The Colorimetric Determination of Traces of Selenium with Dithizone

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The composition of selenium is generally determined by reduction to reddish elemental selenium with such reducing agents as sulfur dioxide. This method is, however, not only insensitive but also subject to interference from other elements. Recently, Cheng reported a useful new method of determining traces of selenium colorimetrically by using 3-diaminobenzidine as an organic reagent[1]. Although Cheng's method is more sensitive and simpler than the former one, it still has some difficulties in the color development and involves complicated procedures.

The present authors have recently found that selenium(IV) can be extracted almost quantitatively by dithizone from an acid solution of a fairly high concentration. In carbon tetrachloride the dithizone complex of selenium is yellow in color and shows a maximum absorption at 420 mμ (Fig. 1).

The fact that selenium can be extracted by dithizone from a highly acidic solution, especially a hydrochloric acid solution of as high as 6N, may be regarded as very favorable for the colorimetric determination of selenium, because the high concentration of hydrochloric acid prevents other metals from complexing with dithizone. Taking these points into consideration, the authors studied the colorimetric determination of selenium with dithizone.

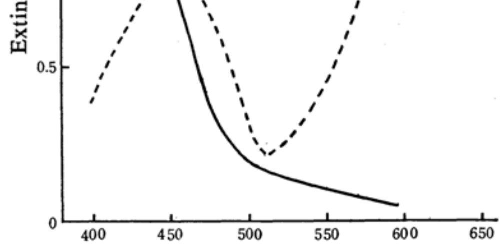

Fig. 1. Absorption curves.
—— Dithizone complex of selenium in carbon tetrachloride
- - - Dithizone in carbon tetrachloride

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[1] K. L. Cheng, *Anal. Chem.*, 28, 1738 (1956).

Experimental

Apparatus and Reagents.—*Spectrophotometer.*—A Beckman model DU spectrophotometer.

Standard Selenium Solution.—Purified metal selenium was first dissolved into a small amount of concentrated nitric acid, and the solution was evaporated to dryness in order to remove any excess nitric acid. Hydrochloric acid was then added to dissolve the residue, and the resulting selenous acid solution was diluted with redistilled water so as to be 0.5∼4 μg. selenium per milliliter.

Dithizone Solution.—The concentration of the dithizone-carbon tetrachloride solution was adjusted to be 40∼60 μmol./l. As for the purification of dithizone, Iwantscheff's method was employed[2].

Other Reagents.—Redistilled water and distilled ammonium hydroxide were used. The other reagents used were of analytical reagent grade.

Proposed Procedure for Determining Selenium.—Preliminary experiments indicated that selenium can be extracted most favorably from a 6 N hydrochloric acid solution. In general, two ways of colorimetric determination by dithizone are applicable to such metals as can be extracted from acidic media: the so-called mono-color method and the mixed-color method. For the present studies, both methods were examined. The proposed procedures for the mono-color and mixed-color methods will be described separately below. The extraction is carried out from a 6 N hydrochloric acid solution in both cases.

Mono-color Method.—Acidify 5 ml. of a sample solution with the same volume of concentrated hydrochloric acid and shake it thoroughly for two minutes with 5 ml. of a dithizone-carbon tetrachloride solution (60 μmol./l.) in a small separatory funnel. Allow the two phases to separate, and draw off the carbon tetrachloride layer into a 10-ml. measuring flask. Repeat the same extraction procedure with small portions of dithizone until selenium is completely extracted. Finally, wash the aqueous solution with one milliliter of carbon tetrachloride, drawing off the latter into the flask. Dilute the combined extracts in the measuring flask to a definite volume (10 ml.) with carbon tetrachloride, and transfer the solution into a separatory funnel. Wash it with 10 ml. of redistilled water, shaking the funnel for thirty seconds. Draw off the carbon tetrachloride layer into another separatory funnel, and add 10 ml. of dilute ammonium hydroxide (1 : 100) to remove the excess dithizone. Repeat the washing with another portion of ammonium hydroxide, and then determine the extinction of the solution at 420 mμ.

Mixed-color Method.—Acidify 2.5 ml. of a sample solution with the same volume of concentrated hydrochloric acid, and shake it thoroughly in a small separatory funnel for two minutes with 5 ml. of a dithizone solution (45 mol./l.). Allow the two phases to separate, draw off the carbon tetrachloride layer into an absorption cell, and determine the extinction at 410 mμ.

Results and Discussion

Absorption Spectra.—The absorption curve of the reagent and the dithizone complex of selenium(IV) in carbon tetrachloride are given in Fig. 1. As may be seen in the figure, the reagent has maximum absorptions at 620 and 450 mμ, while the dithizone complex of selenium has its maximum at 420 mμ. Therefore, extinction measurement may be made at 420 mμ in the mono-color method. As for the mixed-color method, however, it is preferable to measure at 410 mμ, where the absorption by dithizone is rather weak. In fact, in the case of the mixed-color method, it was almost impossible to carry out colorimetric determination at 420 mμ, while good results were obtained at 410 mμ.

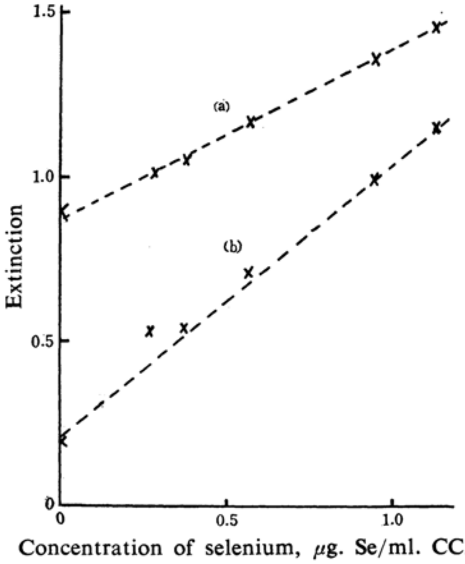

Fig. 2. Calibration curves (referred to carbon tetrachloride)
(a) Mixed-color method (dithizone concentration ∼60 μmol./l)
(b) Mono-color method

In the mono-color method, the calibration curve does not cross the origin. This is likely due to some contamination of other metals or decomposition of dithizone during elimination process of excess dithizone.

TABLE I. EXPERIMENTAL ERRORS OF MIXED-COLOR METHOD

Selenium taken μg.	Selenium found μg.	Error %
0.28_2	0.28_4	+ 0.7
0.37_6	0.36_5	− 2.9
0.56_3	0.58_2	+ 3.6
0.93_8	0.93_8	0
1.12_6	1.12_6	0

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[2] G. Iwantscheff, "Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse", Weinheim/Bergster (1958), p. 60.

TABLE II. POSSIBLE INTERFERING METALS

Metal	Optimum condition for extraction by dithizone	Metal compounds used in this experiment	λ_{max} of dithizonate in CCl_4, mμ
Cu(II)	pH 2 ∼ 4	$CuSO_4$ in H_2O	550
Pd	2 N H_2SO_4	Not tested	640
Ag	pH 2	$AgNO_3$ in H_2O	462
Te(IV)	0.5 N·HCl	TeO_2 in HCl	430
Au	2 N H_2SO_4	Not tested	450
Hg(II)	1 N H_2SO_4	$HgSO_4$ in HCl	485
Bi(III)	pH 6	Bi metal in HNO_3	490

TABLE III. EFFECT OF SEVERAL INTERFERING METALS

Selenium added μg.	Interfering metals present in the aqueous layer	Selenium found under the coexistence of a comparable amount of interfering metal, μg.	Selenium found under the coexistence of a tenfold amount of interfering metal, μg.
0.56_3	Cu(II)	0.70_3	0.91_7
0.56_3	Ag	0.56_3	0.53_9
0.56_3	Te(IV)	0.53_1	0.55_9
0.56_3	Hg(II)	0.68_3	0.53_3
0.56_3	Bi(III)	0.63_7	0.56_9
0.56_3	Cu(II)	0.56_1	–
Preliminary treatment was carried out at pH 7.			
0.56_3	Cu(II), Ag, Te(IV), Hg(II), Bi(III)	0.57_5	–
Preliminary treatment was carried out at pH 2.			

The Calibration Curve and Precision of the Methods.—The calibration curves are given in Fig. 2 for both mono-color and mixed-color methods. Extinction measurements were made at 420 mμ in the mono-color method and at 410 mμ in the mixed-color method. The linearities are good in both cases. The spectrophotometric sensitivity* of the color reaction is, in the mono-color method, 0.001 μg. of selenium in carbon tetrachloride per square centimeters, while it is 0.002 μg. in the mixed-color method.

The experimental errors of the mixed-color method are shown in Table I. From these experimental results, it may safely be said that the proposed mono- and mixed-color methods are both applicable to determining traces of selenium.

Interfering Substances.—The reaction of selenium with dithizone in 6 N hydrochloric acid media is very specific. The substances which would interfere with the determination of selenium with dithizone would include, in the first place, those which oxidize dithizone itself, such

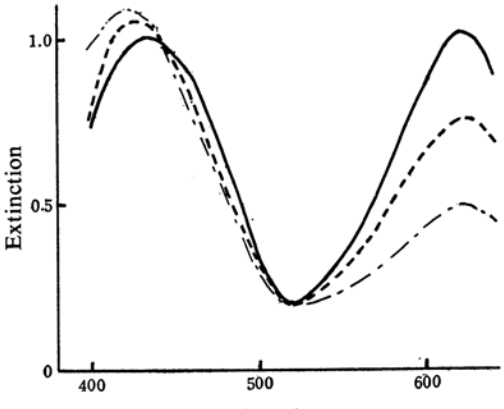

Fig. 3. Changes of absorption curve effected by the presence of copper(II).

—— Absorption curve of dithizone extract of selenium in CCl_4 (0.56 μg. Se/ml. CCl_4).

- - - Absorption curve of dithizone extract when copper(II) is present in the aqueous solution in a comparable amount with selenium.

·—· Absorption curve of dithizone extract when copper(II) is present in the aqueous solution in a tenfold amount of selenium.

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* Here, spectrophotometric sensitivity is defined as follows: the number of micrograms of the element, converted to the colored product, which, in a column of solution with a cross section of 1 cm^2, shows an extinction of 0.001. For details, see E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959), p. 83.

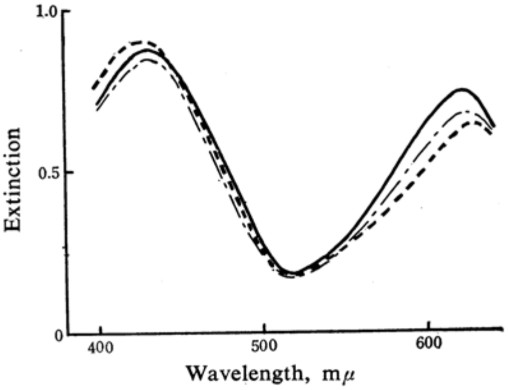

Fig. 4. Changes of absorption curve effected by the presence of mercury(II).

—— Absorption curve of dithizone extract of selenium in CCl_4.

--- Absorption curve of dithizone extract when mercury(II) is present in the aqueous solution in a comparable amount with selenium.

·—· Absorption curve of dithizone extract when mercury(II) is present in the aqueous solution in a tenfold amount of selenium.

as ferric ion, halogens, nitrous acid, permanganate and so forth. These should be removed, of course, from the reaction system. Some metals which react with dithizone in acidic media, such as copper(II), palladium, silver, tellurium(IV), gold, mercury(II) and bismuth(III) may possibly be interfering substances (TableII). The interfering action of these metals was investigated expeimentally and is shown in Table III. We paid no attention to palladium and gold, since they are not so abundant in nature.

From Table III we can conclude that tellurium(IV), silver, and bismuth do not essentially interfere with our method even if any of the three exist in amounts of ten times as much as selenium in the sample solution. This seems to be due to the high acidity and/or the high concentration of chloride ions (which may cause the masking effect) in the extraction system. Copper(II) interferes, and mercury(II) may also be considered to interfere. Changes in the absorption curves of the selenium dithizone complex and of dithizone due to the existence of copper(II) or mercury (II) are shown in Figs. 3 and 4.

Separation of Selenium from the Interfering Metals.—We made several tests of selenium extraction with a dithizone solution, using the radioactive isotope ^{75}Se as a tracer, and observed that, for pH values higher than 2, only less than 1.5% of the total amount of selenium is extracted by a 10^{-3} mol./l. dithizone solution. However, a considerable amount of copper(II) is extracted under the same conditions, so it seems probable that we can exclude the interference of copper by extracting it preliminarily from the sample solution. The procedure of selenium determination including such preliminary treatment is as follows:

First, extract copper from the sample solution with dithizone under neutral or slightly acidic media, and then make the aqueous layer approximately 6 N in hydrochloric acid. An example of determining the selenium content in the sample solution, which contains a comparable amount of copper, by such a procedure is shown in Table III. Table III also gives the results obtained from a similar experiment in which the five kinds of interfering metals described above are contained in the sample solution, each in an amount comparable with that of selenium. Both of these examples give good results, and, as we expected, the extraction from 6 N hydrochloric acid solution is found to be really favorable, since even such interfering metals such as copper(II) and mercury(II) can be separated by a simple preliminary treatment.

Molar Extinction Coefficient.—The extinction coefficient of the selenium dithizone complex in carbon tetrachloride was estimated to be about 70×10^3 per mole-centimeter.

Stability of Color.—The stability of color was carefully examined. The experimental results are given in Fig. 5. It may be observed in Fig. 5 that the color of the dithizone extract of selenium is nearly stable when the extract is separated from the aqueous layer (6 N in hydrochloric acid) immediately after shaking, while the color fades away gradually when the organic layer remains in contact with the aqueous one.

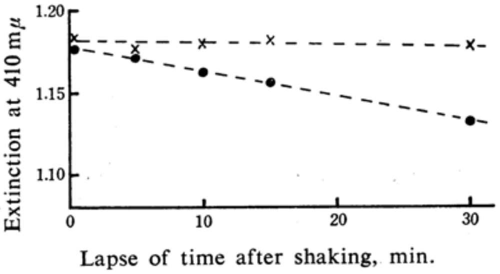

Fig. 5. Stability of color of selenium-dithizone complex in carbon tetrachloride.

×--× Extinction of organic layer which was separated from aqueous layer immediately after shaking.

-•-•-• Extinction of organic layer which has been in contact with aqueous layer after shaking.

Summary

A colorimetric method of determining traces of selenium with dithizone has been studied. Selenium is extracted from a 6 N hydrochloric acid solution with a carbon tetrachloride solution of dithizone almost quantitatively, and the dithizone complex of selenium in carbon tetrachloride has a maximum absorption at the wavelength of 420 mμ. One p. p. m. of selenium can be determined spectrophotometrically, by measuring the extinction at 420 mμ in the mono-color method and at 410 mμ in the mixed-color method.

The errors of these two methods are estimated to be within 3%. Copper(II) and mercury(II) were found to be interfering metals. However, they are easily removed by a preliminary extraction. Finally, attention should be paid to the fact that the color of the dithizone complex of seleium is apt to fade away rapidly when it is left in contact with a 6 N hydrochloric acid solution for some time.

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