



DISCUSSION MEETING OF THE THIRD PROFICIENCY TEST ON SPIRITS, ALCOHOLIC BEVERAGES AND ALCOHOL-BASED PREPARATIONS

**26th January 2017, Prague, Czech
Republic**



AGENDA

- Welcome and adoption of the agenda
- Presentation of the 3rd edition of the proficiency test on spirits, alcoholic beverages and alcohol-based preparations: background, objectives, samples, results, comments, draft report and preliminary conclusions.
- Discussion and interpretation of the analytical results.
- Discussion on tariff classification.
- Conclusions of the meeting
- Any other questions



Previous tests

➤ Proficiency test 2010

- ✓ Good results for parameters: density, alcohol, dry extract, excess pressure, isotopic results and C14 by scintillation.
- ✓ Acceptable results for glycerol, volatile acid, sugars and volatile compounds.
- ✓ Poor results for total acid, acids and butanediol.

➤ Proficiency test 2014

- ✓ 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 - the laboratories have significantly improved since the first test.



Planning and organization of the test

- Preparatory meeting was held in Prague on 3rd March 2016
- 12 participants (Belgium, Czech Republic, Germany, Hungary, Italy, Lithuania, Romania, Spain, Slovakia and United Kingdom)
- Samples: fruits in alcohol, vermouth, suspicious distillate and sweet sparkling wine
- A call for participation to the proficiency test was launched in March 2016 in the e-CLEN community
- 46 Customs Laboratories registered for the test
- The participants received the samples at the end of August 2016 and performed the requested determinations (depending on their available equipment and possibilities)
- 45 Customs Laboratories took part in the test from the following countries: Austria, Belgium, Bulgaria (2), Croatia, Cyprus, Czech Republic (5), Denmark, Estonia, Finland, France (2), Germany (4), Greece (2), Hungary, Ireland, Italy (6), Latvia, Lithuania, Norway, Poland (4), Portugal, Romania, Slovakia, Slovenia, Spain (2), The Netherlands and United Kingdom

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Sample 1 „Fruits in alcohol“



- Main ideas:
- the solid-liquid matrix

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Sample 2 „Vermouth“



- Main ideas:
- containing alpha- and beta-thujone

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Sample 3 „Suspicious distillate“



- Main ideas:
- Fake product (denatured)
- Fruit distillate
- Higher methanol content
- Classification

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Sample 4 „Sweet sparkling wine“



- Main ideas:
- Fermented sample
- Overpressure measurements
- Higher content of sugars
- Classification

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Data evaluation

According to the ISO 13528 Standard "Statistical methods for use in proficiency testing by interlaboratory comparisons"

Individual laboratories results were expressed as z-scores:

$$Z = \frac{(x - X)}{s_X^*}$$

x - the result reported by the participating laboratory;

X - the assigned or "conventionally true" value for the analyte being determined;

s_X^* - the standard deviation for proficiency assessment, which is the robust standard deviation

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

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Not evaluated parameters

Vermouth – low content – glycerol, butanediol, malic acid, lactic acid, succinic acid, tartaric acid, citric acid, fructose, glucose



Alcohol – Sample 1 (Fruits in alcohol)

	Alcohol (l AA/100 kg)
Mean X	12,74
Uncertainty u_x	0,10
StD s_x	0,51
No. of labs	40
No. labs $z < 2$	39
No. labs $z > 2$	1
No. labs $z > 3$	8

Comments:

Units: additional note 4 to chapter 20:
'actual alcoholic strength by mass': the
number of **kilograms** of pure alcohol
contained in 100 kg of the product

Lab 1769 – result in kg PA/100 kg

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Alcohol – Sample 2 (Vermouth)

	Alcohol (% vol)
Mean X	39,87
Uncertainty u_x	0,03
StD s_x	0,13
No. of labs	42
No. labs $z < 2$	36
No. labs $z > 2$	1
No. labs $z > 3$	5

Comments:

s_x (PT 2009; rum): 0,17 % vol

s_x (PT 2014; fruit distillate): 0,29 % vol

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Alcohol – Sample 3 (Suspicious distillate)

	Alcohol (% vol)
Mean X	38,87
Uncertainty u_x	0,04
StD s_x	0,23
No. of labs	42
No. labs $z < 2$	39
No. labs $z > 2$	0
No. labs $z > 3$	3

Comments:

Lab 4020 and 4648 – ethanol content?

s_x (PT 2009; rum): 0,17 % vol

s_x (PT 2014; fruit distillate): 0,29 % vol

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Alcohol – Sample 4 (Sweet sparkling wine)

	Alcohol (% vol)
Mean X	10,99
Uncertainty u_x	0,02
StD s_x	0,09
No. of labs	41
No. labs $z < 2$	40
No. labs $z > 2$	0
No. labs $z > 3$	1

Comments:

Lab 4648 – problem with alcohol determination (4 results)

s_x (PT 2009; sake): 0,04 % vol

s_x (PT 2014; kagor): 0,09 % vol

OIV-method: s_R : 0,16 % vol

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Ethanol – Sample 3 (Suspicious distillate)

	Ethanol (% vol)
Mean X	36,87
Uncertainty u_x	0,16
StD s_x	0,73
No. of labs	34
No. labs $z < 2$	30
No. labs $z > 2$	3
No. labs $z > 3$	1

Comments:

Lab 4784, 5286 – coelution with IPA?

S_R (PT euro-denaturant formulation B): 0,55 %

S_R (PT euro-denaturant screen wash): 0,64 %

s_x (PT 2014; fruit distillate): 0,29 % vol

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IPA – Sample 3 (Suspicious distillate)

	2-propanol (l/hl of ethanol)
Mean X	3,87
Uncertainty u_x	0,03
StD s_x	0,14
No. of labs	32 (+1 excluded)
No. labs $z < 2$	28
No. labs $z > 2$	1
No. labs $z > 3$	4

Comments:

S_R (PT eurodenaturant formulation A): 0,09 l/hl

S_R (PT euro-denaturant screen wash): 0,08 l/hl

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Density – Sample 2 (Vermouth)

	Density (g.cm ⁻³)
Mean X	1,05446
Uncertainty u_x	0,00003
StD s_x	0,00014
No. of labs	43
No. labs $z < 2$	35
No. labs $z > 2$	3
No. labs $z > 3$	5

Comments:

s_x (PT 2009; rum): 0,00014 g.cm⁻³

s_x (PT 2014; fruit distillate): 0,00012 g.cm⁻³

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Density – Sample 3 (Suspicious distillate)

	Density (g.cm ⁻³)
Mean X	0,95302
Uncertainty u_x	0,00002
StD s_x	0,00011
No. of labs	43
No. labs $z < 2$	37
No. labs $z > 2$	3
No. labs $z > 3$	3

Comments:

s_x (PT 2009; rum): 0,00014 g.cm⁻³

s_x (PT 2014; fruit distillate): 0,00012 g.cm⁻³

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Density – Sample 4 (Sweet sparkling wine)

	Density (g.cm ⁻³)
Mean X	1,01547
Uncertainty u_x	0,00002
StD s_x	0,00010
No. of labs	40
No. labs $z < 2$	36
No. labs $z > 2$	1
No. labs $z > 3$	3

Comments:

s_x (PT 2009; sake): 0,00004 g.cm⁻³

s_x (PT 2014; kagor): 0,00011 g.cm⁻³

OIV-method: s_R : 0,000091 g.cm⁻³

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Overpressure – Sample 4 (Sweet sparkling wine)

	Overpressure (bar)
Mean X	4,6
Uncertainty u_x	0,2
StD s_x	0,8
No. of labs	21
No. labs $z < 2$	20
No. labs $z > 2$	0
No. labs $z > 3$	1

Comments:

s_x (PT 2009; cider): 0,4 bar

s_x (PT 2014; beer mix): 0,3 bar

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Glycerol – Sample 4 (Sweet sparkling wine)

	Glycerol (g/l)
Mean X	5,29
Uncertainty u_x	0,04
StD s_x	0,16 (3 % rel)
No. of labs	26 (+3 excluded)
No. labs $z < 2$	23
No. labs $z > 2$	1
No. labs $z > 3$	5

Comments:

s_x (PT 2009; cider): 8,3 % rel
(0,16/1,93 g/l)

s_x (PT 2009; sake): 11,5 % rel
(0,45/3,91 g/l)

s_x (PT 2014; beer mix): 10,7 % rel
(0,08/0,75 g/l)

s_x (PT 2014; kagor): 10 % rel
(0,22/2,20 g/l)

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Butanediol – Sample 4 (Sweet sparkling wine)

	Butanediol (mg/l)
Mean X	366
Uncertainty u_x	33
StD s_x	79 (22 % rel)
No. of labs	9
No. labs $z < 2$	9
No. labs $z > 2$	0
No. labs $z > 3$	0

Comments:

s_x (PT 2009; sake): 44 % rel

s_x (PT 2014; kagor): 15 % rel

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Isotope ratio by IRMS - $\delta^{13}\text{C}$ (ethanol)

	Fruits in alcohol (‰ (PDB))	Vermouth (‰ (PDB))	Sweet sparkling wine (‰ (PDB))
Mean \bar{x}	-28,30	-27,04	-26,59
Uncertainty u_x	0,08	0,09	0,06
StD s_x	0,17	0,19	0,14
No. of labs	7	8	8
No. labs $z < 2$	7	7	8
No. labs $z > 2$	0	0	0
No. labs $z > 3$	0	1	0

Comments:

s_x (PT 2014; kagor):
0,17 ‰

s_R OIV-method:
0,18-0,24 ‰

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Isotope ratio by IRMS - $\delta^{18}\text{O}$ (water)

	Sweet sparkling wine ‰ (V-SMOW)
Mean \bar{X}	3,90
Uncertainty u_x	0,45
StD s_x	0,88
No. of labs	6
No. labs $z < 2$	6
No. labs $z > 2$	0
No. labs $z > 3$	0

Comments:

s_x (PT 2014; beer mix): 0,45 ‰

s_x (PT 2014; kagor): 1,58 ‰

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Isotope ratio by NMR – (D/H)I ethanol

	Fruits in alcohol (ppm)	Vermouth (ppm)	Sweet sparkling wine (ppm)
Mean \bar{x}	92,26	101,58	102,42
Uncertainty u_x	0,22	0,16	0,23
StD s_x	0,43	0,35	0,53
No. of labs	6	8	8
No. labs $z < 2$	6	8	8
No. labs $z > 2$	0	0	0
No. labs $z > 3$	0	0	0

Comments:

s_R OIV-method: 0,35 ppm
 s_x (PT 2014;): 0,10-0,43 ppm
 s_x (FIT-PTS 2016 dry wine):
 0,58 ppm

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

	Fruits in alcohol (ppm)	Vermouth (ppm)	Sweet sparkling wine (ppm)
Mean \bar{x}	127,83	131,81	129,58
Uncertainty u_x	0,20	0,27	0,23
StD s_x	0,40	0,60	0,52
No. of labs	6	8	8
No. labs $z < 2$	6	8	8
No. labs $z > 2$	0	0	0
No. labs $z > 3$	0	0	0

Comments:

s_R OIV-method: 0,62 ppm
 s_x (PT 2014;): 0,14-0,60 ppm
 s_x (FIT-PTS 2016 dry wine):
 0,61 ppm

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C14 activity – Suspicious distillate

	C14 activity dpm/g
Mean X	9,46
Uncertainty u_x	2,06
StD s_x	4,93
No. of labs	9
No. labs $z < 2$	8
No. labs $z > 2$	1
No. labs $z > 3$	0

Comments:

s_x (PT 2009): 1,16 and 1,49 cBq/g of C

s_x (PT 2014): 0,5-0,9 cBq/g of C

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Volatile compounds – Sample 3 (Suspicious distillate)

	Volatile compounds (g/hl PA)
Mean X	416,9
Uncertainty u_x	7,0
StD s_x	26,8 (6,4 % rel)
No. of labs	23 (+2 excluded)
No. labs $z < 2$	22
No. labs $z > 2$	0
No. labs $z > 3$	3

Comments:

Lab 4648, 5562 – overtyping error?

s_x (PT 2014; fruit distillate): 7,4 % rel
(38,1/514,9 g/hl PA)

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Methanol – Sample 3 (Suspicious distillate)

	Methanol (g/hl ethanol)
Mean X	277
Uncertainty u_x	3
StD s_x	15 (5,4 % rel)
No. of labs	31 (+2 excluded)
No. labs $z < 2$	28
No. labs $z > 2$	1
No. labs $z > 3$	4

Comments:

s_x (PT 2009; Rum): 17,2 % rel

s_x (PT 2014; fruit spirit): 4,7 % rel

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Total acidity – Sample 3 (Sweet sparkling wine)

	Total acid (meq/l)
Mean X	75,68
Uncertainty u_x	1
StD s_x	3,57
No. of labs	20
No. labs $z < 2$	17
No. labs $z > 2$	1
No. labs $z > 3$	2

Comments:

s_x (PT 2009; Rum): 0,31 meq/l

s_x (PT 2009; cider): 4,71 meq/l

s_x (PT 2014; beer mix): 0,24 meq/l

s_x (PT 2014; kagor): 1,21 meq/l

OIV-method: s_R : 1,29/1,82 meq/l

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Volatile acidity

	Suspicious distillate (g/l)	Sweet sparkling wine (g/l)
Mean X	0,06	0,47
Uncertainty u_x	0,01	0,05
StD s_x	0,03	0,17
No. of labs	15	15 (+1 excluded)
No. labs $z < 2$	13	14
No. labs $z > 2$	0	0
No. labs $z > 3$	2	1

Comments:

s_x (PT 2009): 0,11 g/l

s_x (PT 2014, fruit spirit): 0,09 g/l

s_x (PT 2014, kagor): 0,06 g/l

OIV-method: s_R : 0,03 g/l

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Malic acid – Sample 3 (Sweet sparkling wine)

	Malic acid (g/l)
Mean X	0,705
Uncertainty u_x	0,076
StD s_x	0,263 (37 % rel)
No. of labs	19
No. labs $z < 2$	18
No. labs $z > 2$	0
No. labs $z > 3$	1

Comments:

s_x (PT 2009; sake): 81 % rel (0,26/0,32 g/l)

s_x (PT 2009; cider): 46 % rel (1,69/3,66 g/l)

s_x (PT 2014; kagor): 14 % rel (0,10/0,72 g/l)

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Lactic acid – Sample 3 (Sweet sparkling wine)

	Lactic acid (g/l)
Mean X	0,754
Uncertainty u_x	0,064
StD s_x	0,217 (29 % rel)
No. of labs	18
No. labs $z < 2$	16
No. labs $z > 2$	0
No. labs $z > 3$	2

Comments:

s_x (PT 2009; sake): 76 % rel (0,55/0,72 g/l)

s_x (PT 2009; cider): 51 % rel (0,46/0,91 g/l)

s_x (PT 2014; kagor): 36 % rel (0,08/0,22 g/l)

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Succinic acid – Sample 3 (Sweet sparkling wine)

	Succinic acid (g/l)
Mean X	0,622
Uncertainty u_x	0,127
StD s_x	0,392
No. of labs	15
No. labs $z < 2$	15
No. labs $z > 2$	0
No. labs $z > 3$	0

Comments:

s_x (PT 2009; sake): 0,73/0,72 g/l

s_x (PT 2009; cider): 0,72/0,79 g/l

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Tartaric acid – Sample 3 (Sweet sparkling wine)

	Tartaric acid (g/l)
Mean X	2,95
Uncertainty u_x	0,10
StD s_x	0,34 (11,5 % rel)
No. of labs	19
No. labs $z < 2$	18
No. labs $z > 2$	0
No. labs $z > 3$	1

Comments:

s_x (PT 2014; kagor): 12 % rel (0,28/2,39 g/l)

35



Citric acid – Sample 3 (Sweet sparkling wine)

	Citric acid (g/l)
Mean X	0,591
Uncertainty u_x	0,023
StD s_x	0,074 (12,5 % rel)
No. of labs	17
No. labs $z < 2$	14
No. labs $z > 2$	0
No. labs $z > 3$	3

Comments:

s_x (PT 2009; sake): 67 % rel (0,08/0,12 g/l)

s_x (PT 2009; cider): 80 % rel (0,08/0,10 g/l)

s_x (PT 2014; beer mix): 8 % rel (0,08/1,0 g/l)

s_x (PT 2014; kagor): 35 % rel (0,17/0,48 g/l)

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Dry extract – Sample 3 (Sweet sparkling wine)

	Dry extract (g/l)
Mean X	82,7
Uncertainty u_x	0,1
StD s_x	0,5 (0,6 % rel)
No. of labs	27
No. labs $z < 2$	22
No. labs $z > 2$	1
No. labs $z > 3$	4

Comments:

s_x (PT 2009; cider): 0,3 % rel.

s_x (PT 2014; kagor): 0,5 % rel.

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Glucose

	Fruits in alcohol (w/w)	Suspicious distillate (w/w)	Sweet sparkling wine (w/w)
Mean x	19,88	0,033	3,10
Uncertainty u_x	0,20	0,003	0,02
StD s_x	0,96 (4,8 % rel)	0,009 (27 % rel)	0,11 (3,5 % rel)
No. of labs	38	18 (+3 excluded)	37
No. labs $z < 2$	33	17	34
No. labs $z > 2$	4	1	0
No. labs $z > 3$	1	3	3

Comments:

s_x (PT 2014; beer mix):

27 % rel (0,07/0,26 g/l)

s_x (PT 2014; kagor):

3 % rel (2,47/78,92 g/l)

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Fructose

	Fruits in alcohol (w/w)	Suspicious distillate (w/w)	Sweet sparkling wine (w/w)
Mean \bar{x}	18,53	0,029	3,13
Uncertainty u_x	0,15	0,002	0,02
StD s_x	0,72 (3,9 % rel)	0,006 (20 % rel)	0,09 (2,9 % rel)
No. of labs	38	18 (+4 excluded)	37
No. labs $z < 2$	34	18	34
No. labs $z > 2$	2	0	0
No. labs $z > 3$	2	4	3

Comments:

s_x (PT 2009; fructose):

4 % rel (2,0/48,2 g/l)

s_x (PT 2014; beer mix):

7,9 % rel (0,42/5,28 g/l)

s_x (PT 2014; kagor):

2,7 % rel (2,10/78,67 g/l)

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Sucrose

	Vermouth (w/w)	Suspicious distillate (w/w)
Mean \bar{x}	28,13	0,896
Uncertainty u_x	0,11	0,012
StD s_x	0,56	0,055
No. of labs	37	33 (+3 excluded)
No. labs $z < 2$	32	29
No. labs $z > 2$	3	1
No. labs $z > 3$	2	6

Comments:

no previous results

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Invert sugar

	Fruits in alcohol (g/100 g)	Vermouth (g/100 g)	Suspicious distillate (g/100 g)	Sweet sparkling wine (g/100 g)
Mean x	35,95	28,70	0,823	5,99
Uncertainty u_x	0,46	0,31	0,101	0,06
StD s_x	1,09	1,16	0,377	0,26
No. of labs	32	22 (+1 excluded)	22 (+3 excluded)	30
No. labs $z < 2$	30	18	19	25
No. labs $z > 2$	1	2	4	2
No. labs $z > 3$	1	3	2	3

Methods used

IS = (Glucose + Fructose) x 0.95

EC Reg. 900/2008 IS = Sucrose + 0.95 x (Fructose + Glucose)

EC Reg. 635/2016 Invert sugar = glucose + fructose + maltose + lactose + (sucrose x 1,05)

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Thujones – Sample 2 (Vermouth)

	Alpha- thujone (mg/l)	Beta- thujone (mg/l)
Mean X	6,3	1,2
Uncertainty u_x	1,1	0,3
StD s_x	2,2	0,5
No. of labs	6	5

Comments:

Presence of alpha-thujone: 11/11

Presence of beta-thujone: 11/12

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Classification – Fruits in alcohol

CN code	Absolute frequency	Relative frequency (%)
2008 60	1	3 %
2008 60 11 (00)	21	58 %
2008 60 19 (00)	11	30 %
2008 99 34	1	3 %
2208 60 11	1	3 %
2208 90 69	1	3 %
Total	36	100 %

Comments:

94 % heading 2008

6 % heading 2208

CN classification - additional note 4 to chapter 20: 'actual alcoholic strength by mass': the number of **kilograms** of pure alcohol contained in 100 kg of the product

10,05 kg PA in 100 kg of the product

More than 30 % of sugar

Declared as cherries

2008 60 11 – Cherries – – Containing added spirit – – – With a sugar content exceeding 9 % by weight – – – – Of an actual alcoholic strength by mass not exceeding 11,85 % mas

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Classification – Vermouth

CN code	Absolute frequency	Relative frequency (%)
2205 10	1	3 %
2205 10 90	8	23 %
2208 70 10 (00)	23	65 %
2208 90 56	2	6 %
2208 90 69	1	3 %
Total	36	100%

Comments:

26 % heading 2205

74 % heading 2208

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Classification – Suspicious distillate

CN code	Absolute frequency	Relative frequency (%)
2207 20	1	3 %
2207 20 00 (19 and 90)	20	55 %
2208 00 00	1	3 %
2208 20 26	7	19 %
2208 90 69	1	3 %
2208 90 91	6	17 %
Total	36	100%

Comments:

58 % heading 2207

42 % heading 2208

Grappa with IPA 3,87 l/hl

HS Explanatory Notes 2207

Ethyl alcohol and other spirits, denatured, are spirits mixed with substances to render them unfit for drinking but not to prevent their use for industrial purposes. The denaturants used vary in different countries according to national legislation. They include wood naphtha, methanol, acetone, pyridine, aromatic hydrocarbons (benzene, etc.), colouring matter.

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Classification – Sweet sparkling wine

CN code	Absolute frequency	Relative frequency (%)
2204	1	3 %
2204 10	1	3 %
2204 10 96	17	48 %
2204 10 98	8	23 %
2204 21 08	1	3 %
2204 10 96 (if P > 3 bar) or 2204 21 08 (if 1 bar ≤ P < 3 bar)	1	3 %
2204 10 98 If P > 3 Bar or 2204 21 09 If > 1 & < 3 BAR	1	3 %
2206 00 39	4	11 %
Total	35	100%

Comments:

89 % heading 2204

11 % heading 2206

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Does your laboratory use this test for:

Parameter	Method accreditation	Quality control	Other purpose
Alcohol	43	51	6
Ethanol	31	56	14
IPA	24	57	19
Density	39	57	4
Pressure	18	68	14
Glycerol	14	64	22
Butanediol	11	67	22
Delta 13C	56	44	0
Delta 18O	67	33	0
(D/H)I	62	38	0
(D/H)II	57	43	0
C14	33	50	17
Volatiles comp.	36	52	12
Methanol	34	52	14



Does your laboratory use this test for:

Parameter	Method accreditation	Quality control	Other purpose
Total acid	35	55	10
Volatile acid	23	77	0
Malic acid	15	65	20
Lactic acid	7	72	21
Succinic acid	9	73	18
Tartaric acid	8	69	23
Citric acid	7	72	21
Dry extract	25	58	17
Glucose	38	55	7
Fructose	37	56	7
Sucrose	34	59	7
Invert sugar	20	52	28
Thujones	0	71	20



3. Proficiency test on spirits, alcoholic beverages and spirit containing mixtures (2016)

Discussion for the preparation of the final report

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3. Proficiency test on spirits, alcoholic beverages and spirit containing mixtures (2016)

Conclusion on the proficiency test and eventual recommendations

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Conclusion

- standard deviation for all parameters good resp. acceptable,
- total acid, volatile acid, butanediol could be improved

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Other questions

- What should be improved in a next proficiency test?
- What kinds of samples would be interesting in a future PT?
- Which parameters should be included?

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