Gas-Chromatographic Determination of Ultramicro Amounts of Selenium in Pure Tellurium Metal

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Selenium (IV) reacts with 4-nitro-*o*-phenylenediamine to form 5-nitropiaselenol, which is detected by means of a gas chromatograph equipped with an electron-capture detector. By this highly sensitive method, the selenium in pure tellurium metal (99.9—99.999%) can easily be determined. Aqua regia oxidizes both selenium and tellurium to the quadrivalent state, and no loss of selenium is found upon this treatment. This method requires only 10—30 mg of a tellurium sample, and the presence of foreign ions does not interfere. It was found that pure tellurium, commercially available, always contains 10^{-3}—10^{-4}% selenium.

Spectrophotometric[1,2] and fluorimetric[3,4] procedures are convenient analytical methods for the determination of traces of selenium. Many organic reagents have been suggested for this purpose, 3,3′-diaminobenzidine[5,6] being widely used. The present author and a coworker[7] have recently proposed a far more sensitive method for detecting selenium in pure sulfuric acid by means of a gas-chromatograph equipped with an electron-capture detector and using 4-nitro-*o*-phenylenediamine. The present paper will describe a gas-chromatographic determination of selenium in pure tellurium. As even about 0.01 μg of selenium can be determined, only a few milligrams of tellurium are needed as the sample. By the oxidation of the pure tellurium with aqua regia, the selenium and the tellurium were converted to the respective quadrivalent states. The selenium in the solution was determined by the gas-chromatographic method using 4-nitro-*o*-phenylenediamine.

Experimental

Reagents. *4-Nitro-o-phenylenediamine Hydrochloride Solution*: This was a 1% acidic solution so stable that the solution could be used after standing for more than 1 week at room temperature.

Stock Selenium(IV) Solution: 351.3 mg of selenium dioxide were dissolved in 250 m*l* of distilled water (1 mg of Se in 1 m*l*). Working solutions were prepared by diluting the stock solution.

Stock Selenium(O) Solution: 3.06 mg of elemental selenium were dissolved in 50 m*l* of carbon disulfide (61.2 μg of Se in 1 m*l*). Working solutions were prepared by diluting the stock solution with carbon disulfide.

Stock Aqua Regia Solution: Concentrated hydrochloric acid and nitric acid were mixed in the volume ratio of three to one. The working solution was the doubly diluted stock solution.

The other reagents were of an analytical reagent grade.

Apparatus. A Shimadzu Model GC-3AE gas chromatograph equipped with an electron-capture detector was used. The glass column (1 m long, 4 mm bore) was packed with 15% SE—30 on 60—80 mesh Chromosorb W. The column and the detector temperature were maintained at 200°C. The nitrogen flow-rate was 48 m*l*/min. A Shimadzu Model 250A recorder was used, and the chart speed was 5 mm/min.

General Procedure. 30 mg of grained pure tellurium was put into a 100-m*l* beaker, and 6 m*l* of aqua regia which has been doubly diluted was added; the solution was then heated in a boiling water bath for 10 min. After cooling, a 3 m*l* portion of concentrated hydrochloric acid was added and the content was transferred to a 100-m*l* separatory funnel and the beaker was rinsed with 10-m*l* of distilled water into the funnel. When the selenium content was too large, an aliquot containing 0.01—0.1 μg of Se was used. Two milliliters of a 1% 4-nitro-*o*-phenylenediamine solution were added and the solution was allowed to stand for 2 hrs. Then, the 5-nitro-piaselenol formed was extracted into 1 m*l* of toluene by shaking for 5 min and the toluene extract was washed with 5 m*l* of 0.2 N sodium hydroxide. Five microliters of the toluene extract were injected into the gas-chromatograph and the peak height was measured.

Results and Discussion

Preparation of the Tellurium Sample. Selenium in the tellurium metal is not present in the form of selenium(IV), but in the elemental form, since the selenium compounds are more readily reduced and less easily oxidized than the corresponding tellurium compounds. Therefore, any selenium in the tellurium must be converted into the 4^+ oxidation state.

In order to dissolve and oxidize both tellurium and selenium to the quadrivalent form, nitric acid, aqua regia or a mixed acid of perchloric acid and nitric acid is usually used. Aqua regia is the most convenient oxidizing reagent, for, unless a considerable excess of nitric acid is used, the basic nitrate and tellurium dioxide are likely to be precipitated. The perchloric acid also lowers the peak height slightly, but the reason is not known. The gas-chromatogram which is obtained with 30 mg of tellurium dissolved in 6 m*l* of aqua regia diluted to two times is shown in Fig. 1. The retention time of 5-nitropiaselenol is four minutes.

Oxidation with Aqua Regia. Usually, when the oxidation of selenium is performed in the presence of hydrochloric acid, a volatile chloride, $SeCl_4$ is formed. This chloride must be responsible for the loss of sele-

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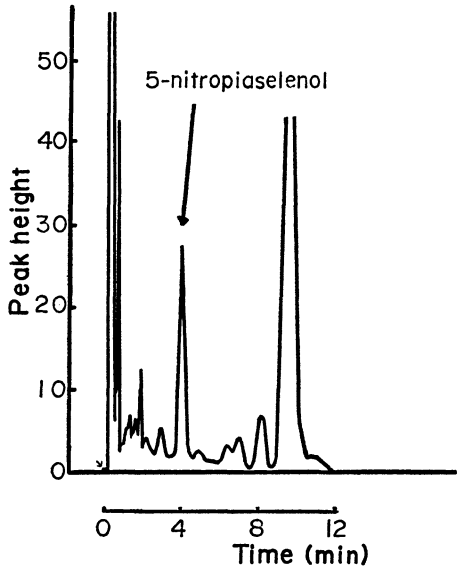

Fig. 1. Gas chromatogram of 5-nitropiaselenol.

Column	15% SE 30/chromosorb W
Carrier gas	N_2 (48 m*l*/min)
Temperature	200°C
Range	0.2 V
Sample	5 μl (0.054 μg Se in 30 mg Te)

nium. The effect of the concentration of aqua regia, the oxidation time, and the oxidation temperature are studied to confirm whether or not there is any loss of selenium.

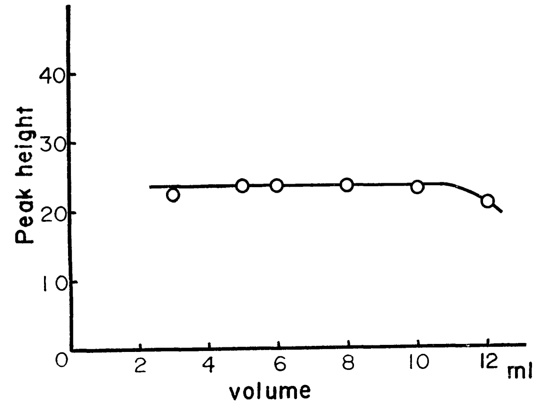

Fig. 2. Effect of the aqua regia concentration (30 mg Te). Range 0.2 V

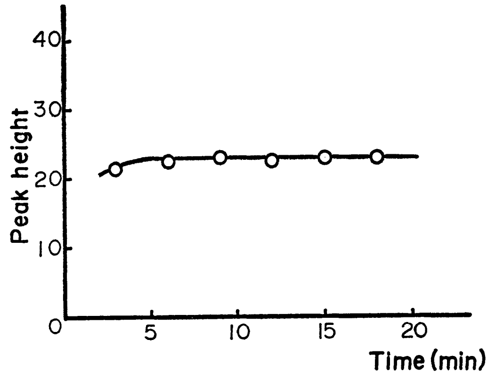

Fig. 3. Effect of the oxidation time (100°C) (30 mg Te). Range 0.2 V

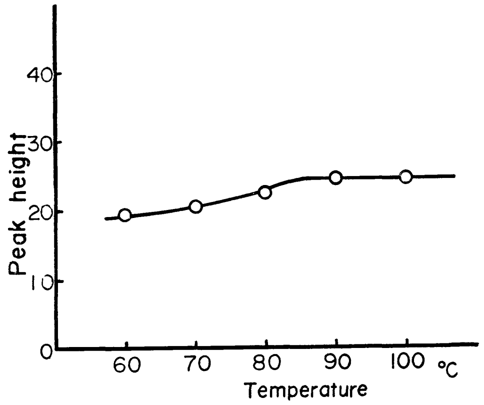

Fig. 4. Effect of the oxidation temperature (30 mg Te). Range 0.2 V

First of all, the effect of the concentration of aqua regia is studied. It is desirable that the concentration of aqua regia required to oxidize both selenium and tellurium be as low as possible. However, if the volume of the solution is too small, the loss of selenium may occur during oxidation in a boiling water bath. Therefore, doubly-diluted aqua regia is used for the oxidation procedure. The results are shown in Fig. 2. Complete oxidation is performed from 5 to 10 m*l* of aqua regia. Therefore, 6 m*l* of aqua regia, diluted to two times, are used in the following experiments. Next, the oxidation time is measured by heating in a boiling water bath (Fig. 3). As the oxidation is complete from 6 to 18 min, a sufficient oxidation time is 10 min. Lastly, Figure 4 shows the effect of the oxidation temperature. When the oxidation is performed at more than 90°C, the peak height shows the maximum and constant value.

Washing the Toluene Extract with Sodium Hydroxide. When the toluene extract is injected directly, without washing with sodium hydroxide, into the gas-chromatograph, an unknown peak appears overlapping the 5-nitropiaselenol. However, it can easily be removed by washing with a sodium hydroxide solution. Though, usually, the nitro compound is readily dis-

TABLE 1. EFFECT OF THE FOREIGN IONS

$$\left(\frac{[X]}{[Se]}=10^4\right)$$

Foreign ion (X)	Se recovery Se(0) in CS_2 (μg)	Se recovery in 30 mg Te (μg)
none	0.067 0.062	0.056 0.053
Fe^{3+}	0.066	0.054
Cu^{2+}	0.065	0.054
Ag^{+}	0.066	0.058
Pb^{2+}	0.064	0.057
Hg^{2+}	0.066	0.059
As^{3+}	0.067	0.058
Sb^{3+}	0.060	0.054
Bi^{3+}	0.061	0.054
$Fe^{3+}+Cu^{2+}+Ag^{+}$ $Pb^{2+}+As^{3+}+Sb^{3+}$	0.067	0.053

solved in an alkaline solution, as long as the toluene extract is washed with at least 5 m*l* of a 10^{-3}—1 M sodium hydroxide solution, the unknown acidic substance is removed and no back extraction of 5-nitropiaselenol can be found.

Effect of Foreign Ions. Although the amounts of foreign metals in pure tellurium would be comparable to that of selenium, the effect of a large amount of various ions is examined. No effect is found, even if 10^4 times as many of foreign ions are present, as is shown in Table 1.

Calibration Curve. The calibration curves are made from both a known amount of selenous acid in a hydrochloric acid solution and the elemental selenium dissolved in CS_2 by the above-mentioned procedure. These two curves are parallel to each other (Fig. 5). This results also shows that the oxidation is complete.

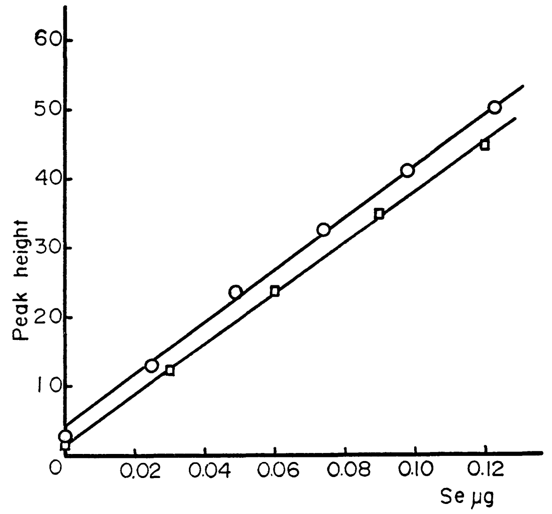

Fig. 5. Calibration curve
Range 0.2 V
—⊖— Se(0) in CS_2
—⊟— Se(IV) as H_2SeO_3

Determination of Selenium in Tellurium. Selenium in 30 mg of commercial pure tellurium was determined by the above-mentioned procedure; the same sample containing a standard addition of elemental selenium was also used for the determination. As its standard addition is always obtained by deducing the former values from the latter values, this method is proved to be suitable and correct for the determination of selenium in pure tellurium metal. The results are shown in Table 2.

Table 2. Selenium content in tellurium

Company	Selenium content in tellurium	
	Analytical reagent grade $\times 10^{-4}$%	Extra pure reagent $\times 10^{-4}$%
A	1.8±0.1	
B	30.0±0.1	22.5±0.2
C	13.5±0.2	7.5±0.1
D	4.0±0.1	31.5±0.2

The mean value of four times mesurement

As the sensitivity of an electron-capture detector tends to vary during operations, a series of experiments should be carried out successively and an unknown content of selenium should be determined along with standard samples which contain similar amounts of selenium. The procedure's outstanding features are that it is simple, highly sensitive, and rapid, and that no special skill is necessary to perform it.

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