



## **ACKNOWLEDGEMENT**

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## **ABSTRACT**

Industrial cathodes have the potential of being extremely nonuniform in impurity content. Obtaining a representative sample is essential in evaluating specifications compliance in industrial cathodes which determine its quality. Knowledge about impurity distribution in nickel cathode is scanty. Again there seems to be no literature regarding proper sampling design on nickel cathode. The thrust of this project was to carry out profile tests on impurity distribution and then design an appropriate sampling method for nickel cathode, using statistical analysis. It was observed that there is no pattern in which the impurities are distributed within the cathode. Random sampling was found to be the best method for sampling nickel cathodes.

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## **CHAPTER 1**

### **1 INTRODUCTION**

Nickel cathodes are currently produced in three separate plants in Southern Africa, Empress Nickel and Bindura Nickel in Zimbabwe and Rustenburg Base Metal Refiners (RBMR) in South Africa. In all these plants nickel is produced from sulphide flotation concentrate that is smelted to produce a matte (Groom J.D.G at el).

Empress Nickel Refinery comprises of Nickel smelter and refinery which operate as a toll refiner of matte for BCL. ENR produces high quality nickel and copper metal from matte supplied by the Selibe Phikwe flash smelter in Botswana. The refinery uses the Outokumpu process for leaching the matte with nickel and copper electro won from the leach solution. Atmospheric leaching of the matte is employed and an insoluble residue containing high copper and low nickel is produced which is then



smelted in a sirosmelt furnace and then returned into the leach process. Empress Nickel Refinery has a capacity of producing a 500 tonnes of Nickel and 400 tonnes of copper per month.

### 1.1 Nickel Refinery by Outokumpu Process

Granulated matte is received from BCL in bags and is ground to 85-90% passing through 53 microns in a ball mill. The cyclone overflow gravitates to a dewatering cone. The cone overflow is used as make up water in the milling circuit and the underflow is pumped to the cementation stage with copper (11) anolyte for nickel leaching. Matte entering the cementation stage consists of 48%Ni, 45%Cu and 5%S. Cementation involves the atmospheric leach in which the matte and copper (11) anolyte are reacted together. The following four reactions take place

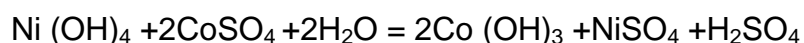
- 1)  $\text{Ni} + \text{CuSO}_4 = \text{NiSO}_4 + \text{Cu}$
- 2)  $2\text{Cu} + 0.5\text{O}_2 = \text{Cu}_2\text{O}$
- 3)  $\text{Cu}_2\text{O} + 2\text{H}_2\text{SO}_4 = 0.5\text{O}_2 + 2\text{CuSO}_4 + 2\text{H}_2\text{O}$
- 4)  $\text{Ni}_3\text{S} + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 = \text{NiSO}_4 + 2\text{NiS} + \text{H}_2\text{O}$

Reaction 1 involves the dissolution of metallic nickel in which copper free solution for nickel electro winning is produced. The cemented copper from reaction 1 along with copper metal in the ground feed is then oxidised to copper oxide by reaction 2. The oxidising agent for reaction 2 is air and oxygen. The oxidised copper is reacted with sulphuric acid and produces more copper ions for reaction 1. The reactions are cyclic and are controlled to obtain the maximum dissolution of nickel and copper. At pH of about 2 the dissolution of copper oxide decreases rapidly and reaction 4 takes over as the rate controlling step. As sulphuric acid is consumed the pH rises and at pH 4 a new reaction is found to take control, which result in the precipitation of a copper sulphate hydroxide compound.



The acid generated in reaction 5 stabilises the pH at around 4 and must be consumed by reaction 4. The hydrolysis of the ferric ions in solution follow a similar manner and the reactions stop when a pH of 6 is achieved. At this point

both the copper and Iron levels in solution have been lowered to acceptable levels. The cementation stage consist of 5 by 50cm<sup>3</sup> reactors, two of which are supplied with oxygen, two on compressed air and one on standby. The product from the last cementation reactor is pumped to thickener 1. To produce high grade nickel cathodes the impure nickel catholyte solution overflowing the thickener gravitates into the hopper where barium hydroxide is added to precipitate dissolved lead, the solution is then pumped to the nickel presses to remove the entrained solids. Further purification is done by removing cobalt by using electrically generated nickelic hydroxide. NiSO<sub>4</sub> in pure catholyte is reacted with an 80g/l solution of NaOH to produce a precipitate of nickelous hydroxide Ni (OH) <sub>2</sub>. The nickelous hydroxide is electrically oxidised using Ni anodes and stainless steel cathodes by the following reaction.



The cobalt precipitation reaction is carried out in aeration tanks and the cobalt concentration is reduced to below 3ppm. Reducing cobalt to this level will ensure a final product containing less than 50ppm cobalt. The precipitate containing the cobaltic hydroxide and unreacted nickelic hydroxide is pumped through the cobalt primary presses and the filtrate is polished using scheiber filters before entering the nickel catholyte storage tank. Nickel catholyte is transferred at a controlled flow rate from storage tank to a steady head tank inside the tank house. The flow is distributed evenly to each nickel cell on line and is controlled by capillary flow meters. Nickel is electro won from the sulphate solution and plated on titanium blanks for the production of starter sheets. These sheets are used in the production of nickel cathode. A nickel cell contains 49 insoluble lead anodes and 48 nickel cathodes with a total of 72 cells being arranged electrically in series. About 10 cells are used in the production of starter sheets and the remainder for cathode production. The cell current is maintained at 15 KA with a cell voltage of approximately 4.0v and a current density of 180A/M<sup>2</sup>. The current efficient of nickel plating decreases rapidly as the acid content of the catholyte increases and therefore the catholyte and anolyte must be separated. This is achieved by using a cathode diaphragm bag. The cathode is suspended in the bag and the flow of catholyte is fed individually to each bag. Good flow control and correct bag

permeability are vital to ensure a hydrostatic head of 5 to 25 mm inside the bag. This will prevent the passage of acid back into the cathode area and subsequent fizzing observed inside the bag. This fizzing is the result of hydrogen gas evolution at the cathode which takes place in preference to nickel plating when acid is present and result in pitted cathodes and poor current utilisation. Nickel cathode exiting the cells overflow into a nickel anolyte launder before being discharged into a sump and pumped to storage for subsequent copper leaching. Nickel cathodes are removed from the cells after a 7 day plating cycle and washed to remove any green nickel sulphate crystals before they leave the tank house. The cathodes are sent to material handling where they are guillotined to 25mm and 100mm squares and finally despatched to market (Empress Nickel Refinery Operating Procedure, 1999).

**Table 1.1 Tank house Configuration and Operating Conditions At ENR**

STARTER CELLS	10
COMMERCIAL CELLS	65
CATHODES PER CELL	48
CURRENT PER CELL (KA)	15
CURRENT EFFICIENCY (%)	96(TARGET)
PULLING CYCLE	NIL
STARTER (d)	2
CATHODE (d)	7
ELECTROLYTE FEED RATE (M <sup>3</sup> /H/CELL)	0.45
pH	2.9
NICKEL	75-80
SODIUM SULPHATE	NIL
BORIC ACID g/l	NIL
SLS ppm	NIL
ΔNi g/L	30
CELL TEMPERATURE	60-65

## 1.2 Justification

The major problem that exists in the nickel cathode production industry is that a small variation in the quality of the metal content can result in a large discrepancy in the financial value of the whole consignment, considering the quantities involved.

Such discrepancies usually causes disputes between producers and buyers, and this might end up involving third parties. There is a need for the design of a sampling method that can produce a representative sample.

### **1.3 Objectives**

- 1) To carry out a profile test of nickel cathode in order to determine impurity distribution.
- 2) To use statistical tools to design an appropriate sampling method.

## **CHAPTER 2**

### **2 LITERATURE REVIEW**

#### **2.1 Electrolytic Refined Nickel Cathode Production**

Control of electrolyte feed to the cathode compartment and of the solution head that develops across each bag are key factors affecting cathode quality. Control of bag

permeability is more difficult requiring strict QA procedures during bag procurement and regular maintenance. Bags that have become blinded or torn are identified during cell inspection. They should be repaired or replaced (Groom *et al* 1985).

## **2.2 Starter Sheet Preparation and Cathode Handling**

Nickel starter sheet quality is important to the quality of the cathode product. Starter sheets are grown on titanium cathode blanks over a period of 1-2 days, after which they are stripped manually from the blank. During starter sheet production process close attention is paid to the following:

- 1) Titanium blank surface quality
- 2) Starter sheet geometry

Finished starter sheets are anodically depassivated at a current density  $90\text{A/M}^2$  for a period of 20 minutes prior to being placed in the commercial cells. This procedure cleans the surface of the sheet, improving deposited adherence and surface quality. After the cathode are pulled, the cells are constantly inspected to check electrode alignment and identify problems such as electrolyte feed disruption, bag failure, poor electrical contacts and electrode short circuits (Kielty 1999).

The anode composition and the behaviour of the dissolved or precipitated impurities in the electrolyte influence cathode quality. Depending on their respective density the precipitated constituents tend to localize on the upper edge or at the bottom section of the cathode. Nodular cathode surfaces can cause severe heterogeneous occlusions of the precipitated impurities. Cathode surface will have to be free of nodulation in order for the impurities to be below the new high-grade specifications. Obtaining a representative sample is essential to evaluating specification compliance (Kielty 1999).

## **2.3 Basics of Nickel Electroplating**

Electroplating is the most widely used method of nickel plating the alternate method is electroless nickel plating (Hofirek 1988).

### **2.3.1 Surface Preparation**

Prior to plating operation the cathode surface should be cleaned from oils, greases, paints and miscellaneous solid particles (Hofirek 1988).

### **2.3.2 Current Efficiency**

Current efficiency is a ratio of the current producing nickel deposit to the total passing current. Anode current efficiency in nickel electroplating is about 100%. It may decrease at high pH, when nickel dissolution is accompanied by discharging hydroxyl ions ( $\text{OH}^-$ ). Cathode efficiency of nickel electroplating is 90-97%, 3-10% of the electric current is consumed by discharging hydrogen ions ( $\text{H}^+$ ) which form bubbles of gaseous hydrogen ( $\text{H}_2$ ) on the cathode surface (Davis *et al* 1994).

### **2.3.3 Anti- Pitting Additives**

Hydrogen bubbles formed on the cathode surface and adhered to it may cause pitting of the deposit. In order to enhance removal of the bubbles wetting agents are added to the electrolyte. Wetting (anti-pitting) agents e.g. Sodium Lauryl Sulphate decrease the surface tension of the cathode and force the hydrogen bubbles out of the surface (Groom *et al* 1995).

### **2.3.4 Air Agitation**

Air agitation by low pressure blowers is used in nickel electroplating to enhance removal of hydrogen bubbles discharged at the cathode.

### **2.3.5 Temperature**

Nickel electroplating processes are conducted at increased temperature, which results in lower electrolyte resistance and therefore permits to decrease the voltage. Additionally high temperature aids dissolution and prevents precipitation of boric acid and other components (Hofirek 1988).

### 2.3.6 Nickel Coating Thickness

Thickness of electroplated nickel coating is calculated from the Faradays law.

$$W = (I \times t \times A) / n \times F$$

Where W is weight of plated metal in grams

I is current in coulombs per second

t is time in seconds

A is atomic weight of the metal in grams per mole.

n is valance of the dissolved metal in solution in equivalence per mole

F is Faradays constant in coulombs per equivalent

F = 96 485 309 Coulombs/ equivalent

## 2.4 Problems and Troubleshooting

Factors that affect quality of nickel cathode are as follows:

### 2.4.1 Roughness

Roughness of nickel coating is generally caused by foreign particles suspended in the electrolyte solution, air dust, torn anode bags, dropped parts, precipitates of boric acid, metallic impurities, or drag in of incompatible solutions. Roughness may be also a result of deposition in low brightener solutions at high current density. Corrective actions proper filtering, preventing drag-in, temperature control (Hofireck *et al* 1990).

### **2.4.2 Pitting**

Pitting is a result of hydrogen bubbles adhered to the cathode surface. It usually occurs at low concentration of wetting agent, low air agitation, high current densities, and low boric acid concentrations. Corrective actions by checking the concentration of anti-pitting (wetting) agent and boric acid, increase air agitation, decrease the current density (Hofireck *et al* 1990).

### **2.4.3 Poor Adhesion**

Poor adhesion (peeling, blister, low adhesion strength) of nickel coatings may be generally caused either by poor pre-treatment cleaning or poor acid activation of the part surface (Kielty 1999).

### **2.4.4 High Stress and Low Ductility**

Different nickel electroplating solutions produce coatings with different levels of internal mechanical stress and ductility. The lowest stress and maximum ductility are provided by nickel sulfamate solutions. Brittle coatings are caused by excessive concentration of organic agents (levellers, brighteners) decomposition products of brighteners, nickel chloride and metallic contaminants (Groom *et al* 1985).

## **2.5 Quality Control**

Achieving high quality involves controlling the bath composition, the purity of the plating solution, and the thickness and uniformity of the deposits. Eliminating rejects, troubleshooting, and the testing of deposits are important aspects of process and product control (Groom *et al* 1985).

### **2.5.1 Control Solution Composition**

Control of the composition of the plating bath is one of the most important factors contributing to the quality of nickel deposits. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter, the composition and pH of the solution must be controlled within specified limits and contamination by metallic and organic substances must be prevented (Hofireck 1988).



### **2.5.2 Purification Techniques and Starting Up a New Bath**

Before any freshly prepared nickel plating bath is used, contaminants such as iron, copper, zinc, and organics present in trace quantities in commercial salts must be removed to obtain the best results.

### **2.5.3 Controlling the Main Constituents**

The following basic constituents of nickel plating baths must be regularly controlled: (a) the nickel metal content; (b) the chloride concentration; (c) the boric acid; and (d) any organic addition agents. Nickel metal concentration is maintained between 60 and 80 g/L. Boric acid is the most commonly used buffering agent for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance (Davis *et al* 1994).

### **2.5.4 Controlling pH, Temperature, Current Density and Water Quality**

The pH of the nickel plating solution will rise during normal operation of the bath necessitating regular additions of acid to maintain the pH within the prescribed limits. (A decrease in pH accompanied by a decrease in nickel ion concentration indicates the process is not functioning properly.) The operating temperature may have a significant effect on the properties of the deposits and should be maintained within specified limits (plus or minus 2<sup>0</sup>C) of the recommended value. In general, most commercial nickel plating baths are operated between 38 to 60<sup>0</sup>C (100 to 1400F). The nickel plating process should be operated at specified current densities by estimating the surface area of the parts and calculating the total current required. The practice of operating the process at a fixed voltage is not recommended. Controlling cathode current density is essential for accurately predicting average nickel thickness, for achieving uniform coating thickness on complicated shapes, and for producing deposits with consistent and predictable properties. Since current density determines the rate of deposition, it must be as uniform as possible to achieve uniformly thick nickel deposits. The quality of the water used in making up the bath and in replacing water lost by evaporation is important. Demineralised water should be used, especially if the local tap water has high calcium content (greater than 200 ppm). Filtering the water before it is

added to the plating tank is a useful precaution to eliminate particles that can cause rough deposits (Kielty, 1999).

### **2.5.5 Controlling Impurities**

Inorganic, organic and gaseous impurities may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities from the plating shop can improve the quality of the deposits, as well as productivity and profitability. The presence of small quantities of inorganic or organic contamination may result in plating defects (Hofireck 1988).

### **2.5.6 Inorganic contaminants**

*Inorganic contaminant* arise from numerous sources, including nickel salts of technical grade, hard water, carry-over from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, dirt from structures above the tank, from parts that fall into the solution and are not removed, etc. Table 8 lists maximum limits for metallic impurities in nickel plating baths. The degree of contamination by many inorganic materials may be controlled by continuous filtration and dummyming; that is, electrolysis of the plating solution at 0.2 to 0.5 A/dm (2 to 5 A/ft<sup>2</sup>).

### **2.5.7 Organic contaminants**

Organic contaminants may arise from many sources including: buffing compounds; lubricating oil dropped from overhead equipment; sizing from anode bags; weaving lubricants on plastic anode bags; uncured rack coatings or stop-off lacquers; adhesives on certain types of masking tape; decomposition products from wetting agents; organic stabilizers in hydrogen peroxide; paint spray; and new or patched rubber tank linings. Many organic contaminants can be effectively removed from nickel plating solutions by adsorption on activated carbon on either a batch or a continuous basis (Hofireck 1988) .

### **2.5.8 Gaseous contamination**

Nickel plating solutions usually consists of dissolved air or carbon dioxide. Dissolved air in small amounts may lead to a type of pitting characterized by a

teardrop pattern. Dissolved air in the plating solution usually can be traced to entrainment of air in the pumping system when the solution is circulated. If this occurs, circulating pump and valves should be checked and modified, if necessary. Nickel plating solutions can be purged of dissolved air by heating to a temperature at least 6<sup>0</sup>C (100F) higher than the normal operating temperature for several hours. The solution is cooled to the operating temperature before plating is resumed. Dissolved carbon dioxide in a nickel plating solution is usually found after nickel carbonate has been added to raise the pH, and is liberated from warm nickel plating solutions after several hours. If solutions containing carbon dioxide are scheduled for immediate use, they should be purged by a combination of heating and air agitation for approximately 1 h at 6<sup>0</sup>C (100F) or more above the normal plating temperature (Groom *et al* 1985).

### **2.5.9 Eliminating Rejects/Troubleshooting**

The production of defective plated parts or rejects may be associated with the presence in solution of soluble and insoluble impurities. The nature of the coating defect is often an indication of the source of the problem. Common defects include roughness, pitting, blistering (often associated with poor preparation of the surface prior to plating), high stress and low ductility, discoloration, burning at high current density areas, and failure to meet thickness specifications (Davies 1994).

### **2.5.10 Pitting**

Pitting is caused by many factors including adhesion of air or hydrogen bubbles to the parts being plated. Air should be expelled as already mentioned. Pitting from adherent hydrogen bubbles can result from a solution that is chemically out of balance; has too low a pH; or is inadequately agitated. Incorrect racking of complicated components; too low a concentration of wetting or anti-pitting agents; the use of incompatible wetting agents; the presence of organic contaminants; the presence of copper ions and other inorganic impurities; incomplete cleaning of the basis material; incomplete dissolution of organic additives that may form oily globules can all result in pitting. Pitting is, therefore, avoided by maintaining the composition of the plating solution within specified limits, by controlling the pH and

temperature, and by preventing impurities of all kinds from entering the solution (Hofireck *et al* 1990) .

### **2.5.11 Discoloration in low current density areas**

Discoloration in low current density areas is most likely the consequence of metallic Contamination of the plating solution. The effects can be evaluated systematically by plating over a reproducible range of current densities on a Hull cell cathode. Hull cells are available from plating supply houses and are shaped so that nickel can be deposited onto a standard panel over a predictable range of current densities. The variation in current density over the face of the panel is achieved by placing the panel at a specified angle to the anode (Groom *et al* 1985).

### **2.5.12 Burning at high current densities**

Can be caused by applying the full load on the rectifier to the lowest parts on a rack as it is lowered into the tank. This can be controlled by applying a reduced load or ramping the current during immersion of the rack. Burning can be caused by exceeding the recommended maximum cathode current density, and is sometimes related to the presence of phosphates in solution introduced via contaminated activated carbon. Incorrect levels of organic additives can cause burning (Green 1997).

### **2.5.13 Failure to meet thickness specifications**

Failure to meet thickness specifications is most frequently due to the application of too low a current and/or too short a plating time. This can be avoided by measuring the area of the parts to be plated, then calculating the total current required for a specified current density, and plating for the appropriate time. Another major cause of failure to meet thickness requirements is non-uniform distribution of current leading to insufficient deposit in low current density areas. Poor electrical contacts and stray currents can also cause thin deposits, and anode and cathode bars, hooks and contacts should be kept clean (Kielty 1999).

## **2.6 Sampling Methods**

A major consideration in the reliability of any analytical measurement is that of sample quality. The analyst often report results obtained on the particular test specimen at the moment of analysis, which may not provide information desired or needed. This is because of uncertainties in the sampling process or in sample storage, preservation, or pre-treatment prior to analysis (American chemical society 1981). The major task for sampling is selection and withdrawal of valid gross sample from the population. Secondly reduction of gross sample to a Laboratory sample suitable for the analytical techniques to be used (American chemical society 1981).

### **2.6.1 Considerations In Sampling**

Poor analytical results may be caused by contaminated reagents, biased methods, and operation errors in procedure or data handling. Most of these errors can be controlled by proper use of blanks, standards and reference samples. The problem of an in valid sample is special neither control standard nor blank will control it (American Chemical Society 1981). Therefore sampling uncertainty is often treated separately from other uncertainties in an analysis. Random errors, the overall standard deviation so is related to the standard deviation for the sampling operation  $S_s$  and to that for the remaining analytical operations  $S_a$  by the expression  $S_o^2 = S_a^2 + S_s^2$ . Youden has pointed out that once the analytical uncertainty is reduced to a third or less of the sampling uncertainty, further reduction in the analytical uncertainty is of little importance ( Youden 1967).The sample under examination must not be biased because any inferences made from them will be also be biased.

## **2.7 Sampling Types**

### **2.7.1 Random Sampling**

Random samples are samples obtained by a random sampling process and form a foundation from which generalisations based on mathematical probability can be made. Even under the most favourable circumstances unconscious selection and biases can occur. The use of random numbers table is recommended as an aid to sample selection. The bulk material is divided into number of real or imaginary segments. Each segment is assigned a number and selection of segments from which sample increments are to be taken is made by starting in an arbitrary place in

a random number table and choosing numbers according to a predefined pattern. Sample those segments whose numbers occur from random number tables until all of the samples decided upon have been obtained. The results obtained should be analysed using some model or plan to identify whether systematic relations exist. This is because of the possibility of introducing apparent correlations due to systematic trends or biases in the measurement process. Hence measurement plans should always be designed to identify and minimise such problems. Sampling at evenly spaced intervals over the bulk is still often used in place of random sampling owing to its simplicity. The procedure is more subject to bias than random sampling. It is not recommended. If the procedure is used the results must be closely monitored to ensure that errors from periodicity in the material are not introduced (Whittaker, 1977).

### **2.7.2 Stratified Sampling**

Where the population embraces a number of distinct categories, the frame can be organized by these categories into separate "strata." Each stratum is then sampled as an independent sub-population; out of which individual elements can be randomly selected. There are several potential benefits to stratified sampling.

First, dividing the population into distinct, independent strata can enable researchers to draw inferences about specific subgroups that may be lost in a more generalized random sample.

Second, utilizing a stratified sampling method can lead to more efficient statistical estimates (provided that strata are selected based upon relevance to the criterion in question, instead of availability of the samples). Even if a stratified sampling approach does not lead to increased statistical efficiency, such a tactic will not result in less efficiency than would simple random sampling, provided that each stratum is proportional to the group's size in the population (Gyp, 1992).

Third, it is sometimes the case that data are more readily available for individual, pre-existing strata within a population than for the overall population; in such cases, using a stratified sampling approach may be more convenient than aggregating data

across groups (though this may potentially be at odds with the previously noted importance of utilizing criterion-relevant strata) ( Gyp, 1992).

Finally, since each stratum is treated as an independent population, different sampling approaches can be applied to different strata, potentially enabling researchers to use the approach best suited (or most cost-effective) for each identified subgroup within the population (Lohr *et al* 1999).

There are, however, some potential drawbacks to using stratified sampling. First, identifying strata and implementing such an approach can increase the cost and complexity of sample selection, as well as leading to increased complexity of population estimates. Second, when examining multiple criteria, stratifying variables may be related to some, but not to others, further complicating the design, and potentially reducing the utility of the strata. Finally, in some cases (such as designs with a large number of strata, or those with a specified minimum sample size per group), stratified sampling can potentially require a larger sample than would other methods (although in most cases, the required sample size would be no larger than would be required for simple random sampling).

A stratified sampling approach is most effective when three conditions are met

1. Variability within strata are minimized
2. Variability between strata are maximized
3. The variables upon which the population is stratified are strongly correlated with the desired dependent variable.

Advantages over other sampling methods

1. Focuses on important subpopulations and ignores irrelevant ones.
2. Allows use of different sampling techniques for different subpopulations.
3. Improves the accuracy/efficiency of estimation.
4. Permits greater balancing of statistical power of tests of differences between strata by sampling equal numbers from strata varying widely in size.

Disadvantages

1. Requires selection of relevant stratification variables which can be difficult.
2. Is not useful when there are no homogeneous subgroups.
3. Can be expensive to implement (Gyp, 1992).

### **2.7.3 Systematic Sampling**

Samples are obtained and analysed to reflect or test some systematic hypothesis, such as changes in composition with time, temperature or spatial location. If samples collected in systematic manner, may each be considered to represent a separate discrete population under the existing conditions. Systematic sampling is one in which there is a random start and then follow systematic interval. Systematic approaches can provide maximum efficiency of data acquisition (Whittaker, 1977).

### **2.7.4 Quota Sampling**

In quota sampling, the population is first segmented into mutually exclusive subgroups, just as in stratified sampling. Then judgment is used to select the subjects or units from each segment based on a specified proportion. For example, an interviewer may be told to sample 200 females and 300 males between the age of 45 and 60.

It is this second step which makes the technique one of non-probability sampling. In quota sampling the selection of the sample is non-random. For example interviewers might be tempted to interview those who look most helpful. The problem is that these samples may be biased because not everyone gets a chance of selection. This random element is its greatest weakness and quota versus probability has been a matter of controversy for many years (Cochran *et al* 1977).

### **2.7.5 Convenience sampling or Accidental Sampling**

Convenience sampling (sometimes known as grab or opportunity sampling) is a type of nonprobability sampling which involves the sample being drawn from that part of



the population which is close to hand. That is, a sample population selected because it is readily available and convenient. It may be through meeting the person or including a person in the sample when one meets them or chosen by finding them through technological means such as the internet or through phone. The researcher using such a sample cannot scientifically make generalizations about the total population from this sample because it would not be representative enough. For example, if the interviewer were to conduct such a survey at a shopping centre early in the morning on a given day, the people that he/she could interview would be limited to those present at that given time, which would not represent the views of other members of society in such an area, if the survey were to be conducted at different times of day and several times per week. This type of sampling is most useful for pilot testing (Black 1999).

#### **2.7.6 Panel Sampling**

Panel sampling is the method of first selecting a group of participants through a random sampling method and then asking that group for the same information again several times over a period of time. Therefore, each participant is given the same survey or interview at two or more time points; each period of data collection is called a "wave". This sampling methodology is often chosen for large scale or nation-wide studies in order to gauge changes in the population with regard to any number of variables from chronic illness to job stress to weekly food expenditures. Panel sampling can also be used to inform researchers about within-person health changes due to age or help explain changes in continuous dependent variables such as spousal interaction (Black 1999)

**Table 2.1 Sampling Techniques: Advantages And Disadvantages**

<b>Technique</b>	<b>Descriptions</b>	<b>Advantages</b>	<b>Disadvantages</b>
Simple random	Random sample from whole population	Highly representative if all subjects participate; the ideal	Not possible without complete list of population members; potentially uneconomical to achieve; can be disruptive to isolate members from a group; time-scale may be too long, data/sample could change
Stratified random	Random sample from identifiable groups (strata), subgroups, etc.	Can ensure that specific groups are represented, even proportionally, in the sample(s) (e.g., by gender), by selecting individuals from strata list	More complex, requires greater effort than simple random; strata must be carefully defined
Cluster	Random samples of successive clusters of subjects (e.g., by institution) until small groups are chosen as units	Possible to select randomly when no single list of population members exists, but local lists do; data collected on groups may avoid introduction of confounding by	Clusters in a level must be equivalent and some natural ones are not for essential characteristics (e.g., geographic: numbers equal, but unemployment rates differ)

		isolating members	
Quota	Select individuals as they come to fill a quota by characteristics proportional to populations	Ensures selection of adequate numbers of subjects with appropriate characteristics	Not possible to prove that the sample is representative of designated population

(Black, 1999)

### 2.7.7 Representative Samples

Representative samples are a single sample of a universe or population that can be expected to exhibit average properties of the population. Obviously such a sample cannot be selected by a random process. And even if it could, to ascertain the validity of its representativeness would require considerable effort. The concept of a truly representative sample would appear to be valid in only two cases. The first case involves samples defined a priori as representative for a specific purpose. For example, the Hazardous Waste Management System prescribes seven protocols for sampling wastes, ranging from viscous liquids, solids, or containerized liquids to reservoirs, to provide samples that will be considered by the Agency to be representative of the waste (Regist, 1980). The second case involves the sampling of truly homogeneous material. Although measurement of samples defined as representative may reduce analytical costs, the information so obtained does not enjoy the status of that obtained from valid random samples of the population. An exception is when the sample is vigorously exerted to homogenize the population prior to sampling. Such process is difficult and is ordinarily only justified when the objective is to produce a number of subsample of essentially similar properties. Because of the difficulties of selecting or producing a representative sample, it is recommended that this concept be discouraged for general purposes and reserved

only for cases where the effort required to prepare such a sample is justified. An appreciation of the compositional information is lost as a result is a further reason to discourage the practice. ( Whittaker, 1977).

### **2.7.8 Composite Samples**

A composite sample may be considered as a special way of attempting to produce a representative sample. Many sampling procedures are based on the assumption that average composition is the only information desired. Such averages may be built averages, time-weighted averages, and flow-proportional averages. Analysis of a number of individual samples permits determination of the average and the distribution of samples with the population. Composite samples provide limited information so full consideration should be given to the consequences before deciding between this approach and the analysis of individual samples ( Whittaker 1977).

### **2.7.9 Sub sampling**

The samples received by the analytical laboratory will be larger than that required for a single measurement so sub-sampling will be required. In general the sub-sampling standard deviation should not exceed one-third of the sampling standard deviation. If a sample is already homogeneous, care may be needed to avoid introducing segregation during sub- sampling. The information on the homogeneity of the samples received should be provided so that the sample can be subsample adequately and efficiently (Dixon 1969).

### **2.7.10 Model Of The Sampling Operation**

The sampling model should consider the population to be studied the substances to be measured, the precision required, and the extent to which the distribution of the substance within the population is to be obtained ( Dixon 1969).

### **2.7.11 Sampling Bulk Material**

Gross samples should be unbiased with respect to the different sizes and type of particles present in the bulk material. The size of the gross sample is often a compromise based on heterogeneity of the bulk material and the cost of sampling operation. When the properties of the sample to be sampled are known, a good approach is to collect a small of samples, making them as representative of the

population of interest. From the analysis standard deviation  $S_s$  of the individual samples can be calculated and confidence limits for the average composition can be established using the relation (Dixon 1969).

$$\mu = \bar{X} \pm t_s S_s / n$$

Where  $\mu$  is the true mean value of the population

is  $\bar{X}$  the average of the analytical measurements

$T$  is obtained from statistical tables for  $n$  measurements at the desired level of confidence usually 95%.

### 2.7.12 Minimum Size Of Individual Increment

Methods have been developed for estimation of the amount of sample that should be taken in a given increment so as not to exceed a predetermined level of sampling uncertainty. Ingamells sampling constant is based on the knowledge that the between sample standard deviation  $S_s$  decreases as the sample size is increased, Ingamells has shown that the relation  $WR^2 = K_s$  is valid in many situations. Where  $W$  represents the weight of sample analysed  $R$  is relative standard deviation (in percent) of sample composition and  $K_s$  is the sampling constant, corresponding to the weight of sample required to limit the sampling uncertainty to 1% with 68% confidence. The magnitude of  $K_s$  may be determined by estimating  $\bar{\delta}_s$  from a series of measurements of samples of weight  $W$ . Once  $K_s$  is evaluated for a given sample, the minimum weight  $W$  required for a maximum relative standard deviation of  $R$  percent can be readily calculated ( Ingamells *et al* 1976).

### 2.7.13 Minimum Number Of Individual Increments

The number of samples necessary to achieve a given level of confidence can be estimated from the relation  $n = t^2 S_s^2 / R^2 \bar{x}^2$

Where  $t$  is the students  $t$  table value for the level of confidence desired.

$S_s^2$  and  $\bar{x}$  are estimated from preliminary measurements on or from previous knowledge of the bulk material and  $R$  is the percentage relative standard deviation acceptable in the average ( Visman 1969).

#### **2.7.14 Sampling A Segregated (Stratified) Material**

Segregation is found in ore bodies, in different production batches in a plant, or in samples where settling is caused by differences in particles size or density. Valid samples can be obtained from a stratified material by dividing the material to be sampled into real and imaginary segments (strata). Major strata can be further divided into real or imaginary substances and the required number of samples is selected by chance (preferably with the aid of table of random numbers). If the major strata are not equal in size, the number of samples taken from each stratum should be proportional to the size of the stratum. It is better to use stratified random sampling rather than unrestricted random sampling. By keeping the number of strata sufficiently small, that several samples can be taken from each, possible variation within the parent population can be detected and assessed without increasing the standard deviation of the sampling step (American Society for Testing and Material, Philadelphia 1979)

#### **2.7.15 Minimum Number Of Individual Increments**

When a bulk material is highly segregated, a large number of samples must be taken from different segments. A useful guide to estimating the number of samples to be collected is given by Visman , who proposed that the variance in sample composition depends on the degree of homogeneity within a given sample increment and the degree of segregation between sample increments according to the relation.  $S_s^2 = A/W + B/N$ . Where  $S_s^2$  is the variance of the average of n samples using a total weight W of sample, and A and B are constant for a given bulk material. A is called a homogeneity constant and can be calculated from Ingamells sampling constant and the average composition by  $A = 10^4 \bar{x}^2 K_s$  ( Visman 1969)

#### **2.7.16 Particle Size In Sampling Particulate Mixtures**

Random sampling error may occur even in well mixed particulate mixtures. If the particles differ appreciably in composition and the test portion contains too few of them. To determine the weight of sample required to hold the sampling standard deviation to a preselected level, the first step is to determine the number of particles n. The value of n may be calculated from the relation (Benedetti-Pichler 1974).

$$N = [d_1 d_2 / d^2]^2 [100(P_1 - P_2) / RP]^2 P(1 - P)$$

Where  $d_1$  and  $d_2$  are the densities of the two kinds of particles,  $d$  is the density of the sample,

$P_1$  and  $P_2$  are percentage compositions of the component of interest in the two kinds of particles.

$P$  is the overall average composition in % of the component of interest in the sample.

$R$  is the % relative standard deviation (sampling error) of the sampling operation and  $p$  and  $1-p$  are the fractions of the two kinds of particles in the bulk material.

With knowledge of the density, particle diameter and  $n$  the weight of the sample required for given level of sampling uncertainty can be obtained through the expression.

Weight =  $(4/3)\pi r^3 dn$  (assuming spherical particles)

## **2.8 Cathode Sampling Methods**

The only reliable basis for sampling must be a mathematical one using statistical probabilities. This means that although not every item or every part of the sample is analysed, the limitation of the selection are carefully calculated and known in advances. After calculating the degree of acceptance risk or margin of variation, the sampling plan is then chosen that will give the maximum information and control that is compatible with a rapid turnover of samples. Sampling from batches the selection of individual samples is carried out according to special random tables which ensure that personal factors do not influence the choice. Sampling procedures involve a number of stages before the analysis of the material. Bulky material usually is heterogeneous. They contain particles of different composition which are not uniformly distributed within the material. In this case a number of increments are taken in a random manner from points in the bulk material, so that each part has an equal chance of being selected. The combination of these increments forms the gross sample. The gross sample is reduced in size to produce sub-sample, the process may require reduction in particle size or thorough mixing, before the analytical sample can be obtained.

### **2.8.1 Current Sampling Methods For Cathodes**

Cathodes were sampled by drilling, saw-cutting and cutting cathode strips. Statistical analysis of data produced shows superiority of saw-cut samples over drill samples for predicting impurity concentration in cathodes. Pressure from the market resulted in the customer calling for chemical specifications for cathode supplied to market. Even though the specification for cathode were put in place by the Landon Metal Exchange (LME) and American Society for Testing Material (ASTM), the challenge of defining impurity contents of cathode with accuracy and precision to allow disputes settlement when cathodes are sold to LME or ASTM specification remained. Medrick and Teague (2) and Publicover and Taubenblat (3) have discussed the question of impurity distribution in individual electrolyte nickel cathode. They emphasized on the nonuniformity impurity distribution throughout the cathode. Publicover and Tanbenblant, in particular, showed Selenium to concentrate near the bottom of the cathode while bismuth concentrates in the greatest amount in the top section of the cathode. The variation of impurity among the cathode within the same production complicates the sampling procedure. The quality of cathodes is often dependent on the position of the cathode in the electrolytic cell. This caused by variation of temperature and circulation variations within the cells. Also variation in circulation rates or reduced temperatures encountered in end cells, resulted in cathode quality difference among the cells in the same production. These sources of variance, coupled with the selective concentration of impurities at various locations in the individual cathodes, make accurate estimation of the average impurity level of production or purchased lot of nickel very difficult. In 1980 Tuddenham presented a discussion on the sampling of electro refined cathodes. Where an estimation of the number of cathodes required reducing the total measurement error to that associated with the analytical method alone was made. Large samples were required for elements possessing greater error and it was suggested that total error standard deviation be brought down to some fraction of a specification tolerance. At that time the specification was not available, but now because of LME contracts and ASTM B115, it is possible to move in that direction.

Producers and consumers in the LME market established a sampling proposal for treatment of disputes when selling to LME contract specifications. The procedure



recommended either punching of cathode in a diagonal pattern or cutting strips. The resultant punching or strips are then melted, cast and sampled. The participant agreed that because of nonuniformity in impurity distribution in single cathodes, simply drilling cathodes and assaying the drilling was an inadequate approach to determining true impurity contents in a cathode. Problem associated with melting and casting, are of equal concern to many. At Kennecott Process Technology Centre, a saw-cut approach was developed, in order to overcome the disadvantage of drill sampling without accepting the disadvantage of melting and casting ( Tuddenhan 1980).

### **2.8.2 Saw-Cut Sampling Of The Cathodes**

The saw-cut sampling procedure involves collection of saw chips from a rotary saw or band saw operation. Saw-cuts are made in the cathode from top, sides, and bottom so as to affect the equivalent of sampling the width of the saw blade for the full length and width of the cathode. Saw chips are collected, blended, and send for analytical determination. A carbide-tipped blade is recommended. If a steel blade is used, trapped iron from the cutting blade is removed with a magnet. Since the loop can entrain electrolyte, one cut is taken close to the loop, no cut is done directly through a loop. Avoiding the loop resulted in an impurity bias, particularly for sulphur, however to cut through the loops would give abnormally high results. Therefore the cut close to but not through the loop would be the best compromise ( Tuddenham 1980).

### **2.8.3 Cathode sampling involves three basic steps**

- 1) Random selecting of an adequate number of cathodes that are representative of a lot.
- 2) Obtaining a sample from the random selected cathodes through a mechanical process such as drilling or sawing on a prescribe pattern.
- 3) Preparing a homogeneous portion from the sample cathodes that is of suitable size and quantity for chemical analysis. The number of cathodes that must be sampled to represent a lot is dependent upon the size of the lot and upon the respective cathode quality.

**Table 2.2 Advantages And Disadvantages Of Cathode Sampling Methods**

	ADVANTAGE	DISADVANTAGE
Drilling	Low cost	Poor to unacceptable representation
	Universally available equipment	High risk of sample contamination
Punching	Easily mechanised	poor representation
	Special equipment	
	Higher capital and lower operating cost	
Sectioning	Improved representation	Highest capital and operating costs
		Specialised equipment
Sawing	Improved representation	High capital cost
	Moderate operating cost	Specialised equipment

The nonhomogeneity of electro refined nickel cathodes has made reliable sampling a difficult task. Because of the nature of the refining process, occlusion of impurities results from mechanical and electrochemical disturbance of the impurities in the electrolyte. Therefore valid sampling procedures that truly represent chemical composition of the cathodes are required.

Several investigation have delved into the problem of cathode sampling, Tuddenham et al conducted an extensive study of impurity distributions in cathodes produced at Kennecott's salt Lake Refinery. Mednck and Teague have evaluated the performance of wire products drown from cathodes with segregate impurities. These studies reaffirm the difficulties encountered by others attempting to effectively sample a product characterised by a high degree of variability within and between pieces.

#### **2.8.4 Current Sampling Method At Empress Nickel Refinery.**

One cathode is selected from each cell using random number table. The cathode is cut into one inch strips. The third strip from top is selected and marked for sampling, as well as the centre strip and a third strip from the bottom. Three holes on each strip are drilled 8 inches from the end and at the centre. All the drillings are collected into a sampling bag.

## **CHAPTER 3**

### **3 RESEARCH METHODOLOGY**

#### **3.1 Selection Of Cathodes**

Nickel cathode was taken from a production on 27 February 2012 to determine the population. The cathode was selected using the random number tables. The cathode was cut into 32 strips of 25mm. Each strip was divided into 27 by 25mm x 25 mm squares of nickel so that all possible sampling points are included. Each square was given a number up to eight hundred sixty four. The squares of 25mm x 25mm were then drilled using a driller to obtain samples which were labelled as Strip 1-32 (S1-S32) and No 1-864. Twenty- seven samples were collected for each strip and a total of 864 samples were collected for the whole cathode. These samples were analysed for Cobalt, Copper, Zinc and Iron because were the major contaminants in the nickel cathode. The values obtained were averaged to determine the true population mean. Due to limited resources and time it was not possible to profile many cathodes. However, a second cathode of different production was taken on 29 November 2012 in order to determine if there was any relationship in impurity distribution between the two cathodes.

##### **3.1.1 Quality Control**

Quality procedures were followed throughout the sampling and analysis phase to ensure that errors were eliminated. The following aspects were addressed to ensure quality during this study.

- 1) During sampling vital information was recorded on the sampling bags, these included sampling date, and strip and sample number.
- 2) All the data generated during analysis was recorded on a work sheet.
- 3) All the equipment used were in good working order and calibrated as per requirement.
- 4) The sample analysed had certified reference material (CRM), and an internally developed control standard.

5) Intra- Lab analysis was done between two analysts to determine the variance when samples are subjected to different conditions.

The values of the CRM and Internally developed standard were as shown in the table below.

**Table 3.1 Values of analytical reference material IARM 190A**

ELEMENT	RANGE (ppm)	AVERAGE VALUE	STANDARD DEVIATION
Cu	12.0-21.3	17	2.6
Fe	94-105	99	4
Pb	6.6-11.0	9.3	1.2
Zn	5.0-10.4	8.1	1.5
Co	5.1-14	8.4	3.0

**Table 3.2 Values of Internally developed standard used nickel production of 03 March 2012**

ELEMENT	CONCENTRATION (ppm)
Cu	61
Fe	56
Co	128
Zn	15

### 3.2 Sampling Design

After analysing the sample, the concentrations were recorded on a spread sheet which resembled the cathode, that is, each concentration was recorded on its exact cathode position. Sampling was done by picking values corresponding to the positions on the spreadsheet.

Profile testing was carried out by drawing graphs of column concentration versus strip numbers and strip concentration versus column numbers. Graphs for average

of column and strip concentrations were also drawn. Systematic sampling was the first sampling method to be considered using nine samples, following the current method, which is being used at ENR. Three strips were taken from top, middle and bottom, from each strip the samples were taken and analysed. Systematic sampling with increased number of samples was carried out. Six strips were taken and five samples were taken from each strip and analysed. Random sampling was carried out taking nine samples following the current method. Selection of samples was done using random number tables, this was repeated ten times. The samples were increased to thirty; the sampling process was repeated ten times. The results obtained were compared with true population mean. The best sampling method was then selected.

### **3.3 Experimental**

#### **3.3.1 Sample Preparation**

The whole sample was cleaned with 1:1 hydrochloric acid to remove grease other solid particles on the nickel drills. The sample was washed with distilled water and dried on a hot plate.

#### **3.3.2 Sample Digestion**

Five grams of nickel sample were weighed into 400ml beaker. The samples were dissolved by 100ml of 1:1 nitric acid on a hot plate. The solution was transferred into 100ml volumetric flask and filled to the mark.

#### **3.3.3 Preparation Of Stock Solution**

1000ppm of cobalt, copper, zinc and iron were prepared by dissolving 1g of each pure metal with 20ml of 1:1 nitric acid and diluted into a litre.

#### **3.3.4 Sub stock Solution**

50 ml each of cobalt, copper, iron and 5ml zinc were pipette into one litre volumetric flask and filled to mark with distilled water to make 50 ppm of cobalt, copper iron and 5ppm of zinc.

### 3.3.5 Samples

Four 50ml volumetric flasks were prepared for each sample. In each of three volumetric flasks 2ml, 4ml and 6ml of sub stock solution were added respectively. Followed by 5ml of samples into each of the four flasks and diluted to the mark.

### 3.3.6 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy Varian 55B was used for analysing all the samples. The burner and spray chamber were cleaned using water and dried using compressed air. Each element was optimised before analysis using the following parameters.

**Table 3.3 Parameters used during atomic absorption spectroscopy analysis.**

PARAMETER	COBALT	COPPER	ZINC	IRON
WAVELENGTH	240.7nm	324.8nm	213.9nm	372.0nm
SLIT WIDTH	0.7	0.5	1.0	0.5
CURRENT	7mv	4mv	5.0mv	6mv
ACETYLENE FLOW RATE	1.5	1.5	1.5	1.5

Each sample was analysed for cobalt, copper zinc and iron using AAS.

# CHAPTER 4

## 4 RESULTS

**Table 4.1 Distribution of Co in nickel cathode (ppm)**

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27
R1	206.63	193.32	178.80	165.09	153.96	149.37	144.66	166.18	143.96	154.73	156.16	164.30	161.87	158.84	147.47	155.43	144.11	164.47	148.90	150.21	159.35	164.77	150.45	166.95	173.12	167.49	175.89
R2	213.45	197.39	163.82	161.30	137.13	134.47	153.23	116.58	131.34	123.89	122.77	132.41	122.64	111.37	126.51	122.35	127.25	114.40	118.20	133.23	150.40	130.29	128.61	153.10	137.94	160.54	139.73
R3	174.18	172.23	151.75	146.98	138.96	134.56	92.21	117.66	116.77	140.41	134.63	133.39	144.85	133.76	114.10	139.90	125.11	124.68	131.41	120.00	127.79	142.21	138.42	148.13	128.13	151.54	152.22
R4	178.32	149.05	146.33	118.82	116.87	114.38	107.09	116.16	102.75	129.41	120.29	126.35	112.66	125.02	117.09	116.94	118.94	113.29	122.37	116.30	114.83	116.80	119.44	124.80	126.02	129.86	145.78
R5	189.91	163.47	125.94	121.18	119.98	135.60	118.55	102.78	106.33	127.39	126.58	131.72	137.50	125.09	119.61	122.80	119.47	116.55	113.99	108.92	114.70	124.51	119.11	111.15	136.28	133.39	164.61
R6	188.00	138.29	130.96	119.59	114.29	126.15	126.30	125.85	124.30	121.93	132.35	115.05	127.32	115.48	112.26	108.83	116.77	110.11	103.81	117.43	113.29	119.02	124.50	119.42	131.27	116.32	110.65
R7	149.40	142.53	131.87	126.79	126.12	148.11	127.23	109.92	112.19	94.78	125.93	119.14	115.19	136.24	121.76	123.02	108.58	125.90	108.17	129.44	129.33	130.54	126.28	108.52	127.83	136.70	148.37
R8	131.31	112.74	108.7	110.87	114.09	124.75	112.87	100.32	126.02	109.84	119.55	123.68	122.92	112.24	119.16	119.96	121.50	130.09	119.93	116.77	114.10	117.62	110.96	117.38	119.70	123.45	150.23
R9	131.96	113.72	125.91	129.72	126.70	122.75	117.67	128.48	106.78	104.66	111.84	83.03	127.61	118.23	116.64	126.37	119.50	124.17	118.09	129.31	119.81	117.32	134.86	137.15	131.42	133.78	122.50
R10	127.93	144.96	133.56	132.99	132.17	126.86	120.40	118.72	122.00	129.93	128.37	135.25	136.01	131.88	124.55	114.58	124.97	109.21	116.84	119.75	112.93	108.48	123.50	127.87	112.95	123.19	150.41
R11	147.53	138.33	130.61	136.83	132.14	136.62	112.32	119.64	122.81	118.08	115.55	115.27	118.98	106.13	101.22	110.28	113.20	115.46	98.06	85.21	97.52	102.15	106.84	111.94	110.72	120.85	134.79
R12	134.48	128.7	118.87	102.11	116.12	111.32	119.51	99.53	102.82	123.98	120.67	122.24	113.65	106.13	127.00	133.13	123.94	121.64	117.53	121.33	129.33	118.95	137.29	124.88	134.32	145.34	180.87
R13	134.08	143.02	150.16	131.58	126.55	129.13	122.91	127.31	123.14	125.10	124.63	132.12	124.61	135.53	131.44	125.41	103.03	113.57	124.74	128.90	125.08	112.01	126.10	106.74	122.24	141.77	154.59
R14	143.68	130.35	141.35	125.26	136.67	136.31	131.82	130.04	120.12	118.78	119.08	124.84	132.57	118.72	127.79	134.89	138.98	135.80	131.18	128.11	125.40	129.10	123.39	129.87	133.83	136.56	127.61
R15	133.90	131.99	126.08	129.38	125.98	108.01	123.72	132.78	124.87	132.26	132.59	136.78	138.37	129.99	105.79	140.27	136.44	142.52	110.33	124.42	131.93	130.19	134.53	121.28	138.74	160.28	287.52
R16	118.75	121.77	127.46	121.32	109.37	128.64	98.24	98.53	102.38	103.35	106.00	117.21	123.41	122.23	117.54	121.43	117.44	119.15	123.05	122.86	127.44	117.19	125.31	123.41	123.84	141.14	162.78
R17	132.54	125.97	139.50	117.43	133.99	135.49	128.93	110.96	137.11	116.59	136.97	119.71	142.23	118.25	110.12	109.60	117.19	92.51	116.67	118.03	124.99	121.32	128.07	105.91	115.53	113.67	135.29
R18	138.37	127.93	135.98	124.24	120.00	126.52	125.97	108.14	124.85	122.47	116.49	124.34	133.64	125.40	119.78	130.19	123.32	125.03	115.20	120.37	121.96	109.24	115.26	115.12	128.27	139.69	191.50
R19	99.40	107.32	103.45	113.21	107.26	97.01	105.92	99.63	107.02	105.92	109.71	110.41	104.90	119.11	109.45	101.84	115.22	117.58	107.36	117.62	102.02	117.29	106.05	103.02	112.85	116.26	134.17
R20	127.46	117.76	125.65	127.50	122.27	118.57	114.90	116.43	118.14	121.73	114.95	121.92	115.41	113.64	118.99	123.24	119.94	120.47	120.56	109.47	109.64	115.78	112.07	114.04	112.84	133.38	146.29
R21	130.43	129.93	124.82	131.90	118.55	122.45	115.51	115.17	121.17	108.53	123.79	122.43	119.95	128.90	129.07	125.40	132.19	134.78	131.35	122.28	121.30	130.79	129.02	135.17	127.53	140.80	123.24
R22	119.22	125.61	134.09	127.92	119.90	124.89	124.34	129.53	127.90	130.96	124.12	111.68	135.91	133.69	130.31	128.17	132.62	136.25	132.96	132.10	130.92	134.35	129.93	136.46	137.69	139.28	157.76
R23	122.93	124.24	117.22	115.88	98.43	109.62	116.39	116.54	111.39	121.18	114.78	113.22	115.65	121.21	111.51	112.16	114.59	114.41	113.58	111.52	110.16	107.90	108.33	118.87	122.22	130.92	140.18
R24	126.60	114.96	128.42	117.87	129.60	132.77	129.23	108.61	118.00	122.15	121.63	119.15	126.50	107.14	119.01	128.12	125.09	78.55	128.74	121.31	121.53	124.05	125.64	116.92	124.61	137.24	144.98
R25	133.90	128.82	129.64	127.98	135.62	132.67	130.34	127.89	135.77	126.93	130.28	132.88	133.86	125.80	127.89	131.82	134.93	130.52	128.48	127.67	127.32	137.55	124.75	126.29	130.41	139.85	128.12
R26	145.60	127.56	132.52	121.59	136.82	126.65	126.09	137.53	137.77	128.32	141.27	130.95	152.30	140.07	148.48	142.35	150.46	142.13	151.84	149.05	135.45	134.71	136.06	126.86	147.22	137.53	136.58
R27	136.41	137.71	112.77	145.70	132.90	135.07	133.77	128.19	127.73	120.25	140.80	129.34	128.24	128.98	124.64	127.97	133.74	108.31	132.56	130.07	124.22	130.92	124.29	126.31	139.69	148.33	156.71
R28	134.10	132.78	125.84	123.10	134.24	128.66	129.85	138.69	132.66	121.81	131.04	130.25	138.02	133.13	120.57	132.27	151.84	137.93	145.81	142.75	132.26	129.14	133.88	145.08	162.54	173.10	155.78
R29	123.57	137.61	149.10	137.75	146.72	139.43	149.37	133.60	138.84	136.60	139.84	140.12	144.42	131.62	139.97	139.42	142.04	132.12	135.50	137.15	135.65	136.48	127.85	141.59	143.09	150.76	170.41
R30	125.83	128.81	135.29	141.60	128.38	130.89	133.75	137.82	129.44	127.64	128.34	130.78	128.86	129.13	134.60	127.66	133.78	126.27	130.55	131.93	130.88	129.10	130.28	127.45	128.37	130.93	151.80
R31	131.35	126.12	122.22	134.06	132.68	130.42	138.48	136.92	132.50	136.48	131.97	131.38	125.31	128.35	124.39	130.47	128.74	125.91	130.00	128.54	127.53	123.27	138.58	131.69	138.25	137.77	146.48
R32	140.94	131.42	136.31	132.50	130.24	129.31	136.04	116.86	128.37	133.36	128.52	133.71	126.64	126.90	131.06	143.67	128.99	144.84	130.65	135.42	136.49	131.56	135.49	136.17	170.04	176.63	181.09



**Table 4.2 Distribution of Cu in nickel cathode (ppm)**

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27
R1	101.77	86.87	75.06	65.22	58.21	57.19	66.09	72.47	58.08	60.59	29.12	36.26	27.71	26.46	41.51	41.14	33.99	59.58	26.32	45.75	30.76	75.29	58.23	60.70	63.03	67.65	69.52
R2	98.15	87.50	60.33	60.75	49.90	46.21	56.44	46.95	53.51	58.26	44.09	47.03	40.68	57.83	46.87	43.24	42.75	40.46	37.61	45.91	57.93	48.50	53.01	56.05	55.75	56.10	56.19
R3	70.69	66.40	55.41	50.39	55.84	59.05	40.03	50.96	45.31	51.19	45.51	55.25	59.62	53.11	43.75	48.63	48.37	47.47	51.65	44.06	53.00	66.55	47.80	63.71	45.74	55.71	71.18
R4	72.22	71.04	61.48	44.16	64.06	57.84	62.94	54.81	48.38	51.52	54.75	56.44	46.26	74.09	82.16	53.62	56.70	55.14	52.61	50.19	52.34	55.31	63.96	50.52	53.22	58.07	77.64
R5	78.63	64.04	54.40	51.40	46.01	55.23	52.40	47.42	66.18	54.46	57.50	51.70	54.64	50.04	28.67	29.03	33.43	36.47	27.95	25.99	29.51	33.20	31.21	32.35	39.53	40.34	59.59
R6	50.95	42.28	42.93	34.48	32.31	34.69	36.71	67.30	37.25	51.22	39.03	32.08	35.30	40.56	40.35	43.11	40.89	40.27	39.70	41.36	43.42	38.52	50.28	38.17	40.03	36.00	41.72
R7	53.15	47.51	44.35	44.55	40.62	45.56	55.59	39.36	42.91	43.57	42.49	43.93	45.30	45.74	36.32	36.68	34.92	35.41	32.76	30.76	28.90	33.18	34.77	33.46	38.54	45.93	50.92
R8	46.16	33.66	28.86	34.99	31.89	40.13	33.98	33.84	37.29	33.37	35.84	34.58	35.32	33.49	35.81	32.68	28.04	29.81	33.48	27.01	25.61	27.54	26.50	38.58	29.61	42.16	71.14
R9	33.63	62.06	39.05	38.19	33.26	37.16	29.81	45.42	55.14	33.51	29.72	33.17	40.12	35.27	29.76	30.75	31.82	36.50	28.59	30.82	29.26	28.38	38.43	40.27	43.21	35.74	34.33
R10	30.73	33.99	33.58	33.84	29.75	42.73	25.16	23.23	25.60	30.36	35.72	28.47	31.93	31.22	46.85	45.76	46.18	43.95	44.53	47.25	42.42	39.88	45.47	52.14	44.38	50.82	59.69
R11	63.85	54.14	51.57	49.92	47.30	51.35	46.45	47.82	44.82	47.75	42.85	42.95	48.74	41.24	39.25	49.57	44.78	44.68	38.05	38.25	62.24	41.02	40.14	53.79	42.04	49.66	60.74
R12	48.38	51.48	42.59	39.92	47.89	46.81	49.99	44.56	36.65	51.12	47.25	69.20	88.34	87.10	49.38	46.44	53.80	59.95	43.37	72.04	46.87	44.98	75.21	49.21	65.39	55.47	77.90
R13	54.96	51.71	51.62	43.60	43.34	45.41	46.76	59.09	41.82	55.38	45.86	46.17	48.05	43.27	48.76	44.99	45.88	64.76	46.43	42.46	40.11	43.56	44.82	42.99	48.97	58.38	61.72
R14	65.31	67.12	73.28	65.30	58.72	63.78	65.91	46.23	49.02	37.29	42.30	38.61	54.08	51.99	45.32	48.43	45.93	43.36	49.14	41.20	42.04	48.34	42.46	46.30	51.44	56.63	56.07
R15	66.95	58.00	71.82	81.97	56.01	50.16	56.94	77.76	89.90	54.71	57.91	108.92	103.68	89.84	49.46	63.36	66.58	59.07	125.56	65.18	58.93	53.07	57.40	46.08	69.19	91.72	98.33
R16	60.52	52.38	54.85	51.06	51.15	52.01	44.86	67.41	44.39	42.02	45.43	48.97	47.36	47.68	45.57	49.64	44.01	42.92	45.61	45.97	57.67	45.45	48.58	46.03	49.46	61.20	73.21
R17	61.01	56.23	54.72	56.38	67.00	48.03	55.17	56.38	49.90	42.10	59.23	44.82	50.31	48.74	47.47	48.21	44.59	47.02	83.70	48.97	45.35	46.45	49.32	43.78	65.53	70.09	60.39
R18	62.78	52.18	58.19	52.35	50.81	53.71	51.12	46.40	54.07	49.80	47.91	61.00	54.64	51.55	47.59	59.71	50.72	51.12	48.95	46.45	48.30	45.34	47.86	46.35	52.05	61.33	105.75
R19	115.86	53.46	42.88	44.90	53.13	39.51	42.93	41.33	44.02	39.75	39.60	41.41	41.15	46.58	42.04	44.25	50.80	47.03	40.69	45.36	38.80	42.33	37.60	37.67	42.93	51.82	69.44
R20	52.36	49.98	50.22	51.91	49.03	50.17	47.78	45.80	46.77	46.82	45.66	51.43	49.77	46.69	46.85	48.82	48.95	47.81	48.39	46.89	44.82	47.47	47.97	49.56	48.28	59.77	63.80
R21	50.32	51.41	49.17	55.38	49.73	45.11	48.05	50.95	48.62	40.33	46.53	45.29	44.47	45.54	44.29	44.04	49.35	48.49	45.97	41.03	45.36	45.31	45.09	47.27	45.79	56.36	60.43
R22	47.19	52.44	50.99	47.31	42.84	48.61	46.47	47.47	48.29	47.74	47.62	45.35	48.54	47.93	47.89	55.63	47.88	48.80	54.14	46.94	48.62	47.94	42.66	50.18	46.15	52.14	58.87
R23	50.38	50.98	48.28	47.21	39.25	42.02	47.79	47.29	45.35	50.18	48.15	48.47	47.84	49.36	47.57	47.51	43.67	49.11	43.47	46.23	44.18	43.28	45.51	52.00	54.09	55.47	63.12
R24	48.39	42.66	55.30	44.04	50.18	51.12	49.02	49.21	45.37	46.79	46.75	44.38	55.58	59.46	48.17	49.22	49.03	30.07	52.69	44.98	49.21	47.45	47.27	42.64	55.00	55.90	63.87
R25	55.63	73.47	60.71	50.74	53.77	54.82	54.80	58.15	58.30	61.20	66.40	65.60	61.57	54.76	55.53	54.23	56.43	50.56	49.19	62.6	63.57	55.86	63.77	53.83	58.11	67.14	58.45
R26	59.49	46.95	47.81	42.32	50.47	48.94	49.85	51.40	51.96	45.12	54.83	45.58	53.76	50.25	54.84	50.66	50.55	46.32	52.14	46.96	49.44	46.8	49.63	43.68	57.92	50.11	58.4
R27	51.86	52.63	40.56	52.77	47.56	49.31	48.50	49.33	48.15	42.31	52.28	48.26	48.13	49.00	44.07	49.06	48.77	40.36	47.99	51.15	47.39	48.80	44.62	46.20	58.56	58.40	67.80
R28	47.16	47.86	44.81	43.74	46.38	46.92	42.18	48.63	46.43	41.48	45.50	48.65	44.31	45.14	42.11	45.68	50.29	46.72	50.73	47.32	42.95	44.12	43.00	49.75	58.22	69.40	63.73
R29	51.97	47.90	51.43	49.02	61.51	47.11	52.72	42.72	48.63	46.71	46.68	46.45	57.54	46.68	47.26	47.18	50.81	43.59	45.68	47.15	45.73	48.12	45.12	49.47	53.56	57.45	67.59
R30	58.51	65.84	66.61	61.30	55.07	58.50	60.33	61.90	57.88	58.84	59.64	58.78	60.04	55.64	58.63	54.54	56.14	54.87	53.27	60.85	54.80	54.25	55.11	54.10	55.75	61.25	72.40
R31	63.26	62.68	54.89	62.01	62.12	74.53	64.87	59.13	61.41	62.02	62.35	58.76	53.54	58.79	55.06	55.91	64.97	55.70	61.16	60.21	55.96	53.59	60.28	53.49	56.53	76.68	74.89
R32	56.89	46.80	49.10	49.60	45.77	41.56	45.54	41.68	42.92	49.03	39.55	50.33	42.15	39.78	53.63	41.88	37.13	37.40	30.09	50.58	53.18	49.64	52.60	57.1	70.90	78.28	89.73

**Table 4.3 Distribution of Zn in nickel cathode (ppm)**

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27
R1	69.35	67.14	62.20	58.69	46.22	24.45	25.34	27.86	51.22	21.56	20.14	19.88	18.34	17.17	18.16	18.22	18.16	19.26	17.08	19.28	18.61	17.48	15.55	14.55	15.95	17.54	18.18
R2	20.87	20.50	16.18	14.89	13.27	12.82	14.01	12.49	18.86	17.50	17.20	16.20	16.37	16.39	16.85	16.16	16.05	16.49	15.77	15.77	15.43	15.17	16.15	18.46	16.59	14.35	17.48
R3	23.26	19.41	21.01	19.31	20.30	19.02	17.67	18.53	17.81	17.45	17.92	18.84	18.66	19.81	17.95	17.03	16.37	16.47	23.22	22.79	22.91	22.35	22.53	21.99	24.63	26.60	26.66
R4	30.55	27.01	26.14	23.70	20.85	19.18	19.97	19.00	18.93	15.88	17.64	16.75	17.51	18.41	20.30	19.35	17.09	22.28	21.70	19.86	20.30	21.92	22.68	24.54	19.79	18.69	23.03
R5	19.77	17.20	18.09	13.37	13.33	12.89	19.90	18.41	21.40	21.80	22.27	21.35	21.50	22.18	11.86	13.81	13.87	12.27	12.17	12.56	11.53	12.29	11.81	12.31	12.17	13.68	18.79
R6	22.94	18.58	16.85	14.63	13.78	15.12	15.53	16.07	16.55	14.51	17.28	14.18	14.87	16.60	16.56	15.94	18.03	15.99	14.27	17.12	15.16	14.58	18.24	16.58	13.13	15.29	13.83
R7	18.64	16.44	14.10	15.90	13.39	13.65	12.30	10.48	9.83	10.09	11.48	11.97	13.35	14.46	13.66	14.35	15.37	14.09	14.07	13.28	12.51	14.52	13.95	12.66	14.18	14.83	17.42
R8	17.23	15.95	16.07	12.72	14.72	14.78	13.27	13.63	13.36	14.96	13.51	12.61	12.37	14.71	19.77	20.47	15.83	14.19	19.62	17.1	16.25	16.58	15.40	17.78	26.51	14.67	23.73
R9	19.92	17.71	19.49	19.44	20.06	16.45	18.86	21.33	17.06	16.16	23.32	26.30	23.08	20.99	15.74	15.83	16.39	17.12	16.74	17.24	13.39	14.07	16.19	17.94	17.07	17.77	16.51
R10	18.26	16.86	17.62	16.33	13.33	16.31	15.42	16.38	19.06	16.29	16.93	19.06	17.87	17.24	15.22	14.01	14.60	13.34	14.76	14.21	14.31	15.24	15.65	16.76	17.42	19.34	19.16
R11	19.23	30.17	18.97	17.62	17.48	19.74	17.31	18.71	16.72	18.18	17.22	18.10	16.20	15.19	15.32	16.10	14.24	13.40	14.2	14.31	16.14	13.12	13.28	13.52	14.13	15.44	17.47
R12	16.61	15.34	14.89	14.43	13.45	14.84	15.11	13.08	12.26	13.26	13.82	13.68	14.70	14.57	23.50	22.22	22.12	21.12	21.13	21.69	20.47	20.43	23.40	20.56	21.97	24.77	30.95
R13	23.07	22.81	23.30	22.07	23.08	22.53	21.64	21.36	21.72	21.00	19.97	19.50	20.26	20.39	18.87	14.75	14.80	13.48	15.24	12.97	12.59	11.78	14.16	13.59	14.58	14.89	19.08
R14	17.65	16.73	14.01	13.47	13.47	14.76	13.91	13.21	17.05	13.80	11.96	14.95	14.35	13.37	15.28	14.92	15.73	13.45	13.61	13.82	13.65	13.18	13.84	13.10	13.51	14.53	18.30
R15	19.14	16.99	17.06	16.14	18.54	17.44	16.45	15.69	15.10	16.61	16.26	18.24	16.46	16.97	15.94	19.43	17.12	15.38	12.48	14.03	15.15	15.83	15.94	15.00	17.11	22.66	30.57
R16	14.06	13.41	14.19	13.45	12.80	14.03	13.91	12.43	11.58	13.46	11.69	13.34	13.19	11.85	12.56	14.04	12.23	12.25	11.66	11.76	13.29	12.53	11.94	12.04	15.18	17.94	17.08
R17	15.22	15.30	15.30	13.45	13.55	12.59	13.11	12.90	14.27	11.35	19.92	12.01	11.79	12.41	14.43	13.70	12.61	14.70	14.71	14.13	13.38	11.72	14.08	11.76	13.62	14.71	18.59
R18	17.68	16.63	16.70	16.33	16.22	15.60	14.83	13.82	14.61	14.46	13.00	16.27	15.46	15.03	13.32	15.78	15.16	17.61	16.55	15.26	13.85	14.25	15.14	13.10	14.44	16.32	21.72
R19	14.52	14.60	16.75	14.85	16.00	14.88	15.76	15.09	16.07	15.88	14.45	15.08	14.74	15.90	14.12	15.40	15.99	14.98	15.69	15.18	13.32	16.24	13.89	13.84	14.43	16.12	18.42
R20	14.69	14.25	13.29	13.98	13.27	13.36	11.64	12.12	12.39	12.11	11.99	13.14	12.32	11.42	12.35	12.97	12.38	13.43	11.82	12.30	13.04	11.75	10.57	12.64	12.42	14.93	15.78
R21	15.15	16.84	15.57	14.87	15.18	14.47	13.40	15.36	13.73	11.03	14.65	14.35	13.27	11.92	12.06	14.06	13.81	13.50	13.42	12.13	13.97	12.58	12.76	12.03	13.27	14.41	14.94
R22	17.99	19.45	18.56	17.98	15.84	16.22	17.45	16.96	15.75	17.16	16.50	13.03	15.43	15.43	15.37	15.99	15.17	16.79	16.10	15.63	15.70	15.51	14.79	16.58	15.98	15.92	19.44
R23	18.58	17.59	17.21	17.44	15.51	17.56	17.14	16.80	17.26	19.97	16.95	17.21	17.14	17.22	16.78	16.04	15.88	16.71	17.04	16.70	16.31	16.37	16.16	18.03	17.99	21.46	20.29
R24	19.36	17.75	19.61	16.53	17.66	18.79	17.81	16.78	17.50	18.83	18.49	17.51	18.89	15.82	17.46	18.11	17.34	11.61	17.06	16.86	16.08	15.76	15.99	15.37	15.97	18.30	20.38
R25	18.50	17.84	17.68	16.77	16.71	17.16	16.34	16.36	18.34	16.67	16.20	16.66	15.96	15.17	16.30	16.72	15.16	16.55	16.00	15.93	13.65	15.71	14.00	14.67	15.75	16.49	15.27
R26	19.12	17.76	17.26	16.81	17.94	18.24	18.28	16.80	18.58	17.82	19.80	19.25	17.83	16.59	18.47	18.28	18.31	16.84	18.26	17.88	17.37	16.46	17.12	15.66	17.53	17.48	19.52
R27	19.91	19.22	17.68	18.66	17.57	18.98	18.29	16.80	16.77	16.50	18.83	17.16	16.65	16.44	15.89	16.98	15.97	14.01	15.67	16.13	16.42	15.58	15.72	15.78	16.39	17.01	20.88
R28	21.40	20.59	21.20	19.02	21.28	19.96	20.05	20.82	19.34	18.96	20.27	20.89	19.76	18.52	18.91	19.71	20.02	20.11	18.31	20.11	19.10	19.31	17.61	19.71	21.06	24.63	23.70
R29	19.50	18.25	21.71	19.28	20.55	17.05	19.37	17.03	19.27	19.82	17.90	16.90	18.73	17.10	18.40	18.58	18.79	18.31	17.96	17.32	17.46	18.09	17.00	17.65	19.76	21.40	22.63
R30	19.28	20.87	19.72	21.54	17.03	21.25	19.77	18.93	19.47	18.35	21.35	18.10	18.73	18.98	19.26	19.56	20.09	15.43	19.31	19.28	18.51	18.26	17.88	17.19	19.19	19.48	24.04
R31	18.30	18.65	18.30	21.33	20.08	18.82	18.61	17.98	18.78	17.82	21.19	17.18	20.12	17.03	18.54	17.73	18.14	18.53	19.53	19.33	18.71	17.38	19.14	18.17	18.19	19.28	20.14
R32	20.81	21.23	19.71	19.82	21.30	24.30	22.56	20.25	18.82	21.17	19.77	19.03	19.92	19.13	17.94	20.32	20.64	21.64	20.15	19.19	21.02	25.96	25.11	26.75	25.67	29.80	50.21

Table 4.4 Distribution of Fe in nickel cathode (ppm)

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27
R1	19.47	13.58	20.69	14.78	8.89	8.30	2.80	2.59	24.29	20.66	88.15	34.66	88.11	14.18	16.86	12.22	11.58	19.76	13.71	42.45	40.31	31.96	33.5	33.79	29.23	61.27	37.16
R2	30.95	38.60	32.76	31.76	22.36	28.92	36.77	89.01	12.61	12.15	7.63	14.15	10.67	17.05	12.99	15.14	10.29	10.69	11.64	13.07	19.13	12.45	8.65	11.59	12.92	13.75	11.34
R3	16.21	15.08	13.08	11.70	43.88	42.79	41.91	46.04	45.41	43.91	45.51	46.36	47.56	46.47	42.95	47.16	40.48	41.10	34.3	51.66	47.15	39.91	26.19	29.51	27.16	40.91	30.06
R4	34.57	32.38	33.00	24.82	31.98	20.04	30.09	27.21	29.39	14.58	21.58	13.07	25.32	30.16	26.00	27.11	22.52	26.97	27.39	28.68	21.69	21.96	84.3	19.17	22.75	71.18	34.66
R5	27.07	23.52	25.51	24.23	24.39	22.96	23.11	26.9	25.06	21.66	27.87	23.57	29.61	28.99	13.25	16.87	22.35	14.07	19.82	20.83	19.87	19.76	22.91	19.05	21.04	16.57	19.13
R6	24.37	19.78	20.38	20.45	22.34	20.50	21.51	24.12	26.66	22.55	24.17	18.42	27.57	38.16	35.75	26.06	30.39	32.10	28.98	31.94	29.01	26.96	30.33	30.9	30.08	24.39	26.83
R7	32.48	32.58	28.71	31.01	31.48	32.76	31.52	29.2	31.98	32.48	33.65	33.88	37.29	38.22	31.14	28.97	30.12	27.17	28.50	28.30	25.72	28.81	28.17	26.62	28.28	30.38	32.55
R8	29.05	25.89	20.95	25.95	24.56	22.65	25.63	29.06	25.52	28.2	31.12	27.46	24.55	26.12	39.19	38.66	34.01	38.30	45.13	32.97	37.65	37.49	36.44	54.05	37.73	33.27	33.15
R9	42.68	45.41	43.52	31.66	31.09	29.21	32.18	33.66	31.43	33.11	32.39	33.17	30.18	28.77	26.32	31.54	26.52	35.31	34.5	31.76	27.51	32.58	30.45	34.29	25.7	29.33	36.41
R10	33.24	31.65	25.09	28.55	27.65	29.70	29.04	27.00	28.29	28.98	30.18	27.68	26.16	24.57	24.83	23.25	20.63	19.60	21.87	22.96	19.87	18.75	21.84	24.53	20.55	21.95	22.08
R11	46.66	25.68	16.40	14.32	15.27	17.63	15.69	16.78	29.57	12.7	17.62	16.76	14.46	15.32	17.93	17.29	16.34	15.22	13.53	18.23	28.23	14.74	16.56	14.67	17.56	15.36	14.81
R12	14.22	16.76	18.01	14.11	17.56	16.75	15.9	15.89	14.26	16.45	18.50	21.49	17.46	16.89	19.16	14.55	12.75	10.44	19.19	35.03	19.75	16.73	16.26	25.09	17.14	17.7	26.96
R13	25.42	25.57	23.75	22.09	19.26	18.81	20.8	20.62	15.03	20.16	15.95	17.55	26.08	26.67	28.91	28.07	26.00	18.23	23.51	28.50	23.63	30.92	31.04	27.37	30.42	30.45	26.67
R14	46.90	43.00	33.23	34.52	45.82	42.13	32.07	37.02	45.53	38.3	36.3	39.68	30.23	45.82	38.25	38.82	40.22	37.63	46.57	38.15	38.82	38.86	47.57	43.36	43.02	36.33	36.30
R15	20.03	18.15	15.83	15.60	19.80	17.83	21.41	20.58	14.17	15.6	18.91	16.86	17.64	26.83	14.25	19.73	18.91	25.17	22.29	17.47	27.37	17.2	18.74	12.3	21.67	31.87	66.27
R16	38.11	24.74	22.02	18.7	20.02	24.62	22.78	27.92	23.61	35.45	29.9	32.12	54.04	35.42	37.36	26.9	27.76	28.05	24.94	24.06	20.99	27.87	31.33	32.34	20.74	17.54	29.72
R17	20.08	35.17	29.87	29.16	18.76	26.75	36.58	25.79	22.95	30.26	29.99	45.61	21.39	28.35	34.02	29.25	24.39	31.61	29.31	29.65	29.61	32.14	44.94	32.31	44.62	28.69	31.76
R18	33.39	29.99	33.17	29.4	28.87	28.33	25.08	21.51	28.31	27.13	27.43	38.71	28.17	26.08	20.8	32.88	42.37	24.77	23.00	24.90	29.54	24.67	28.68	27.39	38.21	41.26	42.59
R19	59.57	14.36	16.15	18.35	15.52	15.06	15.51	15.57	18.22	16.05	13.91	16.72	16.42	20.83	17.25	17.97	18.21	15.35	15.26	17.67	16.03	20.97	16.71	18.45	17.87	18.02	21.58
R20	17.26	15.5	14.57	26.26	12.79	18.62	11.86	17.11	16.21	13.46	7.09	14.5	14.11	15.00	12.93	16.93	15.21	13.09	14.20	11.82	13.46	16.59	15.13	12.34	12.87	17.27	17.09
R21	23.37	17.14	20.11	20.74	22.12	14.45	11.12	17.18	13.42	11.27	16.34	13.46	15.32	14.85	15.9	19.04	12.09	20.19	13.91	12.49	14.99	17.51	17.64	19.14	14.49	22.19	25.36
R22	24.39	16.44	15.97	14	13.03	19.17	15.43	13.87	14.54	13.54	18.93	19.6	20.21	15.33	17.36	17.09	15.57	14.14	17.52	15.29	13.95	19.67	13.16	21.56	12.9	18.04	26.16
R23	14.21	17.63	13.52	16.39	13.28	17.64	18.4	15.2	16.61	12.89	11.2	11.1	15.56	14.53	13.79	13.6	11.98	11.04	8.03	12.33	13.87	14.16	13.42	26.98	8.35	17.00	17.21
R24	20.89	24.48	28.87	16.32	17.54	17.88	18.02	22.68	23.83	23.12	17.67	23.39	27.89	21.03	25.31	24.25	25.05	20.27	24.29	15.77	21.52	18.13	19.98	20.63	19.94	18.75	18.17
R25	27.16	28.87	33.57	28.17	26.09	29.97	24.66	29.86	36.41	23.06	27.64	33.17	25.52	28.07	26.15	27.39	28.22	26.07	22.7	25.88	26.92	26.53	27.14	28.95	27.55	29.22	26.77
R26	24.85	20.2	16.87	22.45	22.47	18.22	17.79	19.7	21.65	17.71	21.07	22.39	25.22	22.81	23.36	23.69	26.07	23.44	23.57	25.4	26.41	21.68	22.46	22.89	23.05	21.21	20.76
R27	20.82	24.2	17.31	22.12	29.53	21.39	21.27	33.64	26.53	33.03	32.82	30.87	36.64	32.73	29.88	37.31	35.42	32.79	34.47	33.28	34.21	33.86	34.6	35.02	35.98	46.13	34.17
R28	35.23	37.42	37.56	31.63	36.2	29.94	34.56	31.99	26.53	34.54	27.54	34.31	27.91	30.54	25.19	28.48	25.44	26.33	23.41	28.59	27.93	24.62	30.68	25.26	26.82	31.72	25.2
R29	21.38	25.09	37.56	21.75	30.39	24.41	29.29	16.18	18.8	24.14	29.67	23.51	26.29	24.14	26.03	21.08	26.43	29.58	28.84	20.8	30.42	12.1	24.66	28.62	26.88	26.22	29.50
R30	27.47	30.13	30.96	36.63	40.04	27.55	35.1	31.67	33.04	30.21	32.47	32.69	32.03	33.46	31.91	30.97	34.84	33.92	34.86	31.29	37.06	33.51	33.28	33.11	31	34.72	36.34
R31	20.83	28.65	25.23	27.48	24.21	25.9	28.96	25.87	27.05	26.27	27.54	26.35	29.42	29.68	29.23	27.68	35.08	29.59	28.71	29.26	30.45	30.86	34.55	28.59	31.34	29.51	31.43
R32	18.5	18.52	18.6	21.45	22.23	21.35	22.37	20.28	23.1	20.56	24.06	26.08	25.61	24.79	17.84	17.61	24.87	24.57	26.55	29.54	25.96	25.11	26.75	25.67	29.8	50.21	20.36

Table 4.5 Intra- Lab analysis  
for Co

SAMPLE No	ANALYST 1	ANALYST S2	DIFFERENCE	WITHIN SPLITTING LIMIT
S <sub>1</sub> 10	143.96	143.69	0.27	YES
S <sub>2</sub> 25	153.1	153.62	-0.52	YES
S <sub>6</sub> 17	108.83	108.04	0.79	YES
S <sub>10</sub> 11	122.00	122.47	-0.47	YES
S <sub>16</sub> 7	128.64	127.65	0.99	YES
S <sub>16</sub> 27	141.14	141.05	0.09	YES
S <sub>21</sub> 2	130.43	129.99	0.44	YES
S <sub>25</sub> 15	125.8	125.88	-0.08	YES
S <sub>30</sub> 24	130.28	130.14	0.14	YES
S <sub>32</sub> 9	116.86	116.79	0.07	YES

The samples analysed by two analysts were all within acceptable splitting limit of +/- 2ppm

**Table 4.6 Intra- Lab analysis for Cu**

SAMPLE No	First Run	Second Run	DIFFERENCE	WITHIN SPLITTING LIMIT
S <sub>1</sub> 10	58.08	57.95	0.13	YES
S <sub>2</sub> 25	56.05	56.38	-0.33	YES
S <sub>6</sub> 17	43.11	42.92	0.19	YES
S <sub>10</sub> 11	25.6	25.78	-0.18	YES
S <sub>16</sub> 7	52.01	52.56	-0.55	YES
S <sub>16</sub> 27	61.2	61.28	-0.08	YES
S <sub>21</sub> 2	50.32	50.44	-0.12	YES
S <sub>25</sub> 15	54.76	54.57	0.19	YES
S <sub>30</sub> 24	55.11	55.26	-0.15	YES
S <sub>32</sub> 9	41.68	41.61	0.07	YES

Intra-Lab analysis for copper the results were within acceptable splitting limit.

**Table 4.7 Intra- Lab analysis for Zn**

SAMPLE No	First Run	Second Run	DIFFERENCE	WITHIN SPLITTING LIMIT
S <sub>1</sub> ,10	51.22	50.89	0.33	YES
S <sub>2</sub> 25	18.46	18.46	0	YES
S <sub>6</sub> 17	15.94	15.48	0.46	YES
S <sub>10</sub> 11	19.06	19.17	-0.11	YES
S <sub>16</sub> 7	14.03	14.14	-0.11	YES
S <sub>16</sub> 27	17.94	17.84	0.1	YES
S <sub>21</sub> 2	15.15	15.1	0.05	YES
S <sub>25</sub> 15	15.17	15.29	-0.12	YES
S <sub>30</sub> 24	17.88	17.81	0.07	YES
S <sub>32</sub> 9	20.25	20.19	0.06	YES

Intra- Lab analysis for copper were within the acceptable splitting limit of +/-2ppm

**Table 4.8 Intra- Lab analysis for Fe**

SAMPLE No	First Run	Second Run	DIFFERENCE	WITHIN SPLITTING LIMIT
S <sub>1</sub> 10	13.71	13.65	0.06	YES
S <sub>2</sub> 25	11.59	14.25	-2.66	NO
S <sub>6</sub> 17	26.06	26.15	-0.09	YES
S <sub>10</sub> 11	28.98	29.89	-0.91	YES
S <sub>16</sub> 7	22.78	22.83	-0.05	YES
S <sub>16</sub> 27	29.72	29.39	0.33	YES
S <sub>21</sub> 2	23.37	23.03	0.34	YES
S <sub>25</sub> 15	26.15	26.24	-0.09	YES
S <sub>30</sub> 24	18.11	18.25	-0.14	YES
S <sub>32</sub> 9	22.33	21.77	0.56	YES

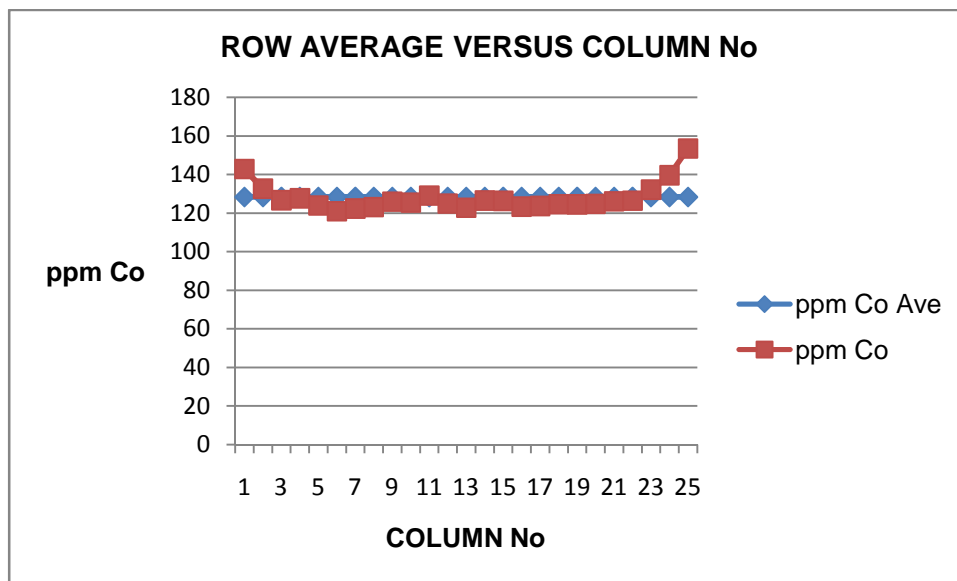
Intra- Lab analysis for iron has one assay that is out of acceptable limit of +/-2ppm

## STATISTICAL ANALYSIS OF TRENDS

a) Variation across cathode ( Left to right)

**Table 4.9 ROW AVERAGES**

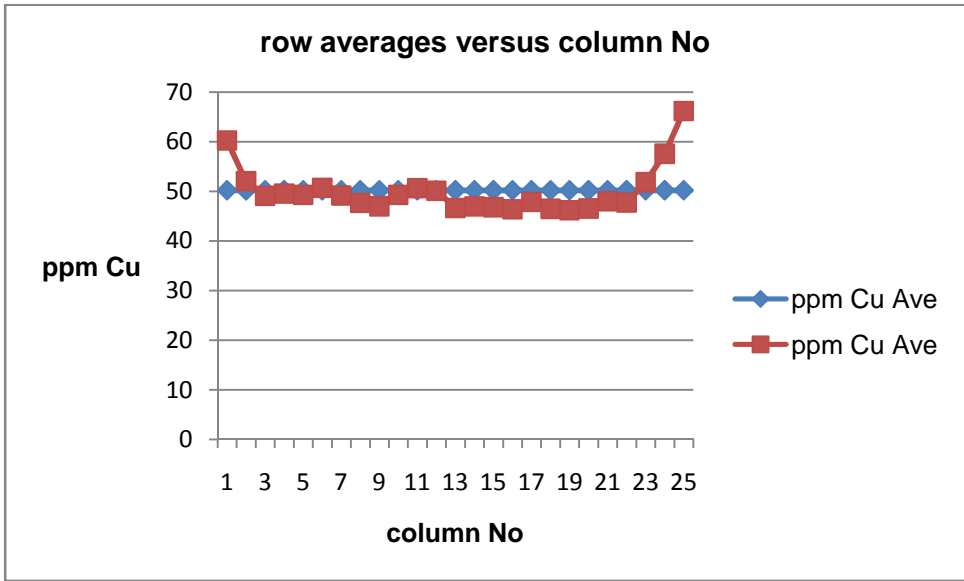
AVERAGE OF COLUMNS		1	3	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
ppm Co Ave	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34	128.34
ppm Co	142.88	132.6559	126.7094	127.7328	123.9878	121.0309	122.4138	123.1075	125.9841	125.4703	129.125	124.9438	122.8053	126.5606	126.3722	123.3944	123.7003	124.6084	124.5484	124.8313	126.1013	126.4231	132.1719	139.6356	153.4041	
ppm Cu Ave	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23	50.23
ppm Cu Ave	60.28469	52.08906	49.09	49.54	49.28688	50.7	49.19125	47.70438	47.00156	49.32156	50.63969	50.15063	46.64969	46.9875	46.81531	46.39906	47.86281	46.49594	46.20844	46.5475	47.99	47.73188	51.84063	57.59906	66.20469	
ppm Zn Ave	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30	17.30
ppm Zn	20.6425	19.26313	17.6175	17.10125	17.03156	16.67063	17.79563	16.57531	17.18344	16.835	16.74438	16.38781	16.47313	16.7675	16.35813	15.97906	16.41563	16.28594	15.92438	16	16.17719	16.25969	17.04938	18.14781	21.06844	
ppm Fe Ave	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64	25.64
ppm Fe	27.83844	24.46313	24.35688	23.50719	24.03781	25.99063	24.68781	23.56813	26.4	25.91688	27.9575	26.30813	24.75281	24.92375	24.75344	24.2675	24.51563	25.93813	26.21969	24.65813	27.75188	26.42375	25.23938	29.45031	28.39219	



**Figure 4.1 Variation of row average (Co) concentration with column numbers of the cathode**

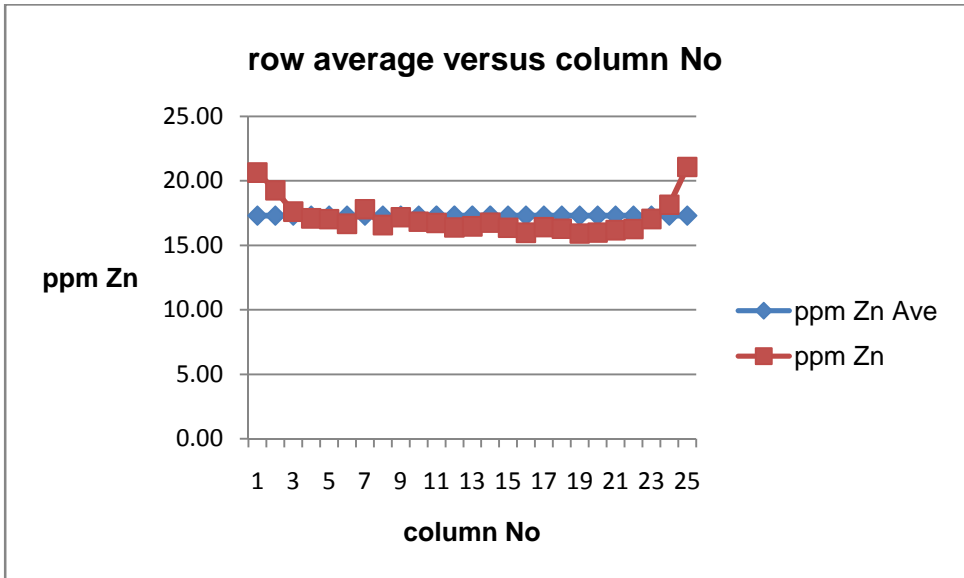
The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that there is no significant difference among most cobalt values across the cathode.





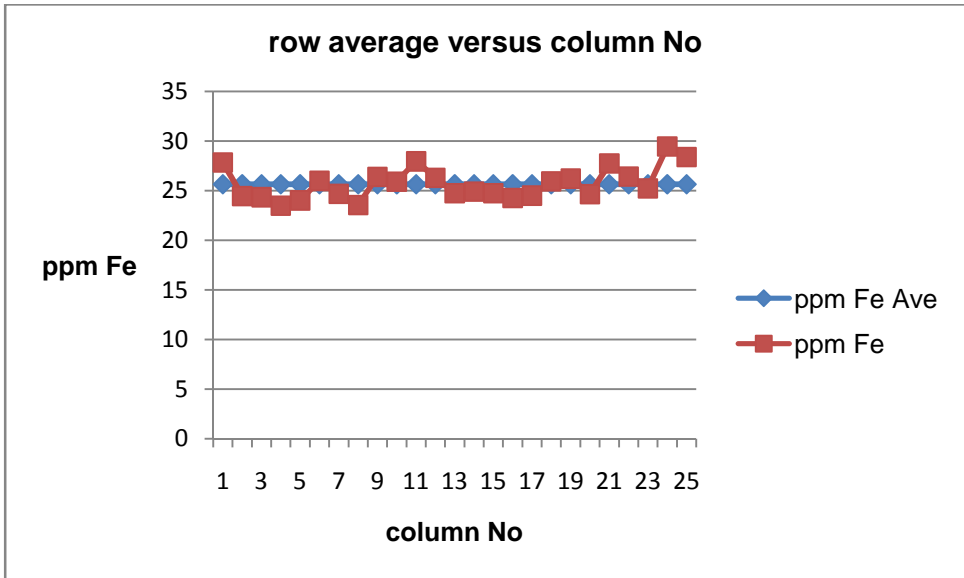
**Figure 4.2 Variation of row average (Cu) concentration with column numbers of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that there is no significant difference among most copper values across the cathode.



**Figure 4.3 Variation of row average (Zn) concentration with column numbers of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that there is no significant difference among most zinc values across the cathode.



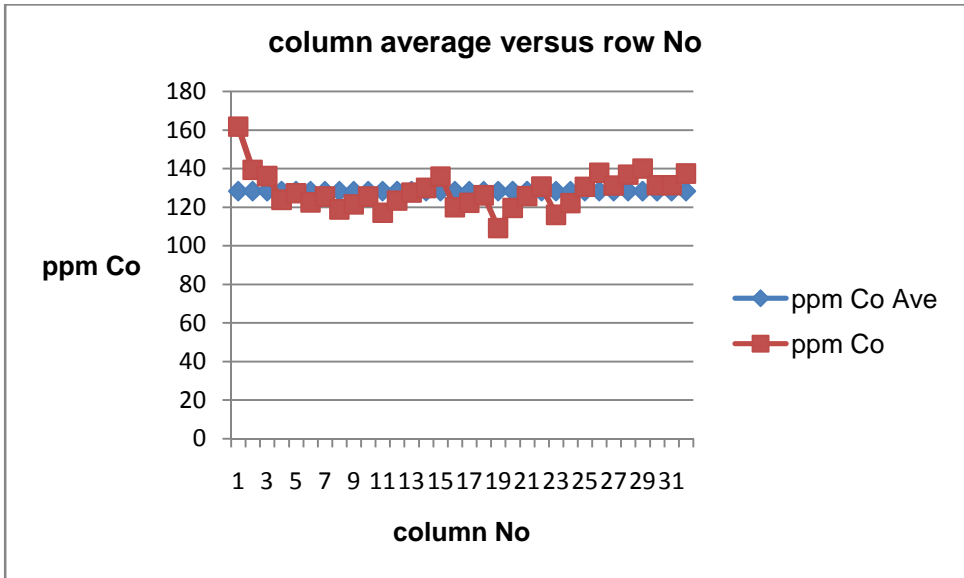
**Figure 4.4 Variation of row average (Fe) concentration with column numbers of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that there is no significant difference among most iron values across the cathode.

b) Variation down cathode

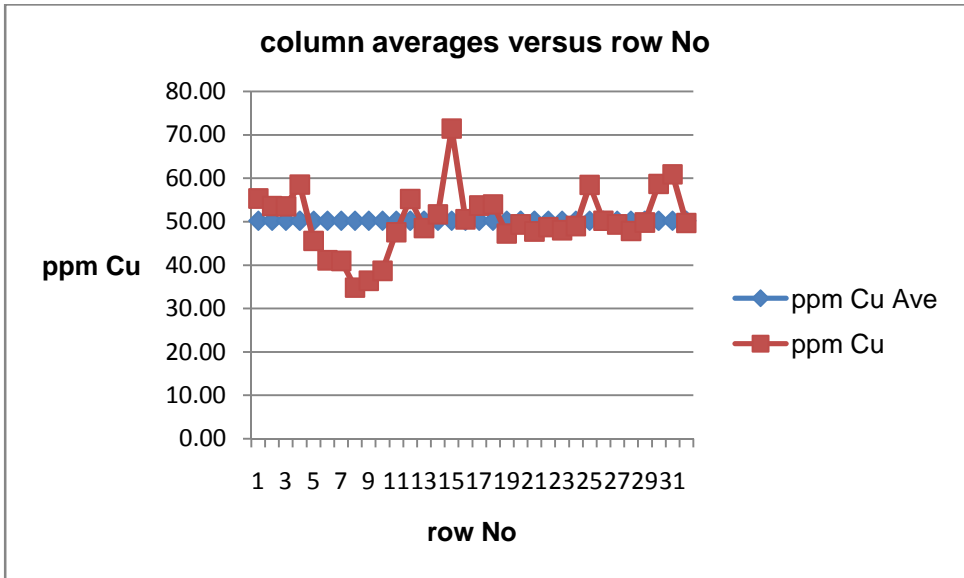
**Table 4.10 column averages**

STRIP NUMBER	ppm Co Ave	ppm Co	ppm Cu Ave	ppm Cu	ppm Zn Ave	ppm Zn	ppm Fe Ave	ppm Fe
1	128.34	161.72	50.23	55.35	17.30	28.06	25.64	20.33
2	128.34	139.42	50.23	53.63	17.30	16.23	25.64	37.20
3	128.34	136.15	50.23	53.57	17.30	20.39	25.64	29.72
4	128.34	123.92	50.23	58.57	17.30	20.85	25.64	22.22
5	128.34	127.30	50.23	45.60	17.30	16.02	25.64	26.47
6	128.34	122.58	50.23	41.14	17.30	16.01	25.64	30.81
7	128.34	125.55	50.23	41.01	17.30	13.74	25.64	32.03
8	128.34	118.92	50.23	34.87	17.30	16.21	25.64	32.62
9	128.34	121.48	50.23	36.42	17.30	18.23	25.64	25.20
10	128.34	125.57	50.23	38.73	17.30	16.33	25.64	18.35
11	128.34	117.23	50.23	47.59	17.30	16.72	25.64	17.96
12	128.34	123.54	50.23	55.23	17.30	18.31	25.64	24.13
13	128.34	127.61	50.23	48.55	17.30	18.28	25.64	39.79
14	128.34	130.08	50.23	51.69	17.30	14.43	25.64	21.20
15	128.34	135.96	50.23	71.43	17.30	17.18	25.64	28.11
16	128.34	120.05	50.23	50.57	17.30	13.26	25.64	30.48
17	128.34	122.39	50.23	53.74	17.30	13.91	25.64	29.88
18	128.34	126.27	50.23	54.00	17.30	15.52	25.64	18.65
19	128.34	109.30	50.23	47.31	17.30	15.27	25.64	14.94
20	128.34	119.74	50.23	49.40	17.30	12.83	25.64	16.88
21	128.34	125.79	50.23	47.77	17.30	13.80	25.64	16.92
22	128.34	130.69	50.23	48.76	17.30	16.40	25.64	14.44
23	128.34	116.11	50.23	48.07	17.30	17.38	25.64	21.32
24	128.34	122.16	50.23	49.03	17.30	17.32	25.64	27.84
25	128.34	130.67	50.23	58.49	17.30	16.24	25.64	22.13
26	128.34	137.92	50.23	50.23	17.30	17.82	25.64	31.11
27	128.34	131.32	50.23	49.40	17.30	17.11	25.64	29.84
29	128.34	136.93	50.23	47.90	17.30	20.16	25.64	25.32
30	128.34	140.02	50.23	49.84	17.30	18.73	25.64	32.97
31	128.34	131.49	50.23	58.69	17.30	19.29	25.64	28.51
32	128.34	131.48	50.23	60.92	17.30	18.78	25.64	24.16
33	128.34	137.53	50.23	49.73	17.30	22.67	25.64	27.59



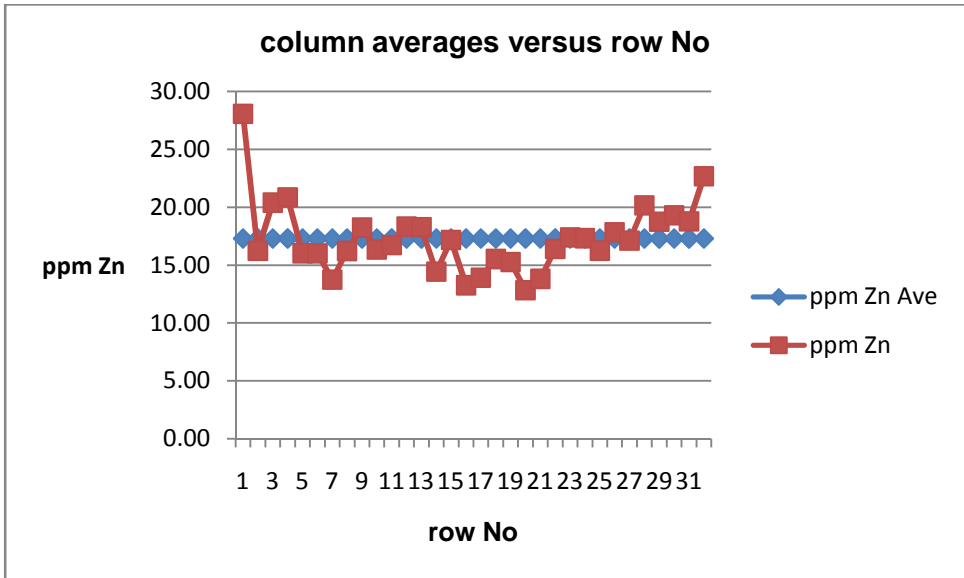
**Figure 4.1 Variation of column average (Co) with row numbers of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that there is no significant difference among most cobalt values across the cathode although there is some slight difference at the top of the cathode.



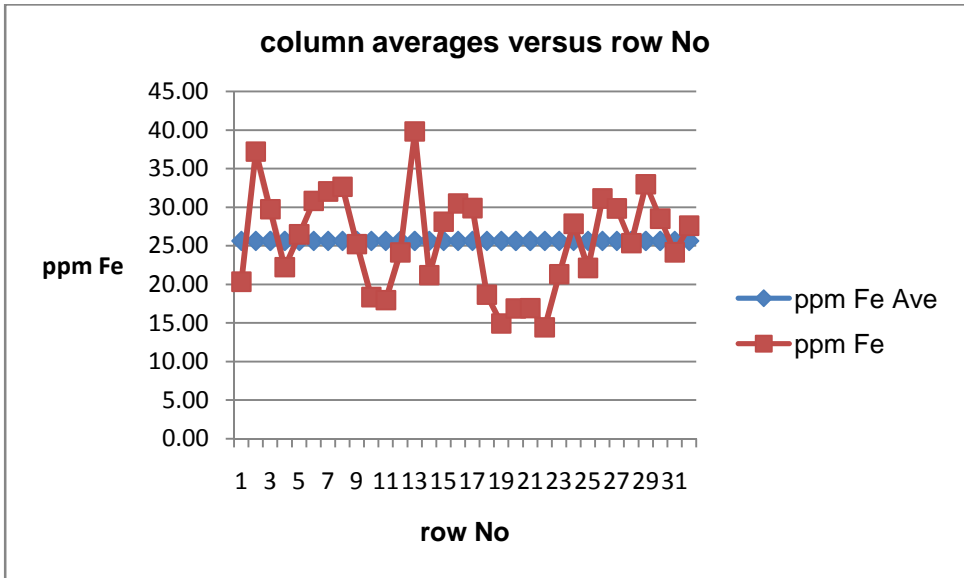
**Figure 4.6 Variation of column average (Cu) with row numbers of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that copper values down the cathode were not the same. Inspection of the graph points to a random distribution, judging by the absence of an obvious trend.



**Figure 4.7 Variation of column average (Zn) with row numbers of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that zinc values down the cathode were not the same. Inspection of the graph points to a random distribution, judging by the absence of an obvious trend.



**Figure 4.8 Variation of column average (Fe) with row number of the cathode**

The data above was also analysed using SPSS (statistical package). The analysis of variation (one way ANOVA) showed that iron values down the cathode were not the same.

**Table 4.11 six groups of similar rows**

The following table shows which rows were the same

GROUP	ROW No
A	1,4,6,7,16,17,18,25,27,28,30,31
B	2,5,11,15,19,21,22,24,26
C	3,14
D	5,6,10,13,15,24,26,29,32
E	8,9,30
F	12,20,22,23

Although the above table shows that there are six groups of similar rows, inspection of the graph in fig 4.8 points to a random distribution, judging by the absence of an obvious trend.



## SAMPLING TECHNIQUES

**Table 4.12 Results of systematic sampling following the current method**

ELEMENT	FIRST	CENTRE	FAR END	AVE	STDEV
Co	117.66	139.9	120.00	125.8533	12.22091
	98.53	121.43	122.86	114.2733	13.65286
	137.82	127.66	131.93	132.47	5.10148
AVERAGE				<b>124.1989</b>	<b>10.32508</b>
Cu	50.96	48.63	44.06	47.88333	3.510076
	67.41	49.64	45.97	54.34	11.46673
	61.9	54.54	60.85	59.09667	3.980959
AVERAGE				<b>53.77333</b>	<b>6.319255</b>
Zn	18.53	17.03	22.79	19.45	2.988177
	12.43	14.04	11.76	12.74333	1.17185
	18.93	19.56	19.28	19.25667	0.315647
AVERAGE				<b>17.15</b>	<b>1.491892</b>
Fe	46.04	47.16	51.66	48.28667	2.974581
	27.92	26.9	24.06	26.29333	2.000233
	31.67	32.67	31.29	31.87667	0.712835
AVERAGE				<b>35.48556</b>	<b>1.895883</b>

Systematic sampling for cobalt using 9 samples give an average of 124,20ppm against a population mean of 128,34ppm.

Systematic sampling for copper using 9 samples give an average of 53,77ppm against a population mean of 50,23ppm.

Systematic sampling for zinc using 9 samples give an average of 17,15ppm against a population mean of 17.30ppm.

Systematic sampling for iron using 9 samples give an average of 35,49ppm against a population mean of 25,64ppm.

**Table 4.13 Systematic sampling using 30 samples (Co) concentration in (ppm)**

	COLUMN						
ROW	5	10	15	20	25	AVE	STDEV
5	119.98	127.39	119.61	108.92	136.28	122.436	10.15996
10	132.17	129.93	124.55	119.75	112.95	123.87	7.782943
15	125.98	132.26	105.79	124.42	128.74	123.438	10.30554
20	122.27	121.73	118.99	109.47	112.84	117.06	5.65894
25	135.62	126.93	127.89	127.67	130.41	129.704	3.557398
30	128.38	127.64	134.6	131.93	128.39	130.188	2.978854
						<b>124.4493</b>	<b>6.740606</b>

Systematic sampling for cobalt using 30 samples give an average of 124,45ppm against a population mean of 128,34ppm.

**Table 4.14 Systematic sampling using 30 samples (Cu) concentration in (ppm)**

	COLUMN						
ROW	5	10	15	20	25	AVE	STDEV
5	46.01	54.46	28.67	25.99	39.53	38.932	11.87833
10	29.75	30.36	46.85	47.25	44.38	39.718	8.891905
15	56.01	54.71	49.46	65.18	69.19	58.91	8.067586
20	49.03	46.82	46.85	46.89	48.28	47.574	1.02212
25	53.77	61.2	55.53	62.6	58.11	58.242	3.711909
30	55.07	58.84	58.63	60.85	55.75	57.828	2.38351
						<b>50.20067</b>	<b>5.992559</b>

Systematic sampling for copper using 30 samples give an average of 50.20ppm against a population mean of 50.23ppm.

**Table 4.15 Systematic sampling using 30 samples (Zn) concentration in( ppm)**

	COLUMN							
ROW	5	10	15	20	25	AVE	STDEV	
5	13.33	21.8	11.86	12.56	12.17	14.344	4.204144	
10	13.33	16.29	15.22	14.21	17.42	15.294	1.624017	
15	18.54	16.61	15.94	14.03	17.11	16.446	1.654216	
20	13.27	12.11	12.35	12.3	12.42	12.49	0.450943	
25	16.71	16.67	16.3	15.93	15.75	16.272	0.430256	
30	17.03	18.35	19.26	19.28	19.19	18.622	0.970963	
						<b>15.578</b>	<b>1.555757</b>	

Systematic sampling for zinc using 30 samples give an average of 15.58ppm against a population mean of 17.30ppm.

**Table 4.16 Systematic sampling using 30 samples (Fe) concentration in (ppm)**

	COLUMN							
ROW	5	10	15	20	25	AVE	STDEV	
5	24.39	21.66	13.25	20.83	21.04	20.234	4.155927	
10	27.65	28.98	24.83	22.96	20.55	24.994	3.422562	
15	19.8	15.6	14.25	17.47	21.67	17.758	3.021567	
20	12.79	13.46	12.93	11.82	12.87	12.774	0.594668	
25	26.09	23.06	26.15	25.88	27.55	25.746	1.640771	
30	40.48	30.21	31.93	31.29	31.00	32.982	4.236799	
						<b>22.41467</b>	<b>2.845383</b>	

Systematic sampling for iron using 30 samples give an average of 22.41ppm against a population mean of 25.64ppm.

**Table 4.17 Comparison of mean of nine random samples with population mean for cobalt**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
RANDOM SAMPLING 9 SAMPLES	Co	119.97	128.34	-8.37
		130.89	128.34	2.55
		134.87	128.34	6.53
		116.99	128.34	-11.35
		132.48	128.34	4.14
		131.95	128.34	3.61
		129.87	128.34	1.53
		128.13	128.34	-0.21
		122.99	128.34	-5.35
		125.19	128.34	-3.15

Comparison of mean of 9 samples against population mean shows that there is wide variation of values, which range from 116.17 to 131.95

**Table 4.18 Comparison of mean of nine random samples with population mean for copper.**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
RANDOM SAMPLING 9 SAMPLES	Cu	49.46	50.23	-0.77
		45.98	50.23	-4.25
		49.25	50.23	-0.98
		46.69	50.23	-3.54
		48.35	50.23	-1.88
		51.2	50.23	0.97
		46.66	50.23	-3.57
		50.73	50.23	0.5
		54.2	50.23	3.97
		44.87	50.23	-5.36

Comparison of mean of 9 copper samples against a population mean of 50.23 shows that the values varies from 44.87 to 54.20

**Table 4.19 Comparison of mean of nine random samples with population mean for zinc**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
RANDOM SAMPLING 9 SAMPLES	Zn	16.92	17.3	-0.38
		19.46	17.3	2.16
		17.27	17.3	-0.03
		16.04	17.3	-1.26
		16.58	17.3	-0.72
		17.11	17.3	-0.19
		21.86	17.3	4.56
		16.69	17.3	-0.61
		15.62	17.3	-1.68
		16.05	17.3	-1.25

Zinc mean values of 9 sample were almost close to the population mean of 17.30

**Table 4.20 Comparison of mean of nine random samples with population mean for iron.**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
RANDOM SAMPLING 9 SAMPLES	Fe	24.02	25.64	-1.62
		23.84	25.64	-1.8
		19.95	25.64	-5.69
		21.93	25.64	-3.71
		26.3	25.64	0.66
		24.04	25.64	-1.6
		24.28	25.64	-1.36
		21.96	25.64	-3.68
		21.47	25.64	-4.17
		25.53	25.64	-0.11

Iron mean values of 9 sample had a wide variation from the population mean of 25.64

**Table 4.21 Comparison of mean of thirty random samples with population mean for cobalt**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x} - \mu$
RANDOM SAMPLING 30 SAMPLES	Co	125.87	128.34	-2.47
		130.76	128.34	2.42
		128.19	128.34	-0.15
		133.84	128.34	5.5
		123.18	128.34	-5.16
		126.59	128.34	-1.75
		130.29	128.34	1.95
		126.08	128.34	-2.26
		130.36	128.34	2.02
		127.51	128.34	-0.83

The mean of thirty cobalt samples were almost around the population mean.

**Table 4.22 Comparison of mean of thirty random samples with population mean for copper**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x} - \mu$
RANDOM SAMPLING 30 SAMPLES	Cu	50.84	50.23	0.61
		50.53	50.23	0.3
		51.30	50.23	1.07
		51.77	50.23	1.54
		51.04	50.23	0.81
		50.84	50.23	0.61
		51.58	50.23	1.35
		46.60	50.23	-3.63
		51.37	50.23	1.14
		46.61	50.23	-3.62

The mean of thirty copper sample were around population mean.

**Table 4.23 Comparison of mean of thirty random samples with population mean for zinc**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
RANDOM SAMPLING 30 SAMPLES	Zn	16.51	17.30	-0.79
		17.13	17.30	-0.17
		17.66	17.30	0.36
		17.2	17.30	-0.10
		16.36	17.30	-0.94
		16.62	17.30	-0.68
		16.6	17.30	-0.70
		17.12	17.30	-0.18
		16.52	17.30	-0.78
		17.4	17.30	0.10

The mean of thirty zinc samples varies around population mean.

**Table 4.24 Comparison of mean of thirty random samples with population mean for iron**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
RANDOM SAMPLING 30 SAMPLES	Fe	27.02	25.64	1.38
		25.7	25.64	0.06
		24.36	25.64	-1.28
		28.23	25.64	2.59
		28.53	25.64	2.89
		27.12	25.64	1.48
		27.23	25.64	1.59
		25.03	25.64	-0.61
		25.16	25.64	-0.48
		25.52	25.64	-0.12

The mean of thirty iron samples varies around population mean.

**Table 4.25 Comparison of mean of nine systematic samples with population mean**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
SYSTEMATIC SAMPLING USING NINE SAMPLES	Co	124.2	128.34	-4.14
CURRENT METHOD	Cu	53.77	50.23	3.54
	Zn	17.15	17.30	-0.15
	Fe	35.49	25.64	9.85

The mean of nine systematic samples varies widely when compared to the population mean.

**Table 4.26 Comparison of mean of thirty systematic samples with population mean**

SAMPLING METHOD	ELEMENT	$\bar{x}$	$\mu$	$\bar{x}-\mu$
SYSTEMATIC SAMPLING 30 SAMPLES	Co	124.45	128.34	-3.89
	Cu	50.2	50.23	-0.03
	Zn	15.58	17.30	-1.72
	Fe	22.41	25.64	-3.23

The mean of nine systematic samples varies widely for cobalt, zinc and iron when compared to population mean, except for copper which is almost the same as the population mean



**Table 4.27 Second production on 29 November 2012 cell 15**

ELEMENT	TOP	MIDDLE	BOTTOM
Co	140.18	126.36	122.64
	131.12	125.08	159.54
	140.19	169.39	165.79
AVE	137.16	140.28	149.32
Cu	99.70	91.92	74.14
	96.73	102.45	101.87
	108.91	108.00	118.76
AVE	101.78	100.79	98.26
Zn	19.67	23.32	15.56
	16.18	24.06	13.85
	23.10	20.19	16.1
AVE	19.65	22.52	15.17
Fe	78.03	65.32	65.66
	62.09	71.59	66.46
	76.95	70.08	83.87
AVE	72.36	69.00	72.00

## CHAPTER 5

### 5 DISCUSSION

#### 5.1.1 Statistical Analysis

SPSS ( one-way ANOVA) statistical analysis was used to determine the trend of impurity distribution in the cathode. Standard deviations, means and the splitting limits were used to determine the best sampling method.

#### 5.1.2 Cobalt Distribution in the Cathode

SPSS ( one-way ANOVA) analysis on cobalt values across cathode from left to right showed that there is no significant differences among most cobalt values. Analysis down the cathode showed that there is no significant differences among most cobalt values. This shows that the cobalt values are randomly distributed in the cathode.

#### 5.1.3 Copper Distribution In The Cathode

Analysis of the copper data using SPSS (one-way ANOVA) showed that there is no significant difference among most copper values across the cathode. Down the cathode the values shows that they are not the same. Hence copper is randomly distributed in the cathode, judging by the absence of an obvious trend.

#### 5.1.4 Zinc Distribution In The Cathode

Analysis of Zinc data using SPSS (one-way ANOVA) showed that there is no significant difference among most Zinc values across the cathode. Down the cathode zinc values shows that they are not the same. However the general trend is that zinc is randomly distributed in the cathode because of the absence of an obvious trend.

#### 5.1.5 Iron Distribution In The Cathode

Analysis of iron data using SPSS (one-way ANOVA) showed that there is no significant difference among most iron values across the cathode. Analysis down the cathode shows that the values were not the same. As shown by SPSS analysis there are six groups of similar rows, inspection of the graph in fig 4.21 points to a random distribution, judging by the absence of an obvious trend.

### 5.1.6 Comparison Of Sampling Methods

Graphs for each individual element that is Cobalt, Copper, Zinc and Iron from Figure 3.1 to Figure 3.236 and the column averages and row averages from Figure 3.237 to 3.244 shows that there is no pattern in which the impurities are distributed within the cathode. This means stratified sampling cannot be applied as a sampling method, for the cathodes. Stratified sampling applies where the cathode can be divided into distinct layers. The results in Table 3. 24, which is the current method being used (systematic sampling using 9 samples) which shows that there is great variance between the population mean of the cathode and the actual values obtained from systematic sampling. Even when the number of samples was increased from 9 to 30 samples, the variance was only reduced for Copper and Zinc but was still high for Cobalt and Iron, as shown in table 3. 25 (systematic sampling using 30 samples). Since the impurities within the cathode are not systematically distributed, the sampling method that can be applied is random sampling. Random sampling using nine samples shows great variance between Cobalt and Copper and much reduced for Zinc and Iron as shown in table 3.16 to 3.19. When increasing samples to thirty, the variation was much reduced for all the elements, even though it was a bit high for Cobalt as shown in Table 3.20 to 3.23. This has proved the fact that as the number of sample increase the closer it will be to the population mean. When comparing systematic sampling and random sampling to the splitting limit acceptable at ENR Laboratory of +/- 2ppm, shows that random sampling is superior than systematic sampling especially with increased number of samples. As shown in Table 3.20 five cobalt samples were within the required splitting limit. For copper and iron eight samples were within the splitting limit while for zinc all samples were within the splitting limit. Systematic sampling using nine samples only zinc was within the splitting of +/-2ppm. When the samples were increased to thirty only copper and zinc were within the splitting limit. Hence random sampling was a better sampling method for cathodes than systematic sampling. The results of samples taken for the second production on 29 November 2012 cell number 15, Table 3.26 shows that there is no relationship with the first production cathode in distribution of cobalt, copper, zinc and iron in nickel cathode. This shows that the distribution of impurities in the cathode depends on the operating parameters of the tank house on the particular production date.

Convenience sampling was not applied because it is a nonprobability sampling technique, hence the sample produced could not be representative enough of the whole population. Quota sampling is applicable where the population can be divided into segments, in this case the cathode could not be divided into segments since the impurities had no pattern in which they are distributed.

## **CHAPTER 6**

### **6 CONCLUSION**

SPSS (one-way ANOVA) analysis shows that there is no significant difference in the impurity distribution in the cathode. Therefore random sampling using random number tables is the best method for sampling cathodes with unevenly impurity distribution. The sampling process involve three basic steps

- 1) Random selection of an adequate number of cathodes that are representative of a lot.
- 2) Obtaining a sample from the random- selected cathodes through a mechanical process such as drilling or sawing.
- 3) Preparing a homogeneous portion from the sampled cathodes that is of suitable size and quantity for chemical analysis.

NB The number of cathodes that must be sampled to represent a lot is dependent upon the size of lot and the respective cathode quality.

## **6.0 RECOMMENDED METHOD**

### **6.1 Application of random sampling on cathode**

#### **6.1.1 Standard Work Procedure**

##### **Title : Sampling Of Nickel Cathode**

#### **1.0 Purpose And Importance**

This procedure describes the steps followed in designing and sampling nickel cathodes.

#### **2.0 Scope**

This procedure applies to the sampling of nickel cathodes for analysis in the Laboratory.

#### **3.0 Responsibility**

3.1 Plant Operator selects the cathode using random number tables from each cell.

3.2 The Chemist design the sampling template

3.3 The Analyst selects the positions to be drilled on the cathode using the random number tables.

3.4 Laboratory Assistant is responsible for drilling and collecting the nickel cathode samples.

3.5 Analyst is responsible for supervising the sampling work and ensuring that samples are collected correctly and on time.

3.6 The Chief Chemist is responsible for the overall implementation and review of this procedure.

#### **4.0 Basic Principle**

Sampling is the process of extracting from a bulky material a portion that is representative of the whole population.

#### **5.0 Special Skills Required**

5.1 Ability to use random number tables

5.2 Operation of the drilling machine.

## **6.0 Tools And Equipment**

6.1 Drilling machine, UCIMU R1299L 30-40

6.2 Drill bits: SOMTA 652 HSS 25/32

6.3 Sample bags/ containers

## **7.0 Designing A Sampling Template**

7.1 Take a spread sheet which is equal in size to the cathode.

7.2 Divide the cathode into 25mm X 25mm squares.

7.3 Number the squares in ascending order.

7.4 Punch a hole on each square

## **8.0 Sampling**

8.1 Select one cathode from each cell from the production pull, using random number tables.

8.2 Determine the sampling positions on the cathode using random number tables.

8.3 Spread the template on the cathode and mark the sampling points on the cathode using a mighty marker.

8.4 Cut the cathode in 25mm strips

8.5 Drill the strips on the marked positions using the drilling machine.

8.6 Collect the drilled samples into the container and label properly.

## **9.0 Special precautions**

9.1 Moving parts of the machine must be guarded

9.2 No loose clothing in the drilling area.

9.3 Gloves must be worn all the time

## **10.0 Prohibition**

10.1 Do not operate the drilling machine without wearing ear plugs.

## REFERENCES

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Appendices

## **Appendix 1 Random number tables**