MEASUREMENT OF ALPHA EMITTING NUCLIDES IN ORGANIC LIQUID WASTE

Adrian van Dalen
Netherlands Energy Research Foundation (ECN)
Martha P. Valdivia
University of Arizona, Tucson, Arizona

ABSTRACT

Radioactive organic liquid wastes are in general processed by incineration. The content of alpha emitting nuclides has to be known for licencing procedures. The main catagories of liquid organic wastes are liquid scintillator solutions, power station oils and mixed organic liquids from laboratories. Depending on the nature of the organic liquid the radionuclides can be extracted with a dilute acid, or after addition of alcohol with a cation exchanger. The radioactivity measurements are performed with α, β and γ spectrometry.

INTRODUCTION

In The Netherlands since 1982 an independent central organization for radioactive waste - COVRA - is in charge of all executional aspects of the management of radioactive wastes. Radwaste will be stored for a period of 50-100 years according to the decision of the government. The processing of low level wastes from hospitals and laboratories is still carried out by the Energy Research Foundation ECN. This practise will be prolonged until the new site of COVRA is ready to receive radioactive wastes including reprocessing wastes from COGEMA and BNFL. Building activities at the new site are just starting (1). It is foreseen by COVRA to install an incinerator for liquid organic radioactive wastes. For these wastes COVRA wants to have a simple analysis scheme for detecting radioactivity in the liquids and in particular alpha activity.

DESCRIPTION OF THE ORGANIC LIQUID WASTES

The largest scheme of liquid organic wastes produced in the country is liquid scintillator counting waste. Practically all users of this counting system take the advantage of the water miscible cocktal solutions. The liquid waste contains therefore 20-50% of water, about 10% of an emulsifier, 40-70% of an organic solvent (monoaromatic), and a small amount of chemicals for the scintillation processes and those from the radioactive samples. Samples to be counted by liquid scintillation may not contain too much salts, no oxiding agents and have to be about neutral regarding pH. The second group consists of solutions used for cleaning and decontamination. They contain more water, organic complexing agents, and neutral detergents. The solutions are neutralized before shipping. Apart form radionuclides the solutions contain corrosion products. The third and last group consists of spent lubricating and cooling fluids from nuclear power stations. These organic liquids are not water miscible and may contain silicon oils. Small amounts of active and inactive corrosion products are present together with some fission products.

The concentration of radioactive material in the waste solutions is in the range of 1 kBq - 1 MBq per kg.

THE DETERMINATION OF ALPHA ACTIVITY

Sample selection

The short range of alpha particles implies that only very thin preparations can be used for counting. This means that the radionuclides have to be separated from the organics. In case the waste solution contains alpha activity with only a minor amount of other beta and gamma activities the detemination of the alpha desintegration rate can be measured directly by liquid scintillation with pulse height analysis. Only a very small number of waste shipments will contain alpha emitting nuclides, so it will be useful to make a selection of the samples to be analysed based on liquid scintillation and knowledge of the origin of the waste. Alpha emitting nuclides are seldom used in laboratories of hospitals, institutes and universities. Liquid scintillation counting of 1 ml samples in a mixture of toluene (9 ml) and Instagel (10 ml) in the channels 0-18-160-300-~ keV, respectively for ^{3}H, ^{14}C, alpha and other beta, gamma activities for 5 minutes per sample gives sample information on the reliability of the declared total content of radioactive material. The liquid scintillator waste contains in general ^{3}H, ^{14}C and other beta activities in the ratio of 100:10:1. Only a few samples will remain for further inspection on alpha activity. Also a few samples will be inspected for gamma emitting nuclides with a calibrated Ge detector e.g. oils from nuclear power stations.

Sample Preparation For Alpha Counting

Several methods exist for the preparation of thin uniform layers on counting disks: direct deposition, electro-02 molecular plating, coprecipitation with $BaSO_4$ or LaF_3 (2,3). In all cases the solutions containing the alpha activities have to be free of organics. The removal of the organics by destruction proved to be of no practical value: oxidation with oxygen or air at elevated temperatures resulted in loss of radioactive material; in case silicon oils are present nearly

all radioactivity has disappeared together with the silica fumes. Destruction with strong oxidants e.g. HNO_3-$HClO_4$ mixtures may result in explosive reactions because the samples to be destructed are too large (1-10 g) for safe handling (100 mg), or result in unacceptable long destruction times if refractory organics are present (hydrocarbons, silicon oils etc.).

For the separation of the radiouclides from the organic solutions two groups have to be distinguished: the water containing - liquid scintillator and decontamination wastes -, and the water immiscible - lubricating oil - . From the first group the radioisotopes are isolated with a strong cation exchange resin after dilution of the sample with ethanol to lower the viscosity of the solution. The second group is treated by solvent extraction with 5 molar HCl also after dilution with hexane to lower the viscosity of the organic solution.

The ion exchange separation is carried out with 0.5 g Dowex 50 W 12 cation exchanger in a small column. After absorption of 5 ml sample diluted with 5 ml ethanol the column is washed with 10 ml ethanol, and the radionuclides are eluted with 10 ml 5 molar HCl. The first fraction including the alcoholic wash contains the main part of the organics with the tritium and carbon-14 activities. After the HCl elution only thorium isotopes remain on the ion-exchanger. In practise these isotopes are not present. The HCl fraction is collected in a teflon beaker, evaporated and treated with concentrated HNO_3 to destruct the last traces of organic material. If some difficult to destruct material persists the nitric acid solution is transferred to a stainless steel crucible and after evaporation heated to 400°C. After this treatment only inorganic material will remain. For alpha counting the material left in the stainless steel crucible is dissolved in a small amount of nitric acid and transferred to a stainless steel counting disk. The solvent extraction is performed with a few fractions of 5 molar HCl. The combined aqueous solutions are washed with hexane to remove entrained organic material. The hydrochloric acid solution is treated in the same way as the fraction from the ion-exchange column.

The Counting Of The Alpha Activity

For licensing purposes the total amount of alpha activity is more important than the specification of the nuclides. Specific and very sensitive alpha counting is best performed by scintillation counting with a ZnS phosphor. The background of the counter is in the range of a few counts per hour, and the counter is insensitive to beta and gamma radiations. The counting efficiency is around 45%.

If more information is needed on the isotopic composition of the main alpha activities then the same counting disks can be used for spectrometry with a silicon surface barrier detector or a gridded ionisation chamber. The determination of alpha activity by element is time consuming by the chemical separations needed; isotopic tracers of the elements to be determined have to be added for recovery determinations. For the purpose of these waste analyses there is, in general, no need for this information.

RELIABILITY OF THE RESULTS

The determination of the alpha activity is carried out without isotopic tracers for yield determinations, thus another feed-back has to be introduced to trace eventual losses during the processing of the samples. Knowledge of the origen of the wastes and the first inspection by liquid scintillation counting gives sufficient information for the selection of non-alpha and probable alpha waste. Fortunately the alpha contaminated liquid scintillator and decontamination waste contains only a small amount of beta and gamma activity. Liquid scintillation counting of the waste with spectrum recording gives quantitatively the alpha desintegration rate. This result should be in accordance with the data obtained from alpha counting or spectrometry. In actual waste samples only low enriched uranium was found.

In waste oils from the nuclear power station also some alpha activity could be measured. The ratio of alpha activity to the ^{60}Co activity was found to be about 10^{-6}. This ratio is in the range of values used for scaling factors H for power plant waste (4). The main alpha activity in this waste is related to curium isotopes. The counting times in this case for alpha spectrometry were long because the total alpha activity was in the range of 0,1 Bq/kg. The determination of these very low activities draws special attention to prevention of cross contamination.

ACKNOWLEDGEMENT

The authors are grateful to COVRA for the initiative and the financial support.

REFERENCES

1. H.D.K. Codée, J. Vrijen, "The Dutch treatment and long-term storage facility for radioactive wastes" Proceedings of the 1989 Joint International Waste Management Conference, Kyoto Vol 1., 115-119 (1989).
2. C.W. Sill, "Determination of Gross Alpha, Plutonium, Neptunium, and/or Uranium by Gross Alpha counting on Barium Sulfate", Analytical Chemistry, 52, 1452-1459 (1980).
3. S.R. Joshi, "Lanthanum fluoride coprecipitation technique for the preparation of Actinides for Alpha-particle spectrometry", J. Radioanal. Nucl. Chem. 90 (2), 409-414 (1985).
4. J.E. Cline, J.R. Noyce, L.J. Coe, K.W. Wright, "Assay of Long-lived radionuclides in low-level wastes from Power Reactors. NUREG/CR-4101 (1985).