

Optimization of Neutron Activation Analyses of ^{129}I in Low-level Radioactive Waste Samples

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Determination of ^{129}I in low-level radioactive waste (LLW) samples from reactors can be a tedious and time consuming procedure often leading to results with large margins of error. This study used an efficient (approx. 2-3 h per sample) and reliable procedure, which could be used for LLW waste samples in various physical forms (solid, liquid, resin). Samples were processed without pretreatment by distillation of the LLW samples, followed by separation using chemical extraction. The extracted ^{129}I solution was then irradiated for 5 min in a 2 MW research reactor (neutron flux of about 10^{13} n/cm²-s), and the activation product, ^{130}I , was analyzed with a high-purity intrinsic germanium detector. A tracer of ^{127}I was also activated to ^{128}I to determine radiochemical yield, which was $29 \pm 7\%$. The lower limit of detection of the procedure was about 30 pCi/g for 4 g samples, 29% recovery, and a 1000 s counting time.

Introduction

This paper describes studies to optimize measurements of ^{129}I in low level radioactive waste samples using neutron activation analysis. The procedure can be used for most liquid, solid, and semi-solid low level waste (LLW) samples. The method uses chemical distillation for separation followed by neutron activation of the separated fraction containing iodine. The objective of this work was to develop an efficient and reproducible procedure for determining ^{129}I concentrations in LLW samples.

Iodine-129 has a half life of 1.572E7 y (ICRP, 1983) and decays 100% by emission of a β particle with a maximum energy of 150 keV (average energy = 48.9 keV) to an excited state of ^{129}Xe . The excitation state yields a 39.6 keV γ ray 7.51% of the time. Internal conversion accounts for the balance of the excitation energy release with the emission of several xenon x rays, the most abundant being 29.8 keV (36.9% of decays), 29.5 keV (19.9% of decays), 33.6 keV (7.1% of decays), 34.4 keV (2.4% of decays) and 33.6 keV (3.7% of decays). These photons could be used to quantify ^{129}I with proper equipment; however, the very slow decay rate of ^{129}I has a significant effect on sensitivity of a photon-counting method. Since ^{129}I emits such low energy x- and γ -rays, self-absorption and absorption within the γ detector can cause decreased sensitivity. For this reason, some procedures try to compensate by using extremely long counting times, even as long as a week.

The principle means of production of ^{129}I is by thermal fission of ^{235}U and ^{239}Pu , with a cumulative thermal fission yield of 1.0% (Blomeke and Todd, 1957) in ^{235}U . The ^{129}I that is released directly from nuclear power plants does not currently present a threat to public health, but the isotope's longevity, its possible accumulation in waste disposal sites, and its potential migration over many years from such sites make it important to determine disposal site inventories. These inventories are important for modelling of future impacts; thus, LLW measurements programs are required to include specific measurements of ^{129}I content in all waste shipments.

Background

Various methods that have been used to quantitate ^{129}I have been described by Brauer (1989) and Strebin *et al.* (1988). Most procedures involve radiochemical separation of the ^{129}I followed by additional processing for counting. New York State, in its studies of environmental ^{129}I , concentrates the sample for direct counting of the isotope on an intrinsic germanium detector (Radiological Sciences Laboratory, 1974). Strebin *et al.* (1988) have concentrated large environmental samples which are processed by oxygen combustion and off gas trapping for neutron activation analysis. Their samples were spiked with ^{125}I for yield determination. Low-level β counting can also be used; however, radioactive tracers for yield determination cannot be used in this method.

Thermal-emission mass spectrometry, accelerator mass spectrometry, and neutron activation are quite sensitive; however, they require specialized equipment. One advantage of neutron activation, if a sufficient neutron source is available, is that it provides good sensitivity with short counting times after the sample is activated.

One uncertainty in all of the current radioanalytical methods for ^{129}I is whether the iodine atoms may be in complex sample matrices, thus precluding consistent and reproducible recovery from sample to sample. Such reproducibility may be a problem for the wide variety of samples from nuclear power plants; therefore, it is essential to use a tracer for radiochemical yield determination on each sample processed. The work reported here for LLW samples used distillation/radiochemical separation, a stable tracer, and neutron activation of LLW samples for comparison to activated ^{129}I standards.

Method

The chemical procedure and the neutron activation method were designed to analyze the ^{129}I content of LLW wastes from the Big Rock Point and Palisades Nuclear Power Plants in Michigan. The waste samples received no pretreatment prior to arrival at the laboratory and were comprised primarily of resins, liquids, filters and smears. Approximately 4 g of each liquid sample was processed; however, the weight of solid samples depended on their availability since they were collected by smearing an area or they were solids that were quite radioactive.

The principle of the chemical process was to first remove the iodine from the sample through a distillation process which has been well documented (Anderson, 1981; Handl and Kuhn, 1980) as a successful method of isolating the iodine from various contaminants such as bromine. Bromine can decrease the sensitivity of the neutron activation method since it has a moderately high thermal neutron cross section (3 barn) and it emits γ rays with energies similar to those of ^{130}I . The object of chemical separation is to isolate the iodine using solvent extraction, converting it into a form which is suitable for neutron irradiation. The extracted iodine is then transferred to polypropylene capsules for neutron activation. Stable iodine is added at the beginning of the distillation process in order to quantify the chemical recovery. A neutron-gamma reaction converts stable ^{127}I to ^{128}I , which has a half-life of 24.99 min. The activated ^{128}I decays with a 16.9% abundant 442 keV (Browne and Firestone, 1986) γ ray, which is used to quantitate its activity and determine chemical recovery.

A neutron-gamma reaction also converts ^{129}I to ^{130}I which has a half life of 12.3 h. The activated ^{130}I decays by a 99% abundant 536 keV γ ray (Browne and Firestone, 1986) which is used to quantify the ^{130}I content to ultimately determine the ^{129}I

concentration. A reference standard of ^{129}I (National Institute of Standards and Technology, Certification No. 4949B-74; $192.43 \pm 3.66 \mu\text{Ci/g}$) was irradiated under identical conditions for quantification of the samples by a ratio of observed activities.

Radiochemical procedure

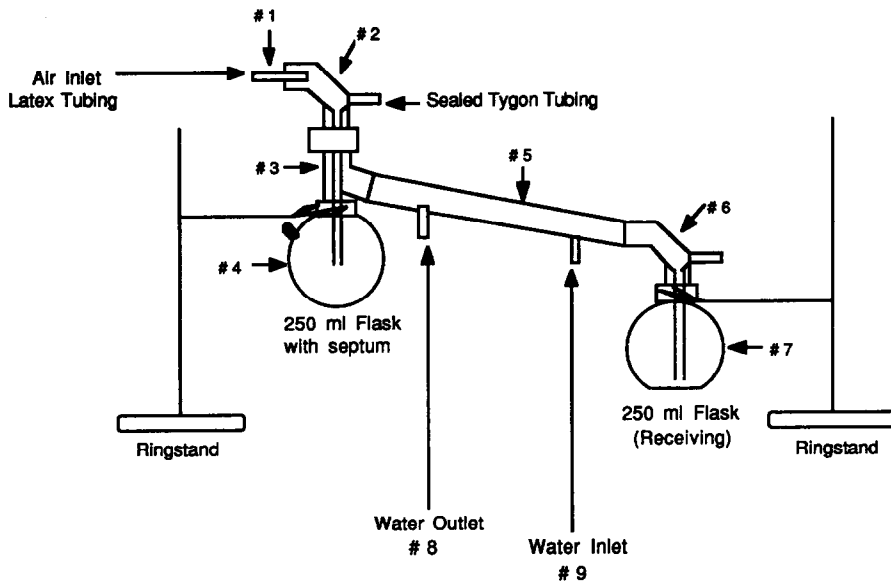
Liquid and solid waste samples were processed by chemical distillation using the apparatus shown in Fig. 1. Prior to distillation, 30 mL of 0.5 M NaOH was added to the receiver flask in order to trap the iodine released from the sample. A pre-weighed aliquot of the sample was added to the distillation flask along with 1 mL of 0.007 M NaI tracer for determining chemical recovery. The distillation apparatus (see Fig. 1) was then assembled with an air supply fitting attached to the top of the distillation flask assembly. After assembly and with the air supply connected, 32 mL of cold concentrated HNO_3 was added to the distillation flask through the syringe attached to the distillation flask. This method was important in order to minimize any iodine losses released by the added HNO_3 . The distillation process was allowed to continue for 35 min (the optimal processing time).

Following distillation, the 30 mL of 0.5 M NaOH in the receiving flask was quickly acidified with 4 mL of 6 M H_2SO_4 . The mixture was then added to a 60 mL separatory funnel containing 1 mL of 1 M NaNO_2 . 10 mL of pre-equilibrated CCl_4 was then added and the mixture was shaken for 2 min.

The organic fraction was then drawn off into another 60 mL separatory funnel containing 5 mL of freshly prepared H_2SO_3 . In order to assure recovery of all the iodine from the original solution, another 1 mL of H_2SO_3 and 5 mL of pre-equilibrated CCl_4 were added and the mixture shaken for an additional 2 min. The organic fraction was then drawn off into the separatory funnel containing the first organic fraction and the 1 M H_2SO_3 . The separatory funnel was then shaken for 2 min after which the aqueous fraction was saved and the organic fraction discarded. The aqueous fractions, which contained the iodine as iodide, were then transferred to a 4 mL polypropylene irradiation vial.

Reference standards of ^{129}I and stable iodine (0.007 M NaI) were prepared and added to an irradiation vial. These standards were not distilled; thus they provided baselines for determining ^{129}I activity and chemical recovery by a ratio method. The activated ^{128}I measured in each sample was ratioed to that produced in the known standard to determine chemical recovery. Likewise, the activated ^{130}I in each sample was ratioed to that produced by activation of the known ^{129}I activity in the standard to determine the ^{129}I in each sample.

The irradiation vials were irradiated in a 2-MW research reactor. The vials were transferred by a pneumatic transfer system to the reactor core and exposed to a neutron flux of approx. $10^{19} \text{ n cm}^{-2} \text{ s}^{-1}$ for



Equipment

1. Small glass adapter- straight connecting, 19/22 joints- Part No. 5035 Ace Glass Co.
2. Adapter, Vacuum Take-off, Long Stem, 24/40 joints- Part No. 5195 Ace Glass Co.
3. Adapter, 75 degree Side Arm, 24/40 joints- Part No. 5040 Ace Glass Co.
4. Flask, Short Neck, with Septum Port, 24/40 joints, 250 ml- Part No. 6933-24 Ace Glass Co.
5. Condenser, 24/40 joints- Part No. 6025 Ace Glass Co.
6. Adapter, Vacuum Take-off, Short Stem, 24/40 joints- Part No. 5195 Ace Glass Co.
7. Flask, Flat-Bottomed, 24/40 joints, 250 ml- Part No. 6896-08 Ace Glass Co.
8. Water Outlet, Latex Tubing, 1/4"x1/16"
9. Water Inlet, Latex Tubing, 1/4"x1/16"

Fig. 1. Distillation apparatus for ^{129}I analysis.

5 min. Upon removal from the neutron flux, the vials were "cooled" so short-lived isotopes could decay to a point that the dose-rate from the vial allowed safe handling. Each vial was then placed on a thin-

window high-purity intrinsic germanium detector and counted for 1000 s. Figure 2 shows a plot of a typical spectrum obtained. The ^{129}I peak occurs at 442 keV, and ^{130}I has peaks at 536, 668 and 748 keV.

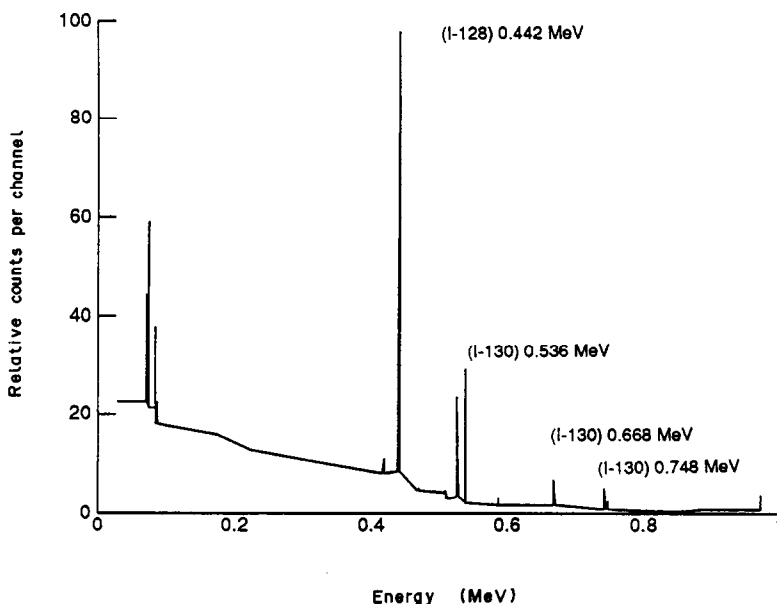


Fig. 2. Typical spectrum from neutron activation of a standard containing ^{129}I and stable ^{127}I using a thin-window high-purity intrinsic germanium detector.

The ^{129}I activity per gram of sample was calculated by the following equation:

$$^{129}\text{I} \text{ (nCi/g)} = \frac{\text{Measured } ^{129}\text{I} \text{ activity (nCi)}}{\text{CR} \cdot w(\text{g})}$$

where, "measured ^{129}I activity" is that obtained by dividing the activity measured under the 0.536 MeV peak (Fig. 2) to that measured per nCi for the NIST-traceable standard; "CR" is the chemical recovery obtained by ratioing the activity measured at the 0.442 peak for each sample to that obtained at the same peak for the known standard (the difference is due to system losses since each was spiked with identical amounts of stable iodine); and w is the sample weight in grams.

Results and Discussion

The chemical yield depended greatly on the proper balance of the distillation time and the amount of nitric acid added in the sample distillation process. The results of varying both of these parameters are shown in Figs 3 and 4, respectively. It was observed that chemical recovery was optimal when the distillation time was about 35 min following the addition of about 30 mL of concentrated nitric acid. However, as shown in Figs 3 and 4, larger values of either of

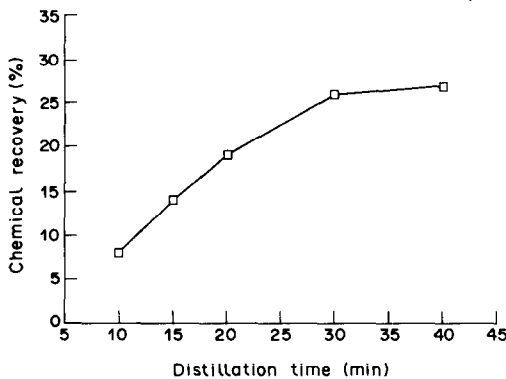


Fig. 3. The effect of distillation time on chemical recovery for solutions containing 30 mL of nitric acid.

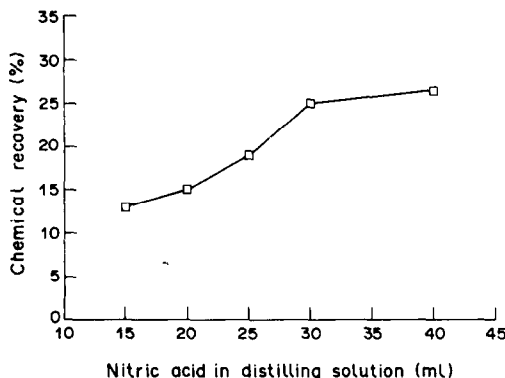


Fig. 4. The effects of nitric acid content on chemical recovery for solutions distilled for 30 min.

these parameters yielded little increase in the chemical recovery; therefore, the procedure used a 35-min distillation time and the addition of 32 mL of concentrated nitric acid. For these conditions, the chemical recovery ranged from 22% to 35%, which is slightly lower than recoveries reported by other authors (Wilkins and Stewart, 1982), probably due to failure to pretreat the samples. The uncertainties in the data plotted in Figs 3 and 4 were less than 10% due to counting statistics.

Some procedures use post-irradiation processing to ensure that samples are free of contaminants, particularly ^{82}Br , which may lower the counting efficiency of the ^{130}I . Such processing was not necessary because clean peaks for quantification were always obtained for the analyses performed. Anderson (1981) and Handl and Kuhn (1980) have shown that distillation sufficiently removes the ^{82}Br , and results of our studies reflect their findings.

Chemical yield is an important determination especially since LLW samples are so diverse in type and history. Consequently, it is essential to use a tracer method for each sample processed. Even then, it is difficult to establish chemical recovery with certainty because the ^{129}I in the sample may be in complex matrices and the behaviour of the tracer may not mirror the behaviour of the iodine in the sample. This problem exists for any method that might be selected. Since the neutron activation technique provides clear identification of the activation products, it is reasonable to expect that both the sample iodine and the tracer are effectively removed by the distillation/nitric acid stripping technique. Known samples were allowed to set for 30–90 min after adding HNO_3 before being distilled and no appreciable differences were noted in observed recoveries. Consequently, it is believed that the concentrated nitric acid equilibrates rapidly with the sample and effectively liberates ^{129}I from the sample matrix regardless of sample type.

Since this method is dependent upon normalizing a sample to the known concentration in a standard, accuracy requires that the irradiation time and the time between irradiation and counting be kept constant due to the short half-lives of both ^{128}I and ^{130}I . The minimum detectable activity (Currie, 1968) for ^{129}I with a counting time of 1000 s and a chemical recovery of 29% was approx. 30 pCi/g for a 4 g sample. Decreasing the background count rates could improve the minimum detectable activity of the procedure; however, to do so requires a longer decay time between irradiation and sample counting. Since the chemical recovery is based on measurement of ^{128}I , which has a half-life of 25 min such decay can affect the accuracy of the chemical recovery determination. It is believed that any gain in the minimum detectable activity for cooling times longer than about 30 min would be offset by increased uncertainty in the ^{128}I count itself. The average labor commitment, working with 10–15 diverse samples, was approx. 2.5 h per sample.

Summary and Conclusions

This study was undertaken to develop a straightforward and relatively non-labor intensive procedure for measuring ^{129}I in different forms of low-level radioactive waste samples (solid, liquid, resin). The procedure used is based on sample distillation followed by radiochemical separation and neutron activation. It has been tested by numerous measurements of an ^{129}I standard and several sets of typical waste samples. Consistent results have been obtained for both. The chemical recovery was $29 \pm 7\%$, which was optimal for a distillation time of 35 min using 32 mL of concentrated nitric acid added as an extractant to the distilled samples. The minimum detectable activity of ^{129}I in the samples was 30 pCi/g based on a 4 g sample, a 29% chemical recovery, and a counting time of 1000 s.

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