A Novel Sample Preparation for Chloride Analysis in Bar Soaps

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ABSTRACT: A simple and rapid sample preparation technique is described for the potentiometric determination of chloride in bar soaps. Usual preparation of soap for potentiometric chloride analysis involves time-consuming dissolution of the sample in water or heating to affect dissolution, followed by a cooling step. Also, when performing potentiometric titrations for chloride under the usual acid conditions, aqueous solutions of soap bars (unlike combination soap/detergent bars) will form insoluble semisolid fatty acids that can occlude some chloride and make clean-up difficult. This paper describes a simple dissolution of bar soap sample in dilute H_2SO_4/methanol at ambient temperature that simultaneously acidifies the sample solution and produces noninterfering methyl esters from the soap fatty acids; water is then added, and the chloride is determined potentiometrically with standardized $AgNO_3$. This procedure has been shown to work well with automatic titrators.

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KEY WORDS: Analysis, automatic titrators, bar soap, chloride, potentiometric titration, silver nitrate, sodium chloride.

Sodium chloride is used in most bar soaps as a processing aid, and analysis of the chloride level is an important part of good quality control. Direct potentiometric titration was considered the procedure most amenable to automated analysis. Many direct titration procedures exist for the analysis of chlorides in a bar soap matrix; however, most require excessive time for sample dissolution, either at ambient temperatures or by warming to dissolve the sample, followed by cooling (1–4). Another problem comes from the soap itself, as most potentiometric titration procedures for chloride are performed after acidification with nitric acid, the fatty acids generated from the soap itself can cause problems by precipitating and forming a sticky semisolid mass (this is not a problem with combination bars that contain anionic surfactants, which keep the fatty acids from solidifying). Several published methods use time-consuming steps to remove the soap or fatty acids by precipitation and filtration (1–4) or by extraction with ethyl ether (5). Others use alcohol or acetone to minimize precipitation of fatty acids (6), but these still require relatively long dissolution times or heating to dissolve the sample, followed by cooling. In this paper we describe a simple one-step acidification/dissolution in H_2SO_4/methanol to simultaneously dissolve the bar soap sample at ambient temperature and to esterify the soap to noninterfering methyl esters to prevent fatty acid interference. Water is then added, and the chloride is titrated potentiometrically; this sample preparation is especially useful for automatic titrators.

EXPERIMENTAL PROCEDURES

Instruments and conditions. Analyses were performed on a Mettler DL 70 automatic titrator, equipped with a DM 141-SC silver combination electrode and an ST 20 sample tray (Mettler-Toledo Inc., Hightstown, NJ). Manual potentiometric titration could also be used.

Reagents and solutions. Standardized 0.1000 N silver nitrate was purchased from Ricca Chemical Co. (Arlington, TX). Methanol and sulfuric acid were each ACS-grade and purchased from Mallinckrodt Specialty Chemicals Co. (Paris, KY). H_2SO_4/methanol was prepared by adding 140 mL sulfuric acid to 4 L of methanol.

Assay procedure and calculation. Three grams of chopped bar soap are weighed (±0.01 g) into a 100-mL polypropylene titration beaker. A stir bar and 40 mL H_2SO_4/methanol is added and stirred for 10 min to dissolve and esterify the sample. The stir bar is then removed, 40 mL water is added, and the beaker is placed in the sample tray for automated direct potentiometric titration with 0.1000 N silver nitrate.

$$\%\ \text{sodium chloride} = \frac{\text{mL AgNO}_3 \times \text{N}_{\text{AgNO}_3} \times 5.844}{\text{g sample}} \qquad [1]$$

RESULTS AND DISCUSSION

Method development. In our laboratory there was a need for a simple, straightforward procedure to determine chloride in bar soaps. Our efforts over the years to simplify this procedure have included a Volhard titration in which ethyl ether kept the fatty acids in solution (but required titration in a fume hood and two standardized reagents) and a direct potentiometric titration with standardized silver nitrate after an anionic surfactant was added to solubilize generated fatty acids. We saw the opportunity to develop a new procedure that would require less operator time, be amenable to automated analysis and provide reliable quantitation. Because we had considerable experience in performing automated potentiometric titrations for chloride in detergent samples and combination/synthetic bars, it seemed natural to use a similar procedure for bar soaps. To prevent agglomeration of semisolid fatty acids (and possible low results due to occlusion of chloride), addition of a small amount of low-chloride synthetic anionic surfactant, such as sodium cocoyl isethionate was tried; this worked adequately but added a small, constant positive error due to the chloride in the anionic surfactant and still required the time-consuming warming/cooling sample preparation steps. It was then found that H_2SO_4/methanol would not only dissolve the sample at ambient temperature but also simultaneously converted the soap to noninterfering liquid methyl esters; this solution was simply mixed with water and automatically titrated.

TABLE 1
NaCl Recovery from Spiked Soap

	Theoretical % NaCl	Experimental % NaCl	% Recovery
Sample 1	0.448	0.443	98.9
Sample 2	0.670	0.669	99.9
Sample 3	0.844	0.842	99.8
Sample 4	1.182	1.181	99.9
Sample 5	1.341	1.334	99.5

Accuracy and precision. Methodology validation studies were conducted in which bar soap samples analyzed by this method compared well to samples containing known amounts of chloride. Also, chloride-free soap was spiked with known amounts of NaCl at realistic use levels and analyzed—recovery averaged 99.6%. The results are detailed in Table 1.

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