

ON THE DETERMINATION OF Am^{3+} IN NATURAL
WATER BASED ON EXTRACTION OF ^{241}Am COMPLEXES
WITH FLUORINATED TRIS- β -DIKETONE

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Abstract

The synthesis and extraction of mononuclear americium (III) complexes with 4,4,4-trifluoro-1-(4-chloro-phenyl)-butane-1,3-dione have been studied. The optimal reaction conditions for the synthesis of Am (III) complex with fluorinated tris- β -diketone have been established at pH next to neutral. Diethyl ether and dichloromethane were proved to be suitable extractants for removal of the complex from the water solution. A novel two-stage extraction procedure for determination of bioavailable americium (III) in natural waters has been developed, permitting long-term preservation of Am^{3+} in its original form after sampling. The extraction yield amounts to $76.2 \pm 0.25\%$ of americium in Am^{3+} form.

Key words: Am^{3+} complexes, β -diketones, Am (III) liquid-liquid extraction, enrichment and γ -spectrometry

Introduction. The input of Am nowadays might be considered to be negligible however its environmental behaviour deserves attention, especially in natural water systems. Studies of the distribution of americium in seas showed Am concentrations between 1 to $12 \mu\text{Bq l}^{-1}$ for the East Sea, the Sea of Okhotsk and the Northwest Pacific [1]. These values are very low to attract public concern

but studies on the uptake and bioaccumulation of Am in marine products reveal that the concentration factors (radioactivity of kg animal weight per radioactivity of litre water) vary between 67 for whitebait to 670 for shell fish [2]. This is a strong indication that bioaccumulation of Am might be very high and deserves attention.

Americium can exist in many different oxidation states mainly III but also IV, V, VI. The bioavailable form of Am is Am^{3+} , which is generally the dominant form at pH values up to 6.5. It is presumed that above this pH various complexes of Am exist. The most important ligands that make complex to actinides in the environment (water) are hydroxide ions (OH^-) and carbonate ions (CO_3^{2-})³. The possibility for direct determination of bio-available americium in natural water with well-known radioanalytical methods is impossible. In some conventional methods, usually strong oxidizing or reducing agents are used, the utilization of which changes the natural actinide forms [4,5].

In a previous paper, we have reported the conditions for complex formation of americium with tris [4,4,4-trifluoro-1-(4-pyridil)-1,3-butanedion] and investigated the possibility for determination of bioavailable Am in natural river water [6] by extraction of the complex with methylisobutylketone.

The aim of the present study was to develop a method for determination of bioavailable americium in natural water (fresh and salt water) including sampling procedure permitting long-term preservation of Am in its original form. The method is based on several novel extraction procedures using fluorinated β -diketones for the first time at acidity near to neutral.

Procedures. Synthesis of ligand. The first procedure was the conventional one described by CLAISEN and CLAPEREDÉ [6]. The second procedure was modified by us applying ultrasonic irradiation of the reaction mixture, which leads to dramatic decrease of the reaction time, higher reaction yields and purity of the target products. The new procedure could be defined as faster, energy saving and therefore environmentally benign.

Extractions procedures. Extraction of americium (III) complex of 4,4,4-trifluoro-1-(4-chloro-phenyl)-butane-1,3-dione (Ligand). 5 ml preliminary prepared americium-241 (4 Bq/ml) solution in 0.1 M HNO_3 , 5 ml (3.2 M) sodium acetate aqueous solution, 2 ml (0.0004 M) 4,4,4-trifluoro-1-(4-chloro-phenyl)-butane-1,3-dione in diethyl ether, or dichloromethane were mixed in a 50-ml-extraction glass vial equipped with a mechanical stirrer and the reaction mixture was vigorously stirred. The pH of the water phase was adjusted by subsequent addition of small portions of sodium acetate. After appropriate extraction time (Table 1), the organic phase has been collected. The γ -activity of both phases (at 59.5 keV for ^{241}Am) has been measured (Table 1).

Two stages extraction of americium (III) with tris- β -diketonate ligand. STAGE 1: 5 ml preliminary prepared americium-241 (0.05 Bq/ml) solution in natural water, 0.3 ml (0.4 M) solution of (Ligand) in diethyl ether were

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Optimization of the extraction conditions of Am-complex with 4,4,4-trifluoro-1-(4-chloro-phenyl)-butane-1,3-dione (Ligand) at pH 7

Extragent diethyl ether						
Experiment	NaOAc [mol/l]/ml	²⁴¹ Am [Bq]	Ligand [mol/l]	Extraction time [min]	Phase ratio, H ₂ O/Org.	Yield [%]
1	3.2/5	5	0.0004	5	2:1	73
2	3.2/5	5	–	5	2:1	0
3	3.2/5	5	0.004	10	2:1	67
4	3.2/5	5	0.0004	0.5	4:1	84
5	3.2/5	5	0.0004	1	3:1	99
Extragent dichlormethan						
6	3.2/5	5	0.0004	5	2:1	63
7	3.2/5	5	–	5	2:1	0
8	3.2/5	5	0.004	10	2:1	57
9	3.2/5	5	0.0004	0.5	4:1	64
10	3.2/5	5	0.0004	1	5:1	79

mixed in a 30-ml-extraction glass vial equipped with a mechanical stirrer and the reaction mixture was vigorously stirred. The pH of the water phase was checked and if necessary adjusted by subsequent addition of small portions of sodium acetate.

STAGE 2: Into the same solution, 1 ml dichloromethane was added and after the corresponding extraction time the organic phase was collected. The γ -activity of both phases (at 59.5 keV for ²⁴¹Am) was measured.

The distribution ratios of americium ion for both procedures were calculated as organic phase content/aqueous phase content. All extraction experiments were carried out at 25 ± 2 °C.

Results and discussion. *Optimization of the extraction conditions.*

Two organic solvents with close polarity and low solubility in water (diethyl ether, dichlormethan) have been investigated for establishing appropriate extraction conditions. The investigated β -diketonates were soluble in both solvents.

The results from the experiments are presented in Table 1. Change of extraction time and stage of extraction did play significant role in the extraction. These results were expected, keeping in mind the high solubility of diethyl ether in water. The best results were obtained (exp. 5) at pH value 7, short extraction times of up to 1 min, six repetitions and phase ratio H₂O/Org. 3:1 (Table 1).

Two-stage extraction procedure for determination of Am³⁺ in water. A water sample spiked with ²⁴¹Am with concentration of 10⁻⁹ M and pH value 7.0 was used for the experiments. This pH was experimentally found for optimal. The results from water extraction confirmed this and showed that if the

T a b l e 2

Optimization of the extraction conditions of Am-complex with 4,4,4-trifluoro-1-(4-chloro-phenyl)-butane-1,3-dione (Ligand) from Am-model solution

Extraction conditions, Am-241 0.05 Bq/ml, pH 7						
Experiment	NaOAc [mol/l]/ml	Solvent	Ligand [mol/l]	Extraction time/ repeats	Phase ratio, H ₂ O/Org.	Yield [%]
1	–	diethylether	0.04	5 min/5	5:1	17.1
2	0.2/0.5	diethylether	0.04	5 min/5	5:1	6.3
3	–	diethylether	0.04	2 min/3	2:1	75.1
4	0.2/0.5	diethylether	–	1 min/6	2.5:1	0
5	–	diethylether	0.04	1 min/6	2.5:1	75.9
6	0.2/0.5	diethylether	0.04	1 min/4	2:1	76.3
7	–	dichloromethane	0.04	5 min/1	5:1	15.1
8	–	dichloromethane	0.04	3 min/5	2:1	76.5
9	0.2/0.5	dichloromethane	0.04	3 min/5	2:1	76.1

pH interval is between 7.0 and 7.5 it is not necessary to add NaOAc as buffer (Table 2). In case of lower pH than 7.0 and higher than 7.5, an appropriate amount of buffer (NaOAc) should be used to adjust pH to normal and to extract Am³⁺ form in range 6.0–8.5 pH.

Table 2 represents the investigated experimental conditions, namely extraction time, repetitions and different phase ratios. The optimal conditions when diethyl ether is used proved to be 1 min extraction and 4 repetitions at 2:1 H₂O/Org. ratio. When dichloromethane is used with ligand – 3 min extraction with 5 repetitions and 2:1 ratio H₂O/Org.

The disadvantage of the high solubility of diethyl ether in water (69 g/l) was turned into advantage in our experiments to propose a two-stage extraction scheme, which allows for field sampling and preservation of the original form of Am until analysis at the laboratory is performed.

STAGE 1: The ligand is introduced to the water sample as highly concentrated ligand solution in diethyl ether.

STAGE 2: The extraction of americium (III) complex from the water solution with pure organic solvent with low solubility in water is performed.

This way of work is appropriate for field sampling because the two stages of the extraction scheme may be separated in time. Normally before the usual radiochemical procedures, the water samples are acidified to prevent losses which lead to a change of the oxidation state and chemical form of the actinides in samples [7]. In the present method, appropriate amounts of ligand solution in diethyl ether and NaOAc (if necessary) are added during sampling. Under these conditions, Am³⁺ makes complexes with the ligand (Stage 1). Americium complexes

T a b l e 3

Optimization of the two stage extraction conditions of Am-complex with 4,4,4-trifluoro-1-(4-chloro-phenyl)-butane-1,3-dione (Ligand) from Am-model solution

Extraction conditions, Am-241 0.05 Bq/ml, pH 7						
Experiment	NaOAc [mol/l]/ml	Solvent	Ligand [mol/l]	Extraction time/ repeats	Phase ratio Org./H ₂ O	Yield
1	0.2/0.5	diethylether	0.4	0.5 min/2	20:1	76.3%
		dichloromethane	–	1 min/12	10:1	
2	–	diethylether	0.4	0.5 min/2	20:1	76.1%
		dichloromethane	–	1 min/12	10:1	

formed this way are insoluble in water and can stay in the water sample for a long time till the laboratory is reached and extraction performed (Stage 2).

The results from the two-stage extraction are presented on Table 3. The additional optimization proved that the extraction time is reduced but repetitions have to be increased in comparison to the results on Table 1 and Table 2. The average yield amounts to $76.2 \pm 0.25\%$ of Am³⁺, which corresponds very well to the results of the single stage extraction procedure (Table 3). This is a good indication for the applicability of the new two-stage extraction scheme, which is extremely appropriate for field sampling.

Conclusion. The conditions for quantitative extraction of Am³⁺ from natural waters as complex with two fluorinated- β -diketones were studied. A two-stage extraction procedure is proposed, permitting field sampling of water and long preservation before analysis. The procedure is characterized with extraction yield $76.2 \pm 0.25\%$.

The procedure permits speciation of Am in natural water, reduction of sampling equipment, and sampling from areas distant from the laboratory at low cost of the analysis.

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