Simultaneous Determination of Radioactive and Stable Isotopes of Cobalt in Environmental Samples by the Isotopic Exchange Method

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The isotopic exchange method is studied for the simultaneous determination of radioactive and stable isotopes of cobalt in environmental samples. Radioactive cobalt is isotopically exchanged with Co-CyDTA in HCl solution of the sample. The solvent extraction method is used for the separation of Co^{2+} and Co-CyDTA species from each other. The amounts of radioactive and stable cobalt isotopes are calculated with activities of Co and Co-CyDTA at the exchange equilibrium. The methods for eliminating interfering ions are discussed. The results are in good concordance with those obtained by the conventional analytical methods.

Key Words isotopic exchange analysis, environmental radioactivity, cobalt, cobalt-60

1. Introduction

The determinations of both the activity of a radioactive nuclide and the amounts of its stable isotope are often necessary and useful in the studies on the behavior of the radio-nuclide in the environment. In this case, the activity is usually determined by some radio-chemical method, and the amounts of the stable isotope is determined separately by some adequate conventional method¹⁾⁻³⁾. If the simultaneous determination of radioactive and stable isotopes of an element could be possible, it would be very much convenient and advantageous. For this purpose, the authors proposed in the previous paper⁴⁾ the substoichiometric method of analysis for determination of radioactive and stable cobalt isotopes. In this work, a new type of the isotopic exchange method has been developed and applied to the simultaneous determination of radioactive and stable cobalt in some environmental samples.

2. Principle

A definite amount of cobalt(II) cyclohexane-diaminetetraacetate (Co-CyDTA) (weight of Co : m) is added to a hydrochloric acid solution of a sample which contains unknown

amounts of the radioisotope (activity : A_x) and the stable isotope (weight : M_x) of cobalt to be determined, and mixed. Then, the following isotopic exchange reaction proceeds rapidly.

After the exchange equilibrium is attained, Co^{2+} ions are separated from Co-CyDTA by extracting Co^{2+} with an appropriate solvent. The activity of each phase is measured (A for Co^{2+} and a for Co-CyDTA). As the specific activity of radiocobalt in the separated phase is unchanged from that in the solution before extraction, the next equation holds.

$$A_x / (M_x + m) = A / M_x = a / m$$

A_x and M_x are then obtained as follows:

$$A_x = A + a$$

$$M_x = m \cdot (A/a)$$

As it is possible to maintain the amount m constant throughout a series of analyses, M_x is proportional to A/a . M_x is, therefore, determined by using a calibration curve which is obtained by plotting the corresponding A/a values against a series of known amounts of Co^{2+} ions. Unknown activity and amounts of radioactive and stable cobalt isotopes, respectively, can be thus determined by only activity measurement.

3. Experimental

3.1 Preparation of Co-CyDTA solution

A definite amount (1 g) of cobalt metal was dissolved in 10 ml of conc. HCl. The solution was evaporated to dryness. The residue was dissolved in 5 ml of 0.01 M HCl. On the other hand, 6 g of CyDTA was dissolved in 20 ml of nearly saturated KOH solution. These two solutions were mixed to form Co-CyDTA complex ions and diluted to 50 ml with 0.01 M HCl. The mixed solution was further diluted to suitable concentration for use. Mixing was done just before use.

3.2 Preliminary experiment

To verify the above-mentioned principle experimentally, the mock sample solution which contains the known activity of ^{60}Co and the known amount of stable cobalt was first analysed.

A 50 ml portion of 0.01 M HCl solution which contains 14–75 $\mu\text{g/ml}$ of stable Co^{2+} ions and 0.3–1 kBq/ml of ^{60}Co in it was taken in a 100 ml separatory funnel. The solution was shaken with 5 ml of Co-CyDTA solution (Co-CyDTA : 0.8 mg-Co/ml, Co^{2+} : 0.1 mg/ml) for 1 min. Then the solution was neutralized with ammonia water and shaken with 20 ml of chloroform and 1 ml of 10% HPDC (pyrrolidinedithiocarbamic acid)⁶⁾–chloroform solution to extract Co^{2+} -species. The activity of each phase was measured by a well-type NaI(Tl) scintillation counter.

It was revealed by the experiments that the isotopic exchange reaction proceeds rapidly and the equilibrium is attained within 1 min at pH 2. As the extractant, DDTC–toluene, DDTC–chloroform or oxine–chloroform is also applicable besides HPDC–chloroform.

3.3 Elimination of interfering ions

It was revealed that the presence of iron, zinc, manganese, copper or nickel of the concentration higher than 1 $\mu\text{g/ml}$ interferes with the determination of 0.2 $\mu\text{g/ml}$ of cobalt. Therefore, cobalt is purified in advance by eliminating the interfering ions as follows: The solution of the sample was adjusted to

8 M in acidity by adding HCl and was shaken with isopropylether for 30 s to extract iron. The organic phase was washed with 8 M HCl. The combined aqueous phase was heated to expel the organic solvent. The solution was then passed through an anion exchange column of MCI GEL (Cl-form, 13 mm ϕ $\times$ 120 mm). The resin was washed with 100 ml of 8 M HCl and 20 ml of 6 M HCl. Finally cobalt was eluted with about 50 ml of 4 M HCl and the effluent was evaporated to dryness. The residue was dissolved in the mixture of 3 M HCl–acetone (1:4)^{6),7)}. The solution was then passed through a cation exchange column of Diaion SK #1 (H-form, 13 mm ϕ $\times$ 100 mm). The resin was washed with 100 ml of the HCl–acetone mixture. Finally cobalt was eluted out with 50 ml of 6 M HCl–acetone (1 : 9) mixture and the eluate was evaporated to dryness. The residue was dissolved in 0.01 M HCl, and subjected to the isotopic exchange analysis.

3.4 Application to the analysis of sea water

No appreciable activity of ^{60}Co was detected in the ordinary sea water. Therefore, the validity of this method was examined by analyzing 1 l of the sea water sample spiked with 24 kBq or 37 kBq of ^{60}Co and 1.5 mg or 2.2 mg of stable cobalt. The concentration and separation of cobalt from sea water was done by the method proposed by the Science and Technology Agency⁸⁾. Finally, the solution was evaporated to dryness and the residue was dissolved in 50 ml of 0.01 M of HCl. The solution was shaken with 5 ml of Co-CyDTA solution (Co-CyDTA : 0.8 mg-Co/ml, Co^{2+} : 0.1 mg/ml) for 1 min. Then the solution was neutralized with ammonia water and shaken with 20 ml of chloroform and 1 ml of 10% HPDC–chloroform solution. Finally, the activity of each phase was measured by a well-type NaI(Tl) scintillation counter.

3.5 Application to the analysis of marine deposits

The dried sample was sieved through a 0.21 mm sieve. The sample of 200 g was heated at 600 °C for 3 h. Then, it was digested with 250 ml of 8 M HCl at about 100 °C for

1–2 h^o. The insoluble matter was filtered off with a sintered glass filter. The residue was re-digested with 8 M HCl and the both filtrates were combined. The combined solution was then treated according to the procedures written in 3.3 to eliminate the interfering ions, and the final evaporated residue was dissolved in 5 ml of 0.01 M HCl.

To a 4 ml portion of the solution, 1 ml of Co-CyDTA solution (0.8 mg-Co/ml) was added and shaken. After the isotopic exchange equilibrium was attained, 0.1 ml of potassium acetate (0.4 g/ml), 0.5 ml of DDTC (sodium diethyldithiocarbamate, toluene solution) (0.2 g/ml), 0.5 ml of nearly saturated KCl solution and 5 ml of toluene were added and shaken for 10 min. Then cobalt ions were extracted as Co(DDTC)₃ with toluene, while Co-CyDTA ions remained in the aqueous phase.

The activity was measured by a low background liquid scintillation counter (Aloka LS-LB1) as follows: To a 4 ml portion of the organic phase obtained by the above-mentioned procedure, 96 ml of the scintillator solution which contain 2.6 g of DPO (2,5-diphenyloxazole) and 0.16 g of DMPOPOP (1,4-bis(2-(4-methyl-5-phenyloxazolyl))-benzene) in 500 ml of toluene was added and mixed⁹. On the other hand, to a 4 ml portion of the aqueous phase, 96 ml of Aquasol-2 (made by New England Nuclear Co.) was added and mixed. Then each activity was measured. The counting efficiency was determined with reference to the ⁶⁰Co standard solution. The external standard ratio method was adopted to correct the quenching effect of each sample.

4. Results and Discussion

4.1 Preliminary experiment

The linear relationship between activity A_x and $A+a$ is shown in Fig. 1. The linear relationship between A/a and amounts of stable cobalt is shown in Fig. 2. Thus, the above-mentioned principle is verified experimentally. Further, by using such a straight line given in Fig. 2 as a calibration curve, the amounts of stable cobalt in the sample can be determined by measuring A and a , and the accurate amount of Co-CyDTA (m) is not necessary

Fig. 1 Linear relationship between A_x and $A+a$.

Fig. 2 Linear relationship between M_x and A/a .

to be known. Only necessary is to keep the volume of the solution added constant in a series of analyses.

4.2 The addition experiment of sea water

The sea water samples spiked with the known amounts of radioactive and stable cobalt isotopes were analysed. The results are shown in Table 1. The observed values are in fairly good concordance with those added. It shows the tendency that the errors are somewhat higher for stable cobalt than for radioactive cobalt.

4.3 Analyses of the marine deposit samples

Table 2 shows the results of the analyses of some marine deposit samples comparing with the results obtained by other conventional methods, i.e. γ -ray spectrometry by a Ge(Li)

Table 1 Simultaneous determination of ^{60}Co and stable cobalt in the spiked sea water sample

Run	^{60}Co activity			Stable cobalt		
	Amounts added (cpm/ml)	Amounts observed (cpm/ml)	Error (%)	Amounts added ($\mu\text{g/ml}$)	Amounts observed ($\mu\text{g/ml}$)	Error (%)
1	144.6 ± 0.2	143 ± 2	-1.1	1.49	1.58 ± 0.04	+6.0
2	222.9 ± 0.3	225 ± 2	+0.9	2.23	2.26 ± 0.04	+1.3

Table 2 Radioactive and stable cobalt contents in marine deposits collected in Urazoko Bay

Sample	^{60}Co activity (Bq/kg)		Stable cobalt (mg/kg)		Specific activity (Bq/mg)	
	This method	Ge(Li)*	This method	ICP**	This method	Ge(Li) and ICP
A	10.5 ± 0.4	12.0 ± 1.0	5.0 ± 0.4	5.0 ± 0.5	2.1 ± 0.2	2.4 ± 0.3
B	9.8 ± 0.9	9.1 ± 0.9	2.5 ± 0.2	2.7 ± 0.4	3.9 ± 0.4	3.4 ± 0.6

* Non-destructive γ -ray spectrometry by a Ge(Li) detector.

** Inductively coupled plasma emission spectrometry.

detector for ^{60}Co and inductively coupled plasma emission spectrometry for stable cobalt. The sample A was taken at the mouth of Urazoko Bay, Fukui Pref. on 19 April 1984. The sample B was taken at the inner part of Urazoko Bay on 20 July 1983. The data for the specific activity were also listed in the table. The values obtained by this method are in fairly good concordance with those obtained by the conventional method.

5. Conclusion

The method proposed in this paper has such advantages as follows:

- (1) The simultaneous determination of radioactive and stable isotopes is possible.
- (2) The procedure is simple and rapid.
- (3) By using the calibration curve, it is not necessary to know the exact concentration of the reagent solution, and the analysis can be done only by the activity measurements.

This method seems suitable for the routine and many samples analyses for radioactive and stable cobalt in such environmental samples as marine deposits, soils and biological ashes, etc.

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References

- 1) Sato, K., Abukawa, J., Higuchi, H. et al.: *Radioisotopes*, **28**, 285-290 (1979) (in Japanese)
- 2) Momoshima, N., Shiki, A., Takashima, Y. et al.: *ibid.*, **34**, 257-261 (1985) (in Japanese)
- 3) Kawamura, S., Izawa, M., Maruyama, T. et al.: *Health Phys.*, **13**, 801-806 (1967)
- 4) Ikeda, N. and Takeda, Y.: *Radioisotopes*, **34**, 99-100 (1985)
- 5) Mitchell, J.W. and Ganges, R.: *Talanta*, **21**, 735-743 (1974)
- 6) Science and Technology Agency: "Manual for Determining Radioactive Cobalt", Tokyo (1985) (in Japanese)
- 7) Fritz, J.S. and Rettig, T.A.: *Anal. Chem.*, **34**, 1562-1566 (1962)
- 8) Japan Chemical Analysis Center: "Manual for Determining Radioactive Species in Environmental Samples with Liquid Scintillation Counter", Chiba (1986) (in Japanese)

要 旨

同位体交換法による環境試料中の放射性および安定コバルトの同時定量

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コバルト(II)イオンは塩酸酸性溶液中で Co-CyDTA 錯体と速やかな同位体交換反応を行う。この反応を利用して、環境試料中の放射性コバルトおよび安定コバルトを同時に定量する新しい方法を考案した。交換平衡に達したのち、溶媒抽出法により、両化学種を相互に分離し、それぞれの放射能を測定して、検量線より放射性コバルトの放射能および安定コバルトの重量を求めた。二、三の海水、海底土試料についての分析結果を、在来法で得られた分析結果と比較したところ、両者の間にはよい一致がみられた。