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Proficiency-testing scheme for essential oils

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Abstract

BIPEA (http://www.bipea.org) organizes regular proficiency-testing schemes (PTS) in many analytical domains, including the analysis of essential oils. As an example, in September and October 2015, two tests were conducted using essential pine oil, with respectively 27 and 32 participating laboratories. The first test was intended for routine quality-control analyses (density, refractive index optical rotation, flash-point, peroxide value, and acid value), whereas the second was intended for the analysis of the composition of this essential oil, by determination of its profile by gas chromatography with flame-ionization detection (for 22 constituents of this particular essential oil). Participating laboratories were required to return their results on a dedicated website within a period of 1 month, and a statistical treatment of the data was as usually performed by BIPEA according to ISO 13528.[1]. Assigned (consensus) values were calculated from the participants' results, and the performances of the laboratories could then be evaluated individually and collectively according to ISO 17043. [2] These tests allow participating laboratories to draw up a general inventory of their analytical skills, and are a very useful tool to detect bias or non-compliant results; they act as a warning signal for the implementation of corrective and/or curative actions in the laboratory.

KEYWORDS

essential oils, GC-FID profile, laboratory performance, proficiency-testing schemes, quality control

1 | INTRODUCTION

Created in 1970, BIPEA is a non-profit organization. Since its creation, it has expanded its activities to many fields and currently offers more than 80 Proficiency Testing Schemes (PTS) to its members.

The PTS, which are organized by BIPEA, allow laboratories to check their performance and represent a tool for quality management, allowing them to control the accuracy of their results and to quantify the bias and the drift of them; they act as a warning signal for the implementation of corrective and/or curative actions.

The Flavourings and Fragrances PTS was created in 2012, and the samples proposed to participants for analysis regularly include essential oils. The examples described below concern samples proposed in September and October 2015, using essential pine oil, with respectively 27 and 32 participating laboratories. The first test was intended for routine quality-control analyses (density, refractive index optical rotation, flash-point, peroxide value, and acid value), whereas the second was intended for the analysis of the composition of this essential oil, by determination of its profile by gas chromatography with flame-ionization detection.

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2 | METHODOLOGY

2.1 | Production and shipment of the samples

Both tests of September and October 2015 were conducted on essential pine oil. One batch of 3 L of this essential pine oil was used to produce the samples. This batch was homogenized in an appropriate glass bottle, using a magnetic stirrer. The 30-mL samples were then distributed under stirring, into small brown glass flasks, one after the other in a very short time. This procedure allowed BIPEA to ensure the homogeneity of the samples. Half of the distributed samples were intended for quality control (QC) analyses of density, refractive index optical rotation, flash-point, peroxide value and acid value, the other half for GC analysis of the profile of this essential oil by gas chromatography with flame-ionization detection, for 22 specific constituents of this essential oil (expressed as relative "area %").

Shipments of the samples were made by express courier at ambient temperature at the end of August 2015 for QC analyses, and at the end of September 2015 for GC analysis. Altogether 27 laboratories registered for the QC analyses, from France (7), USA (5), Switzerland (3), Serbia (2), Germany (1), Argentina (1), Belgium (1), China (1), Colombia (1), India (1),

Indonesia (1), Mexico (1), UK (1), and Singapore (1), and 32 laboratories registered for the GC analyses, from France (8), USA (7), Switzerland (4), India (2), Germany (1), Argentina (1), Belgium (1), Brazil (1), China (1), Colombia (1), Indonesia (1), Japan (1), Mexico (1), UK (1), and Singapore (1).

2.2 | Collection of the results and statistical treatment of the data

Participating laboratories were required to return their results on a dedicated website within a period of 1 month. They had to fill in an online reply form, defining the parameters to be determined, their units and the number of significant digits, the methods to be used and the analysis conditions, using a confidential login and passwords to enter and transmit their results. Before any statistical treatment, BIPEA then checked the whole traceability of the procedure, from the sample production to the results of each participant.

A statistical treatment of the data was performed according to the ISO 13528 standard,[1] which describes in its Annex B some robust statistics (algorithm A).

Assigned values were calculated from the participants' results for each parameter, using the robust mean of the results. No data were removed in this calculation of robust statistics as this iterative process minimized the influence of the most extreme values.

Twice the robust standard deviation of the data obtained by algorithm A was applied as the tolerance value for all the QC parameters except flash point, for which the tolerance value was taken as 3°C.

For the GC analysis, the applied tolerance values depended on the level of the assigned values for each constituent, and are as follows:

Assigned value (%)	Tolerance, as % of the assigned value
0.05–1	50
1–5	20
5–10	15
10–20	10
20–100	5

The results could then be evaluated with regards to this tolerance value, and the performances of the laboratories could be evaluated individually and collectively according to ISO 17043,[2] using z-scores:

$$z = \frac{X - x}{\frac{VT}{2}}$$

where X = assigned value of the analytical parameter.

x = result of the laboratory.

VT/2 = half the tolerance value applied for the analytical parameter.

Parameter	Specific gravity		Refractive index		Optical rotation		Flash point		Peroxide value		Acid value	
Unit					°		° C		$mmol.l^{-1}$		$mg.g^{-1}$	
ASSIGNED VALUE												
X	0,9029		1,4701		-34,91		45		9,2		0,5	
u_X	0,0002		0,0001		0,08		1		1,8		0,1	
s^*_X	0,0008		0,0002		0,29		2		6,1		0,2	
p_X	23		24		19		13		17		23	
PROFICIENCY												
SDPA	0,0008		0,0002		0,29		2		6,1		0,2	
VT = 2 x SDPA	0,0016		0,0004		0,58		3		12,2		0,4	
X + 2 x SDPA	0,9045		1,4705		-34,33		48		21,4		0,9	
X - 2 x SDPA	0,9013		1,4697		-35,49		42		0		0,1	
p_D	3		2		1		2		2		3	
LAB.	x	z	x	z	x	z	x	z	x	z	x	z
1424	0,9035	*0,75*	1,4700	*-0,50*	-34,98	*-0,24*	44	*-0,67*	25,7	*2,70*	(TA) 0,7	*1,00*
1505	0,9033	*0,50*	1,4699	*-1,00*	-34,67	*0,83*	43	*-1,33*			(TA) 0,2	*-1,50*
1551	0,9030	*0,13*	1,4710	*4,50*	-34,60	*1,07*			31,8	*3,70*	(TM) 0,5	*0,00*
1587	0,9032	*0,38*	1,4703	*1,00*	-34,80	*0,38*			***120,0***		(TM) 0,5	*0,00*
1897	0,9034	*0,63*	1,4700	*-0,50*	-34,82	*0,31*					(TM) 0,5	*0,00*
2242	0,9179	*18,75*	1,4701	*0,00*	-35,30	*-1,34*	47	*1,33*	5,5	*-0,61*	(TA) 0,4	*-0,50*
2276	0,9032	*0,38*	1,4702	*0,50*	-35,01	*-0,34*			11,4	*0,36*	(TA) 0,1	*-2,00*
2357	0,9032	*0,38*	1,4701	*0,00*	-35,16	*-0,86*	45	*0,00*	2,5	*-1,10*	(TA) 0,0	*-2,50*
2478	0,9030	*0,13*	1,4700	*-0,50*	-34,58	*1,14*	45	*0,00*	9,9	*0,11*	(TM) 0,4	*-0,50*
2626	0,9032	*0,38*	1,4701	*0,00*	-34,98	*-0,24*	44	*-0,67*	8,6	*-0,10*	(TM) 0,7	*1,00*
2665	0,9034	*0,63*	1,4702	*0,50*	-34,72	*0,66*			0,7	*-1,39*	(TA) 0,4	*-0,50*
3002			1,4702	*0,50*							(TM) 0,4	*-0,50*
3287	0,8989	*-5,00*	1,4710	*4,50*					2,6	*-1,08*	(TM) 2,8	*11,50*
3607	0,9031	*0,25*	1,4697	*-2,00*	-35,10	*-0,66*	45	*0,00*	***156,6***		(TA) 0,7	*1,00*
3703	0,9019	*-1,25*	1,4697	*-2,00*			44	*-0,67*				
3771	0,8996	*-4,13*	1,4697	*-2,00*	-34,51	*1,38*			7,3	*-0,31*	(TA) 0,6	*0,50*
4132	0,9018	*-1,38*	1,4701	*0,00*	-34,75	*0,55*	42	*-2,00*	8,6	*-0,10*	(TA) 1,0	*2,50*
4268	0,9018	*-1,38*	1,4703	*1,00*	***69,39***				8,5	*-0,11*	(TM) 0,6	*0,50*
4305	0,9033	*0,50*	1,4701	*0,00*	-34,8	*0,38*			21	*1,93*	(TM) 0,6	*0,50*
4375	0,9031	*0,25*	1,4704	*1,50*	-35,34	*-1,48*	38	*-4,67*	9,1	*-0,02*	(TM) 0,4	*-0,50*
4381	0,9030	*0,13*	1,4699	*-1,00*	***34,70***		48	*2,00*	9,5	*0,05*	(TA) 0,4	*-0,50*
4439	0,9034	*0,63*	1,4702	*0,50*	-34,90	*0,03*	45	*0,00*	12,3	*0,51*	(TM) 0,5	*0,00*
4588	0,9033	*0,5*	1,4700	*-0,50*	-35,90	*-3,41*	51	*4,00*	5,5	*-0,61*	(TM) 0,7	*1,00*
5039	0,9021	*-1,00*	1,4701	*0,00*	-35,01	*-0,34*			***98,3***		(TM) 0,8	*1,50*

FIGURE 1 Results of laboratories for QC analyses. [Colour figure can be viewed at wileyonlinelibrary.com]

2.3 | Interpertation of the data

The z-scores can be classified as follows:

$\|z\| \leq 2$	"satisfactory"
$2 < \|z\| \leq 3$	"questionable"
$3 < \|z\|$	"unsatisfactory"

A z-sore is calculated for each result, and the laboratories can then classify their results and implement some corrective and /or curative actions if necessary.

3 | RESULTS AND DISCUSSION

The results obtained for the QC analyses are presented in Figure 1. The results were satisfactory for most of the laboratories and most of the analytical parameters.

For specific gravity, refractive index, flash point and acid value, two to three results were out of tolerance.

For optical rotation, two results, given as positive (laboratories 4268 and 4381) were declared as incoherent and were excluded from the statistical calculations.

For peroxide value, the results are more dispersed. Two results were over-estimated (laboratories 1424 and 1551), and three results were declared as incoherent, due probably to wrong units being used (laboratories 1587, 3607, 5039).

The distribution of the results is normal for all the parameters. As an example, the results for refractive index, presented as a histogram, are given in Figure 2.

The results obtained for GC-FID analyses are presented in Figure 3. The results obtained on a polar and non-polar column were requested (without specifying the exact column phase), to know whether one type of column was more appropriate than the other for this specific essential oil.

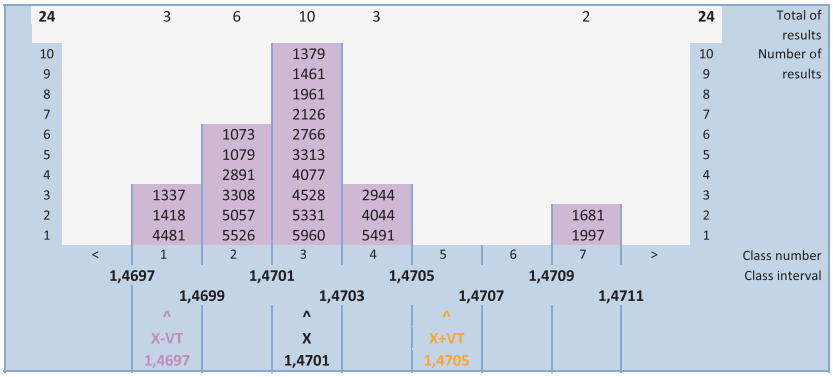

FIGURE 2 Distribution of the results for refractive index. [Colour figure can be viewed at wileyonlinelibrary.com]

Parameter (Unit: %)	Polar column											Non-polar column									
	Bornyl acetate	Alpha-pinene	Beta-pinene	Camphene	Limonene	p-cymene	Delta-3 carene	Myrcene	Beta phellandrene	Terpinolene	Beta-Caryophyllene	Bornyl acetate	Alpha-pinene	Beta-pinene	Camphene	Limonene	p-cymene	Delta-3 carene	Myrcene	Beta phellandrene	Terpinolene	Beta-Caryophyllene
ASSIGNED VALUE																						
X	27,15	13,21	2,22	22,98	4,84	0,10	13,29	0,64	3,60	1,21	1,16	26,94	13,04	2,22	22,90		0,10	13,27	0,65		1,28	1,13
s^*_x	0,41	0,51	0,06	0,37	0,08	0,00	0,28	0,10	0,10	0,03	0,07	0,35	0,12	0,03	0,15		0,02	0,14	0,02		0,03	0,04
p_x	24	22	24	24	24	23	22	21	24	24	24	24	24	24	24		22	23	24		23	24
LAB.	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
1184	32,25	11,91	2,10	20,74	4,77	0,10	11,90	0,54	0,17	1,27	1,40	28,42	12,61	2,26	22,95	8,29	0,20	13,24	0,54	0,16	1,26	1,29
1424	30,20	12,29	2,14	21,98			13,03	0,57	0,17	1,26	1,20	26,28	13,21	2,21	22,55	8,38		12,90	0,64	0,17	1,28	1,15
1551	26,95	13,17	2,23	22,85	4,88	0,10	13,85	0,22	3,68	1,22	1,14	26,56	13,06	2,24	23,07	4,91	0,09	13,27	0,65	3,59	1,29	1,11
1587	26,34	13,23	2,20	23,42	4,78	0,10	13,30	0,63	3,58	1,18	1,09	26,19	13,15	2,23	23,22	4,80	0,09	13,25	0,65	3,62	1,25	1,08
1897	28,03	13,04	2,17	23,14	4,72	0,10	13,12		3,58	1,19	1,26	28,11	13,00	2,22	22,84			13,25	0,65			1,20
2242	27,07		2,20	22,81	4,84	0,09	13,25		3,63	1,22	1,14	26,93	12,89	2,20	22,83		0,09	13,20	0,65		1,29	1,12
2257	26,75	13,43	2,24	23,22	4,88	0,10	13,52	0,68	3,68	1,20	1,12											
2259	27,05	13,08	2,24	22,76	4,95	0,14	13,21	0,69	3,55	1,14	1,26	26,55	12,97	2,25	22,66	4,82	0,13	13,13	0,65	3,63	1,26	1,14
2276	27,00	13,08	2,22	22,82	4,85	0,10	13,87	0,20	3,64	1,22	1,14	26,90	13,06	2,24	22,96		0,10	13,45	0,22		1,33	1,14
2357	27,10	13,00	2,20	22,96	4,80	0,10	13,20	0,60	3,60	1,17	1,20	27,10	12,90	2,20	22,75		0,09	13,30	0,65		1,30	1,14
2478	26,03	13,23	2,27	23,11	4,89	0,10	13,35	0,66	3,68	1,24	1,11	26,87	13,06	2,23	22,93		0,09	13,27	0,66		1,29	1,13
2626	26,97	13,05	2,20	22,84	4,80	0,10	13,15	0,85	3,59	1,20	1,24	26,85	12,98	2,21	22,89	4,16	0,10	13,18	0,64	4,24	1,26	1,12
2665	27,26	15,40	2,25	22,96	4,94	0,07			0,08	1,20	1,23	27,10	13,02	2,21	22,90	8,48	0,11		0,64		1,29	1,14
3607	27,20	13,00	2,20	22,80	4,80	0,09	13,20	0,64	3,60	1,20	1,10	27,20	13,10	2,20	23,10		0,09	13,40	0,66		1,20	1,10
3665												26,40	12,92	2,20	22,88	8,27	0,01	13,04	0,65	0,01	1,26	1,07
3703												26,58	13,07	2,24	22,85	4,83	0,12	13,18	0,85	3,62	1,22	1,25
3760					4,85			0,61														
3771	26,92	14,24	2,37	22,73	4,77	0,10			3,72	1,23	1,14	26,92	13,37	2,02	22,80		0,28	13,06	0,95		1,35	1,19
4132												26,67	12,92	2,23	22,68		0,10	13,26	0,65		1,28	1,14
4305	27,53	13,03	2,31	22,87	4,80	0,09	13,03	0,14	0,85	1,21	0,67	27,11	13,00	2,23	22,81	4,83	0,10	13,26	0,66	3,70	1,29	1,16
4375	26,84	13,30	2,30	23,52	4,94	0,10	13,44	0,68	3,67	1,24	1,07	27,28	13,32	2,27	23,30	4,93	0,10	13,48	0,64	3,66	1,25	1,13
4381	27,30	13,40	2,00	23,80	4,70	0,07	13,50	0,71	3,50	1,00	1,10	27,10	13,20	2,10	23,60	4,80	0,08	13,40	0,57	3,40	1,20	0,99
4439	27,50	13,01	2,19	22,92	4,76	0,10	13,09	0,66	3,58	1,20	1,14											
4575	26,75	11,52	2,20	20,65	4,87	0,09	12,85	0,65	3,60	1,26	1,13											
4588	27,20	13,20	2,20	23,10	4,90	0,10	13,30	0,70	3,70	1,20	1,20	27,20	13,10	2,20	23,00	5,80	0,10	13,40	0,70	2,70	1,30	1,10
4614	26,91		2,25	23,25	4,89	0,09	13,40	0,65	3,66	1,21	1,14	27,30	12,98	2,23	22,90		0,09	13,27	0,65		1,29	1,15
4847	27,00	14,50	2,20	23,30	4,80	0,10	13,30	0,60	3,60	1,20	1,10	27,00	13,00	2,20	22,80		0,10	13,30	0,70		1,30	1,10
5039	27,86	13,65	2,30	24,09	5,02	0,15	13,79	0,79	3,66	1,19	1,26	26,87	13,11	2,23	23,01	8,52	0,02	13,44	0,65	0,16	1,25	1,12
8450	26,79	13,66	2,13	23,31	4,78	0,08	13,44	0,75	3,76	1,18	1,13	26,72	13,07	2,19	22,97	4,64	0,09	13,36	0,64	3,84	1,26	1,10

FIGURE 3 Results of laboratories for GC analyses. [Colour figure can be viewed at wileyonlinelibrary.com]

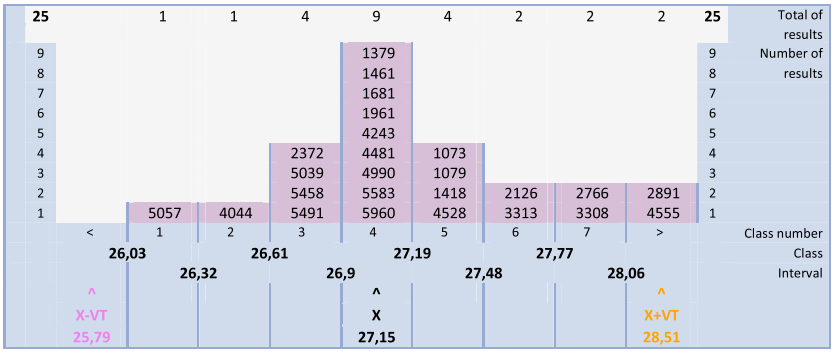

FIGURE 4 Distribution of the results for bornyl acetate, on a polar column. [Colour figure can be viewed at wileyonlinelibrary.com]

The results were satisfactory for most of the laboratories and most of the analytical parameters for polar columns. The observed distribution was normal for all the parameters. An example is given for bornyl acetate using a polar column in Figure 4.

However, for non-polar columns, some co-elutions were detected for some laboratories (1184, 1424, 2665, 3665) between limonene and beta-phellandrene and consequently no assigned value could be estimated for both parameters.

4 | CONCLUSION

The results of these tests were satisfactory for both QC and GC controls and enabled the participating laboratories to draw up a general inventory of their analytical skills. They are very useful to detect bias or non-compliant results and thus act as a warning signal for the implementation of corrective and/or curative actions in the laboratories.

Participation in several proficiency tests per year is of considerable importance, particularly to detect drift or bias in the results, through the use of control charts.

Proficiency tests are an essential tool for the quality management of laboratories and the continuous improvement of their analytical performance.

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