

Novel Approach to Job's Method

An Undergraduate Experiment

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Job's method of continuous variations is a commonly used procedure for determining the composition of complexes in solution. The popularity of this method is indicated by the frequency of its inclusion in a wide variety of analytical chemistry (1–6), instrumental analysis (7–9) and advanced chemical equilibrium (10–13) texts as well as its application in many research articles (14–20). The use of Job's method in the undergraduate laboratory has also been the subject of a number of publications (21–25).

The principle of continuous variations was employed by Ostromisslensky in 1911 (26) to establish the 1:1 stoichiometry of the adduct formed between nitrobenzene and aniline. The principle was used by Denison in 1912 (27, 28) in a study of various liquid mixtures. However, the method of continuous variations is generally associated with the name of Job who in 1928 (29) published a detailed application of the method to the study of a wide range of coordination compounds.

Job's method, as commonly practiced, is carried out in a batch mode by mixing aliquots of two equimolar stock solutions of metal and ligand (sometimes followed by dilution to a fixed volume). These solutions are prepared in a manner such that the total analytical concentration of metal plus ligand is maintained constant while the ligand:metal ratio varies from flask to flask, that is:

$$C_M + C_L = k \quad (1)$$

where C_M and C_L are the analytical concentrations of metal and ligand, respectively, and k is a constant. The absorbance, or more strictly the corrected absorbance, is plotted as a function of mole fraction of ligand or metal in the flasks. The resulting curves, called Job's plots, yield a maximum (or minimum) the position of which indicates the ligand:metal ratio of the complex in solution. For example, a maximum corresponding to 0.5 on the mole ratio fraction of ligand scale suggests a complex of 1:1 composition, while maxima at 0.67 and 0.75 indicate complexes of 2:1 and 3:1 ligand:metal ratios, respectively. (While absorbance is by far the most commonly employed property of the solution for measuring Job's plots, other solution properties can also be used (10, 11, 22, 24, 25, 27, 28, 30)).

Two points from the previous paragraph require explanation. First, the definition of corrected absorbance is somewhat unusual; in words, it is defined as the measured absorbance (at a given wavelength) minus the sum of the absorbances which the metal and ligand would exhibit if no complexation had occurred. Mathematically, the corrected absorbance, Y , is defined as:

$$Y = A - (\epsilon_M C_M + \epsilon_L C_L)b \quad (2)$$

where A is the measured absorbance, ϵ_M and ϵ_L are the absorptivities of metal and ligand, respectively, and b is the optical path length (13, 31). Second, the term mole fraction

as used in this context is not the true mole fraction in that the solvent is omitted from its calculation. The mole fraction of ligand χ_L , is defined as:

$$\chi_L = \frac{C_L}{C_M + C_L} \quad (3)$$

and can evidently vary between zero and unity. Mole fraction of metal is similarly defined.

There are a number of requirements which must be satisfied in order for Job's method to be applicable. The first two requirements relate to the chemical behavior of the system under investigation and the second two relate to how the experiment is actually carried out. These requirements are:

- 1) the system must conform to Beer's law (11, 31),
- 2) one complex must predominate under the conditions of the experiment (10, 11, 29, 32),
- 3) the total concentration of metal plus ligand must be maintained constant (eq. (1)), and
- 4) pH and ionic strength must be maintained constant (11)

It is surprising that Job's method is frequently employed without first checking requirement (1).

For sake of completeness, it is worth pointing out that there are variations of Job's method in which conditions (2) or (3) are not satisfied. Vosburgh and Cooper (31) described an extension of Job's method which allows the compositions of a series of complexes, formed in a stepwise fashion, to be established. However, this variation of Job's method is very limited in that its applicability is conditional upon a fortuitous combination of spectral differences and stepwise formation constants for the individual complexes. Consequently, the method of Vosburgh and Cooper is not generally applicable. In the second modification of Job's method, condition (3) is not satisfied, that is, nonequimolar solutions are mixed and eqn. (1) is no longer satisfied. This modification is one of the techniques by which stability constants of complexes can be obtained from Job's plots (10). However, while Job's plots are frequently used for determining compositions, their use for determining stability constants has been severely criticized (32). Accordingly, the present paper will focus on Job's method as defined by conditions (1)–(4) above and will not deal with the aforementioned variations.

In measuring Job's plots, two experimental crosschecks are often recommended, though not always carried out, in order to evaluate the reliability of the data:

- 1) all readings should be carried out at more than one wavelength (10, 11, 13, 29, 32), and
- 2) the complete experiment should be conducted at more than one metal-plus-ligand concentration, that is, at different values of k in eqn. (1) (10). In order for the method to be applicable, the position of the maximum on the mole fraction axis must be invariant as a function of the changes recommended in crosschecks (1) and (2) above.

These important crosschecks are frequently overlooked in the application of Job's method.

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Objectives

The objectives of this paper are fivefold and are:

- 1) to demonstrate why and how data from a conventional photometric titration can be readily transformed into a Job's plot,
- 2) to compare the advantages of this method to the conventional method for acquiring data for a Job's plot,
- 3) to teach the similarities between photometric titrimetry and Job's method, a relationship which apparently has gone unnoticed in the past,
- 4) to develop a substantive undergraduate experiment (junior or senior level), based upon the above three objectives, that incorporates the requirements and crosschecks that were outlined in the introductory section, and
- 5) to present an overview of Job's method in general and a guide to the literature on the subject.

Clear presentations of the conventional method for implementing Job's method are found in the following references (1, 13) which are recommended for background reading on this subject.

Theory of New Procedure for Measuring Job's Plots

The series of solutions employed in Job's method possesses a fixed total concentration of metal plus ligand (eqn. (1)). Consider now the titration of a metal solution with an equimolar ligand solution. The sum of the analytical concentrations of metal and ligand in the reaction flask remains constant throughout the titration, thus satisfying eqn. (1). (It is assumed, of course, that no contraction or expansion occurs upon mixing the two solutions. This is a reasonable assumption for the dilute solutions normally employed in analytical chemistry (31), and is an implicit assumption invariably made in the calculation of titration curves (e.g., (33, 34).) Thus, the titration experiment and the Job's experiment bear a fundamental relationship to one another in that both encompass solutions of the same compositions. The methods differ only in how they are physically implemented and in how the data are actually plotted. If the titration data were plotted on a mole fraction scale, rather than on the conventional volume scale, the titration data would be transformed into a Job's plot. This transformation can be readily accomplished via the equation

$$x_L = \frac{V_L}{V_L + V_M^0} \quad (4)$$

where V_M^0 is the initial volume of metal titrand and V_L is the volume of titrant added at each point in the titration. It is thus possible to transform titrimetric data into a Job's plot, as pointed out recently (35). The determination of Job's plots by a titrimetric procedure will now be illustrated by means of two examples, one involving a weak complex and the other involving a strong complex. The particular advantages of this alternative approach and its pedagogic significance will then be outlined. The same experimental setup is used for both experiments.

Photometric Titration Assembly

A simple photometric titration apparatus, taken from the literature (36, 37) and illustrated in Figure 1 was used in these experiments. R is modified Erlenmeyer flask having a side tube attached normally (or tangentially) near its base and a second tube emerging from its base; these tubes are connected by means of Tygon tubing to two other glass tubes which are inserted through a tightly fitting rubber stopper into the cylindrical cuvette, C, of a Bausch and Lomb Spectronic 20 spectrometer. The optical path length was 1 cm. Aluminum foil is placed over the top of the optical cell and the adjacent tubing to prevent extraneous light from reaching the detector. A stir bar, S, in flask R is rotated by means of a magnetic stirrer and forces the solution to flow from the flask into the cuvette and return, as indicated by the arrows.

The modified Erlenmeyer flask can be purchased from Burrell Corporation (Pittsburgh, PA). Titrand is placed in the Erlenmeyer flask and titrant is added from a buret through a single-hole stopper. The magnetic stir bar causes effective mixing of the solution in the Erlenmeyer flask and circulation through the optical cell. The effectiveness of the circulation is quite dependent on the combination of magnetic stir bar and flask used. If a wrong combination is chosen, circulation may be very poor. For our experiments we used a 125 mL modified Erlenmeyer flask with a base diameter of 6.5 cm, and a 2.5-cm long stir bar. The circulation efficiency was checked by titrating methyl orange into water and observing how long it required for the spectrophotometer readings at 464 nm to stabilize. In all cases the readings had reached a steady value within 2 min of adding an aliquot of titrant.

The size of titration flask used in these experiments was chosen primarily on the basis of convenience; it would be a simple matter to scale down the experiment considerably so as to use less reagents.

Experiment No. 1: Fe^{3+} - SCN^- System

These experiments were carried out at two different wavelengths, 455 nm and 395 nm (blue-sensitive phototube; no optical filter). The analytical wavelengths were established by recording spectra of the FeSCN^{2+} complex ($5.0 \times 10^{-5} M$ KSCN; $0.050 M$ $\text{Fe}(\text{NO}_3)_3$; $0.15 M$ HNO_3) on a Cary 219 spectrophotometer; a maximum occurs at 455 nm and a minimum at 395 nm. The wavelength scale of the spectrophotometer was checked in advance by running the spectrum of a NdCl_3 solution and comparison with a standard spectrum.

Beer's Law

Adherence of this system to Beer's law at 455 nm was confirmed by measuring the absorbances, A , of six solutions all with an Fe^{3+} concentration of $0.05 M$ and with the SCN^- concentrations varying from zero to $5 \times 10^{-4} M$; a straight line was obtained which covered the absorbance range for the remainder of the experiments.

Solutions for Job's Plots

Solution A: $0.001 M$ $\text{Fe}(\text{NO}_3)_3$; $0.010 M$ HNO_3 . Ionic strength: 0.016.

Solution B: $0.001 M$ KSCN; $0.015 M$ HCl . Ionic strength: 0.016.

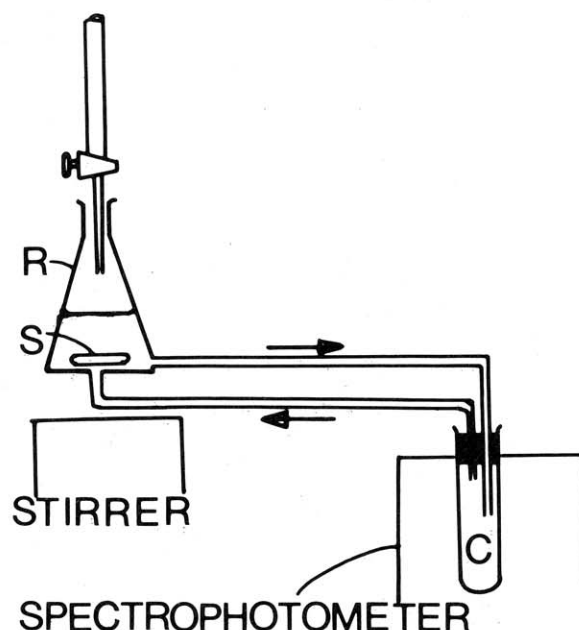


Figure 1. Apparatus for photometric titrimetry; the diagram is explained in the text.

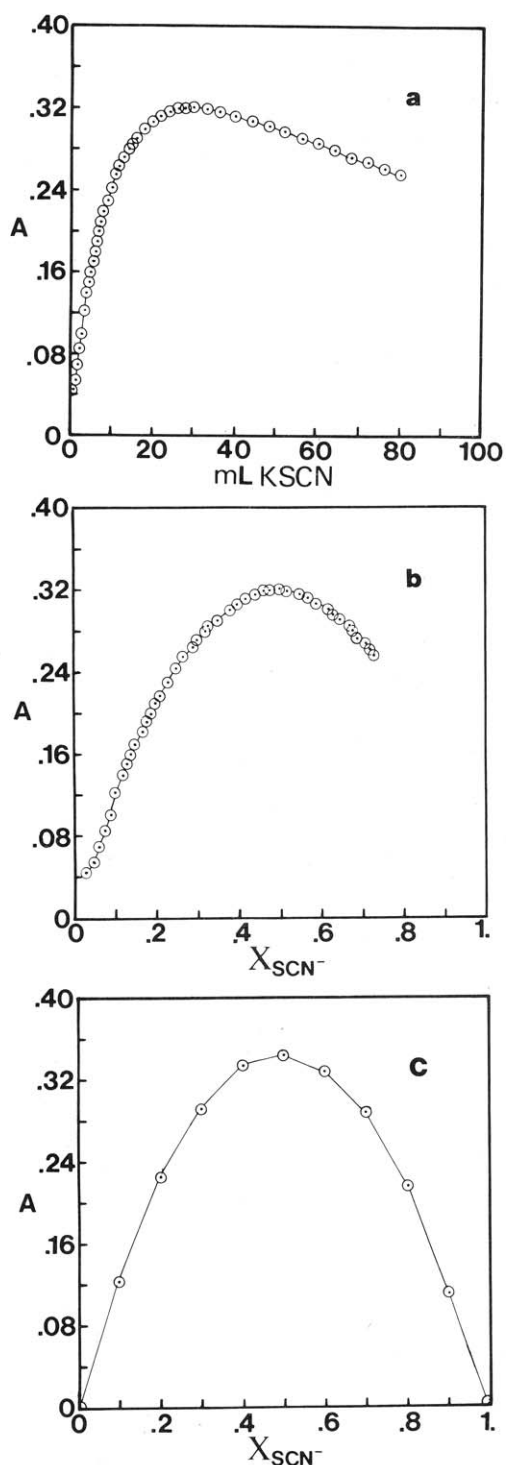


Figure 2. (a) Photometric titration (455 nm) of 30 mL of 0.001 M $\text{Fe}(\text{NO}_3)_3/0.01$ M HNO_3 with 0.001 M $\text{KSCN}/0.015$ M HCl ; (b) Job's plot obtained by transforming curve (a) according to eqn. (4); (c) Job's plot (455 nm) obtained by conventional batchwise method using same stock solutions as in (a).

HNO_3 is used in solution A to minimize hydrolysis of the Fe^{3+} ion without introducing complexing ligands (38); HCl is used in place of HNO_3 in solution B to avoid oxidation of SCN^- .

Results of Experiment 1

Figure 2a shows the photometric titration curve obtained at 455 nm by titrating 30 mL of solution A with solution B. The x axis in Figure 2a represents volume of titrant added. This axis can be transformed into mole fraction of titrant,

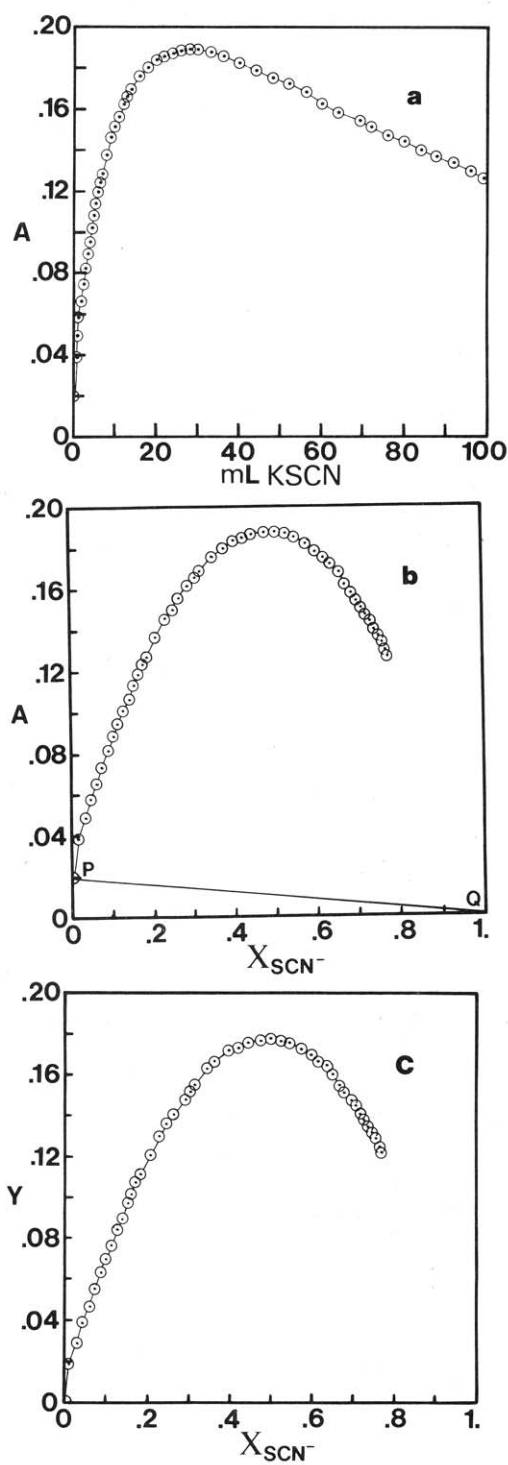


Figure 3. (a) Same as Figure 2a except that 395 nm is the analytical wavelength; (b) curve (a) transformed according to eqn. (4); (c) Job's plot obtained by subtracting PQ from curve in part (b).

χ_L , through eqn. (4). Figure 2b, showing the transformed data, constitutes a plot of A_{455} versus X_{SCN^-} ; since both stock solutions have zero absorbance at this wavelength, $Y_{455} = A_{455}$ (see eqn. (2)). Figure 2c shows a Job's plot obtained by batchwise mixing of solutions A and B in the conventional manner.

Figure 3a illustrates the same photometric titration monitored at 395 nm. Figure 3b shows the titration data from Figure 3a transformed according to eqn. (4); this yields an A_{395} versus X_{SCN^-} plot. Since Fe^{3+} absorbs at this wave-

length, $Y_{395} \neq A_{395}$ (see eqn. (2)). Figure 3c shows the Y_{395} versus χ_{SCN^-} plot; this is obtained graphically, simply by subtracting the area beneath the line PQ in Figure 3b from the total area beneath the experimental curve, consistent with eqn. (2).

Discussion of Experiment 1

Figure 2a is a typical photometric titration curve for a weak complex where the absorptivities of the free metal and ligand are zero and the absorptivity of the complex has a finite value. On transforming the x axis according to eqn. (4) the data are plotted as a function of χ_{SCN^-} ; and since eqn. (1) is satisfied for all data points, Figure 2b is actually a Job's plot for the Fe^{3+} - SCN^- system. This plot is in close agreement with the Job's plot measured in the conventional batchwise manner from the same stock solutions (Fig. 2c). Both plots exhibit a broad maximum at $\chi_{\text{SCN}^-} = 0.5$ indicating formation of a 1:1 complex under these experimental conditions; the broadness of the maxima is consistent with a weak complex ($K_f = 1.4 \times 10^2$). There are a number of noteworthy points of comparison between Figures 2b and 2c:

- 1) The data points in Figure 2b are more closely spaced—the number of data points is determined by the frequency at which titrimetric readings are taken in determining Figure 2a. In the conventional method (Fig. 2c) a completely new experimental must be prepared for each additional datum point required.
- 2) In order to measure 44 data points for Figure 2b, 30 mL of solution A and 80 mL of solution B were required; 30 mL of titrand was used in these experiments due to the size of the modified flask and in order to maintain the level of solution in the flask above the top of the side tube to prevent air bubbles from entering the circulation system. To determine the eleven points for Figure 2c, where all solutions were 30 mL, required 165 mL of each solution. Consequently, the new method for determining Job's plots is more efficient in the use of reagents.
- 3) The curve in Figure 2b is truncated at $\chi_{\text{SCN}^-} = 0.73$. This is because it requires progressively larger volumes of titrant to introduce a unit increase in the mole fraction of ligand as the titration proceeds. This is not a problem in that most compositions determined by Job's method are 1:1 ($\chi_L = 0.5$) or 1:2 ($\chi_L = 0.67$) with occasional 1:3 complexes being found. Furthermore, the right-hand side of the curve is readily accessible by reversing the direction of the titration, i.e., by titrating ligand with metal.

A close examination of Figures 2b and 2c, shows that the maximum in Figure 2b, and in fact all of Figure 2b, lies slightly below Figure 2c. This was shown to be due to the photosensitivity of the FeSCN^{2+} complex (38), where the absorbances of the solutions diminished steadily in the presence of light. For example, the absorbance of a sample stored in darkness remained constant at 0.20 over a two-hour period, whereas the absorbance of a sample left exposed to sunlight decreased from 0.19 to 0.10 during that period. This change due to the influence of light was visually evident. The photometric titration required one to two hours for completion, thus allowing significant exposure of the sample in the flask to sunlight. In the batchwise experiment (Fig. 2c) the absorbances were measured immediately upon preparing each solution. This accounts for the slight discrepancy observed. The above problem could be avoided by "blackening" the titration flask and tubing but that is not necessary for the purpose of these experiments.

Figure 3a illustrates the photometric titration curve monitored at 395 nm, and Figure 3b shows the curve with the x axis transformed according to eqn. (4). In order to obtain the Job's plot (Fig. 3c) the data in Figure 3b have to be corrected as described above, by subtracting the area beneath the straight line PQ from the experimental data in accordance with eqn. (2).

Experiment 1 demonstrates how a Job's plot can be simply obtained from titrimetric data (Figs. 2a and 2b; and Figs. 3a

and 3c). The equivalence of Job's plots obtained by the new method and the conventional technique is illustrated (Fig. 2b and 2c), ignoring the slight discrepancy due to the photosensitivity of the FeSCN^{2+} complex, unique to this example. Once the photometric assembly (Fig. 1) is set up, many more data points can be obtained in a shorter time by the titrimetric method. The new technique is also more conservative in the use of reagents and glassware. Another advantage to the new method is that the optical cell remains undisturbed in the spectrophotometer throughout the complete experiment rather than being constantly removed and reinserted as in the conventional batchwise mode. This minimizes the opportunity for experimental errors.

In carrying out these experiments the ionic strength was maintained fixed at 0.016, and the pH was essentially constant. One of the crosschecks which should always be carried out with Job's method is illustrated here (Figs. 2 and 3), namely, measuring Job's plots at two distinct wavelengths; the maxima occurred at the same value of χ_{SCN^-} in each case, indicating the validity of applying Job's method to this system under these conditions. It should be pointed out that the Fe^{3+} - SCN^- system can display a quite complicated chemistry with the formation of many complexes other than the 1:1 species indicated in this experiment (11, 38, 39). The present results simply indicate that under these particular conditions the 1:1 complex is dominant; at higher reagent concentrations where other species may come into prominence, Job's method may be inapplicable. One should be cautious in extrapolating conclusions arrived at from Job's plots for one set of experimental conditions to that of another set of conditions, such as differences in pH or concentration.

The application of Job's method to the Fe^{3+} - SCN^- system has been described by Carmody (23); the present experiment utilized the same reagents and concentrations as employed by Carmody. However, Carmody does not specify the analytical wavelength that he used, and he employed a 1-inch optical path length; our results are in agreement with his. For higher concentration of Fe^{3+} and SCN^- the position of the maximum of the Job's plots varies, indicating the formation of different complex species (11).

Experiment No. 2: Cu^{2+} -EDTA System

These experiments were performed at one wavelength, 745 nm, and at two total metal-plus-ligand concentrations (red-sensitive phototube with red filter). The analytical wavelength was cited in a number of references (1, 7), and its suitability was further confirmed by recording the spectrum of the Cu^{2+} -EDTA complex on a Cary 219 spectrophotometer, showing a maximum at 745 nm.

Beer's Law

Conformance of this system to Beer's law at 745 nm was established by measuring the absorbances of eight solutions with the concentration of the Cu^{2+} -EDTA complex varying from zero to 0.0125 M; a straight line was obtained which covered the absorbance range for the remainder of the experiments.

Solutions for Job's Plots

Solution C: 0.005 M EDTA (ethylenediaminetetraacetic acid disodium salt).

Solution D: 0.005 M CuSO_4 .

Solution E: 0.0025 M EDTA.

Solution F: 0.025 M CuSO_4 .

Solutions C, D, E, and F were buffered with 0.025 M $\text{HOAc}/0.025 \text{ M NaOAc}$ (pH=4.7); the solutions used in preparing the Beer's law plot were similarly buffered.

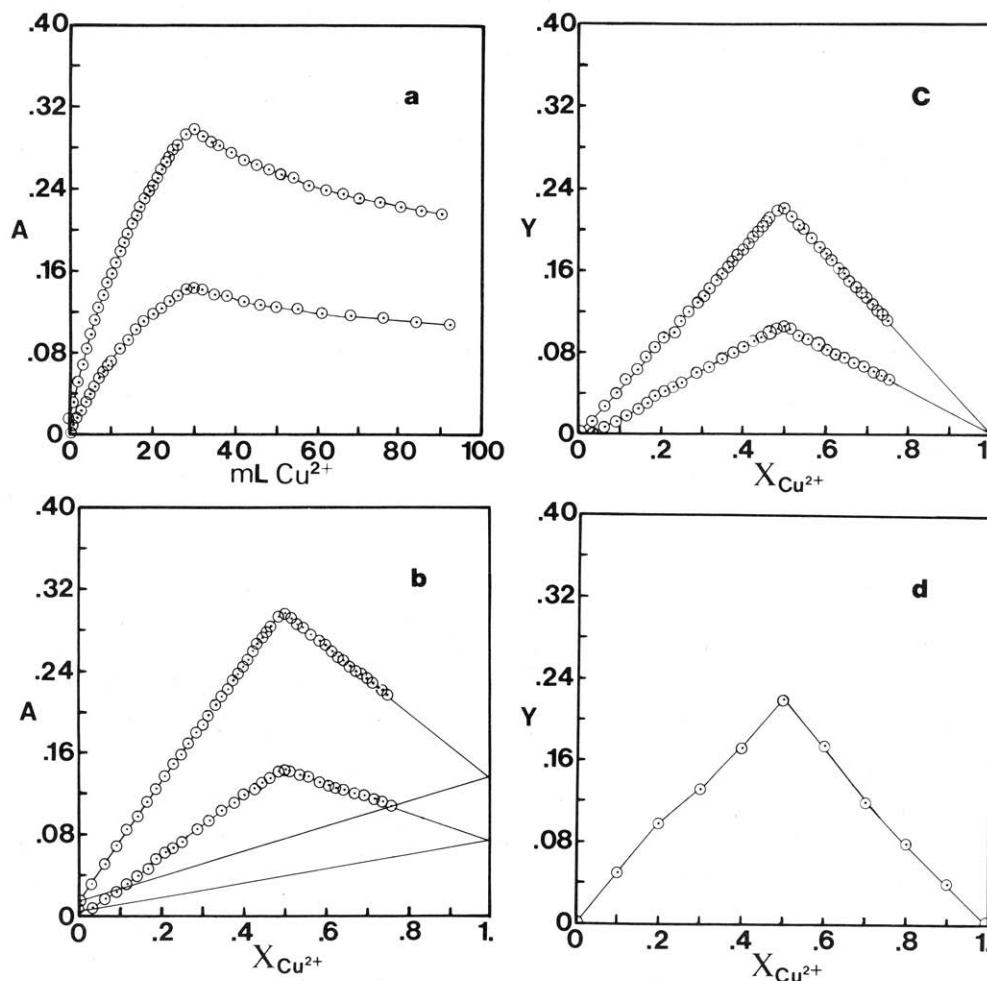


Figure 4. (a) Photometric titrations (745 nm) of 30 mL of EDTA in 0.025 MHOAc/0.025 MNaOAc buffer with CuSO_4 solution in 0.025 MHOAc/0.025 MNaOAc buffer: upper curve, 0.005 M EDTA and 0.005 M Cu^{2+} ; lower curve, 0.0025 M EDTA and 0.0025 M Cu^{2+} ; (b) curves from (a) transformed according to eqn. (4) and extrapolated to $\chi_{\text{Cu}^{2+}} = 1$; (c) Job's plots obtained by correcting curves in (b); (d) Job's plot (745 nm) obtained by conventional batchwise method using 0.005 M EDTA and 0.005 M Cu^{2+} buffered stock solutions.

Results of Experiment 2

Figure 4a shows the photometric titration curves obtained at 745 nm by titrating 30 mL of solution C with solution D and by titrating 30 mL of solution E with solution F. Figure 4b shows the corresponding plots after transformation of the x axis according to eqn. (4), extrapolated to $\chi_{\text{Cu}^{2+}} = 1$. Cu^{2+} absorbs at 745 nm and in order to obtain the Job's plots (Y versus $\chi_{\text{Cu}^{2+}}$) the areas beneath the two straight lines (extending from $\chi = 0$ to $\chi = 1$) in Figure 4b are subtracted from the respective curves, giving the plots of Figure 4c. Figure 4d shows a Job's plot measured for this system by the conventional batchwise method using solutions C and D.

Discussion of Experiment 2

The plots in Figure 4a are typical photometric titration curves for a strong complex. The linearity of the segments in the Job's plots of Figure 4b also indicates the formation of a strong complex, thus justifying the linear extrapolation of the curves to $\chi_{\text{Cu}^{2+}} = 1$. The sharp maxima at $\chi_{\text{Cu}^{2+}} = 0.5$ are consistent with the presence of a strong complex of 1:1 composition as expected ($K_{\text{cond.}} = 2.2 \times 10^{12}$ at pH 5.0).

Points (1)–(3) under "Discussion of Experiment No. 1" and many of the other comments made in that section are also applicable to this example. The Job's plots obtained by the titrimetric method (Fig. 4c) and by the conventional batchwise mode (Fig. 4d) are essentially identical.

In carrying out these experiments the ionic strength was maintained essentially constant at 0.025 by swamping with

the acetic acid/acetate buffer and the pH was maintained constant at 4.7. The second major crosscheck that should be carried out with Job's method is illustrated in Figure 4c; the maxima in the two plots at different total metal-plus-ligand concentrations occur at the same value of $\chi_{\text{Cu}^{2+}}$, indicating the applicability of Job's method to this system.

General Discussion

A method for obtaining Job's plots from titrimetric data rather than by the conventional batch method has been described. The new method has a number of advantages such as the acquisition of many more data points with the use of less reagents. The validity of the method has been demonstrated by comparing Job's plots obtained by this technique with those obtained by the conventional method.

A recent paper (40) subtitled "A titrimetric continuous variations experiment" is unrelated to the content of the present paper and in fact does not pertain to the continuous variations procedure in the normal connotation of Job's method.

The new method has been illustrated by means of two systems which readily lend themselves to undergraduate laboratory experiments. The examples demonstrate the control of important parameters, pH and ionic strength, during the course of the experiment. These experiments also illustrate two important crosschecks which should be employed when using Job's method, that is, carrying out the measurements at more than one wavelength, and also at more than one total metal-plus-ligand concentration. The thorough-

ness of these experiments provides good training for the junior or senior-level student in this area. Examples of both weak and strong complexes are provided thereby illustrating *the two extremes of behavior*. Due to the substantive nature of the experiments described in this paper they would best be accommodated into a multiperiod laboratory or more appropriately be conducted as a team project. In the latter case one student could carry out the photometric titration at one wavelength, another student at a different wavelength, another at a different total metal-plus-ligand concentration while yet another measured Job's plots using the conventional batchwise method.

Besides the actual experiments per se, the underlying concepts presented in this paper have an inherent pedagogic value in that they teach relationships between methods that are normally taught and considered separately. The existence of a close relationship between titrimetry and Job's method has been pointed out in this paper. In the wide variety of analytical chemistry and instrumental analysis texts which discuss these two methods (1-13), they are invariably considered separately with no discussion of their interrelationship. It is these authors' contention that the appreciation of the relationship between titrimetry and Job's method, as presented in this paper, provides a better comprehension of the subject matter as a whole. Titrimetry and Job's method have traditionally been considered as distinct topics. This paper shows how data acquired by one technique can be readily transformed into that of the other. One should make a clear distinction between Job's method and Job's plots; the former refers to a particular methodology for preparing solutions, the latter refers to a mode of plotting data, that is, a plot of Y as a function of mole fraction. *Data for a Job's plot can be acquired directly using Job's method or indirectly from titrimetric data using the transformation described in eqn. (4).*

Note Added in Proof

In a recent issue of THIS JOURNAL, 1985, 62, 680, Clare et al. pointed out a *specific case* where equilateral triangular representation of ternary liquid data, *superimposed on Cartesian coordinates*, appears to be superior for fitting the data to polynomials using a least squares method. Nevertheless, this author considers the right triangular representation to be more advantageous in general, and particularly for pedagogic purposes, for the reasons illustrated here and in a previous paper (1).

Acknowledgment

This research was supported by an L. J. Beckham grant from the Colorado School of Mines.

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