# OIV-MA-AS323-10 Method of determination of phthalates by gas chromatography/ mass spectrometry in wines

Type II/IV methods

## 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 20 µL 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.

5.4.2. Analysing the samples

Start the analysis sequence by analysing the "blank" test (5.3).

Then inject the samples prepared (5.2) in duplicate.

Plan solvent injections after potentially highly contaminated samples.

End the series by injecting one or more calibration standards to check any signal drift during the analysis series and to check several solvent injections..

For each injection, measure the area of the identified peaks and internal standards, and use the calibration curve equation (5.4.1) to determine the concentration in the extract analysed.

5.4.3. Expressing the results

For each sample, calculate the average of the results obtained (5.4.2) for both injections.

The results are expressed in mg/L.

## 6. Quality control

During each analysis series, quality control is provided by the analysis of a wine sample supplemented with phthalates at a concentration level of 0.020 mg/L.

The extract of the sample prepared as per 5.2 is analysed at the beginning of the series, and the results obtained, given in terms of recovery rate, are reflected on a control chart.

## 7. Method characteristics

The analyses performed in the laboratory, under repeatability and intermediate precision conditions, on a red wine and a white wine supplemented with phthalates at two concentration levels (0.040 mg/L and 0.080 mg/L), gave the following repeatability ($CV_r$%), intermediate reproducibility ($CV_{IP}$%), and recovery values:

| 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


**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

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 | Qualifier ions m/z 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.

**Appendix III**

**(for information)**

Validation of analysis of phthalates in wines

Executive Summary

The Institute for Reference Materials and Measurements (IRMM) organised in close

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

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

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

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

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

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

Table 1

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

Participants in the study

Table 2: Participants in the study

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

| | |
|---|---|
| Escola Superior de Biotecnologia Universidade Católica Portuguesa | Portugal |
| Instituto Nacional de Vitivinicultura Departamento de Normas Analiticas Especiales | Argentina |
| Laboratorio Arbitral Agroalimentario | Spain |
| Laboratoire DUBERNET | France |
| Miguel Torres S.A. | Spain |
| SAILab | Spain |
| SCL Laboratoire de Bordeaux | France |
| SCL Laboratoire de Montpellier | France |
| The Australian Wine Research Institute | Australia |

Evaluation of submitted results

The fitness-for-purpose of the calculated reproducibility standard deviation was evaluated. For this purpose, the calculated reproducibility relative standard deviation ( $RSD_R$) 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 ($HORRAT_R$).

Evaluation of systematic effects

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

Evaluation of reported results by analyte

Based on the results of the separate analysis of each analyte and according to the reproducibility results, the method should be considered as either type II (DCHP BBP

DBP DIBP DEP) or type IV (DIDP DINP DNOP DEHP DMP).

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 11 | 10 | 11 | 10 | 10 | 11 |
| Mean | mg/l | 0.020 | 0.073 | 0.018 | 0.031 | 0.053 | 0.027 |
| Median | mg/l | 0.020 | 0.060 | 0.018 | 0.030 | 0.056 | 0.028 |
| Assigned value | mg/l | 0.030 | 0.097 | 0.030 | 0.049 | 0.104 | 0.046 |
| Rel. dev. assign. value | | -33.3% | -38.1% | -40.0% | -38.8% | -46.2% | -39.1% |
| Repeatability s.d. | mg/l | 0.003 | 0.007 | 0.002 | 0.006 | 0.011 | 0.003 |
| Reproducibility s.d. | mg/l | 0.006 | 0.041 | 0.007 | 0.011 | 0.022 | 0.009 |
| Rel. repeatability s.d. | | 9.42% | 7.33% | 8.04% | 13.00% | 10.25% | 7.09% |
| Rel. reproducibility s.d. | | 20.10% | 42.40% | 23.12% | 22.54% | 21.10% | 19.07% |
| Modified Horwitz s.d. ** | | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% |
| HORRATR | | 0.91 | 1.93 | 1.05 | 1.02 | 0.96 | 0.87 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.008 | 0.020 | 0.007 | 0.018 | 0.030 | 0.009 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.017 | 0.114 | 0.019 | 0.031 | 0.061 | 0.024 |
| Rel. limit of repeatability | | 26.09% | 20.32% | 22.28% | 36.00% | 28.38% | 19.64% |
| Rel. limit of reproducibility | | 55.67% | 117.45% | 64.05% | 62.44% | 58.45% | 52.84% |
| No. of laboratories after elimination of outliers | | 9 | 9 | 8 | 8 | 9 | 10 |
| No. of measurement values without outliers | | 18 | 18 | 15 | 16 | 18 | 20 |

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 12 | 11 | 11 | 11 | 10 | 12 |
| Mean | mg/l | 0.048 | 0.065 | 0.030 | 0.039 | 0.021 | 0.059 |
| Median | mg/l | 0.044 | 0.076 | 0.029 | 0.041 | 0.023 | 0.061 |
| Assigned value | mg/l | 0.057 | 0.092 | 0.031 | 0.056 | 0.030 | 0.089 |
| Rel. dev. assign. value | | -22.8% | -17.4% | -6.5% | -26.8% | -23.3% | -31.5% |
| Repeatability s.d. | mg/l | 0.006 | 0.010 | 0.005 | 0.004 | 0.003 | 0.002 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Reproducibility s.d. | mg/l | 0.026 | 0.026 | 0.015 | 0.017 | 0.008 | 0.019 |
| Rel. repeatability s.d. | | 10.49% | 11.32% | 15.28% | 7.00% | 11.41% | 2.53% |
| Rel. reproducibility s.d. | | 45.36% | 28.49% | 47.95% | 29.71% | 25.74% | 20.98% |
| Modified Horwitz s.d. ** | | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% |
| HORRATR | | 2.06 | 1.30 | 2.18 | 1.35 | 1.17 | 0.95 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.017 | 0.029 | 0.013 | 0.011 | 0.009 | 0.006 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.072 | 0.073 | 0.041 | 0.046 | 0.021 | 0.052 |
| Rel. limit of repeatability | | 29.05% | 31.35% | 42.32% | 19.40% | 31.60% | 7.01% |
| Rel. limit of reproducibility | | 125.66% | 78.91% | 132.81% | 82.29% | 71.30% | 58.12% |
| No. of laboratories after elimination of outliers | | 11 | 10 | 11 | 9 | 10 | 11 |
| No. of measurement values without outliers | | 21 | 20 | 21 | 17 | 20 | 22 |

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 11 | 10 | 11 | 10 | 10 | 11 |
| Mean | mg/l | 0.049 | 0.087 | 0.076 | 0.119 | 0.054 | 0.046 |
| Median | mg/l | 0.049 | 0.085 | 0.076 | 0.123 | 0.055 | 0.045 |
| Assigned value | mg/l | 0.035 | 0.076 | 0.058 | 0.107 | 0.061 | 0.045 |
| Rel. dev. assign. value | | 40.0% | 11.8% | 31.0% | 15.0% | -9.8% | 0.0% |
| Repeatability s.d. | mg/l | 0.003 | 0.006 | 0.007 | 0.009 | 0.002 | 0.004 |
| Reproducibility s.d. | mg/l | 0.011 | 0.019 | 0.014 | 0.023 | 0.012 | 0.013 |
| Rel. repeatability s.d. | | 7.43% | 7.71% | 11.55% | 8.81% | 4.04% | 9.54% |
| Rel. reproducibility s.d. | | 32.18% | 25.23% | 24.48% | 21.95% | 19.98% | 28.37% |
| Modified Horwitz s.d. ** | | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% |
| HORRATR | | 1.46 | 1.15 | 1.11 | 1.00 | 0.91 | 1.29 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.007 | 0.016 | 0.019 | 0.026 | 0.007 | 0.012 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.031 | 0.053 | 0.039 | 0.065 | 0.034 | 0.035 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rel. limit of repeatability | | 20.58% | 21.35% | 31.98% | 24.42% | 11.19% | 26.44% |
| Rel. limit of reproducibility | | 89.15% | 69.88% | 67.80% | 60.81% | 55.35% | 78.58% |
| No. of laboratories after elimination of outliers | | 11 | 10 | 11 | 10 | 10 | 11 |
| No. of measurement values without outliers | | 21 | 20 | 21 | 20 | 20 | 22 |

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 12 | 11 | 12 | 11 | 11 | 12 |
| Mean | mg/l | 0.103 | 0.264 | 0.078 | 0.728 | 0.090 | 0.178 |
| Median | mg/l | 0.103 | 0.266 | 0.074 | 0.666 | 0.089 | 0.174 |
| Assigned value | mg/l | 0.107 | 0.281 | 0.057 | 1.039 | 0.032 | 0.153 |
| Rel. dev. assign. value | | -3.7% | -5.3% | 29.8% | -35.9% | | |
| Repeatability s.d. | mg/l | 0.009 | 0.014 | 0.011 | 0.033 | 0.004 | 0.012 |
| Reproducibility s.d. | mg/l | 0.022 | 0.048 | 0.021 | 0.314 | 0.018 | 0.022 |
| Rel. repeatability s.d. | | 8.24% | 5.03% | 19.11% | 3.21% | 13.79% | 7.87% |
| Rel. reproducibility s.d. | | 20.73% | 17.01% | 36.78% | 30.25% | 57.05% | 14.66% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Modified Horwitz s.d. ** | | 22.00% | 19.36% | 22.00% | 15.91% | 22.00% | 21.22% |
| HORRATR | | 0.94 | 0.88 | 1.67 | 1.90 | 2.59 | 0.69 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.024 | 0.039 | 0.030 | 0.092 | 0.012 | 0.033 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.061 | 0.132 | 0.058 | 0.871 | 0.051 | 0.062 |
| Rel. limit of repeatability | | 22.81% | 13.92% | 52.94% | 8.89% | 38.21% | 21.80% |
| Rel. limit of reproducibility | | 57.43% | 47.12% | 101.88% | 83.79% | 158.03% | 40.60% |
| No. of laboratories after elimination of outliers | | 12 | 11 | 12 | 10 | 11 | 11 |
| No. of measurement values without outliers | | 23 | 22 | 23 | 20 | 22 | 22 |

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

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

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Repeatability s.d. | mg/l | 0.002 | 0.001 | 0.003 | 0.004 | 0.003 | 0.003 |
| Reproducibility s.d. | mg/l | 0.008 | 0.004 | 0.005 | 0.011 | 0.015 | 0.007 |
| Rel. repeatability s.d. | | 4.30% | 4.96% | 8.08% | 5.10% | 3.31% | 4.78% |
| Rel. reproducibility s.d. | | 13.71% | 13.82% | 13.93% | 12.72% | 17.00% | 14.00% |
| Modified Horwitz s.d. ** | | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% |
| HORRATR | | 0.62 | 0.63 | 0.63 | 0.58 | 0.77 | 0.64 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.007 | 0.004 | 0.008 | 0.012 | 0.008 | 0.007 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.022 | 0.011 | 0.014 | 0.031 | 0.041 | 0.021 |
| Rel. limit of repeatability | | 11.90% | 13.75% | 22.38% | 14.14% | 9.16% | 13.23% |
| Rel. limit of reproducibility | | 37.98% | 38.27% | 38.58% | 35.23% | 47.09% | 38.77% |
| No. of laboratories after elimination of outliers | | 9 | 8 | 10 | 9 | 9 | 10 |
| No. of measurement values without outliers | | 17 | 15 | 19 | 18 | 18 | 20 |

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

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | S001 | S002 | S003 | S004 | S005 | S006 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 9 | 8 | 9 | 8 | 8 | 9 |
| Mean | mg/l | 0.079 | 0.042 | 0.030 | 0.088 | 0.046 | 0.031 |
| Median | mg/l | 0.076 | 0.044 | 0.033 | 0.091 | 0.050 | 0.033 |
| Assigned value | mg/l | 0.084 | 0.048 | 0.038 | 0.105 | 0.057 | 0.036 |
| Rel. dev. assign. value | | -9.5% | -8.3% | -13.2% | -13.3% | -12.3% | -8.3% |
| Repeatability s.d. | mg/l | 0.005 | 0.006 | 0.003 | 0.005 | 0.002 | 0.001 |
| Reproducibility s.d. | mg/l | 0.024 | 0.008 | 0.005 | 0.011 | 0.011 | 0.006 |
| Rel. repeatability s.d. | | 5.60% | 13.13% | 6.75% | 4.84% | 3.25% | 3.67% |
| Rel. reproducibility s.d. | | 28.46% | 16.05% | 12.93% | 10.20% | 18.83% | 16.37% |
| Modified Horwitz s.d. ** | | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% |
| HORRATR | | 1.29 | 0.73 | 0.59 | 0.46 | 0.86 | 0.74 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.013 | 0.017 | 0.007 | 0.014 | 0.005 | 0.004 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.066 | 0.021 | 0.014 | 0.030 | 0.030 | 0.016 |
| Rel. limit of repeatability | | 15.53% | 36.37% | 18.69% | 13.40% | 9.00% | 10.18% |
| Rel. limit of reproducibility | | 78.83% | 44.46% | 35.82% | 28.24% | 52.15% | 45.35% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| No. of laboratories after elimination of outliers | | 9 | 7 | 8 | 7 | 7 | 8 |
| No. of measurement values without outliers | | 18 | 14 | 15 | 14 | 14 | 16 |

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 12 | 11 | 12 | 11 | 11 | 12 |
| Mean | mg/l | 0.101 | 0.028 | 0.602 | 0.150 | 0.741 | 1.032 |
| Median | mg/l | 0.099 | 0.026 | 0.654 | 0.180 | 0.709 | 1.115 |
| Assigned value | mg/l | 0.217 | 0.046 | 1.049 | 0.328 | 1.569 | 2.013 |
| Rel. dev. assign. value | | -54.4% | -43.5% | -37.7% | -45.1% | -54.8% | -44.6% |
| Repeatability s.d. | mg/l | 0.017 | 0.005 | 0.206 | 0.016 | 0.122 | 0.266 |
| Reproducibility s.d. | mg/l | 0.019 | 0.011 | 0.238 | 0.063 | 0.465 | 0.563 |
| Rel. repeatability s.d. | | 7.72% | 11.54% | 19.66% | 4.82% | 7.78% | 13.20% |
| Rel. reproducibility s.d. | | 8.92% | 24.15% | 22.70% | 19.11% | 29.61% | 27.96% |
| Modified Horwitz s.d. ** | | 20.13% | 22.00% | 15.88% | 18.92% | 14.95% | 14.40% |
| HORRATR | | 0.44 | 1.10 | 1.43 | 1.01 | 1.98 | 1.94 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.046 | 0.015 | 0.571 | 0.044 | 0.338 | 0.736 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.054 | 0.031 | 0.660 | 0.174 | 1.287 | 1.559 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rel. limit of repeatability | | 21.39% | 31.98% | 54.45% | 13.36% | 21.54% | 36.55% |
| Rel. limit of reproducibility | | 24.70% | 66.91% | 62.87% | 52.93% | 82.03% | 77.46% |
| No. of laboratories after elimination of outliers | | 10 | 10 | 12 | 9 | 11 | 12 |
| No. of measurement values without outliers | | 20 | 20 | 23 | 18 | 22 | 24 |

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

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

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Modified Horwitz s.d. ** | | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% | 22.00% |
| HORRATR | | 0.52 | 0.42 | 1.77 | 1.52 | 1.06 | 0.91 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.019 | 0.008 | 0.059 | 0.014 | 0.011 | 0.014 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.027 | 0.008 | 0.064 | 0.105 | 0.023 | 0.030 |
| Rel. limit of repeatability | | 21.73% | 25.61% | 100.62% | 12.50% | 30.97% | 25.56% |
| Rel. limit of reproducibility | | 31.85% | 25.85% | 107.76% | 92.52% | 64.60% | 55.66% |
| No. of laboratories after elimination of outliers | | 9 | 8 | 10 | 9 | 7 | 8 |
| No. of measurement values without outliers | | 18 | 15 | 18 | 16 | 14 | 16 |

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|
| No. of laboratories that submitted compliant results | | 9 | 8 | 10 | 8 | 8 | 9 |
| Mean | mg/l | 0.027 | 0.108 | 1.820 | 0.059 | 0.115 | 0.064 |
| Median | mg/l | 0.028 | 0.116 | 1.497 | 0.058 | 0.136 | 0.051 |
| Assigned value | mg/l | 0.054 | 0.242 | 3.134 | 0.104 | 0.271 | 0.057 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rel. dev. assign. value | | -48.1% | -52.1% | -52.2% | -44.2% | -49.8% | -10.5% |
| Repeatability s.d. | mg/l | 0.004 | 0.019 | 0.520 | 0.005 | 0.010 | 0.003 |
| Reproducibility s.d. | mg/l | 0.006 | 0.027 | 1.067 | 0.019 | 0.072 | 0.040 |
| Rel. repeatability s.d. | | 8.14% | 7.84% | 16.60% | 5.17% | 3.83% | 5.51% |
| Rel. reproducibility s.d. | | 10.27% | 11.18% | 34.06% | 18.41% | 26.60% | 70.59% |
| Modified Horwitz s.d. ** | | 20.00% | 20.00% | 20.00% | 20.00% | 20.00% | 20.00% |
| HORRATR | | 0.51 | 0.56 | 1.70 | 0.92 | 1.33 | 3.53 |
| Limit of repeatability, r (2.77 X sr) | mg/l | 0.012 | 0.053 | 1.441 | 0.015 | 0.029 | 0.009 |
| Limit of reproducibility, R (2.77 X sR) | mg/l | 0.015 | 0.075 | 2.957 | 0.053 | 0.200 | 0.111 |
| Rel. limit of repeatability | | 22.55% | 21.71% | 45.99% | 14.32% | 10.61% | 15.27% |
| Rel. limit of reproducibility | | 28.44% | 30.98% | 94.35% | 50.99% | 73.69% | 195.53% |
| No. of laboratories after elimination of outliers | | 5 | 6 | 9 | 7 | 6 | 6 |
| No. of measurement values without outliers | | 10 | 11 | 17 | 13 | 12 | 12 |

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

| | | S001 | S002 | S003 | S004 | S005 | S006 |
|---|---|---|---|---|---|---|---|

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

References

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[1] Type IV method
[2] Type II method
[3] Type II method
[4] Type II method
[5] Type II method
[6] Type II method
[7] Type IV method
[8] Type IV method
[9] Type IV method
[10] Type IV method