

Analysis by Extraction and High Frequency Measurement

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The usefulness of radio frequency measurements in quantitative analysis has been under investigation in several laboratories for about ten years. Numerous reports have been made on instrumental design, theory and application. Some of the applications have involved titrations, and others have been direct determinations of concentration.

The purpose of this study was to investigate the usefulness of this type of measurement in direct determinations of concentration following extraction of an inorganic substance in an organic liquid. Two specific determinations were selected, the determination of lithium chloride in mixtures with sodium chloride, and the determination of calcium nitrate in mixtures with strontium nitrate. Both determinations are difficult by ordinary chemical methods because of the close chemical similarity between the two substances in each case.

Experimental

A model V Sargent oscillometer was used for all high frequency measurements. The readings are, in effect, in empirical units of capacitance.

For each of the two systems, a series of weighed portions of the substance to be determined was prepared, a portion of the organic liquid was added by pipet, the mixture was shaken until dissolution was complete, and a reading was taken on a portion of the liquid. From these data a calibration curve was prepared. Then a series of standard mixtures was prepared, the organic liquid added, the mixture shaken, and a reading made on a portion of the clear supernatant liquid. For each of the latter readings, the amount of desired substance was read off the calibration curve and compared with the amount used in preparing each sample. All readings were corrected to a fixed temperature, 25° C., by means of empirically determined correction data.

1. Determination of lithium chloride in mixtures with sodium chloride.

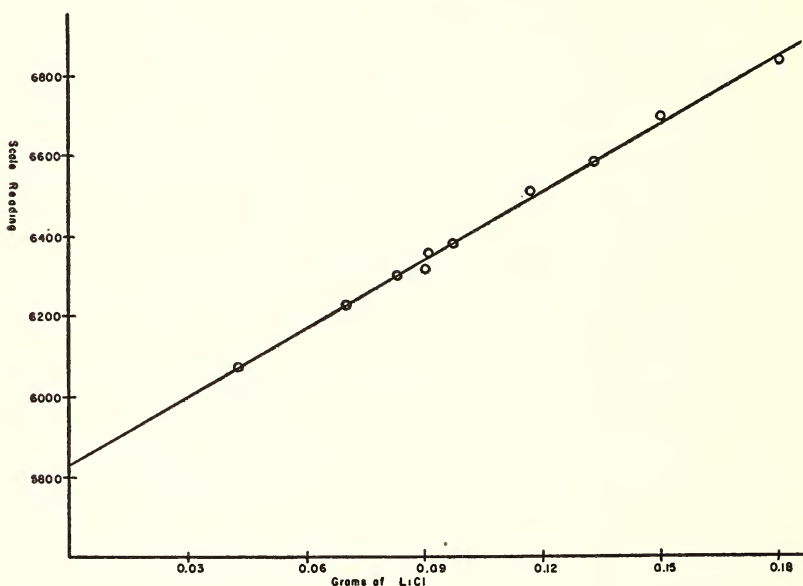
The organic liquid selected to extract lithium chloride was 2-ethyl hexanol. The listed solubilities (gram per 100 ml.) for some alkali chlorides in 2-ethyl hexanol are: Li Cl, 3.0; Na Cl, 0.0001; K Cl, less than 0.00001 (2). Batches of the solvent were purified prior to use by two fractional distillations, collecting the fraction distilling at 184-185° C. Reagent grade lithium chloride and sodium chloride were used, each being dried at 110° C. for 12 hours and stored in a desiccator.

The effect of temperature variation upon the scale reading for the pure solvent was determined by direct experiment. The scale reading decreases by about 57 units per degree C. increase in temperature. The

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temperature dependence of solutions of lithium chloride in 2-ethyl hexanol appeared to be about the same, so an additive or subtractive correction was made upon all subsequent readings to correct them to 25° C.

In obtaining data for the calibration curve, a 25-ml. portion of the organic liquid was used for each sample, and a 10-ml. portion of this was used for the reading. About three hours were required for complete dissolution of the lithium chloride. The calibration curve is shown in figure 1. With larger amounts of lithium chloride, the curve levelled off and above about 0.5 gram, actually reversed its slope, so the linear portion shown in figure 1 was used.

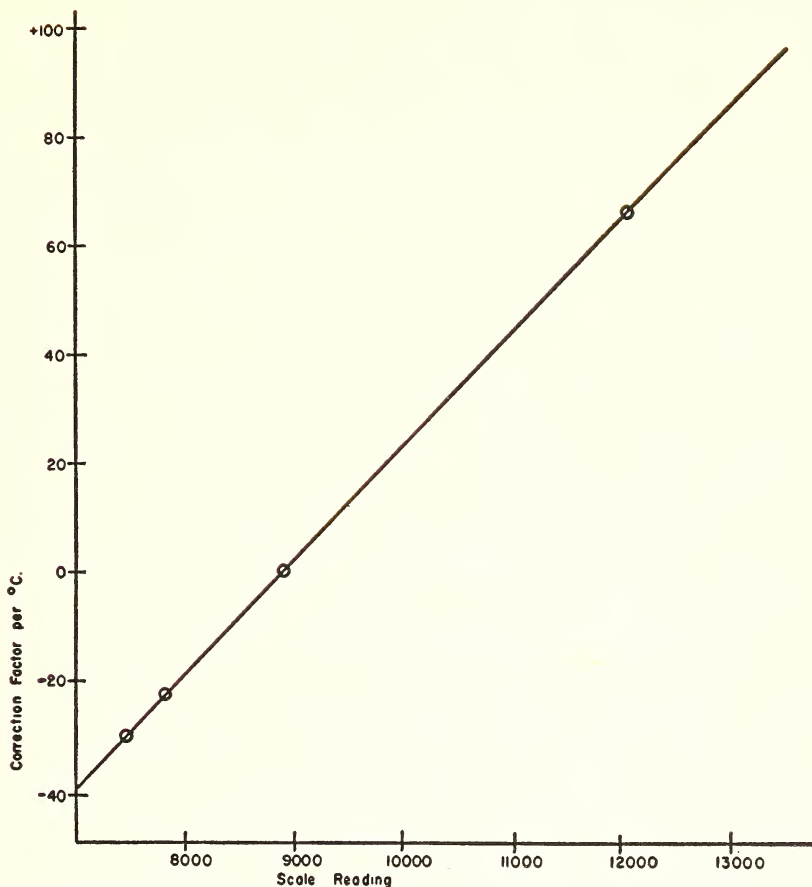


Calibration Curve for Determination of Lithium Chloride

Mixtures of lithium chloride and sodium chloride were prepared, and the amount of lithium chloride in each was determined, by extraction and measurement, with the aid of the calibration curve. Comparative data on the amounts "taken" and "found" are listed in table 1. The standard deviation of an individual result is about 0.0013 gram lithium chloride per 25 ml. of 2-ethyl hexanol, which corresponds to about 3.3% of the smallest amount of lithium chloride and to about 0.9% of the largest amount.

2. Determination of calcium nitrate in mixtures with strontium nitrate.

The extracting liquid selected was butyl cellosolve, in which some listed solubilities (gram per ml.) are: Ca (NO₃)₂, 0.243; Na NO₃, not more than 1.1×10^{-5} ; Ba (NO₃)₂, not more than 2.3×10^{-6} (1). This solvent was also purified by double fractional distillation, retaining the portion distilling at 171-172° C. Reagent grade calcium nitrate and

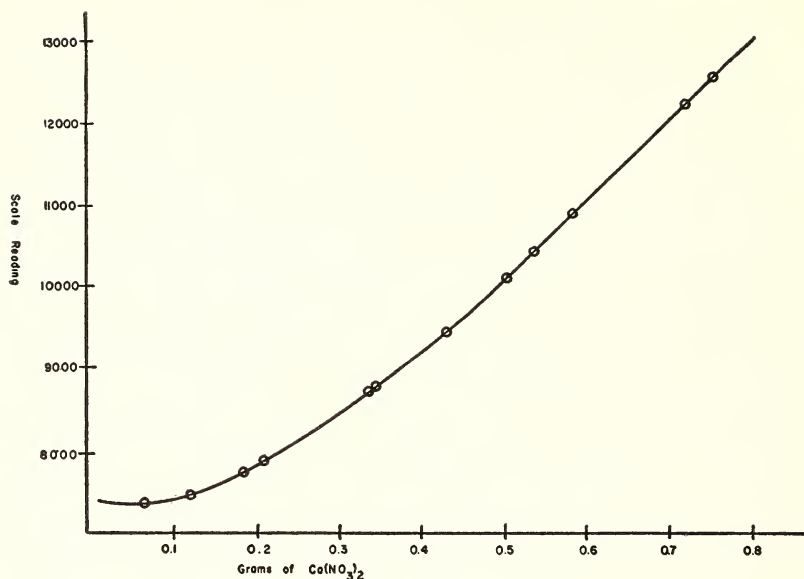


Temperature Correction Curve for Determination of $\text{Ca}(\text{NO}_3)_2$

strontium nitrate were used, the latter after drying at 110°C . for 12 hours. It was necessary to make the calcium nitrate anhydrous by heating at about 175°C . for 30 hours—determination of calcium by a conventional procedure revealed that this material was then stoichiometrically in the anhydrous form.

The effect of temperature variation upon scale reading was found to differ for the solvent and for solutions. The temperature data are summarized in table 2 and plotted in figure 2. A minus sign means that a temperature increase causes a decrease in the scale reading. With the aid of figure 2, all subsequent readings were corrected to 25°C .

In obtaining the data for the calibration curve, it was found that 45 minutes shaking time sufficed, with 25-ml. portions of the butyl



Calibration Curve for Determination of $\text{Ca}(\text{NO}_3)_2$

cellosolve and with amounts of calcium nitrate ranging from about 0.1 gram to 2.7 gram. The calibration data are plotted in figure 3.

Mixtures of calcium nitrate and strontium nitrate were prepared by direct weight, and the amount of calcium nitrate in each was determined, by extraction and measurement, with the aid of the calibration curve. Comparative data on the amounts "taken" and "found" are listed in table 3. The standard deviation of an individual result is 0.0041 gram calcium nitrate, which corresponds to from 4.5% to 0.4% of the amount of calcium nitrate taken.

Conclusion

It has been shown that lithium chloride can be determined in mixtures with sodium chloride with a standard deviation of 3.0 to 0.9 parts per hundred over the range of 0.04 to 0.14 gram lithium chloride by extraction with 2-ethyl hexanol and high frequency measurement and that calcium nitrate can be determined in mixtures with strontium nitrate with a standard deviation of 4.5 to 0.4 parts per hundred over the range of 0.09 to 0.90 gram calcium nitrate by extraction with butyl cellosolve and high frequency measurement. The extraction step is quite time-consuming, but the final measurements are quite rapid after the necessary calibration data are obtained. It is felt that the accuracy and precision in these experiments are limited primarily by residual irreproducibility of the instrument used. It is further felt that

the method of high frequency measurement would be applicable in other analytical determinations in conjunction with the extraction method of separating the desired substance.

TABLE 1. Results of Determinations of Lithium Chloride in Mixtures with Sodium Chloride.

g Na Cl taken	g Li Cl taken	g Li Cl found	difference
0.1319	0.0419	0.0419	± 0.0000
0.1676	0.0570	0.0580	$+0.0010$
0.1114	0.0790	0.0775	-0.0015
0.1211	0.0831	0.0811	-0.0020
0.1316	0.0835	0.0840	$+0.0005$
0.1225	0.0906	0.0899	-0.0007
0.1133	0.1000	0.1019	$+0.0019$
0.1271	0.1069	0.1080	$+0.0011$
0.1337	0.1081	0.1092	$+0.0011$
0.1491	0.1383	0.1374	-0.0009

TABLE 2. Effect of Temperature Variation Upon Scale Reading.

g $\text{Ca}(\text{NO}_3)_2$ /25 ml. solvent	Scale reading @ 25° C.	Change of scale reading per degree C.
0.0000	7469	-29
0.1726	7711	-21
0.3621	8953	+0
0.6197	11196	+66

TABLE 3. Results of Determinations of Calcium Nitrate in Mixtures with Strontium Nitrate.

g $\text{Sr}(\text{NO}_3)_2$ taken	g $\text{Ca}(\text{NO}_3)_2$ taken	g $\text{Ca}(\text{NO}_3)_2$ found	difference
0.3580	0.0901	0.0980	$+0.0079$
0.2460	0.1403	0.1382	-0.0021
0.1826	0.2376	0.2359	-0.0017
0.3990	0.3078	0.3049	-0.0029
0.2412	0.3855	0.3888	$+0.0033$
0.1750	0.4401	0.4435	$+0.0034$
0.2707	0.4418	0.4409	-0.0009
0.2770	0.5433	0.5430	$+0.0003$
0.2162	0.5735	0.5810	$+0.0075$
0.2621	0.6912	0.6872	-0.0040
0.2344	0.8476	0.8481	$+0.0005$
0.2042	0.9060	0.9095	$+0.0035$

Literature Cited

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2. CALEY, E. R., and AXELROD, H. D. 1942. Ind. Eng. Chem., Anal. Ed. **14**:242.