100-ppb concentration range in a continuous fashion can be achieved using the FPD detector and the calibration/monitoring procedure developed and tested in this work.

With the exception of SO_2, the sulfur gases studied can be successfully separated and quantitated in the low ppb concentration range by the use of a cold trap, followed by GC analysis with a specially treated Porapak QS column and an FPD detector.

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Concentration and Determination of Selenium from Environmental Samples

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Radiotracers were used to evaluate a variety of procedures for concentrating selenium for its determination with the heated graphite atomizer (HGA) atomic absorption technique. The concentration procedures studied included extraction, internal electrolysis, coprecipitation, and hydride generation. Although hydride generation using sodium borohydride was chosen as the best method for concentrating and introducing samples into the HGA, the data in this report indicate that published procedures may liberate as little as 10% of the total inorganic selenium from the solution. Optimization of the hydride generation step as well as the other steps necessary for the determination of selenium resulted in a procedure which is sensitive, straightforward, and free from interference.

The importance of selenium as a toxin and carcinogen has been well documented (*1, 2*). The natural abundance as well as the wide use of selenium or its compounds in manufacturing and industrial applications necessitate effective methods for measuring this element, especially at trace levels.

Although numerous methods have been developed for the determination of selenium, no thorough examination has been made of the concentration steps necessary for its determination at the low levels occurring in environmental samples. Adequate studies of possible interferences are also lacking, particularly in the case of recent methods based on the selective volatilization of selenium as its hydride. This study establishes the optimum conditions for the generation of the hydride and its subsequent injection into a heated graphite atomizer. Additionally, several other approaches, both traditional and new procedures for concentrating selenium, have been critically examined. All work was done with the aid of a radioactive selenium tracer.

The selenium hydride results are particularly enlightening due to the fact that they invalidate the popular belief that published procedures for the generation of the hydride are nearly 100% efficient. The ability of selenium to form a hydride has been used for some time to increase the selectivity and sensitivity of its determination. The hydride generation has often been coupled with atomic absorption techniques using flame atomization (*3–6*). Recent innovations have included generation of the hydride with sodium borohydride or aluminum (*7*) in strongly acidic media coupled with the flameless atomizers for increased sensitivity (*5*). Unfortunately little work has been done on the measurement of the efficiency of the generation of the selenium hydride and its transfer to the atomizer. The data obtained from the radiotracer investigations indicate that the efficient generation of the volatile hydride with sodium borohydride and subsequent injection of the sample into the HGA can be accomplished only by the careful selection of several parameters, such as acidity and mechanical design of the apparatus. The data indicate that as little as 10% of the selenium is injected into the HGA by published procedures while the present procedure is about 90% efficient. No interference was noted with the 39 possible interfering species tested.

EXPERIMENTAL

Instrumentation. The Perkin-Elmer HGA 2000 graphite furnace was used with a Perkin-Elmer model 403 atomic absorption spectrophotometer. Nitrogen was used as the inert gas. A demountable hollow cathode lamp from a design by Wolcott (*8*), was used as a light source. Its energy output was 10 times that of conventional hollow cathodes and it proved to have a substantially longer life. It was operated at 50 mA with helium as the filler gas. An electrodeless discharge lamp or a commercial demountable hollow cathode would probably have worked equally well. A Heathkit power supply model PS-4 was used to power the lamp through a 2000-Ω variable resistor. Measurement of radioactivity was done using a scintillation counter with a well-type sodium iodide crystal, a Harrison high voltage power supply and a Canberra model 895 timer and scaler.

Apparatus. The reactor shown in Figure 1 was used for efficient reduction of selenium and volatilization of the resultant hydride when solutions of sodium borohydride were used as the reducing agent. The bubbler frit was of fine porosity (25–50 mm pore size) and the drying tube was 1.9 × 15 cm long. The trap consisted of 6-mm o.d. glass tubing bent into a U and each leg was filled to 13 cm with 3-mm diameter glass beads. It was immersed in liquid nitrogen to a depth slightly higher than the level of the glass beads.

Reagents. All reagents were reagent grade and high quality deionized water was used throughout. The sodium borohydride was obtained as a powder (No. 87658 Aldrich Chemical Co., Inc., Milwaukee, Wis.) except where comparisons were made to published procedures which used alternate reagents. Solutions of sodium borohydride were made immediately prior to use. The radioactive ^{75}Se tracer was obtained from New England Nuclear, Boston, Mass. A selenium stock solution was made by dissolving elemental selenium in a minimum amount of nitric acid. Further dilutions were made when necessary. The calcium chloride and Drierite were 8–16 mesh.

Tracer Procedure. Radioactive selenium added to samples containing 1 μg of selenium was used throughout to determine the efficiency of the various concentration techniques tested. Mass balances were made when possible. Gaseous selenium hydride was absorbed in sodium hydroxide to obtain mass balances when studying the hydride generation procedures. Solids such as copper wire, zinc residue after reaction, and the desiccants were counted for ^{75}Se and included in the mass balance.

Recommended Procedure. A 50-ml sample, after being brought to 4.0 N with respect to hydrochloric acid, containing 0.005–2.0 μg of selenium was placed in the reactor (Figure 1). Twenty-five ml of sodium borohydride solution containing 1.00 g of sodium borohydride were placed in the separatory funnel. Ten g of calcium chloride were placed in the drying tube. The cold trap was placed in liquid nitrogen and allowed to cool for 1 min. After positioning the four-way valve so that the gas would pass through the trap and be vented to a hood, the sodium borohydride solution was slowly added to the sample over a period of 3 min. The system was purged with nitrogen 1 min prior to the sodium borohydride addition and continued to 1 min after the addition of the reagent. The four-way valve was then turned so that the cold trap was by-passed and the connections were changed to by-pass the reactor and drying tube. After connecting the gas flow to the atomizer, the cold trap was warmed at room temperature for 15 s and then at 80 °C in a water bath for 30 s. The instrument was then zeroed, the atomizer heated to the correct temperature, and a baseline was recorded. The four-way valve was then opened so that the hydride was swept into the atomizer and the absorbance was recorded. A microgram of selenium was found to give a response of approximately 0.4 absorbance unit.

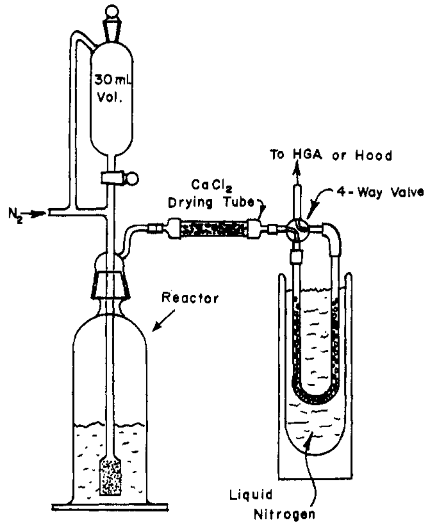

Figure 1. Apparatus to generate, dry, and collect selenium hydride

RESULTS AND DISCUSSION

Although a variety of methods have been reported in the literature for concentrating selenium only those reported in Table I were considered promising enough for further investigation. Recoveries were evaluated using radioactive ^{75}Se. As can be seen from these data, the most promising concentration procedures were the generation of selenium hydride with sodium borohydride and the reduction of selenium on copper wire, i.e., internal electrolysis on copper. Although internal electrolysis was somewhat less efficient than hydride generation, it was rejected primarily because of the mechanical difficulty involved in placing the sample in commercial furnace atomizers. The technique could probably be applied effectively if hollow-T atomizers such as the one developed by Robinson and Wolcott (*9*) were used.

The data demonstrated the need for improvement in hydride generation techniques. It was particularly interesting to note that acid plus zinc produced little selenium hydride. Instead, approximately 88% remained as unreacted material or sludge. Procedures using sodium borohydride (*3–5*) yielded higher recoveries. However, as these studies show, the recoveries were far from optimum. Because radiochemical tracer techniques were not used in the previous studies, experimental evaluations were limited to intuitive judgments. The use of borohydride was sufficiently promising that a detailed investigation using tracer techniques was undertaken to optimize the generation of the hydride. The drying and trapping operations necessary for efficient concentration and injection of the selenium into atomizers such as the HGA were an integral part of the studies.

The use of a liquid nitrogen trap for collection of the selenium hydride was deemed necessary for two basic reasons. First, the trap allowed the hydride to be revolatilized and injected into the HGA in a pulse, producing an increase in apparent sensitivity. Second, the trap removed the selenium hydride from the hydrogen that was generated by the decomposition of the sodium borohydride. The elimination of hydrogen from the input gas stream to the HGA minimized noise levels and prevented damage to the HGA that otherwise resulted from ignition of hydrogen at exhaust ports.

Conditions necessary for maximizing selenium hydride generation required a study of the amount of sodium borohydride to be used and the concentration of acid required. Naturally the mechanical design of the hydride generation