pHOENIX ELECTRODE COMPANY
SURFACTANT ELECTRODE
INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

Introduction

The pHoenix Surfactant Electrode indicates the potentiometric endpoint when titrating anionic or cationic surfactants in solution. Titration procedures for manual titrations are discussed in this manual, though adaptation to automatic titration techniques is quite simple. The electrode comes packaged with one 50 ml bottle of 0.05M Hyamine 1622 (benzethonium chloride) titrant, one 50 ml bottle of 0.01M sodium lauryl sulfate (sodium dodecyl sulfate) titrant, and one 50 ml bottle of sample additive, diluted Triton X-100.

Required Equipment

1. A pH/mV meter, either line operated or portable.

2. A hand controlled delivery system, such as a 10 ml pipet or burette.

3. The pHoenix Surfactant Electrode, Cat. No. SUR1501 (reference electrode necessary), or the pHoenix Surfactant Combination Electrodes, Cat. No. SUR1502 (glass), and SUR1503 (epoxy).

4. The pHoenix Single Junction Reference Electrode, Cat. No. 5731428 (for use with SUR1501).

Required Solutions

1. Distilled or deionized water to prepare all solutions and standards.

2. Titrant for the titration of anionic surfactants is pHoenix Hyamine 1622, 0.05M, Cat. No. SURAS01. To prepare this titrant from your own laboratory stock, add 22.405 grams of Hyamine 1622 and 5 ml of 1 M NaOH to a 1 liter volumetric flask about half full of deionized water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

3.

Titrant for the titration of cationic surfactants is pHoenix 0.01M Sodium Lauryl Sulfate (SLS), Cat. No. SURAS02. To prepare this titrant from your own laboratory stock, add 2.883 grams sodium lauryl sulfate (SLS) to a one liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

4. pHoenix Sample Additive, diluted Triton X-100, Cat. No. SURIS01, keep electrodes clean when added to all samples. To prepare, add 10 ml of reagent-grade Triton X-100 to a one liter volumetric flask about half full of distilled water. Cap the flask and invert several times to mix the solution.

5. pHoenix Electrode Filling Solution, 4M KCl (with Ag^+), Cat. No. R001011, for filling the reference chamber of the electrode.

6. pH Adjuster Solutions for adjusting the pH of both anionic and cationic surfactants (0.01M HCl) and polyacrylates (0.1 M NaOH).

7. Electrode Rinse Solutions consisting of about 50 ml 0.1M HCl diluted to 1000 ml for acidic rinse (anionic or cationic surfactant analysis) and 50 ml 0.1M NaOH diluted to 1000 ml for alkaline rinse (polyacrylate analysis).

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap(s) covering the electrode tip(s) and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode or the reference electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the surfactant membrane.

Prepare 0.0001M SLS by diluting 1 ml of the 0.01M SLS to 100 ml with distilled water. Prior to first usage, or after long-term storage, soak the tip of the surfactant electrode in 0.0001M SLS for 10 minutes before using the electrode each day. Use fresh solution daily. The electrode is now ready for use.

Connect the electrode(s) to the proper terminal(s) as recommended b

y the meter manufacturer.

If the stock solution becomes cloudy or contaminated in any way, discard it.

Titrant Preparation

Based on the recommendations found in **Required Solutions**, select an appropriate titrant. Determine the concentration of titrant needed for the analysis from Table 1.

TABLE 1: Recommended Titrant Concentrations

Recommended Titrant Concentration (M)	Expected Sample Concentration (M)
0.05	0.050 to 0.001
0.005	0.001 to 0.0001
0.001	0.0001 to 0.00001

The titrant concentration may need to be adjusted depending on the concentration of the sample and the method of titration in use. Use the formula:

$$C_t = \frac{C_s \times V_s}{V_t}$$

where: C_t = concentration of titrant

C_s = concentration of sample

V_s = volume of sample

V_t = volume of titrant

For example, for the titration of anionic surfactants, dilute the 0.05M Hyamine 1622 solution provided to the appropriate concentration as calculated above.

Titrate against a known concentration of SLS to standardize the titrant. Calculate the exact concentration of the titrant using the same formula given above.

Units of Measurement

Any convenient unit of measurement may be used for the result. Units may be chosen for samples measured in volume or weight.

If doing the titrations with an automatic titrator, note whether sp

ecific units must be entered for the titrant and/or specific units are required for the result.

Measuring Hints

The sensing membrane is normally subject to water uptake and might appear milky. This has no effect on performance.

All samples and standard should be at ambient temperature for preci se measurement.

Constant, but not violent, stirring is necessary for accurate measu rement. Slow stirring is recommended to avoid foaming.

Always rinse the electrode tip(s) with the slightly acidic (or alka line) rinse solution described in **Required Solutions** and blot dry w ith a fresh tissue between titrations to prevent solution carryover.

Check the electrode for air bubbles adhering to the membrane surfac e after immersion in solution. Agitate the electrode gently to rem ove any air bubbles.

A slow or sluggish electrode response may indicate surface contamin ation of the electrode membrane. Soak the electrode tip in distill ed water for about 5 minutes to clean the membrane. Rinse the memb rane and soak in 0.0001M SLS for about 5 minutes to restore performance.

The electrode should be reconditioned daily before storage as descr ibed in **Cleaning, Reconditioning, and Storage**.

Sample Requirements

To help keep the electrode clean and working properly, add sample a dditive, diluted Triton X-100, to all samples. For every 50 ml of sample, use 1 ml of sample additive.

Samples should be diluted to approximately 10^{-5} to 10^{-4} M to help pr eserve electrode life, help avoid foaming during the titration, and help improve long term results.

Adjust the pH of the sample depending on the method being used.

Anionic surfactants, as well as sulfated and sulfonated surfactants , may be titrated with Hyamine 1622. Adjustment to pH 2.5-4.5 shou ld be done by addition of 0.01M HCl.

Polyacrylates should be adjusted to pH 10-11 with 0.1M NaOH before analysis.

Cationic surfactants should be titrated with an anionic reagent, su

ch as sodium lauryl sulfate, after acidification to pH 3 with 0.01M HCl.

ANALYTICAL PROCEDURES

Sample Analysis

For potentiometric endpoint determination, the surfactant electrode is used as an endpoint indicator. An example of the titration procedure is illustrated using the analysis of an anionic surfactant as an example.

1. Using the acid rinse solution, rinse the surfactant electrode and blot dry with a soft, lint-free tissue before the titration. Fill the single junction reference electrode, or the reference chamber of the combination electrode with fresh filling solution, pHoenix Cat. No. R001011, to a level just below the fill hole.

2. Assure that the electrodes are plugged into the pH/mV meter and that the meter is in the mV mode. To prevent air entrapment, mount the electrode at a 20^{o} angle from the vertical. Using a pipet, add 50 ml of the unknown sample to a 150 ml beaker. Add 3 ml of 0.01M HCl and 1 ml of the sample additive, diluted Triton X-100. Place the beaker on a magnetic stirrer, and start stirring at a constant, but moderate, rate. Lower the electrodes into the solution so that the tips are completely covered and wait until the mV reading is stable, drift is + 1 to 2 mV/minute, before adding any titrant. Remove any bubbles by re-dipping electrode.

3. Add 0.05M Hyamine 1622 titrant to a 10 ml buret until filled. Once mV stability has been reached, add the titrant in 0.5-1.0 ml increments at the beginning of the titration, and in increments of 0.1-0.25 ml in the region of the endpoint. The endpoint is at that volume of titrant where the potential changes dramatically with the slightest addition of titrant. The electrode potential should be recorded after each addition of titrant. Continue titrating until 1 or 2 ml past the endpoint. On standard coordinate graph paper, plot milliliters of titrant added versus mV reading. The endpoint is the point of greatest inflection. Calculate the unknown surfactant concentration:

$$C_{unknown} = \frac{C_{titrant} \times V_{titrant}}{V_{unknown}}$$

where: $C_{unknown}$ = concentration of the unknown

$C_{titrant}$ = concentration of the titrant

$V_{titrant}$ = volume of the titrant in milliliters

$V_{unknown}$ = volume of the unknown in milliliters

Depending on the sample concentration and on the method used, this basic procedure may need to be modified.

ELECTRODE CHARACTERISTICS

Electrode Response

The time for the analysis may vary, depending on the sample, the titrant, the method, and the equipment used. The average time for manual titration of anionic surfactants is 2-5 minutes.

Temperature

The surfactant electrode should be used in the operating range of 0-40°C. The membrane may be permanently destroyed at other temperatures.

Reproducibility

The reproducibility of the surfactant electrode will depend heavily on the good laboratory practices of the technician, but will usually be less than 1% with manual techniques and less than 0.5% with automatic techniques.

Limit of Detection

For anionic surfactants, the lower limit of detection is -10^{-5}M. Good laboratory practice and selection of titrant may allow lower levels of detection for some sample types.

pH Effects

The surfactant electrode has an operating pH range of 2-12. Use at other pH values can adversely affect the membrane.

For anionic, sulfated and sulfonated surfactants, the analysis should take place at a pH between 2.5 and 4.5.

For other samples, the pH range may need to be adjusted. Polyacrylates require adjustment to pH 10, for example.

Interferences

Interferences may be caused by any organic anion or cation which chemically resembles the species of interest.

Cleaning, Reconditioning, and Storage

Acidic (or alkaline) rinse solution should be used to rinse the electrode between measurements.

To recondition an electrode when the response had become noisy, sluggish, or irreproducible, soak in slightly acidic (or alkaline) distilled water for one hour, followed by 10^{-4}M SLS solution for 10 minutes.

The pHoenix Surfactant Electrode may be stored in 0.0001M SLS for short periods of time. For storage over 3 weeks, rinse and dry the membrane element and cover the tip with any protective cap shipped with the electrode(s). The reference portion of the combination electrode (or the reference chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber sleeve placed over the filling hole.

Electrode Life

The surfactant electrode will last six months in normal laboratory use. Continuous titrations on an automatic sample changer might shorten operational lifetime to several months. In time, the response time will increase and the titration endpoint breaks will not be as sharp. At this point, titration is impossible and electrode replacement is required.

ELECTRODE THEORY

Electrode Operation

The surfactant electrode is an endpoint indicator for the potentiometric determination of anionic surfactants in solution. Cationic surfactants may also be determined with this electrode.

The reaction that occurs when a sulfated or sulfonated anionic surfactant is titrated with Hyamine 1622 is as follows:

$$R - SO_3^-Na^+ + R_4N^+Cl^- \; 6 \; RSO_3NR_4 + NaCl$$

where: R = surfactant carbon chain

R_4N^+ = Hyamine ion

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of the problem through checking each of the system components in turn: the instrumentation, the electrodes, the reagents, the sample, and the technique.

Instrumentation

For manual titration, assure that the mV meter is operating correctly and that the glassware is clean. Most meters are provided with an instrument check-out procedure in the instruction manual and a shorting strap for ease of troubleshooting. Consult the manual for complete instructions and verify the instrument operates as indicated.

Clean glassware will drain clean... when rinsed with distilled or deionized water, the water does not bead on the inside walls of the glassware.

If using automatic titration instrumentation, check the instrument instruction manuals/operators' handbook for the correct check-out procedure or call the instrument manufacturer for the check-out procedure.

Electrodes

1. Using distilled or deionized water, rinse the electrodes thoroughly.

2. Titrate a known standard to check the electrode's operation.

3. If the electrode fails to respond as expected, see the section **Measuring Hints.** Repeat Step 2.

4. If the electrode still fails to respond as expected, substitute another surfactant electrode that is known to be in good working order for the questionable electrode. If the problem persists, try the same routine with a working reference electrode.

5. If the problem persists the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. See **Reagents, Sample, and Technique** sections below.

6. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:

- Clean and rinse the electrode(s) thoroughly.
- Prepare the electrode(s) properly.
- Use the proper filling solution, titrant, and sample additives.
- Adjust the pH of the solution according to the method being used for the analysis.
- Measure correctly and accurately.
- Review **TROUBLESHOOTING HINTS**.

Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the reagent solutions. If in doubt about the credibility of any of the reagents, prepare them again. Errors may result from contamination of the titrant, incorrect dilution, poor quality distilled/ deionized water or additive, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode or the reference electrode if the electrodes work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. See **Sample Requirements**, **pH Effects**, and **Interferences**.

Technique

Be sure that the electrodes' limit of detection has not be exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again. Reread **GENERAL PREPARATION**, **ANALYTICAL PROCEDURES**, and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call pHoenix Electrode Company at 1-800-522-7920 and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective instrumentation	check instrument by using instrument check-out procedure
	electrode(s) not plugged in properly	unplug electrode(s) and reseat
	no reference electrode	use reference electrode described in **Required Equipment**
	reference electrode not filled	add filling solution to the the reference electrode
	air bubble on membrane	remove bubble by redipping electrode
	electrode(s) not in solution	put electrode(s) in sufficient solution
Noisy or Unstable Readings (readings continuously or randomly changing)	defective instrument	check instrument using instrument check-out procedure
	air bubble on membrane	remove bubble by redipping electrode
	instruments not properly grounded	ground instruments
	reference electrode junction clogged	clean out junction
	defective electrode(s)	replace electrode(s)
	electrode exposed to interferences	soak electrode in 0.0001 M SLS
	outer filling solution level too low	fill electrode to level just below

		the fill hole
No Endpoint	sample too dilute or titrant solution too concentrated	make sure that the Found sample concentration is greater than 10^{-5}; dilute titrant solution
	sample too concentrated or titrant too dilute	dilute sample or select a different titrant concentration
Poor Reproducibility	sample not completely added, diluted, or poor pipetting	when adding sample or diluent to beaker, avoid splashing on the inside walls of the beaker; use an automated pipet for best results when measuring volumes
	sample carryover	rinse electrode(s), stirrer, and delivery tip thoroughly between measurements; blot excess rinse water
"Incorrect Answer"	incorrect standards	prepare fresh standards
	sample carryover	rinse electrode(s) thoroughly between titrations

SPECIFICATIONS

Minimum level of pure SLS which can be titrated:	10^{-5}M
Maximum level of pure SLS titrable with 0.05M Hyamine:	5 x 10^{-2}M
pH Range:	2-12
Temperature Range:	0-40°C
Resistance:	100 Mohms
Size:	110 mm length 12 mm diameter 1 m cable length
Reproducibility:	±l%
Storage:	store in 0.0001 M SLS or store dry

ORDERING INFORMATION

P/N	DESCRIPTION
SUR1501	Surfactant Electrode, mono (reference electrode necessary), PVC body
SUR1502	Surfactant Electrode, combination, glass body
SUR1503	Surfactant Electrode, combination, epoxy body
5731428	Reference Electrode, single junction, epoxy body
SURAS01	Surfactant Titrant, 0.05M Hyamine 1622
SURAS02	Surfactant Titrant, 0.01M Sodium Lauryl Sulfate (SLS)
SURIS01	Surfactant Sample Additive, dilute Triton X-100
R001011	Reference Electrode Filling Solution, 4M KCl (with Ag^+)

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