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

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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†

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

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interactions with living organisms are largely passive and they have no known biological function.

Transuranic elements are transported through the different compartments of marine ecosystems mainly by means of physical and chemical processes. Adsorption on suspended particulate material plays an important role in determining their accumulation in bottom sediments, which ultimately represent the storage reservoir. Subsequent remobilization is largely dependent upon geological processes. Benthic organisms have a minor role, usually through their own movements causing a rearrangement of upper sediment layers.

Biota are exposed to transuranic elements mainly through surface contact and ingestion (filter-feeding organisms). Transfer to man through the food chains is not relevant: biomagnification phenomena do not occur and concentration factors generally decrease with trophic level. Within the past years, concentration factors for Np, Pu, Am, and Cm have been determined in several species, but most data have been obtained for Pu-239. In algae and invertebrates, concentration factors for this radionuclide are in the range 100–10,000, while in vertebrate tissues lower values ranging from 1 to 100 have been observed.

Transuranic nuclides are of particular concern for the assessment of the radiological impact associated with the disposal of high-level radioactive wastes. Research on the long-term environmental behaviour of these man-made elements is considered with high priority in radiation protection programmes.

E29

Use of Higher Oxidation States of Trans-Plutonium Elements for Their Determination

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Besides the main oxidation state +3, transplutonium elements (TPE) possess a much more rich range of oxidation states than analogous lanthanides. Lately Am(VII), Cm(VI), Cf(IV) and Cf(V), Md(I) have been added to the known Am(IV), Am(V), Am(VI), Cm(IV), Bk(IV), Md(II) and No(II). The number of practical methods for obtaining and stabilizing such forms as Am(IV), Am(V), Am(VI), Bk(IV), Fm(II) and Md(I) have been elaborated during systematic investigations of unusual oxidation states of TPE. This permitted to spread their use in technology and analytical practice.

The use of Am(V) gives a great effect at americium isolation from other TPE. They usually obtain Am(V) in two steps: at first Am(III) is oxidized to Am(VI) and then Am(VI) is reduced to Am(V). Persulphate ions are often used as oxidizer with heating. We have elaborated more suitable methods of oxidation: by the mixture of $(NH_4)_2S_2O_8 + AgNO_3$ without heating and electrochemically. In the latter case Am(III) is oxidized on platinum anode at potential of 2 V in a slight acidic solution (0.02–0.1 *M* $HClO_4$, $\leqslant$0.01 *M* H_3PO_4). It is easy to reduce Am(VI) to Am(V) by lowering the anode potential to 1.27 V. However, there is often no necessity to reduce specially Am(VI) since the extractant or the sorbent can act as reducer.

Am(V) extraction by several extractants: 1-phenyl-3-methyl-4-benzoylpyrasolone-5 (PMBP), di-2-ethylhexylphosphoric acid (HDEHP), ammonium pyrrolidinedithiocarbaminate (NH_4PDTC), mixture of PMBP and tri-n-octylphosphine oxide (TOPO), pycrolonic acid (PA), from different solutions has been studied (Table I).

Am(V) is extracted by different extractants from solutions with pH = 5, while extraction of trivalent actinides can be suppressed by complexing agents—acetate ions or $K_{10}P_2W_{17}O_{61}$(PW). The separation coefficient (K_s) of Am(V) and Cm(III) in these conditions during one-fold extraction cycle reaches 5×10^3. On the contrary, trivalent actinides can be separated by extraction from 0.1 *M* $HClO_4$ or HNO_3 if complexing agents are absent.

Reagent NH_4PDTC can be used also for Am(V) separation from tri-and hexavalent actinide ions by the precipitation method. More than 99% of Am(V) coprecipitates with PDTC at pH = 5, while copre-

TABLE I.

Aqueous phase	Organic phase	Distribution coef.	
		AM(V)	ME(III)
0.01 *M* NH_4NO_3, pH = 5 (acetate buffer)	0.06 *M* NH_4PDTC in the mixture of i-pentanol and ethanol	30	0.02*
0.1 *M* NH_4NO_3, pH = 5 (acetate buffer)	0.05 *M* PMBP in i-butanol	11.6	50
the same + 0.001 *M* PW	the same	12.7	0.002
the same + 0.001 *M* PW	0.5 *M* HDEHP in octane 30	30	0.01
0.1 *M* $HClO_4$ + 0.01 *M* H_3PO_4	0.05 *M* PMBP + 0.025 *M* TOPO in cyclohexane	0.02	900
0.1 *M* HNO_3	0.16 *M* PA in methyl-i-butyl-ketone	0.26	194