• *Technical*

The Analysis of High Molecular Weight Quaternary Ammonium Chlorides[1]

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CERTAIN high-molecular-weight quaternary ammonium chlorides are prepared commercially by the reaction between methyl (or other alkyl) chloride and fatty amines in the presence of sodium hydroxide. The commercial products usually contain small amounts of free amine, sodium chloride, and amine hydrochloride (or free alkali) as impurities. Proper process and product control require methods of analysis for these minor constituents as well as the major constituent, the quaternary ammonium chloride.

Numerous methods are available for the determination of quaternary ammonium halides. Procedures based on the reaction of quaternary halides with dyes to form colored salts (1, 3) are either most suitable for dilute solutions or are not directly applicable in the presence of amines. Methods based on the argentimetric titration of halide are not directly applicable in the presence of amine hydrochloride and sodium chloride. However, after correction for these interferences, a simple argentimetric titration gives straightforward results. This has become the basis for a set of analyses which determine the quaternary chloride, also the various minor constituents in technical fatty quaternary ammonium chlorides.

The following scheme of analysis has been used successfully for several years in the authors' laboratory for routine control. Amine hydrochloride is determined by a titration with standard alkali to a phenolphthalein end-point; or if free alkali is present, it is titrated with standard acid. The sodium chloride is titrated with standard silver nitrate after ashing. A total chloride titration after correction for amine hydrochloride and sodium chloride determines the quaternary ammonium chloride. Free amine is titrated with standard acid to a bromcresol green end point.

DuBois (2) has shown that dichlorofluorescein is a suitable indicator for the argentimetric titration of high-molecular-weight quaternary ammonium halides. This indicator was chosen for the chloride titrations in this work after preliminary studies showed that it gave much better end-points with technical quaternary ammonium chloride preparations than potassium chromate. Dichlorofluorescein functions satisfactorily in a pH range of approximately 4.4 to 10.5 and therefore, as indicated below, requires adjustment of pH in the solutions titrated. The amine hydrochloride (or free alkali) determination should precede the total chloride and the sodium chloride determinations since the latter two may require acidity adjustments dictated by the results of the former.

Reagents

Reagents are as follows.
Aqueous silver nitrate solution, 0.1 N, standardized against sodium chloride with dichlorofluorescein indicator.
Bromcresol green indicator, 0.1% in water.
Aqueous sodium hydroxide, 0.05 N.
Aqueous hydrochloric acid, 0.05 N.
Aqueous hydrochloric acid, 0.2 N.
Dichlorofluorescein indicator, 0.1% in 70% aqueous ethanol.
Phenolphthalein indicator, 1% in ethanol.
Ethanol, 95%.
Toluene, AR.
Ethanol-toluene mixture, 1–1. Heat ethanol to boiling, cool, and mix with an equal volume of toluene. Add 4 drops of phenolphthalein and neutralize to a faint pink color just before use.
Isopropyl alcohol, AR.
Aqueous nitric acid, approximately 1 N.
Aqueous sodium acetate, approximately 1 N.

Procedure

Amine Hydrochloride (or Free Alkali). Weigh 1–2 g. of sample into a 250-ml. Erlenmeyer flask. Add 50 ml. of the ethanol-toluene solvent to dissolve the sample, heating it gently if necessary. Add 10 ml. of water and swirl the flask to mix the contents thoroughly. Add 5–7 drops of phenolphthalein indicator. If the solution remains colorless, titrate the amine hydrochloride with 0.05 N sodium hydroxide to a pink end-point. If the solution turns pink on the addition of phenolphthalein, titrate the free alkali with 0.5 N hydrochloric acid to a colorless end-point.

$$\%\ \text{Amine}\cdot\text{HCl} = \frac{\text{ml.} \times \text{normality of NaOH} \times \text{mol. wt. amine}\cdot\text{HCl}}{\text{wt. of sample} \times 10} \qquad (1)$$

or

$$\text{Alkali number} = \frac{\text{ml.} \times \text{normality of HCl} \times 56.1}{\text{wt. of sample}} \qquad (2)$$

Amine. Weigh 2 g. of sample into a 250-ml. Erlenmeyer flask. Add 50 ml. of ethanol and, if necessary for complete solution, 15 ml. of toluene. Add I ml. of bromcresol green indicator and titrate with the 0.2 N hydrochloric acid to the disappearance of the green color.

$$\%\ \text{Amine}^{a} = \frac{\text{ml.} \times \text{normality} \times \text{mol. wt. amine}}{\text{wt. of sample} \times 10} \qquad (3)$$

[a] If the sample contains free alkali, subtract

$$\left(\text{alkali number} \times \frac{\text{mol. wt. amine}}{561}\right) \text{from \% amine above.}$$

Sodium Chloride. Weigh 1–2 g. of sample into a No. 2 porcelain crucible. If sample contains no free alkali, use Method A below. If the sample contains free alkali, use Method B.

Method A (no free alkali). Ignite the sample by carefully heating the crucible over a Fisher burner. When approxi-

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mately three-fourths of the sample has burned away, in order to prevent loss of sodium chloride by spattering, place a cover over the crucible, leaving a small opening for air. Remove the cover after no more liquid remains and complete the ashing. Cool the crucible, rinse down the sides with 5–10 ml. of water, and heat for 10 min. on a steam bath. Transfer the contents to a 125-ml. Erlenmeyer flask, then rinse the crucible, and cover with 10–15 ml. of water into the same flask. Add 5 drops of the dichlorofluorescein indicator. (If no sodium chloride is visible in the crucible after ashing, use a total of only 10 ml. of water and only 1 drop of indicator for sharper end-points.) Titrate with the 0.1 N silver nitrate to the appearance of red.

$$\%\ \text{NaCl} = \frac{\text{ml.} \times \text{normality of } AgNO_3 \times 5.85}{\text{wt. of sample}} \qquad (4)$$

TABLE I

Titration of Purified Compounds [a]

Titration	Compound	Purity determined
		%
Chloride [b]	Dioctadecylmorpholinium chloride	99.6
	Dioctadecyldimethyl ammonium chloride	99.0[c]
	Dioctadecylamine hydrochloride	99.3
	Trioctadecylamine hydrochloride	100.0
Amine · HCl	Dioctadecylamine hydrochloride	101.0
	Trioctadecylamine hydrochloride	100.2
Amine	Octadecylmorpholine	99.0
	Dioctadecylamine	99.0

[a] All compounds are crystallized laboratory preparations made from starting materials which were purified for alkyl group homogeneity.

[b] Procedure described above under quaternary ammonium chloride.

[c] Sample analyzed 0.5% dioctadecylamine hydrochloride, 0.4% dioctadecylamine, and 0.00% sodium chloride by proposed procedures.

TABLE II

Analyses of Known Mixtures

Titration	Mixture composition				Titration	
	Quaternary	Amine	Amine·HCl	NaCl	Calculated	Found
	%	%	%	%	*ml.*	*ml.*
Chloride [c]	86[b]	8	6	0	15.18	15.23
	81[b]	8	8	3	23.05	23.11
	84[a]	8	4	4	10.59	10.62
	25[b]	50	25	0	16.52	16.70
Amine·HCl	87[b]	5	8	0	3.03	3.12
	25[b]	50	25	0	9.47	9.51
	90[a]	5	5	0	0.48	0.44
Amine	90[b]	5	5	0	1.33	1.28
	89[a]	7	4	0	0.39	0.40
NaCl (after ashing)	98[b]	0	0	2	7.10	7.06
	88[b]	4	4	4	7.25	7.15
	93[a]	2	2	3	5.36	5.31

[a] Dioctadecyldimethyl quaternary ammonium chloride.

[b] Dioctadecylmorpholinium chloride.

[c] Procedure described above under quaternary ammonium chloride.

TABLE III

Reproducibility of Analyses

Determination	Average value			Total No. of determinations	Standard deviation	95% Confidence limits
	1	2	3			
	%	%	%		%	±%
Amine	0.1	0	0.4	30	0.2	0.4
Amine·HCl	4.2	2.0	0.1	27	0.2	0.4
NaCl	0.35	0.27	0.07	21	0.015	0.03
Quaternary	70.2	72.4	72.3	21	0.6	1.2

Method B (free alkali present). Add 10 ml. of isopropyl alcohol and heat on a steam bath till sample is dissolved. Acidify the solution by adding 1.5 times the volume of 0.05 N HCl required to neutralize the free alkali. Heat the crucible gently at first over a Fisher burner, then ignite, and proceed as in Method A.

$$\%\ \text{NaCl} = \qquad (5)$$

$$\frac{\text{ml.} \times \text{normality of } AgNO_3 \times 5.85}{\text{wt. of sample}} - 0.104 \times \text{alkali number}$$

Quaternary Ammonium Chloride. Weigh 1 g. of sample into a 250-ml. Erlenmeyer flask. Add 50 ml. of isopropyl alcohol and heat gently on a steam bath to dissolve the sample. Add 10 drops of dichlorofluorescein indicator. If no fluorescence is evident, excessive amounts of amine hydrochloride are present, and sodium acetate solution should be added dropwise till the fluorescence appears. With samples containing free alkali, add nitric acid dropwise until the indicator is decolorized, followed by sodium acetate solution till the fluorescence reappears. Then titrate with the 0.1 N silver nitrate to the red end-point.

$$\%\ \text{Quaternary} = \text{mol. wt. quaternary} \times (A\text{–}B\text{–}C) \qquad (6)$$

$$A = \frac{\text{ml.} \times \text{normality of } AgNO_3}{\text{wt. sample} \times 10}$$

$$B = \frac{\%\ \text{NaCl}}{58.5}$$

$$C = \frac{\%\ \text{amine·HCl}}{\text{mol. wt. amine·HCl}}$$

Results

Table I contains the results of titrations on purified compounds. In Table II are listed results obtained on known mixtures by using the procedures described above. Dioctadecylamine, dioctadecylamine hydrochloride, and the indicated quaternary were used to prepare these mixtures. In Table III are listed data on the reproducibility of these procedures on three samples of technical grade dimethyldi(hydrogenated tallow) ammonium chloride. These samples contain approximately 20% isopropyl alcohol and 5% water.

Summary

Commercial production of high molecular weight quaternary ammonium chlorides has necessitated methods for their analysis. Available methods were found to be lacking in completeness. A successful scheme of analysis was worked out for determining quaternary ammonium chloride, amine hydrochloride (or free alkali), amine, and sodium chloride. The analytical procedures as described are straightforward and suitable for routine product and process control.

REFERENCES

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