

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/262929559>

# Determination of Po-210 in Drinking Water and Urine Samples Using Copper Sulfide Microprecipitation

ARTICLE *in* ANALYTICAL CHEMISTRY · JUNE 2014

Impact Factor: 5.64 · DOI: 10.1021/ac501164f · Source: PubMed

---

CITATIONS

2

---

READS

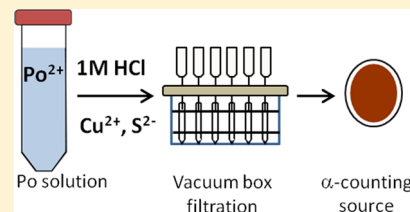
27

# Rapid Preparation of Polonium Counting Sources for Alpha Spectrometry Using Copper Sulfide Microprecipitation

Nicolas Guérin\* and Xiongxin Dai\*

Chalk River Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada, K0J 1J0

**ABSTRACT:** Thin-layer polonium (Po) sources for alpha spectrometry counting can be rapidly prepared using copper sulfide (CuS) microprecipitation. Polonium was coprecipitated with CuS, filtered onto Eichrom Resolve filters, and counted. This simple procedure is faster, cheaper, and more convenient than traditional spontaneous plating on metallic discs, and similar yields were obtained (80–90%). The experimental conditions for the microprecipitation technique were optimized (0.05 mg of  $\text{Cu}^{2+}$  in 10 mL of 1 M HCl); these compare advantageously with conventional preparation and purification procedures for polonium samples (0.1 to 1 M HCl). The results showed that the most likely potential radionuclide interferences (Ra, Th, U, Np, Pu, and Am) for long-lived polonium isotopes ( $^{208}\text{Po}$ ,  $^{209}\text{Po}$ ,  $^{210}\text{Po}$ ) are effectively removed during processing. The effects of several transition metals ( $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$ ) on the yield and the resolution of the alpha peaks obtained were also assessed. Little interference was found, demonstrating the versatility of the present microprecipitation technique for environmental and biological matrices. The procedure has been successfully applied to different amounts of  $^{210}\text{Po}$  using  $^{209}\text{Po}$  as a yield tracer.



Polonium-210 ( $^{210}\text{Po}$ ) is naturally present at trace levels in the environment as a part of the uranium-238 ( $^{238}\text{U}$ ) decay chain. It is considered to be one of the most radiotoxic nuclides: only 1  $\mu\text{g}$  of this alpha emitter ( $t_{1/2} = 138$  d) is sufficient to be fatal to an average adult, making it around 250 000 times more toxic than hydrogen cyanide.<sup>1,2</sup> Due to its important toxicological properties, numerous studies have been undertaken to determine  $^{210}\text{Po}$  in a large variety of sample types, including soils,<sup>3</sup> water,<sup>4</sup> marine organisms,<sup>5</sup> tobacco leaves,<sup>6,7</sup> cigarettes,<sup>8</sup> urine,<sup>9</sup> and biological materials.<sup>10–12</sup>

To date, polonium samples for alpha counting have been almost exclusively prepared by spontaneous plating on metallic discs. Silver discs have been most commonly used for Po plating,<sup>13</sup> but nickel, copper, and stainless steel discs are sometimes employed due to their lower costs.<sup>14,15</sup> Prior to their use, metallic discs are polished and cleaned to remove dust and any oxide layer at the surface.<sup>16</sup> They are then brought in contact with the sample in a minimum volume of diluted HCl solution (0.1 to 1 M) and agitated for 3–6 h at a high temperature (e.g., 80–95 °C) to obtain the highest recoveries possible (usually ~90%).<sup>8,13–16</sup> The metallic discs are subsequently rinsed with water<sup>17</sup> and heated (~300 °C) for few minutes to oxidize the polonium and reduce the risk of contamination to the alpha detector.<sup>16</sup> Although this sample preparation technique is relatively easy to perform, the heating step is inconvenient and time-consuming. In addition, the plating is often performed using in-house assemblies which are not readily available for other laboratories.

In the presence of sulfide,  $\text{Po}^{2+}$  forms polonium sulfide (PoS), which is extremely insoluble in 1 M HCl with a solubility product constant of  $5 \times 10^{-29}$  (Table 1).<sup>18</sup> This very low solubility has been successfully applied to separate PoS from tellurium and bismuth in 1 M HCl.<sup>19</sup> As shown in Table 1, mercury, silver, and copper sulfides are also very insoluble<sup>20</sup>

**Table 1.** Solubility Product Constants of Selected Sulfide Salts<sup>18–20</sup>

salt	solubility product constant
PoS	$5 \times 10^{-29a}$
HgS	$1 \times 10^{-52}$
CuS	$1 \times 10^{-38}$
$\text{Fe}_2\text{S}_3$	$1 \times 10^{-85}$
$\text{Ag}_2\text{S}$	$1 \times 10^{-51}$
PbS	$1 \times 10^{-29}$
NiS	$1 \times 10^{-21}$
FeS	$1 \times 10^{-17}$

<sup>a</sup>Value in 1 M HCl instead of water.

and could potentially be used as coprecipitating agents of PoS for the preparation of thin-layer counting sources by alpha spectrometry. Using a vacuum box system, batches of Po samples can be rapidly processed together, increasing sample analysis throughput. Similar microprecipitation methodologies using lanthanide fluoride for actinides<sup>21–23</sup> and barium sulfate for radium-226 ( $^{226}\text{Ra}$ ) have been routinely employed for the rapid preparation of thin-layer counting sources by alpha spectrometry.<sup>24,25</sup>

The objective of this study was to develop a robust, simple, and fast methodology for the preparation of polonium counting sources for alpha spectrometry using copper sulfide microprecipitation. To our knowledge, this is the first time that such a methodology has been developed for polonium determination. Copper was chosen over silver and mercury, as silver is light sensitive and less stable in solution, while mercury was

Received: May 1, 2013

Accepted: June 7, 2013



avoided due to its toxicity. The optimal conditions for the coprecipitation of PoS were determined, and potential radionuclide and chemical interferences were also evaluated. The utility of using  $^{209}\text{Po}$  as a yield tracer to determine  $^{210}\text{Po}$  was also demonstrated.

## ■ EXPERIMENTAL SECTION

**Reagents and Standards.** All chemical reagents used for this research were purchased from Fisher Scientific (Fair Lawn, NJ), except where otherwise specified. For the copper sulfide microprecipitation, copper chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) were used. All the solutions were prepared using ultrapure water (UPW) from a water purification system (Millipore Direct-Q5, Billerica, MA). Hydrochloric and nitric acids employed in this study were trace metal grade, and ethanol was purchased from Commercial Alcohols (Brampton, ON, Canada). For the assessment of chemical interferences, working solutions were prepared directly from the following salts: silver nitrate ( $\text{AgNO}_3$ ), ferrous ammonium sulfate ( $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ ), ferric ammonium sulfate ( $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ ), nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), lead fluoride ( $\text{PbF}_2$ ), and aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ). For the evaluation of the radionuclide interferences, barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), titanium trichloride ( $\text{TiCl}_3$ ; 10% w/v in 20–30% HCl; all from Sigma Aldrich, St. Louis, MO), 48% hydrofluoric acid (HF; Mallinckrodt Baker, Inc., Phillipsburg, NJ), and isopropanol were used.

Standard radioactive solutions of  $^{209}\text{Po}$ ,  $^{233}\text{U}$ ,  $^{237}\text{Np}$  (Eckert & Ziegler Isotope Products, Valencia, California),  $^{232}\text{Th}$  (Inorganic Ventures, Christianburg, VA),  $^{242}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  (National Institute of Standard, Gaithersburg, MD) were used for this study. Note that  $^{210}\text{Po}$  was directly obtained from the  $^{210}\text{Pb}$  standard solution.

**Method Optimization.** In order to determine the optimal conditions for the PoS microprecipitation, the influence of several important parameters ( $\text{Cu}^{2+}$  quantity, reaction time, HCl molarity, and solution volume) was examined. For all samples, 50 mBq of  $^{209}\text{Po}$  was added in disposable 50 mL conical polypropylene tubes. The optimal amount of  $\text{Cu}^{2+}$  used was first studied by adding known quantities of  $\text{Cu}^{2+}$  from a copper solution (500 mg/L in 1% v/v HCl). The coprecipitation was undertaken in 10 mL of 1 M HCl by adding 1 mL of a 0.3% m/v  $\text{Na}_2\text{S}$  solution. Then, the influence of the precipitation time was determined. Using the previous optimized conditions (0.05 mg of  $\text{Cu}^{2+}$  and 10 min of reaction), the influence of the HCl molarity and volume were also evaluated. Replicate samples were analyzed in each test, and total uncertainties were calculated as combined statistic and systemic errors.

**Microprecipitation Procedure.** In 50 mL of polypropylene conical tubes, 50 mBq of  $^{209}\text{Po}$  was added and mixed into 10 mL of 1 M HCl. For each sample,  $7.87 \times 10^{-7}$  moles of  $\text{Cu}^{2+}$  (50  $\mu\text{g}$ ) followed by  $4.17 \times 10^{-5}$  moles of  $\text{S}^{2-}$  were added, and the sample was vigorously shaken. After sitting for 10 min, the sample was filtered through a 0.1  $\mu\text{m}$  Resolve filter (Eichrom Technologies Inc., Lisle, IL). Prior to the filtration, the filter was rinsed with 1–2 mL of 80% ethanol, followed by 1–2 mL of UPW. The sample was then filtered at minimal flow (approximately 3–4 mL/min) using a vacuum box (Eichrom Technologies Inc., Lisle, IL). After the final rinse with 1–2 mL of 80% ethanol, the precipitate was air-dried for few minutes

and mounted on a stainless steel disc using double-sided adhesive tape for counting by alpha spectrometry.

**Interference Assessment.** Decontamination factors were determined for Ra and actinide (Th, U, Np, Pu, and Am) radionuclides, which could potentially interfere with  $^{208}\text{Po}$ ,  $^{209}\text{Po}$ , or  $^{210}\text{Po}$  measurements. For each sample, approximately 50 mBq of Ra and actinide standards were added in 10 mL of 1 M HCl. The CuS microprecipitation procedure was followed, and the filtrate solution was collected. Radium was determined in the filtrate using a barium sulfate microprecipitation procedure as previously published by Maxwell and Culligan.<sup>25</sup> Actinides were measured in the filtrate using cerium fluoride ( $\text{CeF}_3$ ) microprecipitation as previously described by Dai et al.<sup>24,26</sup> The CuS filter and the filtrate samples were both counted by alpha spectrometry, and the decontamination factor was calculated as the ratio of the Ra or actinide activity in the filtrate to that on CuS filter.

The effects of some transition metals ( $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$ ) that could coprecipitate with sulfide were also evaluated. After the addition of known quantities of these elements and 50 mBq of  $^{209}\text{Po}$ , the CuS microprecipitation procedure was applied to prepare counting sources.

**Determination of  $^{210}\text{Po}$  in Spike Samples.** To examine the performance of the CuS microprecipitation procedure developed, a set of samples, spiked with known amounts of  $^{210}\text{Po}$ , were prepared by adding 5–100 mBq of a  $^{210}\text{Pb}$  standard (in secular equilibrium with its daughter  $^{210}\text{Po}$ ) to 10 mL of 1 M HCl. Then 50 mBq of  $^{209}\text{Po}$  tracer was added to the spike and blank samples for yield monitoring and correction. All the samples were then processed through the microprecipitation procedure, and counting sources were prepared for the determination of  $^{210}\text{Po}$  by alpha spectrometry.

**Alpha Spectrometry.** All the radionuclides were counted using an Octete Plus Alpha Spectroscopy Workstation with eight 450 mm<sup>2</sup> ULTRA-AS ion-implanted silicon detectors (AMETEK/ORTEC Inc., Oak Ridge, TN). The samples were counted for 8 to 24 h, and the alpha spectra were analyzed to determine the  $^{209}\text{Po}/^{210}\text{Po}$  ratios and hence their activities in the samples analyzed.

## ■ RESULTS AND DISCUSSION

**Method Development.** Microprecipitation yields of  $^{209}\text{Po}$  as a function of the amount of  $\text{Cu}^{2+}$  added are shown in Figure 1. Without the addition of  $\text{Cu}^{2+}$ , a yield of  $25 \pm 5\%$  was obtained. By adding 0.001 mg of  $\text{Cu}^{2+}$ , a yield of  $\sim 80\%$  was achieved, and this remained constant for  $\text{Cu}^{2+}$  quantities up to 0.1 mg. The yield obtained was close to that achieved using the spontaneous plating technique ( $\sim 90\%$  in optimal conditions). The low yield observed without adding  $\text{Cu}^{2+}$  indicates that part of divalent or tetravalent Po was precipitated as PoS, which is consistent with its low solubility (Table 1), demonstrating the need to add a coprecipitating agent. Note that  $\text{Po}^{4+}$  is a strong oxidant ( $E^\circ = 1.03\text{ V}$ ) compared to  $\text{S}^{2-}$  ( $E^\circ = 0.14\text{ V}$ )<sup>27</sup> and is reduced to  $\text{Po}^{2+}$  under these conditions, implying that no valence adjustment is required. Lower apparent Po yields (Figure 2) and poor energy resolution (Figure 3) were observed with large amounts of  $\text{Cu}^{2+}$  ( $>0.1\text{ mg}$ ) due to self-absorption of alpha particles in the thicker counting sources. Therefore, a quantity of 0.05 mg of  $\text{Cu}^{2+}$  was chosen for use, but a lower quantity could be justified for a specific sample matrix. Also, adding 0.05 mg of  $\text{Cu}^{2+}$  has practical merit since the formation of the brown colloidal CuS precipitate in the

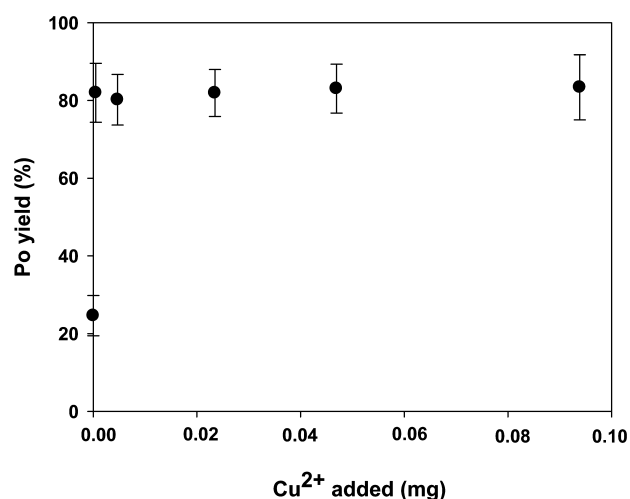


Figure 1. Polonium recovery as a function of  $\text{Cu}^{2+}$  added in 10 mL of 1 M HCl.

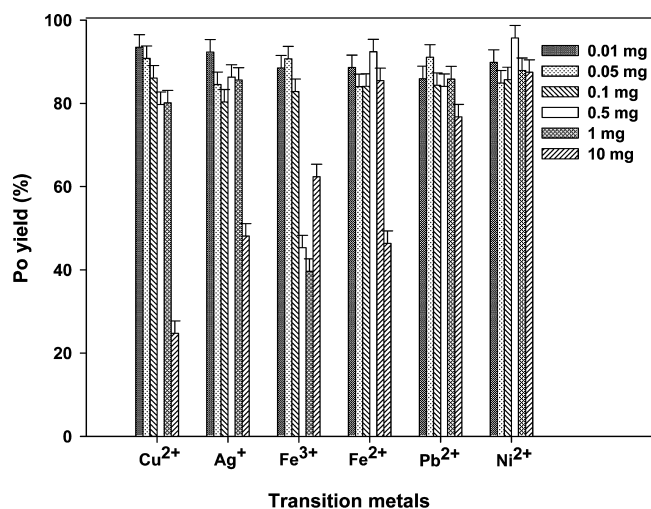


Figure 2. Polonium recovery as a function of the amounts of transition metals added using 0.05 mg of  $\text{Cu}^{2+}$  in 10 mL of 1 M HCl.

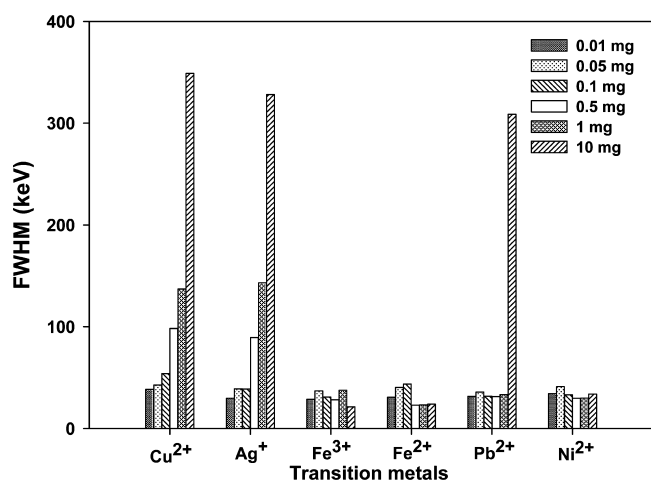


Figure 3. FWHM as a function of the amounts of transition metals added using 0.05 mg of  $\text{Cu}^{2+}$  in 10 mL of 1 M HCl.

solution and on the filters can be easily observed, which is convenient for routine laboratory work.

Using 0.05 mg of  $\text{Cu}^{2+}$  in 10 mL of 1 M HCl, the Po yield as a function of time is shown in Figure 4. A maximum yield of

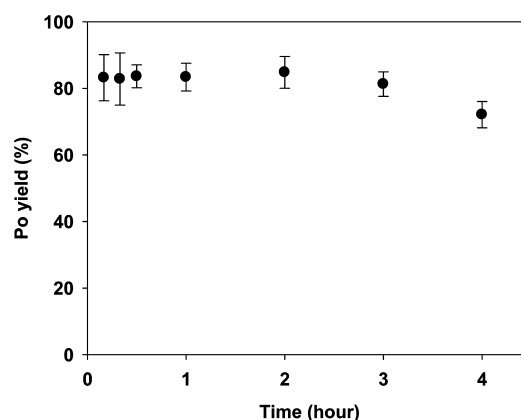


Figure 4. Polonium recovery as a function of time in 10 mL of 1 M HCl using 0.05 mg of  $\text{Cu}^{2+}$ .

~80% was rapidly achieved after 10 min, which remained constant for 3 h and slowly decreased afterward. It was observed that, beyond 3 h, the brown colloidal precipitate slowly coagulated and adhered to the surface of the plastic tubes, reducing recoveries. After 24 h, the precipitate was completely adsorbed on the surface of the tubes, leading to a clear solution. It is suggested that, in order to avoid the loss of the precipitate, the filtration should be conducted within 3 h after the addition of the sulfide. This microprecipitation technique is much faster than the conventional spontaneous plating methods, which take at least 3 h to reach an equivalent yield.

The influence of HCl molarity on the Po yield is shown in Figure 5. For low HCl molarities (0.01 to 1 M), the yield

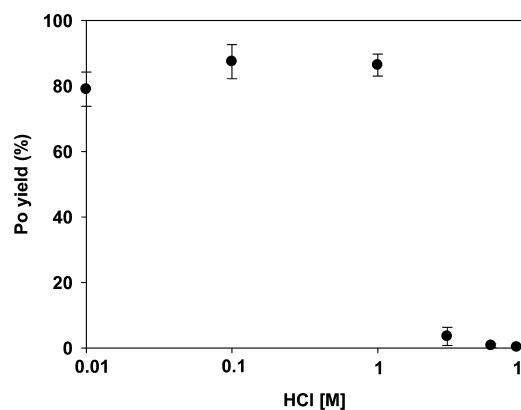


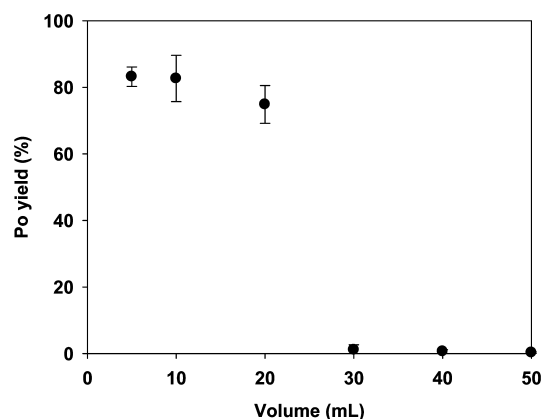
Figure 5. Polonium recovery as a function of HCl molarity in 10 mL of the solution using 0.05 mg of  $\text{Cu}^{2+}$  for 10 min.

remained constant (~80%) but suddenly decreased for higher HCl concentrations. Solutions with acidities higher than 1 M were almost colorless, and only very little precipitate was formed. The precipitates found on the filters for the 0.01 M solutions were darker and less granular than the 1 M samples. The FWHM (Full Width Half-Maximum) of the alpha peak for  $^{209}\text{Po}$  was much wider for the 0.01 M samples (150 keV) in comparison to the 0.1 M (55 keV) and 1 M (32 keV) HCl. At low HCl molarities, a thicker layer of precipitate might have been produced, which led to the observed variation in color and



the poor alpha energy resolution. For the high HCl molarities ( $>1$  M), the loss in Po yield could be explained by two possibilities: (1) PoS and CuS salts are more soluble at high acidities and practically not precipitated, or/and (2) PoS and CuS were not precipitated because  $\text{H}_2\text{S}$  was formed too fast and immediately vaporized, preventing microprecipitation. In order to determine which hypothesis was correct, a few rapid tests were carried out. To a solution of 3 M HCl, 7 times more sulfide than normal was added, which formed the brown precipitate with a yield of  $93 \pm 4\%$ . For a high concentration of HCl (10 M), no precipitate was observed even though an excessive amount of solid sodium sulfide was added to the solution and a significant amount of gaseous  $\text{H}_2\text{S}$  was produced. Another test was performed to first form a CuS precipitate in 1 mL of 1 M HCl. A total of 20 mL of concentrated HCl was then added, which brought the acidity to approximately 10 M, but the brown precipitate remained undissolved with a yield of  $77 \pm 4\%$  for  $^{209}\text{Po}$ . These tests suggested that the low yield in highly acidic conditions was not caused by the dissolution of the precipitate, but rather by the very fast vaporization of  $\text{H}_2\text{S}$  that made the precipitate much more difficult to form. The optimal conditions for the CuS microprecipitation were found to be between 0.1 and 1 M HCl. Since higher acidities would reduce potential interferences from other transition metals that have a higher solubility, 1 M HCl was preferred over 0.1 M HCl.

The variation in sample volume was assessed to determine its effects on the microprecipitation yield (Figure 6). The yields



**Figure 6.** Polonium recovery as a function of volume in 1 M HCl using 0.05 mg of  $\text{Cu}^{2+}$ .

were  $\sim 83\%$  for 10 mL or less, and then slightly decreased for 20 mL ( $75 \pm 6\%$ ). However, for 30 mL or a larger volume, the yields quickly dropped to almost zero. The solutions became colorless, and no precipitates were observed. Note that it is possible to achieve an acceptable yield ( $90 \pm 4\%$ ) by adding 7 times more sulfide to 40 mL of 1 M HCl solution. Since a larger amount of HCl will facilitate the formation of  $\text{H}_2\text{S}$  and prevent the precipitation, more sodium sulfide needs to be added to maintain a sufficiently high concentration of  $\text{S}^{2-}$  in the solution to initiate the microprecipitation.

Copper sulfide microprecipitation can be rapidly performed with high yields ( $>80\%$ ) in 10 mL of 1 M HCl using 0.05 mg of  $\text{Cu}^{2+}$ , which is an excellent alternative to the current spontaneous plating methodology for the preparation of Po alpha counting sources. The microprecipitation method is much faster and easier to operate. Practical experiences have

shown that, using a 12 hole vacuum box for filtration, it was possible to follow all the preparation steps and process 12 samples within one hour. Since most of the current spontaneous plating methods reported for the determination of Po are performed in a minimum volume of 0.1 to 1 M HCl, they can be easily replaced by the CuS microprecipitation technique.

**Interferences. Radionuclide Interferences.** Other alpha emitters, including Ra and actinide nuclides, could potentially interfere with Po isotopes of interest if they coprecipitate with the sulfide. Decontamination factors for Ra and actinides were determined and are given in Table 2,<sup>28</sup> along with the alpha energies and emission intensities of the most susceptible interfering isotopes. A moderate decontamination factor (135) was obtained for Ra, whereas higher decontamination factors ( $>400$ ) were obtained for actinides. These results demonstrate that Ra and actinides do not form insoluble sulfides in hydrochloric acid. Therefore, similar to the spontaneous plating, no purification would be required to remove potential radionuclide interferences for most samples.

**Chemical Interferences.** The influence of some transition metals on the Po yield (Figure 2) and alpha energy resolution (Figure 3) was evaluated by adding known amounts of those elements to the sample solutions.

For  $\text{Cu}^{2+}$ , which is also the coprecipitating agent, the yield remained constant up to 1 mg and then decreased to  $25 \pm 3\%$  for 10 mg (Figure 2). The FWHM increased rapidly for the solutions containing more than 0.1 mg of  $\text{Cu}^{2+}$  to reach 328 keV at 10 mg (Figure 3). The precipitates on the filters became darker as the amount of  $\text{Cu}^{2+}$  increased. Similar results were obtained for  $\text{Ag}^+$ . The yield was relatively stable up to 1 mg of  $\text{Ag}^+$  and quickly decreased afterward (Figure 2). The energy resolution was more affected for the samples with more than 0.1 mg of  $\text{Ag}^+$  (Figure 3), and the filters became darker as the amount of  $\text{Ag}^+$  increased. Because of the low solubility of silver sulfide (Table 1), silver was expected to completely precipitate in the presence of  $\text{S}^{2-}$ , resulting in a lower apparent yield and poor energy resolution due to the self-absorption of alpha particles by the thicker precipitate. Presumably,  $\text{Hg}^{2+}$  would behave similarly due to its extremely low solubility (Table 1). For biological and environmental samples containing a high concentration of either  $\text{Cu}^{2+}$  or  $\text{Ag}^+$ , an additional purification step (e.g., using a Sr resin)<sup>29</sup> would be required to reduce chemical interferences before the microprecipitation.

The microprecipitation yield decreased as the added  $\text{Fe}^{3+}$  surpassed 0.1 mg, and a minimal yield was found at 1 mg ( $40 \pm 3\%$ ). Subsequently the yield increased to  $62 \pm 3\%$  at 10 mg (Figure 2). However, the alpha energy resolution was not affected as the amount of  $\text{Fe}^{3+}$  increased (Figure 3). The characteristic brown color of CuS was observed on the filters for the samples containing 0.1 mg of  $\text{Fe}^{3+}$  or less, but the filters for the samples containing 0.5 and 1 mg of  $\text{Fe}^{3+}$  were white. For the sample of 10 mg of  $\text{Fe}^{3+}$ , the filter was pale yellow. Also, the CuS precipitate formed very slowly for the 0.1 mg of  $\text{Fe}^{3+}$  solutions, and no visible coloration in the solutions was observed for higher  $\text{Fe}^{3+}$  quantities. This indicated that the precipitation of CuS was hampered as excessive ferric ions might compete with  $\text{Cu}^{2+}$  and form a complex with  $\text{S}^{2-}$  in the solution. It is likely that, as the ferric sulfide complex was quickly formed, fast consumption of the  $\text{S}^{2-}$  in the solution and high solubility of ferric sulfide prevented the microprecipitation of CuS from occurring. To verify this hypothesis, the solubility of ferric sulfide was examined. In a 1 M HCl solution

**Table 2. Decontamination Factors and Potential Radionuclide Interferences for Polonium Isotopes<sup>29</sup>**

element	DF <sup>a</sup>	potential interferences (alpha energy (keV) and emission intensity)		
		<sup>208</sup> Po (5116) 100%	<sup>209</sup> Po (4879) 99.2%	<sup>210</sup> Po (5304) 100%
Ra	135		<sup>226</sup> Ra (4784) 93.8%	<sup>224</sup> Ra (5449) 4.9%
Th	750	<sup>229</sup> Th (4901) 10.2%	<sup>229</sup> Th (4845) 56%	<sup>228</sup> Th (5341) 26.7%
			<sup>229</sup> Th (4814) 9.3%	<sup>228</sup> Th (5423) 73%
U	>1114		<sup>234</sup> U (4776) 72.5%	
			<sup>233</sup> U (4783) 13.2%	
			<sup>233</sup> U (4825) 84.4%	
Np	>1407		<sup>237</sup> Np (4788) 47.8%	
			<sup>237</sup> Np (4772) 22.7%	
Pu	>2381	<sup>239</sup> Pu (5157) 70.8%	<sup>242</sup> Pu (4901) 78%	
		<sup>239</sup> Pu (5144) 17.1%	<sup>242</sup> Pu (4856) 22.4%	
		<sup>239</sup> Pu (5106) 11.9%		
		<sup>240</sup> Pu (5168) 73.5%		
		<sup>240</sup> Pu (5124) 26.4%		
Am	413			<sup>241</sup> Am (5443) 12.8%
				<sup>243</sup> Am (5277) 88%

<sup>a</sup>DF: Decontamination factor achieved.

containing 1 mg of Fe<sup>3+</sup>, 10 times more sulfide was added, which changed the yellow complex of FeCl<sub>2</sub><sup>+</sup> to colorless with no precipitate formed. Furthermore, the black Fe<sub>2</sub>S<sub>3</sub> precipitate prepared in water was found to be completely soluble in 1 M HCl, and H<sub>2</sub>S gas was produced. These tests confirmed the high solubility of Fe<sub>2</sub>S<sub>3</sub> in 1 M HCl. In another test, 4 times more sulfide was added to a solution of 1 mg of Fe<sup>3+</sup>, and an improved yield of 93 ± 4% was achieved compared to 39 ± 3% under normal conditions (Table 2). For the sample containing 10 mg of Fe<sup>3+</sup>, a pale yellow precipitate was observed, probably due to the formation of traces of Fe<sub>2</sub>S<sub>3</sub> that adsorbed FeCl<sub>2</sub><sup>+</sup> in the presence of high concentrations of Fe(III) in the solution. For verification, a test was performed by filtering a mixture of S<sup>2-</sup> and 10 mg of Fe<sup>3+</sup> with no Cu<sup>2+</sup> added, and a yellow precipitate was observed. In addition, the alpha energy resolution was not affected by the amount of Fe<sup>3+</sup> added, confirming that the amount of precipitate produced was always small enough to prevent significant degradation of the alpha spectrum.

For Fe<sup>2+</sup>, the yield was consistently high, except for 10 mg of added Fe<sup>2+</sup> (46 ± 3%, see Figure 2), and the alpha energy resolution was not affected (Figure 3). The filters showed the characteristic brown color of a CuS precipitate, except that the samples with 10 mg of Fe<sup>2+</sup> were white. A slower CuS precipitation was observed for the solutions of 1 mg of Fe<sup>2+</sup>. Adding more sulfide to a solution of 10 mg of Fe<sup>2+</sup> increased the yield to 87 ± 4%. Since the ferrous ion is more soluble in 1 M HCl with sulfide than the ferric ion (Table 1), a higher quantity of ferrous iron (10 mg) would be needed to compete for S<sup>2-</sup> and interfere with the CuS precipitation. Such information could be very useful since Fe(OH)<sub>3</sub> preconcentration procedures are often used for the determination of Po in environmental and biological samples.<sup>13,16</sup> A reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> would help alleviate the influence of Fe<sup>3+</sup> on the recovery.

For Pb<sup>2+</sup>, the yields were relatively constant at 85 ± 5% (Figure 2), but the FWHM value increased considerably for the solutions of 10 mg of Pb<sup>2+</sup> (308 keV) as more precipitate was produced (Figure 3). The filters normally showed the characteristic brown color of CuS except with 10 mg of added Pb<sup>2+</sup> when the precipitate was black. The solubility of

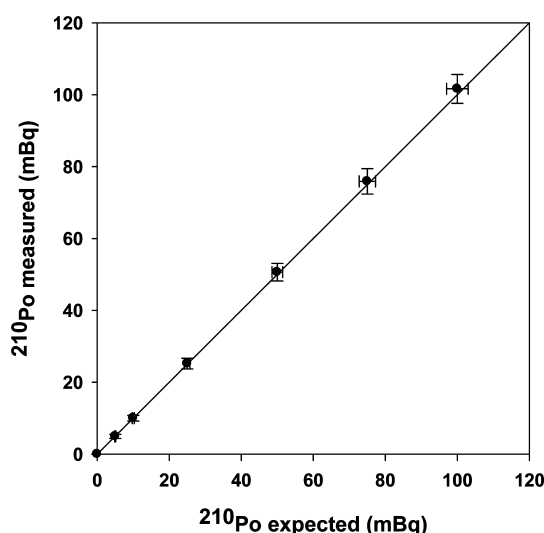
PbS is slightly higher than that of Fe<sub>2</sub>S<sub>3</sub> (Table 1), leading to less interference of Pb<sup>2+</sup> on the microprecipitation than Fe<sup>3+</sup>. For Ni<sup>2+</sup> samples, the yield and the FWHM were not affected in the quantity range studied (Figures 2 and 3). All the filters had the brown color of a CuS precipitate. This was expected since NiS is completely soluble in 1 M HCl.

The results indicated that for samples containing less than 0.1 mg of transition metal impurities, no further purification step would be needed to achieve good Po determinations. Similar to the spontaneous plating technique, all the interfering transition metals for the CuS microprecipitation technique can be removed using additional sample pretreatment steps such as extraction chromatography.<sup>13,29</sup> The insertion of such a purification step may affect final Po yields and should be evaluated depending upon the sample matrix used. However, this is beyond the scope of this study.

**Method Evaluation.** To evaluate the performance of the present microprecipitation method, replicate samples spiked with known amounts of <sup>210</sup>Po were analyzed using <sup>209</sup>Po as the tracer for yield correction. As shown in Figure 7, the measured activities of <sup>210</sup>Po in the spike samples ranging from 5 to 100 mBq agreed well with the expected values, demonstrating that the developed method could be applied for the determination of <sup>210</sup>Po in environmental and biological samples.

## CONCLUSION

A rapid method for the preparation of Po alpha counting sources was developed using a copper sulfide microprecipitation. The method developed is robust, rapid, and simple. It is also easier to perform and faster than the conventional spontaneous plating methods for the measurement of <sup>210</sup>Po by alpha spectrometry. The microprecipitation technique developed can dramatically increase the sample analysis throughput and reduce the analysis cost. Thus, it would be particularly suitable for the radio bioassay of <sup>210</sup>Po in emergency samples. Under optimal conditions (0.1 to 1 M HCl), the method is compatible with most of the current sample preparation procedures for <sup>210</sup>Po using ion exchange or extraction chromatography purification techniques. Potential interferences of alpha emitting radionuclides and transition metals on the microprecipitation yield and alpha energy



**Figure 7.** Comparison of the measured and expected activities of the  $^{210}\text{Po}$  spiked samples.

resolution were examined and found to be unimportant, demonstrating that the technique is either suitable or can be adapted for the determination of Po in a variety of sample matrices by alpha spectrometry.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: 613-584-3311 ext. 43698 (N.G.), 613-584-3311 ext. 46128 (X.D.). E-mail: guerinn@aecl.ca (N.G.), daix@aecl.ca (X.D.).

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors, Nicolas Guérin and Xiongxin Dai, have contributed equally.

### Funding

This research was funded by AECL Research and Development program.

### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Cornett, J.; Tracy, B.; Kramer, G.; Whyte, J.; Moodie, G.; Auclair, J. P.; Thomson, D. *Radiat. Prot. Dosim.* **2009**, *134*, 164–166.
- (2) Harrison, J.; Leggett, R.; Lloyd, D.; Phipps, A.; Scott, B. J. *Radiol. Prot.* **2007**, *27*, 17–40.
- (3) Aoun, M.; El Samrani, A. G.; Lartiges, B. S.; Kazpard, V.; Saad, Z. *J. Environ. Sci.* **2010**, *22*, 1387–1397.
- (4) Gans, I. *Sci. Total Environ.* **1985**, *45*, 93–99.
- (5) Carvalho, F. P. *Radiat. Prot. Dosim.* **1988**, *24*, 113–117.
- (6) Savidou, A. K. K.; Eleftheriadis, K. *J. Environ. Radioact.* **2006**, *85*, 94–102.
- (7) Tso, T. C.; Fisenne, I. *Radiat. Bot.* **1968**, *8*, 457–462.
- (8) Khater, A. E. M. *J. Environ. Radioact.* **2004**, *71*, 33–41.
- (9) Meli, M. A.; Desideri, D.; Roselli, C.; Feduzi, L. *J. Environ. Radioact.* **2009**, *100*, 84–88.
- (10) Hill, C. R. *Nature* **1960**, *187*, 211–212.
- (11) Takizawa, Y.; Zhao, L.; Yamamoto, M.; Abe, T.; Ueno, K. *J. Radioanal. Nucl. Chem.* **1990**, *138*, 145–152.
- (12) Shabana, E. I.; Elaziz, M. A.; Al-Arifi, M. N.; Al-Dhawalie, A. A.; Al-Bokari, M. A. *Appl. Radiat. Isot.* **2000**, *52*, 23–26.

- (13) Matthews, K. M.; Kim, C. K.; Martin, P. *Appl. Radiat. Isot.* **2007**, *65*, 267–279.
- (14) Kelecom, A.; Gouvea, R. C. S. *J. Environ. Radioact.* **2011**, *102*, 443–447.
- (15) Karali, T.; Ölmez, S.; Yener, G. *Appl. Radiat. Isot.* **1996**, *47*, 409–411.
- (16) *Analytical procedures, Lead-210 and Polonium-210 in Water*; Eichrom Technologies, LLC: Lisle, IL, 2009.
- (17) Benedik, L.; Vasile, M.; Spasova, Y.; Wätjen, U. *Appl. Radiat. Isot.* **2009**, *69*, 770–775.
- (18) Bagnall, W.; Robertson, D. S. *J. Chem. Soc.* **1957**, 1044–1046.
- (19) Figgins, P. E. *The radiochemistry of polonium*; National Academy of Science–National Research Council: Washington, DC, 1961.
- (20) Sillen, L. G.; Martell, A. E. *Stability Constants of Metal Ligand Complexes*; The Chemical Society: London, 1964.
- (21) Vajda, N.; Törvényi, A.; Kis-Benedek, G.; Kim, C. K.; Bene, B.; Macsik, Z. *Radiochim. Acta* **2009**, *97*, 395–401.
- (22) Dai, X.; Kramer-Tremblay, S. *Health Phys.* **2011**, *101*, 144–147.
- (23) Maxwell, S. L.; Culligan, B. K.; Noyes, G. W. *J. Radioanal. Nucl. Chem.* **2010**, *286*, 273–282.
- (24) Dai, X.; Kramer-Tremblay, S.; Li, C. *Radiat. Prot. Dosim.* **2012**, *151*, 30–35.
- (25) Maxwell, S. L.; Culligan, B. K. *J. Radioanal. Nucl. Chem.* **2012**, *293*, 149–156.
- (26) Dai, X. *J. Radioanal. Nucl. Chem.* **2011**, *289*, 595–600.
- (27) Schweitzer, G. K.; Pesterfield, L. L. *The Aqueous Chemistry of the Elements*; Oxford University Press: New York, 2010.
- (28) Holden, N. E. *CRC Handbook of Chemistry and Physics* 2013. <http://www.hbcpnetbase.com/> (accessed March, 2013).
- (29) Vajda, N.; LaRosa, J.; Zeisler, R.; Danesi, P.; Kis-Benedek, G. *J. Environ. Radioact.* **1997**, *37*, 355–372.