

Distribution Coefficients of Polonium Between 0.75 M HDEHP in Cyclohexane and Aqueous Hydrochloric and Nitric Acids

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Abstract: The distribution coefficients (D) of polonium between 0.75 M di(2-ethylhexyl)phosphoric acid (HDEHP) in cyclohexane and aqueous hydrochloric and nitric acids have been studied. Results indicate that: (1) D values are ranged from 32.7 to 0.00048 when the HCl acidities vary from 0.10 to 10.0 M, showing that polonium can well be extracted by 0.75 M HDEHP in cyclohexane if the aqueous HCl acidities are ≤ 0.050 M and it will not be extracted if ≥ 0.10 M HCl; (2) D values are ranged from 47.1 to 0.0117 when the HNO₃ acidities vary from 0.10 to 10.0 M, showing that polonium can be extractable by 0.75 M HDEHP in cyclohexane and in a wide range acidity of ≤ 4 M HNO₃. The different extraction behaviours of polonium in 0.75 M HDEHP in cyclohexane and different acidities of HCl and HNO₃ were found. The findings will be very helpful to improve the methods involving polonium decontamination for determination and separation of americium, curium as well as other radioelements in environmental soil, water and biological samples.

Keywords: Polonium, HDEHP, distribution coefficients.

1. INTRODUCTION

The element polonium (²¹⁰Po) was discovered by Marie Curie as the first element separated from pitchblende, and named after her home country, Poland [1, 2]. It has 25 known radioactive isotopes with mass numbers of 192–218, of which only the ²⁰⁸Po, ²⁰⁹Po and ²¹⁰Po have half-lives longer than days. Of these three, ²⁰⁸Po and ²⁰⁹Po, being artificial isotopes are often be used as tracers in the analytical procedures for the determination of natural polonium isotope. However, it is ²¹⁰Po, which lends itself well to industrial applications, particularly in static elimination and control, in neutron generation, and also as a heat source for satellite power supplies etc. Therefore, ²¹⁰Po is of the most interested polonium isotope from health physics and environmental impact viewpoints due to its radiation exposure.

Not like many other elements, studies on the physical properties and chemical behaviours of polonium is relatively difficult and less extent due to the facts that (1) there is no any stable isotope, and (2) a measurable mass of polonium compounds always contains very high specific radioactivity.

As the first evidence, it has long been said that polonium is volatile at high temperature (< 190 °C). But which valence or compound of polonium is volatile is not well known. Some researchers [3] studied the volatility of polonium in soil by fusion method (0.1 g soil sample containing ²¹⁰Po, mixed well with 2.0 g of Na₂CO₃ and Na₂O₂, and fused at 600 °C for different time periods of 10 - 120 min). The obtained average volatility of polonium was $13.9 \pm 3.2\%$, and the effect of the fusion time at 600 °C seems not significant. It means that most of the polonium remains not volatile. The observation of many experiments during polonium determination for some biological samples concluded that oxidation-reduction process can cause a significant lost of polonium. It means that the volatility of polonium significantly depends

on its oxidation state. Therefore, question is raised: which oxidation state is responsible for major polonium volatility, valences of +2, +4, and probably +6?

As the second evidence, there is a lack of information about the chemical extraction behaviours of polonium with many popular used organic extractants [4], such as: Tri-octyl-phosphine oxide (TOPO), di(2-ethylhexyl)phosphoric acid (HDEHP), tri-n-octylamine (TNOA), and tri-n-butyl phosphate (TBP) etc. Uranium and transuranium nuclides, such as ²³⁸U, ²³⁴U, ²³⁵U, ²³⁹⁺²⁴⁰Pu, ²³⁸Pu, ²⁴¹Am etc, represent the highly radiotoxic and/or chemical toxic, long-lived and worldwide dispersed α -emitting radionuclides in the environment [5, 6]. The activity concentration studies of these radionuclides in the environmental matrices can provide basic information on the contamination levels, sources, distributions, inventory estimation and ecological processes of the radionuclides in the environment. Due to the complexity of the matrices and the very low level of radioactivity in it, for most common determination techniques extensive sample preparation, separation and purification procedures are required to achieve accurate results [6-9]. TOPO, HDEHP, TNOA and TBP etc are very popularly used as extractants to separate actinides from the interfering elements in environmental samples. Interference of ²¹⁰Po was observed and is also very critical in the determination of actinides in environmental samples due to the widespread occurrence of ²¹⁰Po as a natural radionuclide. For instance: (1) For the determination of uranium isotope composition in lichen and soil samples [10, 11], ²³²U [$E_{\alpha}=5.2635$ MeV (31%) and 5.3203 MeV (69%)], which has a similar E_{α} to ²¹⁰Po [$E_{\alpha}=5.304$ MeV (100%)], is often used as a yield tracer. Due to the less effective separation of uranium from ²¹⁰Po in the Microthene-TOPO chromatographic column under the experimental conditions and the limited resolution of the α -spectrometry (the best FWHM is about 20-30 keV), trace amounts of ²¹⁰Po can remain in the uranium fraction in the prepared disks of the samples. Owing to the interference of ²¹⁰Po, yield correction from the ²³²U counts can lead to inaccurate results and can make the uranium concentrations of the samples much

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lower than the real values [11]. (2) A similar interference of ^{210}Po can also happen in americium analyses where Microthene-HDEHP chromatographic column was used, as the peaks of ^{210}Po and ^{243}Am ($E_{\alpha}=5.2766$ MeV) as an americium tracer are in the nearly same energy region and can not be resolved by α -spectrometry [8]. (3) If compared with the ^{210}Po concentration, plutonium nuclides only exist in extra-trace amount in environmental samples. The interference of ^{210}Po to the plutonium determinations by Microthene-TNOA chromatographic column can also be possible [6], because the peak of ^{210}Po appears just in the region between the doublet peak of ^{239}Pu [$E_{\alpha}=5.155$ MeV (73.2%)], ^{240}Pu [$E_{\alpha}=5.1681$ MeV (73.5%)] and the peak of ^{238}Pu [$E_{\alpha}=5.465$ MeV (28.3%) and 5.4992 MeV (71.6%)]. Good resolution sources for α -spectrometry measurement are needed in order to reduce the interference of ^{210}Po for plutonium nuclide determination as less as possible.

Therefore, in order to improve the analytical techniques for actinides and some other interested elements it is certainly necessary and important to study the extraction behaviours of polonium in different organic phases (toluene, cyclohexane, xylene etc) of TOPO, HDEHP, TNOA and TBP etc, and aqueous phases (HCl, HNO_3 , H_2SO_4 etc). For this purpose, the distribution coefficients of polonium between 5% TOPO in toluene and aqueous hydrochloric and nitric acids have been studied previously [12]. The objective of this paper is to study the distribution coefficients of polonium between 0.75 M HDEHP in cyclohexane and aqueous hydrochloric and nitric acids in detail. These data are needed to develop more accurate method for determination of americium and curium isotopes by α -spectrometry, and are also helpful to improve the methods involving polonium separation for other element determination.

2. MATERIALS AND METHOD

2.1. Apparatus and Reagents

Polonium-209 as a yield tracer was determined by α -spectrometry with a counting efficiency of 30.2% and a background of $\leq 6 \cdot 10^{-6}$ cps in the appropriate energy region.

A Perspex disk holder for polonium deposition was specially designed to fit 100-250 ml beakers [13]. Silver foil of 0.15 mm thickness was used for ^{210}Po spontaneous deposition and it was cut into disks of 23 mm in diameter.

Polonium-209 standard solution (0.0542 Bq ml^{-1} in 2 M HCl) and di(2-ethylhexyl)phosphoric acid (HDEHP, > 97%) were supplied by Amersham (G. B.) and Merck (Germany) respectively. All other reagents were analytical grade.

2.2. Method

An aliquot of 0.50 ml ^{209}Po standard solution (0.0271 Bq) was added to a 100 ml beaker, which was slowly heated on a hot-plate (200 °C) until incipient dryness. Then the ^{209}Po in the beaker was transferred into a 10 ml graduated centrifuge tube with 3 ml of HCl or HNO_3 solution at different concentrations (0.010, 0.050, 0.10, 0.50, 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 M). 3.0 ml of 0.75 M HDEHP in cyclohexane were added to the tube and shaking was carried out at room temperature (22 ± 2 °C) for 5 min. After centrifuging at 4000 rpm for 5 min, the aqueous phase (extracting solution) was taken out to a 150 ml beaker. The organic phase was diluted to 4.5 ml with benzene and washed with 4.5 ml of distilled

ml with benzene and washed with 4.5 ml of distilled water to lower the acidity of the solution. Finally, the polonium in the organic phase was back-extracted twice with same volume of 0.025 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution. All the washing and back-extracting solutions were combined in another 150 ml beaker. In order to destroy the residue organic matters, the extracting and back-extracting solutions were evaporated to dryness. 1 ml of concentrated HCl was added and the residue was boiled at 100 °C for some minutes with addition some drops of 30% H_2O_2 . After cooling, the pH of the solution was adjusted to 1.5 with 1:5 (v/v) ammonia. The solution was diluted to 50 ml, heated and stirred on a hot-plate magnetic stirrer. A Perspex holder with a silver disk was placed on the beaker and the silver disk was immersed into the solution. Any air bubbles trapped beneath the disk were removed by manipulation of the stirrer bar. The polonium deposition was continued for 5-6 h at 85-90 °C, then the disk was removed, washed with distilled water and acetone, dried and assayed by α -spectrometry. For detailed analytical procedure, please refer to literature [14].

2.3. Distribution Coefficients

The distribution coefficient (D) was calculated as follows:

$$D = \frac{A_o V_w}{A_w V_o}$$

Where, A_o and A_w are the ^{209}Po activities in the organic and aquatic solutions; V_o and V_w are the volumes of the organic and aquatic solutions.

3. RESULTS AND DISCUSSION

It was reported that some polonium compounds are volatile, possibly in its pure and chloride forms [2]. Therefore, the studies on the polonium extraction by HDEHP in cyclohexane and acidified aqueous phases are not easily achievable due to its volatility. In this work polonium yield determination is obliged in order to evaluate the correctness of the obtained distribution coefficients. The yields are defined as the ratios of the total polonium activity obtained from both organic and aqueous phases to that added. Higher yields with less variation are required to derive reliable D values. The most important measure was to evaporate and deposit polonium under the nearly same condition. The standard deviations given in Table 1 for individual data are 1σ , which is obtained from 2-4 times tests.

As shown in Table 1, at each condition the polonium yield ($\geq 50\%$) is relatively constant. Therefore, the obtained D values of polonium are reasonable in both hydrochloric and nitric acids. But an increasing tendency of the yields with the increasing of the acidities in both cases was observed. Low yields, meaning loss of polonium, are not due to its volatility, but to the fact that the polonium deposited on wall of the beaker during the evaporation process needed for the acid medium change can more effectively be washed by the higher acidity.

The distribution coefficients of polonium between 0.75 M HDEHP in cyclohexane and aqueous HCl at different acidities are shown in Fig. (1). It is indicated that: (1) the D values of polonium are decreasing with the increasing of

Table 1. Yields and Distribution Coefficients (Mean \pm 1 σ) of Polonium Between 0.75 M HDEHP in Cyclohexane and Aqueous Hydrochloric and Nitric Acids

Acidity, M	HCl		HNO ₃	
	Po yield, %	D*	Po yield, %	D
0.010	53.7 \pm 0.9	32.7 \pm 7.6	43.9 \pm 0.6	47.1 \pm 0.7
0.050	57.5 \pm 18.8	5.16 \pm 2.70	54.1 \pm 0.1	10.3 \pm 1.3
0.10	88.8 \pm 10.9	0.0077 \pm 0.0002	50.4 \pm 5.3	4.74 \pm 0.18
0.50	97.1 \pm 4.0	0.00048 \pm 0.00006	59.0 \pm 5.0	2.31 \pm 0.05
1.0	83.6 \pm 3.8	0.00259 \pm 0.00142	68.4 \pm 0.4	1.12 \pm 0.14
2.0	98.7 \pm 3.4	0.00119 \pm 0.00070	74.0 \pm 2.6	0.475 \pm 0.041
4.0	91.5 \pm 2.1	0.00056 \pm 0.0005	81.8 \pm 0.8	0.0842 \pm 0.0066
6.0	97.7 \pm 1.5	0.00225 \pm 0.00165	94.9 \pm 0.5	0.0222 \pm 0.0090
8.0	96.9 \pm 1.1	0.00337 \pm 0.00062	97.2 \pm 2.1	0.0133 \pm 0.0039
10.0	86.5 \pm 7.5	0.00219 \pm 0.00234	98.2 \pm 0.1	0.0117 \pm 0.0057

*which are obtained from 2-4 times tests.

HCl acidities; (2) \geq 83.3% of polonium can be extracted by 0.75 M HDEHP in cyclohexane when aqueous HCl acidities are \leq 0.050 M ($D \geq$ 5.16); and (3) nearly all the polonium (\geq 99%) remains in the aqueous phase if the HCl acidities are in the range of 0.10 – 10 M, and it means that polonium is not extractable ($D \leq$ 0.0077) when the HCl acidities are \geq 0.10 M.

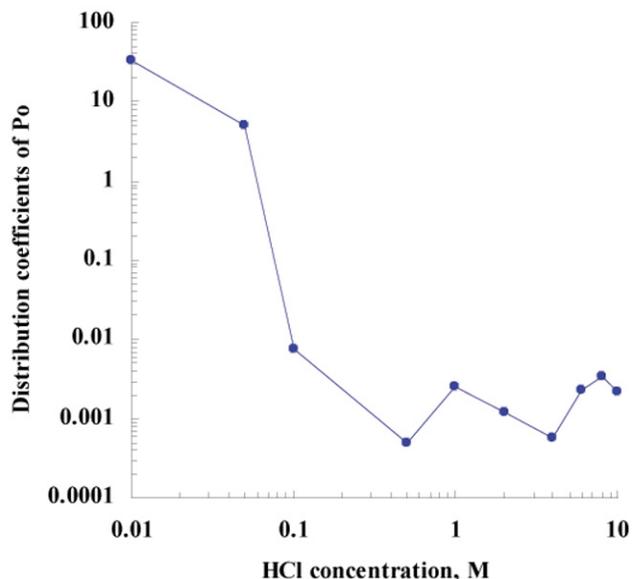


Fig. (1). Distribution coefficients of polonium between 0.75 M HDEHP in cyclohexane and aqueous hydrochloric acid.

The distribution coefficients of polonium between 0.75 M HDEHP in cyclohexane and aqueous HNO₃ at different acidity are shown in Fig. (2). It is indicated that: (1) the D values of polonium are also decreasing with the increasing of HNO₃ acidities from 0.010 to 10.0 M, but the decreasing tendency is less than in the HCl medium; (2) an observable amount of polonium (7.8%) can still be extracted by 0.75 M

HDEHP in cyclohexane and in aqueous solution of 4 M HNO₃ ($D =$ 0.084); and (3) polonium can be considered as not extractable in the aqueous acidities of \geq 8 M HNO₃ ($D <$ 0.0133).

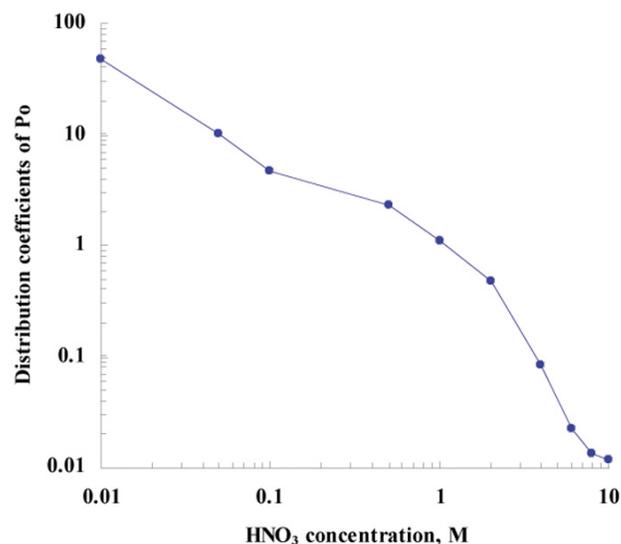


Fig. (2). Distribution coefficients of polonium between 0.75 M HDEHP in cyclohexane and aqueous nitric acid.

The Figs. (1 and 2) clearly show the different extraction behaviours of polonium in 0.75 M HDEHP in cyclohexane and in different acidities of HCl and HNO₃. The findings are very helpful to improve the method for determination of the low-level activity concentrations of americium and curium in environmental soil, water and biological samples. In the most routine procedures for americium and curium separation, 0.10 M HNO₃ was often selected as the washing solution for elimination of polonium. In fact, at this condition the D_{HNO_3} value is 4.74, which is much higher than the D_{HCl} (0.0077). Therefore, to effectively eliminate polonium from americium and curium fraction in the liquid-liquid extraction

and/or column extraction chromatography of HDEHP, 0.10 M HCl should be used as the washing solution instead of 0.10 M HNO₃.

4. CONCLUSION

The obtained results indicate that: (1) D values are ranged from 32.7 to 0.00048 when the HCl acidities vary from 0.10 to 10.0 M, showing that polonium can well be extracted by 0.75 M HDEHP in cyclohexane if the aqueous HCl acidities are ≤ 0.050 M and it will not be extracted if ≥ 0.10 M HCl; (2) D values are ranged from 47.1 to 0.0117 when the HNO₃ acidities vary from 0.10 to 10.0 M, showing that polonium can be extractable by 0.75 M HDEHP in cyclohexane in a wide range acidity of ≤ 4 M HNO₃. The different extraction behaviours of polonium in 0.75 M HDEHP in cyclohexane and in different acidities of HCl and HNO₃ were found. The findings will be very helpful to improve the methods of liquid-liquid extraction and/or column extraction chromatography of HDEHP involving polonium decontamination, such as for determination and separation of americium, curium as well other radioelements in environmental soil, water and biological samples.

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