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## Notes

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### Direct Titrimetric Determination of Aromatic Quaternary Ammonium Salts and Long Chain Aliphatic Sulfates and Sulfonates

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Aromatic quaternary ammonium salts and long chain aliphatic sulfates and sulfonates can be assayed by a rapid, single phase aqueous titration. Sodium tetraphenylboron serves as a direct standard in the assay of the quaternaries and benzalkonium chloride as the titrant for anionic detergents. Bromophenol blue indicator gives a purple to blue color change when the anionic substances are titrated in strongly alkaline solution. The results of this method show excellent agreement with the standard chloroform extraction titration.

THE aromatic quaternary ammonium salts official in U.S.P. XVII and N.F. XII are assayed by many different methods. Sodium lauryl sulfate, the only official long chain aliphatic sulfate, is not directly assayed. It was believed that a single method type, direct titration of large anions with large cations, could be used for all aromatic quaternary ammonium salts and for the long chain aliphatic sulfates and sulfonates.

A direct titration of sodium tetraphenylboron with cetyltrimethylammonium bromide using bromophenol blue indicator was used by Schall (1) in the determination of potassium. This suggested that aromatic quaternary ammonium compounds could be assayed by direct titration of sodium tetraphenylboron, and, conversely, that large anions could be titrated directly with quaternary ammonium compounds.

Cetylpyridinium chloride is officially assayed (2) by titration with standard sodium tetraphenylboron using bromophenol blue indicator. The official method differs from that proposed by Schall in that the end point depends upon the extraction of the indicator from a chloroform layer.

A similar chloroform extraction titration, using tetrabutylammonium iodide as the standard, is official (3) for the assay of the aliphatic sulfonate dioctyl sodium sulfosuccinate. This method is adapted in method A as the general chloroform extraction method against which the proposed method is compared.

#### REAGENTS

**Tetrabutylammonium Iodide (Primary Standard Cation).**—A 0.01000 M solution prepared considering the material to be 100% pure. Titration in triplicate against sodium tetraphenylboron by method A gave 0.01000 M  $\pm$  0.00005 M.

**Sodium Tetraphenylboron (Primary Standard Anion).**—A 0.01000 M solution prepared on the basis of labeled 99.6% assay. This should be freshly prepared before each use because of decomposition on standing in solution.

**Benzalkonium Chloride (Secondary Standard Cation).**—Approximately 0.01 M solution prepared by diluting about 30 ml. of 12.8% benzalkonium chloride<sup>1</sup> to 1 L. and standardized against sodium tetraphenylboron by N.F. XII procedure for cetylpyridinium chloride (2).

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<sup>1</sup> Marketed as Zephirin Chloride by Winthrop Laboratories, New York, N. Y.

TABLE I.—COMPARISON OF METHODS A AND B

Soln.	Method A			Method B		
	No. Assays	Av. <i>M</i>	S. D.	No. Assays	Av. <i>M</i>	S. D.
Benzalkonium chloride I	6	0.00902	0.00001	6	0.00903	0.00001
Benzalkonium chloride II	6	0.01030	0.00001	6	0.01029	0.00001
Diocetyl sodium sulfosuccinate	6	0.01159	0.00001	6	0.01159	0.00001
Sodium lauryl sulfate I	5	0.00906	0.00004	6	0.00910	0.00005
Sodium lauryl sulfate II	3	0.01000	0.00006	5	0.01016	0.00004
Cetylpyridinium bromide	3	0.01135	0.00001	3	0.01136	0.00001

**Sodium Octylphenoxyethoxypolyether Sulfate (Secondary Standard Anion).**—Dilute approximately 20 ml. of alkyl phenoxyethanesulfonate<sup>2</sup> concentrate to 1 L. Standardize against tetrabutylammonium iodide using the N.F. XII procedure for dioctyl sodium sulfosuccinate (3).

**Bromophenol Blue T.S.**—A 0.1% quantity bromophenol blue in a mixture of equal volumes of water and alcohol.

**Salt Solution.**—Prepared according to N.F. XII directions for assay of dioctyl sodium sulfosuccinate (3).

**Chloroform.**—Reagent grade.

**Sodium Hydroxide Solution.**—Twenty per cent.

#### METHODS

**Method A.**—Adapted from N.F. XII Method for Diocetyl Sodium Sulfosuccinate.—Place a sample containing about 25 mmoles cation such as tetrabutylammonium iodide in 25 ml. of water, 50 ml. of salt solution, 25 ml. of chloroform, and 0.4 ml. of bromophenol blue T.S. in a flask. Titrate with an approximately 0.01 *M* anion solution, using a magnetic stirring device to insure thorough mixing of the layers to replace the shaking procedures in the official method. Add the anion dropwise in the vicinity of the end point, allowing sufficient time for mixing and separation. Continue the titration until the blue color is completely removed from the chloroform layer.

**Method B.**—Proposed Direct Method.—This procedure is the same whether the anionic or cationic component is to be determined. Pipet 25 ml. of an approximately 0.01 *M* anion solution into a flask, add 50 ml. of water, 2 ml. of 20% NaOH, and 0.4 ml. of bromophenol blue T.S. The solution will be purple. Using a magnetic stirrer, titrate with the cation, adding it dropwise near the end point, which is a color change to a distinct, bright blue.

Two benzalkonium chloride solutions were prepared as indicated under *Reagents*. These were standardized by titration against the secondary standard anion using method A and the proposed method B. Results are given in Table I.

Diocetyl sodium sulfosuccinate was assayed by titration against standardized benzalkonium chloride solution by both methods. The dioctyl sodium sulfosuccinate solution was prepared by diluting approximately 7.5 ml. of a type of dioctyl sodium

sulfosuccinate<sup>3</sup> to 1 L. and allowing to stand with occasional shaking until complete dissolution was obtained. Results are given in Table I.

Sodium lauryl sulfate was assayed by titration against standard benzalkonium chloride solution, using both methods A and B. Results are given in Table I.

Cetylpyridinium bromide was assayed by titration against standard sodium tetraphenylboron solution, using both methods A and B. Results are given in Table I.

#### DISCUSSION

Tetrabutylammonium iodide can only be used in method A; attempts to use it in method B gave no color change at the end point. Sodium tetraphenylboron can be used in both methods A and B.

As previously stated, the color change in method B is from purple to blue. A trial is necessary to obtain a correct end point, so that a purple-tinged blue may not be mistaken for the true end point by those not thoroughly familiar with the color change.

In method B the formation of a greasy precipitate in the vicinity of the end point has not been found to interfere with end point detection.

The following sulfonphthalein indicators were investigated for use in method B and were found unsatisfactory: thymol blue, bromocresol purple, cresol red, phenol red, dibromopyrogallol sulfonphthalein, pyrogallol sulfonphthalein, pyrocatechol sulfonphthalein.

#### CONCLUSIONS

The data show that the proposed direct titration (method B) yields results in excellent agreement with the chloroform extraction titration (method A) for the compounds studied, which were U.S.P., N.F., or closely related materials. No investigation of interferences was made in this study; the scope was limited to the method types presented in the official compendia. The advantages of method B include: reliable primary standards, inexpensive secondary standards, faster, easier titration. This method also eliminates the use of chloroform, which is both expensive and toxic.

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<sup>2</sup> Marketed as Triton W-30 by Rohm & Haas Co., Philadelphia, Pa.

<sup>3</sup> Marketed as Triton GR-5 by Rohm & Haas Co., Philadelphia, Pa.