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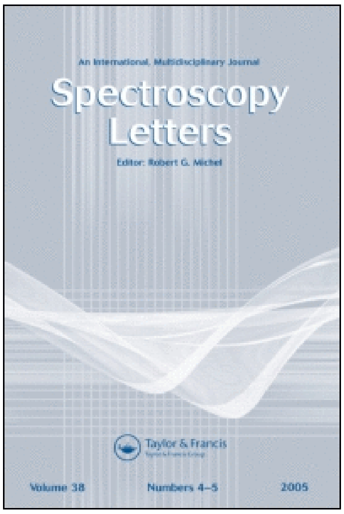

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Application of Experimental Design to the Optimization of a Wet Acid Digestion Procedure for Cd Determination in Plastic Materials by Atomic Absorption Spectrometry

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Application of Experimental Design to the Optimization of a Wet Acid Digestion Procedure for Cd Determination in Plastic Materials by Atomic Absorption Spectrometry

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ABSTRACT A simple and reliable method for Cd determination in plastic materials using optimized wet acid digestion procedure and atomic absorption spectroscopy was developed. In order to obtain the best experimental conditions for plastic digestion, a 2^{7-4} Plackett-Burman design for screening the significant factors and a 2^{4-1} central composite design to optimize the significant experimental variables were carried out. The polyethylene European Reference Material ERM-EC680 with certified Cd content was used in both the screening and the optimization steps. The optimized experimental conditions 0.200 g of plastic material digested with 2 mL nitric acid (30 min, 130°C) followed by 1 mL sulfuric acid (30 min, 140°C). The accuracy and precision was checked using ERM-EC680. The Cd recovery was 101.3% and the relative standard deviation was 5.6%. The limit of detection obtained was 0.23 mg kg^{-1}. The method was applied in the analysis of one PVC plastic material, several commercial packaging materials, and plastic toys.

KEYWORDS atomic absorption spectrometry, cadmium, experimental design, plastic materials, wet digestion

INTRODUCTION

Plastic materials are extensively used in a large variety and quantity of daily products. Those plastics could contain cadmium (Cd) and other unwanted toxic metals. Compounds of cadmium are still used by some manufacturers of plastics as pigment or as a stabilizer. In order to reduce environmental and human exposure to cadmium, the EU Directive 91/338/EC restricts the marketing and use of products that contain Cd above a specified limit. The maximum allowable concentration of Cd in plastics for consumer goods is set at 100 mg/kg.[1] The Restriction of

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Hazardous Substances (RoHs) Directive restricts the use of Cd as well as lead, mercury, and chromium in electrical and electronic equipment.[2]

The accurate and precise analysis of plastic consumer goods is an important task for analytical laboratories. Plastic materials differ in their structure from inorganic objects and also from biological samples. The metal determination in plastics strongly depends on the polymer matrix. This matrix effect cannot be predicted, and it has to be evaluated for each polymer type. Other problems are related to poor homogeneity of many samples and the lack of standard methods for plastics analysis.[3]

A great variety of procedures for metal determination in plastics have been published including nondestructive direct methods such as x-ray fluorescence (XRF) and neutron activation analysis (NAA).[3–6] However, most of the laboratories have opted for digestion methods (among others high-pressure incinerator, classic wet digestion, and closed-vessel assisted by microwave energy). Posterior metal determination has mainly been done using absorption or emission atomic spectroscopic techniques (AAS, ICP-OES, ICP-MS).[3–5,7–12] Microwave (MW)-assisted dissolution presents several advantages over classic techniques such as reduction in the digestion time and decrease of sample contamination. Most of these studies have been carried out using commercial MW systems, which represent a high acquirement cost. Hence, the procedure using the commercial equipment is recommended when a large number of samples have to be analyzed.

A method based in wet digestion procedure that avoids the disadvantages of the open-vessels methods (loss of analytes, longer digestion time, more digestion chemicals) could be an adequate alternative for laboratories that could not acquire the expensive equipment and instrumentation. A reasonable selection of the experimental variables (chemicals, temperature, and time) and a planned experimentation following experimental design could be a useful practice to try to get the best experimental conditions.[13] This kind of approach using screening and optimization design steps has been applied in the determination of organic tin in sediments by electrothermal absorption spectrometry (ETAAS)[14] and lead in foods by flame atomic absorption spectrometry (FAAS).[15] A full factorial design has been used in the optimization of microwave digestion for determination of Zn, Cu, and Ni in tea samples.[16] Therefore, the use of this type of structured methodology should be a short and useful approach to find the best experimental conditions in plastic digestion procedures previous to metal determination.

This work was planned trying to find a simple, inexpensive, and reliable method for Cd determination in plastic based on wet digestion procedure and AAS instrumentation.

MATERIALS AND METHODS

An AAnalyst 200 atomic absorption spectrophotometer (Perkin-Elmer, Shelton, CT) equipped with electrodeless discharge lamp (EDL) was used for the Cd determination. The operating conditions for flame atomic absorption spectrometry (FAAS) are given in Table 1.

Analytical reagent grade nitric acid (65%), sulfuric acid (95–97%), and hydrogen peroxide (30%) were the digestion chemicals used (Panreac, Barcelona, Spain). Standard solutions were prepared just before use from 1000 mg L^{-1} Cd atomic absorption standard (Perkin-Elmer). Throughout all analytical work, double-distilled water was used.

Plastic Samples

The European Reference Material ERM-EC680 was used in the screening and optimization of the wet digestion procedure. This reference material is a polyethylene (PE) with certified contents of several metals including Cd. The sample was acquired from the Institute for Reference Materials and Measurements (IRMM) supplied by LGC-Promochem (Barcelona, Spain). A polyvinyl chloride (PVC) plastic sample (IIS-0557) with accredited Cd content was from the Institute for Interlaboratory Studies (Spijkenisse, The Netherlands).

TABLE 1 Operating Conditions in FAAS

	Cd
Wavelength	228.8 nm
Source	Electrodeless discharge lamp (EDL)
Flame	C_2H_2 2.5 L min^{-1} Air 10 L min^{-1}
Slit width	0.7 nm
Calibration	Standard addition

Different commercially available plastic products used as food containers were acquired from food stores. The abbreviations for the plastic containers used are the following: PS, polystyrene; PE, polyethylene; PET, polyethyleneterephthalate; and PP, polypropylene. Those were the samples analyzed: PS-1 (white tray), PS-2 (yoghurt colorless container), PE-1 (yoghurt white bottle), PE-2 (colorless freezing bag), PET (mineral water bottle), PP-1 (colorless tray), and PP-2 (microwave-use colorless tray). A commercial toy, with different colored tableware pieces was also analyzed. In this commercial toy, the composition of the plastic was not indicated on the label. An attenuated total reflectance (ATR) of the plastic gave PP as a plastic bulk composition. Small parts with different colors were taken and named as T-1 (orange piece), T-2 (brown piece), T-3 (green piece), T-4 (pink piece), and T-5 (violet piece).

Some of the samples were originally present as small granules. The rest of the samples were cut into small pieces. The plastic samples were ground to a grain size of $< 1000\,\mu m$ by a centrifugal grinding mill (Retsch, Haan, Germany) under cooling with liquid nitrogen.

Conventional Digestion Procedure

For comparison, a conventional wet ashing method, similar to that applied in different plastics,[7] was used. Sample digestion was performed in a Digesdahl digestion apparatus (HACH model 23130-20,-21; HACH, Namur, Belgium). Briefly, the sample digestion procedure was as follows: 0.250 g of certified reference material (ERM-EC680) was weighed and transfered to an appropriate 100 mL volumetric flask, and 6 mL concentrated H_2SO_4 acid was carefully added. The plastic was ashed by increased heating. First, the temperature was set at 175°C (10 min), then at 250°C (45 min), and later at 350°C (25 min). A black liquid resulted. After cooling, 3 mL 30% H_2O_2 (v/v) was carefully added, and the solution was heated again, first at 350°C (20 min) and later at 500°C until a clear, colorless solution resulted. After that, the solution was left to cool to room temperature. The content of the flask was then filtered through filter paper, and the filtrate was made up to 25 mL with double-distilled water. Three independent samples were run following the described procedure. The cadmium was quantified using the standard addition method.

Proposed Procedure

Next, 0.200 g of certified reference material (ERM-EC680) was weighed and transfered to a 16×160 mm Pyrex vial. After careful addition of 2 mL concentrated HNO_3 acid, the vial was inserted in a digester block holding up to 18 vials. The digester block is actually used for chemical oxygen demand (COD) evaluation (model Tembloc; P-SELECTA, Barcelona, Spain). The sample with nitric acid was gently heated until the temperature reached 130°C and was maintained for 30 min with this temperature. After cooling, 1 mL concentrated H_2SO_4 acid was carefully added. Again, the sample with acids was slowly heated, and when the temperature reached 140°C it was maintained there for 30 min. The solution was left to cool, was filtered, and the filtrate was made up to 50 mL with double-distilled water. From this solution, the cadmium was quantified by the standard addition method with three standards of 0.2, 0.4, and 0.8 mg L^{-1}. The blank digests were carried out following the procedure.

The experimental designs were performed, and the results were evaluated using the STATISTICA software package (Statsoft, Tulsa, OK, USA).

RESULTS AND DISCUSSION

In order to develop an adequate method for plastic digestion previous to Cd determination, it is necessary to consider and optimize several variables that affect the digestion procedure. An experimental design (involving screening and optimization) was used searching for the best experimental conditions. In all the experiments, the ERM-EC680 certified reference material was used.

The procedure considered a chemical digestion with two sequential steps. After several preliminary runs, two experimental conditions were fixed. Concentrated nitric acid was the first chemical used (2 mL), and 0.200 g of plastic sample was taken. The nitric acid volume and the plastic amount were chosen according to the limitation of the Pyrex tubes size (16-mm diameter, 160-mm height).

Screening Design

Screening is the first step in the efficient assessment of the variables (or factors) involved in the studied analytical systems. If a large number of factors are considered, reduced factorial designs such as Plackett-Burman (P-B) are used. This type of design is useful because it is possible to detect the most significant variables with a reduced number of experiments. In the P-B design, it is assumed that the factors interactions can be completely ignored, and only the main effects are calculated. However, it can be used to try to find the large main effects, which latter can be thoroughly studied using surface response designs.

On the basis of the literature,[3–5,7–12] seven variables were selected to define the experimental field (two qualitative or categorical and five quantitative or continuous). Those were the variables (or factors) considered in the sequential attack with two steps: In the first steps, time and temperature of the digestion with concentrated nitric acid; in the second steps, type of chemical (sulfuric acid or hydrogen peroxide), time and temperature of digestion, and type of digester (chemical oxygen demand reactor or ultrasonic bath). The code and low and high levels for each of the variables are shown in Table 2.

In P-B design, the number of experiments is a multiple of four (4, 8, 12, 16) and exceeds the number of factors by one. In this study, a 2^{7-4} P-B design was applied to evaluate the main effects of seven factors. In total, the design matrix had eight runs. The design matrix and the response for Cd content (in mg kg^{-1}) in ERM-EC680 material is also given in Table 2.

The data obtained were evaluated by an ANOVA test (not included) and the main effects visualized using a Pareto chart (Fig. 1). In the graphic, the bar lengths are proportional to the absolute value of the estimated main effects. The sign of the effect showed that the response would or would not improve on passing a given factor from the lowest to the highest level. The most important variables were the time and temperature of the second step in the digestion procedure and the time in the first step of the digestion with nitric acid. Those three quantitative variables gave higher response at higher levels. The two qualitative variables, second reactive (R_2) and digester type (DigType_2), showed a negative effect for the highest level. Therefore, in

TABLE 2 **Experimental Variables, Levels, 2^{7-4} Plackett-Burman Design Matrix, and Results (mg kg^{-1}) for Cd Determination in ERM-EC680 with Acid Digestion and AAS**

Variable (units)	Coded	Low level	High level
Time 1st step (min)	time_1	15	30
Temperature 1st step (°C)	T_1	90	140
Time 2nd step (min)	time_2	15	30
Temperature 2nd step (°C)	T_2	90[a]	140[a]
		60[b]	85[b]
Reactive 2nd step	R_2	H_2SO_4	H_2O_2
Volume reactive 2nd step (mL)	Vol R_2	0	1
Wet digester type 2nd step	DigType_2	COD reactor[a]	US bath[b]

Run	time_1	T_1	time_2	T_2	R_2	Vol R_2	DigType_2	Cd (mg kg^{-1})
1	15	90	15	140	H_2O_2	1	COD reactor	2.5
2	30	90	15	60	H_2SO_4	1	US bath	7.5
3	15	90	30	60	H_2O_2	0	US bath	1.3
4	30	90	30	140	H_2SO_4	0	COD reactor	30.8
5	15	140	15	85	H_2SO_4	0	US bath	2.5
6	30	140	15	90	H_2O_2	0	COD reactor	3.7
7	15	140	30	90	H_2SO_4	1	COD reactor	22.2
8	30	140	30	85	H_2O_2	1	US bath	29.3

[a] Digestion in chemical oxygen demand (COD) reactor.
[b] Digestion in ultrasonic bath.

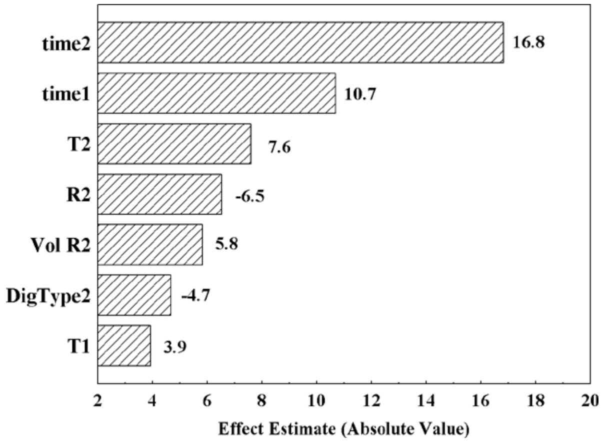

FIGURE 1 Pareto chart of the main effects obtained from 2^{7-4} Plackett-Burman factorial design for Cd determination in ERM-EC680 reference material with acid digestion and AAS.

the two categorical variables, the low level (H_2SO_4 and COD reactor) should be a better selection. The other two quantitative factors (volume of R_2 and temperature of the first step T_1) showed slightly better responses at higher levels. Taking into account these results, three experimental factors were fixed: the two categorical (H_2SO_4 and COD reactor) in the second step and the time of the HNO_3 acid digestion in the first step. In the latter, 30 min was the level chosen due to the highest response obtained. The other four variables were considered in the optimization design described next.

Optimization Design

In order to obtain the best experimental response, a fractional central composite design (CCD) was run out. The four quantitative variables with main effects were taken into account in this optimization step. The four variables and their low, central, and high levels were as follows: time first step (20–30–40 min), time second step (20–30–40 min), temperature second step (100–120–140°C), and volume of reactive second step (0.5–1.0–1.5 mL). These values are shown in Table 3.

Fractional CCD consisted of the points of factorial design (2^{N-1}) increased with ($2N+1$) start points, N being the number of variables. In this work, 2^{4-1} increased with ($2 \times 4 + 1$) start points. The start points were face centered ($\alpha \pm 1$). Also, three runs at the center of the experimental field were performed with independent samples. Therefore, in total the CCD matrix consisted of 19 experimental runs. The matrix and the Cd values (in mg kg^{-1}) are included in Table 3.

A second-degree polynomial model was used including main effects for the four factors and their quadratic components. With this polynomial model, ANOVA showed a lack of fit not significant and a good value for R^2 (0.9114). R^2 is the proportion of the variance accounted for in the respective model in the measurements of the dependent variable. A summary of the ANOVA is included in Table 4. From the four studied factors, the temperature of the second step and the time of the first step gave significant terms (both linear and quadratic terms), showing temperature as the most significant effect.

After checking the adequacy of the model, the next step was to find the conditions of the four factors (or independent variables) that maximized the response of the dependent variable (Cd content). The regression coefficients obtained using the second-degree polynomial model were used in computing predicted values for dependent variable at different combinations of the independent variables levels. Also, there is a program option for predicting values of the dependent variable based on user-defined factor values. The shape of the fitted response can be best visualized in graphs such as three-dimensional (3D) plots. The results for the CCD showing the response (Cd concentration in mg kg^{-1}) as a function of the temperature (T_2) and volume of sulfuric acid (Vol R_2) from the second digestion step are shown in Fig. 2. As can be seen, the highest responses were reached when the temperature was around 140°C and the volume was close to 1 mL. Because the digestion time was not significant ($time_2$) or slightly significant ($time_1$), an intermediate value of 30 min was the chosen level in both digestion steps.

The amount of plastic (0.200 g) and the volume of nitric acid (2 mL) had been previously fixed in the preliminary runs. Taking into account the results obtained with the experimental design, the rest of the working experimental conditions for a two sequential digestion method for Cd determination in plastics were selected. All the process was performed in a COD reactor. For the first step of the

TABLE 3 **Experimental Variables, Levels, Fractional 2^{4-1} CCD Matrix, and Results (mg kg^{-1}) for Cd Determination in ERM-EC680 with Acid Digestion and AAS**

Variable (units)	Coded	Low level	Medium	High level
Time 1st step (min)	$time_1$	20	30	40
Time 2nd step (min)	$time_2$	20	30	40
Temperature 2nd step (°C)	T_2	100	120	140
Volume reactive 2nd step (mL)	Vol R_2	0.5	1.0	1.5

Run	$time_1$	$time_2$	T_2	Vol R_2	Cd (mg kg^{-1})
1	40	40	140	0.5	151
2	40	40	100	0.5	29
3	40	20	140	1.5	155
4	20	40	100	1.5	23
5	40	20	100	1.5	81
6	20	20	140	0.5	131
7	20	40	100	1.5	132
8	20	20	120	0.5	5
9	20	30	120	1.0	138
10	40	30	120	1.0	153
11	30	20	120	1.0	81
12	30	40	100	1.0	135
13	30	30	140	1.0	53
14	30	30	120	1.0	130
15	30	30	120	0.5	110
16	30	30	120	1.5	107
17(C)	30	30	120	1.0	133
18(C)	30	30	120	1.0	128
19(C)	30	30	120	1.0	144

(C), central point.

digestion process using nitric acid: 30 min and 130°C. For the second step using sulfuric acid: 1 mL acid, 30 min, and 140°C.

Analytical Characteristics

Using the selected experimental conditions, limit of detection (LOD), limit of quantification (LOQ),

TABLE 4 **Summary of the ANOVA with the Data Obtained Using Central Composite Design**

Effect	SS	DF	MS	F_{ratio}	P_{level}
A: $time_1$	1960.00	1	1960.00	29.2537	0.0325*
B: $time_2$	28.90	1	28.90	0.4313	0.57880
C: T_2	25806.40	1	25806.40	385.1701	0.0026*
D: Vol R_2	518.40	1	518.40	7.7373	0.10859
A^2	1246.59	1	1246.59	18.6058	0.0498*
B^2	595.95	1	595.95	8.8947	0.09644
C^2	2569.31	1	2569.31	38.3479	0.0251*
D^2	557.70	1	557.70	8.3239	0.10207
Lack of fit	3421.92	8	427.74	6.3842	0.14243
Pure error	134.00	2	67.00		
Total SS	40127.68	18			

$R^2 = 0.9114$.

SS, sum of squares; DF, degrees of freedom; MS, mean squares; F_{ratio}, MS_{factor}/MS_{error}; P_{level}, probability level.

*Significant factor at $\alpha = 0.05$.

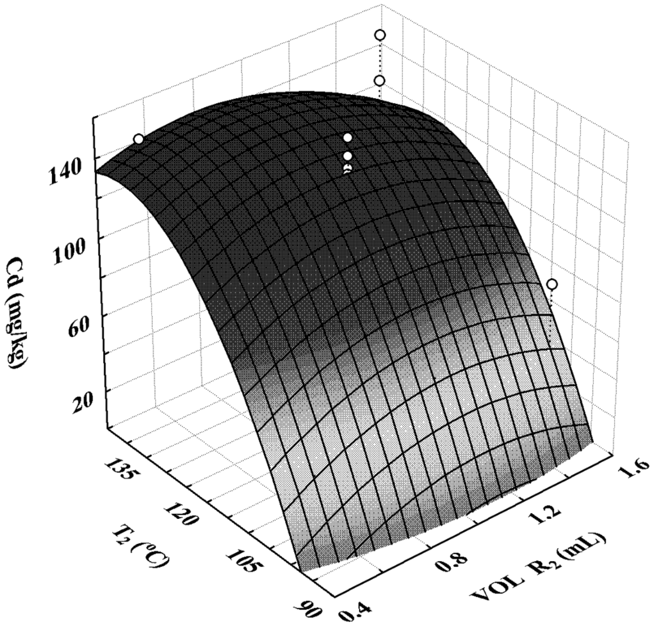

FIGURE 2 Response surface from 2^{4-1} central composite design considering temperature and volume of sulfuric acid in the second step of the digestion procedure for Cd determination in plastic.

accuracy, and precision of the procedure for Cd determination were checked.

LOD and LOQ were calculated according to 3 S_b and 10 S_b criterions, where S_b is the standard deviation of seven replicates of a reagent blank procedure. LOD and LOQ for PE material were calculated by multiplying each of those values obtained in liquid sample by a factor of 50 (0.2 g sample and a final volume of 10 mL). LOD and LOQ, referred to plastic material, were respectively 0.23 and 0.50 mg kg^{-1}. This LOQ value is slightly lower than the 0.88 value obtained working with close microwave digestion and ICP-AES determination.[10] In the later work, the use of more sensitive equipment such as ICP-MS reduced the LOQ obtained value to 0.006 mg kg^{-1}.

The accuracy of the procedure was evaluated by means of the analysis of PE reference material (ERM-EC680), a PVC material used in an interlaboratory study (IIS- 0557), and by spiked recovery experiments. The results of cadmium determination with the two certified plastic materials are given in Table 5. The mean value of Cd obtained following the proposed digestion procedure compared with respectively certified values was 101.3% (ERM-EC680) and 95.8% (IIS-0557). Those recovery values are similar to others obtained working with microwave oven.[10–12] Also, Table 5 includes the data obtained following the conventional wet ashing method with the ERM-EC680 material. Using the latter method, the Cd amount compared with the certified value was 98.4%.

The precision of the procedure was evaluated after the analysis of 10 independent samples for ERM-EC680 and three independent samples for IIS-0557. Repeatability (expressed in RSD) was 5.6% in PE material and 2.5% in PVC material. These data have been included in Table 5. The values are slightly higher than others RSD values obtained working with reference materials and microwave-assisted digestion.[11,12]

To evaluate method performance, we followed the procedure of the uncertainty estimation and the comparison of results with certified values.[17] In this evaluation, Δ_m (absolute difference between measured and certified values) and U_Δ (expanded uncertainty of difference between measurement result and certified value) were compared. With the two certified materials (ERM-EC680 and IIS-0557), $\Delta_m \leq U_\Delta$. Hence, there was no significant difference between the measurement result and the certified value.

The spiked recovery experiments were done using a PE commercial plastic sample without Cd content. Four samples were spiked before digestion with 0.5 mg L^{-1} Cd solution. After the analysis, the

TABLE 5 Summary of Data for Analysis of Cd in Reference Plastic Materials

	ERM-EC680 (PE)	IIS-0557 (PVC)
Certified value ± uncertainty (mg kg^{-1})	140.8 ± 2.5	67.5 ± 14.4
Proposed digestion procedure		
Mean (mg kg^{-1})	147.7	64.7
SD (mg kg^{-1})	8.0	1.6
RSD (%)	5.6%	2.5%
Recovery (%)	101.3%	95.8%
Replicates	n = 10	n = 3
Conventional digestion procedure		
Mean (mg kg^{-1})	138.6	
SD (mg kg^{-1})	12.3	
RSD (%)	8.9%	
Recovery (%)	98.4%	
Replicates	n = 3	

calculated recovery was 98% and relative standard deviation (RSD) was 4.1%.

Application to Commercial Plastic Products

The proposed procedure was applied to a range of plastic products used as food containers and to the colored pieces of the polypropylene plastic toy described in the "Materials and Methods" section. The cadmium was detected neither in the PS, PE, PET, and PP plastic containers analyzed nor in the PP plastic toy pieces.

CONCLUSIONS

A simple and reliable method for Cd determination in plastic material using wet acid digestion and AAS instrumentation was developed using polyethylene reference material (ERC-EC680). The proposed procedure could be useful in studies of Cd in plastics materials.

It was also shown the utility of experimental design in the screening and optimization of the acid digestion conditions in a reasonable number of runs.

A remarkable advantage of the method was based on the simplicity of the equipment used. A heating block used for chemical oxygen demand and an atomic absorption spectrophotometer is the equipment required. Taking 0.200 g plastic material, 2 mL nitric acid and 1 mL sulfuric acid were added for the digestion of the plastic material in two sequence steps. The total time for sequential digestion with two acids was 1 h. This time is longer if it is compared with that of microwave-assisted digestion procedures. However, the proposed method has as advantages the number of digested samples (up to 18 vials in the heating block) and the low cost compared with that of microwave equipment.

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REFERENCES

1. EU Directive 91/338/EC (amending directive 76/769/EC) relating to restrictions on the marketing and use of certain dangerous substances and preparations (cadmium). O. J. L 186, 12.7.1991, 59–63.
2. EU Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment. O. J. L 37, 13.2.2003, 19–23.
3. Ritter, A.; Michel, E.; Schmid, M.; Affolter, S. Interlaboratory test on polymers: Determination of heavy metals in polymer matrices. *Polym. Test.* **2004**, *23*, 467–474.
4. Gimeno Adelantado, J. V.; Peris Martinez, V.; Bosch Reig, F.; Doménech Carbó, M. T.; Bosch Mossi, F. Analysis of toxic elements in plastic components for toys. Multi-elemental determination by x-ray fluorescence. *Anal. Chim. Acta* **1993**, *276*, 39–45.
5. Ernst, T.; Popp, R.; van Eldik, R. Quantification of heavy metals for the recycling of waste plastics from electrotechnical applications. *Talanta* **2000**, *53*, 347–357.
6. Soares, E. P.; Saiki, M.; Wiebeck, H. Determination of inorganic constituents and polymers in metallized plastic materials. *J. Radioanal. Nucl. Chem.* **2005**, *264*, 9–13.
7. Vollrath, A.; Otz, T.; Hohl, C.; Seiler, H. G. Comparison of dissolution procedures for the determination of cadmium and lead in plastics. *Fresenius J. Anal. Chem.* **1992**, *344*, 269–274.
8. Besecker, K. D.; Rhoades, C. B. Jr.; Jones, B. T.; Barnes, K. W. Closed-vessel nitric acid microwave digestion of polymers. *At. Spectrosc.* **1998**, *19*, 55–59.
9. Zischka, M.; Kettisch, P.; Kainrath, P. Microwave-assisted digestion of plastic scraps: Basic considerations and chemical approach. *At. Spectrosc.* **1998**, *19*, 223–227.
10. Perring, L.; Alonso, M.-I.; Andrey, D.; Bourqui, B.; Zbinden, P. An evaluation of analytical techniques for determination of lead, cadmium, chromium and mercury in food-packaging materials. *Fresenius J. Anal. Chem.* **2001**, *370*, 76–81.
11. Skrzydlewska, E.; Balcerzak, M. Multi-elemental analysis of non-food packaging materials by inductively coupled plasma-time of flight-mass spectrometry. *Talanta* **2004**, *62*, 937–944.
12. Sakurai, H.; Noro, J.; Kawase, A.; Fujinami, M.; Oguma, K. Digestion of plastic materials for the determination of toxic metals with a microwave oven for household use. *Anal. Sci.* **2006**, *22*, 225–228.
13. Tranter, R. L. (Ed.). *Design and Analysis in Chemical Research*; Sheffield Academic Press Ltd.: Sheffield, England, 2000, 5, 188–278.
14. Arambarri, I.; Garcia, R.; Millán, E. Application of experimental design in a method for screening sediments for global determination of organic tin by electrotermal absorption spectrometry (ETAAS). *Fresenius J. Anal. Chem.* **2001**, *371*, 955–960.
15. Ferreira, S. L. C.; dos Santos, W. N. L.; Bezerra, M. A.; Lemos, V. A.; Bosque-Sendra, J. M. Use of factorial design and Doehlert matrix for multivariate optimization of an on-line preconcentration system for lead determination by flame atomic absorption spectrometry. *Anal. Bioanal. Chem.* **2003**, *375*, 443–449.
16. Soylak, M.; Tuzen, M.; Santos Souza, A.; Andrade Korn, M. G.; Costa Ferreira, S. L. Optimization of microwave assisted digestion procedure for the determination of zinc, copper and nickel in tea samples employing flame atomic absorption spectrometry. *J. Hazard. Mater.* **2007**, *149*, 264–268.
17. European Reference Materials (ERM). **Application Note 1. Comparison of a measurement result with the certified value**, 2005. Available at www.erm-crm.org.