2014

New Zealand Police

CREWE HOMICIDE INVESTIGATION REVIEW

Report of Wire Analysis (2013)

APPENDIX 12

Appendix 12

Report of Wire Analysis (2013),
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REPORT
1970 CREWE HOMICIDE REVIEW

(Final Ver.16d)

5th – June - 2013

To Andrew J. Lovelock
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P. O. Box 9203
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1.0 Introduction

The New Zealand Police, in conducting a review of the1970 Crewe Homicide, sought expertise from me, through Detective Superintendent, Andrew J. Lovelock, to:

(a) A review and evaluation of scientific methodology applied by Mr Todd, Scientist DSIR, in the forensic examination of wire samples and resultant report/s, findings and conclusions.
(b) A review and evaluation of the evidence presented by Mr Todd in the 1970 Deposition hearing and the 1971 & 1973 High Court Murder Trials of Arthur THOMAS.
(c) A review and evaluation of the scientific methodology applied by Mr DEVEREUX, in the forensic examination of wire samples and resultant report/s findings and conclusions.
(d) A review and evaluation of the evidence presented by Mr DEVEREUX in the 1973 High Court Murder Trial of Arthur THOMAS.
(e) A comprehensive expert report including findings and conclusions that clarify whether the evidence of Mr TODD or Mr DEVEREUX is preferable and why.

As the report concerns in the main the metallurgy and chemical analysis of galvanised steel wire, as background Section 2.0 discusses steel metallurgy & steel wire and Section 3.0, the methods of chemical analysis used to determine the composition of the wire. Section 4.0 examines the Todd Chemical Analysis methodology and results in detail and then specific statements of evidence from the Court Transcript are examined. The following Section 5.0 then, examines the Devereux Chemical Analysis methodology and results in detail and then similarly specific statements of evidence from the Court Transcript are examined. The overall conclusions follow in Section 6.0. All material for this Report comes from the Court Transcript, unless otherwise noted.

2.0 Steel Wire

In steel making the contents of the ladle are called a 'heat' and are given a heat number which is essentially a 'birth certificate' –The Certificate of Analysis and Mechanical Test, which typically contains for structural steel: date, name of the steel works, steel making process, heat number, specification to which steel is made, section type (plate, column etc.), composition, mechanical properties, heat treatment,

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

name of testing laboratory and name of organisation certifying laboratory. Today in New Zealand the testing laboratory must also have international accreditation as must all laboratories certifying structural steel for New Zealand.

The ladle of steel has its composition taken and when this meets specification the steel is poured into ingots, in modern practice it would be con – cast as a continuous product. The ladle analysis is the average composition of the steel in the heat. The composition of the ingots can be taken as the ladle composition, although the analysis of the ingot/product may vary from the specified ladle/cast analysis due to segregation arising during solidification. Segregation occurs when a portion of an element present in the ingot, say C, collects in a particular region, say the centre, of the ingot.

The typical composition *(always in weight %)* of plain carbon steel might be C 0.20, Mn 0.60, Si 0.2, S 0.04, & P 0.4 and these are the most basic elements that would be looked for in a composition analysis to determine if the material is steel and what type. For an alloy steel further alloying elements would be looked for, in particular Ni, Cr & Mo, and for modern micro-alloyed steels small quantities of elements such as V, Nb, and Ti may be added. As a consequence of recycling scrap steel, elements other than those required for a particular specification may be present in small quantities and such elements are called tramp or sometimes trace elements.

As a consequence of the solidification process there is segregation of some elements in the ingot which represents a departure from the average ladle analysis. In steels the element showing the greatest tendency to segregate is S with P, C, Si and Mn segregating to a lesser extent and in that order. This means the composition in the ingot is non-uniform.

Commercial steels also contain non-metallic inclusions, also called impurities, which mainly result from reactions taking place in the melt or solidifying metal and predominately include oxides and sulphides.

Following casting the resulting ingot will thus contain the specified elements, some being partially segregated and also non-metallic inclusions. The ingot will usually be worked by rolling and in the present case of wire, by drawing through a die, where any non-metallic impurities would be strung or drawn out very finely along the length of the wire.

The steel used to make the present wire was most likely rimming steel, so named because of the formation of a surface rim of ferrite during solidification in the mould. There is minimum deoxidation treatment during melt processing. Such steels have very good drawing properties. A typical composition would be: C 0.08 max, Mn 0.25~0.40, P 0.03 max. and S 0.050 max., where the Si is low because of minimal deoxidation. There will still be segregation and non – metallic inclusions, but following

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

drawing to small diameters, this material will be strung out very finely, in a longitudinal direction in the centre of the wire.

The steel maker never makes each melt composition exactly the same rather he keeps within the specification which allows for some variation for certain elements and maximum or minimum values for others, depending on the specification. To produce exactly the same composition each time would make the steel very expensive. Thus each melt is essentially unique, has a heat number and if necessary can be traced back to, provided sufficient key elements, such as C, Si, Mn, S, & P etc. are determined in the composition.

3.0 Chemical Analysis

3.1 Optical Emission Spectroscopy (OES): Todd Analytical Method.

This is the analytical method used by Todd to determine the chemical composition of various wires. To gain an understanding of the method a brief description of the analytical process follows: The sample is excited, in this case with a spark discharge and each element in the sample emits light of a particular wavelength and intensity. The individual wavelengths are separated in a spectrometer and related to a particular element and the intensity to the quantity of that element by comparing the emission intensity with that of appropriate standards of known composition. This method can analyse many elements at the same time and there are only a few elements it cannot analyse for. This, including modern variants of the method, is a standard method used in steel plant for determining melt composition in steel making were several determinations of composition are made before each melt is poured. In modern instruments excitation is achieved with an Inductively Coupled Plasma – ICP. This ICP method is much more sensitive.

3.2 Atomic Absorption Spectroscopy (AAS): Devereux Analytical Method.

This is the analytical method used by Devereux to determine the chemical composition of various wires. To gain an understanding of the method a brief description of the analytical process follows: With Flame-AAS the sample has to be dissolved into liquid form and a small quantity of this is atomised/ionised in a high temperature flame. Light of a particular wave length, characteristic of the element being investigated is shone from a Hollow Cathode Lamp into the atomised/ionised atoms where it is absorbed. The amount of light absorbed, which is related to the amount of the element present, is measured by the instrument. With this method the specimen has to be dissolved to liquid form, the cathode lamp has to generate a wavelength characteristic of the element being investigated and hence a different lamp is required for each element and only one element can be determined at a time. The technique is very sensitive and modern instruments using Graphite Furnace Atomisation are even more sensitive.

A comparison of detection limits for the two techniques, OES and Flame-AAS, for elements of interest in determination of the composition of steel wire, is made in Table 1 below (Zn included for galvanising). Data are included for 1960, from the

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

paper by Robinson and for comparison, for 2012, from technical information from PerkinElmer a major manufacturer of such equipment. For the 2012 data, that for the ICP-OES, was included because that for an OES was not available. Where no information is given for an element, it means none was given by the source information or it was listed as ND, Not Detectable. The detection limits are given in ppm (parts per million) and those data for 2012 were converted from PerkinElmer information.

Element	OES 1960	Flame-AAS 1960	ICP-OES 2012	Flame-AAS 2012
C Carbon	not listed	not listed	no value	no value
Mn Manganese	0.08	0.5	0.0001	0.0015
Si Silicon	40	ND	0.01	0.09
S Sulphur	not listed	not listed	0.01	no value
P Phosphorus	6	no information	0.004	75
Al Aluminium	0.8	ND	0.001	0.045
Ni Nickel	4	1.0	0.0005	0.006
Cr Chromium	2	10	0.0002	0.003
Mo Molybdenum	2	ND	0.0005	0.045
Cu Copper	0.05	0.5	0.0004	0.0015
V Vanadium	4	ND	0.0005	0.06
Nb Niobium	not listed	not listed	0.001	1.5
Ti Titanium	0.4	no information	0.0004	0.075
Fe Iron	0.5	2.5	0.0001	0.005
Zn Zinc	2	0.1	0.0015	0.0002

Table 1 Detection Limits, in ppm, for OES and AAS methods for 1960 & 2012

It is to be noted that C is not detected by either method, in either period and has to be determined using an alternate method. Similarly it would appear S is not detectable by either method during the first period and is only detectable in the second period by the ICP-OES method. Also during the first period no information is listed for Nb. Hence for the first period, 1960, C, Si, S, P, Al, Mo, Nb, V, and Ti could not be detected by the Flame-AAS method of analysis, whereas for the OES method only C, S and Nb could not be detected. By 1970 the Flame-AAS method would have been able to analyse more of these elements. The 2012 information was included to show there are still elements which are not detectable by either method of analysis and that there has been a significant decrease in the detectable limit, although only the 1960 data is of concern in the present review. For the 1960's information, the detectability limits are of the same order, with perhaps the OES method being slightly better. But Robinson, when discussing the OES and Flame-AAS methods, noted that for the period, the limits for quantitative determination of elements for the OES method were usually 10 to 20 times higher than the detection limit concentration whereas for the AAS method they were about the same as the concentration limit. For the OES method small quantities can be detected but to measure with any accuracy the actual quantity present, a greater concentration of the element needs to be available.

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

4.0 Comment: Mr Harry Todd Chemical Analysis

For the following review, attribution of statements by Mr Todd will be made to the Court Transcript, supplied to me by Detective Superintendent Lovelock, by page number. Mr Todd used the OES method of chemical analysis and analysed for eight elements: C, Si, Mn, Ni, Cr, Mo, V and Cu [p.2]. The first three C, Si and Mn are essential for they give an indication of the steel type and deoxidation practice. With this selection of elements I would normally have included S and P because in most specifications they are included as maximums otherwise they can lead to mechanical performance difficulties. Mr Todd had about 30 years of experience with spectrographic type analysis of a wide range of materials, including a large amount of ferrous analysis [p.141: 09.05.0258]

Mr Todd [p2] states that for several elements, measurement of concentration was made to an accuracy of 0.001% (equivalent to 10 ppm) but generally the error was assessed at ± 0.01% (100 ppm). He "subsequently confirmed" a constant error, resulting from small sample size, for the copper determination. Of the eight elements analysed for Mo and V were not detected. Thus six elements, C, Si, Mn, Ni, Cr, and Cu were used for matching samples. Sometimes Si was below the level of detection.

Two reports (attached) from the Chemistry Division of the Department of Scientific and Industrial Research, DSIR, dated 8th October 1970, AR 529 and 28th October 1970, AR 583, are included in the Court Transcript at pages 03.01.0513 to 03.01.0519. Both reports are sent under the hand of Ian K Walker, Director, DSIR, the latter being signed. A further report by Todd, Report of H J Todd, Ref. 17.67, not dated, page 08.13.0034, (attached) details the composition of the most relevant Police Exhibits (see later). In the first report, composition analyses for copper and steel wires are presented. Only the results for the steel wires will be discussed, where C, Si, Mn, Ni, Cr, Mo and V were analysed. The galvanising/Zn on the steel wire was removed before testing and the results are the mean of duplicate tests. It is not clear from the transcript what surface/section of the wire was sparked. With the spark excitation method, each new test is effectively done on different material as the sparking removes/ablates a very small amount of material each time. To check the repeatability of the method and the variation in composition along a wire, two lengths of 16 S.W.G. galvanised steel wire, 2 "feet" long, sample A, and 40 "feet" long, sample B, were analysed at each end, end "1" & end "2", the 40 "feet" sample being analysed three times at each end to check repeatability. All results are the mean of duplicate analyses and some results are given to 3 decimal places, dp. To evaluate this data in more detail, the differences, Δ, in composition between ends "1" and "2" for samples A & B, and the maximum differences between the repeat analyses for ends "1" and "2" of sample B are listed in the following Table 2. Firstly this table must be read in conjunction with the original chemical analysis on page 3 of the report AR 529. This analysis shows samples A and B to be different wires. The 3 repeatability compositions come from 3 duplicate tests, 6 tests in all at each end. This means 6 sparkings each one ablating a very small amount of material. Thus the repeatability in

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testing, in the present situation, with the OES method will depend on the inherent instrument repeatability for a sample which is completely homogeneous with uniform composition throughout its mass and any micro-variation resulting from sparking different micro-regions of material in a steel wire which has segregated material and non-metallic material strung out in the drawn wire, a non-homogeneous material. Thus the variation in composition between each end of the wire will result from instrument repeatability errors, just mentioned, and compositional variation.

From Table 2, the maximum difference between repeat readings for sample B shows there is some very small variation in composition for C, Ni & Cr, with the greatest variation being for Mn, which segregates. If Todd's data from Report AR 529, for repeat tests, are rounded up to his usual error band of ± 0.01%, then there is essentially no variation in composition, apart from that for Mn. In comparing the end-to-end variation in composition, Report AR 529, with the repeat variation (which perhaps has a small compositional element in it), there can considered to be a very small variation with position, being greatest for the element Mn which is not surprising as it segregates and appears in steel in solid solution and as a non-metallic inclusion MnS, manganese sulphide, which segregates. In wire, MnS will be strung out in-homogeneously as thin fibres in the drawing direction. Mn is always present to remove the sulphur as MnS and although sulphur has not been determined in this present situation, it will be present in the steel, for this is not special steel with special sulphur control or vacuum de-gassing during melt processing. It is just plain ordinary wire. Todd notes (page 09.01.0300 or 282 or 284 final paragraph) that for the limits of experimental error he set of ± 0.01%, he could find no variation in composition with length. If the data in Report AR 529, are rounded up to ± 0.01%, then there is essentially no variation in composition, apart from Mn. On pages 282/284 & 283/285 Todd reports "before I assessed my own results I checked possible variations in 100 ft. length of wire; I analysed the two ends and the centre and within the limits of experimental error I set I could find no difference but I am sure that if I had examined these pieces with higher accuracy I would have found differences. The smaller the increment that can be detected, the less significant -- they will become, the less meaningful; ultimately metals are not homogenous". What Todd means is that as the

Elements	Sample A: Δ between ends 1 & 2	Sample B: max. Δ between ends 1 & 2	Sample B 1: max. Δ between repeats	Sample B 2: max. Δ between repeats
C	0.003	0.002	0.002	0.001
Si	0.00	<0.01	<0.01	<0.01
Mn	0.019	0.045	0.014	0.034
Ni	0.00	0.005	0.00	0.005
Cr	0.005	0.004	0.002	0.004
Mo	<0.05	<0.05	<0.05	<0.005
V	<0.005	<0.005	<0.005	<0.005

Table 2 Δ = difference in composition between repeat tests and the ends of lengths of wire.

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

detection sensitivity rises, that is detects ever smaller quantities, with a metal like steel, which is not homogenous, the spatial variation in composition in such a solid may be greater than the detectability limit and thus the increased sensitivity becomes less meaningful. See later for further comment on this matter.

In the second report, composition analyses for copper and galvanised steel wires are presented. As above, only the results for the steel wires will be discussed, where C, Si, Mn, Ni, Cr, Mo and V were analysed for. As previously, the zinc coating was removed and the spark discharge OES method used for chemical analysis. The chemical analysis of various samples was compared. This comparison will be discussed when all testing methods have been considered.

Specific statements from the Court Transcript are discussed below:

- Exhibits 29, scale from steps and 31, scale from wheelbarrow: [p. 143: 09.05.0260]. Is this scale rust? Yes, confirmed on page 196 or 202, but the OES Analysis Report does not appear to be included in the Transcript.
- Note: I make the following observation - Page: 09.04.0205, or 194 or 200 – line 19; This line does not appear to be recorded correctly, as specimens wire 3 & wire 5 are referred to as galvanised iron, whereas previously they were referred to as copper?
- On page 09.01.0273 or 253 or 257, Todd reported in the Court Transcript, he also determined copper in the steel wires by amending his analysis technique, but did not say what the amended technique was. These copper results appear in Report Ref: 17.67 by H. J. Todd.
- Page 09.01.0275 or 255 or 259, Todd said that in steel manufacturing 0.01% is a fine difference. At the time this was certainly true and even today standards quote most elements to two decimal places (2-dp) with some to 3-dp. The BSI Standard, BS EN ISO 16120, specifies for rimming steel C2D1, 11 elements, of which 8 are to 2-dp (C_{max} 0.03, Si_{max} 0.05, Mn 0.01-0.35, Cr_{max} 0.1, Ni_{max} 0.1, Mo_{max} 0.03, Cu_{max} 0.10,& Al_{max} 0.01) and the remaining 3 to 3-dp (P_{max} 0.020, S_{max} 0.020 & N_{max} 0.007).
- Page 09.01.0276 or 256 or 260, line 19: the question is asked by Ryan, "Isn't the spectrographic test you mentioned earlier a little old-fashioned". Todd replied "I would not say so". This technique is still being used and from Table 1, modern ICP-OES (which was being developed in the 1970's) has superior sensitivities to modern Flame –AAS, although the Graphite Furnace-AAS has superior sensitivity but cannot analyse as many elements as ICP-OES. On this and subsequent pages there are also questions asked of Todd about the Flame –AAS method of analysis and wire compositions, but it would appear the method and results from the method had not yet been presented to the Court. I will comment on these matters when the information is presented in the Transcript.
- On page 09.01.0296 or 278 or 280, 19 lines up: Ryan asked Todd to "make a list of the quantity of particles". I presume this is the list which appears at page 08.13.0034, Ref: 17.67, Report of H. J. Todd (attached). It also includes "(Results of Drs. Sprott and Devereux in brackets)", where the results are for the comparison of

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steel wire removed from bodies and a farm. Todd's results come from the signed report mentioned above, apart from for Cu which appears for the first time, but those of Sprott and Devereux appear from no-where. There is a report from T J Sprott and Associates, under their letter head, which details the results of chemical analysis for three elements, Ni, Cr & Cu, in various lengths of steel wire checking for compositional differences along the length of the wires (this report will be discussed later). This report does not include the results for tests on body wires and farm wires. There must be a report or signed letter from T J Sprott and Associates which presents the details of these latter results which are very important for the matter under consideration. I would wish to cite this letter/report.

Todd's data for the Report Ref: 17.67, Report of H. J. Todd, as mentioned above, comes primarily from the Report from the Chemistry Division of the Department of Scientific and Industrial Research, DSIR, dated 28th October 1970, AR 583. Inspection of the data in this report, AR 583, for the composition of body and farm, galvanised steel wires shows that 15 data points in the Report Ref: 17.67, differ from those in Report AR 583. Some of the values have increased and some decreased. I presume for this Report, Ref: 17.67, Todd either re-did the testing or re-worked/re-calculated his existing raw data. As with Devereux's data for this Report Ref: 17.67, there is no official source for Todd's data it just appears in Report Ref: 17.67.

- On page 09.01.0299 or 281 or 283, Todd is questioned about his measurement of silicon, Si, which he detected at 0.001% but quantitatively listed as <0.02%. Ryan said it had "no significance", Todd responded "is exceedingly significant". In terms of a specification, an element can be quoted as a maximum as with the rimming steel mentioned above e.g. Si_{max} 0.05, and thus if silicon is <0.02%, the steel is within specification and it also tells you something about the type of steel.
- On page 09.01.0300 or 282 or 284, Ryan presents the standard deviation, σ, for Sprott's results for the elements Ni 0.0006%, Cr 0.0004% and Cu 0.0001%. Todd questions how they were derived, "multiple tests on the same solution of one dissolved steel wire sample or multiple tests on separate samples of steel wire". Ryan replied that it was the latter, multiple tests on different specimens. Todd noted "then the deviation was then very good". I would wish to see the report from T J Sprott and Associates which details these tests to confirm this data. To get a standard deviation, σ, for Cu say of 0.0001%, would imply that in 5 repeat tests the variation between each result would only be in the 4th dp, and then only by a small amount, like 1,2 or 3.

On this page, Ryan also makes the statement that "all drawn steel wire has carbon content from 0.017 to 0.0017%". Todd said "that is not correct have you heard of high tensile wire". Piano wire, which is used in pianos, is very high tensile steel wire which can have carbon contents of between 0.7 - 1.0%. Development of this wire commenced in the 1840's and the modern form was available in about the 1880's.

Also on this same page the question of manganese, Mn, addition to the wire is raised by Ryan. Todd notes "that for the British Standard BSS 1052 (I find some of these Standards have been withdrawn) the chemical composition is given as P_{max} 0.06 & S_{max} 0.06 and C & Mn are not specified". It is then up to the steel maker to meet the other requirements, strength, ductility, heat treatment etc. by choosing the appropriate composition. With such a composition, Mn will be included because it is needed to control the sulphur by forming MnS, otherwise there could be embrittlement of the steel wire.

- On page 09.01.0302 or 284 or 286, in response to questions, Todd notes the significance of Si in steels," that this wire would have been made/drawn from a rimming steel and that the composition of the wire is in-homogenous with the composition in the rim slightly different from the remainder". Which is correct?
- On page 09.01.0303 or 285 or 287, second to last paragraph, in answer to a question, Todd's response implies when he was testing he made 5 examinations of each sample and all 5 results always fell within his error band of ± 0.01%. In the last paragraph, Todd is asked the question "When it was put to you Dr Sprott's standard deviation was, 0.0006% for manganese ----." Sprott and Devereux did not measure Mn so this must be Ni?
- On page 09.01.0304 or 286 or 288, line 14, in answer to a question, Todd gives further information on his experimental method: "the same piece of wire was used over and over again but each time a fresh surface was sparked and the wire was also cleaned very carefully". Also on page 287/289, line 8, Todd states that he "at least did 2 tests on each wire, often 3 or 4, sometimes 6".
- On pages 09.01.0304 & .0305, or 286/288 & 287/289, Todd is questioned about his and Devereux's comparison of body wires with Thomas farm wires, for each of the elements Ni, Cr & Cu. For each of the elements he argued that his and Devereux's results within the respective error bands, essentially confirmed the body wires were the same as the farm wires and the "fit" was better for some wires than others: "I set an experimental error for every element of plus or minus a certain figure; if the amount was within half that range it was rated "excellent"; if amount was within that range it was rated "good"; if it was outside that range it wasn't rated at all".

5.0 Comment: T J Sprott and Associates Chemical Analysis

Analysts, Industrial and Consulting Chemists
T J Sprott L B Speckman I Devereux

For the following review, attribution of statements by T J Sprott and I Devereux will be made to the Court Transcript, supplied to me by Detective Superintendent Lovelock, by page number. Dr Devereux, who did the analysis, had about 11 years of experience, 6 years as a research chemist with the Institute of Nuclear Sciences, DSIR and 5 with T J Sprott and Associates [see p09.03.0405]. He reports the analysis of three elements Ni, Cr, and Cu for the composition of steel wire when examining the variation in composition along lengths of steel wire [see p08.13.0004] and also when comparing body and farm steel wires [see Ref: 17.67]. As I have said previously, it is usual practice when determining the composition of steel to determine C, Si, Mn, P &

S. The first three C, Si and Mn are essential for they give an indication of the steel type and it is normal to include S and P because in most specifications they are included as maximums otherwise they lead to embrittlement. Analysing only the three elements Ni, Cr, and Cu would give no indication the material was steel and what type. For some of the tests on lengths of wire, Devereux lists the Analysis Certificate which gives the composition for C, Si & Mn, so we know this wire was steel wire. For the body and farm wires Todd's composition analysis shows they were steel wires and what type. Devereux did not analyse for C, Si, S & P because his Flame-AAS method could not analyse these elements (see Table 1 above). I would have expected, that being professional Consulting Chemists, they should have used some other technique to determine these elements rather than relying on Todd's results. Their composition results should have been able to stand alone. On page 411 of the Transcript, Baragwanath asks Devereux whether he agreed with Todd's composition results for each of the elements C, Si, Mn, Mo & V, asking of each element in turn and in that order and Devereux replied he did.

Specific statements from the Court Transcript are discussed below:

- On page 09.03.0405 or 403, line 19, the Transcript refers to work done by Devereux where chemical composition was determined along long lengths of wire to check variation of composition with length. The results are given in a report from T J Sprott and Associates at page 08.13.0004 (attached). The report does not state the method of analysis, the preparation of the wires in that is the zinc coating removed, or if duplicate tests were done at each location and if they were, were they on the same solution of dissolved steel wire or a different sample of steel wire. The only elements analysed for were Ni, Cr & Cu. In a similar exercise Todd analysed for C, Si, Mn, Ni, Cr, Mo & V to look for the compositional variation with length. I would have expected that Devereux should have at least also determined C, Si & Mn, because it was steel wire. The report details tests on a 100 ft coil of 16 gauge, galvanised steel wire, with tests at various locations, also tests on a1000 ft coil of 12 gauge, galvanised steel wire, again with tests at various locations and tests on two 1 ton coils, of 10 gauge, plain steel wire, at the coil ends. These latter coils were each drawn from a single billet, by Ajax TKN (p 09.03.0410 or 408. Note: is TKN not GKN), poured from the same melt with an Analysis Certificate showing C 0.077%, Si <0.02% and Mn 0.35%. To evaluate this data in more detail, the maximum difference, Δ, between measured compositions along each wire are listed in Table 3, where the data in brackets, for galvanised wire, have been rounded up to 3 dp.

Elements	100 ft 16gauge wire: max. Δ between locations	1000 ft 12gauge wire: max. Δ between locations	1 ton coil wire No 1: max. Δ between locations	1 ton coil wire no 2: max. Δ between locations
Ni	0.0025 (0.003)	0.0011 (0.001)	0.0003	0.0007
Cr	0.0014 (0.001)	0.0006 (0.001)	0.0004	0.0002
Cu	0.003 (0.003)	0.001 (0.001)	0.0003	0.0007

Table 3 max. Δ = maximum difference in composition between different locations along steel wires

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

The Table is to be read with the T J Sprott and Associates Report at page 08.13.0004. The differences for the TKN un-galvanised wire, which will not be zinc coated, are generally smaller than for the galvanised wire.

Devereux concludes from his results [p 09.03.0405 or 403, line 34] that "one must come to the conclusion that the composition of wire, especially the proportions of certain trace or tramp metals is very constant along a length of wire". If the errors discussed above for this method of analysis, and the standard deviations presented by Ryan for the method, which for copper was 0.0001, are taken into consideration, the conclusion that the composition is constant along the wire length is not established. For an analytical method with the accuracy stated, the composition difference, Δ, of 0.003 for Cu, in the 16 SWG galvanised steel wire, is significant and I conclude that the composition varies, albeit slightly, along a length of this galvanised steel wire. So that readings in two different locations could be slightly different when determined with a very accurate instrumental method. That there is a variation is not surprising, for as said above, this wire is not a homogenous material. Devereux's conclusions would have been more convincing if C, Si and Mn had also been determined and been shown to be constant. If, for argument, we accept Devereux's conclusion that there is no variation in composition along the length of the wire, then the differences observed in Table 3 must surely come from the experimental error so the accuracy/standard deviation as stated by Ryan of 0.0001 for copper must not be correct and the composition difference, Δ, of 0.003 for Cu in the 16 SWG galvanised steel wire, would be the appropriate experimental error for copper for this method of analysis.

Todd, with his technique noted differences of the same order being to 3 dp, 0.001 – 0.005, (see Table 2) with Mn showing the greatest variation, 0.014 – 0.045, where as noted above, he measured concentration to an accuracy of 0.001%, 3 dp, but generally the error is assessed at ± 0.01%. His measured differences for composition determination along a length of 16 SWG galvanised steel wire, are of the same order as those of Devereux's rounded up data. Todd in assessing the error as ± 0.01%, 2 dp, notes there is no variation in composition along the wire, which would be correct. Devereux who can measure to 0.0001, 4dp, for Cu, with a standard deviation of 0.0001, can readily detect differences in composition of 0.003 for Cu, because his instrumental method has an order of magnitude lower detection limit. Thus the differences reported by Devereux are significant and result from variation of composition along the wire and not from instrumental error. Thus when the AAS technique is used to determine the composition along a wire, it will vary along the length of the wire, showing variation to the 3rd dp. This technique may be able to measure to 0.0001%, 4dp, with a standard deviation of 0.0001, but when the compositions from different locations in a 16 SWG galvanised steel wire are compared, the inherent error that is to be considered must necessarily be of the order of ± 0.001%, the difference in composition reported above. The same outcome will hold when comparing compositions from different 16 SWG galvanised steel wires.

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

If exactly the same volume is analysed, which is possible with the AAS technique because the wire is dissolved in a solution and small portions of the solution can each be analysed, then the performance discussed above, "measure to 0.0001%, 4dp, with a standard deviation of 0.0001 for Cu determination", can be achieved with the AA technique. Ryan in reporting this performance (page 09.01.0230 or 282 or 284), in answer to a question from Todd, "how were they derived, multiple tests on the same solution of one dissolved steel wire sample or multiple tests on separate samples of steel wire", replied "that it was the latter, multiple tests on different specimens". If the standard deviation was derived as reported by Ryan, it is difficult to see how it can be 0.0001, when T J Sprott and Associates measured compositional differences of 0.001 – 0.003 for measurements at different locations along a 16 SWG galvanised Steel wire. Ryan the Counsel may have misunderstood the question and I can find no comment from the Transcript, by Devereux in his testimony on this matter.

On this same page Devereux is asked about the Table Todd was asked to produce of his data for the Court and did he, Devereux, insert in brackets his own data on the same table, which he did. As I said before this crucial information does not seem to appear in a letter or report but rather is just entered in some table which happened to appear in the Court. What do we know about the test method, were there repeat tests and were they on the same liquid of the dissolved sample or different samples ,was the zinc coating removed before testing etc. One has to question the integrity of such data which seems to have been produced under urgency. It does not appear under the letterhead of T J Sprott and Associates, but rather on a document produced by Todd: Report of H J Todd, Ref. 17.67. I also note that this document contains Todd's results for Cu, which do not appear, as far as I can tell from the transcript, in any official report or letter from the Department of Scientific and Industrial Research, DSIR. They also appear to have been produced under urgency. The only metals which were analysed by Devereux and which appear on this document are Ni, Cr and Cu. The results by Todd for Ni and Cr generally agree, within Todd's error band of ± 0.01%, with those of Devereux, for all wires tested. In considering Devereux's results for Ni and Cr, account must be taken of the variation in composition he found for these elements along the length of a 16 SWG galvanised steel wire of 0.003 and 0.001 respectively. This variation can be considered as a positional compositional error because both Todd and Devereux analysed wire from different locations along the same wire. The results for Cu show there is, within the errors stated, a constant difference in composition between the results of Todd and Devereux, which would seem to have arisen from the experimental procedure. Todd mentions, see page 4 above, that he "subsequently confirmed" a constant error, resulting from small sample size, for the copper determination. I have checked the Transcript but can find no further information on this constant error and how it arises.

To evaluate the data from the Todd Report: Report of H J Todd, Ref. 17.67, in more detail the results for Todd and Devereux are listed in Table 4 below, together with the data range as determined by the effective error for each analysis method. Todd can

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

read/measure to 0.001 but the error was assessed at ± 0.01%. Devereux can read/measure to 0.0001 with a standard deviation of 0.0001 for Cu, but when the compositional variation along a wire is taken into account (Devereux found for 16SWG, galvanised, steel wire that the variation in Cu composition along the length of the wire was 0.003%.), and as each test by each analyst is done on a different piece of wire the effective errors for Devereux's results become, see Table 3, for Ni 0.003%, Cr 0.001% and Cu 0.003%, taking the maximum variation into account. Hence rather than using Devereux's errors for determination of Ni, Cr & Cu of 0.0006%, 0.0004% & 0.0001% respectively, the compositional variation discussed above is more appropriately used eg. Ni 0.003%, Cr 0.001% and Cu 0.003%. Devereux's composition results are entered in Table 4 but the data range entered, is that determined by myself and thus the entry is under Devereux – F (Ferguson).

The comparison made of the composition of various Police Exhibits of 16 SWG, galvanised, steel wire in Table 4, includes the results of H J Todd and Drs Sprott and Devereux, but as Sprott and Devereux only analysed for Ni, Cr and Cu, only the results for these three elements are included. Todd analysed for eight elements, but for three, Si, Mo & V, the compositions were less than his instrumental limit of detectability. The composition results in the table are given as a composition range eg. for Todd, Ni, 0.07 ± 0.01%, 0.06 – 0.07 – 0.08. The range is taken from the error range which for Todd is ± 0.01% and Devereux, for 16SWG galvanised steel wire, determined from his results for composition variation with length of wire, as Ni 0.003%, Cr 0.001% and Cu 0.003%, for maximum variation. It should be noted that the Devereux-Ferguson error bars are entered in Table 4 and Figures 1 – 3 as ± values, but that because they come from the maximum variation, they should be read as being either above or below the value but not both above and below. This follows practice in modern Standards: NZS/BS 970.1:1991.

The composition data from Table 4 are re-plotted in Figures 1 – 3 as bar charts for the elements Nickel, Ni, Chromium, Cr, and Copper, Cu, respectively, to give a clearer perspective of the error bands associated with each analytical method, for each Police Exhibit. In Figures 1 & 2, Devereux's data appears under Devereux – F (Ferguson) and in Figure 3, under D/F = Devereux/Ferguson .

In comparing the composition results from each analyst for each element, it is necessary to firstly check the difference between the results in case there are any instrumental effects. Both instrumental methods should produce the same result for a composition, but in some circumstances they may not and there may be a small constant error present. Neither analyst has said what standards they checked their instruments against nor is there information in the Transcript that they both checked against the same standard.

From Table 4 and Figure 1, within the respective error bands, the composition results for Nickel, Ni, from Todd and Devereux are the same, with perhaps a very small

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

Comparison of the Compositions of 16 SWG, Galvanised, Steel Wire, Police Exhibits PE				
Element		Nickel – Ni %	Chromium – Cr %	Copper – Cu %
Error	Todd	± 0.01 %,	± 0.01 %,	± 0.01 %,
	Devereux-F	0.003 %,	0.001 %,	0.003 %,
PE		Ni %	Cr %	Cu %
288/2	Todd	0.06 - **0.07** – 0.08	0.04 – **0.05** – 0.06	0.17 – **0.18** – 0.19
	Devereux-F	0.0700 – **0.0730** – 0.0760	0.0400 – **0.0410** – 0.0420	0.1160 – **0.1190** – 0.1220
320A	Todd	0.06 – **0.07** – 0.08	0.04 – **0.05** – 0.06	0.16 – **0.17** – 0.18
	Devereux-F	0.0700 – **0.0730** – 0.0760	0.0420 – **0.0430** – 0.0440	0.1290 – **0.1320** – 0.1350
323	Todd	0.07 – **0.08** – 0.09	0.04 – **0.05** – 0.06	0.16 – **0.17** – 0.18
	Devereux-F	0.0710 – **0.0740** – 0.0770	0.0420 – **0.0430** – 0.0440	0.1290 – **0.1320** – 0.1350
325	Todd	0.07 – **0.08** – 0.09	0.04 – **0.05** – 0.06	0.16 – **0.17** – 0.18
	Devereux-F	0.0700 – **0.0730** – 0.0760	0.0430 – **0.0440** – 0.0450	0.1300 – **0.1330** – 0.1360
328D	Todd	0.06 – **0.07** – 0.08	0.04 – **0.05** – 0.06	0.15 – **0.16** – 0.17
	Devereux-F	0.0700 – **0.0730** – 0.0760	0.0430 – **0.0440** – 0.0450	0.1280 – **0.1310** – 0.1340
334	Todd	0.06 – **0.07** – 0.08	0.03 – **0.04** – 0.05	0.17 – **0.18** – 0.19
	Devereux-F	0.0700 – **0.0730** – 0.0760	0.0425 – **0.0435** – 0.0445	0.1290 – **0.1320** – 0.1350
288/1	Todd	0.07 – **0.08** – 0.09	0.04 – **0.05** – 0.06	0.135 – **0.145** – 0.155
	Devereux-F	0.0720 – **0.0750** – 0.0780	0.0430 – **0.0440** – 0.0450	0.0890 – **0.0920** – 0.0950
324A	Todd	0.07 – **0.08** – 0.09	0.04 – **0.05** – 0.06	0.12 – **0.13** – 0.14
	Devereux-F	0.0700 – **0.0730** – 0.0760	0.0440 – **0.0450** – 0.0460	0.0840 – **0.0870** – 0.0900

Table 4 Results from Report of H. J. Todd, Ref 17.67, including those of Drs. Sprott & Devereux

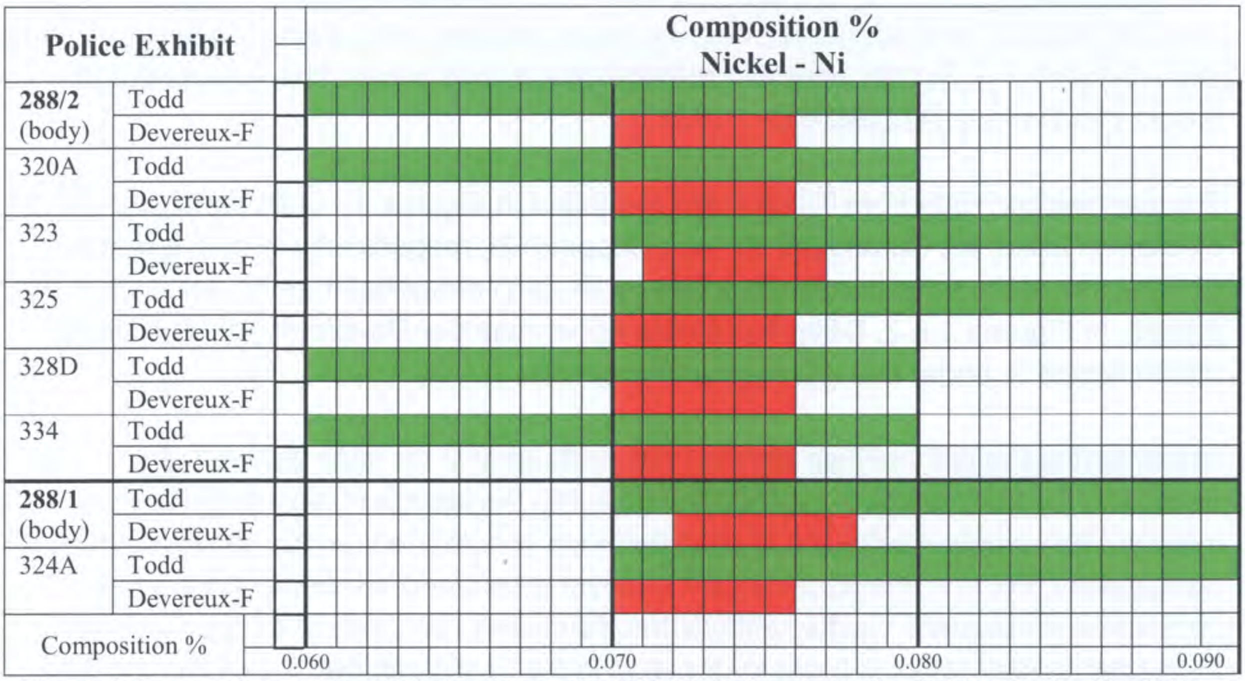


Figure 1 Comparison of the Nickel content of 16 SWG, Galvanised, Steel Wire, Police Exhibits

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

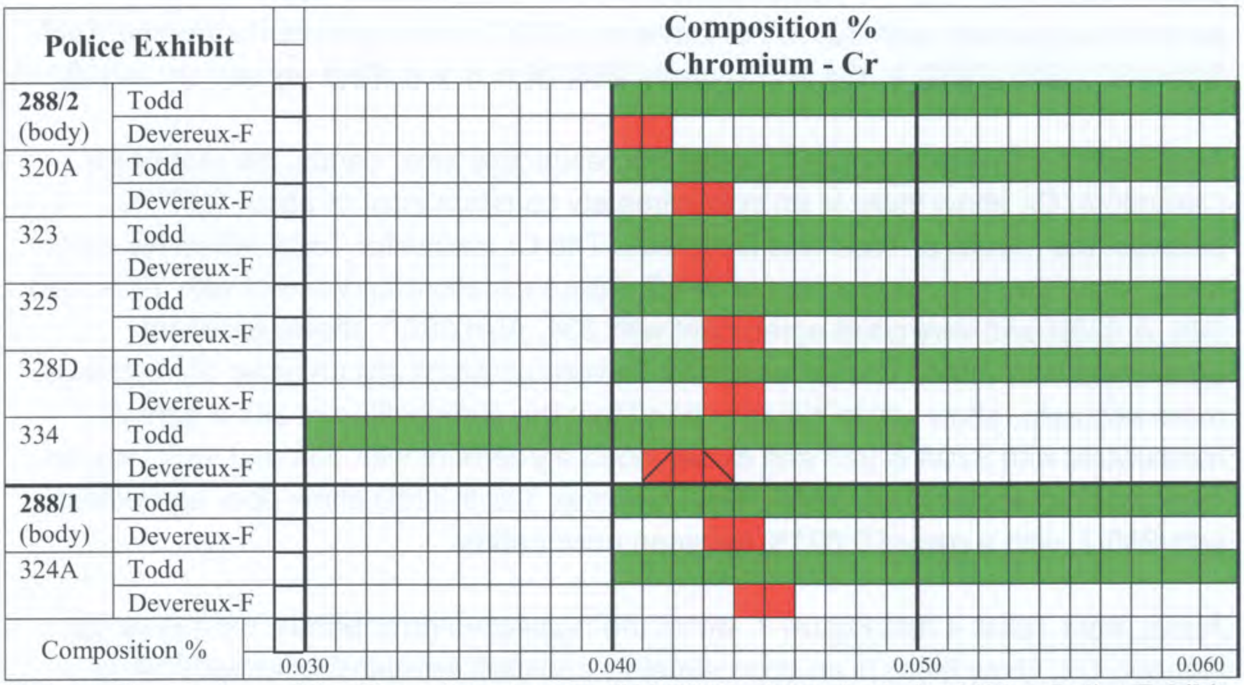


Figure 2 Comparison of the Chromium content of 16 SWG, Galvanised, Steel Wire, Police Exhibits

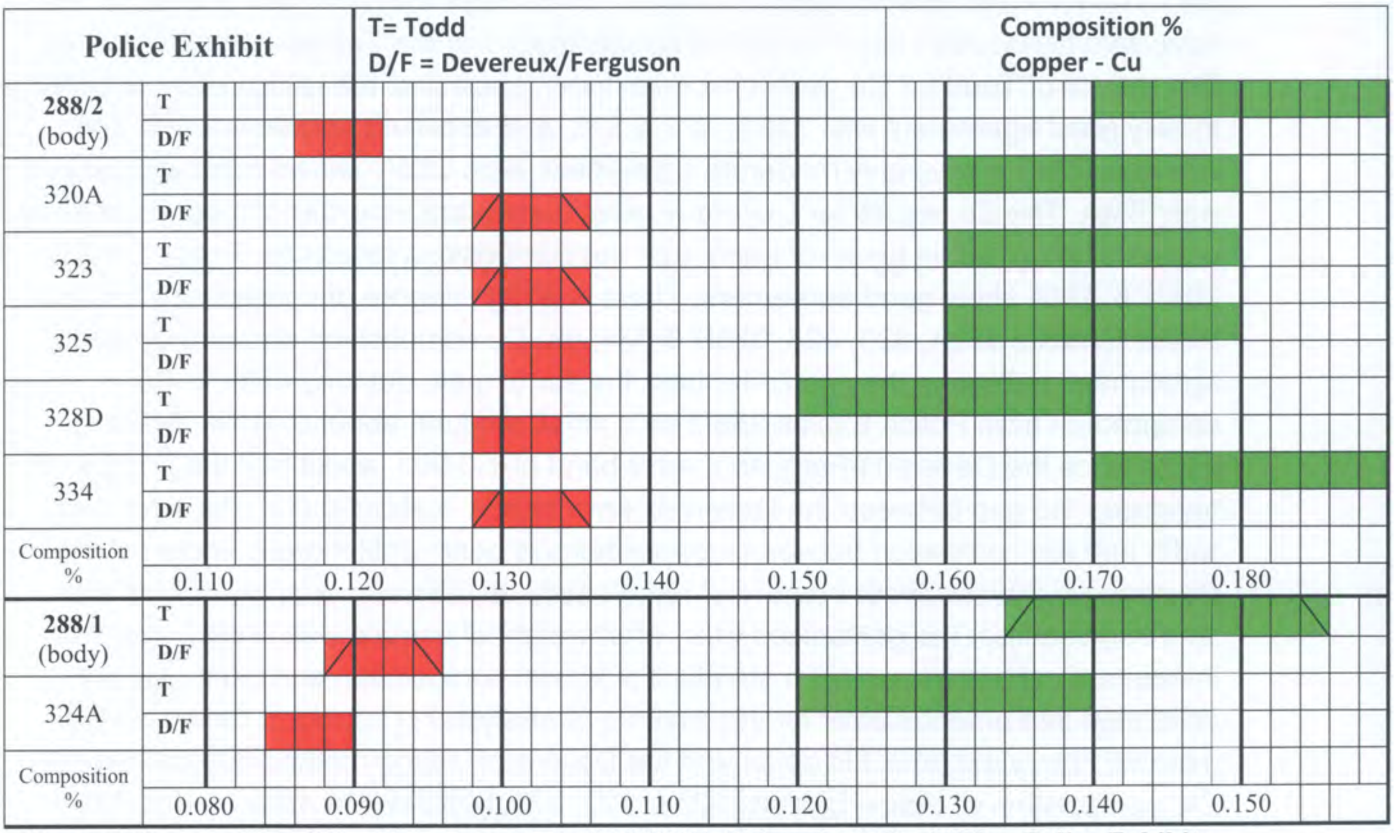


Figure 3 Comparison of the Copper content of 16 SWG, Galvanised, Steel Wire, Police Exhibits

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

constant difference between them. For Todd 288/2 shows excellent agreement with 320A, 328D & 334 and very good agreement with 323, & 325. Also 288/1 shows excellent agreement with 324A. For Devereux 288/2 shows excellent agreement with 320A, 323, 325, 328D & 334 and similarly 288/1shows excellent agreement with 324A.

Also, from Table 4 and Figure 2, within the respective error bands, the results for Chromium, Cr, show there is an approximately constant error of about 0.007% between the results of Todd and Devereux. The Cr results for Todd, within his error band, show that the composition of 288/2 shows excellent agreement with 320a, 323, 325, & 328D and very good agreement with 334. Also 288/1 shows excellent agreement with 324A. The Cr results for Devereux, which are an order of magnitude more accurate, show within his error band that the composition of 288/2 agrees moderately with 320A & 323 and shows good agreement with 334 and 288/1 shows very good agreement with 324A. For Devereux 325 & 328D show poor agreement with 288/2, with a gap of 0.001% between error bands.

Again, from Table 4 and Figure 3, within the respective error bands, the results for Copper, Cu, show there is an approximately constant error/shift of about 0.04 % between the results of Todd and Devereux. Please note that there are two separate x–axis scales in Figure 3, one for Police Exhibits 288/2, 320A, 323, 325, 328D & 334 and the other for Police Exhibits 288/1 & 324A. Todd notes this shift, see above, but as I have said previously I can find no further information in the Transcript on the matter. The results of Todd for Cu, within his error band, show that the composition of 288/2 is in very good agreement with 320A, 323 & 325, and excellent agreement with 334 whereas 328D shows only moderate agreement. Also 288/1 shows good agreement with 324A. The Cu results for Devereux, which again are an order of magnitude more accurate, show within his error band, that the composition results for Police Exhibits 288/1 & 324A show good agreement. There is a high degree of consistency between Police Exhibits 320A, 323, 325, 328D & 334, the Cu composition showing excellent agreement, indicating they could be from the same melt, but they differ in Cu composition from Police Exhibit 288/2 by a small amount, about 0.013%, which is about twice the Devereux-Ferguson error band of ± 0.003, about half the Todd error band and the gap between the Devereux error bands is about 0.006, the error band width and the correlation between compositions is poor. Until more is known of the Devereux testing method: number of repeat tests on different samples of wire, was zinc stripped from the galvanised wire, what weight of sample was tested, was the instrument calibrated against a standard of known composition and what was the calibrated instrumental error for this method of analysis?; I conclude based on the material I have examined in detail and the Devereux testing method that the copper, Cu, composition of Police Exhibits 320A, 323, 325, 328D & 334 differ by one error band width from that for Police Exhibit 288/2 and show poor agreement with same.

Further specific statements, by Devereux, from the Court Transcript are discussed below:

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

- On page 09.03.0407 or 405, line 15, the Transcript refers to Devereux's response to a question from Baragwanath –" Mr Todd had already seen the figures in my first schedule together with our standard deviation". I do not believe I have cited this *first schedule* with the *standard deviation* information. I would like to cite this document please.
- On page 09.03.0408 or 406, line 27, the Transcript reports the following comment by Devereux: "I have carried out analyses of standard iron samples which are internationally accepted using identical method to those in these two schedules and achieved excellent agreement of a similar order to that presented on the schedule with those standards". This represents the instrumental/method calibration I was noting above, but as it stands the statement is meaningless because for what was the experimental method – number of repeat tests, elements analysed, were C, Si & Mn analysed, and most importantly what were the results, the standard deviation and the error band. This work would have been definitive if we had been given the results but we are given not a single number and this work is all about numbers and their significance. Words are of no import.

In the second to last paragraph on this page and the subsequent page, Devereux reports that he analysed for Co, Ni, Cr, Cu, Mo and Sn, but that Co, Sn & Mo levels were very low/small and he was not able to standardise levels in his instrument and his instrument was not capable of differentiating between different steel wires using these elements. Todd also analysed elements, Si, Mo & V which were in concentrations which were less than the detectability limit for his instrument, but in each case he gave us the values of those limits, which were < 0.02, < 0.05 & < 0.005 respectively. Such information gives confidence in the experimental technique and a more complete picture of the composition of the steel wire. It is most disappointing that Devereux did not present the same information and tell us what the levels of Co, Sn & Mo were in the steel wire. He has said previously that his experimental method was very accurate, but he has not told us what the concentrations of Co, Sn & Mo were in the steel wires or his instrumental detectability limit for these elements and because he could not differentiate between steel wires with these elements, did not analyse for them. Devereux in discussing concentration levels (page 09.03.0409 or 407, last sentence) of analysis, states he has analysed down to 0.000001 (0.01ppm), but did not state with what instrument and what element.

- On page 09.03.0410 or 408, of the Transcript there is discussion of the analysis for C, Si & Mn and Devereux reports that it is not possible to examine for C with AAS and that he did not have quantitative results for Si & Mn, so these three important elements for steel were not analysed for. Also Devereux states that "to differentiate between samples of wire from different batches of steel it is necessary to accurately and precisely measure the levels of trace elements which are constant throughout a whole batch of steel", such as Ni, Cr & Cu and that the elements C, Si & Mn can vary, especially Mn which can form segregations. As I have said above, in wire the segregated material will finish up near the centre of the wire and considering Mn, which forms MnS, the segregated material, is strung out as stringers in the wire and is visible as a grey phase under optical microscopy. Now if a small volume of material is occupied by MnS it cannot be occupied by any other elements and the same is true of other segregated material, so in these locations elements such as Ni, Cr & Cu cannot occupy the volume and hence cannot be "constant throughout a whole batch of steel". This effect may be very small but then Devereux's AA analysis method is very accurate.

- On page 09.03.0411 or 409, line 7, of the Transcript, Devereux in answer to a question from Baragwanath "Would you not agree the more elements you can compare the better", responded "if each element is determined accurately enough that would be correct". The question then is why did they not determine more than three. T J Sprott and Associates, must surely have been a competent professional organisation that employed more than one method, AA, for chemical analysis, and have used other methods to determine the concentration of more elements in the steel wire, rather than rejecting the analysis for C, Si & Mn because they varied too much or they segregated, and Co, Sn & Mo because the concentrations were too low. If the concentrations were too low for their analytical instruments to analyse then at least give the limits of detectability of the instruments.
- On page 09.03.0412 or 410, line 11, Devereux in response to a question from Baragwanath, notes that the Standards for 16 SWG steel wire, give values for the amount of C, Si & Mn in the wire, generally a range of values and usually with a maximum value. This is correct. He then implies that most 16 SWG steel wire will have compositions within these standards, which is also correct, but then implies, that because of this, these elements cannot be used to distinguish different wires, all heats having exactly the same composition, which is not correct. His answer would indicate that he does not understand the variation in composition from heat to heat, implying each heat has the same composition. Why did not Devereux determine C, Si & Mn?
- On page 09.03.0413 or 411, line 17, Devereux now gives a figure for his Mo determination, being < 0.05% that determined by Todd, but again does not give his own figure.

6.0 Conclusions:

All though this report is based on the Court Transcript material, for calibration, I have to be more thorough drawn on technical matter and in so doing have tried, where possible to base its relevance to that period around 1970. I make a series of observations as detailed below:

6.1 Steel Wire

Steel can be related back to its original "Heat No.", because for a given class/grade of steel no two heats will have exactly the same composition. The initial elements to investigate to check the composition would be C, Si, Mn, S, & P. Todd determined C, Si & Mn and not S & P, and Devereux looked at Si & Mn, but in the end determined none of the elements. Determining S & P gives some indication of the degree of segregation and the level of non-metallic inclusions/impurities. For the present, the steel is galvanised steel wire, which will have segregated material & impurities strung out along the centre of the wire. The wire composition is not homogenous.

6.2 Chemical Analysis

Two methods are used for chemical analysis of the galvanised steel wire: Optical Emission Spectroscopy – OES, used by Todd and Atomic Absorption Spectroscopy – AAS, used by Devereux. Both methods are suitable for determining elements in steel, with the former method being used routinely in steel works. At the time, both methods were not capable of analysing all the required elements: for the OES method, C & S and for the AAS method a number more. That some elements could not be analysed is not a reason for not determining their concentration, for some other appropriate analytical method should have been used. Both organisations DSIR and T J Sprott and Associates, I would have expected had other analytical techniques available to them. The AAS method is at least an order of magnitude more sensitive than the OES method.

6.3 Todd Chemical Analysis

Todd used the Optical Emission Spectroscopy – OES method of chemical analysis and analysed for the elements: C, Si, Mn, Ni, Cr, Mo, V and Cu, in the 16 SWG galvanised steel wire. In summary, based on his evidence from the Court Transcript, the following is detailed:

- He thoroughly cleaned the specimens before testing.
- He stripped the zinc from the wire before testing.
- For repeat tests the same piece of wire was use over and over again but each time a fresh surface was sparked.
- The results are the mean of duplicate tests and often 3 or 4, or sometimes 6 tests were done.
- He could read results to 0.001 and the error was assessed at ± 0.01% (100 ppm). Reading to 0.001, means Todd could have read all but one of the results obtained by Devereux, which from Report of H J Todd, Ref. 17.67, are only to 3 dp. Todd notes if he made 5 examinations/analyses of each sample, all 5 results always fell within the error band of ± 0.01%. Todd listing all his results to 3 dp, as he did for some, would have been beneficial for comparison purposes even if subsequently rounded up.
- He has not gone into details of the standards he used.
- Of the elements analysed Mo & V were not detected, being less than his detectability limit: Mo <0.05 & V < 0.005. Si was also mostly below his detectability limit of < 0.02 but occasionally was measured at 0.07 & 0.25. It is preferable for such elements, that the detectability limit is quoted, which is standard practice, because it gives a more complete picture of the overall composition. Hence of the 8 elements analysed by Todd, 3 are listed as Si < 0.02, Mo < 0.05 & V< 0.005, being less than the detectability limit and 5 give results which allow for comparison of wires.

- Todd carried out a series of repeatability tests on some wire and also measured the variation in composition at the ends of lengths of wire. If his experimental error of ± 0.01% is assumed and his data, in report AR 529, is rounded up, it essentially shows no variability in composition in the repeat tests, apart from for Mn, and similarly he could find no variation in composition with length, apart from Mn .The difference data in Table 2 shows a very small composition variation with length but when the data in Table 2 are rounded up to ± 0.01%,Todd's observation is confirmed, apart from for Mn.
- Todd determined the concentration of Cu in steel wires by amending his analysis technique, but did not say what the amended technique was. He only seems to have determined Cu during the Second Trial for the results do not appear in Reports AR 529 & AR 583 and are only listed in Report Ref: 17.67, by H. J. Todd, which Ryan asked him to produce during the Court Trial proceedings.
- Todd measured concentration to an accuracy of ± 0.001% but generally he assessed the error at ± 0.01%. Steel Standards quote most elements in a steel specification to two decimal points (2-dp) with some to 3-dp.
- The responses by Todd in the Transcript would indicate he has a sufficient understanding of the metallurgy of steels to appreciate the significance of the elements which make up the composition of steel.

6.4 Devereux Chemical Analysis

Devereux used the Atomic Absorption Spectroscopy – AAS method of chemical analysis and analysed for the elements: Ni, Cr, and Cu, in the galvanised steel wire. In summary, based on his evidence from the Court Transcript, the following is detailed:

- Very little information on the experimental method/procedure:
  - was zinc stripped from the galvanised wire?
  - what was the size of analysis samples?
  - were the results the mean of duplicate (or more) tests?
  - if duplicate tests, were they on the same solution of one dissolved sample or tests on different samples.
- Devereux gives the experimental measurement error for the method for each element as: Ni 0.0006%, Cr 0.0004% and Cu 0.0001%.
- Ryan gives the standard deviation for results from each element as: Ni 0.0006%, Cr 0.0004% and Cu 0.0001%, the same as the measurement error. Ryan, the Counsel, also reported that the standard deviation was determined by multiple tests on different samples of steel wire. Devereux made no statement in the Transcript about this and it conflicts with Devereux results on the composition of lengths of wire.

- Devereux analysed internationally accepted standard iron samples for which he got results of a "similar order to that presented on the schedule" (his list of results). The results from this analysis would have been definitive in terms of instrument and method calibration for element determination in galvanised steel wire, but no results or standard deviations for various elements were presented to the Court.
- Devereux planned to determine Co, Ni, Cr, Cu, Mo and Sn, 6 elements, but his instrument was not capable of differentiating between different steel wires for Co, Sn & Mo, so he did not analyse for these elements. He could not examine for C with AAS and he could not achieve quantitative results for Si & Mn, so these three important elements in steel were not determined. Thus only the tramp/trace elements, Ni, Cr, and Cu were determined. For the other elements he did not list the thresholds, below which his instrument would not detect the element, as Todd did. Such information gives a more complete picture of the composition. He thus only determined 3 elements to enable comparison of wires and did not analyse the other 5, or give the detectability limit for them.
- Devereux measured the variation in composition along lengths of 16 SWG & 12 SWG, galvanised steel wire and also 10 SWG plain steel wire (not galvanised). From these results (see Table 3) Devereux concluded that the composition of trace or tramp metals was very constant along a length of wire. The results do not substantiate this claim. It is most interesting to note that the maximum difference, Δ, in composition between various locations along a wire increases as the SWG number, increases, that is the wire diameter decreases (see Table 3). For the 16SWG (the same gauge as the body wire), galvanised steel wire, these differences, Δ, are for Ni 0.003%, Cr 0.001% and Cu 0.003%. It is these figures which are used for the Devereux-Ferguson experimental error/accuracy and not the figures of Ni 0.0006%, Cr 0.0004% and Cu 0.0001%, reported by Devereux. Devereux assumed the wire composition to be homogenous which it is clearly not and not expected to be with segregation, impurities & non-metallic inclusions in the wire.
- Devereux's determination of standard deviation for each element, as reported by Ryan, of Ni 0.0006%, Cr 0.0004% and Cu 0.0001%, is in conflict with his measurements of variation of composition along a wire. Ryan reported they were repeated tests of different samples of the same wire but Devereux showed that for 16SWG galvanised steel wire, tests along the wire can give differences, Δ, in composition of up to for Ni 0.003%, Cr 0.001% and Cu 0.003%.
- Some of the responses by Devereux in the Transcript would indicate he does not have the same depth of knowledge of the metallurgy of steel as does Todd.

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

6.5 Composition Comparison

The composition results for body and farm Police Exhibit samples for Todd are listed in Report Ref: 17.67, Report of H. J. Todd, which also includes the results of Drs. Sprott and Devereux in brackets, together with the respective experimental errors. Sprott and Devereux's results and Todd's results for copper, Cu, appear to have been produced under urgency during the second trial. Report Ref: 17.67 results are re-tabulated in Table 4 along with their respective error ranges, for the elements Ni, Cr & Cu. The results are also plotted as bar charts in Figures 1, 2 & 3 to give a clearer indication of any comparison of the samples:

- From Table 4 and Fig.1, the composition comparison results for Ni from Todd show, for his error band, that Police Exhibit, PE, 288/2 shows excellent agreement with 320A, 328D & 334 and very good agreement with 323, & 325. Also 288/1 shows excellent agreement with 324A. For Devereux, PE, 288/2 shows excellent agreement with 320A, 323, 325, 328D & 334 and similarly 288/1shows excellent agreement with 324A.

- Also, from Table 4 and Figure 2, the composition comparison results for Cr show there is a small shift in the absolute composition between Todd and Devereux's results. Todd's results show, for his error band, that the composition of 288/2 shows excellent agreement with 320a, 323, 325, & 328D and very good agreement with 334. Also 288/1 shows excellent agreement with 324A. The Cr results for Devereux, which are an order of magnitude more accurate, show within the error band that the composition of 288/2 agrees moderately with 320A & 323 and shows good agreement with 334 and 288/1 shows very good agreement with 324A. For Devereux 325 & 328D show poor agreement with 288/2, with a gap of 0.001% between error bands.
- Again, from Table 4 and Figure 3, the results for Cu show there is a shift in absolute composition between Todd and Devereux's results. Todd's results for Cu, within his error band, show that the composition of 288/2 has very good agreement with 320A, 323 & 325, and excellent agreement with 334 whereas 328D shows only moderate agreement. Also 288/1 shows good agreement with 324A. The Cu results for Devereux, which again are an order of magnitude more accurate, show within his error band, that the composition results for Police Exhibits 288/1 & 324A show good agreement. There is a high degree of consistency between Police Exhibits 320A, 323, 325, 328D & 334, the Cu composition showing excellent agreement, indicating they could be from the same melt, but they differ in Cu composition from Police Exhibit 288/2 by a small amount, about 0.013%, which is about twice the Devereux error band of ± 0.003, about half the Todd error band and

the gap between the Devereux error bands is about 0.006, the error band width of 0.006 and the correlation between compositions is poor.

- Devereux analysed 3 tramp (or trace) elements, Ni, Cr & Cu, to determine a match between the various Police Exhibits. He also looked at Co, Mo, Sn, Si & Mn but could not differentiate between steel wires using Co, Mo & Sn or get quantitative results with Si & Mn, so did not continue to analyse for these elements, which is surprising for an analytical method with very high accuracy. He produced no data for any of these tests or gave any indication of the instrumental detection limit for these elements and hence no conclusions can be made as to whether or not analysis for Co, Mo, Sn, Si & Mn would have contributed to the composition comparison between body and farm wires. It is important to note that Todd in sorting farm wires into groups that matched the composition of body wires and those that did not (see DSIR Report AR.583, Section B Galvanised Iron Wire), used the C, Mn, Si, Ni & Cr compositions as the determinates, with C, Si & Mn and especially C as significant determinates, in the sorting. These latter elements are rejected by Devereux as being unsuitable for this purpose, which on examining Section B above, is definitely not the case. .

  Todd analysed 8 elements, C, Si, Mn, Ni, Cr, Mo, V and Cu, with 3, Si, Mo & V, being below his instrument detection limit, which he always listed, Si < 0.02, Mo < 0.05 & V< 0.005. From Report Ref: 17.67, Todd, within his error band, for C obtained excellent agreement between the composition of PE 288/2 & PE's 320a & 323, very good agreement with 325 & 334, but only moderate agreement with 328D and very good agreement between PE 288/1 & 324A. For Mn he obtained excellent agreement between PE 288/2 and 320A, 323 & 325, very good agreement with 334 but only moderate agreement with 328D and only poor agreement between 288/1 & 324A. For Si, Mo & V the compositions are as given above and they never went above these values. Todd at times listed the result/composition to 3 dp, eg. 0.001. It would have been of assistance to have had all results listed as such, but perhaps he then could not justify the error. As reported above the more elements that are compared, at sufficient accuracy, the better the outcome.
- The final/last report, Report of H J Todd, Ref. 17.67, dealing with the comparison of body and farm samples/PE's of 16 SWG galvanised steel wire, as mentioned above, seem to have been produced under urgency during the second trial. Neither Todd's nor Devereux's results appear to have come out as official documents from their respective organisations, Chemistry Division, DSIR and T J Sprott and Associates

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

Chemical Analysis, or at least not on any document I have been asked to consider. In summary there are matters unable to be answered to do with the experimental method that need to be noted for each of the analysts:

- For Todd, what was the shift in composition for the copper, Cu, and how much was it; what surface was sparked, a curved or flat surface; some data/results were given to 3 dp., why not all results; and the results that went into the final, Report Ref: 17.67, were they reworked data or new results. Where did Report Ref: 17.67, Report of H. J. Todd and the data in the report come from?
- For Devereux, was the galvanising stripped from the steel wire; how many repeat tests were done for each result; were the repeats on different samples; what were the results of the tests on the International Standard iron/steel and what were the results for the other elements investigated; Co, Mo, Sn, Si & Mn and the threshold limit, if appropriate, for these. Where did Report Ref: 17.67, Report of H. J. Todd and the Devereux data in the report come from?

- Both analysts are very experienced with their own instrumental methods and one is not questioning their experimental acumen, but they have both do not have the same experience and exposure to the analysis of steel and steel wire. Hence some of the above comments perhaps mean some of the results are not as reliable as they could be.

6.6 Further Consideration of Results from the AAS Analysis Method

In view of some concern over aspects of the AAS analysis method and the significance of the results in the present investigation it is of interest to know what acceptable level of performance is to be expected with the use of this technique. Two Australian- New Zealand Standards, AS/NZS 1050.37:1994 & AS/NZS 1050.39:1 994, which are technically identical to IS0 Standards (International Organization for Standardization), IS0 4943-1985 & IS0 10138: 1991, respectively, outline in detail the application of the AAS technique for the determination of copper, Cu, & chromium, Cr, in steels & irons, respectively. These AS/NZS Standards are a copy of the ISO Standards, which preceded them and include all the ISO Standard material (see Appendix 5 for details of above Standards). For both these Standards, ISO conducted a series of international analytical trials of the method to determine the **Precision** for each element determination. Samples of steel & iron of known composition were sent to a number of laboratories in various countries to determine the sample compositions using the method of the Standard and from these results the **Repeatability, r,** and **Reproducibility, R,** of the method were determined for copper, Cu, and chromium, Cr. The results from these trials reflect application of the method in very good laboratories in different countries by analysts very experienced with steel & iron analysis and thus represent International Best Practice, and give a very good indication of the performance to be expected from

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

this analytical technique. The copper trials were conducted in 1978 and the chromium in 1987. The copper results would be most applicable to the present analytical work which was done between 1970 – 1973, some 5 to 8 years previously. In that time there would have been at least small improvements in the analytical method and analytical instruments, so that data collected in 1978 would also have been a little more robust than that collected in 1970 – 1973.

The trial data showed a logarithmic relationship between copper content and **Repeatability** and **Reproducibility** for both copper and chromium. **Repeatability** and **Reproducibility** are defined in Appendix 5 below, but essentially are the difference in composition between two data points, that is a composition range or band, in which 95 % of the results will fall (equivalent to a 95 % confidence limit). Of the two, **Reproducibility, R**, would seem to be the most appropriate parameter to employ to examine the present composition results, where for Devereux, as reported in the Transcript, more than one person did the chemical analysis. The **Repeatability**, **r**, and **Reproducibility, R**, results for the ISO Standards Trial, for copper, Cu, and chromium, Cr, are summarized in Tables 5 and 6, respectively as r & R versus composition (see Appendix 5).

Of the composition data in the Report of H. J. Todd 17.67, which includes that of Drs Sprott & Devereux, the Devereux data for chromium, Cr, & copper, Cu, which was determined using the AAS technique, are examined using the findings of the AS/NZS Standards, AS/NZS 1050.37:1994 & AS/NZS 1050.39:1 994 for copper, Cu, and chromium, Cr, respectively. The **Reproducibility, R**, for Devereux copper and chromium data, is determined using Tables 5 & 6, and also appropriate graphical information from the respective Standards. The findings are presented in Table 7 where the **Reproducibility** bands for the body wires, 288/2 & 288/1, are indicated in square brackets for both chromium, Cr, and copper, Cu, and the compositions of the Police Exhibits (PE): 320A, 323, 325, 328D, 334, & 324A are also listed. It can be seen that for chromium, Cr, the respective PE Exhibit farm wire compositions, all fall within the **Reproducibility** bands for body wires 288/2 and 288/1. Similarly for copper, Cu, the respective PE Exhibit farm wire compositions all fall within the **Reproducibility** bands for body wires 288/2 and 288/1.

Re-examination of the composition data for chromium, Cr, & copper, Cu, determined with the AAS technique, using the findings of the ISO Trial for these elements, which would have been carried out by experienced ferrous analysts in different laboratories and countries, has shown that there is a strong correlation between the composition of body wires and farm wires and one would have great difficulty in concluding that PE body wires and respective farm wire, for chromium, Cr, were not of the same composition and similarly so for copper, Cu. Thus in the present assessment the findings produced by application of the **Reproducibility** from the ISO Trial, cannot be ignored. Taking these findings for

Devereux's results for chromium, Cr, and copper, Cu, together with his results for nickel, Ni, and Todd's results for C, Si, Mn, Ni, Cr, Cu and Mo & V, and previous comments on composition comparison in the Report, one would have to conclude with a degree of confidence that, overall, the composition analysis supports the thesis that the respective body wires and farm wires have the same composition. Thus 288/2 and 320A, 323, 325, 328D & 334 have the same composition and come from the same heat and similarly 288/1 and 324A have the same composition and come from the same but a different heat.

Comparison of the Cr & Cu Composition in 16 SWG, Galvanised, Steel Wire, Police Exhibits (PE)			
Element		Chromium – Cr %	Copper – Cu %
Error – bands	Todd	± 0.01 %,	± 0.01 %,
	Devereux	0.0004 %,	0.0001 %,
	Devereux - Ferguson	0.001 %	0.003 %
	Devereux – Std.1050.37		r = 0.008 and **R = 0.014**
	Devereux – Std.1050.39	r = 0.002, R_w = 0.003 and **R = 0.005**	
PE		Chromium Cr %	Copper Cu %
288/2	Devereux – 1050.37	R = Reproducibility	**[0.1190 – 0.014 - 0.1330]**
	Devereux-1050.39	**[0.0410 – 0.005 – 0.0460]**	R = Reproducibility
320A	Devereux		**0.1320**
	Devereux	**0.0430**	
323	Devereux		**0.1320**
	Devereux	**0.0430**	
325	Devereux		**0.1330**
	Devereux	**0.0440**	
328D	Devereux		**0.1310**
	Devereux	**0.0440**	
334	Devereux		**0.1320**
	Devereux	**0.0435**	
288/1	Devereux – 1050.37	R = Reproducibility	**[0.0820 - 0.01- 0.0920]**
	Devereux-1050.39	**[0.0440 – 0.005 - 0.0490]**	R = Reproducibility
324A	Devereux		**0.0870**
	Devereux	**0.0450**	

Table 7 Comparison of Devereux Chromium and Copper Composition in Police Exhibits using the Reproducibility bands defined in AS/NZS 1050.37 and 1050.39

7.0 Concluding Comments

In response to a series of specific queries from Lovelock, concerning the review, I respond as follows:

- In this particular case was optical emission spectroscopy (OES) or atomic absorption spectroscopy (AAS) the most appropriate analytical approach to take. Is one superior to the other and if so why? Do either have limitations or alternatively, greater scope?

The OES method could analyse more elements. Todd analysed for 8, C, Si, Mn, Ni, Cr, Mo, V & Cu of which 5 gave results for comparison and 3 Si, Mo & V, were below the detectability limit, although Si was occasionally above the limit. Todd used the above elements, except Cu, to initially sort the wires, with C being important. Sorting with 5 elements is more convincing than using only 3, Ni, Cr & Cu. Devereux, using the AAS

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

technique, analysed for 6 elements and also attempted to analyse Si & Mn, but only 3, Ni, Cr &Cu, were used for comparison and no information was reported for the other 5. The AAS method is more accurate but in the present case it is not clear how the experimental errors and standard deviations were determined. Todd could read to 0.001% and listed some results to 3dp but generally listed his error as ± 0.01%. Devereux listed his error for Cu as 0.0001 but when compositional variation, which he measured and said was constant, in a length of wire, is considered this error becomes 0.003%, 30 times greater, so effectively measuring to 3 dp. Todd did not always list his results to 3 dp, making comparison in some cases difficult. Using the Reproducibility, R, data determined from the ISO Standard Laboratory Trial, gives a convincing expectation of the level of performance to be expected from AAS technique for the analysis of Cr & Cu in steel. The greater the number of elements determined the more convincing the separation of samples and in this respect the OES technique has advantage The AAS technique will analyse fewer elements and in the present case only 3, Ni, Cr & Cu. The AAS technique is nominally more accurate, but the Reproducibility, R, data mentioned above, gives a much clearer picture of the performance, experimental errors, to be expected for the period in which the compositions were determined, !970 -1973. In steel plants the OES and modern variants are used routinely for composition determination in steel production.

- Was Mr TODD's analysis complete and was he entitled to draw the conclusions he did, based on the results of his analysis?

Yes. He generally explained his experimental method apart from those matters discussed above. He had problems with Cu and it is not clear where the results in Report Ref; 17.67 came from. For comparison it would have been helpful to list results to 3 dp even if rounded up later.

- Was Mr DEVEREUX's analysis complete and was he entitled to draw the conclusions he did, based on the results of his analysis?

Yes. His experimental method has some queries as discussed above and his determination of errors is not justified, his actual errors being at least an order of magnitude greater than quoted and similarly it is not clear where the results in Report Ref; 17.67 came from. His method is more accurate but this accuracy is tempered by the experimental error determined for the experimental method. Also in interpretation of Devereux's results for Cr & Ni, cognizance must be made of the findings of the ISO trial which generally brings the AAS results for Cr & Ni into perspective.

- What is the significance of the difference of the results for copper between Mr TODD and Mr DEVEREUX? It is noted that both individual scientists' results seem to be consistent with themselves however different from each other. Can you explain these differences, and their significance, in words that can be most easily understood by non-experts.

There is a constant difference of about 0.04% between the two sets of results. This most probably results from experimental technique. Todd reported he needed to change his method to determine copper but did not elaborate on this change. He also noted the constant difference between the two sets or results but did not fully explain the reason why, apart from noting it was related to a specimen size effect, which I do not understand.

- Mr TODD stated that results based upon atomic absorption spectroscopy cannot always be relied upon when analysing metals. Is he correct in making this claim?

With the AAS technique some elements cannot be analysed for. In the 1960s the elements, C, Si, S, P, Al, Mo, Nb, V, and Ti could not be analysed for. C, Si, Mn, S & P are very important elements for determining if a steel is in specification and hence need to be analysed. Also the AAS method has a lower detectability limit but if the material is not truly homogeneous unlike steel where there is segregation, non-metallic inclusions and impurities, the variation in composition with position may swamp and far exceed the standard deviation and experimental error of the AAS technique. See previously.

- Mr TODD said that he did not think the differences between Mr DEVEREUX's figures for copper were significant. Again, is he correct in making this claim?

If the Reproducibility, R, data determined from the ISO Standard Laboratory Trial is employed to interpret Devereux's copper, Cu, results as shown in Table 7, then there is a strong correlation between Police Exhibit 288/2 and Police Exhibits 320A, 323, 325, 328D & 334 and similarly between Police Exhibits 288/1 & 324A, and in this respect it can be said that the differences were not significant.

In conclusion I list that stated previously on pages 25 – 26: "Thus in the present assessment the findings produced by application of the **Reproducibility** from the ISO Trial, cannot be ignored. Taking these findings for Devereux's results for chromium, Cr, and copper, Cu, together with his results for nickel, Ni, and Todd's results for C, Si, Mn, Ni, Cr, Cu and Mo & V, and previous comments on composition comparison in this Report, one would have to conclude with a degree of confidence that, overall, the composition analysis supports the thesis that the body wires and farm wires have the same composition. Thus 288/2 and 320A, 323, 325, 328D & 334 have the same composition and come from the same heat and similarly 288/1 and 324A have the same composition and come from the same but a different heat".

8.0 Bibliography:

The intention with this material was to have Reference Material and Standards, where possible, from the period under consideration, the early 1970's. Some more recent material has been assessed to note changes.

Steel Wire:

- Metallurgy for Design Engineers, BHP,1969
- Metallurgy for Engineers, 4th Ed., E C Rollason, Edward Arnold, 1973
- NZS 3471:1974 Galvanised Steel Fencing Wire – Plain and Barbed
- NZS/BS 970.1.1991 Wrought steels for mechanical and allied engineering purposes Part 1.
- Ferrous Physical Metallurgy, Anil Kumar Sinha, Butterworth, 1989
- BS EN ISO 16120-3.2011 Non-alloy steel wire rod for conversion to wire Part 3: Specific requirements for rimmed and rimmed substitute, low carbon steel wire rod.

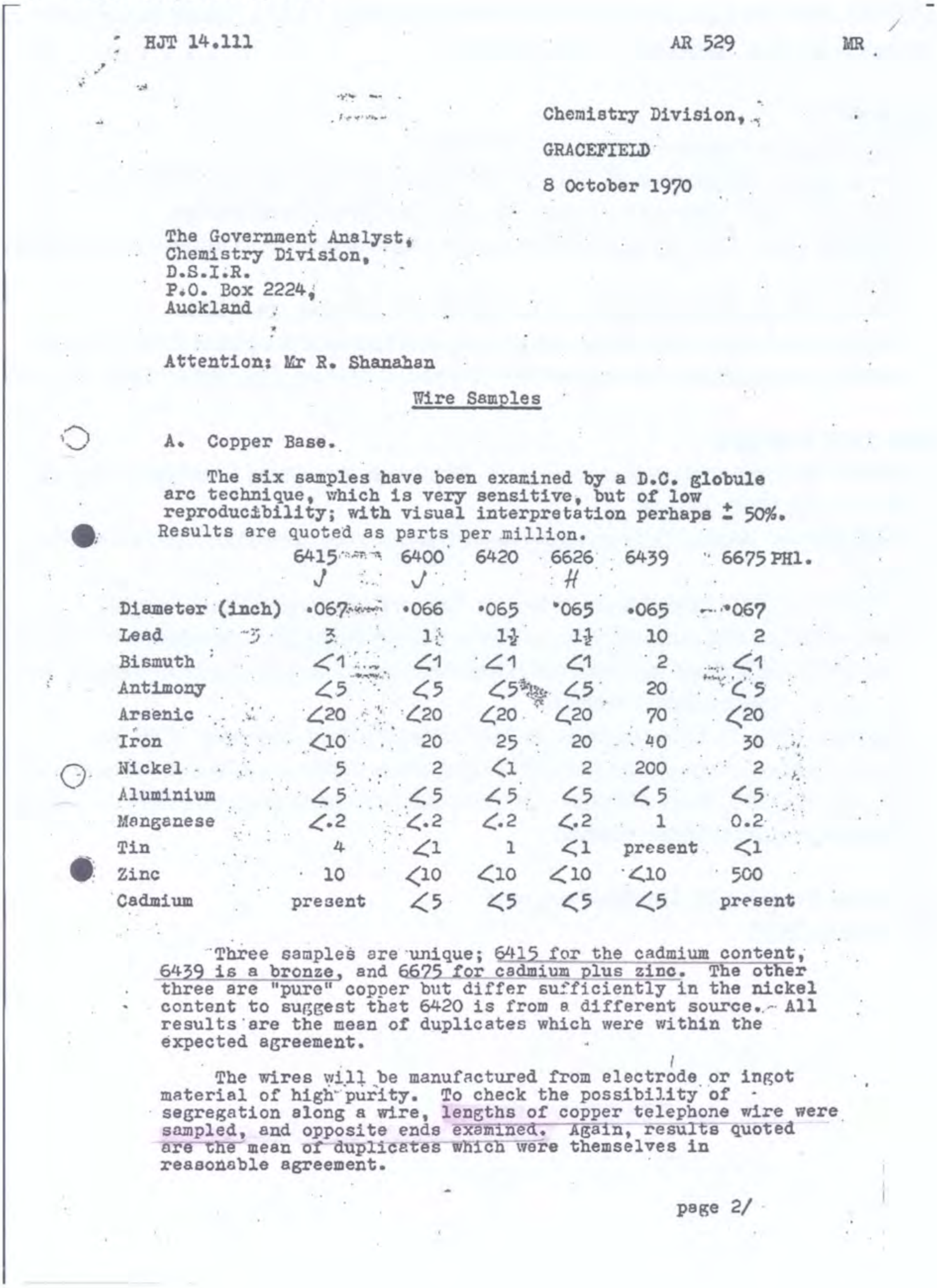
Chemical Analysis:

- Atomic Absorption Spectroscopy, J. W. Robinson, Analytical Chemistry, Vol. 32, No. 8, July 1960, 17 – 29
- PerkinElmer, Atomic Spectroscopy, www/perkinelmer.com/atomicspectroscopy, 2012
- AS/NZS 1050.37:1994 Methods for the Analysis of Iron and Steel Part 37: Determination of Copper Content - Flame Atomic Absorption Spectrometric Method
- IS0 4943-1985, Steel and cast iron-Determination of copper content-Flame atomic absorption spectrometric method
- AS/NZS 1050.39:1994 Methods for the analysis of iron and steel Part 39: Determination of chromium content- Flame atomic absorption spectrometric method
- IS0 10138: 1991, Steel and iron - Determination of chromium content-Flame atomic absorption spectrometric method

Professor Emeritus W. George Ferguson
5th – June - 2013

Appended Material

1. DSIR Report AR. 529



HJT 14.111 AR 529 MR

Chemistry Division,
GRACEFIELD
8 October 1970

The Government Analyst,
Chemistry Division,
D.S.I.R.
P.O. Box 2224,
Auckland

Attention: Mr R. Shanahan

Wire Samples

A. Copper Base.

The six samples have been examined by a D.C. globule arc technique, which is very sensitive, but of low reproducibility; with visual interpretation perhaps ± 50%. Results are quoted as parts per million.

	6415 J	6400 J	6420	6626 H	6439	6675 PH1.
Diameter (inch)	·067	·066	·065	·065	·065	·067
Lead	3	1½	1½	1½	10	2
Bismuth	<1	<1	<1	<1	2	<1
Antimony	<5	<5	<5	<5	20	<5
Arsenic	<20	<20	<20	<20	70	<20
Iron	<10	20	25	20	40	30
Nickel	5	2	<1	2	200	2
Aluminium	<5	<5	<5	<5	<5	<5
Manganese	<.2	<.2	<.2	<.2	1	0.2
Tin	4	<1	1	<1	present	<1
Zinc	10	<10	<10	<10	<10	500
Cadmium	present	<5	<5	<5	<5	present

Three samples are unique; 6415 for the cadmium content, 6439 is a bronze, and 6675 for cadmium plus zinc. The other three are "pure" copper but differ sufficiently in the nickel content to suggest that 6420 is from a different source. All results are the mean of duplicates which were within the expected agreement.

The wires will be manufactured from electrode or ingot material of high purity. To check the possibility of segregation along a wire, lengths of copper telephone wire were sampled, and opposite ends examined. Again, results quoted are the mean of duplicates which were themselves in reasonable agreement.

page 2/

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

	Unused "40 pound" 0.050 inch ends one mile apart		Unused "70 pound" 0.066 inch ends several hundred feet apart		Used "70 pound" 0.066 inch ends about 100 fect apart	
Lead	5	5	5	5	7	7
Bismuth	<1	<1	<1	<1	<1	<1
Antimony	<5	<5	<5	<5	<5	<5
Arsenic	<20	<20	<20	<20	<20	<20
Iron	30	30	20	20	15	15
Nickel	2	2	2	2	2	2
Aluminium	<5	<5	<5	<5	<5	<5
Manganese	0.2	0.2	0.2	0.2	0.1	0.1
Tin	15	15	3	3	15	15
Zinc	20	20	30	30	20	20
Cadmium	present	present	present	present	present	present

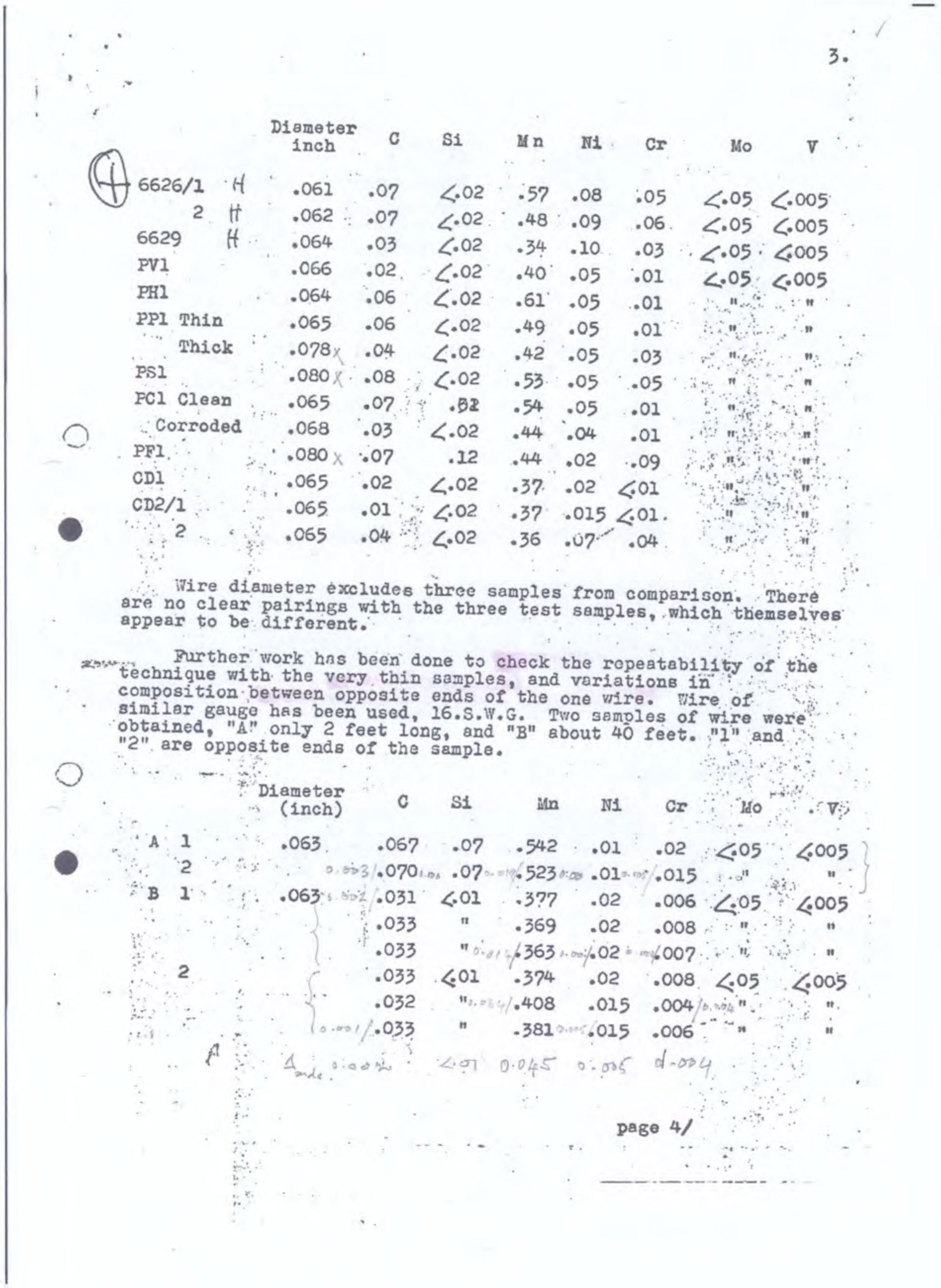
Cadmium is added to increase strength, such wire being used for larger spans. The nominal content is about 1%. A pure copper may be used for short spans. The above three wires could probably be "sorted" by the tin and iron contents. Three other used wires coiled together were sampled at opposite ends and an attempt made to "pair" them. All three were so similar that this was impossible. Wires appear to be fairly homogeneous along the length, but are made from material refined to a fairly uniform purity.

B <u>Steel Wires</u>

As the galvanising on the test samples had been badly corroded, no attempt was made to analyse the zinc coating, which was removed from all samples before examination. The photoelectric spectrometer has been used for the analysis with a "peaked" spark discharge. Results are quoted as percentage, and are the mean of duplicates.

page 3/

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;



	Diameter inch	C	Si	Mn	Ni	Cr	Mo	V
④ 6626/1 H	.061	.07	<.02	.57	.08	.05	<.05	<.005
2 H	.062	.07	<.02	.48	.09	.06	<.05	<.005
6629 H	.064	.03	<.02	.34	.10	.03	<.05	<.005
PV1	.066	.02	<.02	.40	.05	.01	<.05	<.005
PH1	.064	.06	<.02	.61	.05	.01	"	"
PP1 Thin	.065	.06	<.02	.49	.05	.01	"	"
Thick	.078 x	.04	<.02	.42	.05	.03	"	"
PS1	.080 x	.08	<.02	.53	.05	.05	"	"
PC1 Clean	.065	.07	~~.02~~ .12	.54	.05	.01	"	"
Corroded	.068	.03	<.02	.44	.04	.01	"	"
PF1	.080 x	.07	.12	.44	.02	.09	"	"
CD1	.065	.02	<.02	.37	.02	<.01	"	"
CD2/1	.065	.01	<.02	.37	.015	<.01	"	"
2	.065	.04	<.02	.36	.07	.04	"	"

Wire diameter excludes three samples from comparison. There are no clear pairings with the three test samples, which themselves appear to be different.

Further work has been done to check the repeatability of the technique with the very thin samples, and variations in composition between opposite ends of the one wire. Wire of similar gauge has been used, 16.S.W.G. Two samples of wire were obtained, "A" only 2 feet long, and "B" about 40 feet. "1" and "2" are opposite ends of the sample.

		Diameter (inch)	C	Si	Mn	Ni	Cr	Mo	V
A	1	.063	.067	.07	.542	.01	.02	<.05	<.005
	2		0.003/.070	.07	.523	.01	.015	"	"
B	1	.063	0.002/.031	<.01	.377	.02	.006	<.05	<.005
			.033	"	.369	.02	.008	"	"
			.033	"	0.014/.363	0.006/.02	.007	"	"
	2		.033	<.01	.374	.02	.008	<.05	<.005
			.032	"	0.034/.408	.015	.004/0.004	"	"
			0.001/.033	"	.381	0.005/.015	.006	"	"
		Δ ends	0.002	<.01	0.045	0.005	0.004		

page 4/

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

The carbon and manganese results have not been "rounded off". As before, all results are the mean of duplicate exposures. The suggestion of manganese difference between B/1 and B/2 has been examined in more detail. Six analytical results are available for both B/1 and B/2, and the "t" test has been applied to these.

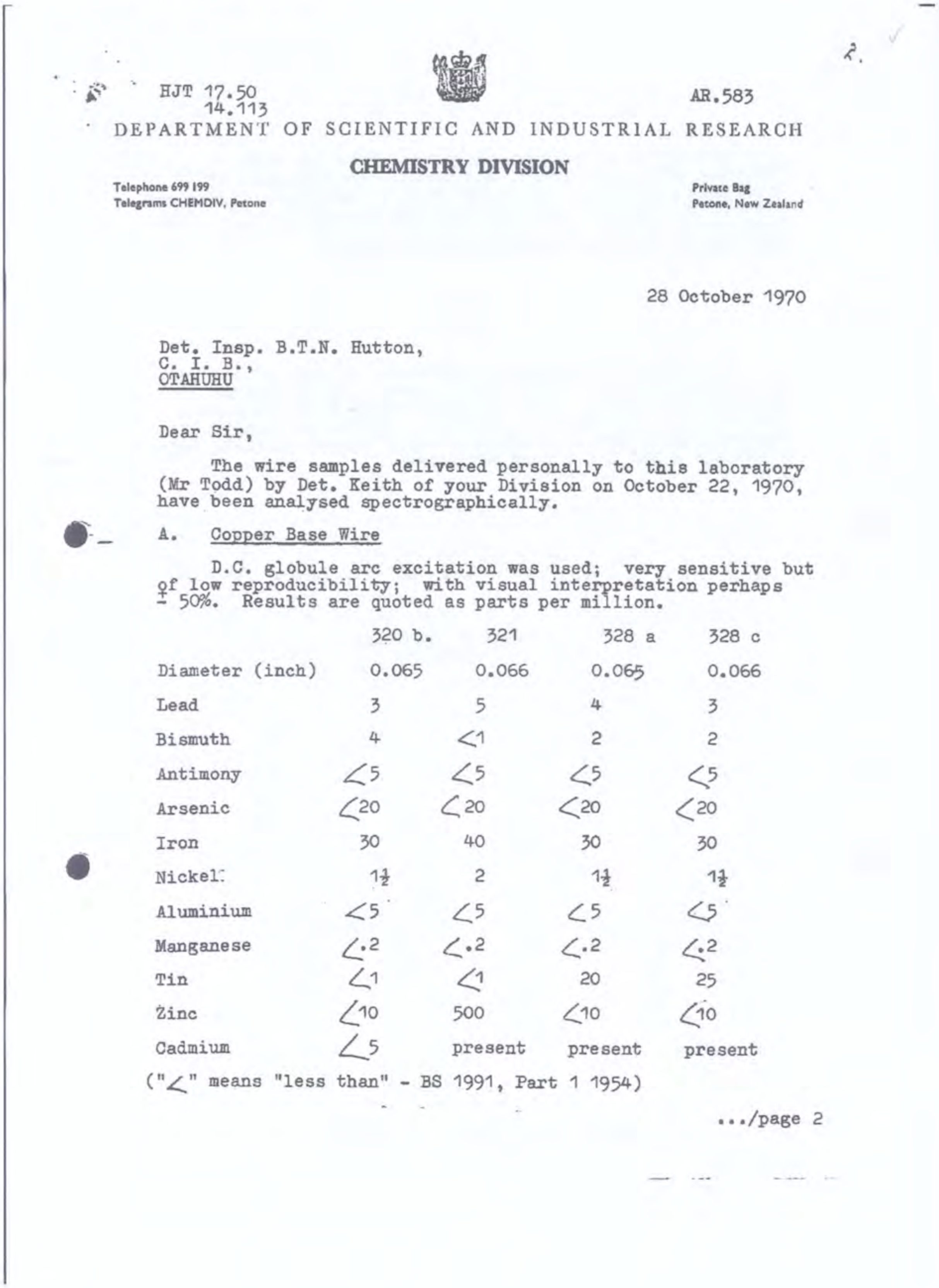
$$t = 1.43$$
$$P = 0.17$$

The slight difference in manganese between B1 and B2 is not significant, being masked perhaps by the poorer repeatability of B. (If repeatability of B had been the same as A, $t = 2.43$ and $P = 0.04$). Within the limits of repeatability, the two ends of A and B appear similar, but certainly A and B are very different.

(Ian K. Walker)
Director

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

2. DSIR Report AR. 583



2.

HJT 17.50
14.113

AR.583

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH
CHEMISTRY DIVISION

Telephone 699 199
Telegrams CHEMDIV, Petone

Private Bag
Petone, New Zealand

28 October 1970

Det. Insp. B.T.N. Hutton,
C. I. B.,
OTAHUHU

Dear Sir,

The wire samples delivered personally to this laboratory (Mr Todd) by Det. Keith of your Division on October 22, 1970, have been analysed spectrographically.

A. Copper Base Wire

D.C. globule arc excitation was used; very sensitive but of low reproducibility; with visual interpretation perhaps ± 50%. Results are quoted as parts per million.

	320 b.	321	328 a	328 c
Diameter (inch)	0.065	0.066	0.065	0.066
Lead	3	5	4	3
Bismuth	4	<1	2	2
Antimony	∠5	∠5	∠5	∠5
Arsenic	∠20	∠20	∠20	∠20
Iron	30	40	30	30
Nickel	1½	2	1½	1½
Aluminium	∠5	∠5	∠5	∠5
Manganese	∠.2	∠.2	∠.2	∠.2
Tin	∠1	∠1	20	25
Zinc	∠10	500	∠10	∠10
Cadmium	∠5	present	present	present

("∠" means "less than" - BS 1991, Part 1 1954)

.../page 2

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

Comparison with the earlier samples reported to Government Analyst, Auckland, our reference AR 529, a copy of which is enclosed, suggests the following.

1. The tin content of 328 a and 328 c precludes any "tie-up" with the actual samples of AR 529 - marked J and H.

2. 321 has far too high a zinc content.

3. 320 b contains bismuth. This is very unusual in copper wire (three of your four samples contain detectable amounts of bismuth). These bismuth results in both groups of samples have been checked, by repeat analysis, and confirmed.

4. All four samples differ in composition from the three "body" specimens.

B. <u>Galvanised Iron Wire</u>

The zinc coating was removed, and the steel base analysed using a "peaked" spark discharge. The thin section precluded very high accuracy, but it is considered that results are comparable with those of AR 529.

	Diameter inch	C	Si	Mn	Ni	Cr	Mo	V
— 320A	.066	.07	<.02	.55	.08	.04	<.05	<.005
322	.065	$.03_5$	"	.52	.04	.02	"	"
- 323	.066	.07	"	.56	.10	.05	"	"
✓ 324A	.066	.07	"	.46	.09	.05	"	"
324B	.067	.02	."	.46	.05	.03	"	"
— 325	.066	.10	"	.54	.09	.05	"	"
326	.065	$.03_5$	"	.48	.04	.01	"	"
328B	.064	.17	.25	.74	.045	.02	"	"
~ 328D	.066	.10	<.02	.54	.08	.05	"	"
- 334 clean	.065	.10	"	.55	.08	.04	"	"
rusty	.063	.03	"	.30	.08	.03	"	"
X6626-1	.061	.07	<.02	.57	.08	.05	<.05	<.005
-2	.062	.07	"	.48	.09	.06	"	"
X6629	.064	.03	"	.34	.10	.03	"	"

1. Diameter is only quoted to show that all samples are a nominal 16 S.W.G. The actual diameter will depend on the corrosion and erosion that has occurred.

2. 328B is completely unlike the three field samples, carbon (C), Manganese (Mn) and Silicon (Si) all being very different.

3. 320A, 323, and to a slightly lesser extent, 325, 328D and 334(clean) are all like X6626-1. [illegible]

.../page 3

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

4. 324A is very like X6626-2.(galvanised)

5. Although 334 (rusty) is very like X6629 (galvanised) with regard to composition, it has lost much of its galvanising, unlike X6629 which is in very good condition. If the small samples are typical of the whole, this factor suggests a difference.

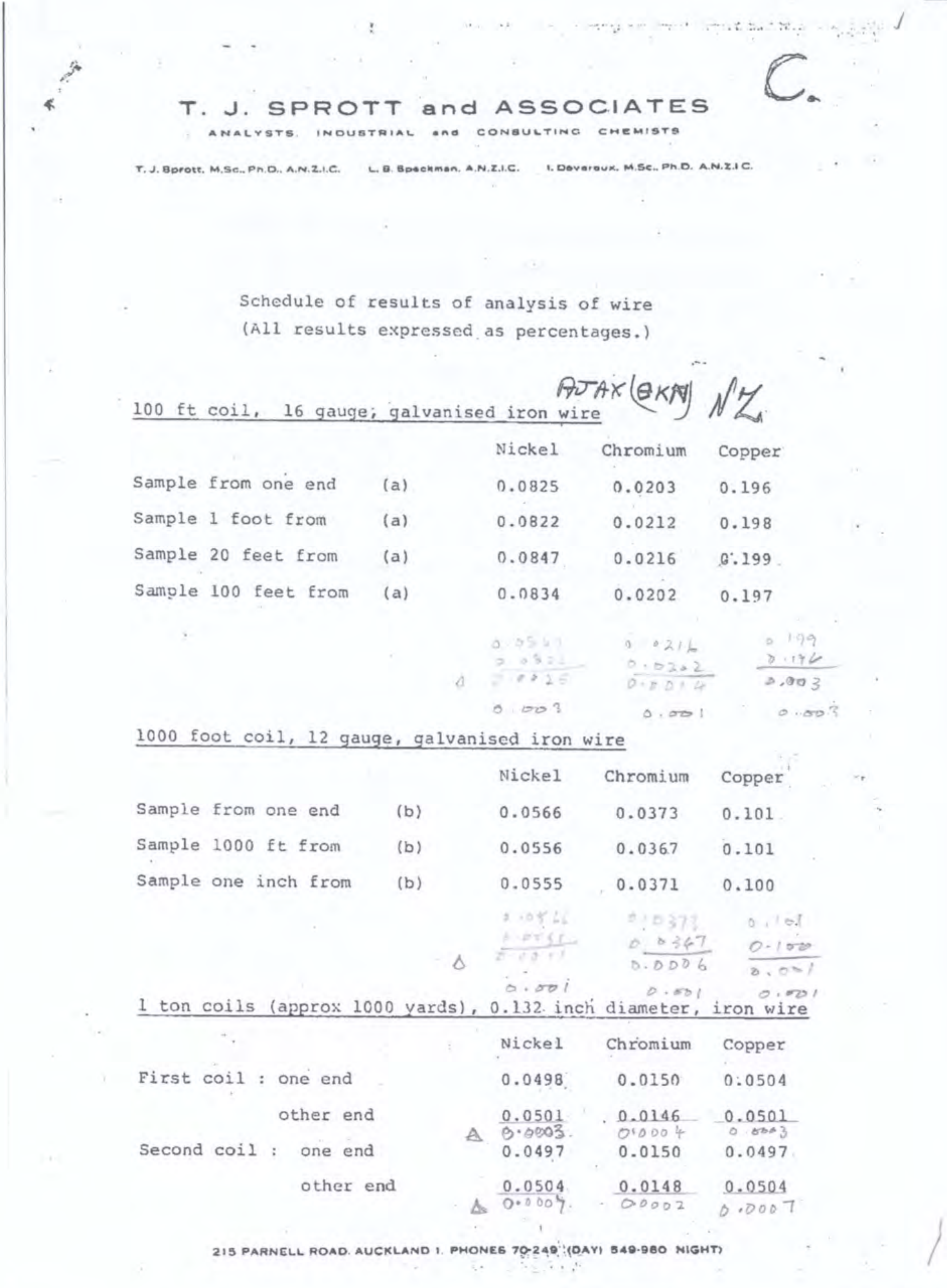
Ian K Walker

(Ian K. Walker)
Director.

...Encl:

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

3. T J Sprott & Associates Report



C.

T. J. SPROTT and ASSOCIATES

ANALYSTS INDUSTRIAL and CONSULTING CHEMISTS

T. J. Sprott, M.Sc., Ph.D., A.N.Z.I.C. L. B. Speckman, A.N.Z.I.C. I. Devereux, M.Sc., Ph.D. A.N.Z.I.C.

Schedule of results of analysis of wire
(All results expressed as percentages.)

AJAX (BKN) NZ

100 ft coil, 16 gauge, galvanised iron wire

		Nickel	Chromium	Copper
Sample from one end	(a)	0.0825	0.0203	0.196
Sample 1 foot from	(a)	0.0822	0.0212	0.198
Sample 20 feet from	(a)	0.0847	0.0216	0.199
Sample 100 feet from	(a)	0.0834	0.0202	0.197
	Δ	0.0847 0.0822 0.0025	0.0216 0.0202 0.0014	0.199 0.196 0.003
		0.003	0.001	0.003

1000 foot coil, 12 gauge, galvanised iron wire

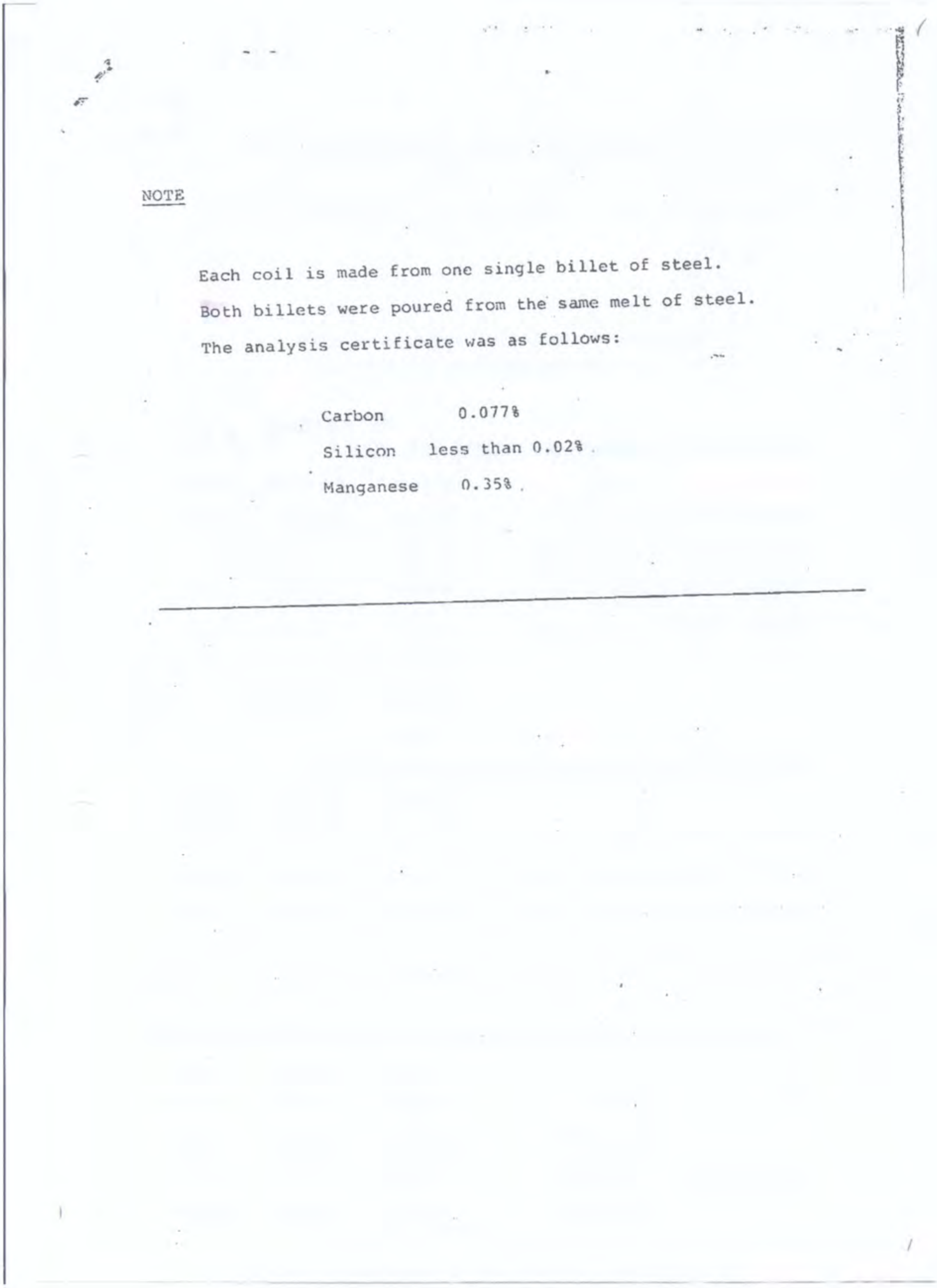
		Nickel	Chromium	Copper
Sample from one end	(b)	0.0566	0.0373	0.101
Sample 1000 ft from	(b)	0.0556	0.0367	0.101
Sample one inch from	(b)	0.0555	0.0371	0.100
	Δ	0.0566 0.0555 0.0011	0.0373 0.0367 0.0006	0.101 0.100 0.001
		0.001	0.001	0.001

1 ton coils (approx 1000 yards), 0.132 inch diameter, iron wire

		Nickel	Chromium	Copper
First coil :	one end	0.0498	0.0150	0.0504
	other end	0.0501	0.0146	0.0501
	Δ	0.0003	0.0004	0.0003
Second coil :	one end	0.0497	0.0150	0.0497
	other end	0.0504	0.0148	0.0504
	Δ	0.0007	0.0002	0.0007

215 PARNELL ROAD. AUCKLAND 1. PHONES 70-249 (DAY) 549-980 NIGHT)

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;



NOTE

Each coil is made from one single billet of steel.

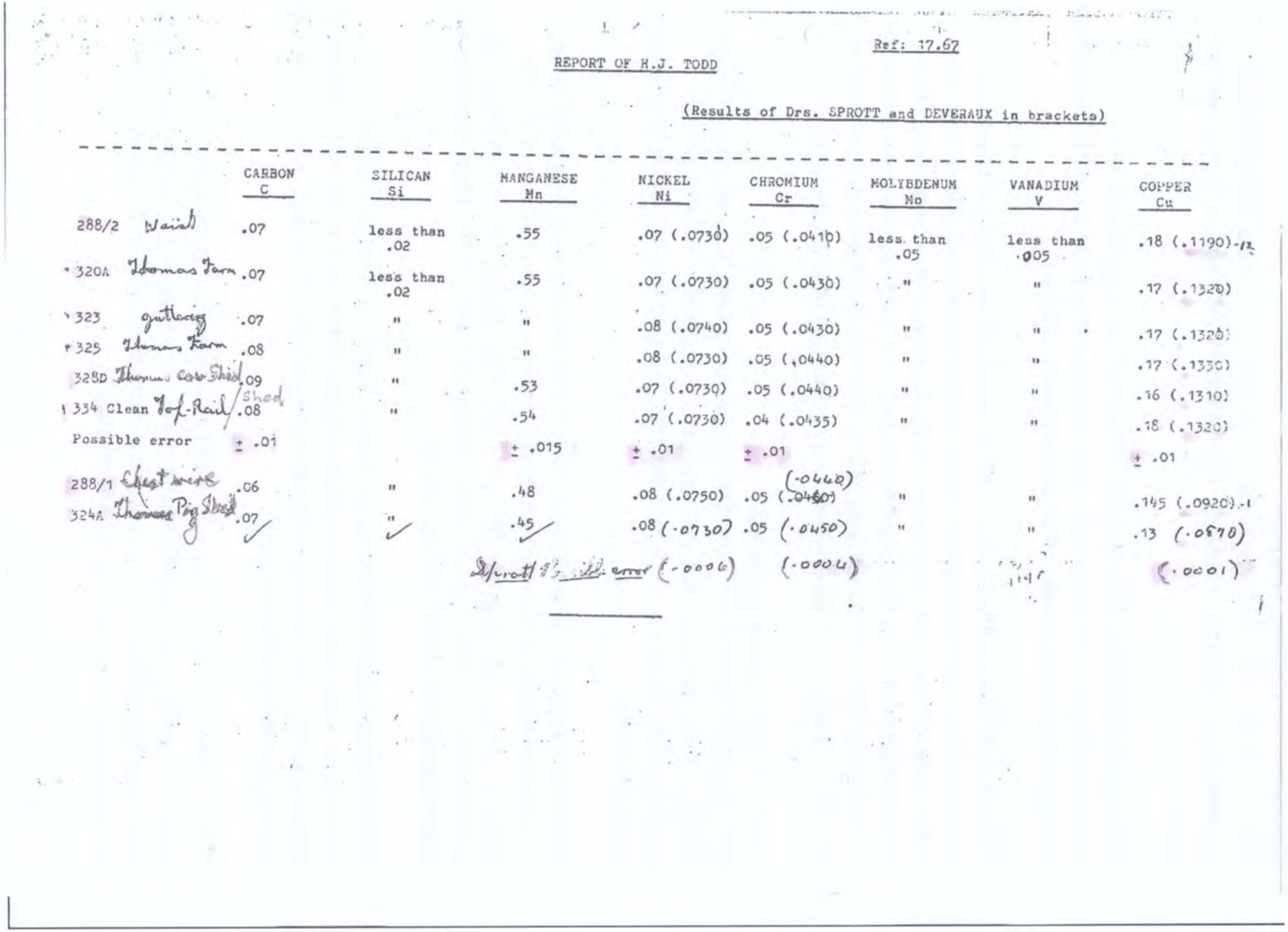
Both billets were poured from the same melt of steel.

The analysis certificate was as follows:

Carbon	0.077%
Silicon	less than 0.02%
Manganese	0.35%

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

4. H J Todd Report Ref: 17.67 (Includes results of Drs. Sprott & Devereux)



Ref: 17.67

REPORT OF H.J. TODD

(Results of Drs. SPROTT and DEVERAUX in brackets)

	CARBON C	SILICAN Si	MANGANESE Mn	NICKEL Ni	CHROMIUM Cr	MOLYBDENUM Mo	VANADIUM V	COPPER Cu
288/2 Waist	.07	less than .02	.55	.07 (.0730)	.05 (.0410)	less than .05	less than .005	.18 (.1190)-12
320A Thomas Farm	.07	less than .02	.55	.07 (.0730)	.05 (.0430)	"	"	.17 (.1320)
323 guttering	.07	"	"	.08 (.0740)	.05 (.0430)	"	"	.17 (.1320)
325 Thomas Farm	.08	"	"	.08 (.0730)	.05 (.0440)	"	"	.17 (.1330)
328D Thomas Cow Shed	.09	"	.53	.07 (.0730)	.05 (.0440)	"	"	.16 (.1310)
334 Clean Top-Rail/Shed	.08	"	.54	.07 (.0730)	.04 (.0435)	"	"	.18 (.1320)
Possible error	± .01		± .015	± .01	± .01			± .01
288/1 Chest wire	.06	"	.48	.08 (.0750)	.05 (~~.0460~~) (·0440)	"	"	.145 (.0920)-1
324A Thomas Pig Shed	.07 ✓	" ✓	.45 ✓	.08 (·0730)	.05 (·0450)	"	"	.13 (·0870)
Sprott [illegible] error				(·0006)	(·0004)			(·0001)

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;

5 Details from AS/NZS Standards and of ISO Analytical Trials

Standards for Copper Analysis

AS/NZS 1050.37:1994 Methods for the Analysis of Iron and Steel Part 37: Determination of Copper Content - Flame Atomic Absorption Spectrometric Method

Technically identical to IS0 Standard (International Organization for Standardization), IS0 4943-1985, Steel and cast iron-Determination of copper content-Flame atomic absorption spectrometric method

This AS/NZS Standard specifies a flame atomic absorption spectrometric method for the determination of copper content between 0.004% (m/m) and 0.5% (m/m) in steel. The procedure involves dissolution of a test portion in hydrochloric acid, nitric and perchloric acids and spraying this solution into an air/acetylene flame for spectrometric measurement of the atomic absorption of the 325.7 nm spectral line emitted by a copper hollow cathode lamp.

Precision for Copper Analysis

ISO conducted international analytical trials for copper, Cu, determination in 1978 on three steel samples and two cast iron samples in four countries involving eight laboratories, each laboratory making four or five determinations on each sample.

*The data obtained showed a logarithmic relationship between copper content and **Repeatability** and **Reproducibility** over the range 0,02 to 5 % (rn/rn) copper of the test results(see Standard IS0 4943-1985), part of the range being summarized in Table 5 below, which is from IS0 4943-1985. **Repeatability** and **Reproducibility** are defined as follows:*

*"The difference between two single results found on identical test material by one analyst using the same apparatus within a short time interval will exceed the **Repeatability**, r, on average not more than once in 20 cases, in the normal and correct operation of the method".*

*"The difference between two single and independent results found by two operators working in different laboratories on identical test material will exceed the **Reproducibility**, R, on average not more than once in 20 cases, in the normal and correct operation of the method".*

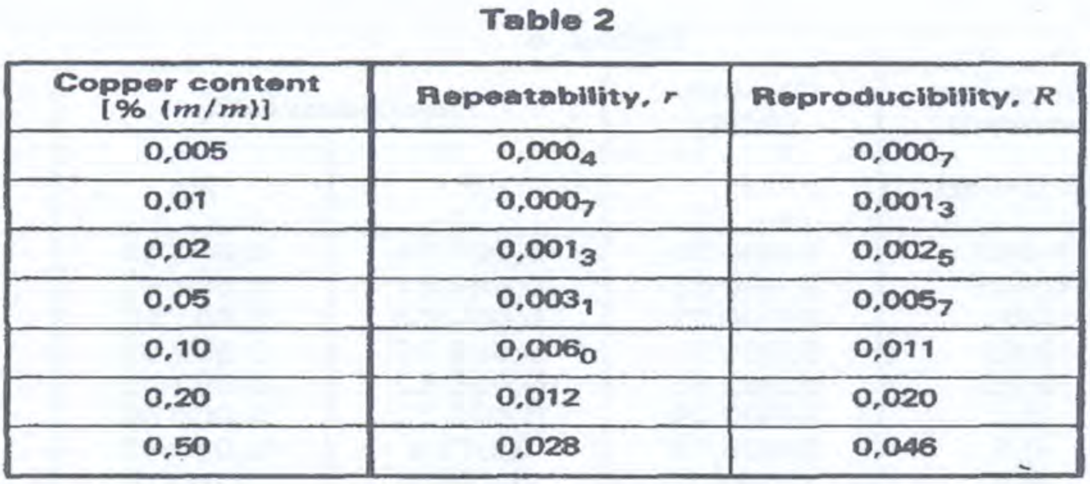


Table 2

Copper content [% (m/m)]	Repeatability, r	Reproducibility, R
0,005	$0{,}000_4$	$0{,}000_7$
0,01	$0{,}000_7$	$0{,}001_3$
0,02	$0{,}001_3$	$0{,}002_5$
0,05	$0{,}003_1$	$0{,}005_7$
0,10	$0{,}006_0$	0,011
0,20	0,012	0,020
0,50	0,028	0,046

Table 5 Repeatability and Reproducibility Data for Copper (Table 2 from IS0 4943-1985)

Standards for Chromium Analysis

AS/NZS 1050.39:1 994 Methods for the analysis of iron and steel Part 39: Determination of chromium content- Flame atomic absorption spectrometric method

Technically identical to IS0 10138: 1991, Steel and iron-Determination of chromium content-Flame atomic absorption spectrometric method

This AS/NZS Standard specifies flame atomic absorption spectrometric method for the determination of chromium content between 0.002% (m/m) and 2.0% (m/m) in non-alloy and low-alloy steel. The procedure involves dissolution of a test portion in acid, oxidation and removal of silica. The remaining material is fused, extracted, then added to the reserved filtrate. This solution is then delivered to a dinitrogen monoxide-acetylene flame for spectrometric measurement of the atomic absorption of the 357.9 nm or 425.4 nm spectral line emitted by a chromium hollow cathode lamp.

Precision for Chromium Analysis

ISO conducted international analytical trials for Chromium, Cr, determination in 1987 on five steel samples and three iron samples in seven countries involving 19 laboratories, each laboratory making three determinations (see Notes 1 and 2) on each sample.

The data obtained showed a logarithmic relationship between chromium content and ***Repeatability*** *(r) and* ***Reproducibility*** *(R and R_w) of the test results (see Note 3) as summarized in Table 6. The graphical representation of the data is given in IS0 10138:1991.*

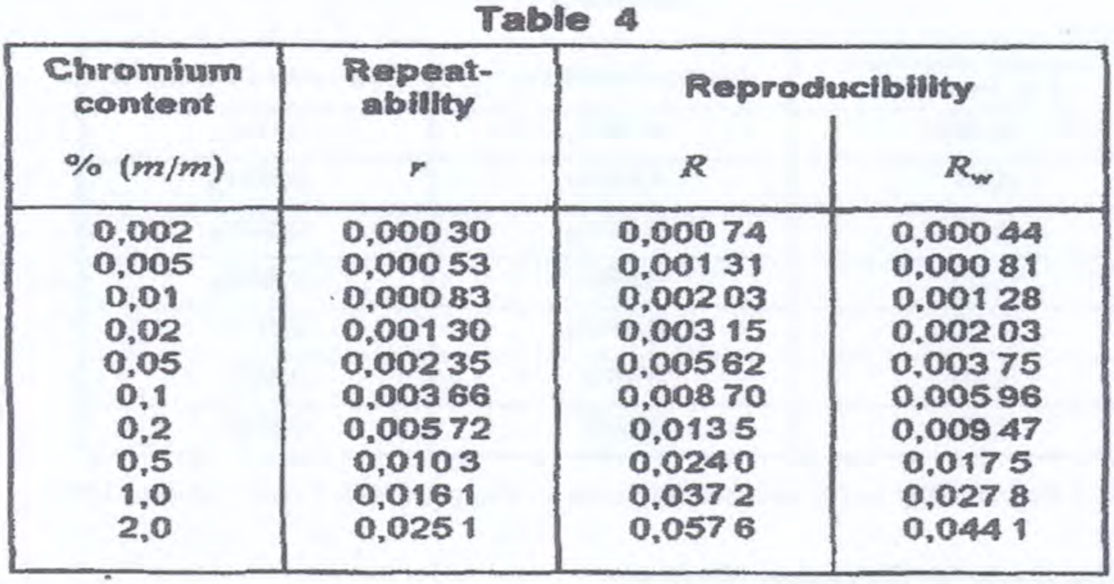


Table 4

Chromium content % (m/m)	Repeat-ability r	Reproducibility R	 R_w
0,002	0,000 30	0,000 74	0,000 44
0,005	0,000 53	0,001 31	0,000 81
0,01	0,000 83	0,002 03	0,001 28
0,02	0,001 30	0,003 15	0,002 03
0,05	0,002 35	0,005 62	0,003 75
0,1	0,003 66	0,008 70	0,005 96
0,2	0,005 72	0,013 5	0,009 47
0,5	0,010 3	0,024 0	0,017 5
1,0	0,016 1	0,037 2	0,027 8
2,0	0,025 1	0,057 6	0,044 1

Table 6 Repeatability and Reproducibility Data for Chromium(Table 4 from IS0 10138: 1991)

"Notes:

*1. Two of the three determinations were carried out under **Repeatability** conditions as defined in IS0 5725, i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.*

2. The third determination was carried out a different time (on a different day) by the same operator as in note 1 above using the same apparatus with a new calibration.

*3. From the results obtained on day 1 the **Repeatability** (r) and **Reproducibility** (R) were calculated using the procedure specified in IS0 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated".*

Carbon, C; Manganese, Mn; Silicon, Si; Sulphur, S; Phosphorus, P; Nickel, Ni; Chromium, Cr; Iron, Fe; Molybdenum, Mo; Copper, Cu; Vanadium, V; Niobium, Nb; Titanium, Ti; Cobalt, Co; Tin, Sn; Zinc, Zn;