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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)

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Executive Summary

The Institute for Reference Materials and Measurements (IRMM) organised in close collaboration with the International Organisation of Vine and Wine (OIV) a collaborative study to assess the performance of an analytical procedure for the determination of ten phthalates in wine by gas chromatography - mass spectrometry (GC-MS). The tested analytical procedure (OIV-MA-AS323-10:2013) was endorsed in June 2013 by the General Assembly of OIV and taken up in the *Compendium of International Methods of Analysis of Wines and Must.*

The design of the method performance study complied with provisions given in ISO 5725-2. It comprised the analysis of six different wine samples as blind duplicates. Test samples consisted of red wine, white wine (both supplied by the *SCL Laboratoire de Bordeaux*), and sweet wine, which was acquired in Belgium at a local store. The wines were spiked at IRMM with the analytes to levels suggested by OIV, bottled into ampoules, and dispatched to the participants of the validation study.

The participants of the study were identified by OIV. They comprised laboratories from Europe, Asia, South America and Australia.

The evaluation of the reported results was performed according to ISO 5725-2 and ISO 5725-4. It revealed acceptable precision of the analytical method for the determination of the analytes in most test materials. Relative standard deviations for reproducibility were mostly within the range of 9 % to 71 %. However, significant method related bias was observed for the determination of several analytes. The application of the analytical method for the determination of phthalates in contaminated wine samples could cause underestimations of the real content by up to about 60 %.

Abbreviations

Abbreviation	Full name
DMP*	Dimethyl phthalate
DEP*	Diethyl phthalate
DBP*	Dibutyl phthalate
DIBP*	Diisobutyl phthalate
DNOP*	Di-n-octyl phthalate
DINP*	Diisononyl phthalate
DIDP*	Diisodecyl phthalate
DEHP**	Bis(2-ethylhexyl) phthalate
BBP*	Benzylbutyl phthalate
DCHP*	Dicyclohexyl phthalate
OIV	International Organisation of Vine and Wine
IRMM	Institute for Reference Materials and Measurements
GC-MS	Gas chromatography mass spectrometry
$HORRAT_R$	Horrat value for reproducibility

* Abbreviations according to EN ISO 1043-3:1999 D

** The abbreviation according to EN ISO 1043-3 is DOP. However DEHP will be applied in this report for referring to bis(2-ethylhexyl) phthalate due to its wide spread use within the analytical community.

Introduction

1,2-Benzenedicarboxylic acid esters, which are commonly denoted as phthalates, form a group of compounds that is mainly used as plasticisers for polymers such as polyvinylchloride (PVC). Other areas of application are adhesives, paints, films, glues, and cosmetics. The number of potential different phthalates is infinite, despite only a few phthalates are produced at the industrial scale. The most important congeners are in that respect bis(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DIDP), and diisononyl phthalate (DINP). Due to their widespread application phthalates have become ubiquitous in the environment, e.g. Hubert et al. estimated the release of DEHP to the environment to about 1.8 % of the annual production (Hubert, Grasl-Kraupp et al. 1996). In addition, phthalates are stable in solution and are able to resist high temperature (Simoneau and Hannaert 1999). They degrade under exposure to sunlight and are readily metabolised under aerobic microbial activity.

Humans are exposed to phthalates via food, the air, water and other sources such as cosmetics or pharmaceutical products.

Food might be contaminated through the migration from packaging materials, via different kinds of environmental sources, or during processing. Consumer protection against high exposures to phthalates is achieved in the EU firstly via the definition of a positive list of substances that may be used for the production of food contact materials and secondly via the specification of specific migration limits (SMLs) (European Union 2012). Specific migration limits are applied also in other countries such as Peoples Republic of China, or are intended to be set such as in Malaysia (People's Republic of China 2008).The specific migration limit is defined in EU legislation as "the maximum permitted amount of a given substance released from the material or article into food or food simulants" (European Union 2011).

Chemical analysis of phthalates in food or food simulants is challenging due to the ubiquity of some members of this group of substances, resulting in an inherent risk of bias due to contamination of chemicals, consumables and analytical instruments.

Hence, it is necessary to provide robust and well characterised analysis methods for the reliable determination of phthalates in food.

The International Organisation of Vine and Wine (OIV) adopted in 2013 a gas chromatography - mass spectrometry (GC-MS) based analytical procedure for the determination of ten phthalates in wine (OIV 2013). The Institute for Reference Materials and Measurement (IRMM) organised in 2014 in close collaboration with OIV the validation of this GC-MS based analytical procedure by collaborative trial, in order to evaluate the performance of the method in different laboratories. This report provides details on the design of the study and the outcome of the method performance study.

Scope

The aim of this study was to assess by collaborative study the accuracy (precision and trueness) of the analytical procedure OIV-MA-AS323-10:2013 for the determination of phthalates in wine. The test samples consisted of white wine, red wine, and sweet wine. The tested substances comprised dimethly phthalate (DMP), diethyl phthalate (DEP) diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), dicyclohexyl phthalate (DCHP), bis-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate. The concentration levels were depending on the analyte in the range from about 0.03 mg/l to 3.1 mg/l. The study was organised and evaluated according to provisions given in ISO 5725-2 and ISO 5725-4 (International Organization for Standardization 1994, International Organization for Standardization 1994).

Participants in the study

Participants in the study were identified by OIV. Most of these laboratories participated also in a pre-trial, which was organised by the *Service commun des laboratoires (SCL) Laboratoire de Bordeaux*.

The organisers of the study would like to thank the participants in the study for their dedication to this project and in particular acknowledge the help of Mr Bernard Medina from *SCL Laboratoire de Bordeaux*. The participating organisations are listed in Table 1

Table 1: 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
Instituto Nacional de Vitivinicultura Departamento de Normas Analiticas Especiales	Argentina
Laboratorio Arbitral Agroalimentario	Spain
Laboatoire 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

The organizers of the study would also like to thank the *Shanghai CIQ Testing Center* for its efforts to participate in the study. However, it was not possible to supply this laboratory with test samples, as they were rejected at the Shanghai customs inspection.

Time frame

The study started end of February 2014 with dispatch of test samples. The laboratories were requested to submit analytical results by mid of April 2014. However, the deadline for submission of results was extended three times to finally mid of September 2014, in order to collect sufficient data for performing statistical data evaluation in compliance with ISO 5725-2. Stopping the collection of results earlier was not possible as it turned out that some laboratories did not report complete data sets. Consequently, the reduced number of data sets would have increased the uncertainty of the derived method performance indicators to an unacceptable level.

Design of the study

The design of the study was agreed with OIV. It comprised the analysis of, in total, twelve blind duplicate samples of white wine, red wine, and sweet wine, which were spiked with phthalates to agreed levels. The analytical procedure for the determination of phthalates was provided by OIV (OIV 2013).

The authors of this report informed OIV prior to the start of the study about issues regarding trueness of the analysis results obtained with the tested analytical procedure. Modifications for improving the performance of the analysis method were proposed to OIV. However, OIV preferred to stick to the analytical procedure as agreed by the General Assembly and as specified in OIV-MA-AS323-10:2013, and to subject this procedure to the method performance study. Details of the analytical procedure are given in ANNEX A.

Most participants in the study were able to familiarize with the analytical procedure in a pre-trial, which was organised by *Laboratoire SCL de Bordeaux*.

In addition to test samples, participants were supplied with a concentrated solution of stable isotope labelled phthalates, in order to eliminate potential restrictions in executing the analyses caused by the access to stable isotope labelled reference materials. This solution had to be used for the preparation of isotope labelled internal standard solutions. Unlabelled analytes had to be acquired by each participant on his/her own. Reporting of analytical results was performed via a dedicated electronic template, which was provided by the organisers.

Test materials

Preparation

The test materials for this collaborative study were white wine, red wine and sweet wine. The white wine and the red wine test materials were produced at *Laboratoire SCL de Bordeaux* under clean room conditions. These materials did not contain measureable quantities of the target analytes. The sweet wine was acquired at a local store. It contained low amounts of DBP.

The test materials were prepared gravimetrically by spiking of two litres of each of the three wines with phthalate standard solutions containing the ten different analytes. The standard solutions were prepared from neat reference materials purchased from Sigma-Aldrich (St. Louis, MO, USA). Single standard stock solutions of each analyte were produced by weighing of neat substances on a micro-balance followed by dissolution in gravimetrically added methanol. Six mixed standard solutions in methanol were prepared gravimetrically from these standard stock solutions, each of them containing the analytes at concentration levels corresponding to the scheme provided by OIV. Exactly 10 mL of the appropriate solution was added to each of the two batches of the three test wines in order to obtain six test materials. Table 2 provides the nominal concentrations of the six test materials. After spiking, each test material was homogenised by intensive stirring. Aliquots of about 20 mL of each test material were flame sealed under inert atmosphere in 25 mL amber glass ampoules. Two test samples were prepared from each of the six ampouled test materials by coding half of the respective ampoules with a different letter. Thereby twelve test samples were obtained, coded with letters from "A" to "H". The correspondence of test materials with test sample codes is indicated in Table 2 as well.

Participants also received a solution of eight stable isotope labelled phthalates in isooctane, which had to be used for the preparation of internal standard solutions. The mix of stable isotope labelled phthalates was also prepared gravimetrically from neat reference materials purchased from Sigma-Aldrich. The composition of this solution and the concentration values of stable isotope labelled analogues of the analytes are provided in Table 3. Aliquots of 1 mL of the mixed solution of stable isotope labelled phthalates were flame sealed under inert atmosphere in 5 ml amber glass ampoules. All ampoules got unique identifiers and were stored refrigerated at 4 °C.

In order to avoid contamination of the test materials by phthalates which might be present in solvents and in the laboratory environment, all solvents including isooctane, isohexane, methanol and ethanol were treated prior to their use with 20 g/l of aluminium oxide, which was activated in an oven for at least 6 hours at 400 °C. All amber glass ampoules were kept prior to their use for at least 12 hours in an oven at 400 °C, and consequently stored in desiccators over activated aluminium oxide.

Table 2: Nominal concentrations of phthalates after gravimetrical spiking of wine samples

Analyte	White wine		Red wine		Sweet wine	
	S001	S002	S003	S004	S005	S006
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
DMP	0.030	0.097	0.030	0.049	0.104	0.046
DEP	0.057	0.092	0.031	0.056	0.030	0.089
DIBP	0.035	0.076	0.058	0.107	0.061	0.045
DBP	0.107	0.281	0.057	1.039	0.032	0.153
BBP	0.057	0.029	0.037	0.088	0.087	0.053
DCHP	0.084	0.048	0.038	0.105	0.057	0.036
DEHP	0.217	0.046	1.049	0.328	1.569	2.013
DNOP	0.086	0.031	0.059	0.114	0.036	0.054
DINP	0.054	0.242	3.134	0.104	0.271	0.057
DIDP	0.275	0.186	0.052	0.281	0.427	3.070
Sample codes	A, H	C, I	E, J	F, G	D, K	B, L

Table 3: Solution of stable isotope labelled phthalates in isooctane; provided for preparation of internal standard solutions

Analyte	Concentration
	µg/mL
DMP-D_4	10.476
DEP-D_4	11.293
DIBP-D_4	11.667
DBP-D_4	10.542
BBP-D_4	12.346
DCHP-D_4	12.322
DEHP-D_4	11.652
DNOP-D_4	10.924

Homogeneity and stability

As the test materials consisted of well mixed solutions of the analytes in liquid matrices of low viscosity (wine), it was justified to assume homogeneity of the test materials. However, a number of 12 randomly selected ampoules were analysed in duplicate for confirmation of the nominal concentrations resulting from the gravimetric preparation of the test material. The contents of the randomly selected ampoules were analysed by GC-MS after liquid-liquid extraction. It shall be mentioned that spiking solutions and standard solutions used for instrument calibration were completely independent from each other. Attention was given to this fact in order to detect potential bias in the preparation of the spiked test materials. Significant differences between measured concentrations and nominal preparation concentrations were only found for DBP in the sweet wine test material, which was contaminated with a low level of DBP.

A modification of the analytical procedure OIV-MA-AS323-10:2013 was applied for the evaluation of homogeneity and stability of test samples (see ANNEX B

Figure B-1 in ANNEX B).

In brief, a wine sample aliquot (12.5 mL) was placed in a 50 mL centrifuge tube, 50 µL of the 10 mg/L isotope labelled internal standard solution (IS) in isooctane was added to each sample. The mixture was shaken vigorously for 30 min in order to equilibrate the

internal standard with the test sample. Afterwards, 6 mL of ethanol and 10 mL of isohexane were added and shaken vigorously (vortex) for 15 minutes. The mixture was then left in an ultrasonic bath for 30 minutes and centrifuged for 5 min at 2800 x g to accelerate phase separation. An aliquot of 8 mL was taken from the organic phase and transferred into a 10 mL test tube. The solvent was evaporated under a stream of nitrogen (0.3 bar) at 35 °C until about one mL of final extract was left. Evaporation to dryness was avoided as well as exceeding a temperature of 40 °C. The pre-concentrated sample extract was then transferred into an autosampler vial, and analysed by GC-MS with electron ionisation (EI) in selected ion monitoring (SIM) mode.

The stability of the test materials was evaluated by analysing the test material at the beginning of the study as well as after the deadline for reporting of results. Statistically significant differences of the results of analysis obtained before and after termination of the study were not found, thus indicating the stability of the test material.

Dispatch of samples

The samples were packed in cardboard boxes and shipped via express mail to the participants. The parcels were delivered mostly within 24 hours after dispatch. Each participant received together with the test samples an accompanying letter (ANNEX C), one 5 mL amber glass ampoule with isotope labelled internal standard mix in isooctane and twelve 25 mL amber glass ampoules containing the test materials of white wine (samples A, C, H and I), red wine (samples E, F, G and J) and sweet wine (samples B, D, K and L).

Evaluation of submitted results

Fourteen laboratories reported analysis results by September 2014. The individual results of the analysis of blind duplicate test samples (M1 and M2) as well as the mean of the reported results are presented per analyte/test material combination in ANNEX D.

The software package Prolab Pro® was used for the calculation of precision values, based on the reported data, according to ISO 5725-2. Only numerical results were included in the data evaluation. The evaluation of precision of the analysis method was

performed in three steps. They comprised in consecutive order the evaluation of systematic effects and exclusion of results from the evaluation which were biased due to potential calibration errors, the identification of statistical outliers and their elimination from the data set according to ISO 5725-2, and finally the calculation of precision parameters with the remaining data. Details on the evaluation of systematic effects are provided below.

Further-on the fitness-for-purpose of the calculated reproducibility standard deviation was evaluated. For this purpose, the calculated reproducibility relative standard deviation (RSD_R) was compared to the relative standard deviation derived from the modified Horwitz equation (RSD_{mH}), 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 ($HORRAT_R$). They were calculated according to Equation 1.

$$HORRAT_R = \frac{RSD_R}{RSD_{mH}} \qquad \textbf{Equation 1}$$

RSD_R: observed reproducibility relative standard deviation

$RSDs_{mH}$: relative standard deviation calculated from the modified Horwitz equation (Thompson 2000)

A $HORRAT_R$ value of 1.0 indicates that the reproducibility standard deviation calculated from the reported analysis results is equal to the standard deviation derived from the modified Horwitz equation. For guidance, European legislation on "methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo[*a*]pyrene in foodstuffs" considers $HORRAT_R$ values of less than two fit-for-purpose (European Union 2011).

Analytical method related bias was assessed in addition to precision. Two parameters were calculated to this end. The relative deviation of the median of reported results from the nominal preparation concentration aims to identify the magnitude of deviation, and the evaluation of the data according to ISO 5725-4 indicates whether the deviation from the nominal preparation concentration is statistically significant. This analysis determines the 95 % confidence intervals for the bias of the measurement method taking into account for a given analyte in a given test material the within laboratory variability, the between laboratory variability, the grand mean of the analyte

content, the uncertainty of the estimate of bias depending on the experimental design, and the true value of the analyte content.

Despite the true values of the analyte contents in the test materials are not known, it is justified to consider the gravimetrical preparation concentrations as good approximations of the true values. The uncertainty of the gravimetrical preparation concentration is not taken into account by ISO 5725-4. The assessment of bias was omitted for dibutyl phthalate in the sweet wine sample for which the assumption of agreement of the true value with the preparation concentration cannot be maintained due to contamination of the native test material. Repeatability and reproducibility standard deviations were applied in the calculations as indicators for the within laboratory variability and between laboratory variability.

Evaluation of systematic effects

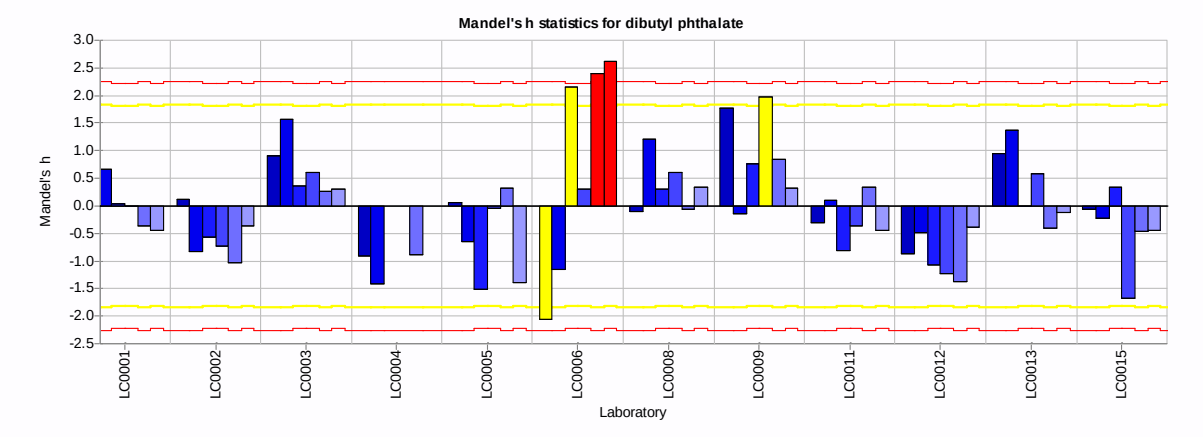
The first step of the data evaluation was the identification of laboratories that deviated significantly from the analytical protocol either intentionally, or unintentionally. Data obtained by the application of such procedures would be considered incompatible with data generated by the tested procedure. Such discordant data have to be removed from the data set according to ISO 5725-2.

Unintended deviations resulting in significant bias were tried to identify by scrutinising the performance of a particular laboratory for a particular analyte across samples. ISO 5725-2:1994 suggests using Mandel's *h* and Mandel's *k* plots for that purpose. The Mandel's *h* statistics indicates whether the mean of the replicate analyses of a particular sample deviates from the grand mean value of all results more than a certain multiple of the standard deviation of the mean results reported for this sample by all participants. The Mandel's *k* statistic compares the within laboratory standard deviation for the measurement of a particular substance in a particular sample with the pooled standard deviation of all participants reporting data for this particular analyte/sample combination. As for the Mandel's *h* statistics thresholds for suspicious performance are set on the 5% significance level and for outliers at the 1 % significance level.

Figure 1 shows as an example the Mandel's *h* plot for the determination of dibutyl phthalate in the six test samples. The columns represent for each participant from left to

right Mandel's *h* values for the test samples S001 (white wine), S006 (sweet wine), S002 (white wine), S005 (sweet wine), S003 (red wine) and S004 (red wine). (Mandel's *h* values exceeding the 5 % significance level are presented as yellow bars, whereas Mandel's *h* values exceeding the 1 % significance threshold are given as red bars.

Figure 1: Mandel's *h* plot for dibutyl phthalate



Mandel's *h* and Mandel's *k* plots are given for all other analytes in the following section.

However, it has to be mentioned that large bias in the results reported by participants might affect the sharpness of the Mandel's *h* test, as the standard deviation of the grand mean might be significantly increased.

Laboratories reporting results that exceeded for one or more analytes consistently 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 correctness of reported analytical results.

Table 4 provides an overview on the outcome of the root-cause-analyses performed by the laboratories and gives information on the decision taken by the study organisers.

Table 4: Outcome of root-cause-analysis and decision taken for data evaluation

Laboratory	Reason provided by the laboratory	Consequences
LC0014	The laboratory was informed about significant systematic deviations from the assigned values. The laboratory suspected a mistake in the preparation of calibration solutions as cause for the deviations. Evidence for the mistake could not be provided as calibration solutions were used only for the purpose of this study, without verification of their concentrations against independent solutions.	All results were excluded from the data evaluation

Statistical outlier tests and elimination of results from data evaluation

Grubbs tests for outlying mean values of the blind duplicates, as well as Cochran's test for excessive variability of the reported blind duplicate results were executed as defined in ISO 5725-2. The tests were repeated after elimination of the outliers identified in the first iteration. However, at maximum two out of nine data sets were eliminated from the data pool.

Results identified as outliers are flagged in the tables presenting the average results reported by the participants for a given analyte in the different test materials by letters, which are placed to the right of the respective value.

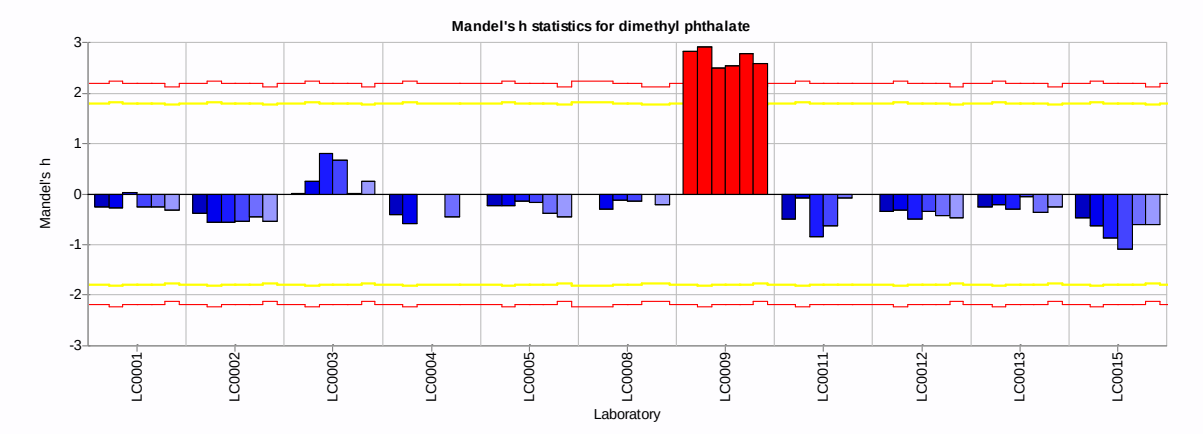
Evaluation of reported results per analyte

Dimethyl phthalate (DMP)

Table 5: DMP - Average results reported by participants and results of outlier tests

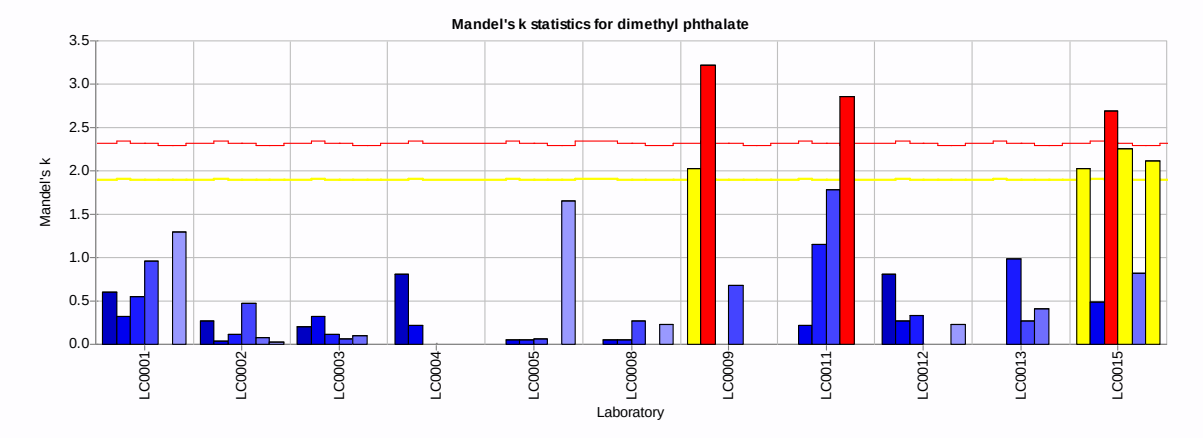
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.021		0.071		0.022		0.030		0.054		0.028	
LC0002	0.017		0.047		0.015		0.023		0.042		0.019	
LC0003	0.032		0.102		0.032		0.052		0.093		0.045	
LC0004	0.016		not tested		0.015		not tested		not tested		0.018	
LC0005	0.023		0.064		0.017		0.026		0.058		0.029	
LC0008	< 0.010		0.065		< 0.010		0.035		0.059		0.028	
LC0009	0.135	B	0.170		0.130	B	0.140	B	0.175	B	0.130	C
LC0011	0.013		0.036		0.028	C	< 0.010		0.038		0.034	
LC0012	0.019		0.049		0.016		0.025		0.050		0.027	
LC0013	0.022		0.057		0.018		0.033		0.062		0.030	
LC0014	0.197	NC	0.588	NC	0.164	NC	0.275	NC	0.563	NC	0.255	NC
LC0015	0.014		0.034	C	0.009		0.020		0.018		0.017	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 2: Mandel's h plot for DMP



From left to right: S001, S006, S002, S005, S003, S004

Figure 3: Mandel's k plot for DMP



From left to right: S001, S006, S002, S005, S003, S004

Table 6: DMP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	significant	significant	significant	significant	significant
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 %
$HORRAT_R$		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
No. of measurement values without outliers		18	18	15	16	18	20

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, 11 to 12 sets of analysis results were received from the participants. Ten to 11 of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's h plot indicates for laboratory LC0009 significant deviation from the mean value for all test materials. The statistical outlier tests identified the results reported by laboratory LC0009 for five out of six test materials as outliers. The results of this laboratory for test material S002 (white wine) were kept in the data set in order to comply with the criterion of eliminating at maximum two out of nine results.

In general higher variability of results reported for test material S002 is reflected in the magnitude of the reproducibility standard deviation, which is in relative terms twice as high as for the other four test materials. $HORRAT_R$ values were for all materials but S002 around 1.0, which indicates good agreement with the target level of precision. A $HORRAT_R$ value of 1.93 was calculated for S002, which however would be still considered fit-for-purpose.

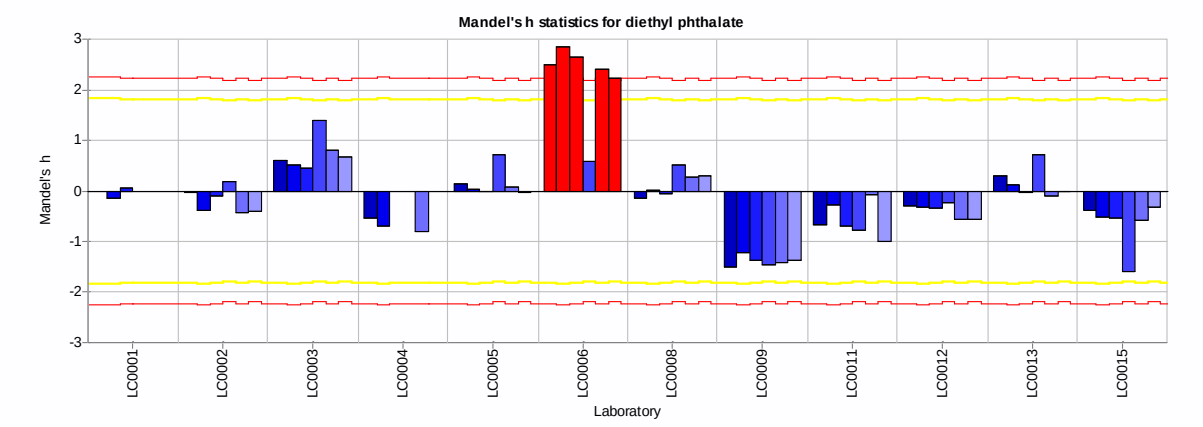
The relative deviations of the median values from the preparation concentrations were about -40 %. The data evaluation according to ISO 5725-4 identified for all test materials significant method related bias.

Diethyl phthalate (DEP)

Table 7: DEP - Average results reported by participants and results of outlier tests

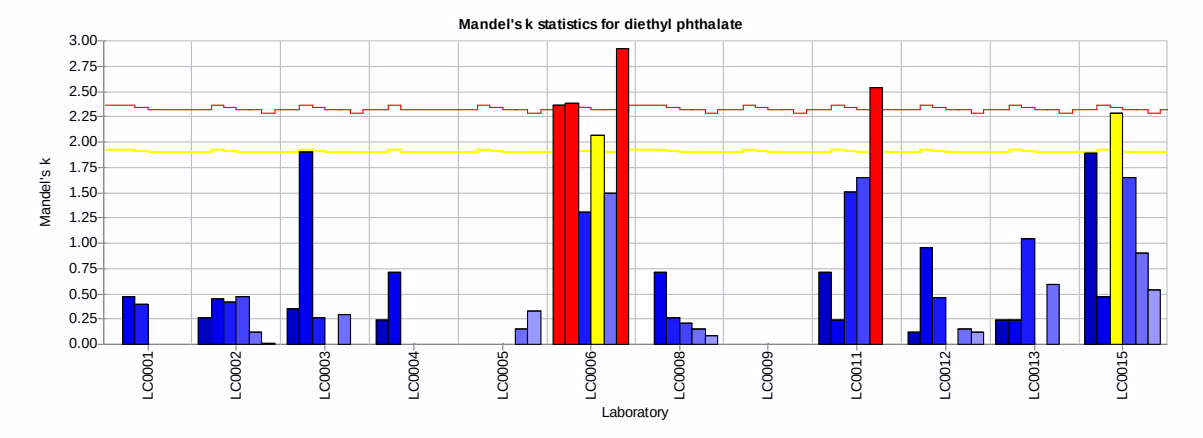
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	< 0.060		0.081		not tested		< 0.060		not tested		0.064	
LC0002	0.047		0.073		0.024		0.035		0.022		0.054	
LC0003	0.063		0.101		0.042		0.064		0.031		0.090	
LC0004	0.034		not tested		0.019		not tested		not tested		0.041	
LC0005	0.051		0.078		0.032		0.045		0.026		0.071	
LC0006	0.110		0.210	B	0.065		0.105	C	0.025		0.185	B
LC0008	0.044		0.076		0.035		0.054		0.025		0.070	
LC0009	0.010		0.010		0.010		0.010		0.010		0.020	
LC0011	0.031		0.044		0.029		0.020		0.015		0.058	
LC0012	0.041		0.061		0.022		0.032		0.019		0.056	
LC0013	0.055		0.077		0.029		0.046		0.026		0.074	
LC0014	0.506	NC	0.784	NC	0.283	NC	0.442	NC	0.235	NC	0.663	NC
LC0015	0.038		0.052		0.022		0.037		0.009		0.048	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 4: Mandel's h plot for DEP



From left to right: S001, S006, S002, S005, S003, S004

Figure 5: Mandel's k plot for DEP



From left to right: S001, S006, S002, S005, S003, S004

Table 8: DEP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		insignificant	significant	insignificant	significant	significant	significant
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 %
HORRAT$_R$		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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, 12 to 13 sets of analysis results were received from the participants. Eleven to 12 of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's h plot indicates for laboratory LC0006 significant deviation from the mean value for five out of six test materials. The statistical outlier tests identified for laboratory LC0006 the results reported for three test materials as outliers.

Reproducibility relative standard deviations were in the range between about 21 % and about 48 %, while all repeatability relative standard deviations were below 15.3 %. $HORRAT_R$ values were in average higher than for DMP, and reached a maximum of 2.18. The calculated data did not indicate any obvious correlation between precision values and analyte content levels.

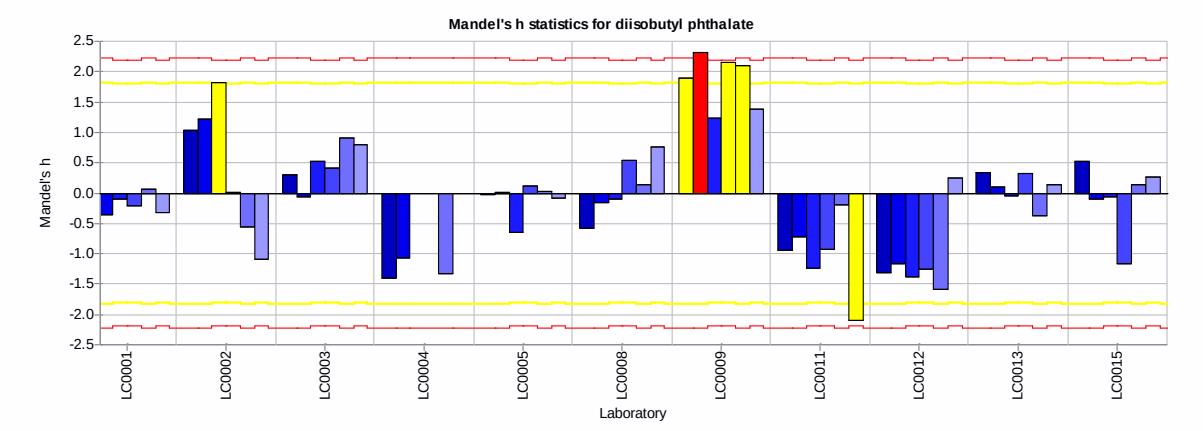
The relative deviations of the median values from the preparation concentrations were between -6.5 % and -31.5 %. However, the relative deviations of the medians from the assigned values were for two third of the test materials higher than 20%. The data evaluation according to ISO 5725-4 identified for the majority of test materials significant method related bias. Insignificant bias was concluded for S003 (red wine) for which the median agreed well with the assigned value, and for S001 (white wine), which was characterised by a high reproducibility standard deviation, causing low power of the test.

Diisobutyl phthalate (DIBP)

Table 9: DIBP - Average results reported by participants and results of outlier tests

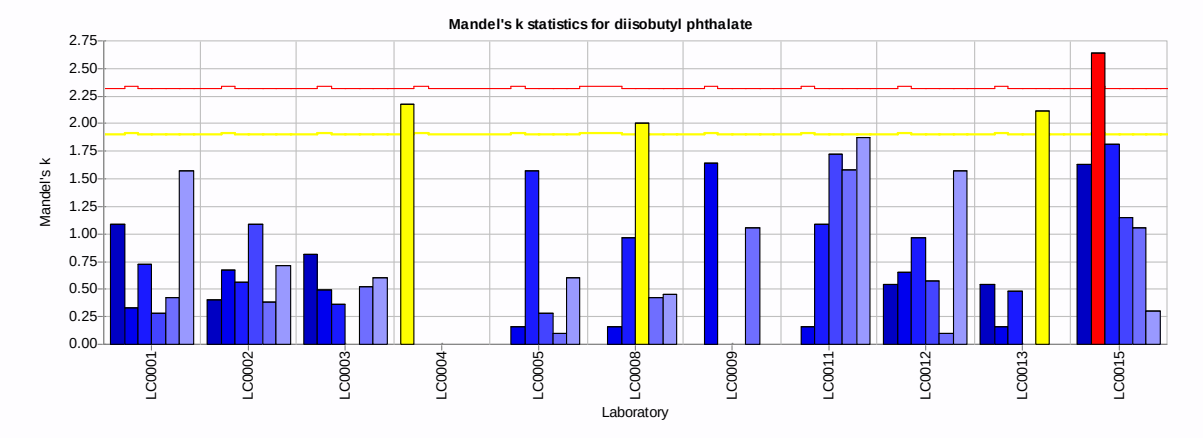
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.048		0.085		0.077		0.112		0.051		0.042	
LC0002	0.061		0.121		0.069		0.095		0.054		0.061	
LC0003	0.052		0.097		0.088		0.137		0.059		0.045	
LC0004	0.034		not tested		0.058		not tested		not tested		0.033	
LC0005	0.049		0.075		0.076		0.117		0.056		0.046	
LC0008	0.043		0.085		0.078		0.136		0.060		0.044	
LC0009	0.070		0.110		0.105		0.150		0.080		0.075	
LC0011	0.039		0.064		0.074		0.072		0.043		0.037	
LC0012	0.035		0.061		0.054		0.125		0.039		0.032	
LC0013	0.053		0.086		0.071		0.122		0.058		0.048	
LC0014	0.418	NC	0.744	NC	0.617	NC	0.981	NC	0.475	NC	0.366	NC
LC0015	0.055		0.085		0.078		0.125		0.040		0.045	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 6: Mandel's h plot for DIBP



From left to right: S001, S006, S002, S005, S003, S004

Figure 7: Mandel's k plot for DIBP



From left to right: S001, S006, S002, S005, S003, S004

Table 10: DIBP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	insignificant	significant	significant	insignificant	insignificant
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 %
HORRAT$_R$		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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, 11 to 12 sets of analysis results were received from the participants. Ten to 11 of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's *h* and Mandel's *k* plots indicated some significant or at least suspicious deviations from the mean values respectively from the average variabilities. However, statistically significant outliers were not identified.

Reproducibility relative standard deviations were in the range between about 20 % and about 32 %, while almost all repeatability relative standard deviations were below 10.0 %. $HORRAT_R$ values were all below 1.5, with the majority close to 1.0. The highest values were found for the lowest analyte concentrations. However, precision values were rather constant at concentration levels above about 0.06 mg/l and the highest tested concentration of about 0.11 mg/l.

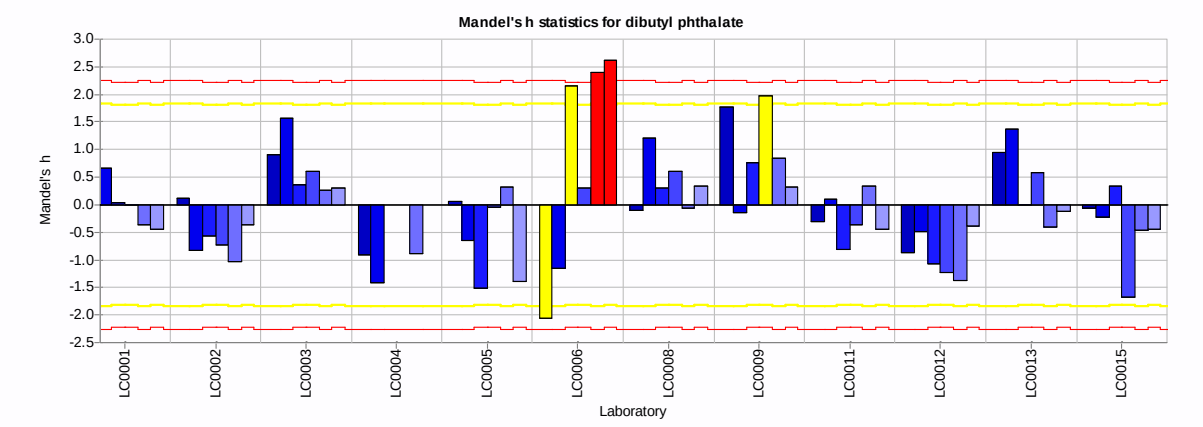
The relative deviations of the median values from the preparation concentrations were between about -10 % and + 40 %. The latter value seems to be high; however, one must consider that the analyte concentration in the test materials was close to the lower limit of the working range of the method. The difference was in absolute terms only 0.014 mg/l. Similar absolute overestimations were found for the second white wine test material (S002) and the two red wine test materials (S003 and S004). Exact match of slight negative bias was found for the sweet wine test materials. A link between magnitude of bias and type of test material can, based on the available information, neither be confirmed nor excluded. The data evaluation according to ISO 5725-4 identified for half of the test materials significant method related bias. Insignificant bias was concluded for test materials with the best match of assigned values and median values.

Dibutyl phthalate (DBP)

Table 11: DBP - Average results reported by participants and results of outlier tests

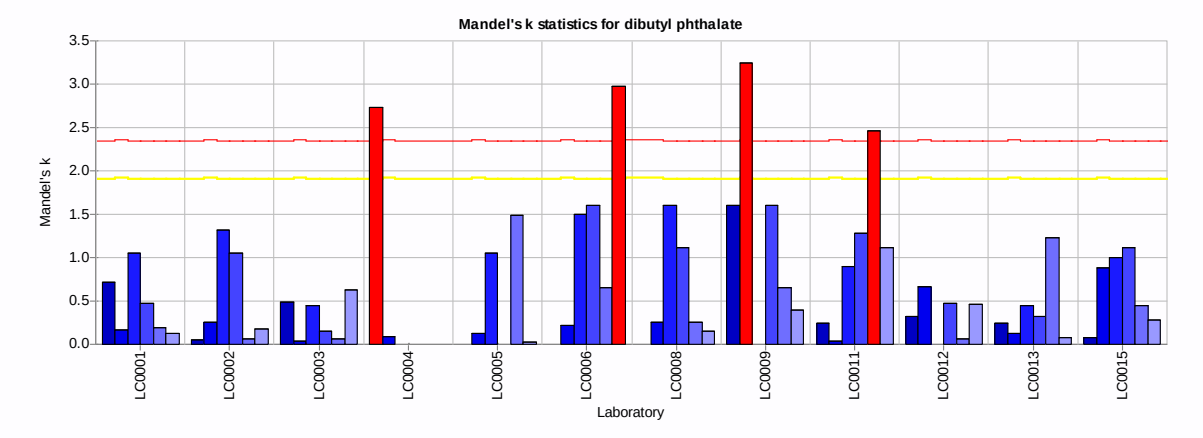
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.113		0.266		0.072		0.621		0.089		0.191	
LC0002	0.105		0.237		0.058		0.666		0.077		0.162	
LC0003	0.122		0.280		0.084		1.067		0.101		0.209	
LC0004	0.084		not tested		0.061		not tested		not tested		0.150	
LC0005	0.104		0.194		0.084		0.050		0.089		0.165	
LC0006	0.060		0.365		0.125		2.450	C	0.095		0.155	
LC0008	0.101		0.278		0.077		1.091		0.101		0.202	
LC0009	0.140		0.300		0.095		1.080		0.125		0.175	C
LC0011	0.097		0.226		0.085		0.623		0.083		0.180	
LC0012	0.085		0.214		0.051		0.649		0.068		0.168	
LC0013	0.122		0.264		0.071		0.815		0.100		0.205	
LC0014	0.996	NC	2.481	NC	0.609	NC	7.798	NC	0.850	NC	1.705	NC
LC0015	0.102		0.280		0.070		0.612		0.059		0.173	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 8: Mandel's h plot for DBP



From left to right: S001, S006, S002, S005, S003, S004

Figure 9: Mandel's k plot for DBP



From left to right: S001, S006, S002, S005, S003, S004

Table 12: DBP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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
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%		
Bias*		insignificant	insignificant	significant	significant		
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 %
HORRAT$_R$		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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, 12 to 13 sets of analysis results were received from the participants. Eleven to 12 of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's *h* and Mandel's *k* plots indicated some significant or at least suspicious deviations from the mean values respectively from the average variabilities. However, only two statistical significant outliers were detected and excluded from further calculations.

Reproducibility relative standard deviations were in the range between about 15 % and about 57 %, while most repeatability relative standard deviations were below 10.0 %. $HORRAT_R$ values were with the exception of test material S005 (sweet wine) all below 2.0, with half of the values below 1.0. The highest values were found for the lowest analyte concentrations. Reproducibility relative standard deviations decreased to a level of about 20 % for analyte concentrations in the range of 0.1 mg/l to 0.3 mg/l.

The relative deviations of the median values from the preparation concentrations were for the two white wine test materials (S001 and S002), rather low. Higher values were encountered for the red wines. This evaluation was omitted for the sweet wine test materials, as the native test materials contained already DBP. A correlation between bias and type of test material was not found, as positive bias was identified for the red wine test material with low analyte content, and significant negative bias for the red wine test material with the overall highest DBP concentration. The high underestimation cannot be explained with the available data.

The data evaluation according to ISO 5725-4 identified for the determination of DBP in both red wine test materials significant method related bias.

Insignificant bias was concluded for test materials with the best match of assigned values and median values.

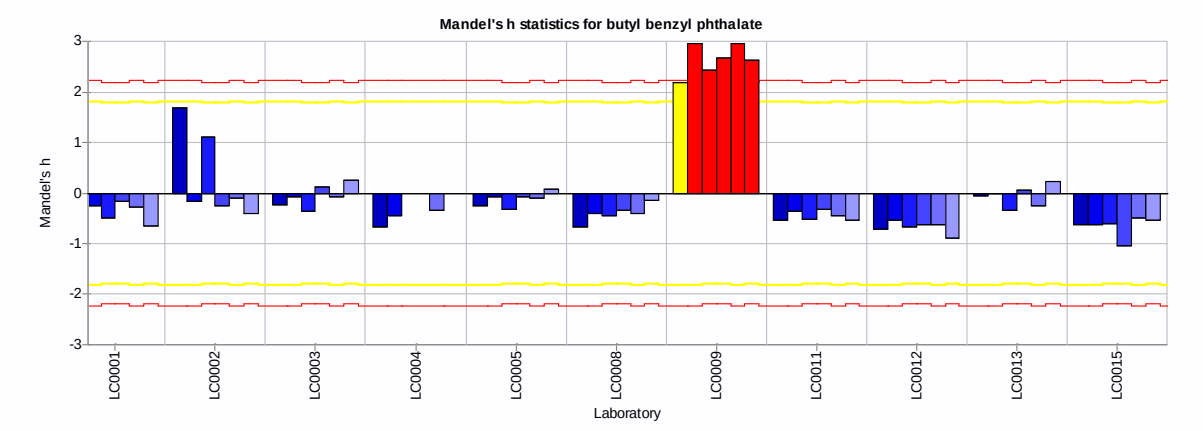
In summary, the analysis method should be suitable for the determination of DBP in wines within the concentration range of about 0.1 mg/l and about 0.3 mg/l. Attention has to be given to contamination issues, which might have significant effects especially at concentration levels below 0.1 mg/l. The high underestimation at high concentrations needs further investigation.

Benzylbutyl phthalate (BBP)

Table 13: BBP - Average results reported by participants and results of outlier tests

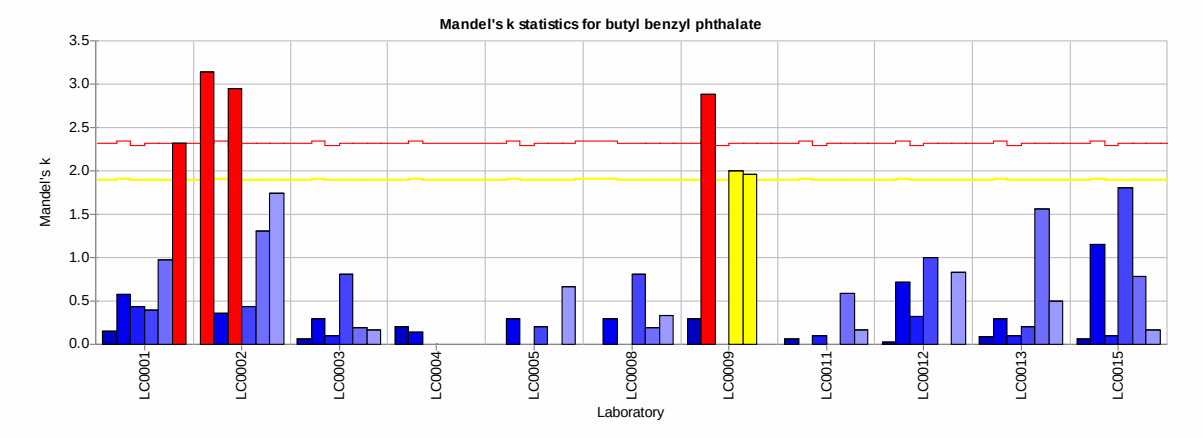
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.050		0.025		0.034		0.065		0.080		0.051	
LC0002	0.119	C	0.071	C	0.038		0.071		0.077		0.054	
LC0003	0.056		0.029		0.038		0.088		0.092		0.057	
LC0004	0.041		not tested		0.032		not tested		not tested		0.044	
LC0005	0.055		0.030		0.038		0.084		0.084		0.057	
LC0008	0.042		0.026		0.030		0.078		0.073		0.046	
LC0009	0.135	B	0.110	B	0.115	B	0.150	B	0.195	B	0.160	C
LC0011	0.046		0.025		0.029		0.068		0.074		0.047	
LC0012	0.041		0.020		0.025		0.058		0.061		0.041	
LC0013	0.061		0.029		0.034		0.087		0.089		0.059	
LC0014	0.447	NC	0.247	NC	0.272	NC	0.672	NC	0.724	NC	0.449	NC
LC0015	0.043		0.021		0.028		0.068		0.044		0.038	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 10: Mandel's h plot for BBP



From left to right: S001, S006, S002, S005, S003, S004

Figure 11: Mandel's k plot for BBP



From left to right: S001, S006, S002, S005, S003, S004

Table 14: BBP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	insignificant	significant	significant	insignificant	insignificant
Repeatability s.d.	mg/l	0.002	0.001	0.003	0.004	0.003	0.003
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 %
HORRAT$_R$		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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, 11 to 12 sets of analysis results were received from the participants. Ten to 11 of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's *h* and Mandel's *k* plots indicated for almost all results reported by laboratory LC0009 significant deviations from the mean values. Significant respectively suspicious exceedance of average variabilities were identified for the participants LC0009, LC001 and LC0002. Consequently, statistical outlier testing identified results reported by LC0009 for all test materials and results reported by LC002 for two test materials as outliers. They were excluded from further calculations. Reproducibility relative standard deviations were for all test materials in the range of about 13 % to about 17 %. Repeatability relative standard deviations were at maximum 8.1 %. $HORRAT_R$ values were for all test materials below 0.77 and seemed to be rather constant over the tested concentration range.

The relative deviations of the median of reported values from the preparation concentrations were for all test materials rather low.

The data evaluation according to ISO 5725-4 identified for the determination of BBP in both red wine test materials significant method related bias. However, this finding has to be put into perspective as the absolute differences between assigned value and median of reported results were at maximum 0.013 mg/l.

Insignificant bias was concluded for the other test materials.

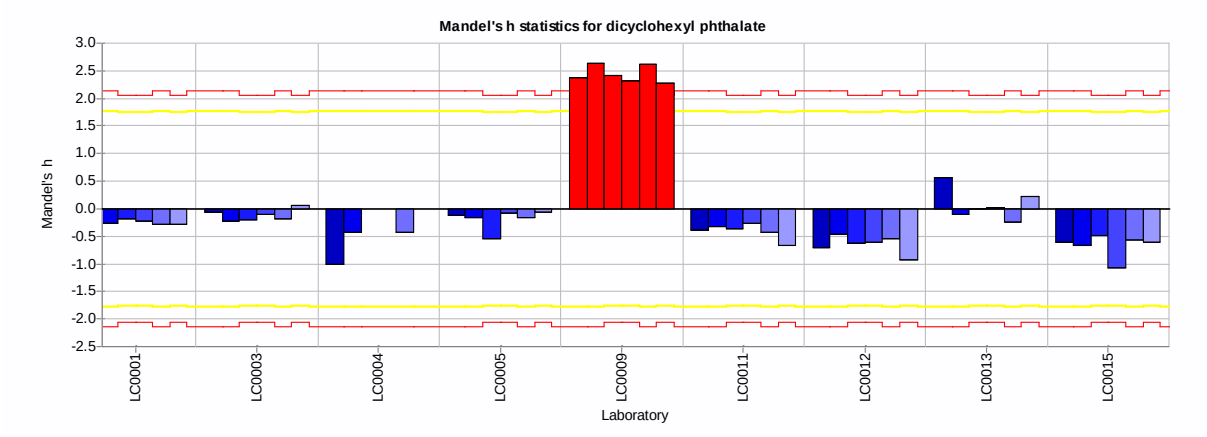
In summary, the analysis method may be considered suitable for the determination of BBP in wines within the tested concentration range.

Dicyclohexyl phthalate (DCHP)

Table 15: DCHP - Average results reported by participants and results of outlier tests

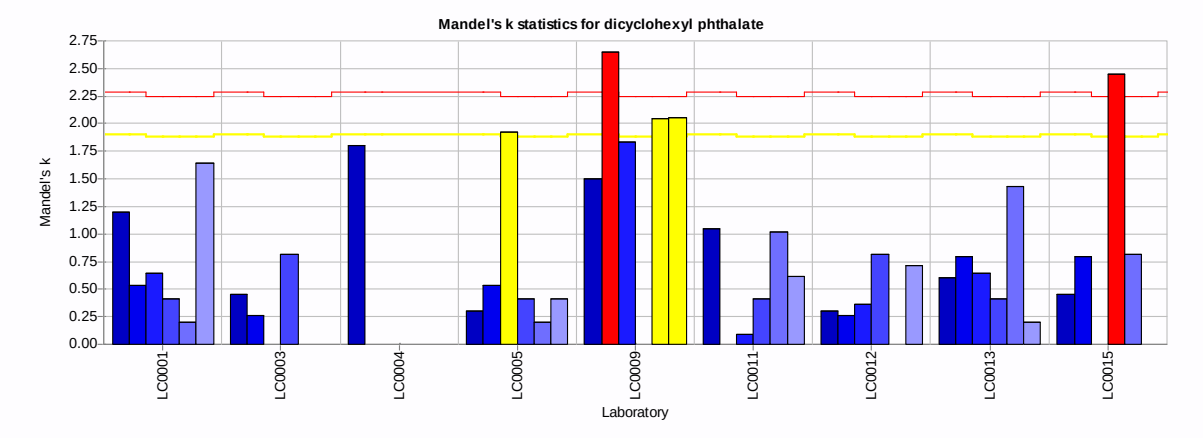
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.078		0.046		0.033		0.089		0.049		0.033	
LC0003	0.077		0.046		0.035		0.097		0.052		0.035	
LC0004	0.055		not tested		0.028		not tested		not tested		0.028	
LC0005	0.076		0.036		0.036		0.094		0.052		0.036	
LC0009	0.135		0.120	B	0.115	B	0.150	B	0.120	B	0.125	C
LC0011	0.070		0.042		0.028		0.080		0.048		0.031	
LC0012	0.062		0.034		0.025		0.074		0.038		0.026	
LC0013	0.092		0.052		0.034		0.101		0.056		0.038	
LC0014	0.605	NC	0.390	NC	0.239	NC	0.753	NC	0.423	NC	0.268	NC
LC0015	0.065		0.038		0.024		0.081		0.025		0.020	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 12: Mandel's h plot for DCHP



From left to right: S001, S006, S002, S005, S003, S004

Figure 13: Mandel's k plot for DCHP



From left to right: S001, S006, S002, S005, S003, S004

Table 16: DCHP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		insignificant	insignificant	significant	significant	insignificant	insignificant
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 %
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 %
HORRAT$_R$		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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, nine to ten sets of analysis results were received from the participants. Eight to nine of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's *h* and Mandel's *k* plots indicated for all results reported by laboratory LC0009 significant deviations from the mean values. Significant respectively suspicious exceedance of average variabilities were identified for the participants LC0009, LC0015 and LC0005. Consequently conducted statistical outlier testing identified results reported by LC0009 for five out of six test materials as outliers. They were excluded from further calculations.

Reproducibility relative standard deviations were for all test materials in the range of about 10 % to about 28 %. Repeatability relative standard deviations were at maximum 13.1 %. $HORRAT_R$ values were for all test materials, except S001, below 1.0.

The relative deviations of the median of reported values from the preparation concentrations were for all test materials slightly negative.

The data evaluation according to ISO 5725-4 did not identify any significant method related bias.

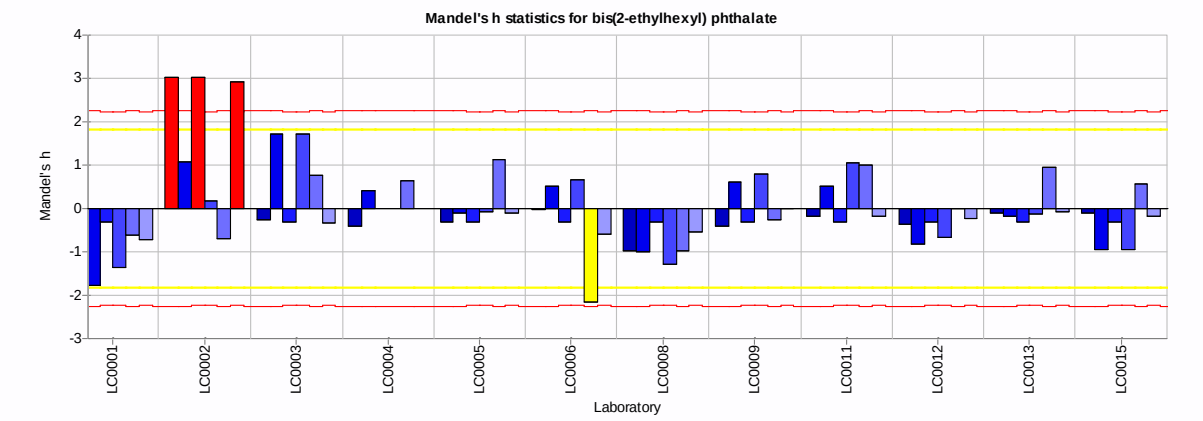
In summary, the analysis method may be considered suitable for the determination of DCHP in wines within the tested concentration range.

Bis(2-ethylhexyl) phthalate (DEHP)

Table 17: DEHP - Average results reported by participants and results of outlier tests

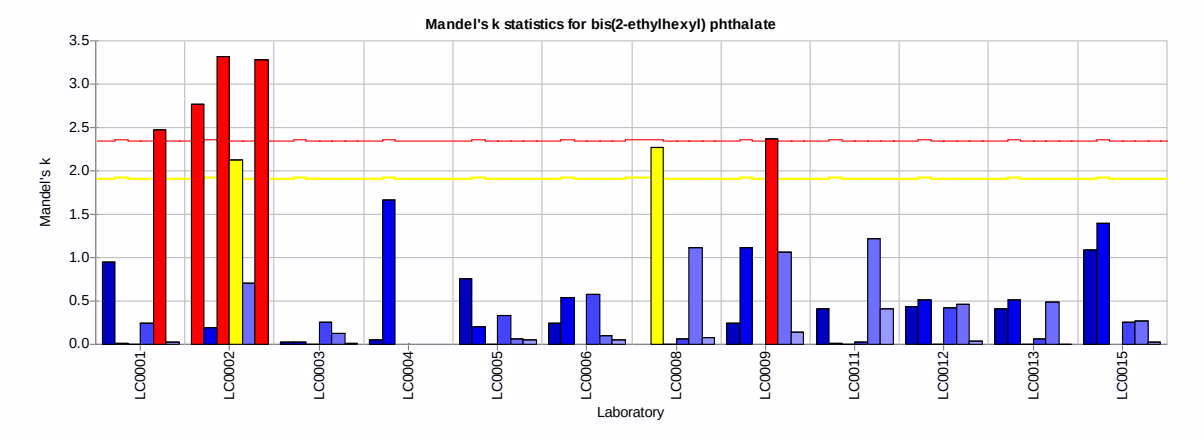
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.084		0.020		0.486		0.051		0.126		0.088	
LC0002	0.454	C	24.781	C	0.473		0.929	C	0.826		1.605	
LC0003	0.102		0.024		0.745		0.142		1.524		1.944	
LC0004	0.086		not tested		0.725		not tested		not tested		1.256	
LC0005	0.095		0.026		0.813		0.202		0.709		0.975	
LC0006	0.125		0.010		0.195		0.080		1.050		1.300	
LC0008	0.023	B	0.025		0.417		0.094		0.151		0.498	
LC0009	0.085		0.050		0.555		0.225		1.105		1.360	
LC0011	0.110		0.035		0.789		0.180	C	1.222		1.305	
LC0012	0.091		0.025		0.602		0.166		0.441		0.595	
LC0013	0.117		0.032		0.781		0.204		0.685		0.935	
LC0014	0.418	NC	0.160	NC	5.778	NC	1.171	NC	4.931	NC	7.470	NC
LC0015	0.118		0.031		0.707		0.182		0.313		0.526	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 14: Mandel's h plot for DEHP



From left to right: S001, S006, S002, S005, S003, S004

Figure 15: Mandel's k plot for DEHP



From left to right: S001, S006, S002, S005, S003, S004

Table 18: DEHP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	significant	significant	significant	significant	significant
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 %
Modified Horwitz s.d. **		20.13 %	22.00 %	15.88 %	18.92 %	14.95 %	14.40 %
HORRAT$_R$		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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, twelve to thirteen sets of analysis results were received from the participants. Eleven to twelve of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's *h* and Mandel's *k* plots indicated for half of the results reported by laboratory LC0002 significant deviations from the mean values, as well as significant exceedance of average variabilities. Consequently conducted statistical outlier testing identified these results as outliers as well as results reported by LC0008, and LC0011 for one test material each. They were excluded from further calculations.

Reproducibility relative standard deviations were for all test materials in the range of about 9 % to about 30 %. Repeatability relative standard deviations were at maximum 19.7 %. $HORRAT_R$ values were for all test materials, except S001, between 1.0 and 2.0.

The relative deviations of the median of reported values from the preparation concentrations were for all test materials negative, and in the range between -38 % and -55 %.

The data evaluation according to ISO 5725-4 identified for the analysis of all test materials significant method related bias.

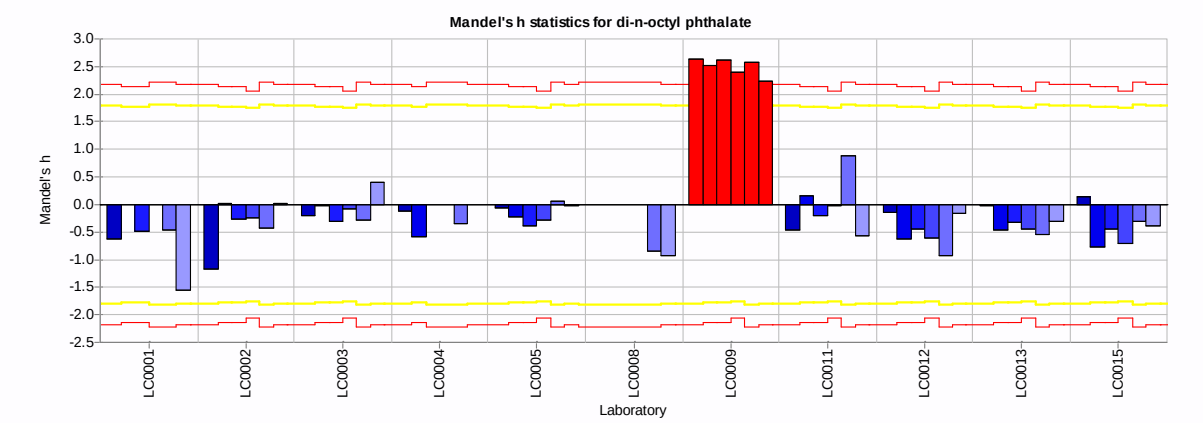
In summary, the analysis method may be considered suitable for the determination of DEHP in wines with regard to analytical precision. However, method related bias will lead to underestimations of DEHP concentrations by about 40 % to 55 %.

Di-n-octyl phthalate (DNOP)

Table 19: DNOP - Average results reported by participants and results of outlier tests

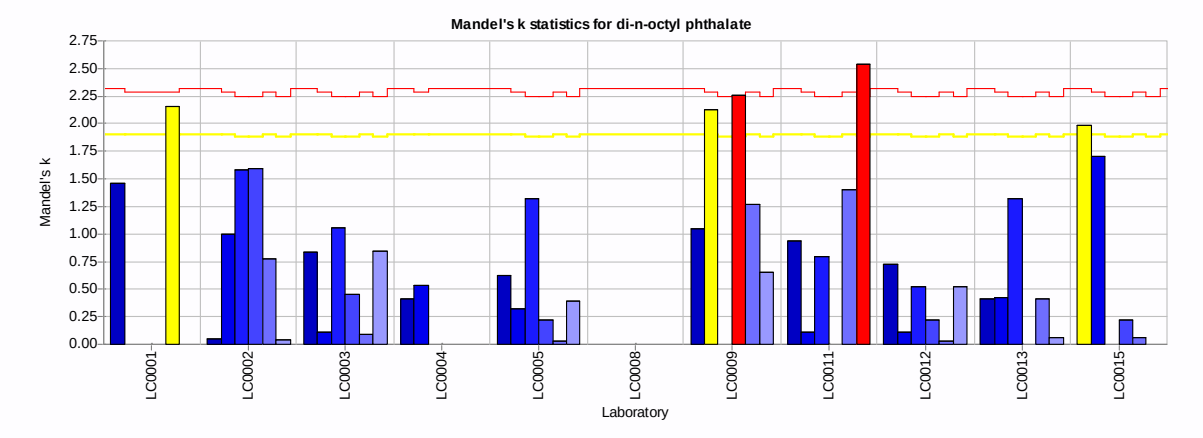
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	0.024		0.012		0.045		0.011		not tested		not tested	
LC0002	0.012		0.017		0.046		0.071		0.02		0.036	
LC0003	0.033		0.016		0.052		0.085		0.024		0.035	
LC0004	0.035		not tested		0.049		not tested		not tested		0.018	
LC0005	0.036		0.015		0.064		0.069		0.018		0.028	
LC0008	< 0.020		< 0.020		0.032		0.035		< 0.020		< 0.020	
LC0009	0.095	B	0.08	B	0.15	B	0.155		0.1	B	0.11	B
LC0011	0.028		0.019		0.092		0.049	C	0.026		0.04	
LC0012	0.035		0.013		0.029		0.064		0.008		0.017	
LC0013	0.037		0.015		0.042		0.058		0.013		0.021	
LC0014	0.163	NC	0.091	NC	0.587	NC	0.394	NC	0.106	NC	0.159	NC
LC0015	0.041		0.013		0.051		0.055		0.005		0.012	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 16: Mandel's h plot for DNOP



From left to right: S001, S006, S002, S005, S003, S004

Figure 17: Mandel's k plot for DNOP



From left to right: S001, S006, S002, S005, S003, S004

Table 20: DNOP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	significant	insignificant	significant	significant	significant
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 %
HORRAT$_R$		0.52	0.42	1.77	1.52	1.06	0.91
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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Summary of evaluation for DEHP

Depending on the test material, 10 to 12 sets of analysis results were received from the participants. Nine to eleven of the data sets were obtained by analyses compliant with the analytical protocol. The Mandel's *h* plot indicated for all results reported by laboratory LC0009 significant deviations from the mean values. Significant exceedance of average variability is indicated by the Mandel's *k* plot for the results reported by LC0009 and LC0011 for one test material each. Consequently conducted statistical outlier testing identified these results as outliers. They were excluded from further calculations.

Reproducibility relative standard deviations were for all test materials in the range of about 9 % to about 39 %. Repeatability relative standard deviations were at maximum 36.3 %, with the majority of values below 10 %. $HORRAT_R$ values were for all test materials below 2.0.

The relative deviations of the median of reported values from the preparation concentrations were for all test materials negative, and in the range between -16 % and -60 %, with the majority of values lying in the range between -45 % and – 60 %

The data evaluation according to ISO 5725-4 identified for the analysis of all test materials except S003 significant method related bias. The results for S003 could be influenced by the high concentration of DINP in the test material, which coelutes with DNOP, causing low within laboratory precision. The rather low deviation from the assigned value in combination with high precision values does not allow identifying statistically significant method related bias for the analysis of this test material.

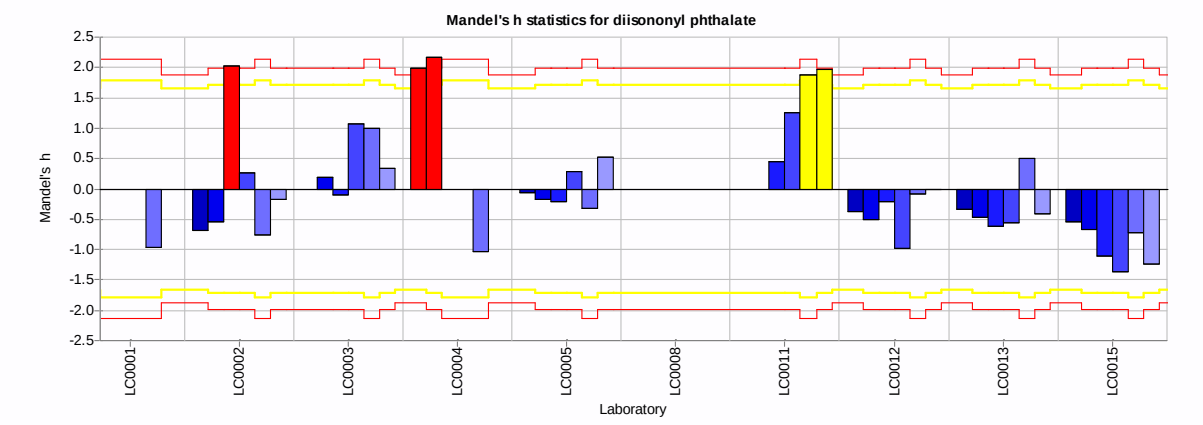
In summary, the analysis method may be considered suitable for the determination of DNOP in wines with regard to analytical precision. However, method related bias will most probably lead to underestimations of DNOP concentrations by about 45 % to 55 %, as demonstrated for five out of six test materials.

Diisononyl phthalate (DINP)

Table 21: DINP - Average results reported by participants and results of outlier tests

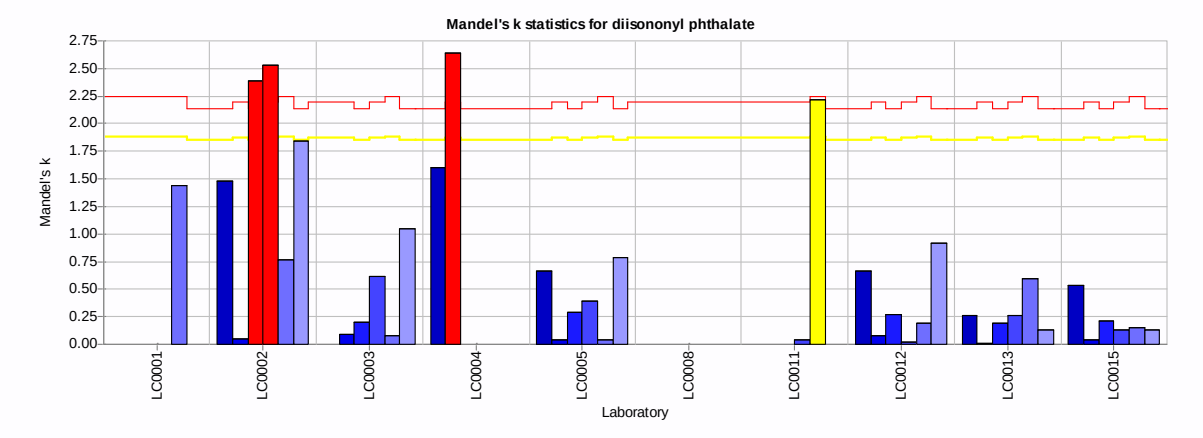
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0001	not tested		not tested		0.843		not tested		not tested		not tested	
LC0002	0.021		0.226	C	1.05		0.055		0.136	C	0.041	
LC0003	< 0.050		0.12		2.838		0.066		0.188		0.135	
LC0004	0.074	B	not tested		0.78		not tested		not tested		0.391	C
LC0005	0.034		0.116		1.497		0.07		0.137		0.087	
LC0008	< 0.020		< 0.020		< 0.020		< 0.020		< 0.020		< 0.020	
LC0011	< 0.050		0.148		3.71		0.102		0.201		< 0.050	
LC0012	0.028		0.116		1.729		0.058		0.053		0.045	
LC0013	0.028		0.096		2.336		0.05		0.081		0.051	
LC0014	not tested	NC	0.56	NC	11.241	NC	0.282	NC	0.491	NC	0.409	NC
LC0015	0.024		0.071		1.081		0.032		0.028		0.026	
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 18: Mandel's h plot for DINP



From left to right: S001, S006, S002, S005, S003, S004

Figure 19: Mandel's k plot for DINP



From left to right: S001, S006, S002, S005, S003, S004

Table 22: DINP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	significant	significant	significant	significant	insignificant
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 %
HORRAT$_R$		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
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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, nine to eleven sets of analysis results were received from the participants. Eight to ten of the data sets were obtained by analyses compliant with the analytical protocol. Noticeably an increased number of laboratories seemed to have difficulties in the determination of DINP in wine, which is indicated by reporting results only for part of the test samples. The Mandel's *h* and Mandel's *k* plots indicated for some results reported by the participants LC0002 and LC0004 significant deviations from the mean values, and/or significant exceedance of average variabilities. Consequently conducted statistical outlier testing identified these results as outliers. They were excluded from further calculations.

Reproducibility relative standard deviations were for all test materials in the range of about 10 % to about 71 %. Repeatability relative standard deviations were at maximum 16.6 %, with the majority of values below 10 %. $HORRAT_R$ values were for all test materials but S006 below 2.0. The high value observed for S006 could be reasoned by the influence of a high concentration of DIDP in this test material, which partially coelutes with DINP.

The relative deviations of the median of reported values from the preparation concentrations were for all test materials negative, and in the range between -10 % and -53 %, with the majority of values being in the range between -44 % and – 53 %

The data evaluation according to ISO 5725-4 identified for the analysis of all test materials but S006 significant method related bias. As seen already for DNOP, the rather low deviation from the assigned value in combination with poor precision values prevents identification of statistically significant method related bias for the analysis of this test material.

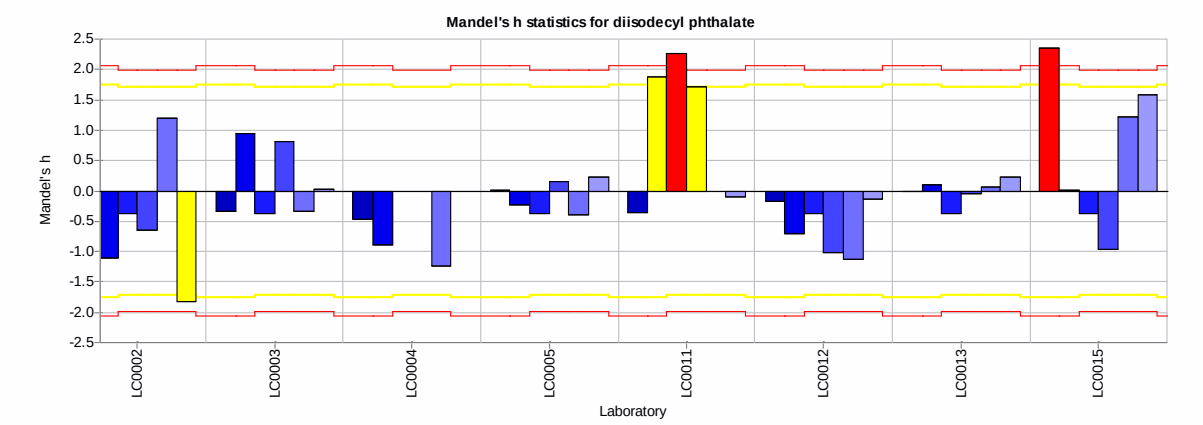
In summary, the analysis method may be considered suitable for the determination of DINP in wines with regard to analytical precision. However, method related bias will most probably lead to underestimations of DINP concentrations by about 44 % to 53 %, as demonstrated for five out of six test materials. The determination of DINP in the provided test materials caused problems for some participants, which is expressed in partially omitting of reporting of analysis results. The method failed in the determination of low contents of DINP in the presence of high contents of DIDP.

Diisodecyl phthalate (DIDP)

Table 23: DIDP - Average results reported by participants and results of outlier tests

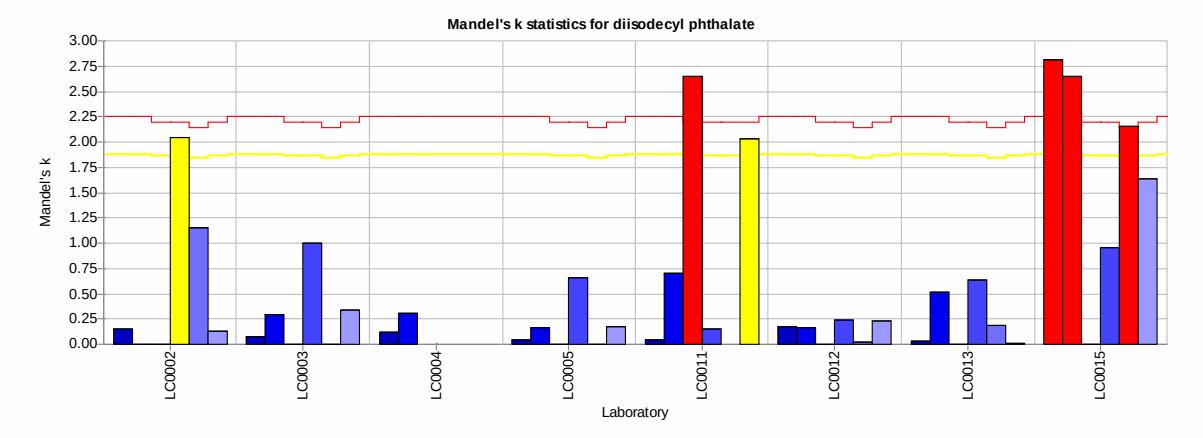
Laboratory	S001		S002		S003		S004		S005		S006	
Unit	mg/l		mg/l		mg/l		mg/l		mg/l		mg/l	
LC0002	0.05		0.107		1.155		0.067		0.116		0.114	
LC0003	0.096		0.097		0.54		0.152		0.273		3.301	
LC0004	0.086		not tested		0.188		not tested		not tested		0.45	
LC0005	0.12		0.096		0.52		0.162		0.203		1.473	
LC0011	0.095		76.065	C	< 0.050		0.147		0.369		4.729	
LC0012	0.107		0.098		0.225		0.145		0.077		0.752	
LC0013	0.119		0.119		0.703		0.163		0.181		1.977	
LC0014	0.467	NC	0.557	NC	2.964	NC	0.709	NC	0.853	NC	11.098	NC
LC0015	0.285	C	0.202	C	1.163		0.226		0.083		1.847	C
Explanation of outlier types												
A: Single outlier			Grubbs									
B: Differing laboratory mean			Grubbs									
C: Excessive laboratory s.d.			Cochran									
NC: Not compliant												

Figure 20: Mandel's h plot for DIDP



From left to right: S001, S006, S002, S005, S003, S004

Figure 21: Mandel's k plot for DIDP



From left to right: S001, S006, S002, S005, S003, S004

Table 24: DIDP – Results of data evaluation

		S001	S002	S003	S004	S005	S006
Method		ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2	ISO 5725-2
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%
Bias*		significant	significant	significant	significant	significant	significant
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 %
HORRAT$_R$		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
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

* Evaluation according to ISO 5725-4

** see (Thompson 2000)

Depending on the test material, eight to nine sets of analysis results were received from the participants. Seven to eight of the data sets were obtained by analyses compliant with the analytical protocol. Noticeably, compared to other analytes, an increased number of laboratories seemed to have difficulties in the determination of DIDP in wine, which is indicated by the low number of reported results in general, respectively by reporting results only for part of the test samples. The Mandel's *h* and Mandel's *k* plots indicated for some results reported by the participants LC0011 and LC0015 significant deviations from the mean values, and/or significant exceedance of average variabilities. Consequently conducted statistical outlier testing identified these results as outliers. They were excluded from further calculations.

Reproducibility relative standard deviations were for all test materials but S003 in the range of about 9 % to about 55 %. The high value, which was observed for S003 (~252%), is reasoned by the influence of a high concentration of DINP in this test material, which partially coelutes with DIDP. Repeatability relative standard deviation was for test material S006 also at the level of about 240 %, whereas values between 3.4 % and 17.1 % were achieved for all other test materials. $HORRAT_R$ values were for two third of the test materials below 2.0. However besides for S003, exceedance of the threshold of 2.0 was also observed in the analysis of test material S006, which contained the highest amount of DIDP in this study.

The relative deviations of the median of reported values from the preparation concentrations were for all test materials but one negative, and in the range between -42 % and -63 %. The exemption was provided by test material S006, for which the DIDP content was overestimated presumably due to the influence of DINP.

The data evaluation according to ISO 5725-4 identified for the analysis of all test materials significant method related bias.

In summary, the analysis method may be considered suitable for the determination of DIDP in wines with regard to analytical precision. However, method related bias will most probably lead to underestimations of DINP concentrations by about 42 % to 63 %, as demonstrated for five out of six test materials. The determination of DIDP at the provided concentration levels caused problems for some participants, which is expressed in partially omitting of reporting of analysis results. The method failed in the determination of low contents of DIDP in the presence of high contents of DINP. The

high reproducibility standard deviation at the highest concentration level requires further investigation.

Summary and conclusions

A collaborative study to assess the performance of an analytical method for the determination of ten phthalic acid esters (phthalates) in wine by gas chromatography mass spectrometry was organised by the Institute for Reference Materials and Measurements (IRMM) in collaboration with the International Organisation of Vine and Wine (OIV). The analytical procedure was developed by OIV. It consisted of the extraction of an aliquot of the wine sample with isohexane followed by concentration of the extract. Stable isotope labelled phthalates were added to the extract prior to injection into the gas chromatograph. Analytes eluting from the non-polar capillary column were ionised by electron ionization and signals were recorded in selected ion monitoring mode. The tested concentration range reached depending on the particular phthalate between about 0.03 mg/l and about 3.1 mg/l. Six test materials were prepared by spiking of white wine, red wine and sweet wine samples. Test samples were provided to the 14 participants from nine countries as blind duplicates.

Analytical precision estimates were derived from the results reported by the participants according to ISO 5725-2, whereas statistically significant method bias was assessed according to ISO 5725-4.

Both repeatability and reproducibility of the analytical method were for most analyte/test material combinations in the acceptable performance range, which is defined in analogy to provisions set EU legislation for other food contaminants by $HORRAT_R$ values below 2.0. However, lack of chromatographic resolution and of mass spectrometric selectivity caused high variabilities in the determination of low amounts of di-*n*-octyl phthalate (DNOP) in the presence of high amounts of diisononly phthalate (DINP). Similarily, this was also found for the determination of low amounts of DINP in the presence of high amounts of diisodecyl phthalate (DIDP) as well as for the determination of low amounts of DIDP in the presence of high amounts of DINP.

The analytical method performed best in terms of both analytical precision and agreement of the median value of reported results with the gravimetrical preparation

concentration for the determination of the contents of benzylbutyl phthalate (BBP) and dicyclohexyl phthalate (DCHP).

Significant method related analytical bias was identified for the determination of especially bis(2-ethylhexyl) phthalate (DEHP), DNOP, DINP and DIDP. The analyte contents of the tested wine samples were in average underestimated for these analytes by about 50 %. This finding agrees with the outcome of the pre-study, which was organised by *Laboratoire SCL de Bordeaux*. Similar discrepancies between the results obtained with the tested analysis procedure and the results obtained with an in-house developed analysis procedure were reported by participant LC0011. The authors of this report came to the same conclusion and informed OIV prior to the start of the study about issues regarding trueness of the analysis results obtained with the tested analytical procedure. Modifications for improving the performance of the analysis method were proposed to OIV. However, OIV preferred to subject the analytical procedure as agreed by the General Assembly and as specified in OIV-MA-AS323-10:2013 to this method performance study.

Correction of analysis results for recovery either intrinsically by the addition of surrogates to the test sample prior to extraction, or by independently determined recovery factors is advised. However, both modifications might have consequences for precision of the method, which would make repeatability and reproducibility estimates derived from this study invalid.

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ANNEX A – Analytical procedure

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS - OIV
Method of determination of phthalates
by gas chromatography / mass spectrometry in wines

Method OIV-MA-AS323-10 Type IV methods

Method of determination of phthalates by gas chromatography / mass spectrometry in wines

1. SCOPE

This method applies to the detection and assay of phthalates in wines.

2. PRINCIPLE

The sample is extracted using isohexane. The extract is concentrated by evaporation. The concentrated extract is analysed by gas chromatography/mass spectrometry (GC/MS) with deuterated internal standards.

3. REAGENTS AND MATERIALS

Unless otherwise specified, all the reagents used are of recognised analytical quality.

3.1 DMP (dimethyl phthalate) [CAS N°: 131-11-3]
3.2 DnBP (dibutyl phthalate) [CAS N°: 84-74-2]
3.3 DEHP (bis (2-ethylhexyl) phthalate) [CAS N°: 117-81-7]
3.4 BBP (butyl benzyl phthalate) [CAS N°: 85-68-7]
3.5 DINP (di-isononyl phthalate) [CAS N°: 068515-48-0/028553-12-0]
3.6 DIDP (di-isodecyl phthalate) [CAS N°: 068515-49-1/026761-40-0]
3.7 DCHP (dicyclohexyl phthalate) [CAS N°: 84-61-7]
3.8 DEP (diethyl phthalate) [CAS N°: 84-66-2]
3.9 DiBP (di-isobutyl phthalate) [CAS N°: 84-74-2]
3.10 DnOP (di-n-octyl phthalate) [CAS N°: 117-84-0]
3.11 DMP-d4: internal standard [CAS N°: 93951-89-4]
3.12 DEP-d4: internal standard [CAS N°: 93952-12-6]
3.13 DiBP-d4: internal standard [CAS N°: 358730-88-8]
3.14 DnBP-d4: internal standard [CAS N°: 93952-11-5]
3.15 BBP-d4: internal standard [CAS N°: 93951-88-3]

3.16 DCHP-d4: internal standard [CAS N°: 358731-25-6]
3.17 DEHP–d4: internal standard [CAS N°: 93951-87-2]
3.18 DnOP-d4: internal standard [CAS N°: 93952-13-7]
3.19 Isohexane [CAS N°: 107-83-5] and Acetone [CAS N°: 67-64-1]

3.20 Standard solutions

All the volumetric flasks used to prepare the calibration solutions are to be rinsed with acetone then isohexane to avoid any contamination.

3.20.1. Stock solutions

- Phthalate - 1 g/L individual solution: for each phthalate weigh 100 mg into a 100 mL flask, dissolve in the isohexane and make up to 100 mL.
- DINP-DIDP - 5 g/L individual solution: for each phthalate weigh 500 mg into a 100 mL flask, dissolve in the isohexane and make up to 100 mL.
- Internal standard - 0.5 g/L individual solution: deuterated standards are packaged in sealed 25 mg ampoules; for each internal standard, all the contents of the bulb are transferred into a 50 mL volumetric flask; make up to 50 mL with isohexane.

3.20.2. Working solutions

- Phthalate 1 mg/L working solution (**S1**)

  Take 100 µL of each 1 g/L and 5g/L stock solution (3.20.1), add the samples to a 100 mL flask, and make up to 100 mL with isohexane.

- Phthalate 10 mg/L working solution (**S2**)

  Take 1 mL of each 1 g/L and 5g/L stock solution (3.20.1), add the samples to a 100 mL flask, and make up to 100 mL with isohexane.

- Internal standard 10 mg/L working solution (IS)

  Take 1 mL of each deuterated standard 0.5 g/L stock solution (3.20.1), add the samples to a 50 mL flask, and make up to 50 mL with isohexane.

3.20.3. Calibration range

The calibration range in isohexane is prepared from the various working solutions (3.20.2), directly into the injection vials that have been heat-treated, rinsed (see § 5.1) and dried under a hood beforehand, according to the following table:

Calibration points	Phthalate concn. (mg/L)*	Vol. of S1 surrogate soln. (µL)	Vol. of S2 surrogate soln. (µL)	Vol. of IS surrogate soln. (µL)	Vol. of isohexane (µL)
C1	0	0	0	50	1000
C2	0,05	50	0	50	950
C3	0,10	100	0	50	900
C4	0,20	200	0	50	800
C5	0,50	0	50	50	950
C6	0,80	0	80	50	920
C7	1,00	0	100	50	900

* to be multiplied by 5 for DINP and DIDP concentrations

4. EQUIPMENT

4.1 Glassware and volumetric laboratory equipment:

4.1.1 50 mL and 100 mL class A volumetric flasks
4.1.2 50 mL glass centrifuge tubes with stopper
4.1.3 10 mL glass test tubes with stopper
4.1.4 Micropipettes with variable volumes ranging from 25 µl to 1,000 µl, checked in accordance with ISO 8655-6
4.1.5 Nitrogen flow evaporator

4.2 Analytical balance

4.3 GC-MS System (e.g. Varian 450GC-300MS)

5. PROCEDURE

5.1 Precautions

Due to the presence of phthalates in the laboratory environment, precautions must be taken throughout the analysis of these compounds:

- Avoid any contact with plastic equipment (especially flexible PVC) as much as possible. If this is not possible, make sure there is no contamination.
- Test the solvents used and dedicate bottles of solvent to these analyses.
- Heat-treat all non-volumetric glassware (400°C for at least 2 hours). Rinse all the equipment carefully (with acetone then isohexane).
- Make sure the septums of the injection vials are phthalate-free.
- Before and after each injection, rinse the injection syringe several times.
- If possible, work in a clean room or in a room reserved for these analyses.

5.2 Preparing the samples

Place 12.5 mL of the sample in a 50 mL centrifuge tube. Add 10 mL of isohexane.

Shake vigorously (Vortex mixer) for at least one minute.

Let the mixture decant until the 2 phases have separated (30 minutes in a 50°C ultrasound bath will accelerate the separation). Recover 8 mL of the organic phase and transfer it into a 10 mL test tube. Evaporate under a flow of nitrogen (0.3 bar) at 35°C and avoid continuing to dryness (warning: the temperature must not exceed 40°C)

Resume with 1 mL of isohexane.

Add 50 µl of the 0.01 g/L internal standard solution to each extract.

Transfer into an injection vial.

NOTE: to minimise matrix effects during analysis by GC-MS, a "protective" agent can be added, such as methyl undecanoate [CAS N°: 1731-86-8].

Add 20µL of this compound is added to each calibration solution and to the extracts from the samples prior to evaporation under a flow of nitrogen.

5.3 Blank test

Prepare a "blank" test by following the procedure described in 5.2 without adding the sample.

5.4 GC/MS analysis

Depending on the apparatus available and its performance, choose between SIM and MRM modes for the mass spectrometry.

For information purposes, analysis conditions are provided in Appendix I and a typical chromatogram is provided in Appendix II.

5.4.1 Calibration

First, carry out several solvent injections (at least 2). Next, inject the standard solutions (3.20.3) in duplicate in increasing order of concentration and end with at least two solvent injections.

Establish a calibration curve for each phthalate:

$$(A_{analyte}/A_{IS}) = f(C_{analyte}/C_{IS}).$$

A: peak area

C: concentration

IS: internal standard

Each phthalate is quantified using to the corresponding deuterated standard, with the exception of DINP and DIDP which are quantified using to DnOP-d4.

Phthalates	Recovery %	CV_r%	CV_{IP}%
DMP (dimethyl phthalate)	67	5	8
DEP (diethyl phthalate)	84	8	11
DiBP (di-isobutyl phthalate)	93	7	10
DnBP (dibutyl phthalate)	95	5	7
BBP (butyl benzyl phthalate)	98	5	6
DCHP (dicyclohexyl phthalate)	97	5	7
DEHP (bis(2-ethylhexyl) phthalate)	98	6	7
DnOP (dioctyl phthalate)	98	6	7
DINP (di-isononyl phthalate)	104	7	8
DIDP (di-isodecyl phthalate)	96	8	11

i.e. the following average values for all the phthalates:

Repeatability (given in CV_r%): **6%**

Intermediate precision (given in CV_{IP}%): **8%**

8. DETECTION AND QUANTIFICATION LIMITS

For each phthalate being analysed for, the detection and quantification limits are provided in the following table:

Phthalates	Quantification limit (mg/L)	Detection limit (mg/L)
DMP (dimethyl phthalate)	0.010	0.004
DEP (diethyl phthalate)	0.010	0.004
DiBP (di-isobutyl phthalate)	0.010	0.004
DnBP (dibutyl phthalate)	0.010	0.004
BBP (butyl benzyl phthalate)	0.010	0.004
DCHP (dicyclohexyl phthalate)	0.010	0.004
DEHP (bis(2-ethylhexyl) phthalate)	0.010	0.004
DnOP (dioctyl phthalate)	0.010	0.004
DINP (di-isononyl phthalate)	0.050	0.020
DIDP (di-isodecyl phthalate)	0.050	0.020

9. REFERENCES

FV 1371. Detection and assay of phthalates in alcoholic beverages. 2011
FV 1234. Questions about phthalates. 2006

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS - OIV
Method of determination of phthalates
by gas chromatography / mass spectrometry in wines

APPENDIX I
(for information)

Gas chromatography conditions

VF-5ms type capillary column: 30 m x 0.25 mm internal diameter, film thickness 0.25 µm

Temperature programming:

For detection in SIM mode:

Oven maintained at 100°C for 1 min; increase to 230°C at a rate of 10°C/min; increase to 270°C at a rate of 10°C/min; maintain for 2 min, increase to 300°C at a rate of 25°C/min; maintain for 8 min.

Note: this programming separates the DEHP and DCHP peaks (which cannot be done with the MRM mode programming)

For detection in MRM mode:

Oven maintained at 80°C for 1 min; increase to 200°C at a rate of 20°C/min; increase to 300°C at a rate of 10°C/min; maintain for 8 min.

Injector: maintained at 150°C for 0.5 min; increase to 280°C at a rate of 200°C/min, in splitless mode at injection

Helium: 1 mL/min at a constant flow rate

Volume injected: 1 µL

Mass spectrometry (MS) conditions

Ionisation in EI mode at 70 eV
Source temperature: 250°C
Transfer line temperature: 300°C
Manifold: 40°C

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS - OIV
Method of determination of phthalates
by gas chromatography / mass spectrometry in wines

Phthalate quantification and identification parameters

For an analysis in SIM mode, table 1 provides the quantification ion and the two qualifier ions for each phthalate and its deuterated homologue.

For an analysis in MRM mode, table 2 reflects the quantifying and qualifying transitions for each phthalate and its deuterated homologue.

Note: DIDP and DINP are each a mixture of compounds. Chromatography cannot separate them completely. They are therefore assayed as a "group".

APPENDIX I
(for information)
Table 1

		Quantification ion m/z	Qualifier ions m/z	
			1	2
DMP	(dimethyl phthalate)	163	77	194
DMP-d4		167	81	198
DEP	(diethyl phthalate)	149	177	222
DEP-d4		153	181	226
DiBP	(di-isobutyl phthalate)	149	167	223
DiBP-d4		153	171	227
DnBP	(dibutyl phthalate)	149	205	223
DnBP-d4		153	209	227
BBP	(butyl benzyl phthalate)	149	91	206
BBP-d4		153	95	210
DCHP	(dicyclohexyl phthalate)	149	167	249
DCHP-d4		153	171	253
DEHP	(bis(2-ethylhexyl) phthalate)	149	167	279
DEHP-d4		153	171	283
DnOP	(dioctyl phthalate)	149	167	279
DnOP-d4		153	171	283
DINP	(di-isononyl phthalate)	149	293	
DIDP	(di-isodecyl phthalate)	149	307	

Table 2

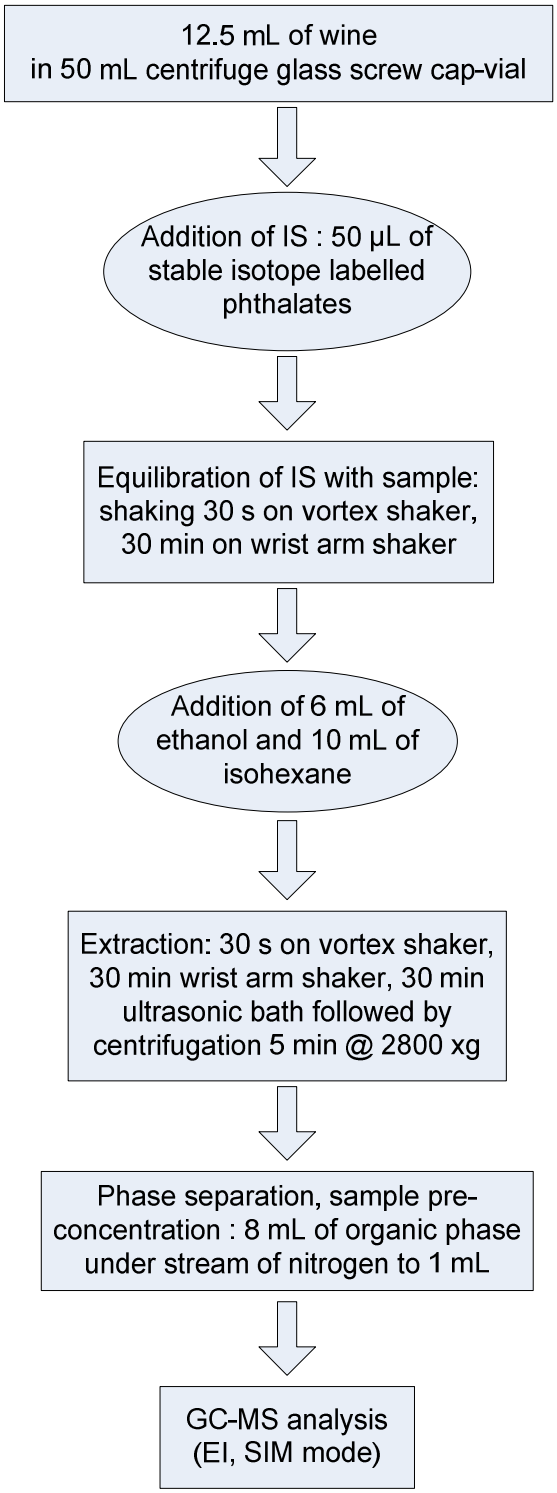
		Quantifying transition	Qualifying transition
DMP	(dimethyl phthalate)	194>163	194>77
DMP-d4		198>167	198>81
DEP	(diethyl phthalate)	177>149	177>93
DEP-d4		181>153	181>97
DiBP	(di-isobutyl phthalate)	223>149	205>149
DiBP-d4		227>153	209>153
DnBP	(dibutyl phthalate)	223>149	205>149
DnBP-d4		227>153	209>153
BBP	(butyl benzyl phthalate)	206>149	149>121
BBP-d4		210>153	153>125
DCHP	(dicyclohexyl phthalate)	249>149	249>93
DCHP-d4		253>153	253>97
DEHP	(bis(2-ethylhexyl) phthalate)	279>149	279>93
DEHP-d4		283>153	283>97
DnOP	(dioctyl phthalate)	279>149	279>93
DnOP-d4		283>153	283>93
DINP	(di-isononyl phthalate)	293>149	
DIDP	(di-isodecyl phthalate)	307>149	

APPENDIX II
(for information)

GC/MS chromatograms of a phthalate standard solution and deuterated internal standards.

ANNEX B

Figure B-1: Method flowchart of the modified OIV-MA-AS323-10:2013 procedure, which was used for the evaluation of homogeneity and stability of samples



ANNEX C – Study description

Ref. Ares(2014)539363 - 28/02/2014

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
Standards for Food Bioscience

Geel, 28.02.2014

Study description

Dear Madame/Sir,

The validation study by collaborative trial of a method specified by the International Organisation of Vine and Wine (OIV) for the determination of phthalates in wine (OIV-MA-AS323-10) has started with the dispatch of the test materials. The test materials comprise twelve ampoules containing at least 15 ml of test sample. The test samples were prepared by spiking of blank wines, which were provided by the SCL in Bordeaux. The concentration levels of phthalates in the test sample range from about 30 µg/l to about 3000 µg/l. The test samples shall be stored at about 20°C in the dark and shall be opened prior to analysis only.

In addition to the test samples, you receive an ampoule containing the isotope labelled internal standards in isooctane. You shall apply this solution, as described in the SOP. The standard solutions of the native phthalates shall be prepared from your own stocks. The aim of this approach is to get a realistic estimate of the variability that can be expected if the tests are performed in different laboratories.
In order to limit the influence of biased standard preparation on the analysis results, we advice you to prepare each concentration level in replicate from, if possible, independent stock solutions of native phthalates, and to evaluate the agreement of the measurement results of the independently prepared standard solutions.

Please note that the replacement of isohexane as solvent for the isotope labelled standard solution by isooctane does not affect the performance of the analysis method. (It was replaced for safety reasons, as isohexane ignites more likely during flame sealing of the ampoules.)

You are requested to analyse each test sample/ampoule once, applying the analysis method OIV-MS-AS323-10. This analysis method is included in the Compendium of International

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571-320.

Methods of Analysis and downloadable from the OIV server. However, a copy of the procedure is provided with the test samples.

The analyses shall be performed under repeatability conditions.

Please follow the analysis procedure as closely as possible! Major deviations will cause the exclusion of your results from the evaluation.

The analysis results for the individual test samples shall be reported in electronic format. A suitable template will be provided to you by email. It consists of a self-extracting data file, which allows you to introduce the measurement results. Detailed instruction is provided with the electronic template.

You will also be requested to fill a small questionnaire that will provide us information on the implementation of the analysis method in your laboratory (e.g. brand of instrument used etc.).

The study is organised by the Joint Research Centre, a Directorate General of the European Commission, in close collaboration with OIV. It is organised according to ISO 5725-2 "Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method".

Deadline for reporting of results is 11 April 2014.

Please contact us immediately (mailto:jrc-irmm-contaminants@ec.europa.eu), if you experience any problem in the execution of the analysis method during the ring-trial?
We will then try to solve the problem, in order to get at the end as many valid data sets as possible.

With best regards

Lubomir Karasek and Thomas Wenzl

Organisers of the study
jrc-irmm-contaminants@ec.europa.eu

ANNEX D – Reported results

Table D- 1: DMP in white wine sample S001

Preparation concentration: 0.030 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.021	0.023	0.020
LC0002	0.017	0.017	0.016
LC0003	0.032	0.032	0.031
LC0004	0.016	0.014	0.018
LC0005	0.023	0.023	0.023
LC0008		< 0.010	
LC0009	0.135	0.130	0.140
LC0011	0.013	0.013	0.013
LC0012	0.019	0.017	0.021
LC0013	0.022	0.022	0.022
LC0014	0.197	0.191	0.202
LC0015	0.014	0.009	0.019

Table D- 2: DEP in white wine sample S001

Preparation concentration: 0.057 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001		< 0.060	< 0.060
LC0002	0.047	0.048	0.046
LC0003	0.063	0.064	0.061
LC0004	0.034	0.033	0.035
LC0005	0.051	0.051	0.051
LC0006	0.110	0.120	0.100
LC0008	0.044	0.044	
LC0009	0.010	0.010	0.010
LC0011	0.031	0.028	0.034
LC0012	0.041	0.041	0.040
LC0013	0.055	0.056	0.054
LC0014	0.506	0.493	0.520
LC0015	0.038	0.030	0.046

Table D- 3: DIBP in white wine sample S001

Preparation concentration: 0.035 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.048	0.050	0.046
LC0002	0.061	0.060	0.061
LC0003	0.052	0.054	0.051
LC0004	0.034	0.038	0.030
LC0005	0.049	0.049	0.049
LC0008	0.043	0.043	
LC0009	0.070	0.070	0.070
LC0011	0.039	0.039	0.039
LC0012	0.035	0.036	0.034
LC0013	0.053	0.054	0.052
LC0014	0.418	0.378	0.459
LC0015	0.055	0.052	0.058

Table D- 4: DBP in white wine sample S001

Preparation concentration: 0.107 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.113	0.117	0.108
LC0002	0.105	0.106	0.105
LC0003	0.122	0.125	0.119
LC0004	0.084	0.101	0.067
LC0005	0.104	0.104	0.104
LC0006	0.060	0.060	0.060
LC0008	0.101	0.101	
LC0009	0.140	0.150	0.130
LC0011	0.097	0.095	0.098
LC0012	0.085	0.087	0.083
LC0013	0.122	0.124	0.121
LC0014	0.996	0.908	1.084
LC0015	0.102	0.101	0.102

Table D- 5: BBP in white wine sample S001

Preparation concentration: 0.057 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.050	0.052	0.047
LC0002	0.119	0.066	0.172
LC0003	0.056	0.057	0.055
LC0004	0.041	0.045	0.038
LC0005	0.055	0.055	0.055
LC0008	0.042	0.042	
LC0009	0.135	0.140	0.130
LC0011	0.046	0.045	0.047
LC0012	0.041	0.041	0.040
LC0013	0.061	0.060	0.063
LC0014	0.447	0.408	0.485
LC0015	0.043	0.042	0.044

Table D- 6: DCHP in white wine sample S001

Preparation concentration: 0.084 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.078	0.082	0.074
LC0003	0.077	0.079	0.076
LC0004	0.055	0.061	0.049
LC0005	0.076	0.075	0.077
LC0009	0.135	0.130	0.140
LC0011	0.070	0.066	0.073
LC0012	0.062	0.061	0.063
LC0013	0.092	0.090	0.094
LC0014	0.605	0.538	0.671
LC0015	0.065	0.063	0.066

Table D- 7: DEHP in white wine sample S001

Preparation concentration: 0.217 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.084	0.104	0.065
LC0002	0.454	0.397	0.511
LC0003	0.102	0.103	0.102
LC0004	0.086	0.087	0.085
LC0005	0.095	0.110	0.079
LC0006	0.125	0.130	0.120
LC0008	0.023	0.023	
LC0009	0.085	0.090	0.080
LC0011	0.110	0.119	0.102
LC0012	0.091	0.082	0.100
LC0013	0.117	0.126	0.109
LC0014	0.418	0.490	0.347
LC0015	0.118	0.095	0.140

Table D- 8: DNOP in white wine sample S001

Preparation concentration: 0.086 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.024	0.031	0.017
LC0002	0.012	0.012	0.012
LC0003	0.033	0.037	0.029
LC0004	0.035	0.033	0.037
LC0005	0.036	0.039	0.033
LC0008		< 0.020	
LC0009	0.095	0.090	0.100
LC0011	0.028	0.023	0.032
LC0012	0.035	0.031	0.038
LC0013	0.037	0.039	0.035
LC0014	0.163	0.205	0.121
LC0015	0.041	0.031	0.050

Table D- 9: DINP in white wine sample S001

Preparation concentration: 0.054 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.021	0.016	0.027
LC0003		< 0.050	< 0.050
LC0004	0.074	0.080	0.068
LC0005	0.034	0.036	0.031
LC0008		< 0.020	
LC0011		< 0.050	< 0.050
LC0012	0.028	0.025	0.030
LC0013	0.028	0.029	0.027
LC0015	0.024	0.022	0.026

Table D- 10: DIDP in white wine sample S001

Preparation concentration: 0.275 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.050	0.059	0.040
LC0003	0.096	0.091	0.101
LC0004	0.086	0.094	0.079
LC0005	0.120	0.118	0.123
LC0011	0.095	0.097	0.092
LC0012	0.107	0.096	0.118
LC0013	0.119	0.121	0.117
LC0014	0.467	0.591	0.343
LC0015	0.285	0.106	0.464

Table D- 11: DMP in white wine sample S002

Preparation concentration: 0.097 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.071	0.076	0.066
LC0002	0.047	0.048	0.046
LC0003	0.102	0.103	0.101
LC0005	0.064	0.064	0.063
LC0008	0.065	0.065	0.064
LC0009	0.170	0.170	0.170
LC0011	0.036	0.025	0.046
LC0012	0.049	0.052	0.046
LC0013	0.057	0.066	0.048
LC0014	0.588	0.590	0.586
LC0015	0.034	0.059	0.010

Table D- 12: DEP in white wine sample S002

Preparation concentration: 0.092 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.081	0.084	0.078
LC0002	0.073	0.077	0.070
LC0003	0.101	0.103	0.099
LC0005	0.078	0.078	0.078
LC0006	0.210	0.220	0.200
LC0008	0.076	0.078	0.074
LC0009	0.010	0.010	0.010
LC0011	0.044	0.033	0.056
LC0012	0.061	0.065	0.058
LC0013	0.077	0.085	0.069
LC0014	0.784	0.788	0.780
LC0015	0.052	0.069	0.034

Table D- 13: DIBP in white wine sample S002

Preparation concentration: 0.076 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.085	0.088	0.082
LC0002	0.121	0.123	0.118
LC0003	0.097	0.098	0.095
LC0005	0.075	0.081	0.068
LC0008	0.085	0.089	0.081
LC0009	0.110	0.110	0.110
LC0011	0.064	0.059	0.068
LC0012	0.061	0.065	0.057
LC0013	0.086	0.088	0.084
LC0014	0.744	0.746	0.743
LC0015	0.085	0.093	0.078

Table D- 14: DBP in white wine sample S002

Preparation concentration: 0.281 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.266	0.276	0.255
LC0002	0.237	0.251	0.224
LC0003	0.280	0.276	0.285
LC0005	0.194	0.183	0.204
LC0006	0.365	0.380	0.350
LC0008	0.278	0.294	0.262
LC0009	0.300	0.300	0.300
LC0011	0.226	0.217	0.235
LC0012	0.214	0.214	0.214
LC0013	0.264	0.268	0.259
LC0014	2.481	2.518	2.443
LC0015	0.280	0.290	0.270

Table D- 15: BBP in white wine sample S002

Preparation concentration: 0.029 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.025	0.027	0.023
LC0002	0.071	0.058	0.085
LC0003	0.029	0.029	0.028
LC0005	0.030	0.030	0.030
LC0008	0.026	0.026	< 0.010
LC0009	0.110	0.110	0.110
LC0011	0.025	0.024	0.025
LC0012	0.020	0.021	0.018
LC0013	0.029	0.030	0.029
LC0014	0.247	0.254	0.241
LC0015	0.021	0.022	0.021

Table D- 16: DCHP in white wine sample S002

Preparation concentration: 0.048 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.046	0.050	0.043
LC0003	0.046	0.046	0.046
LC0005	0.036	0.026	0.047
LC0009	0.120	0.110	0.130
LC0011	0.042	0.041	0.042
LC0012	0.034	0.036	0.032
LC0013	0.052	0.055	0.048
LC0014	0.390	0.406	0.374
LC0015	0.038	0.038	0.038

Table D- 17: DEHP in white wine sample S002

Preparation concentration: 0.046 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.020	0.015	0.025
LC0002	24.781	48.894	0.667
LC0003	0.024	0.027	0.021
LC0005	0.026	0.031	0.022
LC0006	0.010	0.010	0.010
LC0008	0.025	0.029	0.020
LC0009	0.050	0.050	0.050
LC0011	0.035	0.037	0.033
LC0012	0.025	0.031	0.018
LC0013	0.032	0.036	0.027
LC0014	0.160	0.173	0.148
LC0015	0.031	0.031	0.031

Table D- 18: DNOP in white wine sample S002

Preparation concentration: 0.031 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.012	< 0.010	0.012
LC0002	0.017	0.020	0.014
LC0003	0.016	0.018	0.014
LC0005	0.015	0.017	0.012
LC0008		< 0.020	< 0.020
LC0009	0.080	0.080	0.080
LC0011	0.019	0.020	0.017
LC0012	0.013	0.014	0.012
LC0013	0.015	0.018	0.013
LC0014	0.091	0.104	0.079
LC0015	0.013	0.013	0.013

Table D- 19: DINP in white wine sample S002

Preparation concentration: 0.242 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.226	0.360	0.092
LC0003	0.120	0.132	0.109
LC0005	0.116	0.132	0.099
LC0008		< 0.020	< 0.020
LC0011	0.148	< 0.050	0.148
LC0012	0.116	0.131	0.100
LC0013	0.096	0.106	0.085
LC0014	0.560	0.705	0.416
LC0015	0.071	0.059	0.083

Table D- 20: DIDP in white wine sample S002

Preparation concentration: 0.186 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.107	0.098	0.116
LC0003	0.097	0.105	0.089
LC0005	0.096	0.110	0.082
LC0011	76.065	152.000	0.130
LC0012	0.098	0.110	0.085
LC0013	0.119	0.137	0.102
LC0014	0.557	0.689	0.426
LC0015	0.202	0.286	0.118

Table D- 21: DMP in red wine sample S003

Preparation concentration: 0.030 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.022	0.022	0.022
LC0002	0.015	0.015	0.015
LC0003	0.032	0.032	0.031
LC0004	0.015	0.015	
LC0005	0.017	0.017	0.017
LC0008		< 0.010	< 0.010
LC0009	0.130	0.130	0.130
LC0011	0.028	0.042	0.014
LC0012	0.016	0.016	0.016
LC0013	0.018	0.020	0.016
LC0014	0.164	0.168	0.160
LC0015	0.009	0.013	0.005

Table D- 22: DEP in red wine sample S003

Preparation concentration: 0.031 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.024	0.025	0.024
LC0003	0.042	0.043	0.041
LC0004	0.019	0.019	
LC0005	0.032	0.032	0.031
LC0006	0.065	0.060	0.070
LC0008	0.035	0.034	0.035
LC0009	0.010	0.010	0.010
LC0011	0.029	0.038	0.021
LC0012	0.022	0.023	0.022
LC0013	0.029	0.031	0.027
LC0014	0.283	0.284	0.283
LC0015	0.022	0.025	0.019

Table D- 23: DIBP in red wine sample S003

Preparation concentration: 0.058 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.077	0.075	0.079
LC0002	0.069	0.067	0.070
LC0003	0.088	0.091	0.086
LC0004	0.058	0.058	
LC0005	0.076	0.077	0.076
LC0008	0.078	0.076	0.080
LC0009	0.105	0.110	0.100
LC0011	0.074	0.081	0.066
LC0012	0.054	0.055	0.054
LC0013	0.071	0.081	0.061
LC0014	0.617	0.637	0.598
LC0015	0.078	0.073	0.083

Table D- 24: DBP in red wine sample S003

Preparation concentration: 0.057 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.072	0.070	0.073
LC0002	0.058	0.059	0.058
LC0003	0.084	0.084	0.083
LC0004	0.061	0.061	
LC0005	0.084	0.096	0.073
LC0006	0.125	0.130	0.120
LC0008	0.077	0.075	0.079
LC0009	0.095	0.100	0.090
LC0011	0.085	0.104	0.066
LC0012	0.051	0.051	0.052
LC0013	0.071	0.080	0.061
LC0014	0.609	0.633	0.584
LC0015	0.070	0.066	0.073

Table D- 25: BBP in red wine sample S003

Preparation concentration: 0.037 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.034	0.031	0.036
LC0002	0.038	0.035	0.042
LC0003	0.038	0.038	0.039
LC0004	0.032	0.032	
LC0005	0.038	0.038	0.038
LC0008	0.030	0.030	0.031
LC0009	0.115	0.120	0.110
LC0011	0.029	0.028	0.031
LC0012	0.025	0.025	0.025
LC0013	0.034	0.038	0.030
LC0014	0.272	0.285	0.259
LC0015	0.028	0.026	0.030

Table D- 26: DCHP in red wine sample S003

Preparation concentration: 0.038 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.033	0.033	0.032
LC0003	0.035	0.035	0.035
LC0004	0.028	0.028	
LC0005	0.036	0.035	0.036
LC0009	0.115	0.120	0.110
LC0011	0.028	0.026	0.031
LC0012	0.025	0.025	0.025
LC0013	0.034	0.037	0.030
LC0014	0.239	0.253	0.225
LC0015	0.024	0.022	0.026

Table D- 27: DEHP in red wine sample S003

Preparation concentration: 1.049 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.486	0.846	0.126
LC0002	0.473	0.575	0.371
LC0003	0.745	0.726	0.764
LC0004	0.725	0.725	
LC0005	0.813	0.803	0.823
LC0006	0.195	0.180	0.210
LC0008	0.417	0.255	0.580
LC0009	0.555	0.710	0.400
LC0011	0.789	0.612	0.967
LC0012	0.602	0.534	0.669
LC0013	0.781	0.853	0.710
LC0014	5.778	5.993	5.563
LC0015	0.707	0.746	0.668

Table D- 28: DNOP in red wine sample S003

Preparation concentration: 0.059 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.045	0.079	0.011
LC0002	0.046	0.059	0.034
LC0003	0.052	0.050	0.053
LC0004	0.049	0.049	
LC0005	0.064	0.063	0.064
LC0008	0.032	< 0.020	0.032
LC0009	0.150	0.170	0.130
LC0011	0.092	0.070	0.114
LC0012	0.029	0.030	0.029
LC0013	0.042	0.049	0.036
LC0014	0.587	0.608	0.565
LC0015	0.051	0.052	0.050

Table D- 29: DINP in red wine sample S003

Preparation concentration: 3.134 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.843	1.373	0.313
LC0002	1.050	1.332	0.769
LC0003	2.838	2.867	2.809
LC0004	0.780	0.780	
LC0005	1.497	1.483	1.510
LC0008		< 0.020	< 0.020
LC0011	3.710	2.895	4.526
LC0012	1.729	1.801	1.657
LC0013	2.336	2.556	2.116
LC0014	11.241	19.499	2.984
LC0015	1.081	1.137	1.024

Table D- 30: DIDP in red wine sample S003

Preparation concentration: 0.052 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	1.155	1.543	0.767
LC0003	0.540	0.542	0.539
LC0004	0.188	0.188	
LC0005	0.520	0.518	0.521
LC0011		< 0.050	< 0.050
LC0012	0.225	0.217	0.233
LC0013	0.703	0.767	0.639
LC0014	2.964	3.103	2.825
LC0015	1.163	1.890	0.437

Table D- 31: DMP in red wine sample S004

Preparation concentration: 0.049 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.030	0.036	0.025
LC0002	0.023	0.023	0.022
LC0003	0.052	0.052	0.052
LC0005	0.026	0.033	0.019
LC0008	0.035	0.034	0.036
LC0009	0.140	0.140	0.140
LC0011		< 0.010	< 0.010
LC0012	0.025	0.024	0.026
LC0013	0.033	0.033	0.033
LC0014	0.275	0.291	0.259
LC0015	0.020	0.011	0.029

Table D- 32: DEP in red wine sample S004

Preparation concentration: 0.056 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001		< 0.060	
LC0002	0.035	0.035	0.035
LC0003	0.064	0.064	0.064
LC0005	0.045	0.049	0.041
LC0006	0.105	0.140	0.070
LC0008	0.054	0.053	0.055
LC0009	0.010	0.010	0.010
LC0011	0.020	< 0.010	0.020
LC0012	0.032	0.030	0.033
LC0013	0.046	0.046	0.046
LC0014	0.442	0.465	0.419
LC0015	0.037	0.031	0.044

Table D- 33: DIBP in red wine sample S004

Preparation concentration: 0.107 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.112	0.122	0.101
LC0002	0.095	0.099	0.090
LC0003	0.137	0.133	0.141
LC0005	0.117	0.121	0.113
LC0008	0.136	0.139	0.133
LC0009	0.150	0.150	0.150
LC0011	0.072	0.059	0.084
LC0012	0.125	0.114	0.135
LC0013	0.122	0.122	0.122
LC0014	0.981	1.025	0.937
LC0015	0.125	0.123	0.127

Table D- 34: DBP in red wine sample S004

Preparation concentration: 1.039 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.621	0.615	0.628
LC0002	0.666	0.675	0.657
LC0003	1.067	1.035	1.099
LC0005	0.050	0.051	0.049
LC0006	2.450	2.600	2.300
LC0008	1.091	1.084	1.099
LC0009	1.080	1.060	1.100
LC0011	0.623	0.567	0.680
LC0012	0.649	0.626	0.673
LC0013	0.815	0.811	0.819
LC0014	7.798	8.075	7.522
LC0015	0.612	0.626	0.598

Table D- 35: BBP in red wine sample S004

Preparation concentration: 0.088 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.065	0.072	0.058
LC0002	0.071	0.066	0.076
LC0003	0.088	0.089	0.088
LC0005	0.084	0.086	0.082
LC0008	0.078	0.077	0.079
LC0009	0.150	0.150	0.150
LC0011	0.068	0.068	0.067
LC0012	0.058	0.056	0.061
LC0013	0.087	0.086	0.089
LC0014	0.672	0.693	0.651
LC0015	0.068	0.068	0.067

Table D- 36: DCHP in red wine sample S004

Preparation concentration: 0.105 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.089	0.097	0.081
LC0003	0.097	0.097	0.097
LC0005	0.094	0.096	0.092
LC0009	0.150	0.140	0.160
LC0011	0.080	0.083	0.077
LC0012	0.074	0.070	0.077
LC0013	0.101	0.100	0.102
LC0014	0.753	0.777	0.729
LC0015	0.081	0.081	0.081

Table D- 37: DEHP in red wine sample S004

Preparation concentration: 0.328 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.051	0.055	0.047
LC0002	0.929	1.522	0.336
LC0003	0.142	0.139	0.145
LC0005	0.202	0.211	0.192
LC0006	0.080	0.090	0.070
LC0008	0.094	0.108	0.080
LC0009	0.225	0.200	0.250
LC0011	0.180	0.254	0.107
LC0012	0.166	0.158	0.174
LC0013	0.204	0.205	0.204
LC0014	1.171	1.197	1.145
LC0015	0.182	0.187	0.177

Table D- 38: DNOP in red wine sample S004

Preparation concentration: 0.114 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.011	0.011	< 0.010
LC0002	0.071	0.071	0.071
LC0003	0.085	0.079	0.092
LC0005	0.069	0.072	0.066
LC0008	0.035	0.035	< 0.020
LC0009	0.155	0.150	0.160
LC0011	0.049	0.068	0.029
LC0012	0.064	0.060	0.068
LC0013	0.058	0.059	0.058
LC0014	0.394	0.410	0.378
LC0015	0.055	0.055	0.055

Table D- 39: DINP in red wine sample S004

Preparation concentration: 0.104 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.055	0.048	0.062
LC0003	0.066	0.062	0.070
LC0005	0.070	0.073	0.067
LC0008		< 0.020	< 0.020
LC0011	0.102	0.102	< 0.050
LC0012	0.058	0.055	0.062
LC0013	0.050	0.050	0.049
LC0014	0.282	0.303	0.262
LC0015	0.032	0.031	0.032

Table D- 40: DIDP in red wine sample S004

Preparation concentration: 0.281 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.067	0.071	0.062
LC0003	0.152	0.141	0.164
LC0005	0.162	0.168	0.156
LC0011	0.147	0.216	0.078
LC0012	0.145	0.137	0.153
LC0013	0.163	0.162	0.163
LC0014	0.709	0.744	0.674
LC0015	0.226	0.281	0.170

Table D- 41: DMP in sweet wine sample S005

Preparation concentration: 0.104 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.054	0.047	0.061
LC0002	0.042	0.045	0.038
LC0003	0.093	0.094	0.093
LC0005	0.058	0.057	0.058
LC0008	0.059	0.057	0.061
LC0009	0.175	0.180	0.170
LC0011	0.038	0.051	0.025
LC0012	0.050	0.050	0.050
LC0013	0.062	0.060	0.064
LC0014	0.563	0.527	0.599
LC0015	0.018	0.034	0.001

Table D- 42: DEP in sweet wine sample S005

Preparation concentration: 0.030 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.022	0.023	0.021
LC0003	0.031	0.031	0.031
LC0005	0.026	0.026	0.026
LC0006	0.025	0.030	0.020
LC0008	0.025	0.024	0.025
LC0009	0.010	0.010	0.010
LC0011	0.015	0.019	0.011
LC0012	0.019	0.019	0.019
LC0013	0.026	0.026	0.026
LC0014	0.235	0.219	0.252
LC0015	0.009	0.013	0.005

Table D- 43: DIBP in sweet wine sample S005

Preparation concentration: 0.061 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.051	0.051	0.052
LC0002	0.054	0.056	0.052
LC0003	0.059	0.059	0.059
LC0005	0.056	0.056	0.055
LC0008	0.060	0.057	0.064
LC0009	0.080	0.080	0.080
LC0011	0.043	0.046	0.040
LC0012	0.039	0.040	0.038
LC0013	0.058	0.058	0.058
LC0014	0.475	0.440	0.509
LC0015	0.040	0.042	0.038

Table D- 44: DBP in sweet wine sample S005

Preparation concentration: 0.032 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.089	0.088	0.091
LC0002	0.077	0.080	0.073
LC0003	0.101	0.100	0.101
LC0005	0.089	0.089	0.089
LC0006	0.095	0.100	0.090
LC0008	0.101	0.097	0.104
LC0009	0.125	0.130	0.120
LC0011	0.083	0.087	0.079
LC0012	0.068	0.069	0.066
LC0013	0.100	0.101	0.099
LC0014	0.850	0.807	0.893
LC0015	0.059	0.056	0.063

Table D- 45: BBP in sweet wine sample S005

Preparation concentration: 0.087 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.080	0.079	0.081
LC0002	0.077	0.078	0.076
LC0003	0.092	0.090	0.094
LC0005	0.084	0.084	0.083
LC0008	0.073	0.071	0.075
LC0009	0.195	0.200	0.190
LC0011	0.074	0.074	0.074
LC0012	0.061	0.064	0.059
LC0013	0.089	0.089	0.090
LC0014	0.724	0.689	0.759
LC0015	0.044	0.040	0.049

Table D- 46: DCHP in sweet wine sample S005

Preparation concentration: 0.057 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.049	0.048	0.049
LC0003	0.052	0.051	0.053
LC0005	0.052	0.053	0.052
LC0009	0.120	0.120	0.120
LC0011	0.048	0.047	0.048
LC0012	0.038	0.039	0.037
LC0013	0.056	0.056	0.055
LC0014	0.423	0.400	0.447
LC0015	0.025	0.022	0.028

Table D- 47: DEHP in sweet wine sample S005

Preparation concentration: 1.569 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.126	0.146	0.105
LC0002	0.826	0.642	1.010
LC0003	1.524	1.502	1.547
LC0005	0.709	0.738	0.680
LC0006	1.050	1.000	1.100
LC0008	0.151	0.156	0.146
LC0009	1.105	0.900	1.310
LC0011	1.222	1.219	1.224
LC0012	0.441	0.478	0.404
LC0013	0.685	0.680	0.690
LC0014	4.931	4.295	5.566
LC0015	0.313	0.335	0.291

Table D- 48: DNOP in sweet wine sample S005

Preparation concentration: 0.036 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.020	0.013	0.027
LC0003	0.024	0.022	0.026
LC0005	0.018	0.019	0.017
LC0008		< 0.020	< 0.020
LC0009	0.100	0.090	0.110
LC0011	0.026	0.026	0.026
LC0012	0.008	0.009	0.007
LC0013	0.013	0.013	0.013
LC0014	0.106	0.093	0.119
LC0015	0.005	0.006	0.004

Table D- 49: DINP in sweet wine sample S005

Preparation concentration: 0.271 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.136	0.078	0.193
LC0003	0.188	0.174	0.202
LC0005	0.137	0.146	0.128
LC0008		< 0.020	< 0.020
LC0011	0.201	0.200	0.202
LC0012	0.053	0.054	0.053
LC0013	0.081	0.075	0.087
LC0014	0.491	0.472	0.510
LC0015	0.028	0.025	0.031

Table D- 50: DIDP in sweet wine sample S005

Preparation concentration: 0.427 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.116	0.078	0.155
LC0003	0.273	0.254	0.292
LC0005	0.203	0.215	0.190
LC0011	0.369	0.366	0.372
LC0012	0.077	0.082	0.073
LC0013	0.181	0.169	0.193
LC0014	0.853	0.723	0.983
LC0015	0.083	0.101	0.065

Table D- 51: DMP in sweet wine sample S006

Preparation concentration: 0.046 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.028	0.025	0.031
LC0002	0.019	0.018	0.019
LC0003	0.045	0.042	0.048
LC0004	0.018	0.020	0.016
LC0005	0.029	0.030	0.029
LC0008	0.028	0.027	0.028
LC0009	0.130	0.100	0.160
LC0011	0.034	0.032	0.036
LC0012	0.027	0.029	0.024
LC0013	0.030	0.030	0.030
LC0014	0.255	0.217	0.292
LC0015	0.017	0.012	0.021

Table D- 52: DEP in sweet wine sample S006

Preparation concentration: 0.089 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.064	0.063	0.065
LC0002	0.054	0.053	0.055
LC0003	0.090	0.086	0.094
LC0004	0.041	0.043	0.040
LC0005	0.071	0.071	0.071
LC0006	0.185	0.190	0.180
LC0008	0.070	0.071	0.068
LC0009	0.020	0.020	0.020
LC0011	0.058	0.058	0.059
LC0012	0.056	0.058	0.054
LC0013	0.074	0.075	0.074
LC0014	0.663	0.570	0.757
LC0015	0.048	0.047	0.049

Table D- 53: DIBP in sweet wine sample S006

Preparation concentration: 0.045 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.042	0.041	0.043
LC0002	0.061	0.064	0.059
LC0003	0.045	0.044	0.047
LC0004	0.033	0.033	0.033
LC0005	0.046	0.047	0.046
LC0008	0.044	0.044	0.045
LC0009	0.075	0.080	0.070
LC0011	0.037	0.037	0.038
LC0012	0.032	0.034	0.030
LC0013	0.048	0.047	0.048
LC0014	0.366	0.311	0.421
LC0015	0.045	0.053	0.037

Table D- 54: DBP in sweet wine sample S006

Preparation concentration: 0.153 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.191	0.187	0.195
LC0002	0.162	0.155	0.168
LC0003	0.209	0.210	0.208
LC0004	0.150	0.148	0.152
LC0005	0.165	0.168	0.162
LC0006	0.155	0.160	0.150
LC0008	0.202	0.208	0.196
LC0009	0.175	0.100	0.250
LC0011	0.180	0.179	0.181
LC0012	0.168	0.184	0.153
LC0013	0.205	0.208	0.202
LC0014	1.705	1.475	1.935
LC0015	0.173	0.194	0.153

Table D- 55: BBP in sweet wine sample S006

Preparation concentration: 0.053 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.051	0.049	0.053
LC0002	0.054	0.053	0.055
LC0003	0.057	0.056	0.058
LC0004	0.044	0.044	0.045
LC0005	0.057	0.058	0.056
LC0008	0.046	0.047	0.045
LC0009	0.160	0.170	0.150
LC0011	0.047	0.047	0.047
LC0012	0.041	0.044	0.039
LC0013	0.059	0.058	0.060
LC0014	0.449	0.380	0.517
LC0015	0.038	0.042	0.034

Table D- 56: DCHP in sweet wine sample S006

Preparation concentration: 0.036 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.033	0.032	0.034
LC0003	0.035	0.034	0.035
LC0004	0.028	0.028	0.028
LC0005	0.036	0.037	0.035
LC0009	0.125	0.130	0.120
LC0011	0.031	0.031	0.031
LC0012	0.026	0.027	0.026
LC0013	0.038	0.040	0.037
LC0014	0.268	0.224	0.311
LC0015	0.020	0.022	0.019

Table D- 57: DEHP in sweet wine sample S006

Preparation concentration: 2.013 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0001	0.088	0.086	0.091
LC0002	1.605	1.569	1.640
LC0003	1.944	1.949	1.938
LC0004	1.256	1.568	0.943
LC0005	0.975	1.012	0.937
LC0006	1.300	1.400	1.200
LC0008	0.498	0.072	0.924
LC0009	1.360	1.150	1.570
LC0011	1.305	1.304	1.307
LC0012	0.595	0.692	0.498
LC0013	0.935	1.031	0.840
LC0014	7.470	4.127	10.813
LC0015	0.526	0.789	0.264

Table D- 58: DNOP in sweet wine sample S006

Preparation concentration: 0.054 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.036	0.031	0.040
LC0003	0.035	0.034	0.035
LC0004	0.018	0.020	0.015
LC0005	0.028	0.030	0.027
LC0008		< 0.020	< 0.020
LC0009	0.110	0.100	0.120
LC0011	0.040	0.040	0.039
LC0012	0.017	0.017	0.016
LC0013	0.021	0.023	0.019
LC0014	0.159	0.087	0.230
LC0015	0.012	0.020	0.004

Table D- 59: DINP in sweet wine sample S006

Preparation concentration: 0.057 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.041	0.043	0.039
LC0003	0.135	0.131	0.138
LC0004	0.391	0.493	0.289
LC0005	0.087	0.089	0.086
LC0008		< 0.020	< 0.020
LC0011		< 0.050	< 0.050
LC0012	0.045	0.042	0.048
LC0013	0.051	0.052	0.051
LC0014	0.409	0.250	0.568
LC0015	0.026	0.027	0.024

Table D- 60: DIDP in sweet wine sample S006

Preparation concentration: 3.070 mg/l

Lab code	Lab mean	M 1	M 2
	mg/l	mg/l	mg/l
LC0002	0.114	0.112	0.115
LC0003	3.301	3.190	3.412
LC0004	0.450	0.567	0.333
LC0005	1.473	1.537	1.409
LC0011	4.729	4.994	4.464
LC0012	0.752	0.816	0.689
LC0013	1.977	2.172	1.781
LC0014	11.098	5.824	16.371
LC0015	1.847	2.848	0.847

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