Comparison of Microprecipitation Methods for Polonium Source Preparation for Alpha Spectrometry

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Abstract

Detection of radioactive isotopes of polonium is important for understanding natural processes, management and assessment of radioactive waste, and nuclear forensics applications. The most common methods for preparation of polonium samples for alpha spectrometry are electrodeposition and spontaneous deposition which are time consuming. Here, we compare three approaches utilizing rapid microprecipitation from bismuth phosphate, copper sulfide, or tellurium alongside traditional spontaneous deposition methods. From these experiments, results show that copper sulfide microprecipitation recoveries are similar to spontaneous deposition on silver and less time consuming with an approximate five-fold decrease in preparation time, including in the presence of complex matrices like seawater.

Keywords

Polonium, microprecipitation, alpha spectroscopy

Introduction

There are 42 isotopes of polonium including naturally occurring and anthropogenically produced isotopes of polonium that are of interest for understanding natural processes, management and assessment of radioactive waste, and nuclear forensics applications [1, 2]. For example, significant mobilization of polonium-210 (Po-210) has been observed during recovery of unconventional oil and gas [3], and it has been a valuable tracer for understanding nutrient cycling in oceanic systems [4] and atmospheric fallout [2]. In nuclear forensics applications, polonium is also an activation product produced from neutron bombardment of bismuth that has

been monitored in waste and the environment, including the subsurface and atmosphere [2]. In addition, Po-210 has been used previously as a poison leading to significant public health concerns [5].

Polonium isotopes are primarily alpha emitters with Po-210 being the longest lived naturally occurring isotope (half-life of approximately 138 days) and polonium-209 (Po-209) being the longest lived anthropogenically produced isotope (half-life of approximately 124 years). It is important to have fast and reliable methods of preparation of samples for analysis, especially when short-lived isotopes are of interest. To date, the primary preparation methods for alpha spectrometry for polonium are spontaneous deposition and electrodeposition methods which require significant preparation time [1, 6]. When there are large numbers of samples to be analyzed or short-lived isotopes are targeted, there is a need for methods that can be conducted more quickly.

A recent review describes the different methods available for measuring polonium in samples including digestion, purification/separation, source preparation, and analysis methods [7]. When analyzing samples by alpha spectrometry, a thin, homogenous layer of sample is required. Once a sample has been digested or purified/separated, there are three primary methods of source preparation for alpha spectrometry, including spontaneous (or self) deposition, electrodeposition, and microprecipitation. Spontaneous deposition methods are most commonly used with silver flakes or discs (as well as copper, stainless steel, and nickel) with good recoveries (>95%) and selectivity for polonium, although deposition may be less uniform and can be time consuming with optimized procedures generally requiring heated deposition for 2-2.5 hours [1, 6, 8, 9]. In addition, the presence of redox active metals and organics may interfere with deposition or degrade resolution of the alpha spectra [9]. Electrodeposition procedures require a specialized setup with electrodes and a power supply and a similar time of preparation as compared to spontaneous deposition. However, electrodeposition generally results in the highest recovery, uniformity of deposition, and peak resolution [1, 7]. Microprecipitation methods are relatively fast and require minimal equipment in that a simple filter system is required (with or without vacuum). However, microprecipitation techniques may be less selective and result in less uniform precipitates and lower selectivity, peak resolution, and recoveries. Therefore, microprecipitation methods are generally optimized for the element of interest and/or conducted following separation procedures [7].

The objective of this work was to test rapid methods of preparation for alpha spectrometry that still preserve polonium recovery and peak resolution. Rapid microprecipitation methods were tested comparing previously published techniques, including bismuth phosphate [10], copper sulfide [11, 12], and tellurium microprecipitation [13], alongside a standard spontaneous deposition [1, 6].

Experimental

Materials

A Po-209 standard (0.97 pCi/g or 35890 μBq/g) was procured (Eckert and Ziegler, Valencia, CA). All salts were ACS Reagent grade or better in purity with additional chemical details in the microprecipitation methods section. Hydrochloric (HCl) acid, nitric (HNO_3) acid, and ammonium hydroxide (NH_4OH) used were Optima grade (Fisher Scientific, Hampton, NH). All dilutions were prepared with deionized water (DI, > 18 MΩ·cm).

A complex seawater (SW) matrix was prepared for comparison with separation of simple solutions. A highly enriched uranium (HEU) target was irradiated at Washington State University in a natural boron carbide shield. At the same time, an Atlantic Seawater standard from Ocean Scientific International Limited (Havant, UK) was irradiated at Pacific Northwest National Laboratory with a 14 MeV neutron generator. The HEU was dissolved in 3 M HNO_3, while the seawater was dissolved in DI water. Two types of samples were then prepared with and without the irradiated seawater as described in Table 1.

Table 1. Fissions, seawater, and stable tracers added per replicate of the radiological samples processed.

Description	Fissions	Seawater	Stable Tracers (100 μg of each)
No Seawater	5×10^{11}	0	Cu, Mn, Ni, Pt, V, Zn
Seawater	5×10^{11}	1×10^{-4} atoms ^{24}Na/ Fissions	Cu, Mn, Ni, Pt, V, Zn

Methods

Table 2 summarizes the matrix of experiments conducted to compare microprecipitation and spontaneous deposition methods. These methods of preparation for alpha spectrometry are summarized in the sections for microprecipitation and spontaneous deposition, respectively. Three different microprecipitation procedures were tested, including copper sulfide, bismuth phosphate, and tellurium. The alpha spectrometry section details counting methods. Samples were prepared in 0.1 M hydrochloric acid (HCl) either via addition of a polonium standard to 0.1 M HCl for the simplified matrix or via separation and elution of polonium from a complex seawater (SW) matrix (as described in materials section) with an initial volume of 40 mL.

The optimal microprecipitation method identified in the simplified matrix was compared alongside spontaneous deposition for the SW matrix. The SW matrix was eluted from resins following two different isolation procedures. For one of the procedures, polonium was eluted from strontium resin (Sr resin, Eichrom Technologies, Inc., Lane Lisle, IL) in 0.1 M HCl as described previously [14] and summarized in the Supplemental Materials **Fig. S1**. For the second procedure, polonium was eluted from a mixture of Sr resin and KNiFC Pan resin (Eichrom Technologies, Inc., Lane Lisle, IL) in 8 M HNO_3 with transposition via repeated evaporation to near dryness at by setting the hot plate to 150°C with addition of 0.1 M HCl. The transposition was conducted at relatively low temperature to reduce volatilization of polonium [1, 3] and without drying completely, as dry ash procedures have reported significantly lower recoveries [9]. Both isolation procedures were tested for comparison of the microprecipitation method with the best performance in the simple matrix with the SW matrix. The second isolation procedure was also tested with the spontaneous deposition procedure to allow for comparison of standard methods with the best preforming microprecipitation in the SW matrix.

Table 2. Matrix of experiments.

Method	Matrix[1]	Background Solution	Elution Conditions[3]
Bismuth Phosphate	Simple	0.1 M HCl	N/A
Tellurium	Simple	0.1 M HCl	N/A
Copper Sulfide – 1[2]	Simple	0.1 M HCl	N/A
Copper Sulfide – 0.5[2]	Simple	0.1 M HCl	N/A
	SW	0.1 M HCl	Sr Resin

		8 M HNO_3	KNiFC Pan Resin
Spontaneous Deposition	SW	0.1 M HCl	Sr Resin
		8 M HNO_3	KNiFC Pan Resin

[1]The "Simple" Matrix includes addition of only a Po-209/210 standard to acid solutions, while the "SW" matrix includes addition of a background seawater matrix as described in the materials section.

[2]The total copper added in the copper sulfide microprecipitation was tested at 0.5 and 1.0 µg based on previous research [11, 12].

[3]Samples prepared in the SW matrix also went through separations schemes to isolate polonium isotopes for analysis.

Microprecipitation

For the bismuth phosphate method, the following reagents were added in series based on previous research [10]:

(i) 125 µL of 1000 µg/mL Bi stock solution in 2% HNO_3 (High Purity Standards, Charleston, SC) in 0.1 M HCl

(ii) 100 µL H_2O_2 (30% concentration, Fisher Scientific)

(iii) 1 mL of 14.5 M NH_4OH (Fisher Scientific)

(iv) 0.75 mL of 3.2 M $(NH_4)_2HPO_4$ (99+% purity, Thermo Scientific)

For the copper sulfide method, the following reagents were added in series based on previous research [11, 12]:

(i) 1 mL of 0.5 or 1.0 mg Cu/mL from $CuCl_2 \cdot 2H_2O$ (Fisher Scientific) in 0.1 M HCl

(ii) 1 mL of 0.3 wt.% Na_2S from $Na_2S \cdot 9H_2O$ (Fisher Scientific) in 0.1 M HCl

For the tellurium method, the following reagents were added in series based on previous research [13]:

(i) 0.4 mL of 1 mg/mL Te from $H_{10}Na_2O_9Te$ (99.5% purity, Fisher Scientific) in 30% HCl

(ii) 4 mL of 10 m/v% $SnCl_2$ (Fisher Scientific) in 1 M HCl

Approximately 15 minutes after addition, samples for all methods were vacuum filtered onto Resolve filters (Eichrom Technologies, Inc., 0.1 µm pore size, polyethylene). During vacuum filtration, the filter was pre-rinsed with alcohol and deionized water (DI, resistivity >

18 MΩ-cm), before the sample was quantitatively transferred to the filtration unit with three 1 mL rinses of the sample tube with 0.1 M HCl, followed by another round of rinsing with DI and then alcohol.

Spontaneous Deposition

Spontaneous deposition was conducted based on previous research [1, 6]. First, the Po fraction was adjusted to pH 2 via dropwise addition of 10 M NH_4OH and heated to 90-95 ºC in a glass beaker. A polished silver disc was taped on the bottom side to allow for alpha counting of only the top side of the disc before emplacement into the beaker. During deposition, the sample was gently stirred with a magnetic bar for 2 hours with addition of DI periodically to keep the volume from fluctuating during heating. After, the disc was removed, rinsed with DI water, and air-dried in a fume hood.

Alpha spectrometry

Samples were counted on a Canberra Alpha Analyst with Passivated Implanted Planar Silicon (PIPS) detectors. Counting times were approximately 48 hours resulting in an error of < 2% based on counting statistics [15]. The data was analyzed via Canberra software, Apex-Alpha with a library built from the Evaluated Nuclear Structure Data File, which defines peak energies, half-lives, and branching ratios. Regions of Interest (ROI) were taken from the peak energies and extend from +25 keV to -75 keV for a total range of 100 keV surrounding the peak. This ROI can change based on interfering isotopes or sample attenuation, which increases the ROI at the low energy tail. It should be noted that counts may have been attenuated due to sample geometry or precipitate size (for the microprecipitation method) and expanding the ROI only works with neat samples. In addition, the efficiency is slightly increased for the samples prepared on filters (for the microprecipitation method) as the distance from the detectors is slightly decreased as compared to the calibrated geometry.

Results

Comparison of microprecipitation methods

Three different microprecipitation methods and a standard spontaneous deposition method were tested for preparation of polonium for alpha spectrometry. All three microprecipitation methods were effective with recoveries over 90% for clean samples prepared from high purity solutions and a Po-209 stock. However, the copper sulfide method was determined to be the optimal method as the full-width-half-maximum (FWHM) was significantly different for each of the three microprecipitation methods with the average FWHM increasing in the following order: copper sulfide < bismuth phosphate < tellurium, as summarized in **Table 3** and Supplemental Materials **Table S.1** (which compares the methods based on a t-test with an $\alpha = 0.05$). The narrowest FWHM is preferred as it allows for the greatest potential differentiation in alpha energies and suggests less attenuation of the alpha particles due to deposition layer thickness. In addition, there was an increase in the background observed during alpha counting due to chemical impurities for the bismuth phosphate and tellurium microprecipitation methods. Therefore, the copper sulfide method was chosen for further comparison with spontaneous deposition methods for a sample with a SW matrix.

For the bismuth phosphate microprecipitation method, there were visible peaks from naturally occurring U-234/238 (4774.6 and 4198 keV, respectively) likely due to chemical impurities in the $(NH_4)_2HPO_4$ salts (> 99% purity, Thermo Scientific) as shown in the Supplemental Materials **Fig. 1a**. The location of the primary U-234 peak (4774.6 keV) near the Po-209 (4883 and 4885 keV) peaks could lead to loss of approximately 1-2% of the low end of the tail of Po-209. These peaks were observed in the background (reagent blank) and samples spiked with Po-209. This amount of uranium would represent small fraction of the total mass added from the $(NH_4)_2HPO_4$ as U-238 (approximately an 8.7×10^{-7} fraction). Uranium is commonly observed at elevated concentrations in phosphate minerals [16, 17]. Although cleanup of the background natural uranium in these salts is possible, it would be time consuming. Because of the added time for purifying salts and the ease of other microprecipitation methods tested, further testing with this method was not conducted.

The largest FWHM was observed for the tellurium microprecipitation along with the greatest variability, as shown in **Table 3**. Although the FWHM was larger for tellurium, the visual precipitate (Supplemental Materials **Fig. S.2a**) appeared relatively more consistent than copper sulfide. In addition, there were visible peaks from Po-210 likely due to chemical impurities in the $H_{10}Na_2O_9Te$ (>99.5% purity) salt as shown in **Fig. 1b**, potentially concentrated

alongside the tellurium during purification from natural materials. Therefore, if Po-210 measurements are of interest, then this method should be avoided unless chemicals are tested prior to preparation. Because of the larger FWHM and background Po-210, further testing was also not conducted with this method.

Overall, the copper sulfide method led to the narrowest FWHM, did not have significant background peaks due to chemical impurities, and was similarly fast to prepare when compared with the other two microprecipitation methods. The preparation time for the copper sulfide microprecipitation, approximately 30 minutes, as compared to spontaneous deposition resulted in an approximate five-fold decrease in preparation time for alpha spectrometry. In addition, select tests were conducted to determine the optimal mass of Cu to add to samples for precipitation of copper sulfide. Previously published research added between 0.5 and 1 mg of Cu during sample preparation [11, 12]. However, a significant difference was not observed with addition of 0.5 or 1 mg of Cu as summarized in the Supplemental Materials, section S.3, **Fig. S.3** Testing continued with 0.5 mg of Cu.

Table 3. Summary of results for microprecipitation methods with error based on one standard deviation of triplicate samples.

Method	Recovery (%)	FWHM
Copper Sulfide	93±3	32.9±2.6
Bismuth Phosphate	105±5	37.3±1.7
Tellurium	114±1	67.9±15.7

[1]0.5 mg of copper added for microprecipitation

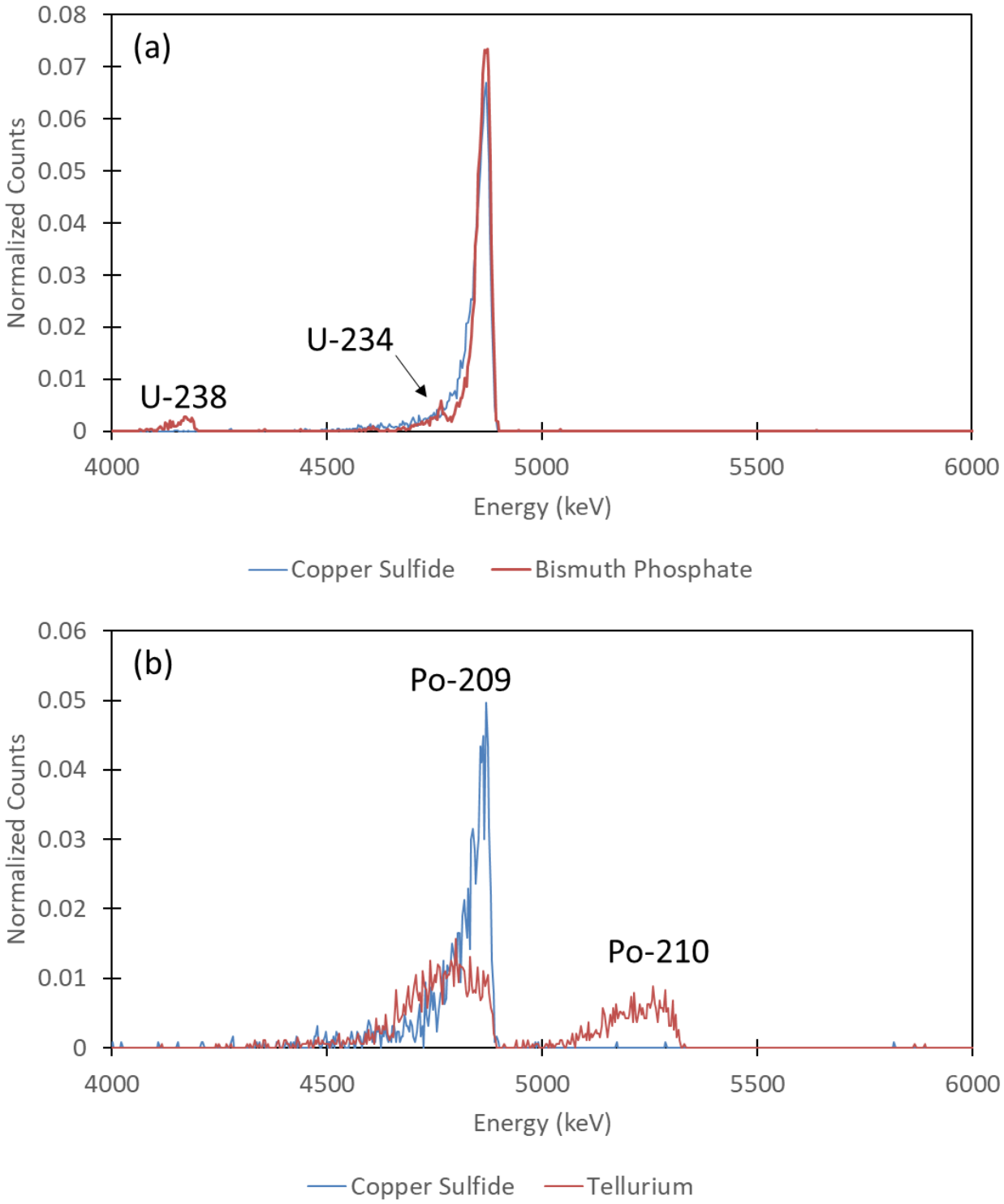

Fig. 1. Comparison of spectra showing salt impurities for bismuth phosphate and tellurium methods with (a) copper sulfide (blue) and bismuth phosphate (red) microprecipitation methods showing peaks for background uranium-234/238 in $(NH_4)_2HPO_4$ and (b) copper sulfide (blue)

and tellurium (red) showing peaks for natural polonium-210 in $H_{10}Na_2O_9Te$. Note: Results are normalized based on the total counts across the entire spectra.

Methods testing on SW matrices

Testing of the copper sulfide method for microprecipitation of polonium with and without the SW matrix, including initial separations procedures described previously [14], resulted in decreased overall recoveries (29.5±1.5% recovery across the entire separation and deposition procedure) as compared to the clean samples. However, the decreased recoveries likely represent losses during separations procedures and not during microprecipitation due to the excellent recoveries observed in the simple matrix samples presented in the previous section.

In addition, both the copper sulfide microprecipitation and spontaneous deposition methods were conducted on split samples following the second developmental separation procedure with a comparison of results with and without the SW matrix following elution in 8 M HNO_3 and transposition into 0.1 M HCl. Overall, the results were similar for both (**Figure 2**), although one of the copper sulfide microprecipitation samples (without SW) included a significant overlapping peak in the low range of the Po-209 peak impacting overall recoveries. Moreover, the FWHM were not significantly different when compared between the simplified matrix and SW matrix for both copper sulfide microprecipitation and spontaneous deposition (SI, section S.4, **Table S2**), although a significant difference was observed when comparing the two different methods (**Table 4**) for the SW matrix and combined comparison with both matrices. The error introduced by the overlapping peak in one of the simplified matrix samples for copper sulfide likely impacted the comparison in those conditions.

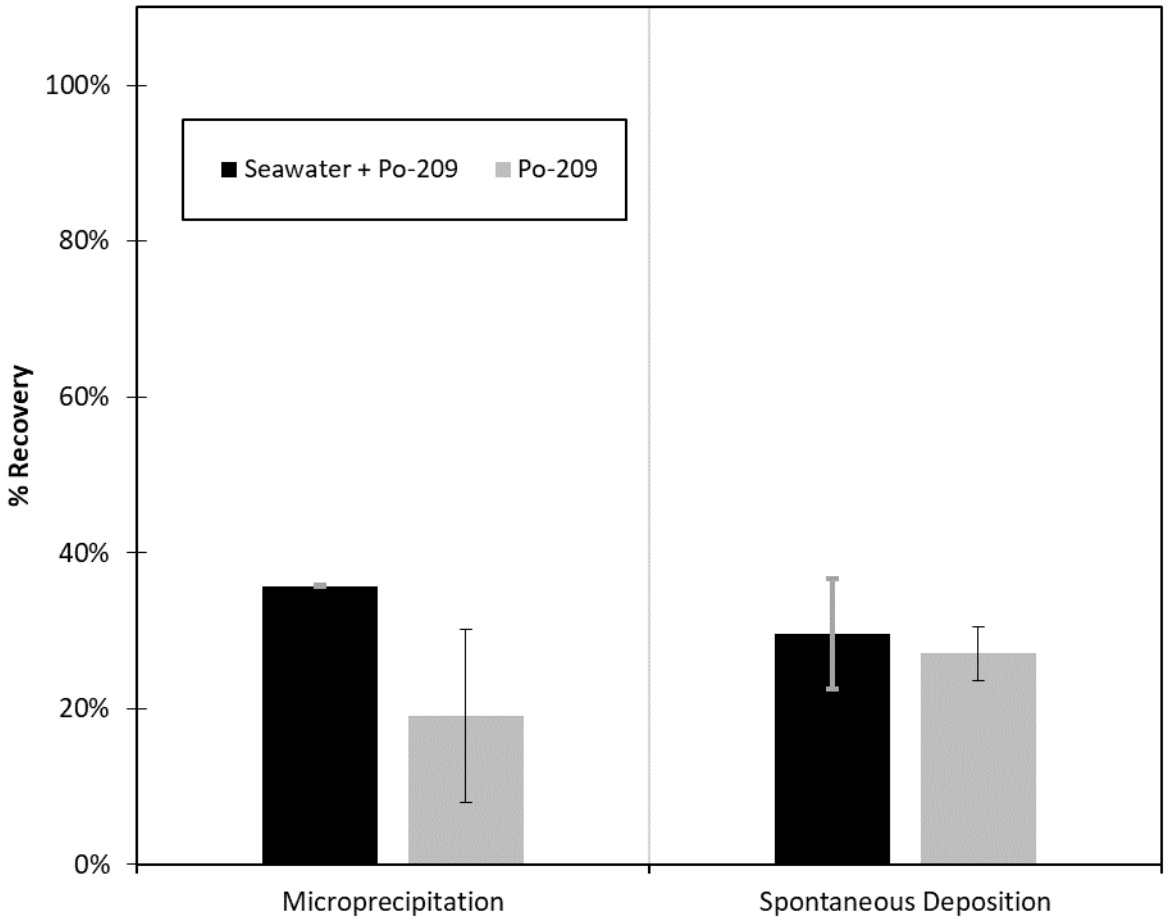

Fig. 2. Comparison of recoveries for Po-209 after separation, elution, and transposition, including microprecipitation and alpha spectrometry and spontaneous depositions and alpha spectrometry for polonium with (*black*) and without (*gray*) seawater.

Table 4. Summary of results comparing copper sulfide microprecipitation and spontaneous deposition method FWHM values with average and one standard deviation, including a comparison t-test for the two sample sets assuming unequal variances for an $\alpha = 0.05$ with the t_{test}/t_{stat} with any comparison ***italicized*** for statistical differences.

Conditions	**Copper Sulfide (FWHM)**	**Spontaneous Deposition (FWHM)**	**t_{test}/t_{stat}**
Simple	31±9	20±2	1.7/6.3
SW	44±2	20±2	***15.2/2.9***

Both	38±9	20±2	***3.7/2.4***

[1]The "Simple" Matrix includes addition of only a Po-209/210 standard to acid solutions, while the "SW" matrix includes addition of a background seawater matrix as described in the materials section.

Conclusions

Bismuth phosphate, tellurium, and copper sulfide microprecipitation methods were compared under simplified conditions for preparation of polonium for alpha spectrometry. From these experiments, the copper sulfide method was the best microprecipitation method tested for polonium, because it had the smallest FWHM and chemicals used for preparation did not require removal of background alpha emitters. In addition, results showed that copper sulfide microprecipitation recoveries for polonium were similar to spontaneous deposition on silver and less time consuming with an approximate five-fold decrease in preparation time, including in the presence of complex matrices like seawater. While the FWHMs were significantly wider for the copper sulfide method as compared to spontaneous deposition, the peaks were sufficient to discriminate between Po-209 and Po-210. Moreover, it is unlikely that peaks would be affected by other major alpha emitters due to the selectivity of the method. Previously, decontamination factors were measured for the actinides and radium, with the smallest measured for radium at 135. Meaning that there was 135× more Ra in solution, as compared to the amount retained on the filter [11]. Consequently, significant quantities would be required to cause interference. If time is the most important factor, the copper sulfide method is the best option of those tested with the reagents used.

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