

Supplementary Information

Standardizing the quantification of trifluoroacetic acid in water: Interlaboratory validation trial using liquid chromatography-mass spectrometric detection (LC-MS/MS)

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Number of pages: 13

Number of figures: 8

Number of tables: 1

SI 1 Test material

Table S 1 water samples, sources, and physical and chemical parameters of the test materials

Abbreviation	Type	Source and comments	conductivity	pH
GW1	Groundwater	PFAS-contaminated (sum 10 µg/L) remediation site Berlin, October 2023	772 µS/cm	6.5
GW2	Groundwater	Stadtwerke Trier, November 2023	365 µS/cm	6.6
OW1	Surface water	Rhine, LANUV, December 2023	345 µS/cm	5.5
OW2	Surface water	Effluent from wastewater treatment plant, January 2024	>1.000 µS/cm	6
RW	Rain water	Collected rain after long dry period, Berlin, September 2023	45 µS/cm	5
TW	Drinking water	Tap water Berlin, January 2024	774 µS/cm	7.2
A1	<i>Matrix addition</i>	GW2 fortified with TFA	365 µS/cm	6.6
A2	<i>Matrix addition</i>	GW2 fortified with TFA	365 µS/cm	6.6

SI 2 Participants

Participants of the interlaboratory comparison for method validation for the determination of TFA in water samples. The alphabetic order of the laboratories does not correspond with the laboratory codes in the graphs in SI 3.

Analytik Institut Rietzler	Fürth, Germany
Bundesanstalt für Materialforschung und -prüfung BAM	Berlin, Germany
Institut für Hygiene und Umwelt	Hamburg, Germany
IWW Zentrum Wasser	Mülheim an der Ruhr, Germany
Landesamt für Natur, Umwelt und Verbraucherschutz NRW	Duisburg, Germany
Landesanstalt für Umwelt Baden-Württemberg	Karlsruhe, Germany
Metrohm IHQ	Herisau, Switzerland
Ruhrverband	Essen, Germany
SWT Stadtwerke Trier	Trier-Irsch, Germany
Thüringer Landesamt für Umwelt, Bergbau und Naturschutz	Jena, Germany
Waters GmbH	Eschborn, Germany
Zweckverband Landeswasserversorgung	Langenau, Germany

SI 3 Results of the interlaboratory comparison

Performance characteristics for the analysis of TFA in tables and graphs.

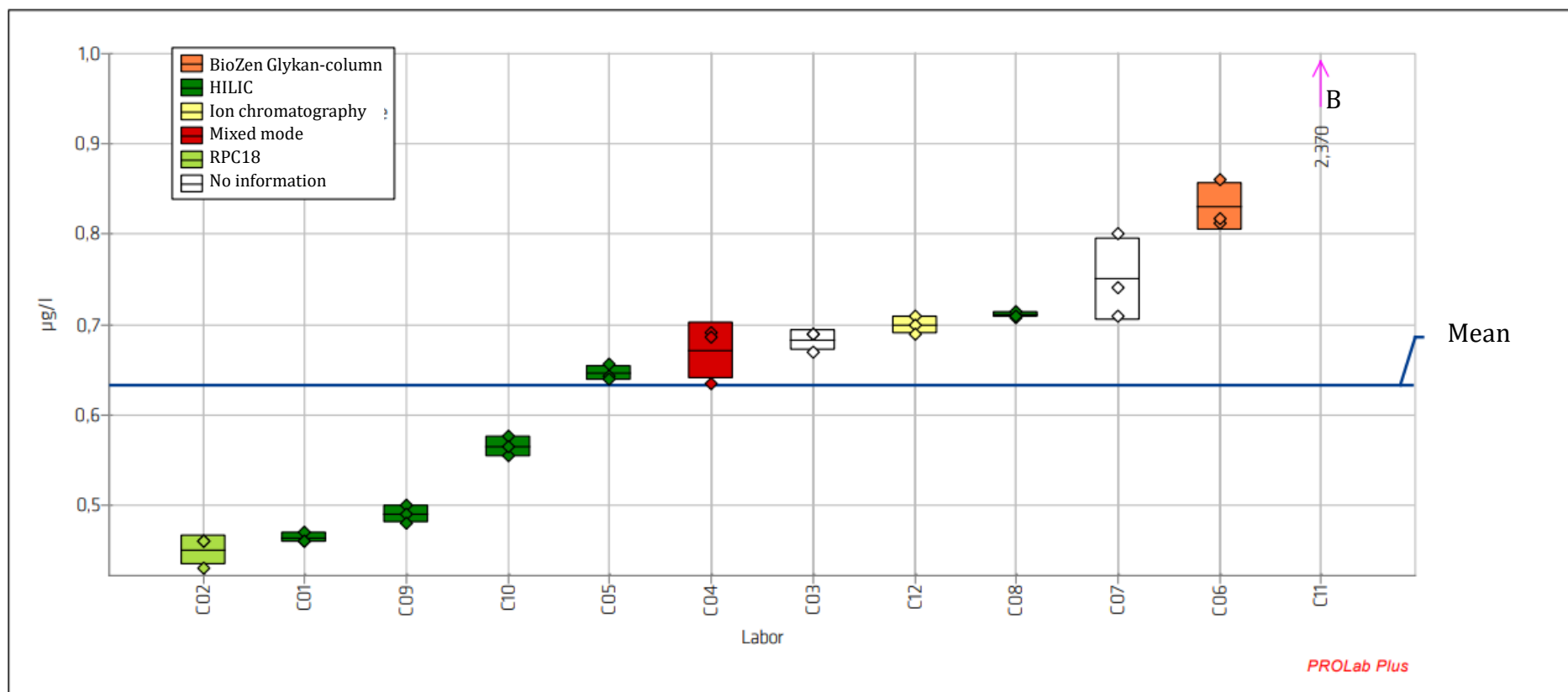
Statistics according DIN ISO 5725-2.

- Fig. S3-1: Graph of performance characteristics for TFA in groundwater (GW1)
- Fig. S3-2: Graph of performance characteristics for TFA in groundwater (GW2)
- Fig. S3-3: Graph of performance characteristics for TFA in surface water (OW1)
- Fig. S3-4: Graph of performance characteristics for TFA in surface water (OW2)
- Fig. S3-5: Graph of performance characteristics for TFA in rain water (RW)
- Fig. S3-6: Graph of performance characteristics for TFA in tap water (TW)
- Fig. S3-7: Graph of performance characteristics for TFA in groundwater with added TFA (A1)
- Fig. S3-8: Graph of performance characteristics for TFA in groundwater with added TFA (A2)

Supplemental material S3-1

Sample: GW1 Groundwater
 Total mean $\pm$ U(mean): 0.633 ± 0.075 $\mu\text{g/l}$
 Assigned value: 0.633 $\mu\text{g/l}$
 Number of laboratories: 12
 Number of laboratories without outliers: 11
 Number of single measurement values: 33

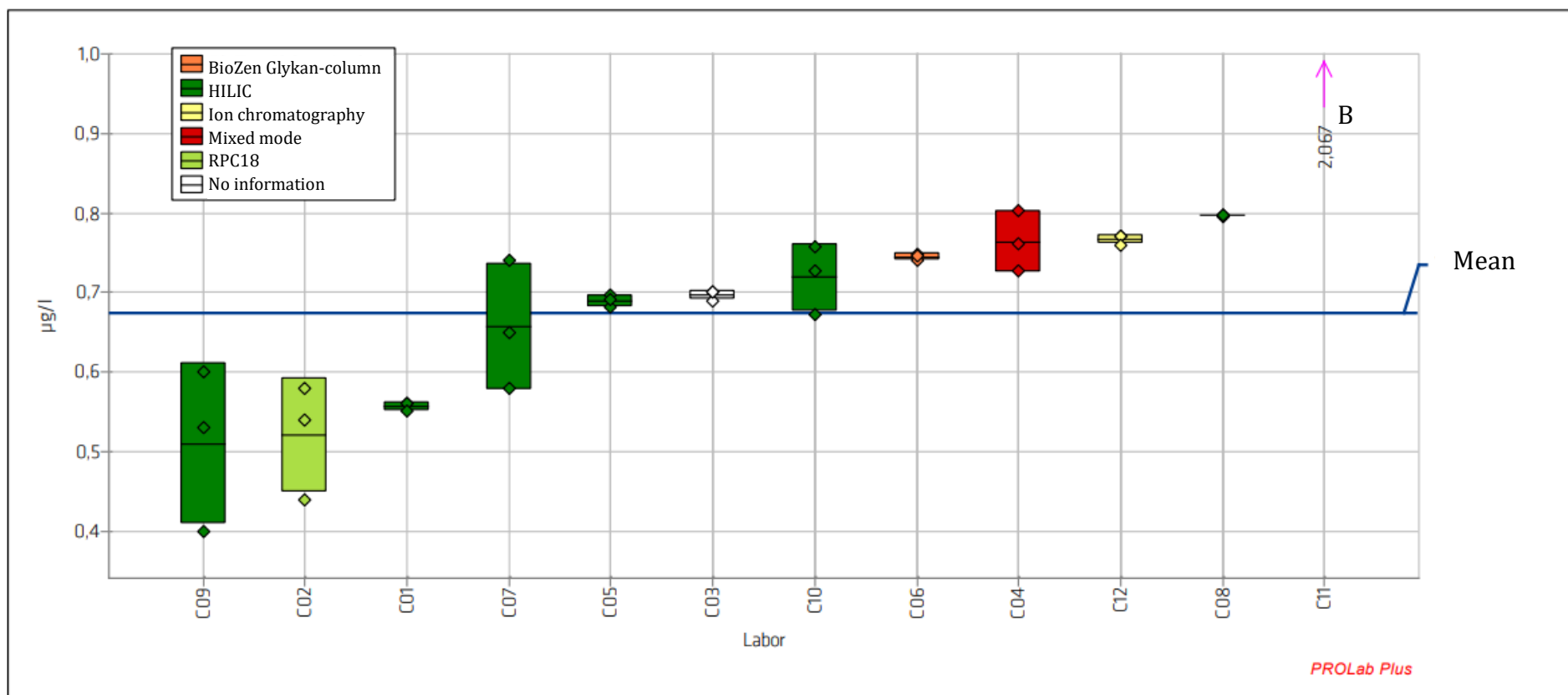
Analyte: TFA
 Coefficient of variation of repeatability: 3.27 %
 Repeatability standard deviation: 0.021 $\mu\text{g/l}$
 Coefficient of variation of reproducibility: 19.83 %
 Reproducibility standard deviation: 0.125 $\mu\text{g/l}$



Supplemental material S3-2

Sample: GW2 Groundwater
 Total mean $\pm$ U(mean): $0.675 \pm 0.062 \mu\text{g/l}$
 Assigned value: $0.675 \mu\text{g/l}$
 Number of laboratories: 12
 Number of laboratories without outliers: 11
 Number of single measurement values: 33

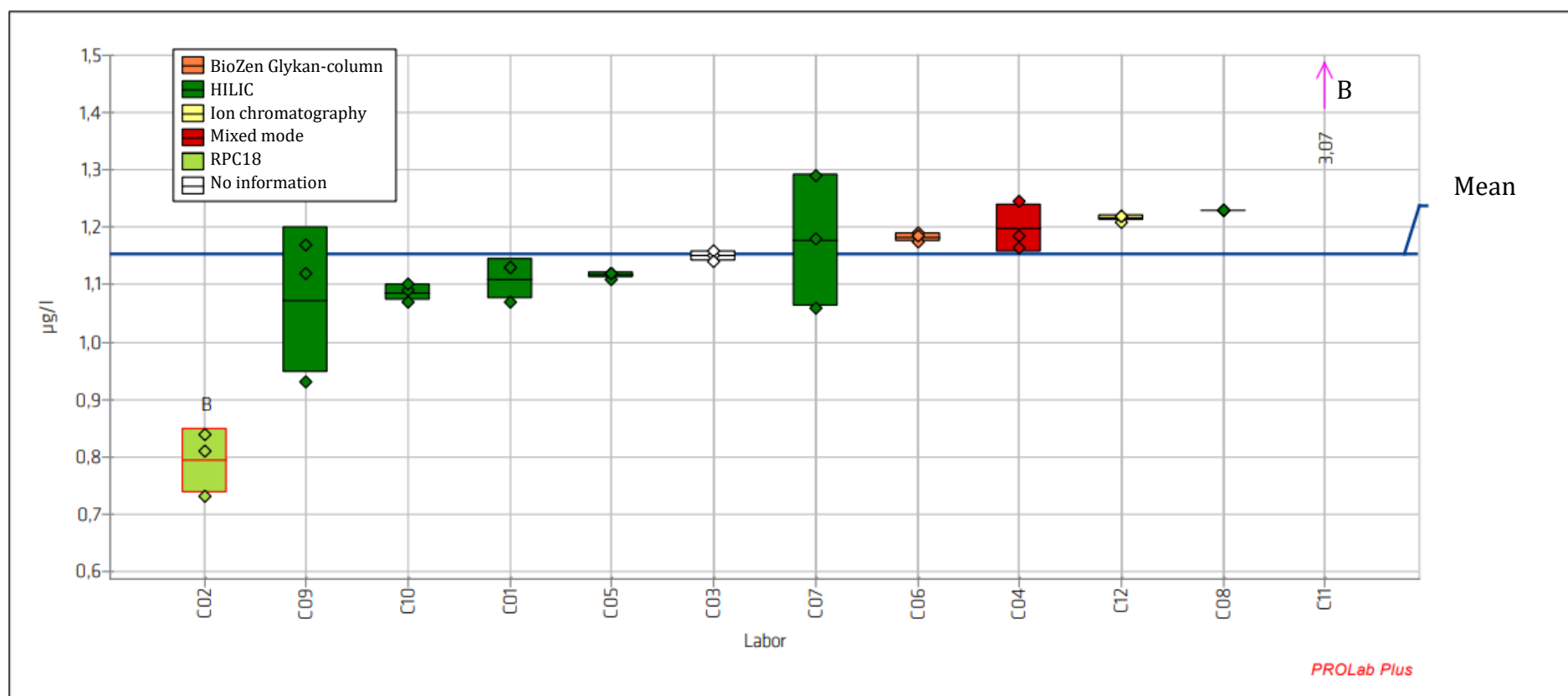
Analyte: TFA
 Coefficient of variation of repeatability: 7.12 %
 Repeatability standard deviation: $0.048 \mu\text{g/l}$
 Coefficient of variation of reproducibility: 16.22 %
 Reproducibility standard deviation: $0.109 \mu\text{g/l}$



Supplemental material S3-3

Sample: OW1 surface water
 Total mean +/- U(mean): $1.15 \pm 0.03 \mu\text{g/l}$
 Assigned value: $0.633 \mu\text{g/l}$
 Number of laboratories : 12
 Number of laboratories without outliers: 10
 Number of single measurement values: 30

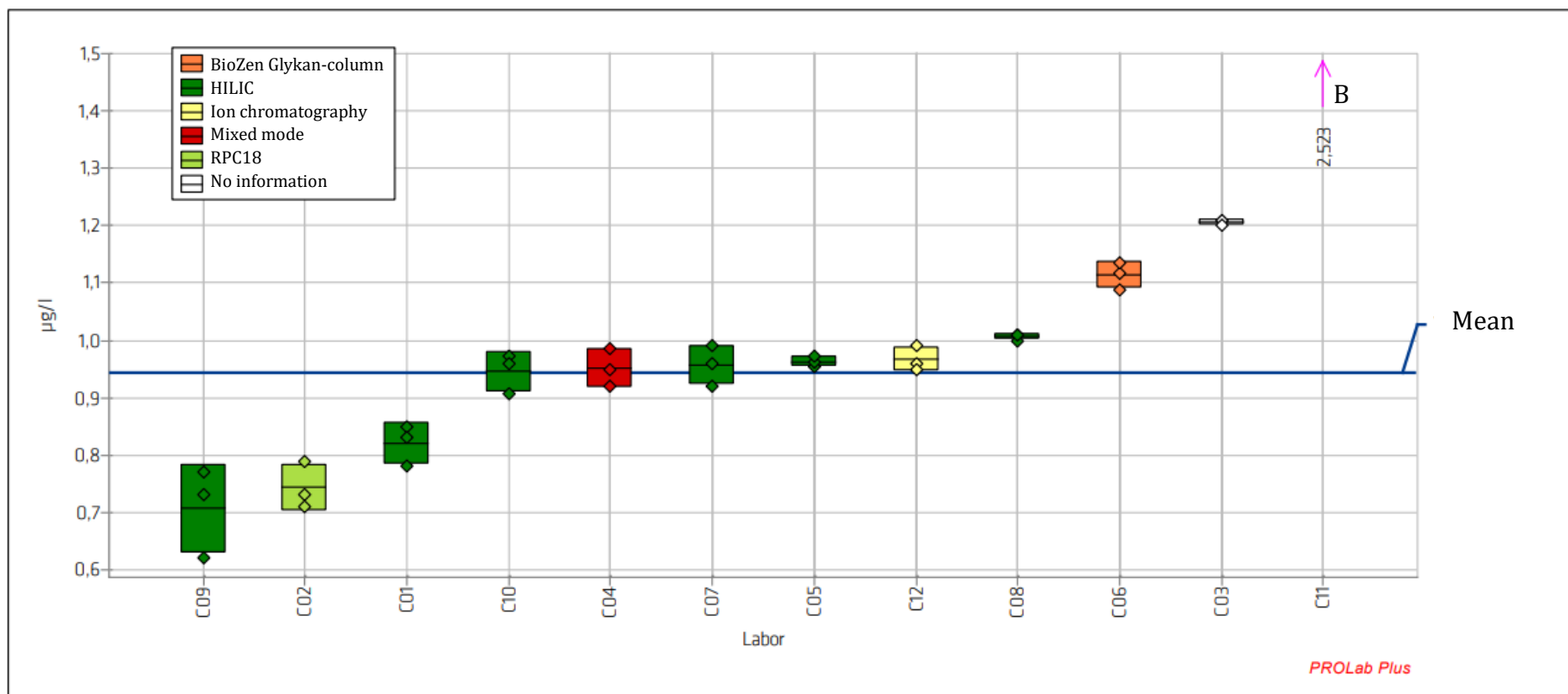
Analyte: TFA
 Coefficient of variation of repeatability: 4.95 %
 Repeatability standard deviation: $0.06 \mu\text{g/l}$
 Coefficient of variation of reproducibility: 6.26 %
 Reproducibility standard deviation: $0.07 \mu\text{g/l}$



Supplemental material S3-4

Sample: OW2 surface water
 Total mean +/- U(mean): 0,944 ± 0.008 µg/l
 Assigned value: 0.944 µg/l
 Number of laboratories: 12
 Number of laboratories without outliers: 11
 Number of single measurement values: 33

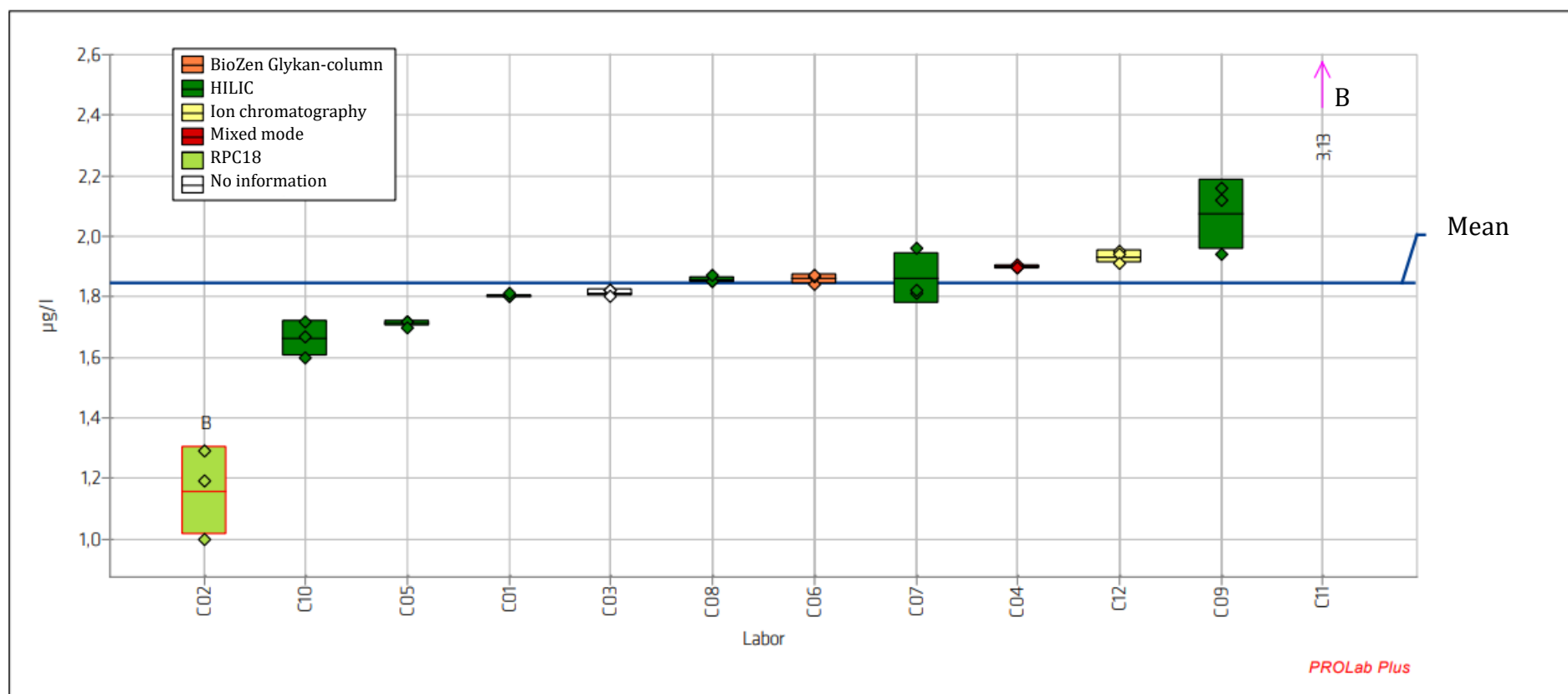
Analyte: TFA
 Coefficient of variation of repeatability: 3.75 %
 Repeatability standard deviation: 0.035 µg/l
 Coefficient of variation of reproducibility: 15.82 %
 Reproducibility standard deviation: 0.149 µg/l



Supplemental material S3-5

Sample: RW rain water
 Total mean +/- U(mean): $1.85 \pm 0.07 \mu\text{g/l}$
 Assigned value: $1.85 \mu\text{g/l}$
 Number of laboratories: 12
 Number of laboratories without outliers: 10
 Number of single measurement values: 30

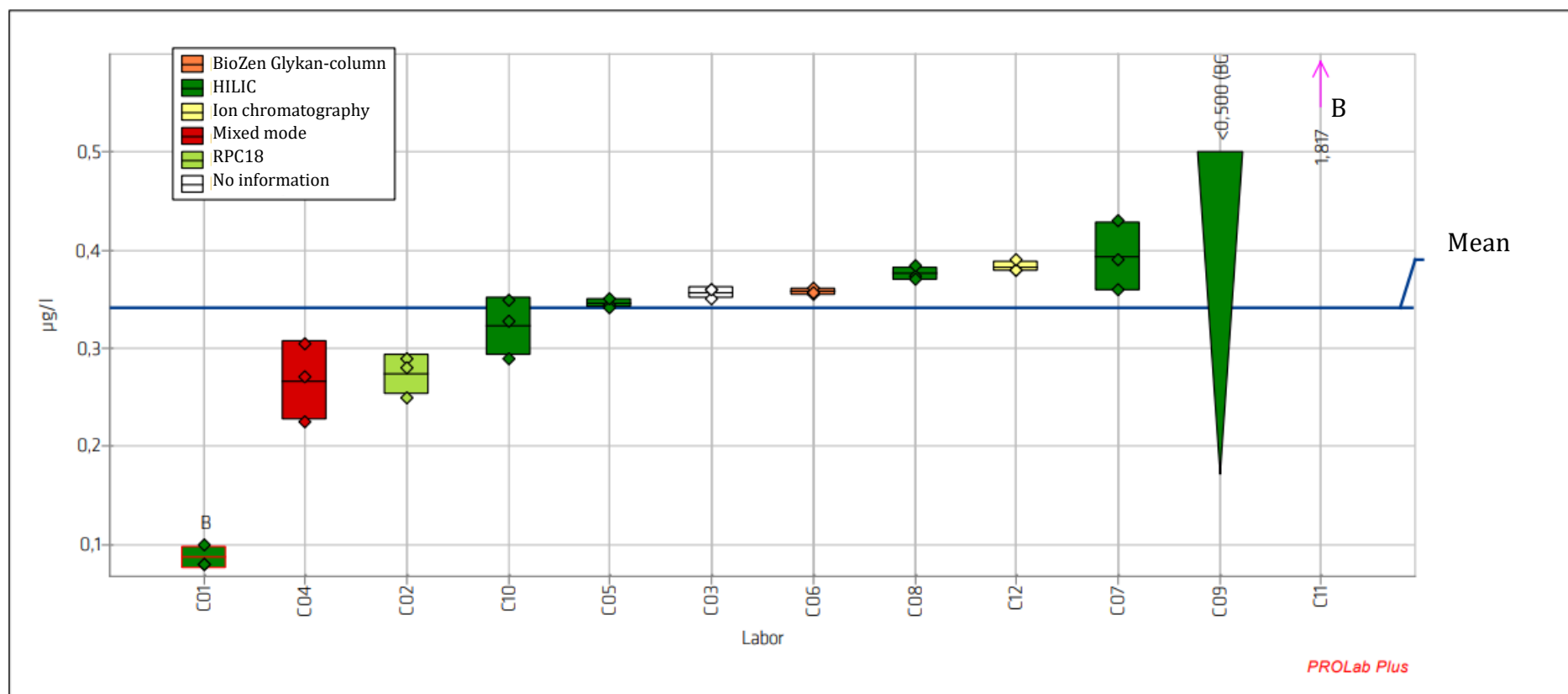
Analyte: TFA
 Coefficient of variation of repeatability: 2.74 %
 Repeatability standard deviation: $0.05 \mu\text{g/l}$
 Coefficient of variation of reproducibility: 6.55 %
 Reproducibility standard deviation: $0.12 \mu\text{g/l}$



Supplemental material S3-6

Sample: TW drinking water
 Total mean +/- U(mean): $0,342 \pm 0.030 \mu\text{g/l}$
 Assigned value: $0.342 \mu\text{g/l}$
 Number of laboratories: 11
 Number of laboratories without outliers: 9
 Number of single measurement values: 27

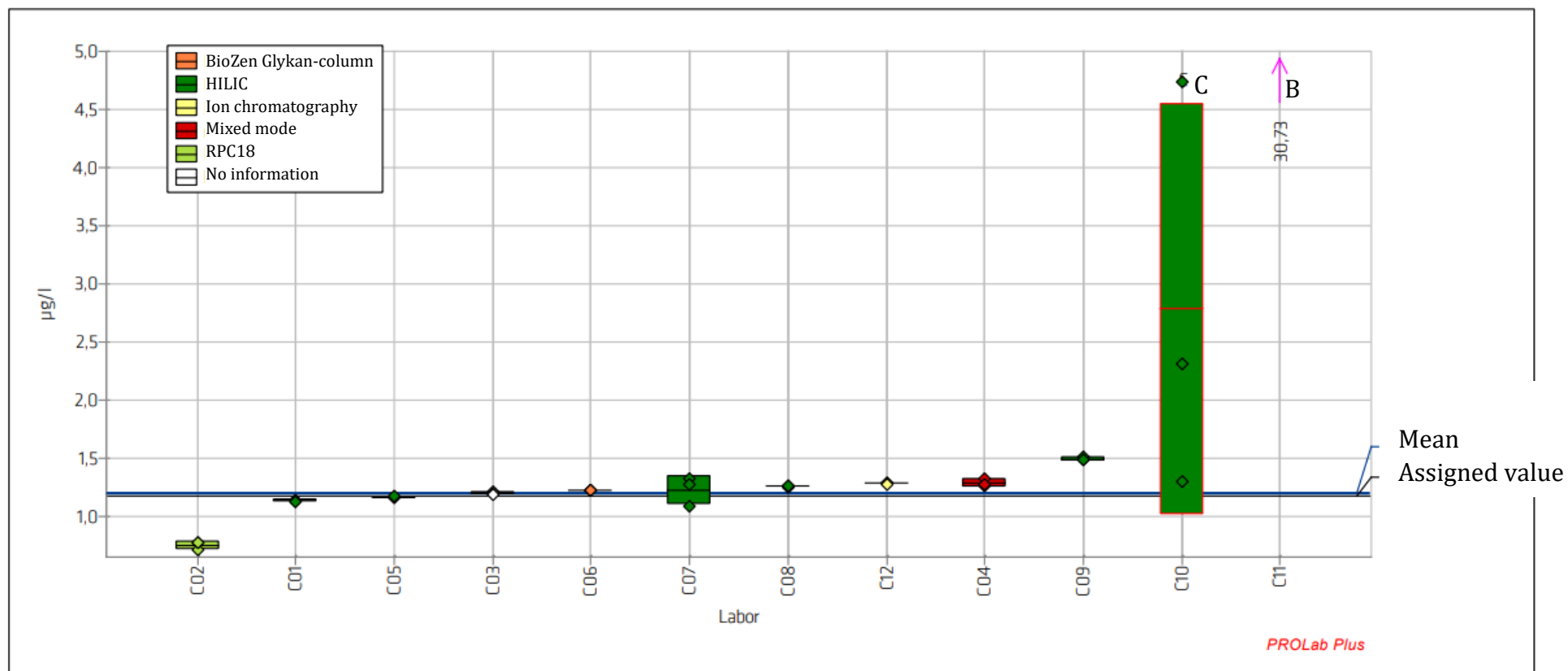
Analyte: TFA
 Coefficient of variation of repeatability: 6.42 %
 Repeatability standard deviation: $0.022 \mu\text{g/l}$
 Coefficient of variation of reproducibility: 14.36 %
 Reproducibility standard deviation: $0.049 \mu\text{g/l}$



Supplemental material S3-7

Sample: A1 (TFA added groundwater)
 Total mean +/- U(mean): 1.20 +/- 0.12 µg/l
 Assigned value: 1.18 µg/l
 Number of laboratories: 12
 Number of laboratories without outliers: 10
 Number of single measurement values: 30

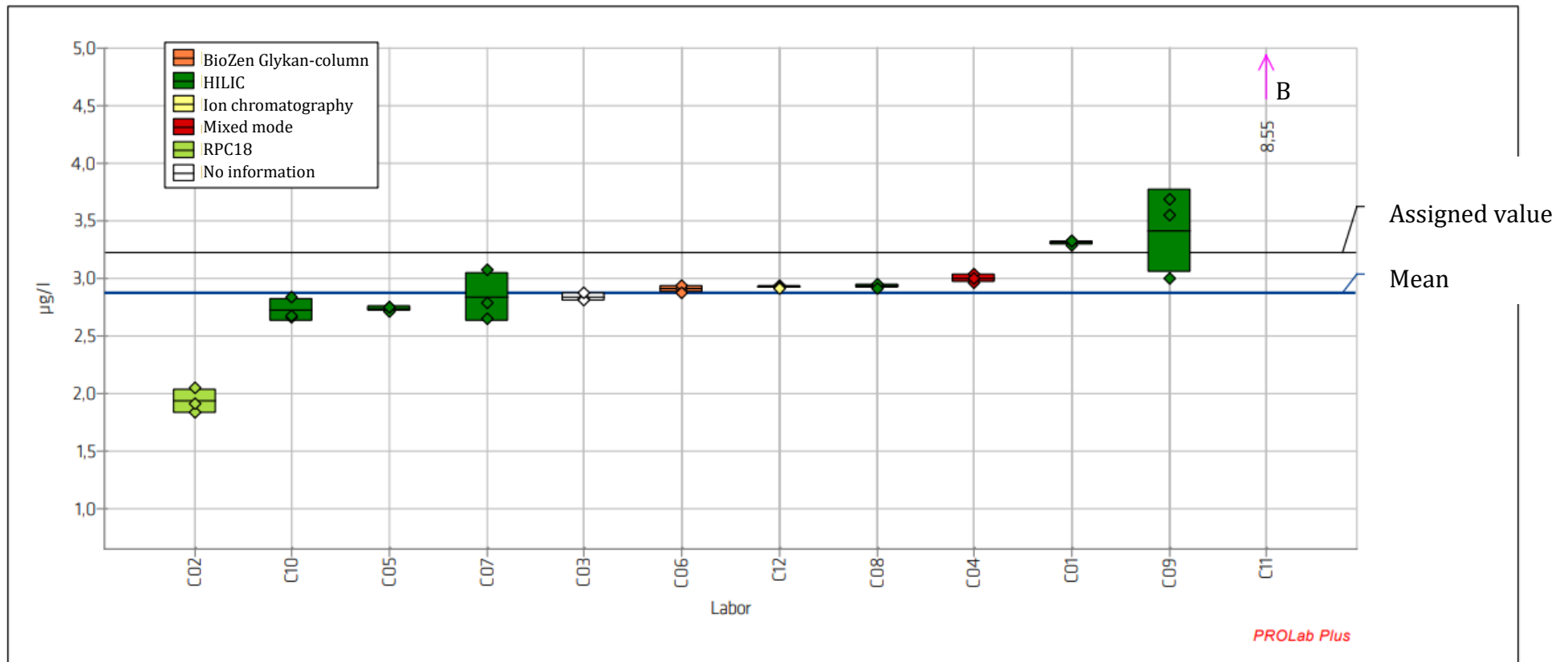
Analyte: TFA
 Recovery rate: 102.17 %
 Coefficient of variation of repeatability: 3.37 %
 Repeatability standard deviation: 0.04 µg/l
 Coefficient of variation of reproducibility: 16.10 %
 Reproducibility standard deviation: 0.19 %



Supplemental material S3-8

Sample: A2 (TFA added groundwater)
 Total mean +/- U(mean): 2.87 +/- 0.23 µg/l
 Assigned value: 3.22 µg/l
 Number of laboratories: 12
 Number of laboratories without outliers: 11
 Number of single measurement values: 33

Analyte: TFA
 Recovery rate: 89.01 %
 Coefficient of variation of repeatability: 4.25 %
 Repeatability standard deviation: 0.14 µg/l
 Coefficient of variation of reproducibility: 12.25 %
 Reproducibility standard deviation: 0.39 %



Supplemental material S4

Method details of participants

Participant	Chromatography type	Column (particle size, length, diameter)	Injection volume	Mobile phase Eluent A	Eluent B	Gradient		Velocity ml/min	Temperature	Blank µg/L	LOQ µg/L
1	mixed-mode	Raptor Polar X (2,7 µm, 50 mm, 2,1 mm)	10 µl	10 mM Ammoniumformiate / 0,05 % Formic acid	0,05 % Formic acid in 60:40 Acetonitrile Methanol	0 – 4.0 min 4.1 – 7.0 min	5% Eluent A 95% Eluent B 45 % Eluent A 65% Eluent B	0.5	40 °C	<0.005	0.03
2	RPC18	Kinetex F5 (2,6 µm, 150 mm, 4,6 mm)	100 µl	0,1 mmol NH ₄ F in Water	Methanol	0 – 1 min 1 – 2 min 3 min	90 % Eluent A 10% Eluent B 60 % Eluent A 40 % Eluent B 10 % Eluent A 90 % Eluent B	0.8	40 °C	0.02	0.1
3	no information										0.1
4	mixed-mode										0.1
5	HILIC	Atlantis Premier BEH C18 AX (1.7 µm, 100 mm, 2.1 mm) and EXP2 Filter Cartridge (3mm, 2µm) with EXP2 Pre-Column Filter Holder	10 µl	0,001 % Formic acid + 2 mM Ammoniumacetate in pure water		isocratic	100 % Eluent A	0.5	60 °C		0.05
6	HILIC	BioZen Glycan (2.6 µm, 150 mm, 2.1 mm)	20 µl	10 mmol/L Ammoniumformiate +0,1 Vol% Formic acid in water	2 mmol Ammoniumacetate und 0,1 Vol% Formic acid in Acetonitrile:Methanol 25:75 (v/v)	0 – 15 min isocratic	40% Eluent A 60 % Eluent B	0.55	30 °C		0.05
7	HILIC	Hypersil Gold HILIC (1.9 µm, 50 mm, 2.1 mm)	2 µl	15 mmol/L Ammoniumacetate in Acetonitrile – Water 8:2 (V/V)		0 – 4.0 min isocratic	100 % Eluent A	0.5	60 °C		0.1
8	HILIC										0.1
9	HILIC										0.1
10	HILIC										0.1
11	mixed-mode									0.2	0.1
12	IC	Metrosep A Supp 17 (5 µm, 150mm, 4.0 mm)	100 µl	5 mM NaCO ₃ , 0,2 mM Na ₂ HCO ₃ with 10% Methanol	1 mmol/L Nitric acid with 10% Methanol	isocratic		1.0	60 °C	0.04	0.1

