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TECHNICAL NOTES

Adaptation of Poly(tetrafluoroethylene) Tips to Mercury Drop Electrodes and Evaluation by Flow Injection Analysis

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INTRODUCTION

A well-known and critical problem that affects dropping and hanging drop mercury electrodes is the tendency of the solutions to creep between the mercury and the internal wall of the glass capillary,¹ chiefly in the presence of substances that react with silicate, such as hydroxide and fluoride. In other solutions, sooner or later, this problem arises and affects the area reproducibility of the mercury drops. This disturbance is also critical in adsorption studies by electrocapillary curves using the drop time method. The detection of the drop fall itself may be done with high accuracy by automatic devices (see ref 2 and references cited therein). In electroanalytical measurements with the hanging mercury drop electrode, HMDE, the problem can become even worse, because the drop neck becomes narrower and unable to sustain the drop's weight.

Different approaches have been proposed to extend the life span of the mercury electrode and its reproducibility. Special designs, in which the capillary internal radius decreases rapidly toward its orifice² were recommended, but their construction is not simple.

Application of silicone-polymeric film coatings to obtain capillaries with a nonwetting inside wall are described by different authors.³⁻⁵ Silanization with dichlorodimethylsilane or application of Desicote is frequently recommended. Coated capillaries present a longer life, but deterioration was noticed after 10 days of normal use³ or even 1 day of contact with the solution.⁵

The coating is inefficient in glass-corroding media; to circumvent this problem, different procedures of prolongation of glass capillaries with solid polymeric materials were proposed in the literature. Clifford and co-workers have constructed a short-length poly(chlorotrifluoroethylene) (Kel-F) capillary and were able to record the first polarograms in hydrogen fluoride medium.⁶⁻⁹ However, the fabrication of this capillary is far from trivial, so much so that only one satisfactory capillary was obtained by the authors in nearly 100 attempts.

Capillaries of polyethylene,¹⁰⁻¹³ polypropylene,¹⁴ and flexible copolymers¹⁵ were also used. The direct application of a Tygon primer to the outside of a polarographic glass capillary was proposed for use in fluoride media.^{16,17}

A PTFE prolongation for a glass DME was described by Raaen.¹⁸ With this electrode, studies in hydrofluoric acid and other media were performed.¹⁹⁻²⁶ They proved that polarograms obtained using a DME with or without the PTFE are interchangeable, favoring the use of the durable PTFE tip in all media. The fabrication process is considered complex,²⁷ requiring special tools,²⁸ and apparently only a few authors²⁹ were able to reproduce this electrode.

An electrical discharge method was developed by Waugh and Wilson²⁷ for punching small holes through PTFE. This method was successfully applied to the construction of a dropping mercury electrode with a PTFE tip by Bond and co-workers,³⁰ but problems were experienced when it was used as a HMDE.³¹

The difficulties associated with the manufacturing of PTFE capillaries can be avoided by using commercial narrow-bore PTFE tubes, now available. A simple and reliable procedure for adaptation of these capillaries to the tip of glass capillaries is described. To demonstrate its suitability in glass aggressive media and under forced convection conditions, the flow injection analysis of As(III) in KOH electrolyte using an automatic mercury electrode³² is described below.

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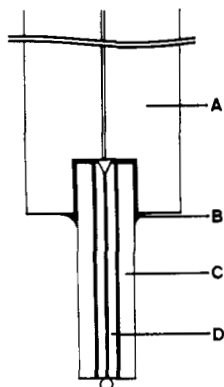


Figure 1. Cross section of the PTFE tip adaptation: (A) glass capillary; (B) epoxy glue; (C) Tygon tube; (D) PTFE tube.

EXPERIMENTAL SECTION

Adaptation of the PTFE Tip to the Electrode. Commercial mercury electrodes from different brands are fitted with glass capillaries. The capillaries' heads present variable shapes and sizes, depending on the design of the coupling with the valve or column, but the tips are usually blunt or conical. Instead of substituting the entire capillary, it was preferred to develop a universal adaptation of PTFE tips.

Narrow-bore PTFE tubes can be ordered with thin or thick walls. The thin-wall ones must be reinforced with an external concentric tube of glueable polymer (Tygon, for example). Otherwise, the same adaptation procedure can be used for both types of capillaries.

The thin PTFE capillary used in this work was ordered from Cole Parmer, Catalog No. 06417-70, and presents nearly 0.051-mm i.d. and 0.35-mm o.d. The internal and external surfaces were inspected by microscope and found to be smooth and clean and with uniform walls, as required for intended use.

A length of approximately 3 cm was cut off, and the ends of the tube were temporarily closed by heating the extremities with a flame and pressing it with pliers. The capillary tube was freed from fat by rinsing with acetone and subsequently immersed in a solution containing metallic sodium dissolved in a mixture of naphthalene and tetrahydrofuran.³³ Preparation and use of this mixture should be done carefully in a foamhead. Tetrahydrofuran is highly flammable and irritating to the eyes and respiratory system, and sodium reacts explosively with water and many other solvents.

After a slight darkening of the polymer surface, the tube is removed from the solution and rinsed with distilled water. This free radical attack process is used to modify the PTFE surface to make it glueable.

To improve the mechanical resistance, the thin PTFE tube was covered with an epoxy glue layer and then introduced into a 1.6-mm-o.d. Tygon tube. After the complete polymerization of the epoxy glue, a 20-mm-long segment of concentric tube is cut off. With the help of a sharp needle, a conical widening of approximately 2 mm in depth is made at the extremity of the tube to be glued to the glass capillary. This operation is best accompanied by a microscope or a magnifying glass. The purpose is to assure the integrity of the mercury column, which can otherwise be disrupted after the filling operation, interrupting electrical contact.

To connect the glass capillary to the polymer tip, the i.d. of the glass tube was enlarged at its tip up to the o.d. of the concentric polymer tube. This apparently difficult operation can be easily made with a dentist's diamond-encrusted drill.

A 4.0-mm-depth cavity with 1.5-mm diameter, shown in Figure 1, was obtained by starting with a conical drill and switching to cylindrical ones when the hole was being finished. As a dentist's drilling machine was not available, the drill was spun with an electrical hand drilling machine. The motor was powered with a step-down variable transformer, to enable adjustment of the

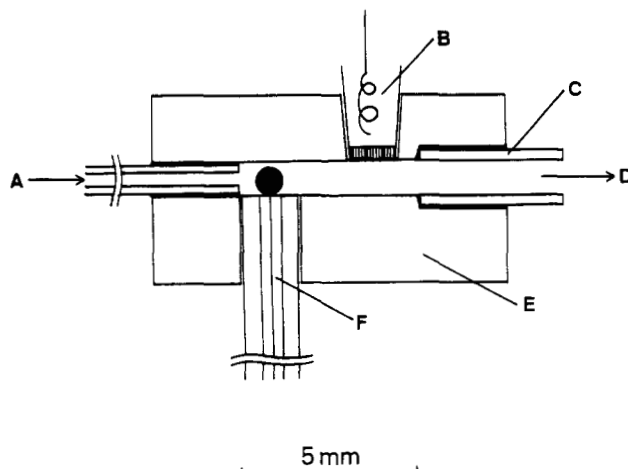


Figure 2. Schematic diagram of the tubular flow microcell: (A) inlet; (B) reference electrode and porous polymer junction; (C) auxiliary electrode; (D) outlet; (E) acrylic block; (F) mercury electrode with PTFE tip.

rotation speed. The drilling operation must be conducted slowly and under a continuous flow of water through the capillary, during the entire operation, to avoid clogging and overheating. A 10-mL plastic syringe, half-filled with air and half with distilled water, connected to the glass capillary and held under pressure with a clamp, serves to feed the water under 2 or 3 bar of pressure.

Once the drilling is finished, additional water is injected, to remove any glass particles. Afterward, the glass capillary is dried. The external surface of the coaxial Tygon/PTFE tube is covered with a thin coating of epoxy adhesive at the widened orifice extremity. Next, the tube is thoroughly embedded into the cavity of the glass tube, to minimize internal dead volume, reducing future risk of air entrapment when the capillary is filled with mercury. After a complete polymerization of the glue, the tip is cut into the desired length, at a straight angle. A new, degreased razor blade must be used to avoid a sloping edge around the circular orifice of the capillary. Any constriction can downgrade the sustentation of the mercury drop. The orifice should be inspected under a magnifying glass and, if necessary, a new slice is cut off.

Subsequently, the capillary is fitted to the mercury column or valve. During the filling operation with mercury, vacuum is applied to the tip, assuring better elimination of air from inside the capillary. A disposable 10-mL plastic syringe with a short length of Tygon tube in place of the needle is well suited to make a vacuum without the risk of mercury spilling. When this operation is finished, the electrode is ready to be used.

The adaptation of commercially available thick-wall PTFE tubes (nearly 2-mm o.d. and 0.34-mm i.d.) is even simpler, because it is unnecessary to glue it to a concentric reinforcement tube. To make the surface modification, a length of 2 cm is enough.

Both types of PTFE tip were successfully adapted to commercial and self-made dropping, hanging, and static drop mercury electrodes. The thin-walled tube was also adapted to the flow-through amperometric microcell described below. For this application, a glass capillary from Metrohm, Code 6.12226.0340, was combined with the high-precision automatic mercury electrode, AME, previously developed by the authors.³²

Flow Cell Design. A new and simple flow cell, presenting little dead volume, is shown in Figure 2. The 10- × 5- × 6-mm Plexiglas block presents a longitudinal orifice with 1.0-mm i.d. (flow channel) in which the three-electrode system is positioned. The PTFE capillary of the mercury electrode is inserted into the cell from the bottom (sessile static drop electrode) by an orifice that is perpendicular to the flow direction. During the drop renovation, the knocked-out drop is removed from the cell with the flowing solution. The microporous polymer junction of the Ag/AgCl reference electrode is positioned downstream with relation to the mercury electrode. A stainless steel needle (size 30/6) serves as the auxiliary electrode and cell outlet.

Apparatus. FIA experiments were made by a gravity-fed system assembled to a homemade pulse polarograph, injector,

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flow cell, automatic mercury electrode, and mini Ag/AgCl reference electrode. The "fiagrams" were obtained on a conventional X-Y recorder, Model RE 0089 (Houston), marketed by EG&G Princeton Applied Research, with an external time base. The response volume and time constant of the flow cell were determined with a Hewlett Packard 7090 measurement and plotting system, by using the pretrigger feature and acquiring data directly from the current to voltage converter of the polarograph.

The reproducibility of the area of the mercury drops generated by the AME using the PTFE tip was determined by weighing the individual drops to the microgram with an AD-6 autobalance from Perkin-Elmer (0.1- μ g sensitivity). The weight of the drops was converted into area by assuming a spherical shape.

Reagents. All solutions were prepared with analytical grade chemicals, and water was obtained from a Millipore, Milli-Q system. Arsenic trioxide was dissolved in 0.1 mol/L KOH and stored as 1×10^{-2} mol/L As(III) stock solution. The synthetic arsenic samples were obtained by dilution with 0.1 mol/L KOH solution. Mercury was chemically purified and distilled twice under vacuum.

RESULTS AND DISCUSSION

Different versions of the thick-wall PTFE tips have been used in the authors laboratory during the last 8 years, some of them fitted only under pressure, welded or not with silicone rubber glue.³⁴ These previous fittings are less reliable in terms of mechanical resistance and tightness, but otherwise indistinguishable in performance from those now described. Routine use in polarographic and chronocoulometric research work in many different aqueous solutions supports the statement that their use is advantageous even in solutions that are not aggressive to glass.

In case of accidents, like loss of electrical contact between the reference electrode and the potentiostat, when any capillary can be ruined, the PTFE tip can usually be recovered by cutting off a slice of the tube. This can be done quickly, without disassembling the electrode. When disassembled, the modified capillary can be chemically cleaned, as is usually done for glass capillaries. PTFE is very resistant to most chemicals, but when the Tygon-shielded tip is used, solvents and reagents that attack this polymer must be avoided.

Hanging mercury drops can last for days suspended at the PTFE tip immersed in aqueous solution. This is a desirable characteristic for electrodes used in stripping analysis. The otherwise required periodical silanization or even substitution of glass capillary justifies the extra effort involved in the PTFE tip adaptation.

The modified capillary can be used directly in media that are mildly aggressive to glass and shorten the useful life span of conventional electrodes. For example, a capillary with the PTFE tip was provided to Instituto Adolfo Lutz (São Paulo, Brazil). It is used routinely with a Metrohm 663 VA stand for the determination of traces of Sn and Pb by anodic stripping voltammetry, first in acid and then in alkaline medium (1.0 mol/L NaOH). Another capillary, adapted to a Model 303 EG&G Princeton Applied Research electrode has been successfully used at Metal Leve Co. (São Paulo, Brazil) in the development of a method for routine checking of urea contents in tetrafluoroborate galvanoplastic baths.

For all techniques examined up to now during last 8 years, the behavior of the modified electrode was essentially the same as that of the conventional glass capillary, assuring that no unusual hydrodynamics or other artifacts have been introduced by the modification. For example, the voltammograms of Figure 3 present the same shape and peak potentials, the same happening with the shape and $E_{1/2}$ values

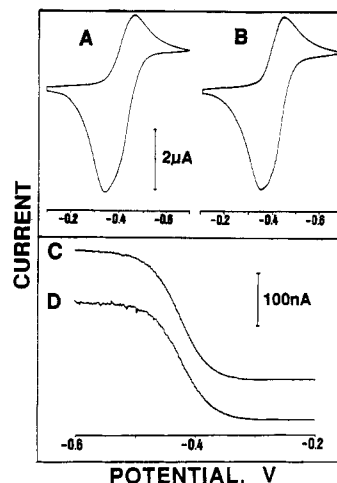


Figure 3. Comparison of cyclic voltammograms (A, B) and fast dc polarograms (C, D) of 10 μ mol/L TK(I) in acidic (0.1 mol/L HClO_4) and alkaline (1.0 mol/L KOH) medium, obtained with the bare glass capillary (B, D) and with a PTFE tip (A, C).

of the fast polarograms. These polarographic measurements were preceded by an aging of both electrodes in 2.5 mol/L KOH solution during 54 h. After that, some difference is observed in the limiting current region, better defined with the PTFE tip. The noncoincidence of peak heights and diffusion currents is originated by differences in mercury drop areas (the flow rate of distinct capillaries is not the same).

Modified and unmodified electrodes also obey in an indistinguishable way the Cottrell equation in chronoamperometric measurements, under nearly linear semiinfinite diffusion conditions. For longer experiments ($t > 0.5$ s), when spherical diffusion cannot be disregarded, the same deviation appears for both capillaries for drops of equal area. Induced adsorption of electroactive metal ions, measured by double potential step chronocoulometry, present no statistically significant differences. Moreover, the absolute surface charges measured during drop extrusion experiments at various potentials agree for both types of tips.³⁴ These observations endorse previous statements about the polarographic use of mercury drop electrodes suspended at PTFE tips^{19,29} and extend them to additional techniques.

In moderately aggressive glass-corroding media, the contact between glass and solution has been precluded by a layer of PTFE tape firmly wrapped around the glass tube. In highly aggressive media, such as HF, the use of the electrode becomes restricted to flow cells, like the one described above, where only the Tygon-shielded PTFE tip is exposed to the solution.

The reproducibility of the area of the drops remains practically the same after adaptation of the tip. When the electrode is modified with the 51- μ m-i.d. PTFE tip and operated with a very accurate mechanical system such as the AME,³² weighting the individual drops shows a relative standard deviation (rsd) of 0.18%, as was calculated for the area of a series of 22 consecutive drops with 0.540 mm². The same rsd was obtained for 0.500-mm² drops generated without the PTFE tip, as previously reported.³² Some increase in dispersion of the area can be observed when the i.d. of the PTFE tube is increased in relation to the glass tube or when very small drops are generated. A probable explanation for this is the greater relative contribution of the irreproducibility of the neck rupture during mechanical drop knocking. However, when larger i.d. tips (around 100 μ m) are used with bigger drops of 3 mm², a rsd below 0.1% was found. An abnormal increase in the area rsd accompanied by mercury column retraction after drop knocking is caused by entrapment of small air bubbles at the glass/PTFE junction. Suction with a disposable syringe (with the mercury valve open, as

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described in the Experimental Section) removes the air bubbles and restores normal operation.

The electric resistance of the capillaries filled with mercury remains nearly the same after the modification, being higher for the narrow-bore Metrohm capillaries (typically 45 Ω). Extra low resistance (1.2 Ω) was attained by drilling a lateral hole near the glass/PTFE junction and inserting a Pt wire, glued with epoxy. These electrodes with low resistance are preferred for chronocoulometric or other transient measurements.

For use in conventional electrochemical cells, the thick-wall PTFE tip presents the advantage of higher chemical inertness. In fact, even the exposure of epoxy can be minimized by removing the glue around the tip as far as possible. This restricts the materials touched by the solution to glass and PTFE. The Tygon-shielded version (Figure 1) presents the advantage of being flexible, simplifying adaptation to flow cells. The cell depicted in Figure 2 explores this potentiality, resulting in a lower dead volume than that reported for glass capillaries with a conically shaped tip.³⁵⁻³⁷ The volume of the longitudinal orifice of the cell is around 6 μL , but the volume from the inlet tube to the drop is below 1 μL . The good mechanical stability of the mercury drop obtained by using the PTFE capillary is improved in the sessile static drop mode, allowing the use of flow rates ranging from zero up to 5.1 mL/min. The upper limit is determined mainly by drop instability and eventual dislodgement.

Peak height reproducibilities were determined for repetitive injections of 115 μL of 5×10^{-7} mol/L Cd(II) in acidic medium, with pulse amperometric detection. A rsd of 0.8% was calculated for the recorded peak heights measuring 8.7 nA above base line. The variation of the drop area (0.18% rsd) contributes to this cipher, but it is not the determining factor. Other components are the irreproducibilities in the injection operation (manual, homemade injector), recording and measurement of the peaks on graph paper, and electronic noise (homemade pulse polarograph). Better precision can be expected by automating the system and substituting peak height measurement for area determination.

To demonstrate the performance of the system in a mild glass-corroding medium, the determination of As(III) in KOH 0.1 mol/L medium are presented. The system was operated without deaeration of the electrolyte, and the anodic oxidation current ($\text{As(III)} \rightarrow \text{As(V)}$) of the synthetic samples was recorded at a constant potential of -0.06 V vs Ag/AgCl. Figure 4 shows peaks for increasing concentrations in the 10^{-5} mol/L region, with drop exchange between peaks. The rsd of each group of six peaks is nearly 0.7%. Data from Figure 4 were examined by linear regression, presenting a slope of 0.0151 ($s = 1.5 \times 10^{-4}$) A·L/mol and an intercept of 6.1×10^{-9} ($s = 2.9 \times 10^{-9}$) A, with a correlation coefficient of 0.9997. A sampling rate of the order of 120 injections/h was used in these measurements, at 1.5 mL/min flow rate and 115- μL sampling loop.

To obtain preliminary information about the response dynamics of the cell, the injection loop was reduced to 20 μL , and the distance from the injector to the cell, to 5.0 cm. The flow rate was maintained at 1.05 mL/min, and the drop area, at 1.71 mm². An average value of 0.083 s was obtained for the time constant of the detector (0–63.2% of peak height, see ref 37). This gives a response volume of only 1.5 μL , far beyond values reported in the literature for other cells with mercury drop electrodes.³⁷

Under the same conditions, standards covering the As(III) concentration range from 2×10^{-7} to 1×10^{-3} mol/L were

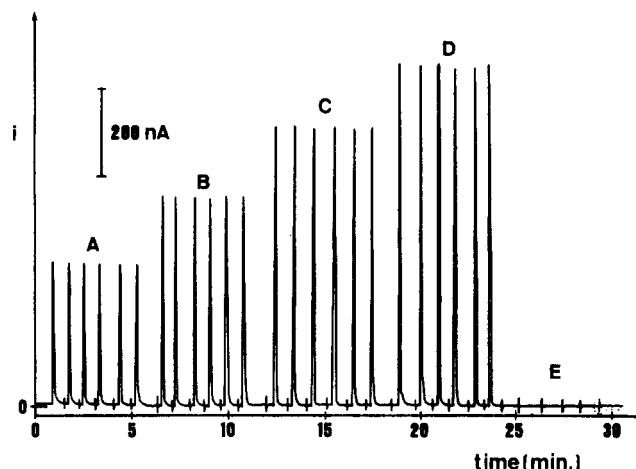


Figure 4. Repetitive amperometric detection using the AME. As(III) concentration: (A) 2.0×10^{-6} mol/L; (B) 3.0×10^{-5} mol/L; (C) 4.0×10^{-5} mol/L; (D) 5.0×10^{-5} mol/L; (E) blank (only electrolyte). The transient observed on the base line after each peak is originated by the exchange of mercury drops. Conditions: flow rate, 1.5 mL/min; Hg electrode potential, -0.06 V vs Ag/AgCl; sample volume, 115 μL ; supporting electrolyte, 0.1 mol/L KOH.

injected. A log I_p vs log C graph resulted in a straight line. Expressing this dynamic range in nanograms of injected electroactive species, as usual, this range corresponds to 0.3–1500 ng, the slope being of 33 nA/ng. This represents a noteworthy improvement in comparison with slope and sensitivity values tabulated in the literature for other electroactive species.³⁷

Each peak of Figure 4 was obtained on a fresh mercury drop. In fact, no response degradation is observed when the same drop is used repeatedly. After 10 sample injections, the same peak height was recorded. This is by far not a rule, solid electrode “fouling” being a well-known limiting factor of amperometric detection in liquid chromatography.^{36,37} Electrochemical activation can be a remedy, but in worse cases the electrode must be disassembled and polished. Some commercial manufacturers also offer disposable glassy carbon electrodes. With the mercury drop, the problem is solved simply by sending a pulse from the computer or pressing a button at the electrode control circuit, to change drops automatically, as done to obtain Figure 4.

Although the mercury electrode is of limited use in the positive potential region, when compared to solid electrodes, in the negative potential domain it is unbeatable. It can be expected that the availability of reliable, simple, and inexpensive mercury electrodes and cells, like those described, will increase the interest in FIA and HPLC with electrochemical detection. When these detectors are preceded by a high-efficiency flow-through deoxygenation device, such as one to be described in a forthcoming paper, fast and direct determinations can be made in the potential range where oxygen is electroactive, with detection limits in the 1×10^{-7} mol/L concentration region. Lower concentrations can be reached using preconcentration and/or catalytic electrode processes.

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