Federal Institute for Materials Research and Testing (BAM)

Federal Institute for Material Research and Testing

in Co-operation with the

International Commission on Glass
- Technical Committee 2 -

The Certification of mass fractions of hexavalent chromium and of total chromium in glass

BAM-S004

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Final certification report

Abstract

This report describes the work done to prepare and certify in co-operation with International Commission on Glass, Technical Committee 2 (ICG-TC2) the BAM reference material BAM-S004 with certified impurity contents in a glass for cosmetics. The certified mass fractions (expressed in mg/kg) are listed below.

ANALYTE	CERTIFIED VALUE	UNCERTAINTY [3]
Cr-hexavalent [1]	94	5
Cr-total [2]	471	25

[1] Mass fraction of hexavalent chromium in the glass, determined by using only one definite analytical procedure as described in the attached document.
[2] Mass fraction of total chromium in the glass, determined by different analytical methods after total wet digestion or after digestion by fusion of the analysed glass sample.
[3] The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) [1] with a coverage factor k = 2.

Informative values

Informative, but not certified values were determined by one of the participating laboratories.

Mass fractions in mass %.

Analyte	SiO_2	Na_2O	CaO	Al_2O_3	BaO	MgO	ZnO	SO_3	K_2O	Cr_2O_3	Fe_2O_3	CuO
Mass fraction	70.9	14.5	9.4	2.15	1.2	0.90	0.33	0.17	0.16	0.07	0.06	0.04

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1 Introduction

1.1 Scope

Enforcement of the Packaging Directive 62/94 [2] has required the development of reliable reference methods for the determination of heavy metals in glass. After considering Pb, Cd and Hg, International Commission on Glass, Technical Committee 2 (ICG TC2), has undertaken a collaborative study for the determination of hexavalent chromium, which is known to be a carcinogen. In this recommended procedure [3] the glass sample is digested with a mixture of sulphuric acid and ammonium hydrogen fluoride at room temperature, then diphenylcarbazide is added to form a violet complex, which is measured with a spectrophotometer.

It is well known, at least for those who are familiar with glass, that the chromium present in packaging containers is almost exclusively in the trivalent form. On the other hand there are containers used for special purposes, such as those produced for the perfumes industry, to which small amounts of hexavalent chromium are intentionally added to the batch in order to achieve a more intense coloration and thus to personalise the final product.

Hence, even though the majority of packaging is produced under reducing conditions, it was nonetheless thought advisable to develop an analytical procedure to measure any hexavalent chromium present in the final product.

The analytical procedure that was developed by the members of ICG TC2 will be applied in many analytical laboratories from different countries. The procedure is complex and may lead to incorrect results if, unwittingly, parameters are slightly changed. Therefore, it was absolutely necessary to establish a reliable tool for checking whether the procedure was applied correctly. A reference material with a certified mass fraction of hexavalent chromium according to the analytical procedure developed by ICG TC2 can act as such a reliable tool. The reference material BAM-S004 was developed by BAM in co-operation with ICG TC2 for this purpose. As a result of a preliminary test (feasibility study) an unacceptable spreading of the results of different laboratories was observed.

Therefore, the procedure [3] was slightly modified. The final interlaboratory comparison for the certification of hexavalent chromium was carried out on the basis of this modified procedure (see appendix 1).

In certain cases the mass fraction of total chromium in the glass is of interest, too. Hence the mass fraction of total chromium was also certified. In this case attention had to be paid to the fact that a diversity of different analytical methods was used by the participating laboratories.

1.2 Certification procedure

A batch of glass bottles for cosmetics was selected by preliminary investigations to be appropriate for the purpose. The distribution of chromium total mass fraction (as an indicator for distribution of hexavalent chromium mass fraction) was checked by a preliminary homogeneity test using 20 pieces of circular glass plates, which had been cut from two sides of the selected bottles of the batch. X-ray fluorescence spectroscopy was used for testing the homogeneity by comparing the results of measurements of the different plates. While the results for two plates coming from the same bottle were found to be correlated, results for plates coming from different bottles differed appreciably. Therefore, the bottles were broken into little pieces. The material was mechanically homogenised. A second step of homogenisation was carried out by hand in the step of filling the sample bottles, whereby a definite procedure of sample taking from the entire material was followed (see 4.2.2).

A second homogeneity test was carried out by using 20 selected sample bottles from the total amount of 290 sample bottles filled with the sample material, which amounted to 15 kg in total. Sample bottles were distributed to 18 laboratories experienced in glass analysis. Most of them were members of ICG TC2. 14 of the laboratories submitted results for the mass fraction of hexavalent chromium and 12 of the laboratories for the mass fraction of total chromium. Six independent measurements were each carried out by the laboratories for the determination of hexavalent chromium and for the determination of total chromium. The spread of the results for the determination of hexavalent chromium was very large.

Therefore, a revision of the procedure as described in [3] was carried out. As the result the procedure [3] was slightly changed (procedure see appendix 1) and a new interlaboratory comparison was started. 15 laboratories participated in this interlaboratory comparison. 13 of them delivered results for the mass fraction of hexavalent chromium according to the revised procedure. All in all results from 15 laboratories for the mass fraction of total chromium were received, some of them in respect of the first interlaboratory comparison and others in respect of the second one. All finally delivered results were trustworthy and could be summarised to the certified values of hexavalent and total chromium mass fractions, respectively. Four different methods were used for the determination of total chromium mass fraction, three of them using wet digestion and one using fusion digestion.

For the final certification, each laboratory carried out 6 independent determinations for the determination of hexavalent chromium, and in most cases also 6 (at least 3), independent determinations of total chromium.

2 Participating laboratories

2.1 Allocation and preparation of the material

- The material was allocated (not produced) by
  Institut Scientifique du Verre, Charleroi (Belgium)

- The glass plates for the first homogeneity test were prepared by
  Institut Scientifique du Verre, Charleroi (Belgium)

- The material was broken into pieces and homogeneized by
  ISOVER Saint-Gobain, CRIR, Rantigny (France)

- The material was filled into sample bottles (following a specific procedure to increase homogeneity of the material) by
  Bundesanstalt für Materialforschung und –prüfung, Division I.1, Berlin (Germany)

2.2 Homogeneity testing

- Preliminary and final homogeneity testing of total chromium mass fraction was carried out by
  Bundesanstalt für Materialforschung und –prüfung, Division I.1, Berlin (Germany)
- Orientating homogeneity testing of hexavalent chromium mass fraction was carried out by Statione Sperimentale del Vetro Murano-Venice (Italy)

2.3 Certification analysis

- The participants of the Interlaboratory comparison for certification are listed alphabetically

Bergakademie Freiberg – Institut für Silikattechnik, Freiberg (Germany)
Bormioli Luigi spa, Parma (Italy)
Bundesanstalt für Materialforschung und –prüfung, Berlin (Germany)
Laboratory: Preparation of Proficiency Testing Samples and Reference Materials for Inorganic Soil and Water Analysis
Laboratory: Trace Element Analysis; Spectral Analysis
Corning Europe Inc., Avon (France)
Forschungsinstitut für anorganische Werkstoffe, Höhr-Grenzhausen (Germany)
Glasforskninginstitutet (GLAFO), Växjö (Sweden)
Glass Institute, Hradec Králové (Czech Republic)
Institut Scientifique du Verre, Charleroi (Belgium)

ISOVER Saint-Gobain, CRIR, Rantigny (France)
Pilkington European Technical Centre, Lathom, Lancashire (Great Britain)
Saint-Gobain Glass Germany, Herzogenrath (Germany)
Schott Glaswerke, Mainz (Germany)
Stazione Sperimentale del Vetro, Murano-Venice (Italy)
Turkiye Şişe ve Cam Fabrikalari A.Ş. Glass Research Center, Istanbul (Turkey)

2.4 Determination of informative values

The determination of mass fractions of 12 oxides of not certified elements was carried out by: Stazione Sperimentale del Vetro, Murano-Venice (Italy)

3 Abbreviations used

Final determination after total wet chemical digestion (1) or after digestion by fusion (2)

ET AAS	Atomic absorption spectrometry with electrothermal atomisation (1)
F AAS	Flame atomic absorption spectrometry (1)
ICP OES	Inductively coupled plasma optical emission spectrometry (1)
XRF	X-ray fluorescence spectrometry (2)

4 Preparation and homogeneity of the material

4.1 Starting material

The starting material for the CRM consisted of 84 bottles for cosmetics (each of them about 120 g in weight), produced from a special container glass. According to the producer all bottles were produced under the same melting conditions and from one starting material. They are regularly produced within a short period or time thus providing a sufficient homogeneity of the material.

The material of the containers is a high quality perfumery glass. This is the reason for the additional BaO content, which is used for increasing the refractive index. The producing company is a medium-sized French glass factory with a specialization in unusual colors and forms. The coloration method is the "feeder coloration" (introduction of a strongly colored and very fusible glass at the end of the process). The containers are used as perfumery bottles of a leading French company.

After a preliminary homogeneity check, the bottles were broken into pieces < 10 mm in size.

4.2 Homogeneity tests, sample preparation and homogenisation

4.2.1 Preliminary homogeneity investigation (Cr total)

In the beginning it was necessary to decide, whether the CRM samples could be delivered in the form of the unbroken bottles. This would have been possible in the case of a uniform distribution of the analytes (Cr and CrVI contents) in the entire number of bottles. If this grade of homogeneity could not be observed, it would be necessary to crush the bottles and to homogenize the crushed material.
To get an impression of the homogeneity of the distribution of total chromium in the bottle material a first (preliminary) homogeneity test was carried out by XRF using 40 pieces (20 pairs from 20 bottles) of circular glass plates, Ø appr. 40 mm, thickness 1 – 3 mm. The bottles had been delivered from the supplier in 4 packages. From each package 5 bottles

had been randomly selected for preliminary homogeneity test. From each bottle were taken two samples in the form of plates. Each pair of plates was taken from the almost flat sides of the same bottle of the starting material. The disks had been lapped with a diamond tool and finally polished with cerium oxide.
The preliminary homogeneity test and its results are documented in appendix 2.
The strong maximum variation of the total chromium mass fraction between the different pairs of glass plates can be concluded from Fig. 1 of appendix 2 ($\pm$ 2,5 % rel.). The results of Cr-concentration seem to be correlated in the four different packages. The maximum variation between two plates deriving from the same cosmetic bottle was much less (about 0,7 %rel.) and the maximum difference of the mass fractions of total chromium of different areas of one plate was very small, see fig. 2 of appendix 2 (about 0,5 % rel.).

The hexavalent chromium in the material of the bottles was assumed to be similarly distributed as the total chromium, because all cosmetic bottles had been produced with the same melting conditions.

4.2.2 Sample preparation and homogenisation

It was concluded that it was necessary to break the cosmetic bottles into pieces small enough that they did not vary essentially in chromium content. From the result of the preliminary homogeneity testing, it was determined to use grain size < 10 mm (down to the powdered fraction). For this purpose a jaw crusher was used, the walls of which were covered by tungsten carbide. As a first step the crusher was cleaned by filling it with 1 kg of the cosmetic glass bottles and applying an extensive crushing procedure. This part of crushed glass was discarded. The other part of the glass (approx. 15 kg) was put into the jaw crusher for 30 sec. The broken pieces were collected in two clean plastic containers, which were closed with a plastic cover and shaken by hand for 15 min. Then half of the material from each of the plastic containers was transferred to the other one. After this each of them was shaken by hand once more for 15 min. For transportation the crushed and homogenised glass material was filled into two clean plastic containers.

Under clean air conditions the contents of each of the containers was poured into a plastic basin and uniformly distributed. Using plastic tweezers all grains with linear dimensions $\geq$ 10 mm (about 1 % of entire sample mass) were separated from the sample batch. The remaining sample material was filled into 290 bottles, each of them containing 50 g of glass material. The small powdered part of the sample, which had been produced by the crushing process, was not removed from the entire sample. During this bottling procedure, the aim was to fill each bottle with representative amounts of sample from different parts of the volume and also a representative grain size spectrum of the starting sample.

4.2.3 Final homogeneity testing (used for Cr total and CrVI)

All bottles were produced under the same redox conditions in the melting procedure. Therefore, it is safe to say that the ratio of CrIII/CrVI content in the glass is the same in each bottle and in each part of the bottle material. As a result we carried out the homogeneity testing for total chromium content only, but applied the results to the chromium content as well as to the content of hexavalent chromium. This test is described in the following.
To carry out the homogeneity test for total chromium in the bottles (see appendix 3) 20 bottles were taken representatively by a combination of random access and systematic selection. From each of the 20 bottles, 4 sub-samples (5 g each) were taken from 4 different parts of their volume. The sub-samples were milled in a planetary ball mill (agate material). From each milled sample 1 g was taken for the preparation of the fused sample.

For comparison a thoroughly homogenized sample was produced. For this purpose a 50 g sample (No. 203) was milled and 27 g of this material were highly homogenized in the “Mixer / Mill” (Spex Ind., USA).

The measurement of the chromium mass fraction was carried out by XRF using a Siemens SRS 303 sequential spectrometer.

The homogeneity test was carried out using fused samples (pellets with a diameter of 26 mm and a thickness of about 4 mm). These pellets were prepared by fusion (propene/air burner) of a mixture of about 1 g glass sample (< 200 μm) with about 6 g Spectromelt A10 (Merck) and about 0.05 g Na-Iodide (Merck) in a crucible (Pt-Au). The fusion procedure lasted about 10 min. The fused pellet was used for X-ray measurement with the top surface, i.e. the surface that had not been in contact with the bottom of the crucible, directed towards the X-ray source.

A homogeneity test (F-test) was made comparing variances “between the samples”. This homogeneity test is an ANOVA, in which different variances resulting from one plot of measurements (20 x 4) were compared. It indicates a “weak” significant inhomogeneity. One can conclude that the Cr-contents ‘between the bottles’ differ significantly, but only slightly more, than ‘within the bottles’.
The second homogeneity test (F-test) was made comparing the mean variance “within the samples” (bottles) and the variance of the thoroughly homogenised sample. This homogeneity results in a comparison of two series of independent measurements (20 x 4 and 1 10). This homogeneity test “within the samples” did not indicate a significant inhomogeneity. One can conclude, that the Cr-contents within the bottles do not differ significantly more than for the thoroughly homogenised sample. All relevant RSD-values are only about 1 % rel. From this one can conclude that any undetected inhomogeneities could not be greater than about 1 % rel. Thus a rather high degree of homogeneity of Cr-contents was detected for the investigated material, as long as the proposed sub-sampling procedure was applied. The contribution of the detected inhomogeneity between the bottles to the total uncertainty was, of course, included in the calculation of the final certified value (see 8).

4.2.4 Orientating homogeneity testing of hexavalent chromium mass fraction

To confirm the positive results of the homogeneity test as described in 4.2.3 for the total chromium mass fraction, a shortened homogeneity test was carried out for the mass fraction of hexavalent chromium following the procedure of ICG-TC2 (see appendix 1). It was not possible to carry out the homogeneity test to the same extent as for total chromium for two reasons:

- the determination of hexavalent chromium in 20 x 4 = 80 samples would demand too much time. The drift of the results would obscure possible inhomogeneities.

- the precision of the method is not high enough to indicate low but relevant inhomogeneities.

But, as explained in 4.2.3, the homogeneity test for total chromium content was used to assess indirectly the homogeneity of hexavalent chromium. Therefore, the direct homogeneity test for hexavalent chromium was used only to confirm roughly the results of the homogeneity test described in 4.2.3. Therefore, a shortened homogeneity test with 6 x 2 sub-samples was carried out. For this test, 6 bottles were filled from different representative volumes of the entire sample before the final bottling of the material was carried out. The hexavalent chromium content was determined in 2 sub-samples from each of the 6 bottles following the revised procedure of ICG-TC2 (see appendix 1). The homogeneity test was made by comparing the variances of the result “between” and “within” the 6 bottles. No significant difference was found between the spreading of the results between and within the bottles and the results lie rather close together (compare appendix 4).

Thus the general positive tenor of the homogeneity assessment for total chromium could be supported by this investigation.

5 Time stability of the material

The total chromium content is not apt to change with time, as long as the material is not debased by contamination. It is widely assumed that the chemical composition of glass is stable over long-term periods [5,6]. Repeated analyses carried out by INAA in 1997 and 1998 within the frame of the certification of BCR CRM 664 showed that the variation of Cr mass fraction and that of other trace elements was essentially negligible over one year (6.54 mg/kg in 1997 vs 6.59 mg/kg in 1998 and within the analytical uncertainty of 0.22 mg/kg) [7].
Also the hexavalent chromium content in the bulk material cannot be changed because of the chemically inert position of the molecules in the material. The concentration of total/hexavalent chromium and the ratio CrIII/CrVI is “frozen” in the glass structure and not subject to changes due to oxidation/reduction phenomena that may occur under normal storing conditions. Possible absorption of moisture from a coarse glass due to weathering can be estimated to be so low that the date of expiry of certification is set to ten years under the storing conditions in BAM (normal humidity conditions). Moreover, it is considered that this glass contains a high amount of alumina that makes it hydrolytically stable and strongly prevents water adsorption. The relatively high surface area of the powdered fraction does not essentially increase the risk for water adsorption. A proper storage under dry environment is nevertheless highly recommended (see 9.3).

6 Analytical methods

6.1 Analytical methods used for certification

This chapter describes the analytical procedures and specific parameters used in the certification campaigns. The methods used for homogeneity testing were described above (see 4.).

6.1.1 Determination of mass fraction of hexavalent chromium

All 13 laboratories that participated in the final interlaboratory comparison for the certification followed the revised procedure (see appendix 1) to determine the hexavalent chromium mass fraction. This procedure is well defined, but for practical reasons the sub-sample mass and the sample aliquots can vary within a certain range. Table 1 (upper part) includes a list of the values of these parameters used by the 13 laboratories that participated in the interlaboratory comparison for determination of hexavalent chromium. The sub-sample masses vary between 0,2 g and 0,61 g, and the sample aliquots between 50 ml and 90 ml. Important for achieving good results are the pH values of the decomposition mixture and of the measuring solution, as demonstrated by results of preliminary investigations in ICG-TC2. In Table 1 (lower part) the measured pH values that were delivered by the majority of participants are listed.

The pH values in the decomposition mixtures vary between 2.4 and 3.6 and most of the values are between 2.7 and 3.4. This is in good agreement with experience for getting trustworthy results. The same holds true for the pH values of the measuring solutions, which are between 0.66 and 1.3, with most of them between 0.8 an 1.3.

Table 1: Determination of hexavalent chromium - parameters of the procedure

Summary of sub-sample mass, sample aliquot, and pH values

sub-sample mass [g] / sample aliquot [ml]

Lab.code no.	sub-sample number											
	1	2	3	4	5	6	1	2	3	4	5	6
1a	0.3064	0.3025	0.3035	0.3154	0.3935	0.3004	70	70	70	70	70	70
1b	0.5005	0.5032	0.5045	0.5036	0.5042	0.5005	50	50	50	50	50	50
2	0.4755	0.4622	0.4583	0.4582	0.4561	0.4796	50	50	50	50	50	50
3	0.5006	0.5006	0.5006	0.4999	0.5011	0.5018	50	50	50	50	50	50
4	0.2000	0.2000	0.2000	0.5000	0.5000	0.5000	50	50	50	50	50	50
8	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000	50	50	50	50	50	50
9	0.2500	0.2500	0.5000	0.5000	0.5000	0.5000	90	90	50	50	25	25
10	0.4880	0.5037	0.4974	0.4973	0.5068	0.488	50	50	50	50	50	50
11	0.5000	0.5000	0.5000	0.5082	0.5025	0.5070	50	50	50	50	50	50
12	0.2500	0.2500	0.2500	0.2500	0.2500	0.2500	90	90	90	90	90	90
13	0.3426	0.3631	0.3774	0.3805	0.3944	0.3844	90	90	90	90	90	90
16	0.6089	0.5025	0.5489	0.5881	0.4499	0.5353	25	50	50	50	50	50
17	0.5000	0.5000	0.5000	0.2500	0.2500	0.2500	50	50	50	90	90	90

pH of decomposition mixture / pH of sample measuring solution

Lab.code no.	sub-sample number											
	1	2	3	4	5	6	1	2	3	4	5	6
1a	3.4	3.4	3.4	3.4	3.4	3.4	1.3	1.3	1.3	1.3	1.3	1.3
1b	3.4	3.4	3.4	3.4	3.4	3.4	1.3	1.3	1.3	1.3	1.3	1.3
2	3.29	3.29	3.29	3.29	3.29	3.29	1.09	0.74	0.96	0.66	0.69	1.13
3	3.1	3.1	3.1	3.1	3.1	3.1	1.3	1.3	1.3	1.3	1.35	1.35
4	2.4						1.3					
8	3.4	3.4	3.4	3.35	3.35	3.35	1.3	1.25	1.3	1.25	1.25	1.2
9	2.74	2.74	2.74	2.7	2.7	2.7	0.96	1.05	1.1	1.17	1.1	1.1
10	3.1	3.1	3.1	3.1	3.1	3.1	1.05	0.98	0.99	1.01	0.99	0.99
11	2.9	2.9	2.9	3.45	3.45	3.45				1.2	1.2	1.2
12	2.9	--	--	--	--	--	1.05	--	--	--	--	--
13	--	--	--	--	--	--	--	--	--	--	--	--
16	--	--	--	--	--	--	1.2	1.2	1.2	1.2	1.2	1.2
17	3.6	3.6	3.6	3.3	3.3	3.3	0.8	0.8	0.8	0.8	0.8	0.8

6.1.2 Determination of total chromium mass fraction

14 of 15 laboratories that participated in the interlaboratory comparison for the determination of total chromium used wet chemical digestion of the samples (see Table 2). The mass of the sub-samples varied between 0.1 g and 1.0 g. Different mixtures of acids were used, mostly a mixture of HF and HNO_3. Most laboratories did not remove the matrix by evaporation. All digestion procedures seem to be suitable for the purpose. 7 participants used matrix matching for calibration, and many of them used more than 2 calibration points. A problem is that not all laboratories followed the rule for metrological traceability of the calibration solutions. The rule demands that either solutions prepared by the participant from pure elements or compounds should be used. Or, in case of using commercially available solutions, they had to be validated by comparison with a solution prepared by weighing pure substances as mentioned above or by comparison with solutions from another commercial producer. Solutions from NIST or traceable to NIST or certified by other National Measurement Institutes or traceable to those solutions were accepted. Three laboratories in table 2 do not fulfil even these “weak” rules. However, all results of the interlaboratory comparison were accepted, because the results of the three laboratories agreed well with the nine “metrologically correct” values. One laboratory used a digestion method by fusion combined with a highly sophisticated calibration and XRF as the method of final determination. 9 laboratories used ICP OES, 4 laboratories FAAS and 1 laboratory used ET AAS for final determination.

6.2 Methods used for homogeneity testing

Homogeneity testing is described in 4.2. Details and results are listed in Appendix 2. XRF was used in combination with different preparation techniques in most cases. An orientating study (see appendix 1) was carried out using the revised procedure for the determination of hexavalent chromium in glass (see appendix 4).

Table 2 Determination of total chromium - parameters of the procedure used by participants

Lab-code	Sample preparation (M = mass of sub-samples)	Calibration	Final determination (see 3.)
1	M: 0.3 g; sample digestion with HF/HNO_3, final sample solution – 5% HCl	BDH Spectrosol 1000 mg/l compared with Fisher Chemicals 1000 mg/l Calibration solution 0.5-1.0-2.5 mg/l were prepared at the date of sample measurement.	F AAS
2	M: 0.25-0.46 g; Digestion in a PTFE beaker with 40 ml from a mixture of (43 g NH_4HF_2 + 80 ml H_2SO_4 (1:1) + 350 ml H_2O) → 15 min stirring and addition 3 g H_3BO_3 and stirring for 10 min. Diluting with 0,1 M H_2SO_4 up to 80 ml and stirring again for 5 min. Digestion of the membrane filter with HNO_3 (under pressure)	High purity $K_2Cr_2O_7$/ASMW compared with ICP-Standard (Merck CertiPUR) Calibration solutions 3-6-9-12 µg/l, matrix matching; control analyses: method of standard addition	ET AAS
3	M: 1.0 g; Digestion with 25 ml HF/2 ml HNO_3, final sample solution 10 ml HNO_3, 8 mol/l → 50 ml	Alfa Product Cr-standard solution 1000 mg/l Calibration solution 1-5-10 mg/l, matrix matching	ICP OES
4	M: 0.5 g; sample digestion with HF/HNO_3, in a platinum crucible on a hot plate until evaporation (2 times) then dissolution of the residue in 5% HCl	Merck standard solution 1,000 g/l Cr compared with 2 home made standard solutions Calibration solution 0-0.50-1.00-2.00-4.00-8.00 mg/l, matrix matching with aliquot of solution (Na+Ca+Al)	F AAS
7	M: 0.5 g Decomposition with HF/HNO_3/$HClO_4$ in carbon-crucible	standard solution 1.000 g/l Cr Calibration solution 4 mg/l Cr_2O_3, matrix matching	ICP OES
8	M: 0.25 g; Digestion with HF/ HNO_3, final sample solution in H_2O/HNO_3, sub-samples 1-3 to 50ml final volume; sub-samples 4-6 to 100 ml final volume	Certified standard stock solution: SPEX CERTIPREP (1000 mg/L) Calibration solution 0-2-4 mg/l (50 ml flask) and 0-1-2 mg/l(100 ml flask), only HNO_3 matching	ICP OES
9	M: 0.5 g; Digestion with HF/ HNO_3 on a sand bath 2 times until dryness; dissolve in 1N HCl → 100 ml flask	$K_2Cr_2O_7$ salt from Merck → 300 mg/l Cr in H_2O (dry weighting) compared with commercial-Standard Merck 1000 mg/l; Calibration solution 0.25-0.50-1-2-3 mg/L	F AAS
10	M: 0.3 g Decomposition with HF/HNO_3/$HClO_4$ acid and evaporated to dryness. the residue is dissolved in HCl and diluted with H_2O (0,3g/100 ml)	NIST SRM 31120 (1003±5) mg/l Cr compared with solution from a different supplier; External calibration, solution 0-0.5-1.0-1.5-2 mg/L were prepared freshly on two different days.	ICP OES

Lab-code	Sample preparation (M = mass of sub-samples)	Calibration	Final determination (see 3.)
11	M: 0.1 g; Decomposition with HF-HNO_3 by micro wave digestion	$K_2Cr_2O_7$; 1 ml = 15 µg Cr calibration solution 2 mg/L, matrix matching	ICP OES
12	M: 1.0 g; Digestion with 10 ml HF/ 5 ml HNO_3 until dryness; dissolve in 5 ml HNO_3 → 100 ml flask	Chemlab commercial solution compared with Baker commercial solution standard addition method (0-1-2-3 mg/L Cr)	ICP OES
14	M: 0.20 g; addition from 10 ml HF, decomposition with pressure digestion system (Paar) 12h at 200°C	Merck standard solution Calibration solution 0-0.5-1.0 mg/l Cr	ICP OES
15	M: 0.1 g; Digestion with 10 ml HF/ 5 drops HNO_3; taken up with 2 ml HNO_3 → 100 ml flask	Merck standard solution 1000 mg/l Cr I. Calibration solution 0-1-3-6-10 mg/l Cr II. Calibration solution 0-3-6-10-50 mg/l Cr	ICP OES
17	M: ; Digestion in open Pt-dish with HF and HNO_3 and diluted into 100 ml	1000 mg/L Accu Trace and 1000 mg/l Merck, checked with in-house glass standard diluted to 1, 3 and 5 mg/l on day of measurements	F AAS
18	M: 0.2 g; Digestion in a PTFE beaker with 40 ml from a mixture (43 g NH_4HF_2 + 80 ml H_2SO_4 (1:1) + 350 ml H_2O) → 15 min stirring and addition 3 g H_3BO_3 and stirring for 10 min. Diluting with 0.1 M H_2SO_4 up to 80 ml and stirring again for 5 min. The solution was transferred to a 100 ml flask, and diluted to volume.	Merck standard solution (1000 ± 5) mg/l Cr matrix matching Calibration solution 0-2-4-6 mg/l, matrix matching	ICP OES
20	M: 1.0 g; fusion with 6 g ($Li_2B_4O_7$ + 0.07% Br) for 25 min in a Claise Fluxer	Johnson Matthey Cr_2O_3 specpure Matrix matching with Na_2CO_3 + $CaCO_3$ + $BaCO_3$+ SiO_2 Calibration: 410-430-450-470 mg/kg; reconstitution analysis	XRF

6.3 Method used for the determination of informative values

XRF method was used by one of the partners to determine main and minor components of the CRM. The mass fractions of oxides of 12 elements are not certified but they can be used for common information for the user.

7 Results and discussion

7.1 Presentation of the data

As soon as all the results of the certification analyses had been submitted, they were summarised and checked by a statistical programme of BCR for evaluation of results of interlaboratory comparisons for certification [4]. After this the data were technically discussed at two meetings of ICG-TC2 where most participating laboratories were represented. Three sets of data for the determination of hexavalent chromium were rejected, because the participants had not followed the revised procedure (as in appendix 1); they had used the original unrevised procedure [3] instead.

The accepted results are listed in Table 3 (for hexavalent chromium) and in table 4 (for total chromium) which contain

- upper part: current laboratory number ("L"); laboratory code number in this interlaboratory comparison (in case of total chromium combined together with the abbreviation of the analytical method used); laboratory mean values and standard deviations of laboratory single values; half width of confidence intervals of the laboratory mean values, all single values from different sub-samples;
- center part: range of all single values; in case of no pooling of all single values: mean of laboratory means, half width of 95% confidence interval and half width of 95% tolerance interval; in case of pooling of all single values (but statistically not allowed in current case): mean of all single values and half width of 95% confidence interval and half width of 95% tolerance interval.
- lower part: based on the specifications of the upper and center parts of the table - a diagram showing the mean of all data sets (vertical line) and the mean of each data set with its 95% confidence interval (horizontal bars) arranged by increasing mean values. These bars are marked by abbreviations of four statistical tests, if results of one or more tests were positive at a level of 5% or even 1%.

7.2 Technical discussion

Certification is justified when the agreement between various laboratories (and in the case of total chromium also between various techniques based on different principles of measurement) indicates that there are no significant differences.

The calculation of the final certified value and its combined uncertainty including contributions from the inhomogeneity of the samples is discussed in chapter 8.

7.2.1 Hexavalent chromium

The certified parameter is dependent on one prescribed procedure of determination (appendix 1). Therefore a variety of different methods - as otherwise commonly used - cannot be claimed. It was concluded from the results of Snedecor F-Test and of Bartlett test that the aggregation of all single values from different sets to one basic population ("pooling") was not allowed.

Only the lowest value was indicated as being suspect by statistical tests (Dixon test and Nalimov t-test), but only at a level of confidence of 5%. The delivering laboratory saw no reason to draw back their value, because they had strictly followed the procedure as described in appendix 1. When additionally a multiple Grubbs test (in the form of a pair test) is used, the results of both laboratories that delivered the lowest values are indicated as being outliers at a level of confidence of 1%. However, both the laboratory with the lowest delivered results and the other laboratory had strictly followed the procedure described in appendix 1. Therefore, the results of both laboratories were not excluded from evaluation, the more so because all mean values were within the 95% tolerance interval. Therefore

participants of ICG-TC2 at their final discussion decided to accept the whole set of data as the state of the art and not to reject any set of data. This was also done in view of the complexity of the prescribed analytical method. The calculation of the final certified value and its combined uncertainty including contributions from inhomogeneity of the samples is discussed in chapter 8.

Table 3 : Hexavalent chromium in CRM BAM-S004 (values in mg/kg)

Current Lab. number	Laboratory code number	Mean	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4	79,150	2,130	2,235	79,300	81,300	76,700	81,600	79,300	76,700
L 2	3	82,000	1,673	1,756	82,000	82,000	84,000	79,000	82,000	83,000
L 3	17	89,658	3,438	3,608	92,130	93,720	87,100	92,000	85,000	88,000
L 4	2	91,708	4,259	4,469	95,450	95,780	94,510	89,280	90,150	85,080
L 5	11	93,933	1,764	1,851	94,400	94,200	92,000	96,700	94,300	92,000
L 6	16	95,218	1,822	1,912	98,540	94,130	95,470	95,520	94,240	93,410
L 7	12	97,383	1,465	1,537	100,100	96,000	97,500	96,300	96,900	97,500
L 8	9	98,000	4,195	4,403	98,000	103,000	93,000	101,000	100,000	93,000
L 9	1a	98,328	1,413	1,483	98,990	96,750	100,520	98,970	97,310	97,430
L 10	10	98,333	2,733	2,868	96,000	96,000	100,000	97,000	98,000	103,000
L 11	1b	98,427	1,255	1,317	100,190	99,650	96,940	98,090	97,480	98,210
L 12	13	98,640	2,360	2,477	98,510	97,770	97,050	97,240	97,930	103,340
L 13	8	99,093	1,408	1,477	96,940	98,350	101,180	99,050	99,520	99,520

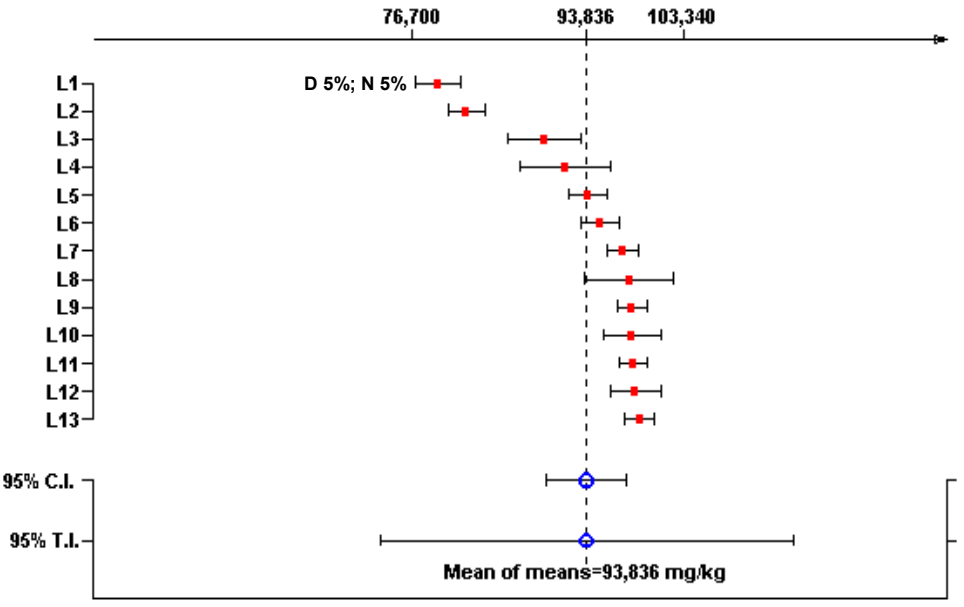
Range [min..max]	[76,700 .. 103,340]
	Case of No Pooling
Mean of means	93,836
95% H.W. Confidence Interval	3,985
95% H.W. Tolerance Interval	20,317
	Case of Pooling
Mean of All	93,836
95% H.W. Confidence Interval	1,529
95% H.W. Tolerance Interval	15,443

Outliers detected by different statistical tests at a = 1% or at a = 5% significance level.

Abbreviations: N = Nalimov t - test
G = Grubbs test (single test)
C = Cochran test
D = Dixon test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Table 3)



7.2.2 Total content of chromium

The certified parameter is not dependent on one prescribed procedure of determination. Therefore a variety of different methods - as commonly occurs - were reported. Certification is justified when the agreement between various laboratories and various techniques based on different principles of measurement indicates no significant differences. As described above (see 6.1.2) some different kinds of sample pre-treatment were used and four different methods for the final determination were applied by 15 participating laboratories.

It was concluded from the results of Snedecor F-Test and of Bartlett test that the aggregation of all single values from different sets to one basic population ("pooling") was not allowed.

5 of the 15 sets of values were indicated as being statistically conspicuous by Cochran test at 1% and 5% level of confidence. But all the intralaboratory RSDs were at sufficiently low levels (below 5% rel.). Thus the result of the Cochran test was ignored. The highest laboratory mean value was indicated as being statistically conspicuous by the Nalimov t-test, but only at a confidence level of 5%. All mean values were within the 95% tolerance interval. Therefore, it was also proposed that this value should not be rejected.

The participants of ICG-TC2 decided at their final discussion to assess the whole set of data as the state of the art and not to reject any set of data.

Table 4 : Total Chromium in CRM BAM-S004 (values in mg/kg)

Current Lab. number	Laboratory code number	Mean	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 F AAS	406,000	10,040	10,536	410,000	404,000	390,000	402,000	420,000	410,000
L 2	10 ICP OES	415,333	0, 577	1,434	416,000	415,000	415,000			
L 3	15 ICP OES	417,400	27,013	28,349	441,400	443,200	441,400	394,200	394,600	389,600
L 4	8 ICP OES	431,450	5,664	5,944	436,700	435,400	437,600	427,100	426,000	425,900
L 5	3 ICP OES	447,333	21,538	22,602	463,000	469,000	468,000	426,000	434,000	424,000
L 6	2 ET AAS	467,117	3,592	3,769	472,110	465,420	467,620	467,020	461,420	469,110
L 7	20 XRF	473,175	2,955	3,101	475,160	469,240	473,200	470,060	476,650	474,740
L 8	1 ET AAS	473,303	4,847	5,087	465,270	469,660	478,160	474,990	476,030	475,710
L 9	18 ICP OES	475,118	1,490	3,701	475,648	473,435	476,270			
L 10	12 ICP OES	480,833	4,167	4,373	480,000	481,000	488,000	480,000	475,000	481,000
L 11	7 ICP OES	489,667	3,055	7,589	487,000	489,000	493,000			
L 12	9 F AAS	499,833	25,151	26,394	506,000	501,000	490,000	456,000	519,000	527,000
L 13	11 ICP OES	510,000	3,950	4,145	513,000	514,000	504,000	508,000	513,000	508,000
L 14	17 F AAS	517,833	17,081	17,926	530,000	526,000	530,000	499,000	529,000	493,000
L 15	14 ICP OES	556,972	5,597	5,874	553,000	566,830	557,000	559,000	555,000	551,000

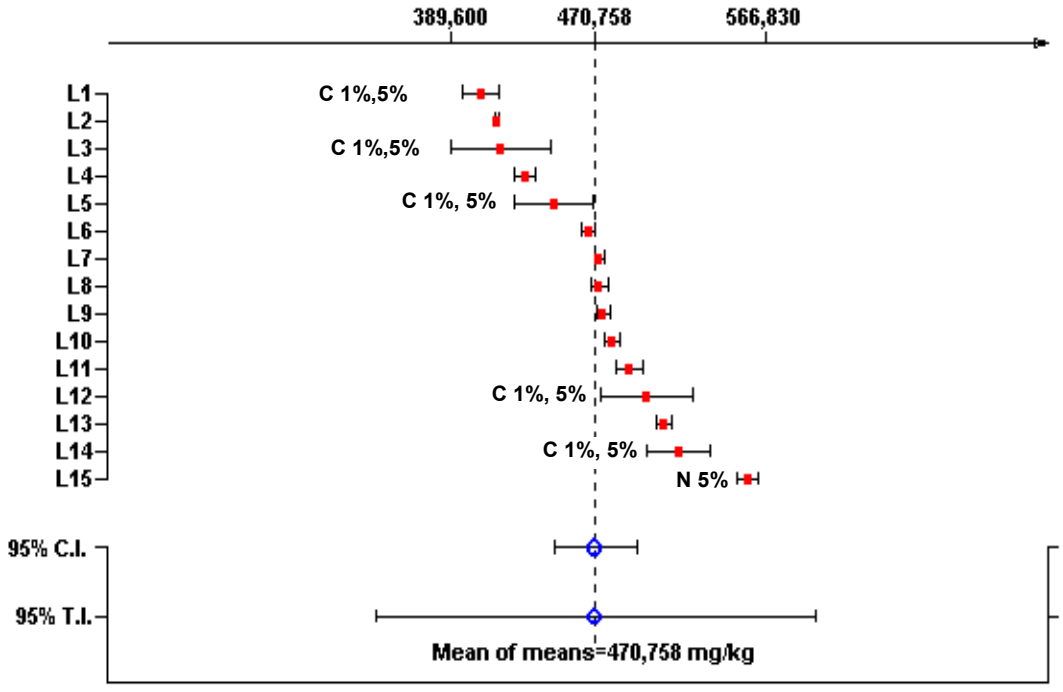
Range [min..max]	[389,600 .. 566,830]
	Case of No Pooling
Mean of means	470,758
95% H.W. Confidence Interval	23,282
95% H.W. Tolerance Interval	124,189
	Case of Pooling
Mean of All	471,949
95% H.W. Confidence Interval	9,569
95% H.W. Tolerance Interval	98,230

Outliers detected by different statistical tests at a = 1% or at a = 5% significance level.

Abbreviations: N = Nalimov t - test
G = Grubbs test (single test)
C = Cochran test
D = Dixon test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Table 4)



7.3 Summary of statistical evaluation

Data and results of the statistical evaluation of the interlaboratory comparison using the BCR program [4] are summarised in Table 5.

Table 5: Results of statistical evaluation

	Hexavalent Chromium	Total Chromium
Number of data sets	13	15
Number of replicate measurements	78	81
Mean of means (a)	93.836	470.751
St. Dev of means (a)	6.594	42.026
Outlying or straggling mean values		
▪ Dixon test	c	no
▪ Grubbs test (single test)	no	no
▪ Nalimov t-test	c	c
Differences between labs statistically significant?		
▪ Snedecor F-test	b, c	b, c
Outlying or straggling variances		
▪ Cochran test	no	b, c
Variances homogeneous		
▪ Bartlett test	b	no
St. Dev. within – laboratories (a)	6.514	42.394
St. Dev. between laboratories (a)	2.512	13.385
Half-width of the 95% confidence interval (a)	3.985	23.273

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

8 Calculation of certified values

8.1 Mass fractions

The certified values of mass fractions of hexavalent chromium and of total chromium were calculated as the mean values "M" of all accepted means from the participating laboratories of the interlaboratory comparison (see 7.2.1 and 7.2.2). The laboratory means are summarized in Table 6.

Table 6: Accepted mean values of interlaboratory comparison for certification [mg/kg]

Current Lab-number.	Cr-(VI)	Cr-total
1	79.1500	406.0000
2	82.0000	415.3333
3	89.6583	417.4000
4	91.7083	431.4500
5	93.9333	447.3333
6	95.2183	467.1167
7	97.3833	473.1750
8	98.0000	473.3033
9	98.3283	475.1177
10	98.3333	480.8333
11	98.4267	489.6667
12	98.6400	499.8333
13	99.0933	510.0000
14		517.8333
15		556.8683
M:	93.836410	470.750956
s_m:	6.594135	42.025863
s_i:	2.301071	9.114967

Additionally the table contains both mean values "M" of the laboratory means, which were used as certified mass fractions, and the standard deviations of the laboratory mean values "s_m".

8.2 Uncertainties

8.2.1 Total chromium

The combined uncertainty of the certified mass fraction was calculated according to

$$u_c = \left(s^2_m/n + s^2_{b,corr} \right)^{1/2} \qquad \text{where} \qquad s_{b,corr} = \left(s^2_b - s^2_{HS} \right)^{1/2} \quad ;$$

u_c = combined uncertainty of certified mass fraction,

s_m = standard deviation of the accepted laboratory mean values,

n = number of accepted laboratory mean values

$s^2_{b,corr}$ = corrected standard deviation in homogeneity testing "between the bottles"

s_b = standard deviation in homogeneity testing "between the bottles"

s_{HS} = standard deviation in homogeneity testing "homogeneous sample"

As a result the combined uncertainty is the square root of the sum of the squares of the standard deviation of the mean of the means in interlaboratory comparison and of the corrected standard deviation "between the samples" from homogeneity testing. This corrected standard deviation is the standard deviation between the samples without the contribution from the standard deviation of the method used in the homogeneity testing. A contribution from the inhomogeneity "within the samples" was not considered, because the homogeneity test did not result in a significant inhomogeneity.

The expanded uncertainty "U" (coverage factor 2) is calculated as

$$U = 2\, u_c$$

The resulting value is the uncertainty of the certified mass fraction of total chromium:

$$U\,(Cr_{tot}) = (24.549 \approx 25)\ [mg/kg]$$

8.2.2 Hexavalent chromium

An extensive homogeneity test (4.2.3) was only carried out for the mass fraction of total chromium, assuming that the distribution of total chromium and of hexavalent chromium is the same in the sample, i.e. the fraction of hexavalent chromium in the total chromium was assumed to be the same in each volume of the entire sample material. This assumption is based on the knowledge of the production of the starting material (see 4.1) and the results of an orientating homogeneity testing for hexavalent chromium (see 4.2.4).

In principle the formulas for the calculation of the uncertainty of the certified mass fraction of hexavalent chromium are the same as for the uncertainty of the certified mass fraction of total chromium. The only difference is that the following substitution has to be made:

$$s_{b,corr}(Cr_{hex}) = s_{b,corr}(Cr_{tot}) \bullet M_{hex}/M_{tot} ,$$

with "M" for the certified mass fractions (see above, Table 5) and the indices "hex" for hexavalent and "tot" for total chromium mass fraction.

Through this, the standard deviations in the homogeneity testing of the mass fraction of total chromium are transformed to the standard deviations of mass fractions of hexavalent chromium by applying a factor, which is the ratio of their certified mass fractions.

Applying this transformation in the formulas above (8.2.1) the expanded uncertainty of the certified mass fraction of hexavalent chromium was calculated:

$$U(Cr_{hex}) = (4.316 \approx 5) \text{ [mg/kg]} .$$

The rounding was made according to the prevailing rules.

8.3 Certified values

According to the previous chapters the certified values are summarised in Table 7.

Table 7: Certified mass fractions [mg/kg]

ANALYTE	CERTIFIED VALUE	UNCERTAINTY [3]
Cr-hexavalent [1]	94	5
Cr-total [2]	471	25

[1] Mass fraction of hexavalent chromium in the glass, determined by using only one definite analytical procedure as described in the attached document.
[2] Mass fraction of total chromium in the glass, determined by different analytical methods after total wet digestion or after digestion by fusion of the analysed glass sample.
[3] The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) [1] with a coverage factor k = 2.

8.4 Informative values

XRF method was used by one of the partners to determine the main and the minor components of the CRM material. Results are shown in Table 8. They are not certified, but meant for common information to the user.

Table 8: Informative values: mass fractions of main and minor elements expressed as mass fractions of their oxides [%]

analyte	SiO_2	Na_2O	CaO	Al_2O_3	BaO	MgO	ZnO	SO_3	K_2O	Cr_2O_3	Fe_2O_3	CuO
mass fraction	70.9	14.5	9.4	2.15	1.2	0.90	0.33	0.17	0.16	0.07	0.06	0.04

9 Instructions for use

9.1 Area of application

The main area of application is checking the trueness of results of the determination of hexavalent chromium in a laboratory according to the approved procedure developed in Technical Committee 2 of the International Commission on Glass (ICG-TC-2) in its revised form (see appendix 1).
The material can also be used for checking the trueness of the determination of the total chromium content in glass by different methods after wet chemical digestion of the material (methods of final determination e. g. ICP OES, AAS) or after digestion by fusion (main method of final determination is XRF).

9.2 Recommendations for correct sampling and sample preparation

For each determination, homogeneity testing of this material was carried out with masses of 1 g of sub-samples taken from different sample subsets of 5 g which had been ground. An increase in uncertainty intervals could result if the sample intake for an analytical determination is less than this. To ensure a representative sub-sampling for the analysis, shake the bottle containing the CRM in different directions before taking sample material for sub-sampling; at least 5 g of sample material must be taken from the bottle before grinding (< 200 µm) and thorough mixing has to be performed. Sub-samples should be taken from this ground material. Close lid of the sample bottle tightly after use.

9.3 Recommendations for correct storage

The sample should be stored in a dust-free and dry environment avoiding contamination and moisture.

9.4 Safety guidelines

1. First aid measures
   In case of contamination of the eyes by dust, rinse thoroughly with water with the eyelids held open. If product is swallowed, induce vomiting and consult a physician.
2. Handling
   Avoid formation and deposition of dust. Ensure adequate ventilation and, if necessary, exhaust ventilation when handling or transferring the product. To avoid injuries do not bring the material into contact with your skin.
3. Exposure restriction and personal protection
   Hand protection: protective gloves
   Eye protection: safety goggles
4. Disposal considerations
   Unused material: reuse if possible.
   Or: may be disposed of in controlled landfills provided local regulations are respected.

10 References

[1] Guide to the Expression of Uncertainty in measurement (1995)
International Organization for Standardization
ISBN 92-67-10188-9

[2] European Directive 94/62 on Packaging and Packaging waste,
OJ No L365, 31.12.94, 10-23

[3] E. Guadagnino, P. Sundberg, and O. Corumluoglu
A collaborative study on the determination of hexavalent chromium in container glasses
Glass Technol., **42** (2001) 148-152

[4] G. Bonas, M. Zervou, T. Papaeoannou and M. Lees
"SoftCRM": a new software for the Certification of Reference Materials
Accred Qual Assur, **8** (2003) 101-107

[5] H. Scholze
Glass-water interactions
J. Non. Crystal. Solid., **102** (1988) 1-10

[6] P. Chartier
La surface du verre: bases scientifiques pour la recherché industrielle
Verre, **3** (1997), 5-11

[7] Ph. Quevauviller and E. Guadagnino
The certification of the content (mass fraction) of antimony, arsenic, barium, cadmium, chloride, chromium, cobalt, lead and selenium in glass CRM 664
EUR 18852, BCR Information (1999), ISBN 92-828.5987-8

11 Appendices

11.1 CERTIFICATION OF THE CONTENT OF HEXAVALENT CHROMIUM IN GLASS
Analytical Protocol/Revised Version (June 2002)

11.2 Preliminary homogeneity test investigation of distribution of chromium and of barium in unbroken candidate glass samples by XRF spectrometric determination

11.3 (BAM-S004): Homogeneity Testing

11.4 (BAM-S004): Orientating Homogeneity Testing of Hexavalent Chromium Mass Fraction

INTERNATIONAL COMMISSION ON GLASS
A SOCIETY OF SCIENTIFIC TECHNICAL ORGANISATIONS
TC2- Technical Committee 2 – Chemical Durability and Analysis

CERTIFICATION OF THE CONTENT OF HEXAVALENT CHROMIUM IN GLASS

ANALYTICAL PROTOCOL/REVISED VERSION

June 2002

1. COLLABORATIVE STUDY AND RESULTS

2. PRINCIPLE OF THE METHOD

The glass sample is digested with a mixture of sulphuric acid and ammonium hydrogen fluoride at room temperature. Diphenylcarbazide is added to form a violet complex with Cr^{6+} ions. The absorbance of the coloured complex is measured by molecular absorption spectrometry at 540 nm.

3. REAGENTS

Water complying with the requirements of Grade 2 water or better in ISO 3696 and reagents of recognized analytical grade shall be used throughout.
Dilutions, e.g. (1+1) refer to 1 volume of the concentrated reagent of the original solution being diluted by one volume of water.

3.1 Sulphuric acid, H_2SO_4, d = 1.84

3.1.1 Sulphuric acid, (1+1)

3.1.2 Sulphuric acid , 0.1M (5.6 ml of conc. H_2SO_4 (3.1) up to 1 liter)

3.2 Ammonium hydrogen fluoride, NH_4HF_2

3.3 Ethylenediaminotetracetic acid, disodium salt dihydrate (EDTA) 0.05M

Dissolve 18.612 g in deionized water and bring to volume in a 1 liter volumetric flask.

3.4 Decomposition mixture
Transfer into a plastic or PTFE beaker 43 g of ammonium hydrogen fluoride (3.2), 40 ml of diluted sulphuric acid (3.1.1) and 350 ml of water. Mix well and check pH be about 3 .

3.5 Stock decomposition mixture
200 ml of decomposition mixture (3.4) are transferred into a 500 ml plastic or PTFE beaker and stirred for 15 minutes. Add 15 g H_3BO_3 (3.8), 2.2 ml H_2SO_4 (3.1.1), dilute with water and stir the solution for a further 10 minutes. Filter through a Whatman No 40 filter paper into a 500 ml volumetric flask and dilute to volume with distilled water.

3.6 Acetone, CH_3COCH_3

3.7 Diphenylcarbazide (C_6H_5-NH-NH-CO-NH-NH-C_6H_5) solution 0.5% (w/v)
Dissolve 0.5 g in 100 ml of a mixture of water and acetone (3.6) (1+1)

3.8 Boric acid, H_3BO_3

3.9 Chromium stock solution
Dissolve 0.8487 g of potassium dichromate ($K_2Cr_2O_7$) with water and dilute to 1 liter on a volumetric flask.

1 ml of this solution = 300 µg Cr^{6+}

3.9.1 Diluted chromium standard solution
Take a 25 ml aliquot portion from the chromium stock solution (3.9) and dilute to 500 ml with deionized water in a volumetric flask.

1 ml of this solution = 15 µg Cr^{6+}

4. APPARATUS

Ordinary laboratory apparatus and usual laboratory glassware made of borosilicate 3.3 glass and complying with the requirements of relevant International Standards.
New containers (beakers, volumetric flasks, storing bottles) should be treated before use by filling to 90% of the overflow volume with hydrochloric acid (1+12) and heating for 2 hours at boiling point, for example using a heating bath.
The containers should be then rinsed with water, filled with water to 90% of the overflow volume and heated as above for 2 periods of 1 hour using fresh water each time.

4.1 Analytical balance, accurate to 0.1 mg or better.

4.2 Pipettes of suitable capacity complying with the requirements of class A in ISO 548.

4.3 Volumetric flasks of suitable capacity complying with the requirements of class A in ISO 1042.

4.4 Agate mortar and pestle

4.5 Magnetic stirrer

4.6 Magnetic bar

4.7 Beakers of polyethylene or PTFE of suitable capacity

4.8 Molecular absorption spectrometer (spectrophotometer)

4.9 Optical cell (normally with a path length of 10 mm; if appropriate, a cell with a path length of 50 mm can be used)

4.10 pH Meter

5. SAMPLE PREPARATION

Grind the sample in an agate mortar (4.4) to a particle size less than 100 μm and store in a desiccator or stoppered bottle.

6. PROCEDURE

6.1 Decomposition and sample measuring solutions

Transfer 0.2000 to 0.5000 g of the powdered glass into a 100 ml plastic or PTFE beaker (4.7), containing a small stirring bar (4.6).
Add 40 ml of the decomposition mixture (3.4), then digest the mixture at room temperature while stirring for 15 minutes. Add 3 g of boric acid (3.8) in order to complex the excess of fluoride ions and stir for about 10 minutes. Cool to room temperature, dilute with 0.1M H_2SO_4 (3.1.2) to about 80 ml and stir again for 5 minutes. Transfer the solution into a 100 ml volumetric flask, cool to room temperature, dilute to volume with deionized water and mix well.

Take a suitable aliquot (up to a maximum of 90 ml), add 5 ml EDTA (3.3) and 2 ml of diphenylcarbazide (3.7) solution then bring to volume with 0.1M H_2SO_4 (3.1.2) in a 100 ml volumetric flask (**sample measuring solution**). Take an aliquot with a plastic syringe, filter the liquid through a pre-washed (with 0.1M H_2SO_4, 3.1.2) cellulose acetate filter (< 0.45 μm) and discard the filtrate. Repeat this procedure twice, then filter the remaining solution, pouring the filtrate directly into a suitable optical cell (4.9) and measure the optical density at 540 nm using the spectrophotometer (see par. 6.3)

Take note of the dilution factor according to the aliquot taken.

Prepare a blank following the same procedure but omitting the sample.

6.2 Preparation of the calibration curve

Transfer by means of a suitable pipette (4.2) aliquots of 0, 1, 2, 3, 4 and 6 ml of the standard chromium solution (3.9.1) into separate flasks of 100 ml capacity. Add to each of the flasks an aliquot of the stock decomposition solution (3.5) equivalent to the sample volume taken. Add to each flask 5 ml EDTA (3.3) and 2 ml of diphenylcarbazide solution (3.7), then make to volume with 0.1M H_2SO_4 (3.1.2) and mix thoroughly.
Measure the optical density of the solutions against the blank in appropriate optical cells (4.9) at 540 nm using the spectrometer (4.8).

Note: If an optical cell with a path length of 50 mm instead of 10 mm is used, appropriate aliquots of the diluted chromium standard solution (3.9.1) should be taken (6 ml may give an absorbance beyond the linear calibration range)

To obtain the calibration graph, plot the observed optical density against the µg Cr^{6+} contained in each solution

N.B. : the calibration curve must be prepared freshly each time. Readings of samples and calibration standards must be taken within 15 min from the development of the coloration

6.3 Determination of hexavalent chromium and expression of the results

Measure the optical density of the sample measuring solution at 540 nm using the spectrometer with the blank as a reference.

Read the chromium content from the calibration graph and calculate the amount of hexavalent chromium in the glass from the following expression :

$$W_{Cr}^{6+} = \frac{C \times V}{A \times m}$$

where :

W_{Cr}^{6+} = Mass fraction of hexavalent chromium in the sample (µg/g = mg/kg)
C = Content (µg) of hexavalent chromium in the sample measuring solution
V = Volume (ml) of the sample decomposition solution (normally 100 ml)
m = Mass (g) of the sample
A = Volume (ml) of the aliquot taken from the sample decomposition solution

APPENDIX 2: Preliminary homogeneity investigation of distribution of chromium and of barium in unbroken candidate glass samples by XRF spectrometric determination

Initially, it was necessary to decide whether the CRM samples could be delivered in the form of the unbroken bottles. This would be possible in the case of a uniform distribution of the analytes (Cr and CrVI contents) in the entire number of bottles. If this grade of homogeneity could not be observed, it would be necessary to crush the bottles and to homogenise the crushed material.
To get an impression of the homogeneity of the distribution of total chromium in the bottle material a first (preliminary) homogeneity testing was carried out by XRF using 40 pieces (20 pairs from 20 bottles) of circular glass plates, Ø appr. 40 mm, thickness 1 – 3 mm. The bottles had been delivered from the supplier in 4 packages. From each package 5 bottles were randomly selected for the preliminary homogeneity test. From each bottle, two samples were taken in the form of plates. Each pair of plates was taken from the almost flat sides of the same bottle of the starting material. The disks were lapped with a diamond tool and finally polished with cerium oxide.
The preliminary homogeneity test and its results are documented in appendix 2.
The strong maximum variation of the total chromium mass fraction between the different pairs of glass plates can be concluded from Fig. 1 of appendix 2 ($\pm$ 2,5 % rel.). The results of Cr-concentration seem to be correlated in the four different packages. The maximum variation between two plates deriving from the same cosmetic bottle was much less (about 0,7 %rel.) and the maximum difference of the mass fractions of total chromium of different areas of one plate was very small, see fig. 2 of appendix 2 (about 0,5 % rel.).

The hexavalent chromium in the material of the bottles was assumed to be similarly distributed as the total chromium, because all cosmetic bottles had been produced on the same melting conditions.

Procedures carried out:

1) Scan over elemental range $92 \geq Z \geq 8$ (uranium-oxygen) of sample no. B15 in a sample-cup with 34mm ∅, C-aperture. By this it was shown that the CrKα line lies in the region of the L-spectrum of barium, which is clearly detectable in the sample. The Ba was measured with the $BaL\beta_2$ line near the CrKα line for studying and taking into consideration the influence of the possibly varying barium mass fraction on the CrKα intensity.

2) Calibration was carried out using brutto intensities by measuring an external glass standard sample. Iron, which has a similar excitation and absorption behaviour to chromium, was used for semi-quantitative determination of chromium mass fraction, because the chromium mass fraction was not certified in this standard sample. From this a chromium mass fraction of approx. 300 mg/kg was estimated in the sample no. B15, which had been selected arbitrarily. Because only the precision of results, and not trueness, was of interest in this homogeneity investigation, this sample no. B15 was used as calibration sample with an assumed chromium mass fraction of 300 mg/kg. In an analogous way, Ba was calibrated and used for comparison.

Attention: The determined mass fractions are only raw estimations because of the calibration procedure described above. However, the enlarged uncertainty is only a systematic one, not affecting the precision needed for homogeneity assessment.

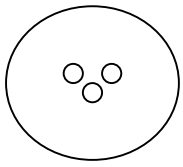
3) Determination of chromium and barium mass fractions in all samples using sample cups with a 34 mm ∅ Au-aperture (see Table and Fig. 1). The deviation of Cr values is rather high (+-2,5% rel). The material is not homogeneous enough.

4) Determination of long time drift (see Table and Fig. 2) for elements Cr and Ba was carried out by making 10 times measurements using sample B15 in the sample cup having a 34 mm ∅ Au-aperture. The measurements were spread temporally over the entire measuring time described in the previous paragraph no.3).

5) Determination of short time drift (see Table and Fig. 3) for elements Cr and Ba was carried out by 10 repeated measurements using sample B15 in the sample cup having a 34 mm ∅ Au-aperture. This was done without changing the position of sample B15 in the sample cup.

6) For determination of the distribution of mass fractions of chromium and barium within one plate (intra-homogeneity) three plates were selected. At each plate 3 positions were selected (see figure below) using an 8 mm Au-aperture. A drift sample was used during the entire measuring time for drift correction. Results show very low deviation of single values from their mean values, i. e. the intra-homogeneity is acceptable (see Table and Fig. 4)

Sample with positions for measurement (intra-homogeneity)



It was decided to crush the material into pieces of dimensions not much larger than the diameters of the irradiated spots in the intra homogeneity investigation and then to mix the material thoroughly.

Table 1 of appendix 2

Determination of chromium and barium contents in the samles

(2x20 samples were selected for realistically representing the entire sample number)

sample plate 1 (S1) *)two samples per bottle: S1 and S2

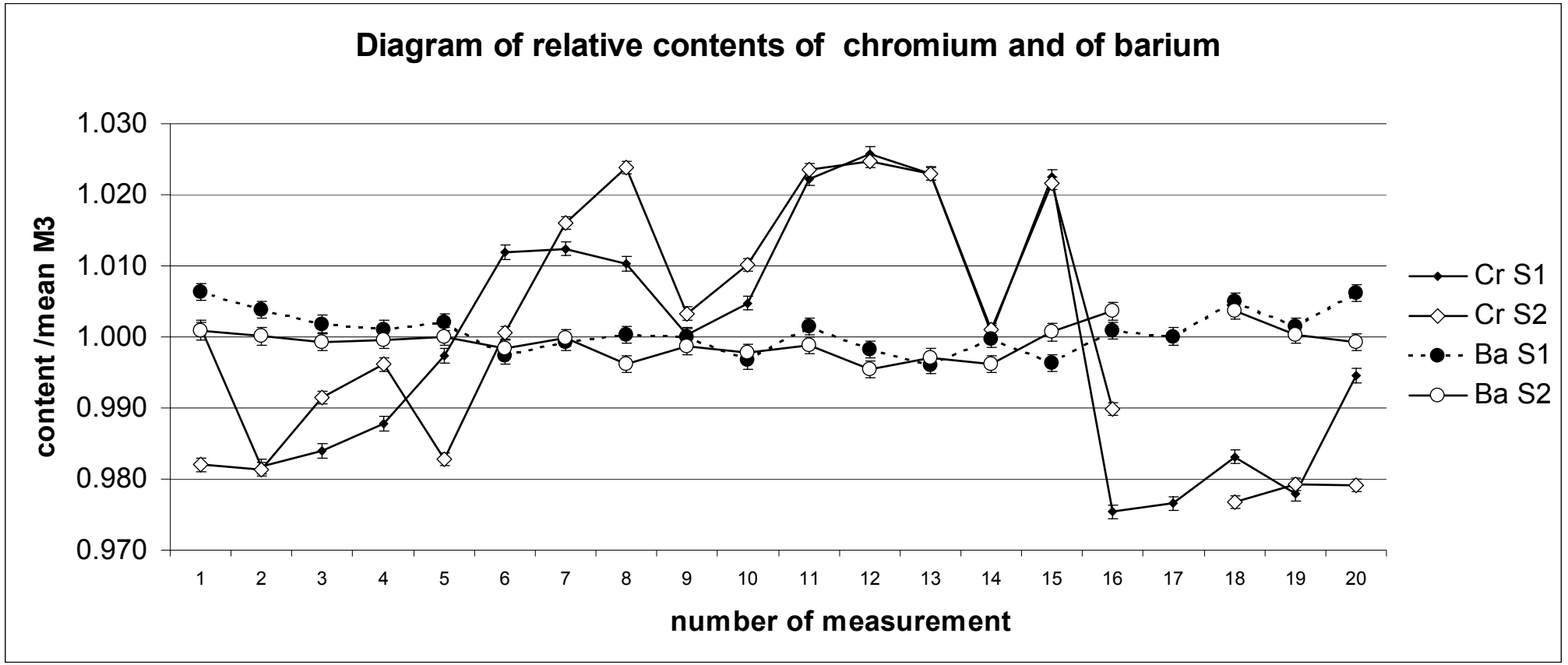
sample code	No	date	time	content Cr S1*) mg/kg	Cr S2*) mg/kg	Ba S1*) %	Ba S2*) %	relative deviation of single values from mean xx Sx content/ mean M3 Cr S1	Cr S2	Ba S1	Ba S2
B11	1	21/3/01	11/55	301.03	295.22	1.4135	1.4058	*1.001*	*0.982*	*1.0063*	*1.0008*
B12	2	21/3/01	11/56	295.15	295.03	1.4100	1.4047	*0.982*	*0.981*	*1.0038*	*1.0001*
B13	3	21/3/01	11/57	295.81	298.06	1.4072	1.4036	*0.984*	*0.991*	*1.0018*	*0.9993*
B14	4	21/3/01	11/59	296.95	299.46	1.4061	1.4040	*0.988*	*0.996*	*1.0011*	*0.9995*
Mean M1drift sample B15	5	21/3/01	10.XX	299.84	295.45	1.4075	1.4047	*0.997*	*0.983*	*1.0021*	*1.0001*
B21	6	21/3/01	12/01	304.20	300.79	1.4008	1.4023	*1.012*	*1.001*	*0.9973*	*0.9984*
B22	7	21/3/01	12/02	304.36	305.47	1.4037	1.4044	*1.012*	*1.016*	*0.9993*	*0.9999*
B23	8	21/3/01	12/03	303.72	307.81	1.4051	1.3992	*1.010*	*1.024*	*1.0003*	*0.9961*
B24	9	21/3/01	12/59	300.72	301.62	1.4046	1.4028	*1.000*	*1.003*	*1.0000*	*0.9987*
B25	10	21/3/01	13/00	302.07	303.69	1.4000	1.4016	*1.005*	*1.010*	*0.9967*	*0.9978*
B31	11	21/3/01	13/02	307.32	307.69	1.4067	1.4030	*1.022*	*1.023*	*1.0015*	*0.9988*
B32	12	21/3/01	13/03	308.38	308.07	1.4021	1.3982	*1.026*	*1.025*	*0.9982*	*0.9954*
B33	13	21/3/01	13/04	307.54	307.52	1.3990	1.4006	*1.023*	*1.023*	*0.9960*	*0.9971*
B34	14	21/3/01	13/05	300.81	300.95	1.4042	1.3993	*1.001*	*1.001*	*0.9997*	*0.9962*
B35	15	21/3/01	13/06	307.41	307.12	1.3994	1.4056	*1.023*	*1.022*	*0.9963*	*1.0007*
B41	16	21/3/01	13/07	293.23	297.59	1.4059	1.4097	*0.975*	*0.990*	*1.0009*	*1.0036*
B42	17	21/3/01	13/20	293.59	x	1.4047	x	*0.977*		*1.0001*	
B43	18	21/3/01	13/21	295.57	293.63	1.4117	1.4098	*0.983*	*0.977*	*1.0050*	*1.0037*
B44	19	21/3/01	13/22	293.99	294.40	1.4067	1.4051	*0.978*	*0.979*	*1.0015*	*1.0003*
B45	20	21/3/01	13/23	299.00	294.36	1.4132	1.4036	*0.995*	*0.979*	*1.0061*	*0.9993*
Mean M3 of contents of samle plates 1&2				**300.6**		**1.4046**					
SD				**5.0**		**0.0038**					
RSD %rel				**1.7**		**0.27**					

sample plate 2

sample code number	date	time of measurement	
2B11	22/3/01	10/47	295.22
2B12	22/3/01	10/48	295.03
2B13 (gen.B15)	21/3/01	12/00	298.06
2B14	22/3/01	10/49	299.46
22B15	22/3/01	11/49	295.45
2B21	22/3/01	10/52	300.79
2B22	22/3/01	10/54	305.47
2B23	22/3/01	10/56	307.81
2B24	22/3/01	10/57	301.62
2B25	22/3/01	10/58	303.69
2B31	22/3/01	11/45	307.69
2B32	22/3/01	11/46	308.07
2B33	22/3/01	11/47	307.52
2B34	22/3/01	11/51	300.95
2B35	22/3/01	11/52	307.12
2B41	22/3/01	11/54	297.59
x			
2B43	22/3/01	11/55	293.63
2B44	22/3/01	11/56	294.40
2B45	22/3/01	12/18	294.36

x - sample broken

Fig. 1 of appendix 2



Result: large deviations between different samples of chromium content: at highest approx. +2.5% ....-2.5% from mean value. The deviations for one bottle (plates 1 and 2) are sometimes (but not in every case) correlated. The deviations of the Ba content are much less (approx. +0.7%....-0.5%). This results from a much more homogeneous distribution of Ba than of Cr. Counting statistics and energy level (and hence the effective analytical volume) of both X-ray lines are very similar and therefore not the reason for the different measured distributions of Cr and of Ba.

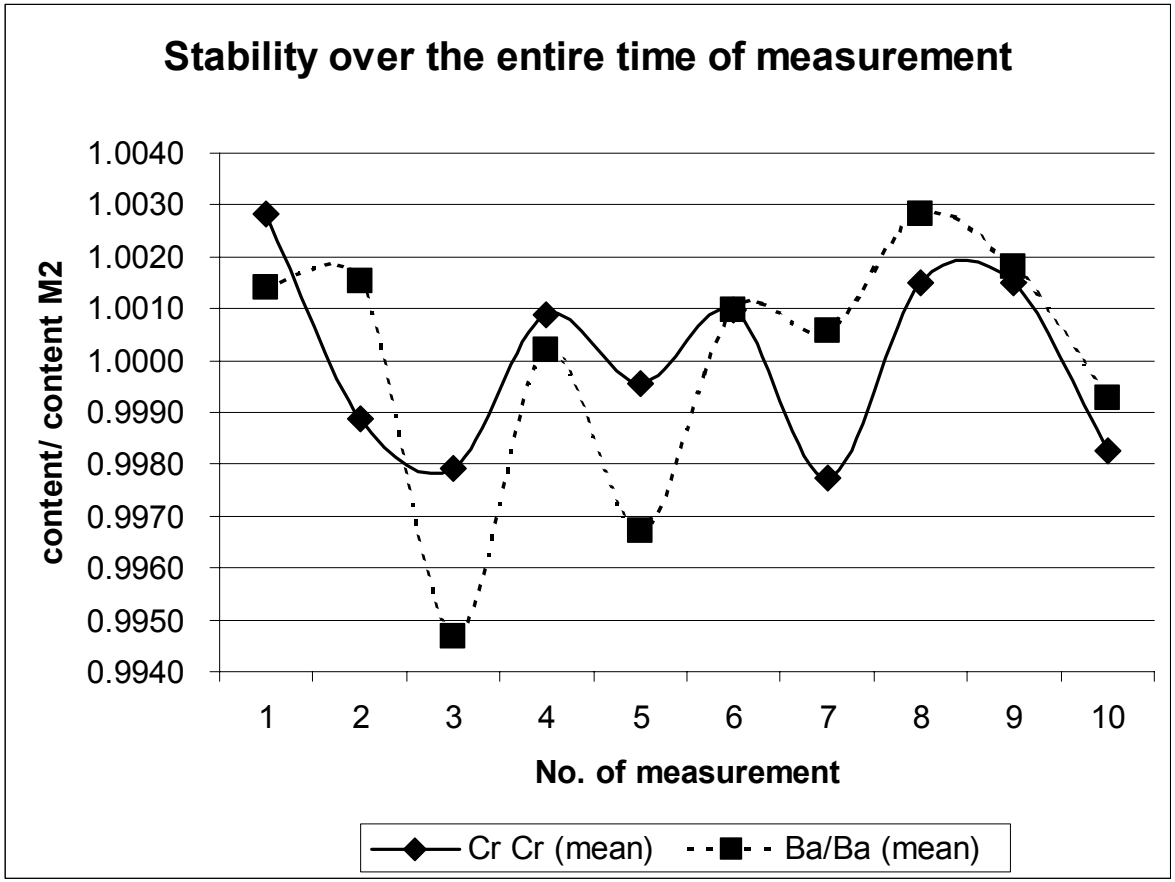
Table 2 of appendix 2 (long time drift)

mean value from short time stability	1	21/3/01 10.XX	299.84	1.4075	*1.0028*	*1.0014*
DB15	2	21/3/01 13/24	298.66	1.4077	*0.9989*	*1.0015*
DB15C	3	22/3/01 08/46	298.37	1.3981	*0.9979*	*0.9947*
KDB15	4	22/3/01 10/50	299.26	1.4058	*1.0009*	*1.0002*
KDB15	5	22/3/01 10/55	298.86	1.4009	*0.9996*	*0.9967*
KDB15	6	22/3/01 10/59	299.29	1.4069	*1.0010*	*1.0010*
KDB15	7	22/3/01 11/44	298.32	1.4064	*0.9977*	*1.0006*
KDB15	8	22/3/01 11/48	299.44	1.4095	*1.0015*	*1.0028*
KDB15	9	22/3/01 11/53	299.44	1.4081	*1.0015*	*1.0018*
KDB15	10	22/3/01 11/58	298.47	1.4045	*0.9982*	*0.9993*

mean value M2	**299.00**	**1.4055**
SD	**0.50**	**0.0033**
RSD %rel	**0.17**	**0.24**
counting statistics error% for comparison	0.18	0.19

Result: No significant drift over whole time of measurement

Fig. 2 of appendix 2



Result: Maximum relative deviations for Cr mass fractions from mean value (same sample in the entire measurement interval) are between +0.3 and -0.2 % and indicate no significant drift

Table 3 of appendix 2

Short time stability, measured without sample change

sample		DATE	TIME	Cr	Ba	*Rel. deviation from me*	
						Cr/Cr mean	*Ba/Ba mean*
sample code	No.of measur.			ppm	%		
KDB15	1	21/3/01	10/41	300.23	1.4052	*1.0013*	*0.9983*
KDB15	2	21/3/01	10/42	299.93	1.4101	*1.0003*	*1.0018*
KDB15	3	21/3/01	10/43	300.04	1.4116	*1.0006*	*1.0029*
KDB15	4	21/3/01	10/44	299.70	1.4024	*0.9995*	*0.9964*
KDB15	5	21/3/01	10/45	300.18	1.4097	*1.0011*	*1.0016*
KDB15	6	21/3/01	10/46	299.73	1.4097	*0.9996*	*1.0016*
KDB15	7	21/3/01	10/47	299.43	1.4045	*0.9986*	*0.9979*
KDB15	8	21/3/01	10/48	300.40	1.4063	*1.0019*	*0.9991*
KDB15	9	21/3/01	10/49	298.64	1.4091	*0.9960*	*1.0012*
KDB15	10	21/3/01	10/51	300.15	1.4065	*1.0010*	*0.9993*
Mean value M1				**299.84**	**1.4075**		
SD				**0.49**	**0.0028**		
RSD %rel				**0.16**	**0.20**		
Counting statistics error %rel for comparison				*0.18*	*0.19*		

Result: No significant short time drift

Fig. 3 of appendix 2

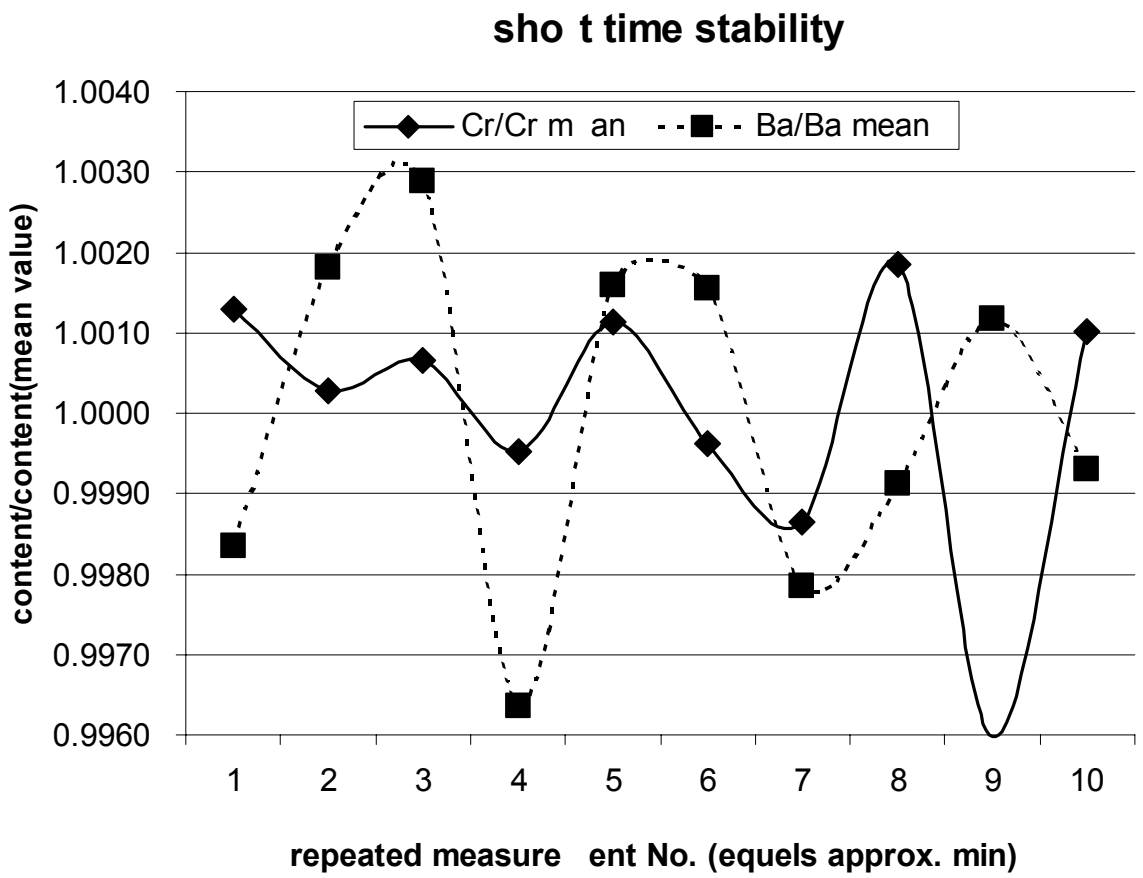


Table 4 of appendix 2

Determination of distribution of chromium within the samples (Intrahomogenity).

Measurements of 3 different samples at 3 different spots each

Measurement of samples

SampleXSpot	DATE TIME	Cr ppm	Ba %	Cr drift corrected ppm
B11X1	27/03/01 12/49	296.03	1.3809	
B33X1	27/03/01 13/09	303.88	1.3929	
B45X1	27/03/01 13/29	296.73	1.3897	
B11X2	27/03/01 15/10	296.87	1.3771	
B33X2	27/03/01 15/31	306.06	1.3869	
B45X2	27/03/01 15/51	300.60	1.3785	
B11X3	28/03/01 07/42	294.28	1.3787	296.47
B33X3	28/03/01 08/03	302.45	1.3722	304.69
B45X3	28/03/01 08/23	294.83	1.3729	297.01
mean value M4		299.1	1.3811	
SD		4.0	0.0068	
RSD % rel.		1.3	0.50	

statistical evaluation

sample**X**measure-spot No.	**Cr** ppm	**Ba** %	sample**X**measure-spot No.	**Cr** ppm	**Ba** %	sample**X**measure-spot No.	**Cr** ppm	**Ba** %
B11X1	296.03	1.3809	**B33X1**	303.88	1.3929	**B45X1**	296.73	1.3897
B11X2	296.87	1.3771	**B33X2**	306.06	1.3869	**B45X2**	300.60	1.3785
B11X3*	296.47	1.3787	**B33X3***	304.69	1.3722	**B45X3***	297.01	1.3729
ıean value M5	296.46	1.3789		304.88	1.3840		298.11	1.3804
SD	0.34	0.0016		0.90	0.0087		1.76	0.0070
RSD rel%	0.12	0.11		0.29	0.63		0.59	0.50

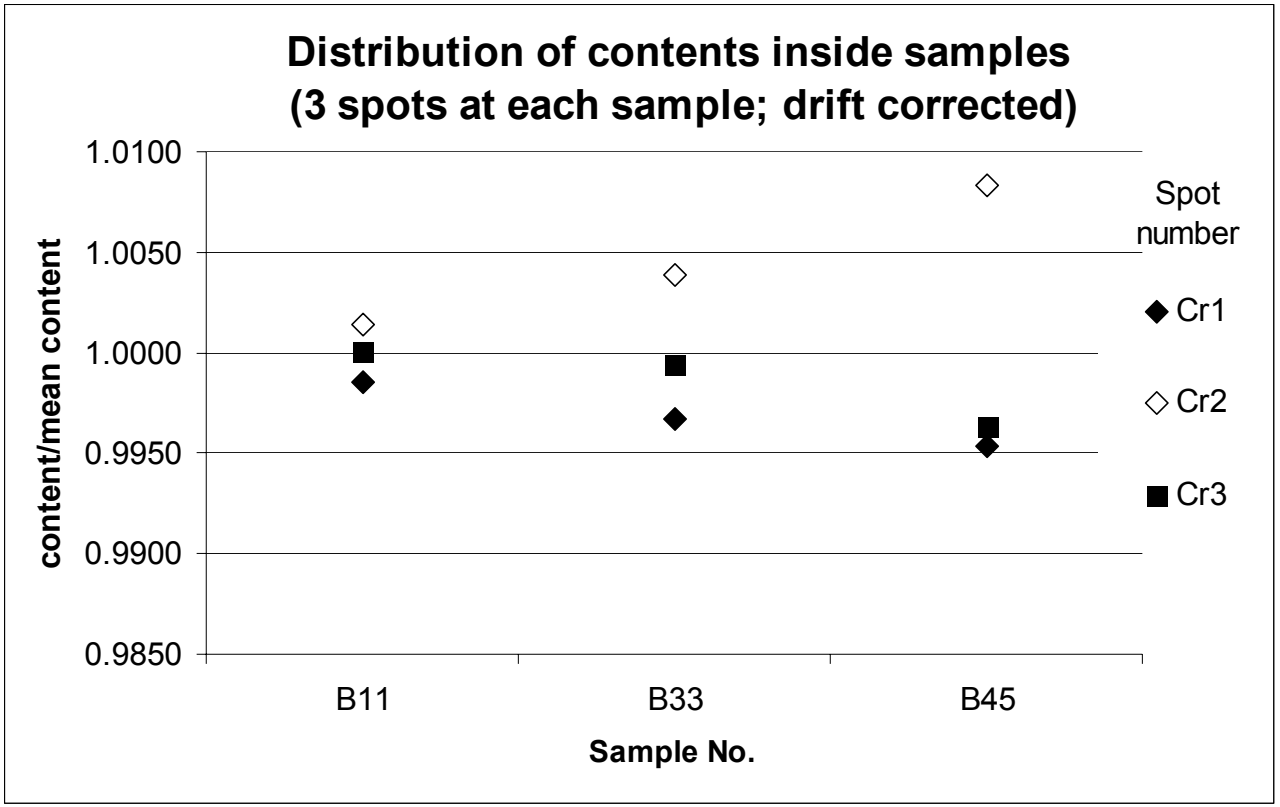
*-drift corrected values

Distribution as relative values

content/content means M5

sample	Cr1	Cr2	Cr3	Ba1	Ba2	Ba3
B11	0.9986	1.0014	1.0000	1.0014	0.9987	0.9999
B33	0.9967	1.0039	0.9994	1.0064	1.0021	0.9915
B45	0.9954	1.0083	0.9963	1.0067	0.9986	0.9946

Fig. 4 of appendix 2



Appendix 3 (BAM-S004): Homogeneity Testing

The starting material (about 2 x 7.5 kg) has been transferred into about 300 bottles, each of them containing 50 g of glass material. During this procedure, all of the crushed starting material was used such that both representative amounts of sample material from different parts of the volume, and a representative grain size spectrum of the starting sample, were transferred into each bottle. Single grains with diameters > 10 mm were excluded in this procedure.

A representative number of bottles was selected from the total number of bottles by random selection for use in homogeneity testing. The following 20 bottles were selected: 8, 22, 38, 53, 66, 82, 91, 106, 124, 134, 147, 161, 179, 186, 207, 217, 236, 250, 258, 268. From each of the bottles, 4 sub-samples (5 g each) were taken from 4 different parts of their volume. The sub-samples were milled to a grain size <200 µm in a planetary ball mill (agate beaker and balls, Retsch, Germany). From each milled sample 1 g was taken for the preparation of the fused sample. For comparison a 50 g sample (No. 203) was milled and 27 g of this material were highly homogenized in the “Mixer / Mill” (Spex Ind., USA) in a polypropylene beaker with polypropylene balls for 3x5min.

The homogeneity test was carried out using fused samples (pellets with a diameter of 26 mm and a thickness of about 4 mm). These pellets were prepared by fusion (propane/air burner) of a mixture of about 1 g of the milled glass samples (< 200 µm) with about 6 g lithium tetraborate (Spectromelt A10, Merck) and about 0.05 g Na-Iodide (Merck) in a crucible (Pt-Au). The fusion procedure lasted about 10 min. The fused pellet was used for X-ray measurement with the flat surface that had been in contact with the bottom of the crucible towards the X-ray beam. The measurement was carried out by XRF using a Siemens SRS 303sequential spectrometer.

The measurement results of the Cr-contents are arranged by increasing bottle numbers (and sub-sample No. 1 …4) in Table 1 of this appendix.

In another table the results of the highly homogenized sample are summarized (see Table 2 of this appendix)

One homogeneity test (F-test) was made for comparing variances “between the samples (bottles)” and "within the samples (bottles)" (see Table 3 of this appendix). This test "between the samples" indicated a weak significant inhomogeneity. One can conclude that the Cr-contents of the sub-samples ‘between the bottles’ differ by a small but statistically significantly amount more than ‘within the bottles’.

A second homogeneity test (F-test) was made comparing the mean variance “within the samples (bottles)" and the variance of the homogenized sample (see Table 4 of this appendix). This homogeneity test “within the samples" did not indicate a significant inhomogeneity. One can conclude, that the Cr-contents of the sub-samples within the bottles do not differ significantly more than in the bottle containing the homogenized sample.

All relevant RSD-values are only about 1 %rel (for comparison: RSD of repeated measurements of the same sample, the "drift sample", was 0.44 %rel). From this one can conclude that the detected inhomogeneity can increase the final uncertainty of the certified value only in the order of 1 %rel as a max. Thus a relatively high level of homogeneity of Cr-content was observed in the investigated material, which was certified as a reference material.

Symbols and relations

$m_{(1-4)}$ Mean value of the determined chromium mass fraction in the 4 sub-samples taken from one bottle [mg/kg]
$s_{(1-4)}$..... Standard deviation (SD) within one bottle
s(rel%) Relative standard deviation (RSD) within one bottle
$s_{(sample\ means)}$ SD of the means $m_{(1-4)}$
M_{total} Mean of all means $m_{(1-4)}$
HS Highly homogenized sample, ten sub-samples
M_{HS} Mean value of the chromium mass fraction determined in HS [mg/kg]
s_{HS} Standard deviation (SD) determined in HS
s_w Mean value of all SD within the bottles calculated by

$$s_w = (\Sigma s^2_{(1-4)} / 20)^{1/2}$$

s_b Mean SD of sub samples between all bottles calculated by

$$s_b = (s^2_{sample\ means} \bullet 4)^{1/2}$$

test value between s^2_b / s^2_w

test value within s^2_w / s^2_{HS}

F-value (inter=between) = Table value of F distribution: $F_{0,05;\ 19;\ 60}$

F-value (intra=within) = Table value of F distribution: $F_{0,05;\ 60;\ 9}$

characteristic no. for homog. between the samples = $(s^2_b / s^2_w) / F_{0,05;\ 19;\ 60}$

characteristic no. for homog. within the sample = $(s^2_w / s^2_{HS}) / F_{0,05;\ 60;\ 9}$

Characteristic no $\leq 1 \rightarrow$ no significant inhomogeneity detected

Characteristic no $>1 \rightarrow$ significant inhomogeneity detected

Table 1 of appendix 3

Measurements between / within the samples

sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
8X1	296.46	299.53	5.834	1.95
8X2	307.94			
8X3	294.91			
8X4	298.82			
22X1	304.52	305.28	5.544	1.82
22X2	313.03			
22X3	303.66			
22X4	299.91			
38X1	301.95	299.38	2.672	0.89
38X2	300.86			
38X3	298.85			
38X4	295.86			
53X1	300.47	299.30	3.712	1.24
53X2	301.06			
53X3	293.80			
53X4	301.88			
66X1	297.31	300.28	2.974	0.99
66X2	303.73			
66X3	298.36			
66X4	301.73			
82X1	298.23	298.24	1.082	0.36
82X2	298.67			
82X3	299.31			
82X4	296.76			
91X1	295.72	297.53	2.592	0.87
91X2	299.24			
91X3	300.22			
91X4	294.94			
106X1	299.25	298.64	1.360	0.46
106X2	299.97			
106X3	298.56			
106X4	296.79			
124X1	297.05	295.63	2.588	0.88
124X2	293.00			
124X3	298.51			
124X4	293.94			
134X1	296.31	296.86	0.740	0.25
134X2	296.98			
134X3	296.30			
134X4	297.86			
147X1	301.98	298.29	2.466	0.83
147X2	297.28			
147X3	296.93			
147X4	296.97			
161X1	302.94	296.83	4.202	1.42
161X2	294.32			
161X3	296.23			
161X4	293.83			

Table 1 (continued) of appendix 3

sample	mg/kg	m $_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
179X1	292.86	295.98	3.115	1.05
179X2	300.29			
179X3	295.17			
179X4	295.61			
186X1	293.54	296.27	2.858	0.96
186X2	299.60			
186X3	294.27			
186X4	297.67			
207X1	296.33	296.36	0.843	0.28
207X2	297.40			
207X3	296.39			
207X4	295.33			
217X1	300.99	295.08	4.670	1.58
217X2	289.76			
217X3	293.78			
217X4	295.80			
236X1	298.74	295.98	2.595	0.88
236X2	297.24			
236X3	292.76			
236X4	295.19			
250X1	296.98	298.56	5.797	1.94
250X2	303.46			
250X3	302.78			
250X4	291.04			
258X1	291.00	291.15	2.258	0.78
258X2	292.02			
258X3	288.12			
258X4	293.46			
268X1	289.38	290.86	3.426	1.18
268X2	287.09			
268X3	291.92			
268X4	295.07			

Mean of the means	**297.30**
s (sample means)	3.112
s (sample means rel.%)	1.05

Table 2 of appendix 3

Measurements of homogenous sample

Homogeneous sample for comparison (HS)

sample	mg/kg
HS 1	300.65
HS 2	297.88
HS 3	299.45
HS 4	305.08
HS 5	301.56
HS 6	299.88
HS 7	301.71
HS 8	304.20
HS 9	298.77
HS 10	298.37

$mean_{HS}$	300.75
s_{HS}	2.4162
RSD_{HS} %	0.80

Table 3 of appendix 3

Cr inter

Homogeneity between the samples			
Analysis of variance $\alpha = 0.05$			
standard deviation within the samples s_w	3.412	M_{total} 297.30	RSD % 1.05
standard deviation between the samples s_b	6.225	F-value	1.768
test value s_b^2/s_w^2	3.328	characteristic no. for homog. between the samples	1.883
Homogeneity between the samples: Significant inhomogeneity			

Table 4 of appendix 3

Cr intra

Homogeneity within the samples			
Analysis of variance $\alpha = 0.05$			
standard deviation of sample for comparison s_{HS}	2.416	M_{HS} 300.75	RSD_{HS}% 0.80
standard deviation within the samples s_w	3.412	F-value	2.79
test value s_w^2/s_{HS}^2	1.994	characteristic no. for homog. within the samples	0.715
Homogeneity within the samples: No significant inhomogeneity			

Appendix 4 (BAM-S004):
Orientating Homogeneity Testing of Hexavalent Chromium Mass Fraction

To confirm the positive results of the homogeneity test as described in Appendix 3 for the total chromium mass fraction, a shortened homogeneity test was carried out for the mass fraction of hexavalent chromium following the procedure of ICG-TC2 (see appendix 1). It was impossible to carry out the homogeneity test to the same extent as for total chromium because of two reasons:

- the determination of hexavalent chromium in 20 x 4 = 80 samples would demand too much time. The drift of the results would obscure possible inhomogeneities.

- the precision of the method is not high enough to indicate low but relevant inhomogeneities.

Therefore, a shortened homogeneity test with 6 x 2 sub-samples was carried out. For this test, 6 bottles were filled from different representative volumes of the entire sample before the finally bottling of the material was carried out. The hexavalent chromium content was determined in 2 sub-samples from each of the 6 bottles following the revised procedure of ICG-TC2 (see appendix 1). The homogeneity test was made by comparing the variances of the result “between” and “within” the 6 bottles. No significant difference was found between the spread of the results between and within the bottles and the standard deviations lie rather close together.
Thus, the generally positive tenor of the homogeneity assessment for total chromium was supported by this investigation.

The results of the measurements of Cr(VI)-contents are arranged by increasing bottle numbers (and sub-sample No. 1 …2) in Table 1 of this appendix.

The homogeneity test (F-test) was made for comparing variances “between the samples (bottles)” and "within the samples (bottles)" (see Table 2 of this appendix). This test "between the samples" indicated no significant inhomogeneity. One can conclude that the Cr(VI)-contents of the sub-samples between the bottles do not differ significantly more than within the bottles.

Symbols and relations

$m_{(1-2)}$ Mean value of the determined Cr(VI)-mass fraction in the 2 sub-samples taken from one bottle [mg/kg]
$s_{(1-2)}$..... Standard deviation (SD) within one bottle
$RSD_{(1-2)}$ Relative standard deviation within one bottle
$s_{(sample\ means)}$ SD of the means $m_{(1-2)}$
M_{total} Mean of all the means $m_{(1-2)}$
s_w Mean value of all SD within the bottles calculated by

$$s_w = (\Sigma s^2_{(1-2)} / 6)^{1/2}$$

s_b Mean SD of sub samples between all bottles calculated by

$$s_b = (s^2_{sample\ means} \bullet 2)^{1/2}$$

test value between s^2_b / s^2_w

F-value (inter=between) = Table value of F distribution: $F_{0,05;\,5;\,6}$

Characteristic no. for homog. between the sample = $(s^2_b / s^2_w) / F_{0,05;\,5;\,6}$

Characteristic no $\leq 1 \rightarrow$ no significant inhomogeneity detected

Characteristic no $>1 \rightarrow$ significant inhomogeneity detected

Table 1 of appendix 4

Measurements between / within the samples

sample	result [mg/kg]	$m_{(1-2)}$ [mg/kg]	$s_{(1-2)}$ [mg/kg]	$RSD_{(1-2)}$ [%rel]
1.1	98	95.5	3.54	3.70
1.2	93			
2.1	93	92.0	1.41	1.54
2.2	91			
3.1	95	93.0	2.83	3.04
3.2	91			
4.1	91	92.0	1.41	1.54
4.2	93			
5.1	87	87.0	0.00	0.00
5.2	87			
6.1	93	92.0	1.41	1.54
6.2	91			
	M_{total}=mean of means	91.9		
	$s_{(sample\ means)}$	2.76		
	RSD $_{sample\ means}$ [rel.%]	3.01		

Table 2 of appendix 4

Homogeneity between the samples			
Analysis of variance α = 0.05			
standard deviation within the samples s_w	2.102	M_{total} 91.9	RSD $_{sample\ means}$ [rel.%] 3.01
standard deviation between the samples s_b	3.909	F-value	4.39
test value s_b^2/s_w^2	3.458	characteristic no. for homog. between the samples	0.788
Homogeneity between the samples: no significant inhomogeneity			