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Certification of n-Heptane (IRMM-441) and Isooctane (IRMM-442): Reference Fuels

Report
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Certification of n-Heptane (IRMM-441) and Isooctane (IRMM-442): Reference Fuels

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ABSTRACT

Certified Reference Materials IRMM-441 and -442 consist of high purity n-heptane and isooctane ampouled in 100 mL units and certified earlier by the National Bureau of Standards, presently National Institute of Standards and Technology, USA, in collaboration with Laboratoire National d'Essais (F) and the Institut Français du Pétrole (F). The certified values were verified by IRMM in 1999. On the basis of these results and on the original certificate, IRMM certified values and uncertainties were determined.

CONTENTS

1. Introduction

SRM 1815a and 1816a (n-heptane and isooctane) were certified in the early eighties through a joint effort of the US National Bureau of Standards (NBS), presenty National Institute of Standards and Technology (NIST), the French Laboratoire National d'Essais (LNE), and the Institut Français du Pétrole (IFP). The reference materials were distributed in the USA by NBS/NIST as SRM, in Europe by LNE. In 1998 the LNE stock was transferred to IRMM with the aim to distribute the materials as IRMM certified reference materials (IRMM – 441 and IRMM – 442). Therefore, both reference materials were reanalysed by IRMM in order to confirm the certified values. As a result of these measurements, which largely confirmed the original certified values (see Table 1), these were slightly corrected and complemented with appropriate uncertainty statements.

Table 1. Original NBS certified values (1985)

	n-heptane (NBS 1815a)	isooctane (NBS 1816a)
Purity	99.987 %	99.987 %
Total organics	0.0011 ± 0.0003 %	0.0010 ± 0.0002 %
Isooctane/n-heptane	0.0007 ± 0.0001 %	0.0002 ± 0.0001 %
Water	0.0002 ± 0.0001 %	0.0003 ± 0.0002 %
Lead	--	--

CRM IRMM-441 consists of high purity n-heptane supplied by ELF Company (France) ampouled in 100 mL units by Laboratoire National d'Essais (LNE), France. and is identical to NIST SRM 1815a. CRM IRMM-442 consists of high purity isooctane supplied by Phillips Chemical Co. (USA) ampouled in 100 mL and is identical to NIST SRM 1816a.
Both materials are intended for use as primary standards in the octane rating of motor and aviation fuels as specified in ASTM test methods (see Volume 05.04, Annual Book of ASTM Standards) and in evaluating ASTM methods for chemical analysis of fuels by gas chromatography (D 2268).

2. Complemental IRMM measurements

2.1 Determination of organic impurities by GC-FID

B. Sejerøe-Olsen, H. Schimmel

The determination of organic impurities was carried out in accordance with ASTM D 2268-93 [1].

2.1.1 Experimental

Procedure. The reference fuel was weighed into a 25 mL volumetric flask. Cyclohexane, p.a., was added (25 µL) as internal standard and reweighed. The volume-% (V_S) of the internal standard was calculated using equation (1), and used in later calculations.

$$V_s = \frac{\left(\frac{wt_{cyclohexane}(g)}{\rho_{cyclohexane}}\right)}{\left(\frac{wt_{referencefuel}(g)}{\rho_{referencefuel}}\right)} * 100\% \qquad (1)$$

Where:

$\rho_{cyclohexane} = 0.7786$, $\rho_{n-heptane} = 0.6838$ and $\rho_{Isooctane} = 0.6919$

Four solutions were prepared for each ampoule. Each solution was filled into two vials and each vial was analysed one time.

Instrumentation. The samples were analysed using a pressure-controlled Hewlett-Packard 5890 II gas chromatograph equipped with a flame ionisation detector (FID) and a Hewlett-Packard 7673 autosampler.

Injector type: *Split/splitless*
Sample size: *0.5 µL (split 1:100) and 1 µL (split 1:50)*
Injector temperature: *150 °C*
Carrier gas type and linear velocity: *helium, 15 cm/s*
Flow rate: *0.85 mL/min*
Column characteristics: *Fused silica, 100m, 0.25 mm ID, coating Squalane, d_f 0.2 µm*
Temperature programme: *Isothermal 32°C (80min)*

The FID was operated under the following conditions:

FID heater: *250 °C*
H_2 flow: *40 mL/min*
Air flow: *450 mL/min*
Makeup gas: *He 10 mL/min*

Two slightly different settings were used. The first one was as described in the ASTM method. (0.5 µL injected, split 1:100). This method however gave a rather low signal for the impurities. Therefore a slightly modified sample size was implied, using 1 µL injected, and a split of 1:50. This gave better response, and was used for determining the impurities of the reference fuels. Compared to the conditions described in the ASTM method it did however not have any influence on the final total purity of the reference materials.

Calculation. All peaks in the resulting chromatograms were integrated. The relative retention time towards *n*-heptane was calculated and the impurities were identified according to table 1 of reference [1]. The corresponding response factor was found in Table 2 of the same reference and used for calculating the volume-% of the impurity. The volume-% of each impurity was calculated using equation (2).

$$V_I = \frac{V_s * PA_I}{PA_s * S_I * (100 - V_s)} * 100 \qquad (2)$$

Where

V_I = Volume-% of the impurity to be determined

V_s = Volume-% of the internal standard, cyclohexane (formula 1)

PA_I = peak area of the impurity to be determined
PA_s = peak area of the internal standard, cyclohexane
S_I = the response per unit volume of the hydrogen flame ionisation detector to the impurity relative to the response per unit volume to cyclohexane (see Table 2 in reference [1])

Blank value of the procedure. Pentane was injected under the same conditions as mentioned above (Fig.1). This was done mainly to check for peaks coming from the chromatographic system (e.g. septum, injector, column etc). Chromatograms of n-heptane and isooctane are shown in Fig. 2 and 3. Comparing Fig. 1 and Fig. 3 it can be seen that no peaks appear on Fig. 1 (pentane) after R_t = 25.35 min and at this time no peaks have eluted yet on Fig. 3 (isooctane), where the internal standard is the first to appear.

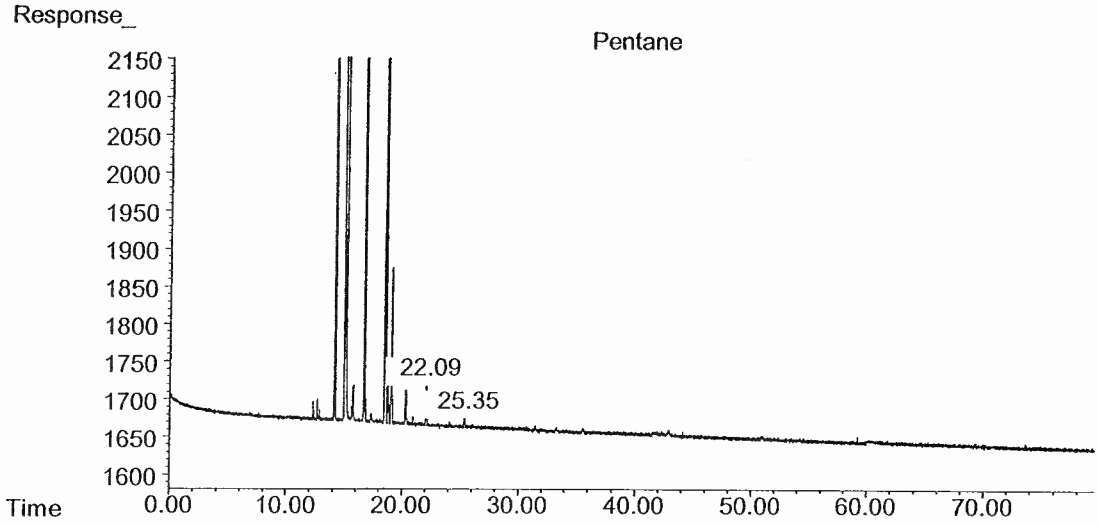

Fig.1. GC-FID Chromatogram of Pentane

As there are no interferences observed from the chromatographic system, all the peaks appearing in the chromatograms for isooctane and n-heptane are considered as "real" impurities and the volume-% calculated using equation 2.

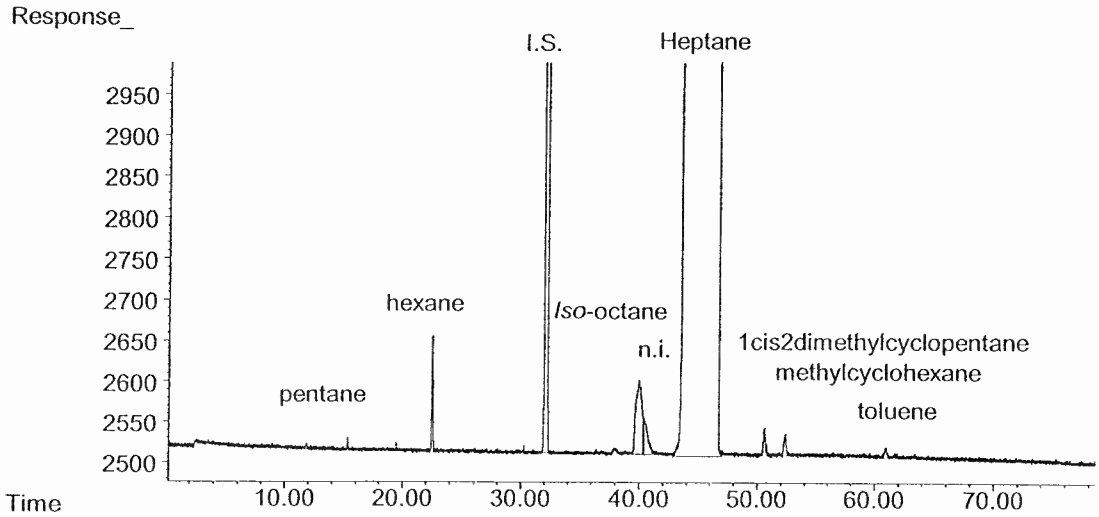

Fig. 2. GC-FID Chromatogram of n-Heptane IRMM-441

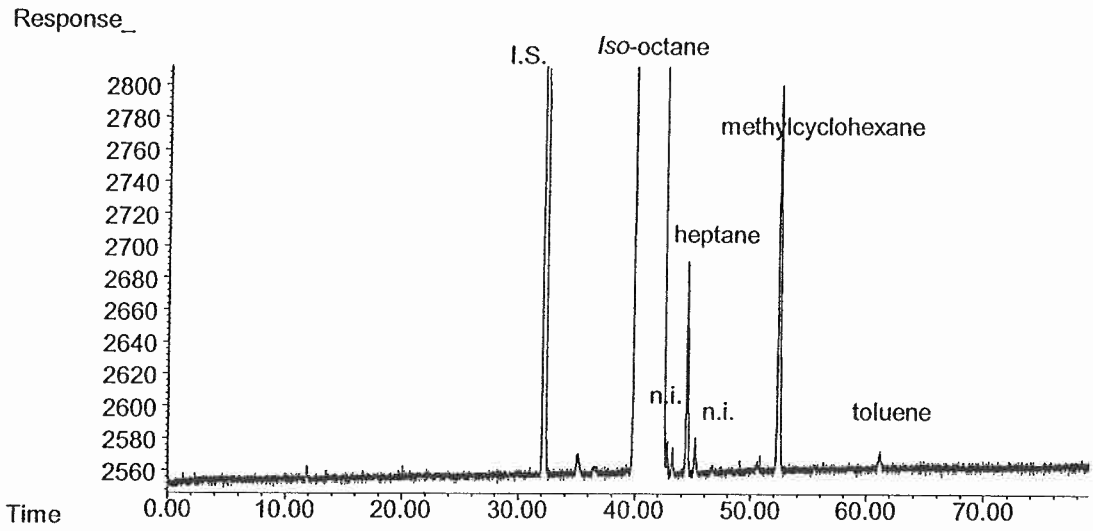

Fig. 3. GC-FID Chromatogram of isooctane IRMM-442

2.1.2 Results and discussion

Originally, two ampoules of n-heptane (9-8 and 14-2) and isooctane (6-24 and 7-2) were selected. From each ampoule 4 solutions were prepared with internal standard (cyclohexane), and each solution analysed twice. The results are given as the mean of two analyses from each solution, and the standard deviation of the 4 replicates. They were calculated using the corrected response factors indicated in the standard (for impurities which could not be identified the response factor was set to 1) and with response factor for all impurities set to 1 (as done by LNE in the original certification).

On the basis of later information originating from documentation handed over by LNE [2] it was, however, realised that, although series are comparable between each other, concentration gradients exist within the individual series. Therefore it was decided to analyse a third sample to cover the full filling range. The ampoules chosen were for n-heptane 14-18 and for isooctane 7-124.
A summary of the results is given in Tables 2 and 3.

These results are in line with the homogeneity observation made in the original NBS certification. They also show a slight negative bias if the LNE method is used. On their basis the following best estimates of the ASTM mean values and uncertainties of the IRMM verification measurements were made:

IRMM-441, n- heptane:

Mass fraction (total organics):	0.0149 % [(1)]
Uncertainty (total organics):	0.0040 % [(2)]
Mass fraction (isooctane):	0.0075 % [(1)]
Uncertainty (isooctane):	0.0022 % [(2)]

[(1)] Average of replicates carried out on the 2 ampoules taken at beginning and end of the filling sequence.

[(2)] Expanded standard uncertainty based on method standard uncertainty (average s on individual ampoules) and within filling series inhomogeneity (difference between extreme values/ $2 * \sqrt{3}$); coverage factor k = 2.

Table 2. Results for IRMM-441, n-heptane

a) Total organics

Ampoule No., solution No.	Total organics (%) acc. to ASTM method	Total organics (%) acc. to LNE method
9-8 1	0.0183	0.0138
9-8 2	0.0174	0.0136
9-8 3	0.0167	0.0124
9-8 4	0.0165	0.0124
MEAN	**0.0172**	**0.0130**
St. DEV.	**0.0008**	**0.0007**
14-2 1	0.0185	0.0144
14-2 2	0.0178	0.0137
14-2 3	0.0178	0.0137
14-2 4	0.0170	0.0131
MEAN	**0.0178**	**0.0137**
St. DEV.	**0.0008**	**0.0007**
14-18 1	0.0129	0.0094
14-18 2	0.0120	0.0088
14-18 3	0.0116	0.0086
14-18 4	0.0117	0.0087
MEAN	**0.0120**	**0.0089**
St. DEV.	**0.0012**	**0.0009**

b) Isooctane

Ampoule No., solution No.	isooctane (%) acc. to ASTM method	isooctane (%) acc. to LNE method
9-8 1	0.0102	0.0091
9-8 2	0.0101	0.0090
9-8 3	0.0086	0.0076
9-8 4	0.0088	0.0078
MEAN	**0.0094**	**0.0084**
St. DEV.	**0.0009**	**0.0008**
14-2 1	0.0085	0.0075
14-2 2	0.0079	0.0070
14-2 3	0.0077	0.0069
14-2 4	0.0073	0.0065
MEAN	**0.0078**	**0.0070**
St. DEV.	**0.0007**	**0.0006**
14-18 1	0.0079	0.0068
14-18 2	0.0070	0.0061
14-18 3	0.0069	0.0060
14-18 4	0.0068	0.0059
MEAN	**0.0071**	**0.0062**
St. DEV.	**0.0011**	**0.0009**

Table 3. Results for IRMM-442, isooctane

a) Total organics

Ampoule No., solution No.	Total organics (%) acc. to ASTM method	Total organics (%) acc. to LNE method
6-24 1	0.0151	0.0130
6-24 2	0.0152	0.0129
6-24 3	0.0150	0.0129
6-24 4	0.0151	0.0129
MEAN	**0.0151**	**0.0129**
St. DEV.	**0.0001**	**0.0001**
7-2 1	0.0152	0.0130
7-2 2	0.0152	0.0131
7-2 3	0.0149	0.0129
7-2 4	0.0150	0.0129
MEAN	**0.0151**	**0.0130**
St. DEV.	**0.0003**	**0.0002**
7-124 1	0.0113	0.0098
7-124 2	0.0118	0.0102
7-124 3	0.0125	0.0109
7-124 4	0.0123	0.0107
MEAN	**0.0120**	**0.0104**
St. DEV.	**0.0006**	**0.0005**

b) n-Heptane

Ampoule No., solution No.	n-heptane (%) acc. to ASTM method	n-heptane (%) acc. to LNE method
6-24 1	0.0037	0.0033
6-24 2	0.0038	0.0033
6-24 3	0.0037	0.0033
6-24 4	0.0036	0.0032
MEAN	**0.0037**	**0.0033**
St. DEV.	**0.0001**	**0.0001**
7-2 1	0.0038	0.0033
7-2 2	0.0038	0.0033
7-2 3	0.0038	0.0033
7-2 4	0.0036	0.0032
MEAN	**0.0037**	**0.0033**
St. DEV.	**0.0001**	**0.0001**
7-124 1	0.0014	0.0013
7-124 2	0.0015	0.0014
7-124 3	0.0016	0.0014
7-124 4	0.0016	0.0014
MEAN	**0.0015**	**0.0013**
St. DEV.	**0.0001**	**0.0001**

IRMM-442, isooctane:

Mass fraction (total organics): 0.0135 % [1]
Uncertainty (total organics): 0.0020 % [2]
Mass fraction (n-heptane): 0.0026 % [1]
Uncertainty (n-heptane): 0.0014 % [2]

[1] Average of replicates carried out on the 2 ampoules taken at beginning and end of the filling sequence.
[2] Expanded standard uncertainty based on method standard uncertainty (average s on individual ampoules) and within filling series inhomogeneity (difference between extreme values/ $2 * \sqrt{3}$); coverage factor k = 2.

For both reference materials there is, however, a small difference in absolute values between the IRMM values and the original NBS certified values (see Table 4). This difference may be due to changes in instrumentation, new development in peak integration, detection limits etc. (e.g. more impurity peaks were observed as e.g. in the LNE results). The difference between the present ASTM method and the method as used by LNE is as well illustrated in Tables 2 and 3.

Table 4. Comparison of IRMM results with original NBS certified values

	IRMM	NBS certificate
n-heptane	No. 441	No. 1815a
total organics	0.015 ± 0.004 %	0.011 ± 0.003 %
isooctane	0.008 ± 0.003 %	0.007 ± 0.001 %
isooctane	No. 442	No. 1816a
total organics	0.014 ± 0.002 %	0.010 ± 0.002 %
n-heptane	0.003 ± 0.002 %	0.002 ± 0.001 %

2.2 Determination of the water content by Karl Fischer titration

S. Rückold, K.H. Grobecker

2.2.1 Experimental

Experimental n-heptane and isooctane samples were measured by IRMM either at Metrohm Belgium NV, Antwerp (December 1998) or at the University of Hohenheim, Institut für Lebensmitteltechnologie, Arbeitgebiet Lebensmittelanalytik, in Esslingen, Germany (July 1999). In both cases a Metrohm 756 KF Coulometer and a coulometric cell without diaphragm were used.
The reagents used were:

Hydranal®-Coulomat AG-H, batch NR. 73450 – 12/97/2002
Hydranal®-Water Standard 0.10, batch NR. 80440 – 2/98/03

Experimental details are summarised in Table 5.

Table 5. Experimental parameters of Karl Fischer titration

control parameters:		Statistics:	off
EP at U:	50 mV	Preselections:	
Dynamics	70 mV	drift corr	auto
max. rate	2000 µg/mL	req. ident.	id1
min. rate	15 µg/mL	req. sample size	value
stop crit.	rel. drift	request and titration	on
rel. drift	5 µg/min	sample unit	g
titration parameters:		limit sample size	off
pause	0 s	text id1	id1 or C21
extr. time	30 s	text id2	id1 or C22
start drift	auto	text id3	id1 or C23
I(pol)	10 µA	cell	no diaphragm
electrode test	on	generator I:	auto mA
temperature	25.0 °C	oven:	no
time interval	2 s	activate pulse:	off
max. titr. time	off		

2.2.2 Results and discussion

The results obtained for n-heptane and isooctane are summarised in Tables 6 and 7.

Table 6. Results obtained for n-heptane

Ampoule No.	Replicate	Replicate results		
5-2	1.	0.0027 %		
	2.	0.0027 %		
	3.	0.0026 %		
	4.	0.0026 %	mean	0.00273 %
	5.	0.0029 %	st. dev.	0.000095 %
	6.	0.0028 %	coeff. of variation	3.48 %
	7.	0.0028 %		
	8.	0.0027 %		
	9.	0.0027 %		
	10.	0.0028 %		
5-18	1.	0.0024 %		
	2.	0.0024 %		
	3.	0.0024 %		
	4.	0.0025 %	mean	0.00247 %
	5.	0.0025 %	st. dev.	0.000071 %
	6.	0.0025 %	coeff. of variation	2.86 %
	7.	0.0026 %		
	8.	0.0024 %		
	9.	0.0025 %		
	10.	0.0025 %		

The values indicate satisfying repeatability even at water contents as low as here, particularly when considering the detection limit of coulometric Karl Fischer titration being nowadays around 0,0005 to 0,0010 %. The differences between the individual

series are, however, significant, as expected from heterogeneity data between bottles from the same filling series.

Table 7. Results obtained for isooctane

Ampoule No.	Replicate	Replicate results		
5-13	1.	0.0035 %		
	2.	0.0037 %		
	3.	0.0037 %		
	4.	0.0038 %	mean	0.00380 %
	5.	0.0038 %	st. dev.	0.000194 %
	6.	0.0039 %	coeff. of variation	4.94 %
	7.	0.0039 %		
	8.	0.0040 %		
	9.	0.0041 %		
	10.	0.0041 %		
5-66	1.	0.0036 %		
	2.	0.0033 %		
	3.	0.0032 %		
	4.	0.0034 %	mean	0.00337 %
	5.	0.0035 %	st. dev.	0.000116 %
	6.	0.0033 %	coeff. of variation	3.44 %
	7.	0.0034 %		
	8.	0.0034 %		
	9.	0.0033 %		
	10.	0.0033 %		
5-148	1.	0.0041 %		
	2.	0.0044 %		
	3.	0.0041 %		
	4.	0.0041 %	mean	0.00414 %
	5.	0.0043 %	st. dev.	0.000126 %
	6.	0.0041 %	coeff. of variation	3.06 %
	7.	0.0040 %		
	8.	0.0041 %		
	9.	0.0042 %		
	10.	0.0040 %		

On the basis of the above results the following best estimates of the mean values and uncertainties of the water content were calculated:

IRMM-441, n- heptane:

H_2O Mass fraction:	0.0025 % [(1)]
Uncertainty:	0.0002 % [(2)]
Estimated expanded uncertainty (k = 2):	0.001 %

[(1)] Mean of all bottles analysed.
[(2)] Between bottles standard deviation.

IRMM-442, isooctane:

H_2O Mass fraction:	0.0038 % [1]
Uncertainty:	0.0004 % [2]
Estimated expanded uncertainty (k = 2):	0.001 %

[1] Mean of all bottles analysed.
[2] Between bottles standard deviation.

These results compare favorable with the results of the original NBS certificate, as illustrated in Table 8.

Table 8. Comparison of IRMM water determination results with original NBS certified values

	IRMM	NBS certificate
n-heptane H_2O	No. 441 0.003 ± 0.001 %	No. 1815a 0.002 ± 0.001 %
isooctane H_2O	No. 442 0.004 ± 0.001 %	No. 1816a 0.003 ± 0.002 %

2.3 Determination of the lead content

A. Walther, K.H. Grobecker

2.3.1 Introduction

The analysis of Pb in n-heptane and isooctane is difficult as can be derived from the disparate results obtained in the original certification. Not only are the Pb concentrations in the sub-ppb range and, therefore, require an analytical method with excellent determination limits like inductively coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrometry (GF-AAS), but tetra-alkyllead compounds are also very volatile (bp: about 40 °C). They can be lost already during the drying step of the GF-AAS technique. In ICP-MS problems arise by the direct introduction of organic solvents because of an overload of the plasma by solvent vapours and the formation of incandescent carbon particles. Therefore, the volatile lead compounds have to be converted before analysis into less volatile species.
Table 9 contains examples of different analytical procedures having been applied for similar analytical tasks.

In procedure [4], described by Lord, tetra-alkyllead compounds are converted into water soluble species by oxidation with I_2 and then quantitatively extracted into diluted nitric acid. Lead is thereby separated from the gasoline matrix in a simple one-step extraction process. This pre-treatment procedure was chosen as the most suited for the determination of Pb in IRMM-441 and 442.

Table 9. Analytical methods used for analysis of Pb in tetra-alkyllead compounds

Ref.	Sample	Procedure	Analytical method
[3]	Isooctane n-heptane	According to ASTM: oxidation with Br_2, extraction into chloroforme/ dithizone solution	**Spectral photometric determination**
[4]	Fuel	Oxidation with I_2 in toluene, extraction in nitric acid	ICP-MS, concentration range: 0.004-1500 mg/kg Pb
[5]	Gasoline	Emulsion of 10 % m/v gasoline in triton x-100/tetralin/water, iodation and complexation with aliquot 336 (tricapryl methyl ammonium chloride) in dekalin	ICP-OES, addition of oxygen to the argon plasma
[6]	Gasoline	Oxidation with iodine chloride	Potentiometric determination with a lead sensitive electrode
[7]	Gasoline	Direct measurement	**ZAAS with dual chamber cuvette**

2.3.2 Experimental

Reagents. Analytical reagent grade iodine, supra pure toluene and nitric acid (Merck) were used for sample pre-treatment. Deionised water was produced by a Milli-Q water purification system (Millipore). Instrumental calibration standards were prepared from 1 g/L aqueous stock solutions of Pb and Bi (Merck).

Procedure. The flow chart of the procedure used is shown in Figure 4.

Oxidation of 5, 10, 15 and 25 mL CRM with 20 µL of a 3 % m/v I_2 in toluene, mixing, reaction time 15 min

⇓

Extraction into 5 mL 10 % nitric acid containing 10 ng/mL Bi, automatically shaken for 15 min

⇓

Separation of the aqueous nitric acid bottom layer

⇓

Analysis of Pb by ICP-MS and ZAAS in the extract solution

Fig. 4. Flow chart of the analytical procedure

Different sample volumes of 5, 10, 15 and 25 mL of isooctane and n-heptane were transferred to glass flasks. 20 µL of a 3 % m/v I_2 in toluene solution were added to the samples and mixed. After 15 minutes reaction time 5 mL of 10 % nitric acid containing 10 ng/mL Bi as internal standard were added to each flask and placed on a mechanical shaker for 20 min. For Pb analysis the aqueous nitric acid bottom layer was removed from the organic top layer. The extracts were analysed using ICP-MS and ZAAS.

Instrumentation. In ICP-MS an Elan 6000 ICP mass spectrometer (Perkin-Elmer/Sciex, Canada) was used to perform lead analysis. Sample introduction was

carried out using a rhyton spray chamber with a cross-flow nebuliser and a peristaltic pump. As internal standard 10 ng/mL Bi was spiked to all solutions. Lead was monitored on all four isotopes 204, 206, 207 and 208 and as total lead.
To study the accuracy of the lead measurements by an independent method a Zeeman Atomic Absorption Spectrometer SM 30 (Grün, Germany) equipped with a Massmann type graphite furnace was used. The extracts were pipetted on a pyrolytically coated graphite platform. All analytical results are based on the peak height of the absorption signals.
The analytical parameters for ICP-MS and ZAAS are summarised in Tables 10 and 11.

Table 10. Analytical parameters of ICP-MS

RF power	1050 Watt
Plasma gas flow	15,5 L/min
Nebuliser flow	0,93 L/min
Auxiliary flow	0,8 L/min
Dwell time	40 ms
Sweeps/reading	20

Table 11. Analytical parameters of ZAAS

	Wavelength (nm)	T_{Drying} (°C)	$T_{Therm.\ Pre\text{-}treatm.}$ (°C)	$T_{Atom.}$ (°C)	$T_{Cleaning}$ (°C)
Pb	283,6	120 for 25s	600 for 25 s	2400 for 4 s	3000 for 3s

Calibration. Calibrations were accomplished using 10 % nitric acid matched standard solutions of the following Pb concentrations: 0.5, 1, 2 and 5 ng/mL. Five replicate measurements per standard and sample were carried out. The calibration curves of Pb obtained by ICP-MS and by ZAAS are shown in the figures below. Detection limits (3σ) of respectively 0.03 ng/mL Pb for ICP-MS and 0.015 ng Pb for ZAAS were achieved.

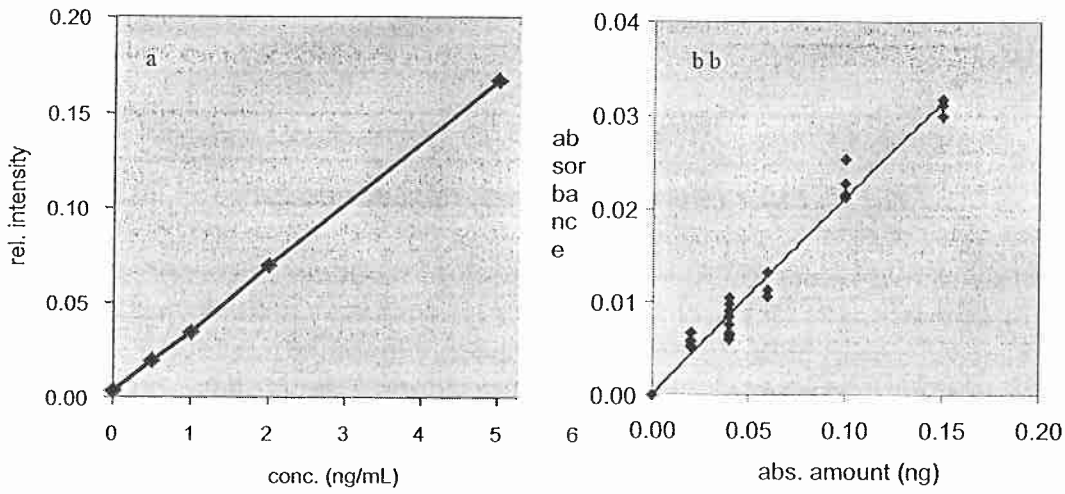

Fig. 5. Calibration of Pb by (a) ICP-MS and (b) ZAAS

Since no significant differences in Pb concentration could be observed for the isotopes 206, 207 and 208, the ICP-MS values taken are based on the determination of the most abundant Pb isotope in order to achieve a better sensitivity. The total lead concentration showed a larger scatter due to the contribution of the insensitive measurement of isotope 204.

Blank value of the procedure. To evaluate the blank of the procedure, 20 µL iodine was added to 5 mL 10 % nitric acid containing 10 ng/mL Bi and placed onto the automatic shaker for 20 minutes. Three blank solutions were produced. The blanks were measured against the external calibration using aqueous nitric acid Pb standard solutions. A mean value of 0.59 ng/mL Pb was calculated on 5 mL of the organic sample (Table 12). The relative coefficient of variation of the blank was 27 %.

Table 12. Procedure blank in ng/mL

Blank 1	Blank 2	Blank 3	Mean ± St. dev.
0.63 ± 0.01	0.42 ± 0.01	0.68 ± 0.01	0.59 ± 0.16

Accuracy of the procedure. As no suitable CRM sample is available, the accuracy of the applied analytical procedure was checked by analysing two different leaded fuel samples. Appropriate sample dilution (1 to 50000) was performed using supra pure toluene. Then the fuels were pre-treated like the n-heptane and isooctane samples. For blank evaluation toluene was oxidised and extracted. The blank corrected results of Pb for both fuel samples are given Table 13.

Table 13. Determination of Pb in fuel samples of different origin

	Fuel 1	Fuel 2	Literature Value
Pb (g/L)	0.17 ± 0.02	0.16 ± 0.01	0.15

The Pb concentrations determined for the two different fuel samples analysed are comparable and show good agreement with the literature value [10].

Precision of the procedure by analysing fuel. From fuel 1 three aliquots of the diluted sample (see above) were taken, oxidised, extracted and analysed as described above in the accuracy study. The obtained data (Table 14) are based on 5 replicate measurements per sample.

Table 14. Study of the precision using fuel 1

	1	2	3	Mean
Pb (g/L)	0.180 ± 0.001	0.165 ± 0.001	0.169 ± 0.002	0.173 ± 0.008

The study shows that the Pb concentration of three parallel extractions agree very well. A coefficient of variation of 4.6 % is calculated on the basis of the mean Pb concentration for the fuel.

2.3.3 Results and discussion

Results for IRMM-441, n-heptane

n-Heptane ampoule 5-4 was analysed by both ICP-MS and ZAAS using external calibration by aqueous nitric acid Pb standard solutions. The Pb concentration in n-heptane ampoule 5-20 was investigated by ICP-MS using both standard addition and external calibration. The standard addition was carried out by means of fuel sample 1 (see above). Three additions of 0.34, 0.68 and 1.02 ng/mL Pb were performed. The Pb concentration in the unspiked sample was also determined by external calibration. The obtained values - not corrected for the procedure blanks - are summarised in Table 15.

Table 15. Uncorrected Pb concentrations (ng/mL) measured in IRMM-441 (n-heptane)

Ampoule No.	Method	E 1	E 2	E 3	E 4	Mean Value
5-4	ICP-MS ext. Calib.	0.53	0.89	0.58	0.32	0.58 ± 0.24
	ZAAS	0.41	0.59	0.78	0.42	0.55 ± 0.17
5-20	ICP-MS ext. Calib.	0.53	0.50	0.44	0.76	0.56 ± 0.14
	ICP-MS standard addition	0.42	0.23	0.42	0.27	0.34 ± 0.10

Though each measurement based on five replicates was quite reproducible (ICP-MS: < 3 %, ZAAS: < 9 %) the values of the different extractions show quite large variations. This is likely due to the fact, that the uncorrected concentration of Pb (in average 0.51 ng/mL with a standard deviation of 0.19 ng/mL for n = 16) is at the level of the procedure blank (0.59 ng/mL with a standard deviation of 0.16 ng/mL for n = 3). Considering these facts, the real Pb concentration can only be estimated as < 0.5 ng/mL, which is in agreement with the value of < 0.4 ng/mL determined by NIST [9]. In contrast to this, LNE [3] reported Pb concentrations between 1.8 and 11.1 ng/mL (mean 5.4 ± 3.1 ng/mL) in 10 different n-heptane ampoules. As the repeatability of determinations on the same ampoule was very poor (variations up to 200 %), these values are not considered as reliable. They are probably the result of high and uncontrolled blanks. IFP [8] gave a Pb concentration of < 5 ng/mL.

Results for IRMM-442, isooctane

Isooctane sample ampoule 5-60 was determined by ICP-MS and ZAAS using Pb standard solutions for external calibration. The Pb concentration in ampoule 5-7 was determined by ICP-MS using standard addition and external calibration. The addition was carried out using the fuel sample 1 (see above). Three additions of 0.34, 0.68 and 1.02 ng/mL Pb were performed. The unspiked samples were also measured against Pb standard solutions. The obtained values - not corrected for procedure blanks - are summarised summarised in Table 16.

Table 16. Uncorrected Pb concentrations (ng/mL) measured in IRMM-442 (isooctane)

Ampoule No.	Method	1	2	3	4	Mean Value
5-60	ICP-MS ext. Calib.	1.36	0.83	1.10	1.04	1.08 ± 0.22
	ZAAS	1.53	0.97	0.94	1.43	1.22 ± 0.31
5-7	ICP-MS ext. Calib.	1.28	0.96	1.18	1.29	1.18 ± 0.15
	ICP-MS standard addition	1.06	0.91	1.13	1.10	1.05 ± 0.10

The results of Pb in different extractions of one ampoule are not very reproducible due to low Pb concentration which is comparable to the procedure blank value (0.59 ng/mL with standard deviation of 0.16 ng/mL for n = 3). However, contrary to the case of n-heptane, Pb is positively identified in isooctane. The uncorrected mean value of all 16 determinations is 1.13 ng/mL, with a standard deviation of 0.20 ng/mL. The agreement between the two ampoules and between the three methods used is, excellent (standard deviation < 0.1 ng/mL). The actual concentration of Pb in isooctane calculated after blank correction is 0.46 ng/mL, the standard deviation on this value being 0.26 ng/mL, and can therefore be certified on the basis of the IRMM measurements as being < 1 ng/mL. This value is comparable to the value of < 0.7 ng/mL as determined by NIST [9].
Both values are again significantly lower than those reported by LNE [3], where in three different ampoules values between 4 and 6 ng/mL Pb (mean 5.8 ± 0.5 ng/mL) were found. But also here a second analysis per ampoule shows variations up to 200 %, suggesting a lack of blank control. IFP [8] stated a Pb concentration of < 5 ng/mL.

3. Basis of IRMM certified values

The results of the IRMM measurements and of the laboratories involved in the original certification are summarised in Tables 17 and 18.

Table 17. Summary of results for IRMM-441

	IRMM	NBS	LNE	IFP
Purity	99.982 (4) %	< 99.99 %	99.985 %	< 99.99 %
Total organics	0.015 (4) %	0.010 (2) %	0.013 (4) %	0.010 (2) %
Isooctane	0.008 (3) %	0.006 (1) %	0.006 (1) %	0.008 (1) %
Water	0.003 (1) %	--	0.002 (1) %	--
Lead	< 0.5 µg/L	< 0.4 µg/L	5.4 ± 3.1 µg/L	< 5 µg/L

Table 18. Summary of results for IRMM-442

	IRMM	NBS	LNE	IFP
Purity	99.982 (2) %	< 99.991 %	99.985 %	< 99.991 %
Total organics	0.014 (2) %	0.009 (2) %	0.012 (1) %	0.009 (2) %
n-Heptane	0.003 (2) %	0.002 (1) %	0.002 (1) %	--
Water	0.004 (1) %	--	0.003 (2) %	--
Lead	< 1 µg/L	< 0.7 µg/L	5.8 ± 0.5 µg/L	< 5 µg/L

On the basis of these results, most probable values were estimated for the parameters certified (see Tables 19 and 20). The quoted uncertainties are estimates of expanded uncertainties as defined in the Guide to the expression of uncertainty in measurement, ISO, 1995 (coverage factor k = 2).

Table 19. IRMM certified values for n-heptane (IRMM-441)

Certified Parameter	Certified value	Uncertainty
n-Heptane, purity by difference	99.985 %	0.005 %
Impurities		
Total organics (other than n-Heptane)	0.012 %	0.005 %
Isooctane	0.007 %	0.002 %
Water	0.003 %	0.002 %
Lead	< 0.5 µg / L	

Table 20. IRMM certified values for isooctane (IRMM-442)

Certified Parameter	Certified value	Uncertainty
Isooctane, purity by difference	99.985 %	0.005 %
Impurities		
Total organics (other than isooctane)	0.011 %	0.004 %
n-Heptane	0.002 %	0.002 %
Water	0.004 %	0.002 %
Lead	< 1 µg/L	

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