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Determination of trace and major elemental profiles in street dust samples by fast miniaturized ultrasonic probe extraction and ICP-MS

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ABSTRACT

A simple, fast and miniaturized ultrasonic probe assisted protocol for acid extraction of trace and major elements from street dust samples, prior to final determination by ICP-MS, has been optimized and validated by standard reference materials and applied during an urban air quality monitoring campaign. 15 mg samples were treated for 3 min with 1 mL concentrated HNO_3–HCl (1:3, v/v) extracting solution, by a 1 mm diameter titanium sonotrode connected to a 200 W and 24 kHz ultrasonic device at 80% amplitude. After centrifugation, the extracts were assayed by ICP-MS with good recoveries for the certified elements. Statistical analysis of real sample results by cluster analysis allowed the correct grouping of the samples according to the influence of traffic and construction/demolition activities. Correlation of street dust and PM10 elemental profiles showed the potential applicability of the proposed analytical protocol as a simple and effective way for urban air quality monitoring.

1. Introduction

Chemical information contained in ambient aerosol particles is relevant for health and environmental impact estimation, and also for pollutant source assignment and apportionment studies. Heavy elements, specifically lead, cadmium, arsenic and nickel, are classified as toxic aerosol components [1,2]; some of them have been proposed as tracers of specific pollution sources as road traffic [3] or biomass burning [4]. Maximum levels of toxic elemental aerosol component are regulated in air quality guidelines and legislation, e.g. by the European Union (Directive 2004/107/EC). Other trace and major elements contained in ambient aerosols serve as indicators of a variety of pollution sources [5]. Dominant analytical methodologies for trace element monitoring in atmospheric aerosols include capturing PM10 or PM2,5 fractions of the aerosol on filters using high volume samplers, acid digestion in hot plate or microwave assisted, and final measurement by ICP-OES and ICP-MS, with reference methods published as European [6] and U.S. EPA [7] standards. Research interest is focused on the search of simplified sampling, pre-treatment and determination strategies for rapid, simple and reliable estimation of elemental profiles in atmospheric deposition.

About sampling, street dust has been widely used as environmental indicator for atmospheric monitoring [8,9], as an accessible and ubiquitous sample that can be easily taken by wiping or brushing, thus avoiding the need of sophisticated active samplers. Most of the studies have reported trace elemental concentrations in street dusts as representative values for their respective cities.

About pre-treatment, ultrasonic extractions have proved to be successful for achieving quantitative recoveries from various environmental matrices, and various parameters associated with the ultrasonic solid–liquid extraction for elemental analysis (total content) has been reviewed [10]. In contrast to intensive sample preparation methods involving high temperatures and pressures, acid extraction of atmospheric samples under mild conditions with ultrasonic bath activation has been described, including particulate matter [11–13], fly ashes [14–16] and dust wipes [17]. Sb speciation in particulate matter by ultrasonic probe extraction has been reported [18].

A single work has been reported about the ultrasonic bath extraction of the heavy metals Pb, Cu, Zn and Ni from street dust samples [19], but no reference was found about the use of ultrasonic probes for the same task. In contrast to ultrasonic baths, the use of high intensity ultrasonic probes can drastically accelerate extraction of analytes from solid samples [20]. The sonication time required with ultrasonic probe is less (up to 100 times) than that needed when using ultrasonic baths, with usual sonication time of 5 min or less. Sample miniaturization typical of probe treatments is also advantageous for reagent saving and potential portability.

In this work we have aimed to explore a simplified strategy for elemental profile in atmospheric monitoring, based on the development of a new miniaturized ultrasound probe assisted

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Fig. 1. Street dust sampling areas in the city of Badajoz, Spain.

pseudo-digestion method for fast and reproducible extraction of inorganic species (major and trace elements) from street dust samples, that can be subsequently assayed by ICP-MS. These samples are ideal from the analytical point of view due to their wide availability and simplicity of sampling. Parameters influencing the procedure such as extraction media, sonication amplitude and time are investigated by using standard reference materials. The proposed pre-treatment has been applied to street dust samples collected during an air quality surveillance sampling campaign in the city of Badajoz, Spain. The results are discussed by marker element ratios, cluster analysis and comparison with by standard elemental profile determination in PM10 by total digestion and ICP-MS.

2. Experimental

2.1. Chemicals and materials

All chemicals used for the preparation of stock and standard solutions were of analytical grade. ICP multielemental standard solutions were obtained from PerkinElmer (Waltham, MA, USA). Working solutions were prepared by dilution with ultrapure water (resistivity >12 MΩ) obtained from a MilliQ (Millipore, Billerica, MA, USA) system. Dilute standards and real samples were adjusted to desired pH with subboiled HNO_3 obtained from a quartz subboiling system (Kürner, Rosenheim, Germany).

Street dust samples were collected in polyethylene auto sealable (ziplock) bags. Ultrasound assisted extraction experiments were carried out with a stand mounted Hierschel (Teltow, Germany) UP200S high intensity ultrasonic device (200 W, 24 kHz), equipped with a 1 mm diameter titanium S1 probe for volumes 0.1–5 mL. The amplitude control of the ultrasonic processor allowed the ultrasonic vibrations at the probe to be set any desired level in the 10–100% range of the nominal power.

Daily PM10 samples were collected on QF20 Schleiser&Schuell MicroScience (Dassel, Germany) 150 mm diameter quartz fibre filters by a Digitel (Digitel Elektronic AG, Hegnau, Switzerland) DAH-80 high volume samplers (30 m^3/h). Total air volume collected was around 775 m^3 per filter. Savillex (Savillex Corporation, Minnetonka, MN, USA) 60 mL PFA digestion vessels with threaded closure were used for filter digestion. Digestion vessels and all glassware were cleaned with diluted nitric acid and rinsed with ultrapure water before use.

NIST Standard Reference Material 2583 Trace Elements in indoor dust was used for accuracy check.

2.2. Sampling

Street dust samples were collected from high, medium and light human activity areas in Badajoz city (southwest Spain, 38.5°N, 6.6°W, 140.000 inhabitants). As depicted in Fig. 1, zone 1 (La Galera gardens) is a quiet area in the heights of the old city, isolated from traffic and other human activities, so it can be considered as urban background. Zone 2 (Belt way) is a heavy traffic urban road. Zone 3 (Meléndez Valdés Street) is a narrow street in the old city, with light traffic. Demolition/construction activities were registered in this area around the sampling period. Zone 4 is a private underground parking lot. The dusts samples were gently swept from

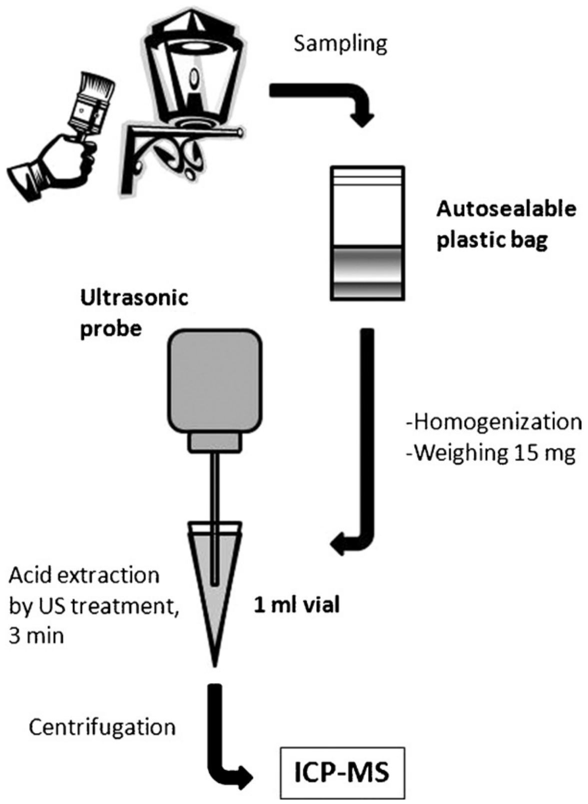

Fig. 2. Overview of the sampling and pretreatment protocol for the street dust samples.

urban furniture to auto sealable polyethylene bags by a clean brush. Three samples from about 1 m^2 areas were taken at each zone. The sampling campaign was conducted simultaneously in the selected zones on July 20th, 2009.

PM10 samples were daily collected at the air quality monitoring unit of Badajoz, which is located in a suburban location with intermediate density of human activities.

2.3. Sample pre-treatment

A schematic view of the sampling and pretreatment protocol is shown in Fig. 2. Street dust samples were transferred to polyethylene vessels, air dried, manually homogenized and stored in desiccators. For the ultrasonic extraction, accurately weighed amounts (15 mg) of sample or reference material were weighed in a 1.5 mL conical bottom Eppendorf micro centrifuge tube with snap cap. 1 mL extraction reagent was added and the titanium ultrasonic probe was immersed. Then the sample–extractant mixture was sonicated at room temperature by varying sonication time and sonication amplitude settings. After sonication, the samples were centrifuged for 10 min at 5000 rpm. 0.5 mL of the supernatant was transferred to a 10 mL flask, 10 ng/mL In(III) and Y(III) were added as internal standards and the volume was completed with water. Blank, reference material and real samples extractions and analysis were carried out in triplicate.

PM10 samples were conditioned and weighed according to EN-12341. After gravimetric analysis, the sampling filters were cut in two equal fractions. Half filters were placed in digestion vessels. 2.5 mL HNO_3 and 5 mL HF were added and the reaction was allowed to proceed for a few minutes under a fume hood, until the bulk of the quartz matrix was dissolved. Then the vessels were closed and placed in an oven for overnight heating at 90 °C. 2.5 mL $HClO_4$ was then added and the solution was evaporated to dryness on a heating plate (200 °C). 1 mL HNO_3 was then added and after evaporation the residue was taken with 5% HNO_3 to a 50 mL flask. 10 ng/mL In(III) and Y(III) were added as internal standards.

2.4. Analytical determination

Digested solutions were assayed by ICP-MS in a PerkinElmer (Waltham, MA, USA) ELAN 9000 instrument equipped with a cross flow nebulizer (resistant to HF and particle clogging), a Scott spray chamber and a gold plated ceramic quadrupole mass analyzer. Instrumental parameters were as follows: RF power 1000 W, carrier gas flow rate 1 L/min, washing time 35 s, 3 replicates per sample. Quantification was performed by internal standards In and Y. To avoid spectral interferences affecting ICP-MS (notably to As) when using concentrated HCl for extraction, some determinations were performed by ICP-OES in a Horiba Jobin-Yvon (Kyoto, Japan) Ultima radial instrument equipped with a Mira Mist nebulizer. The equipment was operated at 1200 W with Ar flow 12.0 L/min, nebulizer pressure 3 bar and pump speed 15 r.p.m.

3. Results and discussion

3.1. Ultrasonic extraction medium

The optimization of the ultrasound procedure was performed by determining the concentrations of As, Pb, Cd, Hg and Cr in NIST SRM 2583 Trace Elements in indoor dust. Different acid media have been explored for ultrasonic bath assisted leaching of elemental species from dust samples. Ashley et al. [11] demonstrated the effectivity of concentrated HNO_3–HCl (1:1, v/v) for the quantitative recovery of As, Pb and Cd from SRM 2583 and aerosol samples, whereas average low recoveries were found for As, Cd and Cr in 25% HNO_3. Pb can be quantitatively extracted from dust wipes [17], SRM 2583 [11] and from workplace particulate matter samples with 25% (v/v) HNO_3 [21]. Elik [19] found equivalent performance of concentrated HNO_3–HCl (1:3, v/v) and HNO_3–$HClO_4$–HF (2:1:1, v/v/v) acid mixtures for extraction of Pb, Cu, Zn and Ni from street dust samples, interestingly showing that HF addition is avoidable in these kind of samples. HF is a typical additive for acid digestion of environmental samples for silicate destruction, but their use in combination with ICP-MS detection is known to be troublesome due to is potential for damaging the torch system [22]. We performed extraction experiments by sonicating 15 mg of SRM 2583 for 5 min with different concentrations (1%, 10% and undiluted) HNO_3 and HNO_3–HCl (1:3, v/v), employing 1 mL extractant solution and 80% sonication amplitude. The resulting solutions were assayed by ICP-MS for As, Pb, Cd, Hg and Cr. Solutions with higher levels of Cl^- (above 10%) were also assayed by ICP-OES due to heavy spectral interferences observed for As determination in ICP-MS. Maximum recoveries obtained in HNO_3 media were 29.3 ± 5.8% for As, 54.3 ± 6.8% for Cd, 36.2 ± 3.7% for Cr, 20 ± 4.8 for Hg and 76.0 ± 19.8% for Pb. Best recoveries were obtained in concentrated HNO_3–HCl (1:3, v/v): 75.0 ± 12% for As, 70.3 ± 9.6% for Cd, 108.0 ± 1.9 for Cr, 101.1 ± 5.5 for Hg and 91.8 ± 12.0 for Pb, so this medium was selected as optimal.

3.2. Sonication parameters

Different authors have extensively investigated the effect of sonication amplitude in the extraction efficiency, since the ultrasonic power delivered by probe is directly related to the amplitude [23]. However, high vibration amplitude generates a great number of cavitation bubbles, which may dampen the passage of ultrasound energy through the liquid [20]. The influence of sonication amplitude on the extraction of the elements from SRM 2583 was inspected in the range 20–80%. Extractant was HNO_3–HCl (1:3,

Table 1
Effect of sonication amplitude on the ultrasonic extraction efficiency of Pb, Cd, Hg and Cr from SRM 2583 Trace Elements in indoor dust, in HNO_3–HCl (1:3, v/v).

Amplitude (%)	Rec Pb (%)	SD	Rec Cd (%)	SD	Rec Hg (%)	SD	Rec Cr (%)	S
20	87.9	8.5	70.7	9.5	97.0	13.6	89.7	7.2
40	85.0	9.8	77.8	6.2	108.3	5.6	92.6	4.2
60	91.6	1.6	75.6	14.3	120.4	7.6	99.8	4.1
80	99.6	8.9	101.9	29.8	125.3	16.2	108.7	1.9

SD: standard deviation.

v/v), extractant volume (1 mL), sonication time (5 min) and sample weight (15 mg) were kept constant. The results are presented in Table 1. We found high recoveries for the selected elements even at the lowest amplitude tested, but the recoveries tended to increase steadily with the increase of amplitude, so 80% was selected as the optimum value.

Extraction efficiency of the elements certified in SRM 2583 respect to sonication time was studied in the range 1 to 5 min. The recoveries increased from 1 to 3 min and then reached plateau, so 3 min extraction time was selected as optimum for the work with the real samples.

3.3. *Method validation*

The optimized method was applied to a set of 5 subsamples of the standard reference material NIST SRM 2583 Trace Elements in indoor dust for accuracy test. The results of these experiments are summarized in Table 2. An excellent agreement between measured and certified values was found for Pb and Cd, whereas the recoveries for Hg and Cr were somewhat high. The precision was in the range of the certified values or better. It is worth noting that the method ensures complete recovery of mercury, which is usually lost in high temperature standard acid digestion protocols in open vessels. Relatively low recovery obtained for As can be connected with the acid nature of the extraction medium. The ultrasonic probe extraction protocol provides a useful means for an average good recovery of the selected elements from the sample matrix in a short time (3 min) using minute reagent amounts (1 mL). Significant time and reagent saving improvements are thus derived from the use of the ultrasonic probe as can be seen by comparison with previously reported ultrasonic bath extraction protocols for atmospheric samples, e.g. 30 min sonication and 10 mL extraction reagents [12], 18 min sonication and 10.5 mL extraction reagents [14], or 30 min sonication and 12 mL extraction reagents [16]. Method detection limits were calculated according to the IUPAC definition by processing 5 blank samples in the same way as the real samples and measuring the final elemental concentrations. The resulting values were 0.03 mg/kg for As, 0.05 mg/kg for Pb, 0.01 mg/kg for Cd, 0.06 mg/kg for Hg and 0.09 mg/kg for Cr, well below the expected values in real street dust samples.

Table 2
Results of the ICP-OES (As) and ICP-MS (Pb, Cd, Hg, Cr) analysis of certified reference material SRM 2583 Trace Elements in indoor dust after the proposed ultrasonic extraction protocol. Sample amount 15 mg; extractant HNO_3–HCl (1:3, v/v), 1 mL; sonication amplitude 80%; sonication time 3 min.

Element	Measured (mg/kg)	Certified (mg/kg)
As	5.2 ± 0.8	7.0 ± 1.6
Pb	85.6 ± 7.6	85.9 ± 7.2
Cd	7.4 ± 2.2	7.3 ± 3.7
Hg	1.95 ± 0.25	1.56 ± 0.19
Cr	87 ± 2	80 ± 22

Table 3
Results of chemical analyses (average and standard deviation) of street dust elemental concentrations at sampling locations in Badajoz: La Galera gardens (LG), Belt way (BW), Meléndez Valdés Street (MV) and underground parking lot (PL).

	LG		BW		MV		PL	
	Ave	SD	Ave	SD	Ave	SD	Ave	SD
Ba	47.2	6.1	195.1	12.9	154.9	14.7	85.1	17.6
Ca[a]	1.68	0.19	3.20	0.07	2.73	0.33	2.21	0.32
Cd	0.4	0.4	0.9	0.1	0.4	0.1	0.3	0.03
Ce	6.2	0.4	9.9	0.6	27.0	7.0	6.6	0.7
Co	3.4	0.4	5.8	0.3	5.0	1.4	6.0	1.1
Cr	14.3	1.6	38.0	4.7	35.1	9.8	27.4	4.6
Cs	0.3	0.03	0.4	0.03	0.5	0.04	0.5	0.04
Cu	46.1	17.4	398.2	24.1	216.4	91.0	140.2	32.2
Fe[a]	1.07	0.050	1.81	0.07	1.30	0.18	1.48	0.24
Hg	0.3	0.04	0.9	0.9	0.6	0.2	0.4	0.1
K[a]	2.02	0.32	0.95	0.11	2.04	0.15	0.81	0.10
La	3.4	0.3	5.3	0.3	16.3	4.8	3.7	0.5
Mg[a]	3.16	0.35	1.43	0.04	1.17	0.12	0.44	0.07
Mn	340.9	35.5	455.8	20.7	282.5	34.6	157.4	15.0
Nd	3.5	0.6	5.5	0.2	7.6	0.3	3.7	0.3
Ni	10.5	3.5	28.3	12.8	21.3	5.3	20.3	4.0
P[a]	0.12	0.01	0.20	0.01	0.17	0.02	0.04	0.00
Pb	51.6	16.2	86.8	2.9	177.2	13.9	136.8	12.1
Rb	5.0	0.5	5.3	0.4	9.3	0.6	7.8	0.7
Sb	1.5	0.3	11.0	1.3	4.5	0.6	6.4	1.7
Sc	1.7	0.0	2.1	0.2	2.2	0.1	1.9	0.1
Se	0.3	0.2	0.5	0.3	0.3	0.1	0.3	0.04
Si	247.1	20.7	278.2	29.1	656.0	72.7	368.9	48.5
Sr	39.2	5.0	324.9	4.4	193.5	27.2	149.7	31.7
U	0.5	0.04	0.6	0.02	4.0	0.2	0.8	0.1
V	139.9	3.4	138.9	12.8	128.3	16.0	124.0	10.1
Zn	101.4	26.5	931.1	60.5	791.1	301.3	415.1	90.5

SD: standard deviation.

[a] All the data are in mg/kg except data for Ca, Fe, K, Mg and P which are presented as percentages.

3.4. *Application to street dust samples*

A set of 27 elements were assayed in the street dust samples from different zones in Badajoz, according with the optimized ultrasonic probe extraction and ICP-MS. The results obtained are presented in Table 3. The data obtained (average of three replicates) are in the range of previously published results for street dust samples in different parts of the world [8,9,19], ranging from mg kg^{-1} for most elements to g kg^{-1} for Ca, Fe, K, Mg and P.

A preliminary inspection of the data was based on the comparison of concentration levels of marker elements in the different zones sampled, according to literature about atmospheric deposition source assignment based on elemental composition [3,4,24,25]. Lower levels of anthropogenic elements were found in La Galera gardens urban background zone (e.g. Ba, Co, Cr, Cu, Hg, Ni, Pb, Sb and Zn). Elevated concentrations of traffic related elements (Cr, Cu, Mn, Sb, Zn) were found in the belt way zone. Some mineral-crustal elements related to construction/demolition activities (Ca, Ce, La) were found to be elevated in Meléndez Valdés St., where these activities were registered at the time of sampling. The levels of other mineral-crustal elements (P, Mn, Mg) were found to be similar in La Galera gardens, the belt way and Meléndez Valdés St., but lower levels were found at the more isolated zone at the parking lot. To better describe and interpret the analytical information, cluster analysis was applied to the database of street dust results.

Hierarchiral cluster analysis of the samples was performed by using Euclidean distance and the Ward agglomerative algorithm. The results, as shown in Fig. 3, clearly distinguished samples collected in the different zones of the city. At the first dissimilarity level, the statistical analysis separated the urban background location at La Galera gardens from the other three sampling zones, more affected by human activities. In a second level, the heavy traffic

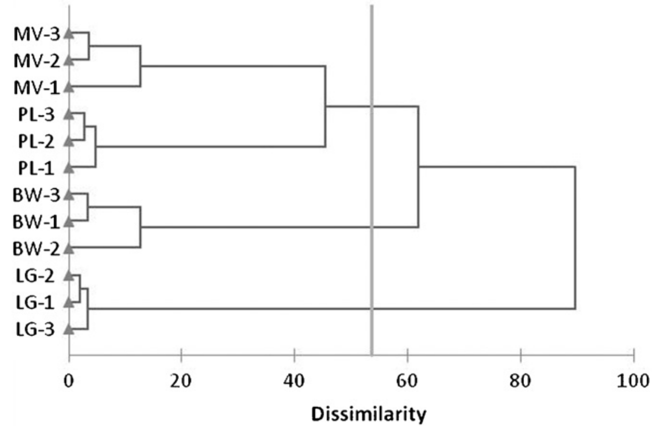

Fig. 3. Hierarchical cluster analysis of street dust samples collected in Badajoz. LG, La Galera gardens; BW, Belt way; MV, Meléndez Valdés Street; PL, parking lot.

location at the belt way zone was distinguished from the light traffic locations at Meléndez Valdés Street and the parking lot.

Cluster analysis of the variables (Fig. 4) revealed three groups of elements: the first mainly contain elements of predominantly anthropogenic origin associated with high traffic density and industry (Ba, Co, Cr, Cu, Hg, Ni, Sb, Zn), but mixed with some elements mainly crustal-mineral in origin (Ca, Fe, Sc, Sr). The second group showed a crustal-mineral profile with elements such as K, Mg, Mn and P, but in this group also appear anthropogenic elements such as Cd and V associated with diesel combustion processes [26]. However, the last one may also have a crustal origin [27]. The same behaviour occurred in the third group, with anthropogenic (Pb) and crustal-mineral elements (Ce, La, Si).

3.5. Street dust vs PM10 elemental profiles

Street dust elemental profiles measured in Badajoz were compared with PM10 aerosol elemental profiles, which are routinely measured in our laboratory as part of the air quality surveillance works carried out in the city. The PM10 set was composed by 72 samples assayed during 2008, collected at a monitoring station which is located in a suburban area with moderate traffic. A correlation between street dust and PM10 elemental profiles was found (r^2 0.97), with more elevated concentrations measured in PM10 respect to the street dust (slope 1.45). This is probably due to the higher presence of organic matter in the street dust, which is not measured in our elemental profile set. The correlation demonstrates that street dust can be used as urban air quality indicator for elemental profiles, confirming previously published results [8,9]. The combination of the simple street dust sampling protocol with the miniaturized and fast ultrasonic extraction proposed, coupled with the standardized ICP-MS measurements, opens a new way for the convenient monitoring of elements in the urban atmosphere.

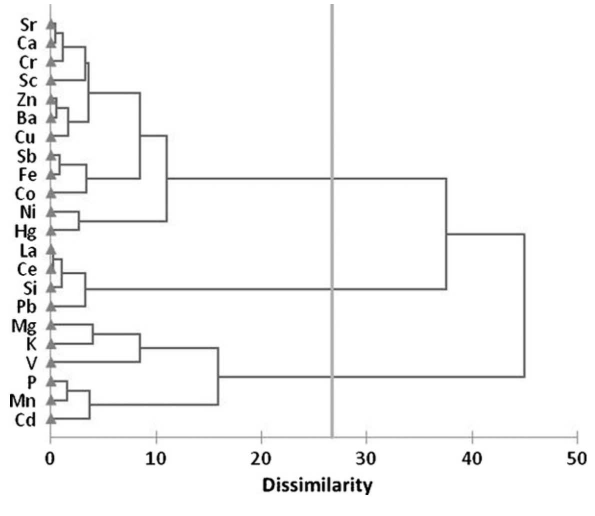

Fig. 4. Hierarchical cluster analysis of the variables (elemental concentrations) measured in street dust samples collected in Badajoz.

4. Conclusions

The optimized ultrasonic probe assisted pre-treatment described offers a fast, efficient and miniaturized sample preparation for extraction of major and trace elemental profiles in street dust samples prior to ICP-MS determination, with potential application for convenient and reliable monitoring of elements in the urban atmosphere. Using 15 mg samples, 1 mL extractant solution, and 3 min sonication time, ultrasound probe assisted extraction can be used as an alternative to traditional sample preparation methods for the estimation of a wide range of major, minor and trace elements in street dust samples. The procedure is also safer as it involves neither high pressure nor high temperature; reagent consumption and the acid waste generation are considerably less than traditional digestion methods.

The effectiveness of the method has been demonstrated with indoor dust reference material and by the consistent results obtained during a sampling campaign in the city of Badajoz, where the method was able to distinguish urban background areas from traffic and construction/demolition affected areas, by the measured concentration of marker elements and hierarchical cluster analysis. Moreover, the applicability of the method for air quality monitoring was confirmed by the correlation found between street dust data and the results obtained by means of standardized sample pre-treatment based on total acid digestion, during routine PM10 air quality surveillance at the same city.

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