

because materials with large surface areas absorb larger quantities of adsorbate, the concentrations of the starting materials should be adjusted so that equilibrium concentrations between 0.05M and 0.2M are used in constructing the isotherm. Likewise, the solid-to-liquid ratio may be diminished when measuring larger areas.

At least three points on the isotherm should be determined for precise work, but a value for the surface area can be calculated from a single point if the isotherm is drawn through the origin. If this is constructed from a point at about 0.2M concentration, an error of from a few to 20% results, depending on the material and the accuracy of the single determination. When using this simplification, it is necessary to establish the accuracy, by first constructing a more complete isotherm. The average working time required for the performance of one of these single-point measurements is 45 minutes; the lapsed time is about 2 hours.

It was not found necessary to outgas the material before use in the cases of dry, precipitated CaHPO_4 and calcium hydroxylapatite. Outgassing is known to change the surface area of hydrates. Also, an effect of outgassing has been reported for the adsorption of acids from toluene onto silica gel (10). Therefore, powders should normally be dried or outgassed prior to surface area measurements, unless evidence shows this to be unnecessary.

RESULTS

Table I lists the surface areas of various phosphates which have been determined by the acetic acid and the conventional BET methods. The precision of the acetic acid adsorption data is 0.2 sq. meter per gram for duplicates up to 8 sq. meters per gram. In this range, the data are more precise than the BET data and are at least as precise at the 70 sq. meters per gram region. The poor agreement between duplicates by the BET method for CaHPO_4 and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ may be due to the sensitivity of the surface area to the degree of surface hydration. Nonreproducible changes could have taken place during the preparation of these two samples for the BET measurements.

The acetic acid adsorption method is not useful for surface area measurements on very basic materials such as lime, which reacts completely with the acid. Results obtained on less polar materials such as silica show surface areas much less than those determined by nitrogen adsorption. This effect can be attributed to the less polar nature of the adsorbent, which would enhance the competitive adsorption of the acid and solvent. Materials which chemically sorb acetic acid might also give complex results when studied by this method.

No solvents other than toluene were studied. However, the choice of solvents is limited by several requirements. The solvent must be miscible with

acetic acid, inert chemically toward it and toward the adsorbent, and nonpolar and nonpolarizable, in order that the adsorption of the solvent on a polar adsorbent does not compete with the acetic acid. Systems where binary adsorption occurs are too complex for routine surface area measurements.

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Spectropolarimetry

Acid-Base Titrimetry with Asymmetric Indicators and Determination of Metal Ions and Asymmetric Substances

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► Because of the recent development of high-precision photoelectric spectropolarimeters, it is possible to purchase or construct instruments which will permit the rapid determination of optical rotation at many different wavelengths. A method is presented, utilizing such an instrument, which allows for the titration of acids or bases using optically active substances as indicators. The titration curves resemble those of conductometric titrations. The method also provides for the determination of metal ions and asymmetric coordinating agents, and permits the determination of the ligand-metal ion ratio in coordination compounds, as well.

BECAUSE of the limitations inherent in making determinations with a visual polarimeter, the instrument is not readily adaptable for titrimetry and, in analysis, has found its prime use in the comparison of optical rotation of samples with that of standards. Mattock (6), Freegard (4), and others have also used the visual polarimeter in continuous variation studies of metal complexes with asymmetric ligands in the determination of ligand-metal ion ratios.

In recent years versatile spectrophotometers of high quality, light sources of high intensity in both the visible and ultraviolet regions, and polarizing prisms with appropriate cements allowing transmission into the ultraviolet

have become commercially available. Some individual investigators have also constructed similar instruments in their own laboratories (2). This has allowed construction of spectrophotometric photoelectric polarimeters which utilize phototubes in place of the human eye as a detector, monochromators in place of special lamp and filter combinations for producing monochromatic light of different wavelengths, and intense light sources for determining the optical rotation of solutions which are also strongly absorbing (3, 5). Several such polarimeters are commercially available (5), and some can fairly readily be adapted for use in titrimetry—e.g., photoelectric polarimeter, Carl Zeiss,

Inc., 485 Fifth Ave., New York 17, N. Y.; Standard-Keston polarimetric attachment, Standard Polarimeter Co., 6 Banta Place, Hackensack, N. J.—but they are limited to a few wavelengths or to a narrow frequency range in the visible region.

The authors and their coworkers (1) have designed a relatively simple spectrophotometric polarimeter for use in the region 2600 to 10,000 Å., which utilizes a Beckman Model DU spectrophotometer with a 10-cm. tube compartment, and which was constructed at a relatively low cost compared with that of commercial instruments of comparable versatility, wavelength range, and precision. In addition, determinations of optical rotation are extremely rapid because they consist of absorbance measurements and because the optically active sample in its solvent and cell acts as its own blank, for both colored and "colorless" solutions. The instrument is particularly applicable to spectropolarimetric titrations of the types described below because (a) the relatively large sample compartment allows for easy handling of suitably large volumes of solution, (b) a multiplier phototube is used to measure light intensities in place of the human eye for the comparison of visual fields, thus avoiding the eye's attendant limitations, (c) a monochromator permits selection of suitable wavelengths in the visible and ultraviolet regions without the problems of special lamps and filters, (d) intense light sources allow the use of relatively optically dense solutions, (e) no solvent blanks are necessary during the determinations, and (f) the optical rotation is determined as a function of the measured optical absorbance difference of the solution between two positions of the analyzer prism (1), which also helps to make for simple, rapid determinations.

PRINCIPLES AND PROCEDURES

Acid-Base Spectropolarimetric Titrimetry with Asymmetric Indicators. INDICATOR SELECTION. For the titration of strong acids and bases, it is necessary to use as an indicator an optically active substance which exhibits a marked change in its optical rotation at the titration end point. For the titration of a strong acid with a strong base, *d*-(or *l*-) tartaric acid is such a substance. It undergoes a marked optical rotation change upon conversion to the monohydrogen salt and undergoes a further marked change upon conversion to the disodium salt, which, in this case, allows determination of the quantity of indicator added to the system. This is also indicative of the potential of this method for titrimetric determination of weak acids, a matter which is now under study.

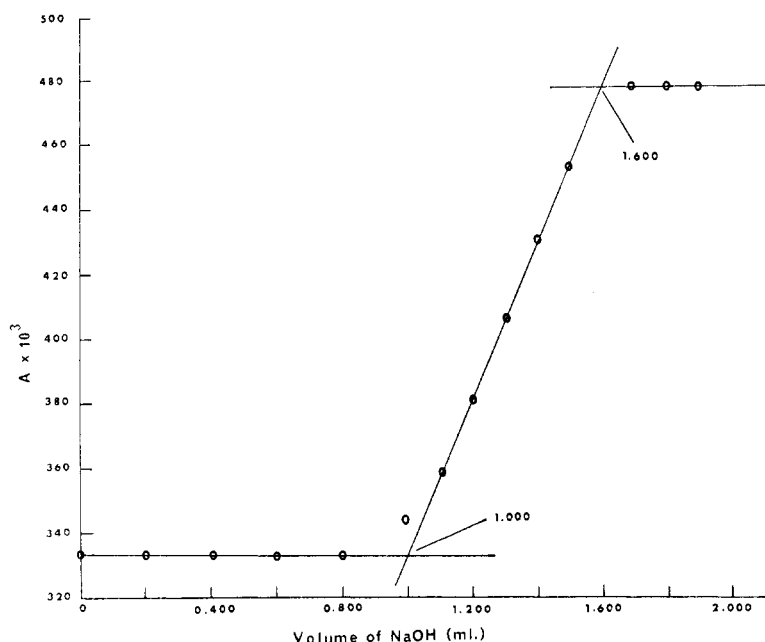


Figure 1. Spectropolarimetric titration of HCl and *d*-tartaric acid with standard NaOH

$\lambda = 4000 \text{ Å.}$

TITRIMETRIC PROCEDURE. If a relatively large volume (>50 ml.) of a relatively dilute (ca. 0.1 *N*) acid of known or unknown concentration, containing an added optically active indicator whose optical rotation changes markedly on going from an acidic to a basic solution—e.g., *d*-tartaric acid—is titrated with a relatively concentrated (ca. 5*N*) base of unknown or known concentration, respectively, using a microburet which is readable to 0.001 ml., measurement of the optical rotation of the system at a few points before and after the end point permits a relatively simple determination of the end point by graphical procedures (Figure 1). The titration resembles a conductometric titration in that it is necessary to obtain only a relatively few points (optical rotation or absorbance difference *vs.* volume of titrant) before and after the end point, to plot the resulting straight lines on graph paper of appropriate size, and then to determine the volume of titrant at the point where the lines cross. It is also possible to determine the concentration of the added asymmetric indicator, if it reacts with the base and undergoes a further appropriate optical rotation change in so doing (Figure 1).

The volume relationship described above is chosen so as to minimize dilution effects. As is often true in conductometric titrations, equilibrium conditions near the end point are relatively unfavorable, and titration points should therefore not be determined too near the end point (see Figure 1). Another factor which may also affect the points in the vicinity of the end point is the acid dissociation constant(s) of the asymmetric

indicator. This question is also under study and will be reported on in a later publication. It is sometimes useful to determine the optical rotatory dispersion of the indicator substance to aid in the selection of the wavelength giving the most appropriate rotation change and transmittance combination for the reaction under study.

Spectropolarimetric Titrimetry of Metal Ions and Asymmetric Substances. INDICATOR SELECTION. For the titration of metal ions by this technique, it is necessary to select as an indicator an optically active substance that rapidly forms a complex of the metal ion having an optical rotation which is markedly different from that of the indicator alone. An example is copper(II)-*l*-(+)-histidine monohydrochloride, which forms 1:1 and 1:2 complexes, both of which have rotations sufficiently different from that of the ligand alone to allow determination by a spectropolarimetric procedure. For the titration of optically active substances by metal ions, a metal ion must be chosen which rapidly forms a complex with the optically active compound with an optical rotation markedly different from that of the compound.

TITRIMETRIC PROCEDURE. As in the previous case, a relatively large volume of a relatively dilute asymmetric coordinating agent—e.g., *l*-(+)-histidine monohydrochloride—of known or unknown concentration may be titrated with a relatively concentrated solution of a metal ion—e.g., copper(II) cation—of unknown or known concentration, respectively, with which it forms a complex (Figure 2.) Excellent use of the

optical rotatory dispersion of the complex can also be made here in the selection of the wavelength and transmittance giving the greatest observable change per unit volume of titrant.

Complexes involving various ratios of ligand to metal ion can be used in these titrations. In fact, it is often possible to determine the ligand-metal ion ratio in compounds by this technique. Figure 2 shows two end points in the titration. The first represents the 2:1 ligand-metal complex, and the second, the 1:1, although, in this case, the lines form too obtuse an angle for an accurate determination of the second end point. As the angle between the two intersecting lines increases, the degree of precision of the end-point determinations decreases, so that system components should be selected to provide as large an optical rotation difference as possible, in order to achieve the smallest possible angle of intersection. Even in Figure 2 the first end point shows so obtuse an angle that it can reasonably be read to only two significant figures. This phenomenon is also being studied further and will be reported later.

RESULTS

The spectropolarimetric titration of 50-ml. of 0.1*M* hydrochloric acid containing 1 ml. of 2*M* *d*-tartaric acid required a volume of approximately 5*M* sodium hydroxide which differed from the calculated volume by 0.32% for three determinations (average). The determination of the concentration of the added *d*-tartaric acid required a volume of standard sodium hydroxide which differed from the calculated volume by an average of 0.41% for three determinations. Both titrations were carried out at 4000 Å.

The spectropolarimetric titration of *l*-(+)-histidine monohydrochloride with 1.5*M* copper(II) chloride at 4000 Å. required a volume of the copper chloride solution which differed from the calculated volume by an average of 0.33% for three determinations using only the first end point (Figure 2), that for the 2:1 ligand-metal complex.

INSTRUMENTAL OPERATIONS

The operation of the instrument itself consists of placing a sample in an appropriate absorption cell (constructed of optically inactive glass, quartz, or other suitable transparent, inactive material, 5 cm. long, 2.5 cm. wide, and 6 cm. high and used in place of a polarimeter tube), adding small known increments (ca. 0.2 ml.) of the concentrated titrant, stirring, allowing the turbulence to cease, and then reading the absorbance of the solution twice—once with the analyzer prism in one of its two

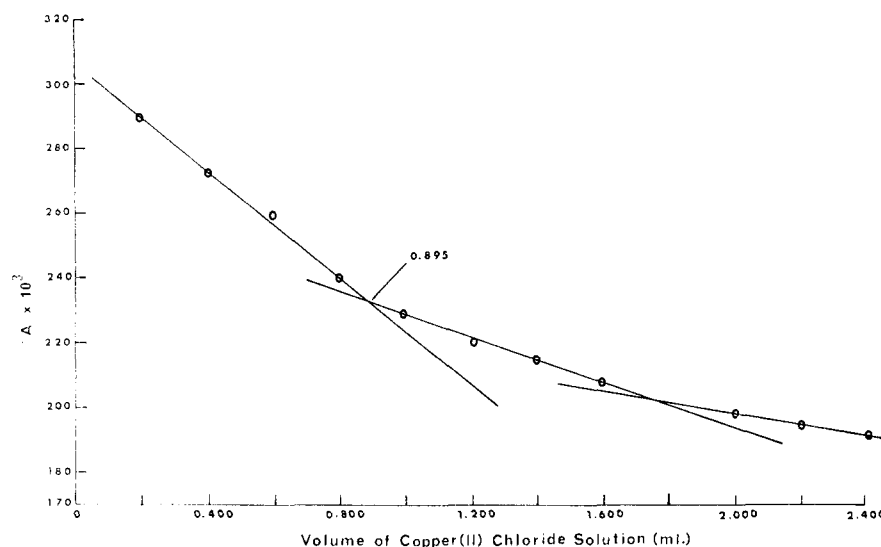


Figure 2. Spectropolarimetric titration of *l*-(+)-histidine monohydrochloride with copper(II) chloride

$\lambda = 4000 \text{ Å.}$

possible positions (1) (where its transmittance is made to read a certain preselected value each time—e.g., 100% or 50%—by appropriate changes in the sensitivity controls of the instrument), and once with the analyzer prism in its other position. The absorbance difference (or absorbance, with the analyzer in its second position) is plotted against titrant volume and the next increment of titrant is added. Four such points obtained both before and after the end point are usually sufficient for an adequate plot. An average titration takes about 30 minutes.

Selection of the most appropriate wavelength is usually not very critical. It can be determined by examination of the absorption spectrum and optical rotatory dispersion of the product (and/or reactants) of the reaction. The wavelength giving the largest rotation change with maximum transmittance will usually be the most appropriate.

CONCLUSIONS

The application of spectropolarimetry to titrimetric procedures for certain systems provides a simple, rapid means for the determination of unknown components of those systems. In particular the method has been applied successfully to the titrimetric determination of strong acids and strong bases utilizing an asymmetric indicator and a spectropolarimeter as an end-point detector. In addition, the method has been used to determine a weak optically active acid by direct titration with a strong base. It has also been used to determine metal ions and optically active coordinating agents which react with each other to produce complexes having optical rotations different from those of the ligands.

Studies are under way to determine whether weak acids and bases may be determined by this procedure, using other optically active indicators which are pH-sensitive. In addition, this method should be applicable to determinations of ligand-metal ratios in complex inorganic compounds, as well as of metals and optically inactive coordinating agents using asymmetric substances which are weak coordinating agents as indicators. Studies on these systems are also under way and will be reported in a later paper.

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