Neutron-activation Analysis of Selenium, Osmium and Ruthenium in Rocks, Sediments and Biological Materials by Successive Distillations with Three Kinds of Strong Phosphoric Acid Reagents*

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A new separation scheme is presented for the neutron-activation analysis of selenium, osmium and ruthenium in solid samples such as rocks, sediments and biological materials. A neutron-irradiated sample accompanying the carriers of the three elements was heated with the bromide-SPA reagent to 250 °C, whereupon selenium came out as gaseous selenium tetrabromide. The second distillation was performed by heating the residual sample with Ce(IV)-SPA reagent till 285 °C to separate osmium as osmium tetroxide gas. The last distillation of ruthenium as ruthenium tetroxide followed under heating the residue with the Cr(VI)-SPA reagent till 245 °C. Each distillate was absorbed in an appropriate absorbing solution from which selenium metal, osmium thiourea chromithiocyanato complex, and ruthenium metal were respectively recovered and they were submitted to γ-counting by means of a Ge(Li) detector coupled with a multi-channel pulse height analyzer. The chemical recoveries of the added carriers were found to be about 80% for selenium and above 90% for osmium and ruthenium.

Because of its excellent decomposing power against various insoluble solid samples, strong phosphoric acid(SPA) is very useful in chemical analysis to avoid tedious treatments for samples such as fusion with flux or dissolution by acids.[1] The SPA treatment of samples can be done in a closed system throughout the analysis, therefore losses of the elements upon the decomposition can be prevented, and the method might be most effectively employed in the activation analysis of various solid samples.

Previously[2] the present authors reported the chemical separation and determination of osmium and ruthenium in the neutron-irradiated samples such as rocks, sediments, and biological materials, where two kinds of strong phosphoric acid reagents, Ce(IV)-SPA and Cr(VI)-SPA, were employed successively. In spite of the excellent results for the separation of the two elements, it was found in the distillation of osmium tetroxide some radioactive nuclides were apt to be accompanied in the distillate: those were selenium, iodine, bromine, mercury and arsenic. Among them Se-75 had to be removed prior to the distillation of osmium because, if it came in the distillate, its photopeaks of 121.0 keV and 136.6 keV locate too close to distinguish from those of 129.4 keV and 139.0 keV of Os-191. In order to make the separation of selenium feasible in the same SPA medium, various reagent-SPA systems were examined, and finally ammonium bromide-SPA reagent has been found most preferable for the purpose.[3] By heating the sample with this ammonium bromide-SPA, selenium(IV) and (VI) can be evolved as selenium tetrabromide in gaseous state, while osmium and ruthenium are not affected at all. Accompaniment of arsenic, iodine, bromine, and mercury to the selenium tetrabromide distillate seemed unavoidable, but these do not interfere the radiochemical determination of selenium. Therefore, the distillation of selenium is well suited as the treatment preceeding the Ce(IV)-SPA treatment for osmium and the Cr(VI)-SPA treatment for ruthenium. Thus, three successive distillations for selenium by ammonium bromide-SPA, for osmium by Ce(IV)-SPA, and for ruthenium by Cr(VI)-SPA could finish the complete separation of the three elements taking only one specimen from the sample.

* Part of this work was done at the Research Reactor Institute, Kyoto University.

Experimental

Reagents. *Strong Phosphoric Acid (SPA)*: SPA was prepared from orthophosphoric acid of extra-pure reagent grade as described previously.[2,3]

Standard Selenium Solution (1 mg/ml): Anhydrous sodium selenite of guaranteed reagent grade was dissolved in 0.1 M hydrochloric acid, and the solution was standardized by iodimetric titration.

Osmium Standard Solution (2 mg/ml) and Ruthenium Standard Solution (2.5 mg/ml): Their trichlorides of guaranteed reagent grade were dissolved in 2 M hydrochloric acid, respectively. They were standardized gravimetrically as thiourea chromithiocyanato complex for osmium and as metal for ruthenium.

Radioactive Tracers: Se-75, Re-186 and Os-191 were prepared by irradiation of each pure metal of them in the KUR, Research Reactor Institute, Kyoto University. On the other hand, As-74, Br-82, Fe-59, Hg-203, I-131, Ir-192, Ru-106, Sb-124, and Sn-113, those purchased from the Radiochemical Centre (England), New England Nuclear Corp. (U.S.A.), Union Carbide Corp. (U.S.A.), Japan Atomic Energy Research Institute (Japan) and Dainabot RI Lab. (Japan). Tc-99 m was obtained by milking of Ultratechnecow which was purchased from Mallincrodt Chemical Works (U.S.A.). Other chemicals were of guaranteed reagent grade.

Apparatus. A well-type γ-ray scintillation counter, Kobe Kogyo Co., Model STL-200 and a 2-cm^3 Ge(Li) detector, ORTEC Model 8100-45 having a resolution of about 2.5 keV for the 1335-keV gamma-peak of Co-60 were used, being coupled with a 400 channel pulse-height analyser, TMC Model 401D, and a printer Model 500P, to determine the radioactivity.

The reaction vessel and the absorption tubes were all the same as those recommended in the previous report.[3]

Procedure. Each 0.5—1.0 g of the finely-ground rocks, sediments or biological materials was accurately weighed and sealed in a clean silica tube. For the standard, about 0.01 ml of 500-ppm standard selenium solution, 10-ppm standard osmium solution and 10-ppm standard ruthenium solution were placed in separate small silica tubes by microsyringe,

respectively, then weighed, dried and sealed. The samples and the standards were irradiated with a thermal neutron flux of 4.65×10^{13} n·cm^{-2}·sec^{-1} for 80 hr at Research Reactor Institute, Kyoto University.

After cooling for 4—5 days, the sample was transfered into the SPA reaction vessel together with non-radioactive carriers of the elements in question, *i.e.*, 10 mg of Se(IV), 4 mg of Os(III), and 10 mg of Ru(III).

About 30—40 g of SPA and about 0.1—0.2 g of ammonium bromide were added to the reaction vessel. The vessel was connected with the absorption tubes which contain each 10 ml of a 1: 1 v/v mixture of 0.3 M hydrochloric acid and 0.6 M perchloric acid. The air was sucked slowly from the last outlet tube with a pump and the reaction vessel was heated with an electric heater to start the reaction. Within 30—50 min the temperature of the contents in the vessel was raised to 250 °C. After the distillation, the heating was stopped and all the connections were disconnected. The absorbing solutions and washings were combined in an Erlenmeyer flask (100 ml), and the solution was made about 6 M in hydrochloric acid, heated on the water-bath, added with about 3 ml of 10% tin(II) chloride solution (in concentrated hydrochloric acid) and digested for 1 hr. The precipitate was filtered off on a previously weighed glass-fiber filter paper (Toyo Roshi, GB-60), washed successively, with 6 M hydrochloric acid, distilled water and ethyl alcohol, then dried at 110 °C and weighed. The final precipitate was wrapped in a "Mylor" film or paraffin-waxed paper and the 136.0 or 264.6 keV photopeaks of Se-75 (121 d) was counted with a Ge(Li) solid-state detector coupled with a 400 channel pulse-height analyser.

After the separation of selenium as described above, about 4 g of cerium(IV) sulfate was put into the reaction vessel which must be cooled to below 100 °C after the selenium distillation. The vessel must be cooled whenever the reagent is added, to make the dissolution of the reagent uniform in the SPA medium. The osmium was distilled by heating the reaction vessel to 285 °C within 30—40 min. The absorbing solution was 1: 1 v/v 2% thiourea and 2 M hydrochloric acid mixture. After distillation the absorbing solution and washings were transfered into a beaker (100 ml) to make the volume about 50 ml. One milliliter of 40% potassium chromithiocyanate solution[4] was added and the contents were stirred vigorously until precipitation was complete. The precipitate was filtered as described in the selenium determination, and washed several times with distilled water, dried at 105 °C for 1 hr, then weighed. Finally, the 129.4 keV photopeak of Os-191 (14.6 d) was counted as same as for selenium.

After the second distillation about 2 g of potassium dichromate (in 2 or 3 portions) was put into the vessel, in the same way for osmium. The ruthenium was distilled by heating the reaction vessel to 240 °C within 30—40 min. The absorbing solution was 1: 1 v/v 6 M hydrochloric acid and ethyl alcohol mixture. After distillation the absorbing solution and the washings were transfered into an Erlenmeyer flask (100 ml) and was diluted with distilled water to about 1 M in hydrochloric acid. About 1.3 g magnesium powder was put little by little into the flask to reduced Ru(III) to Ru(0), followed by heating to coagulate the precipitate on a water-bath. The excess of magnesium was dissolved by a drop-wise addition of concentrated hydrochloric acid to be required and the solution was heated gently. The ruthenium metal thus obtained was collected on a glass-fiber filter paper, and washed several times with hydrochloric acid, distilled water, ethyl alcohol and ethyl ether, successively. The precipitate was dried at room temperature for 2 hr under reduced pressure, and weighed. The 215.8 keV photopeak of Ru-97 (2.88 d) was counted with a Ge(Li) solid-state detector.

Nuclear Data

Naturally occurring selenium consists of six isotopes, Se-74(0.87%), Se-76(9.02%), Se-77(7.58%), Se-78 (23.52%), Se-80(49.82%) and Se-82(9.19%). Some of these isotopes give rise to radionuclides when subjected to the irradiation with thermal neutrons, these are as follows:

$$^{74}\mathrm{Se}(n,\gamma)^{75}\mathrm{Se} \xrightarrow[t=121\,\mathrm{d}]{\mathrm{EC}} {}^{75}\mathrm{As}$$

$$^{78}\mathrm{Se}(n,\gamma)^{79m}\mathrm{Se} \xrightarrow[t=3.91\,\mathrm{m}]{\mathrm{IT}} {}^{79}\mathrm{Se} \xrightarrow[t=6.5\times10^{4}\,\mathrm{y}]{\beta^-} {}^{79}\mathrm{Br}$$

$$^{80}\mathrm{Se}(n,\gamma)^{81m}\mathrm{Se} \xrightarrow[t=57\,\mathrm{m}]{\mathrm{IT}} {}^{81}\mathrm{Se} \xrightarrow[t=18\,\mathrm{m}]{\beta^-} {}^{81}\mathrm{Br}$$

$$^{82}\mathrm{Se}(n,\gamma)^{83}\mathrm{Se} \xrightarrow[t=23\,\mathrm{m}]{\beta^-} {}^{83}\mathrm{Br} \xrightarrow[t=2.40\,\mathrm{h}]{\beta^-} {}^{83}\mathrm{Kr}$$

Among them Se-75 is the most useful nuclide to estimate the total amount of selenium in the present study.

Osmium consists of seven isotopes, Os-184(0.01%), Os-186(1.59%), Os-187(1.64%), Os-188(13.3%), Os-189(16.1%), Os-190(26.4%) and Os-192(41.0%). The nuclear data are as follows:

$$^{184}\mathrm{Os}(n,\gamma)^{185}\mathrm{Os} \xrightarrow[t=94\,\mathrm{d}]{\mathrm{EC}} {}^{185}\mathrm{Re}$$

$$^{190}\mathrm{Os}(n,\gamma)^{191m}\mathrm{Os} \xrightarrow[t=14\,\mathrm{h}]{\mathrm{IT}} {}^{191}\mathrm{Os} \xrightarrow[t=15\,\mathrm{d}]{\beta^-} {}^{191}\mathrm{Ir}$$

$$^{192}\mathrm{Os}(n,\gamma)^{193}\mathrm{Os} \xrightarrow[t=31\,\mathrm{h}]{\beta^-} {}^{193}\mathrm{Ir}$$

Osmium was determined in terms of the nuclide Os-191-(15 d) in all cases, and in some cases in terms of the nuclide Os-185 (31 hr).

Naturally occurring ruthenium consists of seven isotopes: Ru-96(5.57%), Ru-98(1.91%), Ru-99(12.7%), Ru-100(12.0%), Ru-101(17.0%), Ru-102(31.5%) and Ru-104(18.5%). The production and the decay of the radionuclides are represented by the following sequences:

$$^{96}\mathrm{Ru}(n,\gamma)^{97}\mathrm{Ru} \xrightarrow[t=2.88\,\mathrm{d}]{\mathrm{EC}} {}^{97m}\mathrm{Tc} \xrightarrow[t=91\,\mathrm{d}]{\mathrm{IT}} {}^{97}\mathrm{Tc} \xrightarrow[t=2.6\times10^{6}\,\mathrm{y}]{\mathrm{EC}} {}^{97}\mathrm{Mo}$$

$$^{102}\mathrm{Ru}(n,\gamma)^{103}\mathrm{Ru} \xrightarrow[t=39.8\,\mathrm{d}]{\beta^-} {}^{103m}\mathrm{Rh} \xrightarrow[t=57\,\mathrm{m}]{\mathrm{IT}} {}^{103}\mathrm{Rh}$$

$$^{104}\mathrm{Ru}(n,\gamma)^{105}\mathrm{Ru} \xrightarrow[t=4.5\,\mathrm{h}]{\beta^-} {}^{105m}\mathrm{Rh} \xrightarrow[t=45\,\mathrm{s}]{\mathrm{IT}} {}^{105}\mathrm{Rh} \xrightarrow[t=36.5\,\mathrm{h}]{\beta^-} {}^{105}\mathrm{Pd}$$

Taking into consideration of possible interferences from the nuclear reactions: U(n,f)^{103}Ru, U(n,f)^{105}Ru and U(n,f)^{106}Ru, Ru-97 was used for the determination of ruthenium.

Results and Discussion

Distillation Recovery of Selenium. Various solid chlorides and bromides were tested for the SPA decom-

position and distillation, and the amount of selenium distilled was determined radiometrically in every cases. As the results, ammonium bromide was found the most useful for the purpose. The following reactions might take place simultaneously[5]:

$$H_2SeO_3 + 4HBr \longrightarrow SeBr_4 + 3H_2O$$

$$H_2SeO_4 + 2HBr \longrightarrow H_2SeO_3 + Br_2 + H_2O$$

Consequently, in the presence of bromide Se(IV) and Se(VI) can evolve themselves as gaseous selenium tetrabromide from a solid matrix such as rocks, sediments, and biological materials, by heating the samples with ammonium bromide in strong phosphoric acid. Under the condition, elemental selenium and selenide were not affected at all, however, these species could react with bromide after converting them to selenite state by adding 40—50 mg of potassium iodate in the SPA medium as reported previously.[3]

Ammonium bromide together with potassium iodate was found not to react with osmium and ruthenium, and their tetroxide did not appear at all in the absorbing solution as shown in Table 1 which exhibits also the recoveries of selenium, osmium and ruthenium at various temperatures of the SPA media. It is seen that selenium is completely distilled till the temperature reached about 250 °C.

Table 1. Recovery of selenium, osmium and ruthenium at various temperatures of the SPA medium

Reagent (g/30 g SPA)	Temp. °C	Recovery after distillation, %		
		Se	Os	Ru
NH_4Br (0.1) + KIO_3 (0.04)	220	83—85	0	0
	240	93—95	0	0
	250	98—99	0	0
	260	98—99	0	0
	270	94—96	0	0
$Ce(SO_4)_2$ (4)	210		60—70	0
	250		85—90	0
	280		98—99	0
	285		99	0
$K_2Cr_2O_7$ (2)	180			95
	210			99
	230			100
	240			100

Carriers added: Se(IV): 10 mg, Os(III): 4 mg
Ru(III): 10 mg.

Furthermore, the time taken to raise the temperature to 250 °C seemed affect the recovery of selenium tetrabromide. Too fast and too slow heating gave poor recovery of the element. The heating to 250 °C should be done for 30 to 50 min.

Next, various kinds of absorbing solutions were examined for quantitative trapping of the distilled selenium tetrabromide. A 1: 1 v/v mixture of 0.3 M hydrochloric acid and 0.6 M perchloric acid was found to give the best results.

Distillation Recovery of Osmium. The osmium should be oxidized to Os(VIII) and evolved as the tetroxide from the matrix. Spectrophotometric method with thiourea and radioisotopic tracer method were used to find a suitable reagent for the oxidation of osmium. The results show that osmium in various forms, *e.g.*, metal, sulfide, tetrahydroxide and tetroxide, could be distilled quantitatively by means of Ce(IV)-SPA. Ruthenium did not react with cerium(IV) sulfate and not evolve its tetroxide. This fact was explained by Rao's experiments for the formal redox potentials in phosphoric acid of increasing concentrations.[6] The results indicate that cerium(IV) sulfate behaves as a less powerful oxidant than potassium dichromate in SPA contrarily the order of their ordinary oxidation potentials in an aqueous solution. In Table 1, the recovery of osmium is given as a function of temperature. It is seen that the heating to 280 °C or more bring the quantitative recovery of osmium.

Osmium tetroxide evolved could be absorbed in alkaline solution or a mixture of 6 M hydrochloric acid and ethyl alcohol (1: 1 v/v), plus 1 ml of 10% thiourea solution.[2] But in the present study 2% thiourea and 2 M hydrochloric acid mixture (1: 1 v/v) was preferably employed as an absorbing solution for the convenience of the subsequent precipitation of $Os(NH_2 \cdot CS \cdot NH_2)$-$Cr(SCN)_6$. In the presence of ethyl alcohol in the absorbing solution no precipitate appears because the complex can be easily dissolved in ethyl alcohol. The chemical yield is generally 90—95%.

Distillation Recovery of Ruthenium. As described in the previous report[2] potassium dichromate was found the most suitable oxidizing reagent for ruthenium in SPA medium. Ruthenium can be distilled quantitatively by heating with Cr(VI)-SPA to 240 °C and absorbed in 1: 1 v/v mixture of 6 M hydrochloric acid and ethyl alcohol (Table 1).

The time required for completion of reaction was examined and the results showed that the chloride was the most easily decomposed, taking only about 5 min, but sulfide and metallic ruthenium were more resistant, since it took about 30 min to complete the distillation of ruthenium tetroxide.

Table 2. Distillation of various elements by SPA method

Element	Recovery, %		
	Br^--SPA (250 °C)	Ce(IV)-SPA (285 °C)	Cr(VI)-SPA (245 °C)
As(III)	>95	0— 2	0— 2
Br^-	>95	>95	>95
Cl^-	>95	>95	>95
Fe(III)	0	0	0
Hg(I, II)	>95	0—10	10—20
I^-	>95	>95	>95
Ir(IV)	0	0	0
Mn(II)	0	0	0
Os(III)	0	100	100
Re(VII)	0	0	0
Ru(III)	0	0	100
Sb(III, V)	~2	40—60	30—40
Se(IV, VI)	100	0	0
Sn(II, IV)	~3	0	0
Tc(VII)	0	10—20	10—20
Te(IV, VI)	~10	0	0

Behavior of Other Elements. Other elements giving their volatile bromides, oxides as well as volatile acids are believed to be released from their acidic solutions by heating.[7] Table 2 shows that more than 95% of As(III), Br^-, Cl^-, I^- (as hydrohalogenic acid), Hg(I, II), and a few per cent of Sb(III, V), Sn(II, IV) and Te(IV, VI) are driven off from Br^--SPA medium by heating. On the other hand, distillation of As(III) and Hg(I, II) do not exceed a few per cent and 20%, respectively, from Ce(IV)-SPA and Cr(VI)-SPA. In conclusion, not only selenium but other volatilizable elements are almost distilled off on the first Br^--SPA distillation, and hence they do not appear in the absorbing solutions of the second and third distillation with Ce(IV)-SPA and Cr(VI)-SPA. Thus osmium and ruthenium could be separated quantitatively without contaminations except some of technetium species which might be produced secondary from molybdenum [$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow{\beta^-} {}^{99m}Tc(t=6.04\ hr)$ and $^{100}Mo(n,\gamma)$-$^{101}Mo \xrightarrow{\beta^-} {}^{101}Tc(t=14.0\ min)$]. In the present study the interferences by these nuclides were found to be neglible.

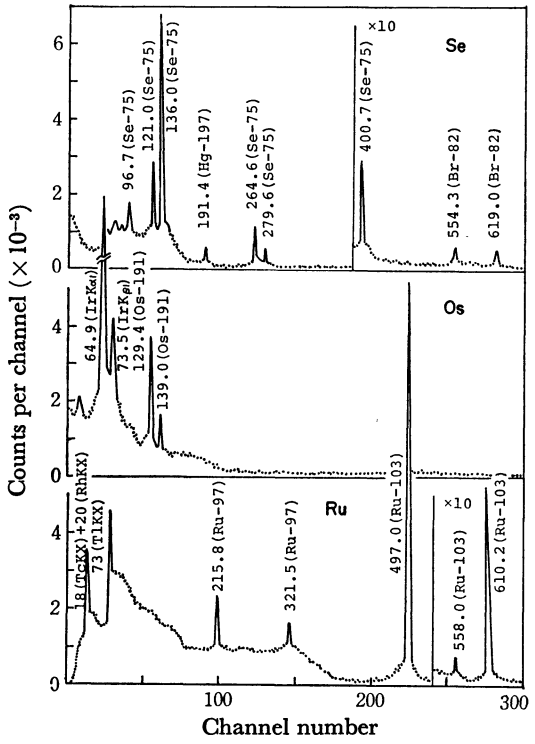

Fig. 1. Gamma-spectra of selenium-, osmium- and ruthenium-fractions after the separation by SPA method (Marine sediment, Japan Sea).

Successive Distillations for Selenium, Osmium and Ruthenium. Successive distillations were tried for marine sediment samples which were collected from the bottoms of Japan Sea, and of Pacific Ocean. One gram of the dried sample was irradiated and processed by the present method as described above, and the final counting samples were submitted to γ-counting. The typical γ-spectra of each fraction separated by the method are shown in Fig. 1. From these spectra, the selenium fraction after Br^--SPA treatment is seen to be contaminated with some of the other nuclides, mainly with Hg-197(65 hr) and Br-82(35.87 hr). However, these radionuclides do not interfere the determination of selenium. On the other hand, the osmium and ruthenium fractions after the Ce(IV)-SPA and then Cr(VI)-SPA treatment were not contaminated with any other radionuclides. In the γ-spectrum of the ruthenium fraction a large photopeak of 497.0 keV appear and it seems to be attributed to mainly Ru-103 produced by fission of uranium existing in the sediment sample. Fission product Ru complicates seriously the determination of ruthenium by the activation analysis. In several sediment samples, ruthenium was characterized by radiation from Ru-103 only and no Ru-97 component could be identified from γ-spectra. According to Gijbels,[8] when the U/Ru ratio is unity the error caused by simply measuring Ru-103 is *ca.* 12%. However, when U/Ru ratio is higher as in the case of marine sediments (10^3—10^4), the ruthenium determination *via* Ru-103 poses a significant problem. It is thus necessary to measure the Ru-97 activity to obtain the reliable results.

Table 3. Selenium, osmium and ruthenium contents of the standard rocks and marine sediments

	Se, ppb	Os, ppb	Ru, ppb
Standard rock			
JG-1 (5)	2.7±0.2	2.7±0.2	n.d.
JB-1 (5)	26 ±2	1.9±0.2	n.d.
Marine sediment			
0°00′00″ N 150°04′07″ E (3)	470	1.0	n.d.
0°48′08″ N 163°59′05″ E (3)	870	9.8	3.6
37°24′ N 132°03′ E (3)	2600	16	8.2
38°33′ N 131°01′ E (3)	910	17	4.3

Determination of Selenium, Osmium and Ruthenium in Rocks and Marine Sediments. The separation and determination of selenium, osmium and ruthenium in standard rock samples and marine sediments were tried by the proposed method. The results are shown in Table 3. Selenium and osmium contents in the standard rocks, JG-1 and JB-1 are the average of five determinations, respectively. Ruthenium was not identified in the present condition. The values for marine sediments are the average of three determinations, respectively. Some sediments were found to contain measurable amount of selenium, while osmium and ruthenium could not be determined, therefore these analytical results are omitted in the table.

The chemical recoveries of the added carriers were in the range 80—85%, 90—95% and 90—95% for selenium, osmium and ruthenium, respectively, within the error of ±10%. The time required for the completion of the radiochemical separation of a sample was about 3 hr.

It will be expected that the present SPA method is applicable for the simultaneous determination of selenium, arsenic, mercury, and bromide from a single

sample and the technique will be described elsewhere.

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References

1) T. Kiba, *Bunseki Kagaku*, **9**, 651 (1960).
2) T. Kiba, K. Terada, T. Kiba, and K. Suzuki, *Talanta*, **19**, 451 (1972).
3) K. Terada, T. Ooba, and T. Kiba, *ibid.*, **22**, 41 (1975).
4) J. W. Morgan, *Anal. Chim. Acta*, **32**, 8 (1965).
5) I. M. Kolthoff and P. J. Elving ed., "Treatise on Analytical Chemistry," Part II, Analytical Chemistry of the Elements, Vol. 7, Interscience Publishers, New York, N. Y. (1961), p. 147.
6) G. G. Rao, *Talanta*, **10**, 1251 (1963).
7) E. B. Sandell, "Colorimetric Determinations of Traces of Metals," 3rd. Ed., Interscience Publishers, New York, N. Y. (1959), p. 72.
8) R. Gijbels, *Talanta*, **18**, 587 (1971).