Analytical methods and results in PTSs for phthalates in wines and spirits

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INTRODUCTION

Phthalates are widely used as additives in the production of plastic materials as well as in certain food packaging materials. Some of these compounds are considered powerful endocrine disruptors, which recently led to a change in regulations concerning their use in materials destined to be in contact with foodstuffs.

Wines and spirits produced, handled and/or transported in contact with plastics (tanks, pipes, pump bodies, plastic container...) could be contaminated with these type of substances and exposed to a refusal of marketing authorization. This is the reason why the request of analyses of phthalates in wines and spirits has gradually increased in recent years, leading laboratories to improve their analytical performances in term of detection and quantification of these molecules. The OIV (International Organization of Vine and Wine) recommended the GS/MS method [1,2] but several laboratories perform these analyses by HPLC/UV, UPLC/UV or develop a specific analytical procedure. Proficiency-testing schemes are being organized by BIPEA since October 2015 proposing wines and spirits spiked with phthalates to allow laboratories to monitor the reliability of their results and validate alternative methods. For each test, a statistical treatment of the data is performed according to ISO 13528 [3]. Assigned (consensus) values are compared to the theoretical concentration of phthalates to evaluate recovery rates. The aim of this work is to discuss about the results obtained in these PTs, making a focus on two different tests, respectively in wine and spirit (tests of October 2018 on white wine and January 2018 on Cognac). Moreover, for the described tests, a specific study was performed comparing the results obtained with the different analytical methods carried out.

MATERIALS and METHODS

Sample preparation: Wines and spirits are spiked with di-ethylphthalate (DEP), di-butylphthalate (DBP), benzybuthylphthalate (BBP), di-methylphthalate (DMP), di-2-ethylhexylephthalate (DHEP), di-isononylephthalate (DINP), di-isobutylphthalate (DIBP), di-n-octylphthalate (DNOP), di-isodecylephthalate (DIDP), at different concentrations. The spiked product is then handled using a specific equipment to ensure homogeneity during the sampling and correctly conditioned to ensure the stability of the manufactured samples. After the production and before the shipment to the laboratories, the homogeneity and stability of the samples for the duration of the test are checked, according to requirements of the ANNEX B of ISO 13528 standard [3].

Analyses: The laboratories participating in PTs are required to return their results, via a dedicated website after a period of 4 weeks, specifying the performed method.

Statistical treatment: The statistical treatments were conducted according to ISO 13528 standard [3]. The assigned values (x_{pt}) were estimated using the means of all results (except incoherent ones), obtained from the application of robust algorithm A.

RESULTS and DISCUSSION

Statistical parameters and recovery rates of each phthalate are given in Table 1 for the test of October 2018 on white wine and in Table 2 for the test of January 2018 on Cognac. The higher response rate is observed for diethylhexyl phthalate (DEHP) and dibutyl phthalate (DBP), which are the most frequently detected compounds in the wines and spirits.
Assigned values (x_{pt}) were estimated for all phthalates except for molecules not added to the product, didisobutylphthlate in wine and diisodecilphthalate in spirit, because participants indicated a qualitative result (as detection or quantification limit). Uncertainties ($u(x_{pt})$, that quantify the confidence to the assigned values, are good and vary according, among other factors, to the phthalate concentration and number of results taken into account to estimate the value. Coefficients of variation $CV(x_{pt})$, reflecting the dispersion of the results according to assigned values, range from 17% to 32% for Cognac and from 21% to 48% for wine. In general, recovery rates (R) of the light phthalates are better than those of the heavy ones, which analyses are more challenging in terms of isolation and spectrum interpretation.
The most widely used method is GS-MS, with, on average, more than 82% of laboratories indicating this technique for Cognac and 64% for wine. Statistics of all analytical parameters *per* method are presented in Tables 3 and 4. The analysis of collected data shows a good consistency of the results obtained from different methods, whatever the matrix, the analyte and the contamination level. For diethylhexyl phthalate (DEHP), benzylbutyl phthalate (BBP) and dibutyl phthalate (DBP), the distribution of the results by method is shown in the histograms just below (Figures 1 and 2)

WHITE WINE – TEST OF OCTOBER 2018

	X µg/L	x_{pt} µg/L	$u(x_{pt})$ µg/L	$s(x_{pt})$ µg/L	$p(x_{pt})$	$CV(x_{pt})$ %	p_{CA}	R (%)
DEP	406	372	36	103	13	28	15	92
DBP	301	424	31	107	19	25	19	141
BBP	61	66	8	26	16	39	18	108
DMP	101	101	8	24	14	24	15	100
DEHP	1012	857	130	415	16	48	19	85
DINP	504	446	59	150	10	34	17	88
DIBP	0	-	-	-	-	-	13	-
DNOP	101	86	8	18	9	21	14	85
DIDP	754	664	67	160	9	24	16	88

Table 1. Summary of the statistical treatment of data and recovery rates on white wine

	HPLC-UV				GC-MS				other methods			
	x^*_m [1]	$u_x{}^*_m$ [2]	s^*_m [3]	p_m [4]	x^*_m [1]	$u_x{}^*_m$ [2]	s^*_m [3]	p_m [4]	x^*_m [1]	$u_x{}^*_m$ [2]	s^*_m [3]	p_m [4]
DEP					377	54	138	10	360	26	36	3
DBP					421	40	129	16	425	21	29	3
BBP					72	11	32	13	52	3	4	3
DMP					102	10	28	12	100	1	2	2
DEHP					817	189	606	16	888	88	122	3
DINP					384	96	232	9	589	114	158	3
DIBP					153	209	325	4				
DNOP	83	5	6	2	62	20	52	11				
DIDP					537	163	392	9	752	105	146	3

[1] Mean (µg/L)
[2] Uncertainty of the mean
[3] Standard deviation
[4] Number of returned results

Table 3. Statistical treatment of data by methods on white wine

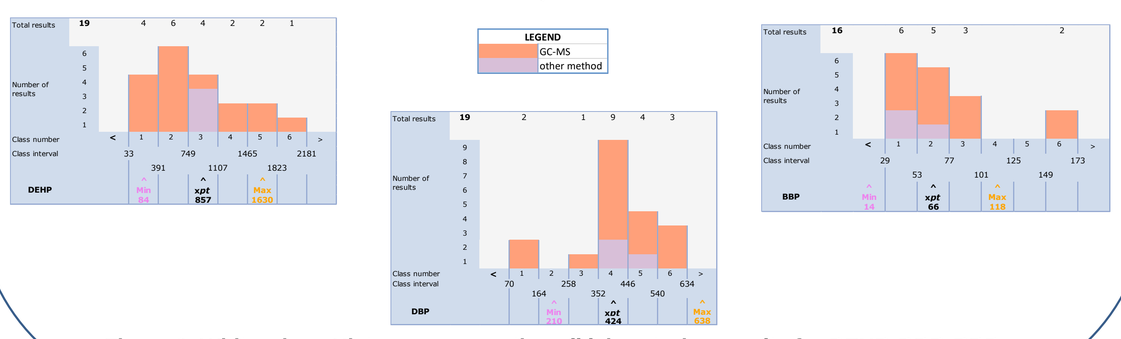

Figure 1. White wine - Histograms reporting all laboratories results for DEHP, DBP, BBP

COGNAC – TEST OF JANUARY 2018

	X µg/L	x_{pt} µg/L	$u(x_{pt})$ µg/L	$s(x_{pt})$ µg/L	$p(x_{pt})$	$CV(x_{pt})$ %	p_{CA}	R (%)
DEP	344	330	38	106	12	32	13	96
DBP	309	278	12	47	22	17	22	90
BBP	757	692	45	135	14	20	14	91
DMP	412	422	57	163	13	39	14	102
DEHP	2118	4178	231	868	22	21	22	197
DINP	8371	6027	524	1920	21	32	21	72
DIBP	279	297	23	69	14	23	14	106
DNOP	5229	4048	281	780	12	19	12	77
DIDP	0	-	-	-	-	-	10	-

Table 2. Summary of the statistical treatment of data and recovery rates on Cognac

	HPLC-UV				GC-MS				UPLC-UV			
	x^*_m [1]	$u_x{}^*_m$ [2]	s^*_m [3]	p_m [4]	x^*_m [1]	$u_x{}^*_m$ [2]	s^*_m [3]	p_m [4]	x^*_m [1]	$u_x{}^*_m$ [2]	s^*_m [3]	p_m [4]
DEP				1	319	48	109	8	397	126	216	3
DBP	320	35	40	2	268	18	51	13	280	18	38	7
BBP				1	681	64	163	10	742	89	124	3
DMP				1	386	59	141	9	471	157	217	3
DEHP	3249	1130	1279	2	4524	290	836	13	3862	260	550	7
DINP	3322	2307	2610	2	6665	709	1880	11	5664	870	1968	8
DIBP				1	282	24	64	11	322	42	47	2
DNOP				1	4354	280	634	8	3622	344	476	3
DIDP				1	1116	517	1014	6				1

[1] Mean (µg/L)
[2] Uncertainty of the mean
[3] Standard deviation
[4] Number of returned results

Table 4. Statistical treatment of data by methods on Cognac

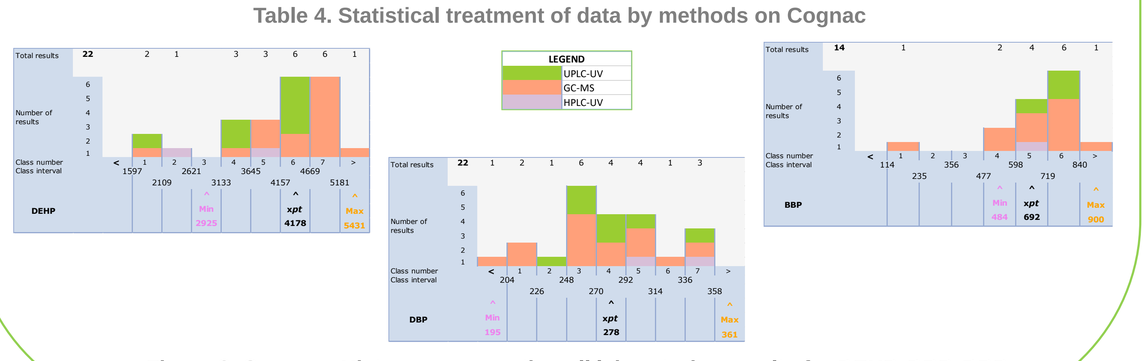

Figure 2. Cognac - Histograms reporting all laboratories results for DEHP, DBP, BBP

TABLE LEGEND

X	Theoretical concentration in the matrix (spiking value).
x_{pt}	Assigned value or conventionally true value, calculated by the robust algorithm A from ISO 13528 standard.
$u(x_{pt})$	Standard uncertainty of the assigned value; this value permits to quantify the confidence that can be given to the assigned value. It depends on the mathematical model applied (algorithm A) and is a function of the standard deviation and the number of results used for the estimation of the assigned value. It is calculated as indicated in § 5.6.2 of ISO 13528 standard.
$s(x_{pt})$	Robust standard deviation of the results, calculated by the robust algorithm A from ISO 13528 from all the results which participated to the estimation of the assigned value.
$p(x_{pt})$	Number of results taken into account for the estimation of the assigned value.
$CV(x_{pt})$	Coefficient of variation, this value permits to measure the dispersion of the results.
p_{CA}	Total number of returned results (including incoherent and qualitative ones)
R	Recovery rate (x_{pt}/X*100)

CONCLUSION

The analysis of results obtained in PTs for phthalates quantification in alcoholic drinks shows that laboratories obtain better results on spirits than wines. The different performed methods give comparable results, but must be refined for the quantification of heavy phthalates in term of recovery rates.
This study confirms that participating in proficiency tests can enable participants to optimize their analytical procedures to improve their performances for phthalates quantification in wines and spirits.

REFERENCES

[1] OIV-MA-AS323-10: Method of determination of phthalates by gas chromatography / mass spectrometry in wines, Compendium of international methods of analysis - OIV
[2] OIV-MA-BS-33: Method of determination of phthalates in spirituous beverages by gas chromatography/ mass spectrometry, Compendium of international methods of analysis of spirituous beverages of vitivinicultural origin - OIV
[3] ISO 13528 - Statistical methods for use in proficiency testing by interlaboratory comparisons.