Construction and Characterization of Fiberoptic Spectrelectrochemical Probes for *In Situ* Analyses

A Research Endeavor by Chad Brenneman
Under the Supervision of Paul Flowers
in the Spring of 1997

ABSTRACT

Two kinds of fiberoptic spectroelectrochemical probes were constructed and characterized *in vitro*. The first probe performed spectroscopy by transmitting light from one end of a Pt cylinder, acting as a working electrode, to the other. The second probe had a mirror at one end of a Pt cylinder, also acting as a working electrode. A ferri/ferrocyanide couple was used as a test system. Cyclic voltammetry at the probe was slightly distorted due to unconventional cell geometry, but otherwise normal. Electrolysis times were long, 9 minutes, despite near thin layer conditions because of a large charging current. A study of absorbance at 420nm vs. concentration of ferricyanide indicated that absorbance spectroscopy obeys the Beer-Lambert Law.

INTRODUCTION

I. Electrochemistry

Electrochemistry is the study of the interaction between electrons and chemical species. Similar to the terminals in a battery, a general electrochemical cell (Fig. 1) has two electrodes, a cathode and an anode. Electrochemical reactions involve the transfer of electrons from one chemical species to another. In the case of the electrochemical cell, an electron is passed from the cathode to an oxidant, which is a chemical species that tends to accepts electrons (Fig. 2). This kind of electrochemical reaction is called reduction. Conversely, an electron can be donated from a reductant to the anode. When a chemical species loses an electron in this manner, it is said to be oxidized.

The standard arrangment for electrodes in an electrochemical

cell is the three electrode geometry (Fig. 3). It consists of the working electrode, the counter electrode, and the reference electrode. The working electrode is the electrode at which the electrochemistry of interest is occuring (reduction or oxidation of analyte). The counter electrode either acts as an electron source or sink, depending on the electrochemical activity at the working electrode (reduction or oxidation, respectively). The reference electrode is used to provide a measure of the potential between itself and the working electrode.

By applying different potentials across the working and reference electrodes, one may oxidize or reduce certain analytes. Each analyte has its own potential at which it is oxidized/reduced. With the technique of cyclic voltammetry, the potential is swept linearly with time, typically from some starting potential to another potential and back to the starting potential. As the potential at which an analyte is electrochemically active is reached, electrochemical reactions occur at the working and counter electrodes, allowing current to flow through an external circuit. When the current is plotted vs. applied potential, a cyclic voltammogram is obtained. A typical cyclic voltammogram is shown in Fig. 4.

Another electrochemical technique is chronocoulometry. Initially, the potential is held at one in which there is very little redox (reduction/oxidation) activity. Thus, very little current flows in the cell. The potential is then stepped to one in which the analyte is essentially completely reduced or oxidized (Fig. 5). Charge flowing in the cell is measured with respect to

time. When this charge reaches a maximum, the potential is then stepped back to the initial value. Fig. 6 is an ideal coulomogram from such an experiment. The time that it takes for the maximal and minimal charges to be reached and the magnitudes of these charges can be used to calculate certain properties of the electrochemical cell, such as, concentration of analyte, area of working electrode, and the rate at which analyte diffuses to the working electrode.

II. Spectroscopy

Spectroscopy is the study the interaction between light and matter. In essense, different kinds of light (infrared, visible, ultraviolet) are used to study certain aspects of a chemical species. Through the use of this technique, an analyte may be characterized as well as quantified.

The spectroscopic method used in this study is called absorbance spectroscopy. Chemical species will absorb light of certain wavelengths, depending on the nature of the chemical bonds that exist between their atoms. If one passes light of appropriate wavelength through a solution containing these chemical species, a drop in transmittance of light will be observed. If one measures the ratio of the intensity of light sent into the solution to the intensity of light that exits the solution, the concentration of analyte may be determined. The logarithm (base ten) of the ratio mentioned above is call the absorbance. An absorbance spectrum is obtained by passing a range of wavelengths through a solution and measuring the absorbance for each wavelength. Absorbance is plotted vs. wavelength of light, as shown in Fig. 7. The Beer-

Lambert law relates absorbance to concentration linearly by the following equation:

$$A=abc,$$

where A is the absorbance, a is an intrinsic property of the analyte called its absorptivity, b is the pathlength that the light travelled through the solution, and c is the concentration of analyte. The Beer-Lambert law is most accurate for absorbances in the range of 0.1 to 1, so solutions were of concentrations calculated to yield appropriate absorbances (between 0.1 and 1).

III. Fiberoptics

Fiberoptics are long cylindrical strands of transparent substance, such as, glass, fused silica, and zirconium, called the core, which is coated with a material of slightly higher refractive index than the core, called the cladding. They are used to efficiently and conveniently transport light.

The property of fiberoptics that allow them to transport light with so little loss of intensity is a phenomon called total internal reflection (Fig. 8). Light is reflected along the interface between the cladding and the core with almost perfect efficiency; that is, almost all the light is reflected at the interface and very little exits the fiber. Ideally, light travels through a fiberoptic with no attenuation, but factors like absorption of light by the core and transmittance at the core/cladding interface cause some loss of light. In spite of these damping factors, fiberoptics remain very efficient light carriers.

IV. Spectroelectrochemistry

Spectroelectrochemistry (SE) is a hybrid analytical technique. The power of SE comes from the combination of the sensitivity of spectroscopy with the selectivity of electrochemistry. There are many different kinds of SE devices, but all of them have one thing in common, they measure some electrochemical aspect of a solution (current, potential, charge buildup) as well as a spectroscopic element (absorption, fluorescence, chemiluminescence). In general, SE monitors spectroscopically what is happening at the working electrode.

Chronoapsorptivity is the measurement of absorbance with respect to time. Chronoabsorptivity is not a SE technique by itself, but it is used in conjunction with exhaustive electrolysis in this study.

EXPERIMENTAL

I. Construction of probes

A. Transmittance geometry, visible spectrum

This probe was built by fixing a 1 cm platinum tube (Alfa Aesar) of diameter 1.32 mm onto the end of a needleless 1 mL plastic syringe. Heat shrink tubing was used to fix the Pt tube to the syringe (Fig. 9). A Pt wire was wrapped around the Pt tube prior to heat shrinking, so that an external electrical connection could be maintained. Holes were then punched in the heat shrink tubing corresponding to the holes machined in the Pt tube. The purpose of these holes is to admit solution into the Pt tube.

Platinum mesh (52 mesh, Alfa Aesar) was then wrapped around the Pt tube. The mesh was to act as the counter electrode. A Pt wire was also attached to the mesh for purposes of electrical

connection. Platinum wire was then wrapped around the tip of the syringe, slightly above the Pt tube, to act as a quasi-reference electrode. The reason this wire can not act as a true reference electrode will be discussed later.

Two acrylic optical fibers (1 mm diameter, Edmund Scientific) were then inserted into both open ends of the Pt tube. These fibers, in turn were connected to a HP8452A Diode Array Spectrophotometer (Hewlett Packard) by an coupler built in-house. Essentially, the coupler consists of a quartz lens (Edmund Scientific) held in place to focus columnated light from the lamp of the spectrophotometer into one fiber, which is used to carry the light into the Pt tube (Fig. 10). The other light was then collected, after passing through the solution inside the Pt tube, by the other fiber to be recolumnated and directed to the detector of the spectrophotometer by another fixed quartz lens.

B. Reflectance geometry, UV visible spectrum

This probe is built in much the same way as the transmittance probe (Fig. 11). A Pt tube is held at the end of a 1 mm plastic syringe with heat shring tubing and acts as the working electrode. Pt mesh wrapped around the Pt tube acts as a counter electrode. A Pt wire wrapped around the syring tip acts as a quasi-reference electrode.

The Pt tube is capped on one end with a thick piece of Pt foil in this probe, however. Also, more holes were machined in the capped Pt tube. Because these holes were much smaller than those in the first Pt tube, a slit was cut in the heat shrink tubing to allow the holes to be exposed to the solution.

A bifurcated fiber optic bundle was constructed to carry the

light to and from the spectrophotometer. The bundle was made by heat shrinking approximately 20 3 meter long fused silica fibers (140 micron diameter, Polymicro Technologies) together for about three quarters of their length. At the three quarter mark, the bundle was split into about 10 fibers each. These two smaller bundles were both encased in heat shrink tubing. The junction was then fortified with another coating of heat shrink tubing. The result was a Y-shaped bundle of fibers (Fig. 12). Each end of the bundle was then fed into glass melting point tubes filled with epoxy.

Once the epoxy had set (over a 24 hour period), the melting point tube around the common end of the bundle was sanded away using the broad side of a glass saw's blade. The diameter of this common end was then about 1 mm, which fit snugly into the Pt tube. All three ends of the bundle were then sanded and polished to a mirror finish. This was done by using successively finer sand paper, then polishing alumina. The other two ends of the bundle were connected to the coupler.

II. Electrochemistry

Cyclic voltammetry was performed in 1-5mM potassium ferricyanide solutions containing 1 M potassium nitrate (used as supporting electrolyte) at both probes. The potential was varied using either a BAS CV-27 Voltammograph (Bioanalytical Systems) or a BAS CV-1B Voltammograph (Bioanalytical systems).

Chronocoulometry was performed in the same solution to determine the time necessary to reduce all the ferricyanide to ferrocyanide inside the Pt tube. The CV-27 was used for this

experiment. The results of this experiment will not be discussed due to an error in the instrumentation of the CV-27, which caused the data to be irreproducible.

III. Spectroscopy

Spectroscopy of the transmittance probe was characterized using the coupler and the HP 8542A spectrophotometer. The absorbance spectrum of a known concentration of potassium ferricyanide was measured with the transmittance probe (Fig. 13).

Because of loss of about three-fourths of light intensity at in the reflectance probe, a more sensitive instrument was needed for spectroscopic characterization of this probe. A 200A atomic absorption spectrometer (Buck Scientific) was used for this purpose. By lowering the burner of the instrument out of the way and modifying the coupler slightly, the highly sensitive detector of the AA spectrometer was made available for absorbance spectroscopy. A plot of absorbance at 420nm vs. concentration of analyte was generated by measuring the absorbance of known concentrations of ferricyanide (Fig. 14).

IV. Miscellaneous Optical Characterization

Other aspects of the optical facet of the reflectance probe were studied. The energy level, which is directly related to the intensity of light received by the 200A absorption spectrometer's detector, vs. separation between the common end of the fiber bundle and the mirror at the end of the working electrode was examined (Fig. 15). Also examined was the effect of throughput on noise levels. Peak-to-peak noise levels decrease with increasing energy level, as depicted in Fig. 16. These characteristics of the

reflectance probe were examined in air.

Another study was conducted to measure the effects of pathlength on noise levels. Absorbance of 5mM ferricyanide was measured at varying pathlengths using the reflectance probe. The results are illustrated in Fig. 17. Signal to noise ratio is plotted vs. pathlength.

V. Spectroelectrochemistry

Because of the unwieldly nature of the transmittance probe, spectroelectrochemistry was only performed on the reflectance probe. Double-step chronocoulometry of 3mM $K_3Fe(CN)_6$ in 0.1M KNO_3 solution was performed while monitoring the absorbance at 420nm with respect to time.

DATA AND DISCUSSION

Shown in Fig. 18 is an example of cyclic voltammetry performed in 2mM ferrocyanide. This voltammetry was performed at a prototype probe of geometry similar to the reflectance probe. The voltammetry is slightly distored because a silver wire is used as a quasi-reference electrode. Also, it is possible that by-products are adsorbed onto the surface of the working electrode after prolonged use. Instead of a mirror capping the end of the working electrode, a drop of epoxy was used to seal the end of the working electrode. The peaks indicate the flow of current through the cell. The downward peak is called the anodic peak and is due to the oxidation of a chemical species at the working electrode. Similarly, the upward peak is due to the reduction of a chemical species at the working electrode and is called the cathodic peak. The ferri/ferrocyanide couple was chosen because it is a well-known

system with a simple 1:1 stoichiometry. Also, there is only one electron transferred during the redox reactions of this system, further simplifying calculations.

As can be seen in Fig. 18, the separation of the peaks is about 30mV. Theory predicts that 58mV peak separation should occur for a one-electron process. This theory assumes conditions, called semi-infinite diffusion, in the cell such that species that have just been oxidized or reduced at the working electrode are free to diffuse away from the working electrode into the bulk solution. Because any analyte that participates in electrochemistry inside the probe is trapped within the working electrode, conditions are said to be partially thin layer. Thin layer conditions can be said to exist when only a small portion of the solution in a cell is exposed to the working electrode, and this portion of solution is fairly isolated from the bulk solution. Peak separations for thin layer conditions are zero. Since conditions in the probe are between semi-infinite diffusion and thin layer, that is, species are somewhat restricted to close proximity of the working electrode, peak separations are expected to be between 58mV and 0mV.

Optimal pathlength, the pathlength that maximizes throughput, in air is ca. 2mm, which is the separation doubled (Fig. 15). Optimal pathlength decreases to ca. 0.6mm for solutions of ferricyanide of moderate concentration (<10M) (Fig. 17). Also, it is observed, as expected, that peak-to-peak noise levels decrease with increasing throughput (Fig. 16). The spectroscopy at the reflectance probe conforms to the Beer-Lambert Law. The

standardization curve (Fig. 14) using the reflectance probe is a straight line with a y-intercept at y=0 and noise levels increasing with absorbance (indicated by increasing magnitude of error bars in Fig. 14).

The double-step chronocoulometry of 3mM ferricyanide indicated that electrolysis times were long for such a small volume of solution. Earlier studies revealed the volume of solution trapped inside the working electrode to be 1-2uL (Brenneman and Flowers, National Conference for Undergraduate Research 1995). Coulomographs such as Fig. 19 show that 9 minutes are required for complete reduction of ferricyanide to ferrocyanide. This may be due to a large charging current along the inner surface of the working electrode.

CONCLUSIONS

The reflectance probe is compact and sturdy enough for *in situ* applications. Lengthy electrolysis times are inconvenient and warrant further investigation. Possible areas of application include environmental chemistry and medicine.

ACKNOWLEDGMENT

There are three kinds of support necessary for research to be carried out: moral, technical, and monetary. The author would like to thank Paul Flowers for supplying the first two and the University of North Carolina at Pembroke for supplying the last.

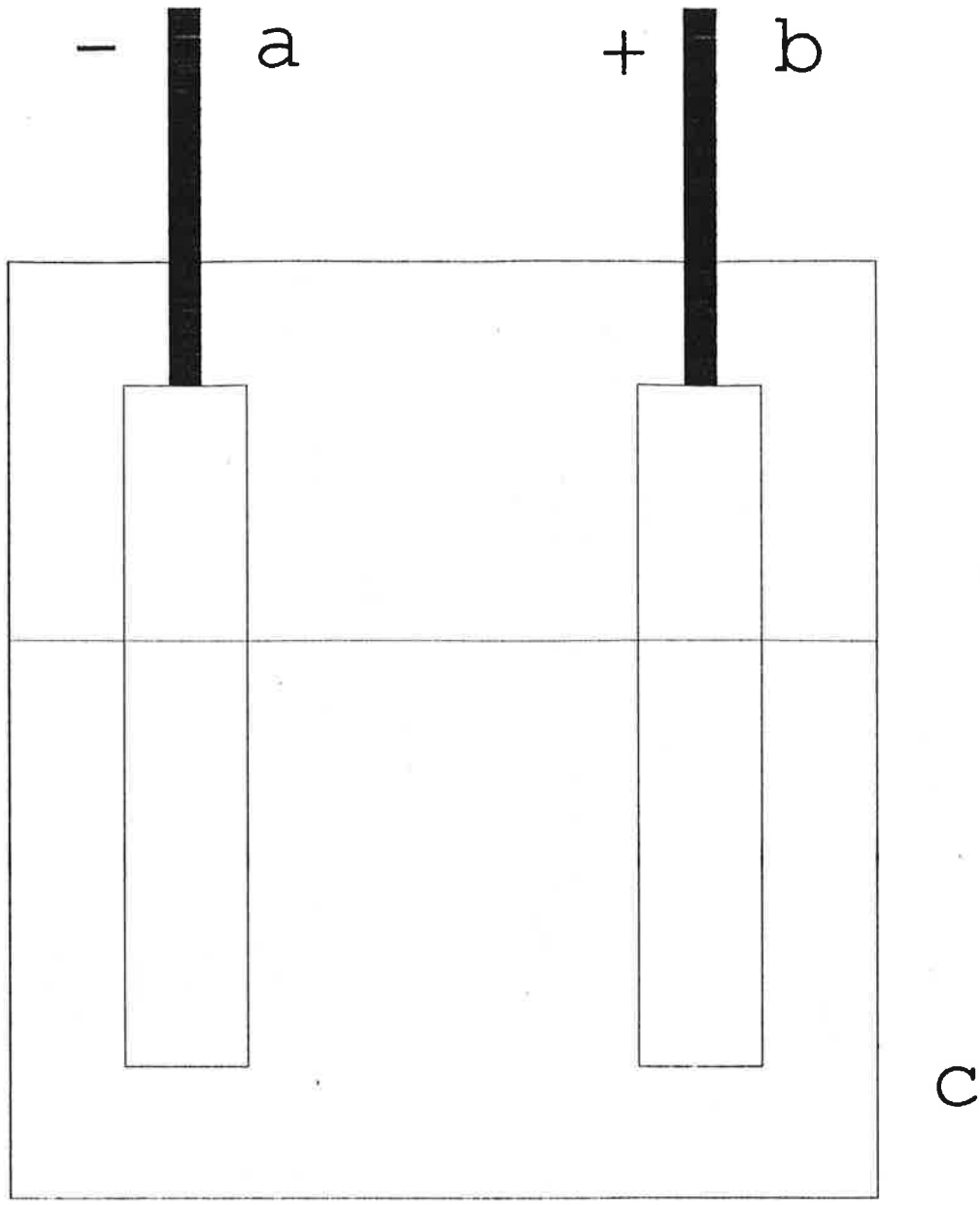

Fig. 1 An electrochemical cell. The cathode(a) and anode(b) rest in a solution containing analyte(c). Reduction occurs at the cathode and oxidation occurs at the anode.

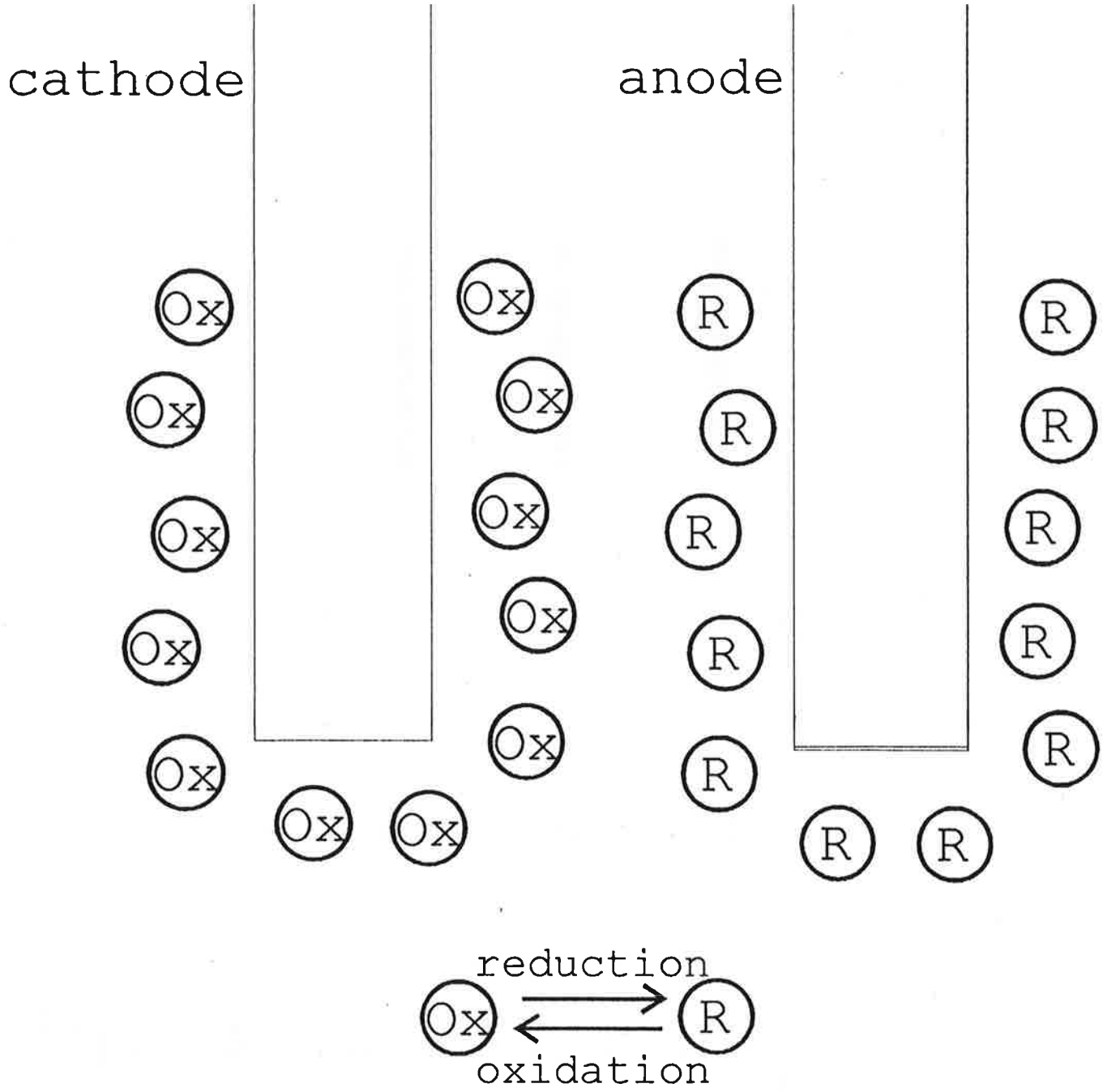

Fig. 2 In this reversible electrochemical reaction, the oxidant(Ox) is reduced at the cathode to produce the reductant (R). Similarly, the reductant is oxidized at the anode.

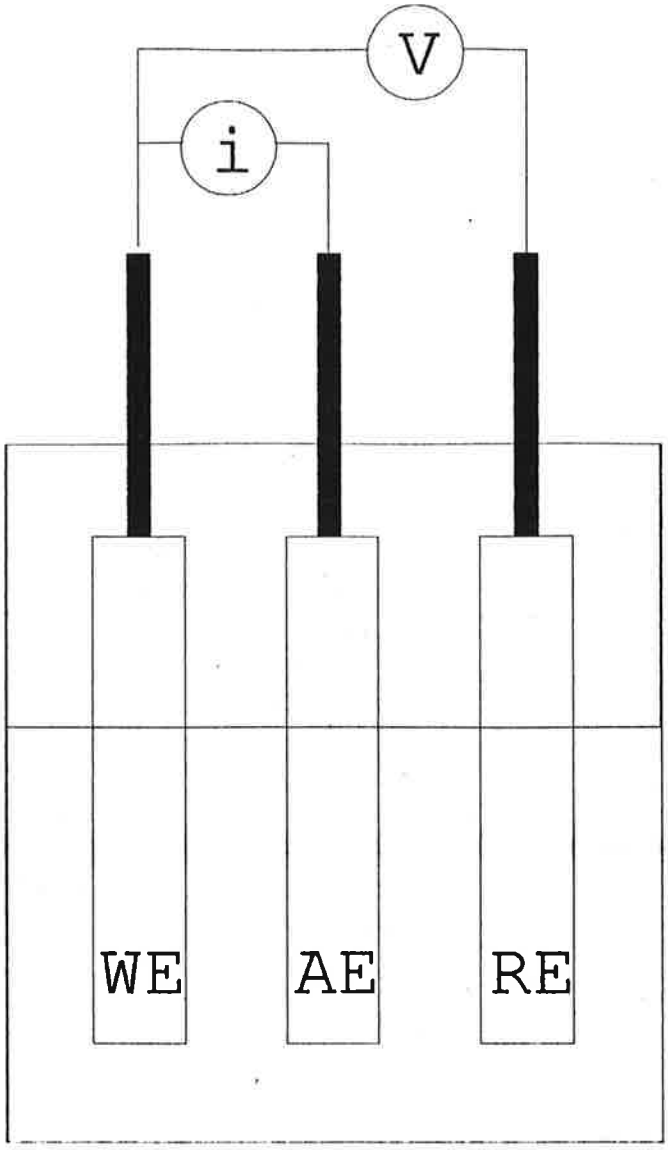

Fig. 3 Standard 3 electrode geometry. The working electrode (WE) and auxillary electrode(AE) reduce/oxidize chemical species, while the reference electrode(RE) serves as a standard against which potential is measured.

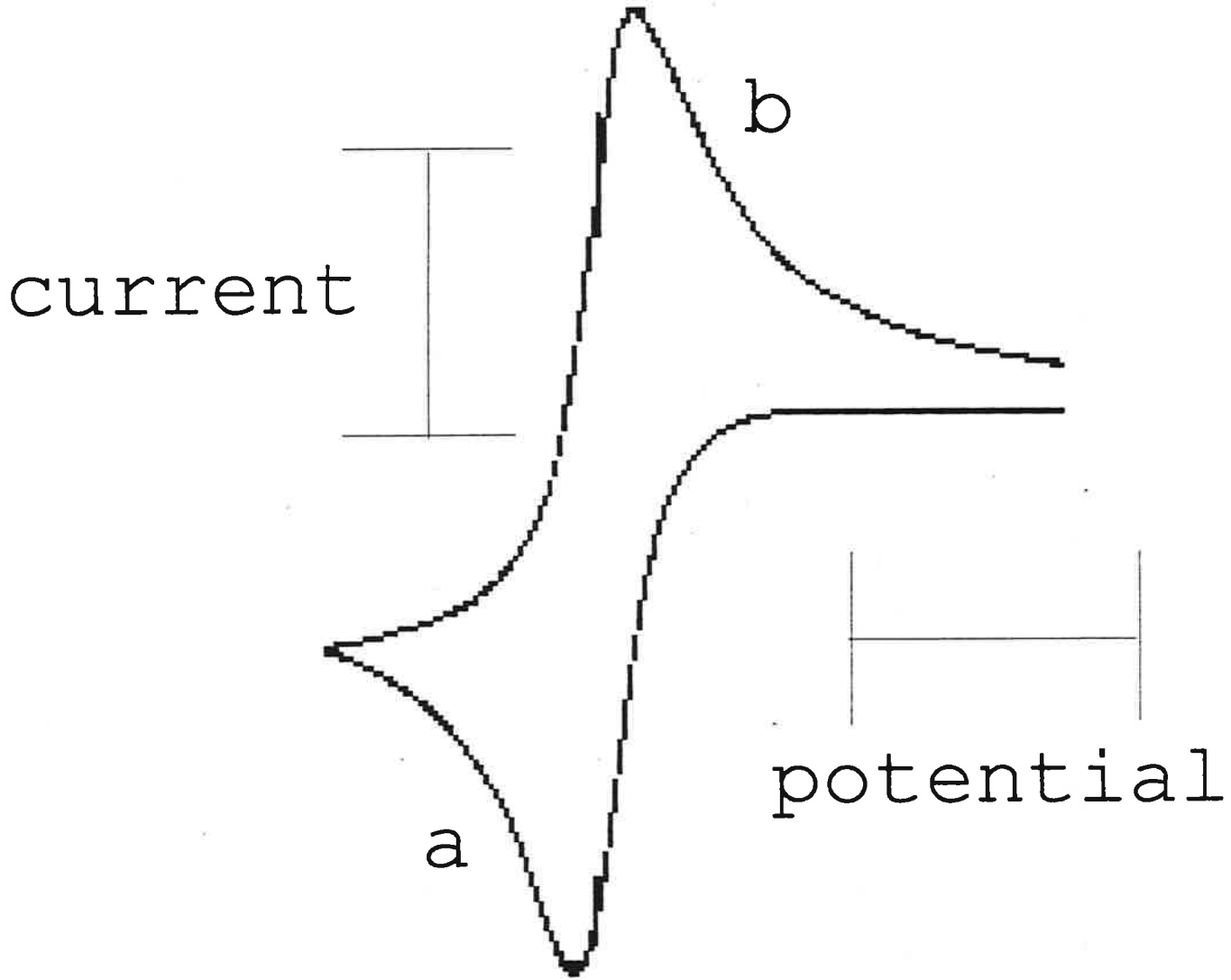

Fig. 4 A theoretical cyclic voltammogram consisting of a cathodic(b) and an anodic peak(a).

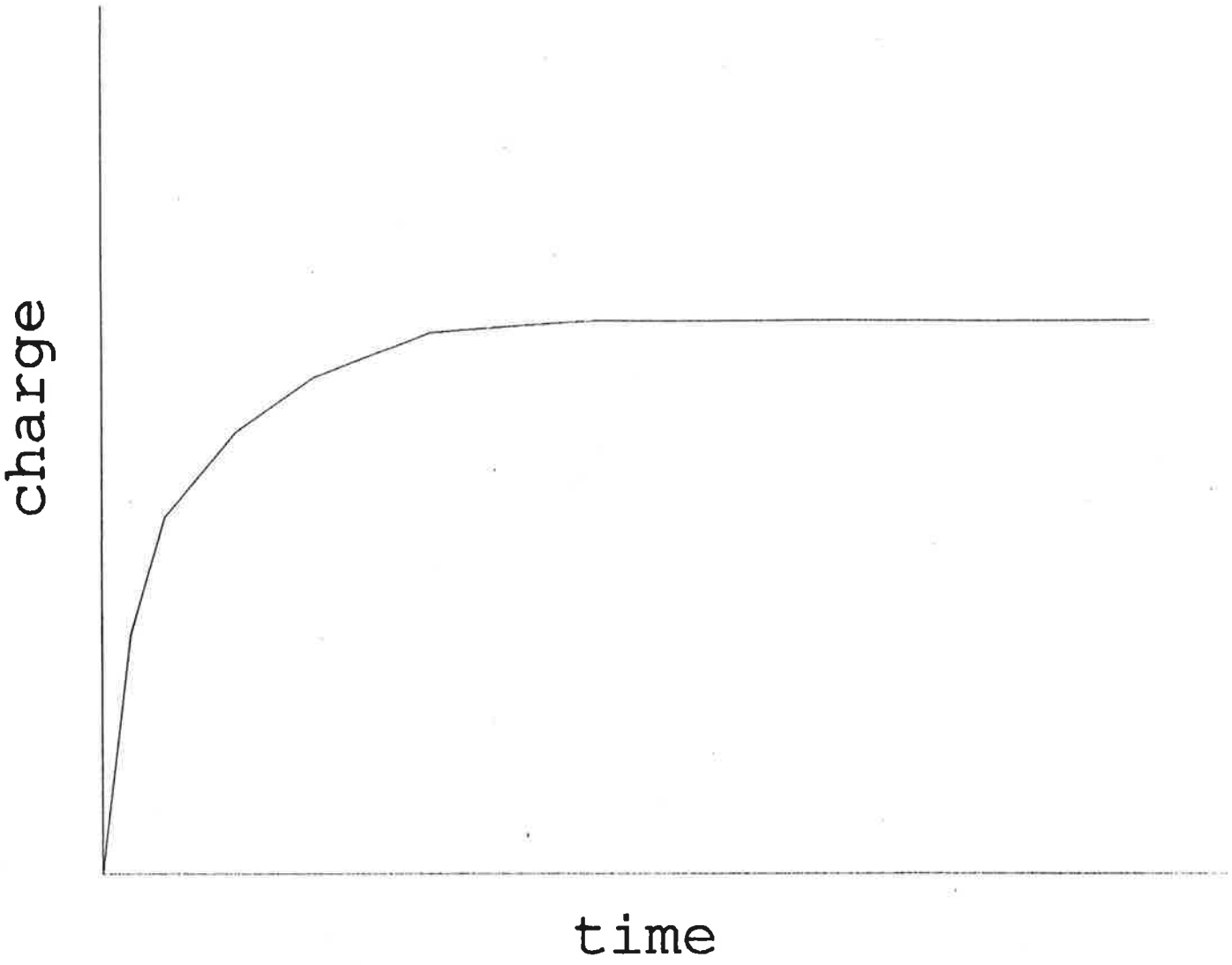

Fig. 5 A coulomogram.

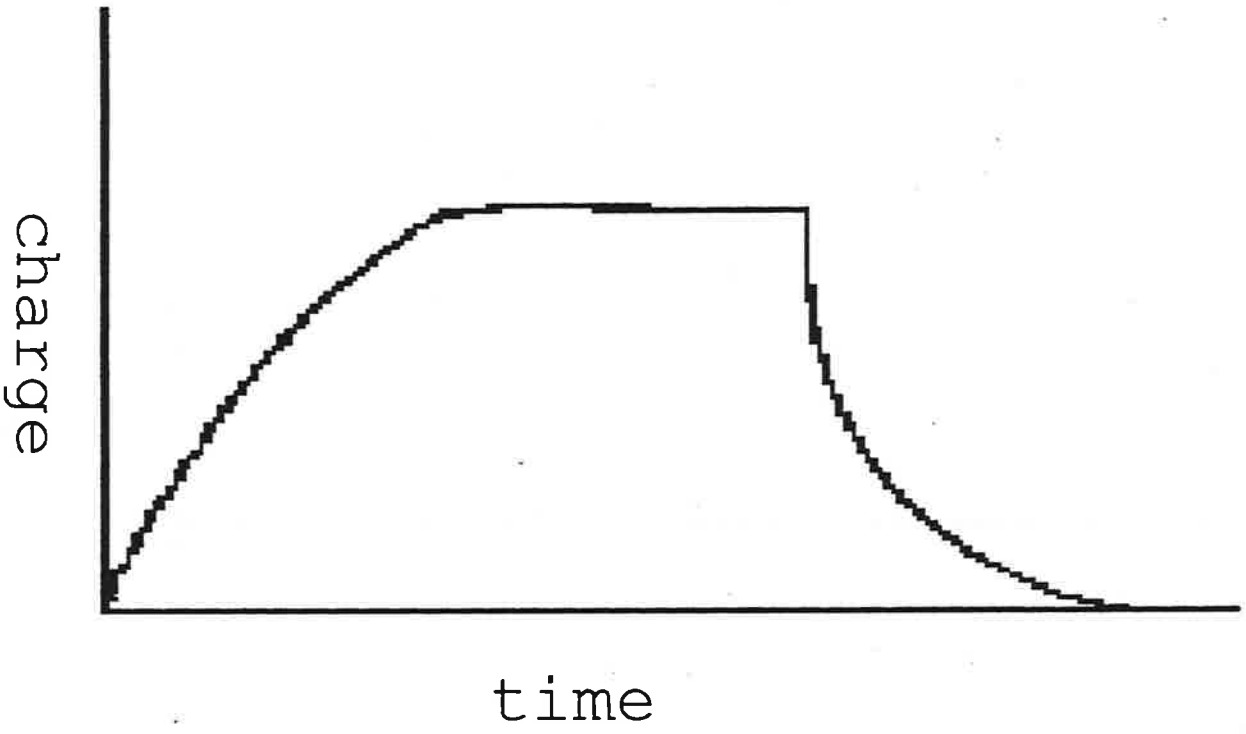

Fig. 6 An ideal double-step coulomogram.

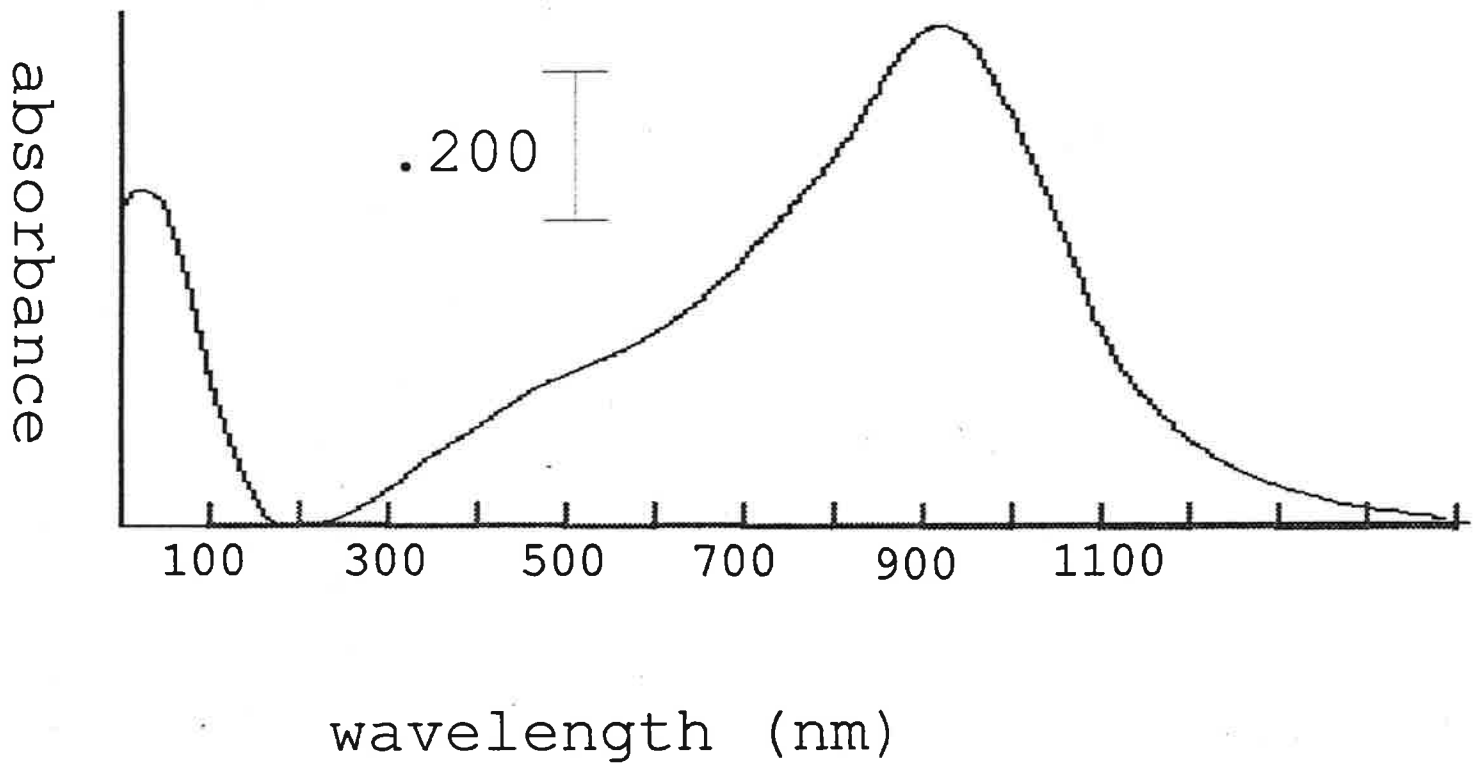

Fig. 7 An absorption spectrum of ferrozine.

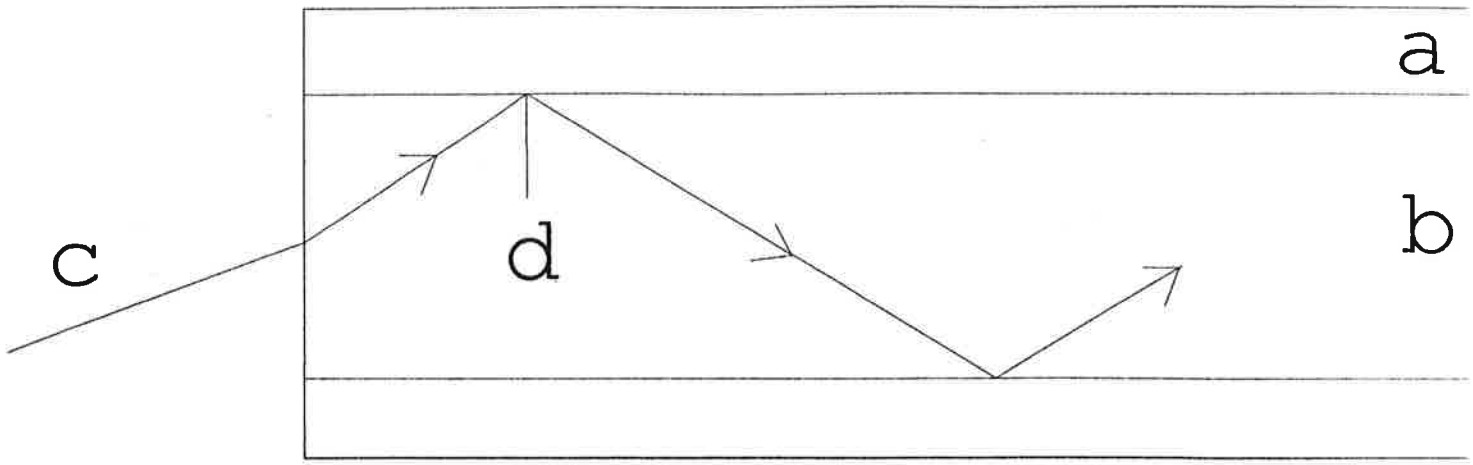

Fig. 8 A fiberoptic is comprised of a cladding(a) around a core(b). An incident light ray(c) enters the core and is reflected at the core/cladding interface(d).

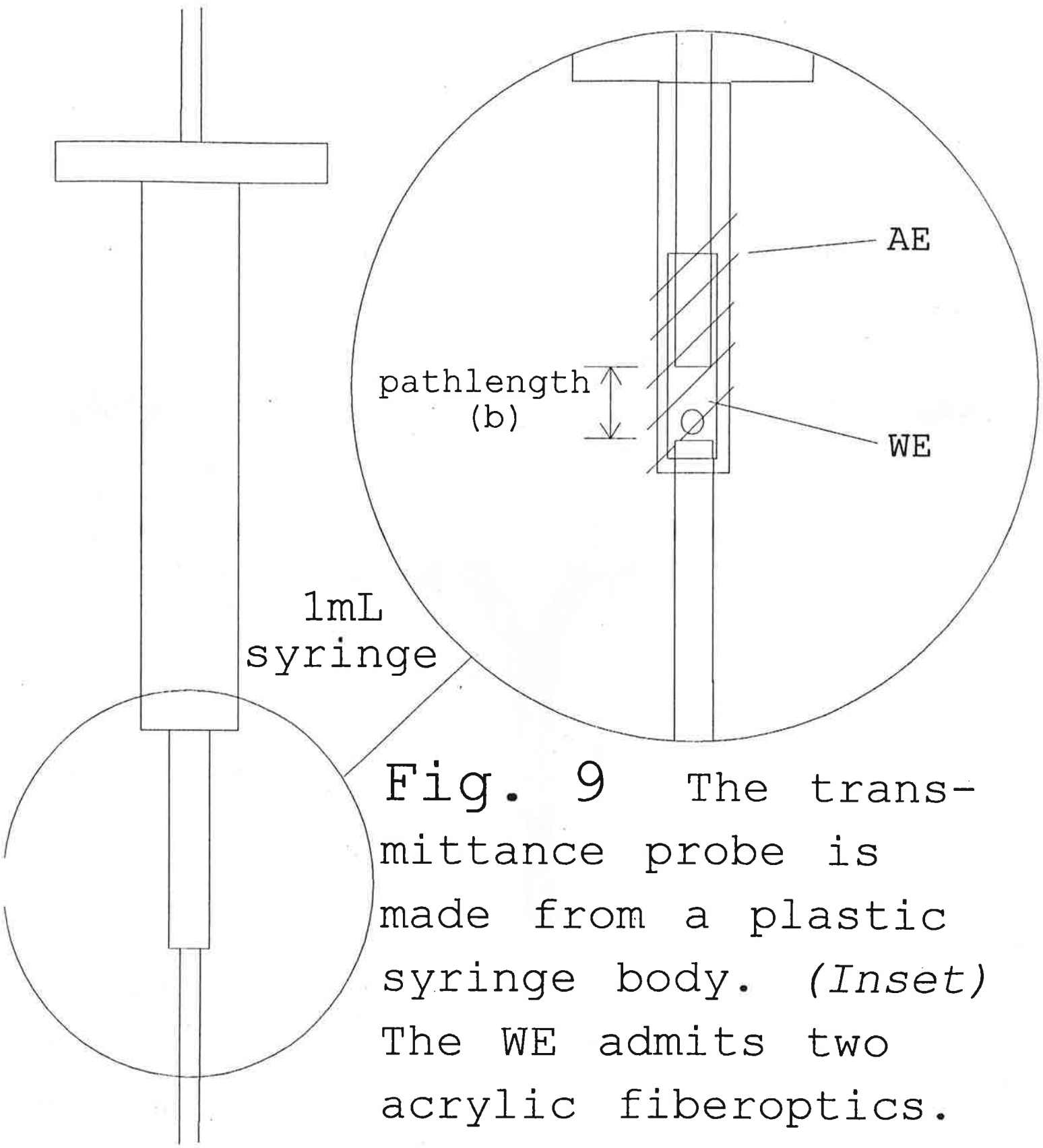

Fig. 9 The transmittance probe is made from a plastic syringe body. *(Inset)* The WE admits two acrylic fiberoptics. Diagonal lines represent the AE.

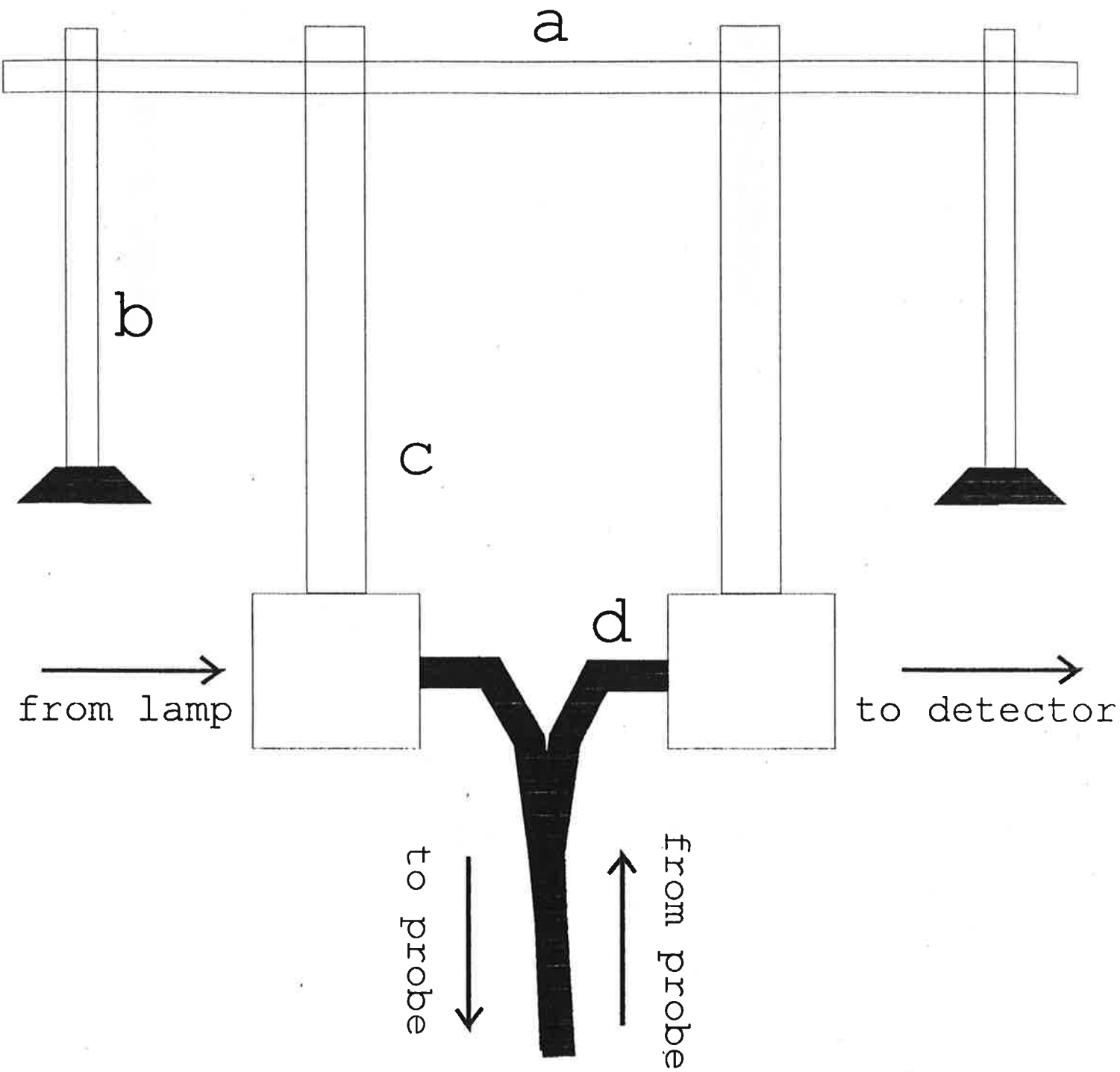

Fig. 10 The coupler's plexiglass base(a) is supported by four bolts(b) capped with rubber stoppers. Clamps(c) hold lenses and bifurcated bundle ends(d).

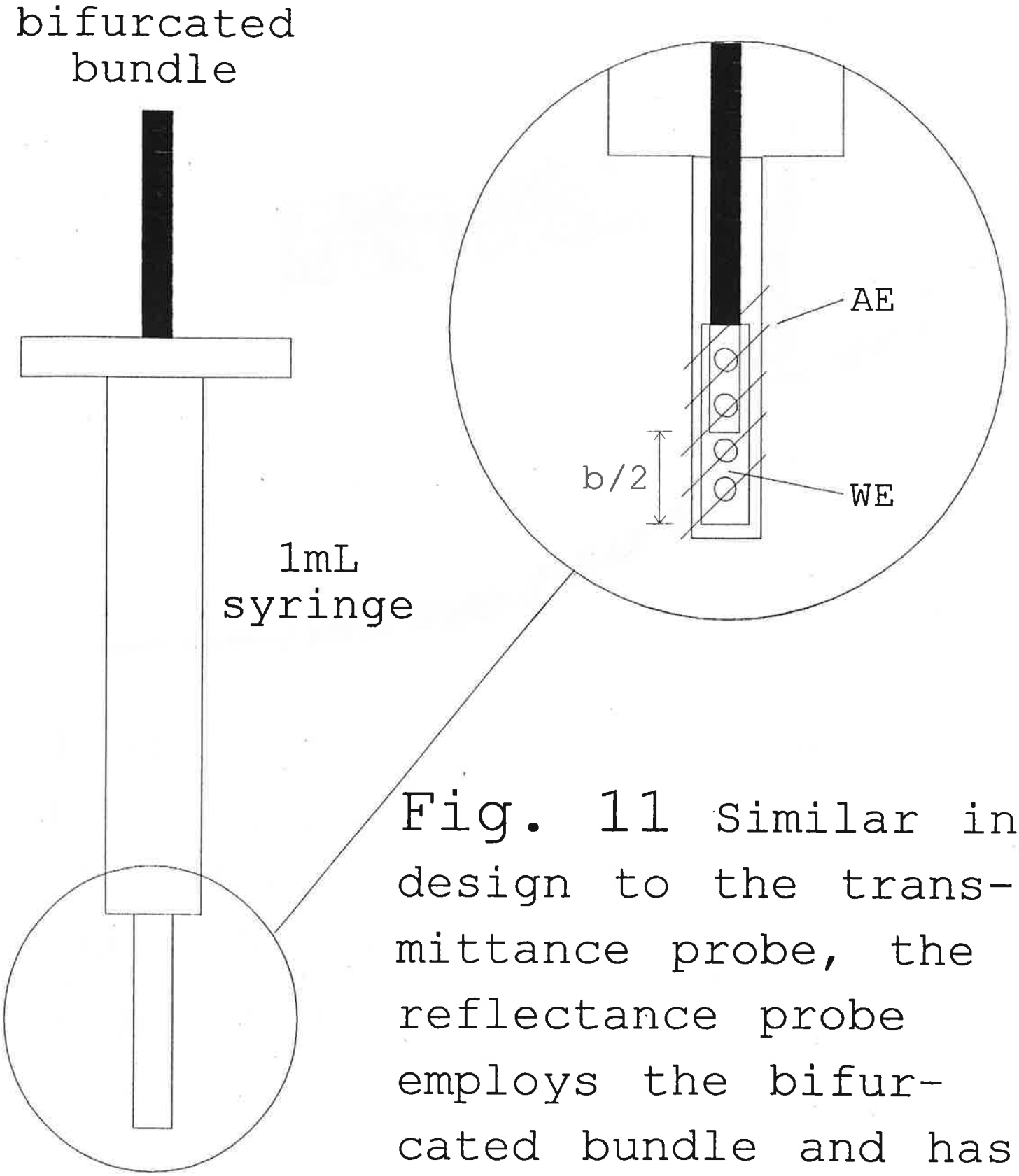

Fig. 11 Similar in design to the transmittance probe, the reflectance probe employs the bifurcated bundle and has a WE that is capped with a Pt mirror.

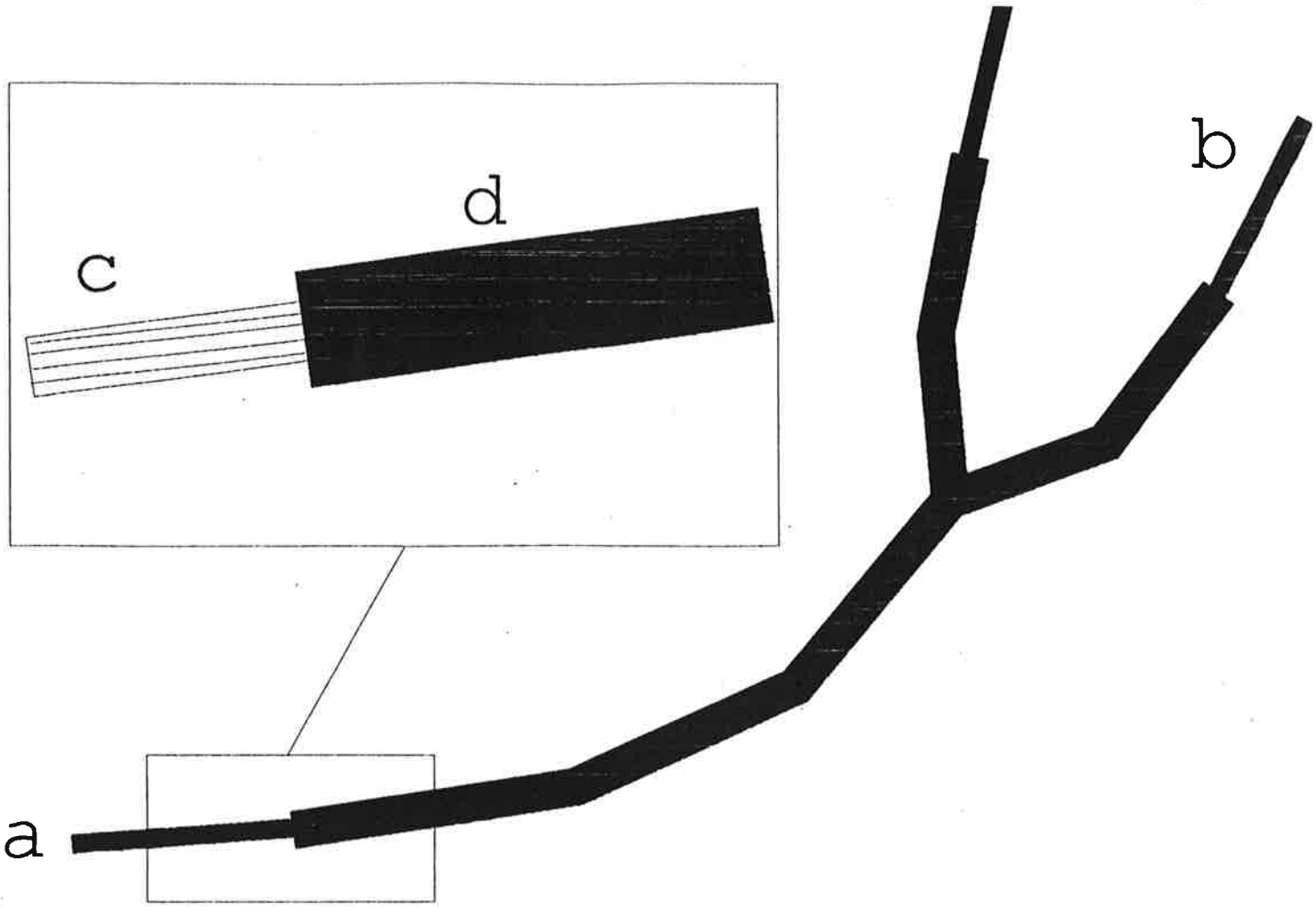

Fig. 12 The bifurcated bundle has a common end(a), where all the fibers are packed in epoxy. The other ends(b) either accept light from instrument lamps or transmit light to instrument detectors. *(Inset)* Fibers are packed in epoxy(c) and covered with protective heat shrink tubing(d).

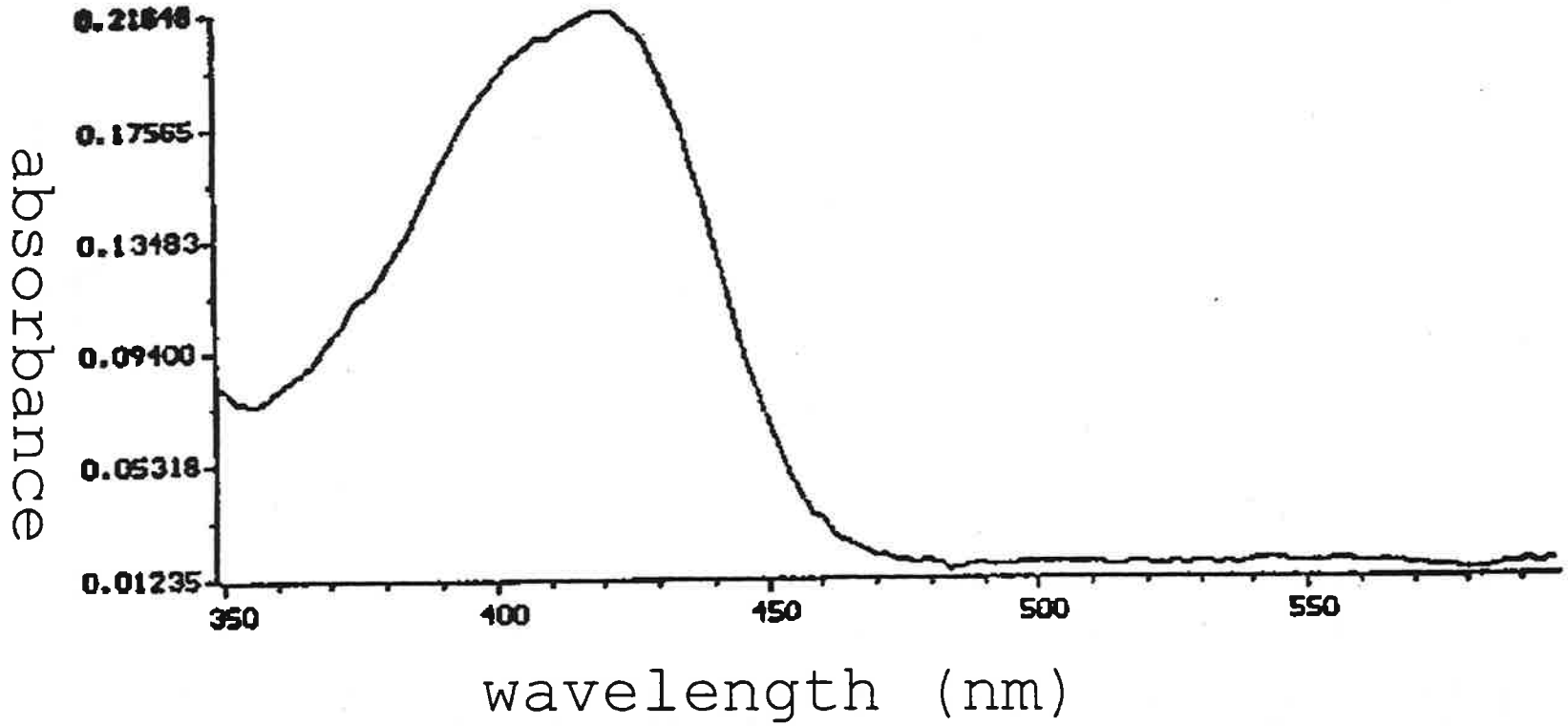

Fig. 13 A typical absorbance spectrum of 3mM ferricyandie measured with the transmittance probe.

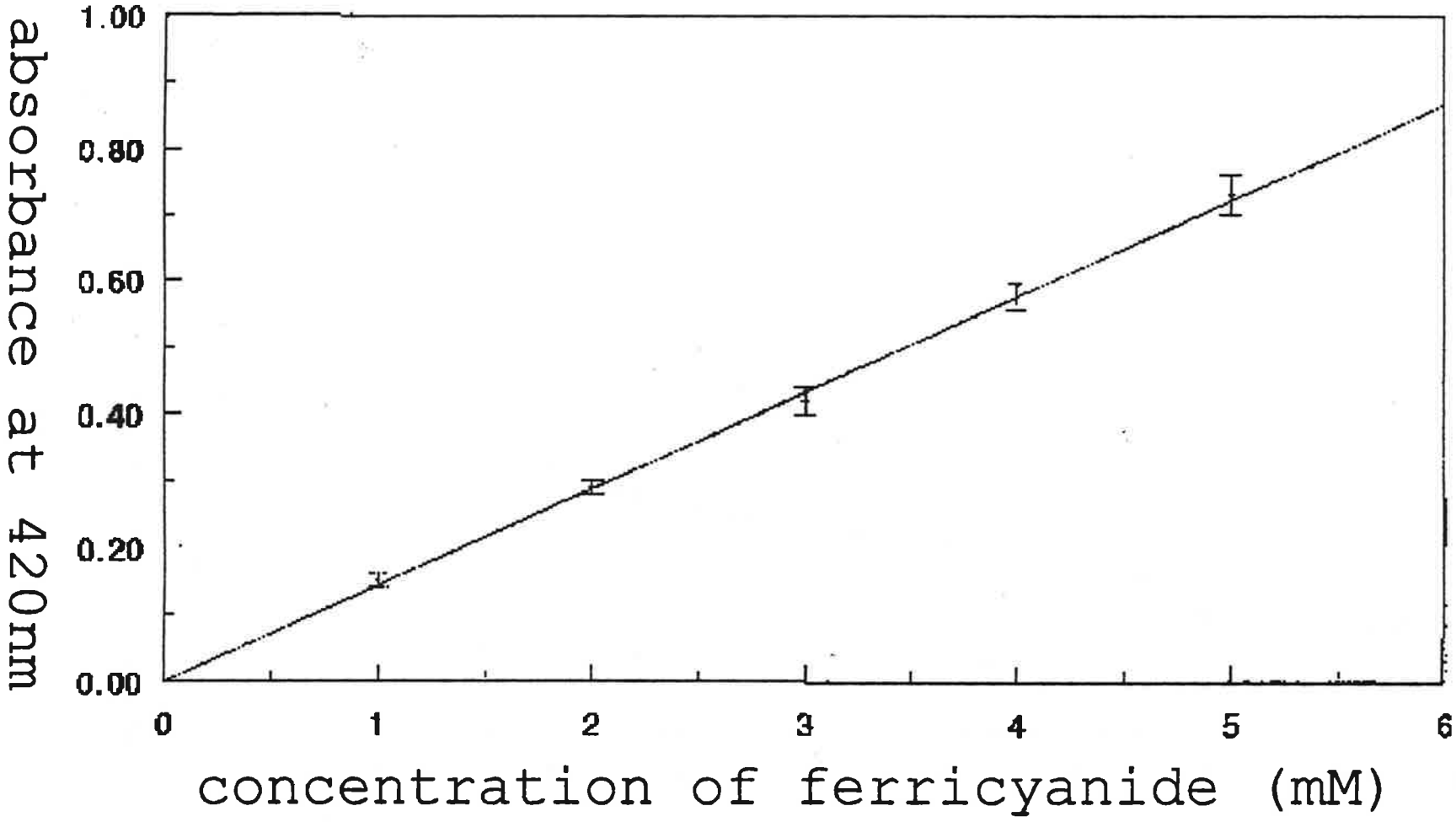

Fig. 14 A calibration curve for aqueous ferricyanide using data obtained from the reflectance probe.

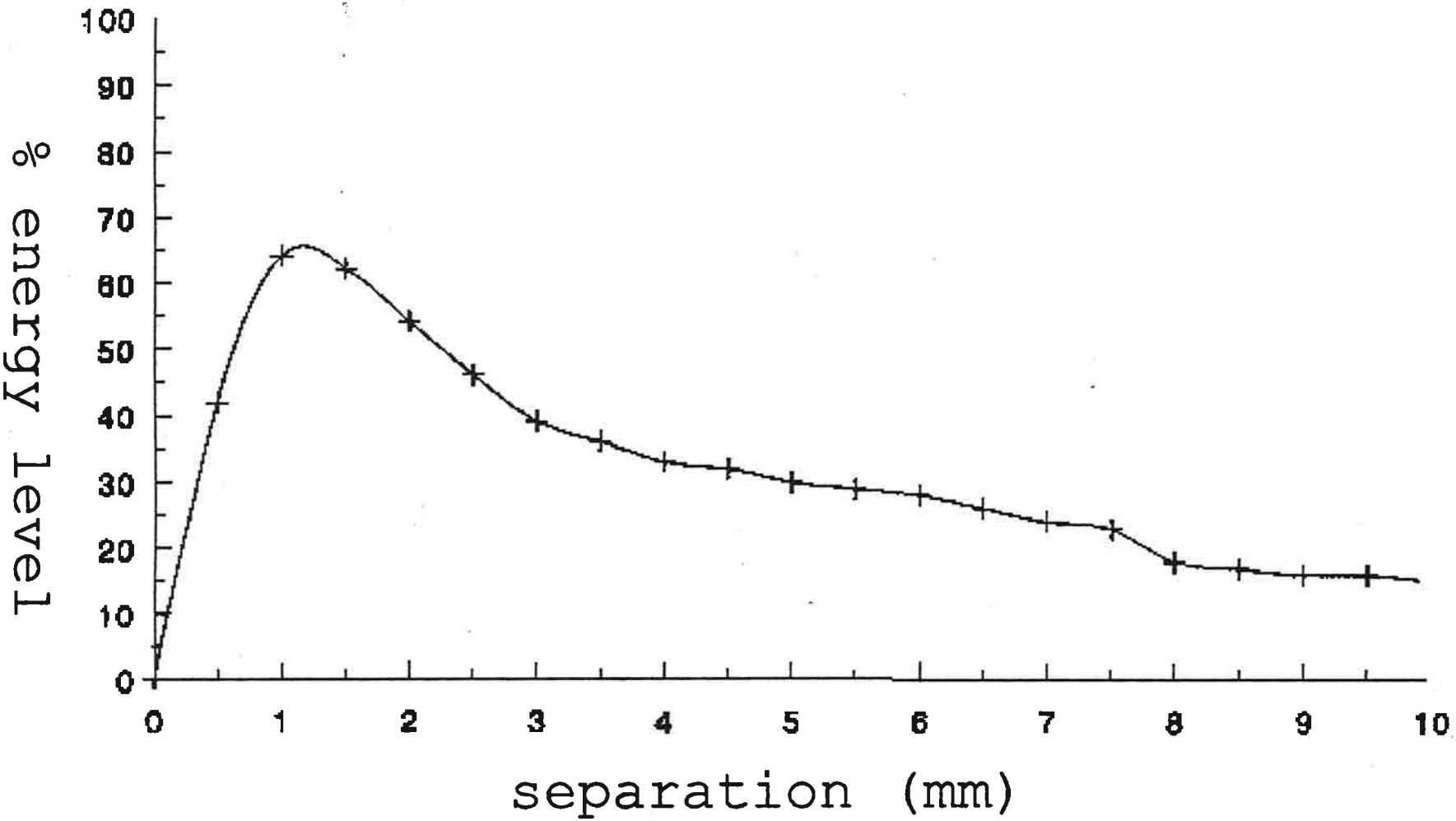

Fig. 15 Detector signal vs. between the common end of the bifurcated bundle and the Pt mirror.

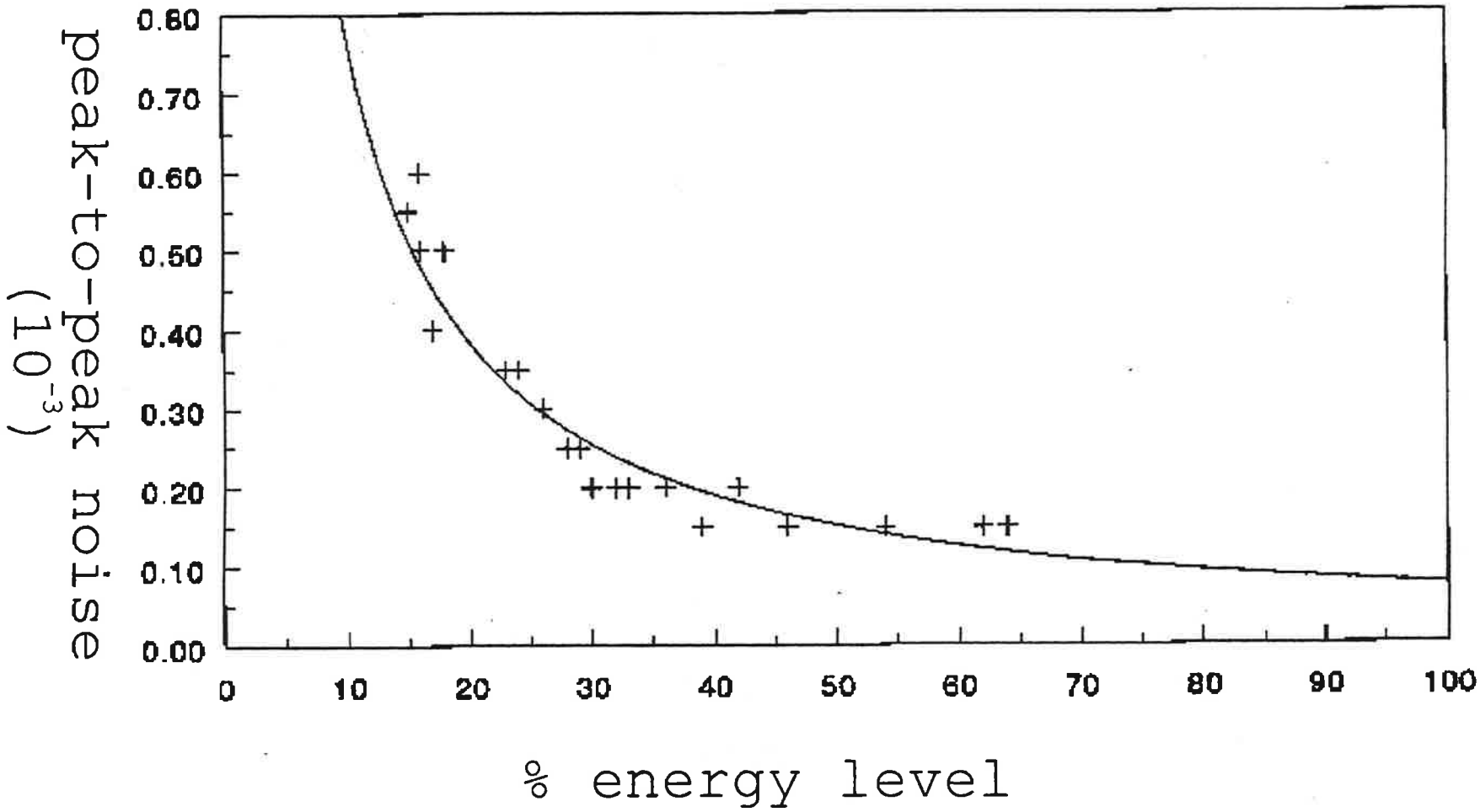

Fig. 16 Noise versus detector signal for the reflectance probe.

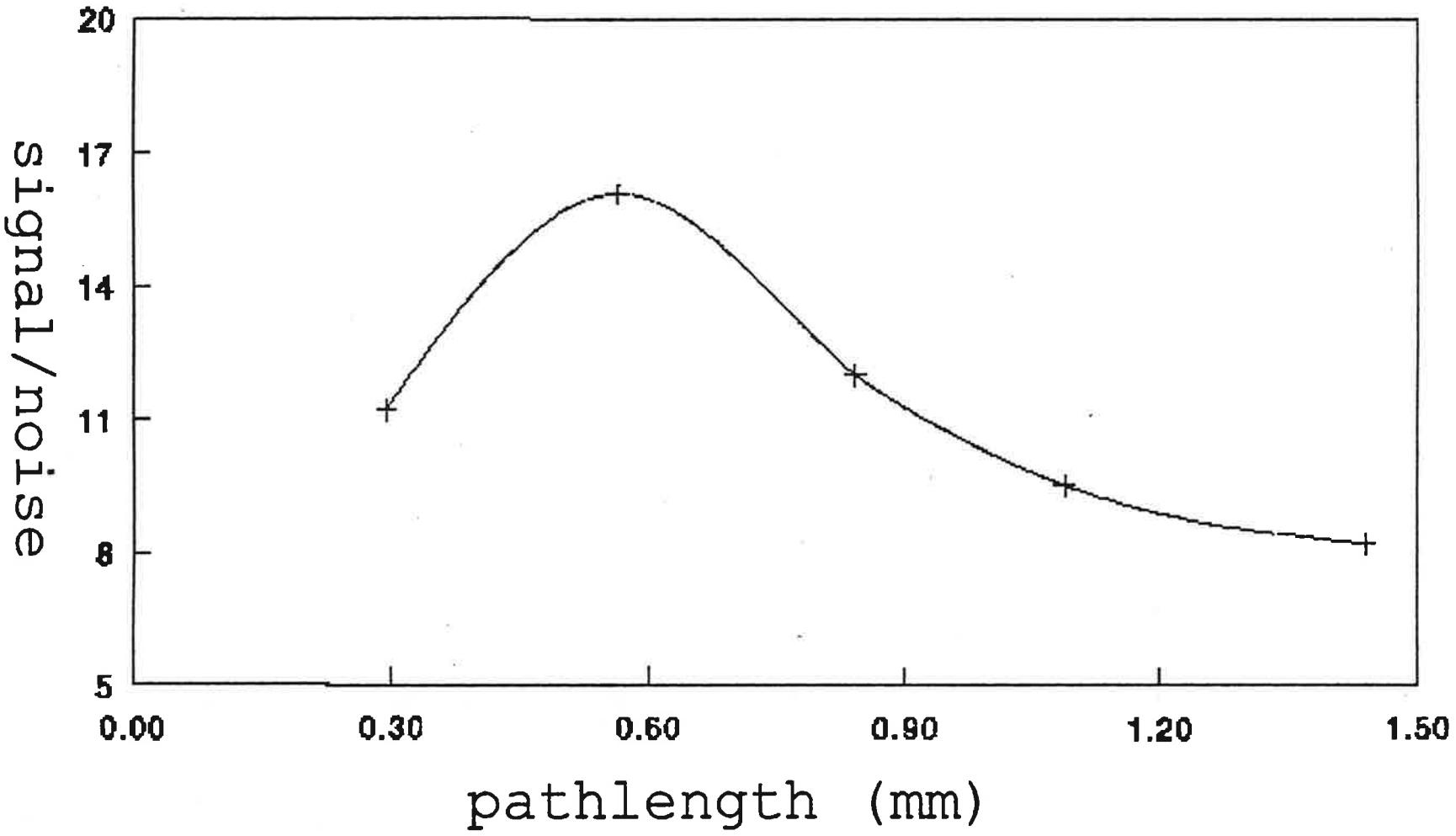

Fig. 17 Signal to noise ratio versus pathlength for the reflectance probe.

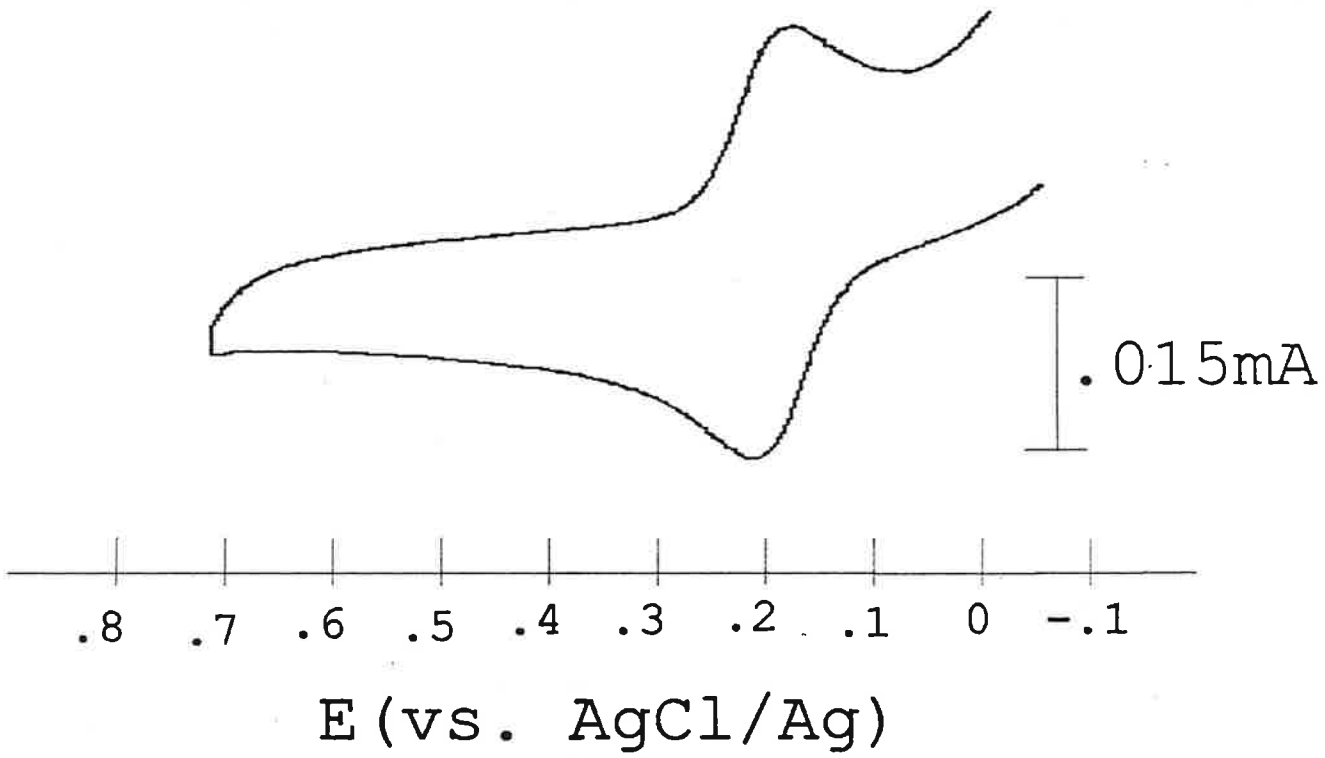

Fig. 18 A cyclic voltammogram of 2mM ferrocyanide in 0.1M potassium nitrate measured in the transmittance probe at a scan rate of 20mV/s.

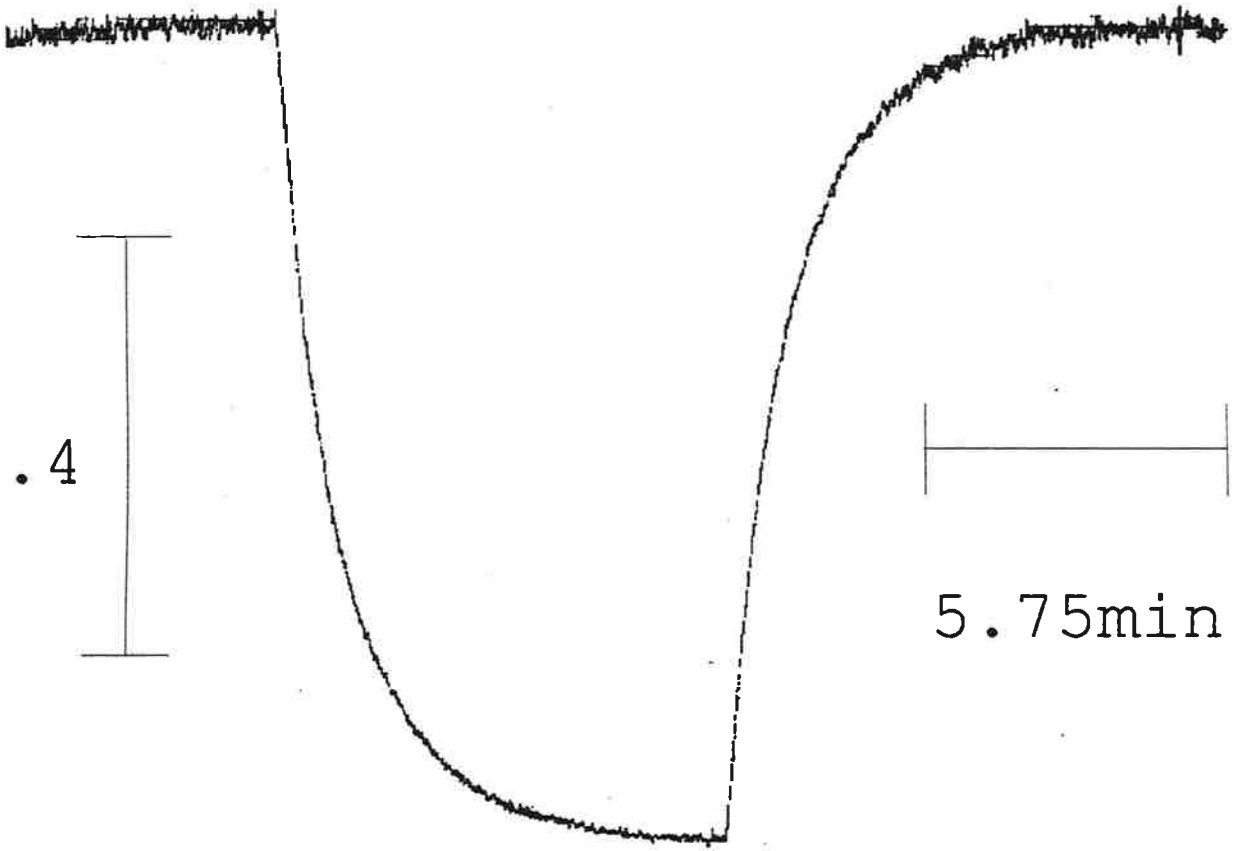

Fig. 19 A chronoabsorptivity study in which absorbance at 420nm is monitored over time in the reflectance probe.

Author's signature Chad Brenneman 4/29/97
(Chad Brenneman)

Advisor's signature Paul Flowers 29/Apr/97
(Paul Flowers)