Supelco®
Analytical Products

Application Note

Bromate in water and drinking water

Photometric determination with 3,3'-dimethylnaphthidine and iodide

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1.0 Introduction

Since bromate has a potentially carcinogenic effect when ingested orally, a limit of 0.01 mg/L has been set in the currently applicable drinking-water regulations like EU drinking water directive[1] or WHO drinking water guidelines[2]. The determination of the concentration of bromate is correspondingly a prerequisite measure for the elimination ofrisks for consumers' health.

Bromate can arise as a by-product of the ozonation of bromide-containing water depending on the conditions (pH, temperature, duration) prevalent at the treatment site. On account of the swift disinfection result that it provides, ozonation is still a method preferentially used in the treatment of water. It is also recognized that by the disinfection of drinking water by sodium hypochlorite, bromate can be found because there are trace impurities of the sodium hypochlorite solutions. If bromate is a possible by-product of the treatment, the process manager should frequently monitor the bromate content.

The bromate concentration in drinking water can be determined, for example, by means of ion chromatography in conjunction with conductivity measurement and suppressions technique. This method is described inter alia in ISO 15061:2001[3], which is also a constituent part of the "German standard method for water, wastewater, and sludge investigation". Furthermore, the measurement may be made using LC/ICP-MS. As these methods require access to lab infrastructure and investment into and training for complex instrumentation, we provide photometry as alternative for on-site analysis in this application note[4].

MilliporeSigma is the U.S. and Canada Life Science business of Merck KGaA, Darmstadt, Germany.

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2.0 Method

This application note describes the determination of bromate in drinking water using 3,3′-dimethylnaphthidine as a sensing dye in photometry.

Bromate oxidizes iodide to iodine in the acidic media provided. This iodine reacts with 3,3′-dimethylnaphthidine to form a pink product which can be determined photometrically.

The methods are preprogrammed on the corresponding Spectroquant® Prove photometers. To eliminate impact of quality changes in the reagents you use, it is strongly recommended to perform regular AQA checks with appropriate reference standards. Please check the Spectroquant® offering of ready-to-use bromate solutions for AQA purposes.

There are two methods available. The Ultra-Low Range (ULR) method requires an additional evaporation step, which may increase the sensitivity by one order of magnitude, but also requires additional handling steps which are also a possible source of additional imprecision.

To make a good choice for your bromate determination, please:

- Select the right method based on your requirements (accuracy, available instrumentation and lab infrastructure) from the overview in **chapter 2.1.**
- Check, if your matrix allows for robust determination, e.g., if the given content of interfering substances is below the threshold for your method provided in **chapter 9.**
- Check, if your analytical process allows for a temperature control within the maximum variation you are willing to accept. Information on impact of temperature changes is provided in **chapter 10.**

2.1 Measuring range

Measuring range [µg/L BrO_3^-]	95% Confidence interval [µg/L BrO_3^-]	Cells size (rectangular)	Evaporation step required	Available for Prove instrument	Name of the application	Procedure in chapter
0.5 – 20.0	± 0.5	100 mm	Yes	600	Bromate ULR (Method number 307)	5
1.0 – 40.0	± 1.0	50 mm	Yes	100/300/600	Bromate ULR (Method number 307)	6
2.5 – 100.0	± 2.5	100 mm	No	600	Bromate LR (Method number 308)	7
5.0 – 200.0	± 5.0	50 mm	No	100/300/600	Bromate LR (Method number 308)	8

2.2 Sample material

Drinking and mineral water, demineralized water, purified water (reverse osmosis)
Before analysis, please check for possible interferences (see **chapter 9** “Influences of foreign substances”).

3.0 Reagents, Instruments and Materials

3.1 Reagents

Cat. No.	Description
1.03122	3,3′-Dimethylnaphthidine
1.00063	Acetic acid 100% for analysis
1.00983	Ethanol abs. for analysis
1.05043	Potassium iodide for analysis
1.00519	Perchloric acid 70–72% for analysis
1.16754	Water for analysis
Optional:	
Analytical quality assurance or user-defined calibration:	
1.33006	Bromate Standard Solution, CRM, 0.0100 mg/L BrO_3^-
1.33007	Bromate Standard Solution, CRM, 0.1000 mg/L BrO_3^-
1.04912	Potassium bromate for analysis ACS, ISO, Reag, Ph Eur 99.8%
1.09925	Potassium bromate solution for 1000 mL; c(KBrO3) = 1/60 mol/l (0.1 N) Titrisol®
Cleaning of the glassware:	
1.00316	Hydrochloric acid 25% for analysis EMSURE®
1.09634	2-Propanol for analysis EMSURE®

3.2 Instruments

For the bromate measurement one of the following Spectroquant® photometers is necessary:

Cat. No.	Description
173018	Spectroquant® UV/VIS Spectrophotometer Prove 600
173017	Spectroquant® UV/VIS Spectrophotometer Prove 300
173016	Spectroquant® VIS Spectrophotometer Prove 100

Software for data maintenance: The Spectroquant® Prove Connect to LIMS software package provides an easy way to transfer your data into a preexisting LIMS system. This software can be purchased under:

Cat. No.	Description
Y.11086	Prove Connect to LIMS

3.3 Material

Cat. No.	Description
1.74011	Rectangular cell 100 mm or
1.14944	Rectangular cells 50 mm
SLAP02550	Syringe filter glass fiber
SLLGM25	Syringe filter 0.20 µm
1.14901	Flat-bottomed long tubes with screw caps (for measurements in 100 mm cells) or
1.14724	Empty cells with screw caps 16 mm (for measurements in 50 mm cells)

- Standard laboratory glass equipment (e. g. glass beakers, 400 mL tall beaker, 25-ml volumetric flask, Erlenmeyer flasks, graduated cylinders)
- Pipettes with high accuracy e.g. piston-stroke pipettes
- Heating plate and boiling granules or
- Magnetic stirrer with heating and stirring rods
- Optional, if sample solution is not clear after evaporation

Cat. No.	Description
SLCR033	Millex-LCR Syringe Filter, Hydrophilic PTFE, Non-sterile or Fluted filter (radius max. 4 cm)

3.4 Preparing the reagents

Pre-treatment of vessels and glassware

Used **vessels and glassware must be clean and free from surfactant residues** or similar substances. Pre-treat the vessels and glassware with a mixture of isopropyl alcohol and hydrochloric acid, if necessary. Subsequently, rinse thoroughly with distilled water.

Prepare the isopropyl alcohol/hydrochloric acid mixture by placing 3 parts isopropyl alcohol in a glass beaker and slowly adding 1 part of hydrochloric acid 25%. Follow the respective safety regulations!

Preparation of an acetic acid/ethanol mixture [1 + 1]:

In a graduated cylinder, measure 25 mL acetic acid 100% and transfer to a 50-ml Erlenmeyer flask with glass stopper. Subsequently, measure 25 mL ethanol abs. in a graduated cylinder, add to the acetic acid, close with the glass stopper and mix thoroughly.

Reagent 1: Dissolve 1.0 g of potassium iodide for analysis in 100 mL water for analysis. The solution is stable for about one year protected from light in a tightly closed container at room temperature.

Reagent 2: In a closed vessel (e.g. 16 mm cells with screw cap) stir 0.025 g 3,3'-dimethylnaphthidine in 5.00 mL of the acetic acid-ethanol mixture [1 + 1] at room temperature (20–25 °C) for 30 minutes (e.g. magnetic stirrer). Should the solution be cloudy or show a bottom sediment it must be filtered with a glass fiber syringe filter **(Cat. No. SLAP02550*)**.

Reagent 2 is stable for 4 weeks, if stored protected from light in closed containers.

* The above-mentioned filter has been checked for interferences. If another filter is used, interferences can occur. Avoid using filters on cellulose acetate basis.

4.0 Important Notes

- All used **vessels and glassware must be clean and free from surfactant residues** or similar substances. Pre-treat the vessels and glassware with a mixture of isopropyl alcohol and hydrochloric acid, if necessary. Subsequently, rinse thoroughly with distilled water.

  Prepare the isopropyl alcohol/hydrochloric acid mixture by placing 3 parts isopropyl alcohol in a glass beaker and slowly adding 1 part of hydrochloric acid 25%. Follow the respective safety regulations!
- Due to the very sensitive measurement, it is important to **work with accurate pipettes** throughout the whole analysis.
- The method is strongly affected by temperature. We recommend **tempering the reagents and sample at 25 °C** before preparing the measurement solution and during the reaction time. For details see **chapter 10**).
- Due to the low bromate concentration, which is accepted as the limit for drinking water (according to WHO and EU Directive 10 µg/L), we recommend **checking the recovery rate of the method** by means of a bromate standard, especially if **new batches of 3,3'-Dimethylnaphthidine or new preparations of Reagent 2 were used**. In case of significant deviations please recalibrate the method.

Instruction for the recalibration can be found in chapter 12 "User-defined calibration".

5.0 Bromate ULR 0.5 – 20.0 µg/L (Prove 600 only)

5.1 Sample preparation

- **Place 250 mL of sample solution** into a 400-mL glass beaker.
- **Add either boiling granules or a stirring bar**.
- Place the glass beaker on the heating plate. If a magnetic stirrer with heating function and a stirring bar is used, start stirring.
- **Evaporate the sample solution** slowly on a hot plate until almost dry (ca. 2–5 mL). **Avoid an evaporation until complete dryness**, otherwise bromate will be decomposed.
- **Transfer the residue** into a 25 mL volumetric flask, **rinse the beaker** a few times with a small amount of water for analysis to quantitatively transfer the remaining solution into the beaker and make up to the mark with water for analysis.
- The solution must be clear. If necessary, **filter** through a small-fluted filter first and subsequently through a 0.20 µm syringe filter (Cat. No. **SLLGM25**). Pay attention, that you only use small-fluted filters (radius e.g. 4 cm) otherwise the sample volume for the determination with the 100 mm cell will not be enough. Alternatively, you can use a syringe filter 0.45 µm (Cat. No. **SLCR033**) instead of a fluted filter.

5.2 Preparing the measurement solutions

The reagent blank and the measuring sample can be prepared at the same time. See the following table for preparation details.

	Measuring sample	Reagent blank	
Pre-treated sample	20.0 mL	-	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Water for analysis	-	20.0 mL	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Reagent 1	0.20 mL	0.20 mL	**Add with a piston-stroke pipette** and mix.
Reagent 2	0.40 mL	0.40 mL	**Add with a piston-stroke pipette** and mix (the solution becomes milky).
Perchloric acid 70–72%	0.40 mL	0.40 mL	**Add with a piston-stroke pipette** and mix.

- **Leave to stand for 30 minutes at room temperature.**
- **Filter** all test samples through a 0.20 µm syringe filter, Cat. No. **SLLGM25**, prior to measurement
- Fill the measurement solutions into a 100 mm rectangular cell. Measure the preparation with water as reagent blank.
  The color of the measurement solution remains stable for about 15 min. (After 15 min the measurement value would have diminished by 3%, after 30 min by more than 7%.)

5.3 Measurement

- Open the method list (<Methods>) and select method No. 307 “Bromate ULR”.
- It is recommended to zero the method each new working day. To do this, open the method, tap the <Settings> button and select the <ZERO ADJUSTMENT> menu item. Follow the instructions shown on the display to proceed.
- Subsequently perform the reagent blank. Therefor tap the <Settings> button and select the <REAGENT BLANK> menu item. Fill the corresponding cell (100 mm) with the reagent blank and insert the cell into the cell compartment. The measurement is performed automatically. Accept the reagent blank by activating the <User RB> field and confirm with <OK>.
- After the reagent blank has been measured, fill the measurement sample into the same or a matched corresponding cell and insert the cell into the cell compartment. The measurement starts automatically.
- Read off the result in µg/L from the display.

6.0 Bromate ULR 1.0 – 40.0 µg/L

6.1 Sample preparation

- **Place 250 mL of sample solution** into a 400 mL glass beaker.
- **Add either boiling granules or a stirring bar**.
- Place the glass beaker on the heating plate. If a magnetic stirrer with heating function and a stirring bar is used, start stirring.
- **Evaporate the sample solution** slowly on a hot plate until almost dry (ca. 2–5 mL). Avoid an evaporation until complete dryness, otherwise bromate will be decomposed.
- **Transfer the residue** into a 25-mL volumetric flask, **rinse the beaker** a few times with a small amount of water for analysis to quantitatively transfer the remaining solution into the beaker and make up to the mark with water for analysis.
- The solution must be clear. If necessary, **filter** through a small-fluted filter first and subsequently through a 0.20 µm syringe filter (Cat. No. **SLLGM25**). Alternatively, you can use a syringe filter 0.45 µm (Cat. No. **SLCR033**) instead of a fluted filter.

6.2 Preparing the measurement solutions

The reagent blank and the measuring sample can be prepared at the same time. See the following table for preparation details.

	Measuring sample	Reagent blank	
Pre-treated sample	10.0 mL	-	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Water for analysis	-	10.0 mL	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Reagent 1	0.10 mL	0.10 mL	**Add with a piston-stroke pipette** and mix.
Reagent 2	0.20 mL	0.20 mL	**Add with a piston-stroke pipette** and mix (the solution becomes milky).
Perchloric acid 70–72%	0.20 mL	0.20 mL	**Add with a piston-stroke pipette** and mix.

- **Leave to stand for 30 minutes** at room temperature.
- **Filter** all test samples through a 0.20 µm syringe filter, Cat. No. **SLLGM25**, prior to measurement.
- Fill the measurement solutions into a 50 mm rectangular cell. Measure the preparation with water as reagent blank.
  The color of the measurement solution remains stable for about 15 min. (After 15 min the measurement value would have diminished by 3%, after 30 min by more than 7%.)

6.3 Measurement

- Open the method list (<Methods>) and select method No. 307 “Bromate ULR”.
- It is recommended to zero the method each new working day. To do this, open the method, tap the <Settings> button and select the <ZERO ADJUSTMENT> menu item. Follow the instructions shown on the display to proceed.
- Subsequently perform the reagent blank. Therefor tap the <Settings> button and select the <REAGENT BLANK> menu item. Fill the corresponding cell (50 mm) with the reagent blank and insert the cell into the cell compartment. The measurement is performed automatically. Accept the reagent blank by activating the <User RB> field and confirm with <OK>.
- After the reagent blank has been measured fill the measurement sample into the same or a matched corresponding cell and insert the cell into the cell compartment. The measurement starts automatically.
- Read off the result in µg/L from the display.

7.0 Bromate LR 2.5 – 100.0 µg/L (Prove 600 only)

7.1 Preparing the measurement solutions

The reagent blank and the measuring sample can be prepared at the same time. See the following table for preparation details.

	Measuring sample	Reagent blank	
Pre-treated sample	20.0 mL	-	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Water for analysis	-	20.0 mL	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Reagent 1	0.20 mL	0.20 mL	**Add with a piston-stroke pipette** and mix.
Reagent 2	0.40 mL	0.40 mL	**Add with a piston-stroke pipette** and mix (the solution becomes milky).
Perchloric acid 70–72%	0.40 mL	0.40 mL	**Add with a piston-stroke pipette** and mix.

- **Leave to stand for 30 minutes** at room temperature.
- **Filter** all test samples through a 0.20 µm syringe filter, Cat. No. **SLLGM25**, prior to measurement
- Fill the measurement solutions into a 100 mm rectangular cell. Measure the preparation with water as reagent blank.
  The color of the measurement solution remains stable for about 15 min. (After 15 min the measurement value would have diminished by 3%, after 30 min by more than 7%.)

7.2 Measurement

- Open the method list (<Methods>) and select method No. 308 “Bromate LR”.
- It is recommended to zero the method each new working day. To do this, open the method, tap the <Settings> button and select the <ZERO ADJUSTMENT> menu item. Follow the instructions shown on the display to proceed.
- Subsequently perform the reagent blank. Therefor tap the <Settings> button and select the <REAGENT BLANK> menu item. Fill the corresponding cell (100 mm) with the reagent blank and insert the cell into the cell compartment. The measurement is performed automatically. Accept the reagent blank by activating the <User RB> field and confirm with <OK>.
- After the reagent blank has been measured fill the measurement sample into the same or a matched corresponding cell and insert the cell into the cell compartment. The measurement starts automatically.
- Read off the result in µg/L from the display.

8.0 Bromate LR 5.0 – 200.0 µg/L

8.1 Preparing the measurement solutions

The reagent blank and the measuring sample can be prepared at the same time. See the following table for preparation details.

	Measuring sample	Reagent blank	
Pre-treated sample	10.0 mL	-	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Water for analysis	-	10.0 mL	**Pipette** into a flat-bottomed long tube with screw caps or glass beakers.
Reagent 1	0.10 mL	0.10 mL	**Add with a piston-stroke pipette** and mix.
Reagent 2	0.20 mL	0.20 mL	**Add with a piston-stroke pipette** and mix (the solution becomes milky).
Perchloric acid 70–72%	0.20 mL	0.20 mL	**Add with a piston-stroke pipette** and mix.

- **Leave to stand for 30 minutes** at room temperature.
- **Filter** all test samples through a 0.20 µm syringe filter, Cat. No. **SLLGM25**, prior to measurement
  Fill the measurement solutions into a 50 mm rectangular cell. Measure the preparation with water as reagent blank.
  The color of the measurement solution remains stable for about 15 min. (After 15 min the measurement value would have diminished by 3%, after 30 min by more than 7%.)

8.2 Measurement

- Open the method list (<Methods>) and select method No. 308 “Bromate LR”.
- It is recommended to zero the method each new working day. To do this, open the method, tap the <Settings> button and select the <ZERO ADJUSTMENT> menu item. Follow the instructions shown on the display to proceed.
- Subsequently perform the reagent blank. Therefor tap the <Settings> button and select the <REAGENT BLANK> menu item. Fill the corresponding cell (50 mm) with the reagent blank and insert the cell into the cell compartment. The measurement is performed automatically. Accept the reagent blank by activating the <User RB> field and confirm with <OK>.
- After the reagent blank has been measured fill the measurement sample into the same or a matched corresponding cell and insert the cell into the cell compartment. The measurement starts automatically.
- Read off the result in µg/L from the display.

9.0 Influences of Foreign Substances

This was checked individually in solutions containing 0 and 20 (ULR) resp. 100 (LR) µg/L Bromate, synergy effects of mixtures of those substances, that may occur with your sample, cannot be reflected here. In case of doubt, please perform a method validation with your sample and an appropriate reference analytics (eg. ion chromatography). Above the given concentrations of the pure substances, the analysis will be impacted in the given manner (too high or too low readings). Cumulative effects were not checked; such effects can, however, not be excluded.

It is known that **substances that take part in a redox reaction, will interfere the analysis**. Please pay attention, if you know that at least one redox substance is contained in your sample and verify your results with a reference analysis.

Surfactants do interfere strongly with the analysis. These may be subjected to your sample by your matrix, but also by insufficient rinsing after cleaning. Please make sure, that all **glassware that you use is free of surfactants**, e. g. by extensive and comprehensive rinsing with ultrapure water.

Table 1. Influence of foreign substance on method

Parameter	Tolerance without interference [mg/L]		Impact of interference
	ULR	LR	
Br^-	25	250	lower readings
Ca^{2+}	100	1000	lower readings
Cl^-	100	1000	lower readings
Cl_2 (free)	0.1	0.05	higher readings
Cl_2 (total)	0.02	0.02	higher readings
ClO_3^-	10	50	higher readings
F^-	100	250	higher readings
Fe^{3+}	0.2	0.2	higher readings
HCO_3^-	100	500	higher readings
H_2O_2	0	0.05	higher readings
I^-	0.5	5	lower readings
IO_3^-	0.001	0.01	higher readings
Mg^{2+}	50	500	lower readings
Mn^{2+}	5	1000	higher readings
Na^+	100	1000	lower readings
NO_2^-	0.01	0.1	higher readings
OCl^-	0.02	0.05	higher readings
SO_4^{2-}	20	250	lower readings
Surfactants, anionic	0.1	5	lower readings
Surfactants, cationic	2.5	500	higher readings
Surfactants, non-ionic	10	100	lower readings
pH	pH 3-10	pH 2-13	< limit lower readings > limit higher readings

10.0 Influence of Temperature

The method is strongly affected by **temperature. We recommend tempering the reagents and sample at 25 °C** bevor preparing the measurement solution and during the whole reaction time.

The temperature influence is shown in **Figure 1**. **Figure 1** shows a comparison of measurement results of the ULR method in a 100 mm rectangular cell for bromate standard solutions with concentrations of 5, 10 and 20 µg/L and incubation at 20, 25, 30 and 35 °C.

Higher temperature leads to higher results, lower temperature leads to lower results (± 5 K = ±25% deviation)!

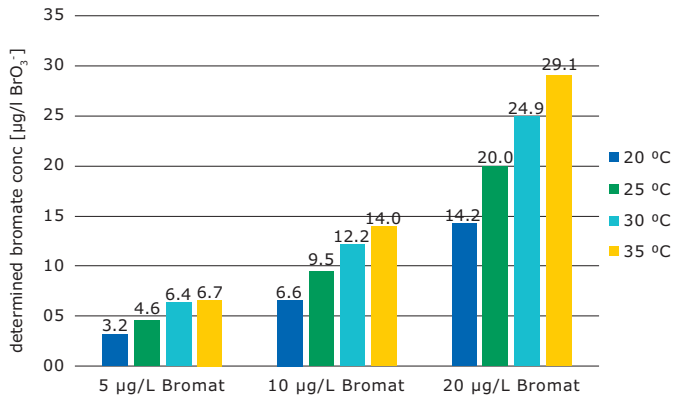

Figure 1: Influences of temperature on method

11.0 Analytical Quality Assurance

The objective of analytical quality assurance (AQA) is to secure correct and precise measurement results.

AQA is recommended before each measurement series. To check the measurement system (test reagents, measurement device, and handling) use the ready-to-use, prediluted CRM bromate standard solution, with the concentrations 0.0100 and 0.1000 mg/L.

In case of deviations, it is recommended to recalibrate the method according to **chapter 12**.

Sample-dependent interferences (matrix effects) can be determined by means of standard addition.

For details on how to perform the AQA check see the instrument-specific manuals.

Moreover, it is recommended to determine the performance characteristic yourself so that all specific factors that may impact the performance (test reagents, measurement device, handling) are considered in the characteristic data.

12.0 User-Defined Calibration

A calibration for this method is preprogrammed in the photometer. It is recommended to check the calibration before the first use of the method as the calibration curve may, however, be influenced by the batch of reagents especially for 3,3'-Dimethylnaphthidine.

In general, to enhance the accuracy of the measurement, it is advisable to perform a "User-defined Calibration" when exchanging batches of the reagents used.

Option 1: Preparation of a 10 mg/L Bromate standard stock solution from Potassium bromate (salt):

Prepare the stock solution out of Potassium bromate for analysis ACS, ISO, Reag, Ph Eur 99.8% (Cat. No. **1.04912**) in the following manner:

Dissolve 1.306 g of $KBrO_3$ (Potassium bromate) with water for analysis in a calibrated or conformity-checked 1000-ml volumetric flask and make up to the mark with water for analysis. The standard solution prepared according to this procedure has a concentration of 1000 mg/L BrO_3^-.

For the preparation of a 10 mg/L BrO_3^- standard solution, place 10.00 mL of the 1000 mg/L BrO_3^- standard solution into a calibrated or conformity-checked 1000-ml volumetric flask and make up to the mark with water for analysis.

Option 2: Preparation of a 10 mg/L Bromate standard stock solution from Potassium bromate solution Titrisol®:

Place the content of the ampoule (Cat. No. **1.09925** Potassium bromate solution for 1000 mL; c($KBrO_3$) = 1/60 mol/l (0.1 N) Titrisol®) into a calibrated or conformity-checked 1000-ml volumetric flask and make up to the mark with water for analysis.

The concentration of this dilution solution is 2.78 g/l $KBrO_3$ or 2.13 g/l BrO_3^-.

For the preparation of a 10 mg/L BrO_3^- standard solution, place 4.70 mL of the prepared solution into a calibrated or conformity-checked 1000-ml volumetric flask and make up to the mark with water for analysis.

12.1 User-defined calibration of the Bromate ULR method

The pre-programmed calibration function of the ULR method is based on measurements with a 50 mm rectangular cell. Therefore, we recommend using the 50 mm rectangular cell also for the user-defined calibration of the ULR method. The Spectroquant® Prove instrument automatically recognizes the used cell size during the measurement and recalculates the concentration accordingly.

Prepare standard solutions in the following manner:

	Standard solution					
	E0	**1**	**2**	**3**	**4**	**5**
	[0.00 µg/L BrO_3^-]	**[5.00 µg/L BrO_3^-]**	**[10.00 µg/L BrO_3^-]**	**[20.00 µg/L BrO_3^-]**	**[30.00 µg/L BrO_3^-]**	**[40.00 µg/L BrO_3^-]**
Bromate standard stock solution 10 mg/L BrO_3^-	0.0 mL	0.500 mL	1.000 mL	2.000 mL	3.000 mL	4.000 mL
Pipette into separate 1000-ml volumetric flasks and make up to 1000 mL with H_2O.						

Sample preparation step

- **Place 250 mL of prepared standard solution** into a 400 mL glass beaker.
- **Add either boiling granules or a stirring bar**.
- Place the glass beaker on the heating plate. If a magnetic stirrer with heating function and a stirring bar is used, start stirring.
- **Evaporate the sample solution** slowly on a hot plate until almost dry (ca. 2–5 mL). Avoid an evaporation until complete dryness, otherwise bromate will be decomposed.
- **Transfer the residue** into a 25 mL volumetric flask, **rinse the beaker** a few times with a small amount of water for analysis to quantitatively transfer the remaining solution into the beaker and make up to the mark with water for analysis.
- The solution must be clear. If necessary, **filter** through a small fluted filter first and subsequently through a 0.20 µm syringe filter (Cat. No. **SLLGM25**). Alternatively, you can use a syringe filter 0.45 µm (Cat. No. **SLCR033**) instead of a fluted filter.

Note: It is possible to perform the user-defined calibration for the "Bromate ULR method" without the sample preparation step (evaporation). In these cases, it is necessary to use standard solutions with 10fold higher concentrations to compensate the concentration step during the sample preparation step (evaporation).

Preparing the calibration solutions:

	Calibration solution					
	E0	**1**	**2**	**3**	**4**	**5**
	[0.00 µg/L BrO_3^-]	**[5.00 µg/L BrO_3^-]**	**[10.00 µg/L BrO_3^-]**	**[20.00 µg/L BrO_3^-]**	**[30.00 µg/L BrO_3^-]**	**[40.00 µg/L BrO_3^-]**
Each standard solution (E0 - 5)	10.0 mL	10.0 mL	10.0 mL	10.0 mL	10.0 mL	10.0 mL
Pipette into a flat-bottomed long tube with screw caps or glass beakers.						
Reagent 1	0.10 mL	0.10 mL	0.10 mL	0.10 mL	0.10 mL	0.10 mL
Add with a piston-stroke pipette to each tube and mix.						
Reagent 2	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL
Add with a piston-stroke pipette to each tube and mix. (the solution becomes milky).						
Perchloric acid 70–72%	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL
Add with a piston-stroke pipette to each tube and mix.						

- **Leave to stand for 30 minutes** at room temperature.
- **Filter** all test samples through a 0.20 µm syringe filter, Cat. No. **SLLGM25**, prior to measurement.
- Fill the measurement solutions into a 50 mm rectangular cell. Measure the preparation with water as reagent blank. The color of the measurement solution remains stable for about 15 min. (After 15 min the measurement value would have diminished by 3%, after 30 min by more than 7%.)

Perform the recalibration

- Open the method list (<Methods>) and select method No. 307 “Bromate ULR”.
- Select the setting menu by tapping the **<Settings>** button and selecting the **<RECALIBRATION>** menu item. An input mask pops up.
- Tap on **<+>** in the numerical keyboard to create an additional input line.
- Select the **"Absorbance"** field in the **"E0"** line (selected fields are shown in a blue frame).
- Fill calibration solution E0 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"1"** line and enter the concentration of **5.00 µg/L** for the first calibration solution.
- Select the **"Absorbance"** field in the **"1"** line. Fill calibration solution 1 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"2"** line and enter the concentration of **10.00 µg/L** for the third calibration solution.
- Select the **"Absorbance"** field in the **"2"** line. Fill calibration solution 2 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"3"** line and enter the concentration of **20.00 µg/L** for the fourth calibration solution.
- Select the **"Absorbance"** field in the **"3"** line. Fill calibration solution 3 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"4"** line and enter the concentration of **30.00 µg/L** for the fifth calibration solution.
- Select the **"Absorbance"** field in the **"4"** line. Fill calibration solution 4 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the "**5**" line and enter the concentration of **40.00 µg/L** for the fifth calibration solution.
- Select the **"Absorbance"** field in the **"5"** line. Fill calibration solution 5 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Activate the **<U-CAL on>** field and the **<linear>** field.
- Optionally enter a batch number for the calibration, selecting the **<Lot number>** field to do so.
- Once all calibration solutions have been measured, save the calibration by pressing **<OK>**

Note: For additional details on how to perform the recalibration of methods please refer to the instrument manual **chapter 9.7.10** User Recalibration (Standard Adjustment) Calibration for Spectroquant® methods.

12.2 User-defined calibration of the Bromate LR method

The pre-programmed calibration function of the LR method is based on measurements with a 50 mm rectangular cell. Therefore, we recommend using the 50 mm rectangular cell also for the user-defined calibration of the LR method. The use of 50 mm rectangular cells for a user-defined calibration has no effects on measurements of sample materials with a 100 mm rectangular cell. The instruments automatically recognize the used cell size during the measurement and recalculates the concentration accordingly.

Prepare standard solutions in the following manner:

	Standard solution					
	E0	**1**	**2**	**3**	**4**	**5**
	[0.00 µg/L BrO_3^-]	**[20.0 µg/L BrO_3^-]**	**[50.0 µg/L BrO_3^-]**	**[100.0 µg/L BrO_3^-]**	**[150.0 µg/L BrO_3^-]**	**[200.0 µg/L BrO_3^-]**
Bromate standard solution 10 mg/L BrO_3^-	0.0 mL	2.000 mL	5.000 mL	10.00 mL	15.00 mL	20.00 mL
Pipette into separate 1000-ml volumetric flasks and make up to 1000 mL with H_2O.						

Preparing the calibration solutions:

	Calibration solution					
	E0	**1**	**2**	**3**	**4**	**5**
	[0.00 µg/L BrO_3^-]	**[20.0 µg/L BrO_3^-]**	**[50.0 µg/L BrO_3^-]**	**[100.0 µg/L BrO_3^-]**	**[150.0 µg/L BrO_3^-]**	**[200.0 µg/L BrO_3^-]**
Each standard solution (E0 – 5)	10.0 mL	10.0 mL	10.0 mL	10.0 mL	10.0 mL	10.0 mL
	Pipette into a flat-bottomed long tube with screw caps or glass beakers.					
Reagent 1	0.10 mL	0.10 mL	0.10 mL	0.10 mL	0.10 mL	0.10 mL
	Add with a piston-stroke pipette to each tube and mix.					
Reagent 2	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL
	Add with a piston-stroke pipette to each tube and mix. (the solution becomes milky).					
Perchloric acid 70–72%	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL	0.20 mL
	Add with a piston-stroke pipette to each tube and mix.					

- **Leave to stand for 30 minutes** at room temperature.
- **Filter** all test samples through a 0.20 µm syringe filter, Cat. No. SLLGM25NS, prior to measurement
- Fill the measurement solutions into a 50 mm rectangular cell. Measure the preparation with water as reagent blank.
  The color of the measurement solution remains stable for about 15 min. (After 15 min the measurement value would have diminished by 3%, after 30 min by more than 7%.)

Perform the recalibration

- Open the method list (<Methods>) and select method No. 308 “Bromate LR”.
- Select the setting menu by tapping the **<Settings>** button and selecting the **<RECALIBRATION>** menu item. An input mask pops up. Tap on <+> in the numerical keyboard to create an additional input line.
- Select the **"Absorbance"** field in the **"E0"** line (selected fields are shown in a blue frame).
- Fill calibration solution E0 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"1"** line and enter the concentration of **20.00 µg/L** for the first calibration solution.
- Select the **"Absorbance"** field in the **"1"** line. Fill calibration solution 1 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"2"** line and enter the concentration of **50.00 µg/L** for the third calibration solution.
- Select the **"Absorbance"** field in the **"2"** line. Fill calibration solution 2 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the **"3"** line and enter the concentration of **100.00 µg/L** for the fourth calibration solution.
- Select the "**Absorbance**" field in the **"3"** line. Fill calibration solution 3 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the "**Conc.**" field in the **"4"** line and enter the concentration of **150.00 µg/L** for the fifth calibration solution.
- Select the **"Absorbance"** field in the **"4"** line. Fill calibration solution 4 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Select the **"Conc."** field in the "**5**" line and enter the concentration of **200.00 µg/L** for the fifth calibration solution.
- Select the **"Absorbance"** field in the **"5"** line. Fill calibration solution 5 into a 50 mm rectangular cell and insert cell into the cell compartment. The measurement starts automatically. The measured absorbance is shown in the display.
- Activate the **<U-CAL on>** field and the **<linear>** field. Optionally enter a batch number for the calibration, selecting the **<Lot number>** field to do so. Once all calibration solutions have been measured, save the calibration by pressing **<OK>**

Note: For additional details on how to perform the recalibration of methods please refer to the instrument manual **chapter 9.7.10** User Recalibration (Standard Adjustment) → Calibration for Spectroquant® methods.

13.0 Conclusion

The determination of the bromate content of water is a challenge that can be met either by using an elaborate ion-chromatography system or a photometric method. Both approaches demand careful handling and a critical appraisal of the result that is yielded. If the necessary working steps are carefully followed, photometry constitutes a true alternative to chromatography for those laboratories that do not possess ion-chromatography systems.[4]

14.0 For More Information

Spectroquant® test kits and spectrophotometers see
SigmaAldrich.com/photometry

Further Application Notes see
SigmaAldrich.com/wfa-applications

References

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2. "Guidelines for drinking-water quality: fourth edition incorporating the first addendum", WHO Library Cataloguing-in-Publication Data, ISBN 978-92-4-154995-0, [accessed 02.11.2020] https://www.who.int/publications/i/item/9789241549950
3. ISO 15061:2001-07, Water quality - Determination of dissolved bromate - Method by liquid chromatography of ions, 2001. www.iso.org/standard/25863.html

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