PROGRESS TOWARDS THE DEVELOPMENT AND IMPLEMENTATION OF AN UNAMBIGUOUS COPPER WIRE FINGERPRINTING SYSTEM

By
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Abstract

The Telecommunications industry in Southern Africa is faced with the problem of theft of the signal carrying copper wire, both from the ground and from telephone poles. In many cases, if the offenders are caught, the prosecuting party has no way of proving that the wire is the property of any one Telecommunication company, as any inked markings on the insulating sheaths have been burned off along with the insulation and protective coatings themselves. Through this work we

- describe the problem,
- specify the necessary and preferred technical properties of a viable solution,
- report the preliminary investigations into the devising of an unambiguous "fingerprinting" of the $\simeq 0.5$ mm wires, including some of those solutions that, upon investigation, appear non-viable,
- describe the development and implementation of an electrochemical marker with detection mechanism which has shown in proof-of-principle to work,
- outline the road-map of necessary future work.

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The undersigned hereby certify that they have read and recommend to the Faculty of Science for acceptance a thesis entitled "**Progress towards the development and implementation of an unambiguous copper wire fingerprinting system**" by **Martin Poole** in fulfillment of the requirements for the degree of **Master of Science**.

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Finally a thank you to Sandra, who has patiently suffered my dedication to completing this work.

Aims and objectives of this work

This thesis is centred entirely around the problem of copper cable theft. The project originated with employees from the Telkom's Technology Procurement Services approaching all the universities possessing a CoE[1] and putting the problem of copper theft to them.

At this time (November 1999, the same time the author was completing his honours degree in telecommunications), the only information given was that no "fingerprinting" system existed that could uniquely identify an arbitrarily selected segment of copper cable (burnt or not) with its owner. It was verbally declared that there was presently no legally tenable method, in the absence of a confession, of prosecuting parties caught in possession of the stolen cables. The general question of "Is there anything anyone can think of that can done to the cable to remedy this" was put to the CoE's. In response, the author and supervisors undertook to perform research into the development of such a "fingerprinting" (as it quickly became known) method.

A method (or technique or solution, used interchangeably throughout this work) in the context of this work, and more generally this problem, is the term used to describe the process or deliberate action that serves to "fingerprint" the cable; i.e. the cable's owner is unambiguously identified with the cable after the implementation and later detection of the method. The work presented in this thesis attempts to simultaneously address the commercial need for a wire marking method, considers and discusses some of the alternatives, that did not prove viable, whilst fulfilling the

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[1] CoE is Telkom's abbreviation for Centre of Excellence. Telkom generously funds research in, and provides bursaries for, research in telecommunication fields they deem pertinent to their business model, and CoE refers to the section of an academic department within a University that performs research specifically for Telkom. These CoE's provide the administrative interface through which money and research findings are channelled. By way of example there is a CoE at Rhodes, which is a research group under Professor Peter Clayton and Mr. Alfredo Terzoli (coordinator) in the department of Computer Science, with a research focus on distributed multi-media.

technical requirements of an M.Sc. in Physics and Electronics (Telecomms) at Rhodes University.

All the investigations and research performed in an attempt to find a solution are fully declared here, including the potential solutions which proved non-viable. When the problem was specified, it was made clear that direct theft prevention (i.e. "guarding") systems were not to be of any concern to *this* research. Telkom felt that a successful prosecution of an offender caught in possession should be the priority, since word would spread amongst the criminal fraternity that legal protection would now exist.

The project was jointly funded by Telkom SA and THRIP.

Chapter 1

Introduction

1.1 Description of the problem

The development of a comprehensive wire identification technique has become necessary in South Africa[1] in recent times. The cables contain highly pure copper, and this copper can be sold to the scrap metal dealers, which is an attractive and seemingly risk-free source of income for people who have no other form of income. Disruptions in telecommunication service provision arising from copper theft have been reported in the press as having grown to around 1700 cables just in March of 2001. See figure 1.1[13].

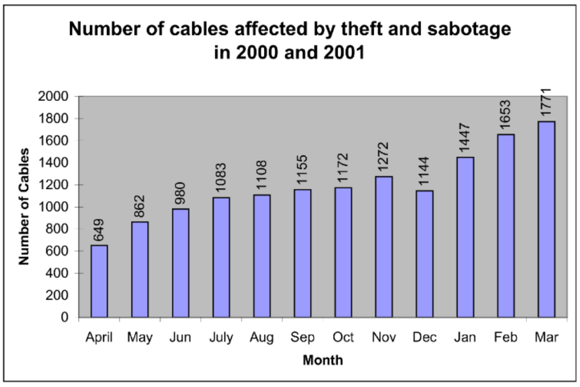

Figure 1.1: Figures published in the press concerning the number of cables lost to vandalism and theft between 2000 and 2001. This data and presentation taken from the Mail & Guardian, 20th July Ed., 2001. [13]

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[1] Apparently, according to sources within Telkom, this problem exists in South America and some other countries in Sub-Saharan Africa too.

Estimates concerning the losses resulting from the theft differ widely, thus no conclusive figure can be provided, but estimates are often given in the region of R300 million a year; a considerable figure.

There is no off-the-shelf (i.e. readily commercially available) technology for uniquely marking the wire, and thus the technology may have commercial value to any competitors wishing to penetrate the South African telecommunication market. It is estimated that the cost of replacing cable is around 3 times the value of the physical wire, and that following the expiry of Telkom's exclusivity rights in May 2002, service disruptions (for all reasons including theft) would translate into loss of custom - not just immediate loss of revenue.

A *cable* is a collection of between 10 and 2400 pairs of individually insulated (with coloured PVC) copper wires bound with wax paper and housed in a larger black PVC sheath (often with an Aluminium inner sheath for the larger cable. An example of a larger cable can be seen in figure 1.2).

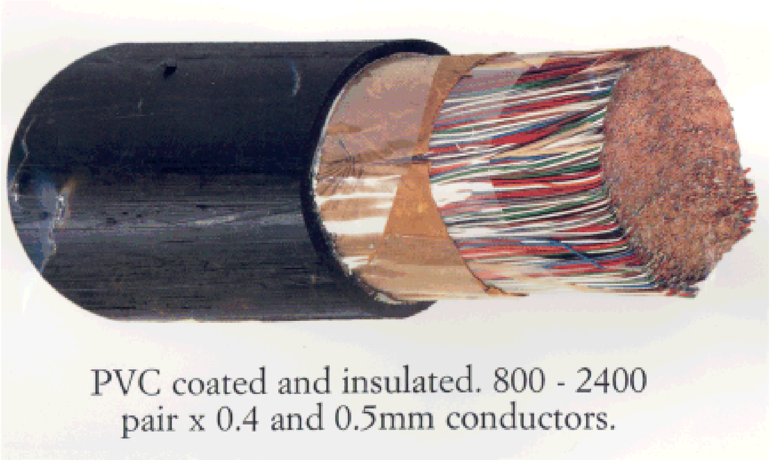

Figure 1.2: A photograph of a cross-section of an example of one of the larger cables. The outer black PVC is clearly visible, and the inner aluminium sheath is visible between the black PVC and the wax paper. Enclosed within the wax paper are the individually insulated and coloured conductors. The different colours are used by maintenance and technical staff for identification. This image kindly provided by Mr. Willie Schutte of Telkom SA.

These cables are found both supported by telephone poles, in the overhead case, or underground, where they are accessed via manholes. Typically the thieves approach the cable with a light duty vehicle, and sever the cable either at the pole or at the manhole often with an axe. The cable is then usually removed by dragging (either by the perpetrators personally or by being affixed to the light duty vehicle) some 200 m or so where the cable is burned. The fire is most often a simple wood fire, aided by the addition of petrol or paraffin. Immediately prior to burning, the outer black PVC sheathing is skinned off, first by first making a length-wise incision with a knife, and then pulling the sheath so that it splits all the way along the cable. The aluminium inner sheath, if present is removed in a similar fashion.

The outer casings are the only components of the cable that carry information on the manufacturer and owner of the wire, and are discarded next to the fire where the police find them later. With the outer casing removed, only the twisted pairs (still coated with their individual coloured polyethylene insulators) remain, and the simplest way to remove them is burning.

The polyethylene coating on each of the wires burns readily, with its combustion becoming exothermic at approximately 120 degrees Celsius (see figure 4.3).

After burning, the wires resemble those shown in figure 1.3. Burned coils of the wire are taken to a scrap metal dealer, where they are sold for approximately R10 per kilogram.

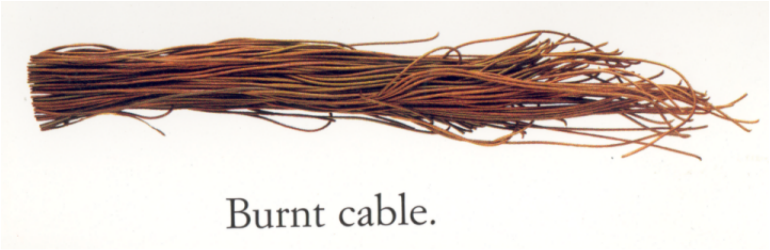

Figure 1.3: Copper wire after burning. Note that there are no visible distinguishing markings, besides some due to surface oxidation, which varies from sample to sample. This image kindly provided by Mr. Willie Schutte of Telkom SA.

Wires used in telecommunications are recognizable to the metal merchants as they often come in large groups of twisted pairs, but there is no way of unambiguously proving that the wire belongs to any one telecommunications company, so there are no legal grounds for prosecution. At the metal merchants, the wire is smelted down and sent back through private smelters for recycling. The actual thieves seldom have the time and wherewithal to smelt the copper themselves, which is fortunate as it provides more opportunities and time for apprehending the criminals while still in possession of the wires.

1.2 Overview of the research progress

In what follows, it is revealed what was considered could possibly be done. Knowing little of the industrial process which results in the finished copper cable (at the time), some candidate techniques were proposed, outlined in chapter 2. One of the questions which had been asked was is there anything that can be done to identify the cable already in the ground? Thus the first investigation was into whether the inherent inhomogeneity of the elements in the wire could be used to identify the cable. To this end, the composition of the wire was determined (presented in section 4.2.1), and simultaneously, much was learned of the production process, as research trips to the cable manufacturers and even to their supplier (see the next chapter for more detail), were undertaken. It is shown in section 5.2 that the inhomogeneities have no application in identifying the existing wires. At that time, assays of the manufacturers copper showed, upon comparison with the LME[2] specification for the appropriate copper, that there might be viability in manipulation of elemental concentrations *before* the raw material is passed to the cable manufacturers. This proved non-viable too, and the reasons for the non-viability are given in section 5.2.

Having obtained all the necessary information on the industrial process, the crucial question of exactly what properties a solution must necessarily have was addressed, and this is explained in detail in chapter 3. Carefully specifying the necessary and desirable properties of a solution helped reveal the non-viability of the inhomogeneity. In turn, identifying the concerns responsible for the non-viability of the inhomogeneity candidate solutions helped clarify the solution criteria.

Electrodeposition of nickel onto the wire as the wire is extruded was investigated for viability, as this method seemed most likely to fulfil the now well-defined solution criteria. There is a full account of the theory and principle behind this solution in

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[2] London Metals Exchange, the authority responsible for dictating the compositional specification of metals and alloys

chapter 6. Briefly, the solution involves depositing nickel onto the surface of the copper wire so that the deposits can later be detected. The deposition occurs as follows. The copper wire is treated as the cathode in an electrochemical cell. An electrolyte of dissolved nickel chloride is gravitationally precipitated over the wire in a thin stream. The anode of the electrochemical cell is some inert substance (e.g. carbon) placed in the stream immediately above the wire. A current is passed from anode to cathode by means of a current source, and this results in nickel ions being reduced to nickel atoms at the cathode, causing plating of metal atoms onto the wire. The detection of the nickel is effected by applying a magnetising field to the nickel-clad wire, and then sensing the residual magnetic field to prove the presence of nickel. This detection is to occur after the wire has been stolen and the insulation burned off.

Ensuring the uniformity of the electrodeposited nickel required a voltage controlled current source (VCCS). Considering the production process (section 4.1.2, particularly figure 4.1), the nickel would have to be applied between the time the wire is drawn to its final diameter, and before it is coated with insulation, point D in figure 4.1. At this time, the wire is moving at approximately 40 m/s.

Simply applying a uniform layer of nickel would certainly identify the wire uniquely as being distinct from an ordinary wire (provided you could detect it, and efforts to do this are revealed in section 7). Since the manufacturers do not supply Telkom only, it would be preferable if the "fingerprint" (in this case the presence of nickel on the surface of the copper) could be manipulated to be unique for each wire, and this unique code could be passed on to any arbitrary purchaser of the cable, and, unknown to a thief, it would be present on the wire even after burning.

The concept of having one solution mark each individual wire with a unique code is termed plurality. The technique described in detail in chapter 6 discusses how plurality is realised in the technique of electrodeposition. Briefly, the deposition current is controlled so that the presence or absence of nickel on the surface of the wire can be patterned. Furthermore, that pattern is chosen to be a "binary code" made up of "bits" where the presence of nickel over some defined length of wire represents a binary "1" and the absence (over an equivalent length) a "0". Thus a unique code can be deposited by ensuring the deposition of n successive "bits", with this code repeated over the entire length of the wire.

To effect the switching of the current with a programmed code, a microcontroller was built into the VCCS and some time was spent developing a VCCS with microcontroller interface, as the commercial versions were both too expensive and difficult to obtain. The account of this is given in section 6.2.3. Once it was shown that the nickel could successfully be deposited, the focus shifted to an important proof-of-principle - could the nickel that is claimed to be present be detected? Showing this consumed the remaining time of the project (presented in section 7) and regrettably the remaining candidate solutions were not investigated.

Chapter 2

Initial proposals for investigation

This chapter details the initial proposals, outlining the basic strategies that were to be investigated for viability for possible employment to fingerprint the wire. At the time that these were proposed, there was little known about the manufacturing of, or even the composition of the wire. As outlined in chapter 3, there are economic as well as scientific concerns and since little was known by the author of the economic aspects initially, these proposals were made largely on the potential scientific viability only.

2.1 Mechanical deformation

It was proposed that mechanical deformation of the wire could be employed, and this technique would involve controlling the cross-sectional diameter of the wire in the final stages of extrusion. A microcontroller would be used to manipulate the dimensions of the diamond die, thereby causing fluctuations in the diameter. These deliberate variations would be detectable using the sensitive capacitance measuring equipment already in place in the process. One other consideration is to reshape the die so as to bevel a groove along the side of the wire as it is extruded.

2.2 Chemical inhomogeneities (intrinsic and artificial)

Using intrinsic inhomogeneities involves using inherent variations within the concentrations of the elements comprising the wires to fingerprint them. For example, if there was, say 10 ppm of Fe in the copper in one batch, and 15 ppm in another, then that information could be used to identify the copper. This solution would require the police to intercept an alleged criminal and take some samples of copper for laboratory analysis. By checking that the concentrations of the elements in the wire taken from the alleged criminals were equal to the concentrations expected for Telkom's wire, a prosecutory case could (theoretically) be made. This was the first avenue the research took, and is documented further in section 5.2

A technique involving artificial homogeneities would employ deliberately manipulating the concentrations of the elements within the wire. For example, if Fe was found to be usually <0.1 ppm, then raising the concentration to 1 ppm would provide an order of magnitude difference for finger printing. The results of further research showed that this idea is non-viable.

2.3 Surface treatments

Surface treatment refers to deploying some chemical, such as a dye or metal, onto the surface of the individual conductors before the insulation is applied. One such treatment which is showing promise has been proposed by a company called BioCode (proposed some time after the initiation of this project). They use trace amounts of a proprietary chemical marker of large molecular mass for marking petrol. The chemical marker reacts with a detecting agent even in minuscule (in order of ppb) concentrations to prove ownership. The technology came out of a similar theft preventative need in North-Central Africa to fingerprint fuel, which was being shipped across international borders duty-free. BioCode has demonstrated their product to Telkom, but at the time of publication, no decision had been made, possibly because the large molecules upon which the solution depends have questionable heat resistance. Surface treatments seem to be the most promising of the concept categories, and electrodeposition is certainly showing strong indications of viability. One such treatment reported in chapter 6 involves the electrodeposition of some nickel onto the copper wires after they are drawn to their final diameter (section D of figure 4.1). Other forms of surface treatment to be considered were laser sputtering, where a laser evaporates a metal (such as nickel) with the copper wire nearby. The molten nickel vapour then clings and alloys to the surface of the copper. The sputtering would also occur at position D in the manufacturing process, and would also take the form of a binary code, where the presence of nickel would denote a logic “1” and the absence a “0”. Similarly, using a laser to physically burn or etch a fingerprint on the outside of the wire might also prove viable.

2.4 Doping the insulation

Each conducting wire has its own insulating coat, made of polyethylene or PVC (depending on the cable’s intended application). In either case, this coat is introduced to the surface of the wire as a molten foam, which rapidly cools and hardens into the familiar coloured plastic coat. The foam is comprised of a base, polyethylene or PVC pellets which make up 90% of the total insulation, and some “masterbatch”, which contains the specific colourant for that insulation, and makes up about 10% of the insulation by mass. Since the cables are most often burned, some sentinel element deliberately included in the insulation, such as zinc or nickel could possibly “drop out” of the insulation as the wire burns and alloy with the surface of the copper, allowing for fingerprinting. An account of this is given by Mitchell[8].

2.5 A sentinel wire

One other option is to introduce a sentinel wire, produced off-line, as the wires are collected together in units. This wire could be made of a different metal like iron, and its presence in a unit could identify the owner of the wire. An account of this technique is given by Mitchell [8].

Chapter 3

Selection of solution criteria

As mentioned before, a solution in the context of this work and field is the term used to describe the process or deliberate action that serves to “fingerprint” the wire; i.e. the wire’s owner is unambiguously identified after the implementation and later detection of the solution.

Furthermore, as before, the focus of this research is developing a solution which will facilitate the successful prosecution of an offender caught in possession of stolen copper cable, and *not* concentrate on directly preventative techniques (such as guarding cameras, padlocks on man-holes, etc.) *at all*.

There are three terms (used in various forms) used throughout this work with respect to a solution, namely uniqueness, unambiguity and plurality. Uniqueness and unambiguity are used interchangeably, and refer to the reliable identification of only one owner with a cable. A solution is considered to provide uniqueness if there is a unique owner identified by the implementation of the solution.

A solution is considered to provide plurality if the solution can be customised so that the cardinality of the set of uniquely (unambiguously) identifiable owners can be greater than unity.

By way of example, consider a solution which involved placing a single dot on the wire every 10 cm to represent Telkom as the owner. Any wire with a dot every 10 cm would uniquely be identified to Telkom *and none other*; hence considered to provide uniqueness, and interchangeably one could consider it unambiguous. However, the solution does not provide plurality, because no other company can be identified by this method. If, in an attempt to provide plurality, the description of the solution was altered so that each owner was ascribed a different symbol, e.g. Telkom was represented by a dot, and Lesotho Telecom by a square, then uniqueness would be preserved, *with* plurality provided, as more than one owner can be uniquely identified to their cable. The cardinality of the set of owners would be determined by the number of unique symbols (dot, square, triangle, cross, etc.).

If the method employed a "serial number" written onto the cable (such as binary sequence), then *whoever* bought the cable would receive the serial number (ensuring uniqueness). Plurality would be provided by the different members of the set of all permissible "serial numbers". This would be preferable to the symbol system as the final owner of the cable would need not necessarily be known *at the time of production*, as would be the case with a system using a different symbol for each different owner.

The first consideration with the method is the point in the cycle at which one wishes to intercept the stolen copper, and prosecute those caught in possession. The point in the cycle targeted depends on the solution one wishes to use to fingerprint the wire.

In most cases such as a solution employing mechanical deformation or surface treatment, you would wish to intercept the wire after it is removed from the ground (or overhead lines) and before it is smelted in the hands of the scrap metal dealers. A solution which employs the manipulation of the compositions of the wire and or insulator could probably withstand the smelting process, as the ratios would not alter with the phase change, provided the stolen wires were not mixed with genuine scrap metal, or other marked wires.

The solution would necessarily have to be unambiguous. There is no sense in developing a system which does not uniquely identify a wire with its owner, as any uncertainty would be revealed in the legal process, resulting in unsuccessful prosecutions.

A solution would have to impact on the electrical and physical characteristics of the wire no more than the electrical specifications of Cu-ETP wire (see table 4.2) would allow.

In addition to the necessary properties, there are some properties which would be preferable. Firstly, there is the consideration of detecting the solution. Consider the police finding a scrap dealer in possession of some cable which resembles the samples shown in figure 1.3. If for instance, the solution involved mechanical deformation - some sort of etching - then a police officer would be able to read directly off the cable what is etched (presumably something like "property of Telkom S.A. Ltd.") on it. Thus they could conclude ownership of the wire on site. If, however, the solution involved manipulating trace concentrations within the conductor, samples of the wire might have to be taken to a laboratory for analysis. This is undesirable, as this would take some time (a few days) to prove, and the alleged thieves would have time to "disappear"; a thief would not await the results of the laboratory analysis, and could not be detained on suspicion alone for any length of time.. Thus we see that being able to detect the solution with a minimum of time and effort is desirable.

A solution would preferably be inherently simple, with the minimum of equipment requirements. The cost of the solution must also not make the production process prohibitively expensive. There is no viability in a solution which costs more than simply replacing the wire despite the labour costs and losses due to loss of custom. Obviously, the cheaper it is to implement, the better.

If some solution allows for variations which allow plurality, then that solution would be preferable since the technology could be sold to competing telecommunications company to mark their wire with the same system, recovering research costs, and perhaps defraying the costs of the wires stolen previously. A simple method for providing plurality is producing a serial code to act as a "fingerprint". Each serial code is unique (uniquely identifying an owner) and the code provides plurality since each cable would have its unique serial code, independent of whether Telkom, Lesotho Telecom, Bel-Atlantic etc. bought the cable.

For reference purposes, the solution properties are listed below. Any viable solution would *necessarily* have to be

- **N.1** fire-proof
- **N.2** unambiguous - each fingerprint must be unique
- **N.3** legally admissible.
- **N.4** unobtrusive in the existing production systems so it can be disabled easily when not desired, and acceptable to the manufacturers

- **N.5** acceptable electrical and physical characteristics after treatment
- **N.6** economically viable - the solution must not make production costs prohibitive.

A viable solution would *preferably* have the following desirable properties

- **P.1** be detectable in the field (i.e. out of a laboratory)
- **P.2** be as easily and inexpensively implementable as possible
- **P.3** provide plurality, possibly through a form of serial code.

Chapter 4

About the Copper, from mining to final product specification

4.1 The manufacturing process

At the outset, knowing the composition of the copper was deemed crucial to understanding the nature of the wire, and (as described on page 10) in determining whether there was a viable solution in intrinsic and artificial homogeneity. A research trip to Phalaborwa Mining Company (PMC) was made to obtain data on the composition of the raw materials from which wire is produced, and the processing of the ore was studied as part of the investigation into methodical manipulation of the composition.

4.1.1 Process the copper-yielding ore

The production is as follows:

STAGE 1 The ore is crushed, milled, separated and hydro-separated, thickened and dried to create what is called Concentrate ($\simeq$35% copper). This process is complicated, and much of the detail is omitted. This is introduced to STAGE 2 as Raw Material. The tailings (mostly gange minerals) from this process are sold to a phosphate mine adjacent to PMC.

STAGE 2 The Reverberatory [1] furnace accepts the (moist) concentrate and fuses

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[1] The reverberatory furnace is the first furnace in which the ore is smelted. It “is a large, rectangular refractory lined furnace fired by pulverised coal”, taken verbatim from the technical documents issued by PMC.

it to produce a “matte” of about 50% Cu. Silicon (Si) is introduced to reduce the melting temperature and help separate the Lithophile elements, which combine to form Silicates. The furnace is maintained at $\simeq$1600 Celsius and pure oxygen forced in to help with the oxidation. The majority of the matte is made up of CuS and FeS, as well as some precious metal traces. The rest is termed Slag and is an environmentally stable[2] substance that is discarded, and is comprised chiefly of oxides (and Silicates) of Fe, Si, Ca, Mg and Al. The matte and slag have significantly different densities, and thus good separation is achieved in the reverberatory bath. Four tap-holes allow the matte to be tapped off to the Converters where the primary chemical process is one of oxidation with air (the air is “blown” in).

The air oxidises the FeS to FeO. SO_2 is the byproduct, which convects up the stack where it is “cleaned” in an electrostatic precipitator before going to the chemical plant to be converted into H_2SO_4. The FeO combines with more Silica to form Iron Silicate Slag, which is periodically removed and reintroduced into the Reverberatory for Cu recovery. A similar process follows for the CuS, which becomes CuO and SO_2. The excess heat of reaction from the oxidation of copper and iron allows frozen reverts and refinery scrap to be re-introduced and melted in the converters.

The copper is conveyed in large bucket-like containers from the Converter to the Anode Furnace where the final CuS is oxidised and a process of “poling” is employed. Poling is the injection of liquid hydrocarbon e.g. propanol into the copper to remove the (dissolved) oxygen. The copper is now said to be fully fire refined. It is $\simeq$99.5% pure and is cast into “Anode Mould” ($\simeq$350kg) which are suitable for the electrolytic refining in STAGE 3.

STAGE 3 The Anodes from STAGE 2 are put into an electrolytic bath in an Anode-Cathode, Anode-Cathode etc. format. The cathodes start as fine sheets or “seeds” of pure copper upon which the copper from the anode deposits. PMC’s electrolysis battery includes 24 sections of 40 cells each. As the current passes through the electrolyte, the copper dissolves off the anode into solution and plates out onto the cathode with the ultimate purity. It takes approximately 10 days for one 350 kg cathode mould to fully form. The current flowing through the electrolyte ranges up to 16 kA.

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[2] Industrial term for substances that are not toxic, and do not leech toxins into the environment over time.

STAGE 4 The cathodes are re-smelted and cast in a continuously revolving "continuous cast" wheel. Upon completing one revolution of the wheel, the copper is solid, but still red hot. It is immediately rolled into rod, the final diameter of the rod dependent on the intended recipient. The rod produced by PMC is the *sole source of raw material for the cable producers in South Africa.* A description, with photographs, of a very similar company's production system is available at `http://www.kennecott.com/copper.html`. An overview is given on page 76.

4.1.2 Extruding the wire from rod and application of insulation

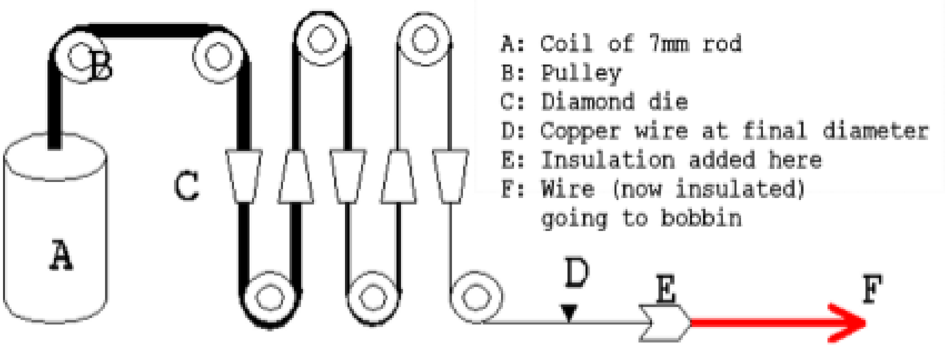

Figure 4.1: A schematic overview of the extrusion process, where the input 7 mm (or 3 mm) rod is drawn down to the final diameter and coated with insulator.

A cable manufacturer (the major manufacturers in South Africa for Telkom are Aberdare and ATC) receives Cathodic Grade A Copper (the copper used to make copper wire as specified by the London Metal Exchange [2]) in the form of a 7 mm or 3 mm rod (represented by A in figure 4.1), and the process commences with the extrusion of the rod through consecutive diamond dies (represented by C in figure 4.1) of decreasing diameter until the ultimate desired diameter (e.g. 0.5 mm) is achieved. As the diameter of the rod approaches the final value, the wire moves faster, since an equal volumes of copper per unit time must pass through all the dies, which are progressively narrower in diameter, with the latter stages moving at approximately 40 m/s.

Following the extrusion, the wire is annealed using a high current to heat the wire (no representation in the figure), passed through an aperture where a specially pigmented (red, green, white etc.) molten foam is introduced. The temperature of the wire is brought as close to the temperature of the molten insulation as possible. This molten foam is water-cooled (for consistency which avoids weaknesses in the final product) over a distance of about 10 m, and hardens, thereby clinging to the surface to act as insulator (represented by E in figure 4.1).

The completely insulated wire is rolled onto a bobbin. The insulated wires are then pulled off the bobbins and combined into twisted pairs; a collection of 10 twisted pairs (or 20 conductors) being termed a unit. Units are in turn combined to form a cable with an appropriate number of pairs (ranging from 10 to 2400 pairs); the final binding being the PVC or polyethylene (for outdoor and indoor applications respectively) sheath. The combined units are set in a petroleum jelly for further water-proofing, and there is an optional inner sheath of aluminium (for the larger cables) providing physical and electrical shielding for the conductors. There is often some wax paper to provide a watertight barrier between the aluminium sheath and the final outer coating of PVC or polyethylene.

The manufacturers do not only supply one Telecommunications Company, and thus any addition to the manufacturing process would have to be configurable for easy enabling, disabling and customisation in accordance with property N.4 (see page 14.

4.2 Copper cable composition and specification

4.2.1 The physical wire

The London Metals Exchange (LME) specifies cathodic grade A copper as containing no more that 0.0065% in total by mass of elements other than copper and oxygen [2]. The specification is general to account for the different ores from which the copper is extracted, allowing for many different impurities and groups of impurities with various maxima. Most companies characterise their copper by declaring a typical assay, and the data produced by PMC is shown in table 4.1.

PMC sample their cathodes in compliance with ISO 9001, and analyse their cathodic copper with 2 methods. To detect for As, Se and Te and S, ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) is used. It is very sensitive, and the limits of detection are in the region of 0.2, 0.02 and 0.01 ppb, for As, Se and Te respectively. There is variation in the detected concentration of these three elements within the cathodic copper. 5 different cathodes each day (according to a schedule) are sampled. Each cathode (approximately 350 kg, and 0.5 m × 0.5 m × 10 cm thick) is sampled 5 times, the samples taken diagonally across the cathode) and sent for analysis to the mine laboratory. Despite variations of up to 100 ppb within any one cathode, the concentration of any one of these three elements very rarely approaches 0.1 ppm. The concentration of sulphur is also determined with $NaBH_4$, and this concentration (for the copper produced by PMC) varies between 5 and 7 ppm.

The remaining elements with the exception of oxygen, mainly metals, are analysed using SAFT (Spark Analysis For Traces), a technique which employs emission spectrometry to determine the elemental concentrations. The detection limits for SAFT are closer to 1 ppm, this concentration corresponding to the minimum for which 99% confidence can be satisfied. Thus when the detection score fails to meet the 99% confidence mark, the element in question is said to have a concentration of less than 1 ppm. This most often satisfies the requirements of LME grade A cathodic copper. Silver often has concentrations above the detection limits of the machine, and as presented in table 4.1, has concentrations which vary between 6 and 10 ppm.

As part of the study into the homogeneity of the wires, samples of the 3 mm raw material rod were collected from Aberdare cables, Port Elizabeth to have their

	Typical Assay	Max. [Min for Cu]	
	Conc. in ppm [% for Copper]		
Element	**PMC rolled rod**	**Grade A**	**Cu-ETP**
Copper	>99.95%	99.95%	99.90%
Bismuth	<0.5	<2	0.2
Selenium	<0.5	<2	0.2
Tellurium	<0.5	<2	0.2
Group	–	<3	–
Arsenic	<0.5	<5	0.5
Cadmium	–	–	–
Chromium	–	–	–
Manganese	–	–	–
Phosphorous	–	–	–
Antimony	<1	<4	–
Group	–	<15	–
Lead	<1	<5	5
Sulphur	5 to 7	<15	–
Cobalt	<1	–	–
Iron	<1	<10	–
Nickel	<1	–	–
Silicon	–	–	–
Tin	–	–	–
Zinc	–	–	–
Group	–	<20	–
Silver	6 to 10	<25	–
Oxygen	300-340	<400	200-400

Table 4.1: Typical assay produced by PMC, the sole supplier of copper to the South African cable manufacturers, is tabulated against the LME spec for Grade A cathodic copper and electrolytic tough pitch copper (Cu-ETP), the copper traditionally used for cabling. PMC data is dated 7th January 1999. Other data taken from [2] and [9].

compositions measured by electron microprobe at the Department of Geology at Rhodes University. For this investigation, 3 samples of 3 mm raw material rod were taken. The three were chosen from 3 separate coils of rod, to investigate the variation within and between coils or “batches” of copper. 10 smaller samples, each about 3 mm long and 3 mm diameter, were taken from each of the 3 rods, and the 30 samples were mounted in araldite cylinders with the samples flush with the bottom side of the cylinders. The cylinders were then polished with progressively finer abrasive media until the surface of the samples was considered smooth enough for electron microscopy to take place, in this case the final grain size used was 1 micron. The araldite cylinders containing the 30 samples were coated with 250 nm of carbon, which is evaporated onto the samples in near vacuum conditions. This thin carbon layer prevent the buildup of charge on the samples. Eight elements were selected for analysis based on their assumed probability of their occurrence copper bearing ore. It was thought that their presence in the ore would result in their inclusion in the final product. However, had more been known about the processing of the ore at the time this experiment was performed, analysis for sulphur and oxygen would have been performed, as these two elements are included in the copper largely by the refinement process. These elements were copper, iron, gold, arsenic, selenium, silver, antimony and cadmium.

The equipment used to perform the analysis was a JEOL 733 superprobe, with an acceleration voltage of 20 kV, and a mean current beam of 40 nA. The standards used for this experiment were copper metal (for determining the concentration of copper), iron metal (for the concentration of iron),gold metal (for the concentration of gold), palladium arsenide (for the concentration of arsenic), silver bismuth selenide (for the concentration of silver and selenium). palladium antimonide (for the concentration of antimony), and cadmium metal (for the concentration of cadmium). Had the expected composition been known at the time of this experiment, sulphur would have been included. The counting time was 200 s (100 seconds “on-peak”, and 50 seconds either side “off-peak”).

The results are shown in figure 4.2. We see from the data in Appendix C that four of the elements (namely iron, selenium, antimony and cadmium) are *never* successfully detected above their specific detection limits. The concentrations were normalised to their respective fractions of the total detected matter. Upon reflection, the absence of analysis for sulphur and oxygen and possibly nickel render these figures good for qualitative reasoning only. Gold, silver and arsenic are only sporadically detected above their detection limits. Copper is obviously detected every sample, but of the 23 points analysed, 7 were discarded for machine error, leaving 17. Arsenic was successfully detected 16 times, with gold and silver detected 5 and 2 times respectively. One important finding of this work is that the trace elements do not occur homogenously throughout the wire (see the data in appendix C). There are instances where the elements have surprisingly high concentrations, and other instances where they are seemingly entirely absent. This inhomogeneous distribution of impurities would have to be considered in any technique employing the inhomogeneities and artificial manipulations of them. Proving that the measured concentrations are equal to the expected concentrations would be complicated by the unreliable distribution of the impurities.

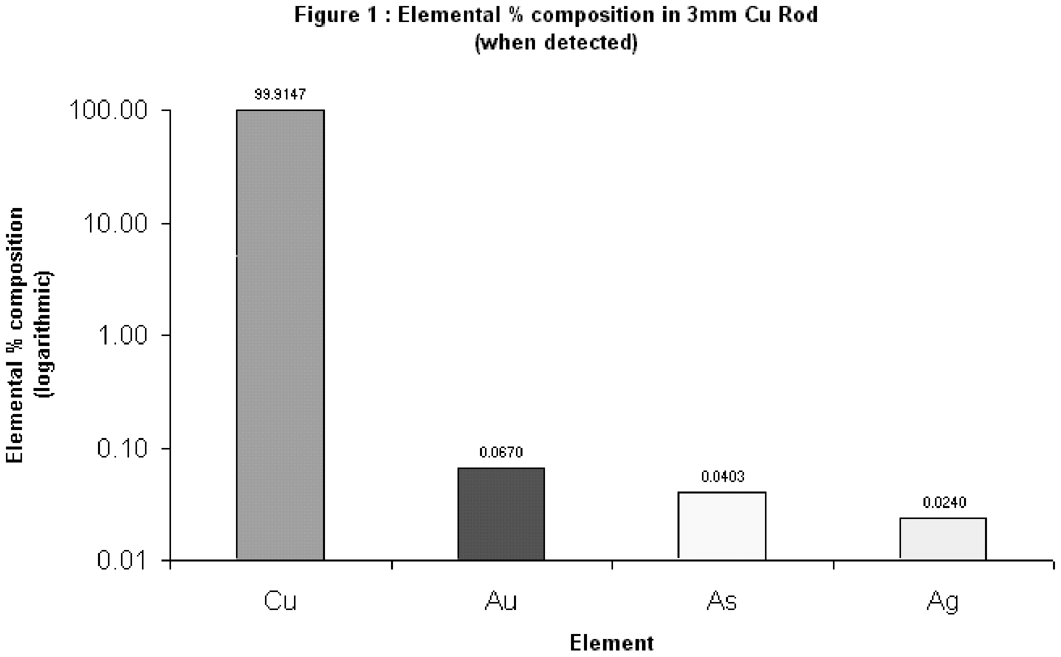

Figure 4.2: Normalised average composition of 3 mm copper rod supplied by Aberdare Telecomms. Note that the elements were not *all* detected in *every* sample, and the averages are only of the instances were the elements actually detected with 99% confidence. The concentrations are normalised to their partial fraction of the total detected matter, and thus are only qualitatively important. The data, together with the detection limits are given in Appendix C.

Electrical characteristics of the wire are listed in table 4.2.

Conductor Diameter [mm]	0.32	0.40	0.5	0.63	0.90
Resistance max ave. [Ω/km]	223	143	91	58	28
Mutual Capacitance max. ave [nF/km]	45 - 59				
Capacitance unbalance max. [pF/500m]	275				
Insulation resistance min. [MΩ/km]	1500				

Table 4.2: Characteristics of the individual conductors taken from http://www.aberdare.co.za, issued August 2000.

Electrical Property	**Typical Value**	**Unit**	**Test Method**
Dielectric constant (50Hz)	$\leq$2.3	-	IEC 60250
Dissipation factor (50Hz)	$\leq$0.0005%	-	IEC 60250
DC Volume Resistivity	$\geq 10^{16}$	Ωcm	IEC 60093
Dielectric Strength	>22	kV/mm	IEC 60243

Table 4.3: The electrical properties of the insulation, taken from http://www.aberdare.co.za. These values are typical to Aberdare and are superior in most respects to the specification. For more on the test method, see http://www.ptli.com/testlopedia/tests/D150Dielectric.asp

4.2.2 The insulation

The insulation of the wire is comprised of either PVC or polyethylene, depending on its intended use. Wires intended for external use are more often coated with PVC, and polyethylene is preferred for indoor applications.

One of the proposed marking techniques involved introducing sentinel contaminants into the insulator molten foam mix, so that they are included in the insulation and could possibly be detected even after the copper is stolen and burned, as the contaminants would (in theory) alloy with the surface of the copper as it is burned.

Introducing sentinel contaminants into the insulation would potentially alter the electrical and physical characteristics, and any solution employing sentinel contaminants would necessarily have to take these into account. The values typical to insulation produced by Aberdare are given in table 4.3, and typical physical properties of the polyethylene insulation are given in table 4.4. It is interesting to note that the insulation must be capable of elongating a minimum of 200% of its length, and also that it must possess the capability to return to its original dimensions (to within 15%).

To determine a little more about the insulation, two experiments were performed.

Physical Property	**ATN**†	**Spec.**	**Unit**	**Test Method**
Density (mixture 95% pellet, 5% masterbatch)	923		kg/m^3	ISO1872-2-B or ISO1183-D
Melt Flow Rate (190C, 2.16 kg)	0.9		g/10 min	ISO1133
Tensile Strength‡	$\geq$15	>12.5	MPa	ISO527
Elongation (250mm/min)	$\geq$300	$\geq$200	%	ISO527
ΔTensile properties*	$\leq$25		%	IEC60811-1-2
Hot Set Test (200C, 0.20MPa)				
Elongation under load	60	$\leq$175	%	IEC60811-2-1
Permanent deformation	0	$\leq$15	%	IEC60811-2-1
ESCR (50C, 10% lgepal),F_{20}	$\geq$96		h	IEC60811-3-1/B
Durometer Hardness (1sec)	52		ShoreD	ISO868
Brittleness Temperature	<-76		C	ASTM D 746

Table 4.4: Physical characteristics of the individual insulators, taken from Aberdare Telecom Networks http://www.aberdare.co.za, issued August 2000. Where possible, the specification has been included too. ATN† = Aberdare Telecom Networks typical value. ‡(250mm/min). *after ageing 240h @ 135C.

The first was Differential Scanning Calorimetry (DSC), performed using a Perkin-Elmer DSC 7 with aluminium pans, interfaced to a P.C. through a Perkin-Elmer TAC 7/3 instrument controller. The principal idea behind DSC is that the sample (in this case a 2.466 mg sample of blue insulation, stripped from the wire) is placed in a pan enclosed within the machine. The atmosphere surrounding the pan is controlled both in composition (the gas of the user's choice is pumped through the machine) and temperature. Typically, the temperature of the atmosphere is controlled through a range and the temperature of a reference sample (known to *not* undergo a phase change in the selected temperature range) is at all times compared with the temperature of the sample. The difference between these two temperatures (the temperature of the standard and the temperature of the sample) is recorded, as the atmospheric temperature ranges through the program selected by the user. In this experiment, the temperature was controlled from 25 degrees Celsius to 500 degrees Celsius and back to 25 at a rate of 10 degrees Centigrade per minute. The difference in temperature between the standard and the sample is converted to a heat-flow in mW and plotted against the temperature, as can be seen in figure 4.3.

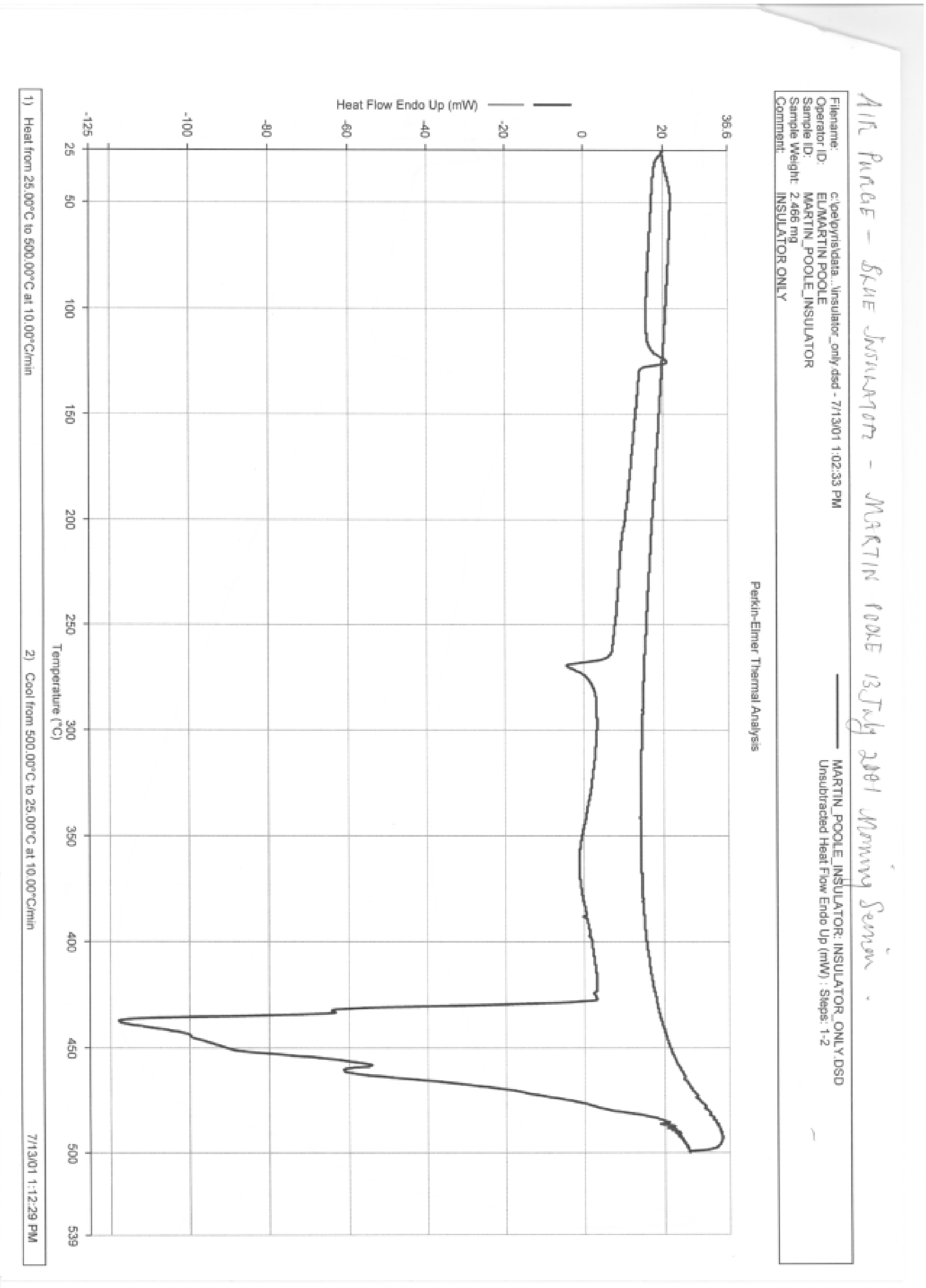

Figure 4.3: Results of Differential Scanning Calorimetry (performed in the Chemistry department at Rhodes University) on a sample of blue polyethylene-coated wire, purged with O_2 gas. The energy released as the insulation burns can be clearly seen beginning at around 120 Celsius, and peaking near 140 degrees Celsius.

Other features to notice on the graph is that some byproduct of the burning is changing phase (probably re-solidifying) at around 260 centigrade. DSC indicates whether energy is being differentially absorbed or released, and to conclude that evaporation, for example, is *definitely* taking place, one needs to perform Thermogravimetric (TG) analysis.

The principle of TG is that, in a similar manner to DSC, the sample is subjected to a controlled temperature program, but the mass of the sample is constantly recorded throughout the controlled temperature range. For this experiment, the sample was subjected to a range from 25 Celsius to 700 Celsius also at a rate of 10 degree per minute. The sample pan is connected to a sensitive microbalance to facilitate the constant mass measurement. The proportion of the initial sample remaining, represented by a percentage, is plotted against the temperature.

Interestingly, an individual (1.175 mg) sample of insulation from a 0.4 mm wire, separated from the wire, completely evaporates in the TG environment at approximately 420 degrees, as evidenced by the TG shown in figure 4.4. The TG was performed using a Perkin-Elmer TGA 7 interfaced to a standard P.C. through a Perkin-Elmer TAC 7/3 instrument controller. This was performed in the department of Chemistry at Rhodes University. No special care to clean the insulation was undertaken as the conditions under which it is usually burned (i.e. 200 m from a manhole and in great haste) has no similar care.

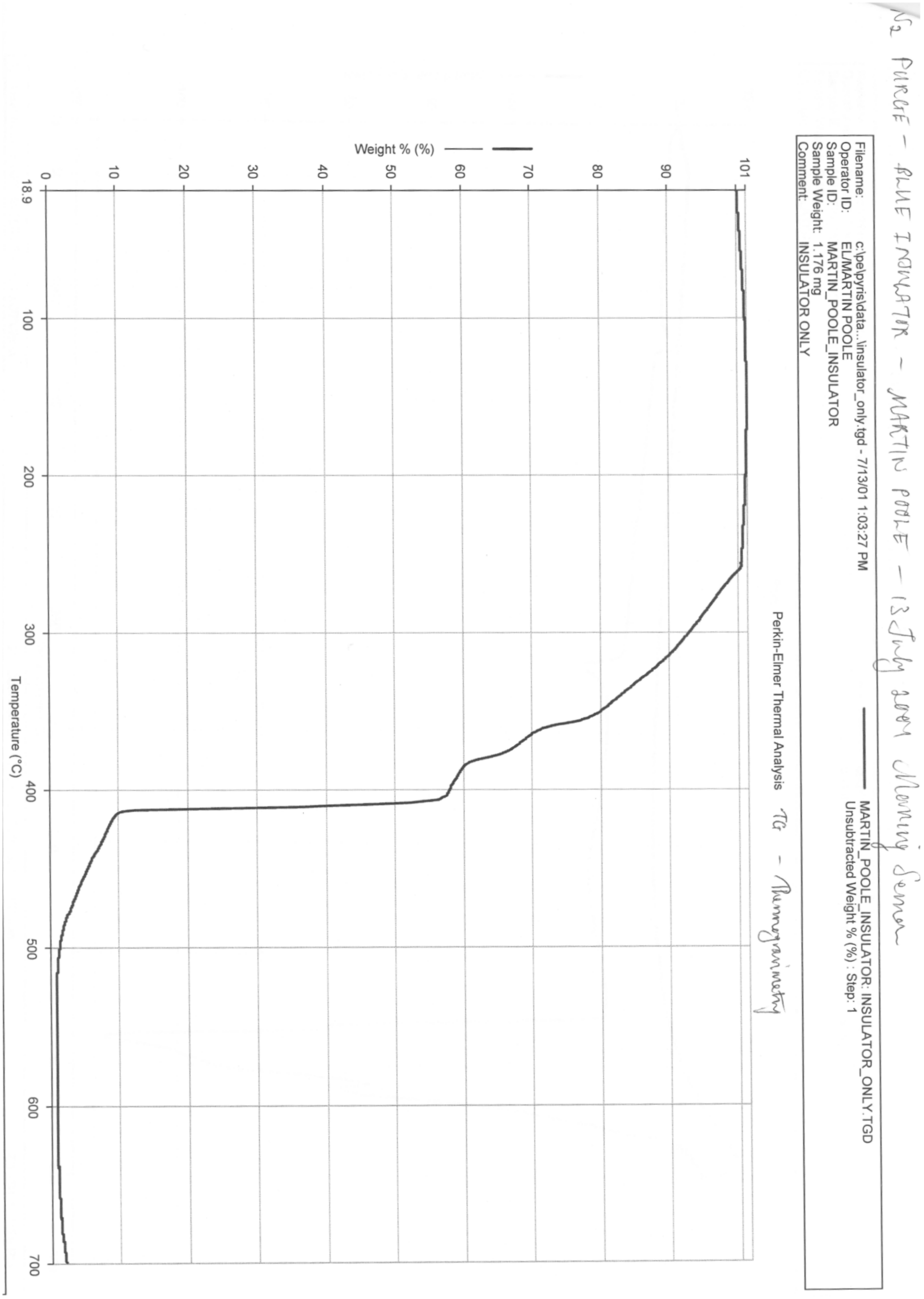

Figure 4.4: Results of Thermogravimetry (performed in the Chemistry Department of Rhodes University) on a 1.175 mg sample of blue insulation, with a N_2 gas purge. Quite clearly, the mass of the sample is evaporating from about 280 degrees Celsius onwards, and has completely evaporated by 520 Celsius.

Chapter 5

Non-viable solutions

This chapter concerns the results of the research that led to certain solutions being deemed non-viable. This chapter does not concern itself with the solutions which were not investigated, such as the sentinel wire. One would expect that much of the data accumulated during the research period would be presented here as evidence of the non-viability. However, the proposals were made before anything was known about the production process and composition of the wire, thus much of the evidence has already been presented in chapter 4, which deals with the composition of the wire, the composition of the insulation and the manufacturing process. That information is referred to when necessary, but not repeated.

5.1 Mechanical deformation

Mechanical deformation was the first considered method. However, after investigating the production process, where it was revealed that the wires are very thin and extruded at rates approximately 40 m/s, it was decided that the mechanical stresses and strains on the wire are sufficiently high that the risk of snapping the wires would be too great. The complexity of any solution employed here would be extreme if it were possible at all, and so the idea was set aside. The manufacturers have acknowledged that it would be possible to implement a groove by modifying the shape of the last of the diamond die. This would cause a groove that would be present on the entire length of the wire, and that the presence of this would identify the wire. This is disadvantageous because the cables containing those wires would have to be specifically set aside for Telkom.

Furthermore, the technique would have little scope for plurality or customisation, as any modified die would have to retain its shape constantly throughout the time that the wire in question is being produced (called a “run”). This would imply that to achieve plurality of the method, many dies with different shapes would have to be designed and built, with replacements as attrition of the part occurs.

5.2 Inhomogeneity - intrinsic and artificial

5.2.1 Intrinsic inhomogeneity

One of the first branches of the investigation was to see whether there is any intrinsic inhomogeneity within and between “batches” of raw material which would provide a unique fingerprint for the batch of wire. This proposal was made at a time when nothing was known about the composition of the wires, or of the manufacturing process. Preliminary electron microscopy (see figure 4.2) showed that the purity of the copper is such that non-copper elements, when detectable, were in sufficiently low concentrations that no field device would have detection limits suitable for this task; thus the intrinsic inhomogeneities solution was eliminated and this implies that chemical composition can not be readily employed to identify copper wire already produced.

5.2.2 Artificial inhomogeneity

This central idea to this technique is artificially enhancing the concentrations of the non-copper elements (henceforth referred to as impurities) within the wire *before* the wire is extruded into its final shape. The investigation was to determine whether it would be possible to deliberately and methodically raise the concentrations of the impurities so that they could be later detected and proved to be different from wire that had not had its concentration altered. Since Palaborwa Mining Company (PMC) sells its product to the cabling companies as pre-rolled rod or ingots, the manipulations would have to take place somewhere in the production of the ingots process outlined in section 4.1.1. Assays of typical copper produced by PMC were analysed (see section 4.2.1), yielding the conclusion that any contaminant would have to be a non-metal element because the trace metals present had concentrations near to the maximum specified (See figure 4.1 on page 21).

There are some concerns associated with the addition of impurities. Data describing the detrimental effect on the resistivity of the cathodic copper due to increasing levels of impurities is already available. It is repeated here in figure 5.1. Firstly, the addition of impurities must not cause the upper limits of concentration, prescribed by the LME specification (see figure 4.1), for the groups of non-copper elements as well as the individual elemental limits to be exceeded. There has been an investigation into wire breakage in wires of various diameters, where over 2500 wire samples were analysed using SEM[5]. Here it is revealed how the vast majority (>90%) of wire breaks (in 0.1 mm wire) were directly ascribed to impurities in the metal lattice. Certain elements have been identified as deleterious to the wire drawing process. Bismuth, Tellurium and Selenium are listed has having a severe effect on wire drawing,

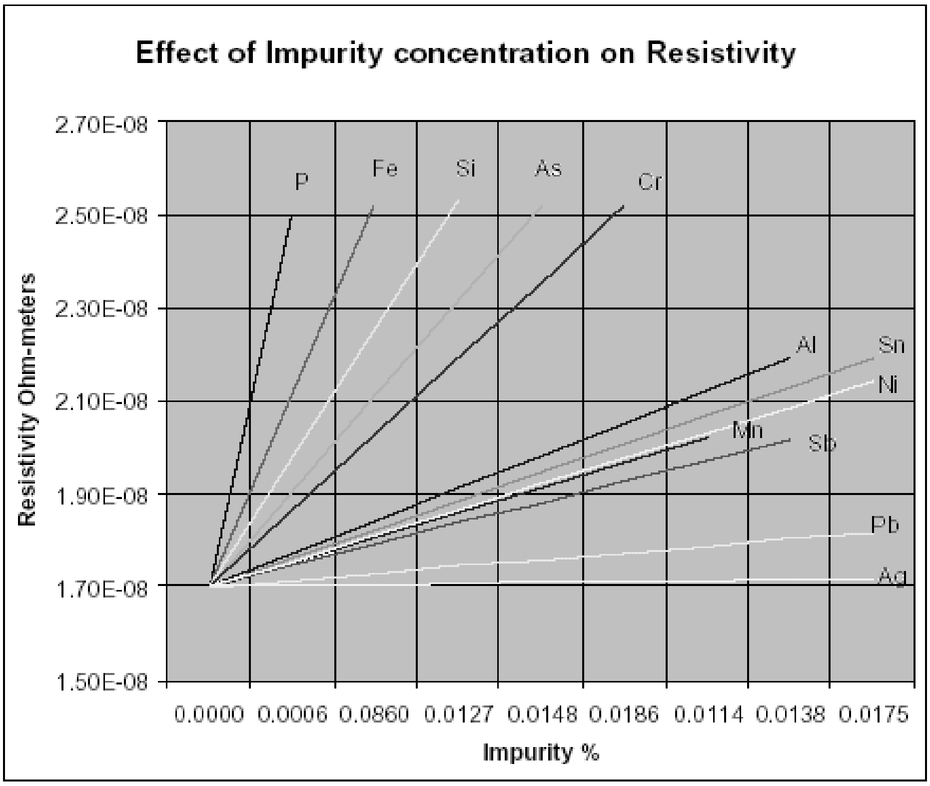

Figure 5.1: Data showing the effect of various impurities on the resistivity of the copper wire. This data taken from Sales information of Rautomead International Ltd. [7]

as they cause grain boundary cracks where they occur in the copper matrix. Lead, Silver, Sulphur and Antimony are thought to have a medium deleterious effect, while Chrome, Iron, Tin, Phosphorous, Silicon and Silver have a mild effect - only harming annealability of the wire[9]. It is also reported in the same article that the refinement process is being updated, using graphite vessels (graphite is said to be unreactive at the temperature of the molten copper) and avoiding any rolling (during which steel becomes incorporated into the copper[9]). The intention of these measures is to minimise these break-causing impurities, so research into elevating the concentration of impurities to facilitate fingerprinting would be contrary to the current industrial trend.

In conclusion, despite the concentrations of the non-metal impurities being more than one order of magnitude lower than the maximum specified, any attempt to augment these impurities could result in

- reduction of the company's copper value
- serious modification to the existing industrial system (in violation of property N.4)
- difficulty with
    - controlling homogeneity of impurities (avoiding "clumping")
    - recording and tracing the correspondence between chemical impurity and product (preference P.2)
    - copper wire having poorer electrical characteristics
    - toxicity of candidate impurities, e.g. Arsenic is toxic
    - designing field test equipment (preference P.1)
    - increased wire breakage.

This attempted solution has proven to be a case of possible scientific viability (and as we have shown even the scientific viability is ultimately minimal), but very little practical viability since the laboratory processes required to detect the elevated concentrations are in conflict with property P.1 (see page 12.

Thus it is the opinion of the author that exploiting inhomogeneity in any form is firstly not advisable, and secondly not viable.

Chapter 6

Electrodeposition - a viable solution?

6.1 Electrodeposition theory

When a current is passed through an electrolytic solution[1] cations are reduced at the cathode to form neutral metal atoms. The rate at which this happens obeys Faraday's Law. These reduced and now uncharged metal atoms adhere or "plate" onto the cathode; a process called electrodeposition. There is a mathematical description of the deposition in the following section, with a more comprehensive and particular description of the deposition process.

It is the intention of this technique to treat the copper wire as the cathode, and constructing apparatus such that an anode, raised in electric potential (so as to effect a current) with respect to the cathode, together with the wire (cathode) are present in a nickel-rich electrolytic solution. The solution employed thus far is prepared by dissolving nickel chloride in distilled water (see subsection 6.2.2). A current is to flow between the anode and the cathode so that the nickel in the solution is reduced to form nickel metal, which plates onto the wire, and this is discussed further in the next section.

It is the presence of this nickel on the wire which provides the unique fingerprint.

In what follows in the subsequent sections, we reveal how this technique has been implemented, and expanded to facilitate plurality.

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[1] a solution containing anions and cations

Nickel differs from copper in one particularly useful way in that it is ferromagnetic, whereas copper is paramagnetic. In short, this means nickel can be magnetised, and copper cannot. Thus, to detect the nickel coating, one can simply apply a magnetic field to the wire under test, and afterwards, measure if there is any residual magnetic field with suitable instruments. This is discussed further in section 7. If one successfully detects a residual magnetic field, then one can conclude that nickel is present, and therefore conclude that the wire is one that was deliberately marked.

6.2 Achieving deposition

The electrodeposition theory mentioned above is adapted to clad the wire with nickel in the following way (figure 6.1 refers). The physical wire currently en route from extrusion to acquiring insulation is to act as the cathode. This corresponds to point D in the extrusion process (figure 4.1 on page 18), and this point is chosen for the electrodeposition because the wire is at its ultimate diameter and has yet to receive insulation. There is a distance of about 10 m between the last pulley of the extrusion process and the annealing prior to the application of insulation, and this provides sufficient area to install the necessary apparatus.

The wire is inherently grounded because the metallic pulleys that constrain the wire (providing good electrical contact by that constraint) are attached to the metallic chassis of the machine performing the extrusion, which is in turn electrically grounded for safety reasons.

An electric pump[2] is immersed in approximately 3 ℓ of electrolyte contained within a cylindrical glass tank of diameter 30 cm and height 10 cm. The pump impels the electrolyte from the tank up a pipe of diameter 1 cm, around to a position 1 cm directly above the wire. Affixed to the output of the pipe is an inert[3] anode which must also make proper electrical contact with the electrolyte to facilitate current flow. The electrolyte is passed through a “nozzle” shaped to be a rectangular slit, the long axis of which is orientated in the plane of the cross-section of the wire. The plane of the rectangular exit of the nozzle is parallel to the surface of the copper wire, and as

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[2] the pump used in this work was a RESUN SP-1100 8 Watt submersible pump commonly used in aquatic tanks and water features

[3] An anode made of nickel could also be used, but as the nickel erodes into the solution, the geometry of the remaining nickel anode would potentially change

mentioned before, is located approximately 1 cm above the wire. For the experiments carried out in the laboratory, the slit has length $l_1 = 1$ cm long width $w_1 = 1$ mm[4]. The electrolyte is thus constrained to precipitate back into the tank, flowing over the wire and hence making good electrical contact, in the shape of a thin veil or sheet of cross-sectional dimensions 1 cm (l_1) by 1 mm (w_1). Connecting a current source between the anode and cathode causes conventional current to flow from the anode to the cathode, and the result is electrodeposition of nickel on the wire (cathode) at a rate principally determined by the current provided by the current source.

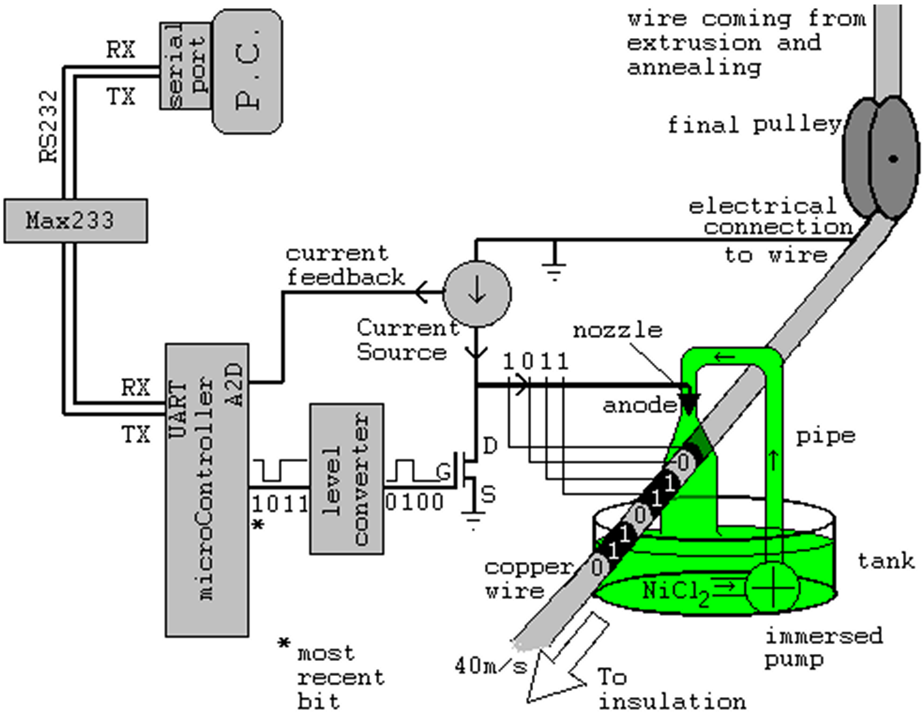

Figure 6.1: A representation of how the prototype plating takes place. The microcontroller switches the current flow by controlling the MOSFET. When the MOSFET is ON the current is shunted to earth, and when OFF the current passes through the $NiCl_2$ causing plating on the wire. The copper wire is earthed inherently through the pulleys attached to the extrusion machine. The microcontroller (Atmel At90S8535) monitors the current source's output current via its analogue to digital converter (A2D) and relays information to the P.C..

To achieve plurality, each individual wire that is produced is assigned a unique binary number (bar-code). Since the plating will only occur when the current is

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[4] See subsection 6.2.1 for more on the importance of this geometry

flowing through the electrolyte, “bits” are set by either applying the current or withholding it as the wire passes. To withhold the current from the solution so that no electroplating takes place, a MOSFET in parallel with the anode-electrolyte-cathode current path “shorts” the current to ground[5]. Through suitable toggling of the MOSFET, the wire (of diameter d) is plated with an n-bit code (allowing for 2^n distinct “fingerprints”), repeated over the entire length of the wire every ℓ metres. Figure 6.2 shows one complete 10 bit pattern (not drawn to scale). A mathematical description of the electrodeposition technique follows. These assumptions are made:

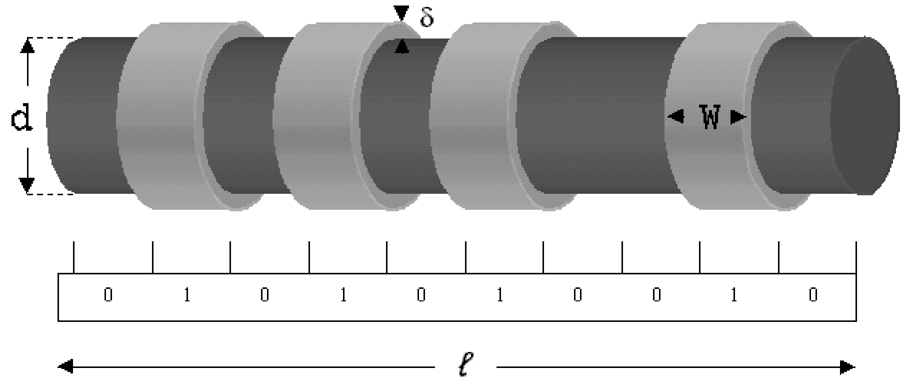

Figure 6.2: A representation of an arbitrary 10 bit sequence. The darker gray represents the copper wire of diameter d, the lighter grey represents the nickel plating of thickness δ. In practice there will probably have to be some “start” and “stop” bits to enable reading of the code - this figure is by way of example only.

- The “bits” are cylindrically symmetrical
- The electroplating is uniform
- There will be no electroless[6] plating when there is no current flowing between anode and cathode

For a given thickness δ of nickel, the volume V of a bit, which is a hollow cylinder of inner diameter d, outer diameter of $d + 2\delta$, and length given by the “bit-width” $w = \ell/n$) is

$$V = \pi[(d/2+\delta)^2 - (d/2)^2]w = \pi[\delta^2 + d\delta]w \qquad [\mathtt{m}^3] \tag{6.1}$$

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[5] The how and why of this is presented in section 6.2.4

[6] “Electroless plating uses a redox reaction to deposit metal on an object without the passage of an electric current.”[12]

But, since $d\delta \gg \delta^2$ (for a 0.6 mm wire, $d\delta \approx 10^6 \times \delta^2$) we can ignore the δ^2 term and say

$$V = \pi \times d \times \delta \times w \tag{6.2}$$

The number of nickel atoms is given by

$$N_{Ni} = \frac{\rho V}{M_{Ni}} N_A = 9.125 \times 10^{28} \times V \tag{6.3}$$

where ρ is the density of Ni metal, taken to be 8908 kg/m^3[16],

M_{Ni} is the molar mass of Ni, taken to be
58.693×10^{-3} kg/mol[17]

N_A is Avogadro's number, 6.023×10^{23} mol^{-1}

The charge of one electron, q_e is 1.602×10^{-19} coulomb. Each deposited atom requires 2 electrons, so the charge required per unit volume of nickel deposit is

$$Q = 2 \times N_{Ni} \times q_e = 2.924 \times 10^{10} \ \ \texttt{[C/m}^3\texttt{]} \tag{6.4}$$

Each bit must be plated over a time

$$\tau = \frac{w}{v} \tag{6.5}$$

seconds, where v is the velocity of the wire. This means the required average plating current, assuming 95% cathodic efficiency [10] is given by

$$I = \frac{Q}{\tau \times 0.95} \times V. \quad \text{[A]} \tag{6.6}$$

Substituting V in from (6.2), and finally recalling $\tau = \frac{w}{v}$

$$I = \frac{Q \times v \times V}{w \times 0.95} = \kappa \times v \times d \times \delta \quad \text{[A]} \tag{6.7}$$

where κ has a constant value of 9.7×10^{10} C/m^3.

$$I = \kappa \times v \times d \times \delta \quad \text{[A]} \tag{6.8}$$

The period τ of each bit is given by $\frac{w}{v} = \frac{\ell}{nv}$ which for $n = 64$ bits, $\ell = 1$ m and $v =$ 40 m/s is approximately 260 μs. This means the current will have to be switched at a frequency ("bit-rate") of 3846 s^{-1}.

For an example example, let us assume an infinitely long wire travelling through the apparatus described above. If we wished to write the code 101..010 (all n bits alternately 1 and 0) onto the wire, we would have the microcontroller produce a square wave of period $T_{sq} = 2 \times \tau$ indefinitely. Every τ seconds, the state of the MOSFET would toggle, alternately allowing and withholding the current required for plating to occur.

6.2.1 The geometry of the nozzle

The electrolyte is constrained to flow in the form of a sheet of fluid transverse to the motion of the wire, because the thickness of the sheet of electrolyte determines the "sharpness" of the edges of the physical nickel bits. To see this, remember that the thickness of the plating at any position on the wire is proportional to the time that position on the wire is exposed to the current flowing through the electrolyte. Consider figure 6.3.

The current density in the electrolyte is given by $I_d = \frac{I(t)}{A_1}$ A/m^2, where A_1 is the surface area over which the plating occurs. We assumed the plating is cylindrically symmetrical, so A_1 is given by

$$A_1 = \pi \times (d + 2\delta) \times w_1 \tag{6.9}$$

The rate at which nickel is deposited ("builds up" on the surface of the copper) or in other words the rate of change of δ with time, is given by

$$X(t,x) = \frac{I(t)}{A_1} \times \frac{1}{Q} \times N(x) \tag{6.10}$$

where Q is taken from equation 6.4, and is interpreted as the charge required for plating per unit volume. $N(x)$ is the generalised nozzle function, a specific example of which is shown in figure 6.3.

Substituting we have

$$X(t,x) = \frac{I(t)}{\pi(d + 2\delta)w_1} \frac{M_{Ni}}{2\rho N_A q_e} = \eta_1 \times \frac{I(t)}{w_1} \times N(x) \quad [\mathrm{m/s}] \tag{6.11}$$

where η_1 contains all the constant terms which are scaling factors unimportant to the demonstration at hand.

Equation 6.11 represents the rate at which the nickel deposit "thickens" on the surface of the copper, and to determine how thick that deposition ultimately is, we

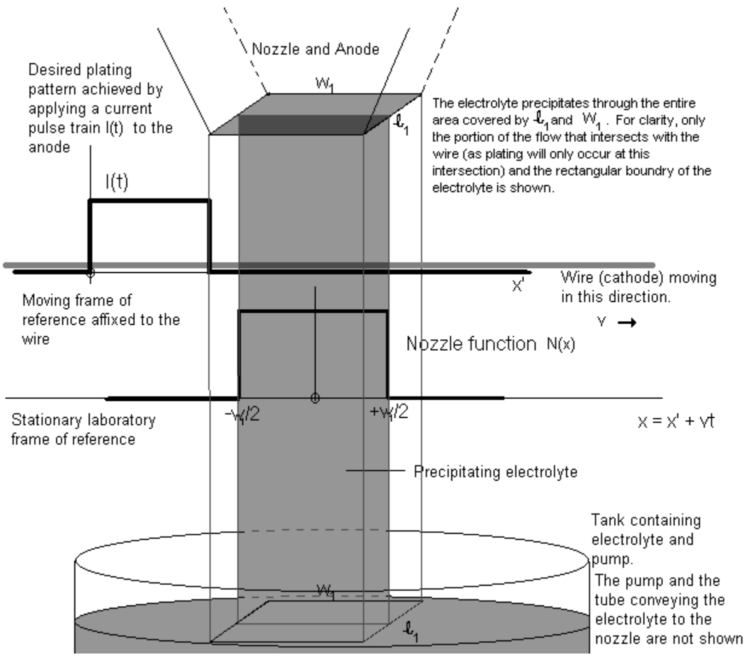


Figure 6.3: A schematic representation supporting the mathematical setup for determining the effect of the nozzle. This nozzle width w_1 is not to be confused with the bit-width w, which is the physical space each bit occupies on the wire. The nozzle is assumed to have a length l_1. The frame x is the fixed laboratory frame of reference with the nozzle centered symmetrically around the origin, and $x^{'}$ is the frame fixed to the wire. The equation $x = x^{'} + vt$ is the well-known Galilean transformation used to transform between 2 co-linear moving inertial frames.

have to integrate $X(t)$ for *all* time. Considering a position fixed in the $x^{'}$ frame (i.e. a fixed point on the wire), we see that deposition only occurs when that point is present between $-\frac{w}{2}$ and $+\frac{w}{2}$ in the laboratory frame.

Rewriting the Galilean transformation, we have

$$t = \frac{x - x^{'}}{v} \quad \text{and} \quad x^{'} = x - vt \tag{6.12}$$

The integral over all time where a point $x^{'}$ is present (i.e. $\frac{-w_1}{2} \leq x \leq \frac{w_1}{2}$) in the aperture is given by

$$\delta(x^{'}) = \int_{-\infty}^{+\infty} X(t,x)dt = \frac{\eta_1}{w_1} \int_{-\infty}^{+\infty} N(x^{'} + vt)I(t)dt \tag{6.13}$$

If we assume the aperture function is a "top-hat" function of width w_1, and exploit the Galilean transformation, and use $dx = vdt$, we have

$$\delta(x^{'}) = \frac{\eta_1}{v} \int_{-\infty}^{+\infty} \sqcap(\frac{+x}{w_1}) I(\frac{x - x^{'}}{v})dx \tag{6.14}$$

which we recognise as the convolution integral

$$\delta(x^{'}) = \frac{\eta_1}{v} \sqcap (\frac{+x^{'}}{w_1}) * I(\frac{-x^{'}}{v}) \tag{6.15}$$

or, because $x^{'}$ gets more negative with increasing t,

$$\delta(-x^{'}) = \frac{\eta_1}{v} \int_{-\infty}^{+\infty} \sqcap(\frac{-x^{'}}{w_1}) I(\frac{+x^{'}}{v}) dx \tag{6.16}$$

We interpret this as meaning that instead of obtaining deposition with spacial form qualitatively described by the current function, we obtain that current function convolved with the aperture function. Remember that the width of aperture function is the width of the nozzle. The effect (described by the convolution) is the well known one of "ramping" (see figure 6.4). In the limit, if the width of w were made equal to the width of t, the result would be a triangle. From above, we see that the more we

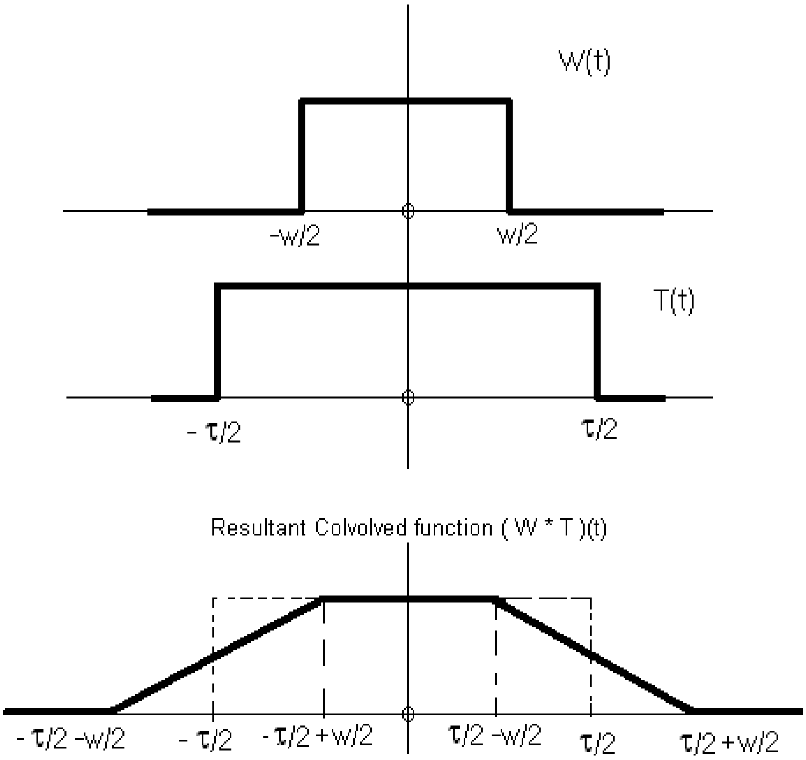


Figure 6.4: Graphical representation of the result of 2 hypothetical top-hat functions, W and T of width w and t respectively, are convolved. There is a ramping effect which can be seen in the lowest of the 3 graphics. The resulting function resembles T in this case, with a ramp of length w on each side.

allow the electrolyte to flow over more of the wire, the larger the ramps will be. As a general rule, the width of the electrolyte w_1 should be made small compared with the bit width, w.

6.2.2 About the electrolyte

Electrodeposition has many applications, particularly in decorative plating (silver plating) and electromechanical systems (MEMS)[3]. Much published research has been performed into optimising the process variables such as bath ingredients, temperature and current density. Benefits to be gained by optimising the bath conditions include less pitting, a condition where the deposited coat is non-uniform in thickness, and is said to be "pitted", and better tensile strength of the deposited lattice resulting from uniform crystal structure and alignment. There was no immediate attempt to use optimal bath ingredients, pH and temperature, because the auxiliary ingredients were not readily available, and it was felt that the focus should have been on proof-of-principle, the optimisation set aside until the principle had been proven. The optimisation has yet to be undertaken.

The electrolyte has to have a high nickel yield, as nickel was selected as the metal to deposit onto the copper. A simple electrolyte of $NiCl_2.6H_2O$ dissolved to the maximum concentration before saturation [14] in distilled water was prepared. For these experiments the nickel chloride was dissolved to approximately 250 g/ℓ of distilled water. Care is taken not to contaminate the electrolyte with other metals to avoid reduced efficiency due to competition at the cathode.

With the recent emergence of MEMS[3] technology, the focus of electrolyte research has shifted back towards solutions which optimise electrical characteristics. One vital consideration in electrodeposition is porosity or pitting, where fine bubbles of hydrogen and water are entrapped in the deposited metal matrix, reducing tensile strength and increasing resistivity. This effect is especially severe for higher DC currents, such as the ones used in this work. Improving the electrolyte is therefore a field requiring much future work.

However, for the purposes of proof-of-principle, and since no one to the author's knowledge has demonstrated plating a rapidly moving cathode before, it was decided to find the electrolyte with the lowest resistivity. The lower the resistivity of the electrolyte, the lower the voltage required to provide the current density described

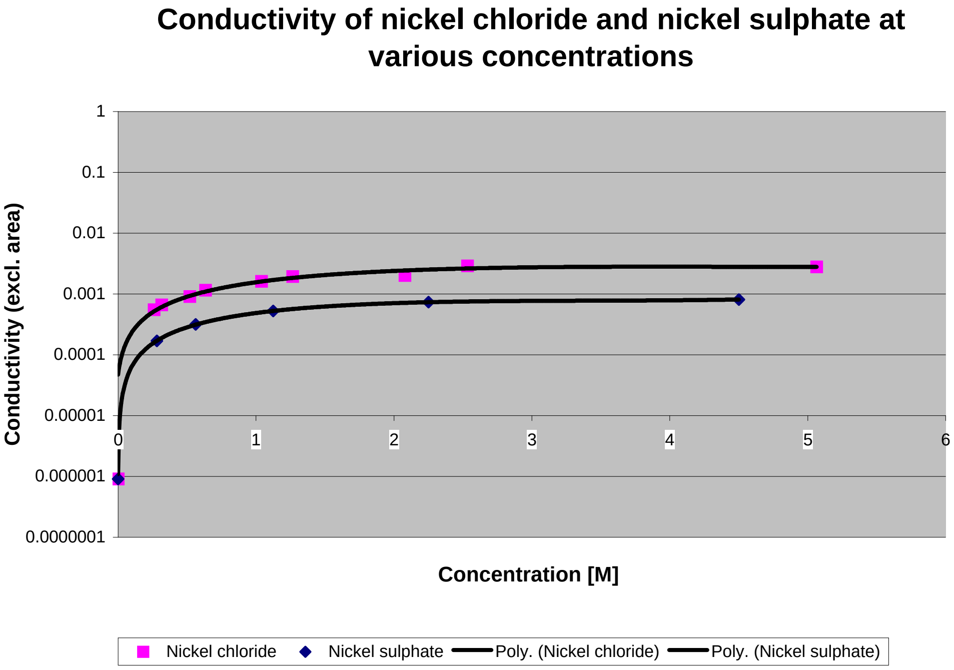


Figure 6.5: The conductivity of $NiCl_2$ and $NiSO_4$ is plotted against concentration of the salt. Not surprisingly, maximum conductivity is achieved when the concentration is greatest. Nickel chloride has a better conductivity than nickel sulphate, with a maximum of $2{\times}10^{-3}$ $\mathrm{m}.\Omega^{-1}$, which corresponds to a resistivity of 500 Ω/m. Thus for a 1 cm anode-cathode separation, we could expect a resistance of 5 Ω.

as follows, and is identical for both nickel sulphate and nickel chloride. Firstly, a solution was made the salt each dissolved (in separate beakers) to approximately 5 molar for nickel chloride, and 4.5 molar for nickel sulphate. A rectangular bath of cross-sectional dimensions 1 cm × 0.75 cm and length 1 m was filled to a marked height with electrolyte. At each end of the bath was a stopper with a plate of nickel metal (on the anode side) and copper metal (on the cathode side) dipped into the bath to the full depth. Current was passed through the electrolyte (thereby plating nickel onto the cathode). A digital voltmeter was used to measure the potential difference between the two probes for separations of the two voltmeter probes ranging from 5 cm

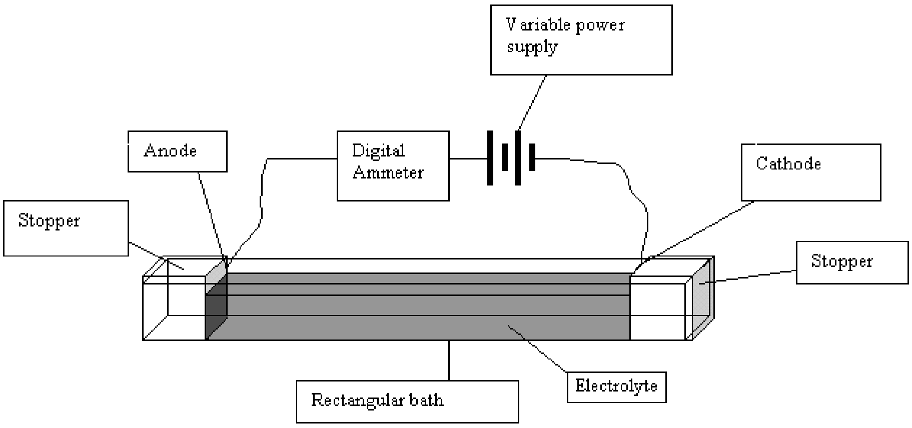


Figure 6.6: The apparatus for determining the conductivity of nickel sulphate and nickel chloride electrolytes. The variable power supply provides current and a digital voltmeter is used to measure the voltage developed across various separations of the probes.

to 70 cm in increments of 5 cm. This information was used to produce a qualitative conductivity per unit area. To get the actual conductivity, one would multiply the value taken off these graphs by the cross-sectional area in question.

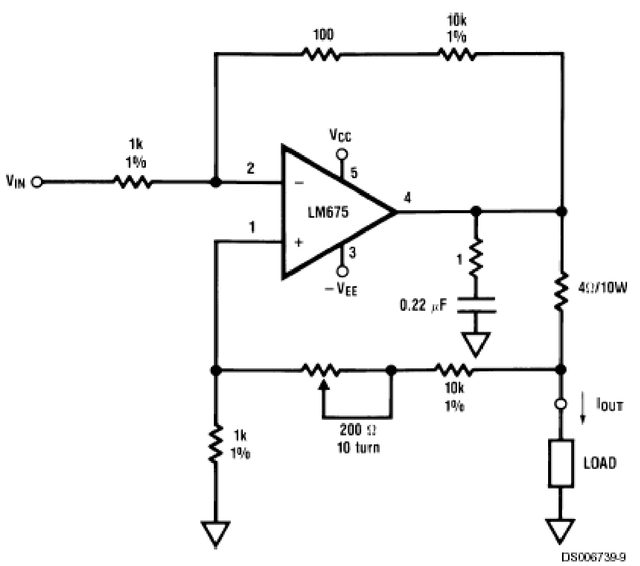
It is clear from figure 6.5 that the electrolytes prepared with nickel chloride have a consistently higher conductivity than electrolytes prepared with nickel sulphate dissolved to the same concentration. Furthermore, nickel chloride has a higher maximum conductivity, and for this reason, a solution of nickel chloride was selected as the electrolyte for all the plating performed in this work.

6.2.3 The current source

The need for a voltage controlled current source became apparent, as the current density in the electrolytic solution determines the rate at which nickel atoms deposit. Fixing the current density will ensure that any variation in resistance of the electrolyte does not result in variation of nickel thickness. It does not correct for variations in the dimensions of the stream of the electrolyte.

Many designs for current sources were considered, the first being an adaptation of the Howland style current source, found on page 182 of H&H [6]. Figure 6.7 shows the schematic diagram for this circuit.

High Current Source/Sink



$I_{OUT} = V_{IN}$ x 2.5 amps/volt
i.e. I_{OUT} = 1A when V_{IN} = 400 mV
Trim pot for max R_{OUT}

Figure 6.7: The Howland style current source, taken from the datasheet for the LM675T power op-amp.

The datasheet for the LM675T, does little to emphasize the sensitivity to oscillation that this circuit suffers. Furthermore, it is sensitive to the accuracy of the resistors employed - they must be very closely matched to ensure a good common mode rejection ratio (CMRR)[7]. High CMRR is desirable because the higher it is, the less sensitive the output of device will be to signal variations common to both inputs. A good example of where a high CMRR is preferable, is when dealing with "mains hum", which is the 50 Hz electromagnetic radiation produced by the 240 V electrical mains. This pollution is manifested as electromagnetic radiation which is received by both inputs of the op-amp[8], particularly if the input wires are long. In figure 6.7, we see that there is a feedback loop from the output back to the input (via the potential divider), and if the output were to change significantly as a result of the common

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[7] CMRR refers to the insensitivity of an amplifier to voltages common to both inputs. It is the ratio of the output with a differential input applied to the input terminals, to the output with an input common to both input terminals applied of the same amplitude[6]. It is most commonly expressed in decibels.

[8] These inputs are acting as antennae which receive the radiation and produce a small voltage signal synchronous with the radiation. Generally, the longer the input leads, the greater the signal strength.

mode feedback (i.e. a low CMRR), then the circuit could “run away” with the positive feedback, causing rail to rail oscillations. Rail to rail in this context refers to the supply voltage of the device. The output of the op-amp cannot exceed the absolute value of the input supply voltages (both positive supply voltage and negative supply voltages), and thus the output voltage is constrained to a maximum of the positive supply voltage, and a minimum of the negative supply voltage.

Much trouble was had with this circuit oscillating. The LM675T would become very hot as a result of the oscillations, and thus a PCB design was never attempted for this circuit. This circuit does have the advantage of being bi-polar, i.e. current can be sourced or sunk by the circuit. However, since the electrodeposition cell-reaction need only occur in the forward direction, i.e. current will always flow towards ground, the device need only be uni-polar.

The author had had no experience with current source design, so the newsgroup sci.electronics.design on usenet was approached and asked to assist with the design of a uni-polar current source, and the consensus was that a voltage-controlled current source (VCCS) like figure 4.11 in the Art of Electronics, 4th ed. page 181 [6] would make an excellent reference point.

Development got underway, and after considerable refinement, the final design used for the current source is shown in figure 6.8.

The current source has a compliance limited by the unregulated supply voltage, and is voltage programmable from 0 to 7 ampere. The unregulated supply voltage must range between 15 and 70 V[9]. Assuming plating was to occur at 3A, the impedance of the electrolytic solution separating the anode and cathode could be up to 23 Ω.

6.2.4 How the current source works

$POT1$ sets the voltage (Vin) at the non-inverting pin of $AR1$, an LF411[10]. The op-amp maintains, through internal feedback, the inverting input at the same voltage, hence fixing the voltage across $R2 + R3$ at Vin. In the quiescent state, there will be

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[9] This is governed by the maximum collector-emitter voltage (V_{CE} for $Trans1$, $Trans2$, and $Trans3$ as well as the maximum V_{CE} of $Q5$.

[10] The LF411 was selected simply for availability. It has disadvantages like not being rail-to-rail, and hence you can see the negative terminal connected to -12V. The LF411 turned out to be adequate in this case, but commercial implementation would warrant a revision of choice.

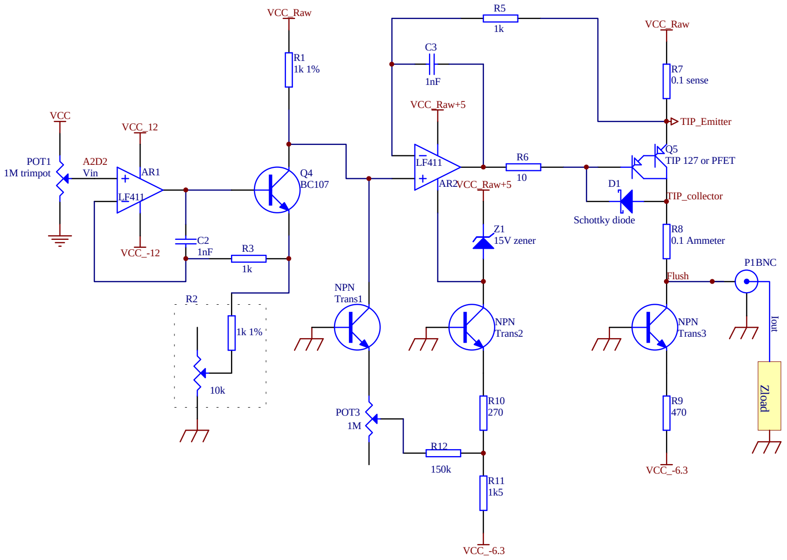

Figure 6.8: The schematic diagram of the current source. This circuit will provide a current set by the voltage V_{in}, provided $R2$ is set to 9.0 kΩ. The output is taken from the BNC connector (also visible in the top right hand corner of figure 6.9). This schematic is realised in the top left hand quadrant of the same figure.

no current flowing through $R3$, so the voltage across $R2$ is equal to the voltage at the inverting input. The 10k pot is included so that the $R2$ can be set to 10.0 kΩ. Thus, a current I_1 given by

$$I_1 = \frac{Vin}{R2} \tag{6.17}$$

flows in the collector of $Q4$ [11]. That current is also present in $R1$, causing the voltage on the collector (drain in the case of a MOSFET) to be

$$Vc = Vraw - (I_1 \times R1) = Vraw - \frac{Vin}{R2} \times R1. \tag{6.18}$$

This voltage is also the voltage present on the non-inverting input of $AR2$, which in a similar manner to $AR1$, is the voltage $AR2$ produces and maintains on its inverting

---

[11] $Q4$ was set to a BC 107 simply on availability and simplicity. There are more suitable transistors, which would allow a higher $Vraw$ and more stability. It is possibly better to use a N channel MOSFET instead as it would give greater stability and voltage range for $Vraw$. These design concerns should be addressed in all future work on the current source.

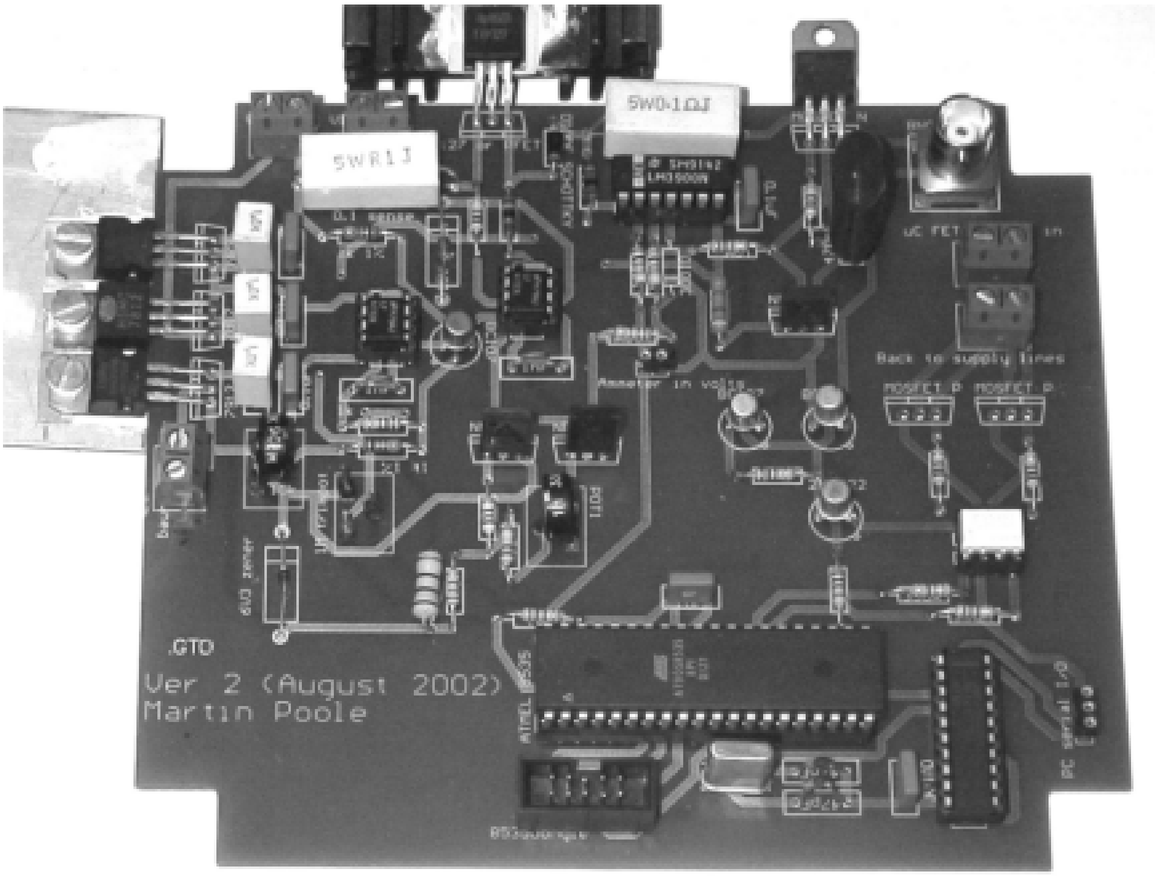

Figure 6.9: A photograph of the populated PCB for the VCCS. The 3 TO220 packages bolted to a heatsink down the left hand side of the board are voltage regulators, providing (in descending order as they appear) 12, 5 and -12V respectively. The TO220 package at the top left is $Q5$ of figure 6.8, which has to have a large heatsink.

input, and therefore the emitter voltage of $Q5$, too. This fixes the current in $R7$ to be

$$I_{R7} = Iout = \frac{Vraw - Vc}{R7} \tag{6.19}$$

Substituting, we see that

$$I_{R7} = Iout = \frac{Vraw - [Vraw - (\frac{Vin}{R2} \times R1)]}{R7} = Vin \times \frac{\frac{R1}{R2}}{R7}. \tag{6.20}$$

Since we have selected $\frac{R1}{R2}$ to be 10 and $R7 = 0.1\Omega$, we see that $|Iout|$ [in amps] is set by $|Vin|$ [in volts].

$R7$ is the sense resistor for the current source, and $R8$ is another sense resistor, used to provide a voltage corresponding to the collector current of $Q5$, for feedback to the microcontroller (q.v. Figure 6.12).

Capacitors $C1$ and $C2$ are provided for more stability, particularly if MOSFETs (an N-channel and a P-channel for $Q4$ and $Q5$ respectively) are used. The capacitor values are determined by the fact that $R2$ and $C2$ form a low pass filter with a critical frequency chosen to be 1 MHz; similarly for $R5$ and $C3$. $Trans1$ with $POT3$ and $R12$ provide a 0.5 to 3.5 μA adjustable current sink used to bias the non-inverting input of $AR2$. $Trans2$ with $R10$ and $R11$ provide a 3 mA current sink used to bias the zener diode $Z1$. This zener is in place so that $AR2$ always has 15 V across its supply terminals, independent of the "raw" or unregulated voltage which can be used to supply the main current.

If $AR2$ was replaced with a rail-to-rail op-amp like the LMC6482, then there would be no need for the extra supply (labelled $OpAmp5$ in figure 6.8) rail maintained at 5 V above the voltage supply rail labelled $Vraw$. The extra 5 V rail was implemented because the LF411 does not have a guaranteed common mode input/output characteristics near the power supply rails, and generally one should provide a voltage 3 V or more above the maximum desired input or output voltage to ensure satisfactory input/output performance. Replacing $AR2$ would also allow a change of $Z1$ to a 10 V zener diode, which would provide enough voltage range so that op-amp's output could drive the base of a TIP127 5 V below the emitter, or bring the gate of a IRF9520 standing in stead of the TIP127[12] 10 V below its source. According to the datasheet (taken from www.irf.com) a base-emitter voltage (V_{BE}) of -5 V is the voltage required

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[12] Note: The IRF9520 has a maximum drain to source current of -6.8 A

to turn a pnp-Darlington transistor like the TIP127 fully on (i.e. allow maximum collector current), or, if the transistor was replaced with a MOSFET like the IRF9520, a gate-source voltage (V_{GS}) of -10 V is required to allow the maximum drain-source current to flow.

A feature of the design is the "through zero" ability of the output current. This is facilitated by the presence of $Trans3$, a 20 mA current sink ensuring that even when no current is being drawn from the output, $Q5$ is on. When 1 mA is drawn from the output, the current in $Q5$ is 21 mA. $R6$ and $D1$ are included for current limiting and over-voltage protection respectively.

To create the desired plating pattern corresponding exactly to the output generated by the microcontroller, the current source is to be switched on and off rapidly (recall from section 6.2 that each nickel bit is set by applying or withholding the current for periods of $\tau \simeq 260\mu$s as the wire moves past at 40 m/s. Since the bits would have to be switched in a patterned way, a microcontroller was introduced to handle the logic, and facilitate communication with a supervisory P.C. or SCADA system. The schematic diagram showing the microcontroller with its interface to the rest of the design is shown in figure 6.10.

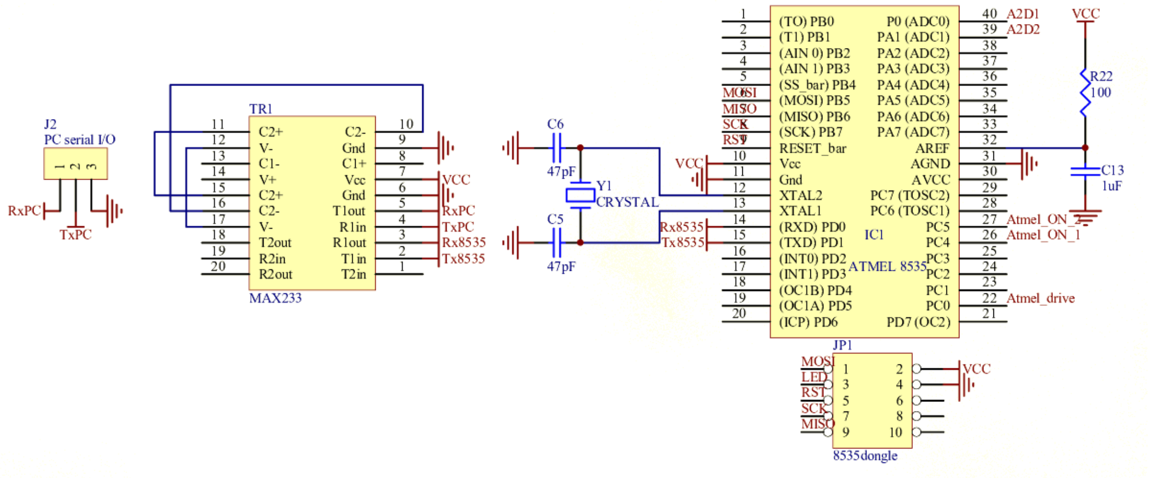

Figure 6.10: The microcontroller (Atmel AT90S8535) with the RS232 interface (MAX 233). These schematic diagrams correspond to the components visible in the bottom right corner of figure 6.9. Examples of the code executed on the microcontroller to effect plating are included on the CD-rom accompanying this thesis.

Discussions on the sci.electronics.design forum on usenet resulted in a decision to shunt the plating current to ground via a MOSFET for the nickel bits where the absence of nickel is to represent a “0”. This has advantages over the alternative of switching the programming voltage at the input. The first disadvantage of switching the programming voltage at the input, is one of ringing. Ringing refers to the “settling time” of the device as the feedback voltage from the output resistor approaches the steady state by successively smaller oscillations about the steady state voltage. Secondly, switching the load to ground minimises thermal cycling[13] in the 0.1 Ω sense resistor, because the current in it remains constant, whether the current is delivered to the electrolyte (deposition) or directly to ground. Finally, shunting the load to ground is electronically simpler than switching an input voltage.

The microcontroller mentioned before switches the MOSFET through a level converter and push-pull. The level converter is necessary because the microcontroller operates on 5 V logic, and to switch the IRF640 MOSFET fully on requires 10 V. The complementary transistor pair act as a push-pull. This is a common technique used to overcome the problem of gate capacitance[6]. The schematic is shown in figure 6.11.

One disadvantage is that there is relatively large power wastage, especially at high current, but this is not important, as the total power wasted is in the order of a few watts, and is thus negligible when compared to the power used generally in the heavy machinery performing the extrusion, annealing and insulation.

The R_{DSon}[14] of the MOSFET (IRF640 in this case) is approximately 30 mΩ, which is 30 mV per ampere of current. Even at 5 A, there would be insufficient voltage across the device, and hence between the anode and cathode to perform electrodeposition. The presence of the switch causes a very brief ($\leq 1\mu$s) voltage spike of double the amplitude of the output voltage on the output waveform, at a time corresponding to the commencement of deposition. This is suppressed in amplitude by 50% by $C9$, a 470 nF capacitor, shown in figure 6.11.

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[13] Thermal cycling refers to the dependence of the resistance of a device upon the heat dissipated within it. As the resistance increases the power decreases, cooling the device, which decreases the resistance etc. While this is inescapable, it is minimal in the steady state case. When the current is toggled, the effect is greater as there is a greater difference in the power dissipation between the toggled states.

[14] The drain to source resistance when the device is switched on

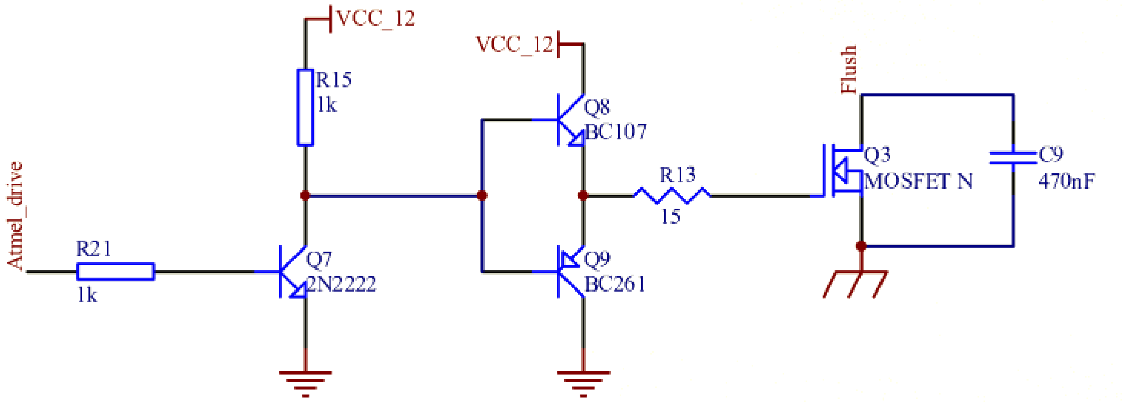

Figure 6.11: The schematic of the MOSFET switch. The signal comes from pin 22 of the AT90S8535 shown in figure 6.10. $Q7$ provides a level converter from the 5 V the microcontoller uses to the 12 V desired for proper switching of $Q3$. $Q8$ and $Q9$ are a complementary pair of BJT's configured in the classic push-pull configuration, to ensure that the gate-source capacitance of $Q3$ is compensated. $R13$ is for protection of the base of $Q3$, and $C9$ is to dampen out voltage and current spikes on the drain caused by the switching. The drain is connected to the Net label marked Flush in figure 6.8.

One aspect left undiscussed is the resistor $R8$, used to sense the current for feedback to the microcontroller. Since Vraw is chosen to be large (anywhere between 20 and 90 V, depending on the selection of the transistors) and unregulated, it could exceed the common mode input of most op-amps. To get around this, a Norton op-amp is used, and the design is taken from the datasheet for the LM3900 for ground referencing a differential voltage. The device accepts input current through resistors $R16$ and $R17$. Both inputs are of the form of the base of a transistor, so the voltage on both the input pins is fixed at approximately 0.7 V. The device produces the difference in the input currents on its output as a current, and this current is passed through the resistor $R20$ to produce a voltage which can be measured by a analogue to digital converter (A2D) on the microcontroller. The design can be seen in figure 6.12. The design was unfortunately sent to the PCB manufacturers with an incorrect net name, and the lower supply of the LM3900 has been connected to -6.3 V. This could be remedied by cutting the track and wiring the pin to ground. The schematic has been modified to show the correct net, and this should be used for further revisions and productions of the design.

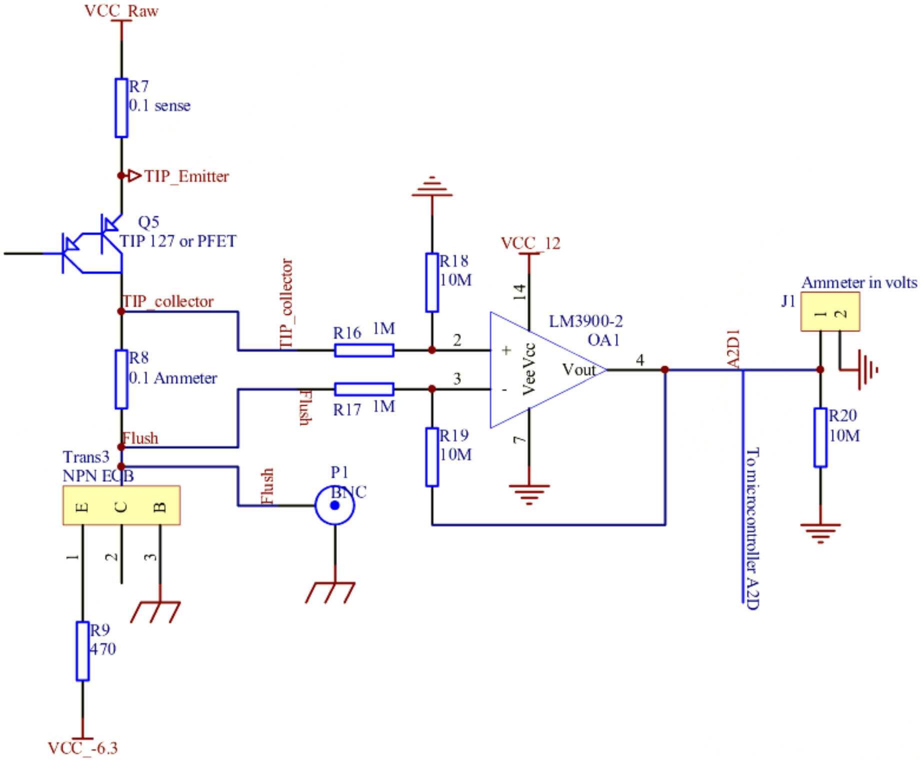

Figure 6.12: The schematic diagram of the circuit used to feed back the current to the A2D of the Atmel AT90S8535. This is the corrected version.

6.3 Considerations arising

6.3.1 Fluid dynamics

In the work presented thus far, we have treated the electrolyte flowing over the wire as being thin by comparison to the bit-width. As can be expected, wire moving through the electrolyte tends to draw the liquid along the length of the wire in the direction the wire moves. Since the current flows through all the electrolyte, it is desirable to minimise the extent to which the electrolyte is drawn along the wire. In simulations performed in the laboratory, the electrolyte was typically drawn approximately 2 cm along the wire with no corrective measures taken. The corrective measures considered were using compressed air to guide the flow of the electrolyte, and "blow off" any electrolyte that adheres to the wire outside of specific boundaries set, and using common kitchen sponges to staunch the progress of the electrolyte. Considerable refinement to these methods, and probably complete revision, will be needed if this technique is to be industrially viable.

6.3.2 Corrosive nature of the electrolyte

One other consideration is that of splashing. The wire does not remain in one position in the flow of electrolyte constantly. It suffers vibrations and other small disturbances, which results in small drops of electrolyte being cast around. Even if the wire is heavily constrained with suitable rollers and pulleys to be disturbed minimally, there will still be a small amount of splashing. The containment of these splashes is essential to the longevity of both the plating equipment and the surrounding existing industrial equipment, as the nickel chloride solution will rapidly oxidise any exposed metal it comes into contact with.

A small amount of whatever electrolyte is chosen is likely to adhere to the surface of the copper despite great effort to reduce such adherence. The effect of this residue on the subsequent insulation stage is to be investigated. If the electrolyte interferes with the insulation stage significantly, then the appropriate cleaning and drying action is to be implemented.

Chapter 7

Detection of deposited nickel

An important part of any viable solution is proving that it has been applied. Recall from before that nickel is ferromagnetic and copper is not. To prove that nickel is present on the copper using electromagnetism, one would apply a magnetic field to the wire, and thereafter use a device for sensing the residual magnetic field. A wire with no deposited nickel would not provide any residual magnetic field, but one *with* nickel deposits would. The varying voltage produced by moving a sensitive magnetic device along a magnetised wire would reveal the magnetic code present on the plated wire. There are many patents and commercially available devices for detecting magnetic fields, codes, differences and polarity. Providing a reliable method for proving the existence of a nickel code on a piece of wire is an integral part of the commercial viability of this solution, but the commercial availability and existence of comprehensive technology for detecting small magnetic fields makes more work on detection scientifically unnecessary. However, this existing equipment is costly, and to prove that nickel had successfully been deposited, a simple magnetic writing device and a simple magnetic reading device were built and tested, with some success.

7.1 Magnetic writing device

The magnetic writing device was designed around the design of a tape-recorder head. Transformer wire (40 AWG) was wound around 2 laminae of iron-core (obtained from a computer floppy-drive stepper motor), with as many windings as possible (between 300 and 350 windings). The wires are then set in glue and taped down to ensure robustness; final d

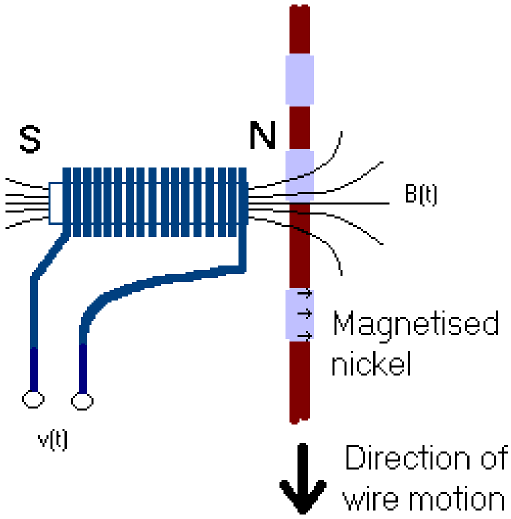

Figure 7.1: A schematic of the magnetic writing device. A bi-polar current induced by v(t) flows through the coils, inducing a magnetic field B(t) in and around the coil. Any nickel in the presence of this field will align its magnetic moments with the field. Copper, being paramagnetic, will not. The wire is propelled by an AC electric motor operating at 1400 rpm.

The electronics which energises the writing device is based on a standard push-pull pnp-npn configuration, and a schematic diagram can be seen in figure 7.2.

A logic hi on the right hand side transistors (causing the pnp to be off, and the npn to be on) will occur simultaneously with the left hand transistors receiving a logic lo (with the opposite transistors on). Thus current will flow from the top left pnp through the inductive and resistive head, through the bottom right npn and to ground. With the complementary logic, the current will flow from the top right, through the inductor (the other way), through the bottom left npn and to ground. High impedance is desirable when the device is inactive, as any deviation from the rails might cause the base of the transistors to be biased half-on allowing current to flow, and a non-zero magnetic field in the coil, causing unwanted magnetisation. The bases of the adjacent transistors are not tied together, despite receiving the same signal as again, because any small leakage current out the base of the pnp would flow into the base of the npn, turning it on, with the result that they both come “full on”, shorting out the supply, and possibly burning out the transistors.

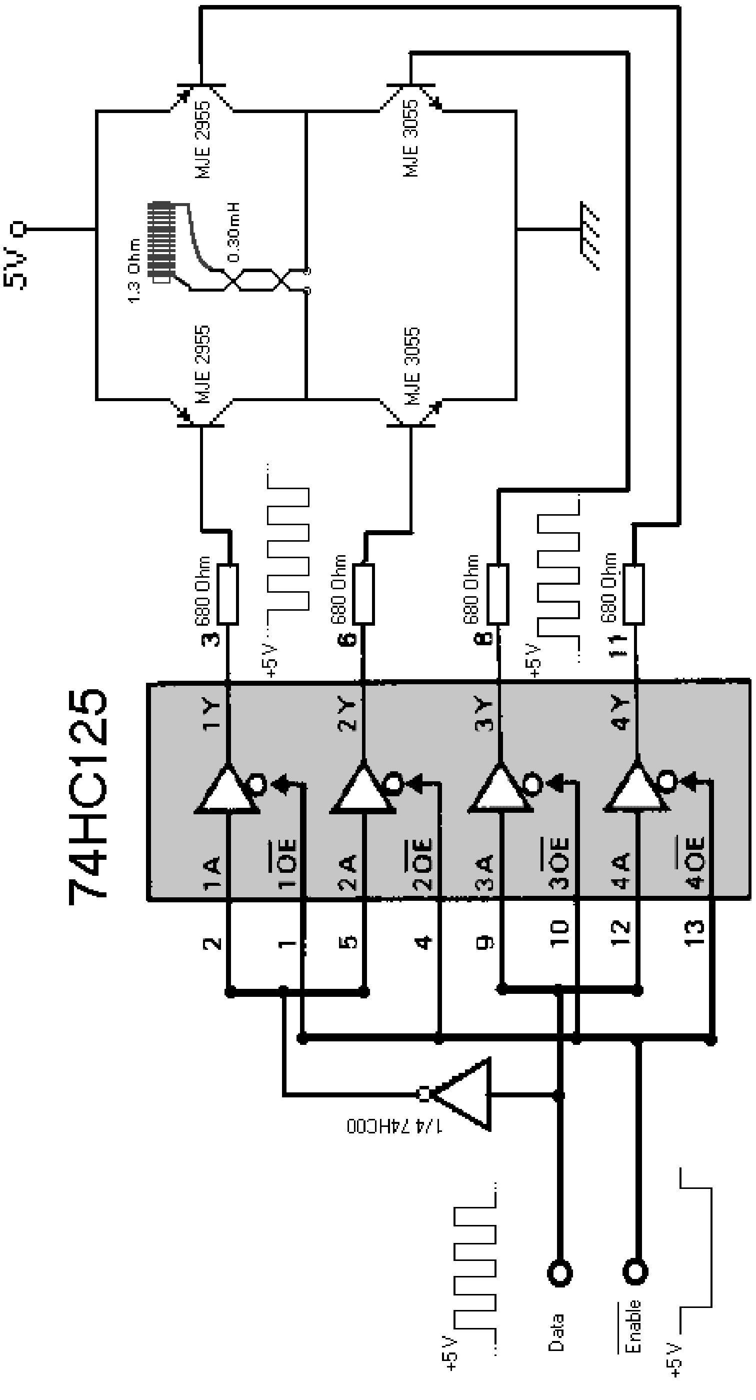

Figure 7.2: A schematic diagram of the electronics used to energise the magnetic write-head shown in figure 7.1. The signal presented on the data inputs are only passed to the output when the enable input is brought low, else the outputs idle with high impedance.

The writing device works by placing a sample of nickel-clad wire on the perimeter of a disc of diameter $D = 16.5$ cm and setting the disk to rotate. The disc is attached to an AC electric motor which rotates the disc in a horizontal plane at a rate of 1400 rpm. The spinning disc has a period of about 42 ms. The writing head described above is placed as close as possible to the wire, also in the horizontal plane. A one-shot pulse generator was employed to deliver a 20 ms $\overline{Enable}$ to the 74HC125. This causes the writing device to be enabled for 1 half of a rotation of the disc. A signal generator perpetually applies a 500 Hz[1] signal to the data line, but this is only piped through to the output when the $\overline{Enable}$ is pulled low (by the one-shot pulse generator, and this is only performed once). This allows 1 half of the clad wire to receive the alternating magnetic signal. An alternating magnetic signal is chosen because the detection method (see below) employs the detection of a *change* in magnetic field, and this change is maximised by alternately swapping the polarity of the field. When this alternating field was applied to a 100% pure nickel wire, the result was astonishingly precise - an "envelope" of alternating B-field being detected. However, applying the same conditions to nickel clad wire (which only has up to a micron of nickel cladding) proved undetectable, and this caused the investigation detailed in subsection 8.1.

The disc spinning at 1400 rpm means the wire is moving with a speed given by

$$V_w = \pi \times D \times \frac{1400}{60} = 12 \ \mathtt{m/s} \tag{7.1}$$

This is important, because for a given frequency f, the spacial wavelength occupied by one cycle of a wave at that frequency is given by

$$\lambda' = \frac{V_w}{f} \tag{7.2}$$

Experiments were carried out with the frequency typically at 500 Hz, which gives a λ' of about 2.4 cm. Recall from section 6.2 that for a 64 bit code, we would have a bit-width of approximately 1.6 cm. This poses a problem, as ideally we would like λ' small compared with the bit-width w so that many wavelengths per bit (corresponding to many polarity toggles per bit) could be written for greater reliability of detection. This could be achieved by using a motor with a lower rpm.

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[1] 500 Hz turned out to be the optimum frequency for this particular write head - 5 kHz exceeded the spatial resolution of the head.

7.2 Magnetic reading device

The principle behind the reading device is moving the wire and detecting the resultant change in magnetic field. The changes in magnetic field would occur as a result of the process described above, where different sections of nickel clad wire are exposed

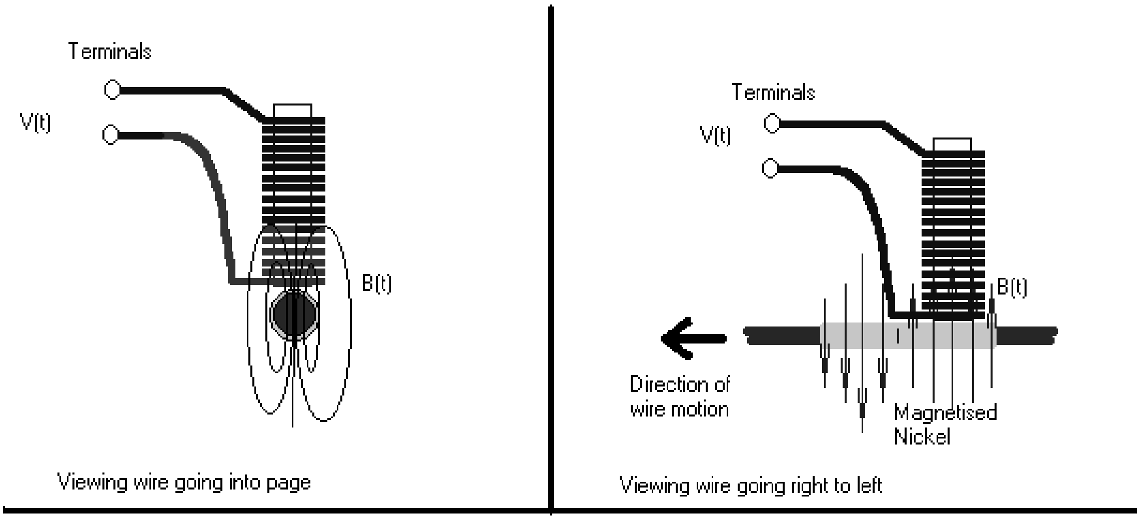

Figure 7.3: A schematic of the reading head. For all the tests conducted, the wire is propelled by an AC electric motor at 1400 rpm.

The experimental apparatus is largely the same as for the writing process. The (now magnetised) wire is affixed to the disc and rotated in the horizontal plane also at 1400 rpm. The same head that is used for writing is used for the reader, and it is also placed as close to the rotating wire as possible. The difference now is that in place of the electronics used to energise the head, there is electronics to amplify the voltage developed across the terminals. The voltage developed across the terminals is given by

$$V(t) = -n \times V_w \times \frac{d(\Phi)}{dx} \tag{7.3}$$

or, using $V_w = \frac{dx}{dt}$,

$$V(t) = \frac{-n}{V_w}\frac{d(\Phi)}{dx} \tag{7.4}$$

where n is the number of turns of wire

V_w is the instantaneous speed of the wire

Φ is the magnetic flux caused by the presence of magnetised nickel.

The voltages are small (in the order of μV), and some amplification is necessary. An instrumentation amplifier taken from figure 7.32 on page 425 of The Art of Electronics[6] was used, and the schematic is shown in 7.4. A highpass filter (of $f_0 =$ 300 Hz) was placed in the front end of the amplifier to try attenuate some (about 18 dB) of the ambient 50Hz noise, without attenuating any of the signal caused by the moving magnetic wire.

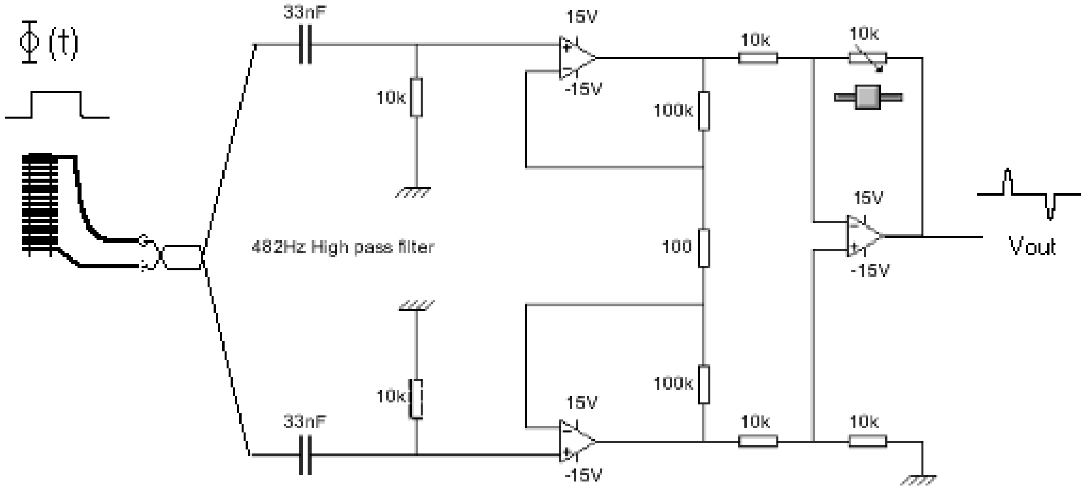

Figure 7.4: The read head and instrument amplifier with an adjustable gain of up to 2000, which was generally the gain used. The op-amps are LF411s, and there are better choices for better CMRR, and again the reason these were used instead is availability.

An alternating constant tone (like the 100kHz biasing tone in audio cassette technology) would be preferable to a direct, uniform magnetisation for 2 reasons. The first is that the alternating field provides a convenient $\frac{d(\Phi)}{dx}$ for better voltage response from the reader, and secondly so that that tone could be used to synchronise the reading equipment so that consecutive “1” bits would be easily counted.

It was found that the reading device could detect wire that was clad with more than about 10μm of Ni with an oscilloscope in the 20 mV range after the 2000×

amplification. But the detection was only possible when the wire was cut into 3 cm pieces, and magnetised for a few seconds with a direct magnetic field[2], before the pieces of wire were attached to the disc and revolved. Along each 3 cm segment of wire the magnetic field is approximately uniform, but it is the abrupt edge of the pieces where the magnetic field falls to zero which induces the voltage in the head. A voltage of opposite sign but equal magnitude is induced when the magnetic field rises abruptly from zero to the uniform value as a piece of magnetised wire moves past the read-head. For thinner Ni deposits, a technique of averaging was necessary, because the weaker magnetic fields resulted in unacceptably weak voltage signals on the oscilloscope. This is discussed below in further detail.

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[2] obtained by stopping the motor, holding the $\overline{Enable}$ of the writing device low with the data pin set for appropriate polarity, and applying the write-head to the wire.

Chapter 8

Checks, tests and verifications of the processes

8.1 Testing the reading/writing devices

8.1.1 Limits of cladding thickness and magnetising current

What is shown above clearly shows the proof-of-principle. Despite this, very little has been finalised, such as the actual thickness of nickel to be deposited. Since the detection was not easily achieved for the thicknesses originally specified (1 nm was the desired thickness initially), work was done on determining what the limits of detection are under different circumstances. Discussions with electrical engineers within Telkom have indicated that an arm synchronous with the wire (i.e. moving at 40 m/s too) as it is extruded (allowing more time for plating to occur) could easily be constructed. This would mean that a lower current density could be used over a longer time for the same resultant thickness of nickel, or the same current density (or higher) could be used to obtain a thicker coating. In short, there are still parameters of the plating process which have not been settled upon, and so some quantitative analysis was performed to attempt to define the boundaries of the parameters. It is entirely plausible that nickel thicknesses that are detectable with magnetic equipment may very well be visible to the human eye. In that case, no magnetisation equipment would be necessary, as an ordinary ruler could determine the bit widths, and thereby prove ownership.

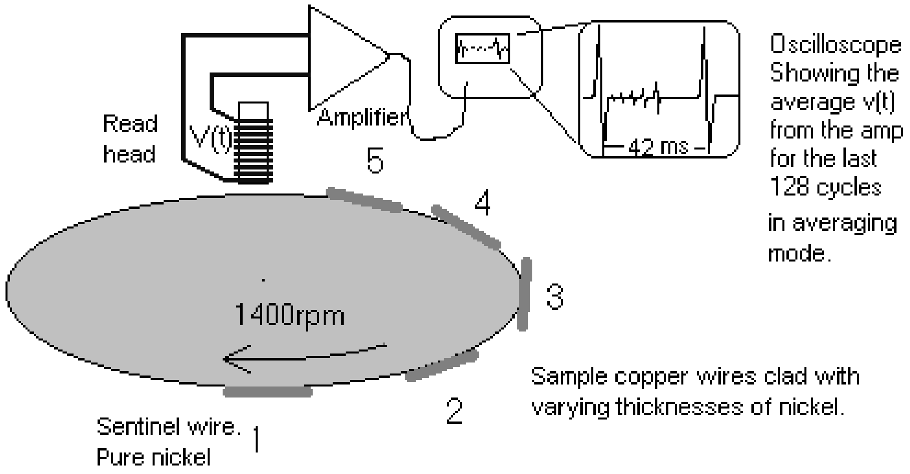

Figure 8.1: A schematic of the apparatus for the investigation into the detection limits of the nickel coating. Sample 1 represents a sentinel piece of pure nickel wire magnetised so that the oscilloscope can trigger on its sharp, clear edge. Between each pass of the sentinel, the samples (numbered 2, 3, 4) pass the head. The oscilloscope synchronously averages over 128 passes and so any voltage that is a result of magnetised nickel should appear, and any noise voltage should average to 0.

The thickness of the nickel determines the strength of the field surrounding the nickel after a magnetic code (whether uni-polar or alternating) is written to the wire. Since the fields are generally weak, and the detector is based on a voltage induced in windings, it is necessary that the magnetised nickel be moving in accordance with equation 7.4 for detection to take place. Thus in this test jig the same motor is used as for the writing process, with wires that had been exposed to ≈ 2 A of deposition current for times between $10\mu s$ and $10s$, mounted on the periphery of the disc as shown in figure 8.1. The nickel clad wires are affixed to the disk, which revolves at 12 m/s past the reading head. The voltage from the read-head passes through the instrument amplifier (see figure 7.4, and that voltage is read by an oscilloscope set up to average over 128 passes. The need for the averaging arose out of the magnetic noise created by the AC electric (wire-brush) motor, which drowns out any small signal produced by the wire by at least 20 dB. One note of import is that the reading head works on the principle of *change* in magnetic field, and since the head is present in a relatively strong magnetic field (the noise from the motor), any bump or regular vibration coherent with the 40 ms (such as the packing-tape used to mount the samples bumping the head each time it passes) leads to a spurious signal, which can mislead the unwary experimenter into believing that a sample is being detected when it is not even there!

It would be useful to obtain a table showing the variance of the signal on the oscilloscope against the change in thickness of the nickel and the length of time that the nickel is exposed to the magnetic field. One of the restrictions on this investigation is that the power transistors used to drive the current back and forth through the writing head do not have high transition frequencies, and so pulses shorter than 1 μs do not fully turn on the transistors, resulting in unreliable exposure times.

It might be asked why the variations in the magnetic field strength is not included in the investigation, rather than subjecting a test wire to varying times of a fixed magnitude field.

In short, it is because the transistors operate in saturation, and since their bases are driven by the CMOS tri-state buffer, there is no mechanism for base current control, and hence no control for the current flowing in the write-head. A range of heads could conceivably be wound, each with a different inductance, and a different magnetic field strength, should the need arise. It seems, however, that the present head is capable of writing to the nickel with adequate spatial resolution at least for purposes of proof-of-principle.

Referring to figure 8.2, we can see that only the wire exposed to 10 s of coating could be detected easily, but interestingly, it required only 10 μs of direct magnetic field from the writing device to get that peak. The height of that peak did not grow with further application of magnetic field, indicating that the magnetic poles of the nickel were all maximally aligned with that relatively short pulse.

The poor quality of the image is regretted, but attempts to improve the quality have proven futile, because the original printout from the oscilloscope was of poor quality. By way of explanation, the text in the bottom left hand corner indicates that the 'scope is showing channel 1, and the scale is 20 mV per division. The M 5.00 ms in the centre of the bottom of the figure indicates that the time scale is 5 ms per division, and the text in the far right corner indicates that channel 1 triggers on a rising edge threshold of 180 mV. The information taken from the right hand side of the figure indicates that the 'scope is in averaging mode, taking a running average of 128 samples.

A control experiment was performed on another piece of wire (also with approx

22 nm of coating) to see whether an alternating B field (of 500 Hz) could be detected on nickel clad wire in the same averaging fashion, as it can be detected very distinctly on a piece of 100% nickel wire. The alternating field would be synchronous with the trigger pulse, and should therefore rise above the noise. The alternating pulses did not prove easily detectable.

From the above, we see that, firstly, the reading (and writing) should be removed from the magnetic interference of the motor. Secondly, the original estimation that 1 nm of nickel would prove sufficient might require revision. Of course, greater sensitivity of the reading and writing equipment are certainly achievable, especially w.r.t. engineering a reading head that smaller dimensions[1]. Thirdly, it is not likely that the apparatus used in these proof-of-principle demonstrations would make for viable field test equipment, unless the nickel cladding was made very thick - more than a micron.

However, it has been shown that seeming small amounts of nickel *can*, in certain cases, be detected with relatively simple and unrefined equipment. Given the results obtained in this work, it might be possible to design and build more sensitive reading and writing apparatus, but it is probably more efficient to buy commercially available sensitive magnetic equipment, and use the research time to improve the VCCS instead.

8.2 Other detection methods

8.2.1 Chemical - Dimethylglyoxime (DMG)

Dimethylglyoxime (DMG) reacts with Ni^{2+} to form Ni(DMG), a red, insoluble solid. An acid like HNO_3 would have to be applied to the nickel-clad copper wire, and the then the DMG, as not enough of the nickel would be oxidised in the natural state. Whether such a small amount of nickel would be sufficient to react to form a visible layer of DMG is not clear, and determining the actual code the nickel represents would be difficult, especially with a long code-length. Time did not permit experimentation with DMG.

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[1] The magnetic field near a magnetised object drops off radially as $\frac{1}{R^3}$, which means that the field is very weak within the head.

8.2.2 Possible visibility of nickel cladding to the human eye

When the idea of deposition was proposed, the initial calculations indicated that for every 2.2 A of current, 1 nm of nickel would be deposited. Despite nickel being silvery white compared to copper's brown copper colour, it was not thought that this layer would be visible, but it was thought that it might be magnetically detectable. Time did not permit investigating what thickness of nickel (and hence corresponding plating current) would cause plating to occur such that the nickel cladding is visible to the naked eye. It is a property worth considering in the future.

8.3 Compliance with the solution criteria

Following chapter 3, particularly page 14, we have a set of solution criteria which a candidate solution must satisfy to be considered viable. Each criterion is addressed separately in what follows.

N.1 The Tamman temperature[4][8] is the temperature equal to half the melting temperature (both temperatures in Kelvin). Below this temperature, the metal is said to be unreactive. Following Mitchell[8], we have that a fire with similar conditions to those under which stolen copper is burned, burns at approximately 390 degrees Celsius. There is no account in that work regarding the experimental procedure except that they used an infrared pyrometer. Whether many such fires were built for aggregation, or whether various types of cables were burned is unclear. However, at that temperature, both nickel and copper are considered unreactive, and so a negligible quantity of cross contamination (where the nickel on one wire alloys with the exposed copper of another during burning) would occur. Regrettably, there was insufficient time to investigate whether the residue left by the burned insulation or the nickel oxidising during the burning interferes with the detection of nickel bar-code, and this is an aspect which must be investigated before viability can be be declared unchallengeable.

N.2 Unambiguity (uniqueness) is achieved by this technique. Each wire has its own n-bit bar-code. Provided care is taken to exclude duplication of the bar-codes, and provided the bar-code is given to the purchaser of the wire in careful correspondence with the code actually on the wire, then both the Telecommunication company concerned and the seller of the cable (ATC or Aberdare) would have a record of that transaction. Thus two different companies could not prove a claim of ownership simultaneously.

N.3 The legal admissibility of the solution is a criterion which the author has attempted to secure throughout the design process, with limited success. Legal authorities have been consulted and the proposed technique has been described to them. Provisional indications are that this method is legally admissible, provided the author is available to testify as a “expert witness”. Only once the technique has been fully refined and declared in its final applicable form with the appropriate patents, can legal admissibility be conclusively evaluated.

N.4 The equipment developed to perform the electrodeposition occupies about 1 m^3, and with more time spent on design, this could be reduced considerably. The equipment can easily be removed when not desired.

N.5 The acceptable electrical and physical characteristics after the application of the solution is a concern that has yet to be investigated. Nickel was selected as the metal for deposition based on its similarity to copper, but no research has yet been conducted in determining the actual effect. See page 71 in the conclusion.

N.6 The cost of implementing the solution is small. By way of example, a continuous nickel coat, i.e. the code 111..., of thickness $\delta = 1\ \mu$m, would only consume 16.7 g of nickel metal for every kilometre of wire. These calculations are based on equations 6.2 and 6.3. It is possible that a sufficiently thick plating would be visible, reducing the cost.

P.1 We have shown that the nickel can be detected with simple and inexpensive equipment under certain conditions. Commercial magnetic detection equipment is available, and should be considered before more research is performed into the magnetic reading and writing equipment. Nonetheless, this solution was designed specifically so that detection of the method could be achieved “in the field”, and it has been shown to be possible.

P.2 The solution is not prohibitively expensive, although minimising the cost beyond its inherent thrift has not been undertaken as part of this work.

P.3 Plurality is provided by encoding a unique binary number consisting of n bits onto each wire. A buyer of cable would receive a list of the codes written to the wires contained within that cable. The number of unique codes is given by 2^n, so $n = 30$ would provide 1.1×10^9 unique codes.

We see from above, there is insufficient evidence for concluding the solution non-viable at this time. If, through further research, N.5, N.3, and N.1 can be shown to be satisfied then the solution can be considered unchallengeable.

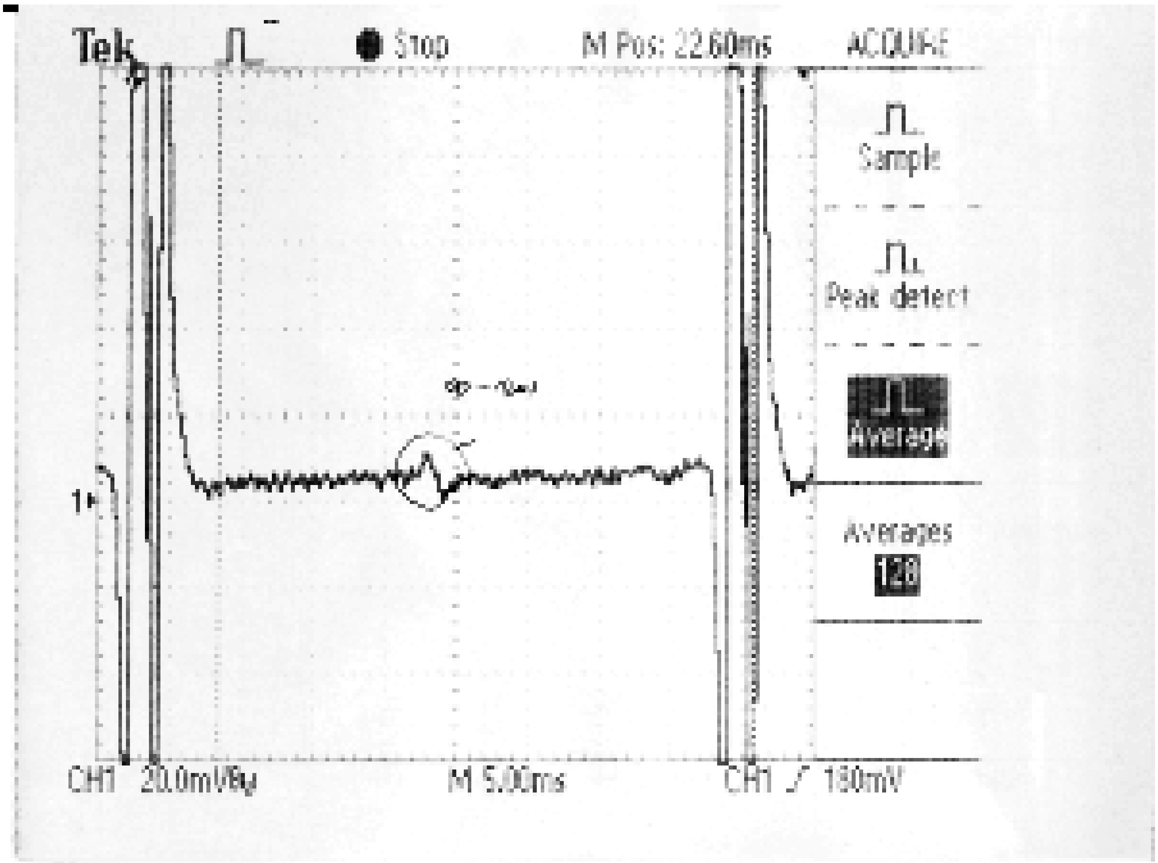


Figure 8.2: A typical screen capture from the oscilloscope, showing the voltage peak caused by the wire exposed to a nickel plating current for 10 s at a current of 2 A. The wires are positioned as in the numbers in figure 8.1, where the wires are placed in decreasing order of thickness in the hopes of obtaining a qualitative comparison of peak height vs. thickness. The other thickness used ranged from 1s down to 1 ms. The sentinel trigger signal is clear on the sides of the trace, but no other wires have fields strong enough to be detected above the ambient noise than the one exposed to 10 s of plating current - seen in the middle. Attempts to improve the quality of the screen capture have proven futile.

Chapter 9

Future work and Conclusion

The author of this thesis has identified the aspects of the problem of copper wire theft which are addressable, declared the properties of a viable solution, and identified some strategies that will not work. It has been shown that electrodeposition is a possible solution, and the author has begun investigating the various aspects implied by electrodeposition, such as how to plate and how to detect the plating.

However, certain questions spring to mind, to which time did not permit attention. Studies show there is more uniformity in the deposited layer if the current is pulsed at a higher frequency[15][11]. For instance, consider a wire normally exposed to 10 ms of current. What if the current was toggled on/off for only 0.1 ms in every ms - or more to the point, what is the optimum duty cycle and frequency for uniform plating? How does the quality (porosity, inclusion of hydrogen bubbles and water molecules in the deposited lattice) of the deposition vary with duty cycle?

There is considerable latitude for research into better plating equipment (more current, etc.), and improved magnetic reading and writing equipment, although it is the author's opinion that purchasing existing reading devices would save considerable time and resource . What has been developed was build to be a quick and cheap proof-of-principle. The technique used to detect the nickel has so far revolved around detecting changes in the magnetic field induced in a coil proximal to the field produced in the nickel cladding. Many companies have developed magneto-resistive techniques which use changes induced by the magnitude of a magnetic field in the resistivity of some substances. It is probable that detection would be improved using such a scheme, and it is the author's opinion that if the layer of nickel is invisible to the human eye, then technology adapted from these magneto-resistive techniques will most likely be the most reliable and accurate. The possibility that the nickel cladding is visible must also be investigated, and the effect of the burning process is to be determined. To what degree does the nickel oxidise, and what is the cumulative effect of the oxidisation and residual polyethylene insulation on the magnetic/optical visibility of the nickel layer.

There are consequences of the electrodeposition which require investigation in or that requirement N.5 (see page 12) be met, i.e. assessing the impact the nickel cladding has on the electrical characteristics. Until now, we have considered nickel to be similar to copper in size, shape and electrical characteristics. Nevertheless, there is a difference, and whether the change in performance will still permit high speed applications like DSL remains to be seen.

There are alternative techniques which have not been ruled out, like High Voltage sputtering and laser burning. There is the possibility that the lack of corrosive chemicals involved in electrodeposition might be preferred, and there is a need to investigate whether the wire needs cleaning (i.e. washing any residual electrolyte off) before the wire can be insulated.

Work in this field is made more complex by factors such as production constraints. There is no other existing research group investigating this matter, and as well as being the initial work, this thesis had the dual mandate of attempting to solve the problem while satisfying the requirements for the degree Master of Science (Physics, Telecommunications). In striking this balance, some compromises have been made.

The outcomes of this thesis, irrespective of how it is considered, include the following. Firstly, the *problem* is fully identified along with a set of solution criteria to which all viable solutions are to be bound. In addition there are some guidelines on what would be preferable properties.

Secondly, some candidate solutions have been shown to be non-viable. This regrettably includes any solution proposed here which was to be applied to the wires already in the ground. More generally, solutions involving manipulating or monitoring homogeneity of the wires are shown to be non-viable on the grounds that controlling the levels would be non-trivial, that there is a general trend towards purer copper in any case. A solution involving inhomogeneity would necessarily involve a large upheaval in the production system and that tracking the adjustments to concentration made would be non-trivial.

This work sorted the candidate solutions in descending order of likelihood of viability. Homogeneities were considered first simply because it had potential to yield a solution which could fingerprint the wire already in the ground. Some techniques remain unexplored, however, including sputtering the nickel onto the copper using a laser, using a laser directly on the copper, as well as a high voltage arcing technique. At this stage, no further conclusion can be drawn on the viability of such techniques as time has not yet permitted any research into these fields.

Finally, a seemingly viable solution involving electrodeposition of nickel onto copper is revealed, including how the nickel is plated to the copper, and how to prove that the nickel is in fact present. Much research effort has been placed in this endeavour, with the current source taking some time to develop, as well as providing reading and writing equipment suitable for proving the presence of deposited nickel. This has been successfully achieved, but regrettably with insufficient time to tackle the necessary optimisations for the industrial process. Much work remains in the improvement of this technique, and the matter should not be considered closed.

Appendix A-1

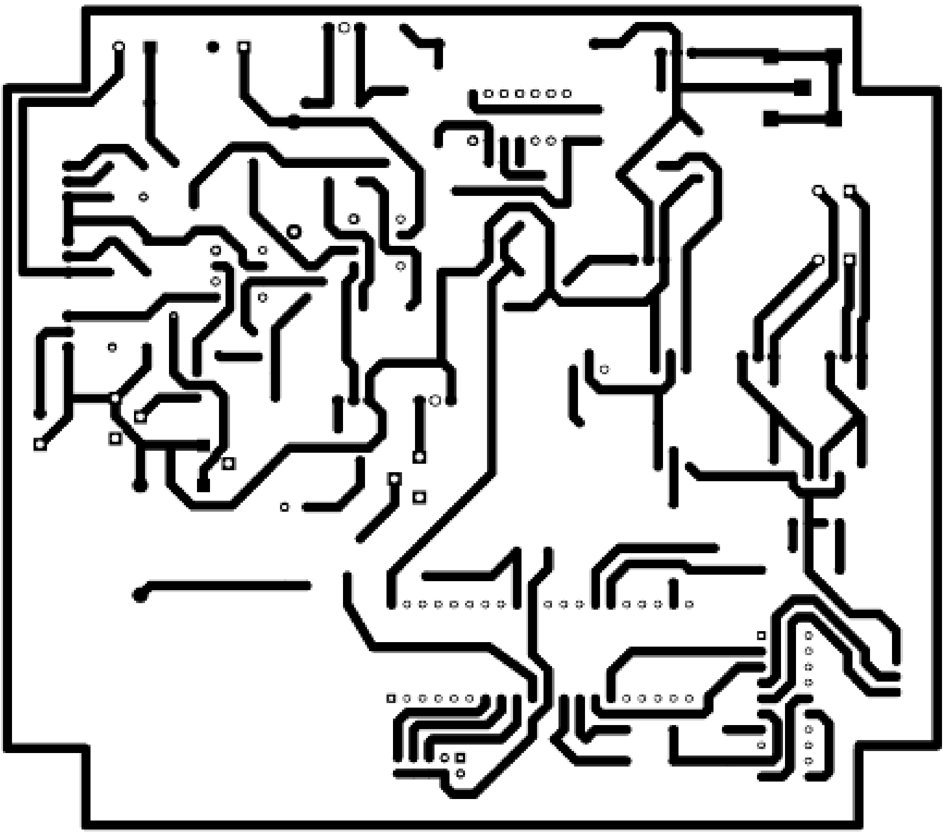


Figure 9.1: The top side of the VCCS PCB, showing the tracks and through-holes.

Appendix A-2

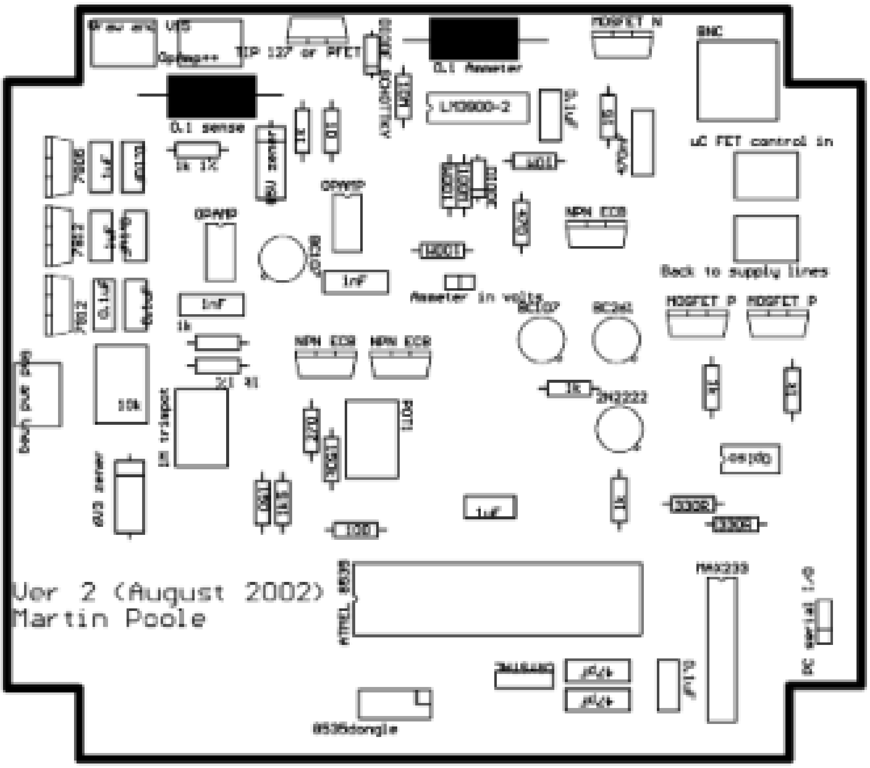


Figure 9.2: The VCCS PCB silkscreen, showing the positions of the various components.

Appendix A-3

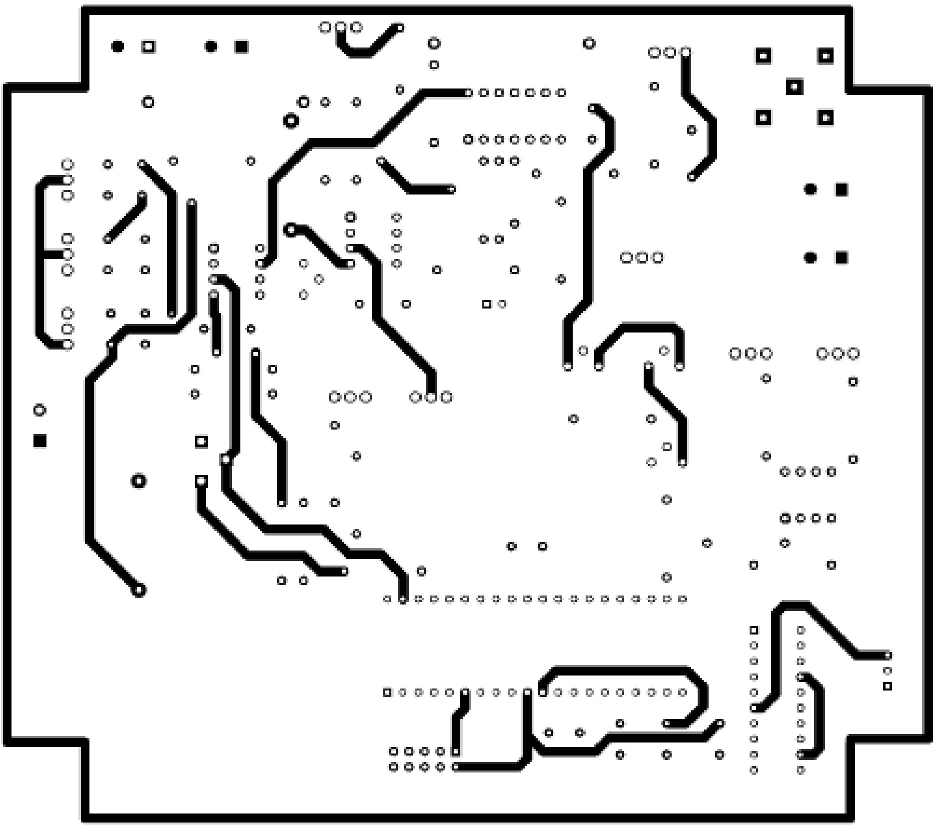


Figure 9.3: The bottom side of the VCCS PCB, showing the tracks and through-holes.

Appendix B

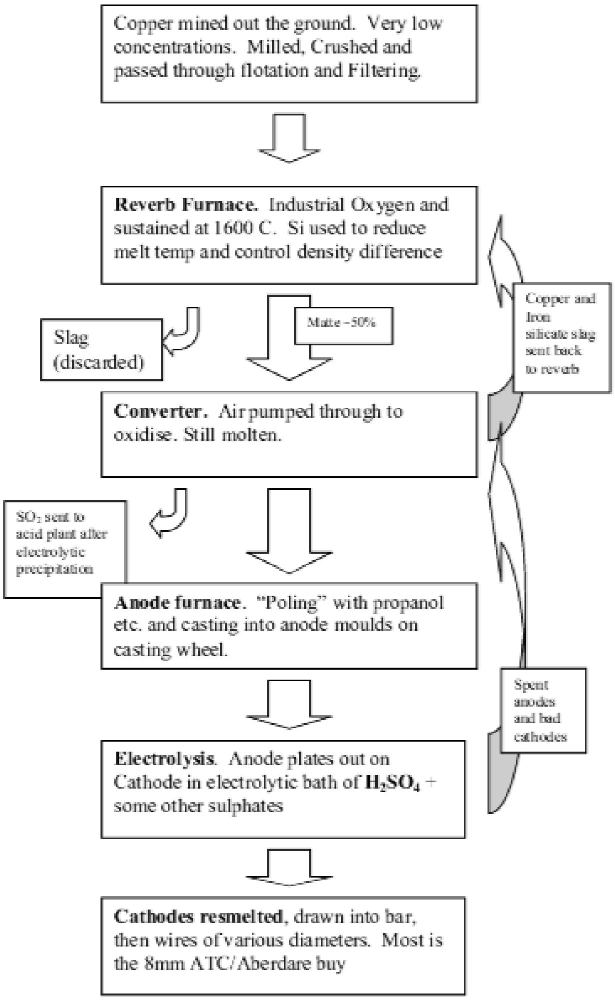
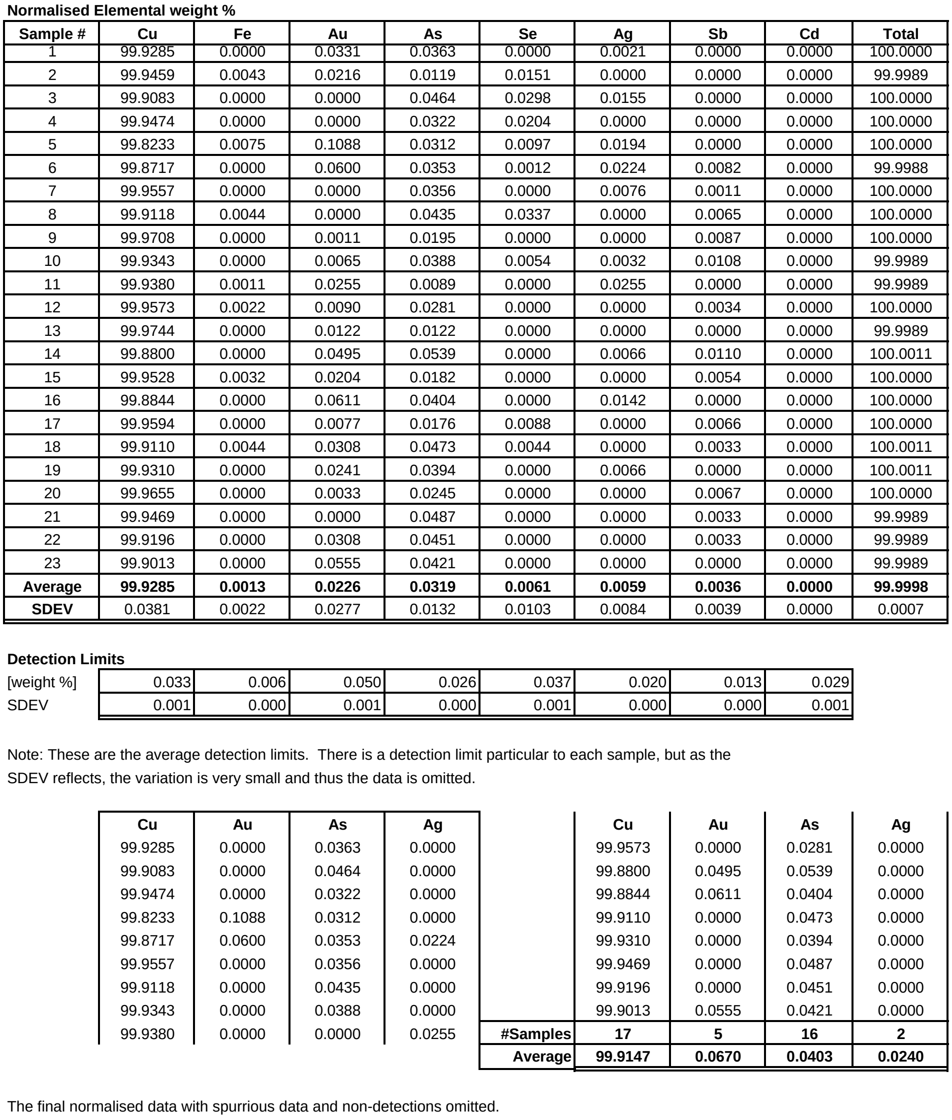


Figure 9.4: Flowchart overview of the process employed to purify copper from the ore. This flowchart is the author's schematic representation of the technical documents kindly provided by Mr. Nico Rheeder of PMC in August of 2001.

Appendix C



Normalised Elemental weight %

Sample #	Cu	Fe	Au	As	Se	Ag	Sb	Cd	Total
1	99.9285	0.0000	0.0331	0.0363	0.0000	0.0021	0.0000	0.0000	100.0000
2	99.9459	0.0043	0.0216	0.0119	0.0151	0.0000	0.0000	0.0000	99.9989
3	99.9083	0.0000	0.0000	0.0464	0.0298	0.0155	0.0000	0.0000	100.0000
4	99.9474	0.0000	0.0000	0.0322	0.0204	0.0000	0.0000	0.0000	100.0000
5	99.8233	0.0075	0.1088	0.0312	0.0097	0.0194	0.0000	0.0000	100.0000
6	99.8717	0.0000	0.0600	0.0353	0.0012	0.0224	0.0082	0.0000	99.9988
7	99.9557	0.0000	0.0000	0.0356	0.0000	0.0076	0.0011	0.0000	100.0000
8	99.9118	0.0044	0.0000	0.0435	0.0337	0.0000	0.0065	0.0000	100.0000
9	99.9708	0.0000	0.0011	0.0195	0.0000	0.0000	0.0087	0.0000	100.0000
10	99.9343	0.0000	0.0065	0.0388	0.0054	0.0032	0.0108	0.0000	99.9989
11	99.9380	0.0011	0.0255	0.0089	0.0000	0.0255	0.0000	0.0000	99.9989
12	99.9573	0.0022	0.0090	0.0281	0.0000	0.0000	0.0034	0.0000	100.0000
13	99.9744	0.0000	0.0122	0.0122	0.0000	0.0000	0.0000	0.0000	99.9989
14	99.8800	0.0000	0.0495	0.0539	0.0000	0.0066	0.0110	0.0000	100.0011
15	99.9528	0.0032	0.0204	0.0182	0.0000	0.0000	0.0054	0.0000	100.0000
16	99.8844	0.0000	0.0611	0.0404	0.0000	0.0142	0.0000	0.0000	100.0000
17	99.9594	0.0000	0.0077	0.0176	0.0088	0.0000	0.0066	0.0000	100.0000
18	99.9110	0.0044	0.0308	0.0473	0.0044	0.0000	0.0033	0.0000	100.0011
19	99.9310	0.0000	0.0241	0.0394	0.0000	0.0066	0.0000	0.0000	100.0011
20	99.9655	0.0000	0.0033	0.0245	0.0000	0.0000	0.0067	0.0000	100.0000
21	99.9469	0.0000	0.0000	0.0487	0.0000	0.0000	0.0033	0.0000	99.9989
22	99.9196	0.0000	0.0308	0.0451	0.0000	0.0000	0.0033	0.0000	99.9989
23	99.9013	0.0000	0.0555	0.0421	0.0000	0.0000	0.0000	0.0000	99.9989
Average	**99.9285**	**0.0013**	**0.0226**	**0.0319**	**0.0061**	**0.0059**	**0.0036**	**0.0000**	**99.9998**
SDEV	0.0381	0.0022	0.0277	0.0132	0.0103	0.0084	0.0039	0.0000	0.0007

Detection Limits

[weight %]	0.033	0.006	0.050	0.026	0.037	0.020	0.013	0.029
SDEV	0.001	0.000	0.001	0.000	0.001	0.000	0.000	0.001

Note: These are the average detection limits. There is a detection limit particular to each sample, but as the SDEV reflects, the variation is very small and thus the data is omitted.

Cu	Au	As	Ag		Cu	Au	As	Ag
99.9285	0.0000	0.0363	0.0000		99.9573	0.0000	0.0281	0.0000
99.9083	0.0000	0.0464	0.0000		99.8800	0.0495	0.0539	0.0000
99.9474	0.0000	0.0322	0.0000		99.8844	0.0611	0.0404	0.0000
99.8233	0.1088	0.0312	0.0000		99.9110	0.0000	0.0473	0.0000
99.8717	0.0600	0.0353	0.0224		99.9310	0.0000	0.0394	0.0000
99.9557	0.0000	0.0356	0.0000		99.9469	0.0000	0.0487	0.0000
99.9118	0.0000	0.0435	0.0000		99.9196	0.0000	0.0451	0.0000
99.9343	0.0000	0.0388	0.0000		99.9013	0.0555	0.0421	0.0000
99.9380	0.0000	0.0000	0.0255	**#Samples**	**17**	**5**	**16**	**2**
				Average	**99.9147**	**0.0670**	**0.0403**	**0.0240**

The final normalised data with spurrious data and non-detections omitted.

Figure 9.5: Normalised data taken from the Electron Microprobe showing the elemental weight percentages and limits of detection. Notice that only 4 elements were successfully detected above their detection limits.

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