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**MT 199 Determination of Quaternary Ammonium Compounds by Potentiometric Titration with an Ionic Surfactant Electrode**

1. **General information on Quaternary Ammonium Compounds:**



The R groups can vary. Examples of R groups:

ALKYL DIMETHYL BENZYL AMMONIUM CHLORIDE

ALKYL DIMETHYLBENZYL DIMETHYL AMMONIUM CHLORIDE

ALKYL DIMETHYL ETHYLBENZYL AMMONIUM BROMIDE

OCTYL DECYL DIMETHYL AMMONIUM CHLORIDE

Note: The chain length on the alkyl group may be a mixture. Labels are given as percentages of each akyl chain length. Example: 40% C12; 20% C14; and 40% C18.

Outline of the Method

This method is suitable for the determination of quaternary ammonium compounds (QAC) in concentrate and ready-to-use (RTU) disinfectant formulations. The method is not suitable for products containing large amounts of alcohol (methanol, ethanol, isopropanol, etc.) and/or hydrochloric acid.

A potentiometric titration, utilizing an ionic surfactant electrode and a titrant of sodium lauryl sulfate (SLS), is used to determine the amount of quaternary nitrogen in the sample. From this value, a total QAC value is calculated.

1. **Apparatus**

Note: Equivalent apparatus may be substituted. All volumetric flasks are Class A.

* 1. Automated titration system – Metrohm 808 Titrando with a 20 mL exchange unit or equivalent
	2. Working electrode – Metrohm Ionic Surfactant electrode (Product # 6.0507.120) or equivalent. Follow manufacturer’s guidelines for conditioning new electrode before use. Typically the new electrode is conditioned by carrying out two or three titrations and discarding this data.
	3. Reference electrode – Metrohm Ag/AgCl reference electrode (Product # 6.0726.107) or equivalent
	4. Beakers – Appropriate size to perform titration, 125 mL
	5. Volumetric flasks – 1000 mL and 2000 mL

1. Reagents
	1. Water – LC grade
	2. Sodium lauryl sulfate (SLS) – 99% or greater purity or a commercially available 0.005 Normal SLS traceable to NIST standard reference material. Metrohm REATI98645, 6 x 1 liter NIST Traceable, or equivalent may be purchased for use.
	3. Boric acid – 99.5% or greater purity
	4. Sodium hydroxide – 2 N or Molar solution
	5. Reference standard – n-Alkyldimethylbenzyl ammonium chloride (trade name Hyamine ® 1622) with 3.126% nitrogen content. Sigma Life Science: *Hyamine® 1622*, C27H42ClNO2, FW 448.08, CAS 121-54-0, and purity ≥ 99.0% (AT), catalog no. 53751-50 G from Sigma Life Science.
	6. SLS solution, 0.005 N – Add 1.44 g of SLS to a 1000 mL volumetric flask containing approximately 500 mL of water. Mix thoroughly. Dilute to volume with water and then mix again. Alternately, a commercially available standardized 0.005 N SLS solution may be purchased for use. Other concentrations of SLS may be used with appropriate adjustments made to sample size and formula for calculations.
	7. Boric acid buffer solution – Add 1.04 g of boric acid to a 2000 mL volumetric flask containing approximately 1000 mL of water. Mix thoroughly. Dilute to volume with water and then mix again. Transfer the resultant solution to a 2000 mL beaker and then adjust the pH to 10.5 by slowly adding 2 N NaOH (approximately 4 mL) while stirring the solution.
2. Preparation of Test Solutions

Test solutions are liquids with no need for vigorous mixing prior to subsampling. Gently mix if solids are observed. Shake gently before sampling. Weigh accurately a test portion of sample to contain approximately 0.060 meq/10 mL of disinfectant quaternary ammonium compound active ingredient into a 100 mL volumetric flask. Dilute to volume with water and take a 10 mL aliquot for analysis. Formula for calculating sample size needed for 12 ml titer using 0.005N SLS titrant:

Sample Weight (g) = 0.006 x MW/ % Label Claim

Where MW is the average molecular weight of quaternary ammonium compounds – calculation found in Table 1.

Example calculation: For a product with 12% Total Quaternary Claim and 359.60 average Molecular weight, 0.006 x 359.60/12 = 0.1798 g or 179.8 mg, 1.798 g into 100 mL final volume, then take a 10 mL aliquot. For very low level quaternary products (less than 1% label claim), a direct weight into the 125 mL sample beaker may be necessary. Table 2 provides further examples.

Evaluation of the titration curve: Some commercial disinfectant products contain inerts which seem to affect the shape of the titration curve. See example curve. Reducing sample size can improve the shape of the titration curve. Instead of an end point at 12 ml titrant, an end point of 4 or 5 ml of titrant is preferred in such cases.

1. Determination
	1. Preparation of titration system –
		1. Rinse and fill the titrant bottle with the SLS solution.
		2. Fill the buret on the exchange unit and dispense 20 mL of titrant a total of four times.
		3. Condition the surfactant electrode by soaking it in the SLS solution for 15 to 20 minutes, then rinse gently with water.
	2. Titrator parameters –
2. Start volume = 5 mL
3. Dosing rate = 3 mL/min
4. Start measured value = off
5. Titration rate = optimal
6. Signal drift = 50.0 mV/min
7. Minimum waiting time = 0 s
8. Maximum waiting time = 26 s
9. Measuring point density = 4
10. Minimum increment = 10.0 µL
11. Maximum increment = off
12. Dosing rate = maximum mL/min
13. Stop volume = 30 mL
14. Stop measured value = off
15. Stop end point = 1
16. Volume after end point = 5 mL
17. Stop time = off
18. Evaluation without window = on
19. End point criterion = 5
20. End point recognition = greatest

* 1. Standardization of SLS solution – Accurately weigh 27 mg of QAC Hyamine ® 1622 into a 125 mL beaker. Add 10 mL of water to dissolve the QAC, then 80 mL of boric acid buffer solution, and titrate the sample. The end point is determined at the maximum of the first derivative of the titration curve. The standardization is performed in triplicate. Alternately, a solution of 2.7 mg/ml of Hyamine ® 1622 may be prepared using an appropriate amount of Hyamine ® 1622 weighed into a volumetric flask, diluted with water. Sonication can be used to dissolve the standard. A 10 ml aliquot will then equal 27 mg of Hyamine ® 1622.
	2. Test Solutions – Previously prepared test solutions are titrated similarly to the QAC Hyamine ® 1622 solution.
1. Calculations
2. The normality (N) of the SLS titrant is calculated as follows:

## N = (Quat nitrogen of standard) (weight of standard in mg)

(mL of SLS used) (1400)

1. The percent quaternary nitrogen found in a sample is calculated as follows:

% Quat nitrogen = (SLS Normality) (mL of SLS used) (1400)

(weight of sample in mg)

1. The percent QAC found in a sample is calculated as follows:

$$\% Total QAC found= \sum\_{}^{}\left[\left(\% Quat nitrogen found\right)\frac{\left(\frac{\% Claimed QAC}{\% Claimed Total QAC}\right)}{\left(\frac{MW of Nitrogen}{MW of QAC\*}\right)}\right]$$

\*Please refer to table 1 for the MW of the Quat and example calculation for a sample with a mixture of different Quats

Frequently products contain multiple QACs in different amounts. The nitrogen percent guaranteed is calculated for the product by adding the percent quaternary nitrogen contributions of all QAC claimed:

$$\% Quaternary nitrogen guaranteed= \sum\_{}^{}\left[\frac{\left(MW of nitrogen\right)}{\left(MW of QAC\right)}\right]\left(\% QAC claimed for product\right)$$

Where MW of nitrogen is 14.007 and MW of QAC is the MW of each individual QAC. Excel spreadsheet in study package for a list of Quat factors for the more commonly used active ingredients.

**Table 1:** Example Table for Calculating Quats Showing Example Calculation

|  |  |  |
| --- | --- | --- |
|  |  |  |
| **molecular weight of each compound** | **claim level %** | **adjusted molecular weight** |
| 359.6 | 1.085 | 143.8135 |
| 305.97 | 0.407 | 45.9011 |
| 362.16 | 0.407 | 54.3307 |
| 334.02 | 0.814 | 100.2183 |
|   |   |   |
|   |   |   |
|   |   |   |
|  |  |  |
|  |  |  |
| Total quats claimed: | 2.713 |  |
|  |  |  |
| Average molecular weight: |  | 344.2636 |
|  |  |  |
| adjusted MW = (claim level%/total quats claimed) x MW of individual compoundAverage molecular weight = sum of all adjusted molecular weights

|  |
| --- |
|  |

 |  |  |
|  |  |  |

**Table 2:** Example Table for Calculating Sample Size for 0.005 N SLS (12 mL end point)

|  |  |  |  |
| --- | --- | --- | --- |
| Average Molecular weight | % total Quaternary claim | meq factor | sample size (g) |
| 405.5 | 0.184 | 0.006 | 13.223 |
| 359.6 | 12.000 | 0.006 | 0.180 |
| 448.09 | 100.000 | 0.006 | 0.027 |

Sample size (g) = 0.006 x MW / % Claim, where MW is the average molecular weight

**Example of titration of Hyamine ® 1622:**

Hyamine®1622 standard titration curve (solid line) with 0.005 N SLS, obtained using the ion surfactant electrode. The endpoint is determined potentiometrically as the maximum of the first derivative of the titration curve (line with dots)



**Example of titration of a sample** **(claim 16.8% total Quaternaries) 118 mg sample size with poor curve shape:**



**Example of titration of the same sample reducing sample size from 118 mg to 47 mg sample size:**

