

Determination of Cadmium, Chromium and Lead in Polymers by ICP-OES Using a High Pressure Asher (HPA)

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The proposed method for an effective assay of Cd, Cr and Pb in several polymer samples has been validated. The determination was carried out using ICP-OES after a high pressure asher (HPA) digestion at pressure and temperatures up to 13 MPa and 320 °C, respectively. Polymer based materials were totally oxidized with nitric acid in a HPA chamber and determined by ICP-OES. Validation parameters such as linearity, matrix effect, limit of detection (LOD), limit of quantitation (LOQ), accuracy and precision (repeatability, intermediate precision and reproducibility) were assessed. The LOD and LOQ in the sample were ranged from 0.98 to 1.18 mg kg⁻¹ and 2.93 to 3.55 mg kg⁻¹, respectively, relying on the analyte. The proposed method had a good accuracy and precision for repeatability, intermediate precision with respect to days and analysts and reproducibility expressed as inter-laboratory study. The developed method was simple to use, suitable and applicable to various kinds of polymers.

Key Words: ICP-OES, High pressure asher (HPA), Metals

Introduction

The Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment, commonly referred to as RoHS,¹ was adopted in February 2003 by the European Union. The RoHS directive came into force on 1 July 2006. This directive restricts the use of six hazardous substances containing lead (Pb), cadmium (Cd) and hexavalent chromium (Cr^{VI}) in the manufacture of various types of electronic and electrical equipment including several polymers. Environmental contamination due to those metals has become a matter of serious concern because of the disposal of industrial and other waste.

Chromium (Cr) is considered essential as well as toxic to mankind, in particular with respect to two oxidation states, which are trivalent chromium (Cr^{III}) and hexavalent chromium (Cr^{VI}). The trivalent form is relatively non-toxic, whilst the hexavalent chromium is harmful to human health and natural environment.² Even though two kinds of chromium have affected human beings differently, the knowledge about total chromium content represents the first step of whether there is hexavalent chromium in the products or not. Therefore, the determination of Cd, Cr and Pb in polymer based products is an important task. The development of the inductively coupled plasma as a source for optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) has provided sensitive analytical techniques to detect such elements. These analytical methods commonly require the sample to be presented as a dilute aqueous solution, simplifying sample preparation. The organic matrix can be removed by diverse digestion methods, including dry ashing, wet digestion (or oxidation) and microwave digestion.

Dry ashing and wet oxidation techniques are slow and can cause losses of metals or contaminaton from external sources.³⁻⁶ However, microwave digestion systems are rapid and enable us to minimize sample contaminaiton and the loss of volatile

elements. In spite of these advantages, microwave-digested samples may not be as fully destroyed and may require further treatment for the removal organic matrices.^{5,6}

In order to guarantee complete or almost complete decomposition of samples, the use of high pressure and high temperature was employed. One of the most useful systems is the high pressure asher (HPA) by Knapp,⁶⁻⁸ which results in a clear solution suitable for the introduction of ICP-OES or ICP-MS. The HPA can be used for the samples at temperatures up to 320 °C or pressure to 13 MPa, under controlled temperature and pressure. In this method the weighed samples are transferred into small quartz vessels with the appropriate acid digestion solution. These are capped with PTFE tape and pure quartz lids, placed in a heating block, and the autoclave chamber closed and pressurized with nitrogen. The nitrogen gas serves to support the digestion vessels by equalizing pressure inside and outside of the vessels, as they are heated. These processes can also allow to eliminate contamination and loss of analytes.

In the present study, a powerful sample preparation method for an accurate and precise determination of these three heavy metals (Cd, Cr and Pb) in polymer matrices utilizing HPA decomposition systems was proposed. In order to validate the proposed method, a series of validation parameters, such as linearity, matrix effect, limit of detection (LOD), limit of quantitation (LOQ), accuracy and precision, were evaluated.⁹⁻¹⁵ Experiment was conducted using six types of polymer matrices including six certified reference materials (CRMs).

Experimental

Reagents. As a diluent, water (resistivity of 18.2 MΩ cm) was deionized in a Mili-DI system (Milipore, USA). An electronic grade of 70% v/v nitric acid obtained from Dongwoo Fine-chem (Seoul, Korea) was used for the preparation of samples, calibration solutions and blanks. The working standard solutions for

constructing the calibration curves of Cd, Cr and Pb were prepared from 100 mg L⁻¹ multi-elemental standard solutions (Perkin-Elmer, USA). A multi standard solution, containing 2.0, 2.0 and 2.5 mg L⁻¹ for Cd, Cr and Pb, respectively, was prepared from AccuStandard (USA) and used without dilution.

Materials. Nine polymer materials were chosen for this method validation. Of all polymers mentioned here, six of them were made up of three kinds of polymer matrices at low and high concentration levels, which are certified reference materials (CRMs). As a CRM, ERM-EC680 and ERM-EC680k based on polyethylene (PE) were produced from the European Reference Material, Institute for Reference Materials and Measurements (IRMM) (B-2440 Geel, Belgium). NMIJ CRM 8103-a and NMIJ CRM 8102-a showing the certified value of Cd, Cr and Pb in acrylonitrile-butadiene-styrene (ABS) were purchased from National Metrology Institute of Japan (Ibaraki, Japan). Moreover, JSAC 0602-2 and JSAC 0601-2 consisting of polyester resin tips were supplied as CRMs by the Japan Society for Analytical Chemistry (Tokyo, Japan). In contrast, the rest were KEPITAL F20-03, KEPAMID-66 2500 and KEPEX 3500, which were made up of polyoxymethylene (POM), polyamide 66 (PA66) and polybutylene terephthalate (PBT), respectively. These three materials used for spiked samples were produced by Korea Engineering Plastics Co., Ltd (Seoul, Korea).

Instrumentation. Sample digestion was performed in 90 mL pure quartz vessels in a high pressure asher (HPA) provided by Anton-Paar GmbH (Graz, Austria). After acid digestion of polymer samples with HPA, the concentrations of heavy metals were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2100DV, Perkin-Elmer, Norwalk, CT, USA). The ICP-OES analysis was carried out on an axially viewed plasma. The emission intensity measurements were made under the conditions listed in Table 1. The spectral lines for the analysis were chosen in order to obtain maximum sensitivity and minimum interference: Cd (228.802 nm), Cr (267.716 nm) and Pb (220.353 nm).

Sample Digestion Procedure. For HPA digestion, ca 0.1 g of a polymer sample was weighed into a 90 mL quartz vessel containing 4 - 6 mL of nitric acid, and spiked appropriately using a standard solution. All glasswares were washed with deionized water and dried in a dust-free environment. The sample vessels were sealed with PTFE tape and quartz lids and then, the vessels were loaded into the HPA autoclave chamber which was filled with nitrogen up to the desired pressure of 10 MPa. A safety valve was used for preventing overpressure caused by heating not to exceed 13 MPa. Samples were subjected to four steps: (1) ramp heating from room temperature to 80 °C, (2) heating from 80 °C to 160 °C within 30 minutes, (3) ramp heating up to 300 °C and (4) holding at 300 °C for 90 minutes.

With the completion of the temperature control program, the chamber should cool down to a temperature of less than 40 °C. It took 20 - 30 minutes to reach room temperature. The nitrogen needed to be slowly released from the chamber in order to allow the gas pressure in the chamber to drop below that inside the sample vessel. After removal from the HPA, samples were diluted to 40 - 50 mL with doubly distilled water before the element analysis. The resulting solutions were clear and colorless. A digestion of a blank sample was also carried out according to the

Table 1. The optimum operating conditions for ICP-OES

RF Power	1300 W
Plasma flow rate	15 L min ⁻¹
Nebulizer flow rate	0.7 L min ⁻¹
Auxiliary flow rate	0.2 L min ⁻¹

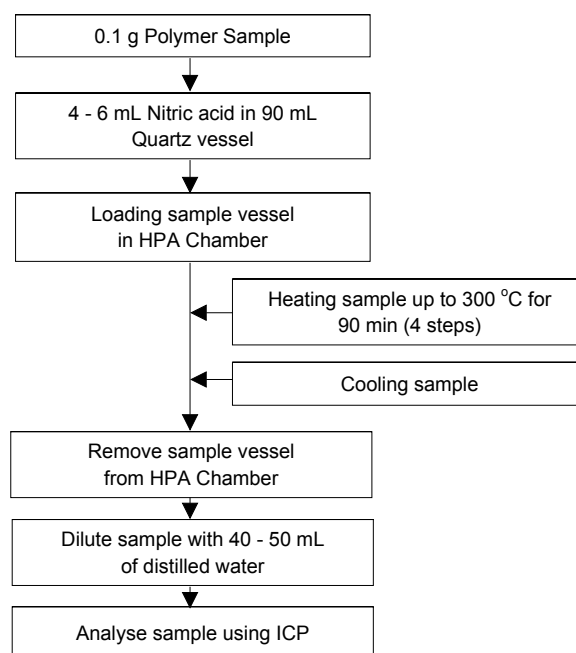


Figure 1. Schematic diagram of sample preparation using HPA chamber.

above procedure. Figure 1 shows the schematic diagram of sample preparation using HPA chamber.

Validation Parameters. The following validation parameters were evaluated: linearity, matrix effect, limit of detection (LOD), limit of quantitation (LOQ), accuracy (bias or recovery) and precision (repeatability, intermediate precision and reproducibility).⁹⁻¹⁵ During the course of this method development, the acceptability of analytical data corresponded directly to the criteria used to validate method. The linearity for calibration curves was required for the correlation coefficient of the lines to be more than 0.995. To examine whether a polymer matrix can interfere the analytes, matrix matching calibration and standard additions method were employed. The LOD, according to the Technical note 17 by NATA,¹¹ was assessed by the analysis of spiked samples with decreasing concentrations of target elements. The LOQ defined as 3 times the LOD was also estimated.^{10,11} The acceptance criteria for accuracy and precision were bias within $\pm 20\%$ of the accepted reference value and relative standard deviation (RSD) of less than 20%, respectively.

Results and Discussion

Linearity and Matrix Effects. The linearity of an analytical method is defined as the ability of the method to obtain test results proportional to the concentration of analyte in the sample.¹⁶ For the establishment of linearity, two methods of

Table 2. Correlation coefficients (R^2) of both calibration graphs and measured values (in mg kg^{-1}) and recoveries of the analytes in ERM-EC680

	Cd		Cr		Pb	
	Conventional calibration	Matrix matching	Conventional calibration	Matrix matching	Conventional calibration	Matrix matching
Correlation coefficient(R^2)	0.9999	0.9999	0.9999	0.9999	0.9999	1.0000
Certified value	140.8	140.8	114.6	114.6	107.6	107.6
Measured value	143.9	143.4	115.7	112.0	111.6	110.4
Recovery ^a (%)	102.2	101.8	101.0	97.7	103.7	102.6

^aRecoveries obtained from 2 replicates of analyses.

Table 3. Results of linear fitting of standard addition data for ERM-EC680, NMIJ 8102-a and JSAC 0601-2

Matrix	CRM	Element	Certified value / mg kg^{-1}	Slope	y-intercept /cps	x-intercept / mg L^{-1}	Measured value ^a / mg kg^{-1}	Recovery (%)
PE	ERM- EC680	Cd	140.8	1001652.7	290927.6	-0.2904	145.2	103.1
		Cr	114.6	1129856.8	267533.6	-0.2368	118.4	103.3
		Pb	107.6	78009.7	18062.2	-0.2315	115.8	107.6
ABS	NMIJ 8102-a	Cd	10.8	1055850.8	23618.9	-0.0224	11.2	103.6
		Cr	27.9	1243695.1	69217.1	-0.0557	27.8	99.7
		Pb	108.9	86301.4	18475.0	-0.2141	107.0	98.3
Polyester	JSAC 0601-2	Cd	5.2	1072307.8	12845.8	-0.0120	6.0	115.2
		Cr	10.8	1230238.7	30012.5	-0.0244	12.2	112.9
		Pb	11.6	61398.5	1667.7	-0.0272	13.6	117.1

^aMeasured values calculated as - x-intercept times total sample volume divided by polymer sample weight.

calibration, matrix matching calibration and conventional calibration, were employed. Calibration solutions containing five concentration levels for each element ($0 - 10 \text{ mg L}^{-1}$) were prepared, with and without addition of POM, one kind of polymers. The correlation coefficient (R^2) expressed as the linearity of the calibration curve, were obtained by calculation of a regression line by the least squares method. To assess the accuracy for both calibration graphs constructed here, two independent replicate determinations on CRM ERM-EC680 were performed.

In Table 2, the correlation coefficient (R^2) and the recovery results are shown. As can be seen, the coefficients of determination for these plots are above 0.999, indicating an excellent linearity relationship between each element and the detector response. Also, these heavy metals were recovered in the range of 97.7 to 103.7%. Despite matrix matching calibrations, the results obtained by HPA and ICP-OES were satisfactory.

In addition, the method of standard additions was applied to investigate whether there exist matrix effects through this proposed method. A standard addition calibration curve was constructed by plotting intensity of an analyte versus concentration. We performed the experiments by spiking known amounts of the target metals to three CRM samples, ERM-EC680, NMIJ 8102-a and JSAC 0601-2.^{11,17,18,19} 0.1 g of CRM was decomposed in the HPA using the nitric acid and increasing amounts of the element standard. After the complete dissolution of the samples, samples were diluted to 50 mL with deionized water.

Table 3 shows experimental results employing the method

of standard additions. It is observed that the recoveries for three metals in JSAC 0601-2 were slightly higher than the others. In the case of JSAC 0601-2, the low levels around 10 mg kg^{-1} probably contributed to the high bias values of analytes. It is known that the range of acceptable recovery percentages tends to be broadened as the analyte concentration is low.¹⁰ This fact gives the reason. Despite the recovery values of JSAC 0601-2, the measurement results for three CRMs were in good accuracy with the recoveries ranging from 98.3 to 117.1%. This demonstrates that a sample matrix has no effect on the accuracy of trace elemental analysis during this procedure.

Another approach for studying matrix effects in the samples was carried out by comparison of calibration slope for the matrix matching samples with that obtained for the conventional standard solutions. The *Student's t* test was applied to both cases of slope values, according to Harris.²¹ The *t* test was used to decide whether two sets of replicate measurements gave the same or different results, within a stated confidence level. To find the answer to this problem, we computed $t_{\text{calculated}}$ with the several formulas described by the Harris's textbook²¹ and compared it with t_{table} obtained from the values of *Student's t* in the same text. If t_{table} is greater than $t_{\text{calculated}}$ at the specified confidence level, the two results are considered to be same.

As can be seen in Table 4, comparing two slopes for each element, no was observed significant differences a 95% confidence, when the *Student's t* test was applied. In other words, it can be clearly seen that both calibration plots were parallel, so

Table 4. Calibration slope data for three elements, with or without a polymer matrix

Sample no.	Cd		Cr		Pb	
	Without matrix	With matrix	Without matrix	With matrix	Without matrix	With matrix
#1	982633.9	1001652.7	1087842.4	1129856.8	68933.8	78009.7
#2	1004275.0	1055850.8	1129945.3	1243695.1	78630.0	86301.4
#3	-	1072307.8	-	1230238.7	-	61398.5
Mean	993454.5	1043270.4	1108893.9	1201263.5	73781.9	75236.5
SD ^a	15302.6	36969.4	29771.2	62205.0	6856.2	12681.0
<i>t</i> _{calculated}	1.735		1.887		0.144	
<i>t</i> _{table} ^b	3.182		3.182		3.182	
	<i>t</i> _{table} > <i>t</i> _{calculated}		<i>t</i> _{table} > <i>t</i> _{calculated}		<i>t</i> _{table} > <i>t</i> _{calculated}	

^aStandard deviation. ^b*t* value for 3 degrees of freedom and 95% confidence from the table in Harris's book.²¹

Table 5. Limits of detection (LODs) and Limits of quantitation (LOQs) for three metals in matrices

Matrix	Material	Element	S ₀	LOD ^a /μg L ⁻¹	LOD ^b /mg kg ⁻¹	LOQ/mg kg ⁻¹
POM	KEPITAL F20-03	Cd	0.1110	0.3	0.27	0.80
		Cr	0.0852	0.3	0.20	0.61
		Pb	0.5668	1.7	1.36	4.08
PA66	KEPAMID-66 2500	Cd	0.0351	0.1	0.08	0.25
		Cr	0.1150	0.3	0.28	0.83
		Pb	0.4122	1.2	0.99	2.97
PBT	KEPEX 3500	Cd	1.0755	3.2	2.58	7.74
		Cr	1.1978	3.6	2.87	8.62
		Pb	0.4992	1.5	1.20	3.59
Overall	-	Cd	-	-	0.98	2.93
		Cr	-	-	1.12	3.35
		Pb	-	-	1.18	3.55

^aLOD = Limit of detection in solution (in units of μg L⁻¹). ^bLOD = Limit of detection in the sample (in units of mg kg⁻¹) taken as the LOD in solution divided by 1.25 because of considering the sample dissolution procedure.

there was no need to compensate for matrix effects.^{2,10,11,14,20} Consequently, since matrix effects were not apparent, we allowed to use the matrix-free calibration.

Limit of Detection (LOD) and Limit of Quantitation (LOQ). The limit of detection (LOD) is defined as the smallest amount or concentration of an analyte that can be reliably distinguished from zero.¹¹ In order to find the LOD, a mass of 0.05 g of each polymer, KEPITAL F20-03, KEPAMID-66 2500 and KEPEX 3500, was used. The decomposed samples by the HPA were brought to a volume of 40 mL with deionized water. The LOD was determined by analysing seven replicate samples at least each of three concentrations, the lowest concentration being nearly close to zero. From a graph of standard deviation (SD) against concentration, we can extrapolate to estimate the standard deviation at zero concentration (S₀). The LOD was calculated as 3 times S₀ (3S₀) under 95% confidence level.¹¹ In contrast to the LOD, the limit of quantitation (LOQ), known as the limit of reporting, is the lowest concentration of an analyte that can be determined with an acceptable level of accuracy and precision during a test.¹⁶ As mentioned above, the LOQ was determined

based on three times the LOD.

In Table 5, the LODs and LOQs for each of the elements are shown. The LOD values were in the range of 0.08 - 2.58 mg kg⁻¹ for Cd, 0.02 - 2.87 mg kg⁻¹ for Cr and 0.99 - 1.36 mg kg⁻¹ for Pb. The average LOQ values for Cd, Cr and Pb were 2.93 mg kg⁻¹, 3.35 mg kg⁻¹ and 3.55 mg kg⁻¹, respectively. These results demonstrate that the proposed method can be applied to determine analyte concentrations greater than the overall mean value of LOQ between 2.93 and 3.55 mg kg⁻¹.

Accuracy and Precision. The accuracy of an analytical method describes the closeness of a result to a true value.^{11,16} Trueness is normally expressed in terms of bias or recovery. The deviation of the mean from the true value serves as the measure of accuracy. This indicates that the trueness of an analysis result improves as bias decreases. In the present work, accuracy was determined by replicate analysis of six CRM samples containing already known amounts of the analytes.

As for the term of precision, the Eurachem Guide defined it as the closeness of agreement between independent test results obtained under stipulated conditions.¹⁶ Since precision depends

Table 6. Testing schemes for repeatability and intermediate precision

Matrix	Repeatability (6 CRMs, n = 7)		Intermediate precision			
			4 different days (2 CRMs, n = 3)		3 different analysts (3 CRMs, n = 5)	
	Concentration level		Concentration level		Concentration level	
	high	low	high	low	high	low
PE	ERM-EC680	ERM-EC680k			ERM-EC680	
ABS	NMIJ 8103-a	NMIJ 8102-a	NMIJ 8103-a		NMIJ 8103-a	
Polyester	JSAC 0602-2	JSAC 0601-2		JSAC 0601-2		JSAC 0601-2

Table 7. Testing schemes for reproducibility

	Sample decomposition/test method	Sample weight/g	Acid
Laboratory-A	HPA	0.10	4 - 6 mL HNO ₃
Laboratory-B	Microwave/EPA 3052	0.20	11 mL HNO ₃
Laboratory-C	Microwave/EPA 3052	0.27 - 0.31	8 mL HNO ₃ + 0.5 mL H ₂ O ₂
Laboratory-D	HPA	0.04 - 0.10	2 mL HNO ₃
Laboratory-D	Microwave/EPA 3052	0.29 - 0.31	7 mL HNO ₃ + 3 mL HCl + 2 mL H ₂ O ₂
Laboratory-E	Wet digestion/EN 1122 (Cd and Cr) and KS M 3211 (Pb)	0.50	10 mL H ₂ SO ₄ + 40 mL HNO ₃ + 20 mL (1:1) HNO ₃

Table 8. Accuracy and precision in repeatability test (n = 7)

Matrix	CRM	Element	Certified value/mg kg ⁻¹	Measured value/mg kg ⁻¹	RSD (%)	Recovery (%)
PE	ERM-EC680	Cd	140.8	136.4	2.5	96.8
		Cr	114.6	111.0	3.5	96.8
		Pb	107.6	110.7	3.4	102.9
	ERM-EC680k	Cd	19.6	19.1	4.7	97.6
		Cr	3-16	3.1	10.9	-
		Pb	13.6	12.1	7.1	88.7
ABS	NMIJ 8103-a	Cd	106.9	104.0	2.1	97.3
		Cr	269.5	273.4	3.0	101.4
		Pb	1084	1142	2.6	105.4
	NMIJ 8102-a	Cd	10.8	9.4	4.3	87.4
		Cr	27.9	24.9	2.7	89.4
		Pb	108.9	115.7	3.2	106.2
Polyester	JSAC 0602-2	Cd	51.7	51.4	4.6	99.4
		Cr	108.8	109.3	4.0	100.4
		Pb	109.3	112.5	4.6	102.9
	JSAC 0601-2	Cd	5.2	4.4	10.4	84.3
		Cr	10.8	10.2	4.9	94.8
		Pb	11.6	10.2	11.1	88.2

only on the spread of results and does not relate to the true value or specified value, it is usually stated in terms of relative standard deviation (RSD) of replicate results.^{11,16} To investigate the precision described here, six CRMs were also used.

Precision is divided into three categories: repeatability, intermediate precision and reproducibility.^{10,11,13,16,20} The three kinds of precision testing schemes were outlined in Table 6-7. Repeatability tests were conducted during a short interval of time

in one laboratory by one operator using the same equipment. Seven replicates at each of 6 CRMs were analysed with the aim of checking repeatability. In the case of intermediate precision, we took into account the within-laboratory variations due to two factors, different days and different analysts. Refer to Table 6. The term reproducibility is assessed by means of the precision between laboratories. Five laboratories accredited by KOLAS (Korea Laboratory Accreditation Scheme)²² took part in this

Table 9. Determination of chromium in ERM-EC680k with the diverse sample decomposition, from the ref. 26

Sample decomposition/acid	Analytical instrument	Sample weight/g	Measured value/mg kg ⁻¹
Microwave/5 mL HNO ₃ + 2 mL H ₂ O ₂	ICP-MS	0.15	13.467
Microwave/15 mL HNO ₃ + 1 mL HF	ICP-OES	0.53	4.633
HPA/4 mL HNO ₃ + 1 mL HCl	ICP-OES	0.25	3.001
HPA/4 mL HNO ₃ + 1 mL HCl	SF-ICP-MS ^a	0.25	2.936
Microwave/two digestion runs: (1) 5 mL HNO ₃ + 1 mL HF + 1 mL H ₂ O ₂ ; (2) 5 mL H ₃ BO ₃	ICP-OES	0.5	9.932
MLS (Milestone UltraClave)/4 mL HNO ₃ + 0.2 mL HClO ₄	ICP-OES	0.06 - 0.12	16.167
MLS (Milestone UltraClave)/4 mL HNO ₃ + 0.2 mL HClO ₄	ICP-MS	0.2	3.482

^aSector field inductively coupled plasma mass spectrometry.

Table 10. Accuracy and precision of the within-laboratory tests due to 4 different days (n = 3)

	Matrix	ABS			Polyester		
	CRM	NMIJ 8103-a			JSAC 0601-2		
	Element	Cd	Cr	Pb	Cd	Cr	Pb
	Certified value/mg kg ⁻¹	106.9	269.5	1084	5.2	10.8	11.6
Day-1	Measured value/mg kg ⁻¹	105.4	270.7	1152.7	4.8	11.1	11.3
	RSD (%)	0.2	3.0	1.3	4.8	7.3	5.4
	Recovery (%)	98.6	100.5	106.3	91.7	103.1	97.7
Day-2	Measured value/mg kg ⁻¹	102.0	268.2	985.8	4.5	9.3	10.5
	RSD (%)	0.3	2.0	2.6	7.7	6.7	9.4
	Recovery (%)	95.4	99.5	90.9	86.5	86.1	90.5
Day-3	Measured value/mg kg ⁻¹	100.9	262.1	1098.7	5.5	11.0	11.7
	RSD (%)	1.1	2.2	0.8	12.2	0.9	11.9
	Recovery (%)	94.4	97.3	101.4	105.1	101.9	101.1
Day-4	Measured value/mg kg ⁻¹	102.2	263.3	1131	5.0	10.7	12.5
	RSD (%)	1.9	2.7	1.4	2.3	1.1	4.4
	Recovery (%)	95.6	97.7	104.4	96.8	99.4	107.5
Overall	Mean/mg kg ⁻¹	102.7	266.1	1092	4.9	10.5	11.5
	RSD (%)	1.9	1.5	6.8	8.3	8.0	7.1
	Recovery (%)	96.0	98.7	100.7	95.0	97.6	99.2

inter-laboratory study. The recovery and RSD were estimated from the analysis of three CRMs, *i.e.* ERM-EC680, NMIJ 8103-a and JSAC 0601-2 under specified conditions in Table 7. The participants were at liberty to choose any method of analysis they wished. All individual laboratories analysed three replicates for each CRM. The measurement data were collected by Korea Engineering Plastics Co., Ltd (laboratory-A). Laboratory-D adopted two ways of sample decomposition including a HPA technique. All laboratories adopted to determine the heavy metal contents with ICP-OES, whereas there were three main methods of sample digestion summarised in Table 7: (1) wet decomposition (*e.g.* BS EN 1122 and KS M 3211); (2) microwave digestion (*e.g.* EPA Method 3052); and (3) HPA method by heating a sample with a strong acid in a pressure vessel.²³⁻²⁵

Repeatability. Table 8 reveals the results of the measurements

of the diverse CRM samples in repeatability experiments. The excellent agreement of the 7 replicates for each material was reflected by the RSD ranging from 2.1 to 11.1% and recovery 84.3 to 106.2%. From a closer look at the data, it can be observed that the accuracy and precision of Cd and Pb in JSAC 0601-2 are relatively low in comparison with other results. These values are probably attributable to the low levels for Cd and Pb, approximately 5 - 10 mg kg⁻¹. As shown previously in Table 5, the LOQs for Cd and Pb varied from 0.25 to 7.74 mg kg⁻¹ and 2.97 to 4.08 mg kg⁻¹, respectively. This corresponds to the fact that higher variability is expected as the analyte levels approach the lower limit of quantitation (LLOQ).^{10,13,14,20} Besides, concerning the low concentrations, a slight difference of measurement data can make a relatively big difference to the recovery and RSD owing to the calculation procedures of obtaining the two validation parameters.

Table 11. Accuracy and precision of the within-laboratory tests due to 3 different analysts (n = 5)

	Matrix	PE			ABS			Polyester		
	CRM	ERM-EC680			NMIJ 8103-a			JSAC 0601-2		
	Element	Cd	Cr	Pb	Cd	Cr	Pb	Cd	Cr	Pb
	Certified value/mg kg ⁻¹	140.8	114.6	107.6	106.9	269.5	1084	5.2	10.8	11.6
Analyst-1	Measured value/mg kg ⁻¹	140.1	115.0	108.1	102.2	273.2	1082	4.4	9.9	10.5
	RSD (%)	1.3	2.1	2.0	4.2	4.6	3.1	5.2	2.1	10.3
	Recovery (%)	99.5	100.3	100.5	95.6	101.4	99.8	85.4	91.7	90.3
Analyst-2	Measured value/mg kg ⁻¹	134.1	111.9	99.8	103.4	274.9	1023	5.1	11.1	12.7
	RSD (%)	1.7	2.6	3.4	0.7	3.6	1.2	6.8	1.4	5.1
	Recovery (%)	95.3	97.7	92.8	96.7	102.0	94.4	98.8	103.1	109.3
Analyst-3	Measured value/mg kg ⁻¹	138.4	112.0	107.0	99.6	261.2	1067	4.8	10.3	10.3
	RSD (%)	2.3	2.8	1.2	3.6	4.5	4.6	5.8	7.9	11.6
	Recovery (%)	98.3	97.7	99.4	93.2	96.9	98.5	93.1	95.4	88.6
Overall	Mean/mg kg ⁻¹	137.5	113.0	105.0	101.8	269.7	1057	4.8	10.4	11.1
	RSD (%)	2.2	1.5	4.3	1.9	2.8	2.9	7.3	6.1	11.9
	Recovery (%)	97.7	98.6	97.6	95.2	100.1	97.5	92.4	96.7	96.1

For ERM-EC680k, we were not able to estimate the recovery for Cr since the Cr content ranges from 3 to 16 mg kg⁻¹, not only one value.²⁶ According to the certification report of ERM-EC680k, inorganic pigments as the form of Cr₂O₃ were added to achieve the Cr content and then, blended with polyethylene and extruded. This report shows that the presence of Cr₂O₃ causes to be difficult to dissolve in acids. Table 9 lists the measured Cr values, described well by the report,²⁶ relying on various sample preparation. The Cr level of ERM-EC680k we detected is 3.1 mg kg⁻¹ that is very close to the Cr concentrations between 2.9 and 3.0 mg kg⁻¹ by HPA decomposition from the Table 9.

As shown from the test results using six CRMs, the accuracy and precision achieved by this method met the chosen performance criteria, irregardless of concentration levels.

Within-laboratory Studies Due to Days and Analysts. To evaluate intermediate precision, two factors, days and analysts, were taken into consideration. At first, each experiment replication (n = 3) was made on four different days. Two CRMs containing the high and low concentration levels, respectively, were analysed. As a result from Table 10, the recoveries varied from 86.1 to 107.5%, while the RSDs varied from 0.2 and 12.2%, indicating that reasonably good accuracy and precision were obtained over a wide concentration range (5.2 - 106.9 mg kg⁻¹ for Cd, 10.8-269.5 mg kg⁻¹ for Cr and 11.6-1084 mg kg⁻¹ for Pb). This confirms that proposed method is valid although these experiments were carried out on 4 different days.

To examine the effects of analysts, furthermore, three CRM samples consisting of a different matrix were analysed by three different operators. Table 11 is a summary of the accuracy and precision results (n = 5), determined by three participants. The measured analyte concentrations showed the RSDs clearly below 12%. However, the low metal contents of JSAC 0601-2 led to the relatively high RSD values due to greater variability at low analyte concentrations. The bias did not deviate by more than 15%, which means all recoveries were within acceptable

limits (80 - 120%). For those reasons, in spite of several analysts, it can be clearly seen that this analytical method complies with established criteria for the accuracy and precision.

Reproducibility. For reproducibility expressed as precision between laboratories, inter-laboratory study on the determination of three heavy metals in polymer matrices was conducted. As shown in Table 12, the participating laboratories analysed the specified CRMs by their method of choice and then, the accuracy and precision for the analysis of those materials were compared. The data obtained from laboratory-D utilizing the HPA to digest samples showed the acceptable accuracy (*i.e.* recovery = 82.5 - 107.0%) and precision (*i.e.* RSD = 1.7 - 17%). It points to the fact that when using the HPA system we suggested very good accuracy and precision can be achieved. For JSAC 0601-2, the measured Cd concentration detected by laboratory-E employing wet digestion showed a high bias, almost +31%. It seemed likely that the LOQ for Cd in laboratory-E was very close to the certified Cd level of 5.2 mg kg⁻¹. Apart from this one exception, the recoveries and RSDs were in the range of 82.5 - 117.6% and 0.5 - 11.9%, respectively, so that good accuracy and precision were reached. Moreover, there were no significant differences in the recoveries and RSDs among the five laboratories. Therefore, the reproducibility assessed by means of an inter-laboratory trial permits the acceptability of this analytical method.

Conclusions

A through study has been carried out on the proposed measurement procedure for Cd, Cr and Pb in polymer matrices. Prior to the determination of trace elements by ICP-OES, efficient sample digestion is recognised as an essential pretreatment. For complete oxidation of organic compounds, the HPA technique was employed. In this work, to validate this suggested method, method validation was done by evaluating a series of

Table 12. Accuracy and precision data in reproducibility

Lab. no.	CRM	ERM-EC680			NMIJ 8103-a			JSAC 0601-2		
	Matrix	PE			ABS			Polyester		
	Element	Cd	Cr	Pb	Cd	Cr	Pb	Cd	Cr	Pb
	Certified value/mg kg ⁻¹	140.8	114.6	107.6	106.9	269.5	1084	5.2	10.8	11.6
Lab.-A	Measured value/mg kg ⁻¹	137.5	113.0	105.0	101.8	269.7	1057	4.8	10.4	11.1
	RSD (%)	2.2	1.5	4.3	1.9	2.8	2.9	7.3	6.1	11.9
	Recovery (%)	97.7	98.6	97.6	95.2	100.1	97.5	92.4	96.7	96.1
Lab.-B	Measured value/mg kg ⁻¹	132.3	111.0	97.5	97.2	254.3	1009	4.8	10.6	11.2
	RSD (%)	3.1	1.8	0.6	1.7	1.3	5.7	2.5	2.9	4.9
	Recovery (%)	94.0	96.9	90.6	91.0	94.4	93.1	92.9	97.8	96.8
Lab.-C	Measured value/mg kg ⁻¹	142.6	112.8	107.0	109.9	262.2	1116.6	5.4	10.1	11.8
	RSD (%)	0.8	1.9	1.3	0.9	0.8	1.1	1.1	1.0	0.8
	Recovery (%)	101.3	98.5	99.4	102.8	97.3	103.0	103.2	93.5	101.7
Lab.-D ^a	Measured value/mg kg ⁻¹	138.8	109.2	109.0	107.8	258.8	1088	4.9	8.9	12.4
	RSD (%)	3.0	3.0	6.5	1.8	1.7	1.9	6.6	17.0	8.4
	Recovery (%)	98.6	95.3	101.3	100.8	96.0	100.3	93.4	82.5	107.0
Lab.-D	Measured value/mg kg ⁻¹	140.3	115.9	107.2	106.1	273.7	1070	4.9	8.93	11.1
	RSD (%)	0.8	0.7	0.8	0.6	0.1	0.5	1.5	2.3	2.6
	Recovery (%)	105.5	106.4	109.9	110.2	108.6	103.2	102.0	85.0	93.9
Lab.-E	Measured Value/mg kg ⁻¹	142.0	113.2	105.8	101.5	255.1	1089	6.79	12.7	13.5
	RSD (%)	1.2	1.4	3.7	1.2	3.4	2.2	4.7	2.8	5.3
	Recovery (%)	100.9	98.7	98.3	94.9	94.6	100.5	130.6	117.6	116.7
Overall	Mean/mg kg ⁻¹	138.9	112.5	105.3	104.1	262.3	1072	5.3	10.3	11.9
	RSD (%)	2.7	2.0	4.3	4.5	3.5	3.4	14.9	13.6	8.1
	Recovery (%)	98.7	98.2	97.8	97.3	97.3	98.9	101.1	95.1	102.3

^aMeasurement results obtained from laboratory-D using the HPA for sample preparation.

method-performance characteristics, such as linearity, matrix effect, LOD, LOQ, accuracy and precision. At the optimal conditions, the technique shows good linearity with a correlation coefficient of more than 0.999 for the calibration curve. Sample matrix has no effect on the measurement of three elements, demonstrating that the HPA-digested samples are fully destroyed. The developed method is very sensitive with the LOD (*i.e.* 0.98 mg kg⁻¹ (Cd), 1.12 mg kg⁻¹ (Cr) and 1.18 mg kg⁻¹ (Pb)) and LOQ (*i.e.* 2.93 mg kg⁻¹ (Cd), 3.35 mg kg⁻¹ (Cr) and 3.55 mg kg⁻¹ (Pb)). Also, the obtained recoveries and RSDs met the specified acceptance criteria in the repeatability and intermediate precision tests. This reveals that the proposed procedure has good accuracy and precision. An important outcome of inter-laboratory study was that there was good agreement between the results obtained by different techniques to digest polymer samples. This method provides substantial benefits to be simple to use, reliable and reproducible and requires instrumentation that is available in many laboratories.

References

1. <http://www.rohs.eu/>; <http://www.rohs.gov.uk>.
2. Gardner, M.; Comber, S. *Analyst* **2002**, *127*, 153.
3. Soylak, M.; Tuzen, M.; Narin, I.; Sari, H. *J. Food Drug Anal.* **2004**, *12*, 254.
4. Mitra, S. *John Wiley & Sons, Inc.* **2003**, *5*, 229.
5. Settle, F. *Prentice Hall PTR* **1997**, *3*, 62.
6. Kumar, S. J.; Ostapczuk, P.; Emons, H.; Fresenius, J. *Anal. Chem.* **1997**, *350*, 171.
7. Maichin, B.; Zischka, M.; Knapp, G. *Anal. Bioanal. Chem.* **2003**, *376*, 715.
8. Matusiewicz, H. *Anal. Chem.* **1999**, *71*, 3145.
9. Peters, F. T.; Drummer, O. H.; Musshoff, F. *Forensic Sci. Int.* **2007**, *165*, 216.
10. Taverniers, I.; Loose, M. D.; Bockstaele, E. V. *Trends Anal. Chem.* **2004**, *23*, 535.
11. *Guidelines for the Validation and Verification of Chemical Test Methods*; National Association of Testing Authorities (NATA), Technical Note, 2006.
12. *Guidelines for the Validation or Analytical Methods for Active Constituent, Agricultural and Veterinary Chemical Products*; Australian Pesticides & Veterinary Medicines Authority (APVMA), 2004.
13. *Validation of Analytical Procedures: Methodology* (Final Guidance); Food and Drug Administration Center for Veterinary Medicine, 1999.
14. *Guidance for Industry: Bioanalytical Method Validation*; U.S. Department of Health and Human Services Food and Drug Admini-

- stration Center for Drug Evaluation and Research (CDER) Center for Veterinary Medicine (CVM), 2001.
15. Burgess, C. *The Royal Society of Chemistry* **2000**, 2, 6.
 16. *A Laboratory Guide to Method Validation and Related Topics*; Eurachem Guide: 1998.
 17. Dean, J. R. *John Wiley & Sons, Ltd* **2005**, 1, 12.
 18. Harvey, D. *McGraw-Hill* **2000**, 5, 110.
 19. Harris, D. C. *Quantitative Chemical Analysis (5th ed.)* **1998**, 5, 101.
 20. Hartmann, C.; Smeyers-Verbeke, J.; Massart, D. L.; McDowall, R. D. J. *Pharm. Biomed. Anal.* **1998**, 17, 193.
 21. Harris, D. C. *Quantitative Chemical Analysis (5th ed.)* **1998**, 4, 77.
 22. <http://www.kolas.go.kr/english/> (KOLAS).
 23. *Plastics - Determination of Cadmium - Wet Decomposition Method*; British Standards Institution, 2001.
 24. *Determination of Lead in Plastics*; Korean Standards Association, 2005.
 25. *Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices*; U.S. Environmental Protection Agency, EPA Method 3052, 1996.
 26. Linsinger, T.; Liebich, A.; Przky, E.; Lamberty, A. *Institute for Reference Materials and Measurements* **2007**, 7, 20
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