RESOLUTION OIV-OENO 596-2019

VALIDATION OF ANALYSIS OF PHTHALATES IN WINES (OIV OENO 477-2013)

WARNING: this resolution amends the following resolution:
OIV-OENO 477-2013

THE GENERAL ASSEMBLY,

IN VIEW of article 2, paragraph 2 iv of the Agreement of 3 April 2001 establishing the International Organisation of Vine and Wine,

CONSIDERING the proposal of the "Methods of Analysis" Sub-commission,

CONSIDERING the resolution OIV-OENO 477-2013 "detection and assay of phthalates in wines", adopted in 2013,

DECIDES to complete the field of application of the resolution OIV-OENO 477-2013 through a footnote by listing the phthalates adopted as type II (DCHP BBP DBP DIBP DEP) and those remaining adopted as type IV (DIDP DINP DNOP DEHP DMP).

The classification of analytical methods is described in the OIV-MA-AS1-03 sheet of the Compendium of International Methods of Analysis of Wines and Musts,

DECIDES to amend the method of analysis OIV-MA-AS323-10 by adding the following document as annexe:

VALIDATION OF ANALYSIS OF PHTHALATES IN WINES

1. Executive Summary

The Institute for Reference Materials and Measurements (IRMM) organised in close collaboration with the International Organisation of Vine and Wine (OIV) this collaborative study to validate Compendium method OIV-MA-AS323-10:2013 for the determination of ten phthalates in wine by gas chromatography - mass spectrometry (GC-MS).

The design of the method performance study complied with provisions given in ISO 5725-2 and those established by the OIV. The test samples consisted of red wine, white wine, and sweet wine presented as blind duplicates (see Table 1).

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The wines were spiked at IRMM, bottled into ampoules, and dispatched to the participants of the validation study.

In addition to the test samples, participants received a deuterated phthalate solution, in order to be able to prepare the internal standard solutions.

The participants of the study were identified by the OIV following a pre-validation study for the method. They comprised laboratories from Europe, Asia, South America and Australia (see Table 2).

The evaluation of the reported results was performed according to ISO 5725-2 and ISO 5725-4, as well as the provisions established by the OIV. Relative standard deviations for reproducibility were mostly within the range of 9% to 71%.

Table 1

Sample	S001	S002	S003	S004	S005	S006
Nature	White wine		Red wine		Sweet wine	

2. Participants in the study

Table 2: Participants in the study

Analab Chile S.A.	Chile
Animal & Plant & Food Inspection Centre, Tianjin Exit-Entry Inspection and Quarantine Bureau	People's Republic of China
Bureau Interprofessionnel du Cognac	France
Central National de Verificare a Calitatii Productiei Alcoolice	Republic of Moldova
Chemisches und Veterinaeruntersuchungsamt Stuttgart	Germany
Escola Superior de Biotecnologia Universidade Católica Portuguesa	Portugal

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Instituto Nacional de Vitivinicultura Departamento de Normas Analiticas Especiales	Argentina
Laboratorio Arbitral Agroalimentario	Spain
Laboratoire DUBERNET	France
Miguel Torres S.A.	Spain
SAILab	Spain
SCL Laboratoire de Bordeaux	France
SCL Laboratoire de Montpellier	France
The Australian Wine Research Institute	Australia

3. Evaluation of submitted results

The fitness-for-purpose of the calculated reproducibility standard deviation was evaluated. For this purpose, the calculated reproducibility relative standard deviation (RSDR) was compared to the relative standard deviation derived from the modified Horwitz equation (RSDmH), as proposed by Thompson (Thompson 2000). The latter provides a concentration dependant guidance level for reproducibility.

The agreement with the guidance level of precision was expressed as HORRAT values for reproducibility (HORRATR).

4. Evaluation of systematic effects

Laboratories reporting results that, for one or more analytes, exceeded the 1% threshold level of either the Mandel's h or Mandel's k tests were contacted by the organisers and requested to check their reported data and to confirm them if appropriate. Results were excluded from data evaluations if the laboratory did not confirm the correctness of the reported analytical results.

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5. Evaluation of reported results by analyte

Based on the results of the separate analysis of each analyte and according to the reproducibility results, the method should be considered as either type II (DCHP BBP DBP DIBP DEP) or type IV (DIDP DINP DNOP DEHP DMP).

Table 3: Dimethyl phthalate (DMP)[1] *– Results of data evaluation*

		S001	S002	S003	S004	S005	S006
No. of laboratories that submitted compliant results		11	10	11	10	10	11
Mean	mg/l	0.020	0.073	0.018	0.031	0.053	0.027
Median	mg/l	0.020	0.060	0.018	0.030	0.056	0.028
Assigned value	mg/l	0.030	0.097	0.030	0.049	0.104	0.046
Rel. dev. assign. value		-33.3%	-38.1%	-40.0%	-38.8%	-46.2%	-39.1%
Repeatability s.d.	mg/l	0.003	0.007	0.002	0.006	0.011	0.003
Reproducibility s.d.	mg/l	0.006	0.041	0.007	0.011	0.022	0.009
Rel. repeatability s.d.		9.42%	7.33%	8.04%	13.00%	10.25%	7.09%
Rel. reproducibility s.d.		20.10%	42.40%	23.12%	22.54%	21.10%	19.07%
Modified Horwitz s.d. **		22.00%	22.00%	22.00%	22.00%	22.00%	22.00%
HORRATR		0.91	1.93	1.05	1.02	0.96	0.87
Limit of repeatability, r (2.77 X sr)	mg/l	0.008	0.020	0.007	0.018	0.030	0.009
Limit of reproducibility, R (2.77 X sR)	mg/l	0.017	0.114	0.019	0.031	0.061	0.024
Rel. limit of repeatability		26.09%	20.32%	22.28%	36.00%	28.38%	19.64%
Rel. limit of reproducibility		55.67%	117.45%	64.05%	62.44%	58.45%	52.84%
No. of laboratories after elimination of outliers		9	9	8	8	9	10

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No. of measurement values without outliers		18	18	15	16	18	20

Table 4: Diethyl phthalate (DEP)[2] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		12	11	11	11	10	12
Mean	mg/l	0.048	0.065	0.030	0.039	0.021	0.059
Median	mg/l	0.044	0.076	0.029	0.041	0.023	0.061
Assigned value	mg/l	0.057	0.092	0.031	0.056	0.030	0.089
Rel. dev. assign. value		-22.8%	-17.4%	-6.5%	-26.8%	-23.3%	-31.5%
Repeatability s.d.	mg/l	0.006	0.010	0.005	0.004	0.003	0.002
Reproducibility s.d.	mg/l	0.026	0.026	0.015	0.017	0.008	0.019
Rel. repeatability s.d.		10.49%	11.32%	15.28%	7.00%	11.41%	2.53%
Rel. reproducibility s.d.		45.36%	28.49%	47.95%	29.71%	25.74%	20.98%
Modified Horwitz s.d. **		22.00%	22.00%	22.00%	22.00%	22.00%	22.00%
HORRATR		2.06	1.30	2.18	1.35	1.17	0.95
Limit of repeatability, r (2.77 X sr)	mg/l	0.017	0.029	0.013	0.011	0.009	0.006
Limit of reproducibility, R (2.77 X sR)	mg/l	0.072	0.073	0.041	0.046	0.021	0.052
Rel. limit of repeatability		29.05%	31.35%	42.32%	19.40%	31.60%	7.01%
Rel. limit of reproducibility		125.66%	78.91%	132.81%	82.29%	71.30%	58.12%
No. of laboratories after elimination of outliers		11	10	11	9	10	11
No. of measurement values without outliers		21	20	21	17	20	22

Table 5: Diisobutyl phthalate (DIBP)[3] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**

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No. of laboratories that submitted compliant results		11	10	11	10	10	11
Mean	mg/l	0.049	0.087	0.076	0.119	0.054	0.046
Median	mg/l	0.049	0.085	0.076	0.123	0.055	0.045
Assigned value	mg/l	0.035	0.076	0.058	0.107	0.061	0.045
Rel. dev. assign. value		40.0%	11.8%	31.0%	15.0%	-9.8%	0.0%
Repeatability s.d.	mg/l	0.003	0.006	0.007	0.009	0.002	0.004
Reproducibility s.d.	mg/l	0.011	0.019	0.014	0.023	0.012	0.013
Rel. repeatability s.d.		7.43%	7.71%	11.55%	8.81%	4.04%	9.54%
Rel. reproducibility s.d.		32.18%	25.23%	24.48%	21.95%	19.98%	28.37%
Modified Horwitz s.d. **		22.00%	22.00%	22.00%	22.00%	22.00%	22.00%
HORRATR		1.46	1.15	1.11	1.00	0.91	1.29
Limit of repeatability, r (2.77 X sr)	mg/l	0.007	0.016	0.019	0.026	0.007	0.012
Limit of reproducibility, R (2.77 X sR)	mg/l	0.031	0.053	0.039	0.065	0.034	0.035
Rel. limit of repeatability		20.58%	21.35%	31.98%	24.42%	11.19%	26.44%
Rel. limit of reproducibility		89.15%	69.88%	67.80%	60.81%	55.35%	78.58%
No. of laboratories after elimination of outliers		11	10	11	10	10	11
No. of measurement values without outliers		21	20	21	20	20	22

Table 6: Dibutyl phthalate (DBP)[4] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		12	11	12	11	11	12
Mean	mg/l	0.103	0.264	0.078	0.728	0.090	0.178
Median	mg/l	0.103	0.266	0.074	0.666	0.089	0.174

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Assigned value	mg/l	0.107	0.281	0.057	1.039	0.032	0.153
Rel. dev. assign. value		-3.7%	-5.3%	29.8%	-35.9%		
Repeatability s.d.	mg/l	0.009	0.014	0.011	0.033	0.004	0.012
Reproducibility s.d.	mg/l	0.022	0.048	0.021	0.314	0.018	0.022
Rel. repeatability s.d.		8.24%	5.03%	19.11%	3.21%	13.79%	7.87%
Rel. reproducibility s.d.		20.73%	17.01%	36.78%	30.25%	57.05%	14.66%
Modified Horwitz s.d. **		22.00%	19.36%	22.00%	15.91%	22.00%	21.22%
HORRATR		0.94	0.88	1.67	1.90	2.59	0.69
Limit of repeatability, r (2.77 X sr)	mg/l	0.024	0.039	0.030	0.092	0.012	0.033
Limit of reproducibility, R (2.77 X sR)	mg/l	0.061	0.132	0.058	0.871	0.051	0.062
Rel. limit of repeatability		22.81%	13.92%	52.94%	8.89%	38.21%	21.80%
Rel. limit of reproducibility		57.43%	47.12%	101.88%	83.79%	158.03%	40.60%
No. of laboratories after elimination of outliers		12	11	12	10	11	11
No. of measurement values without outliers		23	22	23	20	22	22

Table 7: Benzyl butyl phthalate (BBP)[5] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		11	10	11	10	10	11
Mean	mg/l	0.049	0.026	0.033	0.074	0.075	0.050
Median	mg/l	0.050	0.027	0.034	0.075	0.078	0.051
Assigned value	mg/l	0.057	0.029	0.037	0.088	0.087	0.053
Rel. dev. assign. value		-12.3%	-6.9%	-8.1%	-14.8%	-10.3%	-3.8%
Repeatability s.d.	mg/l	0.002	0.001	0.003	0.004	0.003	0.003

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Reproducibility s.d.	mg/l	0.008	0.004	0.005	0.011	0.015	0.007
Rel. repeatability s.d.		4.30%	4.96%	8.08%	5.10%	3.31%	4.78%
Rel. reproducibility s.d.		13.71%	13.82%	13.93%	12.72%	17.00%	14.00%
Modified Horwitz s.d. **		22.00%	22.00%	22.00%	22.00%	22.00%	22.00%
HORRATR		0.62	0.63	0.63	0.58	0.77	0.64
Limit of repeatability, r (2.77 X sr)	mg/l	0.007	0.004	0.008	0.012	0.008	0.007
Limit of reproducibility, R (2.77 X sR)	mg/l	0.022	0.011	0.014	0.031	0.041	0.021
Rel. limit of repeatability		11.90%	13.75%	22.38%	14.14%	9.16%	13.23%
Rel. limit of reproducibility		37.98%	38.27%	38.58%	35.23%	47.09%	38.77%
No. of laboratories after elimination of outliers		9	8	10	9	9	10
No. of measurement values without outliers		17	15	19	18	18	20

Table 8: Dicyclohexyl phthalate (DCHP)[6] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		9	8	9	8	8	9
Mean	mg/l	0.079	0.042	0.030	0.088	0.046	0.031
Median	mg/l	0.076	0.044	0.033	0.091	0.050	0.033
Assigned value	mg/l	0.084	0.048	0.038	0.105	0.057	0.036
Rel. dev. assign. value		-9.5%	-8.3%	-13.2%	-13.3%	-12.3%	-8.3%
Repeatability s.d.	mg/l	0.005	0.006	0.003	0.005	0.002	0.001
Reproducibility s.d.	mg/l	0.024	0.008	0.005	0.011	0.011	0.006
Rel. repeatability s.d.		5.60%	13.13%	6.75%	4.84%	3.25%	3.67%

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Rel. reproducibility s.d.		28.46%	16.05%	12.93%	10.20%	18.83%	16.37%
Modified Horwitz s.d. **		22.00%	22.00%	22.00%	22.00%	22.00%	22.00%
HORRATR		1.29	0.73	0.59	0.46	0.86	0.74
Limit of repeatability, r (2.77 X sr)	mg/l	0.013	0.017	0.007	0.014	0.005	0.004
Limit of reproducibility, R (2.77 X sR)	mg/l	0.066	0.021	0.014	0.030	0.030	0.016
Rel. limit of repeatability		15.53%	36.37%	18.69%	13.40%	9.00%	10.18%
Rel. limit of reproducibility		78.83%	44.46%	35.82%	28.24%	52.15%	45.35%
No. of laboratories after elimination of outliers		9	7	8	7	7	8
No. of measurement values without outliers		18	14	15	14	14	16

Table 9: Bis (2-ethylhexyl) phthalate (DEHP)[7] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		12	11	12	11	11	12
Mean	mg/l	0.101	0.028	0.602	0.150	0.741	1.032
Median	mg/l	0.099	0.026	0.654	0.180	0.709	1.115
Assigned value	mg/l	0.217	0.046	1.049	0.328	1.569	2.013
Rel. dev. assign. value		-54.4%	-43.5%	-37.7%	-45.1%	-54.8%	-44.6%
Repeatability s.d.	mg/l	0.017	0.005	0.206	0.016	0.122	0.266
Reproducibility s.d.	mg/l	0.019	0.011	0.238	0.063	0.465	0.563
Rel. repeatability s.d.		7.72%	11.54%	19.66%	4.82%	7.78%	13.20%
Rel. reproducibility s.d.		8.92%	24.15%	22.70%	19.11%	29.61%	27.96%

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Modified Horwitz s.d. **		20.13%	22.00%	15.88%	18.92%	14.95%	14.40%
HORRATR		0.44	1.10	1.43	1.01	1.98	1.94
Limit of repeatability, r (2.77 X sr)	mg/l	0.046	0.015	0.571	0.044	0.338	0.736
Limit of reproducibility, R (2.77 X sR)	mg/l	0.054	0.031	0.660	0.174	1.287	1.559
Rel. limit of repeatability		21.39%	31.98%	54.45%	13.36%	21.54%	36.55%
Rel. limit of reproducibility		24.70%	66.91%	62.87%	52.93%	82.03%	77.46%
No. of laboratories after elimination of outliers		10	10	12	9	11	12
No. of measurement values without outliers		20	20	23	18	22	24

Table 10: Di-n-octyl phthalate (DNOP)[8] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		11	10	11	10	9	10
Mean	mg/l	0.031	0.015	0.051	0.073	0.016	0.026
Median	mg/l	0.035	0.015	0.049	0.061	0.019	0.028
Assigned value	mg/l	0.086	0.031	0.059	0.114	0.036	0.054
Rel. dev. assign. value		-59.3%	-51.6%	-16.9%	-46.5%	-47.2%	-48.1%
Repeatability s.d.	mg/l	0.007	0.003	0.021	0.005	0.004	0.005
Reproducibility s.d.	mg/l	0.010	0.003	0.023	0.038	0.008	0.011
Rel. repeatability s.d.		7.84%	9.25%	36.33%	4.51%	11.18%	9.23%
Rel. reproducibility s.d.		11.50%	9.33%	38.90%	33.40%	23.32%	20.10%
Modified Horwitz s.d. **		22.00%	22.00%	22.00%	22.00%	22.00%	22.00%
HORRATR		0.52	0.42	1.77	1.52	1.06	0.91

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Limit of repeatability, r (2.77 X sr)	mg/l	0.019	0.008	0.059	0.014	0.011	0.014
Limit of reproducibility, R (2.77 X sR)	mg/l	0.027	0.008	0.064	0.105	0.023	0.030
Rel. limit of repeatability		21.73%	25.61%	100.62%	12.50%	30.97%	25.56%
Rel. limit of reproducibility		31.85%	25.85%	107.76%	92.52%	64.60%	55.66%
No. of laboratories after elimination of outliers		9	8	10	9	7	8
No. of measurement values without outliers		18	15	18	16	14	16

Table 11: Diisononyl phthalate (DINP)[9] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		9	8	10	8	8	9
Mean	mg/l	0.027	0.108	1.820	0.059	0.115	0.064
Median	mg/l	0.028	0.116	1.497	0.058	0.136	0.051
Assigned value	mg/l	0.054	0.242	3.134	0.104	0.271	0.057
Rel. dev. assign. value		-48.1%	-52.1%	-52.2%	-44.2%	-49.8%	-10.5%
Repeatability s.d.	mg/l	0.004	0.019	0.520	0.005	0.010	0.003
Reproducibility s.d.	mg/l	0.006	0.027	1.067	0.019	0.072	0.040
Rel. repeatability s.d.		8.14%	7.84%	16.60%	5.17%	3.83%	5.51%
Rel. reproducibility s.d.		10.27%	11.18%	34.06%	18.41%	26.60%	70.59%
Modified Horwitz s.d. **		20.00%	20.00%	20.00%	20.00%	20.00%	20.00%
HORRATR		0.51	0.56	1.70	0.92	1.33	3.53
Limit of repeatability, r (2.77 X sr)	mg/l	0.012	0.053	1.441	0.015	0.029	0.009

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Limit of reproducibility, R (2.77 X sR)	mg/l	0.015	0.075	2.957	0.053	0.200	0.111
Rel. limit of repeatability		22.55%	21.71%	45.99%	14.32%	10.61%	15.27%
Rel. limit of reproducibility		28.44%	30.98%	94.35%	50.99%	73.69%	195.53%
No. of laboratories after elimination of outliers		5	6	9	7	6	6
No. of measurement values without outliers		10	11	17	13	12	12

Table 12: Diisodecyl phthalate (DIDP)[10] *– Results of data evaluation*

		S001	**S002**	**S003**	**S004**	**S005**	**S006**
No. of laboratories that submitted compliant results		8	7	8	7	7	8
Mean	mg/l	0.096	0.103	0.677	0.152	0.186	1.828
Median	mg/l	0.102	0.107	0.540	0.152	0.181	1.660
Assigned value	mg/l	0.275	0.186	0.200	0.281	0.427	3.070
Rel. dev. assign. value		-62.9%	-42.5%	170.0%	-45.9%	-57.6%	-45.9%
Repeatability s.d.	mg/l	0.009	0.018	0.477	0.048	0.027	0.202
Reproducibility s.d.	mg/l	0.025	0.018	0.505	0.058	0.109	1.676
Rel. repeatability s.d.		3.42%	9.61%	238.49%	17.11%	6.27%	6.57%
Rel. reproducibility s.d.		9.11%	9.61%	252.34%	20.51%	25.43%	54.59%
Modified Horwitz s.d. **		20.00%	20.00%	20.38%	20.00%	20.00%	20.00%
HORRATR		0.46	0.48	12.38	1.03	1.27	2.73
Limit of repeatability, r (2.77 X sr)	mg/l	0.026	0.050	1.321	0.133	0.074	0.559

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Limit of reproducibility, R (2.77 X sR)	mg/l	0.069	0.050	1.398	0.160	0.301	4.642
Rel. limit of repeatability		9.46%	26.62%	660.61%	47.40%	17.37%	18.21%
Rel. limit of reproducibility		25.25%	26.62%	698.98%	56.82%	70.44%	151.21%
No. of laboratories after elimination of outliers		7	5	7	7	7	7
No. of measurement values without outliers		14	10	13	14	14	14

6. References

1. Report on the Method Performance Study of a Method to Determine Phthalates in Wine Determination of Ten Phthalates in Wine by Gas Chromatography Mass Spectrometry (GC-MS), Wenzl Thomas, Karasek Lubomir, Giri Anupam. Publications Office of the European Union 2015 doi :10.2787/666948 (online) https://publications.europa.eu/en/publication-detail/-/publication/b3ebef67-f1db-4fb2-97ce-bfc301c8ce68/language-en

[1] Type IV method

[2] Type II method

[3] Type II method

[4] Type II method

[5] Type II method

[6] Type II method

[7] Type IV method

[8] Type IV method

[9] Type IV method

[10] Type IV method

Certified in conformity Geneva, 19th July 2019
The Director General of the OIV
Secretary of the General Assembly
Pau Roca