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Determination of Selenium by Hydride Generation Ultraviolet - Visible Molecular Absorption Spectrometry With Diode-array Detection

Jesús Sanz,* Félix Gallarta and Javier Galbán
Analytical Chemistry Department, University College of La Rioja, University of Zaragoza, Logroño, Spain
Juan R. Castillo
Analytical Chemistry Department, Faculty of Sciences, University of Zaragoza, Zaragoza, Spain

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A method for the determination of selenium is described that involves hydrogen selenide generation by reduction with sodium tetrahydroborate(III) and subsequent transfer, using nitrogen as carrier gas, into a flow cell placed in a UV - visible molecular absorption spectrometer with diode-array detection. Quantitative determination is performed at 220 nm, taking 8 s for total hydride generation and measurement. The time required for two determinations is 30 s. The limit of detection obtained was 1.8 μg of Se^{IV} in a sample volume of 2 ml and the calibration graph is linear from 10 to 150 μg of selenium in a sample of the same volume. The method has been applied to the determination of selenium in a health-care product.

Keywords: *Selenium hydride generation; UV - visible molecular absorption spectrometry; diode-array detection; health-care product*

The generation of volatile covalent hydrides has been used widely during recent years for the determination of elements that form such hydrides. The method of volatile hydride generation has two major advantages: (i) pre-concentration of the analyte, which results in an increase in the sensitivity; and (ii) selective separation of the analyte from other matrix components, which enables most interferences to be avoided. The generated hydride must be stable enough to be transported to the measuring instrument, the stability depending on the physical and chemical properties of each hydride and also on the conditions used for its generation.

Because of the importance of this technique, many papers have been published that report improvements to the generation conditions, sensitivity, detection limit and detection systems. Atomic absorption spectrometry is the most widely used technique in which hydride generation is employed.[1–6]

UV - visible molecular absorption spectrometry has also been used to determine generated hydride that has been carried into a solution containing a spectrometric reagent which complexes with the hydride-forming element. Arsenic,[7] antimony[8] and bismuth[9] have been determined in this way using silver diethyldithiocarbamate and tin[10] has been determined using phenylfluorone.

Gas-phase molecular absorption spectrometry (GPMAS), an expression first proposed by Cresser and Isaacson,[11] was pioneered by Syty[12] who determined sulphur dioxide, using this method, in 1973. Originally, gas determination was carried out at a fixed wavelength (provided by a strong radiation lamp) using an atomic absorption spectrometer from which the atomisation device had been removed. Syty and co-workers determined several inorganic ions after the generation of volatile compounds such as SO_2,[12] I_2 and Br_2,[13] H_2S,[14] NOCl[15] and HCN[16]; Cresser and Isaacson measured NO_2,[11] Cresser, NH_3[17] and Pleskai, NO.[18]

Other papers have reported the analysis of stored gases by performing a wavelength scan and obtaining a molecular absorption spectrum that offers both qualitative and quantitative information. Significant papers include those by Saturday[19] who determined UF_6 and PuF_6, by Koga *et al.*[20] who determined NO, SO_2, AsH_3 and PH_3, and by Rezchikov *et al.*[21] who performed the determination of volatile covalent hydrides of boron, nitrogen, phosphorus, arsenic, antimony, silicon, germanium and tin, mixed with an excess of inert gas.

The advantages of GPMAS compared with AAS can be summarised as follows: (i) information about the absorbent molecule can be obtained; (ii) simultaneous determination of several generated analytes can be performed; (iii) interferences, such as those due to the atomisation step, do not appear during the measurement process; (iv) a single radiation source is sufficient for determining all the elements; and (v) the measurement step does not destroy the absorbent molecule.

In this paper, a method is proposed for the determination of selenium by GPMAS following volatile hydride generation. The generated hydrogen selenide is carried by nitrogen into the flow cell, which is placed in a UV - visible molecular absorption spectrometer equipped with a diode-array detector. This apparatus is capable of measuring an absorption spectrum from 190 to 820 nm in a very short period of time (0.1 s) and it is possible to obtain a second spectrum after another 0.1 s.[22] The method was applied to the determination of selenium in a health-care product (a shampoo for the treatment of dandruff).

Experimental

Apparatus

All measurements were performed with an HP 8451 diode-array spectrometer equipped with an HP 98155A keyboard, an HP 9121 disk drive for bulk data storage and an HP 7475A graphics plotter.

A Hellma 174QS flow cell (path length 1 cm) was used and three-dimensional and contour-line plots were obtained using a Hewlett-Packard Vectra microprocessor with Golden Graphics System software.

Reagents

All chemicals used were of analytical-reagent grade or better and doubly distilled water was used throughout.

Standard selenium solution, 1000 mg l^{-1}. Extra-pure selenium metal (Merck) (1 g) was dissolved in the minimum volume of 60% *m/V* nitric acid and the solution evaporated nearly to dryness. Doubly distilled water (2 ml) was added and the solution evaporated nearly to dryness (this was repeated

* To whom correspondence should be addressed.

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twice). The residue was subsequently diluted to 1 l with 10% *V/V* hydrochloric acid. Working standards were prepared by serial dilution of the stock solution with doubly distilled water just prior to use.

Sodium tetrahydroborate(III) (Merck) solution, 7.5 g l^{-1}. This solution was prepared immediately prior to use and replaced after 30 min.

Concentrated hydrochloric acid, 1.19 g ml^{-1}, 35% *m/V*. Working standards were prepared by dilution of the concentrated acid with doubly distilled water immediately prior to use.

Concentrated sulphuric acid, 1.84 g ml^{-1}, 96% *m/V*.

Hydrogen peroxide solution, 30% *m/V*.

Results and Discussion

Hydride Generation and Measurement

Initially, the most effective generation vessel to use was determined. The experimental conditions were kept constant and several generation designs were tried, all of which had a threaded neck: a 25-ml round-bottomed flask, a 15-ml test-tube and 15- and 25-ml Erlenmeyer flasks. The best results were obtained with the 15-ml threaded-neck Erlenmeyer flask (Fig. 1); therefore all measurements of hydrogen selenide were performed using this simple generation system. A silicone-rubber septum, fixed by a screw-on cap, was hermetically coupled to the vessel mouth.

The septum was pierced with three stainless-steel hypodermic needles (Fig. 1): 1, for introducing the carrier gas; 2, for injection of the reducing agent; and 3, the widest (1.5 mm i.d.), for the exit of the generated hydride and the carrier gas. This last needle was connected by a silicone-rubber tube to a flux cuvette placed in the spectrometer cell chamber.

Hydrogen selenide molecular absorption spectra were obtained for the range 190–300 nm using the BASIC program given in Table 1. Line 50 enables a spectrum to be obtained every 0.2 s for 8 s, which is long enough for the hydride absorbance to fall nearly to zero. Spectra obtained at different intervals are shown in Fig. 2. The maximum absorbance of hydrogen selenide appears at 220 nm. As no displacements of maxima were observed when the generation conditions were changed, this wavelength (220 nm) was used throughout for the determination of selenium.

Fig. 3(*a*) is a three-dimensional plot of absorbance against time and wavelength. A graphical representation of the variation of the absorbance at 220 nm with time [Fig. 3(*b*)] was obtained using the BASIC program given in Table 2. Peak height and peak area were also obtained using this program and these quantitative determination parameters were used throughout this work.

The different parameters affecting the generation and hence the subsequent determination of hydrogen selenide, such as acidity of the medium, carrier-gas flow, concentration and volume of the sodium tetrahydroborate(III) (the reducing agent) solution and total volume of the sample solution, were studied to achieve the optimum values.

Hydrochloric and nitric acids at various concentrations were used both separately and as mixtures in order to achieve optimum acidity of the medium and to obtain quantitative reduction of selenium using sodium tetrahydroborate(III) solution. Using hydrochloric or nitric acid concentrations greater than 0.4 M a signal with a long tail was produced owing to inefficient transport of the hydride into the cuvette. This was caused by the large volume of gas that formed during the generation reaction. Fig. 4 shows the variation of peak height with hydrochloric and nitric acid concentration and Fig. 5 shows the variation of the maximum absorbance of the peak with the hydrochloric to nitric acid concentration ratio (the total acid concentration was maintained constant at 0.25 M). The optimum results were obtained with 0.25 M hydrochloric acid.

Fig. 6 shows the influence of the nitrogen flow-rate (nitrogen acting as the carrier gas) on a plot of absorbance at 220 nm against time. Flow-rates of nitrogen of less than 300 ml min^{-1} produced a signal which was both wide and poorly defined (Fig. 6, A and B), giving poor reproducibility of the

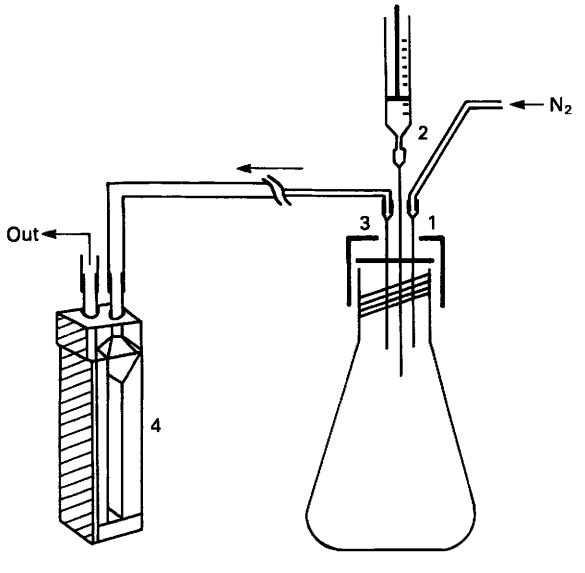

Fig. 1. Device for hydrogen selenide generation. 1, Hypodermic needle for nitrogen flow; 2, hypodermic needle for $NaBH_4$ injection; 3, hypodermic needle for exit of hydride; and 4, flow cell

Table 1. BASIC program used to obtain molecular absorption spectra of hydrogen selenide

```
 10 LAMBDA 190 TO 300
 20 MODE 0, 1
 30 ERASE STANDARD
 40 ABSORBANCE
 50 MEASURE 0.1, 0.2, 0, 8
 60     REM*Obtaining hydrogen selenide spectra*
 70       FOR I = 1 TO 40
 80       IF NMEAS <I THEN 80
 90       TO STANDARD I
100      NEXT I
110 END
120     REM*Plot of spectra on screen. Necessary to type
        RUN 120*
130       OVERLAY 190, 300, 0, 0.025
140       FOR I = 1 TO 40
150       RECALL STANDARD I
160       PLOTTER
170       NEXT I
180 END
```

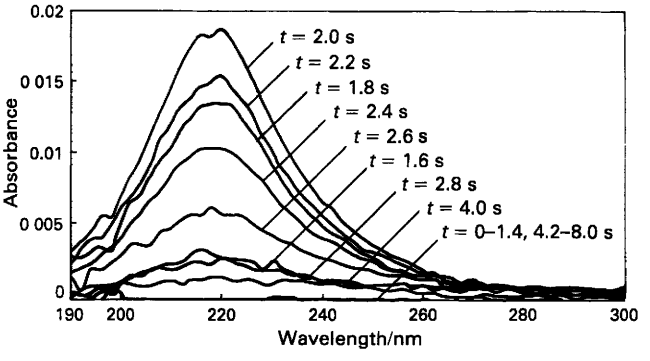

Fig. 2. Hydrogen selenide molecular absorption spectra obtained at different times after injection of reducing agent

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absorbance value. Nitrogen flow-rates in the range 300–600 ml min^{-1} produced a well defined peak (Fig. 6, C). Using nitrogen flow-rates greater than 600 ml min^{-1} (Fig. 6, D), lower peak-height and smaller peak-area values were obtained owing to hydride dilution in the nitrogen flow. When a nitrogen flow-rate of 525 ml min^{-1} was used the best signal resolution and a satisfactory value of the maximum absorbance were obtained.

Aqueous sodium tetrahydroborate(III) solution was used to generate the hydrogen selenide. As the efficiency of hydride generation depends simultaneously on the concentration and the volume of the reducing-agent solution, a combined study of these two variables was performed using different sodium tetrahydroborate(III) concentrations (2.5, 5.0, 7.5, 10, 12.5, 15, 20 and 30 g l^{-1}) and various injected volumes (0.5, 1.0, 1.5, 2.0, 2.5, 3 and 4 ml). The results obtained when measuring peak height can be seen in the contour-line plot shown in Fig. 7. The optimum values were obtained with a concentration of 7.5 g l^{-1} and an added volume of 2.5 ml.

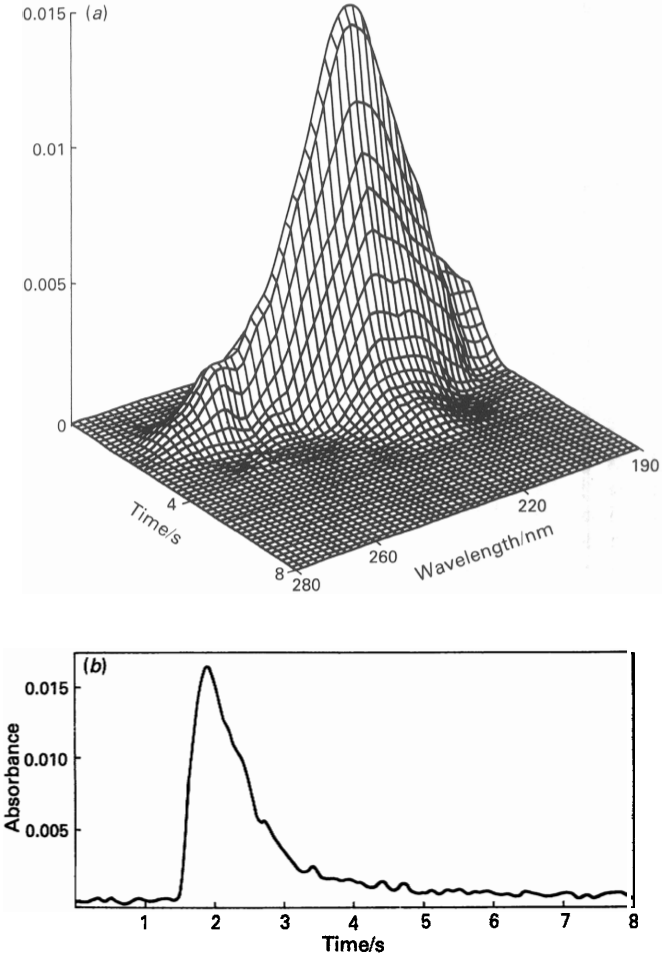

Fig. 3. (*a*) Variation of hydrogen selenide absorbance with time and wavelength. (*b*) Variation of hydrogen selenide absorbance at 220 nm with time

Table 2. BASIC program used to obtain the transient signal, peak area and peak height (maximum absorbance)

```
 10 LAMBDA 220
 20 Y-SCALE
 30 PLOTTER 1
 40 MODE 0, 1
 50 MEASURE 0.1, 0.1, 0, 8
 60     REM*Plot the transient signal on the screen*
 70       FOR I = 1 TO 80
 80       IF NMEAS <I THEN 80
 90       NEXT I
100 END
110     REM*Typing RUN 120, peak height and area are
        obtained*
120       FOR Y = 1 TO 80
130       X = Y/10
140       IF VALUE(X) <0.001 THEN 170 !Background is
          suppressed
150       A = A+VALUE(X)
160       M = MAX(M,VALUE(X))
170       NEXT Y
180     PRINT "Peak area (s)="; A*0.1
190     PRINT "Peak height ="; M
200 END
```

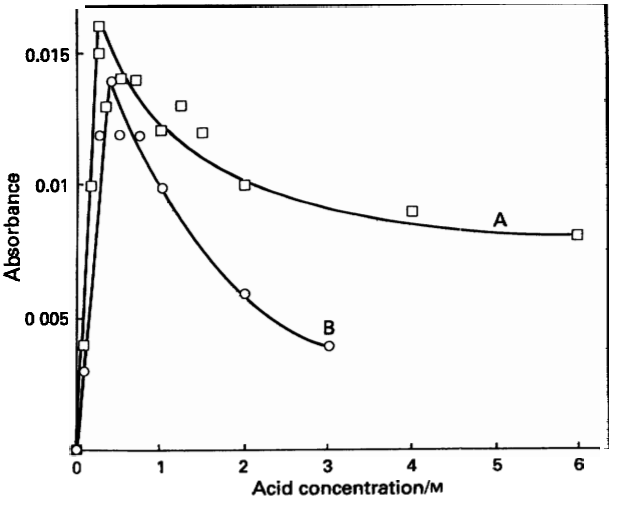

Fig. 4. Variation of hydrogen selenide absorbance at 220 nm with (A) hydrochloric and (B) nitric acid concentration

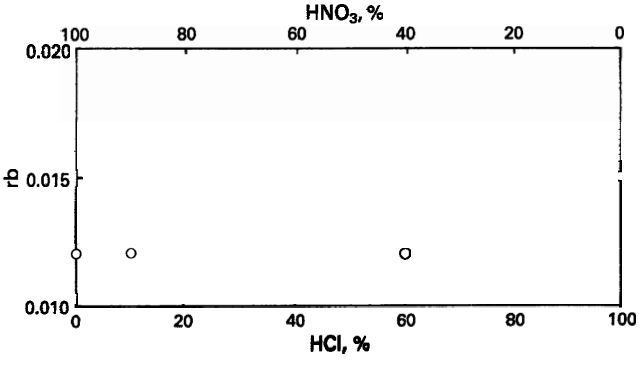

Fig. 5. Variation of hydrogen selenide absorbance at 220 nm with hydrochloric to nitric acid concentration ratio at a total acidity of 0.25 M

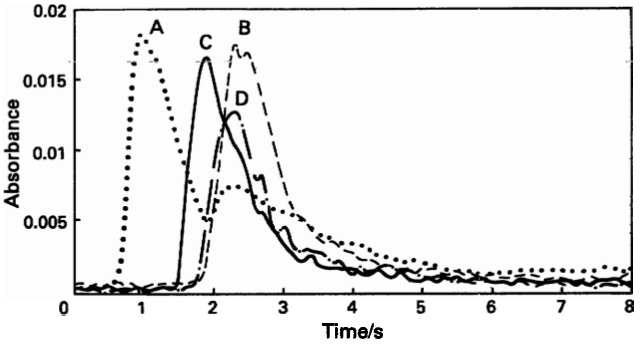

Fig. 6. Variation of hydrogen selenide absorbance at 220 nm with time using different nitrogen flow-rates: A, 10; B, 80; C, 525; and D, 1275 ml min^{-1}

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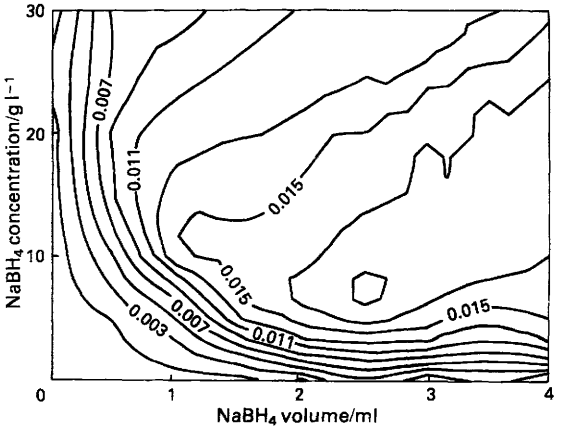

Fig. 7. Variation of hydrogen selenide absorbance with $NaBH_4$ concentration and volume injected

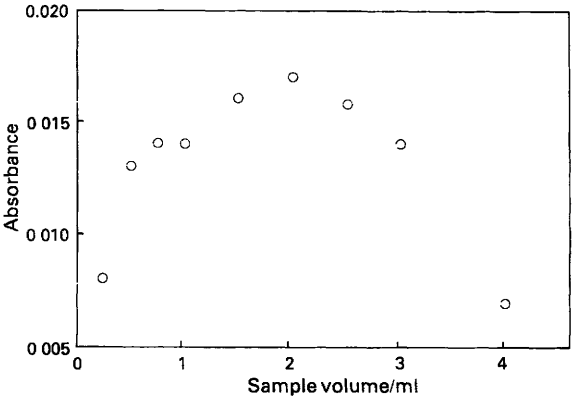

Fig. 8. Variation of hydrogen selenide absorbance at 220 nm with sample volume placed in generator flask

The effect of the total volume of sample solution in the generation flask was also studied. Fig. 8 indicates that the optimum values were obtained using a 2-ml volume of sample.

Table 3 gives the best conditions for the generation and determination of hydrogen selenide by GPMAS. The relative standard deviation (RSD) of ten replicate determinations of 50 μg of Se^{IV} in a 2-ml sample volume was 6.4% for the peak height and 15.4% for the peak area; this latter, anomalous, value is due to the irregular tail of the peak. Hence the maximum absorbance was selected as the quantitative parameter.

Calibration Graph, Sensitivity and Detection Limit

The described method gives a linear response from 10 to 150 μg of Se^{IV} in a 2-ml sample volume. By measuring the peak height at 220 nm the equation of the calibration graph, obtained by the method of least squares, is $y = 0.000337x + 0.000$ (x = μg of Se^{IV}, y = absorbance).

The correlation coefficient was 0.998 and the RSD for ten graphs was 0.11%. The sensitivity was 0.00034 μg^{-1} and the RSD 6.1%.

When more than 150 μg of selenium were present, the injection of reducing agent under the optimum conditions given in Table 3 produced a red - brown metallic selenium precipitate resulting in incomplete generation and the loss of linear response.

The detection limit calculated from a signal twice the height of the background of the blank measurement was 1.8 μg of Se^{IV} in 2 ml. The detection limit calculated from the sensitivity and standard deviation of the blank measurement[23] (k = 3) was 1.7 μg of Se^{IV}.

Table 3. Optimum conditions for hydrogen selenide generation and determination

Wavelength	220 nm
Nitrogen flow-rate	525 ml min^{-1}
HCl concentration	0.25 M
$NaBH_4$ concentration	7.5 g l^{-1}
$NaBH_4$ volume	2.5 ml
Total sample volume	2.0 ml

Table 4. Selenium found in a health-care product*

Method	SeS_2/g l^{-1}	Slope	Correlation coefficient
Interpolation	26.1 ± 1.2	0.00034	0.998
Standard additions	24.4 ± 0.9	0.00036	0.9990

* Manufacturer's value is given as 2.5% *m/V* (25 g l^{-1}) of selenium disulphide.

Determination of Selenium in a Health-care Product

In order to test the described method, selenium was determined in a health-care product (a shampoo for the treatment of dandruff). Sample dissolution was carried out by the procedure described previously.[24] Approximately 1 g of sample was weighed into a 100-ml Kjeldahl flask. Concentrated sulphuric acid (1 ml) was added and the mixture heated for 15 min. The solution was allowed to cool and 5 ml of 30% *m/V* hydrogen peroxide were added. The mixture was boiled vigorously to eliminate excess of hydrogen peroxide and the flask allowed to cool. Finally, dilution to 250 ml with doubly distilled water was followed by the addition of sufficient concentrated hydrochloric acid to produce a solution that was 0.25 M in HCl.

The sample solution (2 ml), containing up to 150 μg of Se^{IV}, was placed in the generation vessel and hydrogen selenide was generated using the conditions given in Table 3. An absorption maximum was obtained at 220 nm. No further spectral peaks were observed in the range 190–820 nm, demonstrating that spectral interferences due to the sample matrix did not appear.

The determination of selenium was carried out both by interpolation on the calibration graph and by standard additions. The results are presented in Table 4.

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