The Determination of Sodium, Potassium and Magnesium in Surfactants by Flame Spectrophotometry[1]

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Abstract

A method for determining sodium, potassium, and magnesium in soaps and detergents by means of flame spectrophotometry is described in detail. Sodium and/or potassium are normally present in high percentages; magnesium is usually found in relatively low concentrations as part of the antioxidant system of bar soaps. The spectrophotometric procedure has the following advantages over commonly used wet methods: 1) rapidity, 2) simplicity, and 3) the cations are determined directly and independently of each other. Soap additives, such as perfumes, colors, super-fatting agents or germicides do not interfere with this method. Possible interferences between sodium, potassium, and magnesium cations were evaluated and eliminated. Typical examples, including toilet soaps, combination soap-detergent bars, and sprayed detergents are described.

Introduction

THE SODIUM, potassium, and magnesium cations in soaps and detergents are usually determined by a variety of standard analytical methods. Foremost of these are the periodic acid method for potassium and the pyrophosphate method for magnesium (1). An alternate method for determining sodium, potassium, and magnesium in soap is by way of flame spectrophotometry.

Flame spectrophotometry has been used to determine sodium and potassium in many areas as, e.g., in the analysis of water (2), minerals (3), soil(4), and animal tissues (5). The method has also been used to estimate magnesium in feldspar (6), cement (7), and biological fluids (8). More recently sodium, potassium, and calcium in leaves have been determined by flame spectrophotometry (9). No reports have appeared discussing the extension of this method to soaps and detergents. It is the purpose of this paper to discuss such a method in detail.

Experimental

Equipment and Reagents

Beckman model DU spectrophotometer with flame attachment
Oxygen, commercial grade
Hydrogen, commercial grade
Potassium chloride, reagent grade
Sodium chloride, reagent grade
Magnesium oxide, reagent grade
Hydrochloric acid, reagent grade
Platinum crucibles
Demineralized water

Procedure

1) Dry the sample at 110C.
2) Ash 0.5000 g of sample in platinum dish.
3) Wash ash with water into a one liter volumetric flask and fill to the mark.
4) Measure luminosity on Beckman model DU spectrophotometer equipped with flame attachment.
5) Operate flame attachment at 10 psi oxygen and 2.50 psi hydrogen pressure.
6) Use instrument selector at 0.1 with specific setting shown:

Element	Wavelength	Resistor	Slit	Photomultiplier
Sodium	589	2	0.02	1
Potassium	766	3	0.1	1
Magnesium	285.3	2	0.04	4

7) Obtain concentration of cation by comparing with standard curve.

Preparation of Standard Curves

Standard Curve for Sodium

A standard stock solution of sodium chloride was prepared so that one ml was equivalent to 1.19 mg of sodium. Aliquots were placed in 100 ml flasks and filled to volume with distilled water. The transmission of the most concentrated solution was set at 100%. The per cent transmission readings of the aliquots plotted against parts per million sodium are shown in Figure 1. Standards were checked before and after each series of unknown samples was analyzed, and also were inserted in the series where the number of samples was large in order to guard against small drifts in oxygen pressure and undefined changes in atomizer characteristicis.

Standard Curve for Potassium

Potassium chloride was dissolved in 1 liter of water to make standard potassium solutions. One ml of stock solution was equivalent to 0.85 mg of potassium. The standard curve (Figure 1) was prepared using the technique described above.

Standard Curve for Magnesium

A liter of magnesium stock solution was prepared from reagent grade magnesium oxide which had been dried at 105C. N_2 HCl (25 ml) was used to bring the salt into solution. One ml of this stock solution was equivalent to 0.130 mg of magnesium. The per cent transmission readings obtained were

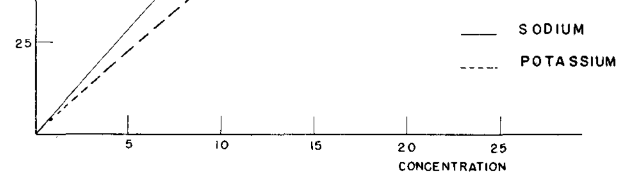

FIG. 1. Standard sodium and potassium emission curves.

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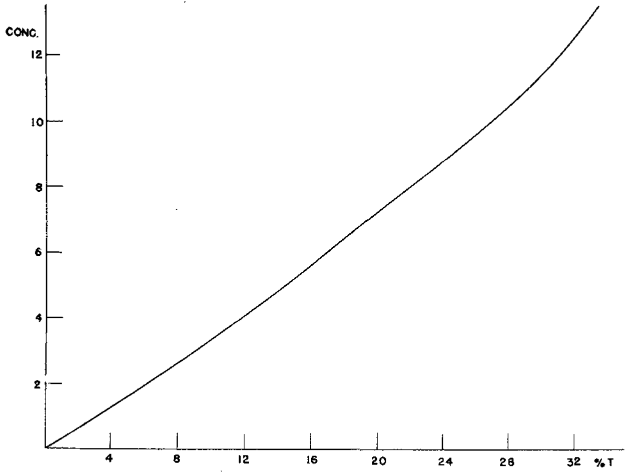

FIG. 2. Standard magnesium emission curve.

plotted against concentration to obtain the standard curve shown in Figure 2.

Discussion

Sodium and potassium are both measured in the visible region of the spectrum: sodium at 589 mμ and potassium at 766 mμ. The analysis of members of Group II-A of the periodic table is beset with greater difficulties than analysis of the alkali metals. Unlike sodium and potassium, the flame spectrum of magnesium is not due entirely to the free atoms, but also contains lines from the ionic species. The only wavelength for magnesium which is free from interference from sodium falls in the ultraviolet region at 285.3 mμ. Using these wavelengths, standard curves were prepared by the usual techniques.

The accuracy of the standard curves was obtained by having unknown solutions prepared from the appropriate stock solution and determining the emission under the same conditions and instrument settings as used for the preparation of the standard curves. The apparent cation concentration was determined from the standard curves. In no case did measured and calculated values differ by more than 0.3 ppm.

Evaluation of Interferences. Some soaps and detergents contain both sodium and potassium salts. In order to evaluate the effect on the presence of potassium on the sodium determination, three standard solutions all containing the same amount of sodium but different quantities of potassium were prepared. Interference of potassium would be indicated by a change in the per cent transmission reading of these samples. Results are shown in Table I. It is apparent from these data that, under these conditions, potassium has no effect on the emission of sodium.

The effect of sodium on potassium emission was determined by reading the per cent transmission of standard solutions containing both sodium and potassium ions under the same conditions used to prepare the calibration curve for potassium. These results are also summarized in Table I. The results indicate that at the upper limit of the calibration curve the presence of sodium at concentrations of 5 or 10 times that of potassium will increase the emission intensity of potassium causing slightly higher results. This interference can be overcome by taking a smaller aliquot, so that the transmission readings will occur in the middle or lower portion of the calibration curve.

TABLE I
Cation Interferences

Sodium ppm	Potassium	Magnesium	%T
17.85	0		85.9
17.85	1.7		85.6
17.85	3.4		85.9
250	25.5		103
125	25.5		103
167	17.0		72.1
83.5	17.0		72.0
83.5	8.5		38.9
41.8	8.5		38.7
0		2.6	72.8
274		2.6	72.9
500		2.6	72.9
0		7.8	86.3
819		7.8	87.0

Standard solutions containing both sodium and magnesium ions were prepared and the transmission determined under the same conditions as used for the preparation of the magnesium calibration curve. These results, shown in Table I, demonstrate that large concentrations of sodium ion have negligible effect on the magnesium determination. This is true only at the particular wavelength selected for magnesium determination.

Effect of Operating Conditions. Variation of the ratio of fuel to oxygen affects the temperature of the flame gases and the dimensions of the flame itself. The pressures and flow rates which produce maximum intensity of an emission line or band vary somewhat, depending upon the element, its concentration, and the wavelength used for measurement. Failure to operate exactly at the maximum intensity does not affect the accuracy of the analysis. However, it is desirable to operate near the maximum emission because the most narrow spectral bandwidths can be used and also, if the approach to the maximum is relatively steep, there is least disturbance from gas pressure variations. To evaluate this variable, the emission intensity of a known amount of sodium was determined as a function of the hydrogen pressure with oxygen pressure as a parameter. Per cent transmission at the initial hydrogen pressure of 2 psi was set at 50% by adjusting the sensitivity. The emission intensity of sodium was then measured as a function of hydrogen pressure alone. This is shown in Figure 3. A final pressure of 2.5 psi was selected to insure that slight variations in the hydrogen pressure would have minimal effect on the luminosity. Using a magnesium standard containing 2.6 ppm magnesium, the emission intensity of magnesium was determined as a function of the hydrogen pressure. The results obtained are shown in Figure 3. Using the same instrument settings, the emission intensity of the same magnesium standard was determined as a function of the

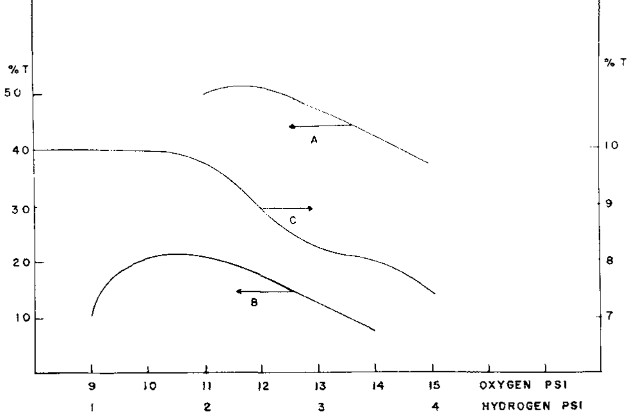

FIG. 3. Emission intensity of sodium as a function of hydrogen pressure (A), and magnesium as a function of hydrogen (B) and oxygen (C) pressure.

TABLE II
Analysis of Soaps and Detergents

Sample	Type	% Cation					
		By flame spectrophotometry			By wet methods (1)		
		Sodium	Potassium	Magnesium	Sodium	Potassium	Magnesium
A	Spray-dried detergent	23.16	0	......	23.76	0	......
B	Light duty liquid detergent	2.10	9.82	......	2.51	10.01	......
C	Heavy duty liquid detergent	2.20	6.94	......	2.31	7.06	......
D	Bar Soap	5.89	2.11	......	6.00	2.17	......
E	Soap-synthetic bar	9.58	0.04	0.03	9.61	0.05	0.03

oxygen pressure with a hydrogen pressure of 1.75 psi, which is the pressure corresponding to maximum emission for magnesium, as a parameter. See Figure 3.

At an oxygen pressure of 10 psi slight variations in the pressure would not affect the luminosity. However, it was found that a calibration curve from 0 to 13 ppm magnesium could not be prepared when the oxygen pressure was 10 psi and hydrogen pressure was 1.75 psi. When the hydrogen pressure was changed to 2.5 psi the readings of the magnesium standard became continuous and a calibration curve could be drawn. If the hydrogen pressure drops from 2.50 psi to 2.45 psi, the transmission readings will increase 0.44 scale division, which amounts to about 0.1 μg of magnesium.

Examples of the Determination of Sodium, Potassium, and Magnesium in Soaps and Detergents. To illustrate the usefulness of the method, five commercial products were analyzed for sodium, potassium, and magnesium. The types of samples analyzed and the results obtained are summarized in Table II. Excellent agreement between results obtained spectrophotometrically and by standard wet methods was obtained. The procedure followed was essentially the same in each case, except that with liquid detergents the samples were dried at 110C prior to ashing. It was found that carbon was more readily burned off when using a platinum rather than porcelain dish. Also, the residue was more easily removed from the platinum than from porcelain or vitreosil dishes.

In conclusion, the determination of sodium, potassium, and magnesium in soap by means of flame spectrophotometry is useful because of the speed and accuracy of the method. Inherent difficulties, such as determining small quantities of magnesium in the presence of large amounts of sodium, were overcome by proper selection of wavelengths and instrumental conditions.

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Kinetic Studies of Detergency. I. Analysis of Cleaning Curves

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Abstract

The kinetics of removal of thin films of pure radioactive tristearin from a stainless-steel surface by .03 M NaOH was studied in a circulation system. The data obtained are consistent with the presence of two species of tristearin, each species being removed simultaneously by a first-order process and behaving independently of the other. The principal evidence for the existence of the two species is the excellent agreement of the experimental data with the mathematical techniques of kinetics over a wide range of experimental conditions. Rate constants for the removal of each species and the relative proportions of the two species are given for different experimental conditions. It is shown that the difference between the two species must be based on some physical factor, and possible explanations are discussed. The presence of two species gives a satisfactory explanation for hitherto unexplained results of other workers.

Introduction

DETERGENCY, A PRACTICAL EVERYDAY OPERATION, usually involves removal of a thin film from a surface by a liquid. Although standards of efficiency are presently high, the literature shows that our understanding of detergent processes lags far behind practice. Most detergent research at the fundamental level has been concentrated on fibers and textiles, even though the cleaning of hard surfaces is conceivably more important as directly related to the wholesomeness of food.

In most detergency studies, the time factor is held constant while other variables are studied. In this investigation of the *rate* of soil removal, in contrast, the main variable under consideration was the time factor.

Rhodes and Brainard (31) pointed out the need for an index of detergent power that would be based on experimental data. They found that log-log plots of detergency vs. time were linear, and suggested that the slopes would be some index of detergent power. Bacon and Smith (4) stressed the importance of mechanical action in detergency and the effect of detergents in reducing the work requirement. They varied the force factor of their mechanical washing device 48-fold and found that their data fitted the equation

$$S = K\ (CFT)^n$$

where S = soil removed, C = detergent concentration, F = force, T = time, K and n are constants, and n is between 0 and 1.

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