

Atomic Absorption Determination of Metals in Superficial Roadside Soils Using Ultrasonic Sample Preparation

A. ELİK

*Department of Analytical Chemistry, Faculty of Art and Science,
University of Cumhuriyet, 58140-Sivas, Turkey
Fax: (90)(346)2191186; E-mail: elik@cumhuriyet.edu.tr*

A fast ultrasonic acid method for leaching of Pb, Mn and Ni from roadside superficial soil samples prior to determination by atomic absorption spectrometry in order to assess the pollution from motor vehicle exhaust has been examined and is shown to be beneficial in the recovery of these metals from surface soils. The best analytical conditions influencing leaching such as exposure time, acid type, acid concentration, sample amount and particle size were determined. A short exposure time (0.5 h), a mixture of concentrated HNO₃-HCl (4:1, v/v), a 0.5 g sample amount (in 25 mL solvent), a particle size < 63 µm were found to be best. Comparable results for the proposed ultrasonic leaching method and the hot-plate acid digestion method for metals in certified reference material and roadside soil samples are obtained, thus indicating the possibility of using mild conditions for sample preparation instead of intensive treatments inherent with the digestion methods. Besides, this method reduces the time required for all treatments with hot-plate digestion method approximately from 14 h to 1.5 h. The precision obtained from 12 replicate ultrasonic leaching method yielded an average RSD of 1.16, 1.73 and 1.34 % for Pb, Mn and Ni, respectively, depending on the analyte. The precision of the method, together with its efficiency, rapidity, matrix free and environmental acceptability, makes it a good alternative for the determination of trace metals in soil material.

Key Words: Sample preparation, Soil, Ultrasound, Leaching, Metals, Atomic absorption spectrometry.

INTRODUCTION

The metal contamination in soils and vegetation is derived in great amount from several anthropogenic activities such as industrial process emissions, vehicular exhausts and mining operations^{1,2}. In particular, lead, manganese and nickel, pollutants from motor vehicle exhaust, are known to cause carcinogenic, physiological and neurological harm to human and animal health^{3,4}. The concentration data of heavy metals in ashes, sediments, vegetation and soils may give information about the pollution degree of the environment and allow to know the availability, mobility and chemical behaviour of these elements.

Sample preparation techniques such as microwave, acid bomb digestion and hot-plate acid digestion have widely been used for the dissolution of target elemental analytes for their subsequent analytical determination and have become established standard methods for trace element dissolution from a large number of matrices prior to quantitative analysis⁵⁻⁷. Such digestion techniques require the use of concentrated mineral acids, high temperatures and high pressure, to affect the dissolution of elemental analytes from solid samples. For metal analysis, the sample preparation procedure employed is, apart from sample collection, ordinarily the most time-consuming step in the overall analysis⁷. Therefore, considerable interest has been expressed for shortened and simplified sample preparation procedures for elemental analysis⁷⁻¹⁰.

Ultrasound is a clean technique and could be used to increase chemical reaction rates which lead to sample dissolution¹¹. 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, fusion and leaching, among others¹²⁻¹⁶. It has been reported that ultrasonic leaching method (ULM) gives high recoveries of elements from sediments^{17,18}, plants¹⁹⁻²¹ and street dust²² in a much shorter time than is required for other extraction procedures. Similar results may therefore also be expected from the analysis of soil samples by ultrasonic leaching method. Ultrasonic leaching of metals from soils, although not yet sufficiently exploited, could be an attractive alternative to hot-plate, acid bomb and microwave digestion since apart from the time required for digestion, cooling of the reactors needs to be accomplished before opening^{6,17,23,24}.

In this work, parameters influencing ultrasound assisted leaching such as exposure time, acid type and concentration, sample amount and particle size are fully investigated. A fast ultrasonic leaching method is here proposed and validated as a good alternative for the leaching of metals from roadside superficial soil samples, for total metal determination. Flame atomic absorption spectrometry (FAAS) was used for quantification of the analytes after leaching, the results being compared with those obtained by hot-plate method (HPM).

EXPERIMENTAL

A UNICAM atomic absorption spectrophotometer Model 929 (Cambridge, UK), functioning with an air/acetylene burner equipped with a deuterium lamp background-correction system was used for metal determination. Hollow 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 217.0, 279.5 and 232.0 nm were employed for Pb, Mn and Ni, 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 0.9-1.1 L min⁻¹ for all metals.

A ultrasonic bath (NEY 300, USA) operating in the nominal frequency range 50-60 kHz was used for leaching the soil samples before analysis and hot-plate was used for a complete dissolution of the sample. The sieving of dried soil 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 leaching was accomplished by centrifugation at 5000 rpm for 10 min with a laboratory-built centrifuge (Mistrial 2000, UK).

All reagents used were of analytical reagent-grade (Merck). 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 prior to use. Stock standard solutions for Pb, Mn and Ni ($1000 \mu\text{g mL}^{-1}$) were made by dissolving the nitrate salts in 2 % v/v nitric acid. Calibration standards of each metal were obtained by suitable dilution of the stock solutions.

Roadside superficial soil samples (3 kg each) were collected from 1 m distance of high, medium and light density 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. 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, 151-212 and $> 212 \mu\text{m}$. The selected soil samples were homogenized and stored in polyethylene vessels at room temperature in desiccators until digestion or leaching. Accuracy was also evaluated using a standard reference material: pond sediment CRM-2 from NIES (National Institute for Environmental Studies, Japan). This reference material was prepared according to the instructions provided by producer. The all materials were dried in air-oven at 110°C for 4 h before use.

Procedures

Ultrasonic leaching method (ULM): For the best analytical conditions, exposure times (10, 20, 30, 45 and 60 min), acid type [concentrated HNO_3 , HCl , HClO_4 and a mixture of HNO_3 - HCl (4:1, v/v), acid concentration (2, 4, 7, 10 and 12 mol/L HCl), sample amounts (0.10, 0.25, 0.50 and 1.0 g, for 25 mL solvent) and particle size (from < 63 to $> 212 \mu\text{m}$) were tested. To evaluate the efficiency of the process, the results obtained with the ultrasonic leaching method were compared with those from hot plate method (HPM).

A portion ($0.50 \text{ g} \pm 0.1 \text{ mg}$) of soil 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 25 min. After sonication, the supernatant liquid was evaporated (*ca.* 1 h) 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.

Hot plate digestion method (HPM): The $0.50 \text{ g} \pm 0.1 \text{ mg}$ of each dried soil sample was placed into a clean 100 mL PTFE beaker, 5 mL of HNO_3 , 10 mL of HF then 10 mL of HClO_4 and 5 mL of HNO_3 were added sequentially after, each addition, complete dryness of the sample was achieved at 150°C . The digestion process took 14 h^{25} . The residue was made up to 10 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.

Analytical determinations: Each result of metal analysis for the leachates was expressed as the average of four readings, which ensured an error of $< 1\%$ of the relative standard deviation (RSD). Three sub-samples of each soil sample were used for analytical determinations with the digestion and leaching procedures. With each series of digestions and leaching a blank was measured. Calculations of metal contents in samples are based on a calibration graph obtained from aqueous standards.

RESULTS AND DISCUSSION

Optimization of the ultrasonic leaching method: The roadside superficial soil samples (from medium density traffic roads) were used for determination of the best analytical conditions. Each result was the average value of three determination performed in separate batches.

Ultrasonic exposure time: The influence of ultrasonic exposure time on metal leaching is shown in Table-1. For three metals, leaching efficiency increased with increasing exposure time from 10 to 20 min and from 20 to 30 min. The ultrasonic leaching method required maximum 30 min to reach the same recoveries given for each metal by hot plate method. There was no significant difference between 20 and 30 min sonication periods for all metals at 0.05 probability but was 30 and 45 min. According to the results, exposure time of 30 min was seen to be suitable for metal leaching.

TABLE-1
EFFECT OF ULTRASONIC EXPOSURE TIME ON THE LEACHING OF THE METALS ($\mu\text{g g}^{-1}$) FROM SOIL SAMPLES (WITH A MIXTURE OF $\text{HNO}_3\text{-HCl}$)

Metal	Exposure time (min)*					HPM*
	10	20	30	45	60	
Pb	73.8 \pm 1.2	81.3 \pm 1.2	85.1 \pm 0.9	85.2 \pm 1.3	84.9 \pm 1.0	82.9 \pm 1.9
Mn	491.7 \pm 9.2	583.2 \pm 9.4	622.4 \pm 7.9	619.7 \pm 10.2	624.3 \pm 8.6	624.1 \pm 13.4
Ni	61.0 \pm 1.3	78.4 \pm 1.4	81.7 \pm 1.1	82.1 \pm 0.9	81.8 \pm 1.6	80.9 \pm 1.5

*Mean \pm standard deviation (N = 3); HPM = Hot plate method.

Solvent systems: Acid type and concentration in the liquid extracting was seen to be the most critical parameter affecting ultrasound leaching. Different acid mixtures such as 15 % $\text{HNO}_3\text{-1\% HCl}$ (1:1, m/m)²⁶, 25 % $\text{HNO}_3\text{-HCl}$ (1:1, v/v)⁷, concentrated $\text{HNO}_3\text{-HCl}$ (1:1, v/v)⁷, $\text{HNO}_3\text{-HCl}$ (4:1, v/v) and concentrated $\text{HNO}_3\text{-HClO}_4\text{-HF}$ (2:1:1, v/v/v)⁶ 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^{6,7,27}. The influence of extractants such as concentrated HCl, HNO₃, HClO₄ and a mixture of HCl-HNO₃ was studied in a univariate way by fixing the other variables at their optimal values. The leaching results obtained with the use of a single acid or acid mixtures are shown in Table-2. It can be seen that high recoveries with ultrasonic leaching method in a concentrated HCl-HNO₃ 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 HCl-HNO₃ are in good agreement with the results found for HCl, except for Pb. The leaching results obtained with the use of a mixture of HCl-HNO₃ and HCl revealed that there is no significant difference between both solvent systems at 0.05 probability, except for Pb. It is also clear that HNO₃ and HClO₄ give less metal leaching than HCl. A concentrated HCl-HNO₃ mixture was chosen for leaching. Different concentrations of hydrochloric acid were also investigated (Table-3). It is clear that highest recoveries with ultrasonic leaching method in concentrated HCl are obtained for metals.

TABLE-2
EFFECT OF ACID TYPE ON THE LEACHING OF THE METALS ($\mu\text{g g}^{-1}$)
FROM SOIL SAMPLES USING THE ULTRASONIC LEACHING METHOD (ULM)

Metal	ULM*				HPM*
	HCl	HNO ₃	HClO ₄	HNO ₃ :HCl	
Pb	79.1±1.3	74.4±1.1	70.6±1.5	85.1±0.9	82.9±1.9
Mn	610.8±10.2	593.9±8.8	574.4±9.2	622.4±7.1	624.1±13.4
Ni	78.3±2.2	76.3±1.2	65.0±1.7	81.7±1.2	80.9±1.5

*Mean \pm standard deviation (N = 3); HPM = Hot plate method.

TABLE-3
EFFECT OF HCl CONCENTRATION ON THE LEACHING OF THE METALS ($\mu\text{g g}^{-1}$)*
FROM SOIL SAMPLES USING THE ULTRASONIC LEACHING METHOD

Metal	Acid concentration (mol/L)				
	2	4	7	10	12
Pb	68.3±1.1	70.2±0.7	76.7±0.5	78.5±0.9	79.2±0.8
Mn	476.9±10.2	523.9±8.8	597.4±10.4	607.4±7.8	611.1±8.4
Ni	70.4±0.8	74.8±1.1	76.9±0.9	78.1±0.6	78.7±0.9

*Mean \pm standard deviation (N = 3).

Sample amount: The 0.10-1.0 g amount interval was investigated for 25 mL solvent volume. Sample amount used largely depends on the procedure followed. A sample amount of up to 0.50 g has been reported in the work with an ultrasonic bath for leaching^{16,18}. As can be seen in Table-4, a significant decrease in metal recovery from soil samples is obtained when the sample amount is larger than 0.50 g. There was significant difference between 0.50 and 1.0 g sample amount for all metals at 0.05 probabilities. The soil amount/solvent volume ratio appears to be an

important parameter for metals which leaching efficiency is affected by the solvent volume. In this work, sample amount/solvent volume ratio was chosen as 0.50 g/25 mL.

TABLE-4
EFFECT OF THE SAMPLE AMOUNT ON THE METAL RECOVERY ($\mu\text{g g}^{-1}$)*
FROM ACID SOLVENT (25 mL) USING THE ULTRASONIC LEACHING METHOD

Metal	Sample amount (g)			
	0.10	0.25	0.50	1.00
Pb	84.9±1.5	86.1±0.9	85.7±0.7	81.2±0.9
Mn	615.3±14.7	614.7±8.6	616.1±9.2	588.4±7.5
Ni	80.9±1.6	81.8±0.4	81.3±1.0	78.7±1.4

*Mean ± standard deviation (N = 3)

Particle size: Particle size was among the more critical parameters influencing ultrasound assisted leaching^{6,16}. As expected, reactions were enhanced on increasing the contact surface. The particle size attempted for metal leaching in this work with the use of ultrasonic bath ranged from less than < 63 up to > 212 μm . The results obtained in this study are shown in Table-5. As can be observed, leaching efficiency decreased when the particle size was larger than 63 μm for the metals. There was no significant difference between < 63 and 63-151 μm particle sizes for all metals at 0.05 probability but was < 63 and 151-212 μm . In this way, the < 63 μm particle size was chosen for evaluation of the accuracy.

TABLE-5
EFFECT OF THE PARTICLE SIZE ON THE METAL RECOVERY ($\mu\text{g g}^{-1}$)*
FROM ACID SOLVENT USING THE ULTRASONIC LEACHING METHOD

Metal	Particle size (μm)			
	< 63	63-151	151-212	> 212
Pb	85.1±0.8	84.9±0.6	82.2±0.6	77.0±1.2
Mn	614.8±10.7	615.7±8.8	591.1±10.8	552.4±13.4
Ni	82.7±1.1	81.2±0.9	78.3±0.7	72.9±1.3

*Mean ± standard deviation (N = 3).

Variables influencing the leaching process and optimum leaching conditions were shown in Table-6. These experimental conditions were applied to roadside superficial soil samples and the results are given in Table-7 and to certified reference pond sediment sample CRM-2 in Table-8. The time required (1.5 h) is shorter than that needed for hot plate method (14 h) and amounts of acids consumed are also less than used for hot plate method for quantitative leaching of Pb, Mn and Ni from soil samples.

Analytical results using ultrasonic leaching method and hot plate method

Calibration and validation: The detection and quantification limits were calculated for flame AAS determinations. Limits of detection [3 (s/m), N = 10] for the ultrasonic leaching method were 2.33, 1.87 and 1.24 $\mu\text{g g}^{-1}$ for Pb, Ni and Mn,

TABLE-6
OPERATING CONDITIONS FOR LEACHING OF THE METALS FROM
ROADSIDE SOIL SAMPLES USING THE ULTRASONIC LEACHING METHOD

Variable	Studied interval	Optimum leaching conditions
Exposure time (min)	10-60	30
Sample amount (g)	0.1-1.0	0.5
Particle size (μm)	< 63 - >212	< 63
Acid type (concentrated)	HNO_3 , HCl, HClO_4 , HNO_3 -HCl	HNO_3 -HCl
HCl concentration (mol/L)	2-12	12

TABLE-7
ANALYTICAL RESULTS ($\mu\text{g g}^{-1}$) FOR THE METALS AS DETERMINED BY
ULTRASONIC LEACHING METHOD (ULM) AND HOT PLATE METHOD (HPM)

Site	ULM*			HPM*		
	Pb	Mn	Ni	Pb	Mn	Ni
High**	116.9 \pm 1.5	858.8 \pm 12.3	87.3 \pm 0.8	114.7 \pm 1.4	863.0 \pm 21.3	86.2 \pm 1.5
Medium**	85.1 \pm 1.0	622.4 \pm 7.1	81.7 \pm 1.2	82.9 \pm 1.8	624.1 \pm 13.4	80.9 \pm 1.1
Light**	63.4 \pm 1.0	519.5 \pm 10.0	57.5 \pm 0.6	63.6 \pm 1.0	512.7 \pm 8.5	58.3 \pm 0.7
Industrial	88.6 \pm 0.8	610.7 \pm 11.4	82.4 \pm 1.4	86.4 \pm 0.8	607.9 \pm 7.2	83.1 \pm 1.2

*Mean \pm standard deviation (N = 3), **According to traffic density.

TABLE-8
COMPARISON BETWEEN RESULTS FOR ULTRASONIC LEACHING METHOD
(ULM) AND HOT PLATE METHOD (HPM) USING CERTIFIED REFERENCE
MATERIAL (CRM-2)

Metal	Concentration ($\mu\text{g g}^{-1}$)*			Recovery (%)†
	ULM	HPM	Reference values	
Pb	104 \pm 2	103 \pm 3	105 \pm 6	98.0
Mn	782 \pm 13	769 \pm 16	770**	101.6
Ni	39 \pm 1	37 \pm 2	40 \pm 3	97.5

*Mean \pm standard deviation (N = 3); †ULM/Reference value \times 100

respectively, being similar to those attained with hot plate method when a 0.5 g sample mass was used for leaching. Limits of quantification [10 (s/m), N = 10] were 7.1, 5.7 and 3.9 $\mu\text{g g}^{-1}$ for Pb, Cu, Ni, Zn and Mn, respectively. The equation for the linear range of the calibration graphs for all metals was found as:

$$\text{Absorbance} = 2(\pm 1) \times 10^{-3} + 0.043 \pm 0.021 [X], (X = 0-7 \text{ mg L}^{-1}), r = 0.9989.$$

Analytical results obtained by ultrasonic leaching method and hot plate method corresponding to the soil samples analyzed are shown in Table-7. Average recoveries for all metals were between 98 and 102 %, thus indicating that there was a good agreement between ultrasonic leaching method and hot plate method. When the average heavy metal values were compared using a significance statistical test it was concluded that there is no difference for the ultrasonic leaching method and

hot plate method at 0.05 probabilities. The main differences between the two methods lie in the time required to complete the digestion or leaching. In precision test, the relative standard deviation (RSD) (N = 3) values for all metals varied in the range of 0.8-1.8 % and 1.0-2.5 % for ultrasonic leaching method and hot plate method, respectively. The precision obtained from 12 replicate ultrasonic leaching method yielded an average RSD of 1.16, 1.73 and 1.34 % for Pb, Mn and Ni, respectively, depending on the analyte. RSDs were calculated from pooled data for method. Besides, the precision of the ultrasonic leaching method was better than hot plate method.

The accuracy of ultrasonic leaching method for the proposed method under the optimized leaching conditions was determined by comparing the results with those obtained using hot plate method for all soil samples, as well as by analyzing pond sediment (CRM-2). Validation of the ultrasonic leaching method is shown in Table-8. A good agreement between the found and certified metal contents can be observed for the all metals studied. The results, presented in Table-8, show that no statistical differences were observed at 0.05 probability, indicating that the ultrasonic leaching method is applicable for this type of sample, opening the possibility of its application for other samples. Ultrasonic leaching method provided (+ 1.7) - (-2.5) % relative error, depending on the analyte and sample, which are acceptable ranges for this kind of studies.

Conclusion

This study indicates that the performance of this technique is equal to the hot plate method and significantly reduces the time required for all treatments with hot plate method (from *ca.* 14 h to *ca.* 1.5 h), the hazardous wastes, contamination risks, the amounts of acids consumed and fume-hood emissions. The ultrasonic leaching method has described offers a fast, easy, reliable and efficient sample preparation for direct determination of Pb, Ni and Mn in roadside superficial soil samples by flame AAS. Exposure time, acid type, acid concentration, sample amount, particle size and sample matrix (chemical properties) are the main factors affecting the leaching process of Pb, Mn and Ni from roadside superficial soil samples. 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 (HPM) based on acid digestion.

It is clear that the ultrasonic leaching method (ULM) is a fast, inexpensive, easy, reproducible and selective technique for the total determination of Pb, Ni and Mn in roadside superficial soil samples which are important in monitoring environmental pollution.

REFERENCES

1. P.F. Scanlan, Effects of Highway Pollutants upon Terrestrial Ecosystem, In: Highway Pollution, Elsevier, Amsterdam, p. 287 (1991).
2. T. Çınar and A. Elik, *Int. J. Environ. Anal. Chem.*, **82**, 321 (2002).

3. D.I. Godbold and A. Hüttermann, *Water, Air, Soil Pollut.*, **31**, 509 (1986).
4. R.W. Linton, D.F.S. Natucsh, R.L. Solomon and C.A. Evans, *Environ. Sci. Technol.*, **14**, 158 (1980).
5. H. Matusiewicz, Wet Digestion Methods, In: Sample Preparation for Trace Element Analysis, Elsevier, Ch. 6, Amsterdam (2003).
6. H. Güngör and A. Elik, *Microchem. J.*, **86**, 65 (2007).
7. K. Ashley, R.N. Andrews, L. Cavazos and M. Demange, *J. Anal. At. Spectro.*, **16**, 1147 (2001).
8. M.D. Luque de Castro and M.P. da Silva, *Trends Anal. Chem.*, **16**, 16 (1997).
9. A. Elik and M. Akçay, *Int. J. Environ. Anal. Chem.*, **80**, 257 (2001).
10. C. Bendicho and I. Lavilla, in ed.: I.D. Wilson, Ultrasound-Assisted Extraction, Encyclopedia of Separation Science, Academic Press, London (2000).
11. T.J. Mason, Practical Sonochemistry, Ellis Horwood, Chichester, UK (1991).
12. M. Akçay, A. Elik and S. Savasci, *Analyst*, **114**, 1079 (1989).
13. K.S. Suslick, Ultrasound: Its Chemical, Physical and Biological Effects, VHC Publishers, Weinheim, Germany (1988).
14. J.L. Luque-Garcia and M.D. Luque de Castro, *Analyst*, **127**, 1115 (2002).
15. J. Mierzwa, Y.C. Sun and M.H. Yang, *Anal. Chim. Acta*, **355**, 277 (1977).
16. A.V. Filgueiras, J.L. Capelo, I. Lavilla and C. Bendicho, *Talanta*, **53**, 433 (2000).
17. J.L. Capelo, I. Lavilla and C. Bendicho, *Anal. Chem.*, **73**, 3732 (2001).
18. A. Elik, *Talanta*, **71**, 790 (2007).
19. C.C. Nascentes, M. Korn and M.A.Z. Arruda, *Microchem. J.*, **69**, 37 (2001).
20. J. Ruiz-Jimenez, J.L. Luque-Garcia and M.D. Luque de Castro, *Anal. Chim. Acta*, **480**, 231 (2003).
21. A. Elik, M. Akçay and M. Sökmen, *Int. J. Environ. Anal. Chem.*, **77**, 133 (2000).
22. A. Elik, *Talanta*, **66**, 882 (2005).
23. J.L. Luque-Garcia and M.D. Luque de Castro, Acceleration and Automation of Solid Sample Treatment, Elsevier, Amsterdam (2002).
24. Y. Mizukoshi, H. Nakamura, H. Bandow, Y. Maeda and Y. Nagata, *Ultrason. Sonochem.*, **6**, 203 (1999).
25. Perkin-Elmer, Analytical Methods for Atomic Absorption Spectrophotometry, USA (1979).
26. P. Reisz, T. Kondo and C.M. Crisha, *Ultrasonics*, **28**, 295 (1990).
27. J. Sanches, R. Garcia and E. Millan, *Analisis*, **22**, 222 (1994).