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Ultrasound assisted pseudo-digestion of street dust samples prior to determination by atomic absorption spectrometry

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Abstract

A sample preparation method based on ultrasound assisted pseudo-digestion of Pb, Cu, Zn and Ni from street dust samples under ultrasonic effect has been described. Parameters influencing pseudo-digestion, such as sonication time, sample mass, particle size and solvent system were fully optimized. Final solutions obtained upon sonication were analyzed by atomic absorption spectrometry. The best conditions for metal pseudo-digestion were as follows: a 25 min sonication time, a 0.3 g sample mass (in 25 ml solvent), a particle size <63 μm and a mixture of concentrated HNO_3–$HClO_4$–HF (2:1:1, v/v/v). Analytical results for the four metals by ultrasound assisted pseudo-digestion, acid bomb and conventional wet digestion methods showed a good agreement, thus indicating the possibility of using mild conditions for sample preparation instead of intensive treatments inherent with the digestion methods. In addition, this method reduces the time required for all treatments (pseudo-digestion or digestion, heating to dryness, cooling and separation) with acid bomb and conventional wet digestion methods approximately from 9 to 1 h. The accuracy of the method was tested either by comparing obtained results with those of acid bomb and conventional wet digestion methods or by application on two standard reference materials. The average relative standard deviation of ultrasound assisted pseudo-digestion method varied between 0.9 and 1.8% for $N = 12$, depending on the analyte.

Keywords: Sample preparation; Ultrasound; Street dust; Pseudo-digestion; Metals; AAS

1. Introduction

Data about the concentration of the metals in fly ash, soil, plant, sediment, street dust, natural waters and snow give information about the pollution degree of the environment and allow us to know the availability, mobility and chemical behaviour of these metals [1–11].

The determination of metals in complex samples by atomic absorption spectrometry (AAS) generally requires the destruction of the sample matrix to render a solution of the analyte ready for analysis. To obtain a solution suitable for AAS analysis of, for instance, biological, environmental and geological samples, conventional wet acid digestion procedures entail tedious and time-consuming manipulations which involve the use of mixtures of corrosive and sometimes explosive acids and long heating periods [12–14]. Sample digestion techniques, such as microwave, acid bomb (ABM) and conventional wet acid (CM) for total heavy metal determination have been used widely for the dissolution of target elemental analytes [12–17]. Such digestion techniques require the use of concentrated acids and high temperatures, and often high pressures, to affect the total dissolution of elemental analytes from solid samples [18]. For elemental analysis, the sample preparation procedure employed is, apart from sample collection, ordinarily the most time-consuming step in the overall analysis [19].

The efficiency of the wet digestion procedures can be enhanced with the use of ultrasound irradiation [19–21]. Ultrasonic radiation can be considered another alternative for solid sample pre-treatment since ultrasound facilitates an auxiliary energy and accelerates some steps, such as dissolution, fu-

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sion and leaching, among others [20–25]. It has been reported that ultrasonic leaching method gives high recoveries of organics from sediment [26], fly ash [27], biological materials [28], and elements from atmospheric particulate [29], sediments [30–33], soils [22,34], plants [35–40] and ores [41,42] in a much shorter time than is required for other extraction procedures. In many situations, ultrasound assisted leaching is an expeditious, inexpensive and efficient alternative to conventional extraction techniques and, in some cases, even to supercritical fluid and microwave-assisted extraction, as demonstrated by application to both organic and inorganic analytes in a wide variety of samples [22,35,43–48].

The aim of this work was to improve sample preparation performance, proposing the development of an ultrasound assisted pseudo-digestion method (UPM) for fast and reproducible recovery of some heavy metals in street dust samples, for total heavy metal determination. Parameters influencing ultrasound assisted pseudo-digestion, such as sonication time, sample mass, particle size and solvent systems are fully investigated. Heavy metal determination in the final solutions is carried out by flame AAS, the results being compared with those obtained by ABM and CM.

2. Experimental

2.1. Materials and reagents

Street dust samples were collected from high, medium and light density traffic roads (>700, 500 ± 200 and 200 ± 100 vehicles/h, respectively) and an industrial area in Sivas city, Turkey (Sivas district, co-ordinates 40°N, 37°E), and used as the matrix to carry out the optimization study. The dusts were sampled directly by gently sweeping of about 2 m^2 area from street surface and were transferred to a polyethylene container. Once in the laboratory, the samples were dried in an air-oven at 110 °C for 24 h, then ground with an agate mortar. Then, the samples were sieved in order to separate the material into different fractions: <63, 63–151 and 151–212 μm. The selected street dust samples were homogenized and stored in polyethylene vessels at room temperature in desiccators until digestion or pseudo-digestion.

Accuracy was also evaluated using two standard reference materials: vehicle exhaust particulates CRM-8 and pond sediment CRM-2 from NIES (National Institute for Environmental Studies, Japan). These reference materials were prepared according to the instructions provided by producer. The all materials were dried in air-oven at 110 °C for 4 h before use.

All reagents used were of analytical reagent-grade. Nitric, hydrochloric, perchloric and hydrofluoric acids were spectroscopic grades (Merck, Darmstadt, Germany) and de-ionized distilled water was used throughout the work. All glassware and plastic ware used were washed with 5% (v/v) nitric acid and rinsed with de-ionized distilled water. Stock standard solutions for Pb, Cu, Zn and Ni (1000 $\mu g\,ml^{-1}$) were made by dissolving the nitrate salts (Merck) in 2% (v/v) nitric acid. Calibration standards of each metal were obtained by suitable dilution of the stock solutions.

2.2. Instrumentation

Ultrasound assisted pseudo-digestion experiments were carried out with an ultrasonic bath (Ney 300, USA), which produced a nominal frequency of 50–60 kHz. An acid digestion bomb (Parr-4749, USA), which consists of a Teflon PTFE (polytetrafluoroethylene) vessel of 23 ml capacity and a stainless steel jacket, and a hot-plate were used for a complete dissolution of the sample. The sieving of dried dust samples was performed with an Endecotts (Octagon-200, London, UK) shaker including suitable sieves. The separation of the final solution from the solid residue at end of each pseudo-digestion was accomplished by centrifugation at 5000 rpm for 10 min with a laboratory-built centrifuge (Mistrial 2000, UK).

For determination of Pb, Cu, Zn and Ni, a UNICAM Model 929 flame AAS, functioning with air/acetylene burner equipped with a deuterium lamp background-correction system (Cambridge, UK), was used throughout this work. Hallow cathode lamps (Unicam, CT, UK) of the different metals were used as the radiation sources and the analytical measurements based on time-averaged absorbance. Resonance lines at 324.8, 217.0, 232.0 and 213.9 nm were employed for Cu, Pb, Ni and Zn, respectively. Lamp intensity (4–6 mA) and band pass (0.2–0.5 nm) were used according to the manufacturer's recommendations. Air/acetylene flow rates were between 0.9 and 1.1 $l\,min^{-1}$ for all metals.

2.3. Procedures

2.3.1. Ultrasound assisted pseudo-digestion method (UPM)

For pseudo-digestion optimization, different solvent systems [concentrated HNO_3, HCl, a mixture of concentrated HNO_3–HCl (1:3, v/v) and HNO_3–$HClO_4$–HF (2:1:1, v/v/v)], sample mass (0.1, 0.2, 0.3, 0.5 and 1.0 g, for 25 ml solvent) and sonication times (10, 15, 25 and 45 min) were tested. A study related to particle size was also performed by varying the particles from <63 to 212 μm. To evaluate the efficiency of the process, the results obtained with the UPM were compared with those from ABM and CM.

A portion (0.3 g ± 0.1 mg) of sample was weighed in to polypropylene beakers (50 ml capacity) and 25 ml of concentrated acid or a mixture of acids were added. Then, the sample was sonicated for 20 min. After sonication, the supernatant liquid was evaporated to approximately 0.5 ml final volume on a heating plate. Final solution was made up to 10 ml with 2% HNO_3 and subjected to sonication for another 5 min. Then, the solutions were centrifuged at 5000 rpm for 10 min, and the final volume was made up to 25 ml with 2% HNO_3. The final solutions were collected in polyethylene flask for AAS determinations of metals. Blanks were also treated in the same way.

2.3.2. *Conventional digestion method (CM)*

The 0.3 g ± 0.1 mg of each dried street dust sample was placed into a clean 100 ml PTFE beaker. A 50 ml volume of a freshly prepared mixture of concentrated HNO_3–$HClO_4$–HF (2:1:1, v/v/v) was added to each beaker and solutions were evaporated to approximately 0.5 ml final volume on a heating plate (∼8 h) [9]. Final solutions were made up to10 ml with 2% HNO_3 and centrifuged at 5000 rpm for 10 min. The final volume was made up to 25 ml with 2% HNO_3, for AAS determinations of metals. Blank digestions were also carried out.

2.3.3. *Acid digestion bomb method (ABM)*

The 0.3 g ± 0.1 mg sample, 5 ml each of concentrated HNO_3 and HF were placed into PTFE beaker. The bomb was closed and heated in an air-oven at 90 °C for 2 h and then increase the temperature to 140 °C and holds it for 4 h at temperature [15]. After cooling the bomb overnight, open the stainless steel cap carefully and residual solutions were evaporated to 0.5 ml final volume on a heating plate. Final solutions were made up to 10 ml with 2% HNO_3 and centrifuged. The final volume was made up to 25 ml with 2% HNO_3, for AAS determinations of metals. Blanks were treated in the same way.

2.4. *Analytical determinations*

Three sub-samples of each street dust sample were used for analytical determinations with the digestion and pseudo-digestion procedures. With each series of digestions and pseudo-digestion, a blank was measured. Each result is the average four readings for sample solutions and standard solutions. The concentrations were obtained directly from calibration graphs after correction of the absorbance for the signal from an appropriate reagent blank. In most cases, the blanks constituted only a small fraction (<1%) of the metal concentration in the samples.

3. Results and discussion

3.1. *Optimization of the UPM*

The street dust samples (from high density traffic roads) were used for optimization purposes. Each result was the average value of three determinations performed in separate batches. Variables influencing the pseudo-digestion process were optimized within the intervals shown in Table 1.

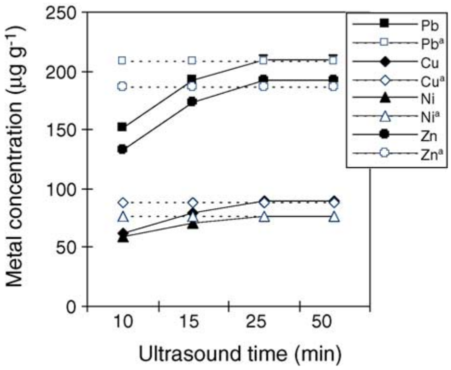

Fig. 1. Comparison of UPM rate curves and recoveries at recommended times with CM for metals in street dust samples, a: CM.

3.1.1. *Sonication time optimization*

The ultrasonic assisted pseudo-digestion rate curves with UPM and the recoveries at recommended times with CM for metals in street dust samples were compared in Fig. 1. While there were some variations in pseudo-digestion time from metal to metal, the UPM required maximum 25 min to reach the same recoveries given for each metal by CM. For the metals, pseudo-digestion efficiency increased with increasing sonication time from 10 to 25 min. There was no significant difference between 25 and 50 min sonication periods for all metals at 0.05 probability but was 15 and 25 min. The results show that 25 min exposure time is enough for metals from the studied samples.

3.1.2. *Sample mass optimization*

In this work, the 0.1–1.0 g mass interval was investigated for 25 ml solvent volume. Sample amount used largely depends on the procedure followed. A sample mass of up to 0.5 g has been reported in the work with an ultrasonic bath for leaching [30,34,49,50]. As can be seen in Fig. 2, a significant decrease in metal recovery from street dust samples is obtained when the sample mass is larger than 0.5 g. There was significant difference between 0.5 and 1.0 g sample mass for all metals at 0.05 probability. The street dust mass/solvent volume ratio appears to be an important parameter for metals which pseudo-digestion efficiency is affected by the solvent volume. In this work, sample mass/solvent volume ratio was chosen as 0.3 g/25 ml.

Table 1

Operating conditions for ultrasound assisted pseudo-digestion of Pb, Cu, Zn and Ni from street dust samples

Variable	Studied interval	Best conditions
Sonication time (min)	10–50	25
Sample mass (g)	0.1–1.0	0.3
Particle size (µm)	<63–212	<63
Solvent systems (concentrated)	HNO_3, HCl, HNO_3–HCl, HNO_3–$HClO_4$–HF	HNO_3–$HClO_4$–HF

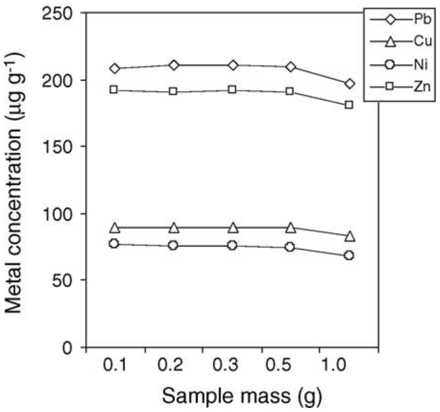

Fig. 2. Effect of the sample mass on the metal recovery from acid solvent with UPM.

3.1.3. Particle size optimization

Particle size was among the more critical parameters influencing ultrasound assisted pseudo-digestion. As was to be expected, reactions were enhanced on increasing the contact surface. The particle size attempted for metal pseudo-digestion in this work with the use of ultrasonic bath ranged from >63 to 212 µm. The results obtained in this study are shown in Fig. 3. As can be observed, pseudo-digestion efficiency decreased when the particle size was larger than 63 µm for the metals. There was no significant difference between 63–151 and 151–212 µm particle sizes for all metals at 0.05 probability but was <63 and 63–151 µm. In this way, the <63 µm particle size was chosen for evaluation of the accuracy.

3.1.4. Influence of solvent systems

The influence of solvent systems, such as concentrated HCl, HNO_3, a mixture of HCl–HNO_3 and a mixture of HNO_3–$HClO_4$–HF was studied in a univariate way by fixing the other variables at their optimal values. Different acid mixtures, such as 15% HNO_3–1% HCl (1:1, m/m) [51], 25% HNO_3–HCl (1:1, v/v) [18] and concentrated HNO_3–HCl (1:1, v/v) [18,49] were reported to be used as solvents for leaching of metals. HF is used in extractions the dissolution of metal species that are bound up in silicate materials and that would otherwise be insoluble, even in other acid solutions [18,52]. The effectiveness of mixtures of concentrated HF and other acids, such as HNO_3, $HClO_4$ and HCl for the ultrasonic leaching of target metals, followed by atomic spectrometric analysis, has been demonstrated previously for bulk certified reference materials, such as sediments, soils and fly ash [52]. The pseudo-digestion results obtained with the use of a single acid or acid mixtures are shown in Fig. 4. It can be seen that high recoveries with UPM in concentrated HNO_3–$HClO_4$–HF mixture are obtained for metals, although there are some differences in recovery depending on the analyte. But, the recoveries with in a mixture of concentrated HNO_3–$HClO_4$–HF are in good agreement with the results found for a mixture of concentrated HNO_3–HCl. The pseudo-digestion results obtained with the use of a mixture of HNO_3–$HClO_4$–HF and a mixture of HNO_3–HCl revealed that there is no significant difference between both solvent systems at 0.05 probability. Therefore, it can be said that street dust samples are not in silicate matrix structure or silicate structure at the level that can be neglible. It is also clear that HNO_3 gives less metal leaching than HCl.

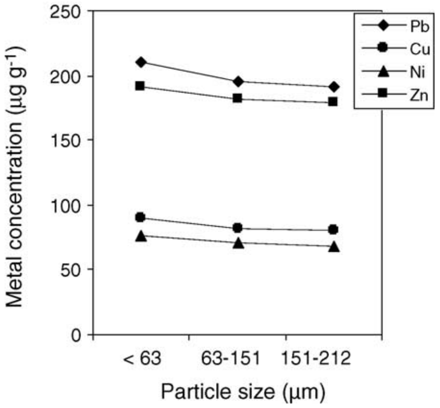

Fig. 3. Effect of the particle size on the metal recovery from acid solvent with UPM.

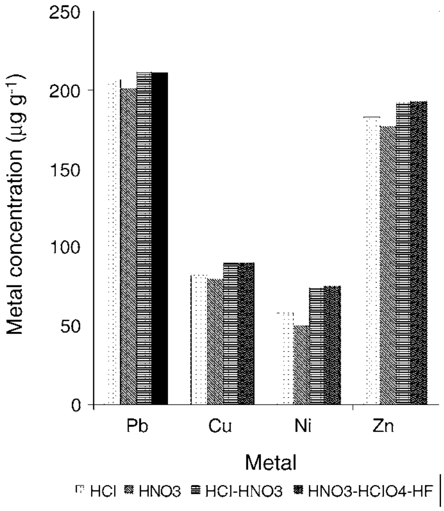

Fig. 4. The effect of solvent system on the ultrasonic assisted pseudo-digestion of metals from street dust samples.

3.2. Analytical results using UPM, ABM and CM

3.2.1. Calibration and validation

The detection and quantification limits, given by limits of detection (LOD) = 3(*s*/*m*), and limits of quantification (LOQ) = 10(*s*/*m*), respectively, where *s* is the standard deviation of 10 measurements of a reagent blank, and *m* the slope of the calibration graph, were calculated for flame AAS determinations. LODs for the UPM were 1.62, 4.11, 2.97 and 0.62 $\mu g\,g^{-1}$ for Cu, Pb, Ni and Zn, respectively, being similar to those attained with CM and ABM when a 0.3 g sample mass was used for digestion. LOQs were 5.4, 13.7, 9.9 and 2.1 $\mu g\,g^{-1}$ for Cu, Pb, Ni and Zn, respectively. The equation

Table 2
Validation of the UPM against the certified reference materials

Metal	NIES CRM-2 ($\mu g\, g^{-1}$)			NIES CRM-8 ($\mu g\, g^{-1}$)		
	Certified value	UPM[a]	Relative error (%)	Certified value	UPM[a]	Relative error (%)
Pb	105 ± 6	102 ± 3	−2.9	219 ± 9	211 ± 6	−3.7
Cu	210 ± 12	213 ± 7	+1.4	67 ± 3	64 ± 3	−4.5
Ni	40 ± 3	38 ± 1	−5.0	18.5 ± 1.5	17.8 ± 0.8	−3.8
Zn	343 ± 17	332 ± 13	−3.2	1040 ± 50	1052 ± 21	+1.2

[a] Average value ± standard deviation ($N = 3$).

for the linear range of the calibration graphs for all metals was found as:

$$\text{Absorbance} = 2(\pm 1) \times 10^{-3} + 0.043 \pm 0.032[X],$$
$$X = 0\text{–}7\,\text{mg}\,\text{L}^{-1}, \quad r = 0.9999.$$

A suitable international standard reference material could not be obtained to test the acceptability of the proposed UPM. But, the accuracy of UPM for the proposed method under the optimized pseudo-digestion conditions was determined by comparing the results with those obtained using different digestion methods (CM and ABM) for all street dust samples, as well as by analyzing different NIES materials, such as vehicle exhaust particulates (CRM-8) and pond sediment (CRM-2). Validation of the UPM is shown in Table 2. A good agreement between the found and certified metal contents can be observed for the all metals studied. The results, presented in Table 2, show that no statistical differences were observed at 0.05 probability, indicating that the UPM is applicable for this type of sample, opening the possibility of its application for other samples. UPM provided (+1.4 to −5.0%) relative error and 0.7–4.7% ($N = 3$) R.S.D. (%), depending on the analyte and sample, which are acceptable ranges for this kind of studies.

Analytical results obtained by UPM, ABM and CM corresponding to the street dust samples analyzed are shown in Table 3. Average recoveries were 100 ± 1, 99 ± 2, 101 ± 1 and 98 ± 1% for Pb, Cu, Zn and Ni, respectively, thus indicating that there was a good agreement either between UPM and ABM or UPM and CM. When the average heavy metal values were compared using a significance statistical test [53] it was concluded that there is no difference for the UPM and CM at 0.05 probability. The main differences among the three methods lie in the time required to complete the digestion or leaching. In precision test, the average relative standard deviation (R.S.D.) ($N = 12$) values for all metals varied in the range of 0.9–1.8, 2.1–2.6 and 1.7–2.4% for UPM, CM and ABM, respectively. R.S.D.s were calculated from pooled data for method [53]. The precision obtained from 12 replicate UPM yielded an average R.S.D. of 0.90, 1.81, 1.76 and 1.80% for Pb, Cu, Zn and Ni, respectively, depending on the analyte. Besides, the precision of the UPM was better than ABM and CM.

An internal standard method was used on both methods (UPM and CM) to verify the leaching recovery of metals. A street dust sample was spiked with a known concentration of each metal before the digestion process by the two methods was carried out (Table 4). The results show that the recovery

Table 3
Analytical results for metals as determined by UPM, ABM and CM

Metal	Method	Metal concentration at the street dust samples ($\mu g\, g^{-1}$)[a]				
		Heavy traffic[b]	Medium traffic[b]	Light traffic[b]	Industry (light traffic)[b]	Average recovery (%)
Pb	UPM	211 ± 2	129 ± 1	74.3 ± 0.5	172 ± 2	
	CM	208 ± 5	129 ± 4	75 ± 2	172 ± 4	
	ABM	209 ± 3	128 ± 3	73.7 ± 0.8	171 ± 5	
	UPM/CM × 100	102	100	99	100	100 ± 1
Cu	UPM	90.1 ± 0.7	70 ± 1	46 ± 1	100 ± 3	
	CM	897 ± 2	71.2 ± 0.9	48 ± 2	102 ± 3	
	ABM	93 ± 2	70 ± 2	46 ± 1	99 ± 2	
	UPM/CMx100	102	98	98	98	99 ± 2
Ni	UPM	76.6 ± 0.8	60 ± 1	35.8 ± 0.6	70 ± 2	
	CM	77 ± 1	61 ± 2	36.6 ± 0.8	72 ± 2	
	ABM	76 ± 1	60.0 ± 0.9	36.1 ± 0.6	70 ± 2	
	UPM/CMx100	99	98	97	98	98 ± 1
Zn	UPM	189 ± 3	164 ± 3	94 ± 1	197 ± 4	
	CM	187 ± 4	161 ± 3	93 ± 3	197 ± 4	
	ABM	187 ± 3	1617 ± 4	93 ± 4	196 ± 3	
	UPM/CMx100	101	102	100	100	101 ± 1

[a] Average value ± standard deviation ($N = 3$).
[b] The sampling sites according to traffic density.

Table 4
Recovery of metals by UPM and CM using an internal standard method

Metal	Original ($\mu g\,g^{-1}$)[a]		Added ($\mu g\,g^{-1}$)[a]	Found ($\mu g\,g^{-1}$)[a]	
	UPM	CM		UPM	CM
Pb	211 ± 2	208 ± 5	70.4	282 ± 4	279 ± 4
Cu	90.1 ± 0.7	89 ± 2	50.6	142 ± 2	141 ± 3
Ni	76.6 ± 0.8	77 ± 1	50.6	126 ± 2	127 ± 2
Zn	189 ± 3	187 ± 4	70.4	260 ± 3	258 ± 4

[a] Average value ± standard deviation ($N = 3$).

is quantitative for each metal and there are no interaction effects between the elements.

4. Conclusion

The method described offers a rapid, easy and efficient sample preparation for direct determination of Pb, Cu, Ni and Zn in street dust samples by FAAS. All parameters studied (sonication time, sample mass, particle size and solvent system) influence the pseudo-digestion efficiency. Under optimum conditions, quantitative recoveries for all metals are reached, and the results obtained are comparable to the obtained ones by means of classical sample pre-treatment based on acid digestion.

The use of the UPM allowed the leaching of the target analyte in a shorter time than required by the ABM and CM that were providing similar results. This method reduces the time required for all treatments (pseudo-digestion or digestion, heating to dryness, cooling and separation) with ABM and CM from approximately 9 to 1 h.

It is clear that the UPM is a rapid, inexpensive, easy, reproducible and selective technique for the total determination of Pb, Cu, Ni and Zn in street dust samples which are important in monitoring environmental pollution.

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