# Determination of the Minute Quantities of Silver in Mineral Waters by the Dithizone Method.

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(Received July 28, 1942.)

Silver is fairly widely distributed in various minerals and it is almost invariably found in the sulphide ores of lead, copper and zinc. As has already been reported, acid springs in Japan always contain a considerable amount of copper and zinc, and the author is of the opinion that the source of copper and zinc in mineral springs is usually their sulphide ores. From this it may be deduced that siler is geochemically associated with copper and zinc and that the minute traces of silver are present in acid springs.*

In the previous papers,⁽¹⁾ volumetric and polarographic methods using diphenylthiocarbazone (dithizone) for determining the minute quantities of copper in large amounts of iron, were studied and these methods were applied to the determination of the element in some mineral springs in Japan. The occurrence of copper in a large number of mineral springs in Japan has recently been found by Prof. Kimura,⁽²⁾ and the presence of silver associating with copper in many mineral springs was also found by him.

In the present paper the author has studied the method and found that the minute traces of silver down to 5 $\gamma$ per litre of spring waters could easily be determined by the dithizone method as in the case of the determination of copper in the mineral waters.

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* The silver content of sea water is believed today to be 0.3$\gamma$ per litre, and if the spring waters contain ten times a larger amount of silver than sea water, it is not so difficult to estimate the amount by suitable methods.

(1) Kuroda, this Bulletin, **15** (1940), 439; **16** (1941), 69.

(2) Not yet published.

I. *Determination of the minute Quantities of Silver by the Dithizone Method.* According to H. Fischer(3), volumetric determination of silver by the dithizone method in the presence of copper, lead, zinc, cadmium, arsenic, antimony, bismuth, mercury, gold, etc. gives a satisfactory result. The volumetric procedure is very tedious, however, when the spring water contains a considerable amount of iron. The author has found in the present work that when a large amount of iron is present, it could be removed by ammonia and ammonium carbonate, as in the case of copper which was described in the previous papers, though the analytical procedure becomes rather troublesome.

(a) *When iron is absent.* Add nitric acid to the mineral water, adjust to *p*H 3 and titrate with a carbon tetrachloride solution of dithizone in a separating funnel, shaking vigorously each time. The orange yellow colour of the carbon tetrachloride layer indicates the presence of silver. When silver is absent and copper is present, the carbon tetrachloride layer turns to the green colour of itself or reddish violet colour of copper.

The amount of silver is obtained from the volume of the carbon tetrachloride solution of dithizone which is used to extract the orange yellow dithizone complex of silver.*

(b) *When a large amount of iron is present.* Add nitric acid to a 500 c.c. portion of the mineral water and boil to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) to slight excess and then 5 c.c. of saturated ammonium carbonate solution.** Warm and filter the solution. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1) and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with dilute nitric acid and evaporate to dryness. Dissolve the residue in nitric acid, adjust to *p*H 3 and titrate with a carbon tetrachloride solution of dithizone.

The efficacy of the method was tested by the following experiments.

(1) A known amount ($10 \sim 100\gamma$) of silver and copper was added to dilute nitric acid solution (*p*H 3) and titrated with the carbon tetrachloride solution of dithizone.

(2) A known amount ($10 \sim 60\gamma$) of silver was added to the sulphate solution which contained 100 mg. of iron and the solution was submitted to the complete process of the separation of iron and the volumetric determination of silver by the carbon tetrachloride solution of dithizone.

The following results were obtained. (Tables 1 and 2).

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(3) Fischer, Leopoldi, and Uslar, *Z. Anal. Chem.*, **101** (1935), 1.

* Each c.c. of the dithizone solution used by the author corresponded to $8.3\gamma$ of silver.

** Silver remains in the solution as complex silverdiamine salt: $Ag(NH_3)_2^+$ ions are formed. (Treadwell, Hall, "Analytical Chemistry" I, p. 101.)

As is described in Treadwell's "Analytical Chemistry", ferrous sulphate precipitates gray metallic silver from boiling solutions.

$$Ag^+ + Fe^{++} \rightarrow Fe^{+++} + Ag$$

It is considered, however, that this precipitated silver is redissolved by nitric acid.

Table 1. Volumetric Determinotion of Silver and Copper.

| No. | Added (γ) | | Found (γ) | | Error (γ) | |
|---|---|---|---|---|---|---|
| | Silver | Copper | Silver | Copper | Silver | Copper |
| (1) | 100 | 50 | 97 | 52 | −3 | +2 |
| (2) | 50 | 50 | 54 | 48 | +4 | −2 |
| (3) | 20 | 50 | 22 | 47 | +2 | −3 |
| (4) | 100 | 10 | 99 | 8 | −1 | −2 |

Table 2. Determination of Minute Amounts of Silver in Large Amounts of Iron.

| No. | Iron added γ) | Silver added (γ) | Silver found (γ) | Error (γ) |
|---|---|---|---|---|
| (1) | 100000 | 10 | 13 | +3 |
| (2) | 100000 | 20 | 19 | −1 |
| (3) | 100000 | 40 | 40 | 0 |
| (4) | 100000 | 50 | 53 | +3 |
| (5) | 100000 | 60 | 56 | −4 |

Down to 5γ of silver could be detected, and the results described in Table 2 show that 10γ of silver in 100 mg. of iron could be quantitatively determined by this method.

The spectroscopic test showed the presence of silver in some of the reagents, but the author could not detect it by the dithizone method. The amount of silver derived from the reagents is therefore considered to be less than 5γ. The dithizone solution was purified as was described in the previous paper. Silver was not detected in distilled water, but the presence of copper, lead and zinc was often found in it. (Table 3)

Table 3.

| No. | | (γ/l.) | | | |
|---|---|---|---|---|---|
| | | Cu | Pb | Zn | Ag |
| (1) | Tap Water of Tokyo …… | 28 | 13 | 65 | <1 |
| (2) | Distilled Water ………… | < 1 | 2 | 28 | <1 |
| (3) | Redistilled Water ………… | < 1 | < 1 | 2(?) | <1 |

II. *Silver Content of Some Mineral Springs in Japan.*

(a) *Arc Spectrographic Detection and Estimation of Silver.*

Nitric acid (0.20 c.c.) was added to suitable quantities (100 to 200 c.c.) of the mineral water and the heavy metals were extracted with the carbon tetrachloride solution of dithizone. Sodium nitrate (10 mg.) was added to the carbon tetrachloride solution and evaporated to dryness. The residue was subjected to arc excitation, a Hilger spectrograph of E 2 type being used.

The following lines were found:

### Table 4.

| No. | Mineral Spring | Prefecture | Spectral Lines of Silver | |
|---|---|---|---|---|
| | | | 3280.68 Å | 3382.89 Å |
| (1) | Netunoyu, Sukayu | Aomori | W | W |
| (2) | Hienoyu, Sukayu | Aomori | W | W |
| (3) | Iron Spring No. 1, Sinyu, Sukayu | Aomori | W | F |
| (4) | Iron Spring No. 2, Sinyu, Sukayu | Aomori | W | F |
| (5) | Gongenyu, Yunohanazawa, Hakone | Kanagawa | — | — |
| (6) | Sea Water, Senami | Niigata | — | — |

Pure silver nitrate was dissolved in water and the solutions containing 1, 0.1, 0.01, 0.001 and 0.0001 mg. of silver per c.c. were prepared. Sodium nitrate (10 mg.) was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001 and 0.0001 mg. of silver respectively. The spectral lines observed at different concentrations are described in Table 5. In this Table, VS signifies that the line in question is very strong, S, that it is strong, W, weak, and F, faintly visible.

### Table 5. Spectral Lines of Silver at Different Concentrations.

| λ (Å) | 1 mg. | 0.1 mg. | 0.01 mg. | 0.001 mg. | 0.0001 mg. |
|---|---|---|---|---|---|
| 3280.68 | VS | S | S | W | W |
| 3382.89 | VS | S | S | W | F |

Table 5 shows that 0.001 to 0.0001 mg. of silver was contained in 100 c.c. of the mineral water of Sukayu, and less than 0.0001 mg. in 100 c.c. of the Gongenyu spring and 200 c.c. of sea water. Therefore, the silver content of the hot springs of Sukayu is considered to be from 1$\gamma$ to 10$\gamma$ per litre and that of the Gongenyu spring and sea water, less than 1$\gamma$ per litre.

(b) *Silver Content of the Hot Springs of Sukayu.* Eleven samples of mineral springs in Japan were tested by this dithizone method, but the presence of silver was detected only in the hot springs of Sukayu, in Aomori Prefecture. The results of analysis are shown in Table 6.

### Table 6.

| | | Ag ($\gamma$/l.) |
|---|---|---|
| (1) | Iron Spring No. 1, Sinyu, Sukayu | 12 |
| (2) | Iron Spring No. 2, Sinyu, Sukayu | 15 |

Netunoyu and Hienoyu were not analysed by this dithizone method, but the silver content of these springs is also considered to be about 10 $\gamma$ Ag per litre from the results of spectroscopic estimation described in (a). According to the analysis by the hygienic laboratory in Tokyo. Netunoyu and Hienoyu belong to acid springs, and Sinyu to bitter springs containing gypsum. The water samples used in this series of experiments were usually collected by the author himself, except the mineral waters of Sukayu which were presented by the owner of the hot spring.

## Summary.

(1) Volumetric and spectroscopic methods, using dithizone for determining the minute quantities of silver in the mineral waters, were studied.

(2) The amount of silver in mineral springs was estimated by the dithizone method. The occurrence of silver in the hot springs of Sukayu was spectroscopically detected and estimated to be about $10\gamma$ per litre. The dithizone method gave $12\sim15\gamma$ Ag per litre.

The author expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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