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The Gas-chromatographic Determination of Selenium in Copper Metal and Copper Salts with 4-Nitro-*o*-phenylenediamine

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The gas-chromatographic method using an electron-capture detector has a high sensitivity for the determination of selenium. Moreover, as the reaction of selenium(IV) with 4-nitro-*o*-phenylenediamine is scarcely disturbed by other elements, the chemical separation from the matrix element is not necessary. The direct determination of very small amounts of selenium in copper and copper salts has been investigated. A mixture of equal volumes of nitric acid, hydrochloric acid, and perchloric acid dissolves the copper sample and also oxidizes the selenium to the quadrivalent state quantitatively. No loss of selenium was observed upon this treatment. The proposed method can determine the selenium in copper samples in amounts as low as 0.005 μg/g.

Trace amounts of selenium are commonly present in metals and alloys. The selenium content in metals influences the mechanical strength. In some instances, small amounts of selenium are added in order to improve the property. The accurate determination of trace amounts of selenium in copper has become increasingly important in recent years. Various methods, such as the spectrophotometric method,[1,2] X-ray spectroscopy,[3] and the atomic-absorption method[4] are widely used. However, chemical separation[5–7] is usually necessary before one can analyze trace amounts of selenium.

The present author has recently proposed a far more sensitive method for determining selenium in sulfuric acid,[8] tellurium,[9] sea water,[10] and plant materials[11] by means of a gas chromatograph equipped with an electron-capture detector using 4-nitro-*o*-phenylenediamine. Cheng[1] has reported that copper is masked with EDTA in the determination of selenium using 3,3′-diaminobenzidine. However, the reaction of selenium(IV) with 4-nitro-*o*-phenylenediamine was not disturbed by a large amount of copper and selenium present in copper salts, and copper metal can be determined without any separation or masking. The present paper will describe the determination of very small amounts of selenium in copper metal and copper salts.

Experimental

Reagents. 4-Nitro-*o*-phenylenediamine dihydrochloride solution (1%): The reagent was purified by repeated recrystallizations of commercial 4-nitro-*o*-phenylenediamine from a hydrochloric-acid solution. One gram of the reagent was dissolved in 100 ml of 1 M hydrochloric acid. Selenium(IV) stock solution: A 704-mg portion of selenium dioxide was dissolved in 500 ml of distilled water. The concentration was determined gravimetrically as 0.98 mg/Se/ml. The working solutions were prepared by dilution. Oxidation mixture: Concentrated hydrochloric acid and nitric acid were mixed in equal volumes. This solution was prepared each time before use. 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. A glass column (1 m long, 4 mm bore) was packed with 15% SE-30 on 60—80 mesh Chromosorb W. The column and detector temperature was maintained at 200 °C. The nitrogen flow-rate was 36 ml/min. A Shimadzu Model 250A recorder was used at a chart speed of 5 mm/min.

Standard Procedure. Accurately weighed copper samples which have been cut into about 10-mg segments are placed in a 100 ml conical flask. Five ml of perchloric acid and 10 ml of the oxidation mixture are added, and the mixture is heated on a sand bath (200—230 °C) in a fume hood (this acid mixture is used for 1 g of copper or less). A vigorous oxidation reaction soon takes place, and a copious brown vapor is evolved. After a few minutes, the main reaction comes to an end. The solution is heated further until a white fume of perchloric acid is evolved. Then the conical flask is removed from the sand bath. After the precipitate has been redissolved with 10 ml of distilled water, the content is transferred into a 50-ml volumetric flask. The solution is diluted to the mark with distilled water. An aliquot containing 0.01—0.03 μg of selenium is transferred into a 100-ml separatory funnel containing 25 ml of 1 M hydrochloric acid which has previously been washed with toluene. A 2-ml portion of 1% 4-nitro-*o*-phenylenediamine is then added, and the solution is allowed to stand for 2 hr. Then, the 5-nitropiaselenol formed is extracted into 1 ml of toluene by shaking for 5 min and the toluene extract is washed with 2 ml of a 7.5 M hydrochloric acid solution. A 5-microliter portion of the toluene extract is injected into the gas chromatograph, and the peak height is measured.

The selenium content in copper salts is always less than that in copper metal. Consequently, in the case of copper salts, after the oxidation procedure all the contents are transferred into a 100-ml separatory funnel and washed with 1 ml of toluene. Then, the aqueous phase is transferred into another 100 ml separatory funnel. A 2-ml portion of 4-nitro-*o*-phenylenediamine is added. The following procedure is the same as that described above.

Results and Discussion

Oxidation of Selenium. Most of the selenium contained in copper metal is present in the form of selenium(II), since, on the electrolytic refining of copper, selenium can easily react with copper to form Cu_2Se. Clark[12] reported that, when a piece of thin copper film was dipped in a hydrochloric acid solution of selenite, the copper was coated with a black film of Cu_2Se. Therefore, the selenium in copper and copper salts must be oxidized to the quadrivalent state. Nitric acid is usually used in order to dissolve

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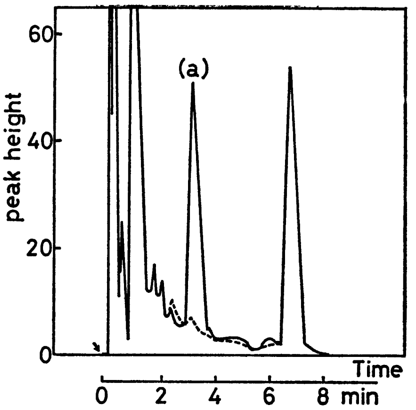

Fig. 1. Gas chromatogram of 5-nitropiaselenol.
—— 0.50 g copper powder (1.59 µg Se/g Cu)
---- blank
(a) 5-nitropiaselenol
Range 0.2 V.

and oxidize both copper and selenium. Gorsuch13) suggested that there was not 100% recovery when a mixture of nitric acid and sulfuric acid was used for plant samples. The mixtures of nitric- and perchloric acid, hydrochloric- and nitric acid, and hydrochloric-, nitric- and perchloric acid were compared in terms of their efficiency in oxidizing selenium in both copper metal and copper salts. Only the last acid mixture can oxidize quantitatively the selenium in both samples. Thus, the mixture of hydrochloric-, nitric-, and perchloric acid was used for the dissolution of copper samples. The bromine–bromide redox buffer8) in a sulfuric acid medium can also be used as a convenient oxidation reagent for copper salts. A gas chromatogram obtained with 500 mg of copper treated by the above-mentioned procedure is shown in Fig. 1.

Dissolution with the Mixture of Hydrochloric-, Nitric-, and Perchloric Acid. Usually, volatile compounds, such as $SeO_2 \cdot 2HCl$ and $SeOCl_2$, are formed during a dissolution in the presence of hydrochloric acid. These compounds must be responsible for the loss of selenium. In order to check whether or not there is any loss of selenium, the effects of the concentration of the oxidation mixture, the oxidation time, and the oxidation temperature were studied. As is shown in Fig. 2, the selenium in 0.5 g of copper metal could be oxidized quantitatively with more than 3 ml of the oxidation mixture in the presence of 5 ml of perchloric acid, and a good recovery was observed. If a smaller amount of the oxidation mixture is used, the back ground of the chromatogram becomes so high that the determination is not accurate. Therefore, 10 ml of the oxidation mixture and 5 ml of perchloric acid were used for the following experiments. If more than 1 g of copper metal is used for the determination, the procedure is disturbed by the deposition of the copper salt during the oxidation procedure. However, this trouble can be overcome by dissolving the precipitate with another 5 ml of perchloric acid.

The oxidation temperature was examined in the approximate range from 130 to 270 °C (sand-bath temperature). The maximum constant peak height was obtained in this region. As a longer oxidation time was needed at a lower oxidation temperature, the optimum oxidation temperature was in the approximate range from 200 to 230 °C. When the heating was continued at this temperature until the color of the solution turned pale blue, the selenium in the copper was oxidized to the quadrivalent state completely. Moreover, no selenium at the 0.1 µg level was lost by volatilization when heated for 20 min, after the evolution of white fumes of perchloric acid. Consequently, the heating was continued at about 230 °C until white fumes of perchloric acid were evolved. The whole oxidation procedure requires about 30 min.

Very small amounts of interfering substances in the distilled water used for dilution often disturb the determination, because the sensitivity of the electron-capture detector is extremely high for the unknown impurities as well as for 5-nitropiaselenol. Therefore, these interfering substances should be remove by washing with toluene. When the selenium content in copper metal is too high, the sample solution is diluted with a 1 M hydrochloric acid solution which has previously been washed with pure toluene. For the copper salts, the sample solution is washed directly with 1 ml of toluene after oxidation. Moreover, the reagent solution also contains small amounts of interfering substances; therefore, 1 ml of the toluene extract after the formation of 5-nitropiaselenol should be washed again with 2 ml of 7.5 M hydrochloric acid.

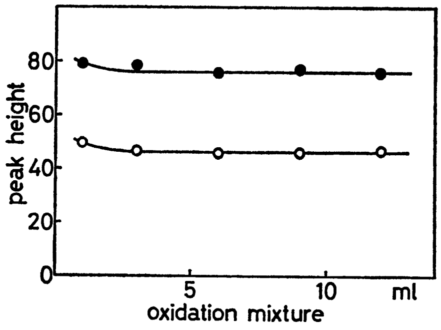

Fig. 2. Effect of volume of oxidation mixture in the presence of 5 ml of perchloric acid.
—○— 0.50 g copper power,
—●— 0.49 µg selenium(IV)+0.50 g copper powder.

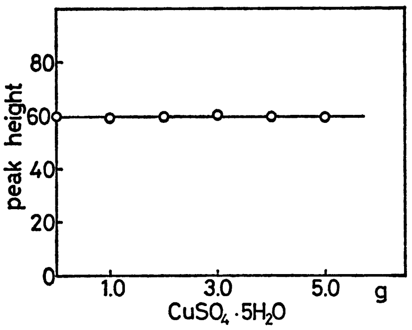

Fig. 3. Effect of copper matrix.
0.0196 µg selenium(IV)+$CuSO_4 \cdot 5H_2O$
No oxidation procedure.

Effect of the Copper Matrix. In order to check the influence of a large amount of copper ions upon the determination of selenium, 0.0196 µg Se(IV) was added to a copper-sulfate solution and determined. As is shown in Fig. 3, the selenium was recovered qunatitatively even in the presence of 5 g of $CuSO_4 \cdot 5H_2O$. Therefore, the masking or separation procedure is not necessary before the determination.

Effects of Foreign Ions. The effects of several foreign ions, such as Fe^{3+}, As^{3+}, and Pb^{2+}, were reported in the previous paper.[9] As is shown in Table 1, even if 10^3 times as many foreign ions are present, no effect is found. In particular, this method is scarcely effected by Mn^{2+} and V^{5+}. It seems that this method can be utilized for the direct determination of selenium in the presence of considerably large amounts of these elements.

Accuracy and Precision. The accuracy of the procedure was evaluated by recovery experiments using copper metal (powder). Recovery was established by dissovling the copper metal to which a known amount of selenium had been added, and by treating the samples as has been described. In all cases, theoretical recovery was obtained within the limits of experimental error (Table 2). The precision was evaluated using a copper metal (powder). The results are shown in Table 3.

Calibration Curve. The calibration curve was made with known amounts of selenous acid in a hydrochloric acid solution. The curve was coincident with that obtained from the same selenous acid by the oxidation procedure. Therefore, the curve obtained without the oxidation procedure is used for the determination. One of the calibration curves obtained at various sensitivities of the gas chromatograph is shown in Fig. 4. More than 0.005 µg of selenium can be determined.

Table 1. Effect of foreign ions

$$\frac{[X]}{[Se]} = 10^3$$

Foreign ion [X]	Added as	Se recovery (µg/g Cu)
None		1.59
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	1.62
Mn^{2+}	$Mn(NO_3)_2 \cdot 6H_2O$	1.56
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	1.55
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	1.67
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	1.58
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	1.57
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	1.57
Mo^{6+}	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.58
V^{5+}	NH_4VO_3	1.58

Table 2. Recovery of selenium added to copper powder

Copper (g)	Added selenium (µg)	Selenium found (µg)	Selenium recovered (µg)	Recovery
0.500	None	0.0159		
None	0.0098	0.0100	0.0100	102
0.300	0.0098	0.0195	0.0100	102
0.300	0.0098	0.0192	0.0097	99
0.500	0.0098	0.0250	0.0091	93
0.500	0.0098	0.0255	0.0096	98

Observed value from one-fifth volume of solution oxidized.

Table 3. Reproducibility of selenium determination in copper powder

Copper (g)	Peak height	Selenium determined (µg/g Cu)
0.501	46.9	1.60
0.501	46.5	1.58
0.500	45.1	1.55
0.500	47.6	1.61
0.501	45.2	1.55
0.500	46.0	1.57
0.500	51.2	1.72
0.500	46.7	1.59
0.500	44.8	1·53
0.501	46.7	1.59
Mean		1.59
Std. dev.		±0.052
Coeff. of var.		3.3%

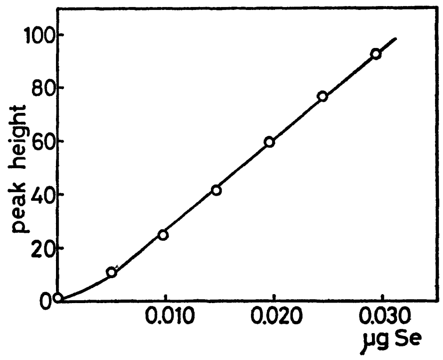

Fig. 4. Calibration curve.
No oxidation procedure.
Range 0.2 V.

Determination of Selenium in Copper metal and Copper Salts. Selenium can be determined successfully even in 0.1 g of copper metal or copper salts, because the ECD gas chromatograph is very sensitive to 5-nitropiaselenol. However, the values obtained in small-sample portions are dispersed widely; this implies that the distribution of the selenium is heterogeneous in copper metal and copper salts. Therefore, in many cases, 10 g or more is mixed well, and a small portion should be taken from the matrix for the determination. However, if copper powder is used, the value of the selenium content is proportional to the powder weight, because the selenium content in copper powder seems to be homogeneous. When 10 g of copper (99.999%) plate was cut into 10-mg segments, and 1—2 g of it was taken after mixing for the determination, the value obtained was reproducible. The peak height of selenium in the sample thus obtained is proportional to the sample weight, as is

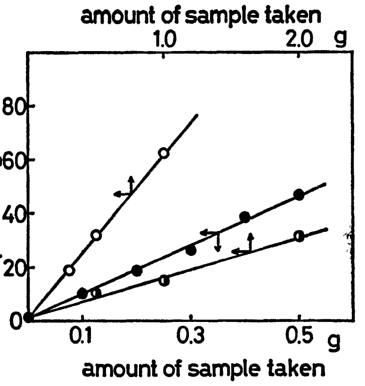

Fig. 5. Effect of amount of sample taken.
—○— $CuSO_4 \cdot 5H_2O$ extra pure (Range 0.4 V)
—●— copper 99% powder (Range 0.2 V)
—◑— copper 99.999% plate (Range 0.2 V).

shown in Fig. 5, and all the lines pass through the same point. The peak height of this point is in fair agreement with the blank value. This indicates that the oxidation is complete and that no loss of selenium occurs during the procedure.

The selenium in 1—2 g of copper metal was determined by the standard procedure; the results are shown in Table 4. The selenium in copper salts can also be determined by the standard procedure, as is shown in Table 5. The selenium in cupric sulfate seems to exist in the form of selenide, because it can not be determined without the oxidation procedure. On the other hand, the selenium in cupric nitrate and chloride may exist in the quadrivalent state, because it can be determined quantitatively without the oxidation procedure (Procedure C in Table 5). To copper metal or copper salts, a known amount (0.0098—0.49 μg) of selenium was added in the quadrivalent state, and the recovery was then examined. The results were satisfactory in all cases, within the limits of experimental error.

Table 4. Selenium content in copper metal

Material	Selenium content[a] $\times 10^{-5}\%$
Copper 99% power	15.9±0.5
Copper 99.99% electrolytic (I)	8.1±0.9
Copper 99.99% electrolytic (II)	1.4±0.1
Copper 99.99% electrolytic (III)	1.9±0.2
Copper 99.999% plate	3.3±0.1
Copper sponge glanular for elementary analysis	5.0±0.5
Copper oxide wire for elementary analysis	2.6±0.3

a) The mean value of five mesurements.

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Table 5. Selenium content in copper salts

Material	Selenium content					
	Analytical reagent grade, $\times 10^{-6}\%$			Extra pure reagent $\times 10^{-6}\%$		
	A	B	C	A	B	C
$CuSO_4 \cdot 5H_2O$	0.2	0.2	—	5.4±0.5	5.1±0.6	—
$Cu(NO_3)_2 \cdot 3H_2O$	0.7±0.5	0.6±0.08	0.8	1.7±0.1	—	1.7
				—	2.6±0.1	—
$CuCl_2 \cdot 2H_2O$	5.1±0.5	—	—	5.4±0.3	—	5.0
				—	6.2±0.2	—

The mean value of five measurements. A: Sample is oxidized with the oxidation mixture. B: Sample is oxidized with 0.1 M Br_2-Br^- redox buffer.[14] C: No oxidation procedure.