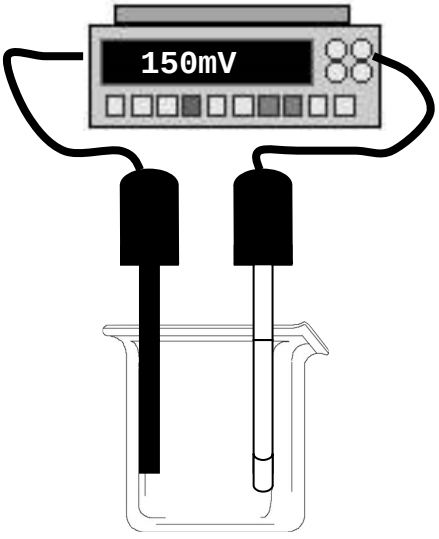
# SENTEK

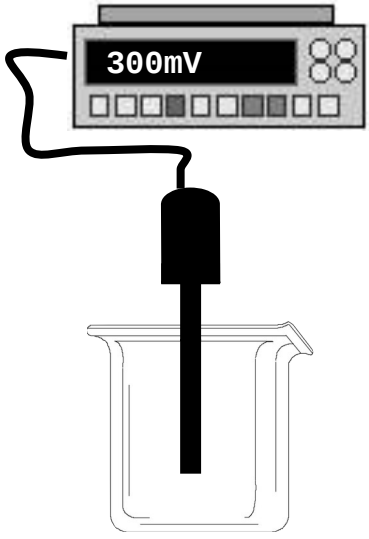
# Ion Selective Electrode

# OPERATING INSTRUCTIONS

CYANIDE




Mono/Reference




Combination

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# Operating Instructions
# Cyanide Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Cyanide Electrode which requires a separate Reference Electrode, and a Combination Cyanide 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.

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# Quick Guide to Cyanide
# ISE

The combination ion selective electrode has a solid state crysytalline membrane with an integral driTEK reference electrode. The electrode is designed for the detection and analysis of Cyanide 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 10ppm Cyanide 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 Hydroxide is ideal as the pH has to be kept above 11 for successful analysis. A typical addition would be 1 ml of 10 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

After use rinse with de-ionised water, wipe clean with a tissue or lint free cloth, replace protective cap and store dry in its box.

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

Should further conditioning be requires rub down the crystal surface with a very fine emery paper until the surface has a grey shiny appearance. Stand electrode in 100ppm Iodide solution for 20 minutes.

**Specification**

Cyanide is a monovalent anion.

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 | 0.03 to 260 ppm |
| Slope | -54 to -59 mV per decade |
| Potential Drift | 2 mV per 8 hours |
| Operating pH range | 11 to 13 |
| Temperature range | 5 to 50 Deg C |
| Endpoint time | Typically 10 to 30 seconds |
| Interferences: Ions with coefficients above 0.001. | Bromide<br>Iodide<br>Sulphide |

# Operating Instructions for Cyanide 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 be measured. The relationship is given by the Nernst Equation:

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

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
$A_{CN}$ is the activity of the Cyanide ions

This equation can be simplified to:

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

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 ions from the Reference Electrode will affect the chloride level

in test solutions, a salt-bridge tube filled with 2M sodium nitrate solution must be place 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 meter or expanded scale pH meter. A meter with digital display is obviously more accurate and most convenient.
The cyanide 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 cyanide ion activity over the range $10^{-2}$ $10^{6}$M. The linear detection limit is around 5 x $10^{-6}$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 cyanide to the solution being measured. All solutions containing cyanide ions should be kept at pH >12 to prevent formation of HCN species which, apart from being quite lethal, do not cause a response to the electrode. This can readily be achieved y using 1.0M sodium hydroxide as an ionic strength buffer, 20ml buffer to 100ml standards and samples. 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.

Daily re-calibration is recommended for analytical use.

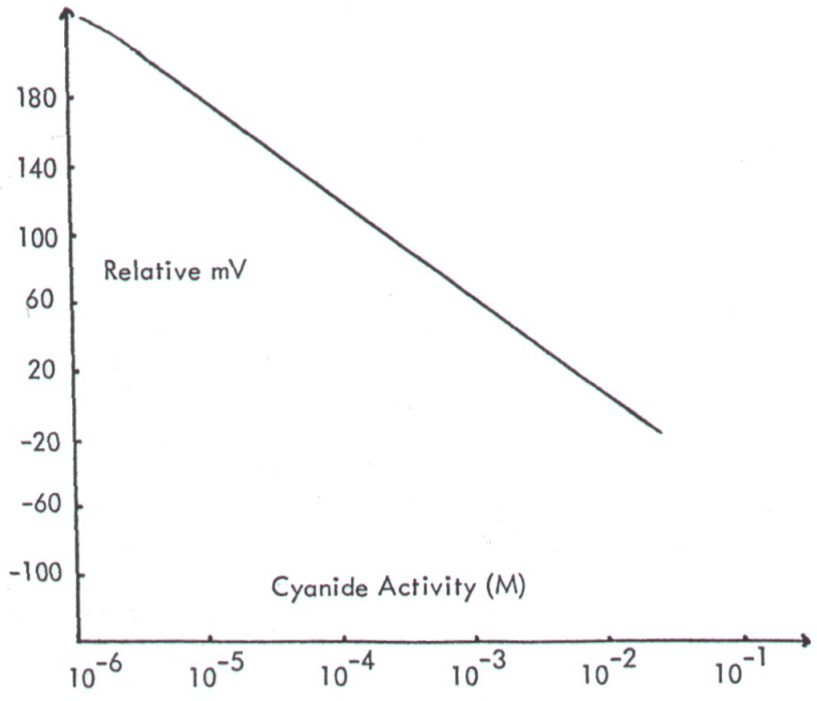


Figure 1

The activity coefficient of cyanide 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 | 0.946 | 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 cyanide electrode is usually in the region of 2.4mV/day.

## 1.5 Selectivity

The cyanide electrode is equally sensitive to iodide ions and the electrode potential will be characteristic of the total cyanide and iodide activity. Sulphide ion also causes interference and should not be present at activities of greater than $10^{-7}$M.
Certain cations which form strong cyano-complexes also interfere by reducing the free cyanide level. Suitable masking techniques must be employed to remove these cations.
The electrode can only be used at pH greater than 10.

## 1.6 Response Time

The electrode response to a step change in cyanide 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 very low ionic strength, i.e. with no ionic strength buffer, the response time may be extended to several minutes.

## 2. Operating and Handling

### 2.1 Initial Setting-Up

On receipt of the electrode remove it from its packing and inspect for damage particularly to the transparent membrane which forms the sensing end of the electrode. Clamp the electrode with its sensing end in a solution of Sodium Iodide ($10^{-2}$M) for about two hours.

### 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 $10^{-2}$M potassium cyanide solution on a magnetic stirrer. Clamp a reference electrode (a double junction Ag/AgCl or SCE should 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 test solution sequentially for $10^{-2}$M, $10^{-3}$M, and $10^{-4}$M cyanide 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 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 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 down-stream of the electrode. The combination

of this electrode with a sampler and pumping system can result in a versatile and low-cost continuous cyanide monitor.

## 3. Applications and Bibliography

The main applications of the cyanide electrode lie in the field of liquid and gases effluent pollution monitoring. The analysis or monitoring of cyanide metal plating baths, metal finishing and metal extraction processes also utilises cyanide electrodes.

Determination of Cyanide in Waste Waters


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Determination of Cyanide in Inorganic Systems


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2. Cigarette smoke - D. G. Vickroy and G. L. Gaunt, Tob. Sci., 174(4), 50, 54
3. Flow systems - B. Flett and H. von Storr, Anal. Chem., 43 (1971) 1575


Determination of Cyanide in Biological Materials


1. W. R. Hussein et al., Anal. Chem. Acta, 61 (1972) 89
2. C. Collombel et al., J. Eur. Toxicol., 3 (1970) 291
3. W. J. Blaedel et al., Anal. Chem., 43 (1971) 890
4. T. S. Light and J. L. Schwartz, Anal. Lett., 1 (1968) 825
5. B. Gyorgy et al., Anal. Chim. Acta, 40 (1969) 318


## 4. Trouble Shooting

4.1 Wildly erratic readings
- i) Air bubble 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 leaking 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 a 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 cyanide 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.