EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

IMEP-18
Sulphur in Diesel fuel (gasoil)
Report to Participants

L. Van Nevel, I. Verbist, C. Harper, S. Bynens, P. Smeyers, Y. Aregbe, P. Robouch and P.D.P. Taylor
IRMM[1]

G. Turk, R. Vocke and W.R. Kelly
NIST[2] , USA

IMEP®

Report EUR 21765 EN

[1] European Commission, Directorate-General Joint Research Centre, Institute for Reference Materials and Measurements
[2] National Institute of Standards and Technology

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

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

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

E-mail: jrc-irmm-imep@cec.eu.int

Tel.: +32 (0)14 571 673
Fax: +32 (0)14 571 865

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

EUR Report 21765 EN
Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

Contents

Summary

The International Measurement Evaluation Programme (IMEP®) is an Interlaboratory Comparison scheme in support of EU policies (e.g. Consumer Protection and Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policy). It is founded, owned and co-ordinated by the IRMM, the European Commission's Joint Research Centre for Reference Materials and Measurements.
The aim of this interlaboratory comparison programme is to picture objectively the degree of equivalence and the quality of chemical measurements. Contrary to most other external quality assessment schemes, participating laboratories in IMEP® can compare their measurement results and uncertainty statements with external certified reference values, obtained completely independent from the participants' result. These reference values are required to demonstrate traceability and they should have a demonstrated and adequately small uncertainty, as evaluated according to international guidelines. Participants in IMEP® use their routine analytical procedures to measure the IMEP-certified test sample (CTS). Therefore they can assess the quality of their results on an international forum by comparing their values to the IMEP-reference values.

In order to meet the new EU air quality standards, car manufacturers are developing a new generation of engines. However S in fuels can impair the effectiveness of existing and emerging automotive technology (S acts as a catalyst poison). The recent published Directive 2003/17/EC intends to reduce the sulphur levels in fuels and states that in 2005 fuels with maximum sulphur amount contents of 50 and 10 $mg \cdot kg^{-1}$ need to be available on the market in the Member States. This report describes the interlaboratory comparison IMEP-18 that allows laboratories to measure a diesel material with a S certified amount content of (42.2 ± 1.3) $mg \cdot kg^{-1}$. The reference value was established by Isotope Dilution Mass Spectrometry and is the result of the BIPM/CCQM key comparison K-35 co-ordinated by NIST to which 4 national metrology institutes participated. In this way, national metrology measurement capability supports measurement capabilities of field laboratories. Measurement results were reported by 141 of the 154 registered laboratories. Customs laboratories were contacted via DG TAXUD and nominated accredited laboratories resulted from the IRMM-European Accreditation collaboration. Besides laboratories from Member States also laboratories from Acceding and Western Balkan countries participated (IRMM's CARDS support).

This report presents organisatorial details about the project. Participants' results are presented in a graphical way together with the reference value and are sorted according to different criteria based on the replies from the questionnaire from which also numerical information is included.

IMEP®

provides reference values with demonstrated traceability and demonstrated uncertainty, independent of the participants' results

invites participants to report results together with the best estimate of the expanded measurement uncertainty

enables result-oriented rather than procedure oriented evaluation of performance

demonstrates a degree of equivalence in measurement results on the international scene

IMEP®

Characteristics of IMEP®

Policy making and policy implementation aims at setting up a legal set of rules providing a maximum of consumer protection within healthy working and living environments and a prospering economy. In many cases implementation of international and national legislation is based on high quality chemical measurement results. Therefore laboratories need to be able to demonstrate that their mea-surement results are reliable, comparable and in compliance with legislation, international standards, and international recognition arrangements that support the free trade goal 'measured once, accepted everywhere'.

In support of this need, the Joint Research Centre - Institute for Reference Materials and Measurements (JRC – IRMM) operates for the European Commission the International Measurement Evaluation Programme (IMEP®), which focuses on the construction of an internationally structured measurement system. IMEP® is a metrological interlaboratory comparison tool publicly available to all laboratories. These laboratories can have different functions in the international measurement infrastructure. IMEP enables laboratories to assess their measurement performance and at the same time allows them to demonstrate their competence on a high quality level to accreditation, authorisation, and inspection bodies as well as to their regular customers.

In IMEP®, participating laboratories can compare their results with certified reference values. They receive the characterised IMEP certified test sample with undisclosed certified reference values. To guarantee the high metrological quality, the refe-rence measurements are performed by institutes with internationally demonstrated and mutually recognised measurement capabilities [1]. Therefore the certified reference values are completely independent from the participants' result. They are required to demonstrate traceability and they should have a demonstrated and adequately small uncertainty, as evaluated according to international guidelines. The underlying philosophy is that the best possible values will serve as reference and these are obtained from well-understood measurement processes in a complete transparent way rather than via a consensus approach.

IMEP® is a metrological Interlaboratory Comparison scheme publicly accessible. It guarantees the confidentiality with respect to the identity of its participants and their reported result. Participants in IMEP® measure the analytes under investigation applying their routine measurement procedures and analytical techniques. In IMEP®, laboratories have always been invited to state uncertainty estimates for their reported results. Contrary to most regular proficiency testing schemes, the IMEP® measurement performance criteria are not only set relative to the reported value, but also to the reported measurement uncertainty. IMEP® interlaboratory comparisons are organised in support of EU policies, therefore IMEP® is addressing different analytes in different matrices. Contrary to regular proficiency testing schemes, IMEP® interlaboratory comparisons are not offered on a regular basis for a specific analyte and matrix. IMEP® intends to picture the state-of-the-practice in measurement capabilities of laboratories at a specific moment in time. These specific features of the IMEP® programme make it a very valuable tool for international and European organisations or reference networks to verify measurement claims and monitoring the efficiency of multilateral arrangements.

A large number of laboratories participating in IMEP® have to comply with the ISO/IEC 17025 standard [2]. They need to meet the requirement of providing reliable measurement results within uncertainties. As laboratories are accredited against this standard, many of them need training to enable them to demonstrate measurement traceability, estimate uncertainty and perform validation. IRMM has already offered training activities to participants who request additional support after the completion of the respective IMEP® comparison. An example is the follow-up of IMEP-12, where underperforming laboratories agreed to assist in general case studies. Results of these activities can be found on the IMEP-EDUC website[3].

Further information about IMEP® including an overview of previous IMEP activities can be found on the IMEP® website[4]. All reports of previous IMEP® interlaboratory comparisons on amount contents of minor and trace elements in various matrices such as water, polyethylene, serum, sediments, car catalysts, wine and rice can be found overthere.

Collaboration with European Accreditation (EA)

By going for accreditation, laboratories prove their commitment to deliver the best quality in mea-surements and services. Accreditation is a way to demonstrate their technical competence to their customers. In addition the accreditation infrastructure is an important component of the European Acquis Communautaire regarding technical infrastructure.
In order to further improve the efficiency of accreditation in chemistry with respect to the evaluation and demonstration of the performance of laboratories, the EA and IRMM agreed to intensify their ongoing co-operation. A formal "letter of intent for co-operation" was signed by the Chairman of the EA and the director of IRMM in the beginning of 2001[5]. The EA-IRMM co-operation focuses on the chemical measurements and aims at improving the metrological basis of accreditation in chemistry. This will be mainly achieved by the organisation of interlaboratory comparisons using traceable reference values obtained in terms of high quality measurements applying the principles of metrology. Accredited laboratories need to meet the requirements, according to the ISO/IEC 17025 standard, of providing reliable measurement results within uncertainties. Recently this became a very important aspect in the collaboration agreement between IRMM and EA, because in general PT providers do not ask participants to report a measurement result within uncertainty. Therefore IMEP® serves as an unique tool for the National Accreditation Bodies to ensure compliance of their accredited laboratories with ISO/IEC 17025.
They may nominate laboratories to participate in IMEP®, in order to evaluate their performance against independent reliable reference values and request the laboratories to take appropriate corrective actions if needed.

Support function of IMEP®

The mission of IRMM is to promote a common European measurement system in support of EU policies, especially internal market, environment, health and consumer protection standards.
IMEP® contributes to this by providing support to EU policies and the chemical measurement infrastructure of the enlarged EU. IMEP® acts as a tool for validation of the proper implementation of the national measurement infrastructure.
By offering IMEP® to testing and calibration laboratories, IRMM supports the EU Member States by ensuring confidence in their national measurement system. IMEP® therefore enables to assess whether national measurement systems are in place to provide for an equivalent implementation of directives across an enlarged EU. To specific groups of laboratories this support can be orga-nised in the frame of collaboration agreements (EA) or specific support programmes (IRMM's CARDS support).
Another way to support the chemical measurement infrastructure, is to link, when possible, laboratories situated on the different levels of the international measurement infrastructure:
- national metrology instritutes at BIPM/CIPM level,
- national reference laboratories via EUROMET
- routine testing laboratories via IMEP.

This is realised by using the same sample material in the various interlaboratory comparison programmes organised on the different levels.

EU legislation and IMEP-18

Directive 2003/17/EC[6]

The revision of Directive 98/70/EC[7] as published in the Official Journal in March 2003, was necessary in order to meet the requirements of Community air quality standards and related objectives and in order to incorporate additional specifications to complement those mandatory specifications already laid down in Directive 98/70/EC. A reduction of the sulphur content of petrol and diesel fuels was identified as a means of contributing to the achievement of those objectives.

The adverse effect of sulphur in petrol and diesel fuels on the effectiveness of catalytic exhaust gas after-treatment technologies is well established for road vehicles. Road vehicles are increasingly reliant upon catalytic after-treatment devices to attain the emission limits laid down in Council Directive 70/220/EEC[8] (measures to be taken against air pollution by emissions from motor vehicles) and Council Directive 88/77/EEC[9] (measures to be taken against the emission of gaseous and particulate pollutants from compression ignition engines for use in vehicles, and the emission of gaseous pollutants from positive ignition engines fuelled with natural gas or liquefied petroleum gas for use in vehicles).

Accordingly a reduction in the sulphur content of petrol and diesel fuels is likely to have a larger impact on exhaust emissions than changes to the other fuel parameters. Therefore introduction of fuels with a maximum sulphur content of 10 $mg \cdot kg^{-1}$ will improve the fuel efficiency attainable with new, emerging vehicle technologies and should lead to significant reductions in emissions of conventional air pollutants when used in existing vehicles. These benefits will compensate for the increased emissions of CO_2 associated with the production of lower sulphur petrol and diesel fuels. The directive states that it is appropriate to lay down measures ensuring the introduction and availability of fuels with a maximum sulphur content of 10 $mg \cdot kg^{-1}$. The widespread availability of fuels with a maximum sulphur content of 10 $mg \cdot kg^{-1}$ will provide a basis for automobile manufacturers to make significant additional progress towards improving the fuel efficiency of new vehicles.

Therefore the directive prescribes that it is necessary to ensure that sufficient quantities of petrol and diesel fuels with a maximum sulphur content of 10 $mg \cdot kg^{-1}$ are available from 1 January 2005 on an appropriately balanced geographical basis in order to permit the free circulation of new vehicles requiring these fuels whilst ensuring that CO_2 emissions reductions from new vehicles outweigh those additional emissions associated with the production of these fuels. The complete penetration of petrol and diesel fuels with a maximum sulphur content of 10 $mg \cdot kg^{-1}$ should be provided for from 1 January 2009 in order to allow the fuel manufacturing industry enough time to make the necessary investments to adapt its production plans. In addition, the full introduction of petrol and diesel fuels with a maximum sulphur content of 10 $mg \cdot kg^{-1}$ from 1 January 2009 will reduce emissions of conventional pollutants from the existing fleet of vehicles leading to an improvement in air quality, whilst ensuring that there is no overall increase in greenhouse gas emissions. A community target of 120 $g \cdot km^{-1}$ CO_2 emissions for the average vehicle is aimed at.

The sulphur amount content in respectively unleaded petrol and diesel fuel is summarised in Table 1.

Table 1: Legislated Sulphur amount content in Petrol and Diesel fuels

	Petrol (Annex III - 2003/17/EC)	Diesel fuel (Annex IV - 2003/17/EC)
	Sulphur content (Maximum Limit)	
01-01-2005 to 01-01-2009	50 $mg \cdot kg^{-1}$ 10 $mg \cdot kg^{-1}$	50 $mg \cdot kg^{-1}$ 10 $mg \cdot kg^{-1}$
After 01-01-2009	10 $mg \cdot kg^{-1}$	10 $mg \cdot kg^{-1}$

According to the definitions: ‘diesel fuels' means gas oils used for self-propelling vehicles as referred to in Directive 70/220/EEC and Directive 88/77/EEC. The terminology 'petrol' means any volatile mineral oil intended for the operation of internal combustion positive-ignition engines.

Concerning monitoring compliance and reporting, the directive states that it is appropriate to provide for a uniform system of fuel quality monitoring or national systems that ensures results of equivalent confidence and for systems of reporting in order to assess compliance with the mandated environmental fuel quality specifications.
Member States shall monitor compliance with the requirements of Articles 3 and 4 of the directive 98/70/EC, in respect of petrol and diesel fuels, on the basis of the analytical methods referred to in European standards EN 228:1999[10] for petrol and EN 590:1999[11] for diesel respectively. Member States may adopt the analytical methods specified in replacement EN 228:1999 or EN 590:1999 standards, as appropriate, if they can be shown to give at least the same accuracy and at least the same level of precision as the analytical methods they replace.

IMEP-18 in support of the directive 2003/17/EC

IMEP-18 provides to the participating laboratories a diesel material with a S certified amount content of 42.2 (1.3) $mg \cdot kg^{-1}$. This diesel material is appropriate for the purpose as the concentration level of the Sulphur in the diesel falls within the limits as prescribed in the directive (2003/17/EC) from 1th of January 2005 onwards. The material represents a “real-life” sample that each laboratory involved in this type of analysis could measure on a regular basis. IMEP-18 enables laboratories to assess their measurement performance and at the same time allows them to demonstrate their competence for the analysis of S in diesel for the given concentration range. Participants were informed prior to the Interlaboratory Comparison of a nominal Sulphur content of 50 $mg \cdot kg^{-1}$ (Annex 3, Announcement letter). This report presents results (in graphical form) from all participants in IMEP-18, in a graphical form.

IMEP-18 in support of the chemical measurement infrastructure

Over the past few years, the International Committee for Weights and Measures (CIPM), the guar-dian of the International Measurement System (the SI), has taken several initiatives to improve the equivalence of chemical measurements worldwide. In October 1999, IRMM and other National Metrology Institutes signed the Mutual Recognition Arrangement (MRA), [12]. The MRA enables National Metrology Institutes (NMIs) to demonstrate their measurement capability by participating in key comparisons and pilot studies.
The material as used in IMEP-18 was also used for a key comparison of the Consultative Committee of Amount of Substance of the CIPM, (CCQM-K35). Four signatories of the MRA, participated using Isotope Dilution Mass Spectrometry as the analytical technique. The derived consensus value from this key comparison is used as certified reference value of IMEP-18. Results of this key comparison will be accessible via the Bureau International des Poids et Mesures (BIPM) web-site [13].
In addition, this material was used in the EUROMET 785 interlaboratory comparison organised for reference laboratories. Results are available on the EUROMET website[14].

Hence IMEP-18 participants can compare their results with the results of laboratories that represent their country at the international measurement structure level and vice versa.

IMEP-18: S in diesel fuel (gasoil)

The IMEP-18 material

The IMEP-18 Certified Test Sample (CTS) was a diesel fuel material available in amber glass ampoules, each one containing about 10 ml of diesel. The material consists of a commercial grade "No. 2-D" distillate fuel oil that was prepared by mixing the reference materials NIST SRMs 1624d (1162 grams) and NIST SRM 2723a (143970 grams) for a target concentration of 42 $\mu g \cdot g^{-1}$.
The material was offered by NIST for use in IMEP-18 and it will be commercially available as NIST Reference Material SRM 2770.

Homogeneity testing was done by WDXRF (Wavelength Dispersive X-ray Fluorescence Spectrometry) on 2 subsamples (3.5 mL) of 24 ampoules, randomly selected from the prepared batch. The measured data was subjected to analysis of variance using the ANOVA, single Factor function[15]. Heterogeneity was quantified [16]. Between bottle variation was found to be less than or equal to 0.8% which is negligible compared to the quality requirements set for evaluating IMEP-18 results. Based on past experience for CRMs certified for S in diesel [17,18], the material is expected to be stable during the duration of this study. Further monitoring of the stability of this material will be performed by NIST (USA).

The CTS arrived at IRMM in February 2004 (Sender: NIST-USA). The 400 ampoules were stored in the dark, in a safety cupboard for chemicals placed in a ventilated room at room temperature. They remained there until dispatch to the participants.

The IMEP-18 Certified Reference value

The certified reference value of IMEP-18 (Table 2) is the BIPM CCQM K35 key comparison reference value (KCRV). This BIPM CCQM key comparison was organised by NIST with the same material as for IMEP-18 and to which besides IRMM, three National Metrology Institutes (NMIs) participated (BAM (D), NIST (USA) and LGC (UK)). All four participants reported a value within uncertainty based on Isotope Dilution Mass Spectrometry (either High Resolution Isotope Dilution Inductively Coupled Plasma Mass Spectrometry or Isotope Dilution Thermal Ionisation Mass Spectrometry). The KCRV and corresponding uncertainty was obtained by applying the Mixture Model median as robust estimate. [19]

All CCQM K35 participants agreed that the KCRV could be used as IMEP-18 certified reference value. Details about the institutes involved are listed as IMEP-18 reference laboratories in Table 3.

As signatories of the Mutual recognition agreement (MRA) [12], NMIs demonstrate their measurement capabilities by participating in key comparisons and pilot studies organised by the BIPM. NMIs support routine laboratories in their country with expert advice and calibration services, and may have a stated responsibility to assure that measurements are traceable. Results of key comparisons are accessible via the BIPM web-site [13].

Note that the certified value on the NIST certificate (Annex 3) is based upon NIST IDMS measurements. These are the same measurement results which were submitted to the CCQM K-35 study.

Table 2: IMEP-18 Certified reference value

analyte	certified value in $mg \cdot kg^{-1}$	expanded uncertainty in $mg \cdot kg^{-1}$ U, k=2
Sulphur	42.2	1.3

Table 3: IMEP-18 Reference laboratories

Logo	Address	Contact
	**European Commission – Joint Research Centre Institute for Reference Materials and Measurements Isotope Measurement Unit Retieseweg 111 B-2440 Geel Belgium**	http://www.irmm.jrc.be/imep/
	**National Institute of Standards and Technology 100 Bureau Drive Gaithersburg MD 20899-3460 USA**	http://www.nist.gov
	**Federal Institute for Materials Research and Testing Unter den Eichen 87 D-12205 Berlin Germany**	http://www.bam.de
	**Laboratory of the Government Chemist Queens Road Teddington Middlesex TW11 0LY Great Britain**	http://www.lgc.co.uk

Laboratory performance assessment in IMEP-18

Laboratories using routine methodologies are not expected to reach the same level of precision as National Metrology Institutes using Isotope Dilution Mass Spectometry. Hence the acceptable range around the IMEP-18 certified reference value will be larger than the IMEP-18 certified range. It is therefore necessary to define a 'fit-for-purpose' quality requirement needed for the performance assessment of participating laboratories.

Setting the quality requirement for performance evaluation: information provided by EU legislation

According to the directive 2003/17/EC, "Member states may adopt the analytical methods specified in the replacement EN 590:1999 standard, as appropriate, if they can be shown to give at least the same accuracy and at least the same level of precision as the analytical methods they replace."

The norm EN 590:2004 [11] indicates three ISO standards that describe methodologies for S analysis in the, for IMEP-18, applicable concentration range: EN ISO20846 [20] (Ultraviolet fluorescence method), EN ISO 20847 [20] (Energy-dispersive X ray fluorescence spectrometry) and EN ISO 20884 [20] (Wavelength dispersive X-ray fluorescence spectrometry). For lower S concentration levels (10 $mg \cdot kg^{-1}$), the EN ISO 20847 is not used. Moreover a note indicates that in cases of dispute concerning the S content, the EN ISO 20847 is unsuitable as an arbitrary method. Therefore this method will not be taken into account for the quality requirement setting for performance assessment evaluation.

According to the latter standards, the precision is linearly related to the S concentration (Table 4). The required precisions presented in Table 5 are calculated using the certified sulphur content (42.2 ± 1.3) $mg \cdot kg^{-1}$. The final quality requirement for performance evaluation is thus obtained by adding quadratically the quantified uncertainty of the certified value (k=1) to the estimated/expected precision of the respective methodology.

(e.g. for UVF : $\sqrt{\left(\frac{0.65}{42.2}\right)^2 + \left(\frac{5.85}{42.2}\right)^2} * 100 = 14\%$)

Table 4: Precision data/reproducibility requirements derived from the relevant ISO standards

ISO Standard	Precision data/reproducibilities	
ISO 20846	1.12+ 0.1120*X	(for S content from 3 to 60 $mg \cdot kg^{-1}$)
ISO 20884	1.9 + 0.1201*X	(for S content from 5 to 60 $mg \cdot kg^{-1}$)

Table 5: Total calculated required precision

ISO Standard	Technique	Required Precision ($mg \cdot kg^{-1}$)	%
ISO 20846	UVF	5.8	14
ISO 20884	WDXRF	7	16.5

The standard deviation/precision directly calculated using the average of all reported results for the respective technique in IMEP-18 confirm the realistic estimate of precision presented earlier.(Table 6)

Table 6 : Precision requirements based on the average of all IMEP-18 results reported for the analytical technique.

Analytical Technique	Number of IMEP-18 results	Precision required ($mg \cdot kg^{-1}$)
UVF	40	5.8
WDXRF	28	7.8

For the purpose of this project, a conservative approach was selected for setting the quality requirement for performance evaluation. Based on the precision requirements for the methods covered by the given ISO standards, the acceptable range around the certified value was rounded from either 14 or 16.5 %, depending on the methodology, to 20 %. This will correspond (as described in the following paragraph) with a performance assessment criterion e.g. for the *z* or *zeta*' score to be equal to 2.
The 'fit-for-purpose' quality requirement hence is set to 10% deviation from the certified value ($0.1\,X_{ref}$).

Performance statistics

As explained in previous paragraph, for IMEP-18, the quality requirement was set based on information available in legislation. This quality requirement can hence be interpreted as an enlarged uncertainty of the certified reference value accor-ding to Equation 1 and which gives for IMEP-18:

$$U = k * u = 2 * 0.1 X_{ref} = 20\% \quad \text{Equation 1}$$

$$\downarrow$$

$$u = 0.1 X_{ref} = 10\ \% \quad \text{Equation 2}$$

Where:

U	The quality requirement expressed as expanded uncertainty
u	The quality requirement expressed as combined uncertainty
k	The coverage factor
X_{ref}	The certified reference value

The quality requirement is derived from measurement methodology which has been submitted to method validation and for which the results are distributed normally. Therefore the coverage factor *k* can be set to 2.

Scoring is the method of converting a participants' raw result into a standard that adds judgmental information about performance[21]. Different perfor-mance assessment criteria/scores are offered in IMEP-18. In addition to the percent difference, IMEP-18 also supplies a *z*-score and a *zeta'* score. The *z*-score is the score that proficiency testing participants are most familiar with seen the wide applicability and acceptance. However since it is the first time that IMEP® offers some of this information, an overview of the different performance criteria/scores in use for IMEP-18 are presented in the next paragraphs.

Percent difference [22, 23]

The 'Percent difference' is expressed using Equation 3:

$$D\% = \frac{(x - X_{ref})}{X_{ref}} * 100 \qquad \text{Equation 3}$$

where:

$D\%$	Percent difference
x	The participants' result
X_{ref}	The reference value

The performance assessment criterion 'Percent difference' discriminates between satisfactory or unsatisfactory results according to the following:

$|D\%| \leq 20\%$ Satisfactory

$|D\%| > 20\%$ Unsatisfactory

***z*-score** [22, 23, 24]

The participants' result is converted into a *z*-score according to Equation 4

$$z = \frac{(x - X_{ref})}{\sigma_p} \qquad \text{Equation 4}$$

Where:

z	The *z*-score
x	The participants' result
X_{ref}	The reference value
σ_p	The fitness-for-purpose based standard deviation for proficiency testing assessment [23,24]

In the case of IMEP-18, σ_p=0.1 X_{ref} which is the quality evaluation requirement based on the legislation and X_{ref} is the certified reference value.

Therefore the formula applicable for IMEP-18 reads as follows (Equation 5):

$$z = \frac{(x - X_{ref})}{(0.1\, X_{ref})} \qquad \text{Equation 5}$$

Where:

z	The *z*-score
x	The participants' result
X_{ref}	The reference value
$0.1\, X_{ref}$	The quality requirement for IMEP-18 (10% deviation from the reference value)

The performance assessment criterion '*z*-score' discriminates between satisfactory, questionable or unsatisfactory results according to the following:

$|z| \leq 2$ satisfactory

$2 < |z| \leq 3$ questionable

$|z| > 3$ not satisfactory

***Zeta*-score and the modified *zeta* score (*zeta'*)** [21, 23]

The *zeta*-score according to the definition given in ISO/DIS 13528[23] and the VAM publication[21], takes also into account the uncertainty reported by the participant. The following formula applies (Equation 6):

$$zeta = \frac{x - X_{ref}}{\sqrt{u_x^2 + u_X^2}} \qquad \text{Equation 6}$$

where:

$zeta$	The zeta-score
x	The participants' result
X_{ref}	The reference value
u_x	The combined uncertainty associated with the participants' result
u_X	The combined uncertainty associated with the reference value

The performance assessment criterion '*zeta*-score' discriminates between satisfactory, questionable or unsatisfactory results according to the following:

$|zeta| \leq 2$ satisfactory

$2 < |zeta| \leq 3$ questionable

$|zeta| > 3$ not satisfactory

According to ISO/DIS 13528 [23] *Zeta*-scores can be used instead of *z*-scores in cases where an effective system is in operation for validating laboratories' own estimates of the standard uncertainties of their results. However when no such system is in operation, *zeta*-scores shall be used in conjunction with *z*-scores as an aid of improving the performance of laboratories. The latter is the approach as followed in IMEP-18 because it might contribute to motivate laboratories to look in detail to the establishment of a correct uncertainty budget for their measurements.

However in the case of IMEP-18 equation 6 as such will never be used because IMEP laboratories do not compare their result with the combined uncertainty of the reference value. They are allowed to compare their results with the quality requirement interpreted as combined uncertainty. This quality requirement is for IMEP hence the 'fit-for-purpose based standard deviation for proficiency assessment' σ_p which equals 0.1 X_{ref} [23, 24].

Therefore the equation for the *zeta*-score as described, needs to be modified for use in IMEP. The modified *zeta*-score (*zeta*') is given by equation 7:

$$zeta' = \frac{x - X_{ref}}{\sqrt{u_x^2 + \sigma_p{}^2}} \qquad \text{Equation 7}$$

For IMEP-18, Equation 7 transforms in Equation 8 since σ_p = 0.1 X_{ref} :

$$zeta' = \frac{x - X_{ref}}{\sqrt{u_x^2 + (0.1\,X_{ref})^2}} \qquad \text{Equation 8}$$

where:

zeta'	The modified zeta-score
x	The participants' result
X_{ref}	The certified reference value
u_x	The combined uncertainty associated with the participants' result
$0.1\,X_{ref}$	The quality requirement for IMEP-18 (10% deviation from the reference value)

The performance assessment criterion for the modified *zeta*-score, the '*zeta'*-score', discriminates in the same way as the '*zeta*-score' between satisfactory, questionable or unsatisfactory results according to the following:

|*zeta'*| ≤ 2 satisfactory
2 < |*zeta'*| ≤ 3 questionable
|*zeta'*| > 3 not satisfactory

Transforming reported uncertainties into combined uncertainties.

Seen the fact that equation 8 propagates combined uncertainties, the following approach was selected in order to convert the reported uncertainties into combined uncertainties.

For laboratories that reported a coverage factor *k*, the combined uncertainty was calculated by dividing the reported uncertainty (assumed to be an expanded uncertainty) by the *k* factor reported.

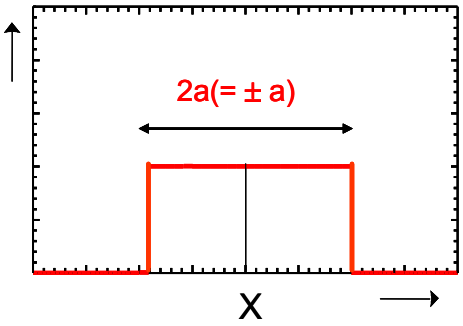
For laboratories who did not report a *k* factor, the following approach was used. When results were reported as X ± a without further explanation about the reported uncertainty, it is assumed that the result is reported as a rectangular distribution. (Figure 1). In order to be able to propagate the reported uncertainty into the formula as given for the zeta'-score, the reported range (a) was converted into the standard deviation according to the following equation (Equation 9). [25] The rectangular distribution is hence transferred into a normal distribution. The resulting standard deviation can now be propagated with the fit-for-purpose criterion (0.1 X_{ref}) which is assumed to be normally distributed.

$$u_x = a/\sqrt{3} \qquad \text{Equation 9}$$

where:

u_x	Standard deviation, combined uncertainty associated with the participants' result
a	Reported uncertainty

Figure 1: a rectangular distribution



IMEP-18 individual certificate

IRMM has issued individual certificates to each participant in IMEP-18. On this certificate, the reported result, the certified reference value for the S amount content in the diesel material, and as performance criteria/scores, the percent difference, the z-score and the modified zeta score were given. A copy of an empty individual certificate is presented in Annex 3 - figure 9.

IMEP-18 regional co-ordinators

Table 7. Regional Co-ordinators for IMEP-18.

Institution/Organisation	Country
NATA	AUSTRALIA
INMETRO	BRAZIL
National Center of Metrology	BULGARIA
Chinese Research Academy of Environmental Sciences	CHINA
State General Laboratory	CYPRUS
Czech Metrology Institute	CZECH REPUBLIC
Danish Institute of Fundamental Metrology	DENMARK
University of Tartu	ESTONIA
Bureau National de Metrologie	FRANCE
Aristotle University of Thessaloniki	GREECE
National Office of Measures	HUNGARY
Semiconductor Physics Institute	LITHUANIA
Centro Nacional de Metrologia	MEXICO
University of Warsaw	POLAND
National Institute of Metrology	ROMANIA
PSB Corporation	SINGAPORE
Slovak Institute of Metrology	SLOVAKIA
Metrology Institute of the Rep of Slovenia	SLOVENIA
CSIR National Metrology Laboratory	SOUTH-AFRICA
SP, Chemistry & Materials Technology	SWEDEN
NMI - Van Swinden Laboratorium	THE NETHERLANDS
Turkish Accreditation Agency	TURKEY
Laboratory of the Government Chemist	UNITED KINGDOM

In view of the collaboration agreement with European Accreditation, European Accreditation (EA) appoints an EA contact person (the EA-coordinator) whose function is to act as mediator between the National Accreditation Bodies and the IMEP co-ordinator.
For IMEP-18, Mrs. Lorraine Turner from UKAS (United Kingdom) was taking appointed for this function. She contacted the National Accreditation Bodies in order to nominate accredited laboratories for participation in IMEP-18.

In addition, over the years a network of Regional Co-ordinators (RCs) was established for IMEP. RCs are typically people that belong to institutions which are directly involved in chemical measurements and preferably experienced and competent in metrological matters, with profound knowledge of the measurement systems of their country or region. The tasks of the RCs are to act on behalf of IRMM in order to liase with participants and administer locally in each comparison, while bridging linguistic, cultural differences and taking into account any local particularities. The general list of RCs can be found on the IMEP website [4]. Seen the fact that IMEP is addressing different matrices, before every planned IMEP ILC, all RCs are contacted to see if they can act as contact person for the particular IMEP ILC to be organised. The active regional co-ordinators for IMEP-18 are given in Table 7.

IMEP-18 Organisatorial details

The planning of the comparison was performed at the beginning of 2004. After informing the regional co-ordinators of the planned activity, the list of IMEP-18 RCs was established and published on the IMEP website.

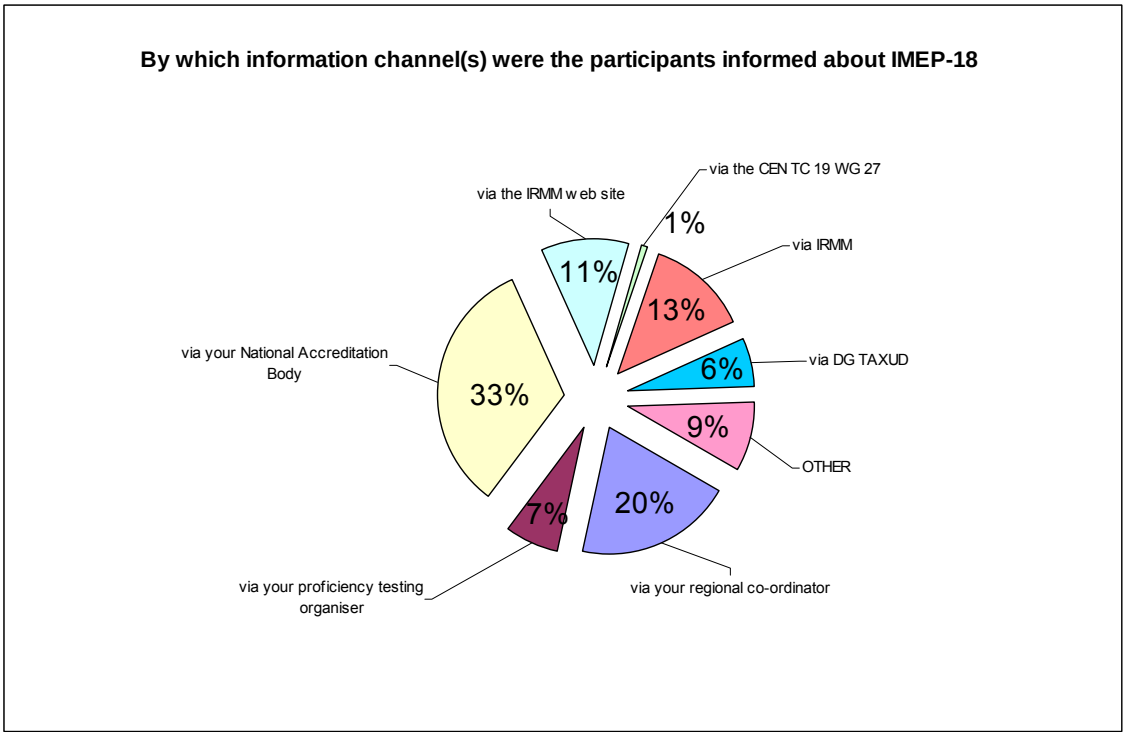
IMEP-18: Contacting laboratories of interest

An announcement letter was prepared for the EA co-ordinator to be sent to the National Accreditation Bodies in the frame of the IRMM-EA collaboration agreement. A general announcement letter (Annex 3) was placed on the IMEP website. This information was sent to the regional co-ordinators for distribution to the relevant laboratories in their country including those that expressed interest for this type of matrix to IRMM prior to the activity. Other laboratories that expressed interest in this type of analysis were contacted directly by IRMM. A commercial proficiency testing organiser volunteered to send the announcement letter to the laboratories in his scheme.
Also laboratories involved in the CEN TC19 working group 27 were contacted by their contact person. In addition, in collaboration with DG-TAXUD, customs laboratories involved in the GCL-action 2 activity were informed about the IMEP-18 initiative.

For the first time in IMEP, interested laboratories could register on-line. In order to facilitate this, guidance documents were prepared (Annex 3). As a result, 154 laboratories from 36 countries registered. (Table 9). From these, 71 laboratories enrolled as EA nominated laboratories, 15 via the DG Taxud collaboration and hence 69 as regular IMEP-18 participants. (One laboratory registered both as EA and DG Taxud laboratory.)
In the frame of the IRMM support to candidate countries and Balkan (CARDS), IMEP opens its activities to laboratories from these countries. In IMEP-18, 26 laboratories from Bulgaria, Croatia, Romania, Serbia-Montenegro and Turkey registered.

At reporting stage, laboratories were asked through which information channels they were informed about the IMEP-18 activity. The following pie-chart sheds light on the distribution, (Figure 2) Multiple replies were possible.

Figure 2: By which information channel(s) were the participants informed about IMEP-18



Diesel fuel CTS material mailing

After the collection of the registration forms, the CTS was distributed to the participants in June 2004.
Individual boxes were prepared at IRMM. These contained the CTS material (2 ampoules of 10 ml) and relevant documents (see Annex 3) which were:

- **An info letter**: giving information relevant to the comparison, pointing out timings and practicalities concerning the on-line reporting including the individual identification number (Password Key).
- **The online reporting guideline**: issued to show how to report results and complete the Questionnaire information electronically through the IMEP web-site
- **The sample receipt form** to acknowledge that the CTS arrived at its destination in good order

The CTS were sent using express mail when possible. For those countries where a regional co-ordinator was identified, the individual boxes were sent to the regional co-ordinator as one batch. The regional co-ordinators were asked to distribute the boxes in their country by the regular national mai-ling system. All other laboratories received their packages on individual basis.

Due to the nature of the material (dangerous goods in excepted quantities), not all countries could be covered by express mailing. For those countries that could receive their package by express mailing, no particular problems were observed. For the other countries, the packages were sent to the laboratories by regular flights. Therefore, IMEP contacted every laboratory concerned in order to identify the nearest airport and laboratories were asked assistance for customs clearance. For some countries organising this transport including customs clearance took some time. In order to give all laboratories sufficient time for measuring the Certified Test Samples, it was decided to shift the initial deadline for reporting (9th September 2004) to 9th November 2004.

Additional samples were supplied to 2 laboratories on request.

Data collection

All IMEP-18 participants reported their measurement results online through the IMEP web-site.

This was enabled by a newly created Oracle-based database. The database was developed in-house at IRMM. IMEP-18 was the first interlaboratory comparison that was organised using this new electronic tool. As a consequence, the management of large amounts of data is faciliated hence reducing the number of transcription errors. Nevertheless, as last step of the reporting procedure, laboratories were asked to print the report form and return it to IRMM signed. Only after receipt of the signed copy, the online result was validated. IMEP accepted and implemented any corrections of submitted results until the reporting deadline.

An example of the IMEP-18 report form is given as figure 11 in Annex 3.

In addition to the result report form also a questionnaire was offered (figure 12 in Annex 3). The purpose of this questionnaire was to enable the organiser to correlate measurement performance with other factors such as analytical technique used, self-assessment of experience, accreditation and to present this to the participants in a graphical form. Additional information gained from this questionnaire will serve to identify the state-of-the-practice in S analysis in road transport fuels and will be used to develop future IMEP interlaboratory comparisons.

All reported information is treated in a confident way. This means that IMEP does not reveal the link between identity of the laboratory and the reported results or information.

Evaluation of reported results

Participation in IMEP-18: country of origin

Samples were distributed to all 154 registered laboratories. Measurement results were reported by 141 participants (92% of the registered laboratories) from 36 countries. For EA, results were reported by 64 laboratories, from the DG TAXUD all 15 labs reported results and 63 laboratories reported as general IMEP-18 laboratories (one laboratory reported both as EA and DG Taxud laboratory). Country selective information about sample mailing (registration numbers) and result reporting is given in Table 9.

Measurement unit

Laboratories were free to report the measurement unit they routinely use in their laboratory. An overview is given in Table 8.
The majority of laboratories reported in $mg \cdot kg^{-1}$ either $\mu g \cdot g^{-1}$ (89%).

The other laboratories reported in volumetric units $mg \cdot L^{-1}$ either $\mu g \cdot mL^{-1}$ (11%). For the graphical displays all results are hence converted into $mg \cdot kg^{-1}$. The density of the material was determined to be 0.817 ± 0.001 in $mg \cdot mL^{-1}$ (23°C). The IMEP-18 certified reference value in the cor-responding unit is given in the last column of Table 8.

Table 8 : The measurement unit as reported in IMEP-18

Measurement unit	Number of particpants	%	IMEP-18 Certified reference value
$\mu g \cdot g^{-1}$	27	19	42.2 ± 1.3 $\mu g \cdot g^{-1}$
$mg \cdot kg^{-1}$	98	70	42.2 ± 1.3 $mg \cdot kg^{-1}$
$\mu g \cdot mL^{-1}$	6	4	34.5 ± 1.1 $\mu g \cdot mL^{-1}$
$mg \cdot L^{-1}$	10	7	34.5 ± 1.1 $mg \cdot L^{-1}$
Total	**141**	**100**	

Table 9: IMEP-18 number of registered and reporting laboratories per country

Country	Registered laboratories	Results received	Country	Registered laboratories	Results received
Austria	3	3	Latvia	1	1
Belgium	4	4	Lithuania	2	2
Brazil	6	4	Mexico	2	2
Bulgaria	7	6	The Netherlands	3	3
China	5	4	Norway	1	1
Croatia	4	4	Poland	17	15
Cyprus	2	2	Portugal	3	3
Czech Republic	11	11	Romania	2	2
Denmark	3	3	Serbia-Montenegro	7	6
Estonia	7	7	Slovakia	4	3
Finland	1	1	Slovenia	2	2
France	9	7	South Africa	1	1
Germany	10	10	Spain	5	4
Greece	2	2	Sweden	3	3
Hungary	6	6	Switzerland	2	2
Ireland	2	2	Turkey	6	6
Italy	1	1	United Arab Emirates	1	1
Kazakhstan	1	1	United Kingdom	8	6
			Total	154	141

IMEP graphical displays

Figure 3 shows how results are displayed in IMEP®. All participants' results of IMEP-18 are plotted in ascending order against the certified reference value (is middle of the reference range). All reported results are included in the graphs. The scale of the graphs is chosen for convenience (± 50% of the middle of the reference value). No results are excluded in IMEP®, but those that are off-scale are presented in textboxes on each graph.

A set of general graphs was prepared where the reported results (in $mg \cdot kg^{-1}$) were sorted according to e.g. region, the criterion 'self-declared experience level', 'accreditation, authorisation, certification status of the laboratory for this type of analysis', 'the analytical technique used' and the 'quality management system in use in the laboratory' based on information from the questionnaire. All graphical displays are plotted in Annex 1 of this report.

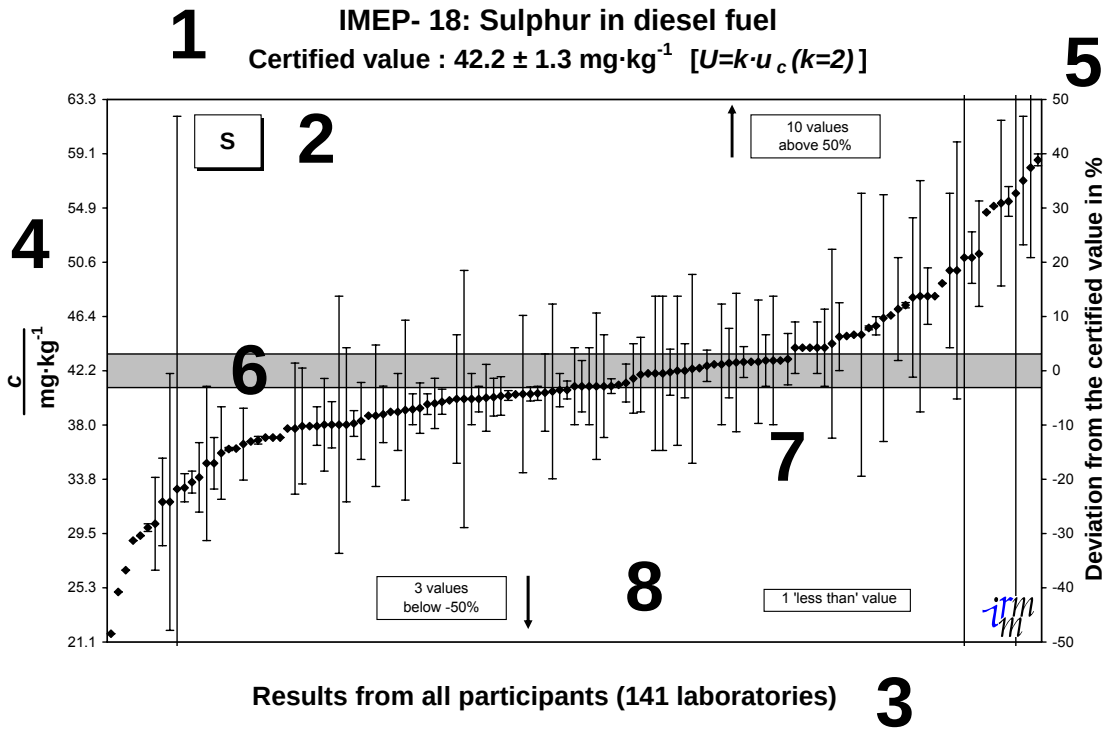


Figure 3: Description of the content displayed in the result graph

1 Legend with project name and certified reference value for the displayed component.

2 Component name

3 Legend explaining details of the graph.

4 Scale with the value of the quantity expressed in absolute numbers.

5 Scale with the value of the quantity expressed in % relative deviation from the certified reference value.

6 Range (shaded) encompassing the certified reference value and its expanded uncertainty.

7 Participants' result and self-declared uncertainty.

8 Box indicating results falling outside the scale of the graph.

Analytical techniques

IMEP® is result-oriented and hence does not focus on studying the different analytical techniques for this type of analysis in detail. To enable the graphical presentation of all results in relation to the analytical technique used, the various reported analytical techniques as presented in the first column of Table 10 are grouped according to the names in column 3. In addition the number of results per reported analytical technique are presented in column 2.

Graphs showing the reported results in relation to the analytical technique-group are given in Annex 1. From Table 10, it can be concluded that the techniques most frequently used by laboratories to analyse the S content in the diesel are EDXRF, UVF, WDXRF and coulometry. They represent 87% of the reported results. All laboratories were informed on registration of the nominal content of the S in the diesel material. (announcement letter Annex 3).

Table 10: Reported analytical techniques and grouping

Analytical techniques	**Number of laboratories**	**Analytical technique group**	**Total number of laboratories**
Coulometric analysis and Oxidative micro coulometric (COU)	15	COU	15
Ultra-violet Fluorescence (UVF)	40	UVF	40
Inductively coupled plasma-atomic emission spectrometry(ICP-AES)	2	ICP-ES	6
Inductively coupled plasma-optical emission spectrometry(ICP-OES)	4		
Wavelength Dispersive X-ray Fluorescence - without internal standard (WDXRF)	27	WDXRF	28
Wavelength Dispersive X-ray Fluorescence - with internal standard (WDXRF-INT)	1		
Energy Dispersive X-ray Fluorescence – Conventional(EDXRF-CON)	38	EDXRF	40
Energy Dispersive X-ray Fluorescence - Polarized X-ray sources (EDXRF-PXS)	2		
Other	12	Other	12

Laboratory performance evaluation

As described in a previous paragraph, in order to calculate the combined uncertainties needed for transforming the result into the *zeta'*-score, the reported coverage factor *k* was used or, when not reported, the reported uncertainty was considered to be of rectangular distribution.

A coverage factor *k* was reported by 48 laboratories (24%). The majority (42) reported the *k* factor to be equal to 2. For the 64% other laboratories, the rectangular distribution approach was used. One of the 141 reporting laboratories reported a 'less than' value and is hence not incorporated in the following statistics.

Table 11 gives an overview of the number of satisfactory, questionable either non-satisfactory results, according to the various performance assessment criteria/scores calculated and how they discriminate between the different categories. As can be seen the quality requirement of 10% was fit-for-the purpose for this population. Some 74% of the laboratories scored satisfactory when the '% difference' either the '*z*-score' was evaluated. Taking into account the reported uncertainties for calculating the *zeta'* score, the number of satisfactory laboratories increases to 80%.

Questionable results were obtained by 9% for the *z*-score and by 7% for the *zeta*'-score. Therefore incorporating realistic uncertainties can help to improve laboratory performance.

A graphical display of *zeta'* scores obtained is given as Figure 19 in Annex 1. An overview of the relative uncertainties as reported by the IMEP-18 participants is given in Figure 4.

Figure 4

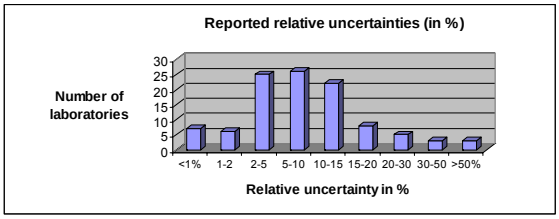


Table 11: Number of laboratories in relation to the different performance assessment criteria

Performance assessment score + criteria:		**Satisfactory**	**Questionable**	**Non satisfactory**
	Criteria	*No. of laboratories*	*No. of laboratories*	*No. of laboratories*
% difference	|D%| ≤ 20% → Satisfactory |D%| > 20 % → Unsatisfactory	104		36
z-score	|*z or zeta'*| ≤ 2 → Satisfactory 2 < |*z* or *zeta'*| ≤ 3 → Questionable	104	13	23
Zeta' score	|*z or zeta'*| > 3 → Unsatisfactory	112	10	18

Evaluation of the questionnaire replies

All except one laboratory completed the questionnaire. The evaluation is hence based on the replies of 140 laboratories. The evaluation of the various replies is given in the following paragraphs. The questionnaire itself is part of Annex 3. The graphical displays which present the participants' results sorted according to the criterion evaluated, can be found in Annex 1, which starts with a list of all figures available.

Self declared experience and number of samples analysed per year

Participants were asked to indicate their level of experience for this type of analysis. Experience was declared by 98 laboratories against 42 less or non-experienced laboratories.

The high number of experienced laboratories (70%) shows that laboratories dealing on routine basis with S analysis in diesel were reached. This can also be concluded from the number of samples analysed per year. Some 75% of the laboratories analyse yearly more than 50 samples Half of this population yearly analyse more than 500 samples.(Figure 5)

Graphical displays for these criteria are given as figures 11 and 12 in Annex 1. The relation between the self-declared experience and the number of samples analysed per year is given in Table 12.

Figure 5: Number of samples analysed per year

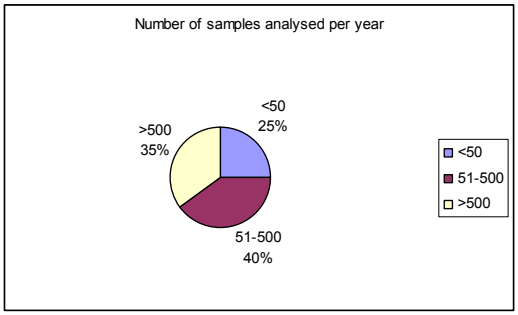


Table 12 : Number of samples analysed per year linked to the self-declared experience for this type of analysis

Number of samples analysed per year	Number of replies	
	(experienced-self declaration)	(non and less-experienced-self declaration)
<50	5	30
51-500	46	3
>500	47	9

IMEP CTS analysed under routine conditions?

IMEP-18 laboratories were asked to analyse the Certified Test Sample (CTS) following the laboratory's routine procedures.

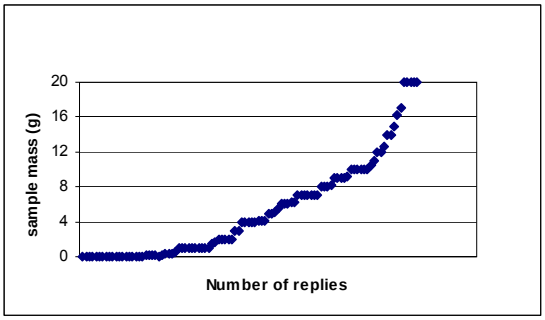
For the majority of laboratories, the IMEP-18 diesel sample was analysed by the routine analyst (96%). From the 6 negative replies, 3 analysts had the same experience as the routine analyst and 1 even more. In addition, 90% of the laboratories treated the sample according to their routine analytical procedure for this sample type. The remaining 10% adapted their experimental protocol due to the limited volume of the sample provided or the different (lower or higher) S concentration.

IMEP-18 results reflect therefore the actual measurement capability for S content measurements for the given concentration range.

Sample mass used

Laboratories received two ampoules of the diesel material each containing 10 ml of diesel. For the majority of the techniques used, this sample volume was sufficient. An overview of the reported sample masses used is given in Figure 6.

Figure 6: sample mass used



Digestion, separation or pre-concentration needed?

Some 5% of the participants incorporate a sample digestion step. The digestion procedures used are microwave digestion (with HNO_3 or HNO_3/H_2O_2); microwave-assisted pressure digestion (with HNO_3/H_2O_2), combustion, Wickbold combustion (0.1 M NaOH) and the use of a digestion bomb system ($HNO_3/HF/H_3BO_3$). No separation step was reported other than drying of combustion gases. No pre-concentration step was involved in the measurement procedure. Approximately 7% of the participants reported that the material was diluted prior to measurement. Deionized water was used after digestion, solvents (petroleum, isooctane, xylene, kerosin) in other cases.

Official method

Some 82% of the laboratories use official analytical methods in their laboratories for S analysis in diesel. The most frequent standards and number of replies are given in Table 13.

Table 13: The standards most frequently used by IMEP-18 participants for S in diesel analysis.

Standard	No. of replies	Standard	No. of replies
ASTM D 2622	7	EN ISO 20847	16
ASTM D 3120	5	EN ISO 20884	10
ASTM D 4294	6	EN ISO 8754	13
ASTM D 5453	6	EN ISO 14596	7
ASTM D 5453-03a	5	EN ISO 16591	2
ASTM D 5456-00	2	NF M 07-059	2
DIN 51400 part 7	2	IP336	2
DIN EN 20846	17		

Certified Reference Material in use in laboratory

81 Laboraties have a diesel certified reference material (CRM) at their disposal (58% of the replies).
From this population, 62 laboratories (76%) indicated the use of these CRMs for procedure validation purposes and 58 (72%) for instrument calibration. Multiple selections showed that 40 laboratories (50%) indicated the use of CRMs for both purposes.
An overview of all reported CRMs is given in Annex 2 as table 1. The graphical presentation of the reported results in view of this criterion is given in Annex 1 as figure 14.

Participation in other interlaboratory comparisons?

100 Laboratories (71%) participated already in other interlaboratory comparisons.
12 of them were involved in the work of the CEN TC19 WG27. They originate from the following countries; Czech Republic, Estonia, France, Germany (2), Slovenia, The Netherlands, Turkey, Sweden (2) and United Kingdom (2).
78% of the laboratories enrolled in proficiency testing schemes. The PT schemes and providers are listed as Table 2 in Annex 2.

Customs related activities

On the question if the laboratory was involved for this type of analysis in customs related activities, 59 laboratories (42%) replied positive. A graphical display of the results of these laboratories is presented in Annex 1, figure 15.
A collaboration agreement with DG TAXUD was established in order to invite customs laboratories for participation in this IMEP interlaboratory comparison. As a result 15 laboratories involved in the DG TAXUD GCL-action 2 activity participated in this interlaboratory comparison. The majority of the results of this group (11 laboratories) are incorporated in figure 15 of Annex 1.

Quality Management System

124 laboratories (89%) work according to the recommendations of a quality management system. Figure 16 of Annex 1 compares results of such laboratories which those of laboratories that replied negative to this question. Which quality management system is followed is summarised in Table 14. Multiple replies were possible. Figure 17 (Annex 1) gives more information about results of laboratories in view of type of quality management system (ISO 17025, ISO 9000 or other).

Table 14: The number of IMEP-18 participating laboratories in relation to the quality management system in use. Multiple answers were possible.

Quality management system in use			
EN 45000 series	**ISO 9000 series**	**ISO 17025**	**Other**
10	48	106	2

Accredited, Authorised or Certified

Results of laboratories that replied positive to the question if they were accredited, certified or authorized (e.g. by law or regulatory authority) for S analysis in road transport fuels, are visualised in figure 18 in Annex 1. The number of laboratories that are accredited, certified or authorised are given in Table 15. Multiple replies were possible. Therefore Figure 7 shows the different combinations and the percentage of laboratories involved.

Table 15: The number of laboratories that replied positive in relation to their status of accreditation, certification or authorisation for S analysis in roadfuels

Status	Number of laboratories	Number of laboratories (%)
Accredited	78	56
Authorised	39	28
Certified	33	24

Reporting and calculating uncertainty

IMEP-18 participants were asked if they are familiar with the Guides for Quantifying Measurement Uncertainty (GUM) issued by the International Organisation for Standardisation (ISO, 1993) and/or EURACHEM (1995).
From the 77% that are familiar with the mentioned guides, 59% also implemented these guidelines to calculate the uncertainty on the reported results. How the uncertainty was evaluated for those laboratories which did not use the above mentioned guidelines is given in Table 3 of Annex 2. Reporting of uncertainties on analytical results to customers is done by 36% of the participating laboratories. About 71% of the latter originate from the population that calculated the uncertainty according to the above mentioned guides.

Motivation for participation in IMEP-18

IMEP-18 participants were asked to indicate the most appropriate reply to the question “Was your participation to this IMEP comparison used to demonstrate your measurement capability to …”. The percentage of replies to the various choice possibilities are given in Figure 8. Internal quality control purposes was the motivation for participation for 36% of the participants, demonstration of measurement capability to other parties such as their management was the motivation for 21%, to customers (18%) or regulating or accreditation body (23%). A minority of the participants (2%), indicated as participation motivation purposes such as development of analytical methods, external assessment of results or as test case for personal measurement capability.

Figure 7: Information about status of certification, accreditation and authorisation of IMEP-18 participants

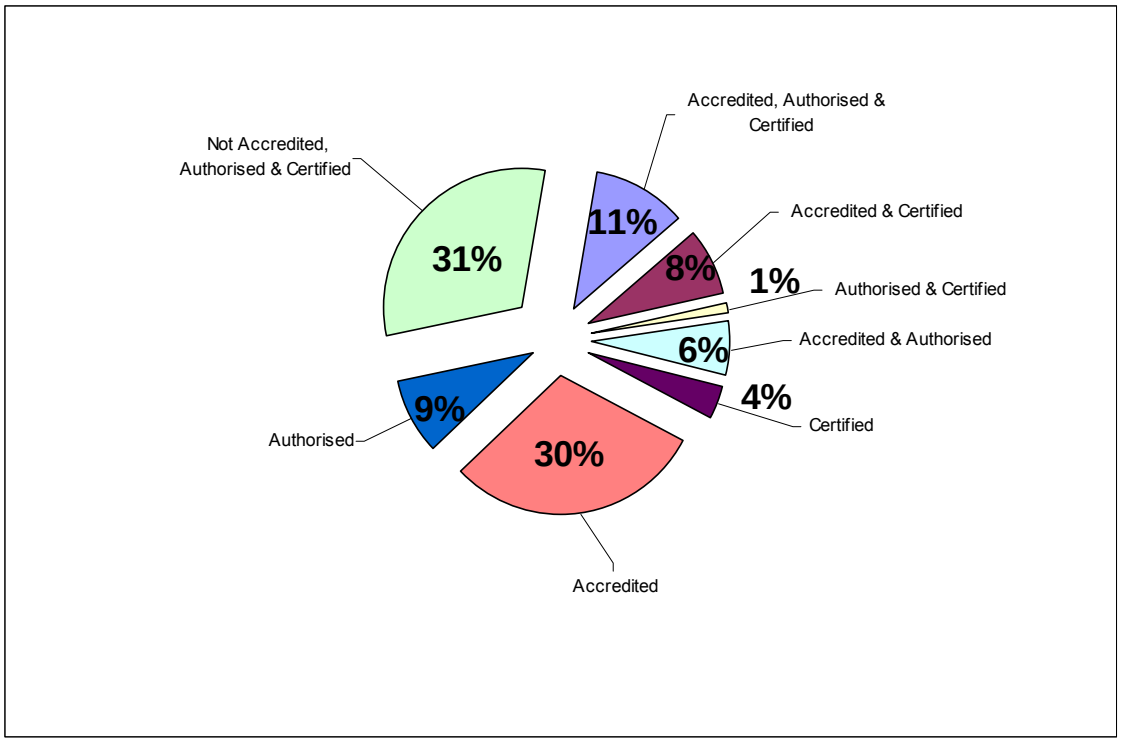
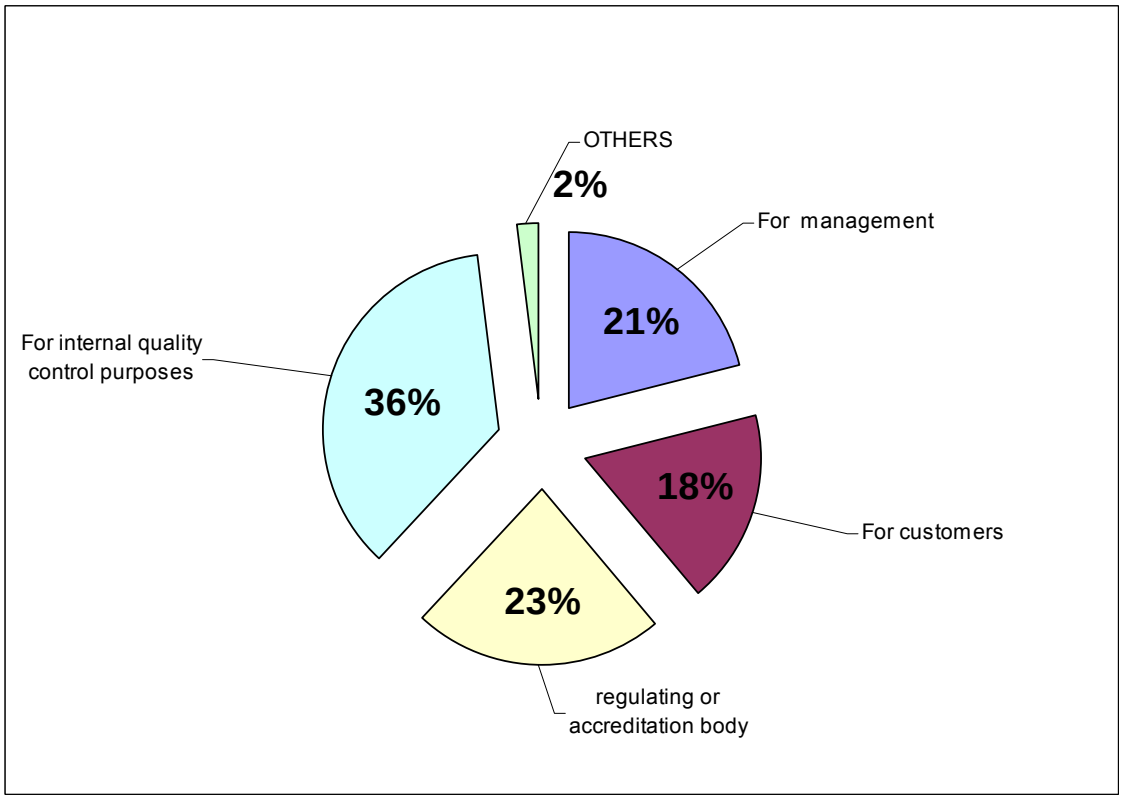


Figure 8: Motivation for participation in IMEP-18



The current analysis of road fuel samples with an S content lower than 10 mg·kg^{-1} ("sulphur-free" fuel)

The purpose of the question was to explore the state-of-the-practice concerning the analysis of S in road fuel samples with a S content lower than 10 mg·kg^{-1} ("sulphur-free" fuel) among the IMEP-18 participants. This type of analysis is done by 46 laboratories (33%). All of them analyse sulphur-free diesel fuel and 35 in addition sulphur-free petrol. The majority of laboratories use the same analytical technique as used for the IMEP-18 samples [UVF (30 participants), WDXRF (10 participants) and other methods e.g. Coulometry EDXRF, EDXRF-PXS, GAUV and TXRF]. Only a few laboratories reported another analytical technique (e.g. coulometry is replaced by UVF, EDXRF by WDXRF). The majority of techniques require a minimal sample volume ranging from about 10 to 20 ml for these S concentration levels. The majority of this population (88% of the laboratories) is interested in an IMEP interlaboratoy comparison on petrol (for S content levels ranging from 8 to 50 mg·kg^{-1}).

Acknowledgements

This IMEP-18 project would not have been possible without the help and support from many people. The authors would like therefore to thank for their support in view of development of/ideas for the ILC ; R. Visser (IIS, the Netherlands), M. Sargent (LGC, United Kingdom), J. Crighton (BP, United Kingdom), C.Stapel, H. Laforce and co-workers (Exxon-Belgium) and T. Linsinger (IRMM).

The authors would like to thank in particular J. Vogl (BAM, Germany), R. Hearn (LGC, United Kingdom), C. Quetel (IRMM), J.Mann (NIST) and other scientists in the various laboratories involved in the production and certification of the material which includes homogeneity testing (J.Sieber) and the logistics to send the material to IRMM (B. Macdonald).

The authors acknowledge the support of the following people in view of contacting interested laboratories: L. Turner and N. Burger (UKAS, United Kingdom) and M. Bednarova (EA-ILC committee) for the EA laboratories; J. Belliardo and M. Dillen (DG-TAXUD), J. Peltzer (Zpam,Munchen, Germany), D. Salvat-Brunaud (Eurofins, France) for the customs laboratories involved in the GCL-action 2, for distributing the announcement information ; R.Visser to members of the PT scheme and J. Crighton to CEN TC19 WG27 members. The authors are very grateful for the continuous support received from the regional co-ordinators: P. Briggs (Australia), R. Martins Horta Borges (Brazil), D. Ivanova (Bulgaria), C. Michael (Cyprus), J. Tichy and F. Vyslouzil (Czech Republic), K. Carneiro (Denmark), I. Leito (Estonia), G. Labarraque (France), A. Voulgaropoulos (Greece), Z. Nagyné Szilágyi (Hungary), A. Galdikas (Lithuania), J. Sainz Uribe (Mexico), E. Bulska (Poland), X. Liu (P.R. China), C. Chin (Rep. of Singapore), S. Duta (Romania), B. Cséfalvayová (Slovakia), N. Majcen (Slovenia), M. Linsky (South Africa), B. Magnusson (Sweden), H. Ent (The Netherlands), P. Yildizlar (Turkey), D. Woods and B. Brookman (United Kingdom).

In addition the efforts of many people working at IRMM are acknowledged; E. Garlick, J. Wylin, J. Alba Sanchez (IPTS) and colleagues from the IRMM Informatics Unit who were actively involved in the development of the new ORACLE based database system that was implemented for the fist time for this IMEP ILC. Many administrative requirements were solved by M. Peetermans and other colleagues from the IRMM administrative services. A word of thank also to former and present colleagues of the IRMM-IM Unit for the assistance in various issues.

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.

List of abbreviations

BAM	Bundesanstalt für Materialforschung und –prüfung (Berlin, Germany)
BIPM	Bureau International des Poids et Mesures (Paris, France)
CARDS	Community Assistance for Reconstruction, Development and Stabilisation
CCQM	Comité Consultatif pour la Quantité de Matière
CIPM	International Committee for Weights and Measure
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRMs	Certified Reference Materials
CTS	Certified Test Sample
DG TAXUD	European Commission – Directorate-General Taxation and Customs Union
EA	European Co-operation for Accreditation
EC	European Commission
EN	European Norm
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
EUROMET	Association of European Institutes for Metrology
GUM	Guide for expression for Uncertainty in Measurement
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IMEP®	International Measurement Evaluation Programme
ILC	Interlaboratory Comparison
IRMM	Institute for Reference Materials and Measurements (EC, Joint Research Centre, Geel, Belgium)
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
MRA	Mutual Recognition Agreement
NAB	National Accreditation Body
NMIJ	National Measurement Institute of Japan (Tsukuba, Japan)
PMM	Primary Method of Measurement
PT	Proficiency Testing Scheme
RC	Regional Co-ordinator
TIMS	Thermal Ionisation Mass Spectrometry

References

1 http://kcdb.bipm.org/appendixC/default.asp
2 ISO/IEC 17025:1999: general requirements for the competence of testing and calibration laboratories
3 http://www.imep.ws go to permanent newsflash
4 http://www.imep.ws
5 P. Taylor, K. Brinkmann, I. Papadakis, L. Cortez, M. Bednarova, Y. Aregbe, Accred.Qual.Assur (2002), 7, No. 4, 168
6 OJ L 76, 22.3.2003, p.10
7 OJ L 350, 28.12.1998, p. 58; Directive as last amended by Commission Directive 2000/71/EC (OJ L 287, 14.11.2000, p. 46).
8 OJ L 76, 6.4.1970, p. 1; Directive as last amended by Directive 2001/100/EC of the European Parliament and of the Council (OJ L 16, 18.1.2002, p. 32).
9 OJ L 36, 9.2.1988, p. 33; Directive as last amended by Commission Directive 2001/27/EC (OJ L 107, 18.4.2001, p. 10).
10 EN 228:1999; Automotive fuels – Unleaded petrol – requirements and test methods
11 EN 590:1999; Automotive fuels – Diesel – requirements and test methods
12 http://www.bipm.org/utils/en/pdf/mra.pdf
13 http://www.bipm.org
14 http://www.euromet.org/cgibin/projectfile.pl?prefno=785
15 NIST Report of Analysis; author:John R. Sieber (January 21,2005)
16 A. van der Veen. T. Linsinger and J. Pauwels, Accr. Qual. Assur. (2001) 6:26-30
17 T. Linsinger, H. Schimmel, J. Pauwels, M. Ostermann, M. Berglund, P.D.P. Taylor, R.D. Vocke Jr., W.R. Kelly, J.L. Mann (2002), The certification of the total sulphur mass fraction of three gas oil reference materials BCR-104R, -671 and -672, European Commission, EUR Report Report EUR 20266 EN
18 Gawlik BM, Lamberty A (2002), private communication (IRMM Internal Report GER/RM/12/2002/May/23, “Stability testing of Reference Materials – results obtained from 01/02 to 04/02”)
19 Duewer, D. L., “*Working document* - A robust approach for the determination of CCQM key comparison reference values and uncertainties”, CCQM/04-15, BIPM, 2004. *available on request from the International Bureau of Weights and Measures,* www.bipm.org.
20 http://www.iso.org
21 Proficiency testing in analytical Chemistry: VAM publication-1997: authors R.Lawn, M.Thompson and R. Walker
22 ISO 43-1: Proficiency testing by interlaboratory comparisons – Part 1: development and operation of proficiency testing schemes – Annex A
23 ISO/DIS 13528: Statistical methods for use in proficiency testing by interlaboratory comparisons: version 2005
24 IUPAC – working document for interested parties meeting on the revision of the IUPAC/ISO/AOAC protocol for proficiency testing
25 Appendix E of the EURACHEM/CITAC guide: the Guide for Quantifying Measurement Uncertainty (GUM) issued by the International Organisation for Standardisation (1995)

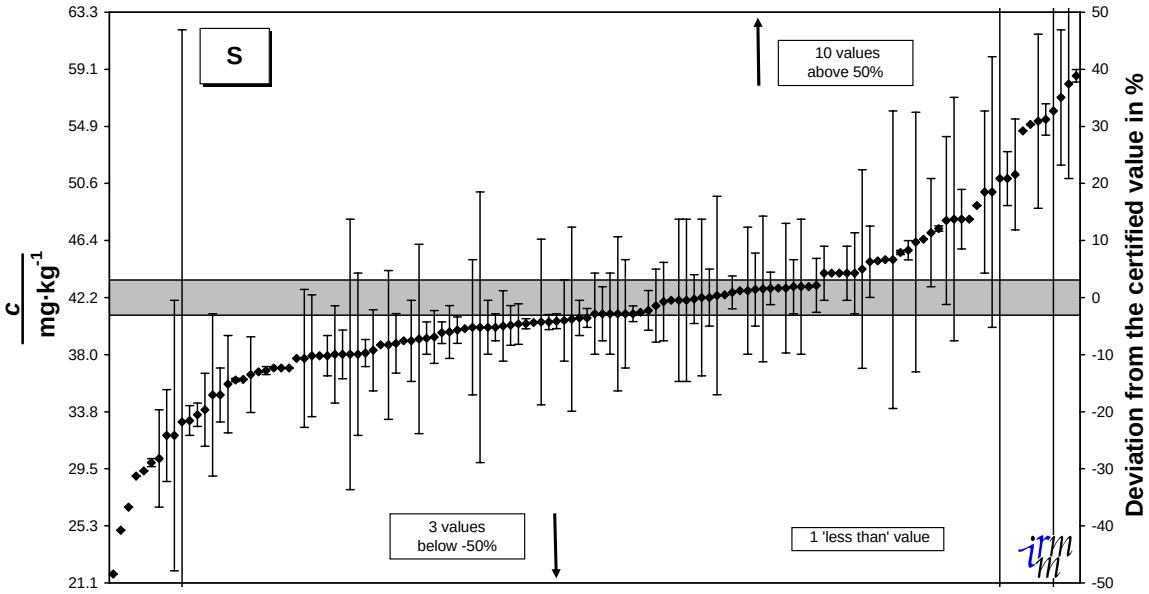
IMEP-18: Sulphur in Diesel fuel

Annex 1 – Participants results – Graphs

Figure 1

IMEP- 18: Sulphur in diesel fuel

Certified value : 42.2 ± 1.3 mg·kg^{-1} [$U=k\cdot u_c\,(k=2)$]

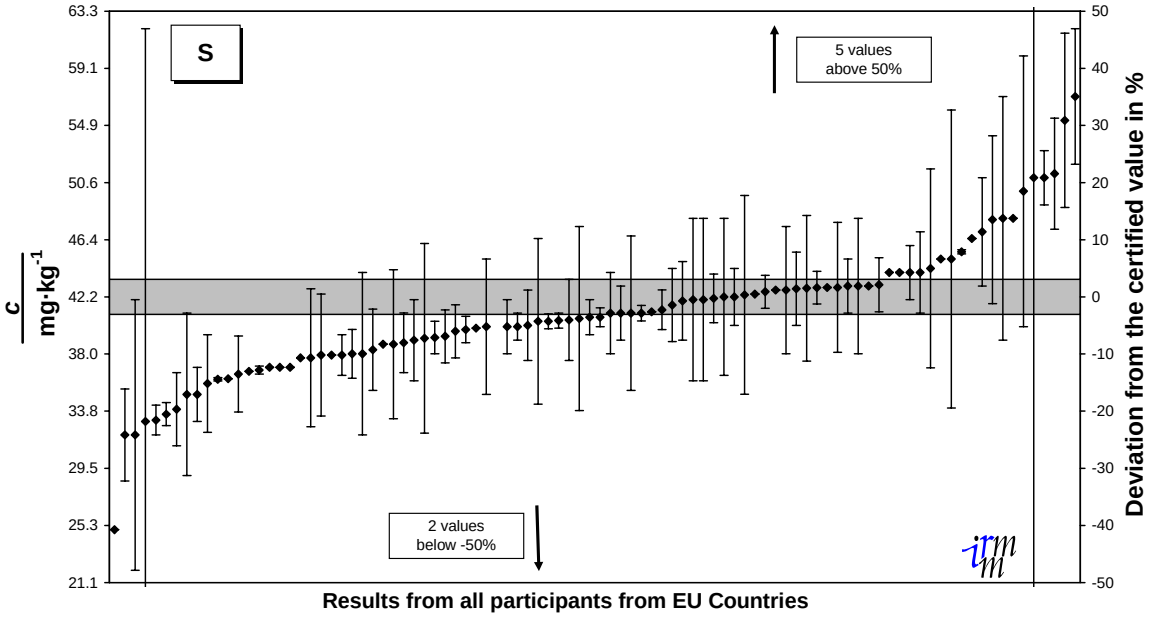


Results from all participants

Figure 2

IMEP- 18: Sulphur in diesel fuel

Certified value : 42.2 ± 1.30 mg·kg^{-1} [$U=k\cdot u_c\,(k=2)$]



Results from all participants from EU Countries

(Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, The Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden and United Kingdom)

Figure 3

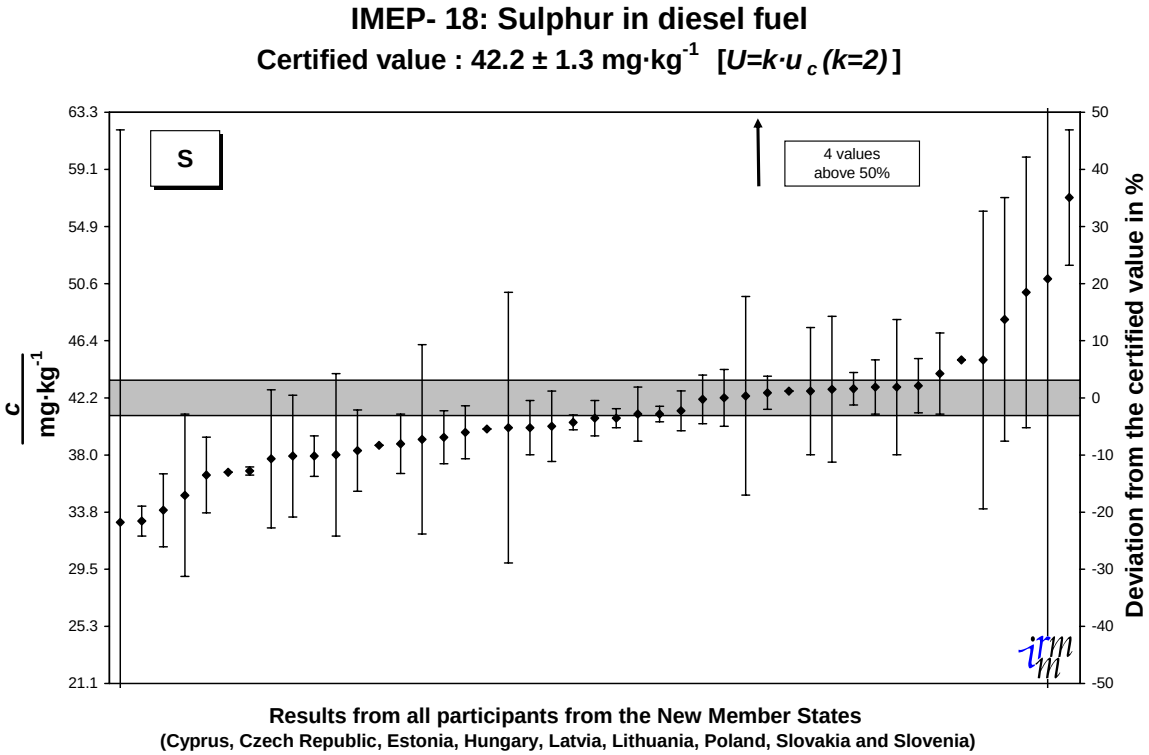


Figure 4

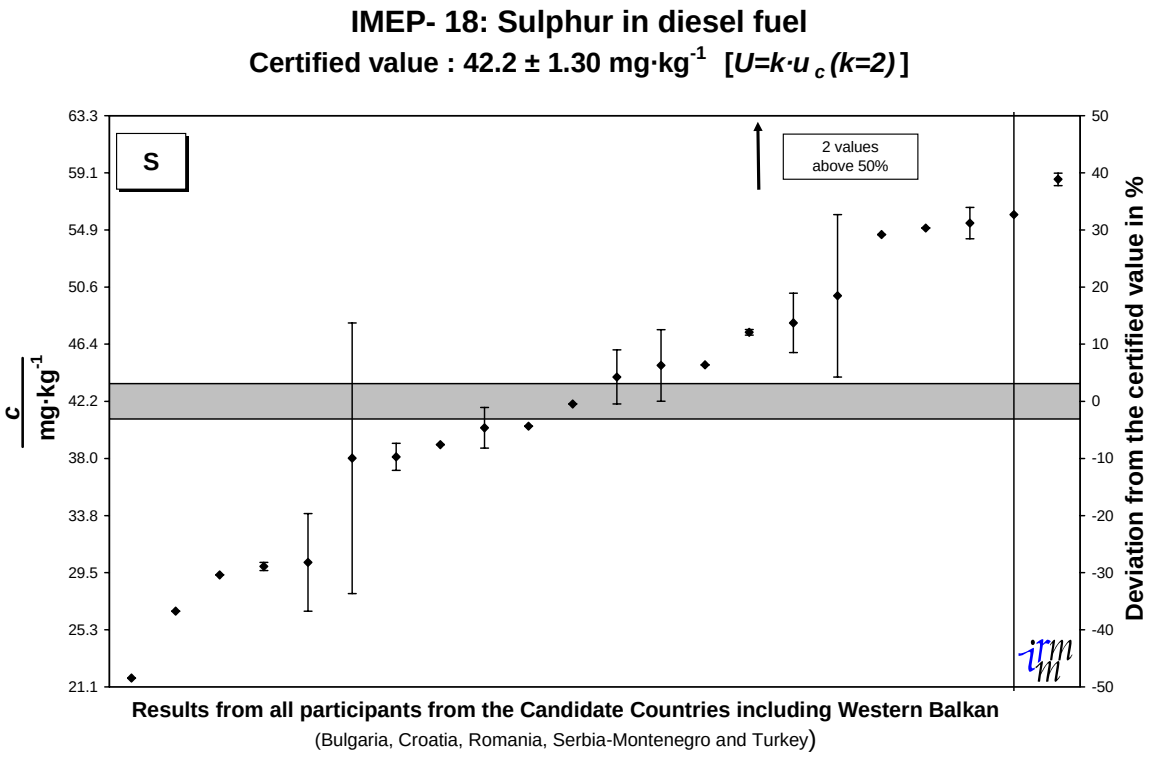
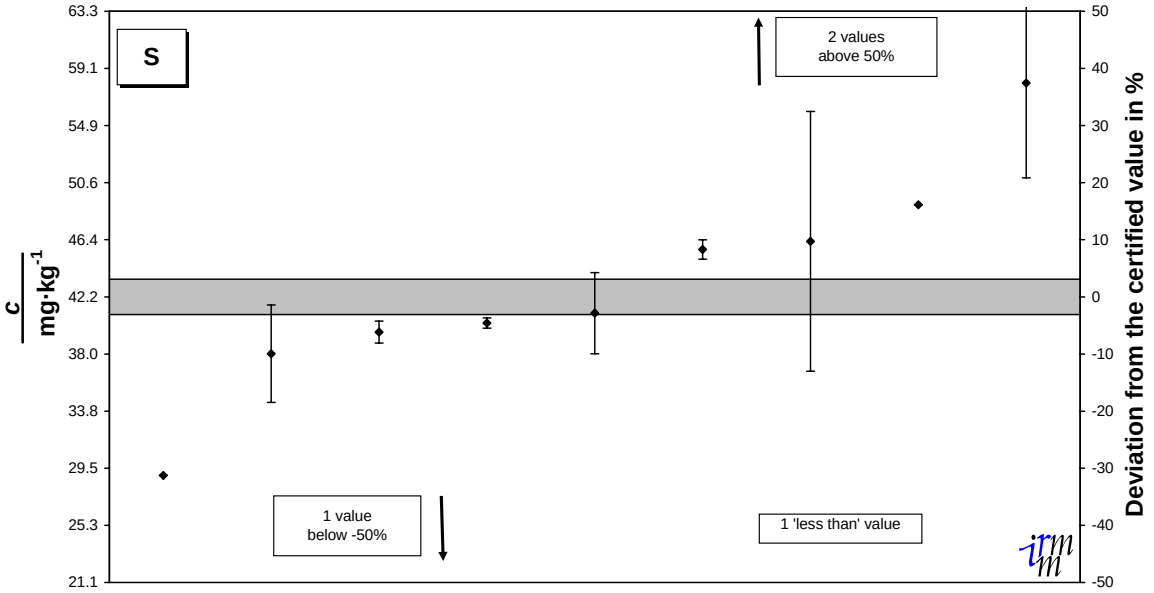


Figure 5

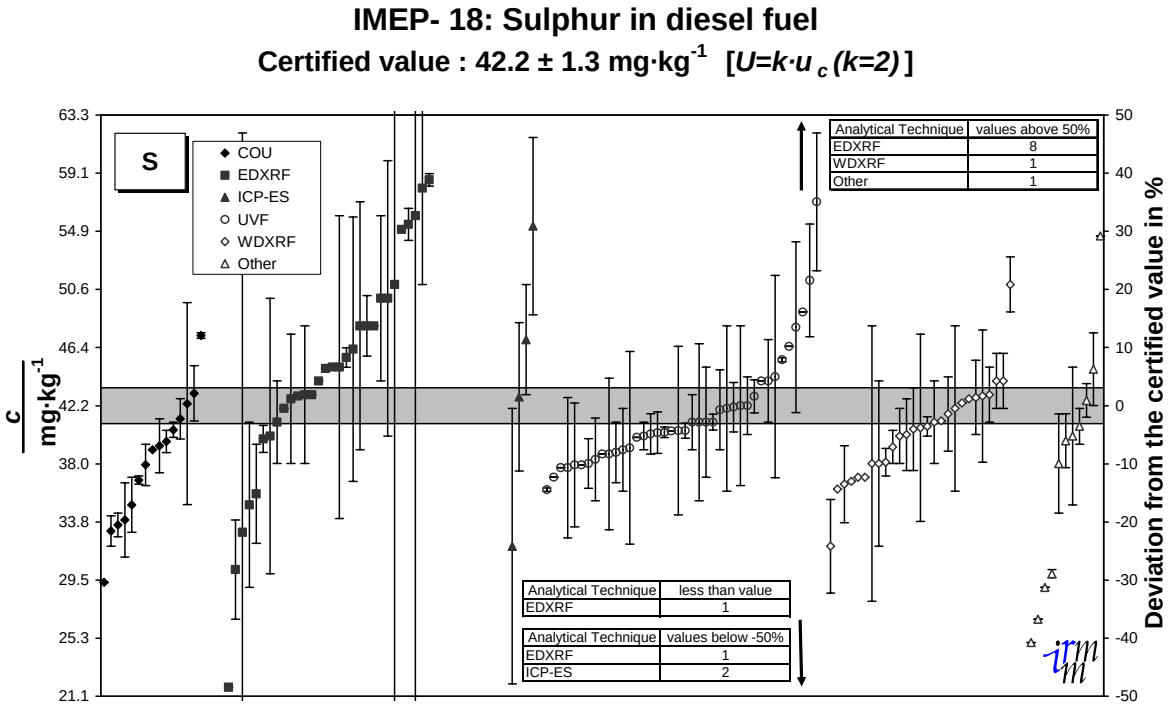
IMEP- 18: Sulphur in diesel fuel

Certified value : 42.2 ± 1.3 mg·kg^{-1} [$U=k\cdot u_c (k=2)$]



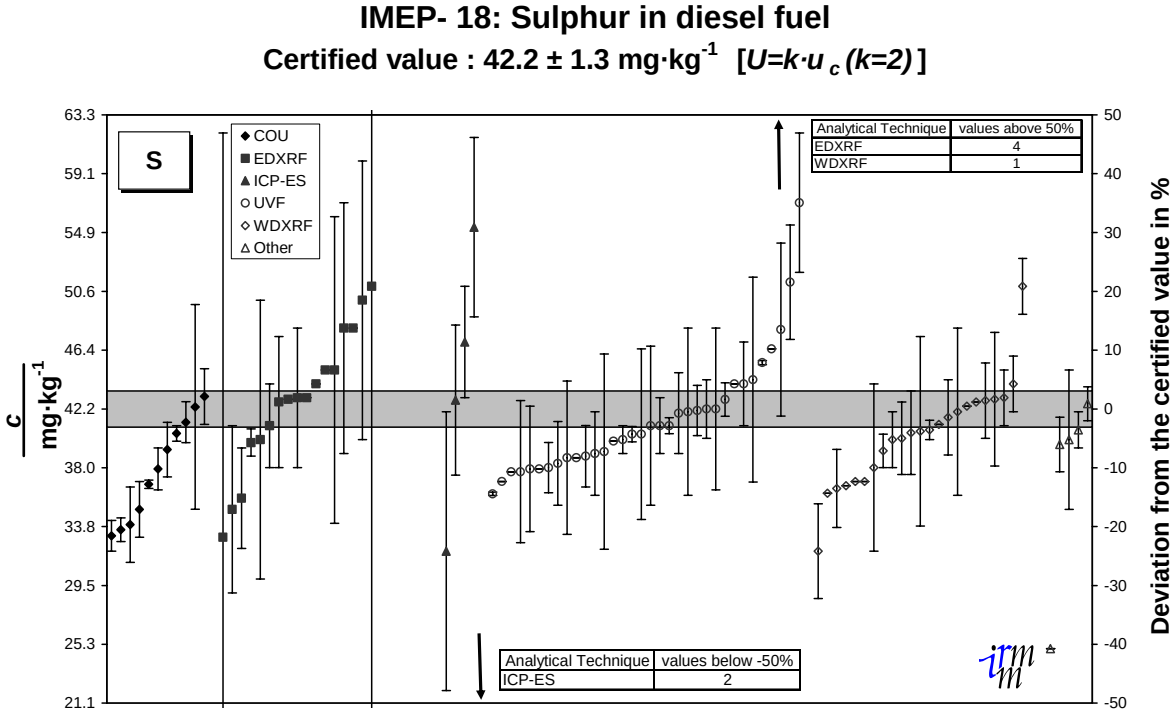
Results from participants from
(Brazil, China, Kazakhstan, Mexico, South Africa and United Arab Emirates)

Figure 6



Results from all participants according to analytical techniques used

Figure 7



Results from all participants from EU Countries (Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, The Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden and United Kingdom) **according to analytical techniques used**

Figure 8

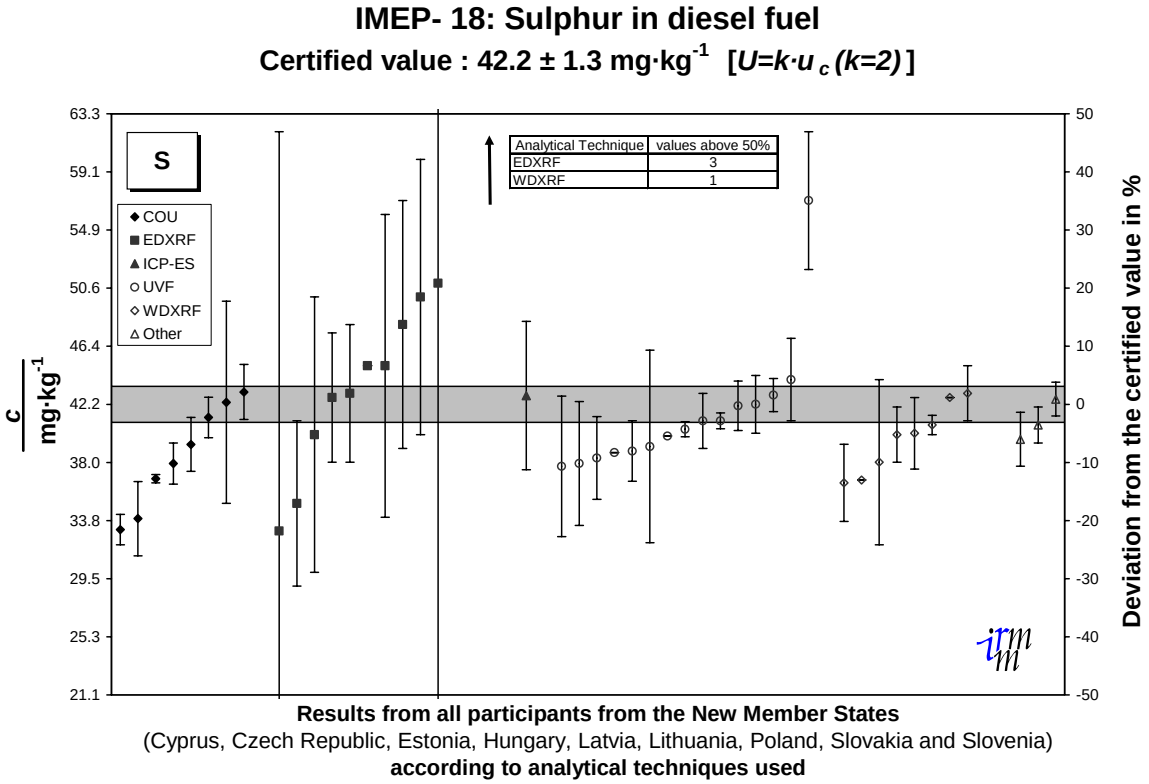


Figure 9

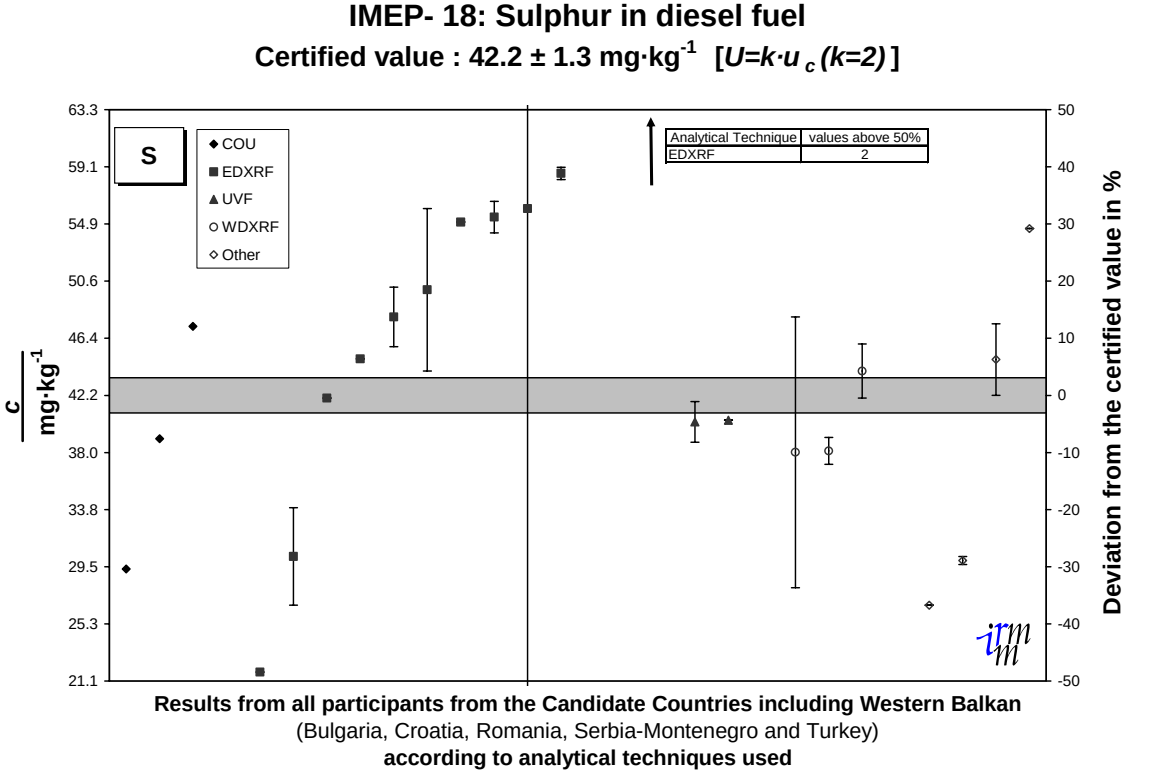


Figure 10

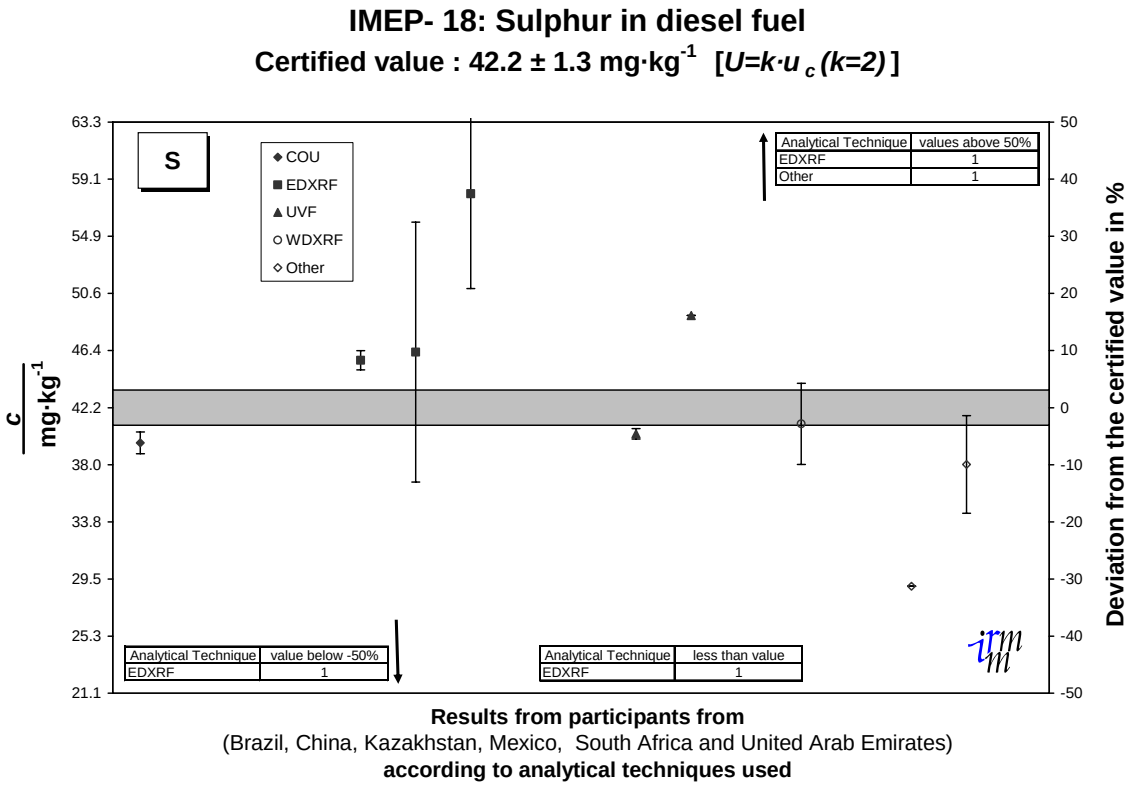
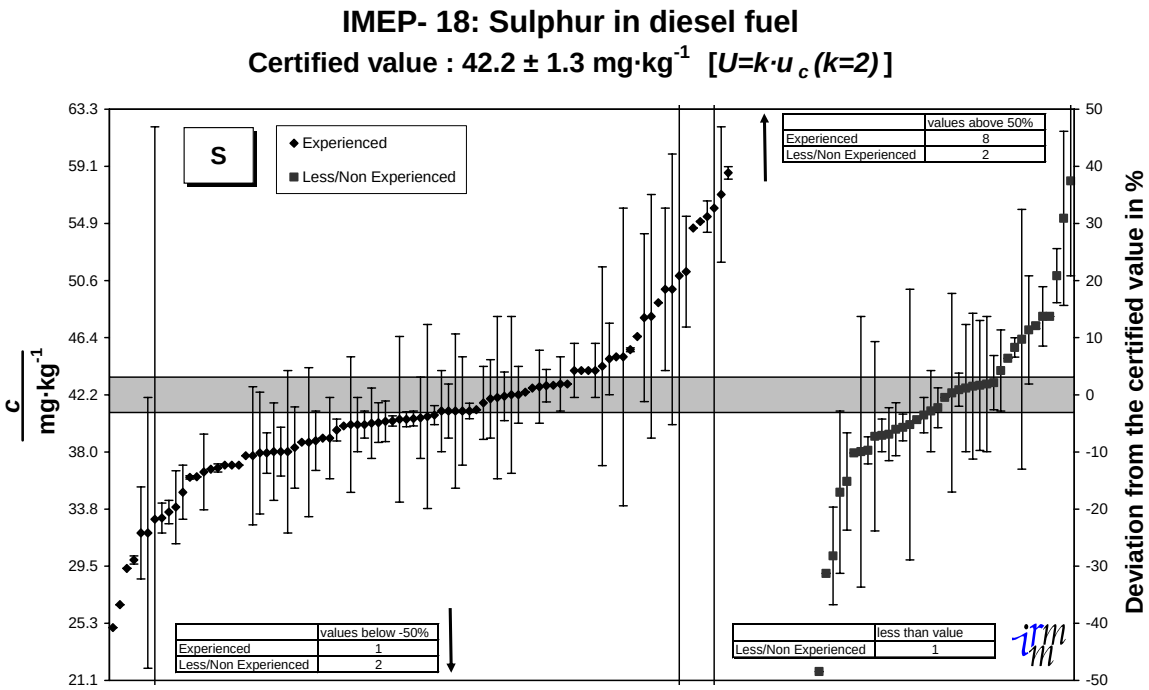
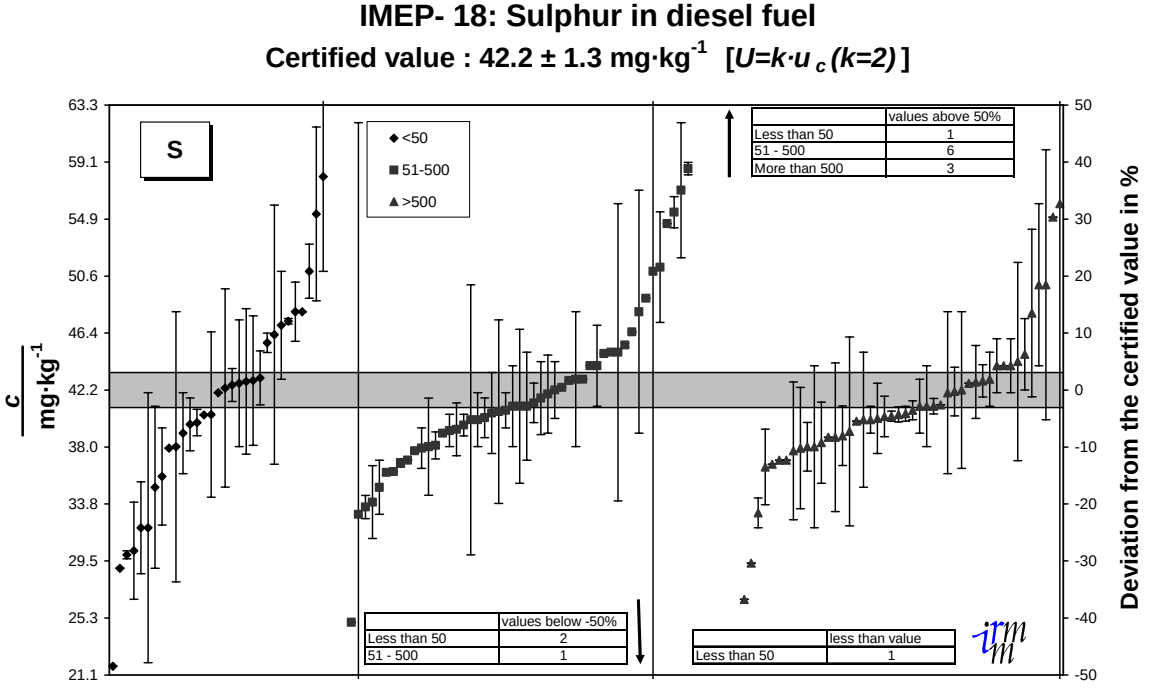

IMEP- 18: Sulphur in diesel fuel
Certified value : 42.2 ± 1.3 mg·kg-1 [U=k·u c (k=2)]
S
COU
EDXRF
UVF
WDXRF
Other
Analytical Technique | values above 50%
EDXRF | 1
Other | 1
Analytical Technique | value below -50%
EDXRF | 1
Analytical Technique | less than value
EDXRF | 1
c mg·kg-1
Deviation from the certified value in %
63.3
59.1
54.9
50.6
46.4
42.2
38.0
33.8
29.5
25.3
21.1
50
40
30
20
10
0
-10
-20
-30
-40
-50
Results from participants from
(Brazil, China, Kazakhstan, Mexico, South Africa and United Arab Emirates)
according to analytical techniques used

Figure 11



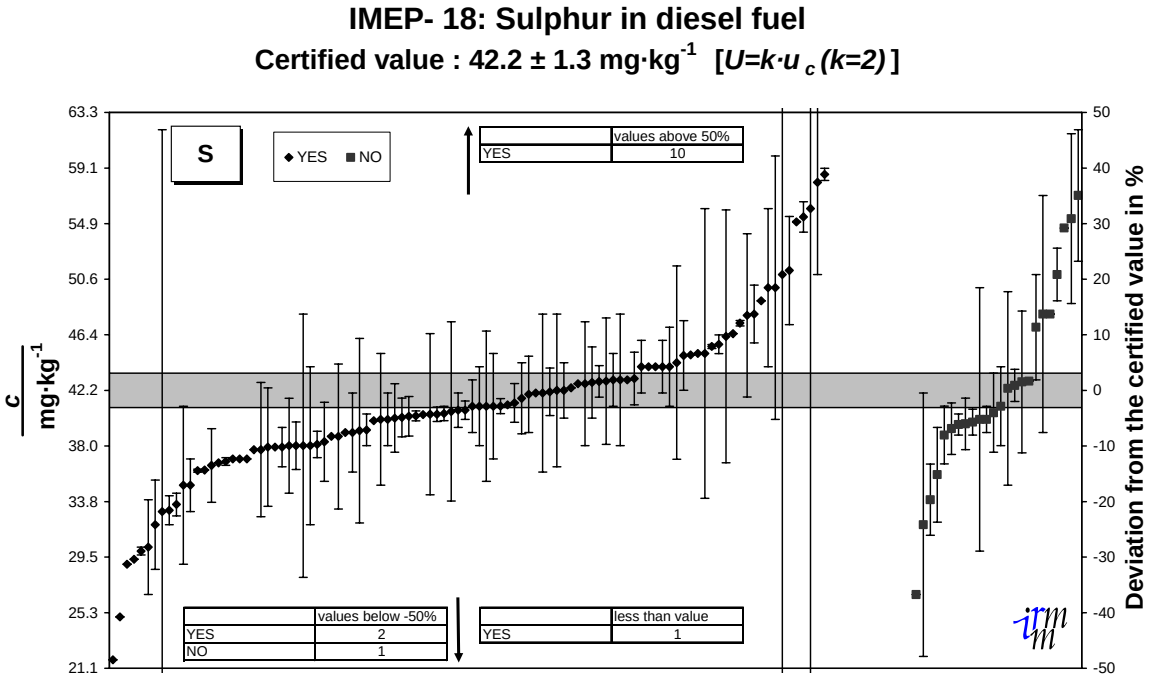
Results from all participants according to the self declared status of experience

Figure 12



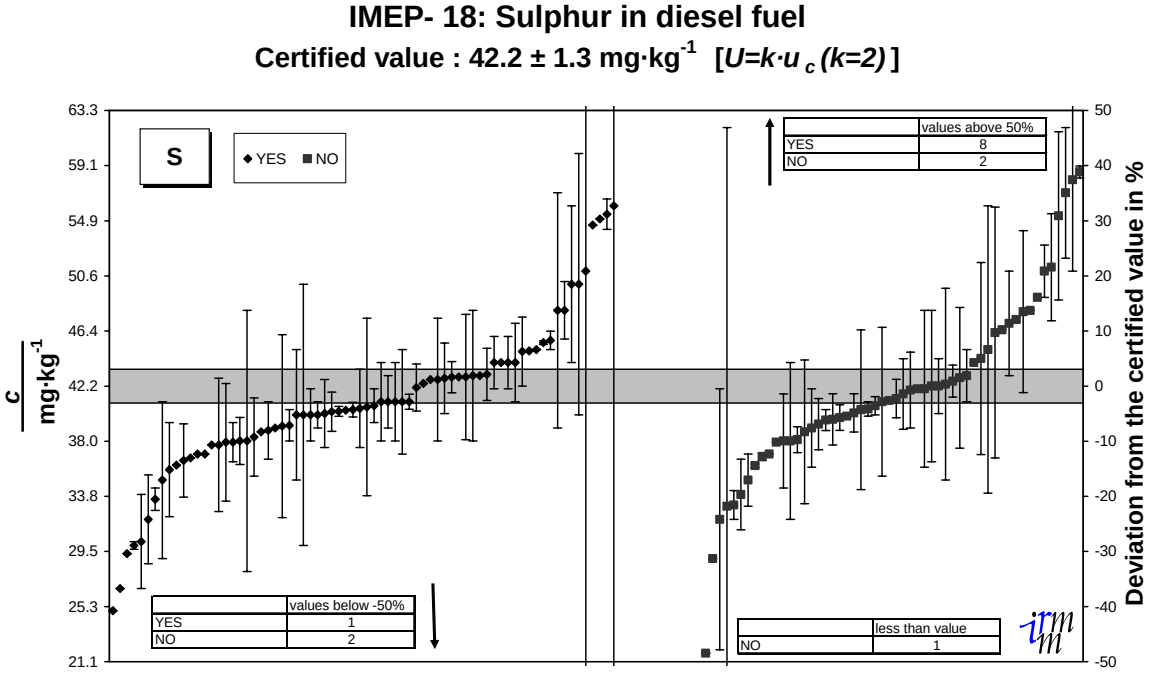
Results from all participants according to the number of diesel samples analysed per year for sulphur content

Figure 13



Results from all participants who analysed the material using any official analytical method

Figure 14



Results from all participants who had in there laboratory diesel Certified Reference Material (CRM)

Figure 15

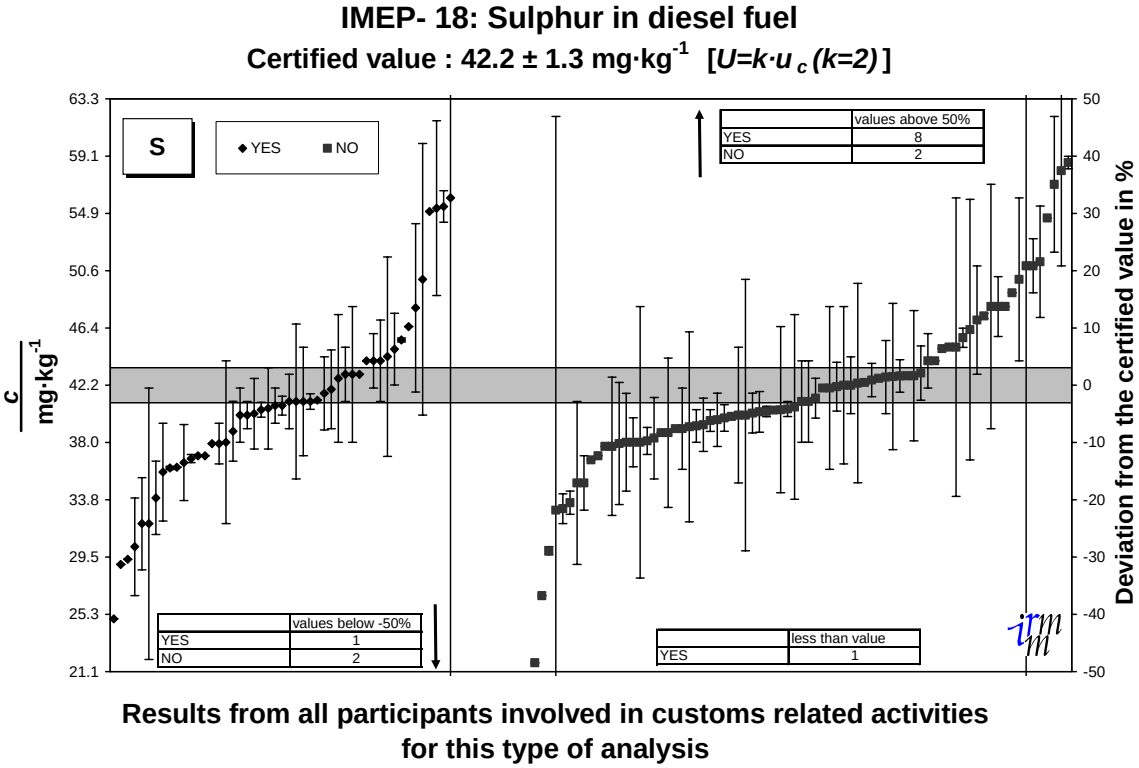


Figure 16

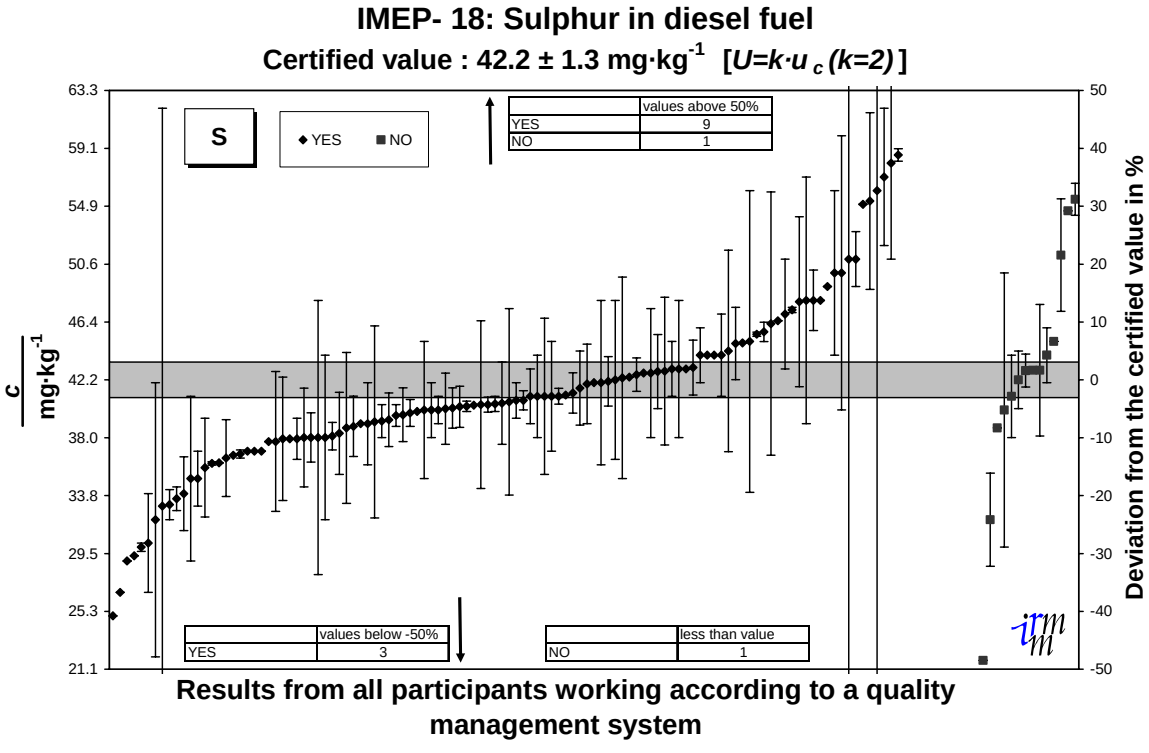
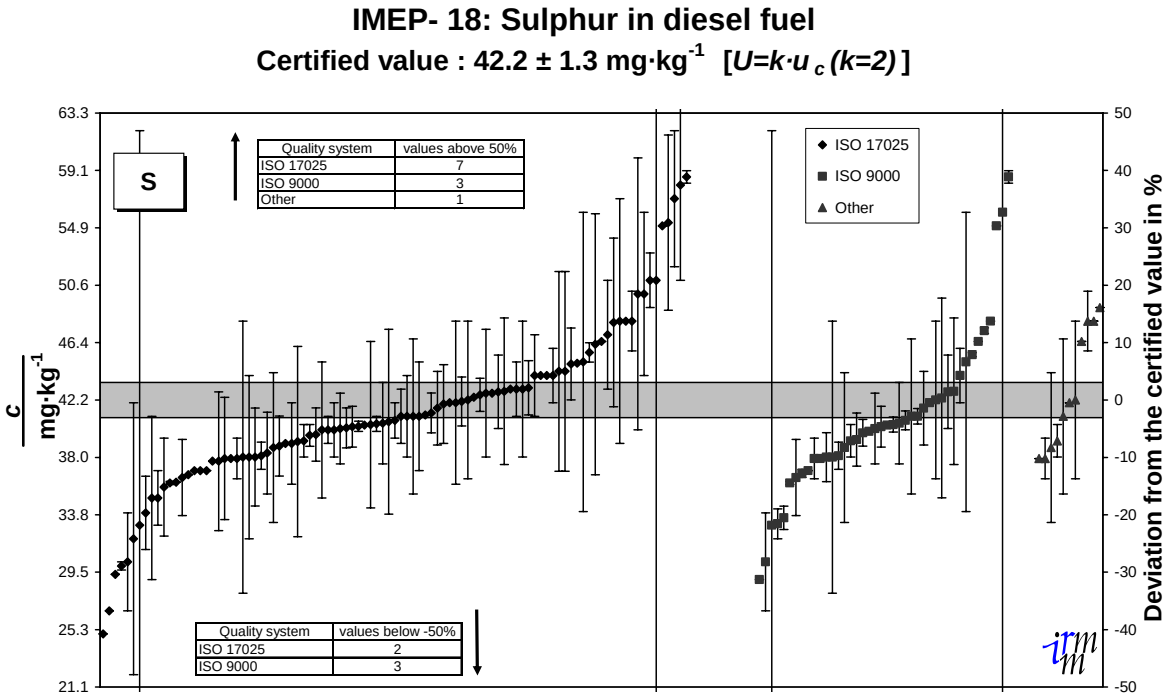
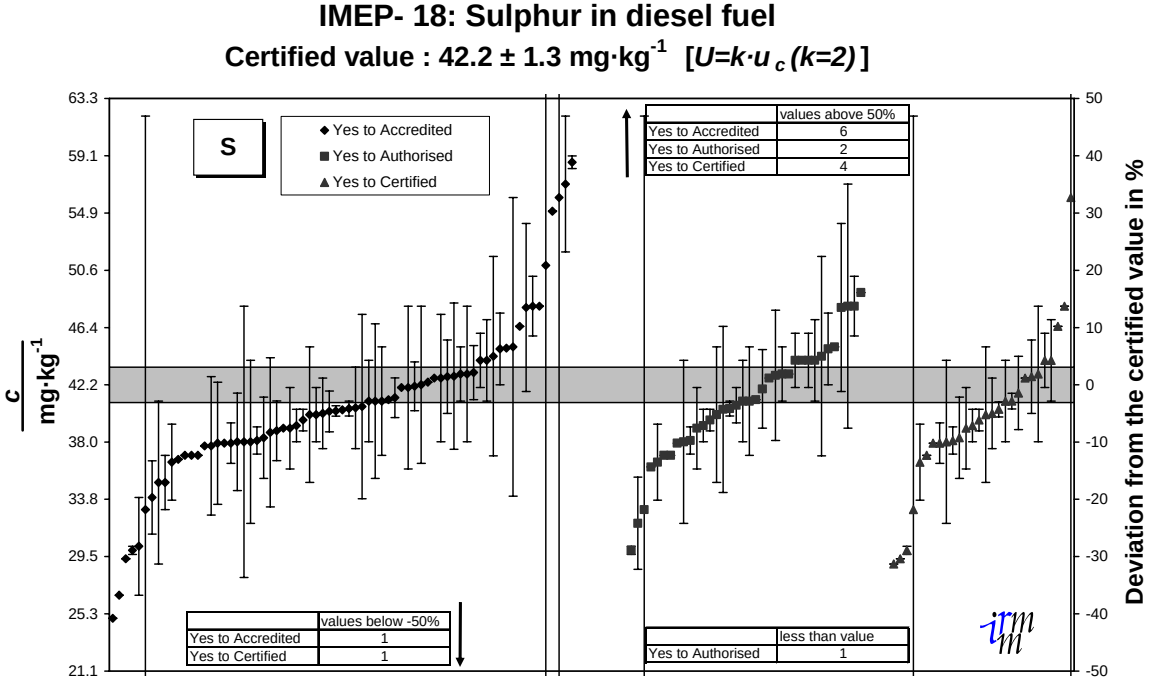


Figure 17



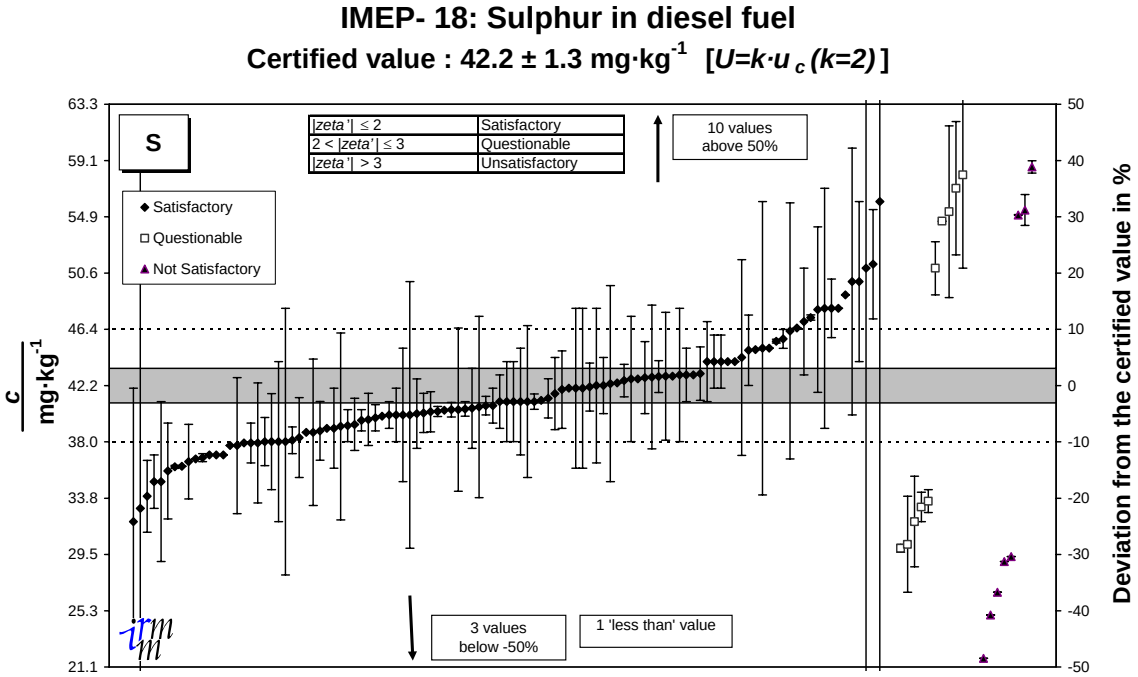
Results from all participants according to the quality system used

Figure 18



Results from participants who replied YES to the question if accredited, authorised or certified

Figure 19



Results from all participants sorted according to the *zeta'* score obtained in view of performance assessment criteria (satisfactory, questionnable either unsatisfactory) which is based on a quality requirement of 10% deviation from the certified value

IMEP-18: Sulphur in Diesel fuel

Annex 2 – Participants results – Tables

Table 1: The CRM as used by the laboratories in relation to the analytical technique used and sorted according to country

Used CRMs as reported by the laboratories	COUNTRY of participant	TECHNIQUE USED by participant
Conostan	AUSTRIA	UVF
NIST 2723a Sulfur in Diesel Fuel I.I.S. GO-12199	BELGIUM	COU WDXRF
Di-n-butyl sulfide and mineral oil from Analytical Services, INC LECO CORPORATION INSTRUMENTS	BRAZIL	EDXRF-CON IR/Leco
SWMO-LT-BL-4, SWMO-LT-1X-4, SWMO-3X-4, SWMO-5X-4, SWMO-LT-7.5X-4, AccuStandard Inc. CRM 105; CRM 106; CRM 107; SDF7 Dibutylsulfid - MERCK	BULGARIA	EDXRF-CON X-RAY
Dibenzothiophene, Standard Material Center of China Accustandard service .USA	CHINA	UVF WDXRF
Dibuthylsulfide in isooctane 100 mg/kg by SARTEC Ltd. NORMA # R 9000, Rofa France SU-GO-497, Rofa France	CROATIA	COU EDXRF-CON WDXRF
LGC3001, 10.0mg/kg Analytical Services, Inc	CYPRUS	EDXRF-CON
BCR ANTEK instruments, LP 0 - 100 ng/ul,.0-100 ng S /ul Canada SCP SCIENSE; USA Alpha Resources, Inc.	CZECH REPUBLIC	EDXRF-CON UVF WDXRF
MBH in UK	DENMARK	EDXRF-CON
AccuStandard		UVF
Sulfur in Diesel Fuel Calibration Standard 0.0500 wt% Analytical Services, Inc. Supplier AmStandard Accustandard S in diesel fuel SDF-BL-4(zero S)SDF-1X-4 (100 mg/kg); Analytical Services similar products accordingly SDF 7 and SDF 1 C VHG LABS Sulphur in #2 Diesel Fuel Standard 100 µg/g, Est-Doma Ltd, Conostan SWMO-7.5X-4; SWMO-15X-4; AccuStandard Inc. USA	ESTONIA	COU EDXRF-CON WDXRF

Used CRMs as reported by the laboratories	COUNTRY of participant	TECHNIQUE USED by participant
SYLAB SPEX or ACUSTANDARD or LGC LNE AND TECHLAB SCT Science	FRANCE	GAUV UVF WDXRF
alpha resources,conostan TOTAL internal standard from Round Robin Tests Di-N-Butylsulfide/Low Viscosity Mineral Oil; Breitländer	GERMANY	ICP-OES UVF WDXRF
OXFORD INSTRUMENTS	GREECE	WDXRF-INT
Stanhope-Seta	HUNGARY	WDXRF
LGC 3000, Lab of Government Chemist, London	IRELAND	EDXRF-CON
Alpha Resources Inc. AR-6201 Ultra low Kerosene 0.0011% w/w	ITALY	WDXRF
VHG Labs	LATVIA	EDXRF-CON
AccuStandard Inc,element: D-5453 Low Level Sulfur;supplier-company Amstandard	LITHUANIA	UVF
Gasoil for sulphur content SU-GO-497, ROFA France A 07074 Merck ULTRA LOW # 2 DIESEL OIL STANDARD ; ALPHA RESOURCES SU-GO- 245 ROFA FRANCE MBH ANALYTICAL LTD,Sulphur in Isooctane Standard 50,0 µg/g,supplier - Tusnovics Instruments Poland Sulfur in Isooctane 30.0 +- 0.3. Supplier: AccuStandard Inc. , D-5453-ML-SET MBH ANALITYCAL LTD e.g. 0,0100% Sulfur in Gasoil, ARMI Sulphur in Diesel Fuel, MBH Analytical Ltd.	POLAND	Combustion EDXRF-PXS UVF WDXRF WDXRF
PAC NIST 1616; #NORMA SU-GO-497;TCI - S0432;	PORTUGAL	EDXRF-CON WDXRF

Used CRMs as reported by the laboratories	COUNTRY of participant	TECHNIQUE USED by participant
MBH Sulfur in mineral oil, supplied by Analytical Services,USA	ROMANIA	UVF WDXRF
AccuStandard ROFA - Low Sulfur in Diesel 0.025-0.072 England,Analytical Services, Inc, supplier-Rofa(Austria) Sulfur in Mineral Oil, Analytical Services, Inc	SERBIA - MONTENEGRO	COU UVF EDXRF-CON
Petrotest Sulfur in Diesel - QC Sample, AccuStandard MBH Analytical Limited	SLOVAKIA	COU EDXRF-CON
CRM supplier is "MBH" from USA NIST CRM's	SLOVENIA	EDXRF-CON WDXRF
Supplier: Alpha Resources, Inc. Materials: AR-2871; AR-2827; AR-2822; AR-2873; AR-2821 VHG S20MIN-25-4 VHG DSL-16 NIST SRM 1616a Sulfur in Kerosine	SPAIN	WDXRF
dibutylsulfid,Analytical Standards	SWEDEN	Antek
BCR 104R	SWITZERLAND	UVF
CONOSTAN-ConocoPhillipsSpecialty Products Inc.,ACCU STANDARD ANTEK Instruments LP, carbon disulfide solutions Analytical Services inc. diesel matrix, 355 mg/kg, normalab analis, in Turkey sulfur limit is very high	TURKEY	EDXRF-CON pyrofluorescence TXRF UOP 357, Raney Nickel Method
NIST CRM supplied by US Department of Commerce NIST, USA.	UNITED ARAB EMIRATES	EDXRF-CON
LGC3021 ,Teddington, UK	UNITED KINGDOM	EDXRF-CON, UVF

Table 2: The Proficiency Testing Schemes laboratories in IMEP-18 participate in

Proficiency testing schemes	**COUNTRY of participant**	**TECHNIQUE used by participant**
FAM IRMM/ Dutch Customes Laboratory	AUSTRIA	UVF WDXRF
ASTM D16 Sulfur in aromatics Round Robin I.I.S. Institute for Interlaboratory Studies	BELGIUM	COU WDXRF UVF
Petrobras-Cenpes Rede Metrológica do Estado do Rrio Grande do Sul - Brasil and Instituto de Pesquisas Tecnológicas - IPT Brasil	BRAZIL	EDXRF-CON IR/Leco
CHEVRON TEXACO-Belgium; GLOBAL LUBRICANTS- LPTP 2001, 2002,2003 and 2004 EU Project QUA-NAS, contract QUA-NAS G7RT-CT-2002-05110, Saybolt WCP	BULGARIA	X-RAY EDXRF-CON
China National Accreditation Board for Laboratories CNAL	CHINA	UVF GB/T380 Petroleum products-Determination of sulphur-Lamp method
ASTM ILCP IFP-France IFP and ASTM	CROATIA	COU EDXRF-CON WDXRF
BP ICPMS	CYPRUS	EDXRF-CON
IMEP	CZECH REPUBLIC	EDXRF-CON
BP Oil International Ltd, Reading. GB	DENMARK	UVF
Institute for Interlaboratory Studies (iis), The Netherlands Norwegian Metrology and Accreditation Service Saybolt LP (Houston, USA) worldwide round robin test for Saybolt group of companies	ESTONIA	COU WDXRF EDXRF-CON
IIS in field of petroleum products	FINLAND	UVF

Proficiency testing schemes	COUNTRY of participant	TECHNIQUE used by participant
BNPé (bureau national du pétrole), TOTAL groupe. BNPé, TOTAL, IFP, IIS	FRANCE	GAUV, WDXRF UVF
BAM a.o. FAM (Fachausschuss Mineralöl- und Brennstoffnormung) ; Saybolt Round Robin FAM (Germany); PetroLab GmbH SGS IIS, Netherlands; FAM, Germany; AGQM, Germany; ASTM D 16	GERMANY	ICP-OES WDXRF UVF
IIS NETHERLAND	GREECE	WDXRF-INT, UVF
IIS, International Interlaboratory Studies	HUNGARY	WDXRF, UVF
UNICHIM	ITALY	WDXRF
Institute for Interlaboratory Studies, the Netherlands	KAZAKHSTAN	EDXRF-CON
IIS	LATVIA	EDXRF-CON
AMERICAN SOCIETY FOR TESTING AND MATERIALS	MEXICO	UVF
ASTM	NETHERLANDS	WDXRF
Institute for Interlaboratory Studies (IIS)	NORWAY	EDXRF-CON
ASTM, POLLAB Institute for Interlaboratory Studies, Dordrecht, The Netherlands Orlen Laboratorium, Poland	POLAND	ICP-AES EDXRF-CON; EDXRF-PXS WDXRF UVF
ASTM iis Round Robin programme SMPCS	PORTUGAL	WDXRF COU EDXRF-CON
Institute for Interlaboratory Studies,The Netherlands	ROMANIA	WDXRF, UVF
IIS IMEP-14	SERBIA - MONTENEGRO	EDXRF-CON UVF

Proficiency testing schemes	**COUNTRY of participant**	**TECHNIQUE used by participant**
Institute for Interlaboratory Studies Dordrecht, the Netherlands	SLOVAKIA	COU, WDXRF
ASTM Institute for Interlaboratory Studies - ICPMS (British Petroleum) - IP - Comite Ibérico de Laboratorios de Ensayo	SPAIN	UVF WDXRF
IIS, Netherlands	SWEDEN	ICP-OES
IIs, ICPMS		Antek
Petro Lab GmbH, Speyer, FAM Germany	SWITZERLAND	UVF
BP ICPMS program Fosfa iis Interlaboratory Studies Netherlands UME	TURKEY	pyrofluorescence UOP 357, Raney Nickel Method EDXRF-CON, COU TXRF
ASTM Interlaboratory Crosscheck Program, Shell Correlation , DNVPS International round robin.	UNITED ARAB EMIRATES	EDXRF-CON
IIS/Esso/ASTM	UNITED KINGDOM	COU

Table 3: Calculation of reported uncertainty in case the guides for quantifying uncertainty (ISO/EURACHEM) were not followed

Reported uncertainty calculated in the following way in case not according to the guides for quantifying uncertainty (ISO/EURACHEM)	**COUNTRY**	**TECHNIQUE**
Exxon guidelines	AUSTRIA	UVF
According rate of confidence of 95% based on standard deviation (10 measurements) By the RSD value on replicates	BELGIUM	COU UVF
By the standard deviation	BRAZIL	EDXRF-CON
EA-4/02 Expression of the Uncertainty of Measurement in Calibration	BULGARIA	EDXRF-CON
It was calculeted as +- standard deviation of 12 measurements	CYPRUS	EDXRF-CON
According to EAL-R2 Standard variation EN ISO 4259	CZECH REPUBLIC	COU UVF
Standard deviation from two single tests ASTM D 5453	DENMARK	EDXRF-CON UVF
Uncertainty was evaluated according to used method	ESTONIA	EDXRF-CON
r value was calculated according to standard EN ISO 20846 (ISO/DIS 20846)	FINLAND	UVF
Internal procedure Relative standard deviation Reproducibility With repeatability and reproducibility	FRANCE	GAUV UVF WDXRF
Standard deviation of 8 measurements standard deviation Reproducibility of EN ISO method used According to the precision data from the norm used Norm ISO 20884	GERMANY	EDXRF-PXS ICP-OES UVF WDXRF

Reported uncertainty calculated in the following way in case not according to the guides for quantifying uncertainty (ISO/EURACHEM)	**COUNTRY**	**TECHNIQUE**
According to the manual of our lab which follows ISO 17025	GREECE	WDXRF-INT
On our own evaluation	HUNGARY	AFS
calculated from the reproducibility of the method on basis of 71% of the interlaboratory reproducibility	NETHERLANDS	UVF WDXRF
at standard deviation for ten value	ROMANIA	UVF
Repeatability ASTM D 3120 by repeatability, which is defined in standard ISO 8754 Instrument data report	SERBIA - MONTENEGRO	COU EDXRF-CON
repeatability	SLOVAKIA	EDXRF-CON
EUROLAB TECHNICAL REPORT Nº1/2002 The uncertainty is evaluated as a standart deviation of the 12 measures we did.	SPAIN	WDXRF
+/- half of the repeatability of the test method R= 5.7 mg/kg (from method); sR=R/2.83 = 2.0; we took sR as combined standard uncertainty to calc. the expanded uncertainty with cov. factor k=2	SWITZERLAND	UVF
Standard deviation was calculated and accepted as uncertainty	TURKEY	COU
Based on IP373 repeatability provided by instrument software	UNITED KINGDOM	COU EDXRF-CON

Annex 3 – Documentation

Contents

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
IRMM
Institute for Reference Materials and Measurements

Geel, March 2004
IM/L/13/04

International Measurement Evaluation Programme

IMEP-18- Sulphur in Diesel fuel (gasoil)

The International Measurement Evaluation Programme (IMEP®) 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 participant's results). Previous IMEP® interlaboratory comparisons have focused on different elements in various matrices such as water, sediment, serum, wine and others. Information about these activities can be found on the IMEP website http://www.imep.ws.

Participating laboratories receive a Certified Test Sample (CTS) (with undisclosed amount content values), which is to be measured using routine analytical procedures. The measurement results of participants will be evaluated against metrological reference values obtained using a primary method of measurement (Isotope Dilution Mass Specrometry). IMEP® is open to all laboratories and full confidentiality is guaranteed with respect to the link between measurement results and the participants' identity.

IRMM is now launching the IMEP-18 interlaboratory comparison that focuses on the analysis of Sulphur in Diesel fuel (gasoil). The nominal amount content of the S in the diesel is approximately 50 µg/g. The CTS is bottled in a 10mL sealed glass ampoule. Participants will receive 2 ampoules of the material. A participation fee of 200 € per laboratory (dispatch costs included) is requested except if the following applies.

> (In the frame of an EU supporting programme to EU acceding and candidate countries as well as Western Balkan countries (Cards program), participation for laboratories from these countries is free of charge. This applies for Albania, Bulgaria, Bosnia-Herzegovina, Cyprus, Croatia, Czech Republic, Estonia, Hungary, Latvia, Lithuania, FYR of Macedonia, Malta, Poland, Rumania, Serbia-Montenegro, Slovakia, Slovenia and Turkey.)

Registration deadline will be 7th of May 2004. The samples will be available in May/June 2004. Deadline for reporting results would be 5th August 2004. As a first feedback, the reference value for the S in the material will be available on the IMEP website in September 2004. Individual certificates will be issued in October 2004. Participants' reports will be available in autumn/winter of 2004.

If you would be interested in joining this IMEP-18 interlaboratory comparison, please register on-line on the IMEP website http://www.imep.ws or via the url-link: http://www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=32.

A list with the regional co-ordinators for this round will be available on the same website address in due time.

Yours sincerely,

Mrs.Lutgart Van Nevel
Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 702 •Fax: +32-(0)14-571 865 • imep@irmm.jrc.be • lutgart.van-nevel@cec.eu.int • www.imep.ws • http://www.irmm.jrc.be

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

Geel, 23rd June 2004
IM/L/46/04

IMEP-18: Sulphur in diesel fuel (gasoil)

Dear «title» «surname»,

Thank you very much for your participation in our interlaboratory comparison.

Together with this letter you will find the sample confirmation form. May we ask you to return this form immediately to IRMM, so that we know if you received the package in good order.

This IMEP-18 interlaboratory comparison involves the determination of the total amount content of S in diesel fuel (gasoil). The Certified Test Sample is bottled in a 10 mL sealed glass ampoule and enclosed are 2 sample sets.

Deadline for reporting the results and returning the completed questionnaire is **9th September 2004**. A first feedback, concerning the IMEP-18 reference value, is foreseen for end September 2004 on our website (www.imep.ws). Individual certificates and the report will be made available in winter 2004.

Result reporting will be done electronically via the IMEP web-site. The result reporting-login will be open from 15th July 2004 onwards and will be accessible via the url-link http://www.irmm.jrc.be/imepapp/jsp/loginResult.jsp . The url-link will also be accessible from our website. At that moment you will find there also a document with information about how to report your results.

You have been allocated a personal code, the 'Password Key', for the on-line reporting of your results. Please fill in this number when requested when you are connected to the on-line reporting page.

Your Password Key = «participation_key»

When you have submitted your results and questionnaire information, you will be prompted to print the result report form. The paper version need to be returned signed to IRMM. Please check your results carefully for any errors before submission. In case you need to adjust any of your results, please contact us on the following address: jrc-irmm-imep@cec.eu.int or by fax to the following number: +32 14 571 865. After result reporting deadline, no amendments of results are accepted anymore.

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

Yours sincerely,

Mrs. L. Van Nevel
IMEP-18 Co-ordinator, IRMM JRC

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

«title» «firstname» «surname»
«companyinstitute_»
«department»
«address1»
«address2»
«address3» «address4»
«zip» «town»
«country»

IMEP-18
Sulphur in diesel fuel (gasoil)

Confirmation of receipt of the IMEP-18 Diesel fuel samples

Please return this form immediately to IRMM, this confirms that the sample package arrived. (in case it is damaged, please contact us immediately).

Please complete or amend the address information in case needed.

(capital letters).

REMARKS ?…….

Date of package arrival:……..

Signature:……

Please return the form to:
Mrs. L Van Nevel
IMEP-18 Co-ordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32 (0) 14 571 865
e-mail : lutgart.van-nevel@cec.eu.int

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

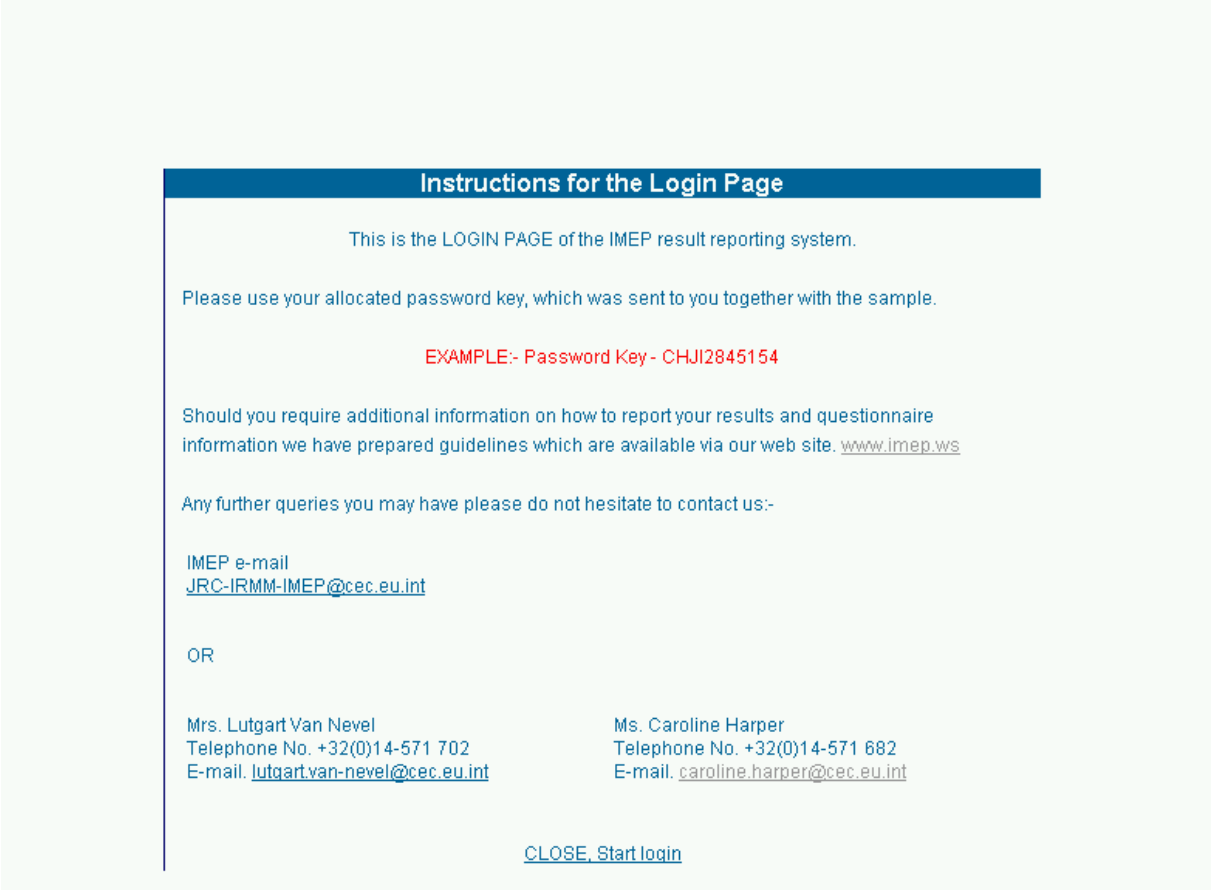
GUIDELINES to Participants on Reporting Results and completing the Questionnaire.

We are pleased to advise that the IMEP® online reporting system is now operational. These guidelines will explain how you can input your measurement result with uncertainty and how to enter the questionnaire information.

The result reporting is done on the Internet, the login page is located using the following URL

http://www.irmm.jrc.be/imepapp/jsp/loginResult.jsp

The following information page will appear. To obtain the login page, close down this screen.



Instructions for the Login Page

This is the LOGIN PAGE of the IMEP result reporting system.

Please use your allocated password key, which was sent to you together with the sample.

EXAMPLE:- Password Key - CHJI2845154

Should you require additional information on how to report your results and questionnaire information we have prepared guidelines which are available via our web site. www.imep.ws

Any further queries you may have please do not hesitate to contact us:-

IMEP e-mail
JRC-IRMM-IMEP@cec.eu.int

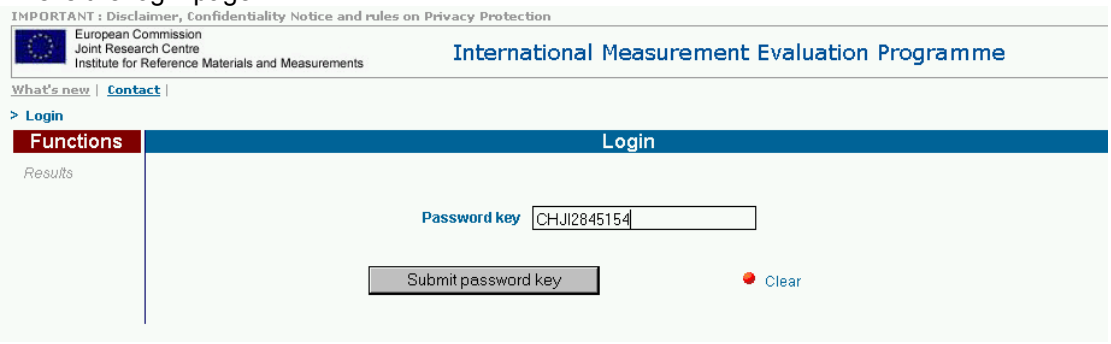
OR

Mrs. Lutgart Van Nevel
Telephone No. +32(0)14-571 702
E-mail. lutgart.van-nevel@cec.eu.int

Ms. Caroline Harper
Telephone No. +32(0)14-571 682
E-mail. caroline.harper@cec.eu.int

CLOSE, Start login

This is the login page.



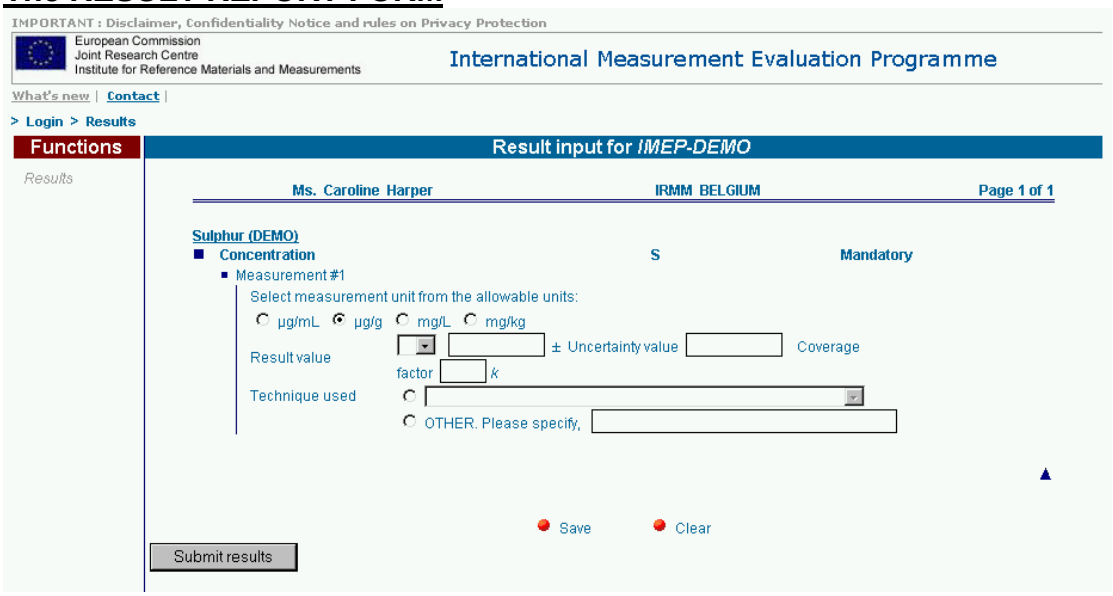
Please use your allocated password key, which was sent to you together with the sample.

EXAMPLE:- Password Key - CHJI2845154

Once you have entered your password key, press the *SUBMIT* button

(Please note that your password key is unique to the comparison you have registered to.)

The RESULT REPORT FORM



Completing the RESULT REPORTING Page.

1. Select the measurement unit from the list provided.

2. In the field marked “Result value” enter your measurement result using the 2nd box to your left.

If you need to report an upper limit as a result you will have to select the “<” from the drop down menu. (1st box from your left) Please be aware that the uncertainty field will now be disabled, so no input can be entered.

3. In the field marked “Uncertainty value” enter your measurement uncertainty. If you have not estimated an uncertainty for your result you will have to leave this field blank.

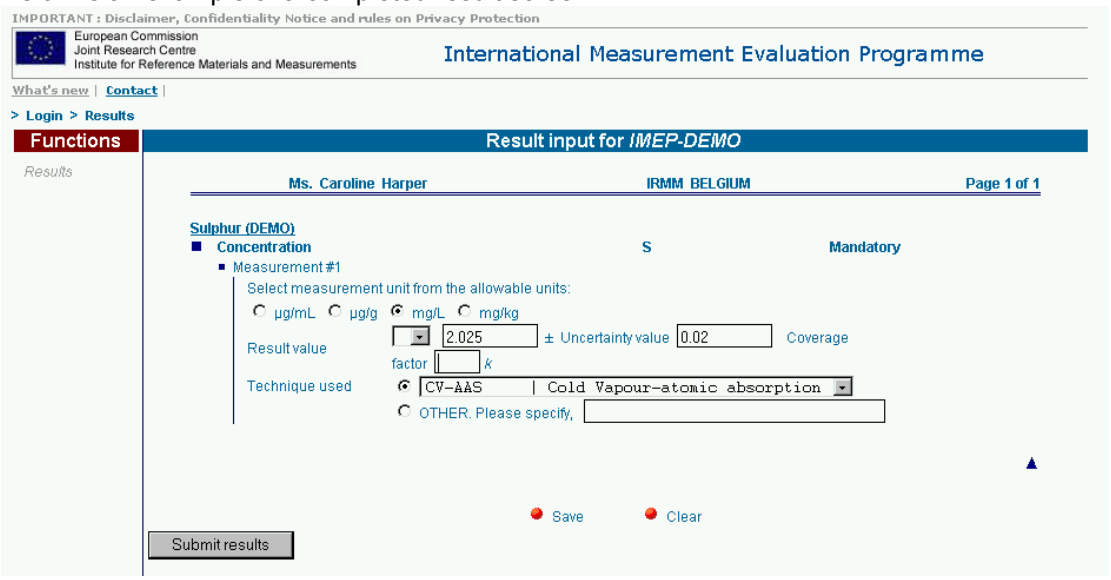
4. Input the coverage factor. (IMEP-18 participants do not have to complete this field, so leave blank)

5. Select the field marked “Technique used” this will activate the drop down menu. Select the technique used. If the technique used is not listed, select the “OTHER” field and then specify.

When the “Technique used” field has been selected the “OTHER” field is disabled and no input can be entered.

Likewise should you select the “OTHER” field then the “Technique used” field is disabled.

Below is an example of a completed result screen.



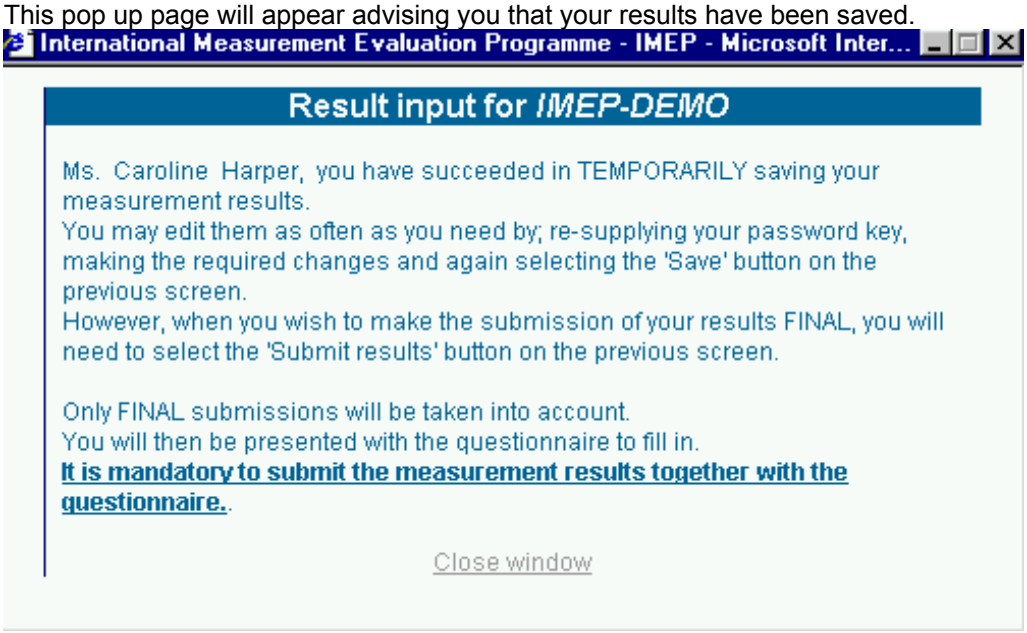
At this stage you can choose to **SAVE** your results or **SUBMIT** them.

SAVE -To SAVE your results press on the *SAVE* button, this will SAVE the data entered with the possibly to edit them as often as you need.

To reconnect to our system use the same URL link http://www.irmm.jrc.be/imepapp/jsp/loginResult.jsp and re-supply your password key. The result form will appear with the data that has already been entered. Make the required changes and select either the *SAVE* button or the*SUBMIT* button.

Remember to submit your results before the deadline date, as ONLY submitted results will be accepted.

This pop up page will appear advising you that your results have been saved.



How to SUMBIT your results
Once the *SUBMIT* button has been pressed, the questionnaire will appear ready for your input.

The QUESTIONNAIRE FORM

Completing the QUESTIONNAIRE Page.

1. You must enter or select data to every question, otherwise your questionnaire information will not be submitted. Should you not complete a question or complete a question incorrectly a message will appear directing you to that relevant question.

2. Text fields are a maximum of 100 characters.

3. Questions that have YES / NO format:-

a. Select your answer.

b. Add comments ONLY where applicable.

Please do not add comments to questions where it is not asked. For any comments entered where not applicable, our system will automatically delete them when you submit your data.

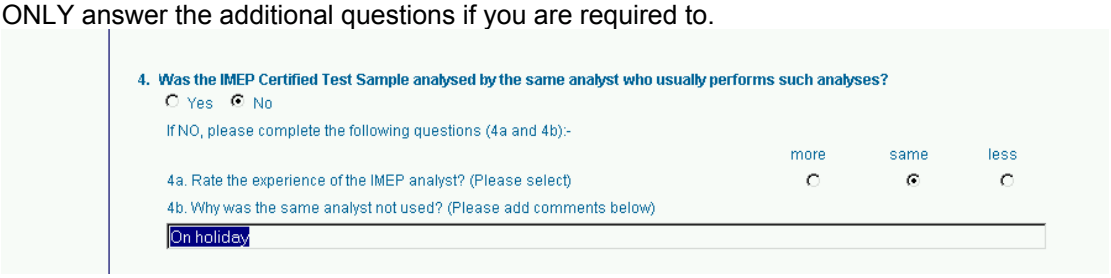
FOR EXAMPLE- If you answer YES to a question, but the comments are only applicable if you answered NO.
PLEASE do not add any text there, **as our system will automatically delete your comments when you submit.**

The same will happen when you answer NO to a question, but the comments are only applicable if you answered YES.

4. In Question No.3, the comment field should only be completed if you have selected “OTHER”.

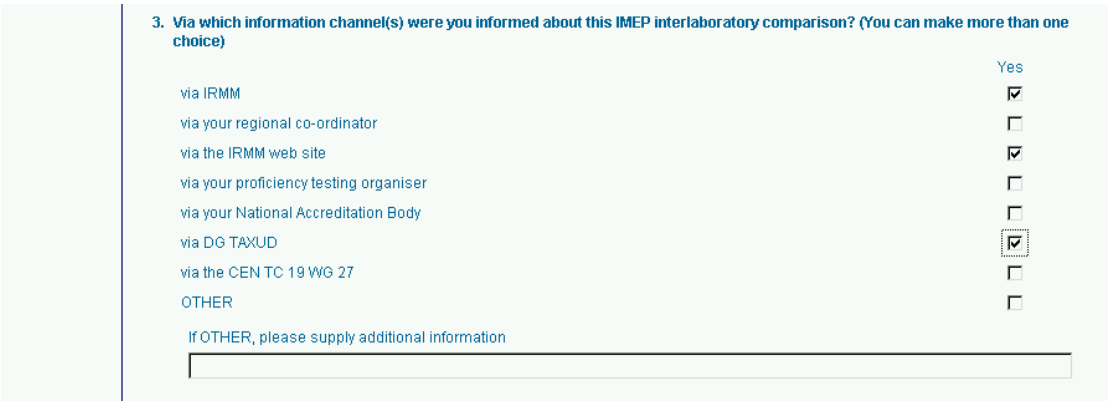
5. Instructions for Questions 4, 7, 12, 13 and 21.

ONLY answer the additional questions if you are required to.



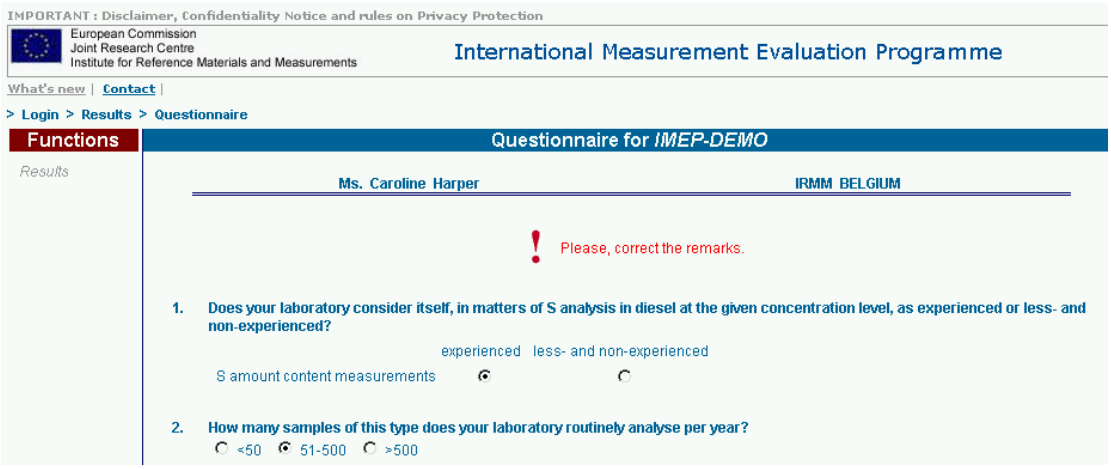
6. Instructions for Questions 3, 15, and 20.

You may select more than one answer.

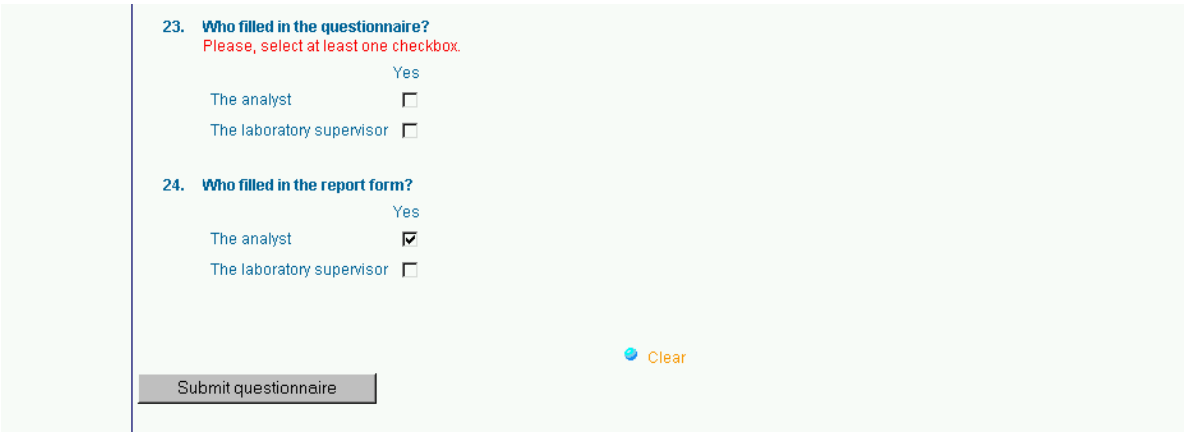


Once you have completed the questionnaire, press the *SUBMIT QUESTIONNAIRE* button.

If you receive an error message, the system will direct you to that relevant question by adding a message in red text.



Below is an example of an error message screen. (Located at the top of the screen)



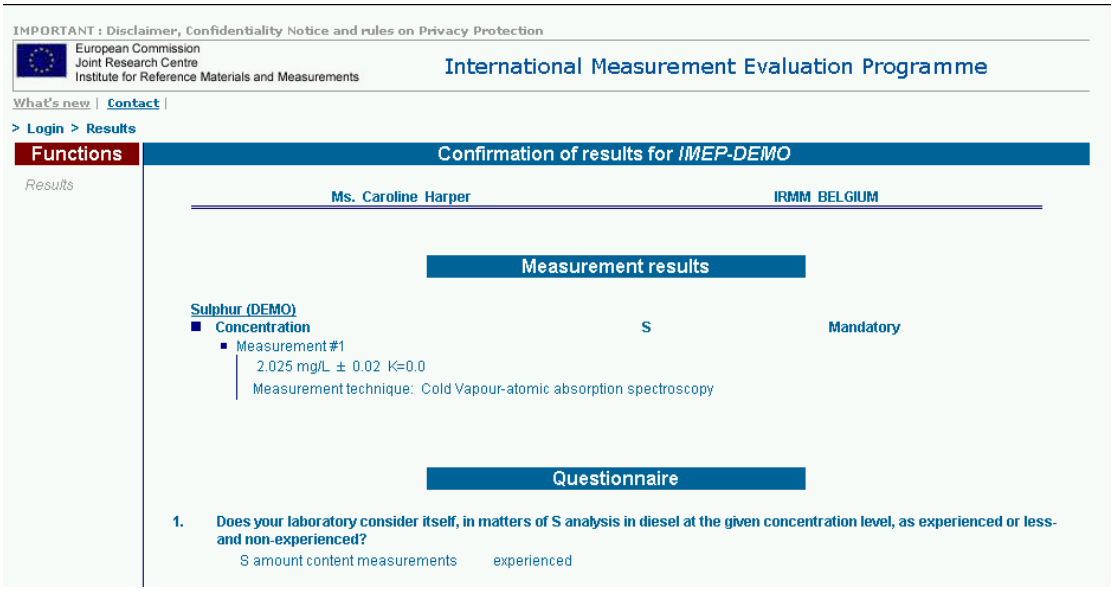
Before re-submitting your data please make sure that the following has been applied:-

a) Ensure all questions have been completed.

b) Ensure that the comment field has only been completed when asked.

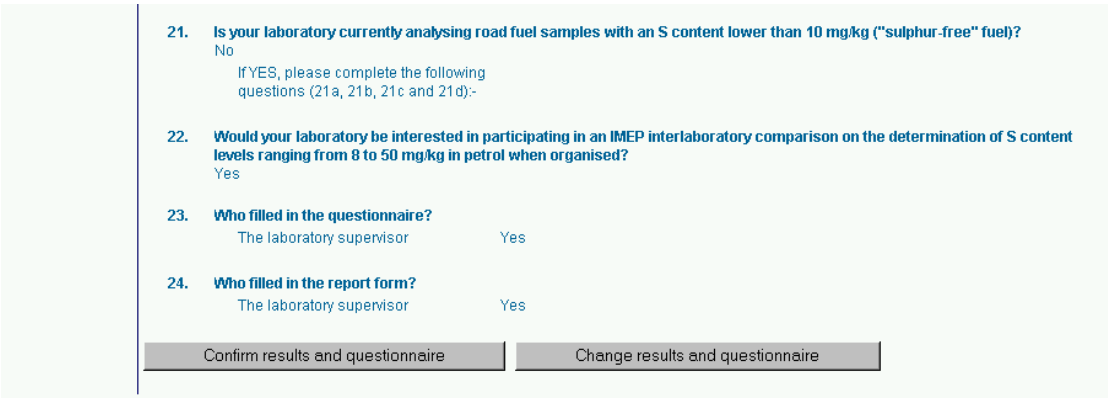
When you have made the necessary changes, press the *SUBMIT QUESTIONNAIRE* button.

A confirmation screen will appear showing the data entered.

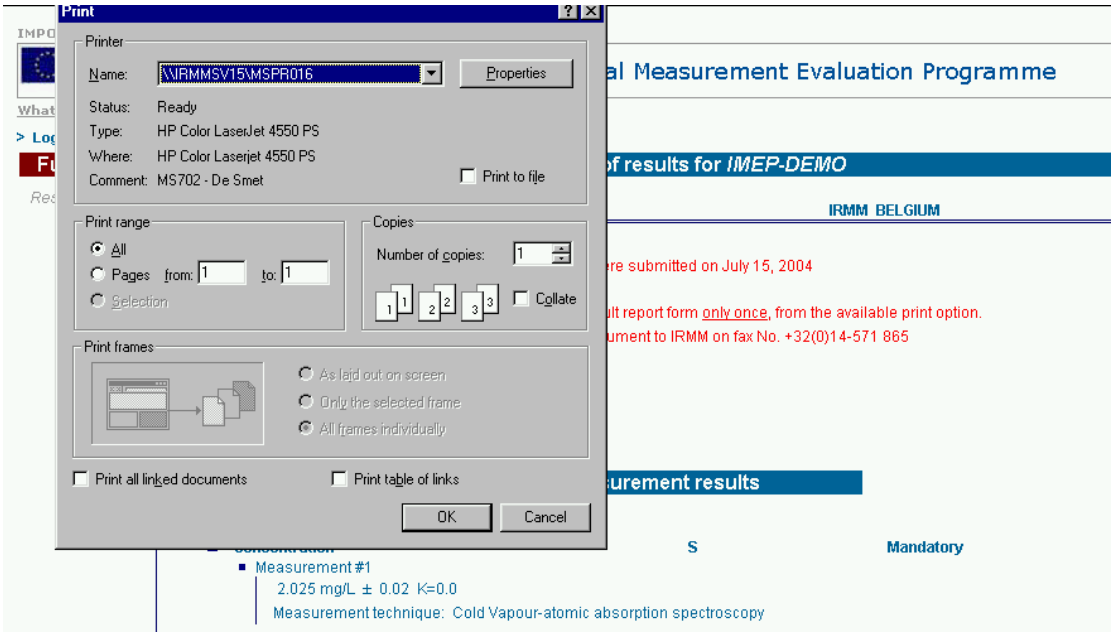


Should any amendments need to be made press the *CHANGE RESULTS AND QUESTIONNAIRE* button, this will return you to the previous screen. Make the required changes and submit your data again.

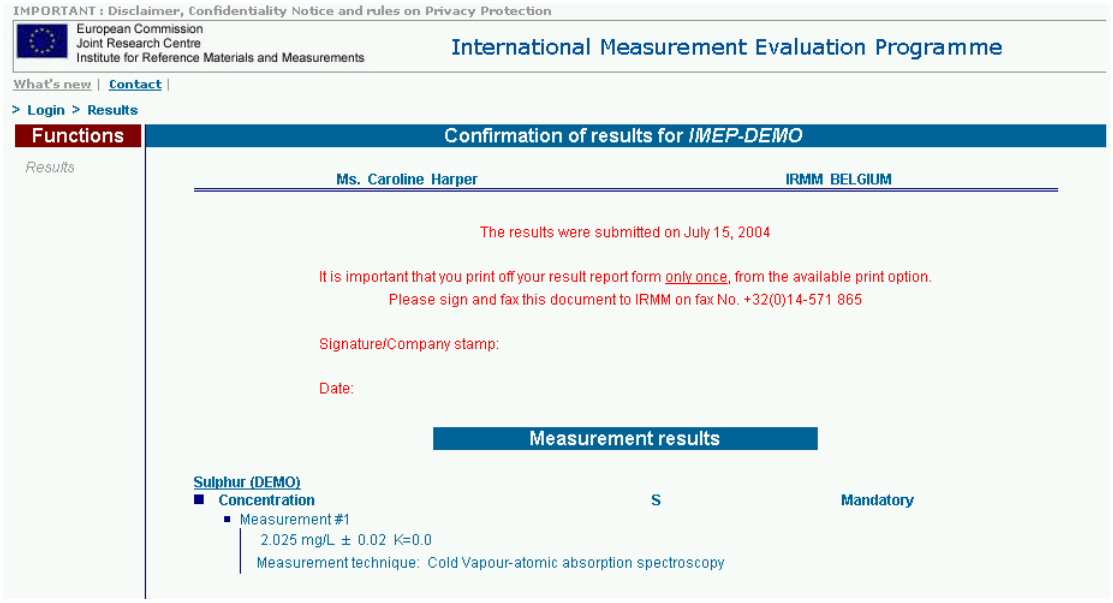
Once more the confirmation screen will appear, check your data again. When all data is correct, press the *CONFIRM RESULTS AND QUESTIONNAIRE* button. (Located at the bottom of the screen)



It is IMPORTANT that you print off your result report form ONLY ONCE, from the available print option.
Please sign and fax this document to IRMM on Fax No. +32 (0)14 571 865



The final screen will conclude that your data has been accepted by IRMM, this message will appear at the top of the screen.



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP®

IM/L/92/04
9 November 2004

IMEP-18

Sulphur in diesel fuel (gasoil)

IMEP Certified Reference Value

analyte	certified value (amount content) mg·kg^{-1}	expanded uncertainty *U*, *k*=2 mg·kg^{-1}
Sulphur	**42.2**	**1.3**

Mrs. L. Van Nevel
IMEP-18 Co-ordinator
IRMM

Institute for Reference Materials and Measurements

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 702 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.imep.ws • http://www.irmm.jrc.be

IMEP: an IRMM programme, with the aim to enable evaluation of performance in chemical measurements and to establish their degree of international equivalence

In IMEP-18 the same sample material was used as in the BIPM/CCQM Key comparison K35 which was coordinated by NIST (USA). Therefore the IMEP-18 certified reference value is the CCQM-K35 key comparison reference value which is derived from results reported by the following National Metrology Institutes. The IMEP-18 certified reference value hence was derived from reference measurements with demonstrated traceability and demonstrated uncertainty.

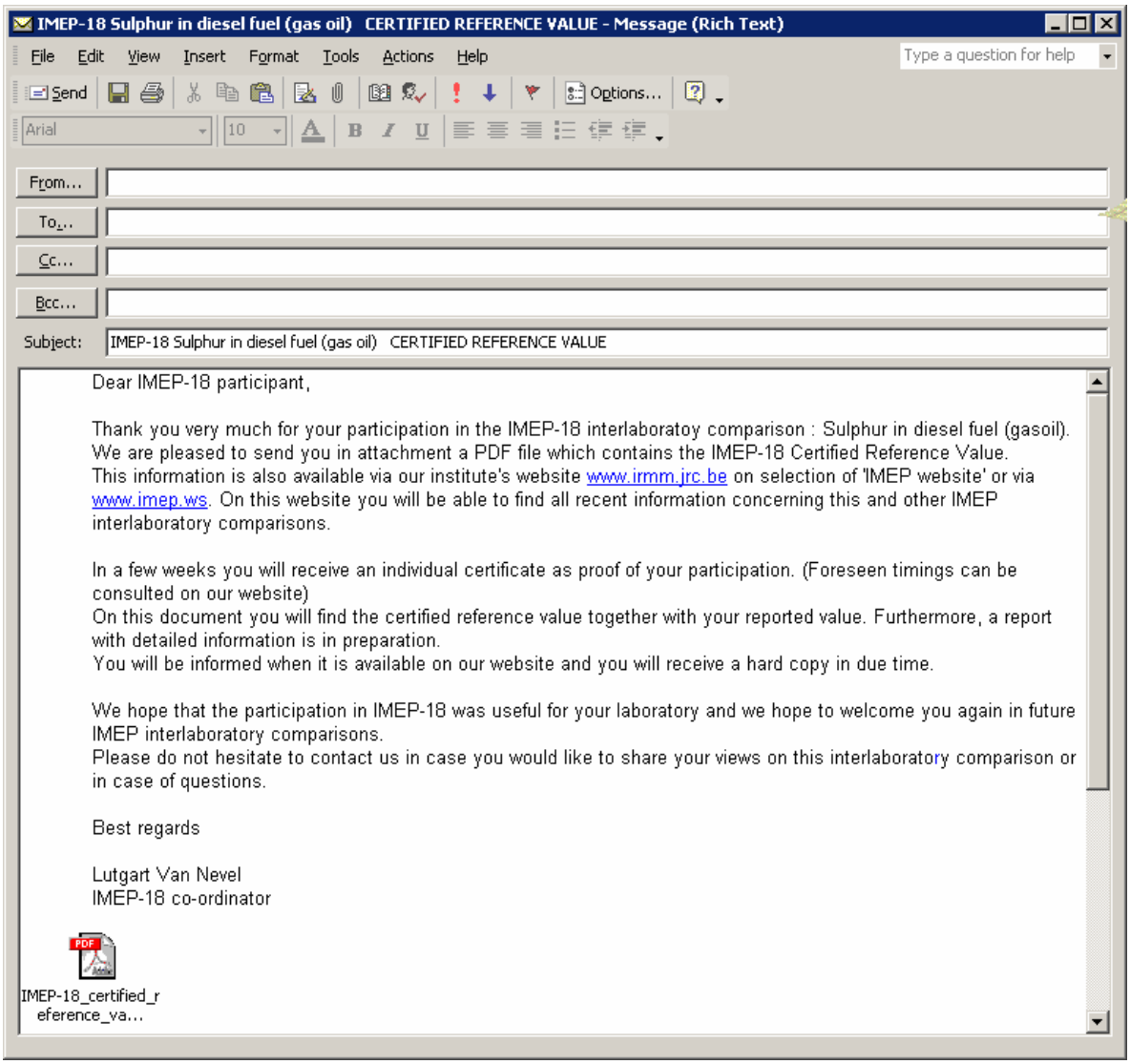
European Commission – Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
Isotope Measurement Unit
Retieseweg 111
B-2440 Geel
Belgium
http://www.irmm.jrc.be/imep/

National Institute of Standards and Technology (NIST)
100 Bureau Drive
Gaithersburg
MD 20899-3460
USA
http://www.nist.gov

Federal Institute for Materials Research and Testing (BAM)
Unter den Eichen 87
D-12205 Berlin
Germany
http://www.bam.de

Laboratory of the Government Chemist (LGC)
Queens Road
Teddington
Middlesex TW11 0LY
Great Britain
http://www.lgc.co.uk

IMEP-18 Sulphur in Diesel fuel - Annex 3
Accompanying e-mail: 'Certified Reference Value' announcement



IMEP-18 Sulphur in diesel fuel (gas oil) CERTIFIED REFERENCE VALUE - Message (Rich Text)

File Edit View Insert Format Tools Actions Help — Type a question for help

Send | Options...

Arial | 10 | B I U

From...

To...

Cc...

Bcc...

Subject: IMEP-18 Sulphur in diesel fuel (gas oil) CERTIFIED REFERENCE VALUE

Dear IMEP-18 participant,

Thank you very much for your participation in the IMEP-18 interlaboratoy comparison : Sulphur in diesel fuel (gasoil).
We are pleased to send you in attachment a PDF file which contains the IMEP-18 Certified Reference Value.
This information is also available via our institute's website www.irmm.jrc.be on selection of 'IMEP website' or via www.imep.ws. On this website you will be able to find all recent information concerning this and other IMEP interlaboratory comparisons.

In a few weeks you will receive an individual certificate as proof of your participation. (Foreseen timings can be consulted on our website)
On this document you will find the certified reference value together with your reported value. Furthermore, a report with detailed information is in preparation.
You will be informed when it is available on our website and you will receive a hard copy in due time.

We hope that the participation in IMEP-18 was useful for your laboratory and we hope to welcome you again in future IMEP interlaboratory comparisons.
Please do not hesitate to contact us in case you would like to share your views on this interlaboratory comparison or in case of questions.

Best regards

Lutgart Van Nevel
IMEP-18 co-ordinator

IMEP-18_certified_reference_va...

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP

Geel, 28 April 2005
IM/L/57/05

«PERSON_TITLE_NAME» «PERSON_NAME» «PERSON_FIRSTNAME»
«ORGANISATION_NAME»
«DEPARTMENT»
«ORG_ADDRESS_LINE1»
«ORG_ADDRESS_LINE2»
«ORG_ADDRESS_LINE3»
«ORG_COUNTRY_CODE» - «ORG_ZIP_CODE» «ORG_ADDRESS_PLACE»
«ORG_COUNTRY_NAME»

IMEP-18 Sulphur in Diesel Fuel (gasoil)

Dear «PERSON_TITLE_NAME» «PERSON_NAME» «PERSON_FIRSTNAME»,

We are pleased to send you your individual certificate for IMEP-18. On this certificate you will find your reported results together with the certified reference value for the S amount content in the diesel material. In addition you will find for your laboratory, performance scores together with the performance assessment criteria. IRMM selected as performance evaluation criterion a range of ± 10% from the reference value. This fit-for-purpose criterion is based on legislation (2003/17/EC).

Enclosed you will also find a hard copy of the material certificate which was sent as electronic version on 18th November 2004 and which is also on-line available on our website. For your information the graphical display of all reported results by participating laboratories displayed together with the reference value can be found in annex.

In order to follow-up the receipt of this information package, may we ask you to return the document 'Acknowledgement of receipt' as soon as possible.

The IMEP-18 participants' report is in preparation and on its completion will be made available on our website (beginning of July 2005). After booklet printing, you will also receive a personal hard copy of the report.

We sincerely hope you have found your participation in IMEP-18 useful. We would like to apologize for any inconvenience that might have occurred due to the fact that we were obliged to postpone some of our timings for this interlaboratory comparison.

We would like to thank you for taking part in this comparison and we hope to welcome you again in one of our future IMEP projects.

Yours sincerely,

Mrs. L. Van Nevel
IMEP-18 Co-ordinator

Attachments: - acknowledgement of receipt
- individual certificate
- graphical display of all reported results
- material certificate

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

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP®

IM/L/28/05/«certificate_number»
April 2005

IMEP-18 Sulphur in Diesel fuel (gasoil)
Individual Certificate

Issued to: «PERSON_TITLE_NAME» «PERSON_NAME» «PERSON_FIRSTNAME»
«ORGANISATION_NAME»
«DEPARTMENT»
«ORG_ADDRESS_PLACE», «ORG_COUNTRY_NAME»

Reported result

«reported_VALUE» ± «reported_UNCERTAINTY» in «reported_UNIT»
Analytical technique used: «TECHNIQUE»

The reported data were converted into mg•kg^{-1} in case reported in another unit.
Density of the material : 0.817 ± 0.001 mg•mL^{-1}(23°C)

	Certified (in mg•kg^{-1})			Reported (in mg•kg^{-1})		
Analyte	Reference Value	Expanded Uncertainty	Coverage Factor, k	Value	Uncertainty	Coverage Factor, k
Sulphur	**42.2**	**1.3**	**2**			

Performance scoring		Score
Percentage difference	$D\% = \frac{(x - X_{ref})}{X_{ref}} * 100$	
z-score	$z = \frac{(x - X_{ref})}{(0.1\, X_{ref})}$	
Zeta'-score	$Zeta' = \frac{x - X_{ref}}{\sqrt{u_x^2 + (0.1\, X_{ref})^2}}$	

Performance assessment criteria

|D%| ≤ 20%	Satisfactory
|D%| > 20 %	Unsatisfactory

|*z or zeta'*| ≤ 2	Satisfactory
2 < |*z* or *zeta'*| ≤ 3	Questionable
|*z or zeta'*| > 3	Unsatisfactory

Where X_{ref} is the reference value; x is the result you reported; u_x is the associated combined uncertainty we recalculated (✠). The fit-for-purpose criterion was set as 10% of the reference value ($0.1\ X_{ref}$), based on legislation.

Mrs. L. Van Nevel
IMEP-18 Co-ordinator

(✠) When laboratories reported a coverage factor (k), the combined uncertainty was calculated dividing the reported uncertainty by k. When no coverage factor was reported, the reported uncertainty was considered as the range of a rectangular distribution ($\pm\ a$); the combined uncertainty was then calculated dividing this range by $\sqrt{3}$, according to Appendix E-of the EURACHEM/CITAC Guide (2000) Quantifying uncertainty

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2770

Sulfur in Diesel Fuel Oil

This Standard Reference Material (SRM) is intended for use in the evaluation of methods and the calibration of instruments used in the determination of total sulfur in fuel oils or materials of a similar matrix. SRM 2770 is a commercial "No. 2-D" distillate fuel oil as defined by ASTM D 975-97 *Standard Specification for Diesel Fuel Oils* [1]. A unit of SRM 2770 consists of 10 amber ampoules, each containing approximately 10 mL of diesel fuel sealed under an argon atmosphere.

Certified Value: The certified sulfur content, provided in Table 1, is based on analyses by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [2]. Homogeneity testing was performed using X-ray fluorescence spectrometry (XRF). A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [3]. The expanded uncertainty for the certified value for sulfur is calculated as a 95 % confidence interval where $U = ku_c$. The quantity u_c is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO and NIST Guides [4]. The coverage factor, $k = 2.31$, corresponds to a t factor obtained from the t-distribution for approximately 8.45 degrees of freedom.

Table 1. Certified Value (mass fraction)

Sulfur:	41.57 mg/kg + 0.39 mg/kg

Information Values: Information values are provided in Table 2 for additional properties of SRM 2770. The values are not certified and are given to provide additional information on the matrix, but insufficient information is available to assess adequately the uncertainties associated with the values [3].

Expiration of Certification: The certification of this SRM is valid until **31 December 2015**, within the uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in the certificate, see "Instructions for Use". However, the certification will be nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: This material is considered to be stable during the period of certification. NIST will monitor this material and will report any significant changes in certification to the purchaser. Registration (see attached sheet) will facilitate notification.

The coordination of the technical measurements leading to the certification of this SRM was provided by W.R. Kelly and G.C. Turk of the NIST Analytical Chemistry Division.

Analytical measurements by ID-TIMS for certification were performed by W.R. Kelly, J.L. Mann, and R.D. Vocke and homogeneity testing by X-ray fluorescence spectrometry was performed by A.F. Marlow and J.R. Sieber of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Robert L. Watters, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 10 March 2005

Statistical consultation for this SRM was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

Blending and ampouling were performed under the supervision of M.P. Cronise of the NIST Measurement Services Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

Each SRM ampoule should only be opened for the minimum time required to dispense the material. Once an ampoule is opened, it is recommended that the material be used within a period of 8 h to avoid a potential change in the sulfur content. To relate analytical determinations to the certified value in this Certificate of Analysis, a minimum sample mass of 150 mg should be used. The unopened ampoules should be stored under normal laboratory conditions away from direct sunlight.

Table 2. Information Values for Selected Properties

Physical Property Test*	ASTM Standard Used	Result
Density @ 15 °C	D 1250-80 (1990)$^{\varepsilon 1}$	818.5 kg/m^3
@ 60 °F	D 4052-96	41.3 API
Flash Point	D 93 (A)-94	93.3 °C
Kinematic Viscosity @ 40 °C	D 445-94$^{\varepsilon 1}$	3.277×10^{-6} m^2/s (3.277 cSt)
Carbon	D 5291-92	85.1 %
Hydrogen	D 5291-92	14.8 %

* These properties were determined by a commercial firm under contract to NIST using ASTM methods. The results are NOT certified and are provided as additional information on the matrix.

ASTM Standards

D 93-94	Standard Test Methods for Flash Point by Pensky Martens Closed Cup Tester
D 4052-96	Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter
D 445-94$^{\varepsilon 1}$	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)
D 1250-80 (1990)$^{\varepsilon 1}$	Standard Guide for Petroleum Measurement Tables
D 2274-94	Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)
D 5291-92	Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants

Source and Preparation of Material: SRM 2770 was prepared at NIST by SRM' by mixing SRM 1624d and SRM 2723a to a target concentration of 42 mg/kg

REFERENCES

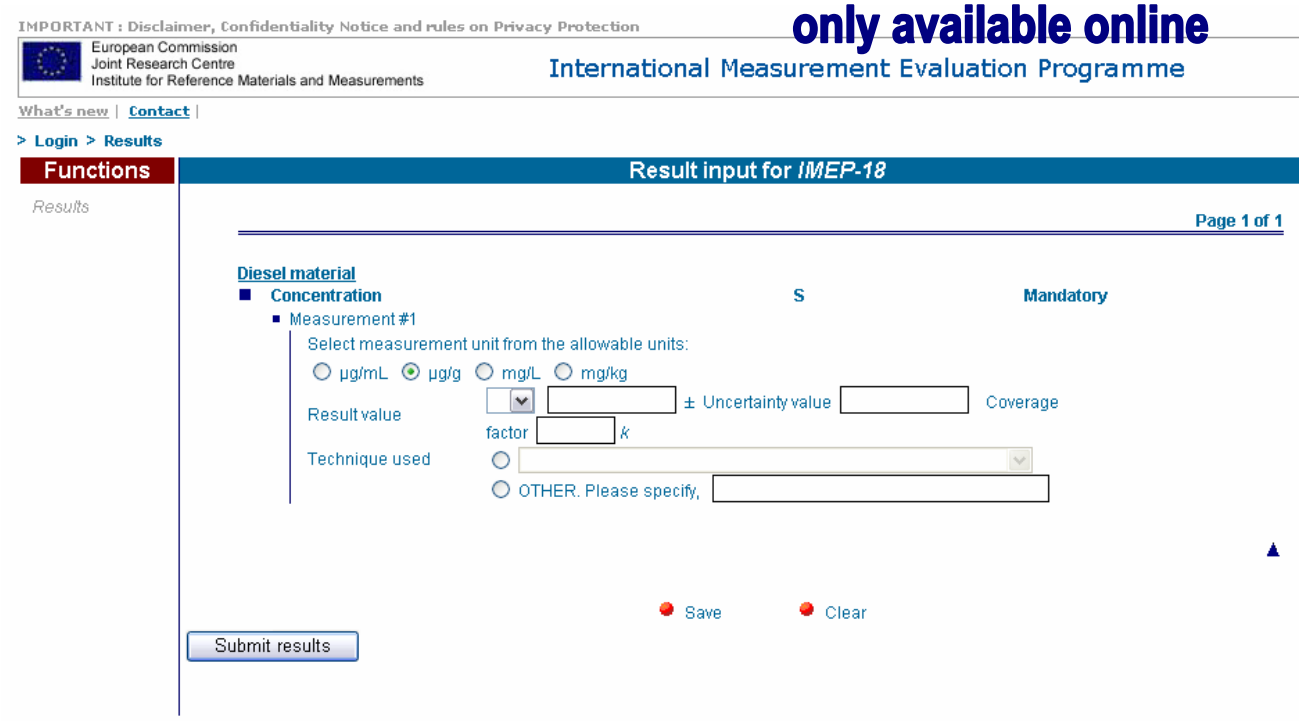
[1] ASTM D 975-97, *Standard Specification for Diesel Fuel Oils*; Annual Book of ASTM Standards, Vol. 05.01, West Conshohocken, PA (1998).

[2] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D., Jr.; Chen, L.-T.: *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, pp. 2505-2513 (1994).

[3] May, W.E.; Parris, R.M.; Beck II, C.M.; Fassett, J.D.; Greenberg, R.R.; Guenther, F.R.; Kramer, G.W.; Wise, S.A.; Gills, T.E.; Colbert, J.C.; Gettings, R.J.; MacDonald, B.S.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136, U.S. Government Printing Office: Washington, DC, p. 16 (2000).

[4] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9. 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926 4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.


IMPORTANT : Disclaimer, Confidentiality Notice and rules on Privacy Protection
only available online
European Commission
Joint Research Centre
Institute for Reference Materials and Measurements
International Measurement Evaluation Programme
What's new | Contact |
> Login > Results
Functions
Results
Result input for IMEP-18
Page 1 of 1
Diesel material
Concentration
S
Mandatory
Measurement #1
Select measurement unit from the allowable units:
µg/mL µg/g mg/L mg/kg
Result value
± Uncertainty value
Coverage
factor
k
Technique used
OTHER. Please specify,
Save
Clear
Submit results

IMEP-18

Sulphur in diesel fuel (gasoil)

PARTICIPANT QUESTIONNAIRE

The purpose of this questionnaire is to enable the organiser to correlate measurement performance with other factors such as analytical technique used, self-assessment of experience, accreditation and to present this to the participants in a graphical form. Additional information gained from this questionnaire will serve to identify the state-of-the-practice in S analysis in road transport fuels and will be used to develop future IMEP inter-laboratory comparisons.

ALL ANSWERS WILL BE TREATED CONFIDENTIALLY,

i.e. non-disclosure of the identity of the laboratories.

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

	experienced	Less- and non-experienced
S amount content measurements		

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

< 50 51-500 > 500

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

via IRMM

via your regional co-ordinator

via the IRMM web site

via your proficiency testing organiser

via your National Accreditation Body

via DG TAXUD

via the CEN TC 19 WG 27

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)

   4a. Rate the experience of the IMEP analyst? (Please select)

   more same less

   4b. Why was the same analyst not used? (Please add comments below)

   …….

   …….

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) (THIS FIELD MUST BE COMPLETED)

   ……

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 which solvents were used and dilution factor
    .....

11. Did you analyse the S in this diesel 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 Diesel Certified Reference Material (CRM) at your disposal certified for S?
    YES NO
    If YES, please complete the following questions (12a, 12b and 12c)

    12a. Is the CRM used in your laboratory for validation of procedures?
    YES NO

    12b. Is the CRM used in your laboratory for calibration of instruments?
    YES NO

    12c. Please state which CRM and supplier
    …….

13. Did your laboratory participate in other interlaboratory comparisons (round robin test/ring tests/collaborative trials)?
    YES NO
    If YES, please complete the following questions (13a and 13b)

    13a. Was the interlaboratory comparison organised by a proficiency testing organiser?
    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

If YES, is your laboratory involved in the interlaboratory comparison “S in mineral oils” which is co-ordinated by DG TAXUD?

YES NO

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

YES NO

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

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 ?

Certified	YES	NO
Accredited	YES	NO
Authorised	YES	NO

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

YES NO

18. Are you familiar with the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1993) and/or EURACHEM (1995)?

YES NO

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

    YES NO

    If "NO", how was the measurement uncertainty evaluated?

    .....
    .....
    .....
    .....

20. Was your participation to this IMEP comparison used to demonstrate your measurement capability to: (You can make more than one choice)

    your management

    your customers

    regulating or accreditation body

    Participation was intended for internal quality control purposes

    OTHERS

    If OTHERS, please supply additional information

    ……...

21. Is your laboratory currently analysing road fuel samples with an S content lower than 10 mg/kg ("sulphur-free" fuel)?

    YES NO

    If YES, please complete the following questions (21a, 21b, 21c and 21d)

    21a. Which type of material – diesel fuel(gas oil)

    …….

    21b. Which type of material – petrol

    …….

    21c. Which analytical technique is used for analysing the S content in "sulphur-free" fuel samples?

    …….

    21d. What is the minimal sample volume required for performing the analysis (in ml or g)?

    …….

22. Would your laboratory be interested in participating in an IMEP interlaboratory comparison on the determination of S content levels ranging from 8 to 50 mg/kg in petrol when organised?

    YES NO

23. Who filled in the questionnaire?

    The analyst

    The laboratory supervisor

24. Who filled in the report form?

    The analyst

    The laboratory supervisor

European Commission

EUR 21765 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements –
IMEP-18 Sulphur in Diesel fuel (gasoil), Report to Participants
Authors:L. Van Nevel, I. Verbist, C. Harper, S. Bynens, P. Smeyers, Y. Aregbe, P. Robouch and P.D.P. Taylor from IRMM;
G. Turk, R. Vocke and W.R. Kelly from NIST , USA
Luxembourg: Office for Official Publications of the European Communities
2005 – 78 pp. – 21 x 29.7 cm
Scientific and Technical Research series

Abstract

The International Measurement Evaluation Programme (IMEP®) is an Interlaboratory Comparison scheme in support of EU policies (e.g. Consumer Protection and Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policy). It is founded, owned and co-ordinated by the IRMM, the European Commission's Joint Research Centre for Reference Materials and Measurements.

The aim of this interlaboratory comparison programme is to picture objectively the degree of equivalence and the quality of chemical measurements. Contrary to most other external quality assessment schemes, participating laboratories in IMEP® can compare their measurement results and uncertainty statements with external certified reference values, obtained completely independent from the participants' result. These reference values are required to demonstrate traceability and they should have a demonstrated and adequately small uncertainty, as evaluated according to international guidelines. Participants in IMEP® use their routine analytical procedures to measure the IMEP-certified test sample (CTS). Therefore they can assess the quality of their results on an international forum by comparing their values to the IMEP-reference values.

In order to meet the new EU air quality standards, car manufacturers are developing a new generation of engines. However S in fuels can impair the effectiveness of existing and emerging automotive technology (S acts as a catalyst poison). The recent published Directive 2003/17/EC intends to reduce the sulphur levels in fuels and states that in 2005 fuels with maximum sulphur amount contents of 50 and 10 $mg \cdot kg^{-1}$ need to be available on the market in the Member States. This report describes the interlaboratory comparison IMEP-18 that allows laboratories to measure a diesel material with a S certified amount content of (42.2 ± 1.3) $mg \cdot kg^{-1}$. The reference value was established by Isotope Dilution Mass Spectrometry and is the result of the BIPM/CCQM key comparison K-35 co-ordinated by NIST to which 4 national metrology institutes participated. In this way, national metrology measurement capability supports measurement capabilities of field laboratories. Measurement results were reported by 141 of the 154 registered laboratories. Customs laboratories were contacted via DG TAXUD and nominated accredited laboratories resulted from the IRMM-European Accreditation collaboration. Besides laboratories from Member States also laboratories from Acceding and Western Balkan countries participated (IRMM's CARDS support).

This report presents organisatorial details about the project. Participants' results are presented in a graphical way together with the reference value and are sorted according to different criteria based on the replies from the questionnaire from which also numerical information is included.

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Community. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.