

Practical Photometric Titrations With An Easily Constructed Reaction Cell

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Introduction

Although the general technique of photometric titration has been known for many years, activity in the field became pronounced with the accessibility of relatively inexpensive filter photometers and spectrophotometers in the decade following about 1945 (1). With the development, in 1959, of an inexpensive titration cell which provided for much larger sample volumes and stirring by circulation (2), interest was further drawn to the technique. That titration vessel, however, although relatively inexpensive and easy to construct, is rather tricky to assemble and difficult for students to employ.

A very simple, large-volume photometric titration vessel has been developed, which is readily constructed from an ordinary beaker and a test tube. It has been thoroughly tested by students who have never before performed a photometric titration and used with a variety of commonly available instruments.

Materials and Methods

The photometric titration vessel (Fig. 1) consists of a pyrex test tube (selected so that the tube fits conveniently into the cell compartment of the instrument to be used), sealed into the bottom of a graduated pyrex beaker of the desired capacity—100 ml is a convenient size, so that titrant volumes as large as 10 ml may be used without significant change in the total solution volume. The length of the actual cell—the test tube—is determined by the working depth of the instrument cell holder, but should be kept as short as possible. The stirrer is constructed from a piece of tygon tubing of appropriate length, cut out as shown in (Fig. 1) to provide thorough solution mixing, into which a piece of glass or plastic rod of the desired length is inserted to serve as a handle.

Operational procedure is simple. After each addition of titrant, the stirrer is raised and lowered rapidly several times, in the cell, so that solution from the test tube is “pumped” up into the beaker, thus stirring the entire solution. Five to ten seconds of such stirring have been found to be adequate. The stirrer is then placed in the “measurement” position, as indicated by the dashed line in the figure, while the instrument reading is taken. Depending upon the size of the beaker used in construction of the cell, the volume of solution titrated may range from a minimum of about 5 ml to a maximum of about 125 ml.

Applications

The photometric titration vessel described may be used with almost any simple colorimeter or filter photometer having a vertical cell compartment

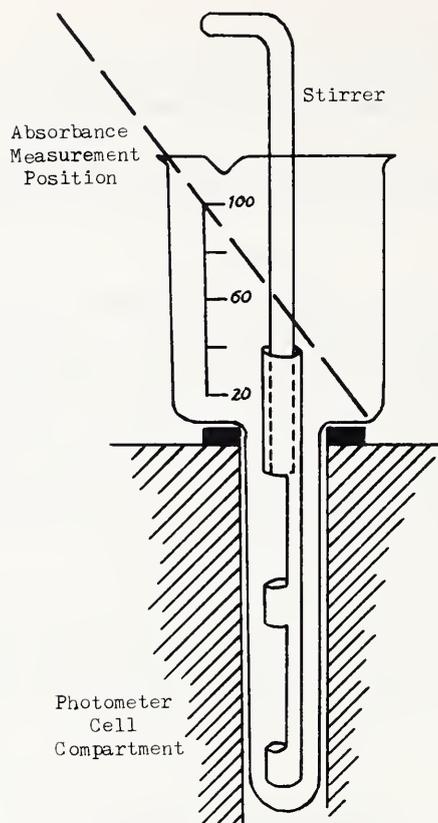


FIGURE 1. *Photometric Titration Vessel.*

which accepts cylindrical cells. Titration vessels have been constructed and tested with the Chemtrix Type 20 Colorimeter, Klett-Summerson Photoelectric Colorimeter, and the Markson J-7453 Colorimeter. Instruments which have an integral shutter actuated by insertion of the sample cell, such as the Bausch and Lomb Spectronic 20 Spectrophotometer, do not yield particularly good results with the cell owing to a light leakage problem—a circumstance also observed with the cell described by Rehm, *et al* (2). Inasmuch as the diameters of the cell compartments vary somewhat with the different brands of instruments, different sizes of test tube cells are generally required.

Two specific analyses have been selected for student experiments with the photometric titration cell (although many others are equally suitable). These are (a) the determination of tannins in tea or coffee by photometric titration with potassium permanganate in the presence of indigo carmine, according to the method of Loewenthal (3), and (b) the analysis of washing soda by titration of the aqueous solution with $N/2$ HCl, using methyl orange as indicator.

Procedures and Results

Determination of Tannins in Tea or Coffee.—The $N/10$ $KMnO_4$ titrant was standardized against USP grade tannic acid (0.500 g per 100 ml) by the same photometric titration procedure used in the analysis. Ten ml (pipet) of the tannic acid solution or an appropriate volume of freshly brewed unknown sample (25.0 ml of tea or 5.00 ml of coffee) were transferred to a clean cell mounted in the

instrument cell compartment. One ml (pipet) of indigo carmine indicator (0.3% in dilute H_2SO_4) and sufficient distilled water to bring the total volume up to about the 80-ml mark on the beaker were added. The titrations were carried out in the usual manner, recording sample solution absorbance at 610 nm and the volume of permanganate solution delivered after each increment of titrant was added and the solution stirred about 5-10 seconds, as previously described. Titrant was added in 1.0-ml increments through a discernible change from green to golden-yellow in the color of the sample solution in the beaker and continued until 4 or 5 increments had been added after minimum (or constant) absorbance was observed. Typical photometric titration curves for samples of tannic acid, tea, and coffee are shown in (Fig. 2).

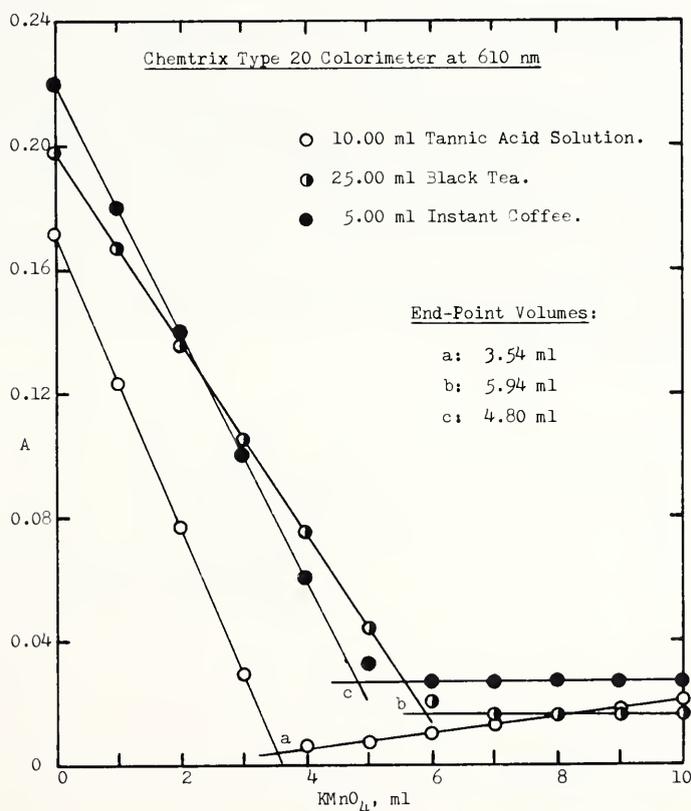


FIGURE 2. Photometric Titration Curves for the Determination of Tannins.

The results of the analyses may be widely varied, depending upon a number of experimental variables. These include time and temperature of brewing, as well as the type and brand of commercial sample analyzed. When all sample variables were fixed, it was found that photometric titrations with the cell described consistently yielded results to well within one relative percent for replicate measurements on the same system. A little imagination may produce an extensive series of interesting student individual or class experimental studies involving tea or coffee.

Analysis of Washing Soda.—This analysis involves the classical titration of sodium carbonate (commercial washing soda) with $\text{N}/2$ HCl , using methyl orange (0.1% in distilled water) as indicator. The end-point color change for this

titration has always been a difficult one for students to observe. In this case, since the HCl used was not standardized by the method to be used, an indicator blank was determined. Approximately 80 ml of distilled water were added to the clean cell mounted in the instrument cell compartment, along with about 5 drops of methyl orange indicator solution. This "blank" solution was then titrated photometrically with 0.10-ml increments of N/2 HCl (previously standardized against standard NaOH solution, using phenolphthalein indicator), until three successive increments produced no change in absorbance (Fig. 3, point A). Then a 10.0-ml aliquot of the commercial washing soda sample solution (prepared by dissolving 5.00 g of the dry commercial product in sufficient distilled water to make 250 ml) was added to the solution already in the cell as a result of the blank titration, and the titration completed, using 0.5-ml increments of acid until the first significant change in absorbance was observed (Fig. 3, point B). Then, 0.1-ml increments were added until point D was reached, after which 3 or more additional 0.5-ml increments were added to complete the titration. The titration end-point volume is the volume at straight-line intercept point C minus that at the blank titration intercept point A. The results were reproducible to within 0.5 relative per cent when the indicator blank volume was applied and the second titration curve break used as the end-point. When the HCl was standardized against primary standard Na_2CO_3 by the same photometric titration technique, the first break in the titration curve (intercept point B) was used as the end-point, leading to equivalent results.

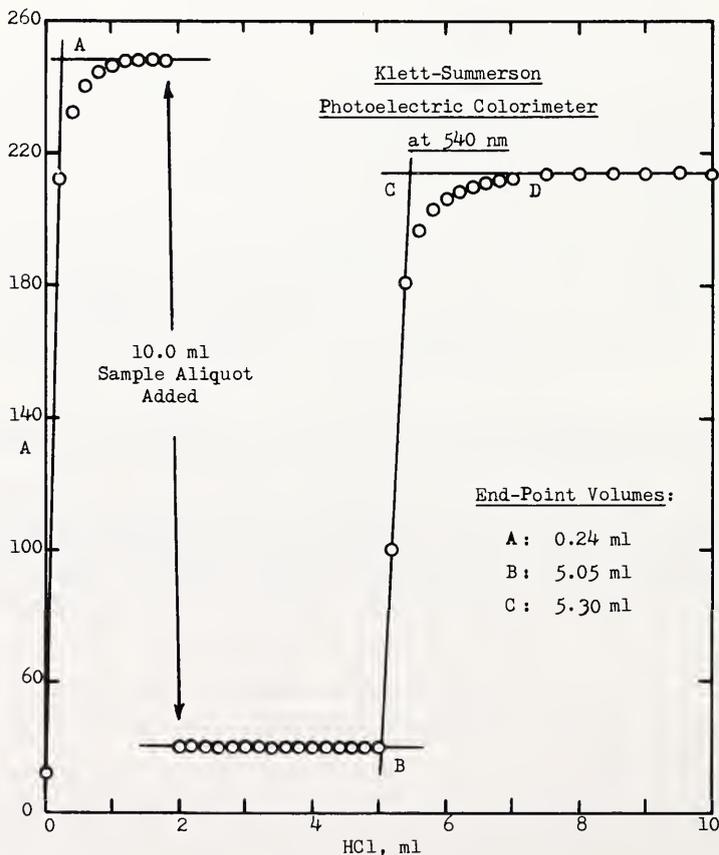


FIGURE 3. Photometric Titration of Washing Soda.

Student interest in these titrations has been high due to the fact that they may provide their own samples, the measurements are rapid and easy to complete, and the results have been exceptionally reliable. The tea/coffee experiment, in particular, has proved to be an interesting one, owing to the many variables and independent "projects" which may evolve from it.

Acknowledgment

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