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# Direct multi-element analysis of plastic materials via solid sampling electrothermal vaporization inductively coupled plasma optical emission spectroscopy

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In this work the determination of Cd, Cu, Cr, Fe and Sb as organic and inorganic additives in in-house plastic materials (ABS, LDPE) using electrothermal vaporization combined with inductively coupled plasma optical emission spectroscopy is described. The influence of  $\text{CCl}_2\text{F}_2$  as gaseous halogenation modifier was investigated. Especially for the carbide forming elements the sensitivity was improved and the memory effects were significantly reduced. Calibration was performed by external calibration and standard addition with aqueous standard solutions added directly into the sample boats. Absolute limits of detection (3 $\sigma$ -criterion) range between 0.1 ng (Cd) and 9 ng (Fe) which corresponds to relative values of 0.1 mg kg<sup>-1</sup> and 1.6 mg kg<sup>-1</sup>, respectively, taking 5 mg as typical sample mass. The detection limits are sufficient to monitor the element contents of plastic materials according to European directives such as European directive on the safety of toys. The developed ETV-ICP-OES method allows a fast analysis with a high sample throughput (3 minutes per analysis), low sample consumption and good trueness and precision for the analyzed elements. Sample preparation is reduced to ashing the samples in a muffle furnace. Furthermore, measurements are possible regardless of the chemical form in the additives. For verification the results obtained with the developed method were compared with measurement results of independent methods ICP-MS/OES after digestion. In addition Cd, Cr, Pb were determined in a solid plastic reference material BAM-H010 to confirm the applicability and accuracy of the method.

## Introduction

Plastic materials are an indispensable part of our daily life. To obtain the desired properties of these materials and to extend their application range additives are often used<sup>1</sup>. Additives are applied as colouring agents<sup>2</sup>, stabilizers against UV radiation<sup>3</sup>, plasticizer<sup>4</sup> and flame retardants<sup>5</sup>. However, some of these additives contain heavy metals e.g. antimony, chromium, cadmium and lead in organic as well as inorganic form, which are known to be hazardous for humans<sup>6</sup>. Therefore, the European Union (EU) has enacted regulations for consumer protection that limit the content and the concentration of harmful compounds in plastic materials.<sup>7,8</sup>

The monitoring of these regulations is challenging since plastic materials are complex matrices for analysis. Conventional methods are based on sample digestion and subsequent analysis of the digestion solution.<sup>9-11</sup> However, the digestion of solid samples is time consuming and the risk of contamination and analyte loss increase with the complexity of the sample preparation. Furthermore, the high dilution of the samples during digestion leads to an increase in the limit of detection of the method. For some plastic matrices, this procedure is very challenging and works only under high pressure and temperature. For this purpose, commonly microwaves<sup>9,12-17</sup> or high pressure ashers<sup>17</sup> are used combined with concentrated acids. An additional limitation of these methods is that they only allow small amounts of sample due to high pressure development by the formation of gases during the digestion procedure. Once the sample is digested the preparation of matrix adapted calibration solutions or standard addition can be performed leading to reliable results.

In contrast, direct solid sampling techniques offer the benefits of reduced risk of contamination, better detection limits and significantly reduced sample preparation times.<sup>18,19</sup> However, for described matrices laser ablation (LA) could not be widely established due to fractionation effects, the lack of matrix-matched standard materials and the high lateral resolution of the measurement which is only suitable for micro homogeneous materials<sup>20,21</sup>. The established method of X-ray fluorescence spectroscopy (XRF) shows high detection limits<sup>22</sup> and light elements are difficult to detect. Furthermore the quality of quantification strongly depends on the matrix, requiring calibration materials with similar composition as the sample to be analyzed.<sup>23</sup>

Electrothermal vaporization (ETV) is meanwhile a well-established effective direct solid sampling technique, which provides in combination with inductively coupled plasma optical emission spectroscopy (ICP-OES) a fast analytical multi-element determination without extensive sample preparation.<sup>24</sup> The technique has the potential to determine approximately 70 elements in various types of samples.<sup>25</sup> In the past, many types of matrices were successfully analyzed by ETV-ICP-OES, e.g. biological samples,<sup>26,27</sup> ceramics<sup>28</sup> and refractory metals.<sup>29,30</sup> It has turned out to be a suitable technique especially for the determination of traces in refractory materials and tasks with limited available sample masses like in forensic applications, analysis of auto paints<sup>31</sup> or hair analysis.<sup>32,33</sup>

The application of this technique for plastic materials is more complex since the presence of volatile carbon matrices causes signal suppression due to plasma load. Additionally, the transport between the graphite furnace and the plasma is significantly affected by an

existing matrix.<sup>34</sup> These factors limit the quantification towards liquid standards.

Resano et al. quantified Cr, Cu, Fe, K, Mn, Pb and Zn in fluorocarbon matrix using ETV-ICP-MS. The sample matrix was removed directly in the ETV furnace in a pyrolysis step before the measurement.<sup>35</sup>

Through the addition of chemical modifiers it is possible to prevent the evaporation of volatile analytes during the pyrolysis step.<sup>36, 37</sup> An addition of HNO<sub>3</sub> or O<sub>2</sub> allows the removal of the matrix at lower temperatures.<sup>36, 38</sup> Furthermore, halogenating agents as gaseous phase modifiers are commonly used for the determination of low volatile forms of analytes or for carbide-forming analytes which react with modifiers and form volatile halides that can be efficiently evaporated.<sup>39</sup> Particles formed by pyrolysis of the modifier can also act as condensation nuclei for sample vapours, which have a positive effect on transport efficiency.<sup>40, 41</sup> Mostly, reactive halocarbons are added to the transport gas stream. The influence of CCl<sub>2</sub>F<sub>2</sub>, CHClF<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, CHF<sub>3</sub> as modifiers was investigated by Hassler et al. for the determination of trace elements in high-purity copper.<sup>42</sup>

The aim of our work was to investigate the applicability of ETV-ICP-OES for the analysis of plastic materials to monitor the contents of additives in these materials. The analyzed plastic materials were doped and prepared by conventional industrial methods.<sup>43</sup> Two different plastic matrices ABS (acrylonitrile butadiene styrene) and LDPE (low-density polyethylene) were used to investigate matrix influences. In this work CCl<sub>2</sub>F<sub>2</sub> as chemical modifier was used to improve the vaporization process. CCl<sub>2</sub>F<sub>2</sub> was added into the furnace as halogenation gaseous reagent to improve the vaporization of carbide-forming analytes. To keep sample preparation as simple as possible and to reduce the risk of contamination no additional modifiers were added for matrix separation in the muffle oven. To avoid possible losses of analytes, the matrix was removed at the lowest possible temperature.

The verification of the method was performed by comparing the results with those obtained using a high-pressure microwave digestion of the samples and subsequent analysis by ICP-MS respectively sodium carbonate/nitrate fusion and analysis with ICP-OES. The suitability of the developed method for determination of elemental content in plastic materials was additionally checked by analyzing a certified reference material.

## Experimental

### Instrumentation

For these studies an electrothermal vaporization system (ETV 4000, Spectral Systems, Fürstfeldbruck, Germany) with an autosampler unit (AWD-50, Ingenieurbüro Schuierer, Ismaning, Germany) coupled to an ICP-OES (IRIS Advantage Duo HR, Thermo Fisher Scientific, Dreieich, Germany) was used. A microbalance (Sartorius RC110D, Göttingen, Germany) with a readability of 10 µg was utilized for weighing the samples. The digestion of the samples was carried out in quartz tubes via a microwave high pressure digestion (Ultraclave III, MLS GmbH, Leutkirch, Germany and Multiwave 3000, Anton Paar, Ostfildern-Scharnhausen, Germany).

The analysis of the digested samples was performed with a sector field ICP-MS (ElementXR, ElementII, Thermo Fisher Scientific, Bremen, Germany). The analysis of dissolved fusion samples for chromium oxide quantification was done with an ICP-OES (Spectro Arcos, SPECTRO Analytical Instruments GmbH, Kleve, Germany).

Water was purified using a Milli-Q water purification system (MilliPore gradient, Merck MilliPore, Darmstadt, Germany). The multi-element calibration standards were prepared by appropriate dilution of 1 g L<sup>-1</sup> single-element standard solutions (Pb, Cd, Cu, Cr, Fe CertiPur® Merck, Darmstadt, Germany, Sb High Purity Standard Alfa Aesar, Karlsruhe, Germany) in quartz volumetric flasks. The acid concentration of the resulting multi-element standard was made up to 1% by adding HNO<sub>3</sub>. HNO<sub>3</sub> was purified by sub-boiling in PFA devices.

For the analysis of digested plastic material with ICP-MS the same 1 g L<sup>-1</sup> standard solutions were used to prepare the multi-element standard. Further internal standards (Sc, Y, CertiPur Merck, Darmstadt, Germany) were added to the calibration and sample solutions to correct for possible losses during the sample preparation step and possible signal drifts during measurements.

### Plastic samples

The in-house plastic samples were prepared according to industrial standard procedures through extrusion of masterbatches and subsequent dilution and mixing in a kneading chamber. Details of this process are described elsewhere.<sup>43</sup> Low density polyethylene (LPDE) and acrylonitrile butadiene styrene copolymer (ABS) were used as matrices. The doping of the polymer was done with organic (Cd(II)-acetate, Cr(III)-acetylacetonate, Cu(II)-bis-(2-ethylhexanoate), Fe(III)-acetylacetonate, Sb(III)-acetate) and for another sample set with inorganic compounds (CdO, Cr<sub>2</sub>O<sub>3</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>). The mass fractions of the analyte elements in the additive compound contained in the samples were in the range of 5 - 80 mg kg<sup>-1</sup>, for Sb up to 220 mg kg<sup>-1</sup> in ABS.

For verification of the developed method analysis of an certified reference material BAM H-010 (ABS doped with Cd, Cr, Pb<sup>44-46</sup>) and additional ABS polymers currently in the certification process with the same analyte elements (BAM-H005, -H008, -H009) were performed.

### Procedure of solid sampling ETV-ICP-OES

The used graphite equipment was not pyrolytically coated. Graphite boats were cleaned in advance with an ETV cleaning program see Table 1. The plastic samples were cut into pieces of about 5 - 10 mg on a metal-free surface using a ceramic knife. After weighing, the material was cleaned in 1% HNO<sub>3</sub> solution for 30 seconds and rinsed with Milli-Q-water for another 30 seconds to reduce surface contaminations. Then the samples were loaded in a graphite boat using titanium tweezers. For pyrolysis the boats were then placed in a muffle furnace (Controller B170, Nabertherm, Lilienthal, Germany) and heated up to 500 °C for 30 minutes. After cooling the graphite boats with the sample residues were placed into the autosampler.

Each sample was measured five times and the average of the five replicates was taken as representative value. A Grubbs test was performed to minimize the possible influence of outliers. Every working day a control sample was measured to check the long term stability and the instrument performance.

**Table 1** Instrumental operating conditions and data acquisition parameters for ETV-ICP-OES measurements

ICP-OES	IRIS Advantage Duo HR axial viewing	
RF power	1150 W	
Auxiliary gas	1 L/min	
Plasma gas	15 L/min	
ETV gas flows	150 mL/min argon mixed with 2 mL/min CCl <sub>2</sub> F <sub>2</sub>	
	400 mL/min argon (bypass gas)	
Sample mass	5-10 mg	
Pyrolysis step	before analysis in muffle furnace	
Oven	ETV 4000	
	temperature [°C]	ramp [s]
Measurement program	400	15
	450	15
	2100	8
	2250	17
	temperature [°C]	ramp [s]
Cleaning procedure	450	12
	480	15
	2250	5
	2350	20

### Quantification

The calibration was carried out with aqueous multi-element standard solutions. The solutions were pipetted into the graphite boats and dried using a heating plate with a temperature of 70 °C. Calibration points with higher absolute analyte masses were achieved by accumulating the solution in graphite boats. For quantification of analytes in ABS polymers calibration by standard addition was necessary. For that purpose ABS raw material, which was placed in the graphite boats, was doped with a liquid multi-element standard solution, dried and ashed. For analysis of LDPE samples external calibration was sufficient.

### Procedure of pneumatic nebulization ICP-MS/OES

About 60 mg of in-house LDPE and ABS samples were weighed. To remove possible surface contamination, the samples were stained in 1% HNO<sub>3</sub> solution for 30 seconds, rinsed with Milli-Q water and transferred into quartz digestion vessels. 4 ml of conc. HNO<sub>3</sub> s.b., 250 µl of an 8 mg L<sup>-1</sup> internal standard solution were added to correct signal drifts, instrument instability and matrix effects. Special processes were required for analysis of iron oxide embedded in ABS matrix. The determination of iron in an ABS-matrix was performed using mixture of 5 ml conc. HNO<sub>3</sub> s.b. and 1 ml conc. HCl. Internal standard was added. Due to a stronger gas formation of this acid mixture a microwave system with pressure compensation has to be used. The microwave digestions were carried out according to the digestion programs shown in table 2.

**Table 2** Microwave program for digestion of plastic samples

Sample mass	60 mg		40 mg	
Acid solution	4 ml HNO <sub>3</sub>		5 ml HNO <sub>3</sub> + 1 ml HCl	
Microwave	UltraClave III		Microwave 3000	
Power	1000 W		1400 W	
Program	time [min]	temperature [°C]	time [min]	temperature [°C]
	10	20 → 110	10	20 → 120
	10	110	40	120 → 220
	10	110 → 160		
	10	160		
	20	160 → 250		
	45	250		

After digestion the solution was diluted with Milli-Q water and measured with ICP-MS. From each digestion solution a double determination was performed. A blank value was determined and subtracted from the results.

Chromium as inorganic chromium oxide additive is not digestible with microwave digestion methods, so it was necessary to perform a melt-fusion. For that purpose 50 mg of the samples were cleaned of surface contaminations. After ashing the samples over a Bunsen burner in a porcelain crucible 300 mg of a 1:1 mixture of NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were added to the residue. This mixture was molten with a Bunsen burner and the cooled melt was dissolved in Milli-Q and after dilution measured with ICP-OES. For quantification an external matrix-matched calibration was applied. The ABS chromium oxide masterbatch was analysed and the content of the analytes in the samples were calculated with respect to the dilution in the extruder.

## Results and Discussion

### Preliminary experiments

#### Choice of spectral lines

For elemental analysis by ICP-OES the selection of the spectral lines to be used is essential. In preliminary experiments multiple lines were compared in respect to low detection limits and a wide linear range of the calibration function. Most useful lines for present matrices and concentration range in the investigated materials were selected and are listed in Table 3.

**Table 3** Limits of detection (3s definition) in ng absolute and limits of quantification for 5 mg sample weigh for trace element determination by ETV-ICP-OES; for calibration dried liquid standards were used; chosen emission lines marked grey; for comparison limits of content in dry, brittle, powder-like or pliable toy material according to European directive on the safety of toys are listed.

	LOD's			Toy	LOD's		
	nm	ng	mg kg <sup>-1</sup>		nm	ng	mg kg <sup>-1</sup>
Cd	226.5	0.1	0.1	1.9	234.3	8.9	5.3
	228.8	0.2	0.1		235.9	8.8	5.3
	326.1	0.3	0.2		248.3	9.9	6.0
	361.0	0.5	0.3		Fe 248.8	9.6	5.8
Cr	266.6	1.2	0.7	37.5 <sup>a</sup>	271.9	9.0	5.4
	276.6	1.4	0.8		272.0	8.9	5.3
	285.5	1.3	0.8		274.6	9.2	5.5
	301.7	1.6	1.0		Pb 261.4	1.9	1.1
Sb	302.4	1.1	0.7		217.5	13	7.8
	222.7	0.4	0.2	622.5	231.1	11	6.4
Cu	224.2	0.7	0.4		217.5	2.0	1.2
	249.2	1.3	0.8		Sb <sup>b</sup> 231.1	1.8	1.1

<sup>a</sup>-Cr (III) for Cr(VI) it is 0.02 mg kg<sup>-1</sup> <sup>b</sup>-without freon as modifier

The limits of detection, given in Table 3 were calculated by 3s-criterion<sup>47</sup> using the slopes of the calibration functions and the standard deviations of measurements of 5 empty graphite boats after cleaning procedure and pyrolysis. Calibration was carried out against dried aqueous multi-element standard solution.

For each analyte at least one emission line with a good linear correlation in the considered content range up to at least 640 ng could be found (Cd 361.0 nm, Cr 302.4 nm, Cu 224.2 nm, Fe 272.0 nm, Sb 217.5 nm). The use of these lines for calibration leads to correlation coefficients  $> 0.99$  for all analytes. The analyte contents in the in-house plastic materials range from 5 – 80 mg kg<sup>-1</sup> equivalent to 25 – 400 ng for a sample size of 5 mg. Especially for cadmium a less sensitive line is needed to be used to achieve a linear calibration function. The lowest limit of quantification 0.1 mg kg<sup>-1</sup> was determined for Cd at 226.5 nm. However Cd was measured at 361.0 nm due to a better linearity of the calibration curve especially for higher analyte content.

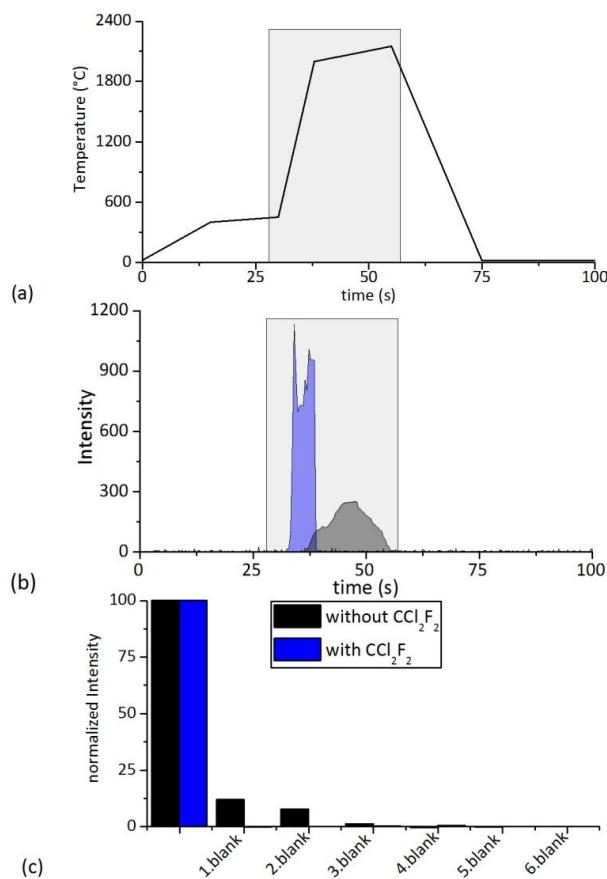
Furthermore limits of quantification were calculated after analysing ashed raw plastic sample materials (LDPE, ABS) as blanks. For the analytes Cd, Cr, Sb the determined limits of quantification analyzing pressed raw plastic sample materials are comparable to the ones determined with empty graphite boats. For Cu and Fe the limitation of the LOQ's is the available purity of the raw material. During the preparation process of the raw polymer material samples a contamination with these elements has been shown to occur<sup>43</sup>. Furthermore a contamination of the sample with ubiquitous iron during sample preparation is difficult to avoid. Therefore highest limit of quantification was observed for determination of iron. The determined 5 mg kg<sup>-1</sup> Fe in the in-house plastic samples is close to the limit of quantification. However, the LOQ's are sufficient to monitor the trace elemental content for the considered elements according to the European directive on safety of toys.

#### Temperature program and gaseous phase modifier

In the experiments the pyrolysis of the samples were performed in a separate muffle furnace. Usually the matrix separation step of the high carbon content matrix is performed in the ETV unit, but this can cause carbon deposition in the transport tubings or might affect the plasma stability and finally leads to an extended analysis time. Furthermore, the ETV furnace is loaded high amounts of CCl<sub>2</sub>F<sub>2</sub> after analysis of the sample – which can be problematic in the ashing step of the next sample. Due to evaporation caused by the modifier analyte losses can occur. Therefore we decided to perform the matrix separation separately in a muffle furnace. Additionally a much slower heating ramp for evaporation can be applied. This procedure leads to more reproducible results for all types of investigated plastic materials. For ashing the samples in the graphite boats were heated from room temperature to 500 °C with a 30 minutes ramp and that temperature was maintained for 5 minutes.

The ETV temperature program was dictated by the special characteristics of Cr, a refractory element which is evaporated at high temperatures under the presence of modifiers only. With the use of CCl<sub>2</sub>F<sub>2</sub> as modifier a complete vaporization of all determined analytes was achieved, which is demonstrated by the signal intensities returning to the baseline before the end of the measurement circle and furthermore significantly reduced memory effects occurred under the experimental conditions.

Without the use of CCl<sub>2</sub>F<sub>2</sub> the determination of a blank value after analysis of a liquid standard solution shows significantly higher signals. This increase can be up to 10% of the signals for previously analyzed samples especially for Cr, Cu and Fe. Up to three blank values after measuring the sample show higher analyte concentrations, which is shown in Figure 1 c. Cd and Sb have a not relevant memory effect that is not influenced significantly by CCl<sub>2</sub>F<sub>2</sub> addition.

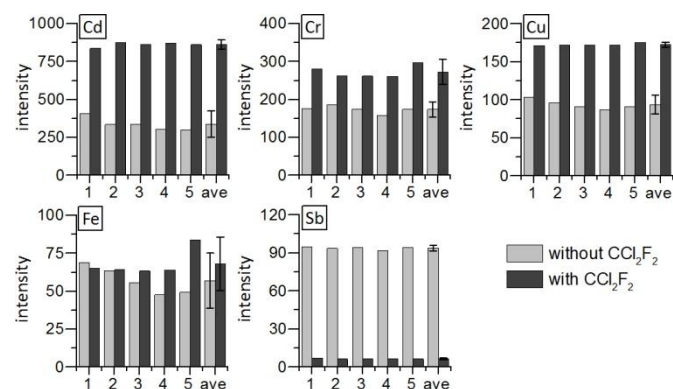


**Fig. 1** *a* - Temperature program for measurement of plastic material; *grey* – integration area for quantification; *b* - Time depending net spectral line intensities for Cr measurement of multi-element standard solution with and without use of CCl<sub>2</sub>F<sub>2</sub>; *c* - Blank determinations of Cr after measurement of multi-element standard solution (160 ng absolute, normalized to 100%) with and without use of CCl<sub>2</sub>F<sub>2</sub>

Because of the complete vaporization the addition of CCl<sub>2</sub>F<sub>2</sub> enhances the precision of the measurements. For Cd and Cu a relative standard deviation of five measurements of 1.8% respectively 1.9% percent could be achieved. Especially for Cd no precise measurement is possible and relative standard deviation rises up to 26% without the use of modifier. For Cu the same trend is visible with a RSD value of 13%.

For iron and chromium only little improvement could be achieved. Therefore a Grubbs-test was carried out after measuring samples to remove outliers caused by contaminations during the sample preparation process in the muffle furnace.

In addition to the reduction of the memory effect and precision improvements, the gaseous modifier increases the signal intensities for the analytes. Figure 2 shows the signal intensities of the investigated elements when measuring dried multi-element standard solutions with and without using CCl<sub>2</sub>F<sub>2</sub> as modifier gas.

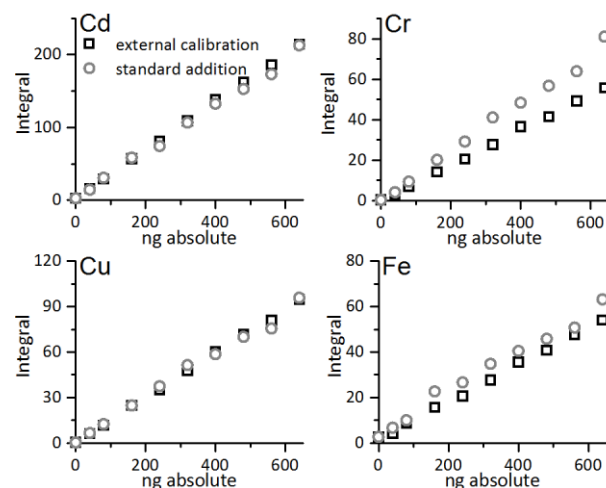


**Fig. 2** Signal intensities of measuring 5 times multi-element standard solution with ETV-ICP-OES with and without  $\text{CCl}_2\text{F}_2$  as modifier gas

For the determination of Cd the use of  $\text{CCl}_2\text{F}_2$  as modifier shows the highest increase of the sensitivity by a factor of 3. Cadmium is a typical carbide forming element and the increase of sensitivity can be explained by the formation of volatile halides. Cr, Cu, Fe showed 1.5-fold higher sensitivities when using  $\text{CCl}_2\text{F}_2$ . For the determination of antimony the addition of  $\text{CCl}_2\text{F}_2$  leads to a drastic decrease in sensitivity by a factor of 10 due to a possible analyte loss by formation of Sb-F. This effect is not fully understood yet and needs further investigations. Without  $\text{CCl}_2\text{F}_2$  the limit of detection for determination of Sb could be improved from 13 ng to 2 ng absolute analyte mass and even the precision is higher when no additional  $\text{CCl}_2\text{F}_2$  is used for antimony determination. RSD of 5 measurements is decreasing from 10% to 2%.

### Comparison of different calibration methods

After ashing of ABS-matrices a residue remains in the graphite boat. LDPE shows no visible residue. Residues may lead to false results of quantification with liquid standard calibration. To investigate possible influence of residues different calibration methods were tested. External calibration was compared with standard addition by spiking ABS raw polymer samples. Examples of the calibration functions are given in Figure 3.



**Fig. 3** Comparison between different calibration methods for ETV-ICP-OES

The calibration curves of external calibration and the method of standard addition have similar slopes for the analytes. However, for chromium the calibration function differed significantly. This must be taken into account when quantifying chromium content in ABS-samples. The sensitivity for external calibration points is much lower than that for standard addition calibration points. Therefore, using slope values from external calibration leads to an overestimation for

chromium in a candidate reference material by a factor of 1.5. By using standard addition a very good recovery of about 100% is achieved compared to the certified value. One reason for this may be the non-complete ashing of the matrix in the muffle furnace. This may result in additional matrix load of the plasma and furthermore different evaporation behaviour of the analyte after ashing and from dried liquid standards resulting in sensitivities not comparable with these obtained by external calibration.

### Quantification and verification

#### Quantitative analysis of ABS and LDPE in-house plastic samples

All following investigations were carried out using the optimized measurement conditions listed in Table 1. We analyzed in-house ABS and LDPE samples doped with organic and inorganic additives.

In Table 4 the contents of analytes determined by ETV-ICP-OES, the results by microwave digestion and subsequent analysis using ICP-MS and the values calculated from weighing the plastic masterbatches and their dilution in the kneading chamber are shown. The determination of antimony was limited to 5 samples (25 measurements) due to the special parameters required for antimony quantification.

For both plastic matrices the determined values are in good agreement with those gathered by ICP-MS analysis after microwave digestion. For chromium incorporated as an inorganic additive the values were compared with those from ICP-OES measurements after fusion and also show a good agreement.

The deviations between the determined values and the weighed values in low density polyethylene especially for copper and iron are attributed to the preparation of the polymer samples in a steel kneading chamber, which resulted in a contamination of the material with these elements.

The determined iron and copper contents show a better precision in the ABS matrix than in the LDPE matrix. This indicates that the content of the doped elements in an acrylonitrile butadiene styrene matrix is more homogeneously distributed than in low density polyethylene<sup>43</sup>. Due to the small sample weight of 5-10 mg homogeneity of the samples is an important factor for the precision of the determination. For inhomogeneous samples more individual analyses have to be performed to improve the precision of the result.

The results demonstrate that the developed method is suitable for determination of analytes independent of the chemical form (inorganic or organic compound) of the additives.

**Table 4** Quantitative results of the analysis of the samples by means of ETV-ICP-OES, the uncertainties are provided as two times standard deviation of the 5 replicates. Reference values obtained by means of solution-ICP-MS and for inorganic chromium by ICP-OES measurements are provided for comparison purposes

ABS	Cd 361.0		Cr 302.4		Cu 224.2		Fe 272.2		Sb 217.5	
	low	high	low	high	low	high	low	high	low	high
<b>inorganic additive</b>										
ETV-ICP-OES	5.5 ± 0.3	56.0 ± 1.3	7.3 ± 0.2	77.8 ± 3.0	11.7 ± 4.0	57.3 ± 1.2	8.7 ± 1.3	60.0 ± 1.5	21.6 ± 4.0	209.6 ± 6.4
weighed value <sup>a</sup>	5.9 ± 0.4	59.0 ± 4.2	7.5 ± 0.5	71.6 ± 5.0	4.8 ± 0.3	46.8 ± 3.3	5.1 ± 0.4	46.7 ± 3.3	21.6 ± 1.5	212.3 ± 15
reference value <sup>b</sup>	5.6 ± 0.1	54.1 ± 0.6	7.6 ± 0.6	72.5 ± 6.0	9.6 ± 0.3	60.1 ± 2.2	7.4 ± 0.6	52.2 ± 4.2	20.9 ± 0.8	214.2 ± 4.3
<b>organic additive</b>										
ETV-ICP-OES	4.7 ± 0.6	53.0 ± 0.8	3.9 ± 0.3	49.8 ± 1.7	15.9 ± 6.4	69.6 ± 1.3	7.9 ± 1.9	55.6 ± 3.1	13.8 ± 2.2	155.3 ± 3.2
weighed value <sup>a</sup>	4.8 ± 0.3	49.9 ± 3.5	5.1 ± 0.4	51.6 ± 3.6	5.0 ± 0.3	49.5 ± 3.4	4.9 ± 0.3	50.2 ± 3.5	15.7 ± 1.1	157.6 ± 11
reference value <sup>b</sup>	4.9 ± 0.2	50.7 ± 2.0	5.5 ± 0.3	54.1 ± 3.2	12.2 ± 0.2	69.0 ± 1.4	5.5 ± 0.3	49.8 ± 3.0	15.0 ± 0.9	151.8 ± 4.6
<b>LDPE</b>										
	Cd 361.0		Cr 302.4		Cu 224.2		Fe 272.2		Sb 217.5	
	low	high	low	high	low	high	low	high	low	high
<b>inorganic additive</b>										
ETV-ICP-OES	4.8 ± 0.3	47.2 ± 0.4	3.9 ± 0.2	49.4 ± 3.4	12.4 ± 5.2	62.7 ± 16	11.0 ± 8.8	55.2 ± 14		
weighed value <sup>a</sup>	4.9 ± 0.3	50.2 ± 3.5	3.7 ± 0.2	49.7 ± 3.4	7.2 ± 0.6	50.0 ± 4.3	5.0 ± 0.6	49.8 ± 6.0		
reference value <sup>b</sup>	4.4 ± 0.1	43.4 ± 1.3	n.a	n.a	9.2 ± 1.8	48.2 ± 9.6	7.1 ± 0.8	52.7 ± 6.3		
<b>organic additive</b>										
ETV-ICP-OES	5.6 ± 0.1	56.1 ± 2.8	6.1 ± 0.7	41.8 ± 6.4	32.5 ± 2.5	78.8 ± 7.5	8.6 ± 2.9	52.1 ± 5.7		42.4 ± 7.8
weighed value <sup>a</sup>	5.2 ± 0.4	49.5 ± 3.7	5.4 ± 0.4	49.4 ± 3.4	4.3 ± 0.3	43.6 ± 3.0	4.5 ± 0.3	46.1 ± 3.3		53.6 ± 3.8
reference value <sup>b</sup>	5.3 ± 0.2	49.1 ± 1.5	5.8 ± 0.4	40.7 ± 2.9	29.7 ± 3.0	71.0 ± 7.1	6.3 ± 0.4	44.2 ± 3.0		44.5 ± 3.6

<sup>a</sup> calculated from dilution of masterbatches

<sup>b</sup> obtained by solution ICP-MS/ for inorganic Cr by ICP-OES

#### Verification of the method by use of reference materials

For further verification of the method for the quantification of trace elements in ABS plastic materials analysis of the certified reference material BAM-H010 and the candidate reference materials BAM-H005, -H008, -H009 was performed. In these samples Cd, Cr and Pb contents are certified. To verify the method these elements were determined. The samples also showed residues after pyrolysis and were therefore quantified by standard addition. The obtained quantitative results are shown in Table 5.

**Table 5** Analysis of the candidate reference materials BAM-H005, -H008, -H009 and certified BAM-H010 by means of ETV-ICP-OES, quantitative results. The uncertainties are provided as two times standard deviation of the 5 replicates. Reference values obtained by means of isotope dilution solution-ICP-MS are provided for comparison purpose, for BAM H-010 the certified values are written

	Cd	Cr	Pb
<b>BAM-H005 (mg kg<sup>-1</sup>)</b>			
ETV-ICP-OES	177.6	43.7 ± 1.6	15.8 ± 0.6
reference value <sup>b</sup>	181.2 ± 0.4	45.6 ± 0.1	15.3 ± 0.1
<b>BAM-H008 (mg kg<sup>-1</sup>)</b>			
ETV-ICP-OES	2.7 ± 0.5	5.6 ± 0.9	26.2 ± 1.1
reference value <sup>b</sup>	2.7 ± 0.1	6.8 ± 0.2	24.6 ± 0.1
<b>BAM-H009 (mg kg<sup>-1</sup>)</b>			
ETV-ICP-OES	51.1 ± 1.3	25.7 ± 0.7	6.0 ± 0.1
reference value <sup>b</sup>	49.9 ± 0.1	25.7 ± 0.1	5.58 ± 0.02
<b>BAM-H010 (mg kg<sup>-1</sup>)</b>			
ETV-ICP-OES	94.1 ± 1.2	472.8 ± 26	489.7 ± 49.2
reference value <sup>c</sup>	93 ± 5	470 ± 36	479 ± 17

<sup>a</sup> sample weight 5 mg

<sup>b</sup> obtained by isotope dilution analysis

<sup>c</sup> certified reference value

The use of standard addition leads to very good recoveries in the quantification of the analytes in the standard samples. For cadmium and lead recoveries of 100 ± 7% are achieved. The chromium contents show recoveries of 100 ± 5% for all investigated reference materials. The precision of the determination is considerably higher due to the better homogeneity of the reference in comparison to the in-house samples.

#### Conclusion

The results presented in this work show that analysis by solid sampling ETV-ICP-OES is able to correctly quantify trace elements in plastic samples after ashing them in a muffle furnace. The limits of detection for Cd, Cr, Cu, Sb and Pb are suitable for monitoring of the European directive on safety of toys. The use of CCl<sub>2</sub>F<sub>2</sub> as modifier significantly improves reproducibility and sensitivity with exception of Sb. It could be shown that the results for analyzing in-house plastic material and the certified reference material (BAM-H010) were in good agreement with results obtained by commonly used techniques. For LDPE matrices quantification against dried liquid standards was possible, but for ABS materials standard addition had to be used. The developed method under optimized conditions enables a determination of the element content independent of the chemical form of the additives. However, the different boiling points of the different forms should be considered, to avoid analyte losses during matrix removal a muffle furnace. In comparison to other more established methods no time and work intensive digestion step is required. Even Cr as Cr<sub>2</sub>O<sub>3</sub> is quantifiable without any special sample preparation. The method enables a fast multi-element analysis of plastic materials, with a high sample throughput (3 minutes per analysis), low sample consumption, good accuracy and precision for the determined elements.

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## Notes and references

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1. R. Pfaendner, *Polymer Degradation and Stability*, 2006, **91**, 2249-2256.
2. P. Patel and B. Puckerin, *Plast Eng*, 2006, **62**, 14-16.
3. *Plast World*, 1975, **33**, 50-50.
4. *Plast Eng*, 1977, **33**, 32-38.
5. R. C. Kidder, *Plast Eng*, 1977, **33**, 38-42.
6. S. Giaccoppo, M. Galuppo, R. S. Calabro, G. D'Aleo, A. Marra, E. Sessa, D. G. Bua, A. G. Potorti, G. Dugo, P. Bramanti and E. Mazzon, *Biological Trace Element Research*, 2014, **161**, 151-160.
7. *Official Journal of the European Union*, 2009, **L170**, 1-37.
8. *Official Journal of the European Union*, 2011, **L174**, 88-110.
9. H. Sakurai, J. Noro, A. Kawase, M. Fujinami and K. Oguma, *Analytical Sciences*, 2006, **22**, 225-228.
10. K. Jankowski, A. Jerzak, A. Sernicka-Poluchowicz and L. Synoradzki, *Analytica Chimica Acta*, 2001, **440**, 215-221.
11. S. Cadore, E. Matoso and M. C. Santos, *Quim Nova*, 2008, **31**, 1533-1542.
12. K. D. Besecker, C. B. Rhoades, B. T. Jones and K. W. Barnes, *Atomic Spectroscopy*, 1998, **19**, 193-197.
13. K. D. Besecker, C. B. Rhoades, B. T. Jones and K. W. Barnes, *Atomic Spectroscopy*, 1998, **19**, 55-59.
14. M. Zischka, P. Kettisch and P. Kainrath, *Atomic Spectroscopy*, 1998, **19**, 223-227.
15. Q. B. Lin, B. Li, H. Song and H. J. Wu, *Food Additives and Contaminants Part a-Chemistry Analysis Control Exposure & Risk Assessment*, 2011, **28**, 1123-1128.
16. N. Longas, R. G. Arrona, M. Ostra and E. Millan, *Atomic Spectroscopy*, 2009, **30**, 47-53.
17. S. Strenger and A. V. Hirner, *Fresenius Journal of Analytical Chemistry*, 2001, **371**, 831-837.
18. V. K. Karandashev, K. V. Zhernokleeva, V. B. Baranovskaya and Y. A. Karpov, *Inorg Mater+*, 2013, **49**, 1249-1263.
19. M. Resano, F. Vanhaecke and M. T. C. de Loos-Vollebregt, *Journal of Analytical Atomic Spectrometry*, 2008, **23**, 1450-1475.
20. R. E. Russo, X. L. Mao, H. C. Liu, J. Gonzalez and S. S. Mao, *Talanta*, 2002, **57**, 425-451.
21. R. E. Wolf, C. Thomas and A. Bohlke, *Applied Surface Science*, 1998, **127**, 299-303.
22. A. N. Kadachi and M. A. Al-Eshaikh, *X-Ray Spectrometry*, 2012, **41**, 350-354.
23. G. W. Tindall, *Analytical Chemistry*, 1977, **49**, 1403-1405.
24. S. Richter, *Plasma Spectrochemistry in Material Sciences—Theory and Recent Applications*, John Wiley & Sons, 2013.
25. A. Asfaw and G. Wibetoe, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2009, **64**, 363-368.
26. A. Detcheva, P. Barth and J. Hassler, *Analytical and Bioanalytical Chemistry*, 2009, **394**, 1485-1495.
27. F. Vanhaecke, M. Resano and L. Moens, *Analytical and Bioanalytical Chemistry*, 2002, **374**, 188-195.
28. M. Lucic and V. Krivan, *Fresenius Journal of Analytical Chemistry*, 1999, **363**, 64-72.
29. J. Hassler, G. Zaray, K. Schwetz and K. Florian, *Journal of Analytical Atomic Spectrometry*, 2005, **20**, 954-956.
30. P. Barth, J. Hassler, I. Kudrik and V. Krivan, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2007, **62**, 924-932.
31. A. Asfaw, G. Wibetoe and D. Beauchemin, *Journal of Analytical Atomic Spectrometry*, 2012, **27**, 1928-1934.
32. J. F. Maurice, G. Wibetoe and K. E. Sjustad, *Journal of Analytical Atomic Spectrometry*, 2002, **17**, 485-490.
33. R. Lam and E. D. Salin, *Journal of Analytical Atomic Spectrometry*, 2007, **22**, 1430-1433.
34. M. A. Belarra, M. Resano, F. Vanhaecke and L. Moens, *Trends in Analytical Chemistry*, 2002, **21**, 828-839.
35. M. Resano, M. Aramendia, W. Devos and F. Vanhaecke, *Journal of Analytical Atomic Spectrometry*, 2006, **21**, 891-898.
36. M. Resano, M. Verstraete, F. Vanhaecke, L. Moens and J. Claessens, *Journal of Analytical Atomic Spectrometry*, 2001, **16**, 793-800.
37. M. Resano, M. A. Belarra, J. R. Castillo and F. Vanhaecke, *Journal of Analytical Atomic Spectrometry*, 2000, **15**, 1383-1388.
38. M. W. Hinds, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 1993, **48**, 435-445.
39. T. Kantor and M. T. C. de Loos-Vollebregt, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2005, **60**, 333-343.
40. J. M. Ren and E. D. Salin, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 1994, **49**, 555-566.
41. J. M. Ren and E. D. Salin, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 1994, **49**, 567-575.
42. J. Hassler, P. Barth, S. Richter and R. Matschat, *Journal of Analytical Atomic Spectrometry*, 2011, **26**, 2404-2418.
43. D. Deiting, paper in progress.
44. M. Ostermann, A. Berger, C. Mans, C. Simons, S. Hanning, A. Janssen and M. Kreyenschmidt, *Accreditation and Quality Assurance*, 2011, **16**, 515-522.
45. C. Mans, C. Simons, S. Hanning, A. Janssen, D. Alber, M. Radtke, U. Reinholz, A. Buhler and M. Kreyenschmidt, *X-Ray Spectrometry*, 2009, **38**, 52-57.
46. C. Mans, S. Hanning, C. Simons, A. Wegner, A. Janssen and M. Kreyenschmidt, *Spectrochimica Acta Part B-Atomic Spectroscopy*, 2007, **62**, 116-122.
47. *DIN 32645*, 2008.