Rapid Colorimetric Determination of Selenium by the Tin(II)-Strong Phosphoric Acid Reduction Method

By Toshiyasu KIBA, Ikuko AKAZA and Hiroaki HACHINO

(Received November 18, 1958)

With the increasing demand of the electronic industry for selenium, the element has become critically important, and a rapid and accurate method of detecting and determining the element is badly wanted in the field and in the laboratory. Although selenium occurs widely in many geological formations frequently accompanied with minerals containing sulfur, the amount is so small that chemical analysis of the element is one of the most difficult of techniques. The procedures which have been presented by most investigators are of two parts: decomposition of samples with oxidizing acids, and estimation of the selenium in the solution. However, it is really regrettable that in all the methods the decomposition of the samples is time-consuming and loss of the element is likely to occur during the evaporation of the solution or filtration of the undissolved residue.

Previously the authors devised a new powerful decomposing and reducing agent, tin(II)-strong phosphoric acid[1], by which sulfur in inorganic substances such as ores[2] as well as in organic compounds[3,4] could be taken out as hydrogen sulfide and readily estimated iodimetrically or colorimetrically. A further attempt was made by the present authors to reduce selenates, selenites, and elementary selenium to hydrogen selenide by treatment with the same reagent. As the result of the preliminary experiments it was found that selenium in various forms could be reduced to hydrogen selenide at somewhat higher temperatures than in the case of sulfur. By the powerful decomposing power of the reagent even pyrite can readily and completely be decomposed without any other treatment, and the selenium can be separated as gaseous hydrogen selenide from the sample. The present paper describes the investigation by which a new method for quantitative analysis of selenium is established.

1) T. Kiba et al., This Bulletin, **28**, 641 (1955).
2) T. Kiba, I. Akaza and N. Sugishita, ibid., **30**, 972 (1957).
3) S. Ohashi, ibid., **28**, 645 (1955).
4) T. Kiba, I. Akaza and S. Taki, ibid., **30** 482 (1957).

Experimental

Apparatus —The apparatus used in this study is shown in Fig. 1. It is composed of two parts, a reaction vessel (A) and an absorbing part (B). The reaction vessel (A) is a round-bottomed flask of hard glass having a glass cap fitted to its top and provided with inlet and outlet tubes for hydrogen gas. The absorbing part (B) is composed of two test-tubes 3 cm. in diameter. A gas delivery tube (G) is connected with a piece of rubber tubing (R) to the outlet arm of the reaction vessel (A) and inserted into the absorbing solution. A Kipp's apparatus is employed for the production of hydrogen, which is purified by four gas-washing bottles (not shown in the figure) and introduced in the reaction vessel

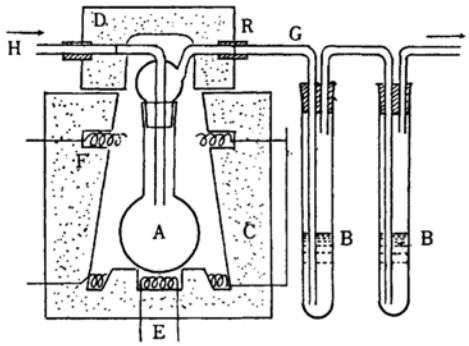

Fig. 1. Apparatus for reduction of selenium and absorption of hydrogen selenide.
A: Reaction vessel, a round-bottomed flask
B: Absorbing vessels
C: Block of diatomaceous earth
D: Cover block of diatomaceous earth
E: Electric heater at the bottom
F: Electric heater around the sides
G: Gas-delivery tube
H: Hydrogen gas introduced into A
R: Short piece of rubber tubing

through the inlet arm. The solution used for the purification of hydrogen is described below.

Reagents. — *Strong phosphoric acid.* — Four hundred grams of commercial orthophosphoric acid of extra pure grade (d=1.7) is placed in a 300 ml. conical beaker, and dehydrated by heating on a 500 W hot plate until a thermometer dipped in the liquid indicates 300°C. If the heating takes too long the liquid will become turbid and viscous and useless for the purpose in view. During the heating, the water vapor and the mist of phosphoric acid coming off should be rapidly removed from the neighborhood of the liquid surface through a glass tube, one end of which is held near the liquid surface, the other end being connected to a suction pump. It saves much time in the dehydration.

Tin(II)-strong phosphoric acid.—Fifty grams of tin(II)-chloride dihydrate of extra pure grade is placed in a 300 ml. conical beaker and on it is poured 250 g. of the strong phosphoric acid prepared as described above. The content is heated to 300°C within about 30 min. in the manner of preparation of strong phosphoric acid. After cooling, the tin(II)-strong phosphoric acid thus obtained, a very viscous and possibly slightly turbid liquid, may be stored in a closed vessel.

Tin(II)-chloride solution.—15% in 9 N hydrochloric acid.

Gum arabic solution.—1% aqueous solution.

Hydrogen gas.—Hydrogen gas produced in the Kipp's apparatus is purified by passing through four gas washing bottles containing respectively, water, 1% potassium permanganate in 10% sodium carbonate solution, 2% vanadium(II) sulfate in 6 N sulfuric acid solution, and 5% barium chloride, and is introduced into the reaction vessel through a glass tube in which a copper net is placed to prevent accidental explosion of the gas.

Standard selenious acid solution. — Elementary selenium is dissolved in concentrated nitric acid and evaporated to dryness, and the selenious acid thus formed is sublimed by gentle heating in another vessel. The sublimate is collected and dissolved in water to make a solution containing 3 mg. of selenium in 1 ml. The solution is diluted to a suitable concentration for the following experiments.

Pyrite ore.—Natural pyrite from the Ogoya Mine near Kanazawa City was ground to 200 mesh size and used as a sample to test the procedure established by the present authors.

Other reagents were all of the pure chemical grade and the utensils were of the ordinary kind for the laboratory.

Procedure.—(1) *Decomposition of samples and evolution of hydrogen selenide.*—Take an accurately measured sample—pipet a solution; weigh a solid—containing selenium and put it into the reaction vessel (A, in Fig. 1). The volume of the vessel should be varied according to the amount of the sample to be analyzed. Evaporate to dryness if the sample is a solution. Pour about 10 to 50 g. of tin(II)-strong phosphoric acid over the sample. Put 5 to 10 ml. of 5 N sodium hydroxide solution into each of the absorbing apparatuses as shown in Fig. 1. Connect all the apparatuses. Pass hydrogen gas very rapidly through the apparatus for five minutes to expel the air from the apparatus. Then reduce the flow of the gas to rate of one bubble per second. Cover the top of the reaction vessel with a block of diatomaceous earth (D) as shown in Fig. 1. Heat the bottom and the sides of the reaction vessel by passing an electric current through nichrome wires placed in the diatomaceous earth blocks (C). The voltage of the current should be regulated by a variable transformer. It is unnecessary to keep the reaction temperature constant, but it should be high enough that the content of the reaction vessel seems to be solidified when cooled after the reaction. After about twenty or thirty minutes the heating is stopped.

Disconnect the absorbing vessels from the gas-outlet arm of the reaction vessel, and transfer the contentin to a 100 ml. Erlenmeyer flask with sufficient washings of the gas-delivery tube. Add 30% hydrogen peroxide solution carefully, drop by drop, since when a relatively large amount of sulfur is present the oxidation takes place explosively. By the above treatment hydrogen selenide is oxidized to selenic acid, and hydrogen sulfide to sulfuric acid. Boil the solution for about ten minutes to decompose the residual hydrogen peroxide completely, and cool the solution by dipping the vessel in running water. Add enough concentrated hydrochloric acid to neutralize the sodium hydroxide and 20 ml. in excess to the solution. Boil the contents for about twenty minutes

with a reflux. By this treatment the selenic acid is reduced to selenious acid, whereas the sulfuric acid remains unchanged.

(2) *Photometric determination of selenium.*—Transfer the content of the flask into a 100 ml. measuring flask, put 4 ml. of gum arabic solution in it, and add water to make the total volume about 95 ml. Place the vessel in a thermostat kept at 45°C, and when the temperature of the liquid has become constant, add 5 ml. of the tin(II) chloride solution and leave the vessel in the thermostat for about twenty minutes. Then, the selenious acid will have been reduced to colloidal elementary selenium having a red color. Add more water till the liquid level comes to the mark, and measure the absorbancy of the solution with a photoelectric colorimeter using a 372 mμ-filter and 10 mm.-cells.

A working curve for the colorimetric measurement should be prepared by carrying out the same procedure with known amounts of selenious acid.

Results and Discussion

Reduction of Selenious Acid by the Tin(II)-Strong Phosphoric Acid.—A definite volume of the standard selenious acid solution was placed in the reaction vessel and the reduction of the acid and the evolution of hydrogen selenide were carried out by the procedure. The recovery of the selenium is satisfactory as shown in Table I, 0.1 to 2.5 mg. of selenium being recovered with relative deviation not exceeding 5%.

TABLE I. RECOVERY OF SELENIUM BY THE METHOD

Se Taken[a)]	Number of Experiment	Se Found (Average) mg.	Standard Deviation
0.094	4	0.096	0.004_5
0.305	4	0.308	0.012_3
0.471	4	0.465	0.001_7
1.016	4	0.99	0.05_4
1.52	4	1.48	0.03_6
2.03	4	2.04	0.06_7
2.54	4	2.54	0.05_0

a) Selenium was taken as selenious acid.

TABLE II. RECOVERY OF SELENIUM IN PRESENCE OF SULFUR

Na_2SO_4 Taken g.	Se Taken mg.	Se Found mg.	Recovery of Se %
0.2	0.102	0.103	100.9
0.3	0.305	0.314	102.9
0.2	0.508	0.508	100.0
0.2	1.02	1.00	98.0
0.2	1.52	1.48	97.4
0.2	2.03	1.98	97.5
0.2	2.54	2.47	97.3
0.8	0.508	0.508	100.0

Determination of Selenium in Presence of Sulfur.—As selenium is often accompanied with a larger amount of sulfur, it was deemed necessary that the effect of sulfur on this method be first examined. A mixed solution of sodium sulfate and sodium selenite in various ratios was employed for the test, and the determination of the selenium was done according to the procedure described above. The results are shown in Table II, from which it is confirmed that the presence of forty to two hundred parts of sulfur for one part of selenium does not interfere with the determination of the latter. When still larger amounts of sulfur are present in the sample, larger amounts of the tin(II)-strong phosphoric acid should be employed to decompose the sample and to remove the sulfur as hydrogen sulfide. In such cases, a larger amount of the absorbing solution of sodium hydroxide should be used.

Determination of Selenium in Presence of Sulfur and Iron.—Before the method is applied to the determination of selenium in a sulfur-containing ore such as pyrite, the effect of iron should be first examined by carrying out the procedure with a synthetic sample. The analysis was performed with a mixed solution of iron(III) sulfate and sodium selenite for this purpose. As shown in Table III, iron has no influence on the determination of selenium. So the procedure presented above may safely be applied to the determination of selenium in pyrite.

TABLE III. RECOVERY OF SELENIUM IN PRESENCE OF IRON(III) SULFATE

$Fe_2(SO_4)_3$ Taken	Se Taken mg.	Se Found mg.
0.4	0.102	0.102
0.4	2.54	2.54
0.4	0.508	0.504

Determination of Selenium in Pyrite.—As all the sulfur and the selenium in the ore could be removed as hydrogen sulfide and hydrogen selenide, respectively, all troublesome treatments such as the dissolving of the ore in nitric and hydrochloric acids and the evaporation of the solution were dispensed with by a single treatment with the tin(II)-strong phosphoric acid. The results obtained by this method are tabulated in Table IV, which are in good agreement with the results obtained by the ordinary acid-dissolving

TABLE IV. ANALYSIS OF SELENIUM IN PYRITE

(a) TIN(II)-STRONG PHOSPHORIC ACID REDUCTION METHOD

Pyrite Taken g.	Se Found mg.	Se Found p.p.m.
1.24	0.111	89
1.03	0.093	90
2.05	0.187	91
2.01	0.178	89
3.02	0.271	90
2.99	0.258	86

(b) HYDROCHLORIC-NITRIC ACID DECOMPOSITION METHOD

Pyrite Taken g.	Se Found mg.	Se Found p.p.m.
10.0	0.843	84
10.0	0.860	86
10.0	0.868	87

method. This method takes about two hours, while the usual method takes five or more hours.

Color System of Selenium. — Many methods have been described for the colorimetric determination of minute amounts of selenium, e.g., coloration of elementary selenium by reduction with tin(II) chloride or other reducing agents[5], colorization by pyrrol[6], and by diaminobenzidine[7], but the tin(II) chloride method is considered the simplest. So the method was preferred in this study. To determine the optimum operating wavelength for absorption spectrometry of selenium, an absorbancy-wavelength curve was plotted by means of a spectrophotometer (Hitachi Ltd., Model EPU-2). covering the range between 320 and 500 mμ. The conditions of the experiment were the same as those described in the procedure, The curves obtained are shown in Fig. 2, in which it is seen that remarkable absorption takes place in the ultraviolet region, but the absorbancy of the blank, the solution containing no selenium, increases also in the same region. The authors chose 372 mμ as the optimum wavelength, at which the absorbancy of the blank is scarcely perceptible, and the absorbancy obeys Beer's law when the selenium concentration is from 0.1 to 0.25 mg. in 100 ml. The relation between the amount of the selenium taken and the absorbancy measured is expressed by the following equation which was computed from twenty-five measurements by the method of least squares

$$x = 3.558\,I$$

where, x is the amount of selenium taken and I the absorbancy measured. A working curve involves a standard deviation of about 1.5%.

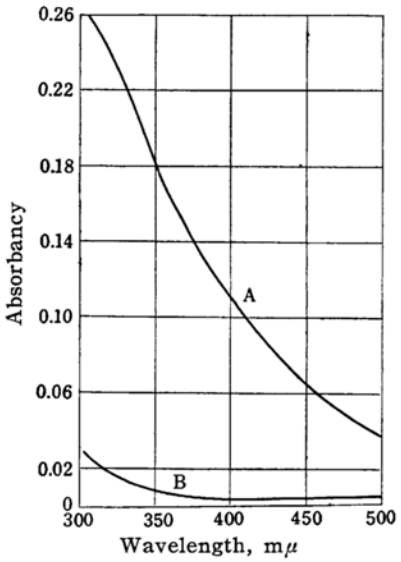

Fig. 2. Spectral absorbance of colloidal selenium.
A: A solution containing 0.6 mg. of selenium, 3 ml. of 15% tin(II) chloride in 9 N hydrochloric acid, and 10 ml. of concentrated hydrochloric acid in 100 ml.
B: The same solution without the selenium.

Summary

A new procedure for a rapid determination of selenium has been devised by the present authors. Tin(II)-strong phosphoric acid, previously prepared by the authors, has a remarkable decomposing and reducing power, and selenium in various forms can be reduced to hydrogen selenide which is evolved as a gas from samples. Sulfur in various forms is reduced to hydrogen sulfide at the same time. Solid samples such as pyrite can be allowed to decompose rapidly by simple heating with the reagent in an atmosphere of hydrogen. The gas evolved is introduced into an absorbing solution of 5 N sodium hydroxide. Then, a small

5) J. Fidler, *Chem. Listy*, **46**, 221 (1952).
6) S. Hirano, M. Suzuki and T. Noguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **55**, 514 (1952).
7) K. L. Cheng, *Anal. Chem.*, **28**, 1738 (1956).
8) H. Goto et al., *Sci. Repts. Research Inst. Tohoku Univ.*, A, **4**, 28 (1952); **4**, 121 (1952); **5**, 34 (1953); **7**, 23 (1955).

volume of 30% hydrogen peroxide solution is added. Thus sodium selenate and sodium sulfate are formed in the solution. After adding an excess of concentrated hydrochloric acid and boiling for about twenty minutes with a reflux condenser, the selenic acid is reduced to selenious acid, while the sulfuric acid remains unchanged. The solution is kept at 45°C for several minutes, and solutions of gum arabic and tin(II) chloride are added successively. The red color of the elementary selenium is measured at 372 mμ by a photoelectric colorimeter. The recovery of selenium is uniform even in the presence of large amounts of sulfur and iron. The analysis of selenium in pyrite was carried out by this procedure, and the results were in good agreement with those obtained by other methods.

The expense of the present research was met in part by a Grant for Scientific Research from the Ministry of Education, to which the authors' thanks are due.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa