Analysis Method

Central composite design for the optimisation of Cd and Pb determination in PVC materials by atomic absorption spectrometry after Kjeldahl digestion

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ABSTRACT

A convenient and simple wet acid digestion method was developed for the determination of Cd and Pb concentrations in polyvinyl chloride matrices by atomic absorption spectrometry. Response surface methodology (RSM) was used to optimise the conditions for maximum recovery and to understand the significance and interaction of the factors affecting the recovery of Cd and Pb. The central composite design was employed to evaluate the effects of nitric acid volume (2.6–9.4 mL), sulphuric acid volume (0.6–7.4 mL) and certified reference material (CRM) amount (0.1–0.5 g) on the metal recoveries (60 min, 200 °C and 20 min, 250 °C). The accuracy was also evaluated using the polyvinyl chloride reference material Fluxana FLX-PVC2. The apparent recoveries of the elements relative to the certified values ranged from 0.94 (Cd) to 0.92 (Pb). The method's detection limits were found to be 1.6 and 6.4 mg kg^{-1} for Cd and Pb, respectively.

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1. Introduction

Plastics are among the most important materials used in daily life and industry today, and the amount of plastic produced is still growing. Optimisation of the material properties can be achieved by using different additives. However, the elemental contents of plastic materials must not exceed the concentration limits specified by regulations, such as the Packaging & Packaging Waste Directive 94/62/EC, the Waste Electrical & Electronics Equipment (WEEE) Directive 2002/96/EC and the Restriction of the use of certain Hazardous Substances in Electrical & Electronics equipment (RoHS) Directive 2002/95/EC, which all regulate the maximum amount of heavy metals (Cd, Cr(VI), Hg and Pb) in different types of plastic materials [1–3]. These compounds might originate from flame retardants, antimicrobial reagents, plasticisers, heat stabilisers or pigments. Tin, lead and other organometallic compounds are added to poly(vinyl chloride) (PVC) to inhibit the dehydrochlorination of labile chlorine atoms.

The increasing needs of the plastic industry and its subsequent new regulations can be met only by improvements in the accuracy and precision of the analytical methods applied to plastic research. The sample preparation step to determine element contents in plastics depends on not only the measurement technique but also on the polymer type. For this reason, the sample preparation step has to be evaluated for each polymer type. The poor homogeneity of many samples and the lack of standard methods for plastics analysis are among the other problems [4]. Sample diversity in commonly applied methods for elemental analyses increases with higher interfering element concentrations; hence the validity of the analytical data must be confirmed by using Certified

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Reference Materials (CRMs) or by comparison of the results of independent analytical methods.

Numerous works have already dealt with the determination of toxic metal concentrations, mainly in polyethylene samples [5–8], by using atomic spectrometry, although optical analytical methods typically require the sample to be dissolved in an aqueous medium. Most conventional approaches are based on sample decomposition procedures, such as dry or wet ashing using high pressures, elevated temperatures and/or microwave (MW) assistance with inorganic acids prior to analysis with atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectroscopy or mass spectroscopy (ICP-AES/MS) techniques [4,8,9]. The application of MW systems shortens the time of sample decomposition, reduces the consumption of acids and is more reproducible than mineralisation in an open system. However, these systems have high acquirement cost.

Another approach is the direct analysis of solid samples using a solid sampling device [10–12] or laser ablation ICP-MS [13] and X-ray fluorescence (XRF) spectrometry [14,15]. These approaches have excellent sensitivity for trace element concentration determination in very small samples. However, homogeneity problems in plastic materials limit the usage of these methods.

A method based on a wet digestion procedure that avoids the disadvantages of open-vessel methods (loss of analytes, risk of contamination, time consuming) could be an adequate alternative for laboratories. However, expensive equipment and instrumentation is needed for closed-vessel methods. In open-vessel methods, the experimental design may contribute to optimising the factors of interest and to identifying the variables that influence such factors, thereby improving the performance of a given methodology or process. Proper experimental design can also facilitate estimation of the significance of different variables and decrease the number of experimental runs per variable, thus reducing the total time needed. Central composite design has been the most successful factorial design for the optimisation of parameters with a limited number of experiments and for estimates based on response surfaces. This type of approach using screening and optimisation design steps has been applied in the determination of cadmium levels in polyethylene samples by AAS [16] and the levels of multiple elements in certified reference plant materials by ICP-AES [17]. A three-level full factorial design has been used in the optimisation of microwave digestion for the determination of Ca, Fe, Mg, Cu, Ni, and Zr concentrations in ceramic samples [18]. Plackett-Burman designs have been used to evaluate the most important variables affecting the process, and central composite designs have been used to find the optimum conditions for microwave digestion to determine trace element concentrations in seafood products using AAS [19].

The aim of this study was to use the Kjeldahl method for digestion to avoid analyte losses for the determination of Cd and Pb concentrations in PVC matrices by AAS. To obtain the best experimental conditions for plastic digestion, a central composite design experiment was performed. The accuracy for the quantification of the mentioned elements was assessed using the Fluxana PVC-set reference material.

2. Experimental

2.1. Apparatus

A Varian AA 220 FS (Victoria, Australia) model AAS was used for atomic absorption measurements (Cd, Pb). This AAS was equipped with a single-slot burner head for air-acetylene flame AAS and a deuterium background correction system. The experimental conditions selected in the AAS analysis of the elements in plastics are given in Table 1.

A Tecator 2012 Digester (Hoganas, Sweden) model digestion apparatus with Kjeldahl flasks was used to dissolve the plastic samples. The system contained twelve Kjeldahl glass flasks (volume, 100 ml; height, 30 cm; diameter, 2.5 cm). All units had glass exhaust manifolds with funnel-shaped adapters that fit into the necks of the flasks, and a water cooling unit to eliminate vapour losses during the heating steps. The temperature program was 200 $^\circ$C for 60 min and then 250 $^\circ$C for 20 min.

2.2. Chemicals

All chemicals used were of analytical reagent grade. Water was purified using a GenPure UV-TOC/UV model ultapure water system equipped with UV-photooxidation, total organic carbon (TOC) and ultrafiltration modules (TKA Wasseraufbereitung-systeme GmbH, Niederelbert, Germany). The conductivity of the deionized water was <0.056 μS.

Concentrated nitric (purity 65%) and sulphuric acids were purchased from Merck (Darmstadt, Germany). Certified Reference Material Fluxana FLX-PVC-2 (Fluxana GmbH & Co.KG, Kleve, Germany) was used for method validation. This reference material is a polyvinyl chloride (PVC) with certified contents of several metals including Cd and Pb. AAS single element standard solutions of 1000 mg L^{-1} for Cd and Pb were obtained from Merck (Darmstadt, Germany).

2.3. Sample preparation

Approximately 100 mg of CRM was weighed and transferred into Kjeldahl flasks. After careful addition of 3 mL of concentrated HNO_3 and H_2SO_4, the flask was inserted into a digester block that held up to 12 vials. The block digester was used for Kjeldahl nitrogen determination. The sample in the acids was gently heated until the temperature reached 200 $^\circ$C for 60 min, after which time the sample was heated to 250 $^\circ$C and then maintained at this temperature for 20 min. The solution was left to cool and was then filtered. The filtrate was brought up to

Table 1
Experimental conditions in AAS analysis.

	Cd	Pb
Wavelength (nm)	228.8	217.0
Flame (air flow, l min^{-1})	13.5	13.5
Flame (acetylene flow, l min^{-1})	2.0	2.0
Slit width (nm)	0.5	1.0
Lamp Current (mA)	4.0	10.0

Table 2
Central composite design of factors with coded values and recoveries.

Exp.	Factors			Metal Recoveries (%R)			
	Volume of HNO$_3$ (mL), X_1	Volume of H$_2$SO$_4$ (mL), X_2	CRM amount (g) X_3	Experimental %Cd	Predicted %Cd	Experimental %Pb	Predicted %Pb
1	−1	−1	−1	79.3	79.2	88.7	86.8
2	1	−1	−1	66.5	57.8	70.9	61.8
3	−1	1	−1	74.9	71.3	78.9	76.2
4	1	1	−1	37.3	34.2	56.6	51.9
5	−1	−1	1	51.9	50.2	49.3	50.2
6	1	−1	1	41.6	40.5	37.5	36.4
7	−1	1	1	63.8	67.9	36.0	41.3
8	1	1	1	47.0	42.5	30.3	28.4
9	−1.682	0	0	84.3	82.8	82.1	79.3
10	1.682	0	0	35.3	43.4	39.2	47.3
11	0	−1.682	0	54.0	58.7	42.3	47.2
12	0	1.682	0	51.8	53.7	30.9	31.5
13	0	0	−1.682	48.1	55.0	76.3	85.4
14	0	0	1.682	37.9	37.6	38.3	34.7
15	0	0	0	43.6	51.5	50.6	56.1
16	0	0	0	48.3	51.5	54.9	56.1
17	0	0	0	60.0	51.5	63.5	56.1
18	0	0	0	55.4	51.5	61.3	56.1
19	0	0	0	43.8	51.5	50.6	56.1
20	0	0	0	58.7	51.5	57.0	56.1

a volume of 25 mL with double-distilled water. From this solution, the cadmium and lead concentrations were quantified by the standard addition method with three standards of 0.1, 0.2, and 0.5 mg L^{-1}.

2.4. Experimental design

A five-level three-factor central composite design was employed in this study, requiring 20 experiments to analyze the plastic digestion parameters. The axial (or star) points were fixed according to the rotatability conditions. The three parameters and their low, central, high and star levels were as follows: volume of HNO$_3$ (2.6-4.0-6.0-8.0-9.4 mL), volume of H$_2$SO$_4$ (0.6-2.0-4.0-6.0-7.4 mL), and CRM amount (0.13-0.2-0.3-0.4-0.47 g). The experimental and predicted data in terms of metal recoveries are shown in Table 2.

A second-order polynomial Equation (1) that includes all interaction terms was used to calculate the predicted response:

$$y = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} b_{ii} x_i^2 + \sum_{i=j}^{2} \sum_{j=i+1}^{3} b_{ij} x_{ij} \qquad (1)$$

where y is the specific activity, b_0 is the offset term, b_i is the linear effect, b_{ii} is the squared effect, b_{ij} is the interaction effect and x_i is the independent variable.

The data were analysed using Design Expert (version 7.1.4), and the coefficients were interpreted using the F-test. Two main analytical steps, analysis of variance (ANOVA) and regression analysis, were performed to establish the optimum conditions for the digestion parameters.

3. Results and discussion

3.1. Optimisation design

The main objective of this work was to develop and evaluate a statistical approach to better understand the relationships between the parameters of plastic digestion. Optimisation of the digestion parameters was performed using a central composite design procedure. Twenty experiments were required in this design using five central points, and the experiments were performed randomly. The coded values and the experimental and predicted metal recoveries are given in Table 2, and the experimental domain is shown in Table 3.

The effects of each factor and each factor's interactions were calculated using Design Expert (version 7.1.4). Fitting the data with various models and the subsequent analysis of variance (ANOVA) showed that recoveries of Cd and Pb were most suitably described with a quadratic polynomial model. The quadratic polynomial equations with significant terms from Design Expert are given in Table 4.

Table 3
Range of coded and actual values for central composite design.

Factors	Levels			Star Points ($\alpha = 1682$)	
	Low (−1)	Central (0)	High (+1)	+α	−α
X_1(volume of HNO$_3$, mL)	4.0	6.0	8.0	9.4	2.6
X_2(volume of H$_2$SO$_4$, mL)	2.0	4.0	6.0	7.4	0.6
X_3 (CRM amount, g)	0.2	0.3	0.4	0.1	0.5

Table 4
The quadratic polynomial equations of recovery (R %).

Compounds	A semi-empirical equation
Cd	$R\% = 51.49 - 11.71x_1 - 5.18x_3 + 6.39x_2x_3$
Pb	$R\% = 56.14 - 9.51x_1 - 4.67x_2 - 15.07x_3 - 5.94x_2^2$

The quadratic polynomial models were highly significant and were sufficient to represent the actual relationship between the response and the significant parameters with very low p-values (0.0041 and 0.0003) according to the ANOVA (Tables 5 and 6). The coefficients of determination ($R2$) values (0.849725–0.917051) indicate a satisfactory relationship between the experimental data and the fitted model.

The effects of the plastic digestion parameters such as the volume of HNO_3, the volume of H_2SO_4 and the CRM amount on the recovery were investigated. The p-values indicate the significance of the coefficients. A value of Prob $> F$ less than 0.05 indicates that the model terms are significant, x_1 (volume of HNO_3), x_3 (CRM amount), and x_{23} were the most significant parameters (Prob $> F$ less than 0.05) for cadmium (Table 5), and x_1 (volume of HNO_3), x_2 (volume of H_2SO_4), x_3 (CRM amount), and x_2^2 were the most significant parameters for lead (Table 6). Sulphuric acid might participate in the formation of the lead sulphate precipitate, though a clear mechanism could not be given. Similar results were obtained by Skuraı et al. [20] who reported the effect of acid on plastic digestion with a microwave oven.

The relationship between the digestion parameters and the lead recovery was investigated using contour plots. Fig. 1 shows the effects of nitric acid, sulphuric acid volume and their mutual interaction on the recovery of lead. A nitric acid volume of 2.7 (mL) and a sulphuric acid volume of 3.0 (mL) led to the maximum recovery (80.2%). The effects of nitric acid volume, the CRM amount and their mutual interaction on the lead recovery are illustrated in Fig. 2. A low nitric acid volume (3.5 mL) and a low CRM amount (0.16 g) increased the recovery (100%). Fig. 3

Table 5
Analysis of variance for the fitted quadratic polynomial model for optimization of digestion parameters for cadmium.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value (Prob > F)
Model	3132.93	9	348.10	6.28	0.0041[a]
HNO_3 (x_1)	1871.87	1	1871.87	33.79	0.0002[a]
H_2SO_4 (x_2)	29.46	1	29.46	0.53	0.4826
CRM amount (x_3)	366.79	1	366.79	6.62	0.0277[a]
x_1x_2	122.46	1	122.46	2.21	0.1679
x_1x_3	67.86	1	67.86	1.22	0.2943
x_2x_3	326.40	1	326.40	5.89	0.0356[a]
x_1^2	243.80	1	243.80	4.40	0.0623
x_2^2	40.36	1	40.36	0.73	0.4134
x_3^2	48.09	1	48.09	0.87	0.3735
Residual	554.05	10	55.41		
Lack of Fit	282.92	5	56.58	1.04	0.4819
Pure Error	271.13	5	54.23		
Cor Total	3686.98	19			
$R^2 = 0.849725$					

[a] Significant at "Prob $> F$" less than 0.05.

Table 6
Analysis of variance for the fitted quadratic polynomial model for optimization of digestion parameters for lead.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value (Prob > F)
Model	5390.93	9	598.99	12.28	0.0003[a]
HNO_3 (x_1)	1234.64	1	1234.64	25.32	0.0005[a]
H_2SO_4 (x_2)	297.49	1	297.49	6.10	0.0331[a]
CRM amount (x_3)	3099.67	1	3099.67	63.57	$< 0.0001^a$
x_1x_2	0.32	1	0.32	6.563E-003	0.9370
x_1x_3	63.85	1	63.85	1.31	0.2792
x_2x_3	1.62	1	1.62	0.033	0.8590
x_1^2	93.15	1	93.15	1.91	0.1970
x_2^2	508.98	1	508.98	10.44	0.0090[a]
x_3^2	27.27	1	27.27	0.56	0.4718
Residual	487.59	10	48.76		
Lack of Fit	342.60	5	68.52		
Pure Error	144.99	5	29.00		
Cor Total	5878.52	19			
$R^2 = 0.917051$					

[a] Significant at "Prob $> F$" less than 0.05.

presents the effects of the sulphuric acid volume and the CRM amount on the lead recovery. An increase in this recovery was observed with decreasing CRM amounts. Sulphuric acid volume of 3.0 (mL) and CRM amount of 0.14 (g) led to the maximum recovery (86%).

Using the model, the optimum cadmium recovery within the experimental region was determined to require 3.0 mL of HNO_3, 2.0 mL of H_2SO_4, and 0.13 g of CRM. The optimum lead recovery within the experimental region was determined to require 4.0 mL of HNO_3, 3.0 mL of H_2SO_4, and 0.15 g of CRM.

3.2. Analytical Characteristics

Quality factors, including the limit of detection (LOD) and repeatability, were investigated to evaluate the
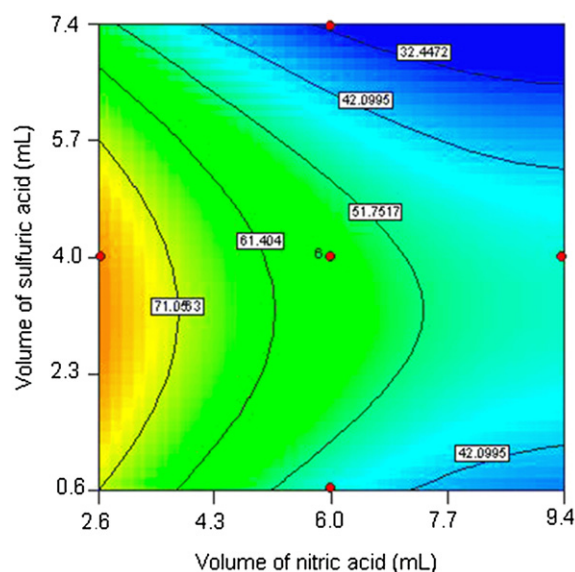
Fig. 1. Contour plot of the combined effects of nitric acid and sulphuric acid volume on the recovery of lead.
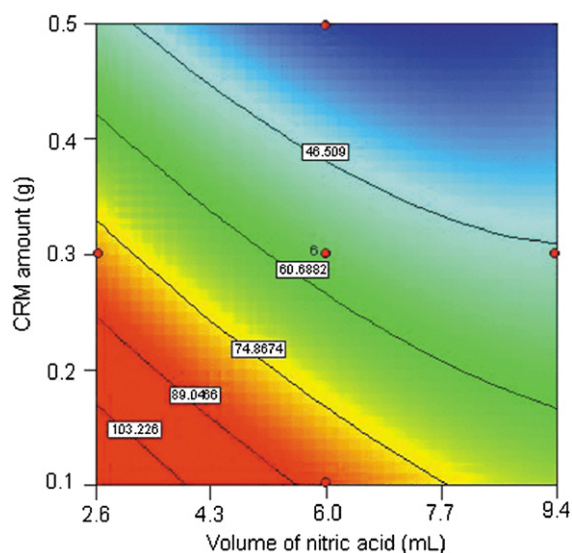
Fig. 2. Contour plot of the combined effects of nitric acid volume and CRM amount on the recovery of lead.

analytical performance of the proposed method under the optimal conditions. The LODs for AAS were calculated for the concentration of analytes corresponding to three times the standard deviation of the blank signal. The LOD for PVC material was calculated by multiplying each of the values obtained in the liquid sample by a factor of 167 (0.15 g sample and a final volume of 25 mL). The LODs of Cd and Pb for the reference plastic material were 1.6 and 6.4 mg kg^{-1}, respectively. This LOD value of Pb is close to the value of 2.25 obtained with closed microwave digestion and ICP-AES determination [5]. The accuracy of the models was validated under the optimal conditions obtained from the central composite design. The results of metal concentration determination with the certified plastic materials are given in Table 7.
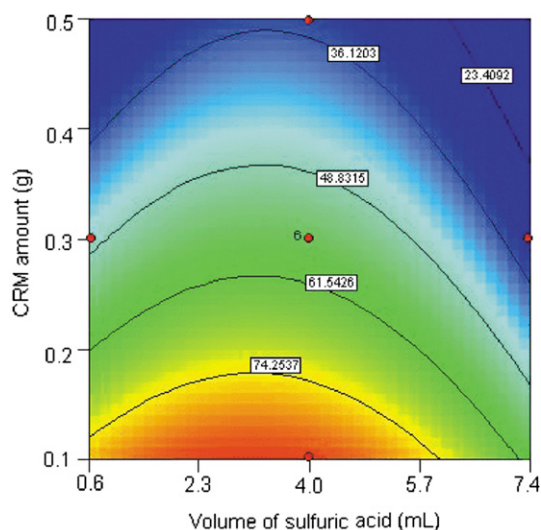

Fig. 3. Contour plot of the combined effects of sulphuric acid volume and CRM amount on the recovery of lead.

Table 7
Results obtained for determination of Cd and Pb in Fluxana PVC2 CRM by AAS ($n = 3$).

Elements	Cd	Pb
Certified value ± uncertainty (mg kg^{-1})	35 ± 3	89 ± 6
Proposed digestion procedure		
Mean (mg kg^{-1})	33	82
Standard deviation (mg kg^{-1})	4	7
Absolute difference, Δ_m	2	7
Expanded uncertainty, U_Δ	5.5	10
Apparent recovery (R)	94	92

The absolute difference (Δ_m) between the mean measured value and the certified value was calculated as $\Delta_m = |c_m - c_{crm}|$, where; c_m is the mean measured value and c_{crm} is the certified value. The difference between the certified and measured values with its uncertainty, i.e., the combined uncertainty of the certified and measured values, was analyzed. The uncertainty of Δm is u_Δ, which was calculated from the uncertainty of the certified value and the uncertainty of the measurement result according to the following formula:

$$u_\Delta = \sqrt{u_m^2 + u_{crm}^2} \qquad (2)$$

where u_Δ is the combined uncertainty of the result and the certified value, u_m is the uncertainty of the measurement result, and u_{crm} is the uncertainty of the certified value. The expanded uncertainty U_Δ, corresponding to a confidence interval of approximately 95%, was obtained by multiplication of u_Δ by a coverage factor (k), usually equal to 2. To evaluate the method performance, Δ_m was compared with U_Δ: If $\Delta_m \leq U_\Delta$, then there was no significant difference between the measurement result and the certified value. As can be seen in Table 7, the expanded uncertainties were larger than the difference Δ_m between the certified and measured values. The measured mean values were, therefore, not significantly different from the certified values.

4. Conclusions

The proposed procedure could be useful in studies of Cd and Pb in PVC materials. Other elements, such as Hg and Cr, that are important for regulation were not studied because of the lack of relevant CRMs for PVC. Spiked samples are not preferred because these samples cannot represent real conditions.

This study demonstrated the utility of experimental design optimisation of the acid digestion conditions in a reasonable number of experiments. A second-order model was obtained to describe the relationship between the recovery of Pb and the acid volumes and CRM amount. The results indicated that volume of nitric acid, the volume of sulphuric acid and the CRM amount were the significant factors in the sample digestion procedure.

A remarkable advantage of the method is the simplicity of the equipment used. A block digester, used for Kjeldahl nitrogen determination, and an atomic absorption spectrophotometer are the pieces of equipment required. The digestion time was longer than that of microwave-assisted

digestion procedures. However, the proposed method has the advantages of being able to process a high number of samples simultaneously (up to 12 vials in the heating block) and of low cost compared with microwave equipment.

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