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Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry†‡§

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This work presents performance data after ultrasonic extraction (UE) for the elemental analysis of a number of metal species in samples of interest in environmental and occupational health. In this study, several National Institute of Standards and Technology (NIST) Standard Reference Materials® (SRMs) were subjected to UE in various acid solutions. The extraction solutions employed were 25% nitric acid (v/v), 25% nitric–hydrochloric acids (v/v) and concentrated nitric–hydrochloric acids (1 : 1). NIST SRMs 1648, 1579a, 2583, 2704, 2710, 3087a, and 8074 were subjected to these acid conditions and ultrasonic energy (about 1 W cm^{-2}), and elemental recoveries were determined following analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES). Observed recoveries were higher overall with HNO_3–HCl mixtures than with nitric acid alone, and recoveries were generally higher for concentrated acid mixtures. Recoveries of $>80\%$ could be achieved for some elements (As, Cd, Cu, Mn, Pb, Zn) when using acidic ultrasonic treatment with no deliberately added heating, even under diluted acid conditions. However, several elements (Ba, Co, Cr, Fe, Mg, Ni, V) yielded $<75\%$ recoveries when using sonication without deliberate heating, even in concentrated HNO_3–HCl. For comparison with UE, selected SRMs were subjected to acid leaching (no sonication) in the above acid solutions. Elemental recoveries from acid leaching without sonication were generally lower overall when compared to results obtained from UE, thereby demonstrating the effect of ultrasound for the dissolution of target analytes. Sonication of chromate-containing certified reference materials and certified filter samples (European Commission Certified Reference Material 545) in slightly basic buffer solutions was shown to be effective for the complete ($>90\%$) dissolution of hexavalent chromium (Cr^{VI}) from both soluble (potassium chromate) and insoluble (lead chromate) Cr^{VI} reference sources. Sonication in HNO_3–HF was used to extract Cd, Fe, Pb and Zn from aerosol filters, water rinsates and aerosol samplers alone; ICP-AES was used for elemental measurement. Sample losses were found for these four elements from rinsates and samples following removal of the aerosol filter, thereby demonstrating the utility of carrying out sonication directly within the aerosol sampler containing the filter. It is hypothesized that UE will be increasingly used for analytical sample preparation purposes.

Introduction

Sample preparation techniques such as hot plate and microwave digestion have been used widely for the dissolution of target elemental analytes for their subsequent analytical determination, and have become established standard methods for elemental extraction prior to atomic spectrometric analysis.[1–3] Such digestion techniques require the use of concentrated acids and high temperatures, and often high pressures (in the case of microwave digestion), to effect the dissolution of elemental analytes from solid samples. For elemental analysis, the sample preparation procedure employed is, apart from sample collection, ordinarily the most time-consuming step in the overall analysis. Hence other strategies for the treatment of solid samples have been tried in efforts to shorten the sample preparation step of the overall analysis.[4]

One of the techniques that has shown promise for speeding up and simplifying sample treatment is ultrasonic extraction (UE). Ultrasonic energy, when imparted to solutions, causes acoustic cavitation, that is, bubble formation and subsequent implosion.[5–7] The collapse of bubbles created by the sonication of solutions results in the generation of extremely high local temperature and pressure gradients, which may be regarded as localized "hot spots." On a timescale of about 10^{-10} s, effective local pressures and energies of about 10^5 atm and about 1 eV, respectively, are generated under sonochemical conditions.[5] These localized high-energy environments formed by the application of ultrasound to solutions can be employed for the purpose of extracting elemental analytes from solid matrices, so that elemental species may then be measured by instrumental techniques such as atomic spectrometry.[4,8]

The utility of UE for analysis by atomic spectrometry and other analytical techniques has been demonstrated for numerous elements within solid samples (bulk or filter).[8,9] Various acidic or, in certain cases, basic extraction solutions

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have been employed in concert with ultrasonic energy in order to dissolve target elements for their subsequent measurement.[8] Sonication can also allow for the preparation of samples directly within the sample container, thereby preventing sample losses and minimizing the likelihood of sample contamination.[10] However, despite its potential usefulness, UE has been under-utilized by analytical chemists.[4,8]

In this paper we present performance data from UE for the analysis of a number of metal species in samples of interest in environmental and occupational health. Also, for purposes of comparison, recovery results from selected reference materials, which were subjected to acid leaching without sonication, are presented. We have endeavored to provide performance results for UE conditions not previously reported, as well as presenting supplementary performance data for pertinent UE experiments previously published in the literature.

Experimental

Materials and reagents

Performance evaluation materials (PEMs) for multi-element analysis consisted of National Institute of Standards and Technology (NIST) Standard Reference Materials® (SRMs): Nos. 1648, Urban Particulate Matter; 2583, Trace Elements in Indoor Dust; 2704, Buffalo River Sediment; 2710, Montana Soil—Highly Elevated Trace Element Concentrations; 3087a, Metals on Filter Media; and 8704, Buffalo River Sediment (NIST, Gaithersburg, MD, USA). Where applicable, SRMs were weighed to the nearest 0.0001 g on an analytical balance (Model AE 163, Mettler, Greifensee, Switzerland). The PEM for hexavalent chromium (Cr^{VI}), CRM (Certified Reference Material) 545, Cr^{VI} in Welding Dust Loaded on Filters, was obtained from the Institute for Reference Materials and Measurements of the European Commission (IRMM/EC, Brussels, Belgium).

Nitric, hydrochloric, perchloric and hydrofluoric acids were spectroscopic grade (Aldrich, Milwaukee, WI, USA), and deionized water (18 MΩ, Barnstead Nanopure system, Dubuque, IA, USA) was used in the preparation of all solutions. Elemental standards (J. T. Baker, Phillipsburg, NJ, USA) and standard solutions of Cr^{VI} (Aldrich), of concentrations *ca.* 1000 μg ml^{-1}, were used for the preparation of calibration solutions. Ammonium sulfate, ammonium hydroxide, sodium carbonate, sodium hydroxide, potassium chromate (all from Aldrich) and lead chromate (Fisher Scientific, Fair Lawn, NJ, USA), were analytical-reagent grade.

Sample containers consisted of 15 or 50 ml centrifuge tubes (Falcon, Becton-Dickinson, Lincoln Park, NJ, USA). Air filters were either mixed cellulose ester (MCE) for multi-element analysis, or poly(vinyl chloride) (PVC) for analysis of chromium species (SKC, Eighty Four, PA, USA). For air samples targeted for subsequent extraction with hydrofluoric and nitric acids, quartz fiber filters (Whatman QMA, SKC) were used for sampling. Samplers for air filters, 25 or 37 mm diameter, were two- or three-piece (closed-face) plastic cassettes (SKC). For chromium work, Cr^{VI} analysis was performed using an ion chromatography system (Dionex Series 4500i, Sunnyvale, CA, USA).

For air samples targeted for subsequent extraction with nitric and hydrochloric acids, performance evaluation air filter samples were generated within an aerosol chamber in the manner described previously.[11] Aerosols were generated from SRM 1579a, Lead-Based Paint (NIST), which was ground to less than 10 μm characteristic diameter. The aerosols were collected at three mass levels onto 25 mm diameter PVC filters housed in plastic cassettes (SKC). Mass loadings on the filters (as measured gravimetrically) were about 0.3 mg, 0.5 mg and 1.6 mg for the three batches of filters ($n = 27$), respectively. The calculated relative standard deviation (RSD) in mass loadings was about 0.07 for each batch of filters.

Extraction and analysis

In experiments to determine the extractability of elements by ultrasonic agitation in acid solutions, samples were treated in accordance with a US National Institute for Occupational Safety and Health (NIOSH) ultrasonic procedure for the extraction of lead.[12] The NIOSH UE procedure was modified in that a higher nitric acid concentration (*i.e.*, 25% HNO_3 v/v[11] rather than 10% v/v[12,13]) was used for some experiments, while in other trials a mixture of 1 : 1 nitric–hydrochloric acid (total acid concentration 25% v/v) was employed. In further UE experiments, 1 : 1 mixtures of nitric and hydrochloric acids (without dilution) were used. UE was carried out in an ultrasonic bath providing about 1 W cm^{-2} power (Model 3510, Branson Ultrasonics, Danbury, CT, USA). Selected SRMs were subjected to acid leaching for 1 h (without sonication) in the above acid mixtures (*i.e.*, 25% HNO_3 (v/v), 25% HNO_3–HCl (v/v) and concentrated HNO_3–HCl). Following extraction in 10 ml of acid solution for 60 min, 5 or 10 ml sample aliquots were filtered through 0.45 μm polytetrafluoroethylene (PTFE) filters (Millipore, Bedford, MA, USA). Aliquots from diluted acid extracts were then analyzed without dilution for elements by inductively coupled plasma atomic emission spectrometry (ICP-AES)[14] (Spectro EOP, SpectroAnalytical, Fitchburg, MA, USA). Aliquots from concentrated acid extracts required 5-fold dilution prior to ICP-AES analysis.

To determine reference concentrations of multiple elements in aerosol samples generated from SRM 1579a, selected filter samples from each batch were prepared and analyzed by NIOSH Method 7300.[14] Briefly, the selected filters were digested in a mixture of concentrated nitric and perchloric acids on a hot plate prior to ICP-AES multi-element analysis after 1 : 10 dilution with water.

For the determination of "total" concentrations of multiple elements, a modification of the French Institut National de Recherche et de Sécurité (INRS) procedure, which uses a mixture of hydrofluoric and nitric acids in concert with UE, was employed.[15] The INRS method describes the UE-HF–HNO_3 dissolution of atmospheric aerosols collected on quartz fiber filters housed in plastic sampling cassettes, but has in some cases been modified for the treatment of bulk samples.[16,17] Briefly, filters and rinsate samples were sonicated in a mixture of 3 ml of HF and 2 ml of HNO_3 (concentrated acids) for at least 10 min. Thereafter, extracted samples were analyzed for elements by ICP-AES after dilution with 10 ml of water.

UE for the dissolution of chromium species (Cr^{VI} and total Cr) was carried out as described previously.[18,19] Briefly, samples were sonicated for 60 min in 10 ml of 0.05 M $(NH_4)_2SO_4$–0.05 M NH_4OH (soluble chromate) or 0.05 M Na_2CO_3–NaOH (insoluble chromate and total Cr) buffer (pH 8). Cr^{VI} was then analyzed without further dilution by using ion chromatography and visible detection (540 nm) after post-column reaction with 1,5-diphenylcarbazide.[20] Total chromium concentration in sample extracts was measured by ICP-AES.[14]

Results and discussion

Ultrasonic extraction of SRMs for elemental analysis

Sonication of SRMs in dilute acid solution for multi-elemental analysis. UE in diluted acid solution has become an accepted sample treatment procedure for the determination of lead in a variety of environmental media, as evidenced by the promulgation of standard reference methods.[12,21–23] An aim of this work is to investigate the potential utility of UE in diluted acid solution for the dissolution of other elements (beyond lead) in environmental matrices such as dust, soil and sediment. Hence representative NIST SRMs were subjected to UE in diluted acid, and the determination of certified as well as non-certified reference elements was carried out by ICP-AES.

Performance data (as measured by percentage recoveries) from UE of several NIST SRMs in 25% v/v nitric acid, followed by multi-element ICP-AES analysis of the extracts, are presented in Table 1. With the exception of Se, excellent recoveries are obtained from SRM 3087a (Table 1). However, such a result is not surprising, as this SRM consists of filter material spiked with the elements dissolved in solution. Hence SRM 3087a does not represent a challenging matrix for elemental extraction into solution. Recovery data obtained from UE of representative SRMs in a diluted mixture of nitric and hydrochloric acids (1 : 1 HNO_3–HCl; total acid concentration 25% v/v) are presented in Table 2. Mean recoveries obtained in dilute 1 : 1 nitric–hydrochloric acid (Table 2) are generally comparable statistically to those obtained from 25% v/v nitric acid (Table 1). It can be seen from the results of Tables 1 and 2 that UE in dilute acid solution does not give high recoveries for most elements within the bulk SRMs (*e.g.*, 1648, 2710, 8704). It is also noted that precision is lower when using dilute 1 : 1 nitric–hydrochloric acid *versus* dilute nitric acid alone (compare standard deviations of Table 2 to those of Table 1); this is attributed to an instrumental reagent effect of HCl.

Although low results were observed for most elements in the bulk SRMs, high recoveries were obtained for several elements (*i.e.*, As, Cd, Cu, Pb, and often Zn; see Tables 1 and 2) in particulate, dust and soil, or sediment materials. This suggests that a subset of elemental species can be determined in environmental media by atomic spectrometry after sample treatment with UE in diluted acid solution. While the application of UE in diluted acid for elemental analysis of environmental samples is admittedly limited, there may be instances when the determination of only one or a few elements is of interest. In such cases, UE in dilute acid may offer a simple, safe and fast alternative to hot plate or microwave digestion techniques that require the use of concentrated acids.[24] Additionally and/or alternatively, UE in dilute acid may offer a time-saving strategy for screening measurements prior to subsequent quantitative elemental analysis.

Table 1 Percentage recoveries of target elements from NIST SRMs subjected to ultrasonic extraction in 25% HNO_3 (v/v), as measured by ICP-AES. (Number of replicates $n=6$; values in parentheses are standard deviations; masses weighed were about 0.25 g for SRMs 1648, 2583 and 2710)

	Standard Reference Material			
Element	1648[a]	2583[b]	2710[c]	3087a[d]
As	83.7 (1.9)	82.8 (2.6)	83.7 (1.7)	99.4 (1.1)
Ba	35.2 (2.8)	N/A[e]	36.9 (1.8)	100.9 (1.9)
Cd	79.4 (2.1)		87.3 (2.2)	100.4 (10.7)
Co	52.1 (2.6)	N/A	58.4 (3.1)	N/A
Cr	13.5 (0.5)	31.8 (1.4)	19.7 (1.3)	105.4 (1.7)
Cu	85.4 (2.4)	N/A	94.4 (2.1)	N/A
Fe	31.0 (1.7)	N/A	32.0 (1.7)	104.0 (1.5)
Mg	62.2 (1.8)	N/A	24.8 (2.5)	109.9 (1.3)
Mn	70.6 (2.3)	N/A	70.2 (2.0)	107.4 (1.5)
Ni	49.2 (1.7)	N/A	42.9 (2.3)	107.3 (1.4)
Pb	88.1 (2.0)	83.4 (7.1)	88.8 (2.0)	108.2 (1.5)
Se	134.9 (5.2)	N/A	N/A	67.6 (17.0)
V	61.1 (1.6)	N/A	34.5 (1.5)	104.6 (1.6)
Zn	79.1 (2.0)	N/A	62.6 (1.2)	102.0 (1.5)

[a]Urban Particulate Matter. [b]Trace Elements in Indoor Dust. [c]Montana Soil—Highly Elevated Trace Element Concentrations. [d]Metals on Filter Media. [e]No certified or uncertified reference values available.

Table 2 Percentage recoveries of target elements from NIST SRMs (about 0.025 g to about 0.50 g) subjected to ultrasonic extraction in 25% HNO_3–HCl 1 : 1 (v/v), as measured by ICP-AES. (Number of replicates $n=6$; values in parentheses are standard deviations)

Element	SRM 1648[a]	SRM 2710[b]	SRM 8704[c]
As	83.5 (12.6)	90.3 (5.3)	N/A[d]
Ba	39.2 (27.2)	35.7 (4.7)	17.4 (1.0)
Cd	85.2 (7.6)	83.4 (18.5)	94.9 (14.2)
Co	49.5 (4.1)	48.2 (18.7)	58.4 (9.9)
Cr	13.6 (1.0)	15.7 (6.6)	43.0 (4.9)
Cu	80.3 (0.9)	94.3 (6.9)	N/A
Fe	30.2 (3.4)	31.5 (3.7)	33.3 (6.1)
Mg	64.4 (5.0)	24.1 (4.4)	51.4 (4.6)
Mn	63.0 (6.0)	64.2 (8.2)	70.0 (3.8)
Ni	50.4 (4.9)	39.3 (5.4)	52.3 (9.3)
Pb	92.4 (6.2)	90.7 (4.9)	95.2 (7.6)
V	61.6 (4.3)	29.1 (8.5)	12.6 (5.4)
Zn	78.1 (5.4)	62.1 (7.5)	81.3 (4.7)

[a]Urban Particulate Matter. [b]Trace Elements in Indoor Dust. [c]Buffalo River Sediment. [d]No certified or uncertified reference value available.

Sonication of SRMs in concentrated nitric and hydrochloric acid solution. The effectiveness of mixtures of concentrated nitric and hydrochloric acids, using heated ultrasonic extraction for multi-element determination by atomic spectrometry, has been previously demonstrated.[9] Our aim here was to investigate the utility of ultrasonic extraction for subsequent multi-elemental atomic spectrometric determination in similar acid mixtures without deliberate heating.

Recoveries obtained from several PEMs, which were sonicated for one hour in 1 : 1 (v/v) mixtures of concentrated nitric and hydrochloric acids, are shown in Table 3. Comparing these data with the results in Tables 1 and 2, it can be seen that UE recoveries are greater for most metals when the acid concentration is increased. High (*i.e.*, >75%[25]) recoveries with UE in concentrated HNO_3–HCl are obtained for about 6 metals (Table 3), although there are some differences in recovery depending on the analyte and on the source matrix material. The results of Table 3 are similar to recoveries reported from a sewage sludge PEM using *aqua regia* and UE, excepting the observed (surprisingly) high recovery reported for Cr.[16] Low recoveries after acid digestion of Cr are not unexpected, since an insoluble oxide is known to form under these (or similar) acid conditions.[24,26,27]

Table 3 Percentage recoveries of target elements from NIST SRMs (about 0.025 to about 0.50 g) subjected to ultrasonic extraction in concentrated HNO_3 : HCl (1 : 1 v/v), as measured by ICP-AES. (Number of replicates $n=6$, excepting $n=3$ in third column; values in parentheses are standard deviations)

	Standard Reference Material				
Element	1648[a]	1648 (+Δ)[b]	2583[c]	2704[d]	2710[e]
As	75.8 (3.6)	130 (2.9)	86.8 (15.9)	N/A[f]	84.1 (10.7)
Ba	56.5 (14.8)	80 (0.6)	N/A	20.5 (2.7)	37.6 (10.3)
Cd	87.4 (5.2)	114 (9.7)	122.4 (38.3)	95.0 (3.6)	97.2 (13.7)
Co	67.6 (7.7)	96 (5.2)	N/A	81.0 (4.5)	99.7 (9.0)
Cr	16.8 (1.3)	23 (0.3)	47.4 (5.7)	60.0 (1.7)	32.9 (10.4)
Cu	99.4 (15.3)	100 (1.4)	N/A	96.7 (11.9)	91.9 (14.3)
Fe	52.2 (4.8)	68 (1.0)	N/A	66.1 (4.2)	51.7 (12.3)
Mg	67.5 (5.5)	—[g]	N/A	64.7 (4.0)	41.2 (12.6)
Mn	78.1 (6.1)	88 (1.4)	N/A	80.3 (2.7)	72.0 (9.3)
Ni	65.1 (5.4)	90 (0.8)	N/A	79.1 (6.2)	68.5 (20.4)
Pb	91.0 (4.2)	95 (1.0)	84.4 (11.3)	89.0 (5.3)	87.4 (11.3)
V	66.3 (5.7)	79 (1.5)	N/A	20.7 (0.8)	48.3 (11.3)
Zn	84.0 (5.3)	97 (3.7)	N/A	92.6 (2.4)	77.7 (12.2)

[a]Urban Particulate Matter. [b]Data from ref. 9: UE with heating (Δ) at 100 °C. [c]Trace Elements in Indoor Dust. [d]Buffalo River Sediment. [e]Montana Soil—Highly Elevated Trace Element Concentrations. [f]No certified or uncertified reference value available. [g]No value reported.

In view of the results in Table 3, it is apparent that elevated temperatures, along with sonication, are needed to effect the complete dissolution of several additional metals from SRMs, which are not fully dissolved by UE without deliberate heating. For instance, compare the results shown in Table 3 for NIST SRM 1648 of unheated (first column) *versus* heated[9] (last column) ultrasonic extracts. Therefore, it appears that the benefit acquired by applying UE with concentrated HNO_3–HCl for the dissolution of multiple elements (compared with UE in dilute acid solution) is limited, unless significant heat is imparted to the ultrasonic bath. Nevertheless, the procedure described was shown to be effective for the extraction of several elements (*e.g.*, As, Cd, Cu, Mn, Pb, Zn) from the SRMs investigated.

Elemental recoveries from SRMs subjected to acid leaching without sonication

It was thought to be necessary to investigate the effect of sonication on extraction efficiency by comparing recoveries from UE with elemental recoveries that were obtained from simply leaching the materials to be analyzed in the aforementioned acid solutions. Hence experiments were conducted by subjecting selected SRMs to acid leaching at room temperature for 60 min *without* sonication. Three representative SRMs (1648, 2704 and 2710) were subjected to leaching for 1 h in the same acid solutions used in UE experiments. Aliquots of sample leachates were then filtered and analyzed by ICP-AES. Afterwards, elemental recoveries were computed; recovery results from leaching experiments are shown in Table 4.

For almost all of the elements measured, recoveries from leaching were observed to be significantly lower than those obtained from UE (compare the data in Table 4 with results from Tables 1–3). A notable exception, however, is lead, whereby simply leaching the SRM sample in acid solution was found to give high recoveries, which were, in most cases, statistically equivalent to the recoveries of Pb obtained using UE (*t*-tests, $p = 0.05$). High recoveries ($>75\%$) from leaching were observed in some cases for several other elements, *e.g.*, As Cd and Cu (Table 4), but these recoveries were nevertheless significantly lower than those obtained using UE (Tables 1–3). These results serve to demonstrate the effect of sonication on recovery. When (not surprisingly) various elements leach into the acid solution to a certain degree, it is clearly demonstrated that more complete dissolution can generally be accomplished through the application of ultrasonic energy.

Table 4 Percentage recoveries of target elements from NIST SRMs (about 0.2 g) subjected to leaching (no sonication) for 60 min in (a) 25% HNO_3 (v/v), (b) 25% HNO_3 : HCl 1 : 1 (v/v), and (c) concentrated HNO_3 : HCl 1 : 1 (v/v), as measured by ICP-AES. (Number of replicates $n = 3$; values in parentheses are standard deviations)

Element	SRM 1648[a]	SRM 2704[b]	SRM 2710[c]
As	(a) 63.4 (1.2)	(a) N/A[d]	(a) 68.3 (0.2)
	(b) 70.9 (3.7)	(b) N/A	(b) 77.3 (2.2)
	(c) 70.8 (6.6)	(c) N/A	(c) 76.5 (2.8)
Ba	(a) 25.1 (0.8)	(a) 12.8 (0.3)	(a) 8.4 (0.1)
	(b) 22.6 (1.3)	(b) 13.6 (0.7)	(b) 8.6 (0.3)
	(c) 28.2 (0.9)	(c) 14.4 (1.4)	(c) 7.4 (1.2)
Cd	(a) 69.4 (1.7)	(a) 75.9 (0.1)	(a) 68.9 (1.3)
	(b) 73.6 (2.9)	(b) 82.7 (0.2)	(b) 73.5 (2.3)
	(c) 73.4 (2.4)	(c) ND[e]	(c) 77.9 (3.1)
Co	(a) 35.0 (0.8)	(a) 17.0 (0.2)	(a) 1.4 (0.1)
	(b) 36.8 (1.8)	(b) 22.7 (9.8)	(b) 8.6 (0.3)
	(c) 42.2 (3.1)	(c) ND	(c) ND
Cr	(a) 10.7 (0.1)	(a) 33.5 (0.1)	(a) 6.1 (0.2)
	(b) 11.5 (0.4)	(b) 35.3 (1.8)	(b) 6.1 (0.1)
	(c) 13.2 (0.6)	(c) 41.4 (2.4)	(c) 7.4 (1.2)
Cu	(a) 73.4 (2.0)	(a) 75.0 (4.0)	(a) 77.1 (1.2)
	(b) 77.5 (4.1)	(b) 77.3 (2.5)	(b) 80.3 (0.5)
	(c) 82.2 (5.3)	(c) 83.4 (3.7)	(c) 77.9 (2.3)
Fe	(a) 19.4 (0.4)	(a) 17.4 (0.1)	(a) 13.9 (0.4)
	(b) 23.5 (0.9)	(b) 18.3 (0.9)	(b) 16.4 (0.4)
	(c) 34.6 (1.5)	(c) 29.1 (2.5)	(c) 29.1 (1.4)
Mg	(a) 59.0 (1.6)	(a) 39.7 (0.2)	(a) 7.5 (0.1)
	(b) 64.0 (1.6)	(b) 41.0 (1.2)	(b) 8.3 (0.3)
	(c) 69.2 (2.4)	(c) 42.9 (2.3)	(c) 18.6 (1.6)
Mn	(a) 51.8 (0.1)	(a) 51.3 (0.1)	(a) 30.5 (0.1)
	(b) 58.0 (2.7)	(b) 57.0 (2.4)	(b) 40.0 (0.1)
	(c) 66.4 (4.2)	(c) 55.5 (3.7)	(c) 57.8 (2.0)
Ni	(a) 40.1 (3.1)	(a) 23.4 (2.7)	(a) 14.4 (1.0)
	(b) 41.9 (1.5)	(b) 23.8 (1.1)	(b) 15.6 (1.0)
	(c) 45.0 (1.0)	(c) 27.0 (1.2)	(c) ND
Pb	(a) 86.9 (2.1)	(a) 86.3 (1.7)	(a) 80.3 (2.5)
	(b) 91.6 (3.2)	(b) 95.5 (1.5)	(b) 87.5 (2.5)
	(c) 84.8 (3.6)	(c) 91.2 (8.6)	(c) 78.9 (2.5)
V	(a) 51.6 (1.0)	(a) 7.5 (0.2)	(a) 17.9 (0.2)
	(b) 53.8 (2.6)	(b) 4.6 (0.2)	(b) 20.1 (0.6)
	(c) 50.4 (1.9)	(c) 5.2 (0.3)	(c) 28.8 (0.9)
Zn	(a) 65.5 (0.2)	(a) 61.6 (3.1)	(a) 31.1 (0.5)
	(b) 72.2 (2.6)	(b) 68.9 (3.2)	(b) 38.8 (2.0)
	(c) 68.0 (13.2)	(c) 84.2 (8.2)	(c) 69.1 (2.6)

[a] Urban Particulate Matter. [b] Buffalo River Sediment. [c] Montana Soil—Highly Elevated Trace Element Concentrations. [d] No certified or uncertified reference value available. [e] None detected.

Ultrasonic extraction of air filter samples for elemental determination

Sonication of air filter samples in basic buffer for the extraction of chromium species. Ultrasonic extraction of industrial hygiene and environmental samples in a slightly basic buffer has been demonstrated to be effective for the extraction of chromium species, including the highly carcinogenic hexavalent chromium, Cr^{VI}.[18,20,28] Following UE, isolation of Cr^{VI} can be accomplished by such means as flow-injection,[29–32] strong anion-exchange solid-phase extraction,[18–20] ion chromatography,[20,33–35] or high-performance liquid chromatographic techniques.[36] Isolated Cr^{VI} can then be measured analytically using a variety of techniques such as the highly popular method using 1,5-diphenylcarbazide,[18–20,33–35,37,38] voltammetric methods,[39–41] or atomic spectrometric techniques.[28,31,32,42–46] For the determination of total chromium, no isolation step is necessary, as has been demonstrated for Cr in a certified reference material (CRM) consisting of welding fumes collected on quartz fiber filters.[20]

Data for the determination of Cr^{VI} and Cr(total) by visible spectrophotometry and ICP-AES, respectively, following UE from spiked filters and from IRMM CRM 545 filters, are illustrated in Table 5. (Although Cr^{VI} was measured using the aforementioned ion chromatographic separation and 1,5-diphenylcarbazide detection method,[20] it is emphasized that equivalent results may be obtained by using atomic spectrometric methods to determine extracted and isolated Cr^{VI}.[43,45,47]) The near 100% recoveries obtained (Table 5)

Table 5 Percentage recoveries of Cr^{VI} and Cr(total) from ultrasonic extraction in pH about 8 0.05 M ammonium sulfate–0.05 M ammonium hydroxide (potassium chromate) or 0.05 M sodium carbonate–0.05 M sodium hydroxide (lead chromate) buffer. PEMs consisted of PVC filters spiked with potassium chromate or lead chromate, and IRMM CRM 545 (Cr^{VI} in Welding Dust Loaded on Filters). (Values in parentheses are standard deviations)

	Mean recovery (%)	
Sample type	Cr^{VI}	Cr(total)
Potassium chromate-spiked PVC filters	96.0 (12.4); $n = 11$	107.4 (7.9); $n = 7$
Lead chromate-spiked PVC filters	92.5 (4.3); $n = 6$	96.6 (2.4); $n = 5$
CRMs (welding dust on quartz fiber filters)	98.4 (3.4)[a]; $n = 6$	111.3 (7.6); $n = 5$

[a] Excludes one statistical outlier (Dixon's Q-test, $P = 0.05$).

demonstrate that UE is an effective technique for the quantitative dissolution of chromium species from industrial hygiene samples. Comparable results for UE of Cr species have been observed elsewhere from environmental samples such as soils and sand spiked with both insoluble and soluble chromate.[29,38]

Sonication of aerosol samples in nitric and hydrochloric acids for multi-element analysis. In previous work, ultrasonic extraction of air filter samples in dilute nitric acid has been shown to give quantitative recoveries of lead.[11,13] In the present study, the effectiveness of UE in both dilute and concentrated acid solutions for the dissolution of numerous additional elements (including lead) was investigated for aerosol samples generated from an SRM paint. The SRM chosen, 1579a, was especially useful for uniform aerosol generation owing to its much smaller mean particle size (mean diameter about 30 μm) compared to other metal-containing SRMs (mean particle diameter about 100 μm). Recoveries of target elements were computed by comparison of UE data against results obtained from a reference analytical method, NIOSH 7300[14] (Table 6). (The NIOSH method 7300 employs hot plate or microwave digestion of air filter samples in a mixture of concentrated nitric and perchloric acids prior to analysis of aliquots of sample extracts by ICP-AES.)

Sonication of air filter samples in dilute nitric acid (Table 6, column 2) was found to give >75% recoveries for six of the eleven metals analyzed. The eleven elements listed in Table 6 were those that were found to give ICP-AES analytical results from the filter samples that exceeded the limit of quantitation. Several other elements were determined by ICP-AES but could not be quantified, and therefore are not listed in the Table. UE with a dilute mixture of nitric and hydrochloric acids resulted in nine of eleven elements having recoveries exceeding 75% (Table 6, column 3). UE with a mixture of concentrated nitric and hydrochloric acids without heating yielded high recoveries for all eleven target elements (Table 6, column 4). These results suggest that UE may be more effective for dissolution of elements from aerosol samples than from bulk materials such as soils, dusts and sediments (Tables 1–3). This is probably due to the smaller mean particle size of the aerosol particulate material (<10 μm) as compared to the bulk SRMs. The results in Table 6 suggest that UE in acid mixtures not employing hydrofluoric acid[1] is an effective technique for the dissolution of numerous elements in at least some types of industrial hygiene samples. Further, UE of air filter samples in diluted acids is shown to be effective for the dissolution of a subset of elements that are extractable using concentrated acids.

Table 6 Recoveries of target elements from ultrasonic extraction of performance evaluation air filter samples generated in an aerosol chamber from NIST SRM 1579a Lead-Based Paint. UE acid solutions were: (a) 25% v/v for dilute HNO_3; (b) 12.5%:12.5% v/v (*i.e.*, 1 : 1 v/v) for dilute HNO_3–HCl; and (c) 1 : 1 v/v (undiluted) for concentrated HNO_3/HCl. (Values in parentheses are standard deviations for n = number of samples yielding results above the analytical limit of quantitation)

	Recovery (%)		
Element[a]	Dilute HNO_3	Dilute HNO_3–HCl	Concentrated HNO_3–HCl[b]
As	97.0 (12.1); $n=3$	84.8 (6.2); $n=3$	118 (8); $n=3$
Ba	90.6 (23.7); $n=9$	88.4 (5.5); $n=9$	93.7 (5.3); $n=9$
Cd	61.0 (5.4); $n=3$	107 (28); $n=6$	101 (24); $n=9$
Co	58.6 (6.9); $n=3$	57.1 (15.1); $n=7$	124 (11); $n=6$
Cu	88.9 (6.1); $n=9$	93.1 (6.1); $n=9$	93.1 (4.7); $n=9$
Fe	20.2 (3.0); $n=9$	49.9 (7.9); $n=9$	79.9 (0.8); $n=9$
Mn	69.4 (6.4); $n=3$	87.2 (7.2); $n=3$	100.6 (2.6); $n=3$
Ni	41.1 (4.0); $n=3$	129 (16); $n=9$	108 (7); $n=3$
Pb	84.0 (2.3); $n=9$	87.4 (6.2); $n=9$	99.1 (5.9); $n=9$
Sr	82.4 (6.7); $n=9$	84.9 (6.9); $n=9$	80.9 (2.1); $n=3$
Zn	81.8 (2.2); $n=9$	87.2 (5.9); $n=9$	101 (3); $n=9$

[a] Observed elemental loadings per filter sample (as determined by NIOSH 7300[14]) were in the following ranges: <0.1 μg for Cd, Co, Ni; 0.1–2 μg for As, Cu, Sr; 2–10 μg for Fe; >10 μg for Ba, Pb, Zn. [b] Samples were diluted 1 : 10 prior to analysis by ICP-AES.

Sonication of aerosol samples in hydrofluoric and nitric acids for multi-element analysis. Hydrofluoric acid (HF) is used in extractions requiring the dissolution of metal species that are bound up in silicate materials and that would otherwise be insoluble, even in other acid solutions.[15–17,24] The effectiveness of mixtures of concentrated HF and other acids such as HNO_3 for the ultrasonic extraction of target elements, followed by atomic spectrometric analysis, has been demonstrated previously for bulk certified reference materials such as sediments, soils, particulates and fly ash.[16,17] HF has also been used successfully in combination with nitric and other acids (*e.g.*, HCl) for multi-element UE from air filter samples for subsequent atomic spectrometric measurement.[10,17,24] Low recoveries observed for Cr and Ni in collected aerosol samples have been attributed to the formation of insoluble oxides.[24]

Previous work has demonstrated problems with aerosol sample losses due to particulates, which adhere to the inside surface of the sampler and are not captured by the filter, and/or are dislodged from the filter during sample transport and handling.[10] A further investigation is presented here, where recoveries of four metals (Cd, Fe, Pb, Zn) from several aerosol samplers were investigated prior to and following washing of the inside surfaces of the samplers with water. Air samples were collected during work activities in a lead refinery, and the filters (quartz fiber) were removed from the samplers (37 mm closed-face cassettes) and subjected to UE in HF–HNO_3. The inner walls of the samplers were then rinsed with about 5 ml of water with a wash bottle, and both the rinsates and the insides of the samplers were subsequently treated by UE in HF–HNO_3. The results of these experiments are presented in Table 7. It is shown from the data of Table 7 (column 4) that significant amounts of the four metals measured may still be present on the inner walls of the sampling cassettes, even after rinsing the samplers with water. Thus, in order to avoid problems from sample losses due to the aerosol which is not captured and retained by the filter, it is recommended to carry out UE directly within the sampler, as described previously.[10,48] This practice would also serve to avoid contamination problems from sample manipulation in removing the filters from the samplers for placement into extraction vessels.

Table 7 Relative recoveries of Cd, Fe, Pb and Zn (after UE in HF–HNO_3) obtained from quartz fiber filters, H_2O rinsates, and the inside walls of aerosol samplers following rinsing of the inner surfaces of the samplers with water. (Values in parentheses are standard deviations; number of samples $n=10$.) Samples consisted of area aerosol samples, collected at various locations in a lead refinery, using 37 mm plastic cassettes housing the filters

	Relative mean recovery (%)		
Metal[a]	Filters	Water rinsates	Samplers (after rinsing)
Cd	72.2 (13.1)	10.1 (6.5)	17.7 (11.5)
Fe	66.5 (19.9)	12.4 (7.8)	21.1 (15.7)
Pb	73.6 (17.9)	11.8 (8.9)	14.6 (10.7)
Zn	75.2 (11.5)	10.1 (6.4)	14.7 (8.6)

[a] Observed ranges of total metal loadings were: 0.29 to 117 μg for Cd (mean 28 μg); 3.1 to 167 μg for Fe (mean 42 μg); 51 to 1674 μg for Pb (mean 459 μg); and 9.8 to 1579 μg for Zn (mean 367 μg).

Conclusions

The utility of ultrasonic extraction for multi-element determination by atomic spectrometry has been demonstrated for samples of interest in the industrial hygiene and environmental fields. Various strategies employing UE for sample preparation have been investigated here and elsewhere. Several benefits offered by UE are: shortened sample preparation times, simplicity, and enhanced safety compared to other more traditional methods of preparing samples for subsequent multi-elemental determination. Another advantage of UE is that there is no possibility of the extraction solution evaporating to dryness. This is often a problem with hot plate digestion, especially when such digestions are carried out in low solution volumes. Potential applications of UE for treatment of workplace air filter samples are especially appealing, since sample preparation can be carried out directly within the sampler, and sample losses from aerosols adhering to the inner walls of the sampler may thereby be avoided.

Dilute acids can be used for the ultrasonic dissolution of a limited number of metals (notably lead[49]) from soils, dusts and air filters, and this may offer possibilities in the development of field-portable equipment. Also, UE in dilute acid mixtures may prove to be useful for screening measurements by atomic spectrometric (and other) analytical methods. Dilute basic buffers may be used to extract hexavalent chromium from environmental and industrial hygiene samples, and this offers a simple preparation method for the subsequent determination of this species by atomic spectrometry. The use of concentrated acids for multi-element ultrasonic dissolution from bulk materials is enhanced with heating. However, UE with concentrated acids without deliberate heating appears to be effective for multi-element dissolution from industrial hygiene air filter samples. Sonication with HF is necessary if it is desired to extract elemental species from otherwise insoluble silicate materials.

Other aspects of ultrasonic treatment for metals analysis, *e.g.*, on-line[4,50] or sequential[51] sonication, as well as ultrasonic slurry sampling,[52] have not been covered here but are mentioned as additional pertinent strategies for ultrasonic sample preparation in metals determination. The use of UE in concert with other extraction techniques has been recognized to be an effective treatment for the dissolution of target elements in many cases.[51,53] It is hypothesized that UE may see wider use for analytical purposes (*e.g.*, in atomic spectrometric analysis) in the future, owing to the simplicity, speed, safety and performance attributes of this sample preparation technique.

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