An-Najah National University
Faculty of Graduate Studies

I- Determination of Lead and Cadmium in Food by Anodic- Stripping Voltammetry

II- Oxidation of Galactose

By

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Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry, Faculty of Graduate Studies, An-Najah National University Nablus, Palestine

2004

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This Thesis was defended successfully on 09/06/2004 and approved by:

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Dedication

To My Mother, Father, Brother, Sisters and my Wife
With Love and Respect

Acknowledgment

After thanking Allah the Merciful the Graceful, who generated me the power and courage to finish this work in a very difficult time, I would like to express my great thanks and gratitude's to Dr. Muhammed Al-Subu and Prof.Dr. Radi Dauod for their supervision, encouragement and guidance during my study.

My deep thanks to Mr. Ibrahim Abu-Shqair for providing important notes during the research period. Thanks to all technicians in the chemistry labs for providing me with all research facilities; they where great helpful, and cooperative.

My great thanks, gratitude and love to my mother, father, brother, sisters and my wife for their support and sincere encouragement.

At last my thanks to my friends and for all whom felling, supporting me during the study period.

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Abstract

In part (I) trace metal concentrations in food, cigarettes and water was determined. Reprehensive samples were taken during May- August 2003. Food samples were digested and then analyzed for their contents of lead and cadmium. Samples were analyzed using anodic stripping voltammetry, which considered being sensitive compared to other methods used in determination of heavy metals.

The results showed very low concentrations that were below the safe limits of lead and cadmium set by the WHO. In part (II) reaction of galactose with potassium hexacyanoferrate (III) in alkaline medium was studied at constant temperature and ionic strength. Stoichiometric studies showed that for each mole of galactose oxidized, two mole of potassium hexacyanoferrate (III) were reduced to produce galactonic acid.

The dependence of rate on the concentration of each of galactose, heacyanoferrate (III) and hydroxide ion was determined. The reaction followed first order rate dependence on both; galactose and hydroxide ion and the rate was independent of the concentration of hexacyanoferrate(III). Addition of potassium hexacyanoferrate (II) to the reaction mixture was found to retard the rate of oxidation. The rate was not affected by added anion but added cations were found to affect the rate of the reaction.

Activation parameters were calculated from rate measurements at different temperatures and a mechanism accounting for the results were suggested.

Chapter One

Introduction

I- Determination of lead and cadmium in food by anodic-stripping voltammetry

1.I.1 General background

The environmental pollution is a matter of great concern worldwide. Consequently contamination of food chain is getting increasingly important in view of its role in human health and nutrition. There is large number of environmental pollutants that constitute a potential danger to humanity (Khan, Ahmand, and Sial *et al.,* 1990).

The term "heavy metals" refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thalium (Ti), and lead (Pb) (Viarengo, 1985).

Heavy metals enter the human body through inhalation and ingestion intake via ingestion depends upon food habits. It is well established that lead (Pb) and cadmium (Cd) are toxic and children are more sensitive to these metals than adults. Other metals such as copper (Cu) and zinc (Zn) are essential micronutrients and have variety of biochemical function in all living organisms; however, they can be toxic when taken in excess. Both toxicity and necessity vary from element to element (Tripathitic, 1999).

Contaminated food and water are sources of illness in human body. Among various pollutants in the environment, heavy metals are directly related to health diseases in human. Although, it is difficult to classify trace metal into essential and toxic groups, yet it is well known fact that an essential metal becomes toxic at sufficiently high intake (Sabir, Khan and

Hayat, 2003). Heavy metals like Cd and Pb do not have any useful biological role and they are considered among the most important contaminants of the environment and are highly toxic even at relatively low concentration (White and Rinbow, 1987).

Toxic and persistent substances in the environment continuously accumulate and increase in the body owing to the anthropic activities. Particular attention is being paid to the presence of heavy metals, because of their irreversible deleterious effects on man. In fact such elements tend to concentrate in all aquatic environment matrices such as biota and sediment. For this reason, they are present in the aquatic food chain and dangerous for humans (Hershko, Shahin and Graver 1984). Lead and cadmium may combine with proteins, amine groups and peptides. This can follow two different ways (Rabiaa, 1999):

1- Toxic metals displace beneficial metal from the active site of enzyme.

2- The toxic metal binds to the deactivating site on the molecule. The binding of metallic cations to enzymes could alter activity, not only by inhibition, but also by simulating the catalytic function of enzymes.

Environmental chemistry is able to determine the minimum values of some heavy metal ions and other pollutants that cause environmental pollution. These are known as “Threshold Limit Values (TLVs)”. For most pollutants, including elemental pollutants, there is no distinct line between safe and unsafe concentrations and the “TLVs” are only guidelines for safe operations (Maxwell, 1987). Table (1.1) shows TLVs for some ions in drinking water that issued by WHO (Christopher and Daniel, 1992).

Table 1.I.1 WHO guidelines (TLVs) for drinking water quality (1992).

Parameter	**Threshold limit value (TLV) (ppm)**
Arsenic	0.05
Cadmium	0.005
Chromium	0.05
Lead	0.05
Mercury	0.001
Selenium	0.01
Aluminum	0.2
Copper	1.0
Iron	0.3
Manganese	0.3
Sodium	200
Zinc	5.0

1.I.2 Toxicity and sources of pollution

1.I.2.1 Toxicity and sources of pollution of lead

The atomic number of lead is 82 and its atomic weight is 207.19. Lead and other heavy metals can persist in the environment for many years even after the closer of the main source of contamination. Due to their chemical stability in soil lead becomes a permanent source of lead exposure for humans living in the area (Small, Nunn, Forslund and Dialy 1995; Chatterjee and Banerjee, 1999).

Lead is considered one of the most toxic metals affecting man, animal and plant. Also toxicity of lead has acummulative nature (Nriagu 1980). Young children are good population for lead exposure assessment studies in contaminated areas due to their naturally tending to hand-to-mouth activity when playing out doors, their higher gas absorption rates, an increased susceptibility to the effects of lead (Baghurst, Tong and *et*

al.,1999). Traditional sources of lead poisoning such as paint flakes and home dirt, are usually ingested by small children at an age when iron deficiency is very common (Hershko, Shahin and Graver, 1984). Lead poisoning has been major public health problem for centuries (Jeng, Lee and Lin, 1994).

Excess lead can cause serious damage to the brain, kidneys, nervous system and red blood cells. The attack of lead on the nervous system effects mental ability and may cause a permanent damage to the brain (Atalah, 1993). Damage to the kidneys occurs through the formation of toxic breakdown products. Lead also affects the blood cells and excessive lead dosage in blood results in anemia (Cheremisinoff and Habib, 1973).

Young children, infants and fetuses are particularly vulnerable to lead poisoning. United States Environment Protection Agency (EPA) concluded that lead might be implicated in causing leukemia (Sabir, Khan and Hayat, 2003). Acute exposure to lead may results in convulsions, cardio respiratory arrest and death. Where, chronic exposure results in weakness of extensor muscles of hands and feet and eventual paralysis (Manahan, 1991). Excessive lead accumulation in children is known to cause hyperactivity, a reduced intelligence and anti-social behavior. In adults, it is associated with heart disease, cancer and infertility. In addition, a high maternal lead is known to lead to miscarriage, reduced birth weight and of fetal malformations (Tuormaa, 1994). Lead interacts with an enzyme active in the breakdown of ribonucleic acid resulting in clumping of ribosomal RNA (Cook, Angle and Stohs, 1986).

1.I.2.2 Sources of lead: Lead is considered one of the most dangerous toxic heavy metals because it is a ubiquitous metal which presents every where including homes, soil, work place, foods and water (Zude, 2000). The main sources of pollution of natural water by lead are lead pipes, mines and effluents of many industries such as those producing automobiles, batteries, metal sheets or paints (US Environmental Protection Agency, 1977). Lead may enter the atmosphere during mining, smelting, refining, manufacturing processes and by the use of lead containing products. Lead intake occurs from the consumption of whisky, fruit juices, food stored in lead lined containers, cosmetics, cigarettes and motor vehicle exhaust (Sabir, Khan and Hayat, 2003).

The automobile exhaust contains leaded gas and particulate lead. Automobile gasoline contains tetra-ethyl lead as knock inhibitor which burns and enters the atmosphere. Roadside plants contain high concentration of lead in their tissues and this has a sub lethal effect on the health of animals (Berthelsen, *et al.*, 1995; Sabir, Khan and Hayat, 2003). High concentrations may occur in these environments with the inevitable result of increasing lead concentration in plant and soil. There are other sources such as storage batteries, building construction, cable coating and other miscellaneous source (Manahan, 1991). Also, there are natural sources such as lead –breaking limestone, galena, volcanic activity and airborne dust (Nriagu, 1980).

1.I.2.3 Absorption of lead

The main ways for lead absorption are the gastrointestinal tract and the respiratory system. Approximately, 90% of lead is concentrated in

bones and next comes liver and kidney as they have somewhat higher lead contents than other parts of body (Pan, Horng and Lin, 1996).

1.I.2.4 Treatment of lead poisoning

In adults and children, the major specific therapeutic objective is the removal of lead from body using chelating agents. The most widely accepted procedure is intravenous infusion of the calcium salt of di-sodium ethylenediamintetra acetate (Ca- EDTA) in doses of 1 to 2g per day for 4 to 5 days. The lead chelate formed by the exchange of Ca by Pb, which is excreted promptly in the urine (Hammond, 1971).

1.I.3 Toxicity and sources of pollution of Cadmium

The atomic number of cadmium is 48 and its atomic weight is 112.40. It is toxic to man and other living things. Cadmium tends to accumulate in the body (Sandstead and Davis, 1974). Cadmium can be found in lead mining areas due to its presence as geological contaminant with lead ore together with zinc. Therefore, cadmium can occur as a by-product from smelting processes involving lead ore (Monica, Eduardo and Fernanda 2002). Cadmium poisoning is known to cause liver damage, kidney failure, and pulmonary diseases. Cadmium also appears to be a contributing factor in high blood pressure, bone diseases, anemia, pulmonary fibrosis, prostates cancer, lung cancer, yellow discoloration of the front teeth near gum line and anosmia (Nogwa, Kido, 1990; Grum and Bresentize, 1990). It was reported that men exposed to cadmium oxide dust exhibited consistent protein-urea and a reduced ability to concentrate urine. It was also reported that the greater the duration of exposure the more is occurred of renal damage (Pan, Horng and Lin, 1996). The mechanism of cadmium

poisoning may involve substitution insertion of cadmium in place of zinc in enzymes. Concern over cadmium poisoning has increased with the awareness that some cadmium is always found in zinc compounds which have many commercial uses (Khan, *et al.,* 1996).

1.I.3.1 Sources of cadmium

Usual sources of cadmium to human and animal are mainly food and inhaled tobacco. In food the usual concentration of cadmium is less than 0.1µg/g. However, some foods accumulate cadmium such as shellfish, liver, and kidneys in which cadmium concentration exceeds 10µg/g (Casarett and Doualls, 1980).

Vapor emissions are considered as a major environmental source of cadmium that contaminates soil and water through fall out during smelling. Contamination is happened between cadmium and sewage sludge which effect plants growth in contaminated soil (Casarett and Doualls, 1980).

The most significant use of cadmium is in nickel / cadmium batteries as rechargeable or secondary power source exhibiting high out put, long life, low maintenance and high tolerance to physical and electrical stress. Other uses of cadmium are pigment stabilizers for poly- vinyl chloride (PVC), alloys and electronic compounds. Cadmium is also present as an impurity in several products including phosphate fertilizers, detergents and refined petroleum products (Sandstead and Davis, 1974; Bazzaz and Govindjee, 1974).

Zinc-refining processes are major sources of cadmium causing environmental pollution. Other sources of environmental pollution with

cadmium in the air are mines, fossil fuel, steal mills, smelters and industrial discharges. Wastes incineration of plastics and cadmium pigments, metal plating and smoking cigarette, are also sources for cadmium pollution (Grum and Bresnitze, 1990). Natural sources of cadmium are volcanic activity, exudates from vegetation, forest fires, windblown dust and weathering of cadmium bearing rocks (Ravlra, 1986).

1.I.3.2 Absorption of cadmium

The greatest concerns about cadmium are its cumulative properties and long biological half – life (20-30) years, possibly leading to nephro-rtoxicity (ATSDR, 1998). As cadmium enters through the lungs and gastrointestinal tract children are under risk of contamination comparable to the risk of lead contamination (Monica, Euardo and Fernanda, 2002).

Steady state concentration of reasonably constant conditions of exposure, while in workers newly exposed to a cadmium-contaminated environment, a new steady state blood concentration was attained in one year. Blood cadmium equilibrates with any given level of exposure within a year (Kjellstrom, 1977).

1.I.3.3 Treatment of cadmium poisoning

Excretion of cadmium from the body is very slow so the use of safe chelating agents such as ethylenediamintetra acetate (EDTA), 2,3-dimercaptopropanal (PAL), and pencillamine (PA) is widely used in the treatment of cadmium intoxication (Anderson, 1989). Additionally, a series of novel dithiocarbamates, and disodium salts are used for the same purpose (Pan, Horng and Lin, 1996).

1.I.4 Methods of analysis used for Lead and Cadmium

Different methods are used for the determination of lead and cadmium. Examples are flame atomic absorption spectrophotometery (FAAS), graphite furnace atomic absorption spectrophotometry (GFAAS) (Hammond *et al.*, 1998), X-ray fluorescence (XRF) (Recai, Somer and Banu, 1999), atomic emission spectrometry (AES) (Camillo, Vians and etal, 1999, Vinas, Pardo and Hernandez, 2000), inductively coupled plasma (ICP) (Boevski, Daskalova and Havezov, 2000) and Anodic stripping voltammetry (ASV). The method of ASV has the advantages of being sensitive and cheap method for the determination of several elements including lead and cadmium (Inam and Somer, 2000).

1.I.4.1 Anodic stripping voltammetry

The demand for the detection and quantitation of trace components in complex samples has come from the public and private sector alike. Heightened awareness of the often detrimental effects of trace elements in the media such as food stuffs, drinking water, and commercial waste water effluents has led to stringent public legislation and industry wide quality programs which have been directed toward monitoring components of a sample at sub-ppm levels. Voltammetric techniques such as anodic stripping voltammetry are capable of determining elements accurately at trace to ultra-trace levels and have demonstrated ability for multi-element determination (Inam and Aydin, 1996).

The technique of stripping voltammetry has been used in trace analysis with relative ease and success in a variety of analytical applications. This technique is routinely capable of identifying and

quantifying trace components from 10^{-5} –10^{-9} M with excellent sensitivity and selectivity. Stripping analysis has received an unusual degree of interest, since it is the most sensitive electro-analytical technique currently available (Btley and Florence, 1974).

Voltammetry is an electrochemical technique in which the current – potential behavior at an electrode surface is measured. The potential is varied in some systematic manner to cause electro-active chemical species to be reduced or oxidized at the electrode surface. The resistant current is proportional to the concentration of the chemical species.

The stripping waveform is a plot of potential applied to the working electrode vs. time, as shown in Fig. (1.1) and consists of several discrete steps (Skoog and Leary, 1992):

1- Deposition: the deposition potential is applied to the working electrode to cause the material of interest to be deposited onto the surface of the working electrode. The solution is generally stirred during deposition to maximize analyte – electrode contact. The deposition potential should be negative with respect to the half – wave potential of the metals to be determined. During deposition, an amalgam is formed by the elemental and mercury on the electrode (Gold and Bethell, 1982).

$M^{n+} + ne^- + Hg \rightarrow M(Hg)$ ……..eq(1.1)

* M represent the metal

(Applied potential more negative than $E_{1/2}$ of M^{n+})

The degree of concentration of metal in this step depends upon the factors discussed below (Skoog and Leary, 1992):

A) The electro-deposition potential: The choice of electro-deposition potential depends on the nature of the analyte.

B) The time of electrolysis: The continuous reduction of metal ions on the electrode during the concentration step causes a continuous depletion of metal ions in the solution. Increasing the time of electrolysis increases the amount of deposited metal and thus increases the sensitivity of the method. For the maximum sensitivity, almost complete deposition of the metal ions form solution has been sometimes used. However, complete deposition takes a very much longer time than deposition of fixed percentage of the metal ions.

C) The rate of stirring: Mass transfer controls the reduction process; the amounts of metal ions reduced in the concentration process are dependent on the velocity of transfer of ions in the solution. This velocity is dependent on the rate of stirring.

2- Equilibration: During this step, the stirrer is switched off for a half to one minute before the stripping process starts. This period helps to eliminate the concentration of gradient in the mercury drop produced during the concentration step. It also gives time for the solution to come to rest during the rest period, the deposition of metal ions does not case completely but continues at a lower rate than during the concentration step.

3- Stripping: In this step, the analyte metal is stripped out of the mercury drop by applying a linear potential sweep in the anodic direction. When the potential approaches the half wave potential, the metal begins to oxidize producing a current:

$M (Hg) \rightarrow M^{n+} + ne^{-} + Hg$ …….eq (1.2)

As a result of scanning in the positive direction, the peak current is proportional to metal concentration. As potential goes more anodic the current increases to reach its maximum at $E_{1/2.}$ When metals in mercury stripped off the current then drops to almost zero. Thus, the current – potential plot, called a voltammogram, shows peaks; each peak corresponding to one metal.

Figure 1.I.1 Potential time wave form used in anodic stripping voltammetry. **(a)** Deposition at $E_{d,}$ stirred solution, **(b)** Rest period, stirrer off, **(c)** Stripping, positive potential scan to E_i

1.I.4.2 Oxygen waves

Oxygen is capable of dissolving in aqueous solution at mille molar level at room temperature and atmospheric pressure. Dissolved oxygen is readily reduced at various electrodes. An aqueous solution saturated with air exhibits two distinct waves attributable to this element. The first result from the reduction of oxygen to peroxide, as seen in equation (1.3)

$O_2(g) + 2H^+ + 2e \rightarrow H_2O_2$ $E_{1/2}$ =0.0V . eq (1.3)

The second corresponds to the further reduction of the hydrogen peroxide.

$H_2O_2 + 2H^+ + 2e- \rightarrow 2H_2O$ $E_{1/2}$= ⁻1.0V….eq (1.4)

Voltametric measurements offer a convenient and widely used method for determining dissolved oxygen in solutions. However, the presence of oxygen often interferes with the accurate determination of other species with half wave potential around (0.0 and ⁻1.0) V. Thus, oxygen removal is ordinarily the first step in voltammetric procedures. Duration of the solution for several minutes with an inert gas (sparring) accomplishes this end; a stream gas, usually nitrogen, is passed over the surface during analysis to prevent reabsorption of oxygen (Skoog and Leary, 1992).

1.I.4.3 Electrochemical cell

A typical cell for stripping analysis is shown in Figure 1.2. The heart of the instrumentation is a three electrode potentiostat. In the potentiostatic circularity a reference electrode of fixed potential e g. (Ag/AgCl) is placed in close proximity to the working electrode and connected through a circuit

that draws no current from it. The cell current is passed between the working electrode and the auxiliary electrode, which is frequently a platinum wire or foil. In many cases, tubing for de-oxygenation and gas blanketing of the solution is required. Many stripping analyzers have a standard cell station. The cell container can be ordinary lab glass beaker, sample vial, or weighing bottle. For ultra trace analysis, acid-washed quartz, Teflon, or disposable plastic beakers are preferable to reduce contamination from leaching or ion loss through surface deposition. As all analytical methods that capable of analysis at the trace level, contamination of sample must be avoided.

Figure 1.I.2 Electrochemical cell for stripping analysis (Working electrode WE, reference Electrode RE; auxiliary electrode AE).

In order to reduce adsorption on glassware, the electrolysis cell, calibrated flasks and pipettes were previously soaked in 30% HNO_3 (v/v) for 24h and rinsed with de-ionized water (Andreu, Gimeno, 1999). A Teflon-covered stirring bar may be used with magnetic stirrer. Erratic stir bar behavior affects results.

1.I.4.4 Supporting electrolytes:

Supporting electrolyte is added to the sample in order to increase the conductivity of the solution to eliminate mass transfer by migration during the deposition step. When potential is applied to the electrochemical cell, the concentration of the metal ions on the electrode surface is practically zero. As the electrolysis proceeds, the concentration of the ions in the sample is constant up to thickness of the diffusion layer from the electrode. As a result of the difference in concentration, the metals ions move towards electrode by diffusion. The ions are influenced by a potential gradient caused by the electrical field around the electrode, namely, migration. To minimize the effect of potential field, an inert supporting electrolyte is added to the sample (thus ionic strength and conductivity of solution increased). Common electrolytes in stripping analysis include inorganic salts (KCl, KNO_3), acids (HCl, $HClO_4$) and buffer solutions (acetate, ammonia) when pH control is needed (Zude, 2000).

1.I.4.5 The Ilkovic equation (Skoog and Leary, 1992)

The diffusion current I_d could be calculated in the polarographic process by applying the following equation:

$i_d = k\,C$ eq. (1.5)

The proportionally constant (k) in the above equation is really collection of terms, some of which are real constants and some of which must be controlled to achieve linearity and reproducibility. An equation showing these terms was given in 1934 by Ilkovic:

$i_d = (607\, nD^{1/2}\, m^{2/3}\, t^{1/6})\, C$ eq. (1.6)

The terms are defined as follows:

- id is the average diffusion current in micro amber.

- the number 607 is the value at 25ºC of a collection of terms including the faraday and density of mercury.

- n is the number of electrons in the process

$Ox + ne^- \rightarrow Red$

- D is the diffusion coefficient of electro-active species in cm2/s (this is a measure of how rabidly the species diffuses in a specified solution under the influence of standard concentration gradient).

- m is the mass of mercury flowing through the capillary per unit time in mg/s.

- C is the concentration of the electro-active species in mMol/litter.

- t is drop time in s

1.I.5 Pollution with heavy metal in Palestine

Because of the importance of water, water pollution is considered as a major problem that is facing the world civilization nowadays. Palestine, as one part of the world is facing the same problem so few researches where done related to water pollution to measure how much our drinking water is polluted with some toxic elements. During the years (1987, 1988 and 1992) three research projects where conducted at An-Najah National University and all were related to water pollution (Salim, Qattawi and *et al*, 1992, Salim, Qattawi and *et al.,* 1987, Salim, Qattawi and *et al.,* 1988). The findings of these studies showed that drinking water in the area is free from polluted elements.

The current study will have a further look on the quality of drinking water; moreover, it expands the search to include food, grains and cigarette.

1.I.6 Aim of the study

Since limited studies were conducted on water and food pollution with lead and cadmium in were conducted in Palestine. The current study aimed at measuring lead and cadmium levels in several water, food and cigarette samples collected in Palestine.

II - Oxidation of Galactose

1.II.1 Oxidation using potassium hexacyanoferrate (III).

Potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$ has been found to be suitable for the oxidation of a wide variety of substrates and has been found to be a good oxidizing agent in alkaline medium (Finar, 1973,Al-Subu,2001; Al-Subu, 2003; Meth, 2000). Hexacyanoferrate (III) is known to be as non-bonded electron-transfer reagent (Gold and Bethell, 1982). It has several advantages that make it suitable for the oxidation of several organic substrates:

1. It is stable over the entire pH scale (Amer, 1992).

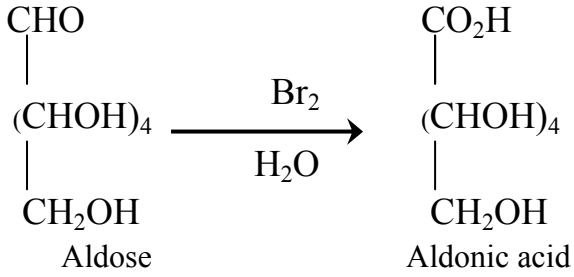
2. It is absorption maximum around 420 nm, with molar absorpitivity ($\varepsilon = 1.0\times10^3$), at which Potassium hexacyanoferrate (II) $K_4[Fe(CN)_6]$ (the reduced form) does not interfere (Al-Subu, 2003). Thus, the kinetics of its reactions can be followed spectrophotometrically.

1.II.2 Oxidation reactions of monosaccharides

A number of oxidizing agents is used to identify functional groups of carbohydrates, in elucidating their structures, and for syntheses. The most important are (1) bromine water (2) nitric acid (3) periodiate (4) Chloramin-T, and (5) Quinquevalent Vanadium

I- Bromine Water: The synthesis of galactonic acids (Morrison and Boyd, 1992).

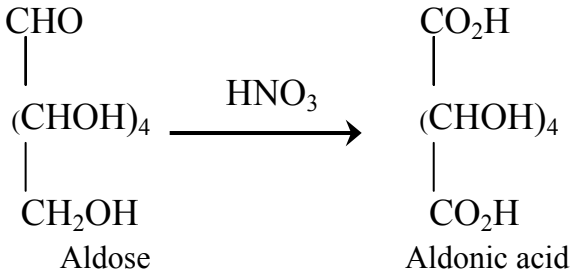
Monosaccharides do not undergo iso-merization and fragmentation reactions in mildly acidic solution. Thus, useful oxidizing reagent for preparative purposes is bromine in water (pH 6.0). Bromine water is a general reagent that selectively oxidizes the ─CHO group to a ─CO_2H group:



Aldose Aldonic acid Eq (1.8)

II- Nitric acid oxidation: Aldaric acids (Morrison and Boyd, 1992)

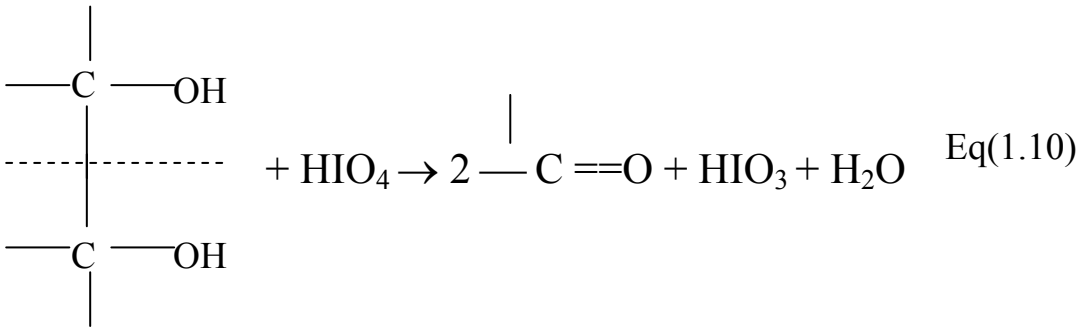
Dilute nitric acid (a stronger oxidizing agent than bromine water) oxidizes both the ─CHO group and the terminal ─CH_2OH group of an aldose to ─CO_2H groups. These dicarboxylic acids are known as aldaric acids.



Aldose Aldonic acid Eq (1.9)

III- Periodiate oxidations: Oxidative cleavage of polyhydroxy compounds: (Morrison and Boyd, 1992)

Compounds that have hydroxyl groups on adjacent atoms undergo oxidative cleavage when they are treated with aqueous periodic acid (HIO_4). The reaction breaks carbon – carbon bonds and produces carbonyl compounds (aldehydes, ketones, or acids). The stoichiometry of the reaction is:



Eq(1.10)

IV- Many other chemical agents are also used, such as Chloramin-T (Mushran, Guupta and Sanehi, 1976), Quinquevalent Vanadium (Bhatangar, Fadnis, 1976).

1.II.3 Aim of this part

The purpose of the present work was:

1- To study the kinetics of oxidation of galactose by potassium hexacyanoferrate (III) in alkaline medium.

2- To calculate the activation parameters: ΔH^*, ΔS^*, ΔG^*, and E_a.

3- To identify the product of the reaction.

4- To propose suitable mechanism for the reaction under consideration.

Chapter Two

Experimental

2.I- Determination of Lead and Cadmium in food by anodic striping voltammetry

2.I.1 Materials

All reagents were of analytical grade (Merck). Lead Nitrate $Pb(NO_3)_2$, $Cd(NO3)_2.4H_2O$ were used in preparation of stock solution (1000mg / L) of metal ions. The required concentrations (1mg / L) were prepared from stock solution by dilution with de-ionized water.

Contaminated mercury was cleaned by passing it successively throughout dilute HNO_3 (0.3M) and water columns in the form of fine droplets. The collected mercury was dried between sheets of filter paper. Before use, a stripping voltammogram of this mercury was recorded, in order to confirm the absence of impurities (Recai, Somer and Banu, 1999).

2.I.2 Preparation of stock solution (1000mg / L)

Stock solutions were prepared by taking the required amount of the salt $Pb (NO3)_2$ (1.59 g), $Cd NO_3)_2.H_2O$ (2.74 g) and dissolved in de-ionized water to give 1000mg /L standard solution.

2.I.3 Supporting electrolyte

Supporting electrolyte is $HClO_4$ perchloric acid (65%), diluted to give 0.1M was used in this study.

2.I.4 Instrumentation

Anodic stripping voltammetry was used to determine the elements using EG&G voltammetric analyzer, model 264-B with 303A static mercury dropping electrode, which operated in the hanging mercury drop

electrode (HMDE). The three- electrode system was completed by means of a platinum wire auxiliary electrode (counter electrode), and an (Ag/ AgCl/ Cl) reference electrode. The voltammograms were recorded using the recorder model RE0089 X-Y- recorder with the vacuum hold down to mask the paper.

2.I.5 Methods

2.I.5.1 Digestion of samples

A sample (1g) of food and cigarettes samples was placed in porcelain crucible, the furnace temperature was slowly increased from room temperature to 450 $^{\circ}$C in 1 hour; then the sample was ashed for about 4 hours until white or grey ash residue was obtained; The residue was dissolved in 5 ml of 25% v/v HNO_3 and the mixture, where necessary, was heated slowly to dissolve the residue; finally the solution brought to the volume of 25 ml with diminerlized water.

2.I.5.2 Voltammetric determination

Five milliliters of supporting electrolyte solution $HClO_4$ (0.1 M) were placed into the voltammetric cell and deoxygenated with high purity nitrogen for 4 minutes with stirring. A fresh mercury drop was suspended and deposition was carried out for 60s. Following deposition, the solution was left to stand for 15s to rest. The differential pulse anodic stripping voltammograme (DPASV) voltamogram was recorded during the potential sweep to the positive direction at scan rate of 10mV/s and pulse amplitude of 25mV. After obtaining the background voltammogram 0.5ml digested sample solution was introduced into the cell, and the oxidation current peaks of the elements were recorded. Standard addition of 50µl of the

analyte metals caused increments of the peak. The above procedure was repeated for all samples (Inam and Somer, 2000).

2.I.5.3 Standard addition method

A polarogram is recorded for the unknown sample, and then a known volume of the unknown is spiked with a known quantity of a standard solution and a second polarogram is obtained. The concentration of the original sample was calculated as follows:

$$C_u = \frac{i_1 \nu C_s}{i_2 \nu + (i_2 - i_1) V}$$

Where:

- i_1 = sample peak height.
- i_2 = standard addition peak hight.
- ν = volume of standard solution added.
- V = volume of original sample.
- C_s = concentration of standard solution.
- C_u = concentration of original sample.

2.II Oxidation of galactose

2.II.1 Method of analysis

In the present work, the kinetic data has been analysed as follows:

(i) Determination of the reaction order by using the method of the initial rate: (Avery, 1978, March, 1977).

If the rate law for a reaction is such that

$r_\circ = k [A_\circ] [B_\circ]$

Then the initial rate of reaction will be given by

$r_\circ = k [A_\circ]^a [B_\circ]^b$

Where:

$r_\circ$ = initial rate of the reaction.

k = reaction rate constant.

$A_\circ$ = initial concentration of A.

$B_\circ$ = initial concentration of B.

a = order of the reaction with respect to $A_\circ$.

b = order of the reaction with respect to $B_\circ$.

If $r_\circ$ is measured using variety of initial concentrations, value of k, a and b can be determined.

If $[B_\circ]$ is kept constant, the last equation becomes:

$r = k' [A_\circ]^a$ and

$\log r_\circ = \log k + a \log [A_\circ]$

A plot of log $r_\circ$ versus Log $[A_\circ]$ should give a straight line of slope a. On other hand, keeping $[A_\circ]$ constant the equation becomes:

$r_\circ = k'' [B_\circ]$ and

$\log r_\circ = \log k'' + b \log [B_\circ]$

Thus, if $r_\circ$ is measured keeping $[A_\circ]$ constant and varying $[B_\circ]$, b can be obtained from the plot of $\log r_\circ$ versus $\log [B_\circ]$.

In the present work, absorbance of hexacyanoferrate (III) versus time was plotted for each run; tangents are drawn at the beginning of the reactions. The negative slope of the resultant tangent line represents the initial rate. The logarithms of the initial rates are plotted versus the logarithms of the corresponding initial concentrations. Slopes of the resulting straight lines represent the order of the reaction.

(ii) Determination of activation parameters: (Avery, 1978, March, 1977).

To determine the energy of activation (E_a), reaction has been studied at different temperatures. The rate constants have been obtained at these different temperatures from rate law of compound, and the energy of activation has been calculated according to Arrhenius equation:

$k = A\, e^{-Ea / RT}$

Where:

k = specific rate constant.
A = frequency factor.
E_a = energy of activation.
R = gas constant.
T = absolute temperature.

The slope of [-lnk vs. 1/T] is equal to E_a / R, hence the energy of activation can be calculated. The entropy [ΔS^*], enthalpy [ΔH^*], and free energy [ΔG^*], was calculated based on the following relations:

$\log (k / T) = \log (k_B / h) + \Delta S4.57 - E_a / 4.57T$

Where:

k, T and Ea, have the same significance as before.

h = Planck constant 6.6256×10^{-27} erg. sec.

K_B = Boltzmann constant 1.381×10^{-16} erg . deg.

$\Delta H^* = E_a - RT$ and

$\Delta G^* = \Delta H^* - T\Delta S^*$

(iii) Stoichiometric determination:

The stoichiometry of the reaction under consideration was determined spectrophotometrically using Beer's law:

$A = \varepsilon cl$

Where:

A = absorbance.

ε = extinction coefficient.

c = concentration M.

l = path length.

The initial concentration ($C_\circ$) and the remaining concentration (C_∞) of hexacyanoferrate (III) corresponding to the initial absorbance ($A_\circ$) and the final absorbance (A_∞) = 0, respectively.

The kinetic of the reaction was determined when hexacyanoferrate (III) is completely consumed, so the absorbance finally (A_∞) = 0. Therefore, to determine stoichiometry large excess of hexacyanoferrate (III) over the galactose was used.

The extinction coefficient (ε) for potassium hexacyanoferrate (III) in aqueous solution determined at 420 nm is 0.990×10^3 or simply it is used as $\varepsilon_{420} = 1000\ dm^3\ mol^{-1}cm^{-1}$ (Amer, 1992, Metha and Tewary, 2001). The ε-value is independent of pH and ionic strength (Bridgart, Wasters and Wilson, 1973, Metha, Tewary, 2001). Thus, the concentration of hexacyanoferrate (III) consumed in the reaction is given by ($C_\circ - C_\infty$). The ratio between ($C_\circ - C_\infty$) nd the concentration of the oxidized species is equal to the stoichiometry of the reaction.

2.II.2 Materials

Potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$, hexacyanoferrate (II) $K_4[Fe(CN)_6]$ galactose, (Riedel-de Haen, AR) was diluted with sodium hydroxide solution, which was prepared and standardized agents potassium hydrogen phthalate. De-ionized distilled water was used for the preparation and dilutions of all solutions were freshly prepared from sample, which were used as received. KCl was used throughout for adjusting the ionic strength.

2.II.3 Instrumentation

All spectra were obtained using ultraviolet spectrophotometer 1601 (SHIMAEZO) equipped with 1-cm glass cells and thermostat cell compartment.

2.II.4 General procedure for kinetic studies

The kinetics of oxidation of the galactose under study by K_3 $[Fe(CN)_6]$, were followed spectrophotometrically by following the absorbance of $K_3[Fe(CN)_6]$ with progress of time at wave length (λ)= 420 nm. The desired hydroxide ion concentration was achieved using sodium hydroxide. Potassium chloride was added to adjust the ionic strength of the reaction mixture to the required value. The required amounts of galactose and K_3 $[Fe\ (CN)_6]$ were dissolved separately in portions of the de-ionized water in two volumetric flasks. The total volume of the reaction mixture in all experiments was kept constant.

A portion of the reaction mixture was transferred into the measuring cell of the spectrophotometer. The absorbance was recorded at appropriate intervals right after mixing. The same procedure was followed to study the effect of added K_3 $[Fe\ (CN)_6]$ and other salts on rate of the reactions by adjusting the amount of de-ionized water to keep the total volume constant (Amer, 1992).

2.II.5 Stiochiometry of the reactions

To determine the number of moles of hexacyanoferrate (III) consumed per one mole of galactose, a reaction mixture containing a known excess of hexacyanoferrate (III) over the galactose was kept at

room temperature in the presence of (0.1M) sodium hydroxide until the reaction was completed.

The mole ratio of consumed hexacyanoferrate (III) to the galactose was discussed in chapter one and their results are shown in table (3.II.1).

Chapter Three

Results and Discussion

3. I Determination of Lead and Cadmium in food by anodic stripping voltammetry

3.I.1 Effect of deposition time

Deposition time is an important experimental parameter that is unique to stripping voltammetry, thus, deposition time must be carefully measured. If more sensitivity is required, the analyst simply increases the deposition time, which increases the degree of pre concentration, making a greater amount of deposited analyte available at the electrode during the stripping step. In order to determine the optimum deposition time, anodic stripping voltammogram for 1 ppm, of lead ion different deposition time periods were used. The results obtained are shown in (Figure 2.I.1).

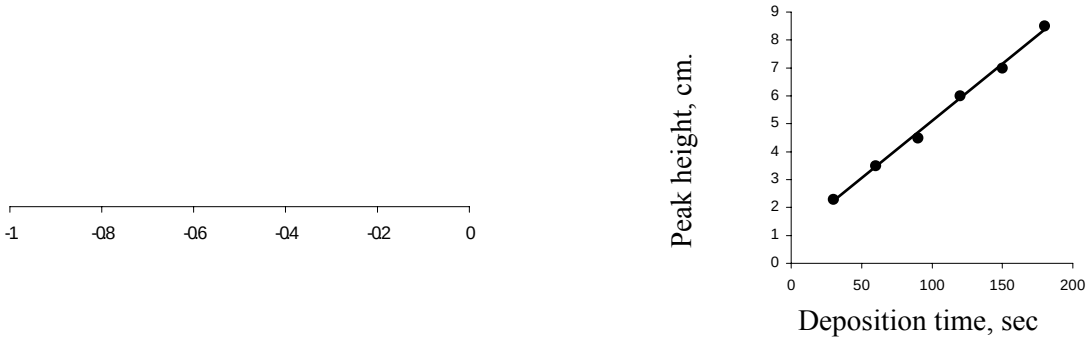


Figure 3.I.1 a. Differential pulse anodic stripping voltammograms

b. Corresponding peak current of 1ppm of lead as the deposition time increased as: 30, 60, 90, 120, 150, 180 second. Peak potential $E_{1/2}$=-0.44 V, scan rate: 20mV/s, purging time: 30s, current range: 5μA.

Based upon the above findings, a deposition of 60 second showed the most sensitive deposition time. All other determinations used in this experiment were kept constant.

3. I. 2 Effect of mercury drop size

The effect of drop size on the peak current of lead oxidation was studied. As surface area of mercury drop (HMDE) increases, the peak current increases due to the increased metal ions accumulated on the surface of the mercury drop.

The effect of the mercury drop size on peaks height was determined experimentally using various mercury drop sizes. The results of these experiments are shown in Figures (3.I.2- 3.I.4). In the current study, medium drop size was selected as it gave suitable and reproducible peak height.

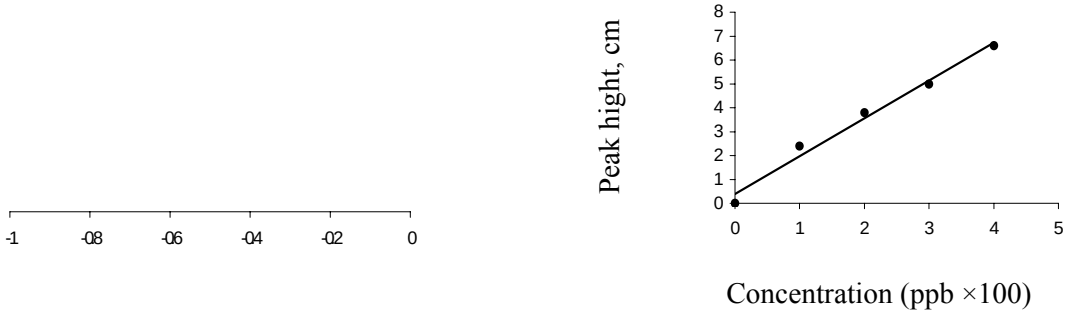


Figure 3. I. 2 **a**. Differential pulse anodic stripping voltammograms, and **b.** anodic stripping voltammetric peak current of lead concentration at drop **small** size and concentration increased 0.01, 0.02, 0.03 and 0.04 ppm. Peak potential $E_{1/2}$= -0.44V, scan rate: 20mV/s, deposition time: 60s, current: 5μA.

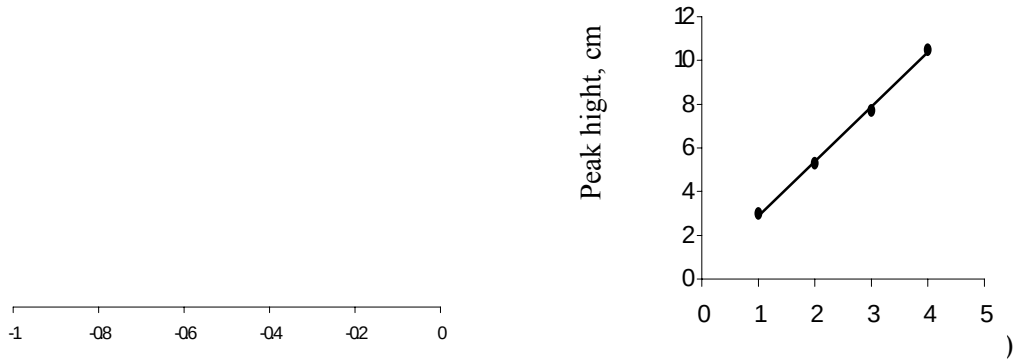


Figure 3.I.3 **a**. Differential pulse anodic stripping voltammograms, and **b.** anodic stripping voltammetric peak current of lead concentration at drop **medium** size and concentration increased 0.01, 0.02, 0.03 and 0.04 ppm. Deposition potential: 0.44V, scan rate: 20mV/s, deposition time: 60s, current: 5μA.

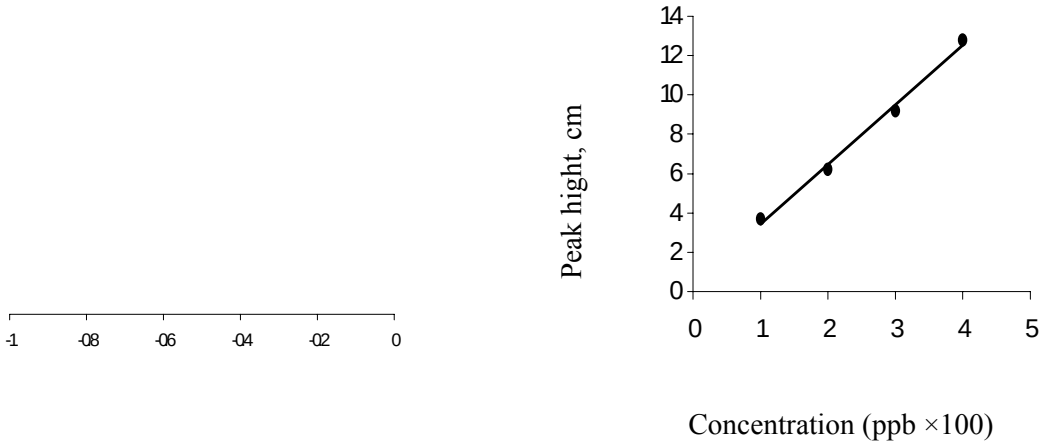


Figure 3.I.4 **a.** Differential pulse anodic stripping voltammograms, and **b**. anodic stripping voltammetric peak current of lead concentration at drop large size and concentration increased 0.01, 0.02, 0.03 and 0.04 ppm. Deposition potential: -0.44V, scan rate: 20mV/s, deposition time: 60s, current: 5μA.

3.I.3 Overlapping peaks

Overlapping stripping signals may arise as a result of similar redox potential of the determined metal ion species. Overlapping peaks may occur during simultaneous measurement of the following ions: Cd and In, Pb and Ti, Pb and Sn, Sb and Bi or Cu and Bi. Resolution in stripping analysis is determined by both peak potential and peak width at half peak height (Nriagu, 1980).

Overlapping peaks during simultaneous measurement of Cd (E1/2 = -0.62) and Pb (E1/2 = -0.43) were missing as shown in Figure 3.I.5.

Figure 3.I.5 Differential pulse anodic stripping voltammograms indicates there no overlapping occurs between lead and cadmium peaks. Deposition potential for lead and cadmium (-0.44V, -0.63 V) respectively, purge time: 4 minutes, Deposition time: 60second, scan rate: 10mV/s, current: 5μA.

3.I.4 Optimal condition for analysis

Table 3.I.1 show the experimentally determined optimum conditions used in this work as they found to be the most reliable and reproducible determinants.

Table 3.I.1 Optimal conditions for analysis.

Working electrode	HDME
Drop size	Middle
Reference electrode	Ag/AgCl
Auxiliary electrode	Pt wire
Initial potential	-0.85 V
Final potential	-0.35 V
Integration set point (Cd, Pb)	(-0.63 V , -0.44 V) respectively
Purge time	4 minute
Deposition time	60 second
Equilibrium time	15 second
Scan rate	10 mV/s
Current	5 μA
Pulse amplitude	25 mv
Recorder X-axes scale	100 mV/cm
Recorder Y-axes scale	250 mV/cm

3.I.6 Water samples

Table 3.I.2 shows the used water samples, their sources and level of contamination of both lead and cadmium. All samples were tested in replicates.

Table 3.I.2 Used water sample and their sources.

TYPE OF WATER	SOURCE	DATE OF SAMPLING	RESULT	
			CADMIUM PPM	LEAD PPB
Tap water	University	7/2003	*	*
Rain-water	Jammain	6/2003	*	*
Tap water	Jammain	6/2003	*	*
Spring water	Ras El-Ein	6/2003	*	*
Spring water	Bet Al-Maa	6/2003	*	*
Spring water	Al-Qareon	6/2003	*	*
Spring water	Al-Sebean	6/2003	*	*

* Value below the detection limit.

Concentration of both lead and cadmium was found to be below the detection level (1 ppb) in all studied water samples, thus indicating that all studied water sources were free of such pollutants.

3.I.7 Grain samples

Several types of grains, commonly used in Palestine, were included in the current study and each sample was tested in triplicates. The majority of the samples were found to be free of lead or cadmium contamination. This might be due to the fact that they were rain fed grains, which was also found to be free of any measurable levels of both lead and cadmium (Table 3.I.3). Few samples were found with high concentration of lead, these samples came from households using homemade flour ground stone mills.

Table 3.I.3 Grain samples from different location.

TYPE OF GRAINS	SOURCE	DATE OF SAMPLING	RESULT	
			CADMIUM PPB	LEAD PPB
Triticum aestivum 1	Jammain	7/2003	*	*
Triticum aestivum 2	Jammain	7/2003	*	*
Triticum aestivum 3	Jammain	7/2003	*	*
Triticum aestivum 4	Nablus	7/2003	*	*
Triticum aestivum 5	Nablus	7/2003	*	*
Vicia faba 1	Nablus	7/2003	*	*
Vicia faba 2	Jammain	7/2003	*	*
Cicer arietinum 1	Nablus	7/2003	*	*
Lens culinaris	Jammain	7/2003	*	*
Cicer arietinum 2	Jammain	7/2003	*	*
Lens culinaris	Jammain	7/2003	*	25.6
Lens culinaris	Jammain	7/2003	*	23.5
Triticum aestivum 1	Jammain	7/2003	*	52.1
Triticum aestivum 2	Jammain	7/2003	*	56.3
Triticum aestivum 3	Jammain	7/2003	*	57.9
Oryza sativa 1	Nablus	8/2003	*	48.9
Oryza sativa 2	Nablus	8/2003	8.1	32.2

* Value below detection limit.

3.I.8 Canned meat

One sample of canned meat was included in this study. The sample was tested in triplicate and the levels of the tested lead and cadmium metals are shown in table (3.I.4).

Table 3.I.4 Canned meat

TYPE OF CANNED FOOD	SOURCE	DATE OF SAMPLING	RESULT	
			CADMIUM PPB	LEAD PPB
Saneora	Nablus	8/2003	22.7	25.5

The findings of high levels of lead and cadmium may be partially due to the process of canning, on the other hand it might be due to the source of used meat.

3.I.9 Soft drinks

Data presented in table 3.5 show the used soft drink samples included in this study. All samples were tested in triplicates. All samples were found free of any detectable levels of either of the studied elements. Such finding indicates that the used water in the manufacturing process was free of contamination.

Table 3.I.5 Soft drink samples

TESTED SOFT DRNK SAMPLES	SOURCE	DATE OF SAMPLING	RESULT	
			CADMIUM PPB	LEAD PPB
Cool orange	Nablus	7/2003	*	*
Cool	Nablus	7/2003	*	*
7 up	Nablus	7/2003	*	*
Merinda	Nablus	7/2003	*	*
Coca cola	Nablus	7/2003	*	*

* Value below detection limit.

3.I.10 Cigarette

Data presented in table 3.I.6 shows the various tested tobacco and cigarette samples. All samples were tested in triplicates and were with high level of contamination of both lead and cadmium. Whether used irrigation water, soil or processing procedures are behind this contamination needs further investigation.

Table 3.I.6 Cigarette sample

TYPE OF CIGARETTE	SOURCE	DATE OF SAMPLING	RESULT	
			CADMIUM PPB	LEAD PPB
Nicotiana tabacum 1	Nablus	6/2003	58	87.9
Nicotiana tabacum 2	Nablus	6/2003	60.1	79.5
Nicotiana tabacum 3	Nablus	6/2003	63.1	89.9
Nicotiana tabacum 4	Nablus	7/2003	56.5	75.4
Nicotiana tabacum 5	Nablus	7/2003	63.6	87.3
Nicotiana tabacum 6	Nablus	7/2003	58.2	39.3
Nicotiana tabacum 7	Nablus	7/2003	52.7	45.3
Nicotiana tabacum 8	Nablus	7/2003	56.2	38
Nicotiana tabacum 9	Nablus	7/2003	37.4	40.8
Nicotiana tabacum 10	Nablus	7/2003	36.9	33.7

3.I.11 Conclusions

The following conclusions can be drawn from the results of this part of the thesis:

1- The concentration of lead and cadmium in all water samples found to be below the detection limit of the studied metal ions by ASV.

2- The concentration of lead and cadmium in most of studied grains was below the detection limit, however, few grain species were found to

contain mainly high levels of lead and these levels were considered to be below the safe limits according to WHO standards.

3- All tested soft drink samples were found to be below the detection limits.

4- The tested canned meat sample was found to contain lead and cadmium levels below the safe limits.

5- Tested tobacco and cigarette samples were found to contain lead and cadmium levels higher than that of the safe limit.

3. II. Oxidation of Galactose

3.II.1 Reaction stoichiometry

The results from the stoichiometry of the oxidation reaction indicated that for each mole of galactose consumed, two moles of Potassium hexacyanoferrate (III) were reduced as shown in table (3.II.1).

The stoichiometry may thus, be represented by the following equation:

$$CH_2OH\ (CHOH)_4\ CHO + 2Fe(CN)_6^{-3} + 2OH^- \longrightarrow$$

$$CH_2OH\ (CH.OH)_4\ COOH + 2Fe(CN)_6^{-4} + H_2O$$

3.II.2 Kinetics

The effect of concentrations of each of galactose**,** $K_3[Fe(CN)_6]$, hydroxide ion, potassium hexacyanoferrate (II), other salts and temperature change were studied.

3.II.2.1 Dependence on reactants concentrations

3.II.2.1 Dependence on potassium hexacyanoferrate (III) concentrations

In order to determine the rate dependence of the galactose, the reaction was carried out using different concentrations of potassium hexacyanoferrate (III), keeping other parameters constant. It was found that disappearance of hexacyanoferrate (III) followed zero order kinetics.

The results of the present study are shown in table (3.II.2) and figure (3.II.1).

Table 3.II.1 Stoichiometric ratio for galactose oxidation by potassium hexacyanoferrate (III),[Galactose] = 1×10^{-4} M, $[OH]^-$ = 0.1M, temperature = 25˚C and time =120 hours

$[Fe(CN)_6^{-3}]$ (Co) × 10^3	$[Fe(CN)_6^{-3}]$ (C∞) × 10^3	$[Fe(CN)_6^{-3}]$ Reacted × 10^3	$[Fe(CN)_6^{-3}]$: galactose
1.00	0.78	0.22	2.00 : 1.00

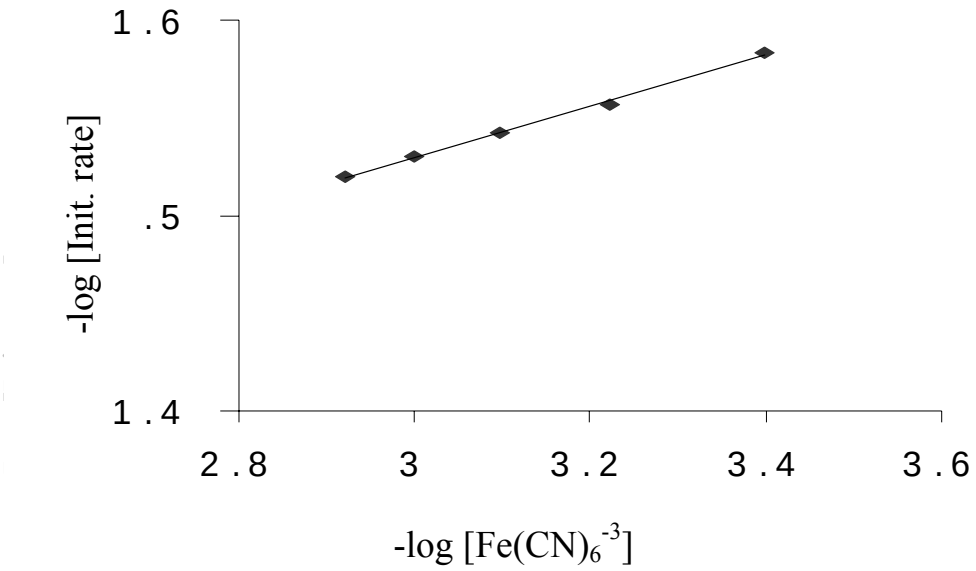


Figure 3.II.1 Effect of varying Potassium hexacyanoferrate (III) concentrations at 25˚C. [Galactose] = 1×10^{-2} M, [NaOH]= 0.1M, and ionic strength = 0.15

3.II.2.2 Dependence on galactose concentration

To study the effect of galactose concentration on the oxidation rate, a series of measurements were carried out using different galactose concentration. Other parameters were kept constant. It was found that the rate constant values were directly proportional to the concentration of

galactose. This indicates a first order dependence of the reaction rate with respect to the galactose as shown in table (3.II.2) and figure (3.II.2).

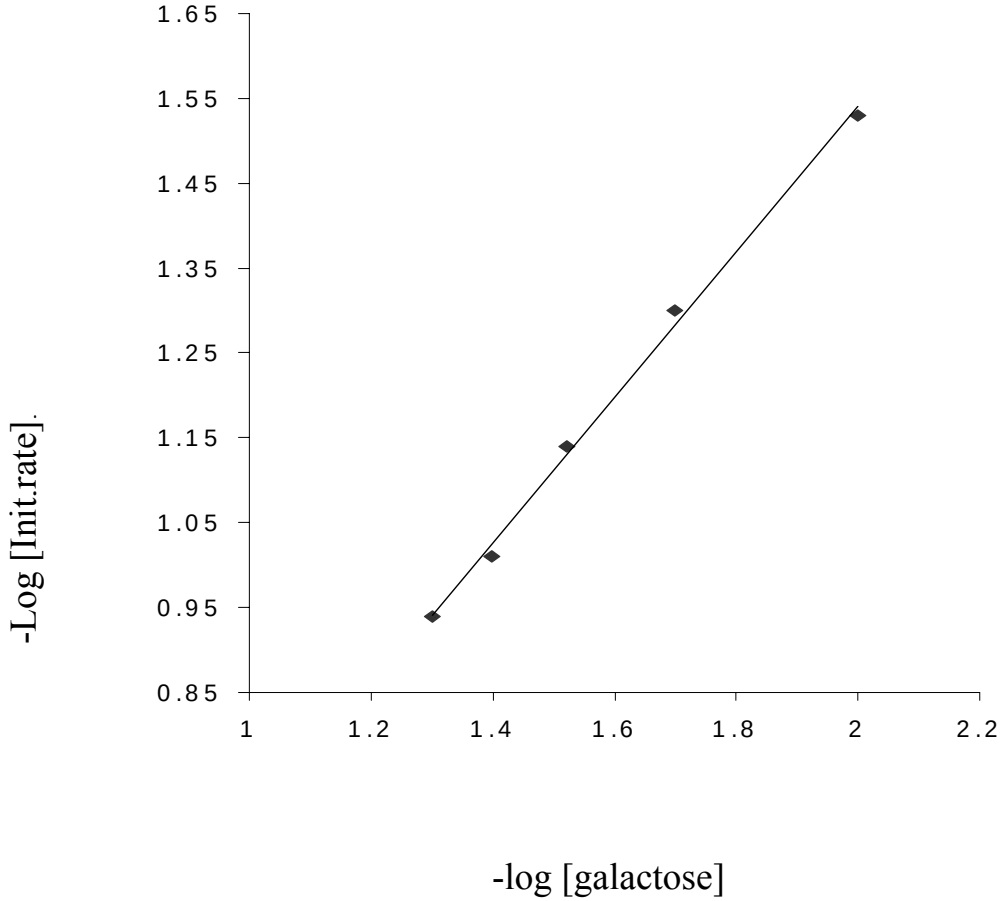


Figure 3.II.2 Effect of varying Galactose at 25˚C. $[Fe(CN)6]^{-3} = 1\times10^{-3}$M, [NaOH]= 0.1M, ionic strength = 0.15.

3.II.2.3 Dependence on sodium hydroxide concentration

For this purpose, different concentrations of sodium hydroxide were studies, keeping everything else constant. The results show that, the reaction rate constant is directly proportional to the concentration of hydroxide ion, which indicates a first order reaction as shown in table (3.II.2.) and figure (3.II.3).

Table (3.II.2) Rate data for the oxidation of galactose at 25°C.

10^2 [galactose] M	10^3 $K_3[Fe(CN)_6]$ M	10[NaOH] M	10^2 Init.rate M Sec
1.0	1.0	1.0	2.95
2.0	1.0	1.0	5.00
3.0	1.0	1.0	7.24
4.0	1.0	1.0	9.77
5.0	1.0	1.0	11.48
1.0	0.40	1.0	2.61
1.0	0.60	1.0	2.77
1.0	0.80	1.0	2.87
1.0	1.00	1.0	2.95
1.0	1.20	1.0	3.02
1.0	1.0	0.10	0.37
1.0	1.0	0.20	0.69
1.0	1.0	0.50	1.58
1.0	1.0	1.00	2.95

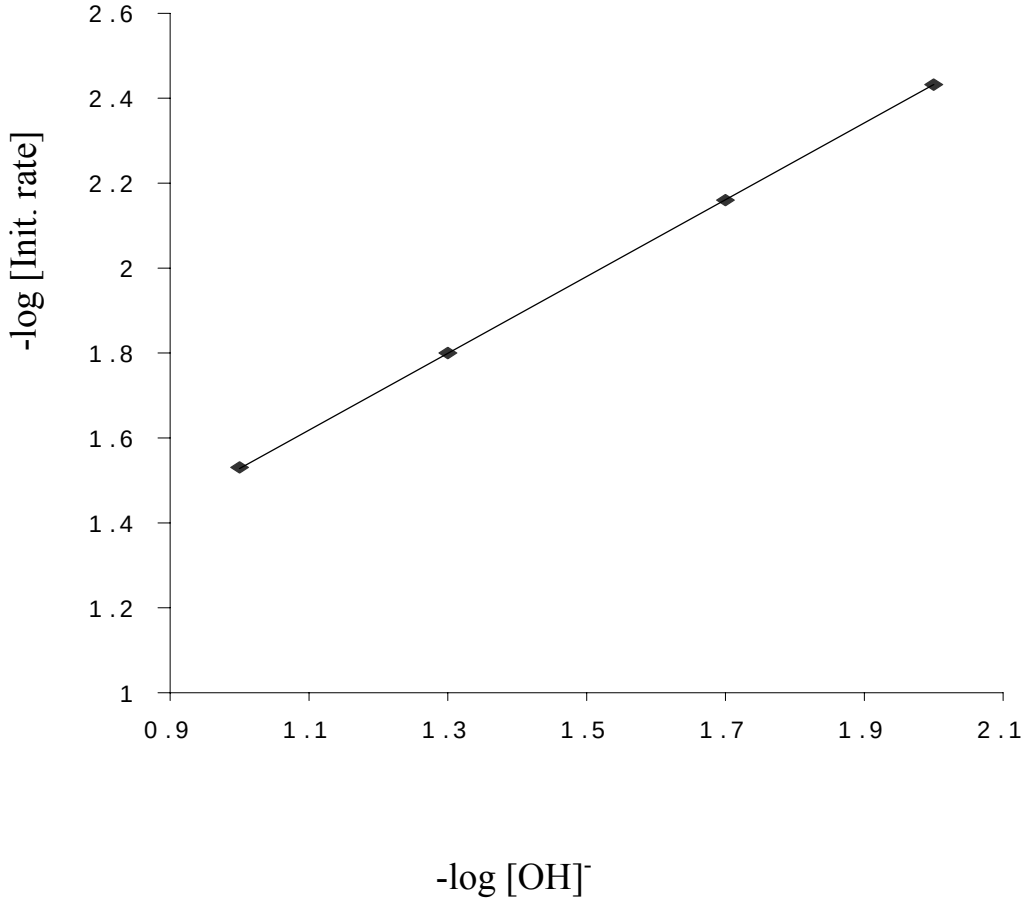


Figure 3.II.3 Effect of varying [NaOH] at 25 ºC. $[Fe(CN)6]^{-3}$ = 1×10^{-3}M, [Galactose] = 1×10^{-2}M, ionic strength = 0.15.

3.II.2.4 Effect of added salts

The reaction between galactose and hexacyanoferrate (III) was carried out using different concentration of potassium hexacyanoferrate (II). It was found that, the rate values decreased with increasing potassium hexacyanoferrate (II) concentrations as shown in Table 3.II.3) and figure (3.II.4).

Table (3.II.3) Effect of varying potassium hexacyanoferrate (II) 10^2 [galactose] = 1M, 10^3 $K_3[Fe(CN)_6]$ = 1M, 10[NaOH] = 1M, Temperature = 25ºC

10^3 $K_4[Fe(CN)_6]$ M	10^2 Init.rate M Sec^{-1}	K_{obs} M^{-1} Sec^{-1}
0.40	2.60	26.3
1.0	2.35	23.5
2.0	1.78	17.8
3.0	1.44	14.4
4.0	0.88	8.8

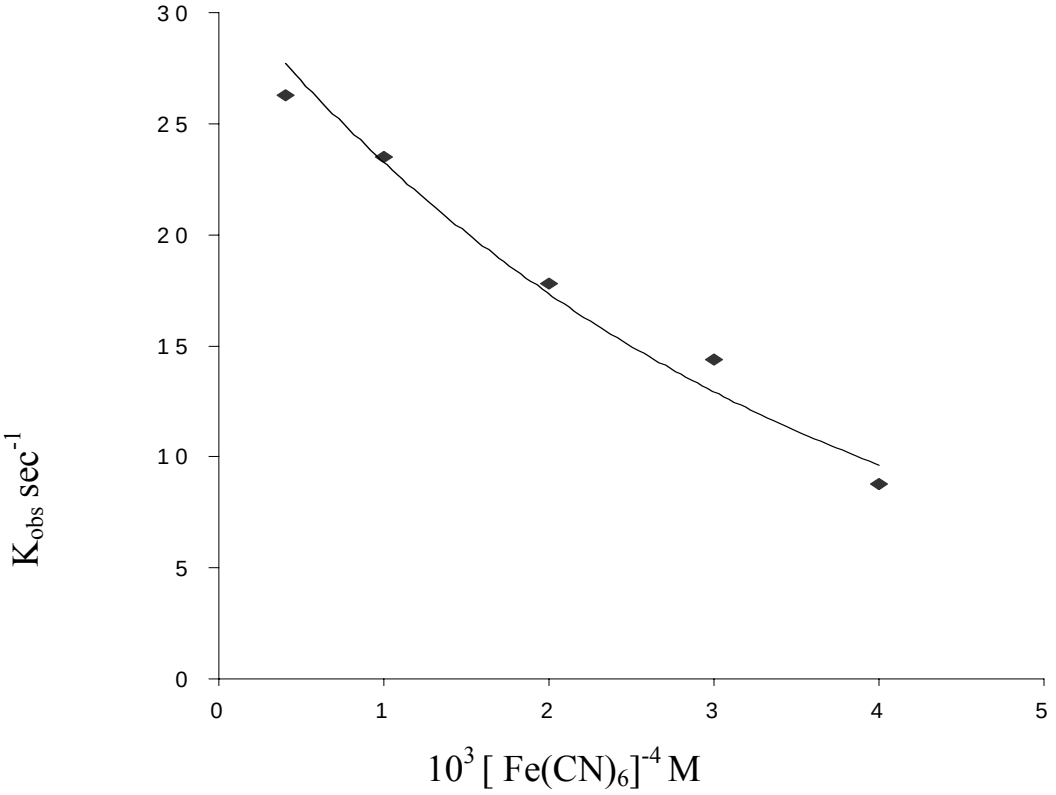


Figure 3.II.4 Effect of varying hexacyanoferrate (II) at 25˚C. $[Fe(CN)_6]^{-3}$ = 1×10^{-3}M,[Galactose] = 1×10^{-2}M, [NaOH] = 0.1M, ionic strength = 0.15.

The effect of varying the cation concentrations (NH_4^+, Na^+ and K^+) on the rate of the reaction showed that the reaction rate was decreased according to the following sequence ($K^+ > Na^+ > NH_4^+$) as shown in table

(3.II.4) and figure (3.II.5). It is worth noting that potassium salt (KCl, KBr, KI) has no significant effect on the reaction rate table (3.II.4) and figure (3.II.6).

Table (3.II.4) Effect of varying salts:
10^2 [salts] = 1M, 10^2 [galactose] = 1M, 10^3 [Fe (CN) $_6$]$^{-3}$ = 1M, 10 [OH]$^-$ = 1M, Temperature = 25ºC.

Salt	10^2 Init.rate M Sec^{-1}	K_{obs} M^{-1} Sec^{-1}
KCl	2.26	22.6
KBr	2.82	28.2
KI	2.69	26.9
NaCl	1.61	16.1
NH_4Cl	0.91	9.1

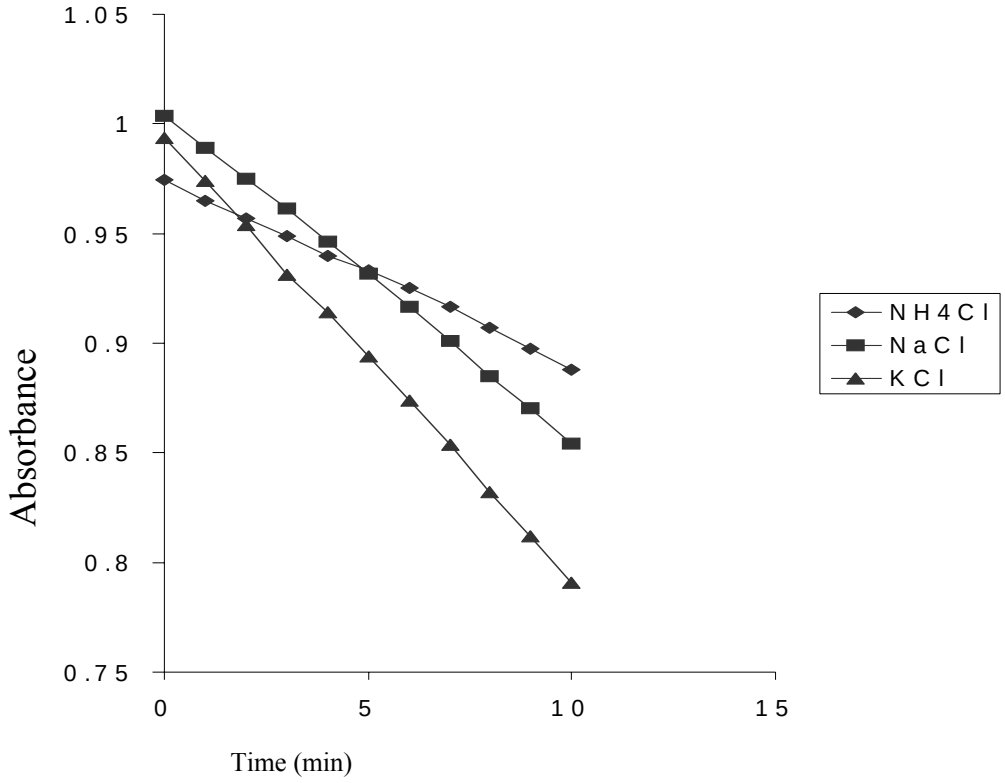


Figure 3.II.5 Effect of varying cations at 25˚C. [Fe (CN) $_6$]$^{-3}$=1×10^{-3}M, [Galactose]=1×0^{-2}M, [NaOH] = 0.1M.

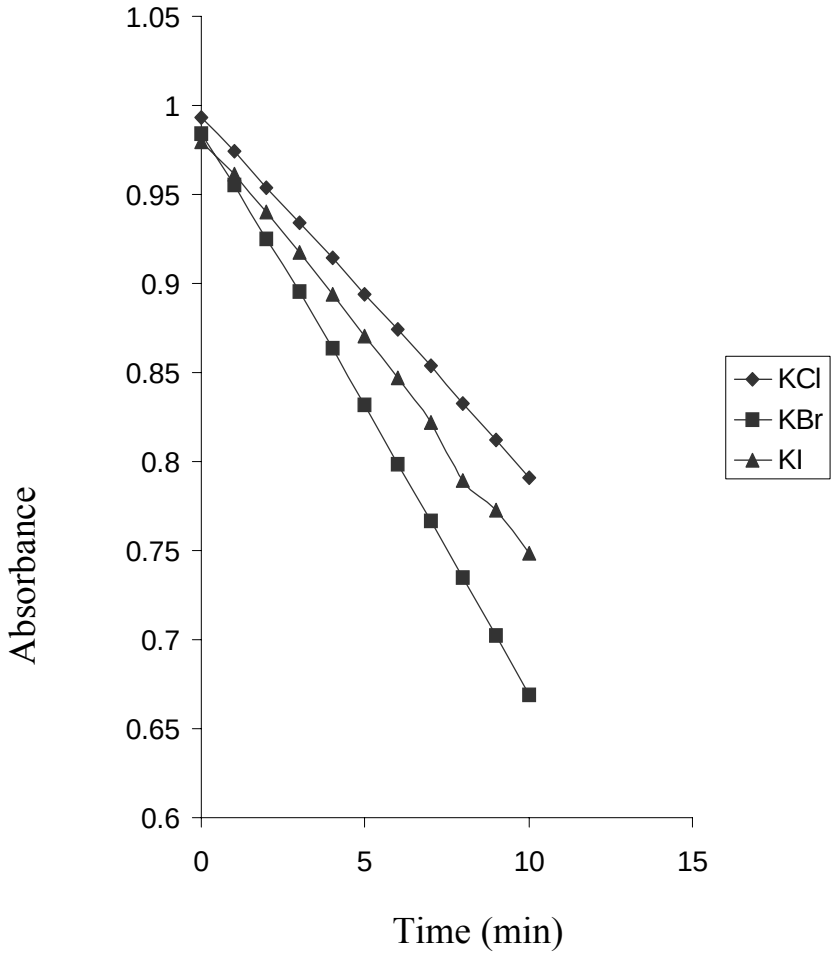


Figure 3.II.6 : Effect of varying anions at 25˚C. $[Fe(CN)_6]^{-3}=1\times10^{-3}$M ,[Galactose]=$1\times10^{-2}$M, [NaOH] = 0.1M.

3.II.2.5 Dependence on temperature

The activation parameters of the reaction between galactose and hexacyanoferrate (III) were calculated by carrying out the reaction at different temperatures (20, 25, 32 and 45 °C). Using the found rate the following equation postulated:

$$\text{Rate} = K_{obs}\,[OH^-]\,[\text{galactose}]$$

The rate constants were calculated at these different temperatures as shown in table (3.II.5) and figure (3.II.7). The activation parameters were calculated and recorded in table (3.II.6) due to the previous discussion in chapter two.

Table (3.II.5) Temperature dependence:
10^2 [galactose] = 1M, 10^3 $[Fe(CN)_6]^{-3}$ = 1M, 10 $[OH]^-$ = 1M.

T / C	10^3 (1/T) k	10^2 Init.rate M Sec	K M Sec	lnK
20.0	3.413	2.63	26.3	3.27
25.0	3.356	2.95	29.5	3.38
32.0	3.226	4.83	48.3	3.88
45.0	3.145	15.19	151.9	5.02

Table (3.II.6) Activation parameters:

Ea Kcal mol^{-1}	ΔS^* cal mol^{-1} deg^{-1}	ΔH^* Kcal mol^{-1}	ΔG^* Kcal mol^{-1}
12.77	- 8.83	12.18	14.81

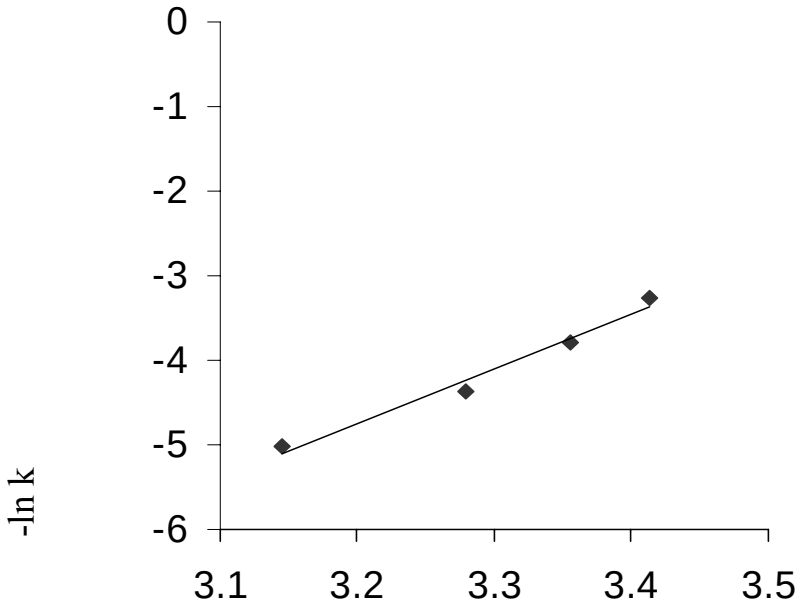


Figure 3.II.7 Effect of varying temperature. $[Fe(CN)_6]^{-3} = 1\times10^{-3}$ M,

[Galactose] = 1×10^{-3} M, $[OH]^-$ = 0.1M and ionic strength = 0.15.

On the basis of experimental data, the rate of the oxidation reactions between the galactose and hexacyanoferrate (III) may be expressed by the following equation:

$$-\frac{d}{dt}[Fe(CN)_6^{-3}] = k\,[\text{Galactose}]\,[OH^{-1}] \quad \ldots\ldots\ldots\ldots\ldots\ldots(3.1)$$

To account for the observed kinetics, the following mechanism was suggested.

This mechanism is consistent with the order proposed mechanism for the oxidation of aldose by (El-Wakil and Wagerrova, 1976; Natha and Singh, 1962). The fact that the rate of the reaction is independent of hexacyanoferrate (III) concentration indicates that the rate determining step may be a step which occurs prior to the oxidation process. This step may be the formation of the galactodiol form catalyzed by hydroxide ion (Srinivassan and Subramaniam, 1990) as seen in the above proposed equation. The galactodiol, being the reactive form reacts with the oxidant in subsequent fast step as in the equation below.

galactodiol $+2[Fe(CN)_6^{-3}] \leftrightarrow 2[Fe(CN)_6^{-4}]$ + galactonic acid $+ H_2O$..(3.2)

The above mechanism is in agreement with those proposed for Cu^{+2} catalyzed oxidation of D-glucose by alkaline potassium hexacyanoferrate (III) in a highly alkaline medium (El-Wakil and Wagerrova, 1976, Natha and Singh, 1962). The above mechanism also enables us to derive the following rate equation:

$$-\frac{d}{dt}[Fe(CN)_6^{-3}] = k_1[\text{Galactose}][OH^{-1}] - k_{-1}[\text{galactodiol}] \quad \ldots\ldots.(3.3)$$

The enediol concentration is assumed to be low an in a steady state. This enables us to neglect the second term of eq. (3.3) relative to the first term. The approximation is in agreement with the experimentally obtained results; the reaction is first order with respect to the galactose concentration, zero order with respect to the potassium hexacyanoferrate (III) concentration, and first order with respect to the hydroxide ion.

Thus the rate equation can be rewritten as:

$$\frac{d}{dt}[Fe(CN)_6^{-3}] = k_1 [\text{Galactose}]^{} [OH^-]$$

Changes in the ionic strength of the medium by the added anion (Br^-, I^-, Cl^-) showed small changes on the affect the oxidation rate. These results suggest the involvement of ions like charges in the rate - controlling step (Powell, Wu and Bruice, 1984). In this case the rate will not depend on ionic strength.

The results clearly revel the existence of specific salt effect of cations; the rate constant increased in the order $NH_4^+ < Na^+ < K^+$. For Na^+ and K^+, this catalytic effect follows the polarizability trend of the cations. The relatively low rate constant value observed for ammonium ion might be due to the fact that the introduced NH_4^+ will react instantly with the hydroxyl ion in the medium to produce ammonia and hence the specific salt effect of a cation no longer exists (Leal, Domingo and *et al*., 1994, Pergel and Buncel, 1993).

A strong retardation by potassium hexacyanoferrate (II) was observed. This indicates that potassium hexacyanoferrate (II) is involved in a reversible step that could affect the rate determining step (Burrows and Rosenblatt, 1983, Hull, Davis and Rosenblaat, 1969, Gupra and Upadhyay, 1992). Since the mechanism proposed is an ionic mechanism, the values of the entropy of activation are expected to be small.

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جامعة النجاح الوطنية
كلية الدراسات العليا

1- قياس تراكيز الرصاص والكادميوم في عينات من الغذاء والماء باستخدام طريقة Anodic Stripping Voltammetry
2- اكسدة الجالاكتوز

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قدمت هذه الأطروحة استكمالا لمتطلبات درجة الماجستير في الصحة العامة بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين

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الملخص

تتناول الدراسة الأولى بقياس تراكيز الرصاص والكادميوم في عينات من الماء في بعض العيون في مدينة نابلس والمياه في قرية جماعين (المياه الموجودة في آبار الجمع والمياه المأخوذة من البلدية). وتم دراسة تراكيز العناصر في بعض عينات من الحبوب والمشروبات الخفيفة والتبغ طريقة القياس المتبعة لتراكيز العناصر هي طريقة Anodic Stripping Voltammetry .

وقد وجد أن التراكيز في معظم العينات كانت اقل من الحد الذي يمكن قياسه من خلال هذا الجهاز وتلك التي ظهر فيه تركيز كانت اقل مما حددته منظمة الصحة العالمية.

ولكن عينات التبغ كانت تحتوي على تراكيز مرتفعة من العناصر السامة وهذه العناصر تدخل إلى الدم وتترسب فيه مسببة مشكلات صحية مختلفة.

تتناول الدراسة الثانية أكسدة سكر الجلاكتوز (Galactose) وذلك باستعمال حديدي سيانات البوتاسيوم $Fe(CN)_6^{-3}$ كعامل مساعد في وسط قاعدي ودرجة حرارة ثابتة.

وجد في هذه الدراسة أن مول واحد من السكر يتأكسد بمولان من مادة $Fe(CN)_6^{-3}$ ليعطي الحامض.

وقد تم بحث تأثير كل من مواد التفاعل مثل تركيز حديدي سيانات البوتاسيوم، تركيز السكر ، تركيز أيون الهيدروكسيد وتبين أن سرعة التفاعل تعتمد على تركيز السكر للدرجـة الأولى وعلى تركيز أيون الهيدروكسيد للدرجة الأولى وجد أن سرعة التفاعل لا تعتمد علـى تركيز حديدي سيانات البوتاسيوم. ومن ذلك وجد أن معادلة معدل سرعة التفاعل هي :

$$-\frac{d}{dt}[Fe(CN)_6] = k\,[Galactose]\,[OH^-]$$

لوحظ أن معدل التفاعل يقل بإضافة مادة حديدو سيانات البوتاسيوم $Fe(CN)_6^{-4}$ ، وهذا يثبت أن التفاعل عكسي . كما وجد أن إضافة أملاح ذات شق سالب (anions) ليس لها تأثير على التفاعل مما يدل على عدم تأثر التفاعل بالشدة الايونيـة ionic strength , ، ونوعيـة الملح المضاف بينما وجد أن أملاح ذات الشق الموجب (cations) تؤثر على التفاعل.

كما تم بحث تأثير درجة الحرارة على سرعة التفاعل ومن ذلك تم حساب المتغيـرات الثيرموديناميكية ($\Delta H^*, \Delta G^*, \Delta S^*, Ea$).

بناء على النتائج السابقة تم اقتراح ميكانيكية مناسبة للتفاعل.