

A UNIVERSAL DIGESTION METHOD FOR THE DETERMINATION OF SELENIUM

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Abstract: Hydride generation atomic absorption spectroscopy (HGAAS) is a precise, accurate, and extremely sensitive method for the determination of selenium. Since Se^{+4} is the only oxidation state that forms a hydride, it is imperative that all other forms of selenium in solution are converted to Se^{+4} prior to analysis by HGAAS. Although this is usually accomplished by heating with hydrochloric acid (HCl), numerous methods have been developed to overcome problems associated with incomplete analyte recovery because of excessive or incomplete heating of samples during the reduction. Most researchers overcome this problem using carefully timed heating procedures. This, however, has led to the proliferation of numerous and confusing methods for accomplishing the simple conversion of Se^{+6} to Se^{+4} . The entire operation can be simplified using closed containers. With closed tubes, extended heating of up to 1 hour and greater is allowable, and numerous methods, one for each sample type, can be reduced to a single procedure.

A series of experiments was performed to demonstrate the efficacy of closed-tube digestion for selenium determination by HGAAS. The use of capped tubes is extremely important to avoid the loss of selenium because of the formation of volatile selenium chloride and other possible selenium species in the presence of the strong HCl used for reduction. The method, along with data from capped-tube digestions using extended heating periods, is presented in a series of experiments leading to the development of this procedure.

Additional Key Words: Selenium, Hydride, Digestion.

Introduction

Although numerous methods are available to select from for the determination of selenium in environmental samples, the choice for most labs is hydride generation with atomic absorption (AA), atomic emission (AE), or atomic fluorescence (AF) for detection. Our lab has chosen hydride generation with atomic absorption measurement after thermally decomposing the hydride in an electrically heated quartz cell. The hydride is generated using a Varian VGA-76 vapor generation accessory (Rothery, 1984) The use and operation of hydride generation accessories, both flow injection and continuous, is an accepted practice in the determination of selenium at low concentrations. As with many techniques, a weak link in the procedure is the sample preparation. In the use of hydride generation, several primary considerations must be addressed prior to analysis:

- Samples must be homogeneous and in a condition usable in digestion procedures. This may entail grinding, splitting of the sample, and drying and, with environmental samples, often the removal of extraneous material, such as plastic, or other items not normally associated with the material being tested.
- Selenium present in the sample must be released from the matrix being studied, and if speciation is not a consideration, the analyte should be in solution in an ionic form.
- For hydride generation, the selenium must be present as Se^{+4} . This is commonly achieved by heating the sample in strong hydrochloric acid for a time and at a temperature sufficient for the conversion from other valence states to Se^{+4} . This paper will address this step.

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For the most part, specific sample preparation methods are specified for various sample types in the literature. There are reasons for this, and often individual researchers, because of the variability of materials being tested, developed guidelines for their particular samples based on finding a reduction method that provided the level of accuracy and precision required. For a lab performing analyses on numerous diverse samples, the problem of digestion methods sometimes comes down to a different variation for each sample type based on published methods for comparable materials.

It has been suggested that the proliferation of methods results from overlooking that sample solutions have redox properties because of the reagents used for digestion of the original sample (Piwonka et. al., 1985). The presence of other reagents makes it necessary to consider the redox properties of the solution throughout the dissolution process (Bye and Lund, 1995).

Because of the controversy and confusing numbers of methods, we decided to select one set of conditions from published literature and develop a single application that could be used for all of the samples normally encountered in our laboratory, including, but not limited to, coal, coal ash, soils, sediments and other geologic materials, liquid fuels, biological materials, and water.

Experimental

Based on the literature, we decided to use a final concentration of hydrochloric acid of 50%. Although there were examples where higher and lower concentrations were successful in achieving the reduction, it appears that 50% is most commonly used. It was also decided that capped tubes would be used at a digestion temperature of 95°C. This temperature was selected as a safe limit to avoid boiling in order to prevent excess pressure from building up during the digestion cycle. An initial experiment was performed to assess the potential for loss from overdigestion using long time intervals.

Ten-mL aliquots of a known concentration (50 µg/L) of selenium, prepared from a stock standard of Se⁺⁶ in dilute nitric acid, were pipetted into a series of digestion tubes, and 0.5 mL of saturated potassium permanganate (KMnO₄) solution was added. For most environmental samples, it is necessary to have an oxidation step to destroy humic materials which forces all of the selenium to Se⁺⁶. The tubes were vortexed, capped, and heated at 95°C for 25 minutes. To minimize pressure at temperature, the tubes were left with the caps loose for a few minutes at the beginning of the heating to allow for expansion of air. After the tubes became warm, the caps were tightened for the duration of the heating period. This procedure for heating of sealed tubes was always followed, in each heating cycle, for safety. After they cooled to room temperature, 0.25 mL of 20% (w/v) hydroxylamine sulfate was added to each tube to reduce excess KMnO₄. In the experiment, 10 mL of concentrated hydrochloric acid (HCl) was added to each tube. The tubes were vortexed and heated at 95°C for several different heating periods. The heating periods chosen were 20 minutes, 1 hour, 2 hours, and 5 hours. Six replicates of each heating period were analyzed by hydride generation AA using a Varian VGA-76 hydride generation accessory, with sodium borohydride as the reductant. The hydride was thermally decomposed to elemental selenium by an electrically heated quartz cell.

Results and Discussion

The experiment showed that analyte is not lost after extended heating periods of up to 5 hours using capped digestion tubes. Table 1 shows the analyte recovery for each heating period.

The advent of flow injection analysis (FIA) and the more common use of closed-vessel and on-line closed-system microwave digestion methods may make the use of a reduction step unnecessary in the sample preparation steps prior to analysis. FIA methods generally incorporate a hydrochloric acid addition step prior to the addition of reagent for producing hydride. Since these systems are essentially sealed, loss of analyte by volatilization is, for the most part, irrelevant. In the use of closed-vessel microwave digestion procedures, a sealed system is available for reduction of Se⁺⁶ to Se⁺⁴. Additionally, it has been suggested that with the proper

Table 1. Results of analyte recovery using extended heating periods, %.

	20 minutes	1 hour	2 hours	5 hours
	49.5	50.8	50.2	50.2
	49.8	50.4	49.7	49.9
	51.0	51.5	50.6	51.0
	50.0	50.5	51.8	50.5
	49.5	50.8	50.1	49.6
	47.9	51.2	49.8	50.0
Average, µg/L	49.6	50.9	50.4	50.2
% Recovery	99	102	101	100
% RSD	1.9	0.8	1.4	0.9

acid digestion mixture, prereduction may not be required. Nast and Jacob (1987) reported that selenium is present only as Se^{+4} during digestion under pressure with HNO_3 (32.5%) at a temperature of more than 230°C. Therefore, an extensive prereduction may not always be necessary.

Conclusions

The development of this simple and versatile method for prereduction of Se^{+6} to Se^{+4} has allowed our laboratory to produce accurate and precise selenium data by hydride generation for a diverse range of sample types for over 5 years. The use of a sealed-tube system allows the use of high concentrations of HCl at subboiling temperatures (95°–98°C) for extended periods of time, thus assuring complete reduction while preventing loss of analyte. The use of subboiling temperatures prevents pressure buildup and, when used properly, is a safe and efficient alternative to multiple prereduction methods for varying sample types.

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