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Determination of metal concentrations in certified plastic reference materials after small-size autoclave and microwave-assisted digestion followed with inductively coupled plasma optical emission spectrometry

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Abstract

The digestion methods for the determination of As, Cd, Cr, Pb, Sb, Sn and Zn concentrations in plastic samples using microwave-assisted digestion (MW-AD) and small-size autoclave digestion was developed. The certified polyethylene, polypropylene, polyvinyl chloride and acrylonitrile butadiene styrene certified reference materials were used in order to find digestion method working properly for several sample matrices. Efficiency of the digestion methods was evaluated by analyzing the residual carbon in digests by TOC analyzer. MW-AD using a mixture of 7 mL of HNO₃ and 3 ml of H₂O₂ as a digestion solution resulted in excellent recoveries for As, Cd, Pb, Sb and Zn, and were in the range of 92- 107 % for all the analytes except Pb in polyethylene material. Autoclave digestion using 5 mL of concentrated HNO₃ as a digestion solution resulted in similar recoveries with the exception of a higher As recovery (98 %). Tin recovery resulted in low level after both MW-AD and autoclave digestion. Autoclave digestion was further developed resulting in a partially open two-step digestion process especially for the determination of Sn and Cr. The method resulted in higher recoveries of Sn and Cr (87 and 76 %) but with the lower concentration of easily volatile As, Cd and Sb.

Keywords: ICP-OES, Autoclave, Microwave, Digestion, Plastic, Determination

1 Introduction

The consumption of commodity plastics, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) has increased rapidly during the last few decades¹. During the manufacturing, the characteristic properties of plastics can be adjusted by using various additives of inorganic, organic and organometallic compounds². Determination of additive compounds in plastics is important due to the regulations related to the final product but in addition processes related to the different recycling possibilities in plastic waste disposal³⁻⁵. The most used methods for the determination of analytes in plastic samples are X-ray fluorescence (XRF) spectrometry⁶⁻⁸, instrumental neutron activation analysis (INAA)⁹ and inductively coupled plasma optical emission or mass spectrometry (ICP-OES/MS)¹⁰⁻¹³. XRF and INAA are nondestructive techniques which allow multi-element analysis without sample pre-treatment and therefore can save time in the analysis. However, lacking of calibration standards in the analysis of plastic materials can reduce the accuracy of the measurements resulting in higher method detection limits. Low detection limits can be obtained using ICP techniques after wet digestion method of plastic samples; but the determination of inorganic impurities in polymers is still a challenge due to the high stability and the number of different polymer grades present in the wet digestion procedures.

The autoclave system, also known as digestion bomb using polytetrafluoroethylene (PTFE) interior reinforced with steel has been widely used in digestion procedures after 1960.¹⁴ The autoclave system was often convectively heated which enabled the digestion of large number of samples, for example in laboratory drying oven. The digestion of inorganic matrices was extensively studied^{15,16} but, however, the research related to digestion of plastics was limited until the development of commercial high pressure asher (HPA) and microwave-assisted (MW-AD) digestion systems. Autoclave digestion for organic materials in microelectronic devices has been studied by Takenaka *et al.*¹⁷ and element concentrations determined resulted in highly comparable with the microwave digestion method. Recent digestion methods, which are used in the routine analysis for polymer materials are high-pressure processes, such as (MW-AD)^{10,18-20}, microwave-induced combustion (MIC)²¹ and HPA^{11-13,22}. These methods use nitric acid as the

main digestion solution combined with hydrochloric acid and/or hydrogen peroxide to enhance the digestion and then efficiency of analyte recovery. The mass of the sample ranges from 100 to 500 mg depending on the sample, and the total volume of the digestion solution varies from 5 to 10 mL. Similar digestion conditions and reagents can be used in the convectively heated autoclave systems described in the literature.¹⁴ Main differences between autoclave systems and commercial MW-AD and HPA methods are that in autoclave digestion, temperatures for biological and organic samples are ≤ 200 °C which results in longer digestion times. Even though different MW-AD and HPA methods are fast and reliable in routine analysis, the conventionally heated autoclave system can be used as an alternative method in the digestion of polymer materials.

In this study, feasibility of different autoclave (digestion bomb) methods and temperature controlled MW-AD digestion methods were tested in the determination of metal concentration in polyethylene, polypropylene, polyvinyl chloride and acrylonitrile butadiene styrene plastics. The aim was to find suitable method working properly for all the plastics investigated. Digestion efficiency was evaluated by determining the carbon concentrations in the digests using a TOC-analyzer.

2 Instrumentation

An inductively coupled plasma optical emission spectrometer (Optima 8300, Perkin-Elmer, Norwalk, CT, USA), equipped with a GemCone™ Low-Flow nebulizer and a cyclonic spray chamber (Perkin-Elmer, USA) was used for the determination of metal concentrations. Operating parameters (Table 1) were tested with all reference materials and were used throughout the work. The optimization procedure and the results are presented in appendix.

Table 1 Instrumental parameters used in the determination of metal concentration in plastic materials by ICP-OES

<i>Parameter</i>	<i>Setting</i>
RF power	1500 W
Plasma gas flow rate	8 L min ⁻¹
Auxiliary gas flow rate	0.2 L min ⁻¹
Nebulizer gas flow rate	0.5 L min ⁻¹
Sample flow rate	1.5 mL min ⁻¹
Sample reading time	Automatic 2-5 s
Flush time	14 s
Measured replicates	3
Viewing	Axial

2.1 Reagents

Ultrapure water (ELGA PURELAB ULTRA, Elga Ltd., Bucks, GB, 18.2 M Ω cm) was used throughout the work. Nitric acid (65 %, p.a.) and hydrochloric acid (37%, p.a.) were supplied by Sigma-Aldrich. Hydrogen peroxide (30 %, p.a.) was purchased from VWR international. Standard solutions for calibration (As, Cd, Cr, Pb, Sb, Sn and Zn) were prepared from 1000 mg L⁻¹ atomic spectroscopy standard solutions (Perkin-Elmer, USA).

2.2 Samples

Four certified reference materials (CRMs), polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC) and acrylonitrile butadiene styrene (ABS) were used as received. The PE material (ERM-EC681k) was produced by European Reference Material, Institute for Reference materials and Measurements (IRMM) (Geel, Belgium). Reference materials produced by National Metrology Institute of Japan (PP material, NMIJ 8123-a, and PVC material, NMIJ 8133-a) were purchased from LGC Standards GmbH, (Wesel, Germany).²³ ABS reference material (BAM-H010) was obtained from Bundesanstalt für Materialforschung und -prüfung (BAM) (Berlin, Germany).²⁴

2.3 Microwave-assisted digestion (MW-AD) method

Milestone Ethos Touch (Soriso, Italy) with tetrafluormethaxil (TFM) digestion vessels and quartz inner vessels was used for the MW-AD procedure. The operational conditions are presented in Table 2. For digestion, 150 mg of each polymer was accurately weighed into a 40 mL quartz interior into which 7 mL of nitric acid (\geq 65 %) and 3 mL of H₂O₂ was added. For equalizing the pressure inside TFM vessel, 4 mL of nitric acid (4 M) was introduced between the quartz and TFM vessels before sealing both containers with respectively quartz and TFM lids. After the digestion program, samples were cooled down for 20 minutes before diluting to a volume of 50 mL with water. After each digestion, the PTFE and quartz vessels were washed with nitric acid (65 %) using the same microwave program presented.

Table 2 Temperature program for microwave-assisted digestion of polymers

<i>Sample</i>	<i>Step</i>	<i>Power (W)</i>	<i>Temperature (°C)</i>	<i>Ramp (min)</i>	<i>Hold (min)</i>
PE + PP	1	1000	120	4	0
	2	1000	180	3	0
	3	1000	220	4	0
	4	1000	220	0	20
PVC	1	1000	220	10	0
	2	1000	220	0	20
ABS	1	1000	220	9	0
	2	1000	220	0	15

2.4 Autoclave digestion method

A laboratory-made small-size autoclave with a PTFE interior (25 mL) and stainless steel exterior were used in autoclave digestion. PTFE interiors and lids were built from a PTFE rod using a lathe, and designed in a way that the system was tightly sealed by a reinforcing steel exterior. It should be noted that in order to avoid the swelling of PTFE, the material was held in an oven (175 °C) for several hours before the final forming. The exteriors made of stainless steel were made from stainless steel rod by G-Tronic Oy, Finland.

Method A: 200 mg of each polymer was accurately weighed into the autoclave system described above. 5 mL of nitric acid was added and the system was then sealed and placed in a conventional laboratory oven for 4-16 hours (130–150 °C). After the procedure, vessels were allowed to cool to room temperature and the sample solutions were transferred to volumetric flasks and diluted to a volume of 50 mL with water.

Method B: The samples were treated according to method A but after cooling, the sample vessels were opened and the solution was reheated in a sand bath. Hydrogen chloride (6 mL) was added for stabilizing Sn and improving the dissolution of Cr. Solutions were then poured into 50 mL volumetric flasks and after cooling diluted to volume with water.

Method C: The samples were treated according to method A but the mixture of 4 mL of HNO₃ and 1 mL of HCl was used as a digestion solution. The autoclaves were cleaned with method A in an oven for 2 hours.

2.5 Evaluation of the residual carbon concentrations after the sample digestion steps

The efficiency of the digestion methods was evaluated by analysis of the carbon content in digests. Both the determination procedure and the results can be seen in appendix.

3 Results and discussion

3.1 Calibration and detection limits

Multi-element calibration standards were prepared for all elements (As, Cd, Cr, Pb, Sb, Sn and Zn). Two most sensitive emission lines, except for Sn, were selected for each element to attain the sensitivity required. The wavelengths for the analysis were chosen on the basis of the limit of detection, higher intensity and without interferences (Table 3). US-EPA method 200.7²⁵ was used in the calculation of the method detection limits (MDLs). It should be noted that the wavelengths were not selected according to the obtained MDL's only. At low concentrations, for example in the case of As 188.979 nm and As 193.969 nm, the first wavelength provided lower RSD values for the plastic samples.

Table 3 Method detection limits (MDL) for the determination of elements by ICP-OES

<i>Element</i>	<i>wavelength (nm)</i>	<i>MDL (mg L⁻¹)</i>	<i>MDL^a (mg kg⁻¹)</i>	<i>Calibration range (mg L⁻¹)</i>
As	188.979	0.0170	5.70	0.02 - 2
	193.696	0.0063	2.10	0.02 - 2
Cd	214.440	0.0006	0.20	0.02 - 2
	228.802	0.0019	0.60	0.02 - 2
Cr	205.560	0.0025	0.90	0.02 - 2
	267.716	0.0028	0.90	0.02 - 2
Pb	217.000	0.0300	10.00	0.02 - 2
	220.353	0.0050	1.70	0.02 - 2
Sb	206.836	0.0190	6.20	0.02 - 2
	217.582	0.0280	0.90	0.02 - 2
Sn	189.927	0.0057	1.90	0.02 - 2
Zn	206.200	0.0025	0.90	0.02 - 2
	213.857	0.0035	1.20	0.02 - 10

Notes: Bold = Wavelength chosen for measurements. MDL^a = Method detection limit when 150 mg of sample was digested and diluted to a volume of 50 mL.

3.2 Microwave-assisted digestion

The MW programs and reagent suggestions by the manufacturer were adjusted for all the CRMs analyzed. This is due to the low sample masses used in the original MW program (in PE and PP) and due to the recommendation to the use of sulfuric acid in ABS and PVC digestions. For PE and PP matrices, the MW manufacturer recommended the maximum use of 100 mg of sample using digestion solution of 6 mL of HNO₃ and 1 mL of H₂O₂. However, the certificate of PE (ERM-EC681k), recommends the use of a minimum sample weight of 150 mg. Because to the higher sample mass, the concentrated nitric acid (10 mL) and a mixture of nitric acid (7 mL) and hydrogen peroxide (3 mL) were tested as a digestion solution for PE reference material. No significant differences were observed between the

digests after the two different digestion solution and visually clear green solutions were obtained. Mixture of the HNO_3 and H_2O_2 was chosen from the two digestion solution and was used in the final digestions for all of the reference materials. In this research, sulfuric acid was not used due to the effect in the ICP-OES nebulization process. Therefore the masses of ABS and PVC samples were lowered to 150 mg (down from 300 and 250 mg) and the MW temperature was raised from 210 to 220 °C resulting in similar MW programs and reagents used for all the plastic materials.

MW-AD was successfully performed for all the elements (Cd, Cr and Pb) in PP and PVC polymers and clear solutions were obtained. The element concentrations determined were in good agreement (Table 4) with the certified values resulting in excellent recoveries: Cd (105 %), Cr (105 %) and Pb (108 %) for the PP material and Cd (98 %), Cr (98 %) and Pb (100 %) respectively for PVC. The organic material in ABS samples was not totally destroyed with the MW program although the recoveries for Cd and Pb were high (97.0 and 96.6 %). A yellowish precipitate was formed when samples were diluted to volume. Precipitate was further investigated due to low recovery of Cr (3 %) with semi-quantitative analysis by XRF, with CHN analysis and was furthermore recrystallized from acetone for single x-ray analysis. Precipitate was confirmed to be p-Nitrobenzoic acid, however Cr was not found to be in the coordination in single x-ray structure. In PVC and PP Cr is added as lead chromate and good recovery rates were obtained PVC (98.6 %) and PP (104.2 %). PE digestion resulted in a visually clear green solution but, however, when diluting to a volume of 50 mL some white suspension appeared in the samples. This suspension was not further investigated but it might be undissolved titanium oxide used as pigment or hydrated tin(II)oxide which explains the low recovery of tin (57 %). Similarly with the ABS material, the Cr in PE is added as Cr_2O_3 and the recovery was very low (46 %). For PE samples, the Cd and Sb resulted in excellent recoveries 101.5 and 104 % whereas Pb and Zn resulted in high 111 and 109 %, respectively. The concentrations determined are summarized in Table 4.

Table 4 Determined element concentrations for certified polymer materials after microwave-assisted digestion followed with ICP-OES analysis

		<i>Certified concentration mg kg⁻¹</i>	<i>Determined concentration mg kg⁻¹</i>	<i>Recovery %</i>			<i>Certified concentration on mg kg⁻¹</i>	<i>Determined concentration mg kg⁻¹</i>	<i>Recovery %</i>
PE - ERM EC681k	As	29.1 ± 1.8	26.9 ± 1.5	92.4	PP - NMIJ 8123a	As	-	< MDL	-
	Cd	137 ± 4	139 ± 3	101.5		Cd	94.26 ± 1.39	98.7 ± 0.7	104.7
	Cr	100 ± 5	46 ± 6	46.0		Cr	895.2 ± 9.6	933 ± 12	104.2
	Pb	98 ± 6	109 ± 6	111.2		Pb	949.2 ± 7.5	1024 ± 12	107.8
	Sb	99 ± 6	103 ± 5	104.0		Sb	-	16.5 ± 1.6	-
	Sn	86 ± 6*	49 ± 15	57.0		Sn	-	5.2 ± 1.4	-
	Zn	1250 ± 70*	1360 ± 30	108.8		Zn	-	105 ± 4	-
PVC - NMIJ 8133a	As	-	< MDL	-	ABS - BAM H010	As	-	< MDL	-
	Cd	95.62 ± 1.39	94 ± 4	98.3		Cd	93 ± 5	90.2 ± 2.0	97.0
	Cr	949.0 ± 9.7	936 ± 30	98.6		Cr	470 ± 36	13.6 ± 3.0	2.9
	Pb	965.5 ± 6.6	972 ± 20	100.7		Pb	479 ± 17	462.5 ± 10.5	96.6
	Sb	-	15.5 ± 1.5	-		Sb	-	2.5 ± 0.8	-
	Sn	-	< MDL	-		Sn	-	3.3 ± 1.1	-
	Zn	-	510 ± 20	-		Zn	-	< MDL	-

*Indicative values

3.3 Autoclave digestions

Development of the autoclave systems described in the literature is presented in Table S1 (Appendix A). In this research autoclave system using HNO₃ as a digestion solution was tested. Heating was performed in temperature controlled laboratory oven. Preliminary autoclave digestions (methods A-C) were tested using polyethylene reference material (ERM-EC681k). Nitric acid, mixture of nitric acid and hydrogen chloride, different temperatures and digestion times were tested. Digestion efficiency was evaluated according to the metal concentrations obtained after ICP-OES analysis and with TOC analysis for 4 and 12 hour digestion. Significant differences in recovery rates were obtained As (82 – 98 %), Cd (89 – 103 %), Cr (27 – 75 %), Pb (95 – 107 %), Sb (96 – 104 %), Sn (0 – 87 %) and Zn (91 – 111 %) in the analysis of polyethylene CRM using different autoclave digestion methods. A summary of the methods A-C for polyethylene digestion is presented in figure 2. According to the results obtained, autoclave method A with 12 hour digestion at 130 °C were chosen for the digestion tests of PP, PVC and ABS reference materials.

Method A (n=4) was tested with PE reference material at two different temperatures, 130 °C and 150 °C, and digestion times of 4, 12 and 16 hours. 5 mL of concentrated nitric acid was used as a digestion solution. After 4 hours of digestion using nitric acid no significant changes in recoveries occurred and digestion was complete (visually

clear) with polyethylene reference material. However, like in microwave-assisted digestion, similar white suspension appeared when samples were diluted to volume which could explain the low recovery of tin. Long digestion times of over 12 hours were used in the overnight digestion. It should be noted that the heating source in autoclave digestion is totally different in comparison to microwave and therefore longer digestion times are needed. Method A was found to be suitable for the determination of volatile elements As, Cd and Sb resulting in excellent recoveries of 98, 103 and 104 %, and those of Pb and Zn were 107 and 111 % respectively. The determination of Sn and Cr cannot be performed after the autoclave method A. In order to increasing the recovery of Sn and Cr, a two-step autoclave method was developed.

Method B (n=16) was performed similarly to method A, after which the PE sample vessels were opened, 6 mL of HCl was added and the cooled digestates were reheated over a sand bath. Samples were then poured into 50 mL volumetric flasks and cooled down before diluting to volume. Method B resulted in excellent recoveries of Pb and Zn at respectively 101, 100 % and higher concentrations for Sn and Cr, respectively 87 and 76 %. Open digestion resulted in slightly lower concentrations for As, Cd and Sb, 82, 91 and 96 %.

Method C (n=4): Samples were treated according to method A (12 h, 130 °C) but 1 mL of HCl was added to the digestion solution resulting in total dissolution. From the results (Fig.2), the effect of the Cl ion can be seen. High deviation in the analysis of Sn can be explained with the lack of sufficient amount of HCl, which is improving the recovery of Cr. However the concentration of HCl was not high enough for the analysis of Sn. Comparing to method A, recoveries of Sb, Pb and Zn were 98-101 % but the recovery of volatile elements were slightly lower.

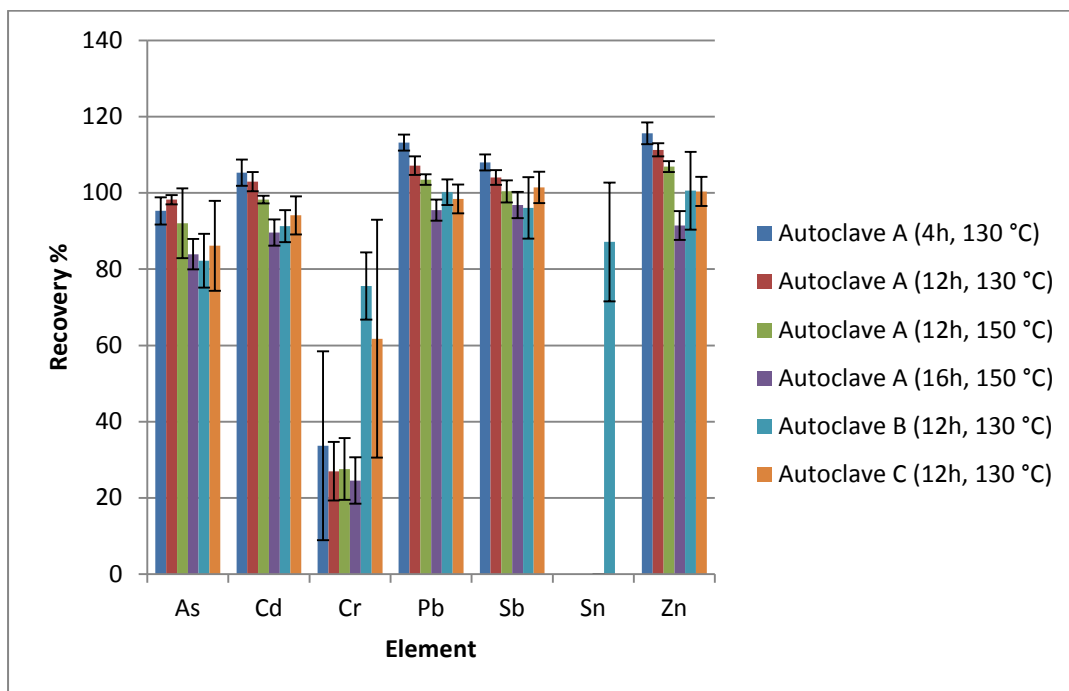


Fig. 2 Digestion efficiency for elements in certified polyethylene reference material, ERM-EC681k after autoclave methods A-C. Method A = 5 mL HNO₃ (Closed), Method B = 5 ml HNO₃ + reheat over sand bath with 6 mL of HCl (Partially open), Method C = 4 mL HNO₃ + 1 mL HCl (Closed)

3.4 Analysis of the ABS, PVC and PP after the proposed autoclave method A

As in the MW-AD method, the ABS material was not destroyed in this autoclave system and a similar yellowish precipitate formed when diluting to volume. The Recoveries of Cd (100 %) and Pb (103.5 %) were excellent but due to the incomplete digestion the determination of Cr resulted in low concentration. For PVC digestion the recoveries were lower than in the MW-AD. The reason for lower recoveries is an incomplete digestion (Figures 3a-b). Interestingly after the digestion fragile white pellets were remaining. According to the semi-quantitative XRF analysis, the white residual (Fig 3b) consists of 53 % of Cl, 34 % of C, 12,5 % of O and small amount of Si, Ca and Al. As a conclusion autoclave method A was found successful for the digestion of PVC material resulting in recoveries of 91 %, 94 % and 90 % for Cd, Cr and Pb, respectively. Digestion of polypropylene material resulted in recoveries comparable with the MW-AD method but higher Cr (111 %) recovery. Summary of the concentrations determined are presented in a Table 7.



Fig. 3a) PVC (NMIJ 8123-a) pellets before autoclave digestion method A 3b) PVC pellets after the digestion method A

Table 7 Determined element concentrations for certified polymer materials after autoclave digestion method A followed with ICP-OES analysis

		<i>Certified concentration mg kg⁻¹</i>	<i>Determined concentration mg kg⁻¹</i>	<i>Recovery %</i>			<i>Certified concentration mg kg⁻¹</i>	<i>Determined concentration mg kg⁻¹</i>	<i>Recovery %</i>
PE - ERM EC681k	As	29.1 ± 1.8	28.6 ± 0.3	98.2	PP - NMIJ 8123a	As	-	< MDL	-
	Cd	137 ± 4	141 ± 4	102.9		Cd	94.26 ± 1.39	96.8 ± 3.7	102.7
	Cr	100 ± 5	27 ± 2	27.0		Cr	895.2 ± 9.6	996 ± 30	111.3
	Pb	98 ± 6	105 ± 3	107.1		Pb	949.2 ± 7.5	1018 ± 40	107.2
	Sb	99 ± 6	103 ± 2	104.0		Sb	-	8.4 ± 0.5	-
	Sn	86 ± 6*	5.2 ± 0.4	6.0		Sn	-	< MDL	-
PVC - NMIJ 8133a	Zn	1250 ± 70*	1390 ± 30	111.2	Zn	-	120 ± 9	-	
	As	-	< MDL	-	ABS - BAM H010	As	-	< MDL	-
	Cd	95.62 ± 1.39	87.2 ± 2.0	91.2		Cd	93 ± 5	93 ± 3	100
	Cr	949.0 ± 9.7	890.5 ± 20.0	93.8		Cr	470 ± 36	15 ± 25,9	3.2
	Pb	965.5 ± 6.6	866 ± 20	89.7		Pb	479 ± 17	496 ± 16	103.5
	Sb	-	7.8 ± 0.8	-		Sb	-	< MDL	-
Sn	-	< MDL	-	Sn		-	< MDL	-	
	Zn	-	490 ± 20	-	Zn	-	< MDL	-	

4 Conclusions

In this research determination of As, Cd, Pb, Sb, and Zn concentrations in PE, PP, PVC and ABS certified reference materials using microwave-assisted digestion (MW-AD) and small-size autoclave digestion followed with ICP-OES was performed successfully. The determination of Sn and Cr concentration was observed to be a challenging after the presented sample pre-treatment methods. The aim of the work was to find suitable digestion method for all the plastics investigated.

The highest metal recoveries by MW-AD were obtained using a mixture of 7 mL of nitric acid and 3 mL of H₂O₂ as a digestion solution at 220 °C for all the sample matrices investigated. The digestion of PE, PP, and PVC was complete; however ABS matrix was not totally mineralized. The concentrations of As, Cd, Pb, Sb and Zn determined

resulted in recovery rates from 92 to 111 % in all the certified reference materials. Closed autoclave digestion method (method A, 130° C, 12 h) using 5 mL HNO₃ as digestion solution was found to be the most suitable for all the plastic matrices. Recoveries of the analytes and digestion behavior resulted in similar with the MW-AD method with the exception of PVC digestion. After the autoclave method, incomplete digestion for PVC material was observed. However, the method was able to dissolve 90 % of the Cd, Cr and Pb in PVC matrix and leaving the high concentrations of chlorine in the PVC matrix.

The current work demonstrates that autoclave method heated in temperature controlled laboratory oven can be used as an alternative method in the digestion of plastic samples. It is easy to operate, requires no controlling, can run multiple different sample matrices at the same time with different acids, and is not labor intensive. However, the drawback is long digestion times compared to microwave-assisted digestion for plastic samples.

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Appendix A. Supplementary data

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