Inventory Control

edited by
DAVID L. BYRUM
Globe High School
501 Ash
Globe, AZ 85301

Potentiometric Titrations Using Pencil and Graphite Sensors

Walter S. Selig
Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

The cost of various commercial indicating electrodes ranges from about \$40 for pH electrodes to as much as \$355 for a potassium ion-selective electrode.[1] This cost can be reduced to less than \$1.50, and in some cases to mere pennies by making sensors from graphite rods and pencils for use in potentiometric titrations. The same sensor can be used for many types of these titrations (acid/base, complexiметric, precipitation, and redox).

Background

Hoke and Collins (*1*) recently used a membrane of polyvinyl(chloride) (PVC) plasticized with dioctylphthalate (DOP) as a sensor in the potentiometric titration of alkyl aromatic sulfonate with a cationic surfactant. We have found (*2*, *3*) that a spectroscopic graphite rod and various pencils can serve as inexpensive support materials for this membrane. This sensor can be considered a variant of the "coated-wire" electrodes introduced by Cattrall and Freiser (*4*) in 1971.

Preparation of Coated-Graphite Electrodes

The graphite rods (Spectroscopic graphite, UF-4S, Ultra Carbon Corp., Bay City, Michigan) were 152.4 mm (6 in.) long and 6.35 mm (¼ in.) in diameter. They cost \$1.29 each and were purchased in 12 in. lengths. Other grades of graphite such as Ultra carbon U-7 and Poco graphite AXF will serve equally well, and the diameter is not critical.

The coating solution is prepared by dissolving 1 g of low-molecular weight PVC and 1 g of DOP in 30 ml of tetrahydrofuran in an Erlenmeyer flask, applying heat, and occasionally shaking to promote solution. The graphite rod is dipped for a few seconds to a depth of about 13 mm (½ in.) into the cooled coating solution and air-dried. This coating process is repeated 3–5 times. The cost of the coating solution is less than \$0.01 per electrode; one batch of the PVC/DOP solution will coat many electrodes and will keep indefinitely in a stoppered glass vessel.

When the coating deteriorates, as indicated by decreasing and/or less steep endpoint breaks, it can be entirely removed with hot tetrahydrofuran. The graphite rod can then be recoated and reused.

Measurements

Any convenient reference electrode can be used in conjunction with the PVC/DOP-coated sensor. We have used a plastic, single-junction, silver/silver-chloride reference electrode containing a salt-bridge of 0.1 *N* sodium nitrate. The electrodes are connected to the measuring instrument, which can be any convenient pH/millivolt meter. The coated graphite sensor is connected to the meter by means of an alligator clip. A typical titration cell is shown in the figure.

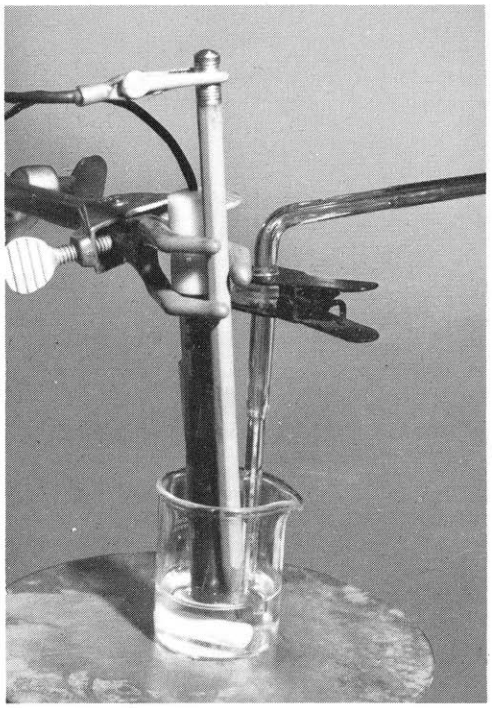

Table 1. Some Feasible Potentiometric Titrations Using a Graphite Sensor Coated with PVC-DOP

Ion measured	Titrant	Titration type	Endpoint break, mV
Perchlorate	Cetylpyridinium	Precipitation	120
Hexafluorophosphate	Cetylpyridinium	Precipitation	220
Peroxydisulfate	Cetylpyridinium	Precipitation	120
Nitroform	Cetylpyridinium	Precipitation	190
Picrate	Cetylpyridinium	Precipitation	170
Tetraphenyl-borate	Cetylpyridinium	Precipitation	450
Dodecylsulfate	Cetylpyridinium	Precipitation	310
Thallous	Tetraphenyl-borate	Precipitation	310
Bromide + iodide	Silver (I)	Precipitation	
Fluoride	Lanthanum (III)	Precipitation	30
Tungstate	Lead (II)	Precipitation	25
Acid phthalate	Sodium hydroxide	Acid-base	70
Ferrous	Chromate	Oxidation-reduction	250
Ethylenediamine tetraacetate	Lead (II)	Complexiметric	

What Type of Titrations can be Monitored?

A list of titrations we have monitored with the coated graphite sensor is given in Table 1. Full details on these titrations are presented in reference (*2*) which gives representative titration curves, magnitudes of endpoint breaks, and standard deviations. No doubt many more are possible, and

Work performed under the auspices of the U.S. Department of Energy at Lawrence Livermore National Laboratory under contract number W-7405-ENG.

[1] These prices were valid in spring 1983.

Table 2. Comparison of Sensors in the Potentiometric Titration of an Aqueous Nitroform Solution versus 0.05 *N* Cetylpyridinium Chloride.

Sensor	Source of supporting material	Mean endpoint break (mV)	Standard deviation	Number of replicates
Fluoroborate	Orion Research	165	0.10	5
PVC/DOP-coated graphite	Ultra Carbon UF-4S	190	0.04	4
PVC/DOP-coated mechanical pencil	Turquoise Eagle Drawing lead	110	0.06	4
PVC/DOP-coated No. 2 pencil	Astro 155 Bondexed lead	30	0.03	4

Titration cell with a coated no. 2 pencil sensor and a single-junction reference electrode.

the writer wishes to learn of titrations which *cannot* be performed. A limitation of the sensor is its applicability in aqueous media only (acids and bases are alright), because organic solvents will attack the membrane.

Pencil Electrodes

The next obvious reduction in cost is to use less expensive graphite-containing materials such as pencils. For one titration, nitroform, $C(NO_2)_3H$, versus cetylpyridinium chloride, we have used the following sensors:

(1) A mechanical pencil "lead" (Turquoise Eagle drawing lead) sealed into a glass capillary for mechanical strength. The cost of each "lead" is \$0.07. It needs to be crimped into a support because it breaks easily.
(2) A No. 2 Astro Bondexed "lead" pencil from which the eraser was removed and the resulting cavity filled with solder to make electrical contact with the graphite core. The cost of the pencil is \$0.04.

Both variants were coated with PVC/DOP as described above. A comparison of mean endpoint breaks and standard deviations for this particular titration is presented in Table 2. Included are previously obtained data using a fluoroborate commercial sensor (*5*). The largest breaks were obtained with the PVC/DOP-coated graphite sensor, followed by the commercial fluoroborate sensor. The smallest break was obtained with the coated No. 2 pencil. It seems that the surface area in contact with the solution, as well as the presence of impurities (the wood of the No. 2 pencil was in contact with the solution) have a significant effect. All PVC/DOP-coated sensors yielded lower standard deviations than the commercial sensor.

Although we have, as a tour de force, tested the No. 2 pencil electrodes in only one type of titration, we have no doubt that many other titrations can be monitored in this manner. In fact, this idea may lend itself to a research project for students.

Simpler Yet—No Coating at All

It is well known that some titrations yield better endpoint breaks in partially nonaqueous media because of reduced solubilities of the precipitated species. This is particularly true for the titration of fluoride versus lanthanum(III) or thorium(IV), and of sulfate versus lead or barium nitrate. All of the variants described above, minus the PVC/DOP coatings, can be used for the following titrations

1) fluoride versus La^{3+} in 60% methanol (*6*),
2) fluoride versus Th^{4+} in 60% methanol (*6*),
3) sulfate versus Pb^{2+} in 80% methanol (*7*),
4) sulfate versus Ba^{2+} in 80% methanol (*7*).

The magnitude of the endpoint break can be improved by dipping the bare sensors for several minutes into a neutral 0.2 *M* potassium permanganate solution. The increased activity resulting from this treatment was explained by Bercik et al. (*8*) as resulting from either the formation of a quinone-hydroquinone redox system on the electrode surface during the activation process, or from the establishment of a mixed potential between separated manganese dioxide on the electrode surface and the solution.

While any graphite rod can be used, including the pencils, we have obtained the largest endpoint breaks with Poco graphite, grade AXF-9QBG1 (Poco Graphite Inc., 1601 S. State Street, Decatur, Texas 76204). However, this material is somewhat more costly, \$6.31 for a 6-in. rod of 1/4-in. diameter (but still inexpensive compared to the \$295 fluoride ion-selective electrode).

In summary, pencils can be used not only to write with or chew on, but also to monitor various potentiometric titrations.

Literature Cited

(1) Hoke, S. H., and Collins, A. G., Report *1979*, BETC/RI-79/10; cf. *Chem. Abstr.*, **93:** 19641q (1980).
(2) Selig, W., *Analyt. Letters*, **15**[A3], 309 (1982).
(3) Selig. W. S., *Energy & Technology Review*, Lawrence Livermore National Laboratory, August 1982, p. ii.
(4) Cattrall, R. W., and Freiser, H., *Anal. Chem.*, **43,** 1905 (1971).
(5) Selig, W., *Mikrochim. Acta*, **II,** 437 (1979).
(6) Selig, W. S., *Microchem. J.* (in press).
(7) Selig, W. S., work in progress.
(8) Bercik, J., Hladky, Z., and Cakrt, M., *Z. anal. Chem.*, **261,** 113 (1972).

Rubber Bulb Modification for Pipetting

Joe B. Davis
Winthrop College
Rock Hill, SC 29733

Learning to use a rubber bulb with a pipet properly is frequently frustrating for all concerned. Placement of the neck of the bulb firmly and squarely against the end of the pipet is difficult for many students to master. Their usual tendency is to force the end of the pipet into the neck of the bulb, resulting in improper filling and contamination of the solution by contact with the bulb. Worse yet, they sometimes become so frustrated with the pipet bulb that they resort to the dangerous practice of pipetting by mouth. A simple modification

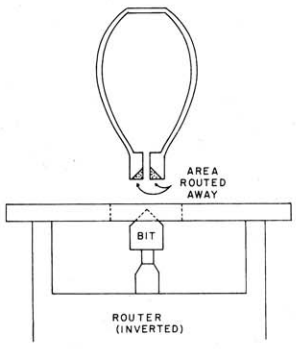

Diagram showing proper procedure for bulb modification.

of rubber bulbs used in my quantitative analysis laboratory has alleviated these problems. The straight opening in the neck was routed to a conical shape with a 45° bit (total included angle–90°). The simplest method is to press the bulb neck against the rotating bit of an inverted router until the desired depth is reached (see figure). Only light pressure, applied intermittently to prevent overheating and melting of the rubber, is required. **CAUTION:** Router speeds are about 25,000 rpm. Preferably, **the router should be mounted on a router table.** Alternately, it may be firmly held or clamped on a bench top with a vibration-damping surface (a folded towel was sufficient to prevent "walking"). The router bit should be in the retracted position and the wrist should be supported on the router base or table. Use of a portable drill is **NOT** recommended. Suction can be applied to the pipet in the usual manner by lightly pressing the self-centering neck of the bulb against the end of the pipet. Pipet aids employing a polyethylene fitting with a conical opening are available from Dynalab Corp., Interex Corp., Cole-Parmer and others. Bulbs modified as described have proved satisfactory for a number of years.