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THE SEQUENTIAL SEPARATION OF ^{99}Tc AND ^{129}I IN WASTE SAMPLES

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A unique procedure permitting the determination of ^{99}Tc and ^{129}I in the same portion of sample is presented. Various matrices of environmental waste samples are spiked with ^{95}Tc and iodide carrier, ashed, fused, and analyzed. The matrices analyzed included various types of filters, resin, evaporator salts, floor silt, sludge and charcoal. The technetium isotopes and iodine isotopes are sequentilly separated by organic extraction techniques.

Introduction

The Idaho National Engineering Laboratory, operated by the United States Department of Energy, encompasses a variety of nuclear facilities. Low level nuclear wastes generated at these facilities must be characterized prior to their temporary disposal at an on site waste management complex.

The complexity of the waste matrices coupled with the small sample size made sequential separation of volatile ^{99}Tc and ^{129}I isotopes desirable. A new laboratory method has been developed which permits the determination of ^{99}Tc and ^{129}I in the same portion of the waste sample. The matrices analyzed included various types of filters, resin, activated charcoal, floor silt, and evaporator salts. Determining both analytes in the same portion of sample is desirable in minimizing the quantity of sample analyzed and thus attaining the lowest possible detection limit for the analytes. Present procedures do not provide for the determination of these analytes in a single sample.

The samples are ashed under basic conditions at 500 °C. A potassium carbonate fusion is completed on the ash. Dissolution of the carbonate fusion is accomplished using water as the solvent. Oxidation of the solution containing the technetium and iodine is completed using a hypochlorite solution. Technetium isotopes are extracted into methyl ethyl ketone under basic conditions. Iodine isotopes remain in the aqueous phase. Extraction of iodine isotopes as I_2 into chloroform is carried out under acidic conditions. Back extraction of the iodine into water is accomplished

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by reducing I_2 to the iodide ion with bisulfite. Further cleanup of the methyl ethyl ketone fraction containing technetium is completed with a basic wash. The yield of technetium is determined by γ-analysis of the ^{95}Tc in the sample as compared to that of a comparator containing a known amount of ^{95}Tc. ^{99}Tc determined by liquid scintillation counting. The iodide fraction is acidified and precipitated as PdI_2. The yield is determined gravimetrically and the ^{129}I is determined by counting the PdI_2 precipitate on a Low Energy Photon Spectroscopy (LEPS) system.

Experimental

The sample is weighed into a platinum dish. Sample weight varied depending upon the matrix type and the overall activity found in the sample. The sample is then spiked with a ^{95}Tc standard and a weighed amount of a known iodide carrier. The samples are thoroughly wet with concentrated ammonium hydroxide and placed in a furnace at 500 °C to ash. Care must be taken to ensure that the temperature remains at or below 500 °C. The ashing time varies with the sample type and the amount to be ashed. The amount of residue left after ashing also varies.

Potassium carbonate is added to the cooled sample in a 10:1 ratio (carbonate: sample). The sample is fused in the furnace at 900 °C until a complete melt is obtained to ensure complete interchange of the analytes with the spike and carrier materials. A different dissolution method was used on the floor silt sample. Approximately 5 g potassium hydroxide is added to the cooled sample and the sample placed in a 500 °C furnace for an hour to char. Up to 2 g magnesium nitrate is then added a bit at a time until the oxidation appears complete.

The fusion cake is dissolved in water and a 6% solution of sodium hypochlorite is added to oxidize the technetium and iodine to TcO_4^- and IO_4^-, respectively. The solution is made 2M in hydroxide with NaOH and TcO_4^- is extracted into an equal volume of methyl ethyl ketone. Two extractions of TcO_4^- are carried out with fresh portions of methyl ethyl ketone. The IO_4^- remains in the aqueous phase. This aqueous phase is acidified with nitric acid and IO_4^- is reduced to iodine (I_2) with hydroxylamine. The I_2 is extracted into chloroform. The iodine is then reduced to the iodide ion with sodium bisulfite and back extracted into an equal amount of water. The floor silt sample was again treated differently. The IO_4^- is reduced to I^- with sodium bisulfite. The I^- is then oxidized to I_2 with sodium nitrite and extracted into chloroform. The rest of the procedure is as described above.

The methyl ethyl ketone fraction containing the TcO_4^- is γ-scanned to ensure that the sample is clean, i.e., contains only ^{95}Tc and no other γ-emitters. Water is added to the methyl ethyl ketone and the methyl ethyl ketone is evaporated using a warm stream of air. The remaining water fraction is placed in a liquid scintillation vial and γ-counted to determine the ^{95}Tc activity. A ^{95}Tc comparator is also counted, and the yield is determined by comparing the counts/gram of ^{95}Tc in the sample to the counts/gram ^{95}Tc in the comparator. A commercial ready-to-use scintillator (InstaGel-XF*) is then added to the sample, mixed well and counted in a liquid scintillation counter. A ^{95}Tc comparator is also counted to determine the amount of liquid scintillation activity present due to the ^{95}Tc in the sample.

The water fraction containing the iodide is acidified with concentrated hydrochloric acid and the I^- precipitated as PdI_2 with 0.2M $PdCl_2$. The yield is determined gravimetrically and the ^{129}I is determined by counting the PdI_2 precipitate on a Low Energy Photon Spectroscopy (LEPS) system.

Results and discussion

Table 1 lists the types of samples analyzed and the yields obtained for the technetium and iodine analytes. It should be noted that several samples are listed with only technetium results. The iodine results on these samples were obtained with direct counting on the LEPS system. We believe that the iodine analysis using sequential separation would have worked well on these matrices if it had been necessary.

Table 1
Sample analysis yield results

Sample type	Tc yield, %	I yield, %
Floor silt	58.3	65.8
Prefilter	67.0	44.8
Evaporator salt	41.0	88.8
Resin	27.0	58.8
Hot cell filter	58.4	56.9
U-3 filter	57.3	44.0
M-130 filter	67.9	–
Water	82.4	–
Charcoal	66.4	–
Black sludge	43.5	–
White sludge	96.9	–

The number of samples analyzed is small; however, the variation in sample matrix is large. More samples of each matrix need to be analyzed to further test and refine the method. We feel the results obtained thus far are encouraging, especially given the difficult nature of some of the sample matrices. We expect to see improvement in the yields with further refinements in the details of the procedure, although the yields obtained with the present procedure are adequate for the purposes of the determinations.

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