ketone was condensed but no reaction product was collected either in the trap or at the trough. The reaction product was mixed with water, the water distilled, and the first fraction collected. Qualitative tests for methyl alcohol and for formaldehyde were negative. The same condensation was carried out in an all-glass system to which a mercury manometer was attached, but no rise in pressure was observed in the manometer during the progress of the reaction.

Summary

Acetophenone and *p*-methoxyacetophenone, in the presence of concentrated sulfuric acid and potassium pyrosulfate, yield 2,4,6-triarylpyrylium acid sulfates in yields about equal to those of the *sym*-triarylbenzenes which are produced at the same time.

In the formation of the pyrylium derivatives one methyl group is lost from three molecules of the methyl aryl ketone, but we have not been able to determine what happens to it or to find that any volatile compound of carbon is produced by the reaction.

CAMBRIDGE, MASS. RECEIVED JUNE 14, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Use of the Concentration Cell in Quantitative Analysis. I. The Estimation of Small Amounts of Chloride in Salts

BY N. HOWELL FURMAN AND GEORGE W. LOW, JR.[1]

The application of the measurement of the e. m. f. of a concentration cell to problems of quantitative analysis appeared to the authors to offer possibilities of the development of an improved technique for the determination of amounts of certain substances ranging from minute traces to small percentages. The primary condition is that the substance to be determined shall be capable of affecting an electrode in a reversible manner.

We deal in this paper with a detailed illustration of the general method in its application to the estimation of small amounts of chloride which appear as impurities in salts. The technique is quite different from any previously used method and it gives results which are reproducible and satisfactory. The usual method for determining small amounts of chloride is the nephelometric procedure, and as has been frequently pointed out[2] this technique is not always satisfactory, especially in the presence of foreign salts. The electrometric procedure described in this paper, on the other hand, is just as applicable in the presence of foreign salts as in their absence.[3]

Theoretical.—The procedure consists in measuring the e. m. f. between two silver–silver chloride electrodes, one of which is dipping into a solution containing the unknown amount of chloride whereas the other dips into a solution containing the unknown amount of chloride *plus* a definite known amount of chloride which is added. Thus a concentration cell is set up, the e. m. f. of which is given by the following expression, at 25°

$$E = 0.0591 \log [f_1(x + a)/f_2 (x)] \qquad (1)$$

where x is the molar concentration of the unknown amount of chloride, a the molar concentration of the known amount of chloride added, f_1 and f_2 the chloride ion activity coefficients in the respective sides and E the observed e. m. f. of the cell. The activity coefficients, f_1 and f_2, depend upon the total ionic strength of the solutions and in the present series of measurements the total ionic strength in each side of the concentration cell is practically identical so that $f_1 = f_2$. Equation 1 therefore becomes

$$E = 0.0591 \log [(x + a)/x] \qquad (2)$$

In these e. m. f. measurements there are two other factors besides activities which must be considered, namely, the liquid junction potential and the solubility of the electrodes. In the present series of measurements the conditions were regulated so that the liquid junction was entirely negligible. This was done by making the solutions into which the two silver–silver chloride electrodes dipped *identical* except for the fact that one side of the cell has chloride of concentration x and the other $x + a$. Now x varies from 10^{-5} to 10^{-3} M and a is 10^{-2} M; and the total ionic strength throughout the cell is at no time lower than 0.25 M and is usually much larger than this.

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[1] J. T. Baker Chemical Co. Fellow in Analytical Chemistry, 1933–1934.

[2] P. V. Wells, *Chem. Rev.*, **3**, 331 (1927); C. R. Johnson, *J. Phys. Chem.*, **35**, 2237 (1931).

[3] Iodides and bromides would be expected to interfere with the determination of chloride by this method.

Since the liquid junction potential depends on the difference in concentration between the two solutions in the cell and since the latter never differ in concentration by more than the difference between 0.25 and 0.26 *M* (*i. e.*, 0.25 plus 0.01, the excess), we can neglect any liquid junction effects.[4] The fact that the results as given in Table I check so well justifies this argument.

The other factor, the solubility of the electrodes, cannot be neglected, especially when x is of the order of magnitude of the solubility of silver chloride, about 10^{-5} *M*. A correction to equation 2 must be applied in order to take care of the chloride which comes from the solution of the silver–silver chloride electrodes. This is made as follows. We have the concentration cell

$$\text{Ag, AgCl}\left|\begin{array}{l} \qquad\qquad \text{Ag}_y{}^+\,\text{Na}^+\,\text{Na}^+ \\ \text{HNO}_3 \\ 0.25\,M\,\text{Cl}_y{}^-\,\text{Cl}_x{}^-\,\text{Cl}_a{}^- \end{array}\right\|\begin{array}{r} \text{Na}^+\,\text{Ag}_z{}^+ \qquad\qquad \\ \text{HNO}_3 \\ \text{Cl}_x{}^-\,\text{Cl}_z{}^-\,0.25\,M \end{array}\left|\text{AgCl, Ag}\right. \quad \text{(cell 1)}$$

in which $\text{Ag}_y{}^+$ and $\text{Cl}_y{}^-$ represent the concentration of Ag^+ and Cl^- ions which come from the solution of the silver–silver chloride electrode in question, and $\text{Ag}_z{}^+$ and $\text{Cl}_z{}^-$ represent the Ag^+ ion and Cl^- ion concentrations from the solution of the other silver–silver chloride electrode; $\text{Cl}_x{}^-$ represents the molar concentration of the unknown amount of chloride and $\text{Cl}_a{}^-$ that of the excess of chloride added to one side. In all other respects the two sides of the cell are identical, *i. e.*, in the case where the unknown amount of chloride in nitric acid is being determined, the concentration of nitric acid throughout the system is 0.25 *M*, so that the only difference between the two sides of the cell is due to $\text{Cl}_a{}^-$, $\text{Cl}_y{}^-$ and $\text{Cl}_z{}^-$. The e. m. f. of cell 1 is then

$$E = 0.0591 \log\,[(x + y + a)/(x + z)] \qquad (3)$$

where x, y, z and a are the molar concentrations of the ions as indicated in cell 1. The values of y and z in equation 3 can be expressed in terms of x and the solubility product of silver chloride P, and the equation becomes

$$E = 0.0591 \log\,[2(x + 0.01)/(x + \sqrt{x^2 + (4P_0/f^2)})] \qquad (4)$$

where 0.01 represents the value of a used throughout this paper, P_0 the solubility product of silver chloride in pure water and f the activity coefficient of the silver chloride when the solubility product is P. The value of P_0 used throughout was $P_0 = 1.69 \times 10^{-10}$.[5] The values for f could not be found in any reference papers for the wide range of concentrations and salts used, so for each particular salt f was determined *experimentally* by measuring E and solving equation 4 for f when x is equal to zero (*i. e.*, in chloride free salts). The value of f thus determined can then be used in solving for x in equation 4, when there *is* an unknown amount of chloride present.

Experimental Part

Apparatus and Materials.—The salts used in these experiments were kindly furnished by Dr. C. R. Johnson, and had been crystallized from chloride-free water until free from chloride or until the chloride was less than an amount which would cause difficulties in the present series of measurements. Similarly, the water and nitric acid used were purified very carefully by distillation of the former through block tin condensers and the latter through quartz apparatus, using atomic weight technique throughout. The electrodes were prepared by electroplating silver on platinum gauze from a cyanide solution and then making them anodes for twenty minutes in a dilute chloride solution, in the manner as described by MacInnes and Parker.[6] The electrodes were discolored somewhat, but the fact that they were not pure white did not appear to affect their usefulness. Experiments showed that the present measurements could be made equally well in ordinary electric light and in the dark. Most of the measurements were made under ordinary electric light in a photographic dark room; the others were made in a photographic dark room using the yellow Wratten safelight. It was found that a slight correction for differences in the electrodes was necessary and this correction was determined for each series of measurements as described below. The cell used for the measurements has been described in detail by Johnson and Low[7] and is shown in Fig. 1. A type of cell was used with all-glass interchangeable joints so that no rubber connections were necessary.

The e. m. f. readings were made on a Queen potentiometer Model E3044 (the student's type) which was calibrated against the laboratory standard Wolfe potentiometer. All measurements were made in a thermostat which remained constant to 25.0 ± 0.05°. Any variation of the temperature within this value was well within the experimental error of the method.

Procedure.—It was decided that the best method for testing this new technique was to use chloride-free salts and add the "unknown" amount of chloride to them, rather than to test salts which already had chloride in them by the new method and by some standard method. This manner of attack was chosen because the electrometric technique turned out to be applicable to cases where no satisfactory standard method of comparison could be found. To a definite known amount (usually 5 g.) of the chloride-free salt to be tested were added 2 ml. of concentrated nitric acid and the "unknown" amount of chloride from a microburet, and the solution was diluted to 100.0 ml. To a 25.0-ml. portion of this solution was added chloride so

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[4] H. S. Harned in Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., N. Y., 1925, pp. 781–788.

[5] "International Critical Tables," Vol. VI, p. 256.

[6] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[7] Johnson and Low, *J. Phys. Chem.*, **36**, 2390 (1932).

that when this was diluted to 30.0 ml. the concentration of chloride was (0.01 + x) molar. Another 25.0-ml. portion was diluted to 30.0 ml with no addition of excess chloride, so that the concentration of chloride in this solution was x molar. This method of making the solutions ensured that they were identical except for the chloride concentrations. One of these solutions was then put in one side of the measurement cell and the other in the other side and the cell was immersed in the thermostat; after temperature equilibrium had been reached, the junction between the two halves of the cell was made by sucking up the liquid in the capillary which joins the two halves of the cell, and the e. m. f. measured. The electrode correction mentioned above was determined in one of two ways: in some cases by measuring the difference in e. m. f. between the two electrodes each of which was in the same solution, usually the more dilute (in chloride concentration) of the two solutions to be subsequently measured; another method of determining the electrode correction was to make a series of measurements on a given salt, then to repeat the series with the electrodes reversed, and average the values. The electrode corrections varied from 0.0001 volt to 0.0004 volt.

TABLE I

SUMMARY OF RESULTS

Sample	u	E. m. f. obsd., v.	f^2	E. m. f. calcd., v.	Grams per liter Added	Grams per liter Found
$(NH_4)_2HPO_4$ + HNO_3	1.18	0.0614	0.319	0.0615	0.03546	0.03567
		.1166		.1172	.00355	.00365
		.1515		.1504	.00036	.00027
		.1559		.1559	....	....
$Al(NO_3)_3$ + HNO_3	0.62	.0615	.388	.0615	.03546	.03546
		.1173		.1174	.00355	.00358
		.1525		.1524	.00036	.00034
		.1584		.1584	....	....
$Cd(NO_3)_2$ + HNO_3	0.55	.0622	.0938	.0615	.03546	.03446
		.1148		.1147	.00355	.00353
		.1371		.1372	.00036	.00037
		.1402		.1402	....	....
$(NH_4)_2SO_4$ + HNO_3	1.21	.0614	.321	.0615	.03546	.03567
		.1166		.1172	.00355	.00365
		.1500		.1505	.00036	.00038
		.1560		.1560	....	....
$Ca(NO_3)_2$ + HNO_3	1.00	.0611	.356	.0615	.03546	.03617
		.1165		.1173	.00355	.00369
		.1511		.1515	.00036	.00039
		.1573		.1573	....	....
$Sr(NO_3)_2$ + HNO_3	0.58	.0613	.379	.0615	.03546	.03585
		.1171		.1174	.00355	.00358
		.1518		.1521	.00036	.00038
		.1581		.1581	....	....
NH_4NO_3 + HNO_3	.77	.0614	.367	.0615	.03546	.03567
		.1169		.1173	.00355	.00362
		.1513		.1518	.00036	.00037
		.1577		.1577	....	....
H_3BO_3 + HNO_3	.25	.0615	.513	.0615	.03546	.03546
		.1168		.1176	.00355	.00369
		.1543		.1550	.00036	.00040
		.1620		.1620	....	....
C_6H_5COOH + C_2H_5OH + HNO_3	.25	.0609	.878	.0616	.03546	.03652
		.1165		.1180	.00355	.00376
		.1607		.1599	.00036	.00032
		.1689		.1689	....	....
KNO_3	.37	.0613	.364	.0615	.03546	.03617
		.1160		.1173	.00355	.00376
		.1507		.1517	.00036	.00043
		.1576		.1576	....	....
$(NH_4)_2HPO_4$	.88	.0614	.218	.0615	.03546	.03567
		.1154		.1167	.00355	.00376
		.1467		.1465	.00036	.00034
		.1510		.1510	....	....
HNO_3	.25	.0613	.493	.0615	.03546	.03585
		.1162		.1176	.00355	.00376
		.1542		.1547	.00036	.00038
		.1615		.1615	....	....
HNO_3 + iodide of 10^{-6} M	.25	.0590			.03546	
		.1005			.00355	
		.1149			.00036	
		.1178			....	
NH_4NO_3 + iodide of 10^{-6} M	.30	.0585			.03546	
		.0990			.00355	
		.1135			.00036	
		.1148			....	

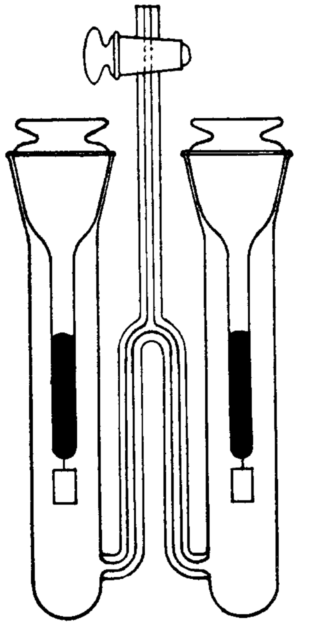

Fig. 1.—Cell for e. m. f. measurement: stopper to base 17 cm.; width 8 cm.; base to capillary junction 8 cm.; inner diameter of electrode vessels 1.5 cm.

In Table I is given a compilation of results obtained for the determination of chloride in a variety of salts. In this table "e. m. f. obsd." gives the observed e. m. f.'s corrected. f^2 is calculated from equation 4. "E. m. f. calcd" gives the theoretical e. m. f.'s calculated from equation 4. "Grams per liter found" are calculated from equation 4. "u" is the total ionic strength of the solution measured in the cell. When nitric acid is present its final concentration is always 0.25 M; therefore the concentration of the particular salt being measured in the final solution is the difference between 0.25 and the indicated total ionic strength. Boric and benzoic acids being weak electrolytes do not contribute to the total ionic strength of the solution.

It is of interest to note that the f^2 is approximately the same for solutions of approximately the same total ionic strength, which would be expected. Characteristically, the cadmium salt behaves quite differently from the others, which would be expected wherever the activity of the solution is a factor. Activity data[8] show cadmium salts to behave very differently from others. The fact that the cadmium nitrate solution measured in this paper agrees with the other data seems to the authors a good confirmation of the theoretical aspects of the paper.

When unknown concentrations of both iodide and chloride are present, it is obvious that a single e. m. f. measurement applied in a modified form of equation (4) will be insufficient for the calculation of both unknowns. The data of Table I indicate that with a constant concentration of iodide, there is a systematic variation in e. m. f. with varying concentrations of chloride. There was no indication of the oxidation of the minute trace of iodide by the nitric acid, and the e. m. f. values became constant very rapidly.

Using the above procedure a sample of C. P. potassium nitrate was analyzed for chloride and was found to contain 0.00027% Cl. According to the analysis on the bottle there was less than 0.005% Cl. No satisfactory method could be found which would serve as a check on the value 0.00027%, but in view of the data put forward in this paper it was assumed to be correct.

Acknowledgment.—Gratitude is here expressed to the J. T. Baker Chemical Co. of Phillipsburg, N. J. The work on this problem was performed with the aid of the Eastern Research Fellowship in Analytical Chemistry established by them.

Summary

A rapid, accurate, electrometric technique for measuring quantitatively small amounts of substances which may occur as impurities in salts has been described, using as an illustration of the general method the determination of traces of chloride in a number of salts, by the use of silver–silver chloride electrodes. The method is comparable in accuracy with the nephelometric procedure, and possesses the advantage that foreign salts do not cause difficulties as they do in the use of the nephelometer. Traces of chloride of as low a concentration as 0.00035 g. of Cl^- per liter of solution were measured accurately by the method, in a variety of salts at various ionic strengths.

PRINCETON, N. J. RECEIVED FEBRUARY 27, 1935

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[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 362.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A Comparison of Several Electrometric and Nephelometric Methods for the Estimation of Small Amounts of Chloride

BY N. HOWELL FURMAN AND GEORGE W. LOW, JR.[1]

In the preceding paper there was discussed a method for the estimation of small amounts of chloride, which consisted in measuring the e. m. f. between two silver–silver chloride electrodes dipping into chloride solutions of different concentrations. It was pointed out that the nephelometric method ordinarily used for the estimation of small amounts of chloride is none too satisfactory, due chiefly to the fact that reproducibility of suspensions is difficult. The present paper describes the results obtained from the use of five different methods for the estimation of chloride, three of them electrometric (one of which was described in detail in the preceding paper), and two nephelometric. For convenience in referring to them in the rest of the paper they shall be designated as follows: "the 0.01 excess method," "the small excess method," "the standard solution method," "the usual nephelometric method" and "the photronic nephelometric method." The same chloride solutions were measured by each of the five methods. Each solution was 0.3 *M* in nitric acid.

Apparatus and Materials.—The same precautions were taken, as described in the preceding paper, for the preparation of all the materials used. The same silver chloride electrodes were used, and all of the e. m. f. readings were made on the cali-

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[1] J. T. Baker Chemical Co. Fellow in Analytical Chemistry, 1933–1934.