EUROPEAN COMMISSION
DIRECTORATE-GENERAL
TAXATION AND CUSTOMS UNION
Customs Policy, Legislation, Tariff
Combined Nomenclature, Tariff Classification, TARIC and integration of trade measures

Customs2020
REPORT
CLEN Action 2
Proficiency test on spirits, alcoholic beverages and alcohol-based preparations (2nd edition)
– Discussion meeting –

18 November 2014 – Brussels, Belgium

Minutes reported by CLENTAS, under contract TAXUD/2013/DE/325.
Final version, 19 January 2015.
Approved by the coordinator, the Action leader and the representative of DG TAXUD Unit A4.
Approved by the meeting participants.
Approved by the Head of DG TAXUD Unit A4.

AGENDA

1/ Welcome and adoption of the agenda.

2/ Presentation of the proficiency test on spirits, alcoholic beverages and alcohol-based preparations (2nd edition) and its results: background, samples, results, comments, draft report and preliminary conclusions.

3/ Discussion and interpretation of the analytical results.

4/ Discussion for the preparation of the final report.

5/ Conclusion on the proficiency test and eventual recommendations.

6/ Any other questions.

ANNEXES

Annex I - List of participants

Annex II - Presentation made by the Chair, coordinator of the proficiency test, during the discussion meeting

Annex III - Complementary homogeneity test performed on sample B by the Belgian Customs Laboratory

I. Welcome and adoption of the agenda

The Chair welcomed the participants. He suggested a round table before starting the meeting and the participants introduced themselves.
The agenda was adopted without modifications.

II. Presentation of the proficiency test on spirits

The Chair started the meeting by presenting the samples chosen for this proficiency test by the preparatory group, their main characteristics and their interest in terms of analysis (**see presentation in Annex II, slides 1 to 8**).
He then provided some explanations regarding the data evaluation and how the results were taken into account. It is to be noted that **clearly erroneous results were not included in the statistical evaluation, as well as zero values**, which were considered as results under the limit of detection/quantification.

III. Discussion and interpretation of the analytical results

The results obtained for each parameter were presented and discussed by the meeting participants (**see presentation in Annex II, slides 9 to 45**).

A. Alcohol content

- **Sample F**

The Chair explained that, against the expectations of the preparatory group, **most of the participants used distillation and not GC** for this determination: the sample was considered as a normal spirit drink. There was **no significant difference** between the results obtained by these two methods.
Compared to the equivalent sample in the previous proficiency test (screen wash), **the performance of the laboratories was a lot better** this time (standard deviation of 0.3 % vol instead of 0.8).
The Chair declared it was likely that one laboratory (3919) did not take into account the dilution of the distillate, as its result is about half the value of the other. A participant confirmed that the laboratory forgot to multiply its result by a factor 2.
A participant noted that all results were taken into account here, even for this laboratory, despite the fact that it seems clearly erroneous.
Another participant explained that it does not have a big impact because robust statistics gives a smaller importance to the extreme values. However, she offered to perform a new statistical evaluation without this value.
The Chair acknowledged that there was no formal procedure to classify a result as erroneous and remove it. As removing this result would not change significantly the statistical data, he declared that it could be kept.

- **Sample S**

For this sample, all laboratories but three used distillation methods. Because of the high amount of volatile compounds in this sample, **the results obtained from GC were lower**. The Chair declared that for him, distillation should be used for the determination of the alcohol content in spirit drinks.
A participant explained that GC was used by the concerned laboratories in some cases, for samples that are not pure hydroalcoholic solutions. For this sample, he explained that the low results are due to the fact that the laboratories determined the ethanol content instead of the alcohol content.

- **Sample B**

For sample B, one laboratory (5053) reported a **significant difference between two samples**.
A second participant declared that one of beer-mix bottles received by her laboratory had different alcohol content. A third participant added that he had the same problem with sugars and organic acids.
The Chair explained that there was however **no evidence for inhomogeneity from the other laboratories**, the problem seems to be only for a few samples. Besides, the homogeneity test performed prior to the sending of the samples gave good results. Another participant noted that this test was only performed on density, for which the results are good, and The Chair answered that this parameter was chosen because it is very sensitive.
Three other laboratories were outliers with results near 2 %vol., which may come from a unit mistake. It has been said this could also be due to the inhomogeneity of the samples.
A participant declared it was possible to have some inhomogeneity, as these were commercial samples. She added that all samples came from the same batch. Following some questions of the other participants, she explained that each sample was coded randomly, so no conclusion could be drawn from the code on the sample.
Despite this problem, the standard deviation is very good and the performance is similar to the one obtained with the cider sample in the previous test.

- **Sample K**

The standard deviation for this sample is good, comparable to the one obtained for the sake sample in the previous test and very similar to the one given in the OIV method.

- **Sample N**

As the alcohol content was very high for this sample, most of the laboratories calculated it directly from the density. Only a few laboratories distilled the sample. The standard deviation is excellent.

B. Density

- **Sample F**

For this sample, there are four outliers. Two of them probably reported the specific gravity instead of the density.

- **Sample S**

For sample S, there is quite a high number of outliers. These results are due to systematic errors and it also seems that two laboratories reported the specific gravity and two other the density of the distillate. A participant confirmed that his laboratory reported the density of the distillate for samples S, B and K.

- **Sample B**

The conclusions are the same for sample B. The performance is not as good as the one obtained in the previous test for the cider sample (standard deviation of 0.00016 g/cm^3 instead of 0.00011), maybe due to the systematic errors.

- **Sample K**

The conclusions are once again the same, with in addition a typing error for one laboratory (4381). The standard deviation is similar to the one given in the OIV method. It is a little higher than the one obtained for the sake sample in the previous test, but this deviation was particularly low. Therefore, the results are overall good.

- **Sample N**

The results are overall good.

C. Pressure

This parameter was measured on sample B only.
One laboratory (3287) is an outlier and reported the pressure instead of the excess pressure (confirmed by a participant). The Chair declared that it was indeed not clearly explained in the results sheet.
The standard deviation is a little better than the one obtained in the previous test for the cider sample. The results are quite good this time.

D. Glycerol

This parameter was determined on samples B and K. There are a few outliers for both samples.
Most laboratories used HPLC (18), many used enzymatic methods (8) and one laboratory used GC.
The Chair declared that, from his experience, there was no difference between HPLC and enzymatic measurements. The result obtained by GC is a little higher, but this may be an accident and not a systematic effect.
One laboratory (2986) most probably reported the result in the wrong unit.
The results are overall similar to those of the first test.
For sample K, it can be concluded from the glycerol results that **most of the alcohol is added distilled alcohol** and only a small part is due to fermentation.

E. Butanediol

This parameter was determined on sample K. For this, 7 laboratories used HPLC and 3 used GC. No significant difference was observed between the two methods in this case.
The results are considerably better than those of the first test; there has been a real improvement of the laboratories between the two tests. The standard deviation is now acceptable (it was not the case in the previous test).

F. Isotope ratio by IRMS

- **δ13C**

For all samples, the results are overall good and the performance is similar to the one given in the OIV method. The result for sample K is quite different from the others, but this does not say much, as it is simply a different product.
A participant said she also measured the δ13C of the residual sugars, which was very different from the one obtained for ethanol, suggesting a different origin.

- **δ18O**

There is no outlier for this parameter. However, **the standard deviation is quite large for sample K**.
One representative said there was a really important dispersion of the results, maybe due to the low number of participants. Another participant declared that, as there was no target value for the isotopic ratio, the value was directly obtained from the results of the participants. Therefore, if the number of participants is low, it is expected to have a large deviation. A third participant added that it could also be an effect of the sample preparation, as there are different preparation techniques for the δ18O.

G. Isotope ratio by NMR

The results obtained are quite good, both for D/H I and D/H II.
One expert declared that it was usual to have a large deviation on D/H II for fermented beverages.

H. C14 activity

The results are overall good. **The standard deviations are far better than in the first test**.
One expert noted that C14 activity should be more or less constant for recent bio-sourced alcohols: it is at a certain average value, independent from the kind of fruit or other material the alcohol is made from. The results are in accordance with this observation.

I. Volatile compounds

For volatile compounds in sample S, the results are overall acceptable.
One laboratory (3944) mixed up the result of ethyl acetate and acetal (confirmed by a participant).
The Chair discussed the case of reporting errors. He declared that, for him, **it was part of the competence of a laboratory to be able to report its results in the correct way and with the correct units.** Therefore, he was not in favour of correcting these mistakes afterwards. He added that such mistakes should make the laboratories think about their procedure and take corrective actions.
The action leader declared that she was in complete agreement with this.
The standard deviations are comparable with those of the first test (except for methanol because the methanol content was much higher here).
There were 4 outliers for the sum of Me-butanols. This comes from an addition of effects. One laboratory (3870) reported the sum of 2-Me-propanol and 2-Me-butanol. The results are nevertheless overall ok and comparable with those of the previous test.

J. Total acid

For sample S, one laboratory (3944) reported a very low amount, due to a mistake in the units. A participant explained that the result was given in % instead of meq/L.
The standard deviation is three times better than in the first test, so **the laboratories have improved a lot**. The results are in accordance with the standard deviation given in the OIV method.

K. Volatile acid

There were some outliers for this parameter. Two laboratories have outlying results for both samples, therefore it may be due to systematic errors.
The results are overall acceptable.

L. Citric acid

For this determination, the participants used 4 different methods: most of them (13 laboratories) used HPLC, but Capillary Electrophoresis (3), Ion Chromatography (2) and enzymatic methods (2) were also used. No significant difference was observed between the results obtained by these methods.
One laboratory (2619) may have made a unit error for sample K.
It should be noted that the standard deviation obtained for sample B is particularly low. It is a very good result and an **important improvement since the previous test**.

M. Other acids (malic, lactic, tartaric, succinic)

These parameters were determined for sample K.
The value obtained for tartaric acid is within the normal range for wine.
There are some outliers, due to systematic effects (laboratories 3919, 3944 and 4500 had several outlying results). One laboratory (2619) most probably reported the results in the wrong unit.

In the previous test, the standard deviation was rather poor, but it is much better this time. The performance here is acceptable.
For succinic acid, no statistical evaluation was performed because of the high dispersion of the results. The Chair declared that the values should not be above 0.5 g/L because succinic acid is a by-product of the fermentation and the sample is only partially fermented. He therefore advised the laboratories which reported a result above 1 g/L to check it. Some laboratories reported separation problems, which may explain these high values.

N. Sugars

- **Sample B**

According to the results of the test, sample B contained very small amounts of maltose, glucose and sucrose. The values are close to the limit of detection or quantification. Therefore, there are only a few results, especially for sucrose (only 8 results reported).
For fructose, the standard deviation is acceptable for such a sugar content. It is very likely some laboratories (2619, 2986, 4869) reported their results in the wrong unit.

- **Sample K**

For sample K, the amounts of glucose and fructose are nearly equal, as expected for a wine. As it is a liquor wine, the high sugar content (nearly 80g/L) is normal.
The results are overall good. The standard deviation is quite similar to the one obtained for fructose in the cider sample of the previous test. There are some outliers, mostly due to reporting errors (laboratories 2619 and 2986).
For sucrose, no statistical evaluation was performed, as most laboratories reported that the value was below their limit of detection.

O. Dry extract

Dry extract is a routine parameter in the analysis of wine.
Quite a high value was obtained for this parameter in sample K. The standard deviation is good. It is likely that one laboratory (3268) reported the sugar free extract instead of the total dry extract.

P. Real and original extract

For the original extract, some outliers (laboratories 2986, 5053) come from the determination of the alcohol content: they were outliers for this parameter, which is part of the calculation of the original extract. One laboratory (1545) must have made a calculation mistake, because its values for real extract and alcohol content are correct.
The standard deviation is acceptable and similar to the literature data.

Q. Sample N

Several parameters were determined on sample N in order to compare the methods described in Regulation (EC) No 625/03 and routine methods.

- **Total acid**

In the Regulation, the limit for total acid in neutral alcohol is defined at 1.5g/L. Therefore, the sample was spiked with an equivalent amount of acetic acid.
The result obtained by the method of the Regulation is around the spiking value, which proves that the spiking was well performed.
It is likely that laboratories 1545 and 2325 made a mistake in the units.

For the routine method, only 4 laboratories participated, therefore no statistical evaluation could be performed. The mean of the 4 results gives a value which is comparable to the one obtained by the method of the Regulation. This is not surprising, given that both methods are similar (titration with NaOH).

- **Esters**

The sample was spiked at the level set in the Regulation (1.3 g/hl) with ethyl acetate.
Here, most of the laboratories participated with their routine methods (GC method, similar to the method used for the determination of the volatile compounds). These methods gave a value which is similar to the spiked value and with a precision in compliance with requirement of the Regulation. For the method of the Regulation, no statistical evaluation could be performed. However, 3 out of the 4 results were near the spiking value, so the method of the Regulation seems to work rather well. Both methods seem suitable.

- **Aldehydes**

The situation is quite similar for aldehydes. The value obtained by the routine methods is very close to the spiking value, which means that both the results and the spiking are good. The precision is suitable.

- **Higher alcohols**

The comments are the same for higher alcohols. The routine methods gave a good result (exactly at the expected spiking level) with a good standard deviation. No statistical evaluation was performed for the method of the Regulation, but the mean of the results is not far from the value obtained by the routine methods, with 2 results very close to the spiking value.
One expert noted that the spiking was only performed with one higher alcohol (2-methyl-1-propanol) and wondered if the analysis would have been so simple in a real case. The Chair agreed that this artificial sample was probably not as complex as a real sample. For a "real" neutral alcohol, there may be a complex mixture of higher alcohols at very low levels, which makes them difficult to detect accurately with GC. The previous participant added that it was also a calculation issue. Another expert explained that indeed, there was a calculation to be made in order to express the result in 2-methyl-1-propanol (ratio with the molecular weight).

- **Methanol**

The routine methods gave a result very close to the spiking level. The standard deviation is acceptable.
There is no significant difference between the results of the two methods, because they are quite similar (GC methods).

R. Classification

- **Sample F**

For this sample, **many different CN codes were proposed**. This is mostly due to a lack of information: **participants did not have all the information they needed for a proper classification of the sample**. **75% of them classified the sample in Heading 3302 and 12% in Heading 2208**. The main problem was to **make the distinction between flavour and spirit**, which was not easy.
For a participant, this sample should be classified as a flavour according to its label. A second expert objected and asked whether the label was so important that the classification should be based on it. He added that this kind of product could be put in a flavour bottle as well as in a spirits bottle. The first expert declared it depended on the amount of aroma. It was also said that some compounds could be highly aromatic even in very low quantities. A third expert declared that the only question

was whether it was drinkable or not. This was agreed by the previous speaker but said that is was very subjective. A fourth expert explained that the procedure in his laboratory was to dilute the sample five times and then perform an organoleptic test to determine if it was an aroma: if there is still a persistence of aroma in the diluted sample, it is an indication that it could be used diluted in food products in order to flavour them. A fifth participant said that some spirits, such as cognac, could also be used to flavour food.

The Chair concluded by saying that it was a **difficult case** as it was tough to determine the objective characteristics of such a product and no quantitative measurements could be made. He declared that he would personally not classify such a product in Chapter 22.

- **Sample S**

For this sample, the Heading was clear: sample S is a **spirit of Heading 2208**. **The problem was to determine the correct subheading, for which it was necessary to know the raw material from which it was produced.** From the data, it was quite difficult to determine this, so the participants had to have some experience in sensory analysis.

This sample was a raspberry spirit, therefore the **correct CN code was 2208 90 48**. **This code was found by 50% of the participants.**

- **Sample B**

Most of the participants classified the product in **Heading 2206**. Some suggested Heading 2203. The Chair declared that for him the sample clearly has the characteristics of a beer mix of heading 2206, given its low alcohol content. The sample was a mixture of beer and lemonade.

The Chair was surprised to see some participants classifying it under 2206 00 59 because all them measured an excess pressure higher than 1.5 bar. Therefore, according to the Additional Note 10, it was a sparkling sample. A participant declared that only 17 laboratories determined the excess pressure, so it could explain this classification.

- **Sample K**

This sample was not so easy to classify: the problem was to **decide between Headings 2204 and 2206**. **The main criterion for this distinction is the kind of added alcohol**. The Chair explained that there has been a **judgment of the European Court of Justice (C-339/09)**, where it was decided that wine to which alcohol other than wine alcohol was added could not be classified under Heading 2204. They therefore classified a Kagor sample under Heading 2206. In this case, most of the participants did not know whether other alcohol was added or not.

One expert said it was not possible to determine this with the isotopic measurement: the parameters are in conformity with ethanol from grape. Therefore, he would classify it under Heading 2204.

A second expert noted that it was determined that the sugar and alcohol were not of the same origin. Therefore one of the two was added. She wondered whether it was possible to add sugar under Heading 2204.

A third expert said the isotopic measurements performed at her laboratory showed that there was an addition of isoglucose from maize. The Chair said that under the European Regulation it was possible to add saccharose in wine but only in small amount. Therefore it was not clear whether this sample could be excluded from Heading 2204 due to the added sugar. The previous participant added that the isotope measurement for oxygen did not show any addition of water. A fourth expert said that in this case isoglucose could not have been added, because it will then be shown by the oxygen isotopic ratio. He declared that it was a borderline case, and that if such a sample arrived to his laboratory he would not be able to reject it as falsified.

Regarding the classification within Heading 2204, more information was needed by the participants (origin, protected designation, varietal wine, etc.). This explains the number of different proposals that were made.

IV. Discussion on the report, conclusions and recommendations

A. Precision data

The precision data were determined on alcohol content, density, pressure, glycerol, methanol, 3-methylbutan-1-ol, total acid, glucose and fructose.

The Chair declared that the precision data study was not so important in a proficiency test because the participants use different methods. He asked whether other parameters should be added. The participants decided that **the parameters of Regulation (EC) 110/2008 could be added** to show that the results were in accordance with the Regulation.

A participant added that in the tables **the name of the second rows should be changed** from "Number of laboratories without outliers" to "Number of laboratories used for the statistics".

B. Homogeneity of the samples

Given the comments made regarding a possible inhomogeneity for sample B, **A participant offered to check this by measuring the alcohol content, density, original and real extracts on the remaining samples**. A second participant said there should be enough samples and that she will check this and organise the shipment to the volunteering laboratory. *Post-meeting note: the results of this test are presented in **Annex II**, no evidence of inhomogeneity was found.*

One expert declared that the alcohol content and density were closely related to the original extract. Moreover, the alcohol content is used for the tax determination, therefore it should be quite stable. He thus suggested choosing another parameter for the homogeneity test, such as organic acids. The Chair said the possible inhomogeneity was observed on the alcohol content determination, it would thus be interesting to check it. He added that the precision for acids and sugars was much lower, so a decision on the homogeneity based on these results would be difficult.

The previous expert explained that sample B is a mixture of beer and lemonade, so different batches may have been used: in case the beer is stronger, the content of lemonade would be adjusted to reach the same alcohol content for all products. Therefore the alcohol content would be the same but organic acids values would be different.

The Chair said that the determinations which will be performed by the volunteering participant should be enough.

C. Conclusions of this proficiency test, in particular regarding the amendment of Regulation (EC) No 625/2003

The Chair declared that the main aim of a proficiency test was to show the performance of the laboratories. For this test, **the standard deviation was good or at least acceptable for all parameters**, including parameters for which the performance was quite poor in the first test. Therefore, **the laboratories have significantly improved since the first test**.

Regarding the neutral alcohol sample, the Chair concluded that the routine methods seem suitable, but that a more detailed study would be necessary before suggesting any amendment to Regulation

(EC) No 625/2003. Indeed, the sample was an artificial one with a relatively simple composition. In addition, he said that he did not know what could be done since this Regulation depends on DG Agri.
A participant declared that the Italian Customs Laboratories would be really interested in continuing this study, because they receive many of these samples.
A second participant said another proficiency test could be organised but only if there were enough Customs Laboratories interested. A third expert noted that only four laboratories analysed the sample by the methods of the Regulation. Therefore, it is quite clear that very few of them receive such samples and that it would be difficult to organise a study.
Another participant asked whether it could be possible to enlarge the participation outside Customs.
It was said by the first speaker that all countries which produce wine and distilled alcohol from wine should have to perform these determinations. It was also declared that the French Customs Laboratories used to receive many samples, but don't analyse so many anymore.
It was suggested having a **study performed internally in Italy**, given that there are seven Customs Laboratories. This study could be opened to a few other laboratories. The Chair said that **this study could be suggested by the Italian delegate at the next Customs Laboratories Steering Group meeting**.
The representative of the EC recommended putting at least **in the conclusion of the report the fact that the Customs Laboratories find the methods of Regulation (EC) No 625/2003 old-fashioned**.

D. Recommendations and wishes for a next proficiency test on Spirits

One expert noted that for all proficiency tests within the CLEN, the little part on the classification always leads to long discussions, even if the analytical results are quite similar. She declared that **classification is the final aim of the Customs Laboratories work**. However, it was already considered as a good result if 50% of the laboratories give the same code. She said the next proficiency test should be more ambitious: **all the needed information should be given to the participants and the original packaging with the label should be kept in order to reflect real practice.** She declared it would then be really useful to discuss with the other laboratories on how they classified the samples.
The Chair agreed with this. He said that, when the test was designed, he was not in favour of adding the classification part, which explains why little information was given. He declared that classification indeed only makes sense if the participants are provided with all the necessary information. A second expert said that in real life, the Customs Laboratories do not necessarily have all the information on the product, therefore it was also good practice. The Chair answered that it would already be interesting to see if with all the information the Customs Laboratories would provide the same answer.
The Chair however pointed out the fact that not all Customs Laboratories were involved in the classification. It was said the classification could be made by the person in charge, as in routine, and that a Tariff section could be included.

Wishes in terms of samples and topics for a possible future proficiency test on spirits were then discussed.

- A participant suggested **a sample containing denaturant**, but another expert answered that this topic was treated within Fiscalis, with a proficiency test already going on, but that it is rather a validation of methods on samples with low concentrations in denaturants.
  Another participant mentioned the case of 50/50 mixtures of alcohol and fuel, which were classified as denatured alcohols. The Chair said it was mentioned during the preparatory

meeting (in particular E95), but that the group got the information that this kind of samples would be dealt with within the proficiency test on mineral oils.
In addition, the Chair was not sure whether working on such samples would make sense, as artificial samples would need to be produced.

- One expert mentioned a kind of sample regularly encountered and for which there is no commercially available test: **solid-liquid samples (like cherries in alcohol)**. The Chair supported this suggestion.
- Another expert suggested testing real **aroma product** like perfumes or eau-de-cologne, as it is important for excise duty to determine their alcohol content.
- A further expert suggested extending the **study on beer** to other parameters. He added that it could be similar to what was done in a test previously performed and coordinated by the Belgium Customs Laboratory, which included 4 common types of beer and in addition a local beer provided by each participant. For the Chair, this would be more than a simple proficiency test, but a separate study as for the neutral alcohol.
  Regarding the beer sample, one of the participant declared that it was good to have the **pressure measurement** because this determination was included in very few commercially available proficiency tests and is essential both for classification and excise. Moreover, as most of the laboratories use the same method, the determination of the resulting precision data can really contribute to the knowledge of the laboratory, as no information is available elsewhere.

The representative of the Commission asked whether it could be possible to have a table of the parameters determined in the test with their purpose (classification/excise). The Chair explained that clear distinction could not be made: many parameters are used for both purposes (e.g. alcohol content, excess pressure, etc.). Parameters related to the exact composition, like the content in sugars, are more for classification purposes.
The representative of the Commission asked if the participant knew any network of Excise laboratories. An expert said that the participants here were almost the same as the one in the Fiscalis group. However, no one among the participants ever heard of a test organised by Fiscalis (except the current test on denaturants, which is organised by JRC).

All the topics of the agenda have been discussed and therefore The Chair closed the meeting by thanking the participants for their contributions and the interesting discussions. He added that he hoped to see this proficiency test renewed.

Annex I - List of participants

Commission:

Ms S. Androni	EC-TAXUD
Mr H. Schepers	EC-TAXUD

Member States

Ms N. Varra	France - *Action leader*
Mr M. Buhmann	DE - *coordinator*
Ms I. Vinckier	BE
Ms R. Kokkinofta	CY
Mr J. Mazáč	CZ
Ms L. Parts	EE
Ms K. Mõts	EE
Ms D. Liouza	EL
Mr F. Lázaro Boza	ES
Mr T. Aholainen	FI
Mr R. Robin	FR
Ms M. Czermann-Toth	HU
Mr D. Ćavar	HR
Mr A. Terracciano	IT
Ms S. Urbonienė	LT
Ms I. Lapele	LV
Mr R. De Groot	NL
Mr C. Niculescu	RO
Ms B. Berlec	SI
Ms T. Vranová	SK

Contractors

Ms E. Messineo	BIPEA CLENTAS
Ms A. Rebours	Eurofins CLENTAS

Excused participants:

Mr E. Bjarnov	DK
Mr P. Sołtys	PL

Annex II: presentation made by the Chair, coordinator, during the discussion meeting

2. Proficiency test on spirits, alcoholic beverages and spirit containing mixtures (2013 -2014)

Introduction

Preparatory meeting

- Preparatory meeting in Berlin in November 2013
- 12 participants

Sample 1 „Alcohol based flavour for food“

Main ideas:

- alcohol based preparation
- high alcohol content
- probably high content of flavour compounds
- expectation: determination of alcohol content with GC

Sample 2 „Fruit spirit“

Main ideas:

- relatively high alcohol content (≈ 50 %vol)
- high amount of volatile compounds
- different matrix than in 1st PT (influence on results)

Sample 3 „Beer mix“

Main ideas:

- low alcohol content (accuracy)
- excess pressure (no precision data in official methods)
- original extract (for excise duty purposes)

Sample 4 „Kagor liqueur wine“

Main ideas:

- classification in dispute (kind of added alcohol)
- total acid, fruit acids (rather poor precision in first PT)

Sample 5 „Neutral alcohol“

Main ideas:

- characteristics of neutral alcohol defined in Reg (EC) no. 110/08
- reference methods described in Reg (EC) no. 625/03: classical, time-consuming, wet chemistry methods
- interest to replace these methods by modern automated methods
- the sample was spiked according the requirements in Reg (EC) no. 110/08

Data evaluation

- mean and standard deviation by applying robust statistics (algorithm A defined in ISO 13528)
- robust standard deviation used for proficiency assessment
- clearly erroneous results were not included in the calculation of mean and standard deviation
- results „0.00“ were treated as qualitative results (like „not detected“ or „under limit of quantification“)

2. Proficiency test on spirits, alcoholic beverages and spirit containing mixtures (2013 -2014)

Discussion and interpretation of the analytical results

Alcohol – Sample F (Flavour)

	Alcohol (%vol)
Mean x	70,0
Uncertainty u_x	0,1
StD s_x	0,3
No. of labs	41
No. labs z>2	4
No. labs z>3	3

Comments:

- no significant difference between GC and distillation
- lab 3919: dilution of the distillate was not taken into account?
- s_x (PT 2009; screen wash): 0,8 %vol

Alcohol – Sample S (Fruit spirit)

	Alcohol (%vol)
Mean x	47,46
Uncertainty u_x	0,06
StD s_x	0,29
No. of labs	41
No. labs z>2	5
No. labs z>3	1

Comments:

- labs 2587, 4288, 4889 determined ethanol content (GC) → low results (z < -2)
- s_x (PT 2009; rum): 0,17 %vol

Alcohol – Sample B (Beer mix)

	Alcohol (%vol)
Mean x	2,39
Uncertainty u_x	0,01
StD s_x	0,04
No. of labs	39
No. labs z>2	2
No. labs z>3	5

Comments:

- 1 lab reported a significant difference between two samples; other results: no evidence for inhomogenity
- labs 1326, 2986, 5053: results between 2,02-2,05 %vol (unit?)
- low s_x; s_x (PT 2009; cider): 0,05 %vol

Alcohol – Sample K (Kagor liqueur wine)

	Alcohol (%vol)
Mean x	15,83
Uncertainty u_x	0,02
StD s_x	0,09
No. of labs	41
No. labs z>2	0
No. labs z>3	3

Comments:

- s_x good; s_x (PT 2009; sake): 0,04 %vol; OIV-method: s_x: 0,068 %vol

Alcohol – Sample N (neutral alcohol)

	Alcohol (%vol)
Mean x	96,30
Uncertainty u_x	0,00
StD s_x	0,01
No. of labs	17
No. labs z>2	0
No. labs z>3	2

Comments:

- most labs: calculation of alcohol content from density (without distillation)
- very small s_x

Density – Sample F (Flavour)

	Density (g/cm³)
Mean x	0,88620
Uncertainty u_x	0,00001
StD s_x	0,00006
No. of labs	41
No. labs z>2	3
No. labs z>3	4

Comments:

- labs 2325, 4869: determination of specific gravity instead of density?
- s_x (PT 2009; screen wash): 0,00008 g/cm³

Density – Sample S (Fruit spirit)

	Density (g/cm³)
Mean x	0,93470
Uncertainty u_x	0,00002
StD s_x	0,00012
No. of labs	41
No. labs z>2	0
No. labs z>3	6

Comments:

- labs 2325, 4869: determination of specific gravity instead of density?
- labs 3870, 4308: density of distillate instead of sample density?
- s_x (PT 2009; rum): 0,00014 g/cm³

Density – Sample B (Beer mix)

	Density (g/cm³)
Mean x	1,00408
Uncertainty u_x	0,00003
StD s_x	0,00016
No. of labs	39
No. labs z>2	0
No. labs z>3	7

Comments:

- labs 1374, 2325, 4869: determination of specific gravity instead of density?
- labs 3039, 4308, 4500: density of distillate instead of sample density?
- s_x (PT 2009; cider): 0,00011 g/cm³

Density – Sample K (Kagor liqueur wine)

	Density (g/cm³)
Mean x	1,04885
Uncertainty u_x	0,00002
StD s_x	0,00011
No. of labs	41
No. labs z>2	0
No. labs z>3	7

Comments:

- labs 2325, 4869: determination of specific gravity instead of density?
- labs 3870, 4308, 4500: density of distillate instead of sample density?
- lab 4381: typing error
- s_x (PT 2009; sake): 0,00004 g/cm³; OIV-method: s_x: 0,000132 g/cm³

Density – Sample N (neutral alcohol)

	Density (g/cm³)
Mean x	0,80622
Uncertainty u_x	0,00001
StD s_x	0,00005
No. of labs	17
No. labs z>2	0
No. labs z>3	2

Comments:

- labs 2325: determination of specific gravity instead of density?
- s_x small; very similar to s_x for sample F

Pressure – Sample B (Beer mix)

	Excess pressure (bar)
Mean x	2,3
Uncertainty u_x	0,1
StD s_x	0,3
No. of labs	18
No. labs z>2	0
No. labs z>3	1

Comments:

- labs 3287: pressure instead of excess pressure?
- s_x (PT 2009; cider): 0,4 bar → s_x OK

Glycerol

	Sample B (g/l)	Sample K (g/l)
Mean x	0,75	2,20
Uncertainty u_x	0,02	0,06
StD s_x	0,08	0,22
No. of labs	26	25
No. labs z>2	3	2
No. labs z>3	3	3

Comments:

- lab 2986: unit g/100 ml or %mas?
- methods: 18 labs HPLC; 8 labs enzymatic; 1 lab GC; no difference between HPLC and enzymatic results, GC: higher amount
- s_x (PT 2009): 8,3/11,5 %rel → s_x OK
- sample K: main part of the alcohol content is added distilled alcohol

Butanediol – Sample K (Kagor liqueur wine)

	Butanediol (mg/l)
Mean x	182
Uncertainty u_x	11
StD s_x	28
No. of labs	10
No. labs z>2	1
No. labs z>3	1

Comments:

- methods: 7 labs HPLC; 3 labs GC; no significant difference between the methods
- s_x (PT 2009; sake): 44 %rel → s_x considerably better (15 %rel)

Isotope ratio by IRMS - δ13C

	Sample S (‰ (/PDB))	Sample K (‰ (/PDB))	Sample N (‰ (/PDB))
Mean x	-28,39	-26,16	-28,08
Uncertainty u_x	0,09	0,08	0,23
StD s_x	0,21	0,17	0,37
No. of labs	8	8	5
No. labs z>2	0	0	0
No. labs z>3	1	2	0

Comments:

- s_x OK; OIV-method: sx: 0,23-0,31‰
- interpretation of the results?

Isotope ratio by IRMS – δ180

	Sample S (‰ (/V-SMOW))	Sample K (‰ (/V-SMOW))
Mean x	-9,60	3,37
Uncertainty u_x	0,25	0,88
StD s_x	0,45	1,58
No. of labs	5	5
No. labs z>2	0	0
No. labs z>3	0	0

Comments:

- s_x OK? (seems to comparatively large for sample K)
- interpretation of the results?

Isotope ratio by NMR – ethanol (D/H)I

	Sample S ppm	Sample K ppm	Sample N ppm
Mean x	97,43	99,02	92,03
Uncertainty u_x	0,20	0,05	0,16
StD s_x	0,43	0,10	0,26
No. of labs	7	7	4
No. labs z>2	0	0	0
No. labs z>3	0	0	0

Comments:

- s_x OK?
- interpretation of the results?

Isotope ratio by NMR – ethanol (D/H)II

	Sample S ppm	Sample K ppm	Sample N ppm
Mean x	123,52	126,97	127,62
Uncertainty u_x	0,21	0,29	0,09
StD s_x	0,45	0,60	0,14
No. of labs	7	7	4
No. labs z>2	0	0	0
No. labs z>3	0	0	0

Comments:

- s_x OK?
- interpretation of the results?

Carbon 14 activity

	Sample F (cBq/g of C)	Sample K cBq/g of C)	Sample N cBq/g of C)
Mean x	22,8	22,8	22,3
Uncertainty u_x	0,3	0,4	0,4
StD s_x	0,5	0,9	0,8
No. of labs	7	7	7
No. labs z>2	0	0	0
No. labs z>3	1	1	1

Comments:

- s_x (PT 2009): 1,16 and 1,49 → s_x considerably better

Volatile Compounds 1 – Sample S (Fruit spirit)

	Acetalde-hyde (g/hl PA)	Ethyl acetate (g/hl PA)	Methanol (g/hl PA)
Mean x	12,4	49,2	838,5
Uncertainty u_x	0,6	0,6	9,1
StD s_x	2,3	2,3	39,4
No. of labs	25	28	29
No. labs z>2	2	2	0
No. labs z>3	0	1	1

Comments:

- lab 3944: result ethyl acetate and acetal probably mixed up
-
- s_x (PT 2009):

  AA: 2,2 (mean: 8,8);
  EA: 3,5 (mean: 28,0);
  ME: 1,5 (mean: 8,4)

Volatile Compounds 2 – Sample S (Fruit spirit)

	2-Me-propanol (g/hl PA)	3-Me-butanol (g/hl PA)	Sum Me-butanols (g/hl PA)
Mean x	63,0	243,9	324,4
Uncertainty u_x	0,5	3,0	2,8
StD s_x	2,3	11,9	11,5
No. of labs	29	25	27
No. labs z>2	1	1	0
No. labs z>3	1	1	4

Comments:

- lab 3870: sum of 2-Me-propanol und 2-Me-butanol
- s_x (PT 2009):
  2-Me-P: 7,8 (95,8);
  3-Me-B: 14,7 (184);

Total acid (titration to pH 7.0)

	Sample S (meq/l)	Sample K (meq/l)
Mean x	2,53	51,06
Uncertainty u_x	0,07	0,33
StD s_x	0,24	1,29
No. of labs	21	24
No. labs z>2	2	2
No. labs z>3	2	3

Comments:

- lab 3944: unit?
- s_x (PT 2009): 0,31 and 4,71 (mean 52,0) → s_x better
- OIV-method: s_x: 1,29/1,82 meq/l

Volatile Acid

	Sample S (g/l)	Sample K (g/l)
Mean x	0,15	0,22
Uncertainty u_x	0,03	0,02
StD s_x	0,09	0,06
No. of labs	15	16
No. labs z>2	0	1
No. labs z>3	3	2

Comments:

- two labs outlying results for both samples
- s_x (PT 2009): 0,11 (mean: 0,35)

Citric acid

	Sample B (g/l)	Sample K (g/l)
Mean x	1,00	0,48
Uncertainty u_x	0,02	0,05
StD s_x	0,08	0,17
No. of labs	18	19
No. labs z>2	0	4
No. labs z>3	2	0

Comments:

- 4 different methods were used (13 HPLC, 3 CE, 2 IC, 2 Enzym) → no significant difference between the results
- sample K: lab 2619: unit (g/100 ml or %mas)?
- sample B: small s_x
- s_x (PT 2009): 0,08 (mean: 0,12)

Other Acids – Sample K (Kagor liqueur wine)

	Malic acid (g/l)	Lactic acid (g/l)	Tartaric acid (g/l)
Mean x	0,72	0,25	2,39
Uncertainty u_x	0,03	0,03	0,08
StD s_x	0,10	0,08	0,28
No. of labs	17	18	18
No. labs z>2	1	1	0
No. labs z>3	3	3	3

Comments:

- lab 2619: unit (g/100 ml or %mas)?
- labs 3919, 3944, 4500 several outlying results
- rather poor s_x in PT 2009, s_x now better

malic: 0,26 (mean 0,32); lactic: 0,55 (mean: 0,72)

Succinic acid: high dispersion of results; expected result: < 0,5 g/l → results > 1 g/l should be checked (separation problem?)

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Sugars – Sample B (Beer mix)

	Maltose (g/l)	Glucose (g/l)	Fructose (g/l)
Mean x	0,32	0,26	5,28
Uncertainty u_x	0,05	0,02	0,10
StD s_x	0,13	0,07	0,42
No. of labs	10	15	30
No. labs z>2	1	1	1
No. labs z>3	0	1	4

Comments:

- maltose, glucose: amount near LOD resp. LOQ
- fructose: labs 2619, 2986, 4869: unit (g/100ml or %mas)?
- s_x (fructose): OK

Sucrose: only 8 results; most labs reported < LOD

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Sugars – Sample K (Kagor liqueur wine)

	Glucose (g/l)	Fructose (g/l)
Mean x	78,92	78,67
Uncertainty u_x	0,55	0,46
StD s_x	2,47	2,10
No. of labs	32	32
No. labs z>2	1	3
No. labs z>3	4	4

Comments:

- labs 2619, 2986: unit (g/100ml or %mas)?
- sx OK; s_x (PT 2009; fructose): 2,0 (mean 48,2)

Sucrose: no data evaluation; most labs reported < LOD

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Dry extract – Sample K (Kagor liqueur wine)

	Dry extract (g/l)
Mean x	184,1
Uncertainty u_x	0,2
StD s_x	1,0
No. of labs	29
No. labs z>2	1
No. labs z>3	4

Comments:

- lab 3268: sugar free extract?
- s_x (PT 2009; cider): 0,3 (mean: 86,9)

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Real and Original extract – Sample B (Beer mix)

	Real extract (g/100g)	Original extract (g/100g)
Mean x	2,38	6,16
Uncertainty u_x	0,02	0,02
StD s_x	0,07	0,09
No. of labs	27	26
No. labs z>2	0	0
No. labs z>3	4	5

Comments:

- original extract lab 1545: calculation error? (real extract and alcohol (%vol) correct
- original extract lab 2986, 5053: outlying results due to low alcohol results
- s_x OK (similar to literature data)

Sample N (neutral alcohol) – Total acid

	Method Reg 625/03 (g/hl PA)	Routine method (g/hl PA)
Mean x	1,65	(1,8)
Uncertainty u_x	0,06	-
StD s_x	0,12	-
No. of labs	8	4
No. labs z>2	0	-
No. labs z>3	2	-

Comments:

- spiked value: appr. 1,5 g/hl PA acetic acid
- no data evaluation for routine method (only 4 results)
- method Reg 625/03 and routine method probably similar (titration with NaOH)
- labs 1545, 2325: unit?

Sample N (neutral alcohol) – Esters

	Method Reg 625/03 (g/hl PA)	Routine method (g/hl PA)
Mean x	(1,3)	1,42
Uncertainty u_x	-	0,05
StD s_x	-	0,14
No. of labs	4	12
No. labs z>2	-	1
No. labs z>3	-	0

Comments:

- spiked value: appr. 1,3 g/hl PA ethyl acetate
- no data evaluation for method Reg 625/03 (only 4 results); 3 of 4 results near spiked value
- routine method: mean ≈ spiked value; precision in compliance with requirements in Reg 625/03

Sample N (neutral alcohol) – Aldehydes

	Method Reg 625/03 (g/hl PA)	Routine method (g/hl PA)
Mean x	(0,4)	0,52
Uncertainty u_x	-	0,07
StD s_x	-	0,17
No. of labs	4	12
No. labs z>2	-	1
No. labs z>3	-	0

Comments:

- spiked value: appr. 0,5 g/hl PA acetaldehyde
- no data evaluation for method Reg 625/03 (only 4 results); 3 of 4 results near spiked value
- routine method: mean = spiked value; precision suitable regarding the limit?

Sample N (neutral alcohol) – Higher alcohols

	Method Reg 625/03 (g/hl PA)	Routine method (g/hl PA)
Mean x	(0,4)	0,50
Uncertainty u_x	-	0,02
StD s_x	-	0,05
No. of labs	4	12
No. labs z>2	-	0
No. labs z>3	-	1

Comments:

- spiked value: appr. 0,5 g/hl PA 2-methylpropanol
- no data evaluation for method Reg 625/03 (only 4 results); 2 of 4 results near spiked value
- routine method: mean = spiked value; precision good

Sample N (neutral alcohol) – Methanol

	Method Reg 625/03 (g/hl PA)	Routine method (g/hl PA)
Mean x	33,7	30,9
Uncertainty u_x	3,1	0,8
StD s_x	5,5	2,2
No. of labs	5	12
No. labs z>2	0	0
No. labs z>3	0	0

Comments:

- spiked value: appr. 30 g/hl PA
- both methods: GC (no further requirements in Reg 625/03)

Classification – Sample F (Flavour)

CN code	Absolute frequency	Relative frequency (%)
3302 10 90	17	53%
3302 10	4	13%
3302 90 10	2	6%
2208 90 69	2	6%
2103 90 90	1	3%
2106 90 20	1	3%
2208 60 91	1	3%
2208 90 90	1	3%
3302 10 10	1	3%
Others	2	6%
Total	32	100%

Comments:

- 75% heading 3302
- 12% heading 2208
- CN classification not possible because lack of information

Classification – Sample S (Fruit spirit)

CN code	Absolute frequency	Relative frequency (%)
2208 90 48	16	50%
2208 90 33	3	9%
2208 90 45	3	9%
2208 90 00	2	6%
2208 00 00	2	6%
2208 20 29 00	2	6%
2208 90 22	1	3%
2208 60 91	1	3%
Others	2	6%
Total	32	100%

Comments:

- Problem: kind of raw material
- 50% correct CN-Code

Classification – Sample B (Beer mix)

CN code	Absolute frequency	Relative frequency (%)
2206 00 39	18	55%
2206 00 59	5	15%
2203 00 01	3	9%
2206 00	2	6%
2206 00 90	1	3%
Others	4	12%
Total	33	100%

Comments:

- characteristics of beer mix beverage → heading 2206
- excess pressure ≥ 1,5 bar → sparkling → subheading 2206 0059 not applicable

Classification – Sample K (Kagor liqueur wine)

CN code	Absolute frequency	Relative frequency (%)
2204 21 98	10	36%
2206 00 59	5	18%
2204 21 90	2	7%
2204 21 91	2	7%
2204 00 00	1	4%
2204 21 00	1	4%
2204 21 50	1	4%
2204 21 94	1	4%
2204 21 96	1	4%
2208 90 56	1	4%
2204 29 9831	1	4%
Others	2	7%
Total	28	100%

Comments:

- problem: heading 2204 or 2206
- criterion: kind of added alcohol (wine alcohol or other; see ECJ judgement C-339/09)
- lack of information for correct classification in heading 2204: origin (EU or other), designation protected?, varietal wine?

2. Proficiency test on spirits, alcoholic beverages and spirit containing mixtures (2013 -2014)

Discussion for the preparation of the final report

2. Proficiency test on spirits, alcoholic beverages and spirit containing mixtures (2013 -2014)

Conclusion on the proficiency test and eventual recommendations

Conclusion

- standard deviation for all parameters good resp. acceptable, including parameters for which the standard deviation was rather poor in the 1st PT (total acid, acids, butanediol)
- analysis of neutral alcohol (Sample N): routine methods are basically suitable; more detailed study required before an amendment of Reg 625/03 can possibly be suggested?

Other questions

- What should be improved in a next profiency test (if there will be a next PT)?
- What kinds of samples would be interesting in a future PT? Which parameters should be included?

Annex III: complementary homogeneity test performed on sample B by the Belgian Customs Laboratory

Following the discussion meeting, a complementary homogeneity test was performed by the Belgian Customs Laboratory on sample B (Beer-mix) on the parameters density, original extract, real extract and alcohol content. The test was performed on 26 November 2014 on 20 samples.

The results obtained showed no evidence of inhomogeneity.

	Density (g/ml)	Original Extract (%m/m)	Real Extract (%m/m)	Alcohol content (%vol.)
1	1.004245	6.19	2.45	2.38
2	1.004234	6.18	2.45	2.37
3	1.004235	6.19	2.45	2.38
4	1.004217	6.18	2.44	2.37
5	1.004223	6.18	2.45	2.37
6	1.004201	6.18	2.44	2.38
7	1.004227	6.19	2.45	2.38
8	1.004185	6.17	2.44	2.37
9	1.004207	6.18	2.44	2.38
10	1.004215	6.19	2.45	2.38
11	1.004227	6.19	2.45	2.38
12	1.004213	6.19	2.45	2.38
13	1.004201	6.18	2.44	2.38
14	1.004193	6.18	2.44	2.38
15	1.004229	6.19	2.45	2.38
16	1.004212	6.19	2.45	2.38
17	1.004205	6.18	2.44	2.38
18	1.004196	6.17	2.44	2.38
19	1.004194	6.18	2.44	2.38
20	1.004197	6.18	2.44	2.38
mean value	**1.004213**	**6.183**	**2.445**	**2.378**
std.dev.	**0.000017**	**0.007**	**0.005**	**0.004**
ringtest result	***1.004080***	***6.16***	***2.38***	***2.39***
sx	***0.000160***	***0.09***	***0.07***	***0.04***