FLUORIMETRIC DETERMINATION OF NANO GRAM AMOUNTS OF SELENIUM IN ROCKS

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A fluorimetric analysis for the determination of nano gram amounts of selenium in rocks has been developed. The analysis has been made up by the procedures of decomposition of rocks, extraction, back-extraction of selenium, and its fluorimetric determination with 2,3-diaminonaphthalene (DAN). The reagent purification steps to minimize its blank value to low as possible have been discussed. Furthermore, the addition of EDTA-NaF to mask coexisting iron in the extraction has been discussed. This fluorimetric method has been applied to the rock reference materials issued by the Geological Survey of Japan.

INTRODUCTION

Trace analysis of nano gram amounts of selenium in rocks has been little reported because of its considerably low content, *e.g.*, 2.7 ppb in granodiorite (JG-1) and 26 ppb in basalt (JB-1)¹⁾. However, using micro gram amounts of selenium many method for rock analyses have previously been summarized²⁾. Neutron activation analysis is one of the highly sensitive methods for the determination of selenium in rocks. However, the following radiochemical steps have been required for the rocks activated by neutron; volatilisation as tetrabromide³⁾ and solvent extraction with 2,3-diaminonaphthalene (DAN)⁴⁾. Fluorimetric analysis is also one of the highly sensitive and convenient methods. The author has presented the fluorimetric method with the DAN reagent for the determination of selenium in sediments⁵⁾, and reported the selenium content of marine sediments to be in the range of 53 - 3177 ppb (47 samples)⁶⁾. However, the previous method is not recommended for the determination of nano gram amounts of selenium in rocks whose selenium content is generally lower than sediments.

In this work, a fluorimetric analysis of nano gram amounts of selenium in rocks has been proposed. This procedure consists of three steps. The first is solvent extraction of selenium with the DAN from rock solutions decomposed by conventional hydrofluoric acid and perchloric acid treatments. The second is back extraction with nitric acid. The third and final step is fluorimetric procedure of selenium with the DAN reagent. In order to determine the nano gram amounts of selenium, the following conditions are essential: (1) reagent blank values should be low and constant, (2) a total reagent blank value throughout all the procedures should be almost equal to the blank value in the fluorimetric procedure, and (3) high precision should be required for the fluorimetric analysis rather than high recovery of selenium in all the procedures. In the proposed analysis, the detailed purification procedure of the DAN reagent to

minimize the blank value has been investigated. Furthermore, the separation procedure of selenium from the interfering ions contained in the decomposed rock solutions has been investigated.

EXPERIMENTAL and RESULTS

Samples, Reagents, and Apparatus

Samples Rock samples issued by Nippon Chikagaku Sha Ltd. were powdered by a steel mortar. The powdered rock was sieved to pass through a 100-mesh size sieve made by plastics, and homogenized by mixing in an agate mill for 10 min and by quartering four times. The segregation and homogeneity of the samples by this preparation have been described by the author⁴⁾⁷⁾. The rock reference materials issued by the Geological Survey of Japan were without the above preparation. All the powder rocks were placed in a desiccator for over 10 days.

Reagents High-purity water, obtained by distilling reverse-osmotic pressed and double-deionized water, was used throughout the present study.

A standard selenium (IV) stock solution (1000 mg/l) was prepared as follows: A 0.1-g portion of high purity metallic selenium (99.999 %) was dissolved with 2 ml of nitric acid and 0.5 ml of 70 % perchloric acid, and then concentrated until white fumes of the perchloric acid appeared. All the selenium in the solution was reduced to selenite by boiling for about 3 min after the addition of 20 ml of 6 M hydrochloric acid. The volume of the selenite solution was made up to 100 ml with the addition of water.

A standard selenium (IV) working solution, containing 0.2 - 10 ng selenium per ml, was prepared by diluting the stock solution with 0.1 M hydrochloric acid.

DAN solution (0.1 % w/v) was prepared by the following purification procedures.

First purification step: A 1-g portion of DAN (2,3-diaminonaphthalene) produced by Tokyo-kase Co. Ltd. or Aldrich Chemical Co. Inc. was dissolved with 20 ml of ethanol on a hot plate. Impurities were filtered with a Toyo No.5 A filter paper, and the filtrate was cooled down to about 0 °C. The recrystallized DAN was filtered with a 3 G glass filter, washed with 20 ml of 50 % cold ethanol, dried in a desiccator for a few days in the dark, and stored in a freezer.

Second purification step: A 0.1-g portion of the dry DAN powder was dissolved on a hot plate with 100 ml of 0.1 M hydrochloric acid containing 0.5 g of hydroxylamine hydrochloride. After cooling, 2 g of sodium anhydride as a salting-out agent was added to the solution in order to extract the fluorescent impurities effectively to the organic phase (see Table 1 and Fig. 1). The DAN solution was adjusted to pH 1 with a few milliliters of hydrochloric acid, transferred to a separatory funnel, and extracted three times using 50 ml of cyclohexane each time (see Fig. 1). The DAN solution was stored in a freezer.

Third purification step: Before experiments, the frozen DAN was dissolved by warming at 50 °C for more than 20 min. After cooling to room temperature, 100 ml of the DAN solution was shaken with 50 ml of cyclohexane, and then the aqueous phase was also shaken with 25 ml of chloroform. The aqueous DAN solution was centrifuged at 3000 rpm for 5 min to separate the chloroform. The DAN solution prepared in the above procedures was used for experiments.

EDTA-NaF solution (0.2 M) was prepared by dissolving 74.5 g of ethylenediaminetetra-

Table 1 Effect of the purification of DAN solutions on the reagent blank values in the fluorimetry of selenium

Purification procedures of DAN solutions	Reagent blank values using DAN solutions (R.F.I.*)
DAN solution (solution No.1)	26.0
Solution No.1 purified by cyclohexane extraction (solution No.2)	18.0
Solution No.1 containing sodium acetate, purified by cyclohexane extraction (solution No.3)	12.3
Solution No.3 purified by chloroform extraction (solution No.4)	10.0
	10.1
	10.4
	10.5
	10.3±0.6
Determination of 10 ng of selenium with the solution No.4	45.3

* Relative fluorescence intensity

Fig. 1 Fluorescent spectra of impurities extracted from DAN solutions

The first extraction of the DAN solution: (1) A Co. Ltd., (2) T Co. Ltd.; The second extraction of the solution: (3) A Co. Ltd., (4) T Co. Ltd.; The third extraction of the solution: (5) A Co. Ltd., (6) T Co. Ltd.

Fig. 2 Calibration curves of selenium

acetic acid disodium salt and 6.7 g of sodium fluoride in water, and making up to 1000 ml with the addition of water.

Cyclohexane and chloroform, commercially available, were used without further purification.

All other reagents and solutions used were of the highest purity available.

Apparatus. Fluorescence- and pH-measurements were made with a fluorescence spectrometer (Hitachi Ltd., model 650-10S, 150 W xenon lamp) and a pH-meter equipped with a glass electrode (Hitachi-Horiba Ltd., model M-7), respectively.

All the glass vessels used throughout this work were free from contamination (see Note 1).

Recommended Procedure of Selenium Analysis

Decomposition Procedure of Rocks Accurately weighed 0.5 g of the finely powdered rock sample was placed in a teflon beaker (Vol. 50 ml), and 6 ml of 46 % hydrofluoric acid and 1 ml of 70 % perchloric acid were added. After being allowed to stand for over one day in a polyethylene box to avoid the contamination of selenium, the mixture in the beaker was concentrated by heating on a hot plate until white fumes of the perchloric acid appeared (see Note 2). To the beaker, 0.5 ml of the perchloric acid was added, and concentrated in the same way. The contents in the teflon beaker was transferred to a 50-ml glass beaker with 4 ml of nitric acid and 0.5 ml of the perchloric acid and concentrated in the same way. One drop of 30 % hydrogen peroxide and 2 ml of 6 M hydrochloric acid were then added, and boiled for about 3 min to reduce chromium (VI) to chromium (III) and selenium (VI) to selenium (IV). After cooling in ice water, 1 ml of acetic acid was added, and the whole volume was made up to about 20 ml with water.

Separation Procedure of Selenium To the decomposed rock solution in the above procedure, specified milliliters (see Table 2) of EDTA-NaF solution and 10 ml of DAN solution (see Note 3) were added. Then the solution was adjusted to pH 1.0 with both saturated sodium acetate solution and 6 M hydrochloric acid. The whole volume of the solution was made up to about 50 ml, and the solution was placed in a thermostat at 50 °C for 10 min. After cooling in ice water, the solution was transferred to a separatory funnel containing 10 ml of cyclohexane, and shaken for 5 min to extract selenium as piasselenol. The organic phase separated was washed by shaking with about 20 ml of 0.1 M hydrochloric acid for a few seconds in order to remove iron and other ions. To the remaining organic phase in the funnel, 5 ml of nitric acid was added, and shaken for 5 min in order to back-extract selenium. The aqueous phase was transferred to a 30 ml-beaker with 1 ml of 70 % perchloric acid, and concentrated on a hot plate until white fumes appeared (see Note 2). To the beaker, 2 ml of 6 M hydrochloric acid was added, and boiled for about 3 min.

Fluorimetric Determination Procedure of Selenium To the selenium (IV) solution separated by the above procedure, 0.25 ml of EDTA-NaF solution and 5 ml of the DAN solution were added. (Use freshly purified DAN solution in the third step.) Then the solution was acidified to pH 1.0 using both hydrochloric acid and saturated sodium acetate solution. The whole volume of the solution was made up to about 20 ml with the addition of water. After being warmed at 50 °C for 20 min (see Note 4), the solution was then cooled, and shaken for 5 min with 10 ml of cyclohexane (see Note 5).

The organic phase was then separated and transferred to a dry stoppered centrifugal tube. This was centrifuged at 3000 rpm for 5 min. The fluorescent spectrum of piazselenol in the cyclohexane was measured at the excitation wave length of 378 nm (see Note 6).

The recovery of selenium throughout the procedures described above was obtained to be 87.3 ± 1.6 % in 3 determinations using 10 ng of selenium. In order to determine the concentration of selenium in a sample solution, the calibration curve was established using a standard solution which was treated by the same procedures as the sample solution.

Calibration Curve of Selenium Figure 2 shows the calibration curve of selenium in the fluorimetric procedure using 10 ml of cyclohexane containing from 0.2 ng to 10 ng of selenium, *i.e.*, corresponding to from 0.02 ppb to 1 ppb of selenium solution. In addition, there was also a same linear line as the calibration in more than 10 ng of selenium. In this fluorimetric procedure, it is essential to minimize the reagent blank value as low as possible to determine the nano gram amounts of selenium (see Table 1). Since there is an experimental fact that the total blank value throughout the procedures was equal to that in the final fluorimetric procedure, the detection limit of selenium in this fluorimetric analysis depends on only the reagent blank value. The actual detection limit of this analysis can be estimated to be 0.05 ng of selenium (corresponding to 5 ppt), although the higher sensitivity can be detected by the fluorimeter.

Effect of the Coexisting Ions on the Extraction of Selenium in Rock Solutions

In the previous paper⁵⁾ concerning the fluorimetric analysis of selenium in sediments, the DAN reagent has been used as a selective chelating agent for extracting selenium into cyclohexane from the decomposed sediment solution. In the extraction, 1 ml of 0.1 M EDTA-NaF solution was added to the sediment solution (0.05 - 0.2 g of sediments) as a masking solution of the coexisting ions; such as iron, copper, magnesium, nickel, titanium, and so on.⁹⁾ Without the existence of the above agents, a precipitate appeared by the reaction of these ions with the DAN.⁵⁾ When the previous method⁵⁾ was applied to rock analyses, selenium content of the rocks could not be determined (*e.g.*, see Fig. 3). This was because large amounts of iron interfered with the fluorimetric analysis of selenium. This occurred even if the definite amounts of EDTA-NaF were added in the decomposed solution.

Figure 4 shows the masking effect of EDTA-NaF against iron in the fluorimetric determination of selenium. In this experiment, 20 ng of standard selenium (IV) solution containing 50 mg of iron (III) was prepared, and determined by the recommended procedure described above. The lack or less amounts of the addition of the masking agents brought a brown precipitate in the reaction of DAN with iron. Also this gave a different spectrum from piazselenol, as shown in Fig. 4. Those spectra were identified as those due to the impurity produced by the decomposition of DAN, whose fluorescent spectra are presented in Fig. 1. As the results of the experiment, it was found that 6.25 ml of the masking solution should be added to the solution containing 50 mg of iron. Since the content of iron in rocks varies with the sort of rocks as shown in Table 2, the amounts of the masking agents to be used can be estimated from the iron content of the rocks. However, the excess addition of the masking agents is not recommended, because a white precipitate

Fig. 3 Fluorescent spectra for rocks by the previous method⁵⁾
 (1) JGb-1 (0.5 g); (2) JB-3 (0.5 g); (3) JB-1 (0.5 g); (4) Standard selenium (15 ng); (5) Reagent blank

Fig. 4 Masking effect of EDTA-NaF against iron on the fluorimetric determination of selenium

Iron (III) 50 mg; Selenium 20 ng;
 0.2 M EDTA-NaF: (1) 0 ml; (2) 1.25 ml;
 (3) 6.25 ml; (4) 12.5 ml; (5) 25 ml

Table 2 Average iron content of rocks and the recommended amounts of masking agents to be added

Rock	Fe ₂ O ₃ * (%)	FeO* (%)	Total Fe (%)	Fe in 0.5 g of rocks (mg)	Masking agents 0.2 M EDTA-NaF (ml)
Granite	1.57	1.78	2.47	12	2 - 3
Andesite	3.33	3.13	4.76	24	3 - 4
Diolite	3.16	4.40	5.36	28	4 - 5
Gabbro	3.16	5.95	6.83	34	5 - 6
Basalt	5.37	6.34	8.69	44	6 - 7
Tholeiite	2.73	9.20	9.60	45	6 - 7

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of the agents may appear and interfere with the separation procedure of selenium.

Selenium Content of Rocks

Table 4 lists the selenium content of rocks determined by the proposed method. The amounts of the masking agents added are also listed in the same Table. Analytical values of selenium in JG-1 and JB-1 were almost equal to those obtained by neutron activation analysis.¹⁾³⁾

Table 3 Selenium content of rocks

Sample	Addition of 0.2 M EDTA-NaF (ml)	Selenium content (ng/g)
Granodiorite G.S.J. JG-1	2	3±2 (n=3) 2.7*
Alkali basalt G.S.J. JB-1	5	21±4 (n=4) 26*
Tholeiite basalt G.S.J. JB-2	6	123±4 (n=3)
High-alumina basalt G.S.J. JB-3	6	54±1 (n=3)
Andesite G.S.J. JA-1	4	9±2 (n=2)
Gabbro G.S.J. JGb-1	6	136±0 (n=3)
Rhyolite G.S.J. JR-1	1	6±1 (n=4)
Rhyolite G.S.J. JR-2	1	3±1 (n=4)
Biotite granite Abukuma, Ibaragi Pref.	2	5 (n=1)
Biotite granite Kitashirakawa, Kyoto	2	less than 0.1 (n=1)
Olivine trachy basalt Toyooka, Hyogo Pref.	6	7 (n=1)
Olivine trachy basalt Fukue, Nagasaki Pref.	6	8 (n=1)
Hornblende quartz diolite Tanba, Gifu Pref.	4	75 (n=1)

* Terada et al.³⁾

n: Number of determinations

NOTES

Note 1: Glass vessels should be usually digested in about 5 M nitric acid for a few days, after the vessels were washed with a neutral detergent commercially available. If the contamination of selenium or fluorescent contamination from the vessels were found, the vessels should be digested in the mixture of nitric acid and sulfuric acid (1+1) for a few hours, and then in the 5 M nitric acid.

Note 2: In the concentration step of the rock solution, the solution should not be dried up, or else selenium will volatilise as halide, *e.g.*, SeCl_4 .

Note 3: It is not necessary to use the most purified DAN solution.

Note 4: In the warming step, the beaker should be covered with a watch glass to avoid any contaminations.

Note 5: If the amounts less than about 10 ng of selenium are contained, use 5 ml of cyclohexane for the extraction.

Note 6: It is essential to measure the fluorescent spectra in order to identify the piasselenol for the fluorimetric analysis of ultra trace selenium, because the other fluorescent spectrum may appear due to the contamination of organic materials or decomposition products of the DAN reagent (see Figs. 1, 3, and 4).

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