CERTIFICATION REPORT

Certification of the sulphur mass fraction in three commercial petrol materials

Certified Reference Materials ERM®-EF211, ERM®-EF212, ERM®-EF213

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

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Certified Reference Materials ERM®-EF211, ERM®-EF212, ERM®-EF213

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SUMMARY

Three petrol reference materials were certified for their total sulfur content in support of Directive 2003/17/EC of the European Parliament and of the European Council, which stipulates that petrol with a maximum S content of 10 mg/kg must be available in all member states by 2009. Commercially available petrol was obtained and filled into borosilicate ampoules without further treatment.

Homogeneity of the materials was tested and no heterogeneity was detected for two of the materials, whereas minor heterogeneity was observed for the third material. Stability of the materials was tested for 8-12 months at 60 °C and no degradation was observed.

Characterisation was based on isotope-dilution mass spectrometry (IDMS) applied as primary method of measurement by three European metrology institutes and certified values were assigned using all results. The certified uncertainties include contributions of (potential) heterogeneity, potential degradation as well as characterisation. The final assigned values are:

ERM-EF211: 48.8 ± 1.7 mg/kg

ERM-EF212: 20.2 ± 1.1 mg/kg

ERM-EF213: 9.1 ± 0.8 mg/kg

The materials are available from IRMM (ERM-EF211), LGC (ERM-EF212) and BAM (ERM-EF213)

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GLOSSARY

ANOVA	Analysis of variance
ASTM	ASTM international
BAM	Bundesanstalt für Materialforschung und- prüfung
CCQM	Consultative Committee for Amount of Substance
CRM	Certified reference material
EC	European Commission
EDXRF	energy dispersive x-ray fluorescence analysis
ERM®	European Reference Materials; www.erm-crm.org
ICP	Inductively coupled plasma
ID	Isotope dilution
IRMM	Institute for Reference Materials and Measurements
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
LGC	LGC Ltd., Teddington, (UK)
MS	Mass spectrometry
$MS_{between}$	Mean sum of squares between groups in an ANOVA
MS_{within}	Mean sum of squares within group in an ANOVA
NIST	National Institute of Standards and Technology (US)
s	standard deviation
SF	Sector-field (MS)
SI	International System of Units
SRM ®	Standard Reference Material
s_{bb}	Standard deviation between units as calculated from ANOVA
s_{wb}	Standard deviation within units as calculated from ANOVA
TIMS	Thermal ionisation mass spectrometry
u_{bb}	Uncertainty of between-unit heterogeneity
u^*_{bb}	Maximum heterogeneity that could be hidden by method repeatability
u_c	Combined uncertainty
u_{char}	Uncertainty of characterisation
U_{CRM}	expanded uncertainty of the certified value
u_{lts}	Uncertainty of long-term stability
u_{meas}	Standard measurement uncertainty
u_R	Uncertainty due to reproducibility
u_{st}	Uncertainty of the calibration standard
u_{sts}	Uncertainty of short-term stability
$u(I)$	Exclusively laboratory dependent uncertainty in a characterisation exercise
$u(II)$	Uncertainty common to all laboratories in a characterisation exercise
$u(III)$	Uncertainty common to groups of laboratories in a characterisation exercise
$u(R)$	Residual uncertainty in a characterisation exercise
UV	Ultraviolet region of the electromagnetic spectrum
WDXRF	wavelength dispersive x-ray fluorescence analysis
δ	Isotopic shift

1 INTRODUCTION

As SO_2 in air gives rise to acid rain, attempts are made to limit the amount of SO_2 in the air. This is most easily done by reducing the sources. As sulfur in fuels is one of these sources, the S content in fuels has been regulated.

Directive 2003/17/EC of the European Parliament and of the European Council [1] stipulates subsequent phasing-in of fuels (both petrol and diesel) containing less than 10 mg kg^{-1} of sulfur by January 1st 2005. These fuels have already a full market share in some European countries. By January 1st 2009 petrol containing 10 mg kg^{-1} must be available in all Member States. Certified reference materials are required in order to enforce this Directive.

Presently there are three reference materials available from NIST (US) certified for sulfur content in petrol (SRM 2299) or synthetic gasolines (SRM 2294, SRM 2298). The latter ones contain twenty-five different organic compounds in contrast to commercially available petrol which contains many hundreds of different organic compounds.

The aim of this project was the certification of the sulfur content in commercially available petrol with a lower uncertainty for the certified values than presently available.

2 TIME TABLE OF THE PROJECT

Procurement of base material: ....September 2004 - March 2005
Processing:...March 2005 – June 2005
Homogeneity study:................................July 2005 – November 2005
Stability study: ....July 2005 – July 2006
Characterisation study:...........................January 2006 – December 2006

3   PARTICIPANTS

The project was jointly managed by the three ERM® partners, the Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin (DE), LGC Ltd., Teddington (UK) and the European-Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel (IRMM) (BE)

Processing and data evaluation:
IRMM (ISO Guide 34 accreditation BELAC 268-TEST)

Homogeneity study
BAM (ISO 17025 accreditation DAP PL-2614.14)

Stability study
Referat Laboratorium Celne, Terespol (PL) (ISO 17025 accreditation PCA AB656)

Characterisation measurements:
BAM (ISO 17025 accreditation DAP PL-2614.14)
LGC (ISO 17025 accreditation UKAS 0003G)
IRMM (ISO 17025 accreditation BELAC accepted; no certificate at 22/1/2007)

4   PROCESSING

Barrels of petrol were supplied from three different European sources. Regular barrels of 200 L were supplied for the lowest (EF213) and highest (EF211) sulphur concentrations. Petrol was delivered in 6 barrels of 20 L for the EF212. The materials were processed in ascending order with respect to the sulfur concentration minimising the possible effects of carry-over and contamination of the filling equipment. For EF213, (low sulfur concentration) petrol was delivered by ESSO Deutschland GmbH, Ingolstadt, Germany. The material for EF212, (intermediate concentration) was delivered by BP CTC, The Manorway, Stanford-le-Hope, Essex, UK and the material for EF211 (high concentration) was delivered by Motor Oil Ltd., Corinth Refineries, Corinth, Greece.

It was decided to use special borosilicate ampoules with a 1 mm wall-thickness to provide a rugged containment for the petrol samples. Borosilicate glass is transparent which is a drawback considering possible break-down of organic compounds containing sulfur if exposed to light and resulting in darkening of the petrol. However, as the ampoules are stored in boxes in the dark this is not regarded as a problem. The ampoules were delivered in a sealed state. The ampoules were first opened and rinsed with Milli-Q-water to remove dust-like or particulate matter discovered in preliminary tests. Preliminary tests had shown that rinsing with acids did not result in a further decrease of the sulphur blank levels. This rinsing step reduced the residual sulfur concentration of a subsequent solution to 1-3 µg/L which is negligible compared even to the S mass fraction of EF213. After rinsing the ampoules were emptied and oven dried at 175 °C over night.

Opened ampoules were filled with approx. 20 mL of the respective petrol samples. The relative standard deviation of the amount of petrol filled in each ampoule was below 1 % (mass) The ampoules were cooled in liquid nitrogen and kept at approx. -50 °C and were flame sealed. Approximately 3000 ampoules of each material were produced.

Processing is described in greater detail in [2].

5   HOMOGENEITY

5.1   BETWEEN-UNIT HOMOGENEITY

28 to 35 ampoules of each material were selected randomly stratified over the whole batch. Each ampoule has been sampled 3 times and each sample has been analysed in triplicate for S using combustion-fluorescence, as BAM had validated this method and the performance characteristics were sufficient for the purpose. The order of analysis was independent of the filling order. Due to problems of the instrument in the beginning, several results for EF211 were clearly technically not acceptable and were therefore discarded.

Grubbs-tests were performed to detect potentially outlying individual results as well as outlying ampoule averages. One outlying sample means was detected for EF211 at a 95 % confidence level. This was most likely due to the instrument problems. It was decided to retain the result, as the mean were not flagged as outlier on a 99 % confidence level and as retaining the results can only lead to a conservative estimate of potential heterogeneity. One outlying individual result was detected for EF213 at a 95 % confidence level. This result was not flagged as outlier on a 99 % level. Taken into consideration that the study comprised 84 results, one outlier on a 95 % level is expected on pure statistical grounds. The finding is therefore most likely a statistical artefact and the result was retained.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trend in the filling sequence was detected for any of the materials on a 95 % level. The trend in the analytical sequence for EF212 was found to be significant on a 95 and 99 % confidence level. As the order of ampoules was randomised, the trend in the analytical sequence will be reflected in the estimation of potential heterogeneity.

It was checked whether the individual data and ampoule averages follow a normal distribution using normal probability plots and whether the individual data are unimodal distributed using histograms. Individual results as well as ampoule means for EF212 and EF213 follow normal distributions. The distribution of ampoule means for EF211 is skewed, but unimodal. The results of these investigations are summarised in Table 1. Individual results of the homogeneity studies as well as normal probability plots are found in Annex A.

Table 1: Results of the exploratory evaluation of the homogeneity results of EF211, EF212 and EF213. As the assessment of unimodality depends on the number of bins, an overall assessment is given.

		ERM-EF211	ERM-EF212	ERM-EF213
Outliers	Individual values	none	none	1 at 95 %, none at 99 %
	Ampoule average	1 at 95 %, none at 99 %	none	none
Significant trends (95 % confidence)	Analytical sequence	no	yes	no
	Filling sequence	no	no	no
Distribution of individual results	Normal	yes	yes	approximately
	Unimodal	yes	yes	yes
Distribution of ampoule means	Normal	no	yes	approximately
	Unimodal	yes	yes	yes

As individual values and sample means follow unimodal distributions, results could be evaluated using ANOVA. Standard deviations within units (s_{wb}) and between units (s_{bb}) were calculated. Furthermore, u^*_{bb}, the maximum heterogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [3]. The results of these evaluations are shown in Table 2.

Table 2: Results of the homogeneity test. n.c.= cannot be calculated as $MS_{among} < MS_{within}$

	Global average ± s [mg/kg]	s_{wb}		s_{bb}		u^*_{bb}	
		[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]
ERM-EF211	52.3 ± 0.6	0.836	1.598	n.c.	n.c.	0.281	0.538
ERM-EF212	20.7 ± 0.6	0.353	1.707	0.481	2.328	0.088	0.425
ERM-EF213	9.19 ± 0.20	0.115	1.254	0.158	1.714	0.029	0.315

A correction (linear regression) for the analytical trend for EF212 is in principle possible, as the sample number is not correlated to the position in the analytical sequence (no risk of eliminating a potential trend in the filling sequence). Data analysis of the corrected samples gave an s_{bb} of 1.83 %, an s_{wb} of 1.66 % and a u^*_{bb} of 0.41 %. This improvement was not seen as significant enough to justify the use of a purely statistical technique and the introduction of another uncertainty contribution due to this correction.

Standard deviation between units could not be quantified for ERM-EF211 as the MS_{among} was below the MS_{within}. However, u^*_{bb} sets an upper limit of between-unit standard deviation of 0.281 mg/kg (0.538 %). Heterogeneities for ERM-EF212 and ERM-EF213 could be quantified as 0.490 mg/kg (2.328 %) and 0.158 mg/kg (1.714 %), respectively (expressed in standard deviation between ampoules).

5.2   MINIMUM SAMPLE INTAKE

Sulfur is present in petrol as a plethora of S-containing organic substances that form a true solution. The material can therefore be regarded as inherently homogeneous. Preliminary investigations indicated that the amount of sulfur mass decreases on evaporation, indicating that the S-containing compounds are also very volatile. The minimum sample intake is therefore mainly defined by the acceptable loss on evaporation.

A minimum sample intake of 0.2 g was set, based on the smallest sample intake used in the characterisation study.

6 STABILITY

Temperature, light, and evaporation were regarded as the most relevant influences on degradation during long-term storage. Evaporation was excluded by flame-sealing of the ampoules. Sensitivity to light is an issue especially for EF211 which turns brown at exposure to sunlight. Very slight browning is also observed for the other materials. However, the materials are stored in the dark, so the influence of light was excluded. The main remaining factor is therefore temperature.

Degradation of petrol occurs by browning and polymerisation. Eventually precipitates are formed ("gumming") that may block the carburator. While this polymerisation appears to occur by a radical mechanism, it apparently stops if the material is no longer exposed to sunlight. Browning and polymerisation of the petrol depends inter alia on the cracking process, source of the petrol and addition of additives. As this process is an organic reaction, it can most likely be speeded up by exposing the samples to higher temperatures. Stability was therefore tested at higher temperatures to allow even better assessment of stability at storage temperature. Time to the market could be decreased in this way.

Stability of the materials was evaluated using two isochronous schemes [4]. For scheme 1, samples were stored for 0, 1 2 and 4 months at 60 °C. Scheme 2 consisted of storage for 0, 4, 8 and 12 months at 60 °C for ERM-EF211 and ERM-EF212. ERM-EF213 was stored for 0, 6 and 8 months at 60 °C and 12 months at 18 °C. Reference temperature for all studies was 4 °C, i.e. samples were moved to 4 °C after each time interval, thus effectively "freezing" its stability status. After completion of the study all samples were analysed under repeatability conditions using ASTM D5453-04 (combustion with subsequent determination of SO_2 by UV fluorescence) ensuring that the analytical sequence did not coincide with the sequence in time. Graphs of the studies are shown in Annex B.

Each of the studies was evaluated individually. No outliers were detected using a Grubbs-test on a 95 % confidence level in any study. Relative standard deviations of the results ranged from 0.6 % to 1.9 %, showing that the data quality was good enough for making useful statements on stability and allow further evaluation. The slopes of the regression lines result versus time were tested for significance. The slope of the 12 month study of EF212 was significantly different from zero on a 95, but not on a 99 % confidence level. No other slope was significantly different from zero on a 95 % confidence level. It was therefore concluded that no evidence of degradation was detected.

Failure to detect degradation does, however, not prove stability. Potential degradation might well be hidden by the analytical variation. The uncertainty of stability (u_{lts}) describes the potential degradation which still can be reconciled with the data, even if the slope is not statistically significantly different from zero. This uncertainty can be determined as uncertainty of the regression line with a slope of 0 multiplied with the chosen shelf life, as described by Linsinger *et al.* [5].

Shelf lives for an uncertainty of stability of 1 % were estimated as described from the 12-months studies. In addition, uncertainty of stability for t = 1 week was estimated to assess potential problems during dispatch from the 4-months studies. The results of this analysis are given in Table 3 and Table 4.

Table 3: Results of the 4 months study at 60 °C for EF211, EF212 and EF213

Material	Average ± s [μg/kg]	Slope ± s [mg/kg/month]	u_{sts} for t = 1 week [%]
EF211	47.77 ± 0.29	-0.037 ± 0.035	0.02
EF212	19.68 ± 0.39	0.062 ± 0.045	0.06
EF213	8.74 ± 0.13	-0.011 ± 0.016	0.05

Table 4: Results of the 12 months study at 60 °C for EF211 and EF212 and the 8 months study at 60 °C for EF213

Material	Average ± s [μg/kg]	Slope ± s mg/kg/month]	Shelf life for u_{lts} = 1 % [months]
EF211	42.31 ± 0.36	-0.005 ± 0.014	30
EF212	17.65 ± 0.12	-0.010 ± 0.004	39
EF213	8.45 ± 0.16	-0.014 ± 0.009	9

The measured results differ from the certified values, probably due to uncertainties in the calibration. This is, however, not a problem as the evaluation is based on a relative assessment (% change) rather than the absolute values.

Stability during dispatch: The slopes were not significantly different from zero. It is not likely that transport takes longer than one week (= 0.25 months). The potential extent of degradation during one week transport was quantified and found to be between 0.02 and 0.06 %. This uncertainty contribution is negligible compared to uncertainties from homogeneity and characterisation.

The material can therefore be dispatched under ambient conditions.

Stability during storage: The variation observed and significant at a 95 % confidence level for EF212 will increase the uncertainty and is thus taken into consideration. None of the slopes were significantly different from zero on a 99 % confidence level, indicating no significant change. This was also clear from the appearance of the ampoules: no visible browning had occurred and no turbidity developed during storage. Shelf lives calculated for an uncertainty of stability ranged from 9 to 39 months.

The shorter shelf life for ERM-BF213 is due to the higher analytical variation at this low concentration as well as the shorter duration of the study (only 8 months at 60 °C rather than 12 months). It can be expected that the material shows similar stability as the two other materials.

Taking into consideration that the study was conducted at 60 °C whereas the material is stored at 20 ± 5 °C, this ensures stability of the materials for more than 3 years. Additional studies to assess stability over longer periods of time are ongoing. The results of these studies will be the basis for prolongations of the shelf life. Further details for storage are given in the section "Instructions for use".

7   CHARACTERISATION

Characterisation was performed by isotope-dilution (ID)-mass spectrometry (MS) methods, independently applied at BAM, IRMM and LGC. Each of these methods has the potential to be a primary method, i.e. to deliver highly accurate results and achieve traceability of the results to the international system of units (SI). Competence of the three partners has been demonstrated by participation in CCQM key comparisons, amongst others one for the determination of S in diesel (gas oil) (CCQM K35; www.bipm.org).

7.1   METHOD EMPLOYED BY BAM

The method employed by BAM is an isotope dilution thermal ionisation mass spectrometry (ID-TIMS) method, which can also be found in the literature [6].

7.1.1   Materials and reagents

Duran$^®$ or quartz glass and precleaned Perfluoralkoxy (PFA) were used for sample preparation to avoid adsorption of S species. Only polypropylene (PP) pipette tips were used.

Ultrapure water (18.2 MΩ, Seral Reinstwassersysteme, Ransbach-Baumbach, Germany), nitric acid and hydrochloric acid (Merck KGaA, Darmstadt, Germany) were tested for their sulfur blank level and were found to be of sufficient quality.

Ammonia solution (Suprapur®) and hydrogen peroxide (Ultrapur®) were obtained from Merck KGaA (Darmstadt, Germany). Arsenic (III) oxide (99.999 %) was obtained from MaTecK GmbH and nitrogen (>99.999 vol. %) was obtained from Messer (Griesheim, Germany). The reagents for the reduction solution, hydroiodic acid (Merck KGaA, Darmstadt, Germany) and phosphinic acid (Fluka) were purchased p.A. grade only, as the reduction solution (75 mL 50 % H_3PO_2, 255 mL 32 % HCl, 155 mL 67 % HI) was refluxed for 5 h to remove all sulfur. The sulfur species were reduced to hydrogen sulfide, which then was evaporated through the reflux condenser.

Spike

Sulfur, enriched in ^{34}S (Chemotrade, Düsseldorf, Germany) was dissolved in HNO_3 to prepare the ^{34}S enriched spike solution. The ^{34}S solution was characterized by reverse IDMS, using two back spike solutions produced by diluting the NIST reference material SRM 3154 (H_2SO_4 solution). In total, 10 blends were prepared.

The isotopic abundances and the molar mass were calculated from the observed isotope abundance ratios. The mass fractionation was corrected by measuring a solution of IAEA-S-1 (solid Ag_2S). The isotopic composition of the BAM ^{34}S spike is shown in Table 5.

Table 5: Isotopic composition of NIST SRM 3154 and BAM ^{34}S spike, measurement results with expanded uncertainties (k=2)

	NIST SRM 3154	BAM ^{34}S spike
Isotope abundance ratio		
$n(^{32}S)/n(^{34}S)$	22.555(26)	0.002120(56)
$n(^{32}S)/n(^{34}S)$	0.17779(50)	0.000253(54)
$n(^{32}S)/n(^{34}S)$	0.00350(42)	0.000015(15)
Molar mass of sulfur		
in g·mol^{-1}	32.06423(12)	33.96343(13)

7.1.2   Sample preparation

The chemical sample preparation consisted of digestion of the samples, reduction of the SO_4^{2-} produced during digestion to H_2S, absorption and precipitation in an ammoniacal As (III)-oxide solution, dissolution of the precipitate and loading on a Re-filament.

Samples in the range of approximately 0.3 g were exactly weighed into the vessel. Approximately 1 g spike solution (exactly weighed), 5 mL HNO_3 and 1 mL H_2O_2 were added and the sample was digested using a high pressure asher system – HPA (Anton Paar GmbH Graz, Austria) equipped with a heating block holding five quartz digestion vessels of 90 mL volume. Then the digestion program started, which worked for 4 h at a maximum temperature of 320 °C and a maximum pressure of approximately 120 bar.

For the reduction of the SO_4^{2-}, produced by the HPA digestion, to H_2S a modified and enhanced version of the apparatus suggested by Paulsen and Kelly [7] was used figure in Annex C). This apparatus consisted of a 100 mL three-necked round-bottom flask (equipped with a thermometer, a port for the nitrogen supply and a reflux condenser), a heating device and a magnetic stirrer. The condenser was connected to a 100 mL gas washing bottle (frit of porosity 1), which in turn was lined up with a tube equipped with a pipette tip at the end. The pipette tip was immersed in 35 mL of an ammoniacal solution of arsenic-(III)-oxide (1000 mg/kg) in a 50 mL Falcon® tube. After refluxing for 30 min to remove traces of S, the solution was cooled down to 30°C and then the sample was added. The whole mixture was refluxed for 45 min with a stirring speed of 350 rpm. The so formed H_2S bubbled through the ammoniacal arsenic solution by means of a nitrogen stream, which was kept constant at 340 mL/min by applying a gas flow meter (Vögtlin Instruments, Germany). The formed oxo-thio-arsenate(III) was precipitated as arsenic-(III)-sulfide by adding HCl. After centrifuging (8000 rpm, 12 min), washing with 1 mL ultra pure water and again centrifuging (8000 rpm, 12 min), the precipitate was dissolved in ammonia solution (25 %) to yield a resulting concentration of 3 µg/µL, which was required for the TIMS measurements.

Co-evaporation of the reduction solution and the transport thereof to the arsenic solution result in varying amounts of HCl for the precipitation, which led to varying procedural blanks and therefore proved critical for the method repeatability. Strict control of these parameters resulted in a detection limit between 0.1 mg/kg and 0.2 mg/kg, which depends on the quality of the acid batch used. This detection limit is calculated as the threefold standard deviation of the blank, and is the lowest published detection limit for IDMS measurements of sulfur in fossil fuels.

7.1.3 Quantification

All mass spectrometric measurements were performed using the multi-collector TIMS (MC-TIMS) instrument Sector54 (Micromass / GV Instruments, Manchester, UK)

Throughout the whole work only rhenium filaments were used. The filaments were degassed under vacuum to remove all impurities. Filaments were prepared by loading 1 µL sample solution, corresponding to 3 µg sulfur, and 1 µL silica-gel suspension (mixed from 0.95 g Aerosil 300, 1.35 mL H_3PO_4 (85%), 2.5 mL NH_3 (25%) and 50 mL H_2O). The filament was heated by a current of 1.5 A to carefully evaporate the sample to dryness, while observing the process through a microscope.

Filament form (band or boat), amount of sulfur (0.75 µg, 1.5 µg, 3 µg and 9 µg sulfur) and amount of silica-gel suspension (1 µL and 3 µL) were tested and found not to influence the result. 27 samples were loaded on the filament in ambient air as nitrogen atmosphere was found not to improve either precision or absolute value.

Measurements with silica-gel suspension only (without sample) were carried out to check for isobaric interferences on the masses 107 and 109 caused by ^{107}Ag and ^{109}Ag. Applying the same measurement conditions as for the samples no interferences could be observed with Faraday detectors.

The loaded filaments were mounted on a turret and were introduced into the TIMS ion source. The current of the rhenium filaments was chosen to yield an ion current of 9 pA for $^{75}As^{32}S^+$ ions or $^{75}As^{34}S^+$ ions, respectively. For samples without spike showing natural-like isotopic compositions mass 107 was used as monitor mass and in terms of blends (isotope diluted samples) as well as spike samples mass 109 was used. During the measurement the

filament current was kept constant. A complete measurement consisted of 200 measurement readings, each integrated over 5 s, which were recorded for all masses (107: $^{75}As^{32}S$, 108: $^{75}As^{33}S$, 109: $^{75}As^{34}S$, 111: $^{75}As^{36}S$) simultaneously. The whole measurement from warm-up until the end takes 35 min. The values of the ion current ratios were calculated from the sum of all 200 single values. The basis of each calculation was mass 109. To control the evaporation and correct for mass fractionation 5 samples of the isotopic reference material IAEA-S-1 have been measured per each turret (20 samples).

7.1.4 Results

The final results are shown in Table 6, the main contributions to the uncertainty are shown in Table 7.

Table 6: Sulfur mass fractions determined by BAM for candidate reference materials EF211, EF212 and EF213 together with their corresponding uncertainties; IUPAC values have been used for the sulfur isotopic composition of the sample.

	ERM-EF211 [mg/kg]	ERM-EF212 [mg/kg]	ERM-EF213 [mg/kg]
Sulfur mass fraction	49.76	20.40	9.60
Uncertainty (k=2)	0.54	0.32	0.64

Blank values dominate the measurement uncertainty for EF212 and EF213, due to the intricate sample preparation.

Table 7: Main contributions to the expanded uncertainty. The sum does not necessarily add up to 100 %, as some minor contributions are not listed here.

Uncertainty source	ERM-EF211 [%]	ERM-EF212 [%]	ERM-EF213 [%]
Sample weight	50	31	< 1 %
Blank	15	55	99
Measured isotope ratio	19	8	< 1 %
Isotopic abundance ^{34}S	10	4	< 1 %
Mass fraction of ^{34}S in the spike solution	5	2	< 1 %

7.1.5 Influence of sulfur isotopic variation on the IDMS results

In literature sulfur isotopic variations $\delta(^{34}S/^{32}S)$, for fossil fuels can be found reaching from -12‰ to +24 ‰. Based on this the isotope ratio $R(^{32}S/^{34}S)$, the isotope abundance $h(^{34}S)$ and the atomic weight M(S) vary. Calculations using the maximum values of $\delta(^{34}S/^{32}S)$ give no significant changes in the sulfur mass fraction of EF211, EF212 and EF213 compared to the calculations using the IUPAC tabulated values.

7.2 METHOD EMPLOYED BY LGC

The method employed by LGC is a double isotope dilution mass spectrometry method described in detail in [8]. The method consists of spiking with isotopically labelled S, microwave digestion and subsequent quantification by SF-ICP-MS.

7.2.1 Materials and reagents

Ultrapure water (18.2 MΩ, Elga - Maxima, UK) and suprapure nitric acid were used throughout.

SRM 3154 (aqueous sulfuric acid solution; for calibration) and SRM 2299 (S in reformulated gasoline; 13.6 ± 1.5 mg/kg S) were obtained from NIST (Gaithersburg, US) and high purity elementary sulfur (99.9995 %) was obtained from Alfa Aesar (Heysham, UK).

Spike

Oak Ridge high purity sulfur isotopically enriched to 94 ± 0.06 % ^{34}S was used to prepare the spike solution. The sulfur was digested in nitric acid and diluted to 19 mg/kg total sulfur with high purity water.

7.2.2   Sample preparation

The sample (0.2 g) was spiked with a solution of enriched ^{34}S to give a predicted ^{32}S:^{34}S ratio of 1. These blends were digested with 6 mL HNO$_3$ in a microwave digester (Perkin Elmer, Multiwave 3000). Total run time of the program was 75 minutes, with a maximum temperature of 260 °C and a maximum pressure of 80 bar. Samples were digested in batches of 8 preparations.

Each batch of preparations consisted of at least one quality control blend (SRM 2299), one sulfur standard blend pure S, Alfa Aesar) and two blanks. After digestion, the solutions were diluted with high purity water to a final sulfur concentration of approximately 200 µg/kg (EF211), 130 µg/kg (EF212) and 90 µg/kg (EF213), respectively.

12 digestions spread over three batches were prepared of ERM-EF211. Respective numbers for the other materials are 15 digestions over 5 batches (EF212) and 13 digestions over 4 batches (EF213).

7.2.3   Quantification

The solutions were measured using a ThermoFinnigan Element magnetic sector inductively coupled plasma mass spectrometer (SF-ICP-MS) at a medium resolution of 4000. The sequence of analysis was as follows: reagent blank, preparation blank(s), standard blend, sample1, sample 2, standard blend. Due to the limited volume of sample solution, samples were bracketed in groups of two and the result was evaluated using equation (1):

$$c'_x = c_z \cdot \frac{m_y}{m_x} \cdot \frac{m_{Zc}}{m_{Yc}} \cdot \frac{R_y - R'_B \cdot \dfrac{R_{Bc}}{R'_{Bc}}}{R'_B \cdot \dfrac{R_{Bc}}{R'_{Bc}} - R_x} \cdot \frac{R_{Bc} - R_x}{R_Y - R_{Bc}} \qquad \text{eq. 1}$$

c'_x mass fraction of S in sample X obtained from one measurement
c_z mass fraction of analyte in primary standard
m_y mass of spike Y added to prepare the blend B (=X+Y)
m_x mass of sample X added to the spike Y to prepare the blend B (= X + Y)
M_{Zc} mass of primary standard solution Z added to the spike Y to make the calibration blend (Bc = Y+Z)
M_{Yc} mass of spike Y added to the primary standard solution Z to make the calibration blend Bc
R'_B measured isotope amount ratio of the sample blend
R'_{Bc} measured isotope amount ratio of the calibration blend Bc
R_{Bc} gravimetric value of the isotope amount ratio of the calibration blend
R_X isotope amount ratio of the primary standardZ (IUPAC value)
R_Y isotope amount ratio of spike material (certified value)

For SRM 2299, a mean S mass fraction of 12.81 ± 0.45 (expanded uncertainty; k=2) was obtained from the 5 replicate determinations. This result agrees with the certified value (13.6 ± 1.5) within the respective uncertainties. Mean recovery of the digested standard blends was 100.3 %.

7.2.4 Results

Uncertainties were estimated taking into account all components of equation 1. This uncertainty is dominated by the precision on the measured isotope ratios and the uncertainty of the isotope amount ratio in the primary standard. Blend to blend variation was assessed by taking the standard deviation of the mean of the 19 replicate analyses used for characterisation. The final results are shown in Table 8.

Table 8: Sulfur mass fractions determined by LGC for candidate reference materials EF211, EF212 and EF213 together with their corresponding uncertainties; IUPAC values have been used for the sulfur isotopic composition of the sample.

	ERM-EF211 [mg/kg]	ERM-EF212 [mg/kg]	ERM-EF213 [mg/kg]
Sulfur mass fraction	47.96	19.81	8.620
Uncertainty (k=2)	0.96	0.49	0.224

Each individual measurement result was assigned an uncertainty in accordance with the GUM/Eurachem Guidelines [16].

7.2.5 Confirmation Analysis

Two IDMS blends of ERM-EF212 were also prepared by NIST using a carius tube digestion technique and an independent ^{33}S and ^{34}S spike solution. The digested samples were measured at LGC using the same measurement technique as described above. Results of 21.8 ± 1.5 mg/kg and 19.0 ± 1.3 mg/kg were obtained. These results agree with the values found for EF212 within the respective uncertainties, indicating that no significant loss occurred during digestion. However, the results must be taken with care, as significant procedural blanks were observed.

7.3 METHOD EMPLOYED BY IRMM

The method employed by IRMM was two-way ID-ICP-MS under as close as possible "exact matching" conditions (ratios of blend ratio values ranged 0.8 – 1.2), as described in detail elsewhere [9]. The analytical procedure developed consisted in the preparation of blend and counter blend samples (using the candidate CRM IRMM-646 as spike material, and SRM 3154 as natural assay material), a sample acid digestion step under high pressure conditions and isotope ratio measurements at medium mass resolution using a single detector sector-field ICP-MS at a medium resolution of 4000. Combined uncertainties associated to measurement results were calculated according to ISO guidelines [16].

7.3.1 Material and reagents

High quality deionised water with resistance greater than 18 MΩcm^{-1} from a Milli-Q system (Millipore, Bedford, MA, US) was used throughout this work. Ultra pure concentrated (70 %) nitric acid (Ultrex, J.T. Baker, Phillipsburg, NJ, US) was used for sample decomposition or dilution. The natural-like isotopic certified reference material IRMM-643 was used to correct for mass discrimination effects. IRMM-646 was used as a link between petrol samples and the sulfur standard solution SRM 3154 (NIST, Gaithersburg, MD, US) natural assay material (diluted to ~ 20 mg/kg of S). Dilutions of the latter as well as the preparation of blend samples were performed exclusively through gravimetry by metrological weighing. SRM 3154 was assumed to have natural isotopic composition, as published by IUPAC [10]. IUPAC reference values were also taken for the atomic masses [11]. Sulfur in gasoline CRMs SRM 2299 and SRM 2298, both from NIST, were used as part of the validation scheme.

7.3.2 Sample preparation

Petrol samples in the range of 0.40-0.60 g were exactly weighed directly in digestion vessels and blended with aliquots of the ^{34}S enriched material IRMM-646. A modified version of digestion program described by Ostermann et al. [12] for the decomposition of diesel

samples was employed. It was found that using 5 mL of HNO_3 (70 %) is not sufficient to decompose more than 0.3 g of petrol, and 8 mL was used instead.

Digested samples were transferred into Teflon Savillex vessels and evaporated at 95 ºC to near-dryness under clean-hood conditions. The residue was taken-up in ~ 10 mL of 2 % HNO_3, transferred in 50 mL-poly(propylene) vessel and further diluted as necessary. The sulfur content in samples run by ICP-MS was estimated to be ~ 120, ~ 160 and ~ 115 ng g^{-1} (^{nat}S) for the EF211, EF212 and EF213 blends, respectively.

All digestions were performed in batches of three samples plus two vessels as procedural blanks to monitor the contamination throughout the whole sample preparation procedure.

Blend samples were prepared in the Ultra Clean Chemical Laboratory of the IRMM. All digestions were carried out in the Sample Digestion Laboratory of the Isotope Measurements Unit of IRMM.

7.3.3   Quantification

The equation for the calculation of the sulfur content was as follows:

$$C_x = f \cdot C_z \cdot \frac{m_z}{m_x} \cdot \frac{m_y}{m_y^{'}} \left(\frac{R_y - K \cdot R_{M1}}{K \cdot R_{M1} - R_x} \right) \cdot \left(\frac{R_z - K \cdot R_{M2}}{K \cdot R_{M2} - R_y} \right) \cdot \frac{\sum_i R_{xi}}{\sum_i R_{zi}}$$

eq. 2

- x petrol sample
- y spike solution (*i.e.* IRMM-646)
- z CRM SRM 3154 standard solution
- $M1$ blend of the petrol sample and spike
- $M2$ blend of CRM SRM 3154 solution and spike
- C sulfur amount content
- m mass
- R $n(^{32}S)/n(^{34}S)$ isotope ratio
- ΣR sum of all ratios (all referenced to $n(^{34}S)$)
- K factor for the correction for the mass discrimination effects calculated as certified-to-measured $n(^{32}S)/n(^{34}S)$ ratio
- f factor equal to unity; serves to cover for the uncertainty associated with isotopic equilibration and potential losses of analyte during sample preparation

All results obtained with the final procedure for SRM 2299 and SRM 2298 were well within the certified range for these CRMs.

7.3.4   Results

All results obtained at IRMM are reported in Table 9. Replicate results were always in agreement with each other within stated uncertainties.

For the three materials, the most important uncertainty component was by far the unity multiplicative factor f (91.3 %, 91.7 % and 86.2 % of the combined standard uncertainty statements for the determined S content in EF211, EF212 and EF213, respectively). Another significant component was the uncertainty on the ^{34}S isotopic abundance (IUPAC data; ~ 4.5 % of the expanded uncertainty). For EF213 the uncertainty associated to the correction for

the procedural blank contributed to ~6 % of the expanded uncertainty. Contributions from other uncertainty components were all < 2 %.

Table 9: Sulfur mass fractions determined by IRMM for candidate reference materials EF211, EF212 and EF213 together with their corresponding expanded uncertainties (k=2); all results in mg/kg

Material	ERM-EF211	ERM-EF212	ERM-EF213
replicate 1	48.9 ± 1.4	20.58 ± 0.57	9.06 ± 0.26
replicate 2	48.1 ± 1.4	20.72 ± 0.58	8.91 ± 0.28
replicate 3	48.5 ± 1.4	20.44 ± 0.57	8.95 ± 0.28
replicate 4	48.5 ± 1.4	20.24 ± 0.56	9.03 ± 0.26
replicate 5	48.9 ± 1.4	20.47 ± 0.57	9.02 ± 0.26
replicate 6	49.0 ± 1.4	20.53 ± 0.57	8.99 ± 0.26
Sulfur mass fraction	48.6	20.50	8.99
Uncertainty (k=2)	1.3	0.56	0.25

7.4 TECHNICAL DISCUSSION OF THE RESULTS

All participants are metrology institutes that participated in the resent CCQM key comparison CCQM-K35 on S in diesel. Furthermore, all participants applied IDMS as primary method of measurement, which guarantees traceability and comparability of results.

An evaluation meeting was held in which the results were discussed. All participants agree that weighing was a crucial step, especially given the volatility of the material. All institutes used capped syringes. Back-weighing was employed by LGC and IRMM whereas BAM used the amount of sample weighed into the digestion vessel.

Control of the blank was a key issue of the sophisticated chemical method applied by BAM, dominating the overall uncertainty. This contribution was less important for the methods used by IRMM and LGC.

Formal differences between laboratories exist, which are based on the very small uncertainties of the participating laboratories. Such uncertainties are not routinely achievable. Therefore, the differences are minor compared to the scatter of routine laboratories (see Table 12). It was therefore concluded that there was no reason to favour one set of results over the others and all sets of results were accepted on technical grounds.

The results for all materials and methods are summarised in Table 10 and compared with the results of the commutability study in Figures 1-3 (section 9.2). The unweighted means of results were adopted as certified values, since all results had been accepted on technical grounds.

Table 10: Summary of results for ERM-EF211, ERM-EF212 and ERM-EF213. Given are mean S mass fractions for each institute and their expanded uncertainties (k=2) in mg/kg.

	ERM-EF211	ERM-EF212	ERM-EF213
BAM	49.76 ± 0.54	20.40 ± 0.32	9.60 ± 0.64
LGC	47.96 ± 0.96	19.81 ± 0.49	8.62 ± 0.22
IRMM	48.6 ± 1.3	20.50 ± 0.56	8.99 ± 0.25

8 CERTIFIED VALUES AND THEIR UNCERTAINTIES

8.1 CERTIFIED UNCERTAINTIES

Uncertainties of the certified value of an individual ampoule (U_{CRM}) consist of contributions for homogeneity (u_{bb}), stability during storage (u_{lts}) and dispatch (u_{sts}) and characterisation (u_{char}). These are combined to the final uncertainties as given in equation 3 [13]

$$U_{CRM} = k \cdot \sqrt{u_{bb}^2 + u_{lts}^2 + u_{sts}^2 + u_{char}^2}$$ eq. 3

Uncertainty of homogeneity was estimated as between-ampoule standard deviation or the upper limit of it, as discussed in 5.1.

Uncertainty of stability during storage was set as 1 %. This results in shelf lives of approx. 3 years for all materials as discussed in 6.

Uncertainty of stability of dispatch for an assumed duration of 1 week and constant exposure of 60 °C was estimated < 0.1 % (Table 3). This uncertainty is therefore negligible compared to the other contributions.

Uncertainty of characterisation was estimated using an approach developed by Pauwels *et al.* [14]. In this approach, the uncertainty of characterisation is split into exclusively laboratory dependent uncertainties *u(I)*, uncertainties common to all laboratories *u(II)*, uncertainties common to groups of laboratories *u(III)*, and an uncertainty component attributed to the disagreement between measurement results *u(R)*.

While the results share some uncertainty components (e.g. all institutes used CRM SRM 3154 as assay material), the main uncertainty contributions vary significantly from laboratory to laboratory. This indicates that the uncertainties stated by the three institutes can be regarded as independent. This is even more true as different methods were employed. Therefore, *u(II)* and u(III) are zero and *u(I)* was therefore calculated as

$$u(I) = \frac{\sqrt{\sum u_i^2}}{n}$$ eq. 4

with u_i being the combined standard uncertainty for the mean value quoted by each laboratory and n the number of laboratories (3).

In the case of ERM-EF211 and ERM-EF213 an additional uncertainty component *u(R)* was added, as the results of the three institutes did not agree within the stated uncertainties. This uncertainty was modelled as a rectangular distribution between the highest and lowest value ad described by Levenson *et al.* [15]. The half-width of this range was converted into a standard uncertainty by division by the square root of three as described in [16]. *u(R)* was therefore estimated as

$$u(R) = \frac{max - min}{2} \cdot \frac{1}{\sqrt{3}}$$ eq. 5

with *min* and *max* being the lowest and highest value for the particular material, respectively.

Using these equations, the individual uncertainty contributions of the three materials listed in are obtained.

Table 11: Uncertainty budgets for ERM-EF211, ERM-EF212 and ERM-EF213. Relative uncertainties are based on the unweighted mean of means as shown in Table 10.

	ERM-EF211	ERM-EF212	ERM-EF213
$u(I)$ [%]	0.58	0.67	1.33
$u(R)$ [%]	1.07	not necessary	3.12
u_{char} [%]	1.21	0.67	3.39
u_{bb} [%]	0.54	2.33	1.71
u_{lts} [%]	1.00	1.00	1.00
u_{sts} [%]	negligible	negligible	negligible
U_{CRM} (k=2) [%]	3.32	5.24	7.86
Average	48.77	20.24	9.07
U_{CRM} (k=2) [mg/kg]	1.62	1.06	0.71

The final certified values and uncertainties therefore are:

ERM-EF211: 48.8 ± 1.7 mg/kg

ERM-EF212: 20.2 ± 1.1 mg/kg

ERM-EF213: 9.1 ± 0.8 mg/kg

9   TRACEABILITY AND COMMUTABILITY

9.1   METROLOGICAL TRACEABILITY

All laboratories applied IDMS as primary method of measurement. All laboratories provided uncertainty budgets showing full understanding of the measurement process and uncertainties were estimated in line with the ISO Guide to the Expression of Uncertainty in Measurement [16]. Either certified spikes or spikes characterised in-house by double-IDMS had been used ensuring traceability of the final quantification step. Absence of bias has been demonstrated by method validation. All relevant influence factors were calibrated to the degree necessary. Each set of results is therefore traceable to the international system of units (SI).

The certified values are combinations of results each traceable to the SI. The certified values are therefore also traceable to the SI.

9.2   COMMUTABILITY

A commutability study was organised to ensure that the certified values could also be obtained by routine methods listed in Table 12. Eleven European laboratories were invited to participate in the study. Samples were distributed on 24.8.2005 and 13.9.2005 and the deadline for delivery of results was the 20.10.2005. Results of all laboratories and their methods used are given below.

Table 12: Methods used and results of the commutability study for EF211 and EF213

Laboratory code	Method	Result EF213 [mg/kg]	Result EF211 [mg/kg]
1	ASTM D5453-04 (Combustion-UV)	10.25	50.18
3	EN ISO 20846 (UV-Fluorescence)	8.6	49
4	EN ISO 20884 (WDXRF)	8.2 ± 1.9	53.1 ± 3.0
5	EN ISO 20884 (WDXRF)	8.9 ± 2.1	48.9 ± 5.6
6	EN ISO 20846 (UV-Fluorescence)	8.4	48.6
7	ASTM D5453-04 (Combustion-UV)	8.8 ± 0.6	47.8 ± 2.3
8	IP-532/05 (EDXRF)	11.7 ± 0.3	53.4 ± 0.5
9	ASTM D5453-04 (Combustion-UV)	10	50
10	EN ISO 20846 (UV-Fluorescence)	9.0	49.3
11	EN ISO 20846 (UV-Fluorescence)	9.7 ± 1.2	50.2 ± 6.0
mean of laboratory means		9.4	50.0
standard deviation of laboratory means		1.1	1.8
95 % confidence interval of the mean of laboratory means		9.4 ± 0.8	50.0 ± 1.4

The result of laboratory 8 for EF213 was an outlier (Grubbs test) on a 95 % confidence level, but not on a 99 % confidence level. The result was therefore retained to calculate the average. No outlying laboratory means were found for EF211 with a Grubbs test on a 95 % confidence level. The distribution of laboratory means was investigated using a normal probability plot, which indicated a deviation from a Gaussian distribution. However, the dataset was not large enough to reject the hypothesis of normal distribution.

The means of laboratory means do not differ significantly from the certified value, proving commutability of both materials, as shown in Figures 1-3.
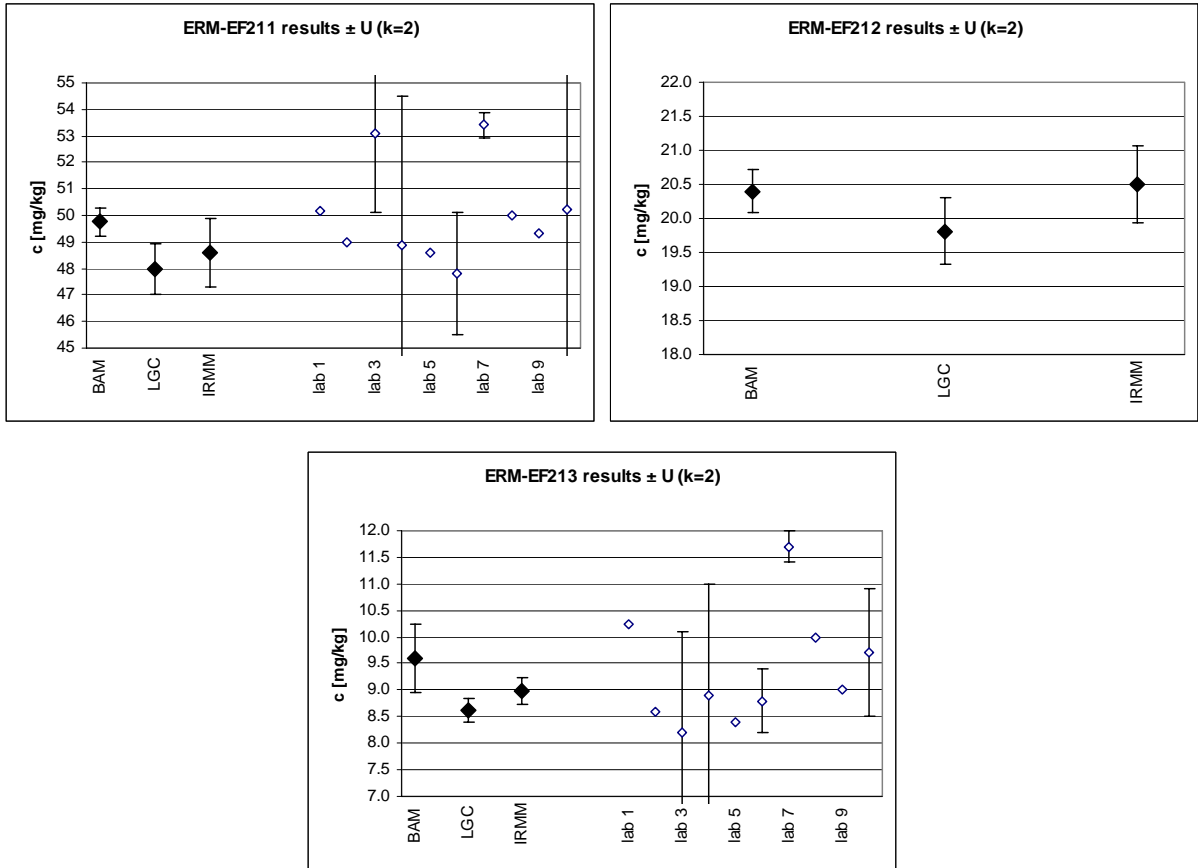
Fig. 1: Results of the characterisation campaign and the commutability study. Solid diamonds: Results of the characterisation study: open diamonds: results of the commutability study. Error bars correspond to expanded uncertainties (k=2) as reported by the laboratories. The shaded area is the certified interval as defined in 8.1. No commutability study was performed for ERM-EF212.

10 INSTRUCTIONS FOR USE

The material is very volatile and great care should be taken when subsampling the material. There is some evidence that the sulphur species are volatile as well. The minimum sample intake of 0.2 g must be respected.

10.1 STORAGE CONDITIONS

The materials should be stored at 20 ± 5 °C in the dark. Exposure to light may lead to browning of the material.

10.2 SAFETY AND PROTECTION OF THE ENVIRONMENT

The following health and safety clauses apply:

R12	Extremely flammable
R38	Irritating to skin
R45	May cause cancer
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R65	Harmful: may cause lung damage if swallowed.
R67	Vapours may cause drowsiness and dizziness.
S2	Keep out of the reach of children
S23	Do not breathe vapour
S24	Avoid contact with skin
S29	Do not empty into drains
S43	In case of fire, use foam/dry powder/CO_2. Never use water jets.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
S53	Avoid exposure - obtain special instructions before use.
S61	Avoid release to the environment.
S62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label.

For non-fuel use only - "Restricted to professional users. Attention - Avoid exposure - obtain special instructions before use."

10.3 USE OF THE CERTIFIED VALUES

The main purpose of the materials is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result. To this end, the following steps are necessary [17]:

1) Assessment of the measurement uncertainty: This uncertainty will depend whether accuracy of one individual result or accuracy of a method in general shall be assessed.

   When using a validated standard method, measurement uncertainty can be estimated from the reproducibility data after having confirmed that one's laboratory performs equally well as those laboratories participating in the validation study. These

reproducibility data do not comprise uncertainty of the calibration. This uncertainty has to be added. The uncertainty is then estimated as

$$u_{meas} = \sqrt{u_R^2 + u_{st}^2}$$

u_{meas} standard measurement uncertainty

u_R uncertainty due to reproducibility (as taken from the validation study)

u_{st} uncertainty of the calibration standard (mainly purity).

    u_{st} can be ignored if it is $< 1/3\ u_R$

2) Determination the standard uncertainty of the certified value of the material in question (u_{CRM}). Standard uncertainty is obtained by dividing the expanded uncertainty as given on the certificate by the k-factor 2.

3) Combination of the two uncertainties to $u_c = \sqrt{u_{meas}^2 + u_{CRM}^2}$

4) The method is significantly biased if the difference between the measured result and the certified value is larger than 2 u_c.

Use in quality control charts

The materials can be used for quality control charts. Different CRM units will give the same result as heterogeneity was found negligible.

Use as a calibrant

It is not recommended to use matrix materials as calibrants. If used nevertheless, the uncertainty of the certified value shall be taken into consideration in the final estimation of measurement uncertainty.

11 ACKNOWLEDGEMENTS

12 ANNEXES

Annex A: Results of the homogeneity study

Annex B: Results of the stability study

Annex C: Reduction apparatus used by BAM

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Annex A: Results of the homogeneity study

ERM-EF211

Annex A Tab. 1: Results of the homogeneity study of ERM-EF211

ampoule number	replicate 1		replicate 2		replicate 3	
	sequence #	result	sequence #	result	sequence #	result
109	25	52.24	60	52.84		
122	6	52.14	66	52.38	72	50.55
188	30	51.88	42	51.75		
283	10	51.83				
431	4	51.73				
522	20	54.16	51	51.08		
635	23	52.63	55	51.31		
730	1	52.61	65	50.84		
740	17	53.29	48	51.88		
866	13	51.75	36	52.8	68	52.59
940	8	51.28	63	51.85		
1043	7	51.51	64	51.55	69	52.73
1120	35	51.69	46	51.96		
1224*	22	54.65	50	53.43		
1357*	33	53.1	38	53.64		
1493	14	52.29	40	51.75		
1516	3	51.65	53	51.74		
1647	18	53.17	61	52.97		
1700	28	51.46	44	51.84		
1846	32	53.02	47	52.76		
1987	26	51.87	59	52.22		
2055	16	52.73	56	51.77		
2068	11	52.54	52	51.71		
2181	27	51.62	39	52.65		
2229	9	50.42	62	52	70	52.77
2337	31	52.25	37	53.28		
2517	2	52.81	67	52.61		
2615	21	53.45	49	52.85		
2758	34	52.72	43	52.43		
2763	29	51.37	45	52.68		
2885	12	51.68	41	52.33		
2898	5	52.05	95			
3048	15	51.91	54	51.72		
3212	19	54.2	58	53.6	71	50.87
3329	24	52.33	57	52.84		

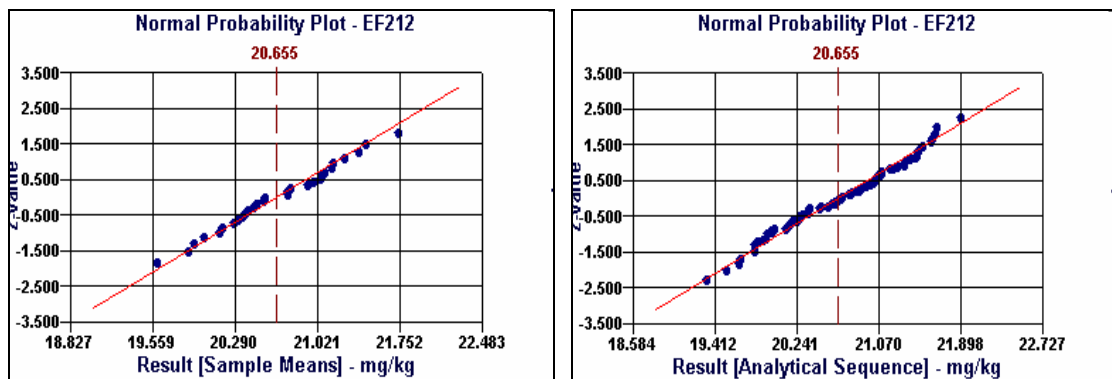*: Outlier on a 95 % but not 99 % confidence level
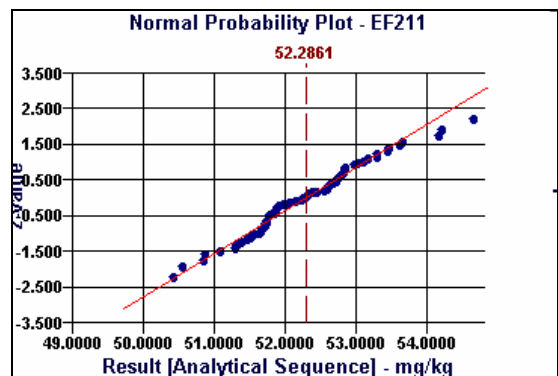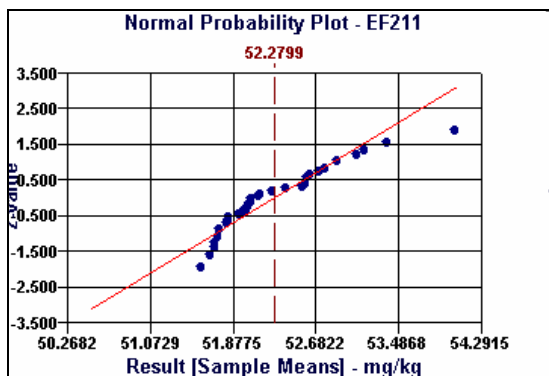
Annex A Fig. 1: Normal probability plots of the results of the homogeneity study of ERM-EF211

ERM-EF212

Annex A Tab. 2: Results of the homogeneity study of ERM-EF212

ampoule number	replicate 1		replicate 2		replicate 3	
	sequence #	result	sequence #	result	sequence #	result
99	52	21.26	53	21.08	54	21.45
182	19	20.8	20	20.98	21	20.47
204	70	19.9	71	19.99	72	20.55
294	4	21.47	5	20.95	6	21.06
430	58	21.01	59	21.05	60	21.08
631	13	21.1	14	19.81	15	19.94
667	28	20.77	29	20.63	30	20.87
759	46	20.01	47	20.17	48	20.36
802	37	19.82	38	21.03	39	20.77
880	82	20.3	83	19.94	84	19.53
1074	10	20.68	11	20.84	12	20.15
1329	34	20.37	35	20.62	36	20.36
1360	61	20.79	62	21.47	63	20.68
1521	85	19.66	86	19.82	87	19.33
1657	49	19.82	50	19.98	51	19.81
1733	25	21.6	26	20.89	27	20.94
1882	16	20.6	17	20.3	18	20.15
1960	76	19.85	77	20.7	78	20.88
2089	1	21.9	2	21.65	3	21.64
2149	64	21.09	65	19.93	66	20.2
2447	22	21.18	23	20.7	24	20.9
2548	79	21.34	80	20.35	81	20.65
2593	7	21.51	8	21.51	9	21.33
2700	31	21.04	32	21.04	33	21.18
2724	73	20.49	74	20.27	75	20.18
2854	67	20.24	68	20.13	69	19.67
2906	40	21.44	41	21.38	42	21.32
3070	43	20.37	44	21.61	45	21.21
3196	55	20.25	56	20.27	57	20.6
99	52	21.26	53	21.08	54	21.45
182	19	20.8	20	20.98	21	20.47
204	70	19.9	71	19.99	72	20.55
294	4	21.47	5	20.95	6	21.06
430	58	21.01	59	21.05	60	21.08
631	13	21.1	14	19.81	15	19.94

Normal probability plots of sample means and individual results (analytical sequence)

Annex A Fig. 2: Normal probability plots of the results of the homogeneity study of ERM-EF212
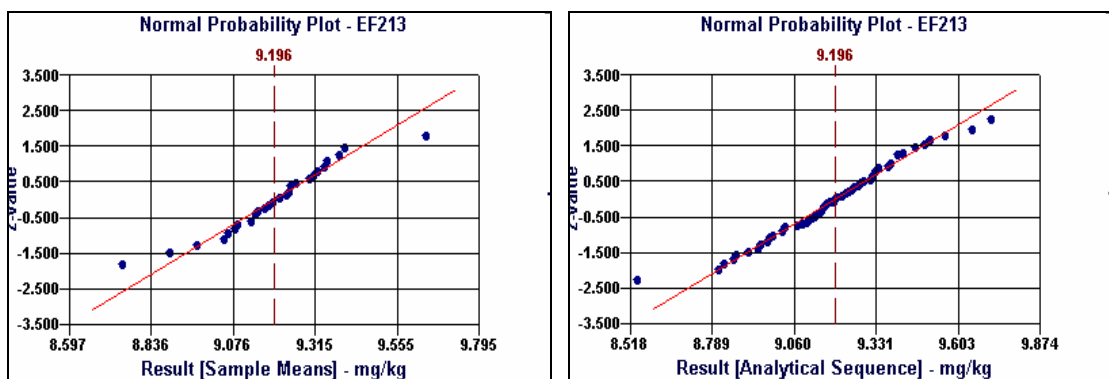
ERM-EF213

Annex A Tab. 3: Results of the homogeneity study of ERM-EF213

| ampoule number	replicate 1		replicate 2		replicate 3	
	sequence #	result	sequence #	result	sequence #	result
40	31	9.03	32	9.02	33	9.14
59	4	9.34	5	9.23	6	9.16
148	10	9.2	11	9.12	12	8.95
368	70	9.14	71	9.03	72	8.98
452	82	9.17	83	9.02	84	9.23
532	22	9.51	23	9.4	24	9.25
664	61	8.83	62	8.86	63	8.98
769	76	9.23	77	9.16	78	9.11
788	52	9.46	53	9.31	54	9.16
955	46	8.94	47	9.02	48	8.95
1131	25	9.32	26	9.38	27	9.33
1207	55	9.11	56	9.38	57	9.4
1262	79	9.1	80	9.22	81	9.13
1302	16	8.87	17	9.49	18	9.34
1533	36	9.12	37	9.09	38	9.18
1659	43	9.42	44	9.46	45	9.33
1726	67	9.2	68	9.22	69	9.31
1865	73	9.33	74	9.15	75	9.15
1934	1	9.27	2	9.26	3	9.24
2047	19	9.26	20	9.32	21	9.14
2098	58	9.56	59	9.65	60	9.71
2276	39	9.17	40	9.2	41	9.17
2375	13	8.91	14*	8.54	15	8.81
2467	64	8.99	65	9.07	66	9.19
2699	28	9.37	29	9.28	30	9.4
2738	49	9.27	50	9.28	51	9.03
2858	7	9.4	8	9.32	9	9.25
3044	34	8.97	35	9.29	42	9.16
40	31	9.03	32	9.02	33	9.14
59	4	9.34	5	9.23	6	9.16
148	10	9.2	11	9.12	12	8.95
368	70	9.14	71	9.03	72	8.98
452	82	9.17	83	9.02	84	9.23
532	22	9.51	23	9.4	24	9.25

*: Outlier on a 95 % but not 99 % confidence level

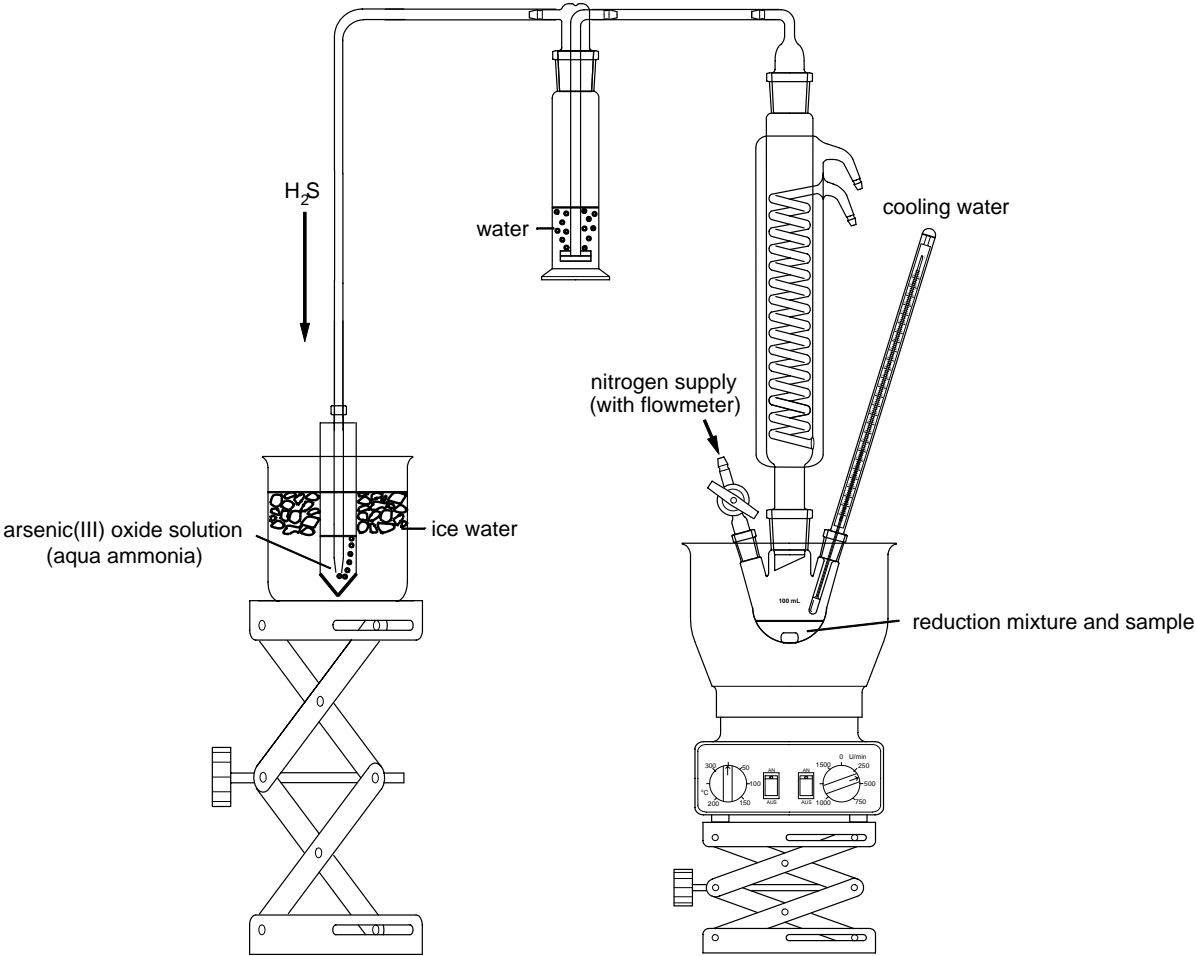Normal probability plots of sample means and individual results (analytical sequence)

Annex A Fig. 3: Normal probability plots of the results of the homogeneity study of ERM-EF211

Annex B: Results of stability studies
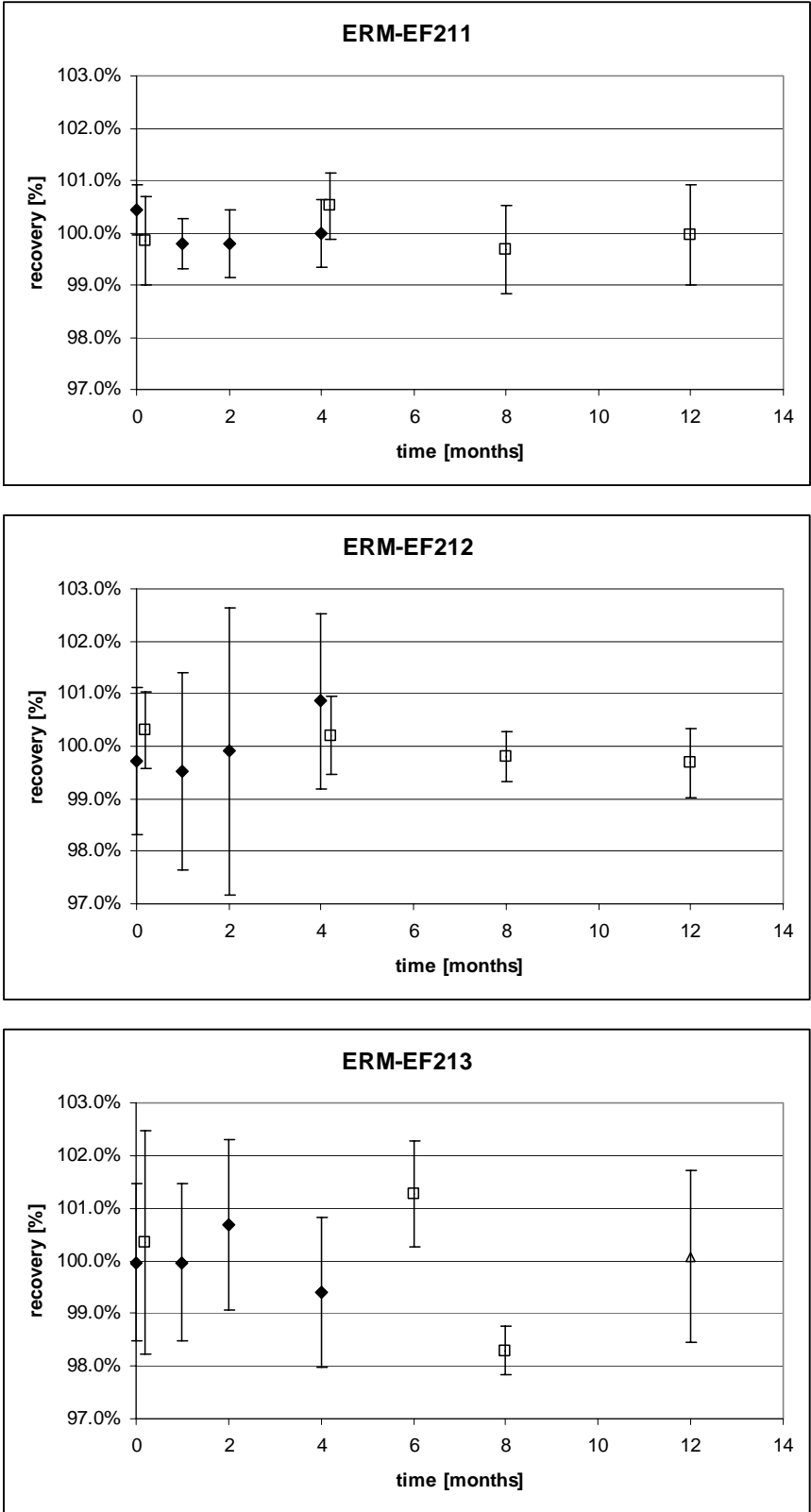
Annex B Fig 1: Results of stability studies of ERM EF211, EF212 and EF213. Shown are averages ± standard deviations for each time point. Results are normalised to the respective grand mean of each study. Solid diamonds: 4 month study at 60 °C. Open squares: 12 months study at 60 °C. Open triangle (EF213 only): 12 months study at 18 °C. Data for t = 0 and t = 4 months were separated graphically.

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Annex C: Reduction apparatus used by BAM

European Commission

Abstract

Three petrol reference materials were certified for their total sulfur content in support of Directive 2003/17/EC of the European Parliament and of the European Council, which stipulates that petrol with a maximum S content of 10 mg/kg must be available in all member states by 2009. Commercially available petrol was obtained and filled into borosilicate ampoules without further treatment.

Homogeneity of the materials was tested and no heterogeneity was detected for two of the materials, whereas minor heterogeneity was observed for the third material. Stability of the materials was tested for 8-12 months at 60 °C and no degradation was observed.

Characterisation was based on isotope-dilution mass spectrometry (IDMS) applied as primary method of measurement by three European metrology institutes and certified values were assigned using all results. The certified uncertainties include contributions of (potential) heterogeneity, potential degradation as well as characterisation. The final assigned values are:

ERM-EF211: 48.8 ± 1.7 mg/kg
ERM-EF212: 20.2 ± 1.1 mg/kg
ERM-EF213: 9.1 ± 0.8 mg/kg

The materials are available from IRMM (ERM-EF211), LGC (ERM-EF212) and BAM (ERM-EF213)

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