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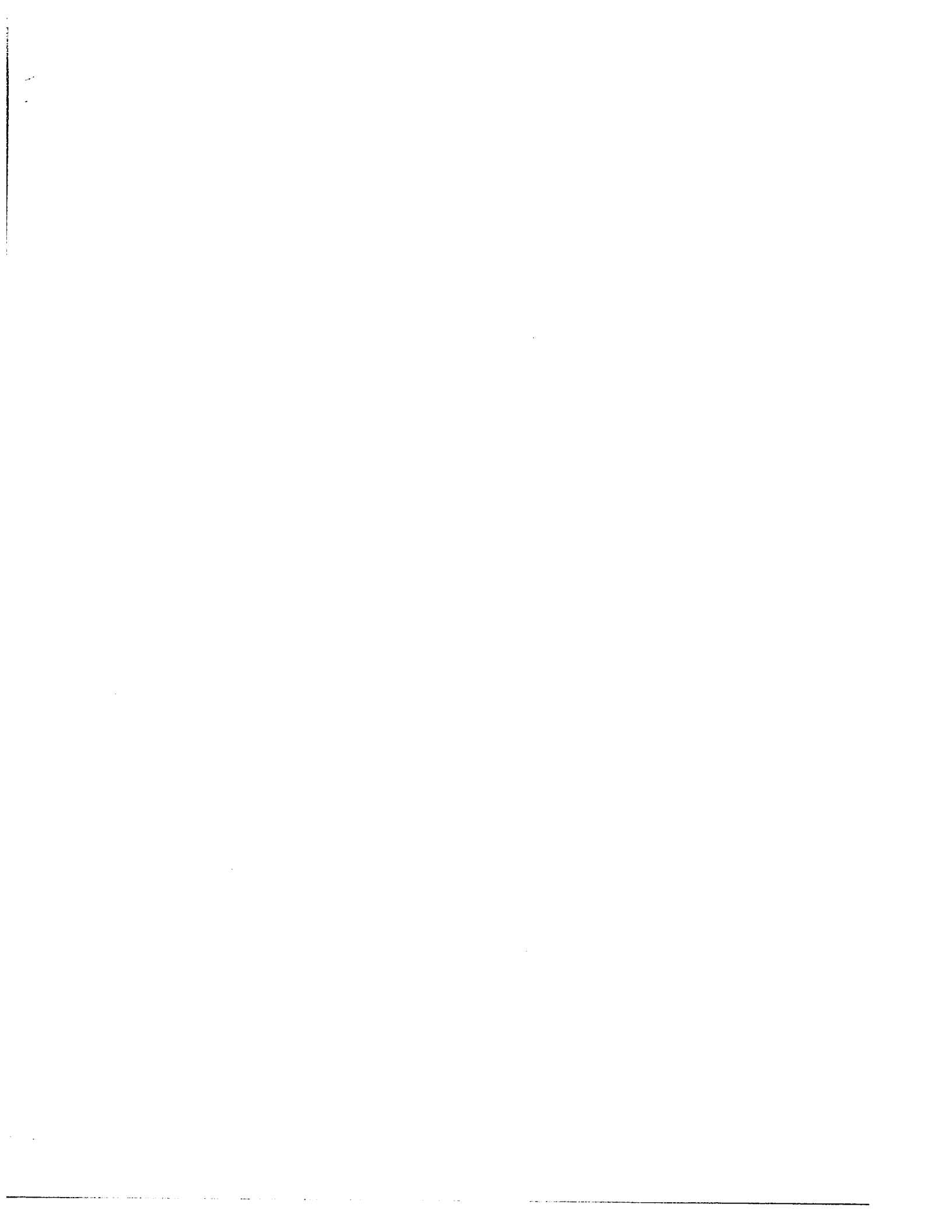
Anodic stripping voltammetry of nickel at a graphite electrode

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San Jose State University, 1994
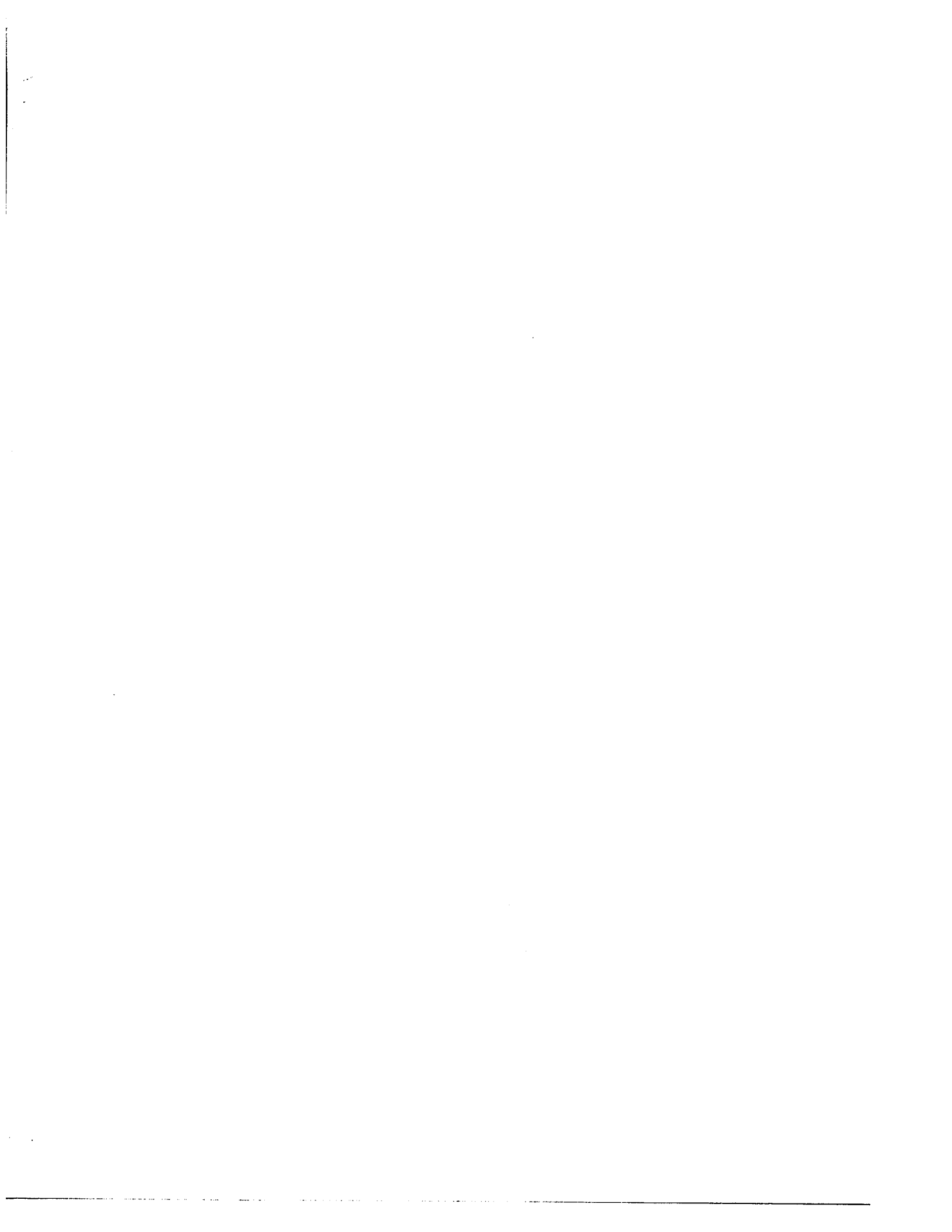
Anodic Stripping Voltammetry of Nickel at a Graphite Electrode

A Thesis
Presented to
The Faculty of the Department of Chemistry
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Satpal Singh
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Abstract

ANODIC STRIPPING VOLTAMMETRY OF NICKEL AT A GRAPHITE ELECTRODE

by Satpal Singh

The determination of nickel ions by anodic stripping voltammetry (ASV) with the Wax Impregnated Graphite Electrode (WIGE) was investigated. It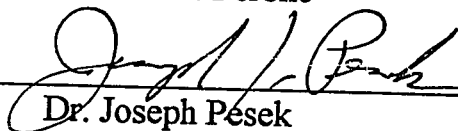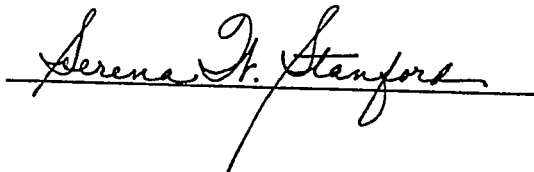 was demonstrated that the graphite microelectode can be used to analyze nickel ions down to trace levels (10^{-4} to 10^{-9}M). Four different types of supporting electrolyte were examined, but Potassium thiocyanate medium was selected for the best results. Nickel was deposited at the graphite electrode at constant potential. The deposited nickel metal was stripped by anodic voltammetry with linearly varying potential, and the total electricity (Coulombs) involved in the stripping peaks was measured. The stripping coulombs are directly proportional to the concentration of nickel ions and electrolysis time.

Our main objective is to develop a graphite microelectrode for chemical sensor applications that involve the use of relatively non-selective microelectrode elements coupled with pattern recognition methods for data analysis. A potential application for this microelectrode is as part of microelectrode arrays for chemical sensors which might be used for monitoring waste treatment plants, quality control in plating processes, or monitoring toxic contaminants in natural, river or sea water. Waste water quality after treating the electroless nickel in Akashic Substrates was investigated. The trace level of nickel ions released to sewer system was determined by using graphite electrode ASV, and test results were compared with Atomic Absorption Spectroscopy.

ACKNOWLEDGMENTS

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Chapter 1

Background

In recent years, an increasing demand for environmental monitoring has stimulated the interest of analytical chemists to develop sensitive, selective and portable detection systems. The substances of interest in environmental water analysis include heavy metals and organic compounds. Analytical chemists from Lawrence Livermore National Laboratory are developing an electrochemical sensor to aid in the waste reduction efforts for plating operations and also in environmental redemption. An important feature of these sensor systems is a solid-state multielement microelectrode array. The individual elements of these arrays are selected so that a variety of electroactive chemical species can be detected by using a single device. [1,2,3]

The Lawrence Livermore National Laboratory chemists also developed a compact electronic package, consisting of a potentiostat, signal generator, and microcomputer with software to use in conjunction with the arrays. They used photolithography and microfabrication techniques to develop the arrays of chemical sensor microelectrodes. [1,3] Electrochemical arrays were used with relatively non-selective individual elements (i.e. each has a substantial response to more than one chemical component) as well as those employing elements with intrinsically greater selectivity. Data analysis using non-selective element arrays involves pattern recognition with the use of artificial neural network techniques.

The work conducted here is directed towards characterization of several different microelectrodes to be used in chemical sensor arrays. For these studies, we are conducting

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a systematic series of experiments to evaluate the information content of voltammetric measurements. These findings will be used for chemical sensor design for various specific goals, such as, to detect specific heavy metals in environmental or waste water streams with complex matrices (organics, surfactants, particulates), and in the presence of multiple metallic interferences.

Procedurally, this work will involve the collection of voltammeteric results for nickel ions using wax impregnated graphite microelectrode (WIGE) materials; evaluation of selectivity and detection limits; and collection of information.

1.1 Objectives

In our work we are attempting to determine the feasibility of using graphite microelectrodes and stripping voltammetry to analyze nickel ions quantitatively and qualitatively down to trace levels (10^{-4} - 10^{-9} M). Another specific goal for this study is to determine if graphite electrode material can be used in an electrochemical sensor array development. The purpose for to developing electrochemical sensor arrays are for: (i) continuous waste treatment plant monitoring, (ii) waste minimization and quality control in plating processes, and (iii) developing portable systems for sample and environmental screening, such as, river water, sea water, and natural water. Graphite electrode materials are relatively inexpensive, non toxic, and can be used repeatedly.

1.2 Background in Solid Electrode Development

Electrolytic analysis with solid electrodes was initiated as early as the 1920s by LeBlanc.[4] Following an investigation of the decomposition voltages of acid and base solutions, LeBlanc studied the electrolysis of metal ions. The results of his investigation have little in common with measurements in the field but serve as an impetus for further study.

Heber and Russ[5] also studied the electrolytic reduction of organic compounds in the 1930's by examining the electrochemical properties of gold and platinum metal electrodes. Theoretical studies of rotated electrodes and stirred solutions developed with the work of Nernst, Merriam, and Brunner.[6] The first comprehensive studies of diffusion conditions at solid electrodes were made by Laitinen and Kolthoff.[7] Zlotowski and Rogers were the first to record the automatic solid electrode polarograms.[8]

In early 1960, M. M. Nicholson investigated the use of solid electrodes (platinum and gold) to detect nickel ions at trace levels by using anodic stripping voltammetry.[9] Perone successfully applied the WIGE to determination of heavy metals (Hg and Ag), which was impossible to analyze by the Hanging Mercury Drop Electrode (HMDE).[10,11,12] Perone and Glass more recently have used graphite electrodes as part of electrochemical microelectrode arrays for chemical sensors in waste stream monitoring.[1]

1.3 Why Use Solid Electrodes

The field of anodic stripping voltammetry the using Hanging Mercury Drop Electrode (HMDE) and Thin film Mercury Electrode (TFME) has grown rapidly for industrial analysis, and environmental monitoring. Presently available anodic stripping methods have some serious disadvantages for routine analysis: (i) Thin mercury film electrodes provide low detection limits (10^{-9} M), but suffer the inconvenience and lack of reproducibility of the preliminary step of depositing the mercury film on an inert substrate, such as Pt, Nickel, or Carbon. (ii) It is difficult to maintain the uniform thickness of mercury films on the substrate, and even more difficult to preserve them in an active state for a length of time or when exposed to air. (iii) Some substrates chosen for thin film stripping analysis introduce serious problems on their own, e. g., Pt and nickel have strongly adherent surface oxide films, low hydrogen potentials and solubility in the mercury to form amalgams. (iv) Problems with mercury electrodes are compounded with attempts to include them in an ultramicroelectrode array. (v) Mercury cannot be used to determine mercuric and silver ions. (vi) Mercury is toxic and can contaminate the sample.

Due to the above mentioned difficulties with mercury electrodes, the Wax impregnated Graphite electrode was investigated as an alternative electrode for heavy metal trace analysis. This work is directed particularly at nickel ion stripping voltammetry.

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Chapter 2

2.1 Introduction

Anodic stripping voltammetry (ASV) is a very sensitive electroanalytical technique. This method consists of two steps: (i) in the first step metal ions in the sample solution are reduced at cathodic potential and concentrated at the electrode under controlled conditions of mass transfer; and (ii) the second step involves stripping the electroactive material by applying a positive (anodic) potential scan and measuring the peak currents produced as the system reaches the oxidation potentials of the metals. The resulting voltammogram provides the analytical information of interest. The peak potential E_p also serves to identify the metal in the sample solution.[13, 14, 15] The reaction mechanism of electroactive material that is supplied to a working electrode by the mass transfer process is listed below:

The general reaction is:

$$Ox \quad + \quad ne^- \quad \Leftrightarrow \quad Red$$

This reaction is composed of individual sub steps:

$$(Ox)_{bulk} \quad \rightarrow \quad (Ox)_{electrode}$$

$$(Ox)_{electrode} \quad + \quad ne- \quad \rightarrow \quad (Red)_{electrode}$$
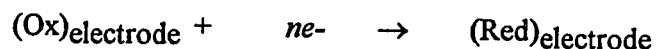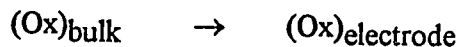
The anodic stripping step involves the reversal of the above process. Analytical correlation's are made between the Faradaic signal obtained in the stripping step, which is proportional to the bulk concentration and the plating time.[7]

Our work involved the application of anodic stripping voltammetry to determine quantitatively the content of nickel ion in waste water. In previous trace nickel determinations by ASV, the Hanging Drop Mercury Electrode (HDME), Thin film Mercury Electrode (TFME), Pt and Gold solid electrodes have been used. Mercury electrodes perform satisfactorily where amalgam formation is involved, but there are some disadvantages: (i) mercury electrodes start oxidizing to mercurous ion at lower than +0.40V vs SCE, (ii) solutions become contaminated with used amalgam drops, and (iii) mercury electrode cannot be used for ASV of noble metals like Hg or Ag.

To circumvent the above mentioned problems with mercury, the Wax Impregnated Graphite Electrode (WIGE) was used in our work. The method involved the controlled-potential deposition of metallic nickel on the WIGE, followed by anodic stripping voltammetry. This report provide the results of anodic stripping measurements on nickel in potassium thiocyanate solutions. The highly irreversible nature of the $Ni-Ni(H_2O)_6^{++}$ couple necessitates the use of a complexing agent to bring the plating and dissolution reactions within a suitable potential range. The amount of metal dissolving was measured by integration of the stripping peak in the current-time curve recorded during a linear anodic voltage scan. All the other variables such as stirring rate, supporting electrolyte concentration, pH of the solution were kept constant. The pre-electrolysis was performed at room temperature. However, the temperature of solution increased slightly with stirring, but this did not show any impact on the experimental results. Experimental results show that the nickel ion concentration can be determined down to 5.0×10^{-9} M.

Chapter 3

Principle and Theory

3.1 Anodic Stripping Voltammetry

Anodic stripping voltammetry is a method for determination of electroactive species that utilizes a bulk concentration step to pre-concentrate the analyte from the solution onto the surface of a working electrode. After the electrodeposition step, the material is anodically stripped back into the solution by Linear potential sweep voltammetry. The amount of metal dissolved can be measured by the integration of the stripping peak in the current-time curve recorded during a linear anodic voltage scan. The total quantity of peak current electricity Q (coulombs) consumed in the electrolysis is proportional to the amount of metal deposit which is related to the bulk ion concentration and the pre-electrolysis time. This type of stripping analysis is widely used for trace metals analysis, and is called anodic stripping voltammetry (ASV). Since ASV is a form of voltammetry; therefore, a basic knowledge of voltammetry is essential for a good understanding of ASV.[13]

3.2 Voltammetry

Voltammetry refers to a class of electroanalytical techniques in which the current at a working electrode is measured as a function of a potential waveform applied to the electrode. In voltammetry, the term "working electrode" is reserved for the electrode at which the reactions of interest occur. The potential of this electrode is a controlled parameter that serves as the driving force for the electrochemical reaction. The reducing

or oxidizing strength of the electrode is controlled by the applied potential. If the potential of the electrode becomes more negative, the electrode becomes a stronger reducing agent (electron source). In a voltammetric experiment, the potential is varied in some systematic manner: linear ramp, staircase, or pulse train. If an electroactive species is present, a current will be recorded when the applied potential becomes sufficiently negative or positive for it to be electrolyzed. The resulting current-potential plot is called a voltammogram. It is a display of current (vertical axis) versus potential (horizontal axis). Depending on the nature of the measurement, a peak-shaped faradaic current along with the background current can be measured. This faradaic current is proportional to the concentration of the electroactive species. [14]

3.3   Quantitative Relationships

For the electrolytic deposition and stripping of nickel, the following simplified reactions occur:

General: $\qquad$ Ni^{2+} $\qquad$ + $\qquad$ $2e^-$ $\qquad$ $\leftrightarrow$ $\qquad$ Ni^0

Sub step: $\qquad$ $(Ni^{2+})_b$ $\qquad$ $\leftrightarrow$ $\qquad$ $(Ni^{2+})_e$

$\qquad$ $(Ni^{2+})_e$ $\qquad$ + $\qquad$ $2e^-$ $\qquad$ $\leftrightarrow$ $\qquad$ $(Ni^0)_e$
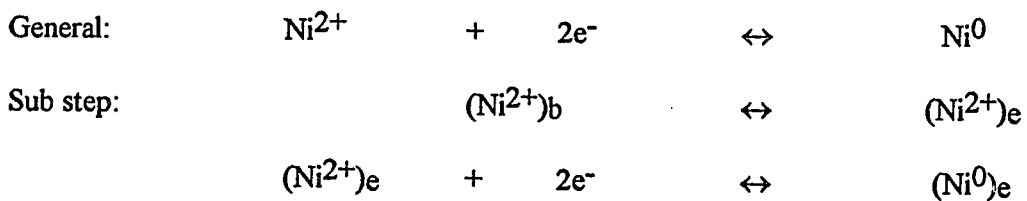
Each step can proceed in either direction, depending on the applied potential. The amount of metal collected/stripped can be measured by the integration of the current-time curve recorded during a linear anodic voltage scan, and that current is proportional to:

* $\qquad$ Analyte bulk concentration

* $\qquad$ mass transfer factors during deposition

* $\qquad$ time of electrolysis

Based on the above facts, we can use a derivation based on by Nernst Diffusion layer theory and Levich convection theory which fits all of the experimental results. With constant convection and large electrolysis potential limiting current condition ($i = i_L$) is obtained which is described by the Levich equation: [15,16]

$$i_L = 0.62 \, nFAD_o^{2/3}\omega^{1/2}\,\upsilon^{-1/6}C_o^b \qquad \text{--(1)}$$

$$i_L = k\,C_o^b \qquad \text{--(2)}$$

See definitions of terms in section 3.4. Anodic stripping theory considers that the amount of material deposited on the electrode is proportional to the limiting current and the electrolysis time. This quantity is related to the numbers of net pre-electrolysis coulombs:

$$Q_e = \int_0^{t_e} i_L\,dt = i_L t_e \qquad \text{--(3)}$$

Substituting equation (2) into equation (3):

$$Q_e = kC_o^b t_e \qquad \text{--(4)}$$

$$k = \frac{Q_e}{C_o^b\, t_e} \qquad \text{--(5)}$$

Equation (1) applies to the mass transfer conditions under forced Convection-Hydrodynamic conditions.

3.4 Definitions:

i_L = Limiting current net (amperes)

F = Faraday constant (Coulombs/equivalent)

n = Number of electron involved in the overall electrode reaction

A = Electrochemical area of the electrode (cm^2)

Do = Diffusion Coefficients (cm^2/sec)

C_o^b = Bulk Concentration of metal ion (mole/mL)

t_e = Electrolysis time, (sec)

ω = Angular velocity, $2\Pi r$ (sec^{-1})

υ = Kinematics Viscosity (viscosity/density of electrochemical solution) (cm^2/sec)

Chapter 4

Experimental Section

4.1 Apparatus:

4.1.1 Sargent Polarograph

The instrument used in this work was the Sargent FS Polarograph, Model-4001, (E. H. Sargent Co., Chicago Illinois). This instrument provides linear potential sweeps from 16.7 mv to 50 mv per second in four steps. In addition, the initial potential can be set either by manual adjustment of the slide wire for the potential scan or by the auxiliary continuously variable low-voltage potential source (+3.0 to -3.0 V range) incorporated into the instrument[10,11]. With the FS polarograph, a three-electrode cell was used.

4.1.2 Electrochemical Cell Set-up

Anodic stripping analysis measurements were carried out in an electrochemical cell, consisting of a Plexiglas flat bottom beaker (100 - 250 mL volume). The plexiglas beaker is acidified (3 parts of dilute nitric acid and one parts of dilute hydrochloric acid) prior to each analysis to reduce the errors from contamination caused by adsorption. The cell also contains three electrodes (working, reference, and counter), which are immersed in the sample solution (Figure 1). These electrodes and the glass tube used for bubbling the high purity nitrogen gas to deoxygenate the solution are supported by clamps. To stir the cell solution during the deposition step, a Teflon-covered magnetic stirring bar (1 inch)

and Auto-Speed Magnetic Stirrer (Model 51000-15, Cole Parmer Instrument Company, Chicago, Illinois 60648) were used. The stirring rate was controlled at 650 ± 2 rpm.

4.1.3 Cell Container Pre-treatment

Each Plexiglas beaker and all glassware used for this experiment was pre-treated for 6-8 hours by submerging into aqua regia solution (three parts of dilute nitric acid and one part of dilute hydrochloric acid) to remove all the adsorbed metallic contamination. All the cell containers were washed with purified water.

4.1.3.1 Electrode Pre-treatment

The initial preparation of a working electrode has been described in the experimental section (1). The working electrode was pre-treated in between the measurements by oxidizing unwanted electroactive species at the potential of +1.25V vs SCE. Furthermore, the working electrode was polished in-between each fold of concentration to remove the deteriorated thin film of electrode which also helps to increase the sensitivity of the electrode. Although the working electrode can be used repeatedly without fine polishing, experimental results were more reproducible and sensitivity was improved by polishing the thin film of the working electrode.

The saturated Calomel electrode solution was changed every time when concentration of analyte is changed. This helps to reduce the nickel cross contamination carried over from the previous sample to the next sample. In addition, contamination in the supporting electrolyte solution was diminished by electrolyzing at -1.25 volt vs SCE

for 60 minutes with a large surface area graphite electrode (approximately 5 cm^2) to continuously deposit metallic contaminants prior to injecting analyte into the solution.

4.1.3.2   Electrodes

The working electrode for this experiment was a 12-inch spectroscopic graphite electrode (National Carbon Co., NY., No. L4309) prepared for use by immersion in melted paraffin wax (Parowax, U. S. P.) for 60 minutes. The preparation of a working electrode involved impregnation with paraffin wax, insulation of the sides, and polishing of the plane circular exposed electrode tip by using 200 fine grid sandpaper. The detail of the procedure has been described previously.[11,12] The exposed area of working electrode was approximately 0.16 cm^2.

The second part of the working electrode system is the reference electrode. Such an electrode provides a known and stable potential that is insensitive to the composition of the solution under study and with which the potential of the working electrode is compared. As a result of its constant composition the reference electrode remains unpolarized during the analysis. For this work a saturated calomel reference electrode was used. This is a double junction type reference electrode, where the outer salt bridged compartment can be filled with an inactive electrolyte.

To minimize errors from cell resistance in controlling the potential of the working electrode, a third counter (auxiliary) electrode was used. The counter electrode is made of a 12-inch spectroscopic graphite electrode (National Carbon Co., NY., No. L4309) with a large surface area. It was placed directly into the test solution.

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4.1.3.3   Purified Water

D. I. water was purified by passing over cation-anion exchange resin bed. The D. I. water was distilled three more times to eliminate all the metallic contamination. Purity of the distilled water was checked by Atomic Plasma Spectroscopy. The absorbance results of purified water (triple distilled water) were compared with regular tap distilled water. The result show that triple distilled water had significantly reduced level of heavy metals compared to regular tap distilled water. Distilled water was used to prepare all the chemical sample solution, clean glassware and electrodes.

4.1.3.4   Supporting Electrolyte (KCNS)

All the chemicals used were reagent grade and were used without further purification. The supporting electrolyte used for experiments was 0.1M Potassium thiocynate (KCNS) or 0.05 M for ultra trace level ($< 10^{-7}$ M). To make the 0.1 M of supporting electrolyte, 9.71 grams of reagent grade Potassium thiocynate was dissolved in one liter of distilled water. Six different kinds of supporting electrolytes may be used for nickel analysis (see section 5.1, Table 1). Potassium thiocynate is the electrolyte chosen for this analysis because the nickel stripping peak is better defined than for the other solutions.

4.1.3.5   Analyte Solution ($NiSO_4. 6H_2O$)

0.0263 grams of dry nickel sulfate reagent grade crystals were dissolved in the 100 mL of distilled water and stored at 10^{-3} M concentration. The nickel sulfate solution was prepared in acidified polyethylene 100 mL flask and stored for six months. The polyethylene bottle was acidified by soaking in dilute nitric acid for 6 - 8 hours. Sample solutions less concentrated than 10^{-3} M were prepared as needed.

4.1.3.6   Waste Water Sample

For determination of nickel in **"waste water,"** the samples were collected from the waste treatment plant of Akashic Substrates, 690 Gibraltar Dr., Milpitas, CA 95035. Akashic Substrates Inc. is plating electroless nickel on hard memory disks, and treats the spent nickel solution down to the ppm level as set by the ordinance of the city of Milpitas. The waste water sample was taken from the final stage tank and prior to release to the sewer line.

The same waste water is analyzed through an independent Sequoia analytical laboratory to determine all the matrix present in the waste water besides nickel. The following matrix are present in the waste water sample used in our experiment:

	Elements		Sample Results	Detection Limits
(a)	Copper	=	0.041 mg/L	0.010 mg/L
(b)	Zinc	=	0.400 mg/L	0.010 mg/L
(c)	Nickel	=	0.310 mg/L	0.010 mg/L
(d)	pH of water	=	9.0 - 10.5	

Although, Sequoia laboratory analyzes for other ions, such as Silver, Cadmium, Lead, Chromium, and Cyanide, but their report shows that they were not present above the stated limit of detection (0.010 mg/L). During the waste water treatment processes, Sulfuric acid, Nitric acid, Caustic soda, and Calcium Carbonate are used to precipitate the heavy metals and to adjust the pH of water. Ultimately, sulfates, nitrates, hydroxyl, carbonate, and bicarbonates ions are also present in the waste water sample.

The waste water samples taken for ASV analysis were stored in an acidified bottle as explained in section 3.1.2. The water sample was analyzed with Atomic Absorption, Perkin-Elmer, Model #2380 to record the concentration of nickel content (see appendix #5).

4.1.3.7   Oxygen Removal

Oxygen is capable of dissolving in aqueous solution to form concentrations as high as 10^{-3} M at room temperature and pressure. Dissolved oxygen can interfere in stripping analysis. Therefore, it is important to remove the oxygen from the sample by bubbling high purity nitrogen gas through the sample. Depending on the pH of the solution, oxygen undergoes reduction in two steps: [16,17]

Step 1:

$$O_2 \;+\; 2H^+ \;+\; 2e^- \;\Leftrightarrow\; H_2O_2 \qquad \text{(acidic medium)}$$

$$O_2 \;+\; 2H_2O \;+\; 2e^- \;\Leftrightarrow\; 2H_2O_2 + \; 2[OH]^- \text{(basic medium)}$$

Step 2:

$$H_2O_2 \;+\; 2H^+ \;+\; 2e^- \;\Leftrightarrow\; 2H_2O \qquad \text{(acidic medium)}$$

$$H_2O_2 \;+\; 2e^- \;\Leftrightarrow\; 2[OH]^- \qquad \text{(basic medium)}$$
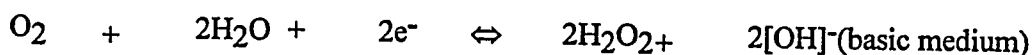
The half wave potentials of these steps are approximately -0.05 and -0.9 V versus the saturated calomel electrode (SCE). These reduction steps result in an increased background current that obscures the stripping peaks of interest[16,17].

4.1.4   Procedure:

Detailed experimental procedures used in this studies have been reported in Appendix 1, but a brief summary is included here. Voltammetric studies were conducted with Sargent Polargraph (Model-4001) system. All the measurements were conducted at room temperature. The working electrode was pretreated by polishing with sand paper and Whatman filter paper 10; in between each experimental measurements the electrode

was held at +1.250 Volt vs. SCE at least one minute to complete removal of deposits. Saturated Calomel and Counter electrodes were used to complete the circuit and the solution was deaerated with nitrogen gas before each experiment. The scan parameters for anodic stripping voltammetry were: Scan rate 1V/minute; Chart speed 10 cm/minute; Scan range from the pre-electrolysis potential is from - 1.25 Volt to + 0.50 Volt vs SCE. The pre-electrolysis scan range Electrolysis potential used for Ni (II) was -1.250 Volt vs. SCE. During pre-electrolysis the Solution was stirred at constant rate of 650 rpm by using the Teflon-covered magnetic stirring bar (1 inch) and Auto-Speed Magnetic Stirrer.

The accurately timed electrolysis step in the stripping analysis procedure was stopped by switching the cell to the off position; stirring was stopped, and 30 seconds were allowed to let the solution come to quiescent state. After this time, the electrolysis cell was switched back into the circuit and an anodic stripping scan was initiated (alternating experiments where the cell was kept in the circuit to 30 sec. after stirring was stopped prior to initiating the anodic scan observed no significant difference in stripping coulombs). Sensitivity of the instrument was adjusted, so the stripped peak current scan can fit on the graph paper. The anodic stripped peak was recorded on the graph paper made by Sargent-Welch Scientific Company, Catalog No. S-72164. The area of the peak was measured to calculate the total amount of electricity (coulombs) produced after stripping the nickel back into solution. Electricity produced by stripping current was used to calculate the concentration of nickel ions in the solution.

Figure 1

Electrochemical Cell with Three Electrodes
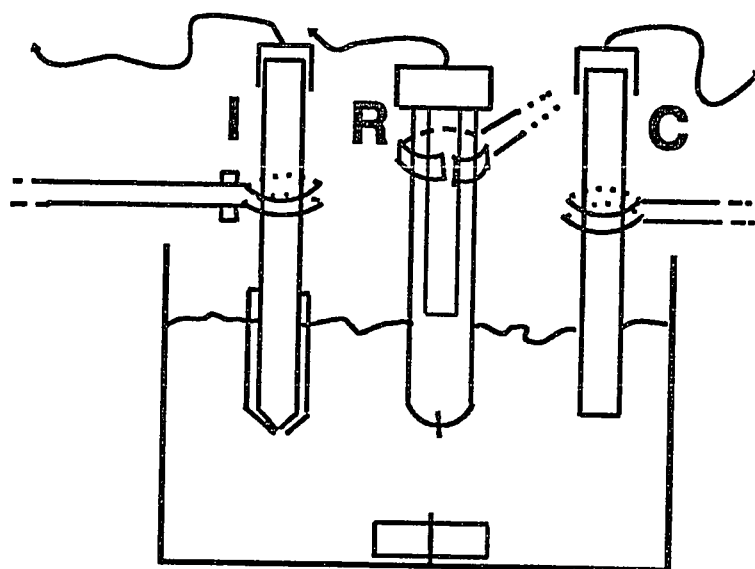
Figure 1. Electrochemical Cell with Three Electrodes. **I,** Indicator (Working); **R,** Reference; **C,** Counter electrode

Chapter 5

Results and Discussion

5.1 Cathodic Voltammetry

In order to select the optimum conditions for the electrodeposition of nickel in a stripping analysis procedure, the cathodic voltammetric behavior of nickel at the WIGE was studied in various complexing media, including: Potassium thiocynate (KCNS⁻), Sodium thiocynate, Ammonium Chloride Buffer (NH_4Cl + NH_4OH), Ammonium Hydroxide, Sodium Hypophosphite (see Table 1). The most reproducible and best defined current-voltage curve was obtained in a Potassium thiocynate medium, and cathodic voltammogram shows that the reversibility of nickel is much better in thiocynate complexing medium. Therefore, Potassium thiocynate electrolyte was chosen for further study. [11]

Table 1

Supporting Electrolyte For Nickel	
Supporting electrolyte	- $E_{1/2}$ vs SCE
0.1 M KCNS	- 0.45
1.0 M NH_4Cl + 1.0 M NH_3OH (pH=9)	-0.75
1.0 M NH_4Cl	-0.65
0.1 M Na_2HPO_4. $6H_2O$	-0.9
0.1 M NaSCN *	-0.45
1.0 M KNO_3+ 0.001 M HNO_3*	-1.1
* Data from Kh. Z. Brainina[18]	

Figure 2 shows the cathodic current-voltage curve which was obtained for 5 ppm (8.5 x E^{-5} M) nickel ions in supporting electrolyte solution (0.1 M Potassium thiocynate). The sample solution was deaerated prior to measurement by bubbling with nitrogen gas. Based on the half-wave potential, -1.25 V vs SCE was chosen to reduce the nickel ions to nickel metal. This potential is well enough along in the limiting current region to compensate for cathodic shift in the half wave potential with dilution, and also not so cathodic as to cause significant interference from solvent reduction.

Figure 2
Nickel Concentration (8.5 X 10⁻⁵ M)

Cathodic Voltammogram
Nickel Concentration 8.5E-5 M
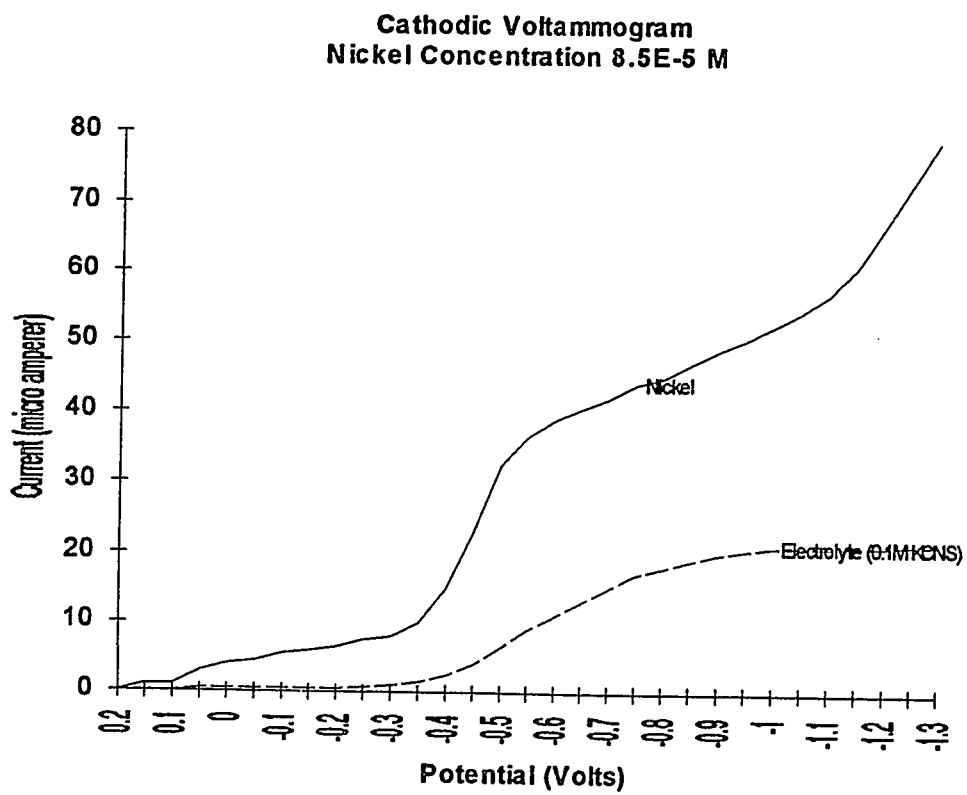
5.2 Anodic Stripping Voltammetry

5.2.1   General Observation

The general procedure described in section 4.1.3 was followed. The nickel samples were made for various concentrations (1.7 X 10^{-4} M, 1.5 X 10^{-5} M, 1.5 X 10^{-6} M, 1.5 X 10^{-7} M, 5 X 10^{-8} M, and 5 X 10^{-9} M) by diluting the nickel stock solution (see section 3.1.2.4). These nickel samples were made as required by the experiment.

The nickel ASV voltammograms obtained by using the WIGE show that the stripping current peak potential varies with the concentration of nickel ions. Figure 3, the voltammogram obtained with nickel concentration 1.7 X 10^{-5} M, shows that the nickel starts oxidizing at -0.80 V and continues until 0.0 volt *VS* SCE. Figure 3 also shows two stripping current peaks; one at -0.65 volt and a second at -0.35 volts *VS* SCE. Figure 4, illustrates that the voltammogram obtained with nickel concentration of 1.5 X 10^{-6} M and lower. Nickel starts oxidizing at about -0.70 volts and continues to about -0.4 volt *VS* SCE. Figure 4 shows only shows one stripping peak at about -0.5 volts vs SCE.

The average thickness of the deposit appeared to be a critical factor in determining the shape of the dissolution curve. Two stripping peaks could be observed for the larger deposits in these our studies. A single stripping nickel peak was obtained as long as the deposit is less than approximately 53 micro-coulombs, the estimated sensitivity corresponding to a monolayer deposit of nickel. The estimated monolayer coverage is calculated as follows:

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$$\text{Electricity Produced by Ni Monolayer} = \frac{(\Pi r^2)_e \times 2 \times 96500 \text{ Coulombs/mol}}{(\Pi r^2)_{Ni \text{ atom}} \times 6.022 \times 10^{23} \text{ atoms/mole}}$$

$$= 53 \ \mu C/cm^2$$

Where:

r_e	=	Radius of Electrode (0.16 cm)
$r_{Ni \text{ atom}}$	=	Radius of Nickel atom(1.246 A° = 1.246 × 10^{-8} cm)[19,20]
$(\Pi r^2)_e$	=	Area of Electrode (3.14 × 0.16^2) = 0.08 cm^2
$(\Pi r^2)_{Ni \text{ atom}}$	=	Area of Nickel atom (3.14 × 1.55×10^{-16})=4.87×10^{-16} cm^2
2	=	No. of electrons/atom oxidized
F	=	Faraday Constant (96500 C/mol)
N	=	Avogadro Number (6.022 × 10^{23} atoms/moles)

The results shown in figure 3 strongly agreed with the Nicholson finding that the double peak pattern was a surface phenomenon.[9] The first peak corresponds to the removal of nickel atoms from what was substantially deposited on a nickel surface, while the second peak involved stripping of nickel atoms attached directly to the carbon atoms of the graphite electrode with a binding energy favoring the deposition process. A similar pre deposition effect was observed by Funkhouser[21] in the deposition of nickel from thiocynate solutions onto a mercury pool.

5.2.2 Measurements at Very Low Nickel Concentrations

Stripping curves from larger deposits (exceeding 320 $\mu C/cm^2$) were more amenable to accurate integration because stripping peaks were larger and well defined. To attain this condition in extremely dilute solution (10^{-6} - 10^{-9} M), it is necessary to carry out the deposition for long times. To carry out the analysis in dilute solution for more than an hour to attain greater than monolayer deposits is not very favorable for electrochemical sensor purposes. As long as the deposition proportionality is constant, the electrolysis time can be reduced to our specific need; but lower electrolysis times will result in sub monolayer nickel deposits. Lower convection rates can also lead to smaller sub-monolayer deposits.

Figure 3

Anodic Stripping Voltammogram of 1.75×10^{-5} M (Nickel)

Anodic Stripping Voltammogram
Nickel Concentration = 1.7E-5 M
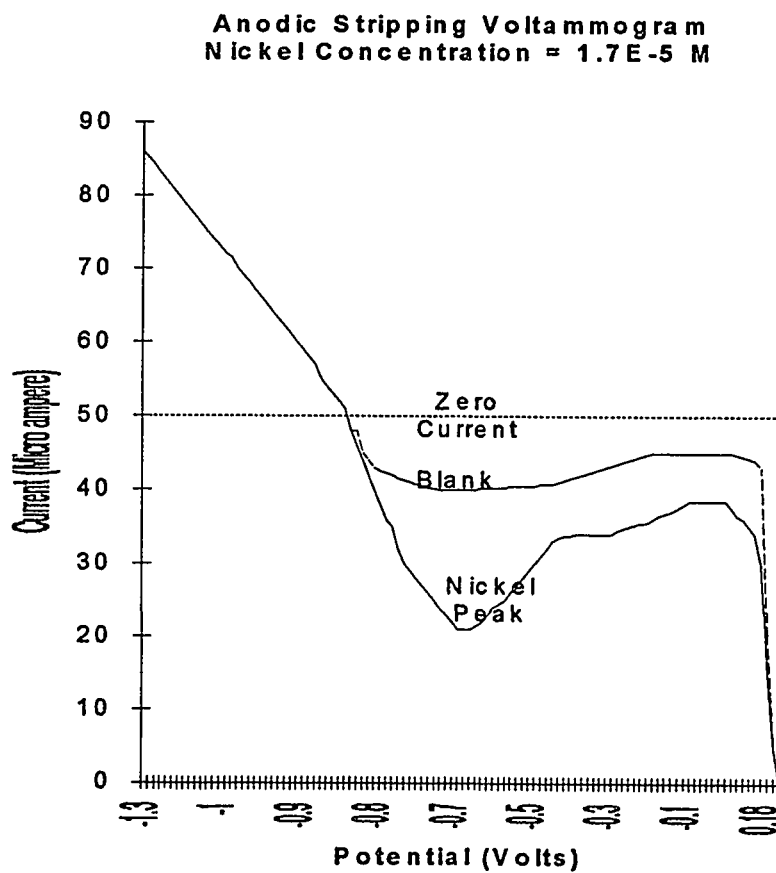
Figure 4

Anodic Stripping Voltammogram of 1.5x10⁻⁶ M (Nickel)

Anodic Stripping Voltammogram
1.5 x E-6 M (Nickel)
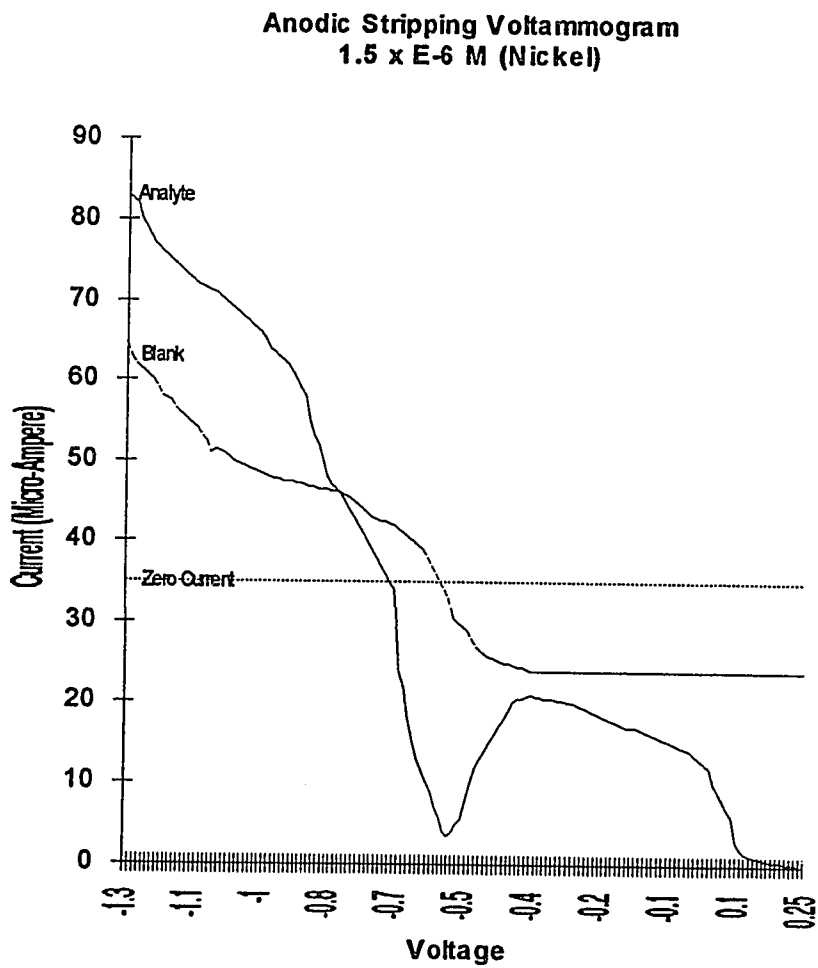
As the nickel concentration approaches the ultra trace level (5×10^{-8}M or below), nickel contamination in the supporting electrolyte became a problem. Listed below are the contamination sources suspected:

(i)   Even with reagent grade supporting electrolyte, heavy metal contamination in the Potassium thiocynate salt was listed as 0.005%.

(ii)   Nickel ions from the previous analysis adsorb on the cell walls.

(iii)   Nickel ions carry over from the working, auxiliary, and reference electrodes.

To minimize the above problems, a pre-treatment procedure was developed and used as explained in section 4.1.3.

5.2.3   Calibration Study

A calibration curve of the stripping current VS nickel concentration was obtained using a high stirring rate of solution (650 rpm) and the results are shown in Table 2. The average of three independent determinations of each concentration was plotted to calculate the proportionality constant (K) value. The raw data for K calculation at high stirring rate are logged in Appendix 2.

Table 2
Anodic Stripping Analysis of Nickel
High Stirring Rate (651 rpm)

Conc.	Electrolysis time	Avg. elec. produced	$k = q/C \cdot t_e$	Rel. Std.
(moles/liter)	(t_e min.)	Q $(10^{-6}$ C)	$(10-6)$	dev.
1.7×10^{-4}	15	756	0.30	0.03
1.7×10^{-5}	19	161	0.50	0.006
1.5×10^{-6}	10.17	7.97	0.52	0.006
1.5×10^{-7}	15	1.2	0.54	0.02
5.0×10^{-8}	25	0.67	0.54	0.02
5.0×10^{-9}	55	0.24	0.83	0.44
		AVG =	0.54	0.17

*   Data refer to three replicate determinations at each concentration.

Similarly, a calibration curve was obtained at a low stirring rates (< 60 rpm) to simulate electrode response in a slowly flowing process stream. For this study a 999 ppm of nickel stock solution was made in 5% nitric acid by dissolving the nickel metal. We used the same stock solution to obtain the calibration curve of 0.66, 1.0, 3.06, 5.84, and 11.5 ppm. The calibration curve data are reported in Table 3 (see next page). The concentration of this experiment was also confirmed with Atomic Absorption, and data are recorded in Appendix 3 (see next page).

Two different industrial waste water samples were obtained from Akashic Substrates as described in section 4.3.1.2. These samples were analyzed by ASV, using a small glass beaker at a low stirring rate to simulate the flow of industrial waste water. The stirring rate was adjusted, so the solution was moving approximately at the same pace as water flows in the river water where a voltammetric sensor will be used to analyze the contamination. The nickel was deposited at -1.25 volt vs SCE. A nickel stripping peak was observed -0.45 volt vs SCE. The average stripping current calculation was made by replicating the analysis two times. The nickel concentration of each sample was calculated by using the average calibration constant K, obtained in Table 3. The waste water nickel results are logged in the Table 4 (see next page). Similarly, we obtained waste water samples 3 and 4 to analyze nickel at high stirring rate and results are logged in Table #5.

The waste water samples concentration were also confirmed by Atomic Absorption at Akashic Substrate. The AA data obtained at Akashic are recorded in the Appendix 4.

Table 3
Anodic Stripping Analysis Calibration Table
Nickel at Low Stirring Rate

Conc.	Electrolysis time	Avg. elec. produced	$k = q/C^*t_e$	Rel. Std.
(moles/liter)	(t_e min.)	Q (10^{-6} C)	(10^{-6})	dev.
1.12×10^{-5}	25	0.53	0.0019	0.0001
1.60×10^{-5}	20	0.74	0.0022	0.0002
5.21×10^{-5}	20	2.05	0.0020	0.0001
9.95×10^{-5}	21	4.77	0.0023	0.0002
1.93×10^{-4}	20	7.6	0.0020	0.0001
		Avg. =	0.0021	0.0001

5.2.4   Interferences

Prior electrolysis of electrolyte solution with a larger surface area graphite electrode for 60 minutes removed unwanted contamination down to parts per billion (see experimental section 4.1.3.1). However, even at this ultra trace level Pb^{++} and Cu^{++} can cause a significant interference, as they are reduced in the same potential range as nickel. They appear in the blank solution, especially when the analysis time is higher than 45 minutes.

An experiment was conducted to determine if Pb^{++} and Cu^{++} stripping peaks overlapped seriously with nickel at the WIGE. We observed that the copper stripping peak in potassium thiocynate interferes with nickel determination at $E_p \cong -0.70$ volts vs SCE. However, the lead contaminant did not affect nickel stripping peaks. Our finding of copper interference at concentrations comparable to nickel agrees with H. Grubitsch and H. Schukoff,[21,22] and they also observed a lead interference for ASV of nickel at Hg electrode.

Table 4

Akashic Waste Treatment Analysis
Anodic Stripping Analysis VS Atomic Absorption
(Nickel)

Sample No.	Electrolysis time	Avg. elec. produced	*C = Q/kt$_e$	Conc. by AA	Differ. ASV vs AA
(Akashic)	(t$_e$ min.)	Q (10^{-6} C)	(mole/liter)	(mole/liter)	(%)
1[a]	25	1.70	3.24×10^{-5}	3.6×10^{-5}	10%
2[b]	27	0.84	1.48×10^{-5}	1.5×10^{-5}	1.2%

* Compare to Table 3 for relevant calibration data (low stirring rate)

a) Industrial waste water was taken on 2/27/94 at 7:30 AM.

b) Industrial waste water was taken on 2/27/94 at 4:30 AM.

Table 5

Akashic Waste Treatment Analysis
Anodic Stripping Analysis VS Atomic Absorption
(Nickel)

Sample No.	Electrolysis time	Avg. elec. produced	*C = Q/kt$_e$ (ASV)	Conc. by (AA)	Differ. ASV vs AA
(Akashic)	(t$_e$ min.)	Q (10^{-6} C)	(mole/liter)	(mole/liter)	(%)
3[ac]	25	25	2.3×10^{-6}	1.3×10^{-5}	82%
4[d]	20	35	3.24×10^{-6}	2.4×10^{-5}	86%

* Compare to Table 2 for relevant calibration data (stirring rate = 652 rpm)

c) Industrial waste water was taken on 3/14/94 at 7:30 AM.

d) Industrial waste water was taken on 3/18/94 at 7:30 AM.

Chapter 6

Observation

We observed that the sensitivity of ASV improved after the first ASV cycle. The first analysis made with the new sample was always less sensitive, but results are very repeatable after the second analysis. Thus, the data in Tables 2 - 5 do not include the very first ASV run at a given concentration.

ASV sensitivity also increases as the mass transfer factor is increased, as can be seen by comparing the average K obtained in Tables 2 and 3. All the analyses were performed at room temperature. Effects of solution temperature increase that are due to stirring actions are small compared to other source of errors (e. g., ultra trace solution handling, cell geometry, effects of contamination, etc.).

It was also observed that the nickel stripped off at two different potentials, when the nickel deposit size exceeds monolayer coverage. The first current peak appearing about at -0.65 volts represents stripping of the Ni-Ni layers, and second peak, appearing at -0.45 volts represents stripping of the Ni-C layer.

The data in Tables 2 and 3 demonstrate that the WIGE electrode is useful for ASV over a broad range of nickel ions. The sensitivity of the WIGE is shifted by changing the condition of electrochemical cell, e.g., by changing the solution of the cell, the geometry of the cell, and the stirring rate of the solution. We observed that the sensitivity of electrode can be improved by (i) re-polishing the working electrode surface, (ii) and

holding the electrode at + 1.25 volts vs SCE to remove the unwanted electroactive material.

The Ni detection limit (D.L.) based on the raw data acquired for Table 2 is 4.5 x 10^{-9} M. This value is obtained from the expression,

$$D.L. = t(S_{mb})/Sens$$

where S_{mb} is the standard deviation of the mean for the blank estimated from the regression analysis standard deviation of the intercept (S_1) for data from the four lowest concentrations in Table 2. The value for student's t is obtained for the 95% confidence level, n = 11, number degrees of freedom + 10. Thus, $S_1 = \pm 0.0043$ µC/min.; $S_{mb} = \pm 0.0013$ µC/min.; Sens = 0.0064 µC/min. -10^{-8}M = sensitivity; and t = 2.22.

The deposition cycle time required by ASV to produce a meaningful stripping peak varies with concentration of nickel ions present in the sample solution. If the concentration of the analyte sample is higher than 10^{-5} M, two to three minutes are sufficient to deposit enough nickel to a get meaningful stripping peak, but if the nickel concentration is lower than 10^{-5} M then the deposition cycle will be higher. The deposition cycle time can be diminished by increasing the stirring rate; also, shorter deposition times can be used for low concentration with diminished accuracy and precision.

We observed that the contamination interference increases as the concentration approaches the ultra trace-level. The effect of interference from other heavy metal ions (most likely Ca^{2+}) is observed in the distortion of ASV data at the lowest Ni^{2+} concentrations. Contaminants are skewing the K value as shown in the 10^{-9} M concentration.

Because our goal is to develop a voltammetric sensor to continuously monitor the contaminants in a flowing stream of waste water, we conducted a concentration study to analyze nickel in waste water at low stirring rate (Table 3). The results for waste water analysis (Table 4) show that ASV analyses are in agreement with AA data within about 10%. At higher stirring rates (Table 5), the ASV analyses of waste water are about 85% lower than the AA data. The reason for the larger error with the higher stirring rate is not understood, but may be related to the larger effect of the different (higher) viscosity of the waste water samples. Nevertheless, it is worth noting that the calibration data in Tables 2 and 3 were obtained for synthetic nickel solutions, and yet were applicable, with reasonable accuracy, to determinations in waste water samples of considerably more complex matrix. If better accuracy is required, a standard addition procedure should be developed.

It is also interesting to note that our ASV results with the WIGE indicate that Ni determinations can be conducted over a broader range and to somewhat lower concentrations than reported previously for other electrodes. [9] This may be due to our rigorous attempts to diminish the presence of interfering heavy metal ions.

Finally, considering that about 1.0 μC Ni deposit is sufficient for good accuracy and precision (Table 2), the detection of the micro molar Ni levels in the waste water sources considered here might require pre-electrolysis times as short as about 60 sec (high stirring rate). Although this might require artificially introducing higher convection rates in the vicinity of the sensor, this observation is very encouraging for practical applications of ASV-based sensors with reasonable response times.

Chapter 7

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Appendix 1

3.2 General procedure to Operate the Sargent-4001 Polarograph for ASV Experiments with Graphite Electrodes:

Start-up Procedure:

Before to the experiment, Sargent-Welch Polarograph's (model - 4001) shall be calibrated as per section 3.2.1. If the instrument calibration is correct then follow to the section 3.2.2 to make sure all the functional switches are in following order.

3.2.1 CALIBRATION:

3.2.1.1 The Model 4001 Polarograph has been fully calibrated at the factory and should not require re calibration unless the calibration settings have been altered or a component has been replaced.

3.2.2.2 GAIN CALIBRATION: Set controls as follows:

Control	Setting
Power	ON
Chart	1 cm/min
Operating Mode	Test
Scan Direction	"-"
Scan Rate	1 volt/ min

Initial V	-.000
Final V	-1.000
Current Sensitivity	10 A F.S.
Icc Compensation	OFF
Damping	OFF
IR Compensation	OFF

3.2.1.3 Turn power switch to RECORD and, with pen down, carefully position pen to chart zero with displacement control. Slowly increase the initial voltage to -1.000V and then adjust the Gain Calibration control (R.36) until the pen indicates full-scale (100) on the chart. The Gain Calibration control is the accessible through the left-hand hole in the back of the instrument case. Return the initial voltage to -.000V and recheck zero. Repeat this procedure, if necessary.

3.2.1.4 DEADBAND SETTING:

- With same settings as in 31-32 above, turn power switch to RECORD and position pen to middle of chart (50) with displacement control.
- Manually displace pen carriage two to three centimeters to the left and it to freely return. Repeat in the right direction.
- The distance between the two steady state traces (trace position after recovering from manual disturbance) represents the DEADBAND. This has been originally set for less than 0.3% of full scale. To adjust this value, adjust the pen servo control (R22) and repeat the above procedure until the desired value is obtained. This control is accessible throughout the right-hand hole in the back of the instrument case.

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3.2.1.5   SCAN RATE CALIBRATION:

- To measure scan rate, set all controls as in 31-32 above.

- Change chart speed to 10 cm/min and turn power to RECORD.

- Carefully position pen to chart zero and, when pen is on a major abscissa line, momentarily depress the Scan Start switch. The pen will move across the chart until it reaches full scale(100) and then automatically return to zero. The length of the trace, measured along the abscissa, should be 10 cm.

- If the scan rate has to be re-calibrated, open the instrument case and adjust the scan Rate control (R45). This control is located on the Scan Rate switch and should be turned in the counter-clockwise direction to increase the scan rate and clockwise to decrease the scan rate.

- Repeat 35.3 and 35.4 above until the proper scan rate is obtained.

3.2.2 Upper Control Panel:

3.2.2.1   Power switch shall be "OFF" position.

3.2.2.2   Chart Switch is a nine position switch which indicate the chart flow rate in cm/min and setting position is an optional.

3.2.2.3   Operating Mode switch shall be in "OFF" position.

3.2.2.4   Scan Direction is a two position toggle switch that determine the polarity of the potential scan and its setting position is optional ("+" for ASV and "-" for LSV reductions).

3.2.2.5   Scan Control switch is a two-position momentary switch which will always be found in neutral position.

3.2.2.6   Meter switch is a five position switch which shall be found in **scan v.** position.

3.2.2.7   Excitation has no function in DC polarography.

3.2.3 Lower Control Switch:

3.2.3.1   **Set Initial V.** switch shall be in "-" ive mode, if the instrument is used for ASV analysis.

3.2.3.2   Set Final V. switch shall be in "+" ive mode, if the instrument was used for ASV analysis.

3.2.3.3   Pen Displacement switch is to adjust the pen position on the graph paper.

3.2.3.4   IR Compensation switch shall be in OFF position.

3.2.4 Setting-up Electrochemical Cell:

3.2.4.1   Prepare the potassium thiocynate solution as per section 3.1.2.2 (recommended electrolyte concentration is 0.1 M)

3.2.4.2   Take 45 mL of electrolyte sample in the cell (beaker) or enough solution to immerse 1-2 cm of the electrodes.

3.2.4.3   Hold the working electrode (wax impregnated graphite), counter electrode (graphite), and reference electrode (SCE) in the cell with the help of clamps and stands.

3.2.4.4   Hook each electrode to the Sargent polarograph (Model 4001) output as labeled.

3.2.4.5	Use sti rrer bar and magnetic to mix the solution.
3.2.4.6	Bubble the nitrogen gas through the electrolyte solution for at least minutes. The nitrogen gas flow rate shall be 10 cc.

3.2.5 Setting up the Sargent-4001 Polarograph for ASV:

3.2.5.1	**Turn-on** the power switch.
3.2.5.2	Set the chart flow rate to **10 cm per minute** position.
3.2.5.3	Set the voltage **scan rate to 1 V** per minute.
3.2.5.4	Set the **scan direction** to "+" .
3.2.5.5	Set the Meter switch to **initial v. position** and adjust **set initial v.** switch to "-" direction.
3.2.5.5	Adjust the initial voltage to the value required to electro-deposit the analyte (initial potential is usually several tenths of a volts more negative than the reversible potential calculated from the Nernest equation; e.g., -1.0 V for Ni^{2+} ions).
3.2.5.6	Move the Meter switch to **final v. position** and adjust final set **finalV.** to "+" direction.
3.2.5.7	Adjust the final voltage to the most positive value desired at the and of the stripping sweep (e. g., 0.5 V for Ni^{2+} ions).
3.2.5.8	Finally, move the Meter switch to **scan v. position.**
3.2.5.9	Adjust the **current sensitivity (4 μA)** switch to the required value to determine the concentration of electro-stripping metal.

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3.2.5.10   **Zero Current Location:-**   Move the operating mode switch to off and

power switch to pen position respectively. Marker pen will move on the

chart, and let the pen stop moving. When pen stop drifting, mark the

position. This is the **zero current** location.

3.2.5.11   Turn power switch to off position.

3.2.5.12   Now the machine is ready to analyze the sample.

3.2.6 Disposition Step:

3.2.6.1   Shut off the nitrogen gas, but leave the stirrer bar on.

3.2.6.2   Turn-on the power and switch the operating mode knob to Auto position.

3.2.6.3   Log the starting time of the deposition cycle (starting time corresponds to

the instant that the operating mode is switched from **Off to Auto mode**).

3.2.6.4   The deposition time t_e must be controlled very carefully, the longer the

deposition time the larger the amount of analyte deposited at the electrode.

The deposition time varies depending on analyte concentration, but

generally the deposition time range is 10 to 60 minutes for analyte

concentrations of 10^{-4} to 10^{-9} M, respectively.

3.2.7 The Rest Period:

3.2.7.1   To stop the forced convection at the end of deposition step, turn the stirrer

bar and Operating mode switch to OFF position, respectively. Let the

solution settle down for 30 second to insure that stripping step is performed in a quiescent solution.

3.2.8 The Stripping Step:

3.2.8.1   After 30 sec of rest period, turn the operating switch to Auto mode.

3.2.8.2   Switch the power switch to **pen position** and adjust the sensitivity.

3.2.8.3   After the pen stops drifting, turn the power switch to plotting mode.

3.2.8.4   Set the pen on the graph paper toggle the start switch on.

3.2.8.5   Repeat the blank analysis one more time.

3.2.8.6   If the electrolyte shows any contamination peak, discard the solution and start with new solution.

3.2.8.7   Now the instrument is ready to analyze the analyte. Simply inject the sample and repeat the step #20-28 at various time analysis.

3.2.8.8   Oxidize the working electrode after every analysis as follows:

- Turn operating switch to off position.
- Switch the **set initial v.** to "+" 1.25V.
- **Turn-on** the stirrer bar.
- Start bubbling the nitrogen through the solution.
- Turn the operating mode switch to **Auto position.**
- After 2 minutes, turn the operating switch to **off,** change the **set initial V. back to "- 1.25 V",** and then go back step #3.2.6.

Nickel Trace Analysis
With Graphite Electrode

Sample #	AA Conc. (ppM)	Conc. (Moles)	Electrolysis time (min.)	Current (Q) (micro-amp)	K = Q/C*t	Stirring Rotatio
1	10.10	1.72 x E-4	15	756.00	0.30	652
2	1.01	1.72 x E-5	19	161.00	0.50	653
3	—	1.25 x E-6	10	8	0.52	652
4	—	1.25 x E-7	15	1.27	0.54	650
5	—	5 x E-8	25	0.67	0.54	650
6	—	5 x E-9	55	0.24	0.83	652
				AVG	0.54	652
				ST. DEV	0.17	

Raw Data for Electricity Produced by ASV

	Concen. (ppm)	Stirring (RPM)	Sample #1 Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	9.60	652	15	840.00	0.33
	9.80	650	15	714.00	0.28
	9.40	651	15	714.00	0.28
	10.00	652			
	10.30	653			
	10.20	650			
	10.40	651			
	10.10	652			
	10.40	650			
	10.50	651			
	10.20	652			
AVG	10.08	651.27	15.00	756.00	0.30
ST. DEV	0.35	1.01	0.00	72.75	0.03

Appendix 2

Raw Data for Electricity Produced by ASV
Sample #2

	Concen. (ppm)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	0.98	650	19	158	0.49
	0.96	650	19	162	0.50
	0.94	651	19	162	0.50
	1.00	652			
	1.03	653			
	1.02	650			
	1.04	651			
	1.01	652			
	1.04	650			
	1.05	651			
	1.02	652			
AVG	1.01	651.09	19.00	160.80	0.50
ST. DEV	0.04	1.04	0.00	2.08	0.006

Raw Data for Electricity Produced by ASV

Sample #3

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	1.25 x E-6	652	10	7.78	0.52
	1.25 x E-6	654	10	7.97	0.53
	1.25 x E-6	653	10.5	8.16	0.52
	1.25 x E-6	653			
	1.25 x E-6	652			
	1.25 x E-6	652			
	1.25 x E-6	652			
	1.25 x E-6	652			
	1.25 x E-6	652			
	1.25 x E-6	653			
	1.25 x E-6	654			
AVG	1.25 x E-6	652.64	10.17	7.97	0.52
ST. DEV	0.00	0.81	0.29	0.19	0.006

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Appendix 2

Raw Data for Electricity Produced by ASV
Sample #4

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	1.25 x E-7	650	15	1.13	0.50
	1.25 x E-7	645	15	1.20	0.53
	1.25 x E-7	650	15	1.35	0.60
	1.25 x E-7	650			
	1.25 x E-7	650			
	1.25 x E-7	645			
	1.25 x E-7	650			
	1.25 x E-7	650			
	1.25 x E-7	651			
	1.25 x E-7	651			
	1.25 x E-7	650			
AVG	1.25 x E-7	649.27	15.00	1.22	0.54
ST. DEV	0.00	2.15	0.00	0.19	0.05

Raw Data for Electricity Produced by ASV
Sample #5

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	5 x E-8	650	25	0.70	0.56
	5 x E-8	649	25	0.67	0.54
	5 x E-8	645	25	0.65	0.52
	5 x E-8	651			
	5 x E-8	645			
	5 x E-8	651			
	5 x E-8	650			
	5 x E-8	645			
	5 x E-8	650			
	5 x E-8	650			
	5 x E-8	650			
AVG	5 x E-8	648.73	25.00	0.67	0.54
ST. DEV	0.00	2.45	0.00	0.03	0.02

Appendix 2

Raw Data for Electricity Produced by ASV

Sample #6

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	⁻K = Q/C*t
	5 x E-9	652	48	0.11	0.46
	5 x E-9	653	68	0.37	1.09
	5 x E-9	652			
	5 x E-9	652			
	5 x E-9	652			
	5 x E-9	653			
	5 x E-9	652			
	5 x E-9	653			
	5 x E-9	652			
	5 x E-9	652			
	5 x E-9	653			
AVG	5 x E-9	652.36	58	0.24	0.83
ST. DEV	0.00	0.50	10.61	0.19	0.44

Appendix 3

Nickel Trace Analysis
With Graphite Electrode

Sample #	AA Conc. (ppm)	Conc. (Moles)	Electrolysis time (min.)	Current (Q) (micro-amp)	K=Q/C*t	Stirring Rotation
1	0.66	1.12 x E-5	25	0.53	1.90E-03	60
2	0.92	1.6 x E-5	20	0.74	2.20E-03	60
3	3.06	5.2 x E-5	20	2.05	2.00E-03	60
4	5.84	9.95 x E-5	21	4.77	2.30E-03	60
5	11.35	1.93 x E-4	20	7.60	2.00E-03	60
				AVG	2.10E-03	60
				St. Dev.	1.41E-04	

Raw Data for Electricity Produced by ASV

Sample #1

	Concen. (ppm)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	0.66	60	25	0.53	1.90E-03
	0.64	60	23	0.48	2.05E-03
	0.68	60	25	0.58	2.06E-03
	0.70	60			
	0.67	60			
	0.65	60			
	0.66	60			
	0.65	60			
	0.63	60			
	0.64	60			
	0.63	60			
AVG	0.66	60	24.33	0.53	2.00E-03
ST. DEV	0.02	0.0	1.15	0.05	8.96E-05

Appendix 3
Raw Data for Electricity Produced by ASV
Sample #2

	Concen. (ppm)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	0.92	60	21	0.72	2.10E-03
	0.94	60	20	0.72	.2.20E-03
	0.94	60	20	0.77	2.40E-03
	0.92	60			
	0.92	60			
	0.94	60			
	0.90	60			
	0.92	60			
	0.92	60			
	0.91	60			
	0.89	60			
AVG	0.92	60	20.33	0.74	2.23E-03
ST. DEV	0.02	0.0	0.58	0.03	1.53E-04

Raw Data for Electricity Produced by ASV
Sample #3

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	3.08	60	20	1.92	1.90E-03
	3.08	60	20	2.11	2.00E-03
	3.09	60	20	2.11	2.00E-03
	3.07	60			
	3.04	60			
	3.01	60			
	3.06	60			
	3.03	60			
	3.05	60			
	3.06	60			
	3.05	60			
AVG	3.06	60	20.00	2.05	1.97E-03
ST. DEV	0.02	0.0	0.00	0.11	5.77E-05

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Raw Data for Electricity Produced by ASV
Sample #4

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	5.82	60	21	4.56	2.10E-03
	5.86	60	21	4.80	2.30E-03
	5.82	60	21	4.94	2.40E-03
	5.84	60			
	5.84	60			
	5.82	60			
	5.86	60			
	5.86	60			
	5.80	60			
	5.83	60			
AVG	5.84	60	21.00	4.77	2.27E-03
ST. DEV	0.02	0.00	0.00	0.19	1.53E-04

Raw Data for Electricity Produced by ASV
Sample #5

	Concen. (Moles)	Stirring (RPM)	Deposition Time (t)	Current (Q) (micro-amp.)	K = Q/C*t
	11.32	60	20	7.40	1.90E-03
	11.31	60	20	7.80	2.06E-03
	11.29	60			
	11.34	60			
	11.31	60			
	11.33	60			
	11.52	60			
	11.38	60			
	11.45	60			
	11.40	60			
	11.32	60			
AVG	11.36	60.00	20.00	7.60	1.98E-03
ST. DEV	0.07	0.00	0.00	0.28	1.13E-04

Appendix 4
Raw Data for Electricity Produced by
ASV
Akashic Sample #1

	Deposition Time (t)	K	Current (Q) (micro-amp.)	Stirring (RPM)	C = Q/K*t	Diff. (%) ASV vs AA
	25	0.0021	1.65	60	3.14E-05	12.3%
	25	0.0021	1.75	60	3.34E-05	7.1%
AVG	25	0.0021	1.7	60	3.0E-05	10%
ST. DEV	0	0	0.07	0	1.414E-06	

Raw Data for Electricity Produced by
ASV
Akashic Sample #2

	Deposition Time (t)	K	Current (Q) (10-6 A)	Stirring (RPM)	C = Q/K*t	Diff. (%) ASV vs AA
	25	0.002	0.72	60	1.37E-05	-10.5%
	29	0.002	0.96	60	1.54E-05	+2.8%
AVG	27.00	0.002	0.84	60	1.49E-05	3.3%
ST. DEV	2.83	0	0.17	0.00	7.07E-07	

Appendix 4
Raw Data for Electricity Produced by ASV
Akashic Sample #3

	Deposition Time (t)	K	Current (Q) (micro-amp.)	Stirring (RPM)	C = Q/K*t	Diff. (%) ASV vs AA
	20	0.54	24.80	651	2.30E-06	82%
	20	0.54	25.15	651	2.32E-06	82%
AVG	20	0.54	24.975	651	2.31E-06	82%
ST. DEV	0	0	0.25	0	1.414E-08	

Raw Data for Electricity Produced by ASV
Akashic Sample #4

	Deposition Time (t)	K	Current (Q) (micro-amp.)	Stirring (RPM)	C = Q/K*t	Diff. (%) ASV vs AA
	20	0.54	34.50	651	3.19E-06	88%
	20	0.54	35.25	651	3.26E-06	86%
AVG	20.00	0.54	34.88	651.00	3.23E-06	87%
ST. DEV	0.00	0	0.53	0.00	0.00E+00	

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Appendix 5

Akashic Samples
Waste Water Nickel Analysis Results by AA

Sample #1 (ppm)	Sample #2 (ppm)	Sample #3 (ppm)	Sample #4 (ppm)
2.05	0.94	0.76	1.46
2.14	0.91	0.78	1.4
2.13	0.92	0.74	1.44
2.1	0.92	0.75	1.44
2.11	0.93	0.74	1.45
2.13	0.9	0.76	1.45
2.13	0.94	0.72	1.48
2.14	0.91	0.74	1.45
2.1	0.92	0.75	1.46
2.08	0.9	0.7	1.47
2.12	0.91	0.7	1.46
2.11	0.94	0.71	1.46
2.13	0.91	0.68	1.49
2.15	0.9	0.77	1.46
2.09	0.89	0.81	1.43
2.11	0.9	0.7	1.47
2.11	0.88	0.77	1.43
2.1	0.89	0.81	1.45
2.1	0.9	0.75	1.42
2.1	0.87	0.74	1.4
2.07	0.89	0.75	1.4
2.12	0.88	0.78	1.47
2.08	0.85	0.75	1.4
2.06	0.87	0.77	1.46

	Sample #1	Sample #2	Sample #3	Sample #4
AVG	2.1066667	0.9029167	0.7470833	1.4458333
ST. DEV.	0.0258199	0.0233087	0.0332944	0.026196

Sample 1 = 2.11 ppm = 3.6 x E-5 M
Sample 2 = 0.90 ppm = 1.5 x E-5 M
Sample 3 = 0.75 ppm = 1.3 x E-5 M
Sample 4 = 1.44 ppm = 2.45 x E-5 M

Appendix 6
Regression Analysis
Linear model: Y = a+bx

Dependent variable: 0.00244, 0.00633, .028,. Independent variable: .5,.5,5,5,5,12.5,1

Parameter	Estimate	Standard Error	T Value	Prob. Level		
Intercept	2.75E-04	3.44E-04	6.34E-02	9.51E-01		
Slope	6.38E-03	6.62E-05	9.64E+01	0.00E+00		

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	Prob. Level	
Model	1.2492	1	1.2492	9286.656	0	
Error	0.0012106	9	0.0001345			

Total (Corr.)   1.2503988   10

Correlation Coefficient = 0.999516
Stnd. Error of Est. = 0.011598

R-Squared = 99.90 percent