

Accuracy

The accuracy of the osmium results obtained with Method 7550, in combination with the pressure-bomb method of sample preparation, was determined using spike recovery results for the nine matrices. The samples were spiked with 10 mg/L Os (as the tetrachloride) prior to digestion. The spike recoveries ranged from 84 to 98 percent, averaging 91 percent (Table 4).

TABLE 6. PRECISION FOR THE FLAME AAS DETERMINATION OF OSMIUM IN THE NINE SAMPLE DIGESTS

Matrix	Os Added (mg/L)	Os Measured (mg/L)	Percent RSD
Trace Elements in Water	10.0	9.83	0.9
Osmium Standard Solution	10.0	9.26	1.5
Synthetic Interference Solution	10.0	9.80	0.9
TCLP Extract of Hazardous Waste	10.0	9.59	0.7
Coal Fly Ash	10.0	9.29	1.5
Municipal Digested Sludge	10.0	8.61	1.5
Marine Sediment	10.0	8.77	2.6
Laboratory Control Sample	10.0	8.70	1.8
Hazardous Waste Site Soil	10.0	8.88	2.0
		Average	1.5

FURNACE AAS METHOD

Optimum Conditions

No reproducible osmium signal could be obtained using furnace AAS, although various combinations of drying, ashing and atomization conditions were used. Since osmium tetroxide boils at 130° C (11), it is possible that the osmium is lost during the drying step of the furnace temperature cycle. Alternatively, osmium may be reduced to the refractory metal which has a boiling point of greater than 5300° C (11). Because graphite sublimes at about 3650° C (11), the maximum temperature for the atomization step was limited to 3000° C. It is possible that osmium metal is produced during the charring cycle and subsequently is not volatilized during atomization.

In an effort to determine which of these scenarios was occurring, radioactive ^{185}osmium was injected into the furnace and the program temperature cycle was initiated. The program was then terminated at various stages and the total radioactivity was determined. Table 7 displays the total percent osmium remaining after different temperature steps.

It is apparent that most of the osmium (81 percent) remains in the graphite tube after being held at 500° C for 30 seconds. Therefore, it is unlikely that the majority of the osmium is in the form of OsO_4. After the atomization steps at 2000° C and 3000° C for 2 seconds, much of the osmium (52 percent and 27 percent, respectively) remains on the furnace walls. Clearly, osmium is probably in the elemental form and is slowly being volatilized from the furnace walls. Furnace AAS analysis of osmium might be improved by the use of matrix modifiers that would release oxygen to osmium during the charring and atomization steps.

TABLE 7. RETENTION OF RADIOACTIVE ^{185}-OSMIUM ON THE GRAPHITE TUBE DURING FURNACE AAS ANALYSIS

Step No.		Temperature (°C)	Time (sec.)	Gas Flow (L/min.)	Percent Os[a] Remaining
1	ramp	amb.-110	30	3	
2	hold	110	45	3	96±2
3	ramp	110-500	70	3	
4	hold	500	30	3	81±3
5A	ramp	500-2000	1	0	
6A[b]	hold	2000	2	0	52±5
5B	ramp	500-2000	1	0	
6B[b]	hold	3000	2	0	27±4

[a]^{185}Osmium with 5 ng stable osmium.
[b]Incomplete atomization occurs at both 2000° C and 3000° C. Temperatures above 3000° C were not explored, due to instrument limitations.

A set of ideal instrument conditions for the furnace AAS determination of osmium was not obtained in this study. Similar difficulties have been experienced by others (9,10).

ICP-AES METHODS

In this section, the results obtained from the evaluation of the four ICP-AES sample introduction methods investigated are discussed.

Optimum Conditions

All optimization procedures were performed using the analytical wavelength of 225.5 nm unless otherwise indicated.

For the majority of the data collected, the sequential spectrometer stepper motor was commanded to the peak position of osmium emission. This was achieved by first nebulizing a 1-mg/L osmium standard and integrating the signal at the stepper motor positions around and including the expected position of maximum intensity. Once the position of maximum intensity was found, the stepper motor was commanded to this position. All ICP-AES data were collected in this manner, with the exception of the Fe and Cr scans, which are discussed in the section on interferences.

Direct Nebulization--

General optimization of the plasma consisted of adjustment of the plasma torch height, such that with manganese (as the instrumental tuning element) a detection limit of 0.6 µg/L at the 257.6-nm analytical wavelength was achieved with 1200 watts of applied power, using a two-second integration time. The

sample flow rate was adjusted to 1 mL/minute. The plasma support gas was delivered at 0.8 L/minute. The sample carrier gas flow rate was 1.0 L/minute. Measurement precision for a 1-mg/L osmium standard typically had an RSD of less than 0.5 percent.

Heated Direct Nebulization--

In general, optimum conditions used were the same as those used for direct nebulization. To find the optimum temperature for heating the sample stream, a variable transformer was used to increase the voltage step wise to the sample stream heating rod. A 1-mg/L osmium tetrachloride standard was aspirated, and signal integrations were taken every two seconds. The osmium signal versus temperature is plotted in Figure 9. A linear relationship was assumed between zero voltage applied at ambient temperature, and the voltage applied for the sample stream to boil at 100° C.

As expected, increasing the temperature of the sample stream caused an increase in the volatility of osmium from aerosol droplets formed during nebulization. The net signal increase at a point just prior to boiling was about twice that for unheated direct nebulization. The precision of the signal measurements remained constant up to approximately 100° C. As the sample stream began to boil, measurement precision decreased dramatically. Precision data (RSD) relative to temperature are presented in Table 8.

TABLE 8. MEASUREMENT PRECISION FOR 1-mg/L OSMIUM SIGNAL VERSUS TEMPERATURE FOR HEATED DIRECT-NEBULIZATION ICP-AES

Temperature (°C)	RSD
25	0.27
50	0.22
75	0.49
ca. 100 not boiling)	0.29

The detection limit at ambient temperature was 0.3 ug/L. At just less than boiling, the detection limit was also 0.3 ug/L, even though the sensitivity had doubled.

It was observed that bubbles from the boiling sample stream caused sporadic 25-percent increases in the osmium signal. This phenomenon may be the result of a more turbid flow through the 1.2-mm i.d. glass coil surrounding the heater. No further investigations on this subject were performed.

Continuous Nebulization--

In order to further investigate the volatile nature of OsO_4, a continuous nebulization apparatus was employed (Figure 3). A 1-mL aliquot of a 1-mg/L osmium tetrachloride standard was injected, and the resulting osmium signal was integrated every 2 seconds. For comparison, a 1-mL aliquot

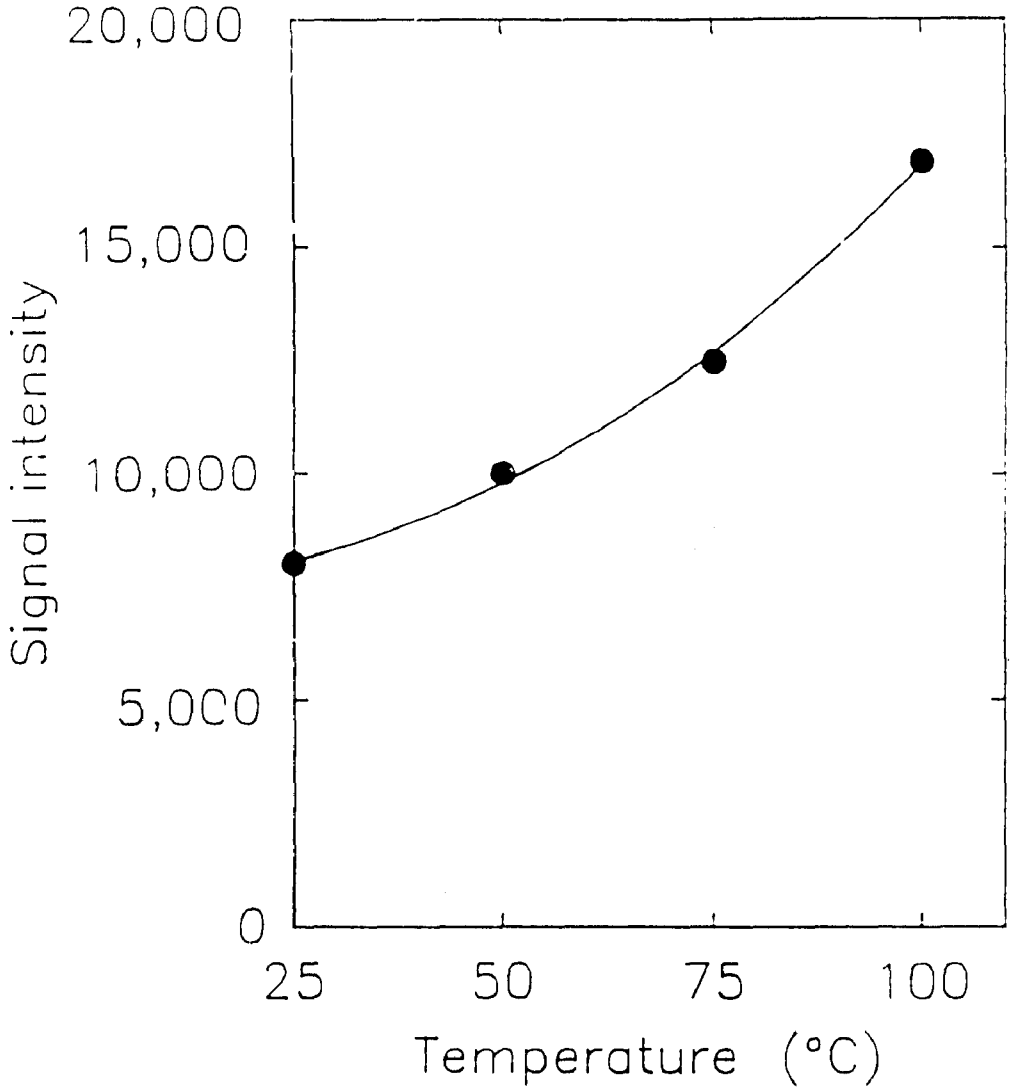

Figure 9. Relationship between osmium signal intensity and temperature for heated direct-nebulization ICP-AES.

of a 1 mg/L copper standard was also injected in the same fashion. Plots of signal response over a 10-minute period for these two elements are shown in Figure 10.

Heated Continuous Volatilization--

This method of sample introduction was employed to take advantage of the volatility of OsO_4, especially at elevated temperature. Additionally, if elements causing spectral interferences were present in a sample, separation of the gas and liquid phases would remove most interferences. These interfering elements would be present in solution as aquo-ligands and would remain in the liquid phase, while the gas phase would contain the OsO_4. Determining the optimum conditions for this sample introduction method consisted of varying power to the sample stream heating rod. A plot of approximate temperature versus signal for a 1-mg/L osmium standard is presented in Figure 11. Corresponding measurement precision data (RSD) are shown in Table 9.

TABLE 9. MEASUREMENT PRECISION FOR 1-mg/L OSMIUM STANDARD VERSUS TEMPERATURE USING HEATED CONTINUOUS-VOLATILIZATION ICP-AES

Temperature (° C)	RSD
25	4.7
50	0.7
75	0.3
ca. 100 (not boiling)	0.4

When the sample stream temperature is increased to a point just below boiling, the osmium signal increases to a level of about eight times that of signal at ambient temperature. Note, however, that the sensitivity at ambient temperature is about eight times less than that for direct nebulization. Measurement precision was poor at ambient temperature (RSD of 4.7 percent), but improved with heating to less than 1 percent RSD. Precision decreased dramatically as the sample stream began to boil. The detection limits at ambient temperature and at a temperature just below boiling were determined to be 2.1 µg/L and 1.4 µg/L, respectively.

Batch Volatilization--

The optimization of this method of sample introduction involved designing the purging cell, choosing the ideal material for the cold trap, and optimizing flow conditions.

Two types of purging cells were investigated. The first was a 500-mL cell containing 100 mL 10-percent H_2SO_4 with 2 percent (w/v) potassium

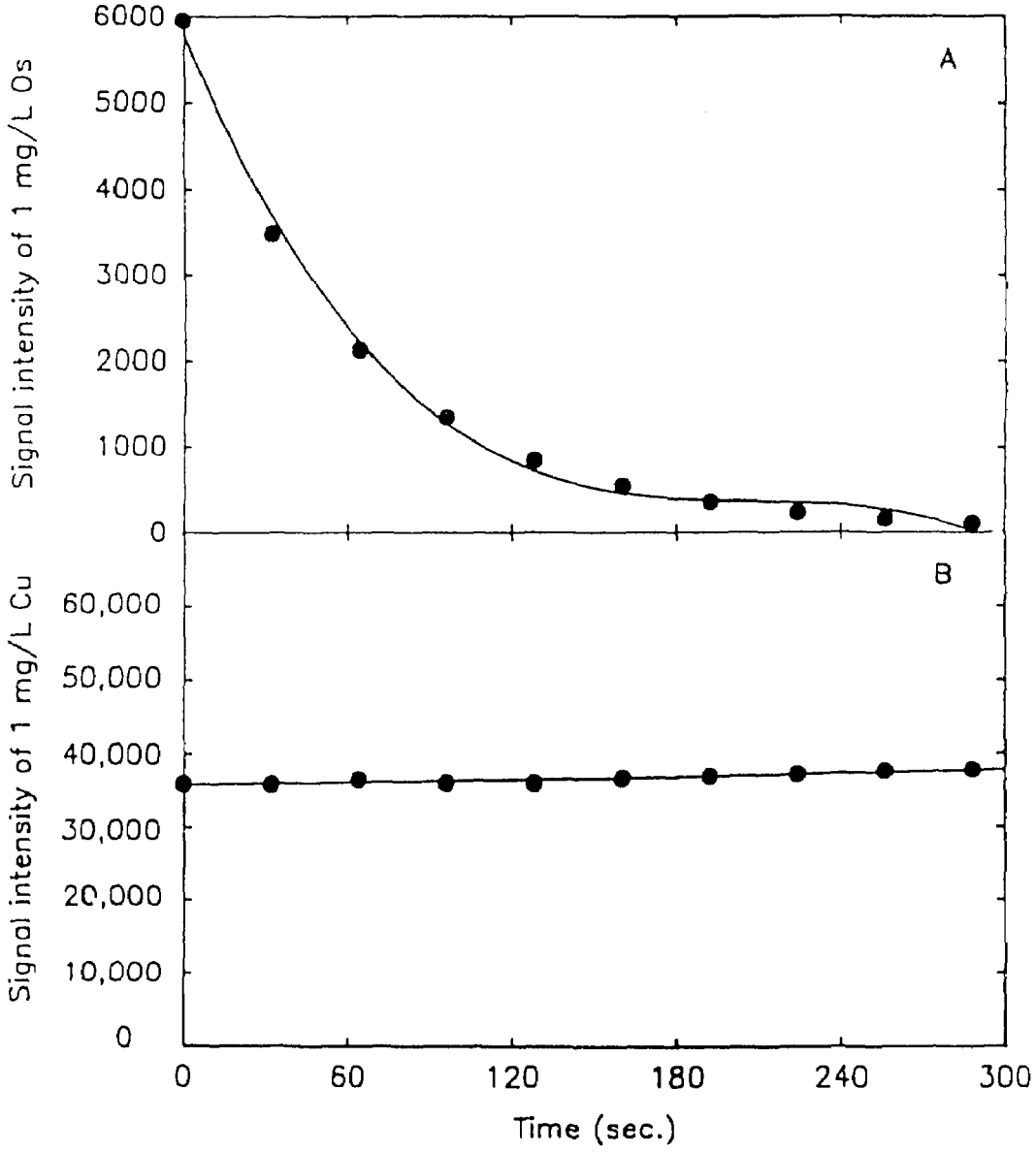

Figure 10. Comparison of time-integrated signals by continuous-nebulization ICP-AES of a 1-mL injection of (A) 1-mg/L osmium standard and (B) 1-mg/L copper.

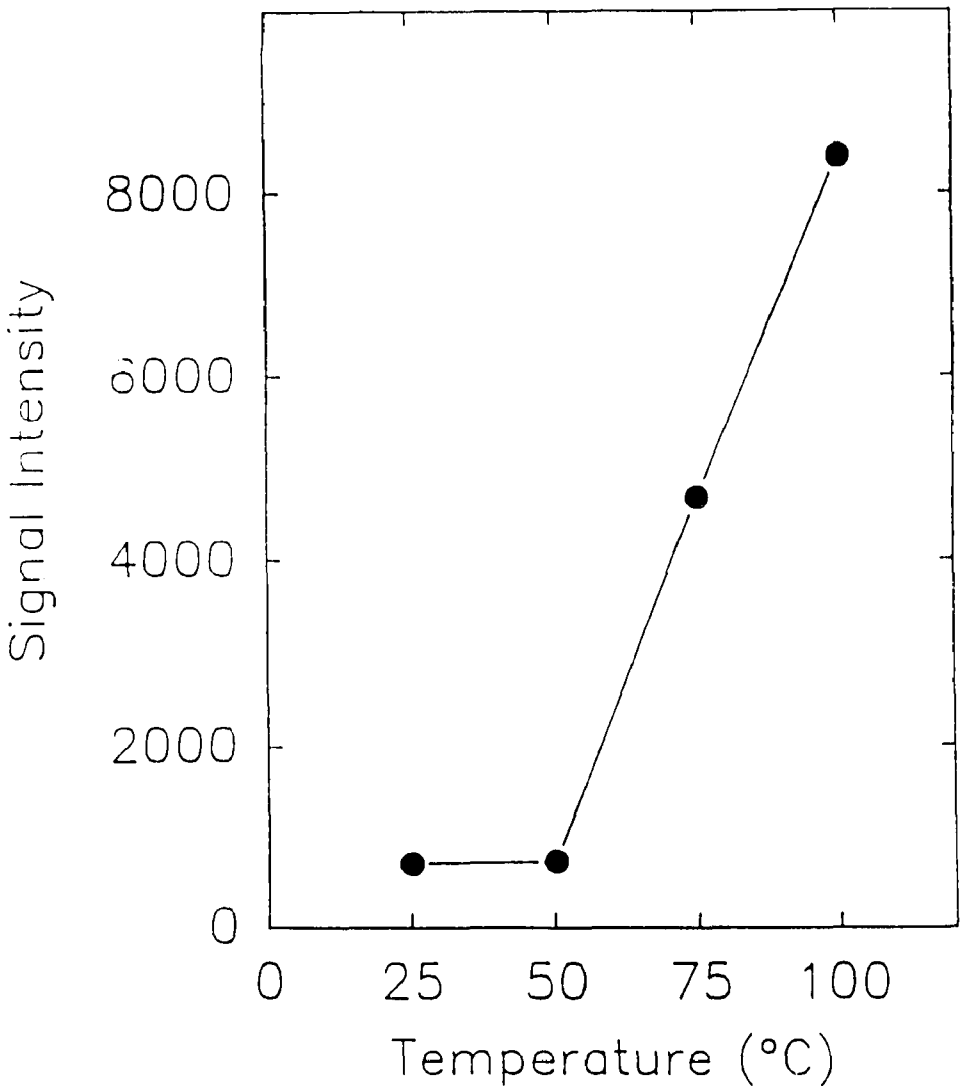

Figure 11. Relationship between emission intensity and temperature for heated continuous-volatilization ICP-AES.

dichromate as the oxidant. The second cell was 100-mL cell containing 22 mL concentrated H_2SO_4 and 3 mL of water (to reduce surface tension). To this solution, 0.3 g of ceric ammonium nitrate was added as the oxidant. The sample volume injected into the purging cell was 1 mL for all standards and samples.

The first arrangement proved unsatisfactory because a large amount of water vapor was generated along with the OsO_4 during the purging cycle. The water vapor caused the the magnesium perchlorate in the drying tube to become saturated after only five determinations. In addition, dry magnesium perchlorate seemed to display some adsorptive properties towards osmium.

The second cell proved more useful in that very little water vapor escaped the sulfuric acid solution; so little that the drying tube could be used without the magnesium perchlorate. Approximately 15 determinations could be performed before it was necessary to change the purging cell solution. Ceric ammonium nitrate was used as the oxidant instead of potassium dichromate. The 100-mL purging cell with H_2SO_4 and ceric ammonium nitrate was used for all remaining investigations of the proper cold trapping material and argon flow conditions.

Cold-trap efficiency was investigated using three materials: borosilicate glass wool, 3-mm glass beads, and crushed borosilicate glass screened to approximately 1 mm. The glass wool was found to bind OsO_4 irreversibly. The 3-mm diameter glass beads trapped OsO_4 during about the first 4 minutes of the purging cycle, but then the osmium signal began to increase, indicating possible leakage, or perhaps saturation of surface area. Best results were obtained using the 1-mm crushed glass, which was used during the remainder of the investigation.

Optimum argon flow rates were determined for both the purging and cold trap heating cycles. For the purging cycle, 200 mL/minute was found to be sufficient. The optimum carrier flow rate for delivering the OsO_4 to the torch from the heated cold trap was 0.8 L/minute. This was determined by varying the argon carrier gas flow rate while purging a 1000-ng injection of osmium with the cold trap in heated condition. Although this flow rate would seem to be the same as that of the plasma (0.8 L/minute), a darker central channel could be seen. The actual carrier flow rate was, therefore, more than 0.8 L/minute. This is probably due to expansion of the argon gas when the cold trap was heated.

To determine the length of time required for integration during the trap-heating cycle, the signal from 100 ng of volatilized osmium from the heated cold trap was monitored, using repetitive two-second integrations. This showed that all of the osmium was released from the trap in less than 12 seconds. Therefore an integration time of 15 seconds was chosen.

The length of time required for the purging cycle was determined by injecting 100 ng of osmium into the purging cell with the cold trap in the heated condition. The osmium signal was then monitored using 15-second integrations for several minutes. The relation of signal intensity versus the time in minutes is presented in Figure 12. A purging time of 10 minutes was

sufficient to remove all of the OsO_4 from the reaction cell, and was used for the remainder of the investigation. Measurement precision, using 1-mL aliquots of a 10-µg/L osmium standard, had a 6-percent RSD.

In summary, the optimum conditions and apparatus arrangement for the batch volatilization are as follows:

1. Utilize a purging cell with sulfuric acid and enough water to reduce surface tension, with ceric ammonium nitrate added as a strong oxidant.

2. Set the water trap in place without a desiccant.

3. Set up the cold trap filled with ca. 1 mm crushed borosilicate glass.

4. Set the argon carrier flow rate at 0.2 L/minute for the purging cycle.

5. Purge for 10 minutes.

6. Set the argon flow rate at 0.8 L/minute for heating the cold trap.

7. Employ a signal integration time of 15 seconds.

Detection Limits

The detection limits were determined for each of the ICP-AES methods, except for continuous nebulization. The detection limits and relative sensitivities for each of the methods are presented in Table 10. Detection limits using heated nebulization and heated continuous volatilization were determined at the temperature just prior to boiling. Sensitivities were determined relative to the direct-nebulization method.

The detection limits obtained using direct nebulization and heated direct nebulization were both 0.3 µg/L at the 225.5-nm wavelength. Heating the sample stream increased the sensitivity by a factor of two; however, the blank noise increased proportionally.

The heated continuous-volatilization method of sample introduction provided the worst detection limit; although, as stated earlier, this method would afford freedom from spectral interferences.

The best detection limit was obtained using the batch volatilization method of sample introduction. Data were gathered using a 1-mL sample volume produced a detection limit of 30 pg, about a ten-fold improvement over that by direct nebulization. Larger sample volumes (within reason) would afford even lower detection limits.

Optimum Concentration Range

The linear range for osmium was determined using only the direct nebulization sample introduction method. Presented here are the recommended

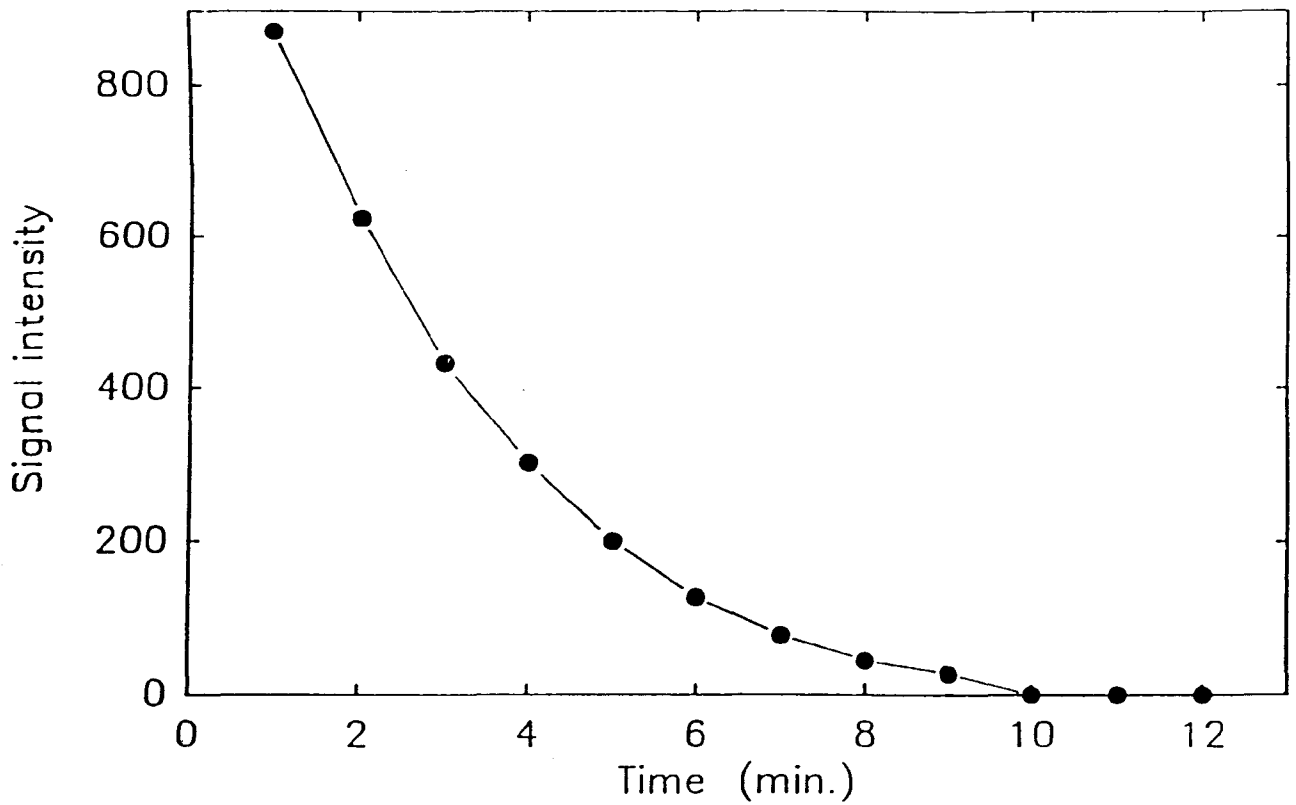

Figure 12. Batch-volatilization ICP-AES purging cycle of 100 ng of osmium injected into H_2SO_4-filled purging cell with the cold trap in the heated condition and the flow rate at 200 mL/min.

TABLE 10. DETECTION LIMITS AND RELATIVE SENSITIVITIES FOR ICP-AES METHODS

Method	Wavelength	Detection Limit (µg/L)	Relative Sensitivity
Direct Nebulization	225.5 nm	0.3	1
	228.2 nm	0.5	0.7
Heated Direct Nebulization	225.5 nm	0.3	2
Heated Continuous Volatilization	225.5 nm	1.4	2
Batch Volatilization	225.5 nm	0.03[a]	320

[a]For 1-mL sample volume.

concentration ranges for the heated direct-nebulization, continuous-heated volatilization, and batch-volatilization sample introduction methods.

Direct Nebulization--

The linear range for this sample introduction method was determined by aspirating a series of standards, and noting any deviation from theoretical concentrations. The standards used ranged from a blank solution to a 20-mg/L osmium standard. The linear range was investigated at both the 225.5-nm and 228.2-nm analytical wavelengths. The results are presented in Figure 13. Data points represent the average result of triplicate measurements of these solutions. As shown in Figure 13A, the increase in the osmium signal at the 225.5-nm line is linear to approximately 20 mg/L. At the 20-mg/L level, the deviation from the theoretical value is 3.8 percent. Similarly, in Figure 13B, one can see that at the 228.2-nm line, the increase in the osmium signal is linear (within 5 percent of the theoretical value) up to 20 mg/L. The deviation at this point was only 2.0 percent. The linear range for osmium at this wavelength probably extends up to 30 mg/L. However, this upper range was not investigated.

Heated Direct Nebulization--

The linear range for osmium was not investigated using this method of sample introduction. However, since the sensitivity of this method is twice that of direct nebulization, a linear range of 10 mg/L might be assumed.

Heated Continuous Volatilization--

The linear range for osmium was not investigated using this method of sample introduction. However, given the sensitivity of the method, a linear range of 10 mg/L might be assumed.

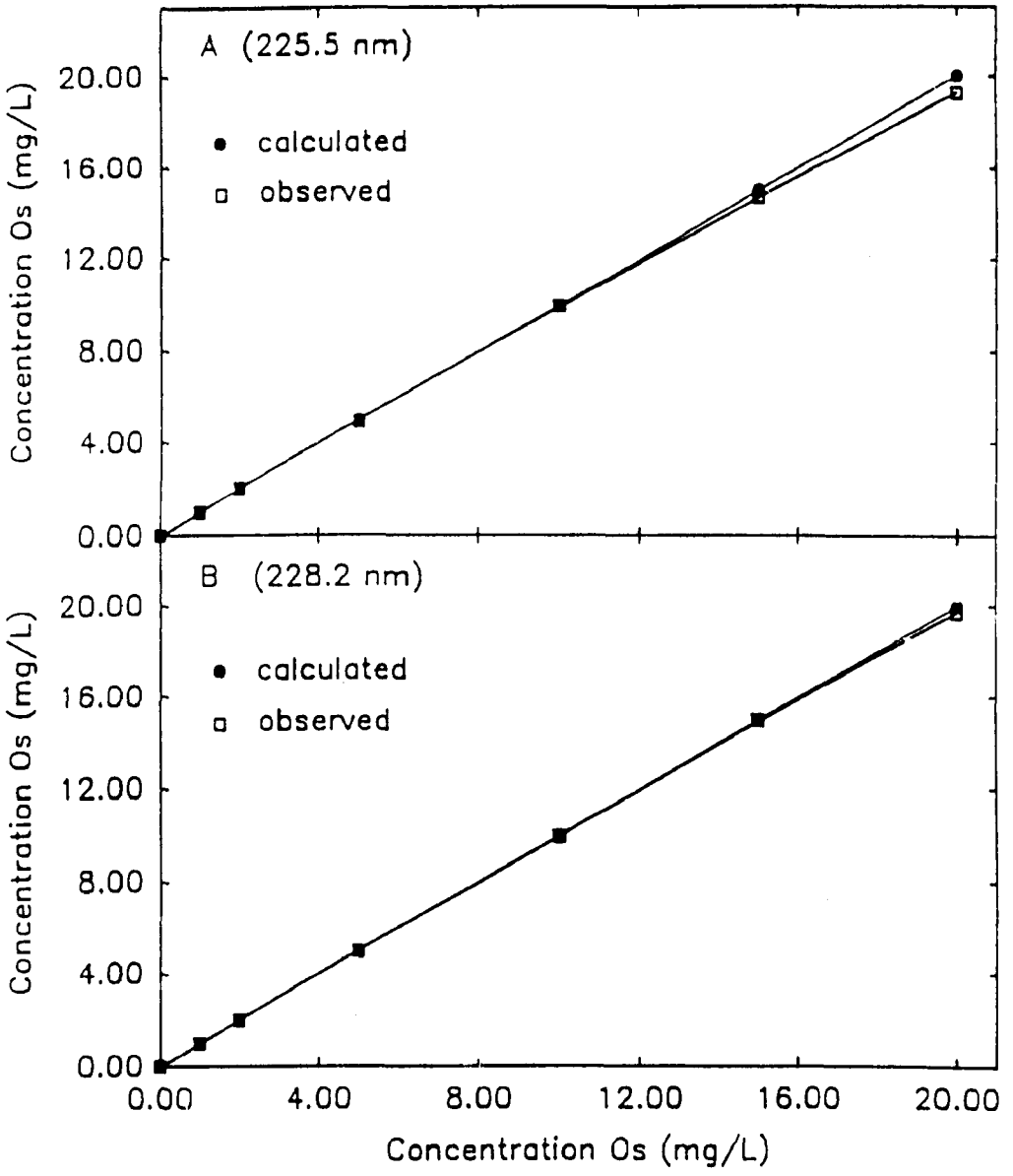

Figure 13. Optimum concentration ranges (linearity) for direct-nebulization ICP-AES of osmium at (A) the 225.5-nm and (B) the 228.2-nm analytical wavelengths.

Batch Volatilization--

The useful range for this method was determined to be from 30 ng/L to 100 µg/L osmium. This is assuming a 1-mL injection volume. Larger sample volumes would allow quantitation at lower concentrations. Samples containing more than 100 µg/L osmium should be analyzed using direct nebulization, which is simpler, faster and possesses a greater linear range.

Spike Recoveries

Two of the target samples (NBS 1633a, Coal Fly Ash, and MESS-1, Marine Sediment) were spiked at the 10-µg/L level and analyzed using the direct-nebulization and batch-volatilization sample introduction methods. A total of three aliquots of each sample were prepared for each matrix using pressure-bomb decomposition. Two of the aliquots were spiked with osmium such that a concentration of 10 µg/L would result in the final volume of 50 mL. The third aliquot was not spiked.

Samples were analyzed using direct nebulization at the 225.5-nm and 228.2-nm wavelengths, and by batch-volatilization at the 225.5-nm wavelength. Analytical results are presented in Table 11.

TABLE 11. RECOVERY RESULTS FOR DIRECT-NEBULIZATION AND BATCH-VOLATILIZATION ICP-AES

	DIRECT NEBULIZATION 225.5 nm (µg/L)	DIRECT NEBULIZATION 228.2 nm (µg/L)	BATCH VOLATILIZATION 225.5 nm (µg/L)
1633A (unspiked)	12.5	<0.5	<0.03
1633A Spike 1	20.4	8.1	7.5
1633A Spike 2	20.4	7.5	8.0
MESS (unspiked)	n/a	0.85	<0.03
MESS Spike 1	n/a	8.2	7.7
MESS Spike 2	n/a	8.0	7.7

The results presented in Table 11 using direct nebulization at 228.8 nm and batch volatilization at 225.5 nm are consistently biased low by about 20 percent relative to the theoretical value of 10 µg/L. This low bias seems to be due to osmium losses during sample preparation through volatilization, rather than due to the analytical method. (See Sample Preparation Methods section.)

Results for the Coal Fly Ash using direct nebulization at 225.5 nm are biased high by approximately 100 percent. A scan of the wavelengths adjacent to, and including, the 225.5-nm wavelength was performed while aspirating the

unspiked Coal Fly Ash digest. The results of this scan are shown in Figure 14. Apparently, there is a spectral interference at the 225.5-nm wavelength, probably caused by the presence of iron (see Interferences, this section). For this reason, the Marine Sediment digest emissions were monitored only at the 228.8-nm wavelength. Analysis of the unspiked Marine Sediment digest by direct nebulization did result in a small positive signal. This is probably the result of minor spectral interferences.

Interferences

Seven elements were investigated to determine if their presence caused spectral interferences at the 225.5-nm and 228.2-nm wavelengths. The direct-nebulization method was used for this interference study. The elements investigated were Al, Ca, Ce, Cr, Fe, Mg, and Na. Cerium was included because it may be used as an oxidant in some sample preparation methods (8). The results of the interference study for the elements listed above are shown in Table 12.

TABLE 12. SPECTRAL INTERFERENCE (APPARENT μg/L OSMIUM) CAUSED BY 1000 mg/L OF TESTED ELEMENTS AT 225.5 nm AND 228.2 nm

Element	Apparent μg/L of Interference	
	225.5 nm	228.2 nm
Al	2	2
Ca	-[a]	-[a]
Ce	-[a]	150
Cr	102 (380)[b]	5
Fe	104 (145)[b]	-[a]
Mg	-[a]	2
Na	-[a]	-[a]

[a]No interference was detected.
[b]Peak of interfering element just slightly off osmium analytical wavelength.

As is apparent in Table 12 and Figures 15 and 16, the interfering effects of iron and chromium are significant. The magnitude of these interferences prohibits the use of the 225.5-nm wavelength for the analysis of soil samples or high-level aqueous samples using the direct-nebulization method. At the 228.2-nm line, only cerium gave a significant positive interference. Therefore, the use of this element as the oxidant in sample preparation is not recommended for direct-nebulization ICP-AES analysis at the 228.2-nm wavelength.

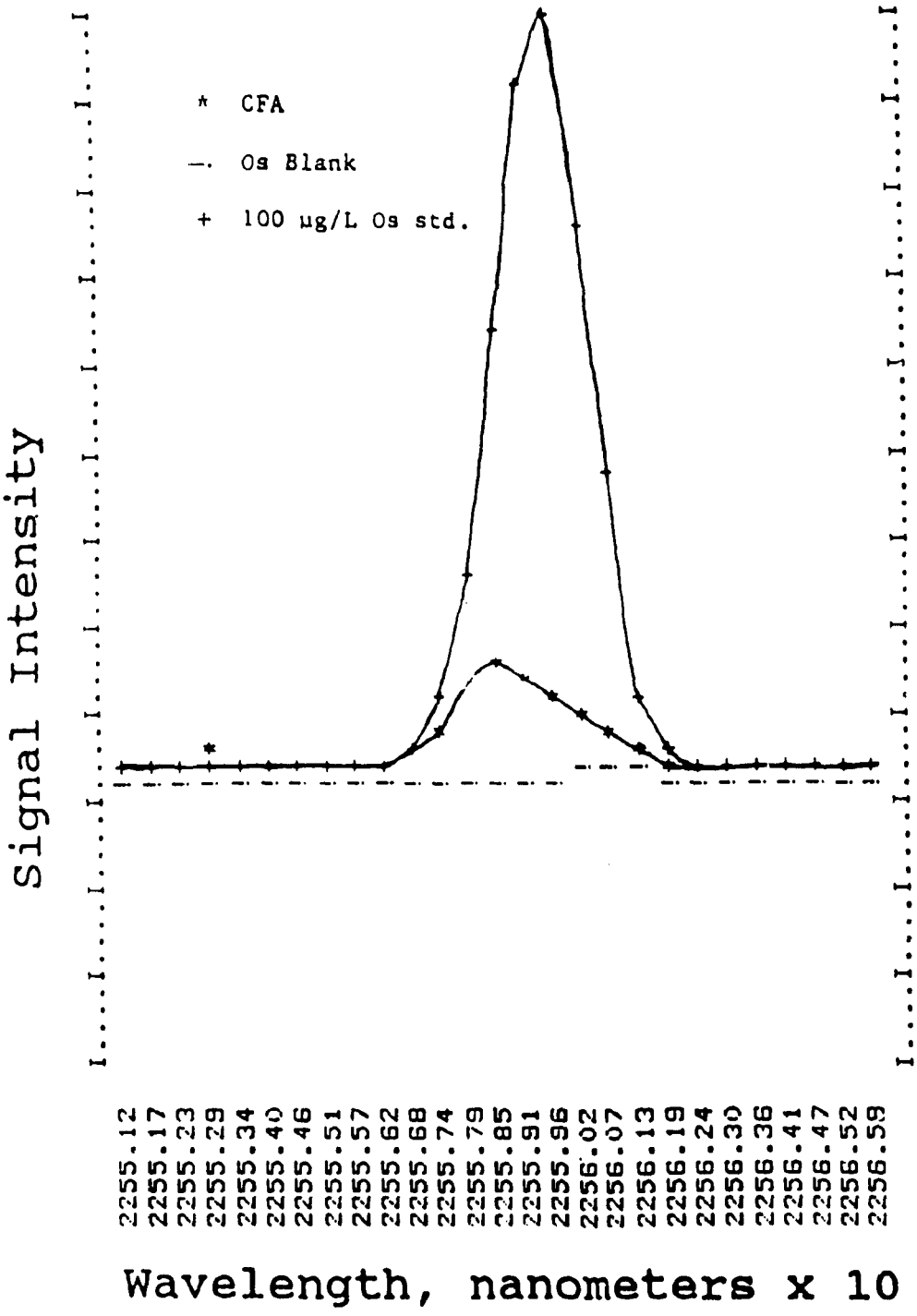

Figure 14. Direct-nebulization ICP-AES of unspiked Coal Fly Ash (CFA), 100 µg/L Os, and Os blank samples at wavelengths adjacent to, and including, the 225.5-nm analytical wavelength for osmium.

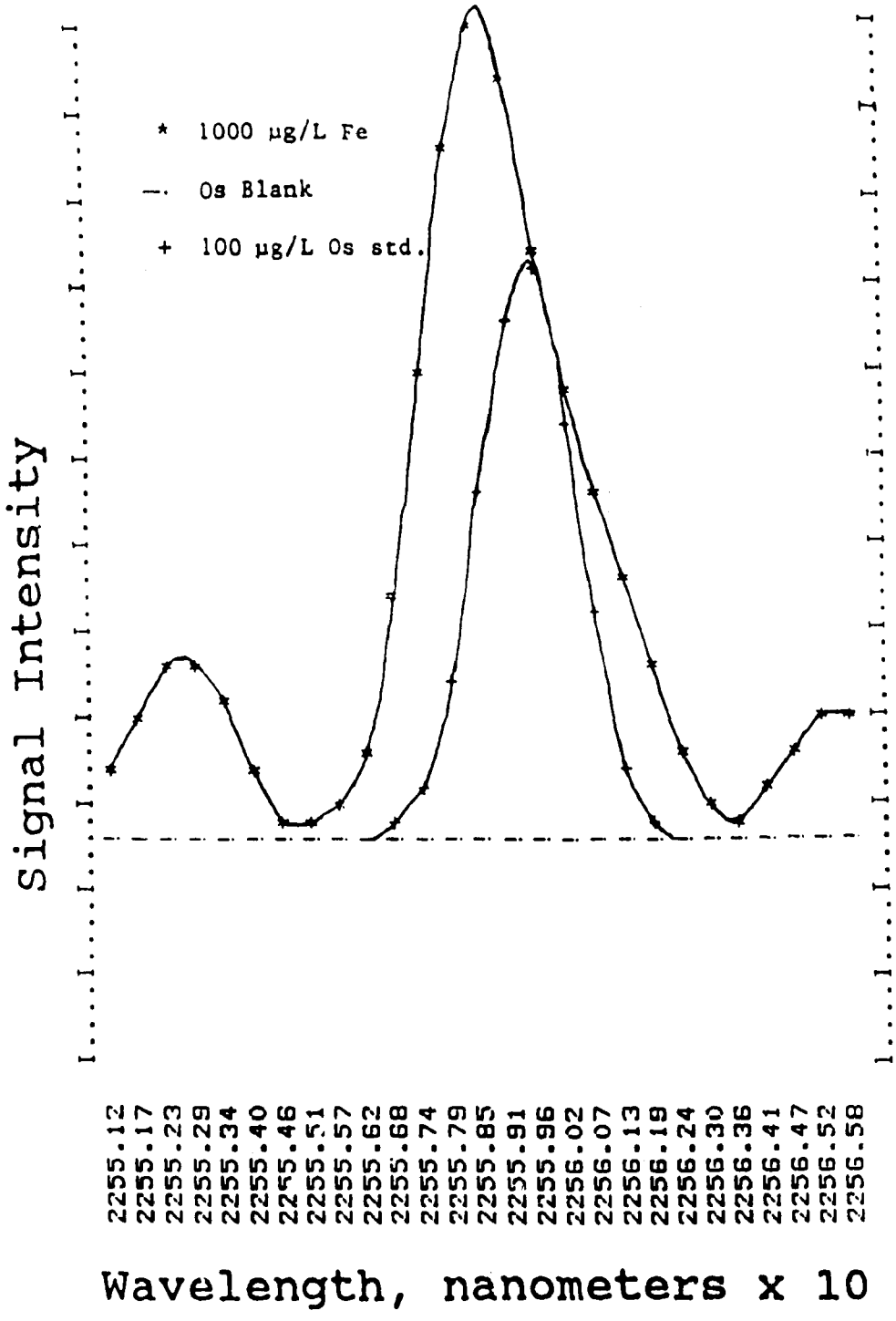

Figure 15. Spectral interference by iron at the osmium 225.5-nm analytical wavelength during direct-nebulization ICP-AES.

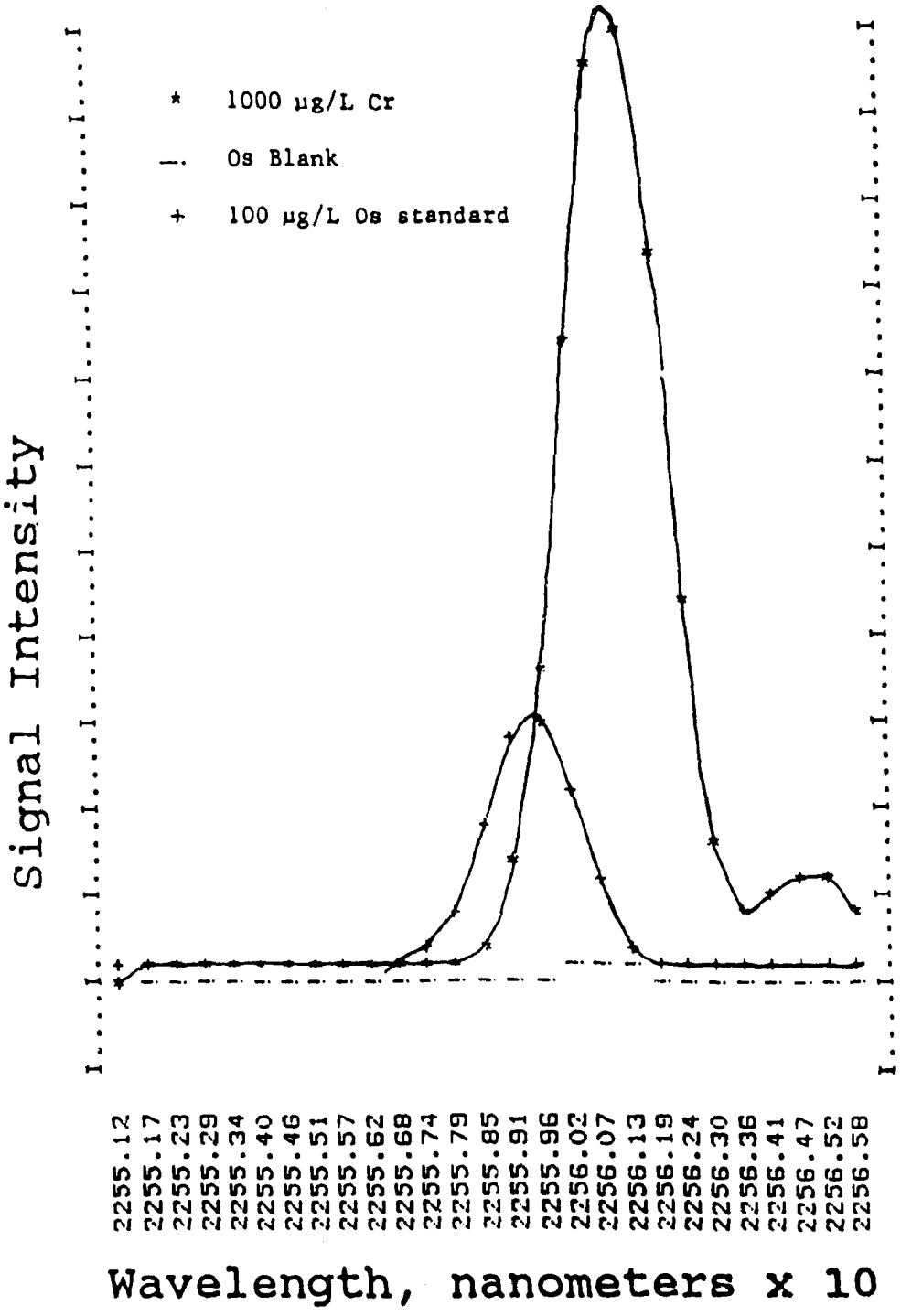

Figure 16. Spectral interference by chromium at the osmium 225.5-nm analytical wavelength during direct-nebulization ICP-AES.

The effects of increasing concentrations of HCl (1 percent (v/v), 3 molar, and 6 molar) on a 1-mg/L osmium standard in a matrix of 1 percent (v/v) each HNO_3 and H_2SO_4 were studied. Figures 17 and 18 show an increasing negative interference with increasing hydrochloric acid concentration relative to a 1-mg/L osmium standard in 1 percent (v/v) each HNO_3 and H_2SO_4 without HCl. This negative interference was the same at both analytical wavelengths. It is possible that hydrochloric acid caused changes in the viscosity or surface tension of the solution such that osmium transport to the plasma was reduced (physical interference). The formation of larger aerosol droplets during nebulization might also be responsible for this result.

SAMPLE PREPARATION METHODS

The results for the four methods of sample preparation investigated are discussed individually below.

Method 7550 Aqueous Sample Preparation

Two aqueous matrices (TCLP extract of soil from a hazardous waste site and Type II water) were spiked with 10 mg/L osmium and digested in duplicate by the procedure given in Method 7550. The average recovery was 71 percent. Flame AAS Method 7550 was used for the determination.

It was not known whether osmium, which might be reduced in solution, would be oxidized by the Method 7550 procedure (1 percent nitric acid, 15 minutes heating). Ascorbic acid (200 mg/L) was used to reduce 1 mg/L osmium in several test solutions. These solutions were digested by the procedure in Method 7550 and analyzed by direct nebulization ICP-AES at the 225.2-nm analytical wavelength. The results showed that osmium remained reduced; no observable signal was detected when the digestion was repeated with 1 mL of H_2SO_4 added prior to, instead of after, heating.

Three strong oxidants, Ce^{+4}, ammonium peroxydisulfate, and 30-percent hydrogen peroxide, were tested to see if they could oxidize the reduced osmium (as well as oxidize the excess ascorbic acid). These reagents were added separately to 100-mL aqueous samples before digestion, along with the nitric acid, at the following levels: 50 mg/L ceric ammonium nitrate; 100 mg/L ammonium peroxidisulfate; and 1 mL 30-percent hydrogen peroxide.

The results of the analysis of these digests showed that both Ce^{+4} and hydrogen peroxide oxidized the reduced osmium at this low level of heating; osmium recovery was 82 percent. Ammonium peroxydisulfate, however, did not fully oxidize the osmium at these temperatures, and the recovery was only 12 percent. It should be noted again that cerium gives a spectral interference in the direct nebulization ICP-AES analysis of osmium at the 228.2-nm wavelength.

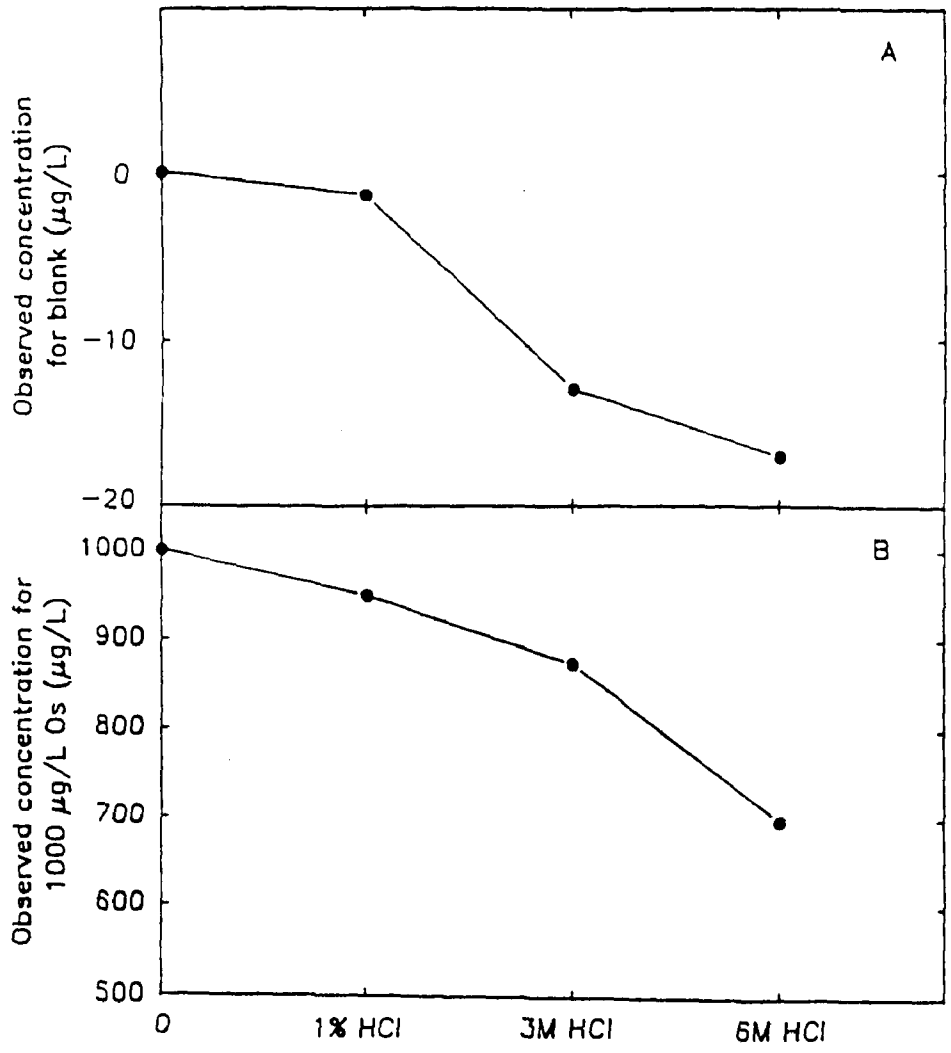

Figure 17. Suppression of 225.5-nm osmium signal in direct-nebulization ICP-AES by HCl.

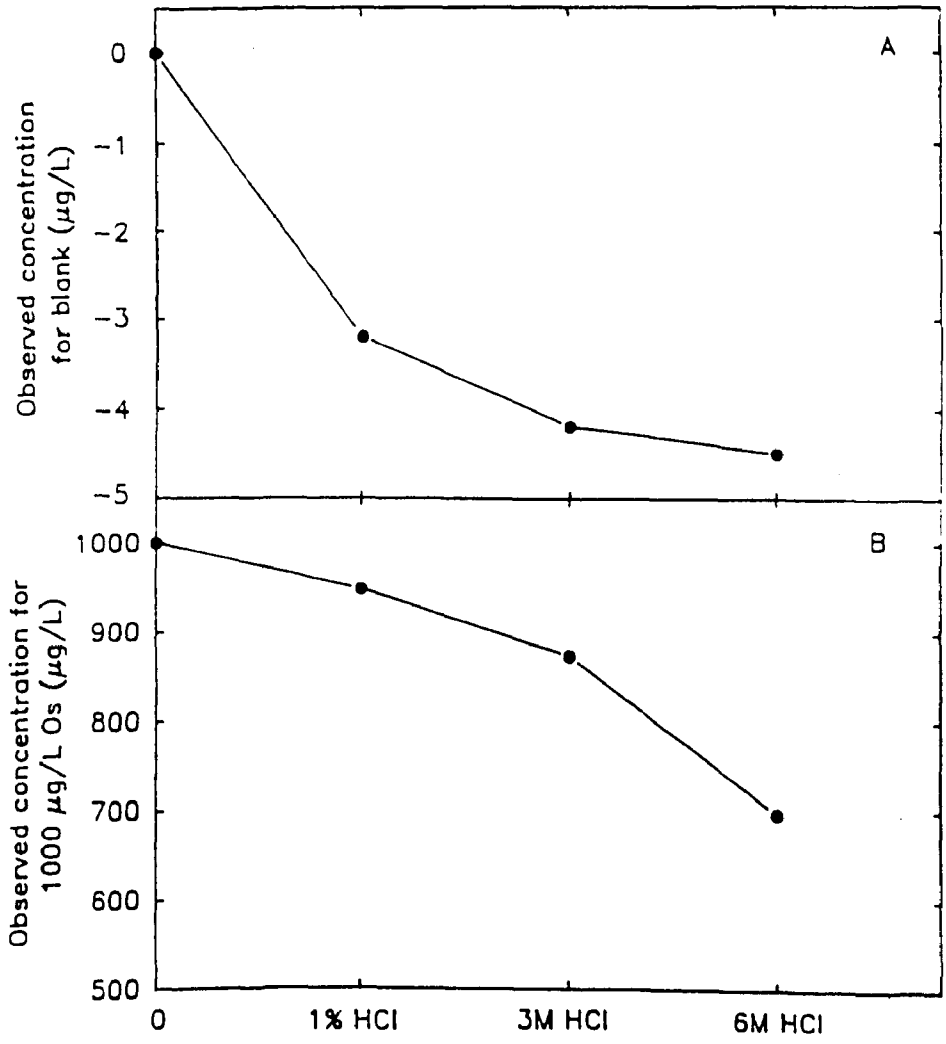

Figure 18. Suppression of 228.2-nm osmium signal in direct-nebulization ICP-AES by HCl.

Method 3050 Solid Sample Preparation

Initial investigation of the Method 3050 digestion procedure for solid samples showed very low spike recoveries (less than 15 percent). A radioactive tracer was used to determine at which steps in the digestion procedure osmium losses were occurring. Radiotracer studies were performed at Scripps Institute of Oceanography. The results of this work are presented in Table 13.

TABLE 13. RETENTION OF RADIOACTIVE ^{185}OSMIUM DURING DIGESTION OF SOLID SAMPLES BY METHOD 3050

Sample	Percent ^{185}Os Remaining After Treatment With:			
	HNO_3[a]	H_2O_2[b]	HCl[c]	Taken to Dryness[d]
LCS (0287)[e]	66±11	53±13	41±6	7±2
1633A[f]	29±5	28±6	27±5	4±2
Municipal[f] Digested Sludge	76±9	60±9	57±10	48±10
MESS-1[f] 14±3		66±10	62±10	55±11
Cu-Ni-Co[f] 5 Reference Ore		58±15	57±15	35±5

[a]After step 7.2.
[b]After step 7.4.
[c]After step 7.5.
[d]Not in procedure. Taken to dryness to determine loss of osmium.
[e]Average of 4 digestions.
[f]Average of 2 runs.

From these results, it is apparent that most of the osmium (>30 percent) is lost, probably through volatilization, during the first step of nitric acid addition. Comparatively little osmium (>13 percent on average) is lost during the subsequent addition of H_2O_2. After the addition of HCl, the amount of osmium lost was very small for some samples, and as much as 22 percent for the Cu-Ni-Co Reference Ore. All samples, with the exception of the Municipal Digested Sludge, lost significant amounts of osmium when taken to dryness. The anomalous results for the Municipal Digested Sludge may perhaps be explained by this sample's very high organic content. Osmium in this digestion might be, in part, reduced by organic matter that has not been

destroyed by the acids and H_2O_2. The consistently low recoveries of osmium for the Coal Fly Ash, NBS-SRM 1633a, might be explained by its relative lack of reduced species. Further investigation is needed to determine whether the above speculations are indeed true.

Sodium Peroxide Fusion Method for Solid Samples

Fusion of 0.5 grams of solid sample with 5 grams sodium peroxide gave good results, with osmium recoveries averaging 80 percent when a solid spiking material was used (Spectromel No. 2 Standard Powder Mixture containing 12.5 percent osmium metal). The recovery was only 20 percent; however, when a dissolved osmium tetrachloride standard was added to the solid sample and then allowed to dry before the fusion.

Pressure-Bomb Method

Initial investigations showed that sample digestion using a pressure bomb yielded good (>85 percent) osmium spike recovery for both liquid and solid samples. Two sets of samples were digested using this method. One set, composed of the nine samples, was spiked with 10 mg/L dissolved osmium chloride, pressure-bomb digested, and analyzed using flame AAS Method 7550. A second set of two sample matrices (Coal Fly Ash, NBS-SRM 1633a and Marine Sediment, MESS-1) was spiked with 10 µg/L osmium, pressure-bomb digested, and analyzed by ICP-AES, using direct nebulization and batch volatilization.

The first set, composed of the nine samples, was prepared in triplicate, spiked prior to digestion with 10 mg/L osmium, and pressure-bomb digested. The results of analysis obtained by Method 7550 are presented in Table 4. As stated previously in Section 2, spike recoveries were good. They ranged from 84 percent to 98 percent, with an average recovery of 91 percent. These sample digests were stored in glass containers and subsequently used in the Concentration-Stability Study, which is discussed below.

The results from the analysis of the second set of samples by ICP-AES methods have been stated previously in the spike-recovery portion of the ICP-AES Methods section heading above.

CONCENTRATION-STABILITY STUDY

The stability of the osmium concentration in pressure-bomb digests of the nine samples was evaluated over a 3-week period. The osmium concentration in each of the solutions was measured twice weekly by using flame AAS Method 7550. As shown in Table 14, osmium remains stable in the sample digests, when stored in glass containers under normal laboratory conditions, for at least 3 weeks; all concentration values stayed within 10 percent of the initial values.

TABLE 14. OSMIUM CONCENTRATION (mg/L) BY FLAME AAS OVER A 3-WEEK PERIOD IN DIGESTS OF THE 9 MATRICES

Matrix	Day						
	0	4	7	11	14	18	21
	(measured as mg/L)						
Trace Elements in Water	9.61	9.80	9.79	9.41	9.56	9.71	9.95
Osmium Standard Solution	9.35	9.31	9.37	8.90	9.19	9.34	9.42
Synthetic Interference Solution	9.83	9.17	9.66	9.52	[a]	9.80	9.80
TCLP Extract of Hazardous Waste	9.56	8.85	9.28	9.22	[a]	9.38	9.62
Coal Fly Ash	9.35	8.87	8.51	8.65	8.97	8.81	8.76
Municipal Digested Sludge	8.35	8.63	8.35	8.45	8.40	8.84	8.32
Marine Sediment	8.81	8.99	8.93	8.97	8.63	8.78	8.65
Laboratory Control Sample	8.49	9.33	9.08	8.87	8.36	8.69	8.97
Hazardous Waste Site Soil	8.62	8.92	8.21	8.42	8.10	8.57	8.46

[a]Not determined.

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APPENDIX

RECOMMENDED CHANGES TO METHOD 7550

METHOD 7550

It is recommended that the existing Method 7550 be revised as follows:

2.0 SUMMARY OF METHOD

2.1 Replace this section with:

Prior to analysis by Method 7550, samples must be prepared for direct aspiration. All sample types (aqueous, sludge, oils, greases and waxes) should be digested by the pressure-bomb digestion procedure discussed in this method.

3.0 INTERFERENCES

A new section, 3.5, should be created. It should state the following:

3.5 Samples that contain high concentrations of chromium will exhibit a positive interference.

5.0 REAGENTS

5.4 The matrix of the standard solutions should be changed from "1% (v/v) HNO_3 and 1% (v/v) H_2SO_4" to "4% (v/v) HNO_3 and 4% (v/v) H_2SO_4."

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.2 This section states that plastic and glass containers are suitable. This should be changed to:

Teflon bottles should be avoided because of absorption of osmium.

7.0 PROCEDURE

7.1 and 7.2 These sections should be completely rewritten as follows:

7.1 Sample preparation: All samples should be digested according to the bomb digestion method described herein. The bomb vessel size for the following procedure is 23 mL. As the bomb vessel size increases, the sample and reagent portions may also be increased

accordingly. Follow all manufacturer's directions on the proper use and assembly of the bomb.

7.2 Pressure-Bomb Digestion of Samples

7.2.1 For aqueous samples, transfer a 10-mL aliquot of the well-mixed sample to the bomb vessel. For sludges, oils, greases, or waxes, weigh out 0.100 g of the sample and transfer to the bomb vessel.

7.2.2 For aqueous samples, add 2 mL HNO_3 to the bomb vessel and close properly. For solid samples, add 2 mL HNO_3 to the bomb vessel and close properly.

7.2.3 Place bombs with aqueous samples in a muffle furnace at 150° C for 2 hours. Place bombs with solid samples in a muffle furnace at 50° C for 4 hours.

7.2.4 After the bombs have been allowed to cool, carefully transfer the entire contents of each into a 50-mL volumetric flask. Do not filter the solutions. Add 2 mL H_2SO_4 and bring to volume with deionized water.

7.3 This section states that a wavelength of "290.0-nm" should be used. This wavelength is incorrect. The wavelength should be changed to "290.9-nm".