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*Mr. W. R. Inman*

**CANADA**

**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT IR 62-26**

**THE APPLICATION OF COMPUTING METHODS  
TO X-RAY FLUORESCENCE ANALYSIS  
2. COPPER AND NICKEL IN ORES**

by

**A. H. GILLIESON & MISS M. J. YOUNG**

**MINERAL SCIENCES DIVISION**

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Mines Branch Investigation Report IR 62-26

THE APPLICATION OF COMPUTING METHODS TO X-RAY  
FLUORESCENCE ANALYSIS  
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A.H. Gillieson\* and Miss M.J. Young\*\*

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SUMMARY OF RESULTS

The application of computing methods to X-ray fluorescence analysis results on copper and nickel in ores, carried out by Geophysical Engineering and Surveys Ltd., North Bay, Ontario, converted a working curve of element content vs. X-ray intensity (non-linear due to variable matrix) to correction formulae, enabling satisfactory analysis to be made to higher contents than previously possible.

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\* Senior Scientific Officer and \*\* Scientific Officer, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

## INTRODUCTION

The firm of Geophysical Engineering and Surveys Limited, 2189 Algonquin Avenue, North Bay, Ontario, approached the senior author for assistance in the X-ray fluorescent determination of copper, nickel, zinc and lead in ore samples. It was explained that the varying composition of the ores, particularly in regard to iron content, resulted in non-linearity of the working curves for copper, nickel, zinc and lead for amounts greater than 1 per cent, produced by the firm's Philips X-Ray Fluorescence Spectrometer.

The senior author considered that the problem might be amenable to treatment by the mathematical method for the correction of inter-element effects in X-ray fluorescence analysis published by H.J. Lucas-Tooth and B.J. Price (1), and already described in detail in Mines Branch Investigation Report No. IR 62-25 (2). Full details of the method of analysis, equipment and operation were requested from the firm, together with chemical results and X-ray intensities for as many samples as possible.

The firm's reply and the data furnished appear in Appendix 1. It was noted that all the X-ray intensities quoted were lower than is customary in Mines Branch work. This was explained in paragraph 3 of the firm's note on "Tests performed on the X-ray Fluorescent Spectrograph", where it was stated that the fluorescent X-rays from the sample were attenuated by 0.01 inch aluminum filter to keep the counts per sec (cps) of the copper and nickel lines below the plateau of the Geiger tube, i.e., 600-700 cps. The low counting rates employed reduced the precision of the X-ray results. This question and the recommendations made are discussed in detail later in the report.

## TREATMENT OF DATA FURNISHED

The results quoted are summarised in Table 1, from which it can be seen that chemical results for copper were given for only 32 out of the 37 samples, and only 12 results were given for nickel, while no chemical analyses were recorded for iron. Five X-ray intensities and four chemical results for zinc were furnished on 5 samples, but no chemical results for copper appear for these samples and no figures were recorded by either method of analysis for nickel or iron.

Consequently, only the data on the 12 samples, for which both copper and nickel chemical results were quoted, could be used for the preparation of the correction formulae. Since it was stated that the samples contained no tungsten, the corresponding X-ray intensities were not included in the calculations. When both chemical and X-ray data are available, the results on at least  $x + 2$  samples are required for the mathematical treatment; where  $x$  is the number of elements present in the sample. In this instance only 3 elements, Cu, Ni and Fe could be considered because the data on at least 5 samples was required. As results on 12 samples were available, the computational matrix was adequately "over-determined". Zinc could not be included since complete results on only 1 element in 4 samples were quoted.

The relevant data on the 12 samples were abstracted and the necessary mathematical treatment in accordance with the Lucas-Tooth and Price method carried out by K. Milliken of the Mines Branch, Physical Metallurgy Division, Computing Section, on the IBM 1620 Computer in collaboration with the Departmental Data Processing Group under K. Shimizu.

Acting on a verbal suggestion made at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, attended March 5-9, 1962 and reported in Internal Report MS-62-42(3), the authors used the reflected tungsten X-ray intensities as an external standard for the computational correlation made between the chemical results and the ratios of net copper or nickel intensities to net tungsten intensities. Although the results of this computation produced a linear working curve, the precision was not as good as that in the direct computational correlation of chemical results with X-ray intensities.

TABLE 1

Data Supplied

Geophysical Engineering and Surveys Ltd.,  
North Bay, Ontario.

Sample No.	Cu		Ni		Fe		W		Zn	
	%	cps	%	cps	%	cps	%	cps	%	cps
1	1.71	559	1.36	370		916		183		----
2	2.23	965	0.13	68		561		273		----
3	0.7	320		2		410		364		----
4	0.6	199	0.52	165		781		200		----
5	0.36	200		1		376		327		----
6	0.89	497		53		388		306		----
7	0.36	182	0.28	116		687		140		----
8	0.13	87		7		355		305		----
9	1.24	608		2		351		547		----
10	2.27	806		---		459		272		----
11	1.82	713		---		538		273		----
12	1.01	436		---		773		251		----
13	0.90	411		---		427		276		----
14	0.17	114		---		497		261		----
15	0.033	30		---		269		321		----
16	1.05	728	0.05	26		351		303		----
17	0.6	213	0.6	241		992		195		----
18		418		---		---		302	0.5	792
19		432		---		---		299	0.5	787
20		420		---		---		299	1.0	1234
21		421		---		---		311	1.0	1240
22		422		---		---		301		247
23	0.69	426		---		494		273		----
24	0.51	293		---		394		285		----
25	0.41	242		---		256		309		----
26	0.29	236		---		397		277		----
36	0.51	188	0.26	81		1019		177		----
37	1.05	335	0.65	172		901		174		----
38	0.15	71	0.09	33		932		235		----
39	0.28	131	0.12	47		928		225		----
40	1.31	421	1.0	239		928		172		----
41	0.8	294	0.3	65		867		190		----
91	0.85	272		---		185		---		----
92	0.84	244		---	+2	253		---		----
93	0.84	217		---	+3	282		---		----
94	0.84	173		---	+6	340		---		----
95	0.84	168		---	+9	385		---		----

## RESULTS

The direct computational correlation of chemical percentages of copper and nickel in the ore samples with their net X-ray intensities produced the following correction formulae:-

$$\text{Percentage Cu} = -0.065223068 + I_{\text{Cu}} (0.0009455618 + 0.00000003995481 I_{\text{Cu}} \\ + 0.0000013209242 I_{\text{Ni}} + 0.0000020776007 I_{\text{Fe}})$$

$$\text{Percentage Ni} = -0.013401833 + I_{\text{Ni}} (0.0011101078 + 0.0000003862387 I_{\text{Cu}} \\ + 0.0000004129664 I_{\text{Ni}} + 0.0000023507453 I_{\text{Fe}})$$

For the twelve sets of results used to derive these two formulae, a comparison of the chemical percentages given, and the percentages derived by the formulae are shown in Table 2. For copper, the difference between the two percentages calculated as a percentage of the chemical result, and the percentage standard deviation of the net total counts are also shown.

The non-linearity of the working curve for copper, relating chemical percentage to uncorrected net X-ray intensities is demonstrated in Figure 1. In Figure 2 the same chemical figures are plotted against the percentage of copper derived by the computational method of Lucas-Tooth and Price, from the net X-ray intensities of Cu, Ni and Fe. It will be noted that the curve in Figure 2 is linear up to 2.25 per cent.

The authors' report of these results to the firm and their acknowledgement appear as Appendices 2 and 3.

The results from the correlation of chemical percentages with the ratios of the Cu and Ni X-ray intensities to those of tungsten are given in Table 3. These results presented no advantages over those employing the intensities directly, were not as precise, and were not communicated to the firm.

TABLE 2

Comparison of Chemical Results and Results Derived by  
Formula from X-ray Fluorescent Intensities

Sample No.	Copper Percentage		Difference	Difference as percentage of chemical results	Percentage standard deviation of net total count	Nickel Percentage		Difference
	Chemical	X-ray formula				Chemical	X-ray formula	
1	1.71	1.81	+0.10	5.85	2.64 1	1.36	1.33	-0.03
2	2.23	2.09	-0.14	6.28	2.02	0.13	0.17	+0.04
4	0.60	0.49	-0.11	18.33	5.11	0.52	0.49	-0.03
7	0.36	0.39	+0.03	8.33	5.63	0.28	0.31	+0.03
16	1.05	1.20	+0.15	14.29	2.38	0.05	0.04	-0.01
36	0.51	0.53	+0.02	3.92	5.29	0.26	0.27	+0.01
37	1.05	0.95	-0.10	9.52	3.55	0.65	0.57	-0.08
38	0.15	0.14	-0.01	6.67	11.82	0.09	0.09	0.0
40	1.31	1.28	-0.03	2.29	3.17	1.00	0.83	-0.17
39	0.28	0.32	+0.04	14.29	7.34	0.12	0.14	+0.02
41	0.80	0.77	-0.03	3.75	3.87	0.30	0.20	-0.10
17	0.60	0.64	+0.04	6.67	4.83	0.60	0.85	+0.15

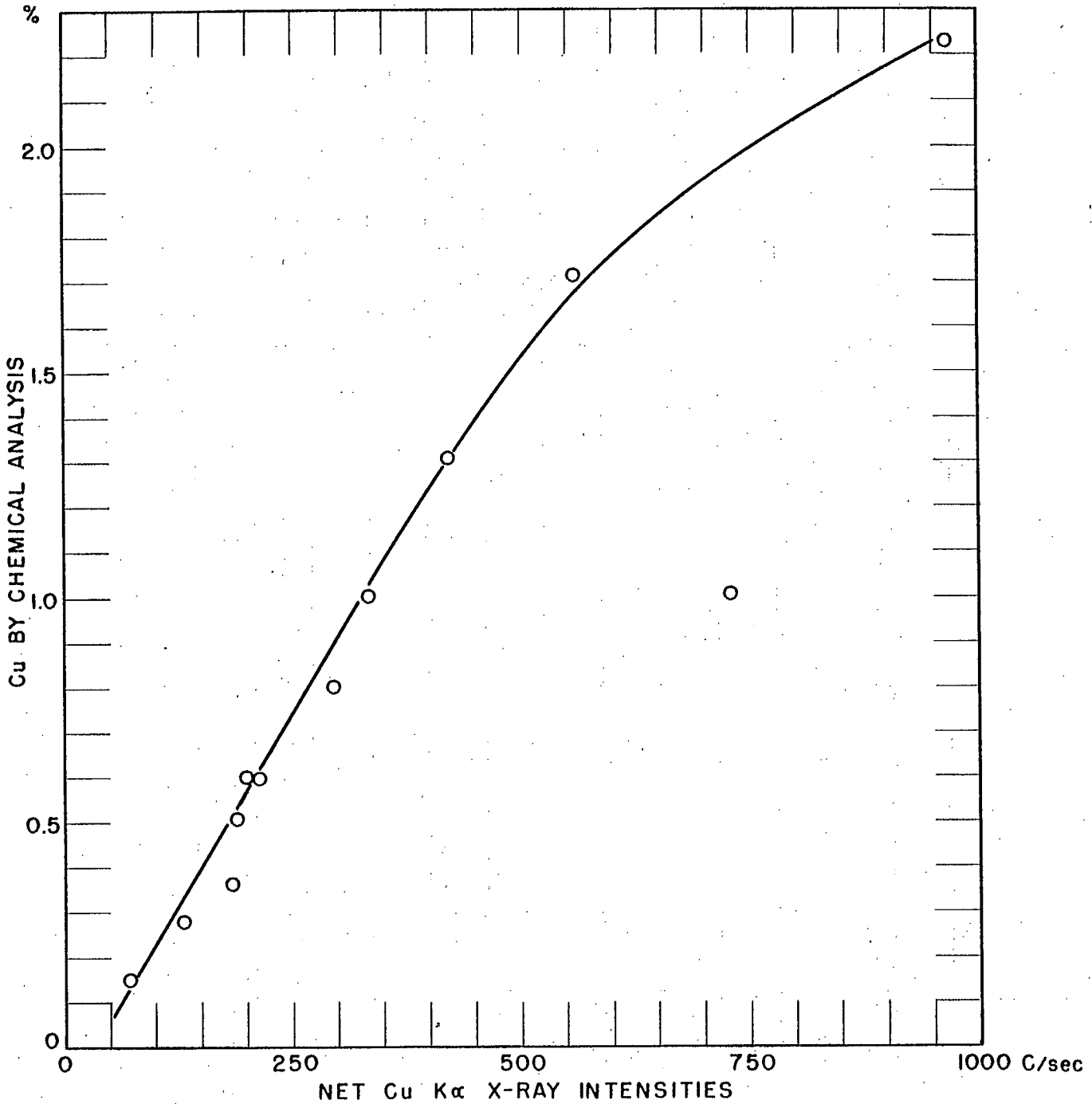


FIGURE 1 X-RAY FLUORESCENCE ANALYSIS OF ORES

CHEMICAL PERCENTAGE OF COPPER VS  
NET INTENSITY OF COPPER K $\alpha$  LINE



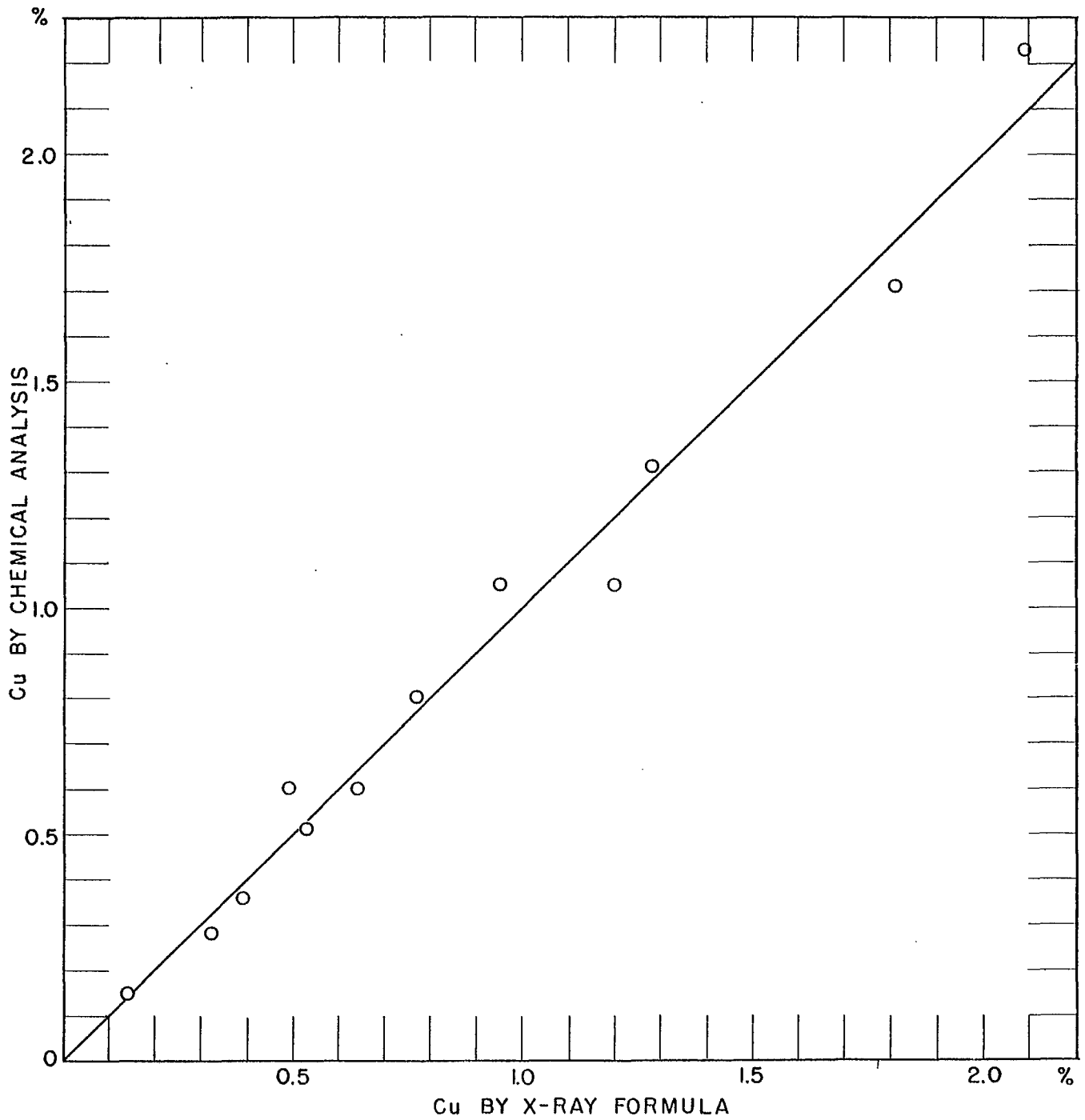


FIGURE 2 X-RAY FLUORESCENCE ANALYSIS OF ORES.

CHEMICAL PERCENTAGE OF COPPER VS PERCENTAGE  
DERIVED FROM X-RAY INTENSITIES BY COMPUTATION.

TABLE 3

Comparison of Chemical Results and Results Derived by  
Formula from X-ray Fluorescent Intensities  
and from Ratio of Intensities

Sample No.	Copper Percentage					Nickel Percentage				
	Chemical	X-ray <sub>1</sub>	Difference	X-ray <sub>2</sub> (Ratios)	Difference	Chemical	X-ray <sub>1</sub>	Difference	X-ray <sub>2</sub> (Ratios)	Difference
1	1.71	1.81	+0.10	1.78	+0.07	1.36	1.33	-0.03	1.29	-0.07
2	2.23	2.09	-0.14	1.99	-0.24	0.13	0.17	+0.04	0.14	+0.01
4	0.60	0.49	-0.11	0.47	-0.13	0.52	0.49	-0.03	0.47	-0.05
7	0.36	0.39	+0.03	0.63	+0.28	0.28	0.31	+0.03	0.48	+0.20
16	1.05	1.20	+0.15	1.23	+0.18	0.05	0.04	-0.01	0.05	0.00
36	0.51	0.53	+0.02	0.49	-0.02	0.26	0.27	+0.01	0.30	+0.04
37	1.05	0.95	-0.10	0.98	-0.07	0.65	0.57	-0.08	0.62	-0.03
38	0.15	0.14	-0.01	0.15	0.00	0.09	0.09	0.00	0.08	-0.01
39	0.28	0.32	+0.04	0.27	-0.01	0.12	0.14	+0.02	0.12	0.00
40	1.31	1.28	-0.03	1.32	+0.01	1.00	0.83	-0.17	0.91	-0.09
41	0.80	0.77	-0.03	0.74	-0.06	0.30	0.20	-0.10	0.21	-0.09
17	0.60	0.64	+0.04	0.53	-0.07	0.60	0.85	+0.15	0.70	+0.10

## DISCUSSION

Because the production of X-ray photons in X-ray fluorescence is a random event, it obeys Poisson Distribution where the theoretical standard deviation is given by the square root of the net total count. Thus in order to obtain a standard deviation of 1 per cent it is necessary to have a net total count of 10,000 counts. Where the amount of the element producing the X-rays in the sample is small and/or the fluorescence efficiency is low, adequate precision can only be obtained by counting for a long time.

In the data supplied, counting times had been kept short for practical reasons, and the original fluorescent X-ray intensity had been attenuated by a filter because of the limited counting-rate capacity of the X-ray detector employed. Compared with the Geiger tube used, scintillation counters have a very much higher counting-rate capacity, and their employment for detection without any filtering was recommended to the firm.

Although, because of the low counting-rates, the data did not have the precision desired for best application of the computational method for correction of inter-element effects, nevertheless the results of its application were significant and of value in this example of the X-ray fluorescence analysis of ores.

## REFERENCES

1. H.J. Lucas-Tooth and B.J. Price, *Metallurgia*, 64, 149 (1961).
2. M.J. Young and A.H. Gillieson, "The Application of Computing Methods to X-ray Fluorescence Analysis 1. Stainless Steels", Mines Branch Investigation Report IR 62-25, June 1962.
3. A.H. Gillieson, "The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5-9, 1962", Mineral Sciences Division Internal Report MS-62-42, March 16, 1962.

APPENDIX 1

GEOPHYSICAL ENGINEERING AND SURVEYS LIMITED

2189 Algonquin Ave.  
NORTH BAY, ONTARIO

February 15th, 1962

Dr. J. Convey,  
Department of Mines and Technical Surveys,  
OTTAWA, Ontario.

Dear Dr. Convey:

In conversation with your Dr. A.H. Gillieson of the Mineral Sciences Division, it was mentioned that you might be able to assist us in preparing working curves for use in connection with our Philips X-Ray Fluorescent Spectrometer.

We are principally interested in doing quantitative work on the elements copper, nickel, zinc and lead on samples gathered in the field by our various field parties.

Our main problem is in absorption and enhancement effects in the amounts present of the stated elements above 1%, as to date we have had very little trouble with the lesser quantities present.

I have checked a number of known chemically assayed samples the results of which are tabulated and attached hereto.

Your assistance in helping us to overcome this problem will be of great assistance in our exploration work and will be greatly appreciated.

Should you require further data from us in this matter it will be forwarded upon request.

Yours very truly,

J.H. BEATSON

## TESTS PERFORMED ON X-RAY FLUORESCENT SPECTROGRAPH

A number of samples with known chemical assays for copper and nickel were prepared for checking in our Philips X-Ray Instrument and a count was taken at the K alpha, first order peak, of the copper and nickel elements in each sample, along with the copper, nickel determinations a count was taken of the element iron of which the amount present was unknown. The peak of the tungsten was also counted and as a wet chemical assay revealed no tungsten present in any of the samples it was apparent that the variations in the count on the tungsten peak was due to the variable matrix effect in the sample.

The intensity of the tungsten is from the tungsten target of the X-ray tube.

The potential on the X-ray tube was maintained at 50 kV and 40 mA, a 0.010 inch pure aluminum filter was inserted between the sample and the analysing crystal (LiF) so that the cps at the copper and nickel lines was kept below the plateau of the Geiger tube i.e., 600-700 cps.

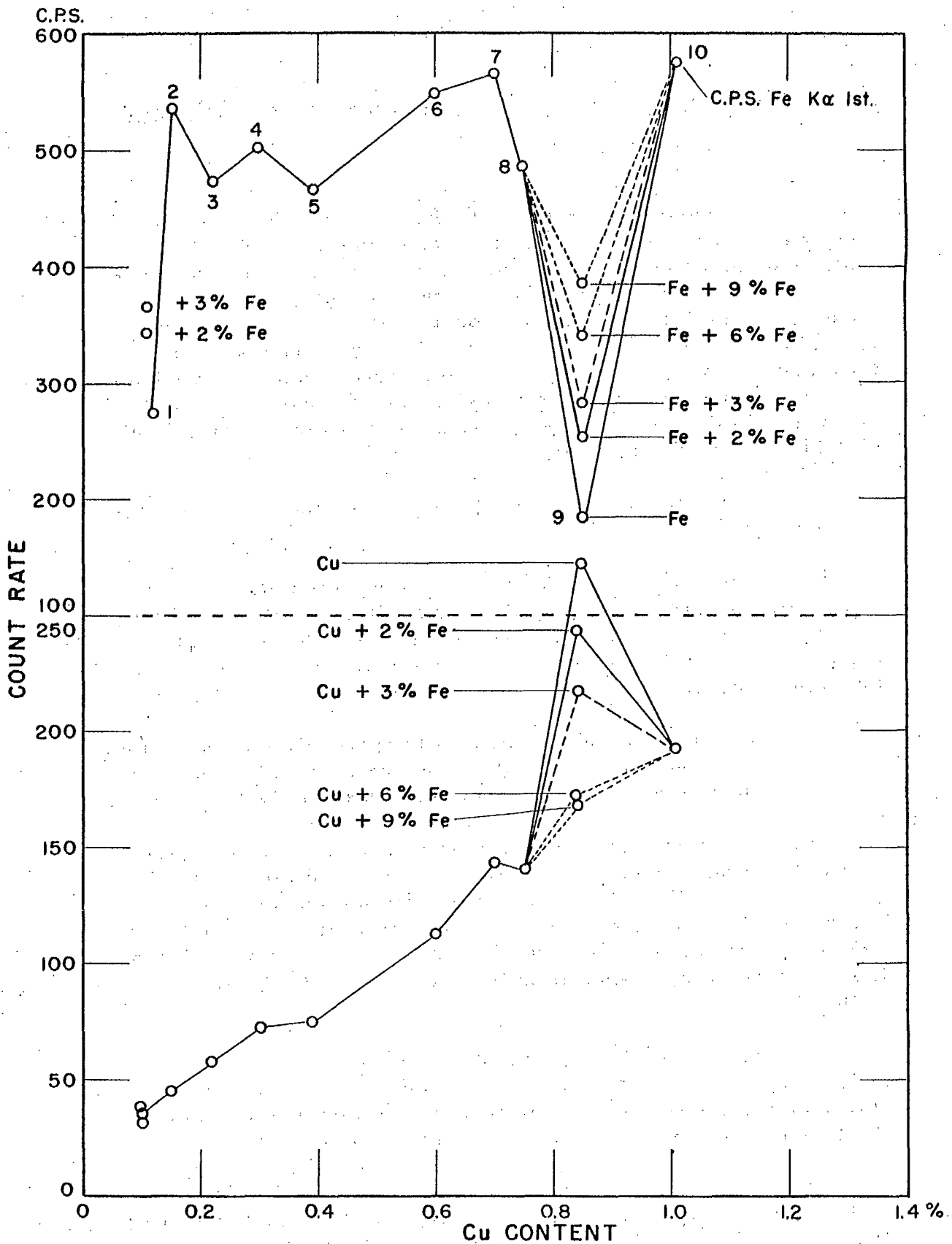
A plot or graph was made with cps vs. known percentage present and it revealed a marked non-linear curve when the element present in the sample was in excess of approximately 1%.

A number of ore samples with different matrices and known chemical assays for copper were prepared for study. The count per second value on each sample was plotted against the known chemical assay percentage, this plot revealed a number of non-linear cases. It was assumed that the non-linearity was due to the variation in the matrix of the samples especially the variation in the Fe present.

To prove this, ten samples were chosen with carefully checked wet assays for copper in the range from 0.1%-1.0% sample No. 9 having 0.84% Cu was chosen as being the most anomalous to the linearity of the other samples. (See Graph No. 4).

The cps of each sample was taken on the  $\text{Fe.Ka}^1$  line and plotted opposite the sample number, when this plot was completed it revealed a low iron count in samples No. 1 and 9.





X-RAY COUNT OF CHEMICALLY ASSAYED ORE SAMPLES.

To sample No. 1 and No. 9, 2% (by weight) of iron was added and the cps taken at the  $K\alpha^1$  peaks of the iron and copper. No change in the copper count was noted in sample No. 1 but sample No. 9 showed a marked decrease in cps on the copper line with the expected increase on the iron line. Additional amounts of iron were added to these samples and when the cps results were plotted it became evident that absorption by the iron of the copper was a factor to be contended with when the amount of copper present was in excess of 0.5%. Below that percentage the variation in the iron content seemed to have very little effect on the copper count. It was also apparent that a variation of plus or minus 50 cps in the iron content had very little effect on the copper count and that working curves could be established for determining the amount of copper present provided that the iron content in cps at the  $Fe.K\alpha^1$  line was taken on each sample thus placing it in an iron category.

J.H. BEATSON

February 15th, 1962.

APPENDIX 2

Mineral Sciences Division,  
A.T. Prince, Chief.

555 Booth Street,  
Ottawa, Ontario.  
March 2, 1962.

J.H. Beatson, Esq.,  
Geophysical Engineering and Surveys Limited,  
2189 Algonquin Avenue,  
North Bay, Ontario.

Dear Mr. Beatson:

X-Ray Fluorescence Analysis of Ores  
Working Curves for Copper and Nickel

Thank you for your letter of February 15th and the attached data on your chemical and X-ray analytical results.

Twelve sets of these results were subjected to mathematical treatment by Mr. Keith Milliken of the Mines Branch, Physical Metallurgy Division, Computing Section, making use of the Department's IBM 1620 Computer and the method described by H.J. Lucas-Tooth and B.J. Price in the September 1961 issue of "Metallurgia" (Photostat attached).

The method of the British authors does not yield a working curve, but a formula for each element to be determined, correlating the intensity of that element with the intensities of the interfering elements.

The two formulas, one for Percentage Copper and the other for Percentage Nickel are as follows:-

$$\text{Percentage Cu} = -0.065223068 + I_{\text{Cu}} (0.0009455618 + 0.00000003995481 I_{\text{Cu}} + 0.0000013209242 I_{\text{Ni}} + 0.0000020776007 I_{\text{Fe}}).$$

continued/...

$$\text{Percentage Ni} = -0.013401833 + I_{\text{Ni}} (0.0011101078 + 0.0000003862387 I_{\text{Cu}} + 0.0000004129664 I_{\text{Ni}} + 0.0000023507453 I_{\text{Fe}}).$$

(Note: These figures can of course be rounded-off to suit your means of calculation e.g., 5-figure logarithms or machine calculator).

For the twelve sets of results used to derive these two formulae, a comparison of the chemical percentages given and those derived by the formulae are shown in the attached table.

In addition for copper the difference between the two percentages, calculated as a percentage of the chemical result, and the percentage standard deviation of your net total counts, are listed for information.

The limit on counts/sec set by your Geiger detector is affecting the precision attainable by X-ray analysis and we would recommend the use of a scintillation counter which permits count rates up to 80,000 per sec, and would enable you to dispense with the attenuating aluminum filter.

It should be noted that, when using the formulae, counts must be recorded for all the elements in the formulae, otherwise the formulae will yield erroneous results.

We were unable to include the zinc figures in the calculations, since there were insufficient results including figures for this element. The calculation cannot be carried out on less than  $x + 2$  sets of results, where  $x$  is the number of elements for which formulae are required.

Photostat copies are attached for:-

- (a) Plot of Percentage Cu vs. X-Ray Intensity (cps).
- (b) Plot of Chemical Percentage Cu vs. Percentage Cu derived by calculation from X-ray Intensities.

It will be noted that the second graph shows satisfactory linearity up to 2.25 per cent Cu.

It is hoped that the above information may be of assistance to you. If you wish to discuss it further, Dr. Gillieson will be ready to answer any questions.

Yours sincerely,

Dr. John Convey,  
Director, Mines Branch.

APPENDIX 3

GEOPHYSICAL ENGINEERING AND SURVEYS LIMITED

2189 Algonquin Ave.  
NORTH BAY, ONTARIO

April 3rd, 1962.

Dr. J. Convey,  
Department of Mines and Technical Surveys,  
555 Booth Street,  
OTTAWA, Ontario.

Dear Dr. Convey:

Thank you for your great assistance in helping us solve some of our problems in connection with our X-Ray Spectrographic work.

The formula you provided has on a trial run overcome a variable matrix problem and we hope that with the installation of a scintillation counter, as suggested in your letter, we will have no great difficulty in assaying for the elements Cu, Ni, Zn, Pb.

Yours very truly,

J.H. BEATSON

AHG:MJY/DV