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Title Page

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Title: Rapid Method to Determine Polonium-210 in Urban Matrices

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Highlights

- Polonium-210 method needed for urban matrices following a radiological emergency, such as detonation of a "dirty bomb"
- Rapid method for determination of polonium-210 developed
- Eliminates Po volatility losses during sample digestion as well as degradation of alpha spectra, which can happen for difficult samples
- Based on rigorous digestion, preconcentration, and extraction chromatography
- Polonium-210 was measured using alpha spectrometry

Abstract

A rapid method for the determination of polonium-210 in urban matrices has been developed that can be used following a radiological event. Samples such as concrete, soil and granite are fused with sodium hydroxide to minimize polonium volatility during sample digestion and to achieve complete sample dissolution. Complete dissolution of samples is important to ensure method ruggedness. Polonium is concentrated and separated from the sample matrix using an iron hydroxide precipitation and extraction chromatography and subsequently measured by alpha spectrometry following microprecipitation with bismuth phosphate. The chromatographic separation removes alpha emitting interferences and matrix constituents which can adversely impact the measurement via alpha spectrometry.

Introduction

Polonium-210 is a naturally-occurring alpha emitting radionuclide ($T_{1/2}$=138.38 days) used in industrial applications, such as static elimination and neutron activation, (Centers for Disease Control, 2019) and is present in the environment as a member of the ^{238}U decay series. Po-210 is one of the most toxic radionuclides, as an ingestion intake of only 1 μg of ^{210}Po may be lethal. Po-210 has already been used in a criminal attack on former Russian intelligence officer Alexander Litvinenko, who died in a London hospital on November 23, 2006. He was deliberately poisoned with ^{210}Po, and it was discovered that those involved in this crime had spread ^{210}Po across many locations throughout London. The incident caused widespread concern and an intense political and public health awareness. (Miller et al., 2012) An explosive or non-explosive radiological dispersive device (RDD) containing ^{210}Po, a so called "dirty bomb", has the capability to trigger widespread panic. Rapid, rugged sample analysis in the aftermath of such an event is very important to determine the scope and impact of the attack. Po-210 is included in a list of radionuclides that might be utilized in a Radiological Dispersive Device (RDD) compiled by the EPA. (Griggs, 2012)

Current analytical methods for determination of ^{210}Po typically involve spontaneous auto-deposition of polonium onto silver or other metal disks followed by counting by alpha spectrometry. (Matthews et al., 2007) Autodeposition times range from 90 minutes to 24 hours or more, with yields that may be less than desired, (Clayton, 1995) particularly when working with matrices other than relatively clean aqueous samples. The analysis of Po in more difficult solid samples, such as urban matrices and environmental and biological samples, via direct autodeposition of Po from sample leachates or digestates is often inefficient, as organic material and red/ox active metal ions can impede autodeposition of Po or degrade resolution of alpha spectra. (Seiner et al. 2014) The accuracy and reliability of ^{210}Po assays following a radiological event is extremely important, and poor yields or degraded spectra will harm the quality of the collected data. In addition, acid digestions employed to treat many solid samples may result in polonium loss due to volatilization. Polonium is often lost in the initial digestion due to its relatively low volatilization temperature, 180 °C. (Martin, 1969; Marbuchi, 1963) This is

extremely problematic, especially during a radiological emergency, where rapid, reliable detection and measurement of ^{210}Po is critical and the safety of the public is at stake.

Vajda et al. (1997) reported a Sr Resin separation for polonium that reduced the chance of degraded alpha spectra. A less rapid autodeposition approach was used to prepare the samples for counting, with reported yields of only 50-70% for polonium. This method is acceptable, however, polonium is recovered from the Sr Resin using 6M HNO_3. As a result, an evaporation step is required prior to source preparation by autodeposition, which requires additional time and increases the risk of polonium losses due to volatilization.

Following the Litvinenko event, the International Atomic Energy Agency (IAEA) administered proficiency testing for the rapid analysis of ^{210}Po in water in concert with the IAEA Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA) Network. The ALMERA network is a worldwide system of analytical laboratories capable of providing timely analysis of environmental samples in the event of an accidental or intentional release of radioactivity. Unfortunately, only 70% of the results reported during this testing met IAEA requirements, and only 19 of 33 labs met the target of a one week turnaround time for this relatively simple matrix. (IAEA, 2006) Solid urban matrices would present even more analytical difficulties than the water samples analyzed in the IAEA study.

Several methods have been reported in the literature for solid matrices (Sethy, 2015). In this review, several different digestion methods, including acid digestion and fusions, were discussed, and the problem of polonium volatilization during sample digestion was highlighted. Jia et al. utilized a sodium carbonate/sodium peroxide fusion in platinum crucibles, followed by acid leaching, and perchloric acid fuming steps to remove organic matter. While the chemical yields for polonium were excellent, the use of perchloric acid can be a safety hazard consideration for many laboratories. In addition, the fusion method did not seem to result in total dissolution, as leaching and filtration were employed. Silicates had to be removed during time-consuming evaporation steps with hydrofluoric acid. The method employed autodeposition for final sample test source preparation, in contrast to utilization of new rapid microprecipitation techniques such as copper sulfide (Guerin and Dai, 2013 and 2014), bismuth phosphate (Maxwell et al., 2013) or

tellurium (Song et al., 2017). All three microprecipitation approaches offer improvements over spontaneous autodeposition.

The Savannah River Environmental Laboratory (SREL) has developed many fast radiochemical methods for the determination of radionuclides in solid building materials samples employing a rapid sodium hydroxide fusion, preconcentration steps and swift sequential purification using extraction chromatography. In this study of polonium in urban matrices, the goal was to determine if an alkaline fusion approach would mitigate the potential polonium volatilization problem, and if this approach could be coupled with extraction chromatography to eliminate the chance of degraded alpha spectra due to sample matrix effects.

A new innovative method to recover and measure ^{210}Po with high chemical yields and effective removal of sample matrix interferences was developed in this laboratory. Following rapid sample fusion with NaOH, polonium is isolated quickly using an iron hydroxide precipitation and separation with DGA Resin (Maxwell et al., 2013). A bismuth phosphate ($BiPO_4$) microprecipitation step performed directly on the DGA column eluate is used to quickly prepare a source for counting using alpha spectrometry.

Experimental

Reagents

The extraction chromatography resin employed in this study was DGA Resin, Normal (N,N,N',N'-tetraoctyldiglycolamide) available from Eichrom Technologies, LLC, (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acid solutions were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS (American Chemical Society) reagent grade. The radiochemical isotopes ^{209}Po and ^{210}Po were obtained from Eckert-Ziegler Analytics, Inc. (Atlanta, GA, USA) and diluted to the activity levels used for spiking samples. MAPEP soil samples were provided by the Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. Single element (Bi, Fe, Y, Ca, La,

Th, Ce, U) atomic absorption standards (10 mg/mL or 1 mg/mL) were obtained from High Purity Standards (Charleston, SC).

Procedures

Column preparation. DGA Resin (2 mL cartridges) and a vacuum extraction system were obtained from Eichrom Technologies, LLC. Flow rates of ~1-2 mL min^{-1} were typically used for this work.

Sample Preparation. Figure 1 shows the sample preparation flowchart for polonium in urban matrices samples. Solid samples were pulverized, homogenized and passed through a 50 mesh sieve prior to sampling so that representative samples could be taken. One gram aliquots of the various urban matrices were prepared and analyzed for ^{210}Po.

Sample aliquots were added to zirconium crucibles, along with 3 mL of a 14.5M ammonium hydroxide solution to prevent polonium loss on drying. Po-209 tracer and ^{210}Po were added to the zirconium crucibles. Sodium hydroxide pellets (15 g) were added, and the crucibles covered with zirconium lids. The crucibles were placed in a furnace at 200 ˚C and the temperature was increased to 300 ˚C to dry the samples. The temperature was increased to 500 ˚C, and the samples were fused for about 20 minutes. The crucibles were removed from the furnace and allowed to cool for 10 minutes in a laboratory hood. Water was added to dissolve the samples, with heating as necessary. Dissolved samples were transferred to 225 mL centrifuge tubes. Residual solids were removed from the crucibles through additional rinsing with 10 mL 3M HNO_3. The nitric acid rinse was then carefully added to the alkaline matrix in the 225 mL centrifuge tube.

Preconcentration of Polonium. Iron (125-150 mg) was added to each tube, as iron nitrate, to coprecipitate polonium on iron hydroxide ($Fe(OH)_3$). For the MAPEP 30 soil sample tested, addition of 25 mg of calcium (as calcium nitrate) seemed to enhance the chemical recovery of the polonium during the iron hydroxide precipitation step, compared to recoveries using $Fe(OH)_3$

194 precipitate alone. No additional calcium was added for granite or concrete samples, which are
195 relatively high in calcium already, and showed higher chemical yields.

196 Following removal of the supernate, the precipitate was dissolved with a mixture of 5 to 7
197 mL 4M HCl-0.2M HF plus 5 mL 0.5M HCl-0.02M HF. After transferring the dissolved precipitate
198 to a 50 mL plastic centrifuge tube, the 225 mL centrifuge tube was rinsed with 15 mL 0.5M HCl-
199 0.2M HF. This rinse was added to the 50 mL tube. Hydrofluoric acid was included in the sample
200 load solution to prevent column clogging due to the formation of colloidal silicates. The HCl
201 concentration in the column load solution was kept relatively low (<1.5M HCl) to prevent
202 significant competition from Fe(III) during Po retention on DGA Resin. Samples were centrifuged
203 to remove any residual solid particulates, and clear solutions were processed using an extraction
204 chromatographic separation with DGA Resin.

205 *Column separation for Po.* In this study, DGA Resin was used to rapidly separate Po for
206 measurement by alpha spectrometry. (Figure 2). Initial experiments showed that addition of a small
207 volume of 30 wt% H_2O_2 to the sample load solution improved recoveries of Po. This improvement
208 may be related to the oxidation state of Po. The most stable oxidation state in aqueous solution is
209 Po(IV), however under certain conditions Po(II) may also be present. The electrochemical potential
210 for hydrogen peroxide reduction in acidic solutions is 1.77 V (USP Technologies, 2019), while the
211 electrochemical potential for Po(II) oxidation to Po(IV) is 1.1V. (Ansoborlo et al. 2012) While
212 hydrogen peroxide redox chemistry can be complex, it appears to oxidize Po(II) effectively to
213 Po(IV), in an similar manner to hydrogen peroxide oxidation of Pu(III) to Pu(IV), which has a
214 similar electrochemical potential of 0.92V. (Wick, 1980) The samples were loaded from a dilute
215 HCl-HF solution, so that silicates remain in solution, and passed through the resin. In early testing,
216 small impurities from thorium isotope peaks were observed in the alpha spectra, possibly due to
217 precipitation of an insoluble fluoride. A column rinse of 1M HCl-0.25M boric acid solution
218 eliminated any traces of thorium, which are removed in the subsequent column rinses. A 0.25M
219 HCl rinse was employed to remove actinides, and an additional rinse with 0.5M HCl-0.02M HF
220 was added to ensure full thorium removal from the resin. An 8M HNO_3 rinse was used to convert
221 the polonium chloride complexes to polonium nitrate complexes so that polonium could be eluted

effectively with dilute nitric acid. It is very important to remove the chloride so that an effective polonium elution can be carried out. As a further enhancement, it was found that by adding 0.005 oxalate to the 0.05M HNO_3 eluent close to 100% of the polonium was eluted. With the 0.05M HNO_3 alone as the eluent, 8-15% of the analyte was sometimes left on the resin. The addition of oxalate improved the chemical yields for polonium substantially. The behavior of Po(IV) on DGA Resin in HCl and HNO_3 is shown in Figure 3. Note the very high Po retention in HCl at all concentrations.

Following the chromatographic separation, purified samples were prepared for alpha spectrometry measurements using a fast bismuth phosphate microprecipitation instead of autodeposition. The microprecipitation was facilitated by addition of 125 µg of bismuth (125 µL of 1000 µg Bi /ml standard in 2% nitric acid), 0.05 mL 30 wt% H_2O_2 and 0.75 mL 3.2M ammonium hydrogen phosphate. Initially, 1 mL 14.5M NH_4OH was added to each sample eluent, followed by additional 14.5M NH_4OH as needed to achieve a medium pink color change with a few drops of phenolphthalein present. An optimal pH 8 to 9 was obtained. After 20 minutes, the solution was filtered through 25 mm polypropylene filters (0.1 µm pore size disposable Resolve™ filter funnel, Eichrom Technologies, Lisle, IL, USA). Filters were rinsed with deionized water, and approximately 3 mL of ethanol to facilitate drying of the filter. The filters were heated briefly under a heat lamp to ensure dryness.

Apparatus

Polonium isotopic measurements were performed using alpha spectrometry. A Canberra Alpha Analyst Integrated Alpha Spectrometer was employed in this study. The alpha system utilized Passivated Implanted Planar Silicon (PIPS) detectors (450 mm^2 active surface) with counting efficiencies of 28-30% and a 3 mm distance between the sample test source and the detector surface.

For the Po elution curve (Figure 4), stable elements were measured on an Agilent 4200 microwave plasma atomic emission spectrometer (MP-AES). Po-210 was measured using a Perkin

Elmer Tri Carb 4910 TR liquid scintillation counter using 7mL glass vials with 5mL of Ultima Gold LLT scintillation cocktail.

Results and Discussion

Table 1 shows the individual results for the determination of ^{210}Po in fifteen 1 g concrete samples spiked with ^{210}Po. The analytical results were corrected for chemical yield using ^{209}Po. The average ^{210}Po result was 370 mBq g^{-1}, with a -0.89% bias relative to the ^{210}Po reference value, with a SD (standard deviation) of 21 mBq g^{-1}. The measured values were corrected for the native ^{210}Po present in the concrete, which was determined by analyzing replicate concrete sample aliquots without adding ^{210}Po. The average tracer yield for ^{209}Po was 88.6% ± 6.8% (SD). The high ^{209}Po tracer recoveries and very good match for ^{210}Po results versus the known value confirm the robust nature of the sample preparation and measurement steps. The chemical yields are reflective of the effective preconcentration steps, minimizing Po volatilization, and the highly efficient extraction chromatography purification using DGA Resin. The uncertainties for the individual ^{210}Po results were typically ± 5-7% (1 SD), with a 12 hour count time. Shorter count times may be used for the analysis of emergency samples, depending on polonium levels and measurement quality objectives for the emergency event.

Table 2 shows the individual results for the determination of ^{210}Po in six 1 g granite samples spiked with ^{210}Po. The average ^{210}Po result was 375.8 mBq g^{-1}, with a 2.47% bias and SD of 13.2 mBq g^{-1}. The average tracer recovery for ^{209}Po was 95.6% ± 5.7% (SD). The uncertainties for the individual ^{210}Po results were typically ± 5-7% (1 SD). The measured values were corrected for the native ^{210}Po present in the granite samples, determined by analyzing replicate granite sample aliquots without adding ^{210}Po. A 12 hour count time was employed for these measurements.

Table 3 shows the individual results for the determination of ^{210}Po in six 1 g MAPEP 32 soil samples spiked with ^{210}Po. The average ^{210}Po result was 377.8 mBq g^{-1}, with a 3.03% bias and SD of 17.9 mBq g^{-1}. The average tracer recovery for ^{209}Po was 82.7% ± 10% (SD). The uncertainties for the individual ^{210}Po results were typically ± 5-7% (1 SD). A 12 hour count time was employed

for these alpha spectrometry measurements. The chemical yields were lower for these soil samples than both concrete and granite samples. While these tracer yields were still acceptable, additional tests were performed to try to increase the chemical yields for this soil type. Since the concrete tested has a very high calcium content and the chemical yields for this sample matrix were very good, a small amount of calcium (25 mg) was added during the iron hydroxide preconcentration step to perhaps facilitate higher chemical recoveries across this key step for soil samples.

Table 4 shows the individual results for six 1 g MAPEP 32 soil samples that were spiked with ^{210}Po, with additional calcium added to test for higher yields. The average ^{210}Po result (corrected for the native ^{210}Po content) was 360.1mBq g^{-1}, with a -1.8% bias and SD of 12.8 mBq g^{-1}. The average tracer recovery for ^{209}Po increased to 95.0% ± 5.0% (SD). The uncertainties for the individual ^{210}Po results were typically ± 5-7% (1 SD). It is not known with certainty why the calcium enhanced chemical yields, however it is likely that that Po precipitation was enhanced either by additional coprecipitation with calcium hydroxide or calcium phosphate during this preconcentration step.

Figure 4 shows a typical alpha spectra obtained when this new analytical method is utilized for urban matrices. The tracer recovery is 92.3% and the FWHM (full width half max) is 50.5 keV. The approach of utilizing alkaline fusion, rapid preconcentration and DGA Resin separation provides high chemical yields, effective removal of interferences and good alpha peak resolution. Poor alpha peak resolution due to degraded spectra can result in poor quality results, perhaps requiring repeat analyses. Following a radiological incident, fast reliable results are required to allow incident commanders to accurately assess the scope and impact of an event to protect the public.

The MDA (Minimum Detectable Activity) for the polonium isotopes measured using this rapid alpha spectrometry method was calculated according to equations prescribed by Currie (1968):

$$MDA = [2.71+4.65\sqrt{B}]/ (CT*R*V*Eff*A*0.060)$$

where B = Total Background counts, = BKG (rate) * sample count time; CT = sample count time (min); R = Chemical Recovery; V = Sample aliquot **(**g) ; EFF = Detector Efficiency ; A = Isotopic abundance (in most cases this will be ~1); 0.060 = conversion from dpm to mBq.

The MDA for the alpha spectrometry results can be modified as needed, depending on the measurement quality objectives, by adjusting the sample aliquot and the count time employed. For a 1g solid urban matrix aliquot, the method MDA for the actinide isotopes with a 12 hour count time is ~700 uBq g^{-1}, assuming a detector efficiency of ~28%, 1 count background per 12 hours and a chemical recovery of 90%. Any changes in detector background, counting efficiency and yields will affect the MDA accordingly. Samples that are counted for only 4 hours, for example, are estimated to have an MDA of ~1.4 mBq g^{-1}.

Figure 5 shows the elution profile for bismuth and other selected elements on DGA Resin under the method conditions employed. It should be noted that the enhanced elution of polonium from DGA Resin with 0.05M HNO_3-0.005M oxalic acid may result in the presence of bismuth isotopes in the final sample test source for counting. Table 5 shows that bismuth isotopes or daughters either do not have a significant alpha emission abundance or do not have interfering alpha energies that overlap with ^{210}Po or ^{209}Po. (Brookhaven, 2019) If bismuth removal is still desired, the use of a 10M HCl bismuth removal rinse on DGA Resin can be employed to remove bismuth isotopes, while polonium remains on the resin. Figure 6 illustrates this potential purification option that would likely be a viable option DGA Resin, however test results indicate this additional bismuth removal step is unnecessary.

This new method for ^{210}Po determination in solid urban matrices has a rapid timeline. The spiking, fusion and preconcentration steps take about 90 minutes, the fast extraction chromatography separation also about 90 minutes, and the sample source preparation using bismuth phosphate microprecipitation requires about 30 minutes. The alpha counting times are set based on expected levels and measurement quality objectives (typically 60-1000 minutes).

Conclusions

A novel method for the fast determination of ^{210}Po in solid urban matrix samples, such

as concrete, soil and granite, has been developed that allows for the separation and measurement of ^{210}Po with high chemical yields and effective removal of sample matrix interferences. The sodium hydroxide fusion technique used to digest the solid samples is quick and robust. The DGA Resin extraction chromatography method employed in this work was effective, removing potential alpha emitting interferences. The test results indicate that ^{210}Po can be determined quickly and reliably following a radiological event.

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Reference

Ansoborlo, E et al, 2012. Review of Chemical and Radiotoxicological Properties of Polonium for Internal Contamination Purposes, Chemical Research in Toxicology 25 (8), 1551-1564

Brookhaven National Laboratory, Chart of the Nuclides, https://www.nndc.bnl.gov/chart/, accessed 1/13/19

Clayton R, Bradley E. 1995. A cost-effective method for the determination of ^{210}Po and ^{210}Pb in environmental samples. Sci Total Environ 173/174:23–28

Currie, L. A., 1968. Limits for qualitative and quantitative determination, Anal. Chem., 40, 586-593.

Griggs, J., 2012. Radiological Laboratory Sample Analysis Guide for Incident Response – Radionuclides in Soil, EPA 402-R-12-006, https://www.epa.gov/sites/production/files/2015-05/documents/402-r-12-006_soil_guide_sept_2012.pdf, accessed 1/10/19

363 Guerin, N. and Dai, X. 2013. Rapid Preparation of Polonium Counting Sources for Alpha
364 Spectrometry Using Copper Sulfide Microprecipitation. Anal Chem, 85, 6524-6529.

365

366 Guerin, N. and Dai, X. 2014. Determination of 210Po in Drinking Water and Urine Samples
367 Using Copper Sulfide Microprecipitation. Anal Chem, 86, 6026-6031.

368

369 Horwitz, E. P. et al., 2005. Novel Extraction of Chromatographic Resins Based on
370 Tetraalkyldiglycolamides: Characterization and Potential Applications. Solvent Extraction and
371 Ion Exchange, 23, 319-344.

372

373 International Atomic Energy Agency (2006) Report on the second ALMERA coordination
374 meeting and the ALMERA soil sampling intercomparison exercise—IAEA/SIE/01, IAEA/AL/
375 164, p 36

376

377 Jia G and Torri G, 2007. Determination of ^{210}Pb and ^{210}Po in soil or rock samples containing
378 refractory matrices, Applied Radiation and Isotopes, Volume 65, Issue 1, Pages 1-8

379

380 Mabuchi H (1963) The volatility of some Po compounds. J Inorg Nucl Chem 25:657–660.
381 Rapid determination of ^{210}Po in water samples

382

383 Martin A, Blanchard RL (1969) The thermal volatilisation of caesium-137, Po-210 and lead-210
384 from in vivo labelled samples. Analyst 94(1119):441–446.

385

386 Matthews K, Chang-Kyu K, Martin P (2007) Determination of ^{210}Po in environmental materials:
387 a review of analytical methodology. Appl Radiat Isot 65:267–279

388

Maxwell, S. Culligan B, Hutchison J, Utsey R, McAlister D. 2013. J Radioanal Nucl Chem Rapid Determination of ^{210}Po in Water Samples 298:1977–1989

Miller C, Whitcomb R, Ansari A, McCurley C, Nemhauser N, Jones R. 2012. Murder by radiation poisoning. implications for public health. J Environ Health 74(10):8

Radiation Studies Branch, Division of Environmental Hazards and Health Effects, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta. http://emergency.cdc.gov/radiation/isotopes/polonium/clinicians.asp, accessed 1/10/19

Seiner B, Morley S, Beacham T, Haney M, Gregory S, Metz L. 2014. Effects of digestion, chemical separation, and deposition on Po-210 quantitative analysis, J Radioanal Nucl Chem 302:673–678

Sethy N,Sutar A, Rath P, Jha V, Ravi P, Tripathi R. 2015. A review of radiochemical analysis and estimation of ^{210}Po in soil matrices. Journal of Radiation Research and Applied Sciences, Volume 8, Issue 4, pages 590-596

Song L, Ma Y, Wang Y, Yang Y, Juo M, Dai X. 2017. Method of Polonium Source Preparation Using Tellurium Microprecipitation for Alpha Spectrometry. Analytical Chemistry 2017 89 (24), pages 13651-13657

USP Technologies, 2019, http://www.h2o2.com/technical-library/physical-chemical-properties/thermodynamic-properties/default.aspx?pid=50&name=Standard-Electrode-Potentials Accessed 3/5/19

Vajda N, La Rosa J, Zeisler R, Danesi P, Kis-Benedek G. 1997. A novel technique for the simultaneous determination of ^{210}Pb and ^{210}Po using a crown ether. J Environ Radioact 37:355–372

Wick, O. J., editor, 1980. Plutonium Handbook- A Guide to the Technology, Item ID: 250005|ISBN: 978-0-89448-023-2, 1st Edition|, 407-422.

Table 1 Results for ^{210}Po Spiked into Concrete Samples

Sample ID	^{210}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	99.6	366.7	486.9	110.9	376.0	2.5
2	99.8	366.7	491.0	110.9	380.1	3.7
3	86.4	366.7	485.1	110.9	374.2	2.0
4	91.8	366.7	494.7	110.9	383.8	4.7
5	81.3	366.7	495.8	110.9	384.9	5.0
6	78.9	366.7	476.2	110.9	365.3	-0.4
7	88.8	366.7	529.1	110.9	418.2	14.0
8	79.8	366.7	495.8	110.9	384.9	5.0
9	94.0	366.7	484.7	110.9	373.8	1.9
10	88.8	366.7	481.0	110.9	370.1	0.9
11	83.6	366.7	462.1	110.9	351.2	-4.2
12	96.6	366.7	465.1	110.9	354.2	-3.4
13	90.4	366.7	465.1	110.9	354.2	-3.4
14	82.8	366.7	439.9	110.9	329.0	-10.3
15	86.5	366.7	460.7	110.9	349.8	-4.6
Avg	88.6		480.9		370.0	0.89
SD	6.8		20.9		20.9	5.69
% RSD	7.8					

Table 2 Results for ^{210}Po Spiked into Granite Samples

Sample ID	^{210}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	96.4	366.7	460.7	97.49	363.2	-1.0
2	92.2	366.7	478.0	97.49	380.5	3.8
3	104.7	366.7	464.4	97.49	366.9	0.1
4	92.8	366.7	494.3	97.49	396.8	8.2
5	98.8	366.7	480.0	97.49	382.5	4.3
6	88.5	366.7	462.1	97.49	364.6	-0.6
Avg	95.6		473.3		375.8	2.47
SD	5.7		13.2		13.2	3.60

Table 3 Results for ^{210}Po Spiked into MAPEP 30 Soil Samples

Sample ID	^{210}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	84.2	366.7	417.7	64.57	353.1	-3.7
2	99.3	366.7	432.2	58.46	373.7	1.9
3	74.0	366.7	442.9	58.46	384.4	4.8
4	78.0	366.7	433.6	58.46	375.1	2.3
5	78.2	366.7	461.0	58.46	402.5	9.8
Avg	82.7		437.5		377.8	3.03
SD	10.0		15.9		17.9	4.89

Table 4 Results for ^{210}Po Spiked into MAPEP 30 Soil Samples (Enhanced with Ca)

Sample ID	^{210}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	88.5	366.7	441.0	64.57	376.4	2.7
2	98.7	366.7	410.7	58.46	352.2	-3.9
3	90.0	366.7	431.8	58.46	373.3	1.8
4	94.0	366.7	414.4	58.46	355.9	-2.9
5	98.4	366.7	401.4	58.46	342.9	-6.5
6	100.5	366.7	418.1	58.46	359.6	-1.9
Avg	95.0		419.6		360.1	-1.8
SD	5.0		14.5		12.8	3.5

Figure 1 Rapid Sample Preparation Method for ^{210}Po in Urban Matrices

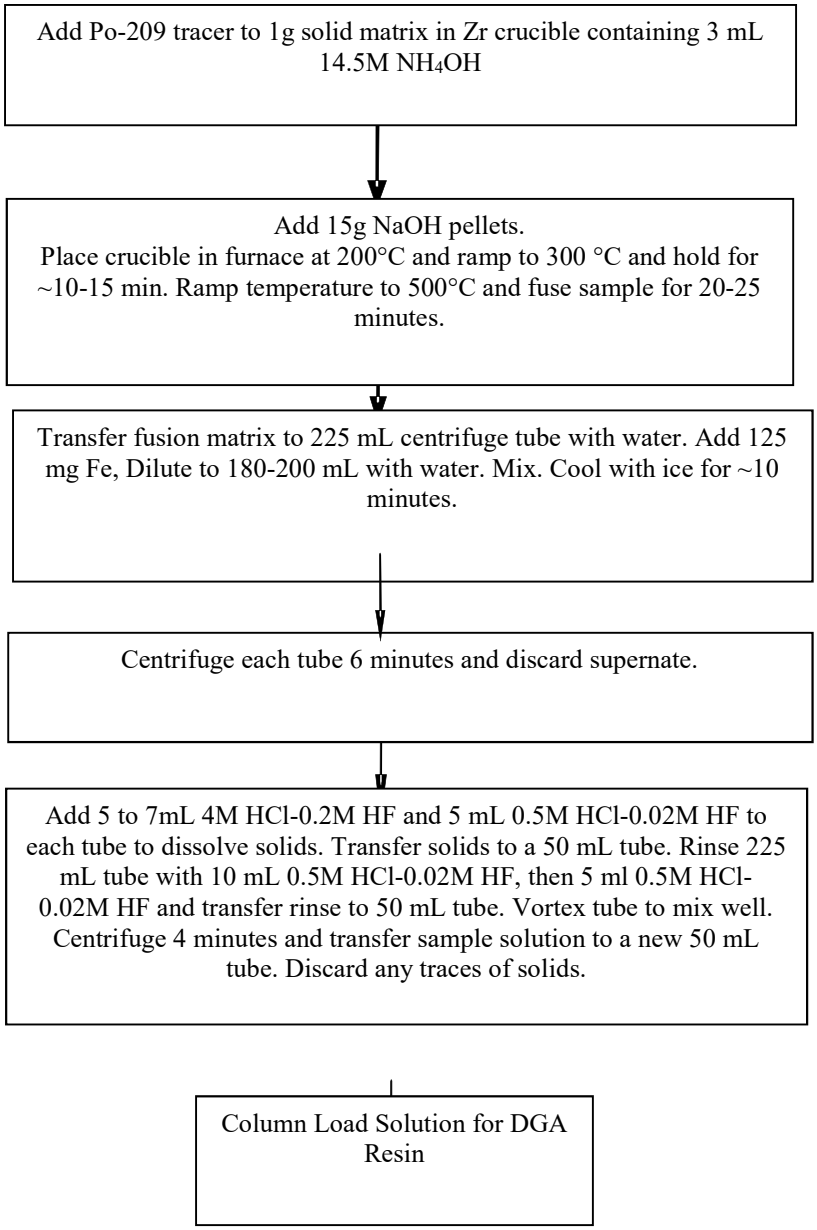
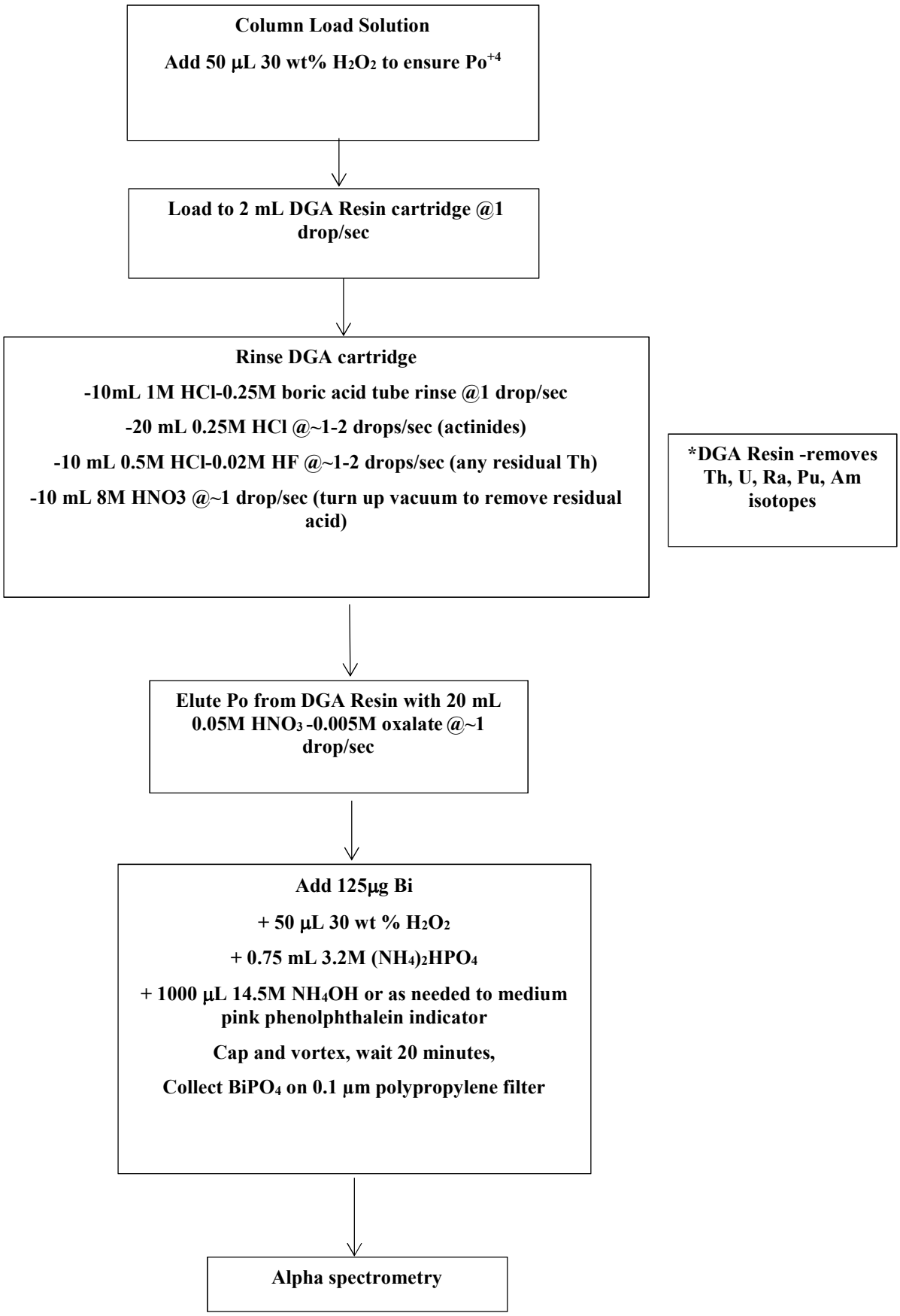


Figure 2 Rapid DGA Resin Separation Method for ^{210}Po in Urban Matrices


Column Load Solution
Add 50 µL 30 wt% H_2O_2 to ensure Po^{+4}
Load to 2 mL DGA Resin cartridge @1 drop/sec
Rinse DGA cartridge
-10mL 1M HCl-0.25M boric acid tube rinse @1 drop/sec
-20 mL 0.25M HCl @~1-2 drops/sec (actinides)
-10 mL 0.5M HCl-0.02M HF @~1-2 drops/sec (any residual Th)
-10 mL 8M HNO3 @~1 drop/sec (turn up vacuum to remove residual acid)
*DGA Resin -removes Th, U, Ra, Pu, Am isotopes
Elute Po from DGA Resin with 20 mL 0.05M HNO_3 -0.005M oxalate @~1 drop/sec
Add 125µg Bi
+ 50 µL 30 wt % H_2O_2
+ 0.75 mL 3.2M $(NH_4)_2HPO_4$
+ 1000 µL 14.5M NH_4OH or as needed to medium pink phenolphthalein indicator
Cap and vortex, wait 20 minutes,
Collect $BiPO_4$ on 0.1 µm polypropylene filter
Alpha spectrometry

555 Figure 3 Retention of Po(IV) on DGA Resin
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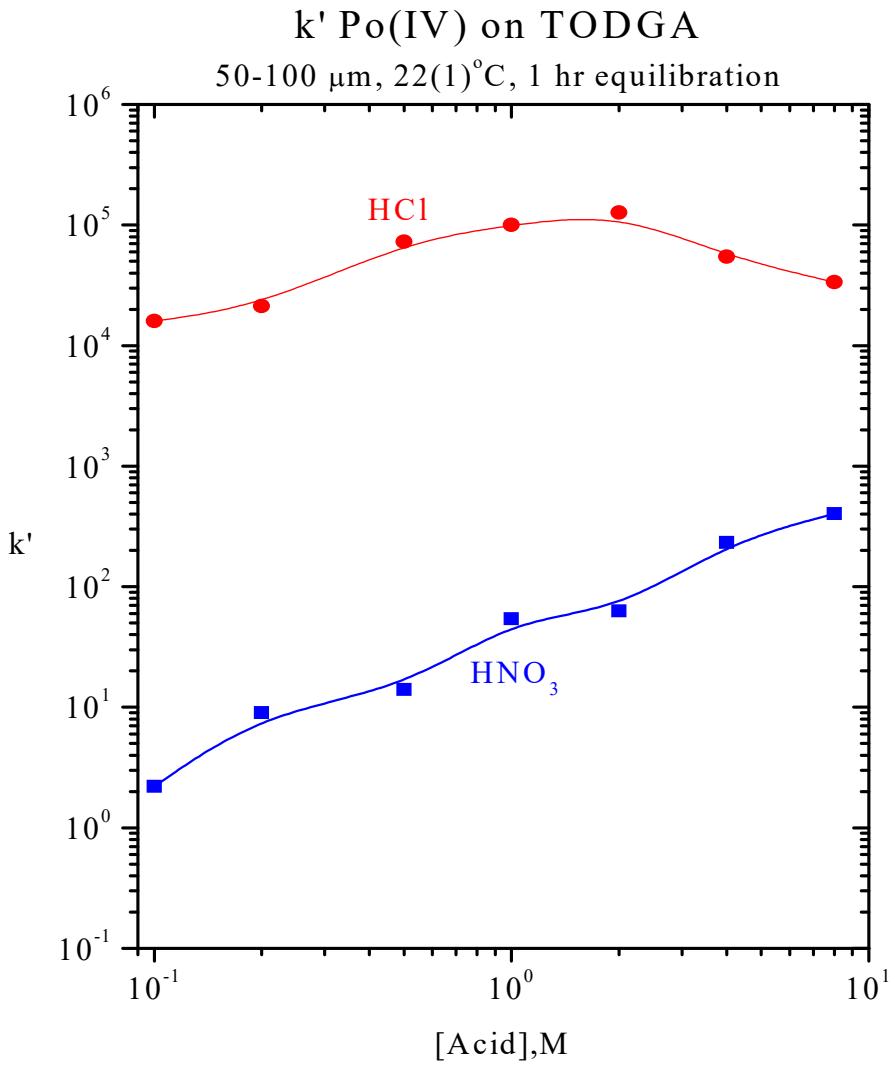

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Figure 4 Typical Alpha Spectra Showing Po Isotopes

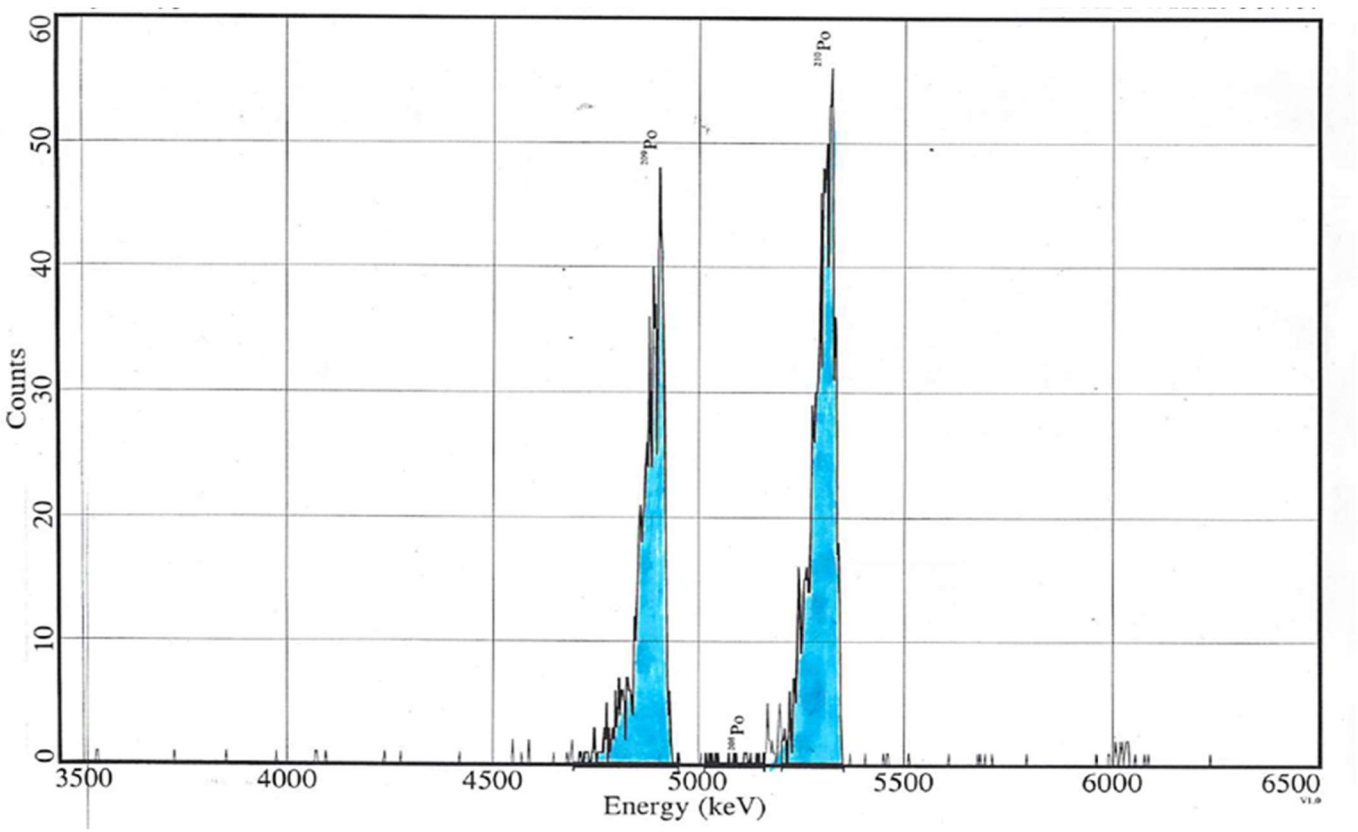
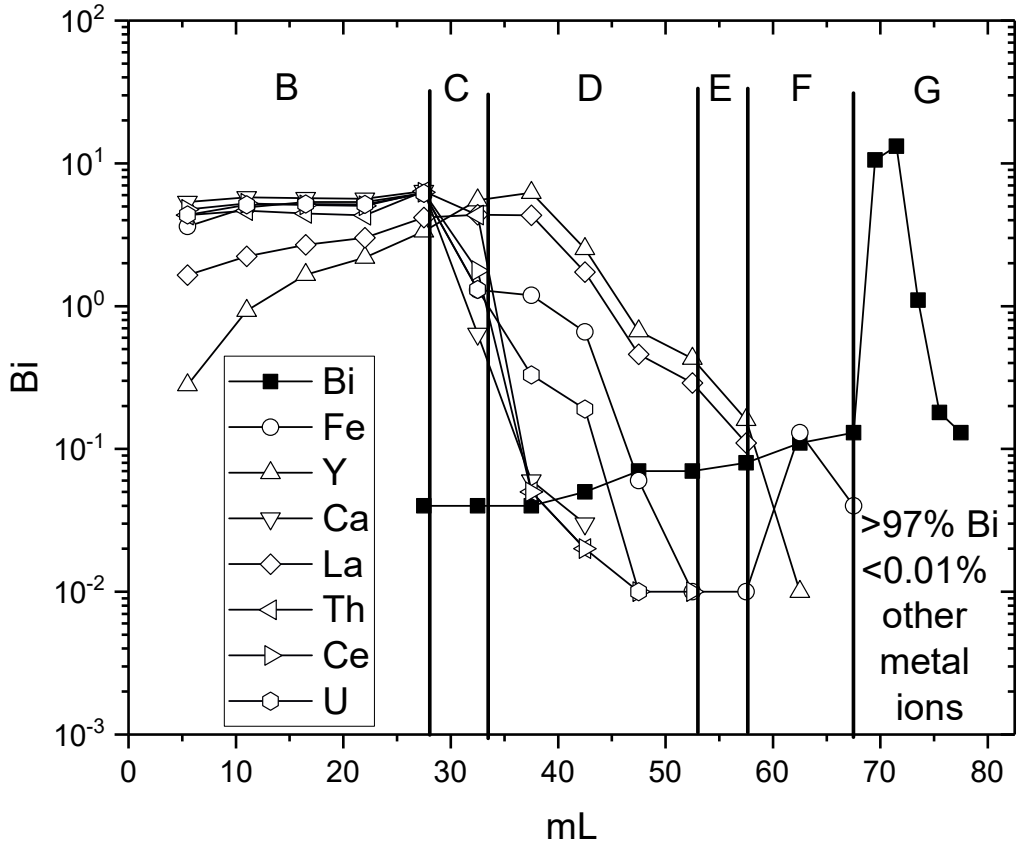


Figure 5 Elution Curve for Po on DGA Resin



A = Precondition 10 mL 1M HCl. B = Load 5 mL 4M HCl – 0.2M HF + 23 mL 0.5M HCl – 0.02M HF. C = 5 mL 1M HCl. D = 20 mL 0.25M HCl. E = 5 mL 0.5M HCl – 0.02M HF. F = 10 mL 8M HNO3. G = 20 mL 0.05M HNO3 – 0.005M ammonium bioxalate.

645 Figure 6 Elution of Bi on DGA Resin
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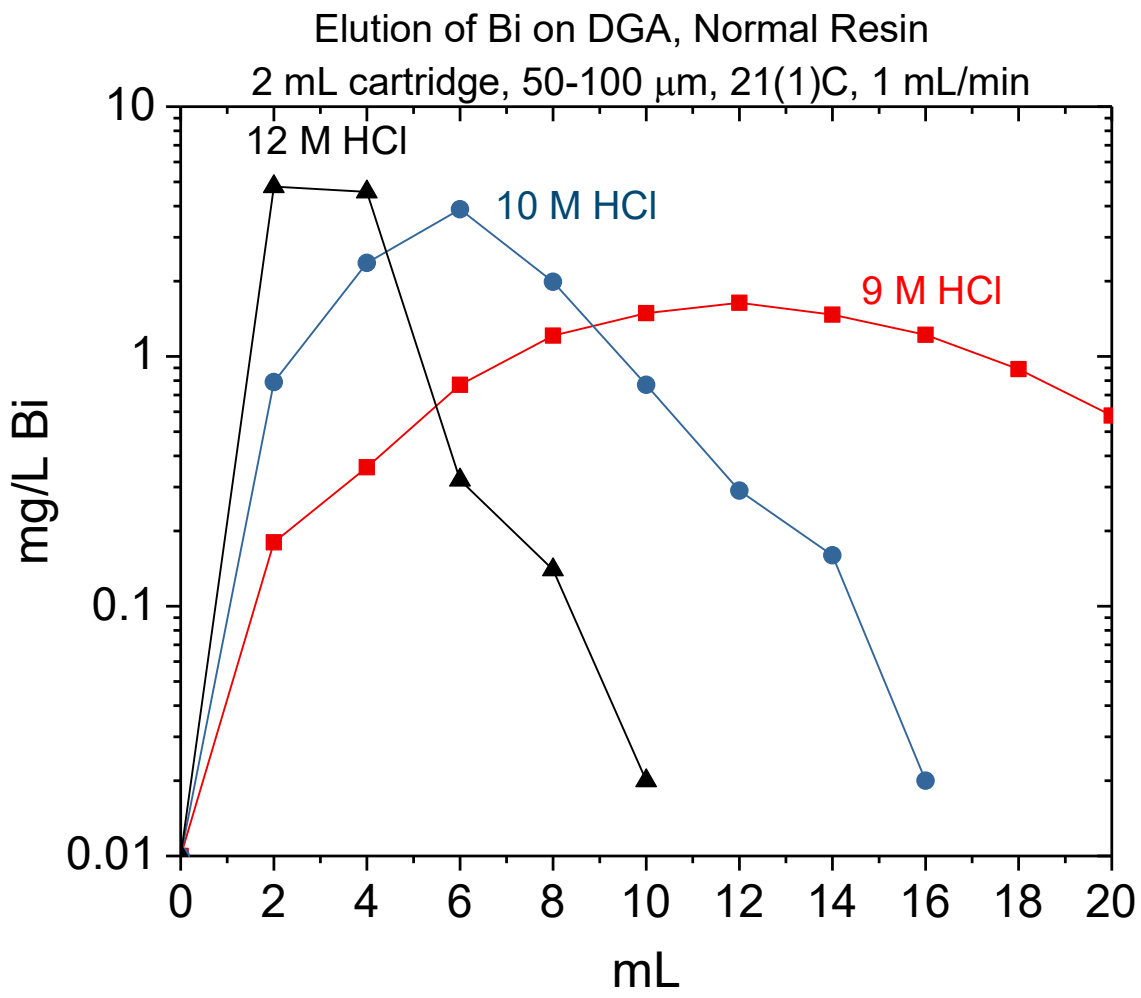

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