THE USE OF NEPHELOMETRIC MEASUREMENTS
TO DETERMINE THE PRESENCE OF CHELATES[1]

A Laboratory Experiment for an Instrumental Course

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NEPHELOMETRY, the measurement of the light scattered by a suspension through an angle of 90 degrees to the incident beam, is a valuable tool in analytical chemistry and will produce accurate quantitative results provided the necessary conditions for the constant reproduction of the suspensions can be found. A typical experiment might involve the estimation of the sulfate content of water by the formation of a suspension of barium sulfate and a comparison of the light scattered from it to that scattered by a prepared standard suspension. Such an experiment fails to indicate to the student the potentialities of the nephelometric method. The following experiment has been developed not only to teach the art and practice of nephelometry but also at the same time to show the student an application of Job's method of continuous variations[2] to the demonstration of the constitution of an inorganic chelate compound.

The formation of a metal chelate may be represented by the simplified equation, $M + n\text{Ke} \rightarrow [\text{MKe}_n]$, where M stands for the metal ion, Ke the ionic chelating ion, and $[\text{MKe}_n]$ the complex. Because many of the chelate complexes of metal ions are quite insoluble in water solutions and can be produced as suspensions, nephelometry can furnish part of the needed information for determining the stoichiometric relationship of the central metal ion to the ligands, e.g., the value of n in the above equation.

A review of Job's method of continuous variations is given before the execution of the experiment. In brief it may be summarized by pointing out that when different amounts of the metal ion species and the chelating ion species are brought together in reaction, but with an imposed restriction that the sum of the concentrations of the metal ion (C_M) and the chelating ion (C_{Ke}) must be in all cases a fixed, constant value, e.g., $C_M + C_{Ke} = C_{total}$, then the total amount of the chelate compound produced not only will depend upon the concentration of the reactant present at the start in limiting amount, but also will approach a maximum value as the ratio C_M/C_{total} approaches the value

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[1] Based on a paper presented before the Chemistry Section of the Alabama Academy of Science, March 30, 1956.
[2] JOB, P., *Ann. chim.*, [10] **9**, 113 (1928).

$1/(1 + n)$. The relative amount of scattered light, which in this experiment furnishes the information as to the quantity of produced chelate, can be plotted versus the C_M/C_{total} ratio to produce the typical inverted V-shaped curve.

The reaction of copper(II) ions and cupferrate ions, which produces very rapidly a precipitate of known composition, is an excellent example for demonstrating the techniques and principles of this experiment.

The student is instructed to:

(1) Prepare 500 ml. each of a copper(II) sulfate and cupferron solution containing exactly 10^{-6} formula weights of solute per ml. of solution, and approximately 10 ml. of a 0.2% by weight starch solution.

[Note: These instructions have been written specifically for the use of a Fisher Nefluoro-Photometer. Therefore an instructor will have to change those instructions that refer to the operation and employment of this instrument to fit his situation.]

(2) The Fisher Nefluoro-Photometer, equipped with the incandescent light source and the 525 mμ filter, is turned on so that the electronic circuits may be warming up and stabilizing. Carry out items 1 through 8 of the manufacturer's instructions.[3]

(3) Make ready a series of ten 150-ml. beakers, numbered consecutively.

(4) Into each beaker measure 50 ml. of distilled water and add three drops of the 0.2% starch solution.

(5) Prepare a copy of the following table in his notebook:

Beaker number	Ml. of H_2O	Ml. of Cu^{++} solution	Ml. of cupferron solution	Ratio C_M/C_{total}	Rel. % scattered light
1	50	18	2	0.90	
2	50	16	4	0.80	
3	50	14	6	0.70	
4	50	12	8	0.60	
5	50	10	10	0.50	
6	50	8	12	0.40	
7	50	6	14	0.30	
8	50	4	16	0.20	
9	50	2	18	0.10	
10	50	1	19	0.05	

(6) By means of a buret measure accurately into each beaker the amount of copper(II) sulfate as indicated in the table.

(7) Starting with beaker No. 1 and progressing consecutively without interruption, except as necessary to refill the buret, measure from a buret the amounts of the cupferron solution indicated in the table. After adding the latter solution, stir vigorously with a glass rod for ten seconds.

(8) With the beakers lined up in consecutive order on the laboratory desk, estimate by eye the one containing the most turbid solution. Fill a black fritted cell with this suspension, transfer it to the Nefluoro-Photometer and follow items 9–16 of the manufacturer's instructions,[3] except in item 13 set the dial scale on 70% rather than 100%. [Note: It is evident that regardless of the type of instrument used, what is desired is the relative per cent of scattered light from these suspensions. One can either take the most turbid suspensions and calibrate the scale of the instrument at some value not too far below 100%, or distilled water can be used as the standard and the scale made to read 0%. This latter procedure was used in determining the data illustrated in the accompanying figure as the concentrations used in these directions do not produce a maximum turbidity over

[3] "Three-way Analysis with the Fisher Nefluoro-Photometer," published by Fisher Scientific Company.

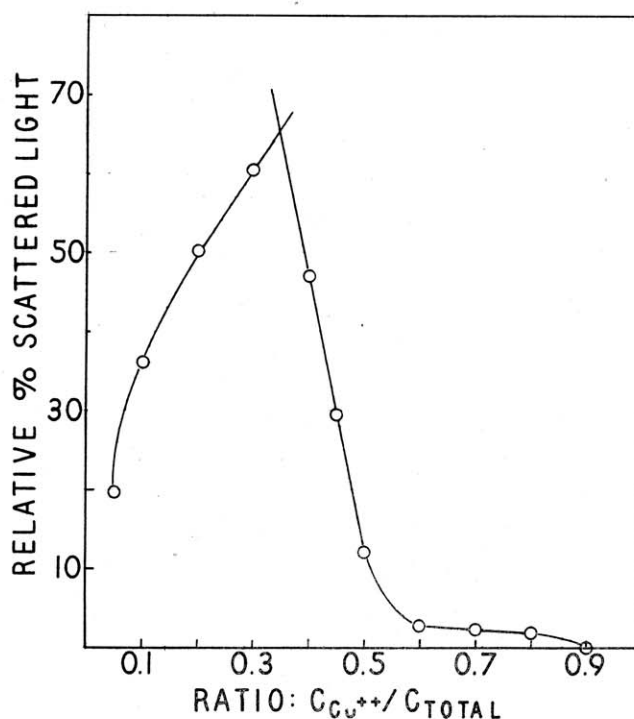100% relative. The use of the most turbid suspension, however, is recommended as the better method to follow.]

(9) With the instrument arbitrarily calibrated, as rapidly as possible determine the relative per cent of scattered light from the samples starting with beaker No. 1 and working rapidly through to No. 10. In running this sequence rerun the sample used to calibrate the instrument in step (8).

(10) Prepare a plot of the per cent of scattered light versus the ratio C_M/C_{total}. Since a suspension containing the exact ratio $1/(1 + n)$ may not be included in a given determination, it is best to draw straight lines through the points on both sides of the maximum and consider where they cross to be the maximum value.

If desired, more combinations of concentrations in the vicinity of the peak of the curve can be included to indicate where the maximum point is going to occur. Experience has tended to indicate that, when many points in the region of the maximum are determined, the peak is rounded in appearance, somewhat reminiscent of the breaks in conductometric curves, so that a better idea of the actual break is obtained by crossing the projections of the two straight lines.

In the accompanying figure a typical set of collected data are plotted to illustrate the formation of the copper cupferrate complex. The straight lines drawn through the points on each side of the maximum cross at a value of 0.33 for the ratio $C_{Cu^{++}}/C_{total}$. This corresponds to a value of two for n or the formula of the chelate is $[CuCf_2]$, where Cf represents the cupferrate ion.

It has been observed that solution temperatures should be 25°C. or above, since at lower temperatures the suspensions form more slowly and erratically.