

Advanced Separation Techniques for Quantitative Determination of Ca-45 in Low-and Intermediate-level Radioactive Wastes

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A new chemical precipitation method for separation of Ca-45 nuclide is developed using the mixed solution of 0.5 M nitric acid and 10% (v/v.) ammonia solution as the solvent. The detailed processes are described below; (1) Stepwise pH adjustments of the aqueous solution, a great part of metals were precipitated as a hydroxide form except for the Ca-45 nuclide. (2) Selective formation of Ca-oxalate complex under strong acidic conditions. Ca-45 was separated from other metals and quantitatively recovered by inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis as well as the gravimetric determination, the recovery results are always above 89.75±4.61% and 83.26±7.25%, respectively. To determine the Ca-45, we introduced the Gas Proportional Counter (GPC). The average of the background values were 4.51 cpm and their counting efficiencies were about 30%. The concentration of Ca-45 in low-and intermediate-level radioactive wastes was 1.20E-02 ~ 2.12E-02 Bq/g.

I. INTRODUCTION

Ca-45 is a commonly used radionuclide with a half-life of 163 days, emitting only beta particles with a maximum energy of 0.257 MeV (Million Electron Volts) and an average energy of 0.075 MeV. The beta particles from Ca-45 travel a maximum of 48 cm in air. The major concern with using Ca-45 is that it cannot be easily monitored while it is used; therefore, it is important to separate Ca-45 from radioactive waste samples.[1]

Calcium is usually separated from isotopes of strontium by Ca(OH)₂ precipitation, but the operation is too difficult and tedious due to exacting control of pH of the solution and removal of the transition metals.[2] Furthermore, there are no separation skills of Calcium from volatile radioactive nuclides such as H-3, C-14 until now.[3]

Herein, we report a simple procedure to separate Ca-45 from low-and intermediate-level radioactive wastes, which relies on the solubility of Ca-45 nuclide in alkaline solution (around pH 8) and insolubility of Ca-45 in acidic solution (around pH 1.5) with oxalic acid. Ca-45 is quantitatively separated from radioactive wastes and more than 90% of Ca was recovered. To remove the volatile radioactive nuclides (H-3, C-14), we tried to use oxidizing agents (K₂S₂O₈ or AgNO₃) and sinter in air at 800 °C for 3 h. Besides, radioactive waste solution was prepared by two ways; 1) Leaching process 2) Ashing process. To confirm the elimination of volatile H-3, C-14, we introduced the Gas Proportional Counter (GPC) to determine beta-ray emission rates of radionuclides.

II. EXPERIMENTAL SECTION

All chemicals were used without further purification and purchased from commercial sources as follows: oxalic acid dihydrate (C₂H₂O₄·2H₂O), acetone (CH₃COCH₃), silver nitrate (AgNO₃), potassium persulfate (K₂S₂O₈) were purchased from Sigma-Aldrich (St Louis, USA). Ammonia solution (25%) and nitric acid (65%) were purchased from MERCK (Germany). The calcium standard solution with 10,000 mg/L was prepared using a CaCO₃(s) powder. Synthetic radioactive waste solutions of Sr (3 mg), Fe (20 mg), Nb (20 mg), Ca (50 mg) were prepared by diluting and combining calibrated standard solutions for the ICP-AES analysis or metal salt solutions to the appropriate concentrations due to the lack of similar certified reference materials for reliability evaluation of the separation procedure confirmed in the study. A radiation shielded ICP-AES system (Thermo Jarrell Ash, USA) composed of an ICP-AES and a stainless steel glove box was employed for the analysis of the radioactive waste samples. DI-water was used a Milli-Q plus Ultra-Pure Water System (Millipore).

III. RESULTS & DISCUSSION

In order to study the determination of Ca-45 radioactive nuclide, the GPC measurement of various samples depending on the synthetic procedures such as LO (Leaching process-Oxidizing agents), LS (Leaching process-Synthesis of CaO) and

AS (Ashing process) was investigated. Leaching process cannot be eliminated the volatile radioactive nuclides. The representative nuclides are H-3, C-14, P-32, S-35 and I-129. Among them, C-14 radionuclide is difficult to remove in particular. Therefore, the samples which made by leaching process include the volatile radioactive nuclides. There are several ways to remove the volatile radioactive nuclides; 1) Oxidizing agents, 2) Heating treatment.

III.A.1. LO (Leaching process-Oxidizing agents) method

In general, AgNO₃ and K₂S₂O₈ are a widely used as oxidizing agents. So, we also used those materials for the oxidation of volatile radioactive nuclides. In the case of LO method, the recovery rates show the quite good results as shown in Table I. However, the GPC values were 10 times higher than blank value. In addition to, the values of Minimum Detectable Activity (MDA) in LO-1, LO-2 and LO-3 were 0.164, 0.197 and 0.181, respectively.

III.A.2. LS (Leaching process-Synthesis of CaO) method

To remove the volatile radioactive nuclides from the synthetic samples, the heating treatment process was introduced in the experimental step. On the average, C-14 radioactive nuclide can be evaporated by thermal treatment. After the separation, white precipitates composed of Ca-oxalate complex were annealed in air at 950 °C for 6 h, yielding about 70 mg of CaO powders. In the case of LS method, LS-1, LS-2 and LS-3 samples showed the excellent recovery rates corresponding to 91.73%, 97.74% and 87.82%, respectively. Furthermore, those samples had the low GPC values similar to the blank value as shown in Table I as well as less than MDA (Bq/g) values.

III.A.3. AS (Ashing process) method

In the case of AS method (Table I), the GPC values of AS-1,2 and 3 samples were higher than blank value which suggest that the samples obtained by ashing process contains volatile radioactive nuclides, especially, C-14.

Sample Name	Recovery (%)	GPC (cpm)	MDA (Bq/g)
LO-1	92.06	21.62	0.164
LO-2	78.47	25.14	0.197
LO-3	85.97	24.08	0.181
LS-1	91.73	3.22	< 1.20E-02
LS-2	97.74	3.64	< 1.73E-02
LS-3	87.82	4.56	< 2.12E-02
AS-1	83.32	10.83	0.107
AS-2	83.40	11.20	0.115
AS-3	93.53	12.53	0.171

Table I. GPC results and recovery percentages of various synthetic samples for the determination of Ca-45. a) LO: Leaching process-Oxidizing agents, LS: Leaching process-Synthesis of CaO, AS: Ashing process.

IV. CONCLUSIONS

A facile chemical precipitation process for separation of Ca-45 nuclide is developed. The key steps are described below; (1) Stepwise pH adjustments of the aqueous solution. (2) Selective formation of Ca-oxalate complex under strong acidic conditions. Ca-45 was separated and quantitatively recovered by ICP-AES analysis as well as the gravimetric determination, the recovery results are above 89.75±4.61% and 83.26±7.25%, respectively. To determine the Ca-45, we introduced the Gas Proportional Counter (GPC). The concentration of Ca-45 in low-and intermediate-level radioactive wastes was 1.20E-02 ~ 2.12E-02 Bq/g. We tried to obtain the valid values by controlling the preprocessing step. As a result, LS route showed the excellent recovery rates which were about 91.73%, 97.74% and 87.82% compared to other routes (LO and AS).

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