



Proficiency test on the determination of mineral oil in sunflower oil

Final Report

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

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Summary

The Rapid Alert System for Food and Feed (RASFF) was notified on 23 April 2008 that sunflower oil originating from Ukraine was found contaminated with high levels of mineral oil. The European Commission has adopted Commission Decision 2008/433/EC of 10 June 2008 imposing special conditions related to the import of sunflower oil from Ukraine due to the risk of contamination with mineral oil.

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Joint Research Centre (JRC) was requested by the Directorate General Health and Consumers (DG SANCO) to organise a proficiency test on the determination of mineral oil in sunflower oil. The aim of this proficiency test was to scrutinise the capabilities of official as well as industrial food control laboratories in Europe to determine the mineral oil content of sunflower oil. The study was announced in September 2008 to interested parties at a workshop on that topic organised jointly by the Food Control Authority of the Canton of Zürich and the European Commission.

The organisation of the study as well as the evaluation of the results was done in accordance with "The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories" and ISO Guide 43. The proficiency test was announced on the JRC-IRMM web-site.

Four test materials were dispatched to the participants: contaminated crude sunflower oil, contaminated refined sunflower oil, spiked sunflower oil and a mineral oil solution in *n*-heptane.

The crude and refined sunflower oil test materials were supplied by the European Federation of the Oil and Proteinmeal Industry (FEDIOL). Spiked oil was prepared by gravimetric addition of mineral oil to blank sunflower oil, which was purchased from local supermarkets in Belgium. The study was free of charge for the participants, and was open to all interested parties.

Altogether 62 laboratories from 19 EU Member States, Switzerland and Ukraine subscribed for participation in the study. The participants were asked to determine the mineral oil content in the test samples by application of their in-house analysis methods. The laboratories were requested to report the results via a web-interface into a secured databank. In total, 55 laboratories, representing official control laboratories, industry and other interested parties reported results to the organisers of the study.

Details regarding the applied analytical methods were requested from the participants too. Forty two participants filled in and returned a questionnaire with the method details back to the organisers.

The assigned values for the mineral oil contents of the crude and refined oil test materials were established by consensus of the participants. The assigned value of the spiked sunflower oil was derived from the gravimetric preparation data. The level of the relative standard deviation for proficiency assessment was agreed on during the workshop in Zurich. A value of 25 % was considered fit for the purpose.

The performance of laboratories in the analysis of the mineral oil solution in *n*-heptane was expressed by the relative bias from the gravimetrically established preparation value. A significant contribution of instrument calibration on the deviation of the results for the sunflower oil samples from the assigned values was detected for at least a quarter of the participants by comparing the relative bias of the results for the sunflower oil samples with that of the mineral oil solution in *n*-heptane.

However, the performance of laboratories in the determination of mineral oil in sunflower oil was expressed by z-scores. They are considered satisfactory if the values of $|z|$ are ≤ 2 . The percentage of satisfactorily performing laboratories was for all sunflower oil test samples at a level of about 80%.

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1. Introduction

Mineral oil is a by-product of the distillation of petroleum during the production of petrol and other petroleum based products from crude oil. It is a transparent, colourless oil composed mainly of alkanes (typically 15 to 40 carbon atoms in the chain) and cyclic paraffins. Its density is around 0.8 - 0.9 g/cm³. Mineral oil is produced in very large quantities.

France notified the European Commission and the EU Member States on 23 of April 2008 via the Rapid Alert System for Food and Feed (RASFF) about the import of sunflower oil from Ukraine with high mineral oil content (5790 mg/kg). The European Food Safety Authority assessed the health risk of this contamination and stated on 29 May 2008 that the contamination level, although undesirable, does not provide any risk to human health [1]. The Standing Committee on the Food Chain and Animal Health agreed on 20 June 2008 on measures to be taken by EU Member States related to this type of contamination and defined requirements on sampling and analytical methods. The European Commission adopted Commission Decision 2008/433/EC of 10 June 2008 imposing special conditions governing the import of sunflower oil originating in or consigned from Ukraine due to contamination risks by mineral oil [2]. On 20 June 2008 the Standing Committee on the Food Chain and Animal Health endorsed provisions on sampling and analysis methods for the determination of mineral oil in sunflower oil [3]. Amongst others it was decided that only alkanes of anthropogenic origin in the range of C10 to C56, or C20 to C56 shall be determined.

The JRC - IRMM was requested by the Directorate General Health and Consumers (DG SANCO) to organise an interlaboratory comparison test in order to assess the ability of laboratories in EU and in Ukraine to determine the mineral oil content of sunflower oil.

The interlaboratory comparison test was free of charge for the participants. The organisation of the study as well as the evaluation of the results was done in accordance with “The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories”, further-on denoted as “Harmonised Protocol” [4] and ISO Guide 43 [5]. It was announced via DG SANCO to the competent authorities of EU Member States and Ukraine. Additionally all participants of the workshop on analytical methods for the determination of mineral oil in sunflower oil, which was held in September 2008 in Zurich (Switzerland), were informed by e-mail. Information concerning the application procedure for the study was also made available on the homepage of the JRC-IRMM (<http://irmm.jrc.ec.europa.eu>). Registration of participants was facilitated via a special web-interface.

Altogether 62 laboratories from 19 EU Member States, Switzerland and from Ukraine subscribed for participation in the study. Receipt of the test samples was confirmed by the participants via the sample receipt form (see Annex 2).

The participants were asked to determine the mineral oil content of the test samples by application of their usual in-house analysis methods. The laboratories were requested to report the results via the web-interface into a secured databank:

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

2. Test Material

2.1 Preparation

The contaminated crude and refined sunflower oil samples were received from the European Federation of the Oil and Proteinmeal Industry (FEDIOL). The blank sunflower oil sample (mineral oil content below 30 mg/kg) was purchased from a local supermarket in Belgium. The material was stored at room temperature.

The contaminated crude sunflower oil material was filtered, stirred overnight and filled in 50 mL serum bottles.

The contaminated refined sunflower oil was diluted with blank sunflower oil in order to lower the mineral oil content of the final sample. The dilution was done gravimetrically in the ratio 2 : 1 (blank : contaminated refined oil). The material was then stirred overnight and filled in 50 mL serum bottles.

The spiked sunflower oil sample was prepared by gravimetrical addition of a mineral oil (Paraffin oil, Merck KGaA, Darmstadt, Germany, Product Number 1.07160.1000) to blank sunflower oil, stirred overnight and filled in 50 mL serum bottles. The certificate of the used paraffin oil is depicted in Annex 4.

All serum bottles were sealed with Aluminium crimp caps and PTFE coated silicon septa.

The mineral oil solution in n-heptane was prepared gravimetrically by dilution of the mineral oil standard (Paraffin oil, Merck KGaA) in n-heptane. The material was filled in 10 mL amber glass ampoules and sealed under inert atmosphere at IRMM.

All vials and ampoules got unique identifiers.

2.2 Homogeneity of the test samples

Sufficient homogeneity was assumed for the test solution in *n*-heptane as it consisted of a well mixed solution of the analyte in a solvent of low viscosity.

Homogeneities of the contaminated crude sunflower oil, the refined sunflower oil, and the spiked sunflower oil test materials were evaluated according to chapter 3.11.1 of the Harmonised Protocol [4].

The contents of ten randomly selected test sample vials were analysed in duplicate by gas chromatography with flame ionisation detection (GC-FID) after bromination and clean up on aluminium oxide. This method was previously validated in a collaborative trial organised by Wagner et al. [6]. In brief, portions of 0.1 g of oil sample were placed into 2 ml bottom tipped vials. Bromination of unsaturated compounds was carried out with a bromine solution in chloroform (5 %, v/v) after addition of the internal standards *n*-tetradecan (*n*-C14), *n*-pentadecan (*n*-C15) and 1-hexadecen (1-C16:1). The brominated sample was passed through a Bakerbond[®] column (6 mL) filled with 3 g of aluminium oxide. The fraction containing saturated hydrocarbons was eluted with 3 mL of *n*-hexane, which was then evaporated by a gentle stream of nitrogen. The block temperature of the evaporator was set to 40 °C. The final volume of the eluate was approximately 100 µL.

The determination of the mineral oil content was performed by GC-FID with on-column injection of 2.5 µL of the final extract. Quantification was performed by internal standardisation using *n*-C14 and *n*-C15 as an internal standards, whereas the completeness of bromination was evaluated from the presence/absence of 1-C16:1 in the injected solution.

The homogeneity of the test samples was proven by subjecting the results of the duplicate measurements to one-way analysis of variance (ANOVA). The variation of the mineral oil content between the ten different sample vials was not significantly larger than the variation within the vials. All analyses complied with the provisions given by the Harmonized Protocol. Hence it was concluded that the sunflower oil test materials were sufficiently homogeneous.

2.3 Stability of the test samples

The mineral oil content of the crude, refined, and spiked sunflower oil test materials was monitored, using the above mentioned protocol, at the beginning of the study, during the study as well as after receipt of the results of the participants as it is suggested in the Harmonized Protocol [4]. Statistically significant differences of the results of analysis obtained before dispatch of samples and after termination of the study were not found, thus

indicating the stability of the test materials. Test samples were kept at room temperature for the period of the study.

2.4 Dispatch of samples

All samples were packed in polystyrene boxes and sent via express mail. The samples were received mostly within 24 hours after dispatch. The participants were asked to fill in the sample receipt form (Annex 2) and send it back to the organisers by e-mail or fax. The samples were dispatched from IRMM on 10 November 2008. Each participant received (together with the shipment) the sample receipt form, an accompanying letter with instructions for sample handling, measurement, and reporting (Annex 3), three 50 mL serum bottles containing the crude, the refined, and the spiked sunflower oil test materials and one ampoule with the mineral oil solution in *n*-heptane. A 50 mL serum bottle with sunflower oil of mineral oil content below 50 mg/kg (blank sunflower oil) was added to the set of test samples to support laboratories in method development.

3. Statistical evaluation of the results

3.1 Assigned value

Assigned values for the mineral oil content of the contaminated crude sunflower oil and contaminated refined sunflower oil test materials were established from the median of the participants' results, as suggested by the Harmonised Protocol. These values were compared to other robust estimates of the mean, which were calculated with an algorithm proposed by the Analytical Methods Committee of the Royal Society of Chemistry (AMC) [7].

The spiked sunflower oil and mineral oil solution in *n*-heptane have been prepared by gravimetric addition of a mineral oil (Paraffin oil, Merck KGaA) to the blank sunflower oil, respectively by dilution with *n*-heptane, therefore the assigned value for these two materials were deducted from the gravimetric preparations.

The standard uncertainties of the assigned values for the contaminated crude, and contaminated refined sunflower oil were determined in accordance with the Harmonised Protocol [4]. They correspond to the standard error of the consensus value, which is given by equation 3.1:

$$u = \frac{\hat{\sigma}}{\sqrt{n}}$$

Equation 3.1

where $\hat{\sigma}$ is robust standard deviation (obtained by AMC algorithm); n is number of results

The relative expanded uncertainty was for both test materials in the range of 8.5 %. The uncertainties of the assigned values for spiked sunflower oil, and for the mineral oil solution in *n*-heptane were estimated from the standard uncertainties of the different preparation steps. The respective values are given in the tables 4.1, 4.3, 4.5, and 4.7.

3.2 Performance indicator and target standard deviation

The performance of an individual laboratory i was expressed by the z_i -score, which was calculated according to equation 3.2:

$$z_i = \frac{x_i - \hat{X}}{\sigma_p}$$

Equation 3.2

z_i : z -score of laboratory i for the respective sample; x_i : reported result of laboratory i for that sample, expressed as the mean of multiple determinations; \hat{X} : assigned value for the respective sample, σ_p : standard deviation for proficiency assessment

The magnitude of the standard deviation for proficiency assessment was set to be fit for purpose, according to the Harmonised protocol [4]. A relative standard deviation of 25 % was considered reasonable for performance evaluation, as agreed upon during the workshop in Zürich [8]. The standard deviations for proficiency assessment were calculated for the individual test samples according to equation 3.3. The appropriateness of this level of tolerated variability of results was confirmed by calculation of the relative standard deviations of the participants' results for the crude, the refined, and the spiked sunflower oil test materials after exclusion of outliers. The calculated relative standard deviations were within the range of 25 % to 26 %.

$$\sigma_P = \frac{25 \times \hat{X}}{100} \quad \text{Equation 3.3}$$

\hat{X} : assigned value for the respective sample, σ_P : standard deviation for proficiency assessment

z-Scores were calculated for the oil test samples only. The acceptability of a laboratory's performance was evaluated according to the following generally accepted limits [4]:

$ z \leq 2.0$	satisfactory
$2.0 < z < 3.0$	questionable
$ z \geq 3.0$	unsatisfactory

The performance of an individual laboratory i in the analysis of the mineral oil solution in n -heptane and the spiked sunflower oil was expressed by the relative bias from the gravimetrically established assigned value, which was calculated according to equation 3.4:

$$Rel. bias_i = \frac{x_i - \hat{X}}{\hat{X}} \times 100 \quad \text{Equation 3.4}$$

Relative bias of laboratory i for the respective sample; x_i reported result of laboratory i for that sample, expressed as the mean of multiple determinations; \hat{X} : assigned value for the respective sample.

4. Performance assessment

4.1 Overview

The deadline for the reporting of results was extended twice on request of the participants to 31 January 2009. Finally 55 data sets were reported to the organisers of the study. The participants were asked to confirm the correctness of submitted results till 18 February 2009.

In order to assure confidentiality, the identities of the laboratories were coded by a unique number between 100 and 300.

Details regarding the applied analytical methods were requested from the participants too. Forty two participants filled in and sent the questionnaire with method details back to the organisers. The details of the applied analysis methods are given in Annex 5.

Data of laboratories that reported measurement results for the mineral oil contents of the sunflower oil samples were considered in the statistical evaluations.

The distributions of the results were checked by kernel density estimations. This analysis is also capable of determining multimodality [4]. In general the results of analysis were not normally distributed, the data sets contained outliers and the respective kernel density plots showed several modes (figures 4.2, 4.4, 4.6 and 4.8).

4.2 z-Scores of the participants

4.2.1 Contaminated crude sunflower oil

A summary of the statistical evaluation is presented in table 4.1.

Eight laboratories out of 55 (14.5 %) reported for the contaminated crude sunflower oil test material results with $|z| > 2$. Laboratory mean values of the determinations of mineral oil in the crude sunflower oil test sample are tabulated with the corresponding z-score in table 4.2. Figure 4.1 shows the plot of z-scores in ascending order.

The distribution of the results was checked for multimodality by kernel density estimation (figure 4.2).

Table 4.1: Summary statistics for the contaminated crude sunflower oil test sample

Number of results		55
Range of results	mg/kg	114 to 805
Median	mg/kg	351
Huber H15	mg/kg	363
Mean of results of participants	mg/kg	373
Mean of results of participants after removal of outliers (according to [7])	mg/kg	358
Assigned value (consensus value of participants' results)	mg/kg	351
Expanded uncertainty (k=2) of the assigned value	mg/kg	30
Robust standard deviation ($\hat{\sigma}$)	mg/kg	118
Target standard deviation (fitness for purpose, $RSD_R = 25\%$)	mg/kg	88
Number (percentage) of results of $ z > 2.0$		8 (14.5 %)

Table 4.2: Results of analysis and z-scores for the contaminated crude sunflower oil test sample; bold printed z-scores mark results outside the satisfactory range

Lab Number	reported result [mg/kg]	z - score	Lab Number	reported result [mg/kg]	z - score
101	362	0.1	185	272	-0.9
104	160	-2.2	188	526	2.0
107	347	-0.1	191	271	-0.9
110	222	-1.5	194	200	-1.7
113	455	1.2	197	396	0.5
116	499	1.7	200	371	0.2
119	390	0.4	203	441	1.0
122	304	-0.5	206	234	-1.3
125	293	-0.7	209	222	-1.5
128	381	0.3	212	502	1.7
131	351	0.0	215	385	0.4
134	369	0.2	218	607	2.9
137	305	-0.5	221	332	-0.2
140	292	-0.7	224	114	-2.7
143	376	0.3	227	295	-0.6
146	176	-2.0	230	304	-0.5
149	448	1.1	233	202	-1.7
152	526	2.0	236	303	-0.5
155	482	1.5	239	498	1.7
158	720	4.2	242	349	0.0
161	505	1.8	245	356	0.1
164	380	0.3	248	283	-0.8
167	580	2.6	251	243	-1.2
170	247	-1.2	254	578	2.6
173	298	-0.6	257	624	3.1
176	313	-0.4	260	340	-0.1
179	422	0.8	263	254	-1.1
182	805	5.2			

Figure 4. 1: Plot of participants' z-scores for the contaminated crude sunflower oil test sample

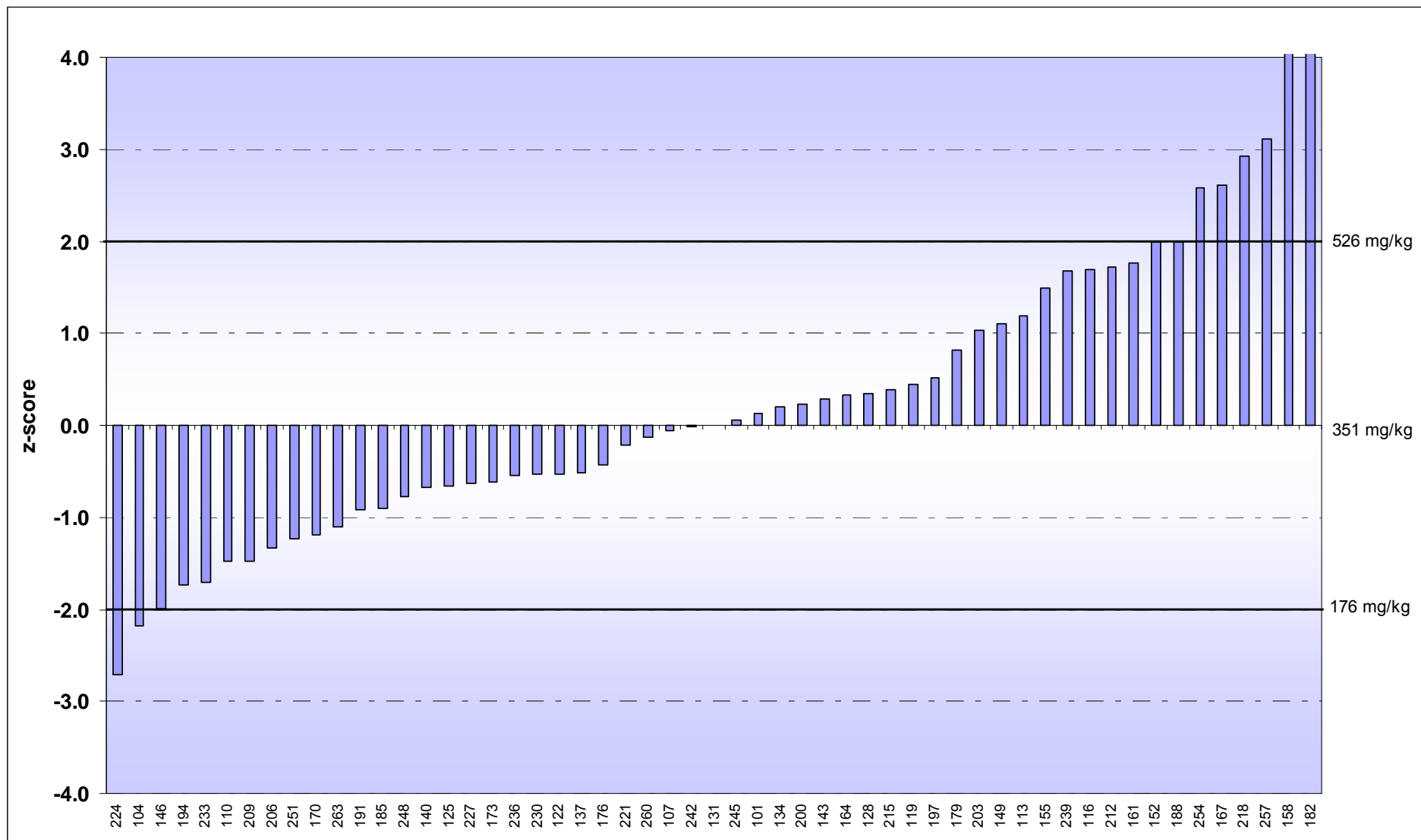
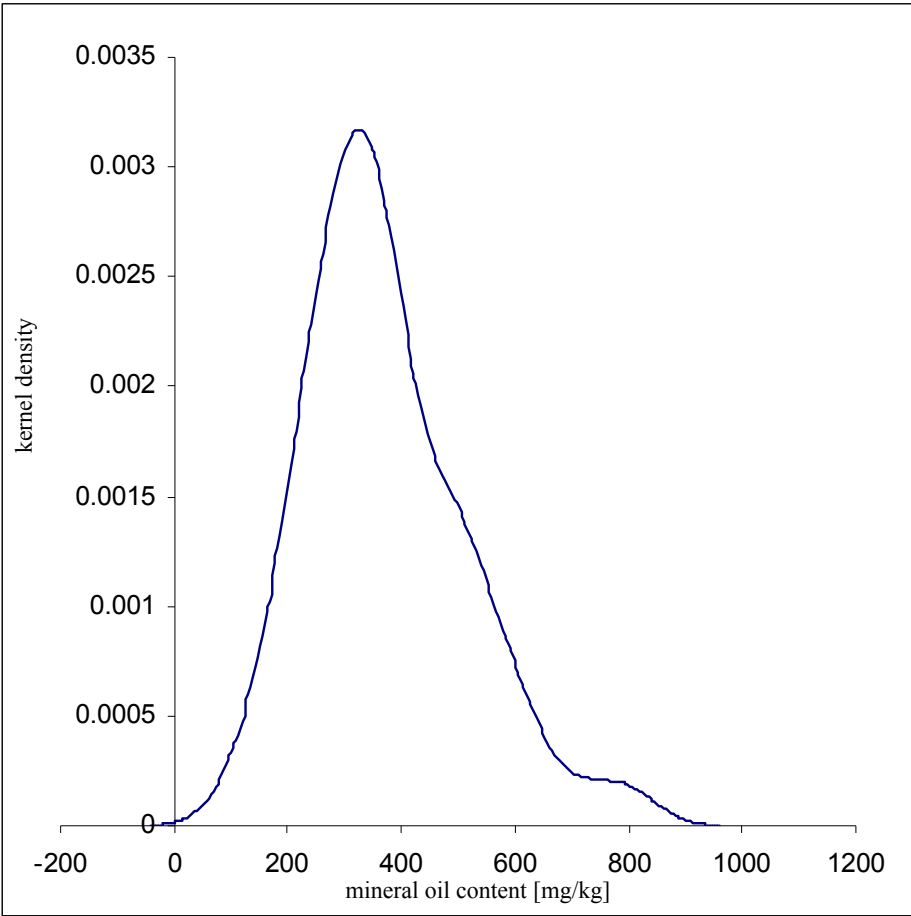


Figure 4.2: Kernel density plot of the participants' results for the contaminated crude sunflower oil test sample



4.2.2 Contaminated refined sunflower oil

A summary of the statistical evaluation is presented in table 4.3. Twelve laboratories out of 54 (22 %) reported results with $|z|>2$. Laboratory mean values of the determinations of mineral oil in the contaminated refined sunflower oil test sample are tabulated with the corresponding z-score in table 4.4. Figure 4.3 shows the plot of z-scores in ascending order.

The distribution of the results was checked for multimodality by kernel density estimation (figure 4.4).

Table 4.3: Summary statistics for the refined sunflower oil test sample

Number of results		54
Range of results	mg/kg	24 to 366
Median	mg/kg	105
Huber H15	mg/kg	113
Mean of results of participants	mg/kg	121
Mean of results of participants after removal of outliers (according to [7])	mg/kg	113
Assigned value (consensus value of participants' results)	mg/kg	105
Expanded uncertainty (k=2) of the assigned value	mg/kg	9
Robust standard deviation ($\hat{\sigma}$)	mg/kg	34
Target standard deviation (fitness for purpose, RSD 25%)	mg/kg	26
Number (percentage) of results of $ z > 2.0$		12 (22 %)

Table 4.4: Results of analysis and z-scores for the contaminated refined sunflower oil test sample; bold printed z-scores mark results outside the satisfactory range

Lab Number	reported result [mg/kg]	z - score	Lab Number	reported result [mg/kg]	z - score
101	112	0.3	185	68	-1.4
104	85	-0.8	188	134	1.1
107	187	3.1	191	80	-1.0
110	75	-1.2	194	105	0.0
113	105	0.0	197	120	0.5
116	24	-3.1	200	109	0.1
119	106	0.0	203	99	-0.3
122	102	-0.1	206	83	-0.8
125	92	-0.5	209	136	1.2
128	123	0.7	212	267	6.1
131	106	0.0	215	108	0.1
134	107	0.0	218	178	2.7
137	137	1.2	221	105	0.0
140	116	0.4	224	63	-1.6
143	190	3.2	227	99	-0.3
149	113	0.3	230	47	-2.2
152	162	2.1	233	89	-0.6
155	158	2.0	236	105	0.0
158	99	-0.3	239	77	-1.1
161	140	1.3	242	151	1.7
164	105	0.0	245	102	-0.1
167	160	2.1	248	100	-0.2
170	65	-1.6	251	60	-1.7
173	130	0.9	254	153	1.8
176	86	-0.8	257	366	9.9
179	328	8.4	260	50	-2.1
182	204	3.7	263	96	-0.4

Figure 4.3: Plot of participants' z-scores for the contaminated refined sunflower oil test sample

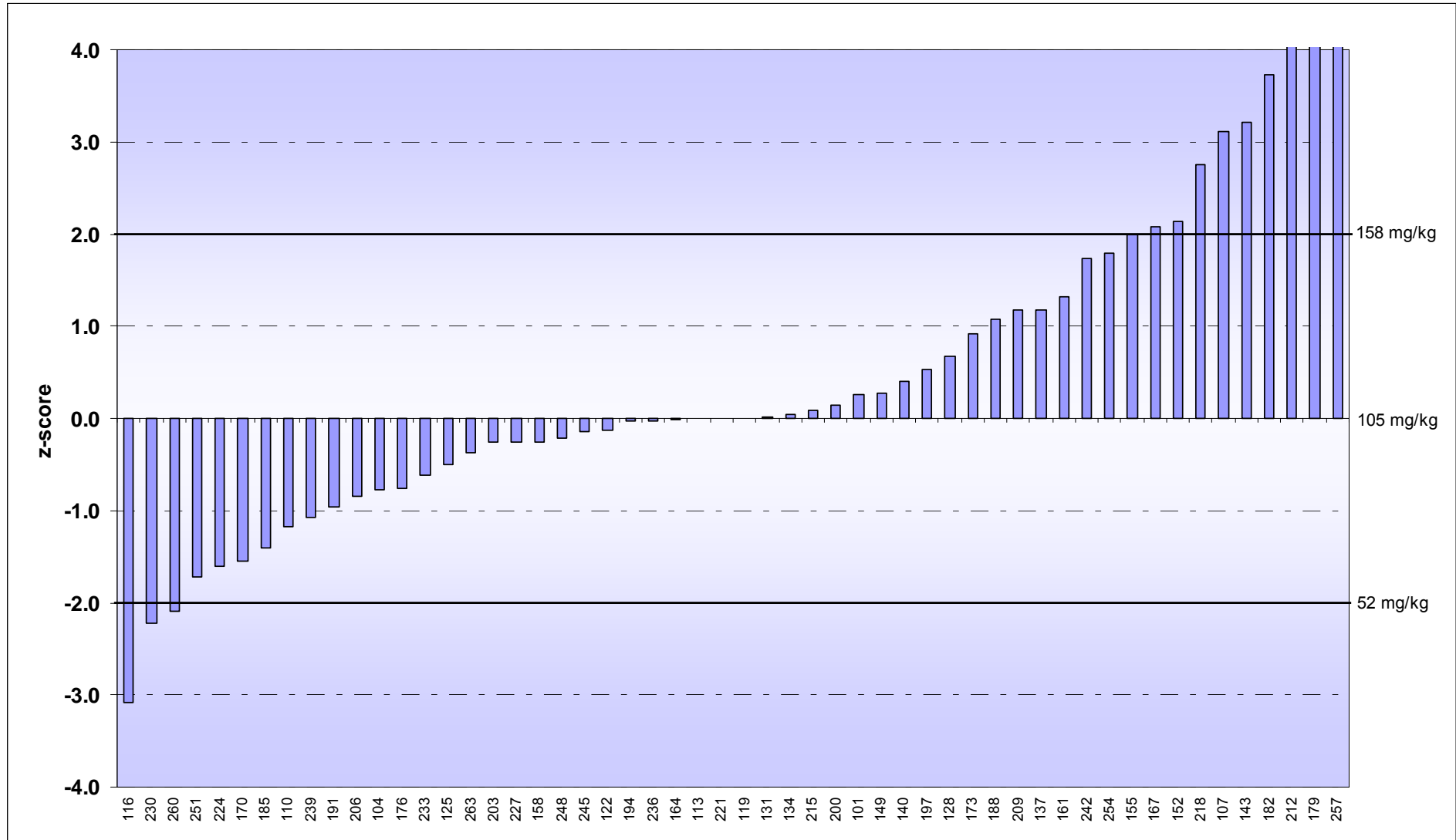
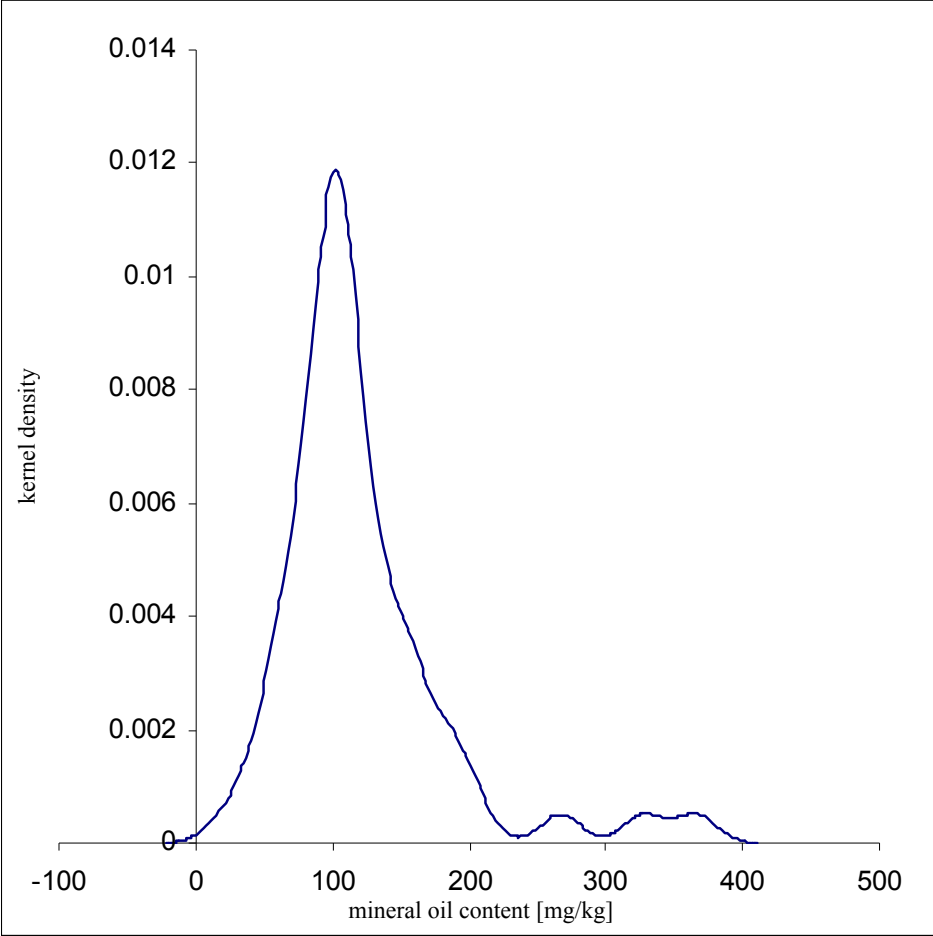


Figure 4.4: Kernel density plot of the participants' results for the contaminated refined sunflower oil test sample



4.2.3 Spiked sunflower oil

Nine laboratories out of 54 (17 %) reported results with $|z|>2$. A summary of the statistical evaluation is presented in table 4.5. Laboratory mean values of the determinations of mineral oil in the spiked sunflower oil test sample are tabulated with the corresponding z-score in table 4.6. Figure 4.5 shows the plot of z-scores in ascending order.

The distribution of the results was checked for multimodality by kernel density estimation (figure 4.6).

Table 4.5: Summary statistics for the spiked sunflower oil test sample

Number of results		54
Range of results	mg/kg	56 to 383
Median	mg/kg	113
Huber H15	mg/kg	120
Mean of results of participants	mg/kg	118
Mean of results of participants after removal of outliers (according to [7])	mg/kg	120
Assigned value (gravimetrically established)	mg/kg	114
Expanded combined uncertainty (k=2) of the assigned value	mg/kg	4
Robust standard deviation ($\hat{\sigma}$)	mg/kg	35
Target standard deviation (fitness for purpose, RSD 25%)	mg/kg	28
Number (percentage) of results of $ z > 2.0$		9 (17 %)

Table 4.6: Results of analysis and z-scores for the spiked sunflower oil test sample;
bold printed z-scores mark results outside the satisfactory range

Lab Number	reported result [mg/kg]	z - score	Lab Number	reported result [mg/kg]	z - score
101	96	-0,6	185	69	-1,6
104	79	-1,2	188	145	1,1
107	110	-0,1	191	91	-0,8
110	71	-1,5	194	97	-0,6
113	124	0,3	197	143	1,0
116	56	-2,0	200	109	-0,2
119	130	0,6	203	93	-0,7
122	122	0,3	206	69	-1,6
125	89	-0,9	209	150	1,3
128	103	-0,4	212	267	5,4
131	139	0,9	215	109	-0,2
134	119	0,2	218	166	1,8
137	113	0,0	221	103	-0,4
140	139	0,9	224	70	-1,6
143	207	3,3	227	109	-0,2
149	112	0,0	230	96	-0,6
152	196	2,9	233	91	-0,8
155	182	2,4	236	124	0,3
158	276	5,7	239	90	-0,8
161	133	0,7	242	142	1,0
164	125	0,4	245	96	-0,6
167	232	4,2	248	122	0,3
170	80	-1,2	251	67	-1,6
173	125	0,4	254	143	1,0
176	103	-0,4	257	383	9,5
179	200	3,0	260	90	-0,8
182	221	3,8	263	114	0,0

Figure 4.5: Plot of participants' z-scores for the spiked sunflower oil test sample

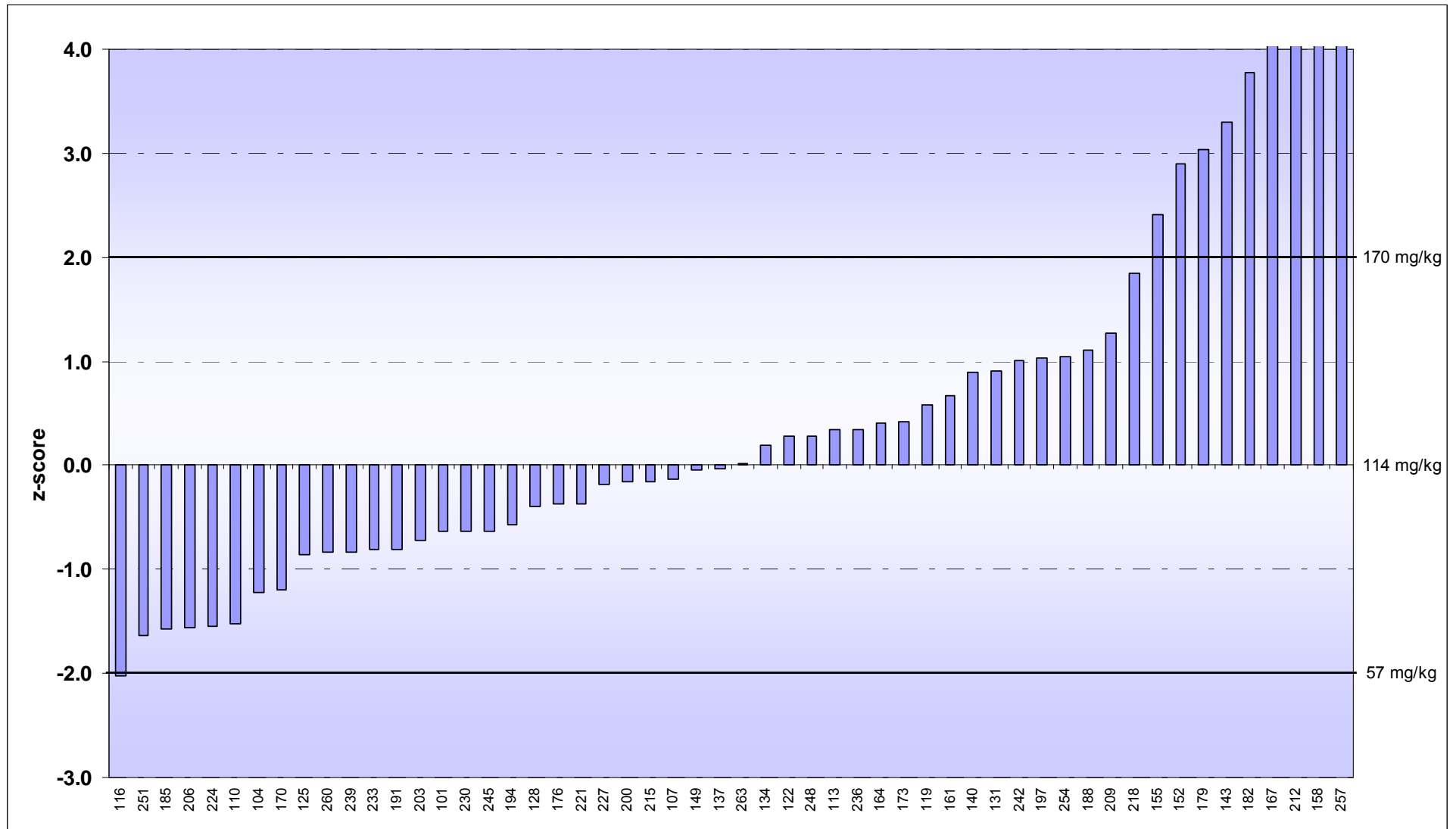
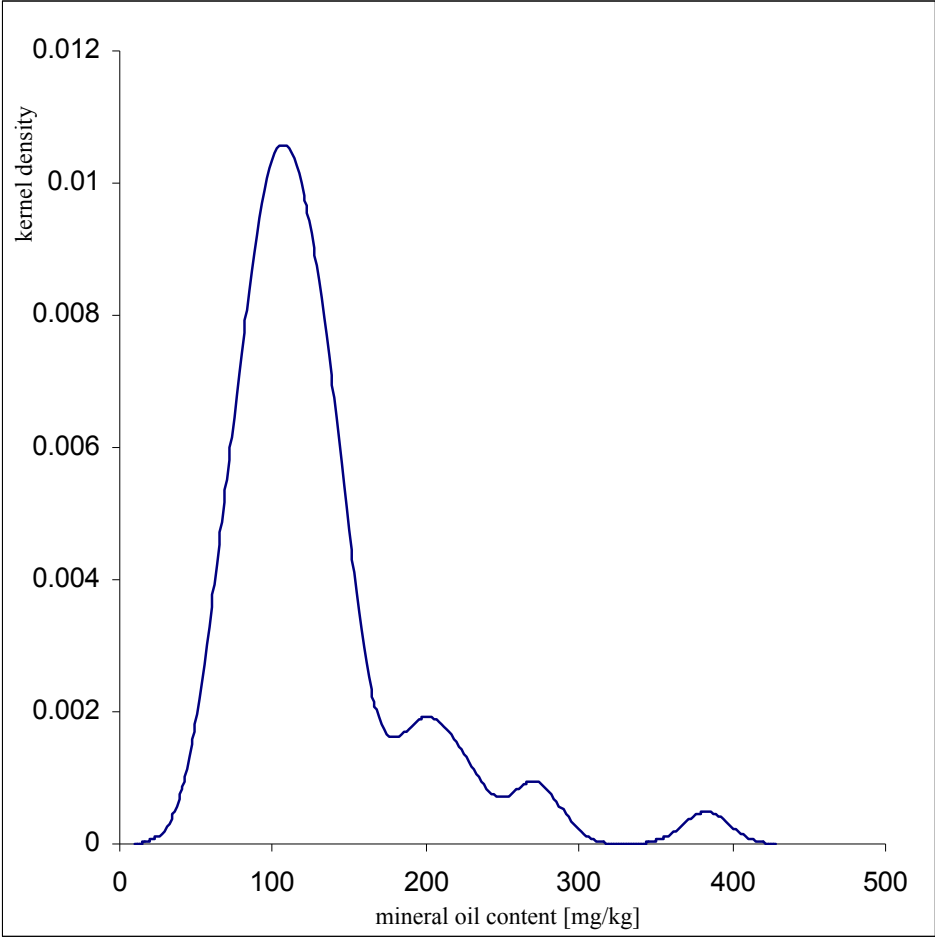


Figure 4.6: Kernel density plot of the participants' results for the spiked sunflower oil test sample



4.2.4 Mineral oil solution in *n*-heptane

Forty nine laboratories reported results for the solution of mineral oil in *n*-heptane. A summary of the statistical evaluation is presented in table 4.7. Laboratory mean values of the determinations of mineral oil in *n*-heptane solution are tabulated with the corresponding relative bias in table 4.8. Figure 4.7 shows the plot of relative bias from the assigned value in ascending order. The respective Kernel density plot is depicted in figure 4.8.

Some participants submitted the results in units other than requested (mg/kg). These results were transferred into the requested units by application of the density of *n*-heptane 0.6795 g/mL and the density equation.

Table 4.7: Summary statistics for the mineral oil solution in *n*-heptane

Number of results		49
Range of results	mg/kg	25 to 1185
Median	mg/kg	77.2
Huber H15	mg/kg	82.6
Mean of results of participants	mg/kg	123
Mean of results of participants after removal of outliers (according to [7])	mg/kg	76.3
Assigned value (established gravimetrically)	mg/kg	88.9
Expanded combined uncertainty (k=2) of the assigned value	mg/kg	1.4
Number (percentage) of results of rel. bias > 20 %		34 (70 %)

Table 4.8: Results of analysis and relative bias for the mineral oil solution in *n*-heptane

Lab Number	reported result [mg/kg]	relative bias [%]	Lab Number	reported result [mg/kg]	relative bias [%]
101	82,3	-7,5	188	99,8	12,2
107	52,3	-41,2	191	70,0	-21,3
110	1184,7	1232,6	194	40,0	-55,0
113	55,1	-38,0	197	512,5	476,5
116	108,5	22,0	203	79,8	-10,2
119	88,0	-1,0	206	576,0	547,9
122	64,2	-27,8	209	107,3	20,6
125	47,8	-46,3	212	185,3	108,4
128	99,0	11,4	215	92,0	3,5
131	52,3	-41,2	218	128,3	44,3
134	62,8	-29,4	221	86,0	-3,3
137	48,3	-45,7	224	48,5	-45,4
140	86,5	-2,7	227	63,3	-28,9
143	110,0	23,7	230	225,5	153,7
149	69,9	-21,4	233	40,8	-54,2
152	135,4	52,3	236	71,3	-19,8
155	111,5	25,4	239	77,2	-13,2
158	50,3	-43,5	242	57,8	-35,0
164	135,0	51,9	248	61,5	-30,8
167	82,0	-7,8	251	25,0	-71,9
170	75,0	-15,6	254	71,5	-19,6
173	96,4	8,5	257	47,0	-47,1
176	101,0	13,6	260	58,9	-33,8
182	126,0	41,7	263	66,3	-25,5
185	25,0	-71,9			

Figure 4.7: Plot of participants' relative bias from the gravimetrically established value of the mineral oil content of the *n*-heptane solution

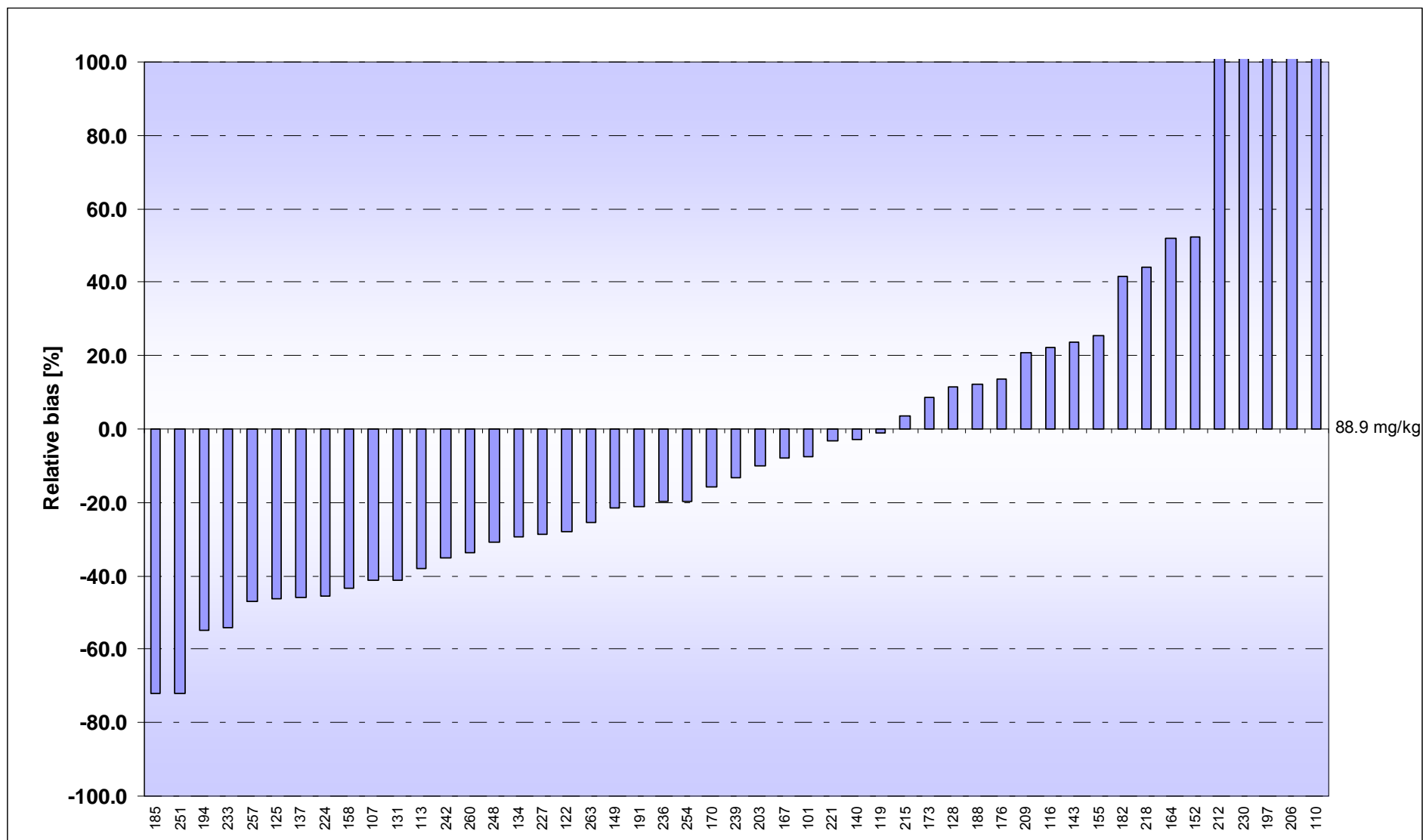
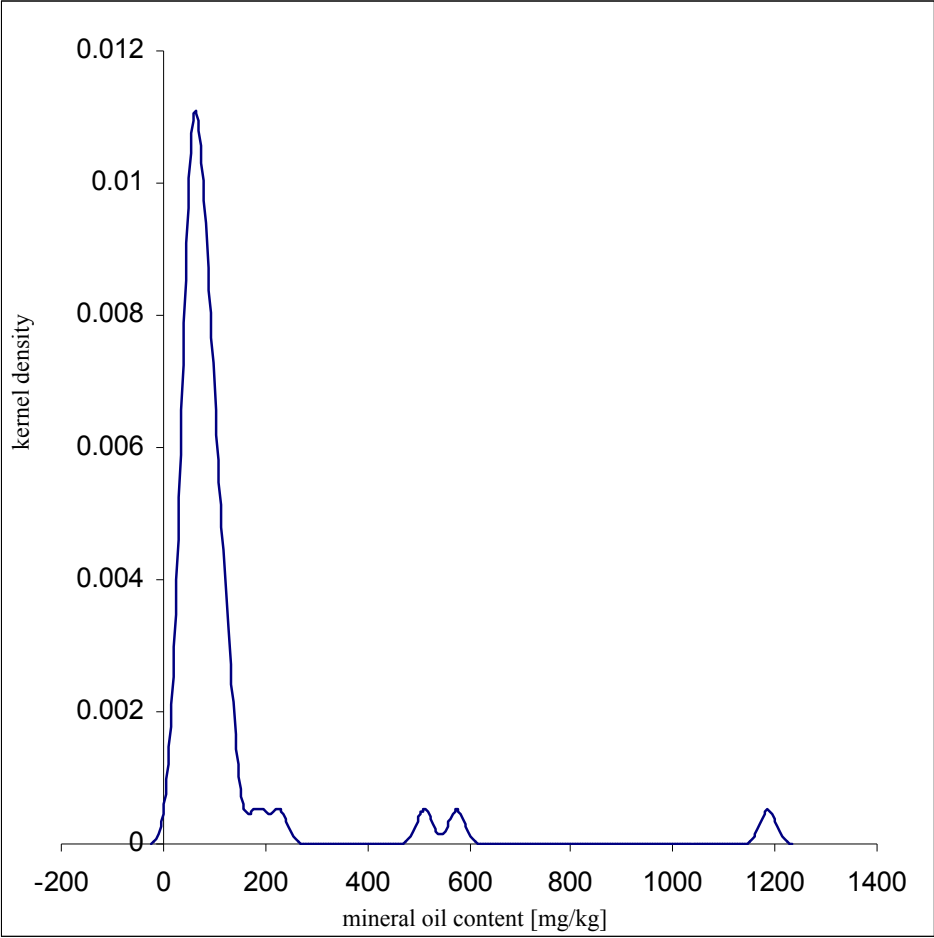


Figure 4.8: Kernel density plot of the participants' results for the mineral oil solution in *n*-heptane



5. Conclusions

- 55 participants reported results for the crude sunflower oil test material, 85 % of them were within the satisfactory performance range (z-score $\leq |2.0|$).
- 54 participants reported results for the refined sunflower oil test material, 78 % of them were within the satisfactory performance range.
- 54 participants reported results for the spiked sunflower oil test material, 83 % of them were within the satisfactory performance range.
- 49 participants reported results for the mineral oil solution in *n*-heptane, a relative bias of less than 20 % was achieved by 30 % of them, and a relative bias of less than 30 % was achieved by 51 % of participants.
- It can be concluded that biased instrument calibration is an important source of error, since more than 25 % of the relative deviations from the assigned values of all results reported by the respective participant for the oil samples, and the relative deviation of the result reported for the mineral oil solution in *n*-heptane from the preparation concentration showed the same sign, indicating constant over- respectively underestimation of the analyte contents. This might be caused by the application of different mineral oil mixtures for standard preparation, but also erroneous standard preparation cannot be excluded. In that respect the application of a common calibration solution was proposed by the participants.
- The critical steps in the analysis of mineral oil in sunflower oil are linked to instrument calibration, peak integration (hump of target compounds), and calculation of results.
- A number of laboratories stated that they just stepped into this field of analysis; therefore they were at the time of the interlaboratory comparison test still busy with the in-house validation of analytical methods, and had a lack of experience with this type of analysis.
- The standardisation of analytical methods for the determination of mineral oil in sunflower oil was proposed by some participants. Application of a well defined, harmonised analysis procedure would also minimise inconsistencies related to calibration and data analysis.

Acknowledgements

The organisers of the study would like to thank Mrs. Claire-Lise Bechert, FEDIOL for the supply of test materials and Mrs. Anne-Mette Jensen for her support in the provision of test materials and the Reference Materials Unit at IRMM, in particular Mr. Håkan Emteborg, for ampouling of the test samples.

6. References

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Annex

Annex 1: Announcement of Study



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for reference materials and measurements
Food Safety and Quality Unit

Geel, 01.10.2008
D08/FSQ/TW/bk/D(2008) 24943

Dear Madame/Sir,

We would like to invite you to participate in the inter-laboratory comparison study (ILC)
on the **determination of mineral oil in sunflower oil**.

Participation is free of charge.

Each participant will receive a solution of mineral oil in cyclohexane for checking proper instrument calibration, one unit of each of blank sunflower oil, spiked sunflower oil, naturally contaminated crude sunflower oil, and naturally contaminated refined sunflower oil. The participants will be requested to perform duplicate analysis per test material with duplicate injections of each preparation into the chromatographic system (altogether four injections per material including standards). The content of exogenous saturated hydrocarbons has to be reported for each sample. Detailed information about the submission of results will be provided together with the samples.

For more information you can contact: JRC-IRMM-Contaminants@ec.europa.eu

Relieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. <http://irmm.jrc.ec.europa.eu>
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-contaminants@ec.europa.eu

Registration of laboratories is open and has to be done via the web interface:

<https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=159>

Deadline for the registration is 20 October 2008.

Mr. Karasek (+32 14 571301) and me are at your disposal for any clarification you may wish!

Please note that registration can only be done via the link above.

With best regards

Thomas Wenzl x



Cc: Franz Ulberth, Donata Lerda, Lubomir Karasek

Annex 2: Sample receipt form



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

Geel, 07.11. 2008

Inter-laboratory comparison study on the determination of mineral oil in sunflower oil

SAMPLE RECEIPT FORM

Name of Participant	
Organisation	
Address	

Please check if the samples (consisting of four 50 mL serum bottles and one 10 mL glass ampoule) have been received undamaged.

Date of sample receipt	
The sample has been received undamaged	Yes <input type="checkbox"/> / No <input type="checkbox"/>

Please store the sample at room temperature!

Please return the completed form by email to: Lubomir.Karasek@ec.europa.eu

or by fax to: **+32-14-571-783**

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 211 - Direct line: 320 •Fax: +32-(0)14-584 343; Email: Thomas.Wenzl@ec.europa.eu
<http://www.irmm.jrc.be>

Annex 3: Study description



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

Geel, 11.11. 2008
D08-FSQ/TW/bk (2008) D 29116

Dear Madame/Sir,

The inter-laboratory comparison study on the determination of mineral oil in sunflower oil starts on **10 November 2008** with the dispatch of samples.

Please, **store the samples at room temperature** in order to maintain sample integrity!

Outline of the study

Test materials

You will receive:

- an ampoule with 5 mL of solution of mineral oil in heptane,
- 50 mL serum bottle of spiked sunflower oil,
- 50 mL serum bottle containing naturally contaminated crude sunflower oil
- 50 mL bottle containing naturally contaminated refined sunflower oil.

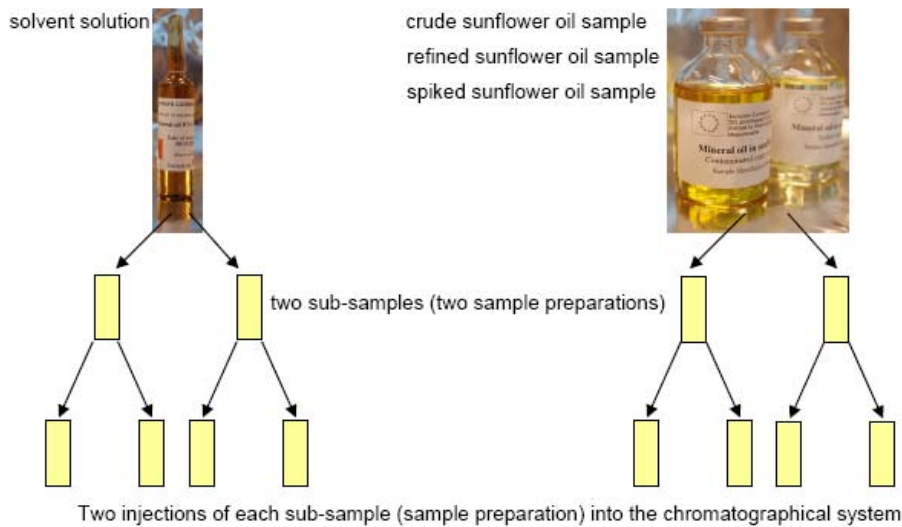
The mineral oil content of the **solvent solution**, **spiked** sunflower oil and **refined** sunflower oil shall be expected within the range of **50 – 300 mg/kg**.

The content of mineral oil in the **crude** sunflower oil shall be expected **below 800 mg/kg**.

- Moreover you will get one 50 mL serum bottle of **blank** sunflower oil (mineral oil content **less than 50 mg/kg**).

You are requested to perform duplicate analysis per test material with duplicate injections of each preparation into the chromatographic system (altogether four injections per material including solvent solution) according to the following scheme:

Retieseweg 111, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 211 - Direct line: 320 •Fax: +32-(0)14-584 343; Email: Thomas.Wenzl@ec.europa.eu
<http://www.irmm.jrc.be>



The content of exogenous saturated hydrocarbons has to be reported for each sample applying a method of your choice. The mean value of the analyses will be applied for calculation of performance indicators.

A set of questions regarding the applied analysis method shall be answered as well. The link to the respective reporting page as well as the login key were sent to you by email.

For more information you can contact: JRC-IRMM-Contaminants@ec.europa.eu

Results have to be reported via the web-interface:

<https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do>

The login key and the sample keys were sent to you by email.

Deadline for reporting of results is: 16 December 2008

Mr. Karasek (Lubomir.Karasek@ec.europa.eu; Tel.: +32 14 571301) and myself are at your disposal for any clarification you may wish!

With best regards

Thomas Wenzl

Retieseweg 111, B-2440 Geel, Belgium
 Tel.: +32-(0)14-571 211 - Direct line: 320 •Fax: +32-(0)14-584 343; Email: Thomas.Wenzl@ec.europa.eu
<http://www.irmm.jrc.be>

Annex 4: Mineral oil spiking standard (Merck Paraffin oil) certificate



Specification

<http://certificates.merck.de>

Date of print: 11.03.2009

1.07160.1000 Paraffin viscous Ph Eur, BP, USP

	Spec. Values
Identity (IR-spectrum)	passes test
Acidity or alkalinity	passes test
Density (d 20 °C/20 °C)	0.845 - 0.890
Dynamic viscosity (20 °C)	110 - 230 mPa·s
Kinematic Viscosity (40 °C)	≥ 34.5 mm ² /s
Residual solvents (Ph Eur./ICH)	excluded by manufacturing process
Aromatic, polycyclic Hydrocarbons	conforms
Solid Paraffines	passes test
Readily carbonisable substance	passes test

Corresponds Ph Eur, BP, USP

Dr. Dietmar Oeter

responsible laboratory manager quality control

This document has been produced electronically and is valid without a signature

Annex 5: Analytical methods applied by the participants

The details of the applied analysis methods are tabulated as they were reported by the participants. The presented data were not at all edited. Not tabulated information was not submitted. It should be noted that the authors do neither claim completeness nor correctness of the given information.

Table 5.1: Number of samples analysed by laboratories per year for the mineral oil content

LAB CODE	Number of samples per year					
	< 20	20 - 50	51 - 100	101 - 200	201 - 500	> 500
101						X
113	X					
119					X	
122		X				
125				X		
128				X		
131		X				
134						X
140				X		
143		X				
146	X					
152	X					
155			X			
158			X			
161						X
170						X
173			X			
176			X			
179			X			
194		X				
197				X		
200		X				
203	X					
206		X				
209				X		
215				X		
218		X				
221			X			
227				X		
230	X					
233	X					
236		X				
239	X					
242			X			
245				X		
248				X		
251						X
254		X				
257	X					
260				X		
263		X				

Table 5.2a: Sample preparation details

LAB CODE	Sample weight in [g]	Further sample preparation					details:
		bromination	epoxidation	saponification	other	no further sample preparation	
101	2.000					X	
113	1					X	
119	0.3					X	
122	1					X	dissolve with 10 ml Hexane
125	1				X		Addition of 1 ml of n-Eicosane 0.05 mg/ml
128	1					X	
131	1				X		Dilution of oil sample with an internal standard (C44H90) solution
134	1					X	
140	2					X	2g oil or fat in 20ml Hexane
143	0.25					X	
146	2					X	
152	0.25				X		+ 250 µl hexane => shake
155	0.025-0.25					X	
158	0.25					X	
161	0,5 / 1				X		Sample solved in n-Hexane.
170	10					X	The melted well-mixed sample is weighed into glass flask, dissolved in 50 ml n-hexane (Fluka, 34484) and shaken up till complete mixing
173	1					X	
176	0.25					X	
179	2						
194	2					X	
197	2					X	
200	10			X			KOH 10% in methanol - 30 min on boiling water with - reflux condenser
203	1					X	

Table 5.2b: Sample preparation details

LAB CODE	Sample weight in [g]	Further sample preparation					
		bromination	epoxidation	saponification	other	no further sample preparation	details:
209	2					X	saponification for mix
215	1					X	
218	10			X			Saponification with KOH in methanol (2N), under reflux, during 45 min. Extraction with hexane/water (1:1) and recovery of the organic layer. Second extraction with hexane. Wash of the organic layer with water / ethanol (1:1). Filtration of the organic layer with anhydrous sodium sulphate. Evaporation till dryness.
221	1					X	
227	1.00					X	
230	1					X	
233	2					X	
236	0.25					X	
239	0.25		X			X	epoxydation only for samples with additional hump or non-typical baseline on the chromatogram; epoxydation with 3-chloroperbenzoic acid in chloroform, next wash with Na2SO3 aq. And Na2CO3 aq.
242	1					X	
245	10	X		X			
248	1					X	
251	1					X	
254	1					X	
257	1					X	
260	3					X	weight 3g of sample in 10mL C5
263	1					X	

Table 5.3a: Sample clean up details

LAB CODE	Column Chromatography	Column dimensions	Aluminium oxide	Silica gel	Florisil	Other	Remarks	sorbent amount [g]	solvent	volume [mL]
101	X	10m x 0,32 mm		X				30.0	hexane	150
113	X	20	X				According to ISO CD Part 2	20	hexane	50
119										
122	X	100 x 17			X		dry column, Florisil activated and cleaned at 600°C	6	hexane	10
125	X	40 cm x 15 mm		X			Silica gel treated with AgNO3			
128	X	180 x16				X	15 g silica gel + 1,5 g AgNO3 + 2 ml H2O	18.5	n-hexane	55
131	X	500X15		X				15	hexane	50
134	X	500x15		X			silica gel activated, 2% water	15	n-hexane	50
140										
143										
146	X			X					hexane	6
152	X	65 x 15		X				2	hexane	4,5
155	X	65x12		X				2	hexane	
158										
161	X	280 x 25	X					25	n-hexane	150
170	X	400x(25-35)	X					200	n-hexane	400
173	X	300x15		X			silica gel + argent nitrate	15	hexane	55
176	X	85x15		X			glass column Chromabond 6ml	2	hexane	4,5
179	X									
194	X	800X20		X				30	hexane	150
197	X			X				30	n-hexane	150
200	X			X						

Table 5.3b: Sample clean up details

LAB CODE	Column Chromatography	Column dimensions	Aluminium oxide	Silica gel	Florisil	Other	Remarks	sorbent amount [g]	solvent	volume [mL]
203	X	300x10	X					3	hexane	20
206										
209	X	500x20		X				30	Iso-octane	150
215	X	300-500 * 15-18		X		X	Silica gel impregnated with silver nitrate	18.5	hexane	40
218	X	400 x 15		X				15	hexane	70
221	X	400 x 15		X			Silica gel is previously treated with silver nitrate, 10% (w/w)	18.5	Hexane	55
227	X	15X500		X				15	hexane	50
230		300x15		X				18.5	n-hexane	70
233	X	500 x 30		X				30	hexane	150
236	X	80 x 13		X				2	n-hexane	4.5
239										
242	X	250x20		X				15	Hexane	60
245	X	200X45		X				10	Hexane	50
248	X	15x500		X				15	hexane	50
251	X	250*10						20	pentane	50
254	X	350 x 12		X				10	n-hexane	50
257	X	200x20		X				20	hexane	70
260			X				In a glass column, put 100mL C5, add 60g of aluminium oxide. Wash with 100mL aluminium oxide. Add the 10 mL of sample in C5 to analysis. Elute with 100mL of C5	60	pentane	100
263	X	500x15		X				15	Hexane	50

Table 5.3c: Sample clean up details

LAB CODE	LC on-line clean up columns, dimensions, solvents, flow rates, etc.	SPE columns, solvents, etc.	Other Clean-up	Final volume of sample [mL]
101				
113				1
119	LC-LC: 1st column: LiChrospher Si 60, 5 µm, 250 x 2 mm i.d.; 2nd column: LiChrospher Si 60, 5 µm, 250 x 2 mm i.d. (or Aluminium oxide 60 active basic, activity I, 0.063-0.2 mm, activated at 400 °C, 100 x 2 mm i.d.); hexane; 300 µL/min; backflush column 1: dichloromethane 1 ml			1.5
122				1 - 2
125				0.5
128				0,6
131				1
134				1
140	Spherisorb Si 5µm, 10cm x 2mm, Hexane 200ul/min			20
143		Empty cartridge (glass, 6 ml capacity). Filled (dry) with 2 g of activated silica gel (Merck 7734, 0.063-0.200 mm) and washing it with 5-6 ml of hexane. Activation of the silica: 16 h at 350 °C, after cooling to room temperature it is stored in a well closed glass bottle. Elution with hexane; first 1.5 ml are discarded, and after it 4 ml of eluate are collected. The solvent is evaporated at room temperature and the sample is washed with 1.5 ml of hexane into a GC vial.		1,5
146				3
152				3
155				5

Table 5.3d: Sample clean up details

LAB CODE	LC on-line clean up Please, specify columns, dimensions, solvents, flow rates, etc.	SPE columns, solvents, etc.	Other Clean-up	Final volume of sample [mL]
158		Silica gel 5g, hexane, 15 ml		0,05 isooctane
161				0,5
170				0,5
173				0,5
176				1
179		2g Si sorbent. Eluted with Heptane		1
194				1
197				1
200				1
203				0.1
206		SPE on silica gel; Method Katell 2008 (Kantonales labor Zurich)		3
209				0,2
215			A volume of 55 ml of elution is collected and evaporated under reduced pressure until dryness and the residue is dissolved in 0.5 ml of n-heptane	0,5
218				1
221				0,2
227				0,2
230				0,5
233				0,5
236				3

Table 5.3e: Sample clean up details

LAB CODE	LC on-line clean up columns, dimensions, solvents, flow rates, etc.	SPE columns, solvents, etc.	Other Clean-up	Final volume of sample [mL]
239		SPE (self prepared) with 2 g silica gel 60 70-230 mesh (Fluka cat. no. 60741), condition and elution with hexane. Sample bring onto column with 250 ul hexane. Discard first 1 ml, and collect next fraction 4 ml.		4
242				0,3
245				2
248				0.2
251				0.5
254				1
257				1
260				1
263				0.2

Table 5.4a: Final determination technique

LAB CODE	GC-FID	GC-MS	HPLC-GC-FID	HPLC-HPLC-GC-FID	Instrument manufacturer	Instrument type
101	X				VARIAN	GC-450
113	X				Agilent	7890
119				X	Thermo Scientific	HPLC pump: Phoenix 40; Trace GC
122	X				Agilent	6890
125	X				Agilent Technologies	HP-6890
128	X				Hewlett-Packard	5890 Series II
131	X				Thermo Finnigan	Trace GC ultra
134	X				AGILENT TECHNOLOGY	7890A
140	X				Thermo	Trace LC-GC
143	X				Agilent	6890
146	X				Varian	3800
152	X				VARIAN	3600
155	X				Agilent-Carlo Erba	6850 Agilent and 5160 Mega Series Carlo Erba
158	X				FISONS	8560 HRGC Mega 2
161		X			Agilent	HP 5890-GC, HP 5972-MSD
170	X				Agilent Technologies, Varian	HP 7890, CP-3800
173	X					GC
176	X				Agilent	Agilent 7890A
179	X				Perkin Elmer	
194	X				Varian	450
197	X				Thermo Scientific	Trace GC
200	X				Perkin Elmer	Autosystem
203	X				Agilent Technologies	AT 6890
206	X				Carlo Erba	5160 mega series
209	X	X			Perkin Elmer for GC-FID, Agilent for GC-MS	Clarus & Agilent HP 6890 -HP 5973 en mode SCAN
215	X				AGILENT TECHNOLOGIES HP	HP 6890
218	X				Carlo Erba Instruments, Italy	HRGC 5160, Mega series

Table 5.4b: Final determination technique

LAB CODE	GC-FID	GC-MS	HPLC-GC-FID	HPLC-HPLC-GC-FID	Instrument manufacturer	Instrument type
221	X				Agilent Technologies	6890 N
227	X				PERKIN ELMER	AUTOSYSTEM XL
230	X				PERKIN-ELMER	Clarus 500
233	X				VARIAN	GC 3900
236	X				Agilent Technologies	6890N
239	X				Varian	CP-3800
242	X				Perkin Elmer	Autosystem
245	X				Fisons	Trace GC
248	X				PERKIN ELMER	AUTOSYSTEM
251	X				Interscience/Thermo	trace GC 2000 series
254	X				Varian	GC3400
257	X				Agilent	6890
260		X			Agilent	GC/MS : GC 7890A, MS 5975 C
263	X				AGILENT	6890N

Table 5.5a: Injection technique - details

LAB CODE	Injection technique						Injection volume [μL]
	on-column	splitless	split	LC on-line	Splitless with CSR	Remark	
101	X					Our injector is a 1079 PTV (on column) injector from VARIAN. Temperature program of the injector : 80 °C to 380 °C 200°C/min ; 380°C 10 min , total time : 11,95 min.	1
113	X						50
119				X		on-column interface, partial concurrent solvent evaporation	450
122	X						2
125	X						2
128	X						2
131	X						1,2
134	X						1
140	X						50
143	X	X				injection is done at 46 °C (below the boiling point of the solvent) and the injector temp is heated as in "track oven" setting (the heating rate is the same as for the oven, the temp is higher by 3°C than the oven temp.	5
146	X					Varian uses an SPI-liner. The column is fitted into this liner. At this way it is similar to On column.	10
152	X						50
155	X	X				Agilent 6850 has been used for splitless injections (3 μl of concentrated sample) while Carlo Erba Mega series 5183 has been used for on column injections (50 μl of sample).	3-50
158	X						1
161		X					1
170			X				1
173	X						2
176	X						2
179			X				1
194		X					1

Table 5.5b: Injection technique - details

LAB CODE	Injection technique					Remark	Injection volume [μ L]
	on-column	splitless	split	LC on-line	Splitless with CSR		
197	X						1
200		X					1
203		X					4
206	X						40
209	X	X				For GC-FID: on-column, for MS: pulse split-less,	1
215	X						1
218	X						3
221			X			Initial temperature: 320°C; Split ratio: 15:1	1
227	X						1
230	X						1
233		X					1
236						LVI injection on PTV injector operated in solvent vent mode	50
239	X						50
242		X					1
245	X						1
248	X					5m Retention Gap	4
251	X						1.0
254		X					1
257	X						1
260		X					2
263	X						2

Table 5.6a: GC conditions

LAB CODE	GC column					Carrier gas				GC oven
	Supplier	Type	Length	ID	Film thickness	Carrier gas type	Flow rate	Constant flow	Constant pressure	Temperature programme
101	VARIAN	CP-SIMDIST	10	0,32	0,1	HELIUM	2	X		80 °C to 350 °C 20°C/min, 350 °C 3 min ; total time : 16,50 min
113	SGE	HAT-5 including 8 m deact. retention gap	25	0,32	0,1	Hydrogen	2	X		for 6 min 71 °C, 20 °C/min to 350 °C, hold 10 min
119	home made	dimethylpolysiloxane PS-255	10	0.25	0.15	H2			X	65 °C (2 min) 25 °/min 360 °C (5 min)
122	J&W	DB-5HT	30	0,32	0,1	He	2,5	X		60°C 2 min, 40°C/min -> 260°C 1 min, 15°C/min -> 370°C 15 min
125	Agilent Technologies	DB-5HT	10	0.32	0.1	Helium	3.1	X		60 °C (1 min) - 350 °C in 10 minutes at 12 °C / min
128	Teknokroma	methylsilicone TRB-1 ht	10	0.32	0.1	hydrogen	20		X	60°C 1min; 12°C/min up to 280°C; 7°C/min up to 340°C; 2.10 min (Total=30 min)
131	Restek	RTX5	15	0,25	0,10	Hydrogen	2	X		85°C, 30°C/min up to 165°C, 2°C/min up to 170°C, 15°C/min up to 335°C for 15 min
134	J&W	DB-1HT	15	0,32	0,10	hydrogen	5		X	80°C for 1 min, rate 15°C/min up to 340°C, 340°C for 10 min
140	J&W	DB1	30	0.32	0.25	H2			60kPa	4min 60celsius; 8celsius/min to 330celsius; 10min 330celsius
143	J&W (Agilent)	HP-1, 100% dimethylpolysiloxane	12	0.2	0.33	Hydrogen	3.0		X	40 °C for 5 min; from 40 to 325°C: 15°C/min; at 325°C: 15 min
146	Varian	WCOT FUSED SILICA Coating Select Mineral Oil	10	0,32	0,10	helium	1,0	X		40(15)-15-350(10)
152	SGE	HT5	7	0,22	0,1	Helium			15 psi	50°C (8 min) to 370°C (9min) with 25°C/min
155	Agilent	HP-1	10	0.32	0.25	H2	2	X		55°C-4min---->25°C/min---->350°C-4min

Table 5.6b: GC conditions

LAB CODE	GC column					Carrier gas				GC oven
	Supplier	Type	Length	ID	Film thickness	Carrier gas type	Flow rate	Constant flow	Constant pressure	Temperature programme
158	Supelco	SPB1	7,5	0,53	0,1	H2	6		X	110°C (5 min) 20°C/min 350°C/min (5 min)
161	Agilent	HP-5 MS	30	0,25	0,25	Helium	1,25	X		60 °C, 1,2 min.; 28 °C/min.; 315 °C, 5 min.
170	Varian	VF-5ht	15	0.32	0.10	He	2.5	X		50 °C - 4 min; rate 10 °C/min to 250 - 1 min; rate 25 degrees/min to 380 - 5 min
173		SGL-5	15	0,32	0,10	helium	2	X	X	50°C-(12°/min)-340°C (10min)
176	VARIAN	capillary WCOT fused silica	25	0,25	0,1	H2	3,5	X		69oC hold 1min, 30oC/min to 270oC, 5°C/min to 350°C hold 5min
179	Varian	VF-1ms	3	0.25	0.1	hydrogen	1	X		90°C to 320°C
194	Varian	VF-1ms	15	0,25	0,25	He	2	X		60°C 2min 60°C/min 180°C 4min 3°C/min 320°C
197	PHENOMENEX	ZB 5 ht	15	0,25	0,1	hydrogen	1 BAR		X	from 100°C to 370°C at 20°C/min, isotherm at 370°C for 12 min
200	Supelco		30	0.32		He				60° 1 min ramp 10°C/min to 300 deg, hold for 10 min
203	Phenomenex Zebtron	ZB-1HT inferno	10	0.25	0.25	N2	1.3	X		45°C(3min)-----360°C(35oC/min)-----360oC(12 min)
206	Mega	dimethyl polysiloxane	10	0.25	0.15	He	4		X	65 °C isotherm for 4 min then to 320 °C at 15 °C/min
209	SGE	BPX5	12	0,25	0,1	H2	1,2		X	70°C,1mn, 35°C/mn to 180°C, 6°C/mn to 310°C
215	VARIAN	WCOT Fused silica CPSil 8CB (5%phenyl 95%dimethylplysiloxane)	10	0,32	0,12	Helium	20	X		Init temp 60°C;Init time 1min.;Rate 12°C/min.;Final temp 350°C;Final time 4min.
218	JW	DB5 - HT	30	0.32	0.1	He	2.5		X	70 to 360 °C with a rate of 5 °C/min

Table 5.6c: GC conditions

LAB CODE	GC column					Carrier gas				GC oven
	Supplier	Type	Length	ID	Film thickness	Carrier gas type	Flow rate	Constant flow	Constant pressure	temperature programme
221	Agilent Technologies	HP-5 5% Phenyl Methyl Siloxane	30	0,32	0,25	Nitrogen	5		X	80°C to 175°C at 25°C/min to 325°C at 8°C/min (held for 29,45 min).
227	RESTEK	RTX-5	10	0.32	0.25	He	4.5	X		80 (0min) RATE 5deg C/min to 340deg C (20min)
230	SUPELCO	SLBTM-5MS	30	0,25	0,25	Helium			20 psi	70°C,10°/min,325°C, hold 15 min
233	VARIAN	VF1ms	15	0,25	0,25	hydrogen	2	X		60°C during 2 min to 180°C (60°C/min) during 4 min then 180°C to 320 °C (3°C/min)
236	Agilent Technologies	HP-5MS, + (deactivated FS pre column)	11 + (5)	0.25(0.32)	0.25	Helium	1,4	X		60C for 4min., 25C/min.to 320C, hold 15.6min.
239	Varian	CP-Sil 5CB with 4 m retention gap 0,53 i.d.	15	0,32	0,25	He			X	75 (5) -> 300, 20/min (23,75); total 40 min
242	Supelchem	SPB1	10	0,25	0,25	hydrogen	2,5		X	60°C stop 5 min 25°C/min to 320°C stop 5 min
245	Phenomenex	DB5	30	0.25	0.1	H2			X	80°C(2 min) -> 320 / Rate 4°C/ min
248	SGE	DB-1	10	0.25	0.15	He	2.5	X		63 deg C (7min) Rate 5 deg C/min to 350 (20min)
251	Chrompack/Varian	CPSil 5CB	15	0.53	0.15	helium				init 50°C, 4 min, rise 25°C/min, final 340°C, final time 5 min
254	SGE	HT5	25	0,22	0,1	Helium	1		X	50 °C (5 min), 25 °C/min to 325 °C (16,8 min)
257	JeW	DB-5	15	0,25	0,25	He	1,3	X		100°C hold 1 min, 10°C/min to 285°C, 7°C/min to 330°C and hold 10 min. Run-time, 35,93 min.
260	Restek	Rxi-5MS	20	0,18	0,18	Helium	1	X		40°C for 5 minutes, rise at 10°C/min until 310°C, 310°C for 10 minutes
263	RESTEK	Rtx-5	15	0,32	0.25	Helium	5.8	X		80C 3C/min 160C 5C/min 340C 10min

Table 5.7a: Chromatographic conditions – detector settings

LAB CODE	Retention time range of target compounds			Detector settings						
	from	to [min]	Remark	FID temperature [°C]	make-up gas type	make-up gas flow [mL/min]	hydrogen flow [mL/min]	air flow [mL/min]	MS ionisation	mass to charge ratios recorded
101	3	15	3,40 min : standard peak, 15 min : end of the hump	380	Nitrogen	30.0	30	300		
113	8	25		350	Nitrogen	25	25	350		
119	15	25		380	none			350		
122	3,3	19,5	C10 3,3 min C16 5,4 min C44 13,7 min C50 15,4 min C60 19,5 min	370	He	17.5	17.5	380		
125	9.5	24		350	Nitrogen	30	30	300		
128	0.5	26		350	nitrogen					
131	8	18		350				450		
134	7	18		360	Nitrogen	5	5	450		
140	5	40		340				400		
143	16	23		340	nitrogen	45	45	450		
146	25	40		350	Nitrogen	30	30	300		
152	8	18,5		350				300		
155	8	14.5	Conditions used with GC Agilent 6850 (splitless)	370				400		
158	6	22		350				50		
161	4,5	14							El	Scan, m/z 50-300
170	1.3	26.9	From C9 to C40	400	He	25	25	350		
173	11	24	approx	350				450		
176	2.5	11		360	H2	20	20	300		
179	6	12		340	nitrogen	40	40	0		
194	12	40	Internal C17 : 5,1min	350	N2	28	28	300		
197	2,6	12		380						
200	20	30	Squalane		N					

Table 5.7a: Chromatographic conditions – detector settings

LAB CODE	Retention time range of target compounds			Detector settings						
	from	to	Remark	FID temperature [°C]	make-up gas type	make-up gas flow [mL/min]	hydrogen flow [mL/min]	air flow [mL/min]	MS ionisation	mass to charge ratios recorded
203	5.2	12		340	N2 5.0	20	20	400		
206	14	24	A 6 m x 0.53 deactivated uncoated precolumn was used	330				300		
209	15	45		330				450	EI	
215	0,35	30		350	Nitrogen	10	10	350		
218	20	55		380	none			100 kPa		
221	1,5	50,6		340	Nitrogen	25	25	400		
227	15	55		350	NONE			400		
230	4	40		350				450		
233	8	45		350	Nitrogen	28	28	300		
236	7	20	C14 at 8min., C40 at 16.4min.	340	N2	20	20	400		
239	12	26	range of integration depends on baseline observation	350	He	29	29	300		
242	9	15		320	none					
245	1	40		350	N2	30	30	360		
248	28	60		380	none			400		
251	4	15		350				350		
254	7,6	21		325	Nitrogen	25	25	250		
257	8,00	29,00		340	N2	45	45	450		
260	18	37							EI	40 - 450 amu SIM ion 57, 85 , 136
263	19	60		320	Helium	10	10	450		

Table 5.8a: Details on calibration

LAB CODE	External calibration	Standard addition	Details on external calibration	Internal standardisation	Details on IS	Amount of IS [µg]	IS added after weighting	IS after sample prep	IS after sample clean-up	Remark
101				X	Hexadecane, C16H34	77.0	X			Hexadecane, C16H34 (concentration of 77 ppm), 1 ml of standard solution is added to the sample.
113				X	C 14 alkane	1			X	According to ISO CD, Part 2
119	X		Paraffin viscous, Merck, 107160							
122	X		Mineral oil without additives, Dr. Ehrenstorfer Nr.: 03009010							
125	X		n-Eicosane (C20)							
128				X	n-eicosane	50	X			
131				X	C44H90	100	X			
134				X	C44 - Tetratetracontane (Sigma Aldrich)	100	X			
140				X	C13	5.15	X			
143				X	hexadecane (C16)	39939	X			5.6 µg internal standard is added, (250 µl; c=0,0224 mg/ml)
146	X		Paraffin Oil, Merck							
152	X		Mineral oil Standard from NMI (ref : RIVM-Nmi-001)							

Table 5.8b: Details on calibration

LAB CODE	External calibration	Standard addition	Details on external calibration	Internal standardisation	Details on IS	Amount of IS [µg]	IS added after weighting	IS after sample prep	IS after sample clean-up	Remark
155	X	X	A standard of mineral paraffins provided by a candy manufacturer							
158				X	Tetracontane (C40H82)	0.025	X			
161	X			X	D40-Nonadecane	58.5	X			
170	X	X	RIVM-NMi-001, Heptacosane (alkane C27) (Fluka, 51559), Nonacosane (alkane C29) (Fluka, 74156), Hentriacontane (alkane C31) (Fluka, 51529), n-Nonane (Riedel de Haën, 46172), Tetracontane (Riedel de Haën, 46409).							
173	X		liquid paraffin	X	eicosane	50	X			
176				X	C16, C40	1.25	X			
179				X	C44		X			
194				X	C17 heptadecane	1000	X			
197				X	1 ml of a solution of octadecane (C18) at 0,1 mg/ml	100 µg	X			response factor equal to 1

Table 5.8c: Details on calibration

LAB CODE	External calibration	Standard addition	Details on external calibration	Internal standardisation	Details on IS	Amount of IS [µg]	IS added after weighting	IS after sample prep	IS after sample clean-up	Remark
200				X	Squalane	1900	X			
203	X		Fluka Cat. No. 69246							
206				X	C13	0.625			X	
209		X	C16 at 50ppm	X	C16	62	X			
215				X	Eicosane (C20)	100	X			
218	X		paraffin oil from Fluka				X			Internal standard (hexadecane) addition for recovery calculation
221				X	n-Eicosane	100	X			
227				X	n-C20	20	X			
230				X	eicosane	100	X			
233		X	C24			500	X			
236	X		Mineral oil standard mixture for DIN EN 14039 and DIN ISO 16703	X	C15, C16:1, C40	12.5	X			
239		X	Mineral oil type A (Fluka 91975), Mineral oil type B (Fluka 78473)	X	Pentadecane (Fluka 76509), heptadecane as verification standard	2.5	X			
242	X		Mineral oil of vacuum pump added to vegetable oil. To check the response factor between internal standards and mineral oil.	X	C20 and C44 saturated hydrocarbon	50	X			

Table 5.8d: Details on calibration

LAB CODE	External calibration	Standard addition	Details on external calibration	Internal standardisation	Details on IS	Amount of IS [µg]	IS added after weighting	IS after sample prep	IS after sample clean-up	Remark
245				X	n-C40	50	X			
248				X	n-C20	4	X			Quantification using Calibration Curve consisted by 5 levels of Paraffin Oil (Liquid Paraffin Merck Cat. No : 1.07160.9026 paraffin viscous)
251				X	decane, Calibration curve of C10 (IS) and RIVM standard, 7 different amounts of min.oil, max. 2000 mg/kg	50				Quantification: addition of IS and calculation of min. oil amount with help of calibration curve
254				X	2,4-dichlorobenzene	10			X	
257				X	C44	128.7	X			
260				X	Naphtalene d8 ion 136	0.4			X	
263	X		Paraffin viscous MERCK 10760	X	n-Eicosane NEOCHEMA Cat. No. 14700-0230	20	X			

Table 5.9a: Details on method working range and integration

LAB CODE	Working range [mg/kg]		Integration		
	lower limit	upper limit	Hydrocarbons range lower limit	Hydrocarbons range upper limit	Details on integration
101	50	5500	18	40	Two integrations are carried out : an integration of the internal standard peak and the integration of the hump followed by the integration of natural hydrocarbons. Then, the peaks of natural hydrocarbons are subtracted from the hump.
113	50	800	10	45	Integration of the hump and subtraction of peaks on the hump
119	5	1000000	12	50	approximation by triangles
122	50	1000	16	44	Column compensation, integration of hump from C16 – C44, subtraction of peaks on hump
125	25	905	10	54	Integration of hump C10-C54 and subtraction of peaks on the hump.
128	20	1000	10	56	Usually, a first integration of peaks and hump from C18 up to C46 is done (a base line is drawn from C18 up to C46). A second integration of sharp peaks on the base line and on the hump (including the internal standard) is done. Area of mineral oil is the difference between first and second integration values.
131	15	1000	20	40	The hump C20-C40 is integrated. The defined peaks on the hump are integrated and subtracted to the total area (hump + defined peaks). The integration of the defined peaks is performed in order to reproduce the theoretic profile of the hump.
134	20	3000	20	48	Integration of hump C20-C48 and subtraction of the peaks of the natural compounds between C20 – C48.
140	2	500	10	40	Integration of hump by subtracting peaks on the hump; Integration software: chrom card
143	50	5000	20	40	The peaks for the natural hydrocarbons (C27,C29 and C31) are subtracted from the area value of the humps.
146	0.1	5	10	40	
152	20	2000	13	40	Calibration curve with 6 levels (from 0,012 mg/ml to 0,39 mg/ml) injected twice. The chromatograms are printed on the same type of paper, the hump is cut up and weight with precision (0,0001g). The axis of the calibration curve are : concentration (mg/ml) and weight (g) of the hump. The weight of the sample's hump is report on the curve to obtain the concentration of the injected solution. The amount of mineral oil contained in the volume of extraction is calculated. As the extraction is supposed to be complete, this value correspond to the quantity of oil mineral contained in the weight of sample (250 mg). The content in mg/kg is then calculated.

Table 5.9b: Details on method working range and integration

LAB CODE	Working range [mg/kg]		Integration		
	lower limit	upper limit	Hydrocarbons range lower limit	Hydrocarbons range upper limit	Details on integration
155	5	800	18	42	integration of the hump C18-C42 subtracting peaks on it.
158	20	1000	20	56	Integration of hump C20-C56 and peaks on the hump subtracted.
161	25	1000	12	36	Integration C12 - C36, hump included; subtraction of natural waxes
170	12	250	9	40	
173	15	300	10	56	integration of hump C10-C56, and peaks on the hump subtracted
176	25	1000	18	40	approximation by triangles
179	300	1000	11	44	
194	50	500			hump - natural hydrocarbur vegetal oil
197			18	50	integration of hump C18-C50 and peaks on the hump subtracted
200	50	1000			
203	50	10000	10	40	
206	10	2000	18	40	integration of hump C18-C40, peaks on the hump subtracted
209	5	2000	20	40	integration in two time, first the hump and second natural hydrocarbons that are subtracted at the hump, in general the column drift is not integrate
215	50	3000	18	42	Two integration types were used for each chromatogram: 1.- valley-valley integration for each peak eluted, from C10 to C60. With this integration mode and by calculating $(\text{Area total} - \text{Area IS}) * m \text{ IS } (\mu\text{g}) / (\text{Area IS} * m \text{ sample}(\text{g}))$, saturated aliphatic hydrocarbons coming from the matrix (sunflower oil) were obtained, SAHm (mg/kg). 2.- Area sum integration for the "hump" in the chromatogram and valley-valley integration for the remainder peaks. With this type of integration and by calculating: $(\text{Area total} - \text{Area IS}) * m \text{ IS } (\mu\text{g}) / (\text{Area IS} * m \text{ sample}(\text{g}))$ total saturated hydrocarbons were obtained (those coming from matrix and those coming from the mineral oil)SAH tot (mg/Kg). The content of saturated aliphatic hydrocarbons of mineral origin, SAHmo, in mg/kg, is obtained by subtracting SAHtot- SAHm.
218	20	500	20	48	Peaks on the hump subtracted. Approximation by measuring the hump maximum height.
221	50		10	50	Integration of hump (C20-C40) and all peaks out of the hump. Reintegration of the chromatogram considering the base line peaks profile. Content of hydrocarbons from mineral oil is the result of the difference between the amount of hydrocarbons obtained from the first integration and the amount obtained from the second integration.

Table 5.9c: Details on method working range and integration

LAB CODE	Working range [mg/kg]		Integration		
	lower limit	upper limit	Hydrocarbons range lower limit	Hydrocarbons range upper limit	Details on integration
227	10	500	20	48	Hump: C21-C48, All Peaks above the hump are subtracted , approximation by normal curve manually integrated
230	30	3000	10	40	peaks on the hump subtracted
233	10	700			
236	20	800	18	41	the hump C18-C42 was integrated by approximation by triangles.
239	25	1000	10	>40	Typically: integration hump between 12-25 min depends on hump and baseline observation (C20-C40) but for mineral oil oil type A&B this range is about 8 to 25 min. Area of hump calculate from subtraction peaks on the hump.
242	50	1100	22	42	Integration of mineral oil hump with subtraction of the natural sunflower oil hydrocarbon present on the hump
245	5	700	10	45	integration of hump (C10-C40), baseline subtraction
248	10	500	20	48	Hump : C21 - C48, All peaks above the Hump are subtracted, approximation by Normal Curve manually integrated
251	10	2500	10	56	Integration of hump C10 to C40, peaks on the hump subtracted
254	50	1000	10	40	peaks on the hump subtracted
257	30	1000	18	44	Integration SIM on the ion 57 of the mineral oil Peaks who don't belong to the mineral oil are manually integrated and subtract. A blank of manipulation is done and subtract.
260	10	300	18	40	
263	40	700	18	48	

Table 5.10a: Details on method quality control

LAB CODE	Quality control						
	QC materials yes	QC materials no	CRM BAM-K010	CRM RIVM-NMi-001	Other CRM	Details on CRM	Internal QC samples, spiking samples - details
101	X				X	A contaminated crude oleisol oil (100 ppm). The result (100 ppm) was confirmed by ITERG. The standard deviation calculated from about 50 samples is 7,5	
113		X					Paraffin (Merck)
119		X					vegetable oils, paraffin oil (C18-C28)
122	X				X	Mineral oil without additives, Dr. Ehrenstorfer	ASTM D5442 C12 - C60 standard, Supelco Nr.: 500623
125	X						Spiked "blank" refined sunflower oil
128		X					
131	X						Oil sample spiked with a known amount of mineral oil and used in an Italian inter laboratory test
134	X					Dr EHRENSTOFER - Mineral oil (DIN 453)	
140	X				X	Paraffin Oil DAB	
143	X						We used "real" technical oil and paraffin oil of pharmaceutical quality for spiking in a concentration range of 50 - 1000 mg/kg.
146	X			X			
152	X			X			the blank sunflower oil as been spiked.
155		X					

Table 5.10b: Details on method quality control

LAB CODE	Quality control						
	QC materials yes	QC materials no	CRM BAM-K010	CRM RIVM-NMi-001	Other CRM	Details on CRM	Internal QC samples, spiking samples - details
158		X					
161							Blank sample, spiked with BAM CRM-5004
170	X			X			Spiking materials (sunflower refined oil + RIVM-Nmi-001), mass fraction of mineral oil 50 mg/kg
173	X						C10-C20-C54
176	X						spiking materials 100mg/kg
179							
194		X					
197	X						internal reference sample (real contaminated sunflower oil sample) at 150 mg/kg
200		X					
203	X		X				
206		X					
209	X				X	a laboratory sample	
215		X					
218		X					spiking with paraffin oil from Fluka and alkane standard solution from Fluka.
221					X	Sunflower oil spiked with mineral oil (lubricant oil).	
227	X						Secondary Reference Material by spiking a blank Sunflower Oil
230		X					
233		X					

Table 5.10c: Details on method quality control

LAB CODE	Quality control						
	QC materials yes	QC materials no	CRM BAM-K010	CRM RIVM-NMi-001	Other CRM	Details on CRM	Internal QC samples, spiking samples - details
236	X		X				Paraffin oil, puriss. for spiking into blank sunflower oil
239	X				X	Mineral Oil Standard Mixture Type A&B for DIN EN ISO 9377-2 (Fluka 18602)	Mineral Oil Type A; Mineral Oil Type B (Fluka)
242		X					
245		X					
248	X						Secondary Reference Material by spiking a blank Sunflower Oil
251	X			X			RIVM Mineral oil standard
254	X			X			Spiked blank sun flower oil + ring test sample as second line test
257		X					
260		X					
263		X					

Table 5.11a: Method performance and additional remarks

LAB CODE	Method performance					Additional remark
	RSDr [%]	Recovery [%]	Recovery correction Yes	Recovery correction No	LOD [mg/kg]	Remarks to PT
101	7,5					Just a remark concerning the quantification : we systematically subtract of all ours results a "natural hump" obtained from a non contaminated refined sunflower oil and which is due to the analytical conditions.
113	2,2	91-103		X	10	
119	10	100		X	5	
122	2,6	100		X	20	
125	6.2 % at 49 ppm level; 10.5 % at 719 ppm level.	89		X	20	The n-Eicosane Standard which was added to the samples, was used just as a rough control tool rather than a pure internal standard. In addition we have available as a possible alternative, a whole set of results obtained by the use of Paraffin as Standard for quantification.
128	10	97		X	10	
131	8	80	X		15	
134	17	98		X	10	
140	7	85		X	2	
143	no data	no data		X	50	Method in under development and detection of recovery will be the next step.
146	0	75		X	0,15	
152		100		X	20	We should have all the same Standard to compare the results. The difference between two preparations may be > 20 %. The sensitivity of the detector is low. For us, it seems difficult to quantify below 50 mg/kg in spite of the large volume injection mode. For our laboratory, it is a new analyse and we would like have more instructions on the method to apply.
155	8	90	X		5	
158		85		X	20	
161	2,3			X	25 (LOQ)	
170	10	89		X	12	
173				X	30	

Table 5.11b: Method performance and additional remarks

LAB CODE	Method performance					Additional remark
	RSDr [%]	Recovery [%]	Recovery correction Yes	Recovery correction No	LOD [mg/kg]	Remarks to PT
176	10	92		X	25	
179	99			X	150	
194					50	
197	20			X	50	
200	15	89		X	50	
203	30	85		X	20	
206		98		X	10	We usually perform mineral oil analysis with LC-GC. Due to technical problem with the instrument we used the manual method proposed by Grob (Katell, 2008, Kantolal Labor Zurich). According to the method authors recoveries higher than 80% are obtained with the manual method. From a duplicate trial we obtained quantitative recoveries (98%)
209					5	
215	5(3000mg/kg)- 10(50mg/kg)				20	The result reported as " mineral origin oil" corresponds to the content in saturated aliphatic hydrocarbons coming from mineral oil (SAHmo). The blank, that is to say the sunflower oil, was analyzed once only, following the same procedure as for the other samples. A content of 30 mg/Kg in SAH mo was obtained for it. No account of this result was taken when reporting results to the interlaboratory (no blank subtraction performed).
218	7	72,5	X		20	
221						
227	4	99		X	10	Even though we determined an amount of 12 mg/Kg Mineral Oil in the blank sample, we have not subtracted this amount from the reported results of the other test materials.
230	20	85		X	30	
233					10	
236	11	90		X	10	
239	12%	87-97	X		25	

Table 5.11c: Method performance and additional remarks

LAB CODE	Method performance					Additional remark
	RSDr [%]	Recovery [%]	Recovery correction Yes	Recovery correction No	LOD [mg/kg]	Remarks to PT
242	8% on 300 ppm	95-100		X	30	
245	10	85-90		X	5	
248	4	99		X	10	Even though we determined an amount of 12 mg/Kg Mineral Oil in the blank sample, we have not subtracted this amount from the reported results of the other test materials.
251		90		X	10	
254	9,6	80		X	25	
257				X		
260				X	10	
263	(for 100ppm) 2	100		X	13	

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Abstract

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Joint Research Centre (JRC) was requested by the Directorate General Health and Consumers (DG SANCO) to organise a proficiency test on the determination of mineral oil in sunflower oil. The aim of this test was to evaluate the comparability of analysis results gained by laboratories in EU and in Ukraine.

The study was free of charge for the participants. The organisation of the study as well as the evaluation of the results was done in accordance with "The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories" and ISO standard 43.

Altogether 62 laboratories from 19 EU Member States, Switzerland and Ukraine subscribed for participation in the study. The participants were asked to determine the mineral oil content in the test samples by application of their in-house analysis methods. In total, 55 sets of results were reported to the organisers of the study.

The performance of laboratories for the oil samples was expressed by z-scores and by relative bias for the mineral oil solution in *n*-heptane.

The percentage of successful laboratories in the determination of the mineral oil content of sunflower oil was for all sunflower oil test materials about 80 %.

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