random distribution of different proportions of two elements in combinations of three. The composition of the glycerol-glyceride fraction in the reaction product is determined by the fraction of glyceryl linkages broken. Reaction time, concentration of reactants and catalyst, and the temperature have no effect outside of determining the number of linkages broken.

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Semi-Micro Analysis of Soap. III. Semi-Micro Determination of Potassium.

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THE classical method for the determination of potassium involves precipitation of the potassium by chloroplatinic acid. This is the basis of the A.O.C.S. Official Method (1). In this laboratory we have secured consistently better reproducibility of results by precipitating sodium as the sodium uranyl zinc acetate (2, 3, 4) and determining potassium indirectly by difference. In addition, the "triple acetate" method, as it has been called, effects a decided saving in time. These facts have accordingly governed our choice of selecting the "triple acetate" method for use on a semi-micro scale. The presence of potassium in a soap can be readily ascertained by a flame test or by the use of p-dipicrylamine (5).

Semi-Micro Determination of Potassium in Soap

Reagents Required

Uranyl Zinc Acetate Solution. Prepare the following solutions:

a) Mix 10 grams of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, 6 grams of 30% acetic acid and 50 ml. of water and warm to dissolve.

b) Mix 30 grams of zinc acetate, $Zn\ (C_2H_3O_2)_2 \cdot 3H_2O$, 3 grams of 30% acetic acid and 50 ml. of water, and warm to dissolve.

Prepare the uranyl zinc acetate solution by mixing equal volumes of solutions a) and b), allowing to stand 24 hours, and then filtering off the precipitate of sodium uranyl zinc acetate usually formed from traces of sodium in the reagents. If no precipitate is formed, add a small amount of sodium chloride to saturate the solution with the triple acetate. Allow the solution to stand with occasional shaking at a controlled temperature of 18 to 20°C. for 12 hours, filter at 18 to 20°C. and use in the method at approximately the same temperature to avoid errors due to solubility changes.

95% Ethyl Alcohol (Saturated With Sodium Uranyl Zinc Acetate)

Shake 95% ethyl alcohol with a small portion of sodium uranyl zinc acetate at room temperature until saturated. The sodium uranyl zinc acetate may be prepared by precipitating sodium chloride with uranyl zinc acetate solution and washing the precipitate with small volumes of the precipitant.

Procedure

Ethyl Ether or Acetone

Transfer about 25 mg. of the sample, accurately weighed, to a 10-ml. beaker. If the sample is a liquid soap or one containing a high percentage of moisture, take sufficient sample to insure approximately 25 mg. of dry soap. Add 5 ml. of water and heat on the steam bath to complete solution. Transfer the solution quantitatively to a 25-ml. volumetric flask and bring to volume with water at room temperature. Transfer a 2-ml. aliquot, very carefully measured by a pipet, to a 10-ml. platinum dish. Evaporate to dryness on the steam bath. Ignite over a low Bunsen flame to complete charring. Add 2 ml. of water and warm on the steam bath to dissolve all soluble matter. Filter through a paper filter (No. 40 Whatman, 35 mm. in diameter) and wash the charred matter with hot water, catching the filtrate in a 25-ml. platinum dish. Return the filter paper and contents to the 10-ml. platinum dish and ash completely. Cool and dissolve the residue in hot water. Add the solution to the filtrate in the 25-ml. platinum dish. Evaporate to a volume of 1 ml. or less.

Add 10 ml. of uranyl zinc acetate solution previously kept at 18 to 20°C. for several hours, mix, and allow to stand for 30 to 60 minutes at 18 to 20°C. An improvised apparatus for maintaining the precipitation vessel at 18 to 20°C. is readily constructed as shown in Fig. 1. If available, a constant temperature bath may be employed instead.

Filter off the precipitate of sodium uranyl zinc acetate in a Gooch crucible, suck dry, and wash the precipitation dish, crucible, and precipitate with 5 to 6 small portions of the reagent, draining the crucible well each time.

Next, wash 5 times with 0.5-ml. portions of ethyl alcohol wash solution and finally with a few small portions of ether or acetone.

Draw air through the crucible for a few minutes to volatilize the ether or acetone. Transfer the crucible and contents to the balance case and weigh after 10 or 15 minutes. Calculate the per cent of potassium present in the sample as follows:

$$\frac{\text{Weight of precipitate} \times 0.01495 \times 100}{\text{Weight of sample in aliquot}} = \%\ \text{Na}$$

$\%$ Na × 1.3479 = $\%$ Na as Na_2O
Total alkali as $\%$ Na_2O − $\%$ Na as Na_2O = $\%$ K as Na_2O
$\%$ K as Na_2O × 1.5196 = $\%$ K as K_2O
$\%$ K_2O × 0.8302 = $\%$ K.

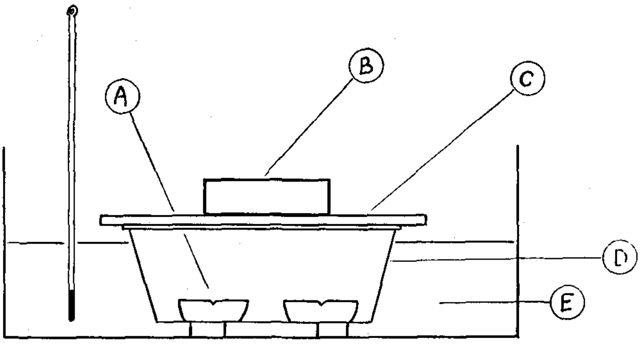

FIG. 1. Improvised apparatus for maintaining precipitation vessels at 18-20°C. *A* are precipitation vessels, *B* is a lead weight, *C* is a transite cover, *D* is a metal dish, and *E* represents water at 18-20°C.

Discussion

The solubility of sodium uranyl zinc acetate hexahydrate in water is 5.85 grams per 100 ml. of solution at 21°C. For this reason the above described precipitation procedure must be closely followed to separate sodium quantitatively. The uranyl zinc acetate solution must be used at approximately the same temperature at which it was prepared (18 to 20°C.) to avoid errors due to solubility changes.

Potassium interferes with the precipitation of sodium when present in relatively large amounts. If more than 50 mg. of potassium as potassium chloride are present per ml. of solution to be precipitated, the solution must be diluted until the concentration falls within this limit. The reagent must be added in the ratio of at least 10 ml. to 1 ml. of the alkali solution to precipitate sodium quantitatively.

TABLE I

Comparison of Results Obtained by the Use of Platinum and Pyrex Vessels

NaCl Present		
By titration	By macro triple acetate method	By semi-micro triple acetate method
%	%	%
39.30	39.32	40.22* 41.94* 41.58* 40.25* 41.00* 38.71** 38.82**

* Pyrex vessels.
** Platinum vessels.

The precipitate is weighed in the air-dry state as Na $(C_2H_3O_2) \cdot$ Zn $(C_2H_3O_2)_2\, 3UO_2\, (C_2H_3O_2)_2 \cdot 6H_2O$.

It has been found that precipitation of the triple acetate in glass beakers produces high results for sodium. For this reason the preparation of the sample and precipitation are carried out in platinum vessels. Use of platinum also insures that the contents of the dish will remain at 18 to 20°C. during the precipitation period inasmuch as platinum is a better conductor of heat than glass.

Table I presents a comparison of results obtained by use of glass and platinum vessels.

Results

Table II presents data showing that the recovery of NaCl from mixtures of the latter and KCl is satisfactory. These values were obtained by dissolving 50 mg. each of mixtures of varying ratios of KCl and NaCl in 50 ml. of water and taking 2-ml. aliquots for analysis. Before precipitation the aliquot was reduced to a volume of 1 ml. or less by evaporation on the steam bath.

TABLE II

Recovery of NaCl From KCl: NaCl Mixtures

Detm. No.	Weight KCl taken	Weight NaCl taken	Weight NaCl found
	mg.	*mg.*	*mg.*
1	0.00	2.00	1.96
2	0.40	1.60	1.54
3	0.80	1.20	1.14
4	1.20	0.80	0.72
5	1.60	0.40	0.27
6	2.00	0.00	0.00

Table III presents a comparison of the results for anhydrous soap content of various commercial soap products obtained by the macro versus semi-micro procedures. Satisfactory agreement is evidenced.

TABLE III

Comparison of the Results for Anhydrous Soap Content of Various Soap Products (Macro vs. Semi-Micro Procedures)

Product	Sodium as Na		Anhydrous sodium soap		Anhydrous potassium soap	
	Macro	Semi-micro	Macro	Semi-micro	Macro	Semi-micro
	%	%	%	%	%	%
Bar soap A	6.56	6.48	16.29*	17.35	71.68	70.67
Bar soap B	6.77	6.70	12.92	13.04	73.50	72.64
Bar Soap C	6.15	6.14	18.07	18.13	62.90	62.85
Spray soap A	11.95	11.89	6.64	7.44	51.47	50.71
Spray soap B	7.10	7.00	17.48	18.75	77.57	76.36
Soap flakes A	6.65	6.50	22.78	24.70	71.74	69.91
Soap flakes B	7.88	7.99	9.62	8.24	85.07	86.38
Soap flakes C	6.15	5.99	29.24	31.40	65.55	63.55
Soap flakes D	7.83	7.89	11.37	10.63	83.84	84.36
Soap flakes E	6.01	5.90	23.44	24.88	70.17	68.81

* Chloroplatinate method gave a value of 17.32%.

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