1980

# The removal of organic films which are formed on platinum electrods during the anodic detection of phenolic compounds in aqueous solution

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# THE REMOVAL OF ORGANIC FILMS WHICH ARE FORMED ON PLATINUM ELECTRODES DURING THE ANODIC DETECTION OF PHENOLIC COMPOUNDS IN AQUEOUS SOLUTION

*Iowa State University* PH.D. 1980

# The removal of organic films which are formed on platinum electrodes during the anodic detection of phenolic compounds in aqueous solution

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1980

TABLE OF CONTENTS


| | | Page |
|---|---|---|
| I. | INTRODUCTION | 1 |
| II. | LITERATURE REVIEW | 3 |
| | A. Distribution, Production and Uses of Phenols and Chlorinated Phenols | 3 |
| | B. Contamination of Chlorophenols by Dioxanes | 6 |
| | C. Determination of Phenols | 8 |
| | D. Chemical Oxidation of Phenol | 12 |
| | E. Electrochemical Oxidation of Phenols | 15 |
| III. | THEORETICAL CONSIDERATIONS | 18 |
| | A. Reactions of Radicals | 18 |
| | 1. Characteristics of phenoxy radicals | 18 |
| | 2. Hetero-radical reactions | 19 |
| | 3. Homo-radical reactions | 21 |
| | 4. Oxidation to the phenoxonium ion | 23 |
| | 5. Reactions with solvent | 24 |
| | 6. Summary | 25 |
| | B. Response of Amperometric Detectors | 26 |
| | 1. General treatment of mass transfer | 26 |
| | 2. Problems associated with tubular flow-through electrodes | 27 |
| | 3. A wire flow-through electrode | 28 |
| | 4. Summary | 31 |
| | C. Coulometric Electrodes | 34 |
| | 1. General principles | 34 |
| | 2. Simultaneous reactions | 36 |
| | 3. Coupled reactions | 37 |
| | 4. Summary | 38 |
| IV. | APPARATUS AND REAGENTS | 40 |
| | A. Flow-injection Analyzers | 40 |
| | B. Flow-through Detectors | 51 |
| | C. Rotated Disc Electrodes | 54 |
| | D. Potentiostat | 57 |
| | E. Miscellaneous Apparatus | 58 |
| | F. Reagents and Chemicals | 59 |

| | | Page |
|---|---|---|
| V. | EXPERIMENTAL PROCEDURES | 60 |
| | A. Flow-injection Amperometry | 60 |
| | B. Coulometry | 61 |
| | C. Voltammetry | 62 |
| | D. Instrumental Characterization of Phenolic Films | 63 |
| | 1. Microscopic examination | 63 |
| | 2. Spectroscopic analysis | 63 |
| | E. Cleaning Procedures | 63 |
| | 1. Disc electrodes | 63 |
| | 2. Flow-through electrodes | 65 |
| | 3. Other methods | 66 |
| VI. | RESULTS AND DISCUSSION | 67 |
| | A. Evaluation of Wire Detector | 67 |
| | B. Flow-injection Amperometry of Phenol | 73 |
| | C. Flow-injection Coulometry | 91 |
| | D. Voltammetry | 103 |
| | E. Instrumental Characterization of Phenolic Films | 125 |
| | 1. Microscopic examination | 125 |
| | 2. Infrared spectroscopy | 130 |
| | 3. Mass spectroscopy | 137 |
| | F. Conclusions | 138 |
| VII. | ANALYSIS OF WATER FOR PHENOLS | 143 |
| | A. Introduction | 143 |
| | B. Chromatography | 143 |
| | C. Analysis of Drinking Water | 161 |
| | D. Conclusions | 164 |
| VIII. | SUMMARY | 172 |
| IX. | SUGGESTIONS FOR FUTURE WORK | 174 |
| X. | LITERATURE CITED | 176 |
| XI. | ACKNOWLEDGEMENTS | 186 |

# LIST OF FIGURES

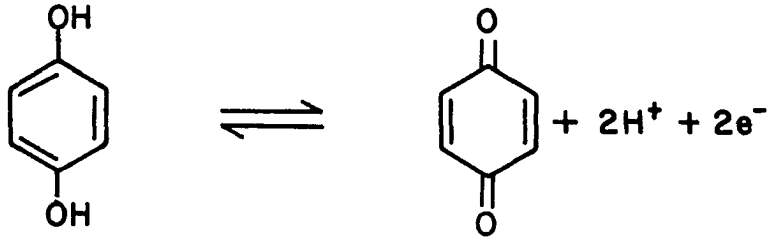

| | | Page |
|---|---|---|
| Figure 1. | Wire flow-through detector | 30 |
| Figure 2. | Annular electrode | 33 |
| Figure 3. | Flow injection analyzer | 42 |
| Figure 4. | Flow control valve | 44 |
| Figure 5. | Actual flow rate versus meter reading for Gilmont flow meter | 46 |
| Figure 6. | Liquid chromatographic analyzer | 48 |
| Figure 7. | Flow rate versus pump setting for Milton-Roy pump | 50 |
| Figure 8. | Tubular detector | 53 |
| Figure 9. | Modified wire detector | 56 |
| Figure 10. | Log of detector efficiency versus log of flow rate for wire detector | 70 |
| Figure 11. | Response of wire detector to repetitive injections of iodide | 72 |
| Figure 12. | Static voltammagram of phenol at a platinum electrode | 76 |
| Figure 13. | Static voltammagram of phenol at a glassy carbon electrode | 78 |
| Figure 14. | Static voltammagram of phenol at a conducting polymer electrode | 80 |
| Figure 15. | Static voltammagram of phenol at a platinum electrode | 82 |
| Figure 16. | Response of wire detector to repetitive injections of phenol | 85 |
| Figure 17. | Effect of electrode deactivation on the anodic detection of phenol and bromide | 87 |
| Figure 18. | Anodic charge which passed due to injections of a standard bromide solution versus the total charge which has passed due to phenol oxidation | 90 |

| | | Page |
|---|---|---|
| Figure 19. | Electron microphotograph of a mechanically polished platinum disc electrode | 93 |
| Figure 20. | Efficiency of coulometric detector versus flow rate | 96 |
| Figure 21. | Observed value of n for phenol versus flow rate | 98 |
| Figure 22. | Observed value of n for phenol versus log of phenol concentration | 100 |
| Figure 23. | Observed value of n for o-cresol versus flow rate | 102 |
| Figure 24. | Response of a platinum disc electrode to reduction of Fe(III) at various stages of electrode inactivation by the anodic oxidation of phenol | 105 |
| Figure 25. | Response of a platinum disc electrode to reduction of Fe(III) at various stages of electrode reactivation | 107 |
| Figure 26. | Residual currents for a clean platinum disc electrode | 111 |
| Figure 27. | Residual currents for a deactivated platinum disc electrode | 114 |
| Figure 28. | Effect of phenolic film on oxygen reduction at a platinum cathode | 117 |
| Figure 29. | Effect of phenolic film on oxygen reduction at a platinum cathode in the presence of Cu(II) | 119 |
| Figure 30. | Effect of phenolic film on oxygen reduction at a platinum cathode in the presence of iodide | 121 |
| Figure 31. | Increase in electrode activity versus cleaning potential | 123 |
| Figure 32. | Electron microphotograph of a platinum electrode covered with a phenolic film | 127 |
| Figure 33. | Electron microphotograph of a partially cleaned platinum disc electrode | 129 |

| | | Page |
|---|---|---|
| Figure 34. | Electron microphotograph of a platinum disc electrode with a partially healed phenolic film | 132 |
| Figure 35. | Electron microphotograph of a platinum disc electrode with a completely healed phenolic film | 134 |
| Figure 36. | Infrared spectrum of polymeric material | 136 |
| Figure 37. | Chromatographic separation of chlorinated phenols | 146 |
| Figure 38. | Effect of column dilution | 147 |
| Figure 39. | Response of wire detector to 0.71 picomoles of phenol | 150 |
| Figure 40. | Response of liquid chromatographic analyzer to 142 picomoles of phenol | 152 |
| Figure 41. | Response of liquid chromatographic analyzer to selected phenols | 155 |
| Figure 42. | Response of liquid chromatographic analyzer to an n-butyl acetate extract of a phenol solution | 157 |
| Figure 43. | Improved chromatographic separation of chlorinated phenols after treatment of chromatographic resin with n-butyl acetate | 159 |
| Figure 44. | Response of liquid chromatographic analyzer to drinking water | 163 |
| Figure 45. | Response of liquid chromatographic analyzer to triply distilled water | 166 |
| Figure 46. | Response of liquid chromatographic analyzer to 1.0 ppm phenol in triply distilled water | 168 |
| Figure 47. | Response of liquid chromatographic analyzer to 1.0 ppm phenol in drinking water | 170 |

# I. INTRODUCTION

The electrochemical activity of organic species in aqueous solution ranges from those for which the reaction is reversible to compounds which completely lack electrochemical activity. The hydroquinone-quinone system is probably the best known of all organic oxidation-reduction couples with a reversible reaction at platinum electrodes. The discovery, in the early 1920's, that the electrode potential of this half reaction is dependent on the hydrogen-ion activity of the solution, as illustrated by equation 1, led to an acceptable instrumental method for the measurement of pH. The hydroquinone-quinone electrode was used routinely for the electrometric measurement of pH during the second quarter of this century (1).




I

Although the hydroquinone-quinone couple is considered reversible and exhibits predictable electrochemical behavior, it is among the relatively few organic systems which react in this manner. Of those organic compounds which are at least partially soluble in aqueous solution, a much more common observation is an irreversible reaction with deactivation of the electrode caused by adsorption of the products of the electrochemical reaction. This phenomenon of deactivation is commonly referred to as "passivation", "blocking", "poisoning", or "fouling" of the electrode.

Electrode deactivation is a serious problem which is not restricted to the electroanalysis of organic species. The presence of organic compounds may also affect the electrochemical reactions of inorganic species, which normally react in a reversible manner.

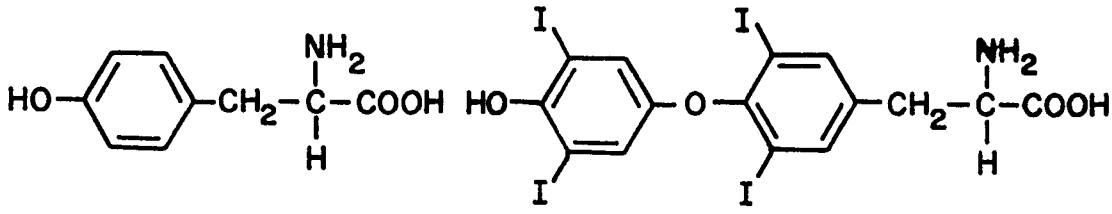
One particular class of compounds which is notorious for its ability to deactivate solid electrodes during electrochemical oxidation is the monohydroxy derivates of aromatic compounds. This class of compounds is generally referred to as "phenols". It should be noted that this name is also commonly used in reference to the polyhydroxy derivatives of aromatic compounds. This thesis is concerned only with the monohydroxy derivatives of benzene. In particular, the electrochemical behavior of phenol itself is described. This work was extended to the chlorinated phenols to demonstrate the applicability of the technology and electroanalytical methodology developed for phenol.

The work which is described in this thesis demonstrates that an amperometric detector is applicable for the flow-injection analysis of water for phenol and chlorinated phenols. An electrochemical detector is described which allows the determination of phenol in aqueous solutions at the sub-picomolar level. A method is described for the in situ reactivation of platinum electrodes which have become deactivated by the adsorption of the products of the electrochemical oxidation of phenols. Finally, a chromatographic procedure is described which achieves the rapid separation and determination of phenol and chlorinated phenols in aqueous samples.

# II. LITERATURE REVIEW

## A. Distribution, Production and Uses of Phenols and Chlorinated Phenols

Unsubstituted phenol seldom, if ever, occurs in nature. Although phenol can be produced in limited quantities from the distillation of coal, there appears to be some question as to whether phenol is actually separated from the coal oils during the distillation process or is produced by chemical reaction during distillation (2). It is common to find substituted phenols present throughout the biological world at low levels (3). Although hormones are substituted phenols and phenols are found in body tissues and intercellular fluids (4-6), biologists are most familiar with the phenolic entities tyrosine and thyroxine (7) which are shown below.



Tyrosine Thyroxine

In the industrial world, the manufacture of phenol and its derivatives is very big business. It is estimated that nearly 1.5 million tons of phenol will be produced in the United States in 1979 (8). The two major reactions used to produce phenol are: 1) peroxidative cleavage of cumene (isopropyl benzene) with acetone as a co-product; and 2) the reaction of chlorobenzene with aqueous sodium hydroxide at elevated temperature and pressure, known as the Dow Process (9).

The uses of phenol are varied; however, the majority of the phenol produced is used in the manufacture of plastics, adhesives and synthetic fibers (8). With the large-scale use of any chemical comes the problem of pollution of water supplies. Since most facilities for water treatment in the United States use chlorination as part of their process for treating water (10), it is not surprising that chlorinated phenols are, on occasion, found in potable water supplies. It has been an established fact for many years that just a few parts per billion of phenol can impart an objectional taste to water following marginal chlorination (11-13).

The toxicity of phenol and its chlorinated derivatives has been both a blessing and a problem to mankind. Early in this century investigators noted the toxicity of phenols to both plant and animal life (14, 15). Although they demonstrated that controlled doses of phenol were useful in the treatment of diseases such as gonorrhea and malaria (16, 17), they also reported that injection or ingestion of phenol, or prolonged contact with phenol, could produce serious maladies and even death (15, 18). The need for accurate, reliable and sensitive methods for the determination of phenol and its derivatives soon became apparent.

Baekeland's discovery of plastics derived from the condensation reactions of phenol and formaldehyde (19, 20) led to large-scale industrial use of phenol and the subsequent discharge of phenolic wastes into waterways. The introduction of substituted phenols, particularly chlorinated phenols, as selective biostatic agents, not only added to the total amount of phenol, but also the variety of phenols in the environment.

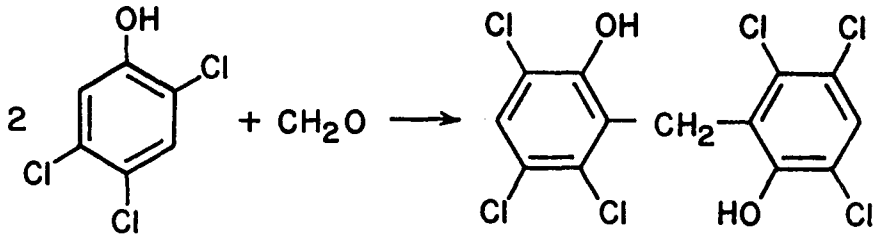
The analysis of aqueous samples for the various chlorinated phenols is becoming increasingly important. These compounds have been identified in ever increasing quantities in water supplies, and in some cases have contaminated entire water reservoirs, both surface and sub-surface. In many cases the source of these pollutants can be traced to indiscriminate, improper or incompetent disposal of chemical wastes (21).

Although these chemicals are considered environmental pollutants, the use of chlorinated phenols has been beneficial to mankind. The introduction of 3,4,6-trichloro-2-nitrophenol into the tributary streams, at a concentration of 30 parts-per-million, virtually eradicated the lamprey eel from the Great Lakes of North America. This predator had threatened to destroy the fishing industry of the entire Great Lakes region (22).

The compound 2,4,5-trichlorophenol has been successfully used as a fungicide and a bacteriocide (23). A derivative of this compound is 2,4,5-trichlorophenoxyacetic acid. This compound, generally referred to as "2,4,5-T", is a naturally occurring plant hormone with herbicidal properties (24, 25). A related compound is 2,4-dichlorophenoxyacetic acid which has similar herbicidal properties and is commonly referred to as "2,4-D". The injection of 2,4-D into old rubber trees has been found to increase latex production (26). Advantage has been taken of the herbicidal properties of the compounds named above in efforts to increase crop production.

Hexachlorophene had been used as a bacteriostatic agent until quite recently (27). It is manufactured by way of an aldol condensation similar

to the reaction used to manufacture Bakelite (28-30). This reaction is shown in equation II. Dichlorophene is another product of the condensation



II

of a chlorinated phenol with formaldehyde. This product is used as an anthelmintic agent and has been found to be effective in the treatment of human cestodiasis (31). Like so many other drugs, dichlorophene produces some undesirable side effects, even when properly administered.

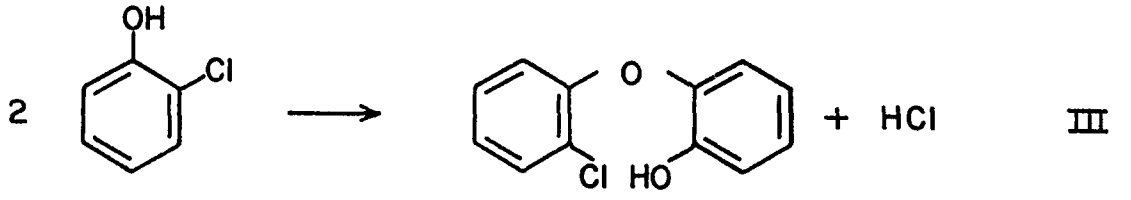
Pentachlorophenol is used on a rather wide scale as a biostatic agent (32). It is usually dissolved in an organic solvent due to its lack of solubility in aqueous systems. Pentachlorophenol is sold in most garden shops and hardware stores for killing vegetation.

It should be noted that not all of the uses of these types of compounds have been with the best of intentions. Thousands of gallons of Agent Orange, a mixture of 2,4-D and 2,4,5-T, and similar chemicals were sprayed on the jungles of Viet Nam during the early 1960s by the United States Air Force. Defoliation of the jungles was desired to decrease the military advantage which the dense jungle offered to opposing forces (33).

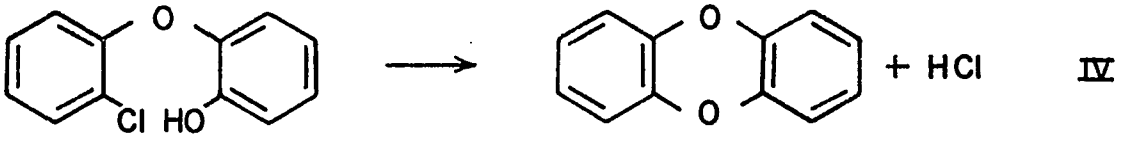
## B. Contamination of Chlorophenols by Dioxanes

The major problem with the use of chlorinated phenols for beneficial purposes is contamination of these products by dibenzoparadioxanes,

commonly referred to as "dioxins". Dioxanes appear to form spontaneously whenever a chlorine atom is in a position ortho to the hydroxy group of the phenol. The sequence of reactions necessary to form the paradioxane is shown in equations III and IV. Although these reactions are nearly identical, the reaction shown in equation III can occur with meta and



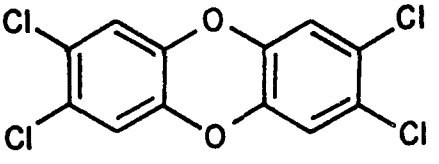

III




IV

para-chlorophenols, while the reaction shown in equation IV cannot occur due to steric hindrance.

The product of the reaction shown in equation IV is dibenzoparadioxane which is not particularly toxic. The toxicity of this particular dioxane is greatly increased with chlorine substitution on the aromatic ring. The most toxic of the 75 possible chloro-isomers of dibenzoparadioxane is 2,3,7,8-tetrachlorodibenzoparadioxane which is shown below. This compound can be spontaneously formed from 2,4,5-trichlorophenol and is one of the



most toxic and mysterious substances known. The $LD_{50}$ level of this compound is as little as 600 nanograms per kilogram of body weight in white mice. Although significant damage in the mice can be found in the hepatic, renal and central nervous systems at this level, no single system is damaged enough to cause death. The toxicity of this compound is observed to vary widely from one species of test animal to another (34). Information concerning the effect of 2,3,7,8-tetrachlorodibenzo-paradioxane on humans is virtually non-existent, as is information about long-term exposure at sub-lethal levels. Exposure to 2,3,7,8-tetra-chlorodibenzoparadioxane has been associated with a skin condition known as "chloracne" (35).

The problem with the use of chlorinated phenols and their derivatives appears to be one of weighing the "good" against the "evil": the "good" being the benefits which can be derived from the biostatic properties of these compounds, and the "evil" being the harmful side effects of the agents used. Some of these harmful effects are the result of contaminants which are present in the starting materials, or are formed in the manu-facturing process of desired compounds. It is interesting at this time to note that 2,3,7,8-tetrachlorodibenzoparadioxane can be spontaneously formed in 2,4,5-trichlorophenol, which is the starting material from which hexachlorophene is manufactured.

## C. Determination of Phenols

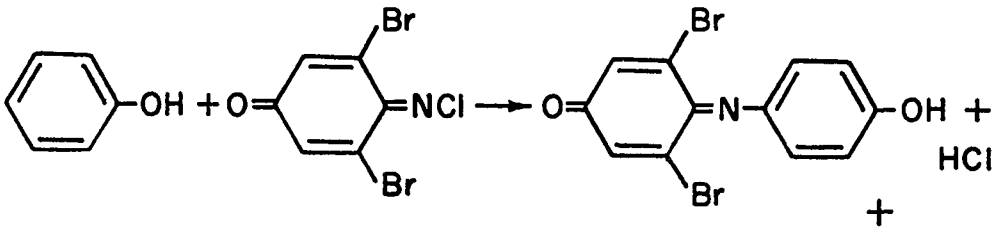
A gravimetric procedure for the determination of phenols was reported in 1871 by Landholt which relied upon the rapid and quantitative reaction

between phenol and bromine, and the insolubility of the resulting brominated product (36). The precipitate was then separated, dried and weighed. Another gravimetric procedure for the determination of phenols, published in 1889 by Messinger and Vortman, involved the iodination of the phenols and was used for the determination of a large number of phenols (37, 38).

Koppeschaar improved upon the bromination procedure by the use of in situ generation of bromine by the reaction of bromate with bromide in acidic solution. He also discovered that the quantity of phenol in solution could be determined by measuring the amount of bromine which remained in solution after the phenol had reacted. This was accomplished by adding excess potassium iodide and titrating the iodine which was generated with a standard solution of sulfite. Furthermore, Koppeschaar noted that this method could be used to measure phenol at levels where the solubility of the bromophenol was not exceeded (39). Mascarelli suggested that the reaction should be carried out in alkaline solution (40); however, the later work of Olivier supported Koppeschaar's method (41). Since the work of Koppeschaar, the only significant alteration of the procedure has been the substitution of thiosulfate for sulfite as the standard reducing agent. This method, and variations of it, are still used today (42, 43). The method can be applied with an accuracy of a few parts-per-thousand at a concentration of 0.01 M.

One of the oldest color-producing reactions of phenol is its reaction with ferric ion (44). The colorimetric detection of phenol based on this

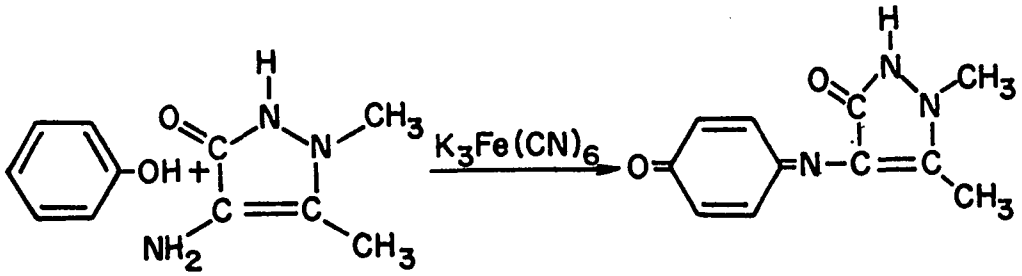
reaction is still useful in isolated situations. In general, colorimetric methods are the so-called "standard methods" for the determination of phenols in aqueous samples. In the Gibbs Reaction, phenol is coupled with 2,6-dibromoquinonechloroimide as illustrated in equation V. The dibromoindophenol formed has a blue color with an absorbance maxima at




V

620 nm. Although this method works well for phenol, it does not work well for para-substituted phenols (45).

The method prescribed by the American Society for Testing Materials (ASTM) for measuring phenols is a colorimetric method which employs 4-aminoantipyrine (46). Upon reaction with phenol, as shown in equation VI, a red dye is formed. The detection limit with this method is 0.10




VI

to 2.0 parts per million (47). The method of the ASTM cannot be used to detect those phenols which are substituted in the para position by aryl, alkyl, nitro, benzoyl, nitroso or carbonyl groups (48).

Nitrous acid will react with phenols in an alcoholic solution of ammonium hydroxide to give a colored quinoid salt. This method has the same sensitivity as the ASTM method using 4-aminoantipyrine (47). Other reagents which have been used in the colorimetric determination of phenols include diazotized sulfanilic acid (49), paradimethylaminobenzaldehyde (50), diazotized para-nitroanaline (51), 3-methyl-2-benzothiazalinone hydrozone (52), titanium salts in chloroform (53), an ethanolamine-molybdate complex (54) and meta-vanadic acid (55). Although these methods are sensitive, they are not ideal. The Gibbs Method is not specific for phenols and may require as long as 24 hours for color development. The ASTM Method may require 4 hours for full color development. The nitrosophenol method may require 24 hours for color development and suffers from a lack of reproducibility (56).

A variety of spectroscopic methods, other than the colorimetric methods mentioned above, have been employed for the determination of phenols. These include ultraviolet spectroscopy (57-67), infrared spectroscopy (68-70), chemiluminescence (71), fluorometry (57), and indirect atomic absorption spectroscopy (72). Of these, ultraviolet spectroscopy has been the most successful; however, other adsorbing species will present serious interferences and this method is not particularly sensitive.

A sensitive fluorometric method has been reported by Afghan et al. (57). This method employs an extraction with n-butyl acetate followed by fluorometric detection. Good sensitivity was reported; however, Raman emission by water at the wavelength of detection does interfere.

Phenols can be determined by non-aqueous potentiometric and amperometric titration (73-76), but these methods do not have appreciable sensitivity. Morris developed an indirect amperometric method for phenols which did show good sensitivity (77).

Many gas chromatographic methods have been developed for the determination of phenols (78-81). Fritz, Chang and Chriswell used an extraction procedure to allow for the use of gas chromatography in their analysis of water for phenol (81); however, the extraction efficiency was poor for many phenols and appeared to be affected by their aqueous solubility (82). These procedures do not appear to be applicable at concentrations of phenol below 1 part-per-million in all cases. A major part of the problem appears to be an inherent incompatibility of aqueous samples with the detectors employed (83).

## D. Chemical Oxidation of Phenol

One of the characteristics of phenol which is frequently listed in textbooks is the ease with which it can be oxidized (84, 85). One thing which is conspicuously missing from these same textbooks is the identification of the products of the oxidation. This omission is probably due to the fact that the oxidation of phenol is a very complex process. Although a considerable number of reports concerning the oxidation of phenol by various oxidizing agents appears in the literature, the mechanism of the reaction does not seem to be well-understood. The reaction may proceed by way of different mechanisms depending on the identity of the oxidizing agents and the conditions employed.

One of the cleanest oxidizing agents which the chemist has at his disposal is the photon. It should be noted that although the photon is a clean oxidizing agent, insomuch as it leaves no readily detectable reduction product, it does have attributes which make it something less than the ideal oxidizing agent. These attributed include, but are not limited to, the inherent relationship of the complexity of the source of the photon to the control of its oxidizing power; and the fact that the quantum efficiency of the process is dependent upon the variables of the system being studied and the apparatus employed for the photochemical oxidation. The fact remains, however, that a photon which possesses sufficient energy to cause the ejection of an electron from the particular species under study can be thought of as an oxidizing agent.

In 1912, Gibbs was the first to report that phenol is decomposed under irradiation by sunlight (86). Several years later, Sierp and Fransemeier (87), reported that the action of sunlight and bacteria will completely decompose phenol in sewage, presumably to carbon dioxide and water (87). Modern photochemical methods were employed by Land, Porter and Strachan to show that the phenoxy radical is produced by these techniques (88); and Roebber reported the cleavage of the 1,2-carbon-carbon bond in the aromatic ring <u>via</u> photolysis (89).

The choice of oxidizing agent appears to affect the nature of the product of the oxidation of phenol. Those agents which have a peroxide nature, such as hydrogen peroxide, persulfate and peracetic acid, appear to favor hydroxylation of the phenol in question. Those agents which are not of a peroxide nature appear to lead to coupled products.

The oxidation of phenol by persulfate, Elbs Method (90), has been studied by several investigators with regard to mechanistic and synthetic application; however, little, if any, analytical utility has evolved from this reaction (91-94). These investigators agree on the hypothesis that a sulfate radical-anion is involved as an intermediate product.

The action of peracetic acid on phenol has been studied by Böeseken et al. (95, 96) who found a considerable amount of cis-cis-muconic acid in addition to quinone in the mixture of reaction products. It is noteworthy that catechol was not found as a product in this reaction. Cosgrove and Waters (97) found that monobenzoates of catechols are produced by the action of benzoyl peroxide on phenols.

The oxidizing agent most extensively employed in the study of the oxidation of phenol has been hydrogen peroxide. In most studies a catalyst has been found desirable. The list of catalysts includes phosphorus compounds (98-100), ultraviolet light (101), various metal oxyanions (102), transition metal cations (103-105), and chelates of metal ions (106). The most frequently employed catalyst is iron as either the ferrous or ferric ion.

The combination of ferrous ion with hydrogen peroxide is Fenton's Reagent. It is thought that ferrous and ferric ions catalyze the generation of hydroxyl radicals from hydrogen peroxide (107). An earlier report by Wieland and Wilhelm proposed that iron also catalyzes the formation of peroxide from dissolved oxygen in aqueous solutions (108). The major products for the oxidation of phenol by hydrogen peroxide are reported to be catechol, hydroquinone and other hydroxylated species with

the products of coupling reactions being reported in lesser amounts (98, 99, 101, 109-111).

Oxidation of phenol by reagents other than peroxides occurs with extraction of one or more electrons. This type of oxidation reaction appears to favor coupling of the products. The action of permanganate ion on phenol was studied by Dore, Legube and Merlet (112). Many of the products found were those which are produced by coupling reactions. Spencer used sulfatocerate to determine phenol in aqueous solution (113); the method relied on the predictable coupling of phenols. Pummerer employed ferric ion and ferricyanide in his extensive studies on the oxidation of organic species (114, 115). Lead dioxide was employed in the oxidation of ortho-cresol by Goldschmidt, Schultz and Berhard (116). In all of these cases, coupling was observed to be the predominant reaction. Taylor and Battersby summarized the conditions and oxidizing agents which are best suited when the coupling reaction is preferred (117). It should be noted that oxidation of phenol by air, in the absence of catalysts, usually results in the coupling reactions (117, 118).

## E. Electrochemical Oxidation of Phenols

Reports of the electrochemical reduction of phenols can be found in the literature, but such reports are rare (119, 120). Reports of the electrochemical oxidation of phenols are more common, but they are not numerous. The major problem with the electrochemical oxidation of phenols is that intermediate products and/or final products of the reaction tend to

form an insoluble polymeric film which adheres to the electrode surface. This film severely retards the transport of electroactive species to the electrode surface and eventually the electrode is insulated from the conducting solution.

During the second decade of this century, Fichter and co-workers extensively investigated the anodic oxidation of aromatic compounds (121-124). While some soluble products were found in solution, the problem of film formation was not solved and no suggestions were offered for dealing with this problem. Other workers have reported similar problems with the formation of films during the anodic oxidation of phenol and other aromatic compounds on solid electrodes (125-133).

Platinum and graphite electrodes have been used most often in the electroanalysis of organic compounds, but other electrode materials have also been employed (134-138). Many investigators describe an adsorbtion phenomenon at the electrode surfaces, but are not clear whether the adsorbed species is the intact phenol or a product of the anodic reaction (138-140). Other investigators flatly state that the adsorbed species is the phenoxy radical produced by the anodic reaction (125, 127, 129, 131, 132, 141-144). The fate of the phenoxy radical determines the overall course of the anodic reaction and this fate is undoubtedly influenced by the local environment of the radical. Little work has been done to investigate the electrochemical oxidation of phenol since the time of Fichter (cited in 145).

The fact remains that the formation of polymeric films on solid anodes is a serious and persistent problem not only with phenol but also

with other organic compounds. Perhaps the problem is best summarized by Hedenburg and Freiser who studied the anodic oxidation of phenol at a platinum electrode (125):

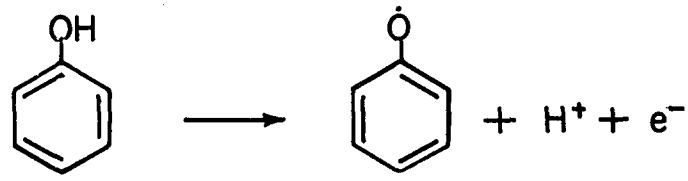
> ...the current rose and then gradually dropped back. If left at this potential long enough, the current dropped back to that of the blank curve. A black deposit was found on the electrode after such treatment. This deposit was insoluble in acetone, dioxane, chromic acid, nitric acid or strong alkali. The formation of the deposit gradually insulated the electrode from the cell, causing the observed current to drop. Attempts to eliminate the formation of the deposit by adding dioxane to the cell and purging with nitrogen failed. The only way found to clean the electrode was to burn off the deposit in the flame of a Bunsen burner for 30 seconds prior to each run.

# III. THEORETICAL CONSIDERATIONS

## A. Reactions of Radicals

### 1. Characteristics of phenoxy radicals

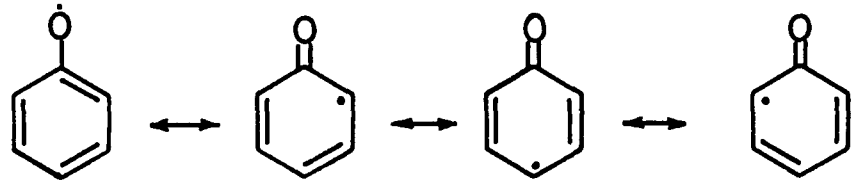
The oxidation of phenol is a complex process which is not well-understood because of the large variety of products which have been identified. The first step in the anodic reaction has been concluded by Gileadi and others (129, 130, 132, 142, 143, 146-148) to be a one-electron oxidation to produce the phenoxy radical as represented by Equation VII. Although this conclusion was based on data obtained for




VII

solid electrodes and may not apply for other oxidizing conditions, it is reasonable to assume that for a multielectron process the electrons are transferred one at a time. Additional evidence for the existence of the phenoxy radical as an intermediate species does exist (149-153).

Since radicals are known to be very reactive in nature, one would not expect a continued buildup of radicals to occur near the surface of the electrode. The fate of the phenoxy radical appears to be affected by its environment. The phenoxy radical is, however, different from many other radicals in that it is stabilized by resonance as shown in equation VIII. This resonance is not only useful in understanding the stability

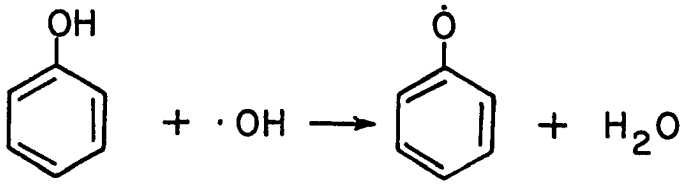


VIII

of the phenoxy radical, but is also helpful in explaining chemical reactions of the radical.

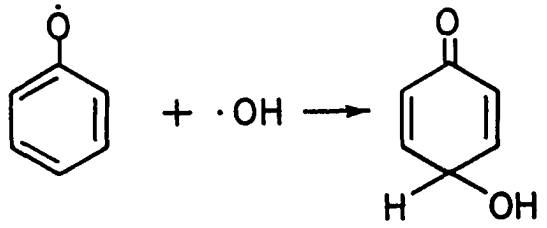
2. Hetero-radical reactions

The simplest reaction which can occur for the phenoxy radical is bond formation with another radical. Consider the reaction of hydrogen peroxide with phenol. The first step is assumed to be the extraction of an electron by a hydroxy radical which is quickly followed by deprotonization of the resulting cation radical. Alternatively, these two steps may occur simultaneously and, taken together, described as a hydrogen-atom extraction as shown in equation IX.




IX

Measurements by ESR spectrometry have proven the existence of the phenoxy radical in reactions of the type shown in equation IX (153). The phenoxy radical can then couple with another hydroxyl radical to form a second intermediate as shown in equation X. This second intermediate product can tautomerize to the corresponding quinone. This reaction

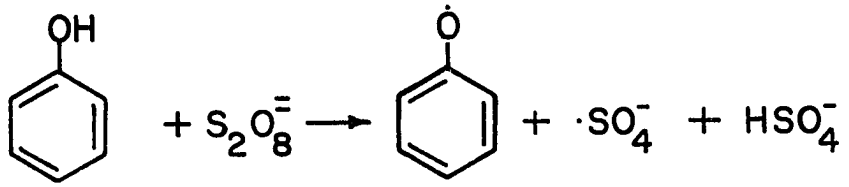



X

sequence seems even more reasonable if one considers the possibility that the hydrogen peroxide molecule enters the hydration sphere of the phenol molecule before dissociating to form the hydroxy radicals. By that mechanism, all the participating species for the entire reaction sequence would be contained within the same hydration sphere.

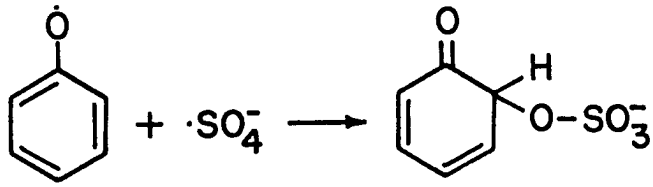
If one considers other peroxides to be simply substituted derivatives of hydrogen peroxide, then ester formation seems reasonable. Monobenzoates of catechols were found as one of the products of the reaction between phenol and benzoyl peroxide (96). During the course of that reaction, the esters formed can also undergo hydrolysis and/or transesterification.

The reaction between phenol and persulfate is also analogous to the case of oxidation by hydrogen peroxide. Equation XI shows the extraction



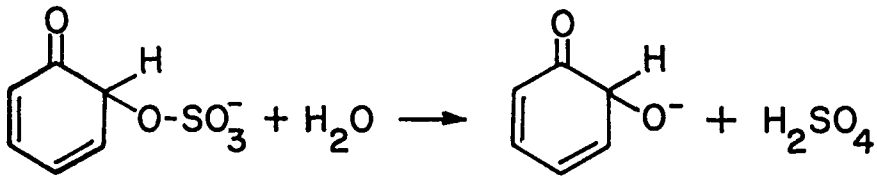
XI

of a hydrogen atom from phenol and the generation of both the phenoxy radical and the radical anion of sulfate. The two radicals can then couple as shown in equation XII (ortho reaction is shown) which produces the phenoxysulfate anion as an intermediate product which can react further



XII

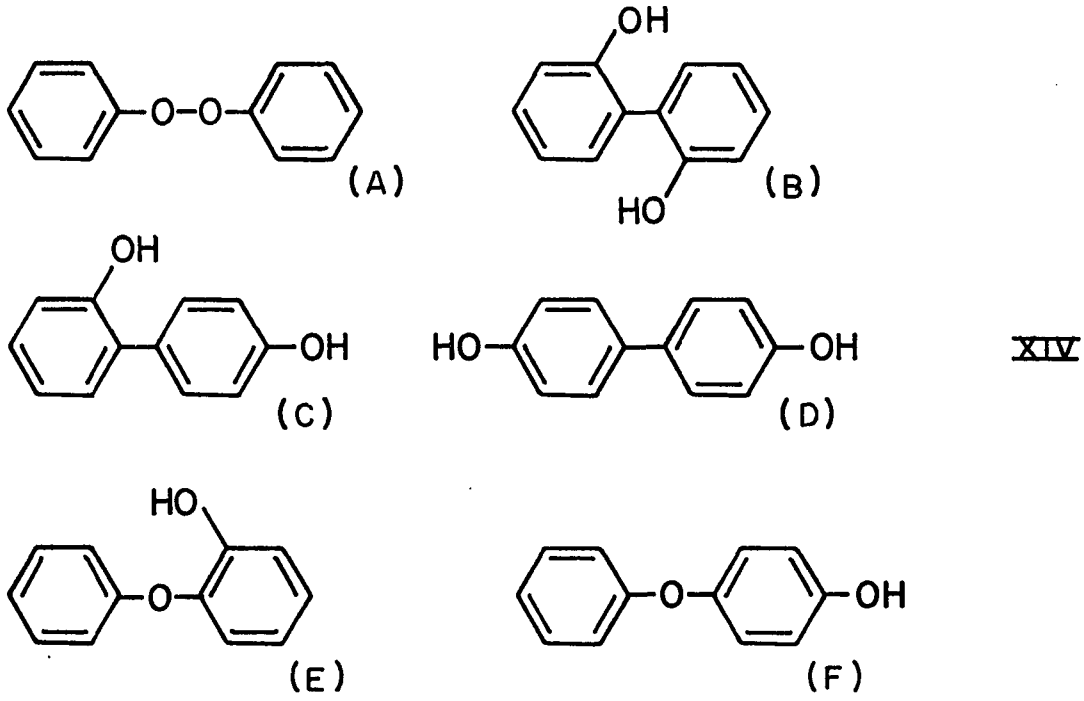
according to equation XIII. The product of reaction XIII will undergo protonation and tautomerization to yield the corresponding quinone.




XIII

3. Homo-radical reactions

Any time phenoxy radicals are formed, one of the possible reactions is the direct coupling of phenoxy radicals with one another. From a consideration of the four resonance structures shown in equation VIII, one concludes that six distinct isomers can be obtained. These are shown in equation XIV A-F. Dimer A is a peroxide and would be expected to be

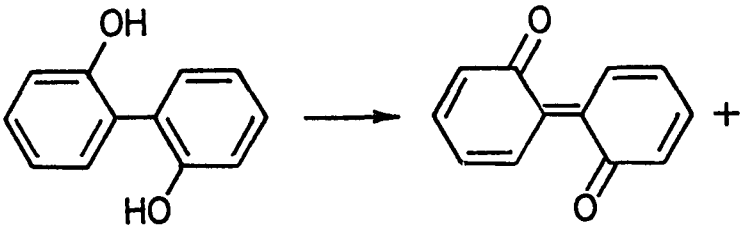



XIV

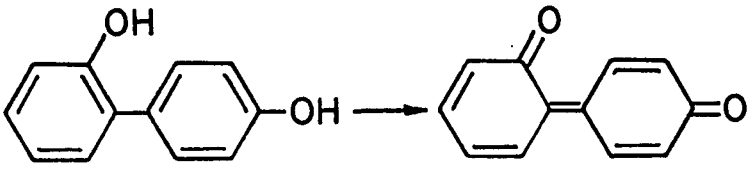
very reactive. The ease with which the oxygen-oxygen bond in peroxides is broken is well-documented. This in turn regenerates the phenoxy

radicals from which the peroxide was formed. Robinson has suggested that the diphenyl peroxide (structure A) can undergo a benzidine type of rearrangement to give structure D (154).

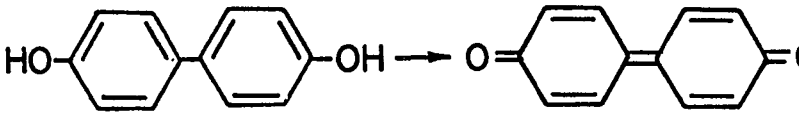
The dimers formed from the coupling of two phenoxy radicals are themselves phenols, and are not immune to further reaction. Structures B, C and D are hydroquinone-type structures and can be expected to undergo oxidation to the corresponding quinones as is illustrated in equations XV, XVI and XVII. Structures E and F cannot undergo a reaction of this type. Therefore, further oxidation of dimers E and F will produce radicals




XV




XVI

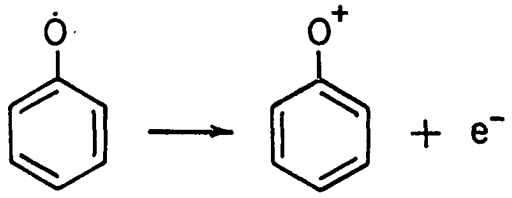



XVII

which are similar in nature to those shown in equation VIII and would be expected to have similarly stabilized resonance structures and undergo reactions similar to those of phenol.

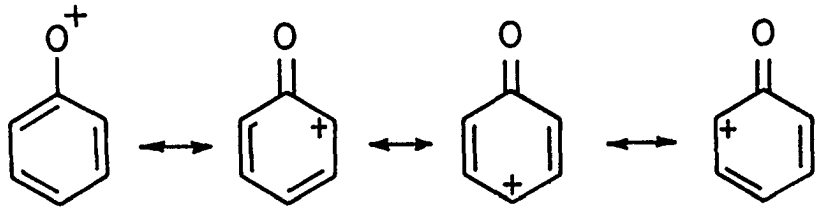
4. Oxidation to the phenoxonium ion

Another possible reaction of the phenoxy radical is oxidation to the phenoxonium ion, as illustrated by equation XVIII. This cation exists



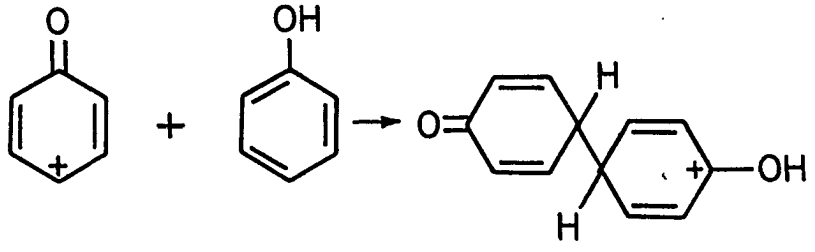
XVIII

in the resonate forms illustrated in equation XIX. The phenoxonium ion



XIX

is a strong electrophile and can attack a neutral molecule of phenol as shown in equation XX (para-para coupling shown). The product of this



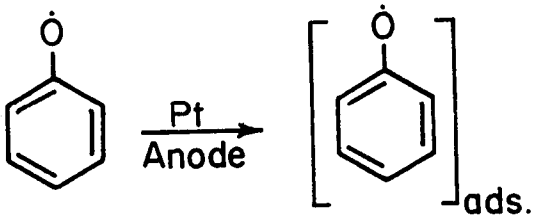
XX

reaction will undergo deprotonation and keto-enol tautomerism to yield product D shown in equation XIV.

It should be noted, at this point, that the coupling of radicals as illustrated by equation XIV (D) and the phenoxonium attack illustrated by equation XX yield the same final products. Note further that although the mechanisms are clearly different, both reactions involve two, one-electron oxidations and two phenol molecules.

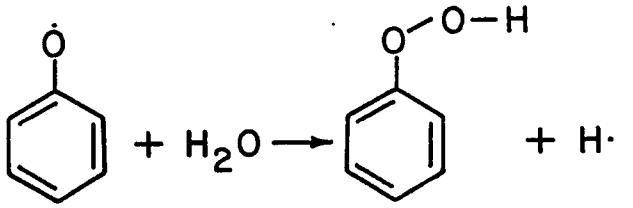
5. Reactions with solvent

Before proceeding further with a discussion of the reactions between phenolic molecules, we must consider the fate of a phenoxy radical or phenoxonium cation in the absence of another aromatic nucleus. In this case the reactive species has only two possible courses to follow. The first is the formation of a bond with the oxidizing agent. This is the reaction described by Gileadi and others (129, 130, 132) and is shown by equation XXI. This reaction is trivial and will not be discussed further.



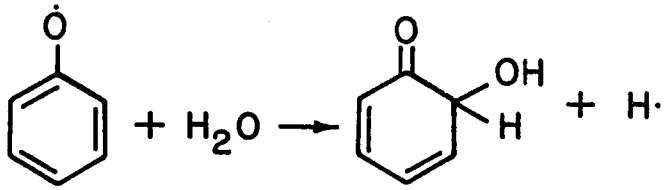

XXI

The second reaction to be considered is that with the solvent. One possible reaction of the phenoxy radical with water is shown in equation XXII. The generation of the hydroperoxide may occur; however, it would




XXII

not be considered a stable species. Should the reaction occur as is illustrated in equation XXIII, the end product would be expected to rapidly




XXIII

tautomerize in protic solvents to catechol. The catechol thus formed could be further oxidized to the corresponding quinone. Hydroquinone can be formed in an analogous manner.

The reaction of the phenoxonium cation with water can occur to produce catecol and hydroquinone with the positive charge being carried by the expelled hydrogen atom. This is in contrast to the reaction of the phenoxy radical, in which the expelled hydrogen carries a single electron. The fate of the hydrogen atom is most certainly oxidation to the hydrogen ion.

## 6. Summary

The first step in the oxidation of phenol is concluded to be a one-electron oxidation to produce the phenoxy radical. The fate of this radical is dependent on its immediate environment. If another radical of virtually any kind is available, radical coupling is expected to occur. If another radical is not freely available, then the phenoxy radical can either react with the solvent or other neutral species, or react again with the oxidizing agent to form the phenoxonium cation. The phenoxonium cation is expected to react readily with protic solvents. In either case, the end product of the initial oxidation may be subject to further oxidation. The products of the dimerization reactions are in some instances nothing more than substituted phenols and can react in the same manner as phenol itself. Hence, it is reasonable to assume that polymers with a highly variable number of monomeric units can be formed by any one, or a combination, of the mechanisms described.

## B. Response of Amperometric Detectors

### 1. General treatment of mass transfer

The limiting response of flow-through electrodes is described by the general equation

$$I = nFAK_1V_f^{\alpha}C \qquad \text{XXIV}$$

In equation XXIV, n is the number of electrons in the reaction (equiv $mol^{-1}$), F is the faraday constant (coul $equiv^{-1}$), A is electrode area ($cm^2$), $V_f$ is the fluid flow rate ($cm^3$ $sec^{-1}$), $\alpha$ is a fraction which is characteristic of electrode geometry and fluid dynamics, and C is the concentration of analyte in the stream entering the detector (mol $cm^{-3}$). $K_1$ in equation XXIV is the limiting, specific, mass transfer coefficient with units $cm^{1-3\alpha}$ $sec^{\alpha-1}$. The limiting detector current for the continuous flow of solution containing analyte, at a bulk concentration of $C_b$, has a steady-state value of $I_{ss}$. The electrolytic efficiency, Eff, of the detector for continuous analysis of a stream at a steady-state concentration is

$$Eff = \frac{I_{ss}}{I_{max}} = \frac{nFAK_1V_f^{\alpha}C_b}{nFV_fC_b} = AK_1V_f^{\alpha-1} \qquad \text{XXV}$$

For injection of a small volume of sample, e.g. $V_s < 1$ mL with concentration $C_b$ into a stream of electrolyte passing through the detector, C will likely be decreased below $C_b$ at all points in the sample plug because of dispersion within the fluid stream. Hence $I_{peak} < I_{ss}$ for the detection peak. Values of $I_{peak}$ may not be a reliable analytical measure of $C_b$ in the sample injected, even with calibration, unless

the factors controlling dispersion are maintained constant. For example, even small changes in the curvature of tubing which connects the sample injection valve to the detector cell can produce changes of several percent in $I_{peak}$ (155). The area of the detection peak, $Q_{peak}$, can be a more reliable analytical measure of $C_b$. For small diameter tubing ($< 1$ mm) and moderately low flow rates (0.2 - 5 mL $min^{-1}$), this area is independent of the extent of sample dispersion as given by equation XXVI.

$$Q_{peak} = \int I_i dt = nFAK_1 V_f^{\alpha} \int C dt = nFAK V_f^{\alpha-1} V_s C_b \qquad \text{XXVI}$$

The efficiency of the detector for flow-injection analysis is given by equation XXVII and is identical to that for steady-state analysis.

$$Eff = \frac{Q_{peak}}{Q_{max}} = \frac{nFAK_1 V_f^{\alpha-1} V_s C_b}{nFV_s C_b} = AK_1 V_f^{\alpha-1} \qquad \text{XXVII}$$

2. Problems associated with tubular flow-through electrodes

The equation of mass transport in a tubular flow-through electrode under laminar fluid flow has been solved (156 - 158) and tubular electrodes made of carbon or noble metals have been popularized as flow-through detectors for continuous analysis of fluid streams (159). The construction of a usable tubular electrode system can be a frustrating experience. The greatest source of difficulty comes from the degradation of the interface between the electrode and the inert material used for construction of the cell. Leakage of the electrolyte solution into the interface can result in a large increase of the residual current and diffusion of analyte into the trapped solution can lead to significant

tailing in applications for flow-injection analysis or liquid chromatography. Irregularities in the dimensions of the inlet channel, resulting from construction error or aging of materials, can result in local turbulence which tends to invalidate the mathematical derivations based on assumptions of laminar flow, and calibration of the detector response is essential (155). These problems have been experienced for a variety of cell materials including Teflon, Kel-F and epoxy.

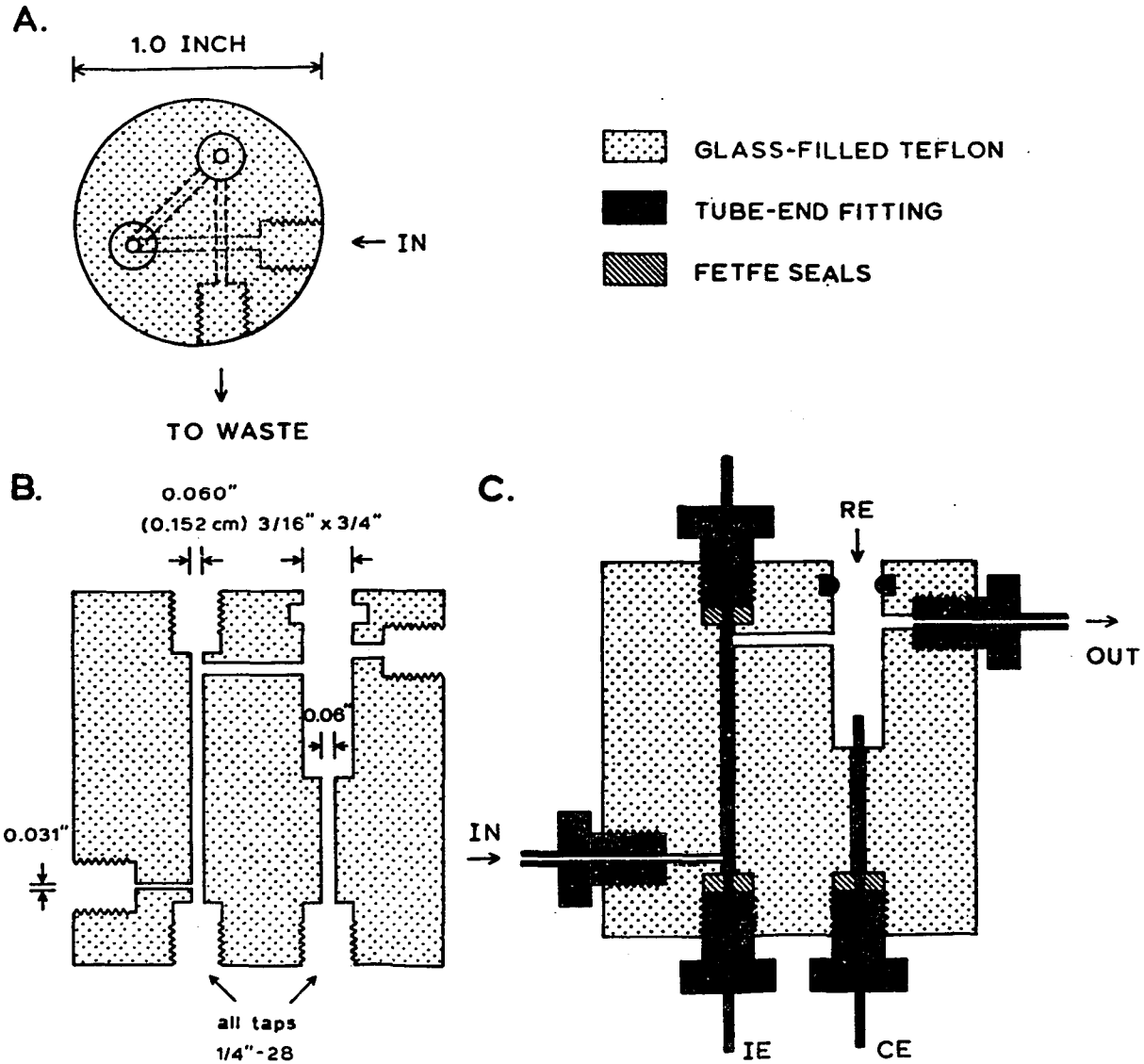
There are other disadvantages with the use of tubular electrodes for analysis. Tubular electrodes made of noble metals are usually constructed by drilling a solid metal rod or disk with the resultant loss of valuable metal. The detector cell of a tubular electrode which has been disassembled for examination and/or physical pretreatment of the electrode surface cannot easily be reassembled.

3. A wire flow-through electrode

A very practical alternative to the tubular electrode is the wire flow-through electrode shown in Figure 1. Further details of the construction are given in section IV-B. This electrode is free of many of the difficulties which plague other flow-through electrodes and since its inception has performed well in the laboratory for a variety of determinations, which include nitrosamines (160), chromate (161), arsenic (162), and phenol (163). The exact treatment of the problem of mass transport in the wire flow-through detector would be a formidable challenge due to the turbulent character of the fluid flow at the entrance of the electrode chamber where the direction of flow makes an abrupt change.

Figure 1. Wire flow-through detector

A. Top view
B. Detector body
C. Assembled detector


A.
1.0 INCH
IN
TO WASTE
GLASS-FILLED TEFLON
TUBE-END FITTING
FETFE SEALS
B.
0.060"
(0.152 cm) 3/16" x 3/4"
0.06"
0.031"
all taps
1/4"-28
C.
RE
OUT
IN
IE
CE

Furthermore, no attempt is made in the assembly of the detector to maintain a uniform spacing between the surface of the wire and the wall of the tubular channel drilled into the Teflon cell block. It should be noted, however, that there is a strong similarity of this detector to the "annular" electrode treated theoretically by Ross and Wragg (164) and illustrated in Figure 2. In their case, laminar flow was assumed for fluid in the annular space surrounding a cylindrical electrode. The value of $AK_1V_f^{\alpha}$ was predicted to be given by equation XXVIII.

$$AK_1V_f^{\alpha} = 3.22\ [\phi(a)]^{1/3} \left[\frac{\pi^{2/3}L^{2/3}r_1D^{2/3}V_f^{1/3}}{d_e^{1/3}\ (r_2^2-r_1^2)^{1/3}}\right] \qquad \text{XXVIII}$$

where D is the diffusion coefficient of the analyte ($cm^2sec^{-1}$). The remaining terms in equation XXVIII are defined as follows:

$$d_e = 2(r_2 - r_1)$$

$$a = r_1/r_2$$

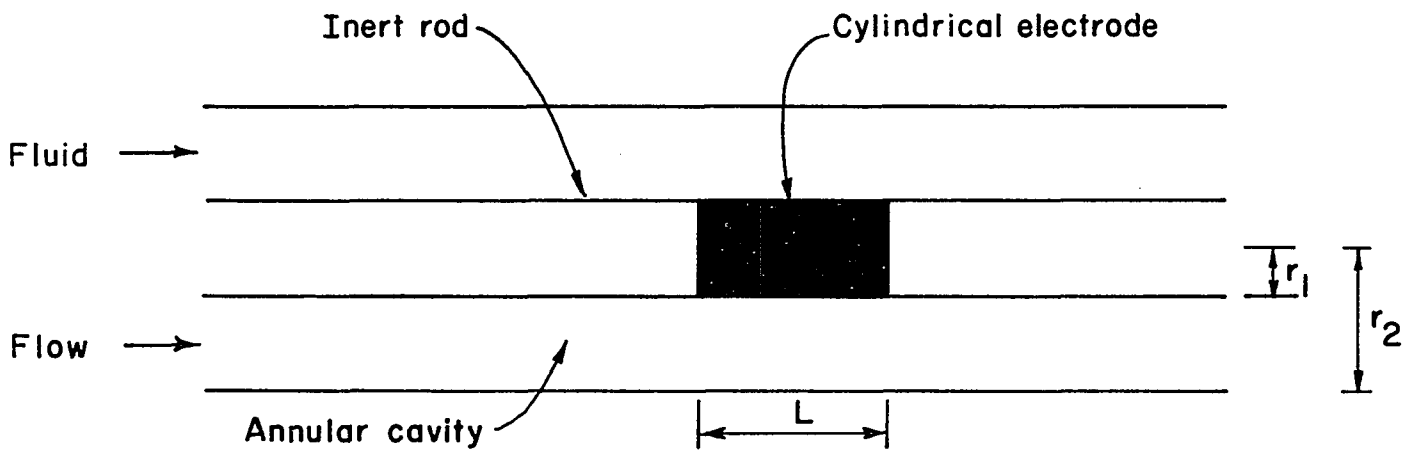
$$\phi(a) = \frac{1 - a}{a} \left[\frac{\frac{a^2}{0.5 - (1 - a^2)}\ \ln(1/a)}{\left\{\frac{1 + a^2}{1 - a^2}\right\} \ln(1/a) - 1}\right]$$

Assuming equation XXVIII is applicable to the wire electrode, $AK_1$ is calculated to be $24.2D^{2/3}$ for $r_1 = 0.0650$ cm, $r_2 = 0.0760$ cm and $L = 2.1$ cm. Since the exponent, $\alpha$, of $V_f$ in equation XXVIII is 1/3, the slope of a plot of log E vs. log $V_f$ is predicted to be -2/3 for applications of the detector to steady-state or flow injection analyses (see equations XXV and XXVII).

4. Summary

Although the mathematical relationship between electrode current and analyte concentration has been solved for a tubular electrode as a

Figure 2. Annular electrode


Inert rod
Cylindrical electrode
Fluid
Flow
Annular cavity
L
$r_1$
$r_2$

function of the experimental parameters, this theoretical response is based on the assumption of laminar flow of fluid through the tube and the existence of turbulent flow can invalidate the equation. The practical result is that, regardless of the care with which the detector was manufactured, the analyst must calibrate the response of the detector with suitable standards. The wire flow-through electrode has performed well and is free of many of the problems associated with the tubular electrode.

## C. Coulometric Electrodes

### 1. General principles

A coulometric flow-through electrode is an electrode which electrolyzes 100% of the electroactive analyte which passes through the electrode. The relationship between the quantity of charge passing in a coulometric electrode, Q, and the number of moles of substance electrolyzed, N, is given by equation XXIX, where n is the number

$$Q = nFN \qquad \text{XXIX}$$

of electrons gained or lost in the electrochemical reaction per molecule of electroactive substance (equiv./mole) and F is the faraday constant. The value of n is observed to have integral values for simple electrochemical reactions. A simple electrochemical reaction, as used in this thesis, is defined as an electrochemical reaction which is not complicated by coupled chemical reactions. Furthermore, the reaction is restricted to that of one, and only one, electroactive species to produce one, and only one, reaction product and the reaction must occur to completion: that is,

the rate of the electrochemical reaction must be mass-transport limited. This last point is considered trivial and will not be discussed further.

Non-integral values of n may be observed when two or more simple electrochemical reactions occur simultaneously, when the electrochemical reaction is coupled to a chemical reaction, or when the flow rate of the solution passing through the electrode has exceeded that for which the electrode can maintain its coulometric character. Observed values of n which are integral, do not guarantee the absence of these conditions nor do they guarantee that the electrode process is a single, simple electrochemical reaction. For example, if a solution contains equivalent quantities of chromium (VI) and iron (III) coulometric reduction of this solution will lead to an observed value of n = 2. The value of 2 resulted from a weighted average of 3 and 1, when the reductions are to chromium (III) and iron (II). If the solution did not contain equivalent quantities of chromium (VI) and iron (III), then the observed value of n would be a non-integral number between 1 and 3.

Consideration of the flow rate deserves further comment here because it deals directly with one of the fundamental characteristics of a coulometric electrode. For a single, simple electrode process, the value of n which is obtained experimentally is independent of flow rate as long as the flow rate is below the maximum value for which the electrode can maintain its coulometric character. This maximum flow rate, $V_m$, can be determined experimentally by observing the value of Q as a function of flow rate for a known amount of an electrochemically active species of known single, simple electrode reaction.

2. Simultaneous reactions

Non-integral values of n may be observed when two or more simple electrode reactions occur simultaneously as discussed in the previous section. Non-integral values of n may also be observed when a single analyte is capable of participating in two or more simple electrode reactions as illustrated by equations XXX and XXXI.

$$A \longrightarrow B + je^- \qquad \text{XXX}$$

$$A \longrightarrow F + me^- \qquad \text{XXXI}$$

Consider the reactions of phenol. Hydroquinone (HQ) can be formed as a result of the oxidation of phenol, (P). Phenol is also known to polymerize; however, at this time only the dimerization reaction will be considered. These reactions are illustrated by equations XXXII and XXXIII where D represents the dimer dibenzohydroquinone. The values of

$$P \longrightarrow HQ + 2e^- \qquad \text{XXXII}$$

$$2P \longrightarrow D + 2e^- \qquad \text{XXXIII}$$

n for these two reactions are 2 and 1, respectively. The value of n observed is a weighted average of the contributions from each of the two simultaneous electrode reactions. Even though the observed value of n is likely to have non-integral values in these situations, that value may be considered independent of flow rate.

The effect of concentration must be considered with respect to the reactions illustrated by equations XXXII and XXXIII. The rate of the dimerization reaction in equation XXXIII has a second-order dependence on the concentration of phenol, whereas the rate of the reaction illustrated by equation XXXII has a first-order dependence on the concentration of

phenol. Although doubling the concentration of phenol will double the rate of the equation illustrated by equation XXXII, it will quadruple the rate of the dimerization reaction. Since the value of n for the dimerization reaction is less than the value of n for the reaction illustrated by equation XXXII, and the observed value of n is a weighted average of the contribution of the two reactions, the observed value of n will decrease as the concentration of phenol increases.

3. Coupled reactions

When the product of an electrochemical reaction spontaneously undergoes a chemical reaction to form another electroactive species, non-integral values of n may be observed. This type of reaction is referred to as having an ECE mechanism and is illustrated by equations XXXIV, XXXV and XXXVI where P, R, DBHQ and DBQ represent phenol, phenoxy radical,

$$P \longrightarrow R + 1e^- \qquad \text{XXXIV}$$

$$2R \longrightarrow DBHQ \qquad \text{XXXV}$$

$$DBHQ \longrightarrow DBQ + 2e^- \qquad \text{XXXVI}$$

dibenzohydroquinone and dibenzoquinone, respectively.

When the flow rate is low, the reaction illustrated by equation XXXV occurs entirely within the coulometric electrode and the reaction illustrated by equation XXXVI contributes fully to the observed value of n. When the flow rate is high, the reaction illustrated by equation XXXV has a high probability of occurring downstream of the electrode and the contribution to Q of the reaction illustrated by equation XXXVI is diminished. Therefore, when coupled chemical reactions occur within a

coulometric electrode the observed value of n is found to be an inverse function of flow rate.

The effect of the concentration of phenol must be considered with respect to this particular sequence of reactions. The rate of generation of R has a first-order dependence on the concentration of phenol; however, the rate of generation of DBHQ has a second-order dependence on the concentration of R and the rate of the reaction illustrated by equation XXXVI are directly dependent upon the rate of generation of DBHQ. Therefore, the contribution of the reaction illustrated by equation XXXVI to the observed value of n will increase as the concentration of phenol increases.

4. Summary

The observed value of n for an electrochemical reaction is independent of the flow rate only for simple electrode reactions. The observed value of n for a coupled chemical reaction shows an inverse dependence on the flow rate. The observed value of n changes in the same direction (not necessarily linearly) as changes in the concentration of phenol for the sequence of reactions representing the ECE mechanism, and inversely with the concentration of phenol for the simultaneous reactions described. The magnitudes of these opposing effects is not known. An increase in the observed value of n with an increase in phenol concentration supports the conclusion of an ECE mechanism; however, an inverse dependence of the observed value of n does not necessarily disprove an ECE mechanism. Whether or not an ECE mechanism is involved must be determined by

determining whether the observed value of n decreases with flow rate or is independent of flow rate. Once the presence or absence of an ECE mechanism has been established, the dependence of the observed value of n on phenol concentration may allow conclusions concerning the existence of simultaneous reactions.

# IV. APPARATUS AND REAGENTS

## A. Flow-injection Analyzers

A schematic diagram of the flow-injection analyzer is shown in Figure 3. All tubing, tube-end fittings and valves were Cheminert from Laboratory Data Control, Riviera Beach, FL. Tubing (0.787-mm i.d.) was made of Teflon; tube-end fittings were polypropylene; and valves were made from Kel-F. The flow rate of the reagent stream was adjusted by a needle valve which was constructed in the Chemistry Shop from Kel-F according to the diagram in Figure 4. The flow rate was monitored by a flow meter from Gilmont Instruments, Inc., Great Neck, NY. Calibration data for this flow meter is shown in Figure 5.

Figure 6 is a schematic diagram of the liquid chromatograph used for isocratic separation of mixtures of chlorinated phenols. The platinum wire detector was employed as the detector. The eluent was 0.05 N $H_2SO_4$ containing 22-29% acetonitrile, by volume.

A Milton-Roy dual piston pump (Model CK) was used to provide eluent flow at pressures of 100 to 400 psi. The output ports of the two pistons were connected in a parallel fashion and then connected to a LDC Pulse Dampener which had an Acco Helicoid gauge to monitor the eluent pressure. The pump and the pulse dampener with pressure gauge were obtained from Laboratory Data Control. The flow rate of the liquid chromatograph was controlled by indexed adjustment of the piston return stops on the Milton-Roy pump. Calibration data are shown in Figure 7. In all cases, both

Figure 3. Flow injection analyzer

A. Helium tank
B. On-off valve
C. Carrier solution reservoir 1
D. Carrier solution reservoir 2
E. Selector valve
F. Flow control valve
G. Flow meter
H. Injection valve
I. Syringe
J. Sample container
K. Detector
L. Potentiostat
M. Recorder

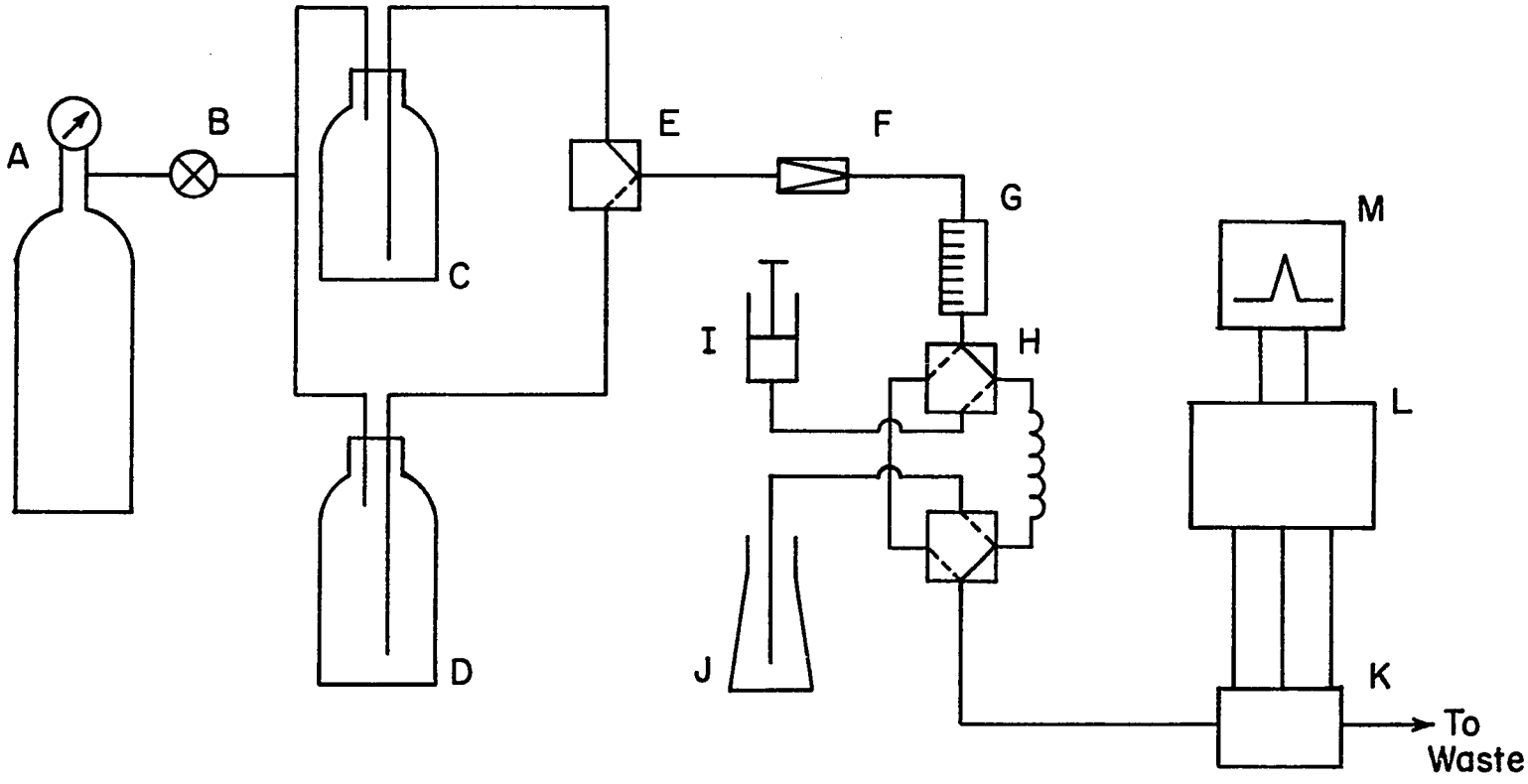

A
B
C
D
E
F
G
H
I
J
K
L
M
To
Waste

Figure 4. Flow control valve

A. 3/4 in. hex
B. Kel-F seating nut
C. 7/8 in. hex
D. Kel-F receiving insert
E. 3" taper
F. Kel-F outer body
G. Fetfe sealing washer
H. 5/8 in. x 18 threads
I. Brass
J. 3/8 in. x 56 threads
K. Aluminum
L. Locking pin
M. Kel-F needle
N. 3/8 in. x 20 threads
P. ¼ in. x 28 threads

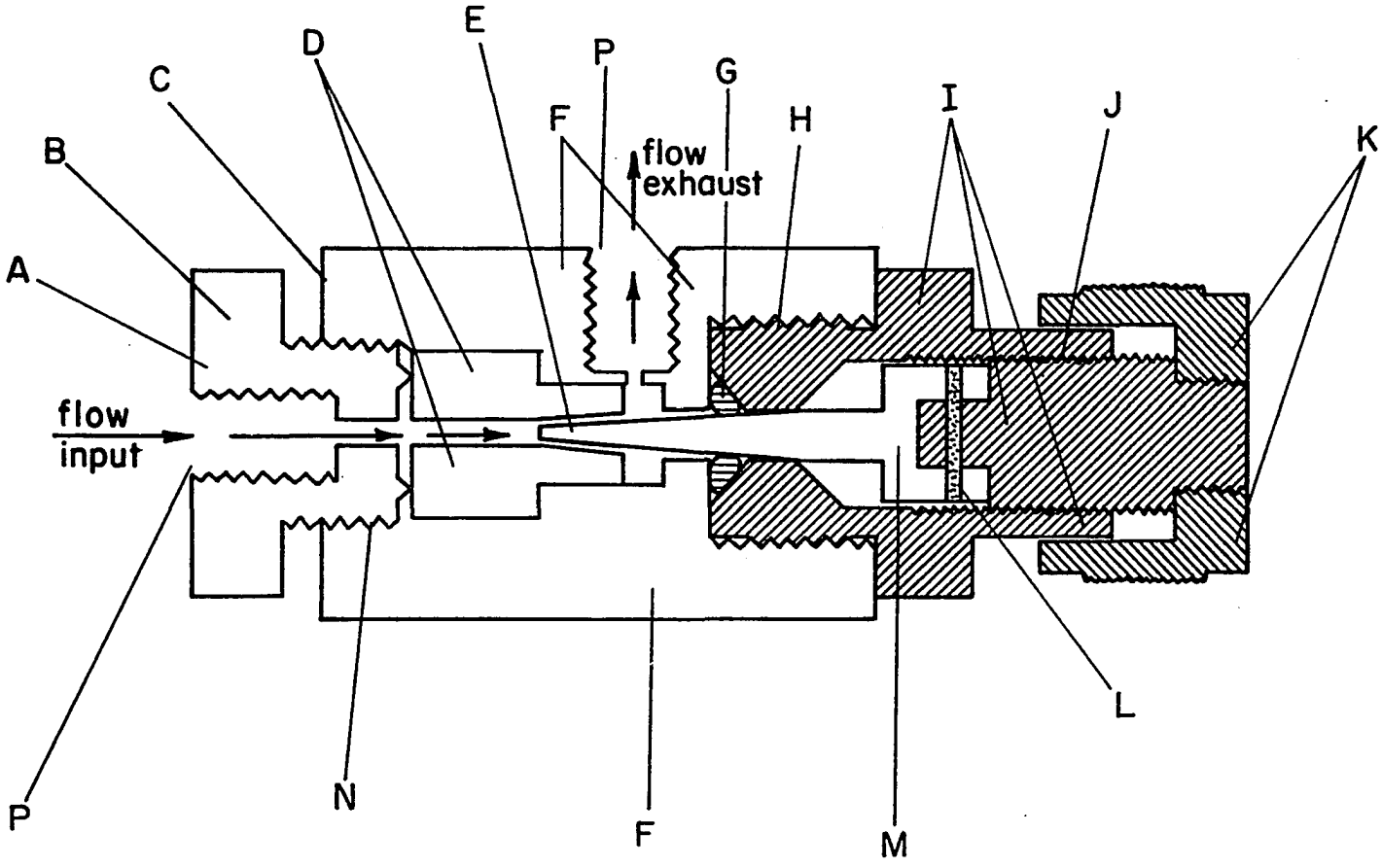

A
B
C
D
E
F
P
G
H
I
J
K
flow
exhaust
flow
input
P
N
F
M
L

Figure 5. Actual flow rate versus meter reading for Gilmont flow meter

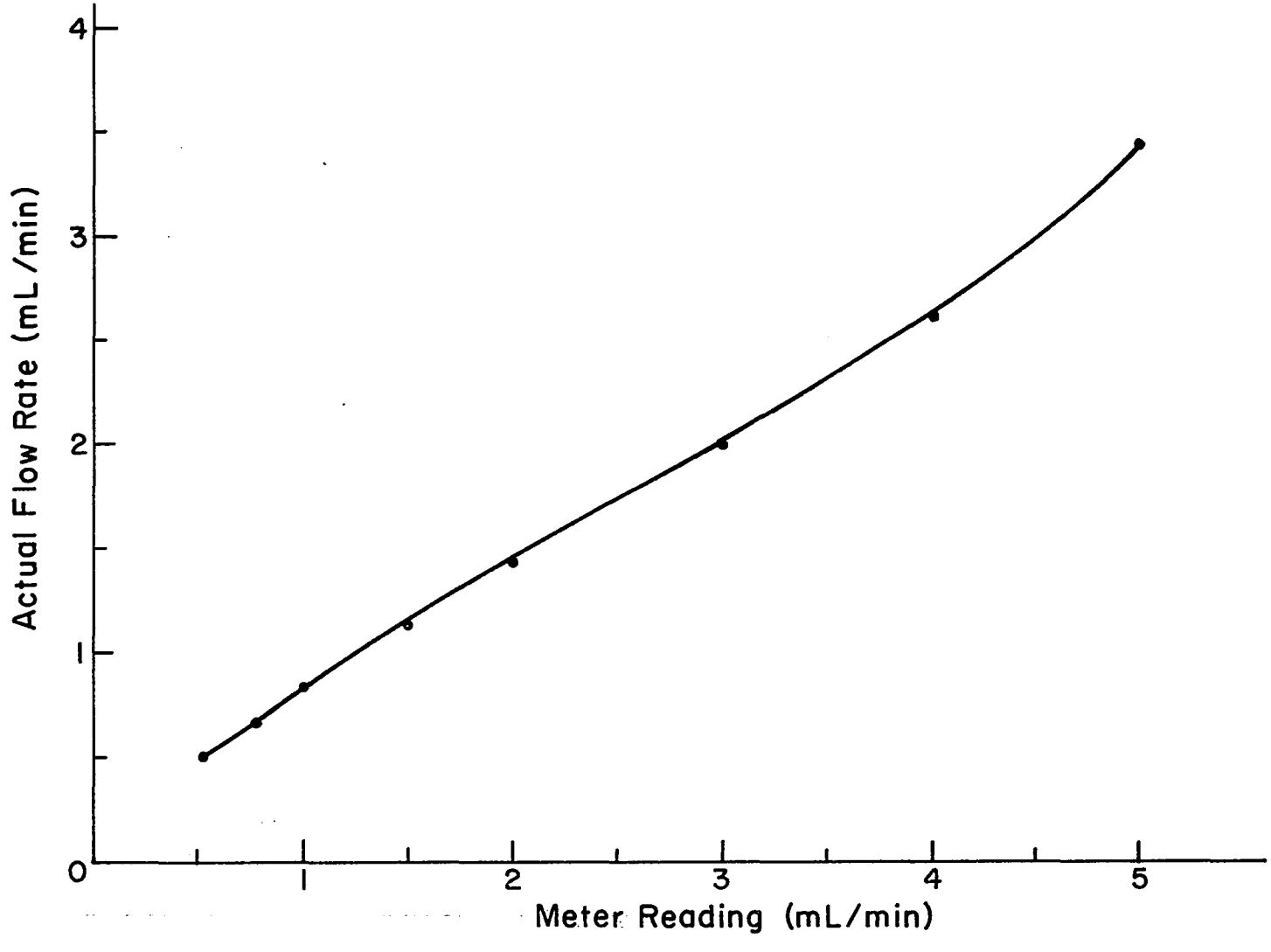

Actual Flow Rate (mL/min)
0
1
2
3
4
1
2
3
4
5
Meter Reading (mL/min)

Figure 6. Liquid chromatographic analyzer

A. Sample reservoir
B. Pump
C. Pressure gauge
D. Pulse dampener
E. Injection valve
F. Syringe
G. Sample container
H. Chromatographic column
I. Detector
J. Potentiostat
K. Recorder

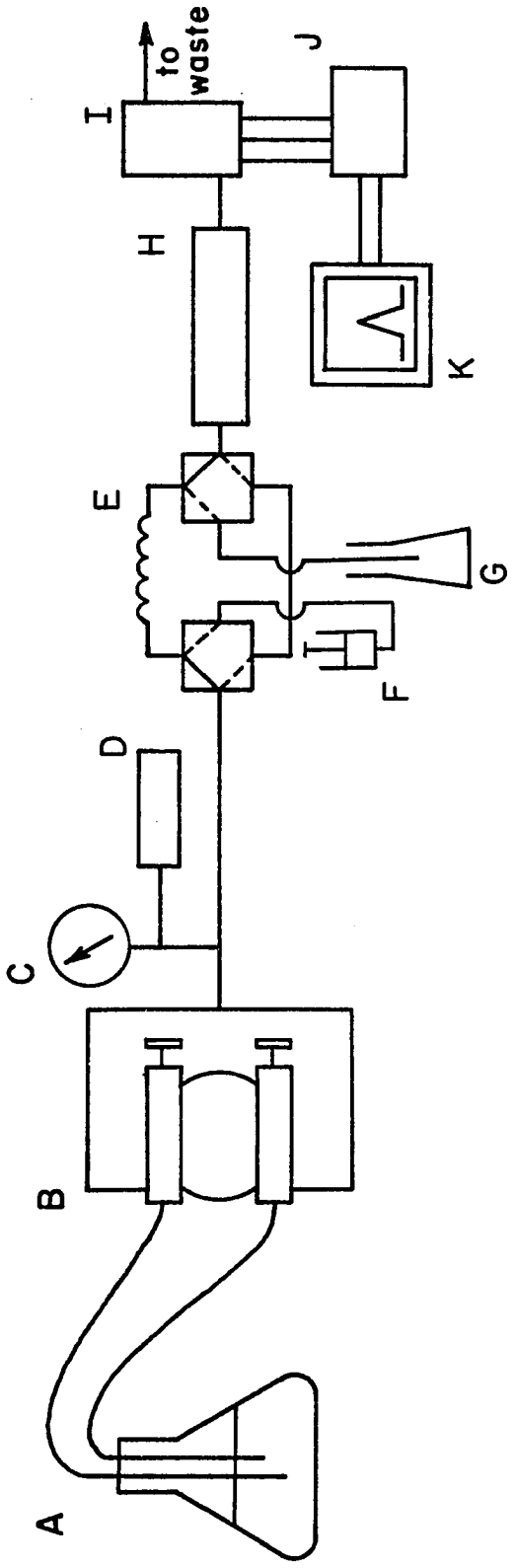
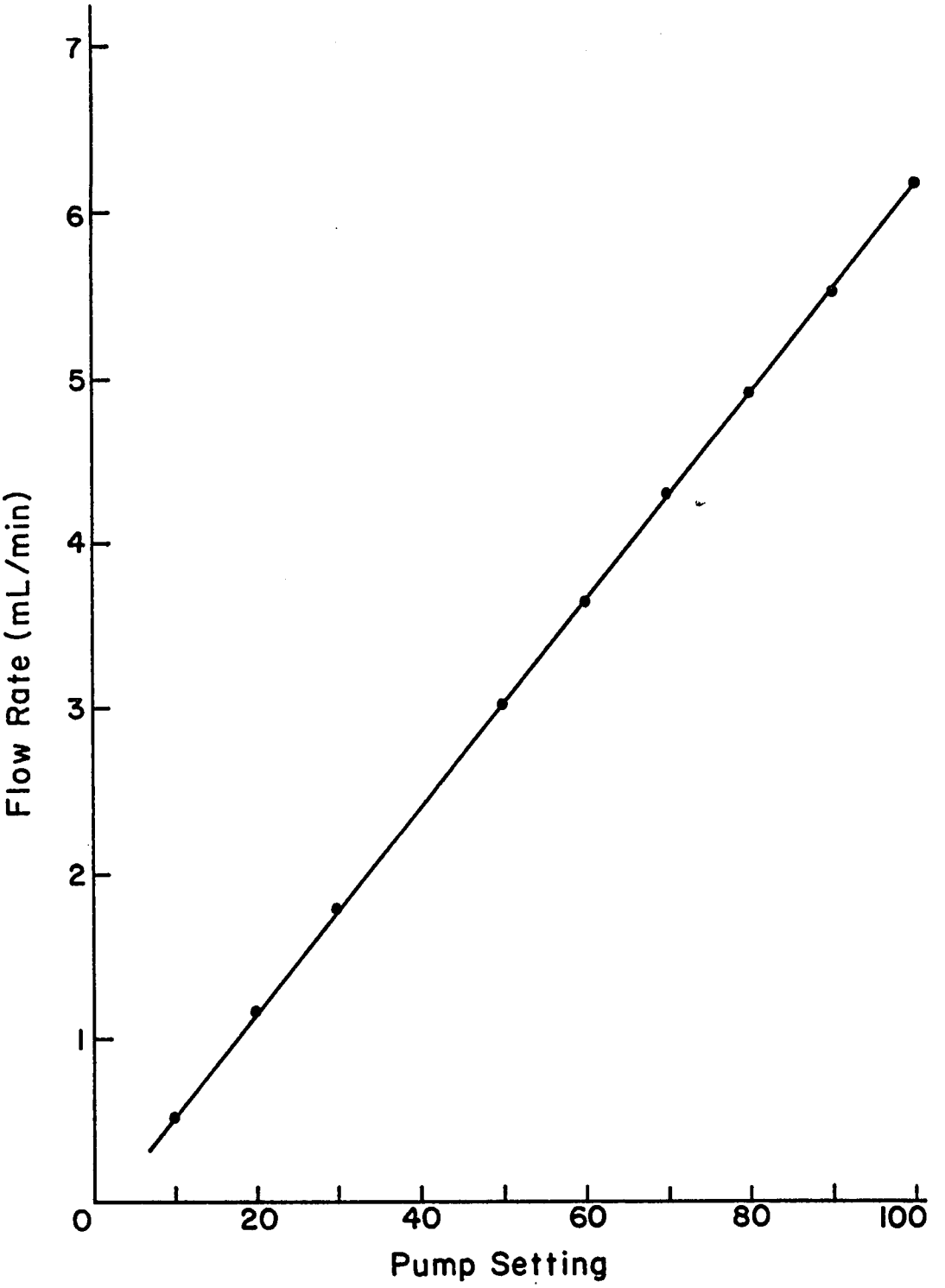

to waste
I
J
H
K
E
G
F
D
C
B
A

Figure 7. Flow rate versus pump setting for Milton-Roy pump


Flow Rate (mL/min)
0
1
2
3
4
5
6
7
0
20
40
60
80
100
Pump Setting

index adjustments were set at the same numerical value.

The chromatographic column (25 cm x 1 cm dia.) was obtained from Dionex Corp., Sunnyvale, CA. The chromatographic resin was fully sulfonated polystyrene with 4% (W/W) crosslinking by divinylbenzene. Particle size of the resin was 23-38 um.

## B. Flow-through Detectors

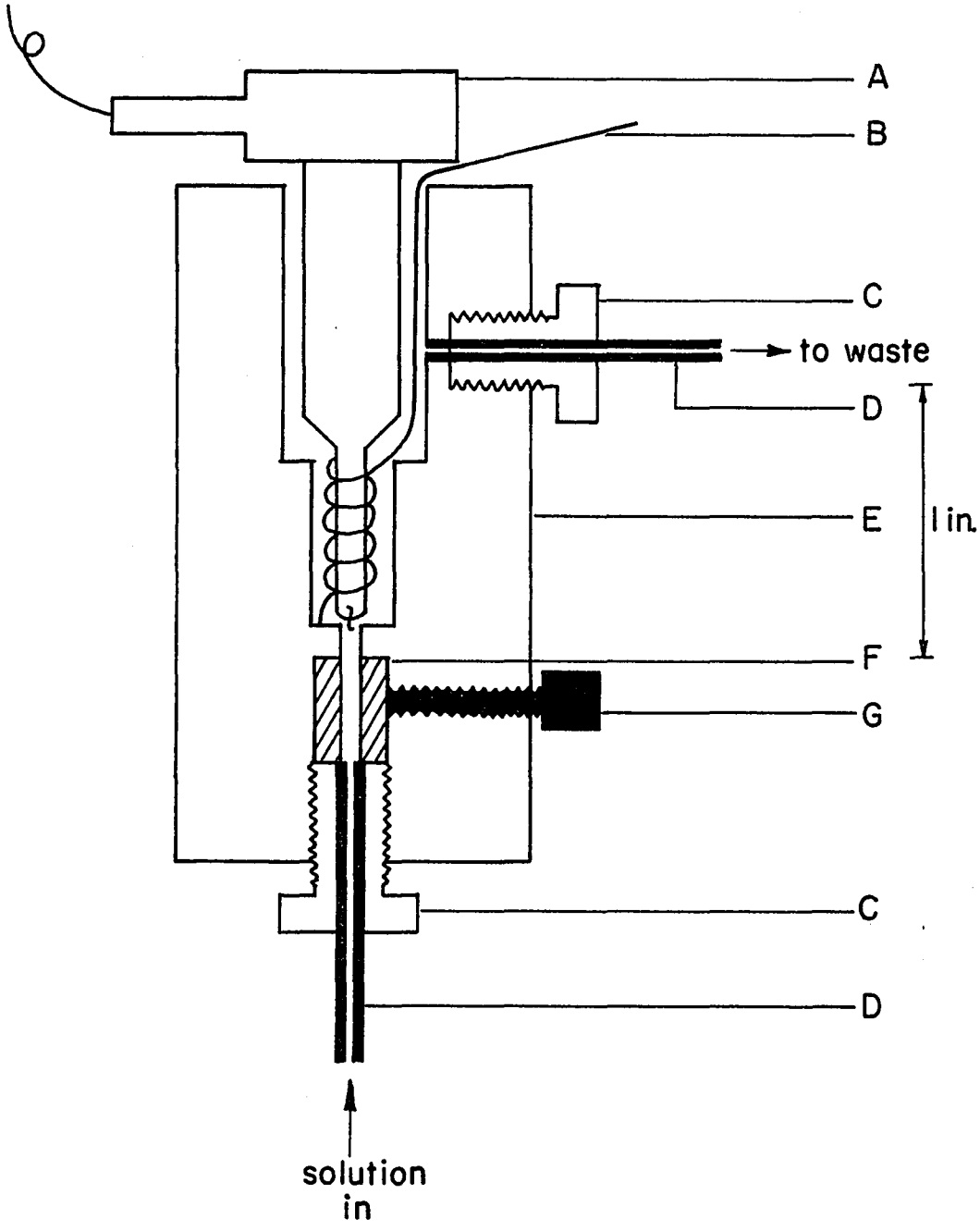
The flow-through electrodes were of three basic configurations: tubular, wire and packed. The tubular configuration was the basis for construction of the flow-through electrodes from glassy carbon and a conducting polymeric material obtained from Dow Chemical Co. The composition of this conducting polymer has been described in the literature (136). A schematic diagram of a typical tubular detector is shown in Figure 8. Note that both the auxiliary and reference electrodes are downstream from the indicator electrode.

A packed flow-through electrode for coulometric detection was employed in an effort to gain insight into the mechanism of the electrochemical oxidation of phenol. This electrode consisted of a tubular platinum electrode which was packed with a large number of small platinum chips. This packing process drastically increased the effective surface area of the electrode and resulted in exhaustive electrolysis of the analyte.

The wire configuration was chosen as the flow-through design to be used with the platinum indicator electrode and is shown in Figure 1. This

Figure 8. Tubular detector

A. Reference electrode
B. Auxiliary electrode
C. Tube end fitting
D. Teflon tubing
E. Detector body
F. Tubular indicator electrode
G. Electrical contact


A
B
C
to waste
D
E
1 in.
F
G
C
D
solution in

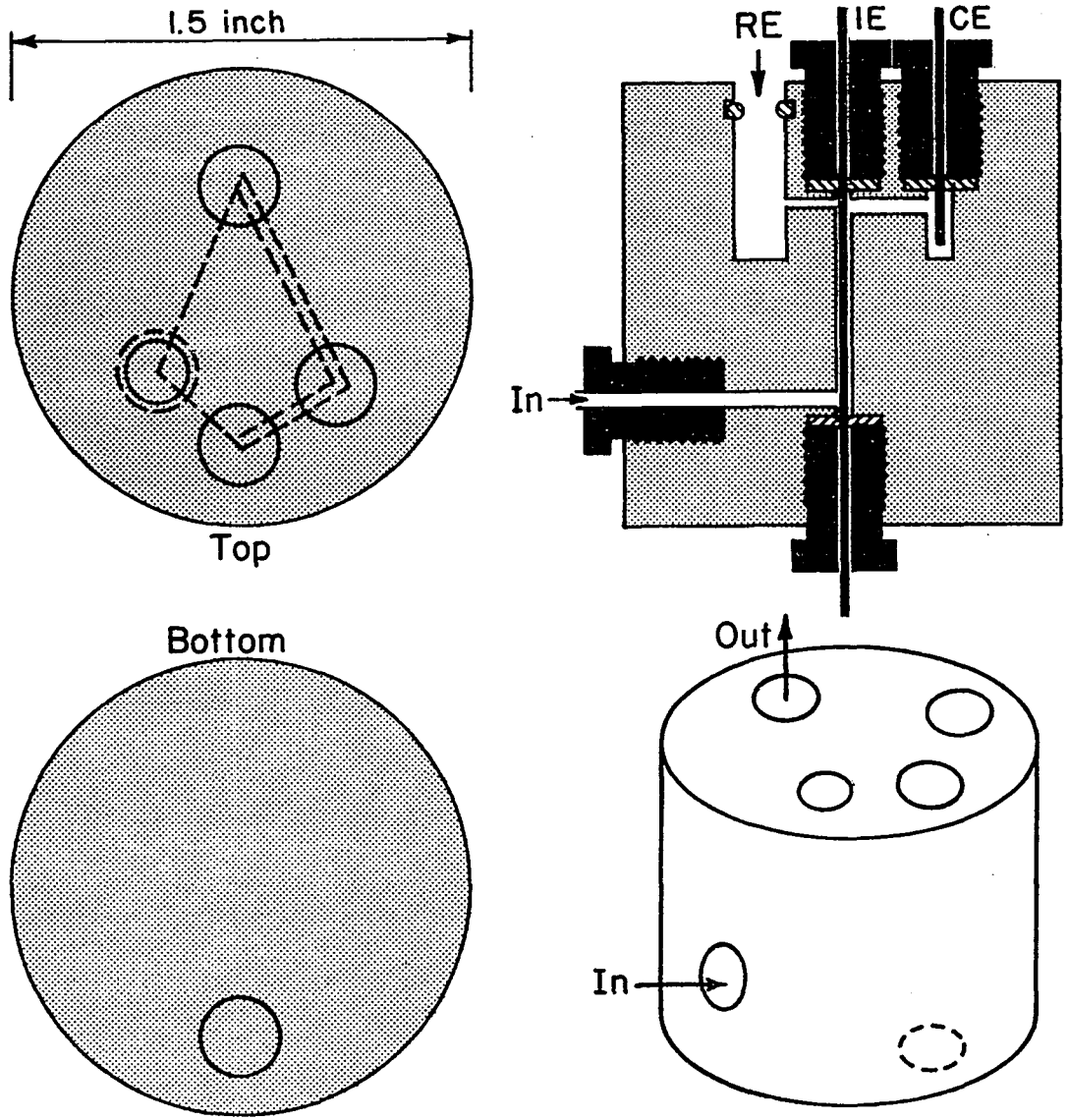
electrode was designed by this author and was manufactured in the Chemistry Shop at Iowa State University. The detector body was machined from a rod of 25% glass-filled Teflon (1.0 in. dia. x 1.5 in.) This material was chosen over Teflon and Kel-F due to its machining properties, mechanical strength and relatively low cost. Fetfe was chosen as the material for constructing compression seals due to its extraordinary resistance to corrosive solutions and its high degree of pliability. Although platinum wire was chosen for the indicator electrode in this research, there is no reason which would prevent the use of other metals or non-metallic conducting materials.

All electrical current which passes in this detector is accompanied by the movement of ions through the channel connecting the indicator electrode with the auxiliary electrode. Thus, any voltage drop due to uncompensated cell resistance within this channel affects the true potential of the indicator electrode with respect to the reference electrode. This problem is significant only if large currents are passed, e.g. $> 1$ mA. To minimize the effect of uncompensated resistance, a second design was developed which is shown in Figure 9. Note that the auxiliary and reference electrodes are in separate chambers. Channel dimensions are chosen to minimize, but not stop, fluid flow through the reference electrode chamber.

## C. Rotated Disc Electrodes

A platinum disc electrode (No. 134) was obtained from Pine Instrument Company, Grove City, PA. This electrode had a geometric surface area of 0.459 $cm^2$. A glassy-carbon disc electrode, 0.451 $cm^2$, was also used for

Figure 9. Modified wire detector


1.5 inch
Top
Bottom
RE
IE
CE
In
Out
In

comparison. This electrode (No. 196) was also obtained from Pine Instrument Company.

A pair of platinum disc electrodes, 0.317 $cm^2$, were constructed in the Chemistry Shop at Iowa State University. These electrodes were considerably smaller than the previously mentioned disc electrodes and the platinum tip was removable. This allowed the disc to be subjected to various types of surface analyses such as Auger Spectroscopy and Electron Microscopy.

A disc electrode, 0.317 $cm^2$, was also constructed from the conducting polymeric material.

## D. Potentiostat

Potentiostatic control for all electrochemical experiments was provided by a three-electrode potentiostat which was assembled in the laboratory from high-gain difference amplifiers and commonly available electronic components. The amplifiers (Models AZ801M1 and AZ801M2, from Zeltex, Inc.) were chosen for their high input impedance. The power supply was Model Z15AZ200DP, also from Zeltex. The circuitry of the potentiostat was of conventional design (165); however, one modification of the conventional circuitry was made to allow the passage of large amounts of current. This modification consisted of the optional switching of a current booster into the circuit between the control amplifier and the auxiliary electrode. At the same time, the current converter was switched out of the circuit and the indicator electrode was attached directly to ground. Calculation of

the current flowing through the electrochemical cell when the booster was operating was made possible by measuring the potential drop across a 10.0-ohm resistor which was also switched into the circuit between the current booster and the auxiliary electrode. The current booster was constructed from a matched pair of Motorola HEP silicon transistors (Models S0015 and S0019). These transistors have a current capacity of 600 mA; however, it should be noted that the booster amplifier could not be used to its maximum capacity because the power supply to the potentiometer had a limit of $\pm$ 200 mA.

## E. Miscellaneous Apparatus

The reference electrode was a miniature Saturated Calomel Electrode (SCE) from the Scientific Instruments Division of the Corning Glass Works, Medfield, MA., with saturated sodium chloride as the internal filling solution. All potentials are reported with respect to this reference electrode. The auxiliary electrode consisted of a platinum wire in contact with the solution analyzed. One additional electrode was constructed in order that relatively large quantities of the polymeric product from the oxidation of phenol could be obtained. This electrode was designated a "flag electrode" and was constructed by spot welding a 10-cm length of 26-ga platinum wire to a piece of platinum sheet metal with the dimensions 2.5 cm x 2.5 cm x 0.025 cm.

All disc electrodes were rotated by a rotator (Model PIR) from Pine Instrument Company. The geometric surface area of each disc electrode was calculated from measurements made with a traveling microscope

constructed in the Chemistry Shop from a microscope (Model 469M) from L. S. Starrett Co., Anthol, MA. Electrical signals were recorded on a Heath-Schlumberger strip chart recorder (Model SR-204) or a Hewlett-Packard X-Y recorder (Model 703513). The infrared spectrum was obtained on a Beckman recording infrared spectrometer (Model IR4250). The mass spectra were obtained on an AEI double focusing mass spectrometer (Model MS 902). The electron microphotographs were obtained on a JEOL scanning electron microscope (Model JSM-U3). Calculations of peak areas were performed on a Hewlett-Packard (Model 19 C) programmable calculator. All potential measurements were made with a Systron-Donner multimeter (Model 7050).

## F. Reagents and Chemicals

Phenol and chlorinated phenols were obtained from Aldrich Chemical Company. Ultraviolet grade acetonitrile was obtained from Burdick and Jackson Laboratories, Muskegon, MI. All other chemicals were obtained from either the Mallinckrodt Chemical Company or Fischer Scientific Company. All chemicals were reagent grade or better, except as specified for several of the chlorinated phenols. Those particular chlorinated phenols were obtained in the purest form available. All chemicals were used without further purification. Water was triply distilled with deionization after the first distillation, and the second distillation was from an alkaline permanganate solution.

# V. EXPERIMENTAL PROCEDURES

## A. Flow-injection Amperometry

Two carrier solutions were used with the flow-injection analyzers. A solution of mixed solvents (29% acetonitrile - 71% 0.05N sulfuric acid) was used for the evaluation of electrode materials and as the chromatographic eluent. All other flow-injection procedures were performed with an aqueous solution of 0.10 M perchloric acid. These carrier solutions were deaerated with helium prior to use.

Analyte solutions were made by dissolving a weighed amount of analyte in the carrier solution employed. This was done in a volumetric flask which was then filled to volume with the appropriate carrier solution. The sample was then diluted to the desired concentration. The chlorinated phenols were dissolved in 60% methyl alcohol - 40% chromatographic eluent due to the very low solubility of the tri-, tetra- and pentachlorophenols in aqueous solution. Dilutions of these phenols were then made with the chromatographic eluent.

The sample loop of the injection valve was calibrated by two different methods. Method A consisted of the collection of ten injections of a standard solution of acid with subsequent titration to the phenolphthalein end point by a standard solution of base. The volume of the sample loop was calculated to be 0.0709 mL from the average of three determinations by Method A. Method B was that employed by Morris (166). A pipette was calibrated and used to deliver a known volume of acid into a flask, which was then titrated with base. Ten injections by the injection valve of

this same acid were then collected and titrated with the same base. The volume of the sample loop was calculated from the ratio of the volume of base used to titrate the acid delivered by the pipette to that required to titrate the acid delivered by the injection valve. A volume of 0.0711 mL was calculated from the average of three determinations by Method B. The final average of the six determinations by the two methods was 0.0710 mL.

Removal of the indicator electrode from the wire detector was easily accomplished by loosening the tube-end fittings at the ends of the wire and pulling the wire out of the channel. To replace the wire, it was pushed through the Fetfe seals and the tube-end fittings were then tightened with the fingers. During both removal and replacement of the wire, neither the tube-end fittings nor the Fetfe seals needed to be removed from the detector body.

Static voltammagrams were constructed by plotting the peak current signal, which resulted from an injection of analyte solution, as a function of electrode potential. The direction of change of the electrode potential has been identified on all figures where the data are plotted.

## B. Coulometry

Cresol was used as an alternate to phenol to test the effect of steric hindrance of the electrode reaction. Solutions containing cresol, phenol and bromide separately were prepared by dissolving a weighed amount of the analytes in 0.10 M perchloric acid in volumetric flasks. The flasks were then filled to the mark and dilutions were made from these solutions.

Current signals were recorded and integrated. Integration was accomplished by Simpson's Approximation. Calculations for this approximation were done automatically on the programmable calculator described in the instrumental section. The observed value of n was calculated as indicated in equation XXIX.

## C. Voltammetry

Voltammetric experiments were performed in 0.10 M perchloric acid. Selected volumes of concentrated solutions of phenol, ferric nitrate and sodium chloride were added to the perchloric acid to obtain solutions of the desired consistency. The voltammetric reduction wave of ferric ion was used as a measure of electrode activity. Phenol was not contained in solutions used for electrode reactivation although ferric and chloride ion were often present in solutions used for electrode deactivation. Chronoamperometric studies of the effect of phenolic films on oxygen reduction were performed at platinum electrodes bearing thick phenolic films. These films were prepared by electrolysis of a solution of 1.0 mM phenol for 24 hours or 0.2 M phenol for 1 hour.

The disc electrodes manufactured in the Chemistry Shop had no inert, protective covering to prevent the shaft of the electrode from participating in electrochemical reactions. This problem was circumvented by touching the disc portion of the electrode to the solution and then raising the disc 2 - 3 mM above the solution surface. Natural adhesive and cohesive forces kept the solution in contact with the flat surface of the rotating disc electrode.

## D. Instrumental Characterization of Phenolic Films

### 1. Microscopic examination

Phenolic films of varying thickness and degrees of perforation were prepared on the smallest of the platinum disc electrodes. These electrodes were then examined by Electron Microscopy in the Engineering Research Institute at Iowa State University. The electrode tips were separated from the shafts, mounted in a sample holder, and placed in the sample chamber of the microscope. The surface of the disc electrode was then observed on a video monitor at magnifications of 300 to 10,000 and polaroid photographs were taken of desired areas. Stereoscopic views were obtained by taking two photographs of the same area at angles differing by $8^{o}$ and then observing the photographs with the aid of a stereoscopic viewer.

### 2. Spectroscopic analysis

Sufficient polymeric material for infrared and mass spectroscopic analysis was obtained by the anodic oxidation of phenol at the flag electrode described in section IV-E. The polymeric material was removed mechanically and incorporated into a potassium bromide pellet for infrared analysis. Additional polymeric material was submitted for mass spectral analysis.

## E. Cleaning Procedures

### 1. Disc electrodes

The recommended procedure for removal of the organic films which are formed on platinum disc electrodes during the anodic oxidation of phenol is as follows:

a. Remove the electrode from the phenolic solution and place it in

contact with a solution which is 1.0 mM in Ferric chloride and 0.1 M in perchloric acid. Place a platinum auxiliary electrode and a saturated calomel reference electrode in contact with this same solution. Make the necessary connections to the potentiostat.

b. While rotating the disc electrode, apply an input potential to the potentiostat such that the anodic current density is 100 mA $cm^{-2}$ or greater.

c. After 30 sec, change the input potential of the potentiostat to 0.0 V vs. SCE.

d. Test the electrode for electrochemical activity.

e. Repeat steps a - d as necessary to obtain an electrode with full electrochemical activity.

The rate of rotation (step b) is not critical. Rotation rates of 400 to 3600 rev $min^{-1}$ have been employed without affecting the cleaning procedure. Changing the input potential of the potentiostat to 0.0 volts (step c) for a brief interval allows reduction of the platinum oxides which are formed during the severe anodic polarization. The most convenient test of the electrochemical activity of the electrode is to measure its activity towards the reduction of iron (III) in the cleaning solution.

The only reasons for the failure of this procedure to produce fully active electrodes have been the existence of excessively thick films and instrumental failure. Excessively thick films would be expected to require longer cleaning times and this problem should be solved by step e. Alternatively, the cleaning time in step c may be increased. Instrumental failure was traced to two sources. The first is that the potentiostat did not have sufficient power output. The second was the placement of the auxiliary electrode behind a fine-porosity glass frit. Uncompensated cell

resistance is an important factor when passing large quantities of current in any electrochemical device. This resistance has been found to cause potential changes within cells of this type in excess of 0.5 volt in the laboratory. Any additional resistance within the cell, such as produced by a glass frit, magnifies this problem.

2. Flow-through electrodes

The procedure for reactivation of flow-through electrodes is slightly easier than for the disc electrodes even though the flow-injection system is more complex in its design. A switching valve is inserted into the system between the chromatographic column and the detector. This valve allows the carrier stream flowing through the detector to be changed from the chromatographic eluent to a solution of 0.1 M ferric chloride in 0.1 M perchloric acid. To reactivate a flow-through detector, the following procedure is recommended:

- Change the carrier stream flowing through the detector from the chromatographic eluent to the cleaning solution by switching the appropriate valve.
- Apply an input potential to the potentiostat such that the anodic current density is 100 mA $cm^{-2}$ or greater for 30 seconds.
- Return the input potential of the potentiostat to the desired value and switch the carrier stream flowing through the detector back to the chromatographic eluent.

It is recommended that the flow rate of the cleaning solution be as high as possible to purge the detector of bubbles which are formed during the severe anodic polarization of the electrode. Reduction of the platinum

oxide layer on the surface of the indicator electrode is not recommended. The detection of phenol is carried out at a potential where the electrode surface is oxidized. Waiting for this surface oxide layer to reestablish itself is considered to be an unnecessary waste of time.

Flushing of the cleaning solution from the indicator electrode chamber of the wire detector by the chromatographic eluent occurs very rapidly due to the low dead volume of this design. The indicator electrode is a platinum wire (0.13-cm o.d.) contained in a cylindrical chamber (0.15-cm i.d.) and the portion of the wire which is exposed to the carrier solution is 2.1 cm in length. The calculated cell volume is 0.037 mL.

3. Other methods

During the course of this research, another method was discovered which resulted in removal of the film. This method consists simply of letting the film air dry for 24 hours or more and then directing a stream of water onto the electrode surface. The intact film was easily removed from the electrode, often in one piece. Unsuccessful attempts were made to remove these phenolic films from platinum electrodes by dissolution in hexane, heptane, pentane, cyclohexane, acetone, methanol, ethanol, ethyl acetate, methylene chloride, chloroform, carbon tetrachloride, toluene, aqueous acid, aqueous base and N,N-dimethylformamide. The film could be removed by the application of extreme heat or abrasive procedures; however, these methods cannot be considered suitable to routine analysis.

# VI. RESULTS AND DISCUSSION

## A. Evaluation of Wire Detector

The investigation of new electrode geometries for hydrodynamic voltammetry, and the solution of the equation of mass transport for those geometries, has long been fashionable for academic electroanalytical research. While the achievement of higher analytical sensitivity and convenience would seem to be sufficient motivation for such research, the work is usually considered unfinished unless equations are presented which quantitatively predict the shapes of current-potential curves and permit quantitative measurement of heterogeneous rate constants. Indeed, from a cursory study of the modern literature on analytical voltammetry, one can hardly avoid the false conclusion that applications of voltammetry for quantitative analysis are possible only if the theoretical relationship between the limiting electrode current and bulk analyte concentration is fully described as a function of all experimental variables. In practice, however, amperometric applications of hydrodynamic voltammetry always rely on calibration with suitable standards. Even for an absolute detector such as the coulometric flow-through electrode (100% efficient), for which the charge is related to the quantity of analyte by Faraday's law, equation XXIX, the careful analyst invariably will analyze a standard sample to verify the assumption of coulometric operation under the experimental conditions appropriate for analysis of the unknown sample (167).

The wire configuration was chosen in an effort to increase the available surface area of the electrode while maintaining the simplicity of the

detector. Application of the wire flow-through detector was made for flow-injection analysis and steady-state analysis of solutions containing $6.81 \times 10^{-5}$ M NaI and $1.64 \times 10^{-5}$ M As (III). The detector efficiency is plotted vs. flow rate on a log-log scale in Figure 10. Also shown is the value of slope ($\alpha$ - 1) for the estimated linear fit of each set of data. The experimental slopes are very nearly equal to the value of -0.667 predicted by Ross and Wragg for their annular electrode under laminar fluid flow (164). The plot of log E vs. log $V_f$ calculated by the function $AK_1V_f = 24.2D^{2/3}V_f^{-2/3}$, using $D = 1.99 \times 10^{-5}$ $cm^2sec^{-1}$ for iodide (168), is shown for comparison.

The precision of results obtained during continuous use of the detector is limited by the precision of the control and measurement of the flow rate. The large variation of efficiency between experiments apparently resulted from disassembly of the detector for inspection. Although clearance between the wire and channel wall was chosen such that the open cross-sectional area of the channel was approximately equal to the cross-sectional area of the incoming fluid stream, no attempt was made to control the position of the wire within the IE channel. According to Ross and Wragg (164), the spacing between the electrode and the channel wall is important in determining the numerical value of $K_1$. Once assembled, the position of the wire did not vary within the channel during normal use and $K_1$ was, therefore, constant.

A typical recording of detection peaks for repetitive injections of $6.81 \times 10^{-5}$ M NaI in 1.0M $H_2SO_4$ is shown in Figure 11. The average area

Figure 10. Log of detector efficiency versus log of flow rate for wire detector

Sample volume: 0.226 mL
Steady state analysis: ◇- $6.81 \times 10^{-5}$ M NaI, E = 0.80 V vs. SCE
□- $1.64 \times 10^{-5}$ M As(III), E = 1.0 V vs. SCE
Flow injection analysis: △- $6.81 \times 10^{-5}$ NaI, E = 0.80 V vs. SCE
○- $1.64 \times 10^{-5}$ M As(III), E = 1.0 V vs. SCE

—— Theory
Values of slope given in figure

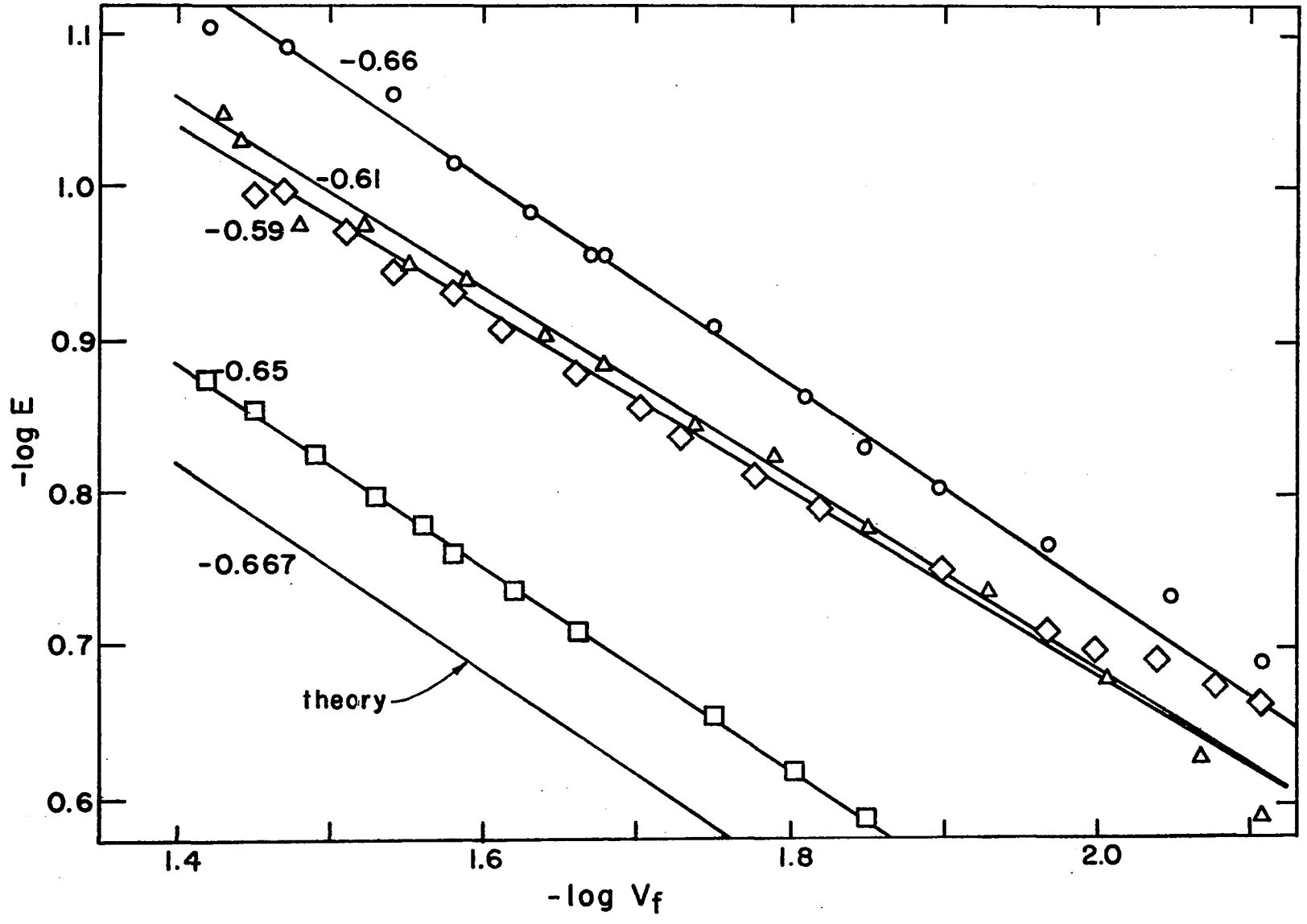
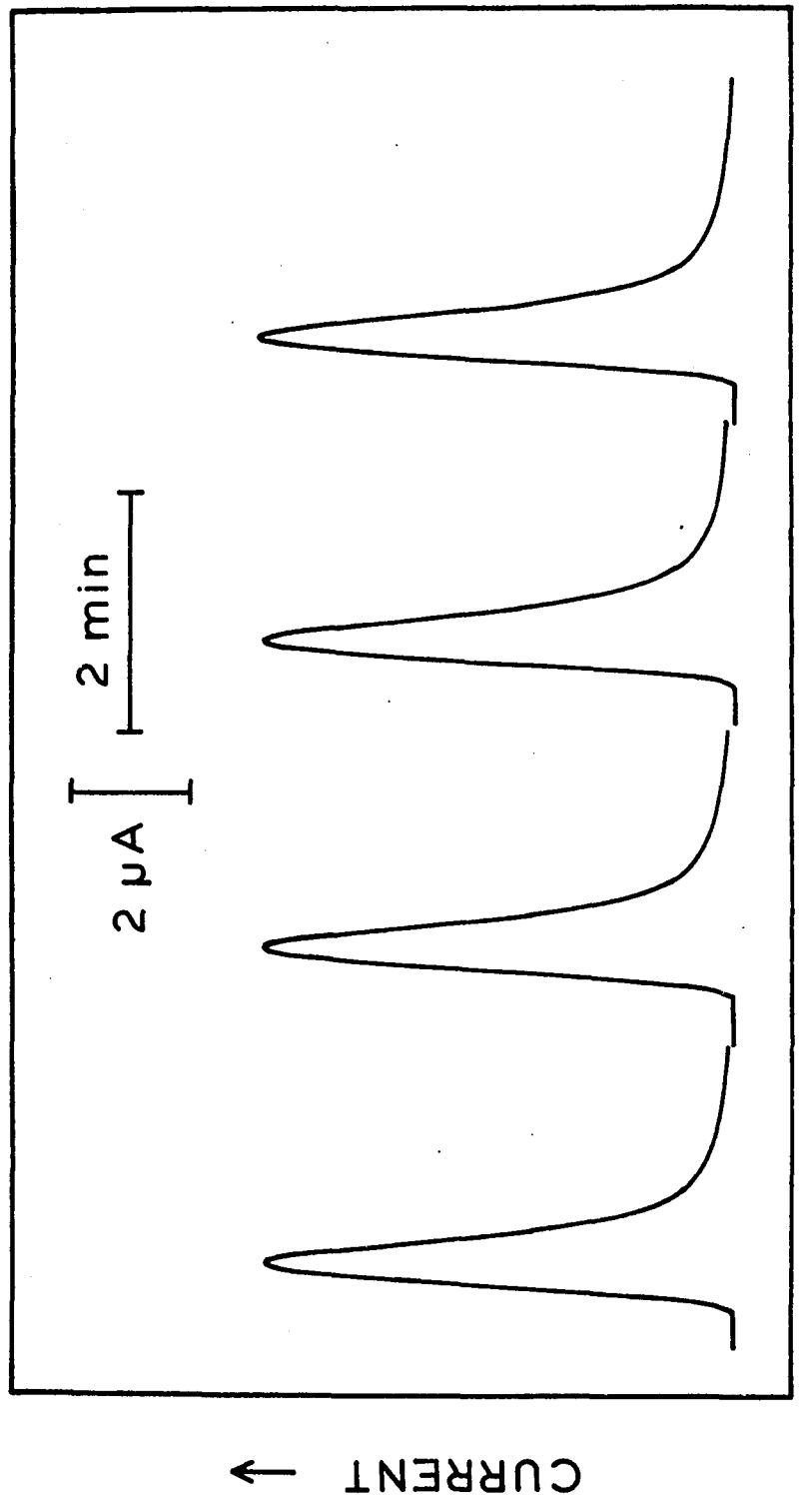

1.1
1.0
0.9
0.8
0.7
0.6
-log E
1.4
1.6
1.8
2.0
-log $V_f$
-0.66
-0.61
-0.59
0.65
-0.667
theory

Figure 11. Response of wire detector to repetitive injections of iodide

Concentration: $6.81 \times 10^{-5}$ M No. I in 1.0 M $H_2SO_4$
Carrier solution: 1.0 M $H_2SO_4$
Sample volume: 0.226 mL
Flow rate: 0.99 mL $min^{-1}$
Applied potential: 0.80 V vs. SCE


2 min
2 μA
TIME →
CURRENT ←

for 4 peaks in the series was 201 ucoul with a relative standard deviation of 27 ppt.[1] These results agree with other reports concerning the performance of this detector (160, 161, 163).

## B. Flow-injection Amperometry of Phenol

When studying the electrochemical oxidation of phenol, the analyst is faced with problems which are not encountered with the majority of inorganic reactions. Normally, electrochemical information can be obtained in the form of current-potential (I-E) curves employing a rotating disc electrode (RDE). This information is useful in choosing an electrode potential for the detection of the analyte at a rate limited by mass transport rather than heterogeneous kinetics. When the products of the electrode reaction do not accumulate on the electrode surface, the reaction is expected to proceed indefinitely without loss of electrode response. During the electrochemical oxidation of phenol, and many other organic compounds, the products of the oxidation can be a major concern to the analyst. As previously mentioned, these products tend to form polymeric films which adhere to the surface of the electrode and distort electrochemical response to such a degree that the response is of little quantitative value to the analyst.

When performing electroanalysis with flow-through detectors, such as is used in flow-injection analysis, the analyst desires to set the potential

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[1] Experimental data presented in this section was obtained by Jean A. Lown, who is presently employed by the Union Carbide Corp., Bound Brook, NJ.

of the indicator electrode such that maximum analytical sensitivity is obtained. When the use of voltammagrams which are obtained under dynamic conditions does not prove fruitful for obtaining this information, the analyst must then resort to other techniques. One technique which has proven to be of significant utility is the construction of static voltammagrams or pseudo I-E curves. This type of voltammagram is obtained by the procedure given in a previous section.

Figures 12, 13, and 14 are static voltammagrams for phenol in a solution containing 71% of 0.05 N sulfuric acid and 29% acetonitrile employing the platinum wire, glassy carbon tubular, and conducting polymer tubular flow-through electrodes. These electrode materials were compared as to their suitability for the detection of phenol. All three electrode materials were found to be deactivated by the electrochemical oxidation products of phenol. The flow-through electrodes were partially deactivated upon a single injection of a solution of phenol whose concentration exceeded 10 μM. Repeated injections of solutions of phenols whose concentration was 10 μM or less resulted in no observable loss of electrode activity. Examination of these static voltammagrams and the observed uncertainty of the residual current of each electrode material, led to the conclusion that platinum is the superior electrode material for the detection of phenol by anodic oxidation.

Figure 15 is a static voltammagram for the oxidation of phenol at a platinum electrode in 0.10 M perchloric acid. A potential of 1.20 V was determined to be the best potential for the flow-injection analysis of phenolic solutions containing phenol in 0.10 M $HClO_4$ after evaluation of

Figure 12. Static voltammagram of phenol at a platinum electrode

Carrier solution: 29% acetonitrile - 71% 0.05 M sulfuric acid
Phenol concentration: 1.0 μM
Sample volume: 0.0710 mL
Flow rate: 1.0 mL $min^{-1}$

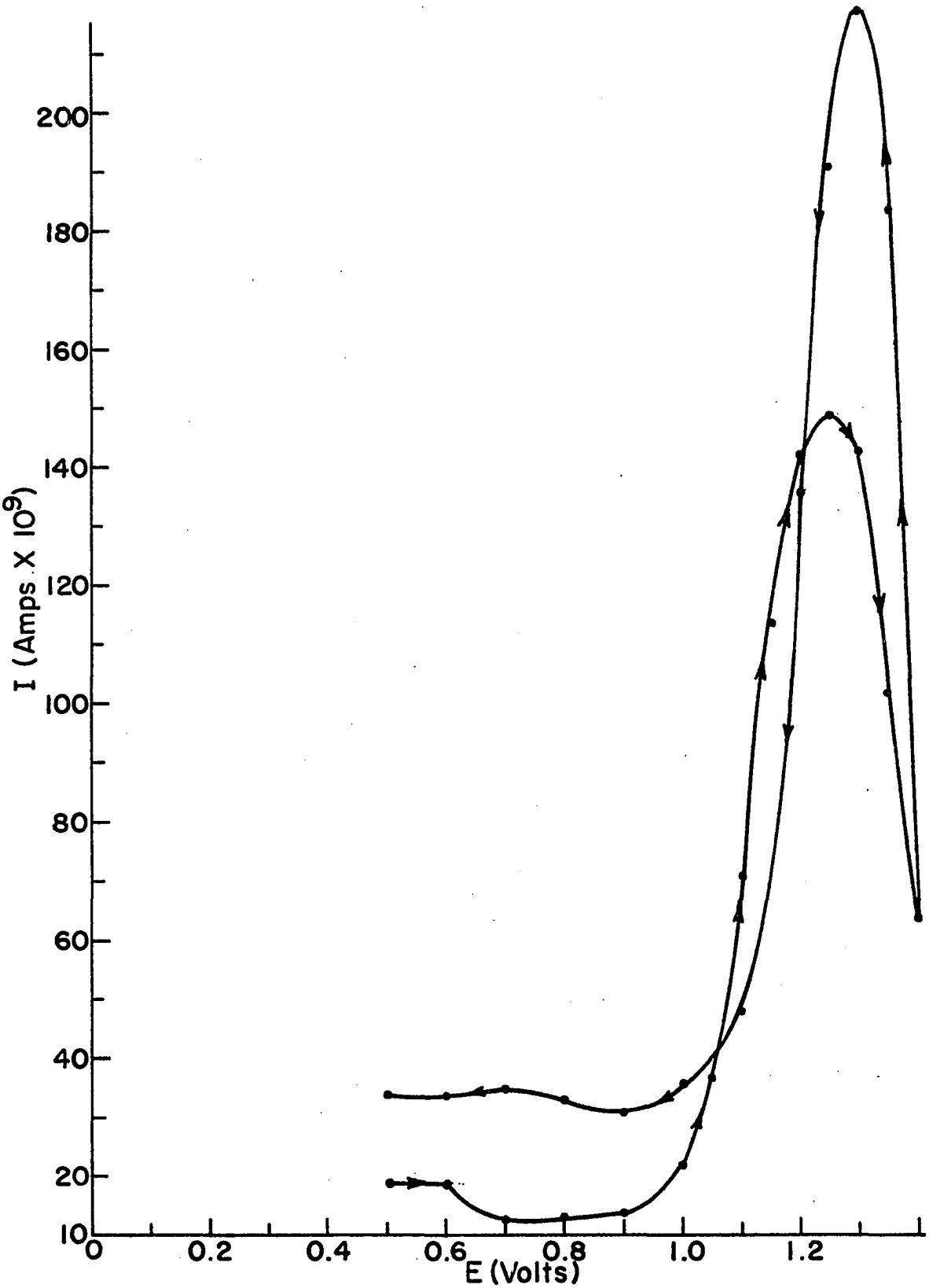

200
180
160
140
120
100
80
60
40
20
10
I (Amps X 10^9)
0
0.2
0.4
0.6
0.8
1.0
1.2
E (Volts)

Figure 13. Static voltammagram of phenol at a glassy carbon electrode

Carrier solution: 29% acetonitrile - 71% 0.05 M sulfuric acid
Phenol concentration: 1.0 μM
Sample volume: 0.0710 mL
Flow rate: 1.0 mL $min^{-1}$

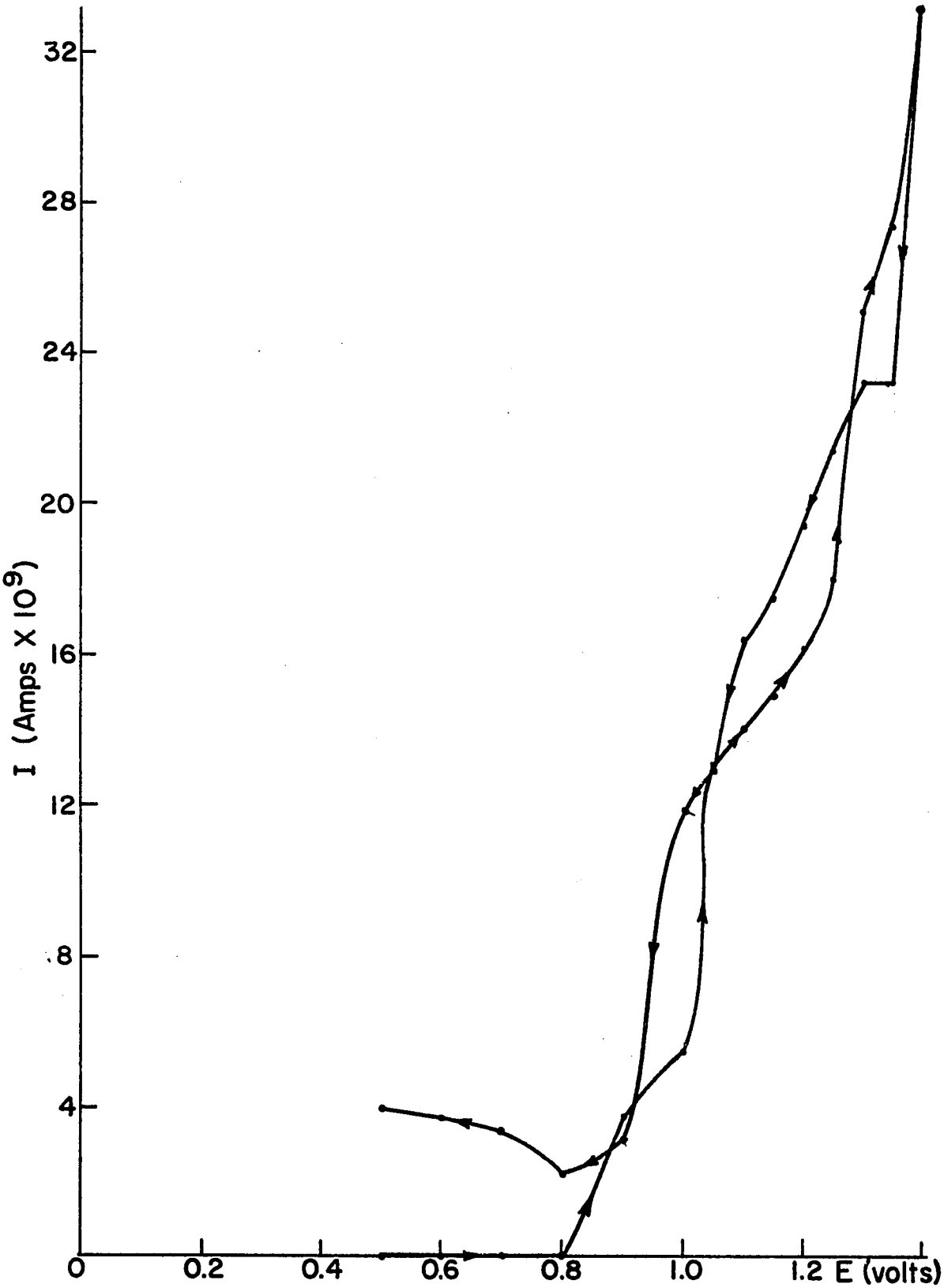

32
28
24
20
16
12
.8
4
0
0.2
0.4
0.6
0.8
1.0
1.2 E (volts)
I (Amps X 10^9)

Figure 14. Static voltammagram of phenol at a conducting polymer electrode

Carrier solution: 29% acetonitrile - 71% 0.05 M sulfuric acid
Phenol concentration: 10.0 μM
Sample volume: 0.0710 mL
Flow rate: 1.0 mL $min^{-1}$

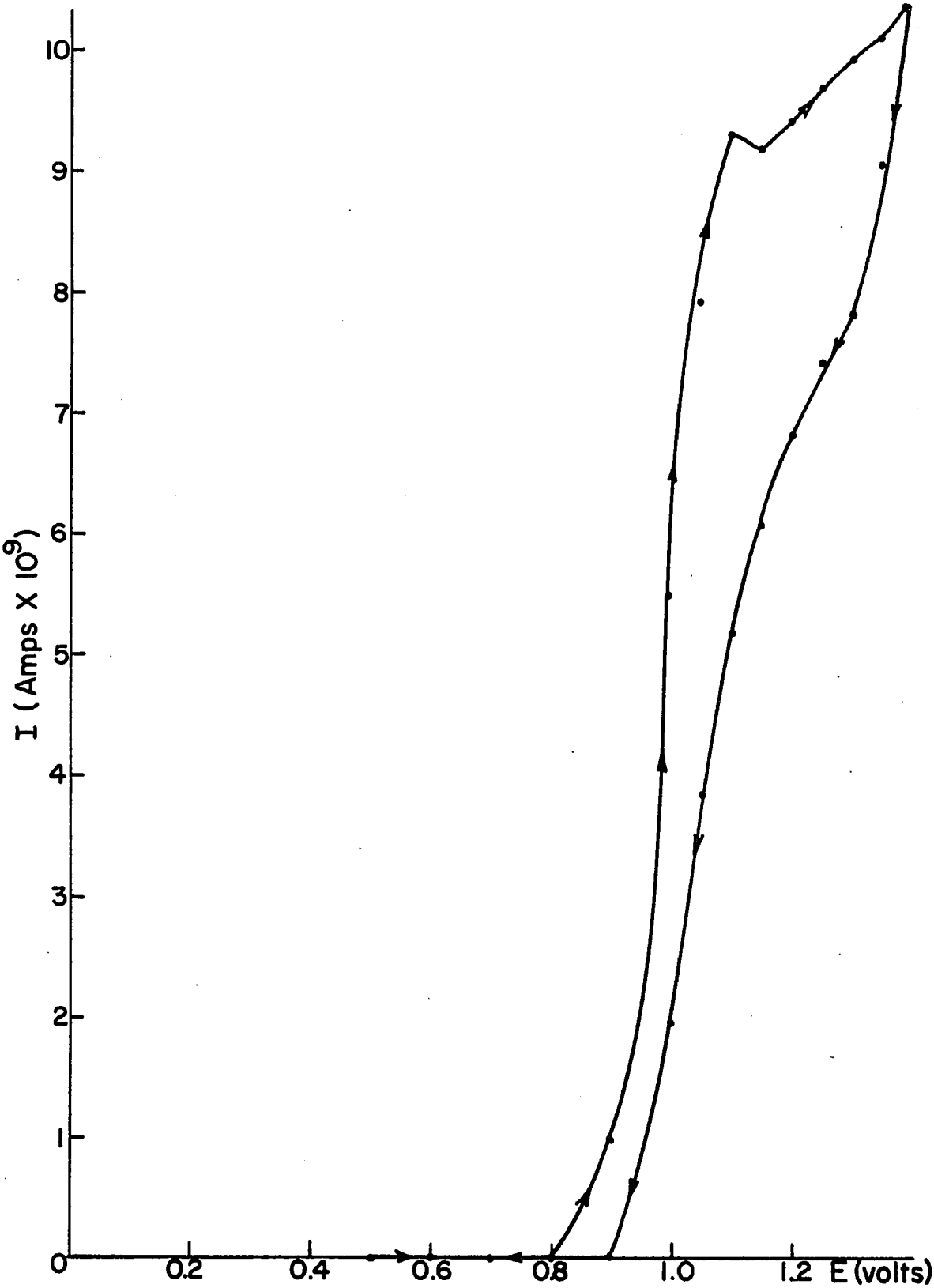
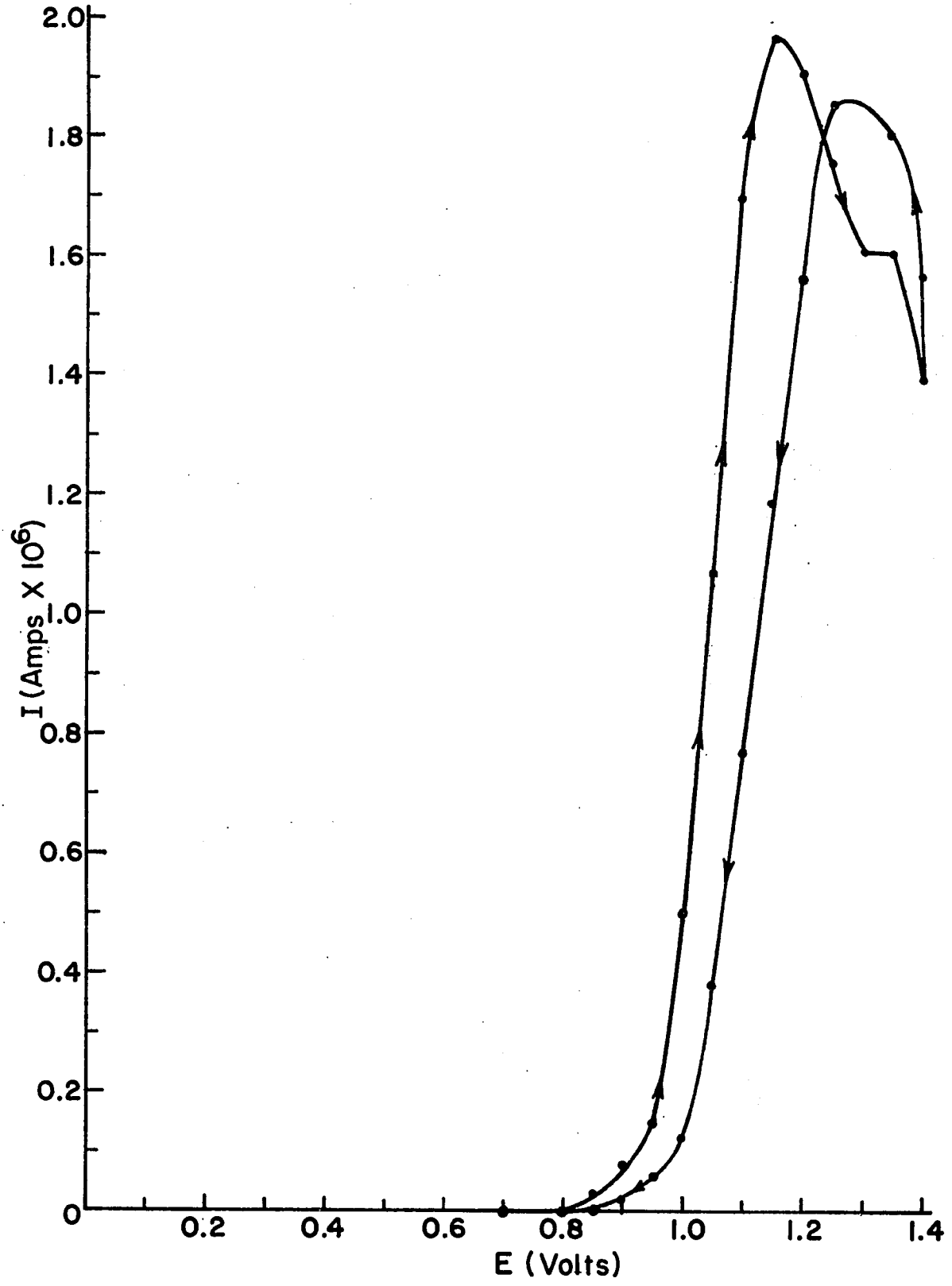

I (Amps X 10^9)
0
1
2
3
4
5
6
7
8
9
10
0.2
0.4
0.6
0.8
1.0
1.2
E (volts)

Figure 15. Static voltammagram of phenol at a platinum electrode

Carrier solution: 0.10 M perchloric acid
Phenol concentration: 10.0 μM
Sample volume: 0.0710 mL
Flow rate: 1.0 mL $min^{-1}$


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
I (Amps X 10^6)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
E (Volts)

the data which are shown in Figure 9. A potential of 1.30 V was chosen as the best potential for the flow-injection analysis of solutions containing phenol in the solution containing 71% 0.05N sulfuric acid and 29% acetonitrile mixture after evaluation of the data shown in Figure 12. These potentials were employed in all subsequent amperometric and coulometric analyses of solutions containing phenol.

Once the proper potential for the oxidation of phenol at a platinum electrode had been obtained, the reproducibility of the detector response was tested. The detector response to successive injections of 10 μM phenol in 0.10 M perchloric acid is shown in Figure 16. No loss of electrode activity was observed and the reproducibility of the detector response was considered satisfactory (relative standard deviation = 9.7 ppt).

Although the electrode responded well to injections of 10 μM phenol, the oxidation of phenol at higher concentrations resulted in electrode deactivation. This deactivation process not only affected the response of the electrode with respect to phenol, but also with respect to other electroactive species. This point was demonstrated by observing the response of the platinum wire flow-through detector to bromide at various stages of electrode deactivation during the anodic oxidation of phenol. Series A of Figure 17 shows the effect of deactivation for the detection of a relatively high concentration of phenol at a flow-through electrode. Series B shows the response of the electrode to a solution 0.10 mM in bromide. The injections of the bromide solution were made alternately with the injections of the phenol solution. Peak 0 was obtained for bromide at

Figure 16. Response of wire detector to repetitive injections of phenol

Carrier solution: 0.10 M perchloric acid
Phenol concentration: 10 μM
Sample volume: 0.0710 mL
Flow rate: 1.0 mL $min^{-1}$

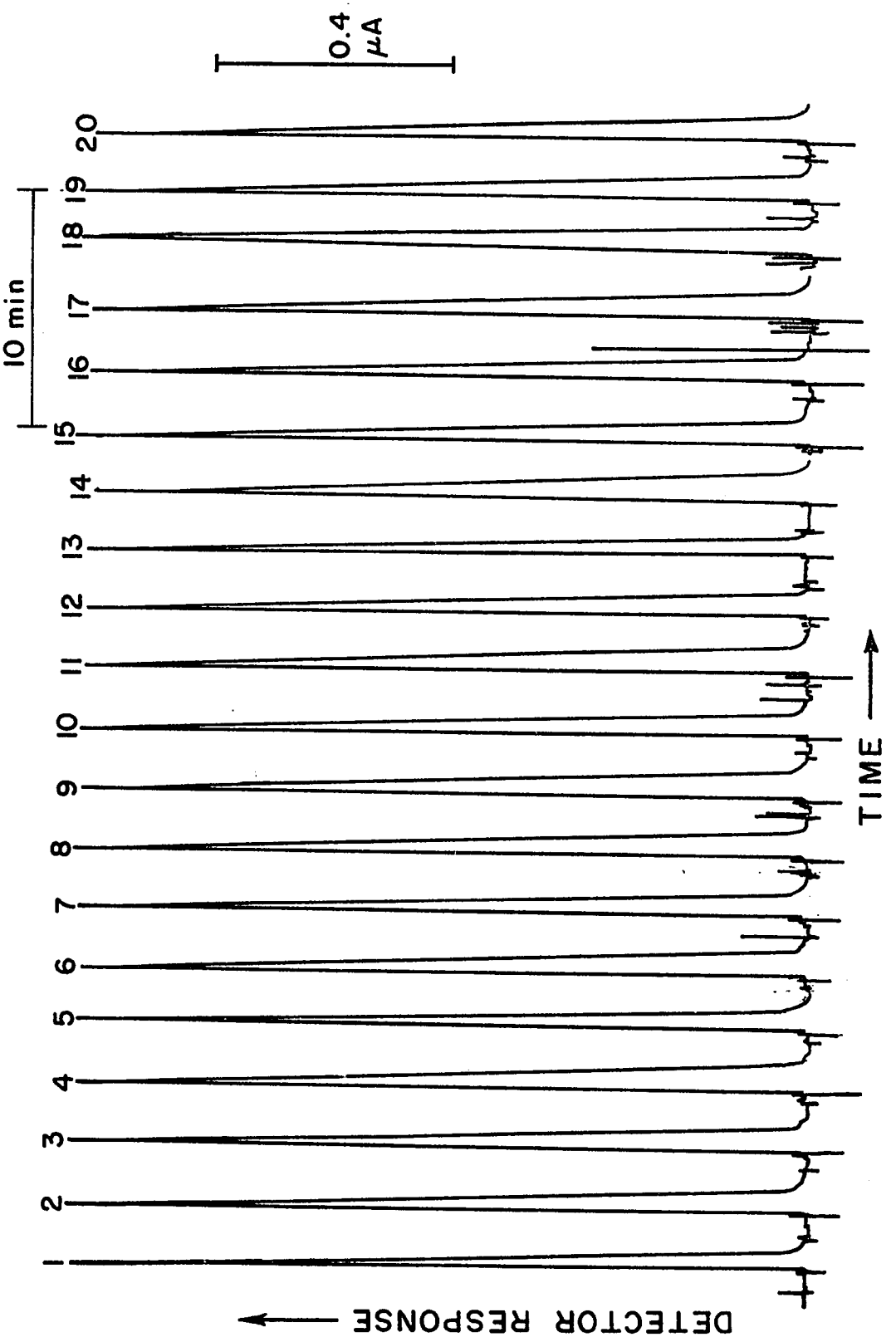
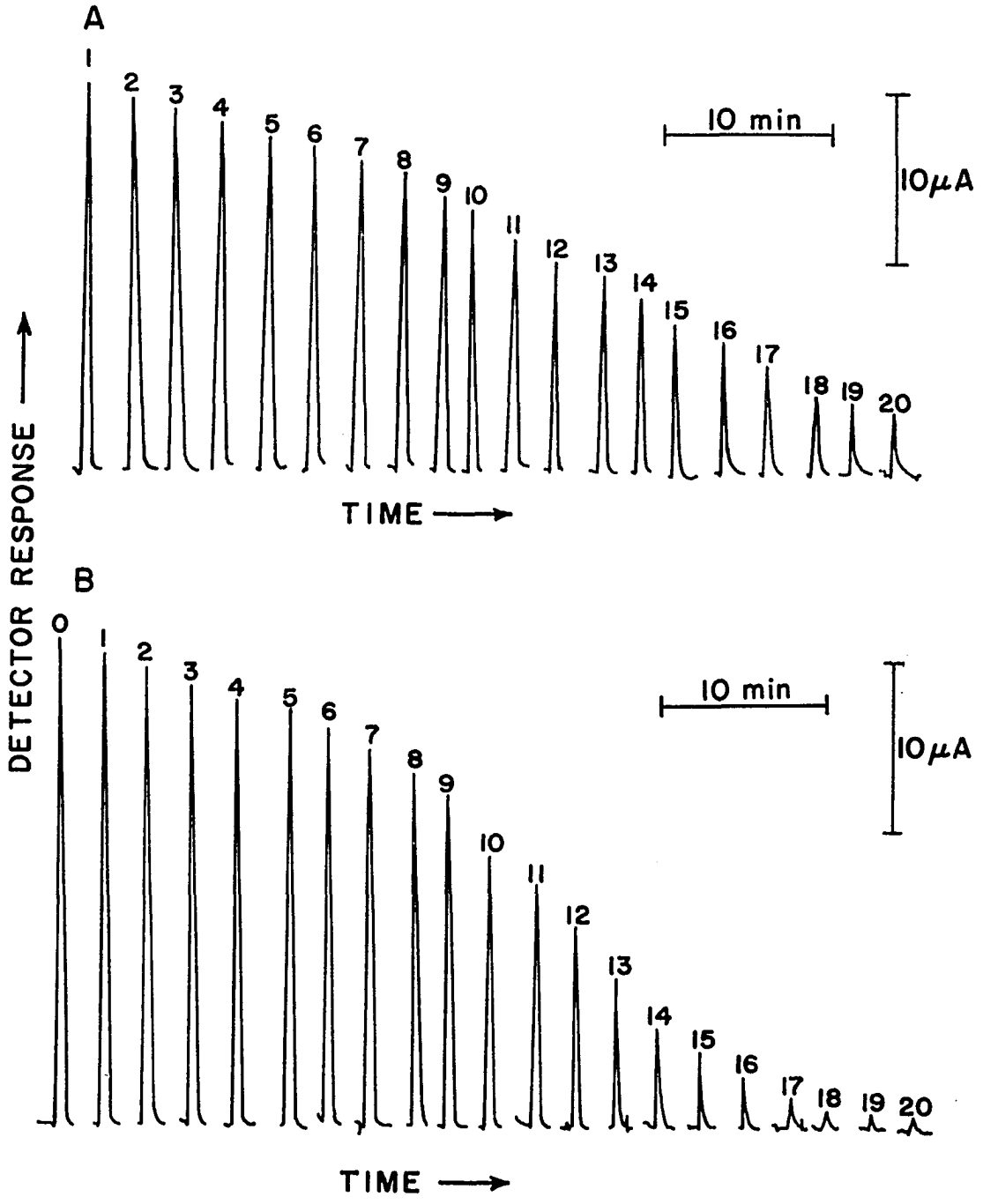

0.4 μA
10 min
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
TIME
DETECTOR RESPONSE

Figure 17. Effect of electrode deactivation on the anodic detection of phenol and bromide

Carrier solution: 0.10 M perchloric acid
Analyte concentration: A - 1.0 mM phenol
B - 0.1 mM sodium bromide
Sample volume: 0.0710 mL
Flow rate: 1.0 mL $min^{-1}$


A
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
10 min
10μA
DETECTOR RESPONSE
TIME
B
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
10 min
10μA
TIME

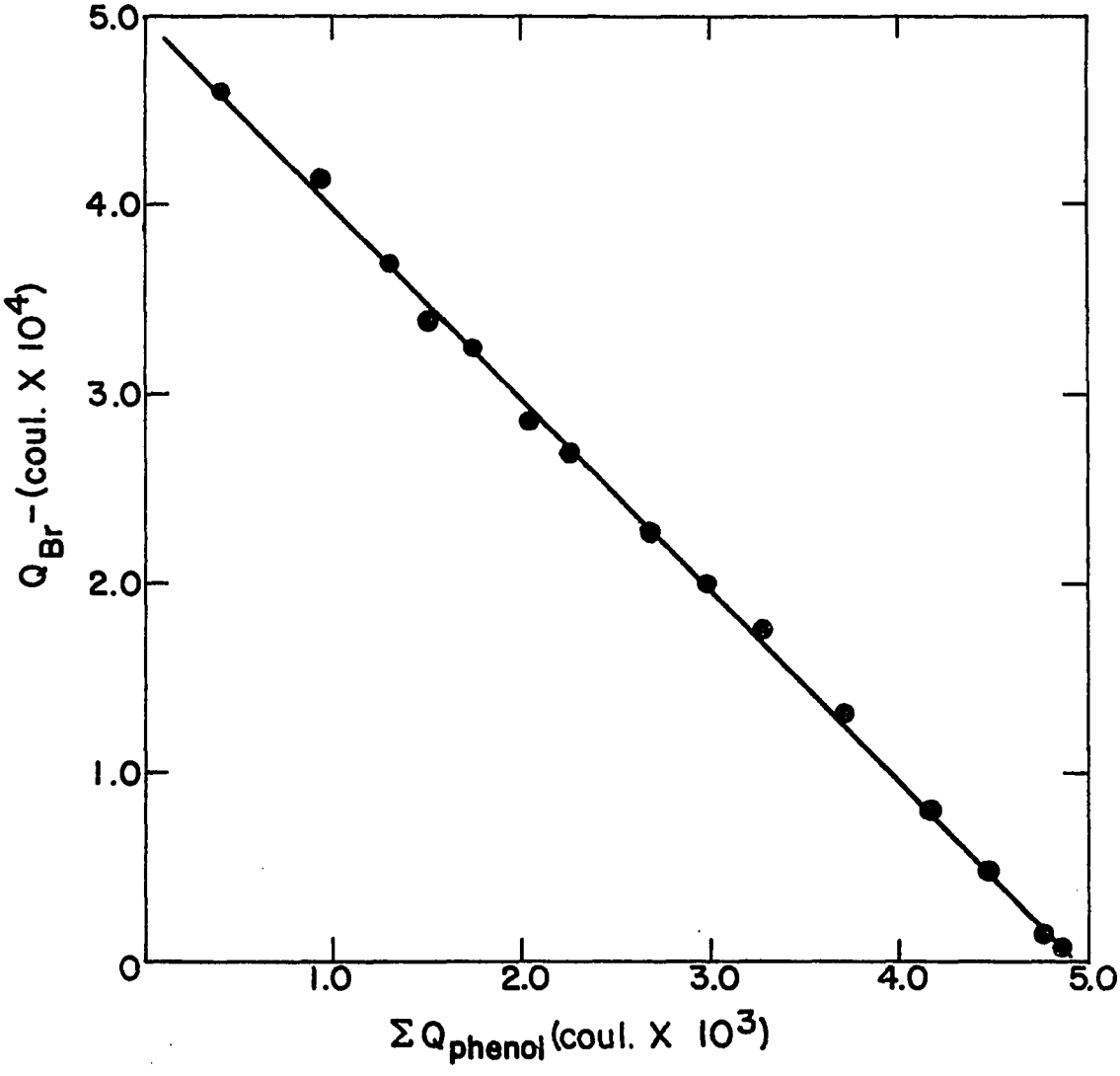
the fully activated electrode prior to the first injection of phenol.

Gileadi calculated the thickness of the film on the electrode surface at the point when the electrode activity is lost, based on data obtained from charge transfer measurements. He reported a value of about 200 monolayers of the phenoxy radical (132). Figure 18 shows the result of a study in which the charge which passed in the electrode due to injections of a standard bromide solution is measured and recorded as a function of the total charge which passed due to phenol oxidation. The quantity of adsorbed phenol producing a complete loss of electrode activity was calculated to be 32 monolayer from the data in Figure 18. This calculation was based on the following assumptions: the electrode reaction produces only the phenoxy radical which is quantitatively adsorbed, the electrode surface is perfectly smooth, and a one-to-one correspondence exists between platinum atoms and adsorbed radicals.

Before taking issue with Gileadi's claim of about 200 monolayers, it is prudent to examine the assumptions on which these calculations were based. First, there was no reason to assume a one-to-one correspondence between phenoxy radicals and platinum atoms. For such an assumption to be valid, one must accept a spacing between phenoxy radicals (center-to-center) which is no greater than 2.8 Å in either direction on the surface plane of the electrode. The assumption that the only reaction which occurred was the oxidation of phenol to the phenoxy radical, cannot be considered valid due to the very nature of the experiment. The only reaction which phenoxy radicals can undergo which does not involve further

Figure 18. Anodic charge which passed due to injections of a standard bromide solution versus the total charge which has passed due to phenol oxidation

Carrier solution: 0.10 M perchloric acid
Analyte concentration: Phenol - 1.0 mM
Bromide - 1.0 mM
Sample volume: 0.0710 ml
Flow rate: 1.0 mL $min^{-1}$


5.0
4.0
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
$Q_{Br^-}$ (coul. X $10^4$)
$\Sigma Q_{phenol}$ (coul. X $10^3$)

oxidation under these conditions is simple coupling. Since a polymeric film was being formed on the surface of the electrode, it is certain that more than dimerization was occurring. To assume that phenoxy radicals were retained quantitatively, one also must assume that numerous layers of radicals are in extremely close proximity and that no following reaction occurs, not even coupling. This is not plausible. Finally, the assumption of a perfectly smooth electrode is easily invalidated. Figure 19 shows an electron microphotograph of the surface of a platinum disc electrode. This photograph shows the surface of the electrode as it appears magnified by a factor of 5000. This same surface appeared to be mirror smooth to the unaided eye.

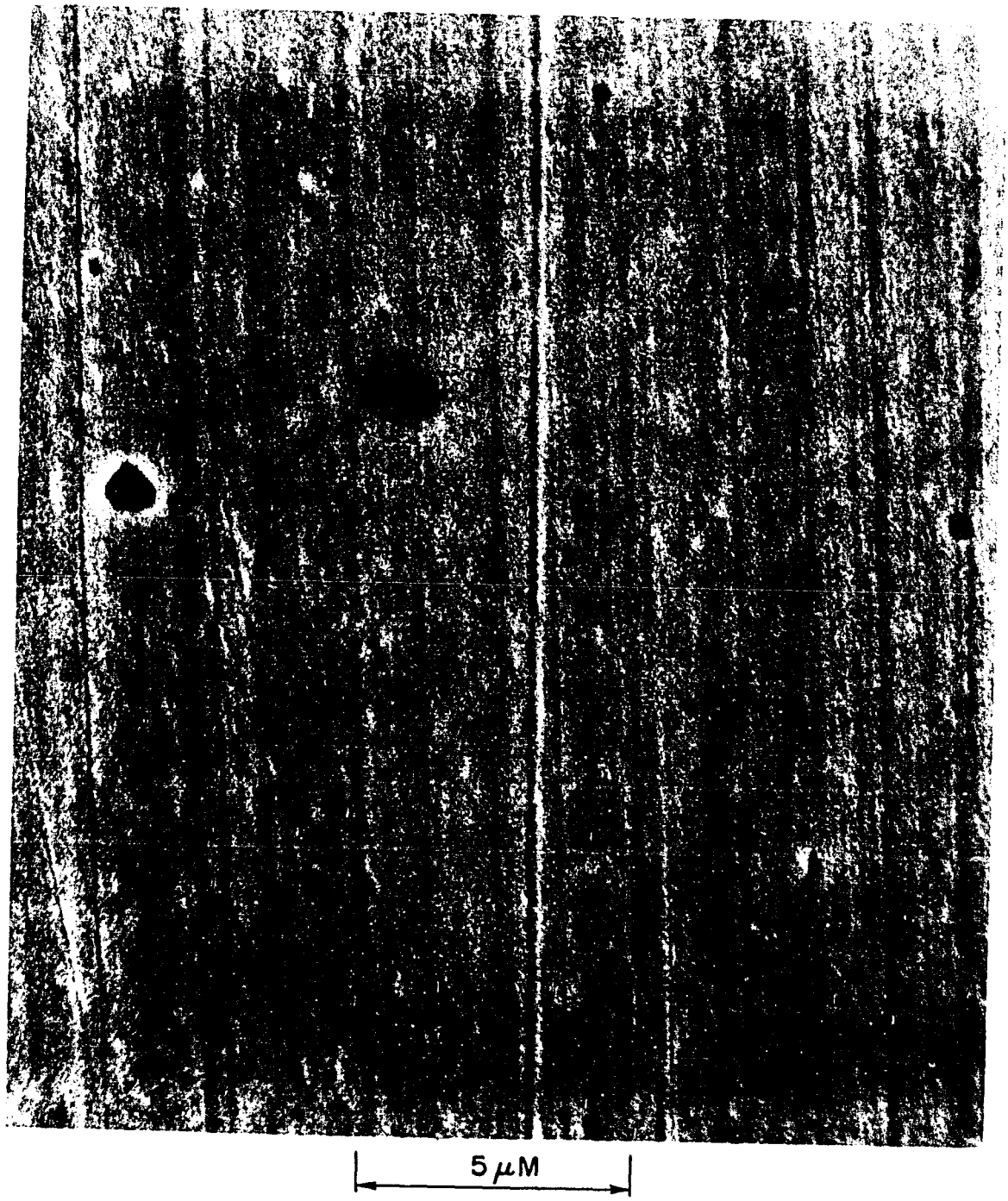
Every assumption which was made in the interpretation of the data in Figure 18 has been shown to be invalid. The calculated number of monolayers of adsorbed phenoxy radical cannot, therefore, be taken seriously. The only thing which may be concluded from this study is that the amount of charge which must pass due to oxidation of phenol to achieve a total loss of electrode activity is a function of the local concentration of phenol during the oxidation process. This conclusion is consistent with a mechanism which involves the coupling of reaction intermediates to form a polymeric matrix.

## C. Flow-injection Coulometry

The value of $V_m$, the maximum flow rate at which a coulometric electrode can maintain its coulometric character, was determined for the coulometric electrode which was used in this study by observing the measured value of n

Figure 19. Electron microphotograph of a mechanically polished platinum disc electrode

Tilt angle: $0^{o}$
Scanning speed: 80 sec
Ion beam voltage: 25 KV
Remarks: Dark areas are holes in the platinum surface


5 μM

for the oxidation of bromide to bromine as a function of flow rate. This reaction is known to be a fast one-electron reaction on platinum electrodes. The results of this study are shown in Figure 20. This study indicated that this particular electrode is coulometric at flow rates below 2.0 mL $min^{-1}$. Once this value had been determined, the effects of concentration, flow rate, and steric hindrance on the observed value of n during the oxidation of phenol was ascertained.

The effect of the variation of the flow rate on the observed value of n is shown in Figure 21. The observed value of n had an inverse relationship to flow rate at all concentrations measured. In consideration of the theory presented earlier in this thesis, it is concluded that the oxidation of phenol on platinum anodes occurs by way of a coupled chemical reaction over the concentration range studied. This process is, in general, referred to as an ECE mechanism: that is an electrochemical-chemical-electrochemical sequence occurs in the reaction mechanism.

The effect of the variation of the concentration of phenol on the observed value of n was also studied. The results of this study are shown in Figure 22. The observed value of n was found to decrease with increasing concentration over the entire range of flow rates studied. Comments and conclusions based on the result of this study are reserved for a later section.

Orthocresol was chosen as a compound which has properties similar to phenol, yet would be sterically hindered in the coupling reactions. The results are shown in Figure 23. The observed values of n for the oxidation

Figure 20. Efficiency of coulometric detector versus flow rate

Carrier solution: 0.10 M perchloric acid
Analyte concentration: 8.83 uM sodium iodide
Sample volume: 0.0710 mL
Applied potential: 0.800 V vs. SCE

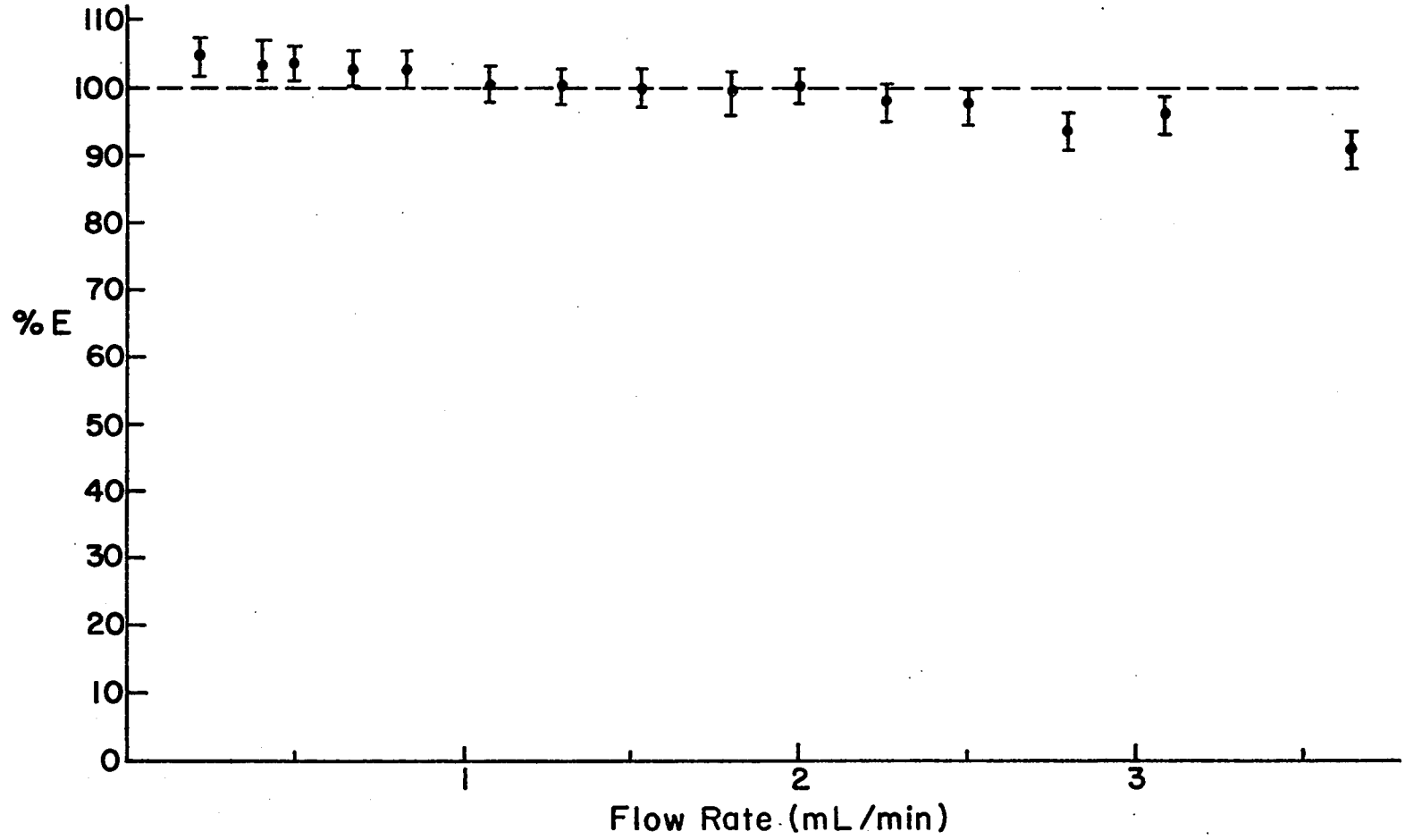

110
100
90
80
70
% E
60
50
40
30
20
10
0
1
2
3
Flow Rate (mL/min)

Figure 21. Observed value of n for phenol versus flow rate

Carrier solution: 0.10 M perchloric acid
Phenol concentration: A - $9.97 \times 10^{-8}$ M
B - $9.97 \times 10^{-7}$ M
C - $9.97 \times 10^{-6}$ M
Sample volume: 0.0710 mL
Applied potential: 1.20 V vs. SCE

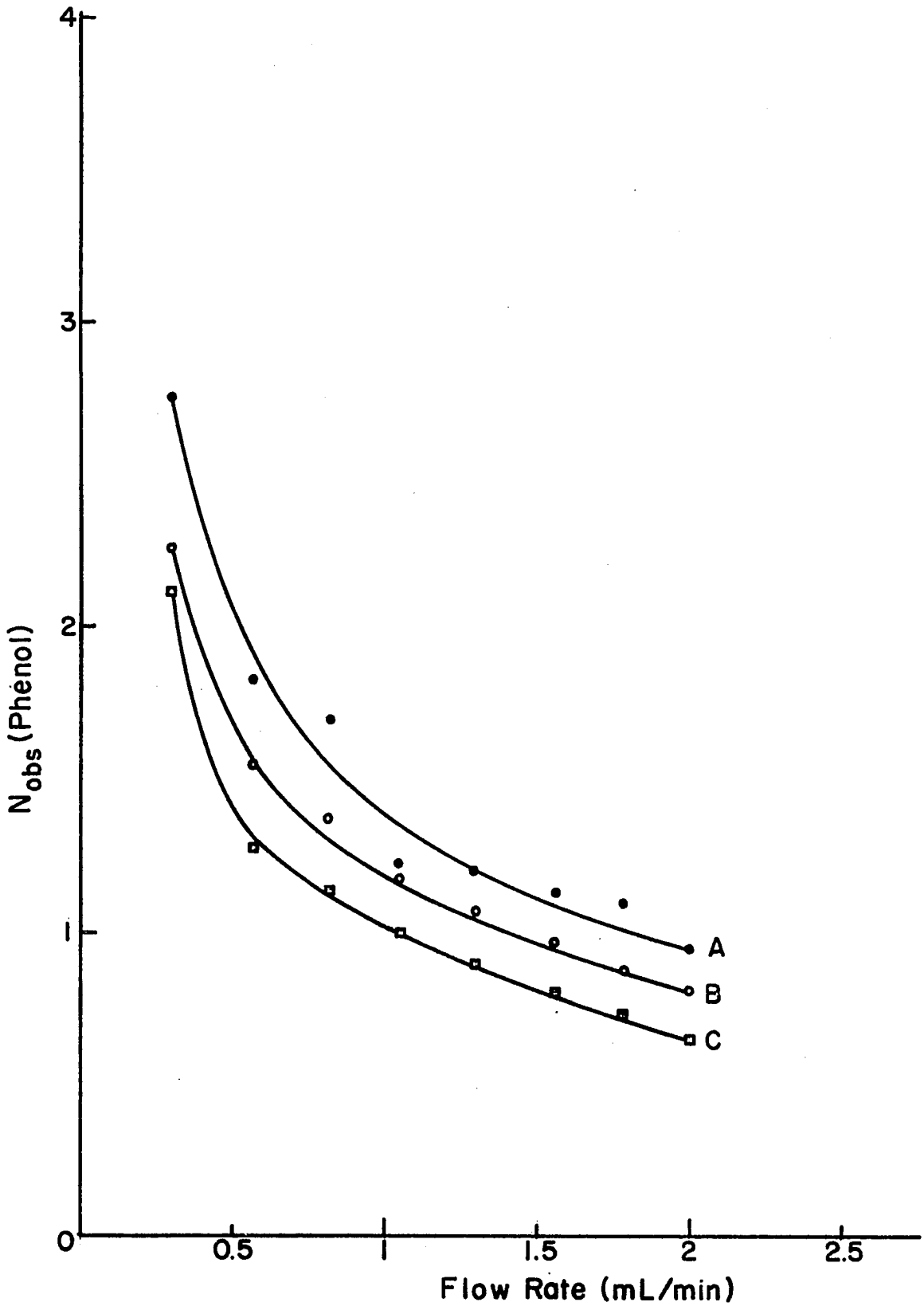

4
3
2
1
0
$N_{obs}$ (Phenol)
0.5
1
1.5
2
2.5
Flow Rate (mL/min)
A
B
C

Figure 22. Observed value of n for phenol versus log of phenol concentration

Carrier solution: 0.10 M perchloric acid
Sample volume: 0.0710 mL
Flow rate: A - 0.57 mL $min^{-1}$
B - 1.05 mL $min^{-1}$
C - 1.56 mL $min^{-1}$
D - 2.00 mL $min^{-1}$
Applied potential: 1.20 V vs. SCE

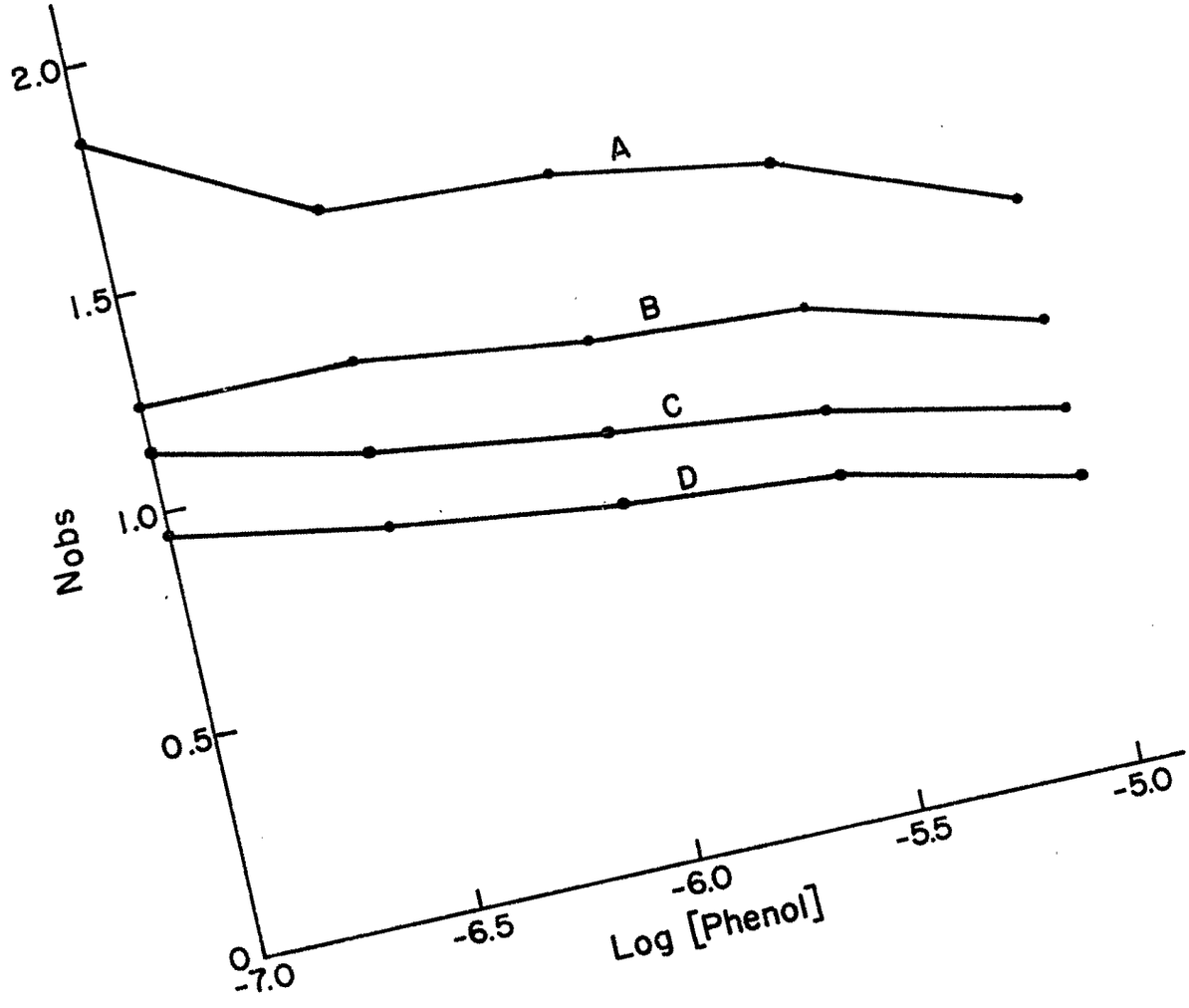
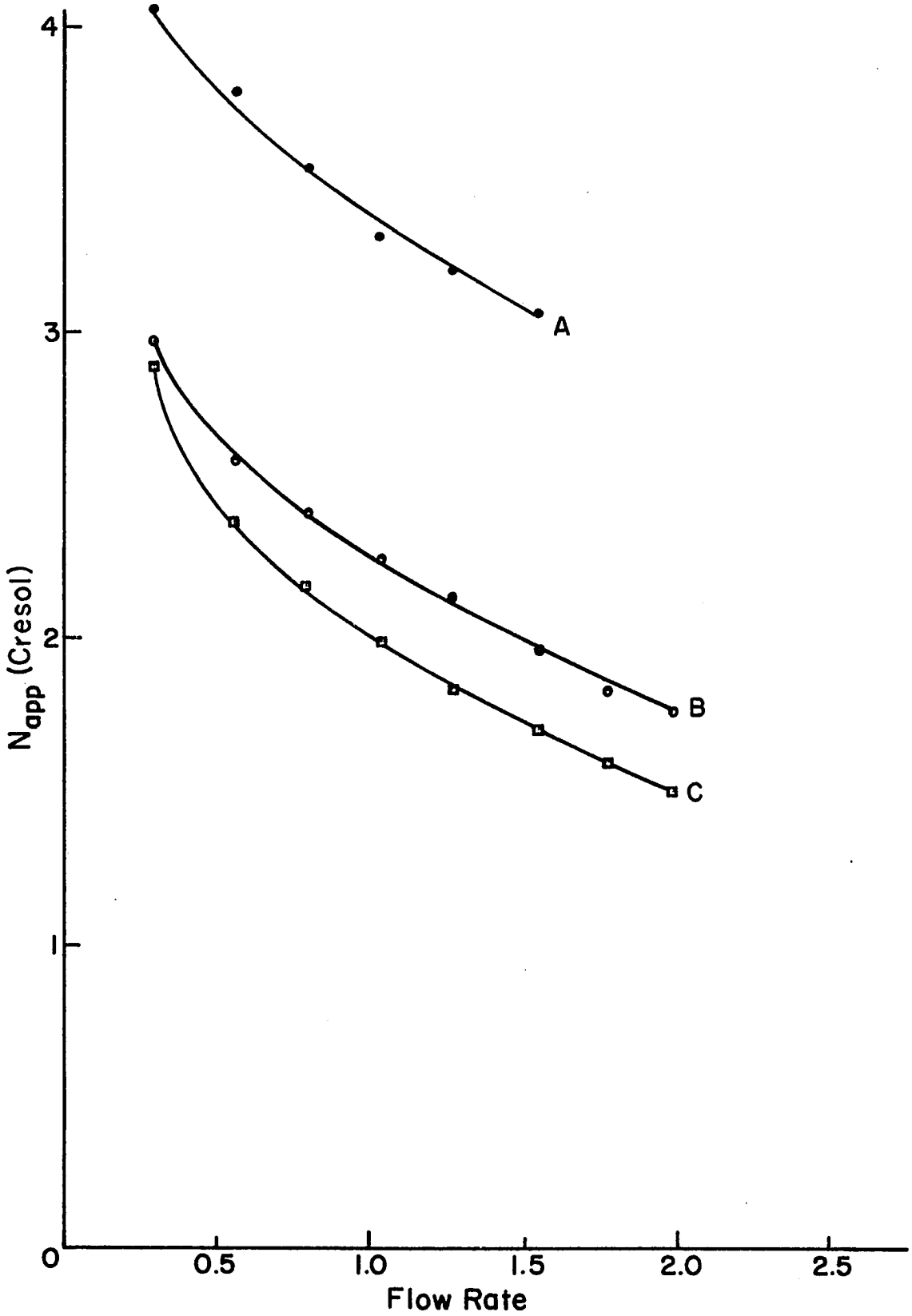

2.0
1.5
1.0
0.5
0
Nobs
A
B
C
D
-7.0
-6.5
-6.0
-5.5
-5.0
Log [Phenol]

Figure 23. Observed value of n for o-cresol versus flow rate

Carrier solution: 0.10 M perchloric acid
o-Cresol concentration: A - $9.44 \times 10^{-8}$
B - $9.44 \times 10^{-7}$
C - $9.44 \times 10^{-6}$
Sample volume: 0.0710 ml
Applied potential: 1.20 V vs. SCE


4
3
2
1
0
$N_{app}$ (Cresol)
A
B
C
0.5
1.0
1.5
2.0
2.5
Flow Rate

of orthocresol are higher than the corresponding values of n for phenol over the concentration and flow rate ranges studied. It is noteworthy that the changes, with respect to flow rate and concentration, in the observed values of n for orthocresol are similar to those observed for phenol. It is also noteworthy that change in concentration had a larger effect on the changes of the observed values of n for orthocresol than phenol. These results are discussed further in a later section.

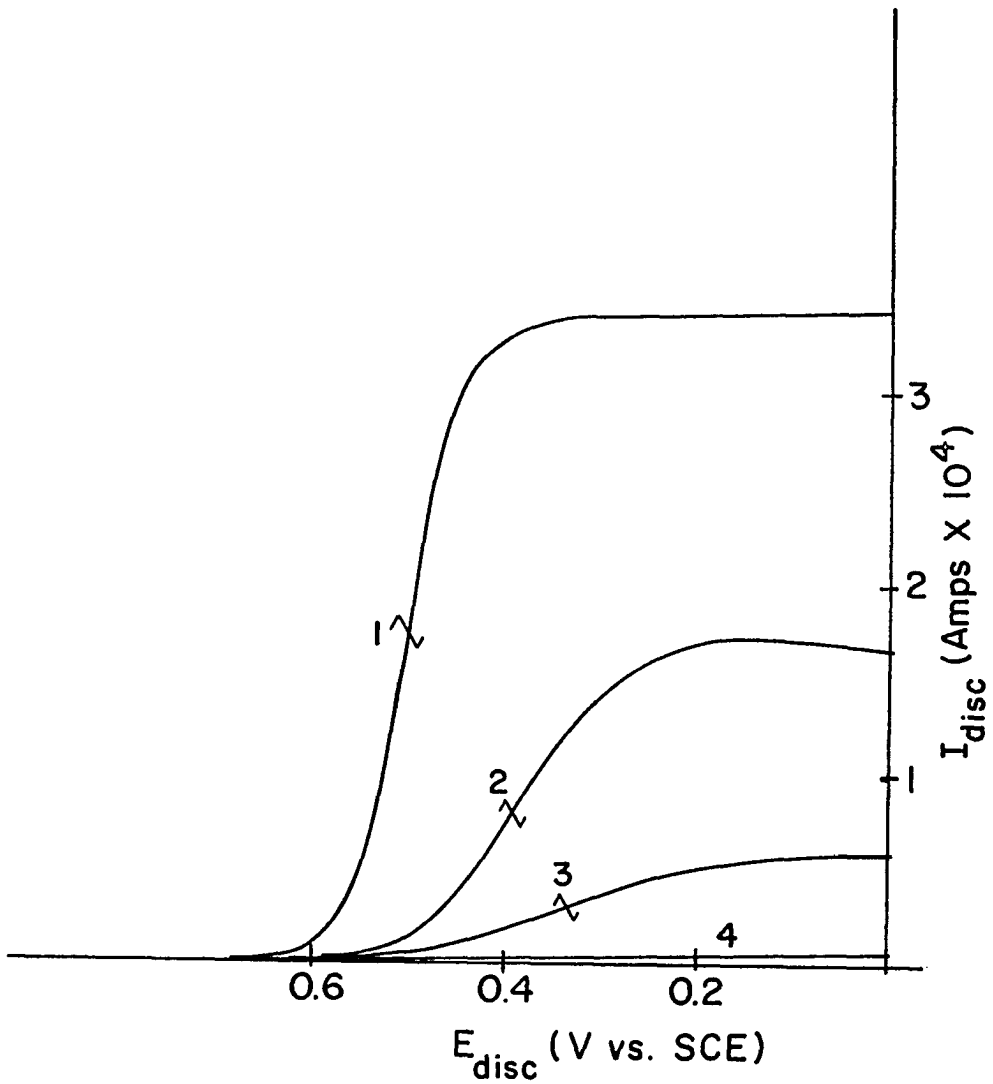
## D. Voltammetry

The formation of adherent polymers on the solid electrode surfaces during the oxidation of phenol has been documented. The formation of the polymer on the electrode surface is concluded to occur as described by equation XXXIII. The polymeric film is rapidly built up on the surface of the anode and effectively hinders the transport of electroactive species from the bulk of the solution to the surface of the electrode. Not only does this film appear to affect the orientation and approach of electroactive species to the surface of the electrode but also to exert control over the outward diffusion of the products of electrode reactions.

The practical result of film formation is that the effective area of the electrode and its electrochemical activity is severely decreased, as illustrated in Figure 24. This figure consists of a series of voltammagrams of the reduction of ferric ion in acidic aqueous solution for various degrees of electrode deactivation. The first voltammagram shows the current which flows as a function of applied potential for a mechanically polished platinum-disc electrode. A well-defined mass transport-limited

Figure 24. Response of a platinum disc electrode to reduction of Fe(III) at various stages of electrode inactivation by the anodic oxidation of phenol

Solution composition: 2.0 mM ferric nitrate in 0.1 M perchloric acid
Rotation speed: 1600 rev $min^{-1}$
Scan rate: 2.0 V $min^{-1}$
Platinum disc electrode No. 134
Z indicates approximate $E_{\frac{1}{2}}$


3
2
1
$I_{disc}$ (Amps X $10^4$)
1
2
3
4
0.6
0.4
0.2
$E_{disc}$ (V vs. SCE)

current is apparent and the sharp increase of the current due to reduction of ferric ion in the range 0.6 - 0.5 V indicates the reaction is kinetically fast.

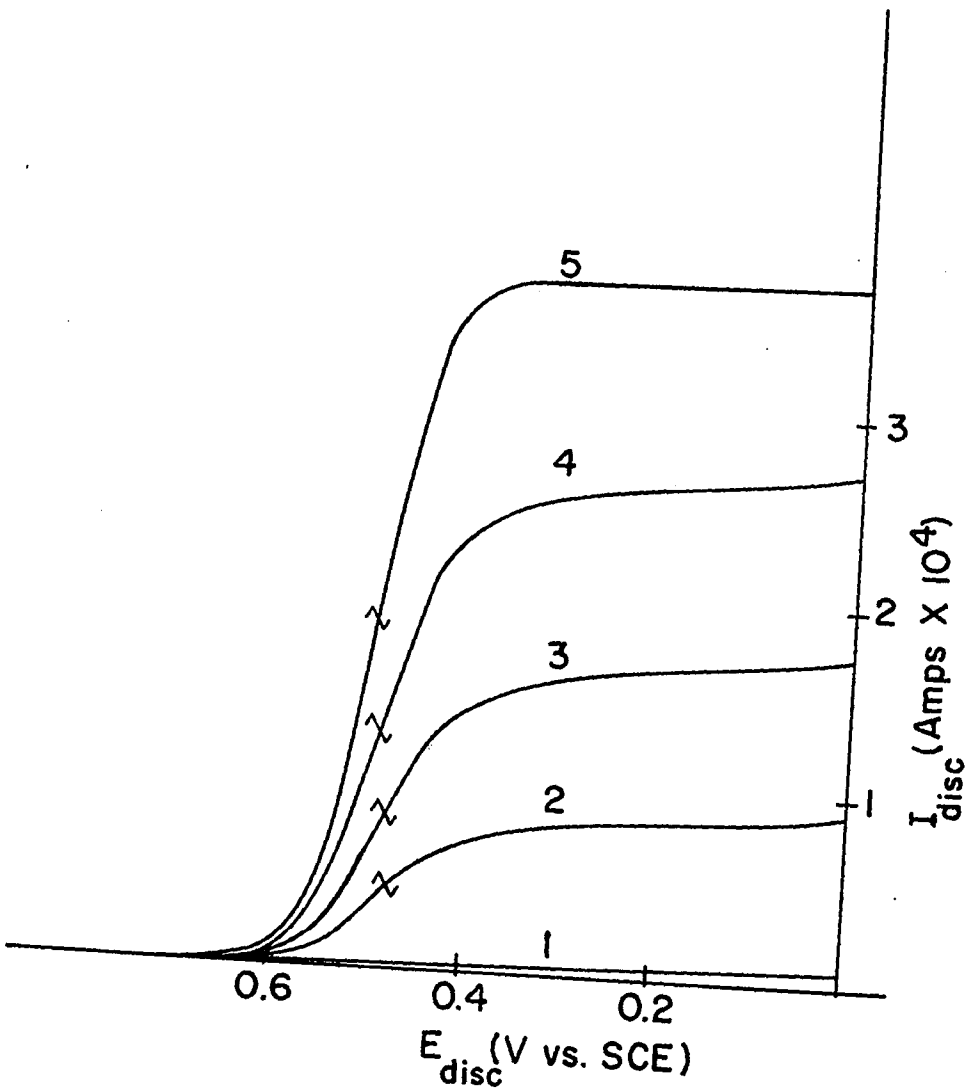
After a small amount of phenol had been oxidized on the electrode, the second voltammagram was obtained for reduction of ferric ion. A comparison of this voltammagram to the first voltammagram quickly reveals two major changes resulting from formation of a film at the electrode surface. The first is the decrease in the mass transport-limited current resulting from the decrease in the effective area of the electrode. The second change is that the half-wave potential ($E_{\frac{1}{2}}$) has shifted significantly in a negative direction. This indicates that the process by which electrons are transferred from the electrode to the ferric ions has been significantly impaired and the heterogeneous constant has been substantially decreased.

Further oxidation of phenol, as shown in the third voltammagram, extends the effects noted in the second voltammagram. The fourth voltammagram shows that the electrode has lost virtually all electroactivity toward ferric ion. Although the small amount of current which does appear in the fourth voltammagram can be assigned primarily to charging current, it is likely that a small amount of this current was due to reduction of ferric ion which managed to penetrate the polymeric film.

Figure 25 is a series of voltammagrams of the reduction of ferric ion at a platinum cathode in acidic solution which were recorded at various stages during the electrochemical cleaning of a severely inactivated electrode. The first voltammagram shows the response of the electrode

Figure 25. Response of a platinum disc electrode to reduction of Fe(III) at various stages of electrode reactivation

Solution composition: 10 mM ferric nitrate and 1.0 mM sodium chloride in 0.10 M perchloric acid
Rotation speed: 1600 rev $min^{-1}$
Scan rate: 2.0 V $min^{-1}$
Platinum disc electrode No. 134
Z indicates approximate $E_{\frac{1}{2}}$


5
4
3
2
1
3
2
1
0.6
0.4
0.2
$I_{disc}$ (Amps X $10^4$)
$E_{disc}$ (V vs. SCE)

before the cleaning procedure has commenced. The second voltammagram shows the increase in the activity of the electrode towards ferric ion reduction after the electrode was exposed to the cleaning procedure for a brief period of approximately 20 seconds. Immediately, one notices the increase in the mass transport limited current. In addition, the half-wave potential is very near to the value of 0.53 V which is predicted on the basis of thermodynamics for a reversible reaction. The third and fourth voltammagrams, which were recorded after the electrode had been successively exposed to the cleaning procedure for additional brief time periods, show further increase in the mass transport-limited current. The fifth voltammagram shows that the electrode had been restored to full electrochemical activity.

Comparison of the voltammagrams of ferric ion reduction during the deactivation procedure (Figure 24) with those obtained during the reactivation procedure (Figure 25) leads one to conclude that the reactivation mechanism is not simply the reverse of the deactivation mechanism. The deactivation process showed not only a decrease in effective surface area of the electrode, but also an effect on the kinetics of the electrochemical reduction of ferric ion. The reactivation process shows an increase in effective surface area of the electrode with little effect on the kinetics of the electrochemical reduction of ferric ion.

The conclusions one may draw from these data are that the polymeric film was built up in increasing thickness uniformly across the surface of the electrode during the deactivation process. The increasing thickness of the film during the deactivation process makes the approach of an

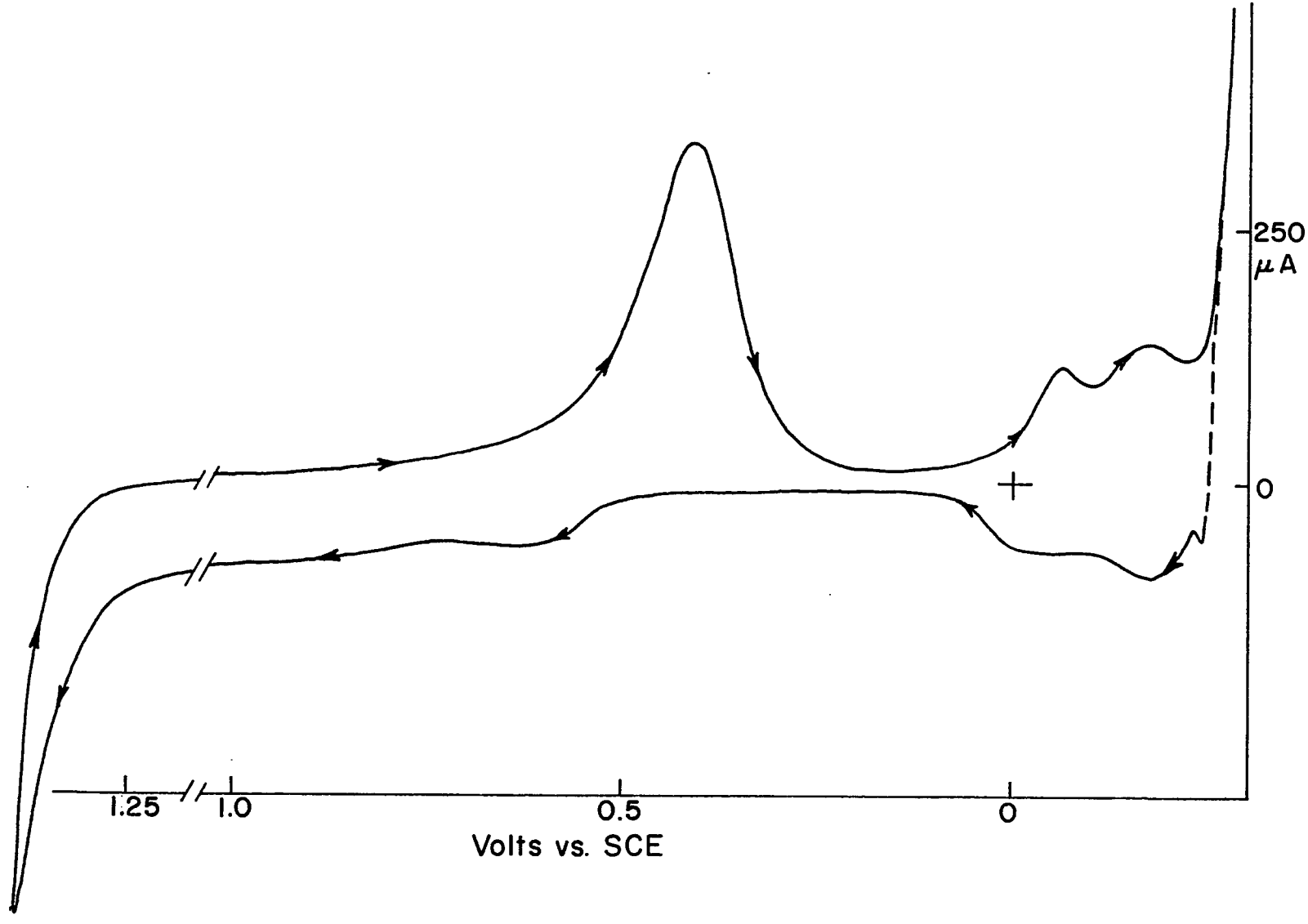
electroactive species more and more difficult. In addition, as the deactivation process continues, the number of active sites on the electrode surface steadily decreases. Furthermore, the flux of any other species whose presence affects the electrochemical reaction, such as electron-transfer catalysts, is decreased. Finally, if orientation of the electroactive species, with respect to the geometry of the electrochemically active site on the electrode is at all crucial, then this orientation may be hindered.

In contrast, perforation of the adherent polymeric film occurs during the cleaning procedure to expose "clean" areas of the electrode at which incoming electroactive species can react. These clean areas act as miniature electrodes whose cumulative geometric area is less than the total geometric area of the electrode; hence, the mass transport limited current which is observed is less than that of a totally reactivated electrode. However, electrochemical reactions which occur on these "clean" portions of the electrode occur by a reversible reaction just as is the case for an electrode which is fully active.

Figure 26 is a recording of the residual currents of a clean platinum disc electrode in 0.10 M perchloric acid. The anodic wave which begins at +0.5 V is due to oxidation of the platinum surface to form a layer of platinum oxide. This is a normal phenomenon and is referred to as the "platinum oxide wave." Species which chemically bond to the platinum surface hinder the onset of this anodic process and the platinum oxide wave to be shifted to more positive values of applied potential. This

Figure 26. Residual currents for a clean platinum disc electrode

Solution composition: 0.10 M perchloric acid
Rotation speed: 1600 rev $min^{-1}$
Scan rate: 2.0 V $min^{-1}$
Platinum disc electrode No. 134


250
μA
0
1.25
1.0
0.5
0
Volts vs. SCE

positive shift is usually quite dramatic for low levels of adsorbing species. For example, 1.0 uM iodide in acidic solutions will cause a positive shift to potentials greater than 1.0 V.

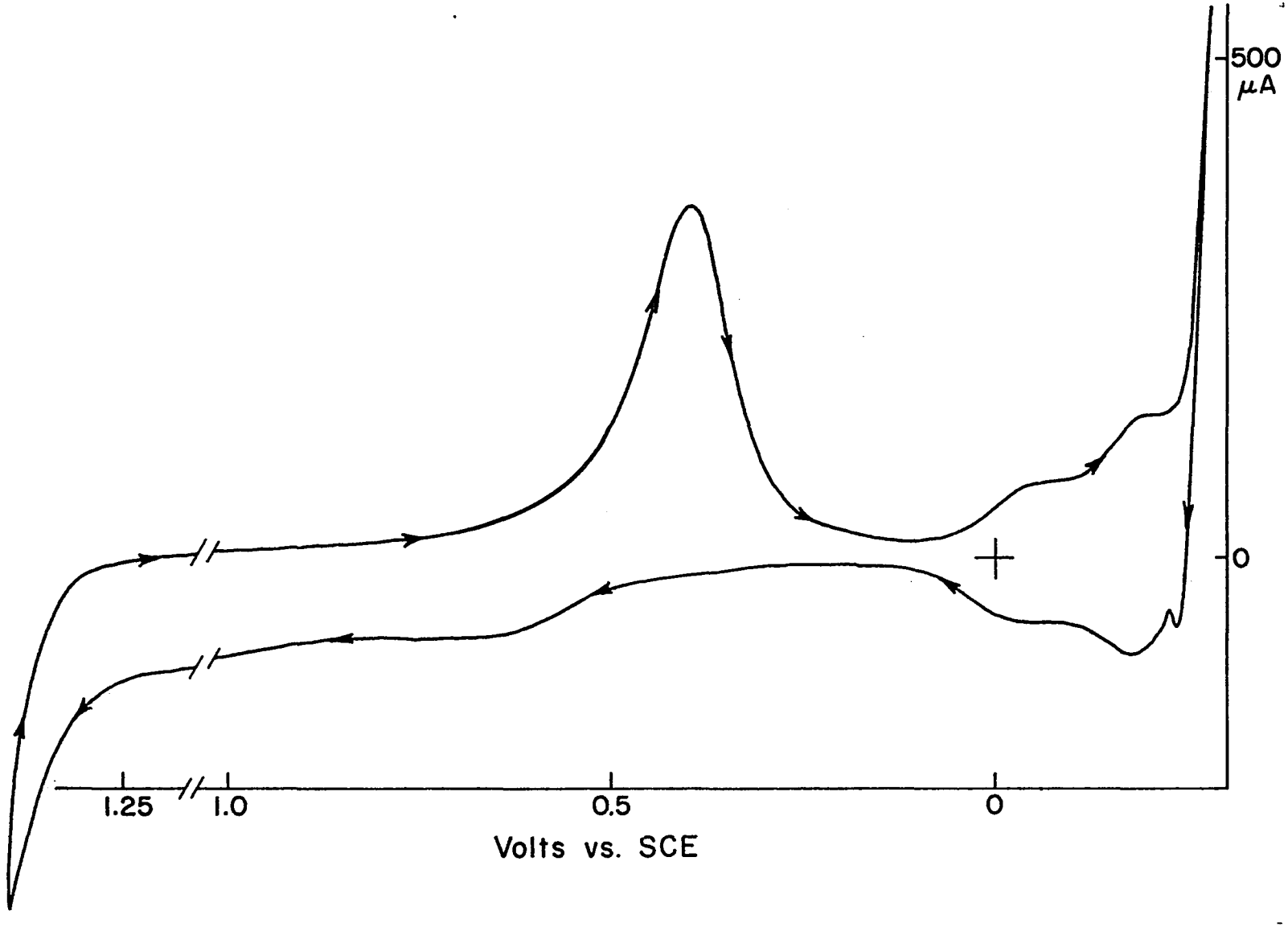
Other normal features of this residual voltammagram include anodic current due to the oxidation of water at potentials greater than +1.20 V; cathodic current due to reduction of the oxides of platinum at 0.4 V; and the anodic and cathodic currents between -0.25 and +0.10 V are due to desorbtion and adsorbtion of hydrogen onto the platinum surface. The large cathodic current which is negative of -0.25 V is due to hydrogen evolution.

Figure 27 is a recording of residual currents of a platinum disc electrode which has been deactivated. The similarity of Figures 26 and 27 is remarkable. The lack of significant difference in the two curves, especially in the region of the platinum oxide wave, leads to the conclusion that the phenolic film is not chemically adsorbed to the platinum surface. Also, the lack of change in the regions of hydrogen evolution and oxygen evolution leads to the conclusion that the phenolic film is permeable to water, hydrogen ion, hydrogen gas and oxygen gas. It is thought that these species diffuse through the film rapidly because they do not have an extensive hydration sphere to impede their progress.

A series of experiments were performed to test this conclusion. A platinum disc electrode was deactivated to the point where the polymeric film was clearly visible to the unaided eye. The ability of this electrode to reduce dissolved oxygen both in the presence and absence of agents which are known to poison the platinum electrode for this reaction was then

Figure 27. Residual currents for a deactivated platinum disc electrode

Solution composition: 0.10 M perchloric acid
Rotation speed: 1600 rev $min^{-1}$
Scan rate: 2.0 V $min^{-1}$
Platinum disc electrode No. 134


500
μA
0
1.25
1.0
0.5
0
Volts vs. SCE

tested. A similar series of experiments was performed on the same platinum disc electrode without the adherent polymeric film. The results of these experiments are shown in Figures 28, 29 and 30. The effect of the polymeric film on the oxygen reduction is shown in Figure 28. Note that the oxygen current decreases with time even when the electrode, without a film is exposed to the solvent only. This slow decrease has been given the name "passivation" and is concluded to be due to the adsorbtion of impurities from the solvent onto the electrode surface. The effect of the film on the poisoning effects of cupric and iodide ions are shown in Figures 29 and 30 respectively. The ability of the film to retard the flux of incoming cupric ions and iodide ions is quite evident. Even after part of the activity of the electrode toward oxygen reduction had been nullified, this lost activity was quickly restored by briefly pulsing the potential of the electrode to a value where the platinum was oxidized and then returning the potential to the previous value.

In an attempt to measure the potential which must be applied to the potentiostat during the cleaning procedure, the following experiment was performed: a disc electrode was fouled until it did not give perceptible response to 2.0 mM ferric ion. The electrode was then cleaned, by applying an input signal of 5.0 V to the potentiostat, until the electrode gave approximately a 100 uA response to ferric ion at 0.0 V. The electrode was then subjected to various cleaning potentials for 60 seconds and the percentage increase in the current due to ferric ion reduction was measured. This data is plotted in Figure 31. This figure indicates that an applied potential of 2.0 V or greater is sufficient to clean the electrode.

Figure 28. Effect of phenolic film on oxygen reduction at a platinum cathode

Solution composition: Air saturated 0.10 M perchloric acid
Rotation speed: 1600 rev. $min^{-1}$
Applied potential: 0.100 V vs. SCE
Platinum disc electrode No. 134
Curve A - Electrode without phenolic film
Curve B - Electrode with phenolic film

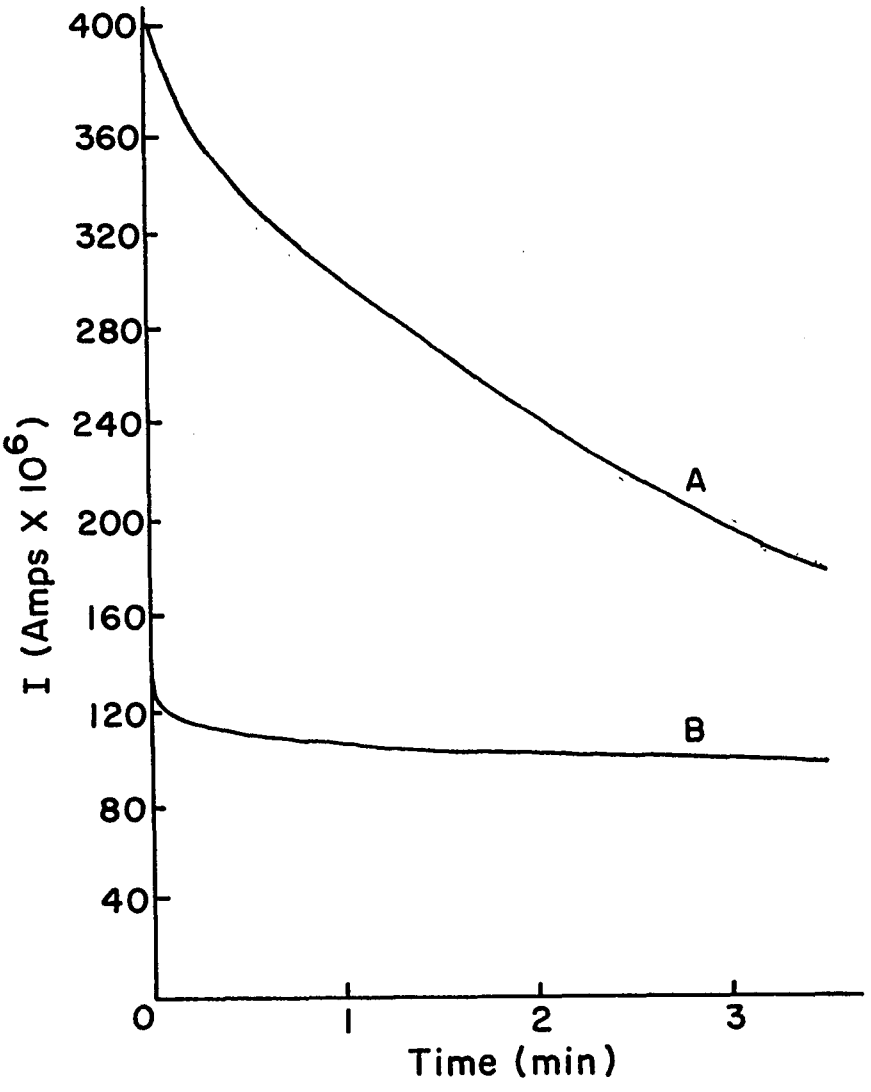

400
360
320
280
240
200
160
120
80
40
0
1
2
3
I (Amps X 10^6)
Time (min)
A
B

Figure 29. Effect of phenolic film on oxygen reduction at a platinum cathode in the presence of Cu(II)

Solution composition: Air saturated 10 μM cupric nitrate in 0.10 M $HClO_4$
Rotation speed: 1600 rev $min^{-1}$
Applied potential: 0.100 V vs. SCE
Platinum disc electrode No. 134
Curve A - Electrode without phenolic film
Curve B - Electrode with phenolic film

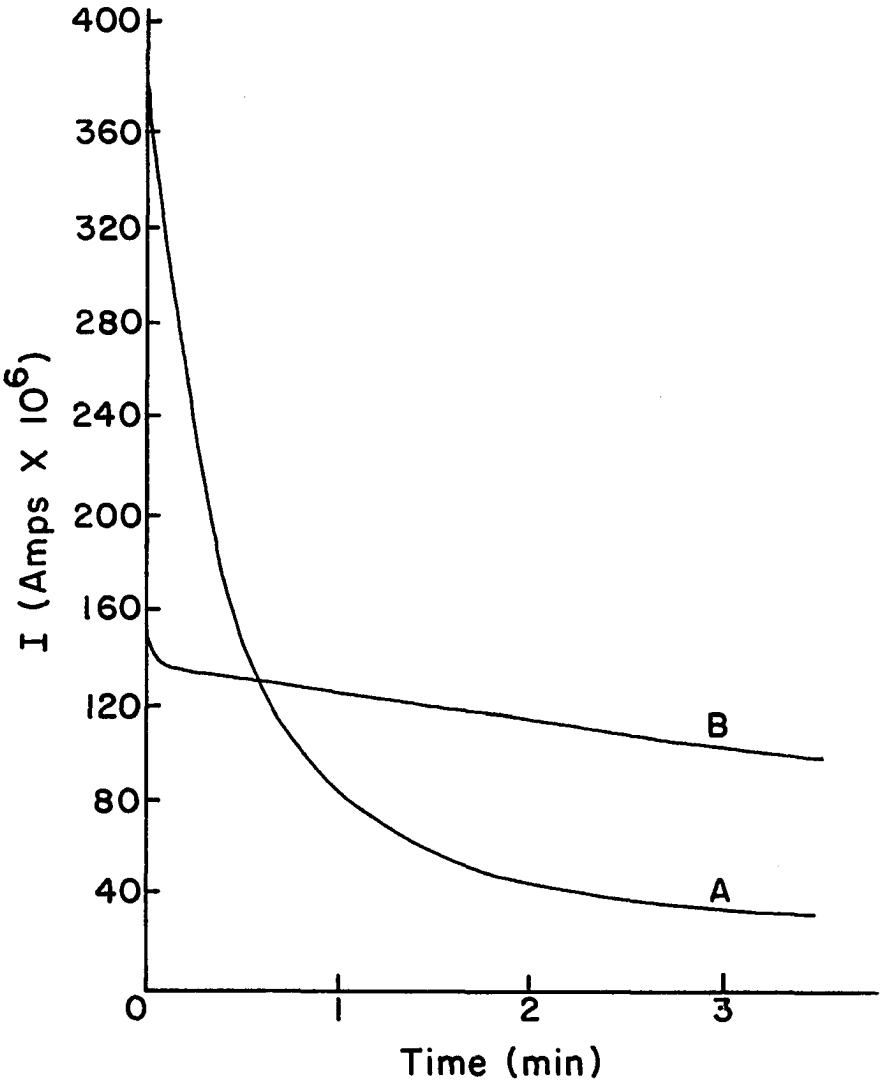

400
360
320
280
240
200
160
120
80
40
0
1
2
3
I (Amps X 10^6)
Time (min)
B
A

Figure 30. Effect of phenolic film on oxygen reduction at a platinum cathode in the presence of iodide

Solution composition: Air saturated 10 μM sodium iodide in 0.10 M perchloric acid
Rotation speed: 1600 rev $min^{-1}$
Applied potential: 0.100 V vs. SCE
Platinum disc electrode No. 134
Curve A - Electrode without phenolic film
Curve B - Electrode with phenolic film

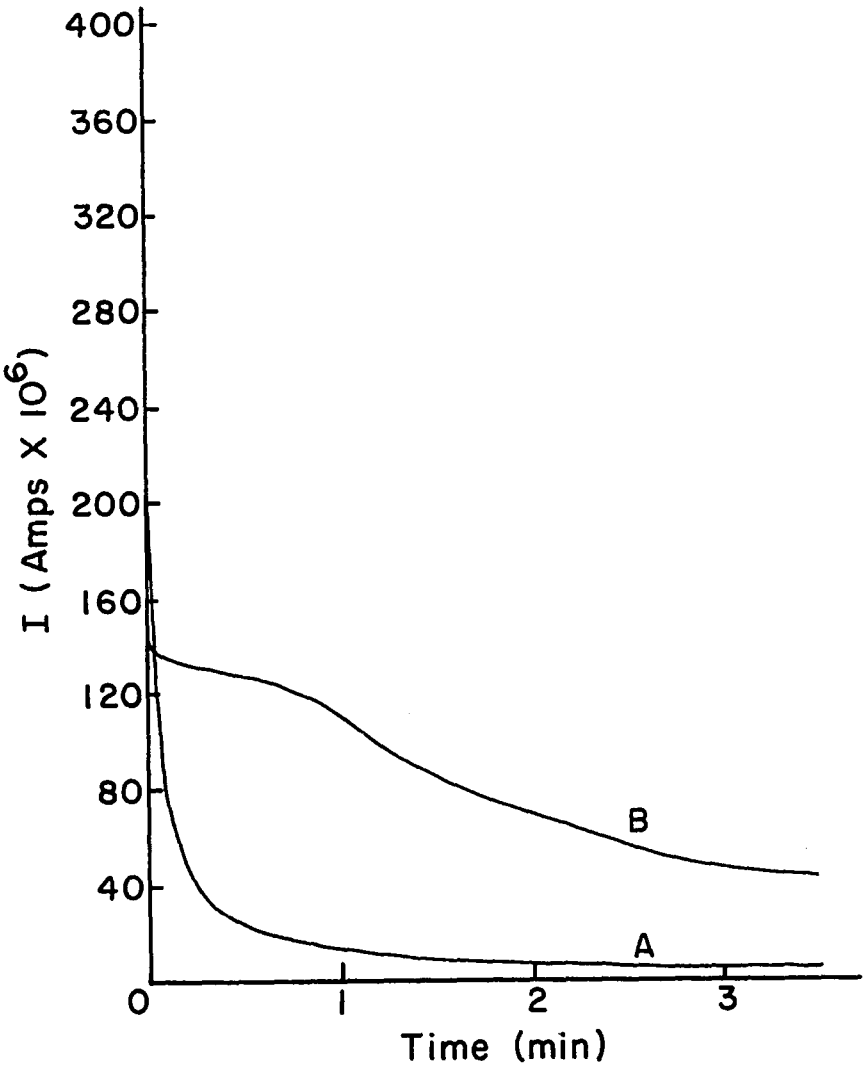
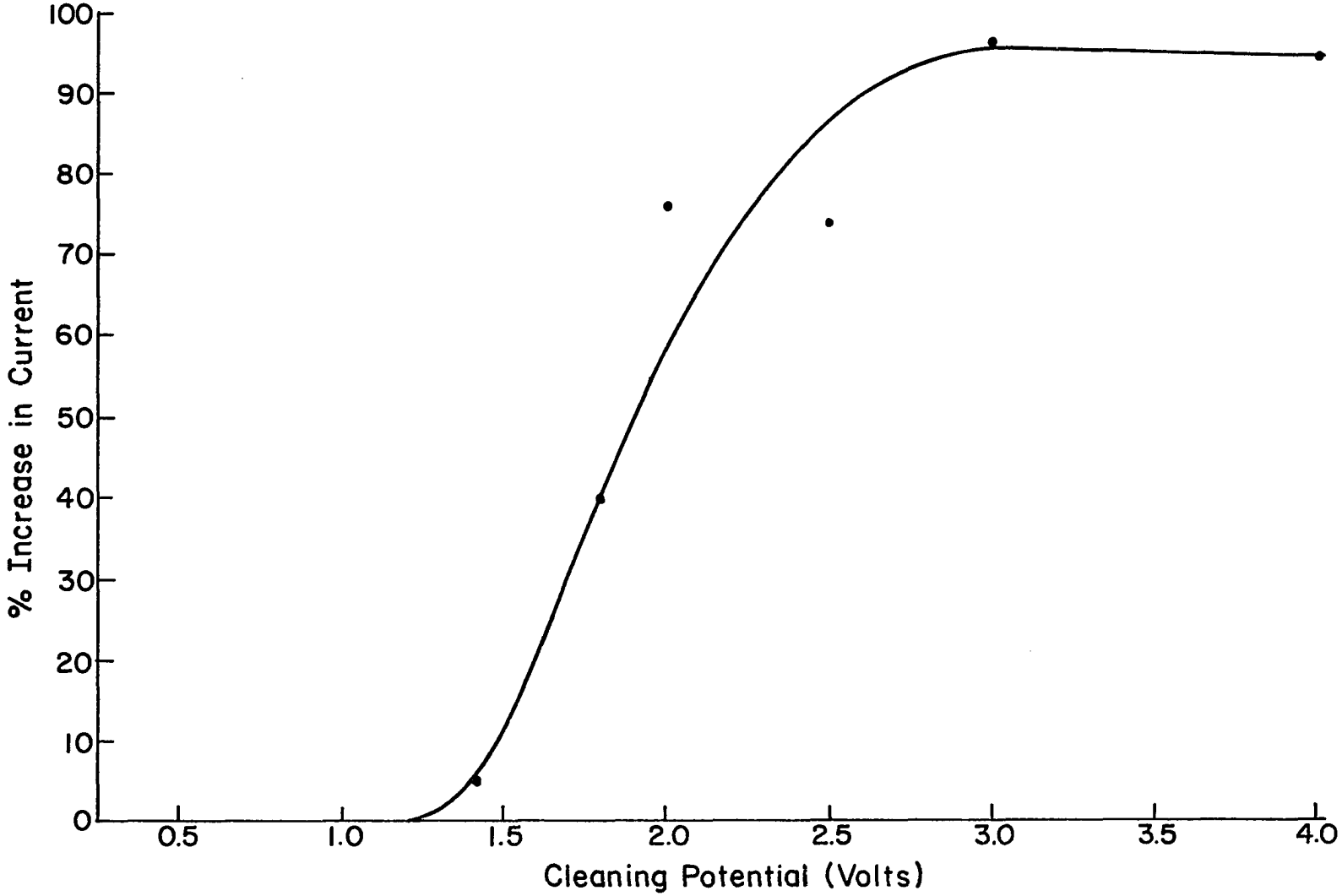

400
360
320
280
240
200
160
120
80
40
0
1
2
3
I (Amps X 10^6)
Time (min)
B
A

Figure 31. Increase in electrode activity versus cleaning potential

Solution composition: 1.0 mM ferric nitrate and 1.0 mM sodium chloride in 0.10 M perchloric acid
Rotation speed: 1600 rev. $min^{-1}$
Platinum disc electrode No. 134


100
90
80
70
60
50
40
30
20
10
0
% Increase in Current
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Cleaning Potential (Volts)

An applied potential of 2.0 V is sufficient to clean the electrode once the cleaning process had been initiated. Note that in the above experiment the electrode was partially cleaned before the measurements were made. An input potential of 2.0 V was found to be insufficient to initiate the cleaning process. The exact nature of the polymeric film is very difficult, if not impossible, to reproduce. Once the electrode has lost its electrochemical activity, the film continues to increase in thickness but at an uncontrolled rate. This makes the starting point, in any experiment attempting to measure the effect of the cleaning process on an intact film, ill-defined at best. It was noted, however, that input potentials to the potentiostat of 3.0 V or greater would rapidly initiate the cleaning process in the presence, of course, of ferric and chloride ions, regardless of the nature of the film. A current density of approximately 400 mA $cm^{-2}$ was observed under these conditions. This high current density is thought to be as important to the cleaning procedure as the presence of ferric and chloride ions.

An attempt was also made to determine the stoichiometric ratio of ferric ion to chloride ion which would provide the maximum efficiency of the cleaning procedure. Although the experiment was considered a quantitative failure, due to the difficulty of reproducing the character of the film, the conclusion can be made that both ferric ion and chloride ion are necessary for the cleaning process to occur.

## E. Instrumental Characterization of Phenolic Films

### 1. Microscopic examination

Figure 32 is an electron microphotograph of the surface of a platinum disc electrode which had been severely deactivated by a thick film of polymeric material. Note that polishing marks can still be identified underneath the film. Figure 33 is an electron microphotograph of a platinum disc electrode which was deactivated to the same extent and then partially cleaned. The perforations in the polymeric film are quite evident.

Three dimensional images of this surface in Figure 33 were obtained by taking a second electron microphotograph of the same area at an angle which is $8^{o}$ different from the first. The two photographs were then viewed with the aid of a stereoscopic viewer. Such three dimensional observations often revealed fragments of the film which were attached to the surface of the electrode on one edge only. Occasionally the remainder of those particular fragments were found to be projecting away from the surface of the electrode at various angles; however, in most observations the fragments of the film were found to be folded completely back onto the surface of the adjoining film.

Voltammagrams for the reduction of ferric ion, which were obtained immediately after partial reactivation of a fouled platinum disc electrode are shown in Figure 25. An electron microphotograph of a partially reactivated surface was shown in Figure 33. The photograph and the voltammagrams have been discussed. If the potential of a partially clean electrode was allowed to scan in a cyclic manner in the range of +0.7 to 0.0 V for several minutes, the value of $E_{\frac{1}{2}}$ for the ferric ion reduction wave was

Figure 32. Electron microphotograph of a platinum electrode covered with a phenolic film

Tilt angle: $0^{o}$
Scanning speed: 50 sec
Ion beam strength: 25 KV
Remarks: None


10 μM

Figure 33. Electron microphotograph of a partially cleaned platinum disc electrode

Tilt angle: $0^{o}$
Scanning speed: 50 sec
Ion beam strength: 25 KV
Remarks: None


10 μM

observed to shift slowly in a negative direction from the thermodynamic value. In addition, the limiting current was observed to decrease simultaneously with the shift of the $E_{\frac{1}{2}}$ value. Subsequent microphotographs of the electrode revealed that the edges of the film surrounding the exposed regions of platinum had become very diffuse as shown in Figure 34. If this process was allowed to continue, the exposed portions of the platinum surface were completely obliterated as shown in Figure 35. Apparently, small organic molecules, oligomers, dissolved in the film, flowed along the surface of the electrode from the intact portion of the film onto the freshly cleaned platinum regions. This resulted in a loss of electrochemical activity on those sections of the platinum surface. Thus, the polymeric films which had been damaged by partial cleaning were able to undergo a "healing" process. When the electrode had been cleaned to such an extent that 80% or more of its full electrochemical activity had returned, then the healing phenomena was not observed to occur, even for extended voltammetric cycling.

2. Infrared spectroscopy

The infrared spectrum of the polymeric material is shown in Figure 36. This spectrum is for the dried material which had been incorporated into a potassium bromide pellet. The broad absorbtion band centered at 3400 $cm^{-1}$ is indicative of hydrogen bonding of the alcoholic (phenolic) groups within the polymer. This band would be expected to be much broader for more acidic hydroxy groups such as those found in water or organic acids. The absorbtion at 1655 $cm^{-1}$ must be assigned to quinoidal structures; however, whether or not the carbonyl groups are on the same ring

Figure 34. Electron microphotograph of a platinum disc electrode with a partially healed phenolic film

Tilt angle: $0^{o}$
Scanning speed: 50 sec
Ion beam strength: 25 KV
Remarks: Diamond particle in center of photograph

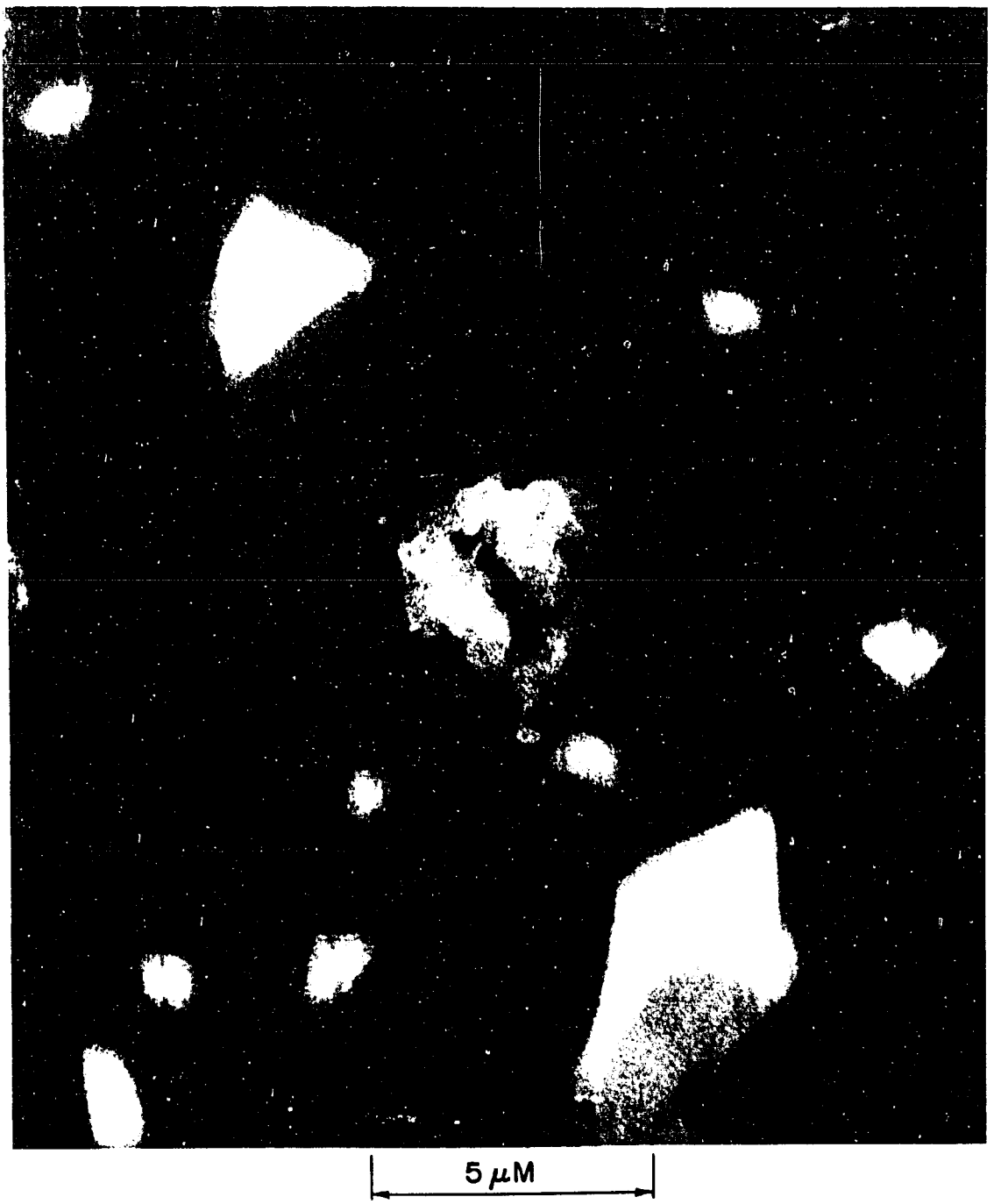

5 μM

Figure 35. Electron microphotograph of a platinum disc electrode with a completely healed phenolic film

Tilt angle: $0^{o}$
Scanning speed: 50 sec
Ion beam strength: 25 KV
Remarks: Diamond particle in center of photograph

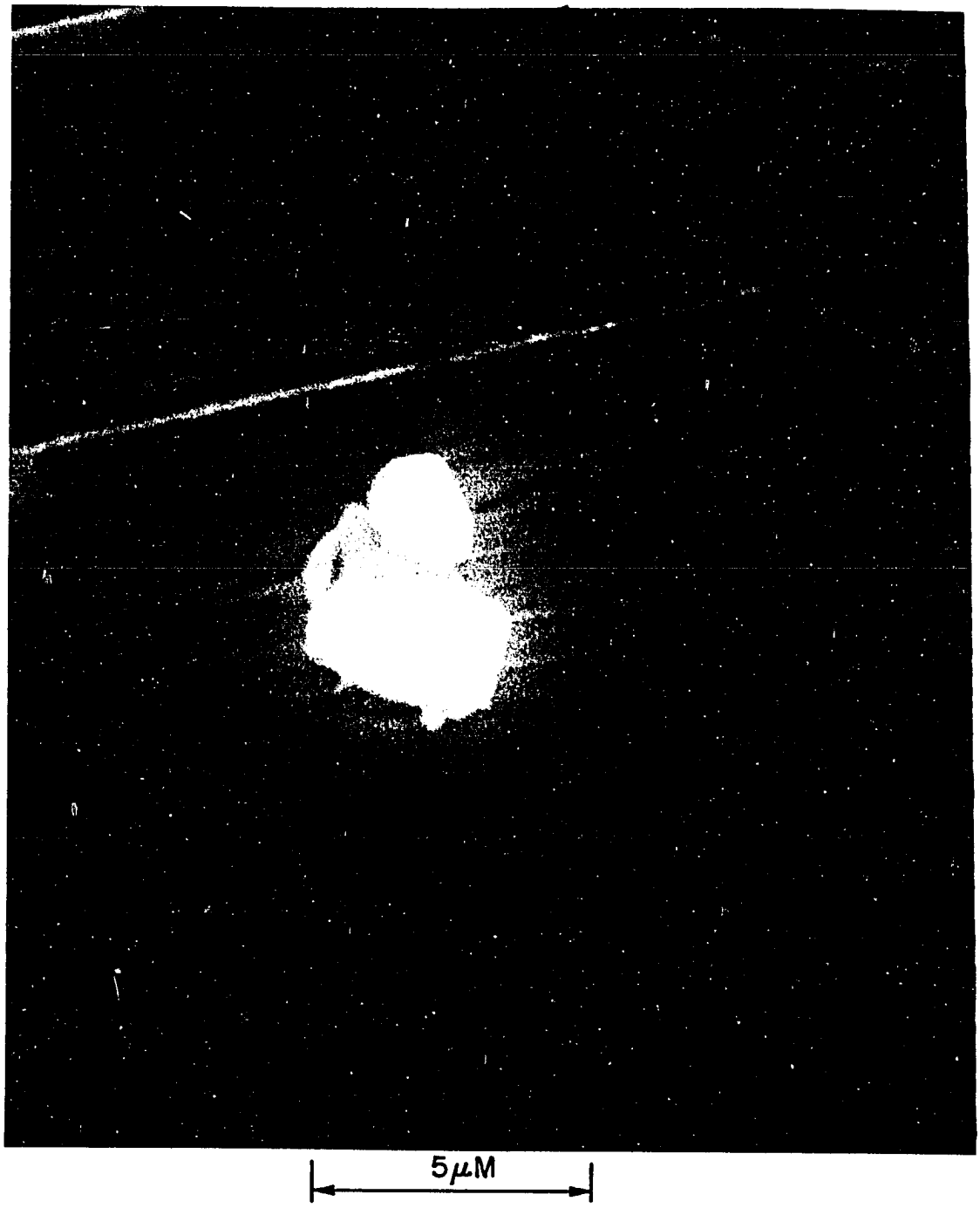
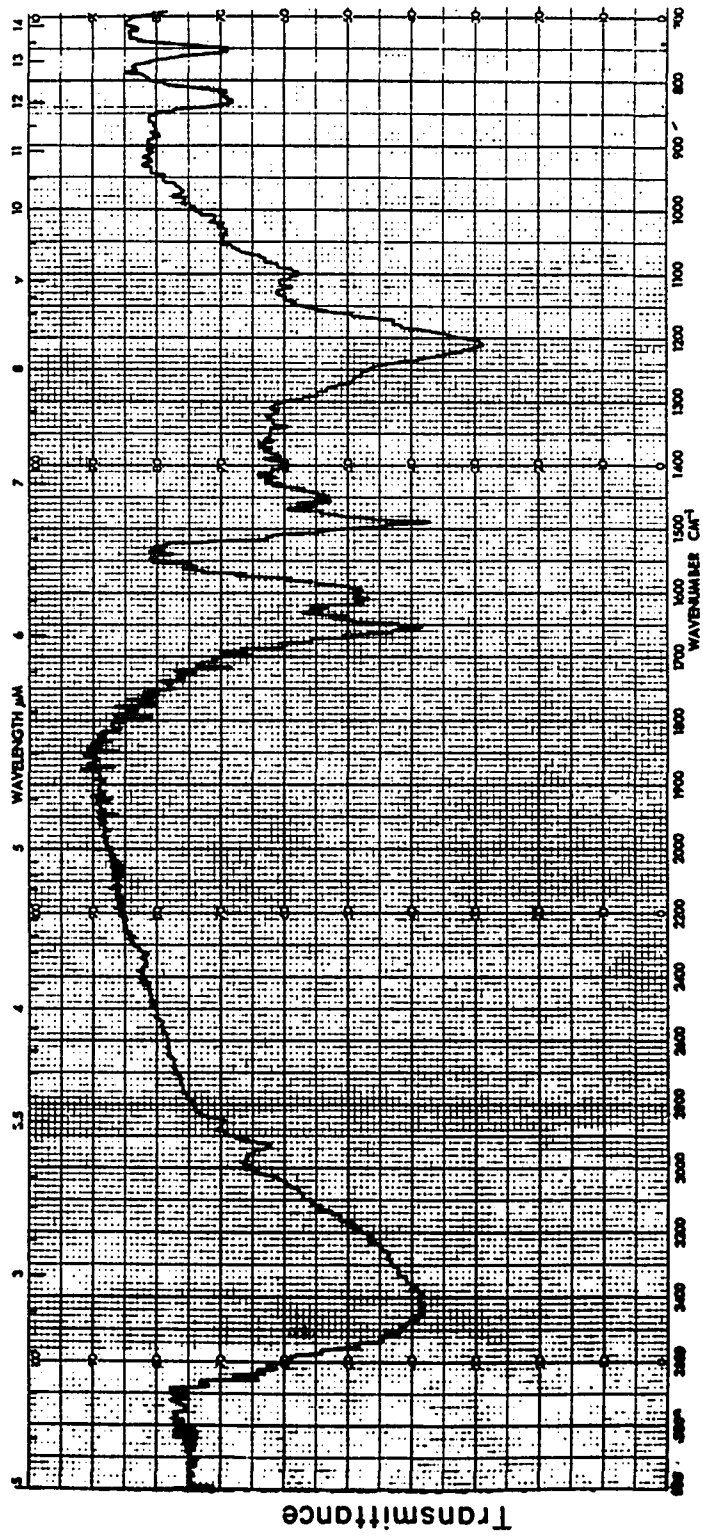

5μM

Figure 36. Infrared spectrum of polymeric material

Phase: Solid-potassium bromide pellet
Speed: 300 $cm^{-1}$ $min^{-1}$
Gain: 1.2
Scale: 20%
Offset: 50


Transmittance
WAVELENGTH μM
WAVENUMBER CM⁻¹

in the conjugated $\pi$ system is not clear. The absorbtion bands centered at 1606 and 1490 $cm^{-1}$ are due to aromatic ring stretching vibrations. The presence of the band at 1450 $cm^{-1}$ and the fact that the band at 1606 $cm^{-1}$ is split is solid evidence for the conjugation of the aromatic ring with another $\pi$ system (169). This could only come about due to the direct coupling of aromatic rings during the electrode reaction.

The strong band at 1210 $cm^{-1}$ is a carbon-oxygen stretching vibration; however, it is not clear whether this bond is due to a phenolic carbon-oxygen stretching vibration, an aromatic ether carbon-oxygen stretching vibration or both. The absorbtion bands at 825 $cm^{-1}$ and 752 $cm^{-1}$ are carbon-hydrogen out-of-plane bending vibrations. They indicate that the aromatic rings are predominantly di-substituted and that the substitution is almost exclusively ortho and para in nature, and that there is little, if any, meta substitution. This is consistent with resonance theory and the proposed reaction mechanism discussed earlier.

3. Mass spectroscopy

Mass spectral analysis of the film indicated the presence of a polymer, oligomers, unreacted phenol and quinones. The presence of a polymer of fairly high molecular weight was indicated by the fact that a large portion of the sample which was placed in the mass spectrometer was not volatile at a temperature of 240° C and a pressure of $5 \times 10^{-7}$ torr. Under these conditions the sample did turn black, which indicates carbonization.

With the probe held at room temperature, prominent peaks were observed at m/e values of 169 and 135 which are probably dimer fragments.

The fact that they were observed with the probe at room temperature, indicates that the parent compound is volatile. A diphenyl ether is a possible identification.

Even mild heating of the mass spectral probe showed the presence of unreacted phenol. Further heating of the probe showed the presence of phenol dimers and trimers, hydroxylated dimers, hydroquinone and quinone. Extreme heating of the probe resulted in weak signals indicating the presence of larger oligomers; however, the evidence for these species is not considered sufficient to allow definite conclusions.

## F. Conclusions

The electrolytic efficiency of the wire detector was slightly less than predicted by equations XXV and XXVII on the basis of equation XXVIII. This undoubtedly is related to the fact that the boundary condition $C = C_b$ was assumed for the solution beyond the diffusion layer in the derivation of equation XXVIII. The wire flow-through detector is similar to a flow-through thin-layer cell wherein the depletion of analyte is significant and the boundary condition given above is not applicable. Hence, the flux per unit area of electrode steadily decreases below the prediction of Ross and Wragg (164) as the fluid passes along the indicating electrode.

The wire flow-through electrode, while not adhering strictly to the published theory for annular electrodes, has proven itself to be a very reliable detector. As for any detector applied for continuous analysis of fluid streams, accurate analytical application requires careful control of the fluid flow rate and calibration with suitable standards.

The changes in the observed values of n as a function of flow rate, concentration and steric hindrance allowed conclusions concerning the mechanism of the electrochemical oxidation of phenol. As mentioned in section III-C, the oxidation of phenol occurs by a mechanism which can result in either the production of hydroquinone (HQ) or dibenzohydroquinone (DBHQ). The former reaction corresponds to a value of n equal to 2 and the latter corresponds to a value of n equal to 1. Both of these compounds are subject to further oxidation to the corresponding quinones.

The reaction which forms DBHQ has a second-order dependence on phenol concentration. Considering just this reaction, an increase in the concentration of phenol increases the rate at which DBHQ is formed. This raises the observed value of n due to the increased contribution of the oxidation of DBHQ to dibenzoquinone (DBQ). The observed decrease in the observed value of n with increasing concentration of phenol leads to the conclusion of simultaneous reactions. Furthermore, it is concluded that the process which results in a lower value of n is favored by this increase in concentration of phenol.

The conclusion that coupled chemical reactions are involved in the oxidation of phenol has been presented. This was due to the inverse relationship between the observed value of n and flow rate. It was also noted that this relationship was observed over the entire concentration range studied. The following sequence of reactions is concluded to occur during the electrochemical oxidation of phenol at platinum electrodes:

1) Oxidative adsorbtion of phenol,

2) oxidative desorbtion of the phenoxonium ion,

3a) reaction with water to form hydroquinone,

3b) reaction with phenol to form a dimer,

3c) reaction with a polymeric unit made up of x monomeric units to form a polymeric unit made up of x+1 monomeric units,

4a) oxidation of hydroquinone to quinone, and

4b) oxidation of dimer to dibenzoquinone or phenoxyphenoxonium ion.

An alternative mechanism is also possible in which the phenoxy radical is desorbed and reacts in solution. This alternative mechanism does not involve the phenoxonium ion product. A combination of these two mechanisms is also possible.

The higher value of n which was observed for orthocresol is the result of steric hindrance of the coupling process. If the coupling process is hindered, then the reaction of the intermediate product with water to form the corresponding hydroquinone is more probable. The observed variation of n with concentration of phenol and cresol is expected to cause calibration curves to be non-linear, even when other parameters are carefully controlled. Hence, careful construction of calibration curves for quantitative analysis is necessary.

Conclusions concerning the manner in which the organic film is built up during the oxidation of phenol at platinum anodes and the manner in which it is removed during the cleaning procedure have been presented. Additional conclusions can be drawn from the data presented. The observed phenomenon of film drying and the result of infrared analysis of the film indicate

that the polymeric film which is formed on platinum electrodes during the anodic oxidation of phenol has a low degree of cross-linking. The infrared spectrum indicated that a large majority of the aromatic rings are di-substituted. Since crosslinking of linear polymeric units requires tri-substitution, the infrared spectrum would be expected to have a different vibrational pattern for the out-of-plane bending if a high, or even moderate, degree of crosslinking existed within the polymer. A high degree of crosslinking is known to reduce shrinking and swelling of chromatographic resins (170).

The observation of the healing phenomenon and the mass spectral analysis of the film support the conclusion that the film consists of a polymeric matrix which contains small units ranging from oligomers to quinones and unreacted phenol. The non-volatile portion of the film which was carbonized during the mass spectral analysis is concluded to be the polymeric matrix. Unreacted phenol, hydroquinone, quinone and dimers were positively identified by mass spectral analysis and the presence of oligomers was indicated but not proven. As previously stated, the healing phenomenon is thought to be the flowing of oligomers and other small phenolic units from the intact portion of the film onto the freshly exposed portions of the platinum electrode.

The similarity of the residual voltammagrams of clean and fouled platinum electrodes, and the fact that the polymer is removed by the gentle force of a stream of water after it has been dried, led to the conclusion that the mode of attachment of the bulk of the film is primarily mechanical in nature. Portions of the film which have formed into and around

irregularities on the surface of the electrode shrink upon drying and release themselves from these irregularities. The observation of the large potential necessary to remove the film from the electrode surface, and the appearance of the electron microphotographs of partially clean electrodes, led to the conclusion that the perforations of the film are the result of miniature explosions on the electrode surface. The partial pressure of oxygen behind the film during the cleaning process is considered to be significant and can literally blow out portions of the film after it has been weakened by the action of the ferric and chloride ions.

Consideration must be given to the possibility that the bulk of the polymeric film is unaffected by the action of the ferric and chloride ions during the cleaning process. The degradation of the points of mechanical attachment of the film to the electrode surface can also result in the observed phenomena. The probability of a section of the film being blown out by the oxygen pressure behind it increases if the attachment points of that section of film are weakened. The exact nature of the action of the ferric and chloride ions is not known. One possibility is that chlorination of the aromatic rings is taking place and this chlorination process weakens the film. Another possibility is that the ferric ion is catalyzing the degradative cleavage of the aromatic rings. Ferric ion has been shown to catalyze reactions of this type (171). If this is the role of ferric ion, then the role of chloride ion is still unknown.

# VII. ANALYSIS OF WATER FOR PHENOLS

## A. Introduction

The applicability of any new analytical procedure to samples as they are found in nature or produced industrially is of paramount importance. Potential interferences must be removed by way of extraction, or precipitation, separated by way of chromatography, or rendered inactive by one or more chemical reactions. Alternately the analyte or analytes may be separated from the matrix by extraction, chromatography, or precipitation. Derivativization is another technique which is used in an effort to aid in separation or detection of the analyte species.

Many procedures are tedious, time consuming and involve extensive sample pretreatment. Current trends are away from these types of procedures. Procedures which involve little sample pretreatment, require small amounts of sample, and can provide analytical information on more than one analyte are desirable. Other characteristics of desirable analytical procedures are low cost of analysis, reduced complexity of the apparatus employed, and good sensitivity and reproducibility.

## B. Chromatography

The electrochemical activity of phenol has been established. The chlorosubstituted phenols are also electrochemically active. This fact has also been reported by others (136). The liquid chromatographic separation of the chlorophenols has also been reported (136, 172). The

chromatographic column material which was described in section IV.A, page 51, of this thesis was found to separate the chlorophenols under isocratic conditions as shown in Figure 37. The methanol in this sample stemmed from the use of methanol as a solvent in the standard solutions as described in Chapter V. Separation was not complete and an improvement in the chromatography was desirable.

Another negative feature of this column was the dilution of the sample during the chromatography. This effect was demonstrated by the chromatograms shown in Figure 38. The peak marked A was the detector response to an injection of 5.0 ppb of phenol with the detector connected directly to the injection valve. The peak marked B was for an injection of 1.0 ppm of phenol with the chromatographic column installed into the flow-injection analyzer. A large portion of this dilution was unavoidable; however, it is thought that at least part of it can be controlled by altering the column dimensions. This particular column appeared to dilute the sample by a factor of approximately 280.

Although the detector was capable of detecting phenol at concentrations as low as 1 ppb as shown in Figure 39, column dilution appeared to raise this detection limit. Figure 40 shows the detector response to 200 ppb phenol in tap water with the column in place between the injection valve and detector. If the detection limit is defined as that level of phenol which produces a signal-to-noise ratio of two, then the detection limit of this particular procedure is calculated to be approximately 50 ppb.

Figure 37. Chromatographic separation of chlorinated phenols

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Analyte concentration: All phenols - 10 uM
Peak identification:
A: Methanol
B: Phenol
C: 2-Chloro,3-chloro & 4-chloro phenol
D: 2,6-Dichloro phenol
E: 2,3-Dichloro, 2,4-dichloro, 2,5-dichloro, 3,4-dichloro & 3,5-dichloro phenol
F: 2,3,6-Trichloro & 2,4,6-Trichloro phenol
G: 2,3,4-Trichloro, 2,3,5-trichloro, 2,4,5-trichloro & 3,4,5-trichloro phenol
H: 2,3,4,5-Tetrachloro phenol pentachloro phenol
Column: fully sulfonated polystyrene, 4% crosslinking, 23-38 uM, 25 cm x 1 cm dia.

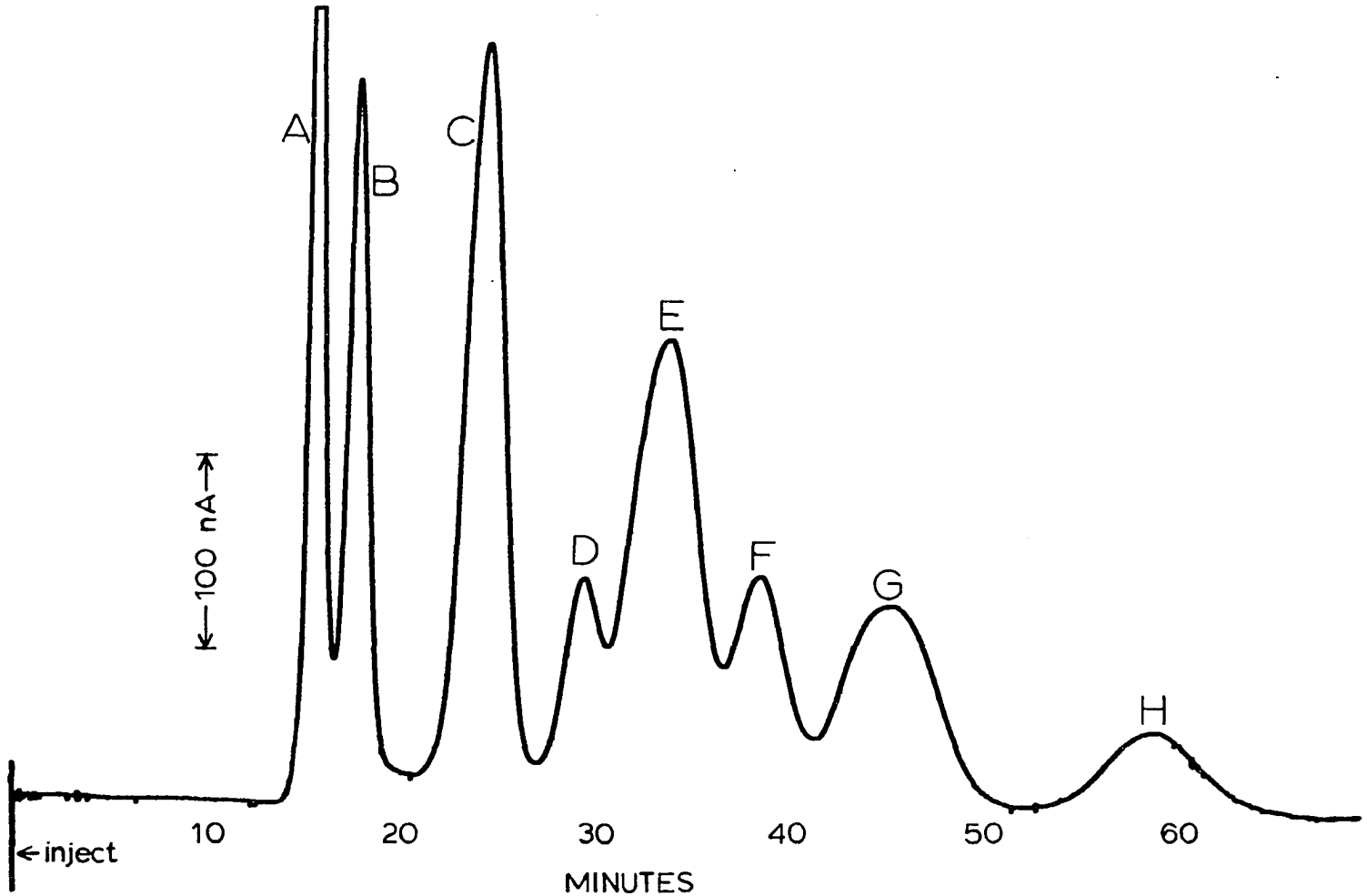

A
B
C
D
E
F
G
H
←100 nA→
←inject
10
20
30
40
50
60
MINUTES

Figure 38. Effect of column dilution

Carrier solution: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Peak A - 5.0 ppb phenol without column in system
Peak B - 1.0 ppm phenol with column in system

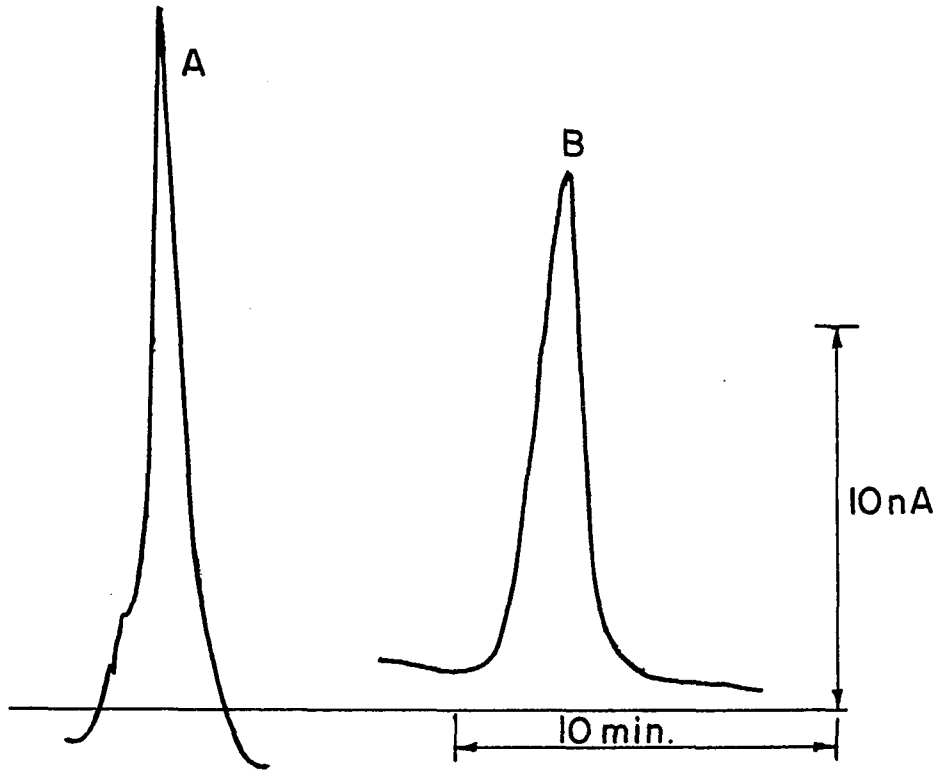

A
B
10nA
10 min.

Figure 39. Response of wire detector to 0.71 picomoles of phenol

Carrier solution: 0.10 M perchloric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.200 V vs. SCE
Sample volume: 0.0710 mL
Analyte concentration: 1.0 ppb
Remarks: Detector connected directly to injection valve

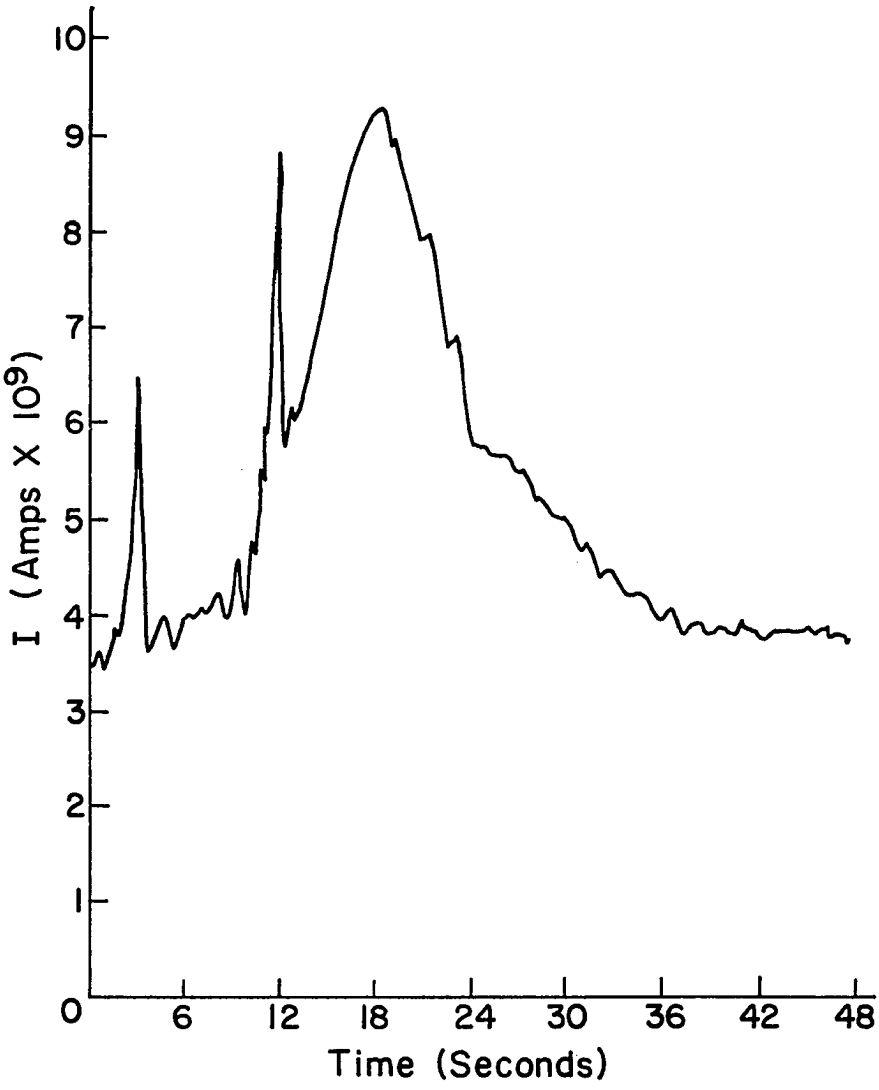
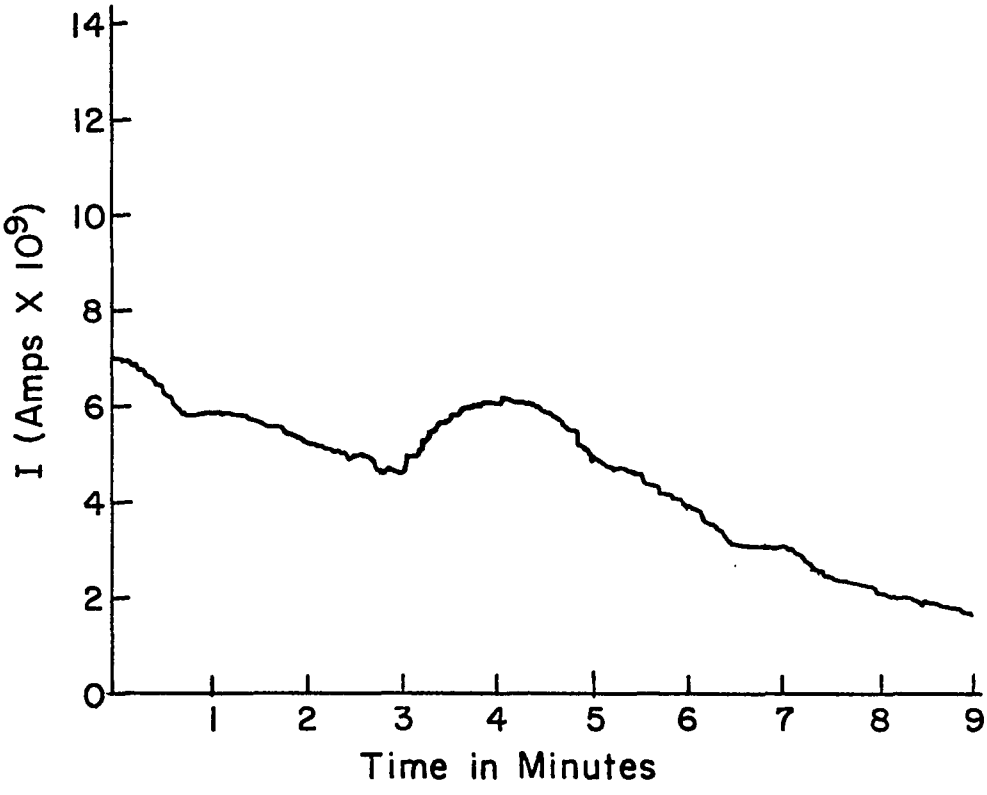

I (Amps X $10^9$)
10
9
8
7
6
5
4
3
2
1
0
6
12
18
24
30
36
42
48
Time (Seconds)

Figure 40. Response of liquid chromatographic analyzer to 142 picomoles of phenol

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Analyte concentration: 200 ppb


14
12
10
8
6
4
2
0
I (Amps X 10^9)
1
2
3
4
5
6
7
8
9
Time in Minutes

Afghan et al. used n-butyl acetate in a successful effort to concentrate phenols at trace levels (57). This procedure was tested for a mixture of phenols in water. The solid line of Figure 41 shows the detector response to a single injection of a solution which was 0.10 mM in each of six phenols. The phenols chosen were: phenol, p-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,5-trichlorophenol and 2,4,6-trichlorophenol. The dashed line shows the detector response to a 1:100 dilution of this same solution with the detector sensitivity unchanged.

Figure 42 shows the detector response to a n-butyl acetate extract of this diluted solution. The extraction procedure consisted of acidifying 1 L of the solution to be extracted with 5.0 mL of concentrated sulfuric acid, and then extracting this solution with 10.0 mL of n-butyl acetate. After mixing thoroughly, the organic layer was allowed to separate in the neck of the volumetric flask. The n-butyl acetate was then injected directly. Although the extraction appeared to have been quite successful, the result was certainly less than ideal. The chromatographic separation was severely reduced in efficiency and the response of the detector to the change in solvent composition was not separated from the phenols. Furthermore, the electrochemical reaction of phenol in the presence of large quantities of n-butyl acetate was not known.

Subsequent injection of the original phenolic solution showed a marked change in the chromatographic separation of the phenols. This effect is shown in Figure 43. Calculation of the number of theoretical plates of the column according to the formula $n = 16(V_r/W)^2$, where n is the number of theoretical plates, $V_r$ is the retention volume of a given peak and W

Figure 41. Response of liquid chromatographic analyzer to selected phenols

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Analyte concentration: Solid line - 1.0 mM in each phenolic compound in aqueous solution
Dashed line - 1.0 uM in each phenolic compound in aqueous solution
Peak identification: A- Solvent front
B- Methanol
C- Phenol
D- 4-Chlorophenol
E- 2,6-dichlorophenol
F- 2,4-dichlorophenol
G- 2,4,6-trichlorophenol
H- 2,4,5-trichlorophenol

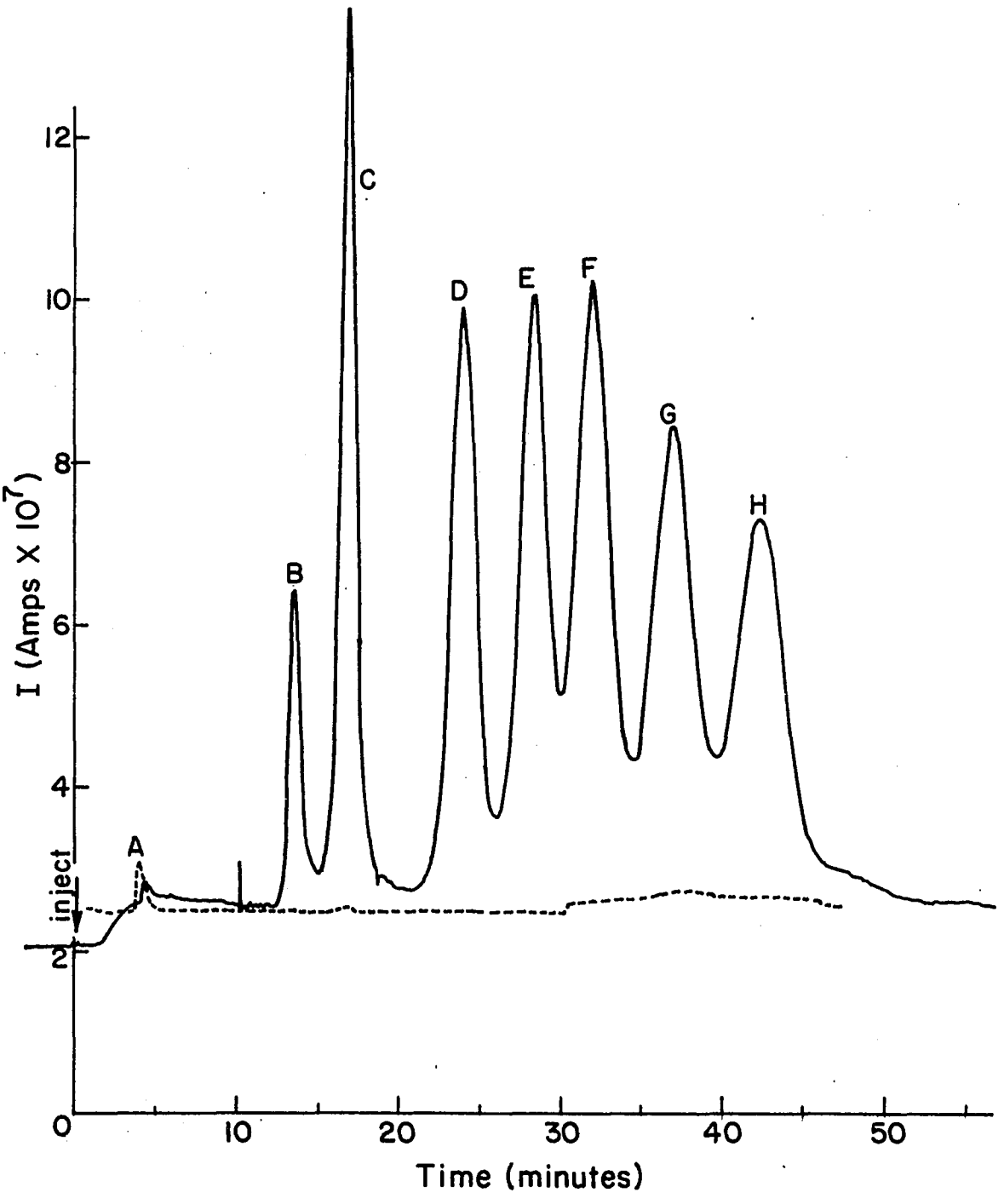

12
10
8
6
4
2
0
I (Amps X 10^7)
inject
A
B
C
D
E
F
G
H
10
20
30
40
50
Time (minutes)

Figure 42. Response of liquid chromatographic analyzer to an n-butyl acetate extract of a phenol solution

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Concentration of phenols in extracted solution:
10 uM in each of phenol
4-chlorophenol
2,4-dichlorophenol
2,6-dichlorophenol
2,4,5-trichlorophenol
2,4,6-trichlorophenol

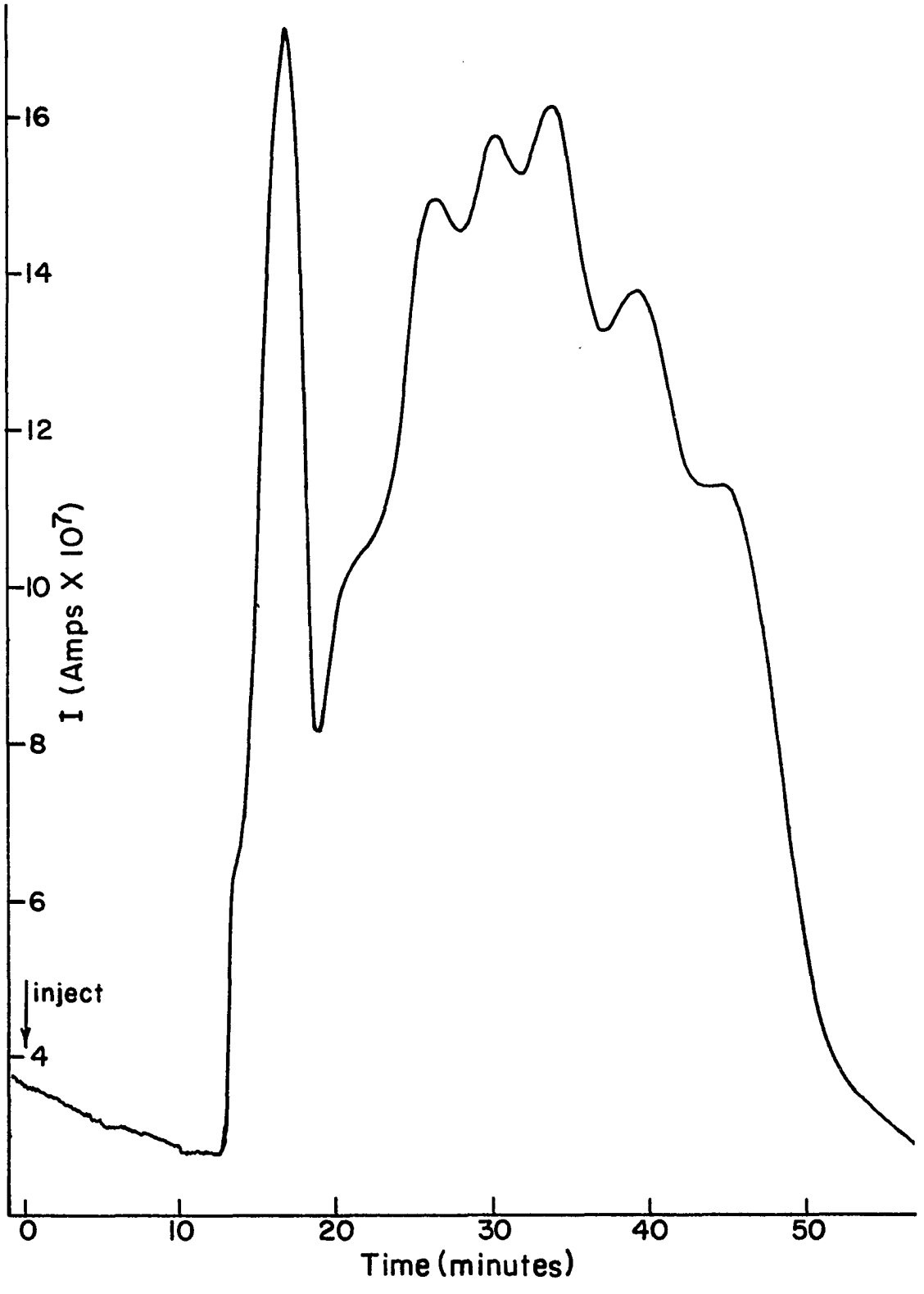
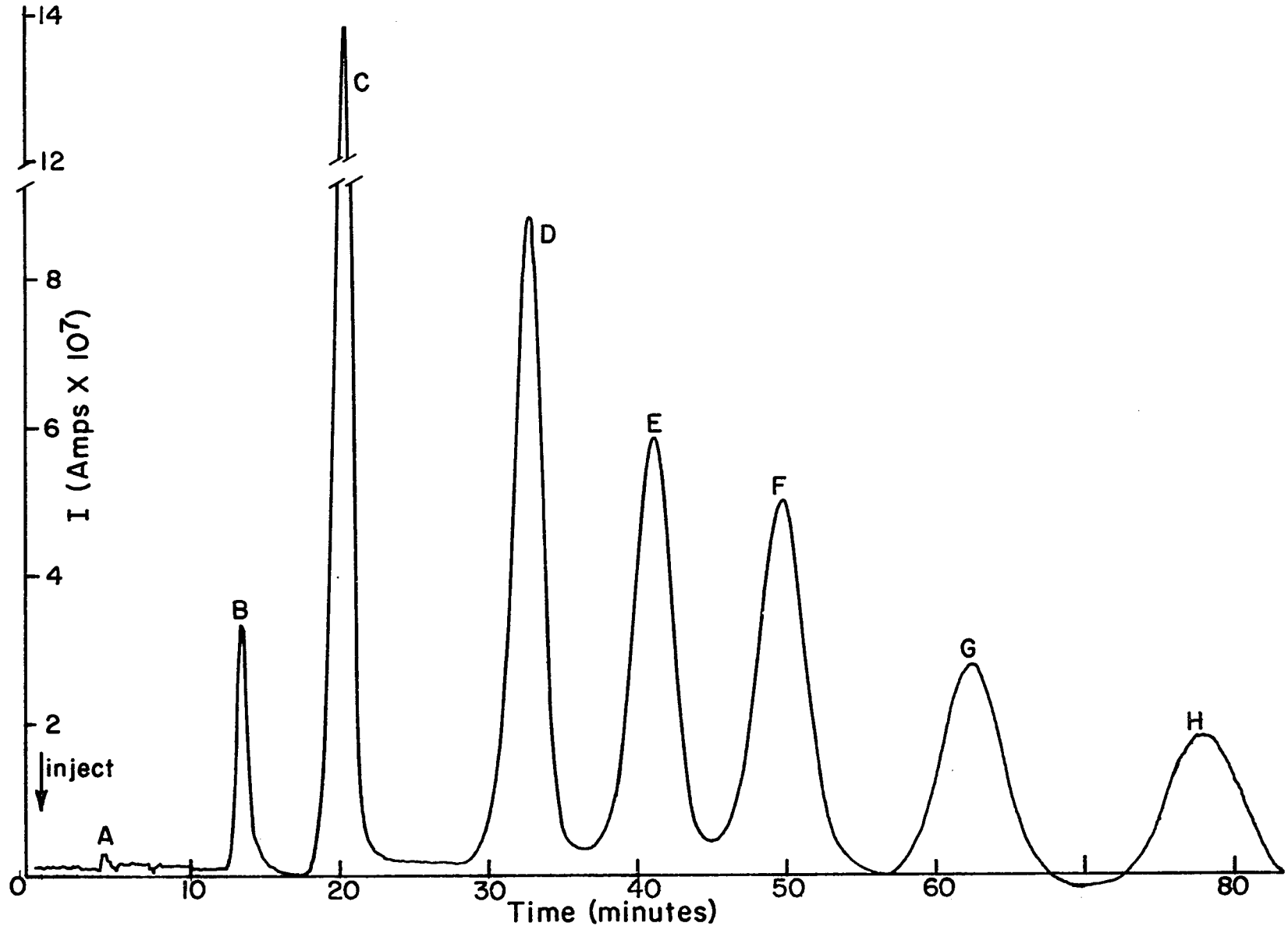

16
14
12
10
8
6
4
I (Amps X 10^7)
inject
0
10
20
30
40
50
Time (minutes)

Figure 43. Improved chromatographic separation of chlorinated phenols after treatment of chromatographic resin with n-butyl acetate

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Analyte concentration: 1.0 mM in each phenolic compound
Peak identification: A- Solvent front
B- Methanol
C- Phenol
D- 4-chlorophenol
E- 2,6-dichlorophenol
F- 2,4-dichlorophenol
G- 2,4,6-trichlorophenol
H- 2,4,5-trichlorophenol


14
12
8
6
4
2
C
D
E
F
G
H
B
A
inject
I (Amps X 10⁷)
0
10
20
30
40
50
60
80
Time (minutes)

is the width of the base of that same peak expressed in volume of eluent, yielded 1156 theoretical plates before exposure of the column to n-butyl acetate and 1271 theoretical plates after exposure of the column to n-butyl acetate. This was an increase of slightly less than 10%. One may have expected the peak resolution to increase by approximately 10%; however, when peak resolution was calculated, it was found to increase by 55% in this particular case. Other similar experiments yielded increases in peak resolution of over 100%.

It is apparent that the entire character of the column was changed by the injection of the butyl acetate. The matrix of the resin was polystyrene which was crosslinked with 4% (W/W) divinylbenzene. The polystyrene was fully sulfonated, which gave it the properties of a strong cation-exchange resin. Since phenol is not cationic, it seems reasonable that the hydrophobic portions of the resin were involved in the separation of phenols. This was solid-liquid chromatography and at this point the presence of the sulfonic acid groups appeared to be of little value in controlling the separation. Two explanations have been put forth as to the function of the sulfonic acid groups, the first of which was suggested by Armentrout, McLean and Long (136). Their explanation is that the sulfonic acid groups merely retain cations such as trace metals and amines which could interfere with the phenol determination. The second explanation was presented by Rich and Johnson of Dionex Corporation (173). Their explanation is that the sulfonic acid groups form an ionic barrier or membrane through which potential adsorbents must diffuse. This sets up a layer surrounding each polystyrene particle which is relatively highly

ordered. Furthermore, since the layer has the polystyrene matrix as one of its boundaries, this area contains a higher proportion of the organic fraction of the eluent. Hence, phenol has a higher affinity for this layer which is higher in organic character.

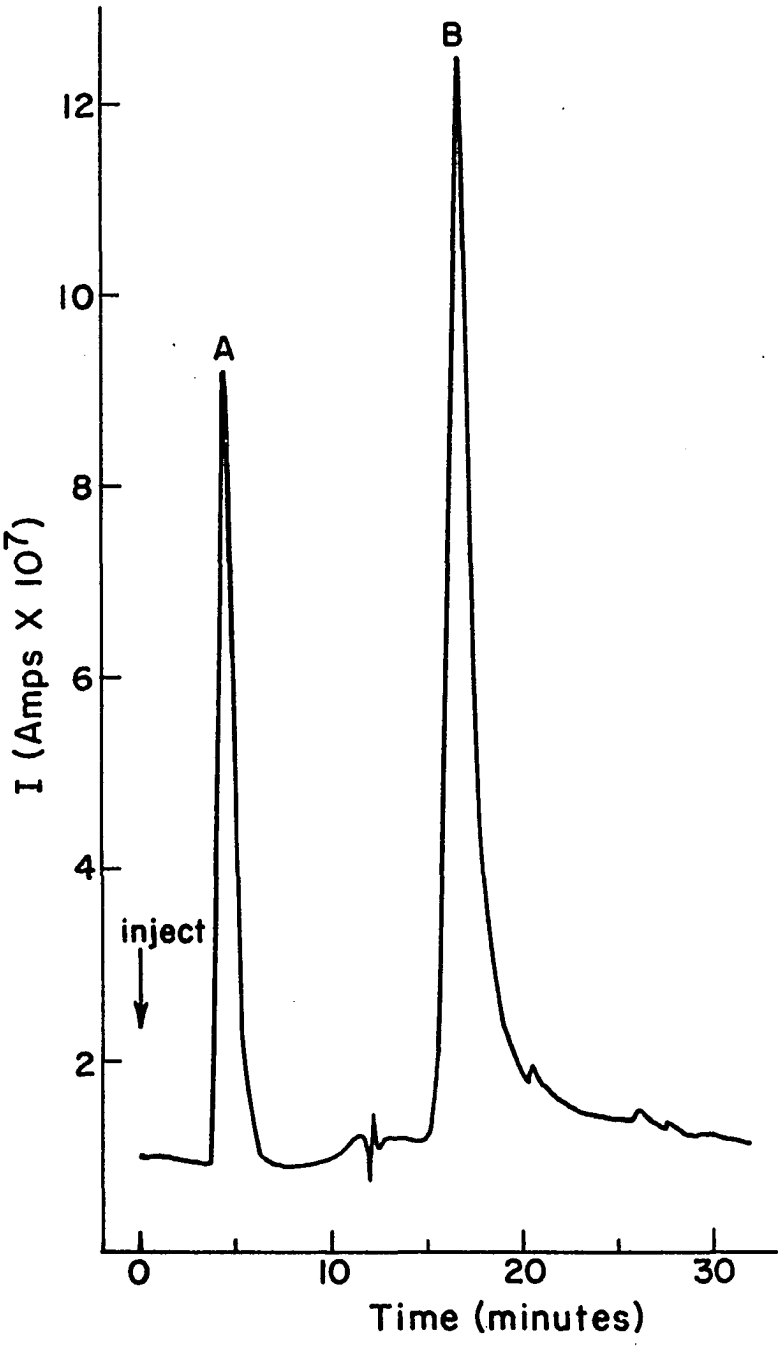
These two effects are not contradictory and both of them may explain the observed phenomena which occurs during sample analysis. The explanation by Rich and Johnson does appear to account, in part, for the increase in peak resolution once the column has been exposed to n-butyl acetate. The n-butyl acetate contained in the layer around each particle of resin can certainly be expected to change the chromatographic characteristics of the column. This is an example of liquid-liquid chromatography with the polystyrene resin functioning as a solid support for the stationary liquid phase of n-butyl acetate. This increased resolution of the chromatographic peaks, which was observed after the chromatographic column had been exposed to n-butyl acetate, would be expected to occur for other solid chromatographic materials such as XAD-2 or XAD-7.

## C. Analysis of Drinking Water

Drinking water from a water fountain in Gilman Hall of Iowa State University was analyzed for phenol and chlorinated phenols. This water is known to originate from the municipal water treatment facility of Ames, Iowa. The procedure consisted of injecting the sample into the flow-injection analysis system and recording the detector response which followed. The response of the detector is shown in Figure 44. Two

Figure 44. Response of liquid chromatographic analyzer to drinking water

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Sample source: Drinking fountain, First floor of Gilman Hall, Iowa State University, Ames, Iowa
Peak identification: A- Solvent front
B- Unknown


B
A
12
10
8
6
4
2
I (Amps X 10^7)
inject
0
10
20
30
Time (minutes)

chromatographic peaks (A and B) were recorded with retention times of 4.5 and 17 minutes. Peak A is the response to the change in solvent composition and this phenomenon is also observed for injection of distilled water as shown in Figure 45.

The exact retention time of phenol was determined to be 24 minutes under the conditions employed by recording the detector response to an injection of 1 ppm phenol in triply distilled water as shown in Figure 46. Phenol was then added to a sample of drinking water such that its concentration was 1 ppm. The detector response to this sample is shown in Figure 47. This amply demonstrates that phenol can be chromatographically separated from potential interfering species in drinking water and detected electrochemically with no sample pretreatment. Drinking water was injected again to determine if detectable levels of chlorinated phenols were present in the sample. No significant signals were recorded over a 3-hour period. The sample was then extracted with n-butyl acetate according to the previously described procedure. The n-butyl acetate extract was injected and, again, no significant signals were recorded over a 3-hour period.

## D. Conclusions

The chromatographic separation of phenol and chlorinated phenols was significantly improved by exposure of the chromatographic material to n-butyl acetate. It is concluded that the chromatographic resin functions as a solid support for a stationary phase of adsorbed n-butyl acetate. The chromatography employed clearly separated phenol and the

Figure 45. Response of liquid chromatographic analyzer to triply distilled water

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Peak identification: A- Solvent front

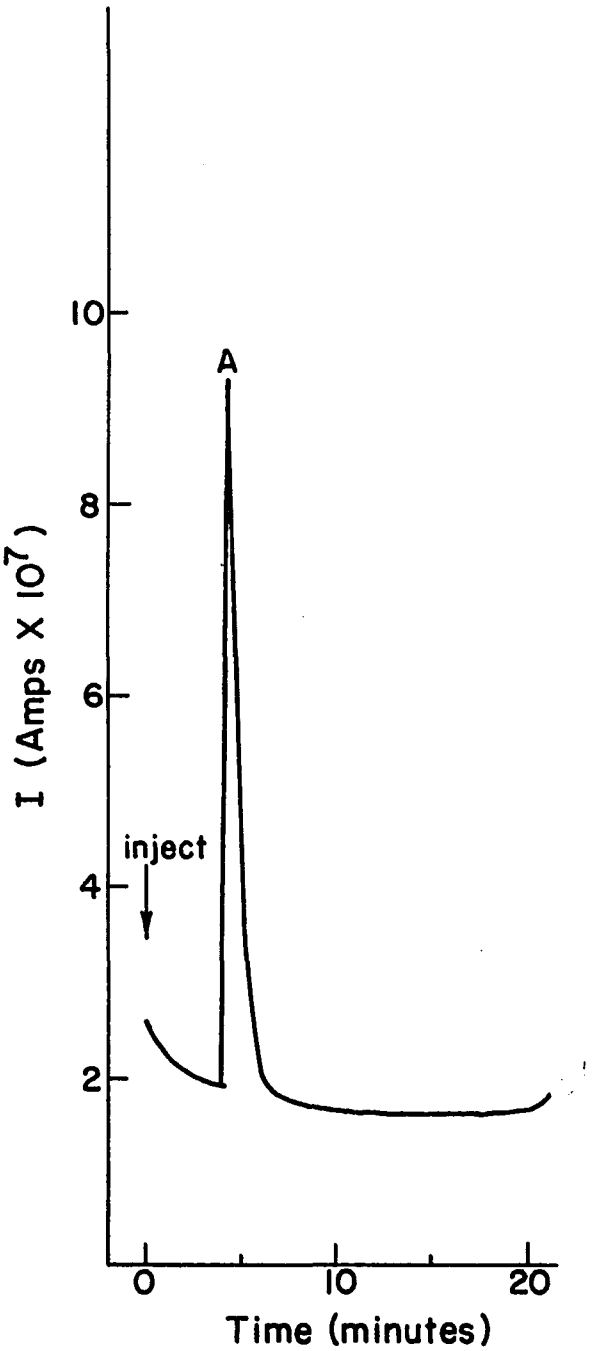

10
8
6
4
2
A
inject
I (Amps X 10^7)
0
10
20
Time (minutes)

Figure 46. Response of liquid chromatographic analyzer to 1.0 ppm phenol in triply distilled water

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volume: 0.0710 mL
Peak identification: A- Solvent front
C- Phenol (1.0 ppm)

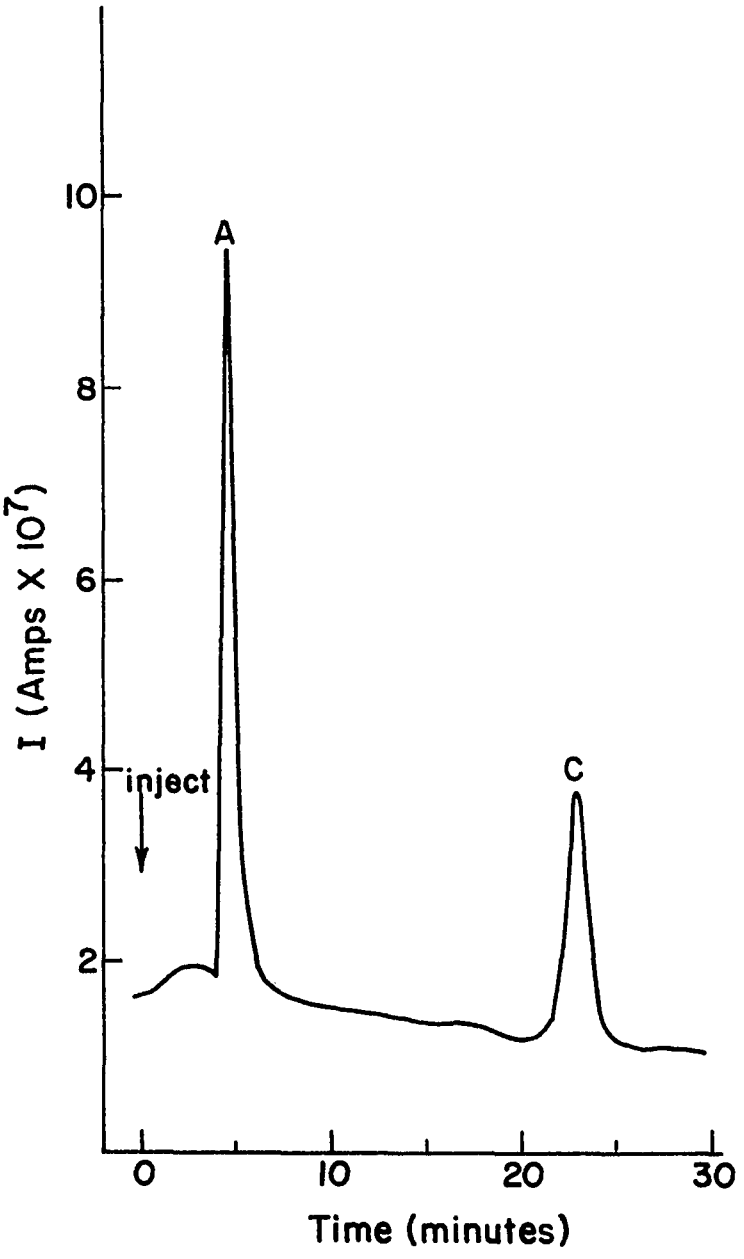
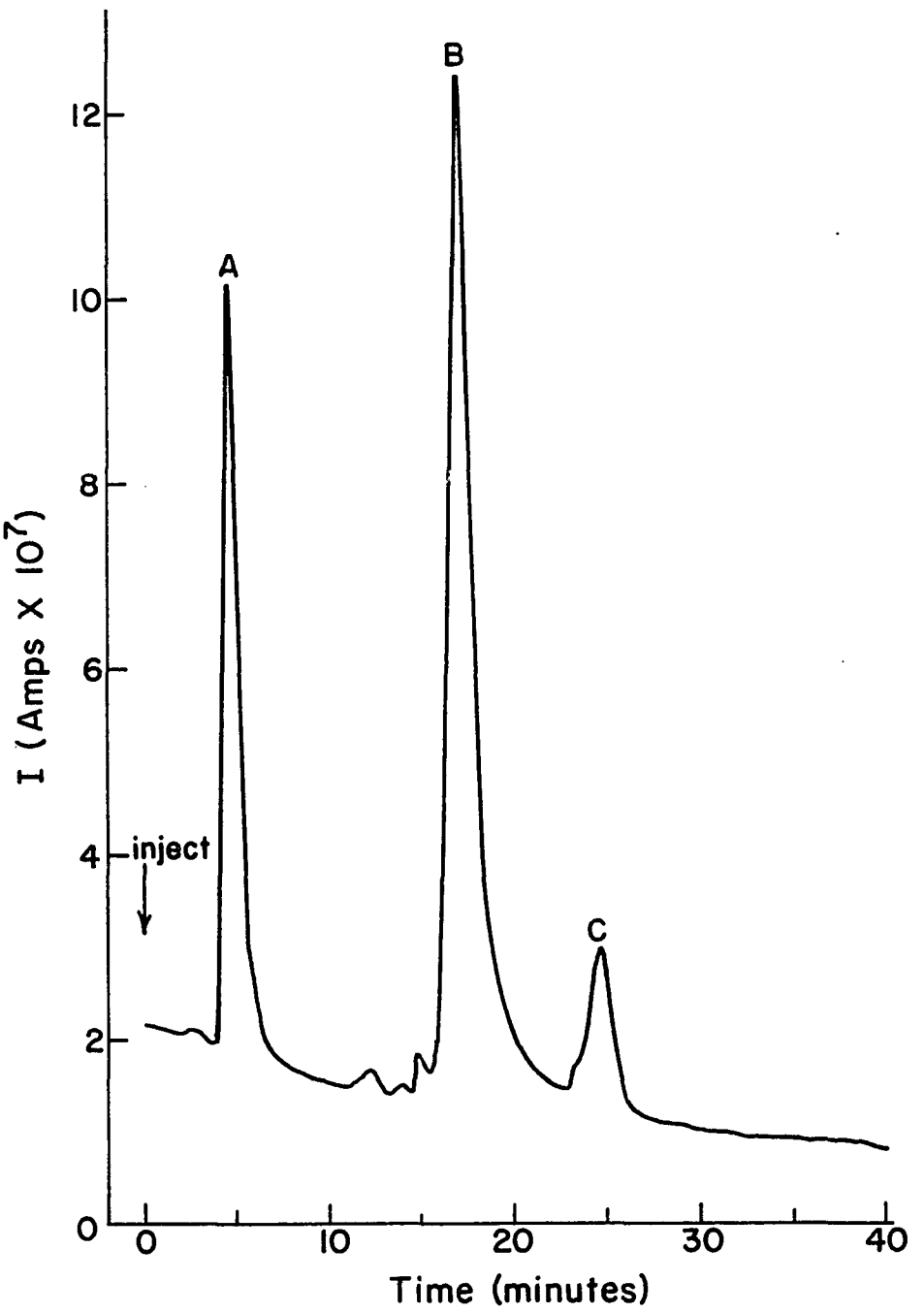

10
8
6
4
2
I (Amps X 10^7)
A
C
inject
0
10
20
30
Time (minutes)

Figure 47. Response of liquid chromatographic analyzer to 1.0 ppm phenol in drinking water

Eluent: 29% acetonitrile - 71% 0.050 N sulfuric acid
Flow rate: 1.00 mL $min^{-1}$
Applied potential: 1.300 V vs. SCE
Sample volune: 0.0710 mL
Peak identification: A- Solvent front
B- Unknown
C- Phenol (1.0 ppm)


A
B
C
inject
I (Amps X $10^7$)
0
2
4
6
8
10
12
0
10
20
30
40
Time (minutes)

chlorophenols from such interferences as the solvent front, methanol and an unidentified peak in the drinking water sample which is thought to be ferrous ion. When extracts in n-butyl acetate were injected, phenol and the chlorophenols were not retained sufficiently on the column to separate them from the detector response to the change in solvent composition.

The procedure developed for the determination of phenol and chlorinated phenols meets the desired criteria listed in the introduction to this chapter. The analysis of drinking water demonstrated that the sample contained no detectable levels of phenol or chlorinated phenols. Although the detection limit for the flow-injection analysis was demonstrated to be slightly less than one picomole of phenol, column dilution in the chromatographic procedure raised the detection limit to 36 picomoles (50 ppb). The detection limit may be lowered by using a larger sample loop and a smaller, more efficient chromatographic column. It is suggested that turbid samples be filtered prior to analysis. Quantitation should be accomplished by the methods of standard additions and internal standards. These methods will alleviate the problems of matrix effects and changes in detector sensitivity. It is also suggested that each liter of sample which is not going to be analyzed immediately be acidified with 5 mL of concentrated sulfuric acid to inhibit air oxidation of phenols in the sample.

# VIII. SUMMARY

The oxidation of phenol at platinum anodes occurs by an electrochemical oxidation followed by simultaneous chemical reactions in the solution. The products of these reactions are subject to further oxidation at the electrode surface. The organic film which is formed on platinum electrodes from the oxidation of phenol at relatively high concentrations is mechanically attached to the surface of the electrode and is not chemically adsorbed to any significant degree. This film severely hinders the mass transport of many electrochemically active species. Dissolved oxygen can diffuse rapidly through this film to react at the electrode surface. The film consists of oligomers and other small phenolic units contained in a polymeric matrix which has a low degree of cross linking.

The anodization of the electrode in an acidic solution of ferric chloride was discovered to remove the polymeric film from the electrode surface. This cleaning process results in perforation of the organic film which exposes electrochemically active regions of the electrode surface. Perforation of the films occurs by a process that weakens the bulk of the film and/or the points of mechanical attachment. The partial pressure of oxygen existent behind the film is then sufficient to rupture the weakened areas.

Phenol and chlorinated phenols can be concentrated by extraction into n-butyl acetate. The presence of n-butyl acetate does interfere with chromatographic separation and electrochemical detection of these phenols. The chromatographic separation of phenol and chlorinated phenols can be

significantly improved by exposure of the chromatographic column to n-butyl acetate. The wire flow-through detector described performs well and is not plagued by the problems associated with tubular detectors. Calibration curves are expected to be non-linear.

# IX. SUGGESTIONS FOR FUTURE WORK

The limitations on future work in this area of electrochemistry are virtually nonexistent. The entire field of the electrochemistry of aromatic compounds appears to be wide open. The most exciting aspect is the possibility of applying electroanalysis to the determination of aromatic and other organic compounds at trace levels in aqueous solution.

The complete characterization of the polymeric films which are formed on the surface of the anode during the oxidation of aromatic compounds is, in itself, a formidable challenge. The determination of the mechanism by which these films are formed may lead to new methods to control their structure. The permeability of these films to dissolved oxygen, while severely hindering the action of species which are known to interfere with the electrochemical reduction of oxygen, may lead to the development of an electrode which is superior to the Clark Electrode in both sensitivity and response time. Investigations into the nature of organic films which are formed during the electrochemical oxidation of other organic compounds should be made. Analine, pyridine, furan, the cresols and the polycyclic aromatic compounds are only a few possibilities. There is ample evidence in the literature of the importance of phenolic films as corrosion inhibitors. The determination of the nature of these films may be useful in determining the strengths and weaknesses of these protective films.

The processes for reactivating electrodes is another area where extensive research should be performed. The substitution of other metal

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ions for ferric ion in the cleaning process, as well as other anions for chloride, may provide insight into the mechanism of the cleaning process. The effects of solvent, pH, and substitution of other electrode materials, such as gold, for platinum on both the deactivation and reactivation processes needs to be investigated. An understanding of the reactivation process could also be beneficial in the development of better corrosion inhibitors.

The design of the wire detector can be modified to increase the signal to noise ratio. Suggested modifications include changing the length of the exposed portion of the wire indicator electrode, changing the diameter of the wire and altering the clearance between the wire and the body of the detector. Isolation of the reference electrode behind an ion exchange membrane is suggested.

One of the more interesting aspects of this research has been the chromatography. The observed increase in peak resolution in the presence of n-butyl acetate is a phenomenon which should be thoroughly investigated. The use of other organic stationary phases, as well as bonded stationary phases, is an area which has great potential for increasing the analytical resolution. These topics hold excellent promise as solutions to the problems of corrosion and the monitoring of environmental pollution. One could spend a lifetime investigating these areas and related phenomena, provided of course, that adequate funding is available.

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# XI. ACKNOWLEDGEMENTS

I would like to acknowledge the support of the members of the electrochemistry group, both past and present, with special recognition going to Dennis Johnson. His free-wheeling research style stimulated this research in all directions at once.

The support of the Chemistry Department, the National Science Foundation and Iowa State University is acknowledged for their financial assistance. I addition, I would like to thank Jerry Amundson of the Engineering Research Institute for performing the microscopy, Willa Jones for performing the mass spectral analysis and Timothy Lindstrom for the use of the programmable calculator which was employed to determine the Simpson Integrals.

A note of thanks is in order to Robert Van Atta, who kindled my interest in analytical chemistry and guided me through undergraduate school with expert skill; Terry Kruger, who made organic chemistry both interesting and enjoyable; and Mr. Kennedy, of the admissions office at Ball State University, who pleaded my case before the admissions board when I could not.

The moral support of my parents, and Kenneth and Betty Weinman, is also greatly appreciated.

Finally and most heartily, I would like to acknowledge the never-ending support of my wife, Wendy, who had faith in my abilities even when I, myself, was in doubt. She was the one who urged me to try college for two academic quarters to see if I could make it.