[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF VERMONT.]

THE DETERMINATION OF POTASSIUM AND SODIUM AS CHLORIDES THROUGH USE OF THE REFRACTOMETER.

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The method about to be described for the determination of potassium and sodium as chlorides, each in the presence of the other, depends upon the facts that the refractive indices of aqueous solutions of potassium and sodium chlorides vary linearly with their concentrations and that the values of the indices of sodium chloride solutions are higher than are those of the corresponding solutions of the potassium salt, the difference increasing with increase in salt concentration. These facts are exhibited in Fig. I, in which the values of Table I are plotted. The indices are those for the D line, and measured at 25°. The instrument used was the Pulfrich refractometer.

The materials used in all of the recorded measurements were prepared as follows: The ordinary laboratory-distilled water was redistilled once, care being taken to prevent passage of spray into the condenser, and the first third of the distillate was discarded. Preserved in a glass container, this water showed uniformly, at 20°, a refractive index of 1.33307.

The potassium chloride of highest commercial purity was once recrystallized, with centrifugal draining. The crystals were heated in a platinum dish to dull redness and preserved in a desiccator.

Table salt was the source of the sodium chloride used. This was twice precipitated from its concentrated aqueous solution through saturating the solution with hydrogen chloride, generated by heating concentrated, chemically pure, aqueous hydrochloric acid. The crystals were drained and the final crystals ignited and preserved as in the case of the potassium salt. Constancy of refractive index indicated that further purification of the salts was not necessary.

TABLE I.

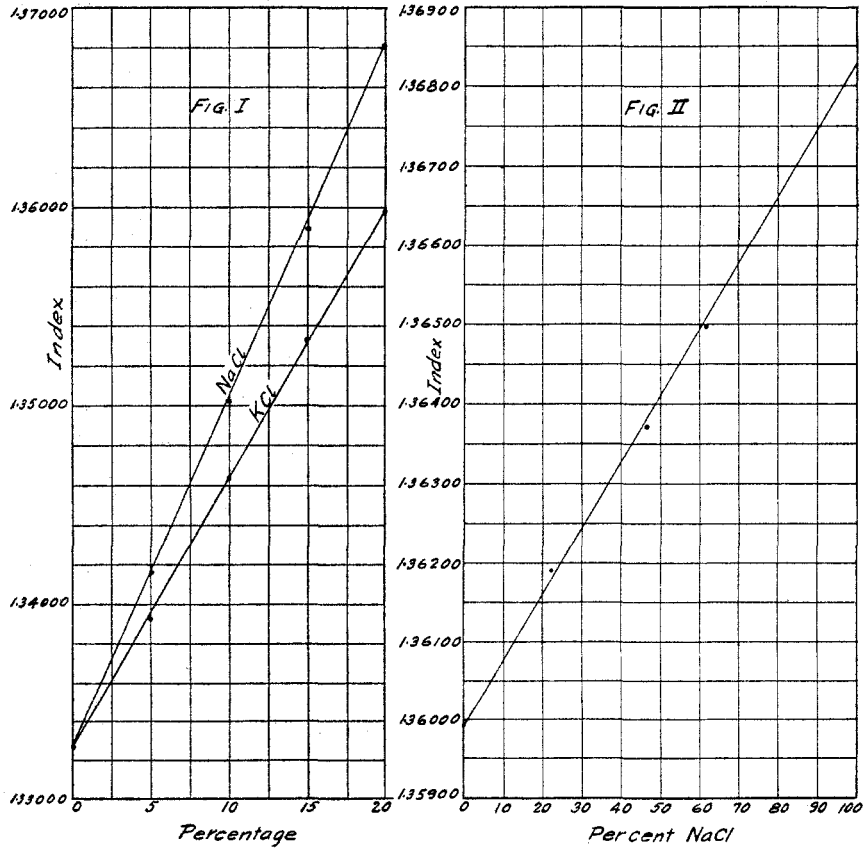
Salt.	G. salt.	G. solution.	% salt.	Index.
KCl	0.0602	1.2042	5.00	1.33931
KCl	0.2770	2.7700	10.00	1.34643
KCl	0.4468	2.9786	15.00	1.35335
KCl	0.5632	2.8162	20.00	1.35992
NaCl	0.2126	4.2520	5.00	1.34172
NaCl	0.9454	9.4536	10.00	1.35021
NaCl	0.9768	6.5118	15.00	1.35893
NaCl	0.9308	4.6536	20.00	1.36829

In Table II are given refractive indices at 25° of solutions of mixtures of potassium and sodium chlorides. In each solution, the total salt concentration is 20%.

TABLE II.

Composition of salt mixture.		
% KCl.	% NaCl.	Index.
00.00	100.00	1.36829
39.20	61.80	1.36499
53.25	46.75	1.36372
67.67	22.23	1.36190
100.00	00.00	1.35992

The values of Table II are plotted as Fig. II. In this plot, the compositions of the salt mixtures dissolved are expressed in terms of their percentage contents of sodium chloride.



The determination is carried out as follows: From the salt mixture to be analyzed, consisting exclusively of potassium and sodium chlorides, a 20% solution is prepared as exactly as possible. This may be done with little expense of time by adding to the mixture, contained in a weighing bottle, slightly more than the calculated weight of water, and evaporating to just this weight, through passing a current of warm air over the

surface of the solution. A single cc. of the solution is ample for the determination. The thoroughly mixed solution is brought to the temperature of 25° in the jacketed cell of the instrument and the index is determined. The necessity of precise control of the temperature is to be emphasized, since a variation of 0.1° in temperature changes the index about 0.00002. From the index of the mixture and those of the pure, single chlorides in 20% solution, the composition of the mixture is calculated by simple proportion. Thus the index of the 20% solution of a certain mixture was found to be 1.36244. The indices of the 20% potassium and sodium chloride solutions are, respectively, 1.35992 and 1.36829 (the first and last values of Table II), whence,

$$\frac{1.36829 - 1.36244}{1.36829 - 1.35992} = \frac{\%\ KCl}{100}.$$

The total difference in refractive indices of 20% sodium chloride and 20% potassium chloride is only 0.00837. A change, then, of 1% in the relative concentration of a salt mixture will change the index only 0.00008, whereas a variation of 0.1% in total salt concentration changes the index about 0.00018. Because of these facts, and because of the marked variation of the index of refraction with variation of temperature, the method is not of high accuracy. Owing, however, to its comparative rapidity and to its avoidance of costly reagents, there may be instances in which it will prove of use.

Table III gives the results of several trial analyses.

TABLE III.

Actual composition (% KCl).	Index.	Composition calculated from index (% KCl).
69.44	1.36244	69.3
43.09	1.36463	43.7
28.95	1.36582	29.0
00.42	1.36820	1.1

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

A NEW METHOD FOR THE SEPARATION OF THE COPPER GROUP FROM THE ARSENIC GROUP, WITH ESPECIAL REFERENCE TO THE IDENTIFICATION OF ARSENIC.

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In qualitative chemical analysis, yellow ammonium sulfide is universally employed for the separation of the copper from the arsenic group. This method is not entirely satisfactory, because some copper sulfide dissolves as well as the sulfides of arsenic, antimony, and tin.[1] To obviate

[1] Rössing, *Z. anorg. allgem. Chem.*, **25**, 407 (1900); *Z. anal. Chem.*, **41**, 1 (1902); Noyes, THIS JOURNAL, **29**, 170 (1907).