Cat. No. 51939-88

Model 51939

Combination ORP Electrode

Instruction Manual

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SPECIFICATIONS

Specifications subject to change without notice.

Construction
Epoxy-body with porous-pin reference junction - resistant to acids, bases and inorganic solvents. Not for use in polar organic solvents.

Length
135 mm

Body Diameter
12 mm

Cable Length
1 m

Temperature Range
Routine Use—0 to 45 ° C (32 to 113 °F)
Occasional Use—0 to 100 ° C (32 to 212 °F)

Storage
-40 to 50 °C (-40 to 122 °F)

Reference Half Cell
Ag/AgCl

Connector
5-pin

OPERATION

DANGER

Handling chemical samples, standards, and reagents can be dangerous. Review the necessary Material Safety Data Sheets and become familiar with all safety procedures before handling any chemicals.

DANGER

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les Fiches de Données de Sécurité des Produits (FDSP) et se familiariser avec toutes les procédures de sécurité avant de manipuler tous les produits chimiques.

PELIGRO

La manipulación de muestras químicas, estándares y reactivos puede ser peligrosa. Revise las fichas de seguridad de materiales y familiarícese con los procedimientos de seguridad antes de manipular productos químicos.

GEFAHR

Das Arbeiten mit chemischen Proben, Standards und Reagenzien ist mit Gefahren verbunden. Es wird dem Benutzer dieser Produkte empfohlen, sich vor der Arbeit mit sicheren Verfahrensweisen und dem richtigen Gebrauch der Chemikalien vertraut zu machen und alle entsprechenden Materialsicherheitsdatenblätter aufmerksam zu lesen.

PERICOLO

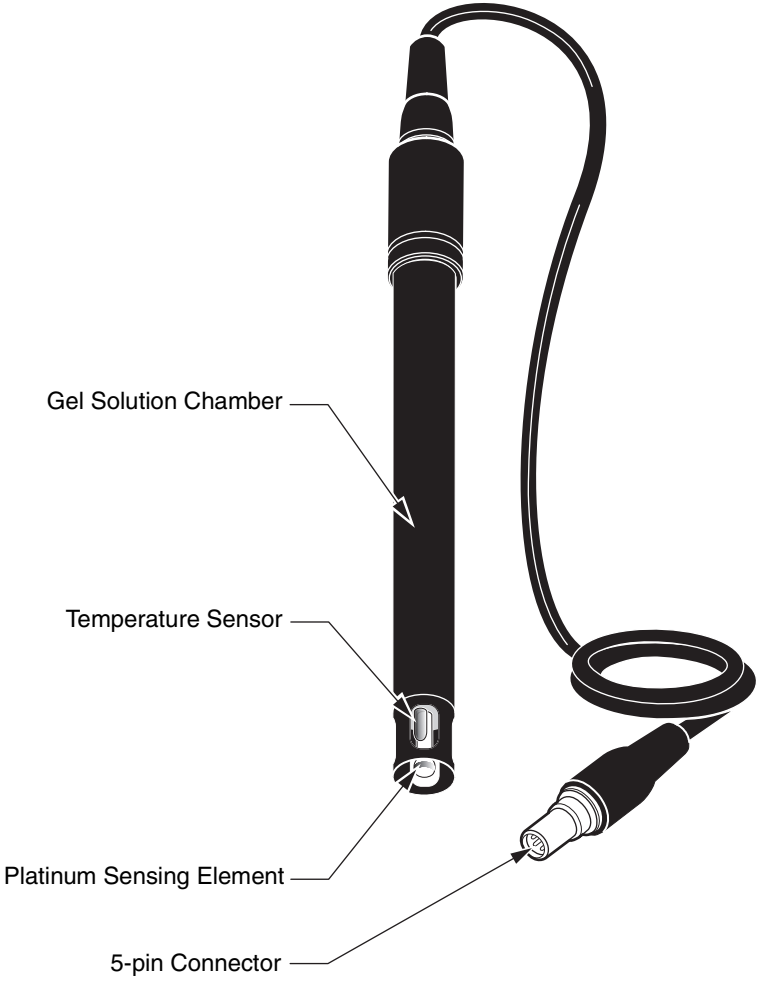
La manipolazione di campioni, standard e reattivi chimici può essere pericolosa. La preghiamo di prendere conoscenza delle Schede Techniche necessarie legate alla Sicurezza dei Materiali e di abituarsi con tutte le procedure di sicurezza prima di manipolare ogni prodotto chimico.

INTRODUCTION

The Model 51939 Combination ORP Electrode is a rugged epoxy-bodied electrode for both field and laboratory applications. This design combines a platinum sensing element and a silver/silver chloride reference electrode in one body. See *Figure 1*.

Use the electrode to make direct measurements of redox potentials or to perform potentiometric titrations. It is not designed for amperometric or constant current titrations, such as the Karl Fischer.

Figure 1 Model 51939 Combination ORP Electrode



Connecting the Electrode to the Meter

Attach the 5-pin connector to the pH input on the meter. Match the arrow on the 5-pin connector with the mark on the meter.

Electrode Measurements

Direct Measurement

Use direct redox potential (ORP) measurements to determine the oxidizing or reducing capability of a solution. These measurements are commonly made in polluted streams, chlorinated waters, industrial waste waters, and other water samples.

Direct Measurement Procedure

1. Connect the electrode to the meter and set the function switch to the millivolt mode. Place the electrode in the sample solution and wait for the reading to stabilize. When stable, record the potential.

2. For some applications it is customary to report redox potential readings relative to the standard hydrogen electrode (SHE). To do this, select the value in *Table 1 Reference Electrode Potentials* that corresponds to the temperature of the solution measured. Substitute that value (C) into the equation and solve for E_{SHE}:

$E_{SHE} = E_0 + C$

where:

E_{SHE} = oxidation reduction potential of the sample relative to the SHE, following the international sign convention.

E_0 = potential developed by the ORP electrode.

C = potential developed by the reference electrode portion relative to the SHE (see *Table 1 Reference Electrode Potentials*).

Table 1 Reference Electrode Potentials shows the potentials, C, developed by the reference electrode portion relative to the standard hydrogen electrode at various temperatures.

Note: *Like all platinum ORP electrodes, the Model 51939 may give unstable readings in solutions containing chromous, vanadous, titanous and other ions that are stronger reducing agents than hydrogen or platinum.*

Table 1 Reference Electrode Potentials*

Temperature (°C)	Electrode Potential in mV (C)
10	231
20	226
25	222
30	219

* Taken from *Reference Electrodes: Theory and Practice*; Ives, D. J. G., Janz, G. J., Eds.; Academic Press: New York, 1961; p 189.

Oxidation Reduction Titrations

Oxidation-reduction, or redox titrations provide a simple, reliable method for determining many substances in solution. A redox titration consists of adding to an unknown sample small increments of a titrant that converts the unknown to a different oxidation state. After each addition of titrant, the ORP electrode develops a potential proportional to the logarithm of the ratio of the activities of the two oxidation states.

At the inflection, or end point, the titrant has completely oxidized or reduced the unknown, causing a sharp change in the logarithm of the ratio of the activities of the two oxidation states. A corresponding sharp change in the potential is developed by the platinum electrode. Often several oxidizing or reducing species can be precisely determined in the same solution by a single titration with several inflection points.

Table 2 Typical Redox Titration Methods lists suitable titrants for different unknowns, the equation for the titration reaction, interferences, and a reference where information about preparing the sample and running the titration can be found. For similar information about unknowns not listed in the table, consult the standard texts listed as references.

The following directions represent a general procedure for performing a redox titration once the sample is prepared for measurement.

Redox Titration Procedure

1. Fill a 10-mL buret with a standard titrant solution with a normality that is 5–10 times that of the sample.

2. Connect the electrode to the meter and set the meter to the millivolt mode.

3. Pipet a 50 mL sample into a 150-mL beaker. Stir with a magnetic stirrer throughout the titration.

4. Begin by adding titrant in 0.5–1 mL increments, recording the potential after each addition. Near the end point, when large potential changes appear, add increments of 0.1–0.2 mL. Continue the titration 3–4 mL past the end point.

5. Plot the electrode potential versus volume of added titrant on linear graph paper and draw a smooth curve through the points. The end point is the point of inflection (the point of greatest slope).

6. Calculate the normality of the sample, N_x, in equivalents per liter:

$$N_X = \frac{V_t \times N_t}{V_X}$$

where:

N_t = normality of titrant (Eq/L)
V_t = volume of titrant at end point (mL)
V_x = volume of sample (mL)

Table 2 Typical Redox Titration Methods

Unknown	Interferences	Suitable Titrants	Titration Reaction	Ref.
antimony (Sb^{+3})	As, Fe, SO_2 V; organic substances and others interfere	potassium permanganate ($KMnO_4$)	$5Sb^{+3} + 2MnO_4^- + 16H^+ \rightarrow 5Sb^{+3} + 2Mn^{+2} + 8H_2O$	2
arsenic (As^{+3})	other reducing agents	sodium bromate ($NaBrO_3$)	$BrO_3^- + 3As^{+3} + 6H^+ \rightarrow Br^- + 3As^{+5} + 3H_2O$	3
hydrogen peroxide (H_2O_2)	preservatives present in commercial H_2O_2 may interfere	potassium permanganate ($KMnO_4$)	$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{+2} + 8H_2O$	5
hypochlorite ion (ClO^-) or chlorine (Cl_2)	Br_2 and other oxidizing agents interfere by liberating I_2	sodium iodide (NaI)	In acid solution: $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$. In basic solution: $2ClO^- + 2I^- \rightarrow I_2 + 2Cl^- + 2OH^-$	1

Table 2 Typical Redox Titration Methods (Continued)

Unknown	Interferences	Suitable Titrants	Titration Reaction	Ref.
iodine (I_2)	other reducing agents	sodium iodate ($NaI0_3$)	$2I_2 + IO_3^- + 5HCN + H^+ \rightarrow 5ICN + 3H_2O$	4
iodine (I_2)	direct sunlight, high acidity, copper salts, and other catalysts promote air oxidation and cause false high results ($Na_2S_2O_3$)	sodium thiosulfate ($Na_2S_2O_3$)	$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$	3
iron (as Fe^{2+}, Fe^{3+}, or in steel)	high levels of organic acids such as acetic, oxalic, tartaric, and alcohols; F^- if present in more then trace amounts; Cl^-; PO_4^{3-}	ceric sulfate [$Ce(SO_4)_2$] (Not recommended for samples containing Cl^-)	$Fe^{2+} + Ce^{4+} \rightarrow Ce^{3+} + Fe^{3+}$	2
iron (as Fe^{2+}, Fe^{3+}, or in steel)	other reducing agents	potassium dichromate ($K_2Cr_2O_7$), recommended for samples containing Cl^-	$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$	3
manganese (as permanganate MnO_4^-)	other oxidizing agents	ferrous sulfate ($FeSO_4$)	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$	2
manganese (as Mn^{2+})	other reducing agents	potassium permanganate ($KMnO_4$)	$3Mn^{+2} + 2MnO_4^- + 7H_2O \rightarrow 5MnO_2 + H_2O + 4H^+$	1
stannous tin (Sn^{2+})	other reducing agents	ceric sulfate [$Ce(SO_4)_2$]	$Sn^{+2} + 2Ce^{4+} \rightarrow Sn^{4+} + 2Ce^{3+}$	4
sulfur (as sulfur dioxide SO_2)	S^{2-} and SO_3^{2-}, remove by shaking with $CdCO_3$ and filtering	iodine (I_2)	$SO_2 + I_2 + 2H_20 \rightarrow SO_4^{2-} + 2I^- + 4H^+$	1
thallium (Tl^+)	other reducing agents	sodium bromate ($NaBrO_3$)	$BrO_3^- + 3Tl^+ + 6H^+ \rightarrow Br^- + 3Tl^{+3} + 3H_2O$	3
thiosulfate ion ($S_2O_3^{2-}$)	S^{2-} and SO_3^{2-}, remove by shaking with $CdCO_3$ and filtering	iodine (I_2)	$I_2 + 2S_20_3^{2-} \rightarrow 2I^- + S_4O_6$	3
uranium (as urnayl ion UO^{2+})	other reducing agents	potassium dichromate ($K_2Cr_2O_7$)	$3UO^{+2} + Cr_2O_7^{2-} + 8H^+ \rightarrow 3UO_2^{+2} + 2Cr^{+3} + 4H_2O$	3
zinc (Zn^{2+})	other reducing agents	sodium iodate ($NaIO_3$)	$ZnHg(SCN)_4 + 6I0_3^- + 6Cl^- + 8H^+ \rightarrow Zn^{+2} + Hg^{+2} + 6ICl + 4HCN + 4SO_4^{2-}$	2

1. Furman, (Ed). *Scott's Standard Methods of Chemical Analysis*, 5th ed.; Van Nostrand: Princeton, N.J., 1938.
2. Hillebrand, Lundell, Bright, and Hoffman. *Applied Inorganic Analysis*, 2nd ed.; Wiley: New York, 1953.
3. Kolthoff and Sandell. *Testbook of Quantitative Inorganic Analysis*, 3rd ed.; MacMillan: New York, 1952.
4. Oesper. *Newer Methods of Volumetiric Chemical Analysis*, Van Nostrand: Princeton, N.J., 1938.
5. Treadwell and Hall. Analytical Chemistry. In *Quantitative Analysis*, 8th ed.,vol. 2; Wiley: New York, 1935.

MAINTENANCE

Cleaning the Electrode

To remove inorganic deposits, immerse the electrode tip in room-temperature 0.1 N HCl for 10 minutes. To remove grease, oil, or other organic deposits, immerse the tip in warm water and detergent and swirl gently. After cleaning, rinse with deionized water.

Storage

When not in use, the electrode may be stored dry, in air. Remove salt crystals on the outside of the electrode by rinsing with deionized water.

Checking Electrode Operation

Checking the electrode is necessary only when there is evidence of malfunction that cannot be traced to other causes.

Procedure A

1. Open an ampule of Light's Solution (Cat. No. 26125-20). Pour the contents of the ampule into a beaker.

2. Immediately place the ORP Electrode tip into the solution.

3. Verify that the potential is 475 ± 10 mV.

   Note: *This potential is the standard reduction potential for* $Fe^{2+/3+}$ *with the reference electrode potential subtracted. The solution is 0.01 M in both* Fe^{2+} *and* Fe^{3+}.

   If it is not, clean the electrode of inorganic deposits by immersing the electrode tip in room-temperature 0.1 N HCl for 10 minutes. To remove grease, oil or other organic deposits, immerse the tip in warm water and detergent and swirl gently. After cleaning, rinse with DI water.

   Repeat Procedure A after cleaning.

Procedure B

1. Prepare solution A (0.1 M potassium ferrocyanide and 0.05 M potassium ferricyanide) as follows:

   a. Weigh out 4.22 g reagent-grade $K_4Fe(CN)_6 \cdot 3H_2O$ and 1.65 g reagent-grade $K_3Fe(CN)_6$. Place in a 100-mL volumetric flask.

   b. Add about 50 mL deionized water and swirl to dissolve the solids.

   c. Dilute to volume with deionized water.

2. Prepare solution B (0.01 M potassium ferrocyanide, 0.05 M potassium ferricyanide, and 0.36 M potassium fluoride) as follows:

   a. Weigh out 0.42 g of reagent-grade $K_4Fe(CN)_6 \cdot 3H_2O$, 1.65 g of reagent-grade $K_3Fe(CN)_6$, and 3.39 g of reagent-grade $KF \cdot 2H_2O$. Place in a 100-mL volumetric flask.

   b. Add about 50 mL deionized water and swirl to dissolve the solids.

   c. Dilute to volume with deionized water.

3. Transfer solution A to a 150-mL beaker. Place electrode in the solution and wait until the reading stabilizes. The potential should be about 234 mV.

4. Rinse the electrode and repeat the measurement with solution B. The potential should be about 66 mV greater in solution B than in solution A.

GENERAL INFORMATION

At Hach Company, customer service is an important part of every product we make.

With that in mind, we have compiled the following information for your convenience.

REPLACEMENT PARTS

Required Apparatus

Description	Cat. No.
Combination ORP Electrode, 5-pin	51939-00

Optional Reagents

Light's Solution, ampules, 20/pkg	26125-20
Hydrochloric Acid Standard Solution 0.1 N, 1 L	14812-53
Sodium Hydrochloride Standard Solution, 0.1 N, 1 L	191-53

Optional Apparatus

Beaker, 100-mL, polypropylene	1080-42
Beaker, 250-mL, polypropylene	1080-46
Beaker, 400-mL, polypropylene	1080-48
Beaker, 600-mL, polypropylene	1080-52
Beaker, 1000-mL, polypropylene	1080-53
Digital Titrator	16900-01
Flask, Erlenmeyer, 125-mL	505-43
Electrode Holder, with electromagnetic stirrer	45300-01
Electrode Holder	45300-00
sensION™ 1 Portable pH Meter	51700-10
sensION™ 2 Portable pH Meter	51725-10
sensION™ 3 Portable pH Meter	51750-10
sensION™ 4 Portable pH Meter	51775-10
Stir Bar, Magnetic, 22.2 x 7.9 mm	20953-50

HOW TO ORDER

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(800-227-4224)
By FAX: (970) 669-2932

By Mail:

Hach Company
P.O. Box 389
Loveland, CO 80539-0389
U.S.A.

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Information Required

- Hach account number (if available)
- Your name and phone number
- Purchase order number
- Brief description or model number
- Billing address
- Shipping address
- Catalog number
- Quantity

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Authorization must be obtained from Hach Company before sending any items for repair. Please contact the HACH Service Center serving your location.

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FAX: (970) 669-2932
E-mail: intl@hach.com

WARRANTY

Hach warrants most products against defective materials or workmanship for at least one year from the date of shipment; longer warranties may apply to some items.

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For a complete description of Hach Company's warranty policy, request a copy of our Terms and Conditions of Sale for U.S. Sales from our Customer Service Department.

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