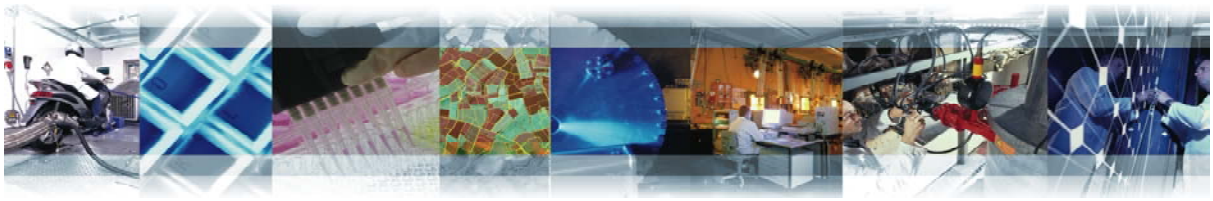

IMEP-22 Sulphur in Petrol

Interlaboratory Comparison Report

J. van de Kreeke, L. van Nevel, S. Bynens, I. Verbist, P. Robouch, B. de la Calle and P.D.P. Taylor

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European Commission
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Contact information
Ms. Lutgart Van Nevel
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

E-mail: lutgart.van-nevel@ec.europa.eu

Tel.: +32 (0)14 571702
Fax: +32 (0)14 571865

http://www.irmm.jrc.be
http://www.jrc.ec.europa.eu

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J. van de Kreeke
L. van Nevel
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Contents

1 Summary

EU Directive 2003/17/EC lays down requirements for the sulphur content in automotive petrol and provides criteria for appropriate methods of analysis to monitor compliance with these requirements. The sulphur content of automotive petrol is currently between 10 and 50 $mg \cdot kg^{-1}$, and will be limited to 10 $mg \cdot kg^{-1}$ as of 2009.

IMEP-22 studies whether the laboratories involved in petrol analysis in the frame of EU legislation are able to measure a sulphur content of 20.5 $mg \cdot kg^{-1}$. This value was certified by IRMM using a primary method of measurement. Most of the 128 participants were routine laboratories located in Europe, and the intercomparison is thought to be representative for this group.

A satisfactory z score was obtained by 70% of the participants. These laboratories fulfilled the legislative requirements laid down in Directive 2003/17/EC. The unexpectedly large share of 30% questionable and unsatisfactory z scores indicates the presence of a discrepancy between the requirements of EU Directive 2003/17/EC and the performance of the average European routine laboratory.

Eighty-seven per cent of the participants had followed the invitation to report an estimate of their measurement uncertainty. A zeta score was calculated for these results, and it was tested whether this uncertainty was within range. Half of the participants obtained satisfactory z *and* zeta scores, and 39% also obtained an additional satisfactory rating for the magnitude of the reported uncertainty. These laboratories fulfilled both legislative and metrological requirements.

Several specific groups of laboratories participated in the frame of IRMM's support to EU policy. Customs laboratories were contacted via DG TAXUD and accredited laboratories were nominated by their accreditation bodies in the frame of the collaboration between IRMM and EA, the European Co-operation for Accreditation. In addition, laboratories from Acceding and Western Balkan countries participated in the frame of the IRMM support to the EU's CARDS programme.

2 IMEP support to EU policy

The International Measurement Evaluation Programme IMEP is organised by the Joint Research Centre - Institute for Reference Materials and Measurements. IMEP provides support to the European measurement infrastructure in the following ways:

- IMEP **distributes metrology** from the highest level down to the field laboratories. These laboratories can benchmark their measurement result against the IMEP certified reference value. This value is established according to metrologically best practice.

- IMEP helps laboratories to assess their estimate of **measurement uncertainty**. The participants are invited to report the uncertainty on their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising intercomparisons in the frame of specific EU Directives, or on request of a specific Directorate-General. IMEP-22 provided specific support to the following parties:

- the **Taxation and Customs Union Directorate General** of the European Commission (DG TAXUD). A collaboration had already been established in the frame of IMEP-18 and was renewed for IMEP-22. Laboratories who participated in the GCL-Action 2 of DG TAXUD were approached and invited to participate. This report does not discern the DG TAXUD affiliates from the other participants. Their results are however summarised in a separate report to DG TAXUD.

- the **European Co-operation for Accreditation** (EA) in the frame of a formal collaboration on a number of metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a number of laboratories for free participation in IMEP-22. Mr. Robert Leubolt (Federal Ministry of Economics and Labour, Austria) liaised between EA and IMEP for this intercomparison. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.

- the Community Assistance for Reconstruction, Development and Stabilisation, or **CARDS programme**. CARDS countries are Albania, Bosnia and Herzegovina, Croatia, Serbia and Montenegro, including Kosovo under United Nations Security Council Resolution 1244 of 10 June 1999, and the Former Yugoslav Republic of Macedonia. Laboratories from these countries participated in IMEP-22 free of charge.

3 Introduction and scope

Air pollution has been one of Europe's main environmental concerns since the late 1970s, and stringent regulations thus apply to the quality of automotive fuels in the EU. One focus is on the sulphur content of fuels. The natural sulphur compounds contained in fossil fuel are released as sulphur oxides upon combustion, and these have a large impact on the environment and human health by causing acid rain and contributing to the formation of smog. Further, sulphur in automotive fuels acts as a catalyst poison, thus decreasing the effectiveness of existing and emerging automotive technology.

Current, stringent requirements as regards the sulphur content of petrol and diesel fuels are set by EU Directive 2003/17/EC [1]. Car exhaust emission limits have been laid down in EU Directives 70/220/EEC [2], 2001/100/EC [3] and 88/77/EEC [4].

Directive 2003/17/EC requires that EU Member States shall monitor compliance with the requirements of Articles 3 and 4 of the Directive 98/70/EC [5], in respect of petrol and diesel fuels, on the basis of the analytical methods referred to in European standards EN 228:1999 [6] for petrol and EN 590:1999 [7] for diesel respectively. Member States may adopt other analytical methods if they can be shown to give at least the same level of precision as the analytical methods they replace.

Current sulphur content of petrol on the European market is between 10 and 50 $mg \cdot kg^{-1}$, and will be limited to 10 $mg \cdot kg^{-1}$ as of 2009. IMEP-22 studies whether the laboratories involved in car fuel analysis in the frame of EU legislation are able to measure a sulphur content of 20.5 $mg \cdot kg^{-1}$ petrol. It provides an indication whether the requirements of Directive 2003/17/EC for analysis of sulphur in petrol are fulfilled by the market. IMEP-22 is complementary to IMEP-18 [8] in which laboratories' performance to measure sulphur in diesel was studied. Both studies share the aim to support Directive 2003/17/EC.

4 Time frame

The certification campaign aiming at establishing the reference value and its associated uncertainty started in autumn 2005. Laboratories were invited to participate in the intercomparison via various channels in October / November 2005. Participants registered in November / December 2005. Samples were dispatched to the participants in January 2006. The initial reporting deadline of 15 March was extended to 27 March 2006. The sample material was certified, and the certified value communicated to the participants in August 2006. The individual certificates of performance were distributed in December 2006. These were accompanied by an individual and comprehensive explanation of the scorings and their settings, which allowed the intercomparison participants to make a detailed evaluation of their performance.

5 Test material

5.1 A CRM

The IMEP-22 material is a certified reference material (CRM) that is on the market since April 2007. It is produced by the European Reference Material (ERM) consortium, the partners of which are the Federal Institute for Materials Research and Testing (BAM, Germany), LGC Ltd (United Kingdom) and the Institute for Reference Materials and Measurements of the European Commission's Joint Research Centre (IRMM, Belgium). The raw material was obtained and processed by IRMM. Characterisation, homogeneity and stability tests were performed by, or under auspices of, the members of the ERM consortium. Relevant details are described below, a comprehensive description can be found in the certification report that is available from the ERM website [9].

5.2 Origin and packaging

The IMEP-22 raw material originated from BP CTC, The Manorway, Stanford-le-Hope, Essex, UK. The material was homogenised and packed in special 20 ml borosilicate ampoules with a 1-mm wall-thickness to provide a rugged containment. In order to prevent degradation of organic sulphur compounds and darkening of the petrol by light (borosilicate glass is colourless and transparent), the participants were asked to store the ampoules in the dark on receipt of the material (for details see chapter 8).

5.3 Homogeneity and stability

The homogeneity study was carried out by BAM. Approx. 30 ampoules were randomly selected from the entire batch and analysed in triplicate for sulphur using combustion fluorescence. The statistical evaluation of the measurement data included an outlier test, a regression analysis to evaluate potential trends in the analytical and filling sequences, a check for normality and quantification of the homogeneity. The between-bottle variation was found to be less than or equal to 2.3%.

The stability study was carried out by a third party under guidance of the consortium. The potential extent of degradation during one week of transport at 60 °C was quantified in terms of a standard uncertainty and equal to 0.01 $mg \cdot kg^{-1}$, which is negligible in the frame of the intercomparison. The potential degradation during a 39 months' storage at 60 °C was quantified in terms of a standard uncertainty and equal to 2.0 $mg \cdot kg^{-1}$. Hence the material was found suitable for distribution to the participants under ambient conditions, and refrigirated storage during the period between receipt and measurement of the sample without the need to undertake any corrections to the reference value and its uncertainty because of limited stability.

6 The certified reference value and its uncertainty

The certified reference value was determined by IRMM by using two-way Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID-ICP-MS), a primary method of analysis. The measured value is traceable to the SI. IRMM has proven its measurement capability by successful participation in the CCQM key comparison K35 on sulphur in diesel [10]. The measured value was confirmed by further measurements performed by BAM and LGC Ltd. The associated uncertainty was determined by combining the uncertainty of characterisation and the contribution for inhomogeneity.

The resulting certified reference sulphur content in petrol and its expanded uncertainty is **(20.5 ± 1.1) $mg \cdot kg^{-1}$**. The estimated expanded uncertainty with a coverage factor $k=2$ corresponds to a level of confidence of about 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement [11]. Further details regarding the homogeneity, stability and characterisation studies are described in the material certification report which is available on request from the ERM website [9].

7 Invitation and registration of participants

Potentially interested laboratories were contacted via various channels. National accreditation bodies were contacted via the EA coordinator for IMEP-22. Customs laboratories involved in the DG TAXUD GCL-action 2 activity were individually contacted by the ILC coordinator. A general letter of invitation (cf. Annex 1) was placed on the IMEP website and distributed via the IMEP regional coordinators. These coordinators assisted IMEP to reach laboratories within their countries. They are usually affiliated with national metrology institutes, accreditation bodies or other national competence centres in the field of chemical measurements. All interested laboratories registered online and confirmed their registration by fax.

There were 141 registrations for participation from 140 laboratories in 35 countries. A total of 127 laboratories in 34 countries (32 of which in Europe) reported 128 measurement results. There were 13 cancellations. From the 127 participants, 74 enrolled as EA nominated laboratories, 17 joined via the collaboration with DG TAXUD, 3 registered as both nominated by EA and affiliated with DG TAXUD and 34 as non-affiliated IMEP-22 participants. In total, 21 laboratories participated in the frame of the IRMM support to EU candidate countries and the CARDS programme.

Table 1 lists the participating countries, the number of registrations and reported results, and the regional coordinators involved in IMEP-22.

Table 1: Participating countries, number of reported results and regional coordinators

Country	Number of registrations	Number of results	Regional coordinator
Austria	3	2	Bundesministerium für Wirtschaft und Arbeit
Belgium	3	3	
Bosnia and Herzegovina	4	3	University of Sarajevo
Bulgaria	5	5	National Center of Metrology
Croatia	3	3	Croatian Accreditation Agency
Cyprus	2	1	State General Laboratory
Czech Republic	10	10	Czech Metrology Institute
Estonia	5	4	University of Tartu
France	4	3	Bureau National de Metrologie
Finland	1	1	
Germany	10	10	Federal Institute for Materials Research and Testing
Greece	2	2	Aristotle University of Thessaloniki
Hungary	3	3	National Office of Measures
Ireland	1	1	
Italy	3	2	
Japan	1	1	
Latvia	5	5	Latvian National Accreditation Bureau
Lithuania	2	2	Semiconductor Physics Institute
FYR Macedonia	2	0	Institute for Accreditation of Republic of Macedonia
The Netherlands	3	3	NMI Van Swinden Laboratorium
Norway	1	1	
Poland	30	27	Warsaw University
Portugal	4	4	Associação dos Laboratórios Acreditados de Portugal
Romania	3	3	National Institute of Metrology
Russian Republic	1	1	
Serbia and Montenegro	8	6	Bureau of Measures and Precious Metals
Slovakia	1	1	Slovak Institute of Metrology
Slovenia	2	2	Metrology Institute of the Republic of Slovenia
South Africa	2	2	National Metrology Laboratory
Spain	5	5	
Sweden	2	2	Swedish National Testing and Research Institute
Switzerland	1	1	
Turkey	1	1	
United Arab Emirates	1	1	
United Kingdom	7	7	Laboratory of the Government Chemist
	total: 141	total: 128	

8 Sample dispatch and data collection

The samples were dispatched to the participants together with a letter with recommendations regarding the storage conditions and instructions on reporting, including timings and the individual participant code (cf. Annex 2), and an acknowledgment of receipt form. Packages were delivered by IRMM to participants via the regional coordinators where possible. Laboratories from countries without a coordinator received their packages directly from IRMM. All participants returned the sample receipt form. The sampels were delivered within one week, only three samples were delivered within two weeks, which was considered acceptable in view of the high stability of the material.

All IMEP-22 participants reported their measurement results online through the IMEP web-site. In addition, laboratories were asked to print and sign the report form and return it to IRMM. The online result was validated only after receipt of the signed copy. IMEP accepted requests for corrections of submitted results until the reporting deadline. In addition, participants were asked to complete a questionnaire (cf. Annex 3). All but one participants completed the questionnaire.

All reported information was treated confidentially. The identity of laboratories who had been nominated by EA was disclosed to EA, as stated in the invitation to this group of participants.

Figure 1: Results from all participants (see chapters 9 and 10)

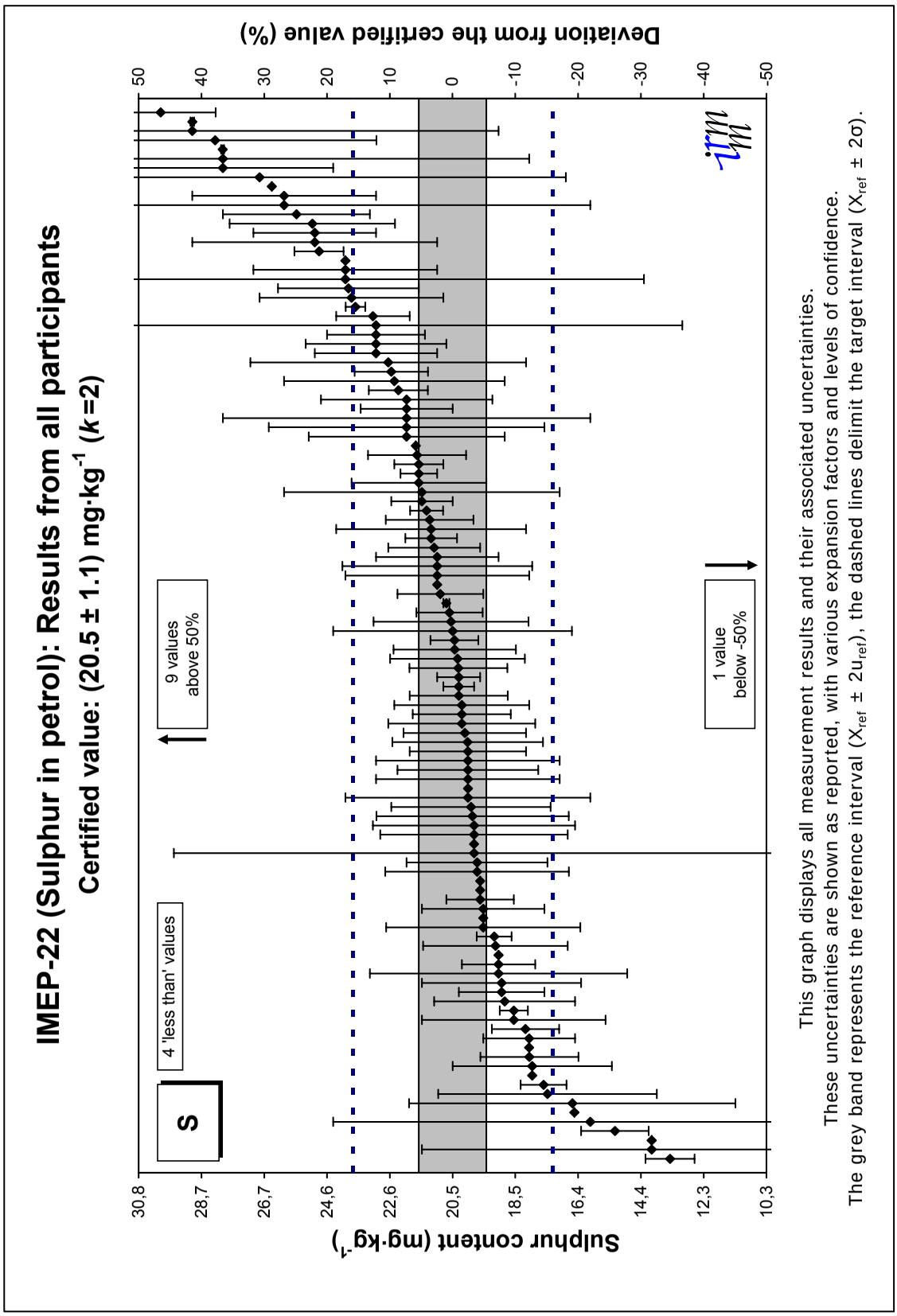
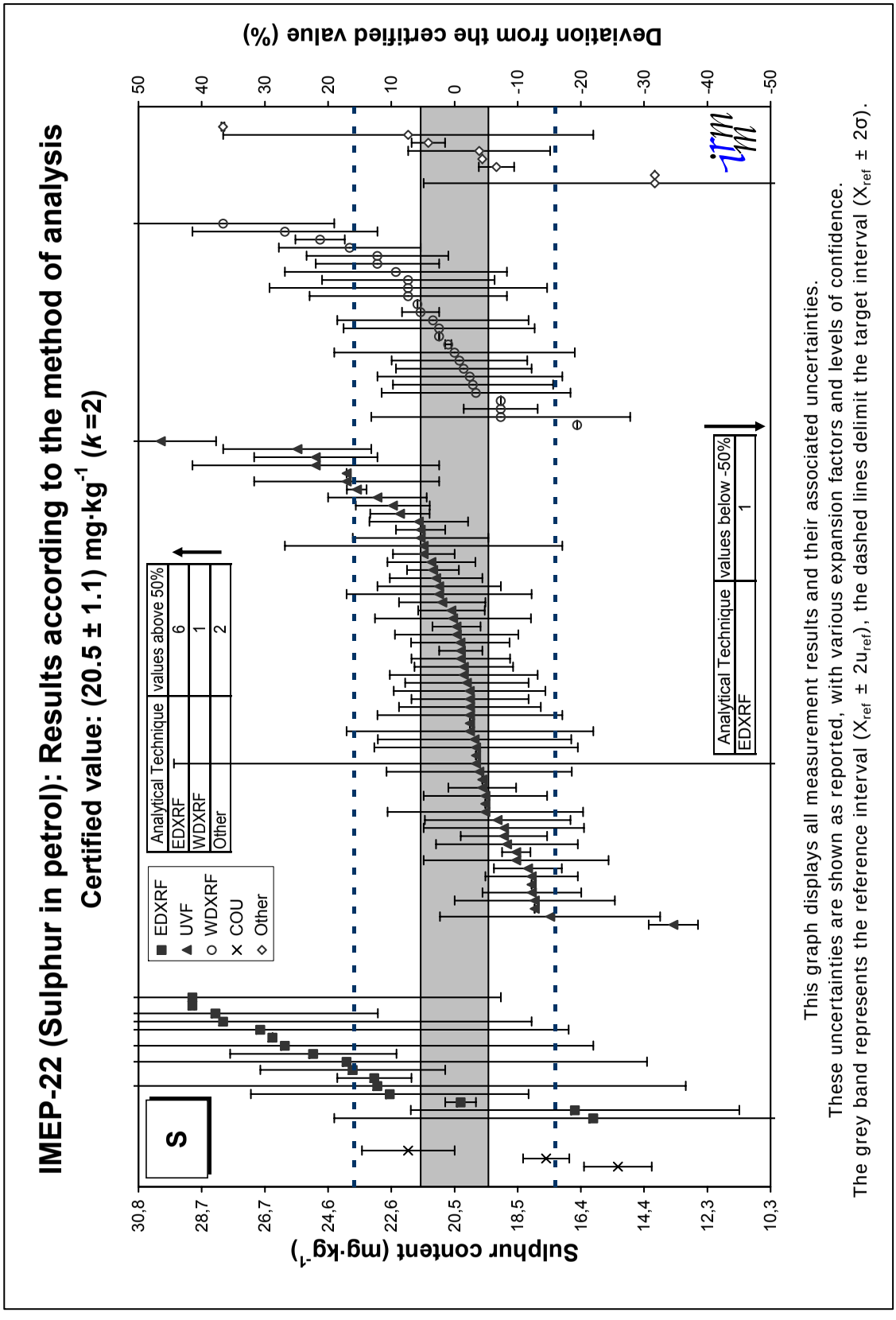


Figure 2: Results from all participants according to their method of analysis
(see chapters 9 and 10)



9 Reported results

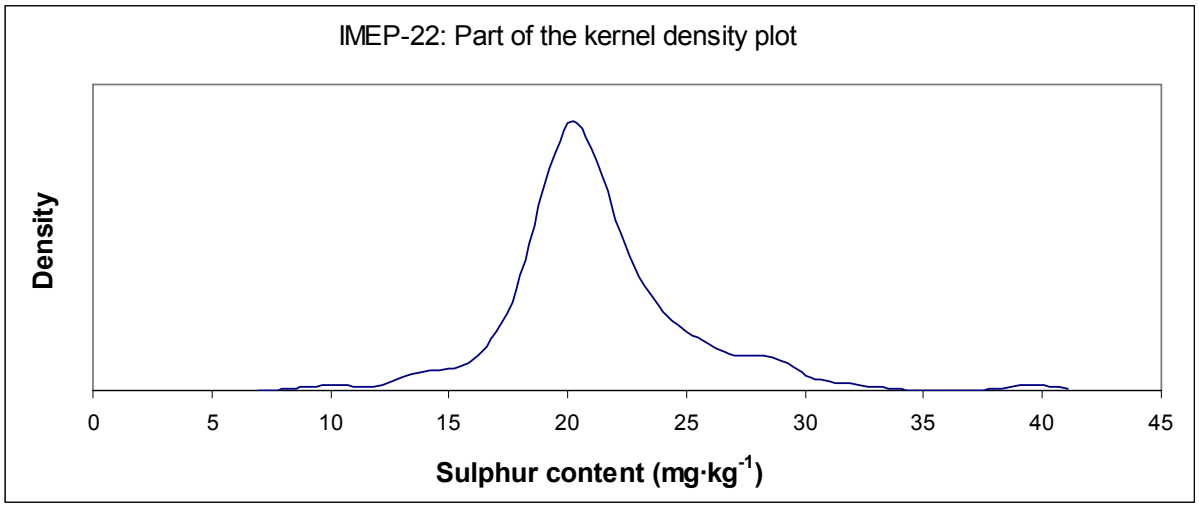
9.1 General observations

A total of 127 laboratories reported 128 measurement results. One laboratory provided two results and is counted in this report as two independent laboratories to ease further analysis. Four "smaller than" values were reported and not further assessed. The evaluation in this report is based on the remaining 124 measurement results. Furthermore, 127 questionnaires were submitted, one participant did not complete a questionnaire. Laboratories reported their measurement results in $mg \cdot kg^{-1}$ or $\mu g \cdot kg^{-1}$. No obvious peculiarities were detected.

9.2 Measurement results

Figure 1 shows the 124 measurement results and their reported uncertainties. The kernel density plot in Figure 3 shows that the results are approximately normally distributed with maximum density at 20.2 $mg \cdot kg^{-1}$. The symmetry of the curve is only skewed by additional density in the range of 23-30 $mg \cdot kg^{-1}$. The robust mean and standard deviation were calculated according to algorithm A of ISO 13528 [12] and found to be 21.4 $mg \cdot kg^{-1}$ and 3.3 $mg \cdot kg^{-1}$, respectively. The robust mean is in agreement with the certified range of (20.5 ± 1.1) $mg \cdot kg^{-1}$.

Figure 3: Part of the kernel density plot of the IMEP-22 dataset



The software used to calculate robust statistics and kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [13, 14].

10 Evaluation of results

10.1 Selection of scores and their settings

The laboratory results are scored with z and zeta scores in concordance with ISO 13528 [12] and the International Harmonised Protocol [15]:

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{and} \qquad zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

where

x_{lab} is the measurement result reported by a participant
X_{ref} is the certified reference value (assigned value): 20.5 mg·kg^{-1}
u_{ref} is the standard uncertainty of the reference value: 0.55 mg·kg^{-1}
u_{lab} is the standard uncertainty reported by a participant
$\hat{\sigma}$ is the standard deviation for proficiency assessment: 1.63 mg·kg^{-1}

Both scores can be interpreted as:

satisfactory result for $|score| \leq 2$
questionable result for $2 < |score| \leq 3$
unsatisfactory result for $|score| > 3$

The IMEP-22 **z score** compares the deviation from the reference value with method performance requirements derived from European legislation. It indicates whether a laboratory is able to operate its method for the analysis of sulphur in petrol, at the given concentration, in compliance with the relevant Directive 2003/17/EC [16]. According to the Directive, compliance should be examined on the basis of the analytical methods referred to in European standard EN 228:1999 [17]. These methods concern ISO 20846 [18] and ISO 20884 [19] which both contain comparable reproducibility limits at the 95% probability level for the sulphur concentration at hand. The largest reproducibility was selected and divided by 2.8 to get the reproducibility standard deviation s_R [20]. This value was used as the standard deviation for proficiency assessment (denominator of the z score equation) $\hat{\sigma}$ = 1.63 mg·kg^{-1}.

The **zeta score** is provided only for laboratories having reported an uncertainty. According to the International Harmonised Protocol [15] it provides an indication of whether the estimate of uncertainty is consistent with the laboratory's deviation from the reference value. The interpretation is similar to the interpretation of the z score. An unsatisfactory score might be caused by an underestimated uncertainty or by a large deviation from the reference value.

The standard uncertainty of the laboratory (u_{lab}) was calculated as follows. If an uncertainty was reported, the reported uncertainty was divided by the coverage factor *k*. If no coverage factor was given, the reported uncertainty was considered as the half-width of a rectangular distribution. The reported uncertainty was then divided by $\sqrt{3}$, in accordance with recommendations issued by Eurachem and CITAC [21].

An **additional assessment** is made related to the reported uncertainty. It aims at giving the laboratory an indication of the plausibility of its uncertainty estimate. The standard uncertainty should fall in a range between a minimal required (u_{min}), and a maximal allowed (u_{max}) reported standard uncertainty. u_{min} is set to the standard uncertainty of the reference value. It is unlikely that a participating routine laboratory is able to measure the measurand with a smaller uncertainty than the reference laboratory itself. u_{max} is set equal to the reproducibility standard deviation s_R as derived from the Directive. Both u_{min} and u_{max} are rounded and set to 0.50 and 2.0 $mg \cdot kg^{-1}$, respectively. If the standard uncertainty $u_{lab} < u_{min}$ it is likely that the laboratory underestimates its uncertainty. If $u_{lab} > u_{max}$ then uncertainty exceeds maximum legislative requirements.

The International Harmonised Protocol [15] suggests that participants can **recalculate the scores** applying their own scoring criteria. The standard deviation for proficiency assessment $\hat{\sigma}$ used in this intercomparison is based on legislative requirements and thought to be fit for the purpose of most of the participants. If this purpose is different, laboratories may recalculate the z score with a $\hat{\sigma}$ which better fits their purposes. In analogy, this also holds for the maximal allowed reported standard uncertainty u_{max}, which is derived from the same legislative requirements.

10.2 Scoring of the laboratory results

A z score was calculated for all results. In addition, a zeta score was calculated for those results that were accompanied by an uncertainty statement, and it was tested whether this uncertainty was within range. Annex 4 lists the scores for all measurement results. Annex 5 and Annex 6 exemplarily show the certificate of performance plus the explanatory notes that were sent to the participants.

Table 2: Overview of performance ratings

Score	Satisfactory	Questionable	Unsatisfactory	no rating
z score	70%	9%	21%	0%
zeta score	58%	10%	19%	13% *
u_{lab} within range	56%	--	31%	13% *

* 13% did not report an uncertainty

Table 2 summarises the distribution of scores. A 70% share of the participants obtained a satisfactory z score. These laboratories fulfilled the legislative requirements laid down in Directive 2003/17/EC. A share of 95% satisfactory z scores could have been expected on the basis of the method reproducibilities provided in ISO 20846 and 20884. There is an obvious discrepancy between legislative requirements and laboratory performance.

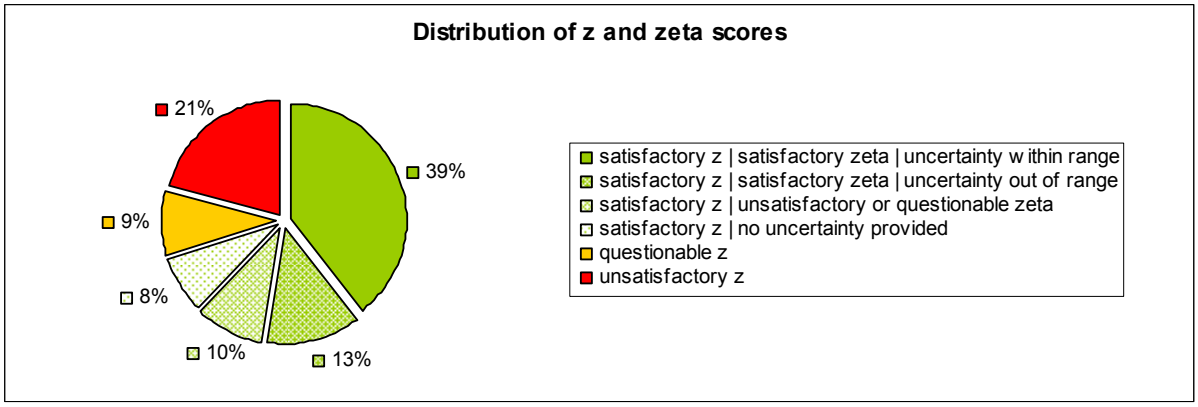
Figure 4 gives more details on the 70% share of participants with a satisfactory z score. It shows that 52% (half of the participants) obtained satisfactory z *and* zeta scores, and 39% also obtained an additional satisfactory rating for the magnitude of the reported uncertainty. These laboratories fulfilled both legislative and metrological requirements.

An uncertainty estimate was provided by 87% of the participants, and 77% of the estimates was accompanied by a coverage factor. These encouraging figures contrast with the modest 39% share of results with satisfactory over-all performance. It shows that many laboratories still encounter difficulties to provide a reasonable uncertainty estimate.

These laboratories are advised to become familiar with the principles of uncertainty estimation as described by ISO [11] and, on a sectoral level, e.g. EURACHEM and CITAC [21]. The questionnaire revealed that the principles contained in these documents were applied by most (78%) of the laboratories that performed best (i.e. the 39% share).

The questionnaire also showed that only 24% of the participants reported the measurement uncertainty to their customers on a regular basis and 50% on request. The difference with the 87% share that reported an uncertainty in IMEP-22 suggests that part of the laboratories had used this intercomparison as a measurement uncertainty reporting exercise.

Figure 4: Distribution of z and zeta scores



11 Further information regarding the results

Further information regarding the participants and their results was inquired during the process of online result reporting. All 128 participants indicated their method of analysis, and the questionnaire was completed by 127 participants. Issues that may be relevant to the outcome of the intercomparison are discussed below.

11.1 Analytical techniques

The participants' methods of analysis resembled their routine methods in 124 cases (97%). The methods that were used most frequently are listed in Table 3 with their respective robust mean and standard deviation, calculated according to algorithm A of ISO 13528 [12]. An exceptionally large robust mean was observed for results obtained with EDXRF. Better results in terms of bias and reproducibility were obtained with WDXRF and UVF, which confirms earlier findings [22]. Figure 2 shows participants' measurement results grouped by analytical method.

ISO and ASTM standards were followed by 89% of the laboratories. The standards that were applied most frequently are listed in Table 4. Several laboratories mentioned ISO 20847 and ISO 8754. These standards are however based on conventional EDXRF methods and state that they are not applicable for sulphur contents below 30 and 300 $mg \cdot kg^{-1}$, respectively.

Table 3: Analytical methods used

Analytical	**Acronym**	**Robust mean [$mg \cdot kg^{-1}$]**	**Robust StD [$mg \cdot kg^{-1}$]**	**Number of results**
Coulometric Analysis / Oxidative Micro Coulometry	COU	18.2	3.9	3
Ultra-violet Fluorescence	UVF	20.3	1.7	62
Wavelength Dispersive X-ray Fluorescence	WDXRF	21.5	2.1	28
Energy Dispersive X-ray Fluorescence	EDXRF	28.7	13.2	25
Other		26.4	13.1	10

Table 4: Official methods used (multiple selections were possible)

Standard	**Number of replies**	**Standard**	**Number of replies**
ISO 20846 (UVF)	44	ASTM D 5453 (UVF)	18
ISO 20884 (WDXRF)	16	ASTM D 2622 (WDXRF)	7
ISO 20847 (EDXRF)	8		
ISO 14596 (WDXRF)	7	Other	8
ISO 8754 (EDXRF)	10	No official analytical method used	14

11.2 A representative study

Most of the samples (98%) were analysed by the routine analyst and according to the laboratory's routine procedures. Many participants (81%) declared to have a large experience with this type of analysis and indeed, 82% indicated analysis of 50 or more samples per year. Most of the participants (97%) stem from various countries in Europe. These figures suggest that IMEP-22 has representatively studied the current capability for routine fuel sulphur content measurements at approx. 20 $mg \cdot kg^{-1}$ in Europe.

11.3 Use of CRMs and participation in PT

The majority of the participants (75%) indicated their participation in similar ILCs during the past three years. Annex 7 provides an overview of all reported ILCs. Many laboratories (65%) indicated to have a petrol reference material at their disposal which has been certified for its sulphur content. Annex 8 provides an overview of all reported CRMs.

11.4 Quality management system

The vast majority (94%) of the participants indicated that their laboratory activities comply with a quality management system: 6% of all participants declared compliance with the ISO 9000 series only, and 88% with ISO/IEC 17025. In addition, the participants were asked whether they were accredited, certified or authorized (e.g. by law or by a regulatory authority) for sulphur analysis in road transport fuels.
Table 5 lists the replies.

Table 5: Laboratory accreditation, certification or authorisation
for sulphur analysis in roadfuels (multiple answers were possible)

Status	Number of laboratories
Accredited	83 (65%)
Authorised	33 (26%)
Certified	23 (18%)
None of these	36 (28%)

11.5 Motivation for participation

The participants were asked to indicate the reason for participation in this intercomparison. Demonstration of measurement capability to other parties such as the accreditation body, regulator, customer or the own management appeared to be the main motivation for participation with a share of 68%. This was followed by participation for internal quality assurance purposes with a share of 31%.

12 Conclusion

This intercomparison studied the capability of analytical laboratories to measure a sulphur content of 20.5 $mg \cdot kg^{-1}$ in petrol. It is thought to be representative for laboratories in Europe that operate this type of measurement on a routine basis. The assessment was made against a reproducibility requirement laid down in EU Directive 2003/17/EC.

A 70% share of the laboratories provided measurement results that were compliant with the requirements laid down in the Directive. They obtained a satisfactory z score. Many laboratories provided a measurement result that also fulfilled metrological requirements: a 52% share obtained satisfactory z and zeta scores, and 39% of all participants also obtained an additional satisfactory rating for the reported magnitude of uncertainty.

The unexpectedly large share of 30% questionable and unsatisfactory z scores indicates the presence of a discrepancy between the requirements of EU Directive 2003/17/EC and the performance of the average European routine laboratory.

13 Acknowledgements

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In addition the efforts of many IRMM colleagues are acknowledged. To conclude the authors would like to express in particular their gratitude to the participating laboratories for their efforts and for their interest in the IMEP interlaboratory comparison programme.

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
ASTM	American Society for Testing and Materials
BAM	Bundesanstalt für Materialforschung und –prüfung (Berlin, Germany)
BIPM	Bureau International des Poids et Mésures (Paris, France)
CARDS	Community Assistance for Reconstruction, Development and Stabilisation
CCQM	Comité Consultatif pour la Quantité de Matière
CIPM	Comité International des Poids et Mésures (Paris, France)
CITAC	Co-operation for International Traceability in Analytical Chemistry
COU	Coulometry
CRM	Certified Reference Material
EA	European Co-operation for Accreditation
EC	European Commission
EDXRF	Energy Dispersive X-Ray Fluorescence
EN	European Norm
ERM	European Reference Materials
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
GUM	Guide to the Expression of Uncertainty in Measurement
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
PT	Proficiency Test or Proficiency Testing
SI	The International System of Units
UVF	Ultra-Violet Fluorescence
WDXRF	Wavelenght Dispersive X-Ray Fluorescence

References

1 Directive 2003/17/EC of the European Parliament and of the Council of 3 March 2003, amending Directive 98/70/EC relating to the quality of petrol and diesel fuels

2 Council Directive 70/220/EEC of 20 March 1970 on the approximation of the laws of the Member States relating to measures to be taken against air pollution by gases from positive-ignition engines of motor vehicles

3 Directive 2001/100/EC of the European Parliament and of the Council of 7 December 2001, amending Directive 70/220/EEC relating to measures to be taken against air pollution by gases from positive-ignition engines of motor vehicles

4 Council Directive 88/77/EEC of 3 December 1987 on the approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous pollutants from diesel engines for use in vehicles, amended by Commission Directive 2001/27/EC

5 Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Directive 93/12/EEC

6 EN 228:1999; Automotive fuels – Unleaded petrol – requirements and test methods

7 EN 590:1999; Automotive fuels – Diesel – requirements and test methods

8 EUR 21765 EN: 2005; Sulphur in Diesel fuel (gasoil) – Report to Participants

9 http://www.erm-crm.org

10 http://kcdb.bipm.org

11 Guide to the Expression of Uncertainty in Measurement, ISO (1993)

12 ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons

13 Robust statistics: a method of coping with outliers (2001), an AMC Technical Brief issued by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry, http://www.rsc.org

14 Representing data distributions with Kernel density estimates (2006), an AMC Technical Brief issued by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry, http://www.rsc.org

15 The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories by M. Thompson et al., Pure and Applied Chemistry (2006), 78, 145–196

16 Directive 2003/17/EC of the European Parliament and of the Council of 3 March 2003, amending Directive 98/70/EC relating to the quality of petrol and diesel fuels

17 EN 228:1999; Automotive fuels – Unleaded petrol – requirements and test methods

18 ISO 20846:2004; Petroleum products - Determination of sulfur content of automotive fuels - Ultraviolet fluorescence method

19 ISO 20884:2004; Petroleum products - Determination of sulfur content of automotive fuels - Wavelength-dispersive X-ray fluorescence spectrometry

20 ISO 5725:1994; Accuracy (trueness and precision) of measurement methods and results

21 Quantifying Uncertainty in Analytical Measurement, Eurachem/CITAC (2000), http://www.eurachem.ul.pt

22 Round Robin Exercise for Sulphur Test Methods for EN 228 and EN 590 Fuel Specifications (2002), CEN/TC 19/WG 27

Annexes

Annex 1: General invitation to participants

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP®

Geel, 24 November 2005
IM/L/112/05

International Measurement Evaluation Programme

IMEP-22: Sulphur in Petrol

IMEP, the International Measurement Evaluation Programme was established and is operated by the Institute for Reference Materials and Measurements (IRMM) in order to picture objectively the degree of equivalence of chemical measurements by comparing them with external reference values (not derived from participants' results). Previous IMEP® interlaboratory comparisons have focused on different elements in various matrices such as water, sediment, serum, fish and others. You can find detailed information about these activities on the IMEP website http://www.imep.ws. Participating laboratories receive a test sample with certified, but undisclosed amount content values, which are to be measured using routine analytical procedures. Participation in IMEP is open to all laboratories.

IRMM is now launching the IMEP-22 intercomparison that focuses on the analysis of **sulphur in petrol**. This study is complementary to the previous IMEP-18 on sulphur in diesel. Both studies are organised in the frame of support to EU[1] and national environmental policies. The test sample is provided in 20 ml glass ampoules and contains approx. 20 µg/g sulphur in a petrol matrix. Each participant receives two ampoules.

The **participation fee** is 200 € per laboratory (dispatch costs are included) except for participants from the new EU member states and the western Balkan countries: Albania, Bulgaria, Bosnia-Herzegovina, Cyprus, Croatia, Czech Republic, Estonia, Hungary, Latvia, Lithuania, FYR of Macedonia, Malta, Poland, Rumania, Serbia-Montenegro, Slovakia, Slovenia and Turkey. For participants from these countries, participation is free of charge. In addition, laboratories involved in DG TAXUD GCL-Action 2 are also free of charge.

Registration deadline will be **23 December 2005**. The samples will be dispatched early 2006, and deadline for reporting results will be one month later. The sample's reference value will be published on the IMEP website in April 2006. Individual certificates will be issued in May 2006. The participants' report will be available in the Autumn of 2006.

[1] EU Directive 2003/17/EC, amending Directive 98/70/EC regarding the quality of petrol and diesel fuels

irmm
Institute for Reference Materials and Measurements

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.imep.ws • http://www.irmm.jrc.be

How to register for IMEP-22:

1. Please use this **link** to register online:
   http://www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=66

2. Once you have submitted your registration electronically (and pressed the button "Register" on the registration form), you will be asked to print the form and return it, preferably by fax to IRMM. It is your **confirmation** of registration.

Please contact us if we can help you further or if you have any questions.

With kind regards

Johanne/ Van de Kreeke

Johannes van de Kreeke
IMEP-22 Coordinator

Institute for Reference Materials and Measurements

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.imep.ws • http://www.irmm.jrc.be

Annex 2: Letter accompanying the sample

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

Geel, 4 January 2006
IM/L/4/06

IMEP-22: Sulphur in petrol

Dear «title» «surname»,

Thank you very much for your participation in this IMEP interlaboratory comparison which involves the determination of the total amount content of S in petrol. In this package you will find the **material**: 40 ml of petrol, packed in two sealed glass ampoules of 20 ml each. The different sample numbers printed on the ampoule labels have no relevance. Included you also find the **sample confirmation form**. Please return this form by fax* *directly* after sample receipt, so as to know whether you received the package in good order. **Store** the material in a cold and dark place (e.g. refrigerator) if you do not undertake your measurement directly after receipt.

Please use the website: http://www.irmm.jrc.be/imepapp/jsp/loginResult.jsp to **report** the measurement **result** (no replicates) with its **uncertainty**, and to complete the **questionnaire**. We will treat the information contained in the questionnaire confidentially and use it for further evaluation of results only. Directly after submitting your results and the questionnaire information online, you will be prompted to **print** the completed report form. Please do so, sign this paper version and **return** it to IRMM by fax* before the deadline for results reporting, **15 March 2006**. Check your results carefully for any errors before submission, since this is your definitive **confirmation**.

The website for reporting your result and completing the questionnaire will be open between **1 February** and **15 March 2006**. For online reporting you need a so-called *password key*.

Your personal password key is: **«participation_key»**.

The preliminary IMEP-22 reference value will be published on our website by early April 2006 (see http://www.irmm.jrc.be/html/interlaboratory_comparisons/index.htm). Individual certificates and the intercomparison report will be available tentatively in July 2006.

If you have any questions or problems, please do not hesitate to contact us.
With kind regards

Johanne Van de Kreeke

Dr. Johannes van de Kreeke
IMEP-22 Coordinator

Cc: Lutgart van Nevel

* If you have no possibility to send a fax you can scan in the document and send it to us by e-mail. You can find both fax number and e-mail details in the footer of this letter.

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-14-571682 • Fax: +32-14-571865
jrc-irmm-imep@cec.eu.int • http://www.irmm.jrc.be

Annex 3: Questionnaire

1. Does your laboratory consider itself, in matters of S analysis in petrol at the given concentration level, as experienced or less- and non-experienced?

	experienced	less- or non-experienced
S amount content measurements	○	○

2. How many samples of this type does your laboratory routinely analyse per year?

○ <50 ○ 51-200 ○ 200-500 ○ >500

3. Via which information channel(s) have you been informed about this IMEP interlaboratory comparison? (You can make more than one choice)

	Yes
via IRMM	☐
via your regional IMEP co-ordinator	☐
via the IRMM web site	☐
via your Accreditation Body	☐
via DG TAXUD	☐
OTHER	☐

If OTHER, please supply additional information

4. Was the IMEP Certified Test Sample analysed by the same analyst who usually performs such analyses?

○ Yes ○ No

If NO, please complete the following questions (4a and 4b):-

	more	same	less
4a. Was the IMEP sample analyst more/same/less experienced?	○	○	○

4b. What was your motivation for this change?

5. Was the IMEP Certified Test Sample treated according to the same analytical procedure as routinely used for this sample type and this concentration level?

○ Yes ○ No

If NO, why not?

6. Indicate the sample mass used (g).

7. Did the analytical procedure involve a digestion step?

○ Yes ○ No

If YES, please complete the following questions (7a and 7b):-

7a. Which acids or reagents used?

7b. What type of digestion procedure and/or equipment used? (microwave, High Pressure Ashing-HPA, bomb, dry ashing ...)

8. Did the analytical procedure involve a separation step?

○ Yes ○ No

If YES, please explain

9. Did the analytical procedure involve a preconcentration step?

○ Yes ○ No

If YES, please supply additional information

10. **Did the analytical procedure involve a dilution step?**

○ Yes ○ No

If YES, please supply additional information concerning the solvents used and the dilution factor

11. **Did you analyse the S in this petrol material following any official analytical method? (e.g. ISO/CEN)**

○ Yes ○ No

If YES, please specify which official analytical method

12. **Do you have in your laboratory a Petrol Certified Reference Material (CRM) at your disposal certified for S?**

○ Yes ○ No

If YES, please complete the following questions (12a, 12b and 12c):-

	Yes	No
12a. Is the CRM used in your laboratory for validation of procedures?	○	○
12b. Is the CRM used in your laboratory for calibration of instruments?	○	○

12c. Please state which CRM and supplier.

13. **Did your laboratory participate in other interlaboratory comparisons (round robin test / ring tests / collaborative trials) in this field over the past 3 years?**

○ Yes ○ No

If Yes, please state which proficiency testing organiser.

14. **Is your laboratory involved in this type of analysis for customs related activities?**

○ Yes ○ No

	Yes	No
If YES, is your laboratory involved in the interlaboratory comparison "S in mineral oils" which is co-ordinated by DG TAXUD?	○	○

15. **Is your laboratory working according to a quality management system?**

○ Yes ○ No

If YES, please state which system. (You can make more than one choice)

	Yes
EN 45000 series	☐
ISO 9000 series	☐
ISO 17025	☐
OTHER (e.g. CEN, GLP, EPA, TQM, national standards)	☐

If OTHER, please supply additional information

16. **Is your laboratory certified, accredited or authorised (e.g. by law or regulatory authority) for S analysis in road transport fuels?**

	Yes	No
Certified	○	○
Accredited	○	○
Authorised	○	○

17. **Do you report uncertainties on chemical measurements to your usual customers?**

○ Yes ○ on request ○ No

18. **Are you familiar with the determination of measurement uncertainty according to the Guide to the Expression of Uncertainty in Measurement (GUM, issued by ISO in 1993) or any sectoral guidance based on the principles of the GUM, e.g. the Guide for Quantifying Uncertainty in Analytical Measurement (issued by Eurachem and Citac in 2000)?**

○ Yes ○ No

19. **Were the reported uncertainties calculated according to the above mentioned guides?**

○ Yes ○ No

If NO, how was the measurement uncertainty evaluated?

20. **Was your participation to this intercomparison used to demonstrate your measurement capability to (you can make more than one choice):**

	Yes
your management	☐
your customers	☐
regulating or accreditation body	☐
participation was intended for internal quality control puposes	☐
other	☐

If other, please supply additional information

21. **Who filled in the questionnaire?**

	Yes
The analyst	☐
The laboratory supervisor	☐
Other	☐

22. **Who filled in the report form?**

	Yes
The analyst	☐
The laboratory supervisor	☐
Other	☐

23. **The limit of quantification is the smallest concentration of the unknown that can reliably be quantified (not only detected) by the instrumental method (usually 10 x the standard deviation of the instrumental noise level). What is your laboratory limit of quantification for S in petrol?**

24. **Do you have any comments regarding the questionnaire?**

Annex 4: Laboratory measurement and scoring results

nr abbreviates for *not reported*. Ratings are colour coded:
red indicates an unsatisfactory, yellow a questionable and green a satisfactory result.

Reported sulphur content [mg·kg^{-1}]	Reported uncertainty [mg·kg^{-1}]	Coverage factor *k*	Calculated standard uncertainty [mg·kg^{-1}]	Analytical method	z score	zeta score	Uncertainty within range?
< 14	nr	nr		EDXRF-CON			
< 19,28	nr			UVF			
< 50	nr			IR/Leco			
< 97	nr			OXFORD LAB-X 3000			
10	7	nr	4,04	EDXRF-CON	-6,4	-2,6	no
13,4	0,8	2	0,40	UVF	-4,4	-10,4	no
14	nr	nr		Internal method based on ASTM D5453	-4,0		
14	7,5	2	3,75	energy-dispersive X-ray fluoresence spectrometry ISO 20847	-4,0	-1,7	no
15,2	1,1	2	0,55	COU	-3,3	-6,8	yes
16	8,4	2	4,20	EDXRF-CON	-2,8	-1,1	no
16,52	nr	nr		WDXRF	-2,4		
16,59	5,33	2	2,67	EDXRF-CON	-2,4	-1,4	no
17,4	3,57	2	1,79	UVF	-1,9	-1,7	yes
17,53	0,75	2	0,38	COU	-1,8	-4,5	no
17,9	nr	nr		UVF	-1,6		
17,9	2,6	2	1,30	UVF	-1,6	-1,8	yes
17,99	1,6	2	0,80	UVF	-1,5	-2,6	yes
18	nr	nr		UVF	-1,5		
18	1,5	2	0,75	UVF	-1,5	-2,7	yes
18,12	1,1	2	0,55	UVF	-1,5	-3,1	yes
18,5	0,46	2	0,23	UVF	-1,2	-3,4	no
18,5	3	2	1,50	UVF	-1,2	-1,3	yes
18,8	2,3	nr	1,33	UVF	-1,0	-1,2	yes
18,9	1,4	2	0,70	UVF	-1,0	-1,8	yes
18,9	2,6	2	1,30	UVF	-1,0	-1,1	yes
19	nr	nr		WDXRF	-0,9		
19	1,2	2	0,60	WDXRF	-0,9	-1,8	yes
19	4,2	2	2,10	WDXRF	-0,9	-0,7	no
19,1	2,36	2	1,18	UVF	-0,9	-1,1	yes
19,14	0,57	2	0,29	BAS ISO 8754, XRF	-0,8	-2,2	no
19,5	nr	nr		UVF	-0,6		
19,5	2	2	1,00	UVF	-0,6	-0,9	yes
19,5	3,17	nr	1,83	UVF	-0,6	-0,5	yes
19,6	nr	nr		ICP-OES	-0,6		
19,6	nr	nr		UVF	-0,6		
19,6	1,1	2	0,55	UVF	-0,6	-1,2	yes
19,7	2,3	2	1,15	Antek	-0,5	-0,6	yes
19,7	3	2	1,50	UVF	-0,5	-0,5	yes
19,8	nr	nr		UVF	-0,4		
19,8	3,06	nr	1,77	WDXRF	-0,4	-0,4	yes
19,8	3,3	nr	1,91	UVF	-0,4	-0,4	yes
19,8	9,8	2	4,90	UVF	-0,4	-0,1	no
19,85	3,14	1	3,14	UVF	-0,4	-0,2	no
19,9	2,6	2	1,30	WDXRF	-0,4	-0,4	yes
20	nr	nr		UVF	-0,3		
20	1,9	2	0,95	UVF	-0,3	-0,5	yes
20	2,3	2	1,15	UVF	-0,3	-0,4	yes
20	3	95	0,03	UVF	-0,3	-0,9	no
20	3	nr	1,73	WDXRF	-0,3	-0,3	yes
20	4	2	2,00	UVF	-0,3	-0,2	yes

Reported sulphur content [mg·kg^{-1}]	Reported uncertainty [mg·kg^{-1}]	Coverage factor *k*	Calculated standard uncertainty [mg·kg^{-1}]	Analytical method	z score	zeta score	Uncertainty within range?
20,01	2,46	2	1,23	UVF	-0,3	-0,4	yes
20,1	2	2	1,00	UVF	-0,2	-0,4	yes
20,2	1,6	2	0,80	UVF	-0,2	-0,3	yes
20,2	2,2	nr	1,27	WDXRF	-0,2	-0,2	yes
20,2	2,4	2	1,20	UVF	-0,2	-0,2	yes
20,3	0,5	2	0,25	EDXRF-CON	-0,1	-0,3	no
20,3	0,7	2	0,35	UVF	-0,1	-0,3	no
20,3	1,6	2	0,80	UVF	-0,1	-0,2	yes
20,31	1,6	2	0,80	UVF	-0,1	-0,2	yes
20,34	2,2	nr	1,27	WDXRF	-0,1	-0,1	yes
20,43	2	2	1,00	UVF	0,0	-0,1	yes
20,44	0,78	2	0,39	UVF	0,0	-0,1	no
20,5	3,9	2	1,95	WDXRF	0,0	0,0	yes
20,55	2,53	2	1,27	UVF	0,0	0,0	yes
20,6	1,08	2	0,54	UVF	0,1	0,1	yes
20,7	0,1	nr	0,06	WDXRF	0,1	0,4	no
20,9	1,4	nr	0,81	UVF	0,2	0,4	yes
21	nr	nr		WDXRF	0,3		
21	2	2	1,00	UVF	0,3	0,4	yes
21	3	2	1,50	UVF	0,3	0,3	yes
21	3,1	2	1,55	WDXRF	0,3	0,3	yes
21,1	1,5	1	1,50	UVF	0,4	0,4	yes
21,2	0,84	nr	0,48	UVF	0,4	1,0	no
21,2	3,1	2	1,55	WDXRF	0,4	0,4	yes
21,25	1,43	nr	0,83	UVF	0,5	0,8	yes
21,35	0,54	nr	0,31	MONOCHROMATIC WDXRF	0,5	1,3	no
21,5	1	2	0,50	UVF	0,6	1,3	yes
21,5	4,5	2	2,25	UVF	0,6	0,4	no
21,6	0,6	0,98	0,61	WDXRF	0,7	1,3	yes
21,6	0,8	2	0,40	UVF	0,7	1,6	no
21,6	2,2	2	1,10	UVF	0,7	0,9	yes
21,66	1,6	2	0,80	UVF	0,7	1,2	yes
21,7	nr	nr		WDXRF	0,7		
22	1,5	nr	0,87	coulometric analysis	0,9	1,5	yes
22	2,8	2	1,40	WDXRF	0,9	1,0	yes
22	3,2	2	1,60	WDXRF	0,9	0,9	yes
22	4,5	nr	2,60	WDXRF	0,9	0,6	no
22	6	2	3,00	ISO 20847 - EDXR	0,9	0,5	no
22,27	0,96	2	0,48	UVF	1,1	2,4	no
22,4	3,6	2	1,80	WDXRF	1,2	1,0	yes
22,5	1,2	2	0,60	UVF	1,2	2,5	yes
22,6	4,5	2	2,25	EDXRF-CON	1,3	0,9	no
23	1,6	2	0,80	UVF	1,5	2,6	yes
23	2	nr	1,15	WDXRF	1,5	2,0	yes
23	2,3	nr	1,33	WDXRF	1,5	1,7	yes
23	10	nr	5,77	EDXRF	1,5	0,4	no
23,1	1,2	2	0,60	EDXRF-PXS	1,6	3,2	yes
23,67	0,32	2,45	0,13	UVF	1,9	5,6	no
23,8	3	2	1,50	EDXRF (oxinst method) ASTM D2 review	2,0	2,1	yes
23,9	2,3	2	1,15	WDXRF	2,1	2,7	yes
24	nr	nr		UVF	2,1		
24	3	2	1,50	UVF	2,1	2,2	yes
24	9,7488	0,982759	9,92	EDXRF-CON	2,1	0,4	no
24,86	0,8	nr	0,46	WDXRF	2,7	6,1	no
25	2	nr	1,15	UVF	2,8	3,5	yes
25	4	2	2,00	UVF	2,8	2,2	yes
25,08	2,7	2	1,35	EDXRF-PXS	2,8	3,1	yes
25,6	2,4	nr	1,39	UVF	3,1	3,4	yes
26	3	2	1,50	WDXRF	3,4	3,4	yes
26	10	2	5,00	EDXRF-CON	3,4	1,1	no

Reported sulphur content [mg·kg^{-1}]	Reported uncertainty [mg·kg^{-1}]	Coverage factor *k*	Calculated standard uncertainty [mg·kg^{-1}]	Analytical method	z score	zeta score	Uncertainty within range?
26,4	nr	nr		EDXRF Spectrometry Using Low Background Proportional Counter	3,6		
26,8	10	2	5,00	EDXRF-CON	3,9	1,3	no
28	3,6	2	1,80	WDXRF-INT	4,6	4,0	yes
28	10	nr	5,77	EDXRF-PXS	4,6	1,3	no
28,01	0,05	2	0,03	BDS 8428	4,6	13,6	no
28,25	5,26	nr	3,04	EDXRF-CON	4,8	2,5	no
29	0,06	2	0,03	EDXRF-CON	5,2	15,4	no
29	10	nr	5,77	EDXRF-PXS	5,2	1,5	no
30,03	1,8	2	0,90	UVF	5,8	9,0	yes
32	nr	nr		WDXRF	7,1		
39,5	2,4	nr	1,39	TXRF	11,7	12,7	yes
43	nr	nr		EDXRF-CON	13,8		
48	11	2	5,50	EDXRF-PXS	16,9	5,0	no
58	10	2	5,00	Wichbold burning, sulfur on IC	23,0	7,5	no
61,8	2	2	1,00	EDXRF-CON	25,3	36,2	yes
63,4	6,4	3	2,13	EDXRF-CON	26,3	19,5	no
91,5	3,672	3	1,22	EDXRF-CON	43,6	52,9	yes
106,3	9	2	4,50	EDXRF-CON	52,6	18,9	no

Annex 5: Individual certificate of performance

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP

Geel, 20 December 2006
Annex to D04-IM(2006)D/31699

IMEP-22 Individual certificate of performance

Issued to: TITLE FIRSTNAME SURNAME
ORGANISATIONNAME
DEPARTMENT
ADDRESS1
ADDRESS2
ZIP CITY
COUNTRY

Measurand and matrix: Total amount content of sulphur in petrol fuel
Your analytical technique: *TECHNIQUE*

Sulphur amount content values

Certified			Reported		
Value [mg/kg]	Uncertainty [mg/kg]	Coverage factor, *k*	Value [mg/kg]	Uncertainty [mg/kg]	Coverage factor, *k*
20.5	**1.1***	**2**	**LVALUE**	**U-REPORTED**	**K-REPORTED**

** This is an estimated expanded uncertainty with a coverage factor k=2, corresponding to a level of confidence of about 95 % (see the attached IMEP-22 material certificate for further details).*

Performance scores

Designation	Formula	Value	Score interpretation	
z score	$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}}$	**Z**	|z|≤2 2<|z|≤3 |z|>3	satisfactory questionable unsatisfactory
zeta score	$zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$	**ZETA**	|zeta|≤2 2<|zeta|≤3 |zeta|>3	satisfactory questionable unsatisfactory
Uncertainty within range ?	$u_{min} \le u_{lab} \le u_{max}$	**RANGE**	yes no	satisfactory unsatisfactory

In this table, x_{lab} is the measurement result you reported; X_{ref} is the certified reference value and u_{ref} the corresponding standard uncertainty; u_{lab} is the (recalculated) standard uncertainty you reported. The standard deviation for proficiency assessment $\hat{\sigma}$ is set to 1.63 mg/kg, based on EU legislation. The acceptable minimum and maximum standard uncertainties are set to 0.50 and 2.0 mg/kg, respectively. Please see the attached explanatory leaflet for further details.

Johannes van de Kreeke
IMEP-22 co-ordinator

Beatriz de la Calle
IMEP group leader

Institute for Reference Materials and Measurements
Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 682 • Fax: +32-(0)14-571 865
jrc-irmm-imep@ec.europa.eu • http://www.irmm.jrc.be

Annex 6: Explanatory notes to the certificate

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Explanatory notes on your certificate

«TITLE» «FIRSTNAME» «SURNAME»

How to interpret your score(s)?

«Explanation on individual z score»

«Explanation on individual zeta score»

«Explanation on individual magnitude of uncertainty»

Why these scores?

The z and zeta scores employed in this intercomparison are used in concordance with ISO 13528.[1] The IMEP-22 **z score** compares your deviation from the reference value with method performance requirements derived from European legislation. More precisely, it indicates whether you are able to operate your method for the analysis of sulphur in petrol, at the given concentration, in compliance with the relevant Directive 2003/17/EC[2]. According to the Directive, compliance should be examined on the basis of the analytical methods referred to in European standard EN 228:1999.[3] These methods concern ISO 20846[4] and ISO 20884[5] which both contain comparable reproducibility limits at the 95% probability level for the sulphur concentration at hand. The largest value of both was selected and devided by 2.8, and thus transformed into its reproducibility standard deviation s_R.[6] This was used as the standard deviation for proficiency assessment $\hat{\sigma}$, i.e. the denominator of the z score.

The **zeta score** is provided only if you reported an uncertainty. According to the International Harmonised Protocol[7] it provides an indication of whether your estimate of uncertainty is consistent with your deviation from the reference value. The interpretation is similar to the interpretation of the z score. An unsatisfactory score might be caused by underestimation of your uncertainty, but might also be due to a large deviation from the reference value.

An **additional check** is performed to give you an indication of the plausibility of your uncertainty estimate. Your standard uncertainty should fall in a range between a minimal required (u_{min}), and a maximal allowed (u_{max}) reported standard uncertainty. u_{min} is set to the standard uncertainty of the reference value. It is unlikely that you, as a participating routine laboratory, are able to measure the measurand with a higher accuracy than the reference laboratory itself. u_{max} is set equal to the reproducibility standard deviation s_R as derived from the Directive. Both u_{min} and u_{max} are rounded and set to 0.50 and 2.0 mg/kg, respectively. If your standard uncertainty $u_{lab} < u_{min}$ it is likely that you underestimate your uncertainty. If $u_{lab} > u_{max}$ your uncertainty exceeds maximum legislative requirements.

irmm
Institute for Reference Materials and Measurements

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 682 • Fax.: +32-(0)14-571 865
jrc-irmm-imep@ec.europa.eu • http://www.irmm.jrc.be

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Recalculate your scores

According to the International Harmonised Protocol, you can recalculate the scores applying your own requirements. The standard deviation for proficiency assessment $\hat{\sigma}$ used in this intercomparison is based on legislative requirements and thought to be fit for the purpose of most of the participants. If the purpose of your measurements is different, you may recalculate the z score with a $\hat{\sigma}$ fit for your purposes. In analogy, this consideration also holds for the maximal allowed reported standard uncertainty u_{max}, which is based on the same legislative requirements and may be altered as well.

How was your standard uncertainty calculated?

If you reported an uncertainty, the standard uncertainty was calculated by dividing the reported uncertainty by the coverage factor *k*. If you did not report a coverage factor, the reported uncertainty was considered as the half-width of a rectangular distribution. The standard uncertainty was then calculated by dividing this half-width by $\sqrt{3}$. This approach is in accordance with recommendations issued by Eurachem and CITAC[8].

References

[1] ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons
[2] Directive 2003/17/EC of the European Parliament and of the Council of 3 March 2003, amending Directive 98/70/EC relating to the quality of petrol and diesel fuels
[3] European standard EN 228:1999; Automotive fuels – Unleaded petrol – requirements and test methods
[4] ISO 20846:2004; Petroleum products - Determination of sulfur content of automotive fuels - Ultraviolet fluorescence method
[5] ISO 20884:2004; Petroleum products - Determination of sulfur content of automotive fuels - Wavelength-dispersive X-ray fluorescence spectrometry
[6] ISO 5725:1994; Accuracy (trueness and precision) of measurement methods and results
[7] The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories by M. Thompson *et al.*, *Pure and Applied Chemistry* (2006), **78**, 145–196
[8] Quantifying Uncertainty in Analytical Measurement, Eurachem/CITAC (2000)

Institute for Reference Materials and Measurements

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 882 • Fax: +32-(0)14-571 885
jrc-irmm-imep@ec.europa.eu • http://www.irmm.jrc.be

Annex 7: ILC participation

Intercomparison(s) designation	Intercomparison(s) designation
IIS (SGS Redwood)	ASTM
For each year we participate in the following interlaboratory comparisons: ASTM (39 samples) and INTA (15 samples)	ASTM Interlaboratory Crosscheck Program, Shell Correlation Shemes, Institute for Interlaboratory Studies, DNVPS International Round Robin Program
ASTM; Petro Lab GMBH; IIS	POLLAB-PETROL
IRMM, PETROLAB GMBH	Mol S.A. Hungary
Round Robin 2/2004 organized by Fortum Oil Research Technology, Finland. IRMM-IMEP-18.	Institut for Interlaboratory Studies, Spijkenisse, The Netherlands
RR Saybolt WCP, RR Saybolt-Russia, IMEP-18 Gasoil	IIS, DIN / FAM, IFP, IMEP-18, CEN TC19 WG27
SWIFT-WFD is funded by the European Commission	IIS, Spijkenisse, the Netherlands
IIS	BP ICPMS
irmm	core laboratory
POLLAB	SMPCS
IIS; IRMM, PETROLAB	RRT's organized by Total
IFP (Institut Francais du Petrole), IMEP 18	Pollab Petrol
INTERLABORATORY EXAMINATION	IIS
IMEP-18 , Pollab-Petrol	IRMM
NIVA, IMEP	SGS IIS, FAM Germany
Association of Analytikal Centers "Analitika" - member ILAC	BP Inter-Centre Precision Monitoring Scheme (ICPMS)
SGS IIS, FAM Germany	ASTM
Institute for Interlaboratory Study ND ,POLLAB PL	IIS
IIS	FAM Hamburg
"GAFTA", ""Hydro Agri", BSI Inspectorate, Estonian Customs.	Fachausschuss Mineralöl- und Brennstoffnormung (FAM)
Saybolt LP(Houston, USA) worldwideround robintest for Saybolt group of companies	Coomet - Russia via National Metrological Institute - Bulgaria
Institute for Interlaboratory Studies	IMEP
EC-JRC IRMM	UNICHIM
Institute for Interlaboratory Studies	Institute For Interlaboratory Studies, EC-JRC IRMM
BP ICPMS	IRMM; CEN; EI; ASTM
ASTM, IIS	IMEP-18
IRMM	IMEP 18, IIS04G03
Institute for Interlaboratory Studies	IIS
INTA (Instituto Nacional Tecnica Aeroespacial) IFP (Instituto Français du Petrole)	Bulgarian Accreditation Service - Executive Agency at the Ministry of Economy and Energy
IMEP-18	POLLAB
FAM Hamburg	IMEP
IMEP 18 - IRMM	DIN /Petrolab GmbH; IMEP-18
ASTM	IRMM IMEP-18, Energy Insitute EI/T401/2004
Collaborative trials	UNICHIM
IIs05B03, IIS05G01, IIS04G03, IMEP-18, IIS04G01, IIS04B02	IMEP-18; Inter-laboratory precision study ASTM D02.03
IRMM, (IMEP 18)	POLLAB
ASTM	IP/ESSO
POLLAB	ASTM, IIS, IFP interlaboratory comparisons
SABS Mapping program	POLLAB
SABS Mapping program	SGS IIS, German FAM
IIS, ELCS, ICPMS	IIS (Holland) and TOTAL(France)
IMEP 18	FAM
IMEP 18	Customs Technical Laboratory Prague
SGS Latvia Ltd.; A/S Ventamonjaks, Ventspils, Latvia	Instytute for Interlaboratory Studies, April 20, 2005
ASTM , IFP	ASTM, Institute for Interlaboratory Studies
Institute for Interlaboratory Studies (The Netherlands), Petrol-Pollab (Poland)	IRMM (round robin test of SY124 in gas oil), iis (Proficiency Test for Summer Gasoil)
POLLAB	POLLAB
	IIS

Annex 8: CRM usage

Certified reference material(s) designation
MidLevel Sulfur calibration set, AccuStandard, USA
Merck de
MBH
Sulfur 10 mg/kg in Mineral Oil, Analytical Service, Inc. is used as RM material, procuct Code SMO1C.
Accustandard D- 5453-ML-SET
Conostan
IIS
analytical reference materials international
PAC, ROFA
AccuStandards
FLUID
AR-6201(0,0011%m/m S - ultra low kerosene), AR-2041(0,053%m/m S - crude oil standard), Alpha Resources, Inc.
SRM 2723a from NIST; D-2622-LL-30X-4 from ISOSTANDARDS; SU-GO-497 from NORMA#R; S = 0.005% from CONOSTAN
NIST SRM 1616a - NIST SRM 1617a
CRM from MERK
Analytical Services, Inc. Code No. SDF1C - 30.0
Set of Calibration standards: Sulphor in Reference fuel-S-RF-I, ROFA Austria
NORMA, ROFA
Set of Calibration standards Sulpfur in reference fuel S-RF-I, Reference standard Sulfur in gasoline 150 +/- 25 mg/kg
Sulfur in Isooctane 10.0+-0.1 Accu Standard
Standards for Low-Level Sulfur Analysis, VHG Labs
0.25 -1000 ng/¿l , ANTEK Instruments, LP
NIST SRM 2299
Standard Reference Material 2724b, U.S. Department of Commerce, National Institute of Standards and Technology
SRM 2298; SRM2299 (NIST); D6428 (Isostandards Material)
NIST-2299
CRM BCR 106 Sulphur 0,502 % ± 0,008 % hm.
Dibutylsulfid - MERCK
The Woodlands
MBH Analytical LTD
Butyl Sulfide
NIST STM1624d and STM 2770
AccuStandard
Normar, Rofa
VHG Labs, Inc.; supplier SIA "Armgate", Latvia
18.2±2.1 Norma France
ASTM D5453 total sulfur by UV fluorescence - Thermo Electron Corporation USA
Sulfur in Isooctane, D-5453-ML-03, D-5453-ML-02, AccuStandard
CRM supplier is "MBH" from USA
AccuStandard Inc.
SDF10C, lot 121505, 0.0000 wt%;0.0015wt%;0.0050wt% Analytical Services Inc.
AccuStandard Inc.

Certified reference material(s) designation
Leco suitable standarts and SWMO-LT-IX-4; SWMO-LT-50X-4, SWMO-LT-400X-4
10ppm Sulfur in Gasoline Analytical Services inc
dibuthylsulphide, Merck - Germany
0.0020% Sulfur in Gasoline, MBH Analytical Ltd.
STD-12 laboratory sample
Acu standard
Sulphur Content for Diesel Fuel: 48.5 mg/kg (interval of confidence=4.1 mg/kg) , ROFA France
ROFA
Supplier IIS
NIST 2723a
Nist CRM 2294 from CROMLAB
NIST CRM's
AccuStandard Inc. Item Number STP-1X-4
OXFORD INSTRUMENTS
NIST
Series SMO8C(L) and (H) by Analytical Service
CRM and supplier Sulfur in Isooctane 20.0+/-0.2 AccStandard Inc.
CHIRON Norway
MBH 258XMN, MERCK CERTIPURE S
Amstandard Ldt
NIST 1624d and 2770
Sulfur in isooctane ; 10.0+-0.1 ; 50.03+-0.5 (supplier: Accustandard Inc.)
8 ppm & 25 ppm from ANALYTICAL SERVICES
NIST1616b, NIST 2723a, NIST 2770, NIST8771
Low level Sulfur Standard (5, 10, 30, 50 ppm)\ Sulfur Blank Standard - Supplier: AccuStandard Inc.
ITN
ULTRAstandard (di-n-butyl sulfide in toluene) - ULTRA Scientific
ULTRASTANDARD (di-n-butyl sulfide in toluene)
SU-GO-497 40 mg/kg
NORMALAB 18 +/- 2.1 mg/kg
AccuStandard Inc.
AccuStandard Inc.element:D-5453 Low Level Sulfur;supplier - Company Amstandard
FAM roudn robin sample
Sulfur 25 ppm in light mineral oil, FLUXANA HD Elektronik Accustandard Ink.
Sulfur in isooctane, Organic Standard Solutions International, LLC
SCP SCIENCE Canada; AlphaResources, Inc. USA;
AccuStandard Inc
Paragaon Scientific
NIST, BCR
France
For calibration D-5453-ML-SET, B4110036-41 . For validation STP+3X+4, B2010222

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IMEP-22 Sulphur in Petrol: Interlaboratory Comparison Report
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Abstract

EU Directive 2003/17/EC lays down requirements for the sulphur content in automotive petrol and provides criteria for appropriate methods of analysis to monitor compliance with these requirements. The sulphur content of automotive petrol is currently between 10 and 50 $mg \bullet kg^{-1}$, and will be limited to 10 $mg \bullet kg^{-1}$ as of 2009.

IMEP-22 studies whether the laboratories involved in petrol analysis in the frame of EU legislation are able to measure a sulphur content of 20.5 $mg \bullet kg^{-1}$. This value was certified by IRMM using a primary method of measurement. Most of the 128 participants were routine laboratories located in Europe, and the intercomparison is thought to be representa-tive for this group.

A satisfactory z score was obtained by 70% of the participants. These laboratories fulfilled the legislative requirements laid down in Directive 2003/17/EC. The unexpectedly large share of 30% questionable and unsatisfactory z scores indicates the presence of a discrepancy between the requirements of EU Directive 2003/17/EC and the performance of the average European routine laboratory.

Eighty-seven per cent of the participants had followed the invitation to report an estimate of their measurement uncertainty. A zeta score was calculated for these results, and it was tested whether this uncertainty was within range. Half of the participants obtained satisfactory z and zeta scores, and 39% also obtained an additional satisfactory rating for the magnitude of the reported uncertainty. These laboratories fulfilled both legislative and metrological requirements.

Several specific groups of laboratories participated in the frame of IRMM's support to EU policy. Customs laboratories were contacted via DG TAXUD and accredited laboratories were nominated by their accreditation bodies in the frame of the collaboration between IRMM and EA, the European Co-operation for Accreditation. In addition, laboratories from Acceding and Western Balkan countries participated in the frame of the IRMM support to the EU's CARDS programme.

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