Determination of QAC surfactants by ISE auto titrator

Keywords
Surfactant, cationic surfactant, quaternary ammonium compounds, QACs, Quats, quaternary ammonium chloride, precipitation titration, quaternary ammonium halides, benzalkonium chloride, BAC, Hyamine, cetrimonium bromide, antimicrobial, disinfectant, biocide, sanitizer, cleaner

Introduction

Quaternary ammonium compound (QAC) surfactants are a common active ingredient in antimicrobial formulations. QACs can be titrated directly with a standard sodium lauryl sulfate (SLS) solution in aqueous acidic solution without the need for a two-phase procedure using an organic solvent. The anionic SLS titrant reacts with the cationic QAC to form a precipitate. The endpoint is sensed by the surfactant ion selective electrode (ISE), such as the one in the Thermo Scientific™ Orion Star™ T9305 Ion Titrator Surfactant Kit. The titrator automatically calculates results and stores the data.

Materials

Equipment

Orion Star T9305 Ion Titrator Surfactant Kit

Solutions

Sodium lauryl sulfate (SLS) titrant, 0.008N (0.008M) – purchased or prepared. Borate buffer solution, pH 9.5 - purchased or prepared. 1% Tween 20 solution. Isopropyl alcohol (IPA), 95+%. Thermo Scientific™ Orion™ pH Electrode Filling Solution for ROSS™ electrodes (Cat. No. 810007) for reference electrode – do not use Orion 900003 that comes with the electrode. Reagent grade water (RGW). Optional: Thermo Scientific™ Orion™ Hyamine 1622 Titrant, 0.05 M, for standardization (Cat. No. 654201).

Note: Use reagent grade chemicals wherever possible for best results. Before working with any chemical, review the safety data sheet (SDS) to identify potential hazards. Observe the recommendations for handling, storage, exposure controls, and personal protection.

Determination of QAC surfactants by automatic ISE titration

Solutions preparation

- SLS Titrant, 0.008M (8 mM) – weigh accurately 2.42 +/- 0.01g of SLS to the nearest 0.1 mg. Transfer to a clean, dry 1L volumetric flask. Dissolve in about 200 mL of RGW, then dilute to volume (1L) with RGW.
- Borate Buffer Solution (pH 9.5) – Dissolve 1.5g of sodium borate decahydrate ($Na_2B_4O_7 \bullet 10\ H_20$) and 1.0 g of boric acid (H_3BO_3) into about 200 mL of RGW with stirring. Adjust the pH to 9.5 with 1N sodium hydroxide (NaOH). Transfer to a 1 L volumetric flask and dilute to volume (1L) with RGW. Note: Do not use a carbonate buffer instead of the borate buffer.
- 1% Tween 20 Solution – Dissolve 1g of pure Tween 20 into 100 mL of RGW. Mix gently.
- Buffer Mix – place 700 mL RGW into a 1000 mL beaker. Add 100 mL of borate buffer solution, 10 mL of 1% Tween 20 solution, and 10 mL of IPA. Mix gently. This amount of buffer mix will be sufficient for 10 titrations. Double the recipe to run 20 titrations, etc. Preparing a buffer mix instead of adding reagents separately makes sample preparation quick and convenient.
- Conditioning solution - Dispense 1 mL of titrant into a 100 mL beaker. Add RGW to the 50 mL mark. Prepare fresh daily. Condition surfactant electrode daily, before samples and between samples, if needed.

Method

Titrator setup

Connect the surfactant electrode, the prepared reference electrode, and the stirrer probe to the titrator. If not previously done, import the preprogrammed QAC by ISE method into the titrator from the Methods screen or program the method according to the Method Program section (to the right). Rinse and fill the 20 mL burette with titrant. See the titrator user manual for details on setting up the titrator.

If bubbles are visible in the tubing, dispense titrant (from the Burette screen) until the bubbles have been expelled. Tap the tubing to dislodge bubbles. Consider standardizing the titrant before titrating samples. See Titrant section of this note (below) for details.

Method Program

Load or copy the method into the titrator.

QAC by ISE Method	
Electrode	
Electrode type	ISE
ISE type	Surfacant
Electrode name	9342BN + 900200
Titrant	
Titrant name	SLS
Titrant ID	Edit as desired
Conc. input mode	Manual
Titrant concentration	8.00 mM*
Titration	
Titration technique	Equivalence point
Number of endpoints	1
Display units	mV
Titration type	Direct
Blank required	No
Titration units	% w/w
Titraion reaction ratio	1
Sample mol. wt.	350**
Sample amount	Variable weight
Pre-dose titrant volume	0 mL
Max total titrant volume	9 mL
Titration process control	User defined
ΔE	15 mV
ΔV_{min}	0.1 mL
ΔV_{max}	0.5mL
dE/dt	10 mV/min
t_{min}	2 seconds
t_{max}	5 seconds
Threshold	50 mV/mL
Precision level	NA
Pre-stir duration	5 seconds
Stir speed	Fast
Sample ID	Manual
Notes	

*Choose units of “mM”
**Edit based on QAC. For benzalkonium chloride = 350

Titrator and electrode care

Refer to the titrator and electrode user manuals for details on cleaning, storage, and maintenance recommendations to keep the titrator and electrode performing well. Main points for care are summarized below.

Daily care

- If bubbles are visible in the titrator tubing, dispense titrant until bubbles have been expelled. Tap tubing to dislodge bubbles that stick.
- If the level of the green inner fill solution in the reference electrode has dropped lower than the level of the outer fill solution, disassemble the electrode and flush according to the instructions noted in Weekly or biweekly care section.
- Add Orion pH Electrode Filling Solution for ROSS Electrodes (Cat. No. 810007)to the outer chamber up to the bottom of the fill hole of the reference electrode and leave the fill hole open during measurement.
- Condition the ISE: soak the surfactant ISE for at least 10 minutes in conditioning solution (1 mL of titrant diluted to 50 mL with RGW).
- Rinse both electrodes thoroughly with RGW before and between titrations.
- Storage of surfactant ISE: Store dry. Thoroughly rinse the ISE electrode with RGW, shake off excess drops, and place the black cover over the end.
- Storage of reference electrode: Cover the fill hole and store in 1 mL of Thermo Scientific™ Orion™ Filling Solution for Orion™ ROSS™ Electrodes (Cat. No. 810007) diluted to 30 mL with RGW.

Weekly or biweekly care

- Flush the outer fill solution and disassemble the reference electrode. Rinse w/ RGW to remove any crystals that may have formed. Drain the green inner fill solution. Replace the green inner fill solution (Cat. No. 900002) and slide the white rubber sleeve up to cover the fill hole. See the user guide for the Orion™ Sure-Flow™ Reference Half-Cell Electrode for details on disassembly and cleaning.
- Reassemble the electrode and refill the outer chamber with ROSS Fill Solution (Cat. No. 810007). Do not use the Orion Filling Solution for Sure-Flow Double-Junction Reference Electrodes (Cat. No. 90003) that comes with the electrode.
- Change the electrode storage solution in the container where the reference electrode is stored.
- Consider standardizing the titrant on a weekly basis, or more frequently, as desired.

As needed

- For slow or drifty response, soak the surfactant ISE for 1 hour in acidic RGW at pH 4 (1 mL of 0.1M HCl added to 1L of RGW). (Do not soak in pH 4 buffer). Condition per Daily Care instructions.
- For a flat titration curve or small mV jump on the titration curve, regenerate the surfactant ISE by soaking 30 minutes in pure titrant. Condition per Daily Care instructions.

Orion Star T9305 Ion Titrator

Sample weight

Calculate the amount of sample to weigh. (EW = equivalent weight of the QAC in g/mol, %Q = expected percent of active QAC in sample.)

If % actives are 10% or less:

g sample = (0.004 *x EW*) ÷ % *Q*

Weigh this amount of sample into a tared clean, dry 150- or 200-mL beaker. Record the exact weight.

If % actives are more than 10%:

g sample = (0.04 *x EW*) ÷ % *Q*

Weigh this amount of sample into a tared clean, dry 100 mL volumetric flask. Record the exact weight. Dilute to volume (100 mL) with RGW. Cap and mix well. Then pipet 10.0 mL into a clean dry 150- or 200-mL beaker. This is a 10x dilution.

Example for a sample with 10% actives or less:
If titrating a 5% actives solution of benzalkonium chloride (EW = 350), calculate weight as follows: weight = (0.004 x 350) ÷ 5 = 0.28 g. Weigh about 0.28 grams of benzalkonium sample into a clean, dry beaker. Record the exact weight. That is the grams of sample that will be titrated.

Example for a sample with more than 10% actives:
If titrating a 50% actives solution of benzalkonium chloride (EW = 350), calculate weight as follows: weight = (0.04 x 350) ÷ 50 = 0.28 g. Weigh about 0.28 grams of benzalkonium sample into a 100 mL volumetric flask. Record the exact weight. Dilute to 100.0 mL, then pipet 10.0 mL into a beaker for titration. Note: the actual weight titrated will be 1/10 of the recorded weight. If recorded weight is 0.295 g, then 0.295 g/10 = 0.0295 g of sample will be titrated.

Sample preparation

After placing sample into the beaker (as described above), add buffer mix to the 70 mL mark on the side of the beaker. The sample is now ready to titrate.

Note: if not preparing buffer mix in batches, add the individual solutions to the beaker separately, after placing the sample into the beaker. Then add RGW to the 60 mL mark, 10 mL of borate buffer, 1 mL of 1% Tween, and 1 mL of IPA. The sample is now ready to titrate.

Sample titration

1. From the Methods screen, select the option to run the saved method QAC by ISE.
2. Rinse the electrodes, stirrer, and dispenser with RGW. Place the electrodes, stirrer, and dispenser into the prepared sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample. Start the titration immediately.
3. When prompted for sample weight, enter the grams of sample placed in the beaker for titration.
   - For samples at 10% or less, enter the recorded weight.
   - For samples more than 10%, enter the recorded weight divided by 10 (because the sample has been diluted by 10x).
4. Touch Save-Run to start the titration.
5. Results are reported as % QAC in sample.
6. Optional: For enhanced accuracy and confidence, prepare the sample again in a new beaker and titrate a replicate by selecting the Run # Cycle option. Repeat as desired. After running 2 to 5 cycles, select the Complete option. The averaged result and precision of replicates

Titration curves

Examples of common QAC surfactant titration curves are shown below.

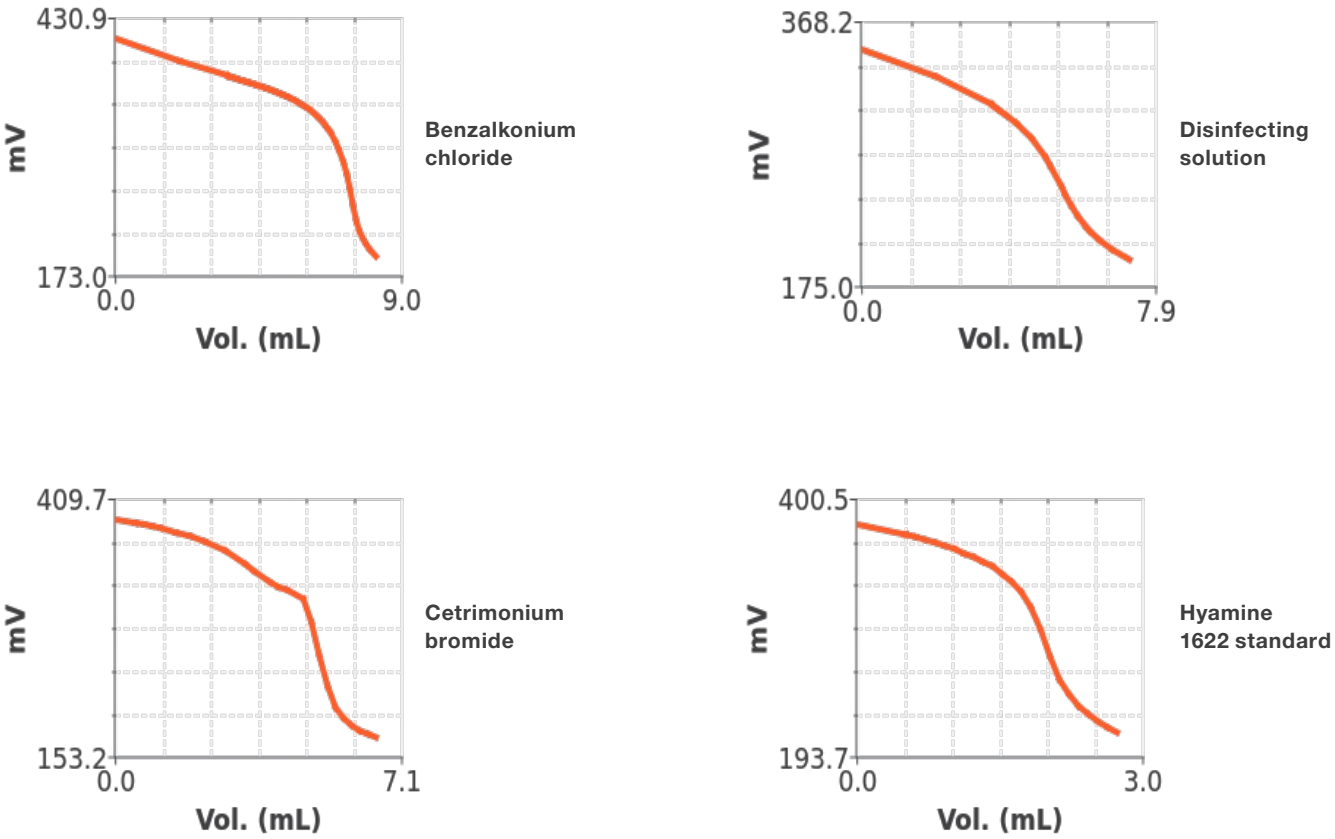

Figure 1. Examples of titration curves for common QAC surfactants.

Range

This programmed method covers a range of < 1% to 100% w/w active QAC.

Results

The automatic titration results are repeatable, accurate, and quick.

Results				
Sample	Results	RSD	% Recovery	Average titration time
Benzalkonium chloride	48.46%	1.00% (n = 5)	Within stated range (50% +/- 2%)	3:30 minutes
Hyamine 1622 standard	2.235%	0.50% (n = 5)	99.8%	2:48 minutes
Cetrimonium bromide	99.72%	0.76% (n = 4)	100.1%	2:33 minutes*
Disinfecting solution	22.54%	1.76% (n = 5)	102.5%	1:51 minutes

* ΔV_{min} = 0.2 mL

Tips for best results

- Create one method for each QAC titrated. For example, if titrating benzalkonium chloride, Hyamine, and cetrimonium bromide, copy the QAC method and save as three different methods – Benzalkonium, Hyamine, and Cetri Br. Edit the Titration section of the Benzalkonium method and enter the molecular weight for benzalkonium chloride (350 g/mole). Save and use for all future benzalkonium chloride titrations. Edit the Titration section of the Hyamine method and enter the molecular weight for Hyamine 1622 (448.1 g/mole). Save and use for all future Hyamine titrations. Repeat for cetrimonium bromide.
- Condition the surfactant electrode for fast titrations and good titration curves. Before the first titration and as needed throughout the testing, soak the surfactant ISE for at least 10 minutes in 1 mL of titrant diluted to 50 mL with RGW. Sometimes the surfactant ISE can be conditioned by titrating a sample 1 or 2 times (cycles) prior to testing. Label those runs as “conditioning”. Then proceed with the sample testing as planned.

Titrant

Over time, standard titrant solutions age and can change concentration. For higher accuracy, determine the exact concentration by standardizing the titrant. It is common to standardize on a weekly basis, but other standardization frequencies may be suitable.

If standardization is not desired, choose option 1 (below) for use of certified standard titrant solutions. If standardization is desired, choose option 2 (below).

1. Certified standard titrant solution option - no standardization, simple, convenient
   - — Some customers may prefer not to standardize their titrant, instead choosing to purchase and use a certified standard titration solution.
   - — In this case, take precautions to protect the titrant from evaporation, air absorption, moisture absorption, light, heat, and/or dust to ensure the integrity of the titrant. Do not keep past the expiration date.
   - — Examples of titrants that change concentration over time include sodium hydroxide and other bases, silver nitrate, iodine, sulfuric acid, potassium permanganate, 2,6-dichloro indophenol (DCP), and any titrant in a volatile solvent (like potassium hydroxide in isopropanol). Use these titrants quickly before they change concentration significantly, or consider standardizing these titrants on a regular basis, as described below.

2. Standardizing titrant option - highest accuracy and confidence
   - — If choosing the option to standardize, edit the Titrant section of the method and choose Concentration Input Mode = Standardization, then enter the program parameters as indicated in the table below. Save the edits, then save the method.
   - — Pipet 1.0 mL standardizing solution, 0.05 M Hyamine, into a clean 150- or 200-mL beaker. Add buffer mix to the 70 mL mark on the beaker. The standard is now ready to titrate.
   - — Select the QAC by ISE method. At the Titration Pre-Check screen, select the Standardize option.
   - — Rinse probes, dispenser, and stirrer, then immerse in solution and start the titration.
   - — At the end of the first titration, the results are shown onscreen. Repeat steps 2. and 3., then select the Run # Cycle option. Repeat for a total of three or more cycles. The results of all cycles will show onscreen. If results agree well, select Complete to end the standardization.
   - — A summary of the results with the new average titrant concentration and the %RSD of the three (or more) cycles will be displayed. This standardized titrant value will automatically be saved and used for subsequent titrations by this QAC by ISE method.

Standardization option	
Titrant	
Titration name	SLS
Titration ID	Edit as desired
Conc. input mode	Standardization
Nominal concentration	8 mM*
Standardize tech	Equivalence point
Number of endpoints	1
Results units	M
Standardize reaction ratio	1
Standard name	Hyamine
Standard amount	Fixed vol, 1.0 mL
Standard concentration	0.05 M
Pre-dose titrant volume	4 mL
Max total titrant volume	9 mL
Standard process control	User defined
ΔE	15.000 mV
ΔV_{min}	0.100 mL
ΔV_{max}	0.500 mL
dE/dt	10.0 mV/min
t_{min}	2 seconds
t_{max}	5 seconds
Threshold	200 mV/mL
Pre-stir duration	5 seconds
Stir speed	Fast
Notes	

*Choose units of “mM”.

Ordering information

Product	Description	Cat. No.
Titrator and electrode	Orion Star T930 Ion Titrator kit (includes surfactant ISE and reference electrode)	START9305
	Orion Star T930 Ion Titrator only	START9300
	Thermo Scientific Orion Surfactant Electrode	9342BN
	Thermo Scientific Orion Reference Electrode	900200
Solutions	Orion Hyamine Standard, 0.05M (Optional for standardizing the titrant)	654201
	Orion pH Electrode Filling Solution for ROSS Electrodes (outer fill solution for reference electrode)	810007
	Orion double junction reference electrode inner fill solution	900002
Reagent grade water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV water Purification System	50129890*
Accessories	150- or 200-mL beakers	
	Analytical balance	
Reagents	Sodium lauryl sulfate**, reagent grade, 98% or better (or purchase sodium lauryl sulfate, 0.008N solution)	
	Isopropyl Alcohol (2-Propanol), reagent grade, 95% or better	
	Boric Acid, reagent grade, 99% or better (or purchase borate buffer pH 9.5)	
	Sodium tetraborate decahydrate, reagent grade, 99% or better (or purchase borate buffer pH 9.5)	
	Tween 20, molecular biology grade	

*Please contact your local Thermo Scientific representative for support on ordering the best water purification system for your application. And visit our website at thermofisher.com/waterpurification.
**Also known as sodium dodecyl sulfate (SDS)

Learn more at **thermofisher.com/titrator**