

Potentiometric Titration Analysis of Real Samples with the Carbon Electrode

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Introduction

Although potentiometric titrations offer perhaps the widest possible applications to the analysis of all types of samples, this technique is often avoided in high schools and small colleges due to the instrumentation required and the inconvenience of the conventional electrode systems. Recently, applications of the carbon electrode to potentiometric titrations have been suggested (2), following a previous evaluation of pyrolytic graphite as an indicator electrode (1). Two analyses suitable for student use, employing a simple, inexpensive, student-constructed potentiometer (4) and home-made electrodes have been developed.

The first of these analyses is the determination of the purity of a commercial table salt (as NaCl) through potentiometric titration of the dissolved chloride with standard silver nitrate. A carbon electrode is employed in the analysis as a reference electrode, along with a piece of bare silver wire as the indicator electrode. The principal advantage of this method is that no salt bridge is required with the carbon electrode, in contrast with the usual types of reference electrodes, *e.g.*, saturated calomel or silver-silver chloride, both of which require non-chloride salt bridges as a part of the cell system for the titration of chloride with silver nitrate.

The second analysis is an acid-base titration, applied to the determination of the active component (hydrochloric acid) of certain liquid household cleaners by titration with standard sodium hydroxide; these cleaners are frequently intensely colored, so that ordinary visual indicator titrations are not feasible. The same student potentiometer is employed as in the first analysis, as is the carbon electrode. However, in this instance, the carbon electrode serves as the indicator electrode, while either a home-made or commercial saturated calomel or silver-silver chloride is suitable as the reference. The advantages of this method lie in the simplicity of the potentiometer and the fact that the carbon indicator electrode is much less expensive and somewhat more durable than the commercial glass combination electrode. This analysis may be performed quite readily with commercial equipment and apparatus.

Materials and Methods

Although any conventional student-type potentiometer may be employed for the titrations subsequently described, a great deal of student interest and experience result from the use of instruments built prior to or as part of the experiments (4). The instrument needs only to be capable of potential measurements to within 1 or 2 millivolts since, in monitoring potentiometric

titrations, changes in voltage are measured (as opposed to the absolute potentials). Consequently, the potentiometer need not be standardized prior to use, since the voltage measurements are relative. Furthermore, absolute measurements with the carbon electrode tend to drift somewhat from one titration to another, as previously reported by Miller (1).

The carbon electrode, used either as indicator or reference, may be made from a carbon rod or stick at least two inches in length. Center rods, removed from dead dry cell batteries (1) or 1/8-inch diameter lead from "kindergarten" pencils serve adequately. Whatever the source, the carbon rod must be pre-soaked in concentrated hydrochloric acid for 15 minutes or so to remove acid-insoluble impurities, washed thoroughly with distilled water, and dried prior to initial use. Electrode sensitivity is maintained if the HCl treatment is repeated after each dozen or so titrations; the electrode should be thoroughly rinsed with distilled water after each titration.

The silver indicator electrode used in the chloride analysis may be made conveniently from a small piece of fairly heavy gauge silver wire, with a 1/4-inch loop bent into the bottom. The wire should be polished with emery paper or cloth, rinsed quickly with dilute nitric acid, and thoroughly rinsed with distilled water before initial use. It should be rinsed well with distilled water after each titration.

The saturated calomel electrode used as reference in the acid-base titration may be readily constructed. Various forms of this electrode, any of which are applicable, have been described by Vogel (5) and others.

The titration vessel itself may consist conveniently of a beaker of appropriate size (150 to 250 ml) containing a magnetic stirrer bar to provide adequate stirring throughout the titrations. A standard 25- or 50-ml buret may be used to deliver the titrants.

Procedures and Results

Analysis of Table Salt.—The N/10 AgNO_3 titrant was prepared and standardized by weight (3). A 5.00-ml aliquot (pipet) of unknown sample solution (prepared by dissolution of an accurately weighed 2.0-g sample of the dry commercial table salt in sufficient distilled water to make 100 ml of solution) was transferred to the titration beaker containing the magnetic stirrer bar. Five ml (graduated cylinder) of dilute HNO_3 (to prevent precipitation of carbonate and other acid-soluble silver salts) were added, along with about 50 ml of distilled water, so that the C/Ag electrode pair was immersed in the liquid. The carbon reference electrode was connected with the positive terminal of the potentiometer and the silver indicator wire with the negative. Using a medium stirrer speed throughout the experiment, the solution was titrated with silver nitrate delivered from the buret, using volume increments as required to yield good definition of the titration curve. The solution was stirred for 5-10 seconds after each titrant addition to provide adequate stirring before voltage measurements were made.

A typical titration curve is shown in (Fig. 1A). The end-points were evaluated in the usual way for potentiometric titration curves. Results obtained

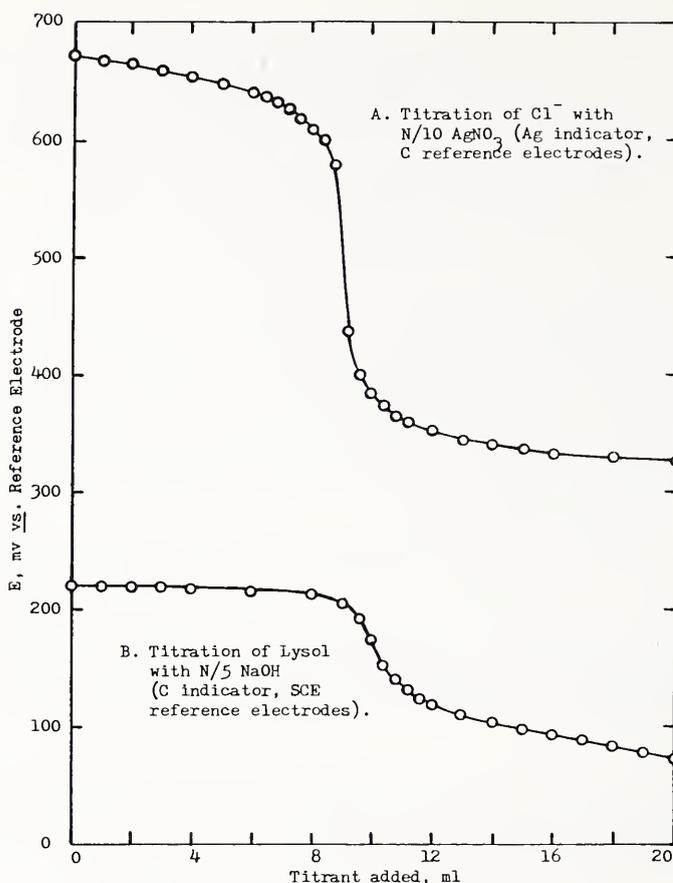


FIGURE 1. Potentiometric Titrations Involving Carbon Electrodes.

TABLE I Potentiometric Analysis of Table Salts.

Commercial Product	Sample Size g/100 ml	Found % NaCl
A	1.34	98.2
	2.48	98.1
	3.55	98.1
B	1.42	97.6
	2.56	97.8
	3.61	97.5
C	1.37	96.4
	2.34	97.0
	3.45	96.6

for three different commercial table salt samples are shown in Table I. The results are independent of sample size, as shown by the data, while replicate titrations yielded values which agreed within 0.5 relative per cent. Analyses of three 2.0-g samples of primary standard grade NaCl (99.9% pure) yielded a result of $99.9 \pm 0.2\%$.

Analysis of Household Cleaners.—The $\text{N}/5 \text{ NaOH}$ titrant was standardized against primary standard potassium acid phthalate by the conventional visual titration with phenolphthalein as indicator (3). A 1.00-ml sample (pipet) of the commercial liquid cleaner was transferred to the titration

beaker containing the magnetic stirrer bar and sufficient distilled water added so that the C/SCE electrode pair was immersed in the liquid. The saturated calomel electrode was connected with the negative terminal of the potentiometer and the carbon indicator with the positive. The titration with sodium hydroxide was performed in the same manner as the chloride titration described previously.

A typical titration curve for the neutralization titration with the carbon indicator electrode is shown in (Fig. 1B). Replicate results obtained for two commercial household cleaners are shown in Table II. Results for the same two cleaners obtained by similar titrations using a commercial pH meter and combination glass electrode were virtually identical with those shown in the table.

TABLE II *Potentiometric Analysis of Household Cleaners.*

Sample Analyzed	% HCl Present	HCl Equivalent Found, %
X	9.25	9.4, 9.3, 9.2
Y	8.50	8.6, 8.4, 8.6

Students have shown considerably more interest in these titration experiments than they have in earlier experiments involving purchased pre-analyzed samples and commercial apparatus. The instruments are less likely to be considered as magical black boxes by beginning students, and the home-made electrode systems (along with the analysis of "real" commercial samples provided by the students) are practical illustrations of the value of the techniques. Commercial product comparison and agreement with labeled package contents are interesting additional factors of this type of experiment.

Acknowledgment

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