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Automated Determination of Total Selenium in Rocks, Soils, and Plants

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INTRODUCTION

With increased interest in the study of selenium for environmental and geochemical investigations, an analytical method for the determination of total selenium has been developed. Automated continuous-flow hydride generation coupled with atomic absorption spectrometry has been applied to the determination of selenium. The method is applicable to a variety of materials including rocks, soils and plants.

A survey of the literature shows several methods have been published describing selenium hydride generation. The proposed method is a combination of methods of Pierce et al. (1976), Goulden and Brooksbank (1974), and Pyen and Fishman (1978) with a few modifications. The modifications include streamlining the manifold system and stripping column, the acidification of the sample stream with 8F hydrochloric acid and the digestion procedure.

EXPERIMENTAL

Reagents

1. Deionized water was used throughout this study. All chemicals were reagent-grade or better.
2. 8F hydrochloric acid solution was prepared from concentrated 12F HCL.
3. 0.5%(w/v) sodium borohydride solution was made by dissolving 5.0 g $NaBH_4$ and 40 g NaOH in 1 L water.
4. Selenium standard solutions. A commercially prepared 1000 µg mL^{-1} selenium atomic absorption standard was used to make serial dilutions of the working standards of 0.01, 0.05 and 0.1 µg mL^{-1} in 10% hydrochloric acid (v/v).

Apparatus

The equipment used for the described method include a Perkin-Elmer* model 306 atomic absorption spectrometer, a Perkin-Elmer model 056 strip chart recorder, a Gilson Mini-Pulse 2, eight-channel peristaltic pump with standard Tygon pump tubing, and a Technicon Auto Analyzer II sampler. The probe on the autosampler was changed from the stainless steel probe to a plastic probe to withstand the high acid concentrations. The stripping column and resistively-heated quartz tube furnace were custom made for the laboratory by Rocky Mountain Scientific Glass Blowing, Arvada, Colorado, and have been previously described in Crock and Lichte (1982) and are shown in figures 1 and 2. The quartz tube furnace is resistively heated and maintained at 850° C with a variable transformer. Instrumental parameters associated with the spectrometer are summarized in table 1.

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*The use of trade and company names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

Sample Preparation

Three digestion methods are described to cover the wide range of sample materials. The digestion for total Se in rocks and soils (Crock and Lichte 1982) is described below.

Method A.

The digestion method for rocks and soils high in organic carbon content (over 5% approximately) is as follows:

1. Weigh 1.000 g of -80 mesh material into a 250-ml Erlenmeyer flask. Slowly add 20 mL of 16F nitric acid, 10 mL of 18F sulfuric acid, and 5 mL of 12F perchloric acid. All acids are of the "Suitable-For-Mercury-Determination" grade. Add several boiling chips.
2. Cover with a watch glass and place on a steam bath overnight.
3. Place the flask on a hotplate and keep covered with a watch glass for the first 2 h of the digestion. Slowly (taking at least 6 h) raise the temperature of the sample until dense, white fumes of sulfuric acid begin to evolve and continue heating for at least 20 min, but not to dryness.
4. Remove from hotplate and cool. Add 10 mL 12F hydrochloric acid, transfer to a 100-mL volumetric flask, and bring to volume with deionized water.

Method B.

The digestion method for rocks and soils low in organic carbon content (less than 5% approximately) or high in silica is as follows:

1. Weigh 1.000 g of -100 mesh material into a teflon 100-mL beaker. Add 10 mL of 16F nitric acid, cover with a teflon lid, and heat on a steam bath for one hour. Remove lid and evaporate to dryness.
2. Cool and add 10mL 16F nitric acid, 12 mL of 18F sulfuric acid, 5 mL 12F perchloric acid, and 10 mL of 48% hydrofluoric acid. Cover with a teflon

lid and heat on a steam bath for 2 h. Remove the lids and heat until the hydrofluoric acid has evaporated.

3. Place on hotplate and slowly heat the solution until dense, white fumes of sulfuric acid begin to evolve. Continue heating for at least 20 min, but not to dryness.

4. Treat the solution as in step 4 of the previous procedure.

The digestion of plants for total Se is more tedious than soils or rocks due to the large amount of organic matter that must be destroyed. The addition of hydrogen peroxide is used to destroy the organic matter.

Method C.

The digestion method for plants is as follows:

1. Weigh 2.000 g of the dry, raw plant material previously ground in a Wiley mill to -80 mesh into a 250-mL glass Erlenmeyer flask. Add 20 mL 16F nitric acid and swirl the contents to mix.
2. Cover the flask with a watch glass or refluxing claw (available from G. Frederick Smith, Columbus, Ohio) and heat gently on a hotplate preset at 100° C. Allow the brown nitric fumes to escape before adding dropwise 30% hydrogen peroxide until a clear solution is attained. Usually 10 mL hydrogen peroxide is sufficient to destroy the organic material.
3. Cool the solution and remove the watch glass or claw head. Add 1 mL 18F sulfuric acid and slowly evaporate to dense, white fumes of sulfuric acid.
4. Cool and add 20 mL of 6F hydrochloric acid. Cover with a watch glass and heat on a steam table for one hour.
5. Cool, filter, and transfer solution to a 50-mL volumetric flask. Analyze solution for total Se by hydride generation atomic absorption spectrometry.

Procedure

The selenium hydride manifold is shown in figure 3. The heated quartz tube furnace must be conditioned prior to analyzing samples. Condition the cell by running samples of the 0.1 µg mL^{-1} Se standard (usually about five samples) until a stable peak height is attained. Since the method requires a standard-additions technique, the unknown sample must be spiked with a given amount of Se. Pipette 5.0 mL of the unknown sample into a glass disposable tube. Spike the sample with 50 µL of 5.0 µg mL^{-1} Se standard giving an effective Se solution of 0.05 µg mL^{-1}. Load the auto-sampler carousel by alternating the unspiked sample followed by its spiked aliquot. Set the instrumental parameters according to Table 1. The absorbance peak heights are measured and Se content determined. There is a small Se blank in the sulfuric acid which must be subtracted from all samples and spiked samples. The calculation of total Se uses the following equation:

$$\frac{a}{b-a} \times (\text{spike concentration } \mu g\ mL^{-1}) \times (\text{dilution factor}) = \text{Se } \mu g\ mL^{-1}$$

a = blank subtracted sample peak height.
b = blank subtracted spiked sample peak height.

dilution factor = mL final volume g^{-1} sample

RESULTS AND DISCUSSION

Optimization and Interferences

The method described was optimized for ease of operation and maximum signal output. The Se signal was optimized by controlling the flow rate of the sample stream, streamlining the manifold system, and interference reduction.

The signal is maximized by maintaining the flow rate of the sample stream at 4.5 mL min^{-1}. A 0.05 µg mL^{-1} Se standard was used during the flow rate experiment. By decreasing the pump speed by 50 percent (i.e., from 1000 pump speed units to 500 pump speed units) and proportionally increasing the sample uptake tubing size to deliver 4.5 mL min^{-1}, the Se signal doubled. The increased signal response is due to a slower flow rate of selenium hydride through the sample stream and a longer residence time in the heated quartz tube furnace.

The manifold where the reagents join and mix, and the stripping column, have been streamlined. The Se manifold of Pyen and Fishman (1978) or Pierce et al. (1976), had either several feet of heated mixing coils or a heated, glass-packed stripping column. Their Se manifold and stripping column were tested for our procedure. However, during the optimization experiments the heated mixing coils and the heated, glass-packed stripping column were either changed or eliminated. The present manifold has a short 40-turn mixing coil and a stripping column with no glass packing. The streamlining of the manifold has reduced memory effects from one sample to the next and decreased the analysis time.

Several researchers (Brown et al. (1981), Kirkbright and Taddia (1978), and Vijan and Leung (1980)), have made suggestions for eliminating or reducing interferences from Fe, Cu, and Ni on the determination of Se by hydride generation. After experimenting with several reagents such as oxalic acid, ethylene diamine tetraacetic acid, hydroxalamine hydrochloride, hexamine, and hydrochloric acid, the results were less than encouraging. Only hydrochloric acid was effective in reducing the interferences by the formation of stable chloro-complexes with these transition metals.

Table 2 shows a comparison of the percent interference effect (i.e., percent loss of signal) Fe, Cu, and Ni have on a .05 μg mL^{-1} Se solution with and without the addition of the 8F hydrochloric acid to the sample stream. As can be seen from table 2, the hydrochloric acid was effective in reducing the interference from Cu and Ni and Fe. Beyond this, no further attempts were made to eliminate the interferences.

Interference studies on selenium hydride have been published by Thompson, et al. (1978), and Pierce and Brown (1977). Elements previously found to interfere by other researchers were investigated using our method by testing their effect on a 0.05 μg mL^{-1} Se solution. Table 3 lists the elements tested. Table 4 lists those elements that were found to have significant effects on the Se signal. Only signal depressions were observed.

The analysis of total Se in geologic materials, soils and plants, As, Sb, Cu, Sn and Ni are commonly encountered in concentrations that potentially could interfere significantly. Therefore, the use of a standard-additions procedure is recommended for the routine selenium hydride analysis. The assumption of the standard-additions procedure is that the effect of the interference is the same for the spiked sample as is for the unspiked sample.

The final parameter in the optimization of the procedure was to test the three listed digestions for total Se recovery. Each digestion procedure was tested for Se recovery of five digested 0.05 μg mL^{-1} Se aqueous solutions and five spiked geologic or plant standards.

There was 99-100% recovery of the Se in both the digested Se aqueous solutions and the spiked andesite rock standard using the digestion method for rocks and soils low in organic carbon and or high in silicon. The recovery for the digested Se aqueous solutions and the spiked coal standard range from 98-100% using the digestion for rocks and soils high in organic carbon. The digestion method for plant material gave 99-100% recovery of the aqueous solutions and spiked orchard leaves standard.

Detection Limits, Precision and Accuracy

With the instrument and manifold setup as outlined in table 1 and figure 3, typical strip chart recorder tracings are shown in figure 4. An instrumental detection limit of 0.000 1 µg mL^{-1} that was determined using a signal to noise ratio of two as the lower limit. The practical detection limit depends on the degree of contamination from reagents. Contamination is minimized by using acids of the "Suitable-For-Mercury-Determination" grade, however, the unavoidable Se blank from the sulfuric acid determines the limit of detection. The detection limit as determined by two times the standard deviation of blanks carried through the entire analytical procedure, using digestion methods A and B was 0.001 µg mL^{-1}. The detection limit determined in the same manner as before except using the plant digestion method was 0.0004 µg mL^{-1}. The plant digestion detection is lower because less sulfuric acid is used.

An estimate of precision was based on analyzing National Bureau of Standards coal 1635 ten times. The relative standard deviation was 2.6%. An indication of the accuracy of the proposed method is given in table 5. The results show good agreement when compared to the literature values. Table 6 is also included to compare the proposed method results with those from a fluorometric method (Ward, 1975).

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Table 1.--Instrumental parameters for the spectrophotometer and strip-chart recorder.

Parameters	Selenium
Wavelength (nm)	196.0
Slit (nm)	0.7
Background correction	Not used
Damping	4 (Maximum)
Mode	Absorbance
Lamp	Electrodeless discharge
Lamp setting	6 W
Strip chart recorder	10 mV full scale response, 5 mm min^{-1} chart speed

Table 2.--Percent interference from Fe, Cu, and Ni with and without 8F hydrochloric acid added to sample stream on 0.05 µg mL^{-1} selenium standard solution.

Element	Percent Interference without HCL	Percent Interference with HCL
Fe - 1000 ppm	65	0
Cu - 50 ppm	44	22
Ni - 10 ppm	30	10

Table 3.--Elements tested for interference on 0.05 μg mL^{-1} selenium standard solution.

Element	Concentration tested
Al	500 ppm
V	100 ppm
Mn	50 ppm
Zn	100 ppm
U	100 ppm
Fe	2000 ppm
Mo	10 ppm
Ce	10 ppm
Co	10 ppm
Cr	50 ppm
Cu	50 ppm
Ni	10 ppm
As	1 ppm
Sb	1 ppm
Sn	5 ppm

Table 4.--Elements most likely to interfere with Se determination, percent loss of signal for indicated concentration and the threshold concentrations where no interference occured. Selenium concentration is 0.05 µg ml^{-1}.

Element	Percent Interference	Threshold concentration where no interference occurred
As - 1 ppm	19	As - 0.5 ppm
Cu - 50 ppm	22	Cu - 20 ppm
Ni - 10 ppm	10	Ni - 5 ppm
Sb - 1 ppm	17	Sb - 0.5 ppm
Sn - 5 ppm	10	Sn - 2 ppm

Table 5.--Selenium content of standard reference materials.

Standard	Se content[a] this study ($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$) Reported	Method of Digestion	Reference
S01 Canadian soil	0.1	0.087	B	1
S02 Canadian soil	0.4	0.44	B	1
S03 Canadian soil	<0.1	0.03	B	1
S04 Canadian soil	0.6	0.55	B	1
NBS 1571 orchard leaves	0.08	0.08	C	2
NBS 1635 Coal	1.0	0.9	A	2
SGR-1 Green River shale	3.4	3.5	A	1
AGV-1 Andesite	<0.1	.01	B	3
GSP-1 Granodiorite	<0.1	.073	B	3

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1) Gladney and Knab (1981).

2) National Bureau of Standards certified value.

3) Erzinger and Purchelt (1980).

a. Mean of 3 samples analyzed 2 times

Table 6.--Comparison of selenium content in various plant materials.

Plant	Se content this study ($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$) Fluorometric method
Slender wheat grass	0.23	0.20
Slender wheat grass	0.08	0.08
Intermediate wheat grass	0.08	0.06
Alfalfa wheat grass	0.42	0.35
Alfalfa wheat grass	0.20	0.30

Figure 1. The resistively heated quartz furnace used in the determination of selenium by hydride generation.

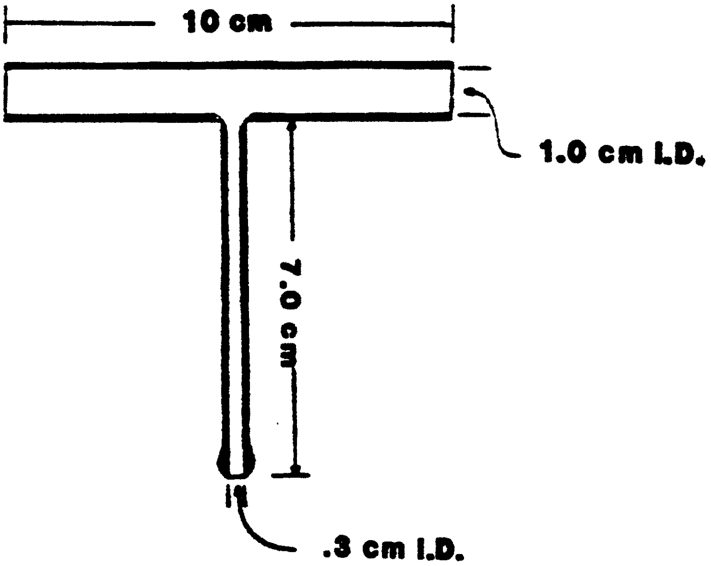

Figure 2. The modified stripping column used for the phase separation in the determination of selenium by hydride generation.

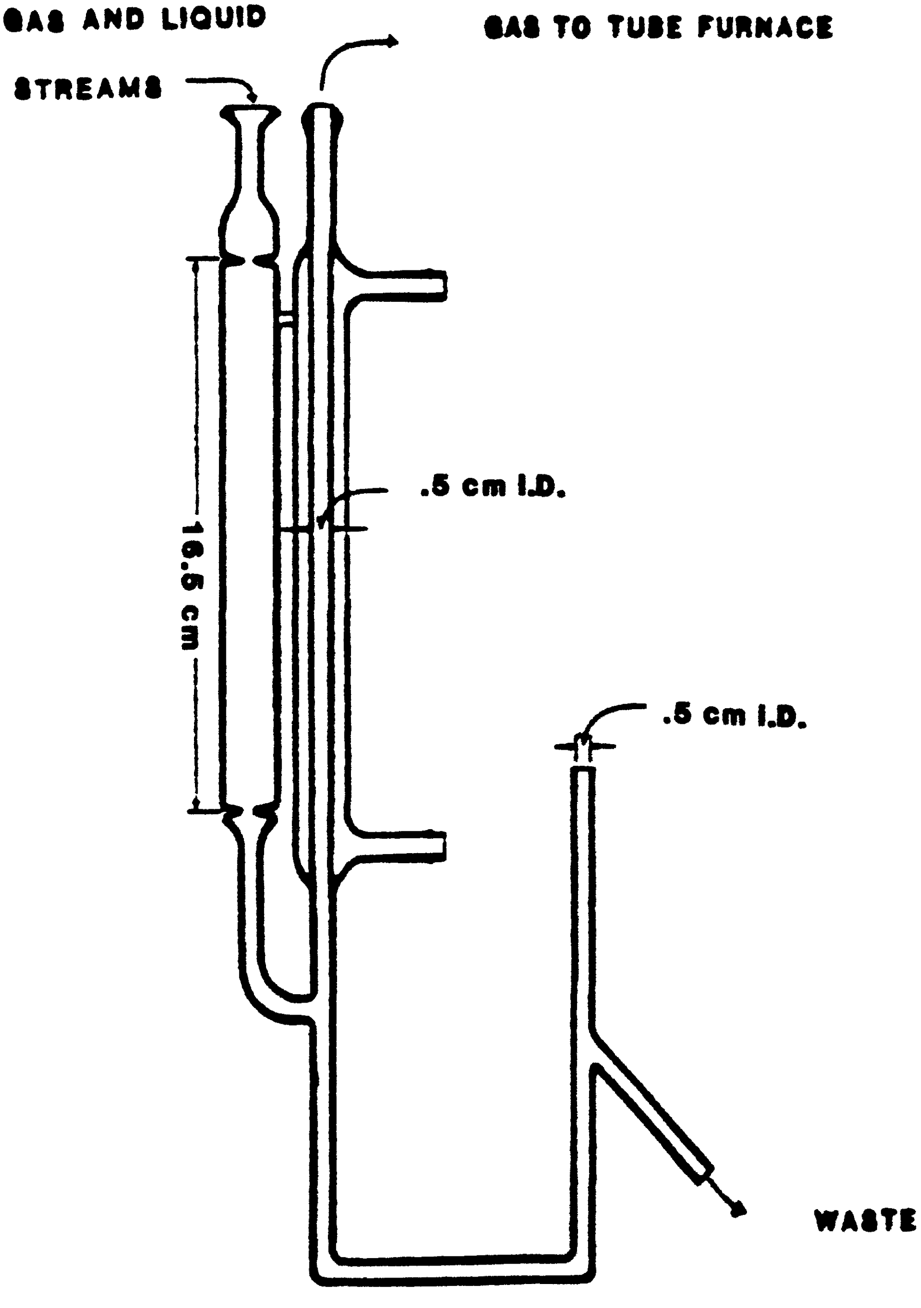

Figure 3. The analytical manifold for the generation of selenium hydride by contineous flow generation.

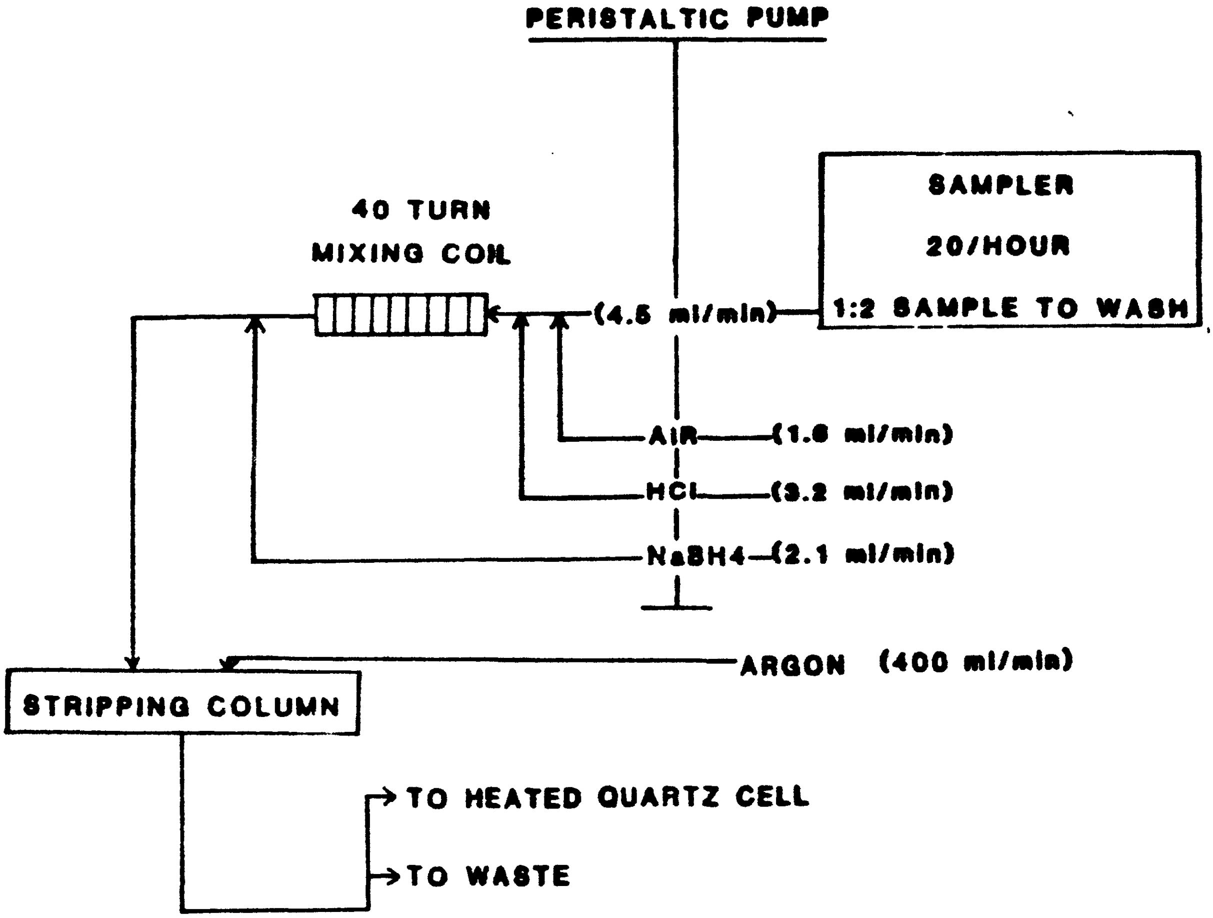

Figure 4. The typical strip chart tracings for standard selenium solutions.