



Project Summary

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, optimum concentration ranges (linearity), spike recoveries, interferences, precision, accuracy, and recommended operating parameters are presented and discussed.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Osmium is a metal, the tetroxide of which is considered toxic to man and other biota and is included on the hazardous substances list for the Resource Conservation and Recovery Act. A single-laboratory study was undertaken to determine the performance

of the atomic absorption, direct-aspiration method for osmium (Method 7550, SW-846) and, secondarily, 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. Included in the investigation was an evaluation of sample preparation and introduction procedures and a study of the stability of osmium concentrations in the sample digests as these factors might affect osmium method performance. The major components of the study are shown in Table 1

Sample-introduction methods compared include direct nebulization, heated direct nebulization, continuous nebulization, heated continuous volatilization and batch volatilization. Method 7550 contains an aqueous sample-preparation method and references Method 3050 for preparation of solid samples. The other two sample preparation methods investigated were a sodium peroxide fusion method and a pressure-bomb digestion method. Details for all these methods are included in the Project Report.

Overall method performance parameters reported include:

- Detection limits
- Optimum Concentration Ranges (Linearity)
- Spike Recoveries
- Interferences
- Precision
- Accuracy
- Ruggedness

Table 1. Study Components^a

Instrument	Sample-Preparation Method	Sample-Introduction Method
Flame AAS	7550 (SW-846)	DN
Flame AAS	3050 (SW-846)	DN
Flame AAS	PB	DN
Flame AAS	Fusion	DN
Furnace AAS ^b	b	b
ICP-AES	PB	DN
ICP-AES	PB	HVN
ICP-AES	PB	CN
ICP-AES	PB	HCV
ICP-AES	PB	BV

^aPB is pressure-bomb digestion, DN is direct nebulization, HVN is heated direct nebulization, CN is continuous nebulization, HCV is heated continuous volatilization and BV is batch volatilization.

^bTesting discontinued when use of radioactive ¹⁸⁵osmium revealed incomplete recovery.

Procedure

Performance characteristics of the methods were determined using 9 types of samples (4 liquid and 5 solid) that included standard reference materials from U.S. and Canadian agencies and a hazardous waste site soil sample; all were well-characterized matrices. Instrument detection limits and optimum concentration ranges were determined with interference-free aqueous standards. The stability of osmium concentrations in digests of the spiked samples was monitored twice a week for three weeks.

Seven elements, Al, Ca, Cr, Fe, Mg, Na and V, were tested individually with Method 7550 to determine if they interfered (caused significant suppression or enhancement) with the osmium signal. Precision was determined from 5 consecutive 4-second readings at each concentration.

The furnace AAS method was studied with radioactive ¹⁸⁵Os to determine the fate of osmium during the analysis. These radiochemical studies were carried out at the Scripps Institute of Oceanography; gamma emissions at 646 KeV and 875 KeV were used to monitor yields.

Five different sample-introduction methods (as listed above) were investigated with ICP-AES to determine the benefits for osmium determinations. The first of these methods was conventional direct nebulization. The other four methods required some modification of the sample-introduction hardware. The

plasma torch, spectrometer and computer hardware were not altered for any of the methods.

Results and Discussion

Method 7550

The average instrumental detection limit obtained for osmium by AAS Method 7550 was 0.3 mg/L. The average method detection limit across all nine sample matrices was also 0.3 mg/L. The optimum concentration range in an interference-free matrix extended from 0.9 mg/L to at least 100 mg/L. Precision (%RSD) of the method ranged from 0.7 to 2.6 across the sample types with an average of 1.5 percent. Method accuracy, determined by assessing predigestion spike recoveries for the nine matrices, ranged from 84 percent to 98 percent with an average of 91 percent recovery. The seven elements listed above were examined as possible interferents in the determination of osmium by AAS Method 7550; of the seven elements tested only three had any effects with calcium and vanadium depressing the osmium signal and chromium enhancing the osmium signal. In general, the method was found to be accurate, precise and relatively insensitive to the presence of other elements in the sample matrices.

Furnace AAS Method

Method performance parameters could not be obtained using furnace AAS

because the osmium absorption signals were not reproducible. The results from the use of the radioactive tracer suggested that the osmium salt converted to the metal or a refractory carbide in the graphite furnace during charring and atomization cycles. The maximum furnace temperature (3000 K) is not high enough to volatilize and recover all of the osmium within a useful time frame.

ICP-AES Methods

The instrumental detection limits obtained for ICP-AES were 0.3 µg/L for both the direct-nebulization and heated direct-nebulization sample introduction techniques, 1.4 µg/L with heated continuous volatilization, and (for 1-mL injection) 0.03 µg/L for batch volatilization. The optimum concentration range with direct nebulization extended from 0.001 mg/L to at least 20 mg/L at the measurement wavelengths of 225.5 nm and 228.2 nm. With heated direct nebulization and heated continuous volatilization the range extended from 0.001 and 0.004 mg/L respectively, to an upper limit of more than 10 mg/L for both. Batch volatilization yielded (based on a 1-mL injection) an optimum range from 0.09 µg/L to 10 µg/L. Precision (as %RSD) for ICP-AES methods was less than 0.5 with direct nebulization, heated direct nebulization and heated continuous volatilization; it was 6 percent with batch volatilization.

Method accuracy for ICP-AES direct nebulization and batch-volatilization

methods were determined by assessing pre-digestion spike recoveries for two different sample matrices. Note that this estimate of the method accuracy (recovery) includes any loss of osmium during the sample preparation using the pressure-bomb digestion method. With direct nebulization the recovery data were biased high by approximately 100 percent. One possible explanation is spectral interference from an iron emission line on the 225.5-nm wavelength used to measure osmium. Both iron and chromium were found to contribute significant spectral interference at the 225.5-nm wavelength. When the 228.2-nm wavelength was used, more realistic values of 80 percent recovery were obtained. With batch volatilization the recovery obtained was 77 percent. Cerium, used as an oxidant in sample preparation, contributes to the osmium signal at 228.2 nm. However, this latter emission line is free of other major interferences, and it is only 30 percent less sensitive than the 225.2-nm wavelength.

Sample Preparation

Osmium spike recovery obtained using the sample-preparation procedure in Method 7550 was 71 percent on average. Digestion Method 3050 for soil sample preparation was also unsatisfactory; less than 50 percent of the radiotracer was recovered. The sodium peroxide fusion method yielded spike recoveries typically

around 80 percent and was considered adequate for solid samples if the spikes were made with osmium metal. When spikes of dissolved osmium (as the tetrachloride) were allowed to air dry prior to fusion, recoveries fell to 20 percent. The pressure-bomb digestion method was found to give recoveries ranging from 84 to 98 percent (average 91 percent) across the sample matrices.

Stability of Osmium Concentrations

Digests of the nine matrices spiked with 10 mg/L osmium (as the tetrachloride) were found to be stable in osmium concentration for at least a 3 week period.

Conclusions and Recommendations

Results of this single-laboratory study show that flame atomic absorption spectroscopy (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. AAS Method 7550 should be revised to show that the analytical wavelength is 290.9 nm and not 290.0 nm. Conventional 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 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 ¹⁸⁵osmium, 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 and is described in detail in the Project Report. The Appendix to the Project 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 interferences because these non-volatilize components do not reach the plasma with this technique.

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Thomas A. Hinnners is the EPA Project Officer (see below).

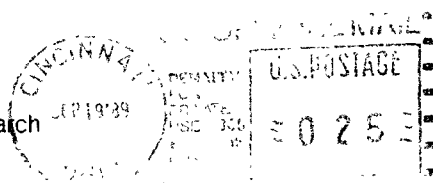
The complete report, entitled "A Single-Laboratory Evaluation of Osmium Analytical Methods," (Order No. PB 89-224 893/AS; Cost: \$15.95, subject to change) will be available only from:

National Technical Information Service
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