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TRACE HEAVY METAL DETERMINATION IN SOIL SAMPLES USING DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

BY

ANGELO RANSIRIMAL FERNANDO

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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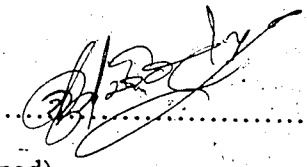

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"Experiment is the Interpreter of Nature,

Experiments Never Deceive

It is Our Judgement Which Sometimes Deceives Itself

Because,

It Expects Results

Which Experiment Refuses."

LEONARDO DA VINCI

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled TRACE HEAVY METAL DETERMINATION IN SOIL SAMPLES USING DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY submitted by ANGELO RANSIRIMAL FERNANDO in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

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Date: MAY 30, 1988

To Manel

My Partner

My Best Friend

and

My Dear Wife.

ABSTRACT

Studies reported in this thesis were carried out employing an anodic stripping system constructed via interfacing a micro computer (Analog Devices Macsym 150) to a commercially available polarographic analyzer (Princeton Applied Research Model 174A). All work was done using an automated hanging mercury drop electrode system (Princeton Applied Research Model 303).

Effects of the background electrolyte on differential pulse anodic stripping voltammetry were investigated. The presence of chloride ions in the solution was found to give higher sensitivity in the determination of cadmium than did the presence of nitrate ions. For lead, this situation was found to be reversed although the difference in sensitivities is not as significant as in the case of cadmium. Apart from the effect on sensitivity, the changing of chloride levels that can arise as a result of leaking from a chloride containing reference electrode was found to affect the precision of the analysis adversely.

Using a matrix exchange procedure and a two way analysis of variance process, oxygen interference in anodic stripping analysis was shown to be confined to the stripping or analysis step.

The applicability of differential pulse anodic stripping voltammetry for the measurement of trace heavy metals in soil samples was investigated by measuring the amount of lead in a sample of soil collected locally as well as in two certified reference soils (SO-1 and SO-2; Canadian Certified Reference Materials Project). Digestion of the soil sample in open Teflon beakers using a nitric : perchloric : hydrofluoric acid mixture was found to be superior to a microwave digestion using nitric and hydrofluoric acids. In the case of the local soil sample the presence of iron led to a noisy response during the analysis of the digested solution using differential pulse anodic stripping analysis.

Dilution of the final analytical solution with deaerated buffer was found to be an effective solution to this problem.

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I wish to thank my wife to whom this thesis is dedicated for her never ending patience, continuous encouragement, and for countless hours spent listening to my boring descriptions of the marvels of Anodic Stripping Voltammetry. My two sons Sumudu and Miyuru are fondly remembered for all the happiness they provided.

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Chapter 1

Introduction to Anodic Stripping Voltammetry

1.1 Anodic Stripping Voltammetry - Principles and Practice

An electrochemical stripping technique can be defined as the use of an electrochemical method to quantify an analyte with prior accumulation onto (or into) an electrode. One may find a direct parallelism between this definition and that of any extraction (solvent or column) procedure which results in an increase in concentration of the analyte. In the case of anodic stripping analysis, which can be considered as a forerunner to all other stripping techniques, prior accumulation consists of a reductive deposition of metals of interest onto an electrode. The usual electrodes of choice are mercury drops or mercury films, because mercury is the only reasonably noble liquid metal at room temperature, so this deposition results in the formation of an amalgam. The concentration of the metals in the amalgam can be controlled by selecting a suitable deposition time. This process is followed by a reoxidation step, usually either under potential control or under current control. Measurement of the uncontrolled parameter during reoxidation yields a greatly amplified signal which can be directly related to the concentration of the analyte in the solution. This amplification results from the increased concentration level of the analyte in the amalgam due to the small volume of the electrode.

Two excellent books[1,2] exist that specifically discuss stripping analysis. Apart from these, almost all modern texts on electroanalytical methods[3,4] or voltammetric and polarographic techniques[5] discuss stripping techniques at an introductory level. References 6,7 and 8 also can be regarded as introductory material. Venkatesan[9] has compiled an extensive bibliography in this area.

In practice anodic stripping analysis is almost invariably performed with either a hanging mercury drop electrode or a mercury film electrode formed on a suitable substrate.

Brainina[10], however, discusses various applications of anodic stripping techniques using solid metal electrodes. Although this practice may have advantages in specific situations, it has limited applications. Recent advances in mercury thin film electrode technologies and the automation of the hanging mercury drop electrodes have ensured the primacy of mercury electrodes in the field of stripping analysis.

Hanging mercury drop electrodes designed by Kemula[11], which used a micrometer head-driven drop forming device, have given way to electronically controlled automatic electrodes such as the stationary mercury drop electrode manufactured by Princeton Applied Research Corporation and the Multi Mode Electrode from Metrohm AG. This has taken away the disadvantages associated with electrode malfunctioning and irreproducibility. Moreover, both of these electrodes can function as hanging mercury drop electrodes or as dropping mercury electrodes, thereby allowing rapid switchover from stripping techniques to polarographic techniques and increasing the possible dynamic range of the system from sub ppb levels to millimolar levels for a particular metal. This allows an analysis to be carried out at the best concentration range to achieve the best accuracy and precision possible. This area of studies directed towards improving the reliability and reproducibility of hanging mercury drop electrodes is still active as evidenced by several reports[12,13,14,15,16] that describe improvements made to existing electrodes, as well as radically new ways of forming and maintaining a drop of mercury at the end of a glass capillary.

The mercury thin film electrode has also undergone considerable modifications mainly as a result of the advancement of the theory and understanding of the behaviour of microelectrodes[17], which are defined as devices with characteristic dimensions smaller than 20μm. Several favourable conditions such as lower interferences from dissolved species in the matrix and lower IR losses[18] can be achieved with this drastic reduction in surface area of the electrode.

Sottery and Anderson[19], Wang et al.[20] and Schulze and Frenzel[21] report on the use of carbon fibers as substrates for thin mercury films as applied to anodic stripping voltammetry. Golas and Osteryoung[22] have studied the nature of mercury films on carbon fibers. Wang[23] reports on a graphite-epoxy electrode that can be used for anodic stripping measurements. Though this is a disk shaped electrode with a radius of 140μm, use of the term microelectrode is warranted in the view of the method of fabrication. Pons and Fleischmann[17] point out the possibility of using a mercury drop with micrometer dimensions deposited on a metallic or other suitable microelectrode for stripping applications as opposed to thin films.

The search for novel substrates for thin mercury films has not been limited to carbon fibers. Liberti et al.[24] have prepared electrodes by incorporating graphitized carbon black into a polyethylene matrix that can be moulded into various shapes and has been shown to have electrochemical properties similar to or superior to glassy carbon. Yoshida and Kihara[25] have evaluated a nickel based mercury film electrode for the purpose of anodic stripping voltammetry. They have found it to have a higher hydrogen overpotential than mercury films based on other metals, which allows stripping determination of both lead and cadmium. They also report on the better stability of a mercury film on nickel. Use of glassy carbon, which is a widely used and preferred substrate for mercury film electrode preparation, has been reviewed by Van Der Linden and Dieker[26]. Florence[27] also has studied the merits of glassy carbon electrodes. Clem, Litton and Ornelas[28] provide a long and informative discussion on preparation and properties of wax impregnated graphite electrodes used as a substrate for mercury films in early studies.

Figure 1.1 (redrawn after Barendrecht[29]) illustrates the entire process of anodic stripping analysis in a compact manner. As indicated the analysis system usually consists of a cell which contains the analytical solution and a stirring mechanism. Stirring increases the flux of analyte to the electrode, increasing the efficiency of the deposition or the accumulation step. As a result of this, deposition is not being done under the diffusion

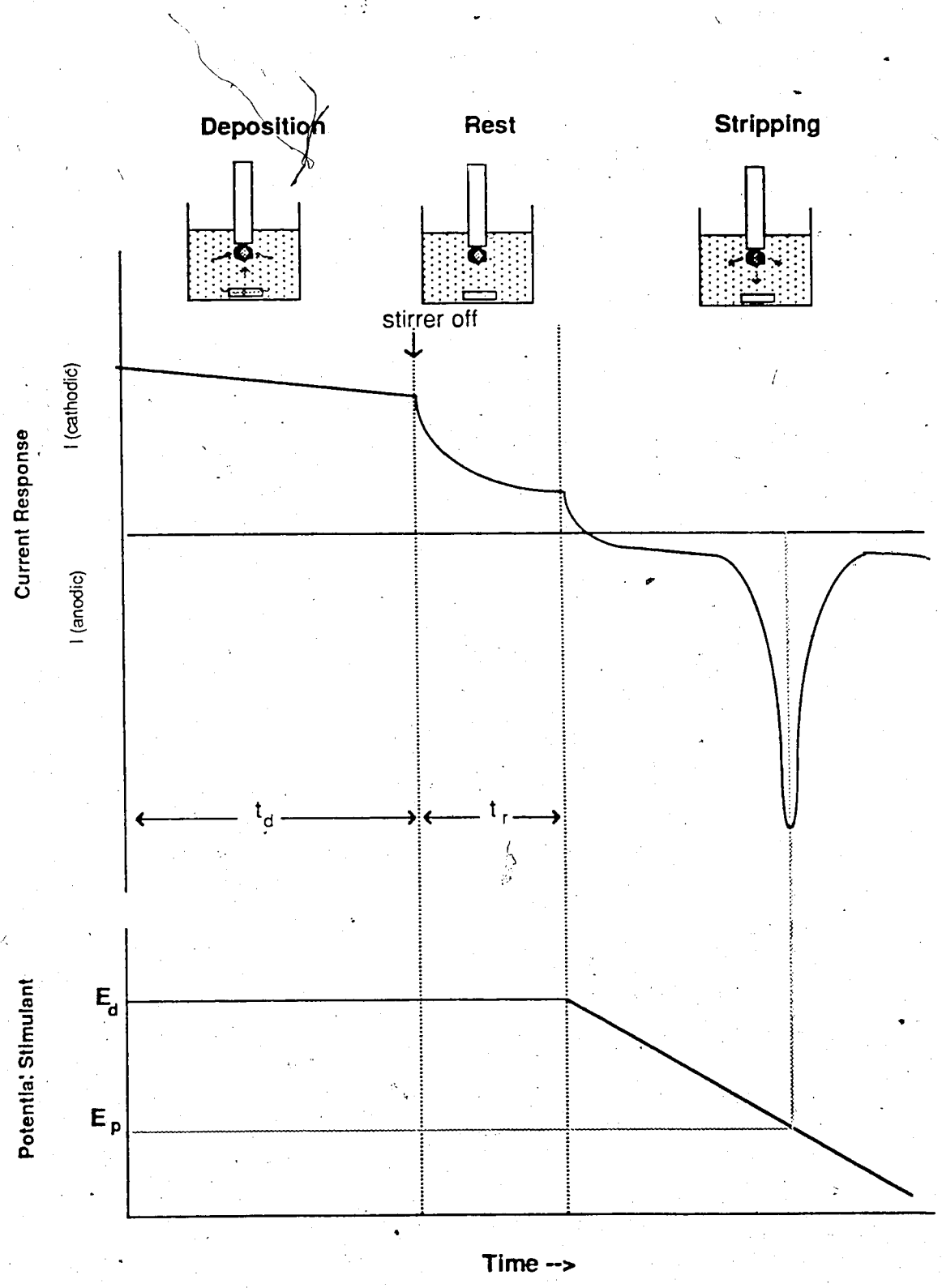


Figure 1.1 Schematic Representation of the Various Steps in Anodic Stripping Analysis (redrawn after Barendrecht(29))

E_d - Deposition Potential

E_p - Peak Potential

controlled conditions that are encountered in polarography, but under convective conditions such as those usually found in coulometric cells. On the other hand deposition is not being carried out to the limit as in coulometric analysis, but is terminated after a reproducible fraction of the analyte has been deposited. In most cases 0.5-5% decrease in the concentration of the metal ion in the solution can be expected. To achieve this, exact reproduction of the stirring conditions is necessary, which depends on the size and speed of the stirring part, shape of the cell, location of the electrode and other related parameters.

An equilibration step has been incorporated prior to the stripping step to allow the solution to become quiescent. This is essential in the case of a hanging mercury drop which is usually operated with a magnetic stirrer to provide stirring. Otherwise disturbances arising from the nonuniform solution flow hinder the measurement process. In the case of a rotating thin film mercury electrode this step can be omitted and the electrode can be rotated throughout the stripping procedure, as a result of the well defined hydrodynamics and the close control one can have on the rotation of a disk electrode. In fact claims have been made on the superiority of using an accurately controlled glass ball shaped stirrer in place of the usual magnetic stirrer[28] and of using a gas flow for stirring purposes[30] On the other hand it has been shown that a magnetic stirrer is equally effective with a stationary thin film mercury electrode[31].

The actual stripping step can be accomplished by a variety of methods. Voltammetric stimulations which are direct adaptations of the waveforms used in polarography are much more popular due to the ready commercial availability of the necessary instrumentation.

Linear scan voltammetric stripping, in which a linear voltage ramp is applied to the electrode, was originated by Nikelly and Cooke[32] in the late nineteen fifties as an alternative to the coulometric estimation methods which were used at that time. In fact the power of anodic stripping voltammetry was demonstrated by the use of coulometric estimation methods as early as in nineteen fifty two by Lord, O'Neill and Rogers[33], who analysed a

12.5 ppb solution of silver with a platinum electrode. Differential pulsed stripping, which has its roots in differential pulsed polarography, has replaced this early stripping technique to a large extent. The differential pulse wave form offers a large sensitivity increase over linear scan, coupled to a better resolution of stripping peaks, with a well defined base line in most situations that simplifies the quantification process (Figure 1.2).

Sensitivity improvement in differential pulsed stripping stems from its ability to suppress charging current contributions to the signal. This gain is further increased by the replating of oxidized metal in between pulsing periods, when the potential of the electrode is more negative than the oxidation potential of the analyte. Some of these aspects as applied to thin mercury film electrodes have been studied by Copeland et al[34].

As shown in Figure 1.3, the differential pulsed wave forms used in normal practice use a slow voltage ramp which increases the analysis time considerably. Lund and Onshus[35] have compared these two techniques as applied to the practical analysis of a sea water sample. Their work is also significant for the theoretical relationships derived for differential pulse anodic stripping voltammetry on a hanging mercury drop electrode.

Longer analysis times with differential pulse stripping can be considered to some extent as an instrumental limitation rather than a fundamental barrier of the method, since it has been demonstrated [19] that faster stripping can be realized by reducing the waiting period between pulses. In general purpose commercial instruments, which are designed to be operated as polarographic analyzers as well as stripping analyzers, the pulse repetition function is usually tied to the mercury drop renewal operation in the polarographic mode. Recent microprocessor based instruments allow more flexibility in this area. Svensmark[36] proposes a staircase voltammetric stripping method with a stripping time of four milliseconds (scan rate of 156 V/s), compared to 150 seconds at a 10 mV/s scan rate using differential pulse stripping voltammetry.

Square wave voltammetric techniques proposed by Barker[37] have also been implemented with microcomputer controlled systems[38] to enhance anodic stripping

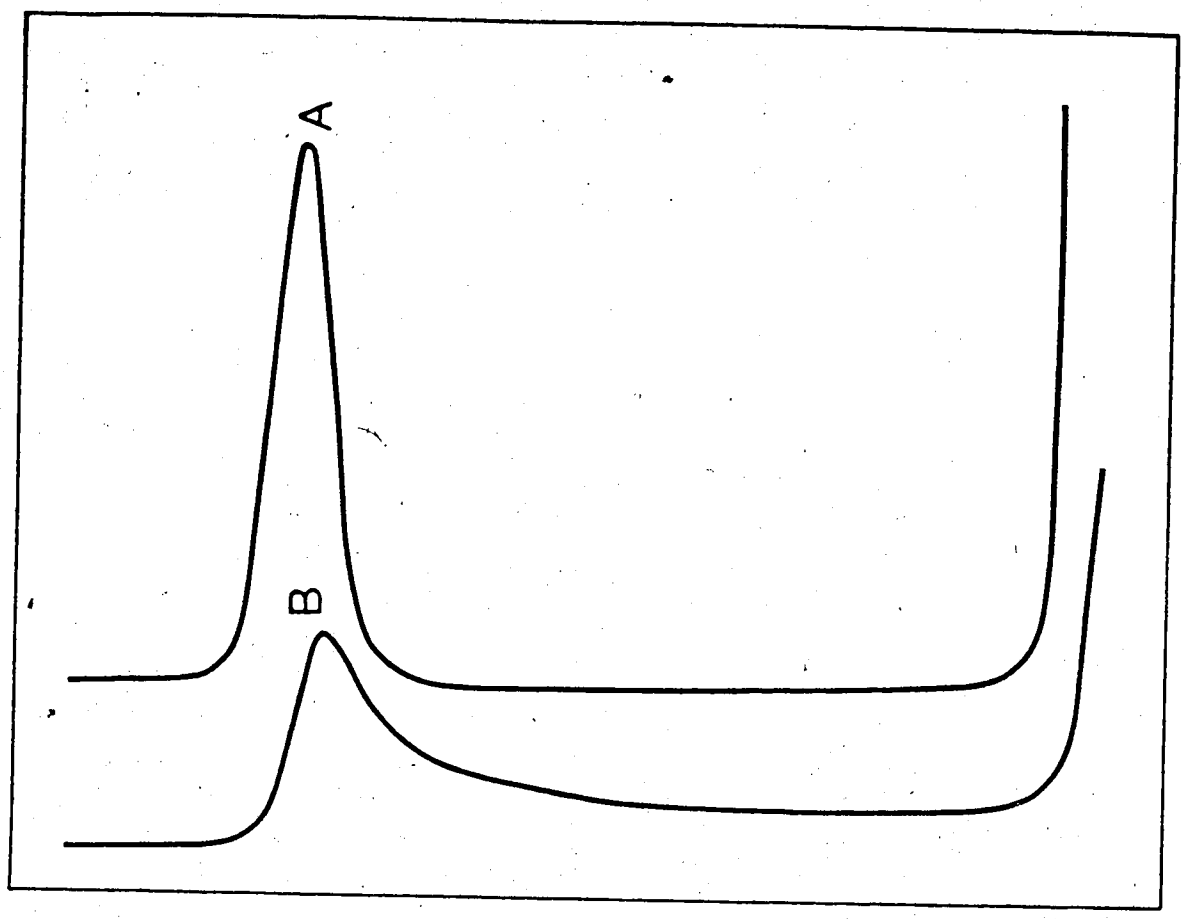


Figure 1.2 Comparison of Linear Scan and Differential Pulse Stripping Curves for a Solution Containing 1ppm Cadmium.

A. Differential Pulse Stripping - Scan rate 5 mV/s
Modulation 50 mV
Peak Height 0.56μA.

B. Linear Scan Stripping - Scan rate 50 mV/s
Peak Height 0.11μA

A 36 s deposition was done in both cases.

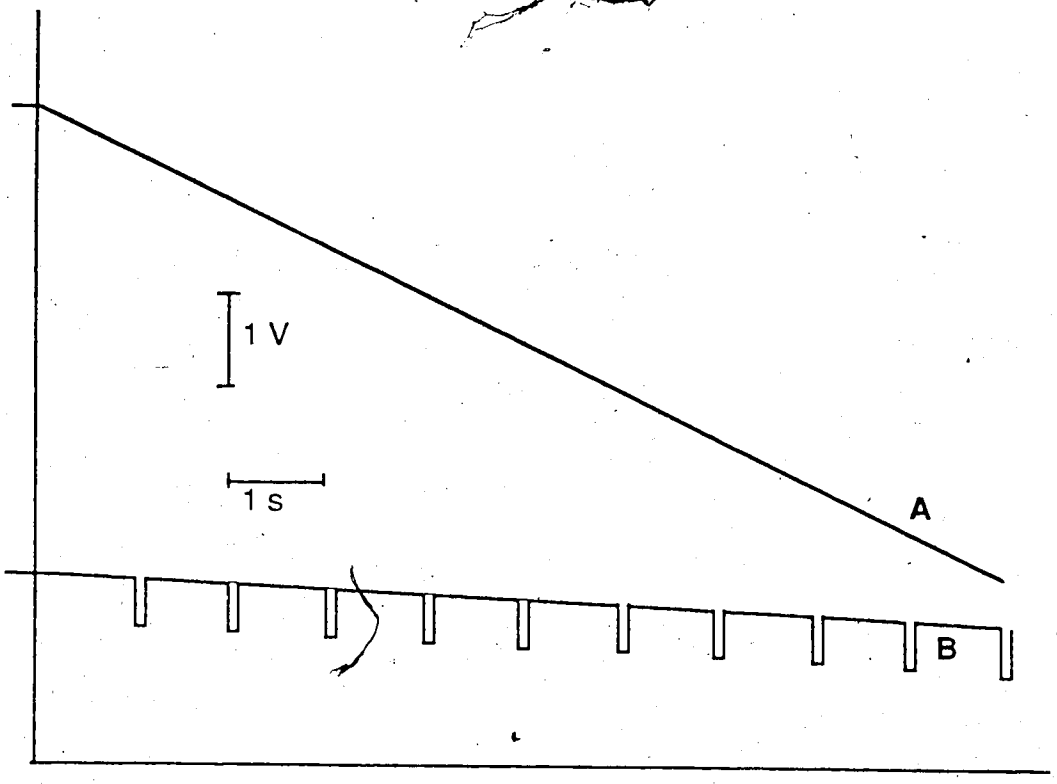


Figure 1.3 Comparision of Stripping Wave Forms: Linear Scan and Differential Pulse.

A. Linear Scan: Scan rate 50mV/s.

B. Differential Pulse: Scan rate 5mV/s; Pulse Height 50mV; Width 50ms; Interval 1s.

techniques. Provisions to perform square wave analysis are provided in several recent commercial voltammetric analyzers. It should be pointed out that in nineteen fifty-two Barker[37] described the anodic stripping analysis procedure in the way it is being practiced today as a technique that can be used to extend the sensitivity of square wave techniques to the 10^{-11}M range, but refrained from promoting it since he did not see any real need for a technique with a sensitivity higher than the 10^{-8}M level that can be achieved with square wave polarography.

In recent years much interest has been directed towards moving away from the standard batch cell process into flow systems. On top of the time advantage, flow systems offer an easy way to perform matrix exchange, which in simple terms amounts to changing the electrolyte or the solution present at the working electrode between deposition and stripping operations[2]. This exchange process allows one to carry out the stripping step under standard conditions in an environment free from other contaminants present in the sample, with the optional advantage of tailoring the stripping solution composition with the use of pH modifiers and complexing agents to enhance the sensitivity of a specific metal or to suppress the signal of an interfering metal.

Ariel's flow system[39] which uses a rotating disk electrode can be cited as representative of the early attempts in using flow systems to automate the stripping analysis. These manipulations were done by incorporating a pump into the system and with relatively minor modifications in the cell design. Buchanan and Soleta's flow through cell system[38] is representative of the next stage of these developments, which incorporate a square wave stripping technique with a matrix exchange system. Though based on an automated hanging drop electrode, a major deviation from the classical configuration is the use of sample flow itself for convective transport of the analyte during the deposition period. The matrix exchange procedure used in this cell has allowed the use of nondeaerated samples with a significant reduction in analysis time. A parallel system which uses a thin mercury film on [illegible]

by Wang and Greene[40]. The flow injection system described by Wise et al.[41] marks the evolution of a new line of thinking in terms of instrumentation. Using a commercially available flow cell and a potentiostat they have demonstrated the capability of the system by performing an indium analysis using differential pulse stripping at a 20pg/ml level, which requires only 1ml of the sample. The main improvement over Buchanan and Soleta's system[37] is the maintenance of a continuous flow even during the stripping step. Gunasingham et al[42] have reported on the use of a wall jet electrode for the same purpose. This electrode, primarily developed for electrochemical detection in high performance liquid chromatography systems, has been claimed to have better defined and well understood hydrodynamic properties, which are useful in this type of application.

Another attractive direction taken by some workers is the use of differential or subtractive stripping systems, where a differential response from two electrodes operated simultaneously is used to correct for background effects such as those arising from oxygen and other dissolved species. Zirino and Healy[43] have used two identical hanging mercury drop electrodes for this purpose. Only one electrode is being plated during the deposition period. The differential signal arising from applying a linear scan stripping ramp simultaneously to both electrodes is used to suppress the high charging currents associated with linear scan stripping. Sub ppb level results have been reported for lead and cadmium with a five minute deposition time and a scan rate of 500 mV/min.

Another subtractive stripping system[30] uses a matched set of graphite electrodes cast in an epoxy resin body to ensure perfect and stable alignment. These electrodes, operated as thin mercury film electrodes, are plated differentially by switching the potential of one electrode to an oxidative value halfway through the deposition step. Sub ppb results are reported for a one minute deposition with a 33mV/s stripping rate, under linear scan conditions. An increase in the deposition time to two minutes provides voltammograms with flat base lines at these concentrations. Wang and Dewald[44] describe a variation of this technique as implemented in a flow injection system, where one thin film mercury electrode

is used. The stripping operation was carried out in the sample solution itself with a stopped flow. Background recorded in the carrier solution is digitally subtracted using a computer data acquisition system. Sub ppb determinations have been performed with one minute deposition using 200µl nondeaerated samples.

As opposed to voltammetric stripping procedures, potentiometric stripping introduced by Jagner and Graneli[45] uses the recording of the potential variations at the working electrode, with oxidative stripping induced by oxygen or mercuric ions present in the solution. The main advantage of this technique is the reduced stripping time and the simplicity of the instrument. Kryger[46] has developed a differential potentiometric technique, which enhances the normal potentiometric stripping outcome. The improvement is similar to the improvement one achieves when going from linear scan stripping to differential pulse stripping. Development of this technique has been accelerated by the early incorporation of computer data acquisition systems, which allow the use of high stripping rates, easy incorporation of flow cells, and sophisticated data manipulations[47]. This method has been used in practical analysis of environmental samples on a routine basis[48]. A novel use of this technique[49] is the quantification of dissolved oxygen in natural water samples through the measurement of stripping time of a standard metal solution.

1.2 Anodic Stripping Voltammetry in Environmental Analysis

Anodic stripping analysis can be considered as a modification of voltammetric techniques for the specific purpose of trace metal determination. Compared to the dominant atomic spectroscopic methods, electrochemical methods have limited scope under given circumstances regarding the number of metals that can be analysed, making them unsuitable as candidates for total elemental analysis. Offsetting this shortcoming is the high sensitivity for environmentally important metals such as lead and cadmium. Our environment being an aqueous one, and many of the important reactions being redox-type reactions, metals or compounds that are highly electroactive in an aqueous solution form a class of

environmentally important species. Most often metals interfere in natural processes through complexation. In this regard, anodic stripping analysis can offer an unparalleled advantage due to its sensitivity to the form of metal species in an aqueous solution, allowing differentiation between different oxidation states as well as different complexes[50,51].

Though a number of significant advances have been made in anodic stripping techniques as well as in the general area of analytical voltammetric techniques, mostly with respect to instrumentation, utilization of this technique in the area of environmental analysis is still limited mainly to the analysis of natural water for possible pollution by heavy metals[52,53]. There seems to be a considerable reluctance to adapt anodic stripping analysis for the analysis of soil and related samples, which form an important class of samples in the environmental monitoring for toxic trace metals. Historically, soil and mineral analysis has been closely related to the development of atomic spectroscopy, which explains to some extent the current trend in this direction[54]. According to Jenkins and Jones[55] "The advent of atomic absorption spectroscopy brought a greater precision and sensitivity for selected trace elements, though it necessitated the dissolution of samples, which is inconvenient for studies of trace elements in the solid phase, but on the other hand proves particularly useful for analysis of extracts. Our knowledge of Cu, Pb and in particular Zn expanded rapidly with the advent of this technique". Ironically Cu, Pb and Zn are three of the metals most often determined using stripping voltammetric methods. It is true that significant advances have been made in atomic spectroscopic techniques in recent years, but the lack of studies regarding applications of anodic stripping techniques in more practical situations hinder any evaluation or comparison. There appears to be only one published report[56] discussing the use of anodic stripping for the analysis of soil for toxic trace metals. An agronomy monograph[57] on methods of soil analysis devotes an entire chapter to anodic stripping voltammetry and differential pulse polarography which forms an excellent introduction to the subject but does not cite a single example or a literature report of a practical application in this field. Nevertheless electrochemical techniques have been

used and have been demonstrated to be capable of having very high sensitivities with various sample matrices[1,2].

Most of the chemical analysis methods being solution analysis techniques, soil samples are digested with an acid or fused with an alkali salt to render the sample soluble before the analysis. Exceptions requiring no sample dissolution are neutron activation and X ray energy dispersive techniques. This digestion step reduces the sample to an aqueous solution that can be analysed using many different techniques. In the view of the environmental scientist or soil chemist it is the amount of metal present that is significant but not the technique. So it is customary to give a very low priority to the reporting of the technique used unless it is an exclusive method for the analysis of a particular sample. This fact complicates the estimation of usage of anodic stripping techniques in this area.

Wang points out " some educational problems" (reference 1, p.3) in discussing acceptance of stripping analysis as a trace analytical technique. Almost half a century ago, Sand[58] stated the existence of a "certain mistrust in applying unfamiliar physical concepts to chemical analysis..." as a reason for the low usage of electroanalytical methods in chemical analysis. Kissinger's statement[59] - "Electrochemistry is not a well understood subject. It is given very little attention in the undergraduate science curriculum. Many scientists who find it useful are not comfortable with its basic principles" - does not show any improvement in this regard. It may be the early development of theoretical concepts and rigorous mathematical treatments of kinetics of electrode reactions that hindered electrochemical techniques from gaining ground as versatile analytical techniques. Fishbein's[60] assessment of the requisite high level of skill required for optimal operation of anodic stripping equipment, which he views as a disadvantage, may also arise from the same reason.

Work reported in this thesis was aimed at assessing the applicability of differential pulse anodic stripping voltammetry to the trace metal analysis of soil. This consisted of an investigation into suitable sample digestion procedures, as well as a study into the effects of

residual anions from an acid digestion process on the outcome of the anodic stripping analysis. Digested soil samples were analysed only for their lead and cadmium content. However, because of its representative nature, most of the results regarding the applicability of anodic stripping analysis can be considered valid for heavy metals generally.

Chapter 2

Introduction to Soil Trace Metal Analysis

2.1 Trace Metals in Soil

In terms of soil science, soil can be defined as, "Unconsolidated mineral matter on the surface of the earth that has been subjected to and influenced by genetic and environment factors of parent material, climate (including moisture and temperature effects), macro and micro organisms and topography all acting over a period of time and producing a product -soil- that differs from the material from which it is derived in many physical, chemical and biological properties and characteristics"[61].

In this definition soil has been viewed as a dynamic living system as opposed to the feeling one might get that a sample of soil being prepared for chemical analysis is no more than a gray powder. This difference in definition complicates the role of the analyst in this important field. At a somewhat intermediate level, we can consider soil as a mixture of two main components: minerals and organic matter. Minerals are crystalline and noncrystalline material derived from the weathering of hard rock at the earth's surface. These can be considered as inorganic in nature and consist mainly of silicates. Organic matter, which originates as residues from a myriad of plants and animals that inhabit soil, may also have undergone numerous changes that have transformed the original substances into forms that are unique and which bear little resemblance to their precursors. Though it can vary with location and history of a sample, in general, the organic phase of soil can be expected to occur as a coating over mineral particles[62,63] In most soils, it is the organic phase together with finer mineral fractions that acts as a binding agent between large mineral particles. Under field conditions, there may be a solution phase and a gaseous phase that share the cavities within soil. These two phases are said to form the soil atmosphere. Disregarding

this soil atmosphere, which is lost when a soil sample is removed from the field and dried, trace metals can be expected to exist in this complex background in two main forms.

1. As atoms or compounds deeply embedded in mineral phase constituents. Metals present in this manner can be assumed to form a stable background concentration of that particular metal.

2. As ions or ionic compounds adsorbed or complexed on to mineral and organic phases. This fraction is weakly bound compared to the first and can be regarded as the more labile fraction. Precipitated salts and organometallic compounds that can be present in soil may also be included in this category.

While the first fraction may be regarded as important in mineral exploration and geochemical studies, the second fraction is important due to its ability to interact with plant and animal life through releasing or accumulating trace metals. It is this phase of soil that acts as the bridge between the more stable mineral fraction and the soil solution, which contains trace elements in the most mobile form.

The mineral fraction of soil can be further subdivided into sand, silt, and clay fractions according to the particle size, silt and clay being microscopic and submicroscopic respectively. These small particles with large surface areas usually carry excess surface negative charges offering perfect adsorption sites for trace metals either through ion exchange or direct chemical bonding. Hydrous oxides of iron, aluminium and manganese also act as sites for surface adsorption. The organic phase, which can be broadly subdivided into humic acid, fulvic acid, and humin fractions, might retain metals through chemical bonding as well as through entrapment of ions and compounds[64].

Trace metals bound in this manner into the chemically active organic and clay fractions are derived from more stable mineral fractions, either through natural weathering activity or through the intervention of man. Geological weathering processes are very slow processes compared to the man made release of metallic pollutants. Realization of the slowness of natural processes, which are usually expected to return these unnaturally

released metals into stable states, darkens this picture[65]. Once pollutant metals reach soil, clay and organic fractions tend to bind these metals, hindering further distribution. Runoff from rain and snow may carry parts of these low density fractions into streams and rivers. They ultimately end up as sediments that settle in calm areas of these water bodies. During this sedimentation process, metals and other elements that have been adsorbed, complexed or otherwise incorporated into these particles are also removed from the bulk of the water body. In this way the clay and organic fractions of soil are directly responsible for metal scavenging actions of water bodies. The sediments thus formed will be transferred back onto the earth's surface in the long run and be incorporated into the surface soil. Davies[65] discusses this aspect of trace metal distribution in soils and provides several illustrative examples.

Because of the similarities that exist between river sediments and soils due to their common origin, many of the analytical and sample treatment techniques can be used interchangeably. For this reason literature discussing analytical techniques applied in the case of river sediments has been quoted in the following discussion without indicating the nature of the specific samples.

2.2 Soil Trace Metal Analysis- Total Analysis and Speciation Studies

From the foregoing discussion it follows that trace elements in soil are expected to be present in a number of retention modes. Apart from the major distinction between mineral-embedded and surface-bound species, the nature of the retention mode can vary within each category, allowing one to define a distribution or a speciation pattern for a given trace element. The analytical scheme that is being used for the analysis of trace element concentrations in a given sample should vary accordingly. It can either be directed towards arriving at a mean concentration of a particular element in the whole sample, which is usually referred to as a total analysis, or at obtaining information on the distribution of metal ions within various bonding modes.

The usual procedure involved in total analysis is to use a dissolution procedure to dissolve the whole sample and to analyse the resultant solution. Emission spectroscopy or X-ray fluorescence analysis can also be used without going through the dissolution step if one is prepared to accept a somewhat higher detection limit[66]. X-ray techniques have the additional advantage of providing information on the mineralogical composition of the sample. Specifically designed extraction procedures are often used to obtain information related to speciation of metals[67]. Because of the close relationship that exists between plant availability and toxicity of soil bound heavy metals and the nature of bonding, these studies have widespread uses in agricultural as well as in environmental investigations[68,69]. The term "extraction" has been used in this area to indicate the transfer of metal analytes into a solution phase from solid soil phase with or without a total dissolution of the solid phase rather than to indicate partial extraction of the metal sought[70]. The term "selective extraction" is used to distinguish studies aimed at fractionating the total metal content on the basis of retention modes. Pickering[67] classifies selective extraction methods into three categories:

(a) selective dissolution of sample components, e.g. dissolution of ferromanganese oxides and carbonates using acetic acid,

(b) selective release of fractions, e.g. use of EDTA solutions to extract exchangeable ions, and

(c) sequential extraction procedures, which are generally a combination of above procedures carried out in a sequential manner.

These procedures are valuable when the amount of information they provide about the sample is considered, but tend to put heavy demands on the analytical techniques that are being used for quantification purposes, due to variations in final matrix composition.

In this work total metal analysis was studied rather than speciation or fractionation techniques. In general one can assume that this goal has been achieved upon one hundred percent dissolution of the sample, provided the analytical technique is not hampered by

adverse matrix effects. However it should be noted that it is not always necessary to dissolve the whole sample, due to differences in metal accumulation properties of the different soil components. An HCl/HNO_3 extraction procedure has been shown to give total metal contents for some metals in a standard sample[69,70]. Ability of these simple methods to indicate total metal levels depends to a large extent on their ability to dissolve the right portion of the sample, which consequently depends on the nature of the sample itself.

2.3 Digestion Methods Used in Total Trace Metal Analysis of Soils

Digestion methods available for the dissolution of soil type samples can be divided into two main categories: acid digestion and alkaline fusion. Acid digestion procedures are wet chemical procedures carried out at moderate temperatures, usually below 250°C. Fusion procedures involve melting a mixture of sample and an appropriate flux at a higher temperature (~ 1000°C)[71]. This technique is usually applied in the case of major element determinations, and has been found to be unsatisfactory for trace metal analysis[72]. The main problems in fusion methods are high blank levels from the use of a large amount of flux and the loss of volatile elements at the high temperatures employed. High salt background salt concentrations in the solutions obtained by dissolving the fused samples in acid can lead to problems in atomic absorption measurements. Nevertheless, fusion techniques, especially lithium tetraborate fusion, have been shown to be effective in the trace metal analysis of soil type samples using atomic absorption methods.

Sulcek, Povondra and Dolezal[73] have reviewed the area of decomposition methods in inorganic analysis and list many variations of these two general techniques. An important modification of fusion techniques are the sintering methods, where a low temperature and a low flux ratio is being used. Though cited literature examples are mainly directed towards the analysis of major components of silicate minerals, many of these digestion methods can be employed for trace analysis as well, if due allowances and precautions are taken. Fusion

techniques and their variations were not considered in the work described in this thesis. Acid decomposition techniques, especially perchloric digestion methods, were thought to be more appropriate for the purpose of trace analysis in soil samples using anodic stripping voltammetry. This decision was based on (1) the low temperatures involved, reducing heating and cooling times as well as equipment requirements, (2) ready availability of ultra pure acids and (3) the widespread use of acid decompositions in the general area of trace analysis.

Acid digestions can be further subdivided into open and closed systems. Digestions carried out under normal atmospheric pressures in open beakers, conical flasks or other containers with or without refluxing attachments to suppress the evaporation losses are classified as "open digestions". These systems, which can be considered as classical digestion techniques, have been improved or rather adapted in recent years by the introduction of Teflon beakers and other implements to be used in trace metal analysis. Almost all mineral acids have been used in these systems for various digestion procedures. For the purpose of trace metal analysis, however, only perchloric, nitric and hydrochloric acids have been used extensively. In soil and other silicate sample digestions hydrofluoric acid is the acid of choice for the disruption of the silicate matrix. Hydrofluoric acid is the only acid that reacts with silicon, silicon dioxide, and silicates, forming soluble H_2SiF_6. Though relatively weak as an acid, with a pK_a of 2.92 (in a medium with an ionic strength of 0.1)[74], its complexing properties make it a superior solvent for many elements. Usually HF is used in conjunction with other acids, primarily $HClO_4$, HNO_3 and HCl, in order to achieve a complete dissolution of the sample. In the case of soil it is difficult to assign individual fractions that are being dissolved by different acids, except for the action of HF on silicates and the oxidative action of HNO_3 and $HClO_4$ on organic matter. This difficulty is due to the unknown composition of a given soil sample. An extensive amount of data exists[73] on the action of these acids on various minerals which can be used in many instances for the selection of suitable acids. Digestion procedures used in trace metal

analysis involve heating with HNO_3, $HClO_4$ or HF or a mixture of these acids followed by evaporation to dryness. The main object of the evaporation step is the removal of fluoride and silicon, through the decomposition of H_2SiF_6 into gaseous SiF_4. Higher oxidative action resulting from the high temperatures attained at this stage is an advantage towards the decomposition of organic and nonsilicate components.

However, there are certain minerals that are resistant to the attack of HF. Breder[75] has found a residue weighing 200mg from the decomposition of a 1g river sediment sample, even after increasing the amount of HF used up to six milliliters. Sulcek et al.[73] cite various examples of this nature, especially with the digestion of rock samples, when high sample weights are being used. Offensive precipitates seem to be due to the formation of fluoro complexes containing iron and aluminium. Once formed these compounds cannot be dissolved easily, even with repeated perchloric treatments. Maqueda[76] reports the inability of the usual HNO_3, HF, $HClO_4$ methods to dissolve the mineral pyrophyllite in clay samples. Bennet[77] notes the inability of HF to dissolve beryl, tourmaline and zircon.

No clear agreement can be found on the order of addition, amounts of acids, heating temperatures, and length of digestion among the large number of reported procedures for silicate-based samples. The only agreement is in the final evaporation to near or complete dryness, after which the residue is dissolved in 1M HNO_3 or HCl. This variability may be due to the tendency to use the least vigorous digestion method possible with a given sample together with other considerations such as avoidance of perchloric acid for reasons of safety. A definite trend in the choice of acids can be seen. Unsuitability of H_2SO_4 for the purpose of trace analysis has been observed[78,79]. Formation of insoluble sulphates of calcium was found to interfere with trace lead analysis through adsorption losses[78,80]. Similar problems have been observed with HCl/HNO_3 mixtures, in addition to volatility losses of metal chlorides. Recent literature reports show a tendency toward, using $HNO_3/HClO_4/HF$ combinations for the purpose of digesting sediments, soils and other associated samples.

High digestion temperatures, which is an advantage of H_2SO_4-based digestions, can be realized with these acids in a closed digestion system or in more common terms in a bomb digestion procedure. Closed vessel digestions where high temperature and pressure conditions can be realized have been used in geological analysis as early as 1894[73]. Most of these early methods used sealed glass tubes to achieve these conditions.

Teflon lined steel bombs have replaced this early apparatus and are widely used for sample digestions. Relative freedom from the need of constant attention and short digestion times that can be realized due to high pressure and temperature can be cited as reasons for this popularity. It has been reported that some of the resistant silicates are amenable to HF attack in a high pressure bomb[76, 77]. Acid mixtures which are used in open beaker systems can be used in bombs too. Contrary to the advice from manufacturers[81] some authors have reported the use of perchloric acid for the digestion of soil and sediment samples in these bombs[69,79] without any adverse results, though the effects of this on the useful lifetime of Teflon liners is not clear. Hsu and Locke[79] report the beneficial effects of increasing the perchloric acid amount in the digestion of resistant deep sea sediments.

Rantala and Loring[82] have designed a Teflon bomb without a steel outer casing, which can be heated up to 100°C (the usual upper limit for high pressure bomb with a steel jacket is 250°C) in a water bath. This bomb has been used successfully in digestions of silicates, sediments, and soil[82, 83, 84, 85, 86, 87] employing various acid mixtures including perchloric.

The most recent advance in this area is the use of microwave ovens for heating samples contained in Teflon and other plastic containers[88, 89, 90]. Unlike conventional heat sources that depend on conductive and convective processes for the transfer of heat from the source to the solution, microwave radiation is converted to heat within the solution. Microwave transparency and low conductivity of Teflon and other plastics makes this method more attractive for digestion of samples in these containers. Unfortunately

metals can absorb and reflect microwaves used in these ovens so metal jacketed Teflon bombs cannot be used. This barrier has been overcome to some extent by constructing a jacket from high strength plastic[91] which is commercially available at a considerable expense. Microwave heating reduces the digestion times drastically. The usual oven heated Teflon bomb digestion which takes three hours can be done within minutes using microwave heating. This reduction results from the quick heating process.

Chapter 3

Instrumental Setup

3.1 Main Components of The System

Though fundamentally simple, anodic stripping analysis demands a carefully monitored and maintained instrumental setup. In any kind of trace analysis, exact reproducibility of the conditions is vital to obtain good results. In anodic stripping analysis the main instrumental parameters that have to be controlled are the deposition potential, the deposition time convection conditions during deposition and the mercury drop size with a hanging mecury drop electrode (HMDE).

The deposition potential can be controlled to a satisfactory level by employing a three-electrode potentiostat. Automated hanging mercury drop electrodes or even micrometer-driven manual electrodes will produce adequate reproducibility of the mercury drop size with proper care and maintenance. Control of timing operations can be carried out in many different ways, including total manual control and use of a micro computer. While there are commercially available voltammetric instruments equipped with provisions for controlling these operations allowing anodic stripping to be done without additional accessories, these microprocessor based instruments tend to have very high price tags, making one question the validity of the well known claim of inexpensive instruments. Moreover, the flexibility of a homemade instrument has prompted various workers to interface commercial as well as homemade potentiostats to microcomputers[42,92].

The anodic stripping system developed for this work consisted of a microcomputer, the Analog Devices Macsym 150; a potentiostat/polarographic analyser, the Princeton Applied Research Model 174A; and an automated hanging mercury drop electrode, the Princeton Applied Research Model 303 static mercury drop electrode (SMDE).

The Analog Devices Macsym 150 microcomputer is specifically designed for measurement and control operations and can be easily interfaced to control any instrument by means of prewired I/O cards. It also uses a specific version of BASIC (MACBASIC) through which any of the control or measurement channels can be accessed via direct commands. In addition a set of graphic commands allows a real time data display routine to be implemented easily. The setup used for this work contained the following cards, which are located in the main card cage of the computer:

DIO-100 DIGITAL INPUT/OUTPUT CARD

Used with AC/DC modules for control functions.

AIM-100 ANALOG INPUT CARD

Used to tap 174A recorder outputs which were used as the data outputs.

AOT-100 ANALOG OUTPUT CARD

Used as an output to an XY recorder.

DS-1100 DUAL SERIAL INTERFACE CARD

Used as a printer port.

The Princeton Applied Research Model 174A polarographic analyzer is a commercial instrument designed for polarographic analysis in normal, sampled DC, pulse or differential pulse modes.

The Model 303 SMDE, is designed to be connected directly to the Model 174A or other Princeton Applied Research instruments via appropriate cables. The operations of this electrode, i.e. drop extrusion, drop dislodge, purge initiation and termination, can be controlled via TTL inputs to appropriate pins on its two back panel sockets. Appropriate logic levels are also available on these ports, so digital output modules on the MACSYM'S DIO-100 card, which are essentially solid state switches, can be conveniently used to control these functions.

3.2 Interfacing

Interfacing between these three instruments was accomplished by modifying the cable supplied by Princeton Applied Research to interconnect the Model 174A to the Model 303 SMDE. Connection to the auxilliary electrode was routed through a relay box which connected the auxiliary electrode input to the summing amplifier input of the Model 174A in the cell off mode. The relay box was under the control of the Macsym 150. Model 303 SMDE functions as well as the scan inhibit/initiate function of the Model 174A were under the direct control of the Macsym 150 through digital input output card DIO-100. Output signals from the Model 174A rear panel banana sockets were connected via AIM-100 analog input card to the Macsym 150. This card was used in a single ended configuration with a +9.995V to -10.00V full-scale and a gain of unity. Table 3.1 lists connections made to the Model 174A via its rear panel Amphenol connectors. Figure 3.1 shows a block diagram of the system while Figure 3.2 gives a more detailed picture in the form of a schematic wiring diagram.

Apart from these three main components, the system also included a magnetic stirrer (Fisher Scientific Catalogue no. 14 511-2) which was powered through a rheostat (OHMITE V_t, Ohmite Corporation) and was controlled via an AC module connected to the DIO -100 card. A XY recorder (Hewlett Packard 7045A) connected to the AOT-100 analog output card was used to obtain hard copies of the stripping curves. An Apple Imagewriter (Apple Computer, Inc) connected via the DS-1100 dual serial interface card served as the system printer.

The stirring rate of the magnetic stirrer was set using the external rheostat rather than the built-in control. This allowed better control of the stirring rate and also better reproducibility.

In effect the Macsym 150 had control over the following functions of the overall system.

Table 3.1 Additional Connections Made to the Model 174A via Rear Panel Amphenol Sockets

J-36 Access External Power Port

Pin No.	Function	Connected to
5	Ramp Control	DIO-100 via ODO-60
7	Clock	DIO-100 via IDO-16
10	Ext. In II (1 V)	Cell Connect Relay
12	-15 V out	DIO-100 (inhibit signal to ramp)

J-37 Drop timer/Cell Connector

Pin No.	Function	Connected to
1 to 7	Ground	Shielding
12	Auxiliary Electrode	To Cell Relay Box

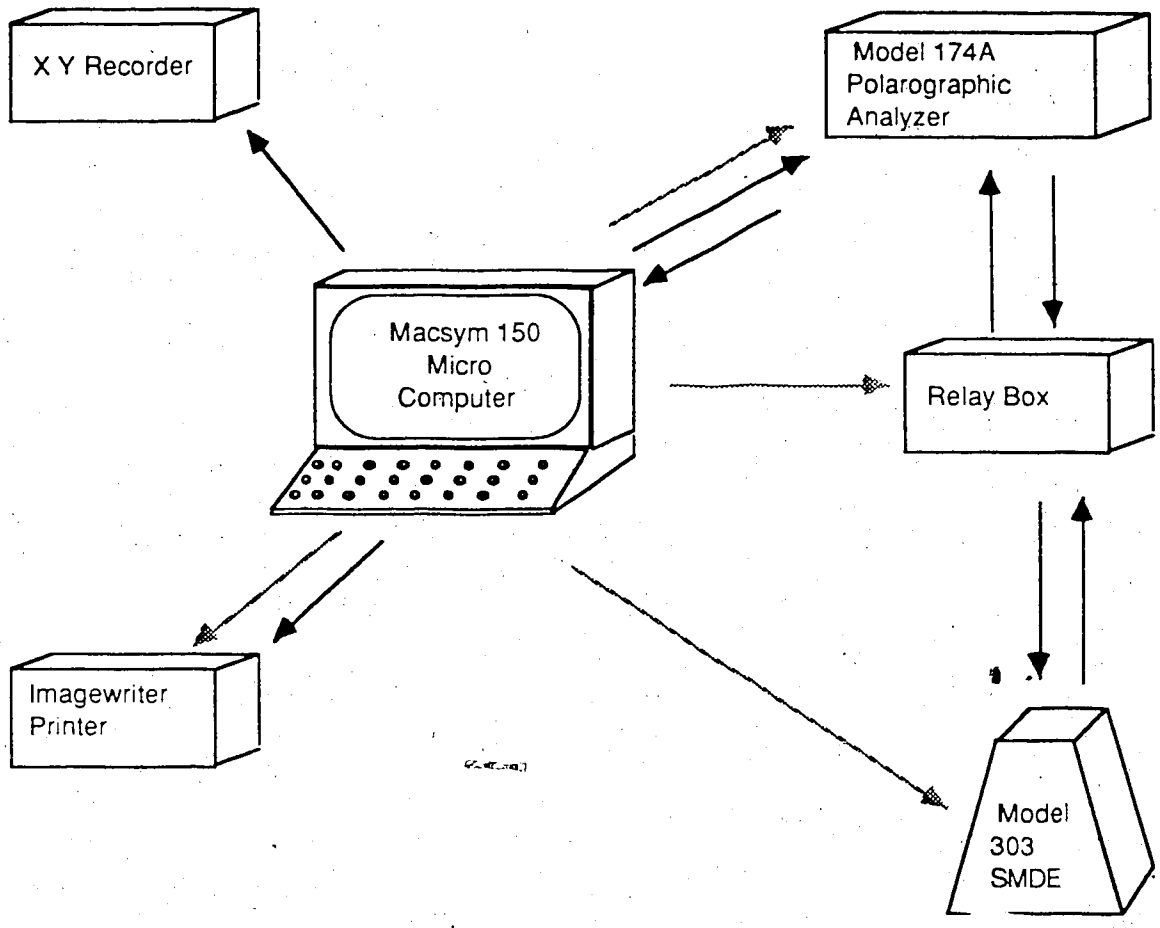


Figure 3.1 Block Diagram of the Instrumental System

Control Lines

Signal Lines

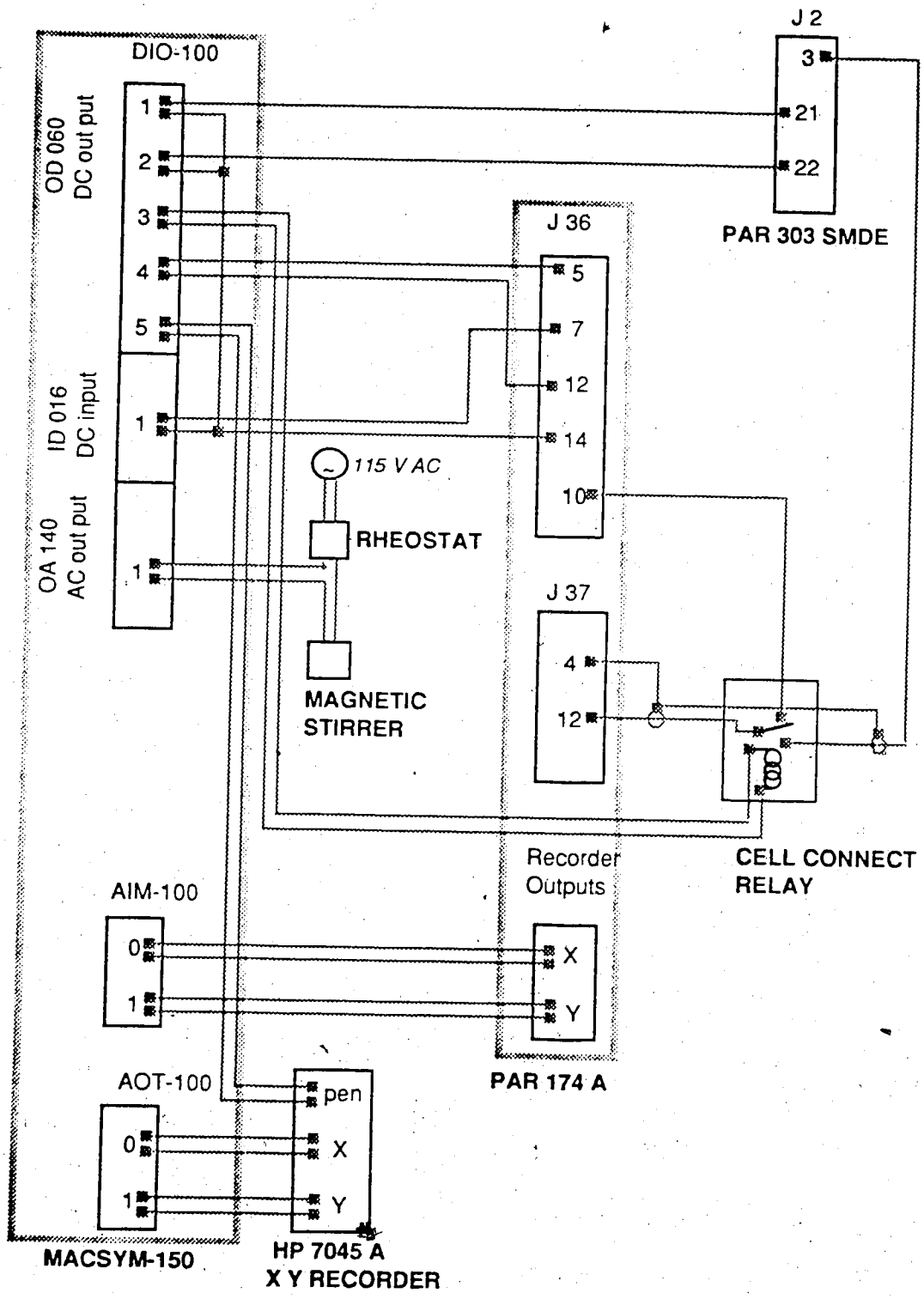


Figure 3.2 Schematic Wiring Diagram of the Instrumental Setup.
Only the modifications to the cable supplied to connect Model 303 to Model 174 A (PAR Catalogue # 6020-0142-02) are shown together with additional equipment connections.

1. Nitrogen purging

2.Formation/dislodge of Hg drop

3. Cell connection /disconnection

4.Magnetic stirrer On/Off

5. Scan initiation/inhibit

6. Data acquisition

7. Data recording

8. Data printout

The Macsym 150 did not have any control over cell potential, stripping mode and associated parameters. These were controlled by the Model 174A according to the settings of its front panel switches. These conditions were manually set at the beginning of each analysis, and were transferred to the Macsym 150 for the purposes of data processing and record keeping. Nevertheless flexibility in the selection of timing cycles, taken together with record keeping and data processing abilities, made incorporation of the Macsym 150 into the system a worthy addition. It should be noted that except for the relay box that was manufactured at the departmental electronic workshop, no other electronic modifications were done. All instruments were tapped using their original and existing ports and no modifications other than those defined by their manufacturers were performed. The final interface between the three instruments, Macsym 150, PAR 174A, and PAR 303 SMDE, is in the form of a single cable with three branches connecting to the back planes of those three units.

3.3 Software for the Anodic Stripping System

The final version of the main control data acquisition program, which was developed over several years and was modified several times to accommodate new requirements, is listed as DPASV in Appendix 1.

This and all other programs were written in MACBASIC (i.e. the version of Basic specifically designed for and supplied with Macsym family of computers) which operates under the MP/M 86 operating system. This operating system is a real time multitasking superset of CP/M 86.

No attempt was made to write any portion of the programs or parts of the programs at more fundamental levels to achieve greater speed[93] since differential pulse analysis itself is a slow procedure. The maximum signal change rate possible with the Model 174A (i.e. its highest clock speed) is 0.5 seconds. The rate of data acquisition that can be realized using macro commands incorporated into Macbasic were found to be adequate to accomplish the necessary data acquisition under these conditions.

The main control program, DPASV, was written as one compact program with several interconnected sections for parameter setting, data acquisition, data recording, and data analysis. Although the program is menu-driven using a main menu for function selection, the whole program is loaded and contained in the memory to avoid loading operations. These might introduce unspecified time delays during analysis runs, especially during repetitions using a single solution portion. Delays between successive repetitions of a single analysis were cut down further using multitasking, which allowed the initiation of the second run while the data of the first run was being processed and recorded.

The main sections of this program that merit detailed discussion are the analysis section which controls deposition, stripping and data acquisition functions, and the data analysis section which performs peak identification and base line correction functions.

Figure 3.3 shows the flow chart for the analysis section. The analysis section can be selected directly from the main menu or via a rerun option in which case the data input section is omitted and the values (for 174A settings and for such parameters as deposition time) that are already defined and present in the memory are used. With reference to Figure 3.3, A to B is the main purge section with purge time determined by user during data input

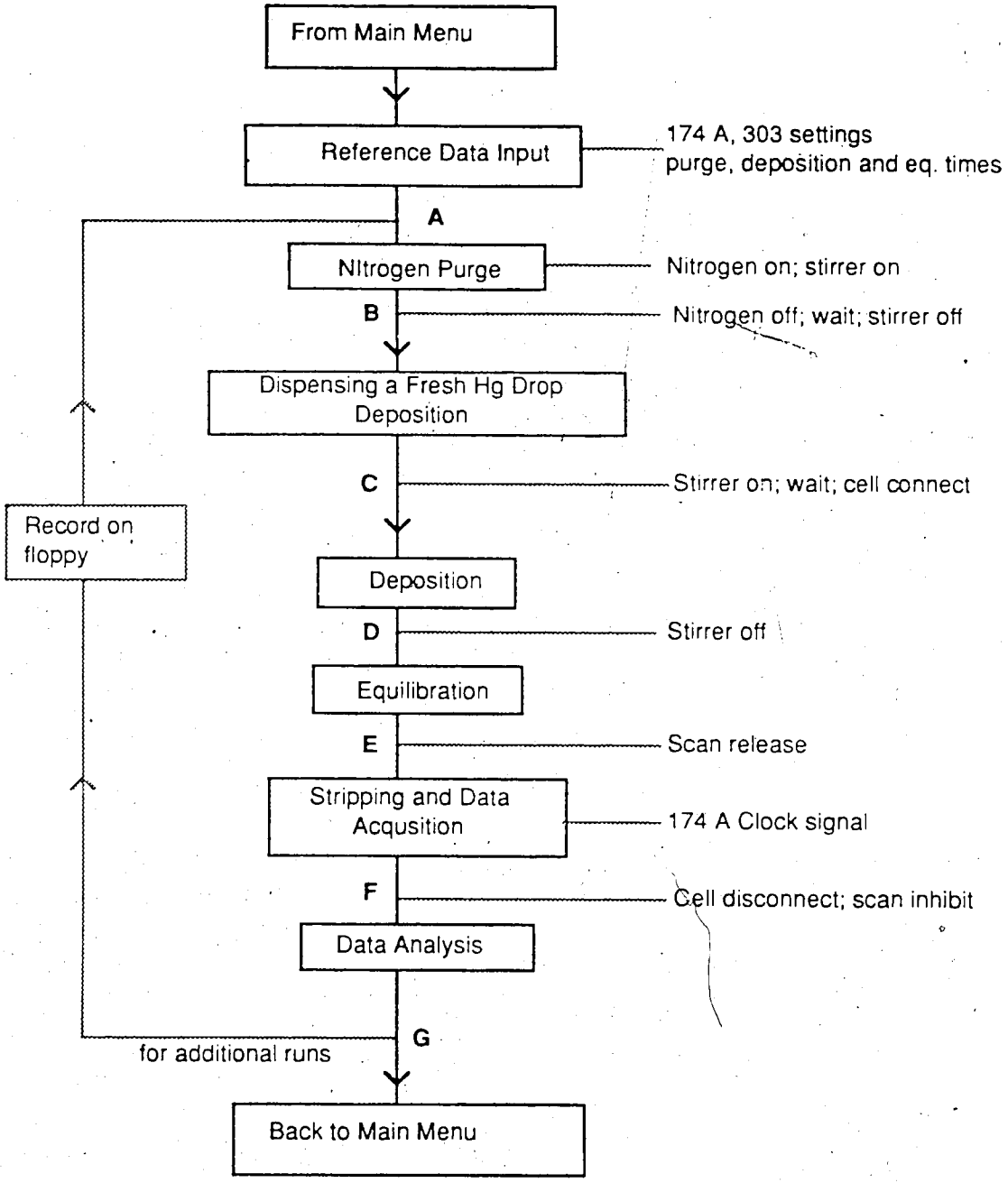


Figure 3.3 Flow Chart for the Analysis Section of the Main Control Program DPASV.

stage. The magnetic stirrer is also active during purging to allow better contact between solution and the purging gas.

After purging is complete nitrogen is routed for blanketing via an appropriate signal to 303 SMDE. The stirrer is driven for few more seconds to eliminate any gas bubbles that remain adhering to the walls of the cell or, with more serious effects, to the electrodes.

During drop dispensing the stirrer is kept switched off and the first drop is discarded. With a fresh drop, the stirrer is activated for a brief interval prior to the application of the deposition potential. This accomplishes two objectives:

1. It allows the solution flow within the cell to attain a steady state prior to the application of the deposition potential, which initiates the deposition process.

2. It mixes the solution between multiple runs on the same sample.

Connection of the cell to the Model 174A automatically initiates the deposition operation, since the Model 174A initial potential is set at the deposition potential during the data input stage. Settings and positions of the Model 174A front panel switches for a typical run are listed in Table 3.2.

At point D in Figure 3.3, which is the end of the deposition interval, as specified by the user during data input stage, the Macsym 150 switches off the stirrer, allowing the solution to come to rest before stripping. This time interval, called the equilibration time, is also set by the user. At the end of the equilibration time, the potential scan function of the Model 174A is activated. One important factor in the above procedure is that deposition is being carried out using a differential pulse wave form rather than a steady DC potential. Theoretically in an ideal situation this should not impose any limitations as far as the deposition is concerned as long as the deposition potential is well away to the negative direction from the reduction potential of the analyte. Under these conditions it is the flux of material to the electrode, which is governed by the diffusion properties of the analyte and the stirring rate that determines the amount of material being deposited. However, if some other impurity is present that can get adsorbed on the surface of the electrode under the

Table 3.2 Settings on the Model 174A Front Panel Switches During a Typical Analysis

Initial Potential	
Sign	-
Volts	0
mV	900
Potential Scan	
Rate	5 mV/S
Direction	+
Range	1.5
Modulation Amplitude	25 mV
Current range	2μA
Clock	1 S
Low pass filter	off
Out put offset	off
Display direction	-

deposition conditions with an adsorption potential within the range of potential change (within 25mV of the deposition potential when a modulation amplitude of 25mV is being used) a change in the kinetics of the reduction process of the analyte can be expected affecting the accuracy and precision of the analysis. But since pulse times used are quite insubstantial compared to steady potential times, 57.ms vs 1 s (i.e. 6%), any degradation that can be expected from this kind of an interference is minimal compared to possibilities of error from irreproducible stirring action that can arise from using a magnetic stir bar.

However, the most significant result of this configuration is a rapidly varying signal during the deposition time. Much of this variation as depicted in Figure 3.4 can be expected to result from current changes that can be associated with the changes in the double layer arising from solution flow past the electrode. The relatively undefined flow conditions in the cell when a stirrer magnet is used do not seem to disappear with tighter control of the stirring mechanism[94]. On the other hand, use of rotating disc electrodes with well documented and studied hydrodynamic characteristics does not seem to make a substantial improvement in precision when compared with a stir bar system [31].

During steps A to E (Figure 3.3) progress of the analysis is displayed on the monitor of the computer together with the real time values of appropriate parameters such as time elapsed and cell current. This allows detection of any abnormal situations or mistakes without delay. At point E, the Macsym 150 display changes its usual format to show a real time plot of current against cell potential in a low resolution graphics mode.

Data acquisition, which comes into effect at point E, is performed using the Model 174A clock signal as a guide. After sensing the clock signal, the system waits for a predetermined time and then starts averaging the current and potential signals provided by the Model 174A, processes them, and plots them on the display before the next sampling operation is initiated by the next clock pulse. Since at least 0.5s is available between two sampling operations there is adequate time to maintain a dynamic display even though the Macsym 150 has an internal clock speed which is comparatively low. It was found that

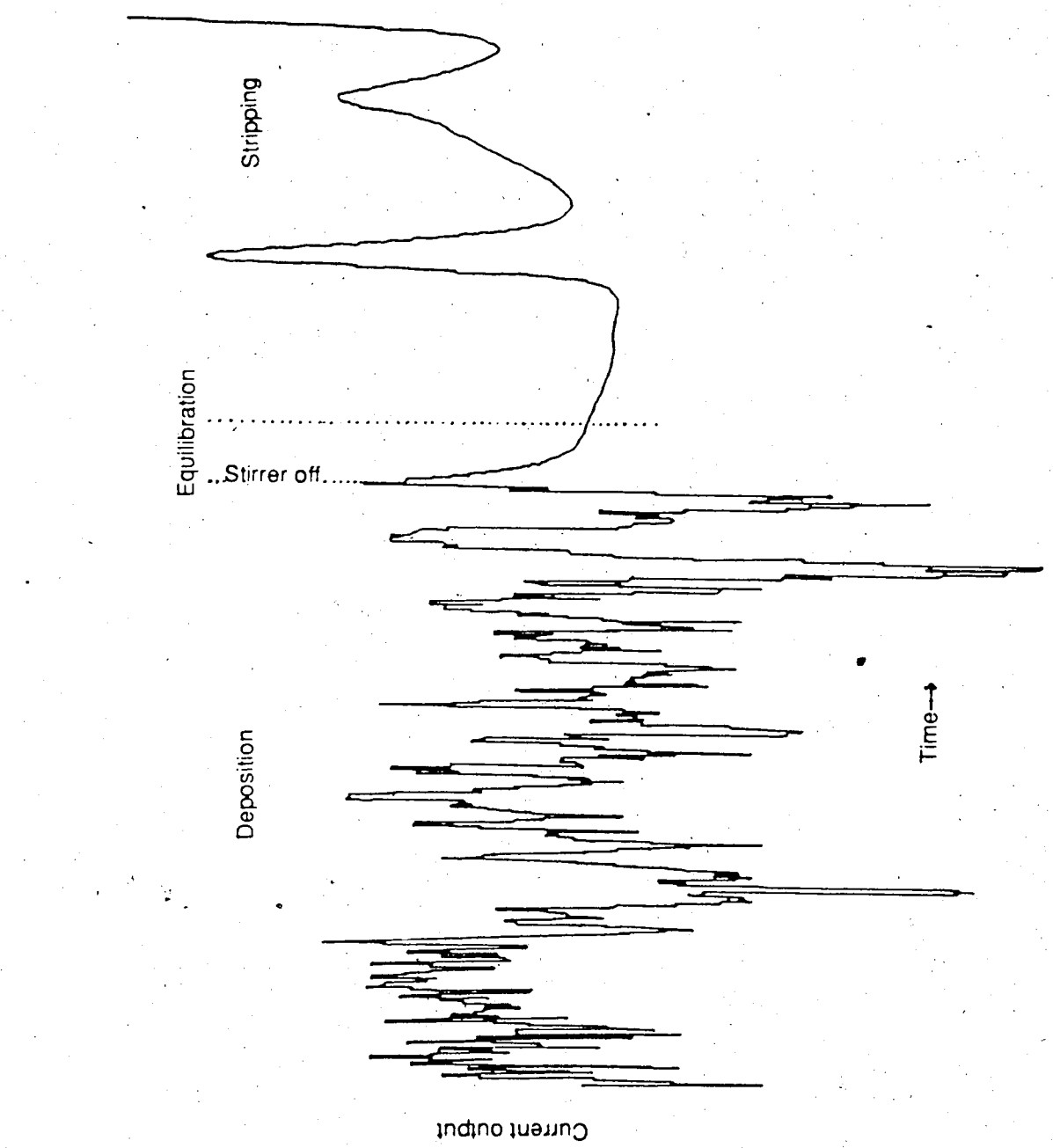


Figure 3.4 Changes in the Current Signal During Anodic Stripping Analysis

performance deteriorated and the system began missing every other data point when memory space was filled to a high level. This may due to the interference from memory keeping or memory refreshing functions associated with a dynamic random access memory such as the one found in Macsym 150. This problem was solved by removing the source code of the program from the memory using MACBASIC'S COMPILE command, which reduced the memory usage significantly. One other possible alternative is to segment the program and to use successive chaining. However, this would increase the analysis time due to the introduction of program loading operations involving the disc drive and may introduce timing errors as mentioned earlier and so was not employed.

When the specified final potential is reached during the stripping operation, the cell is disconnected and scan.inhibit is activated, at which point the program branch t into the peak reader section for data analysis. The peak reader section scans the acquired data points to locate the peak maximum point by comparing differences along the current axis at data points separated by a specified interval. After locating a maximum point it scans forward to locate the next minimum or plateau point which it labels as the peak tail point. Next a backward scan is done to locate the peak start point which is the minimum or plateau portion located immediately to the front of the peak. The line connecting the start and tail points is calculated, and the current value on this line at the point directly below the peak maximum point is used as the base line correction.

After scanning the whole data set and locating and calculating all peak parameters (positions and heights) all this data is recorded on a floppy disk automatically if multiple runs were to be recorded and on demand for single runs. This record file is named using a combination of analysis date and the analysis number allowing a flexible yet simple record keeping system. Any important information about the sample can be incorporated into the sample name, which accepts up to 30 characters. The recording system also creates and maintains an INDEX file for each diskette which can be accessed while the program DPASV is running. This was necessary since MACBASIC does not provide a directory

command that can be used for this purpose. This file also lists peak positions and peak currents found for each voltammogram recorded in the disk so it provides a means of ready access to the data in the disk.

3.4 Hardware Problems and Solutions

Most of the problems encountered during operation of the system were traced to the Model 303 SMDE. On the electronics side, a high frequency noise was observed in the Model 174A output ports (banana sockets) whenever it was connected to the SMDE. It was suspected that the built-in frequency generator of the SMDE was responsible, but since this problem was resolved upon addition of two capacitors to the Model 174A output ports, no modifications or repairs to the Model 303 SMDE were attempted.

The Model 303 SMDE is equipped with a Ag/AgCl reference electrode, which consists of a Ag wire that extends into the cell holding plastic block and glass sleeve with a Vycor plug which serves as the electrolyte holder. The usual internal electrolyte is a solution of saturated KCl (or 4M KCl) that is saturated with AgCl. Though this arrangement works satisfactorily in many situations, leakage of chloride ions through the Vycor plug was found to be substantial. Since chloride ion forms complexes with many metals, it can be expected to interfere with equilibrium concentrations of metals in low concentration solutions such as those used for anodic stripping analysis. This effect will be discussed in more detail in Chapter 5. Further, contamination of the sample solution from any impurities that can leak out around the silver wire or the glass sleeve is also a possibility. This built-in reference electrode might be a drawback in using the Model 303 SMDE for anodic stripping analysis at ultra trace levels.

In the work reported in this thesis an external calomel electrode was used as the reference electrode. This electrode was connected to the cell via a glass salt bridge compartment with a Vycor junction inserted through the side access hole. This salt bridge contained a solution of 2M KNO_3 for most of the work. A specially constructed salt bridge

tube and a calomel electrode for this purpose is also available from Princeton Applied Research Corporation (catalogue no. KO 154 and KO 077).

The internal reference electrode of the Model 303 SMDE is routed to the Model 174A via a voltage follower circuit built into the Model 303 SMDE. This follower does not seem to serve a useful purpose since the Model 174A has adequate input impedance built into its reference electrode input line. This follower can be by passed either by connecting the reference electrode directly to the Model 174A input point if an externally inserted electrode is being used or by connecting the Model 174A cable to the back plane test point of the Model 303 SMDE if the built in reference is being used. No change in performance was observed upon disconnection of this internal follower but the majority of the data was collected with the internal follower connected, since it was decided to use built in connectors whenever possible so as to reduce the number of connections and cables which constitute possible noise sources.

One of the main problems with the Model 303 SMDE electrode was capillary failure. Though the capillary geometry has been improved and changed, useful lifetime of a capillary was found to be a highly inconsistent variable depending upon the capillary. Since capillary removal and reinsertion is not a trivial operation as suggested in the operating instructions, and since it also exposes the operator to metallic mercury with a high possibility of mercury spills, this was found to be an annoying disadvantage of the Model 303 SMDE electrode. Fortunately keeping the capillary tip inserted in mercury when not in use as suggested by one of the many PAR advisory notes was found to extend the capillary life significantly while leaving it in water as suggested by the instructions supplied with new capillaries was a complete failure.

With a properly functioning capillary, reproduction of the mercury drop size was found to be satisfactory and at the levels suggested by the manufacturer. This was checked by collecting five mercury drops into pre-weighed glass vials and by obtaining the weight of

mercury. Six vials were used for each drop size and the whole procedure was repeated once. Results of this study are presented in Table 3.3.

3.5 Performance Evaluation

This integrated system is capable of analysing a given solution portion up to nine times consecutively with the capability of analysing up to ninety-nine samples per day if time permits. These limitations are not inherent in the method but are imposed by the recordkeeping procedures. After each analysis (i.e. after the completion of the specified number of runs for a single solution portion), the system prints out a results sheet showing all the peak positions and heights. An example of this output is found in Figure 3.5.

Another auxiliary program, DAPLOT, can be used to obtain a rough sketch of the stripping curves as shown in the lower portion of Figure 3.5, via the Apple Imagewriter. Using an XY recorder a better output can be obtained for any of the curves recorded on a diskette.

The system was tested by estimating the background signal level for cadmium produced by double distilled water acidified to pH 2 with nitric acid using a standard addition procedure in the range 0.01 to 0.05 ppb. The background signal produced was estimated to correspond to a cadmium level of a negligible 0.033 ppb. This can be either a true signal arising from cadmium or it can be due to background anomalies and electronic noise. Deposition time used for this analysis was ten minutes.

A calibration curve constructed using solutions containing Cd and Pb together in a single sample solution in the range 1 to 5 ppb showed good linearity throughout the entire range of concentrations with a deposition time of only two minutes. The regression line for cadmium under these conditions was found to be $Y = 1.79 \times 10^{-3} + 0.02677X$ with a correlation coefficient of 0.9995 and for lead it was $Y = -6.85 \times 10^{-3} + 0.01569X$ with a correlation of 0.998. So these conditions will give a sensitivity of about 0.03 μA/ppb for Cd and about 0.02 μA/ppb for Pb.

Table 3.3 Mercury Drop Reproducibilty Data for PAR 303 SMDE

Drop Size	1st Six Weighings (5 drops per weighing)			2nd Six Weighings (5 drops per weighing)			Mean Drop Weight per drop (g)	Estimated Radius (sphere assumed) (mm)
	Mean wt. (g)	Std. Dev. (g)	RSD (%)	Mean wt. (g)	Std. Dev. (g)	RSD (%)		
Small	0.0057	1×10^{-4}	2	0.0057	9×10^{-5}	2	0.0011	0.027
Medium	0.0122	2×10^{-4}	1	0.0118	1×10^{-4}	1	0.0031	0.038
Large	0.0252	2×10^{-4}	0.8	0.0252	1×10^{-4}	0.5	0.0050	0.045

```
DATE          mon/da/yr:JA      08      1987
SAMPLE              no:01
SAMPLE            name:CSSM100-06 DIL50 22DE86

INITIAL POTENTIAL  (V):-.8     FINAL POTENTIAL    (V):.4
SCAN RATE     (mV/sec):5       SCAN RANGE         (V):1.5
MODULATION        (mV):25      CURRENT RANGE     (uA):1
CLOCK             (sec):1      DROP SIZE            :M
CONCENTRATION     (ppb):0      PURGE TIME       (min):10
DEPOSITION TIME   (min):2      EQUILIBRATION    (min):.2

 PEAKS FOUND
position(V)  height(uA)  position(V)  height(uA)   position(V)  height(uA)
RUN 1
-.311719     .242469     .1375       .698635      0            0
RUN 2
-.306836     .208208     .142383     .62951       0            0
RUN 3
-.306836     .203918     .1375       .590559      0            0
RUN 4
-.306836     .212183     .142383     .612852      0            0
RUN 5
-.306836     .206614     .1375       .56251       0            0
```

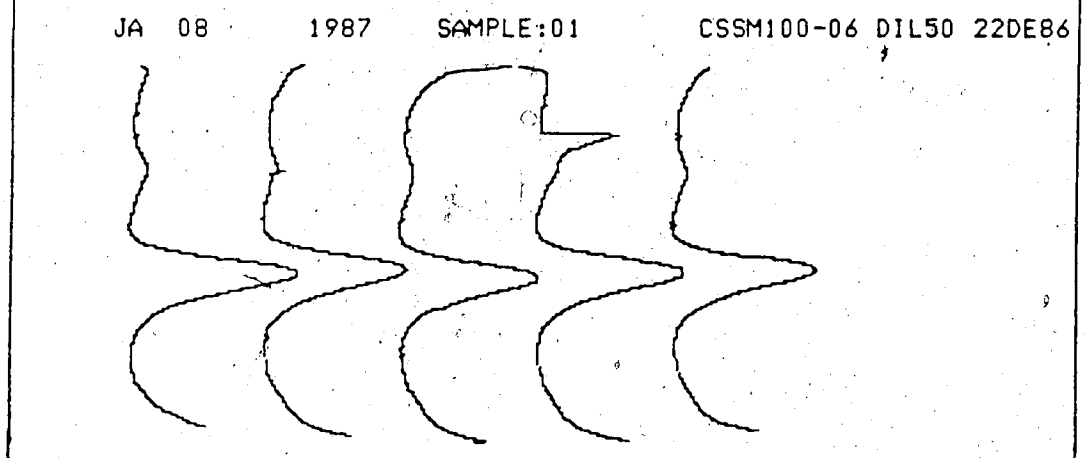


Figure 3.5 Typical Data Output from the Instrumental System

For the above calibration a series of solutions prepared by diluting 1000 ppm stock standard solutions of cadmium and lead were analysed. A single five ml portion was analysed three times. This process was repeated on three portions to give nine data points for each concentration in sets of three points. Precision of these analyses were better within a set of runs , i.e. with a single solution portion, but deteriorates when the data is pooled together to calculate overall values. Though it was not clear from the data available, some form of a slow equilibration process between the solution and the cell may be responsible for the this deterioration. Cadmium shows relative standard deviations for pooled data ranging from 2.5% to just above 5% while Pb data ranges from 8% to 15% (Tables 3.4 and 3.5).

These levels were found to be comparable with the precision levels for anodic stripping determinations reported by various authors as presented in Table 3.6. The poor performance of the lead analyses should be viewed as more acceptable due to lower concentrations compared to cadmium. At the 1 ppb level, cadmium solution is 8.896×10^{-9} mol. L^{-1} while lead is only 4.803×10^{-9} mol.L^{-1}. Relative signal strength does not show this difference clearly because of the separation between lead and cadmium peaks which allows more lead to be deposited while cadmium is being stripped. Differences in complex formation behaviour also can play a part in this which is discussed in Chapter 5.

Table 3.4 Data for Calibration Plots

	Cadmium			Lead		
Conc. (ppb)	Mean Peak height (μA)	Std. Dev. (μA)	RSD (%)	Mean Peak height (μA)	Std. Dev. (μA)	RSD (%)
1	0.0263	0.0004	2	0.0201	0.0003	1
	0.0266	0.0002	0.7	0.0262	0.0006	2
	0.0276	0.0006	2	0.0281	0.0016	6
2	0.0549	0.0030	4	0.0356	0.0013	4
	0.0541	0.0030	6	0.0381	0.0005	1
	0.0593	0.0003	0.4	0.0448	0.0021	5
3	0.0827	0.0013	2	0.0506	0.0038	7
	0.0814	0.0001	0.1	0.0528	0.0012	2
	0.0853	0.0018	2	0.0585	0.0007	1
4	0.1098	0.0015	1	0.0621	0.0015	2
	0.1049	0.0018	2	0.0628	0.0009	1
	0.1141	0.0006	0.5	0.0734	0.0007	1
5	0.1275	0.0021	2	0.0700	0.0008	1
	0.1427	0.0010	0.7	0.0824	0.0020	2
	0.1325	0.0042	3	0.0797	0.0018	2

Table 3.5 Pooled Data for Calibration Plots

Concentration (ppb)	Cadmium			Lead		
	Peak Ht. (μA)	Std. Dev. (μA)	RSD (%)	Peak Ht. (μA)	Std. Dev. (μA)	RSD (%)
1	0.0271	0.00073	3	0.0248	0.00373	15
2	0.0563	0.00290	5	0.0395	0.00431	11
3	0.0832	0.00204	2	0.0535	0.00422	8
4	0.1096	0.00418	4	0.0661	0.00556	8
5	0.1343	0.00712	5	0.0774	0.00579	7

Table 3.6 Literature Data for Precision of Anodic Stripping Voltammetric Determination of Lead

Mode of Analysis	Electrode	Concentration (ppb)	Precision reported RSD (%)	Reference
Linear Scan	HMDE	1000 - 10	3 -6	Sinko and Dolezal (95)
DPASV	TFME	1.8	2.9	Copeland et al. (34)
DPASV	HMDE	22.2 2.3 0.05	0.08 2 8	Valenta et al. (96)
DPASV	TFME	0.5 -0.05	2.5	Valenta et al. (51)
DPASV	HMDE	2.8 0.7	3 4.7	Seelig and Blount (97)

Chapter 4

Experimental Procedures

4.1 Introduction

This chapter lists the more general experimental procedures used together with information regarding chemicals and other reagents. Since the work described in this thesis covers a wide area it is difficult and also not very useful to collect all the experimental procedures into one chapter. Therefore some of the specific details of the experimental techniques used are included in other chapters together with results and relevant discussions.

4.2 Collection and Preparation of a Reference Soil Sample

In order to evaluate the use of anodic stripping methods for the analysis of trace metals in soils and to develop a digestion procedure for this purpose, a bulk soil sample was required. Such a sample was prepared by collecting a large soil sample and processing this sample into a standard sample for local use.

A large sample of soil (~ 5 kg dry weight) was collected from the backyard of a house located at 11736 - 83rd Avenue, Edmonton, Alberta. A location was selected at which grass was growing and where no specific agricultural or other cultivation practices had been carried out for at least ten years. Care was taken to collect only the top soil excluding the grass, vegetation, and roots that abounded in the topmost layer. A steel garden shovel was used for this purpose but soil that came into contact with the shovel was discarded to avoid any contamination from the shovel. Samples were collected in polyethylene plastic pails which had been precleaned with an overnight 10% nitric acid soak. The collected samples appeared black in colour. Two pails of soil were collected and in all subsequent processing these two samples were processed separately.

The samples were dried overnight in an oven kept at 30°C after spreading over pre cleaned aluminium foil. An initial sieving of the dried samples with a number 10 mesh stainless steel sieve was carried out to remove larger stones and other large foreign matter. During this process any lumps formed during the drying stage were crushed using a mortar and pestle but no hard grinding was attempted. Only a very small fraction of each sample (~20g) was discarded as large stones and plant debris that could not pass through a number 10 sieve. The presence of many small root parts such as secondary and capillary roots of small plants was noted; most of these passed through the sieve due to their short wire shape.

Subsequently the samples were resieved through a number 25 mesh sieve with grinding. The portion that had to be ground was about 15g and represented a very minor fraction of the sample. An ordinary blender (Osterizer, Cyclotrol-ten) as well as a grinding machine (CRC Micro Mill, The Chemical Rubber Co., Cleveland, Ohio) was employed for this operation. Care was taken to avoid overgrinding by keeping the grinding durations short with frequent cooling periods. Using similar operations and machinery one of the 25 mesh samples was ground down to pass through a 100 mesh sieve. After these operations the samples were mixed thoroughly by turning them over on a large precleaned polyethylene plastic tray with the aid of a precleaned polyethylene plastic scoop. This operation was done repeatedly to ensure uniform mixing. This step was followed by sectioning the sample and storing in acid leached (50% nitric) one liter size glass jars with paper and vinyl lined phenolic plastic lids.

A dry sieve analysis was carried out on 50 g subsamples of the 25 mesh sample removed after the mixing operation to determine the approximate distribution of the particles in the sample. This was done employing a set of standard stainless steel sieves (Canadian Standard Sieves, W. S. Tyler Co. of Canada Ltd.) and the results are presented in Table 4.1 together with appropriate statistical analysis.

Table 4.1 Sieve Analysis Data for the Reference Sample. A 50g sample was used for each run.

Sieve size (mesh no.)	Retention as a % of sample weight *			
	Run 1	Run 2	Run 3	Mean
40	18	17	17	17.3 (17)
60	19	19	19	19
80	11	11	11	11
100	5	5	5	5
140	7	7	8	7.33 (7)
170	5	5	5	5
200	4	4	4	4
325	10	10	9	9.67 (10)
bottom plate (-325)	21	23	22	22
Total	100	100	101	100.33

48 %

32%

* Rounded off to nearest digit

The two samples collected originally were not of equal size; consequently the 100 mesh sample accounted for only three bottles, while the 25 mesh sample accounted for eight bottles. For all subsequent analyses at the 100 mesh level subsamples were taken from a single bottle after mixing its contents end-over-end overnight on a rotation machine. These subsamples were usually about 20g in weight, and were collected by filling a clean dry weighing bottle with the soil from the top of the storage bottle soon after the rotation operation. A clean, dry Teflon covered spatula was used for this purpose. Weighing bottles containing samples collected in the above manner were kept in an oven maintained at 100°C overnight and cooled in a desiccator over anhydrous calcium sulfate (Drierite, W. A. Hammond Drierite Company, Xenia, Ohio) prior to the weighing out of the analytical samples. Use of a weighing bottle for the sample was found to be necessary because of the weight changes that were observed upon exposure to room atmosphere, arising from the absorption of moisture. On the average an increase of about 0.17% was noted, which introduces an error close to 2mg for a one gram analytical sample (sample size used in open beaker digestions described in subsection 4.5.1) if an open weighing procedure such as weighing boats or watch glasses were used. Weighing bottles also offered the added advantage of taking only one weight measurement per sample in a serial sample weighing operation.

During subsequent digestions (results reported in Chapter 7) the 100 mesh sample was found to be unsatisfactory in terms of precision, indicating possible problems arising from inhomogenity of the sample. To overcome this problem, a portion of the 100 mesh sample stored in a second bottle was sieved through a 200 mesh sieve to remove larger particles. The resulting 200 mesh sample was mixed using rotation as described in the previous paragraph and was used in the same manner to obtain analytical samples.

4.3 Standard Reference Soil Samples

For the purpose of testing the accuracy of the technique certified reference soil samples, SO-1 and SO-2 issued by the Canadian Certified Reference Material Project[98] were used. These samples were kindly provided by Dr. Byron Kratochvil. Figure 4.1 (Certification Sheets for the samples used) gives the compositional and other relevant information for these materials.

According to reference 99, certified values have been calculated by using values reported by thirty-two laboratories using various analytical techniques. None of these laboratories used electrochemical techniques. Specific information regarding the certified value of lead in these samples is presented in Table 4.2.

4.4 Reagents and Chemicals

4.4.1 Water

Any trace analysis system that deals with aqueous solutions must have access to a reliable water supply of very high purity. Purity of water can be measured and expressed in variety of ways, the most common one being the specific conductivity[100]. However, conductivity measurements are not a valid criterion for the measurement of water purity in trace analytical applications. On one hand this measurement, which depends solely on the number of conducting ions in water, cannot indicate any contamination due to nonconducting organic impurities. On the other hand, contributions from trace level metal impurities to the overall conductivity are masked by the high specific conductivity of H^+ and OH^- ions. At pH 7 where the concentrations of H^+ and OH^- are minimum, the conductivity due to these ions is 0.0548 μmho/cm, while the contribution from lead as lead chloride is only 0.0016 μmho/cm at a 10ppb level. With the contributions from dissolved carbon dioxide and oxygen, conductivity measurements may fail to detect trace metal

REFERENCE SOIL SAMPLE SO-1

CERTIFICATE OF ANALYSIS

Recommended Values ± 95% Confidence Interval							
Si	25.72	±	0.22%	Ba	879	±	47 µg/g
Al	9.38	±	0.17%	Sr	328	±	29 µg/g
Fe	6.00	±	0.13%	Cr	160	±	15 µg/g
K	2.68	±	0.08%	Zn	146	±	5 µg/g
Mg	2.31	±	0.11%	V	139	±	8 µg/g
Na	1.97	±	0.08%	Rb	139	±	12 µg/g
Ca	1.80	±	0.07%	Ni	94	±	7 µg/g
Ti	0.53	±	0.02%	Cu	61	±	3 µg/g
C	0.27	±	0.03%	Co	32	±	3 µg/g
Mn	0.089	±	0.003%	Pb	21	±	4 µg/g
P	0.062	±	0.010%	Hg	0.022	±	0.003 µg/g

REFERENCE SOIL SAMPLE SO-2

CERTIFICATE OF ANALYSIS

Recommended Values ± 95% Confidence Interval							
Si	24.99	±	0.23%	Sr	340	±	50 µg/g
Al	8.07	±	0.18%	Zn	124	±	5 µg/g
Fe	5.56	±	0.16%	Rb	78	±	6 µg/g
K	2.45	±	0.04%	V	64	±	10 µg/g
Ca	1.96	±	0.10%	Pb	21	±	4 µg/g
Na	1.90	±	0.05%	Cr	16	±	2 µg/g
Ti	0.86	±	0.02%	Co	9	±	2 µg/g
Mg	0.54	±	0.03%	Ni	8	±	2 µg/g
P	0.30	±	0.02%	Cu	7	±	1 µg/g
Mn	0.072	±	0.002%	Hg	0.082	±	0.009 µg/g
Ba	966	±	67 µg/g				

Figure 4.1 Certification Sheet for Certified Standard Soils SO-1 and SO-2.

Table 4.2 Lead Data for Certification of Standard Reference Soils SO-1, SO-2 (from reference 98).

Parameter	SO-1	SO-2
n	194	193
mean	21	21
low 95% CL high	17 24	17 24
Spread %	36	34
cv%	13.8	13.0

n - number of results
mean- overall mean lead content (ppb)
CL - confidence limits
Spread % - 95% confidence interval as a percentage of mean
cv - average within lab coefficient of variation

impurities even at the 100ppb level. This ambiguity with respect to the level of purity necessitates direct measurement of the impurity level of the water using the analytical method in which that water is going to be used. After analysing several pure water sources available in the Department of Chemistry, it was decided to set up a distillation still to redistill water available through the departmental bulk distillation process. The water available through the departmental bulk distilled supply is referred to as "line distilled water" in the following discussion.

This decision was partly based on the resources available, since some commercial cartridge purification systems were found to be equally effective in reducing trace metal impurities to a level low enough to be used in anodic stripping analysis. In the case of trace metal analysis the pure water requirements include a large amount of water that is used for washing and cleaning purposes in addition to what is required for solution preparation. Alkaline permanganate distillation of line distilled water was found to be more economical and convenient when all these facts were considered, but more importantly, it was a procedure which could not introduce surface active organic material which might affect the anodic stripping measurements. It should be noted that electrochemical procedures do not require the removal of alkali and alkaline earth metals from the water used in sample preparation. In fact an electrocoagulation purification method that removes heavy metal impurities via precipitation and adsorption onto iron hydroxide precipitates has been shown to be effective in producing water of sufficient purity to be used in anodic stripping applications[101].

The distillation unit consisted of a 12 L three neck round bottom flask connected to a vertical fractionation column and a water cooled Liebig condenser. A Glascol heating mantle (Glascol Apparatus Company) with two heating coils rated at 650 W each was used as the heat source. Polyethylene containers (precleaned with a 10% nitric acid soak for a week) were used to collect and store the distillate. An automatic relay switch (Precision Scientific Company) was used to cut off the power to the heater coils at the end of each

distillation operation. This was done by cutting off the power to the heater coils whenever the liquid level in the main flask fell below 1.5 liters.

In order to obtain satisfactory performance from this distillation setup it was found that it is necessary to carry out the distillation at a very slow rate. In a distillation purification procedure, ionic impurities are transferred from the distillation flask to the receiver as splashed out particles and also via a liquid film that can exist on the walls of the tubing (i.e.. the column and the condenser) that connect the distillation and receiver flasks. Ionic salts are unlikely to transfer via evaporation under the conditions that exist in the still. Splashing, which produces solution droplets that can get carried over, results from the boiling action which produces steam bubbles that burst on the surface of the water body. Heat directed from the bottom and sides of the flask sets up convective currents and produces vapor cavities in the liquid layer that is in direct contact with the surface of the flask as a result of low thermal conductivity of water. This process leads to the bubbling action.

Sub-boiling distillation, which is the most advanced purification method available, is also based on this simple fact[102]. In this technique the liquid is heated from the top using an infra-ed radiator to evaporate the surface liquid layer without disturbing the surface. The ideal situation for distillation purification is one in which there is no macro flow, that is, an equilibrium system. This can be realised, for more volatile substances like acetic acid and ammonia, in an isothermal distillation.

Output of a slow distillation system can be increased to some extent by increasing the surface area available for the evaporation to take place but with a corresponding increase in the volume of the apparatus. In the distillation setup used, some form of insulation from particulate or aerosol transfer was offered by placing a vertical fractionation column directly above the distillation flask. This column can be filled with an inert granular material such as glass beads to increase resistance, provided they are precleaned. Use of an open column with baffles or notches, on the other hand, was found to offer more flexible control over

distillation rate via the amount of heat applied to the distillation flask. Heating coils on the heater were operated via two Variac controls (Ohmite Manufacturing Company). All exposed parts of the flask and the column were insulated with fiber glass wool insulation covered with aluminium foil to reduce radiative losses. This allowed the distillation to be carried out at a low power consumption rate. The first one liter of the distillate was discarded and usually this part of the distillation was carried out at a higher heating rate. For the rest of the distillation a lower heating rate was used. Variac settings selected after several trials were 50V for the top heating coil and 60V for the bottom heating coil. Initial heating and the distillation of the first liter of water was carried out at 80V for the upper coil and 100V for the lower coil. With these heating rates, distillation of one batch (amounting to about 10 liters of water) takes between 12 to 16 hours. The lead level of the water produced was found to be below 0.03 ppb upon acidification with ultrapure nitric acid to pH 2. Unless specified otherwise all aqueous solutions cited in this thesis were prepared using water prepared by this purification procedure.

4.4.2 Potassium Nitrate Solutions and Acetate Buffer

These reagents were purified via bulk electrolysis using large volume cells. Aqueous reagents were electrolysed using a cell with a mercury cathode and a locally constructed large volume calomel electrode as the anode. The potential of the mercury pool was kept at -1.4V vs the calomel electrode. A slow and continuous stream of deoxygenated and water saturated nitrogen was used to deoxygenate as well as stir the solution. The potassium nitrate solution had a nominal concentration of 2M to avoid crystallization. The acetate buffer had a nominal concentration of 1M in sodium acetate and acetic acid.

A set of six D size dry batteries was used to supply the necessary potential for these as well as for the mercury purification cell. Cells were connected to the power supply via a simple circuit that contained a potentiometer that allowed setting the operational potential at a desired level, an ammeter, and a voltmeter connected via switches to select the appropriate cell. The electrolysis process was allowed to proceed for about a month before using these

reagents for analytical purposes. Lead and cadmium concentrations in these purified reagents were found to be so low as to be undetectable under the conditions used for the analysis of digested soil samples.

4.4.3 Mercury

Triple distilled mercury was purified by electrolysis before using it in the 303 SMDE. The mercury purification cell was operated using a potassium nitrate solution with mercury at an anodic potential of 0.3 V vs the calomel electrode. A continuous and a slow stream of air (filtered through a glass wool plug) was passed through the mercury pool by applying a mild vacuum to the cell. This continuously agitated the mercury pool and also maintained the aqueous solution at an oxygen saturated condition, accelerating the oxidation of impurity metals dissolved in mercury.

4.4.4 Potassium Chloride

Potassium chloride, used as salt bridge and calomel electrode filling solution, was purified through recrystallization and crystal adsorption[28]. This depends on the ability of the crystalline precipitates to adsorb trace cations that have an ionic radius similar to that of the cation of the predominant crystal phase. Lead, cadmium, and thallium traces exist in an adsorbed state in the presence of excess potassium chloride. Other metal impurities such as copper and zinc are held in the solvent phase.

A saturated solution of potassium chloride was prepared by dissolving an excess of the salt in warm water. Excess salt was allowed to crystallize under turbulent conditions by stirring the solution continuously on a magnetic stirrer. This ensured the formation of small crystals, resulting in a large surface area for adsorption to take place. Supernatant liquid was filtered and was concentrated through evaporation; it was then cooled slowly without stirring to produce the final purified product salt. This salt was filtered, washed, and used to prepare the potassium chloride solutions that were used in the salt bridge and the calomel electrode.

4.4.5 Acetic Acid

Reagent grade acetic acid was purified using isopiestic (or isothermal) distillation[103,104]. An open beaker filled with acetic acid was placed in an acid cleaned glass desiccator together with two Teflon beakers containing water. Approximately 1M acetic acid (as determined from an acid base titration) was removed after about five days. The concentration of the resulting acid solution depends on the volume ratio of the water and raw acid solution[103,105].

This simple process was found to reduce the lead signal of 0.1M acetic acid solutions to an undetectable level under the analytical conditions used for the analysis of digested soil samples.

4.4.6 Nitrogen

Tank nitrogen was purified by bubbling it through an acidified vanadium (II) chloride solution that is in equilibrium with zinc amalgam[106] followed by a washing tower containing water to remove traces of oxygen.

4.4.7 Ultra Pure Chemicals

Suprapur grade nitric acid and sodium hydroxide were obtained from MERCK. Hydrochloric acid of "high purity" grade was obtained from FLUKA. Redistilled perchloric acid (G. F. Smith Chemical Co.) was used in the digestion operations.

4.4.8 Standard metal solutions

Standard 1000 ppm stock solutions for lead and cadmium were prepared from corresponding reagent grade salts and were stored in acid leached (10% nitric) polyethylene bottles. For lead 1.6g of lead nitrate was dissolved in 50ml of nitric acid which was diluted to one liter. Cadmium stock solution contained 2.04 g of cadmium chloride in one liter together with 50ml of hydrochloric acid.

These stock solutions were diluted to obtain working standards, usually of 5 ppm in metal and 0.01M in nitric acid, on a daily basis.

4.5. Volumetric Ware and other Apparatus

Plastic (polyethylene, polypropylene and Teflon) vessels were used whenever possible to avoid contamination from the leaching and adsorption phenomena of glass containers. These were cleaned via acid leaching (10% nitric) followed by repeated washing with water to remove acid traces. Teflon containers used for digestion were occasionally soaked in reagent grade concentrated nitric acid to remove dark colored marks on the outer walls. These marks result from charring of the finger marks during the digestion operation. In the instances where the glass volumetric flasks were used they were cleaned by leaching in 1:1 nitric acid and were equilibrated with the solutions they were to contain. This was done by allowing the solution to stand in the flask overnight. A new solution was prepared after discarding the initial solution without washing the flask. Glass volumetric flasks were used only for dilution of stock standards, preparation of background electrolytes and dilution of acids. They were never used for storage of solutions.

On some occasions glass volumetric flasks were used for serial dilution of standard solutions. In this case partial filling of the flask with water with or without added acid prior to the addition of the metal solution was found to be more satisfactory. Direct addition of a small volume of a concentrated metal solution into an empty flask (even after a prior equilibration) resulted in metal loss, presumably via adsorption on the walls.

The usual glass cells supplied for the Model 303 SMDE were replaced by Teflon cells from the same manufacturer (Princeton Applied Research Corporation, catalogue no. GO 174). Though glass cells can be used with prior equilibration with considerable inconvenience, with low concentration solutions even these procedures resulted in erratic results. At the 10 ppb level a 5ml solution portion left overnight in a glass cell was found to lose almost all the lead it contained. Not surprisingly glass cells used for 100ppb level analyses leached out a considerable amount of lead when soaked overnight with water. The

only disadvantage with Teflon cells was their opaqueness that hinders observation of the state of the hanging mercury drop during the analysis.

Teflon coated stirrer magnets (stir bars) were obtained from Belart Products (Pequannock, N.J.). These were micro size stir bars (10mm X 3mm). Since Teflon is permeable to gases continuous use of these Teflon coated stir bars in high concentrations of nitric or hydrochloric acids can lead to rusting of the magnet and also rupturing of the Teflon coating as a result of rusting. A rust spot develops at a damaged point after overnight soaking in water. This was used to check for damaged stir bars.

4.6 Digestion Procedures

The following sections of this chapter describe the experimental details of the digestion procedures used. In all of these procedures, acids and other chemicals used were of ultrapure quality except for hydrofluoric acid which was of reagent grade. Polypropylene volumetric flasks as well as polypropylene storage bottles were used in handling digested sample solutions. Samples were weighed either on a Mettler AE 160 electronic balance that reads to tenth of a milligram or on a Mettler H51 balance that can read up to hundredth of a milligram.

All temperature values are approximate, except for the oven temperatures for the digestions carried out using Teflon lined steel bombs. Open beaker digestions were carried out on hotplates calibrated using a thermometer dipped into a sand-filled beaker. These calibration curves as well as heating and cooling rate curves were used as guides in timing and planning the described digestion operations. Open beaker digestions that use perchloric acid were all carried out in a stainless steel special perchloric acid fume hood that has washdown as well as independent fume exhaust provisions.

4.6.1 Open Beaker Digestions

The first method tested was an open beaker digestion method which could give a total dissolution of the sample. This was to be used as the basis or the standard for

evaluation of the merits and demerits of the other procedures. Preference was given to a perchloric acid digestion procedure because it will result in a low organic residue. Perchloric acid digestions with a final evaporation step have been used in the analysis of biological samples with anodic stripping analysis and have been found to give good results[107]. After considering several literature procedures mainly developed for the analysis of trace metals in soils and sediments by atomic spectroscopic methods, the procedure described in the manual on soil sampling and methods of analysis published by the Canadian Society of Soil Science[108] was chosen for this purpose. The method as described in the above reference recommends the use of one gram of soil with a mesh size of 300 or below, which is dissolved using HNO_3, $HClO_4$ and HF to result in a final solution having a volume of 50ml which is a solution of metallic components of the sample in a 0.5M HNO_3 background. This method has been developed by Desjardins after considering three reported methods for the total digestion of soil samples and has been employed in a major survey to assess the minor elements in Canadian soils[80].

This procedure is listed below in a stepwise manner.

1. Weigh one gram of oven dried sample into a 100ml Teflon beaker.
2. Add 20ml concentrated HNO_3, cover, boil gently for 1/2 hour (100 - 150 ^oC). Cool.
3. Add 20ml concentrated $HClO_4$, cover, boil gently for 1/2 hour (200 - 250 ^oC). Cool.
4. Add 20ml of concentrated HF, cover and heat for 1 hour at 80 ^oC.
5. Remove covers and take to near dryness (250 ^oC)
6. Cool and wash down walls of beaker with 25ml of 1M HCl or HNO_3.
7. Cover and bring to boil.
8. Cool and make up to 50ml in a volumetric flask with double distilled water.

This procedure was designed for atomic absorption analysis and was employed as described without major modifications. The only change was to use a 100 mesh sample instead of the recommended 300 mesh level. This decision was partly based on the unavailability of facilities to grind down a large sample to the required level. On the other hand it was assumed that the main reason for finer grinding were to accelerate dissolution. Sieve analysis results presented earlier in this chapter indicates the presence of a large fraction of fine particles. The findings of Dudas and Pawluk[109] indicate high Pb levels for the silt and clay fractions of Alberta soils, and the same situation was assumed for the local standard sample since their results can be considered as indicative of general background values. Any alterations in the trace metal burden of a soil that results from man-made pollution can be thought to alter the level of trace metals bound onto these fine particle fractions due to their higher surface area and adsorptive capabilities. Based on these arguments it was decided to use 100 mesh samples, with care being taken to ensure adequate mixing before weighing out subsamples for analysis.

4.6.2 Teflon Bomb Digestions

In order to test and compare the applicability of the digestion procedure described by Reddy et. al.[56] some digestions using only nitric acid were carried out in Teflon lined steel bombs kindly loaned by Dr. Gary Horlick. The procedure used was adapted from the information given in references 110,111 and 56. This procedure is listed below in a stepwise manner.

1. Weigh 0.3g of sample into the Teflon cup.
2. Add 3ml of concentrated HNO_3.
3. Heat in an oven kept at 150 ^{o}C for one and a half to three hours.
4. Cool with air or in ice.
5. Transfer into a 50ml polypropylene volumetric flask and make up to volume with double distilled water.

This procedure was found to be inadequate to dissolve the sample completely. A second bomb digestion procedure tried was a modification of the above incorporating some HF into the acid mixture. In this procedure, 0.2 g of sample was heated in a bomb at 150°C for three hours with 4ml of concentrated nitric and hydrofluoric acids. Hsu and Locke[79] have reported on the superiority of a $HClO_4$, HNO_3, HF mixture for complete dissolution of organic-rich and silica-rich sediment samples. There are also other reports on the use of perchloric acid for soil and sediment sample dissolution in Teflon lined steel bombs but the manufacturer recommends otherwise. This ambiguity and the ability of an HNO_3, HF mixture to give more complete dissolution of the sample used allowed the avoidance of the use of a perchloric acid digestion procedure in these bombs. In the HNO_3, HF procedure, cooled digested solution was transferred into a 125ml polypropylene bottle containing 2.5 g of boric acid and 10ml of double distilled water. After shaking to dissolve all solids the solution was transferred into a 50ml volumetric flask and was made up to the mark with water washings of the bottle.

4.6.3 Microwave Digestions

The microwave oven (Kenmore Model 88760, Sears Canada Inc) as well as the Teflon bombs (Digestion Vessel No. 561, Savillex Corporation, Minnesota) used for microwave digestions were kindly loaned by Dr. Byron Kratochvil. The HNO_3-HF digestion procedure described in the above section was tested using microwave heating. The oven used is a regular oven designed for household use and did not contained any modifications to handle acid fumes. Consequently bombs containing the samples and acid mixture were placed in a plastic container with a snap fitted lid. This allows the containment of any acid fumes that leak out from the bombs (nitric acid invariably gives out nitrous oxide upon heating) without the explosion hazard of a tightly sealed container. This plastic container was placed on a turntable (Litton Canada Inc.) designed to be used in household microwave ovens for the rotation of the cooking vessels to ensure a uniform energy distribution. Eight bombs were used simultaneously. This assembly was heated for seven

minutes at 50% power setting, which corresponds to a microwave power output of 400 W for the oven used[112].

Chapter 5

Effects of the Composition of the Background Electrolyte

5.1 Interferences and Limitations of Anodic Stripping Methods that Arise from Matrix Effects

In stripping analysis, analyte is presented to the system as an aqueous solution. The nature and composition of the background solution has an enormous effect on the analysis; this effect is much more pronounced in anodic stripping voltammetry than in other analytical methods such as atomic spectroscopy. Apart from the classically documented interferences from trace organic compounds, which tend to adsorb to the electrode surface and foul its functions, other chemical entities such as anions and other metal ions can also impose limitations. In many applications undesirable side effects that stem from matrix problems have been dealt with by the incorporation of modifying agents in the form of buffers and complexing agents into the background electrolyte. These either mask the interference signal or move the analyte signal into an interference free region along the potential axis through complexation.

Trace metal analysis, at the level being practiced today (part per billion to parts per trillion range), is very sensitive to contamination from impure reagents. It is much more preferable to work with a minimum amount of reagents to limit contamination problems rather than rely on expensive purification procedures. Though this situation -where only a simple salt or a buffer solution is used as the background electrolyte- can be easily realized in the analysis of a synthetic standard solution, in a real situation such as the analysis of a soil sample it may be impossible to overcome all problems associated with matrix elements without the aid of modifying agents in the background electrolyte. One strategy that can be used in this situation is to optimize the composition of the background electrolyte to give a higher sensitivity towards the desired analyte. The influence of chloride and nitrate on the

anodic stripping analysis of lead and cadmium was studied with this aim. Another distinct aim of this study was to develop a base for the selection of acids for the digestion system. The overall emphasis at this stage was the development of a digestion process that would result in a suitable matrix solution for the final analysis without the necessity of modifying the resultant digested solution.

5.2 Checks for the Assumption of a Normal Distribution for Anodic Stripping Data.

As a preliminary test for the applicability of statistical comparison methods to later results a standard 100 ppb cadmium solution in 0.01 M HNO_3 was analysed 40 times using the apparatus and standard procedure described in the previous chapter. The results were checked for the assumption of a normal distribution. This was done by taking a 5 ml aliquot of the solution and analysing it at least five times consecutively. From this point onwards in this thesis the word "analysis" is used to mean such a collection of several analyses done using a single digestion portion, while the word "run" is used to describe any one of the single analyses included in an "analysis".

Signal values (peak heights in μA units) were tested for a normal distribution using the χ^2 test[113]. As can be seen from Table 5.1 a normal distribution for the results can be accepted with a high degree of confidence.

5.3 Comparison of Chloride and Nitrate Media for Cadmium : Experimental Procedure.

The effect of chloride and nitrate on anodic stripping of cadmium was compared by the analysis of 100 ppb cadmium solutions prepared to contain one of (a) 10^{-2}M HNO_3, (b) 10^{-2}M HCl, or (c) 0.5×10^{-2}M HNO_3 plus 0.5×10^{-2}M HCl. These solutions were prepared by dilution of appropriate volumes of a 1000 ppm cadmium stock solution with concentrated nitric and concentrated hydrochloric acids in precleaned 100ml volumetric flasks.

A 5 ml portion of the solution was pipetted into the cell after washing the pipet and the cell with three 2.5 ml portions of the solution for the first analysis.

Table 5.1 χ^2 Test for Normality of Anodic Stripping Data

Interval upper limit	Frequency within Intervals n_i	$z_i = \frac{(x_i - \bar{x})}{\sigma}$	F_{z_i} ie. $P(Z < z_i)$	Probability within interval p_i	$\frac{[n_i - np_i]^2}{np_i}$
3.0	3	-1.474	0.071	0.071	0.009
3.1	3	-1.125	0.129	0.058	0.119
3.2	3	-0.777	0.218	0.089	0.088
3.3	6	-0.429	0.334	0.116	0.399
3.4	2	-0.080	0.468	0.134	2.106
3.5	8	0.268	0.606	0.138	1.114
3.6	5	0.617	0.732	0.126	0.000
3.7	2	0.965	0.834	0.102	1.060
3.8	3	1.314	0.905	0.071	0.009
3.9	2	1.662	0.951	0.046	0.014
4.0	1	2.010	0.978	0.027	0.0784
4.1		2.359	0.991	0.013	0.443

No of intervals = 12, Degrees of Freedom =11, $\chi^2_{test} = \sum \frac{[n_i - np_i]^2}{np_i} = 6.225$

Since $\chi^2_{0.95,11} = 19.68$ the hypothesis that results are normally distributed can be accepted at 95 % confidence level

Between repetitive analyses (for which a new solution portion was used), the electrodes were washed with doubly distilled water and dried with a Kimwipe. Both cell and pipet were rinsed with a 2.5 ml portion of the solution.

Three runs were carried out for each of the first three analyses. Four runs were carried out for the last two, giving a total of seventeen runs for five analyses. A calomel electrode (Fisher Catalogue No. 13-693-51) connected through a salt bridge was used as the reference electrode. The salt bridge contained 2M KNO_3 for the analysis in HNO_3, 2M KCl for the analysis in HCl and a 1:1 mixture of 2M KNO_3 and 2M KCl for the analysis in HNO_3/HCl. Results of these experiments are listed in Table 5.2.

5.4 Statistical Model for the Comparison of Signal Strength

After reviewing various different statistical procedures available for comparisons of this nature, it was decided to use a hypothesis testing evaluation in a paired sample configuration. Data points were paired according to the analysis run number. Pairing of the data not only simplifies the statistical operations but also removes any ambiguity that can result from adsorption of the analyte to the cell walls. Since a newly precleaned and dried cell was used for each base electrolyte, it was expected to come to equilibrium with the analyte for later runs but could not have done so for the very first run of an analysis.

Though often not observed, ultra-trace levels of oxygen can be present in the solution. The amount of oxygen present decreases during the analysis due to its being reduced at the negative potentials used for the deposition process (i.e. less and less oxygen is present during later runs). Also the presence of an increasing amount of Hg at the bottom of the cell during later runs can alter the flow pattern during stirring. The effect of Hg has been studied by Wang et. al.[114] who has proposed a cell design that removes Hg from the solution. The effects of these two parameters were also minimized through pairing of data.

In a hypothesis testing procedure two types of errors can occur. In a type 1 or α error situation the experimental outcome suggests the rejection of the null hypothesis when

Table 5.2 Mean Peak Heights and Related Statistical Data for the Comparision of the Effect of Chloride and Nitrate on the Anodic Stripping Determination of Cadmium

A. Data Obtained in 0.01 M Nitric Acid Background

Analysis	Number of Runs	Nitric		
		Mean Peak Ht. (μA)	Standard Deviation (μA)	RSD (%)
1	3	2.15138	0.0198	0.92
2	3	2.37261	0.0160	0.68
3	3	2.61334	0.010	0.38
4	4	2.51061	0.0588	2.34
5	4	2.42777	0.0379	1.56
overall		2.40951	0.1517	6.30

B. Data obtained in 0.005 M Nitric Acid and 0.005M Hydrochloric Acid Background.

Analysis	Number of Runs	Nitric/Hydrochloric		
		Mean Peak Ht. (μA)	Standard Deviation (μA)	RSD (%)
1	3	2.61971	0.0832	3.18
2	3	2.89390	0.1107	3.83
3	3	2.97496	0.0968	3.26
4	4	2.83837	0.0552	1.94
5	4	2.88531	0.1514	5.25
overall		2.84473	0.1483	5.21

C. Data obtained in 0.01M Hydrochloric Acid Background.

Analysis	Number of Runs	Hydrochloric		
		Mean Peak Ht. (μA)	Standard Deviation (μA)	RSD (%)
1	3	2.65629	0.1027	3.87
2	3	2.74054	0.1238	4.52
3	3	3.04894	0.1697	5.57
4	4	3.09098	0.1655	5.35
5	4	3.00326	0.1339	4.46
overall		2.92437	0.2158	7.38

the true situation is otherwise. Type 2 or β error occurs when the data suggests the acceptance of the null hypothesis when the null hypothesis is false. It is important to control both situations to obtain a meaningful outcome from a hypothesis test.

One way of doing this is to predefine error levels for these two situations. These defined values, as well as a value for the improvement level δ which defines the magnitude of the acceptable difference in the chosen parameter that is being tested in order to reject the null hypothesis, were used in the hypothesis testing of this model.

For the comparison of analytical signal strength or the peak heights of differential pulse anodic stripping curves, paired data for the two situations that are being compared were subtracted from each other to obtain a new data set as illustrated in the example to follow. The null hypothesis in this case is a zero mean value of this new population. The α and β errors were selected to be at the 0.05 level. An acceptable improvement δ was selected to be $2\sigma_{diff}$, where σ_{diff} is the standard deviation of the population obtained by subtracting the paired data points from each other. In effect a mean value that is more than twice the value of the population standard deviation was used as the criterion of differentiation.

The probability matrix for these selections, shown as Figure 5.1, further clarifies the meanings of α, β and δ. Values chosen for these parameters were based on the available data about the population being studied and the experimental limitations.

Calculation of the sample size based on the above values for error levels was done by following the arguments and formulas presented in reference 115. For example, for the comparison of chloride and nitrate data, denoting cadmium peak height in chloride background as X_c and that in nitrate background as X_n, and defining,

$$X_{diff} = X_c - X_n$$

at each pair, it follows that

$$\mu_{diff} = \mu_c - \mu_n$$

which defines a new population,

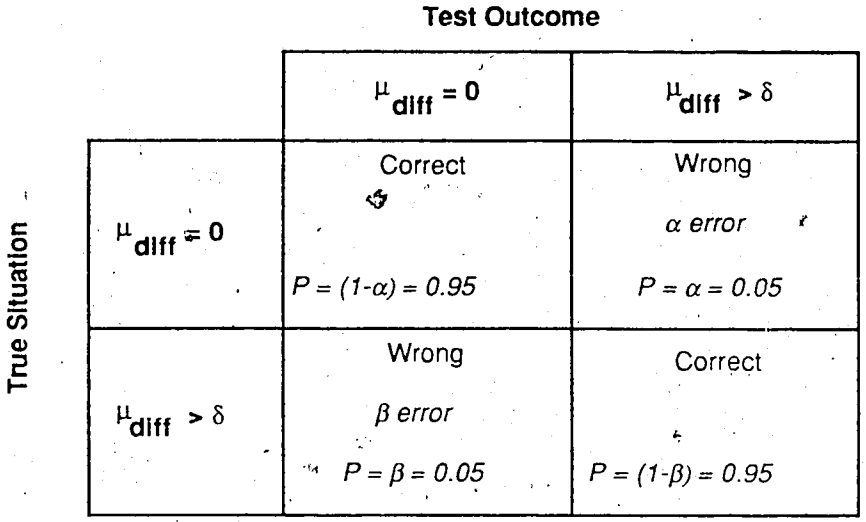


Figure 5.1 Probability Matrix for the Hypothesis Tests for the Comparison of Signal Strength

$$X_{diff} \sim N(\mu_{diff}, \sigma_{diff})$$

since

$$X_c \sim N(\mu_c, \sigma_c)$$

and

$$X_n \sim N(\mu_n, \sigma_n)$$

If the two hypotheses H_o and H_a are stated as H_o: $\mu_{diff} = 0$ and H_a: $\mu_{diff} > 0$ with $\alpha = \beta = 0.05$ and $\delta = 2\sigma_{diff}$, then

$$N_{pairs} = (U_\alpha + U_\beta)^2 \sigma^2 / \delta^2$$

where U_α and U_β are one-sided normal distribution values at the probabilities specified by α and β. For this case the value of both is 1.645, which gives a value of 2.71 for N_{pairs}.

This is the number of data points needed to carry out the above test using population parameters. Since these are being estimated using sample parameters a correction has to be made using the Student t distribution. This involves a recalculation of N using the same equation but with t distribution values for U_α and U_β, at $(N_{pairs}-1)$ degrees of freedom. In this case at 1.71 degrees of freedom, for which $t_\alpha = t_\beta = 3.937$, a final value for N_t is given by,

$$N_t = (1/4)(3.937+3.937)^2 = 15.5 \approx 16$$

The objective criterion for the test can be calculated as

$$\bar{X}^*_{diff} = t_a \, s_{diff}/\sqrt{N_{diff}}$$

where s_{diff} is the sample standard deviation and N_{diff} is the sample size. Upon the condition, $\bar{X}_{diff} > \bar{X}_{diff}$ where $\bar{X}_{diff}$ is the sample mean, H_o can be rejected with at least 90% confidence.

5.5 Statistical Model for the Comparison of Variances

The criterion of differentiation used for the comparison of variances was based on the magnitude of the relative standard deviation. At the concentration levels studied a relative standard deviation below 10% can be considered as acceptable. The lowest relative

standard deviation observed in the data set is 5.21% for the HNO_3/HCl background (Table 5.2). Consequently the criterion of differentiation was taken as twice the relative standard deviation. From the results of the signal strength comparisons which will be presented in section 5.6, it was established that

$$\mu_c \approx \mu_{c/n} \approx \mu_n + 0.5$$

for the comparison of chloride and nitrate media. Allowing the relative standard deviation in chloride media to be twice of that in nitrate media,

$$\sigma_c/\mu_c = 2\,\sigma_n/\mu_n$$

which leads to

$$\sigma_c/\sigma_n = 2\,(\mu_n + 0.5)/\mu_n$$

When substituted with the sample mean for μ_n this provides the estimate

$$\sigma_c/\sigma_n = 2.4166 \approx 2.4$$

Following the arguments in reference 115, the R value for these conditions is given by,

$$R = \sigma_c^2/\sigma_n^2 = 5.76.$$

From the listed R values this corresponds to 15 degrees of freedom, implying a sample size of 16.

This sample size calculation based on relative standard deviation was used in order to avoid employing variance estimates. The effective result is to use the sample mean estimates for the calculation instead of sample variance estimates. Sample means are normally distributed around the population mean for a normally distributed population. Since they are centered around the true population mean, sample means tend to provide a better estimate of the population mean even at smaller sample sizes. On the other hand, sample variances show a chi square distribution which is highly skewed at small sample sizes[115]. Under these circumstances it is better to use sample mean values than sample variance values for the estimation of sample size. At this point it should also be pointed out that the sample standard deviation or s is not an unbiased estimator for the population

standard deviation, though s^2 is an unbiased estimator for the estimation of population variance[115].

These selection criteria change the outcome of the comparison test. Though it is desirable to check whether the variances are equal or not, the sample size selection criteria that have been used only allow checking of whether or not there is a significant difference in the relative standard deviations of the two populations. A significant change is being interpreted as doubling of the RSD. At the concentration levels being used it is approximately equal to a 5% change in RSD.

Though this can be set to the level of equal RSD values which is a more appropriate criterion, it results in a sample size greater than 120, making data accumulation with a reasonable control impossible because each run takes close to six minutes.

Taking the comparison of nitrate and chloride media as an example, the two hypotheses were defined as

$$H_o: \sigma_c^2 = \sigma_n^2$$

$$H_a: \sigma_c^2 \neq \sigma_n^2$$

with $\alpha = \beta = 0.05$ which results in a sample size of sixteen, as pointed out in the last paragraph. The test criterion based on $\alpha = 0.05$ and N=16 is the F value for distribution with (15,15) degrees of freedom, which is designated as F^*. F values for the data were calculated using the identity $F = \sigma_c^2/\sigma_n^2$. Under the condition $F < F^*$, H_o can be accepted with at least 95% confidence.

5:6 Data Analysis

Tables 5.3 list the results of the hypothesis tests for the comparison of peak heights. These results lead to the conclusion that there is a significant difference between cadmium peak height in the presence and absence of chloride. Since it is highest in HCl background followed by the HNO_3/HCl and HNO_3 backgrounds (Table 5.2), this effect appears to depend on the concentration of chloride. The magnitude of chloride effect was

Table 5.3 Hypothesis Test Results for the Comparison of the Effects of Chloride and Nitrate on the Anodic Stripping Determination of Cadmium

For all tests, $H_o : \mu_{diff} = 0$ and $H_a : \mu_{diff} > 0$

See text for the definitions of the symbols used.

	μ_{diff}	$\bar{X}_{diff}$	s_{diff}	n	$\bar{X}^{*}_{diff}$
Chloride vs Nitrate	$\mu_c - \mu_n$	0.5185	0.1366	16	0.0597
Chloride vs Chloride/Nitrate	$\mu_c - \mu_{c/n}$	0.798	0.1616	16	0.0707
Chloride/Nitrate vs Nitrate	$\mu_{c/n} - \mu_n$	0.4294	0.1182	16	0.0517

In all three cases $\bar{X}_{diff} > \bar{X}^{*}_{diff}$. So the null hypothesis can be rejected with at least 95% confidence

quantified by calculating a confidence interval for μ_c-μ_n using X_c-X_n data and assuming a t distribution.

At the 90% confidence level, this interval was found to be (0.52± 0.06) μA, leading to the conclusion.

$$\mu_c \approx \mu_{c/n} \approx \mu_n + 0.5$$

Table 5.4 lists the data and F statistic values for the comparison of variances. Table 5.5 summarizes the results of the whole experiment.

One complication in the analysis of this data arises from the possible intervention of chloride from a salt bridge leak from the reference electrode salt bridge. Though no such effect is easily observable with a KNO_3 salt bridge, with a KCl salt bridge the current level at the final potential of the anodic stripping scan (stripping cycle was terminated at 0.1V) shows a clear systematic increase with the run number (Figure 5.2). This oxidation signal arises from the oxidation of Hg in the presence of Cl^- and the level can be regarded as indicative of the Cl^- level present in the solution at that point.

Though it is possible to measure chloride levels in the solution using the stripping curve itself by extending the final potential to the positive side, it was found to be easier and more appropriate to use differential pulse polarography for this purpose because of the high chloride levels.

5.7 Chloride Level Changes due to Salt Bridge Leak

Though a salt bridge with a Vycor plug at the end was used, leakage of chloride ion into the solution, as shown in Figure 5.2 and explained above, is significant enough to attract attention, especially in a trace analysis situation. This was based on the observation of an increase in sensitivity with the presence of chloride in the background electrolyte. Assuming this effect depends on the chloride concentration, a changing chloride level should contribute towards a deterioration in the precision of the analysis. Addition of a concentrated salt solution may not be an acceptable solution in a trace level analysis,

Table 5.4 Sample Values for the Comparison of the Effect of Different Backgrounds on the Variance of the Cadmium Measurement

Sample Values	$\overline{X}$	s_x	n
Chloride	2.928	0.222	16
Nitrate	2.410	1.517	16
Chloride/Nitrate	2.846	1.531	16

F Test Values	F
Chloride vs Nitrate	2.14
Chloride vs Chloride/Nitrate	2.11
Chloride/Nitrate vs Nitrate	1.02

$H_0 : \sigma_A^2 = \sigma_B^2$ $\quad$ $H_a : \sigma_A^2 \neq \sigma_B^2$

$F_{15,15}$ = 2.40 at 95% cofidence level.

So for all three cases null hypothesis can be accepted with at least 95% confidence

Table 5.5 Summary of Results from the Comparison of the Effect of Chloride and Nitrate on the Anodic Stripping Determination of Cadmium

Comparison of Mean Signal Strength

	95% Confidence Level	99% Confidence Level
Chloride vs Nitrate	$\mu_c - \mu_n > 0$	$\mu_c - \mu_n > 0$
Chloride vs Chloride/Nitrate	$\mu_c - \mu_{c/n} > 0$	$\mu_c - \mu_{c/n} = 0$
Chloride/Nitrate vs Nitrate	$\mu_{c/n} - \mu_n > 0$	$\mu_{c/n} - \mu_n > 0$

Comparison of Variances

	90% Confidence Level	95% Confidence Level
Chloride vs Nitrate	$\sigma_c \neq \sigma_n$	$\sigma_c = \sigma_n$
Chloride vs Chloride/Nitrate	$\sigma_c \neq \sigma_{c/n}$	$\sigma_c = \sigma_{c/n}$
Chloride/Nitrate vs Nitrate	$\sigma_{c/n} = \sigma_n$	$\sigma_{c/n} = \sigma_n$

Rejection of $\sigma_A = \sigma_B$ can be regarded as an indication of a change in RSD by more than 5%.

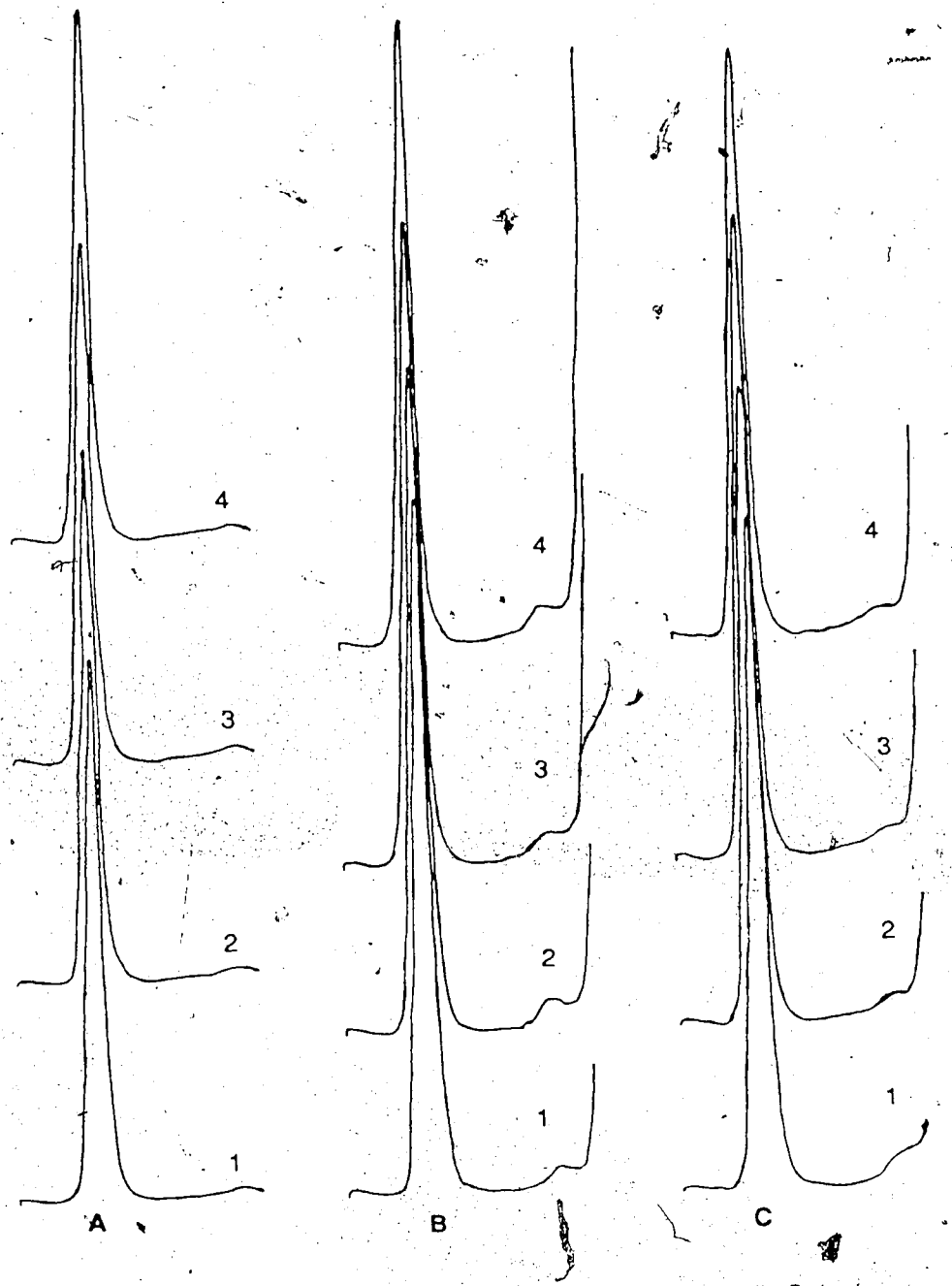


Figure 5.2 Effect of Salt Bridge Leak on the Appearence of Anodic Stripping Curves of Cadmium.

Curves for four consecutive runs obtained with a single solution portion are shown in ascending order for each category.

A. 0.01 Nitric Background; 2M Potassium Nitrate Salt Bridge

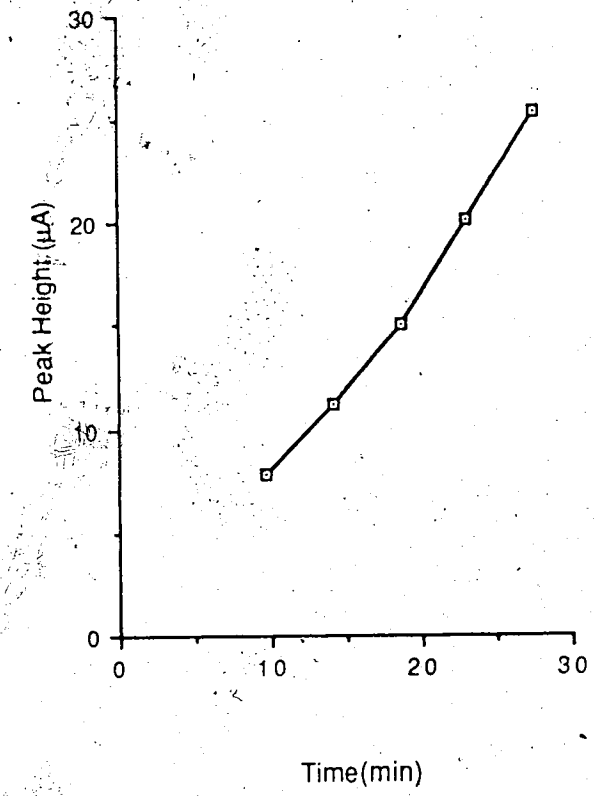
B. 0.01 Hydrochloric Background; 2M Potassium Chloride Salt Bridge

C. 0.005 Nitric + 0.005 Hydrochloric Background; 1M Potassium Nitrate + 1M Potassium Chloride Salt Bridge.

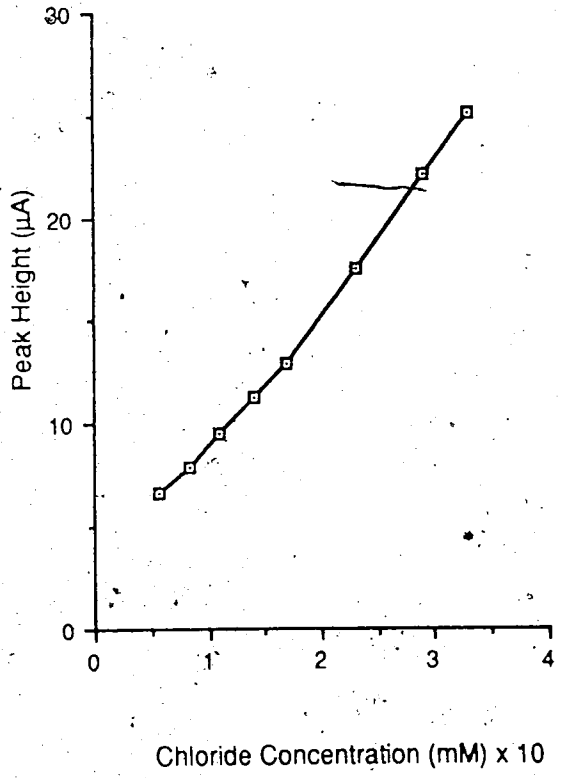
although it would have masked any changes from a salt bridge leak. This prompted further investigations to quantify the level of chloride leakage under experimental conditions.

The same analyte solution as used for previous tests was used as the cell solution with the 2M KCl salt bridge connecting this solution to the reference calomel electrode. Instead of the usual anodic stripping analysis, the potentiostat and the SMDE were switched to operate in differential pulse mode, with the SMDE now operating as a dropping mercury electrode.

Results of five consecutive runs plotted against the time spent in the cell are shown together with a calibration curve for chloride which was obtained using a nitrate salt bridge as Figure 5.3. Comparison of the signal levels show a chloride concentration of approximately 3.5×10^{-4}M at the end of the analysis. Compared to the chloride level in 0.01 HCl this is hundred times lower. Ideally one may not expect any significant change in any behaviour that is dependent on chloride level from a change of this magnitude. It should be noted that the salt bridge used contained 2M KCl. The amount of chloride that can diffuse into the solution will be much higher with a saturated salt bridge, such as direct insertion of the reference electrode into the test solution. The magnitude of this effect is shown in Figure 5.4, which shows a set of linear scan cathodic stripping curves, obtained in a chloride free background electrolyte with the original Ag/AgCl reference electrode system supplied with the 303 SMDE in place. These were obtained by scanning the potential cyclically from 0.0 V to +0.4 V and back at a rate of 30 mV/s. The initial four minute deaeration was followed by 1/2 minute deaerations between successive runs, which mainly served to mix the solution to disperse chloride that leaks into the solution from the reference junction. A second important feature observed in this data set is the development of a secondary peak that grows at the expense of the initial peak. The observed increase in ent at the final potential of the stripping curves presented in Figure 5.2 may be resulting this phenomenon. Growth of the second peak at an intermediate chloride



Chloride Leak Data



Calibration Curve for Chloride Determination

Figure 5.3 Estimation of Chloride Leakage from a 2M KCl Salt Bridge.

Plot Chloride Leak Data shows the observed differential pulse polarographic signal for chloride as a function of time spent in the cell, for a solution containing 0.1M KNO_3 acidified to pH2 with nitric acid. Calibration curve was constructed with a 2M KNO_3 salt bridge in place. Chloride was added as potassium chloride.

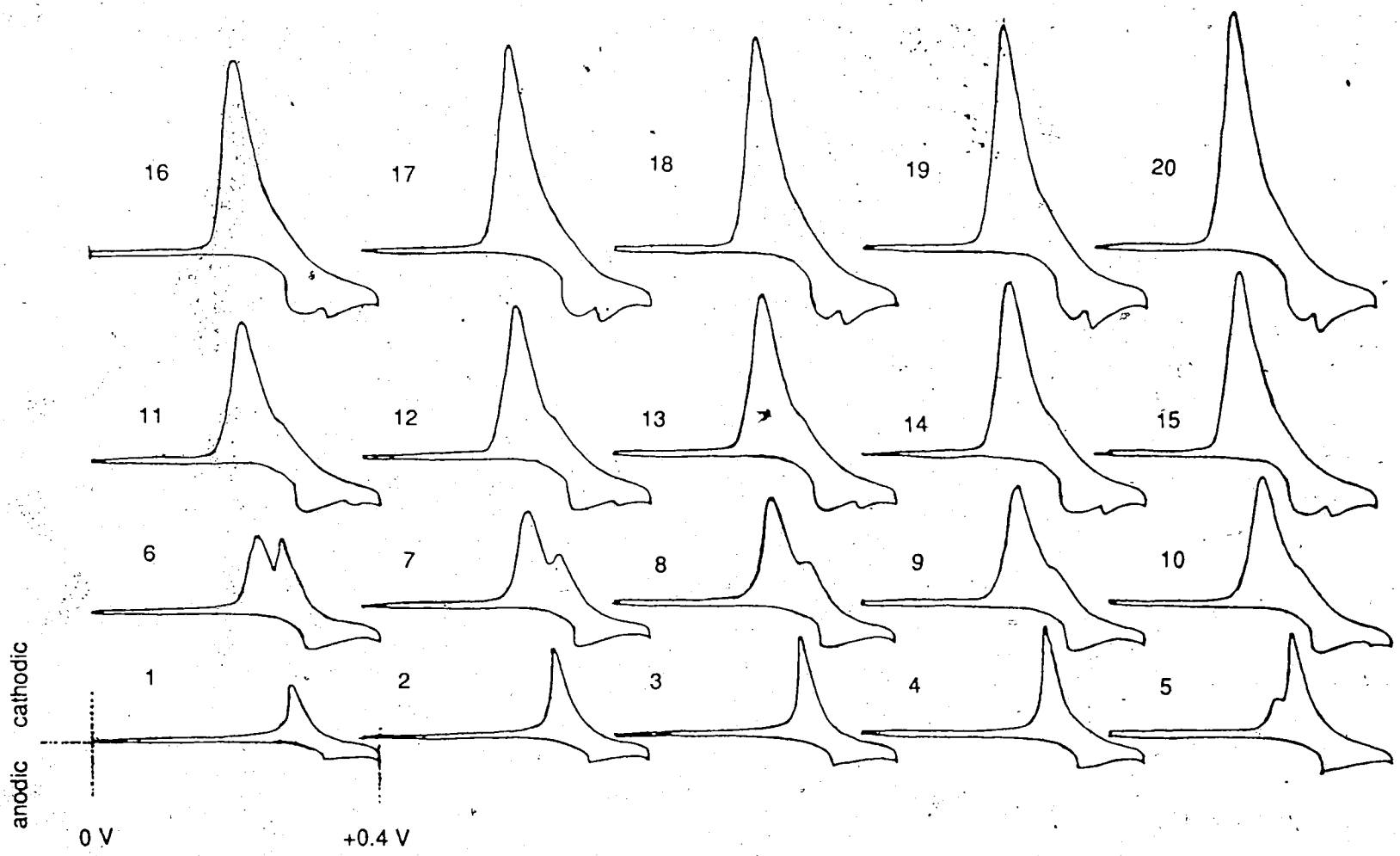


Figure 5.4 Cathodic Stripping Curves Showing Chloride Leak from a Saturated Ag/AgCl Reference Electrode

Current directions and potential values shown for Curve 1 apply to all curves. Background solution contained 0.01M potassium nitrate acidified with nitric acid to pH 2. Curve 1 was obtained soon after a four minute deaeration. A 30 s deaeration was done between successive runs.

concentration is a phenomenon that has been documented[117] and presumably arises from the formation of Hg(I) chloride at low chloride concentrations.

5.8 Effect of Using a Potassium Nitrate Salt Bridge

At this point it was felt that although the amount of chloride transfer into the solution is low, an assessment of the effects of the salt bridge filling solution on the anodic stripping signal of a metal ion at trace level was an appropriate study. Influence of the salt bridge solution upon stripping results can originate either from changes in the solution due to electrolyte leakage or from changes in the conductivity of the salt bridge that may influence the measurement system. One would hardly expect any difference in conductivity between a KCl salt bridge and a KNO_3 salt bridge due to closeness of their transport properties. The equivalent conductivity for chloride ion is 76.34 mho cm^2 while it is 71.44 mho cm^2 for nitrate[3].

Results of a comparison of data obtained by running stripping analyses of 100ppb Cd^{2+} in 0.01M HCl with KNO_3 and KCl salt bridges in place are shown in Table 5.6, which indicates a definite increase in sensitivity with a KNO_3 salt bridge.

A summary of the results obtained for the comparison of variances for all situations studied is presented in Figure 5.5. In this figure each point where three bold lines meet represents a specific situation (solution composition/salt bridge combination). The F statistic tabulated on each line is calculated for the comparison of the two situations connected by that line. The angled line drawn across the diagram separates the situations studied into two groups on the basis of the F test result at the 90% confidence level.

5.9 Comparison of Chloride and Nitrate Backgrounds for the Analysis of Lead

Similar experiments were done for Pb^{2+}in which only a KNO_3 salt bridge was used. The 0.01 M HCl and 0.01M HNO_3 media were compared using the same statistical design and arguments used for the comparison of the Cd^{2+} analyses discussed in Section 5.8.

Table 5.6 Comparison of the Effect of Potassium Chloride and Potassium Nitrate Salt Bridges on the Anodic Stripping Determination of Cadmium in Chloride Media

$$\mu_{diff} = \mu_{KNO_3} - \mu_{KCl}$$

$$H_o : \mu_{diff} = 0 \; ; \; H_a : \mu_{diff} > 0$$

$\bar{X}_{diff}$	s_{diff}	n
0.1613	0.1153	16

($t_{0.05} = 1.75$ at 15 degrees of freedom)

$$\bar{X}^{*}_{diff} = \frac{t_{\alpha} s_{diff}}{\sqrt{N_{diff}}} = \frac{1.75 \times 0.1153}{\sqrt{16}} = 0.0504$$

$\bar{X}_{diff} > \bar{X}^{*}_{diff}$, so the null hypothesis can be rejected with at least 95% confidence.

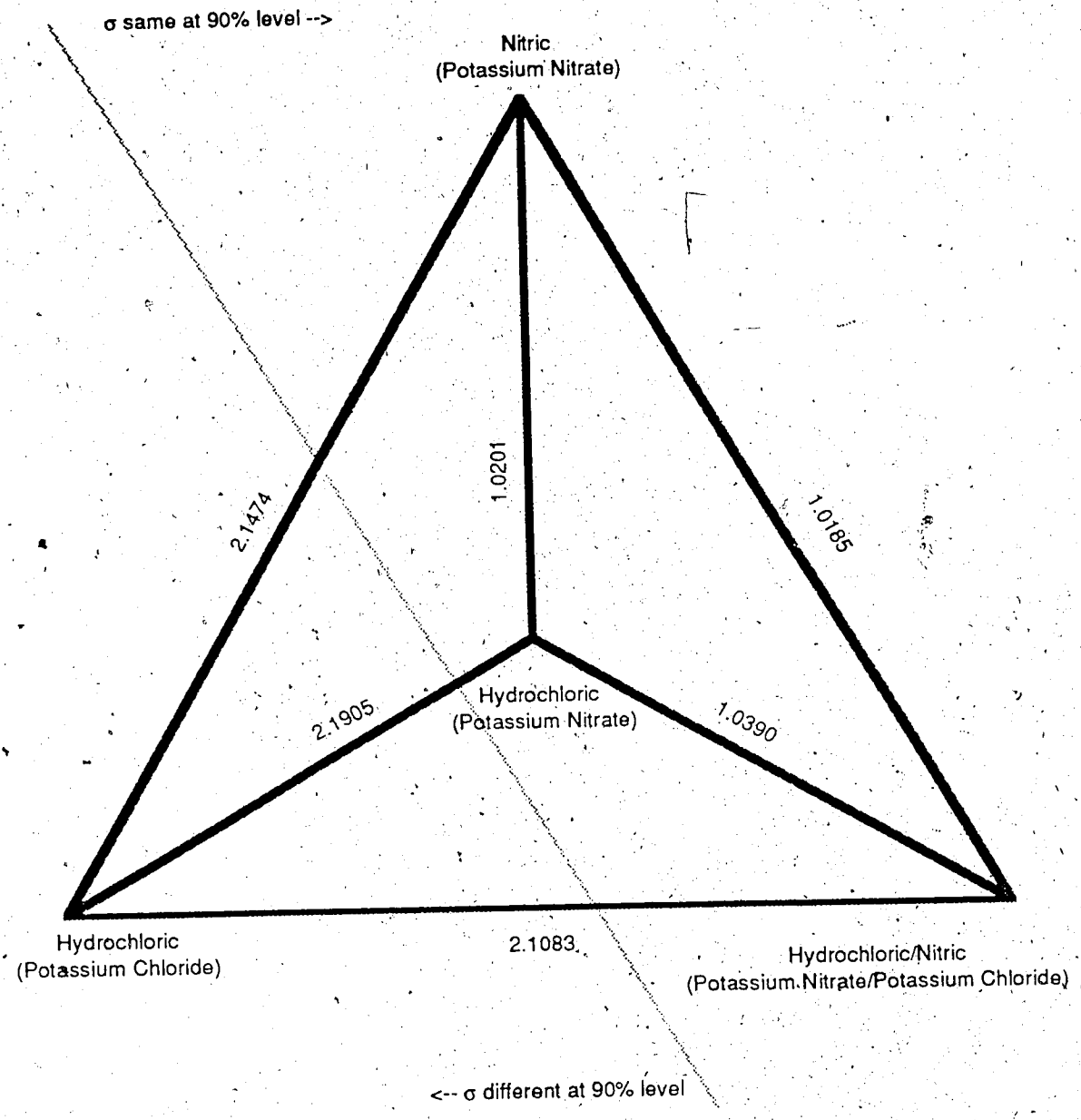


Figure 5.5 Summary of Results from the Comparison of Variance for All Situations.

Calculated F statistic is shown on connecting lines for the two situations marked at the apex.

Salt bridge Composition is shown in brackets.

A summary of the results of this experiment is presented in Table 5.7. Hypothesis test results summarized in Table 5.8 indicate an improvement in signal strength in nitrate media in lead analyses, which is opposite the effect observed in cadmium analyses. But this difference is not large enough to consider as an advantage in a practical analysis. Comparison of variance results in Table 5.9 do not indicate any significant change in variance with the type of background anion used in lead analyses.

5.10 Lead and Cadmium Complexation Properties of Chloride and Nitrate Media

Vydra et. al.[2] gives some data of this nature for linear scan anodic stripping analysis (these data were originally reported by Zarubina and Kolpakova[118]). Data given are averages of peak currents obtained at three different base electrolyte concentrations, 0.02, 0.1 and 0.5M. For cadmium at the 30 ppb level in HCl they report a 41% increase compared to HNO_3 (85 nA vs 60 nA). At 100 ppb level and 0.01M acid concentrations the results of the present study show only a 21% increase (2.9244μA vs 2.4095μA). Though these two observations should not be compared quantitatively due to fundamental differences in the method of analysis and deposition times, and to the fact the literature values are not reported for a specific base electrolyte concentration, it is obvious that there is an increase in sensitivity in chloride media.

This sensitivity change can be expected to arise from differences in complexation behaviour in the two background solutions. Figures 5.6 and 5.7 show the distribution of cadmium and lead among various complexed species that are present in the presence of chloride and nitrate. These diagrams were prepared using the data and techniques reported in the compilation by Kotrly and Sucha[74]. According to these figures only mono ligand complexes can be present under the conditions used for the experiments (i.e. at a ligand concentration of 0.01M). Since these complexes can be expected to be reversible and kinetically labile and since the fraction of the metal tied up is small it is unlikely for them to have any influence on the mechanism of the deposition step. Even if they do, one would

Table 5.7 Mean Peak Heights and Statistical Data for the Comparison of the Effect of Chloride and Nitrate Media on the Anodic Stripping Determination of Lead.

Analysis	Number of Runs	Hydrochloric			Nitric		
		Mean Peak Ht. (μA)	Standard Deviation (μA)	RSD (%)	Mean Peak Ht. (μA)	Standard Deviation (μA)	RSD (%)
1	3	1.463	0.024	2	1.632	0.049	3
2	3	1.694	0.14	8	1.867	0.064	3
3	4	1.604	0.035	3	1.875	0.010	0.5
4	4	1.722	0.028	2	1.907	0.038	2
5	4	1.803	0.030	2	1.668	0.069	4
overall		1.668	0.13	8	1.786	0.13	7

Table 5.8 Comparison of the Effect of Chloride and Nitrate Media on the Anodic Stripping Determination of Lead

$$\mu_{diff} = \mu_c - \mu_n$$

$$H_o : \mu_{difff} = 0 \; ; \; H_a : \mu_{diff} > 0$$

$\bar{X}_{diff}$	s_{diff}	n
0.1170	0.1734	16

$$\bar{X}_{diff} = \frac{t_\alpha s_{diff}}{\sqrt{N_{diff}}} = \frac{1.75 \times 0.1734}{\sqrt{16}} = 0.0758$$

$\bar{X}_{diff} > \bar{X}_{diff}$, so the null hypothesis can be rejected with at least 95% confidence.

Table 5.9 Comparison of Variances for the Determination of Lead in Chloride and Nitrate Media

$$H_o : \sigma_c^2 = \sigma_n^2 \qquad H_a : \sigma_c^2 \neq \sigma_n^2$$

	$\overline{X}_{diff}$	s_{diff}	n
Chloride	1.6946	0.1142	16
Nitrate	1.8116	0.1220	16

$F_{test} = s_n^2 / s_c^2 = 1.142$, $F^* = 2.40$ at 95% confidence level. So the null hypothesis is acceptable.

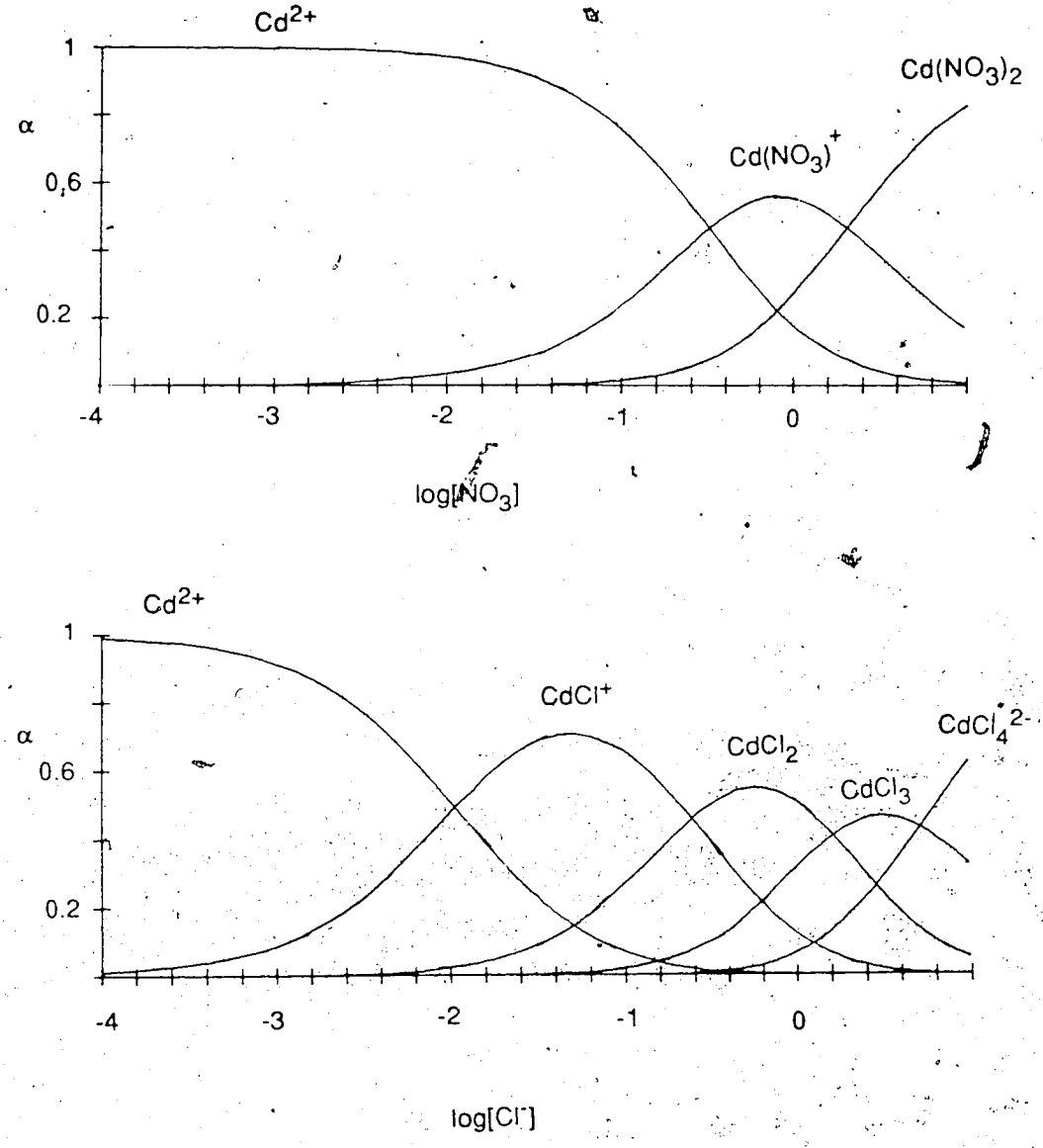


Figure 5.6 Distribution of Cadmium in Nitrate and Chloride Media as a Function of Anion Concentration.

α - Fraction of metal present as indicated species.
A low total metal content was assumed in order to neglect the precipitation of springly soluble species

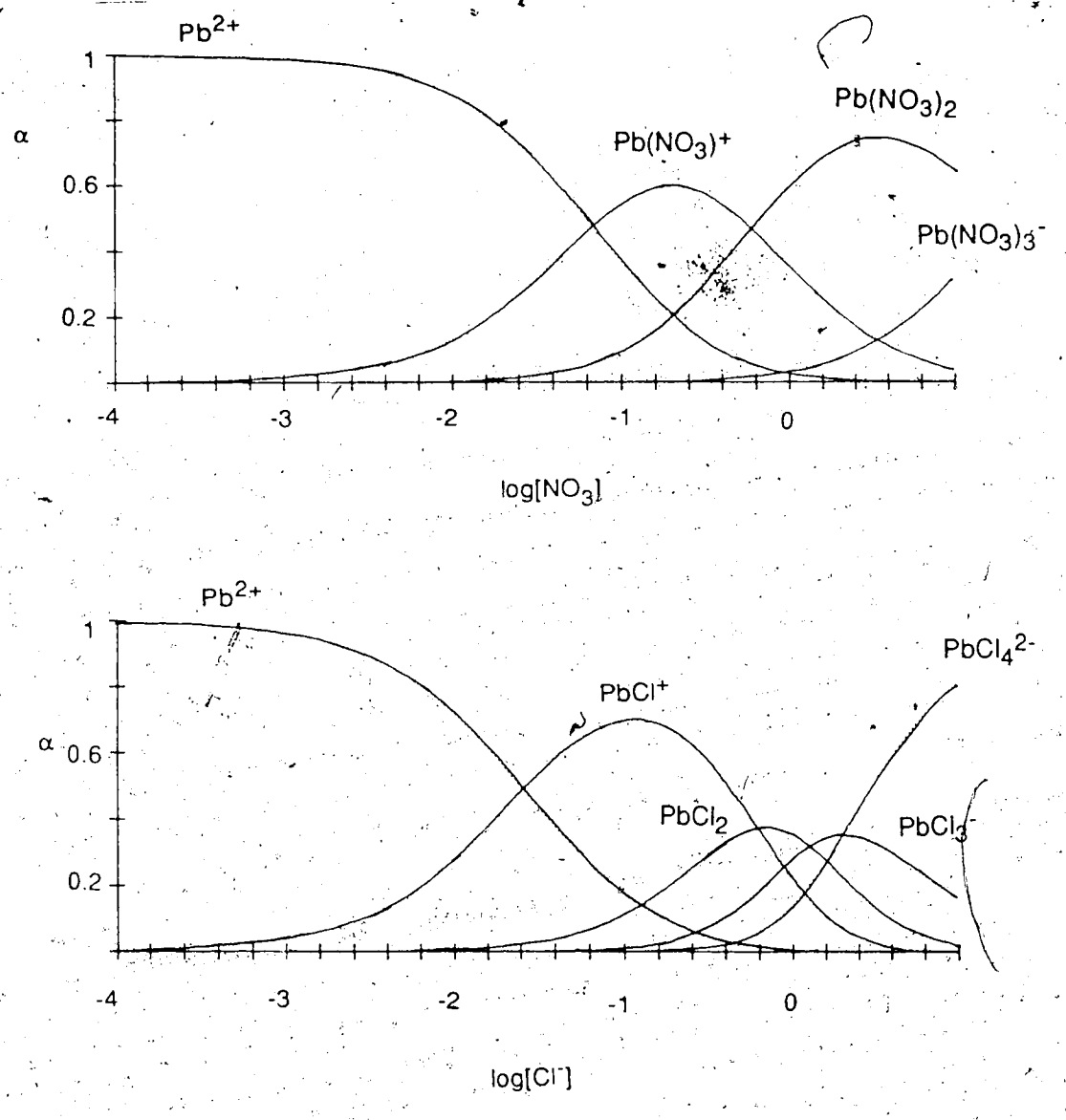


Figure 5.7 Distribution of Lead in Nitrate and Chloride Media as a Function of Anion Concentration.

α - Fraction of metal present as indicated species.
A low total metal content was assumed in order to neglect the precipitation of springly soluble species

expect a decrease in signal strength in chloride media because of the higher complexing capability of chloride relative to nitrate.

Mota et al.[118] have studied the effect of reversible complexation on anodic stripping of metals. Their observations indicate the possibility of a reduction in sensitivity in the presence of a complexing agent through the interaction of the complexing agent at the oxidation or stripping step. Since this involves the production of a high concentration of metal ions at the vicinity of the electrode surface, a low ligand concentration can lead to saturation of the ligand at the electrode surface. The effect of this on the stripping peak is a peak broadening and a corresponding decrease in peak height. Peak broadening occurs via splitting of the peak into two slightly displaced overlapping peaks, the split arising from oxidation of the metal to form both free metal ions and a metal complex.

However, it was observed that the situation with chloride and nitrate is the complete reverse of this. Chloride ion, which forms a stronger complex with cadmium, tends to give a larger signal, while nitrate ion, which is the weaker complexing agent, produces a lower signal.

5.11 Effect of Chloride and Nitrate on Lead in a Buffered Background

Another experiment was done to extend the results obtained in unbuffered chloride and nitrate containing media to buffered solutions. This experiment was carried out using a pH 3 buffer solution prepared by acidifying an equimolar acetate buffer solution with concentrated nitric acid. Potassium nitrate and potassium chloride salts were used as nitrate and chloride sources. The experiment was conducted as a two factor variance analysis experiment. The data obtained and the ANOVA table for these data are shown in Tables 5.10 and 5.11.

Table 5.10 Comparison of the Effect of Chloride and Nitrate on the Determination of Lead in Buffered Media.

Data for the two way analysis of variance test.

A. Raw Data

Potassium Chloride	Potassium Nitrate: 0	Potassium Nitrate: 0.05	Potassium Nitrate: 0.10
0	0.0843 0.0866 0.0879 0.0902	0.0839 0.0855 0.0865 0.0869	0.0913 0.0929 0.0983 0.1010
.05	0.0917 0.1042 0.1076 0.1098	0.0911 0.0924 0.0987 0.0979	0.1029 0.1088 0.1127 0.1155
.10	0.0872 0.0892 0.0908 0.1002	0.0987 0.0989 0.0990 0.1034	0.0853 0.0903 0.1019 0.1027

B. Reduced Data

Mean std. dev. RSD %	0.0872 .0025 3	0.0857 .0014 2	0.0959 .0045 5
Mean std. dev RSD %	0.1033 .0081 8	0.0950 .0038 4	0.1099 .0055 5
Mean std. dev. RSD %	0.0918 .0057 6	0.0999 .0022 2	0.0951 .0086 9

Table 5.11 Anova Table for the Comparison of the Effect of Chloride and Nitrate on the Determination of Lead in Buffered Media

Sources	Sum of Squares	Degrees of Freedom	Mean of the sum of squares	F
Between Rows (KCl Effect)	1.043×10^{-3}	2	0.522×10^{-3}	18.67
Between Columns (KNO_3 Effect)	3.337×10^{-4}	2	1.669×10^{-4}	5.97
Interactions	4.894×10^{-4}	4	1.223×10^{-4}	4.38
Within Cells	7.543×10^{-4}	27	0.280×10^{-4}	

$F_{0.01,2,27} = 5.49$ $F_{0.01,4,27} = 4.11$

According to these results both potassium nitrate and potassium chloride have an effect on the lead signal. However, the effect of chloride is much more pronounced than that of nitrate. Since the differences in variances rather than differences in the signal strength are being considered, these results do not provide enough evidence to deduce the nature of this effect. Moreover, complexation effects from the presence of chloride should be minimal under the conditions used for this study because of the stronger complexing properties of acetate ion. The predominance area diagram for lead in chloride-acetate mixed media shown in Figure 5.8 indicates the near absence of chloride complexes even at the 0.1M chloride level.

5.12 Summary

Figure 5.9 summarizes all the observations in the form of confidence intervals for the mean values. Though hypothesis testing provides a more definite decision making strategy, a confidence interval chart is valuable since it allows one to compare both signal strengths and the standard deviations. Also, it is more useful in a situation where second choices may be required due to limitations imposed by original sample compositions.

Though hypothesis testing shows a definite increase in signal for Cd^{2+} with a KNO_3 salt bridge, the confidence interval chart (Figure 5.9) might lead one to consider this increase as marginal because of the overlapping confidence intervals. Though chloride definitely improves the sensitivity in the case of Cd^{2+}, the situation with Pb^{2+} is reversed.

In anodic stripping voltammetry it is customary to analyze for several metals in a single analysis. This being one of the powerful benefits of the method, a background electrolyte that can be useful in a general practical situation should be able to give optimum, or at least acceptable, results for more than one metal ion. In light of this data it can be concluded that a mixture of chloride and nitrate anions in the form of HCl and HNO_3 is better for the analysis of cadmium and lead. As far as the salt bridge is concerned, preference is for the use of KNO_3. A KCl salt bridge will result in a reduction in

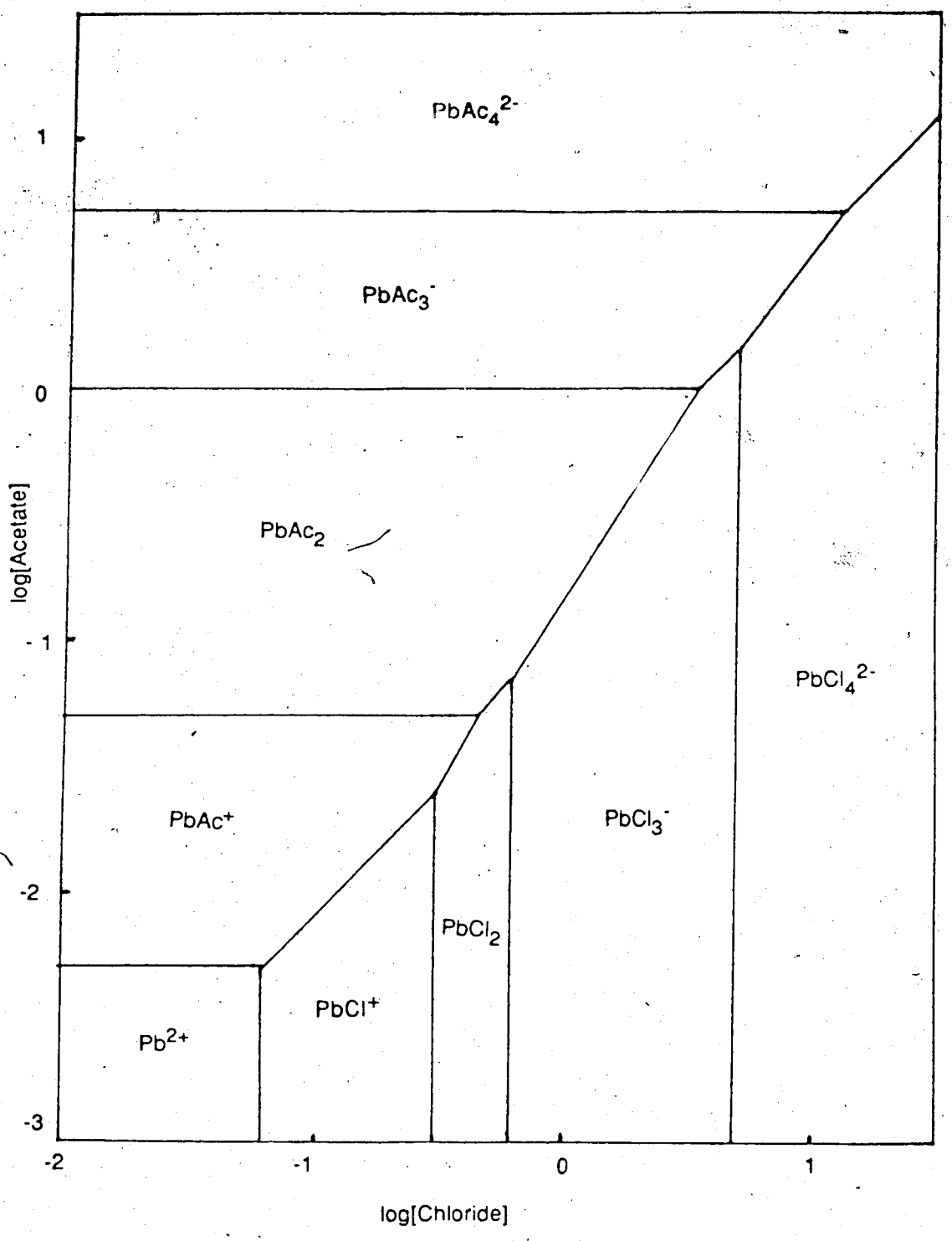


Figure 5.8 Predominance Area Diagram for Lead in Chloride/Acetate Mixed Media

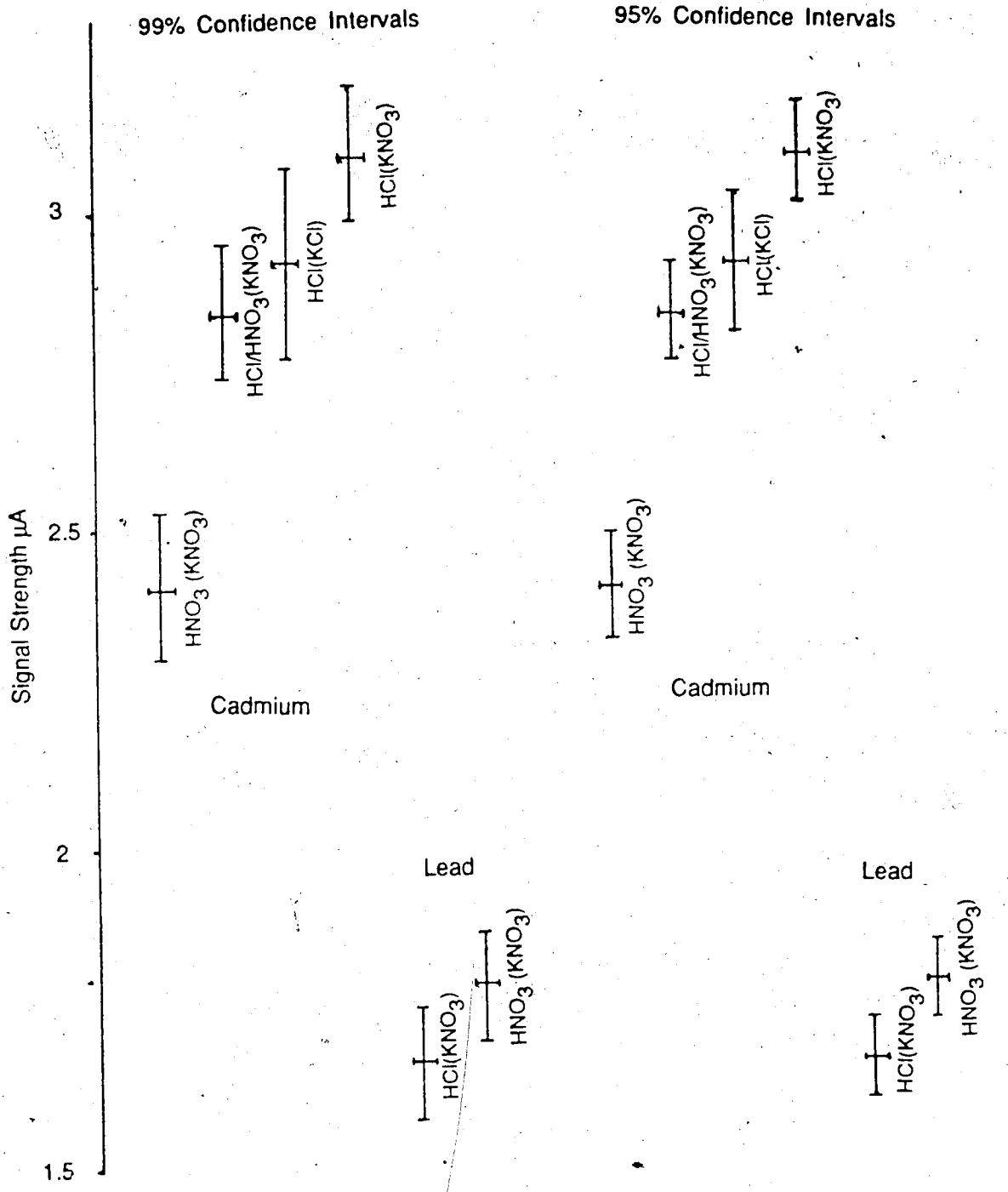


Figure 5.9 Confidence Interval Chart for the Determination of Cadmium and Lead in Chloride and Nitrate Media.

Salt bridge composition is shown within brackets. Metal concentration was 100 ppb in all cases.

performance in terms of sensitivity and precision, but increasing the deposition time will lead to a gain in sensitivity, allowing one to tolerate its use. The main advantage of KCl is the ease of use and system maintenance. All subsequent experiments in this thesis were done with a KNO_3 salt bridge.

Chapter 6

Deaeration and Ox n Interference

6.1 Effects of Dissolved Oxygen: Present Understanding

Oxygen has been considered as an interference in aqueous polarographic and other voltammetric techniques due to the two reduction waves that unfortunately occur near the limits of the useful potential window. Thus deaeration of solutions is an unavoidable step in aqueous voltammetric studies.

Early workers observed interfering effects of oxygen in anodic stripping voltammetric applications: " For the same reasons as in classical polarography, dissolved oxygen must be expelled from the test solution. Oxygen is relatively highly soluble in aqueous solutions at normal pressure and temperature (about 10^{-3}M solutions are formed). The dissolved oxygen is electrolytically reduced and causes a considerable and poorly reproducible increase in the residual current. . . . In addition to an increase in the residual current, the presence of dissolved oxygen may cause other difficulties in stripping determinations. It may oxidize the amalgam already formed, e.g.

$$M(Hg)_x + 1/2\ O_2 + H_2O \longrightarrow x\ Hg + M^{2+} + 2\ OH^-$$

and thus decrease the efficiency of the preelectrolytic step. The formation of hydroxyl ions in the oxygen reduction may cause an undesirable change in the pH of unbuffered solutions, leading to hydrolytic phenomena, etc." (reference 2, page 174)

A recent monograph on stripping analysis also states more or less the same reasons for the necessity to remove oxygen prior to the deposition step:

" The halfwave potentials of these steps (*of the oxygen reduction reaction*) are approximately -0.05 and -0.9 V vs SCE. These reduction steps result in an increased background current that obscures the stripping peaks of interest. Complications in stripping analysis are introduced also through the chemical reactivity of oxygen.

(a) Oxygen may oxidize the metals in the electrode amalgam

(b) Hydroxyl ions formed during the reduction of oxygen in neutral or basic media can precipitate metal ions in the vicinity of the working electrode. For these reasons, oxygen must be removed from the sample solution prior to the deposition step." (reference 1, page 11)

Though there are reports of studies on the nature of oxygen interference in anodic stripping analysis much of the explanation given can be considered as an extension of ideas from the polarographic literature, of which the above excerpts are typical. There is a controversy in this because of the fundamental differences that exist between these two techniques. Use of a stationary electrode in anodic stripping analysis as opposed to a DME in polarography changes the immediate environment of the double layer into a more stationary one. On the other hand the stripping or measurement step in the former is preceded by a relatively long deposition step which is usually carried out under turbulent convective conditions, leading to more bulk changes in the solution. Past and present workers generally have cited three modes by which oxygen can interfere in anodic stripping analysis.

(1) Oxygen reduction increases the background current, so stripping peaks become obscure. This mainly applies to linear scan stripping procedures[38,44].

(2) Oxygen can reoxidize the plated metal during the deposition step, reducing the efficiency of the analysis[120] presumably in a nonreproducible manner.

(3) The oxygen reduction reaction can change the pH of the solution near the electrode, forcing the formation of hydroxy complexes and precipitates of the metal being analysed[121].

Of these processes, the second and third are associated with deposition and equilibrium stages, while background effects predominate only during the stripping stage.

Several recent studies report the disappearance of oxygen interference effects upon matrix exchange, i.e. exchange of the analytical solution for a deaerated buffer solution after completion of the deposition step[38,40,41]. This is preferably done using a flow cell to avoid exposure of the electrode to air and to maintain potential control throughout the exchange process. Since no difference has been observed between deaerated and nondeaerated samples, authors of the references cited above have concluded that oxygen interference is a process that appears only during the stripping step.

6.2 Effects of Oxygen on Lead Analysis: Preliminary Observations

In order to estimate the optimum deaeration time for the system, the effect of variation of the length of the purge time on the outcome of the analysis of lead was studied. This study provided data illustrating the variations of the lead peak with varying dissolved oxygen levels. Efficiency of the deaeration or deoxygenation by nitrogen purge was found to be dependent on the gas flow rate, purge tube geometry and background electrolyte composition as well as on the analyte concentration. In the case of analyte concentration it might have a dependence on the deposition time as well, since deposition time controls the real analyte concentration (i.e. concentration of Pb in the mercury drop at the beginning of the stripping step).

There is a reduction in the oxygen content of the solution during the analysis itself, presumably occurring through exchange with blanketing N_2 and also via reduction reactions that occur in the solution.

Figure 6.1 shows the changes in the Pb stripping peak that occur with changing oxygen levels during consecutive analyses of a 5ml portion of a 50ppb Pb (in 0.01M HNO_3 and 0.1M KNO_3) solution, with a one minute deaeration. Differential pulse anodic stripping curves in Figure 6.2 show the effect of oxygen on the background current. Though high oxygen levels tend to change the background or base line into a deep valley, the lead signal occurs on the bottom of this valley, allowing measurement of the peak

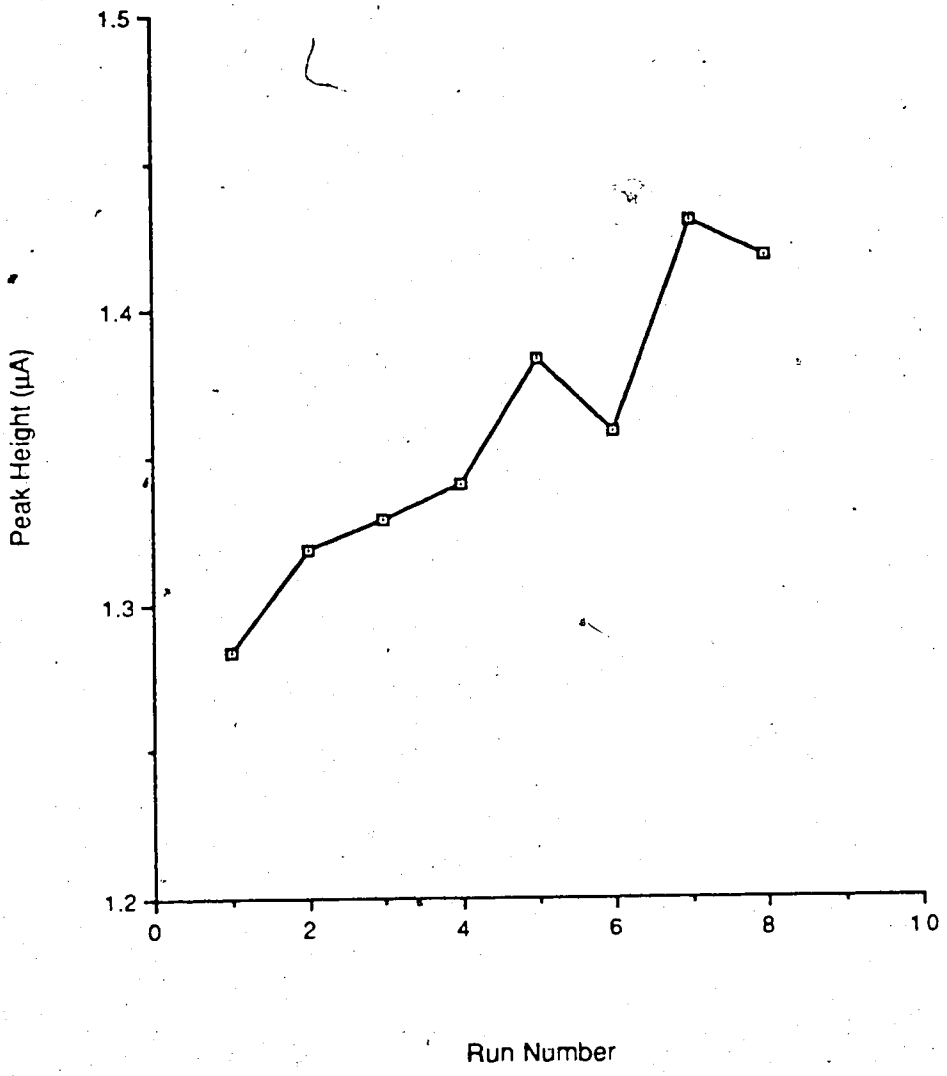


Figure 6.1 Variation of the Lead Signal due to Oxygen Level Changes During Analysis. A 5ml portion of a 50 ppb lead solution (in 0.01M nitric and 0.1M potssium nitrate) was analysed repeatedly after a one minute nitrogen purge. Run number refers to the order of analysis. Observed increase in lead signal strength result from the decrease in the oxygen level in the solution through exchange with blanketing nitrogen.

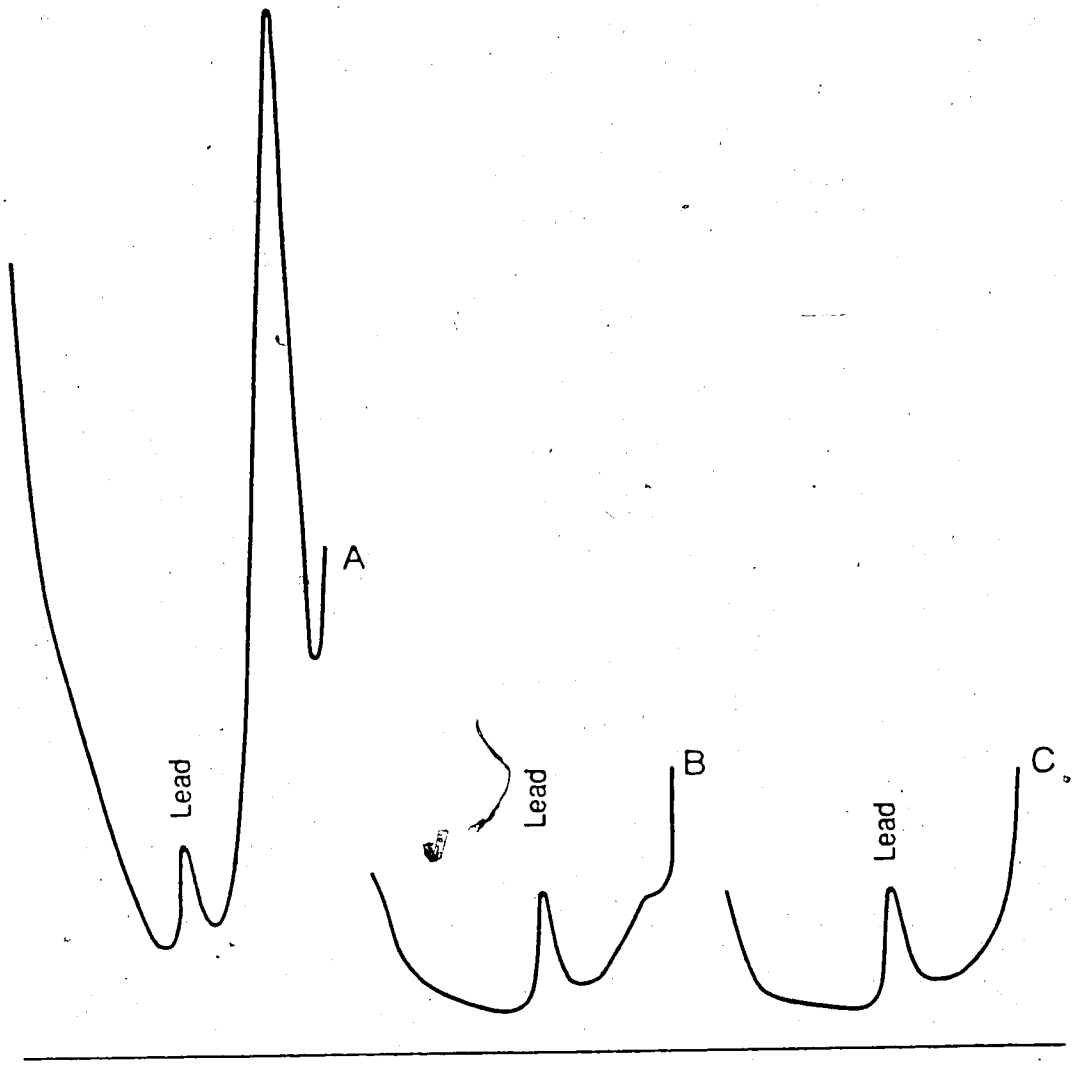


Figure 6.2 Effect of Dissolved Oxygen on the appearence of the Anodic Stripping Curve.

A. No nitrogen purge.

B. Three miunte purge

C. Five minute purge.

A 30 ppb lead solution in 0.01M nitric acid was used with 0.2min deposition in all cases.

height without much interference from the sloping baseline. On the other hand, any changing of oxygen levels has a pronounced effect on the precision of the analysis. In a batch analysis situation where a single sample portion is being analysed several times consecutively this is unavoidable. Longer stripping times encountered in differential pulse stripping procedures allow oxygen level to change rather drastically between deposition stripping cycles.

With a faster nitrogen flow and a smaller diameter purge tube linear variation of the lead stripping peak height begins to level off after about four minutes (Figure 6.3). These conditions were obtained by covering the wide opening (capillary insert hole) on top of the cell holder block of the PAR 303 SMDE with a plastic sheet to maintain a positive nitrogen pressure within the sample cell.

Under these conditions a five minute deaeration time for a 5ml sample, or a 1min/ml deaeration ratio, was selected as the normal operating condition. Although this removes the effect of oxygen, it significantly increases the overall analysis time. This is particularly true with differential pulse stripping, which is slow compared to linear scan stripping. This drawback, and the lack of a satisfactory explanation of the nature of oxygen interference, prompted further investigation of this phenomenon.

6.3 Matrix Exchange System: Details of Construction

A glass cell supplied by the manufacturer as an accessory to the PAR MODEL 303 SMDE (Catalogue no. GO 057)[9] was modified by adding two sidearms, one very close to the bottom of the cell and one near the upper edge of the conical section. To the bottom arm a short length of flexible PVC tubing was attached, which was held in place by a short piece of metal wire bent to form a half loop. The open end of the siphon thus formed was adjusted to rest at level with the upper edge of the conical section of the cell, while the highest point was at a level higher than the upper side arm. This arrangement is shown in Figure 6.4.

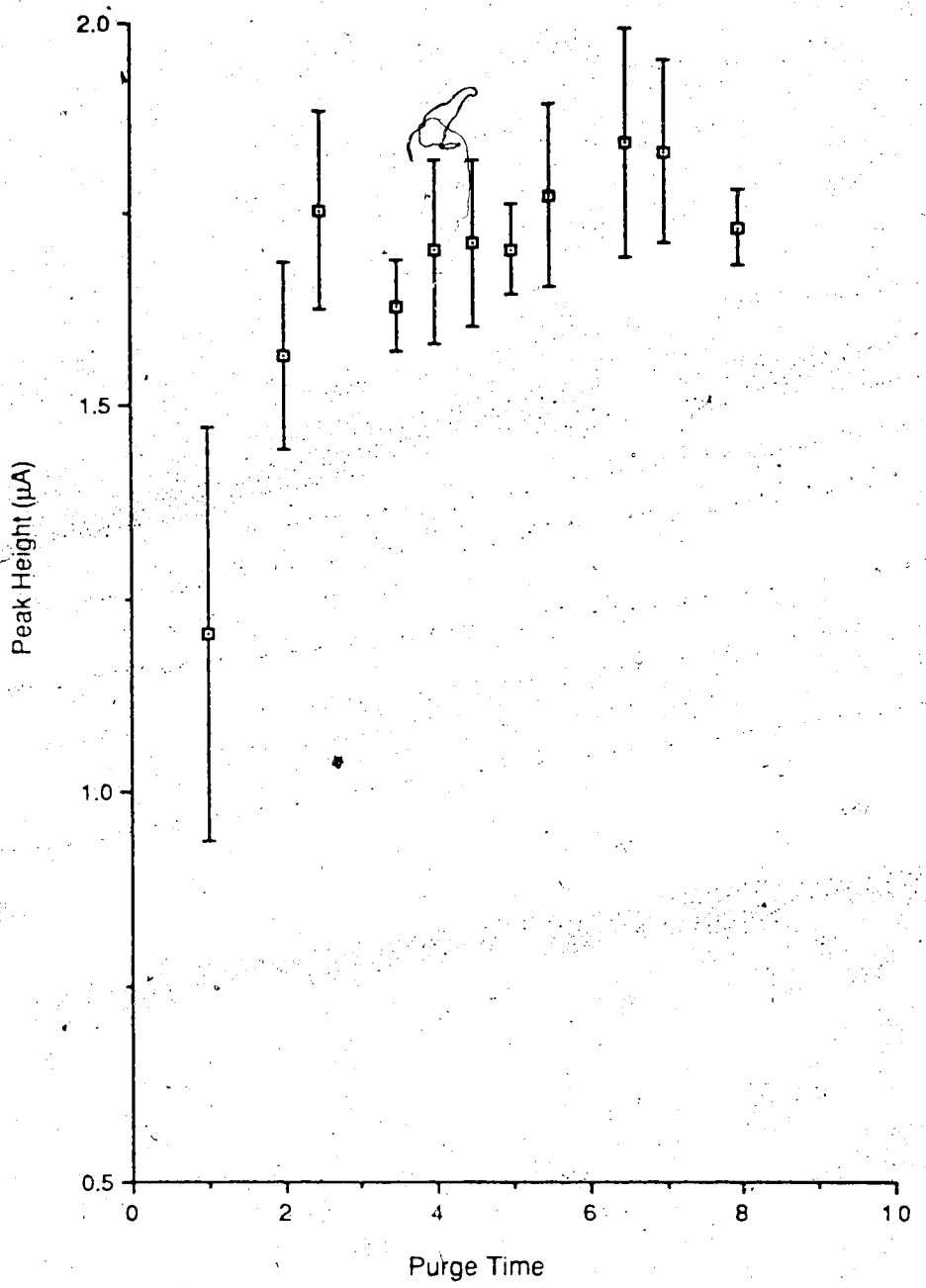


Figure 6.3 Efficiency of Deaeration as Indicated by the Lead Peak Height.

At each purge time at least four measurements were taken. Peak height axis error bars represent ±2 standard deviation points.

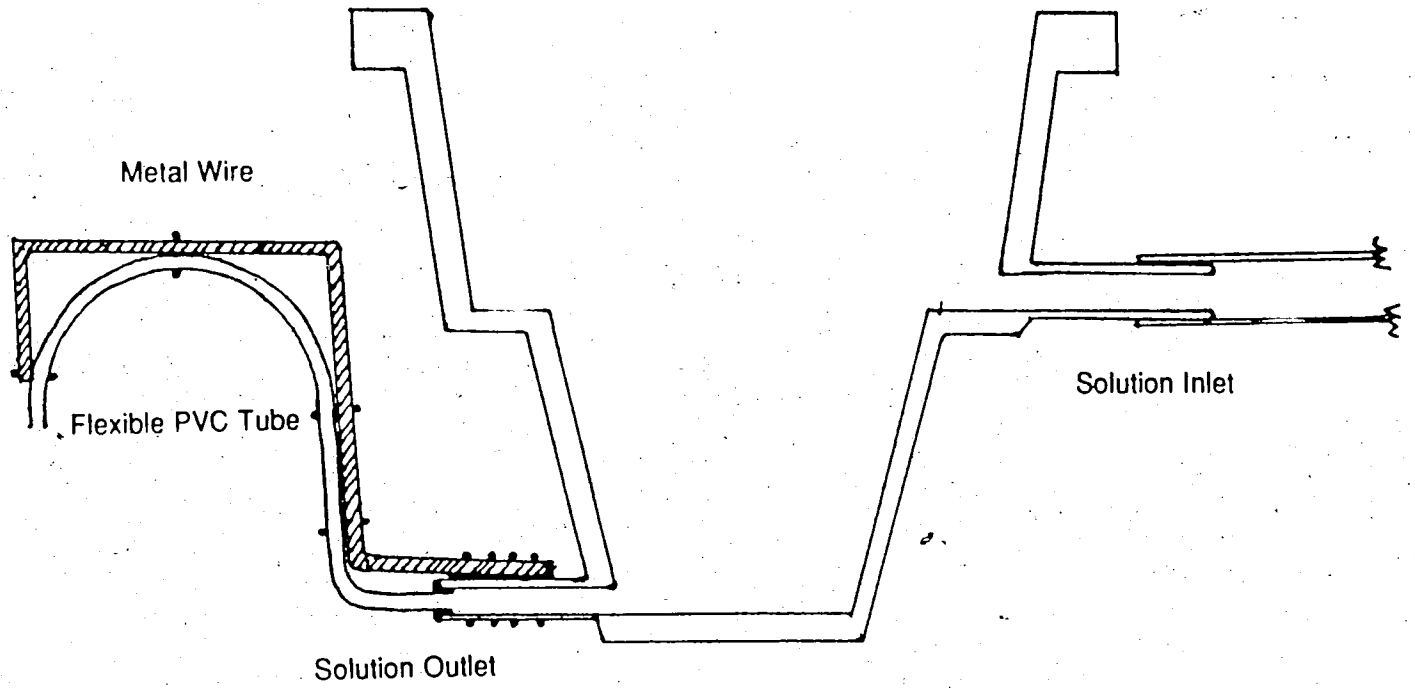


Figure 6.4 Cross Sectional View of the Modified Cell for Matrix Exchange Studies.

A glass cell supplied as an accessory to the PAR Model 303 SMDE was modified as shown.

The upper side arm was connected to a polythene wash bottle (Nalge 500 ml) which served as a solution reservoir. This was placed on a labjack allowing the maintenance of the solution level at a specified level marked on a vertical strip of cardboard attached to the bottom plate of the labjack. A beaker under the open end of the outlet tube acted as a waste reservoir.

During most of the experiments carried out with this setup, analyte solution was pipetted into the empty cell, with the exchange solution flow blocked out by a tube clamp fitted onto the inlet tube. After the deposition step had been carried out to the required extent, flow was started by opening the tube clamp and was stopped on or before initiation of the equilibration step.

Using a $KMnO_4$ solution (5ml) it was found that it is necessary to run at least 20ml of distilled water to remove all the visible color from the cell. Solution flow rate (controlled by the reservoir solution level) and exchange time were selected to satisfy this condition.

Florence and Mann[122] recently reported a similar modification to the PAR 303 SMDE which enables one to perform a matrix exchange procedure. However their cell consists of only a drain arm located at the bottom of the cell, exchange solution being added from a tube inserted through the entry port on the plastic cell holding block. Consequently they had to use 50ml of the exchange solution to remove the analyte completely. A greater chance for solution mixing in their system may be the reason for this high volume. Further, their cell does not ensure a constant presence of a liquid cover in the cell to maintain electrical contact, since accidental opening of the drain can empty the cell completely.

In the cell configuration described above use of a siphon trap at the drain point ensures that this does not occur. Further, the location of the solution inlet at the upper edge of the conical section ensures a smooth flow into the cell with minimum mixing of the exchange and analyte solutions. A design with the lower arm serving as inlet and the upper arm as the outlet was also tried. This led to entrapment of analyte solution just above the

inlet point as revealed by running permanganate solutions. In this situation incoming solution travels over the bottom of the cell, hits the opposite wall, and is directed upwards toward the solution outlet, leading to entrapment of the analyte solution. Use of a magnetic stirrer to break down this flow pattern was also investigated, but it was found to be unsatisfactory because of the large volume of exchange solution required.

6.4 Nature of the Oxygen Interference: Results from Matrix Exchange Studies

The first objective was to determine whether the oxygen interference is limited to the stripping step as suggested by recent reports. There are six possible variations or experiments that can be conducted using a matrix exchange system (Table 6.1). Since it was decided to conduct this investigation using a multivariable variance analysis model with two levels, only deaerated and nondeaerated conditions were considered. Out of the six possible combinations listed in Table 6.1, 1 and 4 do not yield results that are comparable with the results from other situations. This difficulty arises from the continuous matrix exchange procedure, which hinders quantification and reproduction of the deposition interval in a no-exchange situation. As a result of this, the experiment was carried out as a two-level, two-variable situation, allowing comparisons to be carried out with two-factor variance analysis.

The exchange/ background solution was 0.1M KNO_3 acidified with HNO_3 to pH 2, resulting in an HNO_3 concentration of 0.01M. The sample solution contained 50 ppb of Pb^{2+} in addition to KNO_3 and HNO_3. Five analyses were done at each level. The sample solution was deaerated by bubbling N_2 through the solution for 5 minutes after introducing it into the cell. The exchange solution was deaerated in the reservoir (1 min for each ml of the solution).

The results of this experiment are presented as Table 6.2 with the corresponding ANOVA table presented as Table 6.3. These results clearly indicate that deaeration of the sample solution (Factor A) has no significant effect on the outcome. On the other hand

Table 6.1 Possible Combinations of the Conditions that Can be Used to Check the Effect of Oxygen on Stripping Analysis

Experiment	Sample Conditions	Exchange Conditions
1	No Deaeration	No Exchange
2	No Deaeration	Exchange with Nondeaerated Solution
3	No Deaeration	Exchange with Deaerated Solution
4	5 min Deaeration	No Exchange
5	5 min Deaeration	Exchange with Nondeaerated Solution
6	5 min Deaeration	Exchange with Deaerated Solution

Table 6.2 Results from the Two Factor Variance Analysis Experiment

		Sample Solution (factor A)	
		Non Deaerated	Deaerated
Exchange Solution (factor B)	Non Deaerated	0.439	0.737
		0.590	0.635
		0.543	0.738
		0.680	0.689
		0.598	0.684
	Deaerated	0.727	0.721
		0.748	0.693
		0.720	0.779
		0.778	0.725
		0.782	0.758

Table 6.3 Anova Table for the Comparison of the effect of Oxygen on Anodic Stripping Analysis

Sources	Sum of Squares	Degrees of Freedom	Mean of the sum of squares	F
Between Rows (Exchange solution)	0.0602	1	0.0602	20.81
Between Columns (Sample solution)	0.0153	1	0.0153	5.29
Interactions	0.0255	1	0.0255	8.80
Within Cells	0.04628	16	2.892	

$F_{0.01,1,16} = 8.53$ $F_{0.05,1,16} = 4.49$

deaeration of the exchange solution is highly significant. This proves that the dissolved oxygen effect is limited to the stripping step of the overall analysis. It also disproves Vydra, Stulik and Julakova's[2] statement on the negative effect dissolved oxygen has on the efficiency of the deposition step. Even without this evidence it is highly improbable that oxygen would interfere with the reduction of the metal at this stage owing to the working electrode usually being held at a potential well beyond the reduction potential of the metal being analysed. Potentiostatic controlling systems being used for this purpose are capable of supplying currents well beyond the maximum levels required for maintaining the electrochemical reactions that can occur at the electrode surface at these potentials. If H_2O_2 (at the reduction potential of -0.8 V O_2 will not exist but will be converted to H_2O_2) is to reoxidize lead which has been reduced and incorporated into the amalgam, it must accept two electrons per lead atom. The resulting Pb^{2+} ion will move into the diffusion layer but is highly unlikely to move out before it is reduced again. This essentially means that a molecule of peroxide gets reduced at the electrode instead.

Any increase in pH in the vicinity of the electrode as a result of oxygen reduction, which consumes hydrogen ions, can lead to formation of hydroxy complexes and precipitates that can adversely affect the efficiency of the deposition step. However one can expect the stirring process inherent in the deposition step to work against these effects. The increased flux that results from the stirring process should result in solution flow over the electrode surface, changing the environment of the electrode to a dynamic one, as opposed to the relatively stationary conditions that exist in a polarographic experiment.

During the equilibration period, however, if the stirring action is discontinued as it is when an HMDE is used in these studies, it is possible for an increase in pH to occur in the vicinity of the electrode. This will occur only in an unbuffered solution. But even so it is highly unlikely to precipitate the metal being analysed since the effective metal ion concentration is near zero in the vicinity of the electrode and the inward flux now is a mere

trickle maintained by diffusive transport. If the pH of the solution is sufficiently acidic and there are no other elements at higher concentration that can form a precipitate at a higher pH value, one cannot expect complications to arise during the equilibration period either. In solutions of high pH problems can arise but one is always bound to maintain low pH values in trace metal solutions due to solution instability and adsorption losses of metal ions from high pH solutions.

During the stripping stage at the reduction potential of lead, lead in the amalgam is oxidized, giving rise to the desired signal. At the same time, oxygen diffusing to the surface of the electrode is reduced and produces H_2O_2.

Since the potential at the electrode is favourable for the existence of Pb^{2+}, one can expect an interference from this H_2O_2. It is possible that H_2O_2 might react with Pb in the amalgam, though this is highly unlikely given the highly negative $E_{1/2}$ of the H_2O_2 reduction reaction. This possibility was investigated using an exchange solution containing H_2O_2. There was no statistically significant difference at 95% confidence level between the results obtained with solutions containing H_2O_2 and exchange solutions which were H_2O_2 free. On the other hand oxygen getting reduced under the influence of the electrode potential can obtain the necessary electrons from Pb rather than from the electrode; i.e. one might see an addition of these two reactions (an oxidation and a reduction) to give only the net result as the signal.

This argument attempts to explain the nature of oxygen interference, which really manifests itself only during the stripping stage.The oxygen interference results from a chemical reaction which decreases the amount of electroactive substance oxidized during the stripping stage. It does not solely arise as a result of high background current from oxygen reduction.

In polarographic analysis oxygen removal is customary in order to remove the high background signal but this type of an oxidative interference is not usual since most of the reactions that are being used for analysis are reductions.

Wang and Dewald[44] have reported that they were able to overcome the negative contribution from oxygen by subtracting the stripping curve of the background solution from that of the sample using a flow injection analysis system with linear scan stripping. Though this results in a voltammogram with an improved base line, unfortunately they did not compare the performance of their system under deaerated and nondeaerated conditions. However the main problem in this type of a system is the inability to match sample and background oxygen levels. Attempts to duplicate Wang and Dewald's[44] experiment using differential pulse stripping produced inconsistent data because of this problem.

In a differential pulse stripping experiment, however, performing a background subtraction does not remove the negative contribution from the oxygen reduction. This is because of the transformation of any flat portion on a linear scan curve into a zero level signal. A modification at the current sampling stage of the differential pulse operating mode may possibly correct for this, but such a modification would mean a fundamental hardware change in the instrumental system employed for the present study. It might be possible to do such a change relatively easily in a microprocessor based and software controlled instrument.

Chapter 7

Open Beaker Digestions: Anodic Stripping Analysis

7.1 Problems Arising from Background Acidity

In any acid digestion procedure, the final solution obtained is highly acidic as a result of residual acidity from the acids being used for dissolution. Even if one uses a procedure with an evaporation step that removes most of the volatile acids, such as an open beaker digestion procedure, one is forced to employ similar highly acidic conditions in order to dissolve the resulting residue. Attempts to use 0.1M acid in place of the 1M acid the standard procedure calls for consistently failed due to low solubility of the residue in this solution. In order to dissolve the residue in this less acidic solution it was necessary to boil the solution for more than an hour, which made this change unattractive and undesireable.

While a solution with an acid level of 0.5M may not be a problem in atomic spectroscopic techniques[79,86,123], in electroanalytical procedures high acidity can lead to a limitation due to high hydrogen evolution currents at the negative end of the potential range accessible in an aqueous solution. Moreover, in a trace analytical situation where a high sensitivity setting of the instrument is normally used, high hydrogen evolution currents can lead to a significant reduction of the potential window available.

This effect can be seen from the differential pulse polarographic curves shown in Figure 7.1. These data are presented mainly to clarify the situation regarding the definition of the cathodic limiting potentials. With respect to polarographic and other electrochemical methods employing a mercury electrode in an aqueous solution it is usual to define the cathodic limiting potential as the onset of hydrogen evolution. Which is normally given a pH-dependent potential value in the range of 1.2 to 1.5 volts[4,3,5]. But in practice the

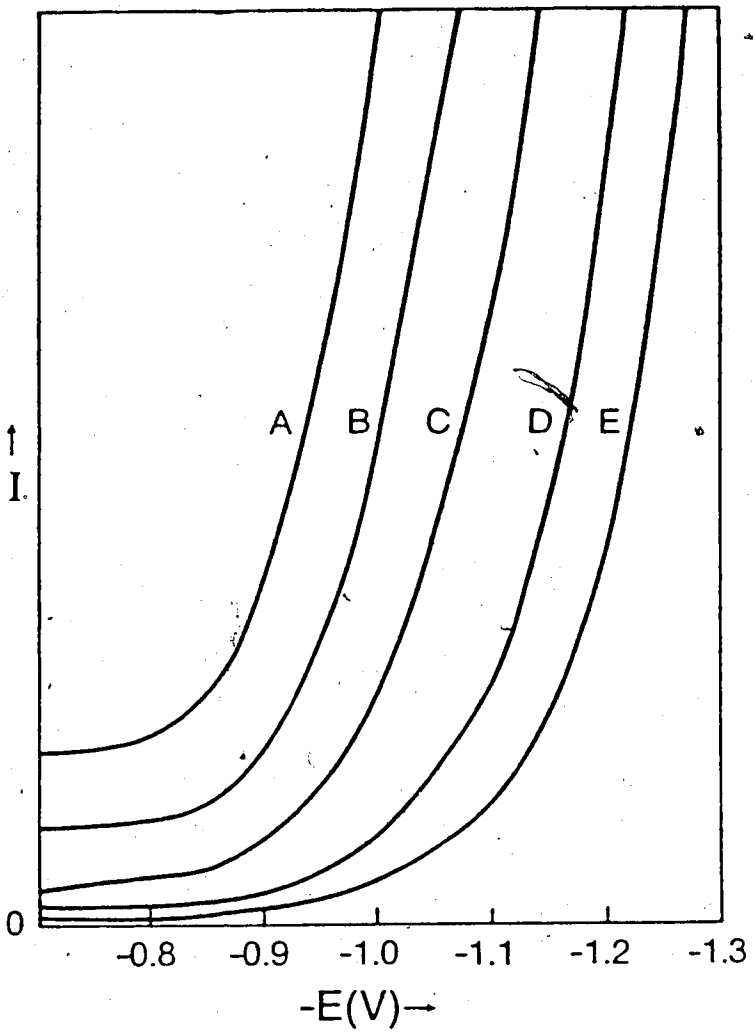


Figure 7.1 Practical Cathodic Limit in Differential Pulse Polarography.

These curves were recorded with a PAR 174A polarographic analyzer coupled to a dropping mercury electrode, with the current range switch set at the following values.

A. 0.5 μA B. 1 μA C. 2 μA D. 5 μA E. 10 μA

Solution used contained 0.1M potassium nitrate and 0.01M nitric acid. At the recorder setting used, current axis scale is (current range)/20 μA per cm. Current zero for all curves is at the indicated point.

sensitivity setting of the potentiostat also affects the limiting point. This is especially true for high sensitivity techniques such as differential pulse techniques.

As illustrated in Figure 7.1, the hydrogen evolution current onset point that limits the accessible potential range moves in a positive direction with increasing sensitivity. With a current range setting of 10μA on the PAR 174A, hydrogen evolution interferes above -1.0 V, while at a 0.5μA setting the region beyond -0.85V is not accessible. This may be more clearly visualized as a signal-noise interaction. At low sensitivity settings or high current ranges (for example, the 10μA range), a comparatively small signal cannot be measured accurately (within the interval -0.85V to -1.0V) because of the low signal to noise ratio that appears to originate from the smaller size of the signal. One cannot improve the situation by moving into a higher sensitivity range (for e.g. 0.5μA range) since this does not change the signal to noise ratio, but amplifies both. The noise in this situation is the hydrogen evolution current. As in the example shown in Figure 7.1 it may increase so rapidly with increasing negative potential that the measurement system reaches saturation even before the potential region of interest is reached.

It is possible to obtain a less acidic solution from an acid digestion process. With small samples, dissolution of the final residue in a small amount of acid and neutralization with a small amount of base can be used. Diluting the final solution after the dissolution of the residue in a relatively concentrated acid solution will also bring down the acid level of the final solution considerably[56,107] but with a corresponding decrease in the analyte concentration. On the other hand it is often desirable to store trace metal solutions as highly acidic solutions rather than use high pH, or large volume dilute solutions, making neutralization or dilution undesirable if one plans to store the solution before analysis.

7.2 Dilution and Neutralization with Sodium Hydroxide

An obvious and straightforward way out of this is to store the resulting digested solution as a highly acidic solution and to dilute a small aliquot of this solution, and

neutralize with a base if necessary, before the analysis. Storing digested solutions becomes necessary in the case of anodic stripping analysis, since digestion of large number of samples or replicates simultaneously ensures equal digestion conditions and a saving of time, while the analysis step is usually long with differential pulse stripping where slow scan rates and standard addition techniques are employed.

After taking this decision the next step was to decide on a dilution ratio and a dilution solution. The problems encountered at this stage and the solutions proposed and tested are discussed in the next several sections of this chapter. These studies were done mainly using solutions obtained by digesting the reference soil sample using the standard open beaker dissolution method.

The first attempts were directed towards diluting 1ml of the digested solution to 5ml and then neutralizing this solution with NaOH to obtain a background with an acidity around pH 2. During the course of these experiments it was discovered that the amount of iron in the sample was significant. Later analyses for iron by atomic absorption placed the iron concentration at 1.25mmol iron/g of soil. The cadmium level of the sample was found to be very low but a reasonably high value was found for lead. As a result it was necessary to change the current sensitivity of the system during the stripping stage if both metals were to be measured. Though this is a simple manipulation in many instances, with the present instrumental setup it called for manual intervention in an otherwise automated analysis. Therefore in subsequent experiments the emphasis was to develop and test procedures for the measurement of lead in the reference soil sample.

The titration curve shown as Figure 7.2 was constructed from the data obtained in a titration of 1ml of a digested solution (diluted to 5ml with water) with 1M NaOH delivered by a micro pipette. The titration curve is marked with a plateau near pH 4. A yellow coloration starts to develop around pH 2.7 to 3 and a cloudiness around pH 6, followed by a yellow/red precipitate of iron hydroxide at higher pH values. These titrations were carried out using a pH meter with glass-SCE electrodes. A continuous stirring action was

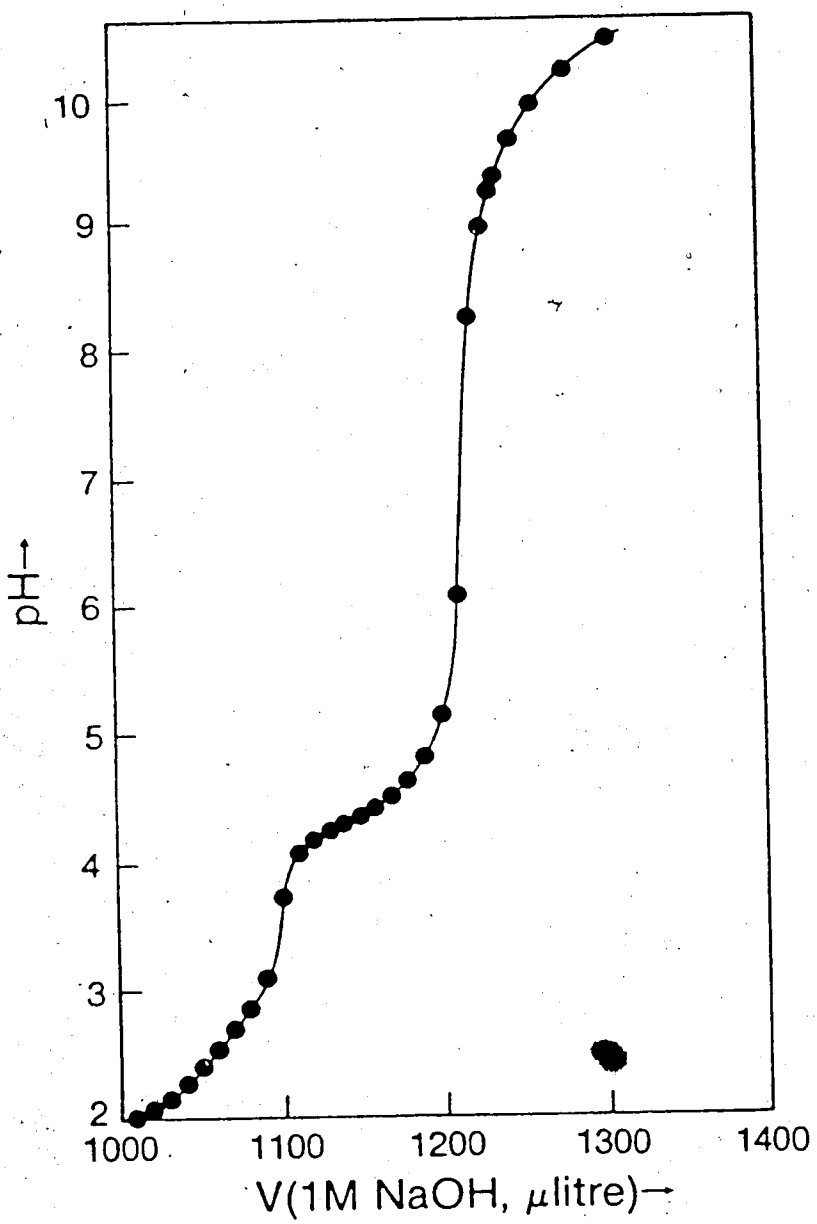


Figure 7.2 Titration of the Digested Sample Solution with 1M NaOH.

1ml of the digested solution diluted to 5ml with water was titrated with 1M NaOH delivered from a micro pipet. pH was measured with a pH meter.

maintained by the use of a magnetic stirrer throughout the titration. Usually a long equilibration time was required between an addition of NaOH and achievemint of a stable pH, especially within the plateau region and while precipitate was forming. The pH and associated colour changes can be attributed entirely to changes induced by iron.

Precipitation and polymerization of iron hydroxides upon neutralization of the solution have significant negative influences upon the analysis of lead due to the adsorption of lead ions into and onto the precipitated or colloidal iron hydroxide. It is necessary to maintain a pH of 2.7 or below in a solution of fivefold diluted sample in order to ensure that no iron colloids exist. Addition of 1M NaOH in the range of 600 -1000µl is required for 1ml of a digested solution to bring the pH of the solution to pH 2 after the fivefold dilution. A single standard volume of NaOH cannot be used due to variations in acidity among digested solutions. These variations may arise from sample weight differences as well as from differences in heating due to nonuniform heat distribution on the hot plates. These factors determine the residual acid content of the residue after the final evaporation step of the open beaker digestion. Since the amount of acid added during the dissolution or take up of the residue is constant for all samples, any variations in the final acid content should originate in the residue after evaporation. In order to find the amount of base required in each case a rapid titration was done for each solution to be analysed. The procedure was similar to the procedure given for the titration of the digested solution described earlier except the titration was terminated upon reaching pH 2. It was necessary to carry out this titration on a separate portion of solution because of impurities introduced by the pH electrode system. Once the amount of base required to bring the pH to 2 had been determined, a fresh portion of solution was diluted, neutralized, and used for the anodic stripping step.

7.3 Effects on Anodic Stripping Analysis:

Figure 7.3 shows the anodic stripping curves obtained for solutions prepared by dilution of 1ml of the digested solution with 4 ml of water and neutralization with 600 to 1000µl of 1M NaOH.

Though the lead peak is clear and well defined it is preceded by a peak near - 0.7 V. This preceding peak shows an abnormal and complicated behaviour. It sometimes appears as a reduction followed by an oxidation, although only an oxidation peak was observed in most of the curves. In some voltammograms only an ill-defined disturbance occurs at this potential region.

This interference is thought to arise from iron, either from a transition involving a hydroxy complex of ferric iron, or through the adsorption of ferric hydroxides onto the mercury surface. But this is hardly likely to occur because of the low pH of the background solution. It could also arise from adsorption of some other species present in the digested solution.

This interference near -0.7 V, though it does not affect the lead peak directly, has a tendency to distort the base line of the voltammogram in an unreproducible manner. This makes it impossible to measure the lead peak height with satisfactory precision,

7.4 Dilution without Neutralization:

The effect or interference at - 0.7V should originate from some phenomena associated with iron since it disappears upon precipitation of ferric iron at a higher pH. But precipitation itself cannot be used as a means of suppressing this effect due to the serious negative effects it has on lead measurement (Figure 7.3). Neither the addition of ascorbic acid nor the addition of hydroxylamine hydrochloride to reduce ferric to ferrous iron gave a satisfactory solution to this problem. Dilution of the solution, however, was effective in removing this effect due to dilution of the matrix components, including iron. Dilution of a 100µl portion of a digested sample to 5ml with water results in a solution with a pH around

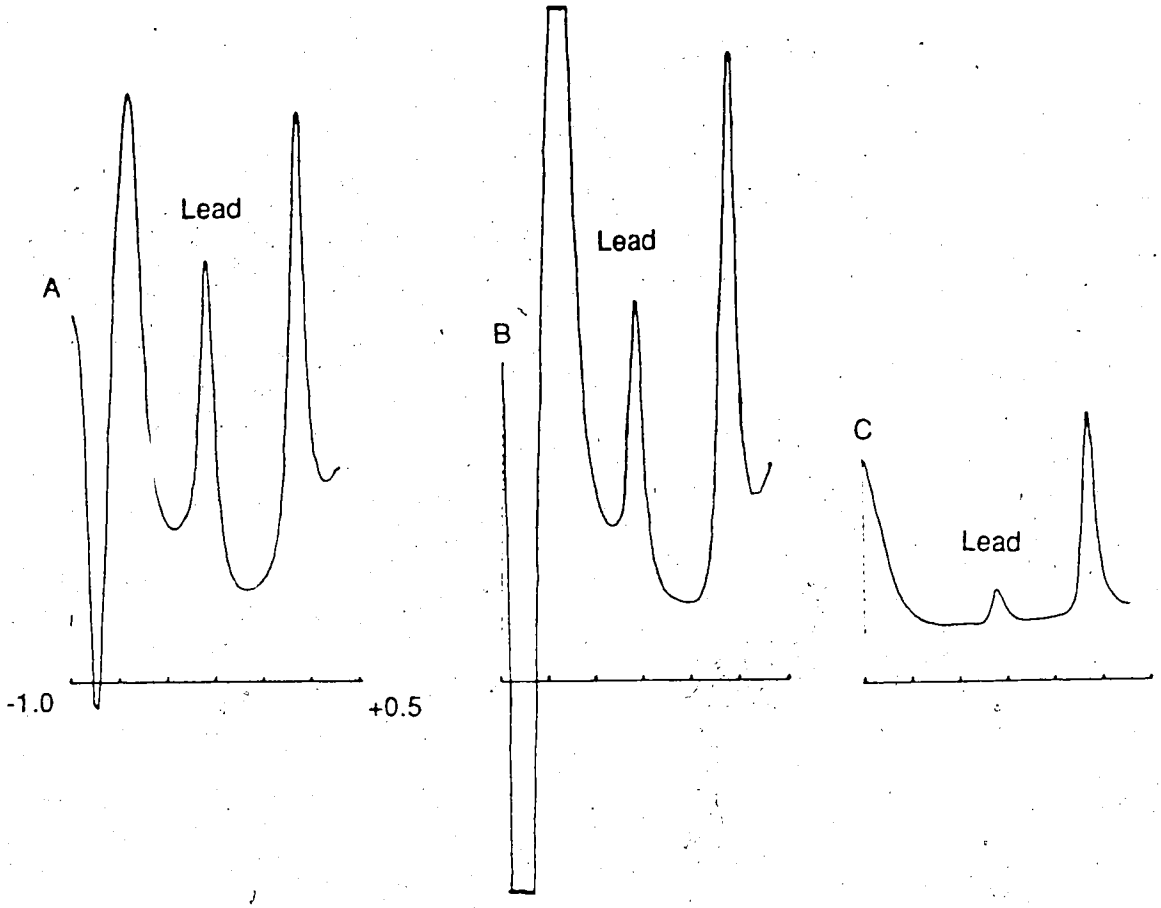


Figure 7.3 Effect of Dilution and Neutralization on Anodic Stripping Analysis.

Stripping curves are shown for the following solutions.

A. 1ml digested solution + 4ml water + 900 µl 1M NaOH. pH = 2.01

B. 1ml digested solution + 4ml water + 900 µl 1M NaOH. pH = 2.18

C. 1ml digested solution + 4ml water + IM NaOH to pH 4.

All curves were recorded at the same sensitivity. Curves A and B show the unpredictable nature of the interference observed near -0.7V. Curve C, recorded at a higher pH shows the effect of iron precipitation on the lead peak. This reduction may be arising from adsorption of lead on to colloidial iron hydroxide precipitate.

2. Under these conditions the corresponding voltammograms show excellent base line stability (Figure 7.4). This dilution drives the solution lead level into the ppb range (usually around 10ppb) however, thus adversely affecting the reproducibility of the total procedure.

7.5 Use of Buffers and Inert Electrolytes:

Though a direct dilution was found to be satisfactory in the terms of anodic stripping voltammograms, it was soon found to be impractical for comparison of results from different digestion systems. Emphasis at this stage was to develop the dilution/analysis procedure to such a level that the main background effects result from the diluent solution rather than from components of the digested solution. This dilution should also act favourably against the effects of any complexing phenomena, since the free metal fraction for a given complex increases with dilution.

Since different digestion procedures use different acid levels and sample weights, acid concentration as well as the analyte concentration varied depending on the procedure being used. This makes it difficult to use the same dilution ratio of 100µl to 5ml for all digestion procedures. It is much more desirable to control the final pH value of the solution by some independent means rather than leaving it dependent on the digested solution composition. Incorporation of a buffer into the background solution or the diluent is the most favourable resolution of this problem because it makes the anodic stripping segment of the analytical procedure independent of the digestion procedures, thereby allowing intercomparison of different digestion systems.

Chloroacetic acid buffers were tried, but were found to have very high background currents beyond -0.8 V. This may be a result of a reduction process associated with this compound or may be due to an impurity. One possibility in overcoming this problem is to use a high current range during the deposition step to avoid saturation of the current measurement circuitry on the potentiostat and to increase the sensitivity during the

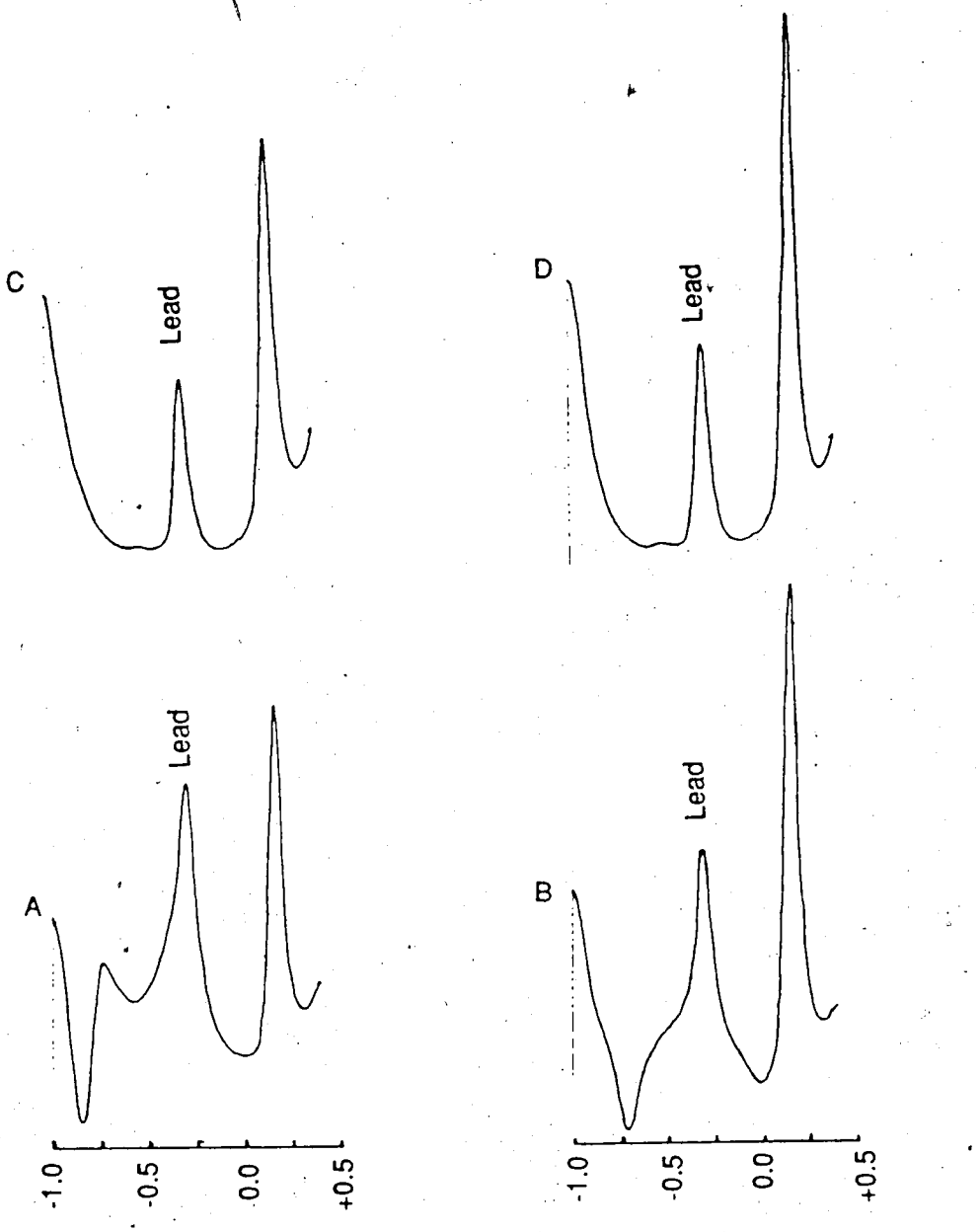


Figure 7.4 Effect of Dilution to ppb Range on Anodic Stripping Results.

Stripping curves are shown for the following solutions.

A. 1ml of sample (a) + 5 ml water adjusted to pH 2 with 1M NaOH.

B. 1ml of sample (b) + 5 ml water adjusted to pH 2 with 1M NaOH.

C. 0.1 ml of sample (a) + 5ml water

D. 0.1 ml of sample (b) + 5ml water.

Deposition time was one minute for A and B and two minutes for C and D.

equilibration step. If some time is allowed for equilibration before the stripping step a satisfactory result can be obtained. This was considered an unnecessary complication and attention was therefore directed to the possibility of using acetate buffers.

Acetate buffers gave good results even when acidified to pH 3. The buffer used was purified via bulk electrolysis at a mercury pool cathode as described in the chapter on reagent purification. One molar buffer solutions obtained by this process were diluted with water. Acidification to pH 3 was done by adding concentrated nitric acid before dilution.

The titration curves such as that shown in Figure 7.5 were used to determine the amount of acid required. As can be seen in this curve the pH 3 point lies at the edge of the acid side of the buffer region. This prompted the use of pure acetic acid instead of acetic acid/acetate mixtures; acetic acid for this purpose was purified using isothermal distillation as discussed in Chapter 4.

7.6 Use of a Predeareated Diluent:

In anodic stripping voltammetry it is customary to carry out the deaeration or purging step in situ, immediately before the deposition step. From the data presented in Chapter 4, it follows that deaeration for the instrumental setup used in these studies should be at least five minutes. Since the developed procedure called for a dilution step before analysis, which can be conveniently carried out in the cell itself, a predeaerated buffer solution was used for this purpose. The result of this was a drastic reduction in the deaeration time, to one minute from the previously required five.

Deaeration of the buffer solution was carried out in a repipette dispenser bottle fitted with a 5ml dispensing syringe. This dispenser was calibrated by weighing the amount of water delivered following pipet and buret calibration procedures[124]. The volume delivered from this dispenser was found to be 4.981±0.006 ml, which translates into a relative standard deviation of 0.1%

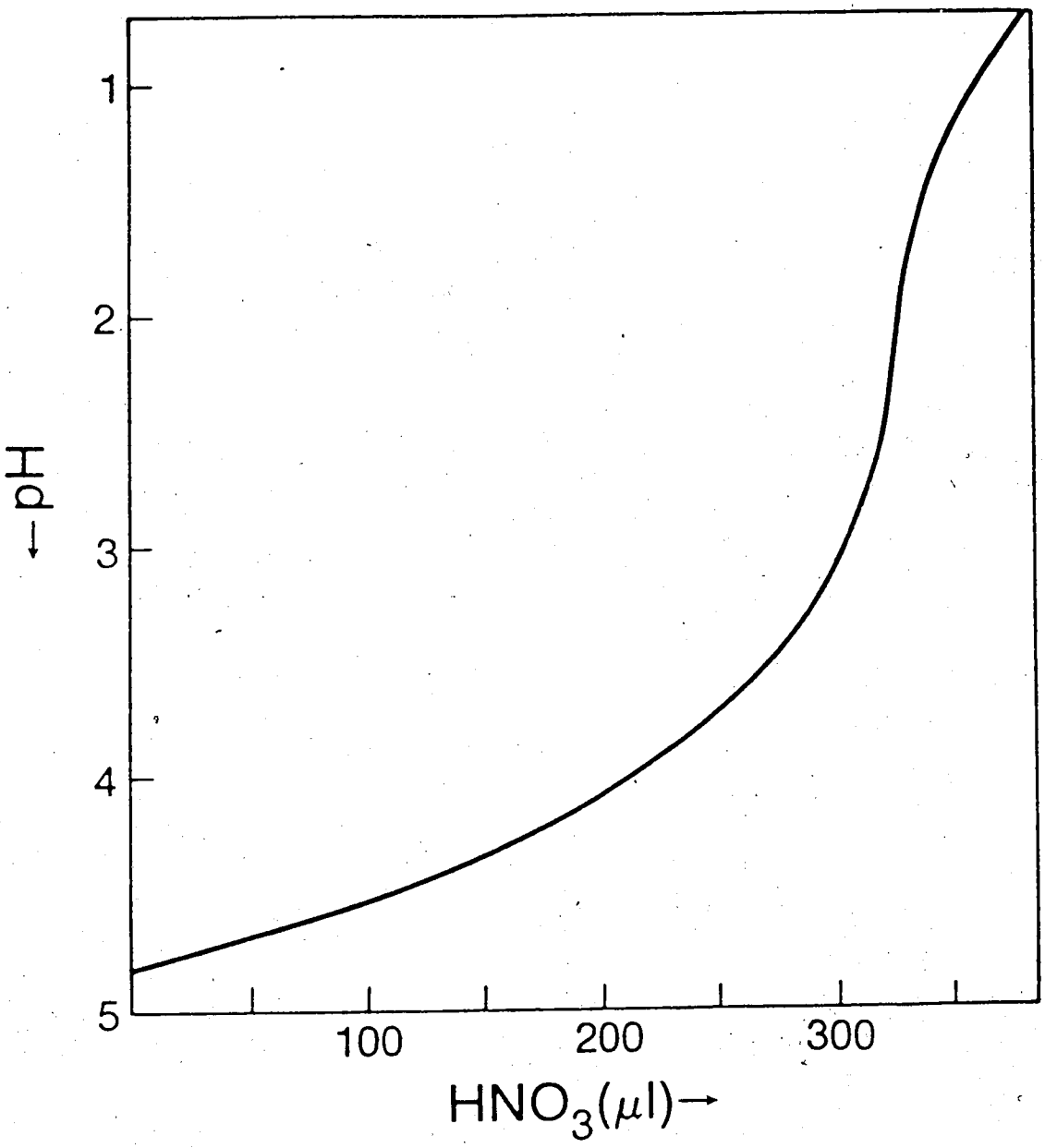


Figure 7.5 Titration Curve for the Titration of Acetate Buffer Solution with Nitric Acid.

5ml of 1M acetate buffer solution was titrated with concentrated nitric acid delivered from a micro pipet. pH was measured with a pH meter.

The storage bottle of the dispenser was filled with the background solution which usually was 0.1M each in acetic acid and potassium nitrate. Deaeration by passing a stream of deoxygenated nitrogen was carried out for a time period that satisfied the purge rate of 1min/ml, i.e. about 8 hours for a 500 ml portion. This operation was conveniently carried out overnight.

Micropipets with pre-calibrated tips were used to dispense sample solutions as well as the standard solutions for the standard addition procedure.

7.7 Method of Quantification; Standard Addition:

The usual method of quantification for voltammetric methods is standard addition, a practice carried over from polarographic measurements. The main reason for standard addition is to compensate for matrix interferences when a large variety of samples are being analysed. Standard addition methods enable one to be more flexible about the sample composition but do not offer any advantage over a calibration curve approach in terms of interfering signals. It will, however, eliminate the effect of adsorbed substances if their interference is physical in nature, that is, if they interfere with the deposition step by increasing or reducing the flux to the electrode or by limiting the available surface area of the electrode. Since it has been demonstrated that organic impurities can act in this fashion in a non-reproducible manner, varying from one sample to another, standard addition techniques were used for quantification in all of the analyses done with digested samples.

The smallest confidence intervals for the standard addition results are obtained when the number of measurements are large and with more measurements at the ends of the concentration range[125]. On the other hand it is advisable to obtain data from at least three concentrations to establish a linear relationship, though it is not necessary to do so if the existence of a linear relationship is certainly known, as it is here. However, at least two additions were done in all analyses to obtain data that would allow more precise understanding of the procedures used.

For open beaker digestions, 100µl to 5ml dilution was found to result in a solution with a lead concentration of about 10ppb. Two 10µl additions of a 5ppm standard solution increased the total lead concentration to about 30 ppb in two 10 ppb steps. At least four voltammograms were recorded at each point giving a total of twelve data points. Standard solutions of 5ppm lead were prepared by diluting a 0.5ml aliquot of a 1000ppm stock standard and 70µl of concentrated nitric acid to 100ml to give an acid level of 0.01 M. The 1000ppm stock standard was prepared according to the procedure described in Chapter 4.

Standard addition procedures suffer from baseline correction errors, so it is essential to correct each data point for baseline values. In a calibration curve procedure a constant baseline value can be tolerated since its final effect will be to shift the calibration curve along the signal strength axis. If the same baseline value is observed for the sample signal, the same value for the sample concentration is obtained. In standard addition methods, this baseline value always translates into a systematic positive error on the final concentration result. For this reason stripping peak heights should be read not from the current zero line, but from the baseline constructed by extrapolating the portions of the curve before and after the peak. The tangential method used to correct for baseline error in the peak read section of the main control program DPASV provides a close approximation for this extrapolation.

7.8 Data Analysis Procedure

The standard addition procedure described above resulted in twelve data points per sample with four points at each concentration. Program DASTA listed in Appendix 1 was used to calculate sample lead values as well as solution lead concentrations and statistical parameters from these data points.

When presented with peak heights with corresponding standard concentrations that are corrected for volumetric calibration errors, DASTA performs a Q test (90% confidence level) at the ends of the signal ranges for each concentration level. Data points that get

through this Q test are used to construct a linear regression line from which the solution lead concentration is calculated. This concentration value and the calculated standard deviation together with the sample weight and the dilution factor (milliliters of analytical solution per sample weight) is used to calculate the lead level of the original sample and its uncertainity.

All the data points, arranged in a descending order within each concentration range, along with the data points rejected on the basis of the Q test, are included in the printout issued at the end of the calculations. The statistical data provided includes both the intercept and the slope of the line together with their respective standard deviations, and the standard deviation and relative standard deviation for both solution concentration and sample lead levels. An example of this output is shown in Figure 7.6.

7.9 Final Analytical Procedure:

The final analytical procedure evolved from preceding studies is written here in a stepwise manner for clarity and simplicity.

1. Deaerate background diluent solution (0.1M acetic acid, 0.1M KNO_3 in water).

2. Pipet required amount of digested solution in to a clean dry Teflon cell containing a magnetic stirbar (100µl for open beaker digestions).

3. Add 5ml of deaerated diluent solution from the dispenser.

4. Insert the cell in SMDE cell holder.

5. Set instrument parameters.

6. Run the analysis (four runs).

7. Add 10µl of 5ppm standard solution.

8. Rerun the analysis (four runs).

9. Repeat steps 7 and 8.

10. Analyse data using DASTA.

STATISTICAL EVALUATION OF STANDARD ADDITION DATA

SAMPLE :CSS M100 13 DATE OF ANAL.:28 DE 87
SPECIES:Pb SAMPLE WT:.99705
DILUTION :2550

DATA	STD.CON	PEAK HT.
1	0	.200909
2	0	.196427
3	0	.193921
4	0	.190226
5	10	.462154
6.	10	.461914
7	10	.460554
8	20	.692715
9	20	.652861
10	20	.612362
11	20	.610237

L.S. LINE Y=a+bX
a=.207052 b=.0223337
s.d.(a)=.0143989 s.d.(b)=.00109559 s.d.(Y)=.030988

SOLUTION CONCENTRATION (ppb)=9.27087
s.d.(ppb)=.788982

SAMPLE CONCENTRATION (ppm)=23.7107
s.d.(ppm)=2.01786
r.s.d.(%)=8.51034

rejected		
1	0	0
2	10	.451513
3	0	0
4	0	0
5	0	0
6	0	0

Figure 7.6 An Example of the Results Output from DASTA.

7.10 Origin of Colour in Open Beaker Digested Samples:

Open beaker digestions carried out using the method described in Chapter 4 sometimes result in yellow-coloured solutions. The crucial point that determines the colour of the digested solution was found to be the final evaporation step. While an evaporation to almost dryness produced a clear solution, stopping the evaporation before this point always led to a yellow solution, the intensity of the yellow colour being inversely proportional to the degree of dryness or the length of the evaporation step.

This observation led to a brief study to determine the origin of this colour. In general, a colourless solution is more desirable; colouration might indicate incomplete digestion. Hsu and Locke[79] present data that leads to the association of colour of the digested solution with incomplete oxidation of organic matter present in the sample. They have observed a decrease in colouration with an increase in the amount of perchloric acid used in a bomb digestion procedure that does not involve any evaporation step.

A prepared reference soil sample which is dark brown grey in colour forms a reddish brown suspension upon heating with concentrated nitric acid in the first step of the open beaker digestion procedure. The next colour change takes place well into the evaporation stage when the solution starts fuming. By this time the initial solution volume of 60 ml has come down to about 20 to 30 ml and the red colour of the solution starts changing to a dark yellow. This solution on evaporation leaves a brown red pasty solid which turns into a light yellow residue if left fuming for some time. This final fuming step tends to yield a colourless solution upon dissolving the residue in 1M nitric acid.

On the other hand, both SO-1 and SO-2 standard soil samples produced a greenish yellow suspension upon heating with nitric acid, which turned into an ash colored one upon the addition of $HClO_4$. All solutions were clear and colorless after the heating step with HF (one hour at 80°C). No solids were present at this stage. All the final solutions obtained from these digestions were colorless.

UV visible spectra of the colored solutions obtained from the digestions of the prepared reference sample (Figure 7.7) show a strong absorption peak around 320nm that tails well into the visible region of the spectrum. These spectra were recorded using a Hewlett Packard Model 8451A diode array spectophotometer. Solutions were read against a 0.5M solution of nitric acid in double distilled water.

Upon dilution, the peak near 300nm seems to move and collapse into the peak near 260nm. This behaviour is not clearly understood. The diluted sample was still yellow and the absorbance value near 400nm was found to be higher for yellow solutions than for colourless solutions (Figure 7.8).

These UV visible spectra show a close resemblance to the UV visible spectra reported in the literature for aqueous solutions of ferric salts[126,127,128,129]. Since these reports do not provide sufficient data for a definite identification, it was decided to record the spectra of ferric ion in 0.5M nitric acid for several common anions. UV visible spectra for the following solutions are shown in Figure 7.9.

a. 1mMol iron (III) sulphate in 0.025 M KCl

b. 1mMol iron (III) sulphate in 0.02 M $K_2C_2O_4$

c. 1mMol iron (III) sulphate in 0.1M EDTA

d. 1mMol iron (III) sulphate in 0.1 M KCl

Iron (III) was added as a sulphate solution, but the addition of an excess of a secondary anion that is capable of forming a complex was assumed to remove any effect from sulphate. All solutions show similar spectra with minor changes in the maximum wavelength of absorption. In general two peaks are observed with peak maxima occurring in the 260 and 320 nm regions.

From these data it was concluded that the yellow colour is due to ferric ions complexed with a complex forming anion (ligand). Colourless digested solutions turned yellow upon addition of KCl, $K_2C_2O_4$ or EDTA, which confirmed the above conclusion. It was also observed that the yellow colour of the digested solutions is extracted into methyl

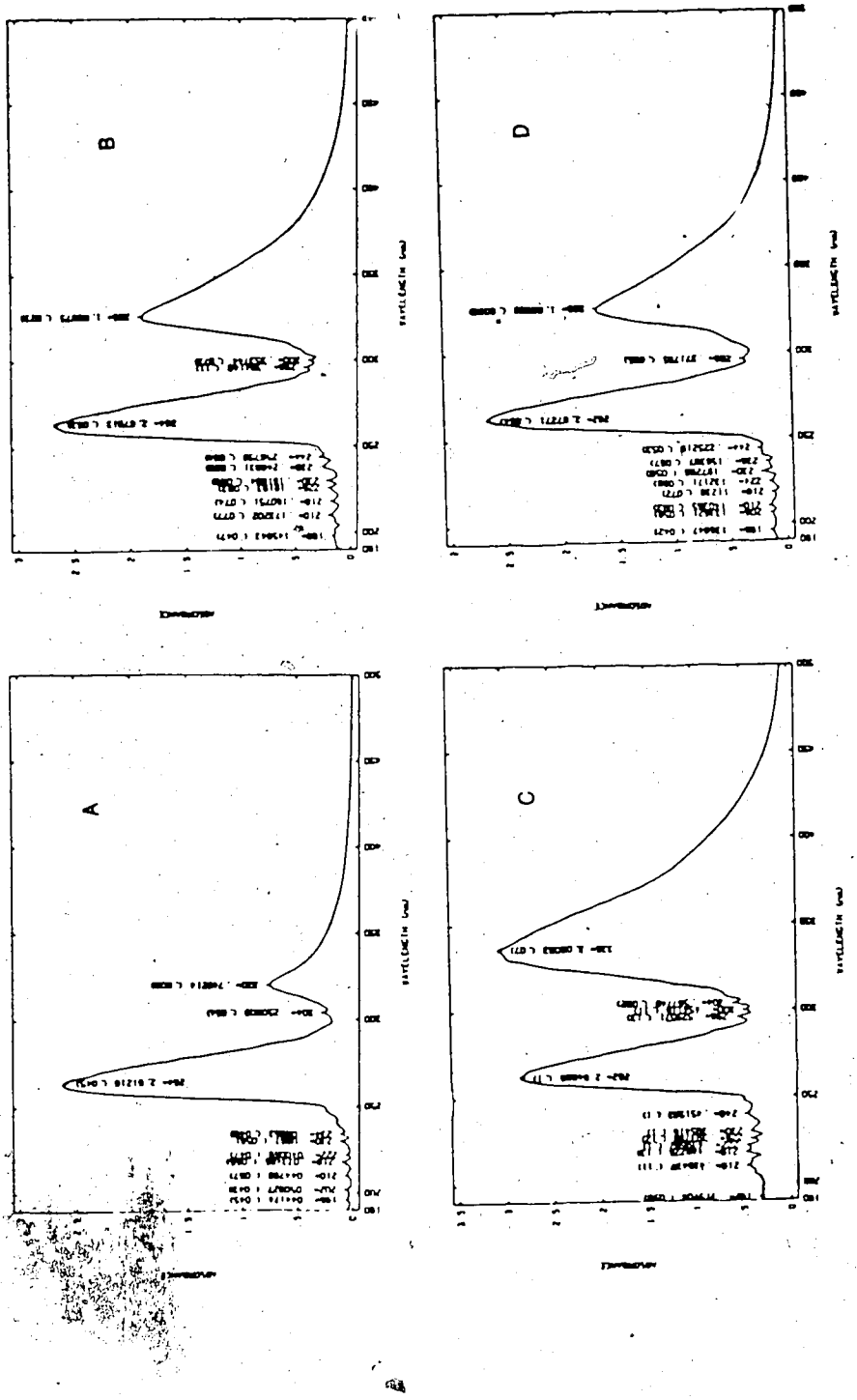


Figure 7.7 UV - Visible Spectra of the Digested Solutions.

Four spectra shown were produced by four different digested solutions. Solutions used for B and C were visibly yellow. D had a slight yellow tint and A was almost colourless.

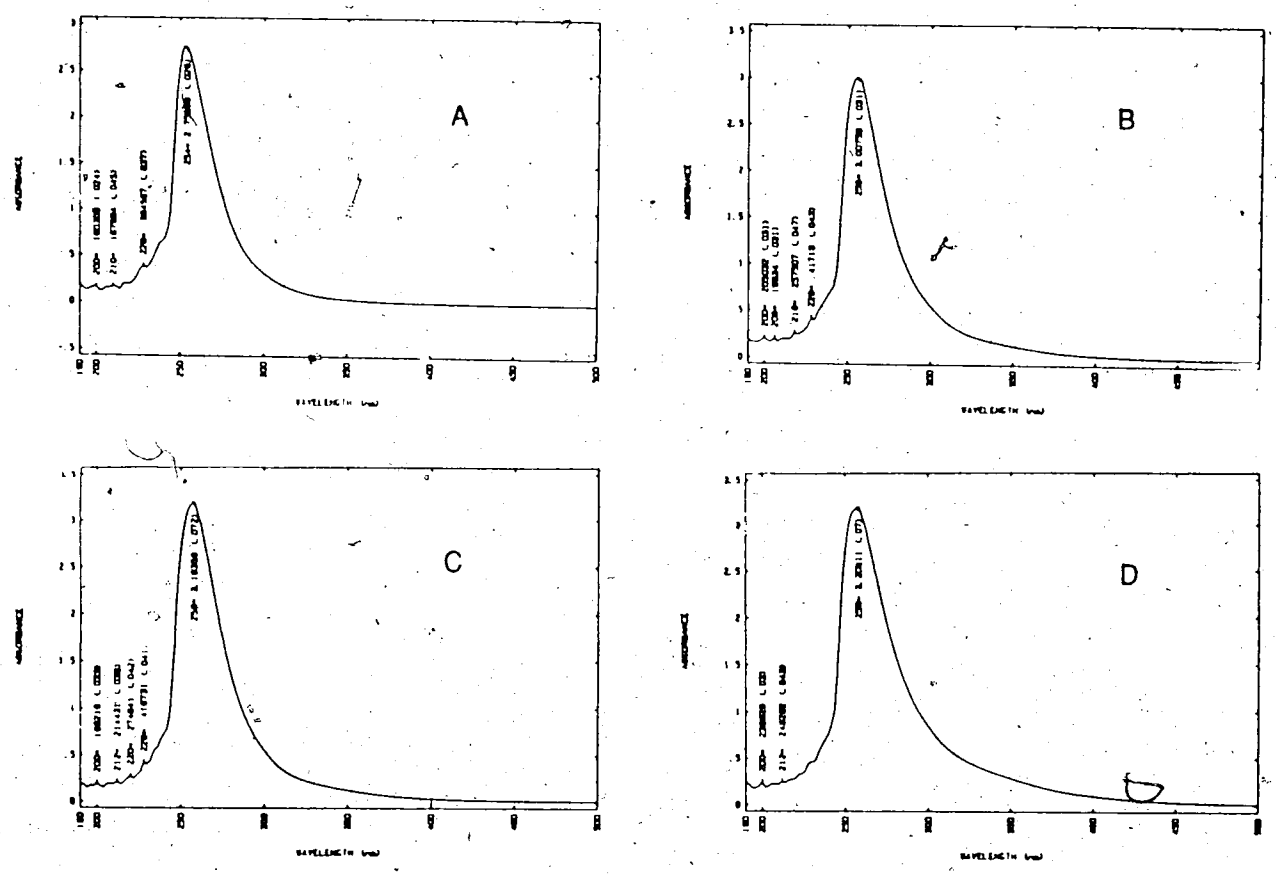


Figure 7.8 UV - Visible Spectra of the Digested Solutions After a Ten Fold Dilution.

Same solutions used to obtain spectra shown as Figure 7.7 were re analysed after a ten fold dilution with water.

Spectra lables correspond to lables in Figure 7.7.

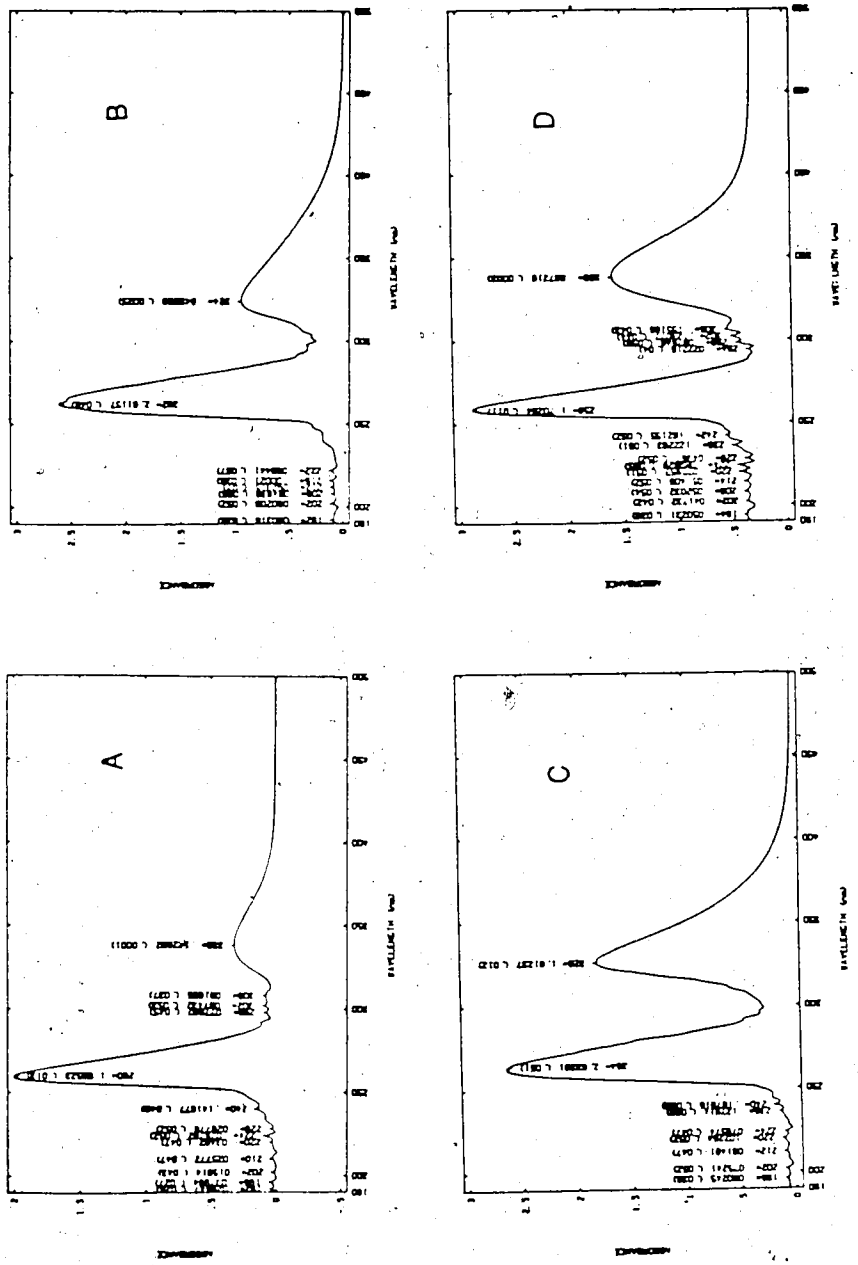


Figure 7.9 UV - Visible Spectra for Ferric Iron in the Presence of Different Complexing Anions.

A. 1ml Iron (III) Sulphate in 0.025 M Potassium Chloride.

B. 1ml Iron (III) Sulphte in 0.02 M Potssium Oxalate.

C. 1ml Iron (III) Sulphate in 0.1M EDTA.

D. 1ml Iron (III) Sulphate in 0.1M Potassium Chloride.

isobutyl ketone, which is a characteristic of chloro complexes of ferric iron. Ferric oxalate solutions prepared failed to show such behaviour. This result indicates a high probability of the existence of one or more yellow ferric chloro complexes in the digested solution. Residual chloride in the final digested solution may either originate in the original soil sample itself or may result from the reduction of perchloric acid. The possibility of formation of oxalic acid upon oxidation of organic matter with perchloric acid has been hinted by Smith[130]. Formation of oxalates upon peroxide oxidation of soil is a known phenomenon[131,132].

An attempt was also made to extract any residual organic compounds into chloroform, but an infrared spectroscopic analysis of the chloroform layer failed to reveal the presence of any such impurities. This may be due to either their nonextractability into chloroform or to their very low concentrations.

7.11 Results of the Anodic Stripping Analysis

Tables 7.1, 7.2 and 7.3 list data for the analysis of samples digested using the open beaker procedure. Data for the certified reference materials SO-1 and SO-2 show good agreement with certified values, indicating that the analysis can be considered accurate. Use of the standard addition technique complicates calculation of the precision of the analysis. When several portions of the same sample has been analysed, the result for each analysis has an associated precision. This value results from the linear regression calculation process (using DASTA). When the data for the whole set of analyses are being considered a mean value for the lead level can be calculated readily from the set of reported concentrations. As a measure of precision one can either use the standard deviation of this set or one can calculate the mean value of the set of standard deviations reported for individual analyses. Figure 7.10 illustrates the origins and the relationships between these values and the analytical scheme. The variance that results from the standard addition calculation is simply a measure of the variability associated with the standard addition

Table 7.1 Anodic Stripping Data for the 100 Mesh Open Beaker Digested Samples

Sample No.	Lead Found (ppm)	Standard Deviation (ppm)	RSD %
01	29.7	1.8	6
02	28	1.1	4
04	38	3.3	9
05	33.5	2.6	8
06	38	4.4	11
07	29.8	0.5	2
09	35.5	3.3	9
10	37.8	3.2	8
11	32.9	3.2	10
13	23.7	2.	8
14	23.1	1.5	7
15	28.7	1.9	7
17	30	0.92	3
19	30.1	0.96	3

Table 7.2 Anodic Stripping Data for the 200 Mesh Open Beaker Digested Samples

Sample No.	Lead Found (ppm)	Standard Deviation (ppm)	RSD %
01	31.5	1.7	5
02	27.3	0.67	2
04	25.3	0.61	2
05	28.0	2.5	9
06	27.0	2.3	9

Table 7.3 Anodic Stripping Data for SO -1 and SO-2 Certified Standard Reference Soils - Open Beaker Digested Samples

	Sample No.	Lead Found (ppm)	Standard Deviation (ppm)	RSD %
SO - 1	01	19.7	0.73	4
	02	18.9	0.91	5
	03	22.9	2.06	9
SO - 2	01	23.1	1.6	7
	02	24.1	1.6	7
	03	21.0	0.65	3

Certified Lead Content for SO-1 and SO-2 is 21±4 ppm.

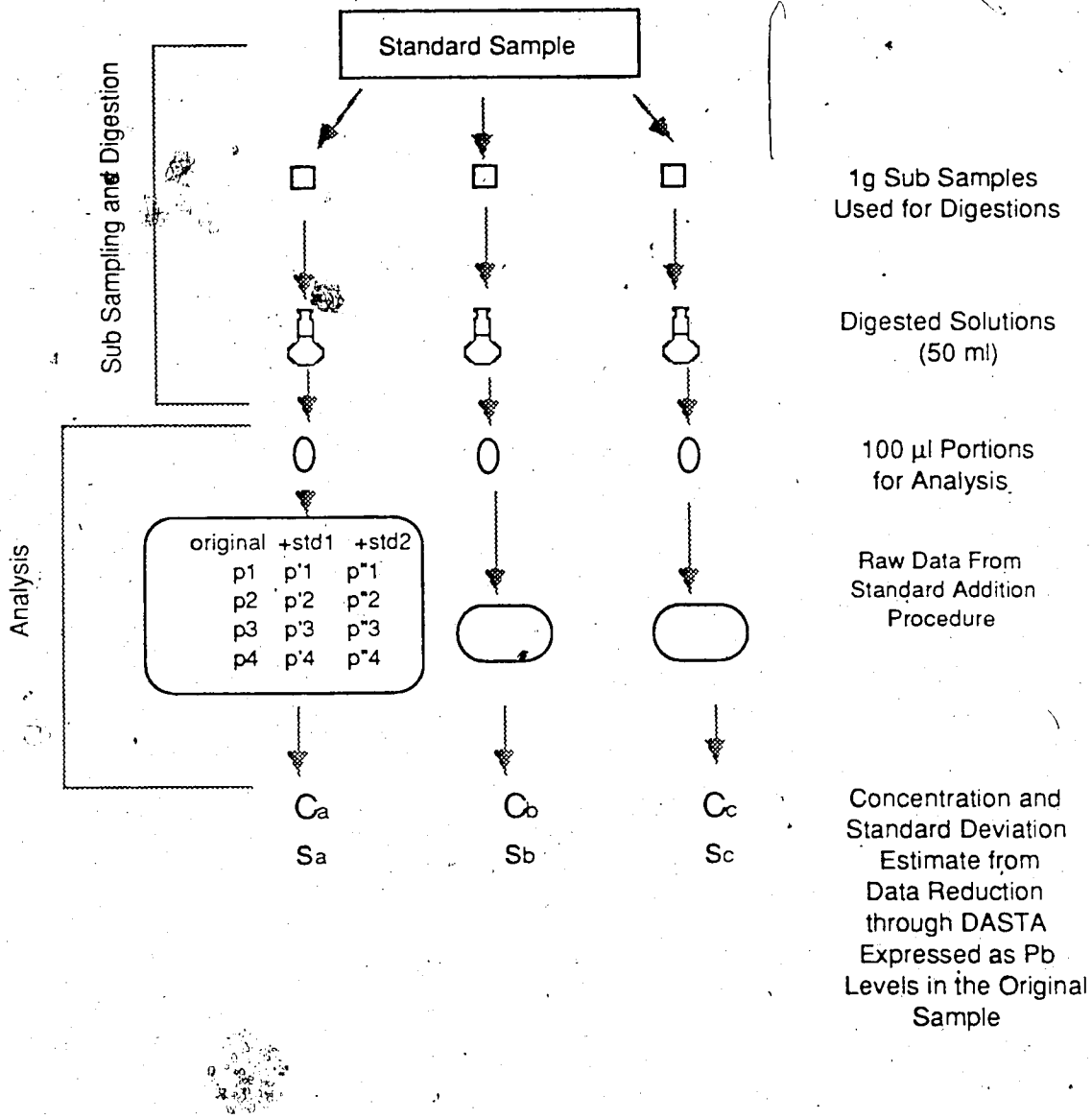


Figure 7.10 Sampling and Data Analysis Procedure and the Relationship Between Statistical Parameters.

Data points p1 to p4 are generated by analysing the diluted 100µl portion four times. Standard solution is added to the cell at this point. Next four runs give data points p'1 to p'4. Third set of data points p"1 to p"4 corresponds to four runs performed after another standard addition.

procedure and the anodic stripping measurement process. If we define the part of the procedure that starts with the introduction of the sample into the anodic stripping system as the analysis step, this value can be considered as a measure of variability associated with the analysis step. A better estimate can be obtained by taking the mean of several individual estimates. It is important to realize that this averaging step is being performed in order to obtain an estimate of the variance associated with the standard addition measurement step. It does not result in an estimate of the variance associated with the mean lead level calculted by averaging the individual lead levels. This estimate can be found by combining the individual variance values following the rules for such a calculation. If X_1.....X_n are independent random variables and if $U=\Sigma a_i X_i$ then $V(U)=\Sigma a_i^2 V(X_i)$[125]. Even an estimate of variability of the mean lead level calculated using this relationship does not reflect the variability associated with the subsampling and digestion operations. An independent estimate of the variance of the individual lead level data set can be considered more satisfactory for this estimation. Table 7.4 summarizes these arguments. Table 7.5 lists the values of these parameters for the samples analysed.

Lead levels found for SO-1 and SO-2 certified reference materials lie within certification limits. This confirms the applicability and accuracy of the analytical procedure developed. From the point of view of precision the results obtained for these certified materials can be considered to be comparable or better than the precision reported for the certification process.

Estimates of the variability of the analytical step (V'_a) show some dependency on the sample type, presumbly arising from the strong matrix dependency of the technique. However, the relative standard deviation values, which are a more comparable measure of the variability, do not show much variation.

The variance estimate for the subsampling and digestion step is abnormally high for the 100 mesh sample which can be considered as an indication of the poor homogeneity characteristics of this coarse sample. From these results the lead level in the prepared

Table 7.4 Definitions of Precision Estimates

Data From Standard Addition Procedure	Over All Values	For the Analytical Step	For the Sampling and Digestion Steps
C_i	$\overline{C} = {}^{1}/_{n}\,\Sigma C_i$		
σ_i^2	$V_{\overline{C}} = {}^{1}/_{n^2}\,\Sigma s_i^2$	$V_a = {}^{1}/_{n}\,\Sigma\, s_i^2$	$V_{s,d} = \Sigma \dfrac{(C_i - \overline{C})^2}{n - 1}$

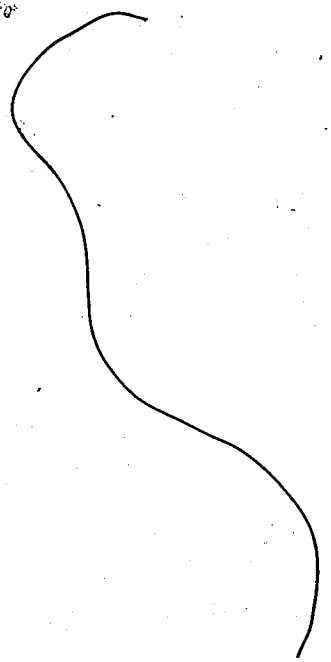
Table 7.5 Values of the Statistical Parameters Defined in Table 7.4

Sample	n	$\overline{C}$ ppm	$V_{\overline{C}}$ ppm	V_a ppm	$V_{s,d}$ ppm
100 mesh	14	31.4	0.4	6.0	24
200 mesh	5	27.8	0.6	3.0	5.2
SO-1	3	20.5	0.6	1.9	4.4
SO-2	3	22.7	0.6	1.9	2.6

Relative Standard Deviation Values for the Standard Deviation Estimates Given Above.

Sample	$V_{\overline{C}}$ %	V_a %	$V_{s,d}$ %
100 mesh	2	8	15
200 mesh	3	6	8
SO-1	4	7	10
SO-2	3	6	7

sample can be stated to be 31± 5 ppm for the 100 mesh sample and 28± 2 ppm for the separated 200 mesh fraction of the soil. These values are based on the variance of the sampling digestion step, the step which shows the highest variability.



Chapter 8

High Pressure Bomb Digestions: Conventional and Microwave

8.1 High Pressure Bomb Digestions: Introduction

One of the disadvantages of open beaker digestions is their length. The open-beaker digestion step alone will usually take at least six hours to be completed with the evaporation steps (especially the final evaporation to dryness) being the most time-consuming steps. However one cannot leave out these evaporation steps since the higher temperatures and concentrated conditions are necessary to achieve total dissolution of the sample. This is particularly true in perchloric acid digestions, since the oxidative properties of perchloric acid are temperature and concentration dependent[130]. On the other hand the differential pulse anodic stripping procedure is also a time intensive process. With a one minute purge, two minute deposition, half a minute equilibration and a potential scan rate of 5mV per second (from -0.9V to 0.0V) a single run takes close to seven minutes. Under these conditions to quantify one solution with two standard additions and four runs at each level, which amounts to four data points at each level, takes about one and a half hours. This is excluding time for calculations and other operations such as system startup and solution preparation.

For these reasons it was felt that any improvements in digestion procedures regarding the length of the digestion were both useful and desireable. As pointed out in Chapter 2, one way to cut down the digestion time is to employ high pressure digestion techniques. This allows one to perform a digestion under more drastic conditions without using lengthy evaporation steps. In this regard the use of a steel jacketed Teflon bomb (which can be termed a conventional bomb) was investigated. Another object of this exercise was to investigate the applicability of a pure nitric acid digestion reported by

Reddy et. al.[56] for the prepared reference sample. Experimental details of the procedure used are listed in Chapter 4.

A second set of digestions was carried out using microwave heating, as an extension of the observations made in conventional bomb digestion experiments. The microwave procedure was thought to be a more attractive technique because of the very short digestion times required. Anodic stripping analyses of the digested solutions were carried out according to the procedure described in Chapter 7 (section 7.9). The following sections of this chapter discuss the observations and results from these experiments.

8.2 Teflon Lined Steel Bomb Digestions

Digestion of the standard sample using nitric acid in a Teflon lined steel bomb failed to dissolve the sample completely. Only four digestions were carried out in this manner. Two were done with 100 mesh samples and the other two with the 200 mesh fraction. In both cases, a residue remained. Since a low sample weight was used in these digestions as indicated in Chapter 4, a corresponding increase was made in the solution aliquot taken for the anodic stripping analysis.

The residue which remained after digestion was red in color, while the solution produced was light yellow, suggesting that most of the iron containing fraction remained undissolved, or perhaps the iron was converted into an oxide that is resistant to the attack of nitric acid under the conditions used. These solutions were filtered through pre-weighed sintered glass filters to separate the undissolved fraction. The undissolved fraction collected was reweighed after drying at 105°C overnight in a glass drying oven. The residue when dried was light brown. Residue weight and analytical data for the 200 mesh samples are presented in Table 8.1. Only about 30% of the sample was dissolved. However the amount of lead found is 28.19 ppm. This value agrees well with the amount of lead found in the open beaker digested samples (27.81 ppm). One explanation might be the complete

Table 8.1 Dissolution Data for Nitric Acid Digestions in Teflon Lined Steel Bombs

Sample	Sample Weight (g)	Residue Weight (g)	% Dissolved	Lead Found (ppm)	Standard Deviation
M200-01	0.3041	0.2109	30.7	27.5	2.3
M200-02	0.3448	0.2429	29.6	28.9	2.9
	Average Values		30.1	28.19	

dissolution of the lead-bearing minerals. A reprecipitation of some compounds after a complete dissolution that removed lead into solution is als. bility.

An improvement in the amount dissolved was sought by adding HF to the digestion mixture. This resulted in complete dissolution of the sample, producing a solution that is more yellow than that produced by nitric acid alone. In this case removal of excess HF is necessary before analysis, because of the adverse effects it can exert on the proper functioning of the hanging mercury drop electrode and the toxicity of HF. Even though the glass etching effect of HF on the glass capillary may be negligible, even at a low concentration the presence of HF can lead to a rapid deteroriation of the tetramethyl silane layer applied to the tip of the glass capillary. This siliconized layer is necessary to increase the hydrophobic characteristics of the capillary. Deterioration of the hydrophobic properties leads to solution creeping into the capillary bore, ultimately resulting in capillary failure. The capillary used in the Model 303 SMDE is especially vulnerable to this problem because of its large bore size. Even washing the capillary tip with concentrated nitric acid, a usual cleaning procedure with polarographic capillaries and manual hanging mercury drop assemblies, was found to affect the capillary lifetime adversely.

Removal of HF can be done either by evaporating the solution to dryness or by using a complexing agent to bind fluoride. With an electrochemical procedure which tends to differentiate and to be seriously affected by complexation of the analyte, an evaporation step is more desireable. The only complication introduced by evaporation is the time it takes to evaporate the solution. In order to minimize loses that can occur via solution splashing and possible volatility of lead salts at higher temperatures, evaporation has to be conducted at the minimum temperature possible, leading to longer evaporation times. For open-beaker digestions using perchloric acid this final evaporation step was conducted at a temperature close to 200°C, and usually took four to five hours. Since the bomb digestion itself takes close to two hours on the average, an evaporation step followed by a redissolution step will bring the length of the digestion operation very close to that of an open beaker

digestion. For this reason a boric acid complexation method was tried with these samples. This procedure, which was described in Chapter 4, gave satisfactory results in a preliminary analysis. A proper experiment with enough data to enable a statistical comparison was not carried out to check the validity of this observation, mainly because of the limited number of bombs that were available and for the reasons given below.

Bomb digestions using Teflon lined steel bombs were abandoned at this stage since it was felt that microwave digestions using Teflon bombs were more attractive and more appropriate. Among the practical problems that were encountered during the digestions using Teflon lined steel bombs, the solution transfer problems should be particularly mentioned. The Teflon liners used in these bombs have a tapered upper edge which makes it difficult to pour out the solution after the digestion operation. One remedy might be to use a Teflon rod to facilitate smooth solution transfer, but since there is no spout (as on a beaker) to hold the rod in place this is not an easy operation. In some instances the Teflon liner was found to become deformed slightly after a digestion which made it difficult to remove the liner from the jacket. In this case cooling the bomb in ice was found to be effective.

8.3 Bomb Digstions Using Microwave Heating

Microwave digestions carried out as described in Chapter 4 produced solutions that are comparable to solutions obtained by conventional bomb digestion procedures. A total of sixteen digestions were done using this procedure. This digestion with a mixture of nitric and hydrofluoric acid was capable of dissolving 98.5% of the sample. Residue after separation as described in the last section appeared black and remained black even after drying at 100 ^{o}C overnight. This is remarkable when compared with the digestion times that were required for open beaker digestions and conventional bomb digestions.

However the blank lead value for this digestion was found to be fairly high. A blank containing no lead produced a signal corresponding to 3.51 ppb of lead in the

analytical solution which was presented to the anodic stripping system. This blank value may result from the reagent grade boric acid that was used for the complexation step. Consequently a blank value subtraction was introduced before calculating the sample concentration from the anodic stripping data.

The lead content found in this manner was significantly lower than that found from the open beaker digestions or with pure nitric acid digestions in conventional Teflon lined steel bombs (Table 8.2). Since the fraction dissolved was found to be high enough for the dissolution to be considered complete this difference in the amount of lead found possibly originate from the presence of some lead in a nonelectroactive form. This can occur via complexation with a sample component. Formation of a lead fluoborate complex is a possibility. On the other hand an adsorption of lead on the undissolved residue as well as nondissolution of a significant lead bearing mineral fraction are also possible.

Microwave-digested samples were found to react with mercury even after dilution with the acetic acid solution which was used as the b ckground electrolyte. This action results from the oxidation of mercury by ferric iron present in the digested samples. This was observed with open beaker digested samples when used without dilution, but disappeared upon dilution. The presence of fluoride ions in the microwave digested samples may be accelerating this reaction. Formation of a mercurous halide film on the mercury drop cannot be ruled out but this should not interfere with the analysis since the potential of the electrode was maintained at a cathodic value throughout the whole analytical procedure. One annoying result from this behaviour is occasional plugging of the capillary. This usually occurred when a sample solution was left in the cell for a time after the analysis. Though extrusion of several mercury drops restored the capillary function, prolonged exposure of the capillary to solution in an open circuit situation may lead to disastrous results. As pointed out in Chapter 3, capillary mulfunction was a major problem with the Model 303 SMDE.

Table 8.2 Anodic Stripping Data for the 200 Mesh Microwave Digested Samples

Sample No.	Lead Found (ppm)	Standard Deviation (ppm)	RSD %
01	22.2	2.1	10
02	20.7	1.0	5
03	22.0	1.1	5
04	18.2	1.4	8
05	20.1	0.9	4
06	15.8	1.8	11
07	23.3	1.9	8
09	19.5	1.0	5
10	14.6	1.3	9
11	20.3	1.8	9
12	18.6	1.5	10
13	15.4	1.0	6
14	15.1	0.5	4
15	14.9	4.9	33
16	18.5	1.4	7

Reduced Data

$\bar{C}$ (ppm)	V_a	σ_a	$V_{\bar{C}}$	$\sigma_{\bar{C}}$	$V_{s,d}$	$\sigma_{s,d}$
18.6	3.5	1.9	0.23	0.48	8.3	2.9

When considered collectively, microwave digestions cannot be considered successful in this analysis. However since pure nitric acid digestions were found to be adequate for the extraction of lead from the 200 mesh standard sample, microwave digestion procedures utilizing that approach can be recommended. In the case of HNO_3/HF digestions an evaporation step to remove HF rather than the boric acid complexation should provide an answer to the problems encountered. Statistical parameters for the microwave digestion results are presented in Table 8.2. When compared with the results obtained for open beaker digestions (Table 7.5), the precision of the analysis step shows slight deterioriation. Obviously the subsampling and digestion steps have performed more poorly.

Chapter 9

Conclusions

In many electrochemical techniques chloride and nitrate anions are treated as somewhat inert species. For example, in polarographic techniques one may not see a difference between these anions except for the effect of chloride on mercury oxidation. However, the results presented in Chapter 5 indicate that this is not so in anodic stripping analysis. The difference in sensitivity in these two mediums may not appear that significant under present analytical conditions, if high detection limits are sought. But the trend towards more and more sensitive analytical techniques, and lower and lower detection limits, may make minor differences like these important. The effects of salt bridge leakage on the precision of the analysis seem to become much more important as the sensitivity increases. Use of a potassium nitrate salt bridge can be strongly recommended in anodic stripping, at least in the case of lead and cadmium analysis.

Oxygen interference in anodic stripping was shown to be confined to the stripping or oxidation step. The presence of oxygen does not pose any adverse effects on the reduction or deposition step. The results presented confirm this observation, which has been reported by many workers. The controversy surrounding the mechanism of oxygen interference can be explained to some extent by the neutral behaviour of hydrogen peroxide; it is the presence of oxygen not hydrogen peroxide that affects the stripping results. The reductive reaction of oxygen can interfere with the oxidation of the analyte during the stripping process. One implication of this observation is the possible adverse effect mercuric ions can have during the use of a thin mercury film electrode plated in situ for anodic stripping analysis.

Use of a predeaerated stripping solution with a nondeaerated sample in a matrix exchange system can be pointed out as a positive application of this observation. Use of a

flow system for this purpose, probably in a flow injection format, will not only allow faster analysis but also an opportunity to incorporate modifications of the stripping solution, enabling better results as pointed out in Chapter 1.

Trace lead analysis of soil samples using differential pulse anodic stripping is a viable technique as demonstrated by the results obtained. This conclusion does not necessarily indicate that anodic stripping methods are preferable to atomic spectroscopic methods. A primary concern is the time factor. One solution might be to employ fast stripping techniques such as the square wave or staircase techniques mentioned in Chapter 1. Mercury film electrodes allow one to cut down the deposition time. These improvements may lead to a more time efficient analytical method but are beyond the scope of this thesis.

Modification of the matrix using a diluent is an effective way to suppress unwanted interferences from sample components. The interference effect disappears not because of the removal of the interferent but because of its low concentration. Increased deposition times can be used to compensate for the loss of sensitivity. Acetate buffers, which are widely used in voltammetric analysis of aqueous solutions, were found to be versatile and useful in the analysis of lead from digested solutions.

Open beaker soil digestions with perchloric acid were shown to be excellent for use with an anodic stripping procedure. In the case of bomb digestions the use of microwave digestions should be investigated further.

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Appendix 1

Computer Programs

The following pages list the two computer programs DPASV and DASTA developed for the instrumental setup described in Chapter 3. Essential features of the program DPASV are discussed in Chapter 3 under section 3.3, Software for the Anodic Stripping System. A description of the program DASTA can be found in Chapter 7 under section 7.8, Data Analysis Procedure.

```
10 ?*************************************************************************?
15 ?     DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY                      ?
20 ?           CONTROL AND DATA ACQUSITION PROGRAM                            ?
25 ?         MACSYM 150/PAR 174A/PAR 303(SMDE) SYSTEM                         ?
30 ?      ANGELO R. FERNANDO,DEPT. OF CHEMISTRY, U. OF A.                     ?
35 ?*************************************************************************?
40 ? THIS PROGRAM WORKS WITH MACBASIC 3 Rev2.00
45 ? REFER TO THE MAIN MENU (FUNCTION SELECT) FOR CHANNEL CONECTIONS.
50 E'=0
55 ON ERROR E',2395
60 TASK 1,2525,5  ? MEMORY CLEARING peak positions
65 TASK 2,2505,5  ? MEMORY CLEARING full data
70 TASK 3,1195,6  ? DATA SAVING
75 PNT 174 PNT 180
80 PNT 27,61,34,48
85 PRINT "    DPASV    "    PNT 183
90  PNT 27,61,40,44
95 ! "DATE  month(in 2 letters):"MON$
100 INP v' IF v'=13 GOTO 110
105 INP v1'  LET MON$=CHR$(v')CHR$(v1')   GOTO 90
110 PNT 27,61,42,44
115 ! "                        date:"DAY$
120 INP v' IF v'=13 GOTO 130
125 INP v1'  LET DAY$=CHR$(v')CHR$(v1')   GOTO 110
130 PNT 27,61,44,44
135 ! "                        year:198"YER$
140 INP v' IF v'=13 GOTO 150
145 YER$=CHR$(v')  GOTO 130
150 PNT 174
155 E'=0 R'=0 ru'=1 B=5.0 Ju'=2 Jp'=5 stp=.02
160 ? B determines the integration time;Ju',Jp' jump lengths,stp stepheight in peak reader.
165 DIM potential(3200),current(3200),para(15),pepot(20),pecur(20)
170 DIM mo$(2),sa$(3),da$(2),yr$(1),ru$(1),sb$(2),sol$(30),nam$(30),P(20),Q(20),K(20)
175 PNT 183 PNT 174 DISPLAY 0
180 PNT 180
185 PNT 27,61,34,36
190 PRINT "    DPASV    "
195 PNT 27,61,36,37
200 ! "POWER ON 174A,303 CONTROL AND RELAY"
205 PNT 183
210 PNT 27,61,37,38
215 ! "DISP CH15;PURGE CH14;SCAN INHIBIT CH13;RECORDER CH12;CELL CH11;STIR CH9;        CLOCK CH1"
220 DOT:0(0,11)=0 DOT:0(0,12)=0 DOT:0(0,13)=1 DOT:0(0,14)=0 DOT:0(0,15)=0
225 PNT 27,61,39,52
230 ! "FUNCTION SELECT"
235 !  "    0   RUN/NEXT RUN     "
240 !  "    1   PLOT ON SCREEN   "
```

```
245 ! "    2  PLOT ON RECORDER  "
250 ! "    3   SAVE DATA       "
255 ! "    4   LOAD DATA       "
260 ! "    5   PARAMETERS      "
265 ! "    6   PEAK READER     "
270 ! "    7   DISK DIRECTORY  "
275 ! "    8   RE RUN          "
280 ! "    9   DATA PRINT (port B) "
285 PNT 27,61,51,32
290 ! "TO SEE PLOTTED DATA ON GRAPHICS PAGE 4 USE SHIFT/SCROL KEYS "
295 PNT 181 PNT 185 PNT 27,61,53,55
300 ! "NEXT FUNCTION ?"
305 INP v' LET f'=v'-47
310 PNT 183 PNT 186
315 ON f' GOTO 325,875,1065,1160,1315,1530,1670,1965,1530,1315
320  GOTO 155
325 ! DATA ACC. FROM 174A/303
330 PNT 174
335 LET sol$="                                "
340 ACTIVATE 2
345 IF f'=9 WAIT .2 PNT 174 PNT 186 GOTO 370
350 LET drp$="                "
355 PNT 174 PNT 186
360 PNT 27,61,34,34
365 INPUT "ADJUST 174A PARAMETERS,SET RELAY TO COMP.RETURN"
370 LET mo$=MON$   LET da$=DAY$   LET yr$=YER$
375 PNT 27,61,35,44
380 INPUT "SAMPLE NO.   (2 chrs):"sb$
385 PNT 27,61,36,44
390 INPUT "SAMPLE NAME (30chrs max):"sol$
395 PNT 27,61,38,32
400 IF f'=9 GOTO 460
405 INPUT "INITIAL POTENTIAL  (V):"para(1)
410 INPUT "FINAL POTENTIAL    (V):"para(12)
415 INPUT "SCAN RATE     (mV/sec):"para(2)
420 INPUT "SCAN RANGE         (V):"para(3)
425 INPUT "MODULATION        (mV):"para(4)
430 INPUT "CURRENT RANGE     (uA):"para(5)
435 INPUT "CLOCK            (sec):"para(6)
440 INPUT "DROP SIZE              :"drp$
445 INPUT "PURGE  TIME       (min):"para(8)
450 INPUT "DEPOSITION TIME   (min):"para(9)
455 INPUT "EQUILIBRATION     (min):"para(10)
460 INPUT "CONCENTRATION     (ppb):"para(7)
465 INPUT "NO. OF RUNS            :"R'
470 finV=(para(12)-para(1))*(1.5/para(3))
475 IF R'<=1 GOTO 505
480 PNT 174 DISPLAY 0
```

```
485 DSKRESET
490 PNT 27,61,40,42
495 INPUT "INSERT DATA DISK,RETURN."
500 R'=R'+1
505 PNT 7 PNT 27,61,53,38
510 INPUT "SET 174A TO SCAN MODE,EXT.CELL. RETURN "
515 t=para(8)  d=para(9)  e=para(10)
520 PNT 174  PNT 185
525 ZERO TIMER
530 DOT:0(0,14)=1      @ N2 flow on
535 PNT 27,61,43,32
540 PRINT "~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~RUN no:"ru'
545 PRINT "/////////////PURGING//////////////////////////TIME ELAPSED:"TIMER/60
550 PRINT "~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~(MIN)~~~~~~~~~~~~~~~~~~~"
555 IF TIMER>t*60 GOTO 565
560 GOTO 535
565 DOT:0(0,14)=0  @ N2 flow off
570 WAIT 15
580 PNT 174
585 @ entry point :return loop from peakred(1755) for multiple runs
590 CLS 4,9
595 GRAPHICS 4 VIEW 6 WINDOW -0.1,1.5,-0.1,10
600 HAXIS 0,0.1 VAXIS 0,0.1
605 HPRINT 0.05,9.2,"RUN:"STR$(ru')
610 FOR I'=1 TO 2
615 PNT 27,61,43,32
[illegible]INT "[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[[RUN no:"ru'
[illegible]"::::::::::::::::DISPENSING A FRESH Hg DROP:::::::::::::::::::::::::::::"
630 PRINT "]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]]"
635 DOT:0(0,15)=1
640 DOT:0(0,15)=0
645 WAIT 2
650 NEXT
655 PNT 174
660 DOT:0(0,9)=1 @ magnetic  stirrer  on
665 WAIT 10
670 DOT:0(0,11)=1 @ cell connect to 174A
675 ZERO TIMER
680 PNT 27,61,40,32
685 PRINT "*******************************************************************run no:"ru'
690 PRINT "#########DEPOSITION PROCEEDING###############TIME ELAPSED:"TIMER/60
695 PRINT "********************************************CELL CURRENT :"AIN:0(1,1)
700 IF TIMER=>d*60 GOTO 710
705 GOTO 680
710 PNT 183
715 DOT:0(0,9)=0 @ STIRRER OFF
720 PNT 174
725 PNT 27,61,42,32
```

```
730 PRINT">>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>run no:"ru'
735 PRINT"::::::::::::::::::::EQUILIBRATION:::::::::TIME ELAPSED:"TIMER/60
740 PRINT">>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>CELL CURRENT:"AIN:0(1,1)
745 IF TIMER=>(d+e)*60 GOTO 755
750 GOTO 725
755 PNT 174
760 @ PLOTTING DATA
765 DISPLAY 4
770 DOT:0(0,13)=0 @ 174A scan release
775 I=1
780 IF DIN:0(0,1)=1 GOTO 790
785 GOTO 780
790 PLOT potential(I),current(I)
795 A1=0.0 A2=0.0  I=I+1
800 FOR J'=1 TO 8
805 A1=A1+AIN:0(1,0) A2=A2+AIN:0(1,1)
810 NEXT
815 potential(I)=A1/8 current(I)=A2/8
820 IF potential(I)>finV GOTO 835
825 IF current(I)>9.9 GOTO 835
830 GOTO 780
835 DOT:0(0,11)=0 @ cell disconnect
840 WAIT .2
845 DOT:0(0,13)=1 @ scan inhibit
850 para(11)=I
855 ru$=STR$(ru')
860 sa$=sb$ru$
865 ru'=ru'+1
870 GOTO 1720  @ End of data acqn section.Peak reader takes over at 1560.
875 @ PLOTTING DATA ON VIDEO SCREEN
880 INPUT"CLEAR SCREEN? (Y/N):"as$
885 IF as$="N" GOTO 905
890 GRAPHICS 4 CLS 4,9
895 @ axis setup.X from -.1 to 1.5,Y from -.8 to 10
900 @ with 0 - 1.5V to X and 0 - 10V to Y.,1 div in X =100mV;            1 div in Y =range*0.0
8
905 GRAPHICS 4
910 DISPLAY 4
915 WINDOW -0.1,1.5,-0.8,10
920 HAXIS -0.3,0.1
925 VAXIS 0,0.8
930 HPRINT 0.5,-0.7,"CELL POTENTIAL" HPRINT -0.1,0,"0.0"
935 VPRINT -0.05,3, "CELL CURRENT"
940 I=1
945 MOVE potential(I),current(I)
950 IPLOT 0.0,0.001
955 I=I+1
960 IF current(I)>=9.9  para(11)=I
```

```
965 IF I=para(11) GOTO 975
970 GOTO 945
975 FOR C'=1 TO 20
980 IF K(C')=0 GOTO 1015
985 IF P(C')=0 GOTO 1015
990 BOX potential(P(C'))-.005,current(P(C'))-.25,.01,0.5
995 BOX potential(Q(C'))-.005,(current(Q(C'))-(pecur(C')*10/para(5)))-.25,.01,0.5
1000 BOX potential(K(C'))-.005,current(K(C'))-.25,.01,0.5
1005 MOVE potential(Q(C')),current(Q(C'))-.25
1010 IPLOT 0.0,0.5
1015 NEXT
1020 JOY X,Y
1025 IF X=U1 GOTO 1060
1030 U1=X U2=Y
1035 X$=STR$((U1/1.5)*para(3)+para(1))"  "STR$(U2*0.1*para(5))
1040 VPRINT U1,5,X$
1045 GOTO 1020
1050
1055
1060 GOTO 155
1065 ! PLOTTING DATA ON THE RECORDER
1070 PNT 174
1075 PNT 27,61,40,40
1080 ! "PLOTTING DATA ON RECORDER, SLOT3 CH0:X CH1:Y"
1085 PNT 27,61,4[illegible]41
1090 INPUT "SET UP RECORDER : PAPER,XY [illegible] etc.  RETURN"
1095 PNT 174
1100 PNT 27,61,50,40
1105 ! "PLOTTING DATA ON RECORDER, SLOT3 CH0:X CH1:Y"
1110 DOT:0(0,12)=1
1115  I=1
1120 AOT:0(3,0)=potential(I) AOT:0(3,1)=current(I)
1125 I=I+1
1130 IF I=para(11) GOTO 1145
1135 WAIT 0.2
1140 GOTO 1120
1145 DOT:0(0,12)=0
1150 AOT:0(3,0)=0 AOT:0(3,1)=0
1155 GOTO 155
1160 ! SAVING DATA ON DISK
1165 PNT 174 DISPLAY 0
1170 PNT 27,61,38,42
1175 ! "SAVING DATA ON DISK "
1180 DSKRESET
1185 PNT 27,61,40,42
1190 INPUT "INSERT DATA DISK,RETURN."
1195 ON ERROR E',2395
1200 OPENW:2 mo$da$yr$sa$
```

```
1205 SAVE ARRAY:2 para(1)
1210 SAVE ARRAY:2 potential(1),para(11)
1215 SAVE ARRAY:2 current(1),para(11)
1220 SAVE ARRAY:2 sol$(1)
1225 SAVE ARRAY:2 drp$(1)
1230 SAVE ARRAY:2 pepot(1)
1235 SAVE ARRAY:2 pecur(1)
1240 SAVE ARRAY:2 P(1)
1245 SAVE ARRAY:2 Q(1)
1250 SAVE ARRAY:2 K(1)
1255 CLOSE:2
1260 OPENA:2 "INDEX"
1265 PRINT:2 mo$da$yr$sa$
1270 PRINT:2 sol$
1275 PRINT:2 pepot(1),pecur(1),pepot(2),pecur(2),pepot(3),pecur(3)
1280 CLOSE:2
1285 IF R'<=2 GOTO 1310
1290 R'=R'-1
1295 ACTIVATE 2
1300 DISMISS
1305 GOTO 1195
1310 ss$=sb$   A'=ru'-1  GOTO 2030
1315 ' DATA LOADING
1320 ACT 2
1325 para(11)=3200 LET sol$="                                   " LET drp$="                    "
1330 PNT 174,185   DISPLAY 0
1335 PNT 27,61,40,42
1340 ! "DATA LOADING "
1345 DSKRESET
1350 PNT 27,61,42,45
1355 INPUT "INSERT DATA DISK,RETURN"
1360 PNT 27,61,44,45
1365 ! "DATE  month(in 2 letters):"mo$
1370 INP v' IF v'=13 GOTO 1380
1375 INP v1'  LET mo$=CHR$(v')CHR$(v1')   GOTO 1360
1380 PNT 27,61,45,45
1385 ! "                        date:"da$
1390 INP v' IF v'=13 GOTO 1400
1395 INP v1'  LET da$=CHR$(v')CHR$(v1')   GOTO 1380
1400 PNT 27,61,46,45
1405 ! "                        year:198"yr$
1410 INP v' IF v'=13 GOTO 1420
1415 yr$=CHR$(v')  GOTO 1400
1420 PNT 27,61,47,45
1425 ! "SAMPLE NO.   (2 chrs):"ss$
1430 INP v' IF v'=13 GOTO 1440
1435 INP v1'  LET ss$=CHR$(v')CHR$(v1')  GOTO 1420
1440 IF f'=10 GOTO 2020
```

```
1445 PNT 27,61,48,45
1450 ! "RUN NO.   (1 chr):"sr$
1455 INP v' IF v'=13 GOTO 1465
1460 sr$=CHR$(v')  GOTO 1445
1465 LET sa$=ss$sr$
1470 OPENR:2 mo$da$yr$sa$
1475 LOAD ARRAY:2 para(1)
1480 LOAD ARRAY:2 potential(1),para(11)
1485 LOAD ARRAY:2 current(1),para(11)
1490 LOAD ARRAY:2 sol$(1)
1495 LOAD ARRAY:2 drp$(1)
1500 LOAD ARRAY:2 pepot(1)
1505 LOAD ARRAY:2 pecur(1)
1510 LOAD ARRAY:2 P(1)
1515 LOAD ARRAY:2 Q(1)
1520 LOAD ARRAY:2 K(1)
1525 CLOSE:2
1530 @ PARAMETER DISPLAY
1535 PNT 174
1540 PNT 27,61,30,32
1545 ! "DATE         mon/da/yr:"mo$,da$,yr$
1550 ! "SAMPLE/RUN          no:"sa$
1555 ! "SAMPLE            name:"sol$
1560 PNT 27,61,35,34
1565 ! "ANALYTICAL PARAMETERS"
1570 ! "INITIAL POTENTIAL  (V):"para(1)
1575 ! "FINAL POTENTIAL    (V):"para(12)
1580 ! "SCAN RATE     (mV/sec):"para(2)
1585 ! "SCAN RANGE         (V):"para(3)
1590 ! "MODULATION        (mV):"para(4)
1595 ! "CURRENT RANGE     (uA):"para(5)
1600 ! "CLOCK            (sec):"para(6)
1605 ! "DROP SIZE             :" drp$
1610 ! "CONCENTRATION    (ppb):"para(7)
1615 ! "PURGE TIME       (min):"para(8)
1620 ! "DEPOSITION TIME  (min):"para(9)
1625 ! "EQUILIBRATION     min):"para(10)
1630 IF f'<>9 GOTO 1655
1635 PNT 27,61,50,38
1640 ! "'R' TO RUN;'return' FOR FUNCTION SELECT
1645 INP v' IF v'=82 GOTO 325
1650 GOTO 155
1655 PNT 27,61,55,40
1660 INPUT "PRESS RETURN FOR FUNCTION SELECT"
1665 GOTO 155
1670 @ PEAK READER SECTION
1675 DISPLAY 4 CLS 4,9
1680 GRAPHICS 4 VIEW 6 WINDOW -0.1,1.5,-0.1,10
```

```
1685 HAXIS 0,0.1 VAXIS 0,0.1
1690 I=1
1695 IF I=para(11) GOTO 1715
1700 PLOT potential(I),current(I)
1705 I=I+1
1710 GOTO 1695
1715 ACTIVATE 1      ! entry point from data acqn section
1720 VIEW 5 WINDOW -0.1,1.5,-10,10
1725 VPRINT -.05,-10,"POTENTIAL" VPRINT -.05,2,"CURRENT"
1730 VPRINT  .0,-10,"  (V)    " VPRINT  .0,2,"  (UA) "
1735 FOR I=1 TO 20 P(I)=0 Q(I)=0  K(I)=0  NEXT I
1740 K=1 I=1
1745 A'=0
1750 A'=A'+1
1755 IF I=para(11) GOTO 1900
1760 IF current(I)<current(I+20) GOTO 1775
1765 I=I+1
1770 GOTO 1755
1775 I=I+1
1780 IF I=para(11) GOTO 1900
1785 IF current(I)>current(I+Ju')+stp GOTO 1795
1790 GOTO 1775
1795 Q(A')=I   ! peak max. point
1800 I=I+1
1805 IF I=para(11) GOTO 1900
1810 IF current(I)<=current(I+Jp') GOTO 1820
1815 GOTO 1800
1820 K(A')=I   ! peak tail point
1825 T'=Q(A')-20
1830 T'=T'-1 IF T'<=Jp'+1 GOTO 1745
1835 IF current(T')<=current(T'-Jp') GOTO 1845
1840 GOTO 1830
1845 P(A')=T'   ! peak start point
1850 bas1=(current(P(A'))-current(K(A')))*potential(Q(A'))
1855 bas2=(current(K(A'))*potential(P(A'))-current(P(A'))*potential(K(A')))
1860 bas3=(potential(P(A'))-potential(K(A')))
1865 base=(bas1+bas2)/bas3
1870 x$=STR$((potential(Q(A'))/1.5)*para(3)+para(1))
1875 y$=STR$((current(Q(A'))-base)*para(5)*0.1)
1880 IF VAL(y$)*10/para(5)<0.5 GOTO 1755
1885 VPRINT potential(Q(A')),-10,x$ VPRINT potential(Q(A')),2,y$
1890 pepot(K)=VAL(x$)  pecur(K)=VAL(y$)
1895 K=K+1 GOTO 1750
1900 IF R'<=1 GOTO 1925
1905 IF R'-1<=1 GOTO 1195 ! Data saving takes over for the last run.
1910 ACTIVATE 3
1915 PNT 174 DISPLAY 0 PNT 185
1920 GOTO 585 ! depart-point:to data acqn for multiple runs
```

```
1925 VIEW 6  WINDOW -.1,1.5,-.1,10 HPRINT 1.0,9,"RETURN"
1930 INPUT
1935 ? END OF "PEKRED"
1940 PNT 174 DISPLAY 0
1945 PNT 27,61,38,42
1950 INPUT "SAVING DATA ON DISK?   (Y/N) "SD$
1955 IF SD$="Y" GOTO 1160
1960 GOTO 155
1965 ? DISK DIRECTORY
1970 OPENR:2 "INDEX"
1975 PNT 174
1980 !"=========================DATA DISK DIRECTORY=============================="
1985 FOR G'=1 TO 20
1990 INPUT:2 dat$
1995 INPUT:2 nam$
2000 ! dat$,nam$
2005 NEXT G'
2010 INPUT "RETURN"  GOTO 1975
2015 ? PARAMETER PRINTER (USE PORT B FOR PRINTER)
2020 PNT 27,61,48,45
2025 INPUT "HOW MANY RUNS ? "A'
2030 I=1
2035 sr$=STR$(I)
2040 LET sa$=ss$sr$
2045 OPENR:2 mo$da$yr$sa$
2050 LOAD ARRAY:2 para(1)
2055 LOAD ARRAY:2 potential(1),para(11)
2060 LOAD ARRAY:2 current(1),para(11)
2065 LOAD ARRAY:2 sol$(1)
2070 LOAD ARRAY:2 drp$(1)
2075 LOAD ARRAY:2 pepot(1)
2080 LOAD ARRAY:2 pecur(1)
2085 LOAD ARRAY:2 P(1)
2090 LOAD ARRAY:2 Q(1)
2095 LOAD ARRAY:2 K(1)
2100 CLOSE:2
2105 IF I>1 GOTO 2330
2110 ? PARAMETER DISPLAY
2115 OPENW:4 "$QTO:1"
2120 PNT 174   PNT:4 27,76,48,49,48
2125 !:4
2130 !
2135 !:4 "DATE      mon/da/yr:"mo$,da$,"198";yr$
2140 ! "DATE      mon/da/yr:"mo$,da$,"198";yr$
2145 !:4 "SAMPLE          no:"ss$
2150 ! "SAMPLE          no:"ss$
2155 !:4 "SAMPLE          name:"sol$
2160 ! "SAMPLE          name:"sol$
```

```
2165 !:4
2170 !
2175 ! "ANALYTICAL PARAMETERS"
2180 !:4 "INITIAL POTENTIAL  (V):"para(1);
2185 ! "INITIAL POTENTIAL  (V):"para(1);
2190 !:4 TAB (4) "FINAL POTENTIAL    (V):"para(12)
2195 ! TAB (4) "FINAL POTENTIAL    (V):"para(12)
2200 !:4 "SCAN RATE     (mV/sec):"para(2);
2205 ! "SCAN RATE     (mV/sec):"para(2);
2210 !:4 TAB (5) "SCAN RANGE         (V):"para(3)
2215 ! TAB (5) "SCAN RANGE         (V):"para(3)
2220 !:4 "MODULATION        (mV):"para(4);
2225 ! "MODULATION        (mV):"para(4);
2230 !:4 TAB (4) "CURRENT RANGE     (uA):"para(5)
2235 ! TAB (4) "CURRENT RANGE     (uA):"para(5)
2240 !:4 "CLOCK             (sec):"para(6);
2245 ! "CLOCK             (sec):"para(6);
2250 !:4 TAB (5) "DROP SIZE              :" drp$
2255 ! TAB (5) "DROP SIZE              :" drp$
2260 !:4 "CONCENTRATION    (ppb):"para(7);
2265 ! "CONCENTRATION    (ppb):"para(7);
2270 !:4 TAB (5) "PURGE TIME       (min):"para(8)
2275 ! TAB (5) "PURGE TIME       (min):"para(8)
2280 !:4 "DEPOSITION TIME  (min):"para(9);
2285 ! "DEPOSITION TIME  (min):"para(9);
2290 !:4 TAB (5) "EQUILIBRATION    (min):"para(10)
2295 ! TAB (5) "EQUILIBRATION    (min):"para(10)
2300 !:4
2305 !
2310 !:4 " PEAKS FOUND      "
2315 !   PEAKS FOUND      "
2320 !:4 "position(V)"TAB(13)"height(uA)"TAB(25)"position(V)"TAB(38)"height(uA)"TAB(51)"position(V)"
TAB(64)"height(uA)"
2325 ! "position(V)"TAB(13)"height(uA)"TAB(25)"position(V)"TAB(38)"height(uA)"TAB(51)"position(V)"TA
B(64)"height(uA)"
2330 !:4 "RUN "sr$
2335 ! "RUN "sr$
2340 !:4 pepot(1);TAB(13);pecur(1);TAB(25);pepot(2);TAB(38);pecur(2);TAB(51);pepot(3);TAB(64);pecur(
3)
2345 ! pepot(1);TAB(13);pecur(1);TAB(25);pepot(2);TAB(38);pecur(2);TAB(51);pepot(3);TAB(64);pecur(3)
2350 I=I+1
2355 IF I>A' GOTO 2365
2360 GOTO 2035
2365 CLOSE
2370 IF f'<>10 GOTO 2385
2375 ! "ANY MORE ?   "
2380 INP D' IF D'=89 GOTO 1315
2385 GOTO 155
```

```
2390 ! ERROR TRAPPING (USE LINE 40 TO DISABLE)
2395 SUSPEND ALL CLOSE  IF E'=17 GOTO 2430
2400 IF E'=46 GOTO 2440
2405 IF E'=111 GOTO 2460
2410 IF E'=122 GOTO 2475
2415 IF E'=43 GOTO 2485
2420 IF E'=221 GOTO 2495
2425 GOTO 155
2430 ! "    DATA NOT FOUND PLEASE CHECK DISK DIRECTORY "
2435 WAIT 1 GOTO 155
2440 PNT 174 ! "  DISK FILE SPACE FULL. PLEASE WAIT "
2445 ERASE mo$da$yr$sa$
2450 INPUT " RESTART WITH A NEW DISK.(return)"
2455 GOTO 155
2460 DISPLAY 0 ! "YOU HAVE USED ALL OF THE MEMORY SPACE ALLOCATED"
2465 INPUT "PRESS RETURN"
2470 GOTO 155
2475 ! "YOU CANNOT USE THIS AS AN INPUT!"
2480 WAIT 1 GOTO 155
2485 ! "IN CORRECT DATE/SAMPLE NO INPUT"
2490 WAIT 1 GOTO 155
2495 INPUT "END OF DIRECTORY. PRESS RETURN FOR FUNCTION SELECT"
2500 GOTO 155
2505 ! TASK 1 AND 2 MEMORY CLEARING
2510 FOR M'=1 TO 3200
2515 potential(M')=0.0 current(M')=0.0
2520 NEXT
2525 !  TASK 1
2530 FOR M'=1 TO 20
2535 pepot(M')=0.0  pecur(M')=0.0
2540 NEXT
2545 PNT 7
2550 DISMISS
2555 IF f'=7 GOTO 2525
2560 GOTO 2505
2565 !=========================END=========================
```

```
10 !*************************************************!
20 ! STATISTICAL EVALUATION OF STANDARD ADDITION DATA. !
30 !   ANGELO R. FERNANDO,DEPT.OF CHEMISTRY,U OF A.    !
40 !*************call name DASTA***********************!
50 DIM X1(20),Y1(20),N(6),MX(6),SX(6),X(20),Y(20),rex(6),rey(6),Q(5)
60 M=1 n'=0  No'=0  KK=2 N(1)=0 C'=0 Q(3)=0.94 Q(4)=0.76 Q(5)=0.64
70 PNT 174
80 PNT 27,61,34,36
90 ! " STATISTICAL EVALUATION OF STANDARD ADDITION DATA "
100 PNT 27,61,37,32   ! "SAMPLE IDENTIFICATION "
110 PNT 27,61,39,32
120 INPUT "SAMPLE NO. :"SAM$ INPUT "DATE OF ANALYSIS :"DAT$ INPUT "SPECIES:"SP$
130 INPUT "SAMPLE WEIGHT(g): "SW  INPUT "DILUTION (ml sol/sam. wt.):"DIL
140 PNT 27,61,44,32    ! "ANALYSIS DATA "
150 PNT 27,61,46,32    PNT 161
160 INPUT "CONCENTRATION OF STD:"C
170 INPUT "NO OF DATA POINTS:"No'
180 FOR I=M TO No'+M-1
190 ! "PEAK HEIGHT ";I-C';INPUT ": "Y(I)
200  X(I)=C
210 NEXT I
220 M=M+No'  C'=M-1
230  N(KK)=C'  KK=KK+1
240 INPUT "enter R for calculations  "R$
250 IF R$="R" GOTO 270
260 GOTO 150
270 FOR K'=1 TO KK-2
280 FOR J'=N(K')+1 TO N(K'+1)
290 I'=J'
300 I'=I'+1
310 IF I')N(K'+1) GOTO 360
320 IF Y(I'))Y(J') GOTO 340
330 GOTO 300
340 STO=Y(J') Y(J')=Y(I') Y(I')=STO
350 GOTO 300
360 NEXT J'
370 ran=Y(N(K')+1)-Y(N(K'+1))
380 IF (Y(N(K')+1)-Y(N(K')+2))/ran)Q(N(K'+1)-N(K')) GOTO 410
390 IF (Y(N(K'+1)-1)-Y(N(K'+1)))/ran)Q(N(K'+1)-N(K')) GOTO 430
400 GOTO 450
410 rex(K')=X(N(K')+1) rey(K')=Y(N(K')+1)
420   FOR I=1 TO N(K'+1)-N(K')-1   X1(I+n')=X(N(K'+1)) Y1(I+n')=Y(N(K')+I+1)  NEXT I     n'=n'+I-1 G
OTO 460
430 rex(K')=X(N(K'+1)) rey(K')=Y(N(K'+1))
440   FOR I=1 TO N(K'+1)-N(K')-1  X1(I+n')=X(N(K'+1)) Y1(I+n')=Y(N(K')+I)  NEXT I    n'=n'+I-1 GOTO
460
450   FOR I=1 TO N(K'+1)-N(K')  X1(I+n')=X(N(K'+1)) Y1(I+n')=Y(N(K')+I)  NEXT I  n'=n'+I-1
```

```
460 NEXT K'
470 SUMX=0.0 SUMY=0.0 SUMX2=0.0 SUMY2=0.0 SUMXY=0.0
480 FOR I'=1 TO n'
490 SUMX=SUMX+X1(I') SUMY=SUMY+Y1(I') SUMX2=SUMX2+X1(I')^2 SUMY2=SUMY2+Y1(I')^2
500 SUMXY=SUMXY+X1(I')*Y1(I')
510 NEXT
520 Sxy=SUMXY-(SUMX*SUMY/n')  Sxx=SUMX2-(SUMX^2/n')  Syy=SUMY2-(SUMY^2/n')
530 b=Sxy/Sxx   a=(SUMY-(Sxy/Sxx)*SUMX)/n'     Zy=(Syy-Sxy^2/Sxx)/(n'-2)
540 sy=SQR(Zy)
550 sb=SQR(Zy/Sxx)
560 sa=SQR(Zy*(1/n +SUMX^2/(n'^2*Sxx)))
570 sab=(sa^2+(a^2*sb^2)/b^2)/b^2
580 OPENW:4 "$QTO:1"
590 PNT 174
600 PNT 27,61,34,32 ! "STATISTICAL EVALUATION OF STANDARD ADDITION DATA "
610 !
620 !
630 ! "SAMPLE :"SAM$;TAB(30);"DATE OF ANAL.:"DAT$
640 ! "SPECIES:"SP$;TAB(30);"SAMPLE WT:"SW
650 ! "DILUTION :"DIL
660 ! "DATA"TAB(13)"STD.CON"TAB(25)"PEAK HT."
670 FOR I=1 TO n'
680 ! I;TAB(13);X1(I);TAB(25);Y1(I)
690 NEXT I
700 ! "rejected"
710 FOR I=1 TO 6
720 ! I;TAB(13);rex(I);TAB(25);rey(I)
730 NEXT I
740 !
750 !
760 ! "L.S. LINE  Y=a+bX "
770 ! "      a="a;TAB(30);"      b="b
780 ! "s.d.(a)="sa;TAB(30);" s.d.(b)="sb;TAB(55);"s.d.(Y)="sy
790 !
800 ! "SOLUTION CONCENTRATION (ppb)="a/b
810 ! "                    s.d.(ppb)="SQR(sab)
820 !
830 ! "SAMPLE CONCENTRATION   (ppm)="(a*DIL)/(b*SW*1000)
840 ! "                    s.d.(ppm)="(SQR(sab)*DIL)/(1000*SW)
850 ! "                    r.s.d.(%)="(SQR(sab)*b*100)/a
860 !:4 "STATISTICAL EVALUATION OF STANDARD ADDITION DATA "
870 !:4
880 !:4
890 !:4 "SAMPLE :"SAM$;TAB(30);"DATE OF ANAL.:"DAT$
900 !:4 "SPECIES:"SP$;TAB(30);"SAMPLE WT:"SW
910 !:4 "DILUTION :"DIL
920 !:4
930 !:4 "DATA"TAB(13)"STD.CON"TAB(25)"PEAK HT."
```

```
940 FOR I=1 TO n'
950 !:4 I;TAB(13);X1(I);TAB(25);Y1(I)
960 NEXT I
970 !:4
980 !:4
990 !:4 "L.S. LINE  Y=a+bX "
1000 !:4 "      a="a;TAB(30);"       b="b
1010 !:4 "s.d.(a)="sa;TAB(30);" s.d.(b)="sb;TAB(50);"s.d.(Y)="sy
1020 !:4
1030 !:4 "SOLUTION CONCENTRATION (ppb)="a/b
1040 !:4 "                    s.d.(ppb)="SQR(sab)
1050 !:4
1060 !:4 "SAMPLE CONCENTRATION   (ppm)="(a*DIL)/(b*SW*1000)
1070 !:4 "                    s.d.(ppm)="(SQR(sab)*DIL)/(1000*SW)
1080 !:4 "                    r.s.d.(%)="(SQR(sab)*b*100)/a
1090 !:4 "rejected"
1100 FOR I=1 TO 6
1110 !:4 I;TAB(13);rex(I);TAB(25);rey(I)
1120 NEXT I
1130 PNT:4 12
1140 CLOSE
1150 FOR I=1 TO n'
1160 X1(I)=0      Y1(I)=0
1170 NEXT I
1180 FOR I=1 TO 6
1190 rex(I)=0       rey(I)=0
1200 NEXT I
1210 GOTO 10
```