## 7. Ordering information

The following components of the $NO_x$ electrode can be supplied separately:

| | |
|---|---|
| – Membrane kit (3 replacement membrane modules + 50 ml electrolyte solution) | Ordering No. **15 231 2000** |
| – 50 ml electrolyte solution | Ordering No. **15 231 1000** |
| – Replacement electrode body | Ordering No. **15 200 2000** |
| AS7 connecting cable consisting of:<br>– AS7 cable socket<br>– ST-Li-Koax 2.8 coax cable<br>– and plug to suit the instrument in use | on request |

## *7. Informations pour commande de matériel*

*Les parties suivantes de l'électrode à $NO_x$ peuvent être commandées séparément:*

| | |
|---|---|
| *– «Membrane-Kit» (3 modules à membrane de remplacement et 50 ml d'électrolyte)* | *No. de cde. **15 231 2000*** |
| *– 50 ml d'électrolyte* | *No. de cde. **15 231 1000*** |
| *– Corps de remplacement de l'électrode* | *No. de cde. **15 200 2000*** |
| *Câble de raccordement AS7 comportant:*<br>*– une prise AS7 pour le câble*<br>*– un câble coax ST-Li-Koax 2.8*<br>*– une fiche correspondant à votre appareil de mesure* | *sur demande* |

## 7. Bestellinformationen

Folgende Teile der $NO_x$-Elektrode können separat bestellt werden:

| | |
|---|---|
| – Membran-Kit (3 Membranmodule und 50 ml Elektrolyt) | Bestell-Nr. **15 231 2000** |
| – 50 ml Elektrolyt | Bestell-Nr. **15 231 1000** |
| – Elektrodenkörper | Bestell-Nr. **15 200 2000** |
| AS7-Verbindungskabel bestehend aus:<br>– Kabelbuchse AS7<br>– Koax-Kabel ST-Li-Koax 2.8<br>– und Stecker passend zum Messgerät | auf Anfrage |

# Operating Instruction for $NO_x$ Electrode

# Manuel d'Instruction pour l'Electrode à $NO_x$

# Anleitung zur $NO_x$ Elektrode

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231-O2-CH



METTLER TOLEDO

## Operating Instructions for Type 15 231 3000 $NO_x$ Electrode

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## *Instructions pour l'Electrode à $NO_x$ Type 15 231 3000*

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## Anleitung zur $NO_x$-Elektrode Typ 15 231 3000

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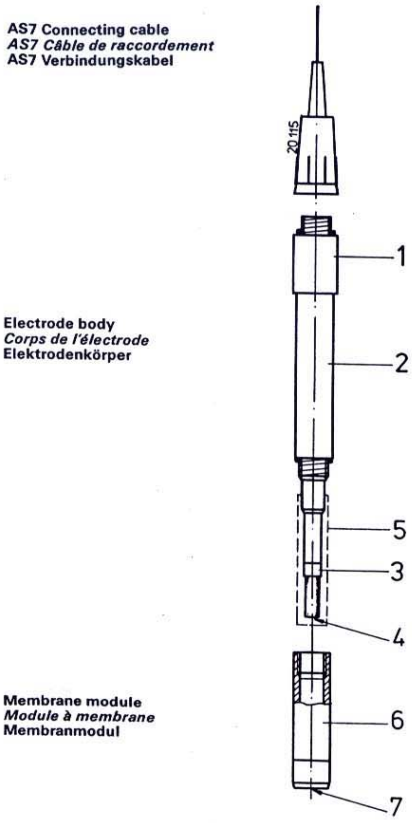
Figure 1: Structural arrangement of a potentiometric $NO_x$ electrode.
*Figure 1: Construction de l'électrode potentiométrique à $NO_x$.*
Abbildung 1: Aufbau einer potentiometrischen $NO_x$-Elektrode.




Structural arrangement of type 15 231 3000 **$NO_x$ Electrode**

1 S7 screw cap
2 plastic electrode body (POM copolymer)
3 Ag/AgCl reference electrode
4 glass pH membrane } pH electrode assembly
5 hydrating cap (only fitted on delivery or for long-term storage of electrode)
6 plastic module body (POM copolymer)
7 gas-permeable membrane (micro-porous)

*Construction de **l'électrode à $NO_x$** type 15 231 3000*

*1 Tête enfichable S7*
*2 Corps en matière synthétique (copolymère POM)*
*3 Electrode de référence à Ag/AgCl*
*4 Membrane de verre sensible au pH* } *électrode combinée de pH*
*5 Capuchon de mouillage (seulement pour l'envoi et pour la conservation à long terme de l'électrode)*
*6 Corps modulaire en matière synthétique (copolymère POM)*
*7 Membrane perméable aux gaz (microporeuse)*

Aufbau der **$NO_x$-Elektrode** Typ 15 231 3000

1 S7-Steckkopf
2 Kunststoffkörper (POM Copolymer)
3 Ag/AgCl-Referenzelektrode
4 pH-Glasmembran } pH-Messkette
5 Wässerungskappe (nur beim Versand und längerem Lagern der Elektrode)
6 Kunststoff-Modulkörper (POM Copolymer)
7 Gaspermeable Membran (mikroporös)

English

## 1. General information

The Type 15 2313000 $NO_x$ Electrode is intended for measuring the $NO_x$ content of aqueous systems. Its preferred applications are to be found in the fields of water and waste water, soil, food analysis etc.

### 1.1 Technical data

| | |
|---|---|
| Primary measured value: | potential in mV, proportional to log [$NO_x$] |
| Measuring range: | $\leq 10^{-6}$ mol/l to $5 \cdot 10^{-3}$ mol/l $NO_x$ |
| Operating temperature range: | 0 to 50 °C |
| Sample medium: | aqueous only (surface-acitive agents will shorten the working life of the membrane module). |
| Maximum permissible ionic strength of the sample medium: | 0.8 mol/l |
| Sample volume: | preferably greater than 20 ml (at concentrations $\leq 10^{-5}$ mol/l, even larger volumes will be required). |
| Interfering substances: | $SO_2$, $CO_2$, $H_2S$, volatile carbonic acids. |
| Electrode poisons: | surface-active agents (e. g. detergents), $H_2S$, etc. |
| Precision: | in the absence of interfering substances and over the linear portion of the characteristic curve it is possible to obtain a precision of better than ±2% of the measured $NO_x$ concentration, corresponding to ±0.5 mV. |
| Response time: | when passing from $10^{-5}$ mol/l $NO_x$ to higher concentrations, about 1 minute, and when passing from high concentrations down to $10^{-5}$ mol/l, several minutes (deviation from final constant value = 1 mV). |
| Electrode dimensions: | length from lower edge of screw cap: 120 mm<br>diameter: 12 mm |
| Materials: | electrode body and membrane module body in chemically resistant plastic (POM copolymer). |
| Working life: | at least 1 year for the pH electrode assembly. The life of the membrane module depends on the operating conditions, but is generally a few months. |
| Connections: | AS7 cable with appliance coupler as specified by the manufacturer of the pH/mV- or ion-meter (see leaflet). |

### 1.2 Scope of delivery

The electrode, or more precisely the electrode body, is supplied fitted with a hydrating cap, and thus is not immediately ready for use. Three membrane modules (of which two are spares), and a 50 ml bottle of electrolyte are supplied in a separate package.

### 1.3 Apparatus and accessories required

- Ion-meter or pH/mV-meter
- Magnetic stirrer with stirring bars
- Closed measuring vessels (titrating vessels) (pressure equalization with the atmosphere)
- Suitable electrode/vessel adapter
- Various pipettes, preferably microlitre pipettes
- Calibrated flasks

The following accessories may be useful, particularly when no ion-meter is available:

- Log/linear graph paper and/or a pocket calculator with scientific and engineering functions.

### 1.4 Chemical solutions required

- Deionized water for preparing solutions
- Electrolyte solution as supplied with the membrane kit (Ordering No. 15 231 2000)
- $NO_x$ electrode storage solution
  Prepare as follows:
  Dissolve 190 g sodium sulphate ($Na_2SO_4$) in about 800 ml deionized water and make up to 1000 ml. Take 100 ml of this stock solution and make up to 1000 ml with deionized water to obtain the storage solution.
- $NO_x$ sample conditioning solution
  Prepare as follows:
  Take the remaining 900 ml of the sodium sulphate solution prepared as described above and carefully add 48 ml concentrated sulphuric acid (96 to 97% $H_2SO_4$) (caution: wear safety goggles).
- 0.1 mol/l standard $NO_x$ solution
  Prepare as follows:
  Weigh out 6.9 g AR grade sodium nitrite ($NaNO_2$), dissolve in deionized water and make up to 1000 ml.
  or:
- 1000 mg/l standard $NO_x$ solution
  Prepare as follows:
  Weigh out 4.93 g AR grade sodium nitrite ($NaNO_2$), dissolve in deionized water and make up to 1000 ml.

## 2. Use of electrode

### 2.1 Preparation for use

Before preparing the $NO_x$ electrode for use, make up an electrode storage solution as described in § 1.4.
Remove the hydrating cap and rinse the pH electrode assembly with deionized water.
Fill app. 15 drops or 0.8 to 1.0 ml of electrolyte solution into the membrane module and remove any air bubbles adhering to the sides by tapping gently with the fingers. Now screw the membrane module to the electrode body and immerse the $NO_x$ electrode in the storage solution.

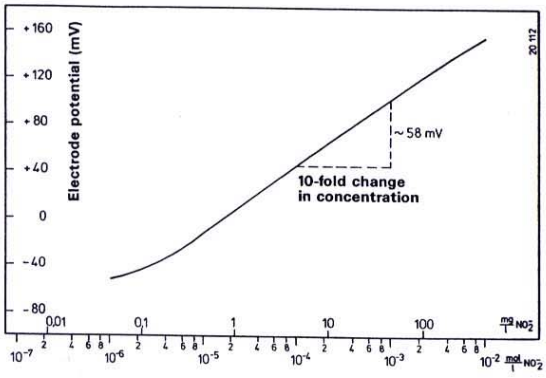
Neither the gas-permeable membrane of the $NO_x$ electrode nor the glass membrane of the pH electrode should be touched with the fingers.
Connect the electrode with the cable to the input socket of the ion- or pH/mV-meter.
Prior to carrying out the first measurement with a new $NO_x$ electrode immerse it for several hours in the storage solution to precondition it. Afterwards, before calibration or measurement, immerse the $NO_x$ electrode at least for 30 minutes in the storage solution.

### 2.2 Calibration and measurement

**Please note!**

- Calibration and sample solutions should always be **at the same temperature** (the measuring vessel should be thermally insulated from possible heating by the magnetic stirrer – generally a sheet of cardboard or plastic foam material will suffice).
- All measurements should be carried out under the **same stirring conditions**, i. e. identical stirring speed, identical stirring bars, identical distance between electrodes and stirring bars, etc.
- When not in use, the $NO_x$ electrode should always be kept immersed in the storage solution (see also § 3).
- In all calibration and sample solutions the **ionic strength should be the same** and should not exceed a **maximum value of 0.8 mol/l.** After addition of the sample preconditioning solution, the pH value should be less than 1.8 (see also § 2.5).
- The electrode should not be immersed to a depth greater than the length of the membrane module, i. e. not more than 6 cm.
- The calibration and measuring vessels should be well closed but allowing a pressure equalization with the atmosphere. They shall have a small volume ratio of the gas phase over the liquid phase.

Figure 2:
Typical calibration curve for an $NO_x$ electrode




### General instructions for determining $NO_x$ content

a) **Calibration**

1) Prepare a series of dilutions of the stock standard $NO_x$ solution (0.1 mol/l or 1000 mg/l), preferably choosing concentrations which bracket that expected from the sample solution. When calibrating for the first time, at least three calibration points should be determined.
2) Run equal volumes of the calibration solutions, beginning with the lowest concentrations, into measuring vessels and stir.
3) Immerse the $NO_x$ electrode in a calibration solution and then add to this solution 1/10th of its volume of sample conditioning solution and immediately stopper the measuring vessel. Gas bubbles adhering to the membrane are removed by tapping the electrode body with the fingers.
4) Once the mV indication has settled down, read off the final constant value.
5) Remove the electrode, rinse it briefly with deionized water and dab off with a paper tissue.
6) Repeat steps 3) to 5) above for all the other calibration solutions.
7) Plot the measured mV values against the logarithms of the $NO_x$ concentrations of the corresponding calibration solutions on log/linear graph paper to obtain a calibration curve:

$NO_x$ concentration → logarithmic axis
mV value → linear axis

b) **Measurement**

For measurement, proceed as for calibration. Read off the $NO_x$ content of the sample solution from the measured mV value with the aid of the calibration curve (see Figure 2), or calculate it with the pocket calculator.

The frequency of recalibration operations depends on the degree of accuracy required and on the measuring conditions.

### 2.3 Particular requirements for determining low $NO_x$ concentrations in the presence of $CO_2$

The measurement of low $NO_x$ concentrations (i. e. less than $10^{-5}$ mol/l) is affected by the following factors:

- flatter $NO_x$ electrode slope
- sluggish response
- interfering substances, particularly $CO_2$
- liberation of adsorbed $NO_x$

Use the largest possible volumes of both calibration and sample solutions. If the electrode has been previously used for determining high $NO_x$ concentrations, it should be left immersed in the storage solution until stable values are obtained. If necessary, the electrolyte should be renewed.

It is advisable to use an addition or enrichment method with several $NO_x$ addition steps when measured in the bent region of the calibration curve, employing a strip chart recorder. Start with an $NO_x$-free ‹blank solution› (such as the storage solution), and renew this repeatedly until the measured electrode potential does not decrease with a further renewal. Then add a definite quantity of the sample solution, followed by standard $NO_x$ solution additions, noting the electrode potential each time.

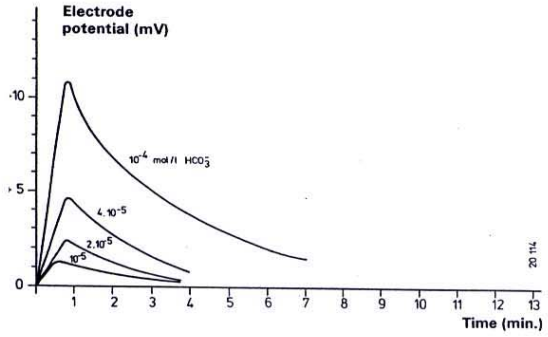
The measured value in the ‹blank solution› then enables the practical limit of detection to be determined, and hence the precision of the subsequent $NO_x$ determinations to be checked (see figure 2).

The interfering substance most frequently encountered is $CO_2$. This is liable to be present in considerable concentrations in samples such as effluent water, tap water, meat, etc. If the display indicates an overshoot when sample conditioning solution is added, followed by a slow fall-off, this is generally due to $CO_2$ interference.

The response behaviour can be seen from figure 3.

Figure 2:

Typical response behaviour of the $NO_x$ electrode in the presence of $CO_2$ or $HCO_3^-$. Addition of sample conditioning solution to a $10^{-5}$ mol/l nitrite solution. For higher nitrite concentrations the $CO_2$ interference is smaller.




## 3. Use and maintenance of the $NO_x$ electrode

### 3.1 Storage

The $NO_x$ electrode should not be kept immersed in the storage solution for more than a few days. For longer periods, remove the membrane module. Thoroughly rinse the pH electrode assembly and the membrane module with deionized water. Fill the hydrating cap with deionized water and fit it to the pH electrode assembly, this, together with the membrane module, then being placed for storage in the original delivery package.

Properly cleaned membrane modules may be kept stored dry for an indefinite period.

### 3.2 Replacing membrane module

Place app. 15 drops or 0.8 to 1.0 ml of electrolyte solution in the new module and remove any air bubbles adhering to the sides by gently tapping with the fingers. Now screw the new module to the electrode (the latter previously rinsed with deionized water) and immerse the complete $NO_x$ electrode in the storage solution.

## 4. Troubleshooting procedures

**Fault:**

| Possible cause: | Remedy: |
|---|---|
| **Value outside measuring range:** | |
| Fault in instrument | Check with input short-circuited. |
| Faulty contact in electrode plug | Insert and withdraw repeatedly. |
| Insufficient electrolyte | Top up electrolyte as necessary. |
| Fault in pH electrode assembly | Remove membrane module, measure potential in pH 7.0 buffer solution containing 0.1 mol/l NaCl (0.58 g NaCl to 100 ml buffer solution), and then in pH 4.0 buffer solution containing an equivalent amount of NaCl (use small volumes). After settling down, the difference in potential should be 160 to 180 mV. |
| **Unstable indication:** | |
| Fault in instrument | Check with input short-circuited. |
| No sample preconditioning | Add sample conditioning solution. |
| Faulty earthing | Check earthing of instrument and magnetic stirrer. |
| Static charges | Treat all plastic parts of the instrument with a suitable antistatic or wetting agent. |
| Air bubble between plastic $NO_x$ membrane and glass pH membrane | Loosen membrane module, tap it with the fingers and then screw it up again. |
| Faulty electrode body | Replace electrode body. |
| **Indication drifts:** | |
| Temperature not constant | Use a thermostatic jacket, or wait until all solutions are at room temperature. |
| No sample preconditioning | Add sample conditioning solution. |
| Membrane module not screwed up tight enough | Tighten membrane module. |
| Insufficient electrolyte | Top up or renew electrolyte. |
| Damage to gas-permeable membrane due to surface-active agents (detergents), ageing or mechanical action | Check for damaged areas, and replace membrane module if necessary. |
| Escape of gases | Check closure of measuring vessel. |
| Ionic strength of sample too high (>0.8 mol/l) | Dilute sample solution. |
| pH electrode assembly stored dry too long | Immerse pH electrode assembly in water. |
| Inadequate preconditioning | Immerse electrode for at least 30 minutes in storage solution before use. |
| Sample solution unstable or contaminated with interfering substances | Modify standard measuring procedure as appropriate and if this does not work, contact your INGOLD Agent for advice. |
| Measurement of low $NO_x$ concentrations after previous measurement of high $NO_x$ concentrations (‹memory effect›) | Immerse in storage solution before the next measurement. |
| **Slope incorrect:** | |
| Calibration solution(s) incorrectly prepared | Prepare new calibration solution(s). |
| No sample preconditioning | Add sample conditioning solution. |
| Membrane module not screwed up tight enough | Tighten membrane module. |
| Membrane damaged | Replace membrane module. |
| Electrode not properly cleaned when passing from high to low concentration | Rinse electrode thoroughly, and immerse in storage solution if necessary. |
| pH electrode assembly damaged | Check in pH 7 and pH 4 buffer solutions as described under ‹Value outside measuring range› above. |

## 5. Conversion tables

**The following conversion factors apply:**

| Given value: | Multiply by: | To obtain: |
|---|---|---|
| mol/l $NO_2^-$ | $46.0 \cdot 10^3$ | mg/l $NO_2^-$ |
| mol/l $NO_2^-$ | $14.0 \cdot 10^3$ | mg/l N-$NO_2^-$ |
| **Given value:** | **Divide by:** | **To obtain:** |
| mg/l $NO_2^-$ | $46.0 \cdot 10^3$ | mol/l $NO_2^-$ |

**Relationship between concentration values:**

| mol/l $NO_2^-$ | mg/l $NO_2^-$ | mg/l N-$NO_2^-$ |
|---|---|---|
| $10^{-1}$ | 4600 | 1400 |
| $10^{-2}$ | 460 | 140 |
| $10^{-3}$ | 46 | 14 |
| $10^{-4}$ | 4.6 | 1.4 |
| $10^{-5}$ | 0.46 | 0.14 |

## 6. Literature


K. Cammann, ‹Working with Ion-Selective Electrodes›, Springer-Verlag, 1979.

D. Midgley, K. Torrance, ‹Potentiometric Water Analysis›, John Wiley and Sons, 1978.

J. Vesely, D. Weiss, K. Stulik, ‹Analysis with Ion-Selective Electrodes›, Ellis Horwood Ltd./John Wiley and Sons, 1978.


Further literature for special applications can be supplied on request.