Data on the HAW denitration will be presented with particular reference to the problem of the precipitation of actinides during this process.

A preliminary indication is also given of the areas of the HDEHP 1 process scheme where further experimental investigations are needed.

E26

Recovery of Grams of Americium from Scraps and Analytical Residues by Means of an Extraction Chromatographic Process Using Dihexyl N,N-Diethylcarbamylmethylene Phosphonate (DHDECMP)

J. KWINTA*, PH. BROSSARD and J. P. TURPAIN

Commissariat à l'Energie Atomique, Centre d'Etudes de Bruyères-le-Chatel, B.P. 561 - 92542 Montrouge Cédex, France

The preparation of americium compounds as well as analytical procedures lead to solid or liquid wastes from which americium must be removed and purified in order to get the oxide to be recycled. The experimental procedure for such a removal depends essentially upon the dissolution medium. Although there is a general tendency for nitric acid media, it is sometimes necessary to treat hydrochloric solutions like those coming from the analytical procedures. In most cases, these solutions are highly acid (from 1 N to 8 N or 9 N) and contain numerous cationic species (Ca, Mg, Al, Na, Li, Fe, Ni, Cr, ...) at great concentrations (10 g/l to 100 g/l). Uranium and plutonium are also present at concentrations up to 100 g/l while the americium concentration is rarely higher than 1 g/l.

If the recovery of uranium and plutonium presents no special difficulty (Purex process, anionic resins, *etc.*) the americium recovery, due to the high acidity of the solution, is a stiffer problem. However some studies [1] have demonstrated that it can be solved using bidentate extractants like the DHDECMP in the case of nitric acid media. Since our waste contains various chloride species, we have studied the extraction of americium from hydrochloric solutions. Even though the extractant appears to be slightly soluble in hydrochloric acid, we successfully removed 4 grams of pure americium from 3.5 liters of liquid waste. The present work describes our main results and the various problems we were faced with.

Americium Extraction in Hydrochloric Acid. The distribution coefficient of americium in the hydrochloric medium was studied and the results were compared with those obtained with nitric acid. One will first notice that at very low HCl concentration the coefficient decreases as the acidity increases. The curve presents a minimum around 0.8 N. This result is very important for practical purposes. At high acidity the coefficient increases but remains smaller than with nitric acid.

Americium Extraction from a Complex Composition Solution. Even though the relatively high solubility of HCl in DHDECMP at high acidities does not give great confidence, we carried on an extraction experiment from a complex solution whose composition is as follows:

Am = 1.16 g/l
Acidity = 0.8 N
Salinity $\simeq$ 100 g/l (mainly Ca^{++}, Li^+, Na^+)
Minor constituants: U, Fe, Ni, Cr at a few g/l
Organic species: TBP, TOPO at unknown but small concentrations

(This solution came from a Purex cycle and has been concentrated by evaporation).

The distribution coefficient of americium between this solution and DHDECMP 0.8 N previously equilibrated with HCl 8.5 N was $D_{Am} = 55$. This results indicates a very strong salting-out effect due to the high salinity of the solution. It gives us confidence to undertake a direct recovery of americium using column chromatography. Therefore we first ran a small scale experiment using a 1.1 cm diameter column filled with 1.5 g of DHDECMP fixed on 3 g of Gas Chrom Q. Through this column we percolated 10 ml of HCl 8.5 N and then a sufficient volume of the americium solution to reach the saturation. (This run was to calibrate a large scale experiment).

The elution step was performed with HCl 0.5 N. The americium balance is as follows:

Americium introduced: 87 mg (±10%)
Americium unfixed: 11 mg (±10%)
Americium recovered during the elution: 70 mg (±10%)

The americium was measured by alpha-spectrometry. Considering the precision of the analysis, the yield appears to be quite good and leads us to run a large scale recovery.

Large Scale Recovery of Americium Using DHDECMP. In order to remove 4 grams of americium contained in 3.5 liters of liquid waste (the same solution was used in the small scale experiment) we filled a column 50 cm high and 5 cm diameter with a 30% DHDECMP–Gas Chrom Q mixture. Then we equilibrated passing through the column a HCl 8.5 N solution under high pressure. Unfortunately, the DHDECMP did not stack on the support but fell down. This problem comes certainly from the solubility of HCl in DHDECMP. To overcome this problem we decided to refill the column with only a 15% DHDECMP–Gas Chrom Q mixture and to stop using a pump to push the solution. The column was then equilibrated with one free column volume of HCl 8.5 N. After the fixation of the 3.5 liters of liquid waste and scrubbing with one free column volume of HCl 8.5 N, the americium was eluted with 1.5 liters of 0.5 N. The result was a pure americium solution from which the oxalate precipitation has been directly performed without any pH adjustment.

The use of DHDECMP allowed us to recover americium from a liquid waste for which there were no other alternate solutions. We pointed out two factors of main importance. On the one hand, the solubility of HCl in the extractant can give serious troubles. On the other hand the very strong salting-out effect is of great help to recycle a liquid waste of complex composition. Numerous complementary studies must be undertaken. However the bidentate organo-phosphorus extraction can already be used in a lot of cases.

1 J. Navratil *et al.*, *ACS Symposium Series* 117, 1980.

E27

Detection Limits for some Transuranic Nuclides Using Low-Energy Photon Spectrometry

G. BARCI-FUNEL and G. ARDISSON*

Laboratoire de Radiochimie, Université de Nice, 28, avenue Valrose, 06034 Nice Cédex, France

During the past 40 years, artificially produced transuranium nuclides have been introduced in the aquatic systems as consequences of atmospheric fallout from nuclear testing and of controlled release from nuclear reprocessing plants; the study of the behaviour of long-lived transuranic elements in oceanic media is of a great importance from the projected development of breeder technology.

Usually, picocurie amounts of these isotopes are mainly determined in environmental samples by α spectrometry after tedious radiochemical separations. Otherwise, we tested [1] the availability of non-destructive low-energy photon spectrometry to measure activity levels of fission products after a nuclear test; in actual experiments, we attempted to give the sensitivities attained by this method for transuranic elements.

The activities were measured with a X-ray spectrometer which consists to a 200 mm^2 area, 10 mm depth planar HPGe detector; the pulses given by the linear amplifier were analysed on a 4096 channels MCA. The energy resolution (FWHM) obtained with this system was better than 180 eV at Fe K_α line.

The samples used for counting were:

a) standard activity sources of ^{241}Am, ^{243}Am and ^{244}Cm provided by L.M.R.I. or by I.A.E.A.

b) brown algae *Fucus vesiculosus* coded AGI/1: intercalibration sample provided by the International Laboratory of Marine Radioactivity (I.A.E.A.).

c) many surface sediments from Nord Cotentin (France).

Standard solutions of transuranic elements were electroplated on stainless disks using the Talvitie's method [2]; as concerns solid samples, accurately weighted quantities were packed in thin plastic containers. The samples were counted for time intervals between 50 and 360 ks. The absolute efficiency of the HPGe system was plotted against energy using counting runs with well known ^{152}Eu, ^{133}Ba and ^{241}Am sources.

The Minium Detectable Activity (MDA) attained by low-energy photon or X-ray spectrometry is related to the branching ratio $\Gamma = N_\gamma/N_\alpha$ or $X = N_x/N_\alpha$ of the isotope under consideration. The MDA (in pCi) is calculated from the formula:

$$\mathrm{MDA} = \frac{27.02 N_p}{\Gamma \cdot \epsilon \cdot t}$$

with t = counting time (s); ϵ = absolute detection efficiency.

The net peak area N_p and the substracted background area N_γ were related by: $N_p \geqslant 3\sqrt{N_b}$. The Table gives the MDA obtained in this method:

^{241}Am		^{243}Am		^{244}Cm		^{237}U	
59.54	1.2	74.67	0.7	42.84	15.3	59.54	1.2
NpL_β	2.5	NpL_α	2.6			NpL_β	2.5
E(keV)	MDA	E(keV)	MDA	E(keV)	MDA	E(keV)	MDA

1 G. Ardisson, *Trends Anal. Chem.*, *1*, No. 12, 281 (1982).
2 N. A. Talvitie, *Anal. Chem.*, *44* 280 (1972.

E28

Behaviour of Transuranic Elements in Marine Food Chains†

P. SCOPPA

Commssion of the European Communities c/o ENEA, Centro Ricerche Energia Ambiente, La Spezia, Italy

In general actinides are present as relatively insoluble compounds in the marine environment and are therefore not considered biologically mobile. Their

---

[†] Contribution n. 2024 of the Radiation Protection Programme of the Commission of the European Communities.