
**Water quality — Determination
of dissolved anions by liquid
chromatography of ions —**

**Part 1:
Determination of bromide, chloride,
fluoride, nitrate, nitrite, phosphate
and sulfate**

*Qualité de l'eau — Dosage des anions dissous par chromatographie
des ions en phase liquide —*

*Partie 1: Dosage du bromure, chlorure, fluorure, nitrate, nitrite,
phosphate et sulfate*



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10304-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition of ISO 10304-1 cancels and replaces ISO 10304-1:1992 and ISO 10304-2:1995, which have been technically revised.

ISO 10304 consists of the following parts, under the general title *Water quality — Determination of dissolved anions by liquid chromatography of ions*:

- *Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*
- *Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*
- *Part 4: Determination of chlorate, chloride and chlorite in water with low contamination*

Introduction

The user should be aware that particular problems could require the specification of additional conditions not provided for in this part of ISO 10304.

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Water quality — Determination of dissolved anions by liquid chromatography of ions —

Part 1:

Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This part of ISO 10304 specifies a method for the determination of dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate in water, e.g. drinking water, ground water, surface water, waste water, leachates and marine water by liquid chromatography of ions.

The lower limit of application is $\geq 0,05$ mg/l for bromide and for nitrite, and $\geq 0,1$ mg/l for chloride, fluoride, nitrate, orthophosphate, and sulfate. The lower limit of application depends on the matrix and the interferences encountered.

The working range may be expanded to lower concentrations (e.g. $\geq 0,01$ mg/l) if an appropriate pre-treatment of the sample (e.g. conditions for trace analyses, pre-concentration technique) is applied, and/or if an ultraviolet (UV) detector (for bromide, nitrate and nitrite) is used.

2 Normative references

The following referenced documents are indispensable for the application 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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

3 Interferences

3.1 Organic acids

Aliphatic organic acids such as mono- or dicarboxylic acids may interfere with the separation of the anions.

3.2 Sulfite

Sulfite may cause a positive bias for sulfate due to autooxidation. In this case the sample may be adjusted to pH 10 and formaldehyde solution is added in order to stabilize sulfite, if necessary.

3.3 Metals

The presence of metals (e.g. alkaline earth metals, transition metals, heavy metals) possibly interfering with the anions of interest, should be checked and can be eliminated with the aid of special cation exchangers (e.g. cartridge in the H-form or Na-form).

NOTE Depending on the sample matrix, the use of cation exchangers in the H-form can cause losses of fluoride and nitrite.

4 Principle

The sample is pretreated in order to remove solids (see Clause 7), sulfite and metal ions, if necessary. The anions of interest (bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate), are separated by liquid chromatography, applying an anion exchange resin as stationary phase, and aqueous solutions of salts of weak mono- and dibasic acids as eluents for isocratic or gradient elution (e.g. carbonate, hydrogencarbonate, hydroxide eluent) (5.10). Detection is carried out using a conductivity detector (CD).

When using CDs it is essential that the eluents show a sufficiently low conductivity. For this reason, CDs are usually combined with a suppressor device (cation exchanger), which will reduce the conductivity of the eluent and transform the sample species into their respective acids.

NOTE A UV detector is not required to carry out this analysis, but can be used for bromide, nitrate or nitrite if a higher sensitivity is required and/or in case of a matrix interference to the CD. If used, bromide, nitrate and nitrite can be measured at $\lambda = 200 \text{ nm}$ to $\lambda = 215 \text{ nm}$.

Check resolution, R , to ensure that it complies with the required separation conditions (6.2). UV may be used in combination with a CD. UV measures the absorption directly.

Calibration is carried out as specified in ISO 8466-1 or ISO 8466-2 (8.2). In special cases, extended working ranges (e.g. two concentration decades) may be applied.

Control experiments are necessary to check the validity of the calibration function. Replicate determinations may be necessary. Use of the method of standard addition may be required when matrix interferences are expected (8.3).

5 Reagents

Use only reagents of recognized analytical grade. Weigh the reagents with an accuracy of $\pm 1 \%$ of the nominal mass, unless stated otherwise. The reagents listed in 5.2 to 5.5 may be considered representative examples for the preparation of eluents (5.10).

5.1 Water, complying with grade 1, as defined in ISO 3696.

5.2 Sodium hydrogencarbonate, NaHCO_3 .

5.3 Sodium carbonate, Na_2CO_3 .

5.4 Sodium hydroxide, NaOH .

5.5 Potassium hydroxide, KOH .

5.6 Bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate stock standard solutions, $\rho = 1\,000\text{ mg/l}$ each.

Single anion and mixed anion stock solutions with adequate and required specification are commercially available. These solutions are considered to be stable for several months.

For an alternative preparation of stock solutions see Table 1. Dissolve the salts accordingly, after appropriate treatment.

Table 1 — Mass portion and pre-treatment for stock solutions

Anion to be determined	Salt to be used ^a	Mass g	Pre-treatment by drying at $(105 \pm 5)^\circ\text{C}$ for at least
Bromide	NaBr	1,287 7	6 h
Chloride	NaCl	1,648 4	2 h
Fluoride	NaF	2,210 0	1 h
Nitrate	NaNO_3	1,370 7	24 h
Nitrite	NaNO_2	1,499 8	1 h
Orthophosphate	KH_2PO_4	1,433 0	1 h
Sulfate	Na_2SO_4	1,478 6	1 h
^a Alternative salts with adequate and required specification may be used.			

5.7 Bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate standard solutions

5.7.1 General

Depending on the concentrations expected, prepare single or mixed standard solutions, of bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate concentrations from the stock standard solution (5.6). Store the standard solutions in polyethene bottles.

5.7.2 Example for a bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate mixed standard solution, $\rho = 10\text{ mg/l}$ each.

Pipette 1,0 ml of each of the stock standard solutions (5.6) into a 100 ml volumetric flask, and dilute to volume with water (5.1).

The solutions are stable for 1 week, if stored in the dark at 2°C to 8°C in polyethene bottles.

5.8 Bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate calibration solutions

Depending on the concentrations expected in the sample, use the standard solution (5.7.2) to prepare e.g. 5 to 10 calibration solutions distributed as evenly as possible over the expected working range.

For example, proceed as follows for the range $0,05\text{ mg/l}$ to $0,5\text{ mg/l}$:

Pipette, into a series of 20 ml volumetric flasks, the following volumes: 100 µl, 200 µl, 300 µl, 400 µl, 500 µl, 600 µl, 700 µl, 800 µl, 900 µl or 1 000 µl of the standard solution (5.7.2) and dilute to volume with water (5.1).

The concentrations of the anions in these calibration solutions are: 0,05 mg/l, 0,1 mg/l, 0,15 mg/l, 0,2 mg/l, 0,25 mg/l, 0,3 mg/l, 0,35 mg/l, 0,4 mg/l, 0,45 mg/l or 0,5 mg/l, respectively.

Prepare the calibration solutions on the day of use.

5.9 Blank

Fill a volumetric flask (e.g. 100 ml flask) with water (5.1).

5.10 Eluents

5.10.1 General

Degas all water used for eluent preparation. In order to minimise the growth of bacteria or algae, prepare eluents freshly after 3 days.

The choice of eluent depends on the chosen column and detector (e.g. UV or conductivity), seek advice from the column supplier. The chosen combination of separator column and eluent shall meet the resolution requirements stated in 6.2.

The example for the eluent composition in 5.10.3 refers to the CD suppressor technique only. Nevertheless, the non-suppressed CD technique (as well as UV detection) is included in this method.

A selection of reagents for common eluents is given in 5.2 to 5.5.

NOTE Preparing the eluent from concentrates has proved to be successful.

5.10.2 Sodium carbonate/sodium hydrogencarbonate concentrate

For the eluent concentrate preparation:

Place 28,6 g of sodium carbonate (5.3) and 8,4 g of sodium hydrogencarbonate (5.2) into a 1 000 ml volumetric flask.

Dissolve in water (5.1) and dilute to volume with water.

The solution contains 0,27 mol/l of sodium carbonate and 0,1 mol/l of sodium hydrogencarbonate.

This solution is stable for several months if stored at 2 °C to 8 °C in glass or polyethene bottles.

5.10.3 Sodium carbonate/sodium hydrogencarbonate eluent

The following eluent is applicable for the determination of the anions according to this standard:

Pipette 20 ml of the concentrate (5.10.2) into a 2 000 ml volumetric flask and dilute to volume with water (5.1).

The solution contains 0,002 7 mol/l of sodium carbonate and 0,001 mol/l of sodium hydrogencarbonate.

6 Apparatus

Usual laboratory apparatus, and, in particular:

6.1 Ion chromatography system. In general, it consists of the following components (see Figure 1).

6.1.1 Eluent reservoir, and a degassing unit.

6.1.2 Metal-free HPLC pump.

6.1.3 Sample injection system, incorporating a sample loop of appropriate volume (e.g. 0,02 ml) or autosampler device.

6.1.4 Separator column, with the specified separating performance (6.2).

6.1.5 Conductivity detector (CD).

6.1.6 Ultraviolet (UV) detector, e.g. a spectrophotometer, operating over the wavelength range: 190 nm to 400 nm, optionally used in combination with a CD or, as an alternative, if only bromide, nitrate or nitrite are to be determined.

6.1.7 Recording device (e.g. a computer with software for data acquisition and evaluation).

6.1.8 Precolumns, if necessary (see 3.3 and Note to 8.3).

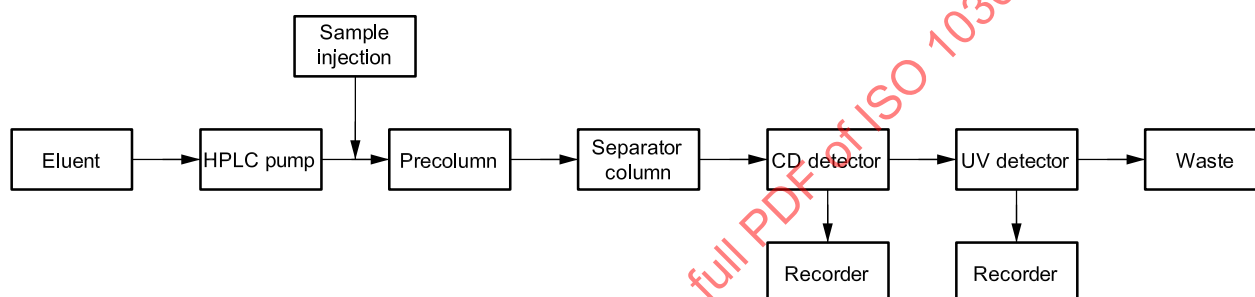
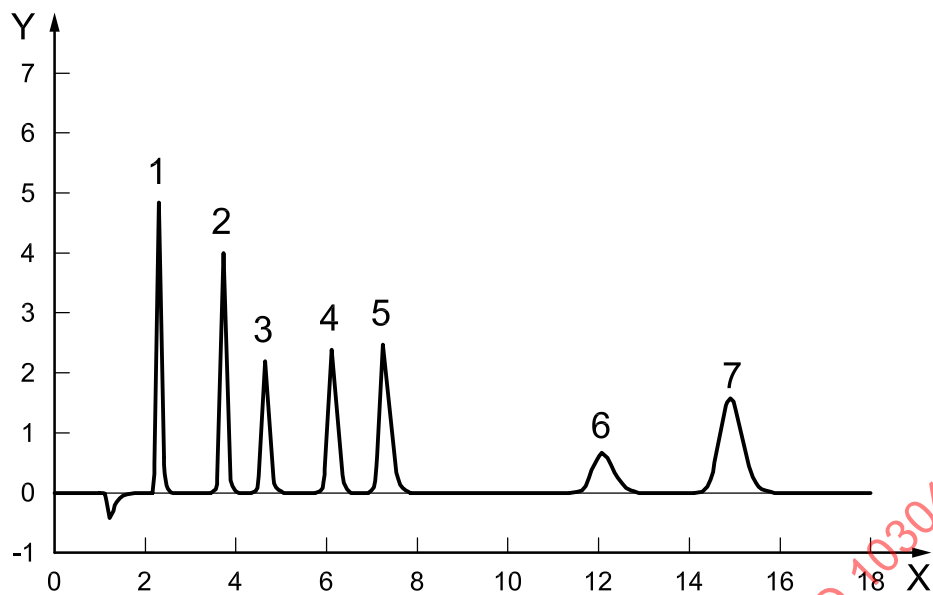


Figure 1 — Ion chromatographic system

6.2 Quality requirements for the separator column

In chromatograms of samples and standard solutions (see Figure 2), the peak resolution, R , between the anion of interest and its nearest peak, shall not fall below 1,3 [see Equation (1) and Figure 3].

Separation conditions shall be such that possible interfering anions will not interfere with the anion of interest.



Key

X retention time, t_R , min
Y conductivity, $\mu\text{S}\cdot\text{cm}^{-1}$

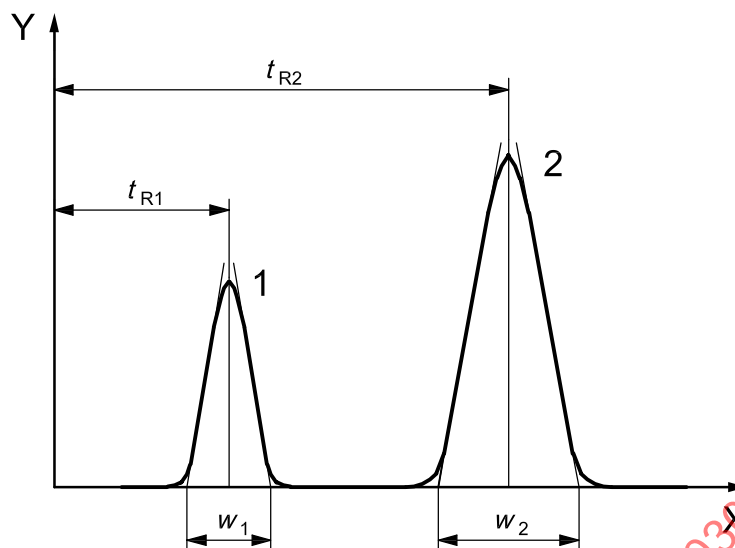
Peak ^a	Ion	Concentration, mg/l
1	Fluoride	3
2	Chloride	5
3	Nitrite	5
4	Bromide	10
5	Nitrate	10
6	Orthophosphate	10
7	Sulfate	10

Conditions

Precolumn	Ion exchanger
Column	Ion exchanger
Eluent	2,7 mmol/l Na_2CO_3 + 1,0 mmol/l NaHCO_3
Eluent flow rate	1,2 ml/min
Detection	CD
Injection volume	25 μl

^a Elution sequences and retention times, t_R , may vary, depending on the type of column and the eluent composition.

Figure 2 — Example of a chromatogram of a standard solution conforming to this part of ISO 10304

**Key**

- X retention time, t_R , s
 Y signal
 w peak width, s
 1 peak 1
 2 peak 2

Figure 3 — Graphical representation of the parameters to calculate the peak resolution, R

Calculate the peak resolution, R , using Equation (1):

$$R_{2,1} = \frac{2(t_{R2} - t_{R1})}{w_2 + w_1} \quad (1)$$

where

- t_{R1} is the retention time, in seconds, of the first peak;
 t_{R2} is the retention time, in seconds, of the second peak;
 w_1 is the peak width on the time axis, in seconds, of the first peak;
 w_2 is the peak width on the time axis, in seconds, of the second peak.

NOTE Base peak widths, w_1 and w_2 , are obtained by constructing isosceles triangles over the Gaussian peaks.

7 Sampling and sample pre-treatment

Use clean polyethylene vessels for sampling.

Stabilize the samples as specified in ISO 5667-3.

NOTE 1 Bacterial activities and adsorption of the anions onto particulate matter can cause conversion of anions (e.g. nitrate, nitrite, orthophosphate). A 0,45 μm filtration step during sampling can remove bacteria and particulate matter.

Store the samples in the dark at 2 °C to 8 °C for transportation.

NOTE 2 Changing pH values can cause precipitation of the sample during analysis. Precipitation can be avoided by an adjustment of the sample pH to the pH of the eluent prior to injection.

Prior to injection into the analyser, filter the sample through a membrane filter (of pore size 0,45 µm) to remove any particulate matter, if necessary.

Prevent possible contamination of the sample from the membrane (e.g. rinse the membrane with a small volume of the sample and discard the first portion of the filtrate).

Treat calibration solutions (5.8) and the blank solution (5.9) in the same way as the sample solutions.

8 Procedure

8.1 General

Set up the ion chromatographic system (6.1) according to the instrument manufacturer's instructions.

Run the eluent and wait for a stable baseline.

Perform the calibration as described in 8.2. Measure the samples, calibration (5.8) and blank solution (5.9) as described in 8.3.

NOTE Low concentrations (e.g. $\geq 0,01$ mg/l) can be determined by this method, but this ability will be limited by the laboratory environmental conditions and the equipment. Also the quality of water and reagents used will influence the accuracy of the analytical results. Pre-concentration techniques can be used in order to achieve lower limits of application.

8.2 Calibration

When the analytical system is first evaluated, and at intervals afterwards, establish a calibration function (e.g. as specified in ISO 8466-1 or ISO 8466-2) for the measurement. An example follows.

Prepare the calibration solutions as described in 5.8 and Clause 7.

Inject the calibration solutions (see 5.8 and Clause 7).

Identify the peaks for particular anions by comparing the retention times with those of the calibration solutions (5.8). Deviation of retention times shall not exceed ± 10 % within a batch.

Use the data obtained to calculate the regression line.

Generally, the calibration method is not restricted to a calibration strategy covering a single concentration decade as specified in ISO 8466-1 or ISO 8466-2 only. When calibrating over a larger range than one concentration decade, a loss of accuracy, compared to that specified in ISO 8466-1 or ISO 8466-2, may occur.

Adjust the established calibration function, if necessary (e.g. measure standard solutions of different anion concentrations in the lower and upper third of the working range).

8.3 Measurement

After establishing the calibration function, inject the sample (see Clause 7) into the chromatograph and measure the peaks as described above (8.2).

NOTE 1 Solid particles and organic compounds (such as mineral oils, detergents, and humic acids) shorten the lifetime of the separator column. They can be removed by applying a filter step through a non-polar phase (e.g. cartridge).

The use of a precolumn is recommended not only for the analyses of waters highly loaded with organics (3.1), but also to protect the analytical separator column.

NOTE 2 In general, two different types of precolumns can be used: those containing the same or similar resin material as the analytical separator column, and those packed with a non-functionalised resin.

If the concentration of the analyte exceeds the calibration range, dilute the sample or establish a separate calibration function for a higher working range and re-analyse it.

If the concentration of the analyte falls short of the calibration range, establish a separate calibration function for the lower working range, and re-analyse it, if necessary.

If matrix interferences are expected, use the method of standard addition to confirm the results (verify the peaks by comparing the retention time of the spiked sample with those of the original sample).

Measure the blank solution (5.9) in the same way as the sample.

9 Calculation

Calculate the mass concentration, ρ , in micrograms per litre, or milligrams per litre, of the anions in the solution using the peak areas or peak heights according to the calibration function used (8.2).

Take into account all dilution steps.

10 Expression of results

Report the results to a maximum of two significant figures.

EXAMPLE

Sulfate (SO_4^{2-}) 51 mg/l

Nitrate (NO_3^-) 0,64 mg/l

The results of nitrate, nitrite and orthophosphate may also be expressed as $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$.

Table 2 — Conversion factors

Multiply results for	by conversion factor	for data
NO_3^-	0,225 9	$\text{NO}_3\text{-N}$
$\text{NO}_3\text{-N}$	4,426 8	NO_3^-
NO_2^-	0,304 5	$\text{NO}_2\text{-N}$
$\text{NO}_2\text{-N}$	3,284 6	NO_2^-
PO_4^{3-}	0,326 1	$\text{PO}_4\text{-P}$
$\text{PO}_4\text{-P}$	3,066 2	PO_4^{3-}

11 Test report

The test report shall include at least the following information:

- a reference to this part of ISO 10304;
- identity of the water sample;
- expression of the results according to Clause 10;
- description of sample pre-treatment, if relevant;
- any deviation from this method and report of circumstances that may have affected the results.

Annex A (informative)

Performance data

Interlaboratory trials were carried out by laboratories in Austria, Belgium, France, Germany, Italy, the Netherlands and the United Kingdom. The variety of instruments and other analytical conditions used conformed with the quality parameters specified in the method.

For the description of sample matrix see Table A.1.

The performance data according to ISO 5725-2 are presented in Tables A.2 to A.8.

The coefficients of variation of the procedure, CV_{xo} (obtained from determined calibration functions analogous to ISO 8466-1) are listed in Table A.9. The data derive from laboratories participating in the above-mentioned interlaboratory trials.

Table A.1 — Description of sample matrix (M)

No	Matrix	Date
M1	Synthetic	1986
M2	Drinking water	1986
M3	Spiked drinking water	1986
M4	Surface water (river Rhine)	1986
M5	Clarified industrial sewage (COD, O: 770 mg/l)	March 1987
M6	Clarified domestic sewage (COD, O: 90 mg/l)	March 1987
M7	Clarified domestic sewage (COD, O: 70 mg/l)	March 1987
M8	Industrial sewage	October 1987
M9	Domestic sewage (COD, O: 300 mg/l; DOC, C: 47 mg/l)	November 1987
M10	Clarified domestic sewage (spiked sample M9)	November 1987
M11	Clarified domestic sewage (COD, O: 60 mg/l; DOC, C: 13 mg/l)	November 1987
M12	Clarified domestic sewage (spiked sample M11)	November 1987
M13	Clarified industrial sewage (COD, O: 400 mg/l; Cl: 3 500 mg/l)	November 1987
M14	Clarified industrial sewage (spiked sample 13)	November 1987
M15	Synthetic sewage, spiked with glucose (DOC, C: 165 mg/l)	November 1987
M16	Synthetic standard solution	March 1989
M17	Domestic sewage	March 1989
M18	Clarified domestic sewage (COD, O: 550 mg/l; electrical conductivity, 1 100 μ S/cm)	March 1989
M19	Synthetic standard solution	October 1988
M20	River water with high organic load (river Rhine)	October 1988
M21	River water (spiked sample M20)	October 1988
M22	Synthetic seawater	October 1988
M23	Refuse-dump seepage with high organic and inorganic load	October 1988
M24	Boggy water. A determination according to the IC method (as well as other methods e.g. photometry) was not possible because of a high load of humic acids.	October 1988
COD: Chemical oxygen demand DOC: Dissolved organic carbon		

Table A.2 — Performance data for bromide

Sample	Matrix	l	n	o %	x_{ref} mg/l	$\bar{\bar{x}}$ mg/l	η %	s_R mg/l	CV_R %	s_r mg/l	CV_r %
M1	Synthetic	29	109	9,2	2,00	1,97	98,6	0,129	6,5	0,08	4,0
M3	Drinking water	26	96	15,8	1,03	1,01	98,1	0,11	10,6	0,057	5,7
M5	Industrial	9	33	0,0	—	54,9	—	7,66	14,0	1,92	3,5
M9	Domestic	16	57	3,5	—	0,17	—	0,044	25,7	0,014	8,2
M10	Domestic	26	95	4,2	8,17	8,32	102	0,49	5,9	0,181	2,2
M11	Domestic	18	65	1,5	—	0,20	—	0,052	25,7	0,013	6,3
M12	Domestic	26	98	6,1	3,20	3,19	99,6	0,156	4,9	0,087	2,7
M13	Industrial	24	89	9,0	—	145	—	6,49	4,5	2,97	2,1
M14	Industrial	24	92	0,0	175	172	98,7	9,88	5,7	2,85	1,7
M15	Synthetic sewage	26	95	8,4	6,00	5,98	99,7	0,309	5,2	0,158	2,6
M16	Synthetic	12	43	8,5	1,50	1,49	99,3	0,06	3,7	0,03	2,5
M17	Domestic	12	44	6,4	—	0,65	—	0,04	6,1	0,03	3,8
M18	Domestic	12	47	0,0	—	0,49	—	0,05	9,8	0,03	6,9

Definition of symbols

l is the number of outlier-free individual analytical values per level;

n is the number of laboratories after outlier elimination;

o is the percentage of outlying values from the replicate determinations;

x_{ref} is the accepted reference value;

$\bar{\bar{x}}$ is the overall mean;

η is the recovery rate;

s_R is the reproducibility standard deviation;

CV_R is the coefficient of the variation of the reproducibility;

s_r is the repeatability standard deviation;

CV_r is the coefficient of the variation of the repeatability.

Table A.3 — Performance data for chloride

Sample	Matrix	l	n	o %	x_{ref} mg/l	$\bar{\bar{x}}$ mg/l	η %	s_R mg/l	CV_R %	s_r mg/l	CV_r %
M1	Synthetic	33	122	5,4	15,0	15,4	103	0,947	6,2	0,279	1,8
M2	Drinking water	30	108	15,6	—	21,6	—	1,03	4,8	0,313	1,5
M3	Drinking water	30	111	12,6	31,6	29,9	94,7	1,44	4,8	0,580	1,9
M4	River water	31	112	11,8	—	13,3	—	1,0	7,5	0,275	2,1
M5	Industrial	7	27	0,0	3670	3658	99,7	122	3,3	52,5	1,4
M6	Domestic	7	27	0,0	236	228	96,5	11,3	4,9	5,02	2,2
M7	Domestic	7	27	0,0	404	377	93,4	11,9	3,2	3,71	1,0
M8	Industrial	13	54	0,0	694	707	102	58,8	9,3	17,7	2,5

Definition of symbols see Table A.2