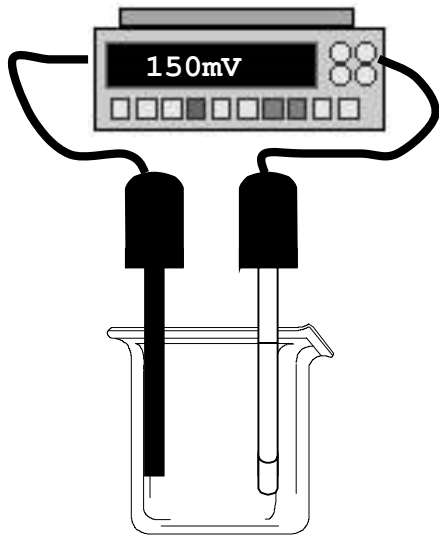
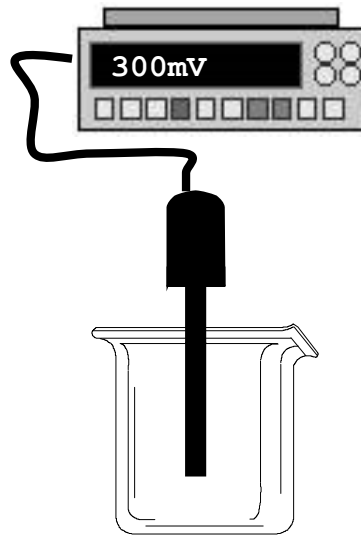


SENTEK

Ion Selective Electrode OPERATING INSTRUCTIONS



Mono/Reference



Combination

N
I
T
R
A
T
E

SENTEK

Unit 6 & 7 Crittall Court, Crittall Drive, Springwood Industrial
Estate, Braintree, Essex, CM7 2SE

Tel: +44 (0) 1376 340 456 Fax: +44 (0) 1376 340 453 Email: sentekuk@btconnect.com

Operating Instructions Nitrate Ion Selective Electrode

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

For extremely low level 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.

SENTEK

Unit 6 & 7 Crittall Court, Crittall Drive, Springwood Industrial
Estate, Braintree, Essex, CM7 2SE

Tel: + 44 (0) 1376 340 456 Fax: +44 (0) 1376 340 453 Email: sentekuk@btconnect.com

Quick Guide to Nitrate ISE

The combination ion selective electrode has a solid state PVC polymer membrane with an integral *dri*TEK reference electrode. The electrode is designed for the detection and analysis of Nitrate ions in aqueous solutions and is suitable for use in the field in the laboratory and in on line analyzers.

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 Nitrate 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). Ammonium Sulphate or Sodium Acetate 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, strong detergents and organic solvents.

Storage and Maintenance

Avoid touching the membrane surface.

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

If performance becomes sluggish, rinse with dilute detergent, rinse with de-ionised water and immerse the tip in a 1000ppm nitrate solution for 1 hour.

Specification

Nitrate is a monovalent anion. A 1 molar solution of Nitrate contains 62.005 grams per litre of Nitrate.

A 1000ppm solution is equivalent to 0.016 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 | 180 mm |
| Resistance at 25 Deg C | < 2.5 Meg Ohm |
| Concentration Range | 0.4 to 62,000 ppm |
| Slope | -54 to 659 mV per decade |
| Potential Drift | 2 mV per day |
| Operating pH range | 2 to 11 |
| Temperature range | 5 to 50 Deg C |
| Endpoint time | Typically 10 to 30 seconds |
| Interferences. Ions with coefficients above 0.001. | Chloride Bicarbonate Nitrite. |

Recommendations for successful analysis

The combination ISE ϕ can be used with any pH/mV meter or Ion meter. If the meter does not have a BNC socket and you have a BNC electrode please contact your distributor who will arrange to have the correct plug fitted. Adapters are also available if the same electrode has to be used on more than one meter.

Meters with a 0.1 mV resolution are recommended whilst dedicated Ion meters will provide direct concentration readouts saving time and effort in constructing calibration curves and performing calculations. Your distributor can advise on the most suitable meter.

Magnetic stirrer/stirrer bars are recommended for laboratory analysis. Please operate at the lowest constant speed available.

Semi-logarithmic (4-cycle) graph paper is required for preparing calibration curves when you are using a mV meter.

Required Solutions

Distilled or de-ionised water will be required to prepare Standards, ISABs and to rinse the electrode between measurements.

1000ppm Stock Standard solution. Used for preparation of Standards. (Prepared by customer)

ISAB. Used to adjust the Ionic strength of all standards and samples. Typical addition is 1 ml of 4 Molar ISAB to 50ml of all standards and samples.

Operation

1. Connect the electrode to the meter being used for analysis
2. Prepare a series (at least 2) of standards that bracket the expected sample concentration. This is best done by serial dilution of the stock solution. Ideally standards should be a decade in concentration apart e.g. 1, 10, and 100ppm.
3. Dispense 50 ml of each standard into analytically clean beakers (100 to 150 ml size is perfect)
4. Add ISAB/TISAB in the appropriate ratio. As a guide with sample concentrations in the 1 to 1000ppm range 1ml of a 4 Molar ISAB to 50 ml sample is satisfactory. For TISAB(Fluoride analysis only) please read the label.
5. Rinse the electrode with de-ionised water and blot dry with a lint free cloth and place in the lowest standard. When the reading is stable record the mV value.
6. Repeat step 6 for all subsequent standards proceeding from lowest to highest.
7. Plot a calibration curve on semi log paper using mV values on the linear Axis and concentration on the log scale.
8. Rinse the electrode in de-ionised water and blot dry. Place the electrode in the sample and record the stable mV value.
9. Using the calibration curve determine the unknown sample concentration.

Hints and tips

1. Ensure that the temperature of all standards and samples are the same to reduce errors.
2. Using a magnetic stirrer for laboratory analysis is recommended but not essential. It is however important to have the stirrer set on a low constant speed which must be reproducible for all measurements.
3. Prior to sample measurement ensure that the electrode is thoroughly rinsed with de-ionised water. It is worth performing this rinse twice given the possibility of carryover being greatest in high concentration solutions.
4. Prepare standards by serial dilution.
5. Make sure your electrode is conditioned by leaving the tip in the lowest concentration standard for 1 hour prior to analysis.

Methods of Analysis

We have described direct potentiometry above. This method is simplified by using a direct reading ion meter. There are several other methods, which are useful.

Known Addition: An incremental technique where the potential of the sample solution is measured followed by addition of a small volume of a higher concentration standard solution. The new potential is measured and from difference in the two values, and using the known electrode slope, the unknown concentration is determined,

This method is ideal for samples whose matrix is not entirely clean or aqueous. In these instances comparisons with clean standards is not appropriate thereby making direct potentiometry unsuitable. Known addition works because both standard and sample are measured in the same matrix.

Typical sample volume is 50 ml, typical standard volume is 5 ml. The standard should be approximately 100 times the sample concentration for accurate analysis.

Sample Addition: An incremental technique where the potential of a dilute standard solution is measured followed by the addition of a small volume of more concentrated sample. The new potential is recorded and the difference noted. Using this value (and the predetermined electrode slope) the unknown concentration is determined.

This method is ideal for dirty or viscous samples with an awkward matrix. The sample however needs to be relatively concentrated i.e. at least 100 times the Electrodes linear detection limit. The analysis does have the benefit of only requiring a small volume.

The sample matrix is basically broken down by dilution with the standard and therefore analysis is carried out in the same media.

End Point Titration: Flow Plus combination ISEs are ideal end point indicators and will produce a significant potential change at the equivalence point. The Ion in question must be contained in the titrand or the titrant and must therefore be in excess or absence at the end point.

Operating Instructions for Nitrate Ion Selective Electrode

1. Introduction

1.1 Construction

The electrode consists of an inert fluorocarbon body with a detachable PVC membrane unit, on the end of which is glued the ion selective membrane. Inside the membrane unit, an internal filling solution makes contact between the membrane and the internal silver/silver chloride reference element. The sensitive membrane consists of liquid ion exchange material immobilised in a poly-(vinyl chloride) matrix. Connection to a millivoltmeter is via a BNC plug, though an alternative plug may be specified.

1.2 Operating Principles

The electrical potential of an ion selective electrode is a function of the activity of certain ions in an aqueous solution. This potential can only be measured against a reference electrode, such as a saturated calomel electrode (SCE), placed in the same solution. Measurements are made with a high impedance millivoltmeter or expanded scale pH meter. A meter with digital display is obviously more accurate and most convenient. The nitrate electrode cannot be used in non-aqueous solvents but the presence of up to 40% organic solvents in an aqueous solution can be tolerated. 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

This electrode will respond to uncomplexed nitrate ion activity over the range 10^{-1}M - 10^{-5}M . The linear detection limit was found to be about $10^{-4.5}\text{M}$, thus Nernstian response was observed in the range 10^{-1} to $4 \times 10^{-5}\text{M}$ nitrate. Curvature of the response was observed at lower concentrations because the solubility of the liquid ion-exchange, leached from the membrane contributes a small but significant amount of nitrate 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 55-59mV/decade. If the total ionic strength of all solutions is maintained constant by the addition of a concentrated (ca. 10^{-1}M) inert electrolyte, such as ammonium sulphate or potassium hydrogen phosphate, the electrode can be calibrated directly in concentration units.

Daily recalibration is recommended for analytical use.

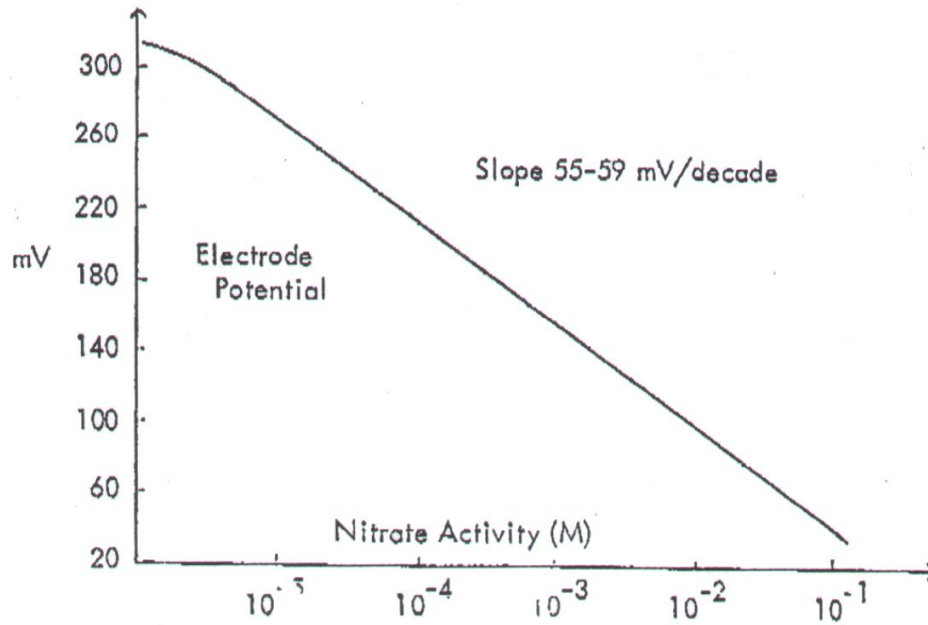


Figure 1. Calibration Curve for Nitrate Electrode

The activity coefficient of nitrate 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. | 0.975 | 0.945 | 0.925 | 0.85 | 0.805 | 0.755 |

Table 1 Activity Coefficients of Nitrate Ion

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

$$\text{Ionic Strength} = \frac{1}{2} \sum_{i=1}^N C_i Z_i^2$$

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:

$$\text{Activity (A}_i\text{)} = \text{Concentration (C}_i\text{)} \times \text{Activity Coefficient (f)}$$

1.4 Stability

The long-term drift in the E_o value of the nitrate electrode is usually in the region of 1-2mV/day.

1.5 Selectivity

The nitrate electrode is subject to interference from a number of inorganic anions, in particular, halides, nitrite, and perchlorate. Relative selectivity ratios for several interfering anions are given in Table 2.

| Interferent Ion | Selectivity Ratio | Activity of Interferent at which measurement made |
|-------------------------------|----------------------|---|
| Cl ⁻ | 9.4×10^{-3} | 0.075 |
| Br ⁻ | 5×10^{-2} | 0.075 |
| F ⁻ | 10^{-6} | 0.1 |
| I ⁻ | 4.1 | 0.001 |
| NO ₂ ⁻ | 3×10^{-2} | 0.075 |
| SO ₄ ⁼ | 3.5×10^{-3} | 0.001 |
| PO ₄ ³⁻ | 10^{-6} | 0.1 |
| ClO ₄ | 16.2 | 0.1 |

It can be seen that the electrode is more sensitive to iodide and perchlorate than to nitrate and both these species must be absent for valid nitrate measurements to be made.

The nitrate electrode can be used in the pH range 4-11 at NO₃⁻ activities 10^{-5} - 10^{-2} . At 10^{-1} M NO₃⁻ pH range 2-12 I usable.

1.6 Response Time

The electrode will respond to a step change in the nitrate ion activity in solution in less than ten seconds. When however, the electrode is removed from one solution and place in another of different nitrate concentration, it may take up to 30 seconds to achieve a new equilibrium.

Temporary erratic response and sluggishness in attaining equilibrium is observed when the electrode has been exposed to strongly interfering anions such as I⁻, Cl⁻, ClO₄⁻. After such exposure the electrode should be reconditioned in 10^{-2} M nitrate for 1 hour.

2. Operating and Handling

2.1 Initial Filling and Setting-Up

On receipt of the electrode remove it from its packing and inspect for damage, particularly to the delicate, transparent membrane which forms the sensing end of the electrode. Unscrew the sensor unit and introduce a few ml of the internal filling solution supplied. Remove air bubbles from inside the unit by tapping or pushing a blunt instrument of suitable diameter down into the unit, placing a finger over the membrane to feel when the instrument makes contact and avoiding rupturing the membrane. Fill the membrane unit to over-flowing with solution and screw it slowly back onto the electrode body. After the first few turns observe the surface of the membrane as the unit is screwed up and when the membrane begins to bulge, stop turning it and back-off very slightly to give a flat membrane. Any sign of solution seeping around the membrane indicates a damaged membrane unit and a replacement should be used.

The electrode is now 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 nitrate solution placed on a magnetic stirrer. Ensure that the liquid level does not come above the membrane unit/electrode body junction. Clamp a reference electrode (a double junction electrode containing 0.1M ammonium sulphate in the outer compartment) so that its end is immersed in the same solution and connect both electrode to a pH or millivolt meter. Record the potential when it becomes steady. Change the test solution sequentially for 10^{-2} M, 10^{-3} M, and 10^{-4} M nitrate solutions and plot the calibration curve, washing and drying the electrode between solutions.

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

2.3 Storage

If the electrode is to be used within a week or so, it can be merely removed from the test solution, washed and dried and be clamped in a vertical position in the air. For longer storage, the internal filling solution should be emptied and the unit stored dry. There is in principle no limit to the storage time but gradual oxidation of the membrane will, however, cause it to harden and lose its response. Shelf life, in its dry state, is better than six months.

2.4 Flow-Through Configuration

A conversion kit is available to enable continuous flow-through measurements 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 flexible nature of the membrane causes the pump pulses to produce rather more

'noise' on the electrode signal than normally found ($\pm 0.8\text{mV}$ as opposed to $\pm 0.2\text{mV}$). This can be mitigated by either damping the recorder input signal or using a pulseless pump.

3. Applications and Bibliography

The nitrate electrode finds wide application in sewage treatment and effluent monitoring as well as nitrate monitoring in the photographic and explosive industries.

The analysis of nitrate in soils is an important use of the electrode. Applications in food and pharmaceutical industries have also been described.

Nitrate in Soil Extracts

1. J. M. Bremner et al., *Anal. Lett.*, 1 (1968) 837
2. A. R. Mack and R. B. Sanderson, *Can. J. Soil. Sci.*, 51 (1971) 95
3. M. K. Mahendrapa, *Soil Sci.*, (1969) 132
4. R. J. K. Myers and E. A. Paul, *Can. J. Soil Sci.*, 48 (1968) 369
5. Orion Research Inc., *Applications Bulletin No. 7*
6. A. Oien and A. R. Selmer-Olsen, *Analyst*, 94 (1969) 888
7. P. J. Milham et al., *Analyst*, 95 (1970) 751

Nitrate in Vegetable and Other Plant Material

1. A. S. Baker and R. Smith, *J. Agr. Food Chem.*, 17 (1969) 1284
2. A. S. Baker et al., *Agron. J.*, 63 (1971) 126
3. P. J. Milham, *Analyst*, 95 (1970) 758
4. J. L. Paul and P. M. Carlson, *J. Agr. Food Chem.*, 16 (1968) 766

Nitrate in Waters

1. N. G. Bunton and N. I. Crosby, *Water Treat. Exam.*, 18 (1969) 388
2. D. R. Keeney et al., *Analyst*, 95 (1970) 383
3. D. Langmuir and R. L. Jacobson, *Environ. Sci. Technol.*, 4 (1970) 834
4. E. C. Shaw and P. Wiley, *Calif. Agr.*, 5 (1969) 11
5. A. Hulanicki et al., *Anal. Chim. Acta.*, 69 (1974) 409

Miscellaneous

1. Nitrate in limestone - P. M. Chalk and D. R. Keeney, *Nature*, 229 (1971) 42
2. Nitrate in oleum - J. M. C. Ridden et al., *Anal. Chem.*, 43 (1971) 1109
3. Nitrate in nitrites - O. G. Gehring et al., *Anal. Chem.*, 42 (1970) 1686
4. Nitrate Complexes of diphenyl thallium III sulphate - J.S. Di Greggorio et al., *Anal. Lett.*, 1 (1968) 811
5. Nitrate in Food Products - C. C. Westcott, *Food Technology (Chicago)*, 25 (1971) 709
6. Nitrogen oxides in air - R. Di Martini, *Anal. Chem.*, 42 (1970) 1102
7. Nitrate in Stainless Steel Pickling Baths - J. O. Burman et al., *Anal. Chim. Acta.*, 80 (1975) 215

4. Trouble Shooting

- 4.1 Wildly erratic readings
- i) Air bubble trapped either inside membrane unit or outside on the surface of the membrane.
 - ii) Wrong filling solution used
 - iii) Excessively violent stirring
- 4.2 Steady continuous drift in one direction
- i) Check membrane for leaks. This can be done by wiping the face of the membrane dry and screwing the membrane unit up a little tighter and observing whether any fluid escapes. Replace membrane.
 - ii) Poor earthing of the mV meter.
 - iii) Excessive leaking from the reference electrode junction leading to continuous changes in the activity coefficients of ions in weaker solutions.
 - iv) Temperature drift if solutions are not thermostatted, or sample vessel insulated from, for example, stirrer motor.
- 4.3 Slope of electrode much less than 50mV/Decade
- i) Membrane unit old and in need of replacing.
 - ii) Presence of an interfering ion in a constant concentration swamping the selected ions - check performance with pure sodium nitrate solutions.