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Technical note

The measurement of ^{129}I for the cement and the paraffin solidified low and intermediate level wastes (LILWs), spent resin or evaporated bottom from the pressurized water reactor (PWR) nuclear power plants

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ABSTRACT

In this paper a relatively simple and low cost analysis procedure to apply to a routine analysis of ^{129}I in low and intermediate level radioactive wastes (LILWs), cement and paraffin solidified evaporated bottom and spent resin, which are produced from nuclear power plants (NPPs), pressurized water reactors (PWR), is presented. The ^{129}I is separated from other nuclides in LILWs using an anion exchange adsorption and solvent extraction by controlling the oxidation and reduction state and is then precipitated as silver iodide for counting the beta activity with a low background gas proportional counter (GPC). The counting efficiency of GPC was varied from 4% to 8% and it was reversely proportional to the weight of AgI by a self absorption of the beta activity. Compared to a higher pH, the chemical recovery of iodide as AgI was lowered at pH 4. It was found that the chemical recovery of iodide for the cement powder showed a lower trend by increasing the cement powder weight, but it was not affected for the paraffin sample. In this experiment, the overall chemical recovery yield of the cement and paraffin solidified LILW samples and the average weight of them were $67 \pm 3\%$ and 5.43 ± 0.53 g, $70 \pm 7\%$ and 10.40 ± 1.60 g, respectively. And the minimum detectable activity (MDA) of ^{129}I for the cement and paraffin solidified LILW samples was calculated as 0.070 and 0.036 Bq/g, respectively. Among the analyzed cement solidified LILW samples, ^{129}I activity concentration of four samples was slightly higher than the MDA and their ranges were 0.076–0.114 Bq/g. Also of the analyzed paraffin solidified LILW samples, five samples contained a little higher ^{129}I activity concentration than the MDA and their ranges were 0.036–0.107 Bq/g.

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1. Introduction

Due to the volatility, solubility and chemistry of iodine, ^{129}I distribution in various waste streams of a reactor operation occurs easily. Waste management activities can further distribute ^{129}I into different waste forms and disposal of them results in the release of ^{129}I into the environment. Since iodine is very much soluble, it migrates along water pathways (Brauer, 1989; Suarez et al., 1996; Verrezen and Hurtgen, 1992). The presence of longer lived nuclides such as ^{129}I ($T_{1/2} = 1.57 \times 10^7$ years) in low and intermediate level radioactive wastes (LILWs) produced by nuclear power plants (NPP) is a crucial meaning to the long-term risk related to their disposal. Consequently, from the standpoint of a radiation protection, ^{129}I of LILWs should be monitored strictly.

Since most LILWs contain a trace amount of ^{129}I or less than a minimum detectable activity (MDA) and its analytical procedure is very complicated, only a few data on ^{129}I have been reported until recently (Brauer, 1989; Suarez et al., 1996). Routine control of a radioactive waste demands an efficient and relatively simple analytical procedure which allows many samples to be analyzed per day with a considerable precision and accuracy.

The low specific activity and low energies associated with an ^{129}I radioactive decay and the presence of other radioactive nuclides in LILWs make the application of direct measurements of ^{129}I by gamma spectrometry difficult. The measurement methods for ^{129}I usually require the separation of iodine from the sample matrix. This removes radioactive and/or chemical interferences in the measurement and reduces the sample to a volume and makes the sample form compatible with the iodine isotopic analyses methods. Thus most ^{129}I measurements for LILWs require laboratory analyses of representative samples (Brauer, 1989).

Simultaneous determination methods of radionuclides that are difficult to measure (DTMs), such as ^{3}H, ^{14}C, ^{36}Cl, ^{129}I, etc., in decommissioning wastes of nuclear facilities using conventional apparatus, were presented (Ashton et al., 1999; Hou, 2007). Currently most low level ^{129}I analyses are being conducted by a neutron activation analysis (NAA), a thermal emission mass spectrometry (TEMS), an inductively coupled-mass spectrometry

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(ICP-MS) or accelerator mass spectrometry (AMS). These methods are at least a factor of 1×10^6 more sensitive than conventional methods such as a beta, X-ray, or gamma ray counting (Brauer, 1989; Smith et al., 1991). The selection of a measurement method depends on the facilities, instrument available in the laboratory, required detection limit of nuclide, etc. All the methods require an iodine separation from a sample prior to a measurement, but the more sensitive methods can use smaller sample sizes. To obtain a reliable iodine separation from LILWs, considerable labor is required. Anion or mixed bed ion-exchange resins can be used to separate and concentrate anionic iodine from complicated compositions of samples (ASTM D4785-00a, 2000; Verrezen and Hurtgen, 1992; Yamamoto and Miyagawa, 1976). Some LILWs that contain a slightly higher radioactivity level are solidified with an inorganic material, i.e. cement or organic material, i.e. paraffin, to immobilize the nuclides contained in them and then placed in steel drums or concrete containers (Kim et al., 2003; Park and Lee, 1991). A relatively simple but applicable analytical procedure for a routine measurement of ^{129}I in cement or paraffin solidified LILWs which were generated from the operation of NPP, pressurized water reactor (PWR), was developed. The experimental procedures were established for a separation of iodide using an anion exchange, solvent extraction after a reduction and an oxidation of iodine and a precipitation as AgI and for a beta counting with a low background gas proportional counter (GPC). The chemical recovery of iodide was reviewed with a variation of the pH and sample weight of the cement powder and paraffin chip. In this work, cement solidified LILWs which contained evaporated bottom or spent resin were analyzed using the established procedure and paraffin solidified LILWs which contained evaporated bottom as well.

2. Materials and methods

2.1. Counting efficiency of a low background GPC for ^{129}I

Seven calibration samples were prepared as follows and a blank sample without an ^{129}I injection as well. Into each of the seven 15 mL capacity centrifuge tube containing 10 mL of distilled water, 0.04, 0.06, 0.10, 0.16, 0.20, 0.24 and 0.30 mL of iodide carrier (I^- 50 mg/mL prepared with KI Merck reagent grade) was added. To the same centrifuge tube 0.1 mL of ^{129}I standard solution (21.8 Bq/mL, Amersham) was added and shaken strongly. And to each centrifuge tube 2 mL of 0.1 M $AgNO_3$ was added and shaken well to mix the contents. After centrifuging the tubes, the supernatant was discarded and the settled AgI salt was washed with distilled water several times and then with ethanol. On the preweighed 1″ copper planchet, the recovered AgI salt was transferred quantitatively and dried for 1 h in a dry oven at 110 °C. After cooling to room temperature in a desiccator, the weight of AgI was weighed and the chemical recovery of iodide was calculated. The ^{129}I activity of each copper planchet was counted for 50 min by a low background GPC (CANBERRA Model SO-SB) and a blank as well. After a correction of the background, the counting efficiency of GPC for the calibration samples of ^{129}I was calculated. A calibration curve was plotted as an X-axis set as a recovered weight of AgI salt and a Y-axis set as the calculated counting efficiency of GPC for the ^{129}I activity.

2.2. Adsorption of iodide on an anion exchange resin with a varying pH

Previously appropriate amount of anion exchange resin (AG 1×2, 50–100 mesh, chloride form, Bio-Rad Laboratories) was washed with distilled water until the wash water showed no change in its pH and stored as a slurry. The conditioned anion exchange resin slurry weighed 2.5 g and was added to each of the four glass beaker, 30 mL capacity, containing 10 mL of pH 4, pH 7, pH 10 and pH 12 buffer solution. And 0.2 mL of an iodide carrier (I^- 50 mg/mL, prepared with KI Merck reagent grade) was added to each beaker while stirring. These beakers were stirred at least 12 h at room temperature to allow a complete adsorption of the iodide on the anion exchange resin.

2.3. Procedures for separation of iodide

The iodide adsorbed anion exchange resin slurry contained in the four glass beakers was transferred into four plastic columns, 15 mm × 150 mm, fitted at the lower end with a perforated disk and drain path hole connected to a flexible tube and a flow control clamp. The flow rate of the liquid from the column was controlled at about 1 drop/5 s by adjusting the flow control clamp. The resin column was washed with three successive 30 mL portions of distilled water. And the resin column was eluted with four successive 5 mL portions of 5–6% NaOCl. The elution rate was controlled at a constant rate, 1 drop/5 s. The NaOCl solution oxidizes the iodide adsorbed on the resin to periodate, which is removed from the anion resin and the eluant is received in a beaker.

The column was washed with four successive 5 mL portions of distilled water and received it into the same beaker. And then the received NaOCl and washing water was transferred into a plastic centrifuge cone of 50 mL capacity. Slowly 1.25 mL of concentrated HNO_3 was added to the plastic centrifuge cone and 5 mL of CCl_4 and 0.5 g of NH_2OHHCl as well. This reagent, NH_2OHHCl, is to reduce the iodate to iodine (I^o). Iodine is preferentially soluble in the CCl_4 phase and can be separated by solvent extraction (ASTM D4785-00a, 2000). As the iodine transfers to the CCl_4 phase, the color of CCl_4 becomes violet due to the dissolved elemental iodine.

At least three successive CCl_4 extractions are required and the extracted organic phase is quantitatively combined in a 50 mL plastic centrifuge cone. The collected dark purple CCl_4 was washed with 5 v/v% HNO_3 until no white precipitate appeared in the aqueous solution with 0.1 M $AgNO_3$. This step is required to remove the halide anions except for the iodide. To the washed organic phase, total volume of 15 mL, 5 mL of 0.1 M $NaHSO_3$ was added and the funnel was shaken for about 3 min. The $NaHSO_3$ reduces the iodine to iodide which is not soluble in CCl_4. The aqueous phase was transferred quantitatively to a 15 mL plastic centrifuge cone and adjusted to pH 2. To the centrifuge cone 2 mL of 0.1 M $AgNO_3$ was added and shaken to disperse the precipitate. After clearly settling the AgI precipitate in the bottom of the centrifuge tube, the precipitate was mounted on a copper planchet quantitatively. The copper planchet was dried at 110 °C for about 1 h and cooled in a desiccator. The chemical recovery of iodide can be calculated from the weight of the AgI precipitate and the added iodide content. The activity of ^{129}I for the AgI precipitate was counted with a low back ground GPC (CANBERRA Model SO-SB) for 50 min.

2.4. Recovery of iodide and the ^{129}I activity depending on the sample weight

To elucidate the effect of a sample weight, cement and paraffin, on the recovery of iodide and the ^{129}I activity, 1–13 g of pure cement powder (Portland I) or pure paraffin chip (fully refined paraffin wax, Aristowax 165), was weighed in 13 beakers, with a 30 mL capacity. In each of the 13 30 mL beaker, 10 mL of pH 10 buffer solution, 2.5 g of anion exchange resin (AG 1×2, 50–100

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