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SENSING STRATEGIES FOR TOXIC VAPOR DETECTION

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ABSTRACT

This work was motivated by the recommendation of the American Conference of Governmental Industrial Hygienists (ACGIH) that threshold limits for hydrazine, $\text{H}_2\text{N-NH}_2$, in air be lowered from 100 to 10 parts-per-billion (ppb) concentration levels. Hydrazine is one of the high-energy propellants used in large volumes in Space Shuttle, Titan, payloads, and other aerospace operations. Since analytical methods presently available for hydrazine detection and/or determination do not satisfy such low levels of detection, the ultimate goal of this research is the development and characterization of a portable and compact chemical sensor ideally capable to detect (in real time) 1 ppb of hydrazine, continuously and reversibly. The laboratory prototype developed as part of this project is comprised of: (1) a reactor part in which $\text{H}_2\text{N-NH}_2$ reacts, generating chemiluminescence emission, with tris[2,2'-bipyridine]ruthenium(III), which is immobilized on an ion-exchange polymeric material of a perfluorinated hydrocarbon containing sulfonate groups as exchange centers (Nafion), (2) an electrochemical three-electrode cell posed at a potential at which the immobilized ruthenium complex could be reoxidized to the III-oxidation state (as to provide reversible and continuous detection), and (3) a low power consumption photomultiplier tube to collect and quantitatively integrate the emitted photons with the help of auxiliary electronics and readout device.

SUMMARY

The scope of this project was to test the feasibility of hydrazine detection with a sensor designed to integrate, in a single unit, chemiluminescence detection and electrochemical regeneration of the main reagent. The unit designed and built as part of this research incorporated the main reagent (a ruthenium complex) immobilized on an ion exchange-polymer (perfluorosulfonic acid). Cyclic voltammetry (an electroanalytical technique based on applying a programmed potential which varies, at a given rate and in a cyclic form, between an initial and a switching potential) was used to characterize the polymeric films with the immobilized main reagent. Limitations of the approach, avenues for improvement, as well as alternatives for further sensor development are presented in the text of this final report.

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I. INTRODUCTION

1.1. THE NEED FOR A HYDRAZINE SENSOR

Hydrazine is one of the high-energy propellants used in large volumes in Space Shuttles, Titan, payloads, and other space operations. Hydrazine has been identified as a carcinogen or potential carcinogen. It may cause lung damage and upper respiratory tract irritation if inhaled, and relatively high concentrations of hydrazine may be fatal. The acute oral LD₅₀ in rats, ingested as hydrazine sulfate, is 50-400 mg.Kg⁻¹ [1]. Allergic skin irritations are known to be caused by skin contact with hydrazine or hydrazine salts.

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended that threshold limits for hydrazine in air be lowered from 100 to 10 parts-per-billion (ppb) [2]. Compliance with this recommendation requires highly sensitive methods of detection, and present methods in use are not capable of satisfying such requirement.

1.2. HYDRAZINE CHEMILUMINESCENCE REACTION WITH TRIS[2,2'-BIPYRIDINE]RUTHENIUM(III)

Chemiluminescence (emission of light resulting from a chemical reaction) offers very high sensitivity (low limits of detection) and wide dynamic concentration ranges for analytical determinations [3]. In 1966 Hercules and Lytle [4] reported the generation of visible light when tris[2,2'-bipyridine]ruthenium(III), Ru(bpy)₃³⁺, was reduced either by hydrazine or hydroxide ion. Since then, several other papers have appeared in the literature discussing the mechanism and kinetics of this chemiluminescence, as well as the reduction by several aliphatic amines leading to light emission [5]. The chemical structure of the Ru(bpy)₃²⁺ is shown in Figure 1.

The chemiluminescence is probably due to the formation of a short-lived amine radical cation resulting from the reduction of Ru(bpy)₃³⁺ by hydrazine, which further reacts with

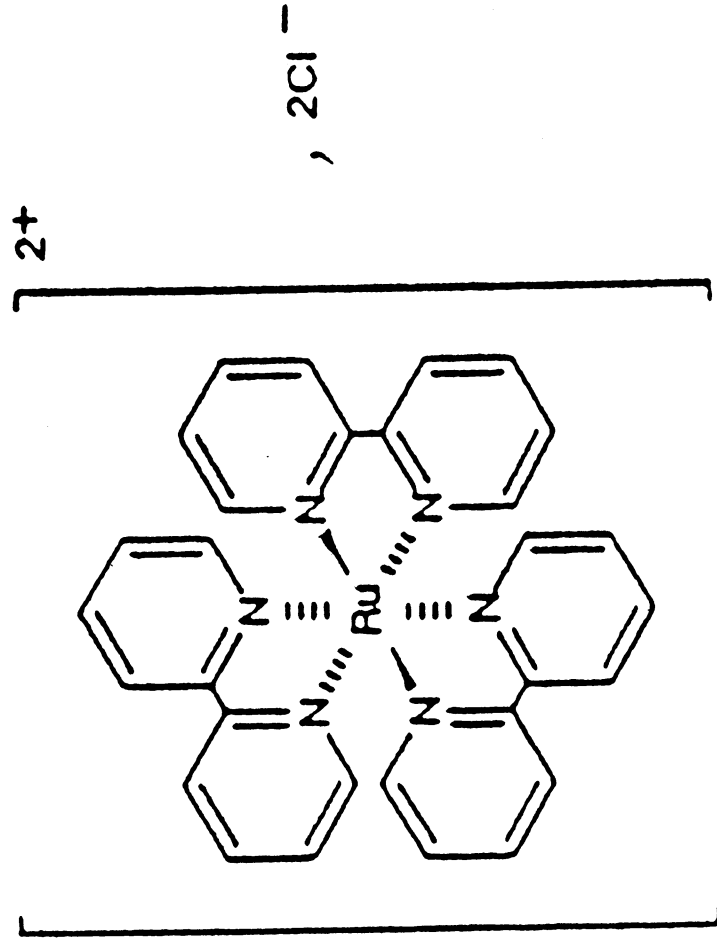
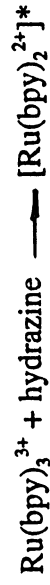


FIGURE 1. Chemical arrangement in the tris[2,2'-bipyridine]ruthenium(II) complex.

$\text{Ru}(\text{bpy})_3^{3+}$ or excess $\text{Ru}(\text{bpy})_3^{2+}$ to form the excited state of the Ru(II)-complex as shown in the following chemico-physical sequence:



in which $[\text{Ru}(\text{bpy})_3^{2+}]^*$ indicates the excited state of the Ru(II)-complex. The process is very rapid and offers the potential of affording very low limits of detection, hence its selection for this project. Lee and Nieman [6] have recently provided a brief review of mechanistic aspects of the chemiluminescent reactions involving $\text{Ru}(\text{bpy})_3^{3+}$ and their analytical applications.

1.3. ELECTROSTATIC IMMOBILIZATION OF TRIS[2,2'-BIPYRIDINE]RUTHENIUM(II/III) AND ELECTROCHEMICAL GENERATION OF THE Ru(III) COMPLEX

The orange-red ruthenium(II) complex can be electrostatically immobilized on a cation exchanger in the general form illustrated below:



in which $(R=SO_3^-)_n$ represents a typically sulfonated cation-exchange site in a polymeric backbone R.

Nafion, the trade mark for a chemically stable perfluorosulfonic acid polymer (E. I. du Pont de Nemours, Wilmington, DE) commonly used in membrane form for the manufacture of chlorine and caustic soda [7], is effective in storing in insoluble form significant amounts of $Ru(bpy)_3^{2+}$ [8]. The green ruthenium(III) complex was prepared and immobilized on Nafion by a similar route during the course of these studies, and for this reason these two complexes were singled out for use in this work. The direct attachment of the ruthenium(III) complex was made part of these studies in an attempt to circumvent that when the ruthenium(II) complex is the main electroactive species on the surface of the screen, only a fraction of its total amount is converted to the III oxidation state and the electrogenerated $Ru(bpy)_3^{3+}$ is the limiting reagent for chemiluminescence.

Oxidation of the immobilized ruthenium(II) complex is possible chemically (e.g. by reaction with lead dioxide or chlorine gas) or electrochemically at an applied potential of about +1.38 V vs. a silver/silver chloride (Ag/AgCl, 3.0 M NaCl) reference electrode,

according to:



Oxidation at potentials higher than +1.50 V need to be avoided because of electrolysis of water at platinum surfaces. Electrochemical oxidation of the ruthenium(II) complex affords a clean avenue for the regeneration of the main reagent [i.e., the Ru(III) complex], and can be incorporated into compact sensing units.

Consequently, with the prototype sensor developed during this work, the utilization of electrochemical regeneration of the main reagent at a platinum screen working electrode as part of a three-electrode cell (Figure 2) was included as part of strategies explored.

Figure 3 provides a closer view of the platinum screen working electrode which also serves as receptacle for the immobilized ruthenium redox couple.

1.4. NEED FOR COMPENSATION OF SOLVENT EVAPORATION

When $\text{Ru}(\text{bpy})_3^{2+}$ is the immobilized species, continuous contact of the polymeric film of Nafion-immobilized Ru(II/III) complex with the air sample (potentially containing the analyte hydrazine) should result in superficial drying of the film impairing the ionic mobility required for sustainment of the electrochemical regeneration of the Ru(III) centers. Moreover, such a drying can result in flaking of the polymer film, and eventual deterioration of the sensing unit. Nafion is a hydrophilic material and can be rehydrated. The rate of rehydration, however, is not fast and air-drying may prevail between these two processes if a device for compensation for solvent evaporation is not part of the overall

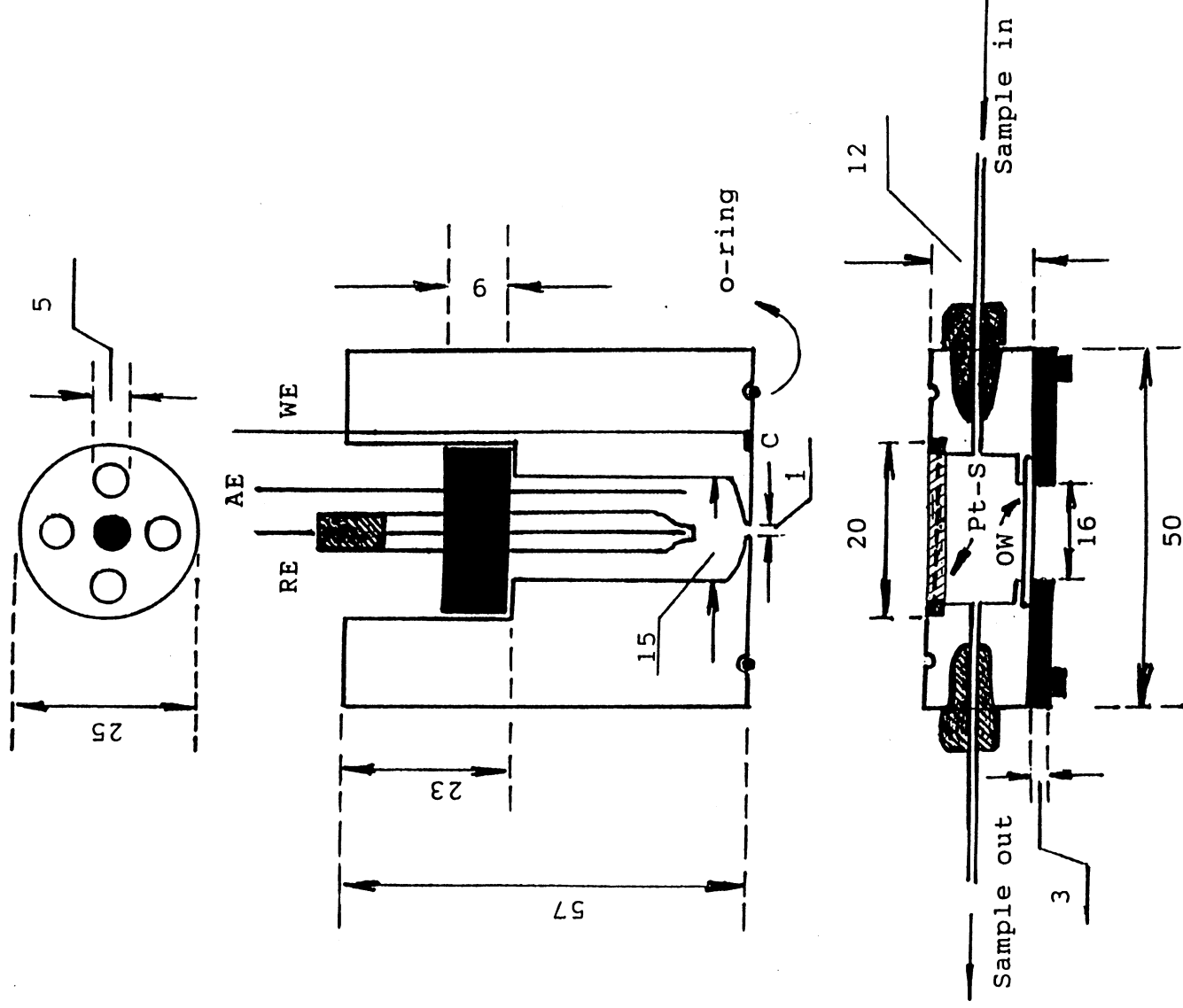


FIGURE 2. Schematic diagram of integrated chemiluminescence reactor chamber, three-electrode reagent regeneration cell, and optical window for photon detection. Measurements in mm. RE: reference electrode (Ag/AgCl/3.0 M NaCl); AE: auxiliary electrode (platinum wire); WE: working electrode connection (working electrode: Pt-S, platinum screen); C: copper contact; OW: optical window (to photomultiplier tube). For further details see narrative (INSTRUMENTATION under MATERIALS AND METHODS).

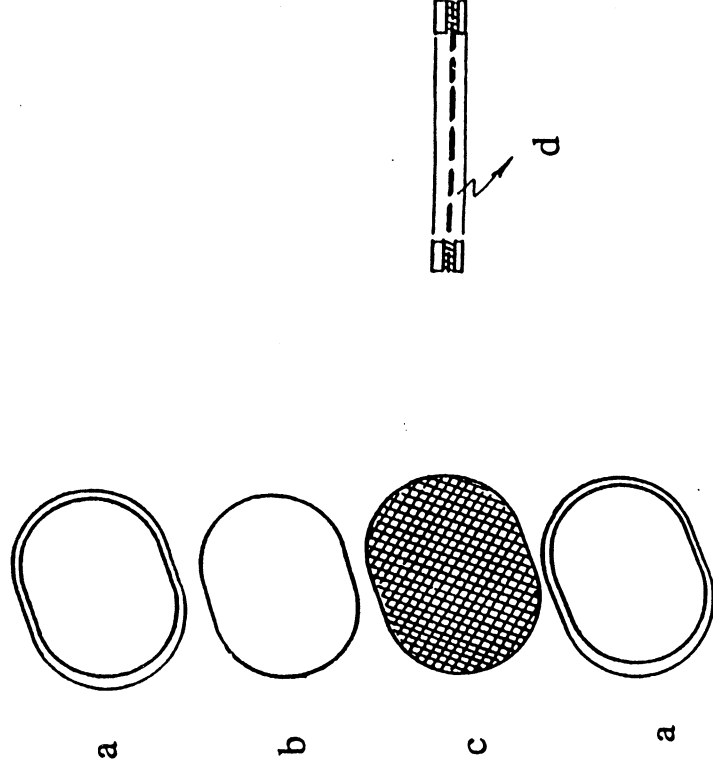
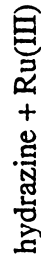


FIGURE 3. Detail of platinum screen anode for regeneration of tris[2,2'-bipyridine]ruthenium(III) reacting centers. a: Platinum rings; b: cellulose-based filter material; c: platinum screen; d: Nafion-immobilized tris[2,2'-bipyridine]ruthenium(II) layer.

sensing device. The semi-solid layer of Nafion-complex in contact with the minigridded platinum working electrode is in direct contact with the cell compartment in which the reference and auxiliary electrodes are located. This compartment can be filled with aqueous supporting electrolyte solution which is in contact with the Nafion-complex layer via the central orifice machined at the bottom of the upper body of the unit. Gravitational flow provides a continuous path for compensating the water loss produced by air-drying. This strategy facilitates electrical as well as ionic communication, both required for the operation of the Ru(II)/Ru(III)/Ru(II) cycle:



This arrangement also provides convenient segregation of the working electrode from the auxiliary one and of the electrochemical and optical parts of the sensor. It requires, however, a compromise between ionic mobility and percolation of the liquid to keep the screen wet. For this reason the intercalation of cellulose-based filter pads (see Figure 3) was implemented.

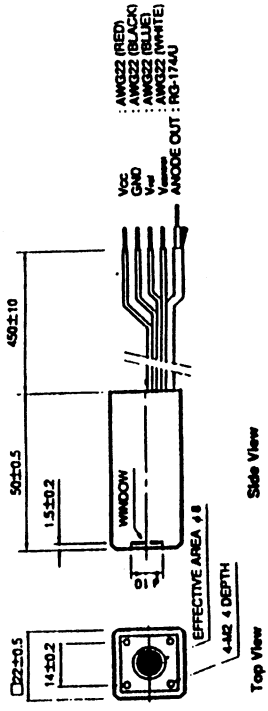
II. MATERIALS AND METHODS

2.1. INSTRUMENTATION

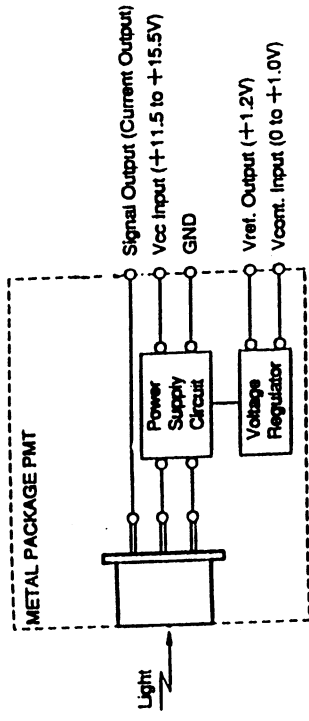
The prototype sensor was constructed of Teflon and black Delrin, and essential details are shown in Figure 2. The platinum rings and platinum screen were cut and forced molded from the reinforcement rim and mesh body of a discarded platinum electrode similar to the type used in electrogravimetric determinations. The reference electrode was a R-5 silver/silver chloride minielectrode with Vycor tip and 3.0 M NaCl filling solution (Bioanalytical Systems, West Lafayette, IN). The Teflon tubing (1 mm i.d.) used for sample transport into and out of the sensor as well as the tube end fittings were of the type used in liquid chromatography and were obtained from Upchurch (Oak Harbor, WA). The optical window was a 0.10 mm thick borosilicate glass circular microscope cover. Cyclic voltammetric information was collected with the aid of a CV-1B Voltammograph connected to a RXY-MF8050 recorder. Amperometric measurements were performed with the help of a LC-4B potentiostat/amplifier, all obtained from Bioanalytical Systems (West Lafayette, IN).

A photosensor module type H5783-01 from Hamamatsu Photonics K K. (Bridgewater, NJ) with broad spectral response (300 to 820 nm range) was attached to the lower part of the cell (just in front of the glass window shown in Figure 2) for light detection. This type of detector exhibits high sensitivity, wide dynamic range, and fast response. Dimensional outlines, module functional diagram, and wiring for sensitivity adjustment are shown in Figure 4. The +11.5 to 15.5 V power supply for sensitivity adjustment was designed by

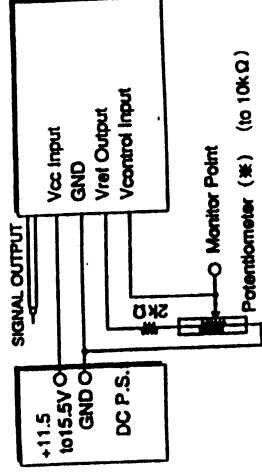
Dimensional Outline (Unit: mm)



Module Functional Diagram



Wiring For Sensitivity Adjustment



※ It is recommended to monitor the control voltage by a multimeter and adjust the voltage within maximum +1.0V. Adjust the potentiometer to set the output.

FIGURE 4. Dimensional outline, module functional diagram, and wiring for sensitivity adjustment (resistance programming) for the Hamamatsu H5783-01 photosensor module.

Carl Mattson and built by David Counts of the Toxic Vapor Detection/Contamination Control Laboratory.

2.2. CHEMICALS AND SOLUTIONS

All chemicals were of analytical reagent grade and used as received, except as noted. Nafion as a 5% (w/w) solution in a mixture of low molecular weight aliphatic alcohols containing 10% water or in a Teflon reinforced membrane (0.007 inch thick) was obtained from Aldrich (Milwaukee, WI). Perchloric acid, sodium perchlorate, 2,2'-bipyridine and the 2,2'-bipyridine ruthenous dichloride were from GFS Chemicals (Columbus, OH). Ruthenium(III) chloride trihydrate was obtained from Aldrich.

2.3. PREPARATION OF THE NAFION-IMMOBILIZED $\text{Ru}(\text{bpy})_3^{2+}$ POLYMERIC FILM ON TOP OF THE PLATINUM SCREEN

The working electrode was assembled by cementing one of the two platinum rings to the copper contact (C in Figure 2) with a fine suspension of silver metal in butyl acetate (GC Electronics, Rockford, IL, distributed by Allied Electronics, Fort Worth, TX) and allowing the organic solvent to air-evaporate. This silver print provides good electrical conductivity, keeps the ring in place, and protects the copper contact. A Nafion solution was deposited onto the screen with the aid of a small brush (of the type used for painting in toy-model construction) until it appeared covered by a fine layer of polymeric film. After air-drying, helped with the use of a heat gun, the film was swollen by immersion of the screen for a minimum of 2 to 4 hours into a 1.0×10^{-3} M $\text{Ru}(\text{bpy})_3^{2+}$, 2 Cl⁻ or $\text{Ru}(\text{bpy})_3^{3+}$, 3 Cl⁻ aqueous solution (on occasions this contact was allowed to last overnight). The assembled working electrode (see Figure 3) was then incorporated into the cell. The screen was kept moisten with electrolyte solution by inserting two or three circles of cellulosic cloth filter (19 mm in diameter and 1 mm thick) between the screen and the upper cell body.

III. RESULTS AND DISCUSSION

3.1. CYCLIC VOLTAMMETRIC STUDIES

Cyclic voltammetry is a powerful technique for the characterization of electron exchange processes taking place at electrode surfaces [9]. Figure 5 shows the typical cyclic voltammogram for $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on Nafion. For thin layer electrochemistry of immobilized species performed under reversible electrochemical conditions (fast electron exchange) the anodic and cathodic peak potentials coincide; with the conditions used here a peak separation of 0.103 V indicates a quasi-reversible behavior (i.e. a moderate slow rate of electron exchange). As expected, peak heights increased with increasing scan rate from 10 to 200 $\text{m V}\cdot\text{s}^{-1}$, and peak separation also increased with increasing scan rate. A plot of cathodic peak current as a function of the square root of the scan rate follows a linear trend with regression coefficients in the 0.975 to 0.990 range, as it should be expected. The voltammogram of Figure 5 was obtained by casting a film of Nafion-immobilized $\text{Ru}(\text{bpy})_3^{2+}$ on a small platinum disk electrode. Voltammograms at scan rates higher than 150 $\text{m V}\cdot\text{s}^{-1}$ developed cathodic and anodic currents out of scale with the instrument used here.

Films deposited on the platinum screen, and assembled as the working electrode in the prototype sensor, exhibit, however, voltammograms as the one illustrated in Figure 6. The appearance of a single reduction peak indicates: (a) the electrochemical process tends toward "irreversibility", i.e. the electron-exchange mechanism is even slower on the screen than on a small platinum electrode directly immersed into a solution of supporting electrolyte (this may be the result of the geometry of the cell, and/or a relatively poor ionic communication between the cell reservoir and the platinum screen), and (b) oxidation does take place during the anodic scan, and $\text{Ru}(\text{bpy})_3^{3+}$ forms in the vicinity of the platinum filaments constituting the screen. Direct visual observation of screens kept for 24 h at a

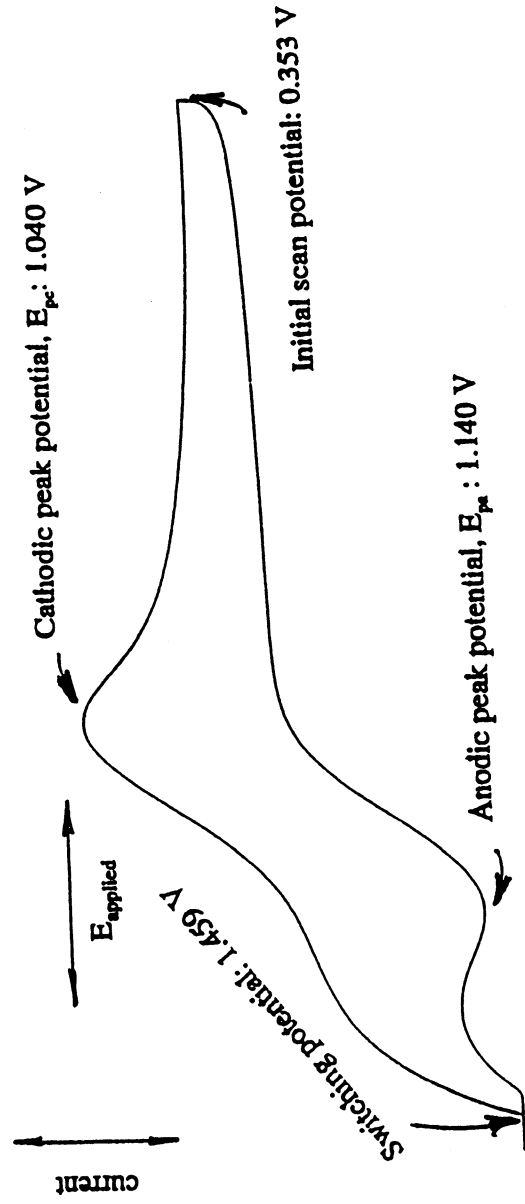


FIGURE 5. Typical cyclic voltammogram of $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on Nafion. Platinum disk electrode (2 mm diameter); supporting electrolyte: $0.025 \text{ M KH}_2\text{PO}_4$, $0.10 \text{ M K}_2\text{SO}_4$, $\text{pH} = 4.04$. Scan rate: $100 \text{ mV}\cdot\text{s}^{-1}$. Reference electrode Ag/AgCl , 3 M NaCl .

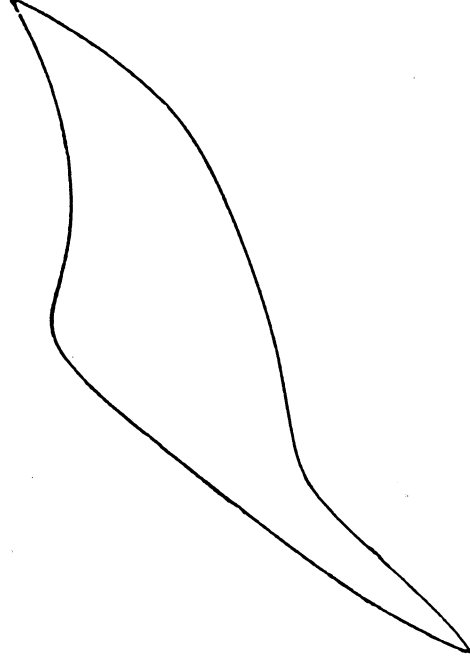


FIGURE 6. Cyclic voltammogram of Nafion-immobilized $\text{Ru}(\text{bpy})_3^{2+}$ on the platinum screen of the sensing unit. Supporting electrolyte: $0.025 \text{ M KH}_2\text{PO}_4$, $0.10 \text{ M K}_2\text{SO}_4$, $\text{pH} = 4.03$. Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$. Initial scan potential: 0.148 V . Switching scan potential: 1.54 V . Reference: Ag/AgCl , 3 M NaCl .

potential of +1.25 to +1.42 V vs. the Ag/AgCl, 3 M NaCl electrode, however, did not show evidence of external green Ru(bpy)₃³⁺ formation. This observation and the cyclic voltammogram of Figure 6 suggest that oxidation occurs in the interior part of the polymeric film deposited on the screen. Microscopic observation of a screen oxidized at constant potential did not rule out such a possibility; it rather pointed in such direction in some isolated portions of the screen. This indicates the development of preferential paths for electron transfer within the screen.

In the suspicion that high concentrations of positively charged metal ions present as part of the supporting electrolyte can compete with ruthenium(II/III) for occupancy of the negatively charged sulfonate groups on Nafion, a cyclic voltammetric test was performed with the small platinum electrode coated with a film of Nafion-immobilized Ru(bpy)₃²⁺. The result of this test is shown in Figure 7. Although rather slowly, supporting electrolytes containing rather high ionic strength removed the ruthenium complex from the Nafion film. The rate of leaching, however, does not seem of consequence with electrolytes of moderate ionic strength which are most likely to be used in sensor development.

3.2. STUDY OF IONIC COMMUNICATION BETWEEN THE SCREEN AND THE SUPPORTING ELECTROLYTE RESERVOIR

As indicated earlier, the need for compensation in solvent evaporation and for the sensor unit to keep a wet environment on both sides of the screen requires a compromise between ionic communication and solution percolation. Cyclic voltammetry, again, provided the guiding information. The original design gave very poor ionic mobility impairing the redox process at the platinum screen. As shown in Figure 8A, no clear redox peaks were visible. By increasing the diameter of the hole that provides communication with the cellulosic pads/screen area, or by decreasing the number of cellulosic pads, the reduction peak of oxidized ruthenium became apparent (Figures 8B and 8C). Although the optimum

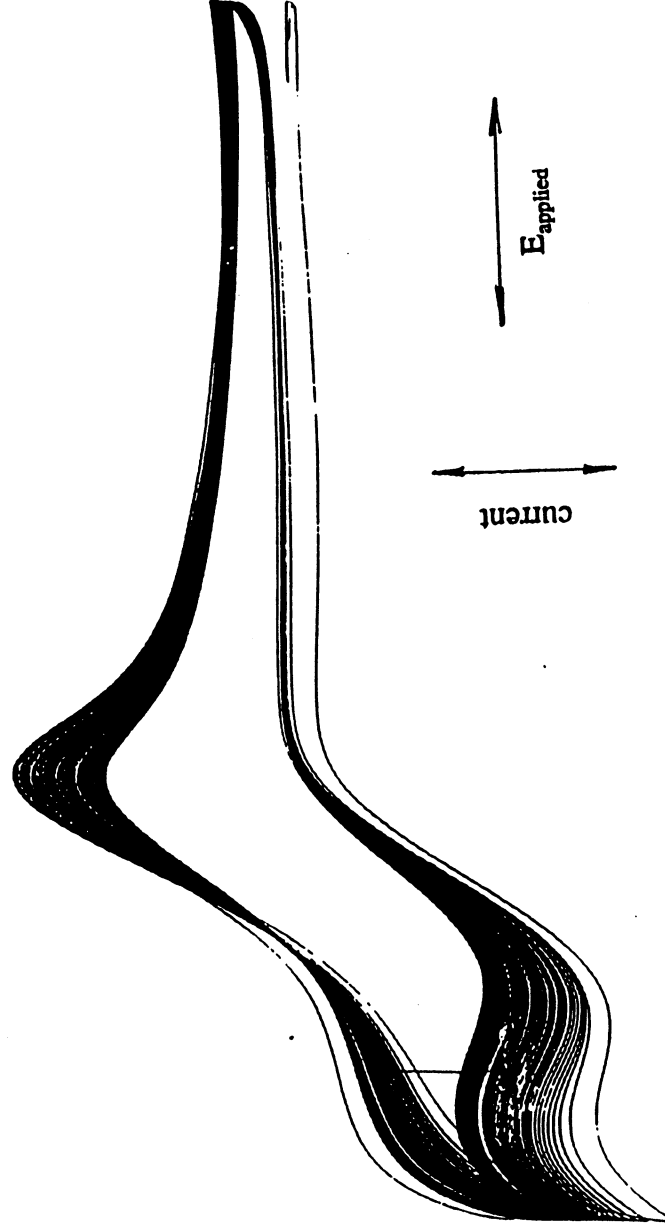


FIGURE 7. Successive cyclic voltammograms of $\text{Ru}(\text{bpy})_3^{2+}$ immobilized on Nafion showing the slow removal of complex by a high ionic strength supporting electrolyte ($0.10 \text{ M KH}_2\text{PO}_4$, $0.50 \text{ M K}_2\text{SO}_4$, $\text{pH } 4.03$). Working electrode: platinum disk of 9 mm diameter. Scan rate: $100 \text{ mV}\cdot\text{s}^{-1}$. Initial scan potential: 0.343 V . Switching potential: 1.435 V . Reference electrode: Ag/AgCl , 3 M NaCl . Leaching is shown by a decrease in current in successive scans. Time between scans: 15 minutes .

compromise was not reached for lack of time, the direction to arrive at such an optimum has been shown.

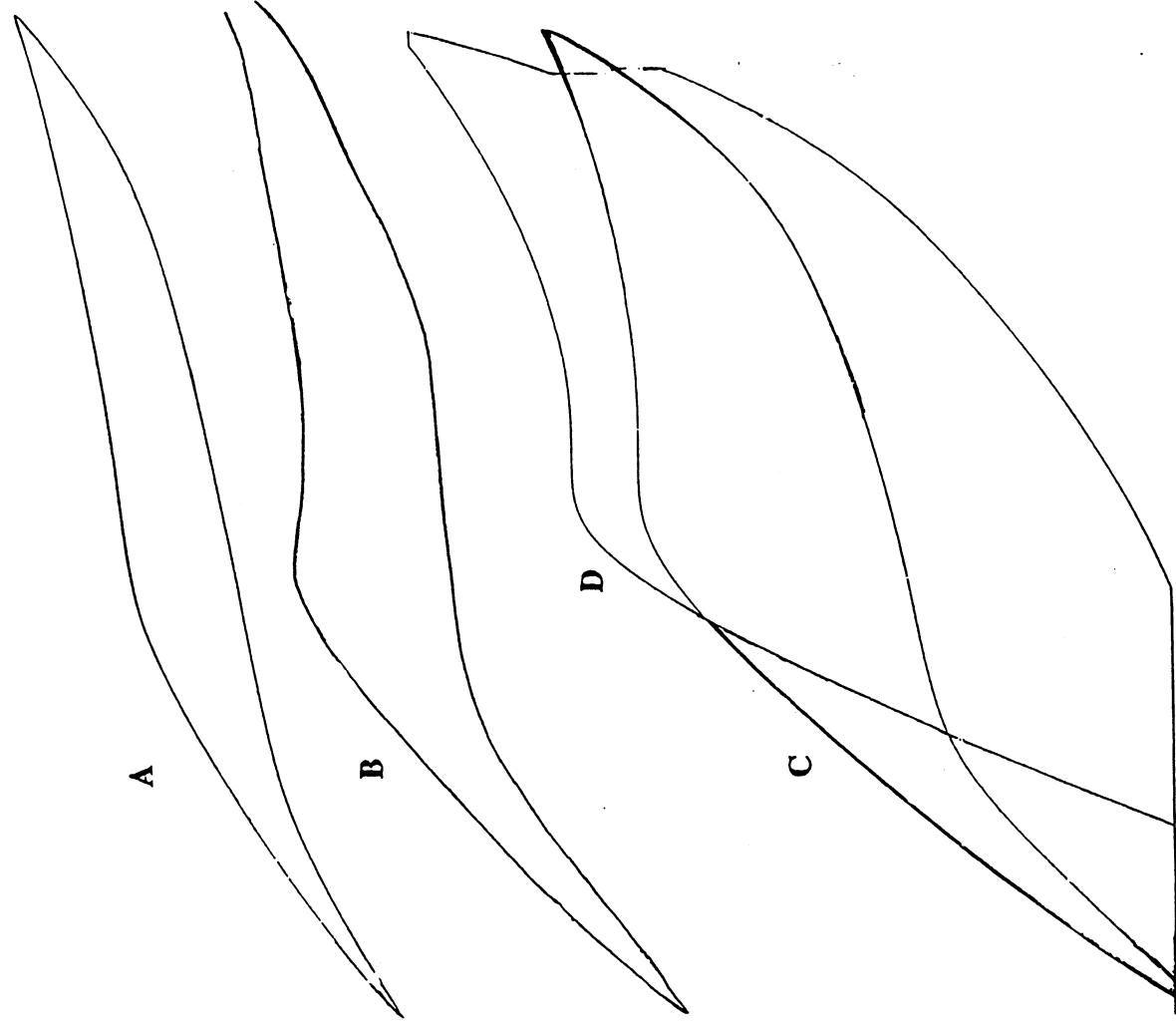


FIGURE 8. Effect of cellulosic filter pads inserted between the bottom of the upper cell body and the platinum screen and the diameter of the perforation at the bottom of the upper cell body which communicates the screen area with the supporting electrolyte reservoir. **A:** 1 mm diameter communicating channel, 4 filter pads; **B:** 1 mm diameter communicating channel, 3 filter pads; **C:** 2 mm diameter communicating channel, 2 filter pads; **D:** 2 mm diameter communicating channel, 3 filter pads. Scan rates: 50 mV. s⁻¹. Initial scan potential: 0.398 V. Switching potential: 1.400 V vs. Ag/AgCl, 3 M NaCl.

IV. CONCLUSIONS

4.1. OBSERVATIONS RESULTING FROM THE PERFORMED WORK

1. Both, $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ immobilize very well and easily on Nafion deposited on solid platinum surfaces as well as on the platinum screen that is part of the prototype sensing unit which was the focus of these studies. The thickness of polymeric films can be controlled within certain limits.
2. Cyclic voltammetry shows that: (a) oxidation takes place on the screen, because no oxidation peak is observed, but a reduction peak is. No reduction peak should be observed if oxidation did not take place, (b) the redox process is slow (polymer films in direct contact with stirred supporting electrolyte solutions show quasireversible electrochemical behavior, and films immobilized on the platinum screen revealed irreversible electrochemistry), (c) high concentrations of positive ions (from supporting electrolyte solutions) compete for the $-\text{SO}_3^-$ sites on Nafion, and remove from the polymeric backbone the immobilized ruthenium complex, and (d) the ionic communication with the present sensor geometry is not fast enough and may be the rate determining step responsible for the observed irreversible electrochemistry (increasing the size of the communicating channel and/or the flow of supporting electrolyte increases the apparent overall rate of electron exchange).
3. The oxidation of all ruthenium(II) centers (when $\text{Ru}(\text{bpy})_3^{2+}$ is the immobilized species) has been unsuccessful. No green color was visually observed when keeping

overnight at a constant applied potential of +1.38, +1.42, +1.55, and even +2.00 V vs. a Ag/AgCl. 3 M NaCl electrode as reference. Potentials of +1.55 and +2.00 revealed considerable oxidation around the copper contact (point C in Figure 2) and the electrolysis of water. Typically, currents of a few tenths of a mA were detected during the oxidation process. This was observed even with very thin polymeric films. However, after an oxidation attempt, and in the process of removing the film, the polymeric material close to the screen appeared pale green. The final portions of washing liquid (a 1:3 solution of 20% nitric acid and acetone) were also of very pale greenish coloration). This and the cyclic voltammetric observations listed above lead to the conclusion that oxidation is limited to the interior part of the polymeric film in contact with the platinum screen. This seems consequential of a very slow charge hopping within the polymeric film.

4. The $\text{Ru}(\text{bpy})_3^{3+}$ complex ion can be prepared reacting RuCl_3 with a large excess of 2,2'-bipyridine in aqueous solution (final pH between 3 and 4).

5. The idea of amperometric monitoring and electrochemical regeneration of $\text{Ru}(\text{III})$ centers is limited to very thin films. Consequently, a sensor based on the strategy studied here would provide very low limits of detection, but restrict the linear response to concentration change. A sensor can be built using $\text{Ru}(\text{bpy})_3^{3+}$ /Nafion films prepared by chemical means. Low limits of detection and wide dynamic concentration range should be accessible by this route. The films will require, however, periodic chemical restoration of the ruthenium central metal ion to the III oxidation state.

4.2. SUGGESTIONS FOR FURTHER WORK

1. Verification that Nafion-immobilized $\text{Ru}(\text{bpy})_3^{3+}$ prepared by direct reaction between Ru^{3+} and 2,2'-bipyridine produces chemiluminescence upon reaction with hydrazine.
2. Preparation of very thin films for efficient electrochemical regeneration of $\text{Ru}(\text{III})$ centers.
3. Optimization of ionic communication/flow of supporting electrolyte solution and pH optimization (compromised pH) for simultaneous operation of both chemiluminescence and electrochemical processes. The compromised pH is needed because the electrochemical process is favored by a pH of or below 4 and the chemiluminescence process operates better at pH values higher than 7.

4.3. ALTERNATIVES OPEN TO CONSIDERATION

1. Search for an inert support other than Nafion for anchoring of the ruthenium complexes.
This inert support should provide reasonably fast charge transfer conditions.
2. Explore the development of a hybrid sensing strategy based on a segmented continuous-flow approach of alternate liquid and gas plugs. This approach should permit operation at the optimum pH for chemiluminescence as well as electrochemical restoration of $\text{Ru}(\text{III})$ centers.

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