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**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

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**MINES BRANCH INVESTIGATION REPORT IR 63-51**

**THE APPLICATION OF COMPUTING METHODS  
TO X-RAY FLUORESCENCE ANALYSIS  
3. MATHEMATICAL DERIVATION OF A  
CORRECTION FACTOR TO COMPENSATE  
FOR VARIATIONS IN SURFACE FINISH  
AND SIZE OF SAMPLES**

by

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**MINERAL SCIENCES DIVISION**

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A.H. Gillieson<sup>\*</sup>, K.S. Milliken<sup>\*\*</sup> and (Miss) M.J. Young<sup>\*\*\*</sup>

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INTRODUCTION

Where absorption or enhancement effects occur in X-ray fluorescence analysis, the recorded intensities are not proportional to the percentages of the elements present, and either:

- (i) the reference standards chosen must approximate closely to the composition of the analytical sample, so that the differences in the absorption or enhancement effects in the sample and in the standards are not significant;
- or (ii) the recorded intensities must be corrected by a formula derived mathematically from the results of a wider range of standards.

Such correction formula have been developed (1, 2, 3, 4, 5, 6) and the application of the method of Lucas-Tooth and Price (5) to materials of interest in the work of the Branch forms the subject matter of the other reports in this series (7, 8, 9).

Basically there are only two methods, the first by Sherman (1) and the second by Lucas-Tooth and Price (5), and both methods require that the

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size and surface finish of the standards and of the sample be strictly comparable.

Because, in practice, it is not always possible to ensure that the size and surface finish of standard and sample be essentially the same, Burnham, Hower and Jones (3) developed a refinement of the Sherman method, which produced a general correction factor S, compensating for variation in form and finish of the sample and permitting normalization of the X-ray intensities from the sample.

Unfortunately this ingenious refinement suffered from a serious drawback, in that the Sherman formulation resulted in equations for the solution of S, which were quadratic for systems of two elements, cubic for three element systems, quartic for four element systems, and so on. In practice only quadratic and cubic equations have a general solution, and thus the method was effectively limited to two- and three element systems.

During the previous work on the Lucas-Tooth method, the first author noted that in the Lucas-Tooth formulation, the introduction of an S-factor would result in quadratic equations for the solution of S, whatever the number of elements present in the system.

This report describes the practical and mathematical work required to confirm the validity of the observation.

## EXPERIMENTAL WORK

As test material for the series of experiments, an inch thick cross section of stainless steel bar of nominal diameter  $1\frac{1}{4}$  in. was obtained from Technical Services Division stock. One circular face was turned to a smooth finish and six measurements of its diameter accurately made with a screw micrometer gauge.

The sample was then placed centrally on the Mylar film of the aluminum sample holder of the Philips 100 kV X-ray Spectrograph, and counts made for the nine elements, molybdenum, niobium, wolfram (tungsten), copper, nickel, iron, manganese, chromium and vanadium. The wavelengths of the elemental X-ray lines and of the related background measurements are shown in Table 1, along with the  $2\theta$  settings of the spectrograph goniometer. A quartz diffracting crystal was used to achieve adequate resolution of the X-ray spectra. The primary tungsten target

X-ray tube was run at 60 kV and 20 mA. The voltage on the photomultiplier of the scintillation counter was 900 V, the amplifier gain was set at 10, and the baseline of the pulse-height analyser was 6 V.

Three readings were taken at each setting of the goniometer, before the sample was repositioned. Each sample was repositioned five times and the mean of the 15 readings recorded:

The sample was then uniformly reduced in diameter by turning, measured carefully as before, and the X-ray analysis repeated. These operations were carried out four times. The resulting samples are referred to as  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$  and  $S_5$ . The turnings resulting from the reductions in diameter were collected and compressed into two pellets, each one inch in diameter and about one-quarter inch thick. These pellets ( $P_1$  and  $P_2$ ) were counted in the same way as the homogeneous samples, and were finally dissolved in acid and analysed chemically.

The experimental data and results used for the calculation of the S-factor are given in Table 2.

It is to be noted that, as the experimental results were obtained over a period of five months, there was the possibility of significant variation in instrumental performance over such a long interval, and in order to permit correction for such variation, a secondary standard used in the calculation of the Lucas-Tooth correction factors for stainless steels (7), was counted at the same time as each of the above seven samples. The results were all normalized to the figures obtained on this secondary standard during the work on the calculation of the Lucas-Tooth correction factors.

How necessary this precaution proved, was borne out in the fact that the photomultiplier initially used had to be replaced during the course of the tests, and the second photomultiplier required operation at 200 V higher than the first.

### MATHEMATICAL CONSIDERATIONS

The basic Lucas-Tooth equation for a particular element in an alloy is as follows:

$$P_{nm} = a_n + I_{nm} (k_{no} + \sum_x k_{nx} \frac{I_{xm}}{I_{nm}}) \quad (\text{Eq 1})$$

where  $P_{nm}$  refers to the percentage of the  $n^{\text{th}}$  element in the  $m^{\text{th}}$  sample, and similarly  $I_{nm}$  refers to the recorded X-ray intensity for the  $n^{\text{th}}$  element in the  $m^{\text{th}}$  sample. The  $a$  and  $k$ 's are constants derived empirically by X-ray analysis of standards of accurately determined composition, whose range of composition embraces that of the alloy of undetermined composition under examination.

The intensities of all the elements determinable by X-ray analysis are recorded, and it is essential for the success of the present method that the sum of the percentages of these elements be as nearly 100 per cent as possible, at least  $> 98$  per cent.

It is then possible to set up for each element determined, an equation similar to (Eq 1). With this difference, that since the size and surface finish of the sample is not necessarily the same as those of the standards, each intensity must be multiplied by the same, as yet undetermined, factor  $S$ . The modified basic Lucas-Tooth equation will now appear as follows:

$$P_{nm} = a_n + SI_{nm} (k_{no} + \sum_x k_{nx} \frac{SI_{xm}}{I_{nm}}) \quad (\text{Eq 2})$$

In the set of  $x$  such equations, the sum of the percentages on the L.H. side is known with sufficient accuracy, and all the constants and intensities are also known. If the  $x$  equations are now added the resulting equation is a quadratic in  $S$ , and can therefore be solved for  $S$  by simple algebra.

$$100 = \sum_1^x a_n + \left( \sum_1^x k_{no} I_n \right) S + \left[ \sum_1^x I_n \left( \sum_x k_{nx} \frac{I_x}{I_n} \right) \right] S^2 \quad (\text{Eq 3})$$

As there is only one sample in question,  $m$  equals 1, and is consequently not shown.

If we denote the coefficient of  $S^2$  by  $a$ , the coefficient of  $S$  by  $b$ , and put  $100 \sum_1^x a_n$  equal to  $c$ , we have the conventional form of the quadratic equation:

$$aS^2 + bS + c = 0, \text{ whose solution is } S = (-b \pm \sqrt{b^2 - 4ac})/2a.$$

The value of the discriminant ( $b^2 - 4ac$ ) determines the nature of the roots of the quadratic equation:

- (i) if this term is negative, the roots are imaginary;
- (ii) if this term is positive, the roots are real and unequal;
- (iii) if this term equals zero, the roots are real and equal.

When a practical case was worked out, this term proved to be very nearly equal to zero, and the departure from zero was clearly due to, and within, the statistical variation in determining the X-ray intensities. The value for  $S$  is then simply equal to  $-b/2a$ .

It will be noted that in the above treatment no restriction was put on the value of  $x$ , and therefore, unlike the treatment of Burnham, Hower and Jones (3), the equation in  $S$  can be solved whatever the number of elements in the alloy.

## DISCUSSION OF RESULTS

Examination of the final results in Table 4, indicate that the correction achieved is excellent for the solid metal samples of differing size, but is less adequate for the pellet samples, where both the size and the density are altered.

It will be noted that the X-ray results for V and W have not been included in the total of the elements present. The V results were not incorporated because they lay near the limit of detection and the occurrence of both small positive and negative values indicated that they were largely the result of the standard deviation of the X-ray counts. The fact that nearly all the W values were negative demonstrated that the element was external to the sample, and the values were actually due to reflection and scattering by the sample of the primary radiation from the tungsten target of the X-ray tube.

For comparison the results obtained from the regression curves of the uncorrected X-ray intensities are shown in Table 5 along with the S-factor results and the improvement, resulting from the use of the correction formula and the S-factor, is demonstrated.

It will be noted that, except in the case of the pellet samples, multiplication of the intensities by the reciprocal area results in over-correction of the percentages.

If all the calculated results are normalized so that the sum of the percentages equals (100-the percentages of C, S, P and Si), i.e., 99.44%, then the results appear as in Table 6. It is clear that of the two methods using regression curves, the second employing correction of the recorded intensities in proportion to the areas, followed by application of the curves and normalization of the sum of the percentages, yields more accurate results than the first, where the area correction is omitted.

Finally, the differences between the chemical percentages and the three calculated percentages from Table 6 are tabulated in Table 7, and indicate the overall superiority in precision resulting from the use of the Lucas-Tooth correction formula and of the S-factor.

It should be noted that on many occasions in practice it may not be possible to measure the irradiated area with the necessary degree of accuracy and that, therefore, the method using area correction cannot be employed. Recourse must then be made to the second less accurate method, or more usually to the use of masks of absorbing metal to cut down the irradiated area of the standard to that of the sample. Not only are all the intensities reduced by this procedure, but longer counting times are required to maintain adequate statistical accuracy of the counts. In addition X-ray lines from the mask may interfere with the measurement of the analytical lines from the sample.

All these difficulties are obviated by the employment of the S-factor, and the correction is derived solely from the recorded intensities.

TABLE 1

Spectrometer Settings

Diffracting Crystal	Element			Background	
	Line	2 $\theta$ angle Mar-Apr.1962	2 $\theta$ angle October 1962	2 $\theta$ angle Mar-Apr.1962	2 $\theta$ angle October 1962
Quartz	MoK	30.05°	29.92°	33.00°	33.00°
Quartz	NbK	31.65°	31.52°	33.00°	33.00°
Quartz	W L <sub>B</sub>	55.70°	55.58°	60.00°	60.00°
Quartz	CuK	68.25°	68.12°	71.00°	71.00°
Quartz	NiK	74.35°	74.22°	71.00°	71.00°
Quartz	FeK	89.70°	89.57°	96.00°	96.00°
Quartz	MnK	99.80°	99.65°	96.00°	96.00°
Quartz	CrK	112.90°	112.80°	105.00°	105.00°
LiF	V K	76.90°	76.75°	75.00°	75.00°



TABLE 2

Net X-ray Fluorescent Intensities of Stainless Steel Samples  
in Counts per Second

Sample	Diameter in inches	I <sub>Fe</sub>	I <sub>Cr</sub>	I <sub>Ni</sub>	I <sub>Mn</sub>	I <sub>Cu</sub>	I <sub>Mo</sub>	I <sub>V</sub>	I <sub>Nb</sub>	I <sub>W</sub>
S <sub>1</sub>	1.255	23508	5638	2676	424	78	277	34	9	164
S <sub>2</sub>	1.138	23615	5657	2698	427	79	282	38	9	174
S <sub>3</sub>	1.011	19628	4521	2251	345	70	242	--	7	146
S <sub>4</sub>	0.867	15349	3591	1731	267	63	182	23	4	130
S <sub>5</sub>	0.747	12325	2887	1375	217	51	143	19	5	96
P <sub>1</sub>	1.00	13886	3210	1577	244	54	194	--	7	126
P <sub>2</sub>	1.00	15104	3474	1730	265	56	206	--	6	127

TABLE 3

The Coefficients of Inter-Element Effect Equations (Programme 2)

Coefficients	Mo	Nb	W	Cu	Ni	Fe	Mn	Cr	V
	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )	(10 <sup>-6</sup> )
a <sub>n</sub>	-2327.0174	-7993.8783	-1809034.6	-53091.872	23218.568	199502.45	33708.02	-263303.15	-21717.233
K <sub>O</sub>	564.19940	8641.4158	45483.251	2739.9590	7313.9324	3914.5542	5467.1471	5359.0333	-4292.0998
K <sub>Mo</sub>	0.0176267	-9.324133	-0.885484	0.103132	-0.116676	-0.001372	0.054687	-0.026621	-0.099325
K <sub>Nb</sub>	0.306859	-0.315563	-0.947227	0.251645	-0.038155	-0.040690	0.127261	0.009913	0.0123780
K <sub>W</sub>	1.038973	3.298784	9.950200	1.859557	3.021137	0.317983	-0.275376	-1.914405	1.861837
K <sub>Cu</sub>	0.436090	-1.767531	-14.190727	-1.086324	-1.066473	-0.158268	-0.555385	-0.825856	-5.384414
K <sub>Ni</sub>	-0.0079101	-6.179243	-0.178412	-0.032736	-0.121623	-0.097946	-0.067911	-0.019799	0.223606
K <sub>Fe</sub>	0.0086225	-0.182170	-0.898500	0.025969	-0.092785	-0.048639	-0.042752	-0.054594	0.128483
K <sub>Mn</sub>	-0.377082	-0.464132	-0.984122	0.148370	-0.224615	-0.164321	0.217079	0.009714	-0.534776
K <sub>Cr</sub>	0.0054209	-0.528807	-2.403625	0.039971	-0.273935	-0.061203	-0.271812	-0.062611	0.405513
K <sub>V</sub>	-1.460516	-10.701902	-26.718607	-3.232156	-4.422136	-1.329604	1.518481	4.713942	0.040902

TABLE 4

Comparison of Chemical and Calculated Percentage Results for Samples

Sample	S-factor	Fe	Cr	Ni	Mn	Cu	Mo	C	S	P	Si	Total less C, S, P, Si
P <sub>1</sub> + P <sub>2</sub>	Chemical Results	69.77*	18.80	9.51	1.14	0.22	--	0.08	0.019	0.027	0.43	99.44
Solid	S-factor							Not included in Total				
								V	Nb	W		
S <sub>1</sub>	1.069	69.25	19.72	8.96	1.06	0.26	0.23	0.03	0.00	-0.62		99.48
S <sub>2</sub>	1.063	69.17	19.69	9.03	1.06	0.26	0.23	0.04	0.00	-0.54		99.44
S <sub>3</sub>	1.300	70.94	17.94	9.73	1.02	0.30	0.27	-0.02	0.00	-0.33		100.20
S <sub>4</sub>	1.638	69.79	18.81	9.26	1.02	0.33	0.24	0.03	0.00	-0.27		99.45
S <sub>5</sub>	2.044	69.66	19.06	9.00	1.04	0.33	0.23	0.03	0.00	-0.45		99.32
	Average	69.76	19.04	9.20	1.04	0.30	0.24					99.58
	Diff. Chem.-X-ray	+0.01	-0.24	+0.31	+0.11	-0.08	-0.24					-0.14
Pellets												
P <sub>1</sub>	1.829	71.27	17.46	9.96	1.02	0.33	0.32	-0.02	0.00	0.07		100.36
P <sub>2</sub>	1.686	71.15	17.61	9.93	1.02	0.31	0.30	-0.02	0.00	-0.08		100.32
	Average	71.21	17.54	9.95	1.02	0.32	0.31					100.34
	Diff. Chem.-X-ray	-1.44	+1.26	-0.44	+0.12	-0.10	-0.31					-0.90

\* Obtained by difference

TABLE 5  
Comparison of Calculated Results

Sample	Normalized Reciprocal Area	S-factor	Fe			Cr			Ni			Mn			Mo			Cu			Total		
			A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
S <sub>1</sub>	1.000	1.069	69.25	70.90	70.90	19.72	18.96	18.96	8.96	9.58	9.58	1.06	1.24	1.24	0.23	0.27	0.27	0.26	0.17	0.17	99.48	101.12	101.12
S <sub>2</sub>	1.216	1.063	69.17	71.06	78.84	19.69	19.03	23.20	9.03	9.65	11.70	1.06	1.25	1.56	0.23	0.28	0.33	0.26	0.25	0.32	99.44	101.52	116.05
S <sub>3</sub>	1.541	1.300	70.94	64.97	81.18	17.94	15.05	23.62	9.73	8.07	12.37	1.02	0.98	1.60	0.27	0.24	0.36	0.30	0.22	0.36	100.20	89.53	119.49
S <sub>4</sub>	2.095	1.638	69.79	58.44	84.09	18.81	11.79	25.57	9.26	6.23	12.92	1.02	0.73	1.69	0.24	0.19	0.37	0.33	0.19	0.45	99.45	77.57	125.09
S <sub>5</sub>	2.822	2.044	69.66	53.83	88.10	19.06	9.33	27.75	9.00	4.98	13.92	1.04	0.56	1.86	0.23	0.15	0.39	0.33	0.15	0.49	99.32	69.00	132.51
P <sub>1</sub>	1.575	1.829	71.27	56.21	67.63	17.46	10.46	16.92	9.96	5.69	8.89	1.02	0.65	1.11	0.32	0.20	0.30	0.33	0.16	0.27	100.36	73.37	95.12
P <sub>2</sub>	1.575	1.686	71.15	58.06	71.31	17.61	11.38	18.37	9.93	6.23	9.74	1.02	0.72	1.22	0.30	0.21	0.32	0.31	0.17	0.29	100.32	76.76	101.25

A - Lucas-Tooth and S-factor

B - Regression Curve

C - Regression Curve after Multiplication of Cts/sec by Reciprocal Area

TABLE 6

Comparison of Normalized Calculated Results

Sample	Normalized Reciprocal Area	S-factor	Fe			Cr			Ni			Mn			Mo			Cu		
			A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
S <sub>1</sub>	1.000	1.069	69.22	69.72	69.72	19.71	18.65	18.65	8.96	9.42	9.42	1.06	1.22	1.22	0.23	0.27	0.27	0.26	0.26	0.26
S <sub>2</sub>	1.216	1.063	69.17	69.60	67.56	19.69	18.64	19.97	9.03	9.45	10.03	1.06	1.22	1.34	0.23	0.27	0.28	0.26	0.24	0.27
S <sub>3</sub>	1.541	1.300	70.40	72.16	67.56	17.80	16.72	19.66	9.66	8.96	10.29	1.01	1.09	1.33	0.27	0.27	0.30	0.30	0.24	0.30
S <sub>4</sub>	2.095	1.638	69.78	74.91	66.85	18.81	15.11	20.33	9.26	7.99	10.27	1.02	0.94	1.34	0.24	0.24	0.29	0.33	0.24	0.36
S <sub>5</sub>	2.822	2.044	69.74	77.58	66.11	19.08	13.45	20.82	9.01	7.18	10.45	1.04	0.81	1.40	0.23	0.22	0.29	0.33	0.22	0.37
P <sub>1</sub>	1.575	1.829	70.61	76.18	70.70	17.30	14.18	17.69	9.87	7.71	9.29	1.01	0.88	1.16	0.32	0.27	0.31	0.33	0.22	0.28
P <sub>2</sub>	1.575	1.686	70.53	75.22	70.03	17.46	14.74	18.04	9.84	8.07	9.57	1.01	0.93	1.20	0.20	0.27	0.31	0.31	0.22	0.28

A - Lucas-Tooth and S-factor

B - Regression Curve and Normalization of Sum of Percentages

C - Multiplication of Intensities by Reciprocal Area, Application of Regression Curve and Normalization of Sum of Percentages

TABLE 7

Differences between Chemical and X-ray Results

Sample	Fe			Cr			Ni			Mn			Mo			Cu		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
S <sub>1</sub>	0.55	0.05	0.05	-0.91	0.15	0.15	0.55	0.09	0.09	0.08	-0.08	-0.08	-0.23	-0.27	-0.27	-0.04	-0.04	-0.04
S <sub>2</sub>	0.60	0.17	2.21	-0.89	0.16	-1.17	0.48	0.06	-0.52	0.08	-0.08	-0.20	-0.23	-0.27	-0.28	-0.04	-0.02	-0.05
S <sub>3</sub>	-0.63	-2.39	2.21	1.00	2.08	-0.86	-0.15	0.55	-0.78	0.13	0.05	-0.19	-0.27	-0.27	-0.30	-0.08	-0.02	-0.08
S <sub>4</sub>	-0.01	-5.14	2.92	-0.01	3.69	-1.53	0.25	1.52	-0.76	0.12	0.20	-0.20	-0.24	-0.24	-0.29	-0.11	-0.02	-0.14
S <sub>5</sub>	0.03	-7.81	3.66	-0.28	5.35	-2.02	0.50	2.33	-0.94	0.10	0.33	-0.26	-0.23	-0.22	-0.29	-0.11	0.00	-0.15
P <sub>1</sub>	-0.84	-6.41	-0.93	-1.50	4.62	1.11	-0.36	1.80	0.22	0.13	0.26	-0.02	-0.32	-0.27	-0.31	-0.11	0.00	-0.06
P <sub>2</sub>	-0.76	-5.45	-0.26	-1.34	4.06	0.76	-0.33	1.44	-0.06	0.13	0.21	-0.06	-0.30	-0.27	-0.31	-0.09	0.00	-0.06

A - Lucas-Tooth and S-factor

B - Regression Curve and Normalization of Sum of Percentages

C - Multiplication of Intensities by Reciprocal Area, Application of Regression Curve and Normalization of Sum of Percentages

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