



A rapid method for the sequential separation of polonium, plutonium, americium and uranium in drinking water

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HIGHLIGHTS

- Sequential separations of Po, Pu, Am and U were carried out in drinking water samples.
- TEVA and TRU chromatography columns were used.
- Copper sulfide micro-precipitation method was used for Po source preparation.
- The alpha spectrometry was used for determination of these radionuclides.

ABSTRACT

A new sequential separation method for the determination of polonium and actinides (Pu, Am and U) in drinking water samples has been developed that can be used for emergency response or routine water analyses. For the first time, the application of TEVA chromatography column in the sequential separation of polonium and plutonium has been studied. This method utilizes a rapid Fe^{+3} co-precipitation step to remove matrix interferences, followed by plutonium oxidation state adjustment to Pu^{4+} and an incubation period of ~ 1 h at $50\text{--}60^\circ\text{C}$ to allow Po^{2+} to oxidize to Po^{4+} . The polonium and plutonium were then separated on a TEVA column, while separation of americium from uranium was performed on a TRU column. After separation, polonium was micro-precipitated with copper sulfide (CuS), while actinides were micro co-precipitated using neodymium fluoride (NdF_3) for counting by the alpha spectrometry. The method is simple, robust and can be performed quickly with excellent removal of interferences, high chemical recovery and very good alpha peak resolution. The efficiency and reliability of the procedures were tested by using spiked samples. The effect of several transition metals (Cu^{2+} , Pb^{2+} , Fe^{3+} , Fe^{2+} , and Ni^{2+}) on the performance of this method were also assessed to evaluate the potential matrix effects. Studies indicate that presence of up to 25 mg of these cations in the samples had no adverse effect on the recovery or the resolution of polonium alpha peaks.

1. Introduction

Polonium-210 ($t_{1/2}$: 138.3 days) is a naturally occurring and widely available isotope of polonium. It exists in the environment at a trace level as a result of decay within the uranium (^{238}U) decay chain (Matthews et al., 2007). Its presence in the atmosphere is mainly due to the decay of ^{222}Rn ($t_{1/2}$: 3.82 days) diffusing from the ground. The ^{222}Rn originates from the decay of ^{238}U in the earth's crust and diffuses from soil to the atmosphere, where it is then adsorbed by aerosols and returned to earth's surface through wet and dry deposition processes (Eisenbud, 1987). Other natural sources of ^{210}Po include volcanic eruptions, fires, combustion of fossil fuels, migration of sea-salt, and

resuspension of soil particles (Poet et al., 1972; Jia et al., 2001). Technologically enhanced sources include effluents and tailings from the ^{238}U mining operations, application of phosphate fertilizers to agricultural soils, operation of coal-fired power plants, combustion of gasoline containing anti-knock compounds containing lead and the use of tobacco products such as cigarettes (Poet et al., 1972; Gesell et al., 1975; Moore et al., 1976; Jaworowski and Grzybowska, 1977; Martell, 1975). Despite its widespread distribution, polonium has received less attention and its chemistry remains only poorly known.

The high specific activity of polonium (1.66×10^{14} Bq/g) is an important aspect of its radiochemistry as well as its radio-toxicity. It is because of this high specific activity that ^{210}Po is considered to be one

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of the most toxic naturally-occurring radionuclides. For example, 1 μg of ^{210}Po emits as many alpha particles per second as 4.5 mg of ^{226}Ra , 262 mg of ^{238}Pu , or 446 kg of ^{238}U (Ansoborlo et al., 2012). The lethal dose for humans is estimated to be fewer than 10 μg . Historically, scientific interest in ^{210}Po in the environment lies in two main areas: (1) its usefulness as a natural tracer to study environmental processes such as the prediction of mixing and cycling behavior of particle-reactive pollutants; and the residence times of lead and other materials in the oceans (Carvalho et al., 1995), and (2) potential radiological impacts on human health. The poisoning of former Russian intelligence operative Alexander Litvinenko with ^{210}Po in December of 2006 brought new interest on polonium and studies on decorporation have been initiated (Miller et al., 2012).

Matthews et al. (2007), and more recently Persson and Holm, 2011 and Ansoborlo et al. (2012), have provided an exhaustive review of analytical techniques available for the assay of ^{210}Po in a variety of environmental matrices. Most of the current analytical methods for the determination of ^{210}Po in water samples have typically involved spontaneous auto deposition of ^{210}Po onto silver or other metal disks from an acidic solution (0.1–1 M HCl) followed by counting by alpha spectrometry. The auto-deposition technique is time consuming, tedious, and often times have recoveries that may be less desirable. Polonium tracers (^{208}Po or ^{209}Po) are frequently employed to measure the recovery of the procedure. However, the micro-precipitation technique has gained popularity in recent years for the polonium alpha source preparation because of its versatility and easy sample preparation. Maxwell et al. (2013) used bismuth phosphate (BiPO_4), Guérin and Dai et al., 2013, 2014 utilized copper sulfide (CuS) micro-precipitation techniques to prepare an alpha source for polonium determination by alpha spectrometry.

Polonium has a tendency to volatilize, which significantly constrains sample preparation techniques and impacts yield assessment. It has been reported that losses begin at temperatures above 100 °C, with 90% loss by 300 °C (Martin and Blanchard, 1969). The volatility of polonium compounds necessitates wet-ashing techniques wherever possible in sample preparation. Dry ashing cannot be used, and the use of the wet-ashing procedure also shows some losses. Henricsson et al. (2011) evaluated the polonium loss during wet-ashing by the use of a double-tracer technique and found values of about 17% when the samples were digested in a microwave oven and about 30% when opened glass beakers were used. Many of the water methods involve low temperature heating with HNO_3 or HCl (Matthews et al., 2007). However, radiochemical separation is often necessary to remove sample matrix and interfering radionuclides that could affect the spectral resolution and/or the recovery of polonium. Separation methods for polonium include liquid-liquid extraction with isopropyl ether, methyl isobutyl ketone (MIBK) and tri-butyl phosphate (TBP), or tri-*n*-octylphosphine oxide (TOPO) in toluene (Matthews et al., 2007; Ansoborlo et al., 2012; Sethy et al., 2015). Extraction chromatography with Sr-resin (Sadi et al., 2016); DGA resin (Maxwell et al., 2013), Pb-resin (Johansson, 2008) and an anion exchange resin (Sethy et al., 2015) has also been used for separation.

In recent years, micro-precipitation techniques for the preparation of alpha counting sources of polonium have been developed for the measurement of ^{210}Po . The micro-precipitation techniques seem to be excellent alternatives to the current spontaneous auto-deposition method for the preparation of polonium alpha counting sources. Maxwell et al. (2013) used bismuth phosphate (BiPO_4) micro-precipitation method to prepare an alpha source for polonium after separating polonium from the sample matrix on DGA resin. This method employed calcium phosphate precipitation, a stacked DGA + TRU column, and alpha spectrometry with very rapid flow rates. The method is rapid and effective in removing interferences, and can be used to determine actinides and ^{210}Po in a sequential manner. The procedure was successfully tested by analyzing several groundwater samples spiked with various levels of ^{210}Po activity. The results showed very

good agreement between the measured and reference values with an overall recovery of about $87.4 \pm 5.8\%$. The sample preparation and column separation steps, including the final micro-precipitation step using bismuth phosphate, could be performed in about 1.5 h. Guérin and Dai (2013, 2014) were the first to report copper sulfide (CuS) micro-precipitation method for the preparation of polonium counting source. Polonium forms extremely insoluble polonium sulfide co-precipitation (PoS) in 1 M HCl with a solubility product constant of (5×10^{-29}) (Guérin and Dai, 2013). This very low solubility has been successfully exploited to separate polonium from other actinides.

The other alpha emitters such as Ra, Th, U, Np, Pu, and Am, commonly found in environmental samples do not co-precipitate and, thus, do not interfere with polonium. Compared to the conventional plating method, CuS micro-precipitation method is found to be much faster as it required no heating step and, thus, could be used for processing large batches of samples with high recovery (80–95%). Additionally, the presence of up to 0.1 mg of transitional metals, which could also form insoluble sulfides along with polonium, had no adverse effects on alpha spectral resolution or polonium recoveries. Later they used this method for the determination of ^{210}Po in 10 mL of drinking water and urine samples (Guérin and Dai, 2014). The results obtained were very good with the high recovery of about 85% being reported.

In this article, a new sequential separation method for the determination of ^{210}Po and Pu, Am and U in drinking water samples has been developed that can be used for emergency response or routine water analyses. The method utilizes a rapid iron (III) co-precipitation method, separation using TEVA (Po and Pu) and TRU (Am and U) followed by rapid micro-precipitation of ^{210}Po using copper sulfide (CuS) and actinide using neodymium fluoride (NdF_3) for counting by alpha spectrometry. The method is simple, robust and can be performed in a day with excellent removal of interferences, high chemical recovery and very good alpha peak resolution.

2. Experimental

2.1. Reagents

All solutions were prepared using ultra-pure water produced from a Millipore water purification system. Trace-metal grade hydrochloric and nitric acids were obtained from Fisher Scientific Inc. Reagent-grade copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), ascorbic acid, sulfamic acid and sodium nitrite (NaNO_2) were purchased from Fisher and were used as received. Trace-metal grade nitric and hydrochloric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). For the assessment of chemical interferences, working solutions were prepared directly from the following salts: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Pb}(\text{NO}_3)_2$; $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. All other materials were ACS reagent grade and were used as received. The resins used in this work are TEVA (Aliquot 336), TRU tri *n*-butyl phosphate (TBP) and (N, N diisobutylcarbamoyl-methylphosphine oxide [CMPO]), and TRU-Resin [tri-*n*butylphosphate (TBP) and octyl (phenyl) N, N diisobutylcarbamoylmethyl-phosphine oxide (CMPO)], obtained from Eichrom Technologies, Inc., (Lisle, IL, USA, 50–100 μm particle size).

The polonium tracer, ^{209}Po , was obtained from Eckert-Ziegler Analytics, Inc.

(Atlanta, GA, USA) and diluted to the appropriate levels. A certified standard solution of ^{210}Pb (Eckert-Ziegler Analytics, Inc.), in secular equilibrium with its daughters, was used as a precursor of ^{210}Po . The stock solutions of ^{242}Pu , ^{243}Am , and ^{232}U were prepared by gravimetric dilution from standards supplied by Eckert-Ziegler Analytics, Inc. (Atlanta, GA, USA). The ^{232}U tracer was prepared by removing its ^{228}Th daughter using barium sulfate precipitation (Sill, 1974).

2.2. Apparatus

An alpha spectroscopy system (Canberra Inc.), equipped with 72

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