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Electrochemical Detection of Aliphatic Sulfur Compounds in Liquid Coal Extracts

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ELECTROCHEMICAL DETECTION OF ALIPHATIC SULFUR COMPOUNDS IN LIQUID COAL EXTRACTS

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The presence of sulfur compounds in coal is a serious environmental problem that affects the coal industry. This problem is due to the fact that organic sulfur is not separated or removed during any physical cleaning process. Organic sulfur is removed only during a more costly chemical desulfurization process. The kinds of organosulfur compounds in coal are generally known, but the quantity of each type of compound and the distribution of these compounds throughout the coal matrix has not been studied extensively.

The objective of this research was to investigate the more reactive and chemically labile organosulfur compounds in liquid coal extracts. Organosulfur compounds such as sulfides, aliphatic thiols, and disulfides were studied using reverse phase HPLC with electrochemical detection in a acetonitrile/water mobile phase.

Coal samples IBC 101 and IBC 105 were extracted with THF and hexane. The liquid coal extracts were fractionated using a simple chromatographic technique. The fractionated extracts were then analyzed using reverse phase HPLC with UV detection, reverse phase HPLC with EC detection, infrared spectroscopy, and selected chemical tests.

From the data collected, one can conclude that THF and hexane solvents did extract organosulfur species that were detectable with UV and electrochemical methods.

THF was found to be a better extraction solvent as compared to hexane. THF extraction resulted in an enrichment of the organosulfur compounds in the coal samples extracted. The chemical reaction for organosulfur compounds was positive in all fractionated samples collected, while IR analysis was negative or inconclusive.

Reverse phase HPLC with EC detection appears to be an ancillary technique that has the potential to provide some pertinent information about organosulfur compounds in liquid coal extracts.

I. INTRODUCTION

Organic sulfur detection, identification, and quantification has received a great deal of attention for many years, because many industries desire sulfur free coal for use. Since organic sulfur is not removed during the physical cleaning process of coal, it has become necessary to develop chemical processes to remove organic sulfur from coal. This requirement for a chemical process has generated a need for information concerning the amounts and types of organic sulfur compounds in coal.[1]

In this study conducted at Western Kentucky University, data was collected for the possible speciation of organic sulfur in two coal samples IBC 105 and IBC 101. The two coal samples were extracted with THF and hexane solvents. The liquid coal extracts were then fractionated using a simple chromatographic technique, examined using HPLC with UV detection, analyzed using HPLC with a electrochemical detector, analyzed with IR spectrometry, and analyzed with selected wet tests. The objective of this study was to determine the feasibility of adequately separating and detecting selected organosulfur compounds such as thiols, sulfides, and disulfides.

A. Coal Structure

Bartle and coworkers reported that coal is now considered to be a cross-linked macromolecular network in which are trapped lower molecular weight materials either in sites readily accessible to solvent or in cages analogous to clathrates.[2] Pajak and coworkers report that all coals can be extracted by organic solvents. The amount extracted varies from 1% to 30% for bituminous coals depending upon the solvent used. Pajak has reported that the solvent action diversity may be explained by the recent concept of electron

donor-acceptor (EDA) mechanism of coal extraction and swelling and by a two-phase model of coal structure.[3]

According to the two-phase model, coals are thought to consist of a three dimensional macromolecular network and separate molecules. The macromolecular network creates a pore system in which the molecules are dispersed and are held in place by electron donor-acceptor interactions between electron donor and electron acceptor sites such as functional groups and hetero-aromatic and aromatic rings occurring in both phases.[3]

Electron donor-acceptor (EDA) complexes vary in strength with hydrogen bonding forming the strongest complex. Pajak reported a possible mechanism for solvent action on coal organic matter may be as follows: solvent molecules substitute for one part of the coal EDA complex thus breaking it up.[3] When the electron donor (ED) or electron acceptor (EA) strength of a solvent molecule is higher than the ED or EA strength of the coal active site, the interphase EDA complexes are destroyed and the coal molecules will be detached from the macromolecular network. Solvents with a higher donor number produce a greater destruction of the interphase EDA complexes resulting in more coal molecules being extracted.[3]

Rubio and coworkers have reported that the mobile phase or trapped molecules may constitute up to 40% of the coal by weight.[4] The more accessible portions would be extracted by non-specific extraction solvents.

A coal extract's composition has been shown to depend on the coal rank, as well as the solvent, and time of extraction.[3, 4] Kershaw has reported liquid coal extracts contain compounds such as branched alkenes, n-alkenes, hydroaromatics, and oxygen containing compounds such as cyclic ethers.[5] Of these chemicals, branched chain and cycloalkanes appear to be the easiest to remove. A typical coal extract contains thousands of compounds with molecular masses that usually range from 100 to 5000.[5]

B. Coal Sulfur

Thiophenic compounds have been the focus of most organic sulfur research as it relates to coal. These compounds are the most stable and the most difficult to remove from coal samples especially as compared to thiols, sulfides, and disulfides. Of the total organic sulfur content in coal, Riley and coworkers have concluded that approximately 45% is thought to be due to aliphatic sulfur compounds.[1] Coal samples usually have a total sulfur content that ranges from 0.2% to 12% by weight with most coal samples having a sulfur content that falls within the 1% to 4% range.[6]

White[7], Lee[7], Stock[8], and Attar[9] have briefly reviewed the organosulfur constituents known to exist in coal and coal-derived products. Other workers such as Yurovskii[10], Kessler[11], and Stock[8] have provided a general overview of the appropriate analytical method to use for detection of specific organosulfur compounds. High resolution mass spectrometry has been used to identify thiophenol and thiophenic compounds in pyridine extracts of a Pittsburgh seam by Kessler, Raymond, and Sharky.[11] Combined gas chromatography-mass spectrometry has been used by Radke[12] and coworkers to identify dibenzothiophene and some alkylate dibenzothiophenes in the aromatic fractions of solvent extracts of coals. Calkins has used GC/MS to identify thiophene, benzothiophene, dibenzothiophene in a Pittsburgh No. 8 coal.[13] In this study evidence exists to suggest that sulfidic and thiolic groups constitute approximately 45% of the organosulfur in mid rank coals.

In a study using thermokinetic analysis, thiols, thiophenols, aliphatic sulfides, aryl sulfides and thiophenic sulfur proportions were determined in five coal samples by Attar and coworkers.[9, 14] In this analysis Attar and coworkers concluded that 15-30% of the organic sulfur in coal is sulfidic, while thiophenic sulfur constitutes 30-55% of the organic sulfur in lignite and 40-60% in bituminous coals with the remaining being thiolic in nature. In another study, Yurovskii[10] determined the types of organosulfur compounds in

alcoholic solutions of phenol coal extracts. In his study 48% of the organosulfur compounds appeared to be thiophenic in nature with thiols, sulfides, and disulfides present as a mixture. In a study using X-ray absorption near-edge structure (XANES) spectroscopy George and Gorbaty determined the distribution of sulfur groups in a Illinois No. 6 bituminous coal and a Rasa lignite.[15, 16] The Illinois No. 6 coal appeared to contain approximately 60% sulfidic and approximately 40% thiophenic sulfur, while the lignite contained approximately 30% sulfidic and approximately 70% thiophenic sulfur. In another study using X-ray absorption fine structure (XAFS) spectroscopy, Huffman and coworkers examined several bituminous coal samples with the general conclusion that the organic sulfur compounds were predominantly thiophenic in nature.[17]

Specific aromatic compounds have been studied extensively by Nishioka and coworkers. Sulfur containing aromatic compounds in crude oil, coal extracts, hydrogenated coal liquids, and catalytically-cracked petroleum bottoms were separated using ligand-exchange chromatography (LEC) employing silica gel impregnated with $PdCl_2$. The isolated compounds were identified by using gas chromatography with flame ionization, flame photometric detection, and combined gas chromatography mass spectrometric techniques.[18-23]

C. Coal Extraction

By using coal extracts or reaction products, solid coal analysis or study is made less difficult. Solvent extraction has been a major technique in coal analysis. Many solvents have been used for extractions - such as tetrahydrofuran, pyridine, and dimethylforamide, each being quite useful. In a study performed by Buchanan, an Illinois No. 6 coal was sequentially extracted with toluene, tetrahydrofuran, dimethylforamide, and pyridine with the coal extract containing approximately 28% of the coal by weight and 29% of the organic sulfur.[23] Calkins and coworkers found tetrahydrofuran gave superior extraction results for Pittsburgh No. 8 bituminous coal as compared to pyridine, ethylenediamine, or

acetonitrile.[24, 25] In other studies, Buchanan and coworkers found hot perchloroethylene extracted elemental sulfur, while little organic sulfur was extracted.[26]

Coal-derived liquids contain numerous organic compounds. As a result, it has become important to develop procedures for the detection and measurement of these organic compounds. Those molecules that are electroactive are likely candidates for electrochemical analysis. This idea has been further supported by the fact that coal-derived liquids usually have simple and reproducible voltammograms.[27]

D. Column Chromatography

An interesting approach to the analysis of coal liquids would be the use of liquid chromatography coupled to a sensitive and selective detector. This method would likely provide two major advantages: (1) straight forward preparation and (2) low detection limits.[28]

Coal liquids, as compared to coal, are relatively clean without significant amounts of inorganic ash material and can be readily dissolved in a variety of electrochemical compatible solvents. Coal liquids are known to contain materials which would be expected to undergo electrochemical oxidation. These species include such things as hydroquinones, phenols, aromatic amines, organosulfur compounds, polyaromatic species, and heterocyclic species.[22]

The complexity of coal-derived material makes it necessary to separate the sample into simpler fractions based on polarity, functionality, or molecular size before detailed characterization is attempted. Column chromatography is an excellent technique for segregating sulfur compounds. By choosing proper conditions it is possible to isolate sulfur compounds from the sample and separate them according to compound type.

Sulfur, in various forms, is present in all fossil fuels. In general they have been categorized according to functionality: thiol, disulfide, sulfide, and thiophene.[22] Polycyclic aromatic sulfur heterocycles (PASH) compounds are the most abundant of

aromatic sulfur compounds. Thiols, sulfides, and disulfides are thought to be contained in coals and crude oils. However, their low abundance has made analysis very difficult combined with the fact that thiols are not stable in air or at high temperatures and tend to form disulfides by a coupling reaction.[22]

The problem of separating sulfur compounds from a sample matrix has received some attention. A major method has been liquid adsorption chromatography. This method has been applied to sulfur compounds as a separation method and for an enrichment step prior to more detailed analysis by other techniques.[29]

In coal liquid extracts, it is necessary to separate and enrich the organosulfur compounds prior to analysis by other methods. In studies conducted by the U.S. Bureau of Mines, workers found alumina useful for the separation of petroleum fractions.[30] Alumina has the ability to separate aromatic compounds from sulfur compounds. By using alumina, large amounts of materials can be prepared for subsequent analysis. In 1966, Orr used liquid-liquid chromatography on mercuric acetate or aqueous zinc chloride to separate alkyl and cycloalkyl sulfides from hydrocarbon, thiophenes, thiols, and aromatic sulfides.[31] At approximately the same time, Synder used a mercuric ion-impregnated cation exchange resin to remove sulfides from nitrogen and oxygen compounds in petroleum distillates.[31] Poirier and Smily used adsorption chromatography using silica gel and/or alumina in the first step to separate PASH compounds containing 1 to 3 rings.[32] Drushels and Sommers reported a more selective method for the isolation of PASH compounds that involves an oxidation/reduction procedure. Sulphones formed by oxidation with peroxides were separated by adsorption chromatography followed by reduction back to the original PASH compound.[33] In 1983, one-ring thiophenic compounds were separated by ligand exchange chromatography on a silver nitrate coated silica column. In this same procedure, ligand exchange chromatography using salts of Hg, Cu, Zn, and other metals was used to coordinate with sulfur compounds. This procedure

was effective for the isolation of aliphatic sulphides but was not in general applicable for the separation of thiophenic compounds.[34] Gundermann used a $PdCl_2$ coated silica gel to separate phenanthrene and dibenzothiophene.[35] Lee and Nishioka used ligand exchange chromatography to isolate 2 and 6 ring PASH from the aromatic fractions of complex mixtures. This two step separation method uses neutral alumina and silicic acid adsorption chromatography to fractionate the materials into seven chemical classes. The hexane fraction contains aliphatic hydrocarbons. The benzene fraction contains neutral polycyclic aromatic compounds (PAC) and after the sulfur separation method will produce polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic oxygen heterocycles (PAOH), and polycyclic aromatic sulfur heterocycles (PASH) fractions. The chloroform/ethanol fraction contains nitrogen polycyclic aromatic compounds (N-PAC). And, the tetrahydrofuran fraction contains hydroxyl polycyclic aromatic hydrocarbons (HPAH) compounds.[36]

E. Oxidative Potentials of Organosulfur Compounds

Most of the important electrochemistry of organic compounds has appeared since 1965. In studying organosulfur compounds, sometimes it is necessary to determine the pertinent electrode potential for a particular functional group.[37] Cyclic voltammetry is frequently used for this purpose.

In cyclic voltammetry, the potential of the electrode is varied linearly with time in a cyclic manner in order to observe the response of the organosulfur compound of interest. The cyclic voltammogram provides some general information such as the electrode potential for the reaction, an indication of the stability of the intermediate, and the rate of the electron transfer.[28]

The oxidative potential of numerous organosulfur compounds has been determined by cyclic voltammetry and polarography. Nicholson studied the voltametric oxidation of aliphatic sulfides at platinum electrodes.[38] Drushel and Miller used this same technique for the qualitative identification of aliphatic sulfides in petroleum and later for quantitative

determination of sulfides in petroleum fractions.[39] Cyclic voltammetry studies have shown that aliphatic and aromatic sulfides are readily oxidized at solid electrodes to the corresponding sulfoxides and sometimes to the sulfone in aqueous solutions. In nonaqueous aprotic solvents, oxidation of sulfides leads to sulfonium ions and products derived from the sulfonium ions.[40]

Only a few examples of oxidative electrochemical studies of disulfides have been reported in the literature. The oxidation of such compounds appears to depend upon the supporting electrolyte. Usually, a radical cation undergoes nucleophilic attack by the solvent which forms a mixture of sulfonium ions.[40]

Oxidation of mercaptans leads to disulfides at platinum and other solid electrodes. Thiols are very easily oxidized to disulfides in solution, but this very favorable redox reaction occurs only very slowly at most electrode surfaces such as the glassy carbon. Most liquid chromatography electrochemical (LCEC) methods for thiols depend on the unique behavior of these compounds at a Hg electrode surface at about +0.10 Volts. The reaction involves formation of a stable complex between the thiol and mercury. It is the mercury that is oxidized and not the thiol:[41]

$$2RSH + Hg \longrightarrow Hg(RS)_2 + 2e^- + 2H^+$$

LCEC can be used to detect thiols directly, whereas with UV detection thiols must be derivatized first in order to be detected.[41]

A review of several articles indicates that many organic functional groups can be electrochemically detected.[37] Table 1 provides a listing of some of the more common functional groups and their approximate potentials. In particular, thiols, sulfides, and disulfides usually have an oxidative potential in the 1 to 2 volt range.[40] Table 2 provides a listing of some selected organosulfur compounds found in the literature.[40] These organosulfur compounds may resemble those organosulfur compounds found in coal liquid extracts in this study. These potentials were establish in acetonitrile with either a Pt or a

TABLE 1

Electrochemical Analysis of Organic Functional Group
(E vs. SCE or Ag/AgCl Electrode)[37]

Functional Groups	Oxidations (Volts)	Functional Groups	Reductions (Volts)
Hydrocarbons	+1.0 to +2.0	Olefins	-1.8 to -2.2
Azines	+1.2 to +2.2	Esters	-0.8 to -2.2
Amides	+0.5 to +1.3	Ketones	-1.2 to -1.8
Phenols	+0.1 to +0.4	Aldehydes	-1.2 to -1.8
Quinolines	+0.2 to +0.6	Ethers	-0.7 to -1.4
Halogens	+0.0 to +0.2	Diazo Comp.	-0.3 to -0.6
Aromatic Hydroxyls	+0.1 to +0.6	Conjugated Esters	-1.0 to -1.7
Amines	+0.5 to +1.3	Nitro Comp.	-0.2 to -0.5
Alkyl Amines	+0.8 to +1.6		
Aromatics	+0.9 to +2.2		
Catechols	+0.0 to +0.5		
Phenyl Ethers	+1.3 to +1.8		
Aromatic Amines	+0.0 to +1.0		
Carbohydrates	+0.0 to +0.7		
Thiophenols	+0.2 to +0.6		
Thiols	+0.5 to +2.0		
Sulfides	+0.5 to +2.0		

TABLE 2

Molecular Mass vs. Oxidation Potential For Model Sulfur Compounds[40]

Chemical Name	Molecular Mass (amu)	Oxidation Potential (Volts)
2-Methyl-2-Propanethiol	90	1.59
1-Methyl-1-Propanethiol	90	1.33
1-Propanethiol	76	1.14
Phenyl Disulfide	218	1.53
Phenyl Methyl Sulfide	124	1.83
Ethylene Sulfide	60	1.51
Dimethyl Sulfide	62	1.41
Diethyl Sulfide	90	1.50
Diallyl Sulfide	114	1.74
1-Butanethiol	90	1.49
Diphenyl Sulfide	186	1.50
Benzyl Phenyl Sulfide	200	1.95
Trimethylene Sulfide	74	1.69
Pentamethylene Sulfide	102	1.42
1,3,5-Trithiane	138	1.47
tert-Butyl Sulfide	146	1.06
sec-Butyl Sulfide	146	1.43
1,4-Dithiane	120	1.46
Tetrahydrothiophene	88	1.45
Dibenzothiophene	122	1.35
Ethyl Sulfide	90	1.50
Phenyl Sulfide	186	1.50
Butyl Sulfide	146	1.45
Thiophene	84	1.84

carbon electrode at ambient temperature. As Figure 1 shows, a plot of these potential values produces an average potential value around 1.5 volts. In the detection process, one must establish the potential window which is the range of electrode potentials accessible. An analyte reaction must occur within the potential window in order to be detected. Mobile phase and electrode material usually limit this potential window in both the positive and negative direction.[41] For a glassy carbon electrode in an aqueous solution at a pH of 4.5, the potential window ranges from -0.8 to +1.2 volts.[41]

F. Sulfur Compound Detection With UV and EC Detection

HPLC has become a widely used instrumental technique for both the qualitative and quantitative analysis of organic, biological, and inorganic compounds. As it relates to sulfur compounds, several articles provide support for the use of HPLC in organosulfur detection. Mockel conducted reverse phase HPLC separation of nonionic sulfur compounds. Mockel reported successful separations for elemental sulfur, aliphatic thiols, aliphatic dithiols, and aliphatic polysulfides.[42] Bossle separated organic sulfides using pre-column derivatization in conjunction with HPLC in addition to direct detection following chromatographic separation.[43] Shoup and Allison were able to simultaneously determine thiols and disulfides using HPLC with a dual mercury amalgam electrode for compounds in plant tissue and human blood.[44] Shea and MacCrehan were able to identify hydrophilic thiols using ion-pair liquid chromatography coupled to electrochemical detection.[45] Electrochemical detectors have also been used in the HPLC analysis of sulfur-containing compounds such as parathion and methyl parathion and biologically active sulfhydryl-containing compounds.[46, 47]

In order to optimize an LCEC determination, one must consider the column and detector together. One of the major limitations is the mobile phase. The mobile phase is usually not a nonpolar solvent because of its inability to support a significant ionic strength required for conductivity. As a result, normal phase separations are not conducted on

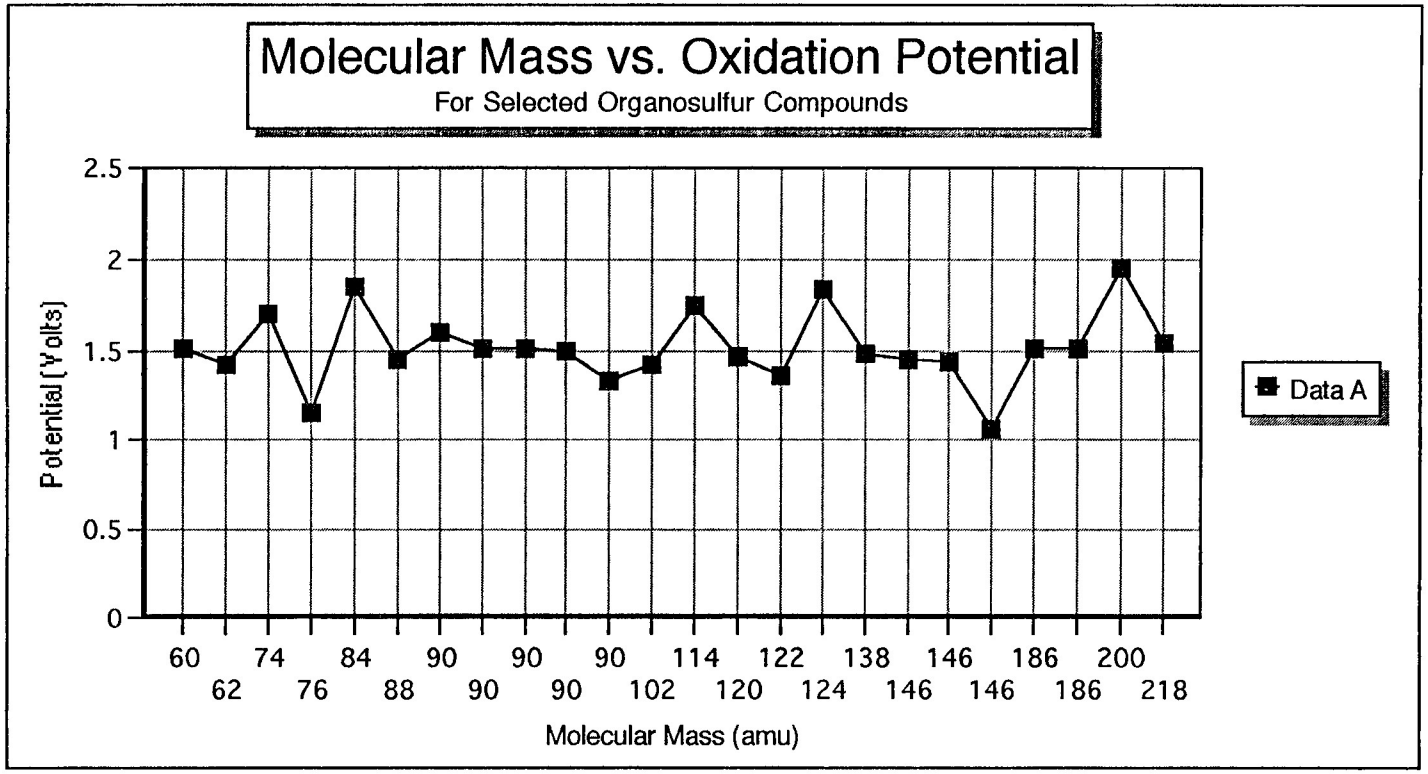

Figure 1. Molecular Mass vs. Oxidation Potential For Model Organosulfur Compounds.

alumina. Most LC separations are reversed phase. In reverse phase the mobile phases are usually aqueous solutions with organic modifiers such as methanol, acetonitrile, and tetrahydrofuran. The retention time of the species is altered by adjusting the modifier concentration, the pH, the ionic strength, temperature, or by adding an ion pairing agent. These mobile phases adjusted as above are excellent for electrochemistry due to their ability to carry an ionic current, to be chemically inert, to be electrochemically inert, and to be able to dissolve the analyte.[41]

Another limitation of the mobile phase is the dissolved oxygen in the mobile phase. This gas must be removed to prevent large background currents even at low potentials. Mobile phases which are totally nonaqueous usually have a distinct advantage as compared to aqueous solutions, because aqueous solutions have a potential range from -1.2 V to +1.2 V whereas in dry acetonitrile the range with salts is from -3 V to +3 V. For mobile phases used with a carbon electrode the following reaction determines the positive limit:

$$2H_2O \text{ ----> } 4H^+ + O_2 + 4e^-$$

The negative limit is defined by the reduction of dissolved oxygen in the mobile phase as shown below:

$$2H^+ + 2e^- + O_2 \text{ ----> } H_2O_2$$

$$2H^+ + 2e^- + H_2O_2 \text{ ----> } 2H_2O$$

To reduce the effect of the above reactions, oxygen is usually removed by nitrogen sparging, vacuum degassing, ultrasonic agitation, and refluxing. If oxygen has been completely removed, the negative potential limit is determined by the hydrogen overvoltage, the reduction reaction is as follows:[41]

$$2H^+ + 2e^- \text{ ----> } H_2$$

HPLC detectors may be divided into two categories. These are usually universal and class specific. Refractive index and UV absorption are universal detectors which are very useful. Many compounds are not responsive to universal

detectors. These compounds may be present at trace levels or they maybe compounds present in complex samples. In the latter case a class specific detector is usually preferred. The electrochemical detector is a class specific detector that has seen rapid development in the last couple of decades. Since the first reported use of electrochemical detectors in liquid chromatography, a wide variety of compounds have been determined at concentrations much lower than is possible with other detectors. The limit of detection of these detectors is influenced by the sensitivity and by the level of noise. When operating at a low potential range with a sensitivity of 0.1 to 1.0 pmole, the lower concentration limits detectable approach 1.0×10^{-9} M to 1.0×10^{-10} M. Many compounds have been successfully analyzed by LCEC: aromatic amines, phenolic compounds, caffeine, NADH, ascorbic acid, sulfides, thiols, disulfides, nitrocompounds, and quinones.[41, 47]

LCEC provides several advantages when compared to other common detectors, such as utilizing absorbance, fluorescence, or refractive index. In LCEC, the oxidation or reduction of an analyte generates the signal. Due to the method of signal generation, the response of the technique is different from that of spectroscopy-based approaches and this is a asset in the analysis of complex samples not completely resolved by the LC column. Furthermore, LCEC selectivity may be adjusted by appropriate choice of applied potential, electrode material, and mobile phase composition. Due to its composition or structure, LCEC may provide very low detection limits on the order of picomole or femtomole.[41]

The cells used in ordinary voltammetry and electrochemistry are fundamentally the same. The instrumentation employs a three-electrode configuration consisting of a working, counter, and reference electrode. The working or indicator electrode may be constructed from a variety of materials such as glassy carbon, pyrolytic carbon, carbon paste, mercury, gold, platinum, and nickel. The working electrode construction depends on the range of potentials needed, the nature of the analyte involved, and the solvent to be used.[41]

Mercury and mercury amalgams demonstrate a high overpotential for hydrogen reduction, and they are useful at negative potentials for reducible analytes. The other electrodes such as glassy carbon and carbon paste are used mainly at positive potentials for analyte oxidation.

The geometry of the electrochemical cell used in LCEC is a thin layer or sandwich type of cell. The elongated cavity formed by the thin spacer allows effluent from the column to pass across the working electrode surface where the analyte oxidation or reduction occurs. This construction provides a low dead volume which serves to minimize band broadening, maximize contact between the solution and the electrode so as to increase the measured current.[41]

A technique widely used in LCEC is constant-potential amperometry. This approach involves just the measurement of the electrochemical current that occurs in response to a fixed potential applied to the working electrode. Following HPLC, the sample passes through an amperometric detector cell, only a fraction of the analyte flows across the surface of the working electrode where the electron transfer reaction and the measurement of current occur. The current produced is dependent on the concentration of the electroactive species in the vicinity of the electrode surface per unit time and on the rate constant of the redox reaction.[41]

The rate of the electrode reaction generally depends on the applied potential. This feature makes the choice of potential important in LCEC. This potential is chosen based on experiments in which the current-potential behavior of the analyte in the eluent is determined by techniques such as cyclic voltammetry (CV) or linear sweep voltammetry. The information generated by techniques such as CV give preliminary information concerning the oxidation or reduction of the analyte as a function of the applied potential and solution conditions.[41] This information is very useful when one is searching for one compound in a complex sample matrix.

In LCEC the working electrode potential is chosen by considering the selectivity required for the specific application and the optimum signal-to-noise ratio. The oxidation or reduction current associated with the analyte increases as the applied potential is made greater. The current reaches a plateau where the oxidation or reduction current becomes limited by the mass transfer of the analyte to the electrode surface. The electrode is usually operated at a potential where the signal-to-noise ratio is at a maximum and eluent electrolysis is at a minimum. Since selectivity is inversely related to the potential employed, the lower the potential chosen, the better the selectivity due to fewer compounds being oxidized or reduced at the lower potentials. When the samples are complex, it may be better to focus on selectivity rather than sensitivity.[41]

G. IR Analysis of Sulfur Compounds

In IR spectrometry, wavelengths in the 2.5-5.0 micrometer range excite transitions between the vibrational energy levels of the molecules present in the sample. The masses of the atoms present and the strength of the interatomic bonds affect the vibrational energy levels. Therefore, the IR spectrum contains information about the atoms present and the way in which they are bonded together (the molecular structure present). Functional groups can be considered to vibrate independently of the rest of the molecule in which they are found. The position of these absorption bands are given in wave numbers called reciprocal centimeters (cm^{-1}).[48]

Some major absorption bands relevant to coal liquids are given in Table 3. IR spectra may be obtained for all materials regardless of physical state. Gas samples can be measured in cells. Liquids can be measured as thin films between NaCl or KBr plates. Solid samples may be prepared as mulls in nujol or mixed with a non-absorbing matrix such as KBr and a small pellet produced in a press.[48]

IR analysis has been applied to coal products. Stompel and Bartle used IR to characterize the structure of tars from fluidized bed pyrolysis of coal.[49, 50]

TABLE 3

Major IR Absorption Bands Found in Coal Liquids[48]

Band Position (cm^{-1})	Functional Group
3600-3500	Free OH stretch
3500-2400	Hydrogen bonded O-H stretch
3400-3200	N-H stretch
3060-3000	Aromatic C-H stretch
3000-2850	Aliphatic C-H stretch
2600-2500	Mercaptan S-H stretch
2560-2550	Thiophenol S-H stretch
1730-1680	Ketone C=O stretch
1800-1740	Carboxylic Acid monomer C=O
1720-1680	Carboxylic Acid dimer C=O stretch
1750-1725	Ester C=O stretch
1680-1640	Amide C=O stretch
1460-1440	Aliphatic C-H bend
1380-1370	Methyl symmetric C-H bend
1300-1100	C-O stretch
900-700	Aromatic C-H bend

II. EXPERIMENTAL

A. Coal Sample Preparation

Two coal samples were selected to quantitatively and qualitatively evaluate for aliphatic sulfur content. Approximately 500 gram samples of IBC 101 and IBC 105 were obtained from the Western Kentucky University Coal and Fuel Lab and ground to -60 mesh. The samples were stored in sealed and labeled containers in a freezer at a temperature of 0 degrees (Celsius) when not in use.

B. Coal Extraction

Solvent extraction work was done using a standard soxhlet extractor. Each soxhlet was insulated with glass wool wrapped in aluminum foil to help prevent heat loss. It was hoped that any heat loss would be confined to the condenser (Figure 2).[51]

A system of six soxhlets were set up, three in a series. The three soxhlet's on the left were used for the THF extraction of IBC 105, and the three soxhlets on the right were used for the THF extraction of IBC 101. A Glas-Col six unit heating mantle was used for the heating of the soxhlet system (Figure 3).[51]

The heated vacuum desiccator used was from Precision Scientific Company in Chicago, Illinois. The vacuum gauge attached to the heated desiccator was used to judge the amount of vacuum on the system. The heated vaccum desiccator was 120 volts, 2 amps. Temperature inside the vacuum desiccator was measured with a thermometer that was built into the heated vacuum desiccator. The vacuum was generated with a Cenco-Hyvac Vaccum Pump from Central Scientific Company.

Weighings were done on a Electronic Analytical Balance from American Scientific Products, catalog number B1240. These weighings were done to the nearest 0.1 mg.

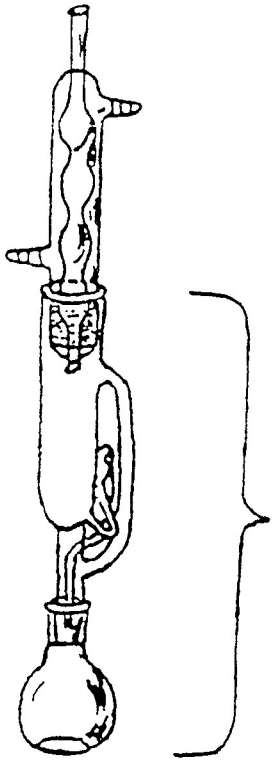

Figure 2. Soxhlet Extraction Apparatus.[51]

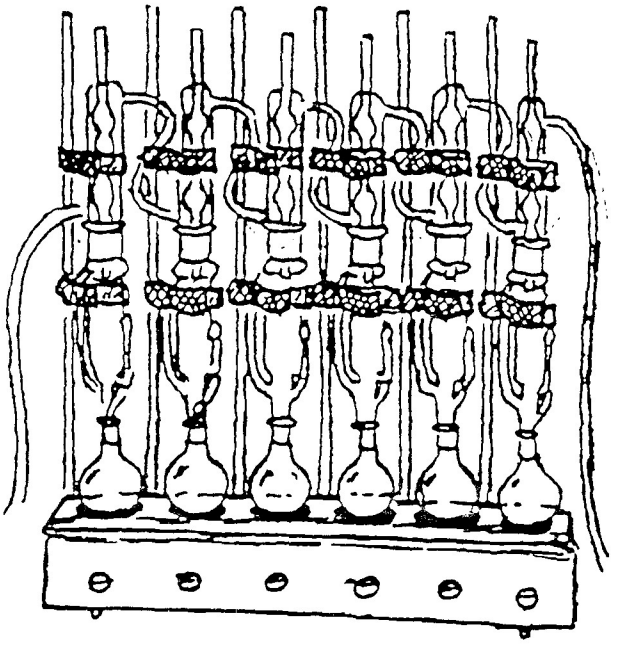

Figure 3. Six unit heating apparatus with soxhlet set-up.[51]

The tetrahydrofuran used was from Aldrich Chemical Company, Inc., Milwaukee, WI, and met A.C.S. reagent grade specifications. It had a boiling point range of 1.2 degrees Celsius and inhibited with 0.025 percent BHT. No extra purification was done to the THF before using it.

The methanol was from Aldrich Chemical Company, Inc., Milwaukee, WI. The methanol was A.C.S. certified and had a boiling point range of 1.0 degrees Celsius. The assay was 99%, and no extra purification was done.

The raw coal was received in sealed five gallon buckets. It was crushed to -8 mesh coal and split, then crushed further into -60 mesh for use. The crushed coal was stored in the freezer at a temperature of zero degrees Celsius until used.

1. Procedure

The procedure used for the solvent extraction work was developed at the University of Kentucky Institute for Mining and Minerals Research by Art Fort.[51] All samples are run in triplicate, and the criterion for good procedure and technique is close agreement of results for members of each group.

a. Dry a beaker at 100-110 degrees Celsius (one hour or more), cool in a desiccator, and weigh to the nearest mg. All subsequent weighings will be to the nearest mg. Weigh in 10 grams of -60 mesh coal.

b. Dry the samples in a vacuum oven at 60 degrees Celsius plus or minus 4 degrees Celsius for a period of six hours. Cool to room temperature in a desiccator and weigh to obtain moisture loss percent. Dry marked thimbles, cool and weigh along with the coal samples. Place dried coal samples in its thimble and weigh again to obtain the weight of dried coal to be extracted.

c. Extract the dried coal samples for a period of 22 hours plus or minus 2 hours, with 150 mL of THF. Insulate the soxhlet extraction assembly to minimize heat loss (we desire most of the heat loss to occur in the condenser). Inspect the extraction assembly from time to time to insure that THF drips rapidly from the condenser drop tip.

d. After cooling, replace THF with methanol and bottle THF extract. Extract the coal sample with methanol for a period of 5 to 6 hours.

e. Remove the thimble from the extraction assembly, allow bulk of methanol to drain and evaporate under the hood. Place the thimble in a vacuum desiccator over calcium chloride lumps (replace calcium chloride periodically as they show evidence of moisture). Evacuate desiccator for a period of one-half hour. Seal vacuum, and allow sample to remain over-night under vacuum.

f. Transfer sample to vaccum oven and dry at 150 degrees Celsius for a period of 6 hours under vacuum. Turn the oven off and leave the samples in the oven under vacuum until they cool to below 50 degrees Celsius (approximately 3 hours). Cool to room temperature (desiccator) and weigh to obtain extraction loss. Store in desiccator under vacuum.

g. Repeat 150 degree Celsius drying for 2 hours, allowing the samples to cool below 50 degrees Celsius before removing them. Continue these 2 hour dryings until the extraction losses are reproducible.

h. Store extracted samples in screw-cap vials. Label each vial and place it in a freezer.

C. Analysis of Coal Samples

The analytical characterization of the coal samples was done using analytical equipment in the Western Kentucky University Coal and Fuel Laboratory. The analysis performed on each coal sample included proximate analysis, ultimate analysis, and forms of sulfur. Proximate analysis (moisture, ash, volatile matter and fixed carbon) values were obtained using the LECO MAC-400; ultimate analysis (carbon, hydrogen, nitrogen, oxygen and total sulfur) data was obtained using the LECO CHN-600 and SC-432. Carbon, hydrogen, and nitrogen were determined using the CHN-600, while total sulfur was determined with the SC-432 high temperature tube furnace combustion method

(ASTM D 4239). The oxygen content of each coal was estimated using the following equation:[52]

$$\%O = 100 - (\%C + \%H + \%N + \%S + \%A)$$

where %O = percent oxygen

%H = percent hydrogen

%S = percent sulfur

%N = percent nitrogen

%A = percent ash

Forms of sulfur (pyritic, sulfate, and organic) were determined using the ASTM D2492 Method.

D. Cyclic Voltammetry

1. Apparatus and Reagents

Cyclic voltammetry scans were obtained with a Bas-100 instrument from Bioanalytical Systems, Inc., Lafayette, Indiana, using a Ag/AgCl reference electrode with carbon and platinum working electrodes.

The acetonitrile was from Aldrich Chemical Company, Inc., Milwaukee, WI. The acetonitrile was A.C.S. certified and had a boiling point of 80.7 degrees Celsius. The assay was 99.95% and no extra purification was done. Sodium perchlorate was from Aldrich Chemical Company, Inc. The sodium perchlorate was reagent grade. The nitrogen was in a steel cylinder. It had an assay of 99.99%.

All sulfur compounds tested were from the Western Kentucky University Chemistry Department. They were used in their present condition.

2. Procedure

The electrode surfaces were cleaned and rinsed throughly with distilled water and acetonitrile solution.[53]

The cell was assembled and filled with 0.05M sodium perchlorate in acetonitrile so that the ends of the electrodes were immersed. The cell was deoxygenated by purging with

nitrogen gas for approximately 15 minutes. Following this, nitrogen gas was directed over the solution to prevent oxygen from re-entering the cell during the remainder of the experiment.

While the cell was being deoxygenated the scan parameters were set. The working electrode was switched off during this procedure. The initial potential was set at 0.00 Volts and the scan limits at +3.0 Volts to -3.0 Volts using the recorder as a monitor. All scans were started in the positive direction.

When deoxygenation was complete, the working electrode was switched on. After allowing the current to obtain a constant value (in about 10 seconds), the potential scan was initiated and a background CV of the supporting electrolyte solution was obtained.

After turning off the working electrode, the cell was cleaned and refilled with 5 mM of the sulfur compound dissolved in acetonitrile which was 0.05 M in sodium perchlorate. Following the same procedure as above, a CV of the sulfur compound was obtained.

The effect of the scan rate on the voltammogram was observed by using the same solution and recording CV's at the following rates: 20, 50, 75, 100, 125, 150, 175, 200 mV/s. Between each scan, initial conditions at the electrode surface were restored by gently moving the working electrode gently up and down without actually removing it from solution or by activating a stirring bar. Care was taken so that no bubbles remained on the electrodes. Two minutes were allowed for the solution to come to rest before obtaining a CV. Once an appropriate CV scan was obtained it was plotted on a plotter connected to the CV instrument using Hewlett Packard plotter paper, catalog number 17801P.[53]

E. HPLC with UV Detection

1. Apparatus and Reagents

A Varian model high performance liquid chromatograph with a UV detector (254 nm), a reversed phase C-18 column, and a 25 microliter syringe were used. The mobile phase consisted of 70% acetonitrile and 30% water. The solution was 0.05 M in sodium

perchlorate. Water and acetonitrile were HPLC grade solvents. Sodium perchlorate was reagent grade. All chemicals were from Aldrich Chemical Company, Milwaukee, WI.

2. Procedure

Mobile phases were prepared one liter at a time. Seven hundred milliliters of acetonitrile and 300 milliliters of water were mixed with 6.10 grams of sodium perchlorate. The solution was filtered using a 250 mL solvent filtration apparatus with Nylon-66 filters (47 mm, 0.45 um pores). While the apparatus was connected to a water aspiration line, the solution was held under vacuum and heated on a hot plate and stirred with a magnetic stirring bar for 15 minutes to removed dissolved oxygen gas. After oxygen removal, the solution was placed in a clean and sealed volumetric flask or placed in the HPLC solvent reservoir.[54]

The HPLC instrument was equilibrated prior to each daily use (2 hours). The flow rate was 1 mL/minute at a pressure of 120 atms and ambient temperature. The UV detector had a sensitivity of 0.44 AUFS and was attached to an integrator with a chart speed of 1 cm/minute.

Model solutions were prepared for various sulfur compounds using freshly prepared mobile phase solution. The total sulfur compound injected onto the column was kept between 10 ng and 100 ng unless higher concentrations were needed for detection. The UV detector and HPLC conditions were set at various settings in order to detect each sulfur compound. Model sulfur compounds of appropriate concentrations were then mixed, and HPLC separation and UV detection were attempted at 254 nm.[54]

Five milliliter samples of liquid coal extract were evaporated to dryness and redissolved in 2 milliliters of mobile phase. The sample was injected onto the column, and UV detection (254 nm) was attempted. The flow rate was 1.0 to 1.5 mL/minute with 120 atms and ambient temperature. The UV detector had a sensitivity of 0.44 AUFS and was connected to an integrator with a chart speed of 1 cm/min.[54]

F. HPLC with Electrochemical Detection

1. Apparatus and Reagents

A Varian model high performance liquid chromatograph with a electrochemical detector, a reversed phase C-18 column, and a 25 um syringe were used. The electrochemical detector was Model LC-4B/17AT from Bioanalytical Systems, Lafayette, Indiana. The reference electrode was a Ag/AgCl electrode, while the working electrode was a glassy carbon electrode.

Acetonitrile and water were HPLC grade solvents. Sodium perchlorate was reagent grade. All chemicals were from Aldrich Chemical Company, Milwaukee, WI. Model sulfur compounds were usually reagent grade. These compounds were obtained from the university's chemistry stockroom.

2. Procedure

Mobile phases were prepared one liter at a time. Seven hundred milliliters of acetonitrile and 300 milliters of water were mixed with 6.10 grams of sodium perchlorate. The solutions were filtered using a 250 mL solvent filtration apparatus with Nylon-66 filters (47 mm, 0.45 micrometer pores). While the apparatus was connected to a water aspiration line, the solution was held under vacuum and heated on a hot plate and stirred with a magnetic stirring bar for 15 minutes to remove dissolved oxygen gas. The freshly prepared solution was placed in a cleaned and sealed volumetric flask or placed in the HPLC solvent reservoir for use.

The HPLC instrument and the electrochemical instrument were equilibrated prior to each daily use (2 hours). The flow rate was 1.0 to 1.5 mL/minute with 120 atms of pressure and ambient temperature. The reference electrode was a Ag/AgCl electrode, while the working electrode was a glassy carbon electrode. The oxidative potential was set at 1.250 Volts.

Model solutions were prepared for various sulfur compounds using freshly prepared mobile phase solution. The total sulfur compound injected onto the column was

kept between 10 ng to 90 ng unless a higher concentration was needed for detection. The HPLC instrument and the electrochemical instrument were set at various settings/conditions in order to detect each model sulfur compound. Model sulfur compounds of appropriate concentrations were then mixed, and HPLC separation and electrochemical detection were attempted at a oxidative voltage of 1.250 Volts or lower (if possible). [54]

Five milliliters samples of the liquid coal extract were evaporated to dryness and redissolved in 2 milliliters of the mobile phase. The sample was injected onto the column and HPLC separation and electrochemical detection were attempted. The flow rate was 1.0 to 1.5 mL/minute with 120 atms of pressure, ambient temperature, and a oxidative potential of 1.250 Volts. The electrochemical detector was connected to an integrator with a chart speed of 1 cm/minute.[54]

G. Liquid Coal Extract Fractionation

1. Apparatus and Reagents

A glass liquid chromatography column was used to fractionate coal liquid extracts (Figure 4). The glass column was 400 mm X 22 mm ID X 25 mm OD column. The column was from Supelco, Canada Ltd., Oakville, Ontario L6K 3V1, Canada. Glass wool and neutral aluminum oxide (Brockman Activity I, 80-200 mesh, Fisher No. A950) were used in the glass column.

Reagent grade solvents of hexane, benzene, chloroform, ethanol, and tetrahydrofuran were used in the coal liquid extract fractionation process. These solvents were from the Aldrich Chemical Company, Milwaukee, WI. They were used with no further purification.

2. Procedure

Approximately 20 grams of the liquid coal extract was dissolved in a few milliliters of chloroform (or used without the chloroform) and adsorbed onto 3 grams of neutral alumina. The solvent was removed from the alumina by vigorously stirring the mixture under a gentle stream of dry nitrogen gas. The alumina with the coal liquid extract sample

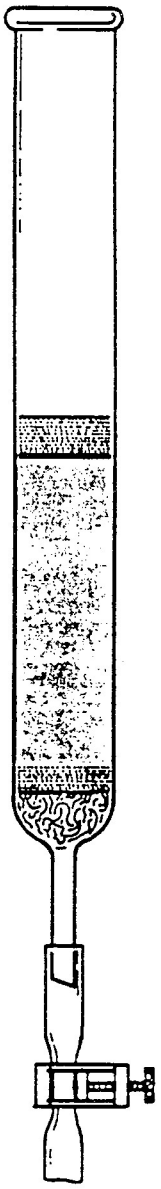

Figure 4. Simple chromatographic column for the fractionation of the liquid coal extract.[56]

was then packed on top of an 22 mm i.d. column which already contained 6 grams of neutral alumina as shown in Figure 4.(56) The sample was then eluted with the following chromatographic grade solvents: fraction A-1, 20 mL of hexane; fraction A-2, 50 mL of benzene; fraction A-3, 70 mL of chloroform; fraction A-4, 50 mL of 10% ethanol in tetrahydrofuran (Figure 5).[36]

The solvent fractions were stored in sealed volumetric flasks of appropriate size (100 mL). Five milliliter samples of concentrated coal liquid extract were evaporated to dryness in an evaporating dish at room temperature. The dry sample was dissolved in an appropriate volume of solvent for UV analysis, electrochemical analysis, IR analysis, and selected wet chemical tests.

H. Infrared Analysis

1. Apparatus and Reagents

Carbon tetrachloride was used as the IR solvent. The solvent was obtained from the Western Kentucky University chemistry stockroom. The salt plates were made of sodium chloride. The instrument model was a Perkin Elmer 16 PC FT-IR.

2. Procedure

Two milliliters samples of the concentrated coal liquid extracts of hexane, benzene, chloroform, and tetrahydrofuran were evaporated to dryness and redissolved in chloroform and placed between two NaCl plates for analysis. The samples were analyzed by scanning from 4400 to 450 reciprocal centimeters.[55]

I. Chemical Tests for the Detection of Mercaptans

1. Reagents and Procedure

Small aliquots of the fractionated coal liquid extracts were tested with saturated lead (II) acetate in ethanol. Thiols produce a yellow precipitate.[56]

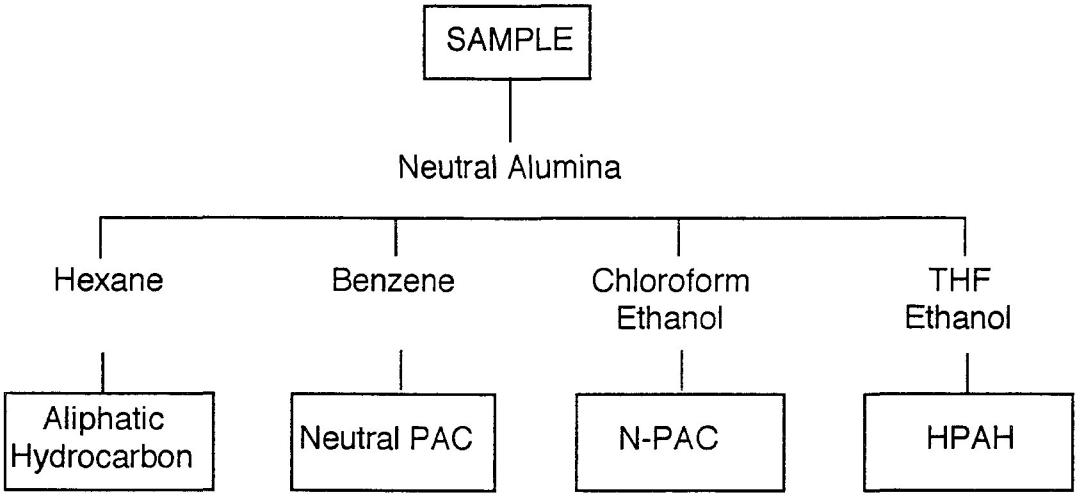

Figure 5. Fractionation Scheme For Coal Liquid Extracts.

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry of Selected Organosulfur Compounds

The initial step in my investigation was to obtain cyclic voltammetry data for model organosulfur compounds in acetonitrile with a concentration of 0.050 M sodium perchlorate using 10 mM of the selected sulfur compound.

Data obtained in this study is listed in Table 4. The data shows a tendency for several oxidative peaks to occur during the oxidation process, in some compounds, while most reductive scans illustrate a single reduction peak.

Scans were conducted for some model organosulfur compounds using a platinum or a carbon electrode (Table 4 and Figures 6 through 41). The data in Table 4 and Figures 6 through 41 show that the oxidative and reductive potentials at the carbon and Pt electrodes were not necessarily the same. The major peaks show similiar potential values, while the carbon electrode demonstrated a overall lower potential for the compounds evaluated (Figure 42).

The oxidative potential of the organosulfur compounds evaluated were generally above 1300 mV's as illustrated in Table 4 and Figure 42. The negative reductive potential values seem to have a wide range. These values were not considered to be important because the aim of my investigation was to attempt a determination of the presence of organosulfur compounds using mild oxidative electrochemical detection.

The CV scans in Figures 6 through 41, Table 4, and Figure 42, clearly show that some compounds are good candiates for detection by electrochemical means while others are not. Oxidative electrochemical detection seems plausible for thiols, sulfides,

TABLE 4

Cyclic Voltammetry Data For Model Sulfur Compounds
in Acetonitrile with 0.05 M Sodium Perchlorate

Chemical Name	Pt Electrode Potential (mV)	C Electrode Potential (mV)
Thioacetic Acid	-1176	none
2-Mercaptoacetic Acid	-1048, 2226	1950
Phenyl Mercaptoacetic Acid	1566, 1962, -698	1659
Thiourea	none	none
Thioacetamide	1545, 1887	1590, -888
Dithiooxamide	-1160, 2337	-1177
2-Mercaptoethanol	1413, -1874	1404, -1883
2-Nitrothiophene	-879	-855
Thionaphthene	1761, -1752	1782
Benzyl Phenyl Sulfide	1542, 1881, -1836	1492
Phenyl Sulfide	1503, 1755, 2145	1602, 1893
Dibenzothiophene	1524, 1842, 2139	1533, 1866
Thiophenol	1497, 2718, -1326	1473
Butyl Sulfide	1491, -1789	1338
1-Decanethiol	1785	1482
Thiophene	2226, 2604, -1758	1859
Benzothiazole	2457, 1077, -1767	none
t-Butyl Sulfide	1629, 1785	1565, 1943
1-Dodecanethiol	1776	1353
Butyl Disulfide	none	1334
Dithiodiglycolic Acid	none	1665

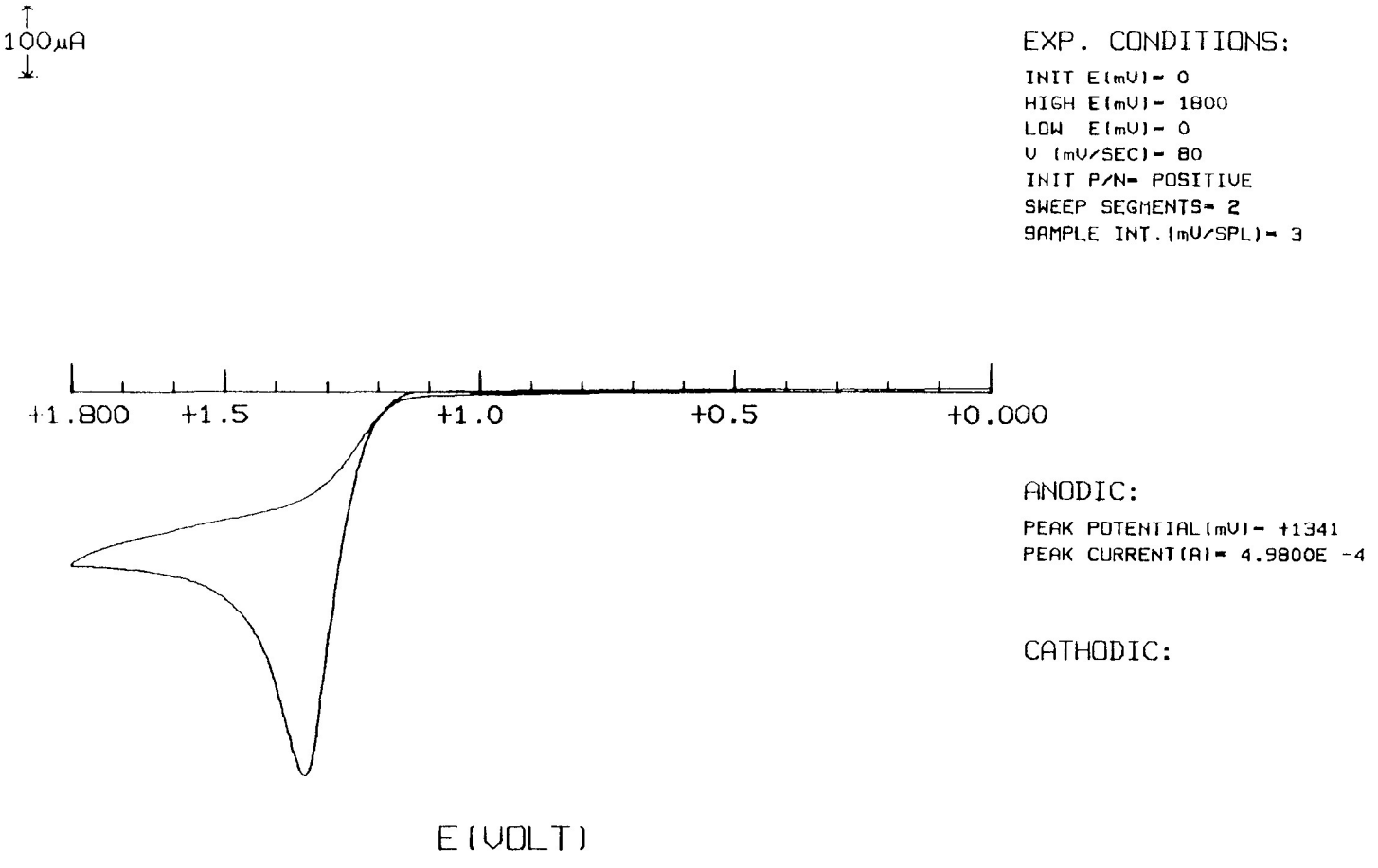

Figure 6. Cyclic voltammogram of 1-decanethiol in acetonitrile using a carbon electrode.

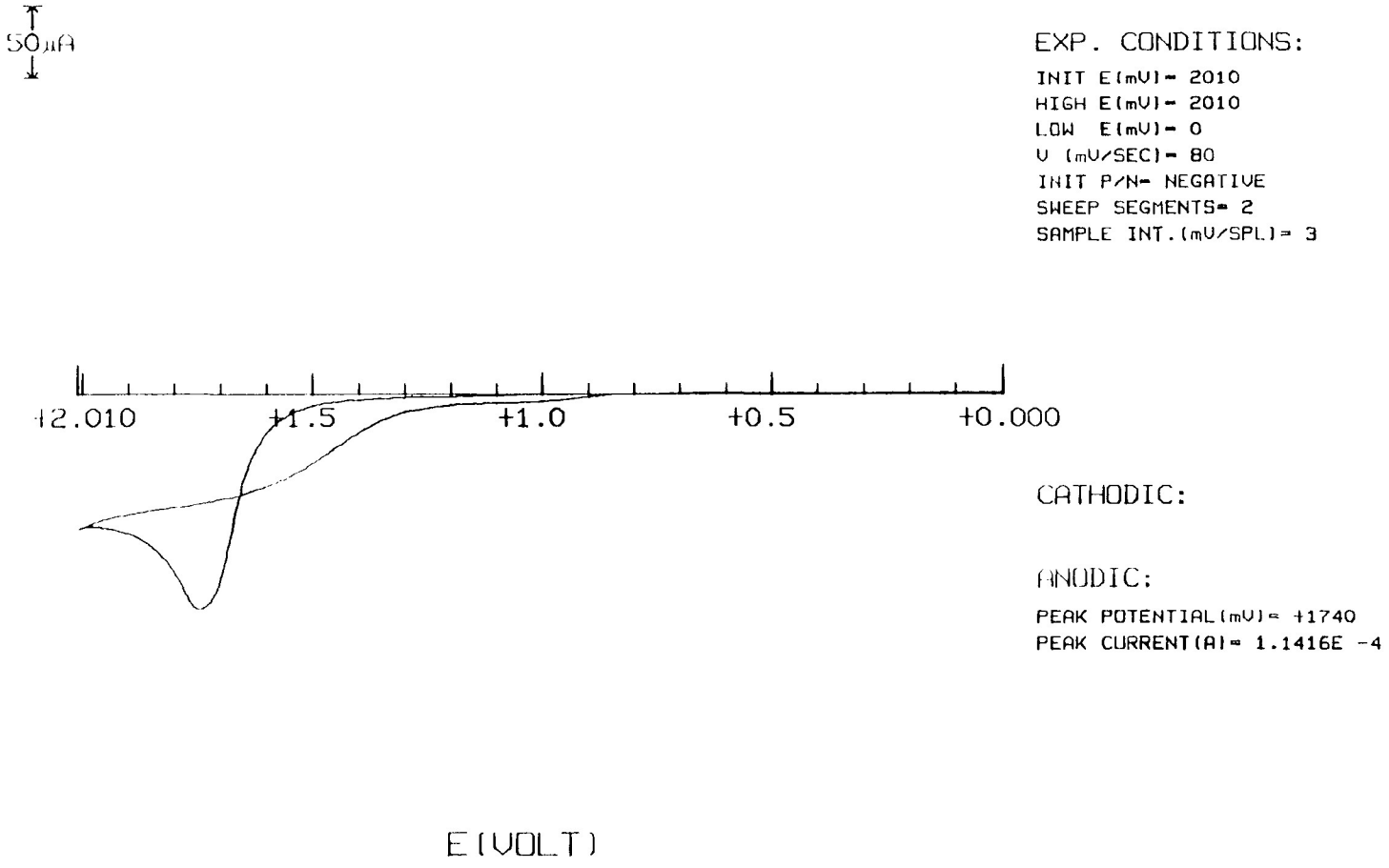

Figure 7. Cyclic voltammogram of 1-decanethiol in acetonitrile using a platinum electrode.

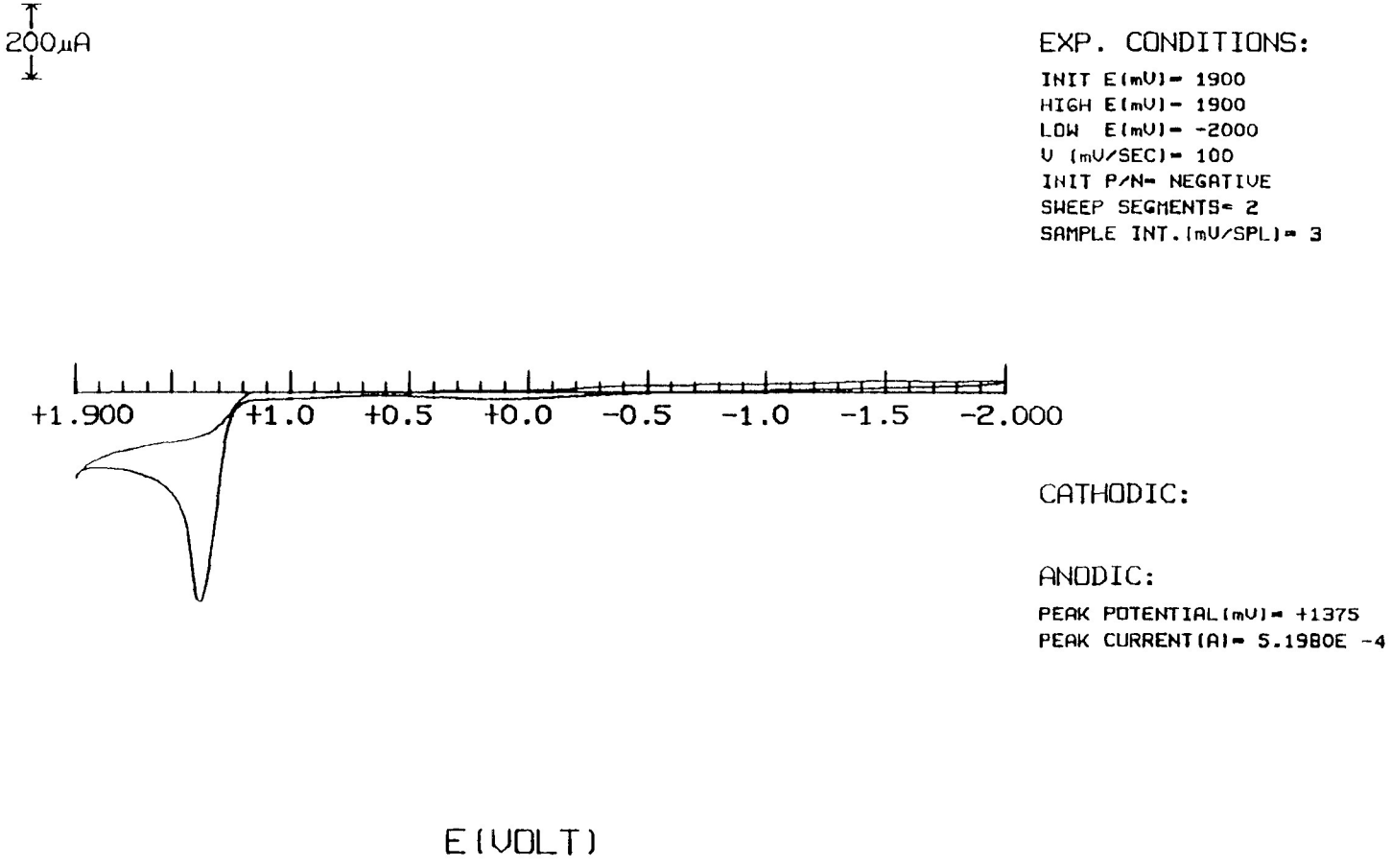

Figure 8. Cyclic voltammogram of 1-dodecanethiol in acetonitrile using a carbon electrode.

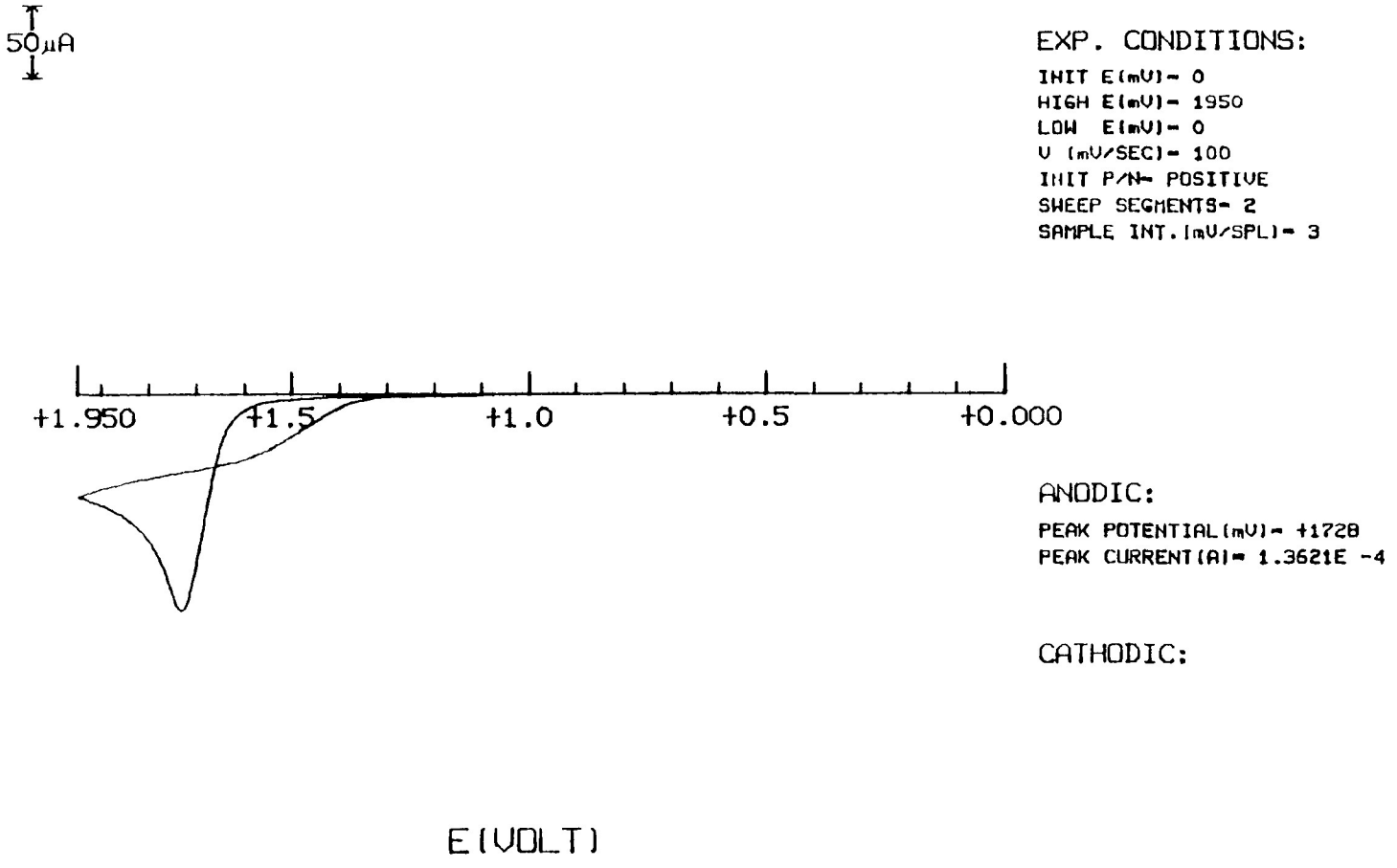

Figure 9. Cyclic voltammogram of 1-dodecanethiol in acetonitrile using a platinum electrode.

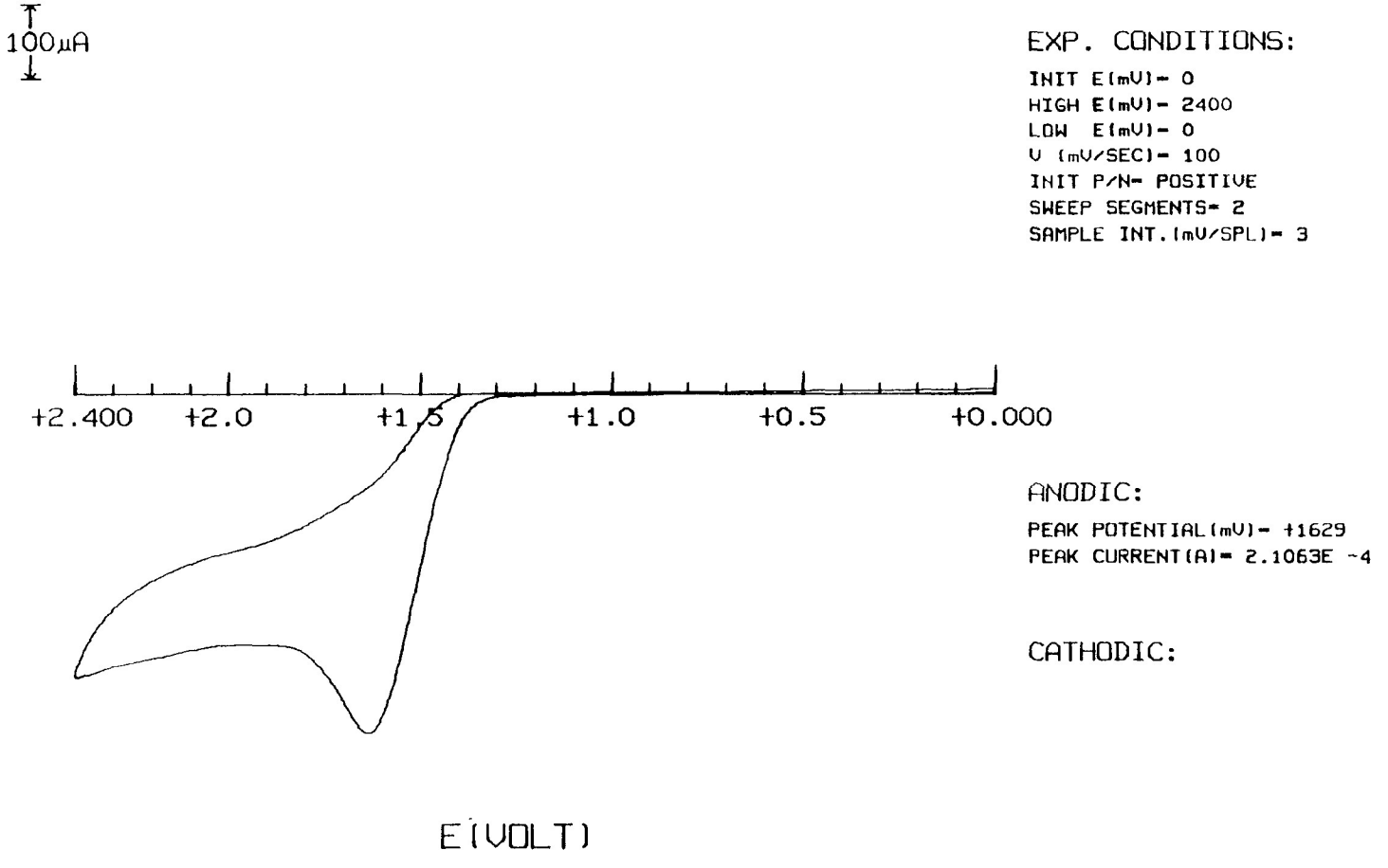

Figure 10. Cyclic voltammogram of phenyl sulfide in acetonitrile using a carbon electrode.

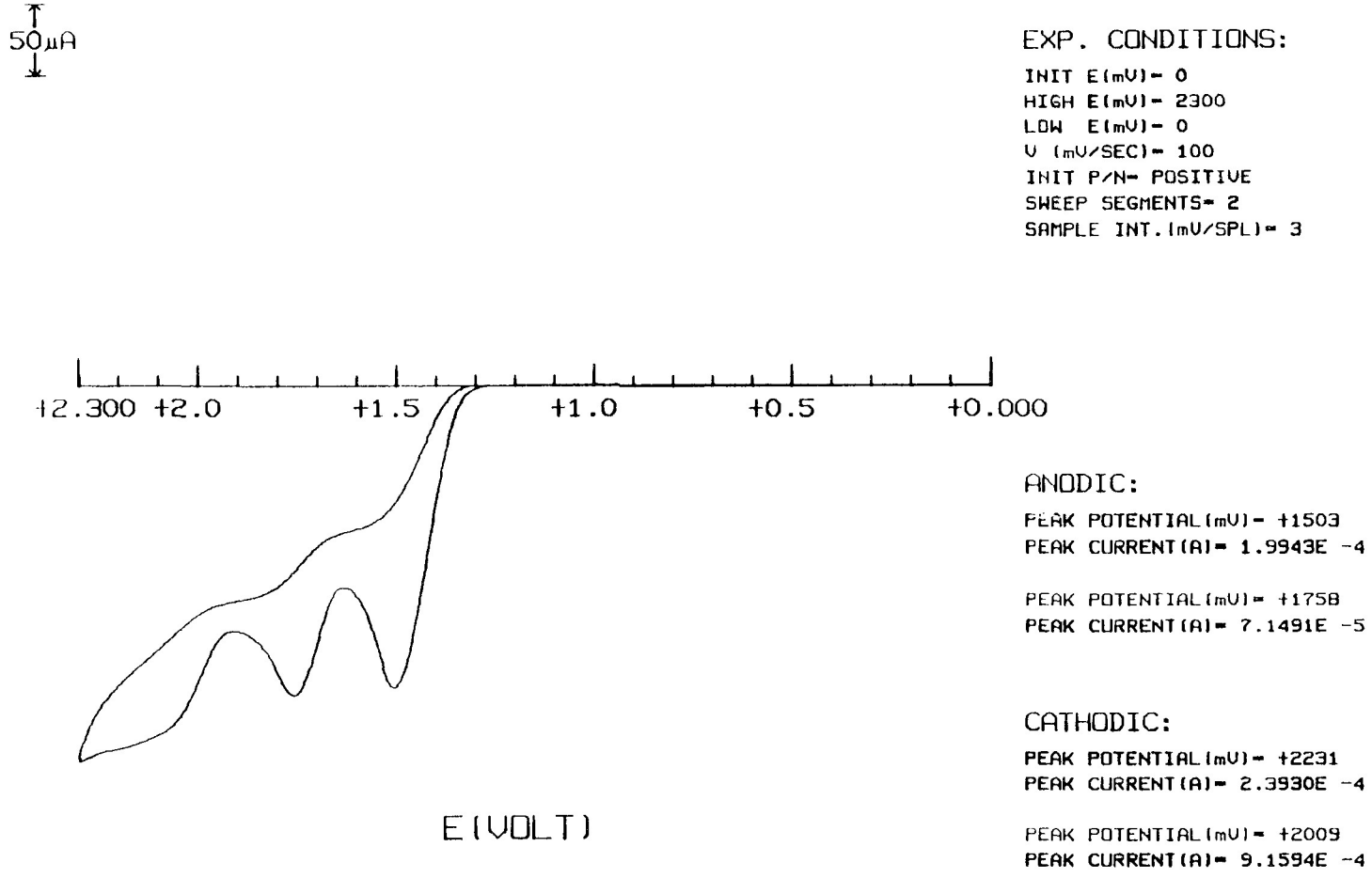

Figure 11. Cyclic voltammogram of phenyl sulfide in acetonitrile using a platinum electrode.

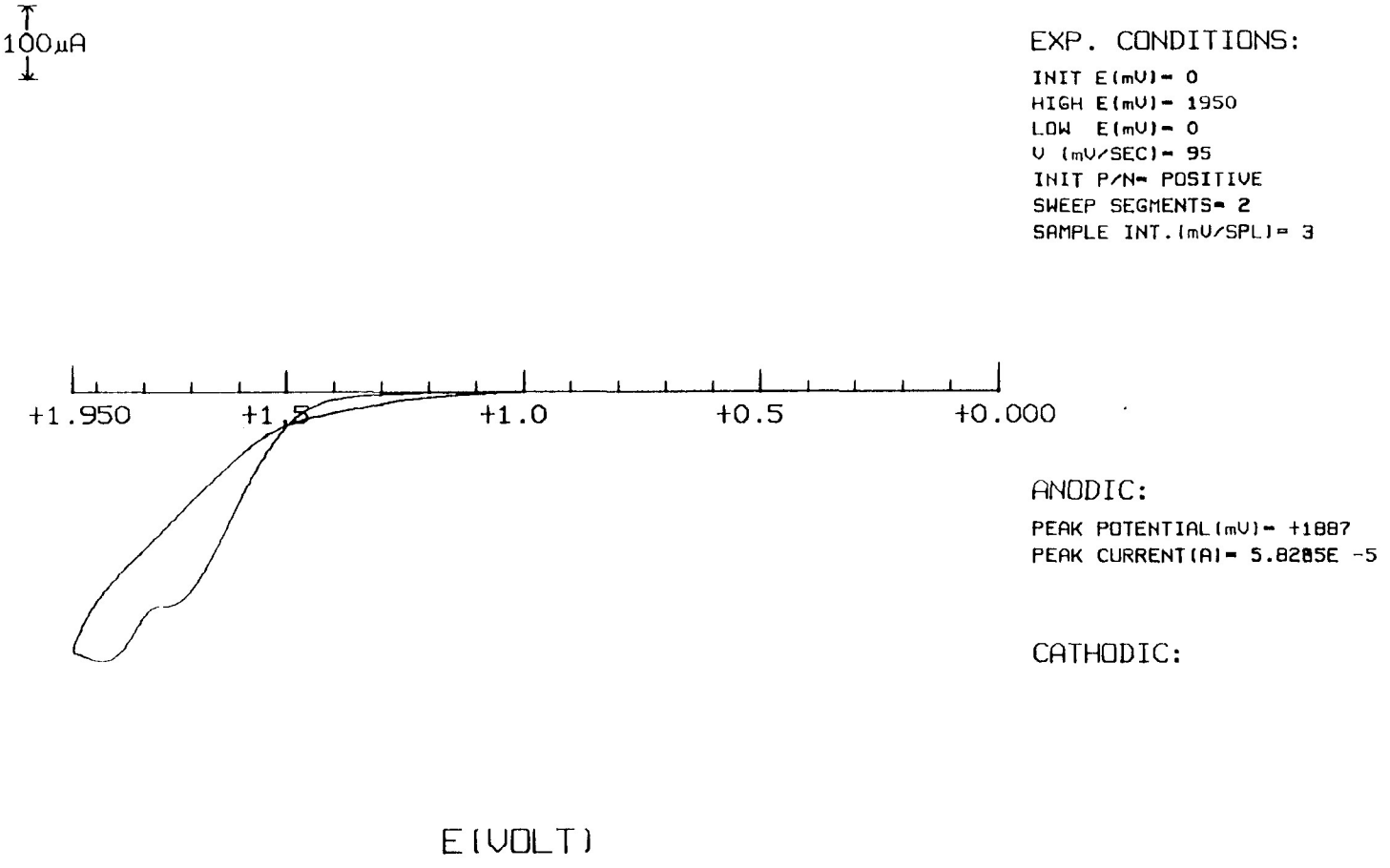

Figure 12. Cyclic voltammogram of t-butyl sulfide in acetonitrile using a carbon electrode.

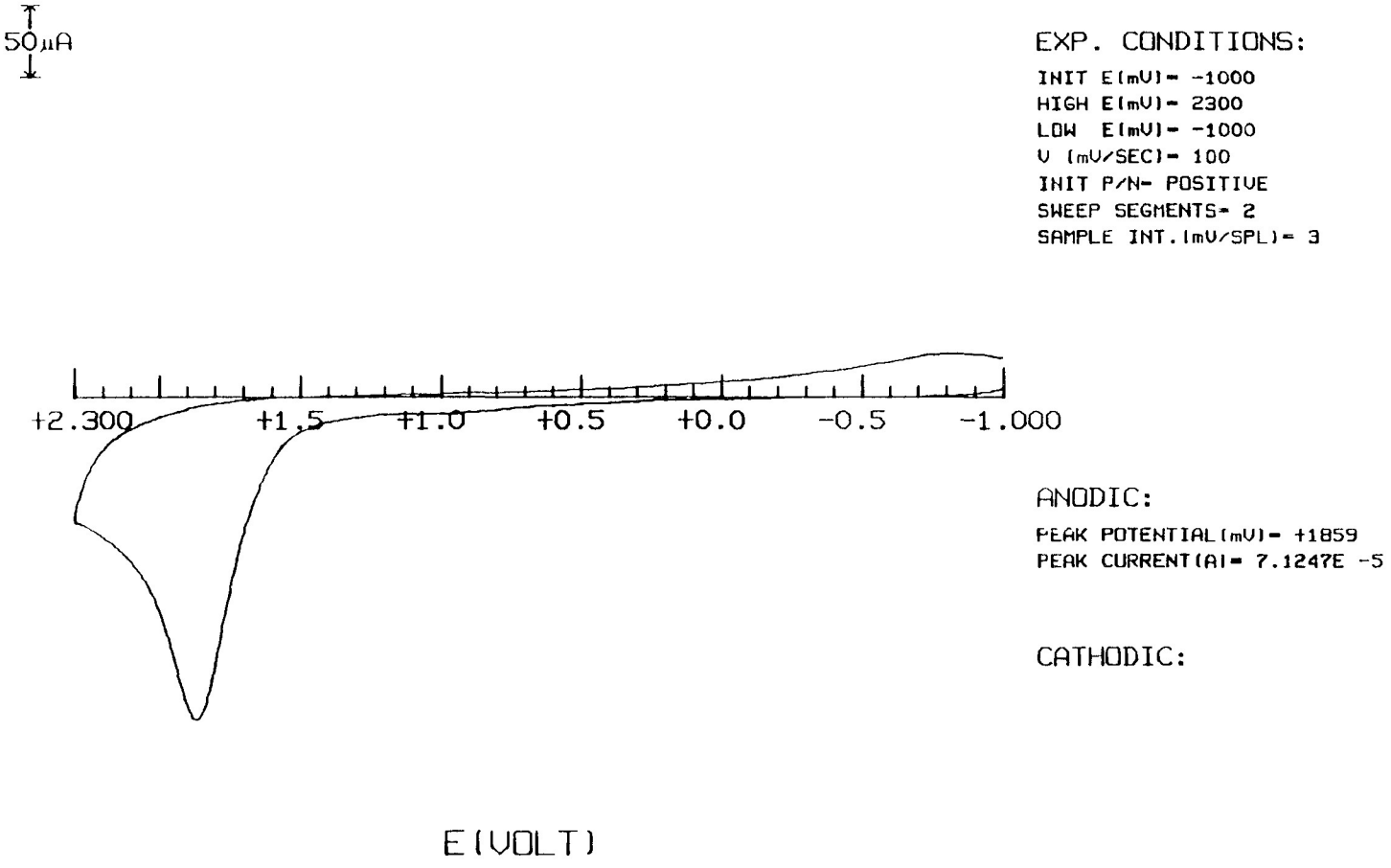

Figure 13. Cyclic voltammogram of thiophene in acetonitrile using a carbon electrode.

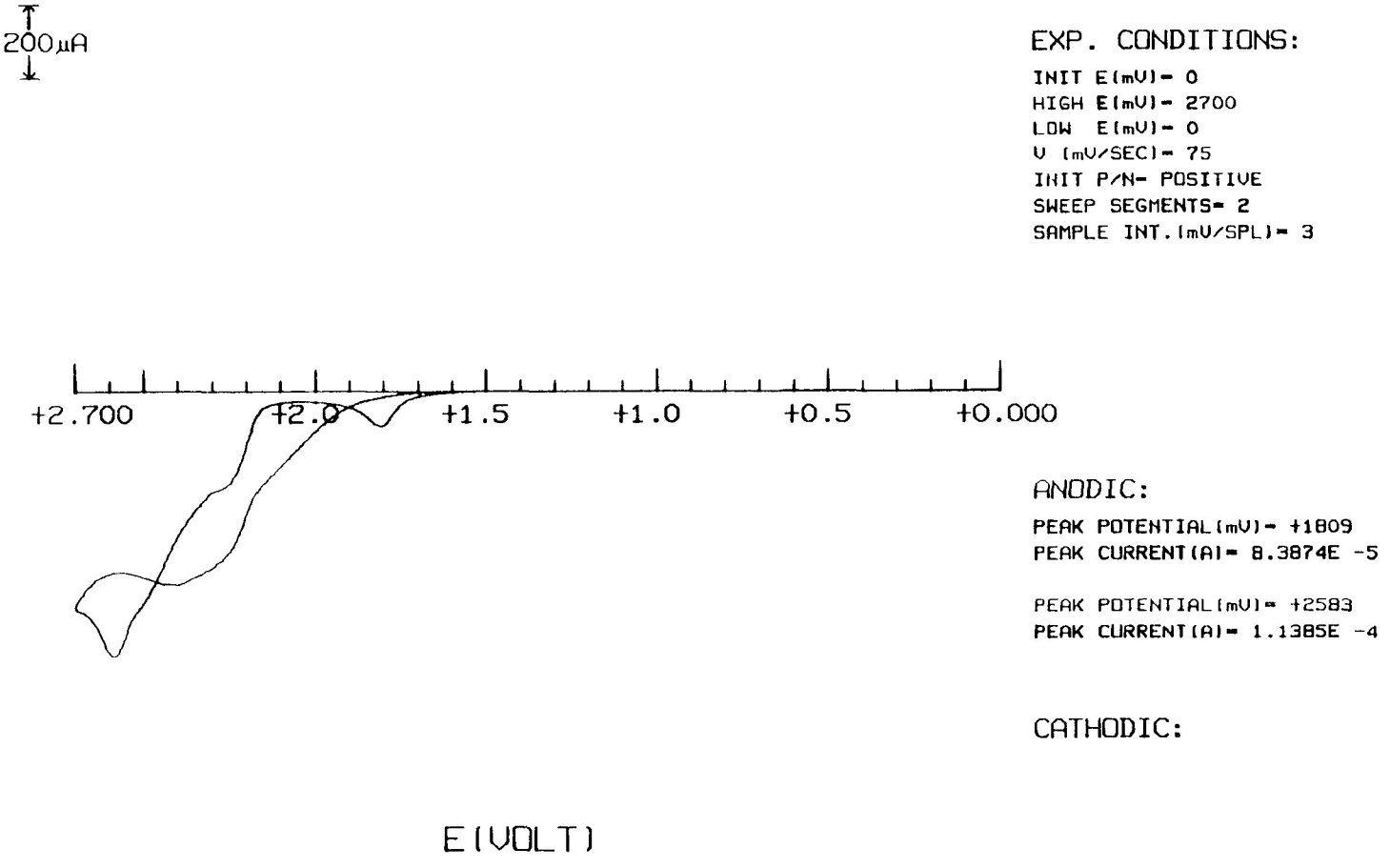

Figure 14. Cyclic voltammogram of thiophene in acetonitrile using a platinum electrode.

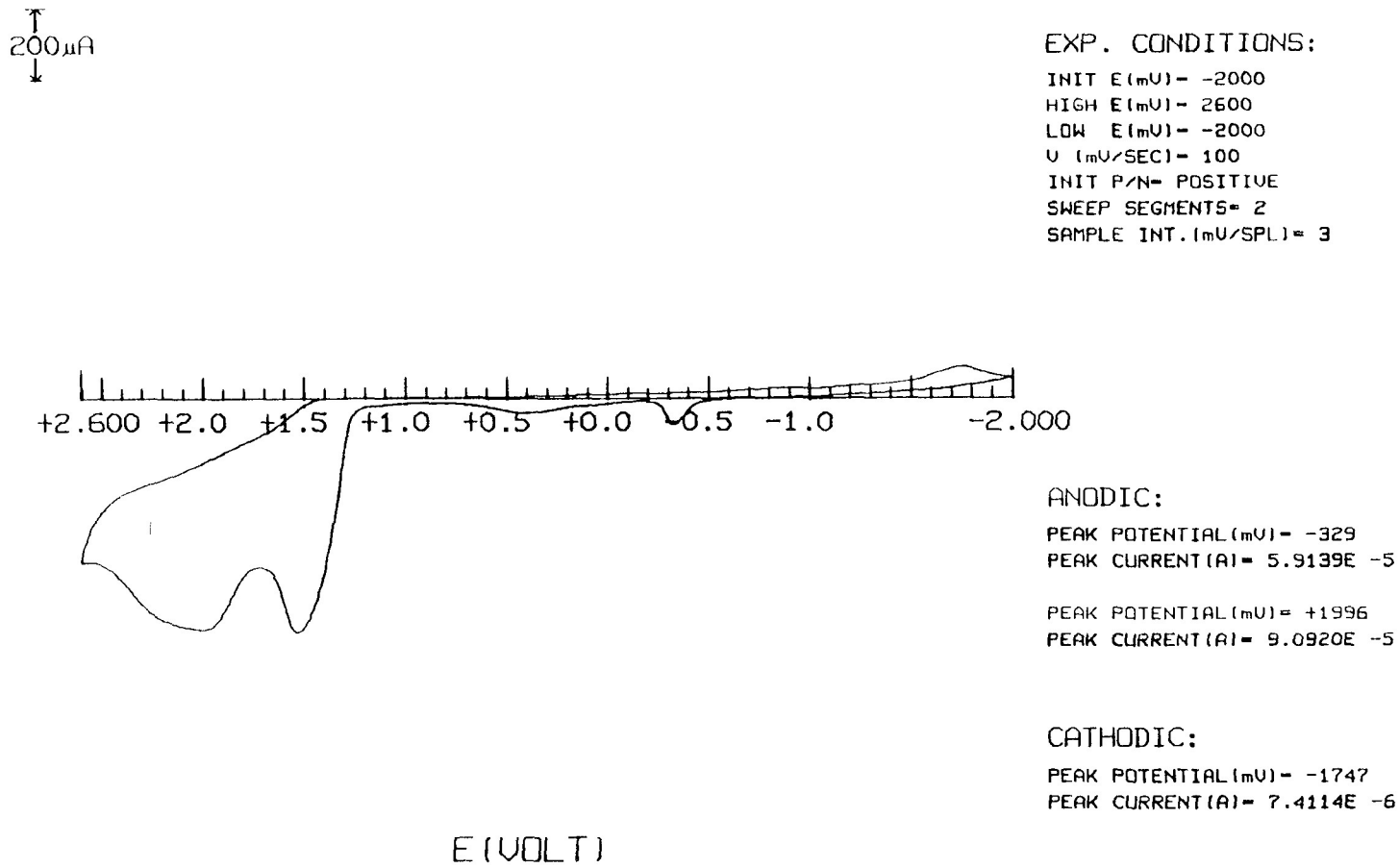

Figure 15. Cyclic voltammogram of benzyl phenyl sulfide in acetonitrile using a carbon electrode.

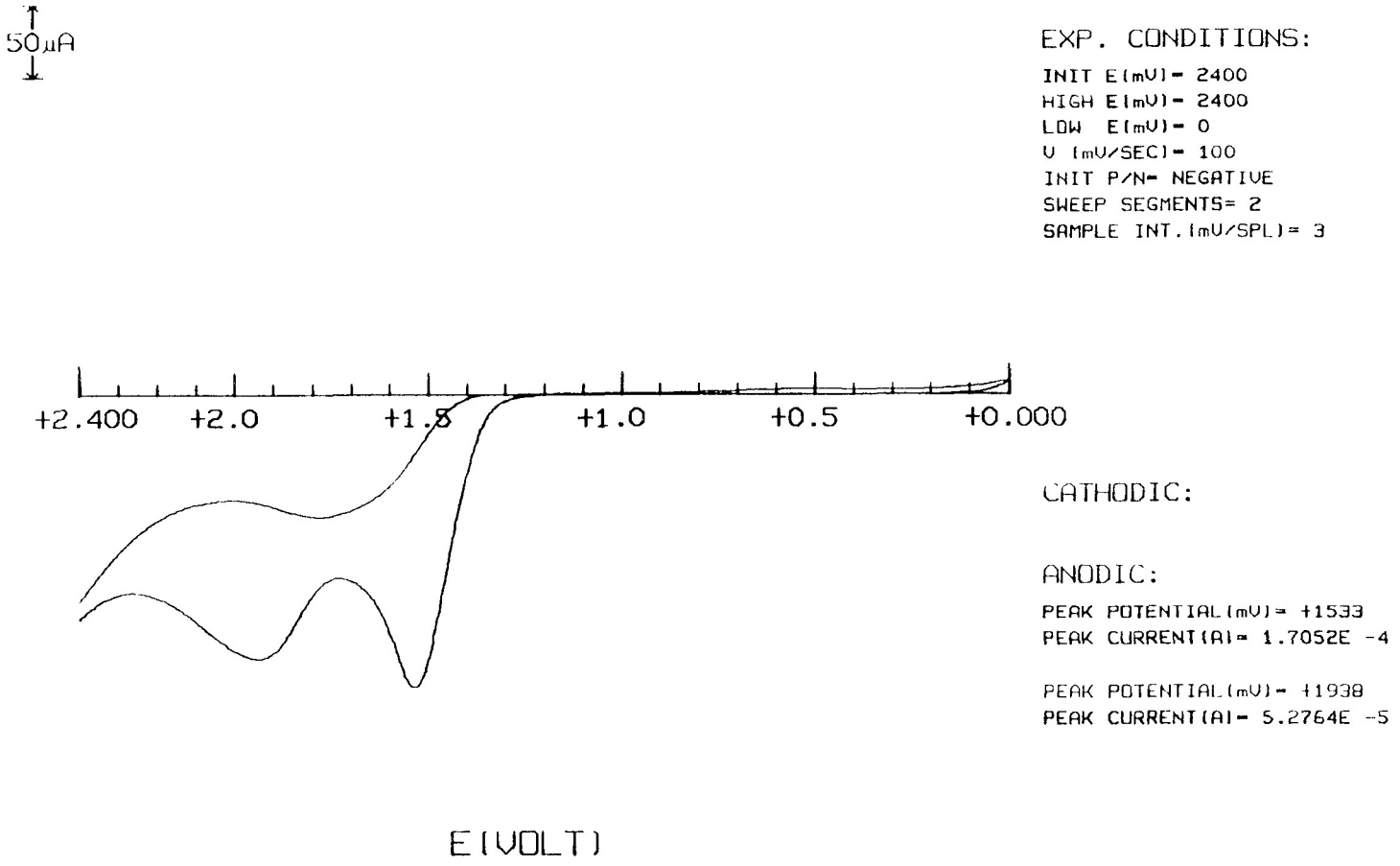

Figure 16. Cyclic voltammogram of benzyl phenyl sulfide in acetonitrile using a platinum electrode.

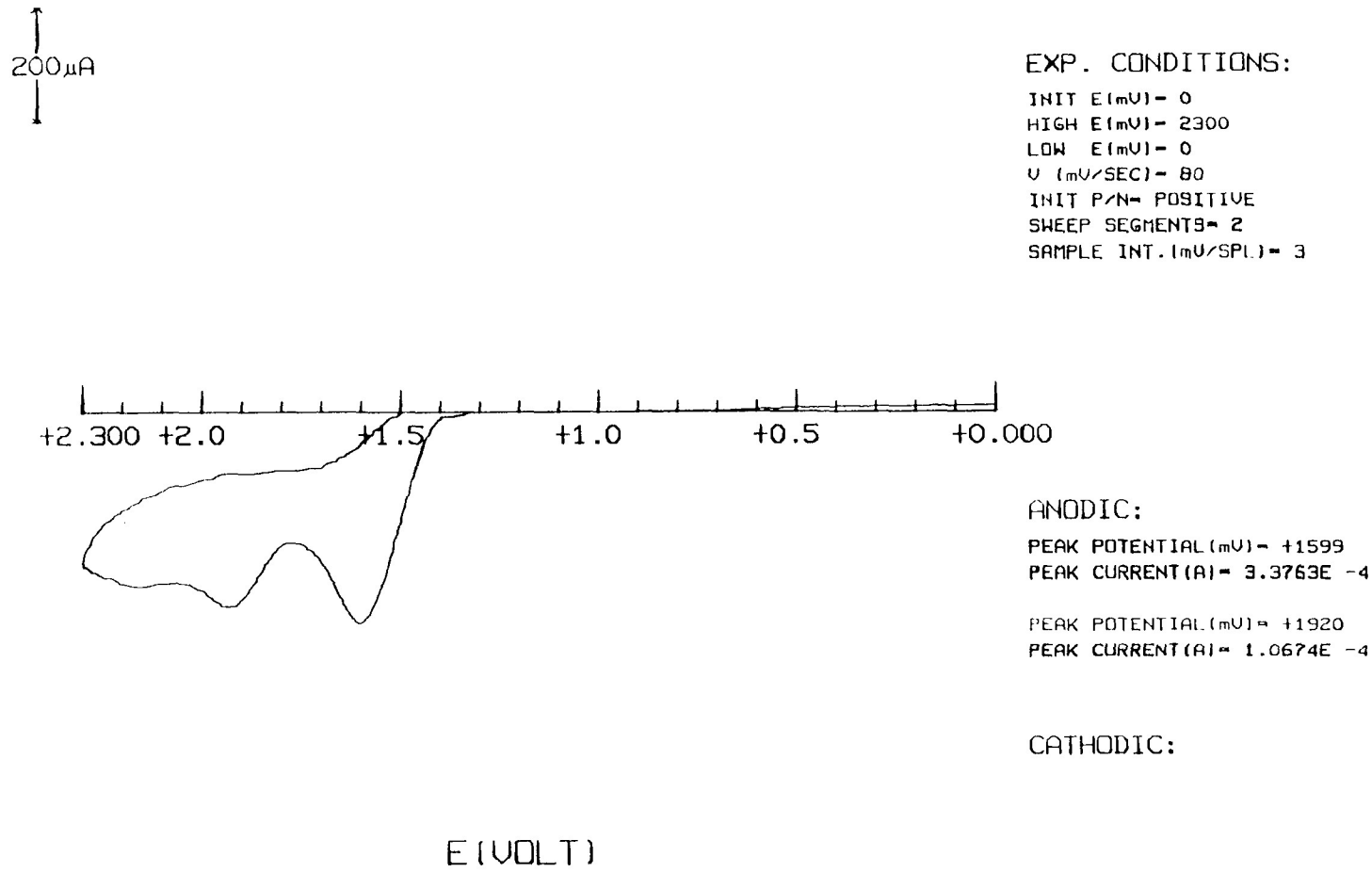

Figure 17. Cyclic voltammogram of dibenzothiophene in acetonitrile using a carbon electrode.

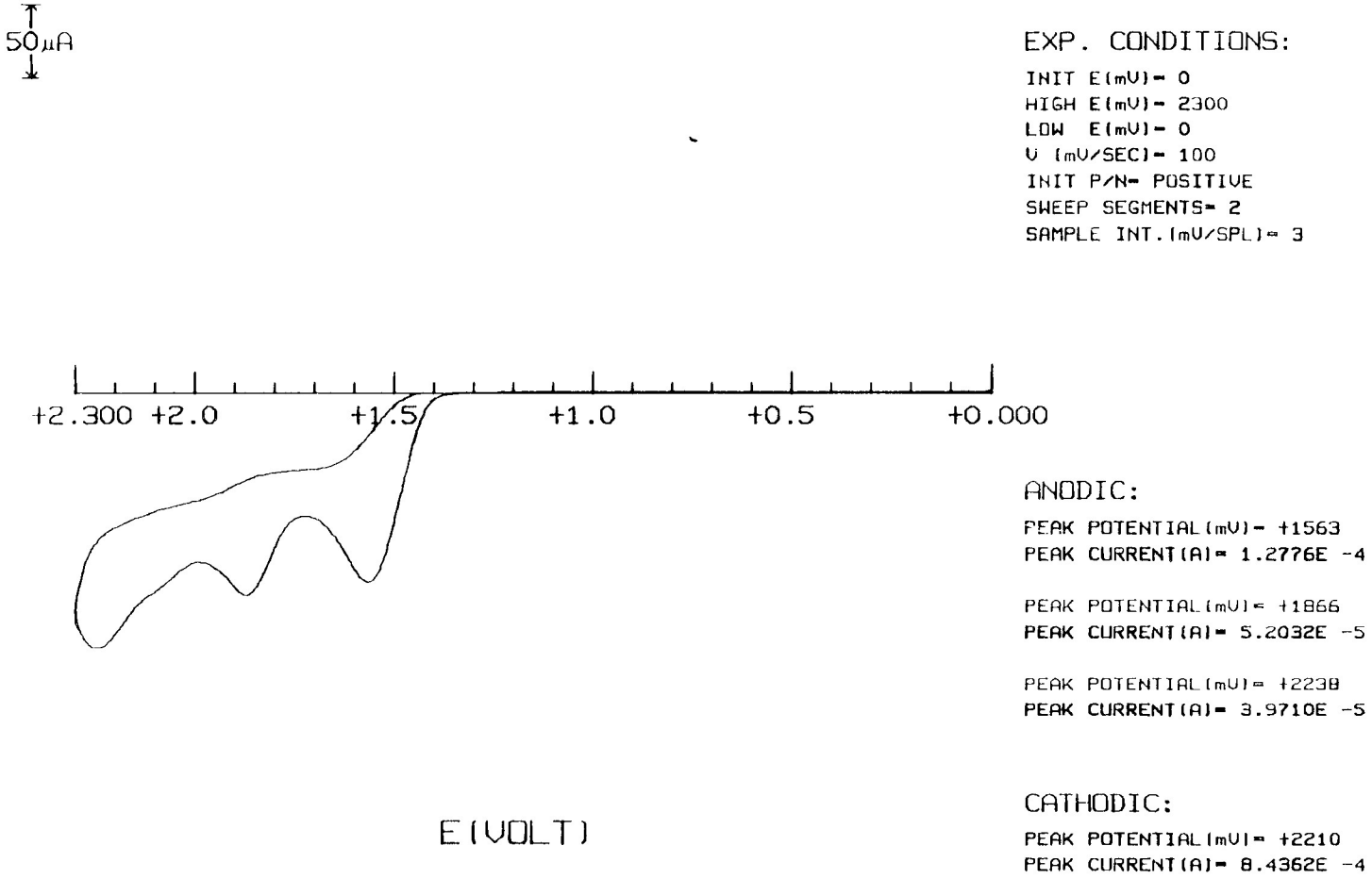

Figure 18. Cyclic voltammogram of dibenzothiophene in acetonitrile using a platinum electrode.

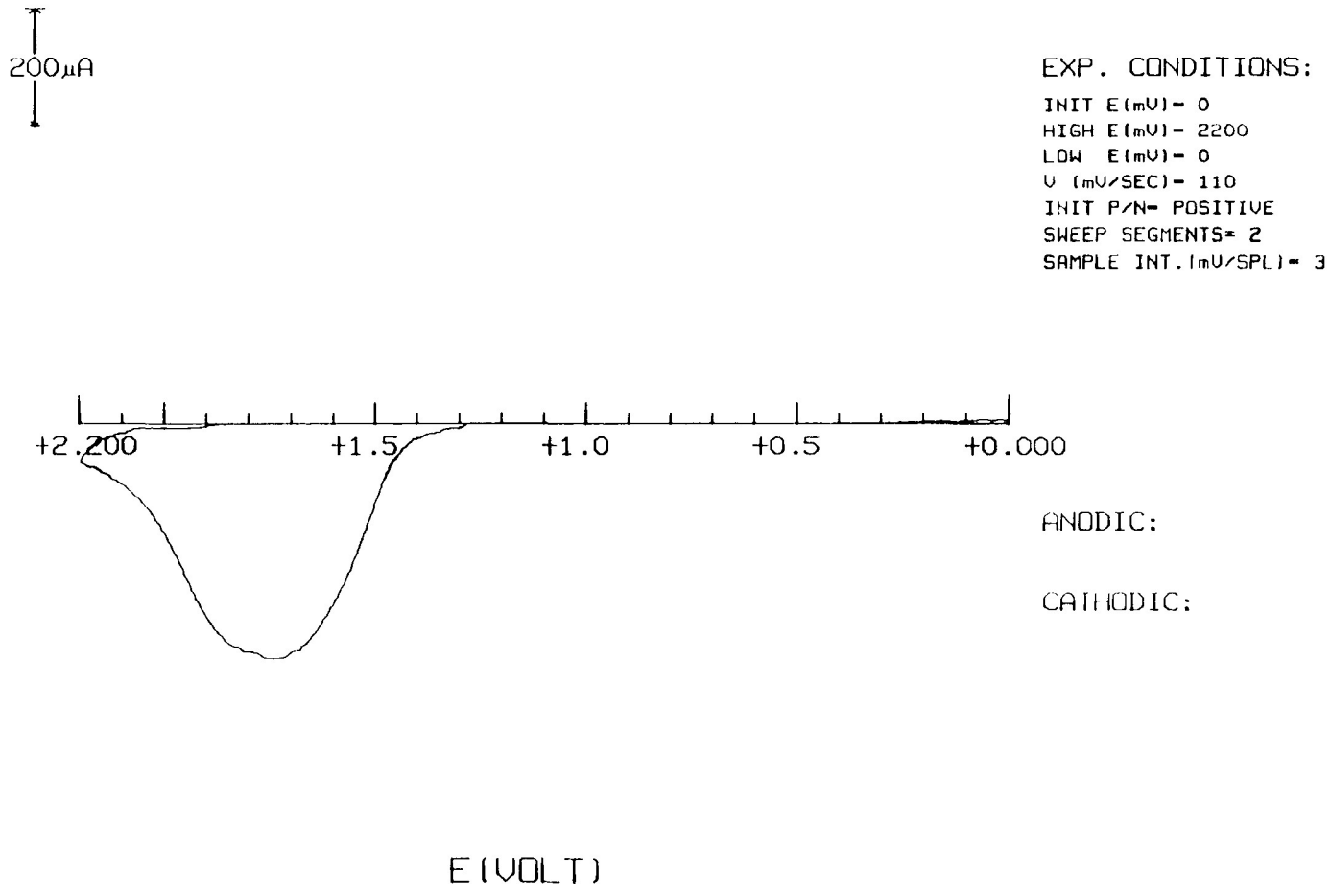

Figure 19. Cyclic voltammogram of thionaphthene in acetonitrile using a carbon electrode.

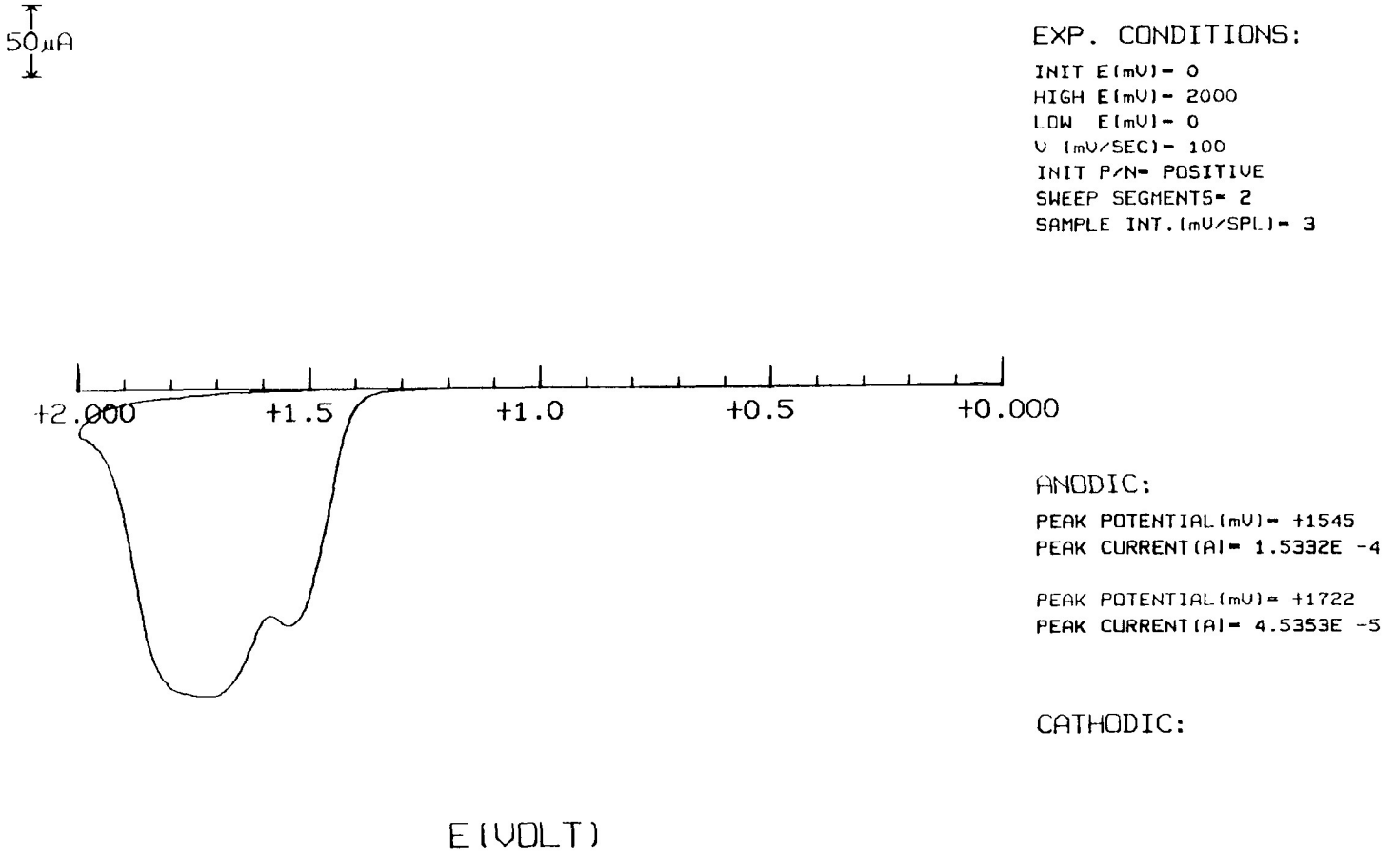

Figure 20. Cyclic voltammogram of thionaphthene in acetonitrile using a platinum electrode.

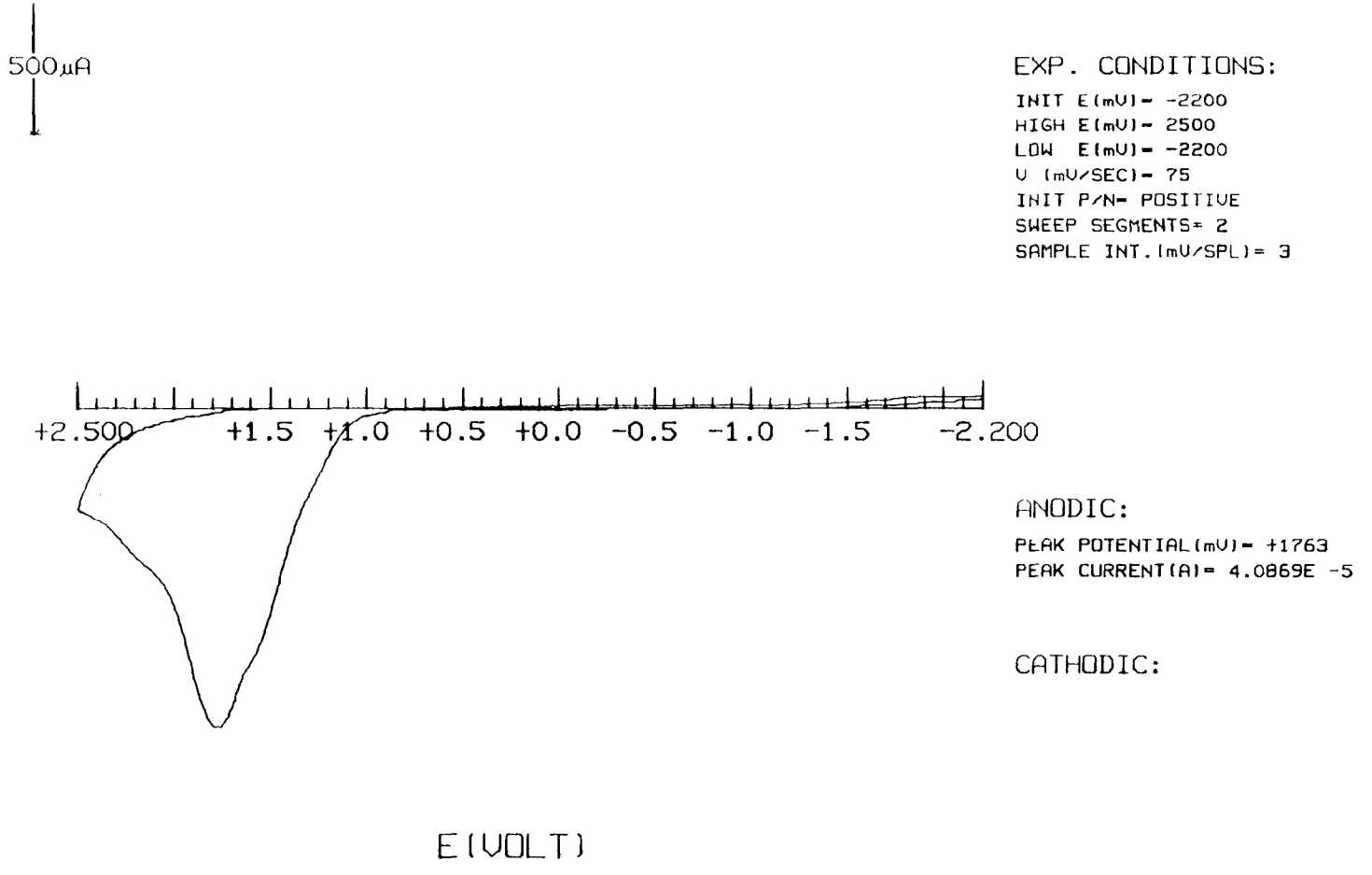

Figure 21. Cyclic voltammogram of thiophenol in acetonitrile using a carbon electrode.

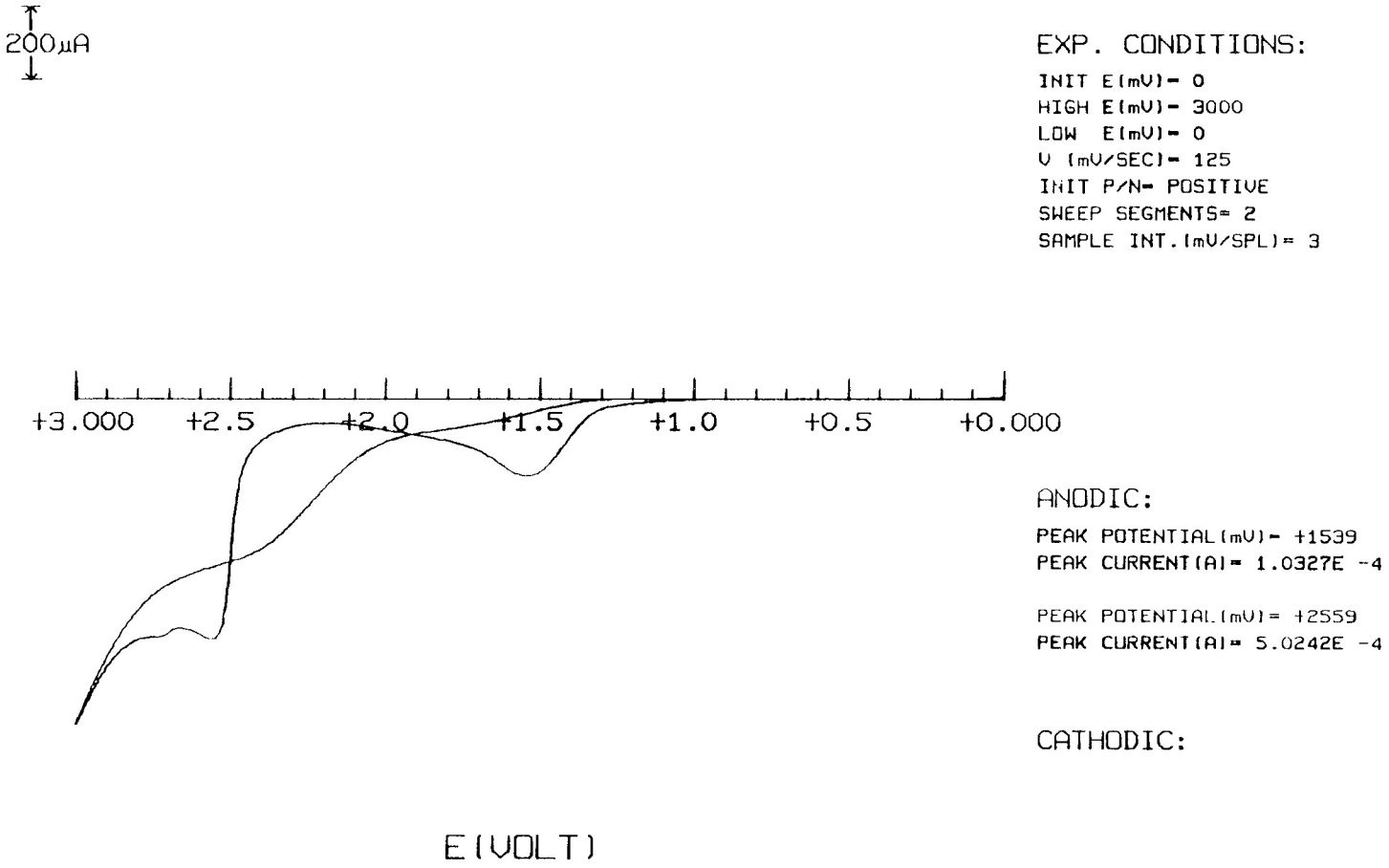

Figure 22. Cyclic voltammogram of thiophenol in acetonitrile using a platinum electrode.

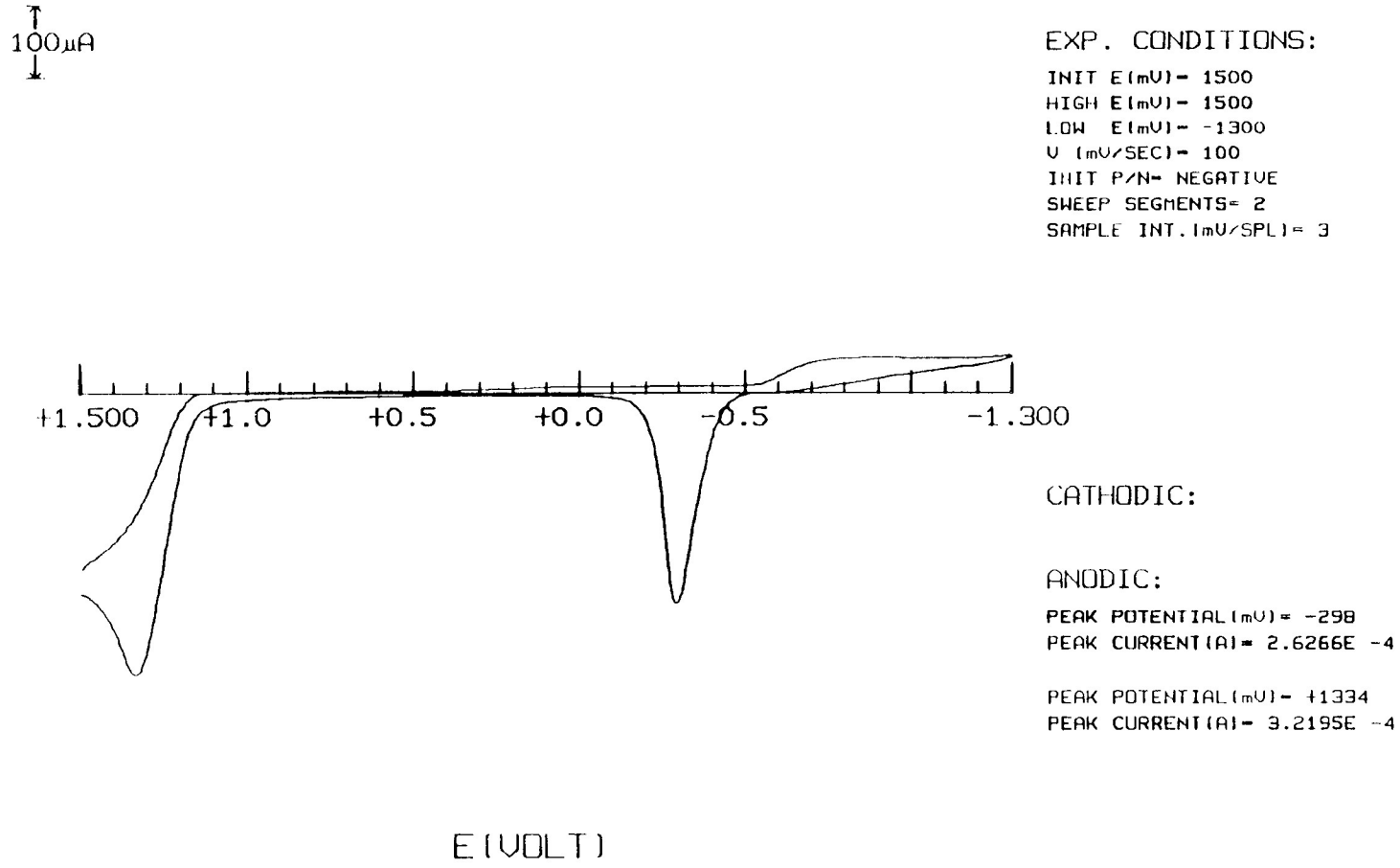

Figure 23. Cyclic voltammogram of butyl disulfide in acetonitrile using a carbon electrode.

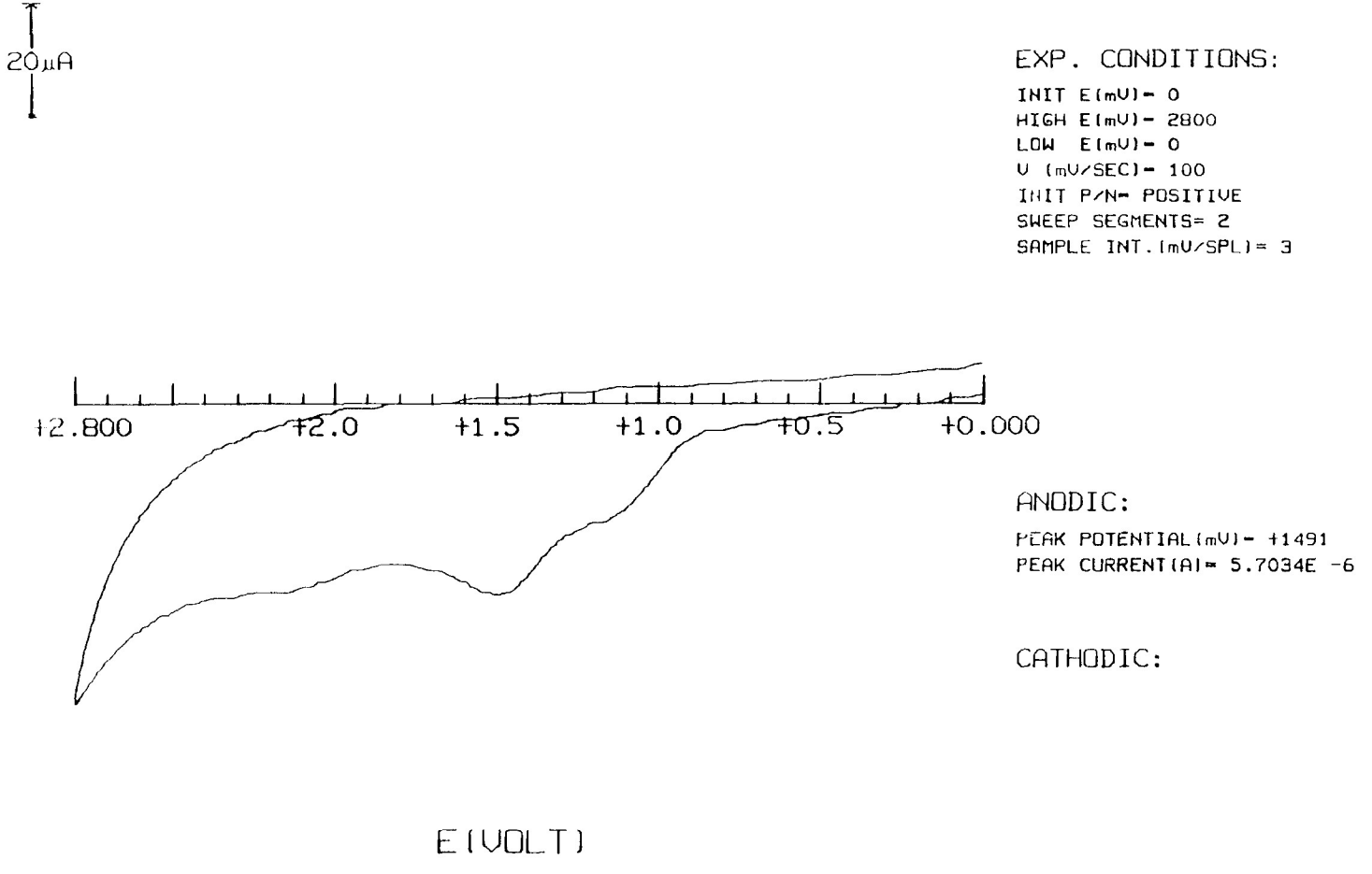

Figure 24. Cyclic voltammogram of benzothiazole in acetonitrile using a carbon electrode.

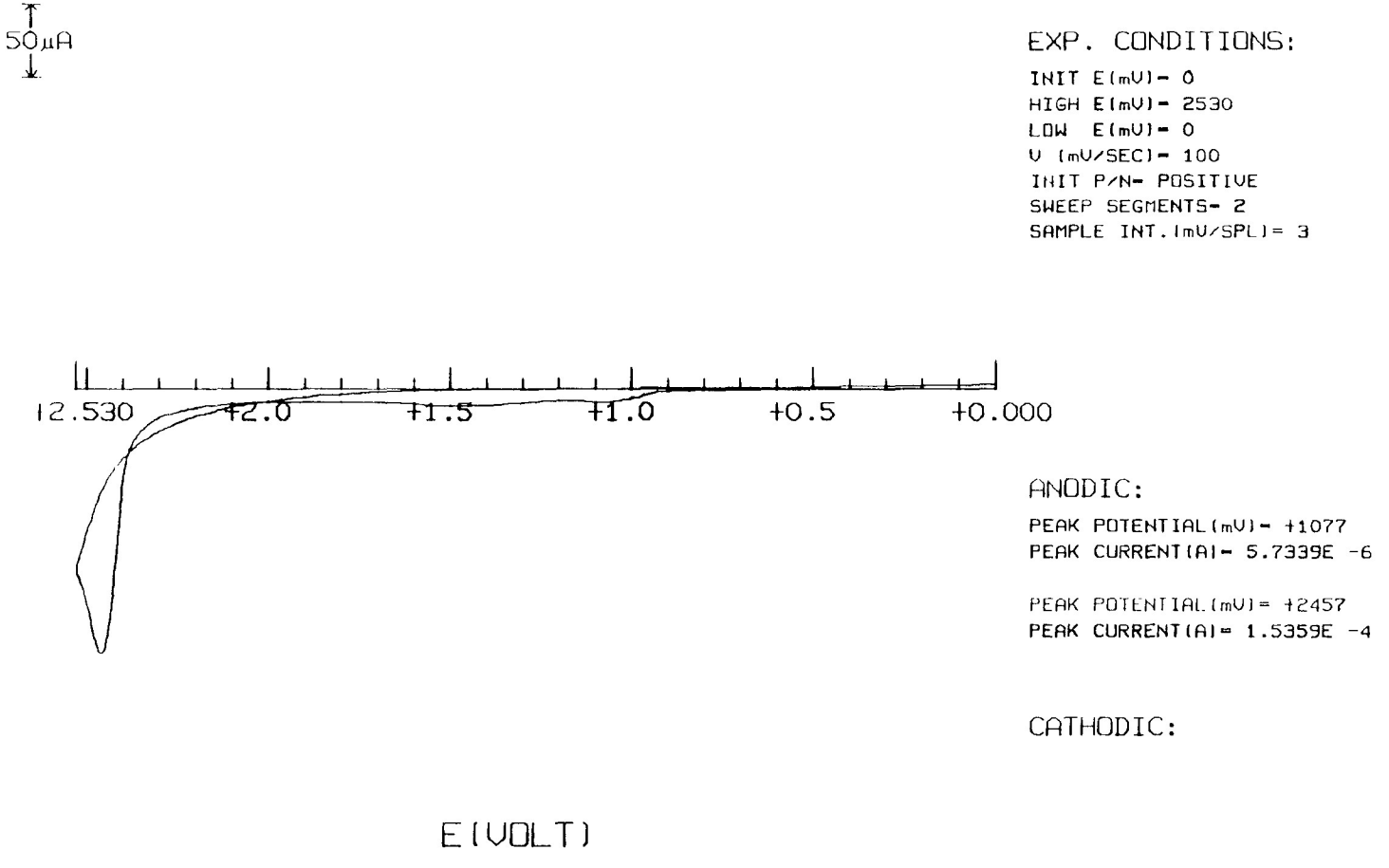

Figure 25. Cyclic voltammogram of benzothiazole in acetonitrile using a platinum electrode.

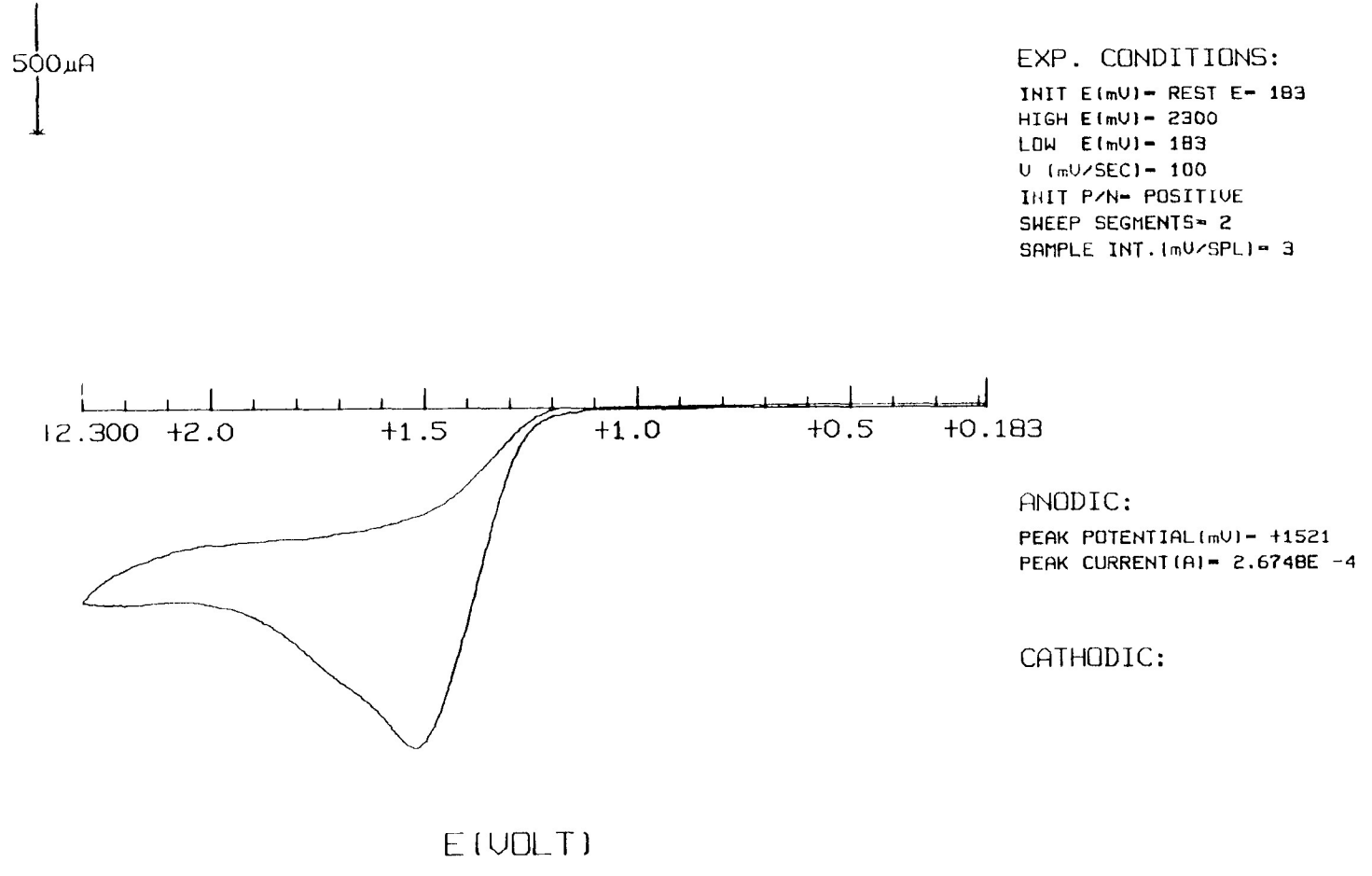

Figure 26. Cyclic voltammogram of 2-mercaptoethanol in acetonitrile using a carbon electrode.

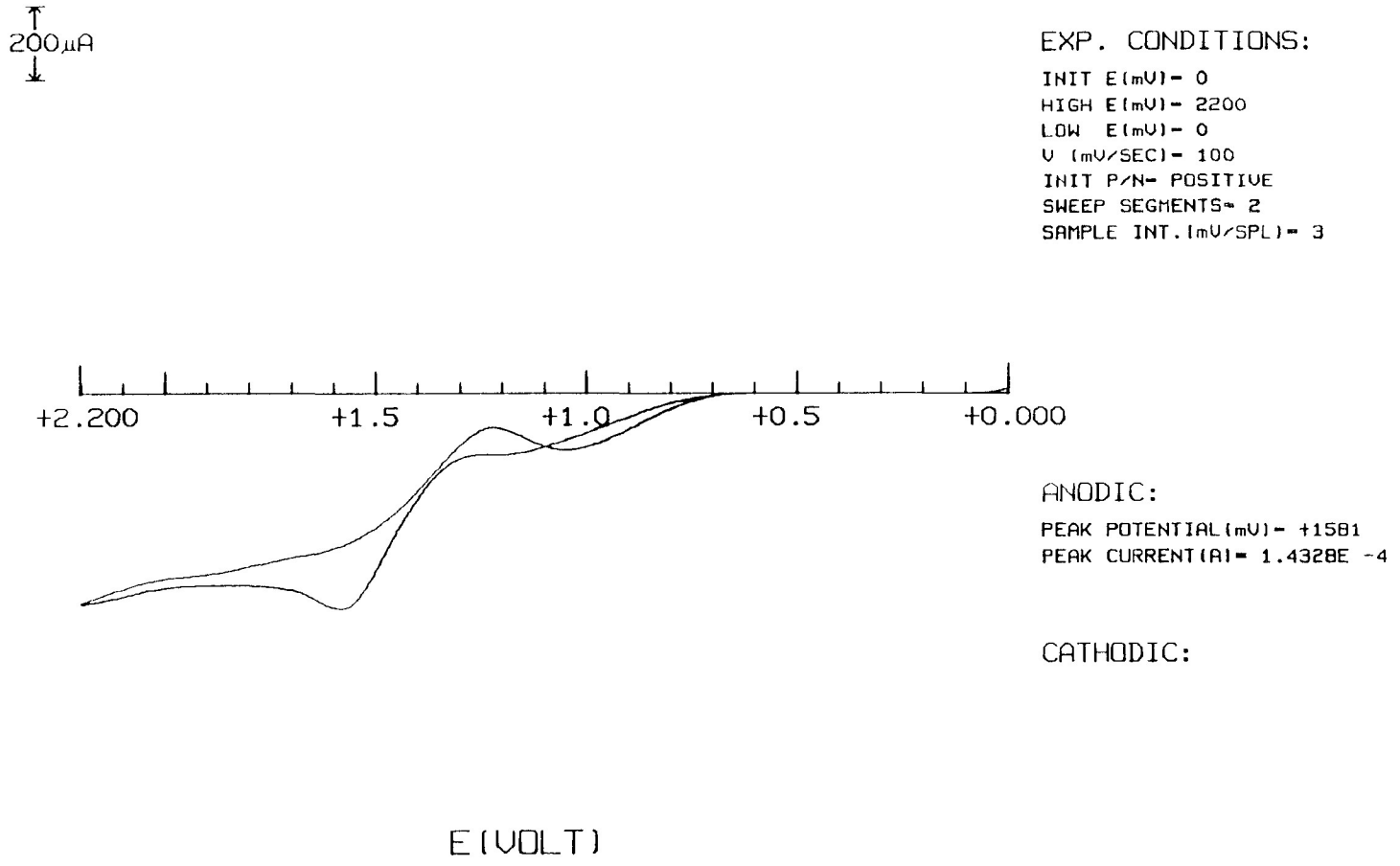

Figure 27. Cyclic voltammogram of 2-mercaptoethanol in acetonitrile using a platinum electrode.

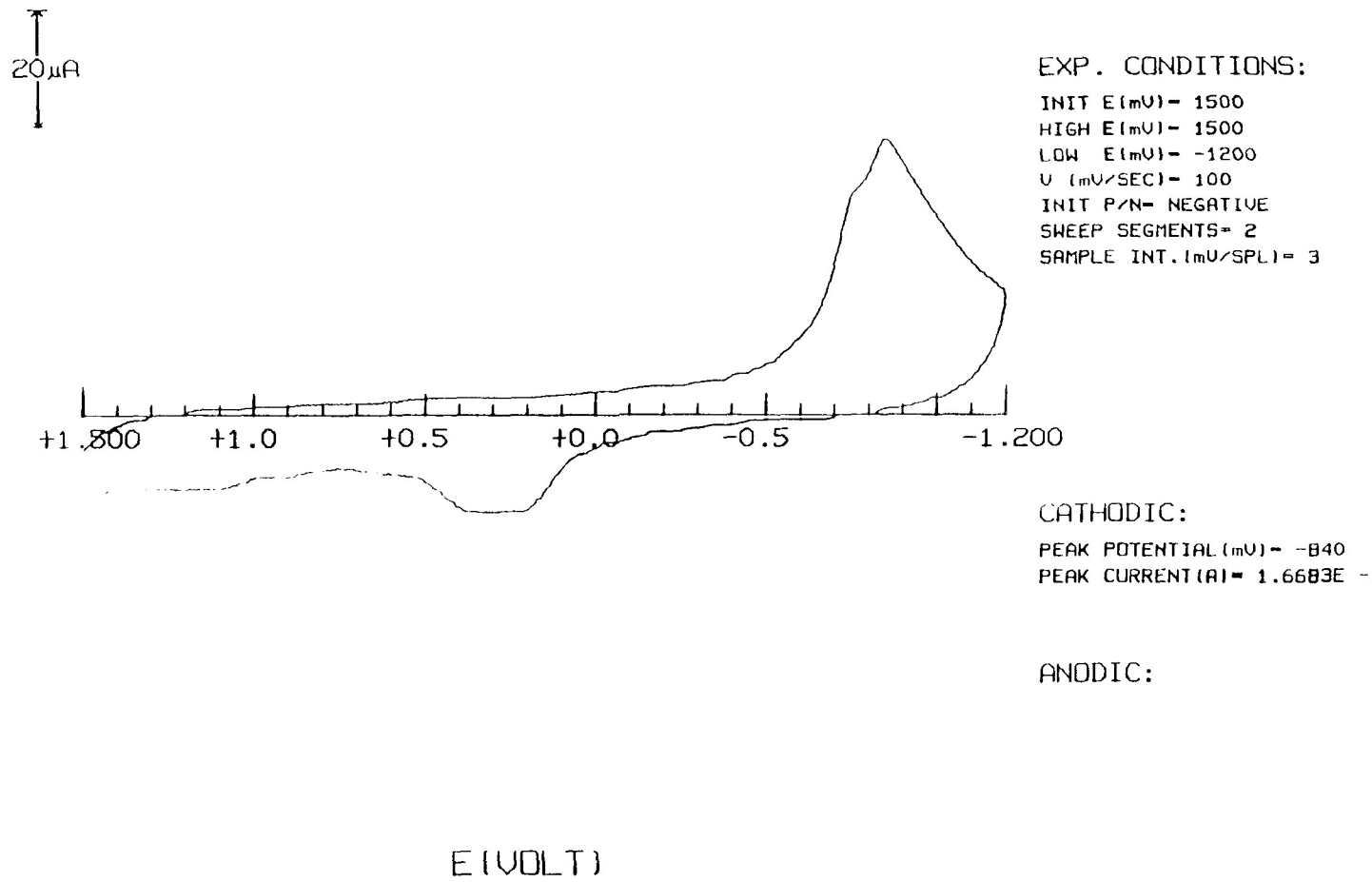

Figure 28. Cyclic voltammogram of 2-nitrothiophene in acetonitrile using a carbon electrode.

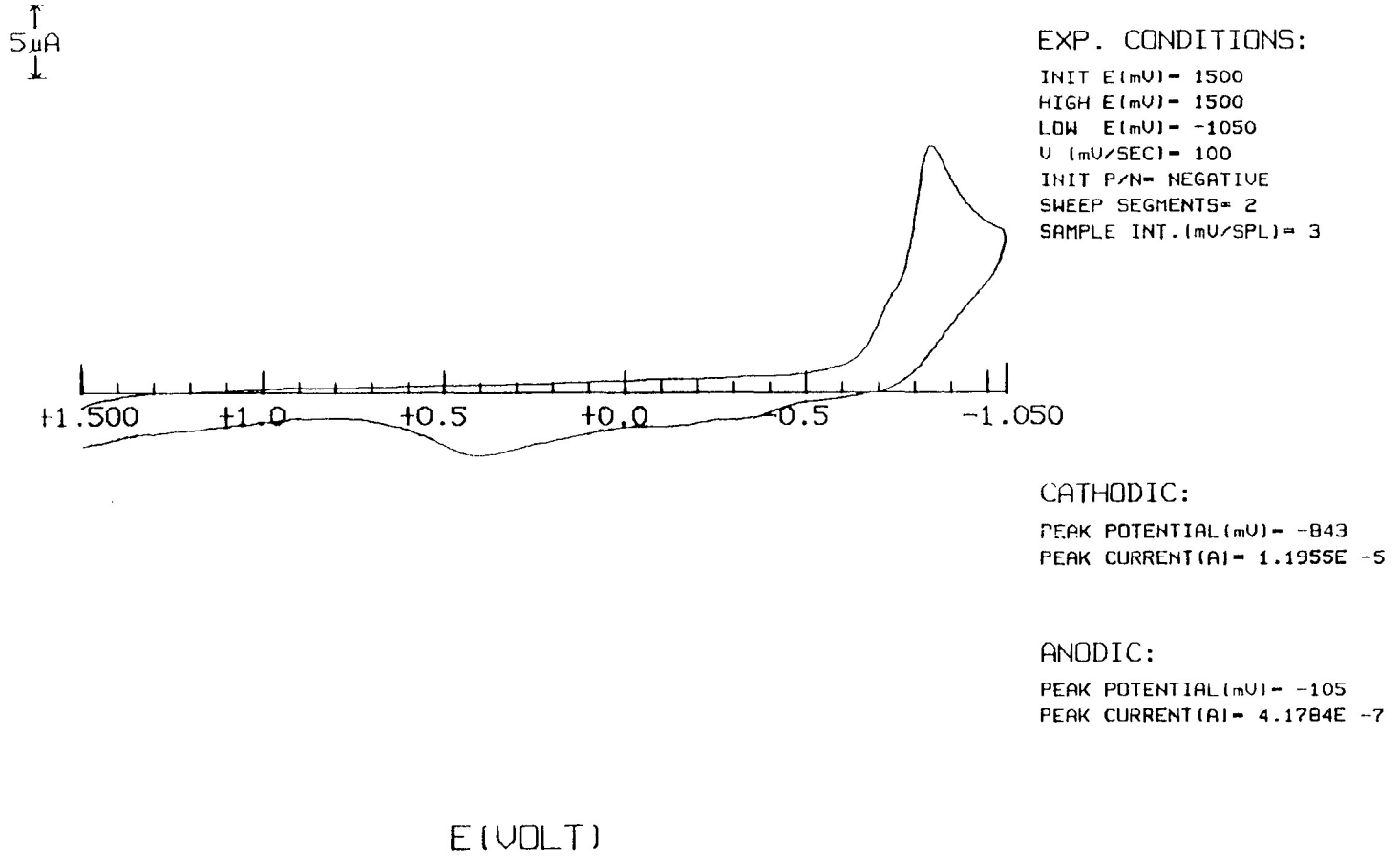

Figure 29. Cyclic voltammogram of 2-nitrothiophene in acetonitrile using a platinum electrode.

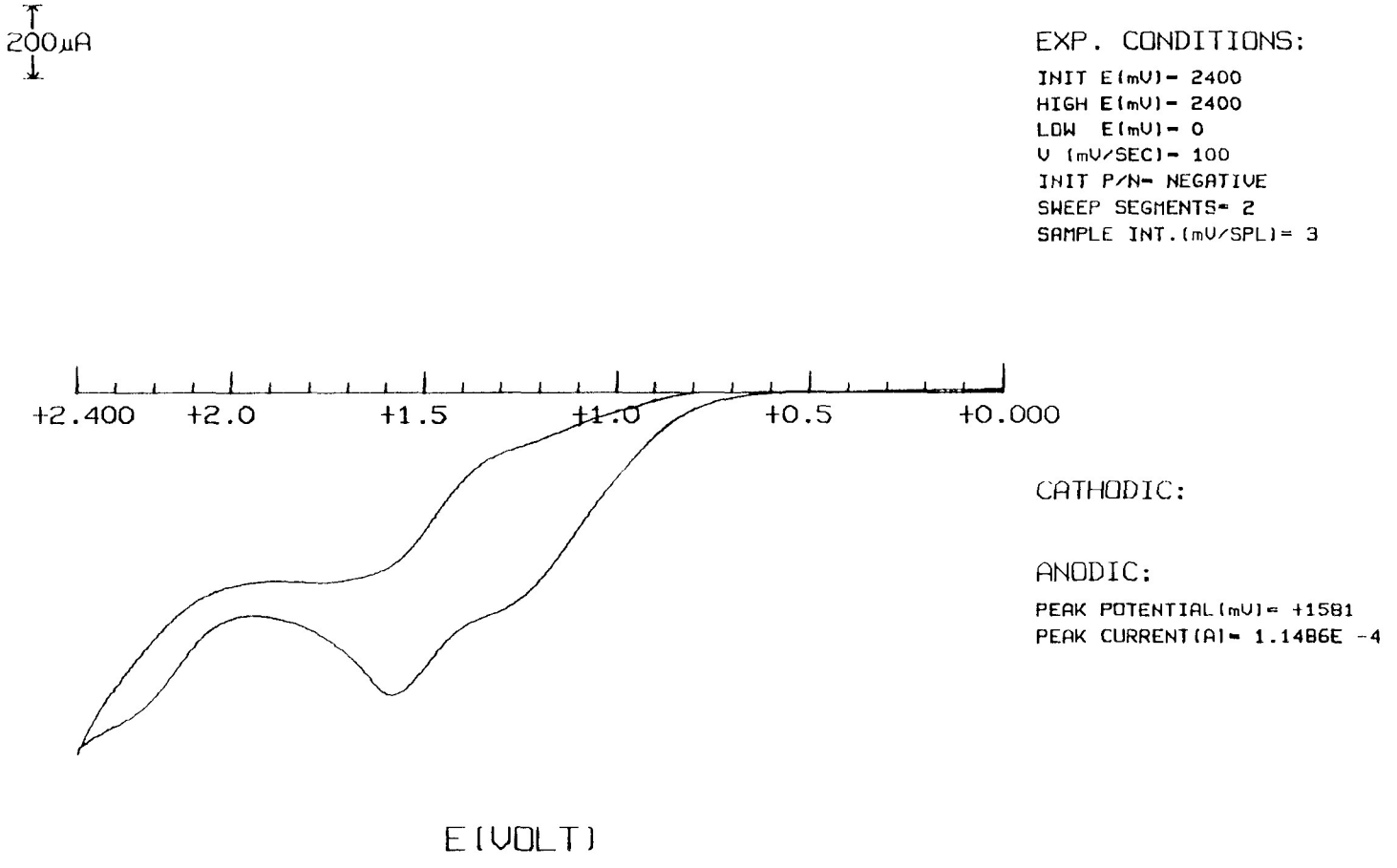

Figure 30. Cyclic voltammogram of thioacetamide in acetonitrile using a carbon electrode.

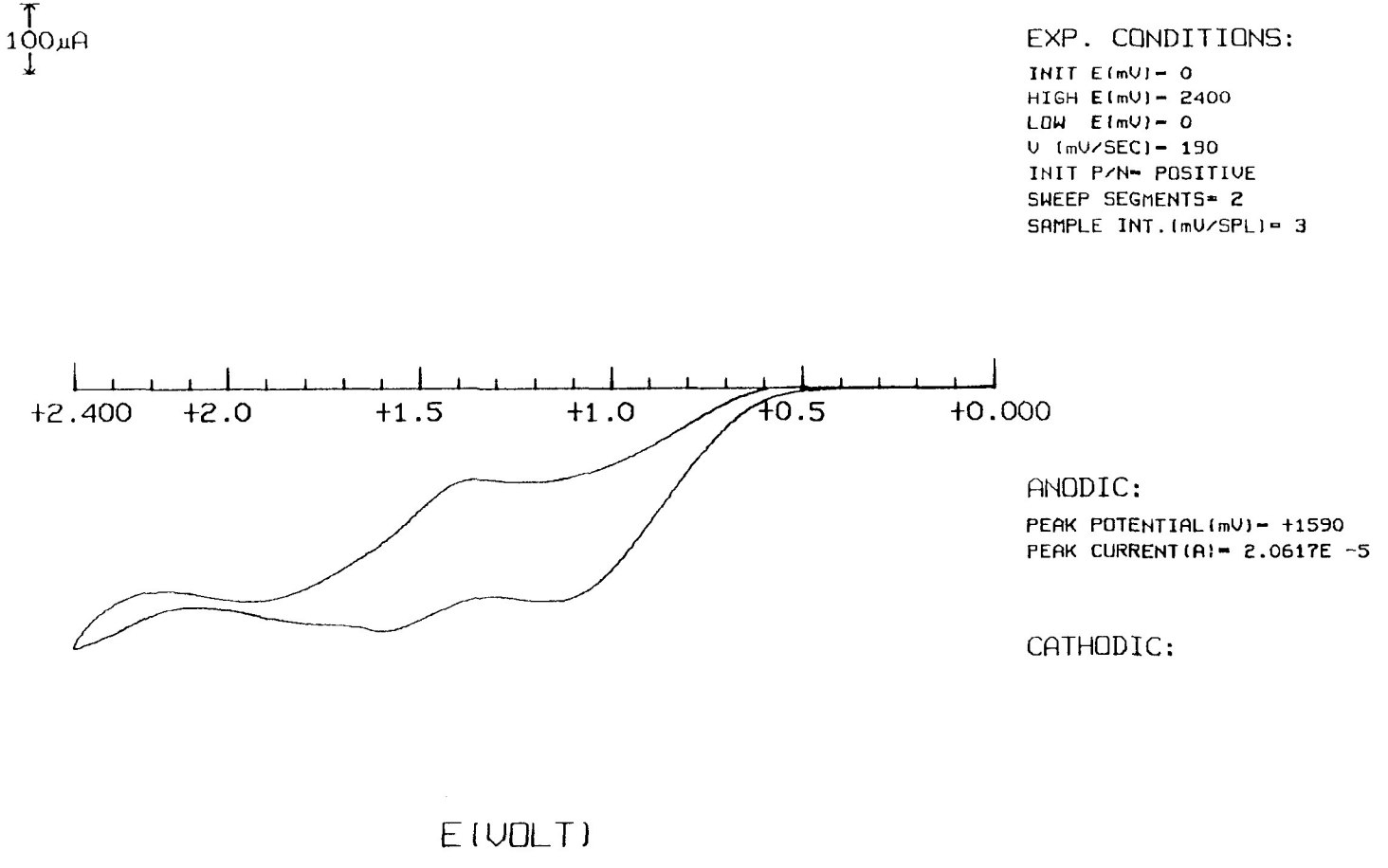

Figure 31. Cyclic voltammogram of dithiooxamide in acetonitrile using a platinum electrode.

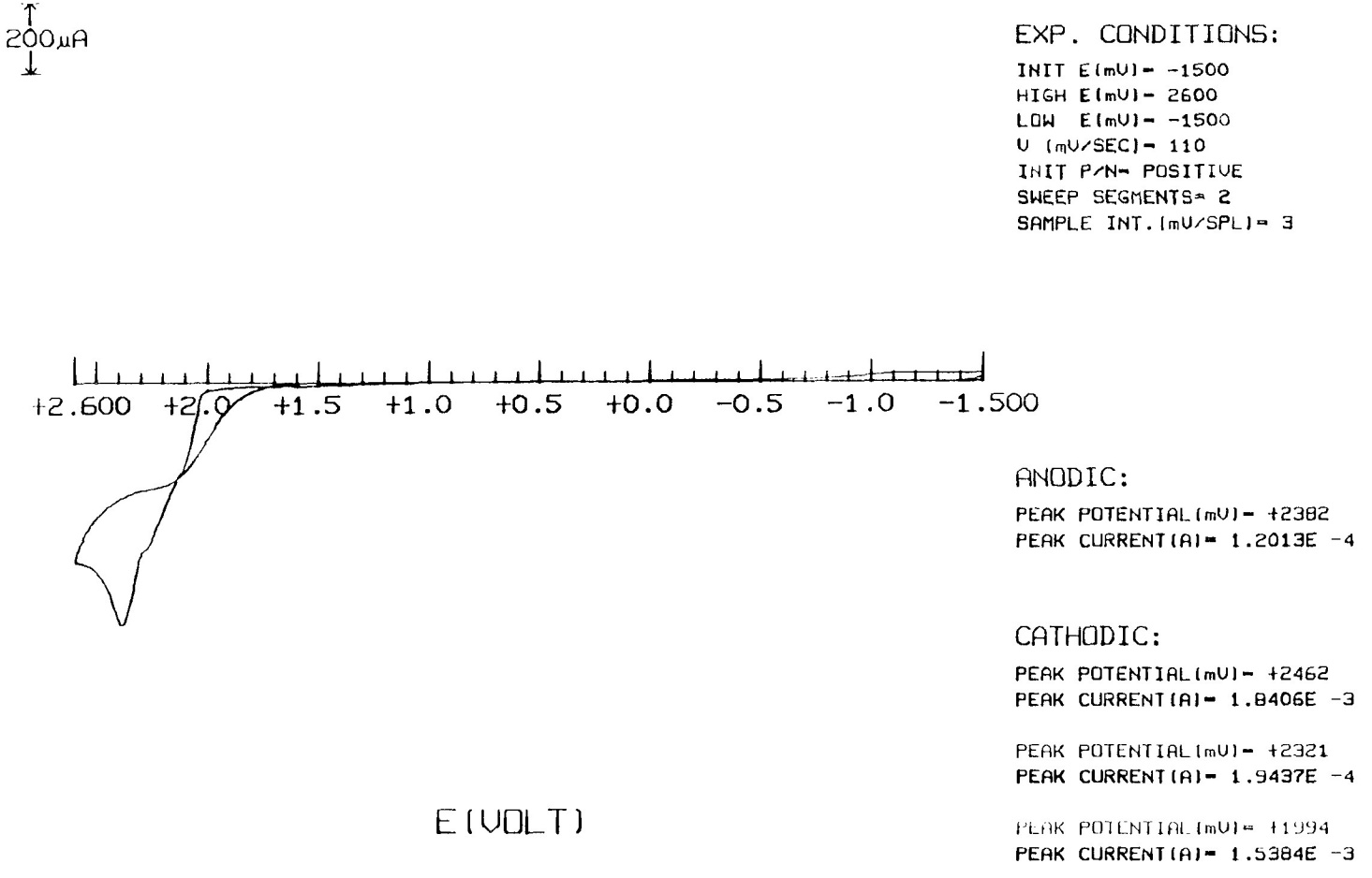

Figure 32. Cyclic voltammogram of dithiooxamide in acetonitrile using a carbon electrode.

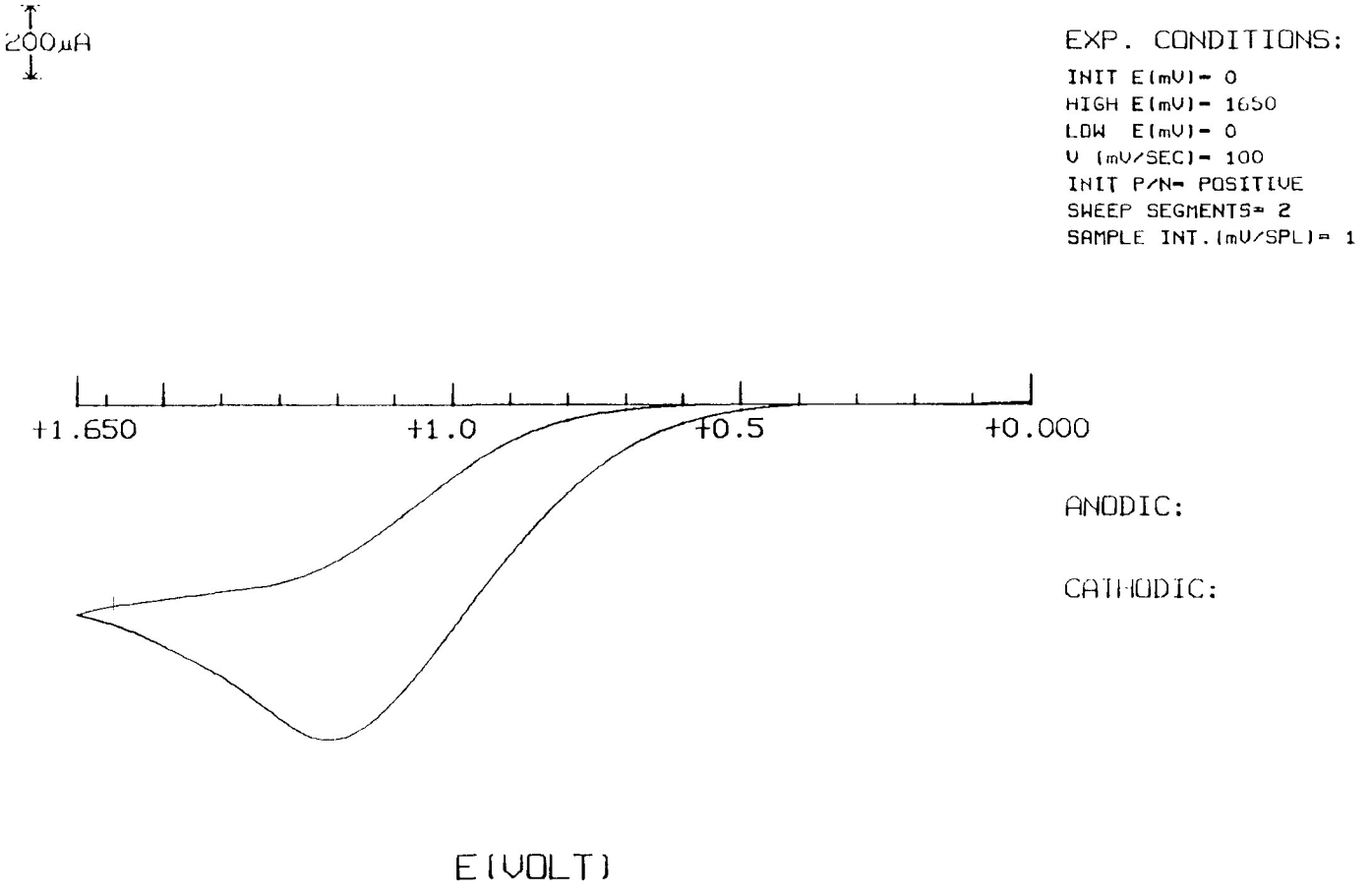

Figure 33. Cyclic voltammogram of thiourea in acetonitrile using a carbon electrode.

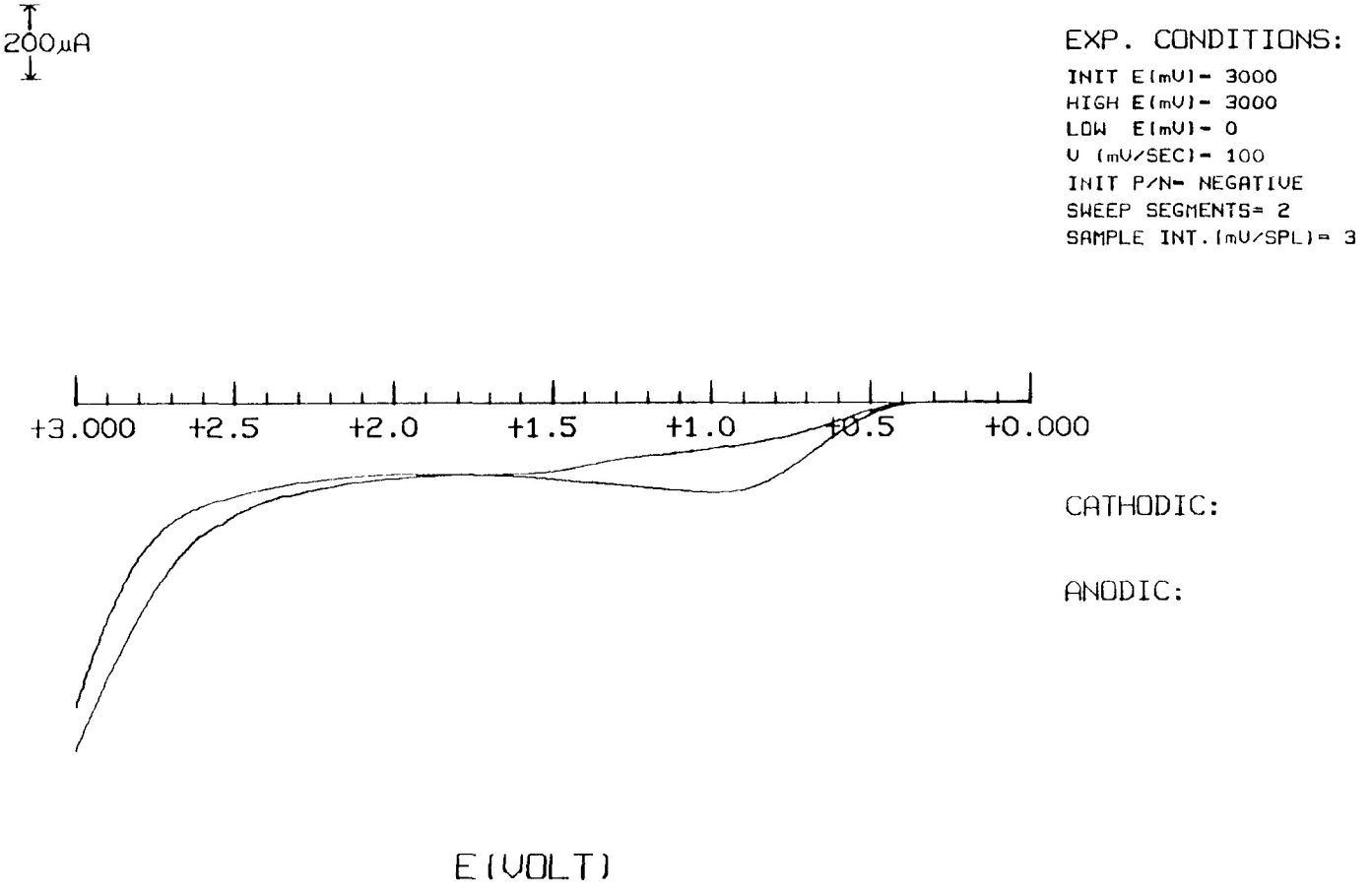

Figure 34. Cyclic voltammogram of thiourea in acetonitrile using a platinum electrode.

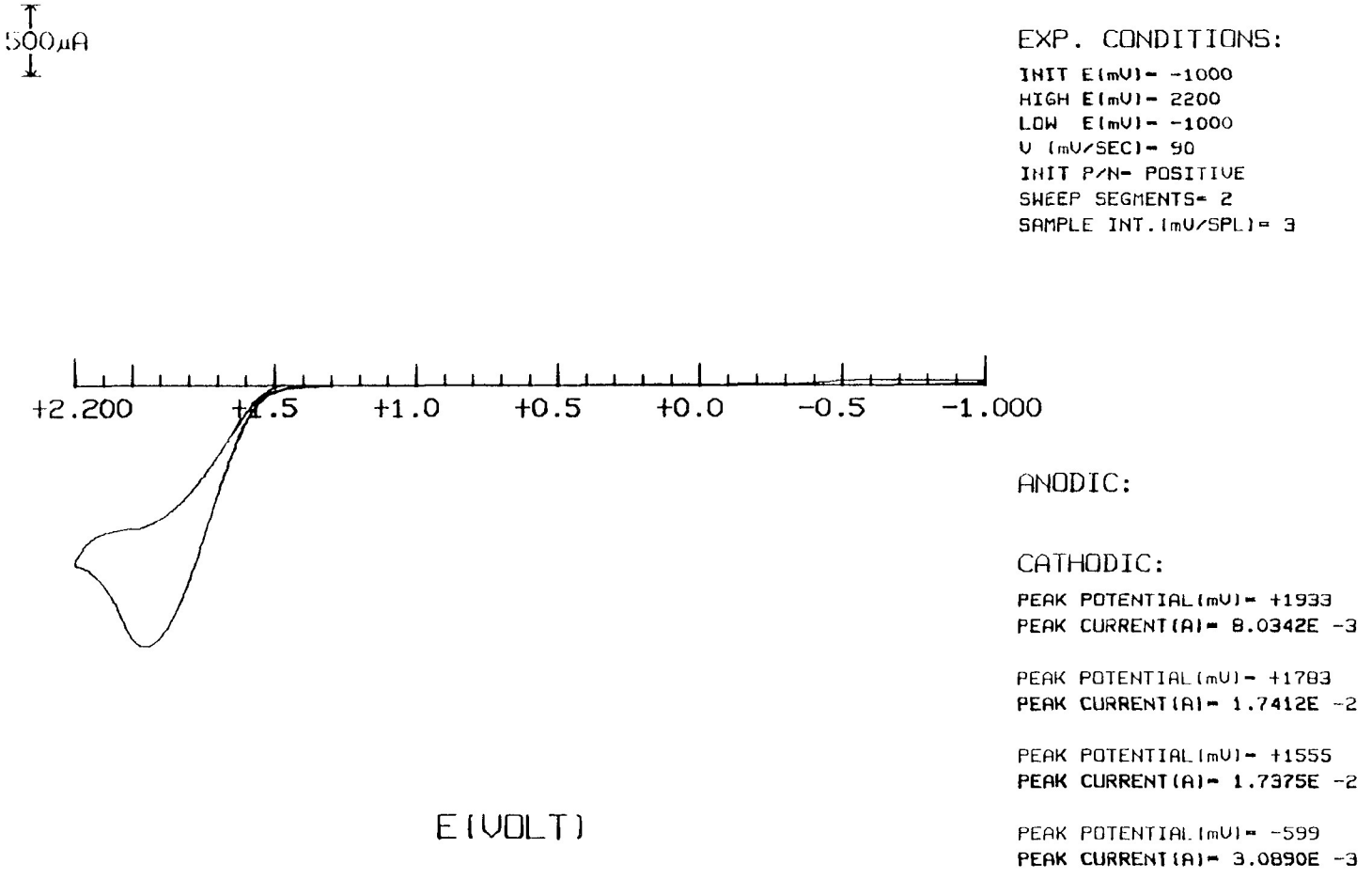

Figure 35. Cyclic voltammogram of 2-mercaptoacetic acid in acetonitrile using a carbon electrode.

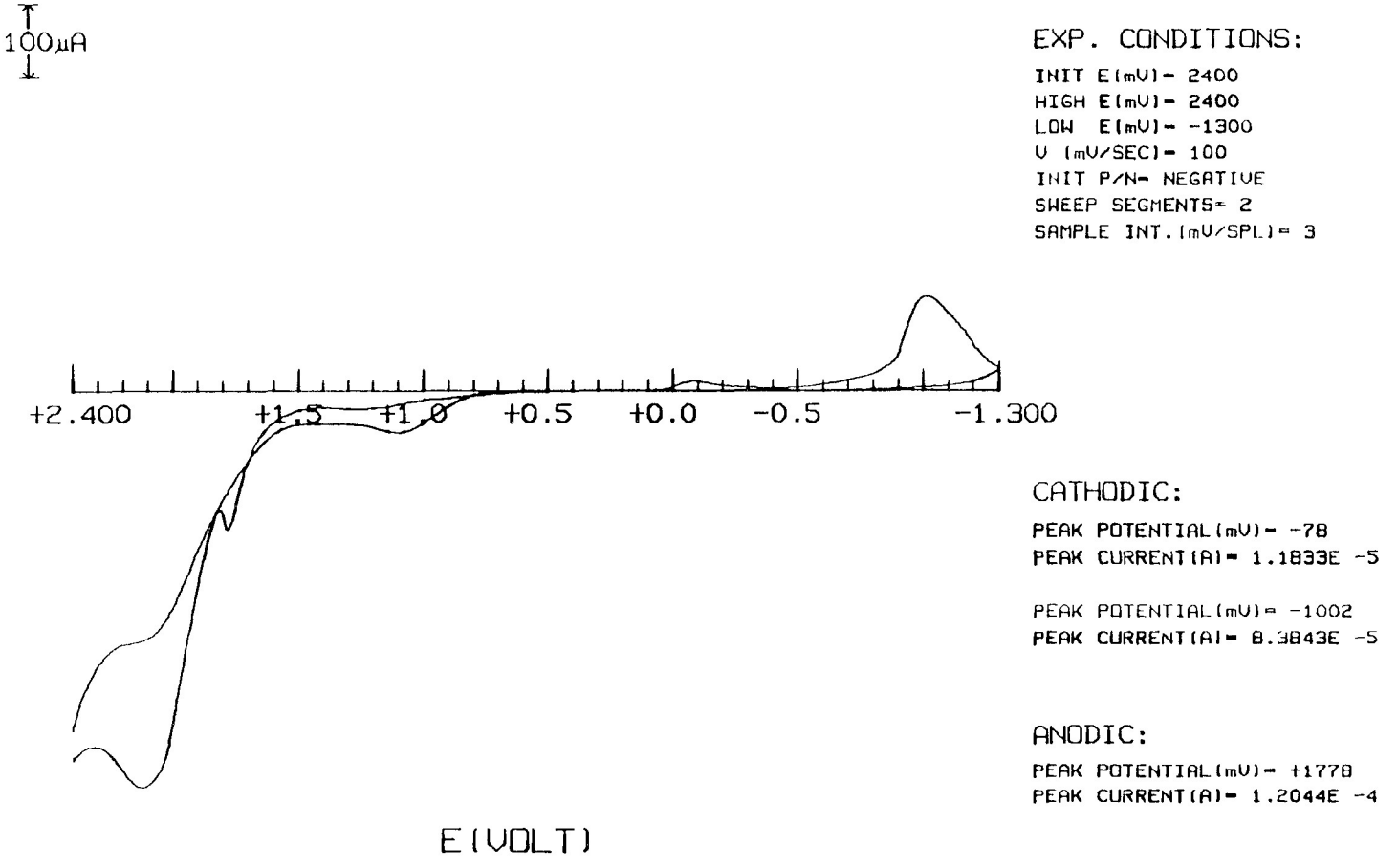

Figure 36. Cyclic voltammogram of 2-mercaptoacetic acid in acetonitrile using a platinum electrode.

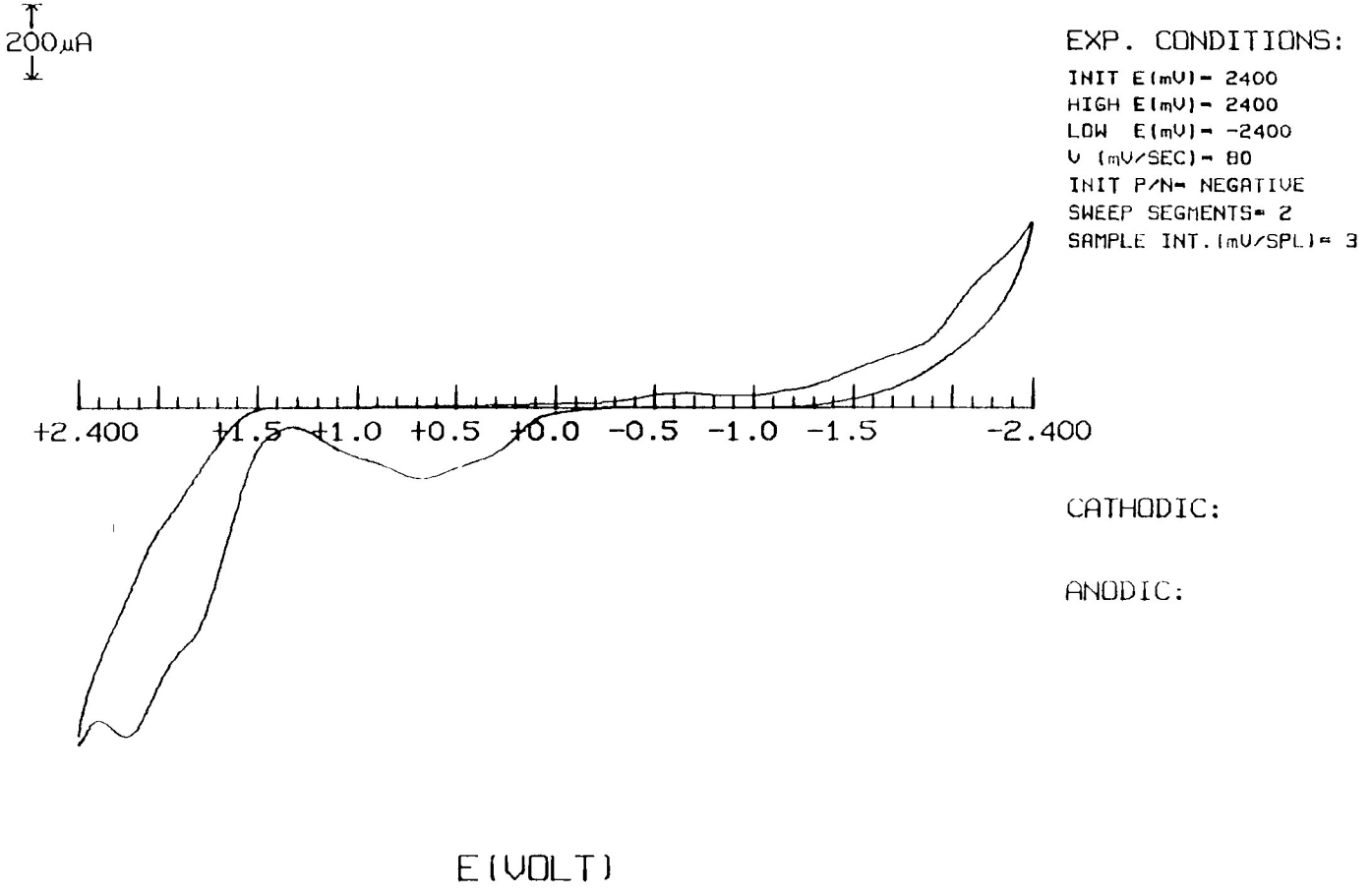

Figure 37. Cyclic voltammogram of thioacetic acid in acetonitrile using a carbon electrode.

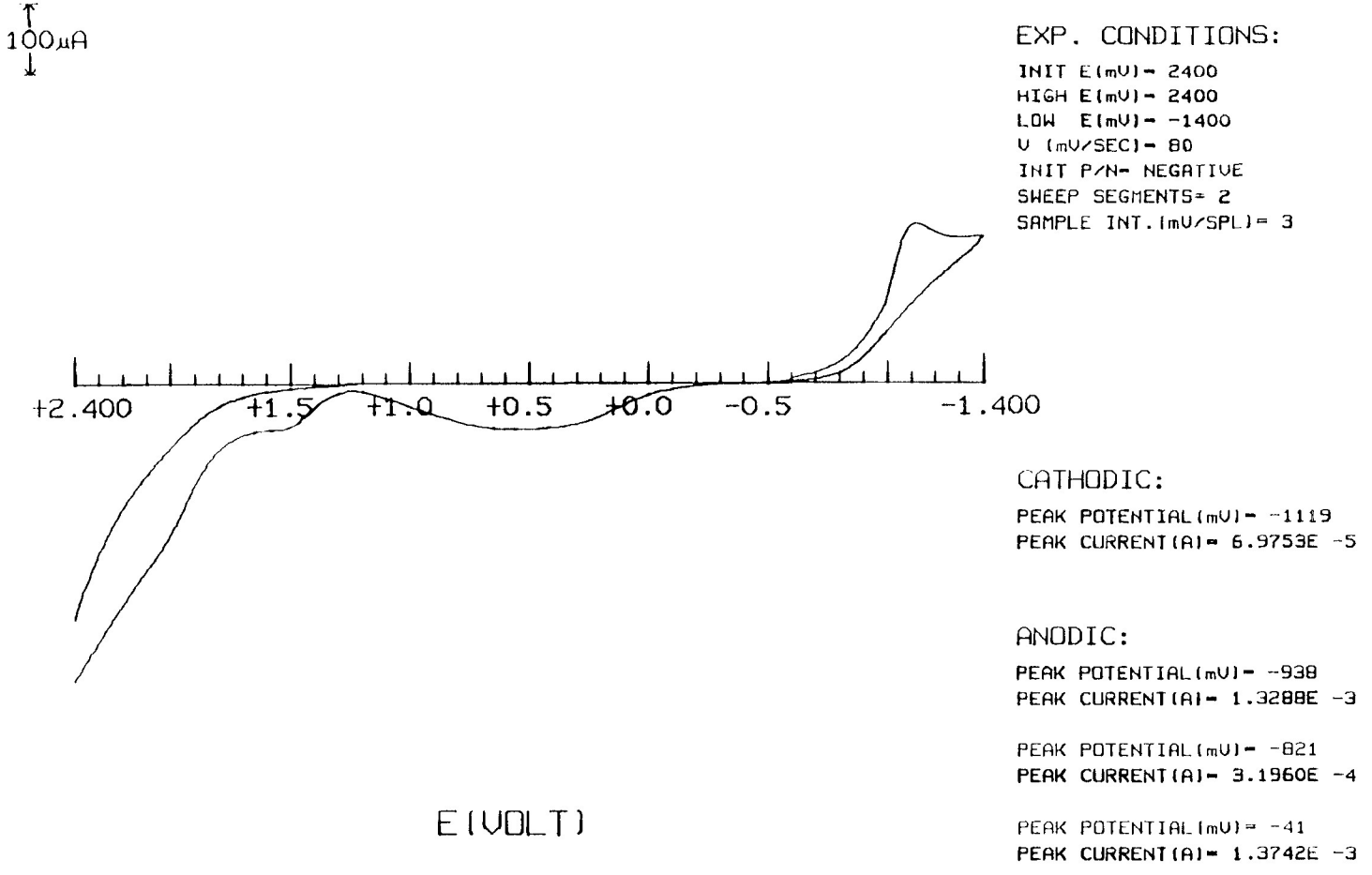

Figure 38. Cyclic voltammogram of thioacetic acid in acetonitrile using a platinum electrode.

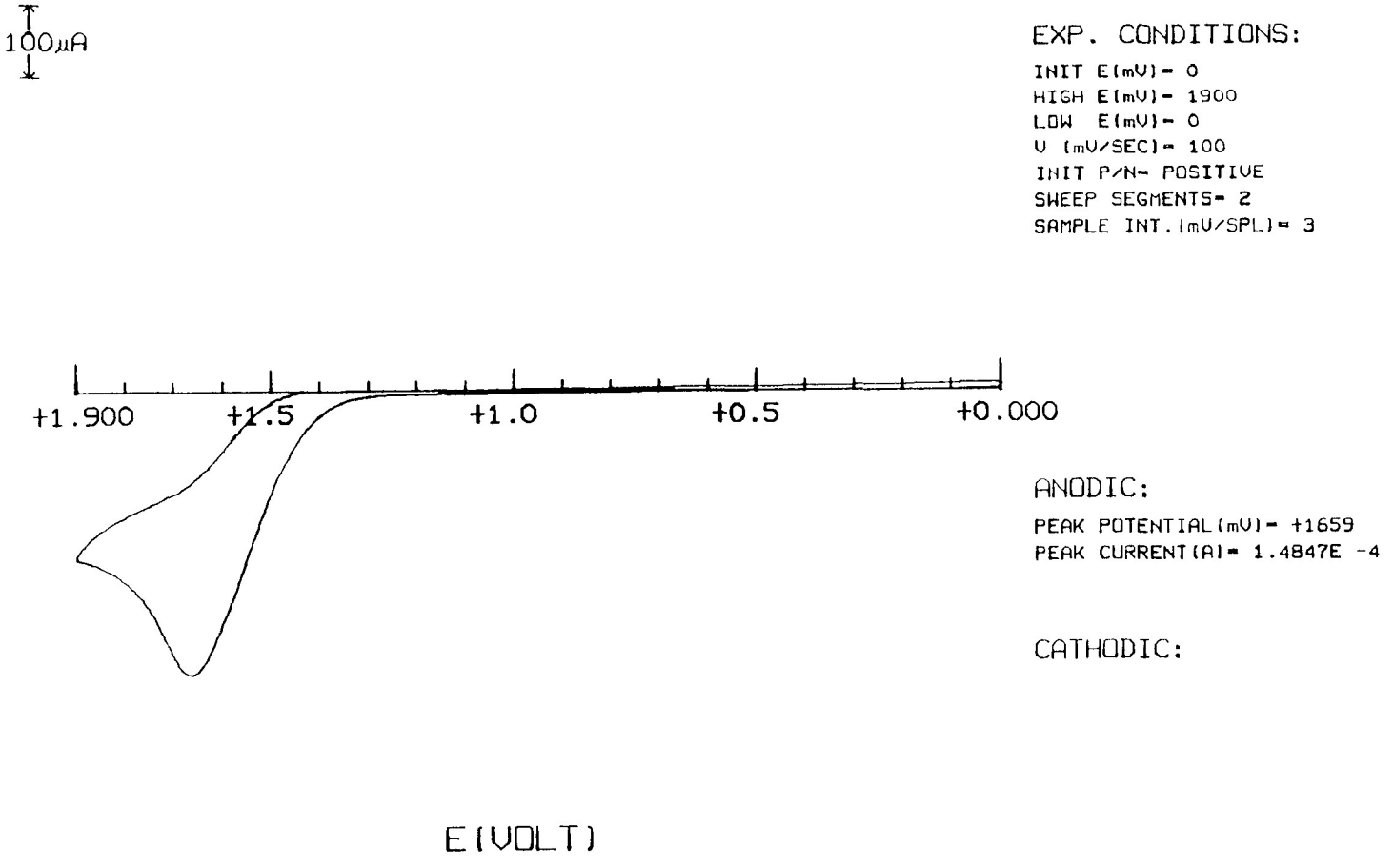

Figure 39. Cyclic voltammogram of phenyl mercaptoacetic acid in acetonitrile using a carbon electrode.

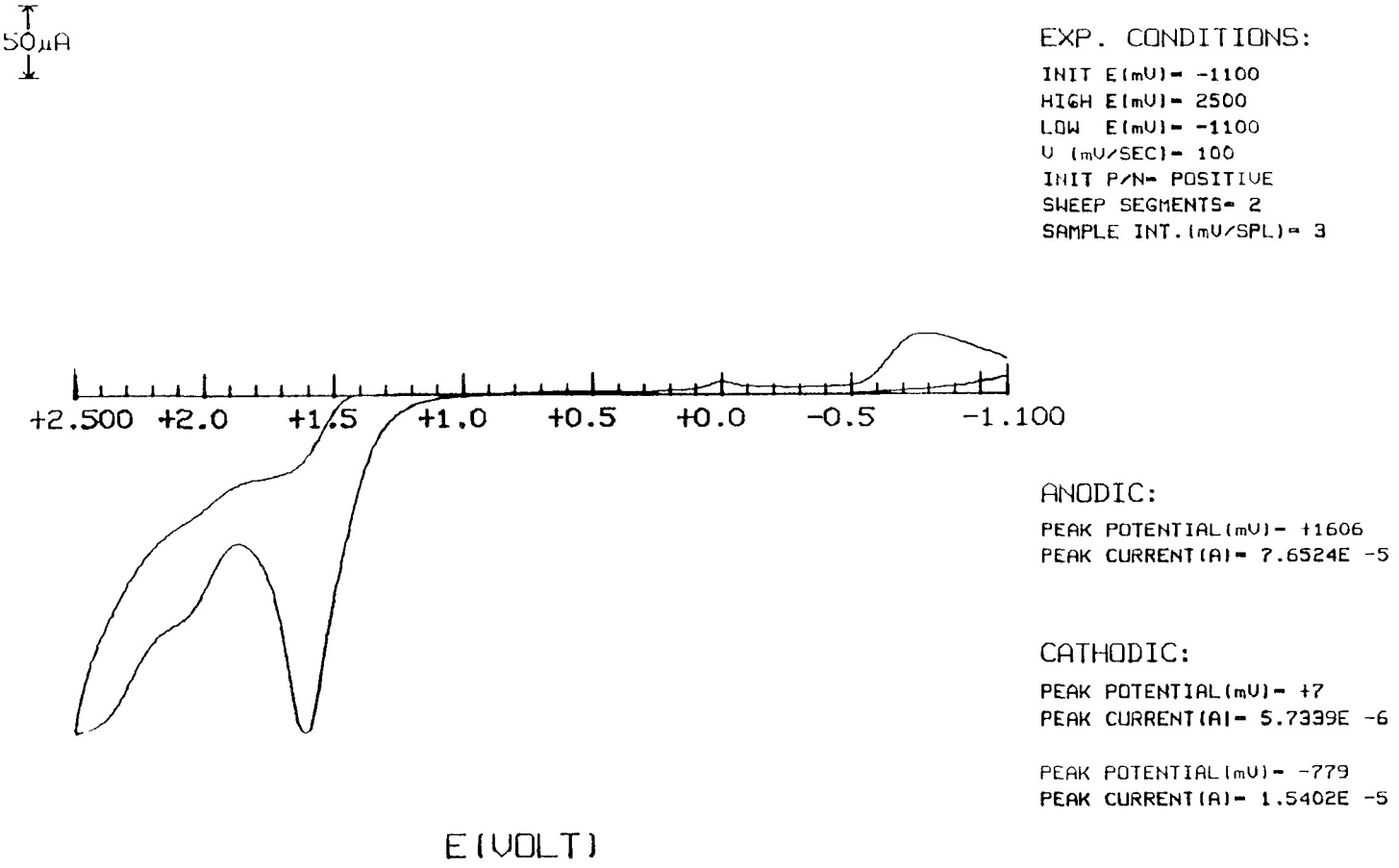

Figure 40. Cyclic voltammogram of phenyl mercaptoacetic acid in acetonitrile using a platinum electrode.

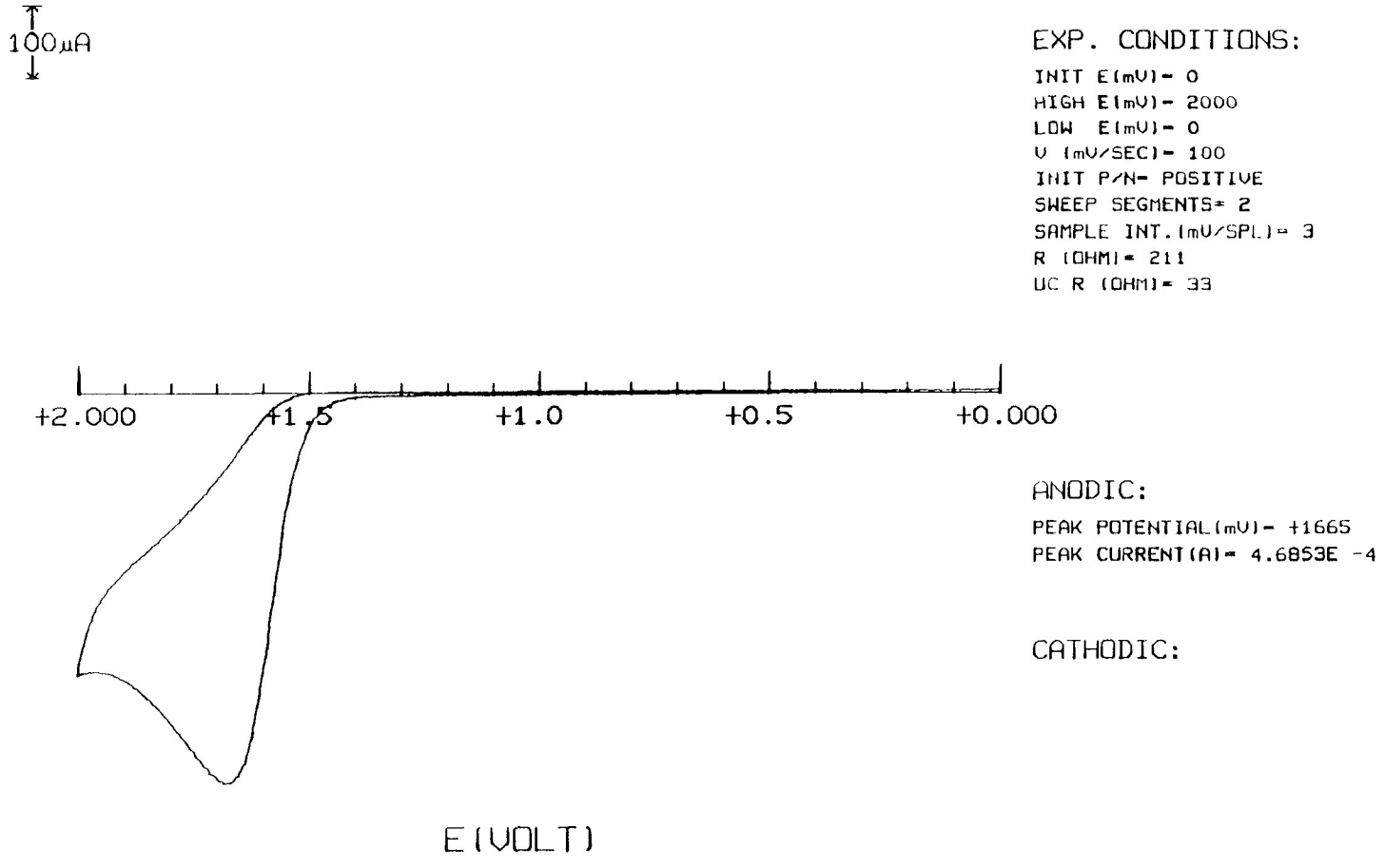

Figure 41. Cyclic voltammogram of dithiodiglycolic acid in acetonitrile using a carbon electrode.

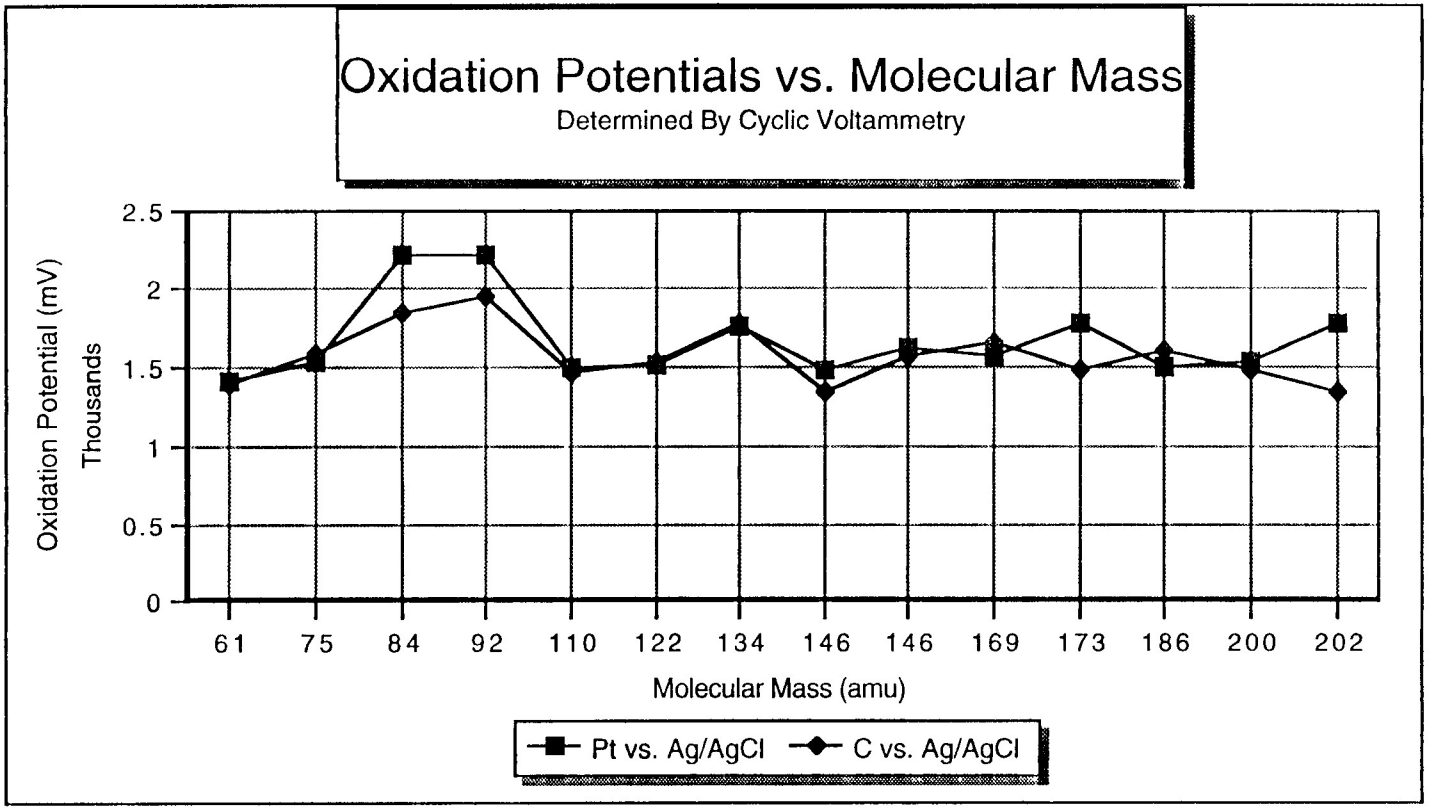

Figure 42. Oxidation Potential vs. Molecular Mass For C and Pt Electrodes.

dibenzothiophenes, while reductive electrochemical detection may be possible for some sulfides, and disulfides in nonaqueous solutions.

B. HPLC and UV Detection of Selected Organosulfur Compounds

The second major step in my research was to determine the feasibility of separating organosulfur compounds using HPLC with UV detection. As Table 5 shows, a variety of organosulfur compounds were selected and evaluated. The data shows many compounds can be detected using UV detection (254 nm).

For the particular mobile phase used, acidic compounds tend to have a short retention time on the reversed phase column. This retention time was less than three minutes for compounds tested. Compounds such as ethanethiol, 1,4-dithiane, butanethiol, propanethiol, and methyl sulfide tend to have retention times between three to five minutes. The retention time appears to be slightly longer due to the more nonpolar nature and the more bulkier molecules. The data indicates small aromatic compounds such as benzyl phenyl sulfide, phenyl sulfide, and dibenzothiophene tended to have retention times that ranged from six to nine minutes. The data indicates that larger molecules such as butyl disulfide and butyl sulfide had retention times that ranged from 11 to 14 minutes. And, even larger molecules such as 1-decanethiol had retention times around 22 minutes.

The compounds appear to elute in the following order: acidic sulfur molecules, small sulfide molecules, small aromatic molecules, and disulfide molecules. This order was established by separately establishing each compound's retention time. As each compound's retention time was established, it was found that one would have to adjust the concentration of the organosulfur compound. Some organosulfur compounds were detected in small concentrations, while other organosulfur compounds required high concentrations in order to be detected. Small aromatic molecules and most sulfide molecules gave good responses, while disulfides gave weak responses even at high concentrations.

TABLE 5

Retention Time, UV Detection, and Electrochemical Detection of Model Sulfur Compounds

Chemical Name	Retention Time (Minutes)	UV Detection (254 nm)	Electrochemical Detection
Methyl Sulfide	3.03	yes	no
Ethanethiol	3.29	yes	no
1,4-Dithiane	3.37	yes	yes
Tetrahydrothiophene	3.60	yes	yes
1-Propanethiol	3.87	yes	yes
Methyl Disulfide	3.80	yes	yes
2-Methylthiophene	4.26	yes	yes
2-Methyl-2-Propanethiol	4.37	yes	yes
1-Methyl-1-Propanethiol	4.65	yes	no
Phenethyl Mercaptan	4.68	yes	yes
1-Butanethiol	4.84	yes	yes
Thionaphthene	4.72	yes	no/yes
Ethyl Disulfide	5.88	yes	yes
Benzyl Phenyl Sulfide	6.64	yes	yes
Phenyl Sulfide	7.77	yes	no
Dibenzothiophene	8.20	yes	yes
Ethyl Sulfide	9.81	yes	no
Butyl Disulfide	11.09	yes	no
Butyl Sulfide	13.52	yes	yes
1-Decanethiol	22.08	yes	no

It is possible to separate and detect a mixture of some of these organosulfur compounds (Table 6). Thionaphthene, benzyl phenyl sulfide, phenyl sulfide, dibenzothiophene, and butyl disulfide were successfully separated and detected using HPLC with UV detection. However, as more organosulfur compounds were included in the mixture, it became more difficult to separate and detect these compounds. Compounds detectable separately were in many cases undetectable in a mixture. This result tends to suggest chemical reactions were occurring which involved certain compounds.

The small aromatic compounds seem to serve as a benchmark. Sulfides tended to elute prior to the small aromatic molecules, while disulfides and 1-decanethiol type of molecules tend to elute after the aromatics (Table 5).

The retention time and elution order of the organosulfur compounds were markedly different in methanol mobile phases as compared to acetonitrile mobile phases. The methanol mobile phases tend to produce undesirably long retention times with adequate separation. The acetonitrile mobile phases provided an acceptable retention time for some organosulfur compounds with moderately acceptable separation. A 70% acetonitrile and a 30% water mobile phase gave the best results for the organosulfur compounds of interest (Table 5 and Table 6).

As Table 7 indicates, most of the organosulfur compounds considered were soluble in methanol.[57] However, their solubilities in water were predominantly insoluble to slightly soluble. This fact affected the mobile phase composition along with electrochemical detection considerations. Methanol mobile phases appeared to provide adequate separation, but methanol mobile phases appear not to be suitable for electrochemical detection due to the large background noise. Acetonitrile gave better results.

C. HPLC and Electrochemical (EC) Detection of Organosulfur Compounds

The third major step in my investigation was the actual determination of the electrochemical nature of some model solutions of some organosulfur compounds.

TABLE 6

Electrochemically Detectable Model Organosulfur Compounds

Chemical Name	Retention Time (Minutes)	UV Detection (Yes/No)	E.C. Detection (Yes/No)	Amount Injected (ng)
1,4-Dithiane	3.37	Yes	Yes	59
Methyl Disulfide	3.59	Yes	Yes	45
Tetrahydrothiophene	3.62	Yes	Yes	104
1-Propanethiol	3.87	Yes	Yes	45
Phenethyl Mercaptan	4.20	Yes	Yes	48
2-Methylthiophene	4.26	Yes	Yes	101
2-Methyl-2-Propanethiol	4.37	Yes	Yes	24
1-Butanethiol	4.61	Yes	Yes	58
Benzyl Phenyl Sulfide	5.20	Yes	Yes	46
Ethyl Disulfide	5.88	Yes	Yes	51
Dibenzothiophene	8.51	Yes	Yes	40
Butyl Sulfide	13.52	Yes	Yes	52

TABLE 7

Model Sulfur Compound Solubility[57]

Chemical Name	Solubility	Water Solubility
Methanethiol	very soluble in al, eth	slightly soluble
Ethanethiol	soluble in al, eth, ace	slightly soluble
1-Propanethiol	soluble in al, eth, ace, bz	slightly soluble
1-Butanethiol	very soluble in al, eth	slightly soluble
Methyl Disulfide	miscible in al, eth	insoluble
Ethyl Disulfide	miscible in al, eth	slightly soluble
Butyl Disulfide	miscible in al, eth	insoluble
Methyl Sulfide	soluble in al, eth	slightly
Ethyl Sulfide	soluble in al, eth	slightly
Butyl Sulfide	soluble in al, eth, ace	insoluble
Diphenyl Sulfide	soluble in al	insoluble
Tetrahydrothiophene	soluble in al, eth, ace, bz	insoluble
Cyclohexanethiol	soluble in al, eth, ace	insoluble
1,4-dithiane	soluble in al, eth	slightly
2-Methylthiophene	soluble in eth, ace, bz	insoluble
Thiophene	soluble in al, eth, ace, bz	miscible
Thiophenol	soluble in al, eth, bz	insoluble
Benzyl Phenyl Sulfide	soluble in al, eth	insoluble
Dibenzothiophene	very soluble in al, bz	soluble
Benzothiophene	soluble in al, eth, ace	insoluble
1-Decanethiol	soluble in al, eth	insoluble

al=alcohol, eth =ether, ace=acetone, bz=benzene

Twenty-three compounds were evaluated for electrochemical oxidation detection using a glassy carbon electrode with a acetonitrile/water mobile phase at a potential of 1.250 Volts.

Table 8 shows a list of organosulfur compounds that gave a detectable UV response. However, these organosulfur compounds did not have an adequate electrochemical response for detection. Detection was attempted separately for each compound.

Table 6 provides a list of twelve compounds that were evaluated for electrochemical detection. These compounds were also detectable using UV detection (254 nm). These compounds had retention times that ranged from 3 to 14 minutes. The compound list includes a cyclic thiol, thiols, disulfides, and small aromatic compounds.

The order of elution appears to be as follows: cyclic thiols, small thiols, small disulfides, small aromatic molecules, and sulfides like butyl sulfide. The small aromatic molecules serve as a benchmark by which to gauge the size and nature of other compounds. The elution order and retention time is essentially the same for both the electrochemical and UV detection process.

EC detection was performed on a mixture of sulfur compounds. These compounds are listed in Table 9, the HPLC chromatogram with UV detection is shown in Figure 43, while the HPLC chromatogram with EC detection is shown in Figure 44. From the data one can conclude that some thiols, sulfides, aromatics, and disulfides can be successfully separated using HPLC and detected electrochemically.

Data were collected for a hydrodynamic voltammogram using a typical thiol, 1-butanethiol (TABLE 10). A plot of the data produced Figure 45. The figure indicates that the glassy carbon electrode should be operated at a potential of 1.0 to 1.3 volts for effective detection of 1-butanethiol. Hydrodynamic voltammograms imply that by selecting a particular potential one can fine tune the electrochemical oxidation detection process. In this investigation, the potential was set a maximum value of 1.250 Volts for the carbon

TABLE 8

Model Organosulfur Compounds Not Electrochemically Detectable

Chemical Name	UV Detection (Yes/No)	Electrochemical Detection (Yes/No)
Methyl Sulfide	Yes	No
Ethanethiol	Yes	No
1-Methyl-1-Propanethiol	Yes	No
Thionaphthene	Yes	No
Phenyl Sulfide	Yes	No
Ethyl Sulfide	Yes	No
Butyl Disulfide	Yes	No
Thiophenol	Yes	No
1-Decanethiol	Yes	No
Thiophene	Yes	No
1,2-Ethanedithiol	No	Yes

TABLE 9

Model Organosulfur Compounds Detected Electrochemically in a Mixture

Chemical Name	Retention Time (Minutes)	EC/UV Detected	Nanograms Injected
1-Propanethiol	3.60	Yes	45
1-Butanethiol	4.70	Yes	58
Benzyl Phenyl Sulfide	5.98	Yes	46
Butyl Sulfide	11.78	Yes	52
Butyl Disulfide	17.38	Yes	40

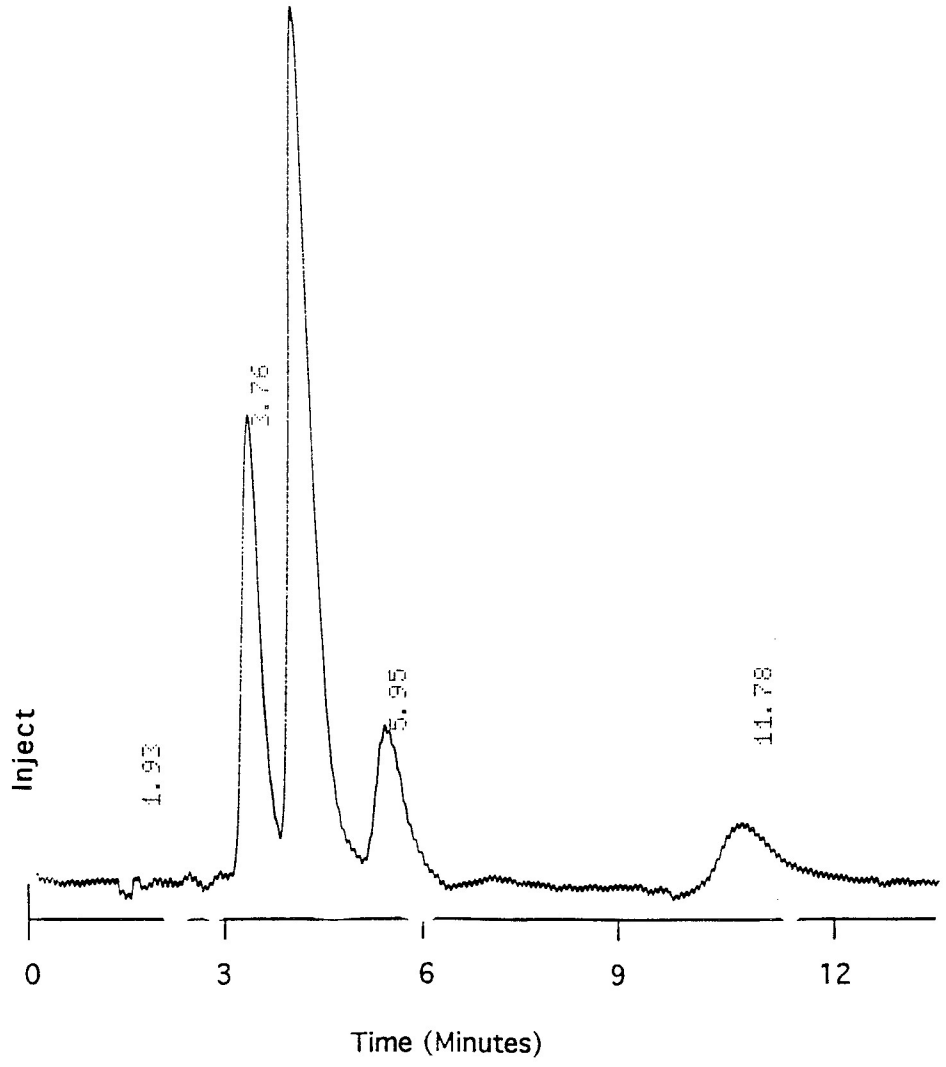

Figure 43. Analysis of model organosulfur mixture using reversed phase HPLC with UV detection (acetonitrile/water).

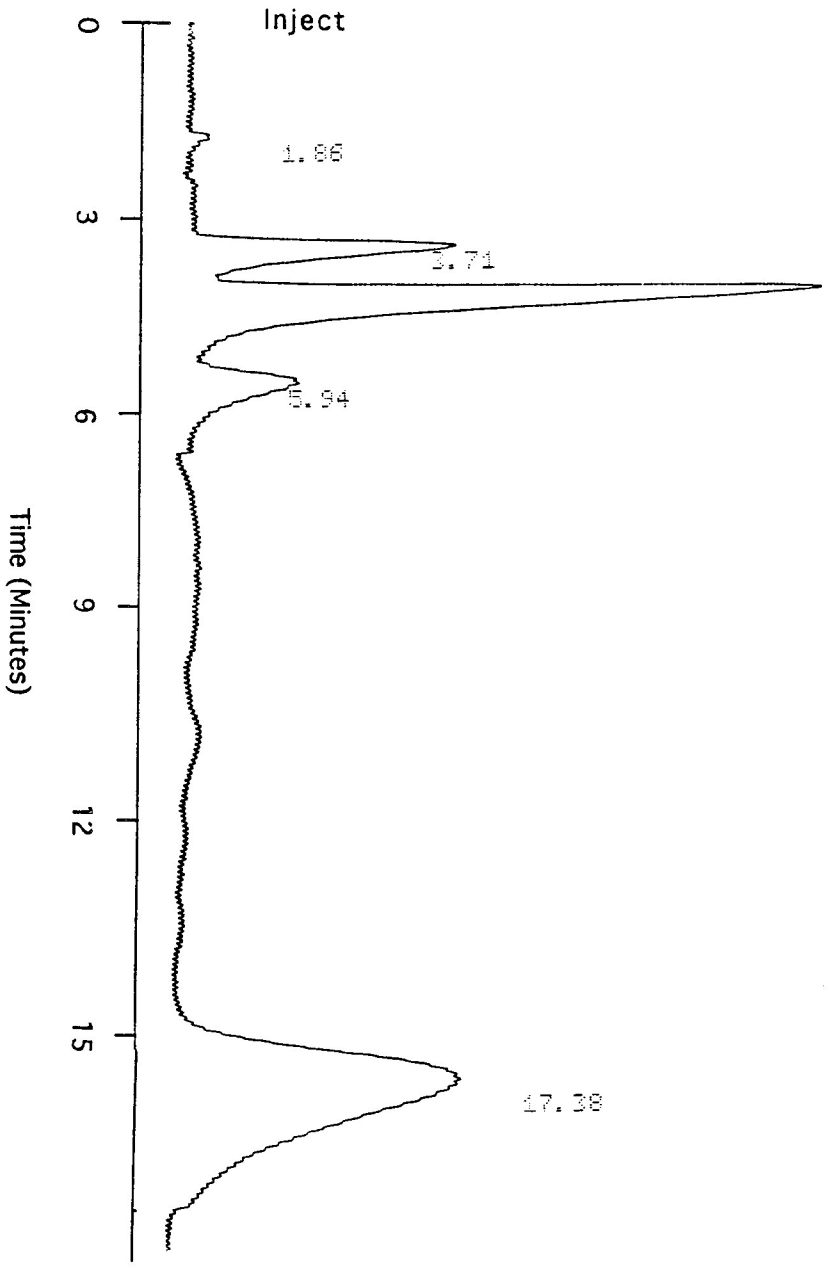

Figure 44. Analysis of model organosulfur mixture using reversed phase HPLC with electrochemical detection; C vs. Ag/AgCl electrode, 70% acetonitrile/30% water, 1.5 mL/min. flow rate, 1.250 volts.

TABLE 10

Hydrodynamic Voltammogram Data For 1-Butanethiol

Potential (Volts)	Current (nA)
0.700	0.0
0.750	1.0
0.850	5.0
0.950	7.0
1.050	32.0
1.150	56.0
1.250	85.0

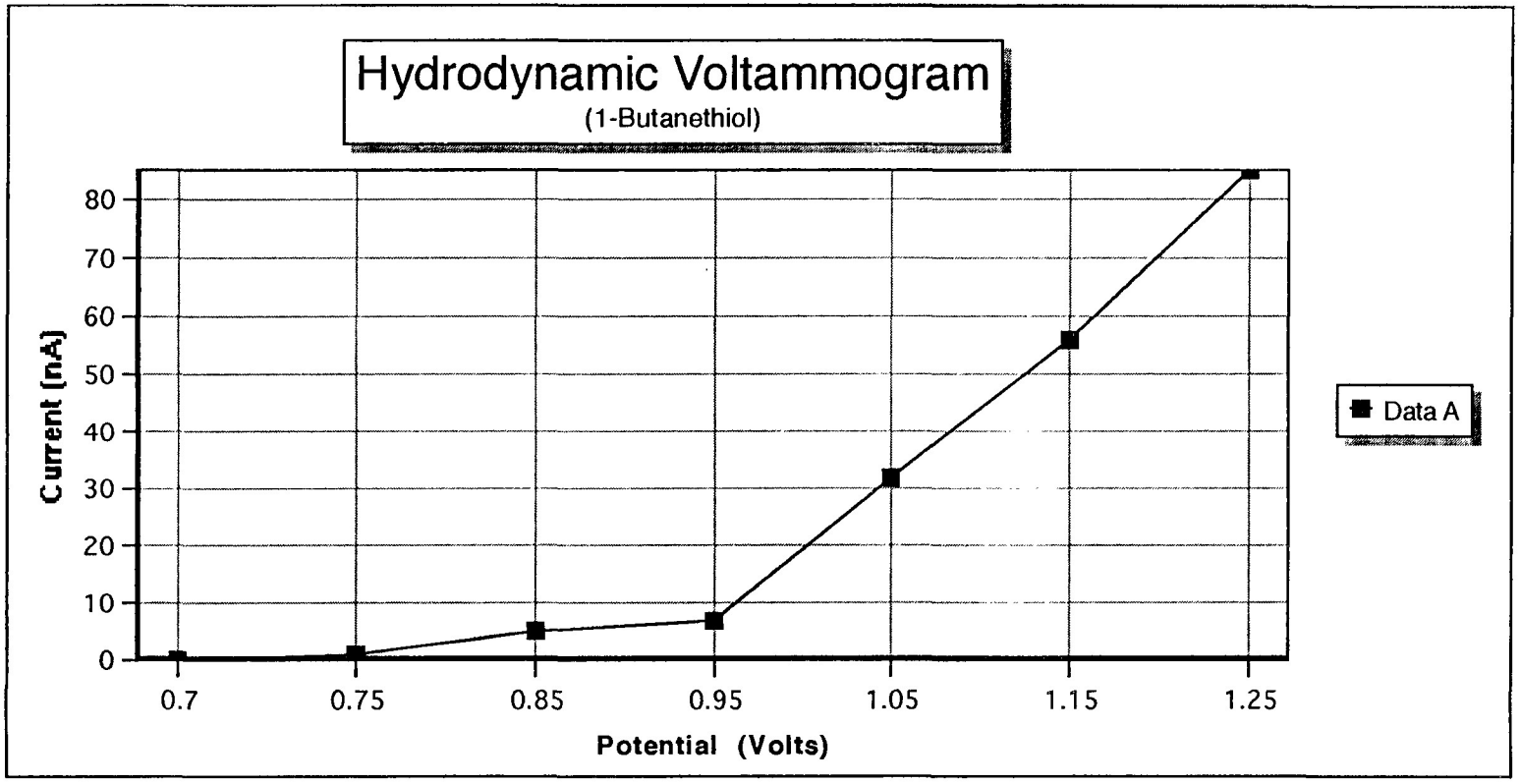

Figure 45. 1-Butanethiol Hydrodynamic Voltammogram.

electrode to insure all possible oxidations occurred. Most organosulfur compounds examined were detectable at a potential around 1.250 Volts (TABLE 6 and TABLE 11), using a 1.5 mL/minute flow rate, a 70% acetonitrile/30% water mobile phase, and a glassy carbon working electrode.

D. UV and Electrochemical Analysis of Liquid Coal Extracts

THF and hexane coal liquid extracts were subjected to electrochemical and UV analysis using reverse phase HPLC. The HPLC chromatograms with UV detection for IBC 105 and IBC 101 liquid coal extracts is shown in Figures 46 through 49, while the HPLC chromatograms with EC detection for IBC 105 and IBC 101 liquid coal extracts is shown in Figures 50 through 53. Data is presented in Table 12 and Table 13.

THF was used as a solvent to extract coal samples IBC 105 and IBC 101 for UV analysis. The UV analysis of the liquid coal extracts of IBC-105 produced 10 detectable UV responses, while the UV analysis of IBC-101 produced 10 detectable UV responses (Table 12). An analysis of the retention times suggest different compounds were responsible for each UV response for both samples IBC-105 and IBC-101.
The retention times ranged from 1.83 minutes to 17.39 minutes for the THF extracted compounds. The data suggest that THF is reasonably successful in extracting compounds or possible organosulfur compounds that can be detected by UV analysis. The retention times of the extracted compounds matched, reasonably well, the retention times for the standard organosulfur compounds examined such as thiols, sulfides, disulfides and small aromatic compounds (Tables 5 and 11).

THF was used as a solvent to extract coal samples IBC-105 and IBC-101 for electrochemical analysis. The electrochemical analysis of the liquid coal extracts of IBC-105 produced 13 detectable oxidative responses, while the electrochemical analysis of IBC-101 produced nine oxidative responses (Table 13 and Figure 54). An analysis of the electrochemical retention times suggests two compounds may both be present in the coal liquid extracts of IBC-105 and IBC-101.

TABLE 11

Electrochemical Retention Time For Model Sulfur Compounds

Chemical Name	Retention Time (Electrochemical Detected) (Minutes)
Thioacetic Acid	1.55
2-Mercaptoacetic Acid	1.62
Phenyl Mercaptoacetic Acid	1.67
Thiourea	2.08
Thioacetamide	2.26
Dithiooxamide	2.33
2-Mercaptoethanol	2.36
Methyl Sulfide	3.03
Ethanethiol	3.21
1,4-Dithiane	3.37
Tetrahyrothiophene	3.66
1-Propanethiol	3.86
Methyl Sulfide	3.88
2-Methylthiophene	4.26
2-Methyl-2-Propanethiol	4.37
1-Methyl-1-Propanethiol	NA
Phenethyl Mercaptan	4.68
1-Butanethiol	4.84
Thionaphthene	4.84
Ethyl Disulfide	5.88
Benzyl Phenyl Sulfide	6.90
Phenyl Sulfide	NA
Dibenzothiophene	8.51
Ethyl Sulfide	9.81
Butyl Disulfide	NA
Butyl Sulfide	13.52

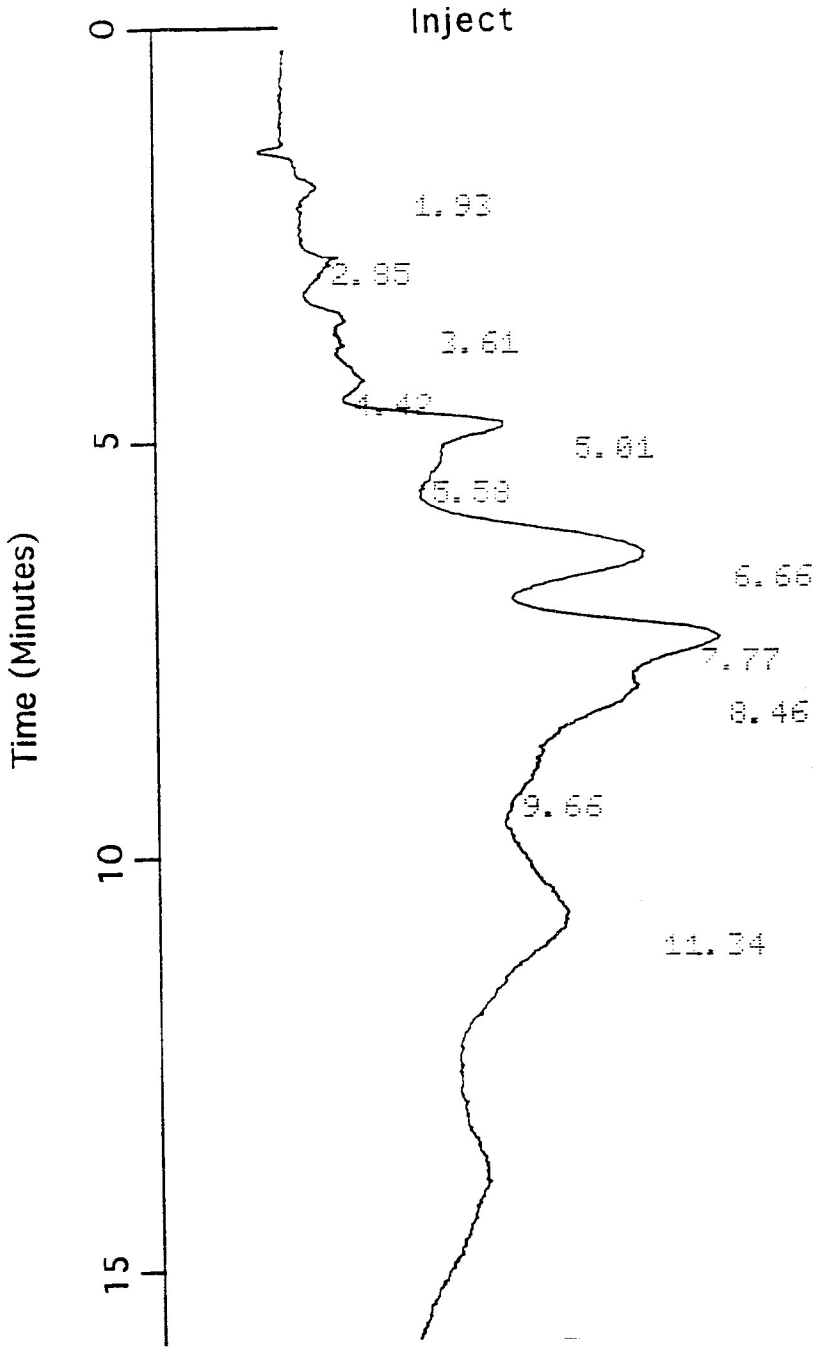

Figure 46. Analysis of IBC 101 THF liquid coal extract using reversed phase HPLC with UV detection, 70% acetonitrile/30% water mobile phase, 254 nm.

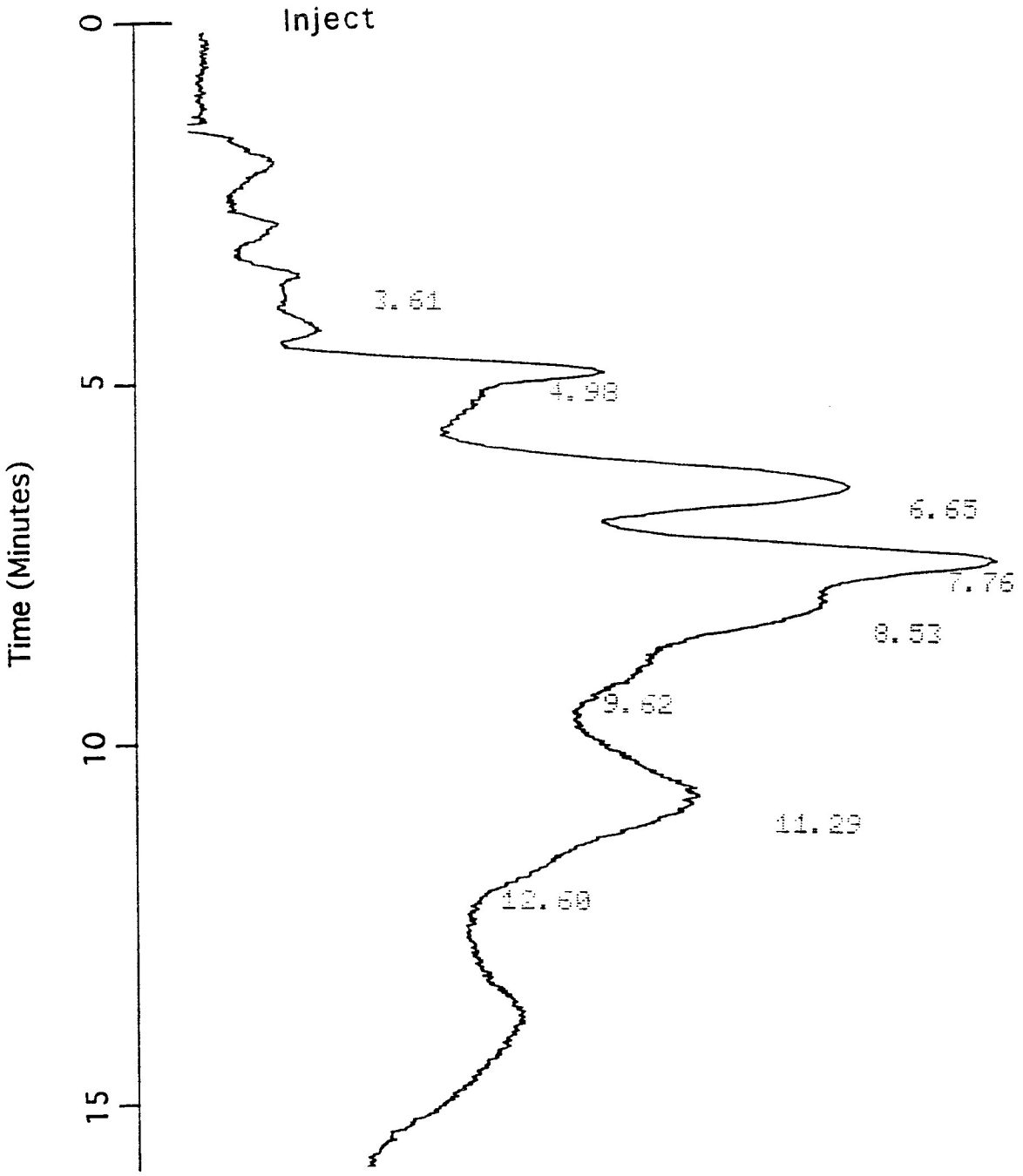

Figure 47. Analysis of IBC 105 THF liquid coal extract using reversed phase HPLC with UV detection, 70% acetonitrile/30% water mobile phase, 254 nm.

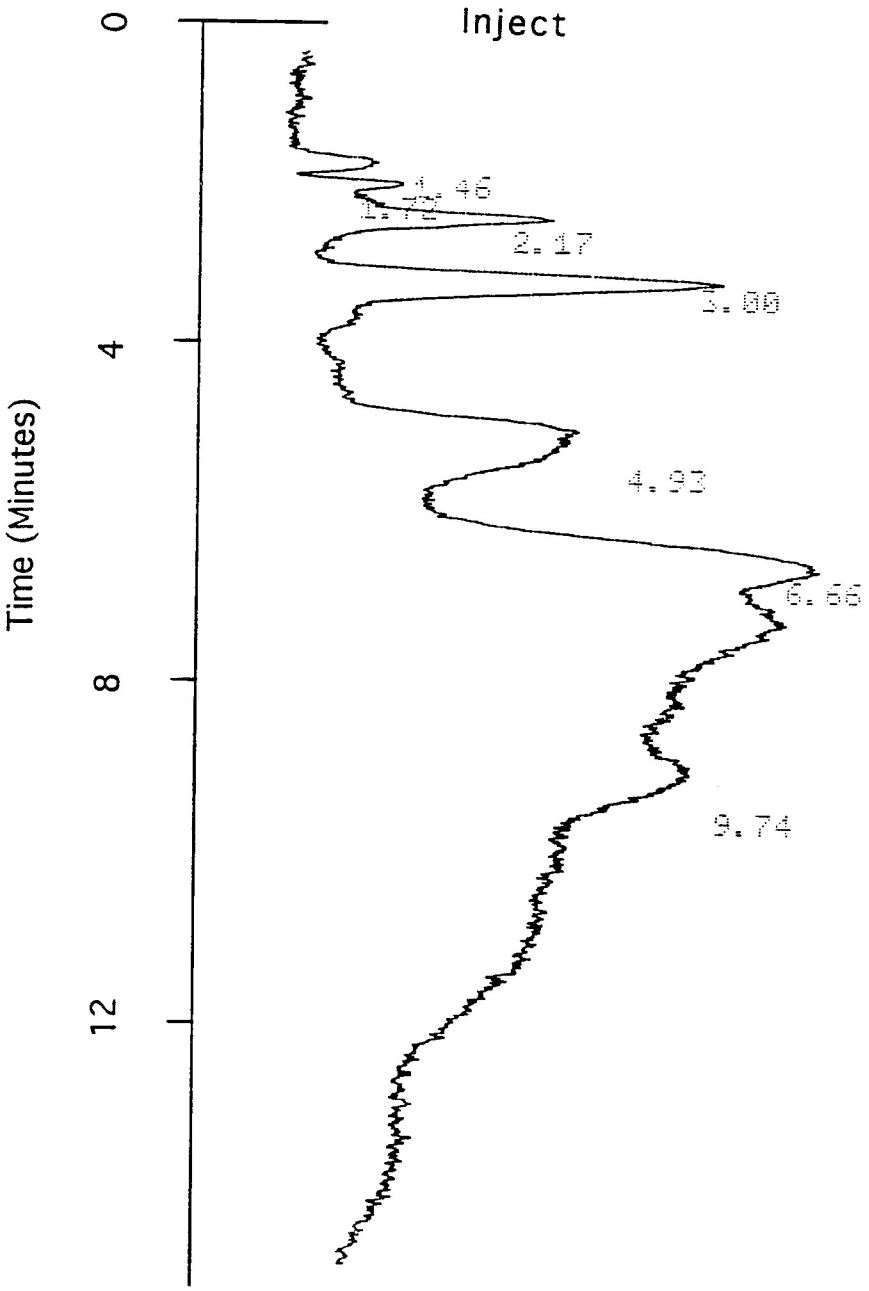

Figure 48. Analysis of IBC 101 hexane liquid coal extract using reversed phase HPLC with UV detection, 70% acetonitrile and 30% water mobile phase, 254 nm.

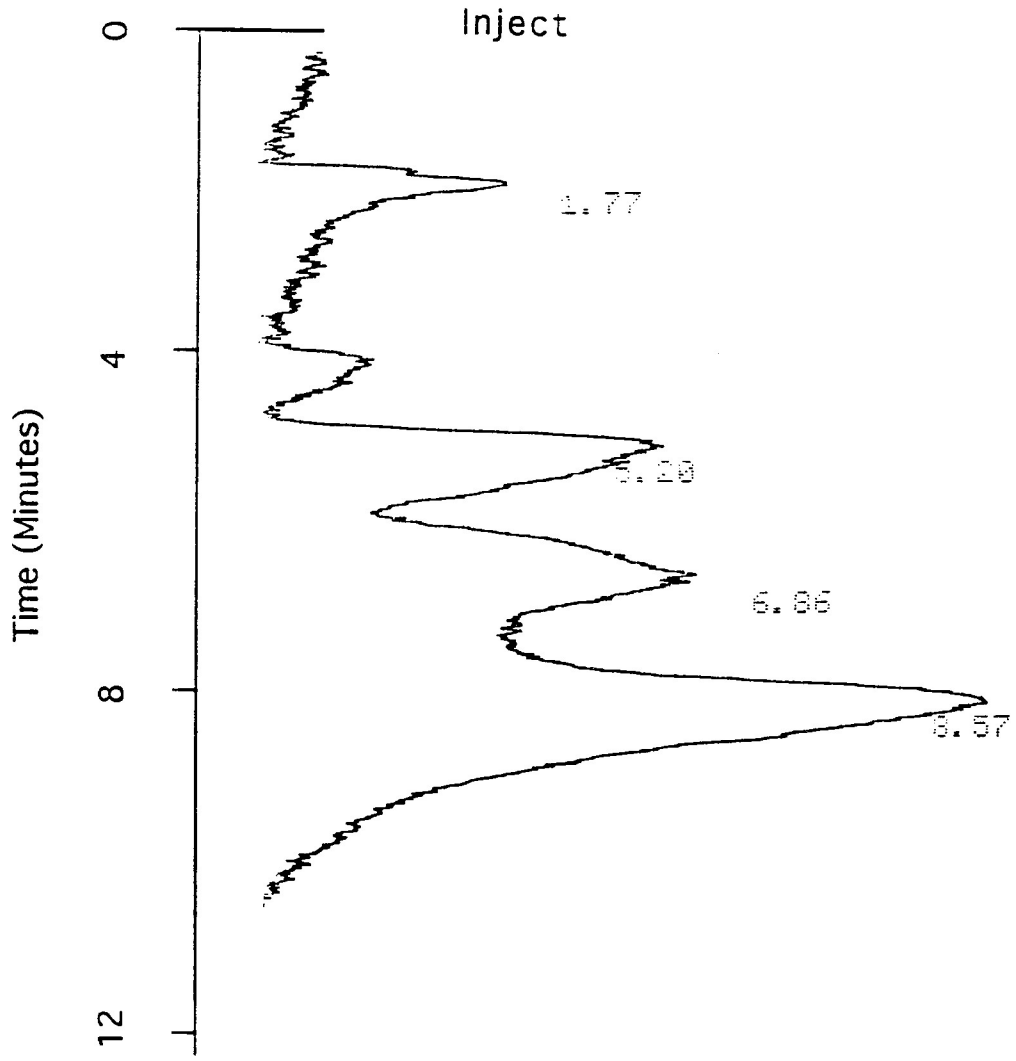

Figure 49. Analysis of IBC 105 hexane liquid coal extract using reversed phase HPLC with UV detection, 70% acetonitrile/30% water mobile phase, 254 nm.

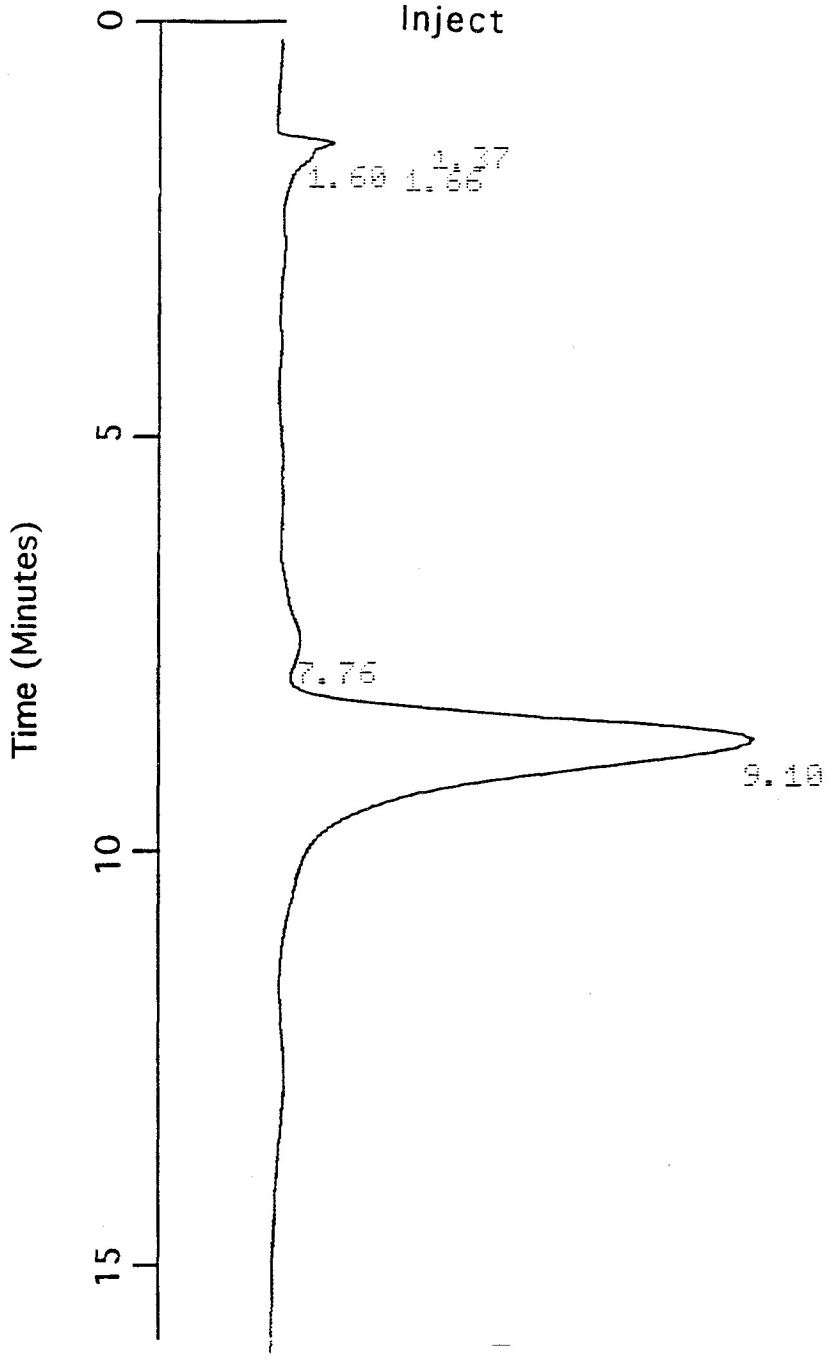

Figure 50. Analysis of IBC 101 THF liquid coal extract using reversed phase HPLC with electrochemical detection; 1.250 volts, 1.5 mL/minute flow rate, C vs. Ag/AgCl electrode, 70% acetonitrile/30% water mobile phase.

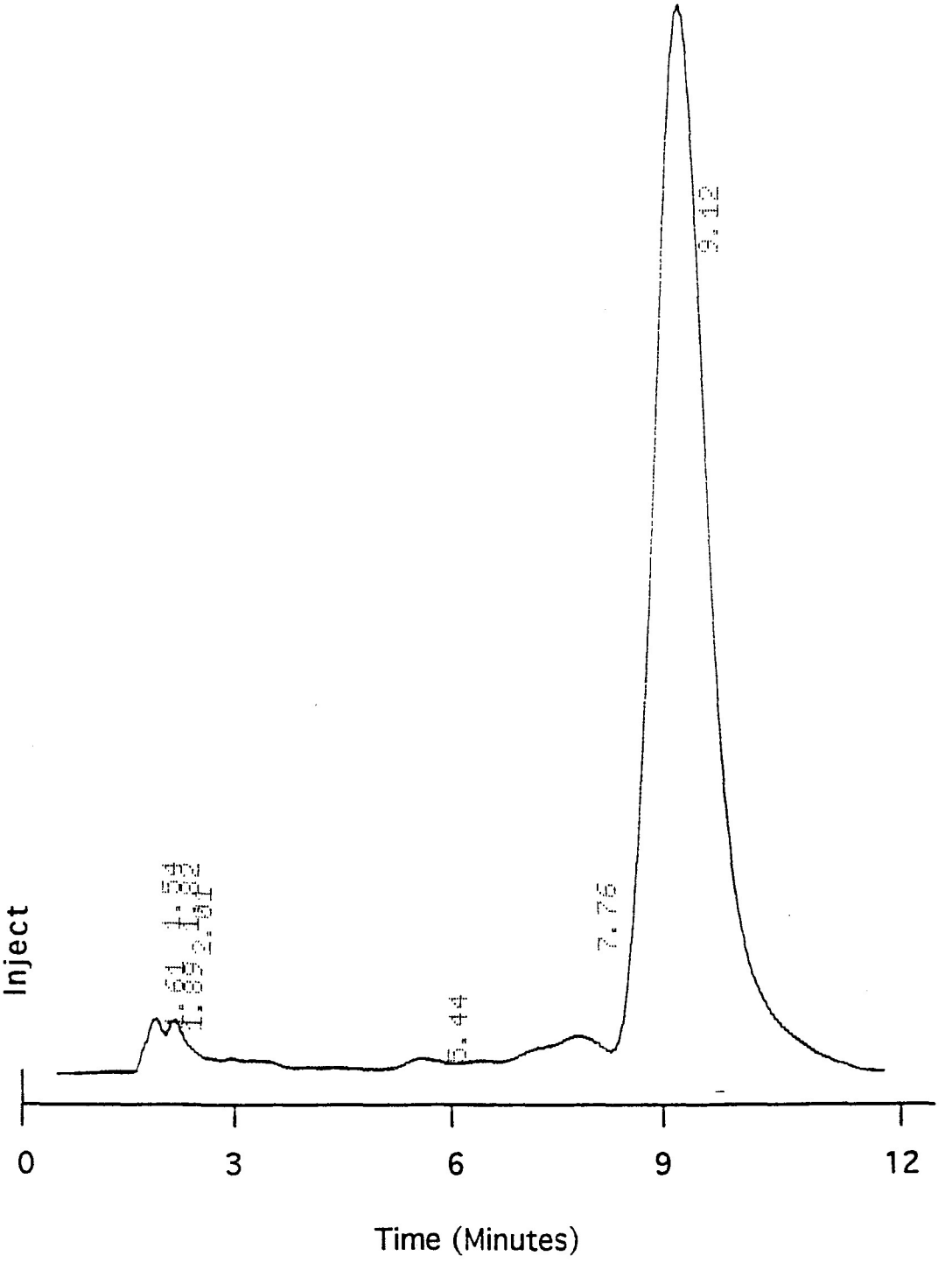

Figure 51. Analysis of IBC 105 THF liquid coal extract using reversed phase HPLC with electrochemical detection; 1.250 volts, 1.5 mL/minute flow rate, C vs. Ag/AgCl electrode, 70% acetonitrile/30% water mobile phase.

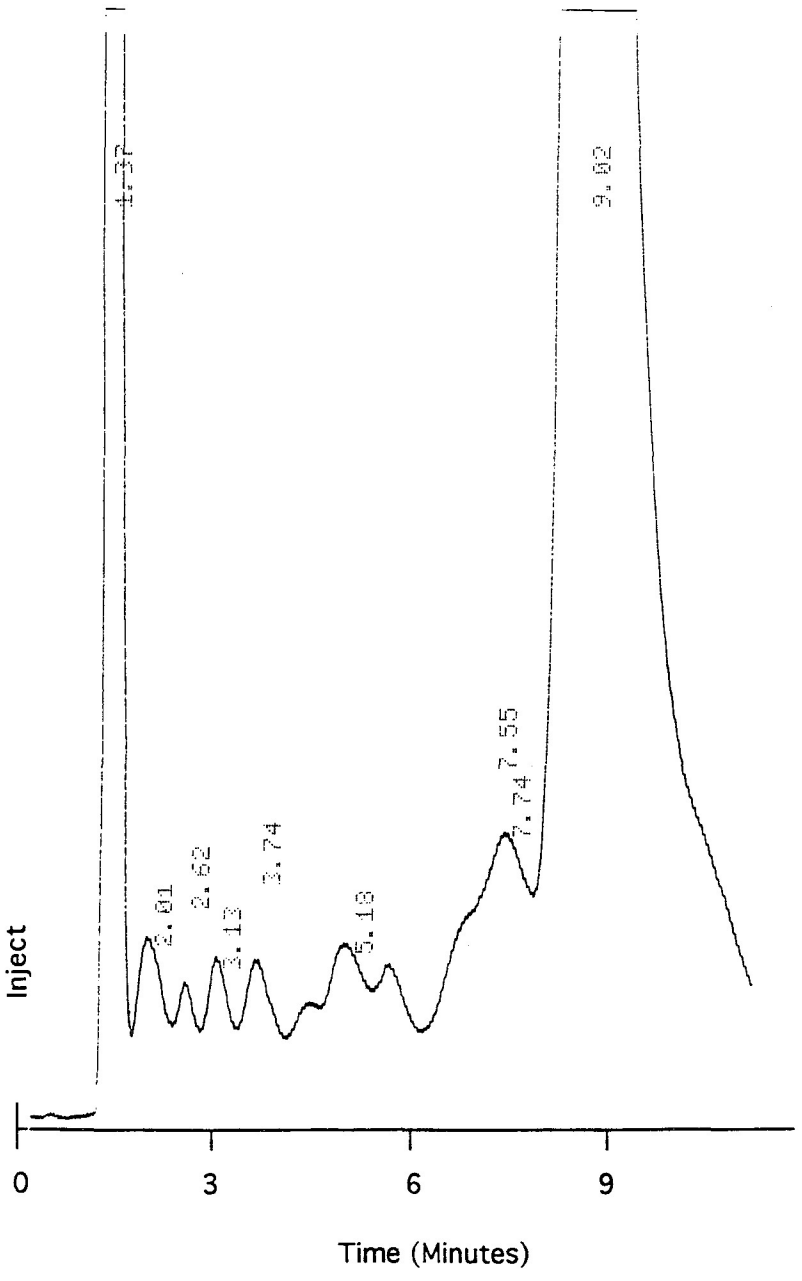

Figure 52. Analysis of IBC 101 hexane liquid coal extract using reversed phase HPLC with electrochemical detection; 1.250 volts, 1.5 mL/minute flow rate, C vs. Ag/AgCl electrode, 70% acetonitrile/30% water mobile phase.

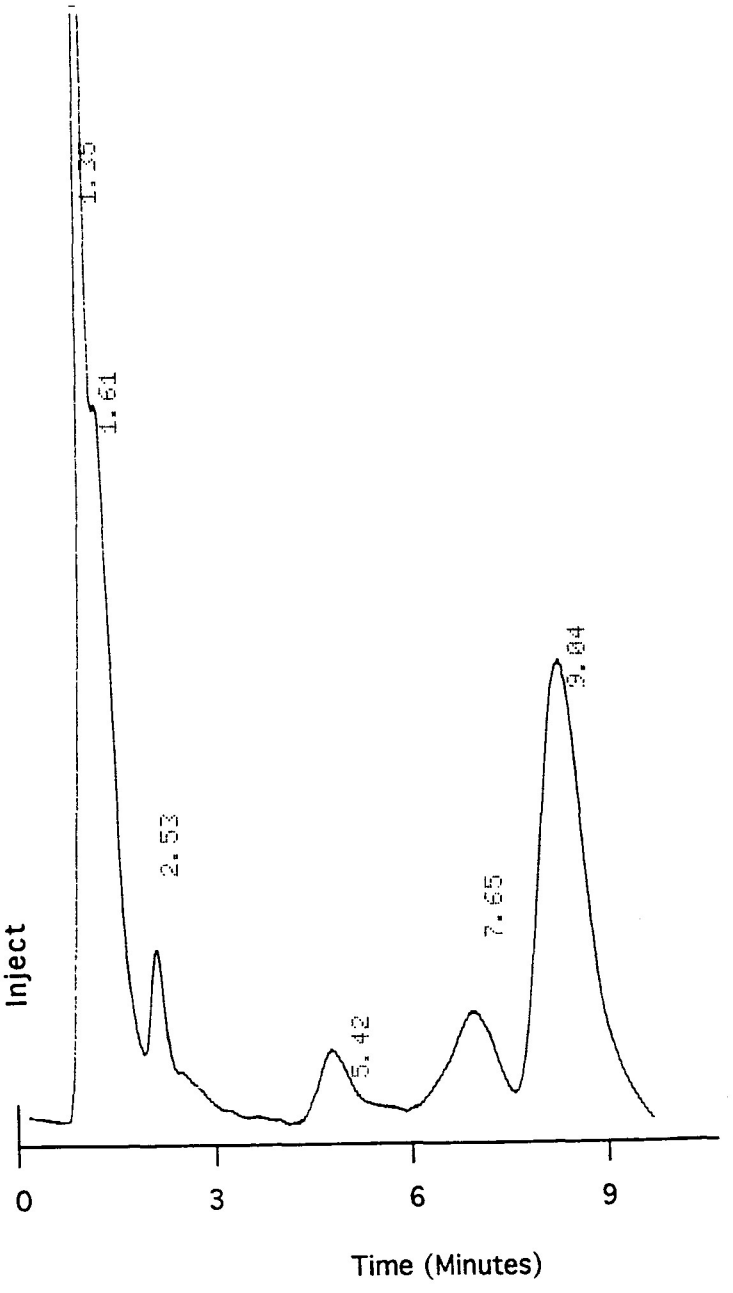

Figure 53. Analysis of IBC 105 hexane liquid coal extract using reversed phase HPLC with electrochemical detection; 1.250 volts, 1.5 mL/minute flow rate, C vs. Ag/AgCl electrode, 70% acetonitrile/30% water mobile phase.

TABLE 12

Retention Times For UV Signals From Coal Liquid Extracts

THF Extractions of Coal		Hexane Extractions Of Coal	
IBC 105 R. T. (Minutes)	IBC 101 R. T. (Minutes)	IBC 105 R. T. (Minutes)	IBC 101 R. T. (Minutes)
2.90	1.83	1.77	1.46
3.60	3.05	5.20	1.72
4.98	3.65	6.86	2.17
6.65	3.69	8.57	3.00
7.76	5.07		4.93
8.53	6.76		6.66
9.62	7.84		9.74
11.29	8.91		
12.60	12.27		
17.39	15.08		

TABLE 13

Retention Times For Electrochemical Signals From Coal Liquid Extracts

THF Extractions of Coal		Hexane Extraction Of Coal	
IBC 105 R. T. (Minutes)	IBC 101 R. T. (Minutes)	IBC 105 R. T. (Minutes)	IBC 101 R. T. (Minutes)
1.54	1.37	1.35	1.37
1.82	1.51	1.61	2.01
1.89	2.68	2.53	2.62
2.01	3.97	5.42	3.13
2.17	5.39	7.65	3.74
2.29	6.03	9.04	5.18
2.83	7.82		7.55
2.95	9.07		7.74
5.44	13.66		9.02
7.76			
8.24			
11.05			
18.03			

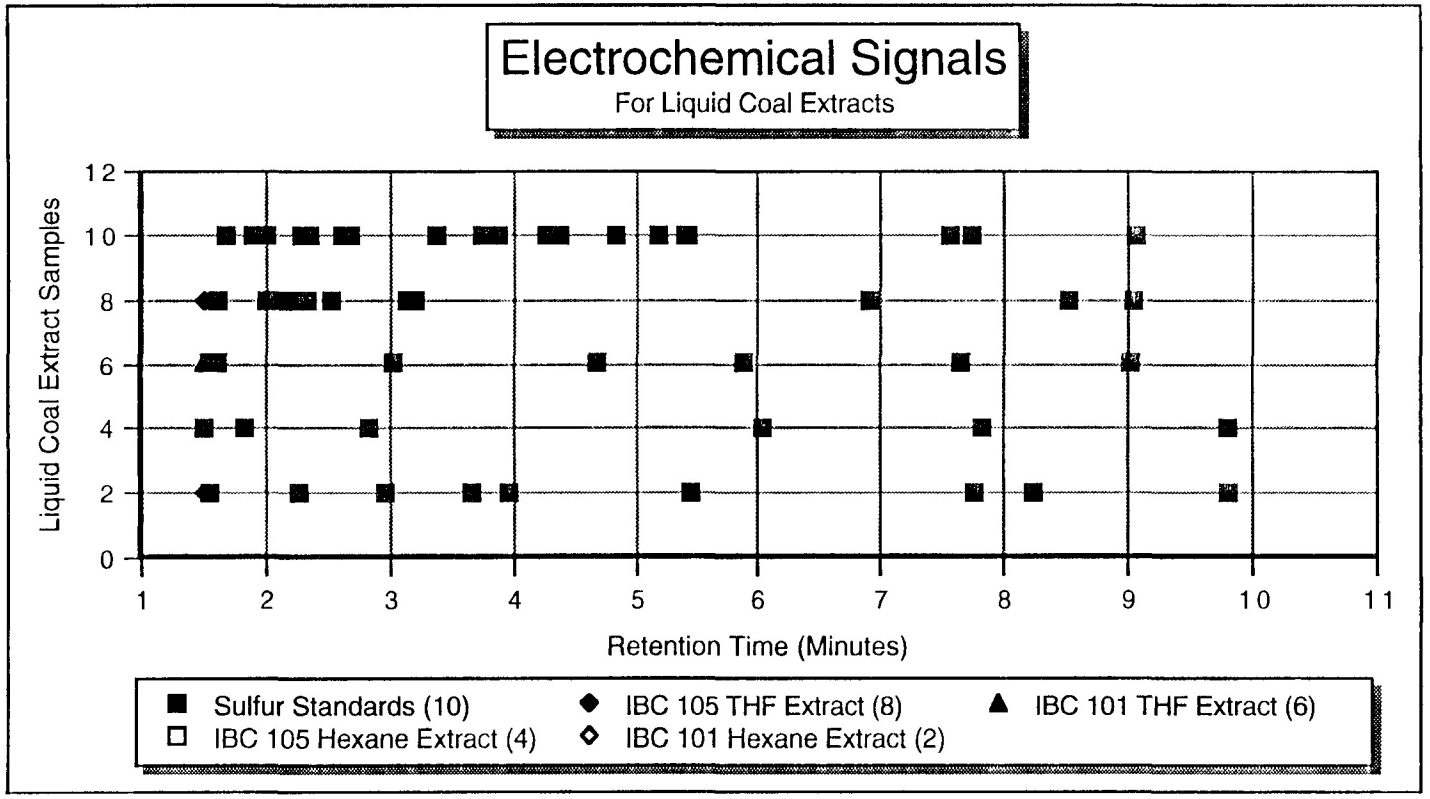

Figure 54. Graph of Data For Electrochemical Signals For Liquid Coal Extracts.

The data suggests that THF is reasonably successful in extracting possible organosulfur compounds that can be detected by electrochemical analysis. The electrochemical retention times of the compounds in the IBC-101 and IBC-105 liquid coal extracts matched, reasonably well, the retention times for the model organosulfur compounds examined such as thiols, sulfides, disulfides, and small aromatic compounds.

The THF extracted coal liquid from IBC-105 produced 13 electrochemical responses, while the UV analysis of the sample produced 10 UV responses (Tables 12 and 13). This information tends to suggest that more compounds are detectable with electrochemical methods as compared to UV methods for this coal sample. If the dibenzothiophene retention time (8.51 minutes) is used as a benchmark, UV analysis suggest that approximately 50% of the detectable compounds are smaller than dibenzothiophene, while EC detection suggests that 85% of the compounds are smaller.

The THF extracted coal liquid from IBC-101 produced nine electrochemical responses, while the UV analysis of this sample produced 11 responses (Tables 12 and 13). This information tends to suggest that more compounds are detectable by UV methods as compared to electrochemical methods for this coal sample. If the dibenzothiophene retention time (8.51 minutes) is used as a benchmark, UV analysis suggests that approximately 64% of the detectable molecules are smaller, while electrochemical detection suggests that 78% of the detectable compounds are smaller than dibenzothiophene.

Hexane was used as a solvent to extract coal samples IBC-105 and IBC-101 for UV analysis. The UV analysis of the fractionated liquid coal extract of IBC-105 produced 4 detectable responses, while the UV analysis of IBC-101 produced 7 detectable UV responses (Table 12).

An analysis of the retention times suggest different compounds were responsible for each UV response for both samples of IBC-101 and IBC-105 (hexane extraction). The retention times ranged from 1.46 minutes to 9.74 minutes for the hexane extracted

TABLE 14

Percent of Retention Times Higher or Lower Than Dibenzothiophene

Coal Sample	UV Lower (%)	UV Higher (%)	EC Lower (%)	EC Higher (%)
IBC 105 (THF)	50	50	85	15
IBC 101 (THF)	64	36	78	22
IBC 105 (Hexane)	75	25	86	14
IBC 101 (Hexane)	86	14	89	11

compounds. The data suggests that hexane does extract some compounds or some possible organosulfur compounds that can be detected by UV analysis. The retention times of the extracted compounds matched, reasonably well, the times for the model organosulfur compounds examined such as thiols, sulfides, disulfides, and small aromatic molecules (Table 4).

Hexane was used as a solvent to extract coal samples of IBC-105/90008 and IBC 101/89020-8 for electrochemical analysis. The electrochemical analysis of the fractionated coal liquid extract IBC-105 produced 6 oxidative responses (Table 13). An analysis of the electrochemical retention times suggest three compounds may be present in both of the hexane coal liquid extracts of IBC-101 and IBC-105. The retention times for the electrochemical detection times ranged from 1.35 minutes to 9.04 minutes for the hexane extracted compounds (Table 13).

The data suggest that hexane does extract some compounds or some possible organosulfur compounds that can be detected by electrochemical analysis. The retention times of the compounds in the IBC-101 and IBC-105 fractionated hexane coal extracts matched, fairly well, the retention times for the model organosulfur compounds examined such as thiols, sulfides, disulfides, and small aromatic compounds such as dibenzothiophene (Table 4).

Hexane extracted coal liquid IBC-105 produced 6 EC responses, while the UV analysis of the sample produced 4 UV responses. This information tends to suggest that more compounds are detectable by electrochemical methods than by UV methods for this coal sample. If the dibenzothiophene retention time (8.51 minutes) is used as benchmark, UV analysis suggests that 75% of the detectable compounds are smaller, while EC detection suggests that 86% of the compounds are smaller than dibenzothiophene.

The hexane extracted coal liquid IBC-101 produced 9 EC responses, while the UV analysis of this sample produced 7 response. This information tends to suggest that more compounds are detectable by electrochemical methods than by UV methods for this coal

sample. If the dibenzothiophene retention time (8.51 minutes) is used as a benchmark, UV analysis suggests 86% of the detectable molecules are smaller, while electrochemical detection suggests 89% of the detectable compounds are smaller than dibenzothiophene.

For IBC-105 (THF extract), an analysis of the data for the electrochemical detection and UV detection shows 7.76 as the only retention time that matched, while two other retention times were close enough to warrant saying they might be due to the same compound (Table 13).

For IBC-101 (THF extract), an analysis of the data for the electrochemical detection and the UV detection shows no matches for retention times. However, electrochemical detection analysis does reveal a retention time that appears in the THF extract for both IBC-101 and IBC-105.

For IBC-105 (hexane extract), an analysis of the data for electrochemical detection and UV detection does not show any matches for retention times. However, electrochemical analysis does reveal a retention time that appears in the THF extracts for both IBC-105 and IBC-101.

For IBC-101 (hexane extract), an analysis of the data for electrochemical detection and UV detection does not show any matches for retention times. However, a retention time of 7.74 appears in the IBC-101 (hexane extract) as well as in the other extracts examined.

THF appears to be a better extraction solvent for UV analysis as compared to hexane. UV analysis of the fractionated THF coal liquid extract produced a total of 21 UV responses; whereas, the UV analysis of the fractionated hexane coal liquid extract produced only 11 UV responses. The UV data indicates several kinds of molecules were present in the extract. The data collected was typical of the model organosulfur compounds evaluated such as thiols, sulfides, disulfides, and small aromatic molecules.

THF appears to be a better extraction solvent for electrochemical analysis as compared to hexane. Electrochemical analysis of the THF liquid coal extract produced a

total of 22 responses, whereas, the electrochemical analysis of the fractionated hexane liquid coal extract produced only 15 electrochemical responses. The electrochemical data indicate several kinds of molecules were present. The data collected was typical of the model organosulfur compounds evaluated such as thiols, sulfides, disulfides, and small aromatic molecules.

E. Fractionation of Liquid Coal Extracts

IBC-105 THF coal liquid extract (15.9946 grams), IBC-101 THF coal liquid extract (20.8630 grams), IBC-105 hexane coal liquid extract (19.6800 grams), and IBC-101 hexane coal liquid extract (19.7419 grams) were each fractionated on a column of neutral alumina. Each column was eluted with hexane, benzene, chloroform/ethanol, and THF/ethanol which resulted in the coal liquid extracts being fractionated into seven possible chemical classes by this method.

The seven fractions should have contained the following groups. The hexane fraction should have contained aliphatic hydrocarbons. The benzene fraction should have contained neutral polycyclic aromatic compounds such as PAH, PAOH, and PASH. The chloroform/ethanol fraction should have contained nitrogen polycyclic aromatic compounds such as 2-PANH, APAH, and 3-PANH. And the tetrahydrofuran/ethanol fraction should have contained hydroxy polycyclic aromatic hydrocarbons.

As the various fractions were collected, they became progressively darker in color suggesting a higher concentration of extracted compounds. The hexane and benzene fractions should have contained the organosulfur compounds of interest. These fractions were a light yellow color which suggested a low concentration of extracted compounds.

The four hexane fractions were the only fractions to be analyzed with HPLC with UV and electrochemical detection. The other fractions contained very high concentrations of extracted compounds which were unsuitable for the present HPLC column.

After analyzing the results, several points became clear. First, the hexane and benzene fractions contained compounds of interest. Second, the extraction procedure

needs to be scaled up so larger amounts of coal liquid extracts can be fractionated. This would produce higher concentrations of the desired compounds in each fraction which would lead to an easier electrochemical analysis. Third, the concentrations of the detected compounds varied a great deal. Chemicals in high concentrations tended to obscure chemicals in lower concentrations. And fourth, the fractionation scheme did produce adequate results for the present investigation of thiols, sulfides, disulfides, and small aromatic molecules in liquid coal extracts.

F. IR Analysis of Fractionated Coal Liquid Extracts

IR analysis is usually important in identifying an organosulfur compound class such as mercaptans, sulfides, disulfides, sulfoxides, sulfones, sulfinic acids, sulfonic acids, sulfonyl chlorides, sulfonamides, sulfonate esters, and sulfates. In this investigation IR analysis was directed at the detection of sulfides, disulfides, mercaptans, and small organic molecules in liquid coal extracts.

The liquid coal fractions were evaporated to dryness and redissolved in carbon tetrachloride. A small aliquot was placed between two sodium chloride plates. The samples were analyzed by scanning from 4400 to 450 reciprocal centimeters.

The most common absorption bands were around the values of 1070, 1470, 3100, 3050, and 800 which suggested C-O stretch, C=C stretch, O-H stretch, and C-H stretch and C-H bend. There was no IR evidence/data to confirm the presence of the organosulfur compounds of interest. This information suggests a great deal more attention should be directed at concentrating the desired compounds in the liquid extracts prior to analysis. However, since the sulfur-sulfur bond in disulfides is readily cleaved with common reagents, the effort to concentrate some of the desired compounds may not produce the desired analytical results.

Mercaptans are characterized by the S-H stretch (2600-2550 cm^{-1}). These compounds produce weak band intensities. The IR scans did not show any evidence of the S-H stretch for any sample analyzed. High concentrations of mercaptans are usually

required for detection. Mercaptans can be easily oxidized to disulfides under mild conditions. IR analysis of disulfides produce very weak and unusable signals. Sulfides are not very well characterized by IR analysis. The most important stretch is the C-S stretch. This stretch is extremely weak and is not usually useful. There was no evidence for the presence of S-H stretch in any of the samples analyzed.

IR spectrometry is not usually useful for detecting disulfides. The C-S and S-S stretches are very weak and usually not useful (Table 15).

G. Chemical Test For Mercaptans

Mercaptans can be detected by the formation of a yellow precipitate when mixed with saturated lead (II) acetate in ethanol. Thiols produce a yellow precipitate as follows:[56]

$$RSH + Pb(II) + 2H_20 \text{ ----> } 2H_30^+ + Pb(SR)_2 (s)$$

Each liquid coal sample, IBC 101 (THF), IBC 105 (THF), IBC 101 (hexane), IBC 105 (hexane), was fractionated using hexane, benzene, chloroform/ethanol, and THF/ethanol solvents (Figure 5). Hexane and benzene fractions were tested for mercaptans using lead (II) acetate in ethanol. All samples produced a precipitate. The data in Table 16 suggests, mercaptans, may be present in low concentrations in the liquid coal extract fractions. THF and chloroform fractions gave positive test for organosulfur compounds. Their high compound concentrations inhibited further analysis. These compounds were not thought to contain compounds of interest.

Other procedures such as the nitrosation of mercaptans and the treatment of mercaptans with Benedict's solution did not produce any positive test results for the liquid coal extracts. All test results were negative.

H. Sulfur Content of Coal Samples

Two coal samples were selected for use in this investigation, IBC 105 and IBC 101. IBC 101 and IBC 105 coal samples were analyzed for total sulfur content prior to extraction with THF and hexane solvents. IBC 101 had a 3.58% sulfur content, while

TABLE 15

Organosulfur Compounds and Related Infrared Data

Compound	General Structure	Important IR Vibrations	Reciprocal Centimeters
Mercaptans	RSH	S-H stretch	2600-2550 (Weak)
Sulfides	RSR	C-S stretch	Extremely weak
Disulfides	RSSR	C-S stretch S-S stretch	Usually not useful Usually not useful
Thiophenols	ArSH	S-H stretch	2560-2550 (Weak)

TABLE 16

Wet Test Results For Organosulfur Compound Detection in Liquid Coal Extracts

Coal Sample Analyzed	Reaction With Saturated Lead (II) Acetate in Ethanol (Precipitate Yes/No)	
	Hexane Fraction	Benzene Fraction
IBC 105 Hexane Extract	Yes	Yes
IBC 101 Hexane Extract	Yes	Yes
IBC 105 THF Extract	Yes	Yes
IBC 101 THF Extract	Yes	Yes

IBC 105 had a sulfur content of 4.12%. This data indicates IBC 105 had a higher sulfur content as compared to IBC 101 (Tables 17, 20, and 21).

IBC 101 and IBC 105 coal samples (solid) were analyzed for total sulfur content after extraction with THF solvent. IBC 101 had a total sulfur content of 3.83%, while IBC 105 had a sulfur content of 4.50% (Tables 17, 22, and 23). These values were higher as compared to the percent sulfur content prior to extraction. THF does not extract mineral sulfur, while it does extract the organic fraction. Consequently, the total sulfur in the residue increases. However, the organic sulfur in the THF extract is higher than it is in the raw coal. The total sulfur content increased 0.257% for IBC 101, while it increased 0.394% for IBC 105. THF is more effective for sulfur enrichment for coal sample IBC 105.

IBC 101 and IBC 105 THF extracted coal samples were treated with nitric acid to remove nonorganic sulfur (Tables 17, 24, and 25). After treatment, IBC 101 had a total sulfur content of 2.20%, while IBC 105 had a total sulfur content of 1.71%. IBC 101 had 1.637% nonorganic sulfur content removed, while IBC 105 had 2.804% nonorganic sulfur removed. This information indicates that IBC 101 had a higher organic sulfur content in the final samples as compared to IBC 105.

IBC 101 and IBC 105 coal liquid extracts (liquid) were analyzed for the total sulfur content. The coal liquid extract of IBC 101 had a total sulfur content of 0.171%, while the coal liquid extract for IBC 105 had a total sulfur content of 0.077%. IBC 101 THF coal liquid extract had approximately 2.22 times more sulfur content as compared to IBC 105. THF extracted more sulfur compounds from the IBC 101 coal sample (Table 17 and Figures 55 and 56).

IBC 101 and IBC 105 coal samples were extracted with hexane. The solid coal extracts were ruined. The procedure should have ended after extraction, I followed the entire procedure. Therefore, there is no data for the hexane extracted solid coal samples of IBC 101 and IBC 105. My investigation focused on the contents of the liquid extract.

TABLE 17

Percent Sulfur in Coal Samples

Coal Sample Analyzed	Percent Sulfur Reported On a As-Determined Basis (%)
IBC 101 (No Extraction)	3.58
IBC 105 (No Extraction)	4.12
IBC 101 (THF Extracted)	3.83
IBC 105 (THF Extracted)	4.51
IBC 101 (THF and Nitric Acid)	2.20
IBC 105 (THF and Nitric Acid)	1.71
IBC 101 (THF Coal Liquid Extract)	0.17
IBC 105 (THF Coal Liquid Extract)	0.07
IBC 101 (Hexane Coal Liquid Extract)	0.06
IBC 105 (Hexane Coal Liquid Extract)	0.05
THF Blank	0.04
Hexane Blank	0.06

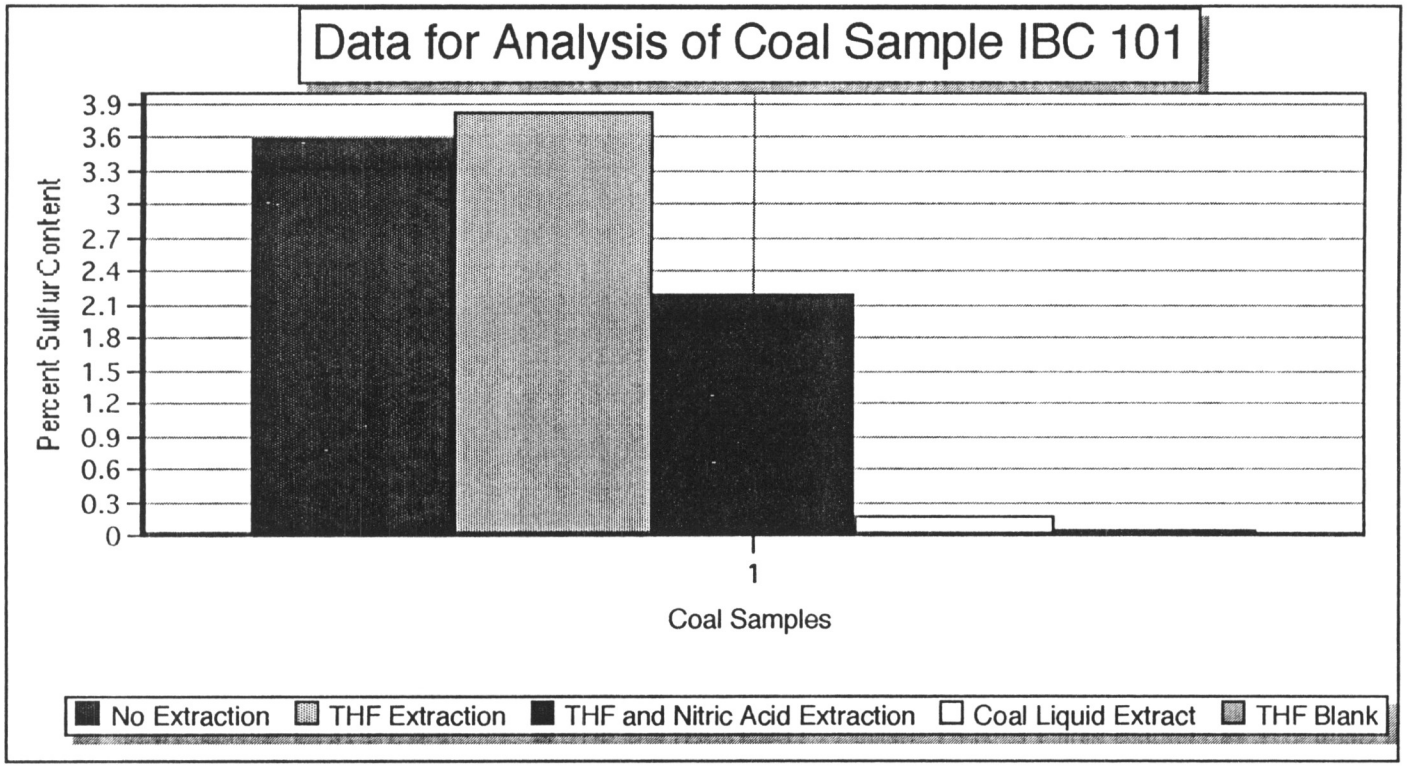

Figure 55. Graph of Data For Coal Sample IBC 101.

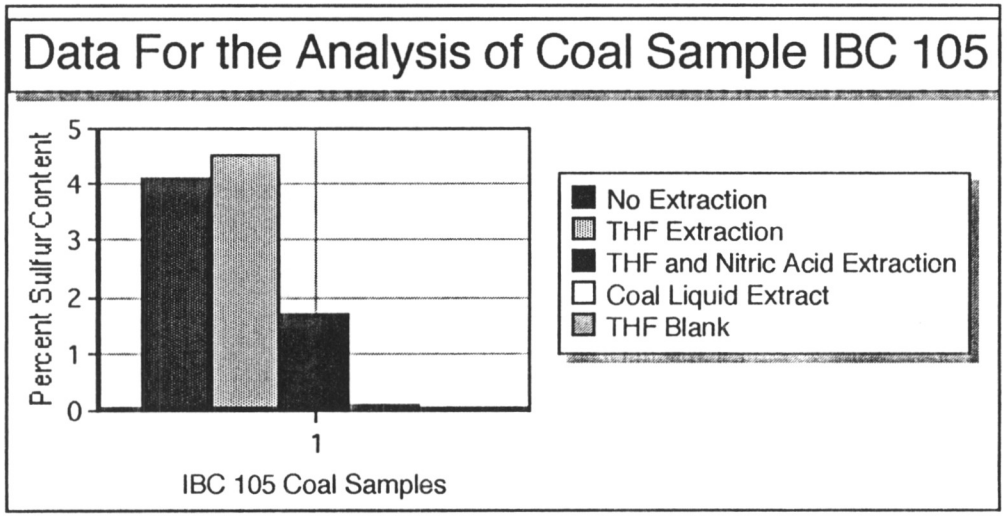

Figure 56. Graph of Data For Coal Sample IBC 105.

The total sulfur content of the hexane coal liquid extracts was 0.06% for IBC 101, while it was 0.054% for IBC 105 (Figure 57). These values are very close to the blank values for hexane (0.058%). Hexane is a very poor extraction solvent for these coal samples. The extracts did develop a very light greenish yellow color suggesting some compounds were extracted.

For THF extracted coal samples, the electrochemical and UV responses seemed to match the total sulfur content. The higher the sulfur content the greater the number of UV and electrochemical responses.

For the hexane extracted coal samples, electrochemical and UV responses seemed to match the percent of organic sulfur present. The higher the percentage of organic sulfur in the sample, the higher the number of responses obtained.

The THF coal liquid extract of IBC 105 gave more UV and electrochemical responses than the liquid extract of IBC 101. The IBC 101 coal sample had approximately 2.22 more sulfur content as compared to IBC 105. Apparently, different kinds of organosulfur compounds were in IBC 101 as compared to IBC 105 or the solvents selectively extract particular types of organosulfur compounds.

In the THF extraction process for IBC 101, a total of 26.3376 grams were extracted with 450 mL of THF solvent (Table 18). The THF extraction process removed approximately 2.1949 grams of material from the coal matrix. This was approximately 8.33% of the total mass. The THF extract had an approximate compound concentration of 4.877×10^{-3} grams/mL. Sulfur analysis of coal sample IBC 101 indicated a 0.171% sulfur composition for the THF liquid coal extract. Calculations suggest the total sulfur content was approximately 8.3396×10^{-4} grams/mL for the THF liquid coal extract.

A sample weighing 20.8603 grams of the IBC 101 coal liquid was fractionated on the neutral alumina column. The material was diluted with 20 mL of hexane. The approximate compound concentration in the hexane fraction was 1.01×10^{-1} grams/20 mL or 5.086×10^{-3} grams /mL for the total compound concentration and 8.69×10^{-4} for the

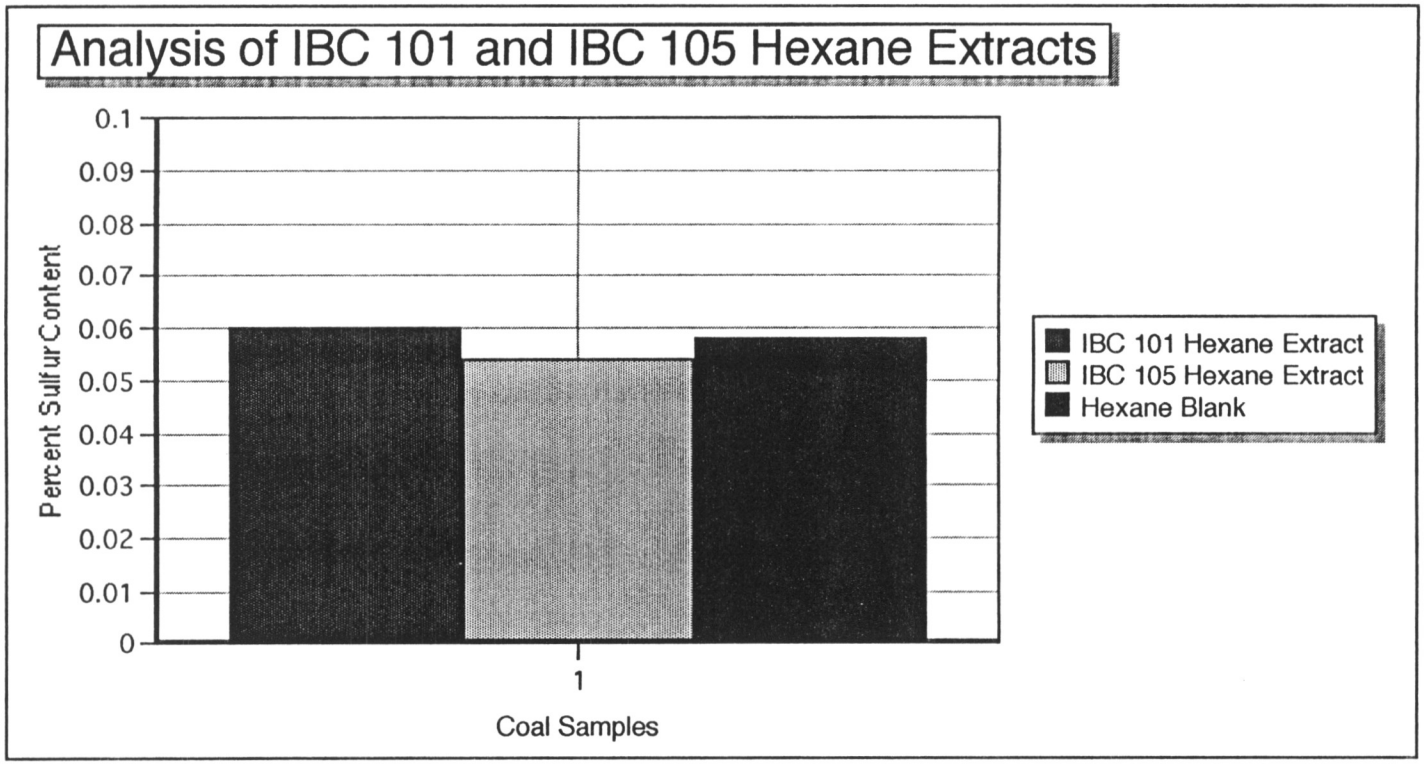

Figure 57. Graph For Percent Sulfur in Hexane Blanks For Samples IBC 101 and IBC 105.

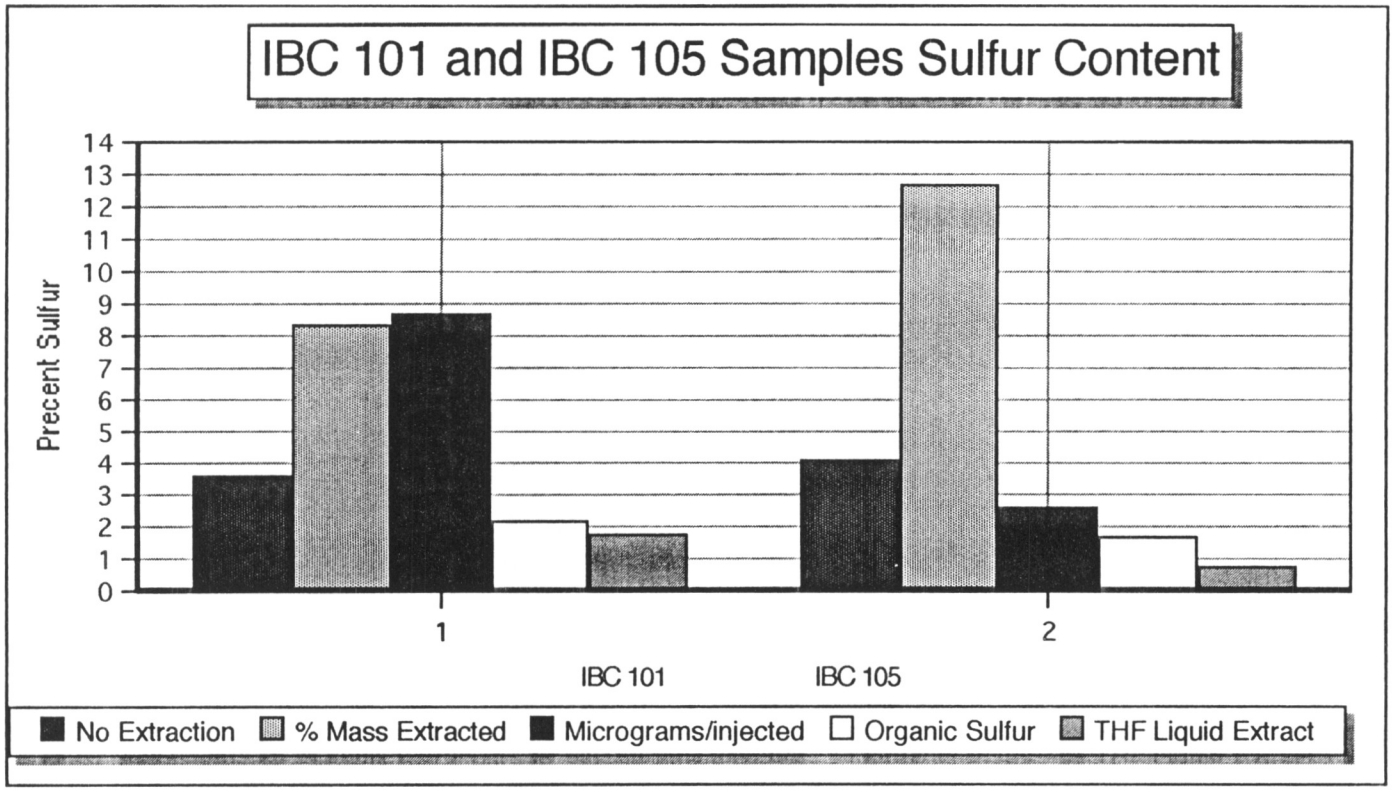

Figure 58. Comparison of the Percent Sulfur in Coal Samples IBC 101 and IBC 105.

TABLE 18

Data For Determination of Mass Extracted From IBC 101 and IBC 105 Coal Samples Using THF as a Solvent

Coal Sample	Mass of Dried Coal and Thimble Prior to Extraction (grams)	Mass of Thimble and Coal After Heating to a Constant Mass After Extraction (grams)	Mass Loss (grams)
IBC 105	13.0408	11.9257	1.1151
IBC 105	12.8831	11.7127	1.1704
IBC 105	12.7621	11.5862	1.1759
IBC 101	12.0676	11.3580	0.7096
IBC 101	12.4829	11.6930	0.7899
IBC 101	12.0799	11.3845	0.9654

sulfur compounds. Five mL aliquots of the hexane extract were evaporated to dryness and redissolved in 2 mL of mobile phase. The total concentration of all the compounds was approximately 2.03 X 10^{-3} grams/mL, while the total sulfur compound concentration was approximately 3.47 X 10^{-4} grams/mL. The total concentration of all the compounds was 2023 ng/microliter, while the total sulfur content was 345 ng/microliter. Assuming a 25 microliter injection syringe was used, the total sulfur concentration injected onto the column per run would be approximately 8625 ng/injection.

In the THF extraction process for IBC 105, a total of 27.3702 grams of IBC 105 was extracted with 450 mL of THF solvent. The THF solvent extracted 3.4614 grams of materials from the coal matrix (Table 18). This was approximately 12.64% of the total mass. The total concentration of all compounds in the THF extract was approximately 7.69 X 10^{-3} grams/mL. Sulfur analysis of coal sample IBC 105 indicated a 0.077% sulfur composition for the THF liquid extract. The approximate sulfur content was 5.92 X 10^{-4} grams/mL.

A sample weighing 15.9946 grams of the IBC 105 coal liquid extract was fractionated on the neutral alumina column. It was diluted to 20 mL with hexane. The total concentration of all compounds in the hexane fraction was approximately 6.788 X 10^{-2} grams/20 mL or 3.39X10^{-3} grams/mL and 2.61 X 10^{-4} grams/mL for the sulfur compounds. Five mL aliquots of the hexane extract were evaporated to dryness and redissolved in 2 mL of the mobile phase for UV and electrochemical analysis. The total concentration of all compounds was 1.35 X 10^{-3} grams/mL, while the sulfur compound concentration was approximately 1.04 X 10^{-4} grams/mL. The concentration of all the extracted compounds was 1350 ng/microliter, while the total concentration of all the extracted sulfur compounds was approximately 104 ng/microliter. Assuming a 25 microliter syringe was utilized, the total sulfur concentration injected onto the column per run would be approximately 2600 ng/injection.

In the hexane extraction process, 27.3639 grams of IBC 105 and 26.4928 grams of IBC 101 (Table 19) were extracted using hexane. Amount of extracted material was not determined due to loss of sample. The procedure was followed completely.

A sample weighing 19.6800 grams of IBC 105 and 19.7419 grams of IBC 101 coal liquid extracts were fractionated on the neutral alumina column. The sample was diluted with 20 mL of hexane. The approximate compound concentration could not be determined for all compounds or the sulfur compounds. Six mL aliquots of the hexane IBC 101 and IBC 105 coal liquid extracts were evaporated to dryness and redissolved in 2 mL of the mobile phase for UV and EC analysis.

Coal IBC 105 had better UV and electrochemical responses with 2600 ng/injection amount for the sulfur compounds, while IBC 101 responses were poorer with higher total sulfur concentration of 8625 ng/injection amount. More sulfur was extracted out of IBC 101 as compared to IBC 105 (approximately 3.31 times more). However, the responses match the amount of organic sulfur in the samples. IBC 105 had a higher organic sulfur content.

TABLE 19

Data For Determination of Mass Extracted From IBC 101 and IBC 105 Coal Samples Using Hexane as a Solvent

Coal Sample	Mass of Dried Coal Added to Thimble For Extraction (grams)
IBC 105	9.0405
IBC 105	9.1048
IBC 105	9.2186
IBC 101	8.7439
IBC 101	8.8936
IBC 101	8.8553

Table 20

IBC 101 Coal Sample-No Extraction

PROXIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Moisture	27.92	13.83	NA	NA
Ash	7.31	8.75	10.16	NA
Vol. Matter	27.16	32.48	37.69	41.89
Fixed Carbon	37.57	44.93	52.14	57.95
Total	99.96	99.99	99.99	99.84

ULTIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Carbon	55.51	66.37	76.98	85.61
Hydrogen	12.31	14.72	17.07	18.98
Nitrogen	00.00	00.00	00.00	00.00
Sulfur	2.99	3.58	4.15	4.61
Oxygen	5.50	6.58	7.60	8.48

FORMS OF SULFUR

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Pyritic	1.36	1.63	1.89	2.10
Sulfate	0.21	0.26	0.30	0.33
Organic	1.83	2.20	2.56	2.84
Total Sulfur	3.40	4.09	4.75	5.27

TABLE 21

IBC 105 Coal Sample-No Extraction

PROXIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Moisture	24.54	9.79	10.84	NA
Ash	14.22	17.01	18.86	NA
Vol. Matter	26.83	32.08	35.56	43.82
Fixed Carbon	34.38	41.11	45.57	56.15
Total	99.97	99.99	110.83	99.97

ULTIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Carbon	55.40	66.24	73.39	90.48
Hydrogen	11.92	14.26	15.80	19.47
Nitrogen	00.00	00.00	00.00	00.00
Sulfur	3.44	4.12	4.56	5.62
Oxygen	1.36	1.63	1.10	2.22

FORMS OF SULFUR

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Pyritic	1.67	2.02	2.21	2.75
Sulfate	0.36	0.39	0.43	0.53
Organic	1.43	1.71	1.89	2.33
Total Sulfur	3.46	4.12	4.53	5.61

TABLE 22

IBC 101 THF Extracted Coal Sample

PROXIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Moisture	17.30	1.13	NA	NA
Ash	8.59	10.28	10.40	NA
Vol. Matter	29.47	35.24	35.65	39.77
Fixed Carbon	44.61	53.34	53.95	60.20
Total	99.97	99.99	100.00	99.97

ULTIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Carbon	51.92	62.08	62.78	70.02
Hydrogen	2.94	3.52	3.56	3.97
Nitrogen	0.91	1.09	1.10	1.22
Sulfur	3.20	3.83	3.88	4.32
Oxygen	16.05	19.19	19.40	21.64

FORMS OF SULFUR

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Pyritic	1.14	1.37	1.38	1.54
Sulfate	0.21	0.263	0.26	0.29
Organic	1.83	2.20	2.22	2.48
Total Sulfur	3.18	3.83	3.86	4.31

TABLE 23

IBC 105 - THF Extracted Coal Sample

PROXIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Moisture	17.27	1.09	NA	NA
Ash	16.69	19.93	20.15	NA
Vol. Matter	26.05	31.15	31.49	39.44
Fixed Carbon	40.00	100.00	99.99	99.99

ULTIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Carbon	49.16	58.78	59.42	74.41
Hydrogen	4.82	3.59	3.62	4.54
Nitrogen	0.92	1.10	1.11	1.39
Sulfur	3.77	4.51	4.56	5.71
Oxygen	10.10	12.08	12.21	15.29

FORMS OF SULFUR

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Pyritic	2.00	2.40	2.42	3.03
Sulfate	0.32	0.39	0.39	0.49
Organic	1.43	1.71	1.72	2.16
Total Sulfur	3.75	4.50	4.53	5.68

TABLE 24

IBC 101 THF and Nitric Acid Extraction

PROXIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Moisture	17.11	0.90	NA	NA
Ash	5.48	6.56	6.62	NA
Vol. Matter	42.98	51.39	51.86	55.50
Fixed Carbon	34.40	41.13	4.51	44.42
Total	99.97	99.98	62.99	99.92

ULTIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Carbon	67.69	80.94	81.66	87.41
Hydrogen	17.24	20.62	20.82	22.26
Nitrogen	00.00	00.00	00.00	00.00
Sulfur	1.84	2.20	2.21	2.37
Oxygen	00.00	00.00	00.00	00.00

FORMS OF SULFUR

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Pyritic				
Sulfate				
Organic	1.84	2.20	2.21	2.37
Total Sulfur				

TABLE 25

IBC 105 - THF and Nitric Acid Extraction

PROXIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Moisture	16.97	0.74	NA	NA
Ash	10.82	12.94	13.04	NA
Vol. Matter	35.27	42.17	42.48	48.83
Fixed Carbon	36.91	44.13	44.47	51.10
Total	99.97	99.98	99.99	99.93

ULTIMATE ANALYSIS

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Carbon	69.58	83.20	83.78	96.34
Hydrogen	16.95	20.27	00.00	00.00
Sulfur	1.43	1.71	1.72	1.98
Oxygen	00.00	00.00	00.00	00.00

FORMS OF SULFUR

ANALYSIS	AS RCVD	AS DETD	DRY BASIS	DAF
Pyritic				
Sulfate				
Organic	1.43	1.71	1.72	1.98
Total Sulfur				

IV. SUMMARY

An analysis of the cyclic voltammetry data indicates that few compounds should be detectable in the acetonitrile/water mobile phase. The oxidation potentials were in general much higher than the 1.20 volt upper limit reported in the literature for the carbon electrode in aqueous solutions.[40] The cyclic voltammetry data collected seem to match those values found in the literature. However, as each standard organosulfur compound was detected separately using HPLC with EC detection, it became clear that most standard organosulfur compounds gave a detectable response at 1.250 volts using the acetonitrile/water mobile phase with a carbon electrode. The HPLC and EC detection system seems to be able to detect compounds at a lower potential (0.30 volts lower) than expected.

An analysis of the coal extraction process would indicate THF to be a better extraction solvent as compared to hexane. The THF extract contained more sulfur compounds as compared to the hexane extract. However, the THF extract also extracted a larger amount organosulfur compounds resulting in an enrichment of sulfur compounds in the solid coal sample. In this type of analytical process, the removal of the sample's organic sulfur content seems to determine the number of UV and electrochemical responses. THF appears to be an acceptable extraction solvent for this research.

After extraction of the coal, the liquid coal extract needs to be reduced to a smaller volume. Volume reduction might produce a higher concentration of the desired compounds, thus leading to more UV and EC responses. The liquid coal extract volume was not reduced enough in the present research. Thiols, disulfides, and sulfides are volatile at fairly low temperatures; thus in order to retain these compounds, a procedure or technique that minimizes loss of these compounds needs to be utilized during solvent

reduction. In this process, one also needs to minimize the sample's exposure to air because thiols readily convert to other compounds in air.[22]

The fractionation process was deemed to be adequate for separating the liquid coal extracts into seven possible chemical classes.[36] However, a great deal more effort needs to be directed at removing the organosulfur compounds from the fractionated extracts by using appropriate techniques mentioned in the literature. The organosulfur compounds were adequately separated by chemical class, but they were not adequately concentrated. The sulfur concentration could probably be performed by a procedure reported by Lee and coworkers.[36] I did not utilize $PdCl_2$ in the chromatographic column. At this point, derivatization should have been considered for the thiols. Derivatization might have produced more consistent results.

The UV analysis of the liquid coal extracts provided information as to whether UV detectable compounds were eluting from the HPLC column. The UV analysis of the standard organosulfur compounds and the liquid coal extracts served as a framework upon which one could evaluate the feasibility of an electrochemical analysis. In this process dibenzothiophene appears to be an excellent compound to use as a benchmark to gauge the nature of the molecules as they elute from the column. Dibenzothiophene provided a fairly good UV and EC response during the research.

The EC analysis did provide some detectable responses. These responses were within the range of responses found for the model organosulfur compounds. The EC analysis of the liquid coal extracts provided a higher number of responses as compared to the UV analysis. Electrochemical analysis is more sensitive and selective as compared to the UV analysis. This sensitivity and selectivity might be greatly enhanced by using a dual Hg electrode at a lower oxidation potential (0.20 volts). There was some sensitivity and selectivity demonstrated in this research with the use of the carbon electrode. The carbon electrode appears to be an all purpose electrode; but for the detection of the thiols, sulfides,

and disulfides in this research, a dual mercury electrode may be more productive. However, the carbon electrode use may be justified in such a procedure as this due to mercury's toxic nature and rapid depletion from the electrode surface.

After equilibrating the equipment, EC analysis appears to be no more difficult than UV analysis. Electrochemical analysis of the liquid coal extracts appears to support the idea that EC analysis can be used in the analysis of complex samples such as liquid coal extracts.

Infrared analysis was performed for each liquid coal extract. There were sixteen fractions produced from the fractionation procedure. In the IR spectra, there was no evidence to suggest thiols, sulfides, and disulfides were present. IR analysis appears to be more appropriate for other classes of sulfur compounds such as sulfones. At this point in the liquid coal extracts' analysis, NMR may have been a more appropriate technique to use to provide supporting evidence for the confirmation of organosulfur compounds.

The combined results of the overall research has demonstrated that it may be possible to use reverse phase HPLC with electrochemical detection to detect a general class of organosulfur compounds or to detect a specific organosulfur compound in a liquid coal extract.

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