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Waste Minimization in Analytical Chemistry through Innovative Sample Preparation Techniques*

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DISCLAIMER

Waste Minimization in Analytical Chemistry through Innovative Sample Preparation Techniques

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ABSTRACT

Because toxic solvents and other hazardous materials are commonly used in analytical methods, characterization procedures result in significant and costly amount of waste. We are developing alternative analytical methods in the radiological and organic areas to reduce the volume or form of the hazardous waste produced during sample analysis.

For the radiological area, we have examined high-pressure, closed-vessel microwave digestion as a way to minimize waste from sample preparation operations. Heated solutions of strong mineral acids can be avoided for sample digestion by using the microwave approach. Because reactivity increases with pressure, we examined the use of less hazardous solvents to leach selected contaminants from soil for subsequent analysis. We demonstrated the feasibility of this approach by extracting plutonium from a NIST reference material using citric and tartaric acids with microwave digestion. Analytical results were comparable to traditional digestion methods, while hazardous waste was reduced by a factor of ten. We also evaluated the suitability of other natural acids, determined the extraction performance on a wider variety of soil types, and examined the extraction efficiency of other contaminants.

For the organic area, we examined ways to minimize the wastes associated with the determination of polychlorinated biphenyls (PCBs) in environmental samples. Conventional methods for analyzing semivolatile organic compounds are labor intensive and require copious amounts of hazardous solvents. For soil and sediment samples, we have a method to analyze PCBs that is based on microscale extraction using benign solvents (e.g., water or hexane). The extraction is performed at elevated temperatures in stainless steel cells containing the sample and solvent. Gas chromatography-mass spectrometry (GC/MS) was used to quantitate the analytes in the isolated extract. More recently, we developed a method utilizing solid-phase microextraction (SPME) for natural water samples. In this SPME technique, a fused-silica fiber coated with a polymeric film is exposed to the sample, extraction is allowed to take place, and then the analytes are thermally desorbed for GC analysis. Unlike liquid-liquid extraction or solid-phase extraction, SPME consumes all of the extracted sample in the analysis, significantly reducing the required sample volume.

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INTRODUCTION

Because toxic solvents and other hazardous materials are commonly used in analytical methods, the analysis itself can become a significant source of new waste. In radiochemical procedures, this waste must often be categorized as mixed waste. Alternative analytical methods can reduce the volume or form of the hazardous waste produced during sample preparation. We are examining high-pressure, closed-vessel microwave digestion to minimize waste from sample preparation operations in the radiological laboratory and microscale extraction techniques for the analysis of polychlorinated biphenyls (PCBs) in environmental matrices in organic analyses.

RADIOCHEMICAL ANALYSIS

The traditional soil dissolution techniques[1,2] of high temperature fusion or prolonged acid digestion are time consuming and generate large quantities of secondary wastes and fume hood emissions. Microwave energy as a heat source for sample digestion was first described over 20 years ago,[3] and today samples are frequently prepared for metal analysis by microwave digestion using strong mineral acids.[4,5] However, this technology has had limited application in the radiochemical laboratory because of constraints on sample size resulting from vessel pressure limitations. As a result, microwave dissolution techniques were not practical for many radiochemical procedures where larger sample sizes are required to achieve required detection limits. However, recent advances in vessel design have eliminated this disadvantage. These new vessels allow for pressures on the order of 110 bar (1500 psi)[6], thereby allowing for larger sample sizes. Additionally, improvements in vessel composition have been made. Noltner et. al have demonstrated that Tetrafluorometoxil (TFM) vessels exhibit significantly lower memory than vessels produced from the more traditional Perfluoroalcoholoxil (PFA).[7] This lower memory results in lower blank values and consequent lower limits of detection, a clear advantage for environmental laboratories. The TFM vessels are also able to withstand higher pressures and temperatures than the PFA vessels.

In previous work, we demonstrated that these high-pressure, closed-vessel systems with strong mineral acids as solvents allow significant improvements in the sample preparation process for soils and vegetations.[8-10] These microwave systems dramatically reduced secondary wastes and acid fume emissions while allowing larger sample sizes, shorter processing times, and reliable sample digestion.

Because reactivity increases as pressure increases, these high-pressure microwave systems enabled us to use alternative, nonhazardous solvents to leach certain contaminants from soils for analysis. In this work, we investigated replacing strong, corrosive acids with milder, nonhazardous complexing agents such as citric and tartaric acids for removing selected contaminants from soils.

Experimental

Instrumentation. A Milestone MLS-1200 MEGA Microwave Digestion System with MDR (Microwave Digestion Rotor) technology was used in this study. A polypropylene rotor holds

six high-pressure TFM vessels that are designed to tolerate exposure to a variety of aggressive acids at elevated pressures up to 110 bar. The power of the magnetron is 1200 W with 1000 W delivered inside the working chamber. The microwave emission is "unpulsed" in the 250 W mode, but pulsed at other wattages. The unpulsed 250 W mode assures controlled oxidation of organics. The microwave digestion protocol has been previously described.[8]

Plutonium and americium samples were electrodeposited onto 1.9-cm stainless steel disks and counted by alpha spectrometry using surface barrier detectors. A sodium sulfate/sodium bisulfate medium described by Kressin[11] was utilized for the electrodeposition.

The behavior of a variety of metals such as strontium, nickel, and zinc was monitored by inductively coupled plasma- mass spectrometry (ICP-MS) using a Fisons PlasmaQuad II with a glass, dual-concentric type nebulizer (Glass Expansion Pty. Ltd., Australia). A water-cooled Scott double-pass spray chamber (also supplied by Fisons) was used in combination with the nebulizer. Samples were transferred to the nebulizer by using a ten-roller peristaltic pump (Miniplus 3: Gilson Medical Electronics, Middleton, WI).

Standards and samples. Plutonium and americium analyses were quantified by isotope dilution employing radionuclides traceable to the National Institute of Standards and Technology (NIST). ICP standards were made from analytical grade reagents and distilled, deionized water.

A variety of soil types were selected for testing. For radiological analyses, the availability of standard reference materials is limited. We used NIST standards SRM 4353-Rocky Flats Soil #1 and SRM 4350B-Columbia River Sediment and MAPEP-97-S4 and QAP9703 soils from performance evaluation programs sponsored by the Department of Energy (DOE). Reference materials for non-radiological metal analyses are more numerous. NIST standards SRM 2709 - San Joaquin Soil and SRM 2711- Montana Soil, as well as CANMET S0-2, SO-3, and SO-4 were analyzed for this project. Soil SO-2 is from the B horizon of a Ferro-Humic Podzol developed in sandy till with an organic content of approximately 10%. Soil SO-3 is of the calcareous till parent material of the Guelpgh series, a gray Brown Luvisol. SO-3 soil has an appreciable content of both calcite and dolomite. SO-4 is from the A horizon of a Black Chernozemic soil developed in silty glacial lacustrine deposits.

Reagents and Materials. All reagents were American Chemical Society reagent grade and were utilized as received. Type-II distilled, deionized water was used for preparation of solutions. Solutions of citric acid, citric acid with hydrogen peroxide, quinnic acid, sodium carbonate-EDTA (ethylenediaminetetraacetic acid), sodium tartrate, and ammonium bioxalate were used as solvents for soil digestion.

Tru SPS and Teva resins, as well as Prefilter Material, an inert support, were received as bulk material (Trademarks of EIChrom Industries, Inc., Darien, IL). Prepacked AG 1-X8 (chloride form, 100-200 mesh) columns were obtained from Bio-Rad Laboratories (Richmond, CA).

Microwave Acid Digestion Procedure. Soils were dried at 110° C for at least 48 hours (or

until dry weight was obtained) and were ashed at 510° C overnight to remove organic material. Two grams maximum of sample were used in each analysis. Each soil-solvent pair was run in triplicate. Each sample was transferred to a clean TFM vessel and treated with 15 mL of the chosen solvent. The vessel was capped and placed into the microwave rotor apparatus. The sample was irradiated and subsequently cooled in a cold water bath. The sample was removed from the vessel, and the leachate was separated by centrifugation. The residue was washed with 5 mL 8 M HNO_3 and centrifuged. The supernatants were combined to form a sample digestate that is 2 M HNO_3.

Separation chemistry. Non-radiological metal analysis required no elemental separation before ICP-MS analysis. However, americium and plutonium had to be isolated prior to their determination by alpha spectroscopy. This step was accomplished through extraction chromatography using Tru SPS and Teva resins (trademarks of EIChrom Industries, Inc) as previously described.[12]

Results and Discussion

The best extractant for the plutonium and americium proved to be 1-2 M citric acid with peroxide. See Tables 1 and 2. It provided the best extraction recoveries and was the easiest to handle during the subsequent separation chemistry. Chemical yields for the separation process were in the range of 60-95 %. At 0.5 M citric acid, the extraction efficiency declined. Sodium tartrate extracted the analytes adequately, but it created gaseous by-products during the microwave procedure resulting in frequent venting of the vessels. Ammonium bioxalate did not extract adequately. Quinnic acid tended to decompose during the separation procedure resulting in channeling on the columns and very poor chemical recoveries. It also fouled the microwave vessels such that they had to be cleaned with aqua regia, a step counterproductive in a waste minimization method. Similar results were observed with sodium carbonate - EDTA. This reagent tended to precipitate during separation, thereby interfering with the analysis.

The strontium extractions were generally quite poor. Of the reagents examined, 2M citric acid with peroxide proved the best extractant, but its average extraction efficiency was only 35%. Citric acid with peroxide was also the best extractant for zinc with an average extraction recovery of 70%. The extraction recovery for nickel from this media was better, 89%. See Tables 3-5.

ORGANIC ANALYSIS

Sample preparation is frequently the most time- and labor-consuming step in the trace organic analysis of environmental samples. The analytes typically have to be extracted and preconcentrated from the matrix before instrumental analysis. In a variety of techniques that have been developed for this purpose, emphasis has been placed on simplicity, usage of organic solvents, time, costs, and ease of automation. We are examining several new approaches to measuring PCBs in natural water and solid samples that are primarily designed to minimize or eliminate the use of organic solvents. We are applying these methods to the determination of

PCBs as a representative subset of the semi-volatile organic compound (SVOC) class. PCBs form a class of 209 chemical compounds in which from 1 to 10 chlorine atoms are attached to biphenyl. These nonpolar compounds are characterized by low aqueous solubility, low vapor pressures, and excellent chemical stability and electrical isolating properties. Thus, PCBs have found many applications in the past. However, their suspected human carcinogenic properties, their widespread environmental occurrence resulting from contamination, their environmental persistence, and their tendency to bioaccumulation have gathered attention, resulting in the development of a myriad of analytical methods for PCB analysis over the last several decades.[13]

To meet regulatory requirements for the measurement of PCBs in environmental solids, large volumes of the samples must be processed to extract the analytes. For solid matrices, Soxhlet extraction, sonication, supercritical fluid extraction (SFE), pressurized fluid extraction (PFE), and microwave assisted extraction (MAE) are currently used. However, long extraction times, large amounts of solvents, or high capital costs (such as in implementation of PFE using commercial instrumentation) are required for these approaches.

We recently demonstrated an inexpensive and instrumentally simple approach to PFE for the quantitative extraction of PCBs in environmental samples of soils and sediments that uses nonhazardous solvents.[14] In this method, stainless steel extraction cells (64-mm-long pipe, 7 mm i.d. and 12 mm o.d., threaded at both ends and fitted with end caps) are filled with a solid sample (~350 mg) and solvent (high purity hexane) and heated for 30 min at elevated temperatures (~300 °C). After cooling the cell to room temperature, PCBs are measured in the extract by direct injection (3-μL sample) to a gas chromatograph with an electron capture detector (ECD). We tested the method on a set of PCB-spiked solid matrices and a PCB-contaminated river sediment (NIST SRM 1939). The recovery results for spiked samples were close to 100% for eight PCB congeners from sand and two different soil matrices. For river sediment, extraction with hexane at 300°C provided higher recoveries for three tested PCB congeners than those reported for a duplicate 16-hr Soxhlet extraction with a mixture of organic solvents. Our adaptation thus extends the PFE approach to an important class of contaminants by using a nonhazardous organic solvent. Furthermore, the method is inexpensive and uses readily available instrumentation, therefore making it more appealing to laboratories that handle small numbers of samples.

For natural water samples, PCBs are typically extracted by either liquid-liquid extraction (LLE) or solid-phase extraction (SPE). In either case, only a small portion of the final preconcentrated extract is introduced to the analytical instrument. In solid-phase microextraction (SPME), all of the extracted sample is introduced into the analytical instrument, significantly reducing the required sample volume. The SPME technique involves exposing a fused-silica fiber coated with a polymeric film to a liquid or gaseous sample. The fiber is usually kept in the sample until the equilibrium of analyte partitioning from the sample to the coating is reached. The analytes then typically are thermally desorbed into the injector of the GC. Thus, the sampling, extraction, concentration, and sample introduction are combined into a single step. SPME[15] has matured into a solvent-free, simple, and inexpensive extraction technique that has found numerous applications in environmental analysis, including PCBs in natural water samples. A comprehensive study of direct SPME of PCBs from water samples was reported by Potter and

Pawliszyn.[16] The SPME conditions were optimized by using a 15-μm-thick poly(dimethylsiloxane)- (PDMS-) coated fiber for two PCB congeners (PCB 18 and PCB 87). However, significant carryover and precision, expressed as a relative standard deviation (RSD) above 15%, were observed for both congeners. Koch and Volker recently reported[17] the results of a detailed study of headspace SPME of PCBs in aqueous matrices using a 100-μm-thick PDMS-coated fiber. In the SPME work reported herein, we examine the effect of the SPME fiber type and sampling time on several analytical figures of merit for a representative group of PCB congeners in aqueous solution.

Experimental

Instrumentation. A Star CX 3600 gas chromatograph (Varian, Sunnyvale, CA) with an ECD and split/splitless injector were employed with hydrogen at a flow rate of 1.2 mL/min as the carrier gas and with nitrogen at 30 mL/min as the detector makeup gas (injector temperature 250°C; ECD temperature 300°C). A 30 m x 0.25 mm, with a 0.25 μm film thickness, SPB-608 column (Supelco, Bellefonte, PA) was used for PCB separation with a split ratio of 100:1. The GC temperature program was started at 150°C and held there for 2 min, ramped to 290°C at 20°C/min, and held at 290°C for 6 min.

The SPME holder for manual sampling and the SPME fibers were obtained from Supelco. Samples (2.5 mL) of water spiked with PCBs were placed in 4-mL clear glass vials and capped with poly(tetrafluoroethylene)- (PTFE-) silicone septa (Supelco, Bellefonte, PA) for the SPME extraction step (2-min desorption time at 250°C).

Materials. A stock solution of the PCB calibration mixture (CB-681M; Ultra Scientific, North Kingstown, RI) was obtained by diluting it 100-fold with acetone. High-purity deionized (18 MΩ) water from a Barnstead NanoPure system (Dubuque, IA), degassed by sonication at reduced pressure, was used for all SPME experiments.

Results and Discussion

Unlike other extraction techniques, SPME is based not on the exhaustive extraction of analyte from a sample, but rather on reaching an equilibrium state of the partitioning of analyte between the sample matrix (usually water) and the polymeric fiber coating. The equilibrium state is characterized by the distribution constant K, which is defined as the ratio of an analyte's concentration in the coating to its concentration in the aqueous phase at equilibrium. The value of the distribution constant is dependent on the nature of the analyte, the sample matrix, and the coating. As a first approximation, the polarity of the analyte and the coating can be used to estimate the distribution constant. Generally, if the polarity of the coating and the analyte are similar and if the sample matrix is of opposite polarity, the analyte will have a strong tendency to partition from the matrix to the coating (characterized by large values of K). Larger values of K will yield a larger mass of analyte in the coating for the same bulk concentration of analyte in the sample, a process that is directly related to attainable limits of detection for the SPME method. However, for the same rate of mass transport, a corresponding increase in the time required to reach the equilibrium state for large values of K will be observed.

Currently, several SPME fibers with different type of coatings are commercially available. Most of the work on the use of SPME for PCB determination has been done with PDMS-coated fibers. In this work, we examined the following coated fibers: 100-μm-thick PDMS, 30-μm-thick PDMS, 85-μm-thick poly(acrylate) (PA), and 65-μm-thick Carbowax/divinylbenzene (CW/DVB). A mixture of nine PCB congeners of the composition described in the experimental section, where each congener of the mixture corresponds to a different degree of biphenyl chlorination, was selected for the study. The GC separation of the congeners was optimized to obtain a baseline resolution of all of the compounds in less than 15 min. Data for 2-chlorobiphenyl are not presented because its signal was barely detectable with the ECD at the concentration of the mixture used for spiking; its initial concentration in the original mixture was low, as is the ECD response factor for this compound.

For the fiber type selection study, 10 mL of the nine-component PCB mixture solution was prepared by diluting the PCB stock solution 100-fold with water; 2.5-mL portions were placed in 4-mL glass vials. Direct SPME extraction at room temperature was performed in triplicate for 15 min for each fiber type. Split GC injections at the ratio of 100:1 were performed to avoid saturating of the ECD. In Figure 1, the peak areas for eight PCB congeners (arranged in the order of elution from the GC column) are compared for different types of fibers by using a 15-min extraction from a 2.5 mL sample. The error bar represents one standard deviation. No dramatic differences in signals were observed for the different fibers. Generally, a higher response was obtained for the 100-μm-thick PDMS fiber versus the 30-μm-thick PDMS fiber. One would expect this to occur if the responses were compared at equilibrium for both fibers. It is, however, unlikely that equilibrium conditions are obtained for any of the fibers examined in such a short period of time (15 min). In the case of the PDMS coating, the values for the octanol-water partition coefficient (K_{ow}) can be directly related to the distribution constant.[17] The PCBs are characterized by large values of K_{ow} (log K_{ow} from 4 to 11).[18] This observation implies that the partition coefficients are also large for PCBs to nonpolar coatings and that long extraction times are needed to achieve equilibrium. The 15-min extraction time was selected as reasonable for practicality. Because the fibers studied differ in the thickness of the coating, the polarity, and the mechanism of extraction (extraction with the CW/DVB coating is based on surface adsorption, rather than absorption as with the other three fibers) and because sampling is finished presumably before equilibrium is reached, clear trends were not observed. It is surprising, however, that the observed differences in response were so mild. When sampling is done under nonequilibrium conditions for analytes with large distribution constants, the precision and the carryover are concerns. Generally, good precision (expressed as an RSD) of less than 10% was observed for most PCB congeners with the 100-μm-thick and 30-μm-thick PDMS fibers. Large RSDs, ranging from 10% to 25% and from 5% to 20%, were obtained for the 85-μm-thick PA fiber and the 65-μm-thick CW/DVB fiber, respectively. The carryover was examined by comparison to a splitless injection. The carryover was defined as the ratio of the peak area obtained for splitless carryover injection divided by a factor of 100 to the peak area obtained with split sample injection. Generally, for both of the PDMS fibers and the CW/DVB fiber, the carryover signals were observed only for the last five PCB congeners. However, the signal did not exceed 2%. Higher carryover was observed for the PA fiber, ranging from 2.5% to 6.0%.

The 30-μm-thick PDMS fiber was further examined to determine the extraction time profiles for the eight PCB congeners. The experiments were run in triplicate for each extraction time. Figure

2 shows the extraction time profiles for the eight PCB congeners with the 30-μm-thick PDMS fiber. The expected shape of an extraction time profile is obtained for most of the PCB congeners studied. The precision of the measurement improves as the extraction time is extended; that is, higher overall precision is observed for the lower-molecular-weight PCBs. Odd-shaped extraction time profiles are observed for PCB-201 and -209. Problems were encountered with the precision and the between-day signal reproducibility for these two congeners.

Using the 30-μm-thick PDMS fiber and an extraction time of 30 min, calibration curves were obtained for the eight PCB congeners. The range of concentrations used for calibration was from 10^4- to 10-fold dilution of the stock solution, which corresponds to a concentration for PCB 50 of 0.1-100 ppb, for example. Linear calibration models ($R \geq 0.99$) were obtained for all PCB congeners studied. Generally, the chromatogram obtained for the lowest concentration examined in the calibration study showed a signal for all PCBs, with a signal-to-noise ratio approximately equal to 3 (even with a 100:1 split ratio used for calibration). By assuming that the response would be increased by factor of 100 when splitless injection is used, limits of detection close to 1 ppt can be expected for all PCB congeners with SPME.

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FIGURE LEGENDS

Figure 1. Comparison of the GC responses obtained for a range of PCB congeners to the four SPME fiber types.

Figure 2(a). Comparison of the effect of sampling time on GC response for a 30 μm PDMS fiber for (a) PCB 5, PCB 29, PCB 50, and PCB 154.

Figure 2 (b). Comparison of the effect of sampling time on GC response for a 30 μm PDMS fiber for PCB 87, PCB 188, PCB 201, and PCB 209.

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Table 1. Plutonium extraction results[a]

Reagent	NIST SRM 4353 [0.217 ± 0.016]	NIST SRM 4350B [0.0137 ± 0.0008]	QAP9703 [3.65 ± 0.46]	MAPEP-97-S4 [1.06 ± 0.07][b]
2M Citric + 1 mL 30% H_2O_2	0.209 ± 0.021	0.013 ± 0.003	3.17 ± 0.21	1.11 ± 0.21
1M Citric + 1 mL 30% H_2O_2	0.195 ± 0.015	0.014 ± 0.003	3.10 ± 0.15	1.14 ± 0.26
1M Citric acid	0.195 ± 0.014	0.014 ± 0.003	3.13 ± 0.23	1.09 ± 0.23
0.5M Citric + 1 mL 30% H_2O_2	0.162 ± 0.013			
0.5M Citric acid	0.158 ± 0.014			
1.5M Sodium tartrate	0.218 ± 0.040		3.26 ± 0.26	1.02 ± 0.10
0.1M Ammonium bioxalate	0.177 ± 0.030		2.73 ± 0.36	0.73 ± 0.07
0.5M Quinnic acid	0.144 ± 0.030	reagent decomposed on columns creating channeling; it also fouled microwave vessels		
2M Na_2CO_3 + 0.1M EDTA	reagent precipitation during sample processing interfered with separation			

[a] Values reported in pCi/g.
[b] Value is a laboratory determined value using strong mineral acids. Certified value not available at the time of this report.

Table 2. Americium extraction results[a]

Reagent	NIST SRM 4353 [0.034 ± 0.003]	QAP9703 [0.154 ± 0.014]	MAPEP-97-S4 [0.539 ± 0.042][b]
2M Citric + 1 mL 30% H_2O_2	0.039 ± 0.007	0.132 ± 0.012	0.513 ± 0.066
1M Citric + 1 mL 30% H_2O_2	0.044 ± 0.008	0.136 ± 0.023	0.525 ± 0.065
1M Citric acid	0.044 ± 0.008		
0.5M Citric + 1 mL 30% H_2O_2	0.046 ± 0.008		
0.5M Citric acid	0.036 ± 0.007		
1.5M Sodium tartrate	0.042 ± 0.012	0.156 ± 0.029	0.515 ± 0.065
0.1M Ammonium bioxalate	0.041 ± 0.012		0.457 ± 0.039
0.5M Quinnic acid	reagent decomposed on columns creating channeling; it also fouled microwave vessels		
2M Na_2CO_3 + 0.1M EDTA	reagent precipitation during sample processing interfered with separation		

[a] Values reported in pCi/g.
[b] Value is a laboratory determined value using strong mineral acids. Certified value not available at the time of this report.

Table 3. Strontium extraction results[a]

Reagent	SO-2[b] [340 ± 50]	SO-3[b] [217 ± 29]	SO-4[b] [170 ± 18]	SRM 2709[c] [231 ± 2]	SRM 2711[c] [245.3 ± 0.7]
2M Citric + 1 mL 30% H_2O_2	97.7 ± 25.7	142.9 ± 4.4	35.4 ± 0.7	87.0 ± 2.2	48.8 ± 0.4
1.5M Sodium tartrate	5.30 ± 0.58	48.9 ± 1.1	31.0 ± 0.7		
0.1M Ammonium bioxalate	5.07 ± 0.21	78.7 ± 1.0	24.8 ± 0.6	65.5 ± 1.6	37.2 ± 0.8
2M Na_2CO_3 + 0.1M EDTA	9.13 ± 0.35	24.1 ± 0.7	28.6 ± 0.4		

[a] Values reported in µg/g (ppm).
[b] CANMET standard reference materials.
[c] NIST standard reference materials.

Table 4. Zinc extraction results[a]

Reagent	SO-2[b] [124 ± 5]	SO-3[b] [52 ± 3]	SO-4[b] [94 ± 3]	SRM 2709[c] [106 ± 3]	SRM 2711[c] [350.3 ± 4.8]
2M Citric + 1 mL 30% H_2O_2	83.8 ± 2.1	31.2 ± 1.1	34.3 ± 1.1	133 ± 4	197 ± 3
1.5M Sodium tartrate	121 ± 2	12.1 ± 0.4	17.4 ± 0.5		
0.1M Ammonium bioxalate	81.2 ± 2.2	15.9 ± 0.5	14.4 ± 0.6	98.0 ± 2.2	120 ± 3
2M Na_2CO_3 + 0.1M EDTA	114 ± 2	20.2 ± 0.7	21.7 ± 0.5		

[a] Values reported in µg/g (ppm).
[b] CANMET standard reference materials.
[c] NIST standard reference materials.

Table 5. Nickel extraction results[a]

Reagent	SO-2[b] [8 ± 2]	SO-3[b] [16 ± 3]	SO-4[b] [26 ± 3]	SRM 2709[c] [88 ± 5]	SRM 2711[c] [20.6 ± 1.1]
2M Citric + 1 mL 30% H_2O_2	5.86 ± 0.22	14.4 ± 0.76	17.9± 0.7	86.9 ± 3.0	23.7 ± 0.5
1.5M Sodium tartrate	6.91 ± 0.17	2.15 ± 0.18	4.93 ± 0.28		
0.1M Ammonium bioxalate	4.11 ± 0.25	3.10 ± 0.25	3.92 ± 0.28	18.1 ± 0.7	6.66 ± 0.28
2M Na_2CO_3 + 0.1M EDTA	7.05 ± 0.27	4.17 ± 0.17	21.0 ± 0.4		

[a] Values reported in µg/g (ppm).
[b] CANMET standard reference materials.
[c] NIST standard reference materials.