

The study of corrosion behaviour of Al, Cu
and Zn in some commercial beverages by
chemical and electrochemical
measurement

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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2012

Abstract

The corrosion behaviour of pure copper, zinc and aluminum in selected commercial beverages was studied. Experiments were also conducted in the presence of citric and phosphoric acid to investigate their role in the corrosion process in these beverages. Two experimental approaches were used to investigate the corrosion behavior: a chemical method in which the dissolved metal concentration was measured after immersion of a sample in a beverage and an electrochemical method using the Tafel extrapolation technique. The metal surfaces were also examined by SEM/EDX after the immersion tests and electrochemical polarization.

Among the important conclusions from this research are that the order in which the various beverages affect the corrosion rate as evaluated by Tafel extrapolation of the polarization curves did not agree with the order based on measurement of the dissolved metal concentration as determined by the immersion tests except when a 1- day immersion test was used for Al. The dissolved Al, Zn and Cu concentrations obtained from short-term immersion tests differed from those measured in long-term tests, although the same ranking of the corrosiveness of the seven soft drinks was obtained after 1- and 3- day immersion tests. These discrepancies likely stem from the complicated dynamics of the corrosion of these metals and the various physical, chemical and electrochemical processes that take place in these beverages. No simple correlation was found between the beverage properties and composition and the dissolved copper, zinc and aluminum concentrations after immersion, whether based on short-term or long-term tests. However, the corrosion rate of copper in the 7 soft drinks as determined by the Tafel extrapolation method was found to depend on the pH. Uniform corrosion was observed in all

cases except for Al immersed in Gatorade. Pitting cavities were observed on the surface of Al after both the 5-day immersion test and Tafel polarization measurements. Of the beverages considered in this study, Gatorade was consistently found to be the most corrosive for the three test metals.

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Chapter 1

Introduction

Nowadays, with hand-held electronic devices becoming increasingly competitive, the demand for better and more reliable products is continually grows. As part of our everyday life, hand-held electronic products are exposed to various environments. For example, corrosion of metal components by spilled beverages is becoming a big concern to manufacturers, distributors, end suppliers and customers. Corrosion may lead to physical failure, but more often to electrical failure because of electrical shorts caused by electrochemical migration. Thus, it is important to investigate the corrosion of these metal components when exposed to commercial beverages commonly consumed by users of hand-held devices. This study focuses on the corrosion of aluminum, zinc and copper, perhaps the most widely used metals in the electronics industry.

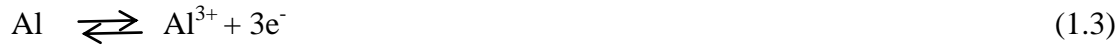
Metal corrosion can take many forms. Uniform and pitting corrosion occurs when the material is exposed to environmental that attack the material surface, such as acids, salts. Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area^[22,52]. For example, a piece of steel or zinc immersed in dilute sulfuric acid will normally dissolve at a uniform rate over its entire surface. The tarnishing of silver and “fogging” of nickel also belong to this type of corrosion. Uniform corrosion can be prevented or reduced by making use of coatings, inhibitors and cathodic protection. On the other hand, pitting is characterized by extremely localized attacks that results in holes in the metal. The nature of these two forms of corrosion may have quite different consequences. Pitting corrosion almost

always causes severe damage and so is the most destructive. At the same time, it is also difficult to predict by laboratory tests. Galvanic corrosion, also call two-metal corrosion, is an electrochemical process involving two dissimilar metals in contact in the presence of an electrolyte and an electronically conductive path.

The corrosion behaviour of aluminum, copper and zinc in acid solutions has been reported^[1-5], but no systematic study of these metals when exposed to common commercial beverages has been found in the literature. Consequently, a series of corrosion experiments were conducted in the presence of sixteen common commercial beverages as test solutions. In order to gain a better understanding of the corrosion behaviour of these metals, their behaviour in the presence of pure citric acid and phosphoric acid, two main corrosive ingredients of these beverages, was also investigated.

The reactions by which corrosion occurs can be chemical or electrochemical in nature or a combination of the two. Chemical degradation does not involve reduction/oxidation ('redox') reactions, whereas electrochemical corrosion does. Electrochemical corrosion reactions have the same features as any electrochemical cell. They involve a reduction reaction at the cathode and an oxidation reaction at the anode. During corrosion, different half-cell reactions occur at the anode and cathode. In the oxidation half-cell reaction, elemental metal is often oxidized which can lead to weight gain/loss or thinning of the solid material. The oxidative dissolution of the three test metals in this work is shown below:





The half-cell reductive reaction can vary depending on the reaction environments. The following are some examples:

(a) In strongly acidic solutions under de-aerated conditions, reduction of hydrogen ions can occur, i.e., $\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

(b) In moderately acidic solutions under aerated conditions, reduction of O_2 to H_2O can occur, i.e., $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

(c) In neutral or basic solutions under aerated conditions, reduction of O_2 to OH^- can occur, i.e., $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

For metals exposed to different environments, the anodic and cathodic electrochemical reactions will vary and have different consequences^[6-9].

The study of corrosion makes use of a variety of techniques to determine the extent of corrosion in a particular environment and the rate of metal loss. Two main types of methods are applied:

- non-electrochemical methods; and,
- electrochemical methods.

The most common non-electrochemical method used is the weight-loss technique. A metal coupon sample is exposed to the test medium and its weight loss or gain is measured as a function of time. This method is most meaningful if the sample corrodes uniformly. When localized corrosion such as pitting occurs, it will not indicate the dangerous nature of the

penetrating attack. In addition to measuring the weight loss of the corroding metal, the amount of metal that dissolves into the test solutions is also commonly measured. Both the amount of metal weight lost and metal dissolved will be determined in this work. The amount of dissolved metal is measured by analyzing solution samples using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Once a metal strip has been immersed in a test solution for a given duration, it is removed and ICP-OES analysis of the solution is conducted to measure the dissolved metal ion concentration. The concentration increase over time enables the corrosion rate to be determined.

Linear polarization techniques are the most common electrochemical methods used to study metal corrosion in aqueous solutions. In this study, the change of the corrosion potential under open-circuit conditions is monitored. Also, experiments under closed-circuit conditions are conducted to measure the rate of oxidation in the test solutions. These include linear potential scans to obtain Tafel plots and estimate corrosion rates.

When the electrode potential is shifted from the equilibrium value for a particular half-cell reaction, this reaction will proceed either in the anodic or cathodic direction. It occurs cathodically if the potential is more negative than the equilibrium value and anodically if the potential is more positive than the equilibrium value. When an electrode has a potential which allows anodic or cathodic current to flow, it is said to be polarized. A condition of zero net current flow occurs when the current due to all anode reactions on an electrode matches the current due to all cathode reactions. The electrode potential at which this state takes place is

called the open-circuit potential or corrosion potential when the reactions lead to corrosion. It is important to note that the system is normally not in an equilibrium state when this condition holds since the anodic and cathodic half-cell reactions typically are part of different redox couples.

When the anodic reaction has slower kinetics than the cathodic reaction, the corrosion rate is said to be anodically controlled and the corrosion potential will lie close to the equilibrium potential of the cathodic half-cell reaction. When the cathodic reaction has slower kinetics than the anodic reaction, the corrosion rate is said to be cathodically controlled and the corrosion potential will tend to be near the equilibrium potential of the anodic half-cell reaction.

In general, when the electrode is polarized and the potential shifts to approximately 100mV from the equilibrium potential, reverse reactions are usually negligible ^[10]. This leads to what is called Tafel behaviour. Information on the corrosion rate can be obtained by determination of the Tafel slope and the exchange current density.

Chapter 2

Research Objectives

The aim of the present work is to perform a systematic study of the effect of 16 common commercial beverages on the corrosion behaviour of the metals aluminum, zinc and copper used in electronic hand-held mobile devices. A set of methods is used to carry out chemical analysis of the beverages including anion, cation and organic acid determination. The corrosion behaviour of the test metals is investigated by measuring the amount of dissolved metal and conducting electrochemical experiments such as open-circuit potential measurements and linear potential scans when the metals are exposed to air.

Preliminary experiments quickly revealed that the determination of weight loss or gain, the traditional non-electrochemical corrosion rate measurement method, is not sensitive enough to accurately determine corrosion rates. Instead, the rate of metal dissolution determined by the more sensitive ICP-OES technique is applied to determine the corrosion rates in this work. The dissolution of metals over short-term (one day and three days) periods is of particular interest. The measurement of the open-circuit potential during corrosion is also used to characterize its behaviour. Other electrochemical parameters such as the corrosion potential, corrosion current and corrosion resistance are obtained from polarization experiments. Knowledge of the corrosion current provides a second way to determine the corrosion rate. A comparison between the corrosion rates determined from the metal dissolution data and from the polarization experiments can then be made. An attempt to correlate the metal dissolution rates during corrosion with bulk beverage properties such as molar electrical conductivity, pH, ion concentration, titratable acidity

and organic acid content has also been made. Finally, the morphology of the corroded surface is also investigated using SEM/EDX technique to gain further insight into the mode of corrosion.

The thesis is organized as follows. Chapter 3 presents a review of the literature on the corrosion of aluminum, copper and zinc and on corrosion test methods. This is followed with a chapter detailing the properties of the commercial beverages including pH, conductivity and titratable acidity, as well as the beverage composition including cation, anion, organic acid and inorganic acid concentrations. The experimental procedure and corrosion test methods used in this study are described in Chapter 5. Chapter 6 contains the results of the experiments to study the aluminum corrosion behaviour using chemical and electrochemical methods. Similar studies on zinc and copper corrosion are presented in Chapters 7 and 8, respectively. The thesis closes with a chapter summarizing the important conclusions from this research and recommendations for future work.

Chapter 3

Literature Review

Aluminum, copper and zinc are some of the most widely used metals in the world. Copper, zinc, aluminium are used for various purposes in the electronic industry. In integrated circuits, the interconnect elements are connected to the printed circuit board (PCB) using a lead frame, which is made of metals such as gold, silver, copper, zinc, aluminum or their alloys. The silicon chips are connected to the lead frame using gold or aluminum wire. A typical PCB consists of a copper connection path integrated in a fiberglass reinforced epoxy polymer.

Numerous research reports related to their corrosion behaviour have been published. Metal corrosion is usually a very complex phenomenon. Different types of corrosion can occur simultaneously in the same media and under the same environmental condition. Corrosion is affected by many factors that are related to the environment and to the metal. However, corrosion mechanisms and behavior are often difficult to explain because the various processes and factors can be difficult to sort out and the theoretical foundations are sometimes insufficient to provide a satisfactory answer^[11]. A metal is most likely to corrode when it is contact with an aqueous solution. Thus, the chemical composition of the solution as well as its physicochemical properties such as temperature and electric conductivity are important factors determining the corrosion rate of a metal.

3.1 Effect of Solution Acidity and Chemical Composition

The pH is an important factor for metal corrosion in aqueous solutions. In general, metals exhibit different corrosion behaviour in acidic, neutral and alkaline media. The pH value of a solution can affect the reaction mechanism and of course can be directly involved in the reaction. The pH has been shown to have a strong effect on the corrosion of Cu and its alloys in NaCl solutions, yielding the highest corrosion rates at pH 1 and the lowest at pH 7^[12]. A further explanation given for this effect is that Cl⁻ acts as a corrosion promoter in acidic media and an inhibitor under neutral conditions. It is well known that steel has a poor corrosion resistance in acidic media, while aluminum has poor resistance in alkaline media containing potassium or sodium hydroxide^[4].

However, when a solution is made up of a complex mixture of anions, cations, organic acids and/or inorganic acids, pH does not always have the dominant effect on the corrosion behaviour of a metal due to the effect of the other components in the aqueous medium. For example, a corrosion study of an aluminum-bronze dental alloy in some beverages showed that no correlation existed between corrosion rate and beverage pH^[13]. In general, the reaction rate increases with the concentration of corrosive agents although this relationship is not necessarily linear. Halide salts (fluorides, chlorides, bromides and iodides) are generally more aggressive towards aluminum than are sulphate and phosphate salts. Somewhat surprisingly, oxidizing salts such as chlorates, persulfates, nitrates and perchlorates generally have little effect^[14]. The influences of pH and phosphate levels on copper release from residential plumbing in a drinking water system have been studied^[15]. Although phosphate is often considered a corrosion inhibitor,

it was shown to lead to both higher and lower dissolved copper concentrations. Two mechanisms were proposed: i) inhibition of oxygen reduction due to the presence of orthophosphate and consequential lower copper oxidation and release into water and ii) hindrance of the precipitation of insoluble copper malachite by phosphate, leading to more copper dissolution.

Cana et al^[16] investigated the corrosion behavior of copper in solutions with different concentrations of citric acid. The corrosion rate rose as the citric acid concentration increased from 0.001 to 1.0M. The effect of oxalic acid on the behaviour of copper in various aerated organic acid solutions has also been studied. Propionic and citric acid were selected as the organic acids in this study. In 60 wt% propionic acid containing 50g/L oxalic acid, the weight of the copper increased quickly during the first 24 hours before increasing more gradually over the next 5 days (Figure 3.1.1). However, when the oxalic acid concentration was increased to 75g/L, the behaviour changed significantly. In this case, the weight increased rapidly over the first day, but then remained virtually constant over the next 4 days before once again rising more sharply thereafter (Figure 3.1.2). From this behaviour, it was concluded that oxalic acid acts as a corrosion inhibitor. The increasing weight of the samples was attributed to the formation of oxide layers on the copper surface.

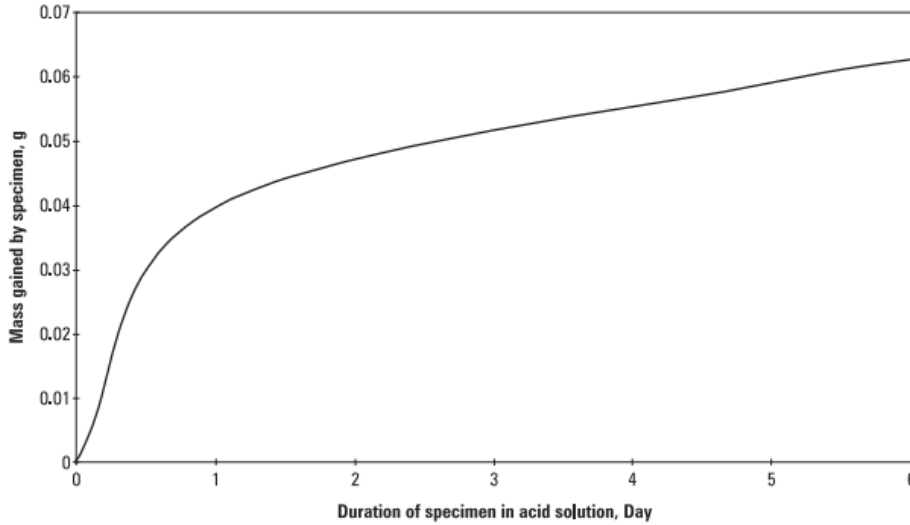


Figure 3.1.1 Inhibition effect of oxalic acid (200g) on copper dissolution [16]

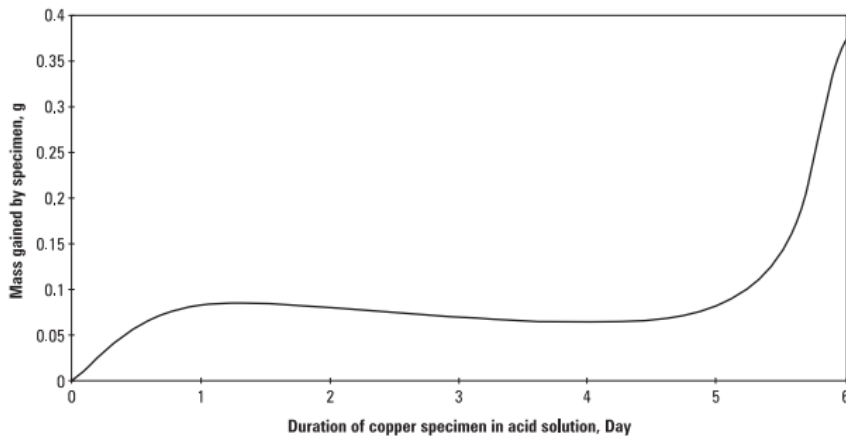


Figure 3.1.2 Inhibition effect of oxalic acid (300g) on copper [16]

The effect of pH on aluminum corrosion in 1M citric acid solution with and without F^- present has also been studied and yielded the results presented in Figure 3.1.3^[17]. In the study, a small amount of F^- added to the citrate solution was found to accelerate the corrosion considerably. Corrosion rates were determined by measurement of the change in metal weight, while the pH

was adjusted using NaOH.

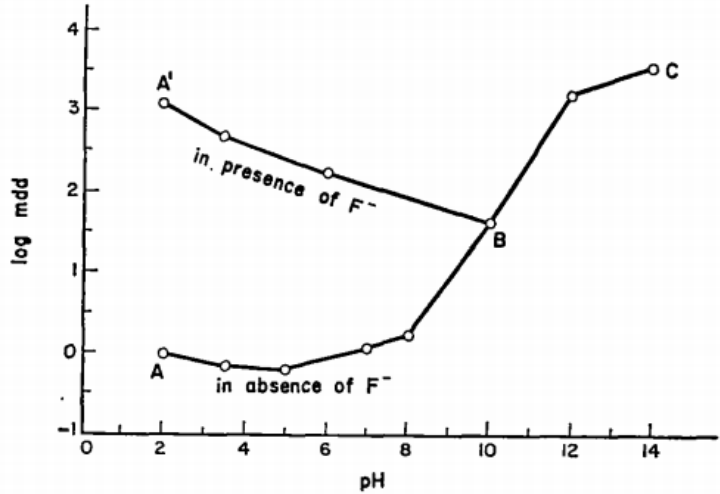
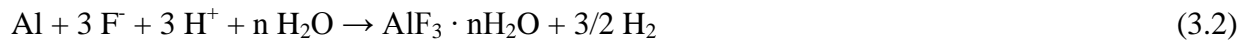
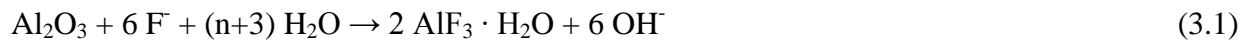


Figure 3.1.3 Corrosion rates of Al in 1M citrate solutions (mdd; mg dm⁻²day) [17]

Al is known to react with citrate ions to form soluble and stable Al-citrate chelates. In acidic and neutral medium in the absence of F⁻, the corrosion rate remains low because of the formation of an oxide film on the surface which hinders citrate ion attack. However, when small amounts of F⁻ are added, the following two reactions are considered to occur:



The first reaction brings about the breakdown of the protective oxide film, while both cause the formation of an AlF₃ film. However, this film is not protective due to the solubility of AlF₃ in citrate solutions and so corrosion of the underlying substrate occurs. The replacement of the oxide film by a film consisting of AlF₃ in the presence of F⁻ has been confirmed by X-ray

analysis (XRD). This effect of the addition of F^- on the corrosion of aluminum is also reflected in the change in corrosion potential and current. As shown below (Figure 3.1.4), the corrosion potential is reduced and the corrosion current increased significantly when as little as 10^{-4} M F^- is added at pH 3.5.

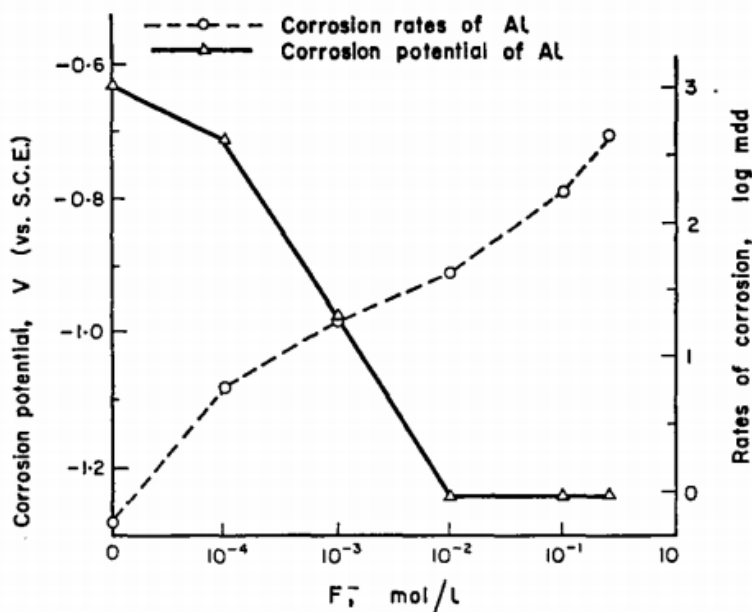


Figure 3.1.4 Effect of F^- in 1 mol l^{-1} citrate solution, $\text{pH}=3.5$ ^[17]

The electrochemical and surface properties of aluminum in 0.05M citric acid have been studied by means of open circuit potential (OCP) measurements, potentiodynamic polarization and chronoamperometry ^[18]. NaOH was added to yield pH values from 3 to 8 and HClO_4 was used to attain pH 2. The author suggested that the corrosion rate depends on the competition between the citrate and fluoride ion from the bulk solution for adsorption sites on the oxide film. The more that fluoride can adsorb, the faster the corrosion rate. Potentiodynamic polarization experiments showed that aluminum exhibits passive behaviour at pH 4–8 due to the formation of a thin oxide

film. Polarization curve provided supporting evidence of hydrogen evolution occurring on oxide-covered Al. E_{corr} , I_{corr} and the Tafel slope β_a suggested that surface processes were probably involved in the dissolution kinetics of aluminum. Rotating disc electrode tests showed that dissolution of Al was controlled by mass transport at pH 2, 7 and 8, but kinetically controlled by a surface reaction such as adsorption and surface complexation at pH 3–6. The inhibitive effect of citric acid on the oxidation of aluminum in 2M NaCl solution at pH 2 using electrochemical techniques has also been reported ^[19]. Oxidation current densities were reduced by increasing the citric concentration in NaCl-containing solutions (Figure 3.1.5) ^[19]. The addition of low concentrations of citric acid in 2M NaCl solution inhibits the corrosion of aluminium. The inhibition efficiency increases with increasing citric acid concentration up to a critical value of $1 \times 10^{-5} \text{M}$, which provides the best protection.

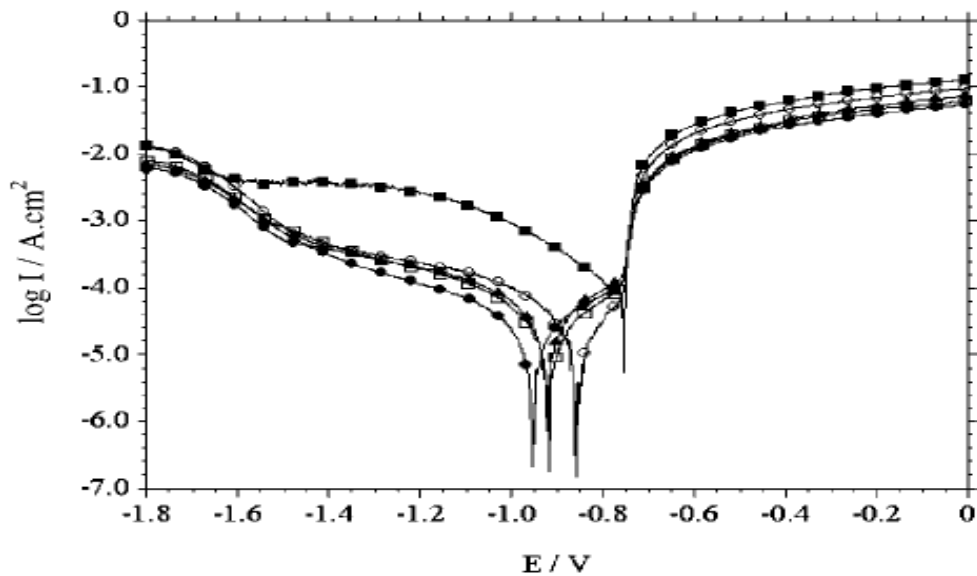


Figure 3.1.5 Polarization curves of Al in 2M NaCl solution with and without different concentrations of citric acids: ■ = blank, ○ = $5.0 \times 10^{-7} \text{M}$, △ = $1.0 \times 10^{-6} \text{M}$, □ = $5.0 \times 10^{-6} \text{M}$, ● = $1.0 \times 10^{-5} \text{M}$ ^[19]

However, when citric acid concentrations greater than $1 \times 10^{-5} \text{ M}$ were added, the opposite behaviour was observed (Figure 3.1.6) ^[19]. Thus, it is necessary to use small concentrations of citric acid for inhibition of aluminium. The explanation given for the increase in oxidation at higher citric acid concentrations is the formation of soluble AlCit complexes that desorb from the electrode surface. Citric acid acts as mixed-type inhibitor with a predominantly cathodic reaction.

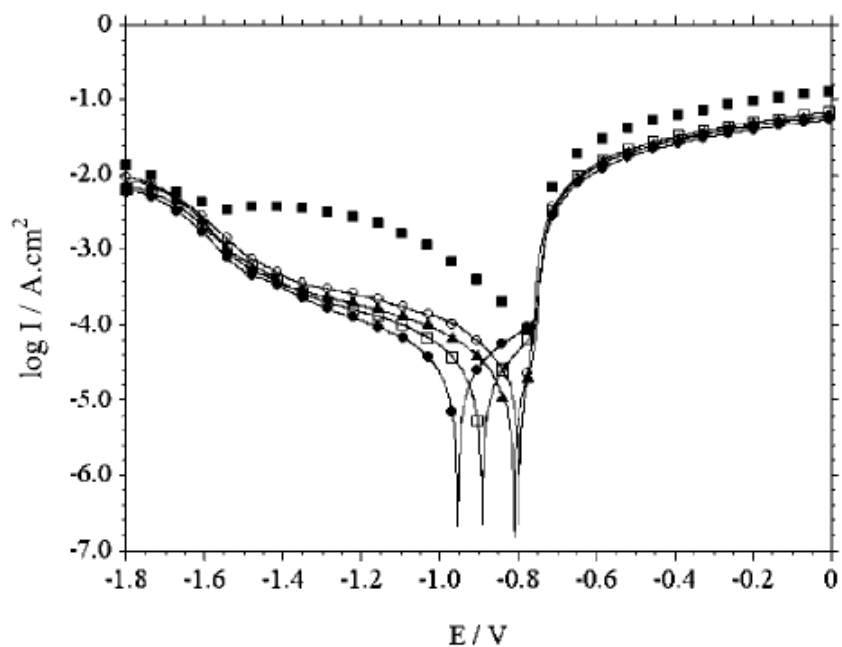


Figure 3.1.6 Polarization curves of Al in 2M NaCl solution with and without different concentrations of citric acids: ■ = blank, ● = $1.0 \times 10^{-5} \text{ M}$, □ = $5.0 \times 10^{-5} \text{ M}$, ▲ = $1.0 \times 10^{-4} \text{ M}$, ○ = $1.0 \times 10^{-3} \text{ M}$ ^[19]

The corrosion behaviour of Al in the presence of ascorbic, citric and tartaric acids with and without chloride ions has also been reported ^[20]. The corrosion potential E_{corr} was found to decrease with increasing pH. The addition of chloride ions to these carboxylic acids caused an

increase in the corrosion rate of Al especially at low pH and high temperatures. On the other hand, the addition of chloride ions to carboxylic acids reduced the corrosion rate over long-term immersion times of 60 hours, presumably due to the formation of a defect-free oxide film.

When several anions and cations are present together, synergistic or antagonistic effects may occur simultaneously or separately depending on the conditions. The corrosion of an aluminum-bronze dental alloy immersed in some beverages was reported ^[21]. No correlation between the corrosion rate and beverage properties such as pH, conductivity and composition was found.

3.2 Corrosion in Commercial Beverages

A large amount of research on copper, zinc and aluminum corrosion in different media can be found in the literature. However, based on our knowledge, only two studies on metal corrosion behaviour in commercial beverages are reported in the open literature. One of these studies was concerned with the corrosion behavior of an aluminum-bronze dental alloy in some beverages and solutions^[21]. The experiments were carried out by means of traditional electrochemical techniques: polarization tests, polarization resistance measurements and weight-loss tests. The aggressiveness of the test beverages and solutions studied was evaluated based on the corrosion rate computed from the weight-loss measurements (Table 3.2.1). Based on these experiments, the media can be ranked in order of increasing corrosivity as follows: artificial saliva, lemon juice, vinegar, 1 M NaCl, white wine, red wine and artificial orange juice. At the same time, the results showed that the aggressiveness of the different liquids is independent of both the pH and electrical conductivity of the solution (Figure 3.2.1). The corrosion resistance (R_p) values of the

beverages on Al-Cu alloy were measured in this work and also found to have no obvious relationship to the corrosion rate computed from weight loss (Figure 3.2.2).

Table 3.2.1 Mean Corrosion Rates (CR) and Standard Deviation expressed as $(\text{cm}^2\text{day})^{-1}$ after 7, 15 and 30 days of immersion to the solution [22].

Solution	7 days	15 days	30 days
NaCl 1 M	$2.87 \times 10^{-5} \pm 0.29 \times 10^{-5}$	$1.76 \times 10^{-5} \pm 0.07 \times 10^{-5}$	$1.01 \times 10^{-5} \pm 0.09 \times 10^{-5}$
Artificial saliva	$8.02 \times 10^{-6} \pm 3.19 \times 10^{-6}$	$6.79 \times 10^{-6} \pm 0.89 \times 10^{-6}$	$5.22 \times 10^{-6} \pm 0.57 \times 10^{-6}$
Vinegar	$2.06 \times 10^{-5} \pm 0.16 \times 10^{-5}$	$1.32 \times 10^{-5} \pm 0.04 \times 10^{-5}$	$7.59 \times 10^{-6} \pm 0.88 \times 10^{-6}$
White wine	$3.42 \times 10^{-5} \pm 1.22 \times 10^{-5}$	$2.92 \times 10^{-5} \pm 1.65 \times 10^{-5}$	$2.00 \times 10^{-5} \pm 0.84 \times 10^{-5}$
Red wine	$7.10 \times 10^{-5} \pm 3.82 \times 10^{-5}$	$4.52 \times 10^{-5} \pm 1.77 \times 10^{-5}$	$3.17 \times 10^{-5} \pm 0.86 \times 10^{-5}$
Lemon juice	$2.53 \times 10^{-5} \pm 0.38 \times 10^{-5}$	$3.89 \times 10^{-5} \pm 0.07 \times 10^{-5}$	$6.06 \times 10^{-5} \pm 0.23 \times 10^{-5}$
Artificial orange juice	$8.28 \times 10^{-5} \pm 2.23 \times 10^{-5}$	$4.47 \times 10^{-5} \pm 1.09 \times 10^{-5}$	$2.81 \times 10^{-5} \pm 0.52 \times 10^{-5}$

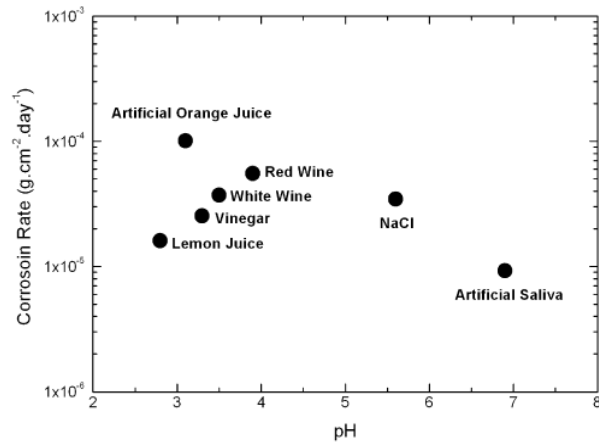


Figure 3.2.1 Mean corrosion rate values as a function of the pH of the solution [22]

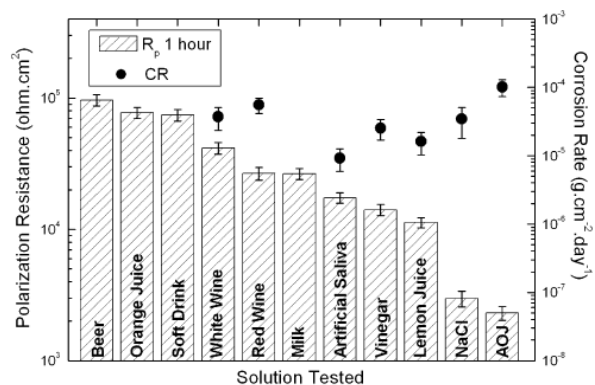


Figure 3.2.2 Polarization resistance (R_p) in decreasing order and corrosion rates (CR) computed from the weight loss measurements.^[22]

Another study^[22] focused on the corrosion behaviour of Al in several soft drinks using potentiodynamic polarization measurement. Polarization curves in selected soft drinks were measured. All experimental polarization curves had similar shapes. The anodic and cathodic branches of these curves were not symmetrical and their Tafel plots did not intersect at E_{corr} . Corrosion parameters and corrosion rates were determined from cathodic polarization curve because its Tafel line was much longer than that of the anodic branch. These results showed that the corrosion of Al in soft drinks is a slow, time-dependent and complex process, strongly influenced by the passivation, complexation and adsorption process. Phosphoric acid is more corrosive to Al than is citric acid.

3.3 Modes of Corrosion

Uniform corrosion, pitting corrosion, stress corrosion, etc. can occur on metal surfaces. The predominant mode of corrosion depends on a number of factors that are intrinsic to the metal, medium and the operating conditions. No form of corrosion is specific to a given metal or its

alloys. With aluminum and its alloys, uniform corrosion is often observed in very acidic or very alkaline media, while pitting corrosion usually occurs in solutions at near-neutral pH^[14]. Using OCP, LPR and ICP-AES measurements, Amin et al^[23] confirmed that both uniform and pitting corrosion occur on aluminum alloy electrode surfaces in KSCN solutions depending on their composition.

Copper and its alloys have been shown to exhibit excellent corrosion resistance in saline solutions, alkaline solutions and solutions containing organic chemicals. However, copper is susceptible to more rapid attack in the presence of oxidizing acids, oxidizing heavy-metal salts, sulfur, ammonia (NH₃) and some sulfur- and NH₃-based compounds. Uniform corrosion was reported in Cu and a CuCrZr alloy in chloride solution at pH 1 and 12^[24]. The interaction of citric, glycolic, acetic, malic and oxalic acids with copper result in a direct surface attack and/or formation of an insoluble chelated surface species^[25].

The corrosion of zinc in solutions is largely controlled by the components present in the solution. In addition to electrolyte composition, other factors such as time of exposure, temperature, etc. can influence the zinc corrosion behaviour in aqueous solutions. In general, zinc corrodes rapidly in both acidic and strongly alkaline conditions. Pitting corrosion of Zn and steel coated with a Zn-Al alloy in pH 2 and 12 NaCl solutions was reported by W. Miao^[26].

3.4. Corrosion Test Methods

Several chemical and electrochemical experimental techniques are used to characterize the corrosion behaviour of metals and their alloys. The National Association of Corrosion Engineers (NACE) Standard Laboratory and ASTM Recommended Practice for Laboratory Immersion Corrosion Testing of Metals provide general guidelines for immersion testing. In most cases, immersion tests can be conducted to determine the corrosion rates of metals in aqueous solutions. The use of specifically designed specimens and conditions also enables immersion tests to provide information on the resistance of the metal to pitting, crevice corrosion, galvanic corrosion, etc. Electrochemical test methods allow corrosion rates to be determined by such techniques as corrosion resistance, linear polarization and potentiodynamic polarization measurements^[27-28].

Chapter 4

Analysis of Commercial Beverages Examined in This Study

Some bulk properties of the commercial beverages were first measured with the idea of later determining whether they play a role in the corrosion behaviour of the metals. These properties include electrical conductivity, pH and titratable acidity. Chemical analysis was also done to obtain the concentrations of various anions, cations and organic acids in the test beverages.

4.1 Preparation of Beverage Samples Prior to Chemical Analysis

The following 16 common commercial beverages including soft drinks, milk products, juices and alcohol were selected for this study:

- Minute Maid™ Apple Juice;
- Alexander Keith's™ India Pale Ale;
- Coca-Cola™;
- Master coffee™
- Dr. Pepper™;
- Gatorade™ Sports Drink (Fruit Punch);
- Canada Dry™ Ginger Ale;
- Carnation™ Rich Chocolate Hot Chocolate;
- Neilson™ 2% Partly Skimmed Milk:Tropicana™ Pure Premium 100% Pure & Natural Orange Juice (No Pulp);
- Pepsi™ Cola;

- Barq's™ Root Beer;
- Sprite™;
- Lipton™ Red Rose Orange Pekoe Tea Heinz™ Canada Fancy Tomato Juice: and,
- Wolf Blass™ Yellow Label 2006 Cabernet Sauvignon.

Prior to analysis, hot chocolate and tea were first prepared strictly following the brewing instructions provided on each package and then allowed to cool to room temperature in order to minimize the data spread due to varying beverage conditions. The hot chocolate sample was prepared by pouring 1 bag (28g) into 175 ml hot water, stirring until it completely dissolved and then allowing it to cool to room temperature. The tea sample was produced by immersing one bag of tea into 180 mL hot water and steeping it for three minutes without stirring before allowing it to cool to room temperature. Master coffee™ was obtained from a coffee machine directly.

Prior to analyses of their chemical compositions, the alcoholic products wine and beer were treated using a VWR heatblock to remove the alcohol in air. The 5 mL samples were air-blown across the surface to evaporate all the ethanol and most of the water down to 2 mL before adding Milli-Q water to bring the volume back up to 5ml. This cycle was repeated two more times to ensure that all the alcohol was removed from the beverages.

All 16 beverages selected were centrifuged, filtered to remove suspended and then extracted by 50 ml dichloromethane (DCM) three times in order to decrease the sugar content in solutions,

filtered using 0.2 micro-syringe filters and diluted 10- or 100-fold before analysis. A Dionex Ion Chromatography system was used to measure the content of inorganic anions and carboxylic acids including malic, tartaric, fumaric, acetic and ascorbic acid as well as an inorganic acid-orthophosphoric acid. Citric and benzoic acid were analyzed using an Agilent Technologies HPLC-MS system. Metal ion concentrations were measured using a Perkin Elmer 3000DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

4.2 Anion Analysis

In ion chromatography, a solution is passed through a column and ions and polar molecules are transferred onto a stationary phase based on coulombic interactions. These charged species are then eluted from the column and their concentrations are measured by a detector (based on conductivity measurement in the Dionex unit used in this study). The various ions present in a sample can be separated and their concentrations measured as they are eluted from the column in reverse order to their affinity to the stationary phase (i.e. ions with weakest affinity are eluted first).

A Dionex AS11-HC column^[29] operated with a 30mM NaOH mobile phase and 1ml/min flow rate was used to determine the concentrations of the following 6 inorganic anions in each beverage: F^- , Cl^- , NO_3^- , NO_2^- , SO_4^{2-} and PO_4^{3-} . The column was calibrated for each anion using standard solutions containing 1, 2.5 and 5.0 ppm of each ion. With appropriate sample preparation prior to analysis, as described in section 4.1, the various ions in a given sample could be detected and their concentrations measured with excellent repeatability (relative standard

deviations of about 2 %), sensitivity (error of ~ 0.1 ppm for each anion) and no interferences between ions and other matrix components. The analysis of the 16 beverages yields the breakdown for the 6 inorganic anions shown below in Table 4.2.1.

Table 4.2.1 Concentration of inorganic ions in the 16 commercial beverages (ppm)

	PO_4^{3-}	F^-	Cl^-	SO_4^{2-}	NO_3^-	NO_2^-
Pepsi	532.8	12.7	17.4	29.2		
Dr. Pepper	470.5	22.2	19.2	32.3		
Coca-cola	670	14.8	32.9	41.4		
Sprite		6.8	14.3	21.9		
Root beer		17.6	30.1	25.2	3.1	
Canada Dry			34.6	27.3		
Gatorade	418		456			
Apple J	197	199	1251	107		
Orange J	401	69	601	84		
Tomato J	234	NA	3373	140		
Beer	222	97.05	85.55	638		98.4
Wine	859	398	260	310	7.08	933
Tea	14.3	21.5	13.8	12.1	2.5	
Coffee	293	148.9	106.8	20.5		
Hot chocolate	333.3	49.9	863.5	28.2		
Milk	1330		991	86.5		

4.3 Cation Analysis

Inductively coupled plasma-optical emission spectroscopy (ICP-OES), also referred to as inductively coupled plasma atomic emission spectrometry (AES), is a widely used analytical technique^[30-31] for trace detection of metals in solution. When a sample solution is injected into a plasma, its components are atomized, ionized and thermally excited. This causes electrons in atoms (i.e., components that are not ionized by the plasma) and ions to jump into higher level orbitals. When these electrons return to their ground states, photons are emitted at wavelengths characteristic of the particular elements. The emitted light is then measured by an optical spectrometer in the visible region of the electromagnetic spectrum.

Table 4.3.1 Elements and their characteristic wavelengths analyzed by ICP.

Elements	Calcium	Iron	Potassium	Magnesium	Sodium
Wavelengths	315.88	259.933	766.455	279.071	588.983

Table 4.3.2 Metal concentrations (ppm) in the commercial beverages

	Calcium	Iron	Potassium	Magnesium	Sodium
Pepsi	1.55	NA	24.2	0.253	2.85
Dr. Pepper	1.68	NA	2.17	0.302	42.8
Coca-cola	12.5	1.06	1.29	2.98	16.2
Sprite	17.2	NA	1.23	4.25	86.3
Root beer	15.8	156	1.5	4.09	92.7
Canada Dry	26.1	NA	36.8	12.9	41.3
Gatorade	2.45	0.58	149	0.886	458
Apple juice	55.1	0.737	1120	42.9	27.6
Orange juice	83.2	0.54	1630	110	5.03
Tomato juice	42.1	9.94	2590	96.6	2120
Beer	88.6	NA	303	76.4	24.3
Wine	70.5	2.46	943	130	37
Tea	0.464	NA	112	6.24	8.27
Coffee	94.2	NA	854	36.2	117
Hot chocolate	22.1	0.019	901	25.7	669
Milk	716	NA	994	69.8	266

Due to matrix effects, it was necessary to make up multi-element standards containing mixtures of different cations with known concentrations. The beverages were analyzed for the following 5 metals: Ca, Fe, K, Mg and Na. Multi-element standards using 1,000 ppm stock solutions of each of these cations were prepared. Three standard solutions containing 0.1, 1 and 5.0 ppm of multi-element analytes were used to calibrate the ICP unit. The measurements were performed using a Perkin Elmer 3000DV Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) instrument equipped with WinLab32™ for ICP software for simultaneous measurement of all analyte wavelengths of interest. The selected analytical wavelengths for the 5 metals are compiled in Table 4.3.1. Chemical analysis of the 16 commercial beverages yielded the metal concentrations presented in Table 4.3.2.

4.4 Organic Acid Analysis

Organic compounds such as citric acid and malic acid are often introduced into carbonated beverages to impart a particular flavor. In addition, some organic acids may be present naturally in the fruit used in juices and beverages. Ion chromatography can be used to separate and measure the concentrations of some of the organic acids in beverages. A Dionex IC system with UV 210 nm detector, Acclaim OA 5 μ m column, 100mM Na₂SO₄ as the MSA mobile phase^[32] was used for determination of some organic acids and an inorganic acid-phosphoric acid in the test beverages of this study. It has been applied successfully to the analysis of lactic, succinic, malic, tartaric, fumaric, acetic, ascorbic acid and phosphoric acids in 16 commercial beverages. Total analysis time is approximately 20 minutes.

Table 4.4.1 Concentration of some organic acids and phosphoric acid in the 16 commercial beverages (ppm)

	lactic	succinic	malic	tartaric	citric	benzoic	fumaric	acetic	ascorbic	phosphoric
Pepsi					55					532
Dr. Pepper						253				459
Coca-cola										509
Sprite					1135	61				
Root beer					152	502				
Canada Dry					1234	190				
Gatorade					3289					367
Apple juice	42	6.7	4125		53			220	11.8	242
Orange juice	121	6.1	2135		7415			82		364
Tomato juice	77	4.6	480		2964				8.3	304
Beer	81	143	143		150		1.8	56		160
Wine	1080	1023	35.4	1345	46			563	15.4	954
Tea			22.6							17
Coffee	108	3.6	104		329		3.8	299		342
Hot chocolate	161	5.7	18.7		335			112		479
Milk			18.4		1270					1662

Liquid chromatography–mass spectrometry (LC-MS, or alternatively HPLC-MS) combines the physical separation capabilities of liquid chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry. High-performance liquid chromatography (HPLC) with mass spectrometric (MS/MS) detection has been demonstrated to be a powerful technique for the quantitative determination of organic acids in beverages^[33-34]. Due to interference between citric acid and oxalic acid, HPLC-MS was applied for citric acid and benzoic acid determination. Cohnm Sonoma C18 column with 60% water/40% acetonitrile as mobile phase, 0.35 ml/min flow rate were chosen as the experimental conditions. The concentrations of some organic acids and phosphoric acid (ppm) in the commercial beverages determined by IC and HPLC-MS are listed as Table 4.4.1.

4.5 pH, Titratable Acidity and Conductivity Measurements.

All carbonated beverages were degassed in an ultrasound bath for 10 minutes before measurement. The pH and conductivity of the beverages were obtained at room temperature using a PC 510 Bench pH/conductivity Meter. Calibrations were performed with pH 4.01, 7.0 and 10.01 buffers and 1414 and 9969 $\mu\text{s}/\text{cm}$ standard conductivity solutions prior to the measurements of the beverages. Table 4.5.1 presents the results obtained for each beverage.

Titrateable acidity is a measure of the total amount of protons available in some beverage and is usually expressed as g/L tartaric acid equivalent. It can be obtained by determining the volume of a 0.1M NaOH solution that must be added to 20 ml beverage in order to raise its pH to 8.2 ^[35].

The titrateable acidity is then calculated using the following formula:

$$\text{g/l} = \frac{\text{ml NaOH} \times \text{normality NaOH} \times 0.075^* \times 1000}{\text{Sample volume (ml)}} \quad (4.1)$$

* = equivalent weight of tartaric acid (kg equiv^{-1})

The values so obtained for the 16 beverages are shown in Table 4.5.2. Comparison of Tables 4.5.1 and 4.5.2 indicates that the pH is not the same as the titrateable acidity. Figure 4.5.1 shows the analytical results for pH and titrateable acidity of the 16 test beverages in a graphical form.

Table 4.5.1 pH and electrical conductivities of 16 commercial beverages.

Beverages	pH	Conductivity($\mu\text{s cm}^{-1}$)
Coca-cola	2.47	1255
Pepsi	2.48	1124
Canada dry	2.82	598
Dr. Pepper	2.86	657
Gatorade	2.92	2200
Sprite	3.26	499
Wine	3.46	2445
Apple juice	3.57	2375
Orange juice	3.8	4295
Beer	3.98	1497
Tomato juice	4.00	15060
Root beer	4.24	433
Red Tea	5.33	506
Coffee	6.04	2555
Milk	6.63	5210
Hot chocolate	7.01	4760

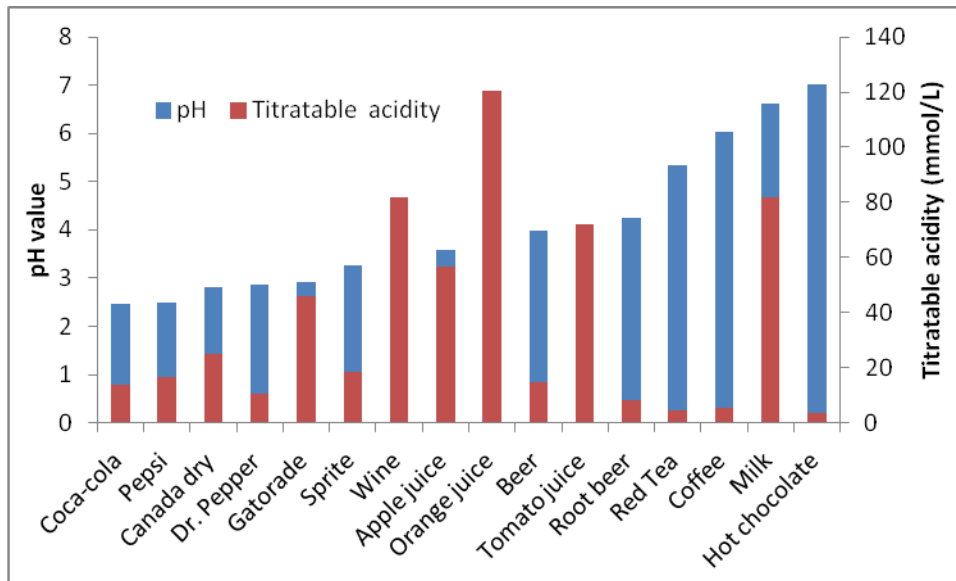


Figure 4.5.1 Variation of pH and titratable acidity of the 16 test beverages.

Table 4.5.2 Titratable acidity of the 16 commercial beverages.

Beverages	Titratable acidity (mmol L⁻¹)		
	Mean value	Range of values	Standard deviation
Canada Dry	24.83	24.25-25.25	0.52
Sprite	18.50	18.00-19.00	0.5
Pepsi	16.58	15.50-17.50	1.01
Coke	13.67	13.50-14.00	0.29
Root Beer	8.00	7.75-8.25	0.25
Dr.Pepper	10.58	9.50-12.00	1.28
Gatorade	46.12	46.00-46.25	0.13
Orange juice	120.42	118.50-122.50	2.01
Apple juice	56.75	56.50-57.25	0.43
Tomato juice	72.00	70.50-73.50	1.5
Tea	4.25	3.75-5.00	0.66
Milk	13.17	12.50-14.00	0.76
Hot Chocolate	3.67	2.75-5.25	1.38
Coffee	5.37	5.10-5.75	0.34
Wine	82.00	81.50-82.50	0.5
Beer	14.50	14.2-14.7	0.25

Chapter 5

Experiment Procedure and Methods for Corrosion Tests

5.1 Sample Preparation

5.1.1 Beverages and Chemicals

As stated previously, the 16 beverages selected for investigation were commercial soft drinks, milk, juices and alcohol products purchased at local grocery stores. Prior to testing, all carbonated beverages were degassed in an ultrasound bath for 5 to 10 minutes until completely de-carbonated. Hot chocolate and tea were prepared as explained in Chapter 4. Master coffee™ was prepared directly from a coffee machine. All tests and measurements were carried out on beverages once cooled down to room temperature. All chemicals were reagent grade acquired from the following sources: citric acid (EMD Chemical Inc, Belgium), DL-malic acid (Mallinckrodt Baker Inc, Canada), phosphoric acid (Fisher Scientific, USA) and NaCl (EMD Chemical Inc, USA).

5.1.2 Metal Specimen Preparation

Aluminium and zinc with purities over 99.0% and 99.95%, respectively, were purchased from Goodfellow Cambridge Limited. Copper ordered from EMD Chemical Inc had a purity above 99.9%. Each metal was in the form of a 0.5mm thick foil. The metal foils were cut into pieces that were 80mm±2mm in length and 25±2mm in width for the immersion tests to determine the corrosion rates in the various beverages. To remove any potential contaminant, the metal strips were rinsed in DI water for 5 minutes while being agitated in an ultrasonic water bath, then

degreased successively for 5 minutes each in reagent grades acetone and isopropyl alcohol in the ultrasonic water bath for 5 minutes, then washed with DI water and finally dried in air before use in the dissolution experiments. The metal samples used in the electrochemical corrosion experiments were prepared by cutting them into circular shapes with 1.4 cm diameter and then mounting them on an electrode tip with exposed areas of 0.785 cm². The same cleaning process described above for the immersion tests was applied to the metal samples prior to the electrochemical experiments.

5.2 Methods and Apparatus

Chemical and electrochemical techniques were chosen to study the corrosion behaviour of the metals.

5.2.1 Chemical method

The chemical method used was to simply measure the dissolved metal ion concentrations in the test solutions as a function of time. A cleaned strip of metal was inserted into a plastic tube containing 50 ml of a particular beverage and fully immersed in the liquid. Three samples of each metal/ beverage pair were prepared to ensure that each experiment could be repeated in triplicate. The tubes were capped and placed in an oven heated to 40°C±2°C to allow the contents to react for the specified amount of time (24 hours, 72hours, or 120 hours). After the designated amount of time, the samples were removed from the oven and the strips removed from the test solutions. Once the pH and conductivity of each solution were measured, a small amount of 2 vol% nitric acid was added and the contents shaken in order to preserve the sample and ensure that all metals were in dissolved form and did not precipitate.

Since the alcoholic content in some beverages caused problems for the analysis by ICP-OES, the alcohol in the beer and wine was vaporized using a VWR heating block prior to ICP analysis, as described previously in Chapter 4. Three standard solutions containing 0.1, 1.0 and 5.0 ppm of each of Al, Cu and Zn were used to calibrate the ICP. Following this, a 1.0 ppm standard solution was introduced into the ICP unit and a measurement made to assess the accuracy. Once the accuracy of the measurement had been satisfactorily verified, the concentrations of the test samples were obtained. All sample solutions were diluted 10-fold first using Milli-Q water and then, if needed, another 100-fold, followed by the addition of 2 vol% nitric acid before the dissolved metal concentrations were measured using the ICP-OES. The selected analytical wavelengths of aluminium, copper and zinc are shown in Table 5.2.1

Table 5.2.1 Aluminium, copper and zinc wavelengths used in OCP-OES.

Elements	Aluminium	Copper	Zinc
Wavelengths	394.4	324.7	213.8

5.2.2 Electrochemical methods

The electrochemical methods chosen were (1) open-circuit potential (OCP) measurements and (2) linear potential scan experiments. A conventional three-electrode cell was used for the electrochemical experiments. Each Cu, Al or Zn working electrode to be used for a corrosion tests was prepared by cutting a 1.4 cm diameter flat circular shape from a thin metal foil. This circular shape was then degreased with acetone and alcohol and ultrasonically washed with deionized water for 5 minutes. Each sample was mounted on an electrode tip holder so as to expose 0.785 cm² exposed area. A Pt rod was utilized as a counter electrode and an Ag/AgCl/3M

KCl electrode was used as the reference electrode. Accordingly, all potentials reported in this thesis are on the Ag/AgCl scale. All experiments were conducted at room temperature using a PGSTAT302 Autolab potentiostat. A glass cell (Metrohm) containing 150 ml solution was used for each electrochemical experiment (Figure 5.2.1).

The open-circuit potential E_{corr} was monitored for 3 hours in the case of copper, 24 hours for aluminum and 10 hours for zinc. The open-circuit potential of each metal electrode was measured in a test solution until a steady state value was attained. After steady state was reached, a linear potential sweep in the anodic direction was performed at a scan rate of 1 mV/s, starting from 0.25 V below the OCP and terminating at 0.25V above the OCP. The output from these experiments yielded a polarization curve showing the current response obtained versus the applied potential.

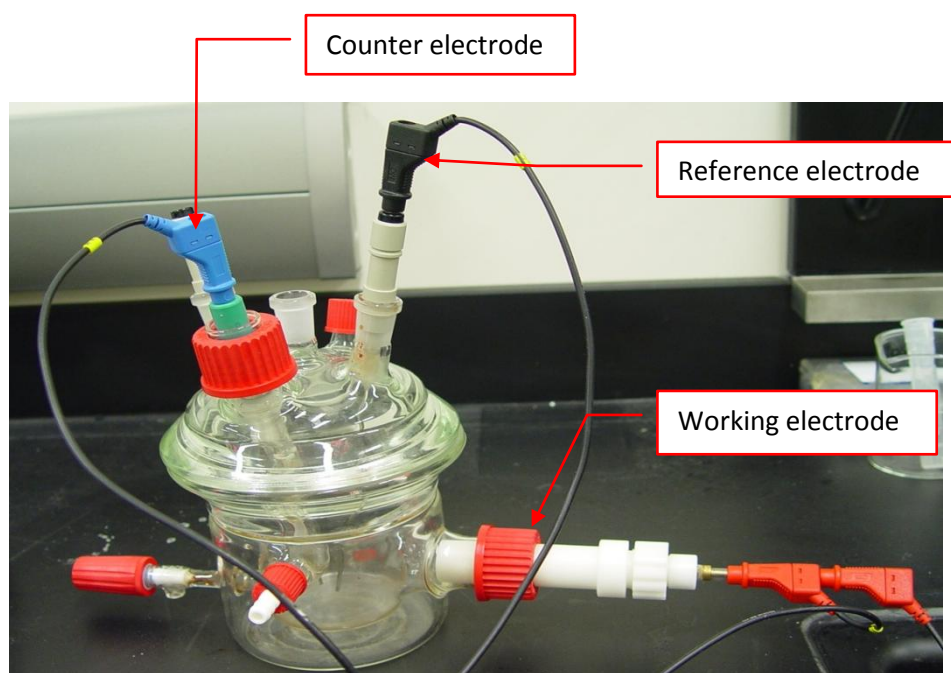


Figure 5.2.1 The Metrohm glass cell used for the electrochemical experiments.

The corrosion current can be calculated using Tafel slope analysis. The relationship between the current density of a half-cell reaction and the electrode potential during polarization is given by the Butler-Volmer equation^[53]:

$$i = i_{corr} [e^{2.303\eta/(b_a)} - e^{-2.303\eta/(b_c)}] \quad (5.1)$$

$$\eta = E - E_{corr} \quad (5.2)$$

where E = electrode potential

i = measured current density

η = difference between applied electrode potential and the corrosion potential

E_{corr} = corrosion potential (same as the open-circuit potential) of a corroding metal

i_{corr} = corrosion current

b_a, b_c = Tafel constants of anodic and cathodic half-cell reactions.

From each polarization curve plotted as $\log I$ versus E , the corrosion current density i_{corr} of the metal is determined by extrapolating the linear Tafel portion until it intersects the open-circuit potential with the aid of the NOVA software package. The NOVA software provides a convenient interface for making Tafel plots, calculating Tafel slopes and corrosion rates. In Figure 5.2.2, a representative current-potential curve for Al immersed in coffee is shown.

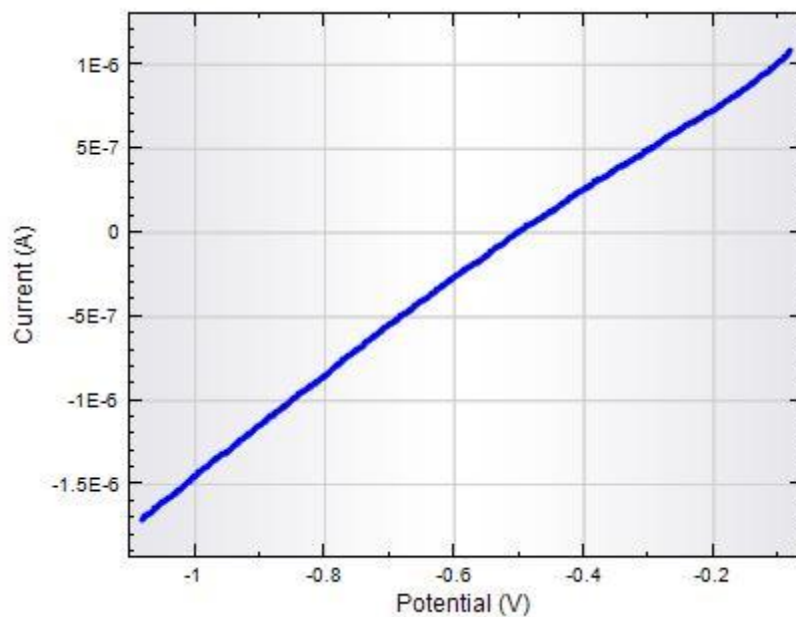


Figure 5.2.2 Current-potential curve for aluminum immersed in coffee

By selecting the Tafel slope analysis tool on the Analysis menu, this plot is converted to its Tafel form shown in Figure 5.2.3

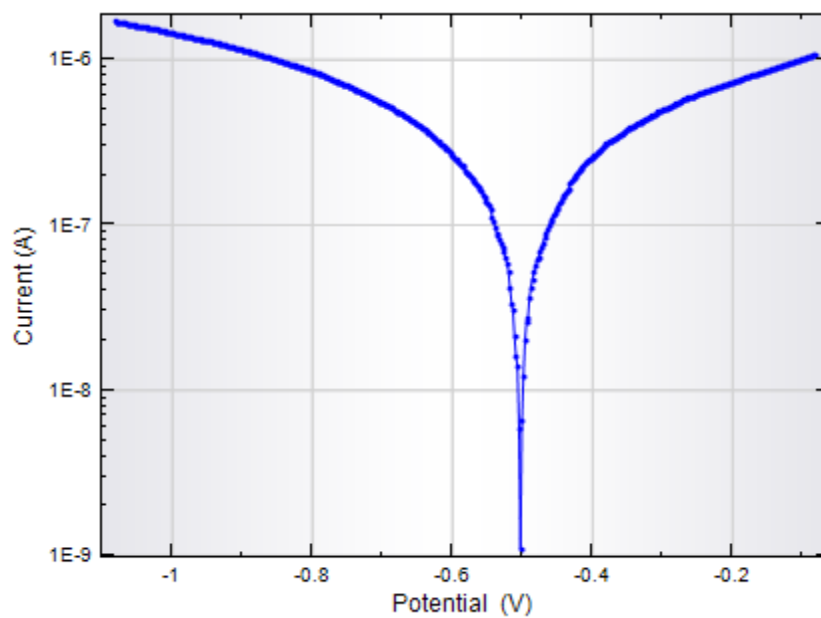


Figure 5.2.3 Tafel plot obtained when aluminum is immersed in coffee.

The anodic and cathodic Tafel regions are specified with the help of arrow markers. Once the regions are selected the NOVA software automatically calculates the Tafel slopes and determines the corrosion current. The Tafel slopes are also automatically plotted on the Tafel plot as shown in Figure 5.2.4.

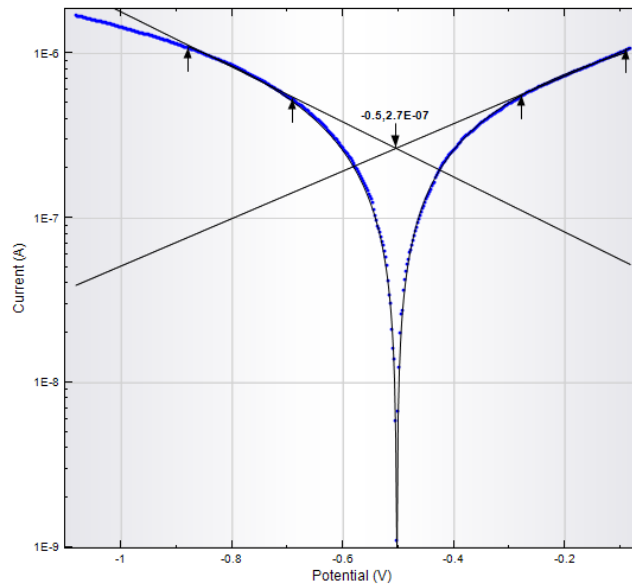


Figure 5.2.4 – Extrapolation of the linear portions of the Tafel plot (identified by arrows) for aluminum immersed in coffee to yield i_{corr} .

In order to obtain the other corrosion parameters, the equivalent weight of the metal, density of the metal and surface area of the electrode are required as input parameters, as shown in Figure 5.2.5. With this information, the NOVA software generates the complete set of corrosion parameters shown in Figure 5.26.

Density (g/cm ³)	2.7
Equivalent weight (g/mol)	8.99
Surface area (cm ²)	0.785
Number of significant digits	2
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Figure 5.2.5 – Input parameters required for the Tafel slope analysis.

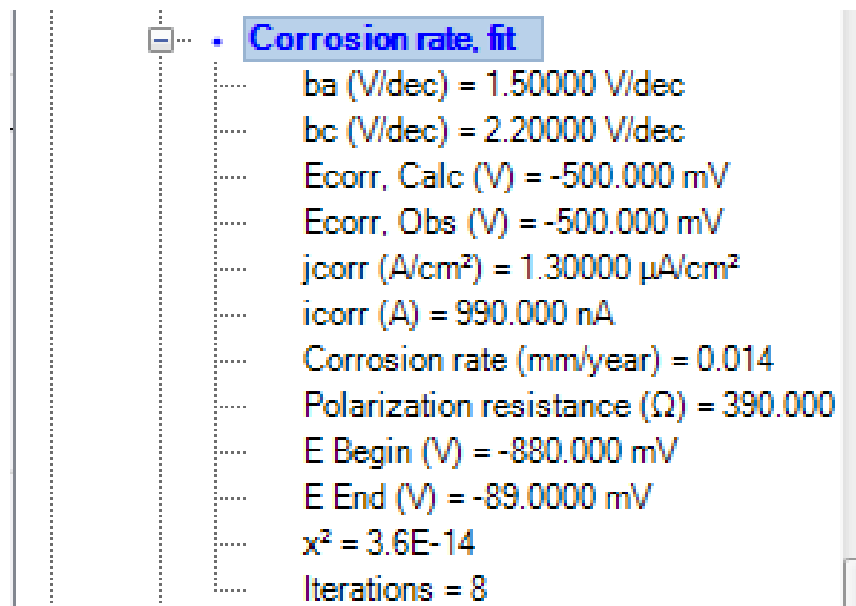


Figure 5.2.6 An output generated by the Tafel slope analysis tool for aluminum immersed in coffee.

An alternate way to determine the corrosion parameters is to use the Corrosion Rate Fit analysis tool which fits the Butler-Volmer expression to the experimental data. This typically provides a more accurate determination of the corrosion current, polarization resistance and corrosion rate.

5.3 Surface Characterization

At the completion of the corrosion experiments, the specimens were rinsed with DI water and then dried in air prior to examination of their surfaces. For examination of the metal surfaces, an optical microscope and JEOL JSM-6460LV scanning electron microscope (SEM) at 20KV with energy dispersive X-ray analysis (EDXA) attachment were used.

Chapter 6

Results and Discussion

Corrosion Behaviour of Aluminum

Aluminum is widely used for many applications due to its low cost, light weight, high thermal conductivity and high electrical conductivity. For example, in the electronics industry, aluminum is the most prevalent metal in a typical die circuit and so Al corrosion is a very common and serious problem. Consequently, the corrosion of Al in the 16 commercial beverages has been studied using both chemical and electrochemical techniques.

6.1 Immersion Test

Aluminum strips were immersed in each of the beverages held at 40 °C in an oven for 1, 3 and 5 days. The dissolved aluminum concentrations reached in each of these beverages over this time period are presented in Table 6.1.1. Each value listed represents an average of 3 independent measurements for the given set of conditions. This enabled the determination of the standard deviation for each measurement which is also included in the table. The data are shown in graphical form in Figures 6.1.1, 6.1.2 and 6.1.3. It was found that the aluminum dissolution rate tended to exhibit 3 types of behaviour depending on the beverage: i) decrease in the rate over time so that the dissolved metal concentration nearly leveled off by the end of 5 days, ii) virtually constant over the 5-day period and iii) little dissolution between 1 and 3 days of immersion followed by a significant increase in the rate thereafter. The results are organized so that the

beverages exhibiting the first type of behaviour are included in Figure 6.1.1, while those in the second category are shown in Figure 6.1.2 and those in the third category in Figure 6.1.3.

Table 6.1.1 Dissolved Al concentrations (ppm) and standard deviations (ppm) after 1, 3 and 5 days of immersion in the test beverages.

Beverages	5 Days	Std. Dev	3 Days	Std. Dev	1 day	Std. Dev
Wine	17.1	3.8	15.5	7.5	6.0	0.4
Beer	16.3	0.9	12.2	1.8	2.3	0.2
Orange Juice	30.0	4.4	12.8	1.0	1.7	0.5
Tomato Juice	21.2	10.3	12.2	2.7	3.7	0.4
Apple Juice	120.0	16.6	76.2	7.9	16.7	0.5
Hot chocolate	45.5	3.1	31.0	2.5	28.1	3.4
Coffee	6.2	0.4	1.7	0.3	0.6	0.1
Tea	23.5	2.9	6.7	0.7	5.3	0.5
Milk	10.7	1.7	1.7	0.2	0.1	0.1
Root Beer	45.2	4.4	32.0	0.8	11.3	1.9
Coca-cola	51.4	4.4	50.4	0.9	35.5	4.6
Pepsi	60.4	1.7	57.0	1.5	38.9	1.0
Dr.Pepper	34.5	4.0	29.7	1.5	14.3	1.5
Sprite	100.1	6.7	53.7	3.4	10.6	0.4
Canada Dry	109.3	4.1	67.7	5.3	15.2	0.9
Gatorade	195.9	8.1	113.7	25.3	38.1	3.5

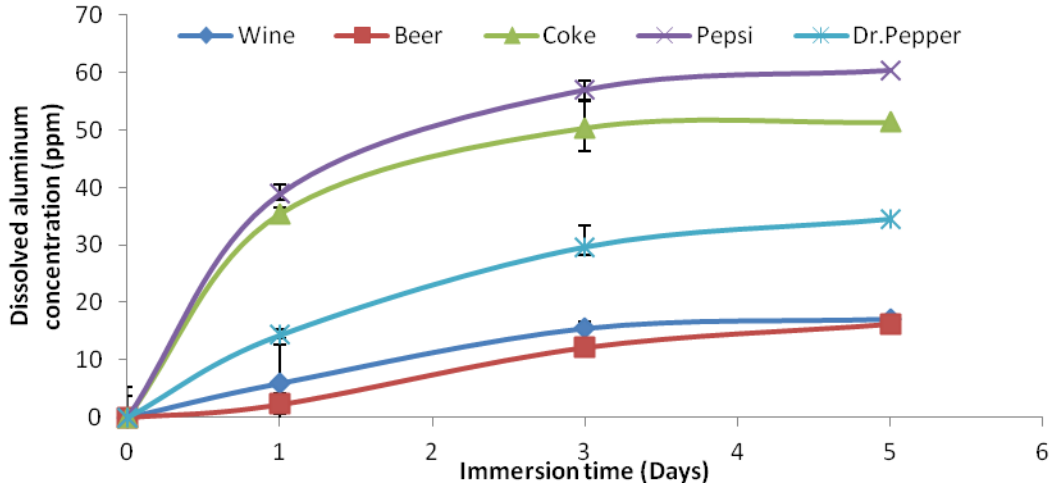


Figure 6.1.1 Dissolved Al concentration as a function of time with error bar when immersed in wine, beer, Coca-cola, Pepsi and Dr. Pepper.

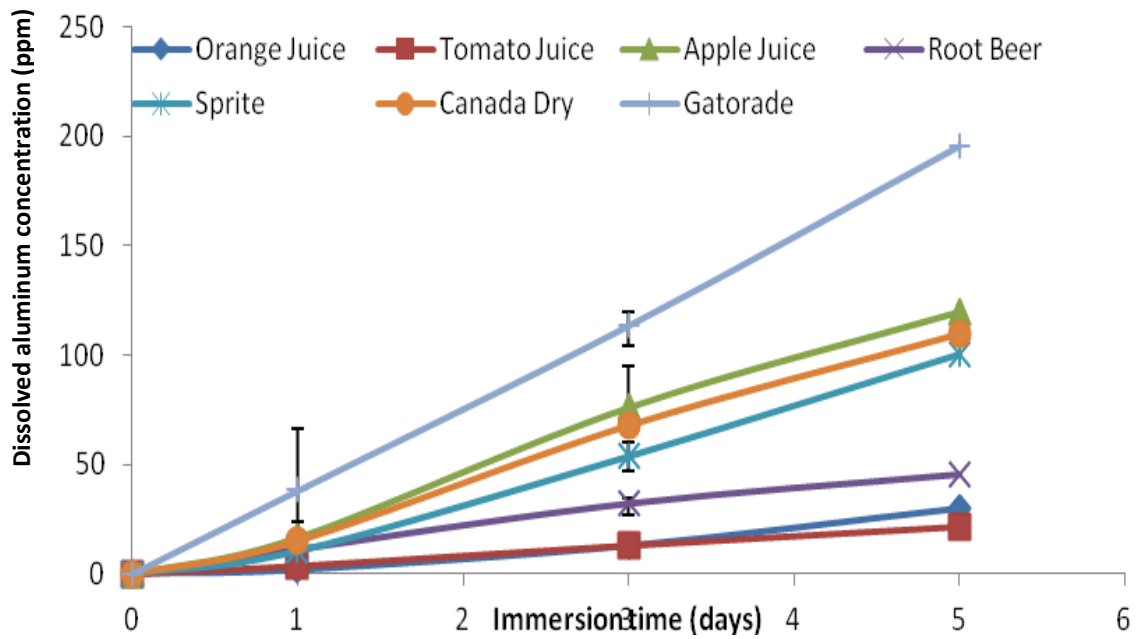


Figure 6.1.2 Dissolved Al concentration as a function of time with error bar when immersed in orange juice, tomato juice, apple juice, Sprite, Canada Dry and Gatorade.

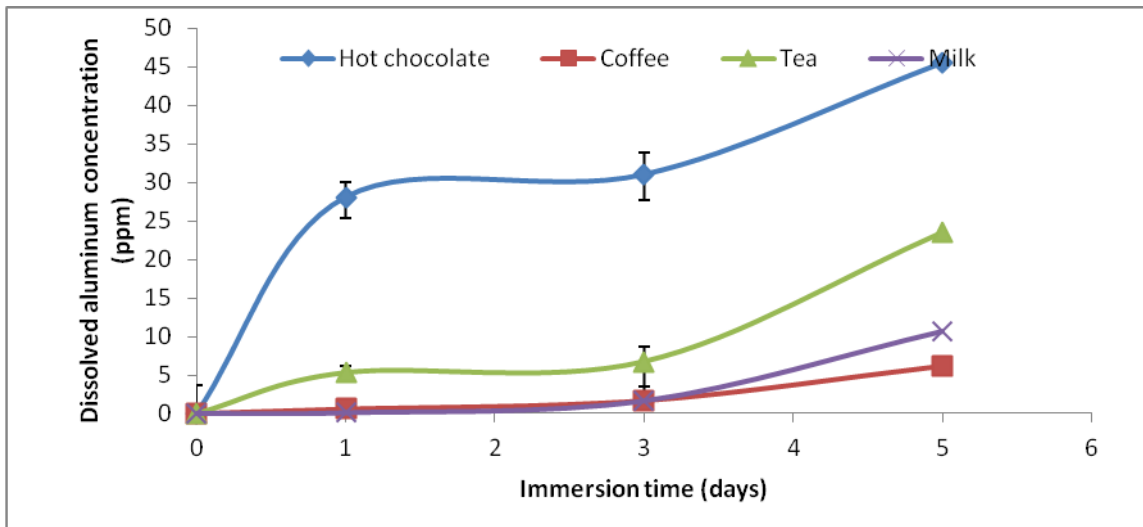


Figure 6.1.3 Dissolved Al concentration as a function of time with error bar when immersed in hot chocolate, tea, coffee and milk.

The beverages in the first group that show a continually declining corrosion rate are wine, beer, Coca-cola, Pepsi and Dr. Pepper (Figure 6.1.1). Examination of Table 4.2.1 indicates that all of these beverages with the exception of beer contain high levels of phosphate. However, phosphate alone does not likely govern the corrosion behaviour since the beverage with by far the highest phosphate content of all sixteen investigated in this study is milk. Corrosion in the presence of milk follows a trend that places it in the third group (Figure 6.1.3), although the amount of corrosion that is observed is very low. The highest amount of aluminum corrosion among the beverages in this 1st group is observed in the presence of Pepsi and Coca-cola. However, it is important to note that the higher corrosion in the presence of these beverages can be attributed almost entirely to events taking place within the 1st day of immersion rather than to anything that occurs thereafter. The dissolved aluminum concentration in the presence of Pepsi and Coca-cola rises from zero up to 38.9 and 35.5 ppm, respectively, over the 1st day. Together with the results observed in the presence of Gatorade, these are by far and away the highest corrosion rates over

this period among all the beverages tested in this study. However, after the 1st day, the increase in dissolved aluminum in the presence of Pepsi and Coca-cola slows dramatically and, in fact, becomes very similar to that observed for the other 3 beverages in this 1st group.

Figure 6.1.2 shows the cases where the corrosion rate remains virtually unchanged over the 5-day period. Apple juice, tomato juice, orange juice, Sprite, Canada Dry, root beer and Gatorade fall in this group. The highest level of dissolved aluminum and the largest corrosion rate is observed when the strips are exposed to Gatorade. In fact, the presence of Gatorade leads to more aluminum corrosion after each of the sampling periods of 1, 3 and 5 days of immersion than does any of the other 16 beverages in this study. The corrosion behaviour of the 3rd group shown in Figure 6.1.3 appears to be somewhat more complicated than in the other two groups, particularly in the case of hot chocolate. Corrosion is relatively fast over the 1st day, but then stops almost entirely over the next two days before accelerating again thereafter. It is interesting to note that the beverages falling in this group are hot chocolate, tea, milk and coffee which are non-alcoholic, non-carbonated and not fruit juices.

An important implication of the results of these experiments is that an One day immersion test is not long enough to satisfactorily assess the long-term behaviour of aluminum when exposed to these beverages. For one thing, the ranking of the beverages according to corrodibility based on short-term tests does not follow in the same order as when based on longer-term tests due to the considerable differences in the dynamics of corrosion among the various beverages.

Furthermore, the chemistry of aluminium in each of the beverages is likely very complex and also varies considerably from case to case. Aluminium can form complexes with various organic compounds (e.g. malic and citric acids) and inorganic ligands (e.g., fluoride, chloride), most of which are soluble. Compounds such as oxides can also form on the aluminum surface to retard dissolution. Of course, the particular species that form depend on additional factors such as the pH and total acid content. A plot of dissolved aluminum concentration after 1, 3 and 5 days immersion against pH of the beverage is presented in Figure 6.1.4, 6.1.5 and 6.1.6, respectively, in order to determine whether a correlation exists between these two quantities. As shown, a weak correlation appears to exist, with a decrease in pH generally leading to an increase in the amount of dissolved aluminum. The most notable outlier to this trend is hot chocolate where a relatively high dissolved aluminum of 28.1 ppm is observed over the first 24 hours although the pH is 7

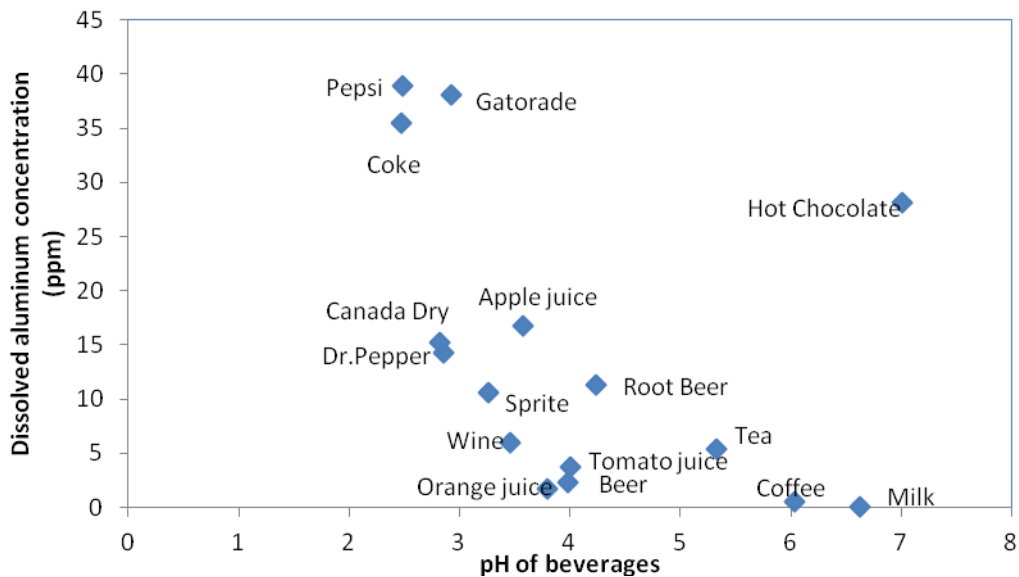


Figure 6.1.4 Mean dissolved aluminium concentration versus beverage pH after 1 day immersion

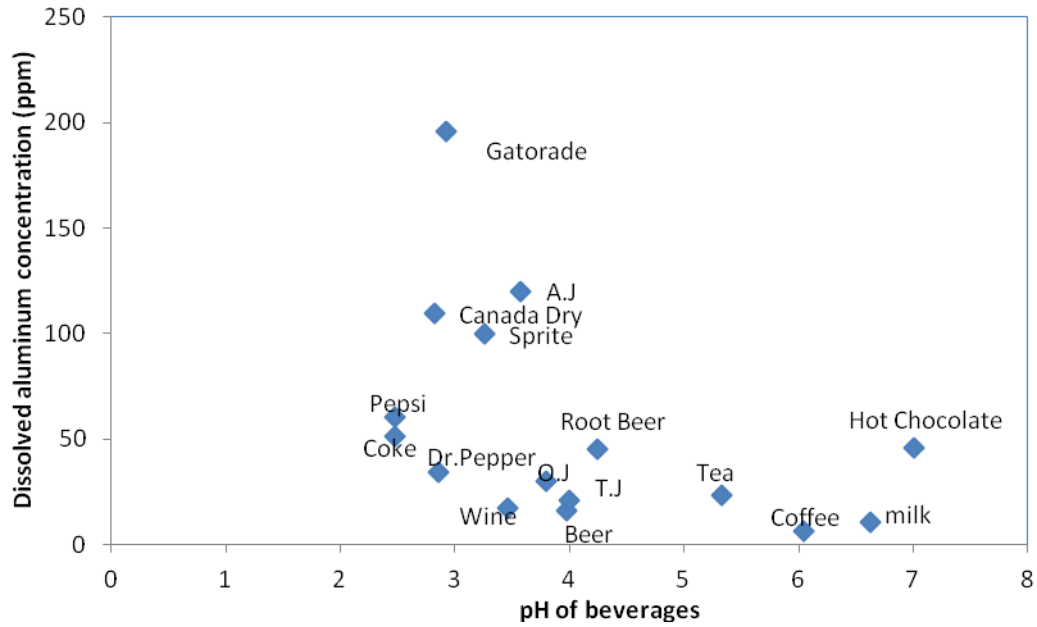


Figure 6.1.5 Mean dissolved aluminium concentration versus beverage pH after 3 days immersion

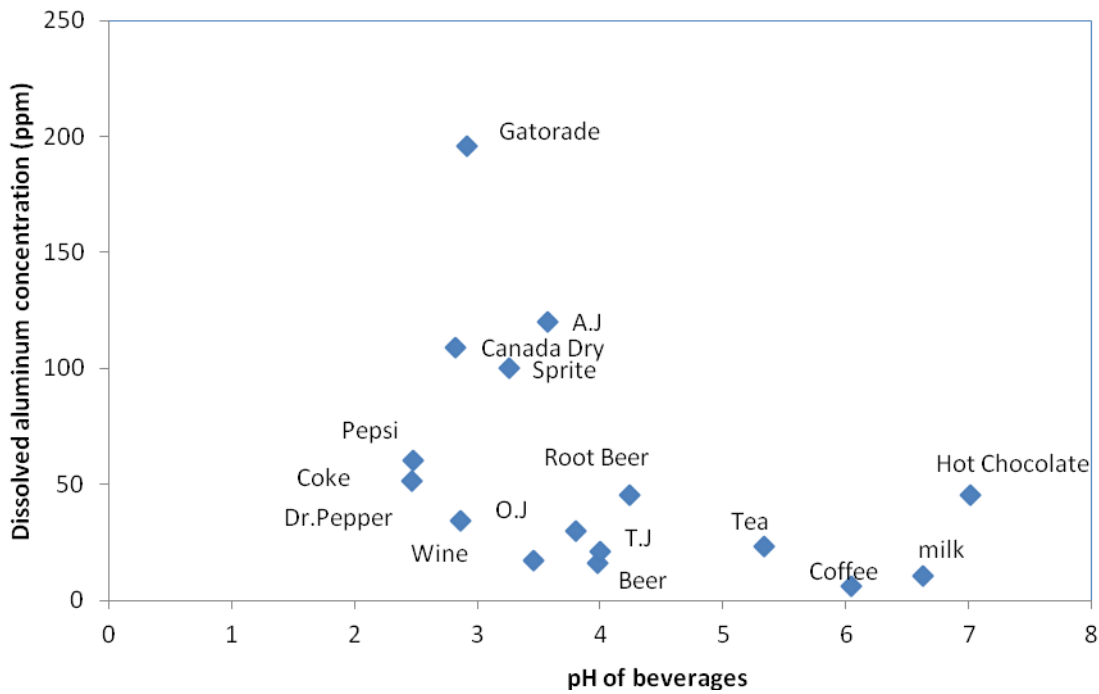


Figure 6.1.6 Mean dissolved aluminium concentration versus beverage pH after 5 days immersion

Many of the ingredients found in beverages may affect the corrosion of Al. Three aggressive ingredients in many of the beverages are phosphoric acid, citric acid and chloride (Cl^-). Their possible effects were investigated by examining whether a correlation exists between the dissolved Al concentration and the concentration of each of these three ingredients in the test beverages. The dissolved Al concentrations after 1, 3 and 5 days of immersion in each of the beverages are listed in Table 6.1.2 together with the corresponding pH, citric acid, phosphoric acid and Cl^- concentrations. No obvious correlation between the amount of aluminum corroded and any single one of these ingredients is evident, particularly as the immersion time increases. For example, aluminum readily corrodes in beverages with large citric acid concentration in some cases (i.e., Gatorade, Canada Dry, Sprite), but not in others (e.g., tomato juice, orange juice, milk). Moderate-to-high corrosion is observed in some beverages with very low citric acid levels (e.g., Coca-cola, Pepsi, apple juice, Dr.Pepper), whereas much less corrosion occurs in other beverages that contain moderately high citric acid concentrations (e.g., coffee, beer, hot chocolate). The results indicate that high phosphoric acid content tends to be associated with lower corrosion levels, but this trend does not always hold. More corrosion occurs when aluminum is immersed in Pepsi and Coca-cola than in milk, orange juice, tomato juice and beer, although the former beverages have higher phosphoric acid content. Finally, large corrosion rates are observed in beverages with both low (e.g., Canada Dry, Sprite) and high (e.g., Gatorade, apple juice) phosphoric acid levels; at the same time, relatively little corrosion is observed in cases where both low (e.g., beer, tea tomato juice) and high (e.g., milk, hot chocolate, tomato juice) amounts of Cl^- are present. However, if only soft drinks are considered, some interesting trends are evident. Histograms showing the dissolved Al concentrations after 1, 3 and 5 days of immersion in these beverages are presented in Figure 6.1.7. More dissolved aluminum is

measured in soft drinks containing high phosphoric acid levels (Coca-cola, Pepsi, Dr.Pepper and Gatorade) than those containing citric acid with no phosphoric acid (Sprite, Canada Dry and Root Beer) after 1 day. This observation suggests that phosphoric acid plays an important role in Al dissolution. However, with further immersion of 3 and 5 days in these drinks, the situation changes and corrosion in the drinks containing citric acid but no phosphoric acid overtakes that of the other group. Recall that the behaviour observed in the case of Coca-cola, Pepsi and Dr. Pepper falls into group 1 (Figure 6.1.1) in which the corrosion rate decreases continuously over the 5-day immersion period, while the corrosion observed upon immersion in Sprite, Canada Dry and Root Beer follows the trend of group 2 and remains at a constant rate (Figure 6.1.2).

Table 6.1.2 Mean dissolved Al concentration after immersion in the various beverages and corresponding pH and citric acid, phosphoric acid and Cl⁻ concentrations.

Beverages	pH	Concentration (ppm)			Dissolved Al concentration (ppm)		
		citric acid	phosphoric acid	Cl ⁻	1 day	3 days	5 days
Pepsi	2.48	55	532	17.4	38.9	57.0	60.4
Coca-Cola	2.47	0	509	32.9	35.5	50.4	51.4
Apple juice	3.57	53	242	1251.0	16.7	76.2	120.0
Dr. Pepper	2.86	0	459	19.2	14.3	29.7	34.5
Canada Dry	2.82	1234	0	34.6	15.2	67.7	109.3
Gatorade	2.92	3289	367	456.0	38.1	113.7	195.9
Sprite	3.26	1135	0	14.3	10.6	53.7	100.1
Root beer	4.24	152	0	30.1	11.3	32.0	58.1
Wine	3.46	46	954	260.0	6.0	15.5	17.1
Tea	5.33	0	17	13.8	5.3	6.7	23.5
Tomato juice	4.00	2964	304	3373.0	3.7	12.2	21.2
Hot chocolate	7.01	335	479	863.5	2.8	3.1	4.5
Beer	3.98	150	160	85.6	2.3	12.2	16.3
Orange juice	3.80	7415	364	601.0	1.7	12.8	30.0
Coffee	6.04	329	342	106.8	0.6	2.9	6.2
Milk	6.63	1270	1662	991.0	0.1	1.7	10.7

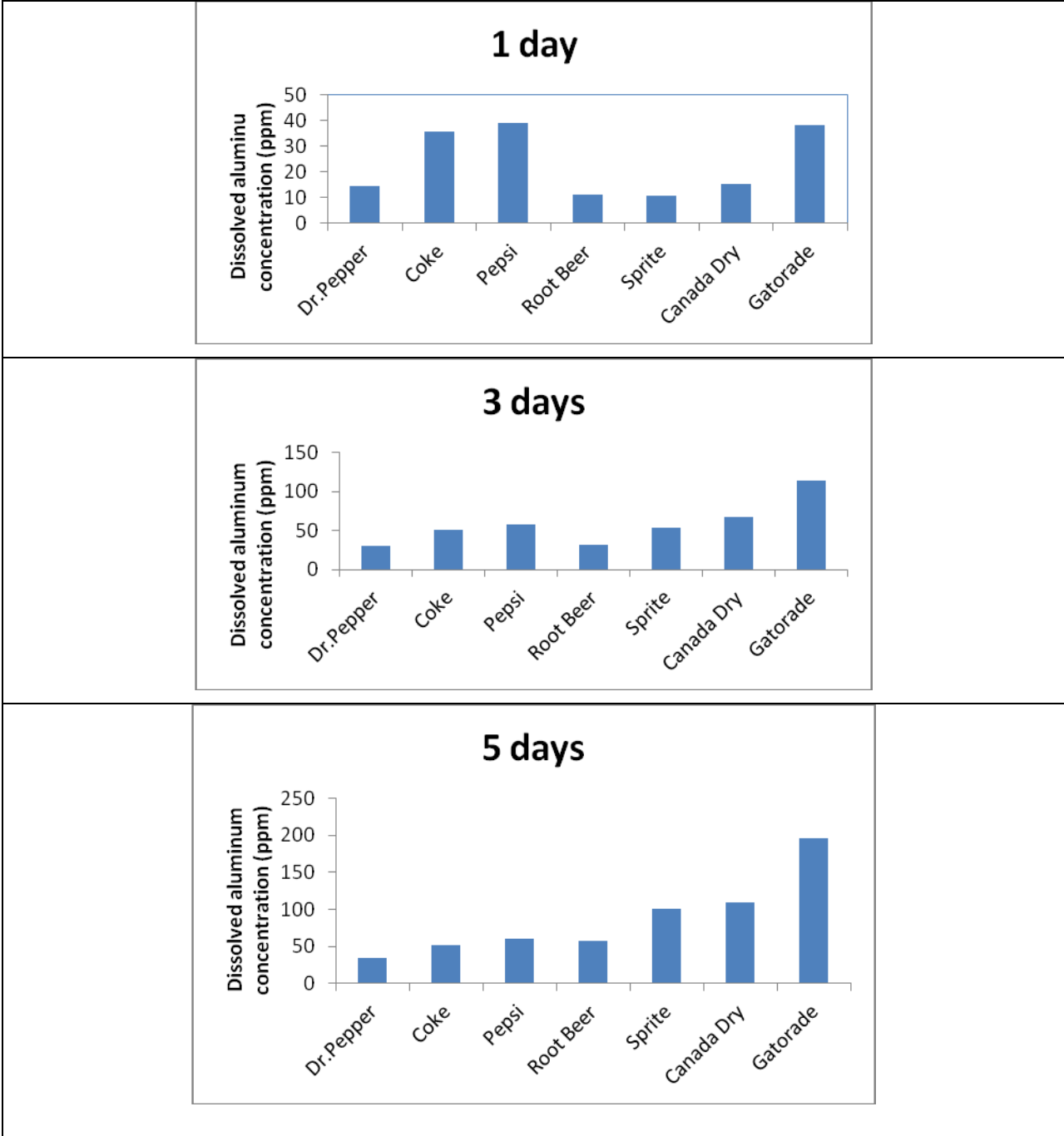


Figure 6.1.7 Mean dissolved aluminium concentrations after 1, 3 and 5 days of immersion in the various soft drinks.

The difference in the behaviour of these two groups suggests that citric acid also appears to be an important factor in Al dissolution. The one case that fit into this pattern is that of Gatorade in which Al continues to corrode rapidly over the entire 5 day period. It is noteworthy that Gatorade is unique among the soft drinks in that it contains high levels of both citric acid and phosphoric acid. However, the trends shown in Figure 6.1.7 are not followed in the other beverage types.

The physical properties and chemical components of beverages affect metal dissolution behaviour in a complex manner.

Obviously, a complex interplay must exist between the various components of these beverages and aluminum. Thus, it is difficult to assess the separate effects of each of the components studied in the present work.

After 5 days of immersion in the various beverages, the aluminum strips were examined by SEM/EDX to determine the nature of the metal attack. With the exception of the sample exposed to Gatorade, corrosion in the other 15 beverages appeared to occur uniformly. Phosphorus (P) and sulfur (S) were detected in the strips after immersion in the phosphoric acid-containing beverages Pepsi, Coca-cola and Dr.Pepper, but absent in the same samples prior to immersion. Representative SEM/EDX images of the sample before and after 5 days of immersion in Coca-cola are shown in Figures 6.1.8 and 6.19, respectively.

The images (Figure 6.1.9) after immersion test show that a rough, porous surface has been produced. The appearance of phosphorus peaks in the EDX spectrum indicates that some sort of phosphate complex or complexes may have formed on the surface during the initial stages of

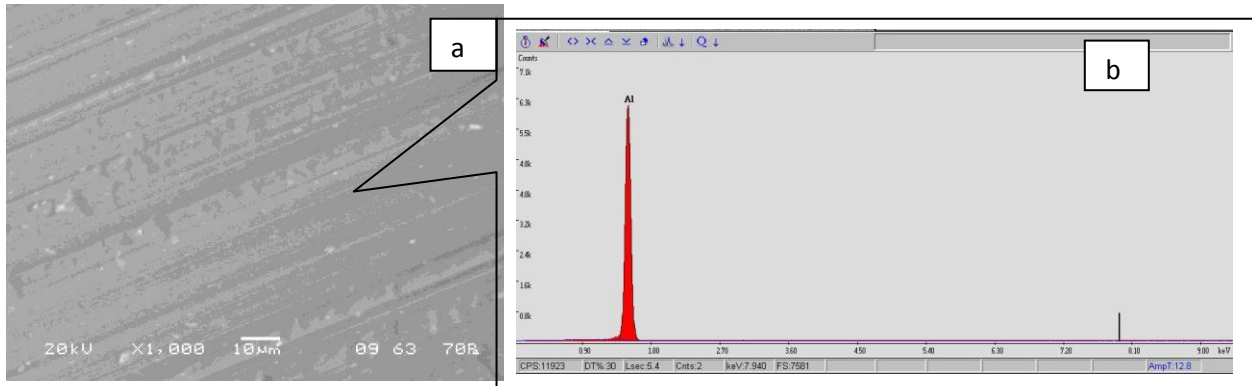


Figure 6.1.8 a) SEM image of Al prior to immersion at magnifications of x1000 and b) EDX spectrum showing elemental analysis of indicated region in a).

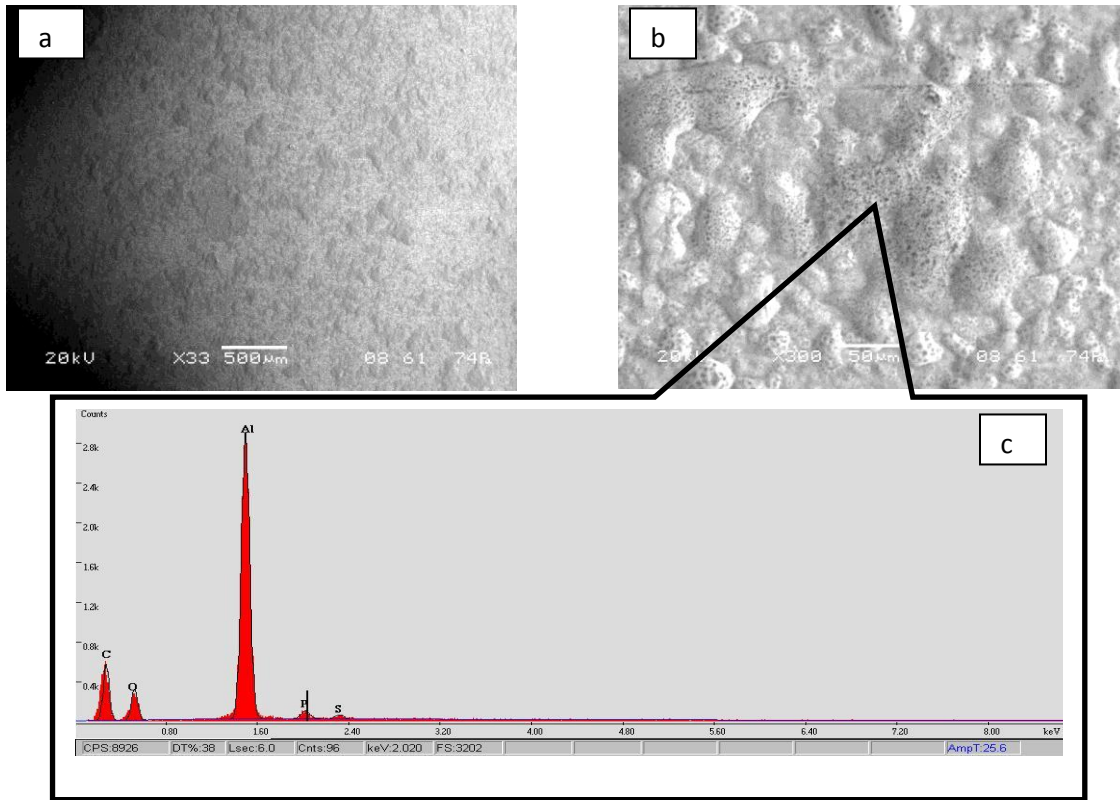


Figure 6.1.9 SEM images of Al at magnifications of a) x33 and b) x300 after 5 days immersion in Coca-Cola. The EDX spectrum in c) shows the elemental analysis of the indicated region in b).

corrosion. If these complexes impeded the subsequent corrosion of the Al surface, this would lead to the gradual slowing down of aluminum dissolution evident in Figure 6.1.1. As reported in the literature, total dissolved Al can exist in the form of soluble Al-phosphate complexes, free Al^{3+} and Al-hydroxyl complexes while the most thermodynamically stable insoluble form is the salt AlPO_4 in addition to aluminum metal^[36]. Although the compound AlPO_4 should only form when the concentrations of Al^{3+} and PO_4^{3-} are high enough to exceed the solubility product of this salt, it may be possible for other insoluble aluminum-phosphate compounds with different stoichiometries to form on the metal surface during corrosion. Therefore, during Al dissolution in the phosphoric acid-containing beverages, the formation of soluble Al-phosphate complexes at the outset may accelerate Al dissolution compared to that observed in the beverages containing citric acid but no phosphoric acid. This would lead to a higher dissolved Al concentration in the phosphoric acid-containing beverages after 1 day immersion. However, the concentration of dissolved aluminum in the vicinity of the metal surface may become large enough to form an insoluble aluminum-phosphate complex on the substrate that covers otherwise exposed metal and slows down subsequent corrosion.

Aluminum-citrate complexes are likely more soluble than aluminum-phosphate complexes. Thus, when immersed in beverages such as Sprite, Canada Dry and root beer that contain citric acid but no phosphoric acid, corrosion should be expected to continue uninhibited by the formation of protective film and exhibit the behaviour shown in Figure 6.1.2. This is further confirmed by the SEM/EDX images in Figure 6.1.10 of an Al strip obtained after 5 days of immersion in Sprite. First, the images reveal the presence of a smooth surface without any evidence of a coating such as what appears when immersed in Coca-cola (Figure 6.1.8). No

phosphorous or sulphur peak appears in the EDX spectrum of this sample. In fact, the spectrum is dominated almost entirely by the aluminum peak with evidence of only trace levels of carbon, oxygen and iron. This reflects that the surface remains “clean” and metallic without the formation of a significant coating during corrosion in the presence of Sprite. Very similar SEM images and EDX spectra are obtained after exposure of the aluminum strips to the other beverages with similar composition as Sprite (i.e., Canada Dry and root beer). Information from the literature indicates that aluminum can form several soluble complexes with citrate such as $\text{Al}(\text{citrate})$, $\text{AlH}(\text{citrate})$ and $\text{Al}(\text{citrate})_2^{3-}$ in addition to various hydroxyl complexes depending on the solution pH^[37-39]. The enhanced solubility of aluminum in the presence of citrate could explain why so little carbon and oxygen are detected on the surface of Al immersed in Sprite, Canada Dry or root beer. As noted previously, Gatorade contains large amounts of citric acid, phosphoric acid and Cl^- . SEM images of Al samples after 1, 3 and 5 days immersion in Gatorade are presented in Figure 6.1.11. This figure also includes the EDX spectrum of the sample exposed to Gatorade for 5 days. Similar to the situation when aluminum is exposed to Sprite, these results suggest that the aluminum substrate remains exposed to Gatorade during corrosion and no citrate salts and /or insoluble Al–phosphate complexes are present on the substrate. However, the corrosion behaviour is different from that in all the other beverages in that pits are beginning to form as early as 3 days after immersion (Figure 6.1.11b). These pits deepen considerably by the end of 5 days (Figure 6.1.11c). A contributing factor for the onset of pitting is likely the presence of higher Cl^- concentration in this beverage which is well known to have this effect^[40]. However, it is important to note that the presence of high Cl^- content alone is not sufficient to cause pitting of aluminum. Five other beverages (apple juice, tomato juice, hot chocolate, orange juice and milk) contain even more Cl^- than does Gatorade, but do not lead to

pitting. Apparently, some complex interaction between the metal surface and the various components in Gatorade causes pitting to occur. Also, it should be recalled that aluminum corrodes more rapidly in Gatorade than in any of the beverages considered in this study.

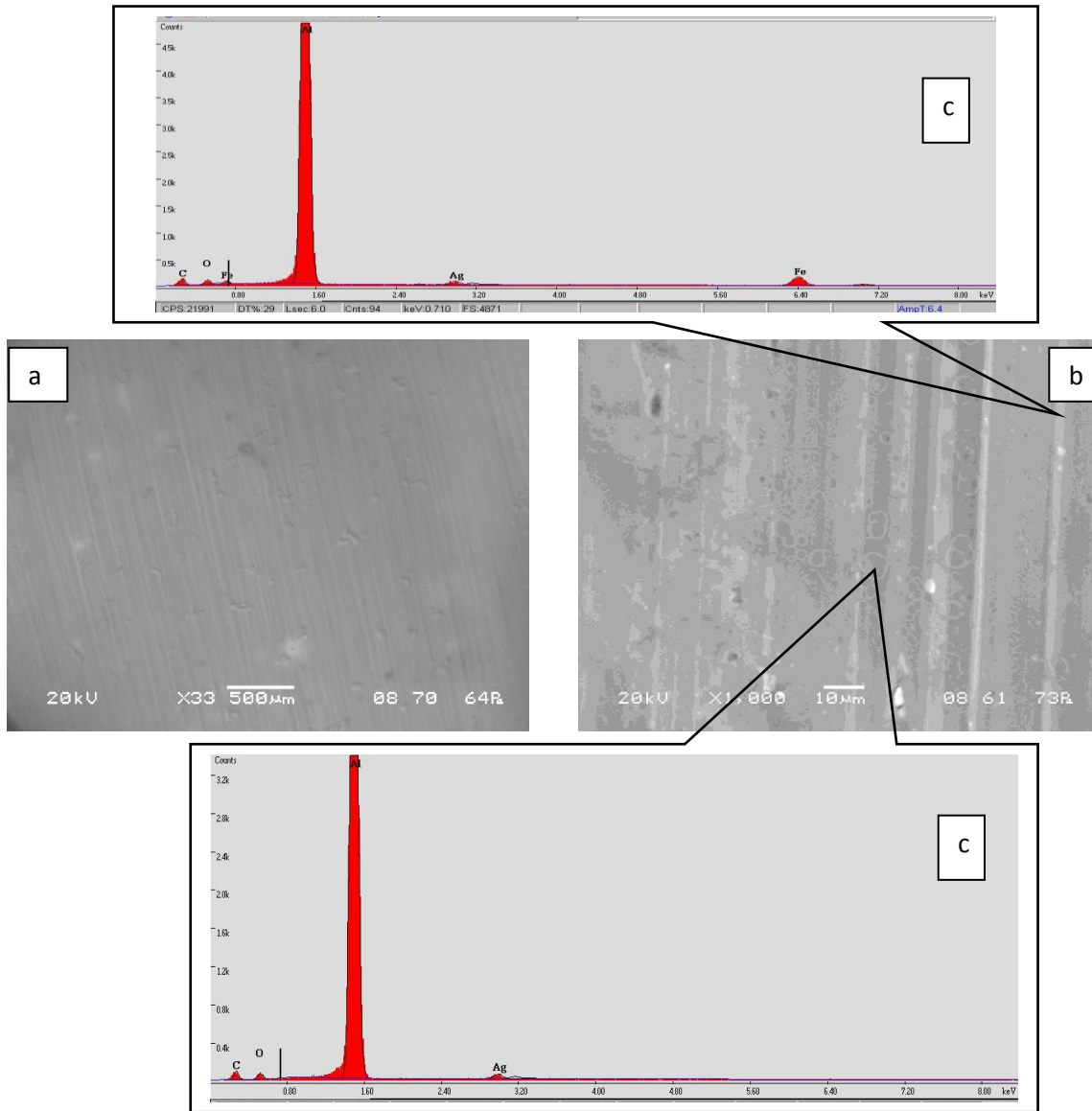


Figure 6.1.10 SEM images of Al at magnifications of a) x33 and b) x300 after 5 days immersion in Sprite. The EDX spectra in c) show the elemental analyses of the indicated regions in b).

It is possible that the presence of citric acid ensures that no insoluble coatings form on the metallic substrate and the metallic substrate remains exposed to the beverage and its high Cl^- content throughout corrosion. In this environment, corrosion can occur rapidly and cause pits to form. However, such a proposal might explain why much less corrosion and no pitting occurs when aluminum is exposed to apple juice, hot chocolate and milk which contain very high Cl^- concentrations, but lower citric acid levels. However, it cannot explain the lower corrosion rates and absence of pitting in the cases of tomato juice and orange juice which contain comparable amounts of citric acid to that of Gatorade. Another contributing factor may be the acidity of the beverage. Gatorade has a lower pH than the five beverages (apple juice, tomato juice, hot chocolate, orange juice and milk) having higher Cl^- concentrations.

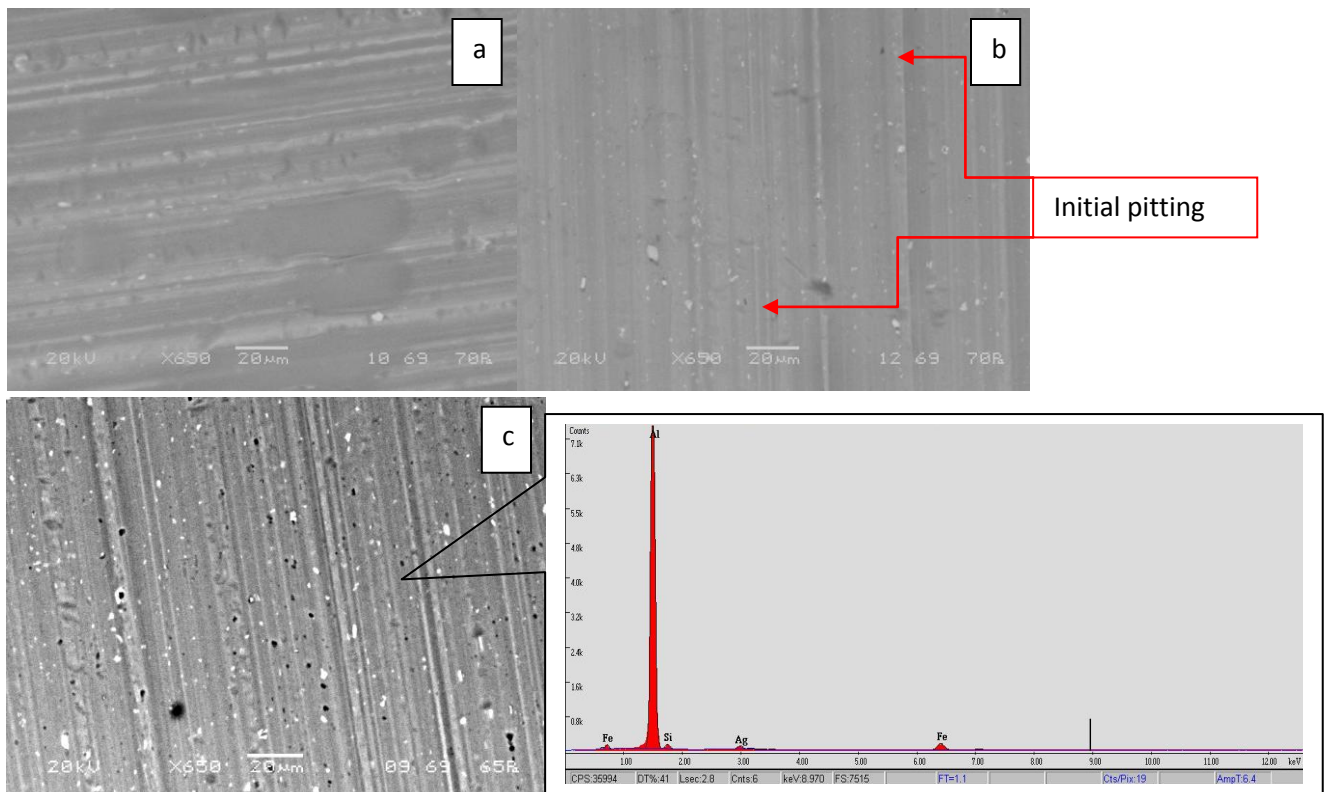


Figure 6.1.11 SEM images of Al at magnifications of x650 after (a) 1, (b) 3 and (c) 5 days of immersion in Gatorade. The EDX spectrum shows the elemental analysis of the indicated region in c).

Beyond citric acid, some beverages contain other organic acids such as malic, lactic, acetic and succinic acids which may affect their Al dissolution behaviour. These organic acids are present in many of the non-carbonated drinks, but not in the soft drinks. An example of one of these non-carbonated beverages is hot chocolate. An SEM image and EDX spectrum of a portion of an Al sample exposed to hot chocolate for 5 days are presented in Figure 6.1.12. The images show a smooth surface with some residues. The EDX spectrum is marked by very large carbon and oxygen peaks as well as smaller ones corresponding to phosphorus, chlorine, sodium and potassium. This suggests that other surface compounds may be present on the surface that affects Al dissolution behaviour.

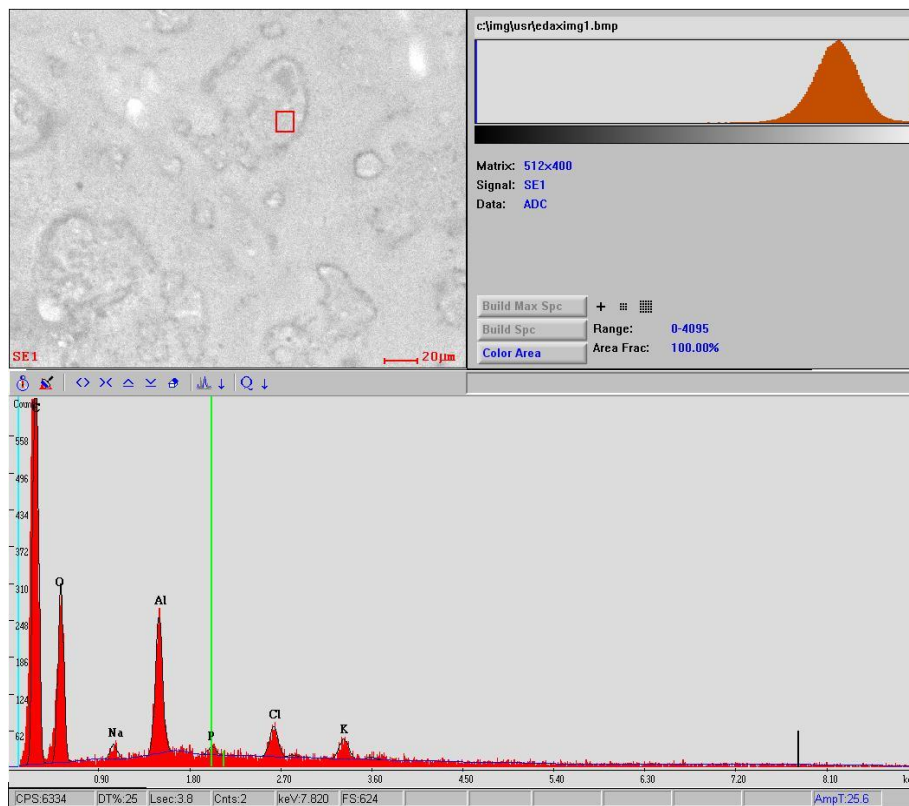


Figure 6.1.12 SEM image of Al (x1000 magnification) and EDX spectrum of indicated region after 5 days immersion in hot chocolate.

The relatively low corrosion rates of aluminum upon exposure to orange juice are surprising given the SEM images and EDX spectra obtained in this case. An SEM image and EDX spectrum of a selected region of an aluminum sample after immersion in orange juice for 5 days is shown in Figure 6.1.13. A relatively clean EDX spectrum is observed after Al has been immersed in orange juice for 5 days. Other than the Al peak, only relatively small carbon and oxygen peaks are detected. It is noteworthy that no phosphorous peak appears in the spectrum despite the fact that orange juice contains a large amount of phosphoric acid (Table 6.1.2). This indicates that no Al-phosphate compounds form on the surface during corrosion. Thus, no evidence of the formation of a protective coating that would moderate the corrosion rate is obvious from this analysis.

An SEM image and EDX spectra of a selected region from a sample immersed in tomato juice for 5 days are shown in Figure 6.1.14. A relatively uniform film with some residue appears on the surface of the metal strip after exposure to tomato juice. The EDX analysis reveals a surface that is intermediate to that of hot chocolate and orange juice with respect to compounds or residues remaining on the substrate after immersion for 5 days. Small carbon, oxygen, sodium, chlorine and potassium peaks are observed. It is possible that some surface film involving some of these components may have formed and helped diminish corrosion. On the other hand, no phosphorous is detected despite the relatively high phosphoric acid content of tomato juice. As in the case of orange juice, no Al-phosphate surface compound appears to form during corrosion. Since tomato juice contains extremely high levels of Cl^- , it is not surprising that a chlorine peak appears in the spectrum below. Nevertheless, no pitting of the surface is evident in the SEM image or in any of the others obtained when aluminum is immersed in tomato juice. Since the pH

of tomato juice is relatively high in comparison to that of many of the other beverages in this study, this suggests that the pH may play an important role in determining the type of corrosion that occurs.

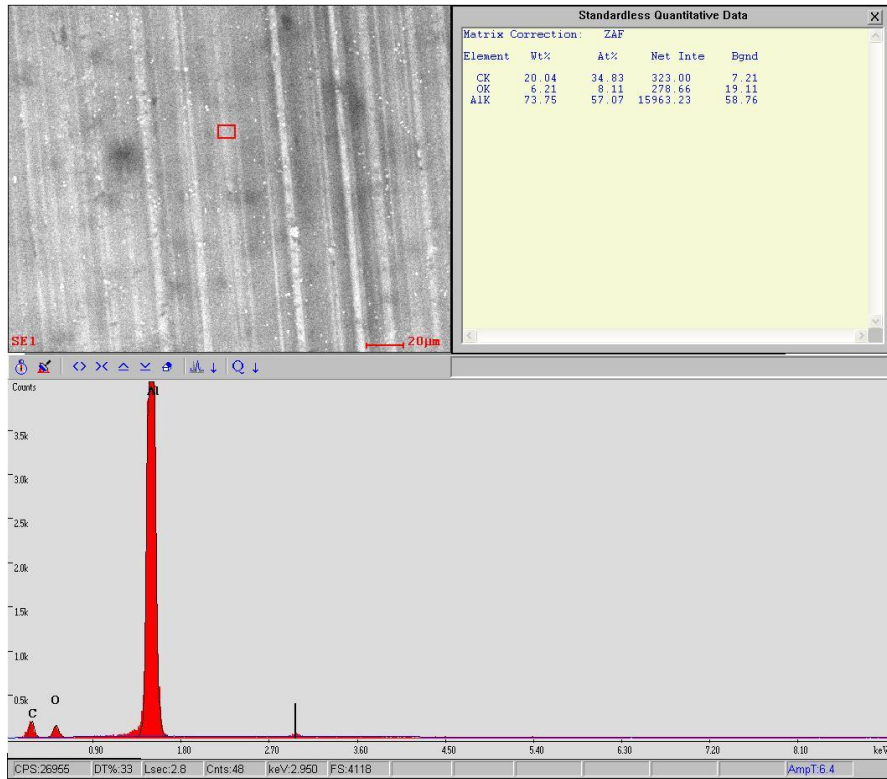


Figure 6.1.13 SEM image of Al (x 500 magnification) and EDX spectrum of indicated region after 5 days immersion in orange juice.

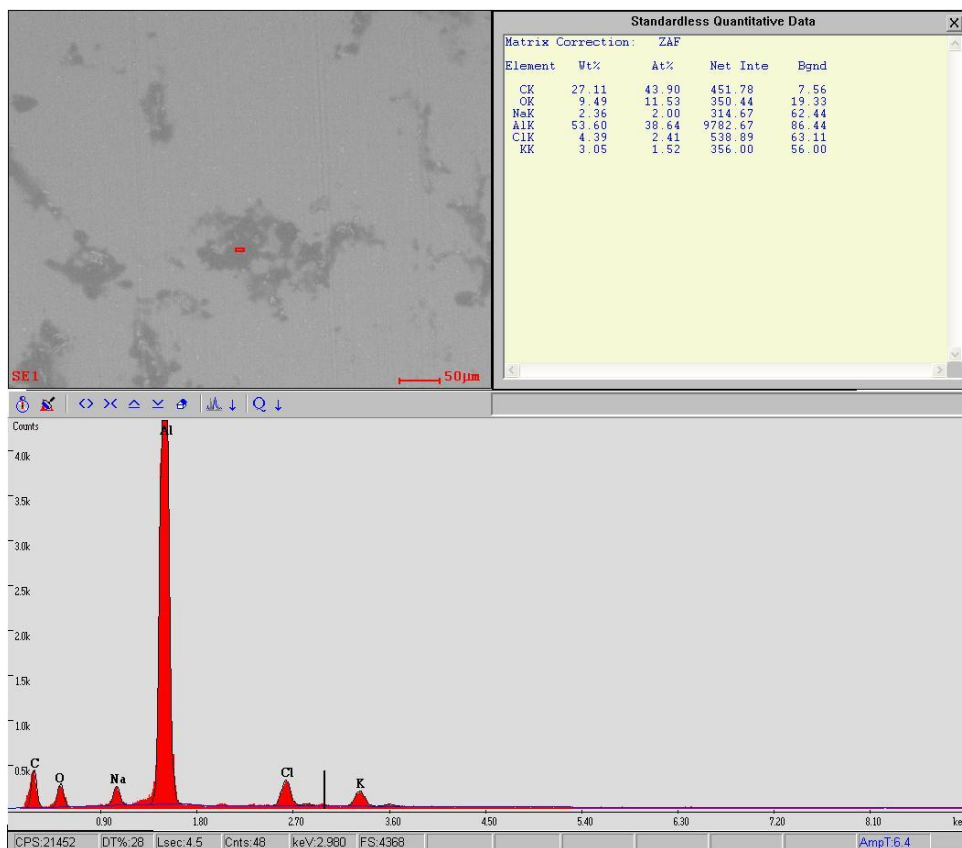


Figure 6.1.14 SEM image of Al (x 500 magnification) and EDX spectrum of indicated region after 5 days immersion in tomato juice.

6.2 Open-Circuit Potential (OCP) Measurements

A conventional three-electrode glass cell was used for electrochemical measurements. An aluminum foil working electrode was immersed in the test beverages along with an Ag/AgCl reference electrode and a Pt wire counter electrode. The potential of the working electrode was measured under open-circuit conditions at room temperature (22°C) as a function of time until steady state was reached or closely approached. A duration of 22 hours in all cases was found to be suitable for this purpose. The variation of the open-circuit potential (OCP) with time obtained

in the six soft drinks is presented in Figure 6.2.1. The steady state OCP in each beverage was taken to be the average recorded over the last 600 seconds of measurement and is listed in Table 6.2.1.

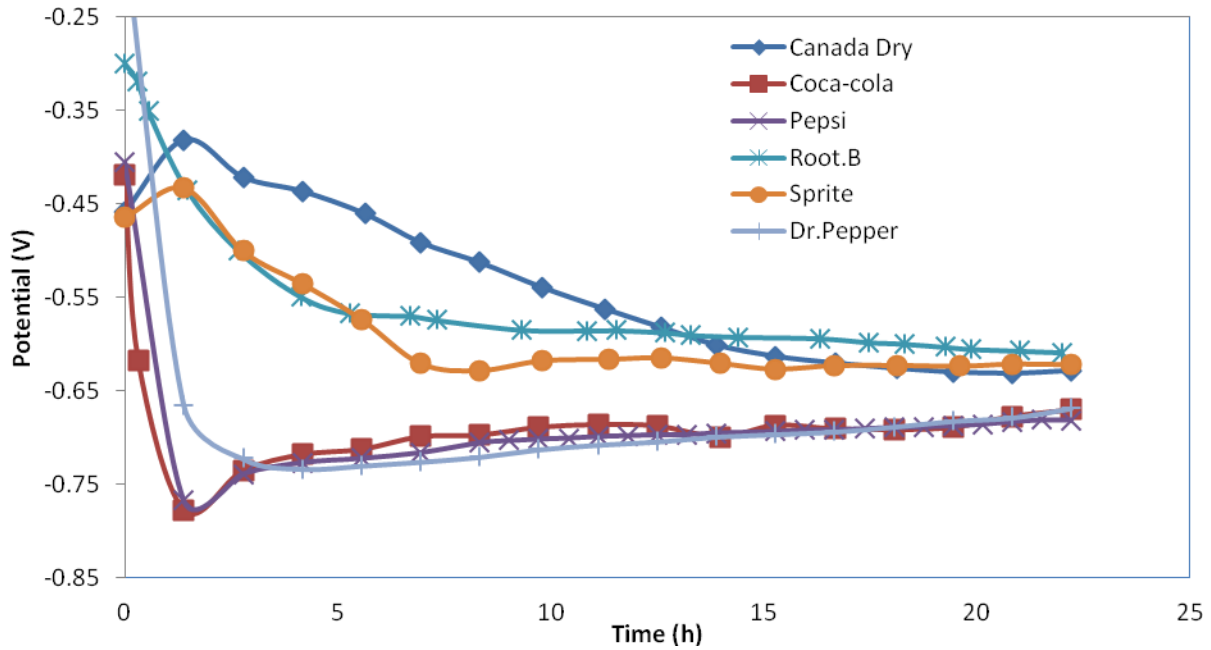


Figure 6.2.1 Variation of the open-circuit potential of aluminum working electrode with time measured in the six soft drinks of this study.

Table 6.2.1 Average open-circuit potentials of aluminum measured in the six soft drinks considered in this study.

Beverages	OCP (V)
Root Beer	-0.608
Sprite	-0.621
Canada Dry	-0.628
Dr. Pepper	-0.668
Coca-cola	-0.670
Pepsi	-0.681

As shown in the previous section, the corrosion dynamics when Al is immersed in the soft drinks falls into two groups depending upon the citric acid and phosphoric acid content of the beverages. A similar grouping is observed with respect to the variation of the OCP over the course of corrosion. The OCP decreases more gradually and reaches more positive values in a range from -0.61 to -0.63 V at the end of 22 hours when Al is immersed in the soft drinks containing high levels of citric acid but no phosphoric acid (i.e., Sprite, Canada Dry and root beer). On the other hand, upon immersion in the beverages containing high levels of phosphoric acid and little or no citric acid (Coca-cola, Pepsi and Dr.Pepper), the OCP decreases more sharply at the outset, reaches steady state more quickly and reaches more negative values of -0.67 to -0.68 V by the end of 22 hours. In general, as an oxidation process becomes more facile, the more negative should be the resulting OCP. Based on a comparison of the evolution of the OCP in the presence of the soft drinks, one would therefore conclude that the corrosion over the first 22 hours occurs more readily in the beverages containing high levels of phosphoric acid than in the beverages containing large amounts of citric acids and no phosphoric acid. This correlates well with the trends shown previously in Table 6.1.2 with respect to the dissolved aluminum concentrations measured after 1 day of immersion. More discussion on this point is provided later.

In order to further investigate the particular effects of citric acid and phosphoric acid on Al metal corrosion, similar OCP measurements were conducted in synthetic solutions consisting of each of these components only. For these experiments, separate solutions containing each of 200, 500 and 1000 ppm phosphoric acid and 200, 500 and 1000 ppm citric acid were prepared. Plots showing the variation of the OCP over a period of 22 hours in solutions containing phosphoric acid are presented in Figure 6.2.2 and the corresponding curves obtained in citric acid solutions

are shown in Figure 6.2.3. Table 6.2.2 lists the steady state OCP values obtained in each case and Figure 6.2.4 presents these results in the form of a histogram. The curves for the phosphoric acid solutions in Figure 6.2.2 are similar in shape to those obtained in the soft drinks containing high levels of phosphoric acid (i.e., Coca-cola, Pepsi and Dr. Pepper). These soft drinks have phosphoric acid levels close to 500 ppm. The steady state OCP of -0.62 V obtained in the solution containing 500 ppm phosphoric acid is somewhat more positive than the values obtained in these soft drinks. This difference suggests that some other component(s) of the soft drinks is contributing to the corrosion of aluminum or interacting with phosphoric acid to do so.

The trends observed in the curves for Coca-cola, Pepsi and Dr. Pepper in Figure 6.2.1 may be explained as follows. The Al surface metal is initially active and attacked by phosphoric acid in pores and active sites, causing a negative shift in the OCP over the first hour or so of exposure. However, as indicated by the SEM/EDX analysis, insoluble Al-phosphate and/or oxide corrosion products may begin to form on the metal surface and inhibit subsequent corrosion. This build-up of products would cause the gradual increase in the OCP over the remainder of the remaining 20 hours of the experiments evident in both Figures 6.2.1 and 6.2.2. This explanation is supported by the trends observed in Figure 6.1.1 whereby the dissolution rate of aluminum in Coca-cola, Pepsi and Dr. Pepper gradually diminishes over time. Relatively high dissolution rates are measured over the 1st day of immersion, but then slow down considerably thereafter.

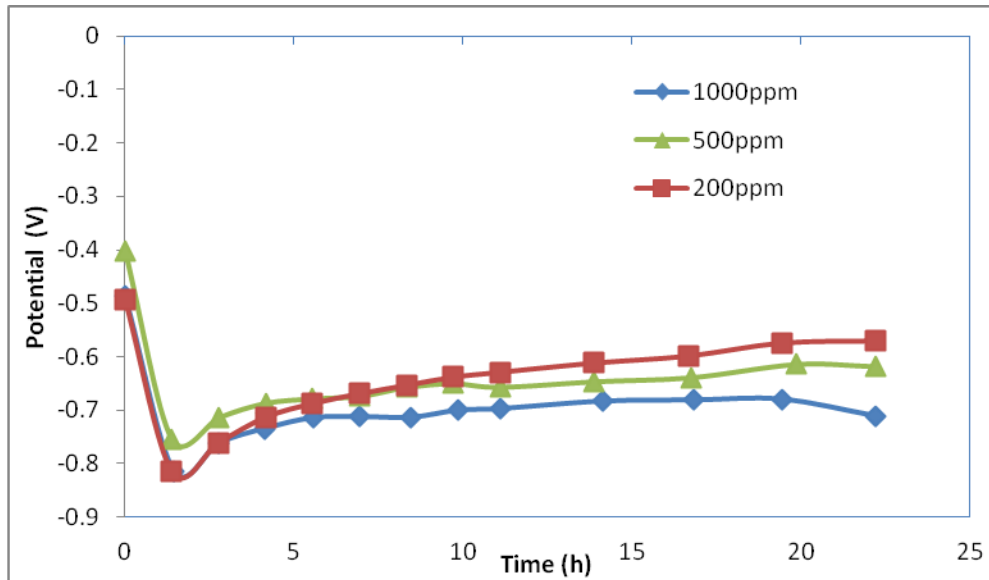


Figure 6.2.2 Variation of open-circuit potential with time of aluminum electrode immersed in solutions containing 200, 500 and 1000 ppm phosphoric acid.

The OCP-time curves obtained in citric acid solutions in Figure 6.2.3 are similar in shape to those obtained in the soft drinks containing high levels of citric acid and no phosphoric acid (i.e., Canada Dry, Sprite and root beer. Steady state OCPs of ~ -0.62 V are obtained when aluminum is immersed in Canada Dry and Sprite (Table 6.2.1) that contain citric acids at concentrations close to 1000 ppm (Table 6.1.2). As shown in Table 6.2.2, these values are somewhat more negative than that obtained in 1000 ppm citric acid solution, a trend similar to that observed in the case of the phosphoric-acid containing soft drinks. Again, some other component(s) of Canada Dry and Sprite other than citric acid is contributing to the corrosion of aluminum.

The evolution of the OCP in citric acid solutions shown in Figure 6.2.3 exhibits the opposite trend to that in phosphoric acid solutions. The potential first shifts in the positive direction before moving in the opposite direction after a few hours. The initial rise in OCP may be due to the formation of an oxide film that tends to partially passivate the metal surface at the outset.

Whether or not such a film actually forms, the situation appears to change after the first few hours and the metal becomes less protected, causing the metal to become more active and the OCP to become more negative. The observation in Figure 6.2.3 that the OCP continues to drop over most of the first 22 hours is consistent with the results presented in Figures 6.1.2 and 6.1.10 that the corrosion rate remains constant and no surface coating appears to form when aluminum is immersed in Sprite for as long as 5 days.

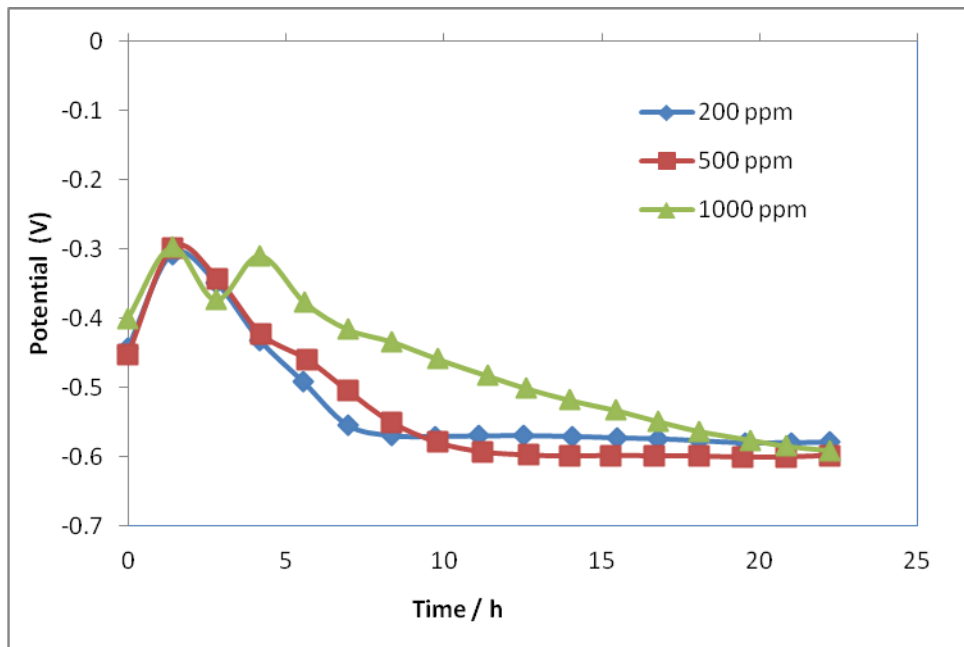


Figure 6.2.3. Variation of open-circuit potential with time of aluminum electrode immersed in solutions containing 200, 500 and 1000 ppm citric acid.

Table 6.2.2 Steady state OCP values measured on aluminum electrodes immersed in solutions containing 200, 500 and 1000 ppm citric acid and phosphoric acid.

Test solutions	OCP (V)
200 ppm citric acid	-0.5769
500 ppm citric acid	-0.5979
1000 ppm citric acid	-0.591
200 ppm phosphoric acid	-0.5701
500 ppm phosphoric acid	-0.6179
1000 ppm phosphoric acid	-0.7113

Figure 6.2.4 shows a histogram summarizing the variation of the steady state OCP measured on aluminum electrodes immersed in the 200, 500 and 1000 ppm citric acid and phosphoric acid solutions over the 22 hours. The value measured in the 500 ppm phosphoric acid solution is more negative than that obtained in the 500 ppm citric acid solution, supporting the conclusion reached from the immersion experiments that aluminum is more readily attacked by the phosphoric acid-containing soft drinks over the first day than by the citric acid-containing soft drinks. The same trend is observed at a concentration of 1000 ppm.

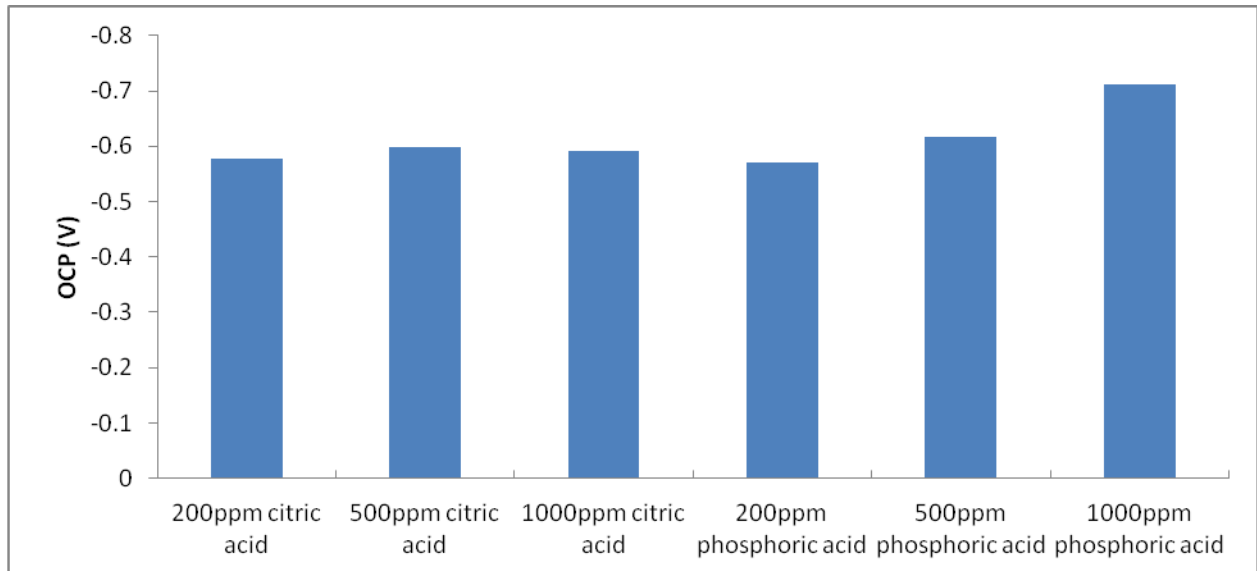


Figure 6.2.4 Histogram summarizing the variation of the steady state OCP measured on aluminum electrodes immersed in 200, 500 and 1000 ppm citric acid and phosphoric acid.

6.3 Polarization Resistance

An electrode is polarized when its potential is forced away from its value at open circuit. The difference between the electrode potential and the open-circuit potential is called the overpotential. If an electrode is sufficiently polarized, current due to an electrochemical reaction at the electrode surface can occur. When the electrode is not strongly polarized, the polarization resistance R_p can be estimated by the following equation:

$$R_p = \Delta E / \Delta I \quad (6.1)$$

where ΔE = overpotential (V)

ΔI = polarization current (A)

R_p is analogous to a simple resistance and can be estimated by taking the inverse of the slope of a current-potential curve within a region of $\sim \pm 10\text{mV}$ on either side of the OCP^[41].

To obtain the current-potential curves, linear sweep voltammetry (LSV) experiments at a scan rate of 0.001 V/s were conducted after the aluminium strips had been immersed in the various beverages for 22 hours under open-circuit conditions. The current-potential data obtained in the region from 10 mV to -10mV relative to the open-circuit potential were fitted by linear regression to obtain the slopes. The results of the regression are shown in Figure 6.3.1. The corresponding polarization resistances R_p calculated from the slopes are listed in Table 6.3.1. These values are also plotted in a bar graph (Figure 6.3.2) so as to rank the beverages in order of increasing R_p value. Interestingly, the order appears to correlate with the chemical content of the beverage. R_p is lowest upon immersion in soft drinks rich in phosphoric acid (Coca-cola, Pepsi, Dr.Pepper) and increases upon immersion in Gatorade, apple juice, soft drinks containing citric acid and no phosphoric acid (Canada Dry, Root Beer, Sprite), and finally beer which contains moderate levels of both phosphoric acid and citric acid.

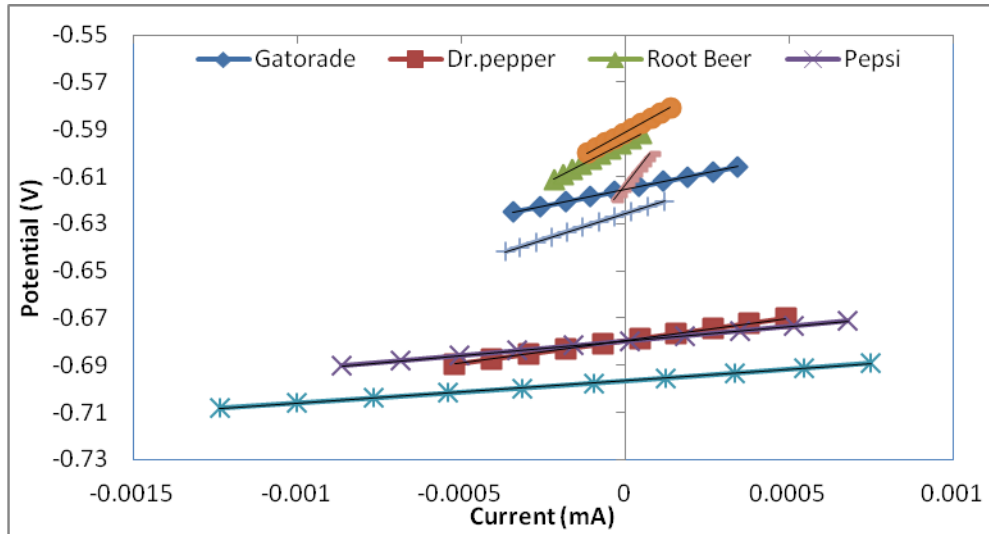


Figure 6.3.1 Linear regression of current-potential data within 10 mV of OCP obtained on aluminum electrodes immersed in various commercial beverages.

Table 6.3.1 Polarization resistances R_p of Al immersed in various commercial beverages.

Beverages	Coca-cola	Pepsi	Dr.Pepper	Gatorade	A.J	Canada Dry	Root Beer	Sprite	Beer
R_p (K Ω)	9.7	12.5	19.0	28.3	43.8	61.0	72.5	76.1	172.5

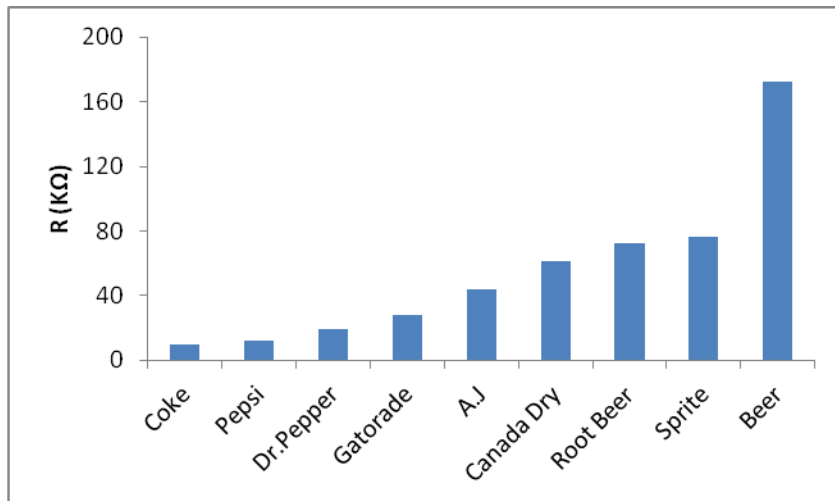


Figure 6.3.2 Polarization resistance R_p among the various beverages sorted in increasing order

A wide range of R_p values from 9 kΩ to 172 kΩ are obtained. The higher R_p values in the citric acid-containing beverages than in the phosphoric acid-containing beverages indicate that Al is less strongly attacked by the former drinks than the latter. The data obtained from the 1-day immersion experiments and the open-circuit and R_p measurements are summarized in histograms presented in Figure 6.3.3. These results show an excellent correlation between these 3 quantities obtained from separate measurements. A more corrosive environment for aluminum leads to a higher dissolved metal concentration, a lower R_p and a more negative OCP value. The fact that a good correlation between these quantities was obtained on the basis of independent experiments provides confidence regarding the quality of the measured data. potential and dissolved aluminum concentration after 1 day immersion in various soft drinks.

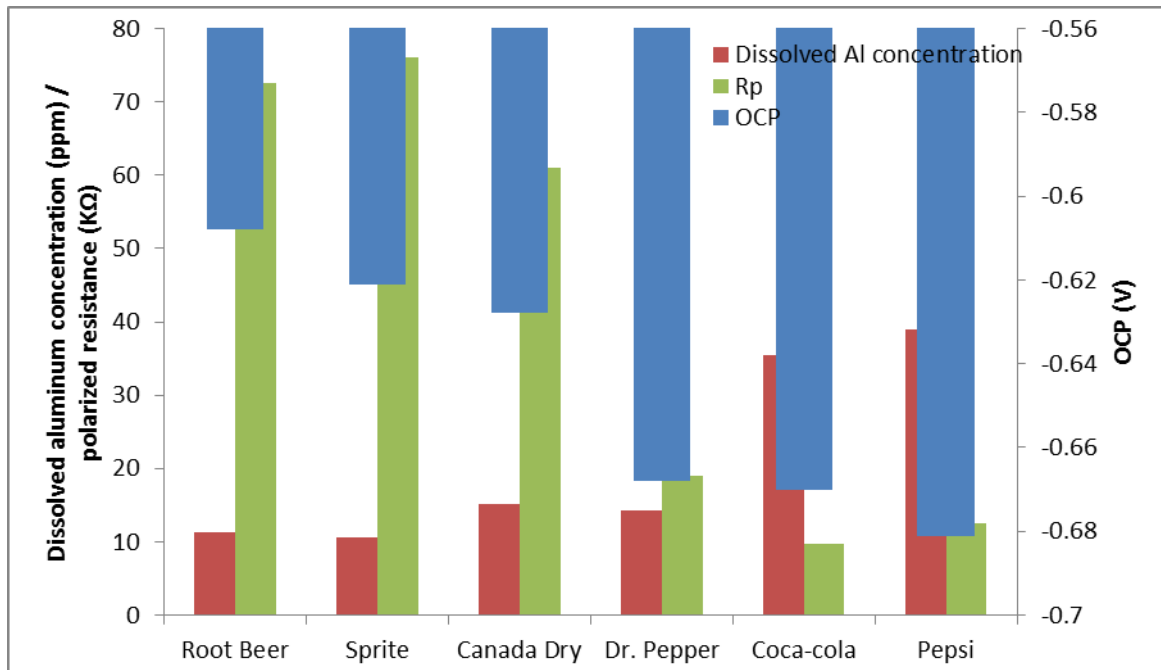


Figure 6.3.3 Histograms show a correlation between polarization resistance, open-circuit potential and dissolved aluminum concentration after 1 day immersion in various soft drinks.

6.4 Tafel Polarization Measurements

Since corrosion is a dynamic process that permanently changes the substrate, it would be useful to assess the response of the metal after it has undergone corrosion for some time. Consequently, the following series of experiments was conducted. The aluminum electrode was allowed to undergo corrosion in the commercial beverages under open-circuit conditions for 22 hours to ensure that steady state had been reached. After steady-state was reached, linear sweep voltammetry experiments were carried out and the current response was measured over a potential range from -250 mv to $+250$ mv with respect to the open-circuit potential at a sweep

rate of 1 mV/sec. At least two scans were conducted in each condition to confirm that reproducible results were obtained.

From the shape of the polarization curves so obtained, the beverages appear to fall into one of four categories types of corrosion behaviour in which aluminum is immersed.

- (1) phosphoric acid-rich soft drinks: Pepsi, Coca-cola and Dr. Pepper (Figure 6.4.1). Anodic current changes slowly with increasing overpotential compared to the behaviour on the cathodic side. Thus, asymmetric polarization curves were obtained.
- (2) soft drinks containing citric acid but no phosphoric acid: Canada Dry, Sprite and root beer (Figure 6.4.2). Compared to phosphoric acid-rich soft drinks, Tafel behaviour on the cathodic side extended over a wider potential range than on the anodic side; also, the anodic current rose more steeply with change in potential than did cathodic current, leading to asymmetric curves.
- (3) beverages containing malic, citric and phosphoric acids: fruit juices, milk and alcoholic products (Figure 6.4.3). Relatively symmetric curve shapes were observed.
- (4) Gatorade (Figure 6.4.4). Pitting corrosion occurred during anodic polarization, leading to a noisy electrode response (Figure 6.4.5).

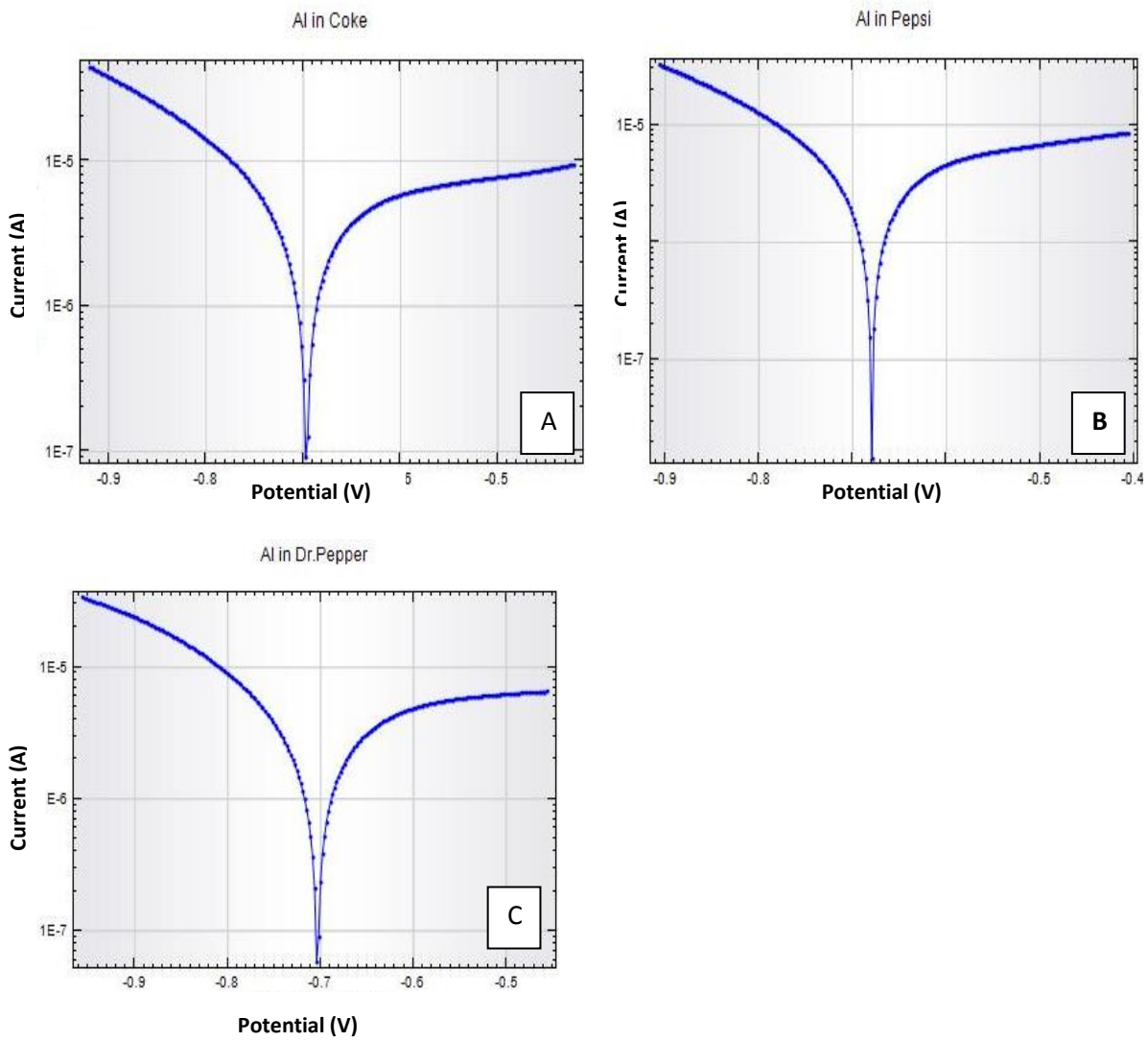


Figure 6.4.1 Polarization curves of aluminum immersed in selected phosphoric acid-containing soft drinks: A) Coca-cola, B) Pepsi and C) Dr. Pepper.

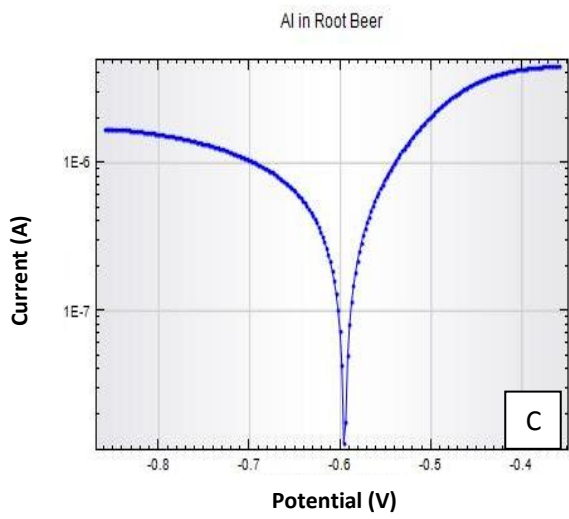
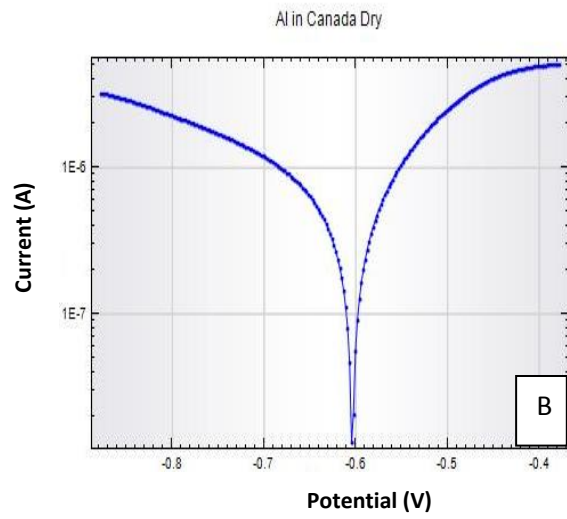
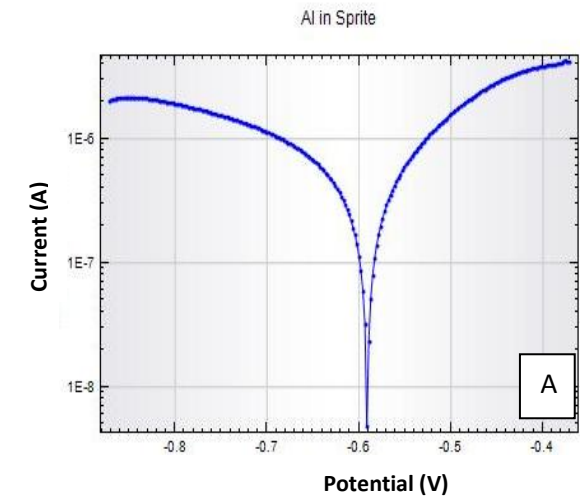


Figure 6.4.2 Polarization curves of aluminum immersed in selected soft drinks containing citric acid but no phosphoric acid: A) Sprite, B) Canada Dry and C) root beer.

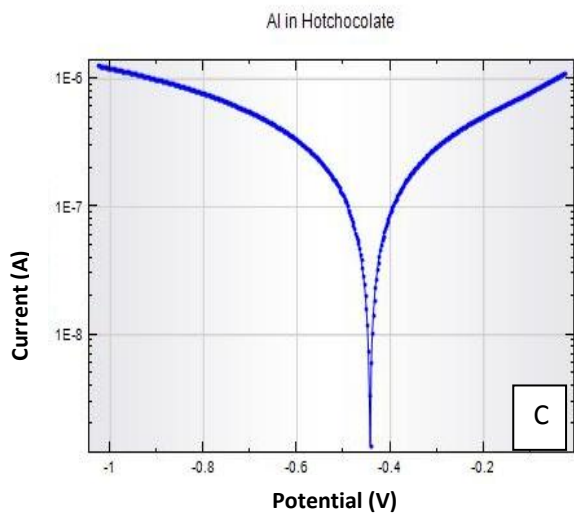
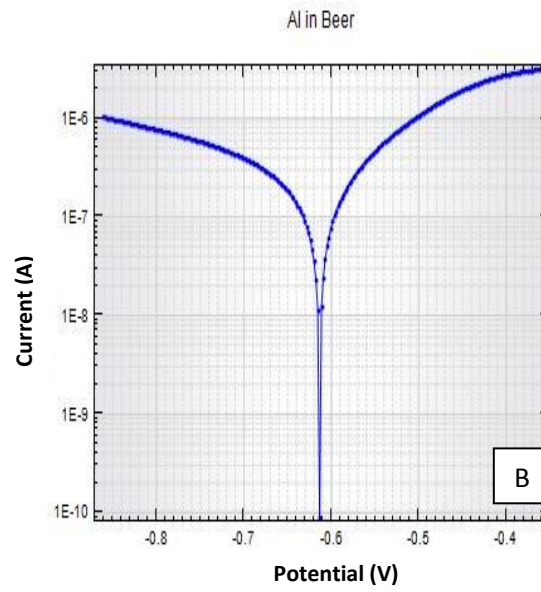
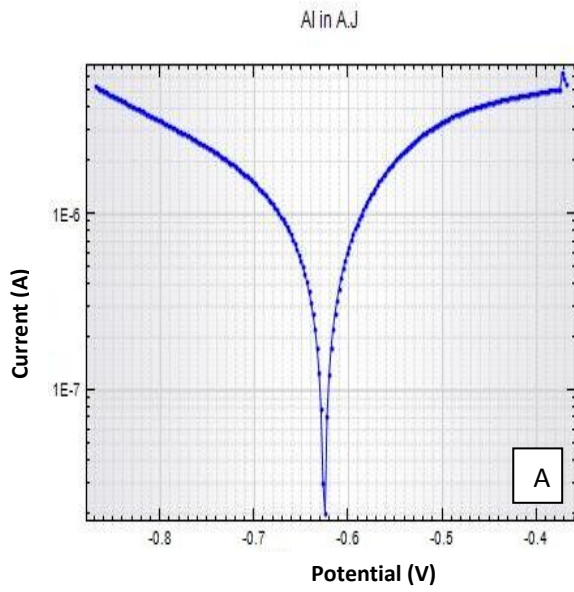


Figure 6.4.3 Polarization curves of aluminum immersed in selected beverages containing malic, citric and phosphoric acids: A) apple juice, B) beer and C) hot chocolate.

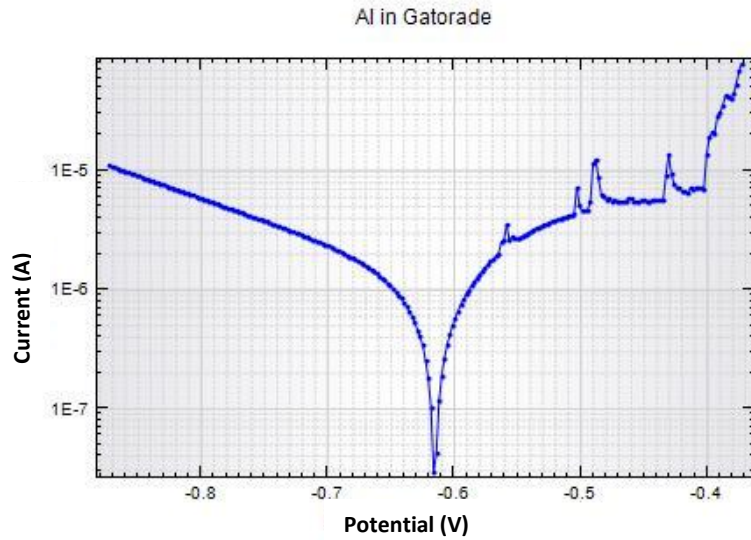


Figure 6.4.4 Polarization curve of aluminum immersed in Gatorade.

Tafel analysis of a polarization curve involves plotting the data as $\log i$ versus E for both the anodic and cathodic branches, obtaining the straight lines that best fit the data at high overpotentials and extrapolating the straight lines until they intersect. The point of intersection yields the corrosion current density i_{corr} and the corrosion potential E_{corr} . Unfortunately, the standard Tafel analysis could not be successfully carried out on many of the anodic and cathodic polarization curves, particularly those of the soft drinks, for several reasons. As shown in Figure 6.4.1, the anodic and cathodic branches of the polarization curves are not symmetrical to each other. Furthermore, the Tafel lines for the anodic and cathodic branches do not intersect at E_{corr} (i.e., where the currents for the anodic and cathodic portions drop off dramatically toward zero). Also, many of the $\log i - E$ polarization curves do not exhibit sufficiently long linear regions at high overpotentials to accurately delineate the Tafel regions and extrapolate to obtain the

intersection points. However, NOVA software available on the Autolab potentiostat was used to perform a more sophisticated numerical fitting of the Butler-Volmer^[53] equation:

$$(i = i_{corr} [e^{2.303\eta/(b_a)} - e^{-2.303\eta/(b_c)}]) \quad (6.1)$$

to the experimental polarization data. The equation was fit to the experimental data by adjusting the values of E_{corr} , i_{corr} , b_a and b_c . The curve fitting method has the advantage that it does not require a polarization curve to exhibit a fully developed linear section. The corrosion kinetic parameters i_{corr} and E_{corr} obtained in this way are given in Table 6.4.1. Also included are the corresponding corrosion rates obtained using the NOVA software. Each of the results in the Table 6.4.1 represents the mean value of two separate measurements.

Table 6.4.1 Corrosion parameters obtained by fitting Butler-Volmer equation to polarization curves obtained after immersing aluminium in selected drinks

Beverage	E_{corr} (V)	i_{corr} ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm year ⁻¹)
Pepsi	-0.67	59.0	0.645
Coca-cola	-0.68	57.0	0.615
Dr.Pepper	-0.69	46.0	0.500
Apple juice	-0.66	17.5	0.185
Sprite	-0.54	2.4	0.026
Canada Dry	-0.6	2.4	0.026
Root Beer	-0.6	1.9	0.021
Hot Chocolate	-0.5	1.3	0.014
Beer	-0.61	0.9	0.0099
Orange juice	-0.64	0.017	0.00024

Some observations that can be made regarding the results obtained from the analysis of the polarization curves include:

1. The corrosion rates of aluminum immersed in the soft drinks rich in phosphoric acid (Coca-cola, Pepsi and Dr.Pepper) are higher than in those containing citric acid with no phosphoric acid (Sprite, Canada Dry and root beer), in agreement with the results shown in previous sections. Consistent with this trend is the observation that more negative E_{corr} values are measured in the phosphoric acid-containing drinks than in the citric acid-containing drinks.
2. The polarization curves for Al immersed in the phosphoric acid-containing soft drinks have different shapes than those obtained in the citric acid-containing beverages. This suggests some difference in the way in which corrosion proceeds in these two types of beverages.
3. As for the fruit juices, milk and alcoholic products, a more complex interaction of the ingredients during corrosion of Al is expected due to the presence of lactic, succinic, malic, tartaric, citric, fumaric, acetic, ascorbic as well as phosphoric acids.
4. Although a polarization curve for aluminum immersed in Gatorade is presented in Figure 6.4.4, a very noisy and non-reproducible response was obtained along the anodic branch due to the onset of pitting corrosion. Consequently, it was not possible to estimate corrosion parameters by fitting Butler-Volmer equation to the data.

Evidence of the pitting that occurs when Al is immersed in Gatorade is provided in the SEM image below in Figure 6.4.5. This sample was examined after the polarization curve in Figure 6.4.4 was obtained. No metastable or stable pits were observed on the surface of Al immersed in

the other test beverages. Some representative SEM images obtained after immersion in these beverages are shown in Figure 6.4.6 for comparison.

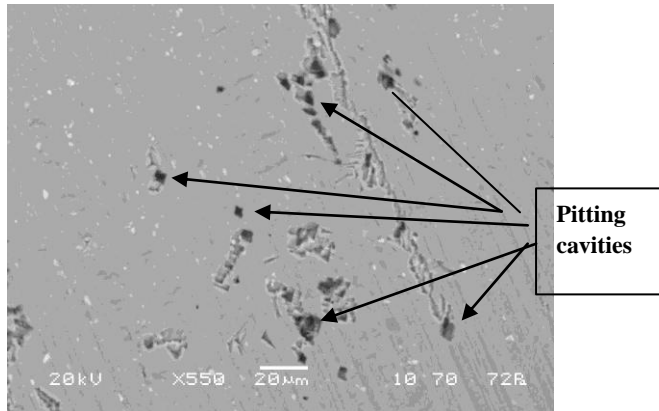


Figure 6.4.5 SEM image showing stable pit cavities on Al surface after immersion in Gatorade and after polarization experiment was conducted.

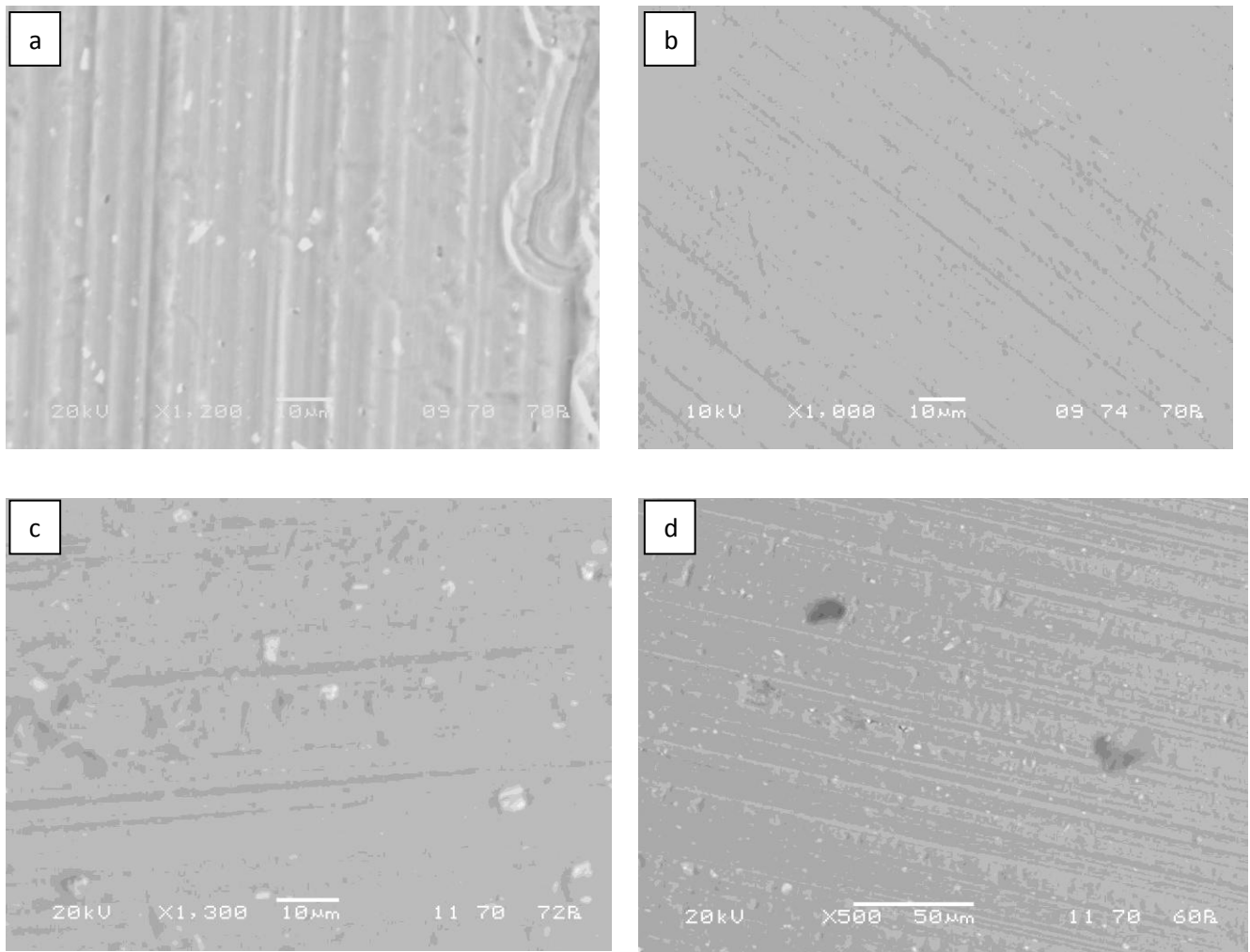
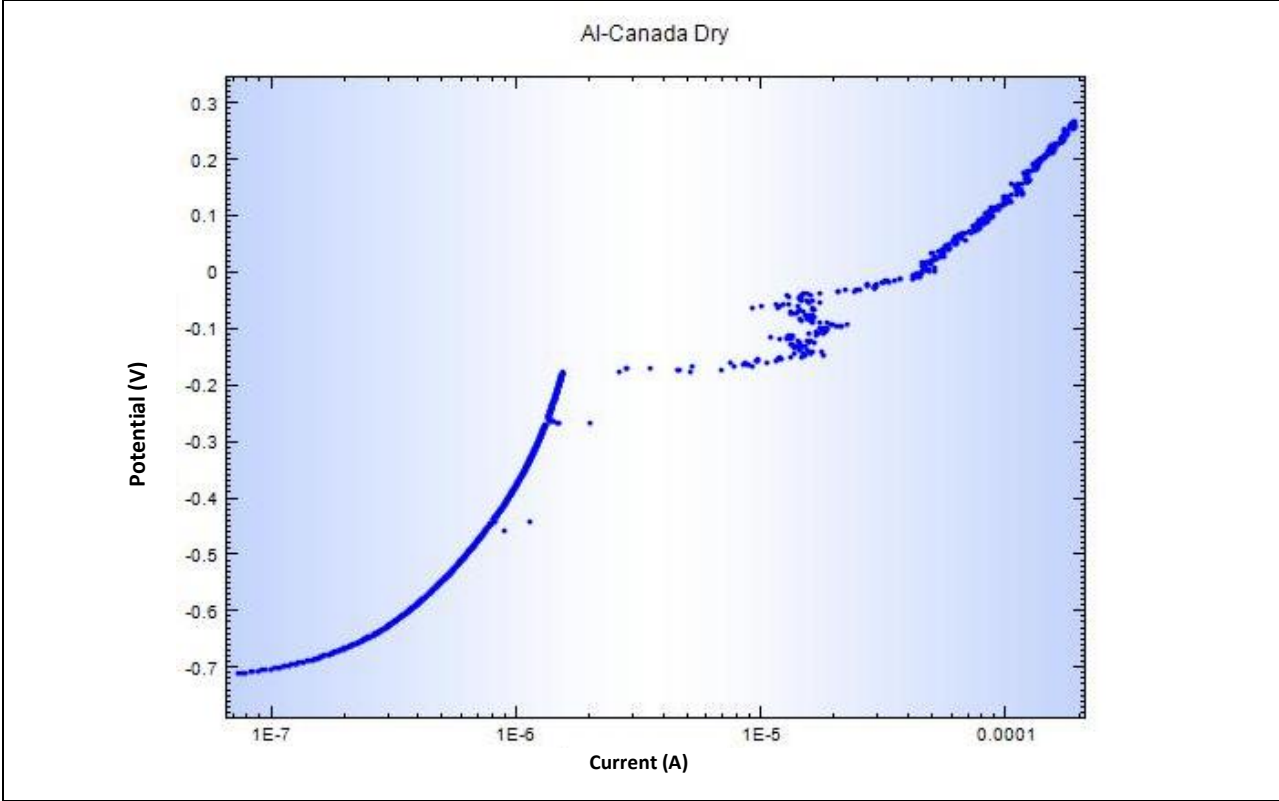
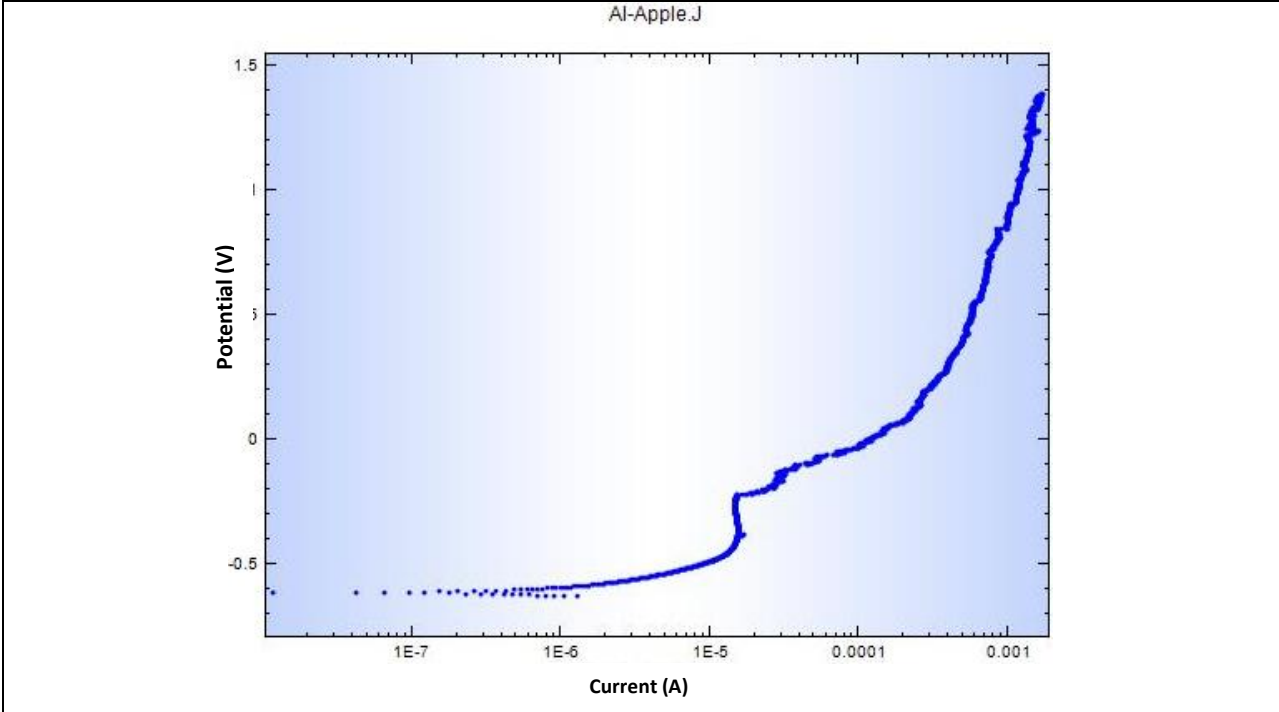


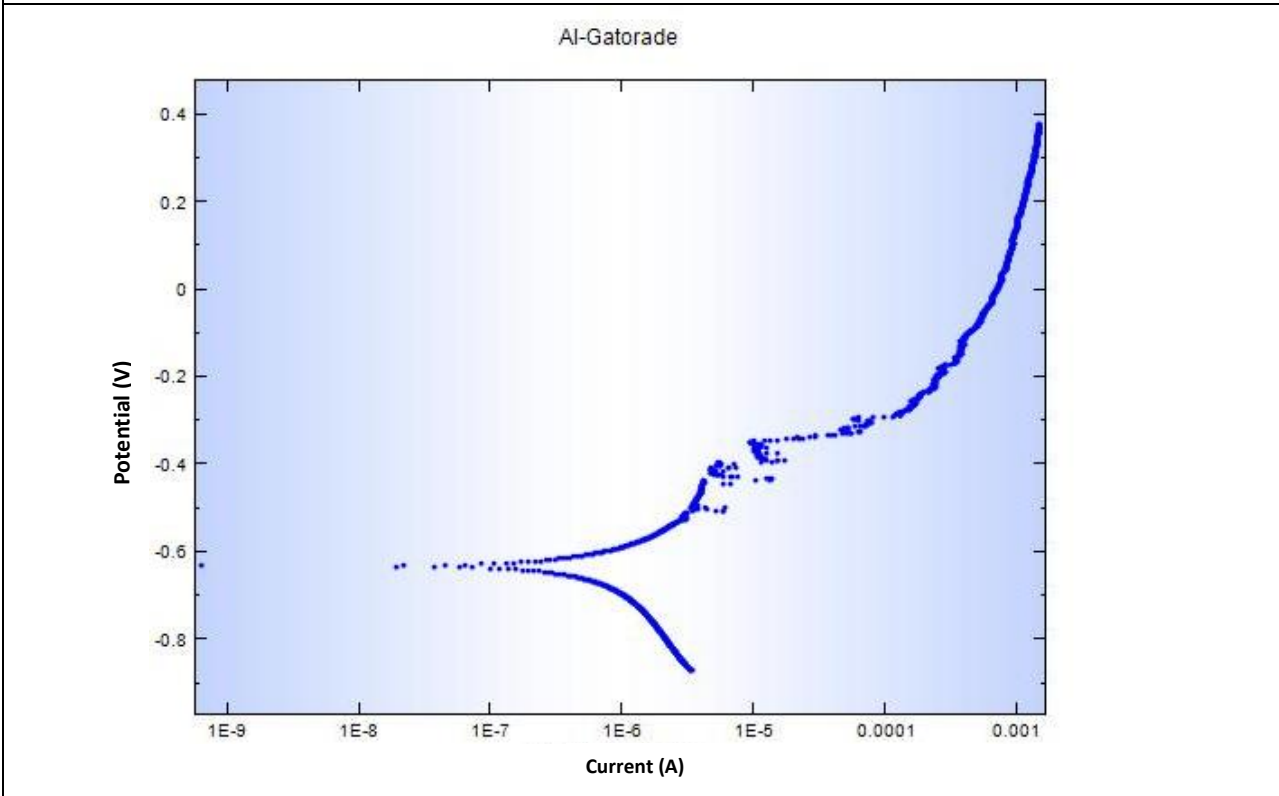
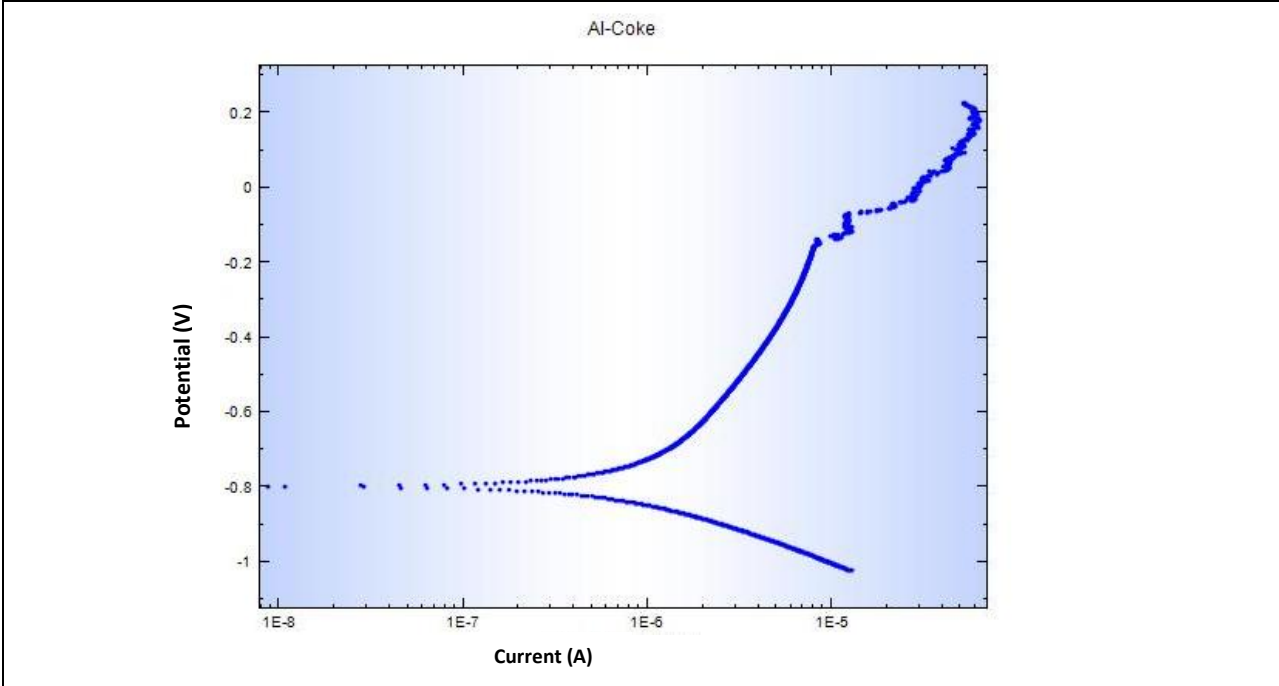
Figure 6.4.6 SEM images of Al surfaces after immersion in (a) Coca-cola (b) Pepsi (c) Dr.Pepper and (d) Canada Dry and after polarization experiments were conducted.

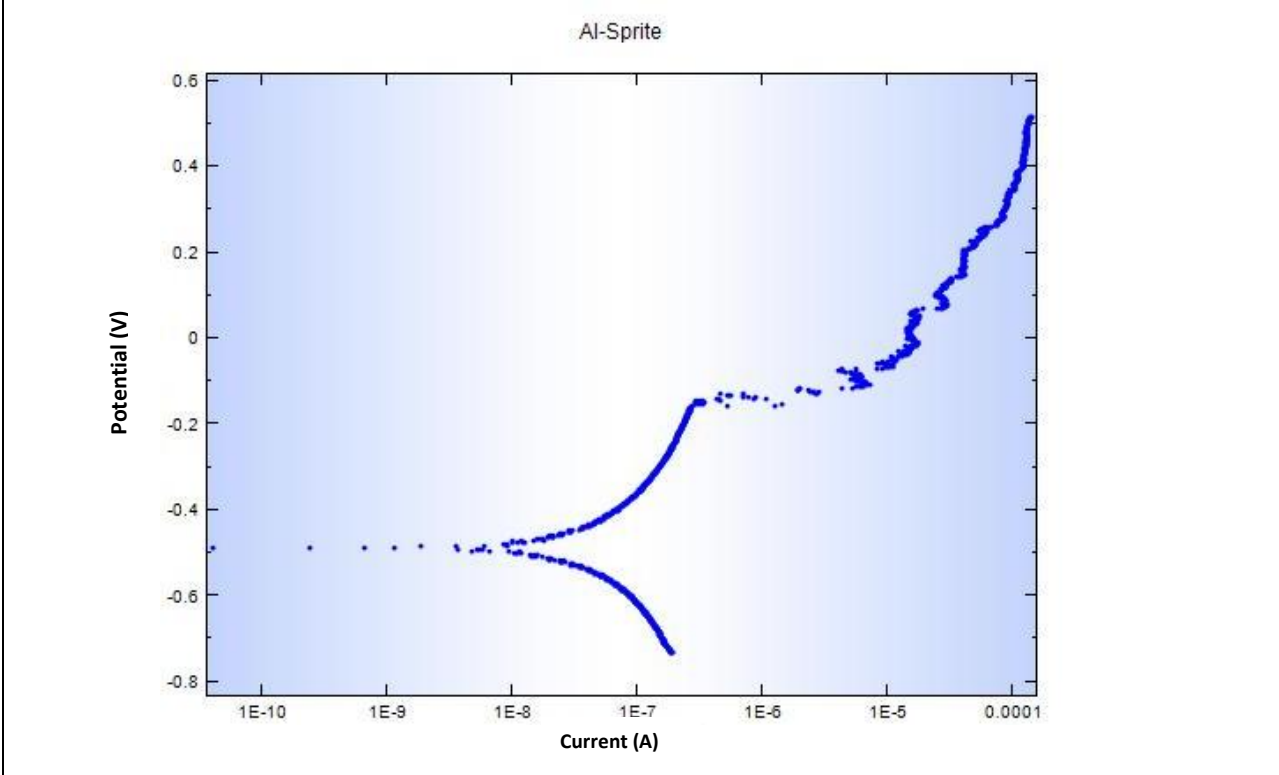
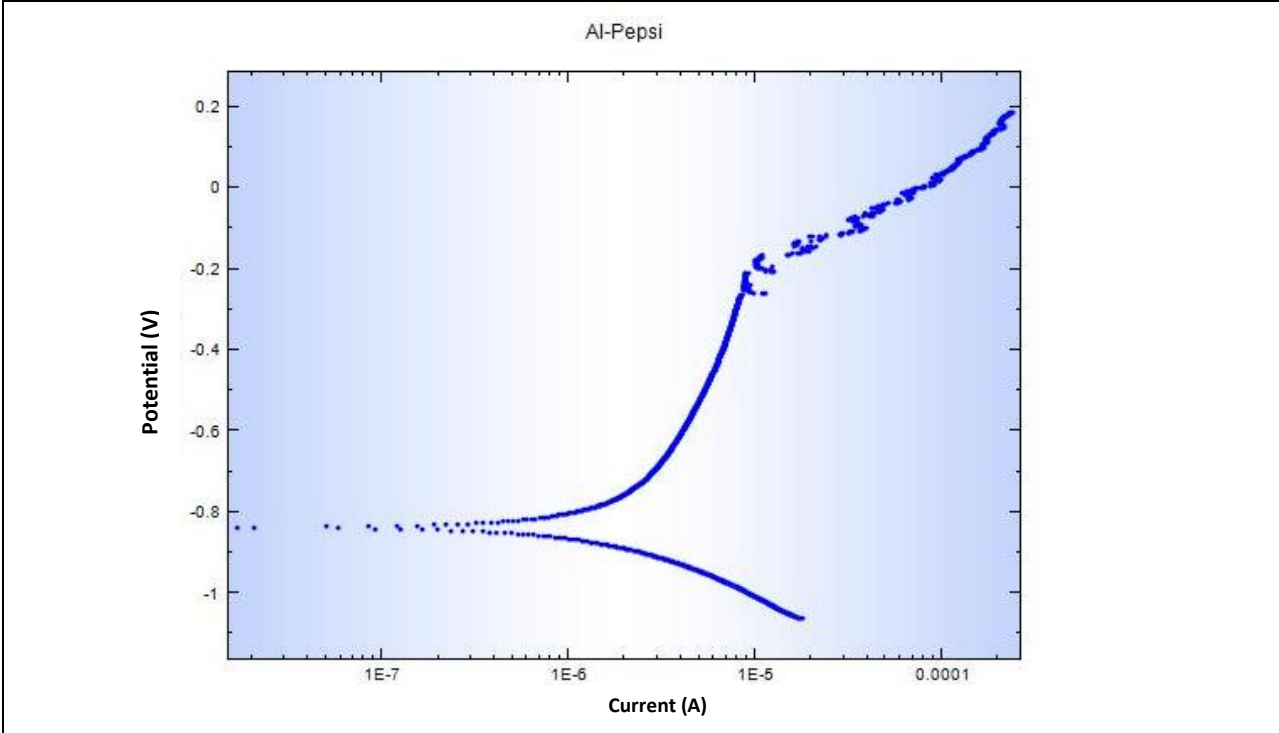
6.5 Anodic Polarization Measurement

In order to gain further insight into the corrosion behaviour of aluminum, an additional set of potentiodynamic measurements was carried out at a 1 mV/s scan rate from 200 mV below the open-circuit potential to 1000 mV above it. Once again, these were conducted at room temperature after the aluminum samples had been immersed in the various beverages for 22

hours under open-circuit conditions. The resulting polarization curves in $E - \log i$ format are shown in Figure 6.5.1. Several common features of the electrode responses are observed during the anodic polarization are observed in all cases. Firstly, as the potential is scanned anodically from the open-circuit value, the rise in anodic current tends to slow down suggesting that passivation of the aluminum surface may be occurring. At some point during each scan, an abrupt increase in current density is observed. The magnitude of this sharp rise varies depending on the beverage. It is interesting to note that once this occurs, the current signal becomes much noisier. These changes suggest that the sudden current increase marks the onset of a transpassive phenomenon such as the breakdown of a passive film that re-activates the aluminum to dissolution and even pitting or the anodic evolution of oxygen. It should be noted that pitting was observed to occur only in the presence of Gatorade during the immersion experiments, but these occurred under open-circuit conditions which are not as severe as those during anodic polarization. This abrupt activation of the electrode response occurs at a different potential and current depending on the beverage, although it is observed to be close to -0.2 V in most cases. The most notable exception again is observed when aluminum is polarized in the presence of Gatorade and the sudden rise occurs at a considerably more negative potential close to -0.4 V. This shift is consistent with the previous finding that pits in the aluminum most readily form when the metal corrodes in this beverage.







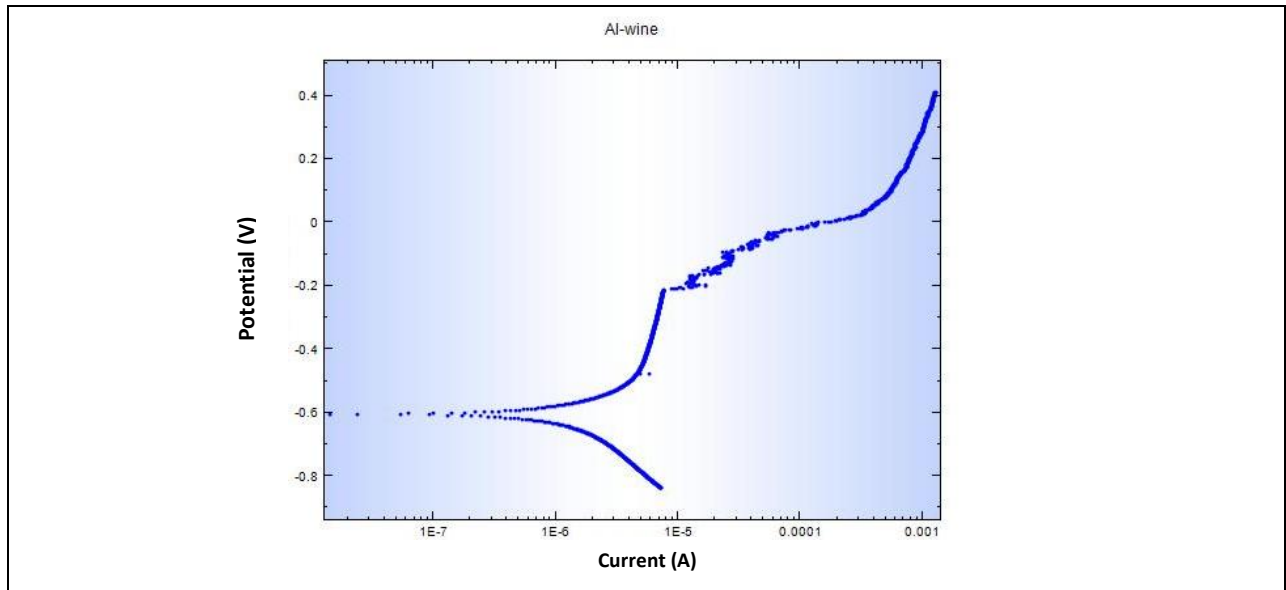


Figure 6.5.1 Anodic polarization curves of Al in selected beverages

Pits are observed on Al surfaces immersed in all of the selected beverages after the potential becomes sufficiently anodic. A representative optical image showing the evidence of this pitting after anodic polarization is shown in Figure 6.5.2 for the case where Al is immersed in Canada Dry.

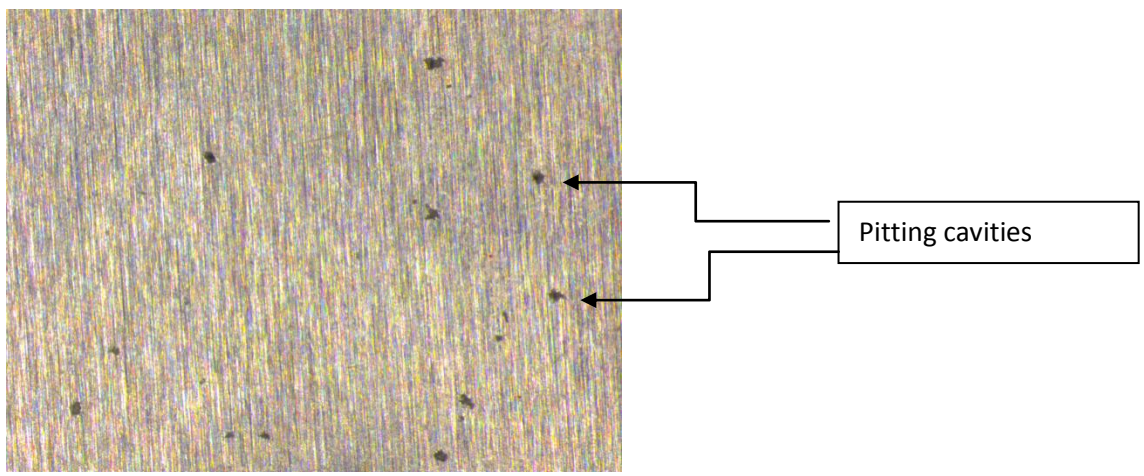


Figure 6.5.2 A representative optical image of Al after immersion in Canada Dry and being subjected to anodic polarization.

The potential at which the current density exceeds 0.1 mA/cm^2 is defined as the breakdown potential E_b ^[42-43]. Comparison of the breakdown potentials in Figure 6.5.3 shows that they vary significantly among the beverages included in this plot. A breakdown potential for aluminum of 0.275 V is observed when immersed in Sprite, 0.12 V in Canada Dry, 0 V in Pepsi and -0.30 V in Gatorade due to extensive pitting. Generally, the more negative is the breakdown potential, the more readily should pitting occur. Thus, the ease with which pitting of aluminum begins in these beverages increases in the following order: Sprite, Canada Dry, Pepsi, Gatorade.

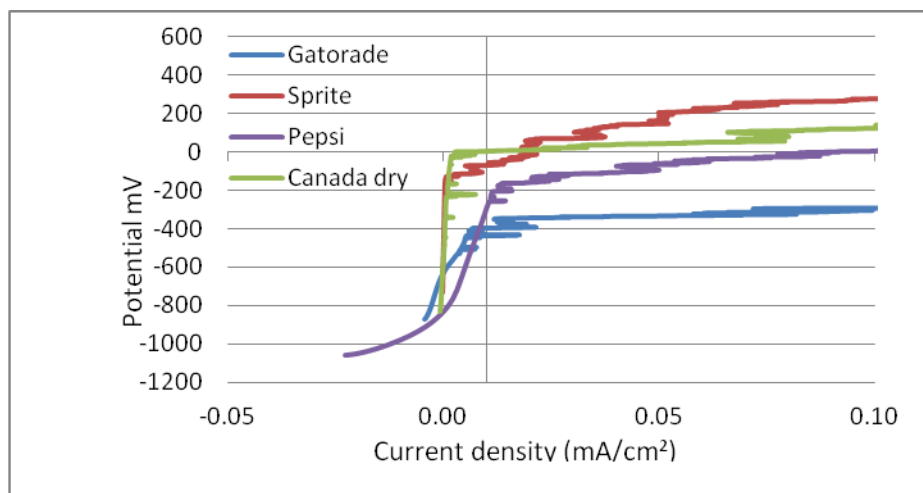


Figure 6.5.3 Anodic polarization curves (with I plotted on a linear scale) of an aluminum electrode immersed in selected beverages showing breakdown potential.

As discussed previously, aggressive components such as Cl^- , phosphoric acid, citric acid, etc., are present in many of the test beverages. Presumably, many of these species compete for sites on a surface that has become passivated. At a sufficiently high surface concentration of chloride, a passive film is likely destroyed and pitting is initiated. Among the beverages included in Figure 6.5.2, Gatorade contains the most Cl^- and so leads to the lowest pitting potential. A linear

dependence of the mean pit propagation rate on the logarithm of the chloride concentration has been reported^[44]. However, pitting corrosion of aluminum and its alloys in chloride media has been shown to be inhibited by other inorganic anions and organic molecules. Evidence for such behaviour among the beverages considered in this study may come in the case of apple juice which contains even more Cl^- than does Gatorade, yet appears to have a more positive pitting potential (Figure 6.5.1). In previous studies, the presence of sulphate in a chloride solution tended was found to shift the breakdown potential to more positive potentials^[45]. It is interesting to note that relatively little corrosion is observed in beverages containing high sulphate levels such as beer, wine, tomato juice, orange juice and milk, whereas higher corrosion is observed in those beverages containing low sulphate including the soft drinks (Table 4.2.1). Nitrite has been reported to inhibit aluminum corrosion in chloride media by strongly adsorbing on the metal surface, but becomes ineffective if the metal is polarized above the pitting potential, whereas chromate acts through repairing the oxide film and aiding oxide growth^[46]. It should be noted that only beer and wine among the beverages considered in this study contain nitrite (Table 4.2.1). Indole and its derivatives can protect aluminium against pitting corrosion^[47]. Clearly, some complicated interaction among the various components takes place to initiate or inhibit pitting.

6.6. Comparison of Two Different Methods of Corrosion Measurement

Figure 6.6.1 shows a comparison of dissolved Al concentration after 1 day immersion in the various beverages as determined by chemical analysis and the corrosion rate determined by

fitting the Butler-Volmer equation to the polarization data. Both sets of data were presented previously in this chapter. The values plotted in this figure are also listed in Table 6.6.1.

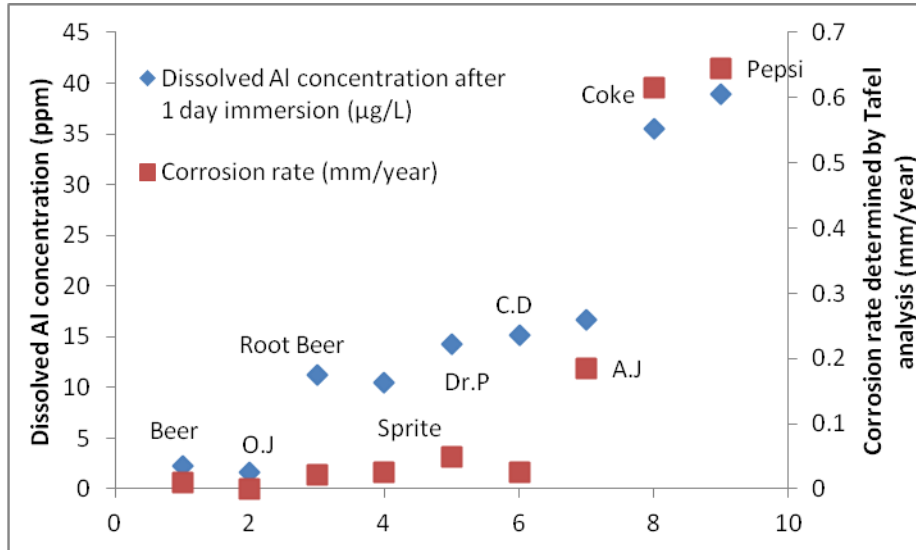


Figure 6.6.1 Comparison of dissolved Al concentration after 1 day immersion determined by chemical analysis and the corrosion rate determined by fitting Butler-Volmer equation to polarization data.

Table 6.6.1 Dissolved Al concentration after 1 day immersion determined by chemical analysis and the corrosion rate determined by fitting Butler-Volmer equation to polarization data

Beverages	Dissolved Al concentration after 1 day immersion ($\mu\text{g/L}$)	Corrosion rate (mm/year)
Beer	2.3	0.0099
Orange Juice	1.68	0.00024
Root Beer	11.27	0.021
Sprite	10.55	0.026
Dr.Pepper	14.33	0.05
Canada Dry	15.21	0.026
Apple Juice	16.71	0.185
Coca-cola	35.5	0.615
Pepsi	38.89	0.645

As shown in Figure 6.6.1, a reasonably good correlation is observed between these two methods of characterizing corrosion. Based on the results presented in Figure 6.6.1, the electrochemical method is able to distinguish the cases where the corrosion rate is high (e.g., in the presence of Coca-cola or Pepsi) from those in which it is low (e.g., beer or orange juice). However, it appears to be less successful at distinguishing the smaller differences in corrosion rates observed in those beverages at the lower end of the range (i.e., corrosion rates measured in the presence of beer, orange juice, root beer, Sprite, Dr. Pepper and Canada Dry).

6.7 Summary

This chapter focuses on the results obtained using electrochemical techniques and chemical analysis to characterize the corrosion of Al in selected beverages. The influences of key components of these beverages such as phosphoric acid, citric acid, Cl^- and pH on Al corrosion were also examined. The breakdown potential where pitting corrosion begins under polarized conditions in several beverages was also determined. The results can be summarized as follows:

1. The order in which the corrosion rates increase depending on the beverage in which aluminum is immersed as determined by the electrochemical technique shows agreement with that obtained by direct chemical analysis of the dissolved Al concentration after 1 day immersion. Phosphoric acid attack on Al under open-circuit conditions is most significant over the 1st day of immersion, but continually slows down over time, reflecting that some sort of passivation is occurring. No evidence of passivation is found when aluminum is immersed in citric acid and consequently a constant corrosion rate can be maintained over a period as long as 5 days. These trends agree well with what is observed in the commercial beverages that are rich in phosphoric acid or citric

acid. On the other hand, no strong correlation is observed between the corrosion rate and beverage properties such as pH, conductivity and total acidity.

2. The trends observed during short-term immersion (i.e., 1 day) often do not agree with those observed during long-term tests (i.e., 5 days), reflecting the importance of the dynamic aspects of Al corrosion in these beverages.
3. Examination of the aluminum samples after undergoing immersion tests shows that they corrode uniformly under open-circuit conditions in all test beverages except Gatorade. Pits are observed on the surface of Al both after 5 days of immersion and Tafel polarization measurement in Gatorade.
4. Anodic polarization measurements show that pitting corrosion can occur on aluminum regardless of the beverage in which it is immersed provided that the electrode potential becomes sufficiently positive. The pitting potential is affected strongly by the beverage in which aluminum is immersed and increases in the following order: Gatorade, Pepsi, Canada Dry, Sprite.

Chapter 7

Results and Discussion-Corrosion Behaviour of Zinc

Zinc is the fourth most widely used industrial metal behind iron, aluminium and copper. It is most commonly used to coat metals in order to improve their corrosion resistance and reduce the damage of the substrate due to corrosion. This chapter is concerned with the results of immersion tests and electrochemical experiments conducted to investigate the corrosion behaviour of Zn immersed in the 7 soft drinks considered previously in this study.

7.1 Immersion Tests

The soft drinks used in the immersion tests and some of their relevant properties (pH, total acidity, conductivity, citric acid and phosphoric acid content) are listed in Table 7.1.1. The test method is the same as described in Chapter 5. These experiments were carried out by immersing zinc samples in the beverages for 1 and 3 days at 40 °C in an oven. For each set of conditions, identical duplicate experiments were conducted. The data presented here are the average values obtained from these duplicate experiments. After removal of the metal sample from the beverage at the completion of an immersion experiment, the beverage was diluted 10 or 100 times using Milli-Q water with 2% nitrate acid added. All samples were analyzed for zinc with the ICP-OES spectrometer and results expressed as $\mu\text{g/l}$. The average dissolved zinc concentrations obtained in each beverage after 1 and 3 days of immersion are listed in Table 7.1.2. Figure 7.1.1 shows the variation in the dissolved Zn levels with immersion time. Figure 7.1.1 shows that the order of the soft drinks in terms of dissolved zinc concentration remains unchanged after 3 days of immersion

relative to that observed after 1 day of immersion. The zinc levels after exposure to the phosphoric acid-rich drinks (Coca-cola, Pepsi and Dr. Pepper) are relatively low compared to those attained in the citric acid-containing beverages (Sprite, Canada Dry and Root Beer). This suggests that phosphoric acid plays an inhibitor role in the zinc dissolution process.

Table 7.1.1 pH, total acidity, conductivity and contents of citric acid, phosphoric acid, chloride ion in test soft drinks.

	Citric acid concentration (ppm)	Phosphoric acid concentration (ppm)	Cl ⁻	pH	Total acidity (mmol/L)	Conductivity (µs/cm)
Gatorade	3289	367	456	2.92	46.12	2200
Canada Dry	1234	0	34.6	2.82	24.83	598
Sprite	1135	0	14.3	3.26	18.5	499
Root beer	152	0	30.1	4.24	8	433
Dr. Pepper	0	459	19.2	2.86	10.58	657
Pepsi	55	532	17.4	2.48	16.68	1124
Coca-cola	0	509	32.9	2.47	13.67	1255

Table 7.1.2 Dissolved Zn concentration (µg/L) after 1 and 3 days of immersion in the test soft drinks.

	1 day	3 days
Sprite	476±8.49	616±6.36
Canada Dry	512±19.80	648±19.09
Coca-cola	95±2.33	154±3.54
Pepsi	108±7.07	161±6.16
Dr. Pepper	110±2.56	172±2.12
Root Beer	140±7.07	185±7.78
Gatorade	784±5.37	861±7.78

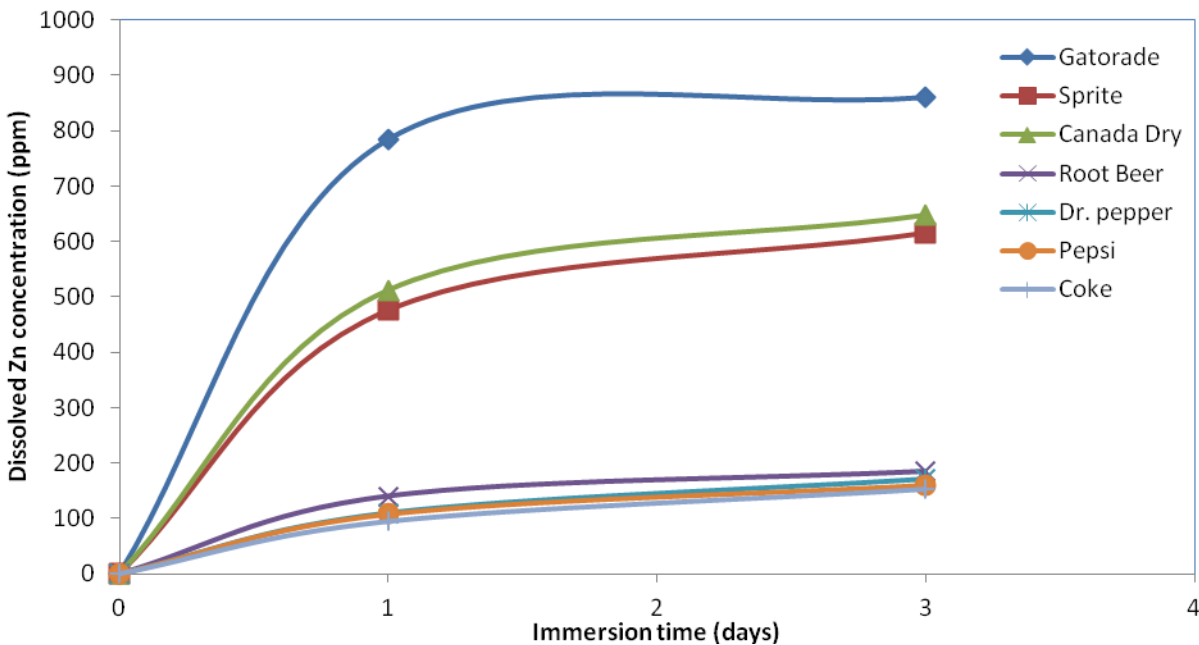


Figure 7.1.1 Variation of dissolved Zn concentration with time of immersion (1 day and 3 days) in the 7 test soft drinks.

SEM/EDX observation of the specimens after immersion in the 7 test beverages shows that the metal is uniformly attacked in all cases. The states of the metal surfaces after 3 days immersion are shown in the SEM images in Figure 7.1.2. In the phosphoric acid-containing beverages, flakes of corrosion products appear to have deposited on the zinc surface (Figure 7.1.2 d, e and f). EDX analysis of these flakes reveals them to contain phosphorus, oxygen, carbon and zinc. As shown in Figure 7.1.3, the atomic ratio of Zn: P: O in these flakes is found to be close to 3:2:8, suggesting that this corrosion product is $Zn_3(PO_4)_2$. The formation of $Zn_3(PO_4)_2$ may lead to the partial inactivation of the zinc surface.

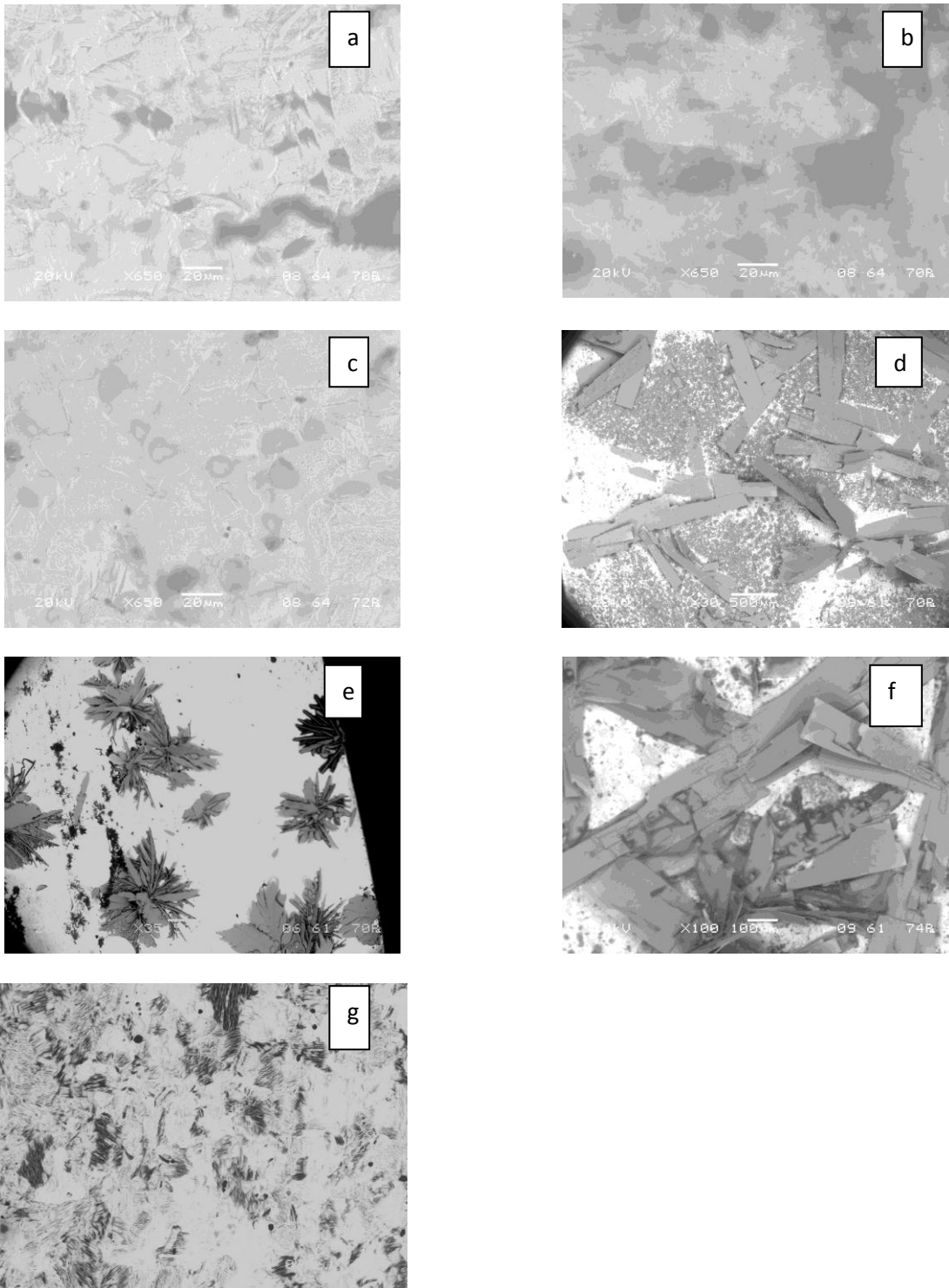


Figure 7.1.2 SEM images of Zn surfaces after 3 days immersion in (a) Sprite, (b) Root Beer, (c) Canada Dry, (d) Coca-cola, (e) Pepsi, (f) Dr. Pepper and (g) Gatorade.

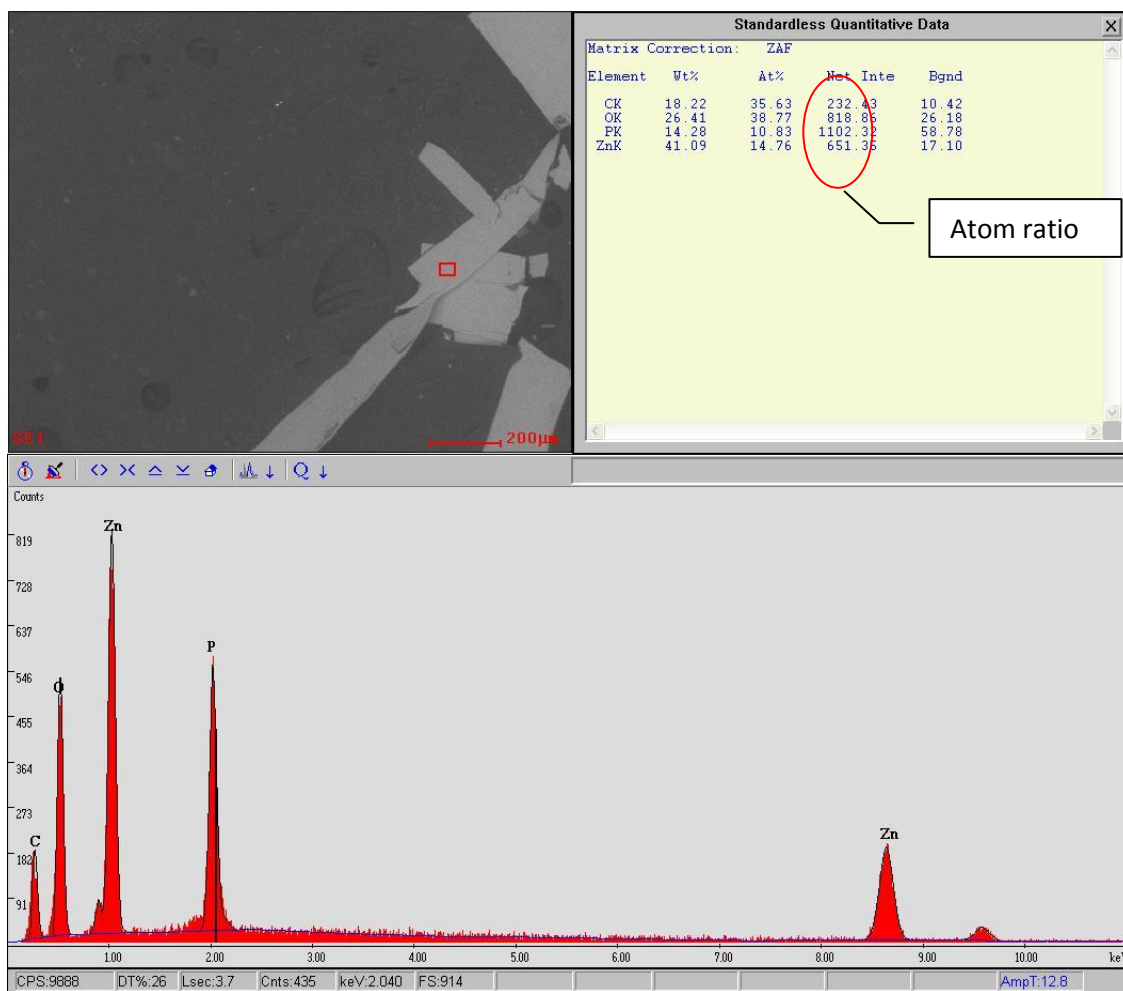
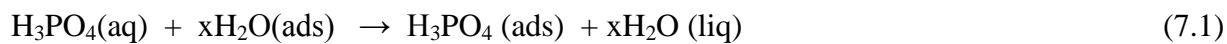


Figure 7.1.3 SEM/EDX spectrum and chemical analysis of corrosion product formed on a Zn surface after 1 day immersion in Coca-cola with a carbon tape background.

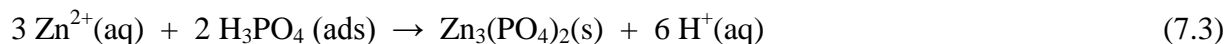
Such a process may begin with the adsorption of phosphoric acid on the zinc surface by replacement of one or more water molecules adsorbed at the metal surface:



In an acidic environment, zinc oxidizes as



These freshly generated Zn^{2+} ion may combine with the adsorbed phosphoric acid to form $Zn_3(PO_4)_2$:



The formation of $Zn_3(PO_4)_2$ on the metal surface is supported by the fact that species is very insoluble (i.e., $K_{sp} = 9 \times 10^{-32}$). When the beverage contains a relatively high concentration of H_3PO_4 , a sufficient amount of insoluble $Zn_3(PO_4)_2$ may form to cover the surface of the metal during the dissolution process and prevent further contact of the solution with the Zn surface. Based on this reasoning, the phosphoric acid concentration in the beverage should play a large role in determining the amount of zinc that corrodes and dissolves. This is supported by the observation that the dissolved Zn concentrations are similar after immersion in Pepsi and Coca-cola which differ only slightly in their phosphoric acid content. An additional factor that may play a role is that Pepsi contains a small amount of citric acid (55ppm), whereas Coca-cola contains none (Table 7.1.1). Citric acid presumably competes with phosphoric acid for interaction with the Zn surface. Similar to the behaviour observed in the case of aluminum, the interaction of citric acid with Zn does not tend to lead to the formation of protective reaction products on its surface and so is expected to promote corrosion, as will be discussed.

The SEM/EDX spectra of Zn films after immersion in Sprite, Canada Dry, Root Beer and Gatorade are shown in Figure 7.1.2 (a), (b), (c) ,(g) and 7.1.4. Relatively clean EDX spectra were observed compared to those obtained in the phosphoric acid-containing beverages. Other than the Zn peak, only relatively small carbon and oxygen peaks were detected. In the presence of citric acid, Zn^{2+} ions form soluble Zn-citrate complexes rather than insoluble species. As the

citric acid concentration rises, the dissolved Zn concentration due to corrosion would also be expected to increase.

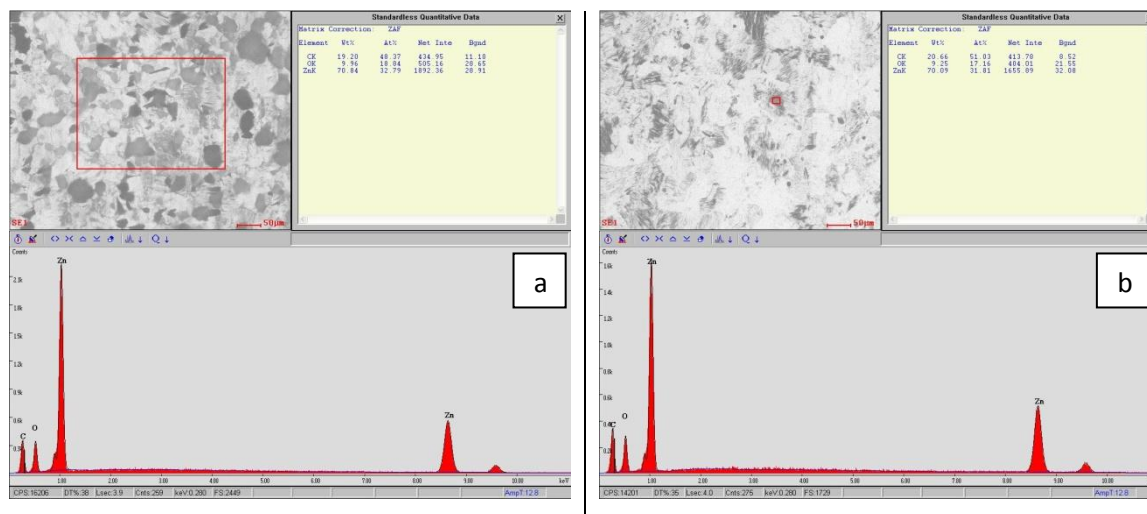


Figure 7.1.4 Representative SEM/EDX spectra of Zn surface after immersion in (a) Sprite and (b) Gatorade.

On the basis of these results, both citric acid and phosphoric acid have a significant influence on the Zn dissolution and surface morphology of the metal after immersion in these soft drinks. Phosphoric acid and citric acid act as an inhibitor and promoter, respectively, during zinc dissolution process in acidic media. Since they presumably compete for the metal surface, the combined effects of these acids help determine the amount of zinc that dissolves. Due to this importance of phosphoric acid and citric acid on Zn corrosion, an attempt was made to quantitatively correlate the dissolved Zn dissolved concentrations to the phosphoric acid and citric acid content of the soft drinks.

Polynomial regression equations predicting the dissolved zinc concentration after immersion in the soft drinks as a function of citric and phosphoric acid concentration were obtained using Minitab software. It turns out that a single equation was found to fit the data extremely well for all 7 soft drinks for each immersion time. The expressions obtained for 1 day and 3 days of immersion are given below in Equations 7.4 and 7.5, respectively:

$$C_{Zn} = 74.4 - 8.03 \times 10^{-4} C_P^2 - 7.4 \times 10^{-5} C_C^2 + 0.442 C_C + 0.447 C_P \quad (7.4)$$

$$C_{Zn} = 97.5 - 1.37 \times 10^{-3} C_P^2 - 1.2 \times 10^{-4} C_C^2 + 0.593 C_C + 0.795 C_P \quad (7.5)$$

where C_P = phosphoric acid content of beverages (ppm).

C_C = citric acid content of beverages (ppm).

C_{Zn} = dissolved Zn concentration in beverages (ppm).

A comparison of the measured and fitted dissolved Zn concentrations according to Equations (7.4) and (7.5) is presented in Table 7.1.3 and shown graphically in Figures 7.1.8 and 7.1.9. As shown below, extremely good agreement between the experimental and fitted values is obtained for both sets of data. These equations can be used to predict the dissolved zinc concentration upon immersion in solutions containing phosphoric acid and citric acid. The fact that a single equation in terms of the phosphoric acid and citric acid concentrations alone can fit the data for all 7 soft drinks reflects that Zn corrosion appears to be controlled almost entirely by these two components.

Table 7.1.3 Comparison of measured and fitted dissolved Zn concentrations after 1 and 3 days of immersion in the various soft drinks.

Soft drinks	1 day immersion		3 days immersion	
	Measured [Zn]	Fitted	Measured [Zn]	Fitted
Gatorade	784	784	860	857
Canada Dry	512	507	648	647
Sprite	476	481	616	616
Root beer	140	140	185	185
Dr. Pepper	110	110	172	174
Pepsi	108	109	161	165
Coca-cola	95	94	154	147

In order to investigate whether the dissolved zinc concentration is correlated to any other important quantities, the dissolved zinc concentration after 1 day and 3 days of immersion is plotted versus the beverage pH, total acidity and conductivity in Figures 7.15- 7.17, respectively.

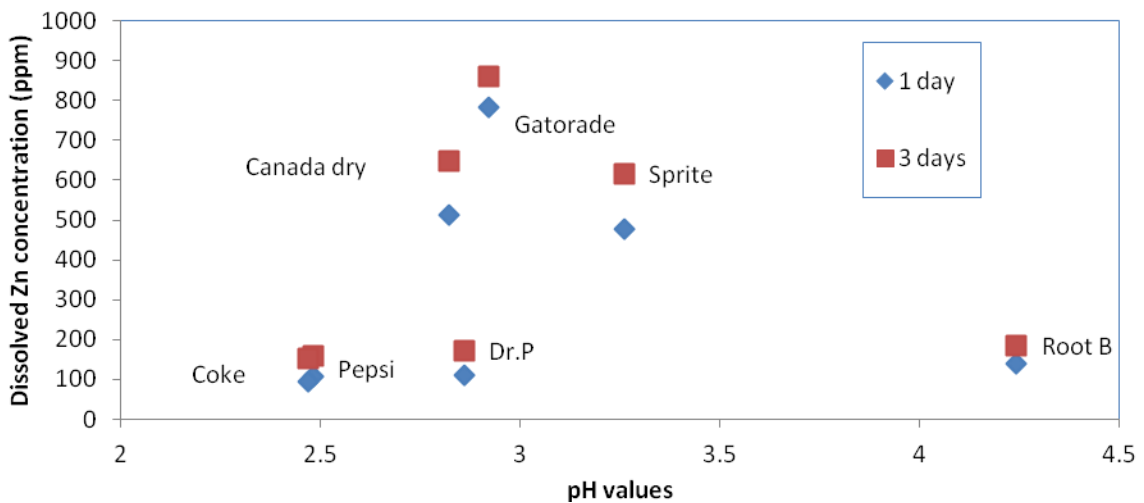


Figure 7.1.5 Relation between the mean dissolved zinc concentrations after 1 and 3 days immersion in the various soft drinks and their pH.

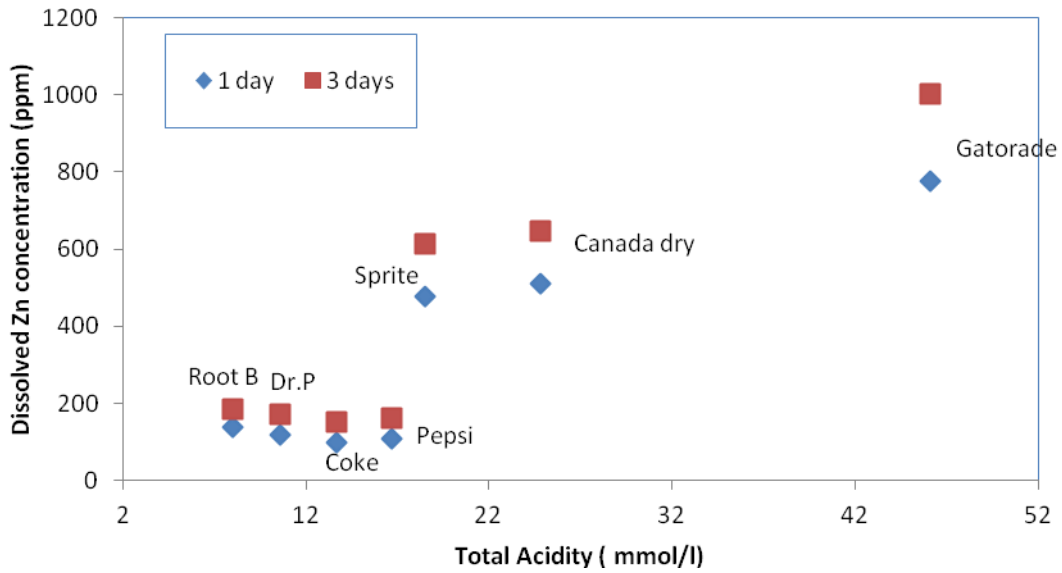


Figure 7.1.6 Relation between the mean dissolved zinc concentrations after 1 day and 3 days immersion in the various soft drinks and their total acidity.

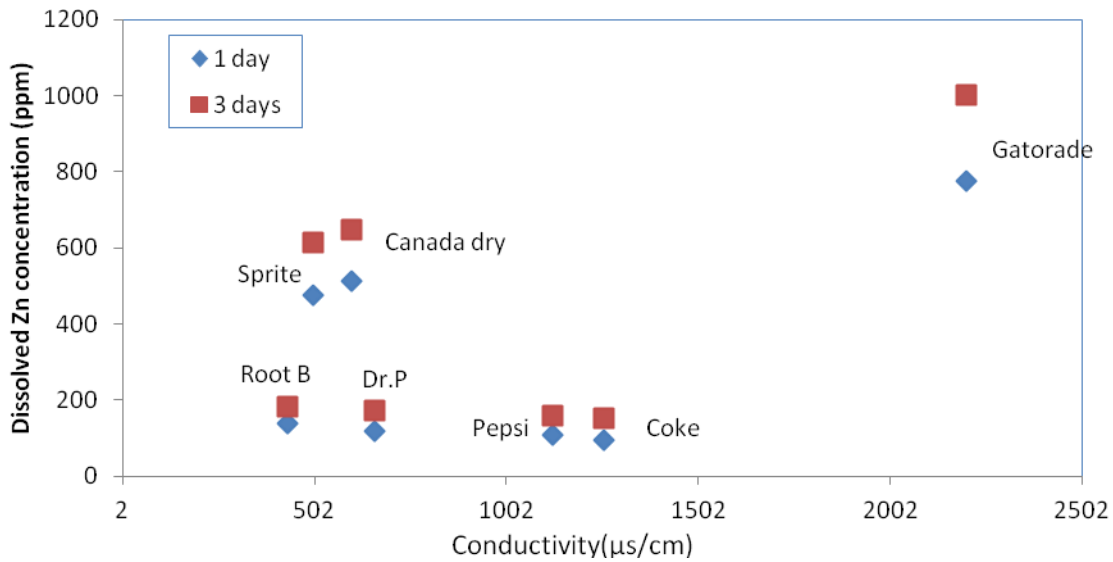


Figure 7.1.7 Relation between the mean dissolved zinc concentrations after 1 day and 3 days immersion in the various soft drinks and their conductivities.

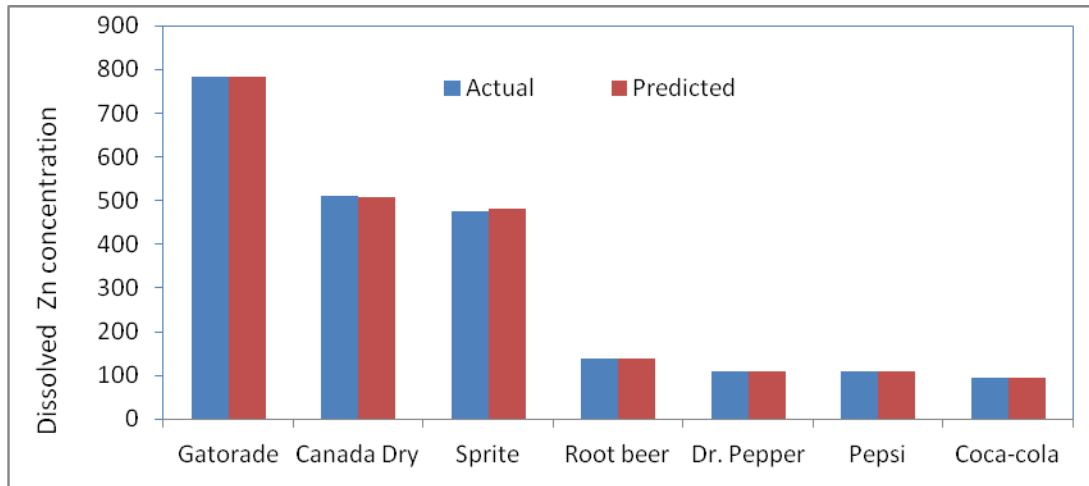


Figure 7.1.8 Comparison of measured and fitted dissolved Zn concentrations after 1 day of immersion.

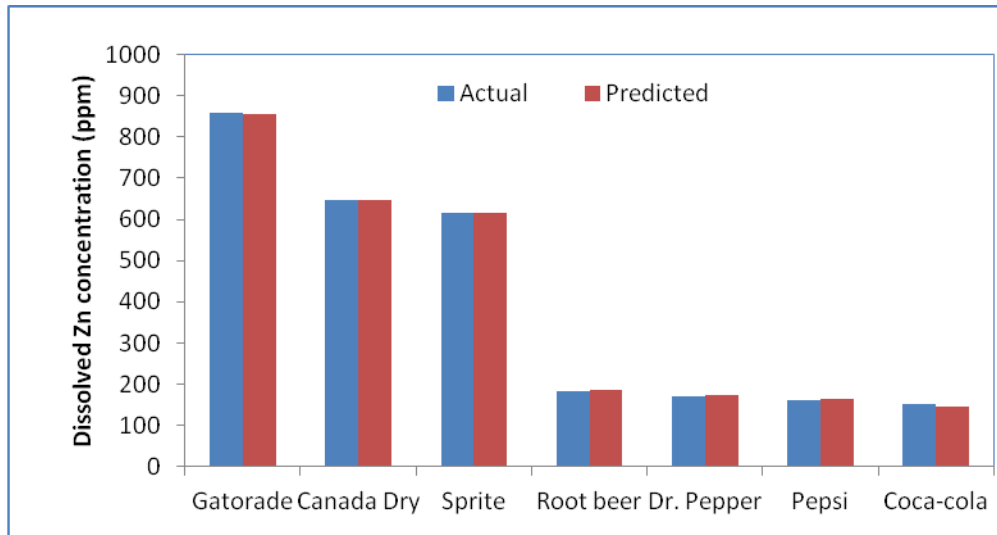


Figure 7.1.9 Comparison of measured and fitted dissolved Zn concentrations after 3 days of immersion.

The relation between the amount of dissolved Zn and the beverage pH or conductivity does not follow any obvious trend (Figures 7.1.5 and 7.1.7). On the other hand, the dissolved zinc concentration appears to increase as the total acidity rises although it remains largely unaffected by the total acidity at lower values. Further discussion on the effect of pH on Zn corrosion is given in section 7.3.

7.2. Open-Circuit Potential Measurements

The evolution of the open-circuit potential measured on zinc electrodes immersed in the various soft drinks was measured for 12 hours. The plots are presented in Figures 7.2.1 and 7.2.2. The open-circuit potential varies similarly with time when zinc is immersed in the soft drinks containing citric acid but no phosphoric acid (i.e., Sprite, Canada Dry and root beer). A rise in potential is observed in the first moments of immersion before shifting and gradually decreasing in the active direction. On the other hand, the OCP values in the soft drinks containing high phosphoric acid levels (i.e., Coca-cola, Pepsi and Dr.Pepper) do not exhibit the rapid rise at the start and instead slowly and monotonically decrease over the course of the immersion. A curve showing the change in the OCP when zinc is immersed in a 500 ppm phosphoric acid solution is also included in Figure 7.2.2 for comparison. The close agreement of this curve with those obtained in the presence of Coca-cola, Pepsi and Dr.Pepper reflects the importance that phosphoric acid plays in the corrosion behaviour of zinc in these beverages. In Gatorade which contains both citric acid and phosphoric acid, the change of OCP is similar to that observed in the phosphoric acid-rich beverages. However, no matters the particular beverage, the change of value in OCP over the 12 hours of immersion remains very small (~ 20-40 mV).

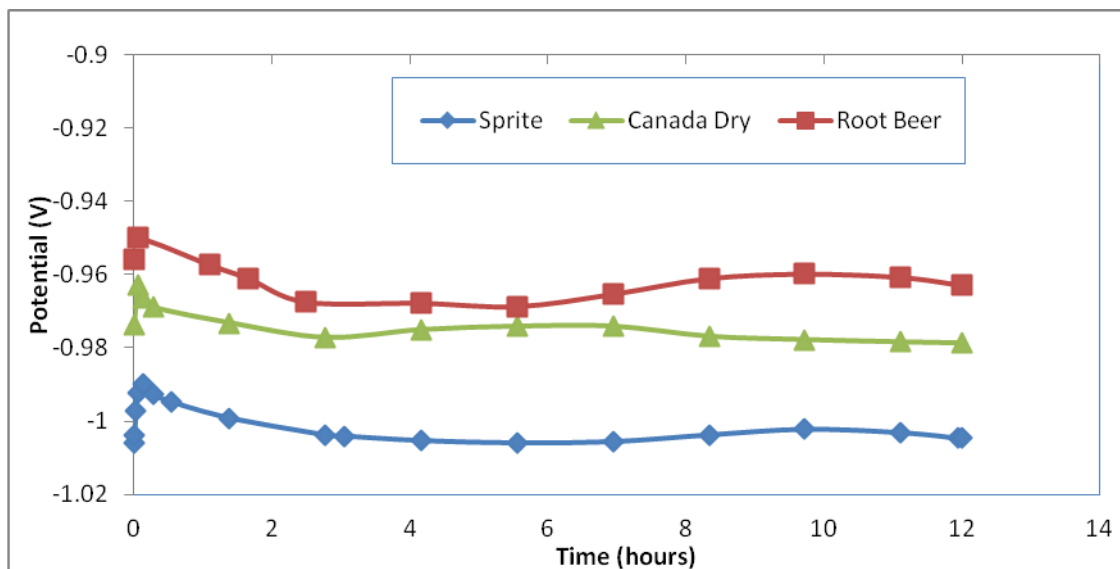


Figure 7.2.1 Variation of open-circuit potential with time for Zn electrodes immersed in Sprite, Canada Dry and root beer.

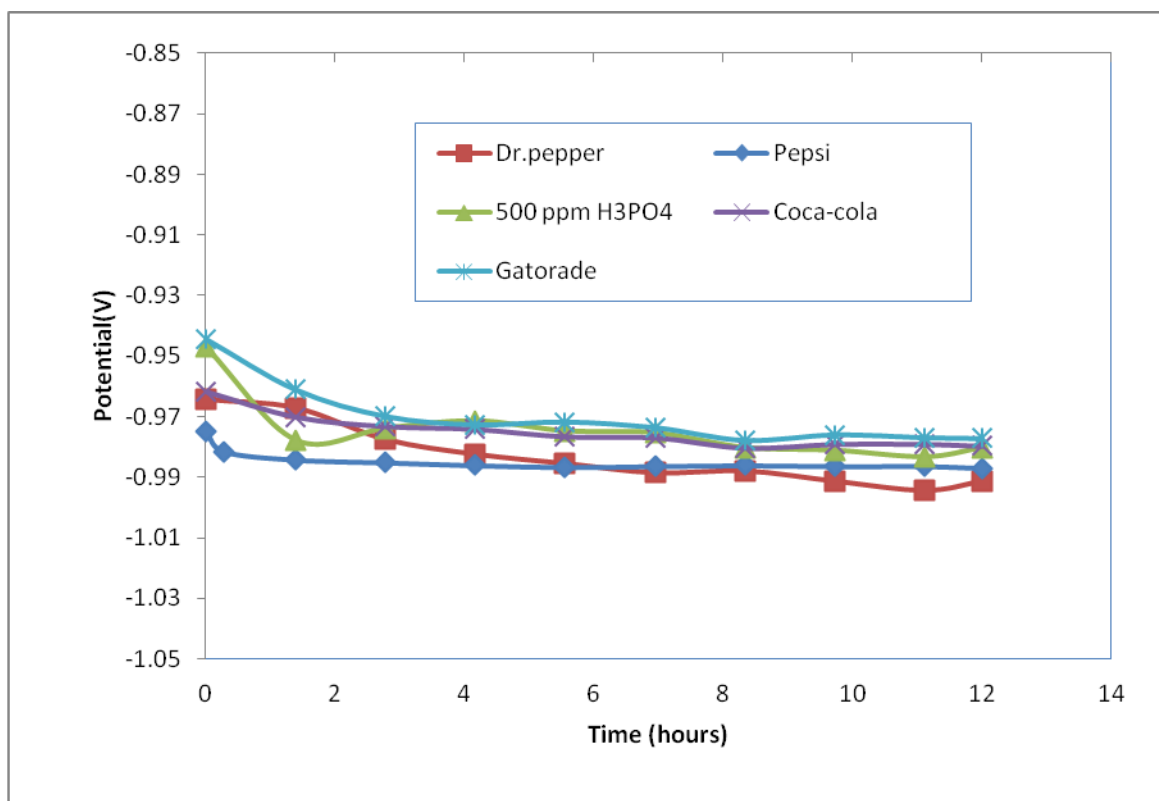


Figure 7.2.2 Variation of open-circuit potential with time for Zn electrodes immersed in 500 ppm phosphoric acid, Pepsi, Coca-cola, Dr. Pepper and Gatorade.

7.3 Tafel Polarization measurements

The Zn electrode was first immersed in a soft drink and maintained at open-circuit conditions for 12 hours in the air. The open-circuit potential was measured over this time. At the end of this period, the Zn electrode was polarized by scanning its potential from -200 mV to 200 mV with respect to the open-circuit potential at a 1mV/s sweep rate. The corresponding current during the scan was recorded to yield the plots of $\log i$ versus potential in Figures 7.3.1 and 7.3.2. With the exception of Gatorade, the polarization curves in the other six soft drinks have similar shapes.

The anodic and cathodic branches are relatively symmetric to each other. The shape of the polarization curve obtained in Gatorade differs from that of the others (Figure 7.3.2). The anodic and cathodic branches are not symmetric to each other and the Tafel lines extrapolated from the high overpotential end of the curves do not intersect at E_{corr} . The cathodic branch exhibits a shorter straight line Tafel region, suggesting a different reaction mechanism may occur in the cathodic region in this beverage. The corrosion kinetic parameters were estimated from these polarization curves by fitting the Butler-Volmer equation ($i = i_{\text{corr}}[e^{2.303\eta/(b_a)} - e^{-2.303\eta/(b_c)}]$) to the experimental data with the aid of the Nova software, similar to the method described in Chapter 6. The corrosion parameters so obtained are listed in Table 7.3.1.

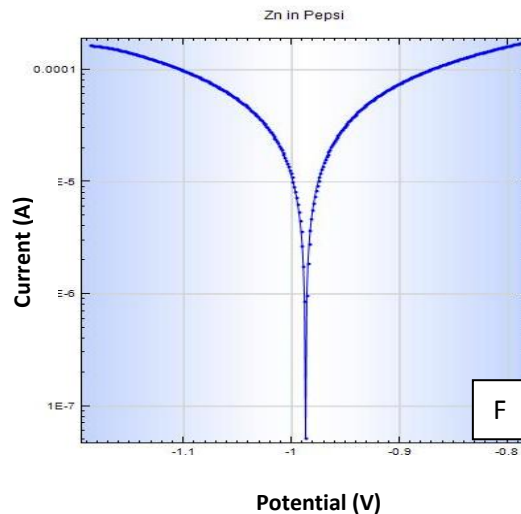
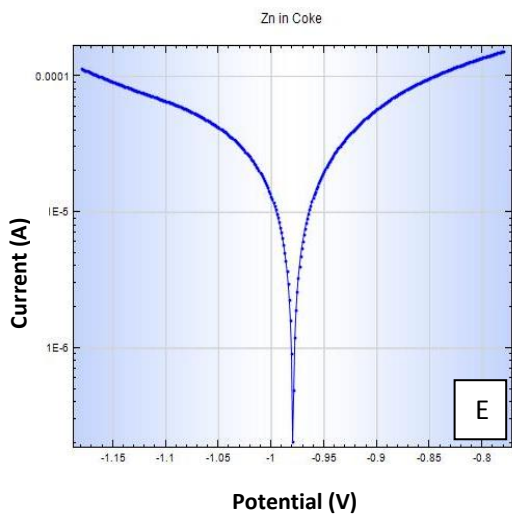
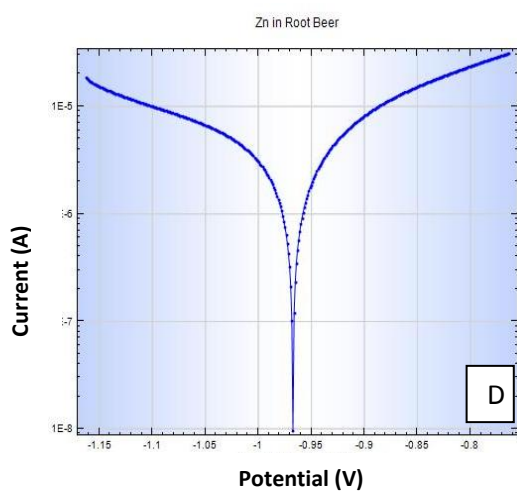
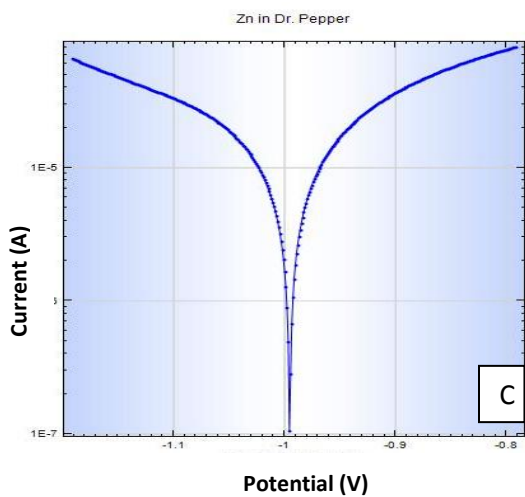
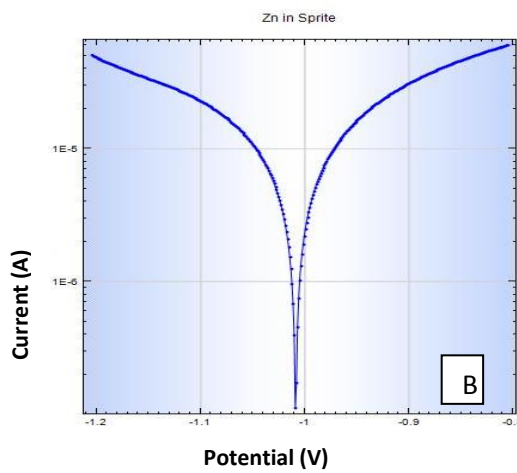
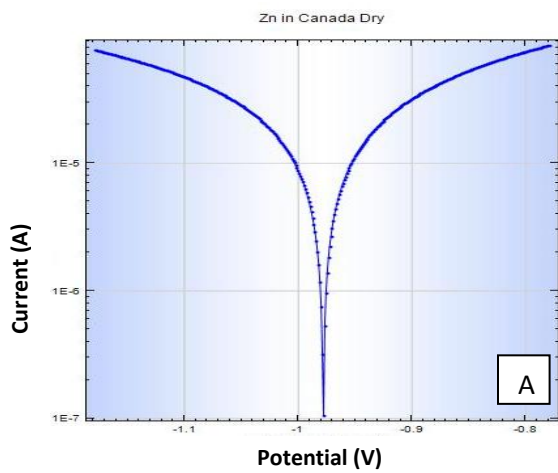


Figure 7.3.1 Tafel polarization curves obtained on Zn electrodes immersed in (A)Canada Dry, (B)Sprite, (C)Dr. Pepper, (D)root beer, (E)Coca-cola and (F)Pepsi.

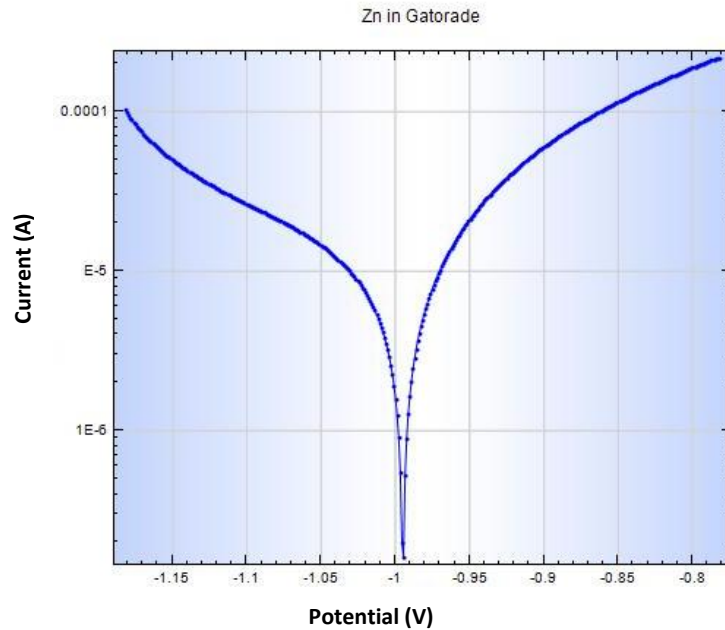


Figure 7.3.2 Tafel polarization curve obtained on a Zn electrode immersed in Gatorade.

Table 7.3.1 Corrosion parameters for Zn electrode immersed in the various soft drinks.

Soft drinks	pH	E _{corr} (V)	i _{corr} (μA/cm ²)	Corrosion rate (mm/year)	Polarization resistance (kΩ)
Coca-cola	2.47	-0.99	570	8.6	1.5
Pepsi	2.48	-0.99	470	7.1	1.2
Canada Dry	2.82	-0.98	330	5	2.5
Dr. Pepper	2.86	-1	190	2.9	2.9
Sprite	3.26	-1	150	2.3	3.8
Root Beer	4.24	-1	89	1.3	10
Gatorade	2.92	-1.1	270	4	2.2

Examination of Table 7.3.1 reveals that the corrosion rate appears to rise as the beverage pH decreases. This trend is also shown graphically in the histogram in Figure 7.3.3. However, an opposite trend compared to immersion test was observed. Zn corrodes faster in Coca-cola and Pepsi than in Canada dry and Sprite. Further discussion on this observation will follow.

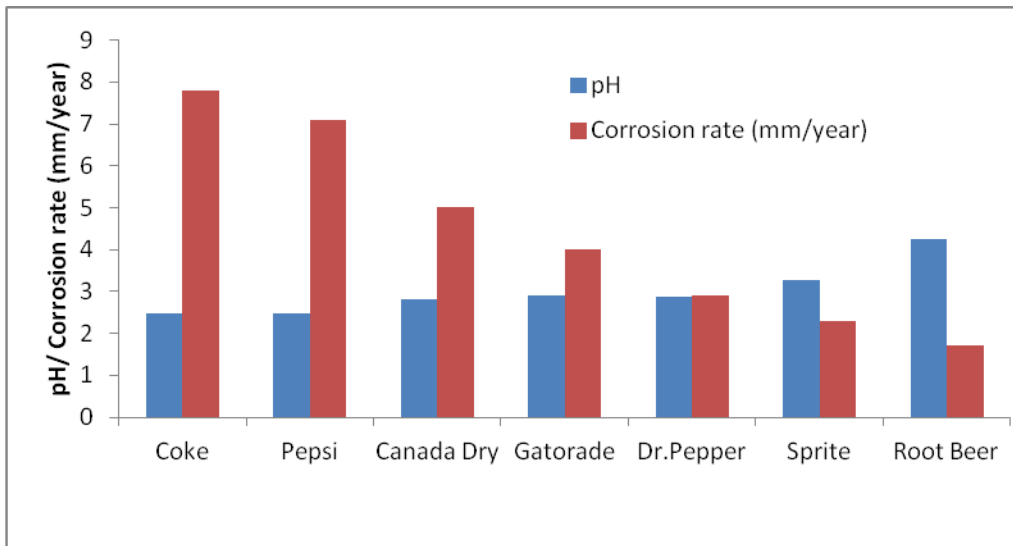


Figure 7.3.3 Histogram comparing the corrosion rate of Zn upon immersion in a soft drink and the beverage pH.

7.4 Anodic Polarization Measurements

To further study the anodic polarization behaviour of the metal, potentiodynamic polarization curves of Zn electrodes were conducted by scanning their potentials from -10 mV to 500 mV relative to the open-circuit potential. A slow scan rate (0.1667 mV/s) was applied to ensure that the electrode response in the active-passive region and the effects of surface film formation^[48-49] could be more accurately captured in the polarization curves according to ASTM guidelines^[50]. Figure 7.4.1 shows the anodic polarization curves obtained in Gatorade, Sprite and Pepsi. The curves in the 3 beverages have similar shapes. The current smoothly and monotonically rises as the anodic overpotential increases with no evidence of passivation or breakdown of a film.

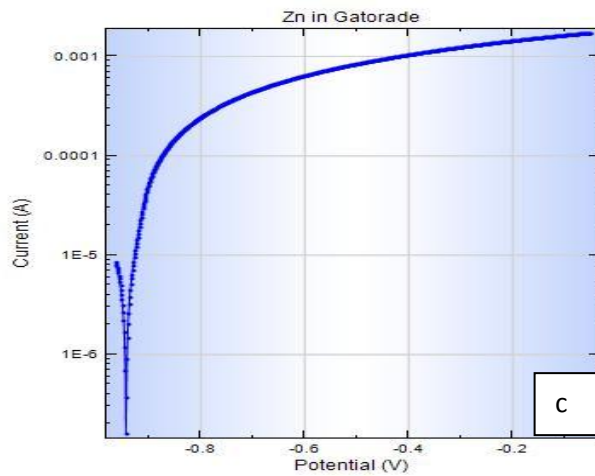
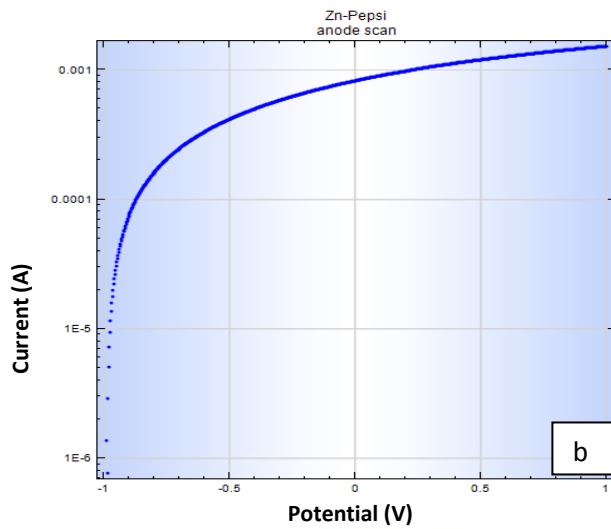
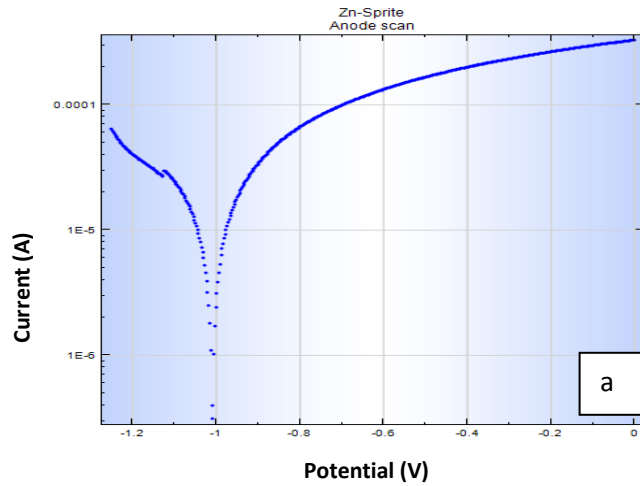


Figure 7.4.1 Anodic polarization curves obtained on Zn electrodes immersed in (a) Sprite (b) Pepsi and (c) Gatorade

SEM examination of the Zn surfaces after the anodic scans were complete showed that uniform corrosion occurred in all of the soft drinks. Representative SEM images and EDX spectra after anodic scans in Pepsi (phosphoric acid-rich), Sprite (citric acid-rich) and Gatorade (rich in both phosphoric acid and citric acid) are shown in Figures 7.4.2 – 7.4.4. The image of the Zn electrode after exposure to Pepsi shows that the presence of patches of a coating ranging in size from a few microns to about 50 microns over the surface (Figure 7.4.2). Some of the larger patches appeared to have formed by the merging of smaller ones. EDX analysis of one of these patches reveals the presence of phosphorus, oxygen and zinc, suggesting that they are made up of a Zn-phosphate complex. When the Zn electrodes are immersed in Sprite and Gatorade, very similar surfaces are obtained (Figures 7.4.3 and 7.4.4). They show evidence of the relatively uniform removal of metal, leaving behind a roughened surface. EDX analysis of the sample that had been immersed in Sprite reveals a remarkably clean Zn surface with only trace amounts of oxygen present (Figure 7.4.3). The spectrum of the sample exposed to Gatorade is also relatively clean and displays only small carbon, oxygen and copper peaks in addition to those of zinc (Figure 7.4.4).

These phenomena reveal differences in the dissolution of the zinc surface in the presence of either citric acid or phosphoric acid. When enough time is provided, the formation of a Zn-phosphate complex film on the metal surface presumably occurs and can inhibit further metal dissolution. Zn-citrate complexes are more soluble and so can quickly dissolve from the metal surface and diffuse into the bulk solution. These trends agree with those obtained from Zn immersion tests, but not from analysis of the polarization curves, as will be discussed in the following section.

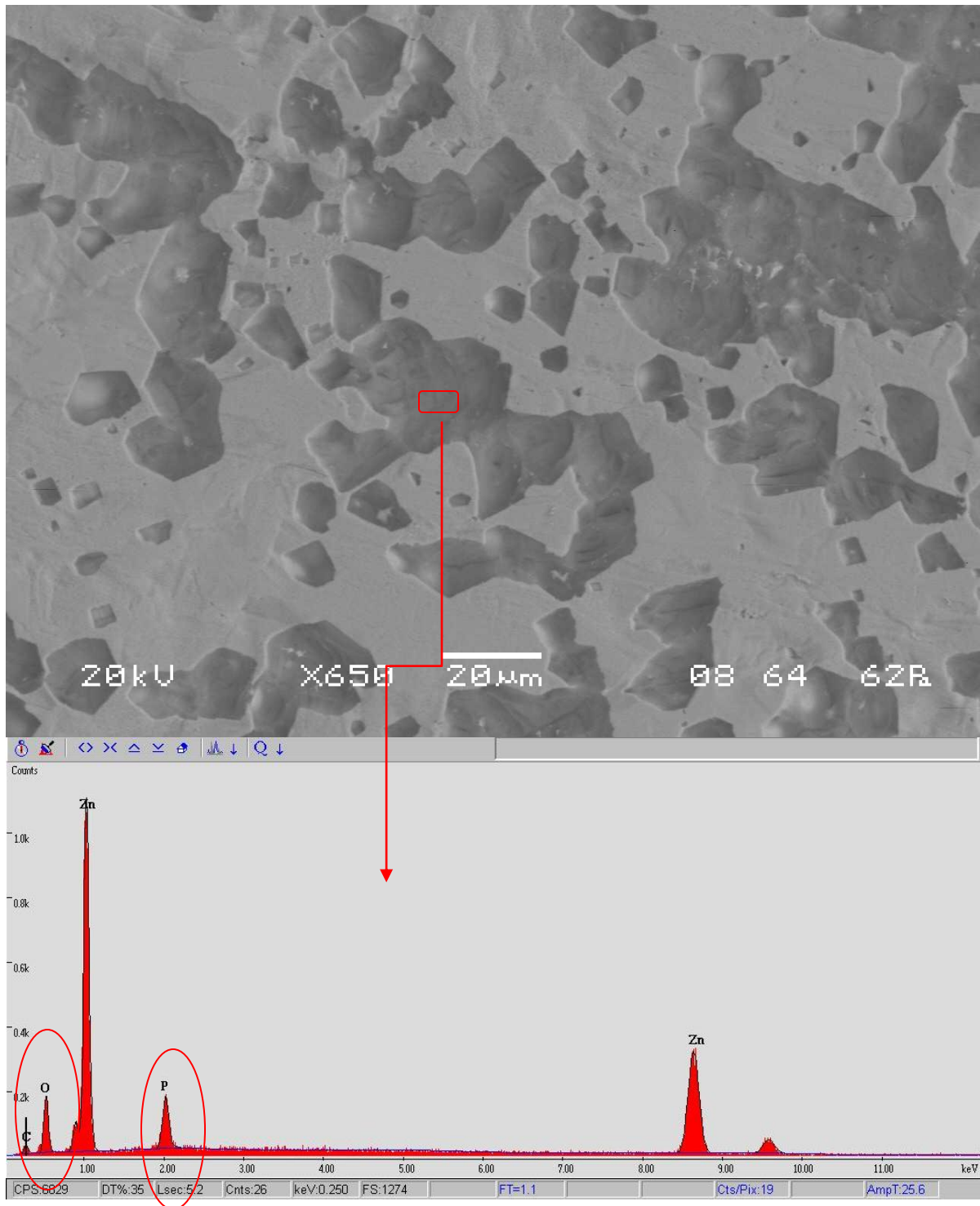


Figure 7.4.2 SEM image of Zn electrode after anodic polarization while immersed in Pepsi and EDX spectrum of the indicated rectangular region on surface.

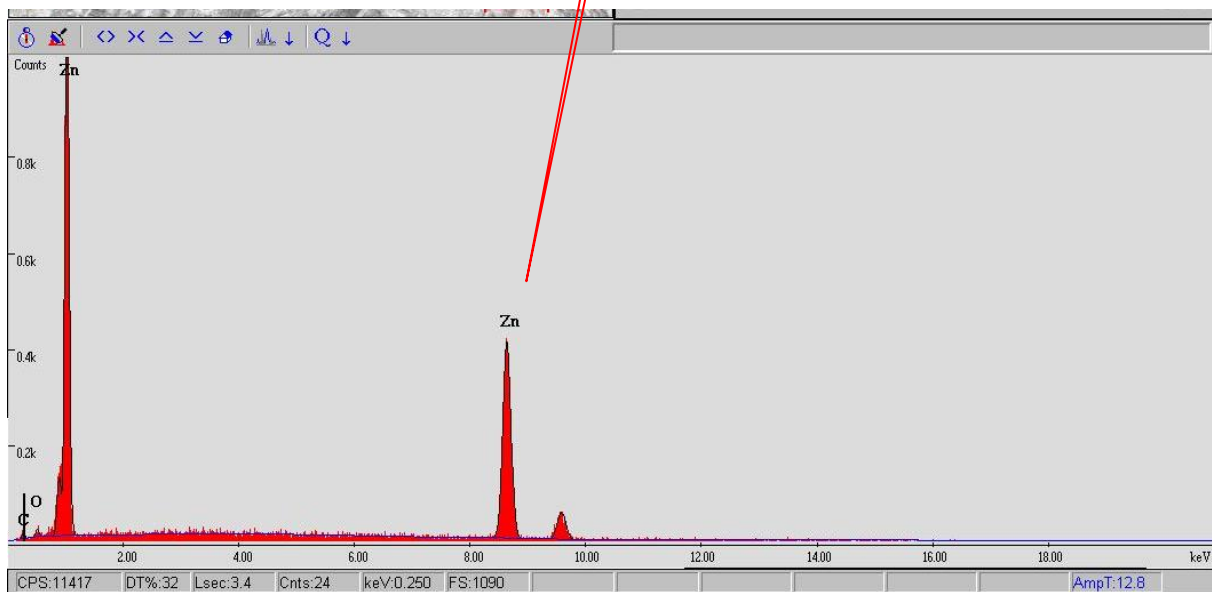
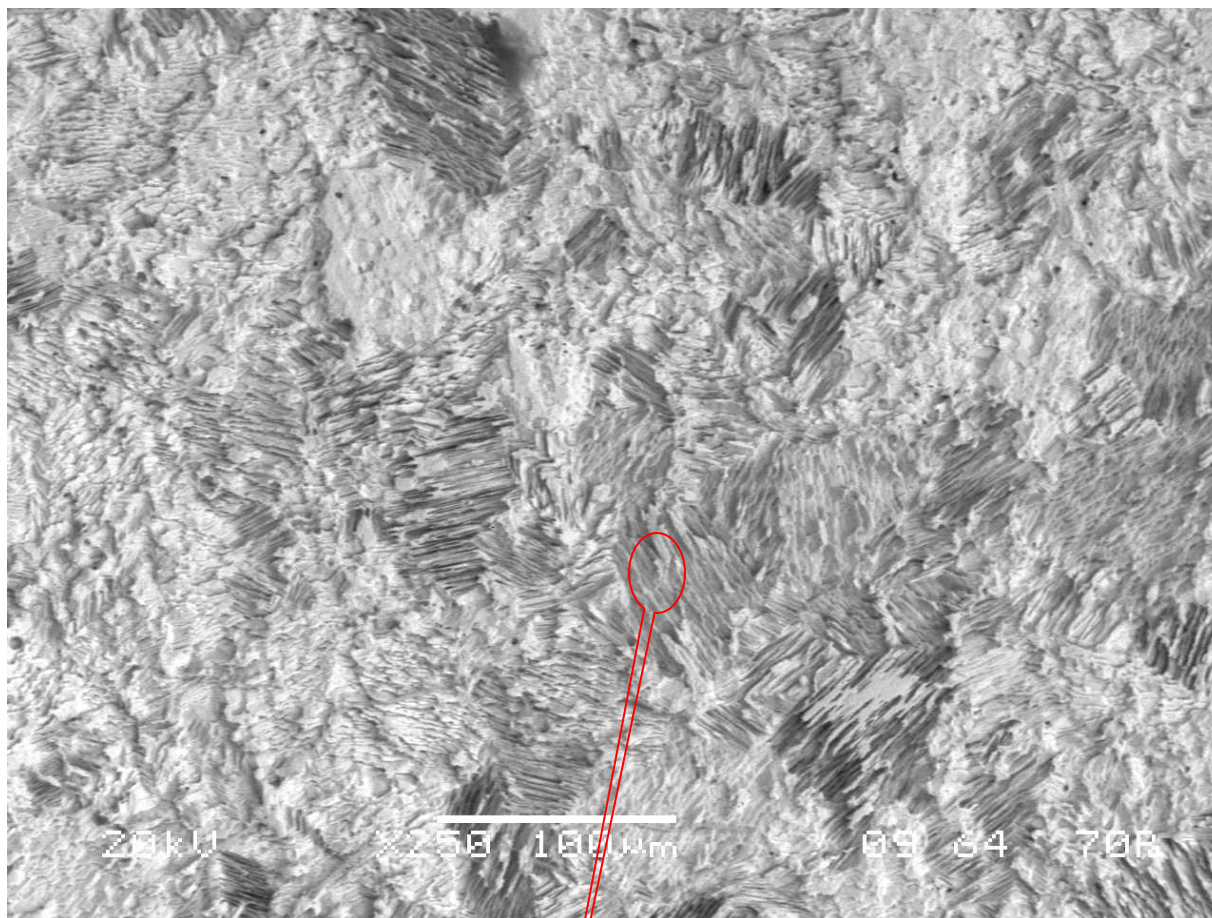


Figure 7.4.3 SEM image of Zn electrode after anodic polarization while immersed in Sprite and EDX spectrum of the indicated region on surface.

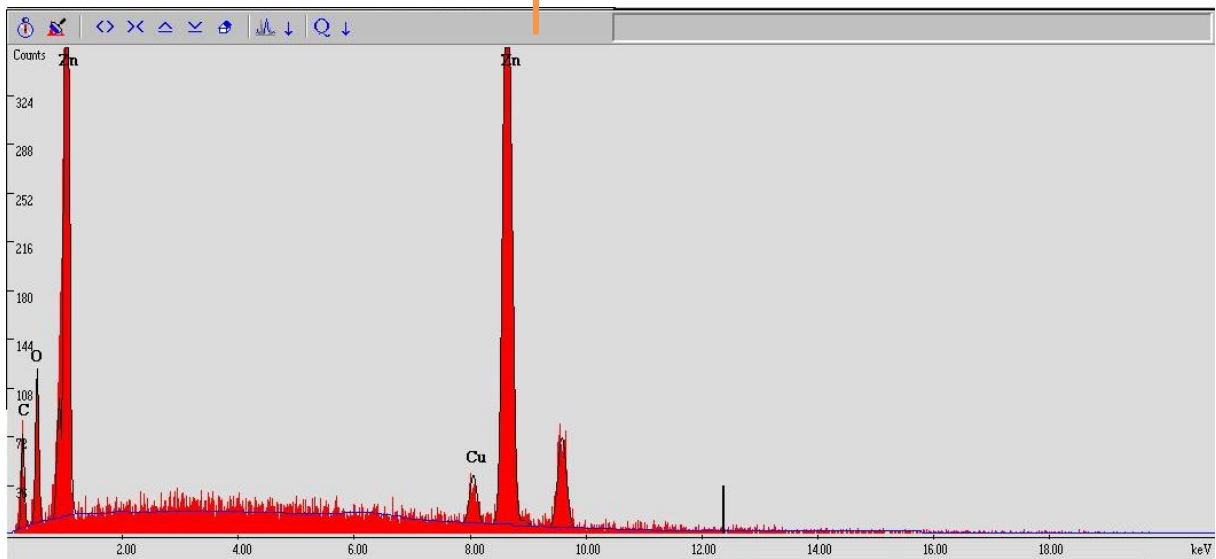
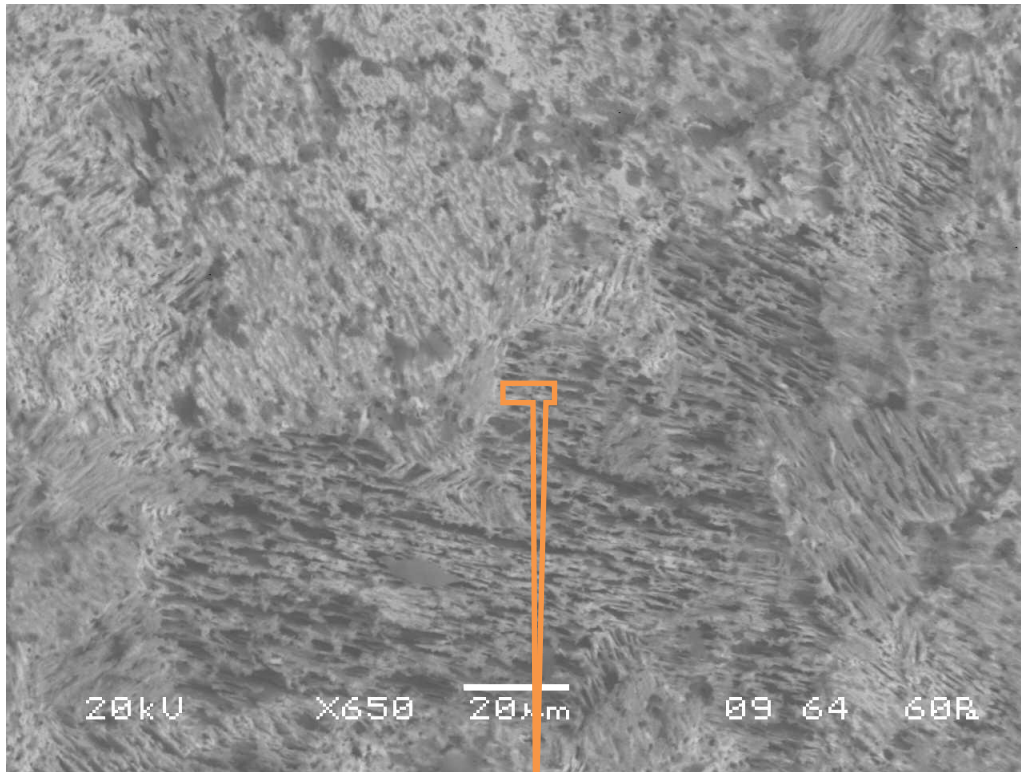


Figure 7.4.4 SEM image of Zn electrode after anodic polarization while immersed in Gatorade and EDX spectrum of the indicated region on surface.

7.5. Comparison between Two Different Corrosion Measurements

Table 7.5.1 and Figure 7.5.1 present a comparison of the dissolved Zn concentrations measured after 1 day and 3 days of immersion and the corrosion rates as determined by analysis of the Tafel polarization curves. No agreement is evident in the trends in the data obtained from these two sets of analysis. This discrepancy may be related to the different durations of the polarization experiments and the immersion experiments. Not enough time may be allowed during the polarization experiments for Zn-phosphate films to form on the metal surface to the same extent as they can during the immersion experiments. Less passivation of the surface would then occur during the polarization experiments. This would lead to much higher corrosion rates being estimated from the polarization experiments than from the immersion experiments in the case of Pepsi and Coca-cola, as observed in the data in Table 7.5.1. Obviously, further research is required to assess the validity of this explanation.

Table 7.5.1 Comparison of dissolved Zn concentrations obtained after 1 and 3 days immersion and corrosion rates determined by Tafel analysis.

	Dissolved Zn concentration (ppm)		Corrosion rate (mm/year)
	1 day	3 days	
Gatorade	784	860.5	4
Canada Dry	512	647.5	5
Sprite	476	615.5	2.3
Root Beer	140	184.5	1.7
Dr. Pepper	110	171.5	2.9
Pepsi	108	160.5	7.1
Coca-cola	95	153.5	7.8

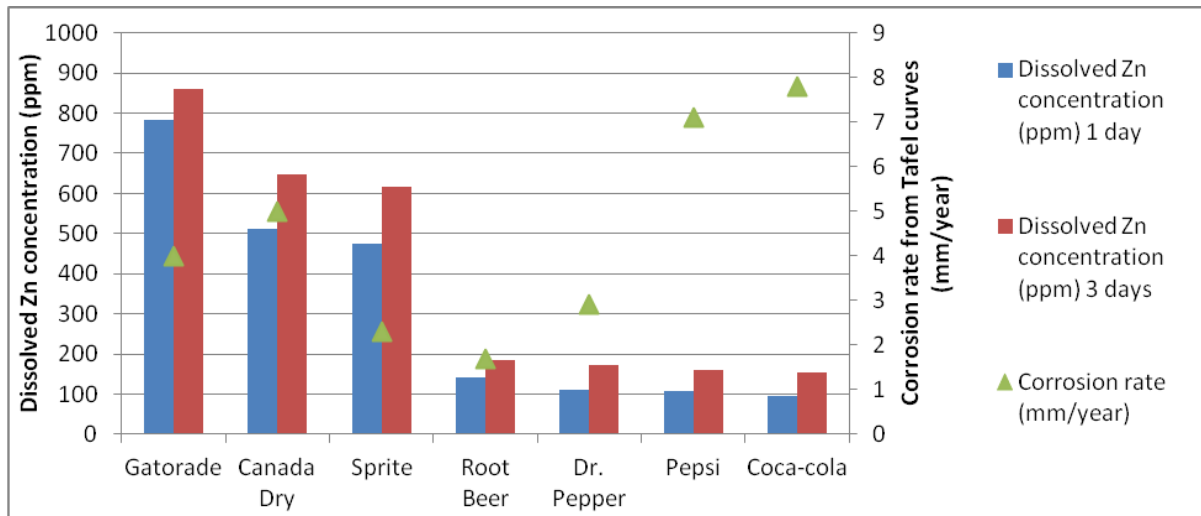


Figure 7.5.1 Comparison of dissolved Zn concentrations after immersion in the various soft drinks and corrosion rates determined from the polarization experiments.

7.6 Summary

In this chapter, the Tafel extrapolation technique and chemical analysis were applied to evaluate Zn corrosion rate in 7 soft drinks. The effects of phosphoric acid, citric acid and pH on the corrosion behaviour were also investigated. The results are summarized as follows:

1. The immersion tests reveal that the corrosion of Zn in 7 soft drinks strongly depends on the type of acid present in the drinks. Phosphoric acid and citric acid act as an inhibitor and promoter, respectively, during zinc dissolution. Relatively small amounts of Zn dissolve when immersed in phosphoric acid-rich soft drinks, whereas much more zinc dissolves when exposed to beverages rich in citric acid. SEM examination indicates that the relatively low amounts of zinc that dissolve in the presence of phosphoric acid-rich soft drinks may be due to the formation of a protective zinc phosphate coating on the metal surface.

2. The order in which the various beverages affect the dissolved Zn concentrations after 1 day of immersion is the same as that obtained after 3 days of immersion.
3. Examination of the samples after immersion testing and Tafel polarization measurements show that they were attacked uniformly in all test beverages.
4. An empirical polynomial expression relating the dissolved Zn concentration obtained after immersion in the 7 soft drinks to the phosphoric acid and citric acid content of these beverages is found to fit the experimental data extremely well. This reflects that Zn corrosion in these soft drinks is controlled predominantly by phosphoric acid and citric acid.
5. The order in which the beverages affect the corrosion rate as determined by Tafel extrapolation of polarisation curves shows the different trend from that obtained from measurement of the dissolved Zn concentration after immersion in these drinks.
6. Tafel extrapolation of the data from polarisation curves shows that the beverage pH has a significant effect on zinc corrosion rates instead of the acid kinds in immersion test.
7. No correlation is found between the corrosion potential and corrosion rate obtained by analysis of the polarization curves.
8. Anodic polarization measurements show none of the telltale signs of passivation or pitting during the oxidation of zinc.

Chapter 8

Results and Discussion-Corrosion Behaviour of Copper

Copper has the second highest electrical conductivity of any element behind silver and so is widely used in the electronics industry. For example, conducting layers in printed circuit board conducting layers are made of thin copper foil. In this chapter, immersion experiments and electrochemical techniques are used to study the corrosion of Cu in 16 commercial beverages.

8.1 Immersion Tests

The beverages used in the immersion tests are listed in Chapter 4 and the experimental procedures are described in Chapter 5. Tests which were carried out in triplicate involved immersing copper samples in the beverages for 1, 3, 5 and 7 days at 40 °C in the oven. After completion of the tests, the beverages were diluted 10 or 100 times using Milli-Q water with 2% nitric acid added and the dissolved copper concentration was measured using ICP-OES.

The concentrations obtained in the 16 beverages are listed in Table 8.1.1, while plots showing the effect of immersion time on the average dissolved concentration are presented in Figures 8.1.1 – 8.1.3. It was found that the variation of dissolved copper concentration with time follows two types of behaviour depending on the beverage. Figure 8.1.1 and 8.1.2 shows those cases where the dissolved copper concentrations rises slowly at the outset before increasing more quickly after about 3 days of immersion and finally leveling off after about 5 days. This behaviour is observed in all of the test beverages except hot chocolate, coffee and apple juice. As

shown in Figure 8.1.3, the dissolved Cu concentration increases only slightly during the first 5 days but then rises rapidly thereafter when copper is immersed in hot chocolate, coffee and apple juice.

Table 8.1.1 Dissolved Cu concentrations (ppm) obtained after 1, 3, 5 and 7 days of immersion in the test beverages.

	1 day	3 days	5 days	7 days
Apple juice	1.5±0.04	4.9±1.13	17.9±7.84	48.3±9.36
Hot chocolate	6.0±0.87	17.3±0.53	25.8±6.14	188.0±20.95
Coffee	6.6±0.23	10.9±1.71	33.6±2.47	170.7±32.39
Beer	14.5±2.02	25.7±1.46	68.1±16.89	41.6±10.29
Milk	15.2±0.35	25.1±8.57	56.0±34.76	26.1±10.83
Orange juice	20.1±2.69	43.8±0.64	109.3±24.44	120.1±46.00
Wine	28.4±3.50	71.1±0.68	128.3±22.50	111.3±1.15
Tomato juice	32.5±4.00	44.0±2.00	170.0±32.60	218.0±52.89
Dr. Pepper	46.5±5.74	129.0±11.14	305.5±65.76	358.5±31.79
Coca-cola	52.2±3.72	150.0±7.00	400.0±30.81	443.0±27.62
Canada Dry	61.5±10.97	157.5±3.54	398.7±11.59	464.0±68.79
Sprite	62.1±3.38	129.0±19.08	479.5±9.19	608.3±69.30
Pepsi	64.4±5.13	143.0±17.06	416.3±65.61	502.5±65.8
Root beer	74.0±8.67	109.9±29.98	301.3±24.50	404.3±42.55
Tea	80.6±26.98	134.0±4.00	388.3±25.54	349.7±33.56
Gatorade	161.3±12.90	338.3±32.32	1,015.0±103.32	1,205.3±105.51

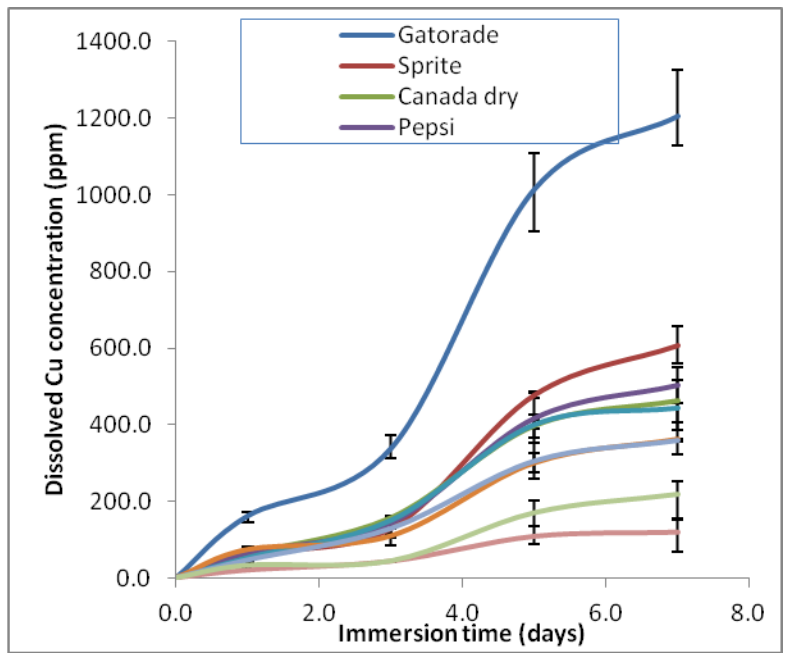


Figure 8.1.1 Variation of dissolved copper concentration with immersion time in 7 soft drinks, orange juice and tomato juice.

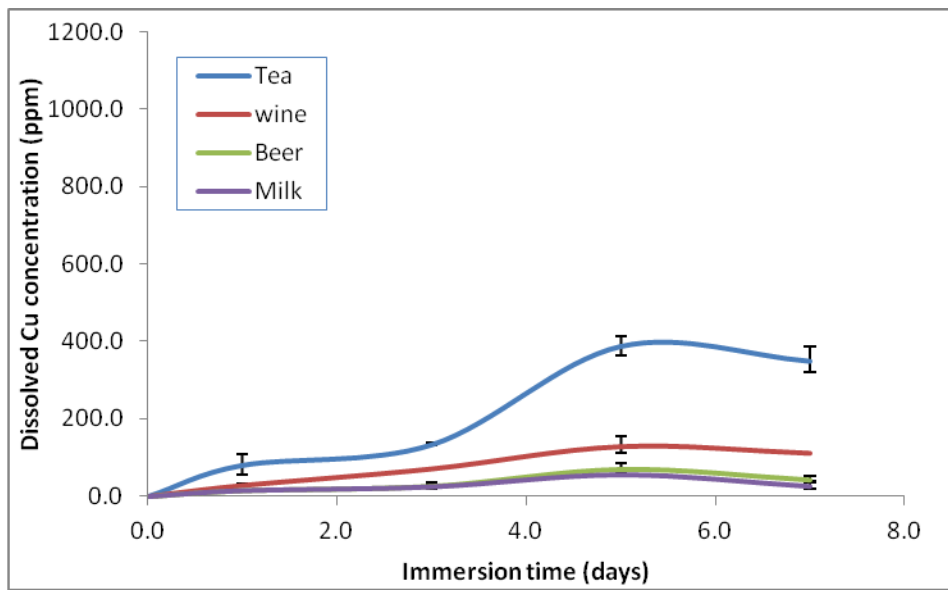


Figure 8.1.2 Variation of dissolved copper concentration with immersion time in wine, beer, milk and tea.

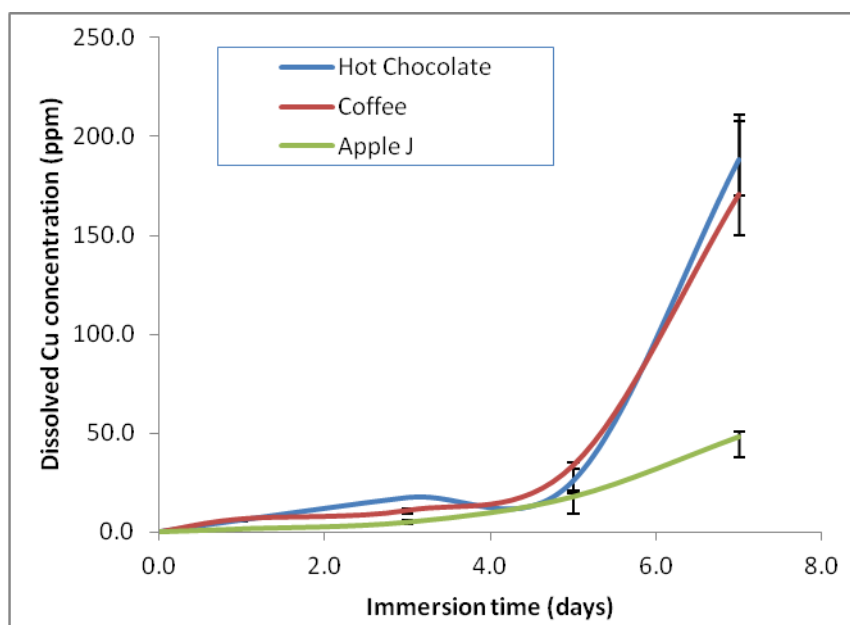


Figure 8.1.3 Variation of dissolved copper concentration with immersion time in coffee, hot chocolate and apple juice.

An important conclusion that can be drawn from these immersion experiments is that the longer term corrosion rates in some of the beverages are not well predicted on the basis of short term 1-day immersion tests. This is due to the fact that their corrosion rates vary significantly over the course of the immersion time. The average corrosion rates can be estimated from the slopes of the curves in Figures 8.1.1–8.1.3. Figure 8.1.4 shows the variation in the corrosion rates (expressed in units of $\text{mg}/\text{cm}^2 \cdot \text{day}$) obtained over the immersion period for all of the beverages. It should be acknowledged that errors likely arise in determining corrosion rates in this way. Nevertheless, with a few exceptions, the dissolution rates are quite variable, both rising and falling at different times. It is interesting to note that apple juice is the only beverage in which the rate increases monotonically.

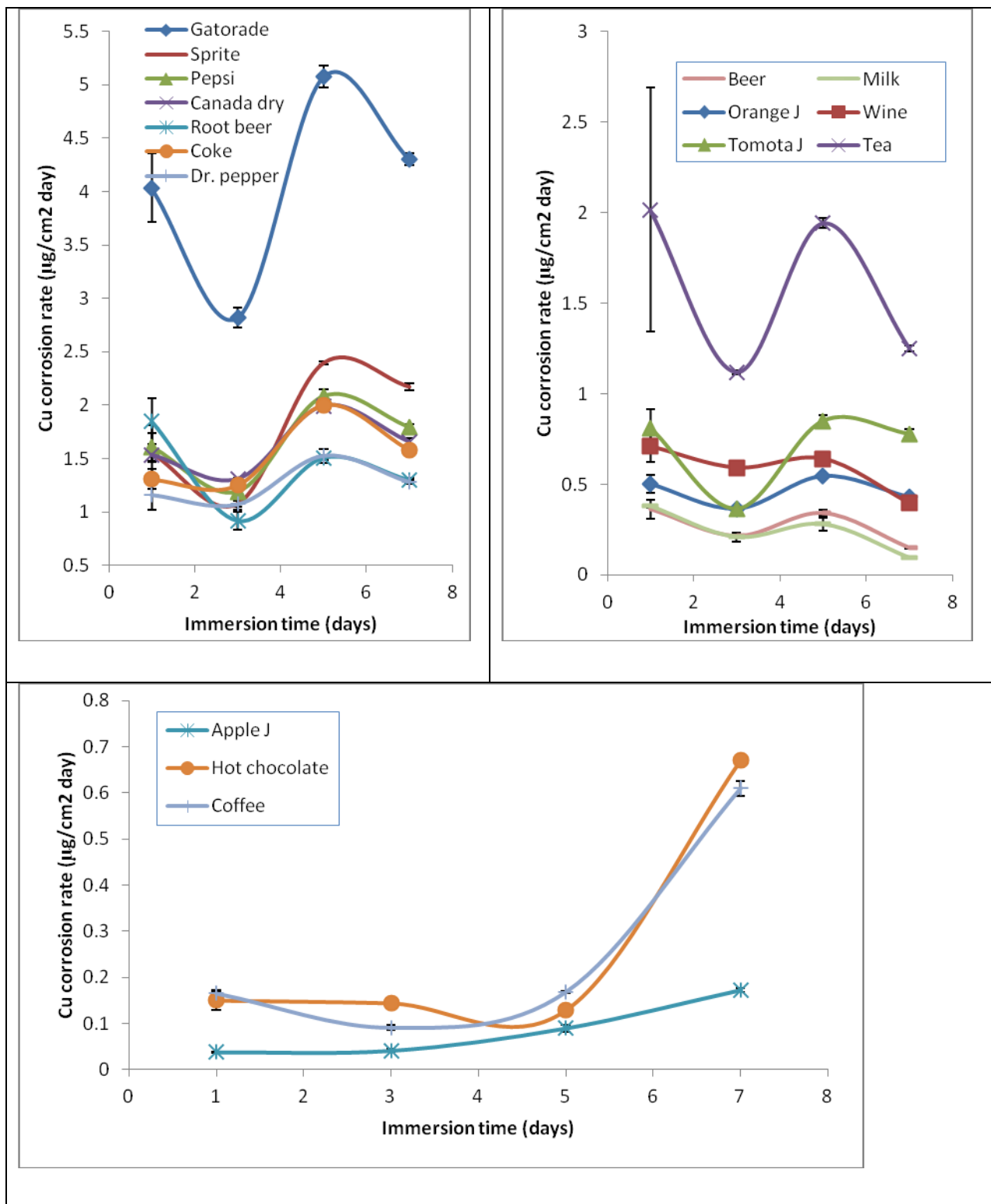


Figure 8.1.4 Variation of copper dissolution rate with immersion time in the test beverages.

The dissolved copper concentrations after 1, 3, 5 and 7 days of immersion are plotted versus the beverage pH in Figure 8.1.5 in order to determine whether a correlation exists between these quantities. Although a few outliers exist (i.e., Gatorade, tea and root beer), a decrease in the beverage pH leads to a rise in the dissolved copper concentration. Although not included here, no strong correlation between the copper concentration and the beverage conductivity or titratable acidity was found.

The effect of pH was investigated more closely by measuring the corrosion of copper after 3 days immersion in a synthetic solution containing 500 ppm NaCl, 500 ppm citric acid and 500 ppm phosphoric acid, which are the main ingredients in many of the beverages. NaOH was added to adjust the pH value without changing any of the other components. As shown below, the corrosion rate of copper was found to decrease as the pH rises from 2 to 4, but then stabilize with a further pH increase from 4 to 6 (Figure 8.1.6). This suggests that the dissolution behaviour in this solution differs at pH below 4 from that above pH 4. Again, a similar trend is observed when copper is immersed in the beverages (Figure 8.1.5). This supports the idea that H^+ plays a significant role in copper corrosion. However, two notable exceptions to the general trend with respect to pH are tea and root beer in which much more copper dissolution than would be expected based on their pH alone is observed. It is not obvious from the chemical compositions of tea and root beer as to why they are outliers (Table 6.1.2). Tea stands out among the beverages in this study by containing a very low level of each of H^+ , citric acid, phosphoric acid and Cl^- . Similarly, the concentration of each of these components in root beer is also relatively low. Thus, it is likely that other constituents can play an important role in copper dissolution. Examination of the composition of inorganic ions (Table 4.2.1) and other organic acids (Table 4.4.1) in these

beverages shows that they do not contain unusually low or high levels of these species except perhaps 502 ppm benzoic acid in root beer. It is possible that some other component(s) not analyzed in this study contributes significantly to copper corrosion. Further research on this topic is warranted.

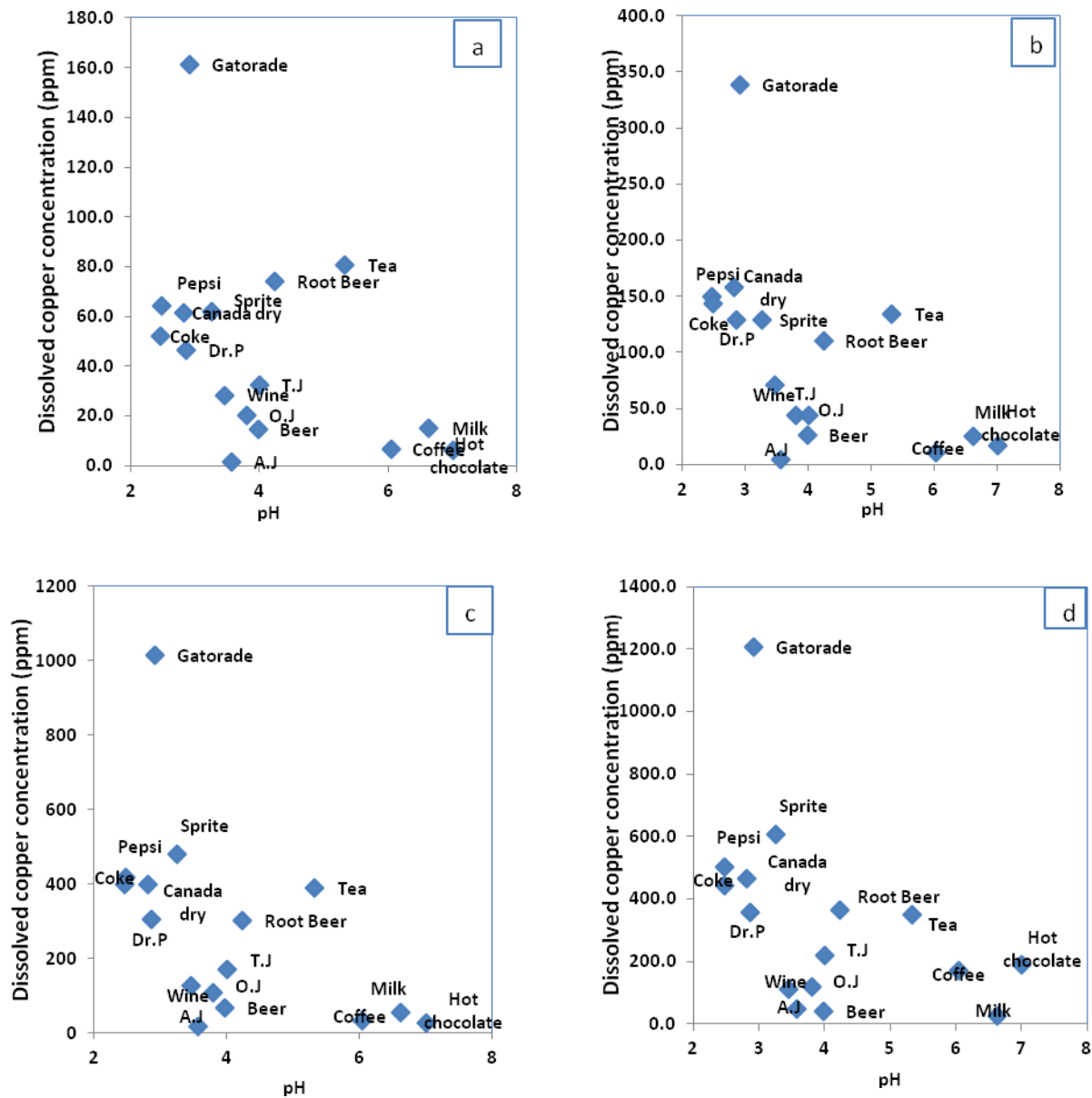


Figure 8.1.5 Dissolved copper concentration after immersion of (a) 1 (b) 3 (c) 5 and (d) 7 days as a function of the beverage pH.

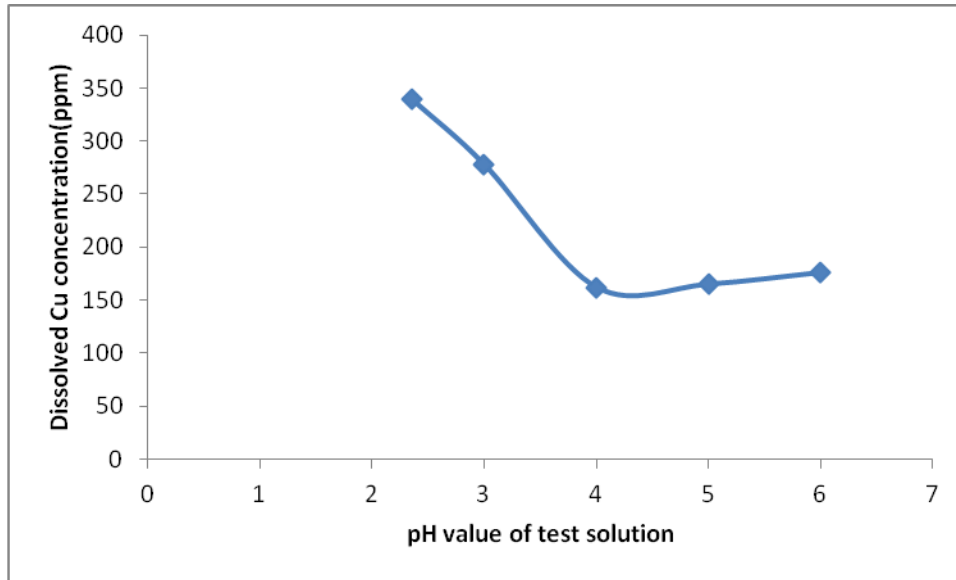


Figure 8.1.6 Effect of pH on dissolved copper concentration in solutions containing 500 ppm NaCl, 500 ppm citric acid and 500 ppm phosphoric acid.

Another implication of the results in this synthetic solution and from the beverages themselves is that a complex interaction between some of the constituents likely occurs during copper dissolution. In order to investigate this aspect further, we conducted a series of experiments to examine the effect of citric acid concentration in a synthetic solution in the presence and absence of NaCl. Figure 8.1.7 compares the effect of citric acid on the corrosion rate when 500 ppm NaCl is present and when none has been added. The addition of NaCl has a significant effect and more than doubles the corrosion rate. It is also interesting to note that the corrosion rate becomes essentially independent of the citric acid concentration above about 1000 ppm regardless whether or not NaCl is present.

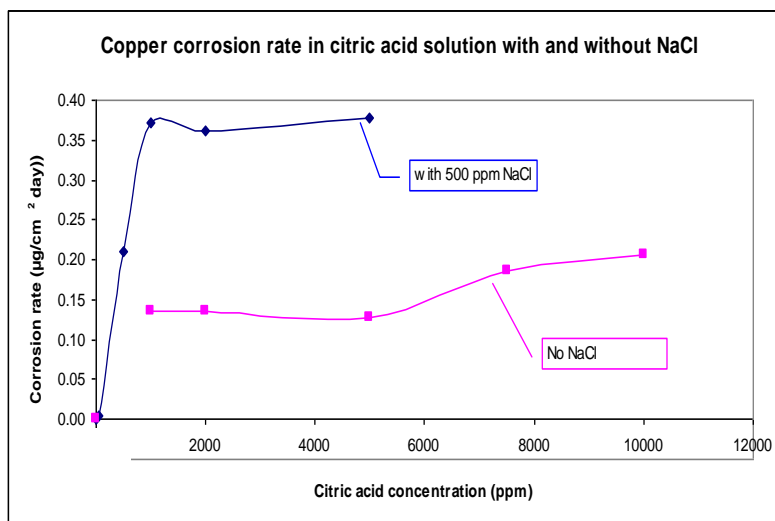


Figure 8.1.7 Effect of citric acid on copper corrosion rate ($\mu\text{g cm}^{-2} \text{ day}$) in the absence and presence of 500 ppm NaCl.

The effects of citric, ortho-phosphoric and malic acids alone at concentrations of 1000, 2000 and 5000 ppm on the dissolution of copper were evaluated in separate experiments. The dissolved copper concentrations after three days of immersion in each of the three acids are listed in Table 8.1.2. These data are shown graphically in Figure 8.1.8. Each of these acids appears to have a different effect on copper corrosion. The amount of copper that dissolves does not depend on the citric acid concentration between 1000 ppm to 5000 ppm, consistent with the results in Figure 8.1.7. On the other hand, phosphoric acid appears to increase the corrosion rate, although the effect is not dramatic. Malic acid appears to have a more complicated effect by enhancing the corrosion rate as its concentration increases up to about 2000 ppm, but then having the opposite effect as anymore is added. However, given the wide range of acid concentrations used in these experiments, the effects evident in Figure 8.1.8 are not large and certainly smaller than the range of solubilities obtained after 3 days immersion in the commercial beverages (Table 8.1.1). Thus,

it is difficult to assess the individual roles of each of these components on copper corrosion when present together with all the other components in the test beverages

Table 8.1.2 Dissolved Cu concentration (ppm) after 3 days immersion in synthetic solutions containing citric acid, phosphoric acid and malic acid.

Acid concentration (ppm)	Copper concentration after 3 days immersion (ppm)		
	Citric acid	Phosphoric acid	Malic acid
1000	163	192	206
2000	162	206	235
5000	162	220	179

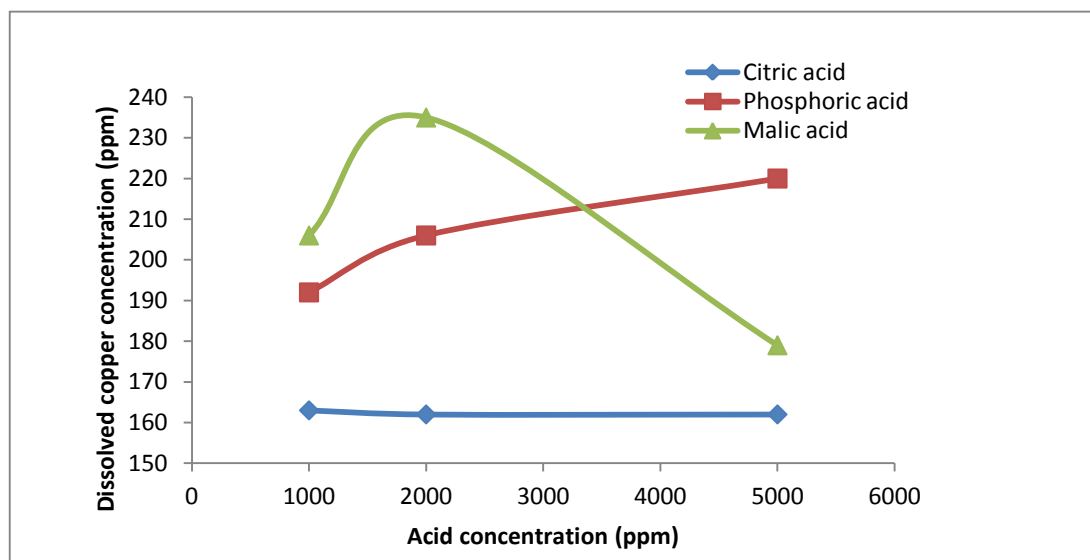


Figure 8.1.8 Effect of the concentrations of citric acid, phosphoric acid and malic acid on dissolved copper concentration.

SEM examination of the Cu surfaces after the immersion test showed that uniform corrosion occurred in all of the drinks. Representative SEM images and EDX spectra in Pepsi (phosphoric acid-rich), Canada dry (citric acid-rich) and Gatorade (rich in both phosphoric acid and citric acid) are shown in Figures 8.1.9-8.1.11. The copper surface remains relatively clean after

immersion in Pepsi and Canada Dry with no evidence of any insoluble film was found on the copper surface. The image of the metal after immersion in Gatorade shows the presence of crystals over its surface (Figure 8.1.11). EDX analysis of the crystals reveals that they contain chlorine and copper with only trace amounts of carbon and oxygen, indicating that they consist of some sort of copper chloride compound.

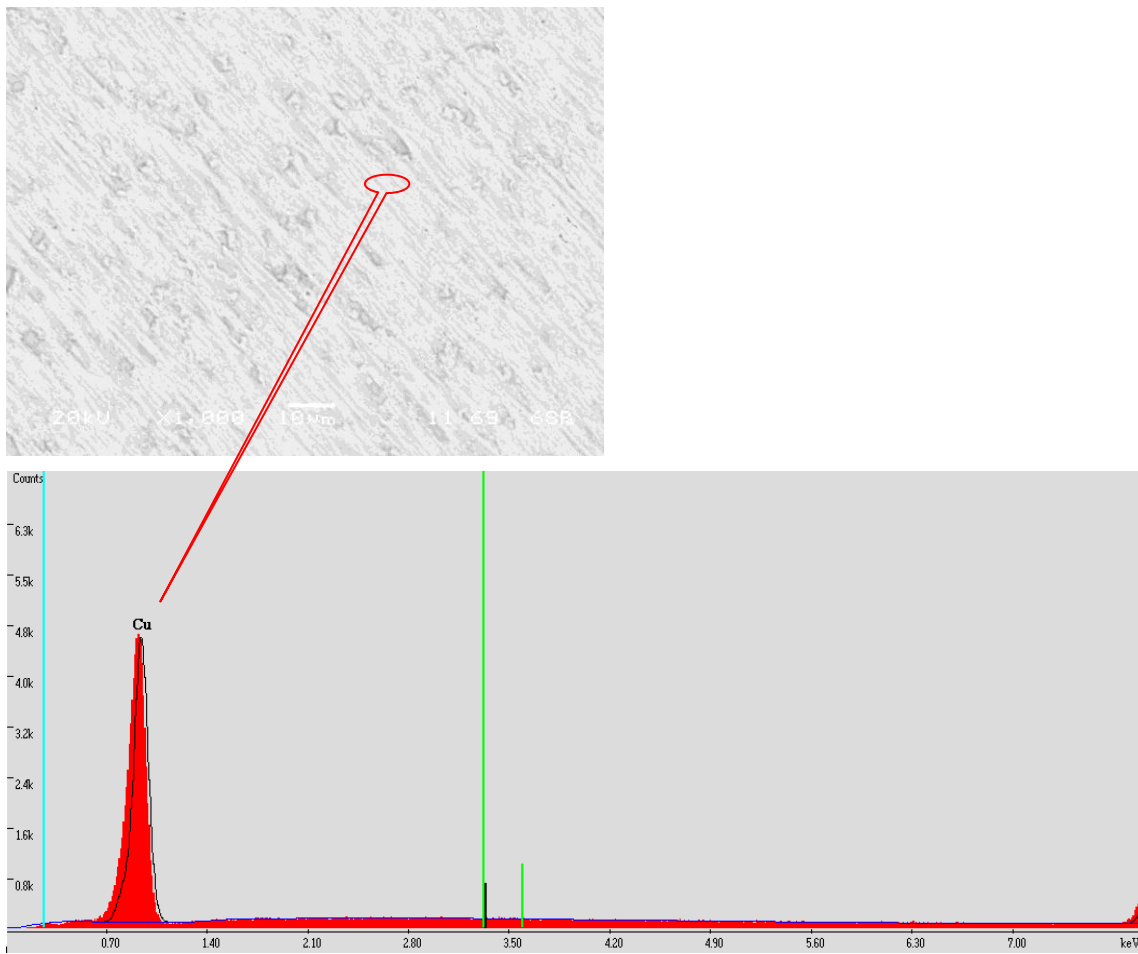


Figure 8.1.9 SEM image of copper at 1000X after 5 days immersion test in Canada Dry and EDX spectrum of the indicated region on surface.

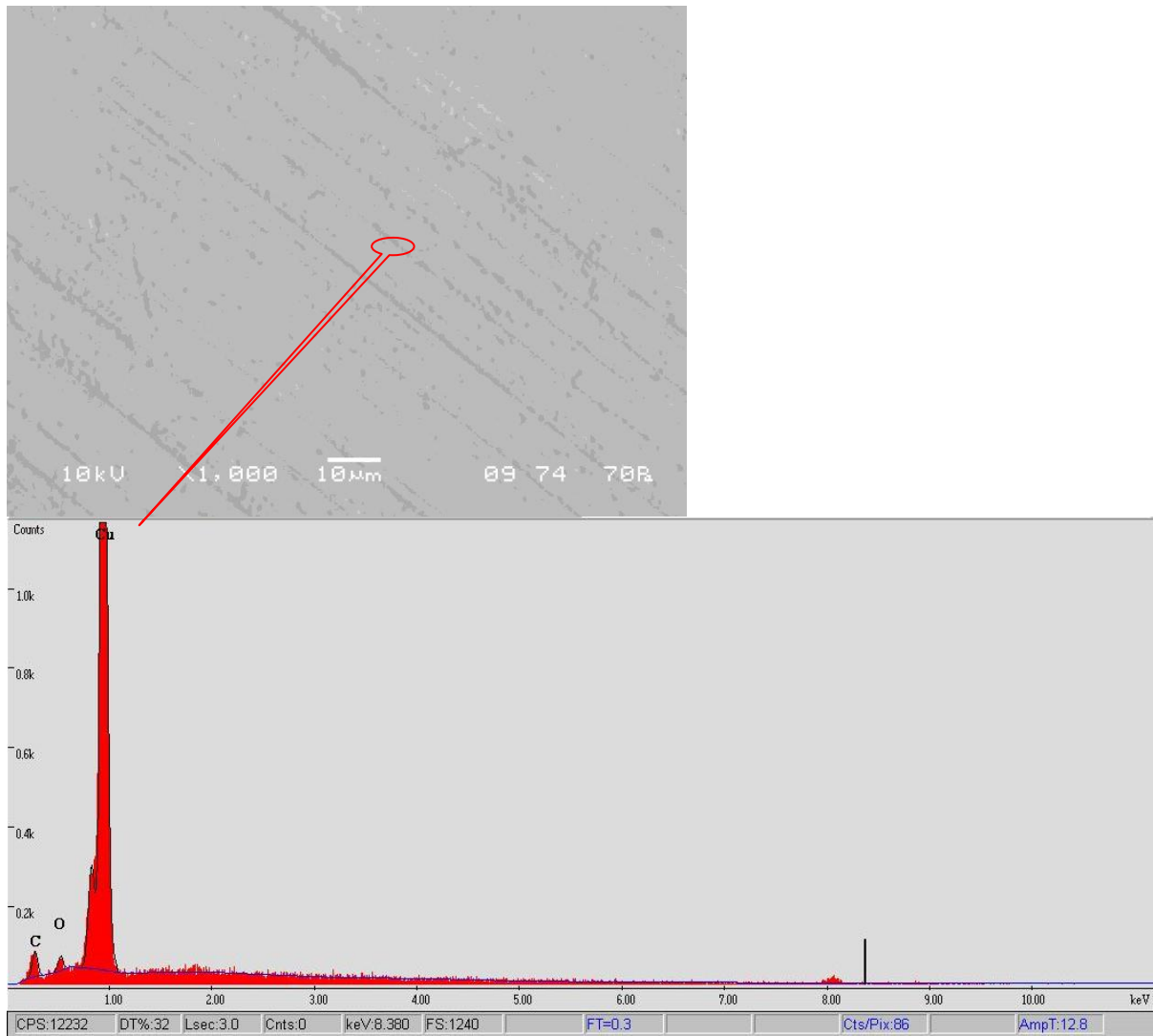


Figure 8.1.10 SEM image of copper at 1000X after 5 days immersion test in Pepsi and EDX spectrum of the indicated region on surface.

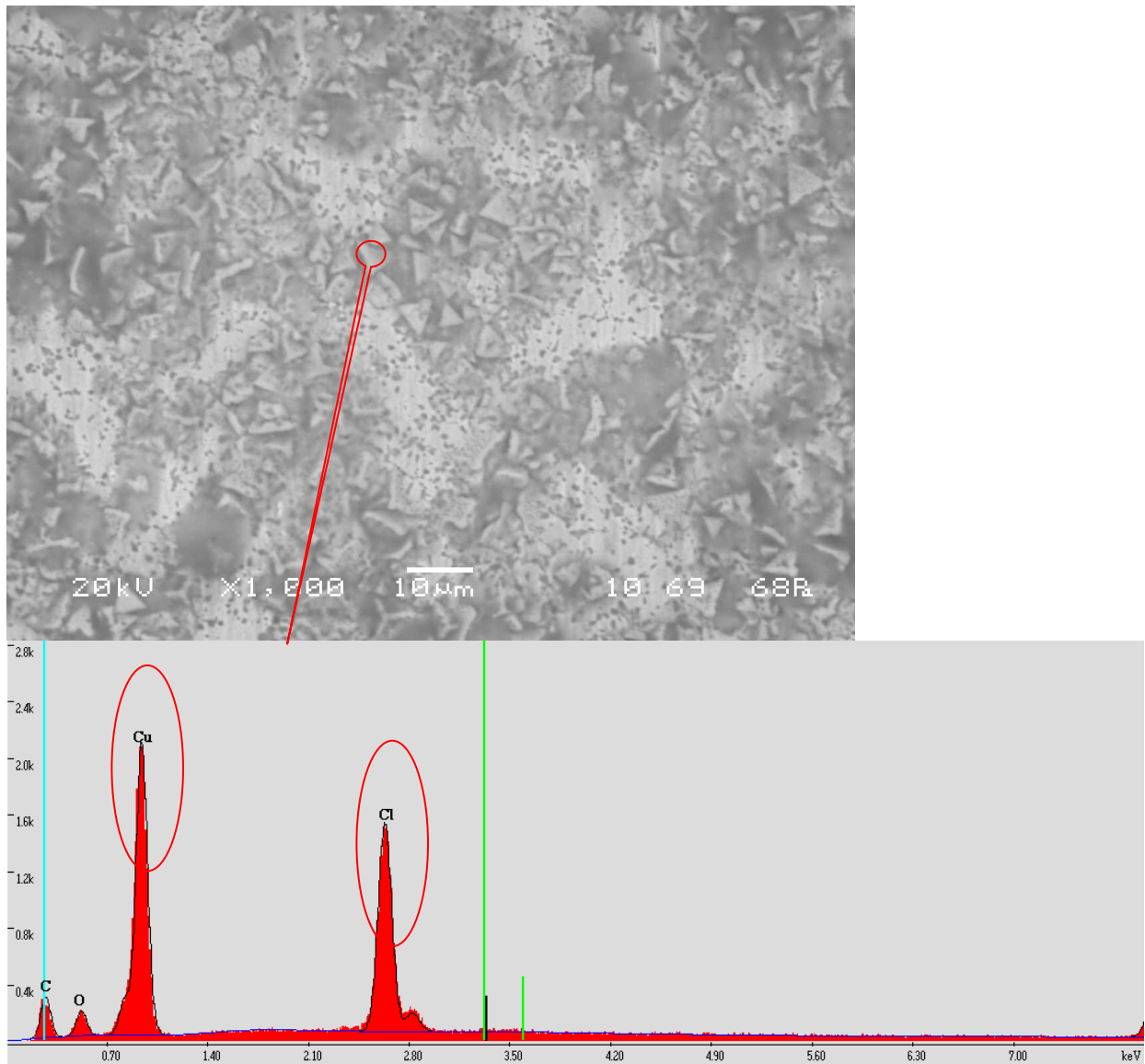


Figure 8.1.11 SEM image of copper at 1000X after 5 days immersion test in Gatorade and EDX spectrum of the indicated region on surface.

8.2 Open Circuit Potential (OCP) Measurements.

The potentials of copper electrodes were recorded as a function of time for 3 hours in 16 commercial beverages under open-circuit conditions. The resulting plots are presented in Figure 8.2.1. In most of the test beverages, the OCP values only vary slightly in the active direction over

the 3-hour period. The most notable exceptions to this trend are observed when copper is immersed in tomato juice and the two alcohol-containing beverages – beer and wine. In these cases, the OCP decrease significantly (by over 200 mV) before steady state is reached. This suggests that a surface oxide film may have formed during the immersion period in these beverages [51].

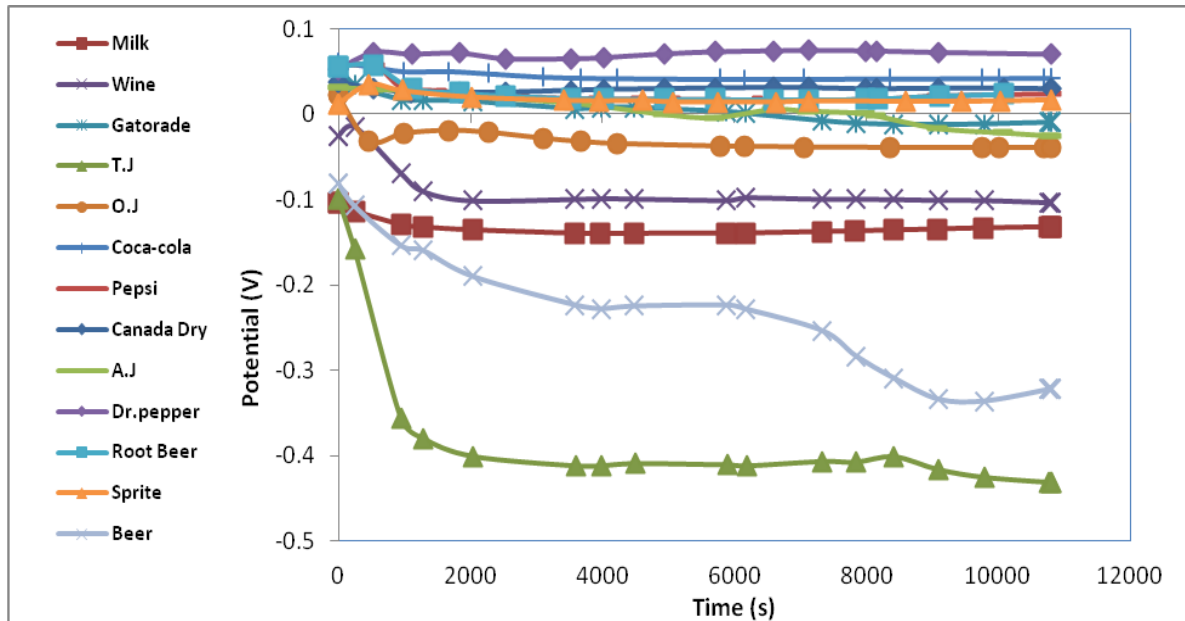


Figure 8.2.1 Variation of the open-circuit potential over time measured for copper electrodes immersed in some of the beverages.

In order to further understand the particular effects of citric acid, phosphoric acid and malic acid, similar experiments were conducted using synthetic solutions containing each of these components. Some representative curves in these solutions are presented in Figure 8.2.2. The OCP values shift continuously in the positive direction in the three solutions containing 200 ppm, 500 ppm and 1000 ppm citric acid (Figure 8.2.2a, 8.2.2b, 8.2.2c). The time required to reach steady state becomes longer as the acid concentration increases. A comparison of the curves in Figures 8.2.1 and 8.2.2 indicates that no strong correlation exists between the dynamics

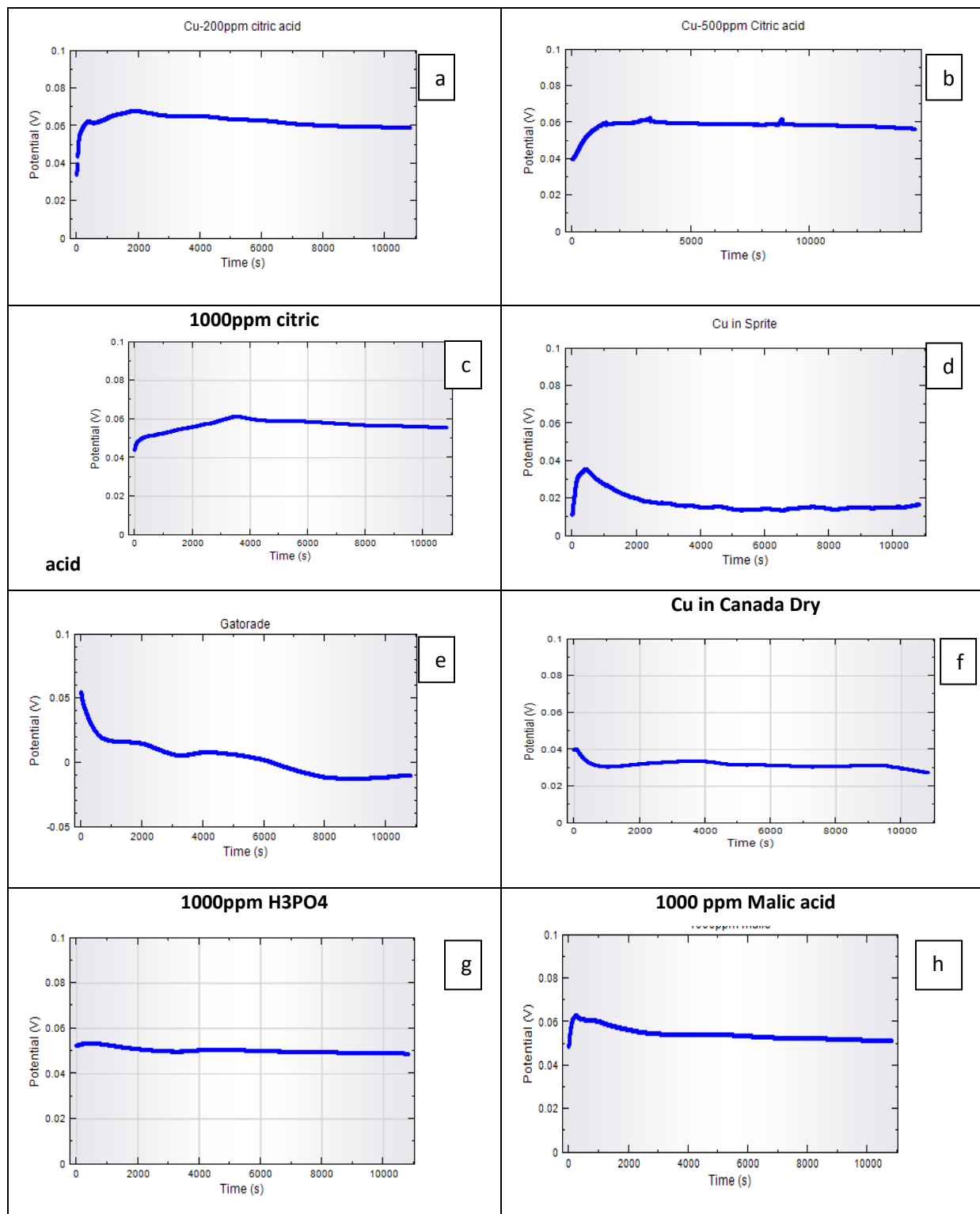
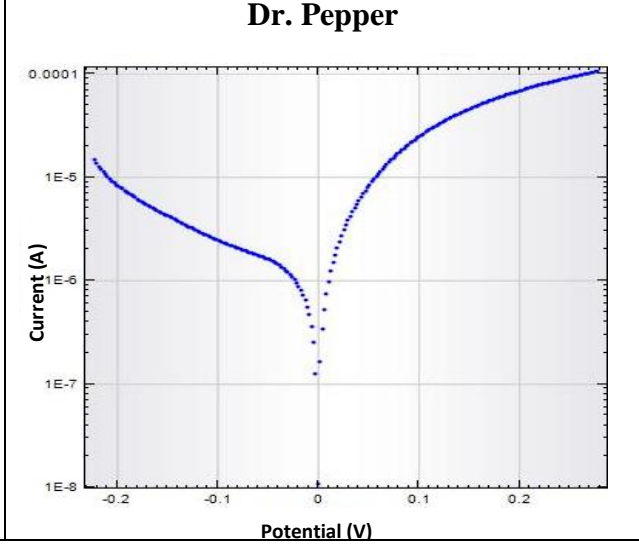
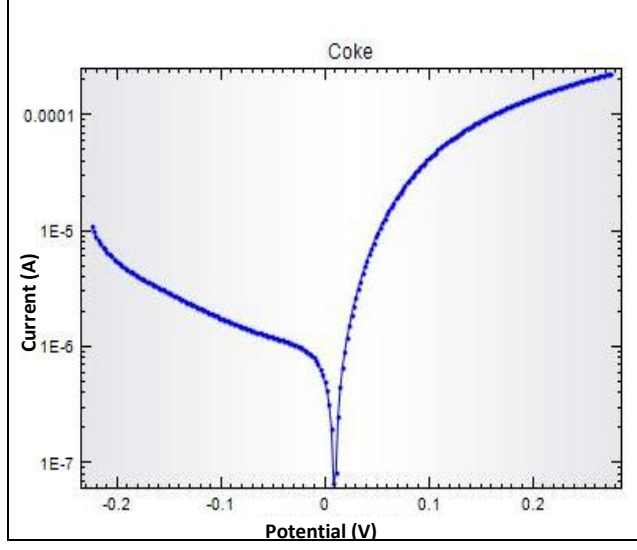
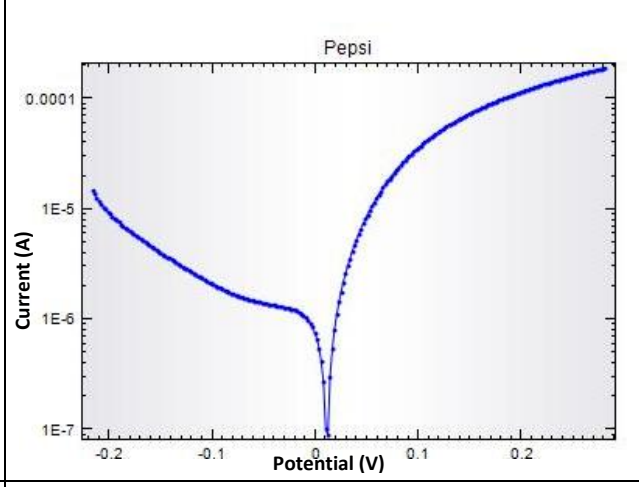
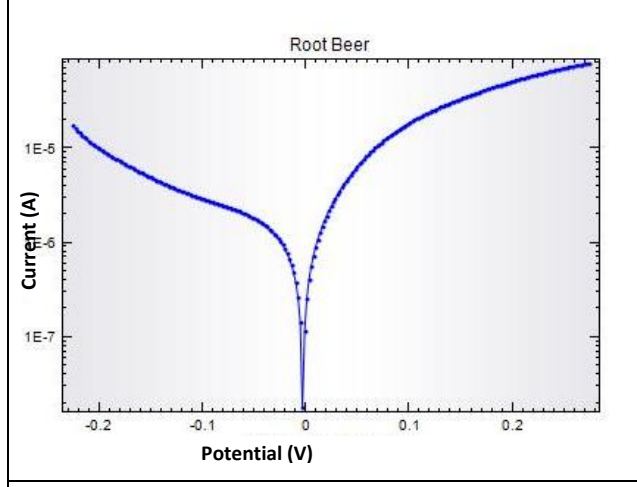
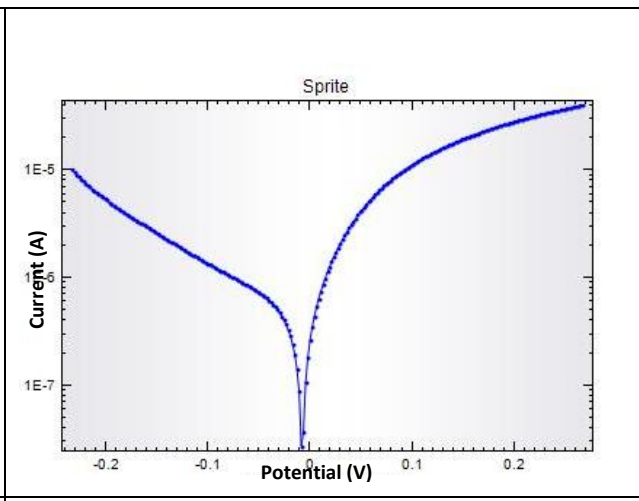
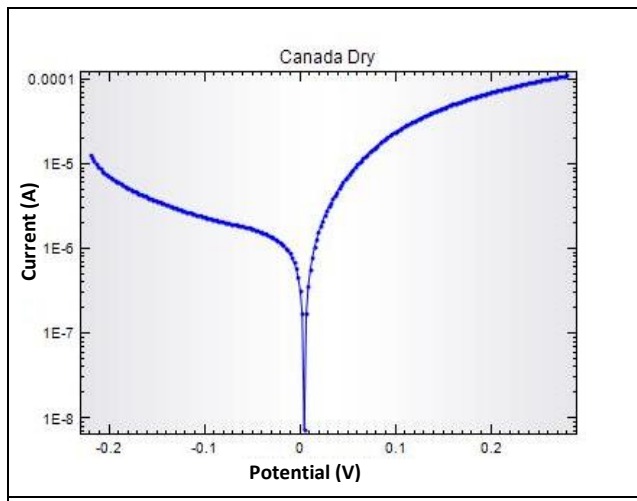


Figure 8.2.2 Variation of the open-circuit potential over time measured on copper electrodes immersed in (a) 200 ppm citric acid, (b) 500 ppm citric acid, (c) 1000 ppm citric acid, (d) Sprite, (e) Gatorade (f) Canada Dry (g) 1000 ppm phosphoric acid and (h) 1000 ppm malic acid solutions.

of the evolution of the OCP when copper is immersed in the beverages and when immersed in the synthetic solutions. For example, the evolution of the OCP in the citric acid-rich beverages such as Sprite, Canada Dry, Root Beer and Gatorade differs from that in the citric acid solutions. The OCP rapidly approaches steady state in the 1000 ppm phosphoric acid solution, suggesting that corrosion quickly reaches a constant rate, whereas it changes rapidly in the early stages before leveling off to different steady state values when copper is immersed in phosphoric acid-rich soft drinks such as Coca-cola, Pepsi and Dr. Pepper. In the malic acid solution, the OCP abruptly shifts in the positive direction at the outset but then begins to slowly decrease. However, the beverages containing large amounts of malic acid (i.e., tomato juice, orange juice and apple juice) do not exhibit this behaviour. This indicates that the copper corrosion is complex, involving the interaction between a numbers of factors

8.3 Tafel Polarization Measurements

Copper electrodes more or less reached a steady state in all test beverages within 3 hours. After the steady-state potential value was reached, the potential was scanned from -250 mV to $+250$ mV with respect to the open-circuit potential at a sweep rate of 1 mV/sec and the resulting current response was measured. Replicate experiments were conducted for each beverage to ensure that the polarization curves obtained were reproducible. Figure 8.3.1 presents the $\log i - E$ polarization curves of copper immersed in 10 of the beverages at room temperature.



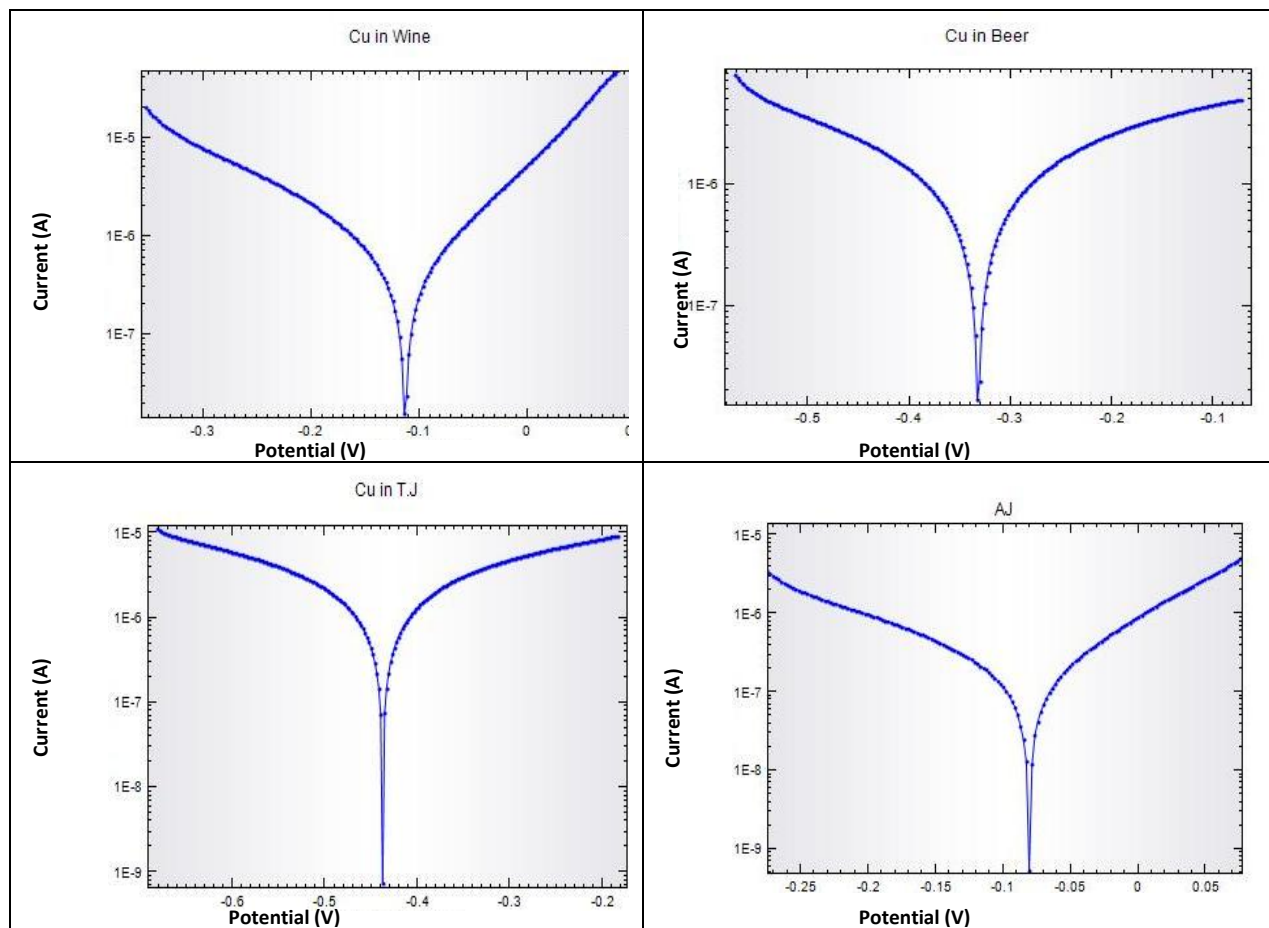


Figure 8.3.1 Polarization curves of copper obtained upon immersion in various test beverages.

With the exception of the behaviour observed in tomato juice and, to a lesser extent, in apple juice, the anodic and cathodic branches of the curves are not symmetric to each other and the anodic and cathodic Tafel curves do not intersect at E_{corr} . The corrosion current densities of copper in the various beverages were determined by fitting the Butler-Volmer equation to the experimental data using the NOVA software, as described in Chapter 6. In all 7 soft drinks, a linear Tafel portion in the anodic regions was observed. Consequently, only the data on the anodic branches were used for the determination of the corrosion parameters in these beverages.

The corrosion parameters obtained are listed in Table 8.3.1. The entries are listed in order of decreasing corrosion rate for convenience.

Table 8.3.1 Corrosion parameters of copper immersed in test beverages with their pH values.

Beverages	Corrosion rate (mm/year)	Polarization resistance (Ω)	E_{corr} (mV)	i_{corr} (mA/cm ²)	pH
Coca-cola	0.44	28	12	3.80E-02	2.47
Pepsi	0.44	58	11	3.80E-02	2.48
Canada Dry	0.28	41	-0.63	2.40E-02	2.82
Dr. Pepper	0.28	81	49	2.40E-02	2.86
Gatorade	0.18	93	-72	1.50E-02	2.92
Tomato juice	0.11	28000	-440	9.00E-03	4
Sprite	0.099	300	-8.1	8.50E-03	3.26
Beer	0.021	1500	-330	1.80E-03	3.98
Milk	0.018	650	-140	1.50E-03	6.63
Root Beer	0.0089	7300	-190	7.60E-04	4.24
Hot chocolate	0.007	9200	160	6.00E-04	7.01
Wine	0.0065	6200	-110	5.60E-04	3.46
Orange juice	0.0062	3800	-74	5.40E-04	3.86
Tea	0.004	370000	230	3.40E-04	5.33
Apple juice	0.0027	160000	-81	2.30E-04	3.57
Coffee	0.0032	10000	0.017	1.70E-04	6.04

The data in Table 8.3.1 indicate that the corrosion rate of copper in the soft drinks tends to decrease with an increase in pH. In other beverages such as juices, hot drinks, milk and alcohol, the corrosion rate is independent of the pH value. No significant correlation between corrosion potential and rate was observed.

SEM examination of the copper electrodes after the anodic scans were complete showed that uniform attack occurred in all of the test drinks. Representative SEM images and EDX spectra after anodic scans in Pepsi and Gatorade are shown in Figures 8.3.2 and 8.3.3, respectively. The SEM image and EDX spectrum of the sample exposed to Pepsi is relatively clean and displays only small carbon, oxygen peaks in addition to those of copper which is very typical of the SEM images and EDX spectra obtained for copper immersed in the other beverages. An SEM image and EDX analysis of a copper sample that had been immersed in Gatorade which contains extremely high Cl^- levels reveals the presence of significant amounts of chlorine on the electrode surface (Figure 8.3.3). This observation is consistent with the SEM images and EDX analysis obtained after copper was immersed in Gatorade for 5 days under open-circuit conditions (Figure 8.1.11).

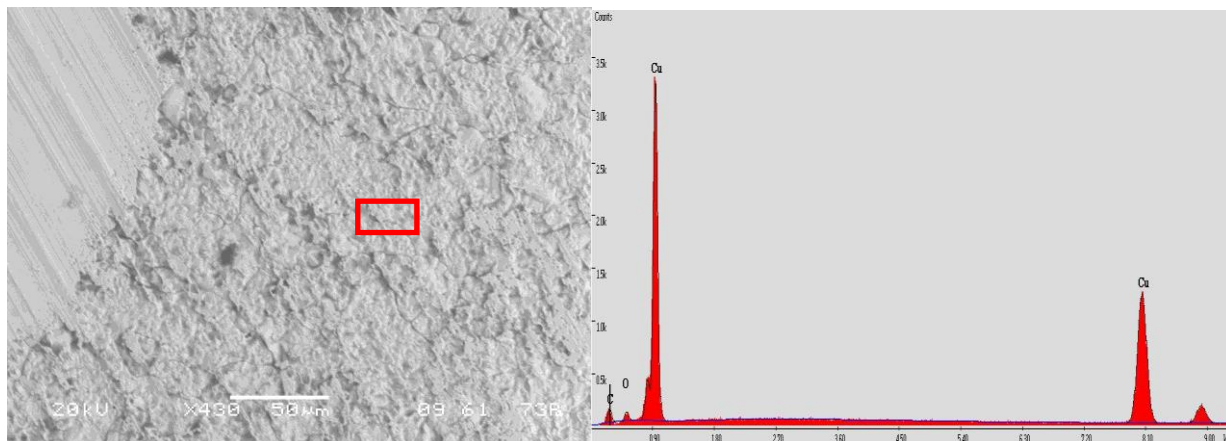


Figure 8.3.2 SEM image of Cu electrode after anodic polarization while immersed in Pepsi and EDX spectrum of the indicated rectangular region on surface.

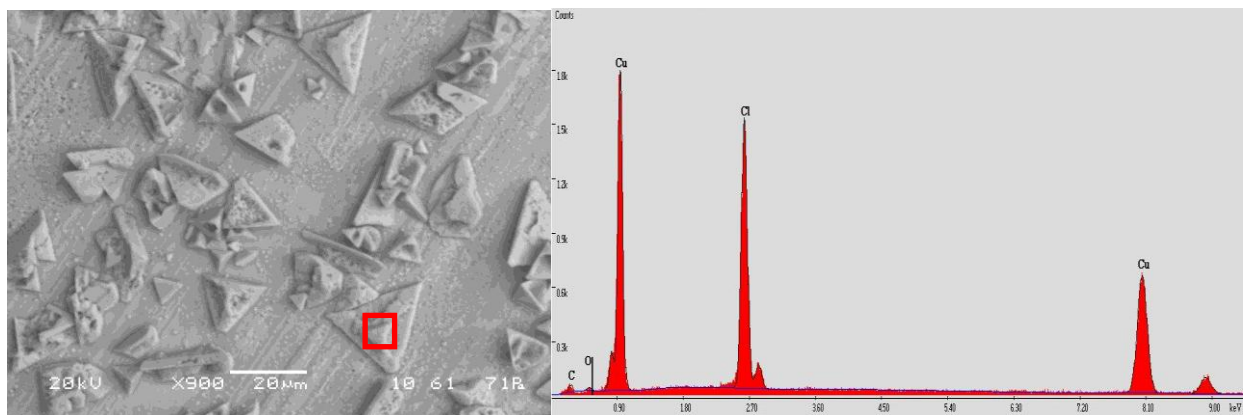


Figure 8.3.3 image of Cu electrode after anodic polarization while immersed in Gatorade and EDX spectrum of the indicated rectangular region on surface.

8.4 Summary

In this chapter, chemical analysis and electrochemical techniques are used to measure the extent of corrosion of copper when immersed in 16 commercial beverages. The influences of phosphoric acid, citric acid, chloride ion and pH have been explored. The main results of these experiments are:

1. The ranking of corrosion rates of Cu estimated from the polarization curves is not in agreement with that based on the measurement of dissolved Al concentrations after immersion in the various beverages for either short- or long-term.
2. The electrochemical measurements indicated that the corrosion rates depend on pH in the 7 soft drinks, but not in other beverages such as juices, hot drinks, milk and alcohol.
3. The ranking of the beverages according to their ability to dissolve copper based on short-term immersion tests (1 day) did not agree with that based on long-term tests (~5 or 7 days). No

correlation was found between the dissolved copper concentrations and beverage properties (e.g. pH, conductivity, etc.) or composition regardless whether short-or long-term immersion tests were conducted.

4. NaCl promotes the corrosion of copper in citric acid-containing solutions.
5. SEM examination of copper surfaces showed that they corroded uniformly in all test beverages. Evidence for the formation of corrosion products containing chlorine was found in both immersion test and the polarization scan when the applied potential increased to 1.0 V above the open-circuit potential.

Chapter 9

Conclusions and Recommendations

The corrosion behaviour of aluminum, zinc and copper has been studied in 16 commercial beverages by measuring the dissolved metal concentration after immersion for different durations using ICP-OES and by using a number of electrochemical techniques (OCP measurement, Tafel extrapolation, anodic scan methods). Physical properties and chemical composition of 16 commercial beverages were also investigated by a set of efficient methods. The metal surfaces after corrosion were examined and characterized by SEM/EDX analysis. The following conclusions can be drawn from the above experiments:

1. For selected beverages, the ranking of corrosion rates of Al estimated from the polarization curves is in agreement with that based on the measurement of dissolved Al concentrations after 1 day immersion tests. However, no correlation was found between the corrosion rate determined from the immersion tests and the corrosion rate obtained electrochemically when Al was exposed to the beverages for 3 days and when Zn and Cu were exposed for any length of time.
2. No strong correlation was found between the properties or composition of the beverages and the dissolved copper and aluminium concentration whether it was based on short- or long-term immersion tests. However, dissolved zinc concentration in soft drinks was strongly correlated to the phosphoric acid and citric acid concentrations. The corrosion rate of copper was found to depend on the pH in the case of the 7 soft drinks as determined by the Tafel extrapolation measurement. The order in which the beverages affect the dissolved Cu and Al concentrations as determined from short-term immersion tests did not agree with that determined from long-term

tests. The order in which the 7 soft drinks affect the dissolved Zn concentration after 1 day of immersion was the same as after 3 days of immersion.

3. The three metals were found to corrode uniformly in all beverages except for Al when immersed in Gatorade. In the latter case, pitting cavities were observed on the surface of Al both after 5 days of immersion. The formation of pits could also be inferred by the shapes of the Tafel polarization curves.
4. Phosphoric acid plays a major role in the corrosion of aluminum in short-term (~1 day) immersion tests, whereas citric acid becomes significant over the longer term. The effects of phosphoric acid and citric acid on corrosion as determined by the immersion tests and polarization measurements were found to be different from each other to Al. No significant difference between phosphoric acid and citric acid was found on the copper corrosion. Phosphoric acid and citric acid act as inhibitor and promoter, respectively.
5. The immersion tests show that Gatorade is the most aggressive beverage toward the three metals.

In order to gain further insight in the corrosion behaviour of metal in test beverages, further research in this area can focus on the following aspects:

1. The electrochemical behaviour of the test metals (Zn, Cu and Al) should be investigated over a range of temperatures. The influence of the temperature on corrosion behaviour of the metals and the corresponding kinetic parameters should be obtained.
2. Surface analysis techniques such as XPS and XRD should be used to obtain more precise information on the chemical and structure nature of the films formed during corrosion and anodic polarization of the metals.

3. Important materials used in the electronics industry are lead-free solders (e.g., Sn-Ag-Cu alloy).

An important topic to investigate is how each of the commercial beverages corrodes these solder alloys. Similar corrosion experiments used in this study can be carried out in such research.

4. Only a limited number of experiments were conducted on the effect of the various organic acids and inorganic anions on the corrosion behaviour of the metals. A more thorough investigation of their effects should be conducted.

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