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AUTOMATIC PHOTOMETRIC TITRATION OF SULFATE

F. J. Miller
P. F. Thomason

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F. J. Miller and P. F. Thomason

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ABSTRACT

The rapid microtitration of sulfate with standard barium perchlorate solutions by use of 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, called Thoron, as an adsorption indicator was adapted for automatic photometric titration. A simple titration-cell assembly was devised that incorporates an interference filter and a phototube. Voltage from the phototube is used to actuate the titrator and is recorded. The end point is determined from the recorded plot of voltage versus volume of titrant added to the test solution. The ORNL model Q-945 automatic titrator is used. Quantities of sulfate in the range 0.048 to 17 mg were titrated.

INTRODUCTION

The technique of a manual titration of sulfate ion with barium perchlorate solution by the use of 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, called Thoron, as an adsorption indicator has been described by Fritz and Yamamura.[1] The color change of the Thoron indicator at the end point from yellow through yellow-orange to pink is difficult for some persons to observe. Each analyst is obliged to standardize his own solutions because of visual disparities. If many successive titrations are done, the precision of the results tends to decrease as the analyst's eyes become fatigued. In addition to these considerations, it is desired to perform the titration remotely within "hot cell" facilities. Many of these cells are equipped with windows that are filled with yellow zinc bromide solution. The color of these windows would prohibit the following of a titration that depends upon the use of a yellow indicator for detection of the end point. A photometric procedure has been devised to overcome these difficulties.

The work of Müller and Partridge[5] and of subsequent authors[2,3,6] has demonstrated the feasibility of photometric titrations. A beam of monochromatic light is passed through a transparent absorption cell that contains a test solution. A photoelectric cell is used to indicate the amount of light absorbed by the solution. If a suitable titrant solution is added in increments and if the absorbancy of the solution in the cell is recorded as a function of the voltage developed by the photocell, titration curves can be plotted.

Either conductometric or potentiometric type titration curves may be obtained in a photometric titration. If the phototube is sensitive to the color of the ion being titrated in the test solution or to the color of an

ion in the titrant solution, a conductometric type curve is obtained. This type curve has all the inherent advantages of the conductometric curve. The region about the end point is not significant since the end point can be located exactly by extrapolation of the two branches of the curve. The precision of the photometric titration is better than that obtained by simple colorimetric measurement because the positions of two branches of the curve are determined from the averages of a number of colorimetric measurements. If the phototube is sensitive only to the color of an indicator solution that has been added in very small quantities to the test solution, a curve is obtained that is very similar to a potentiometric titration curve. An abrupt shift in the potential developed by the photocell results from the sudden change in absorbancy of the test solution caused by the spectral shift of the indicator. The point at which the maximum shift in potential occurs is taken as the end point; thus the region of the curve about the end point is highly significant. The end point cannot be located by extrapolation of the arms of the curve.

The curve that is obtained in performing a precipitation titration with the use of an adsorption indicator is of the potentiometric type. A remarkable similarity can be seen between the adsorption curve shown in Fig. 1 and the curve obtained in the titration of sulfate with barium perchlorate by the use of Thoron as an indicator (see Apx. II). Figure 1 is taken from I. M. Kolthoff's article "Adsorption Indicators" in Chemical Reviews, 16, 87 (1935).

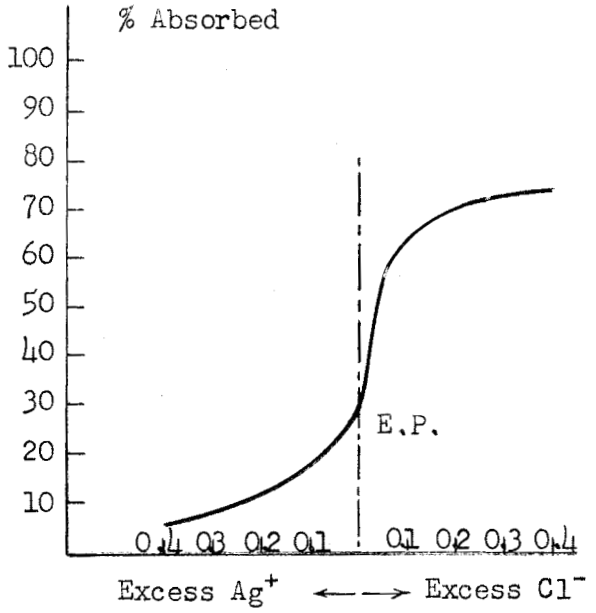


Fig. 1. Adsorption of Methyl Violet by Silver Chloride

Kolthoff's article(4) gives a brief but complete discussion of the use of adsorption indicators and of the mechanism involved in the adsorption of dyes on the surfaces of crystalline precipitates.

SUMMARY

It is expected that the HRT will provide a large number of samples in which sulfate is to be determined. The titrimetric method of Fritz and Yamamura[1] would be adequate except for the difficulties of performance of the titration remotely and of an expected large variance between operators. The automatic photometric titration proposed in this report eliminates the error caused by variance among operators and provides a means for conducting the titration remotely.

Advantage has been taken of existing equipment by designing a titration cell assembly that consists of a light filter, absorption cell, photocell, and load resistor. This cell assembly is used in conjunction with the ORNL model Q-945 automatic titrator.[7]

Amounts of sulfate in the range 0.048 to 17 mg have been titrated with good precision (see Tables 1 and 2 and the discussion following them).

DISCUSSION

The reagents for the titration are prepared according to the directions given by Fritz and Yamamura.[1] The interferences and requisite conditions of the titration are also stated by these authors.

The ORNL model Q-945 automatic titrator has been described previously.[7] The titration cell assembly consists of a box type radio chassis, Bud CU 3006, that is 5 x 3 x 2 inches. The top has a 1-in. wide slot across the center. The light source is a General Electric flashlight bulb, type PR 6, that is connected to an external a-c power supply through a micro switch. The micro switch is actuated by the closing of a lid across the 1-in. slot. The a-c power source consists of a Sola voltage-regulating transformer and a filament transformer that reduces the voltage to 3 v. A potentiometer is connected across the 3-v leads from the filament transformer in order to reduce further the voltage applied to the flashlight bulb. An interference filter, available from the Photovolt Corp., transmits a band of light, approximately 10 mμ wide, in the spectral region of 515 mμ. A flat-sided, pyrex absorption cell, approximately 2 x 7/8 x 1 5/8 in., which can be inserted or removed freely through the slot in the top of the chassis, is located next to the light filter. An RCA 5652 phototube is placed immediately in back of the absorption cell so that light strikes the photosensitive surface of the phototube. Voltage for the phototube is supplied by two 22.5-v batteries (Eveready type 505-E) connected in series. A 1-meg potentiometer serves as a load resistor for the phototube. Voltage developed across the load resistor is fed directly to the automatic titrator by the leads that are normally connected to the electrodes.

The solution in the absorption cell is stirred by means of a glass-covered iron bar, approximately 1/2 in. length x 1/8 in. diameter. The entire chassis is placed on top of the magnetic stirrer. Since the chassis is made of aluminum, the operation of the stirrer is not hindered by the chassis.

The buret used in the titrations is a syringe type buret, calibrated to deliver 3.000 ml of titrant per inch of travel of the syringe plunger. The buret is manufactured by the Micro-Metric Instrument Co. of Cleveland, Ohio. The screw drive of the buret is coupled mechanically to the ORNL model Q-945 automatic titrator by an extensible shaft.

The procedure for this titration is described in Apx. I. It should be noted at this point that the titrant is empirically standardized against a standard sulfuric acid solution, which has been standardized previously against a standard sodium hydroxide solution. The water-to-methanol ratio must be kept constant in any one series of titrations because any change in this ratio will affect the solubility of the barium sulfate precipitate formed in the titration. A change in the solubility of the precipitate will alter the volume of titrant required to reach an end point.

The precision of data taken by the photometric titration method is shown in Tables 1 and 2; the data were obtained by titrating sulfuric acid solutions.

The samples obtained from the HRT solutions can be expected to contain the cations of uranium, copper, potassium, and nickel, as well as the sulfate anion. These cations should be removed by passage of test aliquots of the solution through a column of Dowex 50 cation-exchange resin in accordance with instructions given by Fritz and Yamamura.[1]

Table 1

PRECISION STUDY

Titration of 1.00 ml of 0.0010 N H_2SO_4 with 0.00058 M $Ba(ClO_4)_2$ Solution

(Buret delivered 3.000 ml per inch of travel of buret syringe plunger)

Det'n.	Distance of Buret Syringe Travel, in.	$X - \bar{X}$	$(X - \bar{X})^2$
1	0.289	0.000	0.000
2	0.290	+ 0.001	1×10^{-6}
3	0.288	- 0.001	1×10^{-6}
4	0.290	+ 0.001	1×10^{-6}
5	0.288	- 0.001	1×10^{-6}
			$\Sigma(X - \bar{X})^2 = 4 \times 10^{-6}$

$N = 5$

$\bar{X} = 0.289$ in.

$D.F. = N - 1 = 4$

$$S^2 = \frac{\Sigma(X - \bar{X})^2}{N - 1} = \frac{4 \times 10^{-6}}{4} = 1 \times 10^{-6}$$

S, in. $= 1 \times 10^{-3}$

$$S, \% = \frac{(S)(100)}{\bar{X}} = \frac{(1 \times 10^{-3})(100)}{289 \times 10^{-3}} = 0.346$$

Standard Error at 95% Probability Level, $\% = \frac{tS}{\sqrt{N}} = \frac{1.239 \times 0.346}{\sqrt{5}} = 0.192.$

Table 2

PRECISION STUDY

Titration of 1.00 ml of 0.0100 N H_2SO_4 Solution with 0.0025 M $Ba(ClO_4)_2$ Solution

(Buret delivered 3.000 ml per inch of travel of buret syringe plunger)

Det'n.	Distance of Buret Syringe Travel, in.	$X - \bar{X}$	$(X - \bar{X})^2$
1	0.669	- 0.001	1×10^{-6}
2	0.671	+.0.001	1×10^{-6}
3	0.668	-.0.002	4×10^{-6}
4	0.673	+.0.003	9×10^{-6}
5	0.669	-.0.001	1×10^{-6}
		$\Sigma(X - \bar{X})^2 =$	16×10^{-6}

$N = 5$

$\bar{X} = 0.670$ in.

D.F. $= N - 1 = 4$

$$S^2 = \frac{\Sigma(X - \bar{X})^2}{N - 1} = \frac{16 \times 10^{-6}}{4} = 4 \times 10^{-6}$$

S, in. $= 2 \times 10^{-3}$

$$S, \% = \frac{(S)(100)}{\bar{X}} = \frac{(2 \times 10^{-3})(100)}{670 \times 10^{-3}} = 0.298$$

Standard Error at 95% Probability Level, $\% = \frac{tS}{\sqrt{N}} = \frac{1.239 \times 0.298}{2.23} = 0.165.$

Two 1-ml aliquots of an HRT sample solution were titrated with barium perchlorate solution by the photometric procedure after being passed through the ion-exchange column. Sulfate values of 17.06 and 17.90 mg per ml were obtained. Sulfate values obtained by a gravimetric procedure in which barium chloride was used as the precipitant were 17.8 and 17.7 mg per ml. The agreement between the results by the two methods is reasonable in consideration of the known errors in both methods. More strict adherence to procedures for the use of resin columns to remove cations will probably improve the over-all precision of the photometric titration method of sulfate determination.

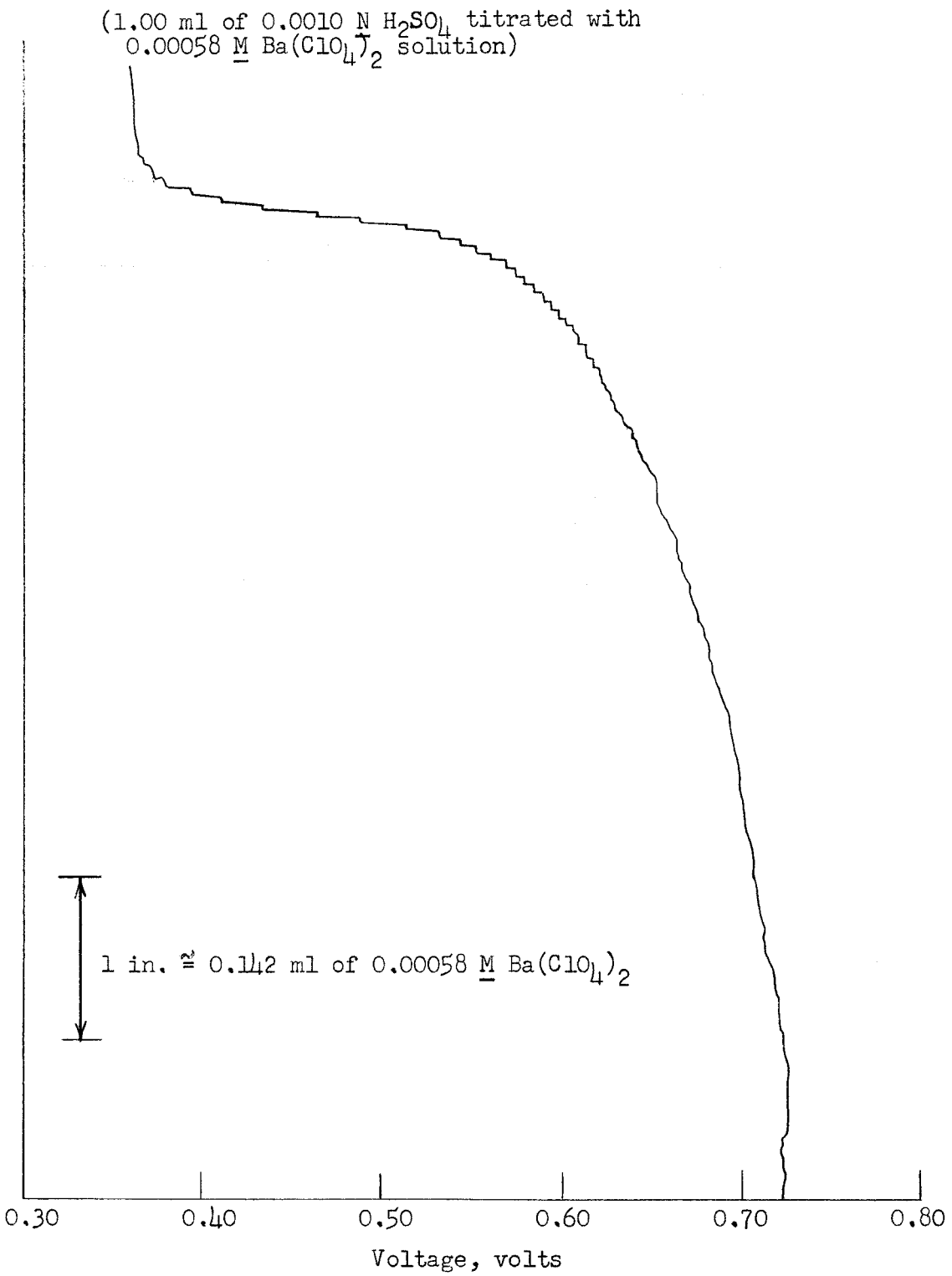
Appendix I

Procedure for Standardizing Barium Perchlorate Titrant Solution

1. Place a 1-ml aliquot of approximately 0.005 M standard sulfate solution in the absorption cell.
2. Add 24 ml of methanol.
3. Add 2 drops of 0.2% Thoron solution.
4. Place the absorption cell in the slot in the cell assembly.
5. Place the lid on the slot, thus activating the light bulb.
6. Place the titration cell assembly on the magnetic stirrer and raise the assembly into position so that the buret tip passes through the hole in the lid and dips into the solution.
7. Set the stirrer into operation, and start the titration by throwing the feed switch on the titrator. The starting voltage should be 1.7 to 1.9 v; the curve produced should be similar to that shown in Apx. II.

Appendix II

Typical Curve Recorded in the Automatic Photometric Titration of Sulfate Solution with Barium Perchlorate



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