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CUSTOMS 2020 REPORT CLEN Action 2 Proficiency test on Mineral oils and Study on aromatics – Discussion meeting –

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approved by the coordinator & the meeting chairman,

and approved by DG TAXUD Head of Unit A4.

FINAL AGENDA

- 1) Welcome and adoption of the agenda.
- 2) Presentation of the proficiency test on mineral oils: backgrounds, samples, parameters, etc.
- 3) Discussion and interpretation of the analytical results of the proficiency test on mineral oils: results, comments, draft report and preliminary conclusions.
- 4) Conclusion on the proficiency test and eventual recommendations.
- 5) Presentation of the study on aromatics: backgrounds, samples, parameters, etc.
- 6) Discussion and interpretation of the analytical results of the study on aromatics: results, comments, draft report and preliminary conclusions.
- 7) Conclusion on the proficiency test and study and eventual recommendations.
- 8) Discussion on an official definition of the term “aromatics”.
- 9) Discussion on the possible amendment of method of Annex A CNEN Chapter 27.
- 10) Any other questions.

ANNEXES

Annex I – List of participants

Annex II – Presentation of the results of the proficiency test on mineral oils by the coordinator

Annex III – Presentation of the results of the study on aromatics by the coordinator

Annex IV – Proposals of amendments to the method of Annex A to Chapter 27

I. Welcome and adoption of the agenda

The meeting chairman (DG TAXUD) welcomed all the participants and thanked the Hungarian coordinator for organising this meeting. He explained that this meeting was important because many problems are encountered on the topic of mineral oils with high aromatics content. There is a very active lobby from the petroleum industry. Several measures were taken by the Customs Committee (such as suspensions) and there also was a court case on this topic. He added that besides the Proficiency test on mineral oils was the classical one with the usual parameters, it was important to have in addition this specific study on aromatics and to discuss this topic in depth. Producers have to check more regularly the aromatic content of their products and face difficulties since the method indicated in Annex A to CNEN Chapter 27 is cumbersome and time-consuming. Therefore, there is a need to be able to respond to the industry regarding whether an easier method can be used.

After this introduction, a round table was suggested and the participants introduced themselves.

The coordinator of these proficiency test and study (HU) welcomed all the participants to this meeting and presented a modified version of the agenda (with the two tests treated one after the other), which was adopted by all.

II. Proficiency test on Mineral oils

The coordinator of the test first presented the background of this proficiency test on Mineral oils (***see presentation in Annex II***). The choices made at the preparatory meeting regarding the design of the test and the samples were presented. The results of the homogeneity tests were also shown and the coordinator pointed out the fact that for one sample the homogeneity criteria were sufficient but near to the limit. However, as the difference in the density values was only on the decimal, the samples were considered homogenous enough. Moreover, the results obtained by the participants on this sample were good and did not show any evidence of inhomogeneity. The schedule of the proficiency test was then presented and the coordinator underlined the fact that the sourcing of the aromatic samples was very difficult and delayed the test. Finally, the parameters which were to be determined were presented, as well as the procedure used in the statistical treatment.

The results obtained for the different parameters were then presented and discussed for each sample.

A. Sample E85 (E85 fuel)

1. Vapour pressure

The Coordinator declared that the results were very good on this parameter, as the calculated limit of repeatability is lower than the repeatability indicated in the standard EN 13016-1.

2. Density

For this parameter, the result of one laboratory was considered as incoherent. The coordinator added that the incoherent value was clearly due to a mistake on the unit and asked the meeting participants whether this data should be modified.

A participant (FR) explained that in some commercial proficiency tests, for such mistakes it is asked to the laboratories if they want to correct the results and it is indicated in the report that the values were modified since the first reporting of the results. The Action leader explained that this is not the usual practice for CLEN tests and suggested to have a comment added instead, which was agreed by the coordinator.

Regarding the methods, the coordinator declared that one laboratory used a Stabinger viscometer, one used ASTM D4052 standard but that no differences were observed in the results. One laboratory measured the density at 40°C instead of 15°C, but it is not sure whether this was for sample E85 or the more viscous samples and the results are consistent with the others.

In the end, the calculated repeatability and reproducibility are very good and lower than those indicated in the standard EN ISO 12185.

3. Sulphur (UVF and XRF)

For the parameter Sulphur by UVF, the results are good and the calculated repeatability and reproducibility are equal or lower than those indicated in the standard EN 15486. The coordinator added that these results will be really helpful for the laboratories given that statistical data are usually determined for mineral oils and does not really apply to E85.

As for the XRF, only four laboratories used this technique. The results obtained were very inhomogeneous and therefore no conclusion can be drawn. One participant (NL) explained that his laboratory did not try XRF on this sample because the sulphur content was too low, i.e. below 5 ppm, which is the limit of the method.

4. Organic oxygenate compounds

For this parameter, GC-O-FID or reformulyzer could be used by the participants. Only a few laboratories took part: five used a reformulyzer, one used GC-O-FID and one used another method.

For ethanol, the coordinator pointed out that laboratory 1049 must have made a calculation or dilution mistake because its result is half the value of the others. One participant (IT) explained he contacted this laboratory to ask if there was a mistake and did not yet receive any answer. If there is a reply, a comment will be added to the report.

Regarding the other oxygenates (other than ethanol), ETBE was detected by three laboratories, MTBE by two and isobutanol and methanol by one laboratory each.

For organically bound oxygen, the results are very dispersed.

On a question of the coordinator, the participants declared that E85 was not analysed routinely in most of the Customs Laboratories.

5. Ethanol content

This parameter was to be determined by regular GC-FID, a very common apparatus. No method was provided and each laboratory therefore used its own method and calibration. This was a new determination and the results are very interesting because they show that regular GC can perfectly be used (with a calibration) to determine the ethanol content measurement and that the laboratories do not have to use any sophisticated GC.

The calculated repeatability and reproducibility are quite good. The repeatability is a little higher than what is indicated in the standard for GC-O-FID, but since it was the first time this determination was included in the proficiency test, this result is nevertheless very good.

The coordinator asked for the feedback of the participants on this determination: was the calibration easy? Do they use this method already in their routine work?

Some participants (RO, NL) explained that it was the first time they performed this determination on a petroleum product and that they used the same method and calibration as for alcoholic product, which worked fine. The coordinator asked whether the sample was diluted before the measurement and one participant (RO) declared he would check this as he did not know the range of calibration.

Another participant (BG) declared that a mandatory field should be systematically added in the result sheets for all the CLEN Action 2 so that the participants indicate detailed description of the methods and procedures used (dilution, type of calibration, etc.). This way it would be easier afterwards to compare methods and evaluate their performances. Indeed, for the moment, the participants do not all feel they have to put a comment in the dedicated field. This should also be mentioned on the first page as a general instruction.

The coordinator declared that this method should be added in ILIADe in the future, once a common procedure is agreed on. Here, different methods were used (different length and type of columns, use of internal standards by some participants, dilution step indicated by two participants with different solvents, etc.). The coordinator therefore asked whether a participant could send a standard operating procedure (SOP) for this method. This procedure could then be circulated for correction and approval and finally be sent to ILIADe. One participant (AT) offered to send his procedure, which requires special equipment as it uses two columns, and the coordinator declared that she will also provide the procedure of her laboratory, which uses a single column. The Action leader approved this creation of a common SOP and added that it could include different options, especially for the column. The coordinator agreed to this last point.

6. Water content

For this parameter, one of the participants reported a very high result, which may be due to a miscalculation.

The calculated repeatability and reproducibility are smaller than in the standard EN15489, therefore this determination was well performed by the participants.

7. GC composition analyses

For this parameter, the coordinator showed the chromatograms sent by the participants.

Some methods are very long (140 minutes for laboratory 1287), other very short (16 minutes for laboratory 1620 and 2054). The spectra are however difficult to compare given the different intensities of the peaks. In general, the separation is good, except maybe for Laboratory 1772 whose choice of column was maybe not the best one. Some laboratories provided GC-MS spectra. For laboratory 4121 many spectra were sent and look like duplicates, this will be check with the laboratory.

The coordinator explained that her laboratory receives mixtures of diesel with gasoline or with E85 (probably resulting from the fact that the tank was not well cleaned between each filling). In this case, they use GC profile not to identify the individual compounds but to see if the diesel contains lighter fractions by looking for the typical peaks of ethanol. They also check the flash point before to see if this GC determination has to be performed. A participant (BE) added that his laboratory also uses this method to do a screening of the samples and then performs the distillation in order to determine the amount of gasoline and diesel. Another participant (RO) declared that in his country only mixtures of benzene solvent and methanol were encountered, because the excise duties are low for methanol.

The coordinator concluded that it was interesting to collect these chromatograms. These chromatograms are not the same, as different methods were used, but still make it possible to compare the results and methods.

B. Sample DIE (diesel with 6-7% FAME)

1. Distillation

For this parameter, it was asked to participants to send back a lot of data, i.e. the temperatures for several distillation yields (from 10 to 95%), the distillation yields at critical points (250 and 350°C), and the temperatures at the initial and final boiling points.

a) Temperatures at several distillation yields

Almost all laboratories obtained satisfactory z-scores. The standard deviations are very similar, although the uncertainty is a little bit higher for the low distillation yields/temperatures. Unfortunately, statistical data are not available for all the distillation yields in standard EN 3405. Therefore the coordinator asked the proficiency test provider (Bipea ^{CLEN}TAS) to calculate the repeatability and reproducibility for the yields for which it was missing. The results obtained are coherent with the standard (imprecision higher for low distillation yields and comparable values). In addition, the uncertainty is also greater in the standard for the final yield, which is not the case here. A participant (EE) asked why the precision data were not calculated at all the distillation yields. The Action leader agreed that it should be done for comparison purpose. The proficiency test provider (Bipea ^{CLEN}TAS) will therefore perform these additional calculations and add the data to the report. Another participant (BG) asked whether all the laboratories performed the automatic method. The coordinator answered that in the comments a few laboratories indicated they used manual distillation.

b) Distillation yields at 250 and 350°C

The coordinator explained that these temperatures were chosen because they are the critical points for Tariff classification purposes. She added that 350°C was the most important one in order to discriminate gasoil and other oils.

There is no outlier for this parameter, which is very good as it means that all laboratories will have the same Tariff classification. There are no statistical data in the standard for these parameters, but the calculated repeatability and reproducibility are good. The coordinator added that in order to calculate the acceptance range, according to the guidelines set in the standard ISO 4259, the reproducibility values are needed. Therefore, having these values calculated based on the results of the test is important for the laboratories.

c) Temperatures at Initial and Final Boiling Points

The highest values of repeatability and reproducibility are of course observed at these two points. The results obtained by the laboratories are however good.

Regarding the parameter distillation in the first Minera oil PT, the coordinator explained that since it was not asked to the participants to provide all the details regarding the method used it was not possible to compare them.

One participant (PL) declared that gasoline was very common and suggested to perform this determination on gasoline in the next proficiency test. The coordinator answered that gasoline was already analysed in the first proficiency test, which is why it was decided to change for diesel this time.

2. Density

For this parameter, the measurements on sample DIE were very precise and the results are excellent, with repeatability and reproducibility better than those of the standard EN ISO 12185. AS for sample

E85, laboratory 3312 reported its result in the wrong unit and was therefore excluded from the statistical analysis. A comment will be added in the report as well.

Since the standard deviation is 0.0, one laboratory (EE) asked which results were also left out from the statistical calculation. The proficiency test provider (Bipea ^{CLEN}TAS) answered that no other results were excluded: the standard deviation is in fact 0.05 but since the results are expressed with one decimal only it was truncated. The Action leader therefore suggested having the exact standard deviation indicated in bracket after the 0.0 value, which was agreed by all.

3. Sulphur

a) Sulphur by UVF

No precision data were calculated, however, the difference between the minimum value (10.4 ppm) and the maximum value (12.5 ppm when the outlier result is excluded) is lower than the reproducibility indicated in the standard EN ISO 20846. Therefore, it can be concluded that the results are quite good.

The coordinator added that, since the calculated mean value is 10.3 ppm, this sample can only be considered as a diesel having a sulphur content lower than 10 ppm by taking into account the acceptance range (according to standard EN ISO 4259).

b) Sulphur by XRF

In the same way, the difference between the minimum and maximum values without the outliers is smaller than reproducibility indicated in the standard EN ISO 20884, therefore the results obtained by XRF are also good.

The coordinator indicated that in her laboratory, in case the sulphur content is around the limit value of 10 ppm the determination is performed by UVF and in the other cases XRF is used. A participant (LT) explained that in her laboratory for samples close to the limit the values obtained with the two methods are indicated with their respective uncertainties.

Regarding the methods, the coordinator asked the participants in which cases they used UVF or XRF if they had both apparatus. One participant (RO) declared that his laboratory uses UVF (for which they are accredited) for low concentrations (up to 10 ppm) and XRF (for which they are not accredited) in case of dark samples or samples with high concentration in sulphur. These samples can also be diluted and measure by UVF. Another participant (EE) said UVF can be used for higher concentration and that his laboratory recently made a calibration curve up to 100 ppm. UVF is indeed easier to use. He indicated that in case of doubt, his laboratory uses both methods. A third participant (AT) said his laboratory uses XRF for gasoline and UVF for diesel. The results of the two techniques are comparable. He added that for high sulphur content his laboratory uses XRF standard-less analysis. Another participant (LT) said gasoline and samples with small quantities of sulphur are analysed in her laboratory by UVF and samples with high quantities by XRF.

A participants (BG) asked whether it was possible with energy dispersive XRF to have such a good determination for small amounts of sulphur. She indicated that the equipment of her laboratory does not make it possible to go below 300 ppm. The coordinator said wavelength dispersive XRF gives better results but added that she heard there now were new models of energy dispersive XRF on the market which apparently are better. The coordinator concluded by saying that the standard allows the three methods: UVF, wavelength and energy dispersive XRFs, but in case of doubt she advised to use UVF or wavelength dispersive XRF.

4. Flash point

For this parameter, the results are good and comparable with those obtained during the first proficiency test. The difference between the minimum and maximum values is a little bit higher than the reproducibility indicated in the standard EN ISO 2719.

Regarding the methods, one laboratory used EN ISO 13736 and another used ASTM D93 but their results were good. Thus it seems there is no difference between the different instruments.

One participant (PL) declared that the result depends on type of apparatus, i.e. if it is automatic, manual or semi-automatic. Another participant (BG) added it also depends on the calibration used.

The coordinator indicated that in the standard there was not different precision data provided for the different type of instruments. Therefore, it can be assumed that the same precision can be achieved. But of course it depends on the calibration of the thermometer and the eye of the person doing the measurement. She indicated her laboratory uses both a semi-automatic and a manual instrument. Another participant (BG) said her laboratory uses a semi-automatic instrument and performed this analysis very regularly.

5. Kinematic viscosity

This parameter was to be determined at 40°C and 50°C.

The precision data were calculated at 50°C and the obtained repeatability and reproducibility are better than the one given in the standard EN ISO 3104. Compared to the first proficiency test, the statistical parameters are better at 40°C for this test and similar at 50°C.

Regarding the methods, many laboratories used capillary viscometers (manual or automatic), some used Stabinger viscometers or other apparatus but no statistical difference can be seen between the methods. One participant (SI) explained that the results for manual apparatus seem worse than for the automatic viscometer. For him, manual viscometers are problematic: indeed, the viscosity constant is for 40 or 100°C but the Customs laboratories have to perform a measurement at 50°C. It is possible to calculate this value with some algorithms but it may explain why the results are not as good. The coordinator suggested to add this remark in the report and added that it would indeed be good to have some CRM with certified viscosity values for 40 and 50°C, so that the laboratories can calculate the constant.

6. FAME content

a) By FTIR

For FTIR, there is only one questionable z-score. The calculated mean value is 6.8 v/v%, The results are however very good. On a question of the coordinator, the participants answered that they did not encounter any problem with this determination.

b) By ATR

For this measurement, a SOP was written by the coordinator and provided to the participants. The coordinator declared she was very pleased with the results because the mean by ATR is the same as for the FTIR determination. She added that the repeatability and reproducibility were a little bit higher than those indicated in the standard but were still acceptable. This method could therefore be an alternative for a quick measurement of the FAME content. She asked for the feedback of the participant on this SOP.

A participant (NL) said his laboratory used only FTIR and GC and is not equipped with ATR. He declared that GC had to be used to check the purity of the FAME. The coordinator answered that it was possible to distinguish FAME and vegetable oil by FTIR. Indeed, there is a shift if the sample contains vegetable oil and there is also an additional different peak patterns at 1200 cm⁻¹.

A second participant (IT) indicated that one of the laboratories of his country uses this method routinely and is happy of it and that another laboratory declared it would be happy to work with an ATR system from now on, even if it is already accredited for the EN ISO 14078 Norm (FTIR). Another participant (SI) declared that the big advantage of this method was that there was no risk of destroying the crystal. The coordinator added that the cleaning was also really quicker.

The coordinator explained that the aim of this determination was to get statistical data which could then be used by the laboratories to get an accreditation for ATR. On the whole, the participants were satisfied with the method and the SOP and declared that the suggested calibration material (methyl oleate) was suitable. The coordinator therefore suggested having this SOP and its statistical data put under ILIADe, which was agreed by all.

c) By GC

Regarding this determination, the coordinator explained that in some cases, the source of the FAME was an important piece of information (for example to determine if the FAME was legally produced). For this reason, it was asked to the participants to measure the fatty acids composition of the FAME. However, only four results were sent: one laboratory had much lower results, but the three other laboratories had comparable results. A participant (EE) suggested this laboratory with low results may have performed the calculation for the whole sample, not only the FAME. Another participant (NL) said it could also be a separation problem.

Regarding the calibration, a participant (NL) declared his laboratory used external standards to perform the calibration on all compounds. The coordinator said her laboratory used an internal standard (separation of the FAME part from the diesel, then re-esterisation process and finally measure with the internal standard).

7. Cold filter plugging point

For this parameter, the minimum value is 11°C and the maximum value is 14°C (without the outliers), therefore the results are in agreement with the reproducibility of the standard EN 116.

The coordinator explained that in Hungary the limit was -20°C, but that this varied depending on the country's weather.

8. Water content

For water content, one laboratory reported an incoherent result and was excluded from the statistical analysis. The water content is very small for sample DIE, however, the calculated uncertainty and standard deviation are very good and much better than in the standard EN 12937.

Most laboratories used same method, i.e. potentiometric titration. One laboratory used colorimetric titration. No differences were observed between these methods.

9. Saponification number

The coordinator declared that the repeatability and reproducibility values in the standard EN 6293-2 were very high, therefore the results are good compared to the standard. The results are also better than in the first proficiency test (standard deviation of 1.58 instead of 3.1). She added that this parameter was important for Tariff classification. If the distillation results do not fulfil the specifications of diesel, the laboratories have to check the sulphated ash content and saponification number to determine the classification of the product.

One incoherent result was reported. The representative from this laboratory explained that it was the first time they had a problem with this analysis. The determination was performed again using a solution at 0.5 instead of 0.1 and a better value was obtained (13.75). In the first proficiency test, this solution at 0.1 was used and the result was however good. This is probably due to the fact that this

time the saponification number of this sample is very high. The coordinator suggested adding this comment to the report.

Another result was low and the representative from this laboratory explained it was because they stopped the titration too soon. When the analysis was performed a second time, the value found was also around 14.

10. GC composition

The coordinator presented and commented the chromatograms sent by the participants.

Different methods were used, but the shape is always similar and typical of a diesel. The resolution can be different as the lengths of the methods are different (for example, laboratory 3011 has a very quick method of 16 minutes). The coordinator declared it was good to see that, even without a common procedure, similar GC profiles are obtained. Some spectra have a different separation as they are GC-MS spectra. Some laboratories also used SIMDIS GC. One laboratory (2054) provided a spectrum with a totally different distribution; this spectrum is most probably a chromatogram of the FAME and should therefore be deleted from the report.

The coordinator declared that this comparison of the spectra shows that most of the Customs Laboratories have very similar results and that determining the composition of a diesel was therefore not a problem for them, which is crucial to tackle the cases of counterfeited diesel.

C. Aromatic Samples: samples PO70 and PO90

1. Density

For sample PO70, the density was measured at a higher temperature because of viscosity issues. Sample PO90 was however too viscous to measure its density.

The standard deviation obtained is quite small compared to the repeatability and reproducibility of the standard. For this determination, the uncertainty and the standard deviation will also be given with more decimals in brackets in the report.

One participant (BG) declared that her laboratory could not perform the determination as the sample was too viscous. Other participants (SI, NL) explained that the instrument had to be heated first (heater in front of the capillary).

A participant (NL) asked why the determination was required at 40°C, since in most cases the temperatures used are 15 or 60°C. The coordinator explained that this problem of high viscosity was not foreseen during the preparatory meeting where it was chosen to have the density measured at 15°C. The coordinator did some tests when the samples were chosen and saw that it could not be done at 15°C but could be done starting from 40°C, thus this temperature was chosen. She added that in usual ring test on gasoline, the densities measured were far lower.

One participant (BG) declared that this method for measuring the density was not appropriate for viscous samples. Another participant (FR) said the measure could be done at 50°C or above and corrections applied. The first participant answered her laboratory had an old equipment in which it was not possible to maintain the temperature constant in the cell. Another participant (RO) said his laboratory used a Stabinger viscometer but had many problems in performing this determination. The repeatability was poor. Finally, a participant (AT) explained he performed the measurement at 50°C as he has not seen the result sheet yet and said he did not encounter any issue at this temperature.

2. Sulphur

Samples PO70 and PO90 did not only have a high content in aromatics, but also a high content in sulphur. Compared to repeatability and reproducibility of the standard, the results of the proficiency test are not good. However, the coordinator added that it was not usual for the Customs Laboratories to analyse samples with such a high content in sulphur. Still, it was important for them to keep their accreditation on the higher range. Some laboratories may have used standard-less method, but there is no proper calibration for that range of sulphur content.

3. Sulphated ash

The coordinator declared it is really difficult to find a sample with a high enough sulphated ash content. Most of the laboratories reported here a value below the limit of detection.

One participant (PL) suggested asking for 3 decimal places next time, as in the standard, to avoid having only zero values. Another participant (EE) explained that was a common practice in commercial proficiency tests to ask for one more decimal place than required in order to have statistically workable results.

One laboratory (RO) wondered why this determination was performed on this kind of sample as it is only useful for classification within Heading 2710. It was explained by the coordinator that the preparatory group could not add one sample only for this determination and was therefore hoping in the end to get aromatics samples containing sulphated ash. Another participant (BG) added that it was still good to be able to practice the technique. A participant (NL) explained that his laboratory received base oils with lots of additives. It was then possible to get high sulphated ash, therefore this analysis was in fact done on many kind of samples.

4. Colour after dilution

The coordinator reminded that the diluted colour number was a requirement for the Tariff classification. According to the standard, this determination is performed by comparing the colour of the diluted sample with some reference colours and indicating if it is equal or lighter than these reference colours.

From the results it seems that the laboratories have some problems with this determination. For sample PO70, at least more than 50% of the laboratories have the same result, but for sample PO90 it is much more heterogeneous. The coordinator acknowledged that this determination is subjective, therefore for PO70 for example results from L 1.0 Dil to 1.1 are possible, but it is very surprising to have 4.0 or 2.0. She wondered what could be the reason for this and asked if it could be a dilution problem.

A participant (FR) wondered how many laboratories used automatic devices and declared that these results could be improved by using such devices instead of doing a visual comparison, which depends on the light used, the person doing the determination, etc.

A second participant (IT) said that one laboratory in his country heated the sample in order to be able to put it in the apparatus. The coordinator declared that with the dilution it was not that much viscous. A participant (SI) explained that his laboratory weighed the sample and then diluted by weight. Another participant (LT) added both the sample and the solvent had to be heated.

This participant underlined that according to the comments, some dilutions were not correctly made (85/15 instead of 100/1). Another participant (BG) said this 85/15 dilution was the one mentioned in the ASTM method. The coordinator read the definition of the diluted colour provided in the Combined Nomenclature. It specifies that this parameter is determined by the ISO 2049 method (equivalent to the ASTM D 1500 method) after one part of the product has been mixed with 100

parts of solvent. This seemed clear enough to her. A participant (BG) said it should be mentioned in the result sheet that the dilution is different to the ISO or ASTM methods. Another participant (FR) said that even in the ISO method it was possible to use a different dilution factor as long as you specified it. The coordinator concluded that in the next proficiency test, the exact definition given in the Combined Nomenclature will be indicated on the result sheet.

A participant (BG) declared that the difference probably mainly comes from the use of visual or automatic apparatus, especially for sample PO90. The coordinator explained that in the CNEN there is no requirement on this and that both types can therefore be used. She added that those samples were good samples for dark colours because they contained no green or yellow additional colorants. She concluded that next time this determination should be repeated, as it is not a very sophisticated measurement but seems nevertheless problematic for the Customs Laboratories.

D. Conclusions of the proficiency test

In conclusion, the coordinator presented the list of parameters on which statistical analyses was performed in the frame of this proficiency test. For some parameters, no statistical analyses could be made because there were not enough results. And finally there were also some qualitative parameters.

The results obtained are in general **better than those of the first proficiency test**, which shows that the laboratories are **more experienced** in these determinations.

This test has shown that **GC-FID can be used for the determination of the ethanol content in E85 fuel**. This is very interesting as this method is much easier. Two SOPs will be created based on the methods of AT and HU, with suggestions of chromatographic conditions. These **SOPs will be circulated among the participants for approval and then sent to ILIADe**.

For the **determination of the FAME content**, an SOP was tested with success for ATR and statistical data were obtained, this SOP can therefore be **sent to ILIADe**.

This test also made it possible to **obtain precision data for some parameters for which they were missing**.

Another conclusion is the fact that **the colour number determination should be repeated** in the future.

Finally, the coordinator mentioned the case of density measurements for viscous samples. A participant (BG) said the conclusion should mention that **high viscosity can be problematic for density measurements**.

The coordinator asked whether the participants had other remarks on this test.

A participant (PL) declared that the sulphated ash content was an important parameter for accreditation purposes and that no statistical treatment was unfortunately possible here. He added that testing the distillation of gasoline and diesel was also very important.

Another participant (AT) added that oxygenates were also important (e.g. gasoline with ETBE), but that there were not many results.

A third participant (SI) declared that his laboratory receives a lot of samples which are mixtures of diesel oil and fluorite. Another (RO) mentioned mixtures of diesel, base oils and vegetable oil (not under the excise duty of heating oil as it contains vegetable oil). The coordinator said it would mean having a proficiency test dedicated to illegal products. The possibility of producing standards or samples was discussed at the last Committee.

A participant (PL) also suggested including the determination of the octane number in a future test. The coordinator answered it was already considered for the first test but only a few laboratories were equipped.

Finally, the chairman said that his DG was thinking of organising small tests on a regular basis. He explained that this would not mean that this proficiency test will not be repeated, but that in addition some limited tests will be organised more frequently. He asked whether the participants thought there would be a need for such a test. All participants were in favour of having a limited test on one or two matrices and a few parameters. A participant (BG) added it could be done for aromatics.

III. Study on aromatics

A. Background of this study and issues regarding aromatics

An expert (BG) presented the background of this study on aromatics to the other participants.

In 2011, her laboratory received sample of fuel oil declared under the CN code 2707 99 99. This product was produced from petroleum oil and it was the first time such a product was declared under this CN code. The laboratory performed analyses to determine the aromatic content of the sample, using for the first time the method of Annex A to CNEN Chapter 27 in their country. The results confirmed that the content in aromatics was higher than 50% and the classification was right. Following this case, more controls were made and the laboratory received many samples of heavy oils classified under Heading 2710 by their producers. These samples were dark oils used for processing and the laboratory discovered that they consisted mainly of aromatic constituents and should thus be classified under Heading 2707.

The French administration then submitted a similar case to the Classification Committee for which they reached the same conclusions. According to the explanatory notes of the Harmonized System (HS), the content in aromatic constituents is the most important parameter for the distinction between 2707 and 2710.

After this, there was a court case in Bulgaria. A producer claimed that the method of Annex A was not appropriate for the determination of the aromatics content and recommended an ASTM method instead. After a very long dispute, the Bulgarian court sent preliminary questions to the European Court of Justice. This was the court case C-330/13. The decision of the court was that the content in aromatic constituents was the decisive parameter for classification.

The expert declared that the method of Annex A should be very carefully checked or maybe reviewed. This method is not a standard, it is a simplified version of an ASTM method, specifically designed and only published in the CNEN. For this reason, she suggested to have this determination included in the proficiency test on Mineral oils and was pleased that this study has been carried out. She added that the samples which were chosen for the study were different from the samples her laboratory received, which were usually residual oils of atmospheric distillation.

The expert then explained that the method of Annex A is time and labour consuming and uses chemicals in too large quantities. She declared that she would like in the future to have a deeper investigation carried out in order to find another technique for this determination.

She added that the other issue which was discussed in these court cases was the definition of the term “aromatic constituents”. In particular, the question was whether it was equal to aromatic hydrocarbons. In the decision of the European Court of Justice it was confirmed that there was no equivalence between the two terms.

She underlined the fact that in the current method of Annex A both terms are mentioned and that it should be corrected.

The expert concluded by saying the choice of the Customs Laboratories on this topic will also have consequences for the producers because in the future they will have to perform this determination for Tariff classification purposes.

B. Results of the study on aromatics

The coordinator presented to the participants the study on aromatics and its results (*see presentation in Annex III*).

The parameter to be studied was the aromatic hydrocarbon content according to different methods: method of Annex A to CNEN Chapter 27, Polish method, ASTM D2007, ASTM D2549, EN 12916 or any other method used by the laboratory. The coordinator briefly presented the main characteristics of these methods. She indicated that ASTM D2549 makes it possible to determine the non-aromatics and aromatics hydrocarbons. ASTM D2007 is probably the most difficult procedure among the four chromatographic methods as it uses of two different columns. Finally EN 12916 is a little different as it is an HPLC method. It was added that the samples were 'real-life' samples as the laboratories did not know the real percentage of aromatics.

The coordinator then presented the results of the study. Statistical treatment was only possible for three methods: method of Annex A to CNEN Chapter 27, Polish method and ASTM D2549 method.

a) Method of Annex A, Polish method and method ASTM D2549

The Annex A method gave the highest aromatic content, followed by the Polish method and then the ASTM D2549 method. The repeatability and reproducibility were calculated for the Annex A and Polish methods and the Annex A method showed better performances.

A participant (PL) pointed out that his results were not included in the proficiency test. These results were sent too late and will therefore only be added as comment in the report of the proficiency test.

Regarding the **Polish method**, an expert (PL) declared he was surprised to see differences in the results obtained by the Annex A method and this method (two low results around 53%). He wondered if this was due to the fact that they were not experienced or to a wrong understanding of the method. He added that the uncertainty was better though for sample PO90. Finally, he declared that if the Customs Laboratories want to introduce this short column method it would be necessary to check it on other levels of aromatic content (e.g. 40 and 50%). The coordinator explained that it was planned to have such samples but they could not be found during the sample sourcing.

A participant (BG) explained that her laboratory checked the eluent phase obtained by IR and saw a small peak around 1600 cm^{-1} for the Polish method, which means that some aromatics are eluted in cyclohexane together with the paraffinic part. This was not the case for the Annex A method and explains the low results obtained for the Polish method. She asked why the solvent was changed for cyclohexane. N-pentane is indeed mentioned both in the Annex A and ASTM D2549 methods. For her, cyclohexane should be used only in case nothing solvates in n-pentane.

The coordinator answered that this was decided at the preparatory meeting because the participants wanted to compare the effect of the solvents. A participant (PL) added the in sample PO90, the results of the Polish method are better, which proves that the analysis in cyclohexane can work.

b) Methods ASTM D2007 and EN 12916

One result was provided for ASTM D2007 and two for EN 12916, therefore no statistical analysis could be performed.

The coordinator then presented the spectra obtained by her laboratory using method **EN 12916**. It can be seen that the method works fine with the standard components and for the calibration; however, the results are very poor for the two aromatic samples of the study and the integration was very difficult to make. The coordinator concluded that the HPLC method is in fact not applicable for all kind of petroleum products. A participant (AT) explained that this standard was for middle distillates. He declared that there was a standard for fuels: ASTM D7419, which is also an HPLC method but with back-flush. The coordinator explained that this method was suggested for the study but no laboratories volunteered to do it as it was too complicated.

A participant (EE) noticed a mistake on the slides for method EN 12916: all the parameters were summed but the parameter POLY-AH was in fact already the sum of DAH and T+. This was corrected during the meeting.

c) Other method: method IP 469

One laboratory also performed method **IP 469**, which is a method based on TLC with FID detection. The representative of this laboratory explained that this analysis was subcontracted (to Intertek). This method is used for saturates, aromatics, resins and asphaltens. It is widely used by the petroleum industry because it is fast (40 minutes) and very simple. The device is quite simple and not very expensive. He declared that it was a way for the Customs Laboratories to have something more automatic. The industry could be very interested in the Customs Laboratories adopting this kind of method because they could analyse a lot of samples in a short time and this method is already described in a standard.

C. Discussion on the methods and definition of aromatics

Following the presentation of the results, the participants discussed the different methods that could be used for the determination of the aromatic content and the meaning of the term aromatics.

An expert (BG) explained that **the global approach used in the method of Annex A was the right one**, because it was not possible to make detailed analyses of all the compounds of these petroleum products. Indeed, they can be very complex mixtures with more than 600 compounds. It therefore makes sense to group them with the paraffinic and naphthenic compounds on one side and the aromatics on the other. The logic of this Annex A method is to separate the paraffinic and naphthenic compounds but it is not sure they are really well separated. The Polish method is based on the same principle only with less solvent consumed as the column is shorter.

A participant (EE) declared that maybe the method was appropriate but **the definition was wrong**. Another participant (PL) agreed that this definition was not in consistent with the current method. He added that the court cases have demonstrated there was not a universal definition of aromatics and that each country had its own definition and analytical method.

A participant (BG) said the definition of aromatic constituents was provided in the Harmonized System. Another participant (AT) indicated that the method of Annex A derived from method ASTM D2549, in which there is a definition of the aromatics fraction.

The coordinator declared that the term “aromatic constituents” was used in the CNEN and that for her this term encompassed all types of compounds with an aromatic part except olefinic constituents. She pointed out the fact that in the method of Annex A the polar and olefinic compounds were not removed and were therefore counted as aromatics. A participant (BG) agreed this was not correct, but that these compounds were only present in small amounts anyway. Extracting only the paraffinic part is for her the simplest way. A participant (EE) wondered whether

the definition should not be rephrased to list several groups of compounds and include polar compounds (and therefore with a different limit, at 60% instead of 50% for example).

Another participant (FR) said that for the industry the definition should only be based on the feasibility of the method. For them, method of Annex A is not appropriate as it is too time-consuming. The issue is first to find a quick method, and only then to provide a definition that fits with this method. It would also be possible to find an existing standard of an easy method which fits the current definition. He declared that it did not matter if this method included polar compounds or asphaltens in the aromatic constituents, as long as it was a simple one.

The coordinator listed the possible options:

- **Stay close to the definition provided in the HS explanatory notes and find an analytical method which measures these chemical groups.**

The coordinator declared she would be in favour of such a method and that **ASTM D2549** could be suitable. However, she acknowledged that this would make the analysis **more complicated**. A participant (PL) confirmed this method was very complex compared to the method of Annex A. It requires the use of several dangerous chemicals and it is time-consuming. He added that he faced difficulties in reaching the constant weight and didn't get a very good recovery. Another participant (BG) declared that it was not a problem for her to determine only the paraffinic part and consider that all the other compounds are aromatic constituents, as done in the method of Annex A.

- **Stay with the method of Annex A and modify it to provide a definition of aromatic constituents.**

The participants all agreed to say that the method of Annex A is very long (about 1 day per sample), uses high quantities of solvent and that the long column is neither convenient to use nor easy to find. A participant (AT) declared it would be better to keep the Annex A method as at least the laboratories know what they analyse with this method. The definition given in method ASTM D2549 could be added.

Another participant (BG) declared that if the method of Annex A is kept, the use of a shorter column should be possible for practical reasons. The method should be **more flexible** and at least leave the possibility to use a long or a short column and specify that for borderline cases the long column should be preferred. She recommended performing additional tests on the short column with n-pentane and cyclohexane as solvents. In this study, the two parameters were changed at the same time (solvent and length of column), therefore it is difficult to conclude.

A participant (IT) was in favour of the **Polish method**. He indicated that one laboratory in his country noticed that he improved its performances by collecting the material in a smaller flask than the size indicated in the method. Another laboratory performed the Polish method a second time and got better result, which shows that the performances of this method could be better once the laboratories are more experienced in it. He declared that having a shorter length of column was a critical point. For these reasons, he would like to **continue this comparison**, in particular by testing samples with content in aromatics at the limit, i.e. around 50%. Another participant (PL) agreed that the Polish method should be checked on at least four or five points. As such samples at 50% aromatics seem difficult to find, the first participant said a solution could be to dilute products in order to produce such samples. Another participant (AT) said his laboratory received residual oils at about 40% aromatics and offered to check if he could provide some material for a test. He added that his laboratory uses a shorter column than in the Polish method and that it usually gives good results, except for aromatic content around 50%. A participant (DE) declared that for her the Polish

method really has the potential to become the new Annex A method because it was really easier and the results obtained were quite similar (for her laboratory, there was just 3% difference compared to the results obtained with the method of Annex A for both samples). However she agreed that a comparison should first be made with n-pentane as solvent.

- **Find an alternative technique for this determination, such as HPLC or FTIR.**

A participant (BG) declared it would be interesting to compare the method of Annex A and **FTIR**. Another participant (FR) said he tried FTIR but could not find a correlation because of the very different numbers of benzene rings in gasoils, atmospheric residues, etc. He added that sometimes the FTIR results looked as if there were no aromatics at all, while the analysis of the same samples by method of Annex A showed aromatics. The coordinator said FTIR was a very simple technique but that her laboratory could not find any existing method. Theoretically, the aromatic compounds have their own peak. However, a calibration should be done and it is difficult to decide what kind of material to use: the mineral oils products contain different aromatic components and the result will therefore depend on the calibration material. A solution could be for everyone to agree on one single calibration material (with an aromatic ring and a side chain) and express the result on the amount of this calibration material: the method will then not really determine the exact amount of aromatics but will at least be reproducible. The coordinator declared every laboratory could at least use quicker methods in order to do a first screening and then apply the official method only for borderline cases. She declared that FTIR also could be used as a control, to check the end point of the elution in the method of Annex A.

Several participants (AT, BG) declared they were also interested in the **method IP 469**, which could be suitable for the industry. For them, it would be good to compare this method with the method of Annex A and check if it is really quicker and if it could be used for routine analysis. The chairman asked whether this method was precise. The expert (FR) answered it was more precise than the others because it was automatic and thus less dependent on the operator. He added that he only tried the methods for the study to see if it had some potential. He declared it would be interesting to do some more investigations to see if could really be used in the future. The representative of the DG TAXUD suggested asking the subcontractor to analyse the samples of the next study in order to compare the results obtained. He was interested by the technique and noticed this equipment could also be used for the analysis of lipids. The coordinator suggested that each Member States checks whether their national mineral oils producers are equipped with such apparatus. The chairman declared it would be nice to be able to say to the industry that they can use an easier method which gives the same results as the method of Annex A.

The chairman declared there were three aspects to be considered in this problem. The first is the fact that the current Annex A method is cumbersome (too long column, time and solvent-consuming method, etc.) and should thus maybe be dropped. The second issue is the fact that the court decided to let each Member State decide on its own method. For the moment it is fine but in the future it may lead to Member States using different methods which is not a good thing. Finally, there are these complains from the industries which have to analyse a lot of products and would therefore need to have an easy and quick method.

The coordinator suggested a round table to ask for the opinion of each participant regarding whether Annex A should be kept or changed and if changed, whether use modified Annex A or other method. Most of the participants declared **they would prefer to keep the method of Annex A with a few modifications to clarify what is its scope** in terms of compounds, in particular change the term

“aromatic hydrocarbons” in “aromatics constituents” and provide a definition which would list all the groups that are included in the aromatic constituents.

The participants were **in favour of the use of a short column**, as in the Polish method, but they agreed to say that for the moment, there was **not enough evidence** that the shorter column gives exactly the same results as the long column. **A study should be performed** with n-pentane and cyclohexane as solvents and with other levels of content in aromatics.

A participant (NL) indicated his laboratory does not use the method of Annex A but GC-FID and GC-MS. However, they do not receive samples with a high content of aromatic compounds. He added that the method of Annex A was not practical and was an old method. However, if the use of a short column was possible, his laboratory would agree to use this modified method.

One participant (SK) declared that his laboratory performed a screening by FTIR and only applies the Annex A method if result was between 43 and 60% of aromatics. For him, the method of Annex A should be changed for another method such as FTIR.

The coordinator declared that from a legislative point of view she would prefer to change the method of Annex A for another method which measures exactly the groups of compounds that are covered by the definition of the Harmonized System. But on the other hand she would like to have an easier method.

The chairman asked who wanted to keep the method of Annex A as it is, only with precisions regarding the scope in terms of components. The participants declared they did not want this as a long-term solution. If another method could be found with enough data they would agree to change the method. The chairman said he understood the laboratories would prefer the safe option and stay close to the Annex A method and its results, but was happy to hear that they were not against a change of method. The first modification to make would surely be to change the column, but he agreed to say that another study has to be made before.

The coordinator declared that of course the laboratories would agree to change the method if an easy and suitable method could be found. However, she pointed out the fact that the range of products covered by this method was very broad and therefore it is possible that several methods have to be used.

A participant (FR) indicated he would prefer in the end to have a more modern method. For him, an HPLC method at least would be better. Another participant (NL) suggested NMR but the coordinator said there would be limitations to this method. A participant (SI) suggested using GC, as done in the Netherlands: indeed, it is a modern technique which is present in all the Customs Laboratories. It was explained that the Dutch laboratory used GC-FID first and then GC-MS with a long column and could achieve a semi-quantification of the aromatics with this method. A participant (DE) asked which method were used by the industry and suggested to apply them in order to see if they give the same results as the Annex A method. Another participant (FR) answered that for the moment the industry uses the IP 469 method and the ASTM D2007 method (not designed for fuels, but used nevertheless), but only in order to check their process, not for importation purposes. This will therefore be a new need for them.

D. Amendment of the method of Annex A to CNEN Chapter 27

Since all participants agreed some modifications had to be made to the method of Annex A, the coordinator suggested agreeing on these changes during the meeting. She proposed to produce two amended versions: one version, which would only contains modifications related to the definition of aromatic constituents and other minor modifications and could be suggested at the next meeting of

the Project Group on mineral oils in April, and another version including the use of a short column, which would be used later as an SOP for the next study and could be suggested to the Commission if the results of the study are good. The participants agreed with these suggestions.

1. Amended method with minor modifications

The suggested amended method is provided in Annex IV.

The main changes suggested were the following:

- **Addition of the scope of the method**

A participant (BG) suggested adding a scope, as in the Polish method. The same sentence was chosen: "This test method covers the determination of the content of aromatic and non-aromatic constituents in mineral oils".

- **Addition of definitions of aromatics and non-aromatics constituents**

As discussed before, definitions of the aromatic and non-aromatics constituents were added. These definitions were taken from the ASTM D2549.

It was decided to keep the term "aromatic constituents" and not "aromatics fraction" as in the ASTM method, because otherwise it would mean that the title of the method would need to be changed. The coordinator pointed out the fact that for the non-aromatic constituents, if the eluent is n-pentane, only hydrocarbons will be eluted, therefore the term "non-aromatic hydrocarbons" would be better. It was decided to keep the same wording everywhere but to add "non-aromatic hydrocarbons" in brackets at the end of the definition.

A participant (EE) pointed out that in this definition compounds containing sulphur, nitrogen and oxygen were included and asked whether this meant that alcohol, ketones, esters, etc. without aromatic ring would also be included. Indeed this method is not only for crude oils. The coordinator declared that such compounds were out of the scope. Another participant (FR) added that in some cases, very rarely though, the method could indeed be used on waste products from the pharmaceutical industry.

A participant (RO) asked about the oxygenated compounds and it was answered that these compounds will be adsorbed on the silica gel.

- **Addition of a step of control by FTIR**

The coordinator suggested adding an FTIR control in order to determine the end of the elution. She explained that it was done in her laboratory and that only a few drops of product were needed for the measurement. For her, this control is necessary as 230 mL of n-pentane were sometimes not enough given the wide range of products and aromatics compounds could therefore still be seen in the eluate. Additional fractions of 50 mL of solvent are added until the control of the eluate by FTIR shows no aliphatic hydrocarbons. A participant (FR) said it could also be possible to decide that 230 mL was a convention for the definition of aromatics. If the practice is the same everywhere, it will not be a problem even if there are still non-aromatics in the column. Finally, it was agreed by all to add this step in this amended version (minor modification because it does not change the chromatographic conditions).

- **Replacement of the term "aromatic hydrocarbons" by "aromatic constituents"**

In the title of the method, the term "aromatic constituents" is used but in the method "aromatic hydrocarbons" is used. It was therefore decided by the participants to use "aromatic constituents" everywhere.

- **Modification of the repeatability and reproducibility values**

The repeatability and reproducibility values were modified according to results of the proficiency test.

- **Other modifications**

Other minor modifications were made, such as the addition of the **number of decimals for the exact weighing** of the sample and the addition of a **definition of the constant weight**.

A participant (PL) suggested adding a requirement only on the distillation starting point and not only the end point. This idea was supported by other participants. The coordinator explained that the end point at 315°C came from standard EN 1553. In the general note 2 of the CNEN, it was specified that this standard should be used for products with distillation end point below 315°C. It was underlined that the ASTM D2549 indicated a starting point at 232°C and that this value could be used here as well. However, the coordinator pointed out that such a modification will create a third case (mixture with a starting point lower than 200°C and a final boiling point higher than 315°C) and that another method would therefore be needed. Therefore, she suggested not mentioning any distillation starting point.

2. Amended method with the use of a short column

The suggested amended method is provided in Annex IV.

In this version, two modifications were made in addition:

- **Addition of the possibility to use a short column**

As discussed before, the possibility to have a second column was added, with the same characteristics as in the Polish method.

- **Addition of cyclohexane as solvent**

This modification was initially planned in the first amended version, however, a participant (BE) pointed out that there were not enough data yet for this. Another participant (BG) reminded that her laboratory found some aromatics compounds in the eluent with cyclohexane but said it could also be a deactivation of the adsorbent and that this point should indeed be investigated more in depth. It was thus decided to mention cyclohexane only in this second version.

A participant (BG) pointed out that it should be made clear that the use of cyclohexane was an exception to the rule, for samples which are not dissolved in n-pentane, and not different options of solvents. It was specified that in this case the sample should also be eluted in cyclohexane.

As for the purity of the cyclohexane, a minimum of 98% was required, as in the Polish method. A participant (EE) wondered why the minimum required purity for n-pentane was 95% and the coordinator explained that this fitted with the characteristics of the commercial solvents.

Because of the poor reproducibility obtained on the Polish method for sample PO70, it was decided not to change the repeatability and reproducibility values yet and to wait for the next test.

A participant (EE) asked if all the laboratories used a vacuum rotary evaporator for the evaporation stage. His laboratory was not equipped and uses a hot plate. He therefore wondered whether the hot plate or oven should also be mentioned here. The coordinator explained that the evaporation should normally be done at room temperature, and therefore a vacuum system was needed. She added that old systems using water to make the vacuum could maybe be used as they are not expensive. Finally, it was decided not to add these systems, as the term “similar apparatus” would cover the other cases.

The coordinator declared she will shortly circulate the amended methods among the participants for validation.

She added that it would be interesting to test the amended version with the short column in a dedicated study rather than waiting for the next proficiency test on mineral oils. She added that this study should also include some synthetic mixtures (aromatics, olefinic compounds, saturated hydrocarbons, etc.) and not only real life samples, so that the aromatics content is known. During this study, some easier method like FTIR or GC-MS could be tested. The chairman declared he was not sure this could be done in 2015, but that it could still be prepare to be able to start it early in 2016.

The coordinator concluded the meeting by saying that it was clear all the participants were in favour of the modification of the Annex A method and would be pleased to find an easier method. For the moment, proposals of small amendments to this method were made. She added that the result of the proficiency test on mineral oils were very good for the majority of the parameters which are important in the field of mineral oils analysis. Moreover, an SOP was produced and validated (FAME content by ATR) and will be sent to ILIADe and another SOP (ethanol content by GC-FID) will be produced shortly and sent to ILIADe as well. She then thanked everyone for their participation.

The chairman closed the meeting by thanking all the participants and thanking the coordinator for the organisation of this meeting. He declared that he was pleased with this meeting as some progress was made on the topic.