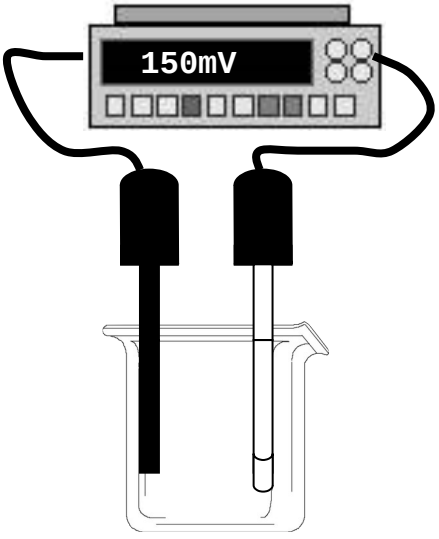
SENTEK

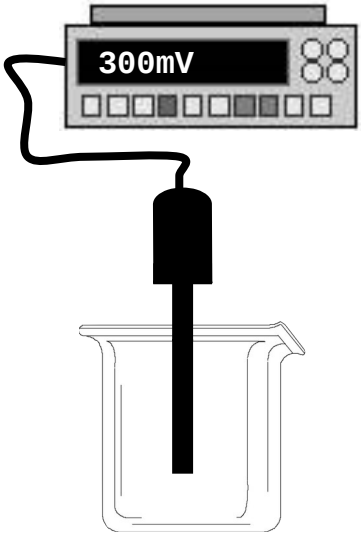
Ion Selective Electrode

OPERATING INSTRUCTIONS

BROMIDE



Mono/Reference



Combination

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Operating Instructions
Bromide Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Bromide Electrode which requires a separate Reference Electrode, and a Combination Bromide Electrode which has the Reference built into the outer shaft.

For extremely low lever work the Half Cell plus Reference Electrode should be used. For general applications the Combination is more convenient.

Depending on the type of ISE chosen you will need to disregard some information for instance if you have the Combination Electrode then disregard any comments about reference electrodes.

A quick guide is included with a more involved section following.

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Quick Guide for Bromide ISE

The Bromide combination ion selective electrode has a solid state crystalline membrane with an integral driTEK reference. The electrode is designed for the detection and analysis of Bromide ions in aqueous solutions and is suitable for use in the field, in the laboratory and in on line analysers.

Installation

Connect the ISE to the mV or ion meter.
Remove the black protective cap and keep it in a safe place.
The ISE can be used immediately but pre soaking for 5 minutes in a 100ppm Bromide solution is recommended.

The ionic strength of the standards and solutions should be kept constant between all standards and samples. This is achieved by the simple addition of an Ionic strength adjustment buffer (ISAB). Potassium Nitrate is ideal. A typical addition would be 1 ml of 1 molar ISAB to 100 ml of standard and sample.

For low level measurements below around 50ppm in relatively pure samples no ISAB is needed.

No temperature correction is necessary however standards and samples should be measured at the same temperature.

Begin calibration from the lowest concentration standard to avoid cross contamination. Calibration should cover the anticipated range of the samples.

Rinse tip with de-ionised water between measurements.

Avoid strongly acidic or alkaline samples, and organic solvents.

Storage and Maintenance

After use rinse with de-ionised water, replace protective cap and store dry in its box.

If performance becomes sluggish carefully polish the membrane with a fine emery cloth or polishing strip, rinse with de-ionised water and immerse the tip in a 100ppm Bromide solution for 10 minutes.

Avoid prolonged exposure to solutions of high concentration.

The Membrane surface should appear shiny and grey in appearance.

Specification

Bromide is a monovalent anion. A 1 molar solution of Bromide contains 79.904 grams per litre of Bromide Ions.
A 1000ppm solution is equivalent to 0.0125 moles per litre
Refer to the table below for the full specification:

Parameter	Specification
Overall length	155 mm
Body Diameter	12 mm
Cap Diameter	16mm
Connector	BNC
Cable length	1000 mm
Resistance at 25 Deg C	< 2.5 Meg Ohm
Concentration Range	0.4 to 81,000 ppm
Slope	-54 to -59 mV per decade
Potential Drift	1 mV per day
Operating pH range	1 to 12
Temperature range	5 to 50 Deg C
Endpoint time	Typically 10 to 30 seconds
ISAB	5 Molar KNO3
Interferences: Ions with coefficients above 0.001.	Iodide must be absent Sulphide must be absent Cyanide must be absent Chloride

Operating Instructions for Bromide Ion Selective Electrode

1. Introduction

1.1 Construction

The electrode consists of an inert polymer body on the end of which is mounted the sensitive membrane. All connections in the electrode are solid-state contacts, there being no liquids of any type inside the body. The high state of surface finish of the membrane is an essential feature for maximum sensitivity and performance. The low-noise shielded cable terminates in a BNC, though an alternative plug may be specified.

1.2 Operating Principles

The electrical potential of an ion selective electrode is a function of the logarithm of the activity of the ion to b measured. The relationship is given by the Nerst Equation:

$$E_{(Measured)} = E^{o} \pm \frac{RT}{zF} \ln A_{Br}$$

where

E^{o} is a constant characteristic of the electrode.
R is the Universal Gas Constant
T is the Absolute Temperature
z is the charge of the ion
F is the Faraday constant
A_{Br} is the activity of the Bromide ions

This equation can be simplified to:

$$E_m = \text{Constant} \pm S \log A_{Br}$$

where S is the slope of the calibration curve. The measured potential E_m can only be measured against a reference electrode, such as a saturated calomel electrode (SCE), placed in the same solution. Since leakage of chloride ion from the Reference Electrode will affect the chloride level

in test solutions, a salt-bridge tub filled with 1M Potassium nitrate solution must be placed between the SCE and the test solution. Alternatively a commercial double junction reference electrode can be used. Measurements are made with a high impedance millivolt or expanded scale pH meter. A meter with digital display is obviously more accurate and most convenient.
The bromide electrode can be used in solutions containing high proportion of organic solvents without ill-effect. For further discussion on the principles of ISE measurements the user is referred to the Technical Bulletin which is available on demand.

1.3 Sensitivity

The electrode will respond to uncomplexed bromide ion activity over the range 10^0 → 10^{-5}M. The linear detection limit is around 5 x 10^{-5}M. Curvature of the response is observed at lower concentrations because the solubility of the membrane material, dissolved from the membrane, contributes a small but significant amount of bromide to the solution being measured. Figure 1 shows a typical calibration plot of the electrode. Values for the slope of this plot should lie in the range 52-59mV/decade. If the total ionic strength of all solutions is maintained constant by the addition of a concentrated (approx 10^{-1}M) inert electrolyte such as Potassium NO_3 the electrode can be calibrated directly in concentration units.

Daily re-calibration is recommended for analytical use.

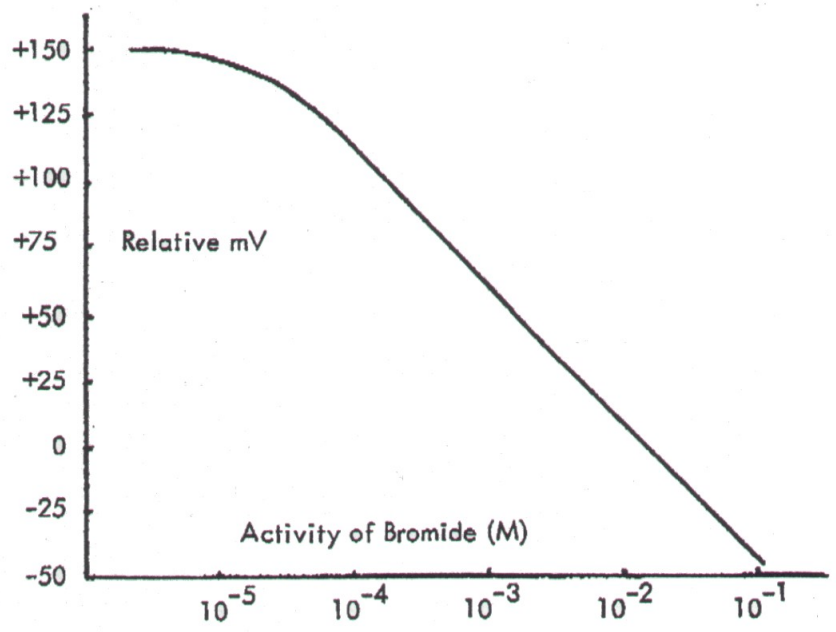

Figure 1.

The activity coefficients of bromide ion depends upon the ionic strength of the solution. The following table can be used to calculate the approximate activity coefficients at various ionic strengths.

Ionic Strength	0.001	0.005	0.01	0.05	0.1	0.2
Activity Coeff. (f)	0.975	0.946	0.926	0.853	0.808	0.755

The ionic strength of the solution to be tested can be calculated from the formula:

$$\text{Ionic Strength} = \tfrac{1}{2} \Sigma C_i Z_i^2$$

where C_i is the concentration of species i and Z_i is its charge, and all species, cations and anions must be taken into account.

Once the ionic strength is calculated and the activity coefficient found from Table 1, then the activity of the ion of interest is found from:

$$\text{Activity } (A_i) = \text{Concentration } (C_i) \times \text{Activity Coefficient (f)}$$

1.4 Stability

The long-term drift in E_o value of the bromide electrode is usually in the region of 2-4mV /day.

1.5 Selectivity

The main interference to the use of the bromide electrodes results from the presence of iodide ions. Any prolonged contact with solutions of iodide ions causes a gradual, permanent change in the membrane structure as the silver bromide is converted to the more insoluble silver iodide. Sensitivity to bromide is thus lost. If only traces of iodide are present in a test solution, the bromide electrode can sometimes be reactivated by light grinding with emery cloth followed by re-polishing to a smooth finish.

Other interferents and their stability ratios are:

OH^- = 3×10^{-5}
CL^- = 2.5×10^{-3}
$S^=$ must be less than 10^{-7}M

The electrode can be used in the pH range 2-12.

The selectivity ratios vary with interferent activity and according to the method of measurement. These figures should be used as a guide only.

1.6 Response Time

The electrode response to a step change in bromide ion activity in solution is extremely rapid, with 95% of the potential change completed in 200 msec. Equilibrium is reached in less than 2 seconds. When, however, the electrode is removed from solution and placed in another of different concentration, it may take up to 20 seconds to regain equilibrium.

The presence of interfering ions does not affect the response time, but in solutions of a very low ionic strength, i.e. with no ionic strength buffer, the response time may b extended to several minutes.

2. Operation and Handling

2.1 Initial Setting-Up

On receipt of the electrode remove it from its packaging and inspect for damage, particularly to the highly polished membrane which forms the sensing end of the electrode. Clamp the electrode with its sensing end in a solution of sodium bromide (10^{-1}M) for about two hours or until the electrode potential, when measured against a double junction SCE, remains constant. Overnight soaking is recommended. After this conditioning the electrode is ready for use.

2.2 Making a Measurement

The electrode should first be calibrated as follows. Clamp the electrode in a vertical position such that the membrane is immersed in a beaker of 10^{-1}M sodium bromide solution on a magnetic stirrer. Clamp a reference electrode (a double junction Ag/AgCl or SCE may be used) so that its end is immersed in the same solution and connect both electrodes to a pH or millivolt meter. Record the potential when it becomes steady. Change the rest solution sequentially for 10^{-2}M, 10^{-3}M and 10^{-4}M bromide solutions and plot the calibration curve, washing and drying the electrode between solutions. If an ionic-strength adjusting buffer is used, add equal volumes of 0.1M buffer to all calibrating and test solutions.

Unknown solutions can now be measured directly. For further details of methods of measurement, the user is referred to Technical Bulletin E1 available from the electrode supplier.

2.3 Storage and Maintenance

When the electrode is no longer needed, it can be merely removed from the test solution, washed and dried and be clamped in the air or returned to its packing container. There is in principle no limit to the storage time. The membrane should be protected from scratching and abrasion during storage. The only maintenance required is an occasional polish with a tissue or soft cloth to keep the membrane surface shiny.

2.4 Flow Through Configuration

A flow through version is available to enable continuous flow through measurement to be made. The reference contact can be made at any point in the solution stream joined to the flow cell by a continuous stream of liquid usually downstream of the electrode. The combination of this electrode with a sampler and pumping system can result in a versatile and low-cost continuous bromide monitor.

3. Applications and Bibliography

The chief commercial application of the bromide electrode is in the photographic industry where it is used to determine un-reacted bromide in the production of emulsions and to detect bromide in wash waters.

The cure rates of epoxies and other functional groups in the plastics industry are determined using a titration technique with the bromide electrode as an indicator.

Bromide in Natural Waters

1. H. F. Wastgestian, Z. Anal. Chem., 246 (1969) 237
2. D. Weiss, Chem. Listy, 65 (1971) 305
3. J. E. Burroughs and A. I. Attia, Anal. Chem., 40 (1968) 2052
4. R. C. Harris and H. H. Williams, J. Appl. Meteorol., 8 (1969) 299
5. J. T. Pearson and K. J. Humphreys, J. Pharm. Pharmacol., 22 (Supp) (1970) 1265

Bromide in Serum and Plasma

1. R. A. Carter, Proc. Ass. Clin. Biochem., 5 (1968) 67
2. H. J. Degenhart, et al., Clin. Chim. Acta, 38 (1972) 217

Bromide Monitoring in Chemical Reactions

1. H. Komiya, Bunsehi Kagaku, 21 (1972) 911
2. E. Koros and M. Burger, Ion Selective Electrodes Sump., 1972, p191 Ed. E. Pungar - Akad. Kiado, Budapest.

Bromide in Soft Drinks

D. L. Turner, J. Food Sci., 37 (1972) 791

Bromide in Non-Aqueous Solutions

W. H. Ficklin, W. C. Gotschall, Anal. Lett., 6 (3), (1973) 317

4. Trouble Shooting

4.1 Wildly erratic readings

i) Air bubbles trapped on outside surface of membrane

ii) Excessively violent stirring.

4.2 Steady continuous drift in one direction

i) Poor earthing of the mV meter.

ii) Excessive leakage from the reference electrode junction leading to continuous changes in the activity coefficients of ions in weaker solutions.

iii) Temperature drift if solutions are not thermostatted, or sample vessel insulated from, for example, stirrer motor.

iv) Not using double-junction reference electrode or salt bridge.

4.3 Slope of electrode much less than 50mV/decade

i) Membrane old and in need of replacing or re-polishing.

ii) Presence of an interfering ion in a constant concentration swamping the selected ions. Check performance with pure sodium bromide solutions.

4.4 Totally incomprehensible results may arise from leakage of solution into electrode via the membrane/body seal. If all fails to cure a problem please ship electrode back to supplier for exchange.