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Oslo, April 2007

Linda Storrustløkken

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SYMBOLS AND ABBRIVATIONS

CRM	Certified Reference Material
EC	European Commission
ERM	European Reference Material
ETV	Electrothermal Vaporisation
GC	Gas Chromatography
HDPE	High Density Polyethylene
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
LA	Laser Ablation
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
LOD	Limit of Detection
LOQ	Limit of Quatification
NAA	Neutron Activation Analysis
PE	Polyethylene
PP	Polypropylene
TOF	Time of Flight
XRF	X-ray Fluorescence

SAMMENDRAG

Plastposer og plastfolier laget fra polyetylen (PE) er ofte gjenstand for bevismateriale i kriminalsaker, enten det er innhentet fra et åsted eller beslaglagt fra personer. Å kunne spore plastmaterialet, beslaglagt fra åstedet eller personen, tilbake til dets kilde vil kunne ha stor betydning i kriminaletterforskning og eventuelle rettssaker.

Hensikten med denne oppgaven var å utvikle en metode for å kunne bestemme spormetaller i transparente plastmaterialer for å se om ett eller flere av grunnstoffene kunne anvendes til å diskriminere mellom plastprøver. Plastmaterialene, som ofte er assosiert med narkotikasaker, er typisk transparente typer av plastfolier, brødposer, fryseposer osv.

I dette arbeidet ble det benyttet Mikrobølgeovn til å dekomponere plastprøvene og ICP-MS til deteksjon av spormetaller i prøveløsningene. Konsentrasjonen av Al, As, Ba, Bi, Cd, Co, Ga, Ge, In, Mg, Mn, Pb, Sb, Te og V ble bestemt i seks plastkilder av typene nevnt over. Al, Ba, Cd, Mg og Mn kunne påvises i samtlige prøver, og hadde derfor størst diskrimineringspotensiale. Disse fem grunnstoffene ble vurdert opp mot fire punkter, (i) konsentrasjonen i prøven sammenlignet med deteksjonsgrensen, (ii) distribusjonen i plastkilden, (iii) variasjonen mellom plastkilder og (iv) spektral interferenser.

Et ideelt diskriminerende grunnstoff har konsentrasjon signifikant over deteksjonsgrensen, er uniformt distribuert gjennom hele prøven, viser signifikante konsentrasjonsforskjeller mellom prøver og er ikke utsatt for spektral interferenser. Mg oppfylte disse kriteriene best, etterfulgt av Mn, Al, Cd og Ba i den spesifiserte rekkefølgen.

Det ble utført både en visuell og statistisk diskrimineringsmetode. Henholdsvis, et ternært diagram basert på isotopratene for Mg, Mn og Al for hver av prøvereplikatene, og en tosidet t-test basert på grunnstoffkonsentrasjonene for Mg og evt. Mn. Alle de seks kildene i dette arbeidet kunne diskrimineres med tosidig t- test (95 og 99% konfidensintervall) ved kun å bruke Mg og Mn.

SUMMARY

Plastic bags and cling films made from polyethylene (PE) features in a variety of crimes, and are often recovered or seized as evidence. It would be of great value, in a criminal investigation and in a court, if this plastic evidence could be traced back to its source.

The aim of this study was to develop a method in order to determine trace metals in transparent plastic materials, often associated with drug trafficking. Cling films, bread bags and freezing bags are frequently being used in order to wrap small quantities of drug.

Microwave decomposition of the samples and ICP-MS as a detection system were used in this work. The concentration of Al, As, Ba, Bi, Cd, Co, Ga, Ge, In, Mg, Mn, Pb, Sb, Te and V were determined in six sources of plastic of the aforementioned type. Al, Ba, Cd, Mg and Mn were detected in all of the samples under study, and were therefore regarded as the elements with the greatest discrimination power. These five elements were tested against four proposed criteria, i.e. (i) the concentration compared to the corresponding detection limit, (ii) the distribution within the plastic sample, (iii) the variation between sources, and (iv) spectral interferences.

An ideal discriminating element has a concentration significant above its limit of detection, is uniformly distributed throughout the entire roll of plastic, shows significant variation between different plastic sources, and are not subjected to any spectral interferences. Mg satisfied these criterions the most, followed by Mn, Al, Cd and Ba in that specified order.

Both visual and statistic discrimination were performed. Respectively, a ternary diagram based on isotope ratios of Mg, Mn and Al for each sample, and a two-sided t-test based on element concentrations of Mg and possible Mn. All six sources of plastic under study in this work could be discriminated with the two-sided t-test (at 95 and 99 % confidence interval), using Mg and Mn.

1 INTORDUCTION

1. 1 Trace element determinations of polyethylene samples; fields of application

Trace element determinations of polyethylene (PE) bags and cling films are useful for several reasons. Section 1.1.1 through 1.1.3 present the forensic, health and environmental, and quality management fields, respectively.

1. 1. 1 In a forensic point of view

Plastic bags and cling films made from polyethylene (PE) features in a variety of crimes and are often recovered or seized as evidence, e.g. sandwich bags, freezer bags and cling films are often divided into smaller fragments in order to wrap quantities of drugs (Ford, 1975). It is also common that drug dealers wrap a small amount of drug into many layers of cigarette papers and cling films respectively. This is called a "drug bubble" and are made in such a way that it can be carried in the mouth and swallowed with minimal effects if the dealer, the so-called body stuffer, is caught (Püschel et al., 2004).

It would be of great importance in a criminal investigation and in a court, if the recovered or seized plastic sample could be traced back to its source (see section 1.4.1 and 1.4.2).

1. 1. 2 In a health and environmental point of view

Many papers concern the need to perform trace element analysis of plastic materials in view of the harmful impact that plastics may have on living organisms and on the environment if it contains large amounts of noxious elements (see references in the text below).

Food contact plastic materials should contain as little as possible of toxic elements due to the potential migration of these elements into the food product (Fordham et al., 1995; Perring et al., 2001; Skrzydlewska and Balcerzak, 2003; Skrzydlewska et al., 2003; Thompson et al., 1996). However, it is of great concern in general as plastic packaging materials are being used on a daily basis in a variety of fields. Landfills are filled up with enormous amounts of plastic materials, which may release toxic elements upon final destruction (Bode, 1993; Nomura et al., 2000; Skrzydlewska and Balcerzak, 2004).

1. 1. 3 In a quality management point of view

Thermoplastic polymer additives are an enormous field of study. The following is drawn from Lutz (1989), if otherwise not stated.

Additives are added to the polymer in order to fulfill specific tasks, and may be antioxidants which prevents oxidation by molecular oxygen, flame retardants which change the flammability of a combustible material, plasticizers which increases the materials workability, pigments imparting color to the material, etc.

It is important to control which additives and in what concentrations they are present in the polymer. The compatibility between the various additives, and between the additive and the polymer matrix are variable. Pigments such as titanium dioxide can promote discoloration of some phenolic antioxidants, as an example of the former, while transition metal ions may have deleterious effects on polymers stability in the latter case. It is also important to control the concentration of noxious elements for the reasons briefly mentioned in section 1.1.2.

1. 2 EC[1] regulation and Certified Reference Materials

The heavy metals present in all types of packaging placed on the market and all packaging waste undergoes EC regulation (94/62/EC) for those reasons mentioned in section 1.1.2. This directive, introduced Dec. 94, states that the sum of concentration levels of Cd, Cr(VI), Hg and Pb should not exceed 100 mg/kg after the year 2001.

The lack of certified reference materials made from polymer material and designed for elemental analysis initiated a collaborative study between laboratories after the introduction of the directive 94/62/EC. The final aim of this work was to certify polymer reference materials for their contents of a range of elements in order to improve the quality control of trace element determinations in polymers. The result was the two certified reference materials ERM®-EC680 and ERM®-EC681 (originally BCR680 and BCR681) available from the Institute of Reference Materials and Measurements (IRMM) (Van Borm et al. 1999; Vogl et al. 2000; Lamberty et al., 2001; Lamberty et al., 2001a).

Only one set with four polyethylene reference materials with Cd mass fractions from 40 to 400 mg/kg (VDA 001- 004), available from IRMM, exist in addition to the aforementioned ERM®-EC680 and ERM®-EC681 (Lamberty et al., 2001a).

1. 3 The manufacturing process of polyethylene bags and cling films

The refined oil or the natural gas is introduced to a cracker where larger molecules are broken down to ethylene. A polymerization process follows which produce the desired polymer depending on the catalyst and production conditions used, e.g. high- or low-density polyethylene (mindfully.org). The manufacturing process that follows is extensive and involves a great deal of contact between the extruded polymer film with the numerous machine parts. Only a very comprehensive version is presented here.

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[1] European Commision

The polymer granulates is melted together with additives before it is extruded through a circular die. The tube is cooled and collapsed between rollers before heat sealed and cut or perforated to form the single bags (Castle et al., 1994; Pierce, 1990; von Bremen and Blunt, 1983). The cling films are also usually being manufactured by this blown film extrusion technique just outlined (Castle et al., 1994). The metals presented in the final product may be due to the various additives added (see section 1.1.3), but also due to contamination from machine parts, catalyst residues etc.

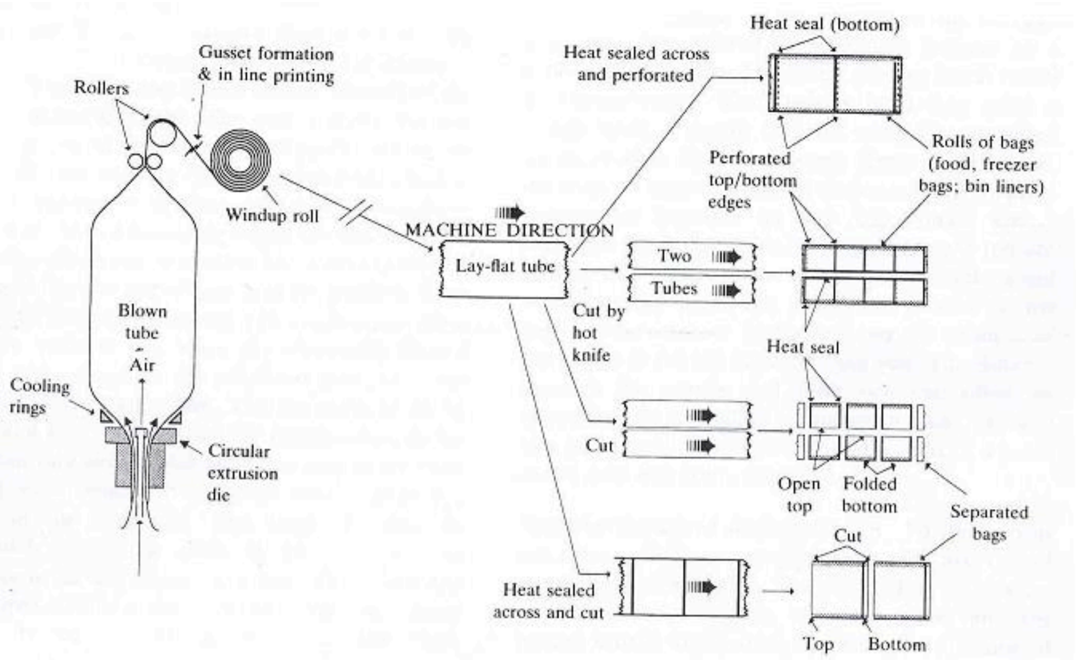

Fig. 1. 1 Principal sketch over the manufacturing process (Castle et al., 1994)

1. 4 Discrimination methods in criminal investigations

1. 4. 1 Discrimination methods based on physical characteristics

Various authors have described one or more of the following techniques; Shadowgraphs imaging, Schlieren imaging, microscopy and/ or the use of polarization filters in order to enhance, magnify or visualize physical characteristics in transparent plastic bags or cling films. These examinations may be of great value in criminal investigations (Castle et al., 1994; Ford, 1975; von Bremen, 1975; Pierce, 1990).

The marks found on plastic products can frequently be attributed to the manufacturing process (see section 1. 3). von Bremen and Blunt (1983) gives a detailed survey of the characteristics found on plastic bags and cling films, and relates these to specific machine parts in the manufacturing process.

Consumers may also impart markings to the plastic products. Stone (1986) examined and compared plastic bags used in home heat sealers. In such cases, not only can the plastic bags be traced back to its source, but it may also be associated with items, in this case a home heat sealer, belonging to the suspect.

However, a physical comparison is not always possible, especially not if only fragments from e.g. an explosion site are available or if the matrix has degraded over time (Nissen et al., 1998). Cling films are also subjected to some difficulties as it is easily distorted (Gilburt et al. 1991).

1. 4. 2 Discrimination based on chemical composition

A survey of the literature revealed only five papers concerning the discrimination of plastic bags or cling films of different origin based on chemical compositions (Cleverley, 1979; Gilburt et al., 1991; Iodine et al., 2005; Nir- El, 1994; Nissen et al., 1998).

All five papers concerned, in various degree, the analysis of transparent polyethylene (PE) samples. Cleverly (1979) used frequencies, shapes and relative intensities of weak IR absorption bands to successfully discriminate between the samples. Gilburt et al. (1991) and Iodine et al. (2005) used GC methods to successfully discriminate between the samples. Unfortunately, the GC chromatogram depends strongly on the sample history, e.g. exposure to sunlight, which makes it less useful in linking samples of common origin but different histories.

Nissen et al. (1998) and Nir-El (1994) used inorganic elemental profiles obtained by ICP-MS and XRF, respectively, in order to discriminate between PE samples. The discrimination of colored PE samples was successfully in both cases. Concerning the transparent samples, Nissen et al. (1998) concluded, based on semi-quantitative measurements that the concentrations of the trace elements were to low and uneven distributed to be of any value as a discriminating element. Nir-El (1994) found that the ratios between peaks' of Fe, Cu and Zn correlated with the origin of the polyethylene.

1. 5 Trace Element Analysis of transparent polyethylene samples

1. 5. 1 Techniques described in the literature

Highly sensitive methods are required concerning the elemental analysis of transparent plastics due to the low analyte concentrations at µg/kg and mg/kg levels (Skrzydlewska and Balcerzak, 2004).

NAA is such a method and has proved to be well suited for analysis of plastics, and organic materials in general, where the major components are C, H and O. These elements do not activate upon irradiation with thermal neutrons, and any trace metals present will be easily detected (Thompson et al., 1997). However, even though NAA is sensitive, non destructive and require no pretreatment of the sample (Thompson et al., 1995), the instrumentation is not commonly available in laboratories.

Alternative methods have been described in the literature for the determination of trace elements in plastics. Fordham et al. (1995) used ICP-MS to determine element residue in food contact plastics. ICP-TOF-MS was used to determine toxic elements in both food contact (Skrzydlewska and Balcerzak, 2004) and non-food contact (Skrzydlewska and Balcerzak, 2003) plastic packaging materials. ICP-MS offers detection limits down to ng/kg and µg/kg for a range of elements, multi elemental capability, selectivity, possibility to simultaneous isotope determinations and high sample throughput (Skrzydlewska and Balcerzak, 2004).

ICP-MS has also been combined with sample introduction techniques such as LA (Resano et al., 2005) and ETV (Vanhaecke et al., 2000) in order to determine trace elements in polyethylene. These techniques make it possible to analyze the solid sample directly, which is of interest if the material cannot be, or are difficult to decompose. Additionally, solid sampling reduces the sample pretreatment and thereby the risk of contamination or analyte loss (Vanhaecke et al., 2002). Resano et al. (2001) evaluated the multi element capabilities of ETV quadropole based ICP-MS and concluded that 20 elements could be monitored for a standard peak width of 1.5-2 s without detrimental effects on the precision, detection limits and sensitivity as long as three to four critical points defined the signal profile.

The determination of inorganic elemental profiles of plastic bags by XRF is also described in the literature (Nir-El, 1994). XRF offers a very broad dynamic range and the technique is capable of detecting concentrations down to sub mg/kg. As for NAA, LA- and ETV-ICP-MS, the technique is multi elemental, and solid samples can be analyzed directly.

1. 5. 2 Trace elements in real samples

Fordham et al. (1995), Nir-El (1994), Nissen et al. (1998) and Thompson et al. (1995) analyzed transparent food contact packaging materials made from polyethylene (PE) for most of the elements in the Periodic Table. Fordham et al. (1995) reported significant concentrations of Al, Cr, Mg and Zr using ICP-MS. Analysis performed by

XRF showed major peaks for Cu, Fe and Zn (Nir-El, 1994). Only Al, Ba, Cd, Cu, Mg, Mn, Ni, Pb, Sr and Ti were detected by ICP-MS at concentrations above their detection limits in the semi-quantitative analysis performed by Nissen et al. (1998). Most of these elements had concentrations lower than five to ten times the detection limits, and only Al, Mg and Ti occurred at concentrations greater than 1 mg/kg. Thompson et al. (1995) detected high concentrations, above 1000 mg/kg, of Ba, S, Ti and Zn. In addition were Al, Ca, Cl, Cu, K, Mg, Na, Si and Sr present in concentrations ranging from 7.9 mg/kg (Cu) to 146 mg/kg (Al). As, Co, Mn and Sb were present at concentrations less than 1 mg/kg. These analyses were performed by NAA.

The raw PE material was also analyzed in the study performed by Thompson et al. (1995). Generally, only Al, Ca, Cl, Co, Cr, In, Mn, Na, Nd, Sb, Ti and Zn were detected in these samples. Cl showed the highest concentration with 1.03 mg/kg.

1. 6 Development of microwave decomposition procedures for polymers

The following is drawn from Kingston and Walter (1998), if otherwise not stated. Especially two parameters are important in developing an optimal microwave decomposition procedure, i.e. the choice of reagents and the temperature profile, which in turn are highly dependent on the matrix. Polymers are generally decomposed using high temperatures. The oxidation efficiency of e.g. HNO_3 is enhanced as the temperature is increased. Long decomposition times may also be required if the polymer is very hydrophobic, floats on the surface of the decomposition reagents or are slowly digested. The acid mixture HNO_3 and H_2O_2 are reported in the literature regarding the decomposition of low-density polyethylene or polypropylene matrices (Nissen et al., 1998; Resano et al., 2005; Skrzydlewska and Balcerzak, 2003; Skrzydlewska and Balcerzak, 2004), while a mixture of HNO_3, H_2O_2 and H_2SO_4 are reported for the decomposition of high-density polyethylene (Resano et al., 2005; Skrzydlewska and Balcerzak, 2004). Eilola and Perämäki (2003) used the latter combination in their work of developing a microwave decomposition procedure for organic materials that are difficult to decompose. Knowledge of the acid chemistry is important regarding the development of a decomposition procedure. Kingston and Walter (1998) gives a brief review of the subject.

1. 7 Visual and statistical discrimination methods

Ternary diagrams have been used to identify the origin of crime scene evidences, e.g. glass, steel (Watling et al., 1997) and document papers (Spence et al., 2000). A description of ternary discrimination plots is given in Appendix L. Ternary plots displays and compares trace elements signatures, but statistical significance tests provides the concluding test for the effectiveness of trace elements in discrimination of samples, e.g. papers (Spence et al., 2000) and colored polyethylene bags (Nissen et al., 1998; Nir-El, 1994). The two sample t-test were applied to test whether the difference between two experimental results were significant.

1. 8 Aim of study

Examinations in forensic laboratories are often based on comparison analysis. The purpose is to establish a link between the recovered evidence with items belonging to a suspect.

It has been an increasingly interest over the past years in identifying the source of the recovered evidence based on trace element compositions, so called fingerprinting. A search in literatures showed that trace metal analyses in forensic connections mainly have been carried out on glass (Duckworth et al., 2002), painting (Hobbs and Almirall, 2003), drug (Watling, 1998) and projectiles (Ulrich et al., 2004). However, bags and cling films made from low-density polyethylene (LDPE) features in a variety of crimes such as shoplifting, drug trafficking, murders etc. and are recovered as evidence from these crime scenes. Despite these facts, few papers describe the trace element analysis of plastic in order to discriminate between samples.

The aim of this study was to develop a method for the trace metal analysis of food contact plastic materials in order to determine weather one or more elements could be used to discriminate between similar plastics of different origin. Microwave oven was used in order to decompose the samples and ICP-MS for detection of trace elements in the sample solutions.

A suitable discriminating element satisfies the following criteria (Spence et al., 2000); it is (i) present at concentrations significant above its limit of detection (LOD), (ii) uniformly distributed throughout the roll of plastic, (iii) unaffected by any spectral interferences and it (iv) shows a statistically significant variation in concentration from one plastic source to another.

2 EXPERIMENTAL

2. 1 Equipment and instruments

Equipment used in laboratory work but not listed in this section will be specified in the text when appropriate.

2. 1. 1 Water purification systems

2. 1. 1a Type I water

Milli-Q® 185 Plus and Synthesis A10 (Millipore, Billerica, USA)
Supplier: Millipore, Norway

Resistance > 18 MΩ cm at 25 ˚C

2. 1. 1b Type II water

Millipore, Automatic Sanitization Module (Millipore, Billerica, USA)
Supplier: Millipore, Norway

Resistance > 1 MΩ cm at 25˚C

2. 1. 2 Analytical balance

Sartorius AG CP 224 S (Goettingen, Germany)
Supplier: VWR International AS, OSLO, Norway

Weighing capacity: 220 g
Readability: 0.1 mg
Repeatability: ≤ ± 0.1 mg

2. 1. 3 Pipettes

Finnpipette® digital (Labsystems, Helsinki, Finland)
Supplier: VWR International AS, OSLO, Norway

Volumes: 100-1000 µL, 1-5 and 2-10 mL

2. 1. 4 Microwave oven

ETHOS 1600 (Milestone, Sorisole, Italy) (See Fig. 2.1)
Supplier: Holger Teknologi AS, Norway

Rotor: HPR[2]- 1000/10S
Number of TFM[3] vessels: 10
Max pressure: 100 bar
Vessel volume: 100 mL
Max temperature: 300°C

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[2] High Pressure Rotor

[3] Hoechst trade name for chemically modified Teflon

The Teflon vessels were equipped with safety shield, Teflon cover, adapter plate, safety spring (see Fig. 2.2), indicator ring and compression screw. A torque wrench was used to properly and safely close the vessels.

The Microwave oven system offers both temperature and/ or pressure control.

Fig. 2. 1 Microwave oven;
ETHOS 1600 (Milestone, Sorisole, Italy)

Fig 2. 2 Accessories;
ETHOS 1600 (Milestone, Sorisole, Italy)

2. 1. 5 ICP MS

ELAN 5000 (Perkin Elmer SCIEX, Norwalk, USA) (See Fig. 2.3)

Peristaltic pump: four channeled operating the flow of both inlet and waste tubes
Nebulizer: cross flow design with nebulizer tips made of PEEK
Spray chamber: Scott design
Torch: demountable design, one piece quartz tubing for plasma and auxillary gas flow
Sampler and skimmer cones: Pt/ Pt

Fig. 2. 3 ICP-MS;
ELAN 5000 (Perkin Elmer SCIEX, Norwalk, USA)

2. 2 Reagents and standards

Table 2.1 and 2.2 list the reagents and standards, with corresponding specifications, used in this study.

Table 2. 1 Specification of reagents

Chemical name/ Trade name	Chem. formula	Conc. (% m/m)	Quality	Supplier
Acids				
Hydrochloric acid	HCl	37	p.a	Fluka Chemie AG, Buchs,Switzerland
Hydrogen peroxide	H_2O_2	35	p.a	Fluka Chemie AG, Buchs,Switzerland
Nitric acid	HNO_3	65	Suprapur®[1]	Merck, Darmstadt, Germany
Nitric acid	HNO_3	65	p.a[2]	Merck, Darmstadt, Germany
Sulfuric acid	H_2SO_4	96	p.a	Merck, Darmstadt, Germany
Water				
Type I[3]			> 18 MΩ cm	Millipore, Billerica, USA
Type II[4]			> 1 MΩ cm	Millipore, Billerica, USA
Gas				
Argon	Ar		≥ 99.999%	AGA, Oslo, Norway

[1] Used for acidifying stock solutions, as decomposition reagent, and for acid matching of calibration standards with sample solution matrices

[2] Used for preparation of cleaning solutions

[3] Used for final rinsing of equipment, and for dilution of following solutions; sample solutions, stock solutions, calibration standards and daily test solutions

[4] Used for pre-rinsing of equipment (see footnote 3)

Table 2. 2 Specification of standard stock solutions

Product No.	**Element(s)**	**Conc. (mg/L)**	**Matrix**	**Supplier**
SS-028314	As, Bi, Ga, Ge, In, Pb, Sb, Se, Sn, Te, Ti, V	50	4.9% HCl	Teknolab AS, Drøbak, Norway
SS-028314	Al, B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, Sn, V, Zn, Zr	50	4.9% HCl	Teknolab AS, Drøbak, Norway
8016	Ba	1000 ± 3	2.5% HNO_3	Teknolab AS, Drøbak, Norway
1014	Cd	1000 ± 0,5	2,5% HNO_3	Teknolab AS, Drøbak, Norway

2. 3 Samples

2. 3. 1 Certified reference material

ERM®-EC681 (EC-JRC-IRMM[4], Geel, Belgium)

The certified reference material (CRM) was used in order to validate the analytical method for trace metal determinations of real samples. The reference material contains certified concentrations of As, Cd, Cr, Pb, Hg, Cl, Br and S in a high-density polyethylene (HDPE) matrix (see Appendix A). In addition, indicative values are reported for Al, Ba, Cu, Sb and Ti in the certification report (Lamberty et al., 2001a). The CRM is in the form of granules of approximately 10 mg each.

2. 3. 2 Real samples

Six sources of packaging materials made from polyethylene (PE) were collected from supermarkets for this study. All samples collected were transparent, i.e. no pigment added, and were intended for food contact applications. See Table 2.3 for specifications.

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[4] European Commission – Joint Research Centre – Institute for Reference Materials and Measurements

Table 2. 3 Specification of real samples

Label[1]	Product[2]	Brand	Matrix[3]	Sampling
S1	Freezing bags	Rul Let	LLDPE	Every fourth bag/ second meter
S2	Cling film	GLAD	PE	Every third meter
S3	Freezing bags	Co- op	90% LDPE, 10% LLDPE	Every tenth bag/ second meter
S4	Cling film	Rimco	Not specified	Every fourth meter
S5	Freezing bags	GLAD	PE	Every fifth bag
S6	Bread bags	ICA	LDPE	Every fifth bag/ third meter

[1] The samples will from now of be referred to by their labels

[2] All samples but S5 were continuous films

[3] See Symbols and abbreviations p. 11 for explanations

2. 4 Cleaning procedures

Section 2.4.1 through 2.4.3 describes the cleaning procedures for the equipment, microwave decomposition vessels and the cones positioned in the ICP-MS, respectively. See Table 2.1 for reagents- and water quality used.

2. 4. 1 Equipment

All equipment was washed in a washing machine at 80˚C prior to use with a Miele Mielabor G 7783 Multitronic (Miele, Germany). A cleaner, Neodisher® A8 (Miele, Rud, Norway), together with 5% (v/v) of HNO_3 were used in order to clean the equipment. Flushing with Type II water completed the washing-program.

The volumetric flasks and PE bottles were then filled up with 2.5% (v/v) of HNO_3 for storage, if not used immediately. The volumetric flasks and PE bottles were thoroughly rinsed with Type I water prior to use. The PE bottles were also rinsed with a small quantity of the sample solution being transferred.

2. 4. 2 Microwave decomposition vessels

Cleaning of decomposition vessels was performed prior to and after decomposition of samples to avoid the potential of carryover between digestions. The cleaning was performed by addition of 7 mL of 65% HNO_3 and 1 mL of 35% H_2O_2 to each vessel and run the microwave program given in Table 2.4. The vessels were thoroughly rinsed with Type I water after ventilation and cooling.

Table 2.4 Microwave cleaning procedure for decomposition vessels

Reagents[1]		Microwave program			
Volume mL	Formula		Step		
			1	2	3
7	HNO_3	Time (min)	5	10	15
1	H_2O_2	Temp (˚C)	180	180	-
		Power (W)	≤1000	≤1000	-

[1] All reagents are concentrated (see specifications in Table 2.1)

2. 4. 3 Skimmer and sampler cones

The cones used in the ICP-MS were cleaned carefully if needed, e.g. when elevated blank values were observed. The alumina washer ring and the rubber ring (O-ring) on the sampler and skimmer cone, respectively, were removed prior to soaking. The cones' respective original packing was used as washing beakers. These were filled up with soapy water and further placed in an ultrasonic bath of the brand Bandelin SONOREX, RK 100H (BANDELIN electronic, Berlin, Germany) for 15 minutes at 30˚C to remove deposit. The cones were then wiped with a Q-tip dipped in 1% (v/v) of HNO_3 before rinsed thoroughly in Type I water and dried at 50˚C in a drying oven.

The cones have a great influence on the sensitivity, as was experienced in this work. A pair of nickel sampler and skimmer cones was replaced with a new set made of platinum after a period where the ICP-MS had suffered from poor sensitivity, i.e. below optimal values. This replacement improved the sensitivity from 2×10^4 to 6×10^4 counts per seconds (cps). Cleaning the cones as described above may be sufficient, but they have to be replaced if worn out, as was the case just descried.

2. 5 Calibration of automatic pipettes

The automatic pipettes were always calibrated prior to preparation of calibration standards and dilution of samples. The calibration was performed as described in the instruction manual from the supplier. For all other usage, the respective volumes of the pipettes were checked on an analytical balance (see section 2.1.2).

2. 6 Preparation of solutions

The performance of the ICP-MS was optimized prior to analysis with the “daily” test solution. Section 2.6.1 describes how this solution was prepared. Table 2.5 sums up the concentration of, and the elements in the “daily” test solution

Two sets of two stock solutions were prepared as described in section 2.6.2 and 2.6.3. These formed the basis of the preparation of the calibration standards (see section 2.6.4). The letters S and M in I-S and I-M refers to which standard stock solution in Table 2.2 they were made from, i.e. S for single element standards and M for multi element standards. I-S and I-M were further diluted in order to give II-S and II-M, respectively (see section 2.6.3). Table 2.5 sums up the concentration of, and the elements in the stock solutions.

Table 2. 5 Concentration of elements in the daily test-solution and stock solutions

Stock solution	**Concentration[1] (mg/L)**	**Elements**
“Daily” test-solution	0.01	Ba, Cd, Ce, Cu, Ge, Mg, Pb, Rh, Sc and Tl
I-S	10	Ba and Cd
I-M	10	Al, As, B, Bi, Ca, Co, Cr, Cu, Fe, Ga, Ge, In, K, Mg, Mn, Na, P, Pb, Sb, Si, Sn, Te, Ti, V and Zn
II-S	0.05	Ba and Cd
II-M	0.05	Al, As, B, Bi, Ca, Co, Cr, Cu, Fe, Ga, Ge, In, K, Mg, Mn, Na, P, Pb, Sb, Si, Sn, Te, Ti, V and Zn

[1] Double concentration of Pb, Sn and V

2. 6. 1 Daily test solution

The daily test solution was prepared from a pre made multi element stock solution containing 5 mg/L of Ba, Cd, Ce, Cu, Ge, Mg, Pb, Rh, Sc, Tb and Tl. 2 mL of this solution was pipetted into a 1000 mL volumetric flask and diluted up to the mark, herein 15 mL of 65% HNO_3 to reach the final concentration of 1% (v/v) of HNO_3. The new concentrations were 10 µg/L.

2. 6. 2 Stock solutions; I-S and I-M

In order to prepare I-S; 250µL each of the two single element standards listed in Table 2.2 was pipetted into a 25 mL volumetric flask and diluted uo to the mark, herein 0.5 mL of 65% HNO_3 to reach the final concentration of 1.5 (v/v) of HNO_3. Element concentrations in the final stock solution were 10 mg/L.

In order to prepare I-M; 5mL each of the two multi element standards listed in Table 2.2 was pipetted into a 25 mL volumetric flask and diluted up to the mark, herein 0.5 mL of 65% HNO_3 to reach the final concentration of 1.5 (v/v) of HNO_3. Element concentrations in the final stock solution were 10 mg/L, except for Pb, Sn and V, which had a concentration of 20 mg/L.

2. 6. 3 Stock-solutions; II-S and II-M

I-S and I-M from section 2.6.2 were further diluted to reach analyte concentrations of 50 µg/L except for Pb, Sn and V, which had a concentration of 100 µg/L. 500 µL was pipetted into a 100 mL volumetric flask and diluted up to the mark, herein 2 mL of 65% HNO_3 to reach the final concentration of 1.5% (v/v) of HNO_3.

2. 6. 4 Calibration standards

The calibration standards were prepared from the stock solutions described in section 2.6.2 and 2.6.3, depending on the analyte and target concentration (see Table 2.6). The calibration standards were acid matched with the sample solutions, i.e. a final concentration of 15% (v/v) of HNO_3 and 1% (v/v) of H_2O_2, respectively.

Table 2. 6 Preparation of calibration standards. All standards were acid matched with the sample solutions and diluted to a final volume of 50 mL

Standard	$C_{analytes}$[1] µg/ L	$V_{stock\ sol}$ mL	I-S or I-M[2]	II-S or II-M[2]
1	0			
2	0.1	0.1		X
3	0.5	0.5		X
4	1	1		X
5	1.5	1.5		X
6	2	2		X
7	2.5	2.5		X
8	3	3		X
9	3.5	3.5		X
10	4	4		X
11	4.5	4.5		X
12	5	5		X
13	6	6		X
14	8	8		X
15	10	10		X
16	15	15		X
17	20	20		X
18	25	0.125	X	
19	50	0.25	X	
20	75	0.375	X	
21	100	0.5	X	
22	500	2.5	X	
23	1000	5	X	
24	1500	7.5	X	

[1] The concentration of Pb, Sn and V is twice the concentration reported in the table

[2] See Table 2.5 for specifications

2. 7 Calibration

External calibration was used for the quantification of the elements of interest for all of the sample solutions in this work. Concentration as a function of intensity was established using calibration standards from section 2.6.4. The ICP-MS software used the least square method and interpolation in order to determine the analyte concentrations.

All of the standards listed in Table 2.6 were used in the linearity analysis (see section 3A.3.1), but only a selection was used for the final analyses of the samples (see section 3A.3.2).

2. 8 Adapting the sample preparation procedure

2. 8. 1 Optimization of the Microwave decomposition procedure

The certified reference material (see section 2.3.1) was subjected to six different decomposition procedures in order to achieve the optimum microwave digestion for transparent polyethylene bags and cling films. The sample amount, reagent volumes and decomposition program for each procedure are given in Table 2.7.

Table 2. 7 Microwave digestion procedures

Procedure	**m_s[1] (g)**	**V_f[2] (mL)**	**Reagents[3]**	**Microwave program**					
				Step					
			Volume/ formula		**1**	**2**	**3**	**4**	**5**
A[4]	0.1	25	6 mL of HNO_3 1 mL of H_2O_2 1 mLType1 water	Time (min.)	4	4	5	36	30
				Temp. (˚C)	120	200	250	250	-
				Max power (W)	1000	1000	1000	1000	-
B[5]	0.1	25	6 mL of HNO_3 1 mL of H_2O_2 1 mLType1 water	Time (min.)	4	4	5	36	30
				Temp. (˚C)	120	200	230	230	-
				Max power (W)	1000	1000	1000	1000	-
C[5]	0.1	25	6 mL of HNO_3 2 mL of H_2O_2	Time (min.)	4	4	5	36	30
				Temp. (˚C)	120	200	230	230	-
				Max power (W)	1000	1000	1000	1000	-
D[6]	0.25	100	3 mL of H_2SO_4 5 mL of HNO_3	Time (min.)	5	10	20	30	
				Temp. (˚C)	-	200	200	-	
				Max power (W)	300	1000	1000	-	
E[7]	0.5	-	4 mL of HNO_3 4 mL of HCl	Time (min.)	20	20	30		
				Temp. (˚C)	200	200	-		
				Max power (W)	1000	1000	-		
F[8]	0.25	-	4 mL of HNO_3 4 mL of HCl	Time (min.)	20	20	30		
				Temp. (˚C)	200	200	-		
				Max power (W)	1000	1000	-		

[1] Sample mass

[2] The final volume after dilution

[3] All reagents are concentrated (see specifications in Table 2.1)

[4] Application note 018, Ethylene (ETHOS 1600 user manual)

[5] Modification of procedure A

[6] Application note 117, Polyester granulate (ETHOS 1600 user manual). The Microwave digestion program is a two- step procedure (see section 3A.1d). Modifications of step 1 were performed (see section 3A.1d)

[7] Application note 119, Ethylene vinyl alcohol c (ETHOS 1600 user manual)

[8] Modification of procedure E

2. 8. 2 Sample preparation for final analyses

All samples, i.e. certified reference material (CRM) and real samples, were microwave digested according to procedure B in Table 2.7 prior to analysis. Approximately 0.1 g of the sample was weighed directly into the decomposition vessels. A plastic spoon was used in the case of CRM, whereas pieces were cut out from real samples with a plastic knife. Proper amounts of the reagent were added to the decomposition vessels before the various vessel parts were assembled (see Fig. 2.2), placed inside the rotor body and subjected to the decomposition program. After completed digestion, the vessels were cooled down to room temperature before the decomposed samples were quantitatively transferred to 25 mL volumetric flasks and diluted up to the mark, ready for analysis. The sample digest in the vessel containing the temperature sensor was poured out right after completed digestion due to possible contamination.

2. 9 Instrumental

2. 9. 1 Optimization of the ICP-MS prior to analysis

The introduction system, cones, torch and vacuum reading were checked, according to the ELAN 5000 user manual, before igniting the plasma.

An acid solution of 1% (v/v) of HNO_3 was introduced to the ICP-MS while the plasma stabilized for approximately 30 min. An acid solution matched with the sample solutions, i.e. 15% (v/v) of HNO_3, was introduced prior to analysis for approximately five min, in order to minimize carryover from earlier analyses.

The ICP-MS was optimized with the daily test solution described in section 2.6.1. ^{24}Mg, ^{207}Pb, ^{208}Pb and ^{103}Rh were measured to ensure sufficient analytical sensitivity. The nebulizer gas was tuned to give the highest possible signal for ^{103}Rh, while the oxide level remind below 3%. The x and/or y position of the cones was manually adjusted if necessary, i.e. if the signal were below the critical values specified in the ICP-MS manual after adjustion of the nebulizer gas flow. The ion-lens settings were adjusted to make the signals of ^{24}Mg and ^{207}Pb or ^{208}Pb to coincide (ELAN 5000 user manual). Ce is most prone to oxide formation, while Ba is most prone to formation of doubly charged ions. Ce and Ba are for these reasons usually used to control the oxide levels and the formation of doubly charged ions, respectively. CeO/Ce and Ba^{2+}/Ba^{+} ratios less than 3% are generally acceptable (Elliot, 1997).

2. 9. 2 Instrument parameters

Table 2.8 reports parameter settings used in this work. The acquisition parameters are described below.

Table 2.8 ICP-MS operating parameters for the ELAN 5000

RF- power (W)	1000	
Argon gas flow rates (L/min)		
Plasma	11	
Auxiliary	8	
Nebulizer[1]	0.82-0.97	
Nebulizer sample uptake rate (mL/min)	~ 1.0	
Sampler and Skimmer cones	Pt/Pt	
MS resolution	Normal, 0.8 amu[2]	
Scanning mode	Peak hop	
Data acquisition Mode	Semi-quantitative	Quantitative
Replicate time (ms)	750	750
Dwell time (ms)	250	250
Sweeps per reading	1	3
Readings per replicate	1	1
Number of replicates	3	5
Points per spectral peak	1	1
Mass ranges[3]/ Specified isotopes[4]	5- 39 41-209 232- 240	^{27}**Al**, ^{75}**As**, , ^{209}**Bi**, ^{137}Ba, ^{138}**Ba**, ^{110}Cd, ^{111}**Cd**, ^{59}**Co**, ^{52}Cr, ^{53}**Cr**, ^{69}Ga, ^{71}**Ga**, ^{72}Ge, ^{74}**Ge**, ^{113}In, ^{115}**In**, ^{24}**Mg**, ^{26}Mg, ^{55}**Mn**, ^{121}**Sb**, ^{123}Sb, ^{206}Pb, ^{208}**Pb**, ^{125}Te, ^{128}**Te**, ^{51}**V**

[1] See section 2.9.1 for optimization procedure

[2] The peak width in atomic mass units at 10% of peak high

[3] Recommended ranges in the ELAN 5000 user manual

[4] Isotopes chosen for final reporting are **bold**

The replicate time, dwell time, sweeps per reading and reading per replicate in Table 2.8 determine the length and precision of the sample analysis. Specifying three of these parameters gives the fourth automatically. The values given in Table 2.8 applies to all specified isotopes. However, a fifth parameter, i.e. the time factor can be set to increase the dwell time for a specific isotope in order to increase the precision of that particular isotope (ELAN 5000 user manual). The time factor in this work was equal to one for all specified isotopes.

The two parameters sweeps per reading and number of replicate were set to scan the mass range three times and to repeat the entire measure protocol five times. The default values were used for points per spectral peak and readings per replicate. The dwell time was used to adjust the total time it took to analyze one sample replicate to an acceptable time, i.e. between three to four min. with the amount of isotopes, or mass ranges, specified in Table 2.8.

2. 10 Validation parameters

The analytical method was validated by means of accuracy, precision, linearity and detection limits.

2. 10. 1 Accuracy

The accuracy was determined in two ways, depending on the analyte in question. Analytes certified or given an indicative value in the certified reference material (CRM) were estimated as described in section 2.10.1a. Analytes not certified were estimated as described in section 2.10.1b. The CRM sample solutions were also diluted in order to match the analyte concentrations in the real samples. This procedure is described in section 2.10.1c.

2. 10. 1a Recoveries

The certified reference material (CRM) was decomposed in three sequences, each including one blank and seven sample replicates of which one contained the temperature sensor (see section 2.8.2). Each CRM digest was diluted in the same manner as the real samples. Each sample replicate was analyzed three times, with days and different operators between, which add up to 54 measure replicates. The recovery was calculated according to equation 2.1.

$$\text{Accuracy as recovery (\%)} = (C_M / C_{CRV}) \cdot 100\% \qquad (2.1)$$

Where C_M is the measured concentration and C_{CRV} is the certified value.

2. 10. 1b Spike recoveries

Six certified reference material (CRM) samples were spiked prior to digestion with 0.25 mL of stock solution II-M (see Table 2.5). The final spike concentrations, after digestion and dilution (see section 2.8.2), were 0.5 µg/L, except for Pb, Sn and V, which had a concentration of 1.0 µg/L. Each sample replicate was analyzed three times, with days and different operators between, which add up to 18 measure replicates. The recovery was calculated according to equation 2.2.

Six of the sample replicates from section 2.10.1a were analyzed in order to determine whether or not any of the spike elements were present in the CRM originally. The spike solution (II-M) was added so that added concentration >> concentration in CRM, see equation 2.2.

$$\text{Accuracy as spike recovery (\%)} = (C_M / (C_{spike} + C_{CRM})) \cdot 100\% \qquad (2.2)$$

Where C_M is the measured concentration, C_{spike} is the added concentration and C_{CRM} is the concentration originally in the certified reference material.

2. 10. 1c Recoveries of analytes in diluted CRM sample solutions

Five sample replicate solutions, from section 2.10.1a, with corresponding blank were further diluted in order to match analyte concentrations in the real life samples. The recoveries were calculated according to equation 2.1. Comparing analyte recoveries between CRM sample solutions with high and low matrix concentration may reveal matrix interferences in addition to, in this work, evaluate the instruments performance at very low analyte concentrations.

2. 10. 2 Precision

The relative standard deviations (RSD) from the accuracy analyses were used as a measure of the precision of both the method and the diluted sample solutions. The repeatability and reproducibility gave the precision of repeated measurements and the precision between days, respectively.

Three sample replicates, analyzed in series, represents the repeatability in this work. All measure replicates were used to calculate the reproducibility.

2. 10. 3 Linearity

The calibration procedure is described in section 2.7. The regression curve, the correlation coefficient and a numerical and graphically presentation of the ICP-MS results described the linearity in this work.

2. 10. 4 Detection- and quantification limits

Limit of detection (LOD) and limit of quantification (LOQ) were obtained from a reagents blank (procedure blank) prepared using the same decomposition and dilution procedure as used for the samples. LOD and LOQ were calculated as three and ten times the standard deviation (S_b), respectively, and divided by the slope of the calibration curve, i.e. the sensitivity (see equation 2.3 and 2.4).

$$LOD = (3 \cdot S_b)/ b \qquad (2.3)$$

$$LOQ = (10 \cdot S_b)/ b \qquad (2.4)$$

Where S_b is the standard deviation of the ICP-MS response and b is the slope of the calibration curve, i.e. the regression line.

3 RESULTS AND DISCUSSION. PART A

- VALIDATION RESULTS

The various validation parameters, i.e. accuracy, precision, linearity and detection- and quantification limits, are explained throughout section 2.10. The results of the validation analyses are presented in part A of chapter 3. An analytical procedure was adapted for the real samples, based on validation results and experiences made during the validation process.

A survey of the optimization of the microwave decomposition procedures, presented in Table 2.7, is presented in section 3A.1.

3A. 1 Results of decomposition procedures

Table 3A.1 sums up the results of the microwave decomposition procedures given in Table 2.7. Results are given in section 3A.1a through 3A.1f. Recall the considerations regarding the development of a microwave decomposition procedure from section 1.6.

Table 3A.1 Results of microwave-decomposition procedures

Procedure	Reagents	Remark	Result
A[1]	HNO_3 and H_2O_2	Original procedure[1]	Ventilation of several decomposition vessels towards the end of the decomposition program. Clear solution without visual sign of precipitate
B[2]	HNO_3 and H_2O_2	Modification of procedure A; reduced max temp.	Clear solution without visual sign of precipitate
C	HNO_3 and H_2O_2	Modification of procedure A; reduced max temp and increased volume of H_2O_2	Fast pressure buildup and ventilation of several decomposition vessels. The decomposition program was aborted
D	HNO_3 and H_2SO_4	Original procedure[3]	Charring never achieved. White precipitate after completed decomposition-program
E	HNO_3 and HCl	Original procedure[4]	Fast pressure buildup and ventilation of several decomposition vessels. The decomposition program was aborted
F	HNO_3 and HCl	Modification of procedure E; reduced sample mass	Melted sample stuck on the vessels wall

[1] Application note 018, Ethylene (ETHOS 1600 user manual)
[2] This method were used in further work
[3] Application note 117, Polyester granulate (ETHOS 1600 user manual)
[4] Application note 119, Ethylene vinyl alcohol c (ETHOS 1600 user manual)

3A. 1a Procedure A

The max pressure monitored using this procedure was close to 50 bar, which caused several of the decomposition vessels to ventilate towards the end of the microwave program. Supplier's specifications stats that the decomposition vessels can handle pressures up to 100 bar, however, this limit will in practice be 50-60 bar when the equipment is worn out (ETHOS 1600 user manual). The decomposed solutions were clear without visible residue. The decomposition graph is given in Fig. E2 in Appendix E.

3A. 1b Procedure B

The max temperature from procedure A was reduced from 250 to 230°C. This had a remarkable effect on the pressure. The highest pressure monitored was lowered by 20 bar compared to procedure A, and the problem with ventilation was avoided. The decomposed solutions were clear without visible residue. This procedure was used for further work. The decomposition graph is given in Fig. E1 in Appendix E.

3A. 1c Procedure C

As stated in section 1.6, the oxidation-efficiency of HNO_3 depends on the temperature. 2 mL of 35% H_2O_2, instead of 1 mL, was added to the decomposition mixture in order to compensate for the temperature reduction performed in procedure B (see section 3A.1b), as H_2O_2 also increases the oxidation efficiency of HNO_3 (Kingston and Walter, 1998; Eilola and Perämäki, 2003). The additional volume of H_2O_2 resulted in rapid pressure buildup and ventilation of decomposition vessels. The program was aborted.

3A. 1d Procedure D

Procedure D was performed in two stages, i.e. charring of the sample with H_2SO_4, followed by oxidation with HNO_3 (Eilola and Perämäki, 2003). In the first step, H_2SO_4 was added into the decomposition vessels containing the sample. The vessels were closed and positioned inside the microwave oven, and the first part of the microwave program was run, i.e. step 1 in Table 2.7. After completion, the vessels were cooled to room temperature, and then vented. Charring of the samples had not been accomplished. HNO_3 was added and the vessels closed and positioned inside the microwave oven. The second part of the microwave program, i.e. step 2 in Table 2.7 was run. The vessels were cooled to room temperature before quantitatively transferred to 100 mL volumetric flasks and diluted to the mark. The sample solutions had white precipitate.

The procedure just described was repeated with some modifications of step 1. The decomposition vessel containing the temperature sensor was opened and checked between different power settings and duration of heating periods. The temperature had reached 190˚C[5] after 18 min. without signs of charring. No further attempts were made to achieve charring of the samples.

3A. 1e <u>Procedure E</u>

The pressure rose rapidly, and decomposition vessels started to ventilate ten min., after start. The microwave program was aborted.

3A. 1f <u>Procedure F</u>

Procedure E was repeated, but only half of the sample mass was weighed into the decomposition vessels. The pressure monitored during the microwave program was lowered as a result of the reduced sample mass and the problem with the ventilation, experienced in procedure E, was avoided. However, the samples were scarcely decomposed, and melted sample was stuck on the vessels wall. p-xylene, a dimethylbenzene compound, was used in order to dissolve the melted samples from the wall. A complete decomposition might have been accomplished if the time of the microwave program had been lengthened (see section 1.6), but no attempt was made.

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[5] The temperature is indicative, as the temperature sensor was not in touch with the sample digest, i.e. less than 8 mL of reagents (ETHOS 1600 user manual). The temperature at the top of the vessel is lower than the temperature in the sample digest solution due to energy absorbed by the acid, and energy released by the vessels (Kingston and Walter, 1998).

3A. 2 Preliminary analysis; TotalQuant II

A selection of real sample solutions were analysed in the semi-quantitative mode, i.e. TotalQuant™. Mass ranges and data acquisition parameters are given in Table 2.8.

Generally, main group elements were detected, and transition metals not. The non-presence of transition metals is in agreement with the fact these may have deleterious effect on the polymers stability (Lutz, 1998), which require careful production control. Al, As, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Ga, Ge, In, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, Te, V, Zn and Zr were further examined. A selection was chosen for final analysis based on the linearity analysis described in section 3A.3.1.

3A. 3 Calibration curves

3A.3.1 Evaluation of the linearity

Appendix B shows the calibration curves for two isotopes, if available, of each of the following elements; Al, As, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Ga, Ge, In, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Sn, Te, V, Zn and Zr. Two ranges were considered, i.e. 0.1 to 10 µg/L[6] and 0.1 to 100 µg/L[7].

A correlation coefficient (R^2) > 0.985 was considered to be satisfactory. The elements under study were separated into three groups with this criterion in mind. (i) As, Ba, Bi, Cd, Co, Cr, Ga, Ge, In, Mg, Mn, Pb, Sb, Sn and Te showed good correlation across the entire concentration range, (ii) Al, B, Cu, K, Ni, Se and Zr had only satisfactory correlation for concentrations higher than 10 µg/ L and (iii) Ca, Na and Zn did not satisfy the criterion at either high or low concentrations. Table 3A.2 sums up the results.

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[6] 0.2 – 20 µg/ L for Pb, Sn and V

[7] 0.2 – 200 µg/ L for Pb, Sn and V

Table 3A. 2 Results of the linearity analysis

Calibration range	Elements showing $R^2 > 0.985$
0.1 to 100 µg/L	As, Ba, Bi, Cd, Co, Cr, Ga, Ge, In, Mg, Mn, Pb, Sb, Sn, Te
10 to 100 µg/L	Al, B, Cu, K, Ni, Se, Zr
-	Ca, Na, Zn

Elements grouped in (ii), except for Al, and (iii) were excluded from further analysis. This decision was based on the results from the linearity analysis and knowledge of analyte concentrations in the real life samples.

The linearity for Ba and Mg were also checked and found satisfactory for concentrations up to 1500 and 1000 µg/L respectively with the OmniRange sat to 20. Appendix C illustrates the effect of different OmniRange settings on the intensity for Ba.

3A.3.2 Calibration procedures for quantification of trace metals in real samples

Table 3A.3 shows the calibration series that were used for the quantification of the trace metals in the samples.

Table 3A. 3 Calibration series[1]

Elements	Calibration standards, µg/L
Ba and Cd	Blank, 0.1, 0.5, 1.0, 1.5, 5.0, 10, 25
Bi, Co, Cr, Ga, Ge, In, Mn, Pb, Sb, Te and V	Blank, 0.1, 0.5, 1.0, 1.5, 5.0, 10, 25
Al and Mg	Blank, 0.5, 2.5, 5, 10, 25, 50, 100, 500

[1] The calibration ranges used for quantification of analytes in the certified reference material included standards of higher concentrations

Calibration was repeated after each set of five samples and a procedure blank. In addition were calibration standards similar to analyte concentrations in the samples ran as control solutions in order to check the instrumental drift. A recalibration was performed if needed.

3A. 4 Detection- and quantification limits

Table 3A.4 sums up the data obtained from the limit of detection (LOD)- and limit of quantification (LOQ) analysis. Limits of detection (LOD_{method}) and limits of quantification (LOQ_{method}) for the method were calculated for each element by taking the dilution factor of 250 into account (0.1 g sample diluted to a final volume of 25 mL).

Table 3A. 4 Results of the LOD and LOQ analysis

Element	Regression equation[1]	R^2	S_b[2]	LOD_{method}	LOQ_{method}
	Y = bX + a		cps	mg/kg	mg/kg
Al	Y = 1412.0X - 25924	0.9999	355.7	0.19	0.63
As	Y = 135.6X + 137.1	0.9604[3]	2.3	0.013	0.042
Ba	Y = 4121.9X + 4035.9	0.9995	125.5	0.023	0.076
Bi	Y = 4832.6X – 41.1	1.0000	4.2	0.00064	0.0021
Cd	Y = 269.4X – 58.4	0.9944	1.2	0.0035	0.012
Co	Y = 3728.5X + 51.7	0.9999	3.1	0.00063	0.0021
Cr	Y = 330.9X + 13.6	0.9983	20.5	0.046	0.16
Ga	Y = 1574.8X – 21.5	1.0000	3.1	0.0015	0.0049
Ge	Y = 638.5X + 15.6	0.9999	1.3	0.0015	0.0052
In	Y = 5474.8X + 53.1	1.0000	2.8	0.00038	0.0013
Mg	Y = 1576.4X + 616.4	0.9738[3]	142.7	0.068	0.23
Mn	Y = 3621.9X + 4112.2	0.9547[3]	29.7	0.0062	0.021
Pb	Y = 3150.6X + 4324.7	0.9850	89.7	0.021	0.071
Sb	Y = 860.8X + 11.0	0.9998	9.3	0.0081	0.027
Te	Y = 159.3X + 2.10	0.9999	2.8	0.013	0.044
V	Y = 2982.0X + 96.7	1.0000	2.7	0.00069	0.0023

[1] Based on the concentration range 0.1 to 10 µg/L

[2] Standard deviation based on nine measure replicates of one procedure blank (see Appendix D)

[3] The regression coefficient for Al, As and Mn satisfied the criterion $R^2 > 0.985$ in the analysis of the real samples (see e.g. the calibration curve for Mn, i.e. Fig. B16 in Appendix B)

3A. 5 Accuracy and precision

3A. 5. 1 Comparison of a measurement result with a certified value

A way of quantitatively compare a measurement result with its corresponding certified value has been explained by Lisinger (2005). The method compares the difference between the certified and measured values with its expanded uncertainty, i.e. the combined uncertainty of certified and measured value multiplied by a coverage factor given in the CRMs certificate (Appendix A). If the absolute difference between mean measured value and certified value is less or equals the expanded uncertainty then there is no significant difference. The results are incorporated in Table 3A.5 and Table 3A.7, and a complete survey is given in Appendix H.

3A. 5. 2a Recoveries

The recoveries of the certified elements in the reference material, i.e. As, Cd, Cr and Pb were in the range 89% (Cd) to 103% (Pb). The recoveries for the elements given an indicative value in the certification report (Lamberty et al., 2001a), i.e. Al, Ba and Sb were in the range 82% (Al) to 112% (Ba). A full description of the data and results from the accuracy analyses of the aforementioned elements are presented in Table 3A.5. Fig. 3A.1 displays the measurement results graphically.

Table 3A. 5 Measurement results of the method of Al, As, Ba, Cd, Cr, Pb and Sb in ERM®-EC681. The conclusion of the quantitative comparison of the measurement result with the certified value is given in the column named remark.

Element	**$C_{CRM} \pm U_{CRM}$[1]**	**$C_M \pm$ 95% CI[2]**	**SD[3]**	**RSD[4]**	**$R_M \pm$ 95% CI[5]**	**n[6]**	**Remark[7]**
	mg/kg	**mg/kg**	**mg/kg**	**%**	**%**		
Al[8]	19	15.9 ± 0.7	2.3	14.8	82.6 ± 3.4	46	No data
As	3.93 ± 0.15	3.78 ± 0.083	0.31	8.2	94.7 ± 1.9	54	Not significant
Ba[8]	306	335.9 ± 5.2	19.5	5.8	112.0 ± 1.5	54	No data
Cd	21.7 ± 0.7	19.6 ± 0.4	1.6	8.0	89.5 ± 2.2	54	Significant
Cr	17.7 ± 0.6	17.4 ± 0.3	1.1	6.2	98.0 ± 1.8	47	Not significant
Pb	13.8 ± 0.7	14.3 ± 0.2	0.8	5.3	103.1 ± 1.4	54	Not significant
Sb[8]	0.82	0.79 ± 0.046	0.17	21.5	98.0 ± 5.5	50	No data

[1] Certified value ± Expanded uncertainty

[2] Mean measured value ± 95% confidence interval

[3] Standard deviation of the measured value

[4] Relative standard deviation of the measured value

[5] Mean recovery of the element ± 95% confidence interval. Each measurement value was calculated as % recovery before R_M and 95% CI were calculated. As a result, $(C_M / C_{CRM}) \times 100\%$ is slightly different from R_M

[6] Number of measure replicates

[7] Comparison of the measurement result with the certified value (see Appendix H)

[8] Indicative value given in the certification report, no data for the uncertainty

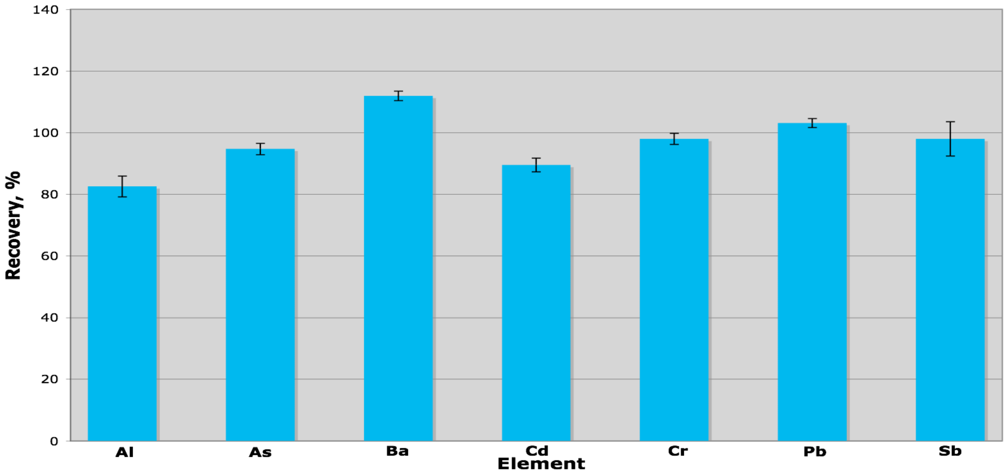

Fig. 3A. 1 Percent recoveries with corresponding 95% confidence interval of Al, As, Ba, Cd, Cr, Pb and Sb in ERM®-EC681

3A. 5. 2b Spike recoveries

Spike recoveries of Bi, Co, Ga, Ge, In and V were in the range 99% (Ge) to 111% (V). Mg and Te were not detected in the spike solutions even though the spike concentration were above their detection limits reported in Table 3A.4, i.e. 0.5 µg/L vs. 0.27 and 0.052 µg/L respectively. Measurement results showed an uneven distribution of Mn with concentrations ranging from 0 to 0.55 µg/L. The spike recovery for Mn was therefore not calculated. A full description of the data and results from the accuracy analysis of the aforementioned elements are given in Table 3A.6. Fig. 3A.2 displays the measurement results graphically.

New spike recovery analyses of Mg, Mn and Te were not performed because of lack of time due to an approaching deadline of which this master thesis was to be hand in. This is very unfortunate, as it turned out that both Mg and Mn were suitable discriminating elements.

The concentration of the analytes in the certified reference material (CRM) was compared to the spike concentration, i.e. 0.5 µg/L. Measurement results of six un-spiked CRM sample solutions (see section 2.10.1b) are reported in the column named remark in Table 3A.6. In general, the concentrations measured in the un-spiked CRM sample solutions were less than 16% of the spike concentration of the elements in the spiked CRM sample solutions. Examples of concentrations of Bi, Co, Ga, Ge, In and V in un-spiked CRM sample solutions are given in Appendix F.

Table 3A. 6[9] Measurement results of the method of Bi, Co, Ga, Ge, In and V in spiked ERM®-EC681. The mean measured concentration of the analytes in questions was determined in six un-spiked CRM sample solutions and compared to the spike concentration. These results are given in the column named remark

Element	**C_{Spike}**[10]	**C_M ± 95% CI**[2]	**SD**[3]	**RSD**[4]	**R_M ± 95% CI**[5]	**n**[6]	**Remark**[11]
	mg/kg	**mg/kg**	**mg/kg**	**%**	**%**		**%**
Bi	0.50	0.52 ± 0.011	0.024	4.6	104.5 ± 2.2	18	8
Co	0.50	0.54 ± 0.017	0.033	6.3	108.1 ± 3.4	15	5
Ga	0.50	0.52 ± 0.0073	0.016	3.1	104.8 ± 1.5	18	4
Ge	0.50	0.50 ± 0.022	0.047	9.5	99.2 ± 4.4	18	4
In	0.50	0.50 ± 0.025	0.054	10.7	100.3 ± 5.0	18	5
V	1.0	1.1 ± 0.041	0.089	8.2	111.0 ± 4.1	18	16

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[9] See also footnotes in Table 3A.6

[10] Spike concentration

[11] Mean measured concentration in un-spiked CRM sample solutions compared to the spike concentration; (C_{CRM} / C_{Spike}) × 100%

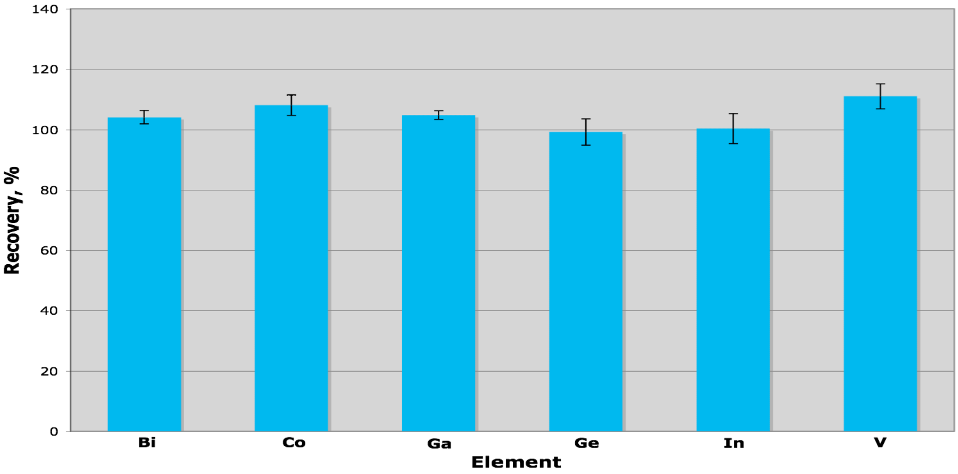

Fig. 3A. 2 Percent spike recoveries with corresponding 95% confidence interval of Bi, Co, Ga, Ge, In and V in ERM®-EC681

3A. 5. 2c Recoveries of analytes in diluted CRM sample solutions

The recoveries of the elements in the diluted CRM sample solutions with certified values, i.e. As, Cd, Cr and Pb were in the range 89% (Cr) to 121% (Cd). The recoveries of the elements given an indicative value in the certification report were 62% (Sb) and 114% (Ba). A full description of the data and results from the accuracy analyses of the aforementioned elements are presented in Table 3A.7. Fig. 3A.3 displays the measurement results graphically.

Table 3A. 7[8] Measurement results and specifications for As, Ba, Cd, Cr, Pb and Sb in diluted ERM®-EC681 solutions. The outcome of the quantitative comparison of the measurement result with the certified value is given in the last column.

Element	**$C_{CRM} \pm U_{CRM}$**[1] **mg/kg**	**$C_M \pm$ 95% CI**[2] **mg/kg**	**SD**[3] **mg/kg**	**RSD**[4] **%**	**$R_M \pm$ 95% CI**[5] **%**	**n**[6]	**Remark**[7]
As[9]	3.93 ± 0.15	3.72 ± 0.80	1.41	37.9	94.6 ± 20.3	12	Not significant
Ba[10]	306[5]	350.5 ± 70.3	129.4	36.9	114.5 ± 23.0	13	No data
Cd[11]	21.7 ± 0.7	25.4 ± 1.3	2.9	11.4	121.1 ± 6.4	18	Significant
Cr[9]	17.7 ± 0.6	18.0 ± 0.6	1.4	7.8	101.6 ± 3.6	18	Not significant
Cr[11]	17.7 ± 0.6	15.7 ± 2.9	6.3	40.1	88.8 ± 16.5	18	Not significant
Pb[9]	13.8 ± 0.7	11.8 ± 2.5	3.8	31.7	93.0 ± 6.1	9	Not significant
Pb[11]	13.8 ± 0.7	13.5 ± 3.7	7.9	58.6	97.8 ± 26.5	18	Not significant
Sb[9]	0.82[5]	0.51 ± 0.065	0.14	28.1	62.4 ± 8.1	18	No data

[8] See also footnotes in Table 3A.6

[9] Dilution factor of 3 100, i.e. approximately 1, 6, 4 and 0.25 µg/L of As, Cr, Pb and Sb respectively

[10] Dilution factor of 62 500, i.e. approximately 5 µg/L

[11] Dilution factor of 12 500, i.e. approximately 2, 1.5 and 1 µg/L of Cd, Cr and Pb respectively

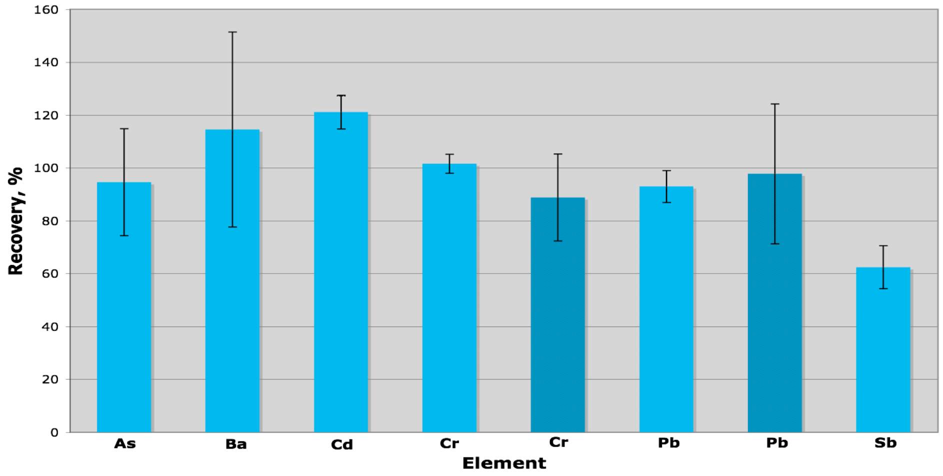

Fig. 3A. 3 Percent recoveries of As, Ba, Cd, Cr, Pb and Sb in diluted ERM®-EC681 sample solutions with corresponding 95% confidence interval. Different dilution factors were used in order to match element concentrations in real sample solutions. Approximate concentrations from left, units in µg/L: 1 (As), 5 (Ba), 2 (Cd), 6 (Cr), 1.5 (Cr), 4 (Pb), 1 (Pb) and 0.25 (Sb)

3A. 6 Precision

3A. 6. 1a Precision of the method

The relative standard deviation (RSD) values obtained in the repeatability calculations were less than 9% (As). RSD values obtained in the reproducibility calculations were less than 14% (Al), with the exception of Sb, which had a RSD value of 21%. Fig. 3A.4 displays the RSD values.

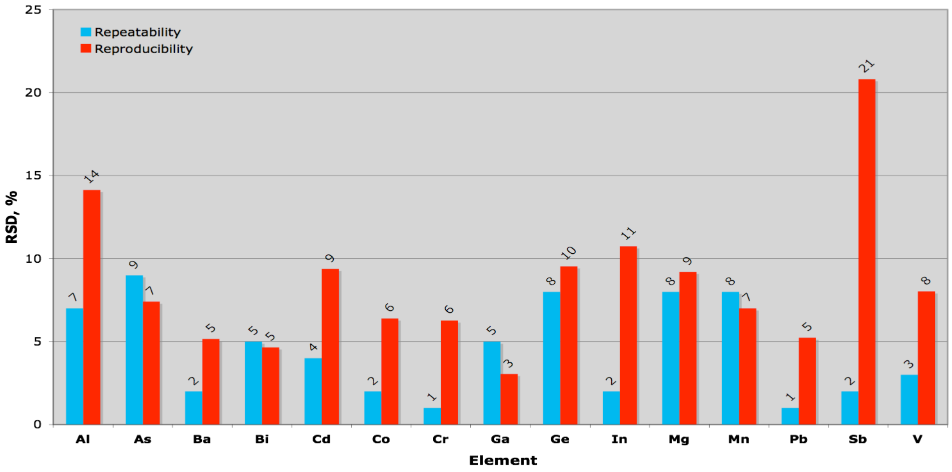

Fig. 3A.4 Precision as repeatability and reproducibility of the method

3A. 6. 1b Precision of the method for diluted CRM sample solutions

Fig. 3A.5 displays the repeatability and reproducibility for As, Ba, Cd, Cr, Pb and Sb at concentrations similar to those in the real sample solutions. As expected, the relative standard deviation (RSD) of the measurement results increases as the analyte concentration in the sample solutions decreases. This is evident for Cr and Pb in Fig. 3A.5. As, Ba and Sb showed the greatest difference between the repeatability and reproducibility (see Fig. 3A.5).

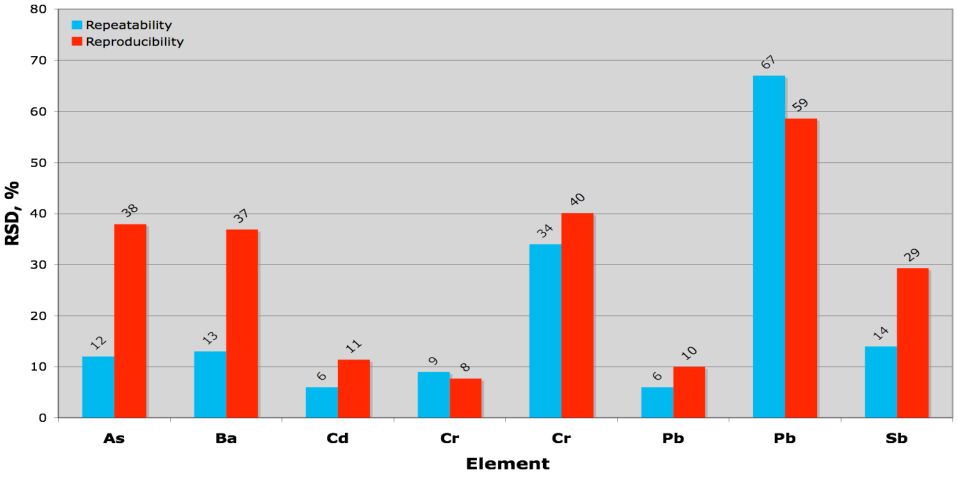

Fig. 3A. 5 Precision as repeatability and reproducibility for diluted ERM®-EC681 sample solutions. Approximate concentrations from left, units in µg/L: 1 (As), 5 (Ba), 2 (Cd), 6 (Cr), 1.5 (Cr), 4 (Pb), 1 (Pb) and 0.25 (Sb).

3A. 7 Interferences

The results from the accuracy analyses and monitoring of two isotopes of the same element was used to check for spectral and matrix interferences. See Appendix K.

3A. 7. 1 Spectral interferences

Table 3A.8 list potential spectral interferences from isobaric, polyatomic and doubly charged atomic ions.

Table 3A. 8 Potential spectral interferences from isobaric, polyatomic and doubly charged atomic ions Bold font means most abundant isotope of an element, or in the case of polyatomic interferences, composed of their respective elements most abundant isotope.

Isotope	**Abundance %**	**Potential interference[1]**
$\mathbf{^{27}Al}$	100	
$\mathbf{^{75}As}$	100	$\mathbf{^{40}Ar^{35}Cl^{+}}$, $\mathbf{^{40}Ca^{35}Cl^{+}}$, $\mathbf{^{59}Co,}$ $\mathbf{^{16}O^{+}}$, $^{150}Nd^{2+}$, $^{150}Sm^{2+}$, $^{150}Eu^{2+}$
^{137}Ba	11,32	
$\mathbf{^{138}Ba}$	71,66	$^{138}Ce^{+}$, $^{138}La^{+}$, $^{122}Sn^{16}O^{+}$
$\mathbf{^{209}Bi}$	100	
^{111}Cd	12,75	$^{111}Nb^{+}$, $^{95}Mo^{16}O^{+}$
^{113}Cd	12,26	$^{113}In^{+}$
$\mathbf{^{59}Co}$	100	
$\mathbf{^{52}Cr}$	83,76	$^{36}S^{16}O^{+}$, $^{35}Cl^{17}O^{+}$, $\mathbf{H^{35}Cl^{16}O^{+}}$, $^{38}Ar^{14}N^{+}$, $\mathbf{^{40}Ar^{12}C^{+}}$, $\mathbf{^{40}Ca^{12}C^{+}}$, $^{36}Ar^{16}O^{+}$, $^{35}Cl^{16}OH^{+}$
^{53}Cr	9,55	$^{37}Cl^{16}O^{+}$, $H^{36}S^{16}O^{+}$, $H^{35}Cl^{17}O^{+}$, $^{40}Ar^{13}C^{+}$, $^{40}Ca^{13}C^{+}$
$\mathbf{^{69}Ga}$	60,4	$^{37}Cl^{16}O^{16}O^{+}$, $\mathbf{^{138}Ba^{2+}}$, $^{138}La^{2+}$, $^{138}Ce^{2+}$
^{71}Ga	39,6	$^{36}Ar^{35}Cl^{+}$, $^{142}Ce^{2+}$
^{72}Ge	27,43	$^{40}Ar^{33}S^{+}$, $^{36}As^{37}Cl^{+}$
$\mathbf{^{74}Ge}$	36,54	$^{74}Se^{+}$, $^{36}Ar^{38}Ar^{+}$, $^{40}Ar^{34}S^{+}$, $^{36}Ar^{37}Cl^{+}$, $^{148}Sm^{2+}$
^{113}In	4,28	$^{113}Cd^{+}$
$\mathbf{^{115}In}$	95,72	$^{115}Sn^{+}$
$\mathbf{^{24}Mg}$	78,7	$\mathbf{^{48}Ti^{2+}}$, $^{48}Ca^{2+}$
^{26}Mg	11,17	
$\mathbf{^{55}Mn}$	100	$\mathbf{^{40}Ar^{14}NH^{+}}$
^{206}Pb	23,6	
$\mathbf{^{208}Pb}$	52,3	$\mathbf{^{192}Os^{16}O^{+}}$
$\mathbf{^{121}Sb}$	57,25	
^{123}Sb	42,75	$^{123}Te^{+}$
^{125}Te	6,99	
$\mathbf{^{128}Te}$	31,79	$^{128}Xe^{+}$
$\mathbf{^{51}V}$	99,76	$^{37}Cl^{14}N^{+}$, $^{35}Cl^{16}O^{+}$

The $RSD_{element}$[8] within the same sample replicate is given in Appendix K. Obviously, a small value of $RSD_{element}$ indicates less probability of spectral interferences. However, some variability appears and the question is weather to assign this difference to (i) a spectral interference or (ii) the instruments precision. The $RSD_{element}$ (also given in Appendix K) was therefore compared to $RSD_{isotope}$[9] for each of the element in question between five sample replicates in order to check what was more probable of (i) and (ii). Having $RSD_{element} < RSD_{isotope}$ it was concluded that spectral interferences for both monitored isotopes of Ba, Cd, Cr, Ge, Mg, Pb and Sb, and ^{71}Ga and^{115}In were minimal. Knowledge of the sample matrix suggests that $^{113}Cd^{+}$ interfere with $^{113}In^{+}$ and $^{138}Ba^{2+}$ interfere with $^{69}Ga^{+}$.

Because the majority of the elements in the Periodic Table have second ionization potentials higher than 15 eV, the amount of doubly charged M^{2+} ions for these elements should be negligibly small. However, doubly charged atomic ions may be serious interferences if the elements producing these (M^{2+}) ions have concentration orders of magnitude higher than the concentration of the element of the isotope being interfered (Hongsen and Houk, 1996; Pupyshev, 2001).

Al, As, Bi and Co are mono isotopic elements. In addition was only ^{51}V monitored due to the very low abundance of ^{50}V, i.e. 0.24%. It was concluded, based on recoveries, that these elements were not subjected to spectral interferences. The recoveries for Al and As were below 100%, while recoveries for Bi, Co and V were 105, 108 and 111 % respectively. However, recall from section 2.10.1b and that these values include both spike concentration and the concentration originally present in the certified reference material.

Critical polyatomic interferences mentioned in literature for the elements listed in Table 3A.8 concern the $^{40}Ar^{35}Cl$ on ^{75}As and $^{40}Ar^{13}Cr$ on ^{53}Cr (Brown et al., 2004). Neither was observed in this work, as recoveries were less than 100%. The interference of $^{40}Ar^{14}NH^{+}$ on ^{55}Mn was not investigated. The concentration of HNO_3 in the sample solutions are equal, however, the nebulizer Ar-gas flow rate was

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[8] Percent relative standard deviation between two isotopes of an element

[9] Percent relative standard deviation between the same isotope

optimized prior to analyses and may impact the formation of $^{40}Ar^{14}NH^+$ within the plasma.

3. 7. 2 Matrix interferences

Some signal enhancement or suppression from ionization/ space charge effects is possible since the decomposed samples contain a high matrix concentration (0.1 g plastic per 25 mL solution). This type of matrix effect was checked by comparison of the recovery data in Table 3A.5 and Table 3A.7, i.e. high and low matrix concentration respectively. The precision of As, Ba, Cr and Pb determinations decreased as the concentration for these elements became very low. However, the accuracy/ recoveries were not affected. From these results it was concluded that matrix effects for these elements were minimal.

The recoveries of Cd and Sb on the other hand, showed significant differences in the two sample solutions. The recovery for Sb decreased from 98.0% in the concentrated matrix to 62.4% in the diluted, while the recovery for Cd increased from 89.5% in the concentrated matrix to 121.1% in the diluted. It is not known why Cd and Sb show contrary behavior due to the fact that these elements do not differ much in atomic mass. However, these results indicate that Cd and Sb are subjected to matrix effects.

The recovery for Al was not determined in the diluted sample solutions. The low recovery of Al may be due to incomplete decomposition, adsorption on the decomposition vessels walls or signal suppression from space ionization/ charge effect.

3 RESULTS AND DISCUSSION. PART B

- RESULTS OF REAL SAMPLES

3B. 1 Results for six sources of real samples

A large amount of data was generated from the analyses of the real samples, i.e. 15 elements in each of the 5 sample replicates sampled from each of the 6 plastic sources. This adds up to a total of 450 numerical data points. Average concentration, median concentration, standard deviation and relative standard deviation were calculated for each element within each sample and are shown in Table 3B.1. See appendix J for the complete dataset. Appendix I give the analyte concentrations in the sample solutions.

Fig. 3B.1 through 3B.6 displays graphically the average concentration, the median concentration and the standard deviation for each element quantified in each sample. Different elements were plotted in different windows if their concentrations differed by orders of magnitudes, e.g. Co (0.0051 mg/kg) vs. Mg (103.8 mg/kg) in S5 (see Table 3B.1). These “extra” windows were incorporated into the first one.

Table 3B. 1 Measurement results of Al, As, Ba, Bi, Cd, Co, Ga, Ge, In, Mg, Mn, Pb, Te and V in six sources of food contact plastic materials (n = 5 for each source).

	Al	As	Ba	Bi	Cd	Co	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample : S1															
Average (mg/kg)	16.7	1.6	4.1	0.061	0.18	0.021	0.046	0.063	-	26.9	1.03	0.17	0,072	0,017	-
SD (mg/kg)	5.8	0.27	5.7	0.011	0.022	0.010	0.0090	0.060	-	9.9	0.11	0.036	0,045	0,016	-
RSD (%)	35.0	17.0	139.6	18.5	11.9	46.9	19.9	95.1	-	36.8	10.6	21.3	64,7	93,8	-
Median (mg/kg)	15.5	1.5	1.2	0.058	0.19	0.019	0.042	0.049	-	23.5	1.02	0.16	0,056	0,025	-
Sample : S2															
Average (mg/kg)	11.2	1.3	1.2	-	0.15	-	-	-	-	9.9	0.75	-	-	-	-
SD (mg/kg)	4.0	0.08	0.93	-	0.011	-	-	-	-	1.7	0.065	-	-	-	-
RSD (%)	35.9	6.5	76.0	-	7.18	-	-	-	-	17.6	8.7	-	-	-	-
Median (mg/kg)	10.1	1.3	0.58	-	0.15	-	-	-	-	9.3	0.75	-	-	-	-
Sample : S3															
Average (mg/kg)	8.3	1.0	0.61	0.0044	0.13	-	0.0024	-	-	1.57	0.50	-	-	-	-
SD (mg/kg)	4.0	0.045	0.28	0.0022	0.039	-	0.00066	-	-	0.39	0.29	-	-	-	-
RSD (%)	47.9	4.3	45.5	51.5	31.1	-	27.3	-	-	24.8	57.2	-	-	-	-
Median (mg/kg)	9.6	1.05	0.72	0.0043	0.11	-	0.0026	-	-	1.5	0.60	-	-	-	-
Sample : S4															
Average (mg/kg)	20.9	1.1	6.0	-	0.22	-	0.0039	-	0.0065	104.5	0.67	0.22	-	-	0.042
SD (mg/kg)	3.0	0.19	5.6	-	0.085	-	0.0012	-	0.00065	10.7	0.091	0.13	-	-	0.012
RSD (%)	14.2	18.0	92.5	-	38.2	-	31.7	-	9.9	10.3	13.7	58.9	-	-	29.8
Median (mg/kg)	20.5	0.95	2.2	-	0.19	-	0.0046	-	0.0067	108.0	0.64	0.25	-	-	0.037
Sample : S5															
Average (mg/kg)	11.8	-	1.6	-	0.18	0.0051	-	-	-	103.8	0.040	-	-	-	-
SD (mg/kg)	1.0	-	0.30	-	0.0060	0.0015	-	-	-	5.2	0.0050	-	-	-	-
RSD (%)	8.4	-	19.2	-	3.1	28.7	-	-	-	5.0	12.9	-	-	-	-
Median (mg/kg)	12.0	-	1.4	-	0.18	0.0048	-	-	-	105.1	0.042	-	-	-	-

- not detected, below the detection limit or below the quantification limit. See specifications in Appendix J

Table 3B. 1 (Continued)

	Al	**As**	**Ba**	**Bi**	**Cd**	**Co**	**Ga**	**Ge**	**In**	**Mg**	**Mn**	**Pb**	**Sb**	**Te**	**V**
Sample : S6															
Average (mg/kg)	8.5	-	1.8	-	0.19	-	-	-	0.16	145.3	0.050	0.046	-	-	-
SD (mg/kg)	4.4	-	0.76	-	0.010	-	-	-	0.18	13.9	0.020	0.027	-	-	-
RSD (%)	51.3	-	42.2	-	7.8	-	-	-	108.6	9.6	37.4	59.2	-	-	-
Median (mg/kg)	7.1	-	1.5	-	0.19	-	-	-	0.054	143.8	0.050	0.039	-	-	-

- Not detected, below the detection limit or below the quantification limit. See specifications

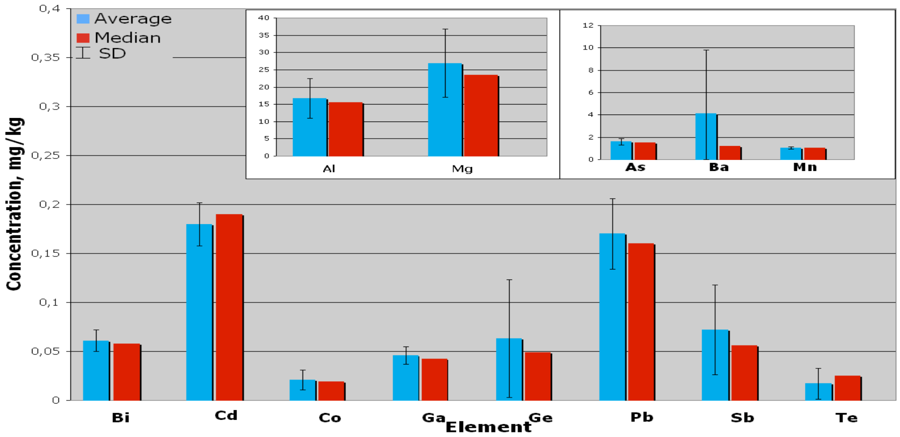

Fig. 3B. 1 Average and median elemental concentrations with SD in S1

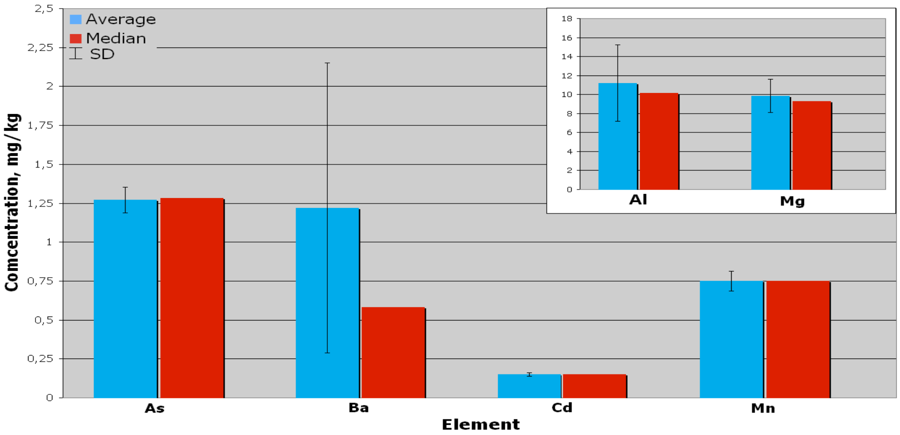

Fig. 3B. 2 Average and median elemental concentrations with SD in S2

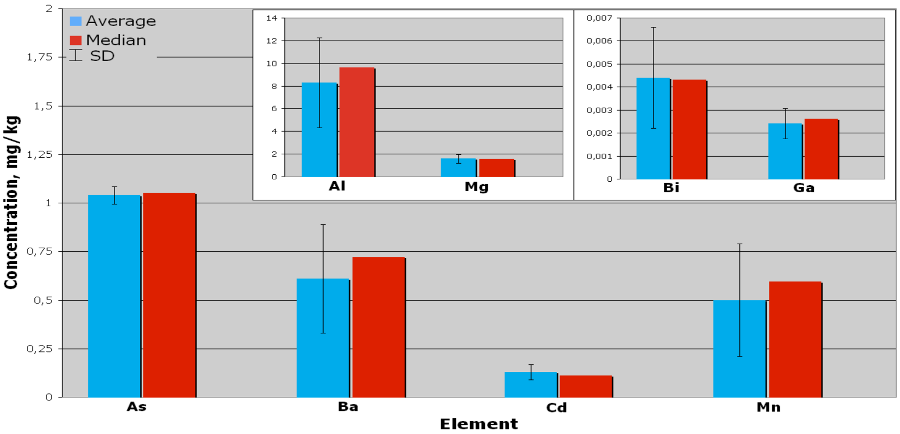

Fig. 3B. 3 Average and median elemental concentrations with SD in S3

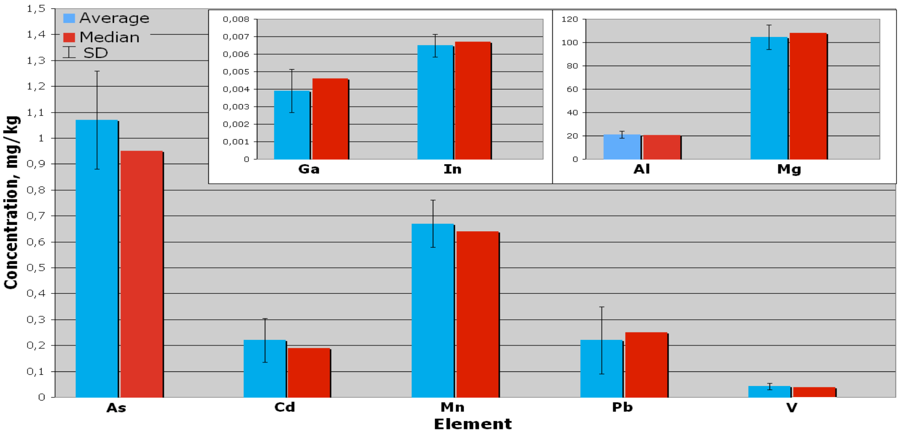

Fig. 3B. 4 Average and median elemental concentrations with SD in S4

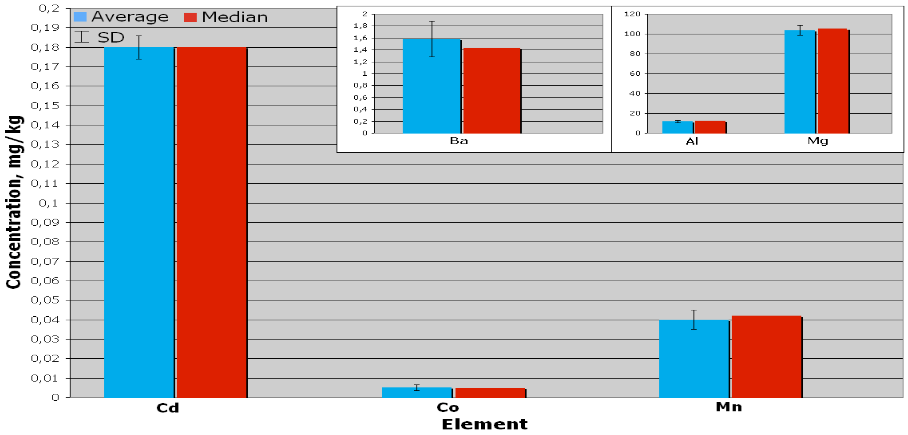

Fig. 3B. 5 Average and median elemental concentrations with SD in S5

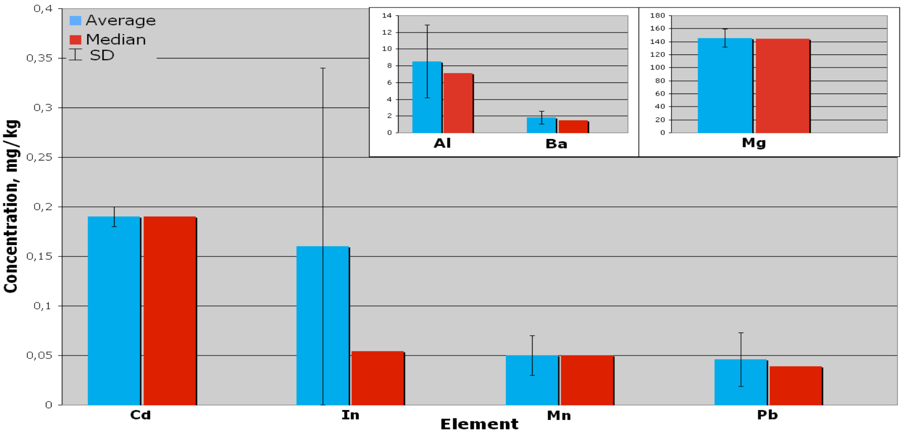

Fig. 3B. 6 Average and median elemental concentrations with SD in S6

3B. 2 Data analyses of real samples

Only 5 out of the 15 elements under study in this work were present in all of the plastic samples. These elements, i.e. Al, Ba, Cd, Mg and Mn had therefore the greatest discrimination power. Recall the criterion, from section 1.8, that each element must fulfill in order to be a suitable discriminating element. The average concentration, median concentration and standard deviation of a particular element, were plotted in the same window for all the samples (see fig. 3B.7 to 3B.11). These plots gave a visual description of how suitable the elements were as fingerprint elements according to criterion (ii) and (iv) stated in section 1.8.

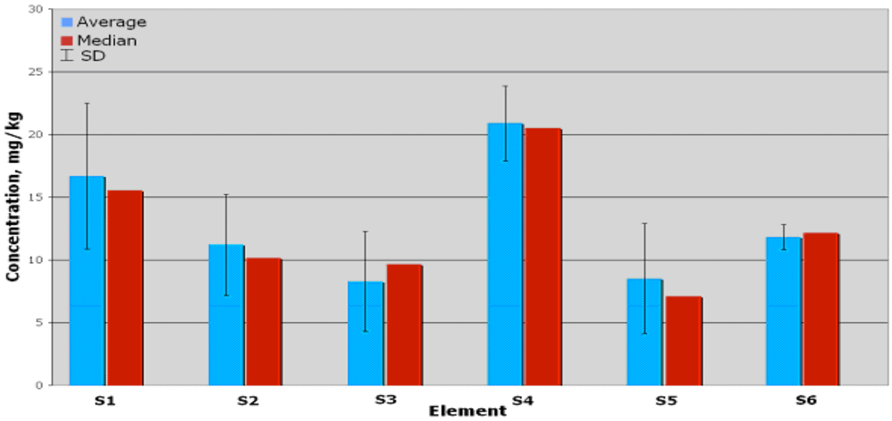

Fig. 3B. 7 Comparison of Al concentration and distribution in six transparent food contact plastic samples.

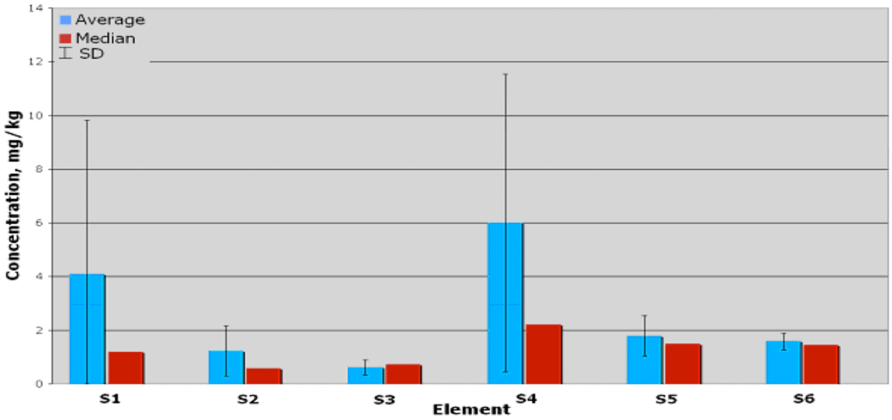

Fig. 3B. 8 Comparison of Ba concentration and distribution in six transparent food contact plastic samples.

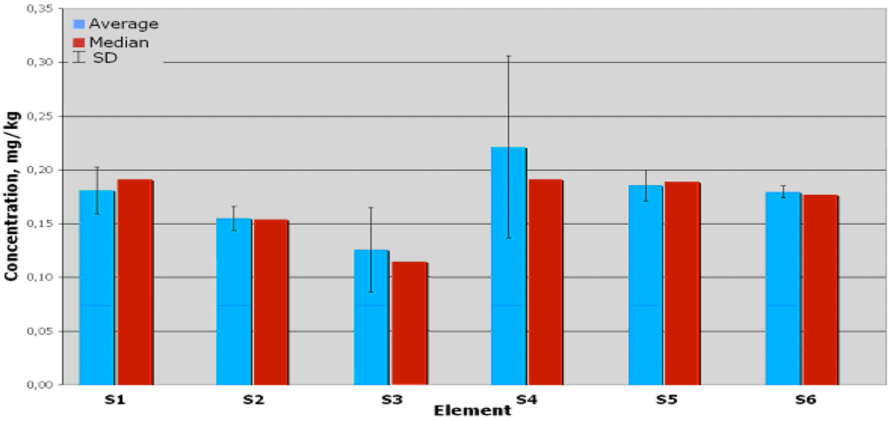

Fig. 3B. 9 Comparison of Cd concentration and distribution in six transparent food contact plastic samples.

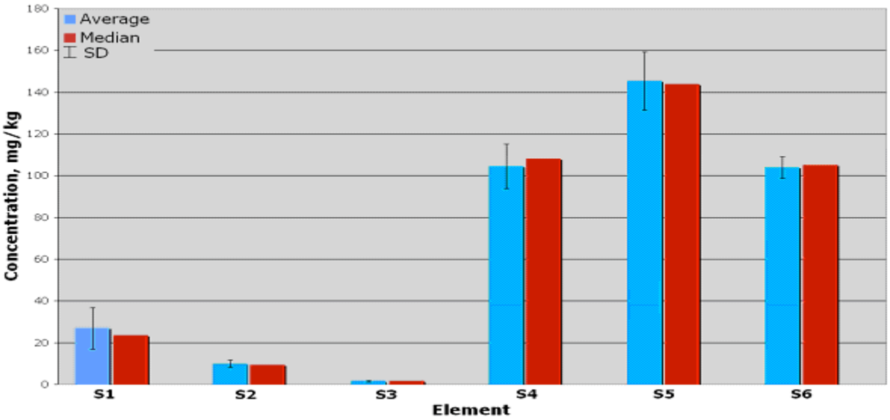

Fig. 3B. 10 Comparison of Mg concentration and distribution in six transparent food contact plastic samples.

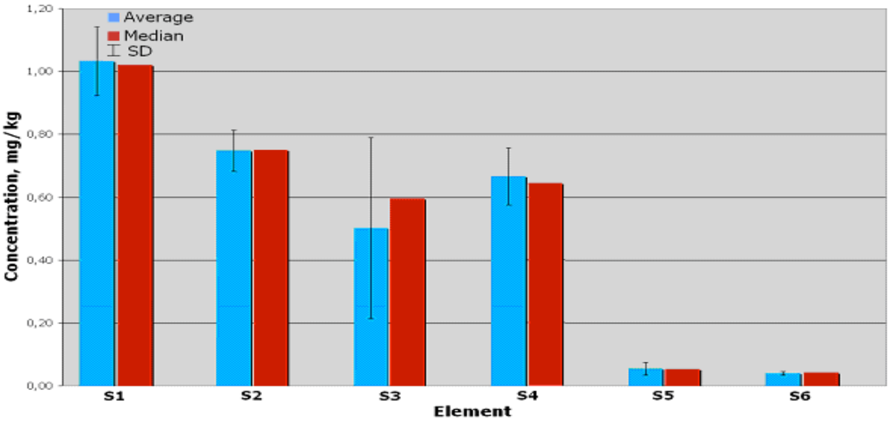

Fig. 3B. 11 Comparison of Mn concentration and distribution in six transparent food contact plastic samples.

3B. 2. 1 Interpretation of Al, Ba, Cd, Mg and Mn as discriminating elements

3B. 2. 1a Criterion (i); Concentration levels

The lowest average concentration of the element in question was compared to its corresponding LOQ. The plastic source denoted S3 showed the lowest average concentration of Al, Ba, Cd and Mg. These elements average concentration vs. LOQ were as follows (units in mg/kg); 8.3 vs. 3.8 for Al, 0.61 vs. 0.071 for Ba, 0.13 vs. 0.012 for Cd and 1.57 vs. 0.23 for Mg. The Mn concentration was lowest in S5 with an average concentration of 0.040 vs. 0.021. See LOD and LOQ values in Table 3A.4. These results showed that all of the elements had concentrations well above their LOD.

3B. 2. 1b Criterion (ii); Elemental distribution

Table 2B.2 shows the repeatability of the method for Al, Mg and Mn and the repeatability for Ba and Cd in the diluted CRM sample solutions. Each relative standard deviation (RSD) for the measurement results of Al, Ba, Cd, Mg and Mn in the real samples was compared to these values. The concentration of the elements in the sample solutions representing the repeatability matches the element concentrations in the real sample solutions. Deviation from the repeatability value is a measure of the distribution.

Table 3B. 2 The relative standard deviation of measurement results of three sample replicates analyzed in series, i.e. the repeatability, against the relative standard deviation of measurement results of real samples

Element	**Repeatability %**		**RSD[1] %**					
	Method	**Diluted**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Al	7		23	36	48	14	8	51
Ba		13	140	76	46	93	19	42
Cd		6	12	7	25	38	3	8
Mg	8		37	18	25	10	5	10
Mn	8		11	9	57	14	13	18

[1] Corrected for outliers (see Appendix J)

The distribution ranges as random standard deviation (RSD) were 8 to 51% for Al and 19 to 140% for Ba. Cd, Mg and Mn showed RSD values generally less than 25%. These results show that Ba has the greatest elemental variation within a sample, Cd, Mg and Mn have the most uniform distribution, while Al shows a variable distribution.

The median compared to the average concentration gave an indication of the symmetry of the elemental distributions. In general, a small RSD value has the median- and the average concentration close together, while larger values for the RSD shows a very skewed distribution.

3B. 2. 1c Criterion (iii); Spectral interferences

See Table 3A.8 and recall the interpretation concerning potential spectral interferences in section 3A.7.1. As for the CRM samples, two isotopes were monitored when analyzing Ba, Cd and Mg in the real samples. It was concluded, based on $RSD_{element}$[10] vs. $RSD_{isotope}$[11], that spectral interferences were minimal. See interpretations of potential spectral interferences on Al and Mn in section 3A.7.1.

3B. 2. 1d Criterion (iv); Elemental variation between samples

The concentration ranges based on average values for each of the elements Al, Ba, Cd, Mg and Mn between the samples were as follows (units in mg/kg); 8.3 to 20.9 for Al, 0.61 to 6.0 for Ba, 0.13 to 0.22 for Cd, 1.57 to 145.3 for Mg and 0.040 to 1.0 for Mn.

These results showed that the concentration of Mg and Mn varied the most between the samples, with two orders of magnitude from the lowest to the highest concentration. The concentration ranges for Al and Ba varied by one order of magnitude. Cd showed the least variation and did not vary by any order of magnitude.

---

[10] Percent relative deviation between two isotopes of an element

[11] Percent relative deviation between the same isotope

3B. 2. 2 Summary

All criterions, i.e. (i) to (iv) in section 3B.2.1a through 3B.2.1d, were taken into account in order to determine which element of Al, Ba, Cd, Mg and Mn that was the most discriminating element. The results of the interpretation according to the proposed criterion are summarized in Table 3B.3.

Table 3B. 3 Review of section 3B.2.1a through 3B.2.1d

	Al	Ba	Cd	Mg	Mn
Concentration vs. LOD	Satisfying	Satisfying	Satisfying	Satisfying	Satisfying
Distribution within sample	Variable	Poor	RSD generally>25%	RSD generally>25%	RSD generally>25%
Spectral interferences	No	No	No	No	$^{40}Ar^{15}NH$ not investigated
Variability between samples	One order of magnitude	One order of magnitude	Poor	Two order of magnitudes	Two order of magnitudes

Table 3B.3 suggest that Mg has the most discriminating power followed by Mn, Al, Cd and Ba respectively, i. e Mg > Mn > Al > Cd > Ba.

3B. 3 Visual discrimination

The three elements with the most discriminating power, i.e. Mg, Mn and Al in this specified order (see section 3B.2.2), were plotted in a ternary diagram in order to visualize variations within a source and between sources. The ideal situation would be (i) no variation within a source (close clustering of sample replicates), and (ii) a large variation between sources (isolation of clusters).

3B. 3. 1 Ternary diagram; inter element associations of Al, Mg and Mn

Fig. 3B.12 displays the inter element association of Al, Mg and Mn for each sample replicate for all of the six plastic sources in this work. The software Origin was used to construct the ternary plot. Each sample replicate is characterized by its position in the diagram, which is determined by the concentration ratios of Al, Mg and Mn. Appendix L explains how the diagram is constructed, and how to interpret it.

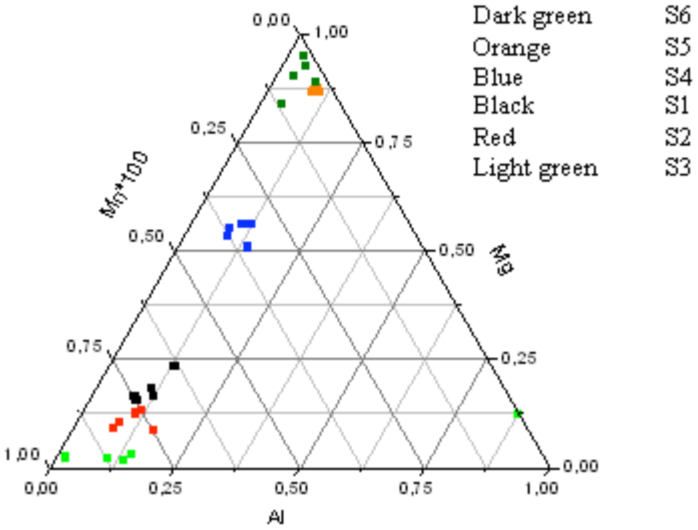

Fig. 3B. 12 Comparison of Al-Mn-Mg ratios for six transparent food contact plastic materials. Each source consists of five sample replicates. Note that Mn have been scaled up by two orders of magnitudes

The five sample replicates of S5 show the lowest variability, evidently from the close clustering. The other five samples do also show clustering of their respective sample replicates, and the six sources can be distinguished from one another. Exception is S2, which has a diffuse transition towards both S1 and S3. Further, one of the sample replicate of S6 coincides with S5.

Ternary diagrams displays concentration ratios, and not absolute concentration values. In addition, two samples of different origin may not be distinguished under some conditions (e.g. one set of three elements), under other conditions (e.g. a new set of three elements) these samples may be distinguished. Statistical significance tests provide the concluding test for the effectiveness of trace elements in discrimination of samples.

3B. 4 Statistical discrimination

A two-sided t-test was used to compare two averages by testing the null hypothesis theorem, i.e. no differences between two experimental means. The statistical analyses were performed according to the protocol proposed by Spence et al. (2000).

The plastic samples were arranged in order of decreasing average Mg concentrations. Adjacent pairs of plastics were compared based on their Mg concentration at a specified significance level using the two-sided t-test. Plastic samples two or more positions away did not have to be tested if adjacent pairs were discriminated. The value for $t_{statistic}$ can only increase as the concentrations becomes more different, i.e. a less probability that the samples came from the same source.

Another discriminating element was used in those cases where the Mg concentrations did not differ significantly. Mn or Al, respectively, would then be the choice.

The software Minitab™ 14 was used to compute the values for $t_{statistic}$ shown in Table.3B.5. These values were compared to the t-distribution critical values given in Table 3B.4.

3B. 4. 1 t-test results

The calculated t-value for two means was compared against its critical t-value given in table 3B.4. If the t-value calculated for the samples ($t_{statistic}$) were greater than the critical t-value ($t_{critical}$), it was concluded that there was a significant difference, i.e. the two samples came from different sources. The results of the $t_{statistic}$ calculations are also given in Appendix M.

Table 3B. 4 t-distribution critical values ($t_{critical}$)

df	**Tail probability**	
	0.025	**0.005**
4	2.776	4.604
5	2.571	4.032
6	2.447	3.707
7	2.356	3.499
	95%	**99%**
	Confidence level	

(Moore and McCabe, 1999)

Table 3B. 5 t-statistic analyses. Mg concentrations are listed in decreasing order, and adjacent means compared using the Student's t-test

Plastic source	**Mg mg/kg**	**$t_{statistic}$[1]**	**Mn mg/kg**	**$t_{statistic}$**
S6	145.3 ± 13.9			
		5.20 (7)		
S4	104.5 ± 10.7		0.67 ± 0.091	
		0.13 (5)		15.46 (4)
S5	103.8 ± 5.2		0,040 ± 0.0050	
		15,38 (6)		
S1	26.9 ± 9.9		1.03 ± 0.11	
		3.78 (4)		4.90 (6)
S2	9.9 ± 1.7		0.75 ± 0,065	
		10.68 (4)		
S3	1.6 ± 0.39			

[1] The degree of freedom (df) is given in parenthesis

Five of the six plastic samples were discriminated at a 95% confidence level using the Mg concentrations. S4 was not discriminated from S5. However, these were discriminated using the Mn concentrations.

Four of the six plastic samples were discriminated at a 99% confidence level using the Mg concentrations. S4 was not discriminated from S5, and S1 was not discriminated from S2. However, these two pairs were discriminated using the Mn concentrations.

4 CONCLUSION AND FURTHER WORK

The present study shows that ICP-MS analysis of trace metals in transparent plastics has a potential in forensic investigations.

Al, As, Ba, Bi, Cd, Co, Ga, Ge, In, Mg, Mn, Pb, Sb, Te and V were detected in one or more of the plastic sources examined in this work. However, only Al, Ba, Cd, Mg and Mn were present in all samples. These five elements had therefore the greatest discrimination power and were further investigated according to four criterions (Section 1.8). Results showed that Mg had the greatest discrimination power followed by Mn, Al, Cd and Ba, respectively.

The different origin of plastics was indicated in the form of a ternary discrimination plot using inter-element ratios of Al, Mg and Mn. The significant difference between these sources was confirmed by a two-sided t-test, performed at both a 95% and 99% confidence level, on the ICP-MS results. The samples were discriminated by Mg, and if necessary, Mn concentrations.

Future work should include accuracy test of Mg and Mn, and the potential interference of ArNH on Mn checked. Further, this work should be extended to include more plastic samples of the kind investigated and the robustness of the method established by comparison of results of day to day analysis of samples.

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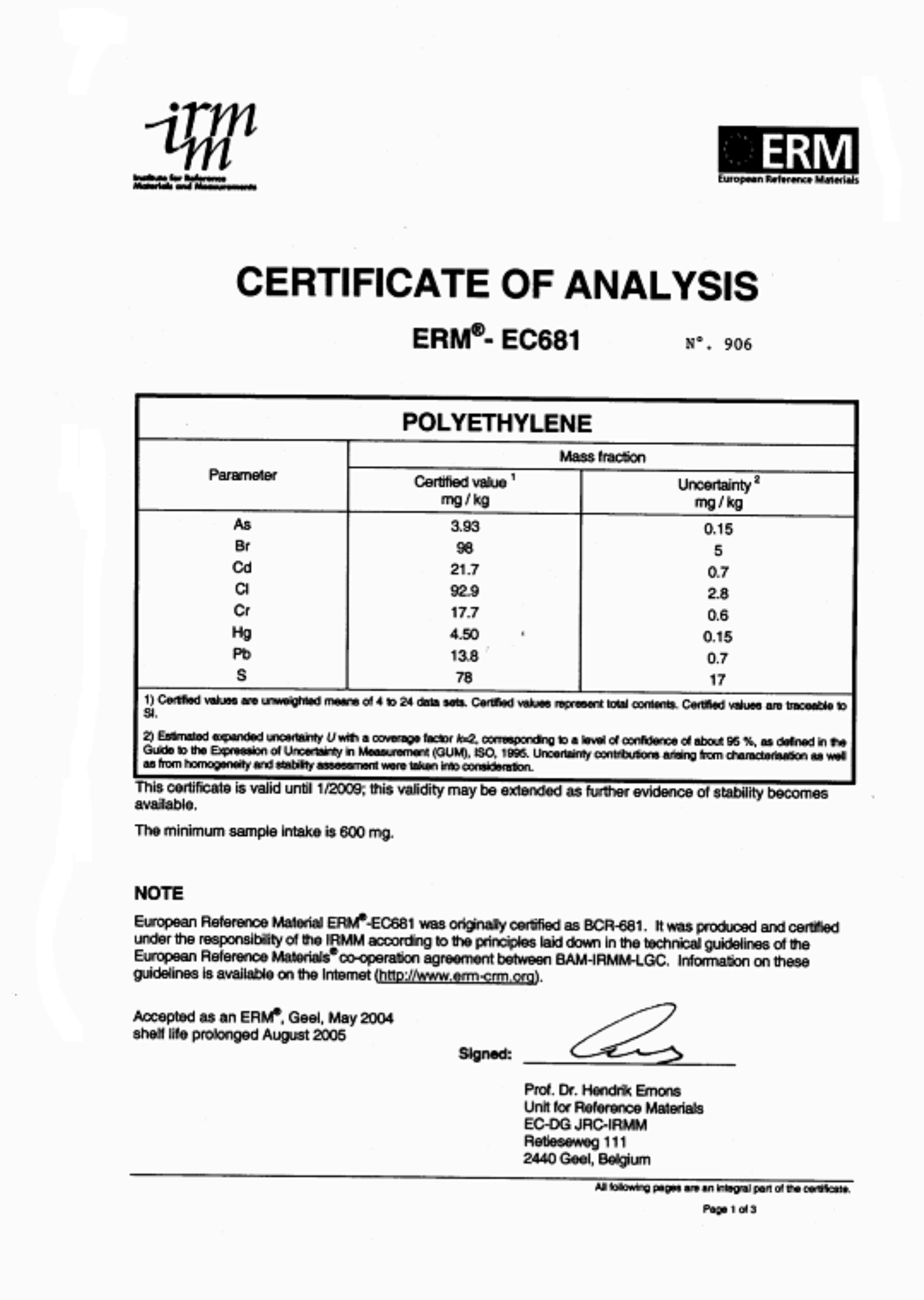
LIST OF APPENDIXES

APPENDIX A: CRM certificate of ERM$^{®}$-EC681



Institute for Reference Materials and Measurements

ERM
European Reference Materials

CERTIFICATE OF ANALYSIS

ERM$^{®}$- EC681

N°. 906

POLYETHYLENE		
Parameter	Mass fraction	
	Certified value [1] mg / kg	Uncertainty [2] mg / kg
As	3.93	0.15
Br	98	5
Cd	21.7	0.7
Cl	92.9	2.8
Cr	17.7	0.6
Hg	4.50	0.15
Pb	13.8	0.7
S	78	17

1) Certified values are unweighted means of 4 to 24 data sets. Certified values represent total contents. Certified values are traceable to SI.

2) Estimated expanded uncertainty *U* with a coverage factor *k*=2, corresponding to a level of confidence of about 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM), ISO, 1995. Uncertainty contributions arising from characterisation as well as from homogeneity and stability assessment were taken into consideration.

This certificate is valid until 1/2009; this validity may be extended as further evidence of stability becomes available.

The minimum sample intake is 600 mg.

NOTE

European Reference Material ERM$^{®}$-EC681 was originally certified as BCR-681. It was produced and certified under the responsibility of the IRMM according to the principles laid down in the technical guidelines of the European Reference Materials$^{®}$ co-operation agreement between BAM-IRMM-LGC. Information on these guidelines is available on the Internet (http://www.erm-crm.org).

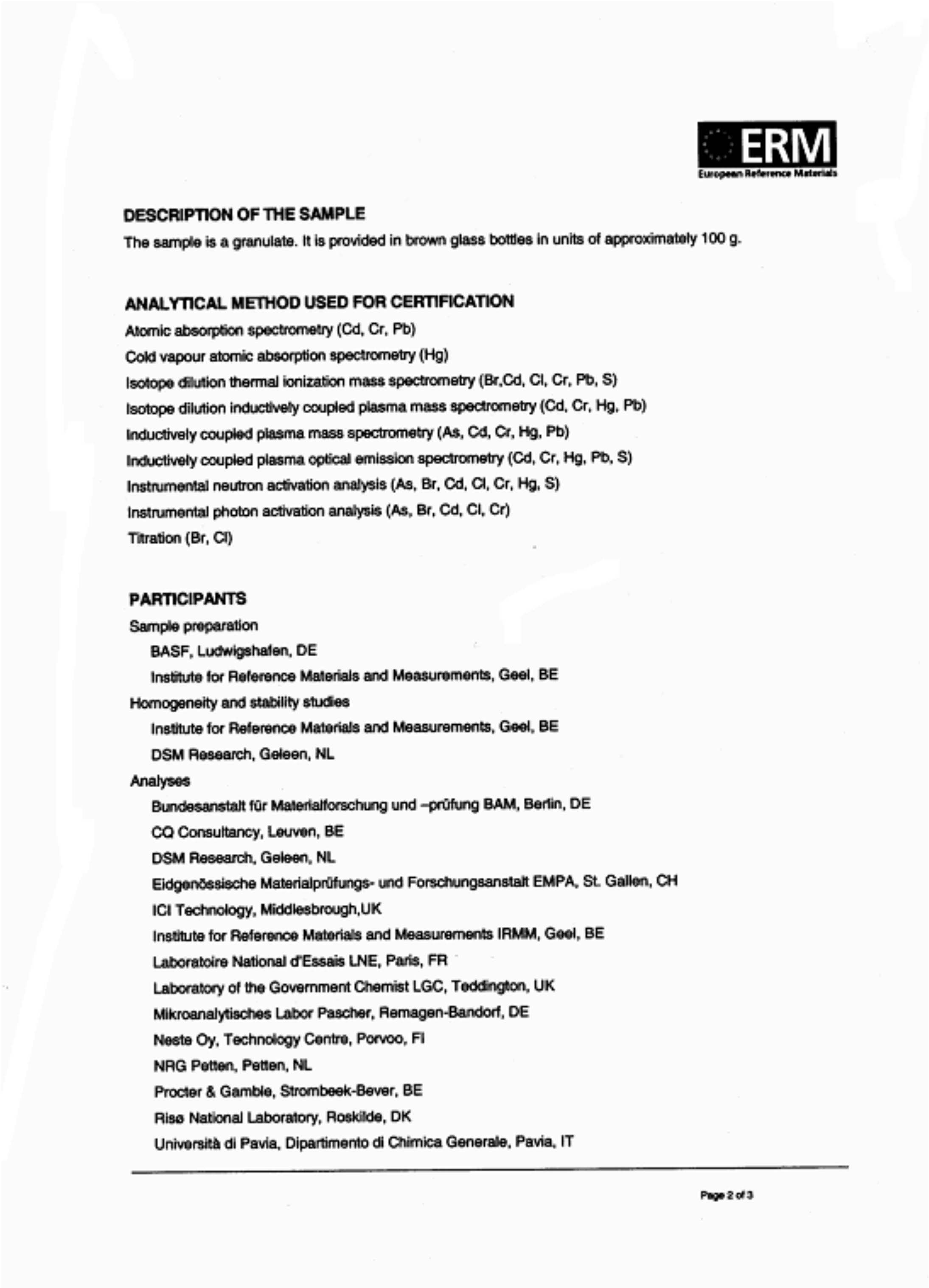
Accepted as an ERM$^{®}$, Geel, May 2004
shelf life prolonged August 2005

Signed:

Prof. Dr. Hendrik Emons
Unit for Reference Materials
EC-DG JRC-IRMM
Retieseweg 111
2440 Geel, Belgium

All following pages are an integral part of the certificate.

Page 1 of 3



ERM
European Reference Materials

DESCRIPTION OF THE SAMPLE

The sample is a granulate. It is provided in brown glass bottles in units of approximately 100 g.

ANALYTICAL METHOD USED FOR CERTIFICATION

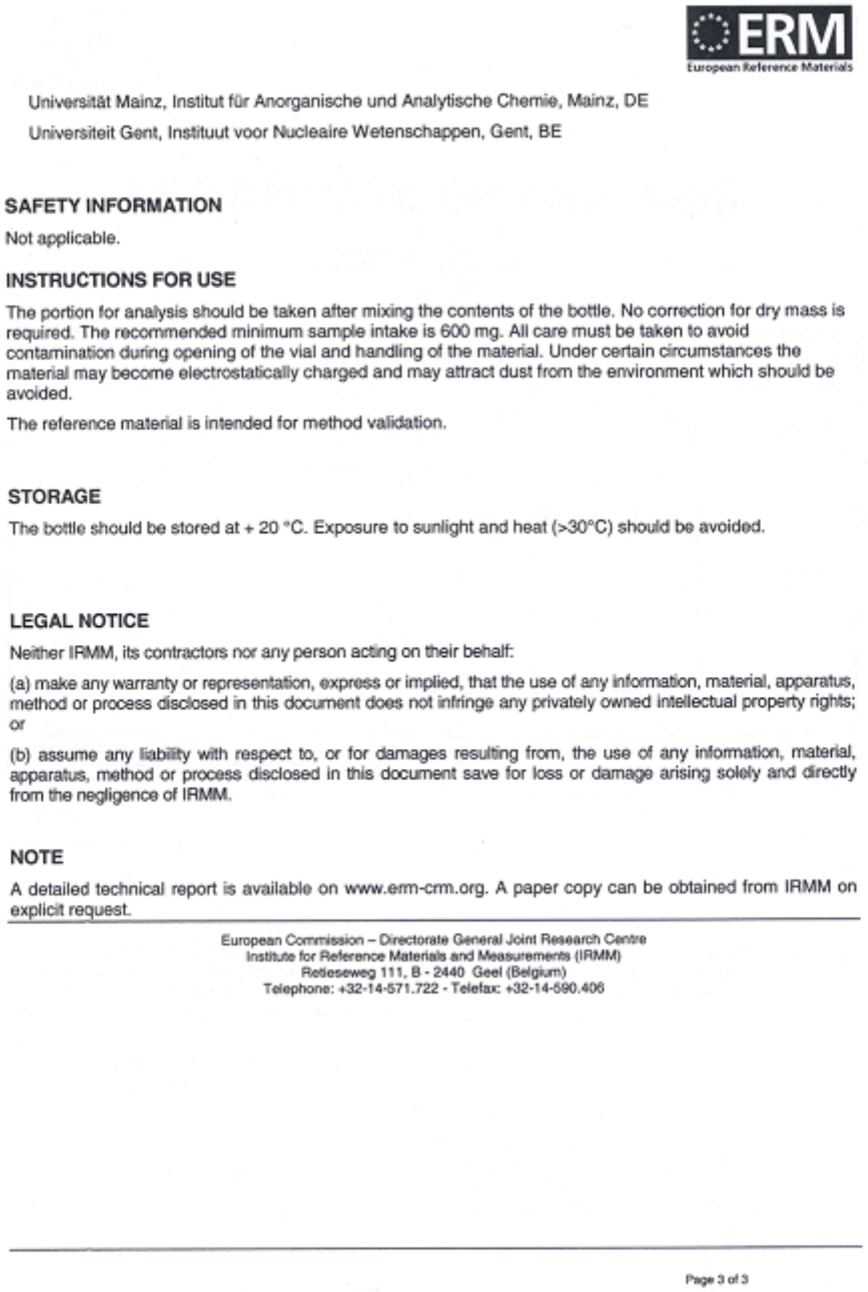
Atomic absorption spectrometry (Cd, Cr, Pb)
Cold vapour atomic absorption spectrometry (Hg)
Isotope dilution thermal ionization mass spectrometry (Br,Cd, Cl, Cr, Pb, S)
Isotope dilution inductively coupled plasma mass spectrometry (Cd, Cr, Hg, Pb)
Inductively coupled plasma mass spectrometry (As, Cd, Cr, Hg, Pb)
Inductively coupled plasma optical emission spectrometry (Cd, Cr, Hg, Pb, S)
Instrumental neutron activation analysis (As, Br, Cd, Cl, Cr, Hg, S)
Instrumental photon activation analysis (As, Br, Cd, Cl, Cr)
Titration (Br, Cl)

PARTICIPANTS

Sample preparation
- BASF, Ludwigshafen, DE
- Institute for Reference Materials and Measurements, Geel, BE

Homogeneity and stability studies
- Institute for Reference Materials and Measurements, Geel, BE
- DSM Research, Geleen, NL

Analyses
- Bundesanstalt für Materialforschung und –prüfung BAM, Berlin, DE
- CQ Consultancy, Leuven, BE
- DSM Research, Geleen, NL
- Eidgenössische Materialprüfungs- und Forschungsanstalt EMPA, St. Gallen, CH
- ICI Technology, Middlesbrough,UK
- Institute for Reference Materials and Measurements IRMM, Geel, BE
- Laboratoire National d'Essais LNE, Paris, FR
- Laboratory of the Government Chemist LGC, Teddington, UK
- Mikroanalytisches Labor Pascher, Remagen-Bandorf, DE
- Neste Oy, Technology Centre, Porvoo, FI
- NRG Petten, Petten, NL
- Procter & Gamble, Strombeek-Bever, BE
- Risø National Laboratory, Roskilde, DK
- Università di Pavia, Dipartimento di Chimica Generale, Pavia, IT



ERM
European Reference Materials

Universität Mainz, Institut für Anorganische und Analytische Chemie, Mainz, DE
Universiteit Gent, Instituut voor Nucleaire Wetenschappen, Gent, BE

SAFETY INFORMATION

Not applicable.

INSTRUCTIONS FOR USE

The portion for analysis should be taken after mixing the contents of the bottle. No correction for dry mass is required. The recommended minimum sample intake is 600 mg. All care must be taken to avoid contamination during opening of the vial and handling of the material. Under certain circumstances the material may become electrostatically charged and may attract dust from the environment which should be avoided.

The reference material is intended for method validation.

STORAGE

The bottle should be stored at + 20 °C. Exposure to sunlight and heat (>30°C) should be avoided.

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NOTE

A detailed technical report is available on www.erm-crm.org. A paper copy can be obtained from IRMM on explicit request.

APPENDIX B: Calibration curves

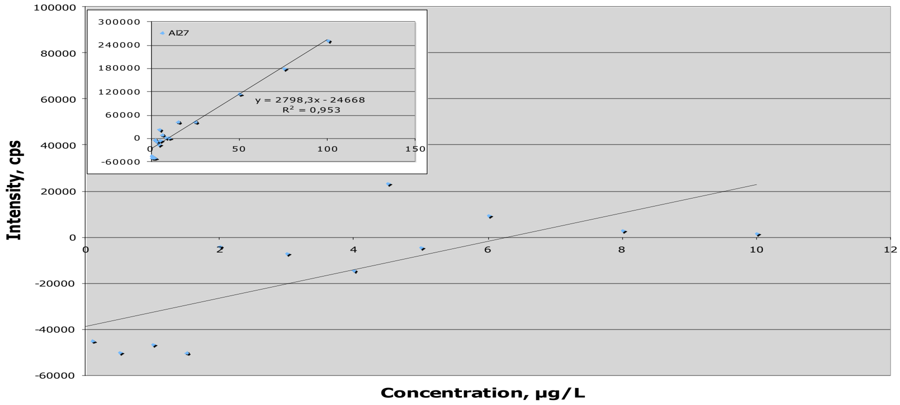

Fig. B1 Calibration curve for ^{27}Al

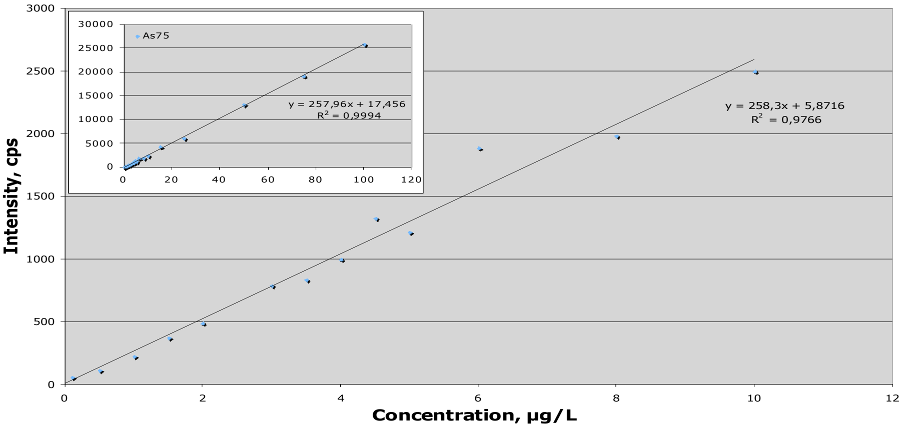

Fig. B2 Calibration curve for ^{75}As

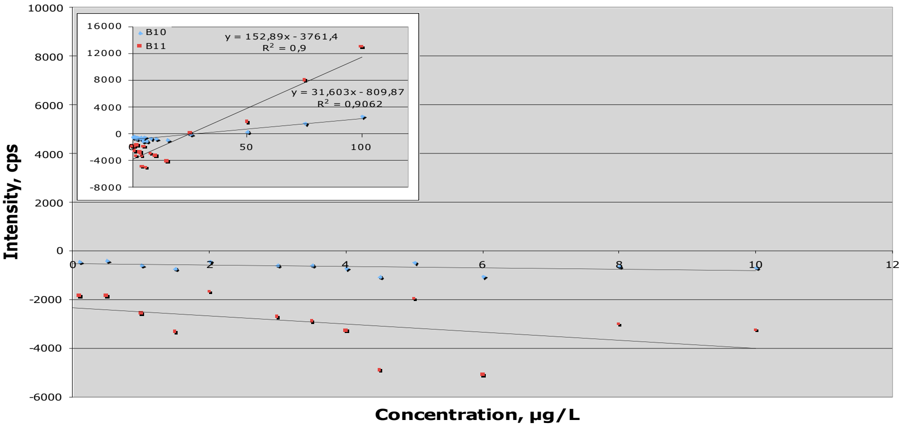

Fig. B3 Calibration curves for ^{10}B and ^{11}B

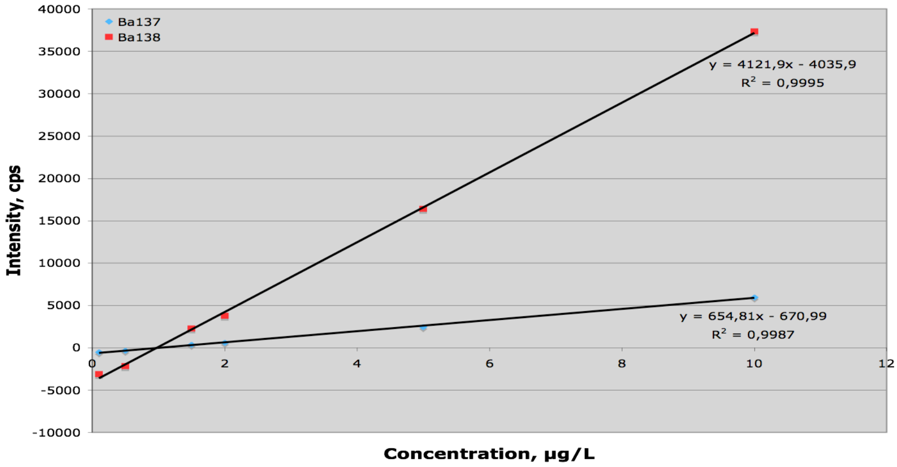

Fig. B4 Calibration curves for ^{137}Ba and ^{138}Ba

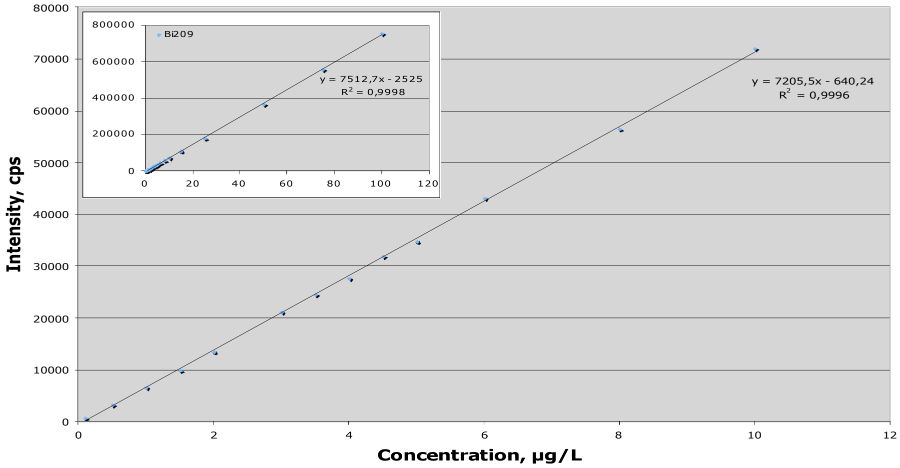

Fig. B5 Calibration curve for ^{209}Bi

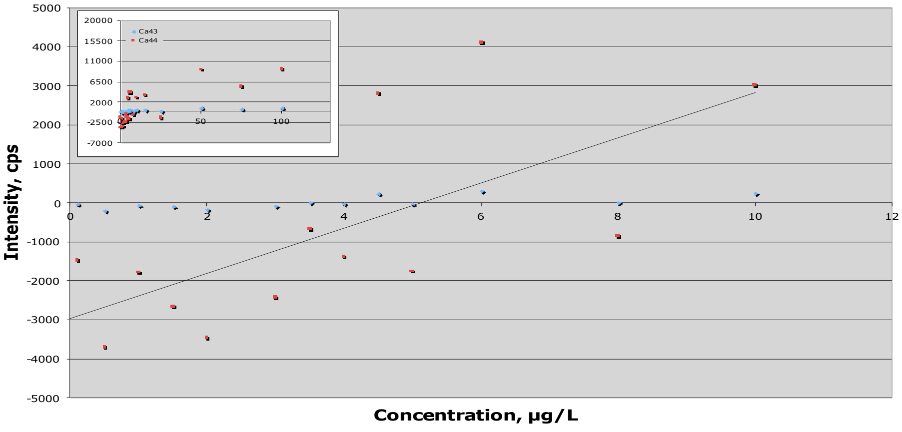

Fig. B6 Calibration curve for ^{44}Ca. Regression analysis of ^{43}Ca not performed

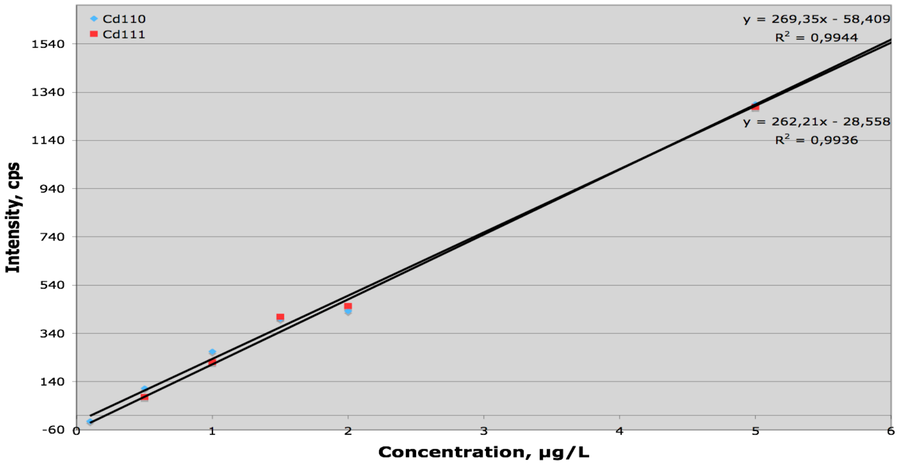

Fig. B7 Calibration curves for ^{110}Cd and ^{11}Cd

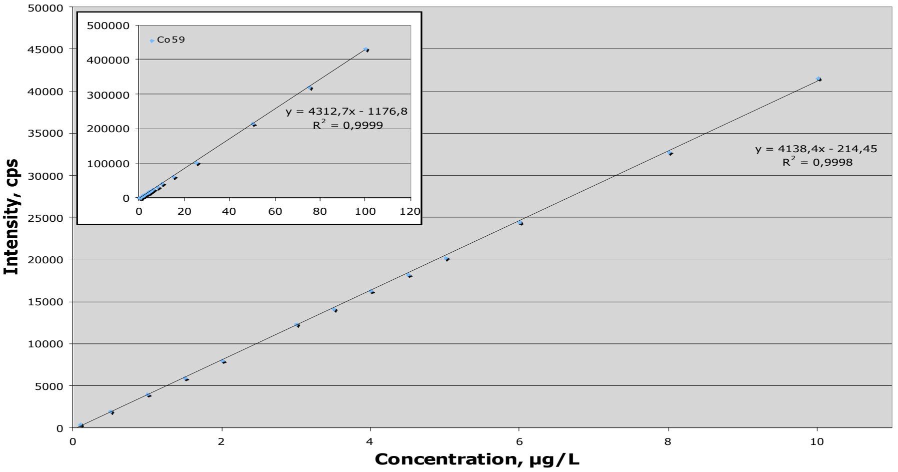

Fig. B8 Calibration curve for ^{59}Co

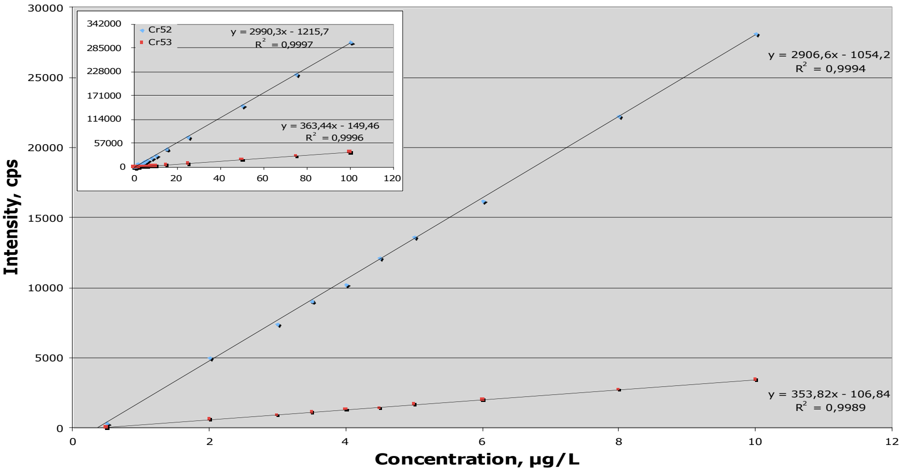

Fig. B9 Calibration curves for ^{52}Cr and ^{53}Cr

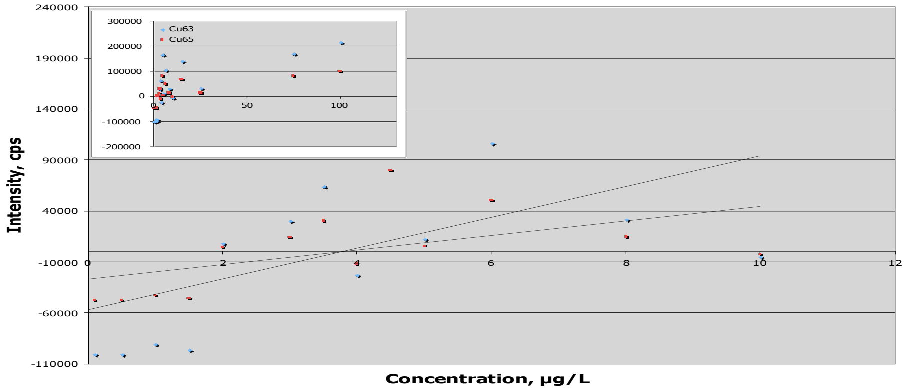

Fig. B10 Calibration curves for ^{63}Cu and ^{65}Cu

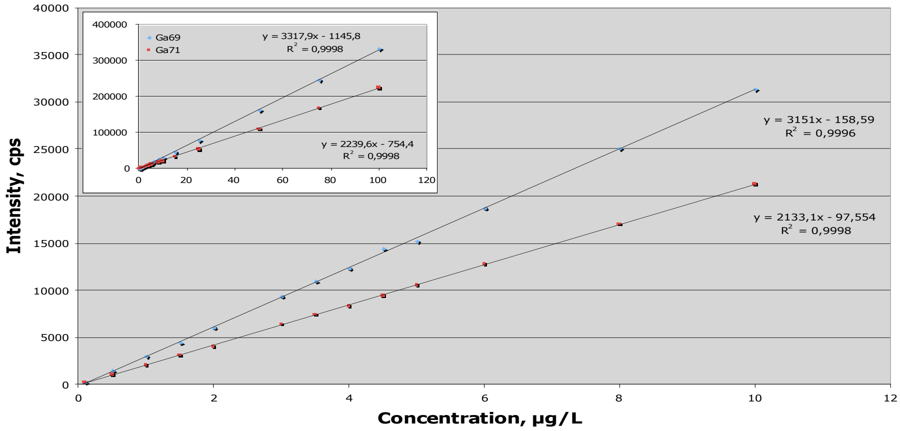

Fig. B11 Calibration curves for ^{69}Ga and ^{70}Ga

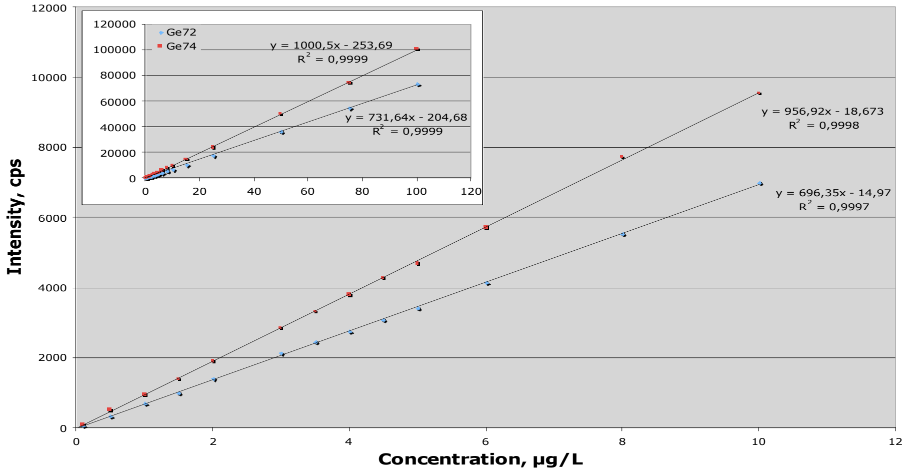

Fig. B12 Calibration curves for ^{72}Ge and ^{74}Ge

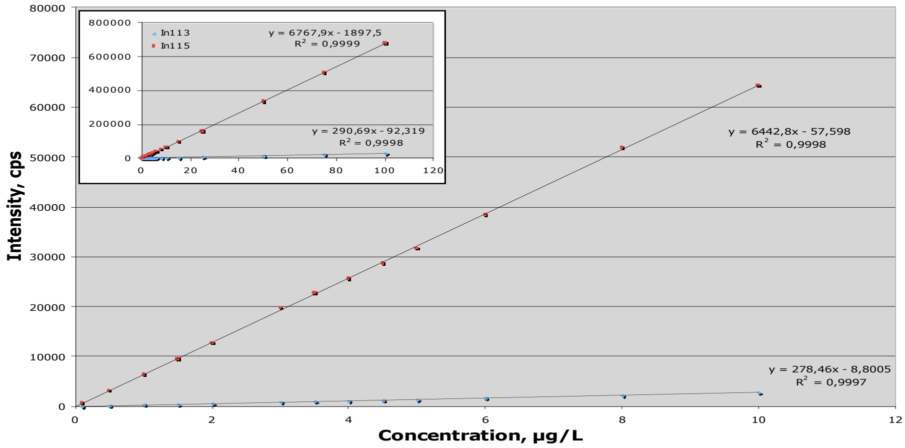

Fig. B13 Calibration curves for ^{113}In and ^{115}In

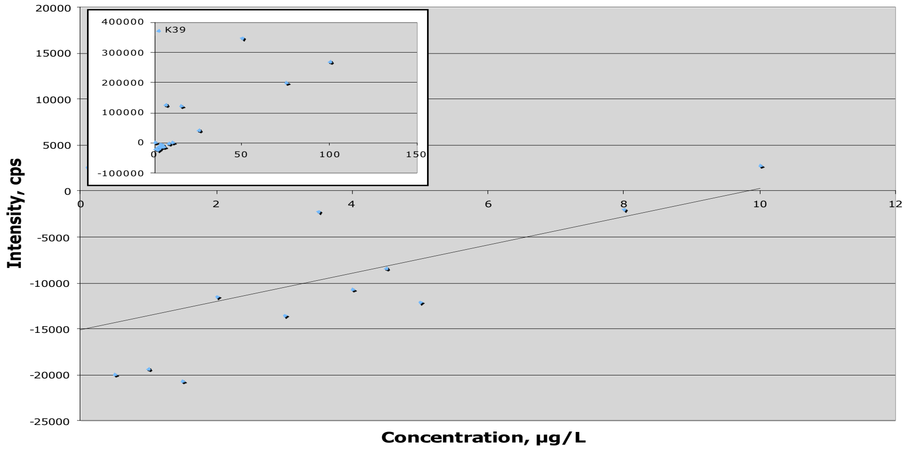

Fig. B14 Calibration curve for ^{39}K

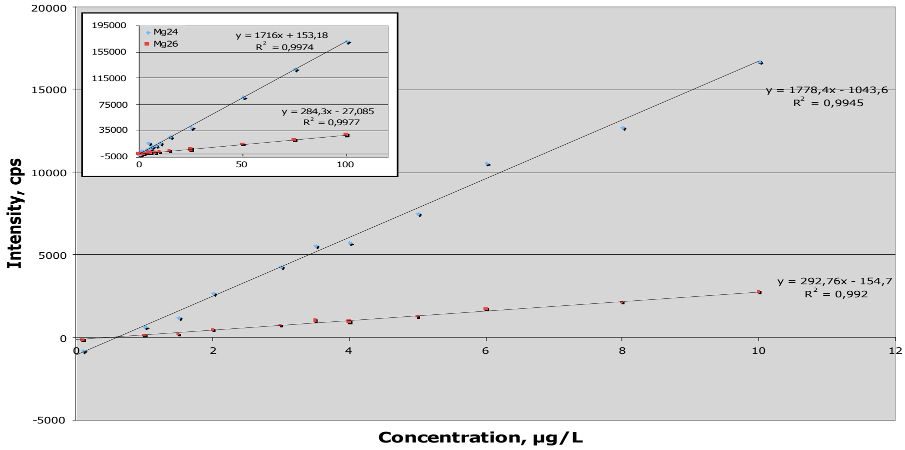

Fig. B15 Calibration curves for ^{24}Mg and ^{26}Mg

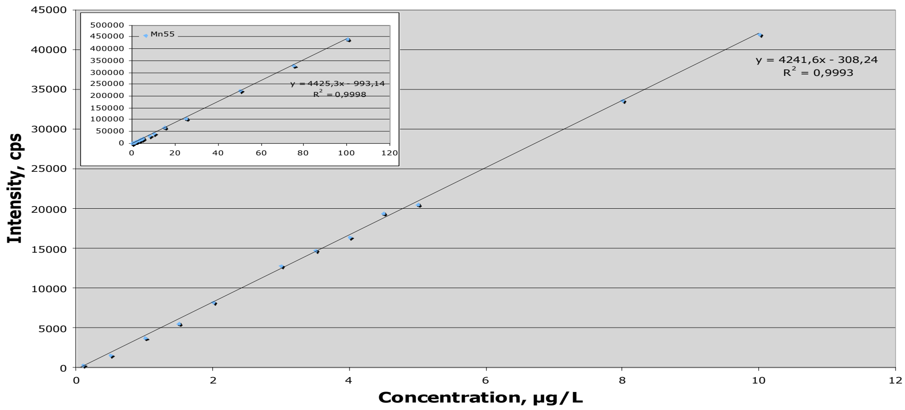

Fig. B16 Calibration curve for ^{55}Mn

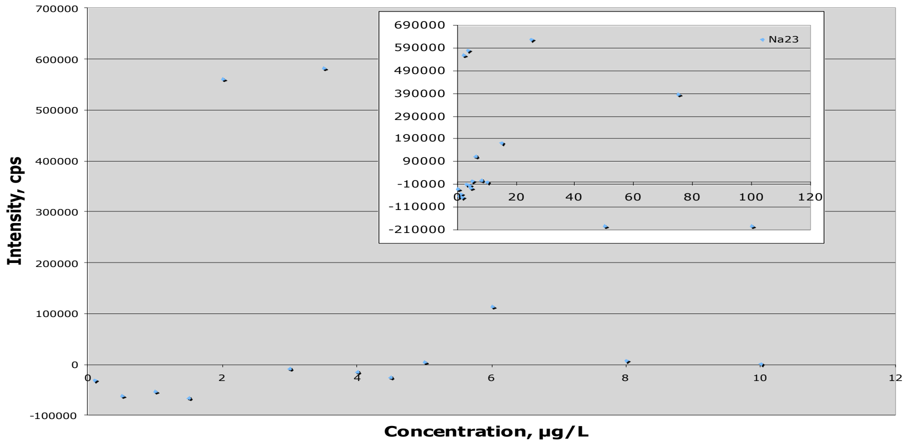

Fig. B17 ^{23}Na

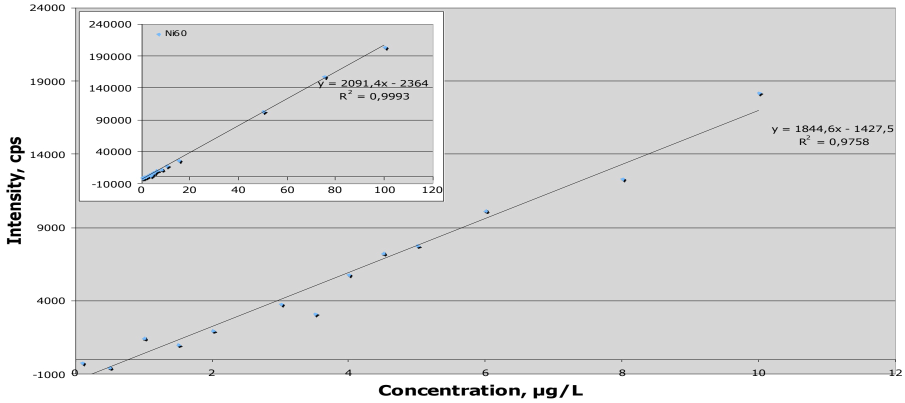

Fig. B18 Calibration curve for ^{60}Ni

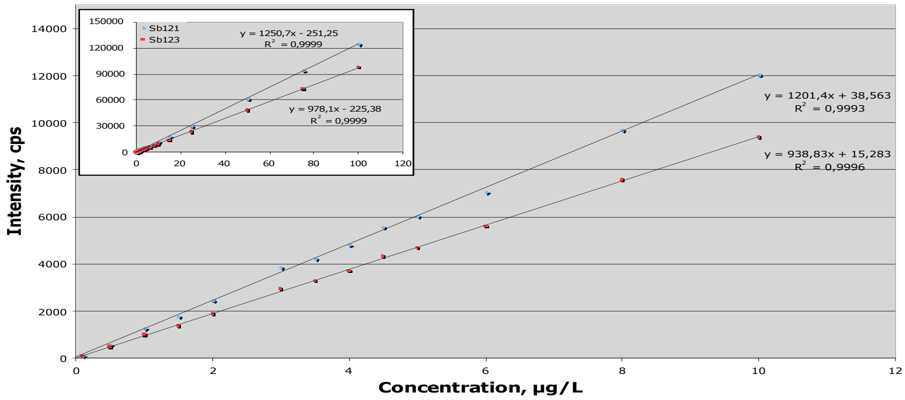

Fig. B19 Calibration curves for ^{121}Sb and ^{123}Sb

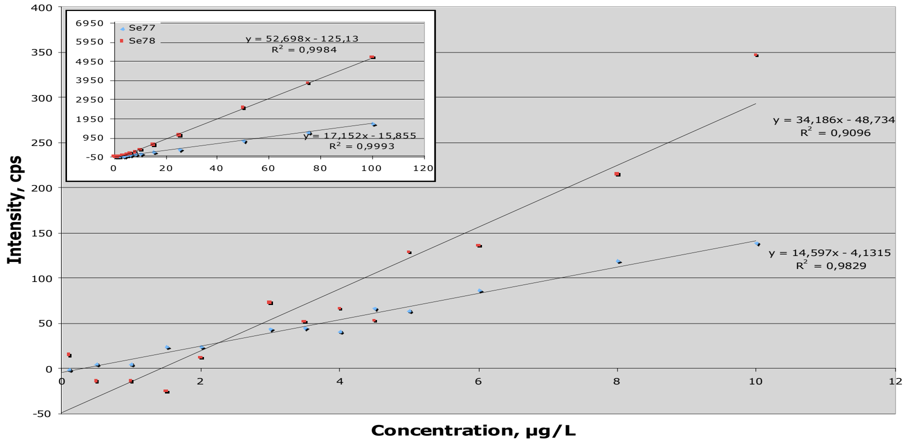

Fig. B20 Calibration curves for ^{77}Se and ^{78}Se

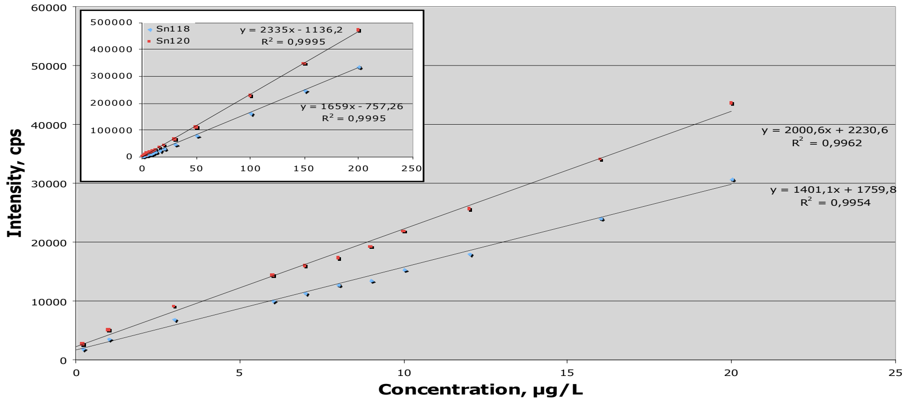

Fig. B21 Calibration curves for ^{118}Sn and ^{120}Sn

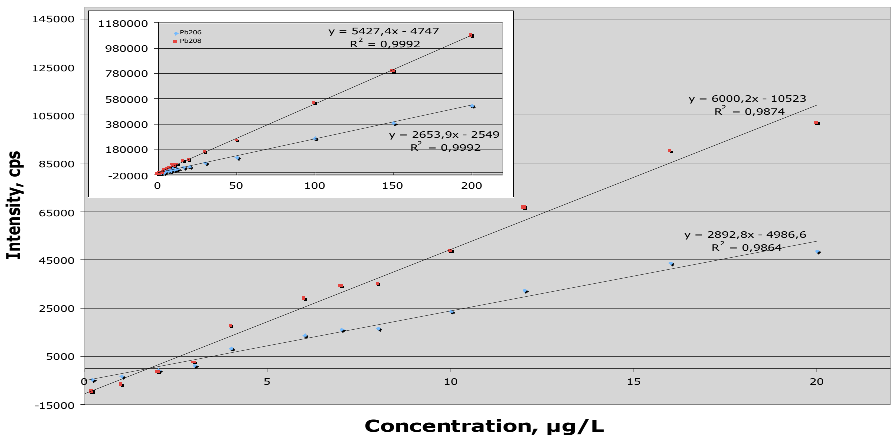

Fig. B22 Calibration curves for ^{206}Pb and ^{208}Pb

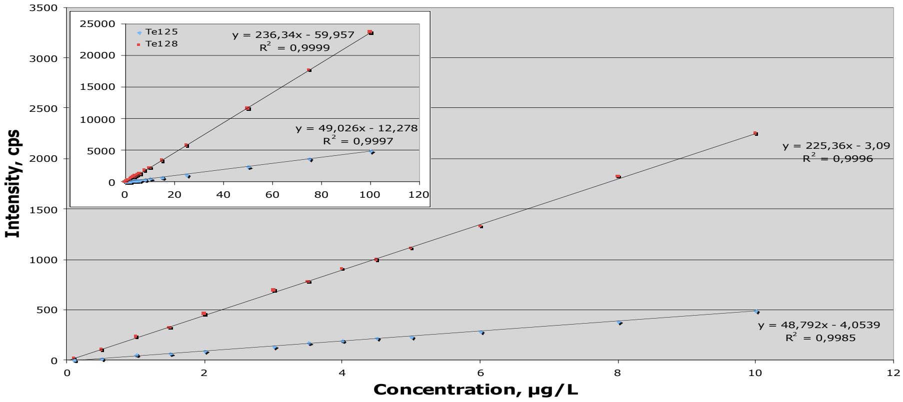

Fig. B23 Calibration curves for ^{125}Te and ^{128}Te

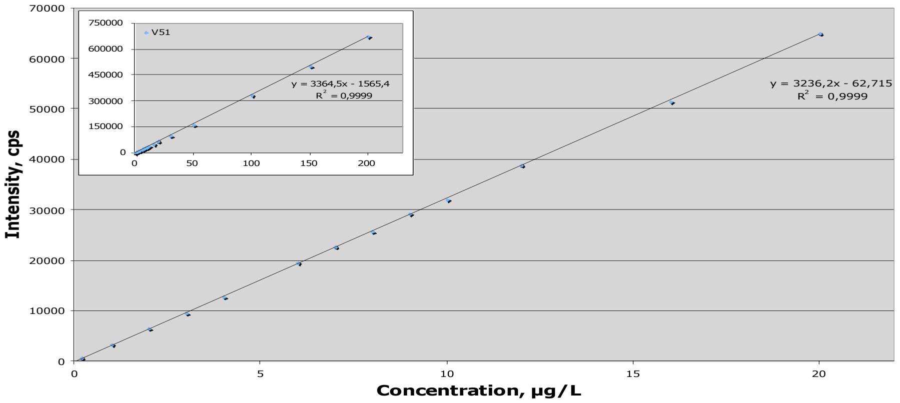

Fig. B24 Calibration curve for ^{51}V

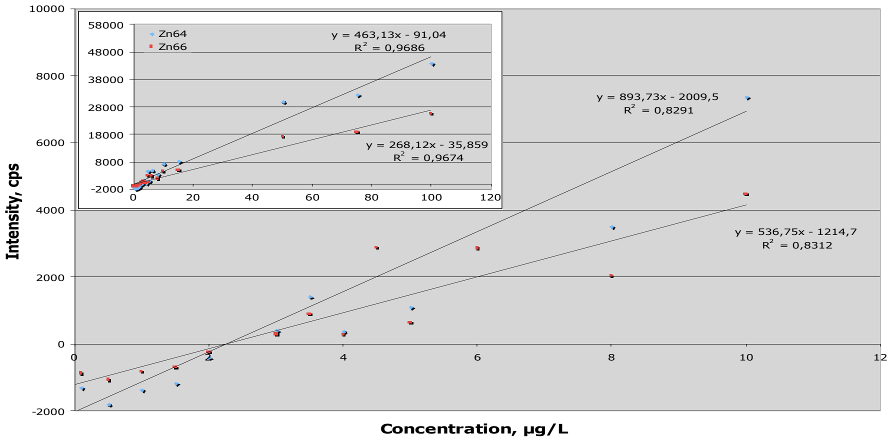

Fig. B25 Calibration curves for ^{64}Zn and ^{66}Zn

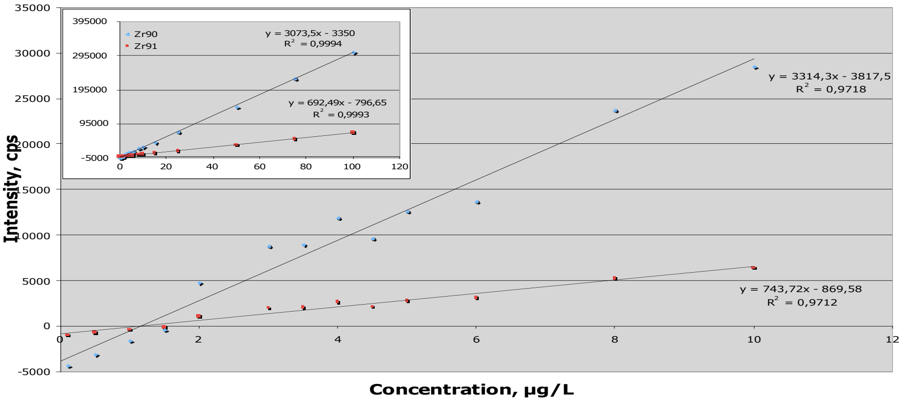

Fig. B26 Calibration curves for ^{90}Zr and ^{91}Zr

APPENDIX C: OmniRange

The OmniRange setting varies the voltage applied to the quadrupole at the exact time that it is transmitting a given mass. This selectively reduces the sensitivity, which makes it possible to analyze concentrations not normally measurable (ELAN 5000 user maual). As Fig.C1 shows, a concentration of 1500 µg/L of ^{138}Ba was beyond the ELANs[12] linear working range for both OmniRange 0 and 10. However, a dramatically decrease in the intensity was observed between OmniRang 10 and 20, and at OmniRange = 50 were almost all ^{138}Ba isotopes deflected.

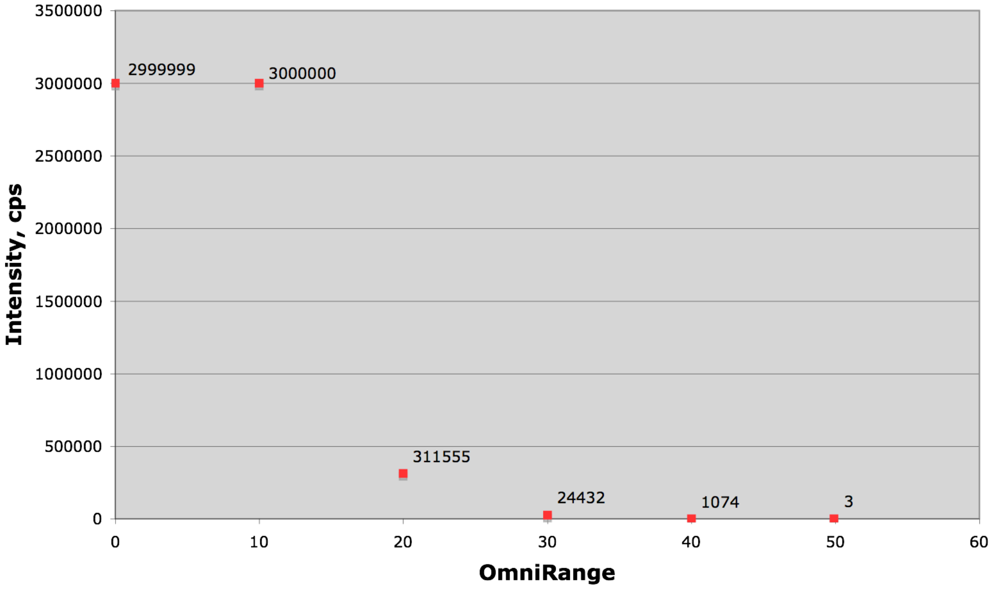

Fig. C1 Intensity as a function of OmniRange of 1500 µg/L of ^{138}Ba

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[12] ELAN 5000 (Perkin Elmer SCIEX, Norwalk, USA)

APPENDIX D: Procedure blank intensities

Table D1 Intensities and standard deviation of nine measure replicates of one procedure blank for the limit of detection analysis

Element	**Intensity**									**Standard deviation, S_b**
	cps									**cps**
Al	7834	7971	7784	7795	7407	7193	7979	7015	7356	355.7
As	12	9	11	9	7	8	12	6	12	2.3
Ba	8573	8552	8641	8643	8669	8865	8760	8912	8774	125.5
Bi	75	78	73	67	73	77	66	71	70	4.2
Cd	20	22	21	21	20	19	19	19	22	1.2
Co	117	127	123	118	124	124	121	121	123	3.1
Cr	383	426	366	409	394	365	379	378	372	20.5
Ga	6	9	8	9	9	11	17	12	10	3.1
Ge	5	5	5	3	2	6	4	4	6	1,3
In	8	12	13	15	11	10	15	7	11	2,8
Mg	3919	3846	3853	3839	3829	3872	3924	4288	3943	142,7
Mn	1058	1057	1072	1101	1084	1099	1129	1144	1089	29,7
Pb	4919	5067	5032	5075	5103	5155	5180	5216	5038	90,0
Sb	241	247	234	236	263	246	236	236	236	9,3
Te	1	3	7	3	5	-2	2	2	-1	2,8
V	36	39	34	40	35	35	35	32	32	2,7

APPENDIX E: Microwave decomposition graphs

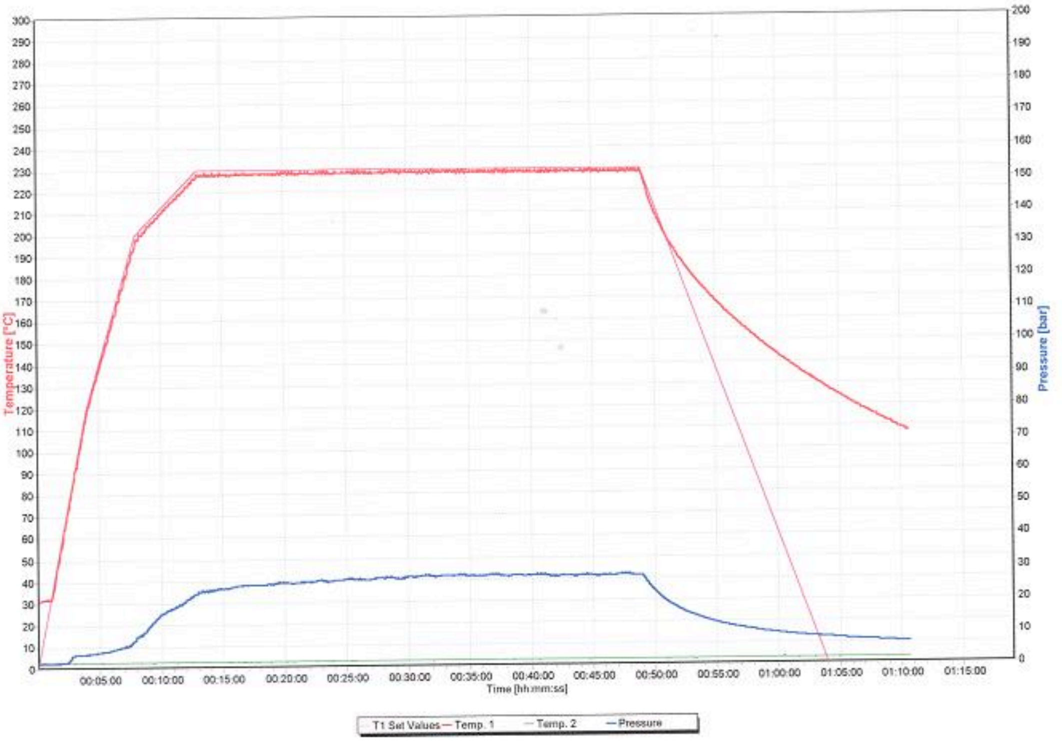

Fig. E1 Microwave decomposition graph using Procedure B in Table 2.7

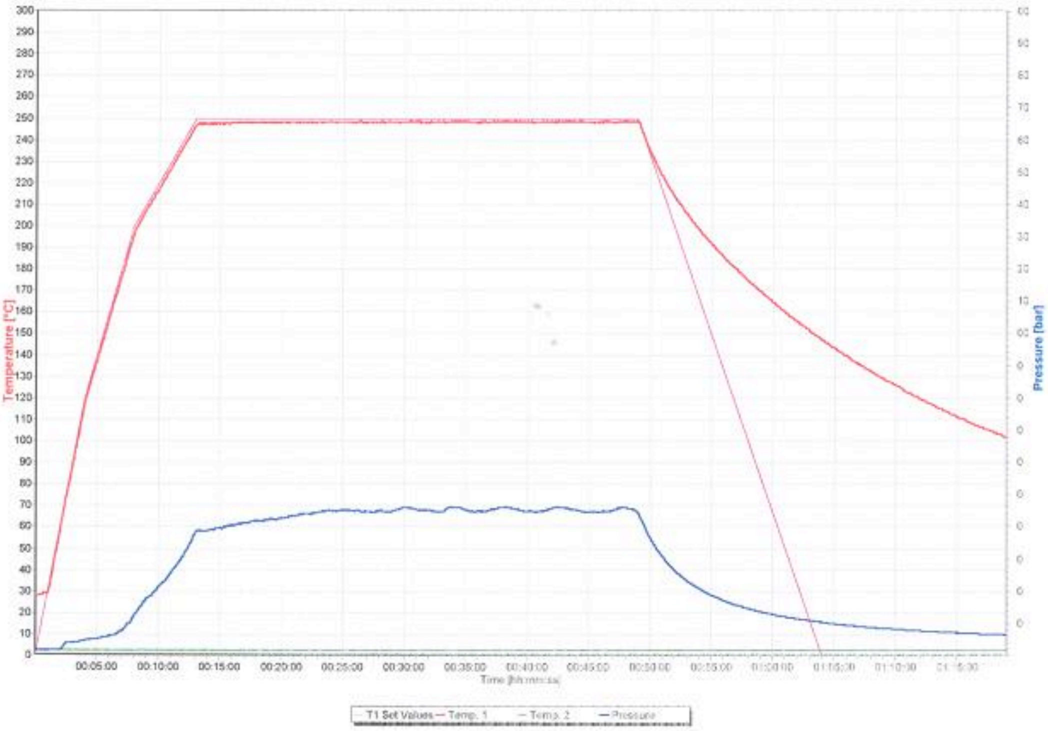

Fig. E2 Microwave decomposition graph using Procedure A in Table 2.7

APPENDIX F: Analyte concentrations in CRM sample solutions

Table E1 Concentrations of Al, As, Ba, Bi, Cd, Co, Cr, Ga, Ge, In, Mg, Mn, Pb, Te and V in ERM®-EC681 decomposed and diluted 250 times. Data for six sample replicates are given. Units are in mg/L, if otherwise not stated.

		Al	As	Ba	Bi	Cd	Co	Cr	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample: EC681																	
Replicate	Mass, g																
1	0,0982	52,5	17,0	1410,8	0,039	69,7	0,020	67,8	0,019	0,014	0,024	nd	0,23	57,9	3,0	nd	0,079
2	0,0999	77,1	13,4	1490,5	0,042	62,5	nd	70,8	0,025	0,015	0,024	nd	0,55	59,1	3,4	nd	0,12
3	0,0920	51,2	13,1	1287,3	0,041	62,9	0,035	63,8	0,020	0,020	0,026	nd	0,51	54,3	3,1	nd	0,23
4	0,0902	60,9	12,9	1261,4	0,15	63,9	0,031	62,5	0,013	0,020	0,023	nd	nd	53,6	3,9	nd	0,079
5	0,0902	52,4	12,5	1300,5	0,040	62,9	0,25	65,7	0,021	0,015	0,023	nd	0,031	54,4	2,7	nd	0,0061
6	0,0932	53,4	13,6	1398,6	13,4	56,5	0,015	68,1	0,019	0,024	nd	nd	nd	55,4	2,7	nd	0,058

[1] Below LOD

[2] Below LOQ

APPENDIX G: Analyte concentrations in solid CRM samples

Table G1 Concentrations of Al, As, Ba, Bi, Cd, Co, Cr, Ga, Ge, In, Mg, Mn, Pb, Te and V in ERM®-EC681. Data for six samplereplicates and corresponding statistical data are given. Units are in mg of element/ kg sample, if otherwise not stated.

	Al	As	Ba	Bi	Cd	Co	Cr	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample: EC681																
Replicate																
1	13,4	4,3	359,2	0,0099	17,7	0,0050	17,3	0,0048^1	0,0034^1	0,0062	nd	0,059	14,7	0,76	nd	0,020^1
2	19,3	3,3	373,0	0,011	15,6	nd	17,7	0,0061	0,0037^1	0,0061	nd	0,14	14,8	0,86	nd	0,030
3	13,9	3,6	349,8	0,011	17,1	0,0095	17,3	0,0054	0,0055	0,0070	nd	0,14	14,7	0,84	nd	0,062
4	16,9	3,6	349,6	0,042	17,7	0,0085	17,3	0,0036^1	0,0054	0,0064	nd	nd	14,9	1,1	nd	0,022^1
5	14,5	3,5	360,5	0,011	17,4	0,069	18,2	0,0059	0,0042^1	0,0064	nd	0,0085^1	15,1	0,75	nd	0,0017^1
6	14,3	3,7	375,2	3,6	15,1	0,0040	18,3	0,0051	0,0064	nd	nd	nd	14,8	0,73	nd	0,016^2
Average (mg/kg)	15,4	3,7	361,2	0,61	16,8	0,016	17,7	0,0052	0,0047	0,0053	nd	0,057	14,8	0,84	nd	0,025
SD (mg/kg)	2,3	0,34	11,0	1,5	1,1	0,026	0,46	0,00090	0,0012	0,0026	-	0,067	0,13	0,13	-	0,020
RSD (%)	14,7	9,4	3,0	238,2	6,7	163,5	2,6	17,4	24,5	49,4	-	115,8	0,85	15,9	-	80,8
Median (mg/kg)	14,4	3,6	359,8	0,011	17,3	0,0067	17,5	0,0052	0,0048	0,0062	-	0,034	14,8	0,80	-	0,021

nd = not detected

[1] Below LOQ

[2] Below LOD

APPENDIX H: Quantitative comparison of CRM- and measurement values

Table H1 Quantitative comparison of CRM- and measurement values of CRM sample solutions, which have gone through the same decomposition and dilution procedure as the real samples

Element	Certified values			Measurement values				Comparison of certified- and measurement values			
	C_{CRM}[1]	U_{CRM}[2]	u_{CRM}[3]	C_M[4]	SD_M[5]	u_M[6]	n[7]	D_m[8]	u_D[9]	U_D[??]	Comment[11]
As	3,93	0,15	0,075	3,78	0,31	0,042	54	0,15	0,09	0,17	Not significant
Cd	21,7	0,7	0,4	19,6	1,6	0,2	54	2,1	0,4	0,8	Significant
Cr	17,7	0,6	0,3	17,4	1,1	0,2	47	0,3	0,3	0,7	Not significant
Pb	13,8	0,7	0,4	14,3	0,8	0,1	54	0,5	0,4	0,7	Not significant

[1] Certified value

[2] Expanded uncertainty of the certified value

[3] Standard uncertainty of the certified value (coverage factor k=2); $u_{CRM} = k \cdot U_{CRM}$

[4] Mean measured value

[5] Standard deviation of the measured values

[6] Uncertainty of the measurement result; $u_M = SD_M \cdot n^{1/2}$

[7] Number of measure replicates

[8] Absolute difference between certified value and mean measured value; $\boldsymbol{\Delta_m} = \left| C_{CRM} - C_M \right|$

[9] Combined uncertainty of result and certified value; $u_\Delta = (u_M^2 + u_{CRM}^2)^{1/2}$

[10] Expanded uncertainty of difference between result and certified value; $U_\Delta = 2 \cdot u_\Delta$

[11] Not significant difference between the measurement result and the certified value if; Δ_m ? U_Δ

Table H2[12] Quantitative comparison of CRM- and measurement values of CRM sample solutions, which have been diluted to match analyte concentrations in the real sample solutions

	Certified values			**Measurement values**				**Comparison of certified- and measurement values**			
Element	**C_{CRM}**[1]	**U_{CRM}**[2]	**u_{CRM}**[3]	**C_M**[4]	**SD_M**[5]	**u_M**[6]	**n**[7]	**Δ_m**[8]	**u_D**[9]	**U_D**[??]	**Comment**[11]
As	3,93	0,15	0,075	3,72	1,41	0,41	12	0,21	0,41	0,83	Not significant
Cr	17,7	0,6	0,3	18,0	1,4	0,3	18	0,3	0,4	0,9	Not significant
Pb	13,8	0,7	0,4	11,8	3,8	1,3	9	2,0	1,3	2,6	Not significant

[12] See footnotes in Table H1

Table H3[12] Quantitative comparison of CRM- and measurement values of CRM sample solutions, which have been diluted to match analyte concentrations in the real sample solutions

	Certified values			**Measurement values**				**Comparison of certified- and measurement values**			
Element	**C_{CRM}**[1]	**U_{CRM}**[2]	**u_{CRM}**[3]	**C_M**[4]	**SD_M**[5]	**u_M**[6]	**n**[7]	**D_m**[8]	**u_D**[9]	**U_D**[??]	**Comment**[11]
Cd	21,7	0,7	0,4	25,4	2,9	0,7	18	3,7	0,8	1,5	Significant
Cr	17,7	0,6	0,3	15,7	6,3	1,5	18	2,0	1,5	3,0	Not significant
Pb	13,8	0,7	0,4	13,5	7,9	1,9	18	0,3	1,9	3,8	Not significant

[12] See footnotes in Table H1

APPENDIX I: Analyte concentrations in sample solutions

Table II Concentrations of Al, As, Ba, Bi, Cd, Co, Ga, Ge, In, Mg, Mn, Pb, Te and V in six sources of food contact plastic materials decomposed and diluted 250 times. Data for five sample replicates are given for each source. Units are in mg/L, if otherwise not stated. See Table 2.3 for sample information

		Al	As	Ba	Bi	Cd	Co	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample: S1																
Replicate	Mass, g															
1	0,0918	48,3	5,1	3,6	0,21	0,75	0,13	0,13	0,18	nd	76,8	3,7	0,52	4,4	0,092	0,22
2	0,0909	67,1	5,6	4,3	0,21	0,69	0,096	0,15	0,20	nd	85,4	3,7	0,75	0,14	0,13	nd
3	0,0871	54,2	5,5	11,5	0,16	0,55	0,047	0,14	0,072	nd	87,5	3,4	0,45	0,12	nd	nd
4	0,0848	87,3	7,0	48,1	0,22	0,65	0,064	0,19	0,078	nd	150,3	4,1	0,69	0,12	nd	nd
5	0,0972	41,1	5,4	3,3	0,30	0,61	0,045	0,21	0,64	nd	77,9	3,5	0,62	0,28	0,10	nd
Sample: S2																
Replicate	Mass, g															
1	0,0888	27,7	4,5	1,9	0,0013^{1}	0,55	nd	nd	nd	nd	28,4	2,7	0,27^{2}	nd	nd	nd
2	0,0842	61,1	4,6	2,0	0,0014^{1}	0,58	nd	0,0025^{1}	nd	nd	31,2	2,7	nd	nd	nd	nd
3	0,0995	40,3	4,8	8,0	nd	0,57	nd	nd	nd	nd	49,6	2,7	0,24^{2}	nd	nd	nd
4	0,0878	32,4	4,6	8,6	nd	0,54	nd	nd	nd	nd	37,4	2,9	nd	nd	nd	nd
5	0,0957	41,2	4,5	2,1	0,57	0,58	nd	0,042	0,40	nd	34,3	2,6	nd	nd	nd	nd
Sample: S3																
Replicate	Mass, g															
1	0,0995	5,32	3,9	0,65	0,024	0,32	nd	0,0053^{2}	nd	0,0058	6,1	2,4	nd	nd	nd	nd
2	0,0987	38,0	4,0	2,9	0,017	0,73	nd	0,010^{2}	nd	0,0047^{2}	4,0	2,3	nd	0,39	nd	nd
3	0,1003	43,6	4,3	2,0	0,0061^{2}	0,46	nd	0,011^{2}	nd	0,0039^{2}	8,3	2,4	nd	nd	nd	nd
4	0,0883	31,4	3,9	2,9	0,025	0,39	nd	0,0083^{2}	nd	nd	6,3	2,6	nd	nd	nd	nd
5	0,0918	39,3	3,9	3,1	0,011	0,52	nd	0,011^{2}	nd	0,0012^{1}	5,4	nd	0,24^{2}	nd	nd	nd

nd = not detected

[1] Below LOD

[2] Below LOQ

Table X (Continued)

		Al	As	Ba	Bi	Cd	Co	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample : S4																
Replicate	Mass															
1	0,0887	87,3	3,4	7,8	nd	0,70	nd	0,017^{2}	nd	0,023	305,9	2,1	0,81	nd	nd	0,11
2	0,0849	69,6	3,2	5,9	nd	0,56	nd	0,016^{2}	nd	0,018	366,9	2,2	0,024^{1}	nd	nd	0,13
3	0,0922	84,3	3,3	8,1	0,0028^{1}	0,68	nd	0,018^{2}	nd	0,026	384,6	2,2	1,2	nd	nd	0,14
4	0,0970	75,8	5,0	54,7	nd	1,4	0,020	0,0076^{2}	nd	0,027	441,4	3,1	1,2	2,3	nd	0,25
5	0,0924	62,6	4,7	38,3	nd	0,71	0,0091	0,013^{2}	nd	0,025	406,4	2,7	0,92	nd	nd	0,14
Sample : S5																
Replicate	Mass															
1	0,0921	44,7	0,0071^{1}	7,4	nd	0,66	0,028	nd	nd	nd	390,7	0,15	nd	0,47	nd	nd
2	0,0940	48,4	nd	5,3	nd	0,66	0,014	nd	nd	nd	391,2	0,13	0,039^{1}	0,083	nd	0,0030^{1}
3	0,0931	38,3	nd	6,6	nd	0,66	0,018	nd	nd	nd	354,2	0,17	0,054^{1}	0,036	nd	nd
4	0,0935	42,8	nd	4,8	nd	0,66	0,018	nd	nd	nd	393,1	0,16	0,018^{1}	0,0031	nd	0,00059^{1}
5	0,0864	42,3	nd	5,0	nd	0,65	0,016	nd	nd	nd	375,7	0,12	nd	0,057	nd	nd
Sample S6																
Replicate	Mass															
1	0,0801	22,6	nd	4,4	nd	0,64	nd	nd	nd	1,2	402,2	0,17	0,096	nd	nd	nd
2	0,0837	54,3	nd	5,0	nd	0,63	nd	nd	nd	0,17	537,0	0,30	0,15	nd	nd	nd
3	0,0839	20,0	nd	5,6	nd	0,65	nd	nd	nd	1,2	482,7	0,19	0,31	nd	nd	nd
4	0,0966	22,6	nd	5,0	nd	0,62	nd	nd	nd	nd	604,6	0,15	0,099	nd	nd	nd
5	0,0821	24,7	nd	10,2	nd	0,62	nd	nd	nd	0,18	460,5	0,13	0,13	nd	nd	nd

nd = not detected

[1] Below LOD

[2] Below LOQ

APPENDIX J: Analyte concentrations in solid samples

Table J1 Concentrations of Al, As, Ba, Bi, Cd, Co, Ga, Ge, In, Mg, Mn, Pb, Te and V in six sources of food contact plastic materials. Values for five samplereplicates and corresponding statistical data are given for each source. Units are in mg/kg, if otherwise not stated. See Table 2.3 for sample information

	Al	As	Ba	Bi	Cd	Co	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample : S1															
Replicate															
1	13.1	1.4	0.98	0.058	0.21	0.036	0.036	0.049	nd	21.6	1.0	0.14	0.038	0.025	0.060
2	18.4	1.5	1.2	0.058	0.19	0.026	0.042	0.055	nd	23.5	1.0	0.21	0.034	0.034	nd
3	15.5	1.6	3.3	0.047	0.16	0.014	0.041	0.021	nd	25.1	0.99	0.13	0.056	nd	nd
4	***25.7***	2.1	14.2	0.064	0.19	0.019	0.057	0.023	nd	**44.3**	1.21	0.21	0.084	nd	nd
5	10.6	1.4	0.86	0.078	0.16	0.012	0.055	0.17	nd	20.0	0.91	0.16	0.15	0.026	nd
Average (mg/kg)	16.7	1.6	4.1	0.061	0.18	0.021	0.046	0.063	nd	26.9	1.03	0.17	0.072	0.017	nq
SD (mg/kg)	5.8	0.27	5.7	0.011	0.022	0.010	0.0090	0.060	-	9.9	0.11	0.036	0.045	0.016	-
RSD (%)	35.0	17.0	139.6	18.5	11.9	46.9	19.9	95.1	-	36.8	10.6	21.3	64.7	93.8	-
Median (mg/kg)	15.5	1.5	1.2	0.058	0.19	0.019	0.042	0.049	-	23.5	1.02	0.16	0.056	0.025	-
Sample : S2															
Replicate															
1	7.8	1.3	0.52	nd*	0.15	nd	nd	nd	nd	8.1	0.75	nq	nd	nd	nd
2	**18.1**	1.4	0.58	nd*	0.17	nd	nd*	nd	nd	9.1	0.81	nd	nd	nd	nd
3	10.1	1.2	2.0	nd	0.14	nd	nd	nd	nd	11.3	0.69	nq	nd	nd	nd
4	9.2	1.3	2.5	nd	0.15	nd	nd	nd	nd	10.3	0.81	nd	nd	nd	nd
5	10.8	1.2	0.56	0.15	0.15	nd	0.011	0.11	nd	11.8	0.67	nd	nd	nd	nd
Average (mg/kg)	11.2	1.3	1.2	nd*	0.15	nd	nq	nq	nd	9.9	0.75	nq	nd	nd	nd
SD (mg/kg)	4.0	0.08	0.93	-	0.011	-	-	-	-	1.7	0.065	-	-	-	-
RSD (%)	35.9	6.5	76.0	-	7.18	-	-	-	-	17.6	8.7	-	-	-	-
Median (mg/kg)	10.1	1.3	0.58	-	0.15	-	-	-	-	9.3	0.75	-	-	-	-

Gribbs' tests for outliers, i.e. $G = |\text{suspect value} - \text{average}| / SD$, have been performed on values in **bold**. Values in ***italic bold*** exceeded the critical value (95% confidence level), i.e. the value can be regarded as an outlier (Miller and Miller, 2000).

nd = not detected

nd* = below LOD

nq = below LOD

Table J1 (Continued)

	Al	As	Ba	Bi	Cd	Co	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample : S3															
Replicate															
1	**1.3**	0.98	0.18	0.0060	***0.080***	nd	0.0013^{nq}	nd	0.0015	1.5	0.61	nd	nd	nd	nd
2	9.6	1.0	0.72	0.0043	0.18	nd	0.0026^{nq}	nd	nq	1.0	0.58	nd	0.10	nd	nd
3	10.9	1.1	0.50	0.0015^{nq}	0.11	nd	0.0029^{nq}	nd	nq	2.1	0.59	nd	nd	nd	nd
4	8.9	1.1	0.82	0.0071	0.11	nd	0.0024^{nq}	nd	nd	1.8	0.73	nd	nd	nd	nd
5	10.7	1.1	0.85	0.0029	0.14	nd	0.0029^{nq}	nd	nd*	1.5	**nd**	nq	nd	nd	nd
Average (mg/kg)	8.3	1.0	0.61	0.0044	0.13	nd	0.0024	nd	nq	1.57	0.50	nq	nq	nd	nd
SD (mg/kg)	4.0	0.045	0.28	0.0022	0.039	-	0.00066	-	-	0.39	0.29	-	-	-	-
RSD (%)	47.9	4.3	45.5	51.5	31.1	-	27.3	-	-	24.8	57.2	-	-	-	-
Median (mg/kg)	9.6	1.05	0.72	0.0043	0.11	-	0.0026	-	-	1.5	0.60	-	-	-	-
Sample : S4															
Replicate															
1	24.6	0.95	2.2	nd	0.20	nd	0.0047	nd	0.0065	86.2	0.59	0.23	nd	0.032	0.032
2	20.5	0.94	1.7	nd	0.16	nd	0.0046	nd	0.0054	108.1	0.64	nd*	nd	0.037	0.037
3	22.9	0.89	2.2	nq	0.19	nd	0.0049	nd	0.0071	104.3	0.59	0.33	nd	0.037	0.037
4	19.5	1.3	13.6	nd	**0.37**	0.0050	0.0020^{nq}	nd	0.0069	113.8	0.80	0.31	0.58	0.063	0.063
5	17.0	1.3	10.3	nd	0.19	0.0025	0.0034^{nq}	nd	0.0067	109.9	0.72	0.25	nd	0.039	0.039
Average (mg/kg)	20.9	1.1	6.0	nq	0.22	nq	0.0039	nd	0.0065	104.5	0.67	0.22	nq	nd	0.042
SD (mg/ kg)	3.0	0.19	5.6	-	0.085	-	0.0012	-	0.00065	10.7	0.091	0.13	-	-	0.012
RSD (%)	14.2	18.0	92.5	-	38.2	-	31.7	-	9.9	10.3	13.7	58.9	-	-	29.8
Median (mg/ kg)	20.5	0.95	2.2	-	0.19	-	0.0046	-	0.0067	108.0	0.64	0.25	-	-	0.037

Gribbs' tests for outliers, i.e. $G = |\text{suspect value - average}| / SD$, have been performed on values in **bold**. Values in ***italic bold*** exceeded the critical value (95% confidence level), i.e. the value can be regarded as an outlier (Miller and Miller, 2000).

nd = not detected

nd* = below LOD

nq = below LOD

Table J1 (Continued)

	Al	As	Ba	Bi	Cd	Co	Ga	Ge	In	Mg	Mn	Pb	Sb	Te	V
Sample : S5															
Replicate															
1	12.1	nd*	2.0	nd	0.18	0.0076	nd	nd	nd	106.0	0.042	nd	0.13	nd	nd
2	12.9	nd	1.4	nd	0.18	0.0037	nd	nd	nd	104.0	0.034	nd*	nq	nd	nd*
3	10.3	nd	1.8	nd	0.18	0.0049	nd	nd	nd	95.1	0.045	nd*	nq	nd	nd
4	11.4	nd	1.3	nd	0.18	0.0048	nd	nd	nd	105.1	0.044	nd*	nd*	nd	nd*
5	12.4	nd	1.4	nd	0.19	0.0047	nd	nd	nd	108.7	0.034	nd	nq	nd	nd
Average (mg/kg)	11.8	nd	1.6	nd	0.18	0.0051	nd	nd	nd	103.8	0.040	nd	nq	nd	nd
SD (mg/kg)	1.0	-	0.30	-	0.0060	0.0015	-	-	-	5.2	0.0050	-	-	-	-
RSD (%)	8.4	-	19.2	-	3.1	28.7	-	-	-	5.0	12.9	-	-	-	-
Median (mg/kg)	12.0	-	1.4	-	0.18	0.0048	-	-	-	105.1	0.042	-	-	-	-
Sample : S6															
Replicate															
1	7.1	nd	1.4	nd	0.20	nd	nd	nd	0.37	125.5	0.052	0.030^{nq}	nd	nd	nd
2	**16.2**	nd	1.5	nd	0.19	nd	nd	nd	0.051	160.4	***0.089***	0.043^{nq}	nd	nd	nd
3	6.0	nd	1.7	nd	0.19	nd	nd	nd	0.35	143.8	0.055	0.094	nd	nd	nd
4	5.8	nd	1.3	nd	0.16	nd	nd	nd	nd	156.5	0.040	0.026^{nq}	nd	nd	nd
5	7.5	nd	3.1	nd	0.19	nd	nd	nd	0.054	140.2	0.038	0.039^{nq}	nd	nd	nd
Average (mg/kg)	8.5	nd	1.8	nd	0.19	nd	nd	nd	0.16	145.3	0.050	0.046	nd	nd	nd
SD (mg/kg)	4.4	-	0.76	-	0.010	-	-	-	0.18	13.9	0.020	0.027	-	-	-
RSD (%)	51.3	-	42.2	-	7.8	-	-	-	108.6	9.6	37.4	59.2	-	-	-
Median (mg/kg)	7.1	-	1.5	-	0.19	-	-	-	0.054	143.8	0.050	0.039	-	-	-

Gribbs' tests for outliers, i.e. G = |suspect value - average|/ SD, have been performed on values in **bold**. Values in ***italic bold*** exceeded the critical value (95% confidence level), i.e. the value can be regarded as an outlier (Miller and Miller, 2000).

nd = not detected

nd* = below LOD

nq = below LOD

Appendix K: Evaluation of spectral interferences

Table K1 Measurement results for two isotopes of the same element for five sample replicates

Isotope	C_A[1]	Sample Replicate					$RSD_{isotope}$
	µg/L	1	2	3	4	5	
^{137}Ba	5	460,3	397,1	351,6	205,6	166,2	39,8
^{138}Ba		443,8	396,1	340,2	198,1	153	41,1
$RSD_{element}$		2,6	0,2	2,3	2,6	5,8	
^{111}Cd	1.5	20,8	20,9	21,6	22,7	22,2	3,8
^{113}Cd		20,9	21,2	21,3	22,4	22,6	3,6
$RSD_{element}$		0,3	1,0	1,0	0,9	1,3	
^{52}Cr	5	16,3	16,6	17,4	20,4	18,1	9,7
^{53}Cr		15,3	16,1	17,5		17,1	5,9
$RSD_{element}$		4,5	2,2	0,4		4,0	
^{52}Cr	1		16,3	7,6	5,2	11,2	48,3
^{53}Cr		11,4	15,7	8,1	6,1	11,5	34,8
$RSD_{element}$			2,7	4,5	11,3	1,9	
^{69}Ga	0.5	12,9	12,1	12,1	12,1	11,2	5,3
^{71}Ga		0,54	0,56	0,55	0,54	0,54	1
$RSD_{element}$		130,1	128,9	129,1	129,3	128,4	
^{72}Ge	0.5	0,52	0,56	0,57	0,53	0,55	4,5
^{74}Ge		0,55	0,55	0,54	0,55	0,54	0,76
$RSD_{element}$		4,0	1,3	3,8	2,6	1,3	
^{113}In	0.5	4,5	3,91	3,11	2,17	2,65	28,8
^{115}In		0,56	0,56	0,57	0,57	0,56	0,77
$RSD_{element}$		110,1	106,0	97,6	82,6	92,1	
^{24}Mg	5	1,5	1	2,1	1,8	1,5	24,8
^{26}Mg		1,7	1,1	2,1	1,7	1,5	22,7
$RSD_{element}$		8,8	6,7	0,0	4,0	0,0	
^{24}Mg	20	8	9,3	12,5	10,6	9	17,6
^{26}Mg		8,1	9	12,4	10,8	9,1	17,4
$RSD_{element}$		0,9	2,3	0,6	1,3	0,8	
^{206}Pb	4	12,4	12,6	13,1			3
^{208}Pb		12,7	13,2	13,4			2,7
$RSD_{element}$		1,7	3,3	1,6			
^{206}Pb	1	5,2	19,6	9,1	19,3	13,6	47
^{208}Pb		6,2	20,9	10,2	19,4	15	43,2
RSD		12,4	4,5	8,1	0,4	6,9	
^{121}Sb	3	1,1	1	1	0,9	0,93	8,8
^{123}Sb		1,1	1	0,95	0,92	0,95	7,2
$RSD_{element}$		0,0	0,0	3,6	1,6	1,5	
^{121}Sb	0.25	0,68	0,66	0,67	0,55	0,77	12,3
^{123}Sb		0,81	0,53	0,67	0,6	0,69	15,3
$RSD_{element}$		12,3	15,4	0,0	6,1	7,7	
^{125}Te		0,14	0,14	0,11	0,011	0,12	51,8
^{128}Te		0,025	0,034			0,026	18,2
$RSD_{element}$		98,6	86,2			91,1	

[1] Approximately analyte concentration in the sample solution

APPENDIX L: TERNARY DIAGRAMS

The following text is drawn from Watling et al., (1997) and Spence et al., (2000) if otherwise not stated. A ternary diagram is a triangle with each apex representing 100% contribution of an element (see Fig. L1), i.e. Al, Mg and Mn in this work. A sample, e.g. S1-1 in Table L1, is characterized by its position on the diagram, which is determined by the ratios of the three elemental concentrations. The contribution from each element is calculated as a percentage of the total concentration of these elements (see footnotes in Table. L1). These percentages are plotted on the diagram.

Samples of different origin are effectively discriminated if they are well separated in the diagram, i.e. a wide range of concentrations across the samples. Close clustering of samples confirms their common origin.

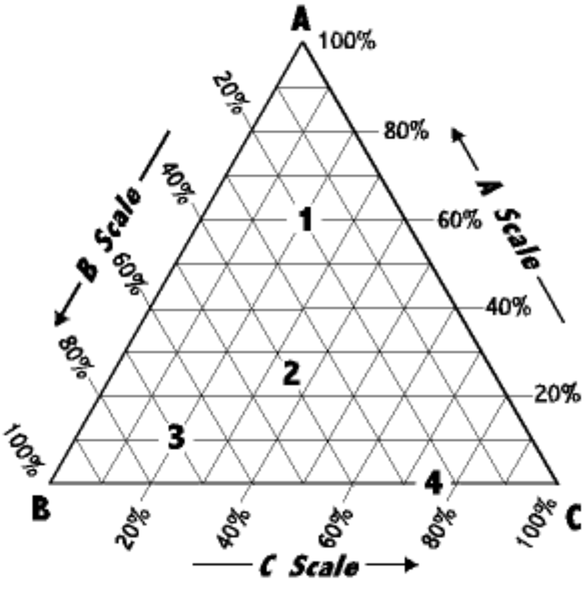

Fig. L1 Principal sketch of a ternary diagram. (http://csmres.jmu.edu/geollab/fichter/SedRx/Images/ternread-d.gif (Accessed: 06.03.07))

Table L1 Datamatrix for the ternary plot

		C_{SS}[1]			C_{Sum}[2]	Percent contribution[3]		
		Al	**Mg**	**Mn**		**Al**	**Mg**	**Mn**
Sample	**S1**							
Replicate	1	13,1	2,2	10,0	25,3	51,9	8,6	39,6
	2	18,4	2,4	10,0	30,8	59,8	7,6	32,5
	3	15,5	2,5	9,9	27,9	55,5	9,0	35,5
	4	25,7	4,4	12,1	42,2	60,9	10,5	28,7
	5	10,6	2,0	9,1	21,7	48,8	9,2	41,9
Sample	**S2**							
Replicate	1	7,8	0,8	7,5	16,1	48,4	5,0	46,6
	2	18,1	0,9	8,1	27,1	66,8	3,4	29,9
	3	10,1	1,1	6,9	18,1	55,7	6,2	38,1
	4	9,2	1,0	8,1	18,3	50,2	5,6	44,2
	5	10,8	1,2	6,7	18,7	57,8	6,3	35,9
Sample	**S3**							
Replicate	1	1,3	0,2	6,1	7,6	17,2	2,0	80,8
	2	9,6	0,1	5,8	15,5	61,9	0,6	37,4
	3	10,9	0,2	5,9	17,0	64,1	1,2	34,7
	4	8,9	0,2	7,3	16,4	54,3	1,1	44,6
	5	10,7	0,2	0,0	10,9	98,6	1,4	0,0
Sample	**S4**							
Replicate	1	24,6	8,6	5,9	39,1	62,9	22,0	15,1
	2	20,5	10,8	6,4	37,7	54,4	28,7	17,0
	3	22,9	10,4	5,9	39,2	58,4	26,6	15,0
	4	19,5	11,4	8,0	38,9	50,2	29,3	20,6
	5	17,0	11,0	7,2	35,2	48,3	31,2	20,5
Sample	**S5**							
Replicate	1	12,1	10,6	0,4	23,1	52,3	45,8	1,8
	2	12,9	10,4	0,3	23,6	54,6	44,0	1,4
	3	10,3	9,5	0,5	20,3	50,8	46,9	2,2
	4	11,4	10,5	0,4	22,4	51,0	47,0	2,0
	5	12,4	10,9	0,3	23,6	52,5	46,0	1,4
Sample	**S6**							
Replicate	1	7,1	12,6	1,7	21,4	33,3	58,8	8,0
	2	16,2	16,0	0,4	32,7	49,6	49,1	1,3
	3	6,0	14,4	0,9	21,3	28,1	67,4	4,4
	4	5,8	15,7	0,3	21,7	26,7	72,1	1,2
	5	7,5	14,0	0,4	21,9	34,2	64,0	1,8

[1] Concentration of the element in the solid sample

[2] The sum of the element concentrations; $C_{Sum}=C_{Al}+C_{Mg}+C_{Mn}$

[3] Percent contribution = $(C_{SS}/C_{Sum}).100$

APPENDIX M: Two-sided t-test

Mg: S6 vs. S4

```
Sample  N   Mean  StDev  SE Mean
1       5  145,3   13,9      6,2
2       5  104,5   10,7      4,8


Difference = mu (1) - mu (2)
Estimate for difference:  40,8000
95% CI for difference:  (22,2501; 59,3499)
99% CI for difference:  (13,3475; 68,2525)
T-Test of difference = 0 (vs not =): T-Value = 5,20  P-Value = 0,001  DF = 7
```

Mg: S4 vs. S5

```
Sample  N    Mean  StDev  SE Mean
1       5   104,5   10,7      4,8
2       5  103,80   5,20      2,3


Difference = mu (1) - mu (2)
Estimate for difference:  0,700000
95% CI for difference:  (-12,976365; 14,376365)
99% CI for difference:  (-20,752365; 22,152365)
T-Test of difference = 0 (vs not =): T-Value = 0,13  P-Value = 0,900  DF = 5
```

Mn: S4 vs. S5

```
Sample  N     Mean    StDev  SE Mean
1       5   0,6700   0,0910    0,041
2       5  0,04000  0,00500   0,0022


Difference = mu (1) - mu (2)
Estimate for difference:  0,630000
95% CI for difference:  (0,516838; 0,743162)
99% CI for difference:  (0,442347; 0,817653)
T-Test of difference = 0 (vs not =): T-Value = 15,46  P-Value = 0,000  DF = 4
```

Mg: S5 vs. S1

```
Sample  N    Mean  StDev  SE Mean
1       5  103,80   5,20      2,3
2       5   26,90   9,90      4,4


Difference = mu (1) - mu (2)
Estimate for difference:  76,9000
95% CI for difference:  (64,6630; 89,1370)
99% CI for difference:  (58,3592; 95,4408)
T-Test of difference = 0 (vs not =): T-Value = 15,38  P-Value = 0,000  DF = 6
```

Mg: S1 vs. S2

```
Sample  N   Mean  StDev  SE Mean
1       5  26,90   9,90      4,4
2       5   9,90   1,70     0,76


Difference = mu (1) - mu (2)
Estimate for difference:  17,0000
95% CI for difference:  (4,5276; 29,4724)
99% CI for difference:  (-3,6826; 37,6826)
T-Test of difference = 0 (vs not =): T-Value = 3,78  P-Value = 0,019  DF = 4
```

Mn: S1 vs. S2

```
Sample  N    Mean   StDev  SE Mean
1       5   1,030   0,110    0,049
2       5  0,7500  0,0650    0,029


Difference = mu (1) - mu (2)
Estimate for difference:  0,280000
95% CI for difference:  (0,140183; 0,419817)
99% CI for difference:  (0,068157; 0,491843)
T-Test of difference = 0 (vs not =): T-Value = 4,90  P-Value = 0,003  DF = 6
```

Mg: S2 vs S3

```
Sample  N   Mean  StDev  SE Mean
1       5   9,90   1,70     0,76
2       5  1,570  0,390     0,17


Difference = mu (1) - mu (2)
Estimate for difference:  8,33000
95% CI for difference:  (6,16434; 10,49566)
99% CI for difference:  (4,73875; 11,92125)
T-Test of difference = 0 (vs not =): T-Value = 10,68  P-Value = 0,000  DF = 4
```

Thesis for the Master's
degree in chemistry

Linda Storrustløkken

Determination of trace metals in transparent polyethylene films by ICP-MS, and its application in forensic chemistry

60 study points

DEPARTMENT OF CHEMISTRY
Faculty of mathematics and natural
sciences
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