Simultaneous Radiochemical Determination of ^{85}Sr and ^{45}Ca by Oxalate Precipitation Method (Determination of Strontium and Calcium, Part II)*

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The following method was established for simultaneous radiochemical determination of ^{85}Sr and ^{45}Ca : ^{85}Sr and ^{45}Ca are precipitated together with calcium oxalate in the presence of 15 mg of Ca in 60 ml of solution (250 ppm). Radioactivity of ^{85}Sr is obtained directly from scintillation measurement. Using the conversion factor previously determined for single radionuclide of ^{85}Sr , the contribution of radioactivity of ^{85}Sr in the sample to G-M counter is estimated. Radioactivity of ^{45}Ca is obtained by subtraction of the estimated counting rate of ^{85}Sr from the total counting rate of G-M measurement.

Prior to the establishment of the method, coprecipitation yield of Sr in calcium oxalate was examined in terms of Ca concentration. A range of 0.002 to 1 mg of Sr in 60 ml of solution (0.03–17 ppm) was coprecipitated in calcium oxalate, with the yield of $95.0 \pm 0.5\%$ in the presence of 15 mg of Ca (250 ppm), and with lower yields at lower concentrations of Ca.

Prior to the studies on the behavior of strontium and calcium in the system of soils and plants, from stand points of geochemistry and environmental radioactive contamination, the methodological studies have been developed. A method for simultaneous radiochemical determination of ^{85}Sr and ^{45}Ca is presented, as a succession to the study on emission-spectrographic determination of Sr for soil analysis¹⁾.

1. Reagents, instruments, and the basic chemical procedure

1.1 Reagents and instruments

Sr carrier solution: Strontium nitrate** was dissolved in re-distilled water, at a rate of 1 mgSr/ml. The stock solution was standardized by EDTA titration, and was diluted quantitatively with re-distilled water to make working solutions.

Ca carrier solution: Calcium nitrate** was dissolved in re-distilled water at a rate of 3 mgCa/ml. The solution was standardized by EDTA titration. The amount of Sr, as an impurity in this Ca reagent, was $0.1_2 \mu\text{g}$ or less per 1 mg of Ca, as tested by emission-spectrography¹⁾.

Ammonium oxalate solution: 0.25 M, a calculated amount of ammonium oxalate** was

dissolved in re-distilled water.

^{85}Sr : Prepared in Oak Ridge National Laboratory, $^{85}\text{Sr}(\text{P})$, $\text{Sr}(\text{NO}_3)_2$ in nitric acid solution, 1.82 mc/ml, 0.173 mgSr/ml, $^{86}\text{Sr} < 0.5\%$ of ^{85}Sr . The radiochemical purity was found to be good enough for the authors' experiment, by the tests of aluminum absorption curves and decay curves measured by both G-M and scintillation counters, in addition to a scintillation spectrometry.

^{45}Ca : Prepared in Oak Ridge National Laboratory, $^{45}\text{Ca}(\text{P-2})$, CaCl_2 in hydrochloric acid, 5.91 mc/ml, 13.8 mgCa/ml, $^{46}\text{Sc} < 0.0025 \text{ mc/ml}$. The radiochemical purity was found to be good enough by the tests of aluminum absorption curve and decay curve measured by G-M counter.

Scaler†: Model 100

Scintillation detector†: NaI(Tl), $\phi 2.5 \text{ cm} \times 2.5 \text{ cm}$

G-M detector†: End window type; thickness of mica: 1.4 mg/cm^2

1.2 Basic chemical procedure for preparation

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** Wako Pure Chemical Industry, LTD., G.R.

** Koso Chemical Co., G.R.

† Made by Scientific Research Institute (Tokyo).

of oxalate precipitate

^{85}Sr or ^{45}Ca was taken in a beaker containing an amount of Ca carrier solution. 6 *N* hydrochloric acid and distilled water were added to adjust the volume of the solution to 50 ml and the concentration of chloride to 0.3–0.6 *N*. The solution was heated to near boiling, added with 5 ml of 0.25 *M* ammonium oxalate solution, and neutralized by 6 *N* ammonium hydroxide using methyl red indicator. The solution, which increased in the volume up to 60 ml, was heated for 10 minutes, and allowed to stand for several hours at room temperature. The precipitate was filtered through a filter paper fitted in a separable filter stick, and rinsed 3 times with distilled water, finally with ethyl alcohol. The precipitate was transferred to a counting dish and dried at 110°C for 1 hour.

2. Examinations of radiochemical yield of ^{85}Sr and ^{45}Ca

2.1 Effect of Ca concentration on the coprecipitation yield of ^{85}Sr

To avoid the difficulty resulting from self-absorption and to attempt a radioassay of high precision, an experiment was designed, based upon the following principle: ^{85}Sr which was not incorporated in calcium oxalate, is recovered from the filtrate by a further oxalate precipitation, after the addition of a fixed amount of Ca carrier to unify the sample thickness, as illustrated in Figure 1.

Fig. 1 Scheme of sample preparation, specially designed for examinations of radiochemical yield of ^{85}Sr and ^{45}Ca .

Aliquots of ^{85}Sr solution were added to beakers containing 2, 10, 15 and 20 mg of Ca carrier respectively. Oxalate precipitate was prepared according to the basic procedure described in 1.2. This precipitate is designated as "main precipitate". The filtrate was acidified by 6 *N* hydrochloric acid, added with 15 mg of Ca carrier, and evaporated to 50 ml. From this solution, "second oxalate precipitate" was prepared according to the basic procedure. The precipitates were counted by scintillation counter.

As results of triplicate experiment, radioactivity of the second precipitate derived from the solution containing initially 15 mg of Ca, was $5.5 \pm 0.6\%$ of the sum of radioactivities of the main and second precipitates. Although still 5 % of ^{85}Sr was expected to escape from second precipitate, this was considered to be negligible. Therefore the sum of radioactivities of the main and second precipitates derived from the solution containing initially 15 mg of Ca, was considered as "total radioactivity", in other words, "dose".

The quantities of ^{85}Sr in all second precipitates were expressed in "per cent of dose". From these values, the quantities of ^{85}Sr coprecipitated in the main precipitates were calculated in terms of "per cent of dose" or "yield".

The result is shown in Figure 2. Coprecipitation yield of ^{85}Sr tends to increase as increase in Ca concentration, but shows a plateau curve reaching to 95–96% yield, at a higher

Fig. 2 Effect of Ca concentration on the coprecipitation yield of ^{85}Sr in calcium oxalate.

concentration than 15 mg of Ca per 60 ml or 250 ppm.

2.2 Effect of Sr concentration on the coprecipitation yield of ^{85}Sr

In the aforementioned experiment, each test solution has contained 0.002 mg of Sr, as the impurity brought by 15 mg of Ca carrier*.

To examine effect of Sr concentration, 0.01, 0.1 and 1 mg of Sr carrier were added respectively to beakers each containing 15 mg of Ca carrier and an aliquot of ^{85}Sr . Preparation of both main and second precipitates, radioactivity measurement and calculation were performed in the same way as in the former experiment. As shown in Table 1, coprecipitation yield of

Table 1 Effect of Sr concentration on the coprecipitation yield of ^{85}Sr in calcium oxalate

Ca added (mg)	Sr added (mg)	Sr present (mg) [†]	Yield of ^{85}Sr (%) ^{††}
15	0	0.002	94.5 $\pm$ 0.6
"	0.010	0.012	95.3 $\pm$ 0.3
"	0.10	0.10	94.8 $\pm$ 0.7
"	1.0	1.0	95.3 $\pm$ 0.3
Average			95.0 $\pm$ 0.5

[†] Including impurity Sr in calcium carrier.

^{††} Average and standard deviation of triplicate experiment.

^{85}Sr in the main precipitate of calcium oxalate was independent from the concentration of Sr, in the range of 0.002 to 1 mg Sr per 60 ml or 0.03 to 17 ppm Sr. The average yield was 95.0 $\pm$ 0.5%.

2.3 Effect of Ca concentration on the precipitation yield of ^{45}Ca

Aliquots of ^{45}Ca solution were added to beakers containing 2, 10 and 15 mg of Ca carrier

Table 2 Effect of Ca concentration on the precipitation yield of ^{45}Ca in calcium oxalate

Ca added (mg)	Yield of ^{45}Ca (%) [†]
2	97.3
10	99.6
15	99.9
	99.9
	99.9

[†] Single determination.

respectively. The experiment was performed in the same way as in the former two experiments, except radioactivity measurement which was made using G-M counter instead of scintillation counter. Table 2 proved that the addition of 15 mg of Ca carrier is good enough to recover 99.9% of ^{45}Ca .

2.4 Discussion on the coprecipitation yield of Sr in calcium oxalate

Uzumasa, et al.²⁾ separated Sr as oxalate precipitate from natural water samples containing 2 to 20 mg Sr per liter in the presence of 25 to 50 mg of Ca, and found the yield of Sr as 95.5 $\pm$ 0.5% by a flame-photometric determination. Uesugi³⁾ and Shigematsu⁴⁾ separated 0.01 to 0.15 mg of Sr as oxalate precipitate from brine samples, after the addition of further 6 to 12 milligrams of Ca, and found the yield of Sr exceeding 97% by a colorimetric determination. The yield was lower at lower concentrations of Ca. The results of these two studies are very close to the authors' result.

In all cases, the coprecipitation yield of Sr in calcium oxalate is much higher than that expected from data of solubility and solubility product of strontium oxalate⁵⁾.

On the other hand, one of the authors Kodaira has performed the survey of ^{90}Sr contamination of polished rice⁶⁾. In such occasion, he has often observed a low velocity of formation of calcium oxalate precipitate and a low coprecipitation yield of Sr, at a low concentration of Ca in test solutions. During the study reported here, the authors observed that the velocity of formation of calcium oxalate precipitate increases critically, when Ca concentration exceeds 15 mg per 60 ml, in other words 250 ppm.

These facts suggest that a special mechanism should be involved in the reaction of coprecipitation of small amount of Sr in calcium oxalate.

In any way the reproducibility of coprecipitation yield of Sr in calcium oxalate is satisfactory in the presence of 15 mg of Ca per 60 ml. Therefore no correction is necessary, when

* Only 0.00001 mg of stable Sr, as a carrier of radiostrontium, was brought in each test solution.

radioassay of ^{85}Sr is made for original or standard solution by the same method as for routine radioassay in tracer experiments. However, when absolute amount of stable Sr is concerned, a correction must be made of course for coprecipitation yield.

3. Examination of radioactivity measurement

3.1 Selective detection and self-absorption

Absorption curves of ^{85}Sr by aluminum absorbers are shown in Figures 3 and 4. The radioactivity detected by scintillation counter was practically γ -rays, and the major part of radioactivity detected by G-M counter was X-rays.

As shown in Figure 5, self-absorption effect of ^{85}Sr can be neglected for usual purpose. Self-absorption curve of ^{45}Ca agreed with the formula, $N/N_0 = (1 - e^{-\mu\theta})/\mu\theta$, where θ is sample

Fig. 3 Absorption curve of ^{85}Sr by scintillation counter.

Fig. 4 Absorption curve of ^{85}Sr by G-M counter.

Fig. 5 Self-absorption curves of ^{85}Sr and ^{45}Ca coprecipitated in calcium oxalate. thickness and μ equals to 0.0107⁷⁾.

3.2 Conversion of radioactivity of ^{85}Sr from scintillation counting rate to G-M counting rate

The ratio of counting rate of ^{85}Sr measured by G-M counter to that measured by scintillation counter was observed, for ^{85}Sr -calcium oxalate samples. As shown in Table 3, the ratio was kept fairly constant.

Table 3 Ratio of G-M counting rate to scintillation counting rate for ^{85}Sr samples

Exp. No.	G-M/scinti.	Time of assay	Numbers	
			assay	samples
1	0.158 ± 0.003	during a period of 55 days	7	1
2	0.155 ± 0.006	at initial time	1	3
3	0.164 ± 0.005	at 30 th day	1	2
Av. 0.159 ± 0.006				

4. Establishment of a method for simultaneous radiochemical determination of ^{85}Sr and ^{45}Ca

Through aforementioned examinations, the authors reached to establish a method for simultaneous determination of ^{85}Sr and ^{45}Ca , as follows.

4.1 Preparation of counting sample

To a sample solution containing ^{85}Sr and ^{45}Ca , an amount of Ca carrier is added to adjust the quantity of Ca to 15 mg. Oxalate precipitate is produced according to the basic procedure described in 1.2. The filter paper and counting dish are previously coupled and weighed. The dried precipitate is weighed.

4.2 Radioactivity measurement and calculation

The sample is counted by both scintillation and G-M counters. Radioactivity of ^{85}Sr is obtained directly from scintillation measurement. Using a conversion factor previously determined for single radionuclide of ^{85}Sr (0.159 in the authors' case), the contribution of radio-

activity of ^{85}Sr to G-M counter is estimated. Radioactivity of ^{45}Ca is obtained by subtraction of the estimated counting rate of ^{85}Sr from total counting rate of G-M measurement. Corrections are made for self-absorption of ^{45}Ca and for radioactivity decay of ^{85}Sr and ^{45}Ca .

4.3 Reliability of the method

The method was applied to a mixed solution containing known amounts of ^{85}Sr and ^{45}Ca . As shown in Table 4, a satisfactory result was obtained from a triplicate experiment.

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Table 4 An example of simultaneous determination of ^{85}Sr and ^{45}Ca

		Scintillation	G-M
Components	^{85}Sr , (cpm) [†]	878±17	—
	^{45}Ca , (cpm) [†]	—	2475±18
Observed, (cpm) [†]		864±9	2582±9
Calculated	cpm ^{††}	^{85}Sr	(864±9)
		^{45}Ca	—
	recovery (%)	^{85}Sr	98±2
		^{45}Ca	—

[†] Average and standard deviation in triplicate experiment

^{††} $^{45}\text{Ca}(\text{cpm}) = \text{G-M}(\text{cpm}) - f \times \text{Scint.}(\text{cpm})$, $f = 0.159 \pm 0.006$

要 旨

シュウ酸塩沈殿法による ^{85}Sr および ^{45}Ca の 放射化学的同時測定法 (ストロンチウムおよびカルシウムの分析法, 第2報)

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^{85}Sr および ^{45}Ca の放射化学的同時測定法をつぎのように確立した。液量 60 ml 中 15 mg (250 ppm) の Ca の存在下で ^{85}Sr および ^{45}Ca をシュウ酸カルシウムとともに沈殿させる。 ^{85}Sr の放射能はシンチレーション測定によって直接求める。あらかじめの ^{85}Sr の単一核種について求めておいた換算係数を使って、G-M カウンターに対する試料中の ^{85}Sr の寄与を推定する。G-M 計測値から ^{85}Sr の寄与の推定値を差引いて ^{45}Ca の計数率を求める。

この測定法の確立に先立って、シュウ酸カルシウムの Sr の共沈収率に対する Ca 濃度の影響を検討した。60 ml 中 0.002—1 mg の Sr (Sr として 0.03—17 ppm) の共沈収率は、Ca が 15 mg (250 ppm) 存在すれば $95.0 \pm 0.5\%$ で、Ca 濃度がこれより低ければもっと低い低を示した。

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