Influence of landfill leachate on growth response and mineral content of Swiss Chard

By

Mohamed Milad Abdulmalek

Student no: 213311151

A dissertation submitted as requirement for the Degree of Master of Technology (MTech) In the Department of Agriculture, Faculty of Applied Sciences, Cape Peninsula University of Technology

Supervisors: Prof. Francis Lewu

Co-supervisor: Prof. Bhekumusa J.Ximba

September 2014
DECLARATION

I declare that the “Influence of landfill leachate on growth response and mineral content of Swiss Chard is a dissertation generated from my own work, that it has not been submitted for any degree or examination in any other University and that all sources I have used or quoted have been indicated and acknowledged by complete references.

Signed ………………

Copyright © University of Cape Peninsula University of Technology

All right reserved
ABSTRACT

In this study, laboratory and greenhouse experiments were conducted to evaluate the effects of utilization of land fill leachate for irrigation purposes on potted soil and Swiss chard, to provide more insight into effects of landfill leachates on the environment. Swiss chard was grown and irrigated with different concentrations of leachates in pot experiments. For several weeks, the experimental soil and Swiss chard leaves was analyzed to assess extent of change in different chemical compositions, post-irrigation.

The leachate samples had a high electrical conductivity (mean = 383 mS cm$^{-1}$) and high soluble salts content (mean values, Na = 714.5 mg/L, K= 56.8 mg/L, Ca = 133.7 mg/L, Mg = 68.8 mg/L, Cl = 983 mg/L); while the composition of heavy metals in these wastewater leachates were of low concentrations. The application of leachates in irrigation resulted in increased soil cation concentrations, particularly those of Na ions (increased sodicity). Similarly, an increase in electrical conductivity and pH were recorded in the soils after irrigation with leachates. The soil metal concentrations were low and there was no significant difference in soil heavy metal concentrations between the soils irrigated with leachate and those of the controls.

The results also show significant (p <0.05) reduction (up to 50%) in Swiss chard growth with application of (100%, 50% and 25%) of leachate as source of irrigation water compared to the growth observed in leachate-free (control) irrigation systems. This reduction in growth was best attributed to the high cation content in plant tissue picked up from the soil which was high in cations as a result of leachate irrigation.
ACKNOWLEDGMENTS

In the name of Allah, the Most Gracious and Most Merciful all praises to Allah the Almighty, for thee (alone) we worship and thee (alone) we ask for help. Praises and Salutations upon Muhammad S.A.W. who guided and led us to the right path.

A special thanks to my wife who stood with me through all the rough times, and my children whose presence gladdened my life.

I would also like to thank my parents, brothers and sisters. Thank you very much for your love, care, prayers, and support during the course of my research work.

I would like to thank my supervisors Prof. Francis Lewu and Prof. B.J Ximba for their support to successfully complete this project.

To the colleagues in department of Chemistry, Cape Peninsula University of Technology, South Africa, I say thank you for the good and the cordial working relationship I enjoyed during my studies.

Lastly, I would like to thank Libyan embassy for financial assistance.
DEDICATION

I dedicate this thesis to

My parents,

My wife,

My sons and daughter

and

All my family in Libya
**GLOSSARY**

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>MP-AES</td>
<td>Microwave plasma-atomic emission spectrometer</td>
</tr>
<tr>
<td>GLS</td>
<td>Green leaves Swiss chard</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>LL</td>
<td>Landfill leachate</td>
</tr>
<tr>
<td>NPK</td>
<td>Nitrogen, Phosphate, Potassium</td>
</tr>
<tr>
<td>SAR</td>
<td>Sodium Adsorption Ratio</td>
</tr>
<tr>
<td>ESP</td>
<td>Exchangeable Sodium Percentage</td>
</tr>
<tr>
<td>OP</td>
<td>Osmotic Potential</td>
</tr>
<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>g m$^{-3}$</td>
<td>Gram per meter cubic</td>
</tr>
</tbody>
</table>
DEFINITION OF KEY TERMS

1. Heavy metals
A heavy metal is defined as any metal that has a relatively high density and is toxic at low concentration such as lead, nickel, mercury and arsenic. Heavy metals belong to a class of pollutants that produce undesirable health effects, even if present in minuscule quantities.

2. Landfill
Landfill is a disposal site where solid waste such as paper, glass and metal is buried between layers of dirt and other materials in such a way as to reduce contamination of the surrounding land. Historically, landfills have been the most common methods of organized waste disposal and remain so in many places around the world. Some landfills are also used for waste management purposes such as the temporary storage, consolidation, and transfer, or processing of waste material (sorting, treatment, or recycling).

3. Leachate
Leachate is the toxic liquid that is collected at the bottom of the landfill. Leachate is formed when water passes through the waste in the landfill cell. The precipitation can be from rain, melted snow or the waste itself. As the liquid moves through the landfill, many organic and inorganic compounds, like heavy metals, are transported in the leachate. The amount of leachate produced is directly linked to the amount of precipitation around the landfill.

4. Composition of Leachate
When water percolates through the waste, it promotes and assists process of decomposition by microorganisms. These processes in turn release by-products of decomposition and rapidly use up any available oxygen creating an anoxic environment. The decomposition processes themselves release further water which adds to the volume of leachate. The leachate also reacts with materials that are not themselves prone to decomposition such as fly ash.
TABLE OF CONTENTS

DECLARATION........................................................................................................i

ABSTRACT.............................................................................................................ii

ACKNOWLEDGMENTS..........................................................................................iii

DEDICATION........................................................................................................iv

GLOSSARY............................................................................................................v

DEFINITION OF KEY TERMS..............................................................................vi

1. Heavy metals..................................................................................................... vi

2. Landfill.............................................................................................................. vi

3. Leachate............................................................................................................ vi

4. Composition of Leachate ................................................................................ vi

TABLE OF CONTENTS............................................................................................vii

LIST OF FIGURES..................................................................................................xi

LIST OF TABLES....................................................................................................xiii

LIST OF APPENDIX..............................................................................................xiv

CHAPTER 1............................................................................................................1

1. INTRODUCTION .............................................................................................1

1.1 Background ...................................................................................................1

1.2 Statement of research problem .....................................................................2

1.3 Research questions ......................................................................................3
1.4 Research objectives ................................................................................................................. 3
1.5 Assumptions ............................................................................................................................ 3
1.6 Delimitations ........................................................................................................................... 4

CHAPTER 2 ................................................................................................................................. 5

2. LITERATURE REVIEW ............................................................................................................ 5

2.1 Leachate generation and composition .................................................................................... 5
2.1.1 Introduction .......................................................................................................................... 5
2.1.2 Stabilization processes in landfills ..................................................................................... 5
2.1.3 Leachate Composition ......................................................................................................... 7
2.1.3.1 Dissolved organic matter ................................................................................................. 8
2.1.3.2 Inorganic macro-components .......................................................................................... 8
2.1.3.3 Heavy metals .................................................................................................................... 9
2.1.3.4 Xenobiotic organic compounds ......................................................................................... 10
2.2 Leachate irrigation .................................................................................................................. 11
2.2.1 Effects of leachate on plant growth .................................................................................... 11
2.3 Effects of leachate salts on soil ............................................................................................... 12
2.3.1 Effects of leachate salts on plants ....................................................................................... 13
2.4 Salt stress symptoms in plants ............................................................................................... 14
2.5 Examples of studies using leachate as irrigation systems ..................................................... 14
2.6 Swiss Chard ............................................................................................................................ 16
6.2.1 Origin and distribution of Beta vulgaris ............................................................................. 17
2.6.2 Climatic and soil requirements of Swiss chard ................................................. 17

2.6.3 Nutritional profiles of Beta vulgaris and effects on health .............................. 18

CHAPTER 3 ................................................................................................................. 20

3. MATERIALS AND METHODS .............................................................................. 20

3.1 Cleaning of glassware ......................................................................................... 20

3.2 Materials .............................................................................................................. 20

3.3 Leachate collection ............................................................................................. 20

3.4 Experimental procedure ..................................................................................... 21

3.4.1 Preparation of pot experiment and trial management ...................................... 21

3.4.2 Soil sampling .................................................................................................... 22

3.4.3 Swiss chard sampling ....................................................................................... 22

3.5 Sample preparation for the analysis .................................................................... 23

3.5.1 Soil samples ....................................................................................................... 23

3.5.2 Swiss chard samples ......................................................................................... 23

3.6 Instrumentation .................................................................................................... 24

3.6.1 Microwave plasma-atomic emission spectrometer (MP-AES) ......................... 24

3.6.2 pH meter ............................................................................................................ 25

3.6.3 Scanning electron microscopy (SEM) ............................................................... 25

CHAPTER 4 ................................................................................................................. 26

4. RESULTS AND DISCUSSION ............................................................................. 26

4.1 Characterization of applied irrigation samples ...................................................... 26
4.2 Chemical characteristics of potting soil used in this study ........................................ 29

4.2.1 The effect of leachate, tap and distilled water irrigation on potting soil properties ........................................................................................................................................ 30

4.2.1.1 Effect of leachate, tap and distilled water irrigation on soil pH ...................... 30

4.2.1.2 Effect of irrigation waters on electrical conductivity of the soil (EC) ............. 31

4.2.1.3 Effect of irrigation waters on the level of trace elements in the soil .......... 33

4.2.1.4 Effect of irrigation waters on the exchangeable cation content of the soil ..... 34

4.2.1.5 Effects of Salinity (EC) and sodicity on Soil Physical Properties ............... 36

4.3 The effect of irrigation waters on test crop (Swiss chard) properties ............... 37

4.3.1 Change in the height of Swiss chard during the experimental period .......... 37

4.3.2 Effect of leachates, tap and de-ionized water irrigations on level of trace elements in Swiss chard species ........................................................................................................... 39

4.3.3 Effect of leachate, tap and de-ionized water on the exchangeable cation concentrations in Swiss chard leaves ........................................................................................................ 39

4.3.4 Effect of irrigation waters on ultra-structural leaves morphology of Swiss chard ......................................................................................................................................... 42

CHAPTER 5 .................................................................................................................................. 46

5. CONCLUSIONS AND RECOMMENDATIONS .................................................................. 46

5.1. Conclusion ................................................................................................................... 46

5.2 Future work and recommendations ............................................................................ 47

References: ......................................................................................................................... 48

APPENDIX ................................................................................................................................ 56
LIST OF FIGURES

Figure 2.1 Bunch of Swiss chard (http://anrcatalog.ucdavis.edu) ........................................ 17
Figure 3.1 Preparation of potting soil .................................................................................. 21
Figure 3.2 Growing of Swiss chard seedling in potting soil ............................................. 22
Figure 3.3 Milestone-MLS 1200 Mega microwave oven .................................................... 24
Figure 4.1 Landfill leachate site at Bellville, Cape Town, South Africa ............................... 26
Figure 4.2 Relationship between SAR and EC of irrigation water to estimate structural
stability ........................................................................................................................................ 28
Figure 4.3 The effect of different irrigation waters on soil pH ........................................... 31
Figure 4.4 The effect of irrigation waters on soil electrical conductivity ............................ 32
Figure 4.5 The change in concentrations of Na in potting soils during second, fifth and
eighth weeks of the experiment as affected by different concentrations of leachate .......... 35
Figure 4.6 The change in concentrations of Mg in potting soils during second, fifth and
eighth weeks of treatment as affected by different concentrations of leachate ................. 36
Figure 4.7 The change in concentrations of Ca in potting soils during second, fifth and
eighth weeks of the experiment as affected by different concentrations of leachate ........... 36
Figure 4.8 The change of Swiss chard height resultant from different irrigation waters .... 38
Figure 4.9 Change in concentration of Na in Swiss chard leaves during second, fifth and
eighth weeks of the experiment ............................................................................................... 41
Figure 4. 10 Change in concentration of Mg in Swiss chard leaves during second, fifth and eighth weeks of the experiment ................................................................. 41

Figure 4. 11 Change in concentration of Ca in Swiss chard leaves during second, fifth and eighth weeks of the experiment ............................................................................. 42

Figure 4. 12 Scanning electron micrographs of (a) 25% Leachate, (b) 100% Leachate, (c) Tap water, (d) 50% Leachate (e) Distilled water, in the first week of the experiment. ...... 44

**Figure 4. 13** Scanning electron micrographs of (a) 25% Leachate, (b) 100% Leachate, (c) Tap water, (d) 50% Leachate, (e) distilled water, in the eight week of the experiment...... 45
LIST OF TABLES

Table 2.1 Nutritional profile per 100g raw Swiss chard.......................................................... 19

Table 3.1 Program for closed microwave oven procedure................................................. 24

Table 4.1 Characteristics of leachate, tap water and distilled water used in the pot experiment..................................................................................................................................29

Table 4.2 Characteristics of soil used in pot experiment...................................................... 30

Table 4.3 Irrigation water ratings based on electrical conductivity................................. 33

Table 4.4 Trace metals content in soil during irrigation with different concentration of leachate, tap water and de-ionized water................................................................. 34

Table 4.5 Trace metals content in Swiss chard leaves during irrigation with different concentrations of leachates, tap and de-ionized water............................................... 39
LIST OF APPENDIX

APPENDIX1: RESULTS OF CALPRATION CURVE OF MICROWAVE PLASMA-ATOMIC EMISSION SPECTROMET ................................................................. 56

APPENDIX2: RESULTS OF LEAVE ........................................................................................................... 60

APPENDIX3: RESULTS OF SOIL ANALY .................................................................................................... 68

APPENDIX4: RESULTS OF ENERGY DISPERSIVE SPECTROSCOPY (EDS) ...... 30
1. INTRODUCTION

1.1 Background

Landfill leachate has been, for a long time, recognized as a potential source of pollution to ground and surface waters (McDougall et al. 1980). Toxic substances which are commonly present in leachate include major ions (as sodium, potassium, sulphate, chloride and iron), heavy metals (like cadmium, chromium, copper, lead nickel and zinc), a wide range of organic compounds and micro-organisms. It is essential to collect and treat leachates before discharge in main/municipal water bodies in order to safeguard aquatic ecosystems. Utilization of municipal wastewaters on lands has been a low-cost treatment and disposal alternative. Municipal wastewater which contains considerable amounts of salts may serve as a source of nutrients for plant growth (Berry et al. 1980). Similarly, it may be possible to recycle landfill leachate by land application; this decontamination is achieved by allowing the soil to act as a filter. Bennett et al. (1975) reported significant water quality improvement and no serious effect on a mature hardwood forest after irrigation with landfill leachate. It has also been demonstrated that forages contained higher concentrations of macronutrients after irrigation with leachate (Menser et al., 1979). However, unlike sewage effluent, landfill leachate has not been considered as a potential resource for plant growth, mainly on account of excessive Fe and Mn. Apart from Fe and Mn, other metals may be present in toxic concentrations. Landfill leachate may also contain salts and organic compounds such as organic acids and phenols in quantities that may restrict biological activity in the root zone (Artiolar-Fortuny et al., 1982). Relatively few studies had been undertaken in recent past to evaluate toxicity, deleterious effects or advantage of leachate on soil and crop yields.
Hence, this study will evaluate the use of landfill leachate as a potential source of water for irrigation purposes, and determine the degree of uptake of essential and trace elements by Swiss chard (*Beta vulgaris var. cicla*) irrigated with such landfill leachate.

### 1.2 Statement of research problem

The management of landfill leachate has become a major focus in landfill environmental management. The leachate is normally generated by the flow of rainfall and surface water into the landfill. Over a period of time, these waters mix with toxic and non-toxic contaminants in landfill sites and results in high concentrated wastewater found in landfill environments which may pose potential threat to the quality of groundwater. The landfill leachates contain complex compositions, such as high concentration of ammonia, nitrogen and salts, suspended solids, and heavy metals, which are also characteristic of leachate contents (Parida *et al.*, 2005).

In recent years, studies revealed that landfills are not properly managed and contamination of water bodies with heavy metals from leachates is evident. Thus, knowledge on influence of possible contamination by irrigation waters used by farmers and safety of the communities around landfill needs to be extended further. It is important to note that the escape of leachate into the main water bodies from landfill is possible under condition of heavy rainfall and improper management of landfill areas. Effect of landfill leachate on the soil properties needs to be assessed, as well as the effect on growth and nutritional composition of cultivated crops.

Hence, Swiss chard was used in a pot experiment for this study. Swiss chard merits the test crop being vegetable that matures in relatively short period and also, the deposition of photosynthate in most vegetables remains in the edible parts of the species, and if
contaminants are absorbed through the plant roots, they could easily find their way into the leaves and fruits and ultimately in human diets.

1.3 Research questions

This study seeks to provide answers to the following questions:

- What is the effect of landfill leachate on soil properties?
- Can landfill leachate be applied as an alternative source of agriculture irrigation system?
- Is there any significant difference in the growth response and mineral content of Swiss chard when different water types landfill leachate water, tap water or distilled water is used for irrigation?

1.4 Research objectives

This research aims to:

- Investigate the effect of landfill leachate on soil chemical properties and assess growth response in Swiss chard (*Beta vulgaris var. cicla*) species.
- Study the possible physiological influence of the uptake of leachate contaminants on the leaf cells of Swiss chard.
- Investigate the influence of landfill leachate on the mineral composition of Swiss chard.

1.5 Assumptions

This study is based on the following assumptions:

- There may be variation in phytochemical and mineral composition of test crop after applying leachates as irrigation water.
• The methods that will be used to analyze the presence and levels of metals in the Swiss chard species are suitable and sensitive to determine the contamination level.

1.6 Delimitations

• The effect of landfill leachate will was studied only on Swiss chard species used for the trial and not on any other vegetable crops.

• Instrumentation including Microwave plasma-atomic emission spectrometer (MP-AES) and scanning electron microscope (SEM) for analysis.

• This will be a pot experiment and not field study, and only one soil type was used.
CHAPTER 2

2. LITERATURE REVIEW

2.1 Leachate generation and composition

2.1.1 Introduction

Landfill leachate is the wastewater that accumulates within a landfill. Leachate forms when the soluble components present in the solid wastes, dissolves and leach out as water moves through the landfill (Monroe et al., 2001). The soluble components can be leached directly from the refuse or can be formed as a result of the physical, chemical and biological processes that take place during decomposition. Rainfall is the main source of water in leachate but surface water, groundwater and the moisture in the waste can also be sources. Landfill leachate is a water based solution containing dissolved organic matter, inorganic components, heavy metals and artificial organic compounds (Kjeldsen et al., 2002). The exact composition of a leachate is a function of the type, age, and stabilization of the landfill waste, and the prevailing physiochemical conditions, microbiology and water content of the landfill.

2.1.2 Stabilization processes in landfills

Leachate composition is mainly a function of the age and degree of stabilization of the waste within a landfill (Reinhart et al., 1998). Once buried, a complex series of chemical and biological reactions occur within a landfill as the refuse decomposes. Chemical and biological reactions stabilize the waste and proceed in a distinct series of phases. The idea of refuse decomposing in phases was first described by Farquhar et al., (1973) and has been the subject of several other studies (Barlaz et al., 1989; Bozkurt et al., 1999). In literature, the exact number of phases involved in degradation of refuse was reported to range from three to seven (Kjeldsen et al., 2002).
Similarly, it is frequently accepted that in the short term, four distinct phases of decomposition takes place (Barlaz et al., 1989; Lisk, 1991; Bozkurt et al., 1999). The rate of production and characteristics of the leachate produced vary from one phase to the next. Descriptions of the first four phases of refuse decomposition are given below:

**Phase 1: Aerobic phase**

The aerobic phase begins when the refuse lands on the landfill and only lasts a couple of days, since oxygen is not replenished once the refuse is covered (Kjeldsen et al., 2002). Aerobic organisms break down the degradable material such as sugars present in the fresh refuse to produce carbon dioxide, organic compounds, heat and water (Barlaz et al., 1989). Small amounts of leachate are produced during this phase as the refuse is not typically containing moisture content at field capacity or above. Most of the leachate produced is a result of moisture being released during compaction of the refuse (Kjeldsen et al., 2002). Phase 1 is characterized by a neutral pH and an increase in the Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) (Taulis et al., 2005).

**Phase 2: Acid phase**

After burial of the refuse, oxygen is not replenished and anaerobic conditions dominate. Hydrolytic, fermentative and acetogenic bacteria take over the decomposition process in the absence of oxygen. During this phase, complex organic material is degraded by hydrolysis to smaller organic molecules such as carboxylic acids, alcohols and carbon dioxide (Bozkurt et al., 2000). The formation of organic acid results in a drop in pH (Kjeldsen et al., 2002). The acidic leachate is chemically aggressive and will increase the solubility of many compounds including metals and other inorganic ions (Kjeldsen et al., 2002; Taulis et al., 2005). Carbon dioxide concentrations reach their maximum values during the acid phase and values of over 90% CO$_2$ have been observed in the landfill gas.
The leachate from the acid phase is characterized by a pH between 5 and 6, high ammonia and BOD concentrations and a high BOD/COD ratio (Robinson et al., 1989).

Phase 3: Initial methanogenic phase

The onset of the third phase begins when measurable quantities of methane are produced (Kjeldsen et al., 2002). Acetogenic bacteria convert the carboxylic acids produced in the acid phase to acetate, hydrogen and carbon dioxide which raises the pH (Barlaz et al., 1989). The increase in pH allows the growth of methanogenic bacteria whose growth is limited in the acidic conditions of the acidic phase (Kjeldsen et al., 2002). The degradation products act as substrate for the methanogenic bacteria which convert it to methane and carbon dioxide (Bozkurt et al., 2000). It is during the initial methanogenic phase that the decomposition of cellulose and hemicellulose begins (Kjeldsen et al., 2002).

Phase 4: Stable methanogenic phase

In the stable methanogenic phase, methane production reaches its maximum and decreases thereafter. Carboxylic acids are consumed at the same rate at which they are produced and methane production is dependent on the rate of cellulose and hemicellulose hydrolysis (Kjeldsen et al., 2002; Taulis, 2005). There is a decline in rate of pH increment and a decrease in the BOD and COD concentrations.

2.1.3 Leachate Composition

Household waste is reasonably consistent in composition; so landfills that accept predominantly municipal solid waste and operate under anaerobic conditions tend to produce leachates with similar constituents, although concentrations vary between landfills. The major components in landfill leachate can be divided into four groups:
1. Dissolved organic matter such as volatile fatty acids, humic and fulvic compounds. These are usually measured as total organic carbon (TOC) or chemical oxygen demand.

2. Inorganic macro components such as calcium, magnesium, sodium, potassium, ammonium, sulphate, chloride, iron and hydrogen carbonate.

3. Heavy metals like cadmium, chromium, and copper, lead, nickel and zinc.

4. Xenobiotic organic compounds which can include aromatic hydrocarbons, phenols and pesticides (Christensen et al., 2001; Kjeldsen et al., 2002).

### 2.1.3.1 Dissolved organic matter

Dissolved organic matter is a bulk parameter covering a wide range of organic compounds including volatile fatty acids, and refractory products such as fulvic and humic-like compounds. The dissolved organic matter content of landfill leachate is usually expressed as biological oxygen demand (BOD), chemical oxygen demand (COD) or total organic carbon (TOC) (Kjeldsen et al., 2002).

### 2.1.3.2 Inorganic macro-components

Inorganic macro-components are the inorganic constituents present in the leachate (Christensen et al., 2001). The common cations and anions found in leachate include sodium, potassium, sulphate, chloride, and ammonia. The concentration of the inorganic macro-components can vary over time depending on the degree of stabilization in the landfill.

The higher pH enhances sorption and precipitation while lower organic matter content allows the formation of complexes with the cations. Sulphate concentrations are lower due to the microbial reduction of sulphate to sulphide (Kjeldsen et al., 2002). Chloride, sodium,
and potassium concentrations are not influenced by the landfill phase as the effects of sorption, complexation and precipitation are minor for these ions (Kjeldsen et al., 2002).

Most of the nitrogen present in leachate is in the form of ammonia which is produced by the degradation of proteins and amino acids. Ammonia concentrations are typically between 500 to 2000 g m\(^{-3}\) (Kjeldsen et al., 2002), but concentrations in excess of 10 000 gm\(^{-3}\) have been recorded (Tatsi et al., 2002). Ammonia concentrations do not decline over time as there is no mechanism for its degradation under anaerobic conditions; therefore any ammonia loss is a result of leaching out of the landfill (Bilgili et al., 2006).

### 2.1.3.3 Heavy metals

Heavy metals are defined as metals with a density greater than 5 g cm\(^{-3}\) (Sayari et al., 2005). Heavy metals present in leachate include arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) (Taulis et al., 2005). Some heavy metals such as copper and zinc are essential for growth but can become toxic at high concentrations (Sayari et al., 2005). Although heavy metals can be toxic, leachate heavy metals generally do not pose a groundwater pollution problem as average metal concentrations are typically low and only a small proportion of the metals that are disposed of in a landfill are leached out (Kjeldsen et al., 2002). Mass balance studies have shown that less than 0.002% of heavy metals are leached from a landfill over the first 30 years of operation (Kjeldsen et al., 2002). Qu et al. (2008), reported that total heavy metals concentration was less than 1% of that deposited in a Chinese Bioreactor landfill during a 20 month study period. Heavy metal concentrations are typically highest during the acid phase when the low pH leachate is chemically aggressive and can increase the solubility of metals (Kjeldsen et al., 2002). As the pH increases and the landfill moves to the methanogenic phase, leachate heavy metal concentrations decrease. Studies
conducted on German landfills (Ehrig, 1983) and in the USA by Krug et al. (1995), showed that magnesium, iron, zinc and manganese concentrations are higher in the acid phase (Taulis et al., 2005). Qu et al. (2008), examined leachate from a full scale bioreactor landfill in China over a 20 month period and reported that cadmium, chromium, copper, nickel, lead, and zinc concentrations were initially high, but after 5 months the methanogenic stage had been reached and the heavy metal concentration had dropped below the Chinese national standards. The relatively low leachate metal concentrations during the methanogenic phase are commonly attributed to adsorption and precipitation processes, binding and immobilizing the metals within the landfill.

Landfills will typically contain significant amounts of soil and organic matter, which absorb the metals, reducing their solubility and mobility (Taulis et al., 2005). Absorption of metals by soil and organic matter occurs more readily at neutral to high pH values, ie. occurs during a landfill’s methanogenic phase (Taulis et al., 2005).

Precipitation is the other mechanism which immobilizes metals. Heavy metals are not always immobilized within the landfill; there are also processes that are capable of increasing the concentrations of metals in the leachate. Complexation of metals to organic ligands, and adsorption onto colloids can increase the concentrations of heavy metals in leachate (Kjeldsen et al., 2002). Long term landfill processes may also lead to heavy metals being mobilized from the landfill into the leachate.

2.1.3.4 Xenobiotic organic compounds

Xenobiotic Organic Compounds (XOCs) are substances derived from anthropogenic sources (Baun et al., 2004). They include aromatic hydrocarbons, phenols and chlorinated aliphatic compounds (Slack et al., 2007) with the most frequently found XOCs being mono-aromatic hydrocarbons and halogenated hydrocarbons (Kjeldsen et al., 2002). XOCs
are commonly associated with industrial or hazardous waste but a large number occur in municipal and domestic waste. Paint, garden chemicals, household cleaning agents, motor vehicle products, batteries, waste electrical and electronic equipment are all sources of XOCs in municipal solid waste (Slack et al., 2007). The number and concentration of XOCs present in leachate can vary between landfills. Baun et al., (2004) monitored 10 different Danish landfills and reported the presence of 55 different XOCs plus 10 degradation products of XOCs with concentrations ranging from <0.1 μg/l to 2220 μg/l. Kjeldsen reported that concentrations of XOCs are higher in older municipal landfills compared to newer landfills. This was attributed to lower acceptance rates of XOCs in the newer landfills rather than any landfill ageing process.

2.2 Leachate irrigation

Leachate can be disposed of by spray or trickle irrigation onto vegetated land. Leachate irrigation is best suited to areas where: (1) high rainfall leads to the production of large volumes of dilute leachate, (2) there is enough suitable land available for irrigation, and (3) the landfill is too far away from any sewer network to make offsite disposal economical (Gray et al., 2005). An advantage of leachate irrigation is that leachate treatment/disposal can be accomplished on site, particularly on closed landfills where irrigation can take place over the capped landfill surface. The other advantage of irrigation is that the nutrients present in the leachate can be recycled and used for plant growth.

2.2.1 Effects of leachate on plant growth

Leachate is rich in nutrients, including nitrogen needed for plant growth, and leachate irrigation has been shown to improve plant growth when managed correctly (Bowman et al., 2002; Maurice et al., 1999; MacDonald et al., 2008; Revel et al., 1999; Shrive et al., 1994). Revel et al., (1999) used leachate with high concentrations of NH$_4^+$ (1520 g m$^{-3}$),
Na\(^+\) (1920 g m\(^{-3}\)), K\(^+\) (2200 g m\(^{-3}\)) and Cl\(^-\) (2130 g m\(^{-3}\)) to irrigate pots containing ryegrass. Increased grass growth was shown when the pots were irrigated with solutions containing up to 400 g m\(^{-3}\) of leachate. Above 400 g m\(^{-3}\) the leachate had a detrimental effect on plant growth which was attributed to sodium toxicity. Shrive et al., (1994) found that irrigation of a high ionic strength leachate significantly increased stem growth in hybrid poplar samplings. The authors also found that direct exposure of the leaves to the potentially phytotoxic compounds (volatile organic compounds and inorganic substances including metals) present in the leachate did not induce phytotoxic reactions in the plants.

2.3 Effects of leachate salts on soil

When discussing the influence of the soluble salts on leachate irrigation, the terms ‘salinity’ and ‘sodicity’ are commonly used. Salinity refers to the presence of soluble salts in the irrigated water or soil, while sodicity refers to the proportion of available sodium ions relative to the available calcium, magnesium, potassium and aluminum ions present in the soil or irrigated water. Salinity and sodicity are common problems in areas where irrigation is employed for agricultural purposes, especially if rainfall is low and evaporation is high (Rietz et al., 2003). Soluble salts present in the irrigation water can accumulate in the soil when the rainfall is insufficient and unable to leach the salts from the soil profile (Rietz et al., 2003). Increased soil sodicity and salinity can cause a reduction in soil hydraulic conductivity and reduce plant productivity.

The sodium adsorption ratio (SAR) is used to quantify the salinity of the irrigating water and the exchangeable sodium percentage (ESP) is used to quantify soil salinity (Balks et al., 1998). The SAR describes the level of sodium relative to other cations (Ca and Mg) present in the irrigation water and is defined by:
The detrimental effects of high sodium concentrations on soils are exhibited through swelling and dispersion of clay minerals (Halliwell et al., 2001).

2.3.1 Effects of leachate salts on plants

Excessive salt concentrations can affect plants in three ways (Parida et al., 2005):

1. Salinity: Excessive salt concentrations affect a plant’s ability to osmotically take up water. As the salt concentrations increase, the water potential between the plant and soil increases, reducing the plant-available water and making it harder for plants to take up water. If soil salinity exceeds a plant’s tolerance, growth reductions occur and in extreme cases can cause plant’s death (Parida et al., 2005).

2. Specific ion toxicity: Excessive concentrations of specific salt such as sodium, chloride and boron can be toxic to some plants. Plants which are sensitive to these elements can be affected at relatively low levels if the soil concentrations are high enough (Seilsepour et al., 2009). The effects of ion toxicities are noticeable in the leaves, particularly the leaf margins where harms including necrotic spots, leaf bronzing and, in the worst case, defoliation can occur.

3. Nutritional disorders: High salt concentrations can cause nutritional imbalances in plants. Many salts are essential plant nutrients. High soil salt concentrations can upset the nutrient balance in plants or affect the uptake of some nutrients (Seilsepour et al., 2009). Plants vary in their response to high soil salinity; generally, there will be no reduction in yield up to a threshold level, which varies for different plant species. Plant species that are

\[
\text{SAR} = \left( \frac{\text{Na}^+}{\left( \frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2} \right)^{1/2}} \right)^{1/2}
\]

(Equation 1)

The detrimental effects of high sodium concentrations on soils are exhibited through swelling and dispersion of clay minerals (Halliwell et al., 2001).
able to grow and complete their life cycle in saline conditions are often termed ‘salt tolerant’. Salt tolerance can be defined as the ability to survive and produce economic yields under adverse conditions caused by salinity. Salt tolerant plants are known as halophytes and can be divided into two groups; obligate halophytes which require saline conditions and facultative halophytes which can survive in saline or freshwater conditions (Parida et al., 2005).

2.4 Salt stress symptoms in plants

Symptoms of salt stress in plants resemble those of plants subjected to drought conditions and are characterized by wilting and reduced growth (Seilsepour et al., 2009). Salt stress affects all major processes in plants such as growth, photosynthesis, protein synthesis, and energy and lipid metabolism (Parida et al., 2005). As a result, plants affected by salt stress grow more slowly and are smaller than unaffected plants. One cause of growth rate reduction is reduced photosynthesis caused by stomatal closure which limits carbon dioxide uptake (Zhu, 2001). The leaves of salt stressed plants are smaller, but may be thicker as salinity can cause increases in epidermal and mesophyll thickness, and elongation of the palisade cells (Bernstein et al., 1975; Parida et al., 2005). The leaves can be a different color to those of unaffected plants as generally the chlorophyll and carotenoid content of leaves decrease under salt stress (Bernstein et al., 1975).

2.5 Examples of studies using leachate as irrigation systems

Hernández et al. (1999) investigated the effects of leachate irrigation on four wild herbaceous species in a greenhouse pot study. Three different leachates were applied to pots containing one of four plant species; two legumes (Trifolium glomeratum and Trifolium tomentosum) and two grasses (Hordeum maurinum and Bromus hordaceus). The results show Leachate irrigation significantly increased soil salinity. The plant response to
the increase in soil salinity differed for each species with the legumes more sensitive to the increase in salinity than the grasses. The dry weight of both the legumes and grasses decreased with increasing electrical conductivity of the leachate.

MacDonald et al. (2008) investigated the effects of leachate irrigation on the capped area of an active landfill in Michigan, USA. Six experimental plots were established and three were irrigated with leachate and left three as control. The leachate had high mean values for electrical conductivity (6000-7000 μS cm⁻¹), chloride (760-900 g m⁻³) and ammonical nitrogen (290-390 g m⁻³) but was low in metals and volatile organic compounds. During the first year of irrigation 320 mm of leachate was applied causing high rates of nitrate leaching and the soil electrical conductivities to rise from 500 μS cm⁻¹ to 2800 cm⁻¹ in the irrigated plots compared to 700 cm⁻¹ in the control plots. In the subsequent year, leachate applications rates were limited to <96 mm y⁻¹ to reduce nitrate leaching and to keep soil electrical conductivities at a level which would not affect plant growth or soil structural stability. After leachate application rates were reduced, soil electrical conductivities reduced to 1400 μS cm⁻¹ in 2004 and 1600 μS cm⁻¹ in 2005. Leachate irrigation did not significantly affect soil metal concentrations and plant metal concentrations were within normal ranges.

Bowman et. al (2002) reported on a two year landfill leachate irrigation trial held at the Newington Landfill, Sydney, Australia. The leachate had high salinity (17,600 μS cm⁻¹) and high concentrations of sodium (3000-4000 g m⁻³), chloride (6700-8000 g m⁻³) and ammonium (250-330 g m⁻³). Plots vegetated with Couch grass (Cynodon dactylon) and Kikuyu grass (Pennisetum clandestinum) was irrigated with town supply water and leachate diluted to 20%, 50% and 100% of its original concentration with town supply water. In the plots irrigated with 50% and 100% leachate, an increase in soil salinity and
bulk density was observed along with a decrease in porosity, aggregate stability and biomass production. The degradation of the soil physical properties was attributed to an increase in the sodium adsorption ratio in the soil. In the 20% leachate plot, biomass production increased while there was no significant change in the soils physical properties compared to the control plot. Nitrogen losses through leaching were significantly less in the 20% leachate plot compared to the 50% and 100% leachate plots. It was concluded that leachate irrigation is sustainable provided that management strategies, such as dilution of the leachate to reduce the electrical conductivity down to 3600 μS cm$^{-1}$ (20% of original concentration), are adopted. Furthermore, pollution due to leaching of nitrogen to groundwater could be minimised by appropriate management of the soil to enhance denitrification (Bowman et al., 2002).

2.6 Swiss Chard

Swiss chard (*Beta vulgaris var. cicla*) is an edible flowering plant that belongs to the family Chenopodiaceae. It is an annual plant that grows quickly and has the ability to survive over winter in temperate regions. Swiss chard leaves are variable in size from about 2–30 cm long and 1–15 cm broad. Larger leaves are found at the base of the plant and small leaves are found higher on the flowering stem (Gilbert et al., 1996). The flowers of Swiss chard are usually yellow-green, 3–4 mm in diameter and mature into several small seeds. Plants may flower in as little as two weeks provided that they are grown in ideal conditions. Chard plants have several names in addition to Swiss chard. Leaf beet, seakettle beet and spinach beet are a few, with regional dialects adding to the list. The most common varieties of chard produce yellow, white or red stalks but there are also stems in pink, purple, orange and hues in between. All types of chard are fast growing plants that thrive in moist, humus-rich soil (Ortmann et al., 2007).
6.2.1 Origin and distribution of *Beta vulgaris*

The ancestral form of all beets (Swiss chard, beetroot, fodderbeet and sugar beet) is the wild Sea Beet (*Beta maritima*), which is distributed throughout the Mediterranean and Near Asian areas. The wild form is very variable and adaptable, with branched tap-roots and varying sugar content. Swiss chard, the main root of which is not swollen, was already cultivated as a leaf vegetable in Greece around 400 BC. Through mutation, varieties have been developed with widened leaf stalks which are used as a vegetable similar to asparagus. (Pathak *et al.*, 2013). Today, China, the United States and Japan are among the largest commercial producers of Swiss chard.

2.6.2 Climatic and soil requirements of Swiss chard

Swiss chard seeds germinate at 2°C to 30°C. However, 7°C to 24°C is optimum temperature for germination. The plant requires a constant and uniform supply of water in order to obtain high quality harvest. During Swiss chard production, the soil should never be allowed to dry out. Swiss chard requires plenty of water, although the soil should have good drainage.
Swiss chard grows well on a variety of soils, although, fertile, potting soils with high organic matter content are preferred. Heavier soils can be quite productive if these are well drained and irrigated. Swiss chard is particularly sensitive to saturated soil conditions and to acidity. The optimum soil pH is 6.2 to 6.9 (Hodges, 1992). Due to the relative fast life cycle of this vegetable compared to other field crops like cereals and legumes, Swiss chard tend to vigorously take up nutrients within very short period of time and therefore has high tendency to pick heavy metals which could affect its food value (http://anrcatalog.ucdavis.edu).

2.6.3 Nutritional profiles of Beta vulgaris and effects on health

Swiss chard contains high levels of minerals and vitamins, rich in phosphorus, iron, potassium, and especially contains calcium and magnesium which are excellent bone-supportive nutrients. A commonly found vitamin in Swiss chard includes vitamin A which is a free radical-scavenger; vitamin K, vitamin B, vitamin E and vitamin C (Table 2.1). Swiss chard also contains vitamin B2, vitamin B6, folate, betaine, copper, protein, manganese, zinc, niacin, selenium and omega-3 fatty acids, which also has a more delicate texture and more nutrients than most other green-leaf vegetables. It is also very rich in antioxidants which scavenge free radicals and adjust blood pressure. These antioxidants are relatively abundant in high levels when Swiss chard is consumed fresh, steamed, or quickly boiled.

Due to its rich nutritional content, Swiss chard has many positive effects on human health. In 2005, studies showed that Swiss chard was the most protective nutrition against cancer risks (Ko et al., 2014). In addition to preventive potential of Swiss chard towards cancer, it is effective in combating cancer cell proliferation. For instance, in a related research, it was found that Swiss chard could prevent breast cancer because it contains high levels of lutein and other carotenoids (Longnecker et al., 1997).
Table 2.1 Nutritional profile per 100g raw Swiss chard

<table>
<thead>
<tr>
<th>Nutrients</th>
<th>Nutritional values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>84KJ(23cal)</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>4.13g</td>
</tr>
<tr>
<td>Sugar</td>
<td>1.1 g</td>
</tr>
<tr>
<td>Dietary fiber</td>
<td>2.1 g</td>
</tr>
<tr>
<td>Protein</td>
<td>1.88 g</td>
</tr>
<tr>
<td>Vitamin A</td>
<td>306 mg</td>
</tr>
<tr>
<td>Folate</td>
<td>9 µg</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>18 mg</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>1.89 mg</td>
</tr>
<tr>
<td>Vitamin K</td>
<td>327 µg</td>
</tr>
<tr>
<td>Calcium</td>
<td>58 mg</td>
</tr>
<tr>
<td>Iron</td>
<td>2.26 mg</td>
</tr>
<tr>
<td>Fat</td>
<td>0.08 g</td>
</tr>
</tbody>
</table>
CHAPTER 3

3. MATERIALS AND METHODS

3.1 Cleaning of glassware

All glassware and containers were thoroughly washed with detergent and tap water, rinsed with distilled water and thereafter soaked in 5% HNO₃ for a period of 48 hours after which they were thoroughly rinsed with distilled water and dried overnight in the oven.

3.2 Materials

All reagents used for this study: super-pure 65% nitric acid, 30% hydrogen peroxide, and 35% hydrochloric acid were analytical grade solvents and were obtained from Merck KGaA Company. Pots (size 15cm diameter by 20 cm high, and hold about 2.5L) were taken from the Horticulture Department in Bellville campus. Potting soil, Swiss chard seedling and organic granular fertilizers were purchased from Stodels Nurseries, Cape Town, South Africa.

3.3 Leachate collection

Leachate samples were obtained from Bellville landfill site near Cape Town. Collection of leachate was done in triplicate at specified time intervals. The leachates were collected in 25 L plastic jerry-can which was rinsed several times with the leachate before being filled with the leachate. A 500 ml sample of leachate was collected in plastic bottle and the pH was measured immediately. This was followed by immediate addition of concentrated HNO₃ for preservation. The acidified leachate sample was stored in a refrigerator at about 4 °C for the MP-AES analysis.
3.4 Experimental procedure

3.4.1 Preparation of pot experiment and trial management

Fifty pots sized 15cm diameter by 20 cm high, and hold about 2.5L of soil, were taken from Horticulture Department, which were washed with tap water and rinsed several times. Each pot was filled up with potting soil and placed inside greenhouse located in the Horticulture Department’s nurseries in Bellville campus. The pots were divided into five treatments; each treatment has ten pots according to the irrigation used. Treatments were; T1 distilled water (first control); T2: Tap water (second control); T3: 100% concentration of landfill leachate (as collected from landfill); T4: 50% landfill leachate (diluted 1:1 volume by volume) and T5: 25% landfill leachate (diluted 1:3 volume by volume leachate and water, respectively). Then each group was irrigated with the respective water samples for 48h prior to transplant of seedling.

![Figure 3.1 Preparation of potting soil](image)

One seedling was planted in each pot and suitable fertilizer was added to each pot at commercial recommended rate to enhance the growth. The Swiss chard seedling was the
same cultivar and age. Treatments (leachate and controls) were applied daily at regular interval throughout the duration of the experiment.

Figure 3.2 Growing of Swiss chard seedling in potting soil

3.4.2 Soil sampling

About 2.5L of Composite soil was potted in 20 cm pots in greenhouse of the Horticulture Department in the Bellville campus of CPUT. The pH of the composite soil was measured using hand-held multi system meter. After potting, initial 80g of organic granular fertilizer was added to all pots and irrigated with the respective treatments. Treatment was applied daily to maintain good soil moisture throughout the study. Clear, unused sampling bags were used for the collection of soil samples. This process of collection was repeated each week to study the effect of irrigation system on soil properties.

3.4.3 Swiss chard sampling

Leaf samples of Swiss chard were collected from each treatment in appropriately labeled brown paper bags for tissue analysis. The Swiss chard leaves were rinsed thoroughly with
CHAPTER 3

tap water and distilled water in order to remove all traces of soil and dust particles and to ensure that there is no contamination. The leaves were then dried in the oven at 60°C. Three samples of Swiss chard leaf were collected in triplicate every week from each treatment over a period of two months to investigate trend in possible accumulation of nutrients over time.

3.5 Sample preparation for different analyses

3.5.1 Soil samples

Soil samples were initially sieved with a 2 mm sieve. The soil was thoroughly mixed to achieve homogeneity and then dried in the oven at 60°C till constant weight was achieved. Once the soil had been cooled, 1.0 g of the dried soil was weighed and transferred to a 50 ml Phillips beaker. To this, 2 ml of nitric acid and 6 ml of hydrochloric acid was added. The solution was transferred to a round bottle flask and heated to approximately 85°C for approximately 30 minutes. Afterwards, the sample was cooled, filtered through Whatman GF/C filter papers, transferred to a 50 ml volumetric flask, and diluted to the mark with distilled water. The sample was then taken for analysis. (EPA Method, 2007).

3.5.2 Swiss chard samples

The Swiss chard leaves were dried in the oven at 60°C till constant weight was achieved. Moisture content was determined by difference. The dried leaves were ground in mortar and pestle, 0.1 g of each sample were weighed out accurately and transferred to a microwave digestion reaction vessel. A 2 ml of 30% hydrogen peroxide and 5 ml of 65% nitric acid were added to the contents of the vessel. The vessels were placed in the carousel digestion proceeded by means of a temperature programmer (table.1). The digestion procedure was carried out in a Milestone-MLS 1200 Mega microwave oven capable of accommodating 6 digestion vessels. After digestion, the samples were cooled, filtered
using Whatman GF/C filter paper and then transferred to the volumetric flask and made up to the mark with ultra-pure water.

**Figure 3.3** Milestone-MLS 1200 Mega microwave oven

**Table 3.1** Program for closed microwave oven procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Power (W)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>5</td>
</tr>
</tbody>
</table>

3.6 Instrumentation

3.6.1 Microwave plasma-atomic emission spectrometer (MP-AES)

Microwave Plasma-Atomic Emission Spectrometer was used for all the sample analysis to determine the concentration of metals in the samples. The MP-AES Spectrometer was chosen for this study for its multi-element capabilities and it is less subjective to chemical
and matrix interferences. The MP-AES which was used for our analysis has several advantages: Runs on air, eliminates need for source/hollow cathode lamps, and simple installation – no chiller. It has a higher resolution, it is more flexible in the number and the selection of lines is infinitely variable, automatic background correction and it is safer as no flammable gases are required.

3.6.2 pH meter

The pH of the soil and leachate samples was measured using a pH meter. The pH of the soil was determined using sieved soil samples. Three grams of soil samples was weighed in clean 50 ml glass beakers. Ultra-pure water was added to form a slurry solution from which pH measurements were done using the pH meter. Before use, the pH meter was first calibrated with standard buffer solution of pH 4 and 7.

3.6.3 Scanning electron microscopy (SEM)

A SEM can generate image for specimens with magnifications from 15X to 30,000X. The fully digital scanning electron microscope or SEM is useful for many purposes such as examining fracture surfaces. SEM was used to study the morphology of the fresh leaves samples of Swiss chard to determine possible structural changes due to heavy metals accumulation and the result was compared with the controls.
4. RESULTS AND DISCUSSION

Experiments were carried out under greenhouse conditions from January to September, 2014. The plants were grown in the sunlight and irrigated with 50 ml/day of distilled water or tap water (for control treatments, not exposed to leachates) or with a similar quantity of different concentrations of landfill leachates (25%, 50% or 100%) for treatments exposed to leachates. The ambient temperature in the greenhouse during the experiment was in the range of 23.8°C to 26.5°C. A total of fifty pots were sown with Swiss chard. Each treatment has ten pots. Three samples of soil and Swiss chard were collected from each treatment every week and analyzed.

4.1 Characterization of applied irrigation samples

The leachates which were collected from Bellville landfill site in Cape Town, South Africa (Fig 4.1) had orange brown to yellowish colour and a malodorous smell, which may be due to the presence of organic acids, resultant of the high concentration of organic matter (Williams, 2004).

![Figure 4.1 landfill leachate site at Bellville, Cape Town, South Africa](image-url)
Several parameters were analysed in the leachate, the tap water and distilled water. These parameters include pH, electrical conductivity (EC), sodium adsorption ratio (SAR), osmotic potential (OP), and concentrations of Cl, Ca, Mg, Na, K, B, Fe and Mn (Table 4.1).

The results of analysis showed the pH ranged from very low (leachate) to medium (tap water) and neutral in the case of distilled water. Typical pH values for other studies of landfills range from 4.5-7.5 with a mean of 6.1 for landfills in the acid phase, to 7.5-9.0 with a mean of 8.0 in the methanogenic phase (Kjeldsen et al., 2002), which would put Bellville Landfill leachate (pH of 7.8) in the methanogenic phase. Other literature reviews and studies have reported pH to be stable and near neutral during the methanogenic phase (Griffith et al., 2006; Heyer et al., 2001).

The electrical conductivity (EC), which defines as the concentration of total salt content in irrigation water, estimated in terms of EC, is 383 mS/m in the leachate and is higher than the considered suitable value for irrigation waters (< 225 mS/m). Leachates also have high concentration of sodium and chloride relative to the other waters.

The Sodium adsorption ratio (SAR) was calculated (using equation 1 in Chapter 2) in order to determine the sodicity or alkalinity hazard of irrigation waters. Based on the SAR (Fig. 4.2) value from (Table 1), irrigation waters can be rated into different categories of sodicity as follows: Safe: < 10, moderately safe: 10–18, moderately unsafe: 19–26, unsafe: > 26 (Richards, 1954). Hence, the leachates were considered moderately safe while the tap and distilled water are safe. Analysis of the SAR and EC of the leachate can be used to predict whether dispersion or swelling of clays is likely to occur when the leachate is irrigated (Table 4.1). The SAR and EC of the leachate in the irrigation collection tank were used to assess the salinity risk for the leachate that was irrigated in potted soil. When the SAR and EC of the irrigated (Table 4.1) were compared with guidelines for the
interpretation of water quality for irrigation (Halliwell et al., 2001), it is appears that soil structural problems are not expected. The plot of the relationship between SAR and EC (Figure 4.2) suggests that soil structural problems are unlikely. Although the SAR of the leachate is relatively high, the EC is great enough to be above the “critical coagulation value” needed for clay dispersion to occur.

![Figure 4.2](image.png)

**Figure 4.2** Relationship between SAR and EC of irrigation water to estimate structural stability.

The Boron concentration in the three types of irrigation water was < 1 mg/l which can be considered as low hazard. The leachate heavy metal concentrations were low (Table 4.1). This correlates with studies reported on other landfill studies (Qu et al., 2008). This may be attributed to the high organic matter content from the vegetable processing waste deposited in the landfill.

Organic matter present in the landfill can absorb significant amounts of metals, hence, decreasing their solubility (Kjeldsen et al., 2002). The mean pH of 7.8 may have also aided the adsorption of heavy metals; this is because the adsorption process occurs more readily
at neutral to high pH values (Taulis, 2005). The sulphate present in the leachate also contributes to the relatively low metal concentrations as metal-sulphite precipitates form readily during the methanogenic phase.

Table 4.1 Characteristics of leachate, tap water and distilled water used in the pot experiment

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Land fill leachate</th>
<th>Tap water</th>
<th>Distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8</td>
<td>8.5</td>
<td>7.1</td>
</tr>
<tr>
<td>EC(mS/m)</td>
<td>383</td>
<td>9.5</td>
<td>1.0</td>
</tr>
<tr>
<td>OP (kPa)</td>
<td>137.88</td>
<td>3.42</td>
<td>0.35</td>
</tr>
<tr>
<td>Na*</td>
<td>714.5</td>
<td>3.42</td>
<td>0.35</td>
</tr>
<tr>
<td>K</td>
<td>56.8</td>
<td>0.1</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu</td>
<td>0.80</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn</td>
<td>0.63</td>
<td>0.14</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.3</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>133.7</td>
<td>16.7</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl</td>
<td>983.0</td>
<td>16.9</td>
<td>3.90</td>
</tr>
<tr>
<td>Fe</td>
<td>0.27</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Mn</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>B</td>
<td>0.42</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>HCO₃</td>
<td>1358</td>
<td>37.4</td>
<td>6.9</td>
</tr>
<tr>
<td>SO₄</td>
<td>49.0</td>
<td>11.0</td>
<td>2.0</td>
</tr>
<tr>
<td>SAR</td>
<td>16.93</td>
<td>0.24</td>
<td>1.37</td>
</tr>
</tbody>
</table>

*All parameters from Na to SO₄ are measured in mg/L (ppm)*

4.2 Chemical characteristics of potting soil used in this study

The determined chemical properties of the soils included pH of soil, electrical conductance of the soil solution, exchangeable cations: Ca, Mg, Na, K, and other trace elements: B, Cu, Zn, Mn, and Fe content. The results of chemical characteristics of uncontaminated potting soil are presented in Table 4.2.
Table 4.2 Characteristics of uncontaminated soil used in pot experiment

<table>
<thead>
<tr>
<th>Property of the soil</th>
<th>pH</th>
<th>EC (ms/m)</th>
<th>Na (cmol/kg)</th>
<th>K</th>
<th>Ca (cmol/kg)</th>
<th>Mg (mg/kg)</th>
<th>Mn (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>B (mg/kg)</th>
<th>Fe (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>7.3</td>
<td>80</td>
<td>2.06</td>
<td>1.87</td>
<td>7.31</td>
<td>4.2</td>
<td>43.5</td>
<td>3.8</td>
<td>26.0</td>
<td>3.4</td>
<td>169.4</td>
</tr>
</tbody>
</table>

4.2.1 The effect of leachate, tap and distilled water irrigation on potting soil properties

Irrigation of soil with leachate, tap water, de-ionized water cause changes in the chemical composition of soil pH, electrical conductivity, sodium concentration and some trace metal elements as discussed below.

4.2.1.1 Effect of leachate, tap and distilled water irrigation on soil pH

Since excessive acidity or alkalinity can be detrimental to plant, determination of soil pH is important. The experimental data of different soil pH resulting from leachate, tap and distilled water irrigations are presented in Fig. 4.3. It was observed that the pH of potting soil increased with leachate concentration (25%, 50% and 100%). The probable reason for this observation may be due to high concentration of monovalent and divalent cation contained in the leachate. The concentration of each constituent of leachate is presented in Table 4.1. The leachate also contained chloride and sulphate anions. As a result of negative charge developed by the soil particles, ions are absorbed on the surface (Li et al., 2010). Any process that encourages presence of high levels of exchangeable bases such as calcium, magnesium, potassium and sodium will reduce acidity and increase alkalinity. Hence pH of the potting soils increases as the leachate concentration increased. In contrast, only a slight variation was observed in pH values of soils irrigated with tap and distilled water.
waters, as the concentration of these cations are low in the control treatments. There was a progressive increase in soil pH over time with every 100% increase in concentration of leachate; suggesting an accumulation of base forming salts in the treated soil compared to the control.

![Graph showing the effect of different irrigation waters on soil pH](image)

**Figure 4.3** The effect of different irrigation waters on soil pH

### 4.2.1.2 Effect of irrigation waters on electrical conductivity of the soil (EC)

Plants are normally sensitive to soil properties such as electrical conductivity (EC). Figure 4.4 shows the change of soil EC during 8 weeks of pot experiment. The result shows continuous increase in EC of the soil when irrigated with 25%, 50%, 100% leachate. The 100% leachate irrigation shows the highest EC ~ 400 (mS/m) in the eighth week after transplant. The obvious reason for this increase is the availability of the high concentration of cations such as Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$ and anions SO$_4^{2-}$, Cl$^-$, HCO$_3^-$, which are responsible for carrying electrical charges and conduct electrical current (Garcia *et al.*, 1993). Consequently, the high concentration of ions in the soil leachate increases the EC of the
soil. On the other hand, the EC of soil irrigated with tap water and distilled water also show minimal to slight change during the eight weeks of the experiment as shown in Fig.4.4. This slight increase in EC from tap and distilled water irrigation may be attributed to the release of cations into soil solution due to irrigation while the significant increase was due to additive and regular accumulation of cations from the leachates treatments.

**Figure 4.4** The effect of irrigation waters on soil electrical conductivity

The EC gives an estimate of the total dissolved salts present in the leachate. Excessive salt concentrations can affect plants ability for water uptake. Therefore EC can be used for prediction if the irrigated leachate is likely to affect the crops (Table 4.3). When the mean EC leachate (383 μS cm⁻¹) was compared to Table 4.3, the Salinity Rating was high, which implies only salt tolerant plants would be unaffected by the high salt content present in the leachate. However, when the controlled sample (95μS cm⁻¹) was compared, the Salinity Rating was very low. The Swiss chard species is moderately salt sensitive
(ANZECC et al., 2000), therefore the growth rate may be affected by the presence of salts in the 100% leachate irrigated treatment.

**Table 4.3 Irrigation water ratings based on electrical conductivity**

<table>
<thead>
<tr>
<th>EC µScm⁻¹</th>
<th>Water salinity rating</th>
<th>Plant suitability (based on salt tolerance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;650</td>
<td>Very low</td>
<td>Sensitive</td>
</tr>
<tr>
<td>650-1300</td>
<td>Low</td>
<td>Moderately sensitive</td>
</tr>
<tr>
<td>1300-2900</td>
<td>Medium</td>
<td>Moderately tolerant</td>
</tr>
<tr>
<td>2900-5200</td>
<td>High</td>
<td>Tolerant</td>
</tr>
<tr>
<td>5200-8100</td>
<td>Very high</td>
<td>Very tolerant</td>
</tr>
<tr>
<td>&gt;8100</td>
<td>Extreme</td>
<td>Generally too saline</td>
</tr>
</tbody>
</table>

**4.2.1.3 Effect of irrigation waters on the level of trace elements in the soil**

The accumulation of copper, zinc and chromium in soils irrigated with different leachate concentrations and the two controlled water treatments during the experimental period are presented in Table 4.4. From the results of the analyzed potting soil, it was observed that there was increase in the concentration of zinc for all the treatments, and the relative level of increase in contamination by the irrigation waters was in the order 100% leachate > 50% leachate > 25% leachate > tap ~ distilled water. Globally, the concentration of zinc in unpolluted soils is expected to be between 10 mg/kg and 300 mg/kg, while the mean concentration is expected to be about 40 mg/kg. The results of this study fall within this range. Also copper and chromium showed gradual increase in accumulation during the treatment period. The highest copper concentration was obtained in 100% leachate irrigated soil (15.0 mg/kg) while the lowest was recorded in the distilled water irrigated soils (4.50 mg/kg). Also the highest chromium concentration was obtained in 100%
leachate irrigated soil (6.00 mg/kg), and the lowest was found in the tap water irrigated soil (3.50 mg/kg). The copper and chromium content of soils obtained in this study are similar to those reported in a study conducted in India (Shridhar et al., 2014). The low accumulation of these trace elements is a resulted of their low concentration in the leachate.

Table 4.4 Trace metals content in soil during irrigation with different concentration of leachate, tap water and de-ionized water.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Trace element (mg/kg)</th>
<th>100% Leachate</th>
<th>50% Leachate</th>
<th>25% Leachate</th>
<th>Tap water</th>
<th>De-ionized water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>W2</td>
<td>5.00</td>
<td>4.00</td>
<td>3.00</td>
<td>2.00</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>11.8</td>
<td>10.0</td>
<td>6.0</td>
<td>5.00</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>W8</td>
<td>15.0</td>
<td>12.5</td>
<td>10.5</td>
<td>5.50</td>
<td>4.50</td>
</tr>
<tr>
<td>Zn</td>
<td>W2</td>
<td>9.5</td>
<td>15.5</td>
<td>9.50</td>
<td>12.5</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>34.5</td>
<td>34.5</td>
<td>17.0</td>
<td>21.0</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>W8</td>
<td>36.0</td>
<td>29.5</td>
<td>24.5</td>
<td>23.0</td>
<td>23.5</td>
</tr>
<tr>
<td>Cr</td>
<td>W2</td>
<td>1.5</td>
<td>2.00</td>
<td>2.00</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>4.00</td>
<td>3.50</td>
<td>4.00</td>
<td>3.50</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>W8</td>
<td>6.00</td>
<td>5.00</td>
<td>4.50</td>
<td>3.50</td>
<td>4.01</td>
</tr>
</tbody>
</table>

*W2: Week two, W5: Week five, W8: Week eight of the experiment

4.2.1.4 Effect of irrigation waters on the exchangeable cation content of the soil

The presence of several ions in the leachates is of potential nutritional value to plants, especially when the heavy metals content are low. However, high concentrations of some ions can potentially increase salinity in soils. In general, the pollutant ions with potential of increasing soil salinity that were assessed in this study include Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺ and Na⁺. The Na content was of greater interest since it is an important contributor to soil salinity. The Na concentrations in the three different leachate concentration had the highest cation content.
The results (Figure 4.5- 4.7) reveal that the salt content in the soils under landfill leachate treatment increased proportionally with the respective salt concentration. Increased soil salinity from week two to week eight reflected increased leachate salinity and the magnitude of the increase depends on the salt concentration in the leachate. However, there was only a slight presence of Na, Ca and Mg in potting soil when tap and distilled waters were used for irrigation, and were under the threshold level as shown in Figure 4.4- 4.6.

**Figure 4.5** The change in concentrations of Na in potting soils during second, fifth and eighth weeks of the experiment as affected by different concentrations of leachate
Figure 4. 6 The change in concentrations of Mg in potting soils during second, fifth and eighth weeks of treatment as affected by different concentrations of leachate

Figure 4. 7 The change in concentrations of Ca in potting soils during second, fifth and eighth weeks of the experiment as affected by different concentrations of leachate

4.2.1.5 Effects of Salinity (EC) and sodicity on Soil Physical Properties

Saline irrigation water contains dissolved salts. Soil water salinity can affect soil physical properties by causing fine particles to bind together into aggregates. This process is known as flocculation and is beneficial in terms of soil aeration, root penetration, and root growth.
Although increasing soil solution salinity has a positive effect on soil aggregation and stabilization, at high levels, salinity can have negative and potentially lethal effects on plants. On the other hand, Sodicity refers specifically to the amount of sodium present in irrigation water. Irrigating with water that has excess amounts of sodium can adversely impact soil structure, making plant growth difficult. Sodium has the opposite effect of salinity on soils. The primary physical processes associated with high sodium concentrations are soil dispersion and clay platelet and aggregate swelling (Parida et al., 2005).

Sand particles are larger and therefore, have larger pore spaces for water to pass through. Under normal irrigation practices, sandy soils will naturally be able to flush more water through the root zone than clay soils. Hence, sandy soils can withstand higher saline irrigation water because more dissolved salts will be removed from the root zone by leaching. The above results also confirmed that the dispersion or swelling of the soil particle was not likely to occur as the EC was great enough to be above the “critical coagulation value” needed for dispersion to occur; although the sodium rate in the potting soil was high (Bernstein et al., 1975).

4.3 The effect of irrigation waters on test crop (Swiss chard) properties

In order to investigate the changes or effects of different types of irrigation waters on growth of the test crop, leaf samples from Swiss chard were taken every week for analysis.

4.3.1 Change in the height of Swiss chard during the experimental period

Figure 4.8 shows the observed change in heights of Swiss chard species during the applications of different leachate concentrations and controls (tap, and distilled water). The result indicated the height of the Swiss chard species gradually increased for all leachate concentrations in the first weeks and reached a steady state after 4 weeks, with a recorded
maximum height of 18.5 cm. The results also showed about 50% drop in height of Swiss chard plant at 100% leachate application compared with distilled water irrigation.

The decline in growth of Swiss chard could be due to the high EC (salinity) value in the potting soil, which is resultant of high salinity of the leachate (Chiemchaisri et al., 2005). As salinity increases each week due to application of irrigation waters, the amount of water available for plants’ uptake decreases as the force with which the remaining water is held in the soil increases, making it progressively more difficult to withdraw water. The irrigation with tap and distilled water showed obvious growth from 9.2 cm in the first week to ~38.3 cm in the eight week of the treatment. It could therefore be conclude that the application of the leachate has a deleterious effect in photosynthate accumulation in Swiss chard species tested in this study due to accumulative toxic level of nutrients, high EC and osmotic limitations between the root and the soil solution.

**Figure 4.8** The change of Swiss chard height resultant from different irrigation waters
4.3.2 Effect of leachates, tap and de-ionized water irrigations on level of trace elements in Swiss chard species

The illustration in Table 4.5 shows the concentration of copper, zinc and chromium in the leaves of Swiss chard irrigated with different leachate concentrations and the two controlled water treatments during the experimental period. The results show accumulation of these metals in the tissue Swiss chard leaves with the highest concentration of 2.00, 11.0 and 2.50 mg/kg for Cu, Zn and Cr respectively after eight weeks of irrigation with pure concentrated leachate (100%). Nevertheless, the concentration of these metals in plant tissue does not exceed the globally expected safe value recommended for human health.

Table 4.5 Trace metals content in Swiss chard leaves during irrigation with different concentrations of leachates, tap and de-ionized water.

<table>
<thead>
<tr>
<th>Trace element (mg/kg)</th>
<th>Water Type</th>
<th>100% Leachate</th>
<th>50% Leachate</th>
<th>25% Leachate</th>
<th>Tap water</th>
<th>De-ionized water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>W2</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>1.00</td>
<td>1.00</td>
<td>1.50</td>
<td>1.50</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>W8</td>
<td>2.00</td>
<td>1.50</td>
<td>1.55</td>
<td>1.06</td>
<td>1.00</td>
</tr>
<tr>
<td>Zn</td>
<td>W2</td>
<td>3.00</td>
<td>2.00</td>
<td>1.50</td>
<td>1.50</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>9.50</td>
<td>7.00</td>
<td>8.50</td>
<td>4.00</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>W8</td>
<td>11.0</td>
<td>6.50</td>
<td>6.00</td>
<td>4.50</td>
<td>4.50</td>
</tr>
<tr>
<td>Cr</td>
<td>W2</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>W5</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>W8</td>
<td>2.00</td>
<td>1.70</td>
<td>1.50</td>
<td>1.30</td>
<td>1.02</td>
</tr>
</tbody>
</table>

*W2 : Week two, W5: Week five, W8: Week eight of the experiment

4.3.3 Effect of leachate, tap and de-ionized water on the exchangeable cation concentrations in Swiss chard leaves

The results show a differential accumulation of the three cations in Swiss chard leaves during the experimental period (Figure 4.9- 4.11). The increase in Na cation in the soils as
a consequence of leachate irrigation was clearly reflected by the content of this element in the leaves of Swiss chard species. The Na content was the most affected nutrient. The uptake of sodium by Swiss chard leaves clearly increased with time when leachate was used in irrigation system, which correlates with the concentration of this element in the leachate and ultimately in the soil.

The results also shows decrease in Ca and Mg concentrations, which has also been described for some grasses under leachate irrigations (Cureton et al., 1991). Calcium deficiency was also reported by Grieve et al., (1998) in salt-stressed maize shoots. This could be due to the replacement of Ca and Mg by Na (Grieve et al., 1998). Such increase in the cation content (mainly Na) in the plants is one of the important aspects that must be taken into account when leachates are used as irrigation water because high concentrations of cation in the plant tissue may inhibit some biochemical processes, which are generally accompanied by a decline in growth (Greenway et al., 1980).

Similarly, the Na, Ca and Mg concentrations also increased gradually in the leaf tissues of Swiss chard when tap and de-ionized water were used for irrigation (Figure 4.9 – 4.11). High Sodicity becomes a problem when enough salts accumulate in the root zone which negatively affects crops growth. As salt concentrations increase in the root zone, the water potential between the plant and soil increases, thereby reducing the plant-available water and making it harder for plants to take up water from surrounding soil. This lowers the amount of water available to the plant, regardless of the amount of water in the root zone. High salinity can also cause increases in epidermal and mesophyll thickness, and elongation of the palisade cell in the leaves. This ultimately negatively affects growth in plant.
Figure 4. 9 Change in concentration of Na in Swiss chard leaves during second, fifth and eighth weeks of the experiment

Figure 4. 10 Change in concentration of Mg in Swiss chard leaves during second, fifth and eighth weeks of the experiment
Figure 4.11 Change in concentration of Ca in Swiss chard leaves during second, fifth and eighth weeks of the experiment

4.3.4 Effect of irrigation waters on ultra-structural leaves morphology of Swiss chard

The authentication of microscopically important ultra-structures using the Scanning Electron Microscope (SEM) plays a vital role in the identification, location and distribution of some botanical features of plants (Vaishali et al., 2008). The micrographs of the Scanning Electron Microscope (SEM) revealed non-uniform granules with rough surfaces of Swiss chard leaves with probable presence of stomata as shown in Figures 4.12 a – 4.12e and Figures 4.13a – 4.13e. After irrigation with different concentrations of leachate, the leaves exhibited agglomerated smooth surfaces and the stomata may have been embedded with Na and Cl, which were confirmed by Energy Dispersive Spectroscopy (EDS). The accumulation of these metals cause increases in epidermal and mesophyll thickness, and elongation of the palisade cells. While, the tissue of Swiss chard leaves irrigated with control water show no change in the surface structure between week one and eight, irregular surface with the presence of stomata. Zooming-in further on figures 4.12a and 4.13a (100% leachate irrigated treatment), the results of the SEM analysis also
revealed possible closure of the stomata opening occasioned by osmotic pressure, deposition of metals and reduced photosynthesis; which would have limited carbon dioxide uptake (Zhu et al., 2001). SEM results correlates well with the trend in plant height from week two to week eight and confirms early studies that the leaves of salt stressed plants are smaller with thick epidermal and mesophyll cells (Parida et al., 2005).
CHAPTER 4

Figure 4.12 Scanning electron micrographs of (a) 25% Leachate, (b) 100% Leachate, (c) Tap water, (d) 50% Leachate (e) Distilled water, in the first week of the experiment.
Figure 4.13 Scanning electron micrographs of (a) 25% Leachate, (b) 100% Leachate, (c) Tap water, (d) 50% Leachate, (e) distilled water, in the eight week of the experiment.
5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

The results of this study indicate that the concentrations of cations, electrical conductivity and pH in the potted soils increased with time when the leachate was used as irrigation water compared with the utilization of tap and distilled water where little or no change was observed. However the heavy metals concentration was within allowed limits and shows no significant difference between leachate irrigated and non-irrigated one, thus indicating the low concentration of these heavy metals in leachate. Also boron toxicity was not observed; as the leachate had very low concentration of B.

The selected crop for this study shows reduction in growth in soil irrigated with 100% leachate and 50% leachate compared with the growth level observed in irrigation with tap and distilled water. This decline in growth could be attributed to the higher Na content in the leachate used for the irrigation of the crop; which tends to replace Ca and Mg in solution thereby limiting their uptake and ultimately affecting structural growth in Swiss chard.

However, Swiss chard species were able to survive up to eight weeks with the applied leachate irrigation. This may be attributed to the fact that Swiss chard has high tolerance to salinity. Furthermore, the results show the concentration of heavy metals in plant tissues over the period of this study falls within globally acceptable values which poses no harm for human consumption and health.
5.2 Future work and recommendations

In future, investigations of the effect of leachate on the other crops such as tomato, carrot and cabbage, which has variable tolerance levels, may be conducted. The study may also be extended to the utilization of different leachate sources and lower concentrations, to investigate their effect on ground water, soil and accumulation of important nutrients like Zn in crop.
References:


MCDOUGALL, W.J., FUSCO, R.A. and O'BRIEN, R.P., 1980. Containment and
treatment of the Love Canal landfill leachate. *Journal of the Water Pollution Control
Federation*, 52(12), pp. 2914-2924.

testing for heavy metals", *Communications in Soil Science and Plant Analysis*, 3(11-14), pp.
1661-1700.

utilization of forage grasses for decontamination of spray-irrigated leachate from a


facilitate access of small-scale farmers in South Africa to input and product markets.
*Agrekon*, 46(2), pp. 219-244.

PARIDA, A.K. and DAS, A.B., 2005. Salt tolerance and salinity effects on plants: A

PATHAK, C., CHOPRA, A.K. and SRIVASTAVA, S., 2013. Accumulation of heavy
metals in Spinacia oleracea irrigated with paper mill effluent and sewage. *Environmental
Monitoring and Assessment*, 185(9), pp. 7343-7352.

QUIRK, J.P., 2001. The significance of the threshold and turbidity concentrations in
1185-1217.


APPENDIX

APPENDIX 1:
RESULTS OF CALPRATION CURVE OF MICROWAVE PLASMA-ATOMIC EMISSION SPECTROMETER

A. Ca (422.673 nm) Calibration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Intensity Replicate 1</th>
<th>Intensity Replicate 2</th>
<th>Intensity Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Ca 422.673</td>
<td>0 ppm</td>
<td></td>
<td>77.87</td>
<td>221.22</td>
<td>284.76</td>
<td>4.78</td>
<td>260.79</td>
</tr>
<tr>
<td>Standard 1</td>
<td>Ca 422.673</td>
<td>0.2 ppm</td>
<td></td>
<td>49637.12</td>
<td>51093.19</td>
<td>50619.18</td>
<td>50449.83</td>
<td>742.66</td>
</tr>
<tr>
<td>Standard 2</td>
<td>Ca 422.673</td>
<td>0.5 ppm</td>
<td></td>
<td>94501.50</td>
<td>96062.67</td>
<td>95442.98</td>
<td>95335.72</td>
<td>786.09</td>
</tr>
<tr>
<td>Standard 3</td>
<td>Ca 422.673</td>
<td>1 ppm</td>
<td></td>
<td>183927.83</td>
<td>181022.87</td>
<td>178535.01</td>
<td>181161.90</td>
<td>2699.10</td>
</tr>
<tr>
<td>Standard 4</td>
<td>Ca 422.673</td>
<td>2 ppm</td>
<td></td>
<td>346303.94</td>
<td>336108.32</td>
<td>327962.44</td>
<td>336791.57</td>
<td>9189.82</td>
</tr>
<tr>
<td>Standard 5</td>
<td>Ca 422.673</td>
<td>5 ppm</td>
<td></td>
<td>877116.43</td>
<td>874764.99</td>
<td>894745.97</td>
<td>882205.80</td>
<td>10924.10</td>
</tr>
<tr>
<td>Standard 6</td>
<td>Ca 422.673</td>
<td>10 ppm</td>
<td></td>
<td>1776962.77</td>
<td>1740141.48</td>
<td>1771994.82</td>
<td>1763033.02</td>
<td>19979.67</td>
</tr>
</tbody>
</table>

\[ y = 175693x + 3361.2 \]

\[ R^2 = 0.9998 \]

Cr (425.433 nm) Calibration

\[ y = 34973x + 1105.6 \]

\[ R^2 = 0.9995 \]
B. Cr (425.433 nm) Calibration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Intensity Replicate 1</th>
<th>Intensity Replicate 2</th>
<th>Intensity Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Cr 425.433</td>
<td>0 ppm</td>
<td>-13.83</td>
<td>9.37</td>
<td>4.85</td>
<td>0.13</td>
<td>12.30</td>
<td></td>
</tr>
<tr>
<td>Standard 1</td>
<td>Cr 425.433</td>
<td>0.1 ppm</td>
<td>7322.66</td>
<td>7374.09</td>
<td>7372.96</td>
<td>7356.57</td>
<td>29.37</td>
<td></td>
</tr>
<tr>
<td>Standard 3</td>
<td>Cr 425.433</td>
<td>0.5 ppm</td>
<td>18154.68</td>
<td>17913.72</td>
<td>17940.85</td>
<td>18003.08</td>
<td>131.99</td>
<td></td>
</tr>
<tr>
<td>Standard 4</td>
<td>Cr 425.433</td>
<td>1 ppm</td>
<td>34862.01</td>
<td>34649.26</td>
<td>34786.53</td>
<td>34765.93</td>
<td>107.86</td>
<td></td>
</tr>
<tr>
<td>Standard 5</td>
<td>Cr 425.433</td>
<td>2 ppm</td>
<td>71291.72</td>
<td>71123.80</td>
<td>70673.79</td>
<td>71029.77</td>
<td>319.52</td>
<td></td>
</tr>
<tr>
<td>Standard 6</td>
<td>Cr 425.433</td>
<td>5 ppm</td>
<td>177233.14</td>
<td>176424.22</td>
<td>175079.07</td>
<td>176245.48</td>
<td>1088.10</td>
<td></td>
</tr>
</tbody>
</table>

C. Ni (305.082 nm) Calibration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Intensity Replicate 1</th>
<th>Intensity Replicate 2</th>
<th>Intensity Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Ni 305.082</td>
<td>0 ppm</td>
<td>10.64</td>
<td>-5.97</td>
<td>-4.59</td>
<td>0.03</td>
<td>9.22</td>
<td></td>
</tr>
<tr>
<td>Standard 1</td>
<td>Ni 305.082</td>
<td>0.1 ppm</td>
<td>659.58</td>
<td>685.31</td>
<td>690.49</td>
<td>678.46</td>
<td>16.55</td>
<td></td>
</tr>
<tr>
<td>Standard 3</td>
<td>Ni 305.082</td>
<td>0.5 ppm</td>
<td>2664.62</td>
<td>2666.60</td>
<td>2726.15</td>
<td>2685.79</td>
<td>34.97</td>
<td></td>
</tr>
<tr>
<td>Standard 4</td>
<td>Ni 305.082</td>
<td>1 ppm</td>
<td>5060.07</td>
<td>5162.27</td>
<td>5169.68</td>
<td>5130.67</td>
<td>61.26</td>
<td></td>
</tr>
<tr>
<td>Standard 5</td>
<td>Ni 305.082</td>
<td>2 ppm</td>
<td>10400.54</td>
<td>10529.14</td>
<td>10621.89</td>
<td>10517.19</td>
<td>111.16</td>
<td></td>
</tr>
<tr>
<td>Standard 6</td>
<td>Ni 305.082</td>
<td>5 ppm</td>
<td>24682.14</td>
<td>25070.45</td>
<td>25100.05</td>
<td>24950.88</td>
<td>233.21</td>
<td></td>
</tr>
</tbody>
</table>
**D. Zn (481.053 nm) Calibration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Intensity Replicate 1</th>
<th>Intensity Replicate 2</th>
<th>Intensity Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Zn</td>
<td>481.053</td>
<td>ppm</td>
<td>-0.42</td>
<td>0.74</td>
<td>-0.32</td>
<td>0.00</td>
<td>0.64</td>
</tr>
<tr>
<td>Standard 1</td>
<td>Zn</td>
<td>481.053</td>
<td>ppm</td>
<td>32.35</td>
<td>37.95</td>
<td>35.92</td>
<td>35.41</td>
<td>2.84</td>
</tr>
<tr>
<td>Standard 3</td>
<td>Zn</td>
<td>481.053</td>
<td>ppm</td>
<td>111.18</td>
<td>111.41</td>
<td>105.43</td>
<td>109.34</td>
<td>3.39</td>
</tr>
<tr>
<td>Standard 4</td>
<td>Zn</td>
<td>481.053</td>
<td>ppm</td>
<td>195.00</td>
<td>206.07</td>
<td>212.95</td>
<td>204.67</td>
<td>9.06</td>
</tr>
<tr>
<td>Standard 5</td>
<td>Zn</td>
<td>481.053</td>
<td>ppm</td>
<td>417.28</td>
<td>405.15</td>
<td>421.37</td>
<td>414.60</td>
<td>8.44</td>
</tr>
<tr>
<td>Standard 6</td>
<td>Zn</td>
<td>481.053</td>
<td>ppm</td>
<td>973.98</td>
<td>977.20</td>
<td>966.73</td>
<td>972.30</td>
<td>5.92</td>
</tr>
</tbody>
</table>

**Co (340.512 nm) Calibration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Intensity Replicate 1</th>
<th>Intensity Replicate 2</th>
<th>Intensity Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Co</td>
<td>340.512</td>
<td>ppm</td>
<td>-0.42</td>
<td>0.74</td>
<td>-0.32</td>
<td>0.00</td>
<td>0.64</td>
</tr>
<tr>
<td>Standard 1</td>
<td>Co</td>
<td>340.512</td>
<td>ppm</td>
<td>32.35</td>
<td>37.95</td>
<td>35.92</td>
<td>35.41</td>
<td>2.84</td>
</tr>
<tr>
<td>Standard 3</td>
<td>Co</td>
<td>340.512</td>
<td>ppm</td>
<td>111.18</td>
<td>111.41</td>
<td>105.43</td>
<td>109.34</td>
<td>3.39</td>
</tr>
<tr>
<td>Standard 4</td>
<td>Co</td>
<td>340.512</td>
<td>ppm</td>
<td>195.00</td>
<td>206.07</td>
<td>212.95</td>
<td>204.67</td>
<td>9.06</td>
</tr>
<tr>
<td>Standard 5</td>
<td>Co</td>
<td>340.512</td>
<td>ppm</td>
<td>417.28</td>
<td>405.15</td>
<td>421.37</td>
<td>414.60</td>
<td>8.44</td>
</tr>
<tr>
<td>Standard 6</td>
<td>Co</td>
<td>340.512</td>
<td>ppm</td>
<td>973.98</td>
<td>977.20</td>
<td>966.73</td>
<td>972.30</td>
<td>5.92</td>
</tr>
</tbody>
</table>
**E. Co (340.512 nm) Calibration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Co 340.512</td>
<td>0 ppm</td>
<td></td>
<td>-28.94</td>
<td>19.76</td>
<td>9.15</td>
<td>-0.01</td>
<td>25.61</td>
</tr>
<tr>
<td>Standard 1</td>
<td>Co 340.512</td>
<td>0.1 ppm</td>
<td></td>
<td>940.09</td>
<td>960.41</td>
<td>968.34</td>
<td>956.28</td>
<td>14.57</td>
</tr>
<tr>
<td>Standard 3</td>
<td>Co 340.512</td>
<td>0.5 ppm</td>
<td></td>
<td>3666.99</td>
<td>3743.27</td>
<td>3699.47</td>
<td>3703.24</td>
<td>38.28</td>
</tr>
<tr>
<td>Standard 4</td>
<td>Co 340.512</td>
<td>1 ppm</td>
<td></td>
<td>7081.18</td>
<td>7056.93</td>
<td>7062.04</td>
<td>7063.38</td>
<td>15.61</td>
</tr>
<tr>
<td>Standard 5</td>
<td>Co 340.512</td>
<td>2 ppm</td>
<td></td>
<td>14277.73</td>
<td>14328.12</td>
<td>14336.51</td>
<td>14314.12</td>
<td>31.79</td>
</tr>
<tr>
<td>Standard 6</td>
<td>Co 340.512</td>
<td>5 ppm</td>
<td></td>
<td>34248.36</td>
<td>34195.05</td>
<td>34371.33</td>
<td>34271.58</td>
<td>90.40</td>
</tr>
</tbody>
</table>

F. Cu (327.395 nm) Calibration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Cu 327.395</td>
<td>0 ppm</td>
<td></td>
<td>23.51</td>
<td>19.91</td>
<td>-43.05</td>
<td>0.12</td>
<td>37.43</td>
</tr>
<tr>
<td>Standard 1</td>
<td>Cu 327.395</td>
<td>0.1 ppm</td>
<td></td>
<td>10967.93</td>
<td>10866.28</td>
<td>11003.39</td>
<td>10945.87</td>
<td>71.17</td>
</tr>
<tr>
<td>Standard 2</td>
<td>Cu 327.395</td>
<td>0.5 ppm</td>
<td></td>
<td>25752.86</td>
<td>25531.85</td>
<td>25661.95</td>
<td>25648.89</td>
<td>111.08</td>
</tr>
<tr>
<td>Standard 3</td>
<td>Cu 327.395</td>
<td>1 ppm</td>
<td></td>
<td>49658.02</td>
<td>49802.03</td>
<td>49707.88</td>
<td>49722.64</td>
<td>73.13</td>
</tr>
<tr>
<td>Standard 4</td>
<td>Cu 327.395</td>
<td>2 ppm</td>
<td></td>
<td>101011.55</td>
<td>101592.57</td>
<td>101408.17</td>
<td>101337.43</td>
<td>296.90</td>
</tr>
<tr>
<td>Standard 5</td>
<td>Cu 327.395</td>
<td>5 ppm</td>
<td></td>
<td>240870.76</td>
<td>240446.6</td>
<td>241256.19</td>
<td>240857.85</td>
<td>404.95</td>
</tr>
</tbody>
</table>
### Mg (518.360 nm) Calibration

![Graph showing the Mg (518.360 nm) Calibration with regression line and equation: \( y = 2544.9x + 1466.1 \), \( R^2 = 0.9992 \).]

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Concentration</th>
<th>Unit</th>
<th>Intensity Replicate 1</th>
<th>Intensity Replicate 2</th>
<th>Intensity Replicate 3</th>
<th>Ave Intensity</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Mg</td>
<td>0 ppm</td>
<td></td>
<td>1.44</td>
<td>-3.94</td>
<td>2.46</td>
<td>-0.01</td>
<td>3.44</td>
</tr>
<tr>
<td>Standard 1</td>
<td>Mg</td>
<td>5 pp m</td>
<td></td>
<td>13551.79</td>
<td>13522.34</td>
<td>13501.57</td>
<td>13525.23</td>
<td>25.23</td>
</tr>
<tr>
<td>Standard 2</td>
<td>Mg</td>
<td>10 ppm</td>
<td></td>
<td>26597.66</td>
<td>26901.05</td>
<td>27028.72</td>
<td>26842.48</td>
<td>221.42</td>
</tr>
<tr>
<td>Standard 3</td>
<td>Mg</td>
<td>20 ppm</td>
<td></td>
<td>54579.30</td>
<td>55364.35</td>
<td>55129.27</td>
<td>55024.31</td>
<td>402.91</td>
</tr>
<tr>
<td>Standard 4</td>
<td>Mg</td>
<td>40 ppm</td>
<td></td>
<td>102746.50</td>
<td>105216.16</td>
<td>105083.31</td>
<td>104348.66</td>
<td>1389.10</td>
</tr>
<tr>
<td>Standard 5</td>
<td>Mg</td>
<td>60 ppm</td>
<td></td>
<td>149903.80</td>
<td>153664.85</td>
<td>154275.30</td>
<td>152614.65</td>
<td>2367.42</td>
</tr>
</tbody>
</table>
APPENDIX 2:
RESULTS OF
LEAVES
ANALYSIS

Code: n.d = not detected
* < 0.1 ppm

A. Ni Concentration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Concentration</th>
<th>Unit</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Ni 305.082</td>
<td>58.32</td>
<td>56.27</td>
<td>66.52</td>
<td>60.37</td>
<td>-0.03</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Ni 305.082</td>
<td>198.90</td>
<td>214.15</td>
<td>214.20</td>
<td>209.08</td>
<td>0.00</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Ni 305.082</td>
<td>233.68</td>
<td>215.00</td>
<td>232.71</td>
<td>227.13</td>
<td>0.01</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Ni 305.082</td>
<td>131.09</td>
<td>149.52</td>
<td>126.06</td>
<td>135.56</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Ni 305.082</td>
<td>169.99</td>
<td>174.70</td>
<td>171.42</td>
<td>172.04</td>
<td>0.00</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Ni 305.082</td>
<td>136.10</td>
<td>116.44</td>
<td>144.09</td>
<td>132.21</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Ni 305.082</td>
<td>124.76</td>
<td>127.34</td>
<td>151.31</td>
<td>134.47</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Ni 305.082</td>
<td>79.41</td>
<td>91.37</td>
<td>72.63</td>
<td>81.14</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Ni 305.082</td>
<td>106.92</td>
<td>136.21</td>
<td>134.07</td>
<td>125.73</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Ni 305.082</td>
<td>193.04</td>
<td>209.06</td>
<td>214.50</td>
<td>205.53</td>
<td>0.00</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Ni 305.082</td>
<td>127.68</td>
<td>141.94</td>
<td>179.44</td>
<td>149.69</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Ni 305.082</td>
<td>211.76</td>
<td>185.57</td>
<td>182.67</td>
<td>193.33</td>
<td>0.00</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Ni 305.082</td>
<td>83.60</td>
<td>111.80</td>
<td>88.38</td>
<td>94.59</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Ni 305.082</td>
<td>71.29</td>
<td>71.49</td>
<td>85.63</td>
<td>76.14</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Ni 305.082</td>
<td>425.82</td>
<td>429.62</td>
<td>417.39</td>
<td>424.28</td>
<td>0.05</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Ni 305.082</td>
<td>106.13</td>
<td>123.60</td>
<td>111.31</td>
<td>113.68</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Ni 305.082</td>
<td>218.45</td>
<td>242.25</td>
<td>239.21</td>
<td>233.30</td>
<td>0.01</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 18</td>
<td>Ni 305.082</td>
<td>135.44</td>
<td>120.72</td>
<td>133.61</td>
<td>129.92</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Ni 305.082</td>
<td>154.15</td>
<td>169.15</td>
<td>148.28</td>
<td>157.19</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Ni 305.082</td>
<td>120.56</td>
<td>132.58</td>
<td>146.43</td>
<td>133.19</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 21</td>
<td>Ni 305.082</td>
<td>-32.79</td>
<td>-25.51</td>
<td>-24.88</td>
<td>-27.73</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Ni 305.082</td>
<td>-43.31</td>
<td>-48.22</td>
<td>-35.79</td>
<td>-42.44</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Ni 305.082</td>
<td>-15.62</td>
<td>-22.86</td>
<td>-21.68</td>
<td>-20.05</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Ni 305.082</td>
<td>-30.44</td>
<td>-36.07</td>
<td>-38.40</td>
<td>-34.97</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 25</td>
<td>Ni 305.082</td>
<td>-33.45</td>
<td>-33.15</td>
<td>-18.89</td>
<td>-28.50</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 26</td>
<td>Ni 305.082</td>
<td>-19.59</td>
<td>-45.48</td>
<td>-31.63</td>
<td>-32.23</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 27</td>
<td>Ni 305.082</td>
<td>-53.01</td>
<td>-17.04</td>
<td>-33.35</td>
<td>-34.47</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 28</td>
<td>Ni 305.082</td>
<td>-38.03</td>
<td>-34.69</td>
<td>-26.53</td>
<td>-33.08</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 29</td>
<td>Ni 305.082</td>
<td>-37.32</td>
<td>-23.48</td>
<td>-43.55</td>
<td>-34.78</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 30</td>
<td>Ni 305.082</td>
<td>-42.42</td>
<td>-44.96</td>
<td>-20.83</td>
<td>-36.07</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
</tbody>
</table>
### B. Cu Concentration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Concentration</th>
<th>Unit</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Cu 327.395</td>
<td>5013.21</td>
<td>5059.95</td>
<td>5015.36</td>
<td>5029.51</td>
<td>0.04</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Cu 327.395</td>
<td>6060.47</td>
<td>6137.86</td>
<td>6094.57</td>
<td>6097.63</td>
<td>0.07</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Cu 327.395</td>
<td>10367.29</td>
<td>10358.62</td>
<td>10340.61</td>
<td>10355.51</td>
<td>0.15</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>Cu 327.395</td>
<td>4588.96</td>
<td>4546.14</td>
<td>4568.26</td>
<td>4567.79</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Cu 327.395</td>
<td>9324.40</td>
<td>9408.46</td>
<td>9380.10</td>
<td>9370.99</td>
<td>0.13</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 6</td>
<td>Cu 327.395</td>
<td>4561.63</td>
<td>4593.27</td>
<td>4604.01</td>
<td>4586.30</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Cu 327.395</td>
<td>6852.56</td>
<td>6874.81</td>
<td>6856.75</td>
<td>6861.37</td>
<td>0.08</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Cu 327.395</td>
<td>4696.90</td>
<td>4725.52</td>
<td>4715.19</td>
<td>4712.54</td>
<td>0.04</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Cu 327.395</td>
<td>4757.02</td>
<td>4691.01</td>
<td>4752.07</td>
<td>4733.37</td>
<td>0.04</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Cu 327.395</td>
<td>8587.67</td>
<td>8544.41</td>
<td>8613.24</td>
<td>8581.77</td>
<td>0.12</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 11</td>
<td>Cu 327.395</td>
<td>5825.18</td>
<td>5774.42</td>
<td>5760.60</td>
<td>5786.73</td>
<td>0.06</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Cu 327.395</td>
<td>8437.64</td>
<td>8437.66</td>
<td>8415.93</td>
<td>8430.41</td>
<td>0.11</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 13</td>
<td>Cu 327.395</td>
<td>4644.31</td>
<td>4661.12</td>
<td>4616.52</td>
<td>4640.65</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Cu 327.395</td>
<td>4211.66</td>
<td>4253.81</td>
<td>4207.13</td>
<td>4224.20</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Cu 327.395</td>
<td>5570.80</td>
<td>5664.18</td>
<td>5642.42</td>
<td>5625.80</td>
<td>0.06</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Cu 327.395</td>
<td>5406.07</td>
<td>5378.48</td>
<td>5384.44</td>
<td>5389.66</td>
<td>0.05</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Cu 327.395</td>
<td>10581.85</td>
<td>10607.38</td>
<td>10650.92</td>
<td>10613.38</td>
<td>0.16</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 18</td>
<td>Cu 327.395</td>
<td>5554.66</td>
<td>5597.98</td>
<td>5577.12</td>
<td>5576.59</td>
<td>0.05</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Cu 327.395</td>
<td>4153.87</td>
<td>4157.29</td>
<td>4158.68</td>
<td>4156.61</td>
<td>0.02</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Cu 327.395</td>
<td>13228.92</td>
<td>13189.28</td>
<td>13309.65</td>
<td>13242.62</td>
<td>0.22</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 21</td>
<td>Cu 327.395</td>
<td>3336.09</td>
<td>3287.52</td>
<td>3321.70</td>
<td>3315.10</td>
<td>0.01</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Cu 327.395</td>
<td>1668.39</td>
<td>1714.18</td>
<td>1713.19</td>
<td>1698.59</td>
<td>-0.03</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Cu 327.395</td>
<td>2198.01</td>
<td>2207.47</td>
<td>2223.80</td>
<td>2209.76</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Cu 327.395</td>
<td>1836.97</td>
<td>1820.80</td>
<td>1820.66</td>
<td>1826.14</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample</td>
<td>Cu 327.395</td>
<td>2351.46</td>
<td>2365.17</td>
<td>2358.08</td>
<td>2358.24</td>
<td>-0.01 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>------------</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>Sample 25</td>
<td>Cu 327.395</td>
<td>2453.46</td>
<td>2434.14</td>
<td>2408.44</td>
<td>2432.01</td>
<td>-0.01 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 26</td>
<td>Cu 327.395</td>
<td>1857.64</td>
<td>1885.20</td>
<td>1864.13</td>
<td>1868.99</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 27</td>
<td>Cu 327.395</td>
<td>2183.26</td>
<td>2214.44</td>
<td>2189.76</td>
<td>2195.82</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 28</td>
<td>Cu 327.395</td>
<td>2278.64</td>
<td>2369.40</td>
<td>2293.32</td>
<td>2313.79</td>
<td>-0.01 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 29</td>
<td>Cu 327.395</td>
<td>1781.49</td>
<td>1769.76</td>
<td>1790.61</td>
<td>1780.62</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 30</td>
<td>Cu 327.395</td>
<td>2032.62</td>
<td>2068.91</td>
<td>2040.40</td>
<td>2047.31</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 31</td>
<td>Cu 327.395</td>
<td>2087.37</td>
<td>2040.96</td>
<td>2058.65</td>
<td>2059.99</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 32</td>
<td>Cu 327.395</td>
<td>1998.78</td>
<td>2031.70</td>
<td>2002.55</td>
<td>2011.01</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 33</td>
<td>Cu 327.395</td>
<td>2229.65</td>
<td>2238.37</td>
<td>2211.70</td>
<td>2224.18</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 34</td>
<td>Cu 327.395</td>
<td>2222.46</td>
<td>2238.91</td>
<td>2211.70</td>
<td>2224.18</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 35</td>
<td>Cu 327.395</td>
<td>2125.53</td>
<td>2147.12</td>
<td>2143.06</td>
<td>2138.57</td>
<td>-0.02 ppm</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>Sample 36</td>
<td>Cu 327.395</td>
<td>2345.19</td>
<td>2328.21</td>
<td>2325.90</td>
<td>2333.10</td>
<td>-0.01 ppm</td>
<td>n.d</td>
<td></td>
</tr>
</tbody>
</table>

C. Mg Concentration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Concentration</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Mg 518.360</td>
<td>27599.32</td>
<td>27581.81</td>
<td>27528.04</td>
<td>27569.72</td>
<td>10.26 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>Mg 518.360</td>
<td>32207.57</td>
<td>31946.93</td>
<td>32073.35</td>
<td>32076.11</td>
<td>12.03 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>Mg 518.360</td>
<td>61740.93</td>
<td>61578.74</td>
<td>61605.11</td>
<td>61588.51</td>
<td>23.63 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>Mg 518.360</td>
<td>39455.11</td>
<td>39548.64</td>
<td>39493.48</td>
<td>39506.46</td>
<td>14.94 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 5</td>
<td>Mg 518.360</td>
<td>64824.92</td>
<td>65155.66</td>
<td>65032.74</td>
<td>65064.31</td>
<td>24.98 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 6</td>
<td>Mg 518.360</td>
<td>30692.63</td>
<td>30824.67</td>
<td>30854.86</td>
<td>30839.71</td>
<td>11.55 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 7</td>
<td>Mg 518.360</td>
<td>45160.90</td>
<td>45318.63</td>
<td>45072.31</td>
<td>45135.79</td>
<td>17.13 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 8</td>
<td>Mg 518.360</td>
<td>31193.14</td>
<td>31131.18</td>
<td>31213.22</td>
<td>31187.20</td>
<td>11.69 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 9</td>
<td>Mg 518.360</td>
<td>35807.52</td>
<td>35879.54</td>
<td>35781.55</td>
<td>35822.87</td>
<td>13.50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 10</td>
<td>Mg 518.360</td>
<td>63470.94</td>
<td>63498.32</td>
<td>63616.47</td>
<td>63525.29</td>
<td>24.42 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 11</td>
<td>Mg 518.360</td>
<td>41414.26</td>
<td>41611.31</td>
<td>41978.19</td>
<td>41673.92</td>
<td>15.80 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 12</td>
<td>Mg 518.360</td>
<td>68383.95</td>
<td>68541.85</td>
<td>68612.26</td>
<td>68592.51</td>
<td>26.38 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 13</td>
<td>Mg 518.360</td>
<td>31352.58</td>
<td>31429.48</td>
<td>31399.45</td>
<td>31413.46</td>
<td>11.76 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 14</td>
<td>Mg 518.360</td>
<td>27251.27</td>
<td>2720.84</td>
<td>27338.72</td>
<td>27270.28</td>
<td>10.14 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 15</td>
<td>Mg 518.360</td>
<td>38322.53</td>
<td>38131.54</td>
<td>38154.50</td>
<td>38143.52</td>
<td>14.42 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 16</td>
<td>Mg 518.360</td>
<td>39673.36</td>
<td>39657.52</td>
<td>39813.75</td>
<td>39714.88</td>
<td>15.03 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 17</td>
<td>Mg 518.360</td>
<td>80632.24</td>
<td>81184.43</td>
<td>80587.10</td>
<td>80801.26</td>
<td>31.17 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Mg 518.360</td>
<td>Intensity Repl 1</td>
<td>Intensity Repl 2</td>
<td>Intensity Repl 3</td>
<td>Ave Intensity</td>
<td>Concentration</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>---------------</td>
<td>---------------</td>
<td>------</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>40807.94</td>
<td>41084.85</td>
<td>41042.13</td>
<td>40978.31</td>
<td>15.53</td>
<td>ppm</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>30504.24</td>
<td>30182.37</td>
<td>30233.39</td>
<td>30306.67</td>
<td>11.33</td>
<td>ppm</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>59214.28</td>
<td>58845.89</td>
<td>59053.02</td>
<td>59037.73</td>
<td>22.62</td>
<td>ppm</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>30827.50</td>
<td>30944.76</td>
<td>30948.29</td>
<td>30906.85</td>
<td>11.57</td>
<td>ppm</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>40905.07</td>
<td>41204.99</td>
<td>41091.83</td>
<td>41067.30</td>
<td>15.56</td>
<td>ppm</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td>43829.75</td>
<td>43856.59</td>
<td>43901.42</td>
<td>43862.59</td>
<td>16.66</td>
<td>ppm</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>38452.53</td>
<td>38350.80</td>
<td>38423.40</td>
<td>38408.91</td>
<td>14.52</td>
<td>ppm</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>34375.24</td>
<td>34429.50</td>
<td>34313.33</td>
<td>34372.69</td>
<td>12.93</td>
<td>ppm</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td>31391.73</td>
<td>31557.82</td>
<td>31661.18</td>
<td>31536.91</td>
<td>11.82</td>
<td>ppm</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>55425.31</td>
<td>55317.80</td>
<td>55379.76</td>
<td>55374.29</td>
<td>21.18</td>
<td>ppm</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td>35025.63</td>
<td>35016.09</td>
<td>35148.63</td>
<td>35063.45</td>
<td>13.20</td>
<td>ppm</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>33925.01</td>
<td>33968.04</td>
<td>33910.79</td>
<td>33934.61</td>
<td>12.76</td>
<td>ppm</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>54016.39</td>
<td>53973.07</td>
<td>54195.60</td>
<td>54061.69</td>
<td>20.67</td>
<td>ppm</td>
</tr>
<tr>
<td>31</td>
<td></td>
<td>31729.94</td>
<td>31901.19</td>
<td>31748.08</td>
<td>31793.07</td>
<td>11.92</td>
<td>ppm</td>
</tr>
<tr>
<td>32</td>
<td></td>
<td>40566.38</td>
<td>40695.44</td>
<td>40691.76</td>
<td>40651.19</td>
<td>15.40</td>
<td>ppm</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td>45980.88</td>
<td>45929.24</td>
<td>46020.61</td>
<td>45976.91</td>
<td>17.49</td>
<td>ppm</td>
</tr>
<tr>
<td>34</td>
<td></td>
<td>30917.86</td>
<td>31052.50</td>
<td>31113.20</td>
<td>31027.85</td>
<td>11.62</td>
<td>ppm</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>35280.93</td>
<td>35248.15</td>
<td>35529.10</td>
<td>35352.73</td>
<td>13.32</td>
<td>ppm</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td>48256.64</td>
<td>48399.89</td>
<td>48414.96</td>
<td>48357.16</td>
<td>18.43</td>
<td>ppm</td>
</tr>
<tr>
<td>37</td>
<td></td>
<td>41815.21</td>
<td>41923.56</td>
<td>41924.19</td>
<td>41887.65</td>
<td>15.88</td>
<td>ppm</td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>43000.39</td>
<td>43055.84</td>
<td>43225.09</td>
<td>43093.77</td>
<td>16.36</td>
<td>ppm</td>
</tr>
<tr>
<td>39</td>
<td></td>
<td>41716.40</td>
<td>41614.18</td>
<td>41886.96</td>
<td>41739.18</td>
<td>15.83</td>
<td>ppm</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>43503.29</td>
<td>43589.98</td>
<td>43435.80</td>
<td>43509.69</td>
<td>16.52</td>
<td>ppm</td>
</tr>
</tbody>
</table>

D. **Zn Concentration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Concentration</th>
<th>Unit</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Zn 481.053</td>
<td>86.95</td>
<td>95.79</td>
<td>86.70</td>
<td>89.81</td>
<td>0.40</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>Zn 481.053</td>
<td>62.58</td>
<td>58.73</td>
<td>61.68</td>
<td>61.00</td>
<td>0.25</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>Zn 481.053</td>
<td>75.10</td>
<td>72.76</td>
<td>69.40</td>
<td>72.42</td>
<td>0.31</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>Zn 481.053</td>
<td>-8.39</td>
<td>-16.62</td>
<td>5.68</td>
<td>-6.44</td>
<td>-0.10</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Zn 481.053</td>
<td>26.89</td>
<td>29.90</td>
<td>30.43</td>
<td>29.07</td>
<td>0.09</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Zn 481.053</td>
<td>43.36</td>
<td>51.17</td>
<td>42.92</td>
<td>45.82</td>
<td>0.17</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 7</td>
<td>Zn 481.053</td>
<td>74.49</td>
<td>76.39</td>
<td>68.70</td>
<td>73.19</td>
<td>0.31</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 8</td>
<td>Zn 481.053</td>
<td>60.32</td>
<td>57.86</td>
<td>62.13</td>
<td>60.10</td>
<td>0.25</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 9</td>
<td>Zn 481.053</td>
<td>27.76</td>
<td>35.20</td>
<td>30.17</td>
<td>31.04</td>
<td>0.10</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 10</td>
<td>Zn 481.053</td>
<td>48.46</td>
<td>52.71</td>
<td>47.44</td>
<td>49.54</td>
<td>0.19</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 11</td>
<td>Zn 481.053</td>
<td>39.58</td>
<td>46.42</td>
<td>26.04</td>
<td>37.35</td>
<td>0.13</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Zn 481.053</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>92.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>91.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>92.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>0.42 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>94.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**E. Cr**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Concentration</th>
<th>Unit</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Cr 425.433</td>
<td>2240.79</td>
<td>2294.58</td>
<td>2306.58</td>
<td>2280.65</td>
<td>0.03 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>Cr 425.433</td>
<td>2127.59</td>
<td>2164.08</td>
<td>2147.60</td>
<td>0.03 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>Cr 425.433</td>
<td>4103.55</td>
<td>4191.85</td>
<td>4202.97</td>
<td>4166.12</td>
<td>0.09</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Cr 425.433</td>
<td>2752.43</td>
<td>2770.85</td>
<td>2745.18</td>
<td>2756.15</td>
<td>0.05</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Cr 425.433</td>
<td>4317.63</td>
<td>4326.48</td>
<td>4322.43</td>
<td>4322.18</td>
<td>0.09</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Cr 425.433</td>
<td>2145.98</td>
<td>2163.26</td>
<td>2180.47</td>
<td>2163.24</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Cr 425.433</td>
<td>2628.06</td>
<td>2659.7</td>
<td>2684.37</td>
<td>2657.38</td>
<td>0.04</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Cr 425.433</td>
<td>2059.36</td>
<td>2056.16</td>
<td>2069.74</td>
<td>2061.75</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Cr 425.433</td>
<td>2056.41</td>
<td>2057</td>
<td>2058.68</td>
<td>2057.36</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Cr 425.433</td>
<td>3357.78</td>
<td>3362.9</td>
<td>3381.54</td>
<td>3367.41</td>
<td>0.06</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Cr 425.433</td>
<td>2636.44</td>
<td>2642.59</td>
<td>2660.12</td>
<td>2646.38</td>
<td>0.04</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Cr 425.433</td>
<td>4185.27</td>
<td>4199.29</td>
<td>4209.97</td>
<td>4198.18</td>
<td>0.09</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Cr 425.433</td>
<td>1934.91</td>
<td>1982.83</td>
<td>1941.42</td>
<td>1953.05</td>
<td>0.02</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Cr 425.433</td>
<td>1703.09</td>
<td>1726.72</td>
<td>1749.52</td>
<td>1726.44</td>
<td>0.02</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Cr 425.433</td>
<td>12560.28</td>
<td>12538.29</td>
<td>12558.5</td>
<td>12552.36</td>
<td>0.33</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 16</td>
<td>Cr 425.433</td>
<td>2048.8</td>
<td>2070.12</td>
<td>2076.2</td>
<td>2065.04</td>
<td>0.03</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Cr 425.433</td>
<td>4409.22</td>
<td>4483.63</td>
<td>4455.9</td>
<td>4449.58</td>
<td>0.10</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 18</td>
<td>Cr 425.433</td>
<td>1938.62</td>
<td>1949.29</td>
<td>1964.92</td>
<td>1950.94</td>
<td>0.02</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Cr 425.433</td>
<td>1620.75</td>
<td>1635.56</td>
<td>1628.58</td>
<td>1628.30</td>
<td>0.01</td>
<td>ppm</td>
<td>*</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Cr 425.433</td>
<td>4742.37</td>
<td>4764.67</td>
<td>4795.75</td>
<td>4767.60</td>
<td>0.10</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 21</td>
<td>Cr 425.433</td>
<td>673.78</td>
<td>701.47</td>
<td>690.49</td>
<td>688.58</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Cr 425.433</td>
<td>654.72</td>
<td>666.64</td>
<td>671.85</td>
<td>664.40</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Cr 425.433</td>
<td>580.14</td>
<td>584.58</td>
<td>601.96</td>
<td>588.89</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Cr 425.433</td>
<td>596.33</td>
<td>611.43</td>
<td>603.46</td>
<td>603.74</td>
<td>-0.01</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 25</td>
<td>Cr 425.433</td>
<td>437.3</td>
<td>455.73</td>
<td>468.28</td>
<td>453.77</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 26</td>
<td>Cr 425.433</td>
<td>430.57</td>
<td>444.47</td>
<td>456.68</td>
<td>443.91</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 27</td>
<td>Cr 425.433</td>
<td>467.8</td>
<td>483.22</td>
<td>495.73</td>
<td>482.25</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 28</td>
<td>Cr 425.433</td>
<td>394.07</td>
<td>402.86</td>
<td>401.32</td>
<td>399.42</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 29</td>
<td>Cr 425.433</td>
<td>385.39</td>
<td>391.04</td>
<td>389.45</td>
<td>388.63</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 30</td>
<td>Cr 425.433</td>
<td>384.34</td>
<td>400.25</td>
<td>389.95</td>
<td>391.51</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 31</td>
<td>Cr 425.433</td>
<td>310.91</td>
<td>321.63</td>
<td>329.9</td>
<td>320.81</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 32</td>
<td>Cr 425.433</td>
<td>459.03</td>
<td>476.54</td>
<td>500.36</td>
<td>478.64</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 33</td>
<td>Cr 425.433</td>
<td>466.65</td>
<td>455.48</td>
<td>462.39</td>
<td>461.51</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 34</td>
<td>Cr 425.433</td>
<td>431.98</td>
<td>444.71</td>
<td>439.87</td>
<td>438.85</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 35</td>
<td>Cr 425.433</td>
<td>556.79</td>
<td>574.32</td>
<td>566.23</td>
<td>565.78</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 36</td>
<td>Cr 425.433</td>
<td>422</td>
<td>433.67</td>
<td>441.99</td>
<td>432.55</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 37</td>
<td>Cr 425.433</td>
<td>420.58</td>
<td>429.37</td>
<td>437.08</td>
<td>429.01</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 38</td>
<td>Cr 425.433</td>
<td>419.88</td>
<td>406.49</td>
<td>420.24</td>
<td>415.54</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 39</td>
<td>Cr 425.433</td>
<td>465.34</td>
<td>463.02</td>
<td>482.16</td>
<td>470.17</td>
<td>-0.02</td>
<td>ppm</td>
<td>n.d</td>
</tr>
</tbody>
</table>
### F. Co Concentration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Concentration</th>
<th>Unit</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Co 340.512</td>
<td>-26.02</td>
<td>-36.36</td>
<td>-21.89</td>
<td>-28.09</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Co 340.512</td>
<td>-36.04</td>
<td>-31</td>
<td>-39.68</td>
<td>-35.57</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Co 340.512</td>
<td>-60.11</td>
<td>-71.02</td>
<td>-73.58</td>
<td>-68.24</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Co 340.512</td>
<td>-50.27</td>
<td>-75.67</td>
<td>-68.87</td>
<td>-64.94</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Co 340.512</td>
<td>-75.93</td>
<td>-85.38</td>
<td>-91.14</td>
<td>-84.15</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Co 340.512</td>
<td>-96.88</td>
<td>-108.74</td>
<td>-127.42</td>
<td>-111.01</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Co 340.512</td>
<td>-79.16</td>
<td>-94.12</td>
<td>-76.81</td>
<td>-76.81</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Co 340.512</td>
<td>-69.91</td>
<td>-72.4</td>
<td>-86.72</td>
<td>-76.34</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Co 340.512</td>
<td>-90.18</td>
<td>-79.97</td>
<td>-91.67</td>
<td>-87.27</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Co 340.512</td>
<td>-63.65</td>
<td>-73.71</td>
<td>-75.8</td>
<td>-71.05</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Co 340.512</td>
<td>-72.36</td>
<td>-61.46</td>
<td>-51.93</td>
<td>-61.92</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Co 340.512</td>
<td>-88.75</td>
<td>-87.43</td>
<td>-111.48</td>
<td>-95.89</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Co 340.512</td>
<td>-74.04</td>
<td>-62.26</td>
<td>-73.65</td>
<td>-69.98</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Co 340.512</td>
<td>-68.79</td>
<td>-75.13</td>
<td>-77.93</td>
<td>-73.96</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Co 340.512</td>
<td>-82.29</td>
<td>-84.04</td>
<td>-60.21</td>
<td>-75.51</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Co 340.512</td>
<td>-59.06</td>
<td>-69.07</td>
<td>-70.52</td>
<td>-66.22</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Co 340.512</td>
<td>-99.65</td>
<td>-114.48</td>
<td>-87.94</td>
<td>-100.69</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 18</td>
<td>Co 340.512</td>
<td>-102.31</td>
<td>-124.12</td>
<td>-119.53</td>
<td>-115.32</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Co 340.512</td>
<td>-63.4</td>
<td>-82.48</td>
<td>-64.75</td>
<td>-70.21</td>
<td>-0.05</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Co 340.512</td>
<td>-176.5</td>
<td>-173.82</td>
<td>-174.72</td>
<td>-175.01</td>
<td>-0.06</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 21</td>
<td>Co 340.512</td>
<td>-17.95</td>
<td>-26.24</td>
<td>-27.27</td>
<td>-23.82</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Co 340.512</td>
<td>-32.81</td>
<td>-27.27</td>
<td>-36.57</td>
<td>-32.22</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Co 340.512</td>
<td>-16.71</td>
<td>-34</td>
<td>-19.34</td>
<td>-23.35</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 27</td>
<td>Co 340.512</td>
<td>-39.37</td>
<td>-30.39</td>
<td>-29.54</td>
<td>-33.10</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 28</td>
<td>Co 340.512</td>
<td>-22.68</td>
<td>-16.52</td>
<td>-24.76</td>
<td>-21.32</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 29</td>
<td>Co 340.512</td>
<td>-37.47</td>
<td>-46.23</td>
<td>-30.37</td>
<td>-38.02</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 30</td>
<td>Co 340.512</td>
<td>-33.4</td>
<td>-18.23</td>
<td>-35.98</td>
<td>-29.20</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 31</td>
<td>Co 340.512</td>
<td>-19.6</td>
<td>-20.21</td>
<td>-34.93</td>
<td>-24.91</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 32</td>
<td>Co 340.512</td>
<td>-32.84</td>
<td>-25.57</td>
<td>-40.69</td>
<td>-33.03</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample 33</td>
<td>Co 340.512</td>
<td>-30.72</td>
<td>-25.47</td>
<td>-28.64</td>
<td>-28.28</td>
<td>-0.04</td>
<td>ppm</td>
<td>n.d</td>
</tr>
<tr>
<td>Sample</td>
<td>Label</td>
<td>Element</td>
<td>Intensity Repl 1</td>
<td>Intensity Repl 2</td>
<td>Intensity Repl 3</td>
<td>Ave Intensity</td>
<td>Conc</td>
<td>Dilution</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>---------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>---------------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>34</td>
<td>Co 340.512</td>
<td>191606.1</td>
<td>192753.49</td>
<td>190053.82</td>
<td>191471.14</td>
<td>1.07</td>
<td>1.50</td>
<td>53.53</td>
</tr>
<tr>
<td>35</td>
<td>Ca 340.512</td>
<td>247859.15</td>
<td>250407.05</td>
<td>250245.23</td>
<td>249503.81</td>
<td>1.40</td>
<td>1.50</td>
<td>70.05</td>
</tr>
<tr>
<td>36</td>
<td>Co 340.512</td>
<td>435444.56</td>
<td>432558.17</td>
<td>430864.95</td>
<td>432955.89</td>
<td>2.45</td>
<td>1.50</td>
<td>122.26</td>
</tr>
<tr>
<td>37</td>
<td>Co 340.512</td>
<td>227379.67</td>
<td>226768.64</td>
<td>224773.15</td>
<td>226307.15</td>
<td>1.27</td>
<td>1.50</td>
<td>63.45</td>
</tr>
<tr>
<td>38</td>
<td>Co 340.512</td>
<td>438816.23</td>
<td>444671.45</td>
<td>444809.89</td>
<td>442656.19</td>
<td>2.50</td>
<td>1.50</td>
<td>125.02</td>
</tr>
<tr>
<td>39</td>
<td>Ca 340.512</td>
<td>188064.86</td>
<td>191888.55</td>
<td>190463.76</td>
<td>190139.06</td>
<td>1.06</td>
<td>1.50</td>
<td>53.15</td>
</tr>
<tr>
<td>40</td>
<td>Co 340.512</td>
<td>310008.38</td>
<td>317066.69</td>
<td>312919.48</td>
<td>315664.85</td>
<td>1.78</td>
<td>1.50</td>
<td>88.88</td>
</tr>
<tr>
<td>41</td>
<td>Ca 340.512</td>
<td>169102.68</td>
<td>169293.5</td>
<td>170947.99</td>
<td>169781.39</td>
<td>0.95</td>
<td>1.50</td>
<td>47.36</td>
</tr>
<tr>
<td>42</td>
<td>Ca 340.512</td>
<td>219986.42</td>
<td>220101.84</td>
<td>219957.21</td>
<td>220015.16</td>
<td>1.23</td>
<td>1.50</td>
<td>61.66</td>
</tr>
<tr>
<td>43</td>
<td>Ca 340.512</td>
<td>396834.57</td>
<td>398263.4</td>
<td>400159.46</td>
<td>398435.81</td>
<td>2.25</td>
<td>1.50</td>
<td>112.43</td>
</tr>
<tr>
<td>44</td>
<td>Ca 340.512</td>
<td>222759.63</td>
<td>223772.02</td>
<td>220544.45</td>
<td>220205.37</td>
<td>1.24</td>
<td>1.50</td>
<td>62.23</td>
</tr>
<tr>
<td>45</td>
<td>Ca 340.512</td>
<td>396176.92</td>
<td>398000.46</td>
<td>396184.71</td>
<td>396787.36</td>
<td>2.24</td>
<td>1.50</td>
<td>111.96</td>
</tr>
<tr>
<td>46</td>
<td>Ca 340.512</td>
<td>210305.35</td>
<td>215390.77</td>
<td>211133.9</td>
<td>212276.67</td>
<td>1.19</td>
<td>1.50</td>
<td>59.45</td>
</tr>
<tr>
<td>47</td>
<td>Ca 340.512</td>
<td>173231.82</td>
<td>173638</td>
<td>173849.77</td>
<td>173573.20</td>
<td>0.97</td>
<td>1.50</td>
<td>48.44</td>
</tr>
<tr>
<td>48</td>
<td>Ca 340.512</td>
<td>232409.55</td>
<td>232225.87</td>
<td>231755.53</td>
<td>232130.32</td>
<td>1.30</td>
<td>1.50</td>
<td>65.10</td>
</tr>
<tr>
<td>49</td>
<td>Ca 340.512</td>
<td>336265.95</td>
<td>335494.99</td>
<td>337229.82</td>
<td>336330.13</td>
<td>1.90</td>
<td>1.50</td>
<td>94.76</td>
</tr>
<tr>
<td>50</td>
<td>Ca 340.512</td>
<td>540889.04</td>
<td>547782.77</td>
<td>536838.45</td>
<td>541836.75</td>
<td>3.06</td>
<td>1.50</td>
<td>153.24</td>
</tr>
<tr>
<td>51</td>
<td>Ca 340.512</td>
<td>237015.56</td>
<td>236425.97</td>
<td>236657.98</td>
<td>236699.84</td>
<td>1.33</td>
<td>1.50</td>
<td>66.41</td>
</tr>
<tr>
<td>52</td>
<td>Ca 340.512</td>
<td>242690.18</td>
<td>245473.18</td>
<td>244556.74</td>
<td>244240.03</td>
<td>1.37</td>
<td>1.50</td>
<td>68.55</td>
</tr>
<tr>
<td>53</td>
<td>Ca 340.512</td>
<td>457090.04</td>
<td>459013.76</td>
<td>459486.32</td>
<td>458530.04</td>
<td>2.59</td>
<td>1.50</td>
<td>129.54</td>
</tr>
<tr>
<td>54</td>
<td>Ca 340.512</td>
<td>59244.69</td>
<td>61476.35</td>
<td>61451.28</td>
<td>60724.11</td>
<td>0.33</td>
<td>1.50</td>
<td>16.32</td>
</tr>
<tr>
<td>55</td>
<td>Ca 340.512</td>
<td>100845.59</td>
<td>100444.64</td>
<td>102396.12</td>
<td>101228.78</td>
<td>0.56</td>
<td>1.50</td>
<td>27.85</td>
</tr>
<tr>
<td>56</td>
<td>Ca 340.512</td>
<td>106309.12</td>
<td>106273.10</td>
<td>107692.84</td>
<td>106758.35</td>
<td>0.59</td>
<td>1.50</td>
<td>29.43</td>
</tr>
<tr>
<td>57</td>
<td>Ca 340.512</td>
<td>92710.12</td>
<td>92056.12</td>
<td>92474.99</td>
<td>92413.74</td>
<td>0.51</td>
<td>1.50</td>
<td>25.34</td>
</tr>
<tr>
<td>58</td>
<td>Ca 340.512</td>
<td>58270.51</td>
<td>59081.25</td>
<td>58922.57</td>
<td>58758.11</td>
<td>0.32</td>
<td>1.50</td>
<td>15.77</td>
</tr>
<tr>
<td>59</td>
<td>Ca 340.512</td>
<td>39170.96</td>
<td>39600.47</td>
<td>39847.56</td>
<td>39593.66</td>
<td>0.21</td>
<td>1.50</td>
<td>10.30</td>
</tr>
<tr>
<td>60</td>
<td>Ca 340.512</td>
<td>115333.44</td>
<td>115894.51</td>
<td>116148.39</td>
<td>115792.11</td>
<td>0.64</td>
<td>1.50</td>
<td>32.00</td>
</tr>
<tr>
<td>61</td>
<td>Ca 340.512</td>
<td>118522.09</td>
<td>119860.16</td>
<td>120177.83</td>
<td>119520.03</td>
<td>0.66</td>
<td>1.50</td>
<td>33.06</td>
</tr>
<tr>
<td>62</td>
<td>Ca 340.512</td>
<td>79987.80</td>
<td>80936.15</td>
<td>81418.70</td>
<td>80780.88</td>
<td>0.44</td>
<td>1.50</td>
<td>22.03</td>
</tr>
<tr>
<td>63</td>
<td>Ca 340.512</td>
<td>119405.39</td>
<td>121181.82</td>
<td>120952.11</td>
<td>120513.11</td>
<td>0.67</td>
<td>1.50</td>
<td>33.34</td>
</tr>
<tr>
<td>64</td>
<td>Ca 340.512</td>
<td>41499.03</td>
<td>42235.44</td>
<td>42001.38</td>
<td>41911.95</td>
<td>0.22</td>
<td>1.50</td>
<td>10.97</td>
</tr>
</tbody>
</table>
Sample 32 | Ca 422.685 | 66323.58 | 67249.00 | 67738.32 | 67103.63 | 0.36 | 1:50 | 18.14 ppm
Sample 33 | Ca 422.686 | 72516.57 | 73974.87 | 67249.00 | 67738.32 | 0.36 | 1:50 | 19.98 ppm
Sample 34 | Ca 422.687 | 67673.77 | 69100.65 | 68707.65 | 67103.63 | 0.37 | 1:50 | 18.60 ppm
Sample 35 | Ca 422.688 | 55783.49 | 55204.51 | 55634.93 | 55783.49 | 0.30 | 1:50 | 14.88 ppm
Sample 36 | Ca 422.689 | 66290.55 | 66832.13 | 66387.24 | 66503.31 | 0.36 | 1:50 | 17.97 ppm
Sample 37 | Ca 422.690 | 87561.82 | 87568.36 | 88433.29 | 87854.49 | 0.48 | 1:50 | 24.05 ppm
Sample 38 | Ca 422.691 | 89008.98 | 90220.27 | 89593.80 | 89607.68 | 0.49 | 1:50 | 24.54 ppm
Sample 39 | Ca 422.692 | 61357.20 | 61544.46 | 61902.49 | 61601.38 | 0.33 | 1:50 | 16.57 ppm
Sample 40 | Ca 422.693 | 41421.58 | 41588.37 | 42387.41 | 41799.12 | 0.22 | 1:50 | 10.94 ppm

APPENDIX 3: RESULTS OF SOIL ANALYSIS

Code: n.d = not detected
*<0.1 ppm

A. Cu Concentration

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Cu 327.395</td>
<td>3007.96</td>
<td>3048.23</td>
<td>3038.74</td>
<td>3031.64</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Cu 327.395</td>
<td>2724.24</td>
<td>2778.95</td>
<td>2800.79</td>
<td>2767.99</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Cu 327.395</td>
<td>2633.94</td>
<td>2643.79</td>
<td>2636.72</td>
<td>2638.15</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Cu 327.395</td>
<td>3321.94</td>
<td>3395.06</td>
<td>3364.39</td>
<td>3360.46</td>
<td>0.04</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Cu 327.395</td>
<td>2185.53</td>
<td>2239.7</td>
<td>2186.82</td>
<td>2204.02</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Cu 327.395</td>
<td>2241.91</td>
<td>2258.1</td>
<td>2261.04</td>
<td>2253.68</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Cu 327.395</td>
<td>2214.34</td>
<td>2279.09</td>
<td>2292.61</td>
<td>2262.01</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Cu 327.395</td>
<td>2321.31</td>
<td>2408.5</td>
<td>2431.31</td>
<td>2387.04</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Cu 327.395</td>
<td>2617.31</td>
<td>2643.08</td>
<td>2595.48</td>
<td>2618.62</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Cu 327.395</td>
<td>2499.07</td>
<td>2495.31</td>
<td>2565.7</td>
<td>2520.03</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Cu 327.395</td>
<td>2607.74</td>
<td>2721.83</td>
<td>2720.63</td>
<td>2683.40</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Cu 327.395</td>
<td>2679.56</td>
<td>2757.36</td>
<td>2703.36</td>
<td>2713.43</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Cu 327.395</td>
<td>2861.15</td>
<td>2895.13</td>
<td>2931.84</td>
<td>2896.04</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Cu 327.395</td>
<td>2504.31</td>
<td>2473.94</td>
<td>2495.98</td>
<td>2491.41</td>
<td>0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample</td>
<td>Cu (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 15</td>
<td>2679.09, 2656.95, 2684.78, 2673.61, 0.03 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 16</td>
<td>2438.55, 2475.49, 2468.8, 2460.95, 0.02 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 17</td>
<td>2485.22, 2489.74, 2523.69, 2499.55, 0.03 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 18</td>
<td>2639.09, 2659.86, 2662.14, 2653.70, 0.03 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 19</td>
<td>2603.47, 2618.08, 2654.56, 2625.37, 0.03 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 20</td>
<td>2383.58, 2367.81, 2374.04, 2375.14, 0.02 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 21</td>
<td>6615.72, 6811.59, 6823.42, 6750.24, 0.10 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 22</td>
<td>5709.98, 5937.41, 6046.14, 5897.84, 0.08 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 23</td>
<td>5846.11, 6071.96, 6207.64, 6041.90, 0.09 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 24</td>
<td>6655.49, 6930.67, 7063.8, 6883.32, 0.10 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 25</td>
<td>6427.14, 6827.55, 6873.63, 6709.44, 0.10 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 26</td>
<td>6678.69, 6929.24, 7051.68, 6886.54, 0.10 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 27</td>
<td>6711.81, 6938.41, 7143, 6931.07, 0.10 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 28</td>
<td>7503.29, 7741.2, 7814.17, 7686.22, 0.12 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 29</td>
<td>12392.59, 12755.61, 13078.89, 12742.36, 0.20 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 30</td>
<td>8815.25, 9057.44, 9086.11, 8986.27, 0.14 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 31</td>
<td>11297.23, 11571.3, 11539.86, 11469.46, 0.18 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 32</td>
<td>15296.62, 15588.69, 15703.03, 15529.45, 0.25 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 33</td>
<td>5455.53, 5527.89, 5522.29, 5501.90, 0.08 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 34</td>
<td>5262.2, 5522.3, 5482.17, 5422.22, 0.08 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 35</td>
<td>5292.36, 5377.25, 5444.02, 5371.21, 0.08 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 36</td>
<td>7096.76, 7158.12, 7185.57, 7146.82, 0.11 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 37</td>
<td>12251.3, 12540.22, 12568.21, 12453.24, 0.20 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 38</td>
<td>11064.07, 11349.75, 11370.18, 11261.33, 0.18 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 39</td>
<td>11131.09, 11266.67, 11295.15, 11230.97, 0.18 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 40</td>
<td>12944.55, 13234.02, 13189.29, 13122.62, 0.21 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 41</td>
<td>6573.68, 6742.74, 6672.14, 6662.85, 0.10 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 42</td>
<td>423.61, 441.34, 490.95, 451.97, -0.01 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 43</td>
<td>2725.66, 2867.72, 2871.04, 2821.47, 0.03 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Cu</td>
<td>327.395</td>
<td>-2315.99</td>
<td>-2309.24</td>
<td>-2321.54</td>
<td>-2315.59</td>
<td>-0.06</td>
</tr>
<tr>
<td>---------</td>
<td>-----</td>
<td>---------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>-------</td>
</tr>
<tr>
<td>No sample</td>
<td>Cu</td>
<td>327.395</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 45</td>
<td>Cu</td>
<td>327.395</td>
<td>5232.13</td>
<td>5267.64</td>
<td>5332.3</td>
<td>5277.36</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 46</td>
<td>Cu</td>
<td>327.395</td>
<td>2702.18</td>
<td>2731.68</td>
<td>2805.82</td>
<td>2746.56</td>
<td>0.03</td>
</tr>
<tr>
<td>Sample 47</td>
<td>Cu</td>
<td>327.395</td>
<td>-647.95</td>
<td>-649.72</td>
<td>-581.25</td>
<td>-626.31</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

**B. Mg Concentration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Mg 518.360</td>
<td>44297.15</td>
<td>44450.43</td>
<td>44553.59</td>
<td>44433.72</td>
<td>12.17</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Mg 518.360</td>
<td>47437.79</td>
<td>47740.23</td>
<td>47630.79</td>
<td>47602.94</td>
<td>13.05</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Mg 518.360</td>
<td>47371.31</td>
<td>46945.97</td>
<td>47293.65</td>
<td>47203.64</td>
<td>12.94</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Mg 518.360</td>
<td>45180.16</td>
<td>44992.17</td>
<td>45029.33</td>
<td>45067.22</td>
<td>12.35</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Mg 518.360</td>
<td>52599.06</td>
<td>52654.84</td>
<td>53046.35</td>
<td>52766.75</td>
<td>14.49</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Mg 518.360</td>
<td>45836.57</td>
<td>45967.48</td>
<td>45911.84</td>
<td>45905.30</td>
<td>12.58</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Mg 518.360</td>
<td>50494.81</td>
<td>50762.29</td>
<td>50765.16</td>
<td>50674.09</td>
<td>13.91</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Mg 518.360</td>
<td>48635.43</td>
<td>48461.5</td>
<td>48508.28</td>
<td>48535.07</td>
<td>13.31</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Mg 518.360</td>
<td>51323.83</td>
<td>51132.38</td>
<td>51324.15</td>
<td>51260.12</td>
<td>14.07</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Mg 518.360</td>
<td>42455.63</td>
<td>42644.76</td>
<td>42489.32</td>
<td>42529.90</td>
<td>11.64</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Mg 518.360</td>
<td>48959.82</td>
<td>49050.43</td>
<td>49292.02</td>
<td>49100.76</td>
<td>13.47</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Mg 518.360</td>
<td>47719.31</td>
<td>47420.22</td>
<td>47799.78</td>
<td>47646.44</td>
<td>13.06</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Mg 518.360</td>
<td>45302.15</td>
<td>45482.87</td>
<td>45136.53</td>
<td>45307.18</td>
<td>12.42</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Mg 518.360</td>
<td>41239.13</td>
<td>41388.31</td>
<td>41409.21</td>
<td>41345.55</td>
<td>11.32</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Mg 518.360</td>
<td>44266.62</td>
<td>44726.87</td>
<td>44401.14</td>
<td>44464.88</td>
<td>12.18</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Mg 518.360</td>
<td>45134.85</td>
<td>45738.17</td>
<td>45462.84</td>
<td>45445.29</td>
<td>12.45</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Mg 518.360</td>
<td>52638.59</td>
<td>52871.8</td>
<td>52926.15</td>
<td>52812.18</td>
<td>14.50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 18</td>
<td>Mg 518.360</td>
<td>45873.75</td>
<td>45728.86</td>
<td>45701.68</td>
<td>45768.10</td>
<td>12.54</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample</td>
<td>Mg</td>
<td>518.360</td>
<td>42651.55</td>
<td>42869.87</td>
<td>42792.58</td>
<td>42771.33</td>
<td>11.71</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>---------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Mg</td>
<td>518.360</td>
<td>40904.78</td>
<td>41186.27</td>
<td>41552.8</td>
<td>41214.62</td>
<td>11.28</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 21</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 25</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 26</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 27</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 28</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 29</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 30</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 31</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 32</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 33</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 34</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 35</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 36</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 37</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 38</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 39</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 40</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 41</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 42</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 43</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 44</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Sample 45</td>
<td>Mg</td>
<td>518.360</td>
<td>45352.17</td>
<td>45664.25</td>
<td>45392.84</td>
<td>45469.75</td>
<td>12.46</td>
</tr>
<tr>
<td>Sample 46</td>
<td>Mg</td>
<td>518.360</td>
<td>46978.91</td>
<td>47051.16</td>
<td>47137.36</td>
<td>47055.81</td>
<td>12.90</td>
</tr>
<tr>
<td>Sample 47</td>
<td>Mg</td>
<td>518.360</td>
<td>51703.17</td>
<td>51466.36</td>
<td>51456.03</td>
<td>51541.85</td>
<td>14.15</td>
</tr>
<tr>
<td>Label</td>
<td>Sample</td>
<td>Element</td>
<td>Intensity Repl 1</td>
<td>Intensity Repl 2</td>
<td>Intensity Repl 3</td>
<td>Ave Intensity</td>
<td>Conc</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>---------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>---------------</td>
<td>------</td>
</tr>
<tr>
<td>Sample 1</td>
<td>Zn</td>
<td>481.053</td>
<td>23.59</td>
<td>32.05</td>
<td>19.13</td>
<td>24.92</td>
<td>0.08</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Zn</td>
<td>481.053</td>
<td>12.97</td>
<td>28.76</td>
<td>23.95</td>
<td>21.89</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Zn</td>
<td>481.053</td>
<td>31.05</td>
<td>29.7</td>
<td>20.06</td>
<td>26.94</td>
<td>0.09</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Zn</td>
<td>481.053</td>
<td>13.2</td>
<td>35.05</td>
<td>20.96</td>
<td>23.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Zn</td>
<td>481.053</td>
<td>44.8</td>
<td>36.49</td>
<td>30.44</td>
<td>37.24</td>
<td>0.13</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Zn</td>
<td>481.053</td>
<td>21.43</td>
<td>27.48</td>
<td>27.2</td>
<td>25.37</td>
<td>0.08</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Zn</td>
<td>481.053</td>
<td>34.58</td>
<td>25.53</td>
<td>24.77</td>
<td>28.29</td>
<td>0.09</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Zn</td>
<td>481.053</td>
<td>21.56</td>
<td>34.57</td>
<td>37.96</td>
<td>31.36</td>
<td>0.11</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Zn</td>
<td>481.053</td>
<td>48.42</td>
<td>53.74</td>
<td>52.09</td>
<td>51.42</td>
<td>0.19</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Zn</td>
<td>481.053</td>
<td>38.75</td>
<td>45.36</td>
<td>44.03</td>
<td>42.71</td>
<td>0.15</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Zn</td>
<td>481.053</td>
<td>42.24</td>
<td>31.74</td>
<td>36.85</td>
<td>36.94</td>
<td>0.13</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Zn</td>
<td>481.053</td>
<td>32.14</td>
<td>36.73</td>
<td>36.85</td>
<td>35.24</td>
<td>0.12</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Zn</td>
<td>481.053</td>
<td>32.32</td>
<td>22.73</td>
<td>30.16</td>
<td>28.40</td>
<td>0.09</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Zn</td>
<td>481.053</td>
<td>24.99</td>
<td>25.63</td>
<td>24.58</td>
<td>25.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Zn</td>
<td>481.053</td>
<td>18.85</td>
<td>23.84</td>
<td>27.6</td>
<td>23.43</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Zn</td>
<td>481.053</td>
<td>20.11</td>
<td>22.94</td>
<td>22.13</td>
<td>21.73</td>
<td>0.06</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Zn</td>
<td>481.053</td>
<td>43.48</td>
<td>49.32</td>
<td>43.75</td>
<td>45.52</td>
<td>0.17</td>
</tr>
<tr>
<td>Sample 18</td>
<td>Zn</td>
<td>481.053</td>
<td>28.53</td>
<td>31.01</td>
<td>45.24</td>
<td>34.93</td>
<td>0.12</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Zn</td>
<td>481.053</td>
<td>38.75</td>
<td>35.58</td>
<td>34.52</td>
<td>36.28</td>
<td>0.13</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Zn</td>
<td>481.053</td>
<td>30.32</td>
<td>40.55</td>
<td>35.39</td>
<td>35.42</td>
<td>0.12</td>
</tr>
<tr>
<td>Sample 21</td>
<td>Zn</td>
<td>481.053</td>
<td>112.78</td>
<td>100.94</td>
<td>104.68</td>
<td>106.13</td>
<td>0.42</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Zn</td>
<td>481.053</td>
<td>107.01</td>
<td>113.68</td>
<td>99.5</td>
<td>106.73</td>
<td>0.43</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Zn</td>
<td>481.053</td>
<td>129.12</td>
<td>131.78</td>
<td>120.9</td>
<td>127.27</td>
<td>0.51</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Zn</td>
<td>481.053</td>
<td>119.76</td>
<td>116.71</td>
<td>104.63</td>
<td>113.70</td>
<td>0.46</td>
</tr>
<tr>
<td>Sample 25</td>
<td>Zn</td>
<td>481.053</td>
<td>80.91</td>
<td>86.22</td>
<td>94.36</td>
<td>87.16</td>
<td>0.34</td>
</tr>
<tr>
<td>Sample</td>
<td>Element</td>
<td>481.053</td>
<td>481.053</td>
<td>481.053</td>
<td>481.053</td>
<td>0.18</td>
<td>ppm</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>26</td>
<td>Zn</td>
<td>49.06</td>
<td>47.88</td>
<td>47.33</td>
<td>48.09</td>
<td>0.18</td>
<td>ppm</td>
</tr>
<tr>
<td>27</td>
<td>Zn</td>
<td>126.35</td>
<td>127.17</td>
<td>130.69</td>
<td>128.07</td>
<td>0.52</td>
<td>ppm</td>
</tr>
<tr>
<td>28</td>
<td>Zn</td>
<td>69.82</td>
<td>65.08</td>
<td>77.51</td>
<td>70.80</td>
<td>0.27</td>
<td>ppm</td>
</tr>
<tr>
<td>29</td>
<td>Zn</td>
<td>173.83</td>
<td>164.06</td>
<td>168.81</td>
<td>168.90</td>
<td>0.69</td>
<td>ppm</td>
</tr>
<tr>
<td>30</td>
<td>Zn</td>
<td>118.05</td>
<td>123.73</td>
<td>114.59</td>
<td>118.79</td>
<td>0.48</td>
<td>ppm</td>
</tr>
<tr>
<td>31</td>
<td>Zn</td>
<td>206.7</td>
<td>206.74</td>
<td>214.61</td>
<td>209.35</td>
<td>0.86</td>
<td>ppm</td>
</tr>
<tr>
<td>32</td>
<td>Zn</td>
<td>149.04</td>
<td>142.05</td>
<td>143.94</td>
<td>145.01</td>
<td>0.59</td>
<td>ppm</td>
</tr>
<tr>
<td>33</td>
<td>Zn</td>
<td>94.38</td>
<td>94.62</td>
<td>89.46</td>
<td>92.82</td>
<td>0.37</td>
<td>ppm</td>
</tr>
<tr>
<td>34</td>
<td>Zn</td>
<td>99.39</td>
<td>102.28</td>
<td>106.13</td>
<td>102.60</td>
<td>0.41</td>
<td>ppm</td>
</tr>
<tr>
<td>35</td>
<td>Zn</td>
<td>113.62</td>
<td>107.16</td>
<td>112.13</td>
<td>110.97</td>
<td>0.44</td>
<td>ppm</td>
</tr>
<tr>
<td>36</td>
<td>Zn</td>
<td>115.9</td>
<td>110.41</td>
<td>122.64</td>
<td>116.32</td>
<td>0.47</td>
<td>ppm</td>
</tr>
<tr>
<td>37</td>
<td>Zn</td>
<td>171.41</td>
<td>170.77</td>
<td>160.04</td>
<td>167.41</td>
<td>0.69</td>
<td>ppm</td>
</tr>
<tr>
<td>38</td>
<td>Zn</td>
<td>174.15</td>
<td>157.13</td>
<td>156.64</td>
<td>162.64</td>
<td>0.66</td>
<td>ppm</td>
</tr>
<tr>
<td>39</td>
<td>Zn</td>
<td>186.59</td>
<td>186.3</td>
<td>179.69</td>
<td>184.19</td>
<td>0.76</td>
<td>ppm</td>
</tr>
<tr>
<td>40</td>
<td>Zn</td>
<td>173.17</td>
<td>167.5</td>
<td>189.58</td>
<td>176.75</td>
<td>0.72</td>
<td>ppm</td>
</tr>
<tr>
<td>41</td>
<td>Zn</td>
<td>34.3</td>
<td>20.17</td>
<td>24.78</td>
<td>26.42</td>
<td>0.08</td>
<td>ppm</td>
</tr>
<tr>
<td>42</td>
<td>Zn</td>
<td>44.96</td>
<td>40.32</td>
<td>34.56</td>
<td>39.95</td>
<td>0.14</td>
<td>ppm</td>
</tr>
<tr>
<td>43</td>
<td>Zn</td>
<td>-418.47</td>
<td>-426.62</td>
<td>-419.06</td>
<td>-421.38</td>
<td>-1.82</td>
<td>ppm</td>
</tr>
<tr>
<td>No sample</td>
<td>Zn</td>
<td>481.053</td>
<td></td>
<td></td>
<td></td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>Zn</td>
<td>-0.09</td>
<td>7.52</td>
<td>-3.45</td>
<td>1.33</td>
<td>-0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>46</td>
<td>Zn</td>
<td>-8.62</td>
<td>3.62</td>
<td>6</td>
<td>0.33</td>
<td>-0.03</td>
<td>ppm</td>
</tr>
<tr>
<td>47</td>
<td>Zn</td>
<td>-384.61</td>
<td>-380.21</td>
<td>-381.78</td>
<td>-382.20</td>
<td>-1.66</td>
<td>ppm</td>
</tr>
<tr>
<td>48</td>
<td>Zn</td>
<td>-0.07</td>
<td>-4.85</td>
<td>0.76</td>
<td>-1.39</td>
<td>-0.03</td>
<td>ppm</td>
</tr>
</tbody>
</table>

**D. Cr Concentration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Cr</td>
<td>452.39</td>
<td>430.94</td>
<td>451.52</td>
<td>444.95</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Cr</td>
<td>321.56</td>
<td>346.27</td>
<td>350.28</td>
<td>339.37</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Cr</td>
<td>360.3</td>
<td>370.26</td>
<td>362.88</td>
<td>364.48</td>
<td>0.02</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample</td>
<td>Cr</td>
<td>425.433</td>
<td>335.25</td>
<td>336.14</td>
<td>338.11</td>
<td>336.50</td>
<td>0.02</td>
</tr>
<tr>
<td>---------</td>
<td>-----</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Cr</td>
<td>425.433</td>
<td>482.51</td>
<td>505.21</td>
<td>494.35</td>
<td>494.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Cr</td>
<td>425.433</td>
<td>426.92</td>
<td>428.31</td>
<td>445.76</td>
<td>433.66</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Cr</td>
<td>425.433</td>
<td>297.95</td>
<td>303.95</td>
<td>308.79</td>
<td>303.56</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Cr</td>
<td>425.433</td>
<td>482.51</td>
<td>505.21</td>
<td>494.35</td>
<td>494.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Cr</td>
<td>425.433</td>
<td>309.52</td>
<td>319.71</td>
<td>321.53</td>
<td>316.92</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Cr</td>
<td>425.433</td>
<td>297.95</td>
<td>303.95</td>
<td>308.79</td>
<td>303.56</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Cr</td>
<td>425.433</td>
<td>242.78</td>
<td>255.29</td>
<td>259.99</td>
<td>252.69</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Cr</td>
<td>425.433</td>
<td>2196.65</td>
<td>2223.55</td>
<td>2236.18</td>
<td>2218.79</td>
<td>0.06</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Cr</td>
<td>425.433</td>
<td>2123.83</td>
<td>1237.89</td>
<td>1240.21</td>
<td>1233.98</td>
<td>0.04</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Cr</td>
<td>425.433</td>
<td>2196.65</td>
<td>2223.55</td>
<td>2236.18</td>
<td>2218.79</td>
<td>0.06</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Cr</td>
<td>425.433</td>
<td>2498.15</td>
<td>2509.05</td>
<td>2520.3</td>
<td>2509.17</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Cr</td>
<td>425.433</td>
<td>3199.1</td>
<td>3192.52</td>
<td>3204.48</td>
<td>3198.70</td>
<td>0.08</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Cr</td>
<td>425.433</td>
<td>4227.94</td>
<td>4232.4</td>
<td>4221.11</td>
<td>4227.15</td>
<td>0.11</td>
</tr>
<tr>
<td>Sample 18</td>
<td>Cr</td>
<td>425.433</td>
<td>3132.52</td>
<td>3140.65</td>
<td>3151.58</td>
<td>3141.58</td>
<td>0.08</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Cr</td>
<td>425.433</td>
<td>4704.35</td>
<td>4662.12</td>
<td>4631.28</td>
<td>4665.92</td>
<td>0.12</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Cr</td>
<td>425.433</td>
<td>5657.35</td>
<td>5748.12</td>
<td>5769.93</td>
<td>5725.13</td>
<td>0.14</td>
</tr>
<tr>
<td>Sample 21</td>
<td>Cr</td>
<td>425.433</td>
<td>3969.75</td>
<td>3975.42</td>
<td>3992.02</td>
<td>3979.06</td>
<td>0.10</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Cr</td>
<td>425.433</td>
<td>2383.97</td>
<td>2355.54</td>
<td>2387.15</td>
<td>2375.55</td>
<td>0.06</td>
</tr>
<tr>
<td>Sample</td>
<td>Cr 425.433</td>
<td>Intensity Repl 1</td>
<td>Intensity Repl 2</td>
<td>Intensity Repl 3</td>
<td>Ave Intensity</td>
<td>Conc</td>
<td>Dilution</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>----------------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>Sample 32</td>
<td>4863.39</td>
<td>4894.07</td>
<td>4924.29</td>
<td>4893.92</td>
<td>0.12 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 33</td>
<td>2926.83</td>
<td>2934.3</td>
<td>2940.06</td>
<td>2933.73</td>
<td>0.08 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 34</td>
<td>2782.09</td>
<td>2761.1</td>
<td>2772.93</td>
<td>2772.04</td>
<td>0.07 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 35</td>
<td>1219.48</td>
<td>1226.34</td>
<td>1230.92</td>
<td>1225.58</td>
<td>0.04 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 36</td>
<td>2782.09</td>
<td>2761.1</td>
<td>2772.93</td>
<td>2772.04</td>
<td>0.07 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 37</td>
<td>425.433</td>
<td>4924.16</td>
<td>4865.08</td>
<td>4910.29</td>
<td>0.11 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 38</td>
<td>4690.95</td>
<td>4710.4</td>
<td>4762.69</td>
<td>4721.35</td>
<td>0.12 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 39</td>
<td>4191.62</td>
<td>4212.23</td>
<td>4226.42</td>
<td>4210.09</td>
<td>0.11 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 40</td>
<td>4945.92</td>
<td>4985.01</td>
<td>4976.87</td>
<td>4969.27</td>
<td>0.12 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 41</td>
<td>-148.54</td>
<td>-143.43</td>
<td>-126.7</td>
<td>-139.56</td>
<td>0.01 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 42</td>
<td>298.48</td>
<td>301.43</td>
<td>311.29</td>
<td>303.73</td>
<td>0.02 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 43</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 44</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 45</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 46</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 47</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 48</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Ca Concentration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc</th>
<th>Dilution</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Ca 422.673</td>
<td>26274.54</td>
<td>26330.76</td>
<td>25705.1</td>
<td>26103.47</td>
<td>0.32</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Ca 422.673</td>
<td>20117.7</td>
<td>20240.04</td>
<td>19846.4</td>
<td>20068.05</td>
<td>0.27</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Ca 422.673</td>
<td>21467.74</td>
<td>21740.05</td>
<td>21566.52</td>
<td>21591.44</td>
<td>0.28</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Ca 422.673</td>
<td>22737.94</td>
<td>22535.94</td>
<td>22398.43</td>
<td>22557.44</td>
<td>0.29</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Ca 422.673</td>
<td>20314.37</td>
<td>20240.17</td>
<td>20629.93</td>
<td>20394.82</td>
<td>0.27</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Ca 422.673</td>
<td>19563.26</td>
<td>20497.9</td>
<td>20114.32</td>
<td>20058.49</td>
<td>0.27</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Ca 422.673</td>
<td>19070.19</td>
<td>19016.31</td>
<td>19144.22</td>
<td>19076.91</td>
<td>0.26</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Ca 422.673</td>
<td>20457.06</td>
<td>20374.32</td>
<td>20218.32</td>
<td>20349.90</td>
<td>0.27</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Ca 422.673</td>
<td>29580.75</td>
<td>29127</td>
<td>28834.16</td>
<td>29180.64</td>
<td>0.34</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>Sample</td>
<td>Ca 422.673</td>
<td>21742.12</td>
<td>21522.76</td>
<td>21740.53</td>
<td>21668.47</td>
<td>0.28</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>Sample 11</td>
<td>Ca 422.673</td>
<td>20356.75</td>
<td>19961.3</td>
<td>20159.23</td>
<td>20159.09</td>
<td>0.27</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 12</td>
<td>Ca 422.673</td>
<td>27702.49</td>
<td>27162.84</td>
<td>27490.21</td>
<td>27451.85</td>
<td>0.33</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 13</td>
<td>Ca 422.673</td>
<td>22068.99</td>
<td>22103.76</td>
<td>22509.17</td>
<td>22227.31</td>
<td>0.28</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 14</td>
<td>Ca 422.673</td>
<td>21101.94</td>
<td>21438.5</td>
<td>22103.76</td>
<td>21422.92</td>
<td>0.28</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 15</td>
<td>Ca 422.673</td>
<td>22689.24</td>
<td>22992.87</td>
<td>22639.09</td>
<td>22773.73</td>
<td>0.29</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 16</td>
<td>Ca 422.673</td>
<td>30402.49</td>
<td>30245.09</td>
<td>30829.11</td>
<td>30492.23</td>
<td>0.35</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 17</td>
<td>Ca 422.673</td>
<td>25667.5</td>
<td>26135.41</td>
<td>26327.77</td>
<td>26043.56</td>
<td>0.31</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 18</td>
<td>Ca 422.673</td>
<td>22711.1</td>
<td>22769.31</td>
<td>23134.72</td>
<td>22871.71</td>
<td>0.29</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 19</td>
<td>Ca 422.673</td>
<td>19858.91</td>
<td>19636.24</td>
<td>19813.36</td>
<td>19769.50</td>
<td>0.26</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 20</td>
<td>Ca 422.673</td>
<td>22375.62</td>
<td>22021.48</td>
<td>22421.77</td>
<td>22272.96</td>
<td>0.28</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 21</td>
<td>Ca 422.673</td>
<td>178660.12</td>
<td>179116.77</td>
<td>181389.92</td>
<td>179722.27</td>
<td>1.56</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 22</td>
<td>Ca 422.673</td>
<td>143741.18</td>
<td>144161.07</td>
<td>142939.22</td>
<td>143613.82</td>
<td>1.27</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 23</td>
<td>Ca 422.673</td>
<td>186060.55</td>
<td>183946.1</td>
<td>185805.97</td>
<td>185270.87</td>
<td>1.60</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 24</td>
<td>Ca 422.673</td>
<td>179981.82</td>
<td>181047.36</td>
<td>180475.38</td>
<td>180501.52</td>
<td>1.56</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 25</td>
<td>Ca 422.673</td>
<td>165285.31</td>
<td>161528.95</td>
<td>166392.86</td>
<td>164402.37</td>
<td>1.43</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 26</td>
<td>Ca 422.673</td>
<td>204274.01</td>
<td>204355.57</td>
<td>205477.7</td>
<td>204702.43</td>
<td>1.76</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 27</td>
<td>Ca 422.673</td>
<td>220974.87</td>
<td>221606.63</td>
<td>218087.59</td>
<td>220223.03</td>
<td>1.89</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 28</td>
<td>Ca 422.673</td>
<td>185812.95</td>
<td>183880.97</td>
<td>184274.09</td>
<td>184656.00</td>
<td>1.60</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 29</td>
<td>Ca 422.673</td>
<td>256688.69</td>
<td>257472.56</td>
<td>259299.08</td>
<td>257820.10</td>
<td>2.19</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 30</td>
<td>Ca 422.673</td>
<td>208155.53</td>
<td>208093.9</td>
<td>207540.29</td>
<td>207929.91</td>
<td>1.79</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 31</td>
<td>Ca 422.673</td>
<td>303716.59</td>
<td>305363.74</td>
<td>304148.09</td>
<td>304409.46</td>
<td>2.57</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 32</td>
<td>Ca 422.673</td>
<td>300323.47</td>
<td>302135.54</td>
<td>299944.57</td>
<td>300801.19</td>
<td>2.54</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 33</td>
<td>Ca 422.673</td>
<td>158767.18</td>
<td>159243.39</td>
<td>159287.12</td>
<td>159099.23</td>
<td>1.39</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 34</td>
<td>Ca 422.673</td>
<td>132085.68</td>
<td>133085.88</td>
<td>133447.55</td>
<td>132873.04</td>
<td>1.18</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 35</td>
<td>Ca 422.673</td>
<td>150730.93</td>
<td>150215.4</td>
<td>149001.43</td>
<td>149982.59</td>
<td>1.32</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 36</td>
<td>Ca 422.673</td>
<td>169153.59</td>
<td>167449.98</td>
<td>169756.55</td>
<td>168786.71</td>
<td>1.47</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 37</td>
<td>Ca 422.673</td>
<td>279847.49</td>
<td>282952.99</td>
<td>283066.83</td>
<td>281955.77</td>
<td>2.38</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 38</td>
<td>Ca 422.673</td>
<td>261629.84</td>
<td>257411.74</td>
<td>261904.64</td>
<td>260315.41</td>
<td>2.21</td>
<td>1:50 ppm</td>
<td></td>
</tr>
<tr>
<td>Sample 39</td>
<td>Ca 422.673</td>
<td>Intensity Repl 1</td>
<td>Intensity Repl 2</td>
<td>Intensity Repl 3</td>
<td>Ave Intensity</td>
<td>Conc 1:50 ppm</td>
<td>Dilution 1:50</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>--------------</td>
<td>----------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>324546.13</td>
<td>322814.21</td>
<td>320730.38</td>
<td>322696.91</td>
<td>2.71</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 40</td>
<td>Ca 422.673</td>
<td>341900.54</td>
<td>337519.65</td>
<td>332565.38</td>
<td>2.83</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 41</td>
<td>Ca 422.673</td>
<td>148014.6</td>
<td>149499.53</td>
<td>150047.09</td>
<td>1.31</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 42</td>
<td>Ca 422.673</td>
<td>22123.36</td>
<td>21883.41</td>
<td>21338.94</td>
<td>0.28</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 43</td>
<td>Ca 422.673</td>
<td>418486.58</td>
<td>410930.16</td>
<td>414321.37</td>
<td>3.46</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No sample</td>
<td>Ca 422.673</td>
<td>656.14</td>
<td>950.28</td>
<td>798.55</td>
<td>0.11</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 45</td>
<td>Ca 422.673</td>
<td>26924.55</td>
<td>26986.26</td>
<td>26848.64</td>
<td>0.32</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 46</td>
<td>Ca 422.673</td>
<td>359429.54</td>
<td>351048.7</td>
<td>352312.63</td>
<td>2.97</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 47</td>
<td>Ca 422.673</td>
<td>1877.37</td>
<td>1834.54</td>
<td>1701.09</td>
<td>0.12</td>
<td>1.50 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**E. Ca Concentration**

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc 1:50 ppm</th>
<th>Dilution 1:50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Ca 422.673</td>
<td>26274.54</td>
<td>26330.76</td>
<td>25705.1</td>
<td>26103.47</td>
<td>0.32</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Ca 422.673</td>
<td>20117.7</td>
<td>20240.04</td>
<td>19846.4</td>
<td>20068.05</td>
<td>0.27</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Ca 422.673</td>
<td>21467.74</td>
<td>21740.05</td>
<td>21566.52</td>
<td>21591.44</td>
<td>0.28</td>
<td>1.50 ppm</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Ca 422.673</td>
<td>22737.94</td>
<td>22535.94</td>
<td>22398.43</td>
<td>22557.44</td>
<td>0.29</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 5</td>
<td>Ca 422.673</td>
<td>20314.37</td>
<td>20240.17</td>
<td>20629.93</td>
<td>20394.82</td>
<td>0.27</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 6</td>
<td>Ca 422.673</td>
<td>19563.26</td>
<td>20497.9</td>
<td>20114.32</td>
<td>20058.49</td>
<td>0.27</td>
<td>1.50 Pm</td>
</tr>
<tr>
<td>Sample 7</td>
<td>Ca 422.673</td>
<td>19070.19</td>
<td>19016.31</td>
<td>19144.22</td>
<td>19076.91</td>
<td>0.26</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 8</td>
<td>Ca 422.673</td>
<td>20457.06</td>
<td>20374.32</td>
<td>20218.32</td>
<td>20349.90</td>
<td>0.27</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 9</td>
<td>Ca 422.673</td>
<td>29580.75</td>
<td>29127</td>
<td>28834.16</td>
<td>29180.64</td>
<td>0.34</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 10</td>
<td>Ca 422.673</td>
<td>21742.12</td>
<td>21522.76</td>
<td>21740.53</td>
<td>21668.47</td>
<td>0.28</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 11</td>
<td>Ca 422.673</td>
<td>20356.75</td>
<td>19961.3</td>
<td>20159.23</td>
<td>20159.09</td>
<td>0.27</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 12</td>
<td>Ca 422.673</td>
<td>27702.49</td>
<td>27162.84</td>
<td>27490.21</td>
<td>27451.85</td>
<td>0.33</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 13</td>
<td>Ca 422.673</td>
<td>22068.99</td>
<td>22103.76</td>
<td>22509.17</td>
<td>22227.31</td>
<td>0.28</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 14</td>
<td>Ca 422.673</td>
<td>21101.94</td>
<td>21438.5</td>
<td>21728.33</td>
<td>21422.92</td>
<td>0.28</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 15</td>
<td>Ca 422.673</td>
<td>22689.24</td>
<td>22992.87</td>
<td>22639.09</td>
<td>22773.73</td>
<td>0.29</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 16</td>
<td>Ca 422.673</td>
<td>30402.49</td>
<td>30245.09</td>
<td>30829.11</td>
<td>30492.23</td>
<td>0.35</td>
<td>1.50 Ppm</td>
</tr>
<tr>
<td>Sample 17</td>
<td>Ca 422.673</td>
<td>25667.5</td>
<td>26135.41</td>
<td>26327.77</td>
<td>26043.56</td>
<td>0.31</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 18</td>
<td>Ca 422.673</td>
<td>22711.1</td>
<td>22769.31</td>
<td>23134.72</td>
<td>22871.71</td>
<td>0.29</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 19</td>
<td>Ca 422.673</td>
<td>19858.91</td>
<td>19636.24</td>
<td>19813.36</td>
<td>19769.50</td>
<td>0.26</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 20</td>
<td>Ca 422.673</td>
<td>22375.62</td>
<td>22021.48</td>
<td>22421.77</td>
<td>22272.96</td>
<td>0.28</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 21</td>
<td>Ca 422.673</td>
<td>178660.12</td>
<td>179116.77</td>
<td>181389.92</td>
<td>179722.27</td>
<td>1.56</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 22</td>
<td>Ca 422.673</td>
<td>143741.18</td>
<td>144161.07</td>
<td>142939.22</td>
<td>143613.82</td>
<td>1.27</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 23</td>
<td>Ca 422.673</td>
<td>186060.55</td>
<td>183946.1</td>
<td>185805.97</td>
<td>185270.87</td>
<td>1.60</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Ca 422.673</td>
<td>179981.82</td>
<td>181047.36</td>
<td>180475.38</td>
<td>180501.52</td>
<td>1.56</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 25</td>
<td>Ca 422.673</td>
<td>165285.31</td>
<td>161528.95</td>
<td>166392.86</td>
<td>164402.37</td>
<td>1.43</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 26</td>
<td>Ca 422.673</td>
<td>204274.01</td>
<td>204355.57</td>
<td>205477.7</td>
<td>204702.43</td>
<td>1.76</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 27</td>
<td>Ca 422.673</td>
<td>220974.87</td>
<td>221606.63</td>
<td>218087.59</td>
<td>220223.03</td>
<td>1.89</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 28</td>
<td>Ca 422.673</td>
<td>185812.95</td>
<td>183880.97</td>
<td>184274.09</td>
<td>184656.00</td>
<td>1.60</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 29</td>
<td>Ca 422.673</td>
<td>256688.69</td>
<td>257472.53</td>
<td>259299.08</td>
<td>257820.10</td>
<td>2.19</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 30</td>
<td>Ca 422.673</td>
<td>208155.53</td>
<td>208093.9</td>
<td>207540.29</td>
<td>207929.91</td>
<td>1.79</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 31</td>
<td>Ca 422.673</td>
<td>303716.59</td>
<td>305363.74</td>
<td>304148.06</td>
<td>304409.46</td>
<td>2.57</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 32</td>
<td>Ca 422.673</td>
<td>300323.47</td>
<td>302135.54</td>
<td>299944.57</td>
<td>300801.19</td>
<td>2.54</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 33</td>
<td>Ca 422.673</td>
<td>158767.18</td>
<td>159243.39</td>
<td>159287.12</td>
<td>159099.23</td>
<td>1.39</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 34</td>
<td>Ca 422.673</td>
<td>132085.68</td>
<td>133085.88</td>
<td>133447.55</td>
<td>132873.04</td>
<td>1.18</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 35</td>
<td>Ca 422.673</td>
<td>150730.93</td>
<td>150215.4</td>
<td>149001.43</td>
<td>149982.59</td>
<td>1.32</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 36</td>
<td>Ca 422.673</td>
<td>169153.59</td>
<td>167449.98</td>
<td>169756.55</td>
<td>168786.71</td>
<td>1.47</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 37</td>
<td>Ca 422.673</td>
<td>279847.49</td>
<td>282952.99</td>
<td>283066.83</td>
<td>281955.77</td>
<td>2.38</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 38</td>
<td>Ca 422.673</td>
<td>261629.84</td>
<td>257411.74</td>
<td>261904.64</td>
<td>260315.41</td>
<td>2.21</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 39</td>
<td>Ca 422.673</td>
<td>324546.13</td>
<td>322814.21</td>
<td>320730.38</td>
<td>322696.91</td>
<td>2.71</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 40</td>
<td>Ca 422.673</td>
<td>341900.54</td>
<td>337519.65</td>
<td>332565.38</td>
<td>337328.52</td>
<td>2.83</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 41</td>
<td>Ca 422.673</td>
<td>148014.6</td>
<td>149499.53</td>
<td>150047.09</td>
<td>149187.07</td>
<td>1.31</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 42</td>
<td>Ca 422.673</td>
<td>22123.36</td>
<td>21883.41</td>
<td>21338.94</td>
<td>21781.90</td>
<td>0.28</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 43</td>
<td>Ca 422.673</td>
<td>418486.58</td>
<td>410930.16</td>
<td>414321.37</td>
<td>414579.37</td>
<td>3.46</td>
<td>1:50</td>
</tr>
<tr>
<td>Sample 45</td>
<td>Ca 422.673</td>
<td>656.14</td>
<td>950.28</td>
<td>798.55</td>
<td>801.66</td>
<td>0.11</td>
<td>1:50</td>
</tr>
</tbody>
</table>
### Table 1: Element Concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc</th>
<th>Dilution</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na</td>
<td>588.995</td>
<td>520205.83</td>
<td>508986.20</td>
<td>520140.46</td>
<td>1.45</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>2</td>
<td>Na</td>
<td>588.995</td>
<td>468635.20</td>
<td>470836.22</td>
<td>473150.91</td>
<td>1.32</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>588.995</td>
<td>446520.07</td>
<td>457523.39</td>
<td>457645.48</td>
<td>1.28</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>4</td>
<td>Na</td>
<td>588.995</td>
<td>348101.61</td>
<td>347377.00</td>
<td>350310.63</td>
<td>0.97</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>5</td>
<td>Na</td>
<td>588.995</td>
<td>824255.55</td>
<td>834042.19</td>
<td>832339.00</td>
<td>2.36</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>6</td>
<td>Na</td>
<td>588.995</td>
<td>826987.39</td>
<td>854896.68</td>
<td>840444.52</td>
<td>2.38</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>7</td>
<td>Na</td>
<td>588.995</td>
<td>800459.76</td>
<td>820677.63</td>
<td>819690.55</td>
<td>2.32</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>8</td>
<td>Na</td>
<td>588.995</td>
<td>780169.62</td>
<td>804860.20</td>
<td>797652.58</td>
<td>2.25</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>9</td>
<td>Na</td>
<td>588.995</td>
<td>743827.23</td>
<td>735538.70</td>
<td>741495.46</td>
<td>2.10</td>
<td>1:50</td>
<td>ppm</td>
</tr>
<tr>
<td>10</td>
<td>Na</td>
<td>588.995</td>
<td>518809.85</td>
<td>521600.38</td>
<td>512115.58</td>
<td>1.46</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>588.995</td>
<td>543274.68</td>
<td>545487.07</td>
<td>541470.76</td>
<td>1.53</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>12</td>
<td>Na</td>
<td>588.995</td>
<td>579263.66</td>
<td>577489.82</td>
<td>591837.19</td>
<td>1.64</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>13</td>
<td>Na</td>
<td>588.995</td>
<td>484730.28</td>
<td>498260.84</td>
<td>495887.80</td>
<td>1.39</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>14</td>
<td>Na</td>
<td>588.995</td>
<td>492911.37</td>
<td>473354.72</td>
<td>474656.54</td>
<td>1.35</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>15</td>
<td>Na</td>
<td>588.995</td>
<td>498786.57</td>
<td>487488.51</td>
<td>488943.95</td>
<td>1.38</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>16</td>
<td>Na</td>
<td>588.995</td>
<td>405120.36</td>
<td>401276.66</td>
<td>412731.56</td>
<td>1.14</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>17</td>
<td>Na</td>
<td>588.995</td>
<td>674292.55</td>
<td>661697.37</td>
<td>679615.61</td>
<td>1.90</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>18</td>
<td>Na</td>
<td>588.995</td>
<td>544734.84</td>
<td>540637.05</td>
<td>542772.24</td>
<td>1.53</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>19</td>
<td>Na</td>
<td>588.995</td>
<td>557718.85</td>
<td>548234.68</td>
<td>538816.06</td>
<td>1.55</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>20</td>
<td>Na</td>
<td>588.995</td>
<td>556567.91</td>
<td>550563.45</td>
<td>550632.96</td>
<td>1.56</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>21</td>
<td>Na</td>
<td>588.995</td>
<td>381326.63</td>
<td>40175.65</td>
<td>41807.69</td>
<td>0.09</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>22</td>
<td>Na</td>
<td>588.995</td>
<td>29740.41</td>
<td>32070.58</td>
<td>32677.70</td>
<td>0.07</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>23</td>
<td>Na</td>
<td>29180.54</td>
<td>30290.99</td>
<td>30613.62</td>
<td>30028.38</td>
<td>0.06</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
</tbody>
</table>

### F. Na Concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na</th>
<th>Intensity Repl 1</th>
<th>Intensity Repl 2</th>
<th>Intensity Repl 3</th>
<th>Ave Intensity</th>
<th>Conc</th>
<th>Dilution</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>Ca</td>
<td>422.673</td>
<td>26924.55</td>
<td>26986.26</td>
<td>26848.64</td>
<td>0.32</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>47</td>
<td>Ca</td>
<td>422.673</td>
<td>359429.54</td>
<td>351048.7</td>
<td>352312.63</td>
<td>2.97</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>48</td>
<td>Ca</td>
<td>422.673</td>
<td>1877.37</td>
<td>1834.54</td>
<td>1701.09</td>
<td>0.12</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 24</td>
<td>Na 588.995</td>
<td>35124.98</td>
<td>35544.38</td>
<td>36123.68</td>
<td>35597.68</td>
<td>0.08</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 25</td>
<td>Na 588.995</td>
<td>111805.31</td>
<td>113345.93</td>
<td>113603.88</td>
<td>112918.37</td>
<td>0.30</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 26</td>
<td>Na 588.995</td>
<td>141550.49</td>
<td>142208.61</td>
<td>142705.31</td>
<td>142154.80</td>
<td>0.38</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 27</td>
<td>Na 588.995</td>
<td>102974.72</td>
<td>104483.38</td>
<td>102854.62</td>
<td>103437.57</td>
<td>0.27</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 28</td>
<td>Na 588.995</td>
<td>145100.89</td>
<td>142208.61</td>
<td>142705.31</td>
<td>142154.80</td>
<td>0.38</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 29</td>
<td>Na 588.995</td>
<td>149419.31</td>
<td>151872.25</td>
<td>148940.37</td>
<td>150077.31</td>
<td>0.40</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 30</td>
<td>Na 588.995</td>
<td>109056.83</td>
<td>108744.87</td>
<td>105731.14</td>
<td>107844.28</td>
<td>0.28</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 31</td>
<td>Na 588.995</td>
<td>110454.80</td>
<td>109743.74</td>
<td>109882.15</td>
<td>110031.90</td>
<td>0.29</td>
<td>1:50</td>
<td>Ppm</td>
</tr>
<tr>
<td>Sample 32</td>
<td>Na 588.995</td>
<td>70964.77</td>
<td>72438.93</td>
<td>0.18</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 33</td>
<td>Na 588.995</td>
<td>31654.41</td>
<td>32158.44</td>
<td>0.07</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 34</td>
<td>Na 588.995</td>
<td>26847.42</td>
<td>26984.82</td>
<td>0.05</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 35</td>
<td>Na 588.995</td>
<td>23442.78</td>
<td>23565.77</td>
<td>0.04</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 36</td>
<td>Na 588.995</td>
<td>32062.31</td>
<td>32722.05</td>
<td>0.07</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 37</td>
<td>Na 588.995</td>
<td>78143.56</td>
<td>77219.43</td>
<td>0.20</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 38</td>
<td>Na 588.995</td>
<td>72181.13</td>
<td>72081.28</td>
<td>0.18</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 39</td>
<td>Na 588.995</td>
<td>72988.75</td>
<td>72082.32</td>
<td>0.18</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 40</td>
<td>Na 588.995</td>
<td>84707.61</td>
<td>0.22</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 41</td>
<td>Na 588.995</td>
<td>63246.12</td>
<td>64145.88</td>
<td>0.16</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 42</td>
<td>Na 588.995</td>
<td>18294.90</td>
<td>17871.92</td>
<td>0.03</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 43</td>
<td>Na 588.995</td>
<td>4313293.94</td>
<td>4286610.87</td>
<td>12.25</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 44</td>
<td>Na 588.995</td>
<td>4659.84</td>
<td>-0.01</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 45</td>
<td>Na 588.995</td>
<td>4681.64</td>
<td>4659.84</td>
<td>-0.01</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 46</td>
<td>Na 588.995</td>
<td>29774.21</td>
<td>0.06</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 47</td>
<td>Na 588.995</td>
<td>3859253.98</td>
<td>11.03</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 48</td>
<td>Na 588.995</td>
<td>4424.74</td>
<td>-0.01</td>
<td>1:50</td>
<td>Ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 4: RESULTS OF Energy Dispersive Spectroscopy (EDS).