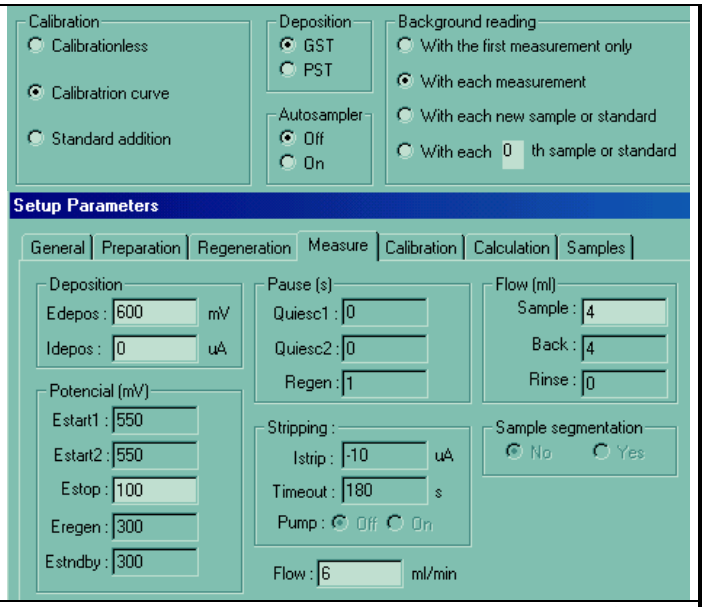
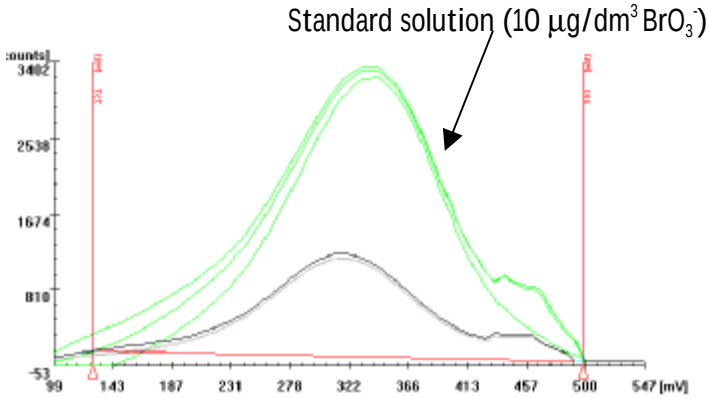
Application list No.	38
Title	Determination of bromates in water samples
Types of samples	All kinds of disinfected water samples
Principle	The bromate anions in the stabilised water sample are reduced to bromine with an acidified bromide solution: $BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ The formed bromine is then determined by in-electrode coulometric titration through its electrochemical reduction to bromide ions: $Br_2 \rightarrow 2\ Br^- - 2\ e^-$ During this step the chronopotentiometric signal is recorded and evaluated. Possible interfering species are removed by boiling and addition of Fe(II) ions.
Reagents	§ HCl, p.a., conc. § $FeSO_4.7\ H_2O$, p.a. § Certified reference material for bromate, e.g. dried $KBrO_3$ or $NaBrO_3$
Solutions	§ R-013 *Carrier electrolyte, 0,1 mol/*dm^3 HCl § R-025 *Ethylenediammine (EDA) in water, 100 mg/*cm^3 *)* § R-026 *(*Fe^{2+}*solution: 0.5 g* $FeSO_4.7\ H_2O$ *dissolved in 100 ml 0.3 mol/*dm^3 H_2SO_4*)* § R-027 *(KBr solution)* § Bromate standard solution in water (50 mg/dm^3 BrO_3^-)
Standard solutions for the calibration curve	The calibration solutions are prepared from the bromate standard solution (see above) in water containing 50 mg/dm^3 EDA:: Standard No. 1: 5 µg/dm^3 BrO_3^- Standard No. 2: 10 µg/dm^3 BrO_3^- Standard No. 3: 20 µg/dm^3 BrO_3^- *Note: If appropriate, adjust the composition of the standard solutions to the sample !* The shelf life of the calibration solutions is one day. The calibration solutions are treated in the same way as the samples – see the sample preparation procedure.
Sampling and sample preservation	*U.S. EPA Method 300.1:* 1. The water samples are sampled into amber glass flasks. 2. Add ethylenediammine (*R-025*) so that the final concentration is 50 mg/dm^3. The samples can be stored at or below 6 °C but not longer than 28 days.
Sample preparation	1. Boil samples containing disinfection byproducts such as chlorine, hypochloride, chlorammines, ozone, chlorine dioxide, chlorates, as well as carbon dioxide for 5 min and let it cool to laboratory temperature. 2. To a dry 100 ml volumetric flask add 0.5 ml of *Fe(II) solution (R-026)* (1.0 ml for samples with HCO_3^{2-} contents over 500 mg/l) 3. Adjust the volume to 100 ml with the sample (*or with the calibration solution in the case of a calibration*) and on mixing let the solution stay for 2 to 10 min. Important: the pH must lay in the range of 5 - 6 ! (In the case of the calibration solutions it may be pH 3 to 6) 4. Add 2 ml of *concentrated HCl* and mix the solution: Solution A 5. To a dry 50 ml volumetric flask add 0.1 ml of the *R-027* reagent and adjust the volume to 50 ml with the solution A. Mix the solution: Solution B. 6. Solution A serves as the blank for the treated sample (or standard). Solution B serves as the sample (*or standard*). These solutions are stable not longer than 30 min and therefore must be immediately analysed.
Electrode	E104 C (moist the new electrode with ethanol before setting into the cell)
Experimental parameters	Galvanostatic mode



Typical signal



Data evaluation	Calibration curve
Metrological data	*Concentration range*: 0.5 to 50 µg/dm³ BrO_3^- *Reproducibility*: 6,8 % at 5 µg/dm³ BrO_3^- in the measured solution 3,1 % at 20 µg/dm³ BrO_3^- in the measured solution
Interferences	§ High Fe(III) contents (over 10 mg/l) deteriorate the results. Use a cation exchanger to remove Fe species. § High nitrate contents (over 50 mg/dm³) interfere
Notes	§ Samples with bromate contents over 50 µg/dm³ should be diluted with water prior to analysis. § The reagent solutions should be stored in a refrigerator. § The analyses can be accelerated by enhancing the flow rate to 6 ml/min through replacing the pump tube. § If on addition of the Fe(II) reagent to the sample solution the resulting solution gains a yellowish colour, it indicates a pH value of the resulting solution over 6 and the analysis would probably be wrong. In such a case adjust the sample pH, e.g. by adding some diluted HCl, so that on adding the Fe(II) reagent the resulting solution would have a pH in the range of 5-6: the solution should be virtually colourless. § Removal of air bubbles from the system: - Immerse the sampling tube to ethanol - Start the „Preparation“ routine - Make 2-3 measurement of a standard solution, e.g. 10 µg/l BrO_3^-.