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

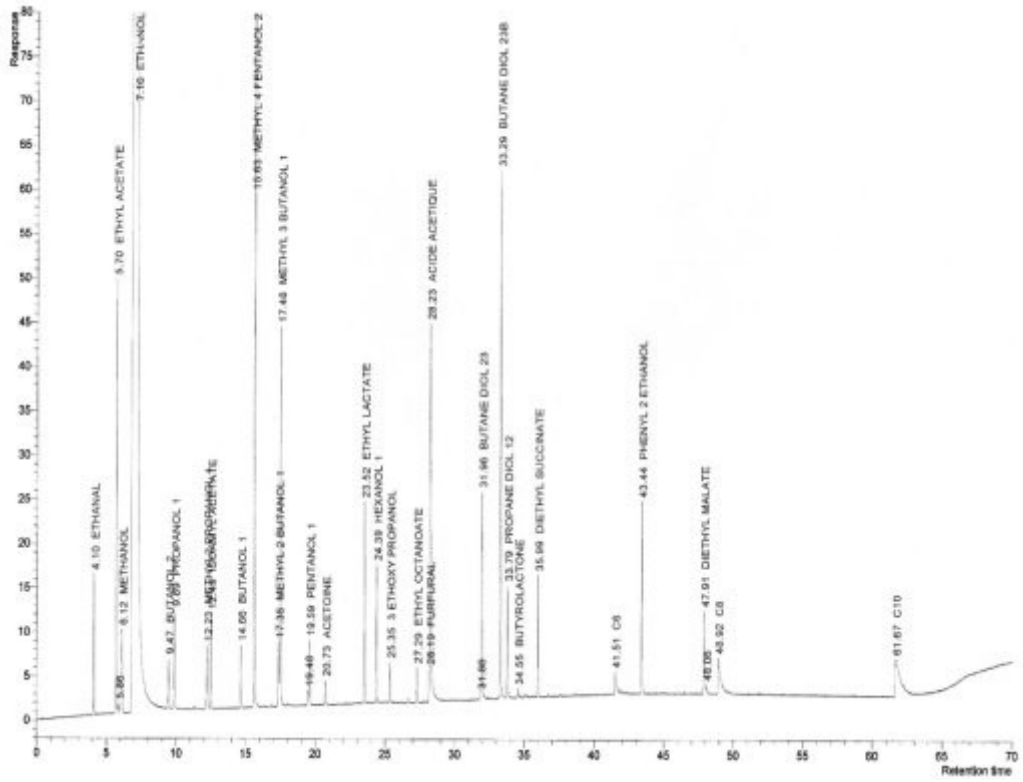


Figure 1: chromatogram of a standard solution of volatile compounds

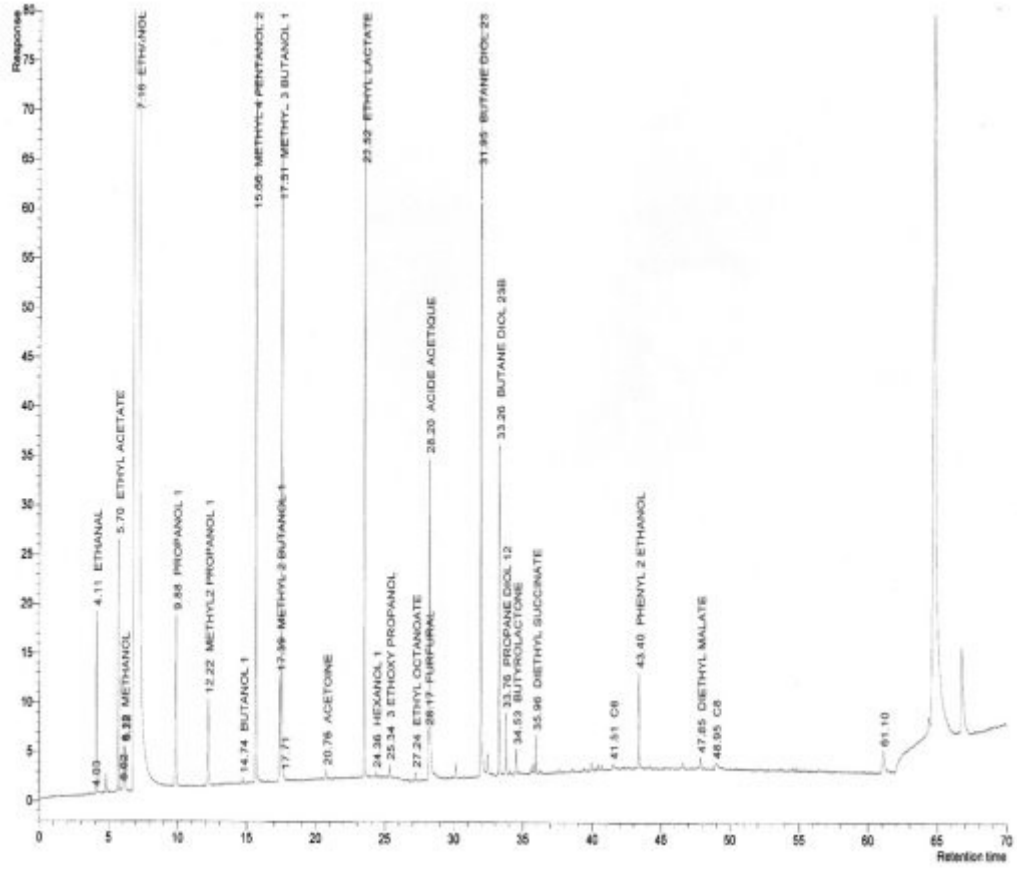


Figure 2 : chromatogram of volatile compounds in a white wine (sugar < 15 g/L)

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

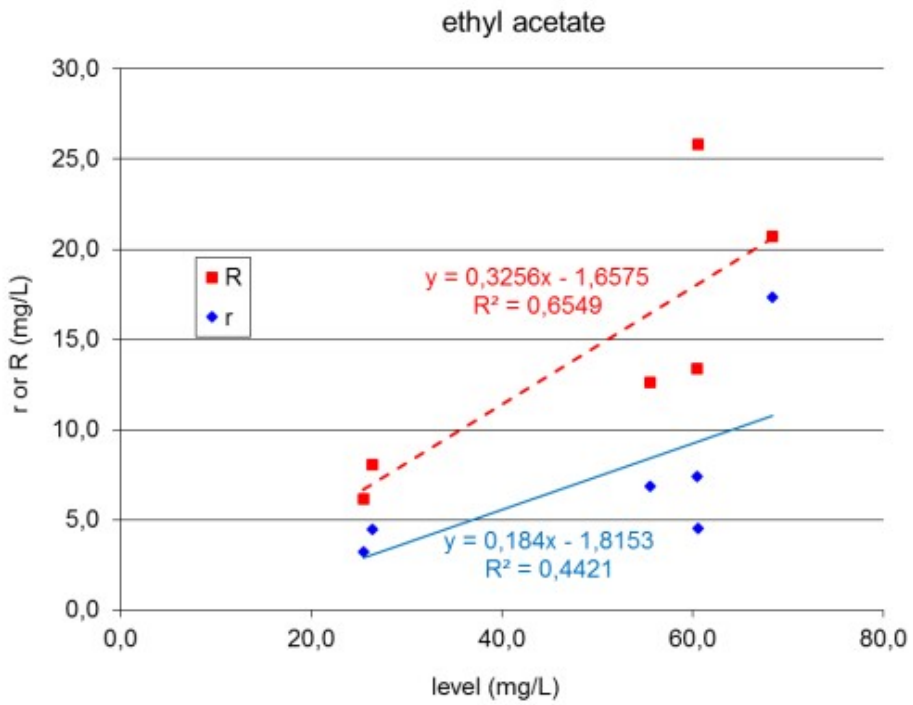
where x is the measured concentration

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

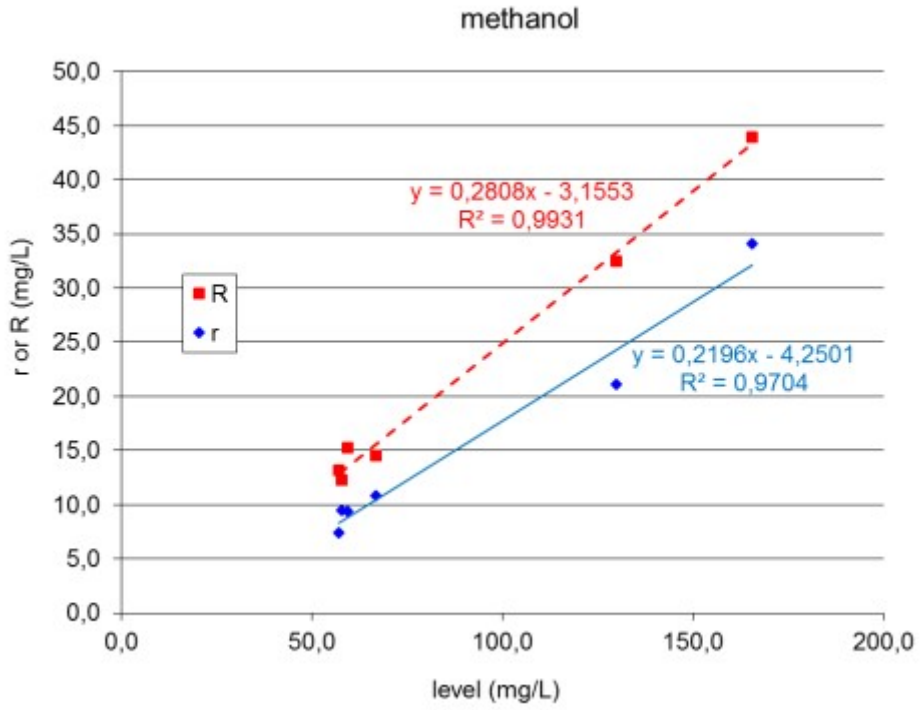


Methanol - Fidelity

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

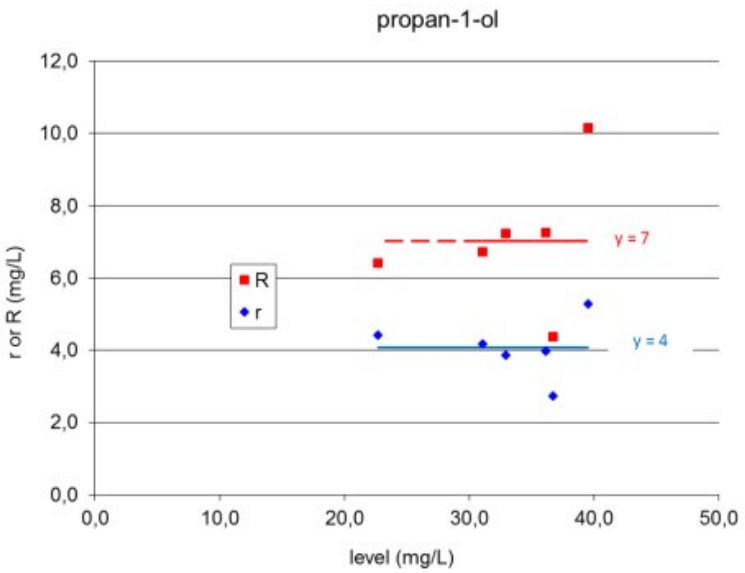


Propan-1-ol - Fidelity

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

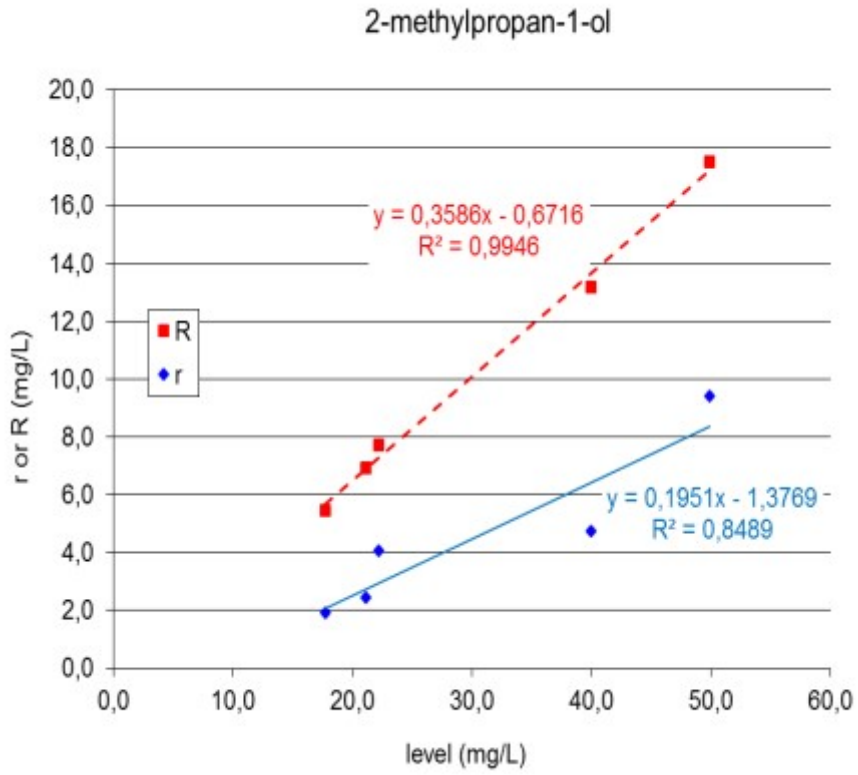


2-methylpropan-1-ol - Fidelity

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

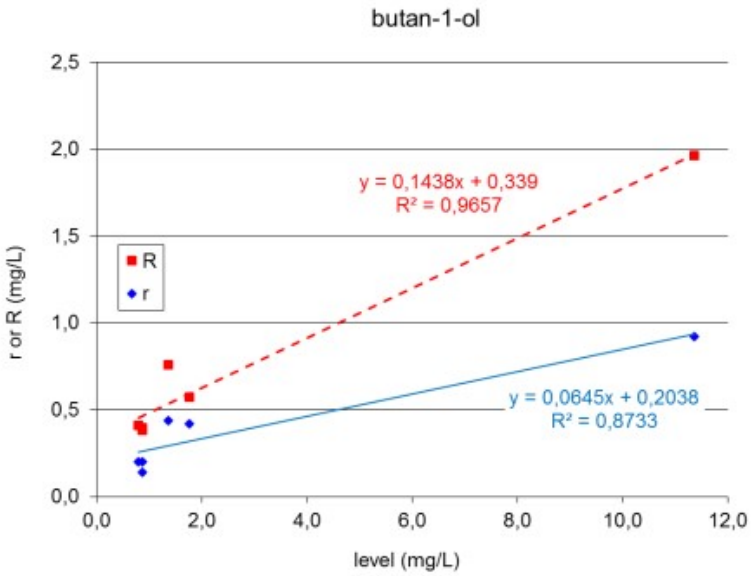
*presumed outlier, not considered for computation of fidelity.



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

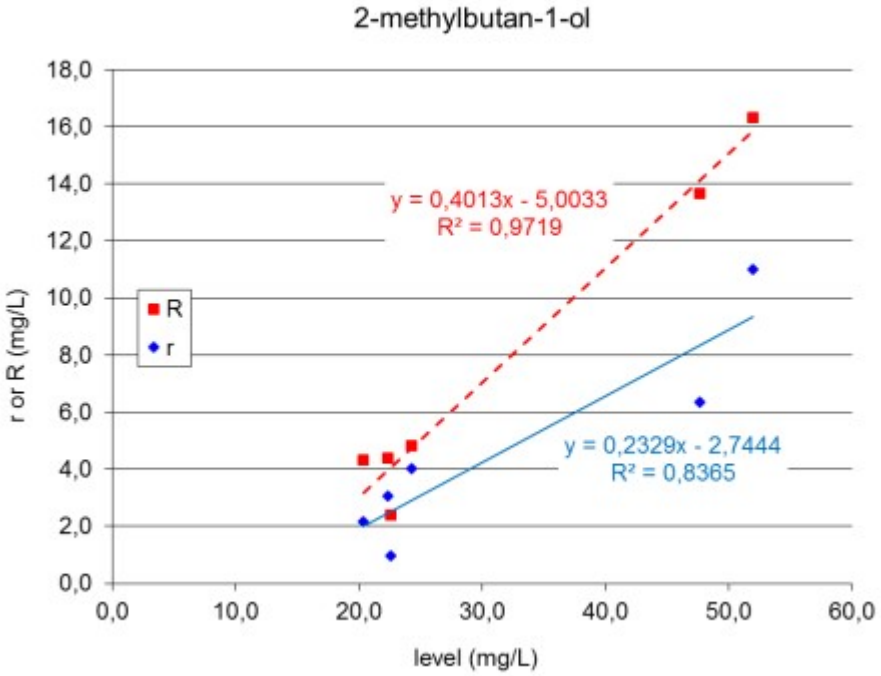
Number of measurement values without outliners	28	26	34	23	28	32
Mean (mg/L)	0.87	0.87	1.77	11.36	0.81	1.36
Repeatability s.d. Sr	0.05	0.07	0.14	0.29	0.07	0.15
RSDr %	5.5	7.8	8.2	2.6	8.4	11.0
Limit of repeatability r	0.14	0.20	0.42	0.92	0.20	0.44
Relative limit of repeatability r%	16.2%	23.1%	23.9%	8.1%	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.



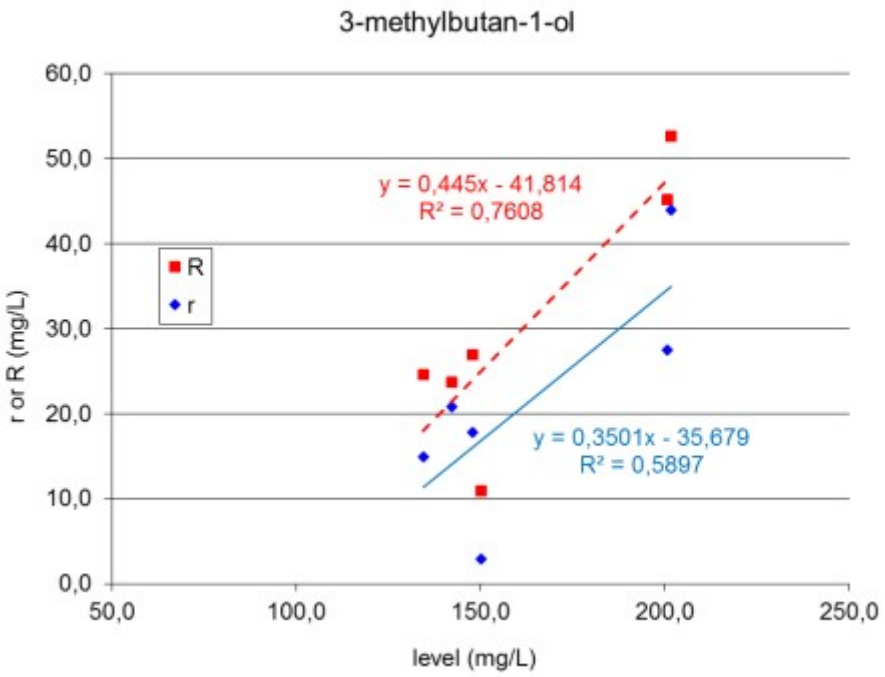
3-methylbutan-1-ol - Fidelity

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.

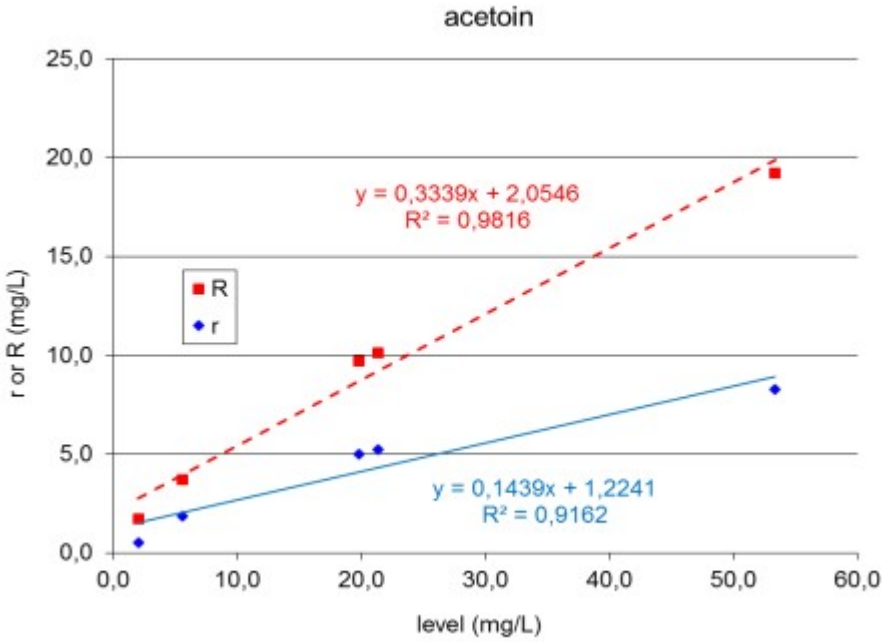


Acetoin - Fidelity

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

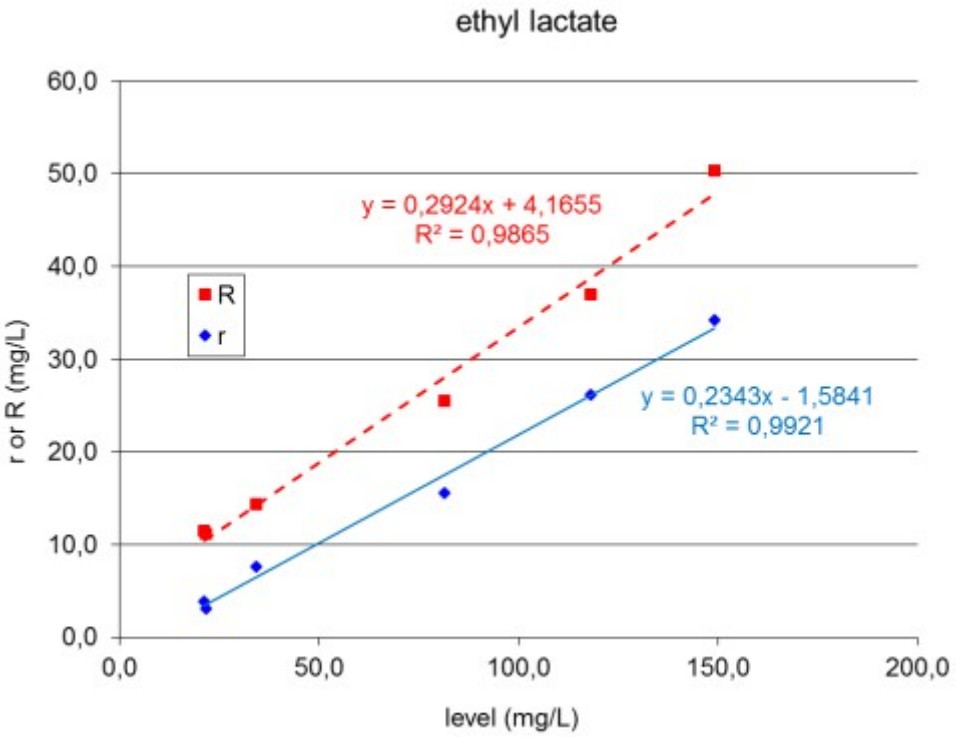


Ethyl lactate - Fidelity

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

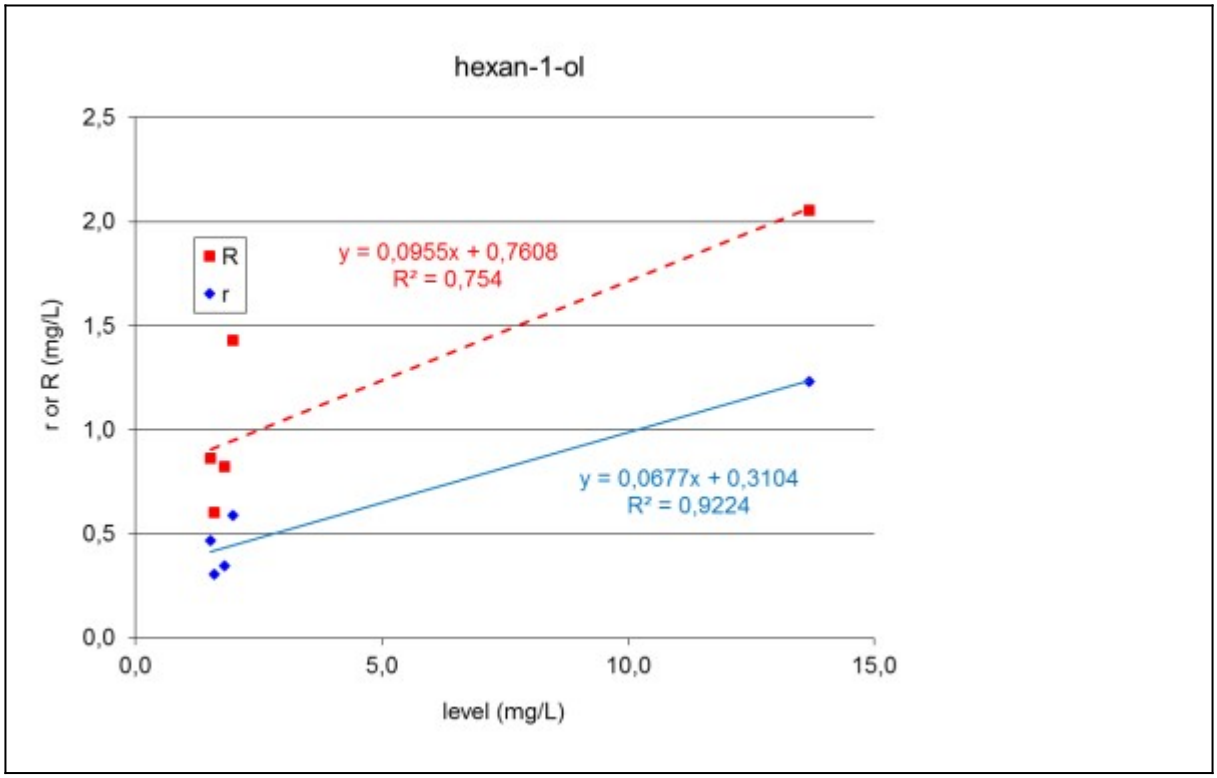


Hexan-1-ol - Fidelity

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.



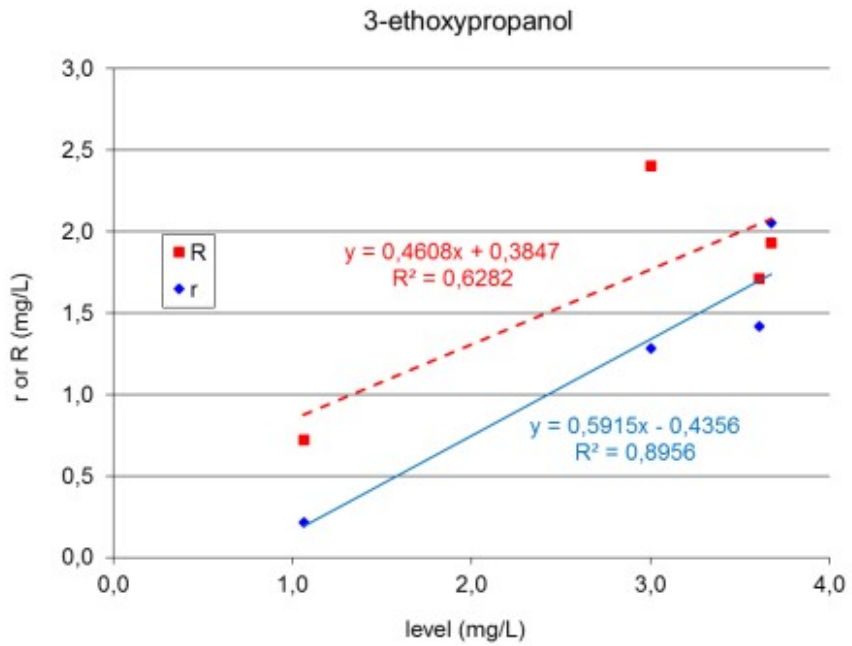
3-ethoxypropanol - Fidelity

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.

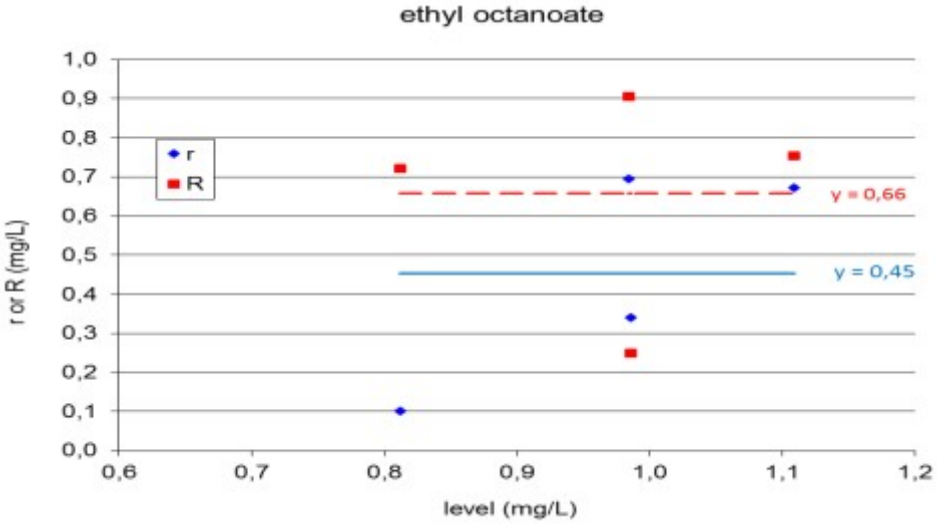


Ethyl octanoate - Fidelity

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.



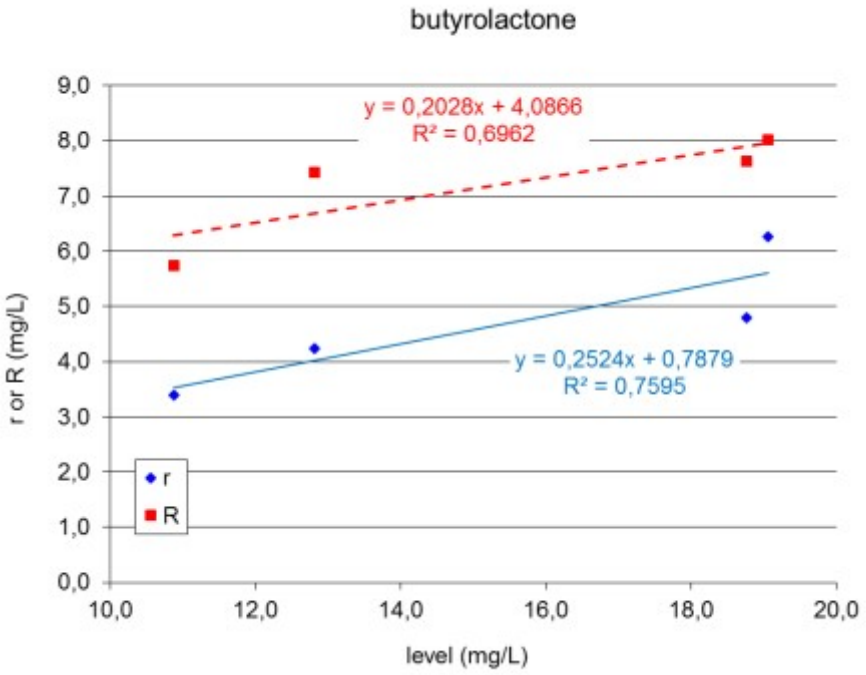
Butyrolactone - Fidelity

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.

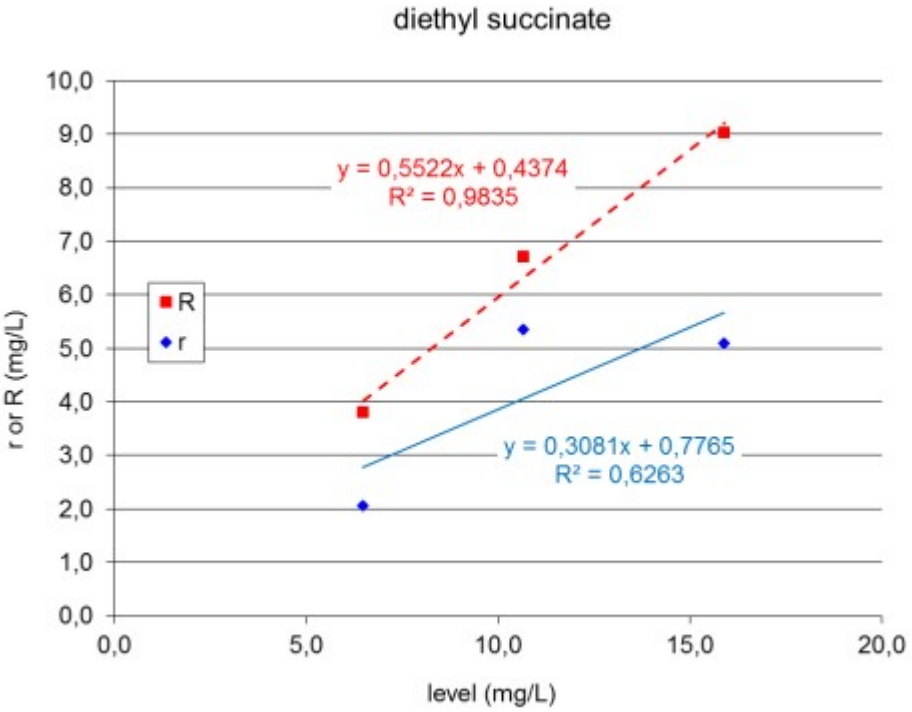


Diethyl succinate - Fidelity

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.

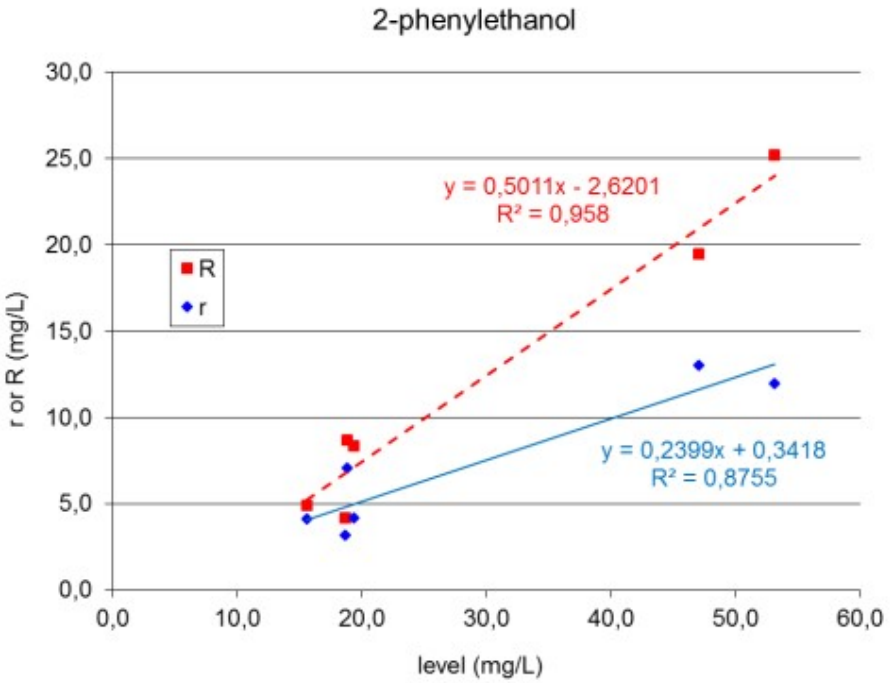


2-phenylethanol - Fidelity

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