At present there are no heat data with which these results may be compared.

Summary

Measurements have been made on the following cell at several acid concentrations and varying concentrations of vanadic acid and vanadyl chloride.

$VOCl_2$ (c' f. in c_A f. HCl)
Pt, HVO_3 (c'' f. in c_A f. HCl), HCl (c_A f.), HgCl(s), Hg(l)
HCl (c_A f.)

The electromotive force of the cell varies greatly with the acid concentration, and normally with the concentration of vanadic acid and vanadyl ion. An explanation for the effect of the acid is offered.

The reduction potential E' at 25° with reference to the molal hydrogen potential as zero was found to be -1.0216 volts in molal hydrochloric acid, slightly greater than the bromine potential (-1.0659 volts) and considerably more positive than the chlorine potential (-1.3594 volts). The corresponding potentials at other acid concentrations are presented in Table II.

From the temperature coefficient of electromotive force the heat content increase accompanying the reduction by hydrogen of one mole of vanadic acid in hydrochloric acid solution to vanadyl ion and water was found to be $-29,350$ cal.

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The Nephelometric Determination of Chloride

BY I. M. KOLTHOFF AND HENRY YUTZY

Two procedures for the nephelometric determination of chloride have been described in the literature, one by T. W. Richards and R. C. Wells,[1] the other by A. B. Lamb, Carleton and Meldrum.[2] The former is of historical interest, since it was the first real nephelometric method described. The method of Lamb and co-workers is recommended by J. H. Yoe[3] for general use. However, in its application to the chloride determination in unknowns, it should be remembered that foreign electrolytes may affect the light reflecting power of the silver chloride suspensions, whereas the method has been developed and recommended by the authors for the determination of traces of chlorine in war gases. Preliminary experiments on its application yielded many unexpected difficulties and a

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(1) Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904).

(2) Lamb, Carleton and Meldrum, THIS JOURNAL, **42**, 251 (1920).

(3) Yoe, "Photometric Chemical Analysis," Vol. II, Nephelometry, John Wiley and Sons, New York, 1929, p. 137.

systematic study was thought desirable, the more so since H. Kleinman[4] after extensive investigations arrived at the conclusion that silver chloride suspensions are unsuitable for nephelometric work.

Various factors which affect the reliability of the results of a nephelometric determination are briefly discussed in the following paragraphs.

Reproducibility of the Suspension.—P. A. Kober's[5] statement that the greatest source of error in nephelometry or colorimetry is practically an instrumental one is completely at variance with P. V. Wells'[6] insistent statements that the limiting factor is the reproducibility of the dispersion rather than the precision of the instrument. From the experience gained in the present work we are inclined to agree entirely with P. V. Wells. The first condition of reproducibility is determined by the fact that the average size of the particles should be the same, if the suspension is made each time under identical conditions. T. W. Richards[7] insisted that the unknown and standard be treated in the same way and protested against the use of permanent standards for any other purpose than for investigating the change in the light reflecting power of a suspension with time.

The multitude of influences affecting the light refracting power of a dispersion makes it very difficult to decide what particular factor causes a given effect. The size of a suspension formed by interaction of its components in solution is primarily determined by the competition between the speed of formation of the nuclei and the growth of the latter to crystals of larger dimensions. Since adsorption phenomena are of great influence upon the crystallization velocity, it may be expected that the homogeneity of the medium during the formation of the slightly soluble substance will be of great importance in obtaining good results. If, for example, an excess of silver ions is added to a chloride solution, the latter will be in excess at the very beginning of addition of reagent, thus giving rise to formation of negatively charged particles; later silver will be in excess and the charge of the particles will be reversed. Therefore it is not surprising that the rate of addition of the one solution to the other may have considerable influence upon the optical density of the resultant system. The effect of the speed of addition of silver nitrate to the solution upon the density of the suspension has been investigated by Kleinman,[4] A. F. Scott and G. L. Moilliet[8] and by Kober.[9]

In nephelometric work another factor, namely, the time elapsed between the moment of mixing the solutions and their nephelometric measurement, is of great importance. The turbidity ordinarily increases immediately after the precipitation has been made as a result of a more nearly complete

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(4) Kleinman, *Biochem. Z.*, **99**, 141 (1919).

(5) Kober, *J. Biol. Chem.*, **13**, 490 (1915).

(6) Wells, *Chem. Rev.*, **3**, 331 (1927).

(7) Richards, *Am. Chem. J.*, **35**, 510 (1906).

(8) Scott and Moilliet, THIS JOURNAL, **54**, 205 (1932).

(9) Kober, *Ind. Eng. Chem.*, **10**, 556 (1918).

precipitation and the ripening of the suspension. After a certain time the optical density becomes a maximum and decreases on further standing due to coalescence and flocculation of particles. It is advantageous to select a time of reading at which the opalescence time curve shows a flat maximum.

R. C. Wells[10] found that electrolytes aid in producing the maximum opalescence and hasten the speed of its formation. Lamb and co-workers shortened the time for attainment of maximum opalescence by heating the suspensions formed according to their procedure. Moreover, they noticed that by heating their suspensions for thirty minutes at 40° a constant opalescence was obtained which was stable for at least one hour.

In the present work a procedure has been developed in which the chloride was added to a relatively large excess of silver nitrate, since under these conditions the environment remains virtually constant, although one must realize that the degree of supersaturation of the silver chloride will depend upon the speed of mixing. In the following work various factors affecting the results of a nephelometric chloride determination have been studied systematically.

Experimental

Recrystallized C. P. chemicals, chloride free, have been used.

The stationary plunger movable cup type Klett nephelometer was used.

Readings with the Nephelometer.—The precautions mentioned by Lamb[2] in the use of the nephelometer were carefully considered. It should be mentioned that a certain skill both in the preparation of suspensions and in the use of the nephelometer should be acquired by any one applying this method of analysis before he may rely upon his results.

Instead of using the method of Lamb and co-workers for the elimination of any error due to a defect in the optical system of the instrument, we decided to use one side of the instrument as tare, filling one cup with either the unknown or the standard, setting it at an arbitrary reading, filling the opposite cup with unknown and adjusting it, then filling the latter with standard and adjusting it again. This method was used in the experimental work. In all experiments the value given as the "reading" is the average of ten settings of the scale, whereas the data reported in the tables are the average of at least three independent determinations.

Influence of the Concentration of Alcohol in Lamb's Procedure.—The claim made by Lamb and co-workers of an average accuracy of their procedure of 3 to 4% was found to be quite legitimate if foreign electrolytes were absent. Since Lamb's procedure does not specify exactly how much alcohol should be used, and it is conceivable, as the procedure is worked, that at times the standard might be made up with a different alcohol content than the unknown, the effect of changing the alcohol concentration upon the turbidity was investigated. It was stated by Lamb and co-workers that the opalescence of silver chloride in water is about 15% greater than in 50% alcohol or 50% acetic acid. In the present work a much larger alcohol effect was noticed. The experiments were carried out in the following way: 10 cc. of 0.1 *N* nitric acid, 10 cc. 0.005 *N* silver nitrate and *x* cc. of alcohol were made up to 50 cc. with water. This mixture was poured into a flask containing 5 cc. of a solution of sodium chloride with a concentration of 17.5 mg. of

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[10] Wells, *Am. Chem. J.*, **35**, 99 (1906).

NaCl per liter. The mixture was heated at 40° for thirty minutes, cooled rapidly and read. In some cases it was very hard to obtain good reproducibility; for this reason seven runs were made at each alcohol concentration. The mixture containing 40% alcohol is taken as standard in the following table.

TABLE I

EFFECT OF ALCOHOL UPON LIGHT REFLECTING POWER

Alcohol content in %	0	10	20	30	40	50	60
Reading 40% alcohol/x% alcohol	1.47	1.37	1.25	1.17	1.00	0.85	0.76

Approximately there seems to be a linear relation between the alcohol concentration and the light reflecting power of the suspension. A difference in the alcohol concentration of 5% in the neighborhood of 40% alcohol causes a difference in the readings of about 8%. Therefore it is necessary to have the same alcohol concentration in unknown and standard.

The influence of other factors upon Lamb's procedure will be given with the discussion of the results of a revised procedure.

Procedure.—To one of two solutions containing 25 cc. of ethyl alcohol, 1 cc. of 0.5 N silver nitrate and 5 cc. of 0.5N nitric acid, rapidly add with shaking 10 cc. of the unknown solution containing chloride, to the other add 10 cc. of a standard chloride solution. Allow the resulting suspensions to stand at room temperature in a dark room for one hour before comparing in the nephelometer. If the ratio of the chloride concentrations in the unknown and the blank is between 1.5 and 0.7, the concentration of the unknown may be calculated on the basis of an inverse proportion between concentration and depth. The procedure can be applied over a concentration range between 0.08 to 42 mg. of Cl per liter, and yields *an accuracy of approximately 2%.*

Effect of Varying the Silver Ion Concentration.—In the recommended procedure the silver nitrate concentration in the final suspension is of the order of 0.0125 N. Experiments showed that a small variation of this excess of silver did not affect the turbidity of the silver chloride suspension nor the stability of the latter. The turbidity of the suspension increases slightly with increasing concentration of silver between 0.0001 and 0.01 N, as shown in Table II.

TABLE II

INFLUENCE OF EXCESS OF SILVER UPON TURBIDITY

Ratio = Reading for soln. 1: Reading for soln. x

Silver concentration (N)	0.0012	0.0024	0.0036	0.006	0.0084	0.01	0.0125
Ratio	1.00	1.02	1.11	1.12	1.18	1.19	1.19

Effect of Heating, Time of Standing and Alcohol upon Turbidity.—1. Ten cc. of sodium chloride solution (containing 35 mg. of NaCl per liter) was added to a mixture of 1 cc. of 0.5 N silver nitrate, 25 cc. of alcohol and 5 cc. of 0.5 N nitric acid (standard reagent). The resulting suspension was allowed to stand a few minutes at room temperature, then transferred to the nephelometer and readings taken after various times of standing. In these and the following experiments comparison was made against a constant standard, composed of a frosted glass reflector which reflected light through a copper sulfate solution of the proper strength necessary to impart a blue color similar to the color of the light reflected by the suspension. Curve 1 in Fig. 1 gives the turbidity–time curve.

2. The suspension was made up as in 1, but after mixing heated at 40° for thirty minutes, cooled rapidly and examined in the nephelometer (Curve 2, Fig. 1).

3. The solution was made up as in 1 save that 25 cc. of water was substituted for

the 25 cc. of alcohol; the suspension was allowed to stand for a few minutes at room temperature and placed in the nephelometer (Curve 3, Fig. 1).

All experiments were repeated a few times; the results were reproducible within a few per cent. The data show that: (a) according to the revised procedure the turbidity remains constant from sixty to one hundred and twenty minutes after the mixing, if the suspension is kept at room temperature. Therefore comparisons can be made between one to two hours after the preparation of the suspensions. Heating the suspension for half an hour at 40° has a harmful effect; the turbidity reaches a maximum after about seventy to eighty minutes and then gradually decreases. It must be stated that in working according to Lamb's procedure the favorable effect of heating as recommended by him and his co-workers was substantiated by our experiments.

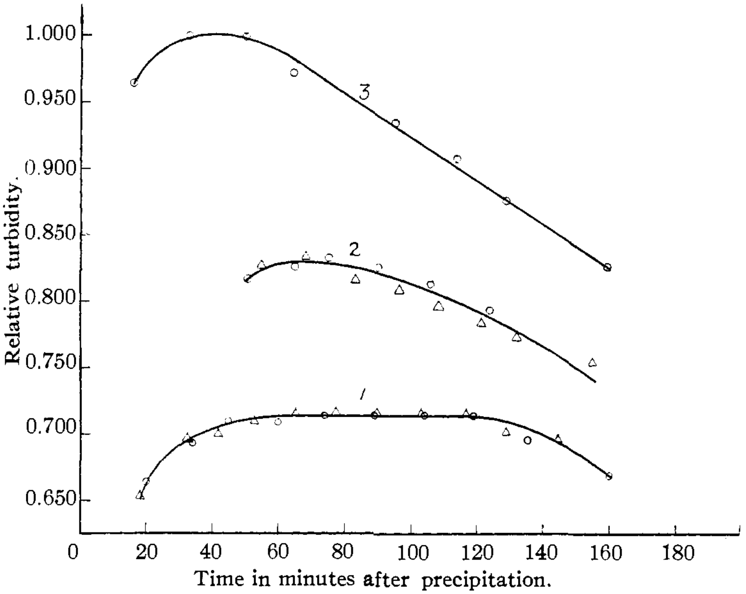

Fig. 1.—O and △, two runs by the same procedure, showing the reproducibility.

(b) The presence of alcohol in a concentration recommended in the procedure has a decided stabilizing effect.

Effect of Shaking.—It was found that continuous shaking of the suspensions for ten to fifteen minutes results in a coagulation of the silver chloride into particles of filterable size. Therefore in preparing the suspensions it is recommended to mix the reagent and solution by careful shaking, just enough to ensure thorough mixing and repeat shaking before the measurements are made.

Relation between Chloride Concentrations and Readings.—The turbidities of solutions containing various concentrations of chloride were determined by the procedure of Lamb and the revised one proposed in this paper. The chloride concentration was varied between 21 and 35 mg. of sodium chloride per liter. The solution containing 28 mg. per liter was taken as a standard. Table III gives the results obtained and shows that according to the new procedure a linear relation between concentration and reciprocal of the reading exists, if the concentrations of the unknown and the standard do not differ by more than 25%.

TABLE III

RELATION BETWEEN TURBIDITY AND CONCENTRATION

Ratio calculated	0.75	0.87	1.00	1.12	1.25
Ratio found with new procedure	0.72	0.88	1.00	1.16	1.27
Ratio found with Lamb's procedure	0.70	0.83	1.00	1.15	1.30

This relation was also tested at the extreme chloride concentration (0.08 and 42 mg. of Cl per liter, respectively) and found to hold true within 2%.

Influence of Foreign Electrolytes upon the Turbidity.—The influence of foreign electrolytes upon the turbidity of suspensions obtained according to Lamb's procedure and the revised one has been investigated. The electrolyte concentrations reported in the following tables are final concentrations in the suspensions. The ratio reported is that of the reading of the standard without any special addition to the reading of the suspension with the indicated concentration of electrolyte. An increase in the ratio indicates a stronger turbidity of the suspension than of the corresponding blank.

In Table IV the influence of the presence of foreign cations with increasing charge is given. In all cases the final electrolyte concentration in the suspensions was 0.002 *N*.

TABLE IV

INFLUENCE OF THE VALENCE OF CATIONS UPON TURBIDITY

Electrolyte		KNO_3	$Ba(NO_3)_2$	$Al(NO_3)_3$	$Zr(NO_3)_4$
Ratio (new procedure)	1.00	0.98	1.04	0.96	1.13
Ratio (Lamb's procedure)	1.00	1.05	1.03	0.98	0.70

At a final concentration of 0.002 *N* the influence of potassium, barium and aluminum is negligibly small. It is interesting to notice that zirconium ions increase the turbidity of the suspensions prepared according to the new procedure, whereas these ions have the opposite effect in Lamb's procedure. In the latter case the suspension is prepared by adding the silver solution to the chloride, at the moment of precipitation the quadrivalent zirconium ions undoubtedly will have a different effect upon the negatively charged suspension than in the case in which there is an excess of silver during the formation of the silver chloride.

The influence of the concentration of nitric acid is found in Table V. The second column gives the ratio determined if the nitric acid was in the silver solution. The suspensions were prepared according to the revised procedure, save that instead of 5 cc. of 0.5 *N* nitric acid a concentration corresponding to that in the first column was used. It was impossible to make an exact reading of the suspension without any acid. The data reported in the third column were obtained by adding the acid to the chloride solution and substituting the 5 cc. of 0.5 *N* nitric acid recommended in the standard procedure by 5 cc. of water. The figures in the fourth column are obtained according to Lamb's procedure. The ratio given is that of the reading in 0.25 *N* acid divided by the reading in any of the other suspensions. (Decreasing ratio indicates decreasing turbidity.)

TABLE V

INFLUENCE OF NITRIC ACID UPON THE TURBIDITY

Final concentration of nitric acid in suspension (normality)	Ratio (new procedure) Acid added to silver soln.	Acid added to chloride soln.	Ratio (Lamb's procedure)
0.25	1.00	1.00	1.00
.125	0.98	1.03	0.98
.050	.97	1.02	.92
.025	.87	0.97	.88
.00	< .5	< .5	< .5

From the data it may be inferred that the influence of a change of the nitric acid concentration is negligibly small at normalities between 0.05 and 0.25*N*. In the recommended procedure a final concentration of 0.05 *N* nitric acid is used, thus allowing chloride determinations in nitric acid solutions of a concentration of 1 *N*. The acid concentration recommended in Lamb's procedure corresponds to a final normality of 0.025 *N*; the results in Table V indicate, however, that it would be advantageous to double the amount of acid.

Table VI gives the influence of larger concentrations of potassium and barium nitrate upon the results of the proposed and of Lamb's procedure. The chloride solution used contained as in former cases 35 mg. of NaCl per liter. The reading without any salt addition was taken as a standard.

TABLE VI

INFLUENCE OF LARGER CONCENTRATIONS OF POTASSIUM AND BARIUM NITRATE

KNO_3, final normality	Ratio, new procedure	Ratio, Lamb's procedure	$Ba(NO_3)_2$, final normality	Ratio, new procedure	Ratio, Lamb's procedure
0.00	1.00	1.00	0.00	1.00	1.00
.001	1.01	1.02	.001	0.99	1.01
.002	1.00	1.00	.002	.99	1.01
.025	1.02	1.01	.025	.99	1.01
.045	1.02	1.02	.045	.99	1.03
.06	1.00		.06	1.00	

The data show that potassium and barium nitrate at the indicated concentrations do not interfere with the new procedure nor with Lamb's method.

Finally the influence of a divalent anion in the form of sodium sulfate was investigated. Since the suspensions formed are positively charged by the excess of silver, a harmful effect of the sulfate was anticipated. The suspensions prepared according to the new procedure and that of Lamb are much less stable in the presence of sulfate, and, on standing, show a tendency to deposit some silver chloride. It appeared necessary to have the suspensions ripen in the flasks in which the precipitations had been made and to shake carefully before they were placed in the nephelometer. Even then the readings have to be made as quickly as possible since the turbidity decreases fairly rapidly on standing in the nephelometer cups. Suspensions without the sulfate can be kept in the cups for a longer time without any changes. It is not recommended to shorten the time between the preparation of the suspensions and the readings, since the shape of the time–turbidity curves was found to be similar to those in Fig. 1.

The influence of sodium sulfate upon suspensions prepared according to the new procedure and that of Lamb is given in Table VII.

TABLE VII

INFLUENCE OF SODIUM SULFATE UPON TURBIDITY

Na_2SO_4 final normality	0.00	0.001	0.002	0.025	0.065
Ratio revised procedure	1.00	0.85	0.83	0.85	0.84
Ratio Lamb's procedure	1.00	1.11	1.12	1.13	1.24 (flocculation)

It is interesting to notice that even traces of sulfate decrease the turbidity of suspensions obtained according to the revised procedure and that constant readings are obtained with final concentrations of sulfate between 0.001 and 0.065 *N*. Therefore in cases in which the unknown contains sulfate in a concentration less than 0.3 *N* it is recommended to add so much sulfate to the blank that its final concentration is of the order of 0.01 *N*.

At sulfate concentrations larger than 0.3 N the nephelometric determination is made impossible due to flocculation of the silver chloride. The influence of sulfates on suspensions prepared according to Lamb's procedure is the reverse of that found by our method.

Summary

A procedure for the nephelometric determination of chlorides has been given in which the chloride solution is added to a mixture of alcohol, silver nitrate and nitric acid. The method can be applied to the determination of from 0.008 to 0.42 mg. of chloride in a 10-cc. sample, and gives results reproducible within 2%. The influence of electrolytes upon the turbidity of suspensions prepared according to Lamb's and the revised procedures has been investigated.

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The Medium Effect of Various Solvents upon Silver Bromate at 25°

BY BENTON BROOKS OWEN

As a means of studying the effect of variation in solvent upon the activity coefficient of an electrolyte, solubility measurements possess, under favorable conditions, the combination of experimental simplicity and thermodynamic rigor. This method has been applied in the present research to a study of the medium effect of a number of mixed solvents upon a single electrolyte, silver bromate, with a view of determining to what extent it depends upon the dielectric constant in accordance with the Born[1] equation, and to what extent it is a specific property of the components of the solution. Previous studies of this nature have often been performed under unfavorable conditions. Experimenters making use of pure organic solvents have had to choose between the difficulties of measuring minute solubilities in non-aqueous solutions, and the uncertainties of evaluating activities in aqueous solutions in which the solubility is too great to permit the use of the limiting equation of Debye and Hückel.[2] Even under more favorable conditions, comparisons of data from different sources with calculations based upon dielectric constants, variously determined, have been somewhat inconsistent. In the present research, therefore, an especial effort has been made to attain consistency. A uniform analytical procedure was used throughout, and the solvents were prepared from the same stock from which Åkerlöf[3] prepared solutions for dielectric constant measurements. Since Åkerlöf employed a uniform technique in his

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[1] Born, *Z. Physik*, **1**, 45 (1920).

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).