

ORION

Orion Research Incorporated

IONALYZER INSTRUCTION MANUAL

thiocyanate electrode
model 94-58

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general information

introduction

The Model 94-58 thiocyanate electrode allows thiocyanate ion in aqueous solutions to be measured quickly, accurately, and economically. All apparatus and solutions required for measurement, general analytical procedures, electrode characteristics, and electrode theory are discussed in this manual. The 94-58 electrode is intended to measure thiocyanate in the range 5×10^{-6} M to 1 M.

required equipment

meter — Orion Model 801A or 701 digital pH/mv meter for precision laboratory measurements, or Orion Model 407A specific ion meter for laboratory, field, or plant measurements.

reference electrode — Orion Model 90-02 double junction reference electrode.

magnetic stirrer — recommended for laboratory measurements.

graph paper — (for use with digital pH/mv laboratory meters) 4-cycle semilogarithmic paper for preparing calibration curves.

polishing strips — Orion Cat. No. 94-82-01, for polishing dirty or etched sensing membranes.

required solutions

distilled or deionized water — to prepare all solutions and standards.

standard solution — 0.1 M NaSCN. To prepare, place 8.107 g reagent-grade sodium thiocyanate in a one-liter volumetric flask. Add about 500 ml distilled water and swirl to dissolve. Dilute to the mark with distilled water.

ionic strength adjustor (ISA) — to keep a constant background ionic strength. For samples with a total ionic strength less than 0.1 M (see page 20 for how to calculate ionic strength), prepare 5 M NaNO₃ by dissolving 42.5 g reagent-grade sodium nitrate in 100 ml distilled water. 2 ml ISA is added to 100 ml standard or sample solutions to bring the background to 0.1 M. For samples above 0.1 M in ionic strength, prepare standard solutions similar to the sample composition.

reference electrode outer chamber filling solution — use the filling solution provided with the electrode (Orion Cat. No. 90-00-03).

connecting electrodes to meter

Insert the reference electrode phone-tip connector and the sensing electrode connector into appropriate jacks on the digital pH/mv meter or specific ion meter. Non-Orion meters may require special adaptors. Consult your meter instruction manual.

checking electrode slope with 801A or 701 digital pH/mv meter

Note: Check electrode slope daily.

1. Put 100 ml distilled water into a 250 ml beaker. Add 2 ml ISA. Turn Function Switch to MV position. Place electrodes in the solution to a depth of about 3 cm (1 inch).
2. Pipet 1 ml 0.1 M standard into the solution. Stir thoroughly. Read electrode potential in millivolts and record.
3. Add 10 M 0.1 M standard. Stir thoroughly. Read electrode potential in millivolts and record. Determine the difference between the first and second potential reading. Correct electrode operation is indicated by a difference of 57 ± 1 mv, assuming the solution temperature is between 20°C and 25°C . If the change in potential is not within this range, see the troubleshooting check list in the centerfold.

NOTE: The above procedure measures electrode slope. Slope is defined as the change in potential observed when the concentration changes by a factor of ten.

checking electrode slope with 407A specific ion meter

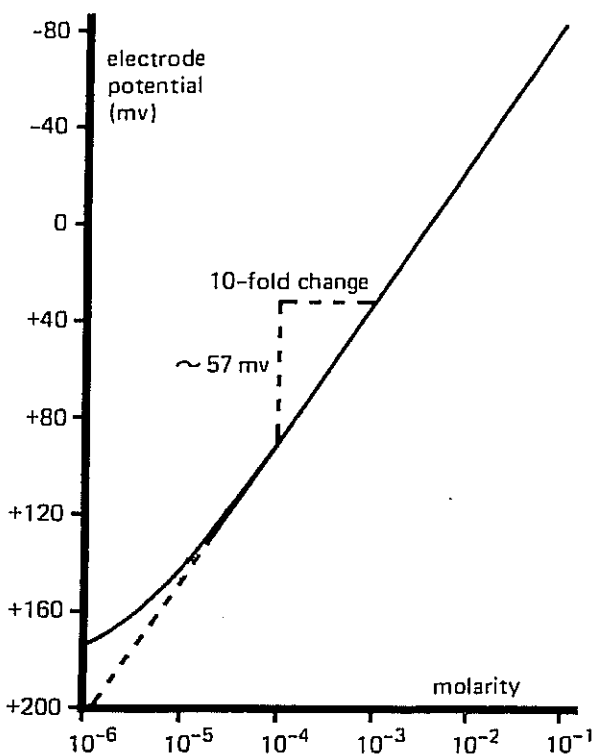
Note: Check electrode slope daily.

1. Put 100 ml distilled water into a 250 ml beaker. Add 2 ml ISA. Turn Function Switch to the X^- position. Place electrodes in the solution to a depth of about 3 cm (1 inch).

2. Pipet 1 ml 0.1 M standard into the solution. Stir thoroughly. Adjust the Calibration Control until the meter needle points to "1" at the center of the red logarithmic scale.
3. Add 10 ml 0.1 M standard. Stir thoroughly. Adjust the Temperature Compensator until the meter needle points to "10" at the extreme right of the red logarithmic scale. Turn the clear Slope Indicator dial until the white arrow on the Temperature Compensator points to the temperature of the solution. Read the percent electrode slope on the lower scale of the dial. Correct electrode operation is indicated by a percent slope between 95 and 97. If the slope is not within this range, see the troubleshooting check list in the centerfold.

figure 1

typical thiocyanate electrode calibration curve



In the direct measurement procedure, a calibration curve is constructed on semilogarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only three standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. The direct measurement procedures in this manual are given for concentrations in the region of linear electrode response. Low-level measurement procedures are given for measurements in the non-linear region.

using the electrode

units of measurement

Thiocyanate can be measured in units of moles per liter, parts per million, or any other convenient concentration unit.

sample requirements

The epoxy body is resistant to inorganic solvents. Common non-polar organic solvents, including methanol, ethanol, benzene, and acetonitrile, cause no damage at room temperature. Polar organic solvents slowly attack the epoxy; contact the Orion Technical Service Department for recommendations on using the electrode in other organic solvents.

Samples must be aqueous; they must not contain organic solvents. Samples and standards should be at the same temperature. A 1°C difference in temperature will give rise to about a 2% measurement error.

Interferences should be absent (see pages 16-18).

analytical procedures

Direct measurement is a simple, direct procedure for measuring a large number of samples. Only one meter reading is required for each sample. The temperature of samples and standards should be the same.

Direct measurement results can be verified by a known addition procedure. The known addition procedure involves adding a standard of known concentration to a sample solution. From the change in electrode potential before and after addition, the original sample concentration is determined.

Known addition is also a useful method for measuring occasional samples, as the preparation of a calibration curve is not required. As in direct measurement, any convenient concentration unit can be used.

direct measurement using 801A or 701 digital pH/mv meter

1. Prepare 100 ml 10^{-2} M, 10^{-3} M, and 10^{-4} M standards by serial dilution of the 0.1 M standard. Add 2 ml ISA per 100 ml standard prepared.
2. Place electrodes in the 10^{-3} M standard. Stir thoroughly. Set the meter reading to 000.0 by pressing the Restandardization button on the 801A or by turning the Calibration Control on the 701.

3. Rinse electrodes, blot dry, and place in the 10^{-4} M standard. Stir thoroughly. Wait for a stable reading and record.
4. Rinse electrodes, blot dry, and place in the 10^{-2} M standard. Stir thoroughly. Wait for a stable reading and record.
5. Plot the millivolt readings (linear axis) against concentration (log axis) on standard 4-cycle semilogarithmic paper. See the typical calibration curve in figure 1. The calibration curve may be extrapolated down to about 10^{-5} M.
6. Transfer 50 to 100 ml sample to a 150 ml beaker. Add 2 ml ISA per 100 ml sample.
7. Rinse electrodes, blot dry, and place in sample. Stir thoroughly. Record the millivolt reading. Determine the unknown concentration from the calibration curve.
8. Recalibrate every two hours. If the ambient temperature has not changed, repeat step 2 above. If the ambient temperature has changed, repeat steps 2 through 5 above.

low-level measurements using 801A or 701 digital pH/mv meter

1. Prepare a low-level ISA by diluting 20 ml ISA to 100 ml with distilled water. Add 1 ml low-level ISA to every 100 ml standard or sample for low-level measurements.
2. Prepare a 10^{-3} M standard by diluting 1 ml 0.1 M Orion standard to 100 ml. Add 1 ml low-level ISA.
3. Place 100 ml distilled water in a 250 ml beaker. Add 1 ml low-level ISA. Place electrodes in the water. Stir thoroughly. Add increments of the 10^{-3} M standard using the steps outlined in table 1, page 8. Measure the electrode potential after each increment and plot on semilogarithmic paper the potential (linear axis) against the concentration (log axis). See figure 1, page 5. Save final solution for checking calibration.
4. Rinse electrodes, blot dry, and place in sample. Stir thoroughly. Determine the concentration from the low-level calibration curve.
5. Prepare a new low-level calibration curve daily with fresh standard.

table 1

preparation for low-level measurements

Additions of 10^{-3} M standard to 100 ml distilled water, plus 1 ml low-level ISA. "A" is a 1 ml graduated pipet. "B" is a 2 ml pipet.

step	pipet	added volume	resulting molarity
1	A	0.1 ml	1.0×10^{-6}
2	A	0.1	2.0×10^{-6}
3	A	0.2	4.0×10^{-6}
4	A	0.2	6.0×10^{-6}
5	A	0.4	9.9×10^{-6}
6	B	2.0	2.9×10^{-5}
7	B	2.0	4.8×10^{-5}

direct measurement using 407A specific ion meter — moles per liter

1. Prepare 100 ml 10^{-2} M and 10^{-3} M standards by serial dilution of the 0.1 M standard. Add 2 ml ISA per 100 ml standard.
2. Set Function Switch to X^- . Place electrodes in the 10^{-3} M standard. Stir thoroughly. Adjust the meter needle to "1" (center scale) on the red logarithmic scale with the Calibration Control.
3. Rinse electrodes, blot dry, and place in the 10^{-2} M standard. Stir thoroughly. Turn the Temperature Compensator knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.
4. Transfer 50 to 100 ml sample to a 150 ml beaker. Add 2 ml ISA per 100 ml sample.
5. Rinse electrodes, blot dry, and place in the sample. Stir thoroughly. Multiply the meter reading on the red logarithmic scale by 10^{-3} M to determine sample concentration in moles per liter.

off-scale readings in sample

If the needle goes off-scale right, rinse the electrodes, blot dry, and place them in the 10^{-2} M standard. Adjust the Calibration Control until the needle points to "1" on the red logarithmic scale. Rinse the electrodes, blot dry, and replace in sample. Multiply the meter reading on the red logarithmic scale by 10^{-2} M to determine sample concentration in moles per liter, i.e., a reading of "1" on the meter is 10^{-2} M.

If the needle goes off-scale left, rinse the electrodes, blot dry, and place them in the 10^{-3} M standard. Adjust the Calibration Control until the needle points to "10" on the red logarithmic scale (full-scale right). Rinse the electrodes, blot dry, and replace in sample. Multiply the meter reading on the red logarithmic scale by 10^{-4} M to determine sample concentration in moles per liter, i.e., a reading of "1" on the meter is 10^{-4} M.

low-level measurements using 407A specific ion meter

1. Prepare a low-level ISA by diluting 20 ml ISA to 100 ml with distilled water. Add 1 ml low-level ISA to every 100 ml standard or sample.
2. Prepare 10^{-3} and 10^{-4} M standards by serial dilution of the 0.1 M standard.
3. Set Function Switch to X^- . Calibrate the meter by placing the electrodes in the 10^{-4} M standard and adjusting the meter needle to "1" (center scale) on the red logarithmic scale with the Calibration Control. Rinse electrodes, blot dry, and place in the 10^{-3} M standard. Stir thoroughly. Turn the Temperature Compensator knob until the meter needle reads "10" (full-scale right) on the red logarithmic scale.
4. Rinse electrodes, blot dry, and place them in the 10^{-4} M standard. Stir thoroughly. Adjust the Calibration Control until the meter reads "10" (full-scale right) on the red logarithmic scale.
5. Rinse electrodes, blot dry, and place in 100 ml distilled water. Stir thoroughly. Record the blank correction, "A", on the red logarithmic scale.
6. Transfer 50 to 100 ml sample to a 150 ml beaker.
7. Rinse electrodes, blot dry, and place in the sample. Stir thoroughly. Record the reading on the red logarithmic scale and subtract "A" from the reading. Multiply the result by 10^{-5} to find the sample concentration.

known addition

Known addition is convenient for measuring occasional samples because no calibration curve is needed. Because an accurate measurement requires that the concentration double because of the addition, sample concentration must be known to within a factor of three. Total thiocyanate concentration is measured in the absence of complexing agents or in the presence of a large excess (50 to 100 times).

using 407A specific ion meter

To measure an unknown sample, place electrodes in 100 ml of sample and add 2 ml ISA. Turn the Function Switch to X^- , set the Slope Indicator dial to the percent slope determined in the daily checkout, and turn the Temperature Compensator knob to the sample temperature. Follow steps 1 through 4 below.

To check the results of a direct measurement, leave the electrodes in 100 ml of sample and follow steps 1 through 5 below.

1. Set the needle to " ∞ " on the green increment scale by turning the Calibration Control.
2. Prepare a standard solution about 100 times as concentrated as the sample concentration by diluting the 0.1 M standard. Add 2 ml ISA to each 100 ml standard.
3. Pipet 1 ml standard solution into 100 ml sample. Stir thoroughly. Record the reading, Q, from the green increment scale.
4. To determine the original sample concentration, use the following equation:

$$C_0 = (Q/100)C_S$$

where:

C_0 = sample concentration

Q = reading from green increment scale

C_S = concentration of added standard

5. Compare the concentration obtained from the red logarithmic scale and the concentration obtained by the known addition check procedure. If they differ by more than $\pm 4\%$, the measurement is suspect. Check the measuring hints section, page 14, and the troubleshooting check list section, in the centerfold, before repeating the direct measurement procedure.

For example, suppose direct measurement gave 3.6×10^{-4} M as the sample concentration. After adding 1 ml standard, Q, from the increment scale, is 3.5. Then:

$$C_o = \frac{Q}{100} (C_s)$$

$$\begin{aligned} C_o &= \frac{3.5}{100} (10^{-2}) \\ &= 3.5 \times 10^{-4} \text{ M} \end{aligned}$$

The two methods agree within $\pm 4\%$, so the direct method is probably correct. A known addition result significantly higher than 3.5×10^{-4} M would indicate the presence of complexing agents in the sample.

using 801A or 701 digital pH/mv meter

To measure an unknown sample, place electrodes in 100 ml sample and add 2 ml ISA. Turn the Function Switch to X^- , set the Slope Indicator dial to the percent slope determined in the daily electrode check-out, and turn the Temperature Compensator knob to the sample temperature. Follow steps 1 through 4 below.

To check the results of a direct measurement, leave the electrodes in 100 ml sample and follow steps 1 through 5 below.

1. Turn the Function Switch of the meter to REL MV (801A) or EXP MV (701). Set the reading to 000.0 by pressing the Restandardization button on the 801A or by turning the Calibration Control on the 701.
2. Prepare a standard solution about 10 times as concentrated as the sample concentration by diluting 0.1 M standard. Add 2 ml ISA to each 100 ml standard.
3. Pipet 10 ml standard into the sample. Stir thoroughly. Record the potential difference, ΔE , directly from the meter.

troubleshooting check list

SYMPTOM	POSSIBLE CAUSES
Off-Scale or Over-Range Reading	defective meter electrodes not plugged in reference electrode junction is dry reference electrode not filled calibration control not turned far enough sample potential out of expanded scale of 701
Noisy or Unstable Readings (readings erratically changing)	defective meter reference electrode junction clogged wrong reference electrode meter or stirrer not grounded
Drift (reading slowly changing in one direction)	samples and standards at different temperatures incorrect reference filling solution membrane dirty or etched
Low Slope or No Slope	standards contaminated or incorrectly made standard used as ISA ISA not used
"Wrong Answer" (but calibration curve is "OK")	incorrect scaling of semi-log paper incorrect sign 407A function switch in wrong position 407A incorrectly calibrated incorrect standards complexing agents in sample interferences present

NEXT STEP

check meter with shorting strap
(see meter instruction manual)

reseat electrodes

hold cap and lift outer sleeve to expel a few
drops of filling solution

be sure inner and outer chambers of
double junction electrode are filled

continue turning the calibration control. It
provides 10 turns of coarse calibration range,
and is more difficult to turn after the 270° fine
tuning range has been exceeded.

recalibrate 701

check meter with shorting strap

clean reference electrode

do not use calomel or Ag/AgCl (frit or
fiber type) reference electrode

ground meter or stirrer

allow solutions to come to room
temperature before measurement

use recommended filling solution in outer
chamber of reference electrode (page 2)

polish membrane (page 16)

prepare fresh standards

use ISA!

use ISA!

plot millivolts on the linear axis. On the log axis,
be sure concentration numbers within each
decade are increasing with increasing concentration.

be sure to note sign of millivolt number correctly

set function switch to X⁻ position

set first standard to center scale reading with the
calibration knob, second standard to the end of the
scale with the temperature knob

prepare fresh standards

use known addition, or remove complexing agents

remove interferences

4. From table 2 find the value, Q , that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_0 = QC_s$$

where:

C_0 = sample concentration

Q = reading from known addition table

C_s = concentration of added standard

5. Compare the concentration obtained from the calibration curve and the concentration obtained from the known addition check procedure. If they differ by more than $\pm 4\%$, results are suspect. A known addition result significantly larger than a direct measurement indicates the presence of complexing agents in the sample. Check the measuring hints section below, and the troubleshooting check list section in the centerfold.

For example, suppose direct measurement gave 8.29×10^{-3} M as sample concentration. After adding 10 ml 0.1 M standard, the potential change is 17.8 mv. The corresponding Q value is 0.0834. Sample concentration is:

$$C_0 = QC_s$$

$$C_0 = 0.0834 \times 0.1$$

$$= 8.34 \times 10^{-3} \text{ M}$$

The two methods agree within $\pm 4\%$, so the direct method is probably correct.

measuring hints

- For maximum precision allow all standards and samples to come to ambient temperature before measurement.
- Stir sample and standards during measurement. For best results stir at a rate that will not cause a vortex. Magnetic stirrers are recommended, but some models generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard, or styrofoam between the stirrer and heater.
- Rinse the electrodes and blot dry with a clean, dry tissue between measurements to prevent solution carryover.

table 2

known addition table, values for Q vs. ΔE at 25°C
for 10 ml added to 100 ml

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
-5.0	0.297	10.0	0.160	-20.0	0.0716	30.0	0.0394
5.1	0.293	10.2	0.157	20.2	0.0707	30.2	0.0390
5.2	0.288	10.4	0.154	20.4	0.0698	30.4	0.0386
5.3	0.284	10.6	0.151	20.6	0.0689	30.6	0.0382
5.4	0.280	10.8	0.148	20.8	0.0680	30.8	0.0378
5.5	0.276	11.0	0.145	21.0	0.0671	31.0	0.0374
5.6	0.272	11.2	0.143	21.2	0.0662	31.2	0.0370
5.7	0.268	11.4	0.140	21.4	0.0654	31.4	0.0366
5.8	0.264	11.6	0.137	21.6	0.0645	31.6	0.0362
5.9	0.260	11.8	0.135	21.8	0.0637	31.8	0.0358
6.0	0.257	12.0	0.133	22.0	0.0629	32.0	0.0354
6.1	0.253	12.2	0.130	22.2	0.0621	32.2	0.0351
6.2	0.250	12.4	0.128	22.4	0.0613	32.4	0.0347
6.3	0.247	12.6	0.126	22.6	0.0606	32.6	0.0343
6.4	0.243	12.8	0.123	22.8	0.0598	32.8	0.0340
6.5	0.240	13.0	0.121	23.0	0.0591	33.0	0.0336
6.6	0.237	13.2	0.119	23.2	0.0584	33.2	0.0333
6.7	0.234	13.4	0.117	23.4	0.0576	33.4	0.0329
6.8	0.231	13.6	0.115	23.6	0.0569	33.6	0.0326
6.9	0.228	13.8	0.113	23.8	0.0563	33.8	0.0323
7.0	0.225	14.0	0.112	24.0	0.0556	34.0	0.0319
7.1	0.222	14.2	0.110	24.2	0.0549	34.2	0.0316
7.2	0.219	14.4	0.108	24.4	0.0543	34.4	0.0313
7.3	0.217	14.6	0.106	24.6	0.0536	34.6	0.0310
7.4	0.214	14.8	0.105	24.8	0.0530	34.8	0.0307
7.5	0.212	15.0	0.103	25.0	0.0523	35.0	0.0304
7.6	0.209	15.2	0.101	25.2	0.0517	36.0	0.0289
7.7	0.207	15.4	0.0997	25.4	0.0511	37.0	0.0275
7.8	0.204	15.6	0.0982	25.6	0.0505	38.0	0.0261
7.9	0.202	15.8	0.0967	25.8	0.0499	39.0	0.0249
8.0	0.199	16.0	0.0952	26.0	0.0494	40.0	0.0237
8.1	0.197	16.2	0.0938	26.2	0.0488	41.0	0.0225
8.2	0.195	16.4	0.0924	26.4	0.0482	42.0	0.0216
8.3	0.193	16.6	0.0910	26.6	0.0477	43.0	0.0206
8.4	0.190	16.8	0.0897	26.8	0.0471	44.0	0.0196
8.5	0.188	17.0	0.0884	27.0	0.0466	45.0	0.0187
8.6	0.186	17.2	0.0871	27.2	0.0461	46.0	0.0179
8.7	0.184	17.4	0.0858	27.4	0.0456	47.0	0.0171
8.8	0.182	17.6	0.0846	27.6	0.0450	48.0	0.0163
8.9	0.180	17.8	0.0834	27.8	0.0445	49.0	0.0156
9.0	0.178	18.0	0.0822	28.0	0.0440	50.0	0.0149
9.1	0.176	18.2	0.0811	28.2	0.0435	51.0	0.0143
9.2	0.174	18.4	0.0799	28.4	0.0431	52.0	0.0137
9.3	0.173	18.6	0.0788	28.6	0.0426	53.0	0.0131
9.4	0.171	18.8	0.0777	28.8	0.0421	54.0	0.0125
9.5	0.169	19.0	0.0767	29.0	0.0417	55.0	0.0120
9.6	0.167	19.2	0.0756	29.2	0.0412	56.0	0.0115
9.7	0.165	19.4	0.0746	29.4	0.0408	57.0	0.0110
9.8	0.164	19.6	0.0736	29.6	0.0403	58.0	0.0105
9.9	0.162	19.8	0.0726	29.8	0.0399	59.0	0.0101

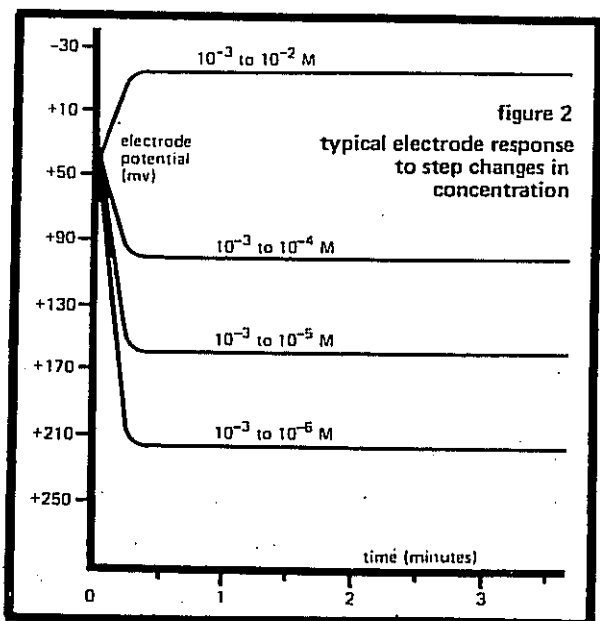
electrode characteristics

electrode response

Electrode potential plotted against thiocyanate concentration on semilogarithmic paper results in a straight line with a slope of about 57 mv per decade change in concentration. See figure 1, page 5.

The electrode exhibits good time response (99% response in one minute or less) for thiocyanate concentrations above 5×10^{-5} M. See figure 2.

If the electrode response drops off or the potential reading becomes drifts, the membranes may need repolishing. Use the special Orion polishing strips, Cat. No. 94-82-01. To polish, cut off a one-inch length of paper and wet the frosted side. Using a circular motion, polish the electrode sensing element for about thirty seconds. Rinse and soak in a standard solution for about five minutes before use.



interferences

High levels of ions which form very insoluble salts of silver may deposit a layer of the salt on the membrane, causing electrode malfunction. In addition, strongly reducing solutions may form a surface layer of silver. In either case, restore performance by polishing.

Mercury ion must be absent from samples.

Measurements can be made in solutions containing oxidizing agents such as MnO_4^- .

Table 3 gives the maximum allowable concentration of the more common interfering ions expressed as the ratio of the interfering ion concentration (moles per liter) to the sample thiocyanate concentration (moles per liter). If the ratio is exceeded, the measurement will be in error. If the ratio is less than that listed in the table, neither the accuracy of the measurement nor the surface of the electrode membrane will be affected.

table 3

maximum allowable ratio of interfering ion to thiocyanate (moles/moles)

interference	maximum ratio
(a) S^-	10^{-6}
I^-	10^{-6}
Br^-	3×10^{-3}
(a) CN^-	7×10^{-3}
S_2O_3^-	0.13
Cl^-	20
(b) OH^-	100

(a) Sulfide and cyanide may be removed by adding a nickel (+2) solution.

(b) Hydroxide interference may be removed by acidifying to pH 4 with 1 M HNO_3 .

For example: What is the maximum level of bromide tolerable in a sample whose thiocyanate concentration is 10^{-3} M? From table 3 the maximum ratio is:

$$\frac{[\text{Br}^-]}{[\text{SCN}^-]} = 3 \times 10^{-3}$$

$$\begin{aligned} \text{or } [\text{Br}^-] &= 3 \times 10^{-3} [\text{SCN}^-] \\ &= 3 \times 10^{-6} \text{ M maximum bromide concentration for no interference} \end{aligned}$$

limits of detection

The lower limit of detection is determined by the very slight water solubility of the membrane. At low levels, electrodes respond to thiocyanate ions in the sample as well as to ions dissolved from the membrane. The dashed line in figure 1, page 5, shows the theoretical linear response compared to actual response (full line); the discrepancy between the curves is due to response to the dissolved membrane. For measurements in the nonlinear region below 10^{-5} M, a low-level procedure is recommended.

reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the electrode's operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to $\pm 2\%$ can be obtained.

complexation

Thiocyanate ions form complexes with some metal ions. Since the electrode responds only to free thiocyanate ions, the presence of any complexing agents lowers the measured concentration. Table 4 lists the levels of complexing metals causing a 10% error at several thiocyanate concentrations.

Total thiocyanate concentration in the presence of a large excess (by a factor of at least 50 to 100) of complexing agent can be measured by the known addition method (pages 10 - 15).

table 4

maximum levels of complexing agents for a 10% error

complexing agent	10^{-4} M	10^{-3} M	10^{-2} M SCN^-
Ag^+	10^{-4} M	10^{-3} M	10^{-2} M
Cu^+	10^{-4}	10^{-3}	10^{-2}
Cu^{++}	2×10^{-2}	2×10^{-2}	3×10^{-2}
Fe^{+++}	5×10^{-3}	5×10^{-3}	8×10^{-3}

electrode storage

Rinse electrode, blot dry, and replace the protective rubber cap for storage.

temperature effects

Changes in temperature will cause the electrode response curve to both shift and change slope. Table 5 indicates the variation of theoretical slope with temperature. At the 10^{-3} M thiocyanate level, a 1°C change in temperature gives rise to a 2% error. Samples and standards should be at the same temperature: for convenience, room temperature.

table 5

values of theoretical slope vs. temperature

$T^{\circ}\text{C}$	S	$T^{\circ}\text{C}$	S
0	54.20	30	60.15
10	56.18	40	62.13
20	58.16	50	64.11
25	59.16		

theory of operation

The thiocyanate electrode consists of a silver thiocyanate/silver sulfide membrane bonded into the tip of an epoxy electrode body. When the membrane is in contact with a thiocyanate solution, silver ions dissolve from the membrane surface and the electrode develops a potential due to the silver ion concentration. This concentration is, in turn, determined by the sample thiocyanate ion concentration. This potential is measured against a constant reference potential with a digital pH/mv meter or specific ion meter. The measured potential corresponding to the level of the thiocyanate ion in solution is described by the Nernst equation:

$$E = E_0 - S \log (A)$$

where:

E = measured electrode potential

E_0 = reference potential (a constant)

A = thiocyanate ion level in solution

S = electrode slope

The level of thiocyanate ion in solution, A , is the activity or "effective concentration". The thiocyanate activity, A , is related to the thiocyanate ion concentration of free thiocyanate ions, C_f , by the ionic activity coefficient, γ :

$$A = \gamma C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength.

Ionic strength is defined as:

$$\text{ionic strength} = \frac{1}{2} \sum C_i Z_i^2$$

where:

C_i = concentration of ion i

Z_i = charge of ion i

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration.

Ionic strength adjustor (ISA) is added to all standards and samples so that the background ionic strength is high and constant relative to variable concentrations of thiocyanate. For the thiocyanate electrode, NaNO_3 is the recommended ISA. Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to thiocyanate.

ordering information

945800	thiocyanate electrode
900200	double junction reference electrode
900002	inner chamber reference electrode filling solution (5 2-oz bottles)
900003	outer chamber reference electrode filling solution (5 2-oz bottles)
920014	microsample dish
948201	polishing strips
040720	model 407A specific ion meter with carrying case
040721	model 407A specific ion meter without carrying case
070100	model 701 digital pH/mv meter
080110	model 801A digital pH/mv meter

specifications

concentration range	1 M to 5×10^{-6} M
pH range	pH 2 to 10; pH <4 is to recommended to avoid OH^- interference
temperature range	0 to 50°C continuous use 51 to 100°C intermittent use
electrode resistance	<100 K ohms
reproducibility	$\pm 2\%$
minimum sample size	3 ml in a 50 ml beaker, 0.3 ml in Orion Microsample Dish (Cat. No. 92-00-14)
storage	dry, with protective rubber cap in place
size	length: 13.9 cm diameter: 12 mm cap diameter: 16 mm cable length: 75 cm

specifications subject to change without notice.

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