GROSS ALPHA DETERMINATION IN URINE

Jia Guogang (贾国纲)
(*China Institute of Atomic Energy, Beijing 102413, China*)

ABSTRACT

A short review is given for the determination of gross alpha activity in urine; detailed information is collected including urine mineralization, separation of alpha emitters and source preparation.

Keywords Urine, Gross alpha, Mineralization, Internal contamination, Alpha spectrometry, ZnS(Ag) scintillation detectors

1 INTRODUCTION

Internal contamination by α emitters is assessed by bioassay techniques, since direct counting methods in vivo can not be used in this case. Alpha spectrometry or α global detection is commonly used to determine gross alpha activity in urine when people are exposed simultaneously to different α emitters. The usual procedure for the gross α determination in urine mainly consists of three steps i.e. pretreatment and concentration, purification, and source preparation and counting.

2 PRETREATMENT AND CONCENTRATION

Urine is a complicated material to work with. It is composed of inorganic salts and complexes, and organic compounds. One of the difficulties in urine analysis is to convert urine into an inorganic salt solution by ashing. Organic compounds in urine must be removed, otherwise the final recovery would be quite low because of complexes formation. Kramer[1] ashed the urine sample by boiling it with 10%~20% HNO_3 and evaporating to dryness, then more concentrated HNO_3 was used repeatedly to evaporate until clear and almost colourless solution was got. This conventional wet and dry ashing method is time-consuming and presents some risks of forming refractory oxides during the dry ashing step.

Coprecipitation technique has become a method of choice widely used since many years for the precipitation of actinides. The main advantages are time-saving and a good separation of actinides from the bulk of inorganic and organic materials present in urine.

In general, 1000~1500 ml urine is wet ashed with 100~200 ml concentrated HNO_3 and 30 ml 30% H_2O_2 at 80~90°C for 3~4 h. Meanwhile, Ca^{2+}, Fe^{3+} and concentrated H_3PO_4 are added. After mineralization, the pH of the solution is adjusted to 8~10 with ammonia to form phosphates and hydroxides. The precipitate is allowed to settle for 4~10 h. The majority of the supernatant is removed by careful aspiration and the

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precipitate is collected by centrifugation or filtration. The precipitate is then heated in muffle furnace at 500°C until a pure white residue is obtained. The residue is dissolved in 1 mol/L HNO_3 and centrifugalized to remove silica; since the silica residue has not been found to contain any measurable activity from spiked sample analysis. The final solution is then ready for further purification.

3 PURIFICATION

3.1 Surface adsorption

In 1968 Eakins[2] reported a method to determine gross α activity in urine by adsorption on a glass filter paper; the solution obtained by dissolving the ashed urine precipitate was adjusted to pH=5 with ammonia and passed through a glass fiber paper; then, the adsorbed actinides were eluted with 6 mol/L HCl. Nearly the same pH range and eluting solutions were employed in other methods which use different adsorbents, such as alumina, bentonite, silica gel and Dextrangel Sephadex. The effects of valence, pH and age of radionuclide solution have been studied.

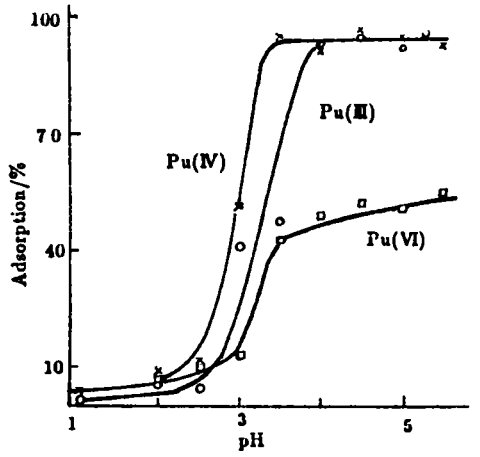

Fig.1 Adsorption curves of Pu(III, IV, VI) from calcium phosphate solutions[2]

Fig.1 shows that the adsorption curves of Pu (III) and Pu(IV) are very similar and they are almost quantitatively adsorbed by a glass fibre filter paper at pH>4.0. On the contrary Pu(VI) is less adsorbed being PuO_2^{2+} less subject to hydrolysis than Pu^{4+} and Pu^{3+}. As a matter of fact a divalent ion is also likely to be less strongly retained by ion exchange mechanisms. The same problems were also met for U(VI) and Np(V) [2,3]. As (V) and (VI) valences are poorly adsorbed, it was considered advisably to reduce the elements to (III) or (IV) with suitable reductants before the adsorption.

Fig.2 represents the percentage variation of radionuclide adsorption on alumina as a function of pH. Adsorption was highest at $3 \leq pH \leq 6.5$; this is due to the formation of positively charged soluble hydrolyzed species of the elements at such pH, which could be attracted on the negatively charged alumina surface. According to Vold[4], the major attraction forces are long Van der Waal's forces and electrical double layer interaction.

Fig.2 shows the percentage adsorption of the radionuclides as a function of pH. A number of effects may be responsible for this behavior, such as change of the ion state in the solution, or an alteration in binding properties of the active groups.

Fig.2 also shows that the percentage adsorption decreases as the age of the radioelement solution increases. Okenden *et al.*[5] claimed that ageing of Pu(VI), Am(III) and

U(VI) solution, at different pH, causes a change in the charge versus size ratio of the particles. Aged particles are larger and less charged; variation of charge would cause a variation in the force of attraction or repulsion between the radioelement particle and the alumina surface. It could be assumed that the decrease in adsorption as the age of the particle increases is due to the disappearance from the solution of small positively charged particles as these ones combine to form negatively charged colloids, which due to their negative charge are repelled by the alumina surface.

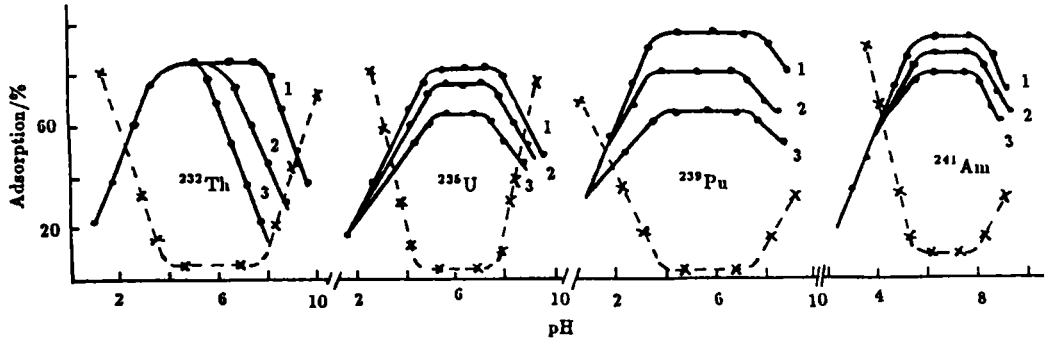

Fig.2 Variation of adsorption percentage of different radionuclides from aqueous solutions, at different age times T as a function of pH

T is the time after adjusting the pH; 1. T=5 min; 2. T=60 min; 3. T=180 min; ----- eluent, -×-×- effluent[38]

3.2 Solvent extraction

Tri-n-octyl phosphine oxide (TOPO), di-2-ethylhexyl phosphoric acid (HDEHP) and thenoyltri-fluoroacetone (TTA) have been extensively used for the determination of actinides in biological samples[6–8]. However, amines are most often used as extracting agents for the quantitative determination of U, Th, Pu and Np in urine. The most useful amines are tri-lauryl amine (TLA), tri-iso-octyl amine (TIOA), Aliquat-336 and Alamine-336.

Butler[9] utilized TIOA as an extracting agent for the extraction and determination of U, Np and Pu from urine samples. Extractions were carried out from 8 mol/L HCl solutions obtained after the complete wet ashing of urine samples with HNO_3 and H_2O_2 and the removal of HNO_3. Plutonium was backextracted with 8 mol/L HCl+0.05 mol/L NH_4I, neptunium with 4 mol/L HCl+0.02 mol/L HF and uranium with 0.2 mol/L HCl. In the case of emergency, when the detection of gross alpha activity is required, the three actinides can be stripped together by 0.1 mol/L HCl. Veselsky *et al.*[10,11], however, claimed that a direct precipitation of U, Np and Pu with calcium phosphate without any wet ashing of urine samples, followed by an extraction with Alamine-336 from 10 mol/L HCl, was better and gave radiochemical recoveries of about 95% for all three actinides.

Later on, Bulter and Hall[12] tested a new organophosphorous compound, the bibutyl-N, N-diethylcarbamylphosphonate (DDCP), for the determination of trivalent actinides (Am, Cm and Cf) in urine. After extraction of U, Np, Pu with TIOA from 8 mol/L

HCl, transplutonium elements were extracted from 12 mol/L HNO_3 into 1 ml of undiluted DDCP by mixing vigorously for 10 s. DDCP was then diluted with toluene (5 ml) and transplutonium elements were back-extracted to 2 mol/L HNO_3. As gross alpha determination is concerned, the same procedure as that for transplutonium was employed by using DDCP, because all actinide elements (from Th to Es) can be extracted from 12 mol/L HNO_3 and back-extracted to 2 mol/L HNO_3. It is suggested that the methylene derivatives of DDCP, such as caramoylmethylphosphine oxide (CMPO), is by far the best extracting agents for Am, Cm and other actinides, because the extractions can be performed at high acid concentrations; 0.01 mol/L HNO_3+0.001 mol/L $NH_2OH{\cdot}HNO_3$[13] or 1 mol/L HCOOH+0.05 mol/L $NH_2OH{\cdot}HCOOH$ solution[14] can be used as the eluent from which the actinides can be directly electroplated; moreover a good separation of the actinides from each other can also be achieved by only changing the acidity of the eluent.

3.3 Ion-exchange

Other authors prefer ion-exchange separation techniques to solvent extraction. Several investigators have used the method reported by Kressin and Waterbury[15] in which some actinides are adsorbed onto an anion-exchange column from a 7~8 mol/L HNO_3 medium. Since Pu, U, Np and Th are strongly adsorbed on the column, all these elements can be determined simultaneously. If a separation is necessary, after washing the column with 7~8 mol/L HNO_3 to remove U and Fe, thorium is first eluted with 10 mol/L HCl, followed by the elution of Pu with NH_4I in HCl and of Np with 4 mol/L HCl+0.02 mol/L HF.

Table 1
Distribution coefficients of actinides on Dowex 1×4 from 1 mol/L HNO_3-93% methanol

	Th(IV)	U(VI)	Pu(IV)	Am(III)	Cm(III)
K_d	4×10^4	4×10^2	4×10^3	1.4×10^3	10^3

An analogous procedure was used by Henley [16] for sequential determination of actinides in urine; the feed solution containing 10 mol/L HCl+0.01 mol/L HNO_3 was passed through an anion-exchange column; elution were performed with 10 mol/L HCl +0.02% HI for Pu, 6.8 mol/L HCl+0.002 mol/L HF for Pa, 4 mol/L HCl for Np and 1 mol/L HNO_3 for U, respectively. The effluent was evaporated to dryness; after washing, bismuth phosphate precipitation was carried out; the precipitate was then dissolved in HCl and Am, Cm were coprecipitated by LaF_3. The overall recoveries were 93% ± 3% for Pu, 70% ± 10% for Pa, 72% ± 5% for Np, 80% ± 5% for U and 90% for transplutonium elements.

Holm *et al.*[17] developed another method to separate actinide elements: they used 1 mol/L HNO_3+90% methanol mixture as a feeding solution containing Th, U, Np, Am and Cm to be passed through an anion-exchange column with a final elution of the actinides with 0.5 mol/L HNO_3. This technique has been used for environmental and some other biological samples[1,18]. Distribution factors of actinide elements[1] are shown in Table 1. By the method a better separation could be reached; the source so obtained presents a good resolution for alpha spectrometry.

4 SOURCE PREPARATION AND COUNTING

ZnS(Ag) scintillation detectors and alpha spectrometry are commonly used in gross alpha determination. The source preparation for the former is simple and easy: in general, the eluting solution is evaporated or boiled to a small volume which is transferred to a watch glass or platinum tray for counting. Due to the need of uniform and adherent sources for high-resolution alpha spectrometry, two techniques are used, *i.e.* electrodeposition of actinides on a platinum or stainless steel disk and coprecipitation of actinides with lanthanum, cerium or neodymium fluorides.

Actinides can be electrodeposited from ammonium media, such as formate[19], oxalate[1,20], chloride [15,21,22] or sulphate[23,24]. Ammonium sulphate is the most commonly used medium for electrodeposition, as organic materials present in the solution can be easily decomposed in the presence of H_2SO_4 or $NaHSO_4$. U, Th and Pu are routinely electrodeposited onto platinum discs from all kinds of biological sample. Schadel *et al.*[25] claimed that most actinides can be electrodeposited in 5~10 min using a dimethyl sulfoxide method. Liu[26] developed a new system for simultaneous electrodeposition of actinides; the system consists of $(NH_4)_2C_2O_4$+H_2SO_4+HCl; quantitative recovery for ^{233}U, ^{237}Np, ^{242}Pu, ^{241}Am and ^{244}Cm can be attained.

Some laboratories choose coprecipitation of actinides with rare earth metals rather than electrodeposition for the source preparation. This technique has also been used as a separation step of actinide elements after bismuth phosphate coprecipitation[27,28]. Mercier *et al.*[29] quantitatively entrained actinides by a microprecipitate of lanthanum fluoride on a cellulose acetate filter of very low porosity. This procedure has three basic advantages, *i.e.* excellent counting geometry, negligible self-absorption (weight of the precipitate 25 $\mu g/cm^2$) and good spectrometric resolution. The average chemical separation efficiency is 90%. A similar method using 50μg of La^{3+} was reported by Jia *et al*[30]. Kramer *et al* coprecipitated actinides from a 3.4 mol/L HCl solution of bismuth phosphate with 1 mg of cerium[28]; the precipitate was filtrated with a 2.4 cm diameter filter paper (pore size 0.8 μm Millipore). Sill *et al*[31] used 50μg of cerium hydroxide to precipitate actinides from an alkaline EDTA solution of barium sulphate. Hindman[32] claimed that neodymium fluoride precipitation is better than ceric hydroxide precipitation for alpha spectrometric determination of U, Pu and Am.

When liquid scintillation counting is used, the source preparation is particularly simple. In this case the end solution after purification can be mixed with a suitable scintillation liquid into a counting vial. The scintillation liquid is generally composed of a primary scintillator [PPO(2,5-diphenyloxazole) or *p*-terphenyl, 1~7 g/L] and a secondary scintillator {POPOP[1,4-bis–2(5-phenyloxazolyl)benzene], 0.05~5 g/L} dissolved in 1 L of toluene. The solvent may contain ethyl alcohol to permit complete solubility of the aqueous solutions or, alternatively, may be composed by dioxane containing dissolved naftalene (100 g/L).

Extraction-scintillation counting is also very useful. A simpler technique was used by Keough and Powers[33]. After dry and wet ashing, the residue is dissolved in hot

2 mol/L HNO_3 containing 0.2 mol/L boric acid. Up to 10 ml aliquot of the resulting solution is transferred into a 20 ml counting vial containing a drop of 4 mol/L urea. If a smaller aliquot was taken, it had to be diluted with sufficient 2 mol/L HNO_3 to bring the volume to 10 ml. Then 4 ml of an extractant-scintillation solution (200 ml HDEHP in 800 ml toluene, 4 g *p*-terphenyl, 0.05 g POPOP) was added. The vial was shaken repeatedly until constant counting. Some other authors reported that TNOA, TOPO, dibutyl phosphoric acid (DBP)[34] were also useful as extractants for scintillation counting. These techniques have primarily been used for Pu, but can be used for other actinides with proper selection of extractants, solvents and aqueous systems.

The main advantages for liquid scintillation counting are ease of sample preparation and high counting efficiency (about 100%); alpha spectrometric measurements are also possible; the resolution in the range is 200–300 keV FWHM. One drawback of this technique is the relatively high background count.

Alpha track and fission track methods have also been developed for actinide elements counting; both the methods are very sensitive; the fission track method can lower the minimum detectable limit 50 to 100 times[35], but it is limited to fissionable isotopes.

5 DISCUSSION

The concentration procedure can be considered as a first purification stage, since it allows a certain degree of separation of the actinides from the matrix. Alkaline earth phosphate coprecipitation at pH 8~10 is now widely used as an easy and suitable procedure. Alternative ways of concentration actinides are coprecipitations of bismuth phosphate at pH 1, yttrium phosphate at pH 2[36], iron phosphate at pH 4[37], titanium phosphate or calcium oxalate at pH 1~2.

After coprecipitation, some organic matter still remains in the precipitate, which can cause a big fluctuation of the recovery; therefore, the precipitate must be ashed further. As a simple oxidation with nitric acid is not sufficient to assure reproducible results, a dry ashing in a muffle at 450~500°C was chosen by many authors. Some analysts still prefer a wet ashing by repeated boiling with HNO_3 alone or in the presence of H_2O_2.

The work described in some papers demonstrates that the phenomenon of surface adsorption can be used to further purify alpha emitters. There are several advantages compared with conventional ion exchange or extraction methods, such as ease of handling, cheapness and rapidity. Table 2 shows the recoveries of actinides in some methods using different adsorbents. All these results are satisfactory; a disadvantage of these methods is the poor selectivity as some stable elements are adsorbed; therefore the sources so obtained suit only to count gross alpha activity without any alpha spectrometry.

Th,U,Np and Pu can be easily adsorbed all together by anion exchange resin. Adsorption of transplutonium elements (Am, Cm) also is possible when they are in the form of thyocyanate complexes. This procedure is adopted in particular for their separation from the lanthanides.

Table 2
Actinides yields using different adsorbents

Adsorbent	Adsor. condi.	Elu-HCl /mol·L^{-1}	Yield /%					
			Th	U	Np	Pu	Am	Cm
Anion exchange resin[1]	1 mol/L HNO_3 93% methanol	1 mol/L HNO_3	70±19	–	–	64±12	74.0±11	–
Alumina[38]	pH 5.0	2	88.6±2.3	87.0±2.0	–	90.0±2.7	84.1±5.6	94.1±1.7
Bentonite[39]	pH 5.0	0.4	–	94.9±1.1	94.5±1.5	93.6±1.8	93.9±1.4	–
Silica gel[40]	pH 5.0	6	90.2±1.5	90.4±2.5	–	94.0±1.8	91.9±2.9	93.6±1.8
Dextramgel sephadex[3]	pH 5.0	0.5	74.1±6.9	75.9±7.0	84.6±2.8	90.8±1.4	88.8±3.0	–
Glass fibre filter paper[2]	pH 5.0	6	79.7±3.5	56.2±2.0	84.9±3.3	90.2±4.1	81.7±3.8	86.1±4.3

Electrodeposition is the preferred and commonly used technique for the source preparation; however, coprecipitation of actinides with ceric hydroxide, neodymium or lanthanum fluoride is becoming very popular. Fluoride coprecipitation is very simple and convenient, as it can be used without any critical control of the test condition. The fluoride can be precipitated in a 1~8 mol/L HCl or ≤2mol/L HNO_3 medium[41] and the presence of 0.005~0.05 mol/L Fe^{3+} or Al^{3+} does not affect the coprecipitation[31].

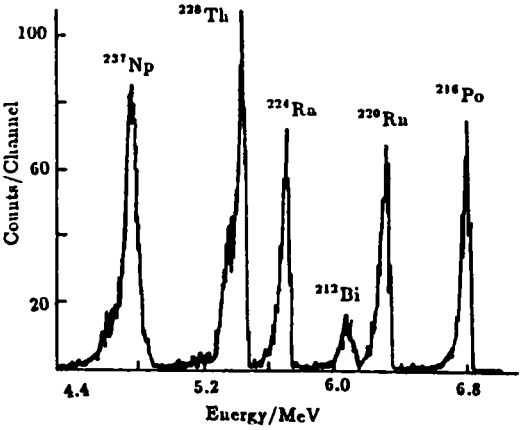

Fig.3 Alpha-spectrum of a source obtained from an 1000 ml urine sample spiked with ^{237}Np and ^{228}Th

The simultaneous determination of alpha emitters with the aid of alpha spectrometry is the most useful technique for routine analysis. Fig.3 shows the alpha spectrum of a source prepared as LaF_3 precipitate from a urine sample by Jia *et al.*[30]; a resolution of 50 keV is the ideal resolution for biological samples. Sometimes, appropriate internal tracers are required to check the final yield of the procedure because of the inevitable loss at some steps. The alpha energies of the actinides of interest are shown in Table 3.

The detection limit depends on separation methods, detection instruments and counting time. The best result was reported by Mereier *et al.*[29]; the average chemical yield of their method is 90%, the counting efficiency is 46% by the ZnS scintillation technique and 32% by the surface-barrier technique; the selected counting times are 900 min for measurement with ZnS and 4320 min for the surface-barrier detector; the detection limits are 0.55 mBq (15 fCi), and 0.11 mBq (3 fCi) respectively.

Background measurement on urine was carried out by Eakins[2]; six 1400 ml urine

samples of unexposed people were analyzed for gross alpha activity; the sources obtained were counted in a ZnS(Ag) alpha counter for 4 h and the results were 4.8±1.5 mBq.

Table 3
Alpha energies of actinides of interest

Nuclides	Energies /MeV				Nuclides	Energies /MeV					
Uranium series					^{241}Am	5.49	(85%)	5.44	(13%)		
^{238}U	4.20	(75%)	4.15	(25%)	^{237}Np	4.78	(75%)	4.65	(12%)		
^{234}U	4.77	(72%)	4.72	(28%)	^{242}Cm	6.12	(74%)	6.07	(26%)		
^{230}Th	4.68	(76%)	4.62	(24%)	^{243}Cm	6.06	(6%)	5.99	(6%)		
^{226}Ra	4.78	(95%)	4.60	(6%)		5.79	(73%)	5.74	(11.5%)		
^{210}Po	5.305	(100%)			^{244}Cm	5.81	(77%)	5.77	(23%)		
Thorium series					Tracers						
^{232}Th	4.01	(76%)	3.95	(24%)	^{232}U	5.32	(68%)	5.27	(32%)		
^{228}Th	5.43	(71%)	5.34	(26%)	^{229}Th	5.05	(7%)	4.97	(10%)		
^{240}Pu	5.17	(76%)	5.12	(24%)		4.90	(11%)	4.84	(58%)	4.81	(11%)
^{239}Pu	5.16	(88%)	5.11	(11%)	^{242}Pu	4.90	(76%)	4.86	(24%)		
^{238}Pu	5.50	(72%)	5.46	(28%)	^{243}Am	5.28	(87%)	5.23	(11.5%)		

Notes: Data in brackets are decay branching ratio

An obvious drawback of the gross alpha determination is that the nuclides which have very near alpha energy can not be distinguished in alpha spectrometry; in this case a further separation is needed.

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Jia Guogang, male, associate Professor. Born in January 21, 1952. Education: 1975-09~1979-02, dept of technical physics, Peking University; 1987-11~1989-11, Urbino University, CRE Casaccia, Italy. He has published 26 academic papers on domestic and overseas publications. Interests: studies of new separation methods for radionuclides in environmental and biological samples; studies of ecological migration processes of radionuclides in the environment; occupational exposure monitoring and dose estimation; environmental control and assessment