Van London Co.

"When Accuracy Matters"

Surfactant Electrode

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GENERAL INSTRUCTIONS

Introduction

The Van London Co. 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 & Solution

1. A Titrator or Ion Meter.
2. Deionized or distilled water for standard and titrant preparation.
3. An automatic or hand-controlled delivery system, such as a 10-ml pipet or burette.
4. Surfactant Electrode (supplied in electrode box).
5. Reference Filling Solution, R001013 125ml (30ml supplied in electrode box).
6. Titrant for the titration of anionic surfactants, SURAS01, 125ml.
7. Titrant for the titration of cationic surfactants, SURIS02.
8. Sample Additive is diluted Triton X-100 to keep electrodes clean when added to all samples.
9. pH Adjuster Solutions for adjusting the pH of both anionic and cationic surfactants (0.1M HCl) and polyacrylates (0.1M NaOH).
10. 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 small black shipping cap from the bottom of the electrode and lower the rubber insert covering the filling hole of the reference chamber to expose the fill hole. Fill the electrode with the reference filling solution shipped with the electrode to a level just below the fill hole. 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. Prior to first usage, or after long term storage, immerse the electrode in deionized water for thirty minutes. Connect the electrode to the meter with the BNC connector at the end of the electrode cable as recommended by the meter manufacturer. To prevent air entrapment, use the electrode at a 20° angle from the vertical.

Titrant Preparation

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

Measuring Hints
1. The sensing membrane is normally subject to water uptake and might appear milky or white. This has no effect on performance.
2. Constant, but not violent, stirring is necessary for accurate measurement. Slow stirring is recommended to avoid foaming.
3. Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove any air bubbles.
4. A slow or sluggish electrode response may indicate surface contamination of the electrode membrane. Soak the electrode tip in deionized water for about five minutes to clean the membrane.

Sample Requirements
1. To help keep the electrode clean and working properly, add sample additive, diluted Triton X-100, to all samples. For every 50 ml of sample, use 1 ml of sample additive.
2. Samples should be diluted to help preserve electrode life, help avoid foaming during the titration, and help improve long term results.
3. Anionic surfactants, as well as sulfated and sulfonated surfactants, may be titrated with Hyamine 1622. Adjustment to pH 2.5-4.5 should be done by addition of 0.01M HCl.
4. Polyacrylates should be adjusted to pH 10-11 with 0.1M NaOH before analysis.
5. Cationic surfactants should be titrated with an anionic reagent, such as Sodium Lauryl Sulfate, after acidification to pH 3 with 0.01M HCl.
6. All samples and standards must be aqueous. They must not contain organic solvents.

ANALYTICAL PRCEDURES

Sample Analysis by Manual Titration
(For an Automatic Titrator, follow the Titrator manual recommendations and settings)

The surfactant electrode is used as an endpoint indicator during titration. 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, lintfree tissue before the titration.
2. 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 electrode into the solution so that the tip is 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:

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

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.

1. The sensing membrane is normally subject to water uptake and might appear milky or white. This has no effect on performance.
2. Constant, but not violent, stirring is necessary for accurate measurement. Slow stirring is recommended to avoid foaming.
3. Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove any air bubbles.
4. A slow or sluggish electrode response may indicate surface contamination of the electrode membrane. Soak the electrode tip in deionized water for about five minutes to clean the membrane.
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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^{o}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 ppm. 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) deionized water for about one hour to clean the membrane.

The Van London Co. Surfactant Electrode may be stored in deionized water 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.

TROUBLESHOOTING HINTS

*Remember to remove the black protective shipping cap on the bottom of the electrode and expose the refill hole underneath the electrode cap. Fill the electrode with the Reference Filling Solution shipped with the electrode to a level just below the fill hole.

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 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 in0.0001 M SLS
	outer filling solution level too low	fill electrode to level just below the fill hole
No Endpoint Found	sample too dilute or titrant solution too concentrated	make sure that the sample concentration is greater than 10^{-5}M; 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:	5×10^{-2}M
pH Range:	2-12
Temperature Range:	0-40^{o}C
Resistance:	100 Mohms
Size:	110 mm length 12 mm diameter 1 m cable length
Reproducibility:	$\pm$l%
Storage:	store in 0.0001 M SLS or store dry

ELECTRODE THEORY

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