Differential Electrolytic Potentiometric Detector in Flow Injection Analysis

by

Mustafa Emrah Koken

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

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BY

MUSTAFA EMRAH KOKEN

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بسم الله الرحمن الرحيم

مصطفى عمرو كوكين

طريقة فرق الجهد التفاعلي ككاشف في تحليل الحنف الانسيابي

كمية: ١٤١٧
٣ ربيع الأول

تم في هذا البحث استخدام طريقة فرق الجهد التفاعلي لأول مره ككاشف في تحليل الحنف الانسيابي حيث استخدمت هذه الطريقة في عمليات المعايير الصغرى جدا ساعد في ذلك استخدام حالت مبرمج بالحاسب الآلي. تم معايير النتائج من خلال الرصاص ونيتيامين ج حمول السيرم. وضمن أن هذه المعايير لها اثر كبير في الحصول على نتائج جيدة أخرى بد من استخدام تيار مناسب سواء في المعايير أو في حالة الحنف الانسيابي. ولقد استخدمت الطريقة بنجاح في التحليل بالحنف الانسيابي في كل من تفاعلات الأكسيد والاختزال وفي تفاعلات الترسيب. تم الحصول على الظروف المثلى من حيث شدي التيار ومعدل انسياب السائل وكذلك حجم الميلين. تم قليل نيتيامين ج وال الحديد الثنائي باستخدام حمول السيرم واقتباب البلاتين. وتم تقسيم كل من الكلوريد والبروميد والايوئيد باستخدام اطباقي الفضه واقتباب الفضه/كلوريد الفضه واقتباب البلاتين مع الفضه واقتباب الفضه الملتصق بالإرثيق.
ABSTRACT

Flow injection analysis is based on the injection of a liquid sample into a moving, non-segmented, continuous carrier stream of a suitable liquid. The injected sample forms a zone transported toward a detector that continuously records a physical parameter such as absorbance, electrode potential. The system consists of a pump to propel carrier stream through a tube of certain length and diameter, an injection port from where the well-defined volume of a sample is injected into a carrier stream. A reactor in which the sample zone disperses and reacts with carrier stream a detector that senses forming species and a recorder.

The detector is the heart of the system that gives the analytical signals related to the concentration. Among them the optical detectors especially spectrophotometric ones are the most commonly used. However for the spectrophotometric detectors, the detection is limited to the formation of colored complexes. Although electrochemical detectors are also widely used it is first time that differential electrolytic potentiometric detector was introduced in flow injection analysis.

The purpose of this work is to check the applicability of the polarized solid electrodes as detectors in the flow injection analysis and to investigate the parameters that are involved such as flow rate, current etc, in several types of reaction systems.
Chapter 1

INTRODUCTION

1.1 Differential Electrolytic Potentiometry

As a contrast of classical potentiometry where the potential is related to the logarithm of concentration, differential methods is a technique that gives titration curves in the form of a peak resulting in precise end point location. However they remain unsatisfactory in dilute solutions due to the slow electrode response speed long equilibrium time and non reproducibility.

The high speed to attain the electrode equilibrium potential is provided with polarization methods. The polarization was done on indicator electrode with respect to a reference electrode. However the use of single polarized electrode (1) cannot be used in endpoint location since it gives inaccurate results. When a pair of identical electrodes are polarized accurate results are obtained with high response speed of electrodes. Salomon, Nerst (2) were the earliest workers who used the system.

Differential electrolytic potentiometry (DEP) is a technique used for the study of electrode processes and titrimetric reactions (3,4). A heavily stabilized current passed through a pair of identical electrodes immersed in a vigorously stirred solution and the potential difference ($E_d$) between them is measured. At the equivalence point $E_d$ will give a sharp peak representing the first differential of S-shaped potentiometric curve.
Considering the advantage of the faster response of polarized electrodes with respect to zero current electrodes DEP gives better results during titration. The instrumentation is simple and the reference electrode which is the source of contamination for titrand solution and difficulties caused by salt bridge are eliminated.

The polarization of electrodes can be done by various ways. Direct current periodic current or alternating current both can be used and the name of method is given by the polarizing current. In this work the direct current was used to polarize the electrodes.

Direct current DEP (dc DEP) has been applied to all types of oxidation-reduction reactions using platinum and gold electrodes (5,6,7); precipitation reactions using silver and silver halide coated electrodes (8,9); and complexation reactions using gold amalgam electrodes (10,11) in both aqueous and non-aqueous media.

1.1.1 Theories of DEP

The mass and charge transfer processes become pertinent since the titration curves are affected by many titrimetric and electrical parameters.

Kolthoff (12) defines the polarization an electrode in the means of a passing current through it. The potential of the electrode will change and it will be different from that of the zero-current potential. Depending on the type of polarization the anodic polarization will make the potential of the electrode more positive than that of the zero current. In the case of cathodic polarization, the electrode will attain more negative potential than the zero current electrode. The differences in potentials are due to overpotentials.
1.1.2 Overpotentials

In the absence of net current flowing in the external circuit the sum of cathodic and anodic current is equal to zero

i.e. \( i_c + i_a = 0 \) and \( i_c = -i_a = i_0 \)

\( i_0 \) represents the exchange current that flows continuously in the compact layer. When \( I = 0 \), the electrode potential will have the equilibrium zero-current value, \( E_{eq} \) with respect to saturated hydrogen electrode.

When a net current is passing through the electrodes its potential will have a new value, \( E_{we} \) which is the potential of the working electrode. The difference between \( E_{we} \) and \( E_{eq} \) is called the overpotential \( \eta \) i.e. \( \eta = E_{we} - E_{eq} \)

\( \eta \) consists of three components, \( \eta_a \) charge transfer or activation overpotential, \( \eta_c \) the mass transfer or concentration overpotential and \( \eta_r \) the resistance overpotential.

\( \eta_a \) occurs due to the slowness of the electrode process, depending upon the nature of electrode surface, its surface conditions and the concentration of electroactive species present in the medium.

\( \eta_c \) arises when the passage of current causes a net reaction at the electrode surface and independent of the nature of electrode. This results in a difference in concentrations of reactants and products at the electrode surface from those in the bulk of solution forming concentration gradients. Hence reactants migrate towards and products migrate away from the electrode.

\( \eta_c \) could be defined as \( \eta_{cs} \) which represents the overpotential that results from the passage of current as \( \eta_{cb} + \eta_{cs} \), where \( \eta_{cb} \) is independent of current and constant for a given bulk concentration.
\[ \eta_{cs} = \frac{RT}{nF} \log_{e} \frac{[OX]_{S}}{[\text{Red}]_{S}} - \log_{e} \frac{RT}{nF} \frac{[OX]_{B}}{[\text{Red}]_{B}} \]  

(1.1)

and the potential of an electrode \( E = E'_{O} + \eta_{cB} + \eta_{cs} + \eta_{a} \)  

(1.2)

\[ *E = E'_{O} + \eta_{c} + \eta_{a} \]  

(1.3)

The resistance overpotential \( \eta_{r} \) (13), defined by Bowdon and Agar, depends upon the conductivity of the electrolyte solution and the amount of current flowing but not on electrochemical processes. Adding supporting electrolyte in a proper concentration is sufficient to lower \( \eta_{r} \) to an insignificant value.

1.1.3 Parameters involved in the theoretical treatment

In order that the theoretical treatment in the following sections may be easily followed, a list of the parameters involved is provided here.

- A - Projected area of the electrode
- \( \partial_{x} \) - Thickness of the diffusion layer
- \( r \) - Roughness factor of the electrode surface
- D - Diffusion coefficient
- \( I \) - current
- \( k \) - The conditional overall rate constant
- a - The charge transfer coefficient
- n - Number of electrons involved in the reaction
E\textsubscript{we} - Working electrode potential
E'\textsubscript{0} - Conditional potential
[Ox]\textsubscript{B} - Concentration of the oxidized form in the bulk solution
[Ox]\textsubscript{S} - Concentration of the oxidized form at the surface of the electrode
[Red]\textsubscript{B} - Concentration of the reduced form in the bulk solution
[Red]\textsubscript{S} - Concentration of the reduced form at the surface of the electrode
'f' and 'b' Refer to the forward or backward electrode reaction
k\textsubscript{f} - Specific rate constant for forward reaction
k\textsubscript{b} - Specific rate constant for backward reaction
a\textsubscript{ox} - Activity of oxidized species
a\textsubscript{red} - Activity of reduced species

The kinetics of an electrode reaction depends on the rates of mass and charge transfer reactions at electrode surface.

Mass transfer exits in three different forms: diffusion, convection and electro migration. Diffusion occurs due to the change in concentration of electrolyzed species near the electrode forming a concentration gradient between the electrode surface and the bulk of solution.

Convection is formed by density and concentration gradients. Rapid stirring of solution results in a uniform concentration in the bulk.

Since ions carry the current, electromigration of reacting species will occur. The addition of a background electrolyte minimizes such migration.

In order to calculate [Ox]\textsubscript{S} and [Red]\textsubscript{S} under conditions where \eta\textsubscript{a} is negligible, it is assumed that the electromigration is negligible (14).
Consider the oxidation-reduction reaction

\[ \text{Ox} + n\text{e} \rightleftharpoons \text{Red} \]  

(1.4)

For which the electrode potential is given by

\[ E_{\text{we}} = E'_0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]_S}{[\text{Red}]_S} \]  

(1.5)

At equilibrium for a given current:

rate of electrolysis = rate of diffusion

therefore \[
\frac{I}{nF} = D_{\text{ox}} \cdot A \cdot r \cdot \frac{[\text{Ox}]_B - [\text{Ox}]_S}{dx} \]  

(1.6)

and \[
\frac{I}{nF} = D_{\text{red}} \cdot A \cdot r \cdot \frac{[\text{Red}]_S - [\text{Red}]_B}{dx} \]  

(1.7)

Solution of equation (1.6) and (1.7) gives the ionic concentrations of the oxidized and reduced species at the electrode surface:

\[ [\text{Ox}]_S = [\text{Ox}]_B - \frac{I \cdot dx}{nF Ar D_{\text{ox}}} \]  

(1.8)

\[ [\text{Red}]_S = [\text{Red}]_B + \frac{I \cdot dx}{nF Ar D_{\text{red}}} \]  

(1.9)

Substitution of (1.8) and (1.9) in (1.5) gives \( E_{\text{we}} \) corresponding to a given value of the current.
\[ E_{we} = E'_0 + \frac{RT}{nF} \ln \frac{[Ox]B}{[Red]B} - \frac{I dx}{nFArD_{Ox}} + \frac{I dx}{nFArD_{\text{red}}} \]  

(1.10)

When the process becomes limited by the diffusion of oxidant to the electrode surface, \([Ox]s \to 0\), so that from (1.6) the limiting current for cathodic reactions is given by

\[ I_L \stackrel{[OX] s \to 0}{=} \frac{nFArD_{Ox} [Ox] B}{dx} \]  

(1.11)

\[ E \to -\infty \]

Similarly from (1.4) the limiting current for anodic reaction is

\[ I_L \stackrel{[Red] s \to 0}{=} \frac{nFAr D_{\text{red}} [Red] B}{dx} \]  

(1.12)

\[ E \to \infty \]

This current is approached asymptotically and would only be obtained for cathodic reactions at \(E_{we} = -\infty\); at higher potentials, the current corresponding to a given potential is obtained by solving (1.10) for I, hence
\[
I = \frac{nFA D_{ox} D_{red}}{dx} \frac{[Ox] B - B [Red]B}{B D_{ox} + D_{red}} \quad (1.13)
\]

where
\[
B = \exp \frac{nF (E_{we} - E_{o})}{RT} \quad (1.14)
\]

By applying equations (1.10) and (1.13) the potential at a specified current and the current at a specified potential both can be calculated. Furthermore, using the convention that a net cathodic current is positive and a net anodic current is negative, the above equations can be applied to both anodic and cathodic reactions.

Considering equations (1.11) and (1.12), the parameters that are unknown or difficult to be measure, but which are constant for a given set of conditions may be grouped together in an overall conditional mass transfer rate constant \(K_{mass}\).

\[
K_{mass,ox} = \frac{D r_{ox}}{x L_{ox}} = - \frac{I}{(nFA [Ox])} \quad (1.15)
\]

\[
K_{mass,red} = \frac{D r_{red}}{x L_{red}} = - \frac{I}{(nFA[RED])} \quad (1.16)
\]
1.1.4 The Charge Transfer Problem

In order to obtain \([\text{OX}]_S\) and \([\text{Red}]_S\) for substitution in the charge transfer equations, the mass transfer equations have to be applied. There is a connection between mass transfer and charge transfer.

Considering again the general reaction

\[
\begin{array}{cccccc}
\text{Ox} & + & \text{ne} & \rightarrow & \text{Red} & \leftarrow \text{Red} \\
\text{i} & \text{c} & & & \text{i} & \text{a}
\end{array}
\]  
(1.17)

and on the passage of a net current \(I\) through the electrode, the rate equation is

\[
\frac{d a_{\text{ox}}}{dt} = \frac{d a_{\text{red}}}{dt} = k_f a_{\text{ox}} - k_b a_{\text{red}} = \frac{I}{nF} \quad (1.18)
\]

where \(a_{\text{ox}}\) and \(a_{\text{red}}\) are the activities of the oxidized and reduced species, \(k_f\) and \(k_b\) are the forward and backward reaction rate constants and \(I\) is the net current flowing.

The specific rates, \(k_f\) and \(k_b\) can be written in terms of the theory of absolute (15) reaction rates as

\[
k_f = k_B^B \frac{T}{h} \text{e}^{-\Delta G_f/RT} \quad (1.19)
\]
\[ k_b = \frac{k_B T}{h} e^{-\Delta G_b/RT} \quad (1.20) \]

where \( \Delta G_f \) and \( \Delta H_b \) are the corresponding free energies of the activated state

\[ KB \text{ is Boltzman's constant, } h \text{ is Plank's constant.} \]

If the potential of the electrode with respect to some reference point such as N.H.E. is \( E_{\text{vol}} \) and \( k'_f \) and \( k'_b \) are the rate constants at \( E = 0 \) and \( a \) is defined as the fraction of the potential favoring the forward reaction, i.e. cathodic reaction, then there will be a free energy change of \( nFE \) per mole and hence the specific rate of the forward reaction becomes

\[ k_f = k'_f \exp \frac{anFE}{RT} \quad (1.21) \]

and similarly a fraction \( (1 - a) \) of the potential \( E \) will favor the backward, i.e. anodic, reaction and thus the specific rate of the backward reaction becomes

\[ k_b = k'_b \exp \frac{(1 - a)nFE}{RT} \quad (1.22) \]

Substituting these values in the overall rate equation (1.19) gives

\[ I = nF A_{\text{ox}} k'_f \exp - \frac{anFE}{RT} - \text{ared } k'_b \exp \frac{(1 - a)nFE}{RT} \quad (1.23) \]
At zero current: When no net current is flowing through the external circuit, \( I=0 \), and \( i_c = -i_a = i_0 \), where \( i_0 \) is the exchange current; the electrode potential \( E_{\text{we}} \) will then have the equilibrium value, \( E_{\text{eq}} \), and \([\text{Ox}]\) and \([\text{Red}]\) will be the bulk concentrations.

Thus \( i_c = nFA \, a_{\text{ox}} \, k'f \, \exp \left( -\frac{nF \, E_{\text{eq}}}{RT} \right) \)  \( (1.24) \)

and \( i_a = nFA \, a_{\text{red}} \, k'b \, \exp \left( \frac{(1-a)nF \, E_{\text{eq}}}{RT} \right) \) \( (1.25) \)

Substituting in the equation \( i_c + i_a = 0 \) gives, after simplification

\[
E_{\text{eq}} = \frac{RT \, \log e}{nF} \frac{K'_f}{K'_b} + \frac{RT \, \log e}{nF} \frac{a_{\text{ox}}}{a_{\text{red}}} \]  \( (1.26) \)

Which is the Nernst equation at zero current and from which the definition of \( E_0 \) can be seen:

\[
E_0 = \frac{RT \, \log e}{nF} \frac{K'_f}{K'_b} = \Delta G - \Delta G_f \]  \( (1.27) \)

Similarly insertion of \( f_{\text{ox}} \) and \( f_{\text{red}} \), the activity coefficients of OX and Red into equation (1.26) gives the definition of \( E'_0 \)

\[
E'_0 = E_0 + \frac{RT}{nF} \log e \frac{f_{\text{ox}}}{f_{\text{red}}} \]  \( (1.28) \)
By using an overall rate constant, \( K \), which is defined as

\[
K = k' f_{\text{oX}} \exp \left( -\frac{a n F E_0}{RT} \right) = K'_b f_{\text{red}} \exp \left( \frac{(1-a) n F E_0}{RT} \right)
\]

(1.29)

or

\[
K = k' f \exp \left( -\frac{a n F}{RT} E'_0 \right) = K'_b \exp \left( \frac{(1-a) n F}{RT} E'_0 \right)
\]

(1.30)

and substituting these values in equation (1.23) using the fact that

\[
E = E_{\text{eq}} \text{ at } I = 0 \text{ and the relation } E_{\text{eq}} = E'_0 = RT \log e \frac{[\text{OX}]}{[\text{Red}]} \text{ gives } n F \frac{[\text{OX}]}{[\text{Red}]} = 0
\]

(1.31)

But

\[
i_0 = i_c = -i_a
\]

\[
* i_0 = n \text{FAK } [\text{OX}]^{(1 - a)} [\text{Red}]^a
\]

**At net current:** When \( I \neq 0 \), then \( i_c \neq i_a \). In order to calculate \( I \) from equation (1.23), \( E \) is not equal to \( E_{\text{eq}} \) but equal to the working electrode potential, \( E_{\text{we}} \). Using the definitions of the overall rate constant, \( K \), in (1.29) and (1.30) and substituting into (1.23) gives

\[
I = n \text{FAK } [\text{OX}] \exp \left( -\frac{a n F (E_{\text{we}} - E'_0)}{RT} \right) \left[ \text{Red} \right] \exp \left( \frac{(1-a) n F (E_{\text{we}} - E'_0)}{RT} \right)
\]

(1.33)
When \( I = 0 \), \([\text{Ox}]\) and \([\text{Red}]\) are the bulk concentrations and \( E_{\text{we}} = E_{\text{eq}} \), but when \( I \neq 0 \) the concentrations are \([\text{Ox}]_S\) and \([\text{Red}]_S\). From Equation (1.3)

\[
E_{\text{we}} = E'_0 + \eta_a + \eta_c \quad \text{and therefore (1.33) becomes}
\]

\[
I = nFAK[\text{Ox}]_S \exp \left( \frac{-a_nF}{RT} \right) \eta_c + \eta_a - [\text{Red}]_S \exp \left( \frac{(1-a)nF}{RT} \right) (\eta_a + \eta_c) \tag{1.34}
\]

Equation (1.34) can be solved for \( \eta_a \) by substituting from (1.7)

\[
\eta_c = \frac{RT \log_e [\text{Ox}]_S}{nF} \left[ \frac{[\text{Ox}]_S}{[\text{Red}]_S} \right] \tag{1.35}
\]

which gives after simplification.

\[
I = nFALK[\text{Ox}]_S (1-a) [\text{Red}]_S \exp \left( -a_nF \right) \eta_a - \exp \left( \frac{(1-a)nF}{RT} \right) \eta_a \tag{1.36}
\]

Which is the charge-transfer and mass-transfer overpotential equation. Calculation of the potential at a given current may be achieved by direct solution of equations (1.33), (1.34) and (1.36), but in each case the mass transfer problem must be solved in order to determine \([\text{Ox}]_S\) and \([\text{Red}]_S\) for substitution into (1.36). Equation (1.36) is straightforward to solve for supplied values of \( \eta_a \), \( K \) and \( a \). It is also possible by numerical methods (16,17) to resolve this equation for \( \eta_a \) in terms of supplied values of the current. Finally substitution of the calculated values for \( \eta_c \) and \( \eta_a \) in

\[
E_{\text{we}} = E'_0 + \eta_a + \eta_c \tag{1.37}
\]

gives \( E_{\text{we}} \) at the chosen current, the sign of the current will give the correct solution for either anodic or cathodic process.
1.2 Flow Injection Analysis

The injection of a liquid sample into a moving non segmented continuous carrier stream of a suitable liquid (18) is the basis of the flow injection analysis (FIA). A physical parameter develops as a result of transportation of the zone formed by the injected sample toward a detector. This physical parameter is absorbance, electrode potential or any other parameter that continuously changes due to the passage of sample material through the flow cell.

A basic FIA configuration (19) as shown in Fig.1 consists of
a) propelling unit to drive one or more flowing stream solutions at a constant rate,
b) injection port to introduce an accurately measured sample volume into flow,
c) a reactor formed by a piece of tubing along the reacting mixture is transported.
d) a detector, measuring device that transduces the signal generated to a recorder.

1.2.1 Propelling System

On the account of the constant flow rate which is one of the most important prerequisite to be met peristaltic pumps are most frequently used (20). For instance an ALITEA FIA LAB was used for this purpose.

1.2.2 Injection System

The injection system is important to give a well defined volume of sample into carrier system.
Fig. 1  (a) Scheme of a basic FIA system. C: carrier (with or without a dissolved reagent); PS: propelling system; IV: injection valve; R: reactor; D: detector; W: waste. (b) Slow recording—the commonest in this technique—corresponding to injection of triplicate standards and quintuplicate samples. (c) Fast recording,
The earliest injection unit employed was a simple syringe and hypodermic needle (20). Currently the injection system most frequently used are the rotary valve (20) and proportional injector (21) although the former damage easily and give non reproducible volumes.

For this work a computerized injection system was used. A stepper motor controlled by a card equipped with a computer program is linked to normal plastic syringe. The metallic needle is replaced by a plastic one in order to prevent acid attack.

1.2.3 Transport and Reaction System

Transport system normally consists of small tubes of a small inner diameter (22). They are most commonly Teflon, polyethylene and polypropylene made.

The reactor is the major component of the transport system that influence residence time. Straight open tubes, coiled tubes and mixing chambers and packed ones are used where the coiled tubes are the most common. A piece of tube is coiled around a rigid cylinder of a desired diameter which was also preferred for this work.

1.2.4 Detectors

FIA utilizes a variety of analytical detection techniques such as optical (spectroscopic and non spectroscopic), potentiometric (23,24), amperometric, conductimetric (25,26), coulometric (27,28) and thermochemical.
Optical detectors are the most common detector system in flow injection analysis (29). Potentiometric detectors were also commonly used especially ones that contain ion selective electrodes. The technique of DEP has not been applied yet as a detector for FIA.

1.2.5 FIA readouts

The physical foundation of FIA is related to the behavior of sample in the flow, characterized mathematically by means of so called dispersion (30). It was shown before that the signal observed by a detector has the form of a peak of height H, width W and area A (31).

Peak height is the most commonly used measured peak dimension since it is easily identified and directly related to detector response like absorbance, potential or current. Hence in the absence of chemical reactions detector response is a linear function of concentration (C) then

\[ H = k \cdot C \] where k is proportionality constant.

However in the presence of chemical reactions FIA peak is a combination of physical aspect (dispersion) and chemical aspect (chemical reactions).

In potentiometric detector systems composed of an indicator electrode and a reference cell the peak is expected to be linear giving a Nerstian response (potential is related to log of the sample concentration).

In the case of differential electrolytic potentiometric detector Nerstian response is replaced by a direct proportionality.
Chapter 2

OBJECTIVES

In the first part of the work, Differential Electrolytic Potentiometric micro titrations were performed for the determination of two substances. These titrations are

i) Microtitration of nitrite using Pt electrodes

ii) Microtitration of Vitamin C using Pt electrodes

In the second part of the work the objective was the application of differential electrolytic potentiometric detector to flow injection analysis. For this application several systems which can be classified mainly to two groups were analyzed. These systems are

i) Oxidation Reduction Reactions

1) Vitamin C / Ce(IV) System using Pt electrodes

2) Fe(II) / Ce(IV) System using Pt electrodes

ii) Precipitation Reactions

1) Cl⁻, Br⁻, I⁻ Analysis using Ag electrodes

2) Cl⁻ Analysis using Ag/AgCl electrodes and selective polarization

3) Cl⁻ Analysis using Ag/AgCl and Pt electrodes

4) Cl⁻ Analysis using Ag/AgCl and Pt(Hg) electrodes

5) I⁻ Analysis using Ag and Pt electrodes
Chapter 3

EXPERIMENTAL

3.1 General instrumentation

A constant current polarization source which does not require a standard reference necessary cell was designed for the early experiments. This source provides an adjustable dc current of the range 100 μA -- 100mA which is usually used in dc differential electrolytic potentiometry. Tests on this source showed that the drifts in potentials during a period of 30 min. were insignificant.

For the other experiments a Keithley Instruments 225 Constant Current Source was used. The potentiometer used is Corning Scientific Instruments Model 12 Research pH Meter for oxidation reactions and changed to digital Fisher Accumet Selective Ion Analyzer Model 750 for the other experiments.

A Cole Parmer chart recorder was used for all experiments and all the data were recorded with a speed of 0.3 cm/min.

The test solutions were propelled by a peristaltic pump of Alitea USA/ FIA lab for all experiments.
A Gateway 2000 computer with RS 332-098 4 phase unipolar stepper motor drive board introduced into the hard disk was used for the injection of samples into carrier streams to provide a highly precise and reproducible volume.

The injector used was a plastic syringe with the metallic needle replaced with a plastic one to prevent the corrosion and the attack of the acid to the metal.

100, 500, 1000 ml volumetric flasks and micro burette were used for the preparation of solutions.

3.1.1 Constant Current Source

Different dc polarizing sources have been employed in the dc DEP technique. For example, high tension batteries and high value ballasts have been used as polarizing sources (32,33). The high tension batteries, when they become scare, have been replaced by solid state high voltage sources (34). A stable low current source has been constructed from operational amplifiers (35). This source requires a Mallory mercury cell which acts as a reference voltage, hence, a regulated current will be obtained. However, the Mallory cell discharges and it has to be replaced frequently.

A constant current source which does not require a reference Mallory cell in its configuration was constructed. Instead it uses a semi conductor reference diode to act as a reference voltage. This set up does not require any frequent replacement such as in the case of the Mallory cell. The stability of the output current of this source is also reported.

The constant current source consists of two components. These components, which are shown in Figures 2 and 3 include a dc power supply unit and a circuit which provides a very small adjustable dc current. Fig.2 represent the dc power supply which is directly
connected to the main ac voltage which is of 110V/6Hz. The transformer T steps down the main ac voltage from 110V to 28V. The output of the transformer T is fed into a rectifying and filtering unit. This unit, which consists of the diodes D1 through D4, the capacitors C1, C2, C3 and the resistor R2, converts the ac voltage into a dc voltage. It also minimizes the ripple at the output. The integrated circuit IC1, which is supported by the resistors R3 and R4, the capacitors C4 through C6 and the diode D6, gives a constant dc voltage of 30 V.

The circuit which acts as a constant current source is shown in Fig.3. This source consists of four integrated circuits IC2 through IC5. The integrated circuit IC2 acts as a reference diode and provides a constant voltage to the buffer amplifier IC3.

The latter acts as a constant voltage source at the non-inverting input of the integrated circuit IC5. The potentiometer VR2 is used to vary the output voltage of the buffer amplifier IC3. The integrated circuit IC4, the diodes D7, D8 and the potentiometer VR5 all act as a shunt regulator which provides a clamping voltage at the junctions of resistors R7 and R8. The fine and coarse controls which adjust the output current are represented by VR3 and VR4, respectively. VR6 represent a trimming potentiometer which acts as an offset adjustment of the integrated circuit IC5.

The voltage or the current through the load are monitored by the switch S2 at the terminals J2-A and J2-B. The load current is allowed to pass through a standard 10 kohm resistor R9. The potential drop, which is proportional to load current, is measured across the resistor R9.

The complete circuit shown in Figures 2 and 3 was assembled on a metallic chassis. The two controls which vary the current and the voltage were provided on the front panel of the chassis.
Tests were done by allowing a current of 1 mA to pass through standard resistors of 1 megohm and 10 megohms as well as through a solution. The voltage drop across the resistors and the solution were measured during a period of 30 minutes. The changes in these voltages, which represent the drift in the current, were found to be insignificant.

The behaviour of the dc source was examined by changing load resistances at different settings of the output current, which were from 100 hA- 100 mA. The load was varied from 0 - 10 megohms. It is apparent from Fig.4 that the output current was highly stable, particularly for current values below 10 mA which are normally applied in the technique of dc DEP. Moreover, currents to 100 mA can be applied to solutions with impedances up to 1 megohm.
Fig. 2 A d.c. Power Supply Unit
Fig. 3 A Circuit that acts as a constant current source
Fig. 4 The output current
3.2 DEP Titrimetry

3.2.1 Micro titration of Nitrite with Pb(IV)

i) Chemicals and Reagents

AnalaR Sodium Nitrite was used to prepare nitrite solutions.
Fluka Lead Tetraacetate and Fluka concentrated acetic acid were used for the preparation of Pb(IV) solutions.
Thorn Smith Sodium Chloride was used to prepare supporting electrolyte solution.
0.69 grams of sodium nitrite was dissolved with distilled de ionized water in 1000 ml volumetric flask to give 0.01 M nitrite stock solution. The stock solution was diluted with required volume of distilled de ionized water to produce $10^{-3}$ M, $10^{-4}$ M nitrite solutions and more dilute solutions were prepared in the same way.
0.443 grams of lead tetraacetate was dissolved with concentrated acetic acid in 100 ml volumetric flask to give 0.01 M Pb(IV) stock solution. More dilute solutions were prepared by diluting required amount with concentrated acetic acid.
0.0558 grams of sodium chloride was dissolved with distilled de ionized water in 100 ml volumetric flask to produce 0.01 M sodium chloride supporting electrolyte solution.

ii) Electrodes

A pair of platinum electrodes were used for the experiments. The platinum electrodes were
SargentWelch type 30-415 and 30-415 respectively. They were cleaned with concentrated sulfuric and/or nitric acid before each experiment as a pre treatment, rinsed with distilled de ionized water and placed in the cell.

iii) Cell

The titration was done in a 10 ml beaker. A rubber stopper that contains three holes was attached into the beaker. The injector plastic needle and electrodes were immersed via these holes. Titration cell is shown in Fig.5. The computer controlled stepper motor that delivers reproducible and precise small volumes was used as micro burette.

iv) General Measuring Conditions

The same apparatus was used as described in the previous micro titration. In the case of the 10-4 M nitrite titration 0.01 M Pb(IV) solution was used and 10^-3 M Pb(IV) was preferred for 10^-5 M and 10^-6 M nitrite solutions. The titration was done while the beaker was containing 1 ml of nitrite solution and 4 ml of sodium chloride solution.
Fig 5  Apparatus for DEP Titrimetry
T : Titration Cell
M : Constant Current Source
C : Computerized injector
P : Potentiometer
3.2.2 Micro titration of Vitamin C with Ce(IV)

i) Reagents and Chemicals

Analytical grade chemicals were employed for the preparation of reagents. C-249 certified ceric ammonium sulfate by Fisher Scientific Company and 30743 concentrated sulfuric acid (95-97%) by Riedel de Haen were used for the preparation of the stock solution of 0.1 M Ce(IV) in 0.5 M sulfuric acid.

95200 Vitamin C by Fluka was used to prepare a stock solution of 1000 ppm.

0.1 M Ce(IV) in 0.5 M sulfuric acid was prepared by dissolving 63.6 grams of ceric ammonium sulfate in 28.2 ml of concentrated sulfuric acid and 300 ml distilled water in 1000 ml volumetric flask and made up to 1000 ml with distilled water. The solution was left overnight and then used for the preparation of different solutions by dilution.

1000 ppm solution of vitamin C was prepared by dissolving 1 gram of vitamin C solid in 600 ml of distilled water and the volume was completed to 1000 ml. Other vitamin C solutions were prepared by diluting with distilled water.

1 M Sulfuric was prepared by adding 55.4 ml of concentrated sulfuric acid to 200 ml of distilled water in 1000 ml flask and then completing till the mark.

ii) Electrodes

Platinum electrodes were used for the micro titration. They were the same as described in the micro titration of nitrite with Pb(IV).
iii) Cell

The same cell was used as in the case of the micro titration of nitrite with Pb(IV).

iv) General Measuring Conditions

For the titration of 100 ppm solutions of Vitamin C, 0.5 M Ce(IV) in 0.05 M sulfuric acid was used. The concentration of Ce(IV) solution was decreased to 0.05 M for the titration of 1 ppm of Vitamin C keeping the acidity constant.

The titration beaker contains 1 ml of Vitamin C sample and 5 ml of 1 M sulfuric acid and the resulting solution was titrated with standard solution of Ce(IV).
3.3 DEP Detector in FIA

3.3.1 Oxidation Reduction reactions

3.3.1.1 Ce(IV) and Vitamin C System

i) Chemicals and Reagents

The same reagents were used as described in the microtitration of Vitamin C with Ce(IV).

ii) Electrodes

The same platinum electrodes were used as described in the microtitration of Vitamin C with Ce(IV).

iii) Cell

While one-manifold system was used in the absence of the vitamin C carrier it was changed to two-line manifold with single congruence point as shown in Fig. 6. This part was made of glass and combined with a coiled tube formed using a plastic tube of 40 cm length and 1.14 mm in inner diameter around a rigid cylinder of diameter 0.7 cm. This part is combined to a Teflon made rigid cylinder of 3 cm in length where two electrodes are placed 0.5 cm far from each other.
Fig 6  Types of FIA manifolds used
A  single line
B  two line with a single confluence point
C  reagent premix into a single line
iv) General Measuring Procedure

The optimum conditions were determined experimentally.

For 10-90 ppm samples of vitamin C a volume of 140 µl of samples were injected through the injection port. For 1-9 ppm samples only the sample volume was increased to 200 µl. In both cases the samples were injected to the carrier of 20 ppm vitamin C content while passing from the other line 0.001 M Ce(IV) in 0.05 M sulfuric acid.

For 100-250 ppm vitamin C samples the content of carrier was increased to 150 ppm and the volume of samples injected was 140 µl. The second line had a content of 0.01 M Ce(IV) in 0.25 M sulfuric acid.

3.3.1.2 Ce(IV) and Fe(II) System

i) Reagents and Chemicals

Analytical grade chemicals were employed for the preparation of reagents. C-249 certified ceric ammonium sulfate by Fisher Scientific Company and 30743 concentrated sulfuric acid (95-97%) by Riedel de Haen were used for the preparation of the stock solution of 0.1 M Ce(IV) in 0.5 M sulfuric acid.

Pro analysi Merck (NH₄)₂FeSO₄.6H₂O and concentrated sulfuric acid were used to prepare 0.05 M Fe(II) solution in 0.05 M sulfuric acid.

1 M sulfuric acid was prepared by adding 55.4 ml of concentrated sulfuric acid to 200 ml of distilled water in 1000 ml flask and then completing till the mark.
All the other reagents were prepared by diluting stock solutions with distilled water in appropriate volumetric flasks.

0.1 M Ce(IV) in 0.5 M sulfuric acid was prepared by dissolving 63.6 grams of ceric ammonium sulfate in 28.2 ml of concentrated sulfuric acid and 300 ml distilled water in 1000 ml volumetric flask and completing the total volume to 1000 ml with distilled water. The solution was left overnight and then used for the preparation of different solutions by dilution with distilled water and 1 M sulfuric acid.

0.05 M Fe(II) was prepared by dissolving in 19.6 grams of ferrous ammonium sulfate six water in 28.2 ml of concentrated sulfuric acid and 300 ml of distilled water in 1000 ml volumetric flask and then completed to the mark to have the final concentration. The solution was left overnight and then used for the preparation of solutions in different concentrations by using distilled water and sulfuric acid.

**ii) Electrodes**

A pair of platinum electrodes were used for the experiments. The platinum electrodes were SargentWelch type 30-415 and 30-415 respectively. They were cleaned with concentrated sulfuric and/or nitric acid before each experiment as a pre treatment, rinsed with distilled deionized water and placed in the cell.

**iii) Cell**

In the major part of the experiment the reactor consists of one line manifold as shown in Fig.6 made of glass and combined with a coiled tube formed using a plastic tube of 25 cm
length and 1.14 mm in inner diameter around a rigid cylinder of diameter 0.7 cm was used. It was linked to the detector made of Teflon in the form of a cylinder of 3 cm in length where the two electrodes are placed 0.5 cm far from each other. For the lower detection of Fe(II) two line manifold reactor was used.

iv) General Measuring Conditions

The optimum conditions were determined experimentally. For $10^{-4}$ to $15 \times 10^{-4}$ M samples of Fe(II) in 0.05 M sulfuric acid, a volume of 140 μl of samples were injected through the injection port.

The samples were injected to the carrier of 0.001 M Ce(IV) in 0.05 M sulfuric acid.

For the detection of Fe(II) in $10^{-5}$ M range standard addition method was used. 10$^{-4}$ M of Fe(II) in 0.05 M sulfuric acid was added to all samples adjusting the final acidity to 0.05 M sulfuric acid using 1M sulfuric acid.

For the detection of 10-6 M Fe(II), Ce(IV) concentration was decreased to $10^{-5}$ M. The acidity of this solution was maintained at $5 \times 10^{-3}$M.
3.3.2 Precipitation Reactions

3.3.2.1 Chloride Analysis

i) Chemicals and Reagents

Thorn Smith Standard Sodium Chloride was used to prepare chloride ion solutions. Analar Sodium Nitrate and Potassium Nitrate were used to prepare supporting electrolyte solutions. Fisher Scientific Company hydrochloric acid and Baker Analyzed nitric acid were used for the required purposes. Fluka Iron(III) Chloride was used for the preparation of the solution that is required in the plating of silver electrodes with silver chloride. Fluka Silver Nitrate was used for the preparation of silver nitrate solution. Degussa Mercury was used for the preparation of amalgamated electrode.

0.01 M chloride solution was prepared by dissolving 0.585 grams of sodium chloride using distilled de ionized water in 1000 ml volumetric flask. Corresponding 10⁻⁴ M chloride solutions were prepared by diluting the required proper amount hundred times in 100 ml volumetric flasks using distilled de ionized water. 0.01 M chloride solution was diluted ten times with distilled de ionized water in 100 ml flask to give 10⁻³ M chloride solution and then the required amount from this solution was used for the preparation of 10⁻⁵ M of chloride. 0.8494 grams of silver nitrate was dissolved in distilled de ionized water and the final volume made up to 500 ml to give 0.01 M silver nitrate stock solution. The stock
solution was diluted 10 and 100 times with distilled de ionized water to produce $10^{-3}$ M and $10^{-4}$ M silver nitrate solutions respectively.

0.845 grams of sodium nitrate was dissolved in 100 ml of distilled de ionized water in 1000 ml volumetric flask and then completed till mark with distilled de ionized water to produce 0.01 M supporting electrolyte solution. Potassium nitrate supporting electrolyte solution was prepared in the same way by dissolving 1.01 grams of potassium nitrate instead of 0.845 grams of sodium nitrate.

0.5 M Iron(III) chloride solution was prepared by dissolving 8.11 grams of Iron(III) chloride in 8.06 ml of concentrated hydrochloric acid and 50 ml of distilled de ionized in 100 ml flask then completing till the mark with distilled de ionized water.

6 M nitric acid was prepared by diluting 49.7 ml of concentrated nitric acid with distilled de ionized water to 100 ml.

Aqua regia was prepared by mixing one part of concentrated hydrochloric acid with three parts of concentrated nitric acid.
ii) Electrodes

a) Silver Electrodes

Silver wire electrodes were used in the halide analysis. They were cleaned with 6 M nitric acid as a pre treatment before each experiment. The electrodes then were rinsed with distilled de ionized water and placed in the cell.

b) Silver/Silver Chloride Electrodes

Silver/Silver chloride electrodes were prepared by surface oxidation of silver electrodes in 0.5 M Fe(III) chloride solution which was found more effective than the traditional anodic oxidation process (36). The electrode was immersed in the solution, left overnight then rinsed with distilled de ionized water and placed in the cell.

c) Platinum Electrodes

The platinum electrodes were SargentWelch type 30-415 and 30-415 respectively. They were cleaned with concentrated sulfuric and/or nitric acid before each experiment as a pre treatment, rinsed with distilled de ionized water and placed in the cell.

d) Platinum/ Mercury amalgamated electrode

Platinum electrode was cleaned by dipping in boiling aqua regia and then rinsed with
distilled de ionized water. It was immediately immersed into pure mercury for thirty seconds, rinsed and placed in the cell.

iii) Cell

A two line manifold was used as shown in Fig.6. Silver nitrate solution was passed from one line and supporting electrolyte from the other. The reactor was the same as described in Fe(II) and Ce(IV) system. The detector was changed to a transparent plastic cube instead of a Teflon cylinder that enables the visual control of the flowing of the solutions and the electrodes were introduced into holes designed on it.

iv) General Measuring Conditions

All optimum conditions were determined experimentally. For the analysis with silver electrodes 140 μl of samples were injected while for the rest 100 μl were chosen as sample volume.

3.3.2.2 Bromide Analysis

i) Chemicals and Reagents

Fluka Sodium Bromide was used to prepare bromide solution. 0.01 M bromide solution was prepared by dissolving 1.03 grams of sodium bromide in 1000 ml volumetric flask using 100 ml of distilled de ionized water and then completing till
the mark with distilled de ionized water. Corresponding $10^{-4}$ M solutions were prepared by dilution as described in the chloride solution preparation.

Supporting electrolyte solutions were the same as in chloride analysis. They were prepared in the same way as described previously.

Silver nitrate solution used was prepared in the same way as described in the chloride analysis.

\textbf{ii) Electrodes}

A pair of silver electrodes were used. They were the same electrodes used in chloride analysis.

\textbf{iii) Cell}

The same cell was used as described in the chloride analysis.

\textbf{iv) General Measuring Conditions}

The optimum conditions were determined experimentally. A 140 μl of bromide sample solutions were injected.
3.3.2.3 Iodide Analysis

i) Chemicals and Reagents

Fluka Sodium iodide was used to prepare iodide solution. 0.01 M iodide solution was prepared by dissolving 1.498 grams of sodium iodide in 1000 ml volumetric flask using 100 ml of distilled de ionized water and then completing till the mark with distilled de ionized water. Corresponding $10^{-4}$ M and $10^{-5}$ M solutions were prepared as described in the chloride solution preparation.

Supporting electrolyte solutions were the same as in chloride analysis. They were prepared in the same way as described previously.

Silver nitrate solution used was prepared in the same way as described in the chloride analysis.

ii) Electrodes

Silver and platinum electrodes were used for the analysis. They were the same electrodes used in chloride analysis.

iii) Cell

The same cell was used as described in the chloride analysis.
iv) General Measuring Conditions

All optimum conditions were determined experimentally. For the analysis with silver electrodes 140 µl of samples were injected while for the rest 100 µl were chosen as sample volume.
Chapter 4

RESULTS and DISCUSSION

4.1 DEP Titrimetry

4.1.1. Microtitration of Nitrite with Pb(IV)

Pb(IV) is a strong oxidizing agent (37) and prepared from lead tetraacetate and the potential of Pb(IV)/Pb(II) couple can be shown as

\[
Pb(CH_3COO)_4 + 4 H^+ + 2 e^- \rightarrow Pb^{2+} + 4 CH_3COOH
\]

where the potential depends on pH (38). The standard solution of Pb(IV) was commonly used in strongly acidic media for iron and titanium determination (39) in almost neutral 1 M or 0.1 M sodium chloride solution for the determination of nitrite (40).

Nitrite can be easily oxidized by strong oxidizing agents. The nitrate/nitrite potential couple can be shown as

\[
NO_3^- + 2 H^+ + 2 e^- \rightarrow NO_2^- + H_2O
\]

The chemistry involved in the titration of nitrite samples with Pb(IV) can be summarized as follows. At the early stages of the titration, dissolved oxygen reduces at cathode and nitrite oxidizes at anode i.e.

\[
cathode : O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O
\]

\[
anode : NO_2^- + H_2O \rightarrow NO_3^- + 2 H^+ + 2 e^-
\]
At the equivalence point there will be no nitrite and Pb(IV) but nitrate and Pb(II) i.e.

$$\text{NO}_2^- + \text{Pb(CH}_3\text{COO)}_4 + 2 \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Pb}^{+2} + 4 \text{CH}_3\text{COOH} + \text{NO}_3^-$$

Then the anode reaction changes to oxidation of Pb(II) to Pb(IV) i.e.

anode: $\text{Pb}^{+2} + 4 \text{CH}_3\text{COOH} \rightarrow \text{Pb(CH}_3\text{COO)}_4 + 4 \text{H}^+ + 2 \text{e}^-$

A potential difference will develop due to this change where the peak will reach to its maximum height.

Beyond the equivalence point there will excess Pb(IV) which will make the potential of cathode similar to that of anode.

For more concentrated sample solutions higher currents should be applied and the resulting peak is shown in Fig.7 but for dilute solutions the current should be decreased as shown in Fig.8 otherwise the potential jump decreases. This becomes clear when peaks are compared as shown in Fig.9.

$10^{-6}$ M nitrite was found to be determined easily by applying lower currents although the equilibration time for electrodes were slower. The sample volume was relatively small for real titration i.e. 1 ml in this case and the use of computer controlled injector gave the opportunity to titrate $10^{-6}$ M nitrite with $10^{-3}$ M Pb(IV). The titration system was found to be a rapid and sensitive technique for nitrite determination.
Fig 7 Titration of 10-3 M Nitrite
Sample Size 1 ml
Current 1.0 μA
Fig 8  Titration of 10-5 M Nitrite
Sample Size 1 ml
Current 0.3 µA
Fig 9 (a) Titration of 10-6 M Nitrite
Sample Size 1 ml
Current 0.17 μA
Fig 9 (b) Titration of 10-6 M Nitrite
Sample Size 1 ml
Current 0.5 μA
4.1.2 Microtitration of Vitamin C with Ce(IV)

It is known that Ce(IV) (41) is one of the most common titrant and strong oxidizing agent used for years. The solution once prepared is very stable hence it is reliable titrant solution. Ce(IV)/Ce(III) couple is a reversible system

\[
Ce^{4+} + e^- \rightarrow Ce^{3+}
\]

where the potential depends on pH and Ce(IV) is a more powerful oxidizing agent in strongly acid media.

Vitamin C, known also as ascorbic acid, is a very unstable compound and can be easily oxidized in acidic solutions to its dehydro form. Vitamin C/Dehydro Vitamin C couple can be shown as

\[
C_6H_6O_6 + 2H^+ + 2e^- \rightarrow C_6H_8O_6
\]

So Ce(IV) solution is a suitable titrant for the determination of vitamin C in acidic media and many organic substances do not interfere.

The chemistry involved can be summarized as follows. At early steps of the titration of vitamin C solutions with Ce(IV) titrant, the reduction of dissolved oxygen occurs at cathode and the oxidation of vitamin C at anode i.e.

- Cathode: \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \)
- Anode: \( C_6H_6O_6 + 2H^+ + 2e^- \rightarrow C_6H_8O_6 \)

At equivalence point, there will be no more vitamin C and Ce(IV) but Ce(III) and dehydro vitamin C i.e.

\[
Ce^{4+} + C_6H_8O_6 \rightarrow Ce^{3+} + C_6H_6O_6 + 2H^+
\]

Hence the anode reaction changes to the oxidation of Ce(III) to Ce(IV) i.e.

- Anode: \( Ce^{3+} \rightarrow Ce^{4+} + e^- \)
This will cause a big potential difference and the peak will reach to its maximum height. Beyond the equivalence point there will be excess Ce(IV) ions in the medium which will put the potential of cathode to a value similar to anode potential.

Theory predicts that the current applied should be low for dilute solutions. This was experimentally confirmed. For 100 ppm solutions of vitamin C the optimum current was found to be 1 μA. The titration result is shown in Fig.10. However the same current was found to be completely inconvenient for 1 ppm solutions of vitamin C. Instead 0.3 μA was experimentally suitable. The titration result is shown in Fig.11.

The system was found to be suitable for quick determination of vitamin C. For dilute samples, since lower currents were applied, the equilibration time for electrodes was found to be slower but still much more faster than the zero current conditions. This does not cause a disadvantage when the sensitivity of the system was considered.

The use of computer controlled injector gave the opportunity to titrate dilute solutions with highly concentrated titrant solutions and keep the sample solution volume relatively smaller i.e. 1 ml for this case. The change in concentration for titrant solution that can be produced from its dilution was also eliminated.
Fig 10  Titration of 100 ppm Vitamin C
Sample Size 1 ml
Current 1 μA
Fig: Titration of 1 ppm Vitamin C
Sample Size 1 ml
Current 0.2 μA
4.2 DEP Detector in FIA

4.2.1 Oxidation Reduction Reactions

4.2.1.1 Vitamin C -- Ce(IV) System

The design of the reactor was the main problem to be solved for the work. Sample size that is injected should be very precise and reproducible so that the reproducibility of the reactor has to be considered further. As mentioned in experimental section a computer controlled injector was used for this purpose and this requirement was obtained. The peaks obtained using this injector were highly reproducible as shown in Fig.12 compared with those obtained with convectional system in Fig.13. Many different types of cell (straight tubes or mixing chambers) were used but resulted in non reproducible peaks. When coiled tubes were used the results obtained were very good due to the proper mixing as a consequence of radial geometry.

The reaction between vitamin C and Ce(IV) is observed from many aspects. The chemistry involved can be summarized as follows. Before the injection of the vitamin C sample solution the reduction of Ce(IV) to Ce(III) occurs at cathode and consecutive oxidation of Ce(III) back to Ce(IV) at anode which results in a stable base potential for the system i.e.

\[
\text{cathode: } \text{Ce}^{+4} + e^- \rightarrow \text{Ce}^{+3} \\
\text{anode: } \text{Ce}^{+3} \rightarrow \text{Ce}^{+4} + e^-
\]

When the sample is injected, vitamin C begins to react with Ce(IV) while diffusing so Ce(III) and dehydrovitamin C are formed i.e.
Fig 12  Recorder Trace

Peaks obtained using traditional injection systems
Fig 13  Recorder Trace

Peaks obtained using computerized injector
2 Ce⁴⁺ + Vitamin C $\rightarrow$ 2 Ce³⁺ + dehydr vitamin C + 2H⁺

This zone reaches the detector and the anode reaction changes to oxidation of the solvent which is water i.e.

anode: 2 H₂O $\rightarrow$ O₂ + 4H⁺ + 4 e⁻

while the cathode reaction remains the same. As a result a potential difference arises which results in the form of a peak. After the zone passed from the detector, coming Ce(IV) ions change the base potential to its initial value.

In the first part of the experiment vitamin C samples were injected into Ce(IV) carrier. For the optimization of the system, one parameter was changed while the other were kept constant. First current effect was analyzed. The applied current is considered to be one of the most important factor that affects both the peak height and the peak shape. The electrodes are active within a certain range. At low currents, electrodes lose their activity or their equilibration becomes very long.

As a consequence the peak height is small and it is broad or at extremely low currents it is absent. At high currents drift from the baseline becomes greater and the charging current is effective. Theory predicts the increase of peak height with increase in current which was also found experimentally true. Recorder trace and current -- peak height relation is shown at Fig.14.

Similarly the effect of flow rate was analyzed. Actually flow rate indicates the residence time of sample in the system. As flow rate decreases the peak height increases and so does diffusion in any other detector system resulting in broadening of the peaks. This is completely true for the new detector as well. At low flow rates the return to baseline is also very slow. At high flow rates peaks become sharper in the expense of their heights.
Fig 14 (a) Recorder Trace

Flow Rate 0.93 ml/min

140 μL of 10 ppm Vitamin C injected

in 10-3 M Ce(IV) in 0.5 M Sulfuric acid

a) 0.3 μA  b) 0.5 μA  c) 1.0 μA  d) 1.5 μA  e) 2.0 μA  f) 3.0 μA
Fig 14b Current-peak height relation
Flow Rate 0.93 ml/min
140 μL of 10 ppm Vitamin C injected in
10-3 M Ce(IV) in 0.5 M sulfuric acid
Fig.15 shows the recorder trace and plot of flow rate versus peak height. After the optimization of conditions calibration graph and recorder trace are shown in Fig.16. The calibration curve was linear as expected however the differentiation for the peaks in different concentration was not very good. Diluting Ce(IV) solution to detect lower concentrations of vitamin C, as shown in Fig.17, did not give good results due to the effect of acid concentration in the medium which was discussed later.

Since its concentration is quantitatively less than Ce(IV) concentration, passing a known concentration of vitamin C does not change the approach mentioned above except the concentration of Ce(IV) in the medium.

Although the completion of a reaction is not the aim in the flow injection analysis, passing a known concentration of vitamin C from a second line is preferred since the direct injection of vitamin C in Ce(IV) carrier was not found very sensitive as mentioned above. Actually this has similar effects as standard addition. Standard addition method has only the advantage to increase the concentration of the sample. However passing a known concentration of vitamin C for is superior in the sense to decrease the concentration of the carrier Ce(IV) so that the peaks obtained from different concentrations differentiate better.

Since its concentration is quantitatively less than Ce(IV) concentration, the theoretical approach on electrode reactions will not change.

So in the second part of the experiment, the manifold used as reactor was changed from one line system to two lines one and 20 ppm of vitamin C was passed from this second line. Similarly the current effect on the system were analyzed as shown in Fig.18. The experimental results were alike as in the absence of vitamin C carrier with better sensitivity obtained as shown in calibration graph and recorder trace in Fig.19.
Fig 15  a. Recorder Trace

Current 1.5 μA

140 μL of 10 ppm Vitamin C injected in 10-3 M Ce(IV) in 0.5 M Sulfuric acid

Flow Rate  a) 0.55 ml/min  b) 0.93 ml/min  c) 1.17 ml/min  d) 1.26 ml/min
Fig 15b Flow rate - peak height relation

Current 1.52 μA
140 μL of 10 ppm Vitamin C injected in
10-3 M Ce(IV) in 0.5 M sulfuric acid
Fig 16a  Recorder Trace

Current 1.52 µA  Flow Rate 0.93 ml/min

140 µL of sample injected in 10-3 M Ce(IV) in 0.5 M Sulfuric acid
a) blank  b) 10 ppm  c) 20 ppm  d) 30 ppm  e) 50 ppm  f) 70 ppm
Fig 16b Calibration Curve
Current 1.52 μA Flow Rate 0.93 ml/min
140 μL of samples injected in
10-3 M Ce(IV) in 0.5 M Sulfuric acid
Fig 17  Recorder Trace
Current 1 \( \mu \text{A} \)  Flow Rate 0.93 ml/min
140 \( \mu \text{L} \) of \( x \) ppm Vitamin C injected in
10-4 M Ce(IV) in 0.5 M sulfuric acid
\( x : \) a) blank b) 1 c) 3 d) 5 e) 7
Fig 18a  Recorder Trace

Flow Rate 0.93 ml/min

140 μL of sample injected in 20 ppm Vitamin C

Other line 10-3 M Ce(IV) in 0.5 M Sulfuric acid

a) 0.1 μA  b) 0.2 μA  c) 0.3 μA  d) 0.4 μA  e) 0.5 μA  f) 0.6 μA  g) 0.8 μA
Fig 18b Current - Peak height Relation
Flow Rate : 0.93 ml/min
140 µL injected of 10 ppm vitamin C
injected in 20 ppm vitamin C
The other line 10-3 M Ce(IV) in 0.5 M sulfuric acid
Fig 19a  Recorder Trace

Current 0.5 μA  Flow Rate 0.93 ml/min
140 μL of sample injected in 20 ppm Vitamin C carrier
Other line 10-3 M Ce(IV) in 0.5 M Sulfuric acid
a) blank  b) 10 ppm  c) 20 ppm  d) 30 ppm  e) 40 ppm  f) 50 ppm  g) 60 ppm
Fig 156 Calibration Curve
  Current 0.5 µA  Flow Rate 0.93 ml/min
  140 µL of samples injected in 20 ppm vitamin C carrier
  Other line 10-3 M Ce(IV) in 0.5 M Sulfuric acid
The acidity of the medium is extremely important. The role of the acid is complex due to many reasons. First Ce(IV)/Ce(III) potential depends on the pH of the medium and precipitation of ceric hydroxides occur in low acid concentrations. Second, the platinum electrodes are affected by acid concentration since at low pH anodic platinum electrodes were almost completely deactivated (42). The third function of the acid is that it acts as supporting electrolyte. The final effect of pH is on the oxidation rate of vitamin C since in highly acidic media the oxidation of vitamin C is retarded. Each of these functions have important consequences. In the first and second part of the experiment the lower sensitivity obtained was also due to the acid concentration. Lowering acid concentration to the extent that precipitation would not occur - that was 0.05 M sulfuric acid - resulted in an important change in the peak height. The effect of the pH on peak height is shown in Fig.20.

In the third part of the experiment the acid concentration was lowered and the parameters were re-established. The current and flow rate effects on the system are shown in Fig.21 and Fig.22 respectively where the experimental results were the same as obtained in previous parts but with higher sensitivity and resolution when the calibration curve was considered as shown in Fig.23.

For the detection of lower concentration of vitamin C the sample volume that is injected in the medium was increased. The calibration graph and recorder trace are shown in Fig.24.

Using same approach for the detection of higher concentration of vitamin C the lowest acid concentration found to be 0.25 M. The current and flow rate effects on the system
Fig 20a  Recorder Trace

Current 0.5 μA  Flow Rate 0.93 ml/min

140 μL of sample injected in 20 ppm Vitamin C carrier

Other line 10-3 M Ce(IV) in x M Sulfuric acid

x : a) 0.05  b) 0.1  c) 0.5
Fig. 20b: Acidity-peak height relation
Current 0.5 μA  Flow Rate 0.93 ml/min
140 μL of 10 ppm Vitamin C injected in 20 ppm Vitamin C carrier
Other line 10-3 M Ce(IV) in different acid concentration
Fig 21: Recorder Trace

Flow Rate 0.93 ml/min

140 μL of sample injected in 20 ppm Vitamin C

Other line 10-3 M Ce(IV) in 0.05 M Sulfuric acid

a) 0.1 μA  b) 0.3 μA  c) 0.5 μA  d) 0.6 μA  e) 0.8 μA  f) 1.0 μA  g) 1.5 μA
Figure 2.4: Current - Peak Height Relation
Flow Rate 0.93 ml/min
140 μL of 10 ppm Vitamin C injected in 20 ppm Vitamin C
Other line 10-3 M Ce(IV) in 0.05 M sulfuric acid
Fig 2a. Recorder Trace

Current 0.5 μA

140 μL of sample injected in 20 ppm Vitamin C

Other line 10-3 M Ce(IV) in 0.05 M Sulfuric acid

Flow Rate  a) 0.23 ml/min b) 0.55 ml/min c) 0.93 ml/min d) 1.17 ml/min
Fig 22b  Flow rate and peak height relation
Current 0.5 μA
140 μL of 10 ppm injected  Vit C in 20 ppm Vitamin C carrier:
Other line 10-3 M Ce(IV) in 0.05 M sulfuric acid
Fig 23. Recorder Trace

Current 0.5 μA  Flow Rate 0.93 ml/min
140 μL of sample injected in 20 ppm Vitamin C
Other line 10-3 M Ce(IV) in 0. M Sulfuric acid
a) blank  b) 10 ppm  c) 30 ppm  d) 50 ppm  e) 70 ppm  f) 90 ppm
Fig 23b Calibration Graph
Current 0.5 μA  Flow Rate 0.93 ml/min
140 μL of samples injected in 20 ppm Vitamin C in carrier
Other line 10-3 M Ce(IV) in 0.05 M sulfuric acid
Fig 24a. Recorder Trace

Current 0.5 μA  Flow Rate 0.93 ml/min
200 μL of sample injected in 20 ppm Vitamin C
Other line 10-3 M Cs(IV) in 0.05M Sulfuric acid
a) blank  b) 1 ppm  c) 3 ppm  d) 5 ppm  e) 7 ppm  f) 9 ppm
Fig 24 Calibration Curve

Same conditions as indicated for high concentration range
200 μL of samples injected in the same vitamin C carrier
were shown in Fig.25 and Fig.26 respectively with similar results obtained in previous parts of the work. The recorder trace and calibration graph are shown in Fig.27.

The system was applied to the analysis of vitamin C in the pharmaceuticals. Final calibration is shown in Fig.28.
Fig 25a. Recorder Trace

Flow Rate 0.93 ml/min

140 μL of sample injected in 200 ppm Vitamin C

Other line 10-2 M Ce(IV) in 0.25 M Sulfuric acid

a) 1.02 μA  b) 1.52 μA  c) 2.32 μA  d) 4.06 μA  e) 4.52 μA
Fig 25. Peak height - current relation
Flow Rate 0.93 ml/min
140 µL of 100 ppm Vitamin C injected in 200 ppm Vitamin C
Other line 0.01 M Ce(IV) in 0.25 M sulfuric acid
Fig 26a  Recorder Trace

Current 0.5 μA

140 μL of sample injected in 200 ppm Vitamin C

Other line  10-2 M Ce(IV) in  0.25 M Sulfuric acid

Flow Rate  a) 0.55 ml/min  b) 0.93 ml/min  c) 1.17 ml/min  d) 1.26 ml/min
Fig 26: Peak Height - Flow Rate relation
Current 4 μA
140 μL of 100 ppm Vitamin C injected in 200 ppm Vitamin C carrier
Other line 0.01 M Ce(IV) in 0.25 M sulfuric acid
Fig 27. Recorder Trace

Current 4.0 μA  Flow Rate 0.93 ml/min

140 μL of sample injected in 200 ppm Vitamin C carrier

Other line 10-2 M Ce(IV) in 0.25 M Sulfuric acid

a) 100 ppm  b) 150 ppm  c) 200 ppm  d) 250 ppm  e) 300 ppm
Fig. 27: Calibration Graph

- Current 4 \( \mu \text{A} \), Flow Rate 0.93 ml/min
- 140 \( \mu \text{L} \) of samples injected in 200 ppm vitamin C carrier
- Other line 0.01 M Ce(IV) in 0.25 M sulfuric acid
Fig 28  Recorder Trace

Current 0.5 µA  Flow Rate 0.93 ml/min
100 µL of sample injected in 20 ppm Vitamin C
Other line  10-3 M Ce(IV) in 0.05 M Sulfuric acid
a) 10 ppm  b) 0 ppm  c) 0 ppm  d) 0 ppm  e) 0 ppm
f) Sample A  g) Sample B
4.2.1.2 Fe(II) -- Ce(IV) System

The chemistry involved can be summarized as follows. Before the injection of the Fe(II) sample into the Ce(IV) carrier the reduction of Ce(IV) to Ce(III) occurs at the cathode and consecutive Ce(III) oxidation to Ce(IV) at the anode i.e.

\[
\text{cathode : } \text{Ce}^{+4} + e^- \longrightarrow \text{Ce}^{+3} \\
\text{anode : } \text{Ce}^{+3} \longrightarrow \text{Ce}^{+4} + e^-
\]

When the Fe(II) samples are injected, Ce(III) and Fe(III) will form while the injected zone diffuses toward the detector i.e.

\[
\text{Ce}^{+4} + \text{Fe}^{+2} \longrightarrow \text{Ce}^{+3} + \text{Fe}^{+3}
\]

The cathode potential will change since Fe(III) will reduced instead of Ce(IV) i.e.

\[
\text{cathode : } \text{Fe}^{+3} + e^- \longrightarrow \text{Fe}^{+2}
\]

while the anode reaction remains constant. The resulting potential difference will cause the formation of the peak. The introduced Ce(IV) ions will change the cathode reaction hence the same initial base potential will be obtained.

The geometry and length of the reactor are considered to be the very important parameters since the physical parameter which is diffusion is influenced by the geometry of the cell. Straight tubes were used for fast reactions (43) since there is no need for prolonged mixing formed by coiled tubes, however for Fe(II) and Ce(IV) system the situation was found to be completely different. Due to improper mixing incomplete peaks doubled in opposite site were developed. This observation was found to be the same over a certain range of currents when other parameters were kept constant as shown in Fig.29.
Fig 29  Recorder Trace

Flow Rate 1.17 ml/min

140 μL of 10-4 M Fe(II) in 0.05 M sulfuric acid injected in 10-3 M Ce(IV) in 0.05 M Sulfuric acid
a) 0.5 μA  b) 0.8 μA  c) 1.0 μA  d) 1.5 μA
Coiled tubes in reactor system was found to be suitable. However longer tubes require high flow rates to establish a rapid equilibrium and quick return to baseline. Tests were made to find the optimum length which was found to be 25 cm.

After choosing proper dimensions for reactor geometry the parameters were adjusted in the same as described in vitamin C case.

At low currents the peaks are completely in reverse direction due to the insufficient electrolysis. While increasing the current changed the direction. However they are very broad at relatively low currents. The best working range was found to be 1.52 - 1.90 μA.

At high currents the peaks were found to loose their reproducibility due to the higher sensitivity of the electrodes and the drift from baseline was noted. The peak height was found to increase when the current increased for a certain range as theory predicts. The recorder trace and the plot of peak height versus current are shown in Fig.30.

Low flow rates are not suitable due to the slow equilibrium process. Some of the total peak occurred in the reverse direction. Increasing flow rate removed this observation. The best flow rate was found to be 1.17 ml per minute. The recorder trace and the plot of peak height versus flow rate are shown in Fig.31.

As the sample size increased peak height also increased since peak height is related to concentration as shown in Fig.32.

With these optimizations the calibration graph was found to be linear for the range of 3 × 10⁻⁴ - 10⁻³ M Fe(II) as shown in Fig.33.

For the concentration below 10⁻⁴ M Fe(II) standard addition method was required when the stoichiometry of the reaction was considered. 10⁻⁴ M Fe(II) was added into all
Fig. 3: Recorder Trace

Flow Rate 1.17 ml/min
140 μL of 10-4 M Fe(II) in 0.05 M sulfuric acid injected
in 10-3 M Ce(IV) in 0.05 M Sulfuric acid

a) 0.2 μA  b) 0.5 μA  c) 0.8 μA  d) 1.0 μA  e) 1.5 μA  f) 1.6 μA

 g) 1.9 μA  h) 2.3 μA  i) 2.5 μA
Fig 30b  Current - Peak height relation

Flow rate 1.17 ml/min
140 µL of 10-4 M Fe(II) in 0.05 M Sulfuric acid injected in 10-3 M Ce(IV) in 0.05 M Sulfuric acid
Fig 3: Recorder Trace
Current 0.5 μA

140 μL of 10-4 M Fe(II) in 0.05 M sulfuric acid injected in
10-3 M Ce(IV) in 0.05 M Sulfuric acid

Flow Rate  a) 0.23 ml/min  b) 0.55 ml/min  c) 0.93 ml/min  d) 1.17 ml/min  e) 1.26 ml/min
Fig 34-3 Flow rate peak height relation

Current 2.5 μA
10-4 M Fe(II) in 0.05 M sulfuric acid injected
in 10-3 Ce(IV) in 0.05 M sulfuric acid
Fig 32  Recorder Trace

Current 0.5 µA  Flow Rate 0.93 ml/min
x µL of 10-4 M Fe(II) in 0.05 M sulfuric acid injected in
10-3 M Ce(IV) in 0.05M Sulfuric acid
x:  a) 80 µL  b) 140 µL  c) 160 µL
Fig 33 a  Recorder Trace

Current 2.5 μA  Flow Rate 1.17 ml/min

140 μL of x 10⁻⁴ M Fe(II) in 0.05 M sulfuric acid injected in
10⁻³ M Ce(IV) in 0.05 M Sulfuric acid
Fig 12 Calibration Graph
Current 2.5 μA  Flow rate 1.17 ml/min
140 μL injected in 10-3 M Ce(IV) in 0.05 M sulfuric acid
samples keeping the final acidity of samples as 0.05 M sulfuric acid. The resulting calibration graph which was found to be linear is shown in Fig.34.

Acidity is one of the most important factors due to the same reasons mentioned in the case of vitamin C especially for the detection of lower concentration of Fe(II) samples. In addition Fe(III)/Fe(II) potential is also affected by pH of the medium and Fe(II) should be prepared in acidic media in order to prevent oxidation of Fe(II) to Fe(III). Although the concentration of Ce(IV) was decreased to stoichiometric amount for the reaction with Fe(II), the determination failed at $10^{-6}$ M. Also, the ratio of acid concentration to Fe(II) concentration is important since acid is when acting as supporting electrolyte put the electrodes in highly stable potential and any change in the potential is suppressed. So the acidity must be controlled to differentiate between the peaks in different concentrations.

As a result for the determination of Fe(II) samples in $10^{-6}$ M range the pH of the samples were adjusted with concentrated NaOH a decrease in peak height was observed with increasing the concentration as shown in Fig.35. This can be explained by oxidation of Fe(II) to Fe(III).

A buffer can also be used for acidity adjustment. An acidic buffer (acetic acid/sodium acetate) was tried for this purpose. The effects of current and flow rate change on peak height are shown in Fig.36 and Fig.37 respectively with no major change in experimental approach mentioned previously. The resulting calibration curve is shown in Fig.38.
Fig 34a  Recorder Trace

Current 2.5 μA  Flow Rate 1.17 ml/min

140 μL of x 10^-4 M Fe(II) in 0.05 M sulfuric acid injected in
10-3 M Ce(IV) in 0.. M Sulfuric acid

x : a) 1  b) 1.2  c) 1.4  d) 1.6  e) 1.8
Fig 14: Calibration graph
Same conditions mentioned for higher concentration samples
Fig. 35  Recorder Trace

Current 1.0 \mu A  Flow Rate 1:17 ml/min

140 \mu L of x M Fe(II) injected in
10-5 M Ce(IV) in 5 10-3 M Sulfuric acid

x : a) 1 b) 3 c) 5 d) 7 e) 9
Fig 36a  Recorder Trace

Flow Rate 1.17 ml/min

140 µL of 5 10-6 M Fe(II) injected

First line  10-5 M Ce(IV) in 5 10-3 M Sulfuric acid

Second line buffer solution

a) 0.2 µA  b) 0.5 µA  c) 0.8 µA  d) 1.0 µA  e) 1.3 µA  f) 1.5 µA
Fig 3. Current - peak height relation
Flow rate 1.17 ml/min
140 µL of 5 10^-6 M of Fe(II) injected
First line 10-5 M Ce(IV) in 5 10^-3 M Sulfuric acid
Second line buffer solution
Fig 37 - Recorder Trace

Current 1.5 µA

140 µL of 10-6 M Fe(II) injected

First line 10-3 M Ce(IV) in 0.05 M Sulfuric acid

Second line buffer solution

Flow Rate: a) 0.55 ml/min  b) 0.93 ml/min  c) 1.17 ml/min
Fig 37b: Flow rate - Peak Height relation

Current 1.5 µA
140 µL of 5 x 10^-6 M Fe(II) is injected
First line 10-5 M Ce(IV) in 5 x 10-3 M Sulfuric acid
Second line buffer solution
Fig 28a. Recorder Trace

Current 1.5 μA  Flow Rate 1.17 ml/min

140 μL of x 10^{-6} M Fe(II) injected

First line 10^{-5} M Ce(IV) in 5 10^{-3} M Sulfuric acid

Second line buffer solution

x : a) 1  b) 3  c) 5  d) 6  e) 7
Fig 38 Calibration graph

Current 1.5 μA  Flow rate 11.17 ml/min
140 μL of samples injected
First line 10 -5 M Ce(IV) in 5 10-3 M sulfuric acid
Second line buffer solution
4.2.2 Precipitation Reactions

The results and discussions are given according to the electrode pair used for the indicated analysis in the detector system.

4.2.2.1 Silver electrodes for Halide Analysis

Polarized silver electrodes are the ones that are used for the detection of halides and cyanide (44). The chemistry involved may be summarized as follows. Before the injection of the halide X where X is chloride, bromide or iodide the reduction of silver ion to silver metal occurs at cathode and oxidation of silver metal to silver ion at anode consequently i.e.

\[ \text{cathode: } \text{Ag}^+ + e^- \rightarrow \text{Ag} \]

\[ \text{anode: } \text{Ag} \rightarrow \text{Ag}^+ + e^- \]

However when the chloride sample is injected chloride ions will react with silver ions forming an insoluble precipitate while diffusing toward detector.

\[ \text{Ag}^+ + \text{X}^- \rightarrow \text{AgX} \text{ (ppt)} \]

So silver ion concentration will decrease and the insoluble precipitate will reduce at the cathode i.e.

\[ \text{cathode: } \text{AgX} + e^- \rightarrow \text{Ag} + \text{X}^- \]

Then the potential difference will form the peak. The introduced silver ions will normalize back the situation by changing the cathode potential to its initial value.
At low currents, the sensitivity of electrodes was found to be low and the currents higher than 0.8 µA were found to be not suitable for such systems. The current and peak height relation is shown in Fig.39. Peak height increases as theory predicts.

Peak broadening occurs at low flow rates although its height to be maximum. While increasing flow rate the peaks become sharper on the expense of the height due to decrease in the residence time of the sample. The recorder trace and the plot peak height versus flow rate are shown in Fig.40.

The calibration is linear as expected and shown in Fig.41 for samples in 1-9 $10^{-4}$ M of Cl⁻. However silver electrodes are not suitable for very dilute chloride analysis due to the solubility product of silver chloride and for lower range they were found to be inactive. Instead silver chloride coated siver electrodes are more convenient and preferred for chloride analysis.

Similarly silver electrodes can be used for the determination of bromide and iodide. Since AgBr and AgI are more insoluble than AgCl, silver electrodes behave better for bromide and iodide analysis. Instead silver chloride coated siver electrodes are more convenient and preferred for chloride analysis.

For the bromide analysis the current peak height relation is shown in Fig.42. The peak height was found to increase with increasing of current as predicted. The calibration graph was found to be linear for the indicated range as shown in Fig.43.

The analysis was performed with iodide samples in the same optimized conditions found for bromide analysis. Again the calibration was found to be linear as shown in Fig.44.
Fig 29 - Recorder Trace
Flow Rate 0.93 ml/min
140 μL of 10-4 M Cl- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
a) 0.2 μA  b) 0.4 μA  c) 0.6 μA  d) 0.8 μA  e) 1.0 μA
Fig 3a & b Current and peak height relationship
Flow rate 0.93 ml/min
140 µL of 10-4 M Cl- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
Fig 40-a  Recorder Trace

Current 0.6 μA

140 μL of 10-4 M Cl- injected

First line 10-3 M Silver nitrate

Second line 0.01 M Potassium nitrate

Flow Rate  a) 0.55 ml/min  b) 0.93 ml/min  c) 1.17 ml/min
Fig 44 Flow rate peak height relationship

Current 0.6 μA
140 μL of 10-4 M Cl- injected
First line 10-3 M Silver nitrate
Second line 0.01M Potassium nitrate
Fig 4.1 a Recorder Trace

Current 0.6 µA  Flow Rate 0.93 ml/min

140 µL of x 10⁻¹ M Cl⁻ injected

First line 10⁻³ M Silver nitrate

Second line 0.01 M Potassium nitrate

x : a) 1  b) 3  c) 5  d) 6  e) 7  f) 9
Fig 4.1b Calibration graph
Current 0.6 μA  Flow rate 0.93 ml/min
140 μL of samples injected
First line 10-3 M  Silver nitrate
Second line 0.01 M  Potassium nitrate
Fig 42a  Recorder Trace

Flow Rate 0.93 ml/min

140 \( \mu \)L of 10-4 M Br- injected

First line  10-3 M Silver nitrate

Second line  0.01 M Potassium nitrate

a) 0.2 \( \mu A \)  b) 0.4 \( \mu A \)  c) 0.6 \( \mu A \)  d) 1.0 \( \mu A \)
Fig 42b Current peak height relation

Flow rate 0.93 ml/min
140 μL of 10-4 M Br- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
Fig 4.3a  Recorder Trace
Current 0.6 µA  Flow Rate 0.93 ml/min
140 µL of x 10-4 M Br- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
x : a) 1  b) 3  c) 5  d) 6  e) 7  f) 10
Fig 43: Calibration graph
Current 0.2 \mu A Flow rate 0.93 ml/min
140 \mu L of samples injected
First line 10^{-3} M Silver nitrate
Second line 0.01 M Potassium nitrate
Fig 44a  Recorder Trace
Current 0.2 µA  Flow Rate 0.93 ml/min
140 µL of x 10-4 M I- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
x : a) 1  b) 3  c) 5  d) 6  e) 7  f) 9
Fig. \textit{b} Calibration Graph

0.2 \( \mu \)A Flow rate 0.93 ml/min
140 \( \mu \)L of samples injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
4.2.2.2 Platinum-Silver Electrode Pair for Iodide Analysis

Polarized platinum electrode pair was also used for chloride analysis with standard silver nitrate reagent (45). The response of the platinum electrode can be explained by adsorption of silver chloride precipitate on the platinum surface. Similarly iodide can also be determined using the combination of Pt and Ag electrodes.

Before the injection of sample into silver nitrate carrier, the reduction of silver ions to silver metal occurs at the cathode and consequently silver metal oxidizes to silver ions at the anode i.e.

\[
cathode \text{(platinum)}: \quad \text{Ag}^+ + e^- \rightarrow \text{Ag} \\
anode \text{(silver)}: \quad \text{Ag} \rightarrow \text{Ag}^+ + e^-
\]

When the sample containing iodide is injected into silver nitrate carrier silver ion concentration will decrease as result of the formation of insoluble silver iodide precipitate while diffusing toward the detector.

\[
\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}
\]

The cathode reaction changes from the reduction of silver ions to metallic silver to silver iodide reduction i.e.

\[
\text{AgI} + e^- \rightarrow \text{Ag} + \text{I}^-
\]

As a consequence a potential difference will arise between the cathode and the anode which will be reflected in the form of a peak. Here the benefit of platinum electrode use is that its response is expected to be slower to silver ions than that of silver electrode. So the potential difference between the anode and cathode are expected to be higher and this was verified experimentally.
The current peak height relation is shown in Fig.45. Similar behavior was obtained as mentioned in previous case. The calibration graph was found to be linear as shown in Fig.46.
Fig 45-α Recorder Trace

Flow Rate 0.93 ml/min
100 μL of 3 × 10⁻⁵ M I⁻ injected
First line 10⁻⁴ M Silver nitrate
Second line 0.01 M Sodium nitrate

a) 0.5 μA  b) 1.0 μA  c) 3.0 μA  d) 4.0 μA
Fig 45b Current - Peak Height relation
Flow Rate 0.93 ml/min
100 μL of 3 10^-5 M I- injected
First line 10-4 M Silver nitrate
Second line 0.01 M Sodium nitrate
Fig 46a  Recorder Trace

Current 3.5 μA  Flow Rate 0.93 ml/min

100 μL of x 10−5 M I− injected

First line 10-4 M Silver nitrate

Second line 0.01 M Sodium nitrate

x : a) 1  b) 3  c) 5  d) 6  e) 7  f) 9  g) 15  h) 25
Fig 4b. Calibration graph
Current 3.5 μA Flow Rate 0.93 ml/min
100 μL of samples injected
First line 10-4 M Silver nitrate
Second line 0.01 M Sodium nitrate
4.2.2.3 Platinum - Silver/Silver Chloride Electrode Pair for Chloride Analysis

Alternatively silver halide coated electrodes can substitute silver electrodes and even their sensitivity is better (46). However their lifetime is limited especially for silver bromide and silver iodide coated electrodes, being 48 hours only for the latter. Since silver electrode performance and sensitivity are suitable for bromide and iodide only silver chloride coated silver electrodes were substituted for chloride analysis.

One of the most important facts about the silver chloride coated electrode is that the electrode will loose its coating while it is being polarized cathodically after a certain period of time. It is known that this electrode is always used as anode since the anode responds to chloride due to the reaction $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$. Polarized platinum electrode pair was also used for chloride analysis with standard silver nitrate reagent. The response of the platinum electrode can be explained by adsorption of silver chloride precipitate on the platinum surface. It is then possible to make a combination of platinum and silver/silver chloride electrode platinum being cathode. Combining these facts, a pair of platinum and silver/silver chloride electrodes can also be used for the determination of chloride.

Before the injection of chloride into the silver nitrate stream anodic and cathodic reactions can be summarized as follows.

\[
\text{cathode : } \text{Ag}^+ + e^- \rightarrow \text{Ag} \\
\text{anode : } \text{Cl}^- + \text{Ag} \rightarrow \text{AgCl} + e^- \\
\text{since } \text{AgCl} \rightarrow \text{Ag}^+ + \text{Cl}^- *
\]
When the sample is injected silver ion concentration will decrease since silver ions will precipitate with chloride ions and the equilibrium will shift to right. As a result chloride ion concentration in the precipitate that is on the surface of electrode.

The potential difference will develop between the anode and the cathode. Hence the peak will arise. Introduced silver ions will normalize the potential back to its initial value and the base potential is restored.

The current and peak height relation was shown in Fig.47. The peak height was found to increase with increasing current.

The calibration was found to be linear as shown in Fig.48.
Fig 47b  Recorder Trace
Flow Rate 0.93 ml/min
100 µL of 4 ppm Cl- injected
First line  10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
a) 0.2 µA  b) 1.0 µA  c) 2.0 µA  d) 3.0 µA  e) 4.0 µA
Fig 4. Peak height - Current Relation
Flow rate 0.93 ml/min
100 μL of 4 ppm Cl- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
Fig 42a  Recorder Trace

Current 2.0 μA  Flow Rate 0.93 ml/min
100 μL of x ppm Cl- injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
x : a) 1.8  b) 4.2  c) 18.2  d) 29.8  e) 42.7  f) Sample A  g) Sample B
Fig 4.4. Calibration Graph

Current 2 µA  Flow rate 0.93 ml/min
100 µL of samples injected
First line 10-3 M Silver nitrate
Second line 0.01 M Potassium nitrate
4.2.2.4 Platinum-Mercury Amalgam Electrode and Silver/Silver Chloride Electrode For Chloride Analysis

In the same way the different combination of electrodes can be applied. Silver/silver chloride can be combined with mercury amalgam electrode.

The chemistry can be summarized as follows. Before the injection of the chloride sample into silver nitrate stream the expected reactions are

- **cathode**: \(2 \text{ Hg} + 2 \text{ Ag}^+ \rightarrow \text{Hg}_2^{+2} + 2 \text{ Ag}\)
- **anode**: \(\text{Cl}^- + \text{ Ag} \rightarrow \text{AgCl} + e^-\)
  \(\text{AgCl} \rightarrow \text{Ag}^+ + \text{ Cl}^-\)

When the sample that contains chloride is injected, the precipitation of silver chloride will occur while diffusing toward the detector. The anodic response will change as a result of chloride concentration change on the coated surface of silver/silver chloride electrode. There will be a change in the cathodic change as well since mercurous ion will also respond to chloride ion according to the following reaction:

\[
\text{Hg}_2^{+2} + 2 \text{ Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2
\]

The potential difference will arise and it will form the peak. Introduced silver ions will normalize the potential back to its initial value.

The current peak height relation and the calibration graph are shown in Fig.49 and Fig.50 respectively.
Fig 49 a  Recorder Trace

Flow Rate 0.93 ml/min
100 μL of 4.5 ppm Cl- injected
First line 10-3 M Silver nitrate
Second line 0.1 M Potassium nitrate
a) 0.1 μA  b) 0.3 μA  c) 1.2 μA  d) 1.5 μA  e) 2.0 μA
Fig 4.4 Current - peak height relation
Flow rate 0.93 ml/min
100 μL of 4.5 ppm Cl- injected
First line 10-3 M Silver nitrate
Second line 0.1 M Potassium nitrate
Fig 50a Recorder Trace

Current 2.0 μA  Flow Rate 0.93 ml/min
100 μL of x ppm Cl- injected
First line 10-3 M Silver nitrate
Second line 0.1 M Potassium nitrate
x : a) 1.8  b) 3.0  c) 18.2  d) 29.8  e) 42.7
Fig 76b Calibration graph
Current 2 \mu A Flow rate 0.93 ml/min
100 \mu L of samples injected
First line 10-3 M Silver nitrate
Second line 0.1 M Potassium nitrate
4.2.2.5 Silver/Silver Chloride Electrode Pair for Chloride Analysis

A different approach was developed for the chloride analysis. It was mentioned the chloride analysis in water samples without precipitation reaction but only by injecting the sample solution in the supporting electrolyte carrier and recording the change in potential between the silver/silver chloride anode and a reference cell (47). Although the method is simple, the response of the electrode changes due to the concentration of the sample being nerstian for concentration higher than 10 ppm and linear for lower than this concentration. Special precautions should be taken for the contamination of the carrier that comes from the reference electrode hence the use of a double junction reference electrode is required that can result in high junction potential.

The elimination of the reference electrode in DEP eliminates this problem and two polarized silver/silver chloride electrode was used for the experiment. A pair of silver/silver chloride coated electrode was used with one line reactor system where supporting electrolyte was passed. The recorder trace and calibration graph are shown in Fig.51. The relation was found to be nerstian since the electrode response is maintained constant at a certain concentration and the peak arises due to the difference in concentration between the carrier and sample content.

For the detection of lower concentration of chloride a two line manifold was used passing from one line a supporting electrolyte and a known concentration of chloride from the other. The latter is beneficial to prevent the electrode to be vacuum (48). The calibration graph was found to be linear as shown in Fig.52.
Fig 51 a Recorder Trace

Current 0.8 µA  Flow Rate 0.93 ml/min

100 µL of x 10-4 M Cl- injected in 0.1 M Potassium nitrate

x : a) 3  b) 5  c) 7  d) 9  e) 15
Fig 5.1 Calibration graph
Current 0.8 μA Flow Rate 0.93 ml/min
100 μL of samples injected in 0.1 M potassium nitrate
Fig 52 a. Recorder Trace

Current 0.8 μA  Flow Rate 0.93 ml/min

100 μL of x 10-6 M Cl- injected in 10-4 M Cl- carrier

Other line 0.1 M Potassium nitrate

x : a) 70 b) 40 c) 20 d) 9 e) 1
Fig. 52.4  Calibration Graph
Current 0.8 µA  Flow Rate 0.93 ml/min
100 µL injected of samples in 10-4 M Cl- carrier
Other line 0.1 M potassium nitrate
In both cases using higher concentrations of supporting electrolyte is not advisable since it provides a high stability to the electrode's base potential, consequently the change in potential will be suppressed.

At high dilute solutions and in the absence of foreign electrolyte, possible functions of the current were mentioned to supply the charging current for the double layer capacitance, to provide the activation energy of charge transfer in addition to its normal function. It can be concluded that current has also similar task of supporting electrolyte and removing the supporting electrolyte from the medium resulted in perfectly stable base potential with non suppressed peak height. The relation between the peak height and concentration did not change and the calibration graph is shown in Fig.53.

However this was found to be not suitable for the application of the real samples without pretreatment since their ionic strength is much more higher.

The chemistry involved can be summarized as follows. Before the injection of chloride sample into the system the cathode and anode reactions are as follows.

- Cathode: \( \text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^- \)
- Anode: \( \text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + e^- \)

When the sample was injected chloride concentration will change as a result the potential difference will arise as a result of change in anode potential. Coming known concentration of chloride will normalize the base potential back to its initial value.
Fig 5.3a Recorder Trace

Current 0.3 μA  Flow Rate 0.93 ml/min

100 μL of x 10-6 M Cl- injected in 10-5 M Cl- carrier

a) 7  b) 20  c) 50  d) 100
Fig 53 b Calibration Graph

Current 0.05 μA Flow Rate 0.93 ml/min
100 μL of samples injected in 10-5 M Cl- carrier
4.2.2.6 Reference (Silver/Silver Chloride) Electrode and Silver/Silver Chloride Electrode for Chloride Analysis

It is known that selective (anodic or cathodic) polarization with respect to a reference cell give inaccurate results in the location of end point in DFP titrimetry (49). Since the completion of the reaction is not a requirement in the FIA, this method can be applied. Due to the fact that silver/silver chloride electrodes loose their coating after some time when they are polarized cathodically and the anode actually responds to chloride ion, anodic polarization was preferred. The cathode potential was remained unchanged throughout the experiment and the anode potential produced the change i.e.

\[ \text{anode: } \text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^- \]

The problem caused by supporting electrolyte in the previous case is solved by selective anodic polarization of the silver/silver chloride electrode with respect to the same type reference electrode taking precautions for the chloride contamination from the reference electrode.

The current behaviour was examined and it is shown in Fig.54. It is interesting that the peak height reaches its maximum while increasing the current but tends to decrease with further increase in current and this supresses the peak height. The working range for the current was found to be higher than the case where reference electrode was absent. However the technique was found to be improved when compared with the zero current case.

Similarly the flow rate peak height relation is shown in Fig.55. It was found that the decrease in peak height with the increase in flow rate which had no critical effect.
Fig 54a  Recorder Trace

Flow Rate 0.93 ml/min
100 µL of 4.5 ppm Cl- injected
First line  10-3 M Silver nitrate
Second line 0.1 M Potassium nitrate

a) 0.1 µA  b) 0.3 µA  c) 0.5 µA  d) 0.8 µA  e) 2.0 µA  f) no current
Fig 54b Current peak height relation
Flow rate 0.93 ml/min
100 μL of 18 ppm Cl- injected
First line 0.6 ppm Cl
Second line in 0.1 M potassium nitrate
Fig 55: Recorder Trace

Current 0.3 μA

100 μL of 4.5 ppm Cl- injected
First line 0.6 ppm Cl-
Second line 0.1 M Potassium nitrate
Flow Rate a) 0.23 ml/min  b) 0.93 ml/min  c) 1.26 ml/min  d) 2.2 ml/min
Fig 54 Flow rate peak height relation
Current 0.3 μA
4.5 ppm Cl- injected
First line 0.6 ppm Cl-
Second line 0.1 Potassium nitrate
The calibration is shown in Fig. 56. The relation between concentration and peak height was found to be Nernstian as expected for concentration higher than 10 ppm and linear for those lower than this value.
Fig 5.6a Recorder Trace

Current 0.3 μA  Flow Rate 0.93 ml/min

100 μL of x ppm Cl- injected in 0.6 ppm Cl- carrier

Other line 0.1 M Potassium nitrate

x : a) 0.6 b) 1.8 c) 4.2 d) 6 e) 18 f) 30 g) 42 h) 60

Fig 56 Calibration curve
Current 0.3 μA Flow Rate 0.93 ml/min
100 μL of samples injected
First line 0.6 ppm Cl-
Second line 0.1 M Potassium nitrate
Fig 56 b2  Calibration curve
Same conditions as mentioned in high concentration range
REFERENCES