



## Determination of quaternary ammonium chloride surfactants by argentometric auto titration

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### Introduction

Quaternary ammonium compound (QAC) surfactants are a common active ingredient in antimicrobial formulations. Quaternary ammonium chlorides and other halides can be titrated directly with silver nitrate in aqueous solution. The silver ions in the titrant react with the chloride or bromide anion of the QAC salt to form insoluble silver salts. The endpoint is sensed by the silver ion selective electrode (ISE). The titrator automatically calculates results and logs the data.

### Materials

#### Equipment

Thermo Scientific™ Orion Star™ Ion Titrator Kit with Silver Billet Electrode (Cat. No. START930), or an Orion Star Ion Titrator (Cat. No. START9300), and a Thermo Scientific™ Orion™ Silver/Sulfide Electrode (Cat. No. 9616BNWP). When choosing between the kit with silver billet electrode or the titrator and a silver/sulfide electrode, keep in mind that the silver billet is the traditional choice and has a lower replacement cost. The silver/sulfide electrode is easier to maintain and will not clog but has a higher replacement cost.

# Determination of quaternary ammonium chloride surfactants by argentometric auto titration

## Solutions

Silver nitrate titrant, 0.1N (0.1M). Isopropyl alcohol (IPA), 99%. Reagent grade water (RGW). Optional: Orion Chloride Standard, 0.1M, for standardization (Cat. No. 941706).

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.

## Solution preparation

Combine 500 mL of IPA with 500 mL of RGW to make the IPA/RGW mix.

## Methods

### Titration setup

Connect the electrode and the stirrer probe to the titrator. If not previously done, import the preprogrammed QAC by Ag method into the titrator from the Methods screen or program the method according to the Method Program section (below). 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 later in this document for details.



The Thermo Scientific Orion Star Ion Titrator.

## Method Program

Load or copy the method into the titrator

QAC by Ag method	
Electrode	
Electrode type	ISE-Titration
ISE type	Silver (Ag+)
Electrode name	Silver
Titrant	
Titrant name	AgNO <sub>3</sub>
Titrant ID	Edit as desired
Conc. Input mode	Manual
Titrant concentration	0.1N (0.1M)
Titration	
Titration Technique	Equivalence pt.
Number of endpoints	1
Display units	mV
Titration type	Direct
Blank required	No
Titration units	%w/w
Titration reaction ratio	1
Sample mol. wt.	Enter g/mole*
Sample amount	Variable weight
Pre-dose titrant volume	0.5 mL
Max total titrant volume	20 mL
Titration process control	Quick
Pre-stir duration	5 sec
Stir speed	Fast
Sample ID	Manual
Notes	
*Edit based on QAC. For benzalkonium chloride = 350	

## Titration 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	Weekly or biweekly care	As needed
<ul style="list-style-type: none"><li>• If bubbles are visible in the titrator tubing, dispense titrant until bubbles have been expelled. Tap tubing to dislodge bubbles that stick.</li></ul>	<ul style="list-style-type: none"><li>• Drain and replace the fill solution of the electrode.</li></ul>	<ul style="list-style-type: none"><li>• For slow or drifty electrode response, soak the electrode in 1% laboratory detergent solution with vigorous stirring for 15 minutes. Rinse well with RGW. Drain and refill the electrode.</li></ul>
<ul style="list-style-type: none"><li>• Add Orion electrode fill solution up to the bottom of the fill hole and leave the fill hole open during measurement.</li></ul>	<ul style="list-style-type: none"><li>• Change the electrode storage solution in the container that the electrode is stored in.</li></ul>	<ul style="list-style-type: none"><li>• For a more rigorous cleaning, use Orion pH Electrode Cleaning Solution C (Cat. No. 900023). Follow instructions. Rinse well with RGW. Drain and refill the electrode.</li></ul>
<ul style="list-style-type: none"><li>• Wipe the electrode sensor gently with a moistened lint-free wiper as needed to keep the surface clean.</li></ul>	<ul style="list-style-type: none"><li>• Consider standardizing the titrant on a weekly basis, or more frequently, as desired.</li></ul>	<ul style="list-style-type: none"><li>• See the electrode user manuals for maintenance details.</li></ul>
<ul style="list-style-type: none"><li>• Rinse electrode well with RGW before and between titrations.</li></ul>		
<ul style="list-style-type: none"><li>• Storage: Thoroughly rinse the electrode with RGW and cover the fill hole. For silver billet electrode: store in Orion pH Electrode Filling Solution (Cat. No. 900011) or 3M KCl. For the Ag/S electrode: store in Orion Optimum Results C Filling Solution for Silver ISE (Cat. No. 900067) or 1M KNO<sub>3</sub>.</li></ul>		

## Sample weight

Calculate the sample size to titrate as follows:

$$g \text{ sample} = (0.15 \times EW) \div \%Q$$

where EW = equivalent weight of the QAC in g/mol and %Q = expected percent of active QAC in sample. For example, if titrating a benzalkonium chloride (EW = 350) solution expected to have 50% active QAC, calculated weight =  $(0.15 \times 350) \div 50 = 1.05$  g. Therefore, weigh about 1.0 grams of benzalkonium sample.

Weigh the calculated amount of sample into a tared 100- or 150-mL beaker. Record the exact weight of sample to the nearest 0.01 g.

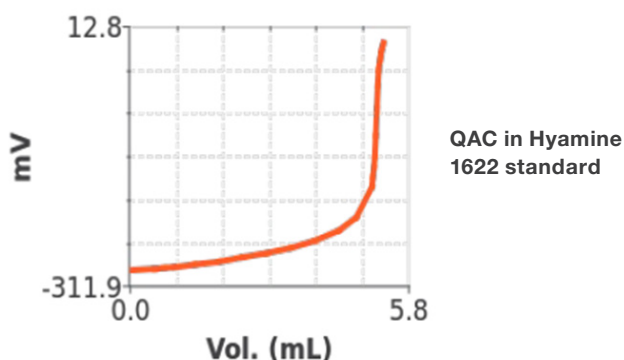
## Sample preparation

After placing the sample into the beaker (as described above), add about 60 mL of the IPA/RGW mix. The sample is ready to titrate.

## Sample titration

1. From the Methods screen, select the option to run the saved method QAC by Ag.
2. Rinse the electrode, stirrer, and dispenser with RGW. Place the electrode, 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 into the beaker for titration.
4. Touch Save-Run to start the titration.
5. Results are reported as % QAC in the sample.
6. Optional: For enhanced accuracy and confidence, prepare the sample again and titrate a replicate by selecting the Run # Cycle option. Repeat as desired. After running 2 to 5 cycles, select the Complete option. The average result and precision of replicates (in % RSD) are automatically calculated, displayed, and logged by the titrator.

## Titration curve



**Figure 1. Titration curve for active QAC in Hyamine 1622 standard.**

## Range

This programmed method covers a range of about 0.30 to 60% active QAC.

## Results

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

## 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

- a. Some customers may prefer not to standardize their titrant, instead choosing to purchase and use a certified standard titration solution.
- b. 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.

- c. 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

- a. 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 below. Save the edits, then save the method.
- b. Pipet 2.0 mL standardizing solution, 0.1M (0.1N) standard sodium chloride, into a clean 100 mL beaker. Add about 60 mL of IPA/RGW mix to the beaker.
- c. Select the QAC by Ag method. At the Titration Pre-Check screen, select the Standardize option.
- d. Rinse probes, dispenser, and stirrer, then immerse in solution and start the titration.
- e. At the end of the first titration, the results are shown onscreen. Repeat steps b. and d., then select the Run # Cycle option. Repeat for a total of three to five cycles. The results of all cycles will show onscreen. If results agree well, select Complete to end the standardization.
- f. 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 Ag method.

## Results

Sample	Results	RSD	% recovery	Average titration time
Benzalkonium chloride	48.46%	0.10% (n = 4)	Within stated range (50% +/- 2%)	3:39 minutes
Hyamine 1622 standard	2.248% (0.050M)	0.12% (n = 4)	100.6%	2:18 minutes
Cetrimonium bromide	0.4787%	0.10% (n = 4)	NA	1:52 minutes

Standardization option	
Titrant	
Titration name	AgNO <sub>3</sub>
Titration ID	Edit as desired
Conc input mode	Standardization
Nominal concentration	0.1N (0.1M)
Standardize tech	Equivalence pt.
Number of endpoints	1
Results units	M
Standardize reaction ratio	1
Standard name	NaCl
Standard amount	Fixed vol, 2.0 mL
Standard concentration	0.10 M
Pre-dose titrant tolupe	0.5 mL
Max total titrant volume	4 mL
Standard process control	Routine
Pre-stir duration	5 seconds
Stir speed	Fast



**Thermo Scientific™ Orion™ Silver Billet Electrode, included with the purchase of an Orion Star T930 Ion Titrator kit.**

### Ordering information

Product	Description	Cat. No.
Titrator and Electrode	Orion Star T930 Ion Titrator kit (includes silver billet electrode and cable)	START9301
	Orion Star T930 Ion Titrator only	START9300
	Orion Silver/Sulfide Electrode	9616BNWP
Solutions	Orion Chloride Standard, 0.1M (Optional for standardizing the titrant)	941706
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV water Purification System	50129890*
Accessories	100- or 150-mL beakers	
	Analytical balance	
Reagents	0.10 N (0.10 M) standard silver nitrate solution	
	Isopropyl alcohol (2-propanol), 99%, reagent 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](http://thermofisher.com/waterpurification).