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SPECIAL ISSUE PAPER

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Comparison of microwave-assisted extraction and waste extraction test (WET) preparation for inductively coupled plasma spectroscopic analyses of waste samples

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Abstract The Waste Extraction Test (WET) is used in California as a complement to the Toxicity Characteristic Leaching Procedure (TCLP). The WET protocol consists of shaking a sample with citrate buffer and determining the metal content in the solution produced. This procedure requires a 1-to-10 waste-to-liquid ratio and 48 h for extraction. Although the WET protocol proves to be very useful, it is a time-consuming step in the determination of leaching and mobility. Therefore, a microwave extraction procedure was optimized to emulate the relative extraction efficiency obtained by the WET protocol. Lead, arsenic, and copper concentrations were measured by inductively coupled plasma mass or atomic spectrometry (ICP-MS or ICP-AES), following a strict quality assurance protocol. Results obtained with this new methodology were statistically comparable to those obtained by the WET protocol. This microwave extraction approach proved simple and fast, reducing sample treatment by almost 280%. A significant reduction also occurs in waste production, materials, labor, and chemical usage. Therefore, the microwave extraction procedure is recommended as a rapid and cost effective monitoring tool for waste samples when combined with or supplemented by the traditional WET protocol.

Keywords Microwave-assisted extraction · Waste extraction test (WET) · Inductively coupled plasma spectroscopic analyses · Waste

Introduction

Leaching protocols used for the analysis of metals in soil, wastes, and other solid materials give an indication of metal release and mobility. This information is needed to protect human health and environment. Traditionally, leachants such as synthetic acid rain or deionized water are use to evaluate the metal leachability of a sample [1, 2]. Among the batch leaching protocols, the Toxicity Characteristic Leaching Procedure (TCLP) has been widely adopted by the US Environmental Protection Agency to evaluate the release of contaminants from wastes. The TCLP utilizes acetic acid as leachant, since it was developed to predict the potential for mobility under rigorous environmental conditions, in an actively decomposing landfill, where carboxylic acids, such as acetic acid, are generated [3]. However, it has been reported that this protocol fails in predicting extraction of elements from some alkaline wastes [4].

California also has adopted the Solute Threshold Limit Concentration (STLC) to identify wastes that may contaminate groundwater. When a target analyte exceed the STLC limit (e.g., As 5 ppm, Pb 5 ppm, and Cu 25 ppm), the waste is classified as hazardous. The STLC analysis determines the amount of each analyte that is soluble in the California “Waste Extraction Test” (WET) leachate. The main difference between the TCLP and the WET protocol are the anion used as leachant. While acetate is used for TCLP, citrate is used for WET. The citrate is a trident ligand that forms chelates with free metal ions in solution. The metal chelates are more stable than the complexes/ion pairs with mono-dentated ligands, such as those formed with acetate. Therefore, the WET procedure is a more aggressive test to evaluate leachability [1, 3].

The WET procedure requires a 1-to-10 waste-to-liquid ratio and 48 h for extraction. Although the WET protocol proves to be very useful, it represents a lengthy step in the determination of leaching and mobility. Therefore, in this work we propose substituting microwave extraction for the mechanical shaking extraction.

Microwave energy has been widely used in analytical chemistry as a tool for sample treatment. A large number of total or partial digestion methodologies, generally with mineral acids, using microwave heating have been created to replace traditional methods, because the use of microwave systems accelerates chemical procedures. Microwave

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energy has also found applications for extraction procedures generally using mineral acids such as nitric acid [5] or aqua regia for soil samples [6]. Determination of mobility of metals in soils has also been tested using microwave energy. The approach produced results appropriate for the assessment of environmental risk and reducing sample treatment time from 20 h to 2 h [7, 8, 9].

In this work a commercial microwave system is explored as an alternative to traditional shaking in the WET protocol to speed up the metal extraction by citric acid from waste samples. Operational parameters such as power, temperature, and time were optimized to emulate the efficiency obtained by the WET protocol. Lead, arsenic, and copper were determined by ICP-MS or ICP-AES. Other factors such as buffer concentration and sample weight also were evaluated. Results obtained by microwave heating methodology were statistically compared to those obtained by the WET protocol.

Experimental

Instrumentation. All samples were extracted in a commercial microwave sample preparation system (MDS 2000, CEM Corporation, Matthews, NC, USA) supplied with a power range from 0 to 100% (630 W). The control software allows setting the microwave power, extraction time, and maximum reaction temperature reached. The CEM microwave system is equipped with a Thermo-Optic temperature control and a high throughput accessory (CEM High Throughput Vessel set, DV-50 turntable, DV-50 Thermowell). The high-throughput turntable can hold 52 (50-ml) polypropylene centrifuge tubes simultaneously. The centrifuge tube cap has a small hole to allow venting and pressure equalization. Extractions take place at atmospheric pressure. Temperature was monitored with a temperature probe in a Thermowell placed in a control vessel (usually the vessel with the largest sample amount). New centrifuge tubes were used without further treatment for each extraction; the lids were cleaned with soap and then soaked in 10% HNO_3 overnight.

Table 1 ICP-MS instrumental and operational parameters for Pb, As, and Cu determinations

TICP system	Elan 5000a
Rf Power (kW)	1.0
ICP torch	Fassel type
Torch injector	Ceramic alumina
Outer argon flow rate (L/min)	14.8
Intermediate argon flow rate (L/min)	1.0
Central argon flow rate (L/min)	1.0
Sample pump rate (ml/min)	1.0
Nebulizer	Gem Tip Cross Flow
Spray chamber	Ryton Scott Double Pass
Resolution (amu at 10%)	0.8 (normal)
Scanning mode	Peak hop
Replicate time (ms)	250
Dwell time (ms)	250
Sweeps/reading	1
Readings/replicate	1
Number of replicates	25
Points per spectral peak	1
Spectral masses used	^{208}Pb, ^{75}As, ^{65}Cu

Table 2 ICP-AES instrumental and operational parameters for Pb, As and Cu determinations

ICP system	Spectro Ciros^{CCD}
ICP torch	Fixed Quartz Torch
Frequency (MHz)	27.12
Power (kW)	1.4
Viewing	Axial
Outer argon flow rate (L/min)	14.0
Auxiliary argon flow rate (L/min)	1.0
Sample pump rate (ml/min)	1.0
Nebulizer	Modified Lichte
Nebulizer flow (L/min)	1.0
Spray chamber	Cyclonic
Readings	3
Wavelengths (nm)	Pb 168.215 As 189.042 Cu 324.754

All solutions were analyzed using ICP-MS (Perkin-Elmer ELAN 5000a, Norwalk, CT, USA) or ICP-AES (Spectro Ciros^{CCD}, Spectro Analytical Instruments, Fitchburg, MA, USA). The instrumental operating parameters for the detection of Pb, As, and Cu are listed in Tables 1 and 2. A benchtop centrifuge (Fisher Scientific, Centrific Model 225, Pittsburgh, PA, USA; maximum: 5100 rpm/3400×G) was used to centrifuge the treated samples.

Reagents. Dilution and solutions were prepared with distilled deionized water (Barnstead NANO pure system, Sybron/Barnstead, Boston, MA USA). Nitric acid was purified by sub-boiling distillation in a quartz apparatus. A 5% nitric acid solution was prepared by direct dilution of sub-boiling nitric acid in double distilled water.

A 0.2 mol/L citric acid buffer at pH 5 was prepared by dissolving 38.4 g of citric acid (anhydrous powder, reagent grade, J.T. Baker, Phillisburg, NJ, USA) in water, adjusting the pH to 5 with NaOH (25% v/w, VWR, West Chester, PA, USA) and diluting to 1 L.

A multielement calibration standard, 100 μg/ml of As, Cu, and Pb (CALMIX7, SPEX, Metuchen, NJ, USA) was used to prepare calibration curves and study the effect of the microwave power on the recovery of a standard solution. Standards were prepared by direct dilution in 5% nitric acid solution, and adding 4% citric acid buffer.

Samples. Samples correspond to materials from several waste treatment plants. They were stored closed at room temperature and extracted without pretreatment. All samples were physically different; they ranged from powder to muddy-like materials. The extractable concentrations of Pb, As, and Cu in each sample, determined by using the traditional WET procedure, were supplied by the treatment plants that provided the samples.

Extraction procedure. A 1-g aliquot of sample was transferred to a 50-ml polypropylene centrifuge tube, and 10 ml of citrate buffer was added. The tube was closed with a vented cap, and swirled manually for 30 s to wet the entire sample. For each batch the temperature probe was placed in the centrifuge tube with the largest sample amount. The microwave controller automatically shuts down power when the temperature in this control vessel reaches a preset maximum. During this study the effect of microwave power, temperature, and time at that temperature were examined. The optimized extraction conditions found were a one-step program for 15 vessels with a power of 45%, lasting for 10 min, and at a maximum temperature of 100 °C.

After microwave treatment the samples were allowed to cool to room temperature. The sample tubes were centrifuged for 5 min at 4080 revolutions per minute (rpm). A 1-ml aliquot of the resulting solution (measured with an Eppendorf pipette with disposable tip) was transferred into a fresh, calibrated 50-ml polypropylene centrifuge tube, and the solutions were diluted to 25 ml with a 5% nitric acid solution. The concentrations of Pb, As, and Cu in this final solution were determined by ICP-MS or ICP-AES.

Quality assurance/control. A quality assurance protocol based on EPA SW 846 Method 6020 was implemented for the ICP-MS measurements to control analytical measurement errors. The ICP determination protocol included the following steps:

1. Precalibration routine is applied to maintain the optimum instrument response.
2. Initial calibration is used with multielement standards prepared in nitric acid and citrate buffer to emulate sample conditions.
3. Initial calibration verification is used with a standard mixture prepared as the samples by another analyst with different stock solutions.
4. Continuing calibration verification, every ten solutions, is applied to identify significant instrument drift during measurements.
5. After these steps blank and samples are measured.
6. Potential matrix interferences are evaluated by comparing sample concentrations obtained from an original solution and a fivefold diluted solution.
7. Several samples are analyzed a second time every day to identify any significant difference in instrumental performance.

Results and discussion

The Waste Extraction Test (WET) used to determine the amount of extractable substances in a sample requires shaking the sample in the citrate buffer solution for 48 h, while controlling the temperature to less than 40 °C. Since the objective of this work is to apply a microwave system to emulate as closely as possible the traditional WET protocol, while increasing the extraction speed, a high-throughput, open-vessel system was employed. This commercial High Throughput Accessory allows treating of up to 52 disposable centrifuge tubes simultaneously per run. Thus, the use of this system can accelerate treatment, reduce total analysis time, and increase capacity. To compare both procedures relative extraction efficiency was defined as the ratio of the concentrations obtained by the microwave extraction and the WET protocol. Concentrations obtained by the WET protocol were provided by the treatment plants that supplied the samples.

Preliminary studies

Centrifuge tubes tests

One of the initial concerns during this study was the interaction of the citrate solution (containing the elements of interest Pb, As, and Cu), with the polypropylene centrifuge tube, since no information was available. Therefore, a multielement standard was spiked into the citrate buffer to produce a 2.5 mg/L solution of Pb, As, and Cu. This solution was treated in the microwave as a sample, and the resulting solution was diluted 25 times with 5% nitric acid solution. When recoveries were evaluated for different maximum temperatures (25, 40, 60, 80, and 100 °C), with 50% power and 5 min holding time (after reaching the desired temperature), recoveries averaged 103±5%, indicating neither analyte adsorption or desorption occurred with the polypropylene tube under microwave influence. Therefore, new polypropylene centrifuge tubes were used for the extractions. The vented caps were reused and were cleaned with soap and by soaking them overnight in a 10% HNO_3 acid bath.

Microwave extraction conditions optimization

Assuming that all the samples would behave similarly during the microwave extraction, sample *A* was chosen as the trial sample, because it was the largest. This sample was used to optimize the microwave parameters to produce 100% relative extraction efficiency. The parameters evaluated were the microwave power, the maximum extraction temperature, and the time at maximum temperature. Maximum of extraction was observed at 50% power (Fig. 1), even when it was larger than 100% for some elements. Although the three elements were extracted in different proportions, all behaved similarly with applied microwave power. The effect of maximum extraction temperature on the relative extraction efficiency was evaluated for seven samples. As illustrated in Fig. 2, the relative extraction efficiency increased with an increase of the maximum temperature for most samples and elements. The As relative extraction efficiency was influenced most by the extraction temperature. Results in Fig. 2 also demonstrate that all the samples behaved differently during microwave extraction. For instance, copper extraction for some samples was not efficient (samples *C*, *D*, *F*, *G*), while efficiency was around 100% for others. Sample *F* showed a decreasing extraction efficiency with an increase of extraction temperature. Standard additions and dilutions were performed to rule out measurement errors. Filtering through 0.45-μm filters and pregrinding samples were also evaluated without success to improve relative extraction efficiency for these samples. Holding times longer than 5 min did not improve the extraction efficiency significantly for all the samples used during this study.

These results demonstrated that samples behaved differently when extracted using microwave energy. Therefore, to evaluate seven test samples for all conditions, a simplex optimization procedure was designed. The parameters evaluated were power, maximum temperature, and holding time at maximum temperatures. The initial vertexes were taken based on the preliminary results, and subsequent vertexes conditions were calculated following the procedure from Miller and Miller [10]. The parameter optimized was the relative extraction efficiency. The target was to obtain extraction efficiencies between 85 and 115% for most elements and samples. For each vertex condition 15 vessels were used, and each sample was treated in duplicate, except for the muddiest sample *G*, which was treated in triplicate.

The simplex optimization progressed properly for some of the samples, but by the tenth experiment it became clear that a maximum for the optimum extraction

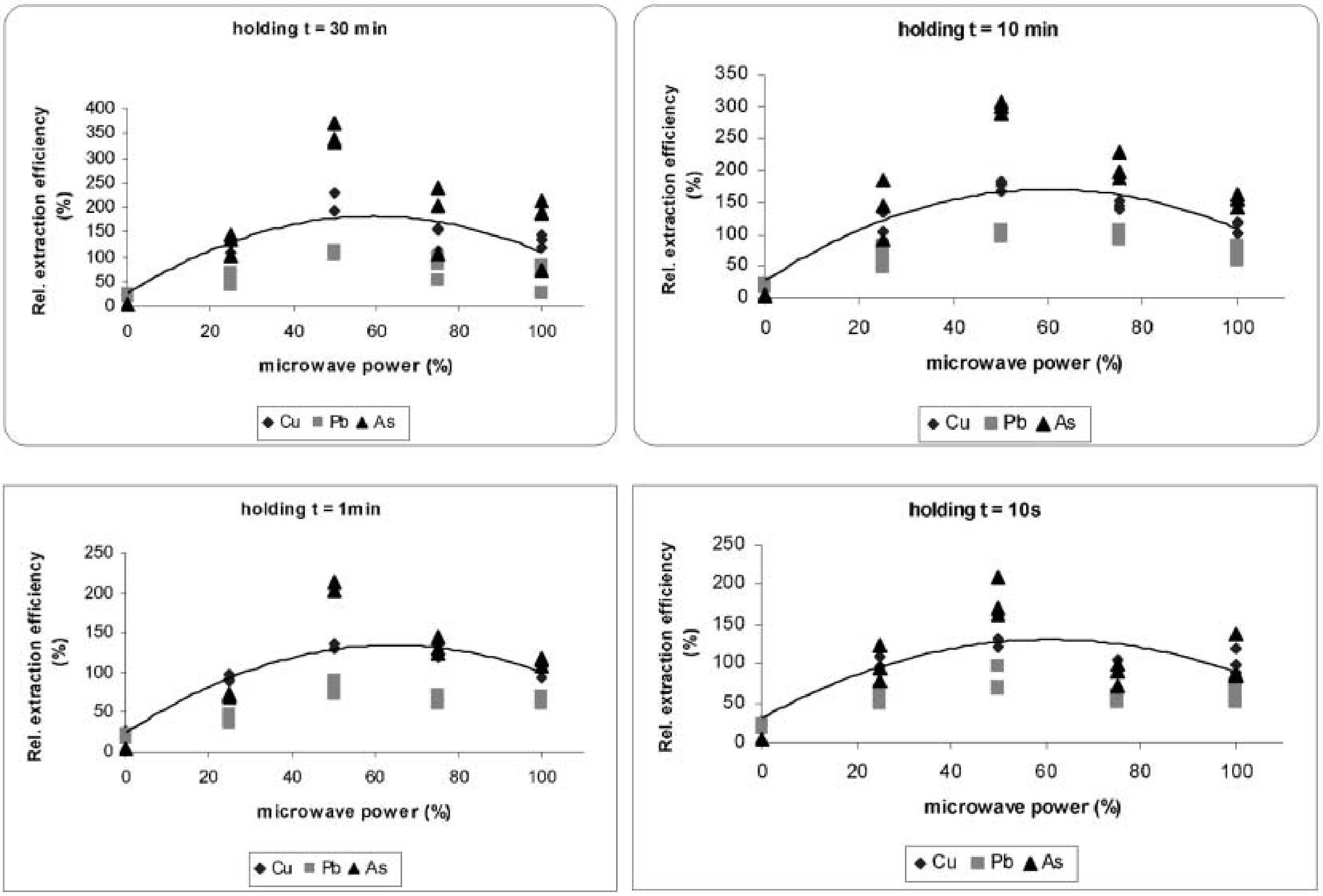

Fig. 1 Effect of microwave power on extraction efficiency for sample A and 10-s, 60-s, 600-s, 1800-s holding times at 85 °C. Microwave extraction compares with traditional shaking extraction

was different for different samples and sometimes for each element. This series of experiments pointed to a set of conditions optimal for most of the samples (i.e., 45% power, 85 °C maximum temperature, and 4 min holding time, for a total 10-min run), and these conditions were used for the remainder of the investigation.

Evaluation of the proposed microwave method

Throughout the previous study copper extraction from some samples was not efficient. Therefore several tests were designed to evaluate the relative extraction efficiency of Cu. The results indicated that the relative extraction efficiency was not significantly affected by buffer concentration (from 0.02 to 0.8 mol/L), sample mass (ranging from 1 to 5 g), or mass to buffer ratios (ranging from 1:1 to 1:50). Samples were also ground and the extraction solution was filtered through a 0.45-µm filter to eliminate potential physical effects resulting from particle size or suspended particles in the centrifuged solution. However, no significant differences were observed. These results indicated that the extraction procedure is promising and robust, although results, however very reproducible, were not always statistically similar to those reported by the treatment plants.

Because of these differences between our results and those reported, standard addition analyses were tested to rule out a possible matrix effect in the ICP-MS measurements. Additionally, ICP-MS results were compared to those obtained by ICP-AES. Both test showed that the solutions did not have a significant matrix effect that could explain the differences between the microwave and WET protocol results.

Comparison of microwave assisted extraction and WET protocol

The microwave extraction procedure accuracy was evaluated by determining Pb, As, and Cu in different sets of samples from different waste treatment plants. Since no certified reference material is available, only reported values obtained by traditional WET procedure in each treatment plant were compared. Fifty samples were evaluated in duplicates over a period of five months.

Lead extraction

An excellent correlation was found (Fig. 3a) when comparing lead extraction results by microwave with those re-

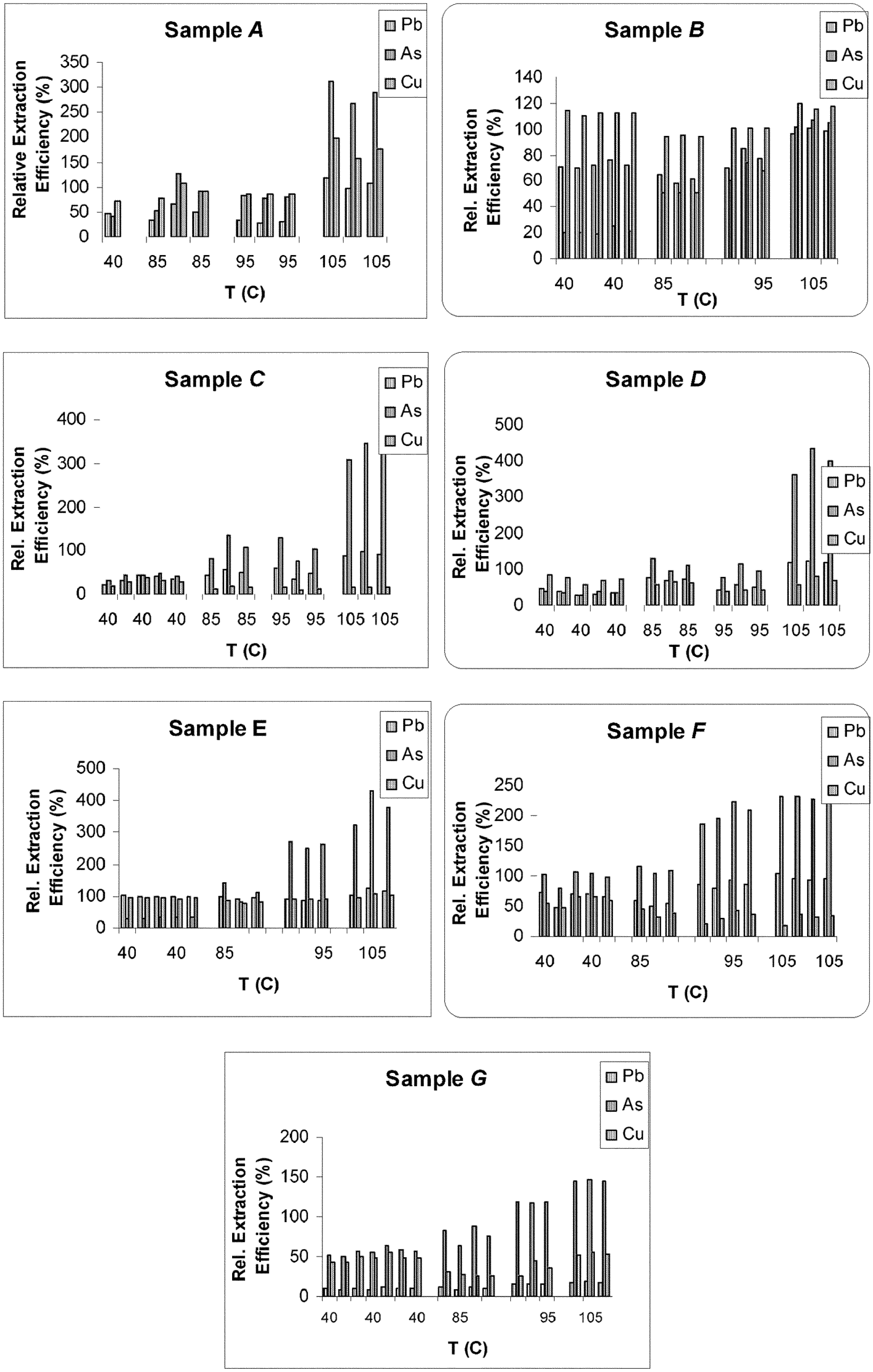

Fig. 2 Effect of maximum temperature reached during microwave extraction for seven samples. Microwave Power 75%, 30 min holding time at the set temperature

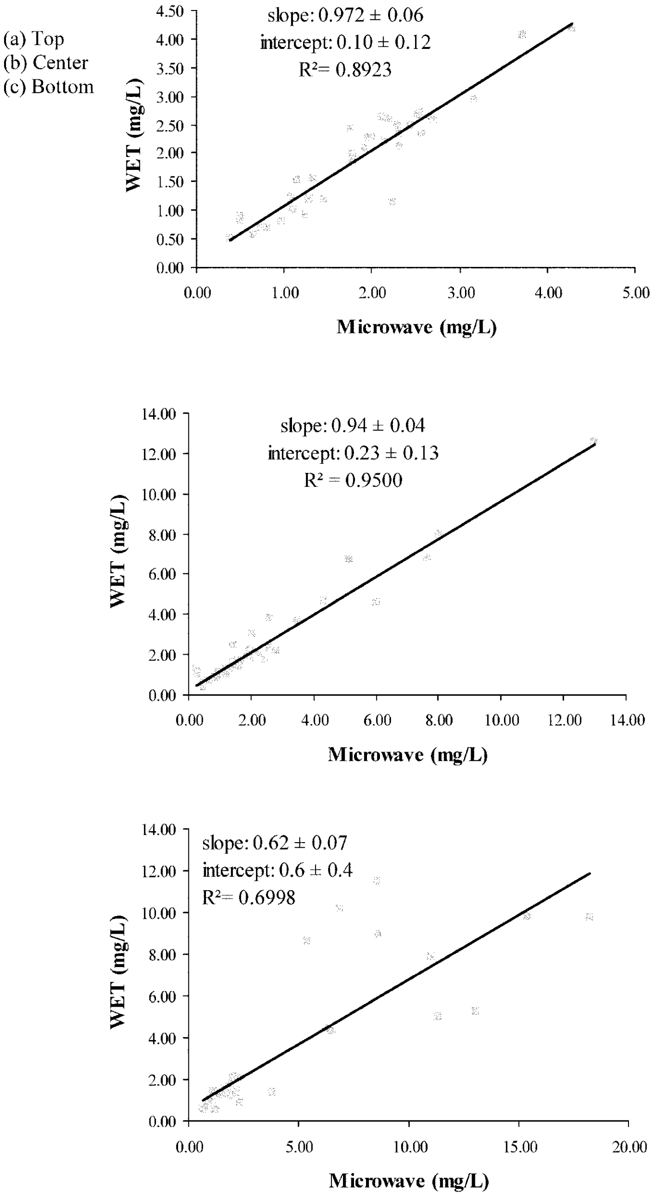

Fig. 3a–c Comparison of: **a** Pb; **b** Cu; **c** As extraction by microwave assisted extraction and Waste Extraction Test (WET) results

ported by the treatment plants by WET protocol. Extraction solution concentrations ranged from 0.01 to 5 mg/L, and Pb extraction was efficient in most cases (between 85 and 115% efficiency). This implies that the microwave extraction is highly reliable for Pb extraction when compared to the WET protocol, and similar STLC concentration limits for Pb may be applied.

Copper extraction

Copper microwave extraction results were comparable to the WET protocol for most samples, as demonstrated by the good correlation in Fig. 3b. However, when evaluating the data, copper extraction was low for a set of samples originating from the same source (such as sample *F)*. This phenomenon was found for all samples of the same origin, while As and Pb extractions were efficient for those samples. The results indicated that the relative extraction efficiency is very reproducible but was approximately 50% for this sample set. Previous investigations reported similar microwave power effects for Cu extraction [7, 8]. Perez-Cid et al. reported that Cu extraction was diminished with an increase of microwave extraction power (such as sample *F*, Fig. 2). They attribute this phenomenon to an irreversible readsorption process enhanced by microwave heating. Therefore, to apply the microwave protocol results deciding about the fate of these sample types, the copper STLC threshold should be reduced from 25 mg/L to 12.5 mg/L to account for 50% extraction efficiency, but only for samples from the unique source. No further studies were undertaken to identify unique properties of these samples leading to the low extraction efficiency.

Arsenic extraction

Upon evaluating arsenic results and comparing them with the WET protocol data, good correlation was obtained between both methods for samples with less than 4.5 mg As/L (Fig. 3c). However, for samples with As concentrations greater than 4.5 mg/L, the results were statistically different for many samples. In most of these cases As concentrations obtained by microwave extraction were higher, sometimes almost double those obtained by WET protocol. No measurement errors were identified, and these differences may be due to sample characteristics, even though no clear pattern or previous reports, as in the case for Cu, have been found. The reproducibility of these results indicate that the microwave protocol is as good as the WET protocol to identify samples with As content less than 4.5 mg/L. For samples with higher As content, the results by microwave may be larger, in general around 35% larger, than obtained by WET protocol for a significant fraction of the samples. These discrepancies may be due to the binding characteristics of the arsenic in the samples that might be possible to identify if the exact composition, characteristics, and history of the samples were known.

Based on these results, we recommend that when applying the microwave extraction protocol, the samples with As content larger than 6.75 mg/L (corresponding to the WET STLC threshold level of 5 mg/L As) should be reevaluated by using the traditional WET protocol to verify the exact As concentration.

Conclusions

This study demonstrates that microwave extraction with citrate buffer offers a statistically reliable alternative to the conventional WET procedure extraction for the use in analysis of solid waste samples. Application of microwave extraction reduces treatment time from 48 h (WET procedure) to 10 min, allowing the analysis of at least seven duplicate samples per run (as demonstrated in this work).

Employing minimal reagent chemicals is a promising characteristic of microwave extraction, since the extraction uses only 1 g of sample and 10 ml of extraction solution. Thus, a 50-fold reduction of chemical reagents and waste is achieved. This characteristic may also be a drawback for highly heterogeneous samples or samples with very low metal content, since the microwave system used in this work limits the sample size to less than 5 g. However, these limitations were not apparent for the 50 samples analyzed during the progress of this work.

Furthermore, the microwave conditions used do not require 100% of the microwave power. This allows future parameter adjustment for 52 extractions per batch.

Results show that Pb extraction by microwave is highly reliable. Copper extraction is also very reliable for specific source samples. However, for a group of samples originating from the same step of the waste treatment, microwave extraction yields consistently and systematically about half of the WET extraction result. Because this low copper relative extraction efficiency from those samples has been very reproducible, we propose that all samples from those sources will behave predictably the same. Therefore, we recommend that the copper STLC applied for these sample types be changed from 25 to 12.5 mg/L.

Arsenic has been a special case. Results indicate that by microwave extraction As results are usually 35% larger than reported by WET protocol over the range of concentrations examined, 0.6 to 11 mg/L As. Therefore, we recommend that the arsenic concentration STLC limit be changed to 6.75 mg/L when using this microwave extraction.

In general, the microwave extraction protocol using either ICP-MS or ICP-AES to determine the concentration of Pb, As, and Cu has proven to be simple and rapid, reducing sample treatment time almost 280%. The reduction in chemical usage and waste production, along with the replacement of sample filtering by centrifuging and the use of disposable centrifuge tubes, involves an important per sample processing cost reduction. Labor costs are also reduced. Therefore, the microwave extraction procedure is strongly recommended as a rapid and cost effective monitoring tool for samples from waste treatment plants, when combined with or supplemented by the traditional WET protocol.

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