

Study on the Volatility of Cesium in Dry Ashing Pretreatment and Dissolution of Ash by Microwave Digestion System – 13331

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ABSTRACT

Based on the regulation of the activity concentration of Cs-137, Co-58, Co-60, Fe-55, Ni-59, Ni-63, Sr-90, Nb-94, and Tc-99, and the total alpha from the radioactive waste acceptance criteria, the measurement of the activity concentration of these nuclides in low and intermediate levels of radioactive waste such as in paper, cotton, vinyl and plastic samples was investigated. A dry ashing method was applied to obtain a concentration effect of the samples. Owing to the temperature dependence of the volatility for cesium, the temperature of 300 to 650 °C was examined. It was found that 450 °C is the optimum dry ashing temperature. After dry ashing, the produced ash was dissolved with HNO₃, HCl, and HF by a high-performance microwave digestion system. The ash sample, for the most part, was completely dissolved with 10 mL of HNO₃, 4 mL of HCl, and 0.25 mL of HF by a high-performance microwave digestion system using a nova high temperature rotor at 250 °C for 90 min until reaching 0.2 g. To confirm the reliability of cesium loss after the performance of the dry ashing procedure, a cesium standard solution for AAS and a Cs-137 standard solution for gamma spectrometry were added to a paper towel or a planchet of stainless steel, respectively. Cesium was measured by AAS, ICP-MS, and gamma spectrometry. The volatility of cesium did not occur until 450 °C ashing.

INTRODUCTION

To measure the activity concentration of a nonvolatile nuclide such as Cs-137, Co-58, Co-60, Fe-55, Ni-59, Ni-63, Sr-90, Nb-94, and Tc-99, and the total alpha in low and intermediate levels of radioactive waste samples such as paper, cotton, vinyl, and plastic as shown in Fig. 1, a sample treatment procedure should be established to obtain a clear solution before performing a separation procedure. A dry ashing method has been used for a sample pretreatment method owing to such advantages as the decomposition of a large sample size, no reagents, a relatively safe technique, and mass production. However, because of the possibility of cesium volatility during ashing in an electric muffle furnace, the temperature dependence of the volatility of cesium was examined from 300 to 650 °C.

METHODS AND RESULTS

Dry ashing pretreatment

An electric muffle furnace (Thermo Fisher Scientific, NJ, USA) was used to ignite the dry active waste samples. To prevent the formation of soot or a flame during ashing, the temperature was increased step by step from room temperature to 110, 200, 250, 300 °C, and maintained for 4 or 5 hrs at every step. To measure the recovery of cesium using a paper towel, two kinds of cesium solution, standard solutions for atomic absorption spectrometry and gamma spectrometry, were utilized. The recovery of Cs-137 activity using a planchet was performed without a dissolution procedure. The effect of ashing temperature on the recovery of cesium was not observed from 300 to 450 °C. In addition, the effect of ashing time elapsed on the recovery of cesium was not also observed from 4 to 12 hr at 450 °C. The volatilization of cesium began at 550 °C. The recovery difference between 450 and 550 °C was 9.7%. And the relative recovery of cesium at 650 °C was $42.8 \pm 4.6\%$ based on the results of 450 °C. The recovery of cesium decreased with increase ashing temperature above 550 °C. It was found that the volatility of cesium did not occur until 450 °C ignition, which was in a good agreement with Green and Finn results [1], the volatility of cesium did not occur in milk samples during ashing at 450 °C.



Figure 1. Photos of dry active waste sample before and after ignition

Dissolution of ash by high-performance microwave digestion system

Distilled and demineralized water (DDW), with a specific resistance of $18.5 \text{ M}\Omega \cdot \text{cm}$, was prepared using a Milli-Q plus Ultra Pure Water System (Millipore, Billerica, MA, USA). Chemicals including HCl, HF, H_2SO_4 , and HNO_3 used (Merck, Darmstadt, Germany) were of analytical grade. After dry ashing, the produced ash was dissolved with a mixed acid of

HNO₃-HCl-HF by a high-performance microwave digestion system (HP-MDS) (Ethos one; Milestone, Sorisole, Italy). The operating conditions of the HP-MDS are shown in Table I.

Table I. Operating condition of HP-MDS

Step	HP-MDS	
	Temperature (°C)	Time (min)
1	25-250	30
2	250	60
3	250-25	60

The amount of hydrofluoric acid is very important because the precipitation of CaF₂ ($K_{sp} = 4.0 \times 10^{-11}$) was formed by a reaction between Ca⁺² in the presence of the sample and excess HF as shown in Fig. 2. In addition, though sulfuric acid is a good reagent, as microwaves cannot easily pass through the acid in a vessel, it should not be used in the case of an ash sample containing alkaline earth metal owing to the formation of alkaline earth metal sulfate salts {(Ca, Sr, Ba) SO₄}, which have a low solubility product constant. Most samples were completely dissolved with 10 mL of HNO₃, 4 mL of HCl, and 0.25 mL of HF using an HP-MDS with a nova high-temperature rotor at 250 °C for 90 min. However, other samples containing calcium and titanium as major compositions were not dissolved with the same experimental conditions. In addition, the dissolution of ash was affected by the sample weight. Generally, the maximum sample amount for complete dissolution was till 0.2 g. About a 0.3 g sample was not completely dissolved. Thus, to obtain a clear solution described above, the solution and insoluble matter were separated by centrifugation after operation of the digestion system, and the residue could be dissolved by a second digestion.

After the dissolution of ash produced from a paper towel with a mixed acid of HNO₃-HCl-HF by an HP-MDS, the constituent of the paper towel ashed was present in order of Ca, Si, Mg, Na, Fe, Sr, and Zn. In addition, the content of total organic carbon (TOC) in the solution decreased with an increase in the ashing temperature. The amount of TOC after 450 °C ashing was less than 1 mg/L. Further study will be performed to completely dissolve ash sample containing Ca and Ti as major constituents.

CONCLUSIONS

To meet the requirements for the disposal of low and intermediate level radioactive waste in a repository, a sample pretreatment procedure for the determination of the activity of 10 nuclides in dry active radioactive waste was established. It was found that the volatility of cesium did not occur until 450 °C ashing. Although 0.3 g of the ash sample could not be completely dissolved by an HP-MDS, most of the Cs-137 activity was present in the solution. In addition, the activity of nuclides in the residue was at a negligible level. Most ash samples produced could be completely dissolved with a mixed acid of 10 mL of HNO₃, 4 mL of HCl, and 0.25 mL of HF by a high-performance microwave digestion system (HP-MDS).

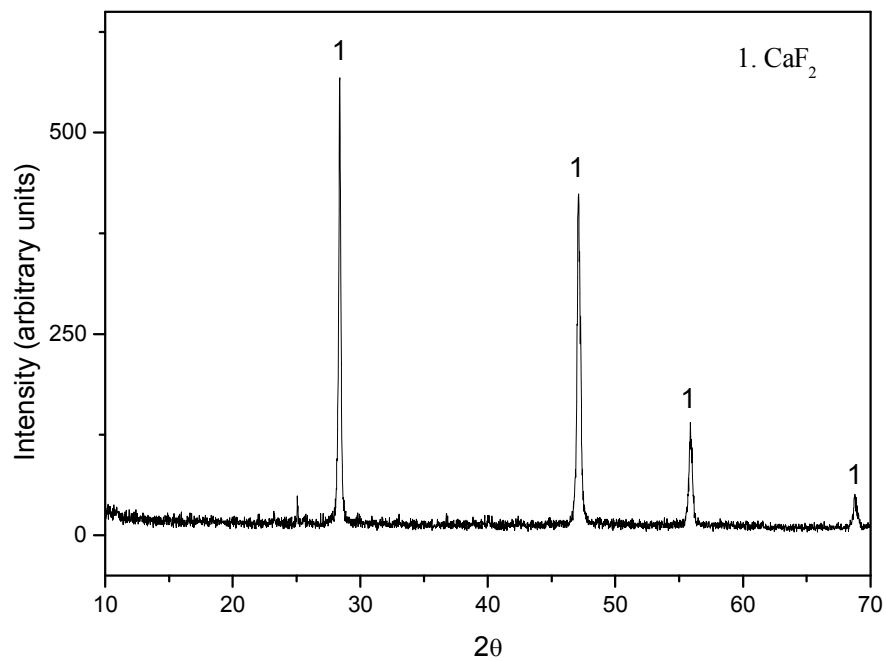


Fig. 2. XRD patterns of insoluble residue

References

- [1] R.M. Green and R.J. Finn, Loss of cesium-137 in the ashing of milk samples. *Anal. Chem.*, 1964, 36: 692-693.