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Natural gas — Upstream area — Determination of hydrogen sulfide content by laser absorption spectroscopy

Gaz naturel — Zone amont — Détermination de la teneur en sulfure d'hydrogène par spectroscopie par absorption laser

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 3, *Upstream area*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Four methods for determination of sulfur compounds in natural gas already exist as International Standards:

— ISO 6326-3, *Natural gas — Determination of sulfur compounds — Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry*;

— ISO 6326-5, *Natural gas — Determination of sulfur compounds — Part 5: Lingener combustion method*;

— ISO 16960, *Natural gas — Determination of sulfur compounds — Determination of total sulfur by oxidative microcoulometry method*;

— ISO 19739, *Natural gas — Determination of sulfur compounds using gas chromatography*;

— ISO 20729, *Natural gas — Determination of sulfur compounds — Determination of total sulfur content by ultraviolet fluorescence method*.

Laser absorption spectroscopy is a more efficient method compared with chemical titration because it is an optical and instrumental method. It offers a more convenient and more stable means to analyse H_2S in upstream area natural gas.

Natural gas — Upstream area — Determination of hydrogen sulfide content by laser absorption spectroscopy

WARNING — The use of this document can involve hazardous materials, operations and equipments. This document does not aim to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and to determine the applicability of any other restrictions prior to use.

1 Scope

This document specifies a method for the determination of hydrogen sulfide content in working field natural gas of upstream area by laser absorption spectroscopy. The analytical range expressed as mole fraction is 10×10^{-6} to 20 %. The analytical range can be expanded to higher content with specific instrument requirements.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10715, *Natural gas — Sampling guidelines*

ISO 11095, *Linear calibration using reference materials*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

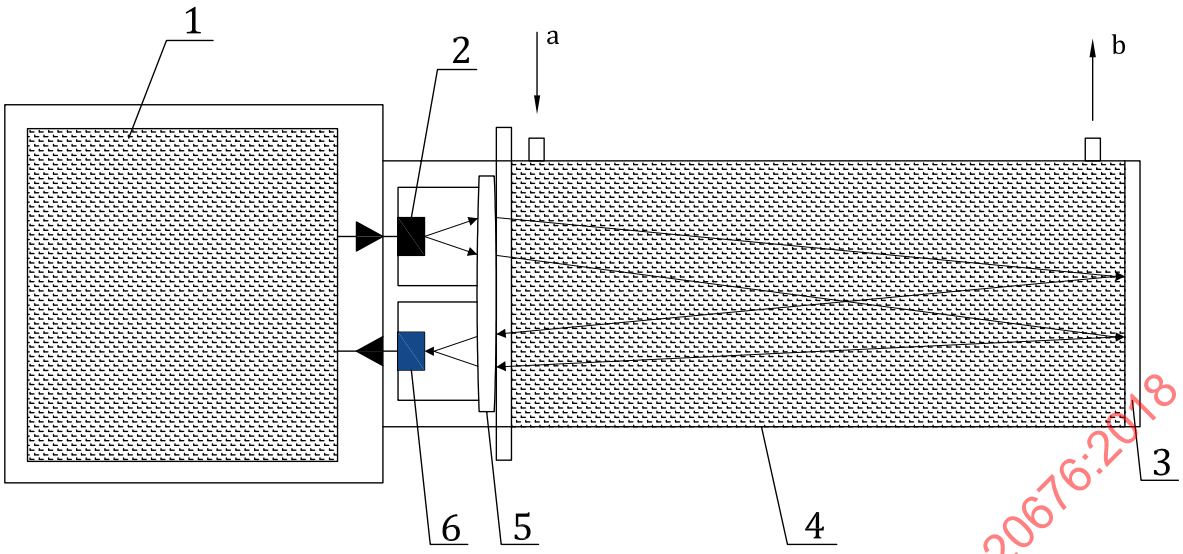
— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

4.1 Working principle of the hydrogen sulfide laser absorption analyser

The sketch of the measuring principle is shown in Figure 1. Semiconductor laser generator generates a laser beam, the laser beam goes through the sample. Then, the laser beam is detected by the photoelectric sensor. The energy of the laser beam is attenuated because of the absorption by the testing sample. The absorbance obeys the Lambert-Beer law.



Key

1 analytical unit
2 laser generator
3 mirror
4 gas chamber
5 lens
6 sensor
a Gas input.
b Gas output.

Figure 1 — Working principle of the hydrogen sulfide laser absorption analyser

4.2 Calculation formulae

If the analytical signal is absorbance, the content of hydrogen sulfide is calculated by Formula (1):

$$C_s = \frac{A_s}{A_{ref}} C_{ref} \quad (1)$$

where

C_s is the content of hydrogen sulfide in the natural gas sample;

A_s is the absorbance of hydrogen sulfide in the natural gas sample;

C_{ref} is the content of hydrogen sulfide in the calibration gas;

A_{ref} is the absorbance of hydrogen sulfide in the calibration gas.

NOTE The reference conditions are preferably 20 °C, 101,325 kPa.

5 Measurement device

5.1 Laser hydrogen sulfide analyser

5.1.1 Laser analyser

The type of laser hydrogen sulfide analyser is selected according to the content of hydrogen sulfide in natural gas. The signal/noise ratio should be higher than 2:1 over the whole analytical range. The light transmission should be higher than 10 % before introducing any sample.

5.1.2 Laser generator

The laser generator should be warmed up according to the operating instructions of the analyser before its first application and also after each switching on. If the operating instructions do not state warming-up period, the laser generator should be warmed up for at least 48 h before its first application and 1 h after the analyser is turned on.

5.2 Gas pressure regulator

The gas pressure regulator should have a minimum interior volume. It shall be made of stainless steel or shall be deactivated; it should show no effect on the analytical result of hydrogen sulfide content.

5.3 Flow rate meter

The sample flow rate through the analyser should be set in accordance with the operating instructions of the analyser.

5.4 Hydrogen sulfide absorber

Beakerflask, flask etc. filled with basic solution can be used as hydrogen sulfide absorber in order to eliminate hydrogen sulfide from the measured natural gas sample.

6 Reagents and material

6.1 Calibration gas

The hydrogen sulfide calibration gas should be certified with proper content to cover the analytical range of the instrument. The balance gas of the calibration gas should be methane.

6.2 Methane

The purity of methane should be higher than 999 mmol/mol. The H_2S impurity mole fraction shall not be more than 0,1 µmol/mol. Methane is used as zero point gas and sweeping gas.

6.3 Absorb solution of hydrogen sulfide

Technical pure sodium hydroxide is used to prepare a 10 % (mass fraction) solution as absorber of sulfur contained in the natural gas sample. Other types of hydrogen sulfur absorbing compounds can also be used to prepare this solution.

7 Measurement

7.1 Preparation

The calibration gas or the sulfur-containing natural gas sample is connected with the analyser according to Figure 2.

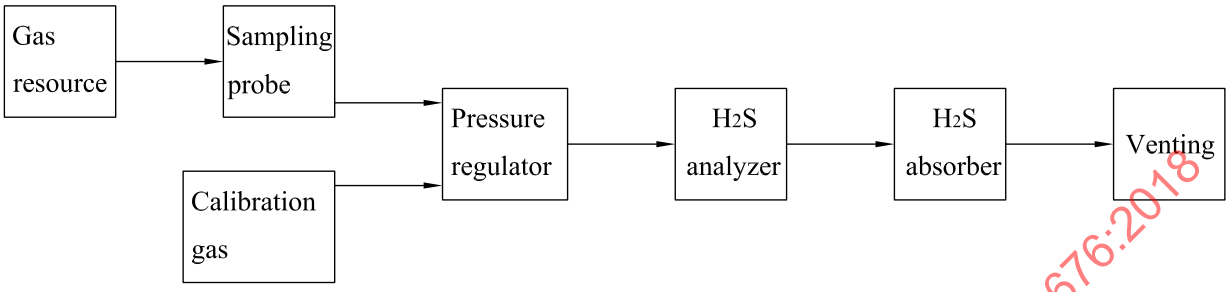


Figure 2 — Analytical procedure of the measurement/calibration

7.2 Calibration of analyser

7.2.1 Calibration frequency

The laser hydrogen sulfide analyser should be properly calibrated. The hydrogen sulfide analyser should be recalibrated according to the needs of the user (at least annually).

7.2.2 Calibration procedure

Before the laser hydrogen sulfide analyser is used to carry out the analysis, the calibration gas specified in 6.1 is used to perform the calibration.

Connect the calibration gas with the analyser according to Figure 2. Adjust the input pressure to 0,2 MPa to 0,4 MPa by the gas pressure regulator. Keep a constant and stable flow rate. The change of the flow rate should be less than 10 %. Sweep the analyser with the gas flow for at least 2 min.

After the sulfur-containing calibration gas is used, it should go through the absorption solution before it is vented.

7.2.3 Calibration method

Using ISO 11095, the user should choose the calibration method depending on the analytical accuracy that is required. The following are candidate methods and their requirements:

— bracketing calibration: the difference between calibration gas and analytical result should be less than relatively 20 %;

— response formula simulation: no less than three calibration gas should be used to cover the analytical range;

— one point calibration: the difference between calibration gas and analytical result should be less than relatively 20 %.

If the method is used to monitor fixed natural gas source with constant H_2S concentration, one point calibration or bracketing calibration should be applied. If the method is used to analyse a non-constant natural gas source with changing H_2S concentration, response formula simulation should be applied.

7.3 Sampling

Sampling shall be performed in accordance with ISO 10715.

All the materials used for sampling equipment and transfer lines shall be inert to sulfur compounds. For direct sampling, it should include sample conditioning to ensure the gas injected into the analysis unit does not contain any liquid water, dust or liquid hydrocarbons.

WARNING — H_2S is poisonous, it is important for the user to establish appropriate safety and health practices.

7.4 Measurement of hydrogen sulfide in natural gas sample

Suitable instrument should be selected according to the content of hydrogen sulfide and accuracy requirement.

The analyser should be in the measurement mode while doing the measurement. Connect the gas sample with the analyser according to Figure 2. Adjust the input pressure to 0,2 MPa to 0,4 MPa by the gas regulator. Keep a constant and stable flow rate. The change of the flow rate should be less than 10 %. Sweep the analyser with the gas flow for at least 2 min.

After the sulfur-containing sample is tested, it should go through the absorption solution before it is vented.

7.5 Data processing

When the analyser is in measurement mode, if the listed result is the content of the analysis, testing result should be read directly. If the listed result of the analyser is the absorbance, the content of hydrogen sulfide shall be calculated according to Formula (1). The analytical result should have three significant digits.

8 Repeatability

In the analytical range given by this document, under repeatability conditions, the difference of two test results in a short time interval (30 s) should not exceed the values listed in Table 1 at a 95 % level of confidence. Annex A gives an example of the statistical procedure of the repeatability estimation.

Table 1 — Repeatability of different concentration ranges

Content range	Repeatability limits
10 µmol/mol – 50 µmol/mol	5 µmol/mol
50 µmol/mol – 1 mmol/mol	10 µmol/mol
1 mmol/mol – 4 mmol/mol	100 µmol/mol
4 mmol/mol – 20 mmol/mol	600 µmol/mol
20 mmol/mol – 200 mmol/mol	2,5 mmol/mol

9 Uncertainty evaluation

9.1 Principle

The H_2S concentration is calculated using Formula (1). The uncertainty of the final result is based on Formula (1) with some mathematical computing.

9.2 Uncertainty of A_S

The uncertainty of A_S is the standard deviation of the analytical data (S_S), and the relative uncertainty of A_S is calculated by Formula (2).

$$u_{\mathrm{rel},As} = \sqrt{\frac{\sum_{i=1}^{n}(A_i - \bar{A})^2}{n(n-1)}} \tag{2}$$

where

$u_{\mathrm{rel},As}$ is the relative standard uncertainty of the absorbance(signal) of the sample;

A_i is the absorbance (signal) of each test;

$\bar{A}$ is the mean of all the absorbance values in one analysis.

9.3 Uncertainty of A_{ref}

The uncertainty of A_{ref} depends on the calibration procedure. In the one point calibration procedure, the uncertainty of A_{ref} is evaluated in the same procedure as A_S.

9.4 Uncertainty of C_{ref}

The uncertainty of C_{ref} is given by the producer of the calibration gas and is listed in the certificate of the calibration gas.

9.5 Uncertainty of result

The relative standard uncertainty of the result is calculated by Formula (3).

$$u_{\mathrm{rel},Cs} = \sqrt{u_{\mathrm{rel},As}^2 + u_{\mathrm{rel},Aref}^2 + u_{\mathrm{rel},Cref}^2} \tag{3}$$

where

$u_{\mathrm{rel},Cs}$ is the relative standard uncertainty of the final analytical result;

$u_{\mathrm{rel},As}$ is the relative standard uncertainty of the H_2S absorbance(signal) of the sample;

$u_{\mathrm{rel},Aref}$ is the relative standard uncertainty of H_2S absorbance of the calibration gas;

$u_{\mathrm{rel},Cref}$ is the relative standard uncertainty of H_2S content in calibration gas.

Annex A
(informative)

Example of statistical procedure for estimation of the repeatability

A.1 Background

In order to test the repeatability of the method, a series of experiments was designed and carried out. It involved nine instruments in five laboratories. The instruments used in the experiments are listed in Table A.1.

Table A.1 — Analytical instruments used in the experiments

Instrument	Analytical range	Repeatability	Manufacturer	Laboratory
A	1 % – 20 %	≦1 % F.S.	FPI (Hangzhou)	RINGT. PetroChina
B	1 % – 20 %	≦1 % F.S.	FPI (Hangzhou)	RINGT. PetroChina
C	0 – 200 × 10^{-6}(C-1) 0 – 2 000 × 10^{-6}(C-2)	≦1 % F.S.	FPI (Hangzhou)	RINGT. PetroChina
D	0 – 0,7 %	≦1 % F.S.	FPI (Hangzhou)	Chongqing Purification Plant. PetroChina
E	0 – 50 × 10^{-6}	≦1 % F.S.	FPI (Hangzhou)	Chuan Xibei Purification Plant. PetroChina
F	0,1 % – 2 %	≦2 % F.S.	MIZI (Wuhan)	In manufacturer
G	2 % – 20 %	≦2 % F.S.	MIZI (Wuhan)	In manufacturer
H	0 – 100 × 10^{-6}	≦2 % F.S.	MIZI (Wuhan)	In manufacturer
I	0 – 200 × 10^{-6}	≦1 % F.S.	FPI (Hangzhou)	In manufacturer

A total of 15 cylinders of calibration gas were used to test the behaviour of all the instruments. All the raw data were processed in order to obtain the repeatability of the method. All the experiments used H_2S/CH_4 as calibration gas, with methane as balance gas. The different concentrations of H_2S and related uncertainty are listed in Table A.2.

Table A.2 — Cylinders of calibration gas used in the experiments

No.	Cylinder No.	Concentration (10^{-2} mol/mol)	Uncertainty (k = 2)
1	52804153	0	—
2	52804113	10,8 × 10^{-4}	1 × 10^{-6}
3	52804024	49,9 × 10^{-4}	Rel 2,5 %
4	52804072	98,7 × 10^{-4}	Rel 2,5 %
5	52804119	775 × 10^{-4}	Rel 4,5 %
6	52804094	0,163	Rel 2,8 %
7	52804022	0,285	Rel 2,8 %
8	52804005	0,406	Rel 2,8 %
9	50303002	0,557	Rel 2,8 %
10	50303143	0,770	Rel 2,8 %
11	50303126	1,11	Rel 2,8 %
12	50303046	1,57	Rel 2,8 %

Table A.2 *(continued)*

No.	Cylinder No.	Concentration (10^{-2} mol/mol)	Uncertainty (k = 2)
13	50303042	3,98	Rel 2,8 %
14	50303106	7,90	Rel 2,8 %
15	50303202	15,8	Rel 2,8 %

A.2 Experiments

Acording to the analytical range of the different instruments, the different laboratories used the suitable calibration gas to test the analytical range repeatability. A total of 11 tests were performed on each calibration gas, on each instrument.

The following procedure was used:

— before starting the 11 tests, connect the calibration gas with the instrument, sweep the pipe and instrument for more than 5 min, and then read the analytical result every 30 s;

— after completing 11 tests, another calibration gas is used in the test.

The repeatability of the method was calculated according to ISO 4259-1 and ISO 4259-2, using the analytical result of the same calibration gas on each instrument. After obtaining all the 11 testing results of each analysis, S_r is calculated according to the raw data. The obtained S_r is multiplied with 2,8 according to ISO 4259-1 and ISO 4259-2. Rounding off is applied to the product for final repeatability.

A.3 Raw data of the test

The raw data of the different tests with the different calibration gases on the different instruments are given in Table A.3. There are 2 to 4 instruments tested on different calibration gas. Other instruments were not able to be tested on such calibration gas with improper H_2S concentration.

Table A.3 — Data obtained with the cylinders of calibration gas used in the experiments

No.	Cylinder No.	Reference value	Instrument No.	Raw data of 11 tests										
1	52804153	0 (µmol/mol)	B	0	0	0	0	0	0	0	0	0	0	0
			C-1	12,5	8,00	7,68	6,53	9,05	11,0	14,4	11,1	8,41	6,69	6,40
			E	7,70	7,67	7,57	7,57	7,44	7,44	7,55	7,58	7,65	7,71	7,62
			I	0,06	0,41	0,16	0,10	0,73	0,56	0,71	0,16	0,60	0,27	0,32
2	52804113	10,8 (µmol/mol)	E	5,32	5,32	5,33	5,21	5,28	5,36	6,17	6,39	6,23	5,99	5,92
			H	15,4	19,1	19,3	16,5	13,6	19,8	18,5	14,6	16,1	15,5	14,2
			C-1	12,6	9,87	10,9	12,1	11,8	11,4	15,5	12,8	11,6	14,2	13,6
			C-2	13,2	11,9	12,0	11,4	13,4	15,2	15,6	13,9	14,1	14,8	16,2
			I	10,9	10,9	10,8	10,8	10,8	10,7	10,9	10,9	11,0	11,2	11,3
3	52804024	49,9 (µmol/mol)	C-1	49,1	50,0	50,1	49,1	48,8	48,2	49,5	49,0	48,8	48,7	48,0
			C-2	48,3	48,0	50,3	52,6	47,7	46,6	45,2	45,6	46,0	46,5	47,0
			E	41,0	41,2	40,9	40,9	40,8	40,8	40,9	41,0	41,0	41,1	41,0
			I	54,1	53,9	54,4	54,6	54,6	54	54,3	54,3	53,7	53,2	54,1
4	52804072	98,7 (µmol/mol)	H	80,6	82,1	87,3	85,2	82,3	89,2	81,5	85,5	83,4	84,3	88,2
			C-1	91,3	92,3	90,8	87,9	89,9	90,1	92,6	91,4	92,6	92,1	92,6
			C-2	112,7	117,1	116,0	112,5	109,4	110,7	107,4	104,7	104,9	106,3	104,5
			I	105,1	105,2	105,2	105,3	105,3	105,3	105,2	105,2	105,3	105,6	105,9
5	52804119	755 (µmol/mol)	D	612	615	614	614	615	616	615	614	617	617	618
			C-2	499	501	503	510	508	507	506	508	506	505	506
			I	612	613	613	613	613	613	612	612	612	612	612
6	50303143	0,163 (10 mmol/mol)	A	0,099	0,102	0,093	0,095	0,096	0,098	0,095	0,098	0,093	0,102	0,104
			B	0,135	0,129	0,130	0,123	0,124	0,122	0,123	0,132	0,134	0,125	0,120
			D	0,175	0,175	0,175	0,175	0,175	0,175	0,175	0,175	0,175	0,175	0,175
			F	0,088	0,088	0,094	0,092	0,085	0,085	0,092	0,096	0,096	0,098	0,098
7	52804094	0,285 (10 mmol/mol)	A	0,224	0,227	0,226	0,230	0,222	0,224	0,225	0,220	0,218	0,224	0,222
			B	0,207	0,209	0,213	0,213	0,21	0,210	0,213	0,210	0,212	0,211	0,216
			D	0,317	0,317	0,317	0,317	0,317	0,317	0,317	0,317	0,317	0,317	0,317
			F	0,229	0,234	0,233	0,237	0,220	0,225	0,226	0,232	0,232	0,235	0,233
8	50303002	0,406 (10 mmol/mol)	A	0,311	0,314	0,307	0,306	0,311	0,310	0,317	0,306	0,312	0,317	0,314
			B	0,341	0,344	0,345	0,342	0,343	0,343	0,338	0,349	0,343	0,340	0,337
			D	0,426	0,427	0,426	0,426	0,426	0,426	0,426	0,426	0,426	0,426	0,426
			F	0,337	0,335	0,328	0,325	0,327	0,336	0,328	0,335	0,335	0,335	0,337

Table A.3 *(continued)*

No.	Cylinder No.	Reference value	Instrument No.	Raw data of 11 tests										
9	52804022	0,557 (10 mmol/mol)	A	0,490	0,477	0,483	0,470	0,493	0,500	0,491	0,476	0,460	0,464	0,470
			B	0,483	0,485	0,484	0,492	0,487	0,487	0,486	0,489	0,493	0,492	0,489
			D	0,627	0,627	0,627	0,627	0,627	0,627	0,627	0,627	0,627	0,627	0,627
			F	0,523	0,519	0,523	0,527	0,536	0,528	0,525	0,527	0,522	0,518	0,525
			G	0,365	0,236	0,306	0,275	0,314	0,281	0,260	0,315	0,352	0,340	0,340
10	50303126	0,770 (10 mmol/mol)	A	0,693	0,69	0,685	0,682	0,683	0,687	0,686	0,687	0,675	0,683	0,674
			B	0,731	0,740	0,736	0,735	0,736	0,741	0,743	0,740	0,735	0,731	0,731
			F	0,765	0,766	0,756	0,764	0,767	0,766	0,759	0,766	0,770	0,771	0,771
			G	0,622	0,608	0,617	0,620	0,640	0,638	0,649	0,670	0,700	0,723	0,710
11	52804005	1,11 (10 mmol/mol)	A	1,03	1,03	1,03	1,04	1,03	1,04	1,04	1,04	1,03	1,04	1,04
			B	1,05	1,04	1,05	1,05	1,05	1,04	1,01	1,04	1,05	1,05	1,04
			F	1,13	1,13	1,13	1,13	1,12	1,13	1,14	1,13	1,14	1,12	1,14
12	50303046	1,57 (10 mmol/mol)	A	1,45	1,46	1,47	1,46	1,46	1,46	1,46	1,44	1,45	1,46	1,47
			B	1,51	1,51	1,52	1,51	1,51	1,52	1,52	1,52	1,53	1,52	1,52
			F	1,60	1,60	1,60	1,60	1,61	1,61	1,61	1,61	1,61	1,61	1,60
			G	1,76	1,67	1,59	1,64	1,66	1,66	1,66	1,62	1,63	1,60	1,63
13	50303042	3,98 (10 mmol/mol)	A	3,67	3,66	3,66	3,67	3,66	3,68	3,67	3,68	3,67	3,67	3,67
			B	3,79	3,78	3,78	3,78	3,79	3,78	3,78	3,78	3,78	3,78	3,77
			F	3,88	3,87	3,88	3,91	3,90	3,89	3,90	3,90	3,90	3,89	3,89
			G	4,30	4,15	4,26	4,11	4,28	4,32	4,40	4,43	4,41	4,32	4,39
14	50303106	7,90 (10 mmol/mol)	A	7,23	7,25	7,26	7,26	7,26	7,26	7,26	7,25	7,26	7,25	7,25
			B	7,37	7,38	7,36	7,36	7,35	7,34	7,34	7,35	7,35	7,34	7,35
			F	7,04	7,05	7,04	7,05	7,05	7,05	7,05	7,04	7,04	7,03	7,03
			G	8,10	8,11	8,08	8,06	8,01	8,01	8,01	8,00	8,00	8,06	8,05
15	50303202	15,8 (10 mmol/mol)	A	15,1	15,1	15,1	15,1	15,0	15,0	15,0	15,1	15,0	15,0	15,0
			B	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0
			G	13,1	13,3	13,1	13,1	13,2	13,1	13,3	13,4	13,3	13,3	13,3

A.4 Calculation of the mean of each analysis

After obtaining the raw data, the mean of each analysis is calculated. All the means are listed in Table A.4.

Table A.4 — Means of each analysis

p	Instrument N°	Level, cylinder N°, reference value (10 mmol/mol)														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
		52804153	52804113	52804024	52804072	52804119	50303143	52804094	50303002	52804022	50303126	52804005	50303046	50303042	50303106	50303202
		0	0,00108	0,00499	0,00987	0,0755	0,163	0,285	0,406	0,557	0,770	1,11	1,57	3,98	7,90	15,8
1	A	—	—	—	—	—	0,098	0,224	0,311	0,479	0,684	1,035	1,457	3,669	7,254	15,045
2	B	0,00000	—	—	—	—	0,127	0,211	0,342	0,488	0,736	1,04	1,52	3,78	7,35	15,00
3	C-1	0,00093	0,00124	0,00490	0,00912	—	—	—	—	—	—	—	—	—	—	—
4	C-2	—	0,00138	0,00476	0,01097	0,05054	—	—	—	—	—	—	—	—	—	—
5	D	—	—	—	—	0,06152	0,17500	0,31700	0,42609	0,62700	—	—	—	—	—	—
6	E	0,00076	0,00057	0,00410	—		—	—	—	—	—	—	—	—	—	—
7	F	—	—	—	—	—	0,09200	0,23055	0,33255	0,52482	0,76555	1,13091	1,60545	3,89182	7,04273	—
8	G	—	—	—	—	—	—	—	—	0,30764	0,65427	—	1,64727	4,30636	8,04455	13,22727
9	H	—	0,00166	—	0,00845	—		—	—	—	—	—	—	—	—	—
10	I	0,00004	0,00109	0,00541	0,01053	0,06125	—	—	—	—	—	—	—	—	—	—

A.5 Calculation of repeatability

After obtaining the mean of each analysis, S_r is calculated according to the means and the raw data from Table A.3 and Table A.4. The statistical repeatability is calculated by 2,8 × S_r, and then the obtained value is rounded off. All the data are listed in Table A.5.