

WCSR Advice 2017-13 B

SCIENTIFIC COMMITTEE REACH (WCSR)

ADVICE ON MEASURING METHODS FOR CERTAIN RESTRICTED
SUBSTANCES OF THE ANNEX XVII OF REACH – PART B : CR(VI)
IN LEATHER, PB IN ALLOYS, PB IN PLASTICS



www.reachinbelgium.be

WCSR Advice 2017-13 B

MEMBERS OF THE SCIENTIFIC COMMITTEE

The members are :

Willy Baeyens; Johan Bierkens; Marie-Noëlle Blaude; Steven Broekx; Peter Dubruel; Lieve Geerts; Lode Godderis; Walter Hecq; Birgit Mertens; Guy Schroyen; Stefaan Soenen; Nicolas Van Larebeke; An Van Nieuwenhuyse; Guido Vanermen; Jeroen Vanoirbeek; Reinhilde Weltens.

CONFLICT OF INTEREST

No member has declared any conflict of interest.

RAPPORTEUR

The Scientific Committee REACH thanks the rapporteur Willy Baeyens.

PUBLIC CONSULTATION

A comment from Centexbel was received in the Public Consultation ending on 2 February 2018.

ADOPTION OF THE ADVICE

The Scientific Committee REACH advice was adopted by consensus on the meeting of 19/4/2018.

LEGAL FRAMEWORK OF THE ADVICE

Cooperation agreement of 17 October 2011 between the Federal State, the Flemish Region, the Walloon Region and the Brussels Capital Region concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

Ministerial decree of 8 July 2014 appointing the members of the Scientific Committee REACH established under Article 3, § 3 of the Cooperation Agreement of 17 October 2011 between the Federal State, the Flemish Region, the Walloon Region and the Brussels Capital Region concerning the Registration, Evaluation, Authorisation and restriction of Chemicals (REACH)

Ministerial decree of 2 June 2016 on dismissal and appointment of members of the Scientific Committee REACH

Ministerial decree of 5 October 2016 on appointment of members of the Scientific Committee REACH

DISCLAIMER

The Scientific Committee REACH reserves, at any time, the right to change this advice when new information and data become available after the publication of this version.

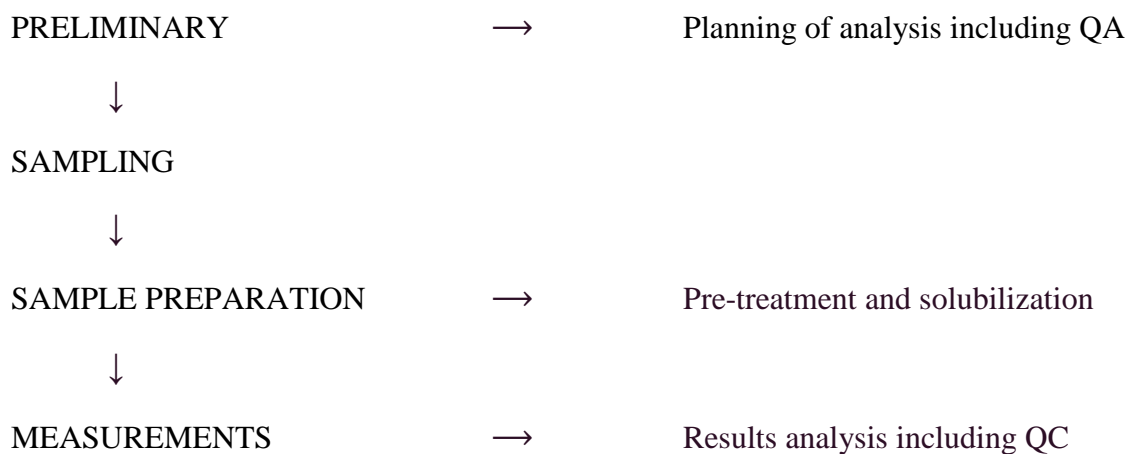
CONTENTS

Contents

1	DETERMINATION OF Cr(VI) IN LEATHER.....	5
1.1	ANALYTICAL STEPS - FROM SAMPLING TO REPORTING.....	5
1.2	PROPOSED METHOD:.....	8
2	DETERMINATION OF Pb IN ALLOYS.....	11
2.1	ANALYTICAL STEPS - FROM SAMPLING TO REPORTING.....	11
2.2	PROPOSED METHOD:.....	15
3	DETERMINATION OF Pb IN PLASTICS.....	17
3.1	ANALYTICAL STEPS - FROM SAMPLING TO REPORTING.....	17
3.2	PROPOSED METHOD:.....	21

1 DETERMINATION OF Cr(VI) IN LEATHER

1.1 Analytical steps - from sampling to reporting



Quality assurance (QA) claims to assure the existence and effectiveness of procedures that attempt to make sure that expected levels of quality will be reached (Rauf & Hanan, 2009).

Quality control (QC) refers to procedures that lead to control different steps in measurement process (Rauf & Hanan, 2009). Accuracy and precision belong to QC. Accuracy is the measurement of how close an experimental value is to the true value. It is realized by use of control samples with known compositions, which are treated in the same way as the unknown samples. Nowadays, to demonstrate accuracy of the method, analysis of (standard, certified) reference materials (CRMs) is the most commonly used. Another way to confirm accuracy of the method of interest is to compare results with those obtained with well established (reference) methods (Intra-laboratory) or independent procedures by other laboratories (Inter-laboratory). Recovery studies by means of standard additions is also part of the accuracy estimation.

Precision (reproducibility) is the degree to which further measurements or calculations show the same or similar results. It is expressed by means of relative standard deviation on the average of the series of measurements (RSD).

Cr(VI) in leather can be measured in a liquid solution after extraction of the element followed by a clean-up and photometrical determination of the red/violet diphenylcarbazone-chromium complex at 540 nm or by ICPMS analysis of the liquid extract after separation of Cr(VI) from Cr(III).

The Standard Operational Procedure (SOP).

The standard operational method for determining Cr(VI) in leather is ISO 17075:2007 and is based on the photometrical determination of the red/violet diphenylcarbazone-chromium complex at 540 nm.

Extraction technique

Two g of ground leather is immersed for 3h in a degassed phosphate buffer solution. This solution is filtered followed by a clean-up step with a Solid Phase Extraction cartridge (SPE) to remove all interfering compounds and substances. Ten mL of eluate is collected and diluted with extraction solution.

SOP measurement technique

The measurement proposed in the SOP is a spectrophotometer. To the eluate of the SPE cartridge, phosphoric acid solution and color forming diphenylcarbazide solution are added. After 15 min the absorbance of the red/violet complex is measured at 540 nm with the spectrophotometer. The detection limit reported for this method is 3 mg/kg.

Alternative measurement technique

Chromium can be detected at much lower concentrations with ICPMS, however, a separation step between the chromium ions (III and VI) prior to measurement is necessary because the mass spectrometer makes no difference between the two ions. Chromium speciation in water solution is possible using the chromFAST low pressure anion exchange speciation kit (CF-KIT-Cr36 anion exchange column) and the SC-DX FAST autosampler system from ESI for ICPMS. The fully automated and easy-to-use system can switch between multi-element ICPMS sample to chromium speciation in minutes.

The column separates chromium ions as well as other potentially interfering compounds in about 10 minutes via low pressure liquid chromatography. If other interfering compounds will still be present than it is possible, in view of the ultra-low concentrations that can be measured to further dilute the sample extract (see further detection limits).

Cr can be measured at different mass units but the most abundant are 52 (83.8%), 53 (9.5%) and 50 (4.3%). There are many polyatomic interferences (ions composed of 2 or 3 elements), with as the most important on ^{52}Cr ($^{40}\text{Ar}^{12}\text{C}^+$, $^{36}\text{Ar}^{16}\text{O}^+$, $^{38}\text{Ar}^{14}\text{N}^+$, $^{36}\text{Ar}^{15}\text{N}^1\text{H}^+$, as well as a number of chlorine and sulfur polyatoms). Therefore, Cr is measured in medium resolution (MR) mode avoiding those interferences.

Blanks are extract solutions without leather sample that follow the same analysis procedure as the extract solutions with leather sample.

Detection Limit

The detection limit depends in the first place on the IDL (instrument detection limit) and the dilutions of the sample. The instrumental detection limit provided for Cr by THERMO for the Element II (HR-ICPMS) is 95 pg/L, obtained in their laboratory in Bremen. However, Cr(VI) has first to be separated from Cr(III) with the speciation system, increasing the detection limit to 4 ng/L (Application Note – Low Pressure Cr speciation from Elemental Scientific).

With a detection limit of 4 ng/L and assuming that 2 g leather is extracted in 100 mL phosphate buffer solution, the lowest concentration we can detect with the HR-ICPMS (Element II) is then 0.2 µg/kg (ppb). This is about 10 000 times more sensitive than the spectrometric analysis method. This also means that analyses of further dilutions of the sample extract (10 are 100 times) are still more sensitive than with the spectrometric method. In this way interferences during measurement can be avoided.

Instrument settings

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min ⁻¹ (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min ⁻¹
Cool argon flow rate	16 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10 ⁶ cps per 1 ng mL ⁻¹ ¹¹⁵ In (in Low Resolution)
Isotopes monitored	Cr ⁵² , Cr ⁵³
resolution	medium
volume injected	50µl
sample time	0.2s
mass window	125
samples per peak	20
Number of acquisition	150 (150 passes, 1 run)
Analysis time	12 min
Search window MR	60%
Integration window MR	60% for each isotope
Scan type	E scan for each isotope

Reference Materials

There are no reference materials for Cr(VI) in leather. Following reference materials are used instead

SRM 2700 and 2701 Cr(VI) in Soil (from National Institute of Standards and Technology (NIST)).

BCR 545 Cr(VI) in welding dust on a filter (EC-JRC-IRMM, Geel).

The proposed extraction method is the same as in the SOP (ISO 17075:2007), but the measurement method is different because the lowest detection limit is obtained with a high resolution ICPMS.

1.2 Proposed Method:

Extraction Method.

Degassed extraction solution: Dissolve 22,8 g dipotassium hydrogen phosphate ($K_2HPO_4 \cdot 3H_2O$) in 1,000 ml water, adjusted to pH $8,0 \pm 0,1$ with phosphoric acid. Degas this solution with either argon or nitrogen.

Weigh $2 \text{ g} \pm 0,01 \text{ g}$ of ground leather to the nearest 0,001 g. Pipette 100 ml of degassed solution into a 250 ml conical flask. Displace oxygen by passing oxygen-free argon (or nitrogen) into the flask for 5 min ($50 \text{ ml/min} \pm 10 \text{ ml/min}$). Remove the aeration tube, add the leather and close the flask with a stopper. Record the extract volume as V_0 .

Shake the leather powder suspension $3 \text{ h} \pm 5 \text{ min}$ on a mechanical shaker to extract the chromium(VI).

Gently shake the suspension in a smooth circular movement to keep the leather powder from adhering to the wall of the flask. Avoid shaking it too quickly.

Immediately after completing 3 h of extraction, filter the content of the conical flask through a membrane filter into a glass bottle with screw cap. Check the pH of the solution. The pH of the solution shall be between 7,5 and 8,0. If the pH of the solution is not within this range, start the complete procedure again.

Measurement method:

Chromium speciation in water solution is possible using the chrom*FAST* low pressure anion exchange speciation kit (CF-KIT-Cr36 from ESI) and the SC-DX *FAST* autosampler system for ICPMS. The fully automated and easy-to-use system can switch between multi-element ICPMS sample to chromium speciation in minutes. In addition, a low-pressure LC system is much easier

to handle than a high-pressure LC system. The separation conditions are set according the manufacturer's (Elemental Scientific) directions.

Cr(VI) is analyzed in 10 mL final sample with HR-ICPMS at mass 52 and 53.

The settings of the HR-ICPMS are summarized below:

Instrument settings

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min ⁻¹ (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min ⁻¹
Cool argon flow rate	16 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10 ⁶ cps per 1 ng mL ⁻¹ ¹¹⁵ In (in Low Resolution)
Isotopes monitored	Cr ⁵² , Cr ⁵³
resolution	medium
volume injected	50µl
sample time	0.2s
mass window	125
samples per peak	20
Number of acquisition	150 (150 passes, 1 run)
Analysis time	12 min
Search window MR	60%
Integration window MR	60% for each isotope
Scan type	E scan for each isotope

Reference Materials

There exist no Cr(VI) reference materials in leather. Following reference materials are used instead:

SRM 2700 and 2701 Cr(VI) in Soil (from National Institute of Standards and Technology (NIST)).

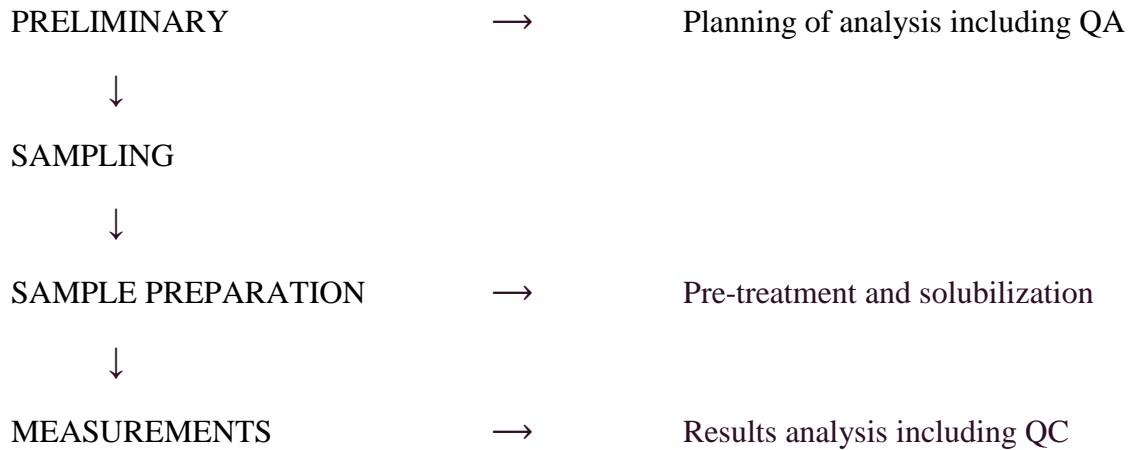
BCR 545 Cr(VI) in welding dust on a filter (EC-JRC-IRMM, Geel).

Detection Limit: 0.2 µg/kg (ppb).

Users that prefer a High Pressure LC system for separation and detection (the full measurement method is described), instead of the Low Pressure one described here, can find an application note from Agilent joint in annex.

2 DETERMINATION OF Pb IN ALLOYS

2.1 Analytical steps - from sampling to reporting



Quality assurance (QA) claims to assure the existence and effectiveness of procedures that attempt to make sure that expected levels of quality will be reached (Rauf & Hanan, 2009).

Quality control (QC) refers to procedures that lead to control different steps in measurement process (Rauf & Hanan, 2009). Accuracy and precision belong to QC. Accuracy is the measurement of how close an experimental value is to the true value. It is realized by use of control samples with known compositions, which are treated in the same way as the unknown samples. Nowadays, to demonstrate accuracy of the method, analysis of (standard, certified) reference materials (CRMs) is the most commonly used. Another way to confirm accuracy of the method of interest is to compare results with those obtained with well established (reference) methods (Intra-laboratory) or independent procedures by other laboratories (Inter-laboratory). Recovery studies by means of standard additions is also part of the accuracy estimation. Precision (reproducibility) is the degree to which further measurements or calculations show the same or similar results. It is expressed by means of relative standard deviation on the average of the series of measurements (RSD).

Pb in alloys can be measured in a liquid solution after solubilization of the sample (this is the most common way of analysis) or with non-destructive methods such as laser ablation ICPMS or XRF (X-ray Fluorescence) on homogeneous metal materials.

The Standard Operational Procedure (SOP).

The standard operational method for determining total lead in alloys is CPSC-CH-E1001-08.3 and we have added the method used in the interlaboratory calibration study by BV, INTERTEK, MTS, SGS and UL-STR (Analytical method: Detection and Determination of Total Lead in Metal and Metal Alloy by ICP-AES, ICP-MS and AAS).

Although non-destructive methods are also mentioned in the SOP, solubilization of the alloy followed by spectrometric detection is the most common used method. These 2 steps will be discussed in detail.

Solubilization techniques

Solid samples were solubilized by wet decomposition, with or without microwave-assistance (MW). In the SOP, digestion on a hot plate or in a microwave oven is described. The advantage of MW-assisted digestion compared to the open vessel system is: shorter dissolution times, no contamination from the environment, less amounts of reagents, no loss of volatile elements. For example, Szymczycha-Madeja & Mulak (2009) tested four digestion procedures for determination of major and trace elements (Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn) by ICP-OES in a spent catalyst. Two MW-assisted and two conventional hot-plate wet digestion procedures were applied. MW digestion with an HCl, HNO₃ and H₂O₂ mixture was the most effective one. Quality of results was evaluated by analysis of CRM (CTA-FFA-1, fine fly ash). The proposed method provided a better solubilization of the matrix and much better reproducibility.

In the SOP, 30 to 100 mg alloy are digested with 6 mL acid mixture (4.5 mL of nitric acid and 1.5 mL of hydrochloric acid) at 175 °C in a microwave oven. For the inter-comparison exercise either pure nitric acid or aqua regia (mix of nitric and hydrochloric acid in a ratio of 1:3) was suggested. To 100-200 mg of alloy, maximum 10 mL of acid was used. In literature digestions were in fact carried out with nitric acid and hydrochloric acid in various ratios. The SOP digestion procedure in a microwave oven or on a hot plate are both valid methods.

Measurement technique

The digested solution is measured, after appropriate dilution with Milli-Q water, with either Atomic Absorption Spectrometry (AAS), Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Induced Coupled Plasma Mass Spectrometry (ICP-MS). The ease of analysis, the sample throughput, the interferences and the detection limits are, however, different between these 3 techniques.

Table 1: Evolution of Measuring Techniques for Pb.

Acronym	Dates	Method	LOD ppb = ng/g = μg/L
UV-Vis	1920-1960	Complexation with Dithizone	20-500 ppb
AAS	1960-1970	Flame Atomic Absorption Spectroscopy	20-50 ppb
GFAAS	1970-1985	Graphite Furnace Atomic Absorption	1 ppb
XRF		X-ray Fluorescence	0.9 mg/cm ²
ICP-AES	1980s	Inductively Coupled Plasma Atomic Emission	20 ppb
ICP-MS	1990s	Inductively Coupled Plasma Mass Spectroscopy	1-10 ppt

Since the ICP-MS method is the most sensitive and easy to measure Pb, we will only discuss this method in detail. Pb can be measured at different mass units but the most abundant are 206 (24.1%), 207 (22.1%) and 208 (52.4%). Polyatomic interferences (ions composed of 2 or 3 elements) are only coming from Pt and Ir oxides ($^{190}\text{Pt}^{16}\text{O}^+$, $^{191}\text{Ir}^{16}\text{O}^+$ and $^{192}\text{Pt}^{16}\text{O}^+$). Because these polyatomic interferences are extremely rare, the ICP-MS can be run in low resolution mode. To correct for instrumental fluctuations use is made of Bi as internal standard.

Detection Limit

Detection limits are 0.034 mg/kg (Agilent application note) and 0.040 mg/kg (Mochizuku et al., 1990). The detection limit depends in the first place on the IDL (instrument detection limit) and the dilutions of the sample. The instrumental detection limit provided for Pb by Thermo for the Element II (HR-ICPMS) is 87 pg/L, obtained in their laboratory in Bremen. This value corresponds to the instrumental detection limit (IDL) reported in their application note 30003 (Determination of Trace Elements in Clinical Samples by HR-ICPMS on Element II), which equals 50 pg/L. Correcting the IDL for the dilution factor (50), a Method Detection Limit (MDL) of 2.5 ng/L is obtained. We also determined on our HR-ICPMS (Element II) the MDL for Pb is 6 ng/L. These values correspond thus to the range 1 to 10 ppt as mentioned in Table 1.

With a MDL of 5 ng/L and assuming that 100 mg alloy are solubilized in 100 mL solution, the lowest concentration we can detect with the HR-ICPMS (Element II) is then 5 μg/kg (ppb).

Blanks are digest solutions without alloy sample that follow the same analysis procedure as the digest solutions with alloy sample.

Instrument settings

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min ⁻¹ (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min ⁻¹
Cool argon flow rate	16 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10 ⁶ cps per 1 ng mL ⁻¹ Bi (in Low Resolution)
Take-up time	15 s
Wash time	10 s
Number of acquisition	6 (3 runs and 2 pass)
Search window LR	0% for each isotope
Mass window	20%
Integration window LR	5% for each isotope

Reference Materials

SRM 897 to 899 Nickel Alloy (from National Institute of Standards and Technology (NIST)).

SRM 361 to 364 Low Alloy Steel (from National Institute of Standards and Technology (NIST)).

SRM 2165 and 2166 Low Alloy Steel (from National Institute of Standards and Technology (NIST)).

SRM 1151a to 1154a Stainless Steel (from National Institute of Standards and Technology (NIST)).

JSS 168-2 Carbon Steel (from the Japan Iron and Steel Federation (JISF)).

JSS 152-5 Alloy Steel (from the Japan Iron and Steel Federation (JISF)).

The proposed digestion method is the same as in the SOP (CPSC-CH-E1001-08.3), but the measurement method is different because the lowest detection limit is obtained with a high resolution ICPMS.

2.2 Proposed Method:

Microwave Digestion Method.

1. If the item is coated with paint or a similar surface coating (it may contain Pb), the coating shall be removed and analyzed separately from the base metal for lead content, as described in the CPSC Standard Operating Procedure for Determining Lead (Pb) in Paint (<http://www.cpsc.gov/businfo/leadsop.pdf>). Care should be taken to remove as little of the substrate metal as possible.
2. Weigh out a 30–100 mg piece of metal alloy into appropriate microwave vessel equipped with a controlled pressure relief mechanism. Samples should be cut or ground into many small pieces to increase the rate of dissolution. If used, grinding apparatus (such as a rotary grinding tool with disposable grinding bits) must be cleaned thoroughly to prevent cross-contamination. Record actual weight to the nearest 0.1mg.
3. Add 4.5ml of concentrated nitric acid and 1.5ml of concentrated hydrochloric acid to each vessel. Wait for initial reaction of acid and sample at room temperature to be complete (to the point of no obvious fuming or bubbling) before sealing vessels. Seal vessels in accordance with the manufacturer's directions.
4. The microwave method should involve increasing the temperature of each sample to 175°C in approximately 5.5 minutes, and holding at 175°C for 4.5 minutes.
5. Allow the samples to cool for a minimum of 5 minutes before removal from the microwave. Vent the microwave vessels in fume hood before uncapping.
6. Quantitatively transfer the sample to 50 ml volumetric flask or disposable volumetric digestion cups. Dilute to 50 ml with deionized water (final sample).

Measurement method:

1. Pb is analyzed in 10 mL final sample (see point 6 hereabove), to which Bi (1 µg/L) is added, with HR-ICPMS at mass 208.
2. Perform calibration using calibration blank and at least three standards. Calibration shall be performed a minimum of once a day when used for analysis, or each time the instrument is set up. Results for each standard shall be within 5 percent of the true value, and the calibration blank should be < 5 times MDL. If the values do not fall within this range, recalibration is necessary. The operational blank signal should be subtracted from the sample signal before concentration calculations.
3. At least one certified reference material (CRM) should be analyzed with each batch of samples. The CRM should be similar material as test specimen with a known amount of Pb. Analyte recoveries should be within ±15 percent of expected values. If recoveries

are outside this limit, the source of the problem should be identified and resolved before continuing analyses.

4. Dilute any samples that have Pb values exceeding 1.5 times the high calibration standard and reanalyze.
5. The settings of the HR-ICPMS are summarized below:

Instrument settings

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min ⁻¹ (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min ⁻¹
Cool argon flow rate	16 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10 ⁶ cps per 1 ng mL ⁻¹ Bi (in Low Resolution)
Take-up time	15 s
Wash time	10 s
Number of acquisition	6 (3 runs and 2 pass)
Search window LR	0% for each isotope
Mass window	20%
Integration window LR	5% for each isotope

Reference Materials

SRM 897 to 899 Nickel Alloy (from National Institute of Standards and Technology (NIST)).

SRM 361 to 364 Low Alloy Steel (from National Institute of Standards and Technology (NIST)).

SRM 2165 and 2166 Low Alloy Steel (from National Institute of Standards and Technology (NIST)).

SRM 1151a to 1154a Stainless Steel (from National Institute of Standards and Technology (NIST)).

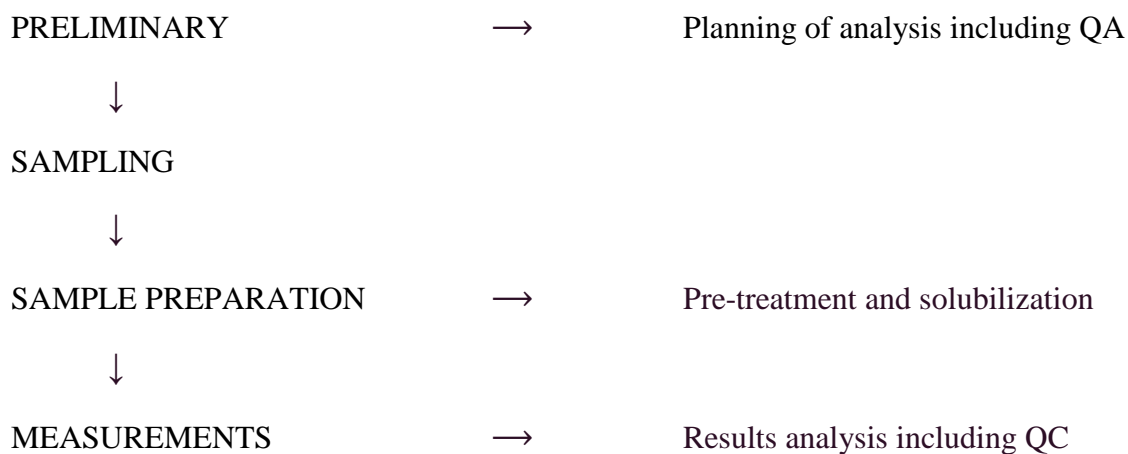
JSS 168-2 Carbon Steel (from the Japan Iron and Steel Federation (JISF)).

JSS 152-5 Alloy Steel (from the Japan Iron and Steel Federation (JISF)).

Detection Limit: 5 µg/kg (ppb).

3 DETERMINATION OF Pb IN PLASTICS

3.1 Analytical steps - from sampling to reporting



Quality assurance (QA) claims to assure the existence and effectiveness of procedures that attempt to make sure that expected levels of quality will be reached (Rauf & Hanan, 2009).

Quality control (QC) refers to procedures that lead to control different steps in measurement process (Rauf & Hanan, 2009). Accuracy and precision belong to QC. Accuracy is the measurement of how close an experimental value is to the true value. It is realized by use of control samples with known compositions, which are treated in the same way as the unknown samples. Nowadays, to demonstrate accuracy of the method, analysis of (standard, certified) reference materials (CRMs) is the most commonly used. Another way to confirm accuracy of the method of interest is to compare results with those obtained with well established (reference) methods (Intra-laboratory) or independent procedures by other laboratories (Inter-laboratory). Recovery studies by means of standard additions is also part of the accuracy estimation. Precision (reproducibility) is the degree to which further measurements or calculations show the same or similar results. It is expressed by means of relative standard deviation on the average of the series of measurements (RSD).

Pb in plastics can be measured in a liquid solution after solubilization of the sample (this is the most common way of analysis) or with non-destructive methods such as laser ablation ICPMS or XRF (X-ray Fluorescence) on homogeneous polymeric materials.

The Standard Operational Procedure (SOP).

The standard operational method for determining total lead in plastics is CPSC-CH-E1002-08.3

Although non-destructive methods are also mentioned in the SOP, solubilization of the polymer sample followed by spectrometric detection is the most common used method. These 2 steps will be discussed in detail.

Solubilization techniques

Solid samples can be solubilized in different ways but microwave-assisted (MW) digestion compared to the open vessel digestion has several advantages: shorter dissolution times, no contamination from the environment, smaller amounts of reagents, no loss of volatile elements. In the SOP, a microwave procedure is described with only nitric acid as digestion reagent. To 150 mg of plastic material five mL of nitric acid are added. The vessel is placed in a microwave oven up to 200 °C and after digestion the solution is cooled down and diluted to 50 mL.

The choice of a MW-assisted digestion is a very important step, because other digestion techniques often yielded poor results. Lehtimäki and Väisänen (2017) tested various digestion methods on polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC) and acrylonitrile butadiene styrene (ABS). They found good recoveries of Pb (97 to 11%) in certified reference materials (CRMs) adding either 10 mL of nitric acid or 7 mL of nitric acid and 3 mL of hydrogen peroxide to 150 mg of plastic material and digesting it at 220 °C in a microwave oven. The samples were further diluted to 50 mL.

In the Agilent application note from 2013, 200 mg of polypropylene (PP) and high-density polyethylene (HDPE) were digested with 5 mL of nitric acid and 2 mL of hydrogen peroxide in a microwave oven at 220 °C and afterwards diluted to 50 mL. Recoveries on CRMs were between 93 and 109%.

Ritter et al (2004) report the results of an intercalibration exercise on PVC and polyurethane (PU). The sample preparations produced their best recovery rates for Pb in PVC and PU when high-pressure incinerators or microwave digestions were used. The addition of hydrogen peroxide to the mineral acids was not mandatory. The results were independent of the subsequent analysis methods. The key step in obtaining an accurate result was the use of a suitable digestion method.

Measurement technique

The digested solution is measured, after appropriate dilution with Milli-Q water, with either Atomic Absorption Spectrometry (AAS), Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Induced Coupled Plasma Mass Spectrometry (ICP-MS). The ease of

analysis, the sample throughput, the interferences and the detection limits are, however, different between these 3 techniques.

Table 1: Evolution of Measuring Techniques for Pb.

Acronym	Dates	Method	LOD ppb = ng/g = µg/L
UV-Vis	1920-1960	Complexation with Dithizone	20-500 ppb
AAS	1960-1970	Flame Atomic Absorption Spectroscopy	20-50 ppb
GFAAS	1970-1985	Graphite Furnace Atomic Absorption	1 ppb
XRF		X-ray Fluorescence	0.9 mg/cm ²
ICP-AES	1980s	Inductively Coupled Plasma Atomic Emission	20 ppb
ICP-MS	1990s	Inductively Coupled Plasma Mass Spectroscopy	1-10 ppt

Since the ICP-MS method is the most sensitive and easy to measure Pb, we will only discuss this method in detail. Pb can be measured at different mass units but the most abundant are 206 (24.1%), 207 (22.1%) and 208 (52.4%). Polyatomic interferences (ions composed of 2 or 3 elements) are only coming from Pt and Ir oxides ($^{190}\text{Pt}^{16}\text{O}^+$, $^{191}\text{Ir}^{16}\text{O}^+$ and $^{192}\text{Pt}^{16}\text{O}^+$). Because these polyatomic interferences are extremely rare, the ICP-MS can be run in low resolution mode. To correct for instrumental fluctuations use is made of Bi as internal standard.

Detection Limit

The detection limit depends in the first place on the IDL (instrument detection limit) and the dilutions of the sample. The instrumental detection limit provided for Pb by Thermo for the Element II (HR-ICPMS) is 87 pg/L, obtained in their laboratory in Bremen. This value corresponds to the instrumental detection limit (IDL) reported in their application note 30003 (Determination of Trace Elements in Clinical Samples by HR-ICPMS on Element II), which equals 50 pg/L. Correcting the IDL for the dilution factor (50), a Method Detection Limit (MDL) of 2.5 ng/L is obtained. We also determined on our HR-ICPMS (Element II) the MDL for Pb is 6 ng/L. These values correspond thus to the range 1 to 10 ppt as mentioned in Table 1.

With a MDL of 5 ng/L and assuming that we solubilize 150 mg plastic in a 50 mL solution, the lowest concentration we can detect with the HR-ICPMS (Element II) is then 1.7 µg/kg (ppb).

Blanks are digest solutions without plastic sample that follow the same analysis procedure as the digest solutions with plastic sample.

Instrument settings

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min ⁻¹ (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min ⁻¹
Cool argon flow rate	16 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10 ⁶ cps per 1 ng mL ⁻¹ Bi (in Low Resolution)
Take-up time	15 s
Wash time	10 s
Number of acquisition	6 (3 runs and 2 pass)
Search window LR	0% for each isotope
Mass window	20%
Integration window LR	5% for each isotope

Reference Materials

ERM-EC680m and EC681m LDPE (from EC-JRC-IRMM, Geel, Be).

NMIJ-8102a ABS, acrylonitrile-butadiene-styrene ter polymer (from National Metrology Institute of Japan)

BAM-H010 ABS (from Bundesanstalt für Materialforschung und -prüfung (BAM))

NMIJ-8123a PVC (from National Metrology Institute of Japan)

SRM-2859 PVC (from National Institute of Standards and Technology (NIST))

NMIJ-8133a PP (from National Metrology Institute of Japan)

SQC1093 PP (from MERCK)

JSAC-0601-3 Polyester (from Japan Society for Analytical Chemistry)

The proposed digestion method is the same as in the SOP (CPSC-CH-E1002-08.3), but the measurement method is different because the lowest detection limit is obtained with a high resolution ICPMS.

3.2 Proposed Method:

Microwave Digestion Method.

1. Cut the test specimen into small pieces. Hard to digest plastics may need to be cryomilled to get finer powder. Weigh out 150 mg of the milled or cut plastic into an appropriate microwave vessel equipped with a controlled-pressure relief mechanism. Ensure that the milling apparatus is thoroughly clean between test specimens to avoid cross-contamination. Record actual weight to the nearest 0.1 mg.
2. At room temperature, add 5 ml of concentrated nitric acid to each vessel. Wait for completion of the initial reaction of the acid and the sample before sealing vessels. Seal vessels in accordance with manufacturer's directions.
3. The microwave method should involve increasing temperature of each sample to at least 200°C in approximately 20 minutes, and holding for 10 minutes.
4. Allow the samples to cool for a minimum of 5 minutes before removal from microwave. Vent the microwave vessels in a fume hood before uncapping.
5. Quantitatively transfer the sample to a 50 ml volumetric flask or disposable volumetric digestion cup. Dilute to 50 ml with deionized water (final sample).

Measurement method:

6. Pb is analyzed in 10 mL final sample (see point 5 hereabove), to which Bi (1 µg/L) is added, with HR-ICPMS at mass 208.
7. Perform calibration using calibration blank and at least three standards. Calibration shall be performed a minimum of once a day when used for analysis, or each time the instrument is set up. Results for each standard shall be within 5 percent of the true value, and the calibration blank should be < 5 times MDL. If the values do not fall within this range, recalibration is necessary. The operational blank signal should be subtracted from the sample signal before concentration calculations.
8. At least one certified reference material (CRM) should be analyzed with each batch of samples. The CRM should be similar material as test specimen with a known amount of Pb. Analyte recoveries should be within ±15 percent of expected values. If recoveries are outside this limit, the source of the problem should be identified and resolved before continuing analyses.
9. Dilute any samples that have Pb values exceeding 1.5 times the high calibration standard and reanalyze.
10. The settings of the HR-ICPMS are summarized below:

Instrument settings

Instrument	ELEMENT2 Thermo Finnigan
Forward power	1,350 W
Reflected power	< 2 W
Nebuliser	Concentric
Solution uptake rate	0.4 mL min ⁻¹ (pumped)
Spray chamber	Cyclonic
Sampling and skimmer cones	Ni (Thermo Finnigan)
Sample gas flow	1 to 1.5 L min ⁻¹
Cool argon flow rate	16 L min ⁻¹
Auxiliary argon flow rate	1.0 L min ⁻¹
Torch	Capacitive decoupling Pt shield torch
RF frequency	27.12 Mhz
Sensitivity	1 x 10 ⁶ cps per 1 ng mL ⁻¹ Bi (in Low Resolution)
Take-up time	15 s
Wash time	10 s
Number of acquisition	6 (3 runs and 2 pass)
Search window LR	0% for each isotope
Mass window	20%
Integration window LR	5% for each isotope

Reference Materials

ERM-EC680m and EC681m LDPE (from EC-JRC-IRMM, Geel, Be).

NMIJ-8102a ABS, acrylonitrile-butadiene-styrene ter polymer (from National Metrology Institute of Japan)

BAM-H010 ABS (from Bundesanstalt für Materialforschung und -prüfung (BAM))

NMIJ-8123a PVC (from National Metrology Institute of Japan)

SRM-2859 PVC (from National Institute of Standards and Technology (NIST))

NMIJ-8133a PP (from National Metrology Institute of Japan)

SQC1093 PP (from MERCK)

JSAC-0601-3 Polyester (from Japan Society for Analytical Chemistry)

Detection Limit: 1.7 µg/kg (ppb).

President

PROF. DR. WILLY BAEYENS

c / o

Federal Public Service Health, Food chain safety and Environment

Risk Management of Chemicals Unit

Victor Hortaplein 40 box 10
1060 Brussels