# OIV-MA-AS315-27 Analysis of volatile compounds in wines by gas chromatography

**Type IV method**

1. **Object**

This method is applicable to the analysis of volatile compounds in wines containing less than 20 g/L sugar.

For wines with a sugar content higher than 20 g/L and for mistelles, prior distillation (identical to that practised to obtain the ABV) is necessary; however distillation sometimes removes a significant part of the compounds.

2. **Scope of application**

The present method may be used for the quantification of the following compounds (non-exhaustive list):

ethanal,
ethyl acetate,
methanol,
butan-2-ol,
propan-1-ol,
2-methylpropan-1-ol,
isoamyl acetate,
butan-1-ol,
2-methylbutan-1-ol,
3-methylbutan-1-ol,
pentan-1-ol,
acetoin,
ethyl lactate,
hexan-1-ol,
3-ethoxypropanol,
ethyl octanoate,
furfuraldehyde,
(2R,3R)-butane-2,3-diol,

(2R,3S)-butane-2,3-diol,
propane-1,2-diol,
butyrolactone,
diethyl succinate,
hexanoic acid (semi-quantitative),
2-phenylethanol,
diethyl malate,
octanoic acid (semi-quantitative),
decanoic acid (semi-quantitative).

*Note: diacetyl and acetic acid cannot be quantified by this method yet they appear in the chromatograms.*

## 3. Principle

Volatile compounds are quantified by gas chromatography after direct injection of the sample, added with an internal standard, into a capillary column coated with a bonded polar phase and detection using flame ionisation.

## 4. Reagents and products

*The quantities and **method** of preparation **are given by way of example and may be adapted as necessary to the type**s of wine.*

4.1. Demineralised water (e.g. ISO 3696 type II or resistivity ≥ 18 MΩ.cm);
4.2. ethanol [CAS no. 64-17-5], purity ≥ 96%;
4.3. high-purity hydrogen for GC (e.g. $H_2O$ ≤ 4 ppm; $O_2$ ≤ 2 ppm; $C_nH_m$ ≤ 0.5 ppm; $N_2$ ≤ 4 ppm);
4.4. high-purity helium for GC ($H_2O$ ≤ 3 ppm; $O_2$ ≤ 2 ppm; $C_nH_m$ ≤ 1 ppm; $N_2$ ≤ 5 ppm);
4.5. high-purity compressed air for GC;
4.6. ethanal [CAS no. 75-07-0], purity ≥ 99%;
4.7. ethyl acetate [CAS no. 141-78-6], purity ≥ 99.5%;
4.8. methanol [CAS no. 67-56-1], purity ≥ 99.8%;
4.9. diacetyl [CAS no. 431-03-08], purity ≥ 99%;

4.10. butan-2-ol [CAS no. 15892-23-6], purity ≥ 99.5%;
4.11. propan-1-ol [CAS no. 71-23-8], purity ≥ 99.5%;
4.12. 2-methylpropan-1-ol [CAS no. 78-83-1], purity ≥ 99.5%;
4.13. isoamyl acetate [CAS no. 123-92-2], purity ≥ 97%;
4.14. butan-1-ol [CAS no. 71-36-3], purity ≥ 99.5%;
4.15. 4-methylpentan-2-ol (internal standard) [CAS no. 108-11-2], purity ≥ 99%;
4.16. 2-methylbutan-1-ol [CAS no. 137-32-6], purity ≥ 99%;
4.17. 3-methylbutan-1-ol [CAS no. 125-51-3], purity ≥ 99.5%;
4.18. pentan-1-ol [CAS no. 71-41-0], purity ≥ 99%;
4.19. acetoin [CAS no. 513-86-0], purity ≥ 96%;
4.20. ethyl lactate [CAS no. 687-47-8], purity ≥ 98%;
4.21. hexan-1-ol [CAS no. 111-27-3], purity ≥ 99.0%;
4.22. 3-ethoxypropanol [CAS no. 111-35-3], purity ≥ 97%;
4.23. ethyl octanoate [CAS no. 106-32-1], purity ≥ 99%;
4.24. furfuraldehyde [CAS no. 98-01-1], purity ≥ 99.0%;
4.25. acetic acid [CAS no. 64-19-7], purity ≥ 99%;
4.26. (2R,3R)- and (2R,3S)-butane-2,3-diol [CAS no. 513-85-9], purity ≥ 98%;
4.27. propane-1,2-diol [CAS no. 57-556], purity ≥ 99.5%;
4.28. butyrolactone [CAS no. 96-48-0], purity ≥ 99%;
4.29. diethyl succinate [CAS no. 123-25-1], purity ≥ 99%;
4.30. hexanoic acid [CAS no. 142-62-1], purity ≥ 99.5%;
4.31. 2-phenylethanol [CAS no. 60-12-8], purity ≥ 99%;
4.32. diethyl malate [CAS no. 7554-12-3], purity ≥ 97%;
4.33. octanoic acid [CAS no. 124-07-2], purity ≥ 99.5%;
4.34. decanoic acid [CAS no. 334-48-5], purity ≥ 99.5%.

*Note: diacetyl and acetic acid cannot be quantified by this method yet they appear in the chromatograms.*

Preparation of reagent solutions *(the quantities are given by way of example and may be adapted as necessary to the types of matrix to be analysed)*

4.35. 10% Aqueous-alcoholic mixture to be made up with ethanol (4.2) and water (4.1).

4.36. Internal standard solution

Transfer 1 mL 4-methylpentan-2-ol (4.15) into a 100-mL flask (5.2). Fill up to the calibration mark with ethanol (4.2). Divide into flasks on which the date of preparation

is noted. Keep refrigerated.

4.37. Internal or external reference wine (a CRM (Certified Reference Material) wine or a wine used as a reference material from a proficiency-testing programme between laboratoriesfor example).

4.38. Stock calibration solution

The compounds are individually weighed at ± 1 mg (nominal weights given in the table below) using a precision balance (5.4). In order to avoid losses through evaporation, quickly add a small amount of ethanol (4.2). Mix and pour into a 1-L flask (5.3). Rinse with ethanol. Add 2.5 mL 4-methylpentan-2-ol (4.15). Make up to 1 L with ethanol (4.2) and mix. Divide into flasks and store in the freezer. Record the exact weights.

| **Compound** | **Nominal weight (mg)** | **Final concentration in the working calibration solution 4.39 (mg/L)** | **Compound** | **Nominal weight (mg)** | **Final concentration in the working calibration solution 4.39 (mg/L)** |
|---|---|---|---|---|---|
| Ethanal (4.6) | 500 | 50 | Hexan-1-ol (4.21) | 300 | 30 |
| Ethyl acetate (4.7) | 1500 | 150 | 3-Ethoxypropanol (4.22) | 160 | 16 |
| Methanol (4.8) | 650 | 65 | Furfuraldehyde (4.24) | 50 | 5 |
| Diacetyl (4.9) | 50 | 5 | Ethyl octanoate (4.23) | 120 | 12 |
| Butan-2-ol (4.10) | 160 | 16 | Acetic acid (5.25) | 5000 | 500 |
| Propan-1-ol (4.11) | 350 | 35 | Butane-2,3-diol (4.26) | 4000 | 400 |
| 2-Methylpropan-1-ol (4.12) | 240 | 24 | Propane-1,2-diol (4.27) | 1000 | 100 |
| Isoamyl acetate (4.13) | 250 | 25 | Butyrolactone (4.28) | 50 | 5 |

| | | | | | |
|---|---|---|---|---|---|
| Butan-1-ol (4.14) | 160 | 16 | Diethyl succinate (4.29) | 500 | 50 |
| 2-Methylbutan-1-ol (4.16) | 160 | 16 | Hexanoic acid (4.30) | 250 | 25 |
| 3-Methylbutan-1-ol (4.17) | 1000 | 100 | 2-Phenylethanol (4.31) | 500 | 50 |
| Pentan-1-ol (4.18) | 160 | 16 | Diethyl malate (4.32) | 1000 | 100 |
| Acetoin (4.19) | 250 | 25 | Octanoic acid (4.33) | 500 | 50 |
| Ethyl lactate (4.20) | 1500 | 150 | Decanoic acid (4.34) | 750 | 75 |

4.39. Working calibration solution

Just before use, dilute the stock calibration solution (4.38) ten times.

5. **Apparatus**

5.1. 20-mL volumetric flasks (class A);

5.2. 100-mL volumetric flasks (class A);

5.3. 1-L volumetric flasks (class A);

5.4. precision balance with an accuracy of ± 1 mg;

5.5. gas chromatograph equipped with:

"split-splitless" injector,

autosampler (optional),

detector: flame ionisation (FID);

5.6. fused-silica capillary column:

Carbowax 20 M type with a bonded polar phase,

50 m in length,

internal diameter of 0.32 mm,

film thickness of 0.45 µm.

*Note: other systems may be used on condition that they are capable of satisfactorily separating the different compounds.*

6. **Preparation of the samples**

Conduct a preliminary degassing of sparkling wine samples (for example, by first taking a sample using an automatic pipette and collecting it in a tube).
Distil the wines containing more than 20 g/L of sugar and the mistelles prior to preparation.
Introduce the sample into a 20-mL flask (5.1). Add 0.5 mL internal standard solution (4.36) and fill up to the calibration mark with wine.

7. **Procedure**

Analyse using the gas chromatograph (5.5) equipped with a capillary column (5.6).
Analytical conditions (given by way of example):
Carrier gas (4.4): $P_{helium}$ = 90 kPa
*Note: another carrier gas such as hydrogen may be used, but nitrogen is best avoided.*
Septum flow rate: 2.5 mL/min
Split flow rate: 40 mL/min
Split mode of injection
Volume injected: 1 µL
Temperature of the injector: 200 °C
Detector: FID (flame ionisation)

- Detector temperature at 250 °C
- Flame: $P_{hydrogen\ (4.3)}$ = 50 kPa and $P_{air\ (4.5)}$ = 130 kPa

Temperature programming:

- temp. 1 = 32 °C at 2.5 °C/min, up to 80 °C - $t_1$ = 0 min
- temp. 2 = 80 °C at 4 °C/min, up to 170 °C - $t_2$ = 20 min
- temp. 3 = 170 °C at 10 °C/min, up to 220°C - $t_3$ = 20 min

Calibration
Inject the working calibration solution (4.39) before each analysis series.
Calculation of response factors:
$RF_i$ = ($area_i$ x $Cc_{is}$) / ($Cc_i$ x $area_{IS}$)
$Cc_i$ = concentration of the constituent of the calibration solution
$Area_i$= area of the constituent of the calibration solution
$Cc_{IS}$= concentration of the internal standard in the calibration solution
$Area_{IS}$= area of the internal standard in the calibration solution

It is also possible to use a calibration curve.

By way of example, chromatograms of a standard solution and a wine sample are given in the Annexes.

8. **Calculations**

In the case of use of a response factor, calculation of the concentrations is as follows: $Cc_i = (area_i \text{ x } Cc_{IS}) / (RF_i \text{ x } area_{IS})$.

9. **Precision**

See Annex C.

10. **Quality assurance and control**

Traceable to the international references through mass, volume and temperature.

Synthetic mixtures or samples coming, for instance, from proficiency ring test are used as internal quality control. A control chart may be used.

11. **Results**

Express concentrations in mg/L to the number of decimal places indicated below.

| Analytical parameters | No. of decimal places | Analytical parameters | No. of decimal places |
|---|---|---|---|
| Ethanal | 0 | Ethyl lactate | 0 |
| Ethyl acetate | 0 | Hexan-1-ol | 1 |
| Methanol | 0 | 3-Ethoxypropanol | 0 |
| Butan-2-ol | 1 | Ethyl octanoate | 0 |
| Propan-1-ol | 0 | Furfuraldehyde | 1 |
| 2-Methylpropan-1-ol | 0 | (2R,3R)-Butane-2,3-diol | 0 |
| Isoamyl acetate | 1 | (Meso)-butane-2,3-diol | 0 |

| | | | |
|---|---|---|---|
| Butan-1-ol | 1 | Propane-1,2-diol | 0 |
| 2-Methylbutan-1-ol | 0 | Butyrolactone | 0 |
| 3-Methylbutan-1-ol | 0 | Diethyl succinate | 0 |
| Pentan-1-ol | 1 | 2-Phenylethanol | 0 |
| Acetoin | 0 | Diethyl malate | 0 |

**Annex A Bibliography**


- BERTRAND A., GUEDES DE PINHO P. and ANOCIBAR BELOQUI A. (1994). *Les constituants majoritaires du vin*, FV 971, OIV, 15 pages.


**Annex B Example chromatograms**

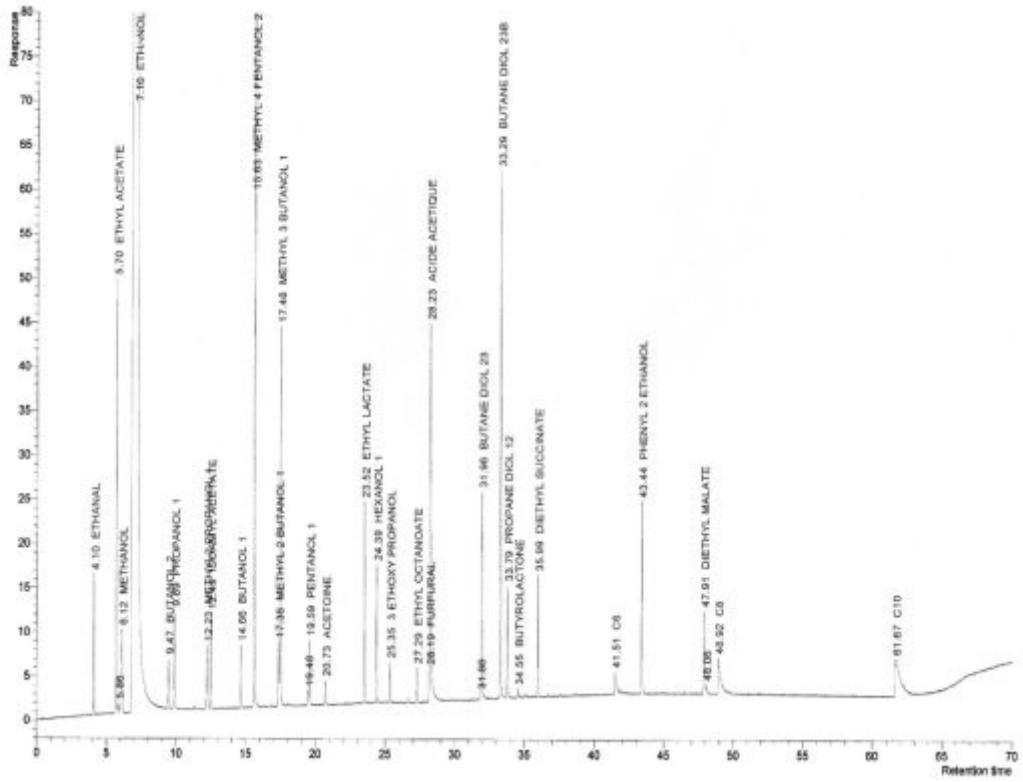


*Figure 1: chromatogram of a standard solution of volatile compounds*

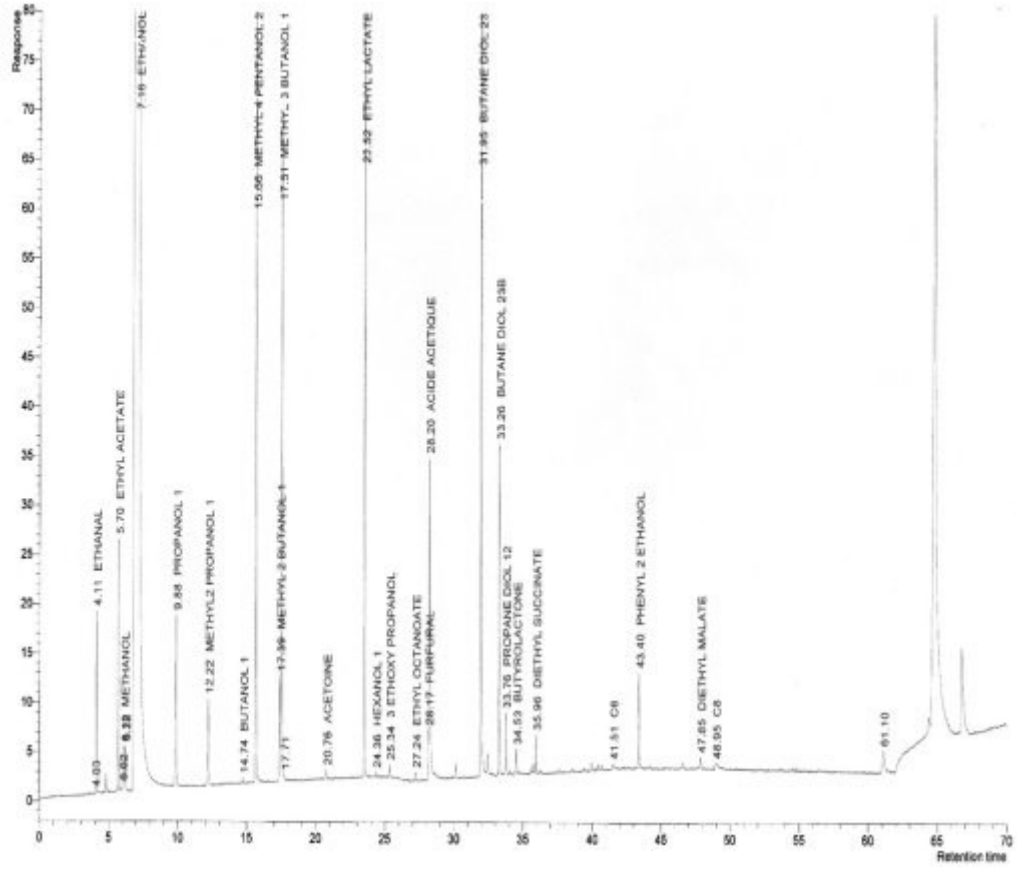



**Figure** 2 : chromatogram of volatile compounds in a white wine (sugar < 15 g/L)

**Annexe C**

**C1 – Organisation of the study - Samples**

This study was carried out by the Comité Interprofessionnel du Vin de Champagne in Epernay. A prevalidation occurred during October/December 2015 and actual interlaboratory during March/April 2016.

The trial involved 11 samples: two white wines identified B and E, two red wines identified C and F and one rosé wine identified A (blindly replicated) + one of the samples spiked with butan-2-ol, butan-1-ol, acetoin, hexan-1-ol and diethyl malate (identified D).

**C2 - Fidelity**

13 laboratories participated in the interlaboratory study:
Autoridade de Segurança Alimentar e Económica, Lisbon, Portugal;
Bundesinstitut für Risikobewertung, Berlin, Germany;
Bureau National Interprofessionnel du Cognac, Cognac, France;
Comité Interprofessionnel du vin de Champagne, Epernay, France;
Czech Agriculture and Food Inspection Authority, Brno, Czech Republic;
Instituto dos Vinhos do Douro e do Porto, Porto, Portugal;
Laboratoire DUBERNET, Montredon Corbières, France;
Laboratorio Arbitral Agroalimentario, Madrid, Spain;
Landesuntersuchungsamt, Mainz, Germany;
Miguel Torres S.A.- Finca, Barcelona, Spain;
Service Commun des Laboratoires Bordeaux-Pessac (SCL MINEFI), Pessac, France;
Service Commun des Laboratoires Montpellier (SCL MINEFI), Montpellier, France;
Union Nationale de Groupements des Distillateurs d'alcool (UNGDA), Malakoff, France.
The results were evaluated according to the OIV protocol (Collaborative study OIV□MA-AS1-07:R2000).
ISO 5725-2 §7.5 recommends to look for any functional relationship between the fidelity values and the content, which is expressed by the graphs below the data tables for each product.

**C3 - Results tables**

| compound | r | R |
|---|---|---|
| ethyl acetate | 0.18x – 1.8 | 0.33x – 1.7 |
| methanol | 0.22x – 4.3 | 0.28x – 3.2 |
| propan-1-ol | 4 mg/l | 7 mg/L |
| 2-methylpropan-1-ol | 0.20x – 1.4 | 0.36x – 0.7 |
| butan-1-ol | 0.07x + 0.2 | 0.14x + 0.3 |

| | | |
|---|---|---|
| 2-methylbutan-1-ol | 0.23x – 2.7 | 0.40x – 5.0 |
| 3-methylbutan-1-ol | 0.35x – 35.7 | 0.45x – 41.8 |
| acetoïn | 0.14x + 1.2 | 0.33x + 2.1 |
| ethyl lactate | 0.23x – 1.6 | 0.29x + 4.2 |
| hexanol | 0.07x + 0.3 | 0.10x + 0.8 |
| 3-ethoxypropanol | 0.59x – 0.4 | 0.46x + 0.4 |
| ethyl octanoate | 0.5 mg/l | 0.7 mg/l |
| butyrolactone | 0.25x + 0.8 | 0.20x + 4.1 |
| diethyl succinate | 0.31x + 0.8 | 0.55x + 0.4 |
| 2-phenylethanol | 0.24x + 0.3 | 0.50x – 2.6 |

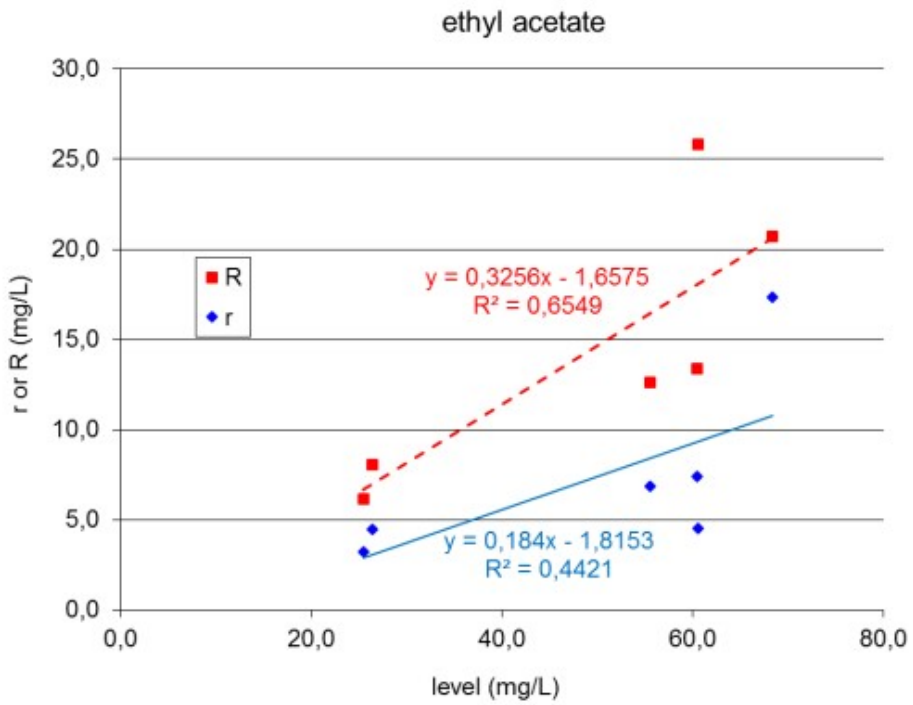
where x is the measured concentration

**Ethyl acetate - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 12 | 12 | 12 | 13 | 12 | 13 |
| Number of measurement values without outliners | 42 | 42 | 42 | 23 | 42 | 46 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Mean (mg/L) | 26.4 | 60.5 | 55.5 | 60.6 | 25.5 | 68.4 |
| Repeatability s.d. Sr | 1.6 | 2.6 | 2.4 | 1.4 | 1.1 | 6.0 |
| RSDr % | 5.9 | 4.2 | 4.3 | 2.4 | 4.3 | 8.8 |
| Limit of repeatability r | 4.5 | 7.4 | 6.9 | 4.5 | 3.2 | 17.3 |
| Relative limit of repeatability r% | 16.9% | 12.2% | 12.3% | 7.4% | 12.5% | 25.3% |
| Reproducibility s.d. SR | 2.8 | 4.7 | 4.4 | 8.8 | 2.2 | 7.3 |
| RSDR % | 10.7 | 7.7 | 8.0 | 14.5 | 8.5 | 10.6 |
| Limit of reproducibility R | 8.1 | 13.4 | 12.6 | 25.8 | 6.2 | 20.7 |
| Relative limit of reproducibility R% | 30.5% | 22.1% | 22.7% | 42.6% | 24.2% | 30.3% |
| HORRAT R | 1.1 | 0.9 | 0.9 | 1.7 | 0.9 | 1.2 |

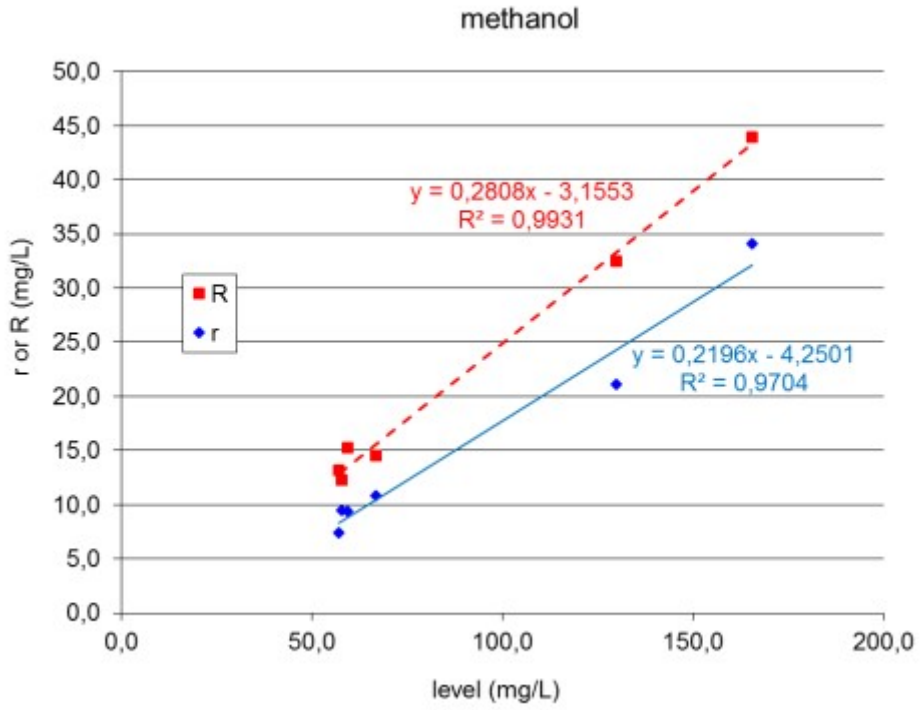


**Methanol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 13 | 13 | 13 | 13 | 13 | 13 |
| Number of measurement values without outliners | 46 | 46 | 46 | 23 | 46 | 46 |
| Mean (mg/L) | 66.8 | 57.2 | 129.8 | 57.8 | 59.4 | 165.6 |
| Repeatability s.d. Sr | 3.8 | 2.6 | 7.4 | 3.0 | 3.3 | 11.9 |
| RSDr % | 5.6 | 4.5 | 5.7 | 5.2 | 5.5 | 7.2 |
| Limit of repeatability r | 10.8 | 7.4 | 21.2 | 9.5 | 9.4 | 34.1 |
| Relative limit of repeatability r% | 16.2% | 12.9% | 16.3% | 16.3% | 15.8% | 20.6% |
| Reproducibility s.d. SR | 5.1 | 4.6 | 11.4 | 4.2 | 5.4 | 15.4 |
| RSDR % | 7.6 | 8.1 | 8.8 | 7.3 | 9.0 | 9.3 |
| Limit of reproducibility R | 14.5 | 13.2 | 32.5 | 12.3 | 15.3 | 43.9 |
| Relative limit of reproducibility R% | 21.7% | 23.1% | 25.0% | 21.3% | 25.7% | 26.5% |

| | | | | | | |
|---|---|---|---|---|---|---|
| HORRAT R | 0.9 | 0.9 | 1.1 | 0.8 | 1.0 | 1.3 |

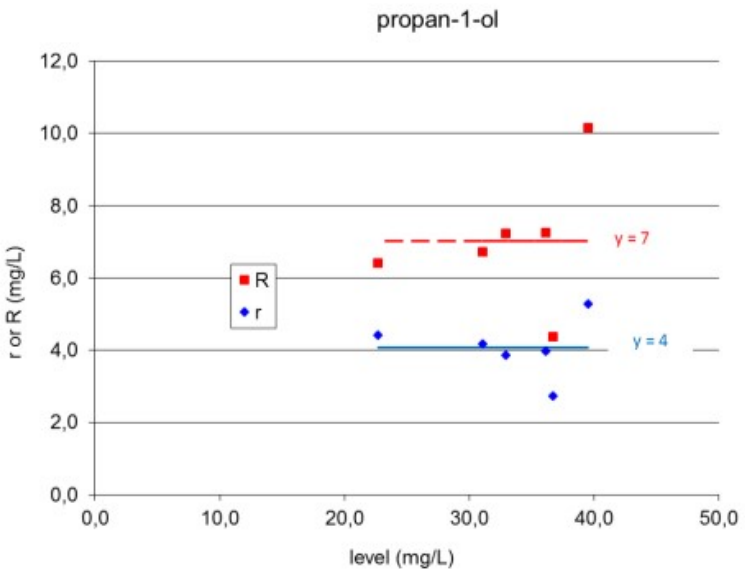



**Propan-1-ol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 13 | 13 | 13 | 13 | 13 | 13 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Number of measurement values without outliners | 46 | 46 | 46 | 23 | 46 | 46 |
| Mean (mg/L) | 31.1 | 36.1 | 39.5 | 36.7 | 32.9 | 22.7 |
| Repeatability s.d. Sr | 1.5 | 1.4 | 1.8 | 0.8 | 1.4 | 1.5 |
| RSDr % | 4.7 | 3.8 | 4.6 | 2.4 | 4.1 | 6.8 |
| Limit of repeatability r | 4.2 | 4.0 | 5.3 | 2.7 | 3.9 | 4.4 |
| Relative limit of repeatability r% | 13.4% | 11.0% | 13.4% | 7.4% | 11.8% | 19.4% |
| Reproducibility s.d. SR | 2.0 | 2.1 | 3.0 | 1.5 | 2.1 | 1.9 |
| RSDR % | 6.3 | 5.9 | 7.5 | 4.1 | 6.4 | 8.3 |
| Limit of reproducibility R | 6.7 | 7.3 | 10.2 | 4.4 | 7.2 | 6.4 |
| Relative limit of reproducibility R% | 21.6% | 20.1% | 25.7% | 11.9% | 22.0% | 28.3% |
| HORRAT R | 0.7 | 0.6 | 0.8 | 0.4 | 0.7 | 0.8 |

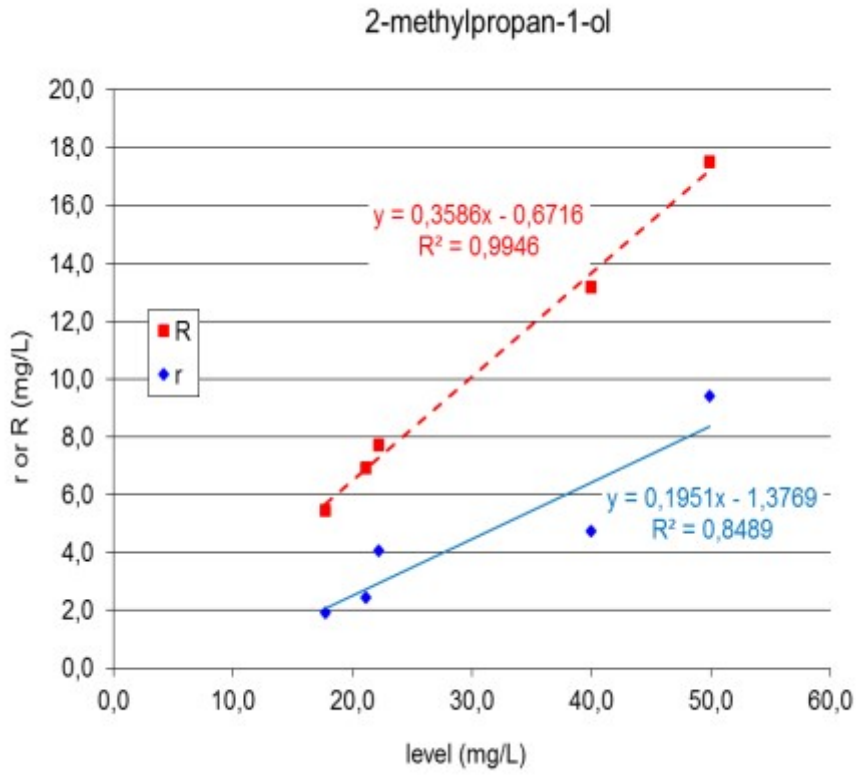


**2-methylpropan-1-ol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 13 | 13 | 13 | 12 | 13 | 13 |
| Number of measurement values without outliners | 46 | 46 | 46 | 21 | 46 | 46 |
| Mean (mg/L) | 21.2 | 22.2 | 40.0 | 30.8 | 17.7 | 49.9 |
| Repeatability s.d. Sr | 0.9 | 1.4 | 1.6 | 3.0 | 0.7 | 3.3 |
| RSDr % | 4.0 | 6.4 | 4.1 | 9.6 | 3.7 | 6.5 |
| Limit of repeatability r | 2.5 | 4.1 | 4.7 | 9.5 | 1.9 | 9.4 |
| Relative limit of repeatability r% | 11.6% | 18.3% | 11.8% | 30.8% | 10.8% | 18.9% |
| Reproducibility s.d. SR | 2.4 | 2.7 | 4.6 | 7.5 | 1.9 | 6.1 |
| RSDR % | 11.5 | 12.2 | 11.5 | 24.2 | 10.8 | 12.3 |
| Limit of reproducibility R | 6.9 | 7.7 | 13.2 | 22.0 | 5.5 | 17.5 |
| Relative limit of reproducibility R% | 32.8% | 34.7% | 33.0% | 71.5% | 30.8% | 35.1% |
| HORRAT R | 1.1 | 1.2 | 1.3 | 2.5* | 1.0 | 1.4 |

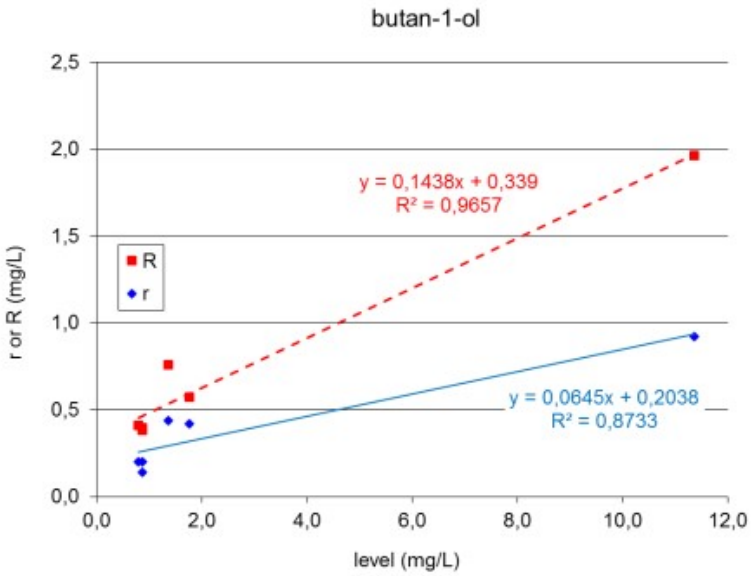
*presumed outlier, not considered for computation of fidelity.




**Butan-1-ol – Fidelity repeatability et reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 9 | 8 | 10 | 13 | 9 | 10 |
| No. of laboratories after elimination of outliners | 9 | 8 | 10 | 13 | 9 | 10 |

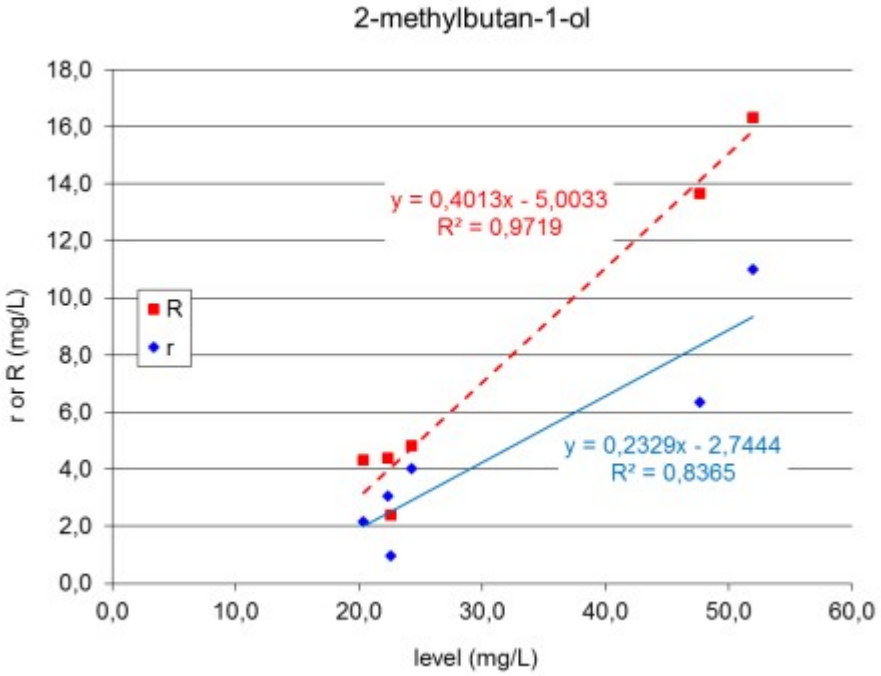
| | | | | | | |
|---|---|---|---|---|---|---|
| Number of measurement values without outliners | 28 | 26 | 34 | 23 | 28 | 32 |
| Mean (mg/L) | 0.87 | 0.87 | 1.77 | 11.36 | 0.81 | 1.36 |
| Repeatability s.d. Sr | 0.05 | 0.07 | 0.14 | 0.29 | 0.07 | 0.15 |
| RSDr % | 5.5 | 7.8 | 8.2 | 2.6 | 8.4 | 11.0 |
| Limit of repeatability r | 0.14 | 0.20 | 0.42 | 0.92 | 0.20 | 0.44 |
| Relative limit of repeatability r% | 16.2% | 23.1% | 23.9% | 8.1% | 24.8% | 32.1% |
| Reproducibility s.d. SR | 0.14 | 0.13 | 0.20 | 0.67 | 0.14 | 0.26 |
| RSDR % | 15.6 | 15.0 | 11.3 | 5.9 | 17.5 | 19.3 |
| Limit of reproducibility R | 0.39 | 0.38 | 0.58 | 1.96 | 0.41 | 0.76 |
| Relative limit of reproducibility R% | 45.2% | 43.9% | 32.5% | 17.3% | 50.9% | 55.7% |
| HORRAT R | 1.0 | 0.9 | 0.8 | 0.5 | 1.1 | 1.3 |



**2-methylbutan-1-ol - Fidelity**
**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 9 | 9 | 9 | 9 | 9 | 9 |
| No. of laboratories after elimination of outliners | 9 | 9 | 9 | 9 | 9 | 9 |
| Number of measurement values without outliners | 32 | 32 | 32 | 16 | 32 | 32 |
| Mean (mg/L) | 24.3 | 22.4 | 47.6 | 22.6 | 20.4 | 52.0 |
| Repeatability s.d. Sr | 1.4 | 1.1 | 2.2 | 0.3 | 0.7 | 3.8 |
| RSDr % | 5.7 | 4.7 | 4.6 | 1.3 | 3.6 | 7.3 |
| Limit of repeatability r | 4.0 | 3.1 | 6.4 | 1.0 | 2.2 | 11.0 |
| Relative limit of repeatability r% | 16.6% | 13.7% | 13.3% | 4.3% | 10.6% | 21.2% |
| Reproducibility s.d. SR | 1.7 | 1.5 | 4.7 | 0.8 | 1.5 | 5.7 |
| RSDR % | 6.9 | 6.8 | 9.9 | 3.5 | 7.3 | 10.9 |
| Limit of reproducibility R | 4.8 | 4.4 | 13.7 | 2.4 | 4.3 | 16.3 |
| Relative limit of reproducibility R% | 19.9% | 19.6% | 28.6% | 10.6% | 21.2% | 31.4% |
| HORRAT R | 0.7 | 0.7 | 1.1 | 0.4 | 0.7 | 1.2 |

The laboratories that summed the peaks of 2-methylbutan-1-ol and 3-methylbutan-1-ol are excluded.



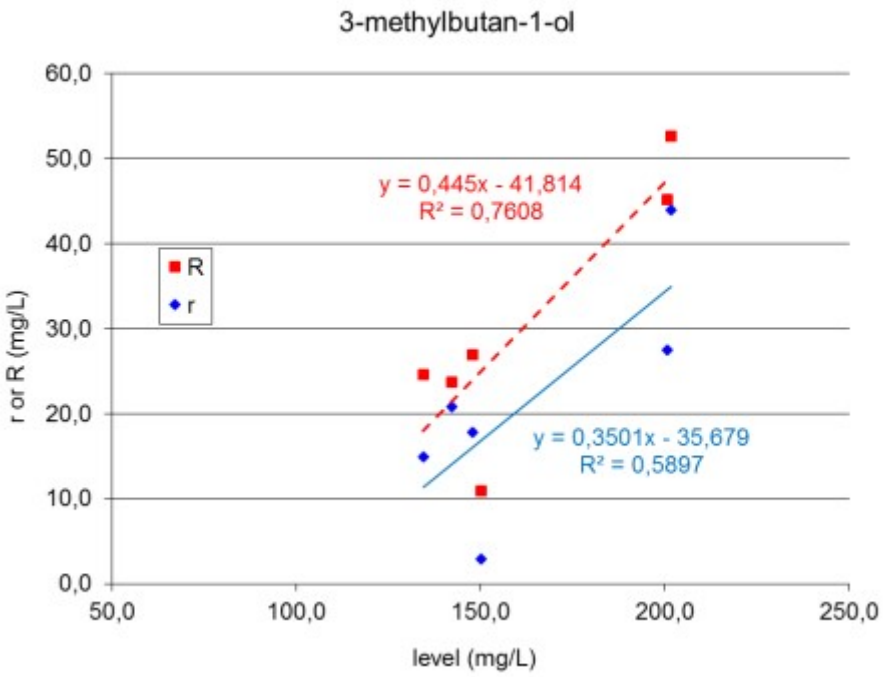

**3-methylbutan-1-ol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 9 | 9 | 9 | 9 | 9 | 9 |
| No. of laboratories after elimination of outliners | 9 | 9 | 9 | 9 | 9 | 9 |
| Number of measurement values without outliners | 32 | 32 | 32 | 16 | 32 | 32 |
| Mean (mg/L) | 142.2 | 147.8 | 200.5 | 150.2 | 134.4 | 201.7 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Repeatability s.d. Sr | 7.1 | 6.1 | 9.4 | 0.9 | 5.1 | 15.0 |
| RSDr % | 5.0 | 4.1 | 4.7 | 0.6 | 3.8 | 7.5 |
| Limit of repeatability r | 20.8 | 17.8 | 27.5 | 2.9 | 14.9 | 44.0 |
| Relative limit of repeatability r% | 14.6% | 12.1% | 13.7% | 1.9% | 11.1% | 21.8% |
| Reproducibility s.d. SR | 8.2 | 9.3 | 15.7 | 3.6 | 8.5 | 18.2 |
| RSDR % | 5.8 | 6.3 | 7.8 | 2.4 | 6.3 | 9.0 |
| Limit of reproducibility R | 23.7 | 26.9 | 45.2 | 10.9 | 24.6 | 52.6 |
| Relative limit of reproducibility R% | 16.6% | 18.2% | 22.5% | 7.3% | 18.3% | 26.1% |
| HORRAT R | 0.8 | 0.8 | 1.1 | 0.3 | 0.8 | 1.3 |

The laboratories that summed the peaks of 2-methylbutan-1-ol and 3-methylbutan-1-ol are excluded.

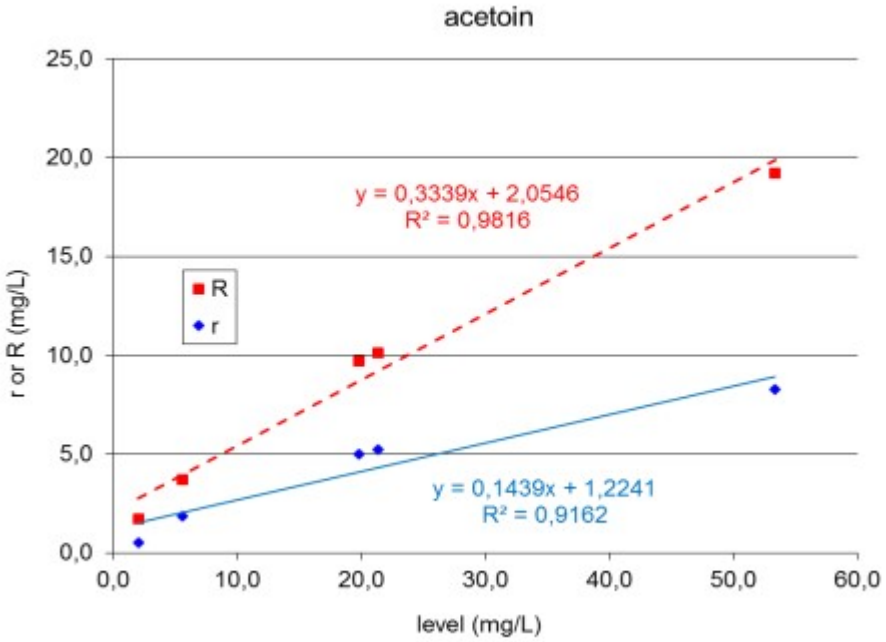


**Acetoin - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 12 | 13 | 13 | 12 | 13 |
| No. of laboratories that submitted compliant results | 12 | 9 | 13 | 13 | 10 | 13 |
| No. of laboratories after elimination of outliners | 11 | 7 | 13 | 13 | 9 | 13 |
| Number of measurement values without outliners | 38 | 24 | 46 | 23 | 30 | 46 |
| Mean (mg/L) | 5.6 | 2.1 | 19.8 | 53.4 | 2.4 | 21.4 |
| Repeatability s.d. Sr | 0.7 | 0.2 | 1.7 | 2.6 | 0.5 | 1.8 |
| RSDr % | 11.5 | 8.3 | 8.8 | 4.9 | 19.7 | 8.5 |
| Limit of repeatability r | 1.9 | 0.5 | 5.0 | 8.3 | 1.4 | 5.2 |
| Relative limit of repeatability r% | 33.4% | 24.7% | 25.2% | 15.5% | 58.0% | 24.3% |
| Reproducibility s.d. SR | 1.3 | 0.6 | 3.4 | 6.5 | 0.7 | 3.5 |
| RSDR % | 23.1 | 28.3 | 17.2 | 12.2 | 30.2 | 16.6 |
| Limit of reproducibility R | 3.7 | 1.7 | 9.7 | 19.2 | 2.1 | 10.1 |
| Relative limit of reproducibility R% | 66.2% | 82.8% | 48.9% | 36.0% | 87.3% | 47.3% |
| HORRAT R | 1.9 | 2.0 | 1.7 | 1.4 | 2.2* | 1.6 |

*presumed outlier, not considered for computation of fidelity

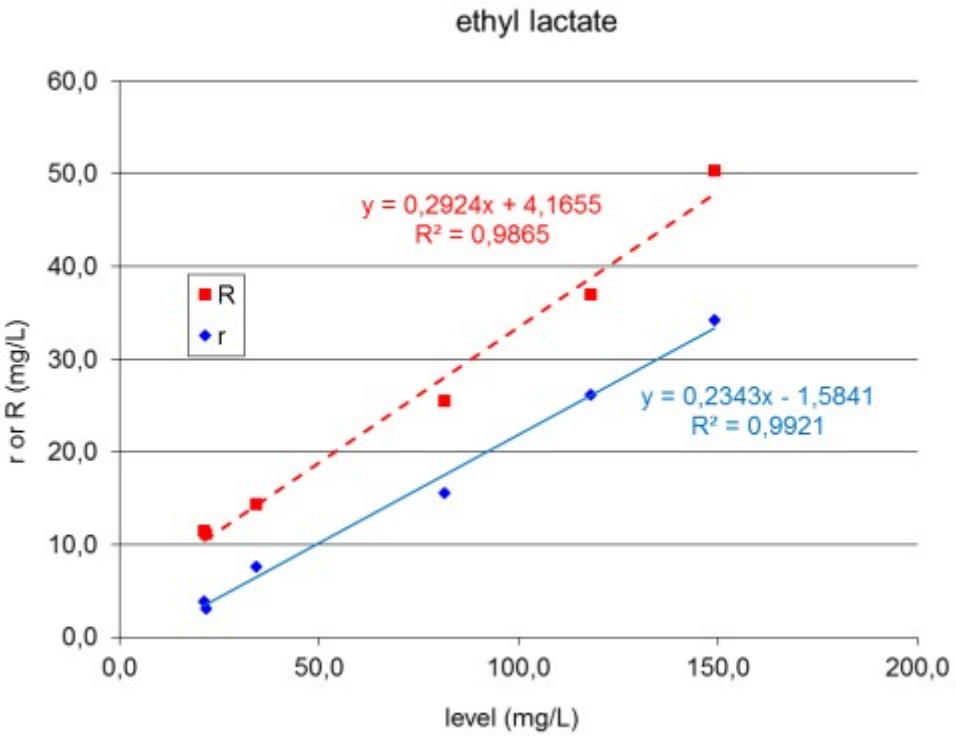



**Ethyl lactate - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 13 | 13 | 13 | 13 | 13 | 13 |
| Number of measurement values without outliners | 46 | 46 | 46 | 23 | 46 | 46 |
| Mean (mg/L) | 81.5 | 21.4 | 149.2 | 21.8 | 34.3 | 118.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Repeatability s.d. Sr | 5.4 | 1.3 | 11.9 | 1.0 | 2.7 | 9.1 |
| RSDr % | 6.6 | 6.3 | 8.0 | 4.6 | 7.7 | 7.7 |
| Limit of repeatability r | 15.5 | 3.9 | 34.2 | 3.1 | 7.6 | 26.1 |
| Relative limit of repeatability r% | 19.0% | 18.0% | 22.9% | 14.2% | 22.2% | 22.1% |
| Reproducibility s.d. SR | 8.9 | 4.0 | 17.7 | 3.8 | 5.0 | 13.0 |
| RSDR % | 11.0 | 18.9 | 11.8 | 17.4 | 14.7 | 11.0 |
| Limit of reproducibility R | 25.5 | 11.5 | 50.3 | 11.1 | 14.3 | 37.0 |
| Relative limit of reproducibility R% | 31.3% | 53.8% | 33.7% | 51.0% | 41.7% | 31.3% |
| HORRAT R | 1.3 | 1.9 | 1.6 | 1.7 | 1.5 | 1.4 |

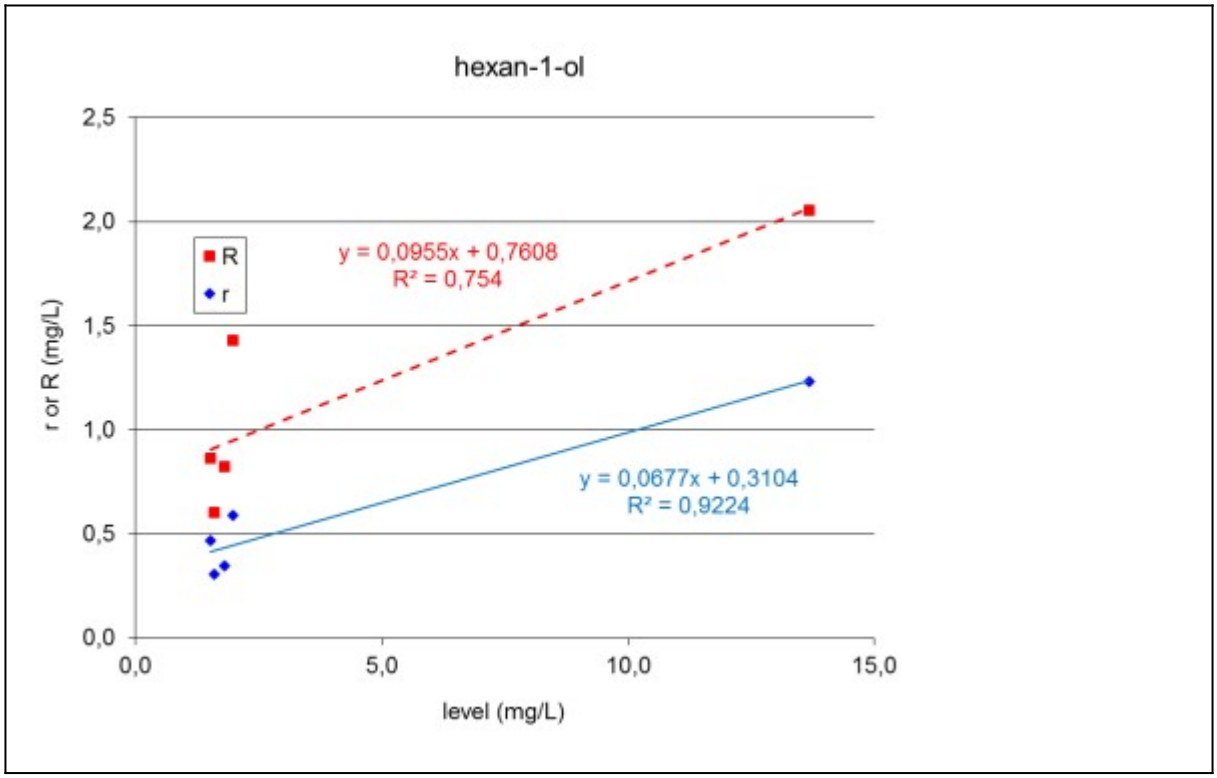


**Hexan-1-ol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 11 | 12 | 11 | 13 | 11 | 10 |
| No. of laboratories after elimination of outliners | 11 | 12 | 11 | 13 | 10 | 10 |
| Number of measurement values without outliners | 36 | 38 | 38 | 23 | 34 | 34 |
| Mean (mg/L) | 1.81 | 1.53 | 1.99 | 13.68 | 1.60 | 1.22 |
| Repeatability s.d. Sr | 0.12 | 0.16 | 0.20 | 0.39 | 0.10 | 0.32 |
| RSDr % | 6.6 | 10.6 | 10.2 | 2.9 | 6.6 | 26.1 |
| Limit of repeatability r | 0.35 | 0.47 | 0.59 | 1.23 | 0.31 | 0.93 |
| Relative limit of repeatability r% | 19.2% | 30.7% | 29.7% | 9.0% | 19.2% | 76.2% |
| Reproducibility s.d. SR | 0.29 | 0.30 | 0.50 | 0.70 | 0.21 | 0.65 |
| RSDR % | 15.8 | 19.8 | 25.1 | 5.1 | 13.1 | 53.2 |
| Limit of reproducibility R | 0.82 | 0.87 | 1.43 | 2.05 | 0.60 | 1.87 |
| Relative limit of reproducibility R% | 45.4% | 56.7% | 71.9% | 15.0% | 37.7% | 152.9% |
| HORRAT R | 1.1 | 1.3 | 1.7 | 0.5 | 0.9 | 3.4* |

*presumed outlier, not considered for computation of fidelity.



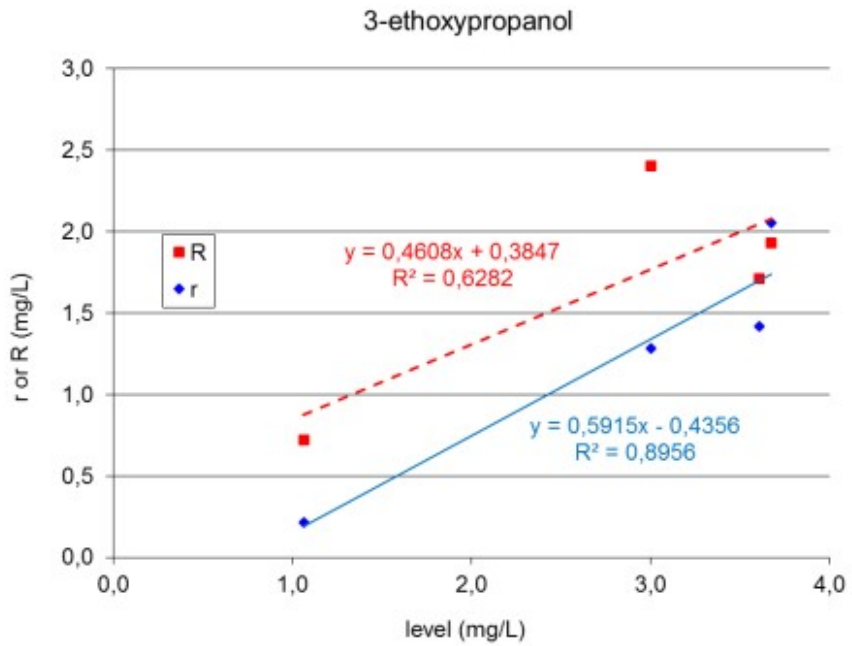

**3-ethoxypropanol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 12 | 12 | 12 | 12 | 12 | 11 |
| No. of laboratories that submitted compliant results | 7 | 11 | 8 | 11 | 11 | 6 |
| No. of laboratories after elimination of outliners | 7 | 11 | 8 | 10 | 11 | 6 |
| Number of measurement values without outliners | 21 | 37 | 23 | 17 | 30 | 17 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Mean (mg/L) | 1.7 | 3.6 | 1.4 | 3.7 | 3.0 | 1.1 |
| Repeatability s.d. Sr | 1.0 | 0.4 | 0.1 | 0.4 | 0.4 | 0.1 |
| RSDr % | 62.4 | 10.9 | 7.5 | 11.3 | 14.4 | 6.5 |
| Limit of repeatability r | 3.2 | 1.4 | 0.3 | 2.1 | 1.3 | 0.2 |
| Relative limit of repeatability r% | 189.2% | 39.3% | 22.7% | 55.9% | 42.7% | 20.2% |
| Reproducibility s.d. SR | 1.4 | 0.6 | 0.5 | 0.7 | 0.8 | 0.2 |
| RSDR % | 81.3 | 16.5 | 33.3 | 17.6 | 27.7 | 22.6 |
| Limit of reproducibility R | 4.0 | 1.7 | 1.4 | 1.9 | 2.4 | 0.7 |
| Relative limit of reproducibility R% | 239.8% | 47.5% | 97.7% | 52.6% | 80.1% | 67.7% |
| HORRAT R | 5.5* | 1.3 | 2.2* | 1.3 | 2.0 | 1.4 |

*presumed outlier, not considered for computation of fidelity.

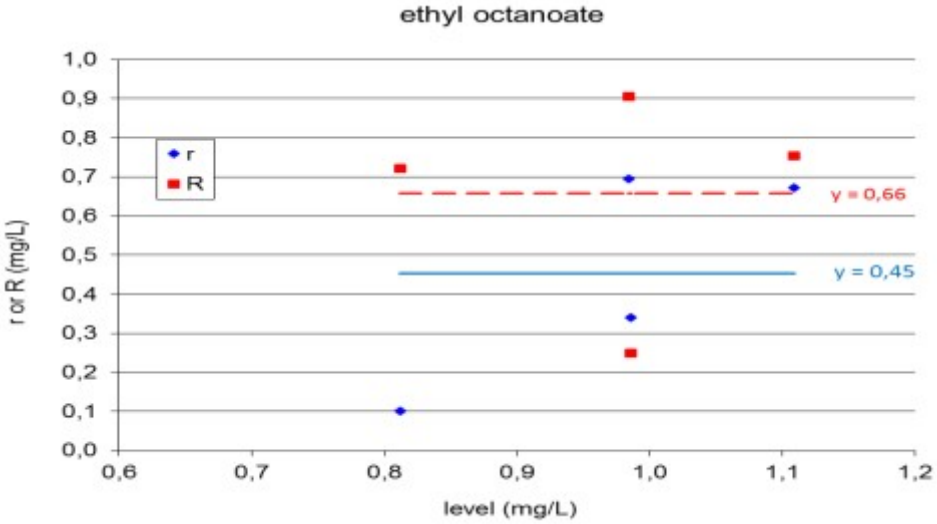


**Ethyl octanoate - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 12 | 12 | 12 | 12 | 12 | 12 |
| No. of laboratories that submitted compliant results | 7 | 9 | 5 | 9 | 9 | 4 |
| No. of laboratories after elimination of outliners | 7 | 9 | 5 | 8 | 9 | 4 |
| Number of measurement values without outliners | 19 | 30 | 10 | 13 | 30 | 10 |
| Mean (mg/L) | 0.8 | 1.1 | 0.7 | 1.0 | 1.0 | 0.8 |
| Repeatability s.d. Sr | 0.03 | 0.2 | 0.3 | 0.1 | 0.2 | 0.4 |
| RSDr % | 4.1 | 20.6 | 47.0 | 10.3 | 24.0 | 49.5 |
| Limit of repeatability r | 0.1 | 0.7 | 1.2 | 0.3 | 0.7 | 1.4 |
| Relative limit of repeatability r% | 12.5% | 60.7% | 171.1% | 34.4% | 70.6% | 171.3% |
| Reproducibility s.d. SR | 0.2 | 0.3 | 0.6 | 0.1 | 0.3 | 0.8 |
| RSDR % | 29.9 | 23.5 | 91.4 | 8.2 | 31.8 | 90.3 |
| Limit of reproducibility R | 0.7 | 0.8 | 2.0 | 0.3 | 0.9 | 2.4 |
| Relative limit of reproducibility R% | 88.8% | 67.9% | 292.8% | 25.3% | 92.0% | 288.8% |
| HORRAT R | 1.8 | 1.5 | 5.4* | 0.5 | 2.0 | 5.5* |

*presumed outlier, not considered for computation of fidelity.



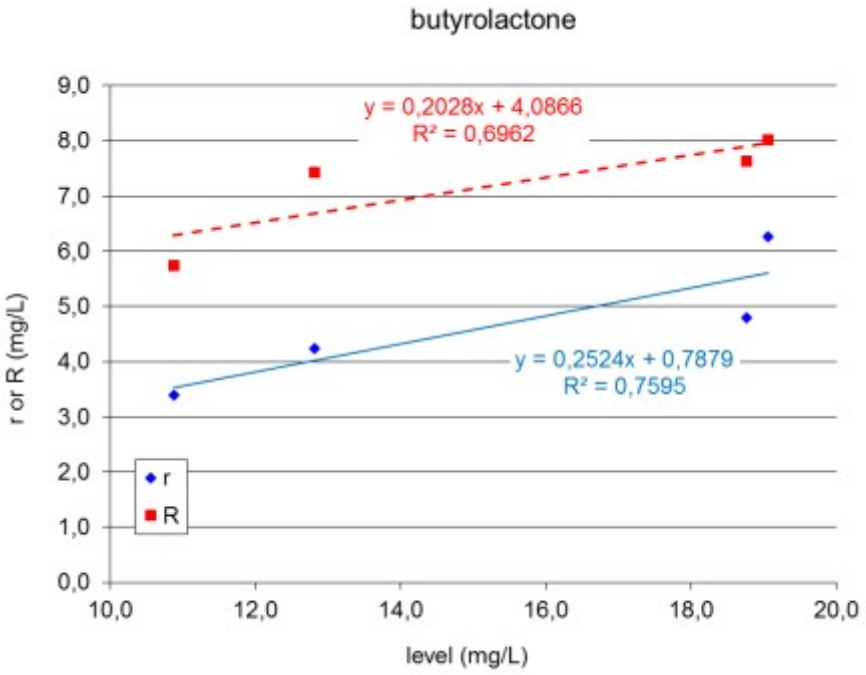

**Butyrolactone - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 10 | 10 | 10 | 10 | 10 | 10 |
| No. of laboratories that submitted compliant results | 10 | 10 | 10 | 10 | 10 | 10 |
| No. of laboratories after elimination of outliners | 8 | 8 | 7 | 10 | 9 | 8 |
| Number of measurement values without outliners | 26 | 28 | 24 | 17 | 30 | 28 |
| Mean (mg/L) | 12.8 | 10.9 | 18.8 | 11.3 | 8.2 | 19.1 |
| Repeatability s.d. Sr | 1.4 | 1.2 | 1.6 | 1.2 | 2.9 | 2.1 |
| RSDr % | 11.1 | 10.6 | 8.6 | 10.3 | 34.9 | 11.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Limit of repeatability r | 4.2 | 3.4 | 4.8 | 3.9 | 8.5 | 6.3 |
| Relative limit of repeatability r% | 33.1% | 31.2% | 25.5% | 34.3% | 102.7% | 32.8% |
| Reproducibility s.d. SR | 2.6 | 2.0 | 2.6 | 3.9 | 2.9 | 2.8 |
| RSDR % | 19.9 | 18.2 | 13.9 | 34.4 | 35.6 | 14.5 |
| Limit of reproducibility R | 7.4 | 5.7 | 7.6 | 11.6 | 8.5 | 8.0 |
| Relative limit of reproducibility R% | 57.9% | 52.7% | 40.7% | 103.1% | 102.9% | 42.1% |
| HORRAT R | 1.8 | 1.6 | 1.4 | 3.1* | 3.1* | 1.4 |

*presumed outlier, not considered for computation of fidelity.

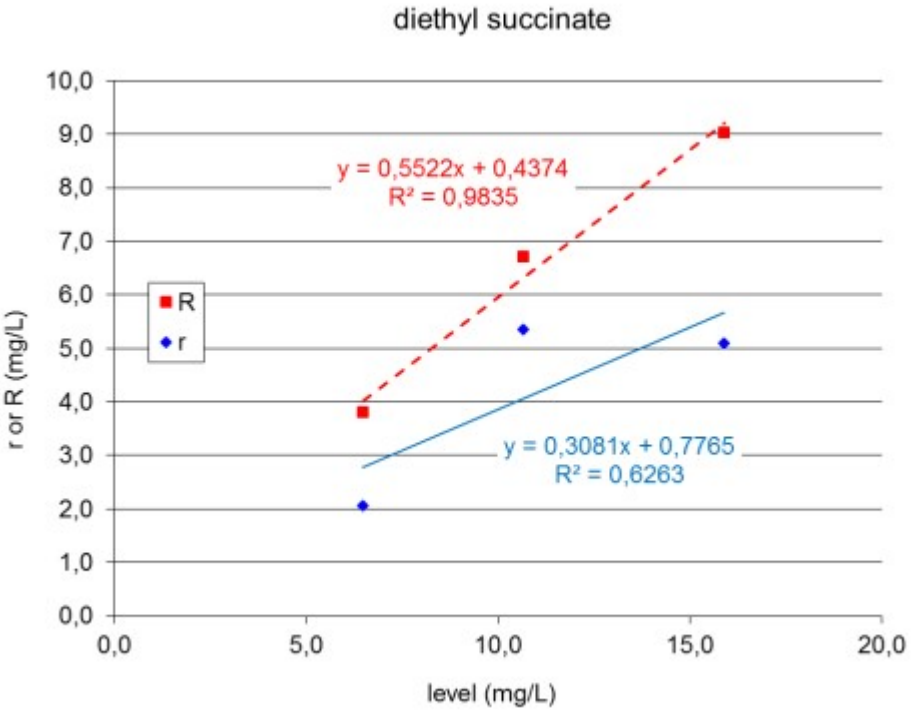



**Diethyl succinate - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 10 | 13 | 10 | 12 | 13 |
| No. of laboratories after elimination of outliners | 11 | 10 | 13 | 10 | 12 | 12 |
| Number of measurement values without outliners | 40 | 34 | 46 | 17 | 35 | 42 |
| Mean (mg/L) | 6.5 | 3.3 | 15. 9 | 4.0 | 3.7 | 10.7 |
| Repeatability s.d. Sr | 0.7 | 0.4 | 1.8 | 1.5 | 0.6 | 1.9 |
| RSDr % | 11.0 | 11.2 | 11.2 | 37.8 | 16.1 | 17.4 |
| Limit of repeatability r | 2.1 | 1.1 | 5.1 | 5.0 | 1.7 | 5.4 |
| Relative limit of repeatability r% | 31.7% | 32.6% | 32.1% | 126.4% | 47.1% | 50.2% |
| Reproducibility s.d. SR | 1.3 | 1.5 | 3.2 | 1.9 | 1.3 | 2.4 |
| RSDR % | 20.5 | 44.9 | 20.0 | 48.6 | 35.4 | 22.0 |
| Limit of reproducibility R | 3.8 | 4.3 | 9.0 | 5.8 | 3.7 | 6.7 |
| Relative limit of reproducibility R% | 58.6% | 129.2% | 56.9% | 145.6% | 101.7% | 63.0% |
| HORRAT R | 1.7 | 3.4* | 1.9 | 3.7* | 2.7* | 2.0 |

*presumed outlier, not considered for computation of fidelity.

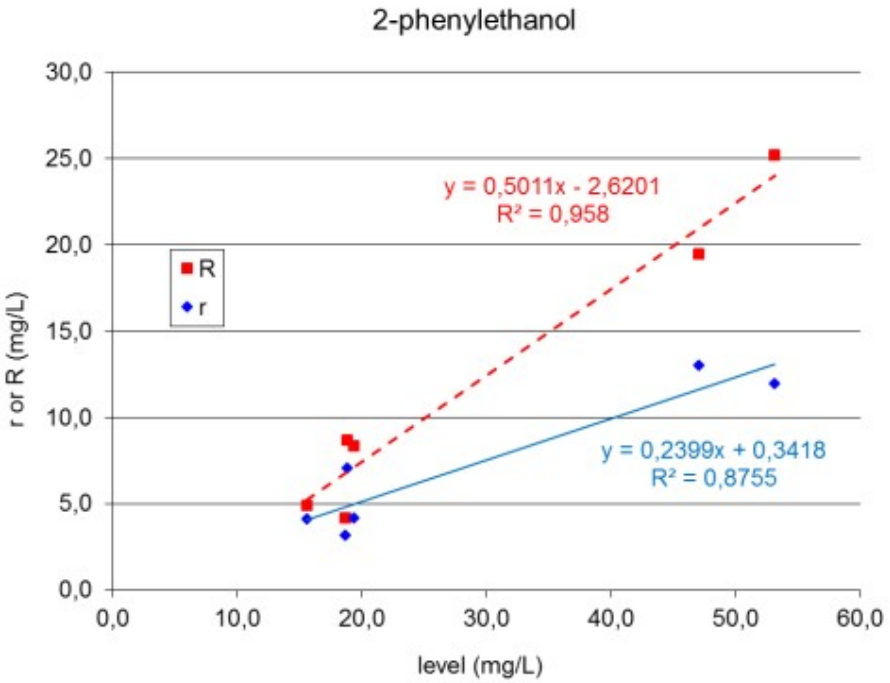



**2-phenylethanol - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 12 | 12 | 12 | 12 | 12 | 13 |
| Number of measurement values without outliners | 42 | 42 | 42 | 21 | 42 | 46 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Mean (mg/L) | 19.4 | 18.8 | 47.0 | 18.7 | 15.6 | 53.1 |
| Repeatability s.d. Sr | 1.4 | 2.4 | 4.5 | 1.0 | 1.4 | 4.2 |
| RSDr % | 7.4 | 13.0 | 9.6 | 5.3 | 9.1 | 7.8 |
| Limit of repeatability r | 4.2 | 7.0 | 13.0 | 3.2 | 4.1 | 11.9 |
| Relative limit of repeatability r% | 21.5% | 37.4% | 27.7% | 17.1% | 26.3% | 22.5% |
| Reproducibility s.d. SR | 2.9 | 3.0 | 6.8 | 1.4 | 1.7 | 8.8 |
| RSDR % | 15.1 | 16.2 | 14.5 | 7.6 | 11.0 | 16.6 |
| Limit of reproducibility R | 8.4 | 8.7 | 19.5 | 4.2 | 4.9 | 25.2 |
| Relative limit of reproducibility R% | 43.1% | 46.2% | 41.4% | 22.4% | 31.5% | 47.4% |
| HORRAT R | 1.5 | 1.6 | 1.6 | 0.7 | 1.0 | 1.9 |



**Ethyl acetate - Fidelity**

**repeatability and reproducibility**

| | wine A | wine B | wine C | wine D | wine E | wine F |
|---|---|---|---|---|---|---|
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| No. of laboratories that submitted results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories that submitted compliant results | 13 | 13 | 13 | 13 | 13 | 13 |
| No. of laboratories after elimination of outliners | 12 | 12 | 12 | 13 | 12 | 13 |
| Number of measurement values without outliners | 42 | 42 | 42 | 23 | 42 | 46 |
| Mean (mg/L) | 26.4 | 60.5 | 55.5 | 60.6 | 25.5 | 68.4 |
| Repeatability s.d. Sr | 1.6 | 2.6 | 2.4 | 1.4 | 1.1 | 6.0 |
| RSDr % | 5.9 | 4.2 | 4.3 | 2.4 | 4.3 | 8.8 |
| Limit of repeatability r | 4.5 | 7.4 | 6.9 | 4.5 | 3.2 | 17.3 |
| Relative limit of repeatability r% | 16.9% | 12.2% | 12.3% | 7.4% | 12.5% | 25.3% |
| Reproducibility s.d. SR | 2.8 | 4.7 | 4.4 | 8.8 | 2.2 | 7.3 |
| RSDR % | 10.7 | 7.7 | 8.0 | 14.5 | 8.5 | 10.6 |
| Limit of reproducibility R | 8.1 | 13.4 | 12.6 | 25.8 | 6.2 | 20.7 |
| Relative limit of reproducibility R% | 30.5% | 22.1% | 22.7% | 42.6% | 24.2% | 30.3% |
| HORRAT R | 1.1 | 0.9 | 0.9 | 1.7 | 0.9 | 1.2 |