A GENERAL QUANTITATIVE SPECTROGRAPHIC METHOD FOR THE ANALYSIS OF ORES, AND ASSOCIATED METALLURGICAL PRODUCTS

by

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CONTENTS

S U M M A R Y.

Methods are described for the determination of P, As, Sb, Ba, Bi, B, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Sr, Zn, W, Be, Mo, Ge, Nb, Ta, V, Ti, and Zr in ores and associated metallurgical products. Mixtures of Te, Cd, Au and Pt in graphite were used as combined buffer -- internal standard diluents.

With two exceptions, namely Ba and As (in siliceous materials) the accuracy and standard deviations of the methods were within ± 15%.

1. INTRODUCTION

The work described in this thesis was carried out at the Johannesburg laboratories of Goldfields of S A Ltd., and of the Government Metallurgical Laboratory.

In both these laboratories samples were received of ores, both before and after metallurgical concentration techniques. In some cases a mineralogical analysis was also undertaken in the mineralogical section, but frequently this was not required The samples were generally submitted for analysis for the more economically important elements, and for any other elements that might affect the cost of their recovery. In many cases the sample was at least -150 mesh on arrival, and was submitted under a sample number, with no information given as to its history.

Under these circumstances, the main object of the work was to obtain general methods of spectroscopic analysis, using as few internal standards as possible that could be applied to the wide variety of sample matrices found in the ores submitted for analysis. It was also desirable that the methods should be applicable to as many elements as possible, whether of economic value or not.

/With...

With no knowledge of the sample history it was frequently necessary to do a preliminary analysis of a composite sample from a batch, to determine the approximate concentrations of the major elements, in order to make up a representative matrix for the standards. These standards were always prepared, artificially, from spectrographically pure substances. Internal standard mixtures were prepared in quantity in spectrographically pure graphite, and mixed in the correct prcportions, with samples submitted for analysis.

As the methods were intended to be quantitative as opposed to semi-quantitative, the methods of Harvey[1], Mitchell[2] and Von Tongeren[3], were not considered. In 1955, Jaycox[4] introduced a general method of analysis, using one part of sample mixed with one part of germanium dioxide, and diluting one part of this mixture with nineteen parts of cupric oxide and twenty parts of graphite. He obtained results for Al, Cr, Fe, Mn, Ni, Pb, Si, and Sn, using weak copper lines for comparison. While of value for many elements of intermediate volatility, this method has the disadvantage that it cannot be used for the simultaneous determination of copper and other elements. In the mining industry copper is always of interest, and, in fact was requested in over seventy per cent of the samples submitted for analysis.

/In...

In 1955 Dennen and Fowler[5] published a method using alumina as a variable internal standard. They found the ratios of the concentrations of the normal matrix elements as oxides, to that of aluminium, and, hence the percentage of the total sample that was there as SiO_2, TiO_2, Al_2O_3, total iron (as Fe_2O_3), MgO, MnO, CaO, Na_2O and K_2O. This method, while useful for a preliminary determination of the composition of the matrix would not appear to be applicable to samples of high halide or carbonate concentration, or for minor constituents, without simultaneous chemical determinations.

In 1957 Frisque[6] published a method for the spectrographic determination of Al, Ba, B, Ca, Cr, Co, Fe, Pb, Li, Mg, Mn, Mo, Ni, F, Si, Na, Sn, Ti, V and Zn. He mixed 30 mg of sample with 400 mg of a 1 : 3 GeO_2 - Graphite diluent, and the analysis lines were compared with Ge 2829. This method would appear to be very useful, especially in cases where the high dilution, and consequent loss of sensitivity, is not of importance.

Biber and Levy[7] mixed the sample with an equal quantity of a grapnite - GeO_2 mixture containing 1% of GeO_2. Small amounts of sample were arced in electrodes with narrow craters, in order to reduce the matrix effects, and germanium was used as internal standard.

Addink[8,9,10] individually, and with co-workers[11,12] determined up to 38 elements, in a variety of materials using untapered, large diameter electrodes to minimize the variation of temperature within the arc.

/Five...

Five or ten mg of sample was packed into a shallow cavity in the anode, and arced at 10 amp.

Hawley and MacDonald,[13] described a method in which a Stallwood jet is used, the removal of the outer layer of the arc by the airstream facilitating the use of ground state lines that would normally self-absorb.

Hirst and Nicholls[14] describe a method for the determination of Pb, Ga, In, Ge, Cu, Bi, Sn, Cd, and Zn in limestones, by concentrating with acetic acid, and using thallium as an internal standard. Using this same procedure, and Pd as internal standard, they also obtained good results for Ni, Co, V, Cr, Mo, Ag, and Be.

Ahrens[15,16] describes methods for the analysis of silicate minerals, rocks, soils, and meteorites. Several internal standards are used, according to the particular group of elements required, e.g. Na for K, Li, Rb and Cs. However, indium and palladium are the two main standards when the elements are considered as a whole, and not in groups. Indium is used for the more volatile elements, and palladium for the involatiles. This method has been used for over thirty five elements.

/Lingard...

Lingard[17] gives a method for the spectrochemical determination of common elements in rocks and minerals. To a hundred milligrams of sample he adds nine hundred milligrams of nickel oxide and three grams of graphite. Arcing at 12 amps d.-c. for 30 seconds, he determines the following elements in the percentage ranges given in brackets Al (5-50), Ca(10-50), Fe (1-10), Mg (1-15), Mn (1-15) Si (5-80) and Ti (0.1-3).

Nomokonova[18] (1960) gives a method for the determination of Sn, Li, In, Be, Nb, Ta, Zr, Ti, Rb, Ga, Ge, Sc, La and Y in ores. In the same journal Vitushkina and Ginzburg[19] give a method for Cu, Ni, Co, Mn, Cr, Ti, V, Ag, Ga, Ge, In, Co, Zn, Mo, and Pb, using wine glass shaped electrodes. The samples were mixed with a buffer of 50% graphite and 50% iron powder, and arced at four amps or eight amps, according to the elements to be determined. An error of 15 - 35% is claimed, according to the element being investigated. Unfortunately, it is difficult to obtain English translations of this journal, Spektr. Analiz. v. Tsvetnoi Met., Sbornik 1960, but these articles would appear to be of great interest.

Neuberger, Schoffmann, and Herkenhoff[20] give a method for the determination of Fe, Mn, Si, P, Ca, Mg, Al, Cu, Cr and Pb in ores, by first fusing

/with...

with borax, and then using photometric, and flame photometric methods, but the time taken for analysis for all the elements mentioned would appear to be longer than when using straight spectrographic techniques.

As the method decided upon was to be used by several people, with various degrees of training, any chemical pre-treatment was considered undesirable. Similarly it was felt that as few internal standard mixtures as possible should be used, consistent with the determination of those elements most commonly required.

In the method described in this work the element considered were P, As, Sb, Ba, Bi, B, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Sr, Sn, Zn, W, Be, Mo, Ge, Nb, Ta, V, Ti, and Zr. The alkali metals were not included, as it was felt that, in general, they could be determined easily by flame photometric methods which had given satisfaction in the laboratory for a considerable period. The internal standards used were tellurium, cadmium, gold, and platinum.

/Method...

2. METHOD FOR LOWER REGION VOLATILES.

2.1 General.

Arsenic, antimony and phosphorus are extremely volatile elements, and were treated as a separate group, exposures being taken in the wavelength range 2340 - 3150 Å. The spectrograph used throughout this investigation was a large Hilger Littrow type with quartz optics. Analysis and standard lines were chosen, whenever possible, so as to lie between 2480 and 3600 Å, so that one arcing would suffice for the medium to volatile elements, and one for the involatile elements. This was not possible for arsenic, for reasons given below, so a further subdivision was made of the lower region volatiles, arsenic, antimony, and phosphorus.

For development work, an "average" matrix was used consisting of approximately 50% SiO_2, 20% $CaCO_3$, 10% Fe_2O_3 and 20% Al_2O_3. An internal standard was chosen for the elements under consideration, particular attention being paid to the following factors:-

(a) Volatility, - other factors being equal, the internal standard was chosen so as to have approximately the same volatility as that of the element sought.

(b) Mutual occurrence, - an element was not chosen as internal standard if it was likely to occur naturally with the analysis element.

(c) Detectable occurrence, - whenever possible an element was not chosen as internal standard if it was likely to be detectable in any sample received in the laboratory, so as to ensure the maximum applicability of the method.

/The procedure...

The procedure adopted in developing methods was as follows. Standards of the elements were made in the "average" matrix given above. Once a method was found to give a straight line concentration curve using this matrix, analysed samples of soils and ores were arced, and an approximate evaluation made of their matrices. If these differed greatly from the "average" matrix, standards were then made in artificial matrices corresponding as closely as possible to those determined, and the method developed was used. If the calibration curve obtained with these new standards differed significantly from that obtained with the "average" matrix, or, if the results obtained on the analysed samples differed significantly from the chemical figures, then an investigation was undertaken to find the cause, e.g. small quantities of alkali metals in the natural matrix might affect the rate of volatilisation of the element to be determined. Once the cause had been ascertained, and the difficulties overcome by changing the conditions, the method was used on all samples submitted for analysis for the element concerned.

As stated above, analysis lines were usually chosen with wavelengths above 2480A, but in the case of arsenic, As 2349 was the most sensitive line available without using specially sensitised plates, and as arsenic was considered to be of importance when present as a minor constituent, it was decided to use this line.

Yu Yokoyama[21] compared As 2349 and Sb 2598 with Cd 3261, using calcium nitrate as a buffer. He obtained good reproducibility (a coefficient of variation of approximately 10%), although the cadmium line appears to be somewhat distant from the two analysis lines, and, in fact, could not be used on the large Hilger, as its range does not extend from 2349 - 3261 A on a single arcing.

As a special range was necessary for arsenic, it was decided to include antimony in this method for the following reasons:-

(a) if the method was suitable for arsenic, it was likely to be suitable for antimony, because of their similarity in the arc,

(b) as arsenic and antimony usually occur together, there was a strong possibility that if the concentration of arsenic was required, that of antimony would also be of interest. If antimony had been classed with the upper region volatiles, two exposures would have been necessary, with different ranges, to determine both elements.

Phosphorus was included in this method because of its volatility, and the proximity of its line to that of the internal standard.

/Choice...

2.2 Choice of internal Standard.

Tellurium was chosen as internal standard as it seemed suitable, being rare, and therefore not liable to occur in any samples received for analysis, and also because its volatility was similar to the volatilities of the elements under consideration, and it had lines of suitable wavelength for comparison. A 0.1 per cent mixture of tellurium (using Spec. pure TeO_2) was made in S.P. 2 graphite, and samples and standards were mixed with this, in the ratio of one part of sample to nine parts of internal standard mixture. A Wig-L-Bug converted dental amalgamator was used for all small bulk mixing, and an agate pestle and mortar were used for mixing large quantities of matrices of internal standard mixtures.

Table 1.

Data on the lower region volatiles.

Element	B.Pt°C	Cpd. added	B.Pt°C	Wavelength A	Intensity	Excitation ptl. eV
Te	1390	TeO_2	s.450	2385.76	600	5.8
P	280	KH_2PO_4	d.P_2O_5 s.347	2554.93	60	7.1
As	615	As_2O_3	s.193	2349.84	250	6.6
Sb	600	Sb_2O_4	-O, 930 s.1550	2877.91	250	5.3

Details of the elements and lines considered are given in Table 1. P2554.93 is weaker than P2535.65 (100) and P2553.28 (80), but was chosen for the reasons given in 2.7.

/Throughout...

Throughout this thesis, the lines and intensities quoted are taken from the M.I.T. wavelength tables.

2.3 Conditions of arcing.

The calculated amounts of KH_2PO_4, As_2O_3, and Sb_2O_4 were added to the "average" matrix, to give a mixture equivalent to 10% P, As, and Sb. This was diluted one part to nine with the internal standard mixture, and an exposure was taken using the following procedure.

(a) the electrode, described below, was filled with the mixture

(b) slit length; 1mm.

(c) with a current of five amps an exposure was taken for five seconds, then, without closing the shutter, the current was increased to fifteen amps, and the plate holder racked down 2mm each second for thirty seconds.

An examination of the plate showed that, at fifteen amps, all the elements of interest had volatilised completely after ten seconds. The conditions of arcing were therefore chosen as follows:-

Spectrograph:		Large Hilger, quartz optics
Plates	:	Ilford thin film half ton
Developer	:	D19b for 5 minutes
Electrodes	:	United Carbon 101L,
		National Carbon L4036

/Slit...

Slit : nominally 20 microns, length 8mm.

Exposure : 5 seconds at 5 amps, then 10 seconds at 15 amps, with step sector.

Optics : Lens F1025 (Hilger) 2cm from slit
Diaphragm 1 cmx1cm 36cm from slit
Lens F958 (Hilger) 54cm from slit
Source 63cm from slit
The lens F958 was protected from pitting by replaceable quartz slides.

2.4 Calculations.

Plate readings were taken on a Jarrell Ash comparator-microphotometer, and the calculations were performed on the Respectra calculating board. A step sector was used throughout the investigation, and, on examining the standard spectrograms, it was decided which step of the analysis line to compare with the standard line, e.g. if the analysis line were weak and the standard line strong, it might be decided to compare the first step of the analysis line with the third step of the standard line. This was to facilitate the comparison of several analysis lines, of sometime vastly different strengths, with the same standard line, using the same scale for the log intensity ratios on the graph paper. The graphs plotted were of percentage element versus log intensity ratio. The slit of the spectrograph was usually masked with black film, so that only the steps of interest were exposed.

/Arsenic...

2.5 Arsenic.

Arsenic determination is of interest to the gold mining industry, as complications are caused in the cyanide process by its presence. Samples were therefore received from many different types of deposits. Those from the Witwatersrand usually consisted of highly siliceous material, whereas some samples from Rhodesia, and South West Africa were predominantly calciferous. As the presence of arsenic, or antimony, in large quantities, frequently makes it necessary to roast the ores before using the cyanide process, the determination of the Sb - As content is routine in mine cost evaluation.

The spectrochemical determination of arsenic has been investigated by several workers. Goldschmidt and Peters[22] determined its concentration in iron ores, using As 2780 and As 2860 as analysis lines. As 1890 is the most sensitive line, but has too short a wavelength to be useful with a photographic instrument on a routine basis. This line would, however, probably be very useful for vacuum spectrographs and photo-electric measuring techniques.

/The detection...

The detection limit for arsenic is normally of the order of 100 p.p.m., as in the method described here, although Hall and Lovell[23] determined approximately 20 p.p.m., in anthracite coal ash, using 'boiler' electrodes. Sb2614.30 was used as internal standard line, and, as Sb and As are very similar chemically, due to their external electronic configuration, it is probable that their chemical behaviour in the arc would be very similar. They also have very similar boiling points, and should therefore be good internal standards for each other. However the use of antimony as an internal standard was impracticable in the present investigation, as, in nearly every sample submitted for arsenic determination, antimony was not only present, but also required. Tellurium, however, suffered from no such disadvantage, and equal step sector steps of As2349 and Te2386 were compared.

No background corrections were made. When highly siliceous materials were analysed interference from a component of a SiO band was apparent. Such interference was corrected by measuring another line in the silica band of known intensity ratio to that interfering with the arsenic line. A correction could then be made on the calculating board.

/The difficulty...

The difficulty in using this method was the identification of one specific component of the band for use as reference. This was solved by using the line interfering with Au 2349.84. Gold was unlikely to occur in detectable concentrations, and its presence could be checked by reference to Au 2675.95. The line could easily be found by comparison with a gold - arsenic - tellurium standard plate. It was found that, in the absence of gold and arsenic, the ratio of the two lines in the band is given by

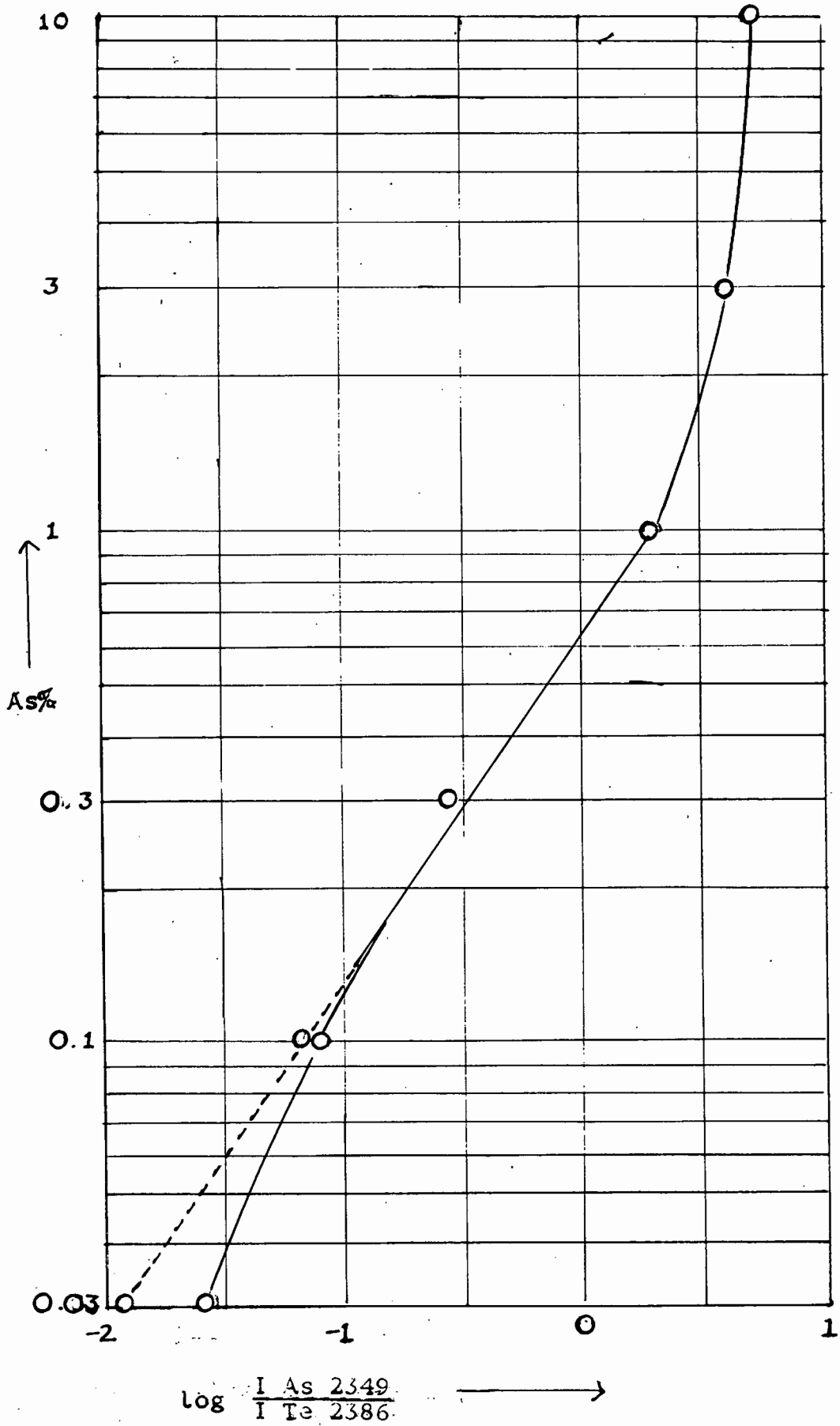
$$\log \frac{\text{Intensity Si02428}}{\text{Intensity Si02350}} = -0.28.$$

This compensation technique is very similar to that employed by Ahrens[24], for obviating the effect of SiO 2497.73 on B 2497.73. In this case the correction was made by using Si02497.56, a component next to Si02497.73 and of the same intensity.

The curve for As% v. $\log \frac{\text{Intensity As2349}}{\text{Intensity Te2386}}$ is given on page 16. It will be seen that there is self absorption for arsenic values in excess of approximately two per cent, and that the background becomes significant for values below 0.1% As. The dotted line gives the curve when background corrections have been applied at the 0.1 and 0.03% levels.

Figure 1

The graph of percentage arsenic versus $\log \frac{I\ As\ 2349}{I\ Te\ 2386}$



The dotted line gives the shape of the curve with background corrected.

A comparison of the spectrographic and chemical results for arsenic are given in Table 4 on page 118. Unfortunately the chemical results could not be regarded as highly accurate, as the samples were not chemical standards. Assuming, however, the chemical results to be correct, an accuracy of ± 14% was obtained for the samples that needed no silica band corrections and 25% for the others. Throughout this work the accuracies and the coefficients of variation were calculated as given in Appendix 1.

For the purpose of preparing a working curve, each standard was arced in triplicate, whereas in the actual determinations unknowns were arced in duplicate. Although only twenty checked samples were analysed, the method was used on a further thirty three unchecked samples, and it was found that for non-siliceous base materials the coefficient of variation was 11%, whereas, in the case of highly siliceous ores, this increased to 19%, probably due to the error in correcting for SiO band interference.

2.6 Antimony.

Very few chemically analysed samples were available for checking the antimony method, and those that were came from two sources, an iron - manganese ore deposit, and a Rhodesian gold mine. The only checked samples that were available from the latter deposit were metallurgical concentrates. The nature of these samples made it seem preferable to use Sb2878 as the analysis line, instead of the more commonly employed Sb 2528.535 and Sb 2598.062 for the following reasons.

/Silica...

Silica was always present in the samples, and Si 2528.56 was very strong, so that Sb 2588.535 could not be resolved. Sb 2598.062 would probably be very useful for many ores, but Fe 2598.028 (listed intensity of only 4) was found to interfere in iron - manganese ore.

A detection limit of approximately 20 p.p.m. is quoted by Ahrens[25], whereas in the present method the limit found was 600 - 700 p.p.m.. This low degree of sensitivity is partly due to the use of a relatively insensitive antimony line, and partly to the nine fold dilution with graphite. However, in the ore dressing questions involved, antimony was only of importance when present in quantities in excess of 0.1 per cent, so that higher sensitivity than that given by the present method was not required.

Many authors have given methods for antimony, one of the most interesting being that of Veselovskii[26] who employed vacuum sublimation in a hard glass tube at pressures of approximately 10^{-4} - 10^{-5} mm Hg, and temperatures of up to 880 ^{o}C. The sublimate was then analysed. However, this method was not necessary in the present case, as the sensitivity obtainable by direct excitation of the sample powder was more than was required. It must also be born in mind that the object in view was to develop methods that could be used as a matter of routine, by several people, some having little or no previous training, on samples whose history was frequently unknown.

/Although...

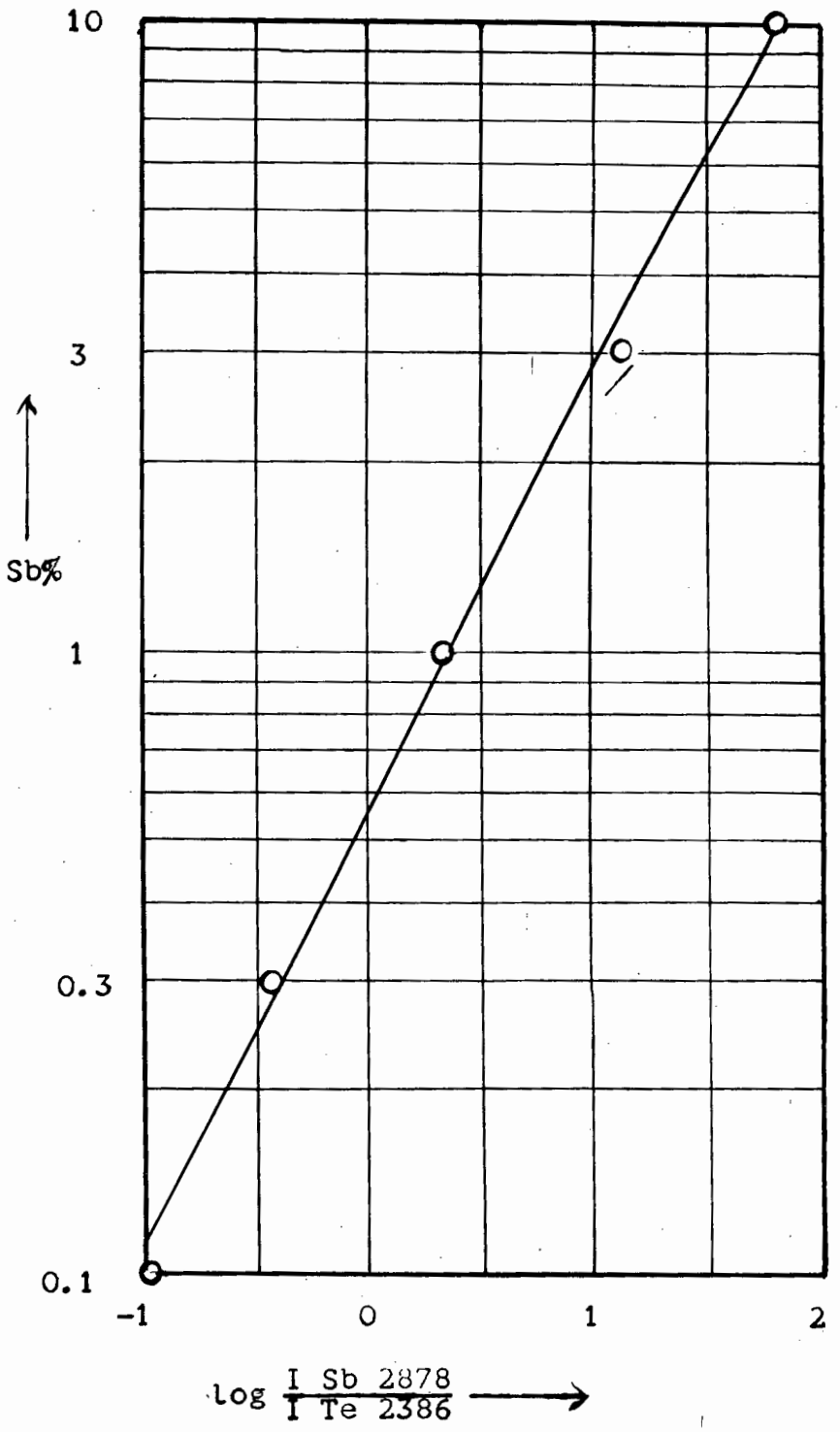
Although it seems probable that arsenic is one of the best internal standards for antimony, it was impractical to use it - as antimony was for arsenic- because arsenic is so frequently present with antimony, and often required in the same analysis.

A suitable step-sector step of Sb 2878 was compared with a higher step of tellurium, e.g. third step of antimony to second step of tellurium. The antimony working curve is given in Figure 2 on page 20, and the sample results in Table 5, page 119. The samples were arced in duplicate, and the working curve was obtained from triplicate determinations. As stated above, few analysed samples were available for antimony, but, on the basis of the ten examined, an accuracy of ± 13% was obtained. The method was used on approximately thirty samples, in duplicate, and the coefficient of variation was 10%.

In all cases the accuracies of the methods were calculated by comparting the chemical results with those found spectrographically on the same samples, assuming the chemical results to be completely correct. This was frequently a dangerous assumption, as many samples were not chemical standards, and, if the error in the chemical estimation was high it could result in a greater variation being assigned to the accuracy than was actually obtained, although the coefficient of variation of the spectrographic method itself would not be affected.

Figure 2

The graph of percentage antimony versus $\log \frac{I\ Sb\ 2878}{I\ Te\ 2386}$.



2.7 Phosphorus.

Calcium phosphate is widely used as a fertiliser, and is therefore of great interest to the mining industry when present in economic deposits. When the P_2O_5 content is of the order of 3% or over, the ore body is usually considered as being worthy of evaluation. During the mapping of a deposit, samples of a wide range of concentrations will be encountered, but the samples with a phosphorus content of less than 0.3% P are unlikely to be of interest in economic geology. It was not therefore considered necessary to try to increase the sensitivity of the method below this level.

Phosphorus is not very sensitive spectrochemically, the most common detection limit quoted being of the order of 100 p.p.m. P2535.65 (100) is the strongest available line for the analysis of phosphorus in ores, but it almost invariably suffers from interference from Fe2535.65 (1000). P2553.28 (80) is the next strongest line, but, in practice, this always appeared to suffer interference from Fe2553.185 (10), which could not be resolved. This is suprising, as the line finally chosen, P2554.93 (60) should be even more strongly affected by interference from Fe2555.066 (20), which would have been sufficiently different in wavelength to be distinguished, though not resolved. This, however, was not found to be the case, and it would appear that either Fe2555.066 was depressed in comparison to Fe 2553.185 with the arcing conditions used, or, perhaps more likely, the interference was a composite effect from this line and Ni 2553.377 (20).

/Nickel...

Nickel was known to be present in small amounts in this deposit, but Ni 2528.1 (20) was not detected. Ni 2419.3 (2) was faintly visible, however, and, in common with 2553.4, this is a ground state line. The interference on P2553 was such that a line persisted at this wavelength on all the plates, even when phosphorus could not be detected chemically. Such a pronounced effect could not be expected from the listed intensities of the iron and nickel lines.

There is little literature on the spectrographic determination of phosphorus in ores. Braun[27] used Co3044 as internal standard for P2535 in determining phosphorus in plant ash. Although several types of plates have a fairly constant gamma between 2,500Å and 3,100 Å, this seems to be a somewhat large wavelength difference.

Standards were made in the 'average' matrix, and arced in triplicate. Equal steps of P2555 and Te2386 were compared, and a working curve was drawn. This curve was checked with analysed samples, but the results were found to be systematically lower by 50% than given by chemical analysis, and a matrix effect was suspected. As phosphorus usually occurs, when in workable concentration, as calcium phosphate in rocks that are predominantly carbonatites, it was decided to ascertain whether a matrix effect was responsible.

/Standards...

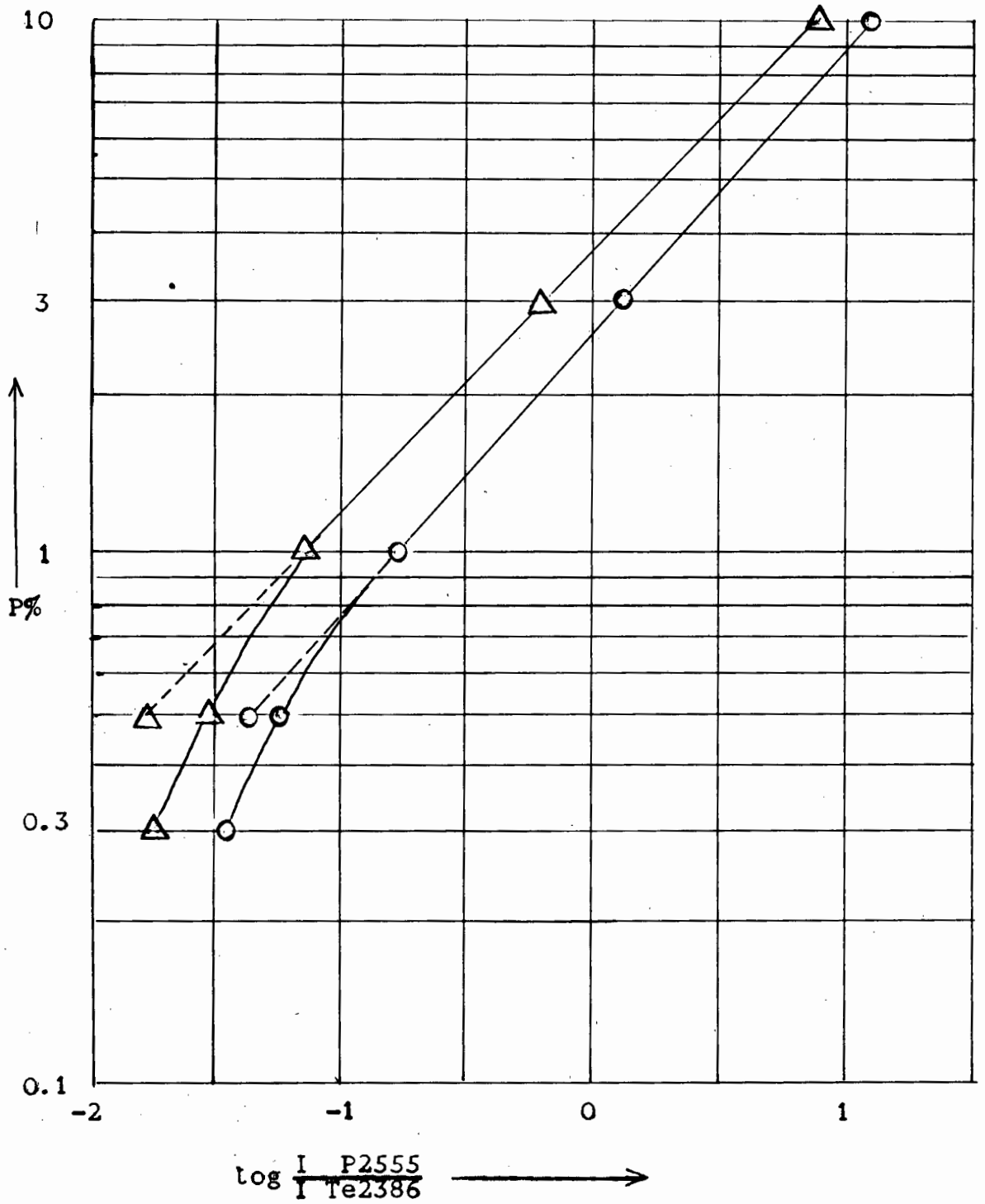
Standards were therefore made with calcium carbonate, and arced in triplicate. The working curve was found to be considerably displaced from that obtained previously, as shown in Figure 3, page 24.

The results calculated from the calcium carbonate curve are given in Table 6. The accuracy was found to be approximately ± 14%, although it was lower when dealing with high phosphate concentrations. This figure was again calculated assuming the chemical results to be correct, although the samples were not chemical standards.

The method was used on approximately fifty samples, and the coefficient of variation was ± 11%.

Figure 3

The graph of percentage phosphorus versus log $\frac{I\ P\ 2555}{I\ Te\ 2386}$



—O— P in 'average' matrix

— · — P in $CaCO_3$

----- Background corrections made.

3. METHODS FOR VOLATILE AND SEMI-VOLATILE ELEMENTS IN THE UPPER REGION.

3.1 General.

As stated in 2.1, analysis lines were usually chosen above 2480A. The elements in this category were subdivided into a volatile - semi-volatile group, and the involatiles. This section deals with the former, consisting of Bi, Cu, Pb, Zn, Ba, Sn, Ni, Co, Sr, Cr, Mn, Fe, B, Mg, and Ca. As this group covers a large range of elements of different volatilities, it was decided to use two internal standards, the choice being governed by the considerations given on page 7.

The matrices of the samples used for checking the method were found to vary considerably, and it was decided to use a more complex 'average' matrix for the preliminary investigations. This consisted of 70% SiO_2, 10% $CaCO_3$, 7½% Fe_2O_3, 2½% MgO, 2½% $MnSO_4$ and 7½% Al_2O_3. The procedure adopted in developing methods was the same as that given in section 2.1.

3.2 Choice of internal standards.

In dealing with so many elements at once, the question of interferences became marked. It seemed probable that any internal standard of suitable volatility would occur naturally in some rock or soil submitted for analysis.

/It was...

It was therefore decided to use relatively high concentrations of rare elements as internal standards. By doing this the method would not be affected by traces of these elements being present in the sample. The elements chosen as internal standards were gold and cadmium, and mixtures were prepared of 1% gold, using the calculated amount of ammonium chloroaurate, in graphite, and similarly 1% and 2% of cadmium in graphite. The cadmium mixture used depended on the dilution considered advisable for the sample in question. The lines used, and other relevent data, may be found in Table 2 on page 27.

These lines were chosen for their freedom from interference, and also for their position in the spectrum. As no dilution with alkalies was used, in the majority of cases, it was decided to choose lines as far from the cyanogen bands as possible. These lines had to be on the ultraviolet side of the CN bands, as plate characteristics vary rapidly at higher wavelengths, unless panchromatic plates are used, and for the majority of the elements these are not necessary. The plates finally chosen were Ilford thin film half tone.

Two lines are given for manganese and gold. The gold line nearer to the analysis line was generally used. The choice of manganese lines is discussed below.

/Table 2...

Table 2.

Element	Boiling Pt °C		Line Å	Intensity	Excitation ptl. Ev.
Barium	Ba	1140	3071.6	100R	4.04
	BaO c.	2000			
Bismuth	Bi	1470	3067.7	3000R	4.04
	Bi_2O_3	1230			
Boron	B	2550	2497.7	500	4.96
	B_2O_3	1500			
Cadmium	Cd	767	3261.1	300	3.80
	CdO	975			
Calcium	Ca	1240	3158.9	100	7.05
	CaO	2850			
Chromium	Cr	2200	2975.5	100R	5.13
Cobalt	Co	2900	3453.5	3000R	4.02
Copper	Cu	2310	3274.0	3000R	3.78
Gold	Au	2600	2675.9	250R	4.63
			3122.8	500	5.10
Iron	Fe	3000	2723.6	300	6.64
Lead	Pb	1610	2833.1	500R	4.40
Magnesium	Mg	1110	3096.9	150	6.72
	MgO m.	2700			
Manganese	Mn	1900	2593.7	200R	4.77
	Mn_3O_4 m.	1650			
	Mn_2O_3 m.	1700	2576.1	300R	4.81
Nickel	Ni	2900	3002.5	1000R	4.16
	NiO	3380			
Strontium	Sr	1150	3464.8	200	6.62
	SrO m.	2430			
Tin	Sn	2270	3175.1	500	4.33
Zinc	Zn	907	3345.0	800	7.78
	ZnO s.	1800			

3.3 Conditions of arcing.

A one percent mixture of all the elements was made in the new "average" matrix, and a 'time plate' was taken using the procedure described in 2.3. An examination of the plate showed that after five seconds at five amps followed by fifteen seconds at fifteen seconds at fifteen amps the analysis lines had either disappeared, or were of insignificant intensity (transmission of over 80%). The exposures were always started at five amps as this seemed to prevent material from jumping out of the electrode.

The electrodes used were National Carbon L4000, and United Carbon products 101U. The wavelength setting was 2480 - 3600A, and the exposure five seconds at five amps followed by fifteen seconds at fifteen amps. All the other conditions were as given in section 2.3.

3.4 Barium.

The spectrochemical estimation of barium has been studied by many workers, among the first being Von Engelhardt[28] (1936), who used cathode layer excitation and lanthanum as internal standard for the determination of barium in minerals and rocks. Ruehle and Jaycox[29] (1940) described a method for the determination of barium when in solution, using rotating electrodes, and obtained accuracies of 5 - 10%.

/In 1950...

In 1950 Farmer[30] used the cathode layer technique for the determination of barium, and other elements, in plant ashes. Potassium sulphate was used as a buffer, while silver and chromium, incorporated in carbon powder, provided internal standard lines. Lanthanum was also employed as an internal standard by Shaw[31] (1954) for the determination of barium in silicates. He used the ion lines Ba 4934: La 4921, instead of the line pair Ba 4554 : La 4558 used by Von Engelhardt.

The use of calcium as a variable internal standard is described by Ahrens and Taylor[32] for the determination of Ba in plagioclase feldspars. The The line pair used was Ba 4554 : Ca 4435. A similar method was employed on alkali feldspars using the line pair Ba 4554 : Ca 4455. Barium was also determined by Heier and Taylor[33] in alkali feldspars, using palladium as internal standard. One part of sample was mixed with five parts of graphite containing 10%$(NH_3)_4Pd(NO_3)_2$, and the line pair used was Ba 4934 : Pd 4473.

In 1956, Birks[34] determined barium, and many other elements, in alpha active materials, using a copper spark method. Mo was used as internal standard, and the line pair chosen was Ba 3891.8 : Mo 3903.0.

/These...

These methods all used lines with wavelenghts that were outside the range that had been chosen in the present method as being best for the majority of elements. Had barium been of such economic importance that traces were of interest to the mining industry, it would have been necessary to develop methods using the strongest lines, Ba5535.5 and Ba 4554 (1000R). This however was not the case and it was possible to choose the much weaker Ba 3071.6 (100R) as a suitable analysis line.

The procedure adopted in treating samples and synthetic standards will be called Method A to avoid repetition.

Method A

The samples and standards were mixed 1 : 1 with the graphite containing 1% gold. Approximately 15 mg (15 ± 2) were packed into the electrodes. These were then arced under the conditions given above. In many cases the weighing of matter into the electrode only took place for the first few samples, and when the general level of the mixture in the electrode had been noted, the quantity was judged visually. The amount was not critical, as an internal standard was being used.

Ba 3071.6 and Au3122.8 were the analysis lines second step of barium being compared with the fifth step of gold.

/No...

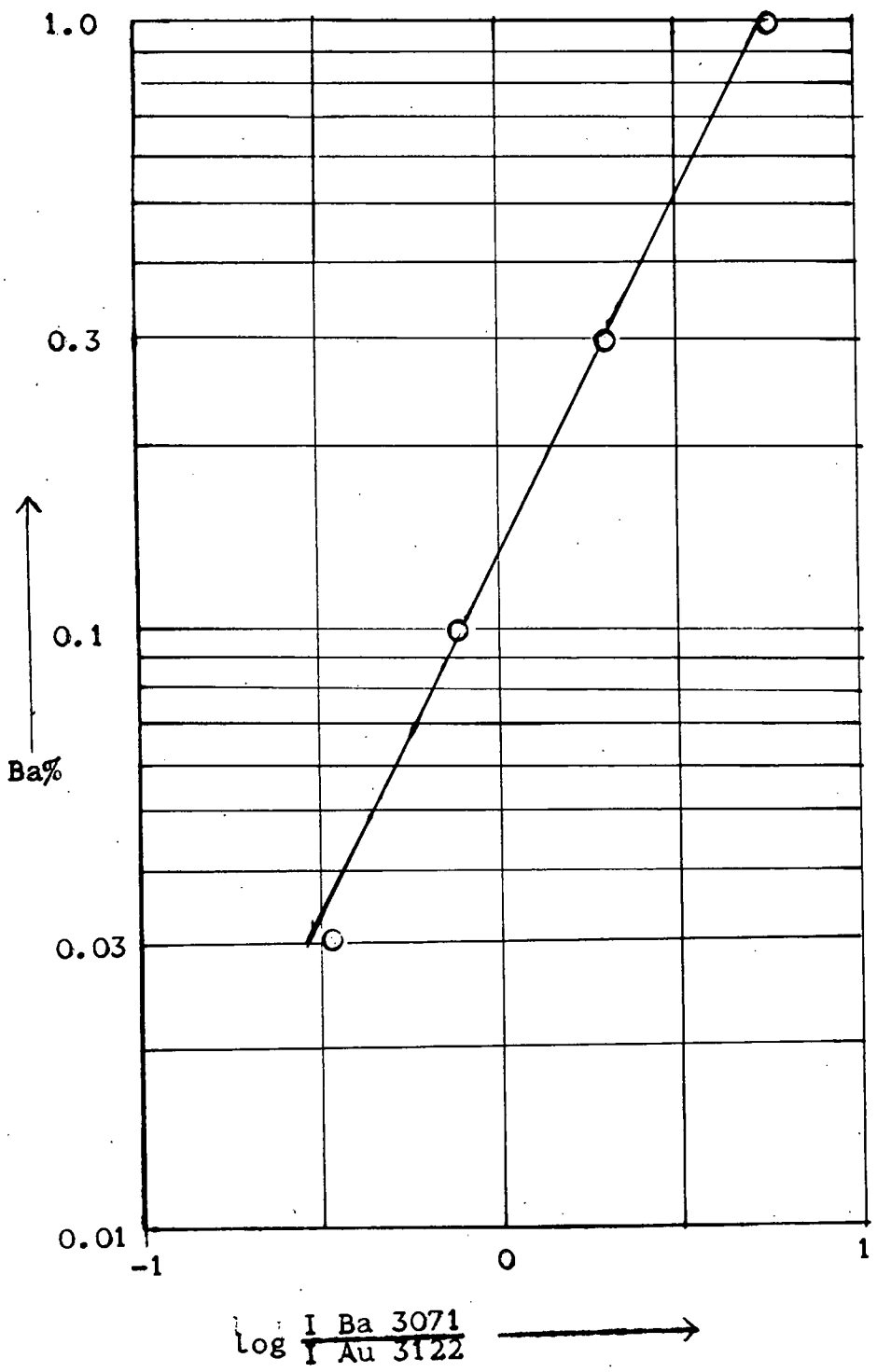
No background readings were taken, as the lines were in a relatively clear region of the plate. The barium working curve is given in Figure 4 on page 32.

The standard curve was obtained from triplicate determinations, and the samples were analysed in duplicate. Unfortunately there were only six analysed samples available for checking the method. These appeared to be mainly calcites, and the standards were therefore made in calcium carbonate. The results are given on page 121. These give an accuracy of ± 19%, assuming the chemical results to be correct. However, as the samples were not fully checked chemical standards, and had simply been analysed in a routine manner, the assumption may be invalid. For this reason, and because there were so few samples, a detailed statistical analysis was not undertaken.

One sample was burnt ten times, and the coefficient of variation was calculated to be ± 11%.

Figure 4

The graph of percentage barium versus log $\frac{I\ Ba\ 3071}{I\ Au\ 3122}$



3.5 Bismuth.

Few, if any, references are to be found in the literature for the determination of bismuth in ores, using spectrographic procedures. In 1949, Hustler and Hammaker[35] published a method for the determination of bismuth, and several other elements, in sand, using silver nitrate as a combined buffer and internal standard. Morris and Pink[36] (1957) developed a method for the determination of trace quantities of bismuth and other elements, by taking them into solution and drying on non-absorptive graphite electrodes. Molybdenum was used as internal standard, and spark excitation employed. Hegemann and Kostyra[37] (1955) developed a method for the determination of bismuth in sphalerite. Nine parts of sample were added to one of graphite, containing beryllium as internal standard, and this mixture was packed into deep electrodes, and the fractional distillation effect thereby obtained was utilized for maximum sensitivity. The line pair employed was Bi 3067 : Be 3321.4. This method was used by Hegmann and Sybel[38] (1955) for the estimation of bismuth in galena. The detection limit obtained was approximately 5 p.p.m..

Unless present in relatively high concentrations, bismuth is of little interest to the mining industry. For this reason, it was not necessary to develop a method giving optimum sensitivity.

/The...

The lines chosen were Bi 3068 : Au3123, and Method A (3.4) was employed. The second step of the bismuth line was compared with the fifth step of the gold line, and the working curve obtained from triplicate determinations is given on page 35. It will be seen that self-absorption takes place at concentrations of bismuth in excess of 0.3%.

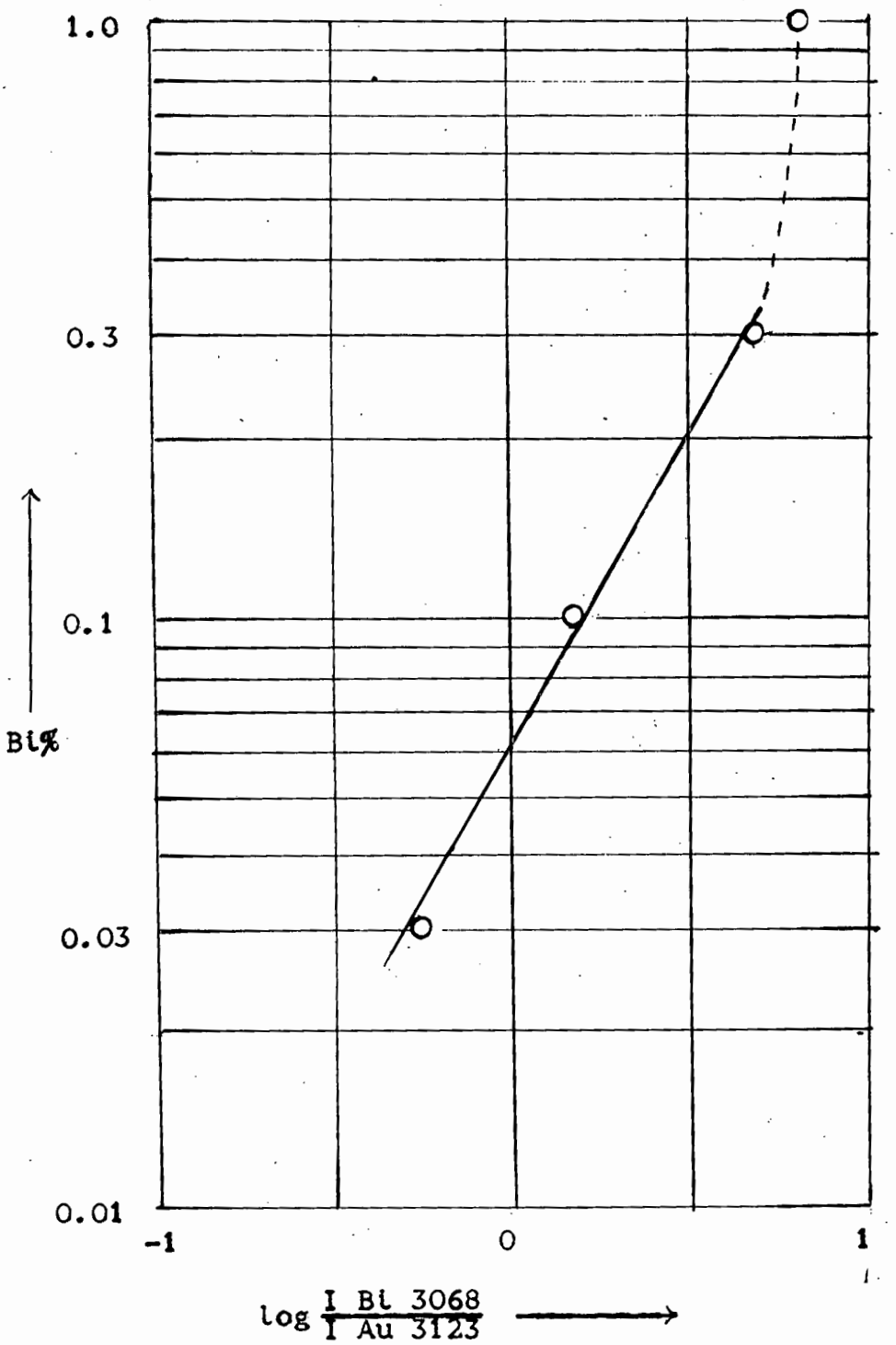
Deeke and Crosswhite[39] (1943) have shown that the most important factors affecting the self absorption of a line are the intensity, and the lowness of the low level of the line. As Bi 3068 is a very intense (3000) ground state line, and the low excitation potential is 0.0 eV, it is not suprising that this line self-absorbs.

As in the case of barium, there were few analysed samples available for checking the method. These were finely ground, and appeared to be clays. The spectrographic results are compared with those given chemically on page 121. The deviation of Bi 1 appears to be high, but including this result, a mean accuracy of ± 14% is obtained.

In order to calculate the reproducibility, one sample was thoroughly ground and thirty aliquots were analysed spectrographically. A coefficient of variation of ± 10% was obtained.

Figure 5

The graph of percentage bismuth versus log $\frac{I\ Bi\ 3068}{I\ Au\ 3123}$



-------- The portion of the curve showing self reversal.

3.6 Boron.

Although the most commonly used boron lines, B 2496.8 and B 2497.7, are perfectly free from cyanogen interference, the earlier workers on the spectrochemical analysis of this element were obliged to use copper electrodes for their determinations, as it was impossible to obtain graphite electrodes that did not contain significant traces of boron. Thus Goldschmidt and Peters[40] (1932) used copper electrodes, and cathode layer excitation, when investigating the geochemistry of boron. Landergren[40] (1945) used an intermittent arc to stop the copper electrodes from melting during the exposure, and added antimony, as 5% Sb_2O_5 in pure feldspar, to the samples to act as internal standard.

However, even by 1942 it appears that pure graphite was available, and Parks[42] investigated the boron content of soils using graphite electrodes. The samples were mixed with $CaCO_3$ containing tin as internal standard, and the effect of various salts on the boron - tin ratio was examined. It was found that NaOH and $AlCl_3$ had a disturbingly high effect on the ratio, even in the presence of 200% $CaCO_3$. The limit of detection was 15 p.p.m.. Graphite electrodes were also used by Ahrens[43], for the determination of boron in rocks

/Correction...

Correction for the interference of SiO 2497.73 on B 2497.73 was made using SiO 2497.56, the two band component being found to have the same intensity.

In 1953 Ota[44] studied the boron content of ooze from the bottom of the sea, using copper rods, the tellurium as internal standard. However, in the present investigation copper electrodes were not considered, as with the high grade graphite at present available from the National Carbon Co., and the United Carbon Co., no contamination was noted, even when examining uranium for boron at the 0.3p.p.m. level, by another method.

The samples that were available for checking the boron method were slags, so a special matrix had to be made containing 15% Na_2CO_3, 40% SiO_2, 20% Fe_2O_3, 10% $CaCO_3$, 5% MgO and 10% Al_2O_3.

Method A was again employed for boron, and equal steps of the most sensitive line, B2497..7 were compared with those of Au 2675.9. B 2496.8 was a possible alternative, but frequently suffered interference from Fe 2496.533 (40), whereas Fe 2497.8 (15) was rarely visible. The working curve for boron is given in Figure 6.

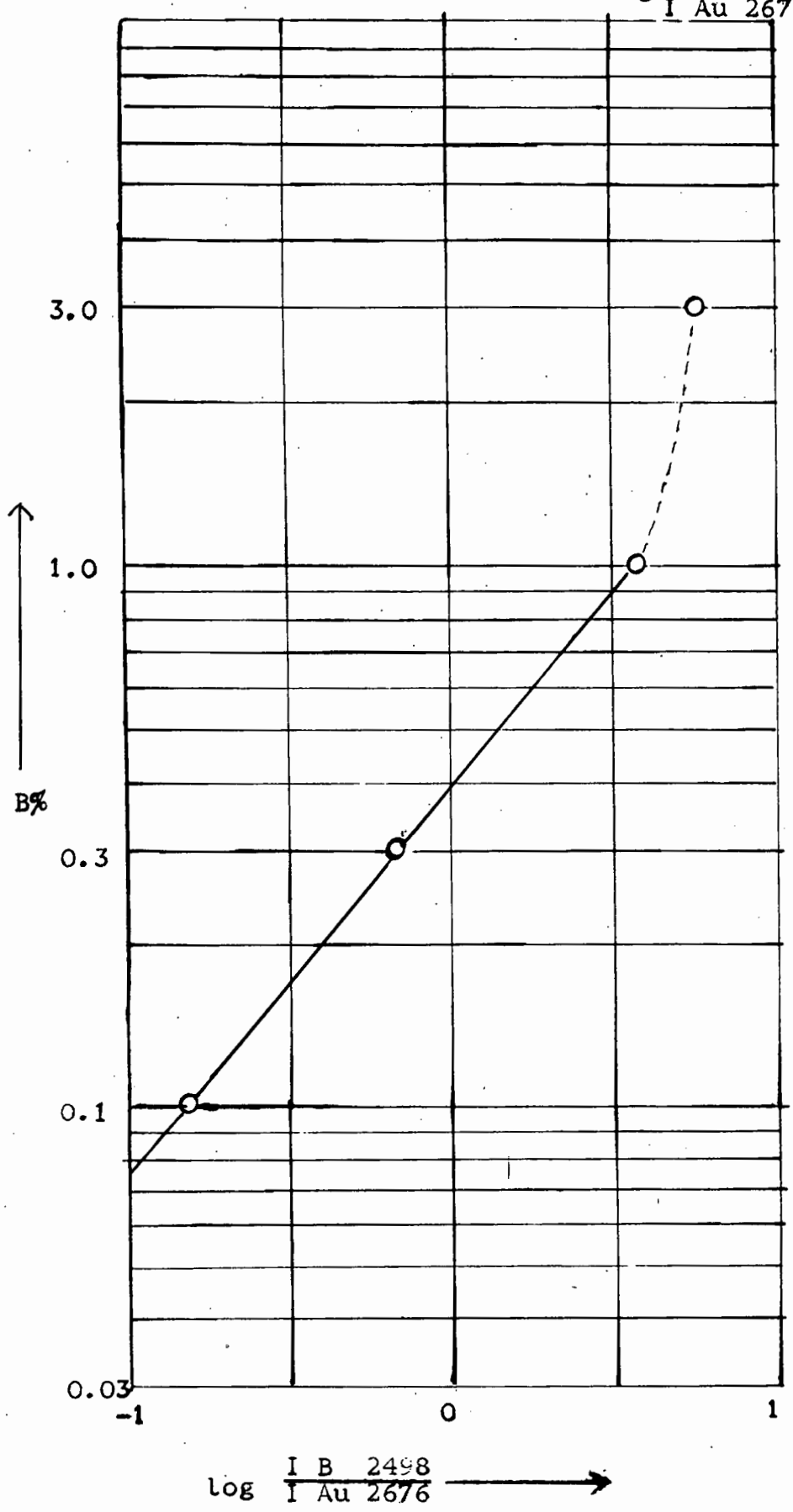
/It...

It is clear from the figure that there is self absorption of the boron line at concentrations of over 1% As B 2497.9 is a strong (500) ground state line, this is in accordance with Dieke and Crosswhite's[39] conclusions for iron.

The results are given on page 122, and, assuming the chemical results to be correct, the accuracy is $\pm$ 12%. One sample was analysed ten times and the coefficient of variation was $\pm$ 11%.

Figure 6

The graph of percentage boron versus $\log \frac{I\ B\ 2498}{I\ Au\ 2676}$



- - - - - - - The portion of the curve showing self reversal.

3.7 Chromium

The spectrographic analysis of chromium in steels has been studied by many workers, and Cr is included in most general methods for several elements. In 1939, Ashton[45] studied the analysis of chromium in plant ash, using molybdenum as internal standard, and adding a preponderance of lead oxide to suppress the cyanogen bands. Helz and Scribner[46] when studying several elements, including chromium, in cement, used cobalt oxides as internal standard, and graphite and KNO_3 as buffers. Hustler and Hammaker[35] used the same method of determining chromium in sands[3] as is described in 3.5 for bismuth. In 1955, a method was published by Astaf'ev, Rubinovich, and Yakovleva[47] for the spectrographic determination of Ni, V, Cr, and Cu in clay, using carbon electrodes, a constant current arc, and cobalt as internal standard. Their limit of detection was of the order of 20 p.p.m..

Nachtrieb, Johnson and Dress[48] employed a fusion technique for the determination of Cr, Fe, V, and Sb in titanium ores. These were fused with twenty times their own weight of potassium bisulphate, and graphite electrodes were dipped into the molten mixture, so as to obtain a thin vitreous coating. 2200 V. a.c. spark excitation was used, and a detection limit of 50 p.p.m. obtained.

/Nikitina...

Nikitina[49] (1955) described a method for the determination of chromium, and several other elements, in sand, quartz, and other highly siliceous materials. The samples were fired for 5 - 10 seconds in a separate arc (25 - 27 amp) and then put into the graphite electrode craters and exposed at 10 amp. with an arc gap of 2mm.. The spectrogram was free from SiO bands when 2mg samples were used, and the sensitivity of the method was 10 p.p.m..

The chemically analysed samples that were available for checking the method, and all the subsequent samples that were submitted for analysis were from a chrome - iron ore deposit, and were therefore very high in chromium. It was therefore possible to use a method involving quite high sample dilution. The samples were diluted 1 : 9 with "average" matrix, before mixing with the graphite - internal standard mixture, which contained both gold, and also one per cent of cadmium, as CdO. As these were the two main internal standards of the present work, a mixture containing both was frequently employed for preliminary work. The standards and samples were then arced in triplicate. On examining the resultant spectrogram, it was found that the variation of Cr 2975.5 with Cd 3261.1 was much more reproducible than with Au 3122.8. This was surprising, as cadmium is much more volatile than chromium. The method adopted was therefore to dilute the sample with "average" matrix, as given above, and then to mix 1 : 9 with graphite containing one per cent of cadmium.

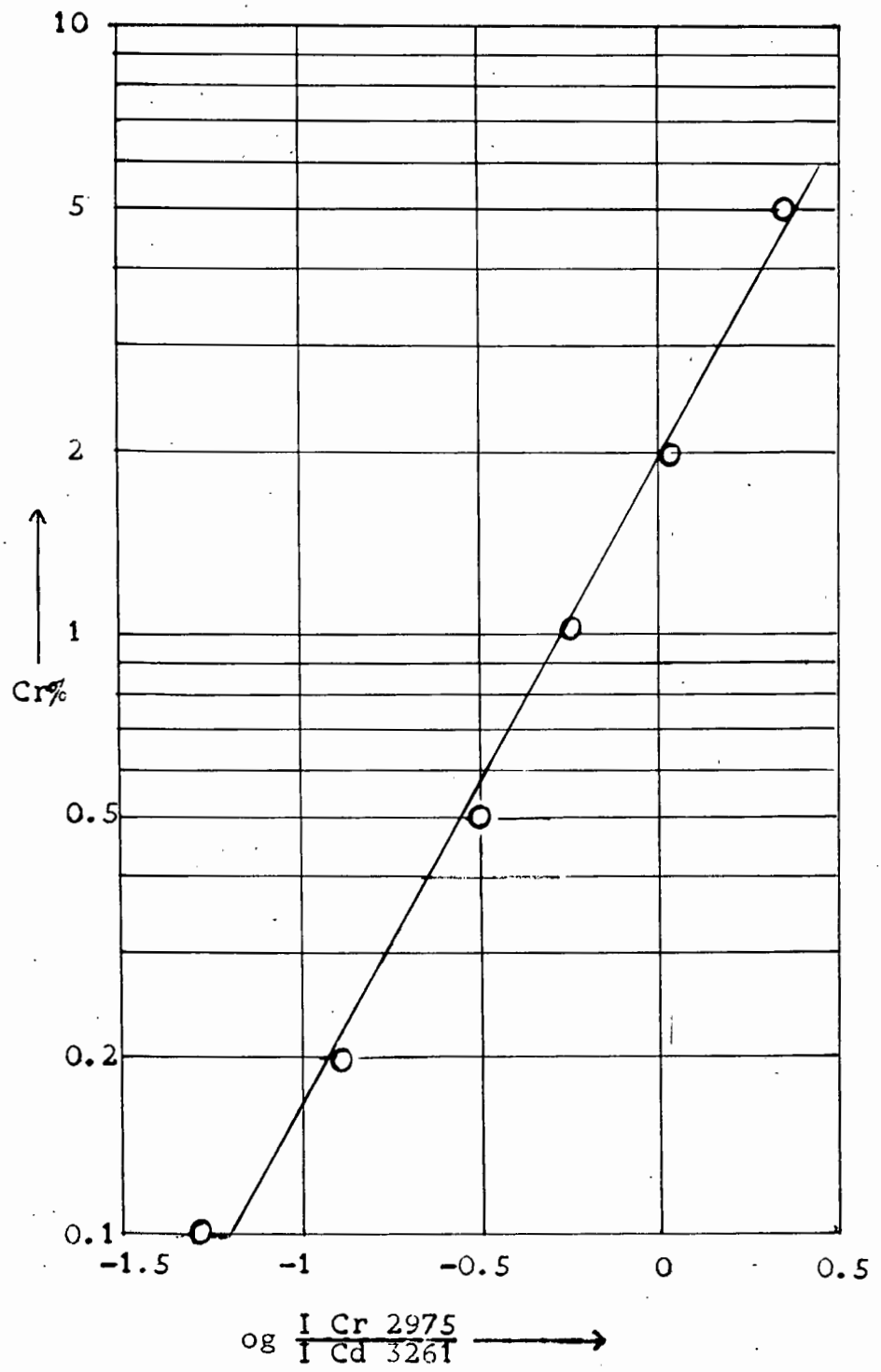
/The lines...

The lines used were Cr 2975.5 and Cd 3261.1 Cr 2975.5 was chosen instead of the three most sensitive lines, Cr 4289.7, 4274.8 and 4254.3 for three reasons: firstly these lines were not in the range that was suitable for the majority of the elements; secondly, because trace quantities of Cr were not required, Cr being of economic importance only when present as a major constituent; and thirdly, because the plates had a far lighter background in the region chosen than in the 4100 - 4300A range, and the emulsion characteristics were more constant.

The first step of Cr 2975.5 was compared with the third step of Cd 3261, and the working curve obtained is given on page 43. The chemical and spectrographic results are tabulated on page 123. Assuming the chemical results to be correct, an accuracy of ± 10% was obtained. A coefficient of variation of ± 8% was calculated from the results given by analysing two samples ten times each. In Cr 3, the deviation of the spectrographic from the chemical result is 48%. As the analyses were done in duplicate, and this deviation is six times the standard deviation of the method, the probability that the chemical result was in error is very high.

Figure 7

The graph of percentage chromium versus log $\frac{\text{I Cr 2975}}{\text{I Cd 3261}}$



3.8 Copper and Nickel.

The spectrographic determination of copper and nickel has been studied by many workers, and these elements are included in nearly all the general methods given in section 1. In 1953, Galakhovskaya[50] studied the determination of these, and several other elements in the soluble portion of halite, sylvene and sylvinite, by applying the saturated solution to the surface of a plate shaped lower electrode, and slowly evaporating. Molybdenum was used as internal standard.

The method previously described for the determination of chromium, by Astafe'v Rubinovich, and Yakovleva[47], was also employed for copper and nickel. The internal standard element was cobalt.

Hegemann, von Sybel and Wilk (1955)[51] determined copper and nickel in pyrites and chalcopyrite, using a d.c. arc method. The sample was mixed with pure graphite, and, in the case of the pyrites, Cu 3274 was compared with Fe 3171, and Ni 3051 with Fe 3058, for the chalcopyrites Cu 2824 was prefered.

Lovering, Nichiporuk, Chados and Harrison Brown[52] (1957) used Pd 3242.7 as internal standard for the spectrographic determination of copper in meteorites.

/The samples...

The samples were diluted 4 : 1 with graphite powder containing palladium.

Carobbi and Pieruccini[53] (1943) determined copper in sedimentary rocks using iron as a variable internal standard. Samples were packed into deep (12mm) electrodes, and arced for five minutes using cathode layer excitation. These authors corrected for matrix and electrode contamination by comparing the copper line in the blank with the CN band component CN3160.

Hustler and Hammaker[35] in the method previously described in 3.5 and 3.7 used silver nitrate as a composite buffer and internal standard for the determination of nickel in glass sands.

Landergren and Muld[54] (1955) determined copper, and several other elements, in igneous rocks, sediments and ores by fusing with 5 parts of Li_2CO_3 and 9 parts H_3BO_3 until decomposed. The cooled melt was powdered, mixed with graphite, to which CeO had been added, for use as internal standard, formed into pellets, and sparked.

During the investigation of chromium, which is described in 3.7, it had been found that chromium could be determined with more reproducibility using cadmium as an internal standard than with gold. It was therefore decided to see whether copper and nickel could be determined using this element as internal standard, in spite of the wide difference in volatility.

/The method...

The method would also be of use in the analysis of other elements in gold concentrates, when the high concentrations of gold present would significantly interfere with the gold internal standard method.

The method described below will hereafter be referred to as Method B.

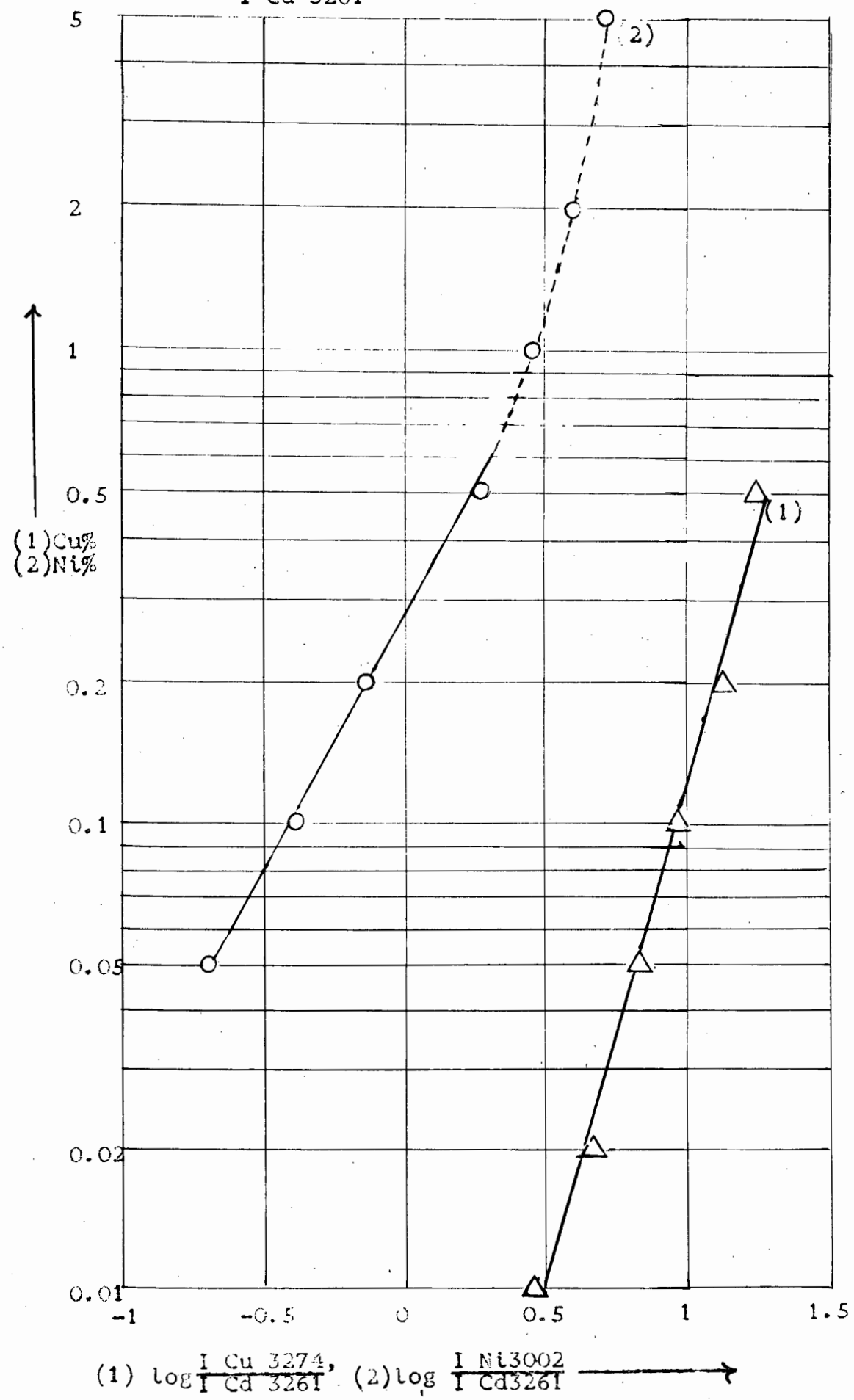
METHOD B.

The standards were made in the same 'average' matrix as in Method A, and one part of standard or sample was mixed with nine parts of graphite containing 1% cadmium as CdO. Approximately 20 mg of this mixture was packed in an L4000 electrode, and arced at 5 amps for 5 seconds, followed by 15 amps to completion.

The fourth step of Cu 3274 and Ni 3002 were compared with the fourth step of Cd 3261, and the working curves obtained are shown on page 47. Three batches of samples were analysed, the first being mainly siliceous, while the others appeared to be clays. The results of the first batch were not included in the accuracy calculations as the copper content was so low that only one significant figure was reported. If one assumes the chemical results to be correct, although the samples were not chemical standards, an accuracy of 16% for copper, and 23% for nickel is obtained. A coefficient of variation of 14% was calculated for both elements from 25 sets of duplicate results.

Figure 8

The graph of (1) Cu % (2) Ni % versus (1) $\log \frac{I\ Cu\ 3274}{I\ Cd\ 3261}$ and (2) $\log \frac{I\ Ni\ 3002}{I\ Cd\ 3261}$.



3.9 Lead.

The spectrographic determination of lead has been investigated by many workers. Schnopper and Adler[55] (1949) determined its concentration in zinc and other ores, using a buffer consisting of one part graphite and two parts lithium carbonate. A centre-post electrode was used, with an exposure of 20 seconds at 14 amps.

The determination of lead is included in most of the general methods given in section 1, and also in the previously described methods of Hustler and Hammaker[35] (in which $AgNO_3$ was used as buffer and internal standard) and Galakhovskaya[50] (who studied the soluble portion of halite using molybdenum as internal standard).

Bismuth has been used as an internal standard for lead by several workers. Waring and Worthing[56] in 1953, determined lead concentrations in zircon, apatite, sphene, and several other minerals, by comparing Pb 2833 and Bi 2898. 12.5 mg of the powdered mineral sample was mixed with three parts of Na_2CO_3, containing 0.1% of Bi or 0.05% Bi for low-lead samples. Calibration curves were obtained from SiO_2-Pb - Bi standards. Wedepohl[57] added equal weights of carbon powder containing 0.1% Bi to his samples with lead content above 100 p.p.m., and 25% $CaCO_3$ containing 0.04% Bi_2O_3 to his lower samples. Waring and Worthing's analysis pair was used.

/Hamaguchi...

Hamaguchi and Kuroda[58] (1955) also used bismuth for the determination of lead in silicate rocks. Samples of the powdered minerals were mixed with half their weight of NaCl which contained 2.9% of Bi_2O_3. The samples were arced using d.c., and lengths of spectra recorded through a logarithmic sector were used for estimating the lead concentration.

Heier and Taylor[59] (1959) determined lead in alkali feldspars using sodium as a variable internal standard. The samples were only arced for the period of the alkali distillation, so that the cyanogen bands were suppressed by the low arc temperature, and it was possible to use the strongest line Pb 4057 when necessary. This line usually suffers severe interference from the CN band with head at 4216A. A relative deviation of 5% was obtained.

It was decided to use Method B for the analysis of lead, as cadmium seemed a more suitable internal standard than gold, both from the point of view of its volatility and its chemical characteristics. Pb 2833 was used, instead of Pb 4057 for the following reasons:-

(a) no alkali dilution was being employed at this stage, so that there was cyanogen interference with Pb 4057

(b) maximum sensitivity was not required, as lead is only of economic significance when present at concentrations of well over 1000 p.p.m.

/Method...

Method B was followed, mixing the sample 1 : 9 with graphite containing 1% Cd. The working curve obtained comparing the first step of Pb 2833 with the second step of Cd3261 is given in Figure 9, (1). Nine chemically analysed samples were available for checking the method, and it was found that the spectrographic results did not agree with the chemical figures. Except for the fact that all the spectrographic results were low, the disagreement appeared to be random, the spectrographic figures being anything from 50% to 10% of the chemical figures. The reproducibility of the spectrographic method for a single sample was, however found to be ± 10%.

In order to see if the presence of any other elements in the samples was causing this disagreement, weighed quantitied of the samples were arced and an inspection was made to see if any elements were present in quantities that could be correlated with the deviation of the spectrographic from the chemical results. It was found that the samples had differing alkali contents, and that the higher this content the greater the difference obtained between the chemical and spectrographic results. The samples appeared to be dolomitic, with clay intrusions, but as they had been finely crushed, it was hard to be sure of this.

/To test...

To test this theory of alkali effect, standards were prepared and diluted 1 : 9 with an internal standard mixture consisting of 2% Cd as CdO in a diluent of 2 : 1 Li_2CO_3 : Graphite. This was found to give far less sensitivity for lead, as shown in (2) Figure 9.

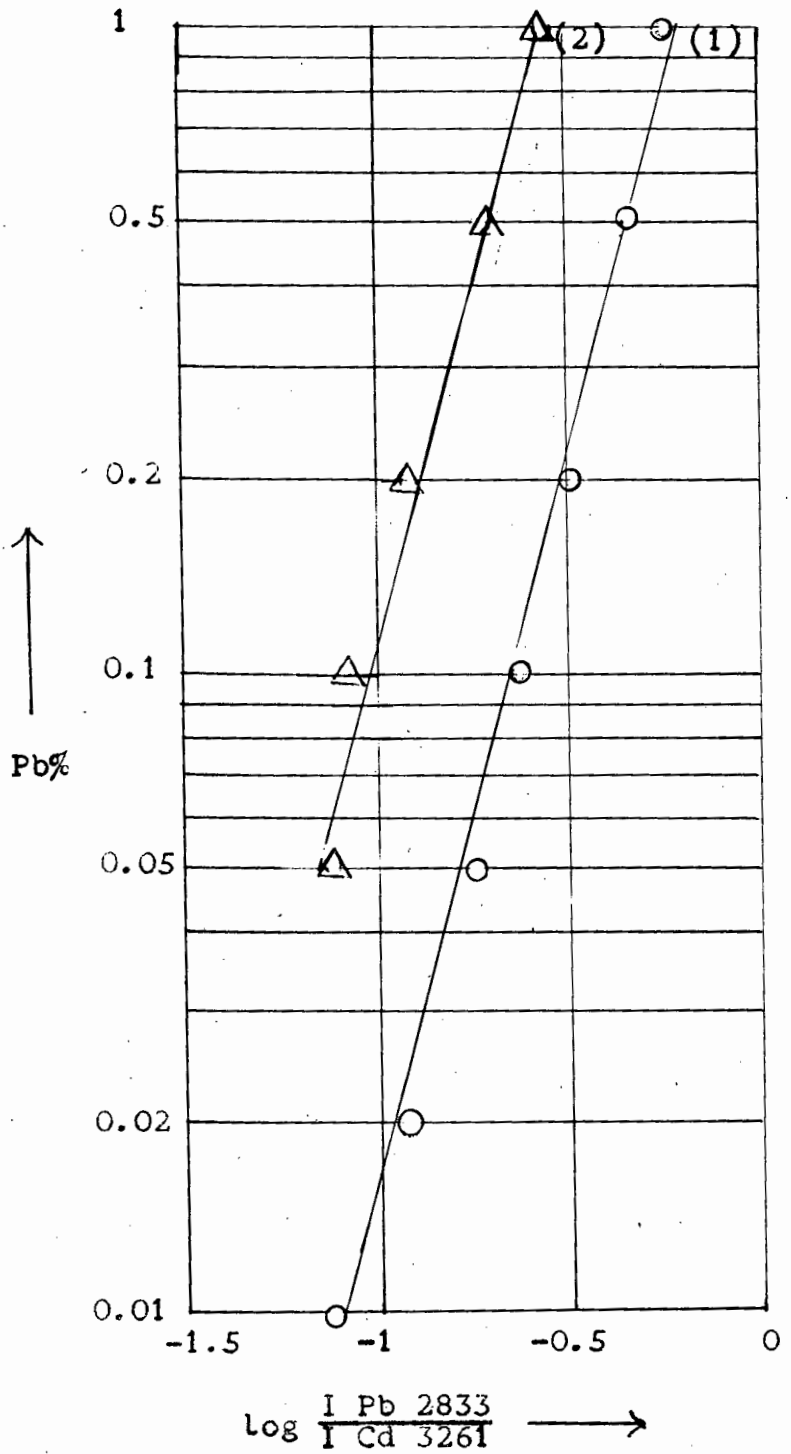
The samples were then treated in the same manner and agreement was obtained with the chemical figures. Considering the chemical results as correct, an accuracy of ± 12% was obtained.

The standard deviation was calculated from duplicate analyses on twenty five samples, and was found to be ± 11%.

Figure 9

The graph of Pb% versus log $\frac{\text{I Pb 2833}}{\text{I Cd 3261}}$

(1) without Li_2CO_3, (2) with Li_2CO_3.



(1) with no Li_2CO_3

(2) with Li_2CO_3.

3.10 Calcium and Magnesium.

Calcium and magnesium have been determined in clays by several workers. In 1943 Austin and Bassett[60] used graphite containing Mo as internal standard, for the determination of Fe and Mg in clay samples. Gillis and Eeckhout[61] determined Ca, Mg and several other elements, using Cu and Li as internal standards. Synthetic mixtures could not be used as standards, and analysed clay samples had to be employed.

Kvalheim[62] (1947) determined Ca and Mg, as well as other common elements, in minerals, rocks and slags using $SrCO_3$ as internal standard. A relative error of less than 10% was obtained. Hegemann[63] in 1953 obtained an accuracy of 3% for Mg, Ca, Si, Al and Fe in silicates. The sample was placed on the edge of a filter paper (diameter 3.15cm) which was then rotated at a rate of approximately one revolution per minute through an a.c. carbon arc.

In 1955 Sherstkov[64] analysed ores for Fe, Ti, Ca, and Mg by spraying the sample, mixed with cobalt as internal standard, into a 2.5mm gap and sparking. Landergren and Muld[54] in the fusion method previously described, used Ca 3159 and 3179 and Mg 2795 and 2803 as analysis lines.

/Vainshtein...

Vainshtein, Borovik-Romanova, and Korolev[65] in 1955 determined the oxides of Si, Al, Fe and Mg in clays of various geological ages. CuO was the base and charcoal powder and diluent. A 10 amp 250V d.c. arc was used and the results of the spectroscopic and chemical analysis agreed within 4 - 6 per cent.

Roubault and Sinsou[66] (1956) determined Al, Mg, Fe, Ca, Mn, Ti, Na, and K in crystalline silicate rocks. Four parts of the powdered sample were mixed with twelve parts of Ni powder, forty parts graphite, and one part H_3BO_3 and excited with an interrupted arc. The line pairs used for analysis were Mg2582/Ni3080 and Ca3159/Ni3129.

Heier and Taylor[33], in the method previously described for barium, used Pd as internal standard for the determination of Ca in alkali feldspars. Analysis lines were Ca 4454 and Pd 4473.

In the present work it was decided to use Method A, the lines chosen being Ca3159, Mg 3096.9 and Au 3122.8. Ca 3159 was used instead of the stronger Ca 4227, 3968 and 3934 and Mg 3096.9 instead of Mg 5184, 3838 and 2852 for the following reasons:-

(a) the other lines were found to be too strong in all the samples available for analysis.

/(b) with...

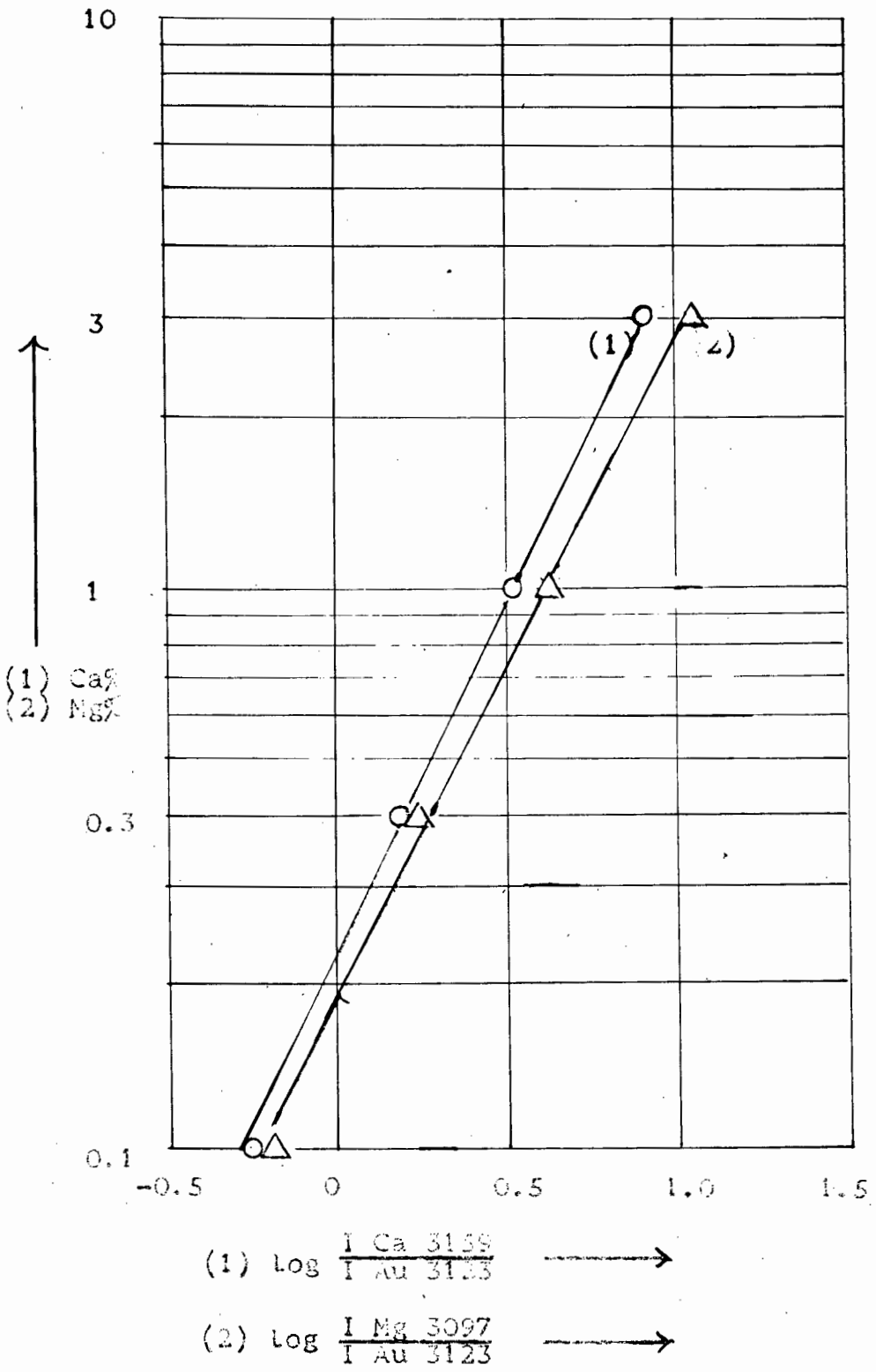
(b) with the exception of Mg 2852, these lines were outside the range that was suitable to the majority of elements using Method A.

At first the only samples available for checking the method were descloizites so the working curves given on page 61 are for standards in a descloizite matrix. However, the method has since been used on soil samples, for which an artificial matrix of 70% SiO_2, 20% Al_2O_3, and 10% Fe_2O_3 was employed. The accuracy for Ca and Mg in descloizite was $\pm$ 5% and $\pm$ 7% respectively. One sample was arced ten times and the coefficient of variation was calculated to be - 5% for both elements. For the soil samples, the accuracy was found to be - 11% for Ca, and $\pm$ 13% for magnesium, assuming the chemical results to be completely correct. One sample was again arced ten times and the coefficient of variation was $\pm$ 9% for both elements.

Figure 10

The graph of (1) Ca%, (2) Mg% versus

(1) log $\frac{\text{Ca } 3159}{\text{Au } 3123}$ and (2) log $\frac{\text{Mg } 3097}{\text{Au } 3123}$



3.11 Iron and Manganese.

Iron and manganese have been investigated by numerous workers, in many types of ores. Churchill and Russell[67] (1945) determined iron in aluminium ores. Tablets were made of one part ore, five parts NaF and twelve parts graphite. These were sparked, and Al used as internal standard.

In 1944, Ahrens[68] published a method for the determination of iron in glass sands. Silicon was used as internal standard, and was found to be satisfactory unless potassium was present at over 0.3%. Fe 3020 was rejected as an analysis line because it exhibited strong self reversal, but Fe 2973 and Fe 2600 were satisfactory. A coefficient of variation of approximately 5% was obtained.

Nachtrieb, Johnson and Dress[48] determined iron and manganese in titanium ores, by fusing the sample with 20 parts of $KHSO_4$, dipping a flat electrode in the melt, and arcing with a 2200V. a.c. arc. The impurities were compared with titanium lines.

Kuraoka, Takahashi and Hara[69] (1951) used strontium as internal standard for Fe and Mn in silicates. A mixture was made of 11 parts sample to 1 part $SrCO_3$ and 4 parts graphite, and packed into centre - post electrodes.

/Iron...

Iron could be determined in the range 0.01 – 15% Fe_2O_3, and manganese between 0.01 – 5% MnO_2. Kvalheim[62] also used $SrCO_3$ as internal standard in his analysis of rocks and minerals.

Hegemann and Leybold[70] (1953) determined Fe, Mn, and several other elements, in galena. A homologous line pair method was employed, with Ni as internal standard. Reproducibilities of better than 10% were obtained. Ni was also used for the determination of manganese in iron ores by Nadezhdina[71] (1954). The samples were formed into briquettes, and the line pair chosen was Mn 2879.5 / Ni 2865.5. Roubault and Sinsou[66] also used Ni for the determination of Fe and Mn in crystalline silicate rocks.

Fe and Mn have also been determined in common with many other elements in most of the general methods described in Section 1, and also by the $AgNO_3$ internal standard method of Hustler and Hammaker[35], and by Galakhovskaya[50] in the method described in 3.9.

It was decided to use Method A for the determination of Fe, and Mn, as Au seemed a more suitable internal standard than the very volatile Cd. Mn 2576.1, the strongest Mn line in the spectral range exposed in Method A, was used when Mn was present in trace quantities, but when the concentration was higher than 0.1% Mn, Mn 2593.1 was found to be more suitable.

/Traces...

Traces of iron were not required, as, in the mining industry, iron is rarely of importance, either as a contaminant, or economically unless present in amounts well in excess of 1000 p.p.m.. A relatively weak line was therefore required, and Fe 2723.6 was found to be satisfactory.

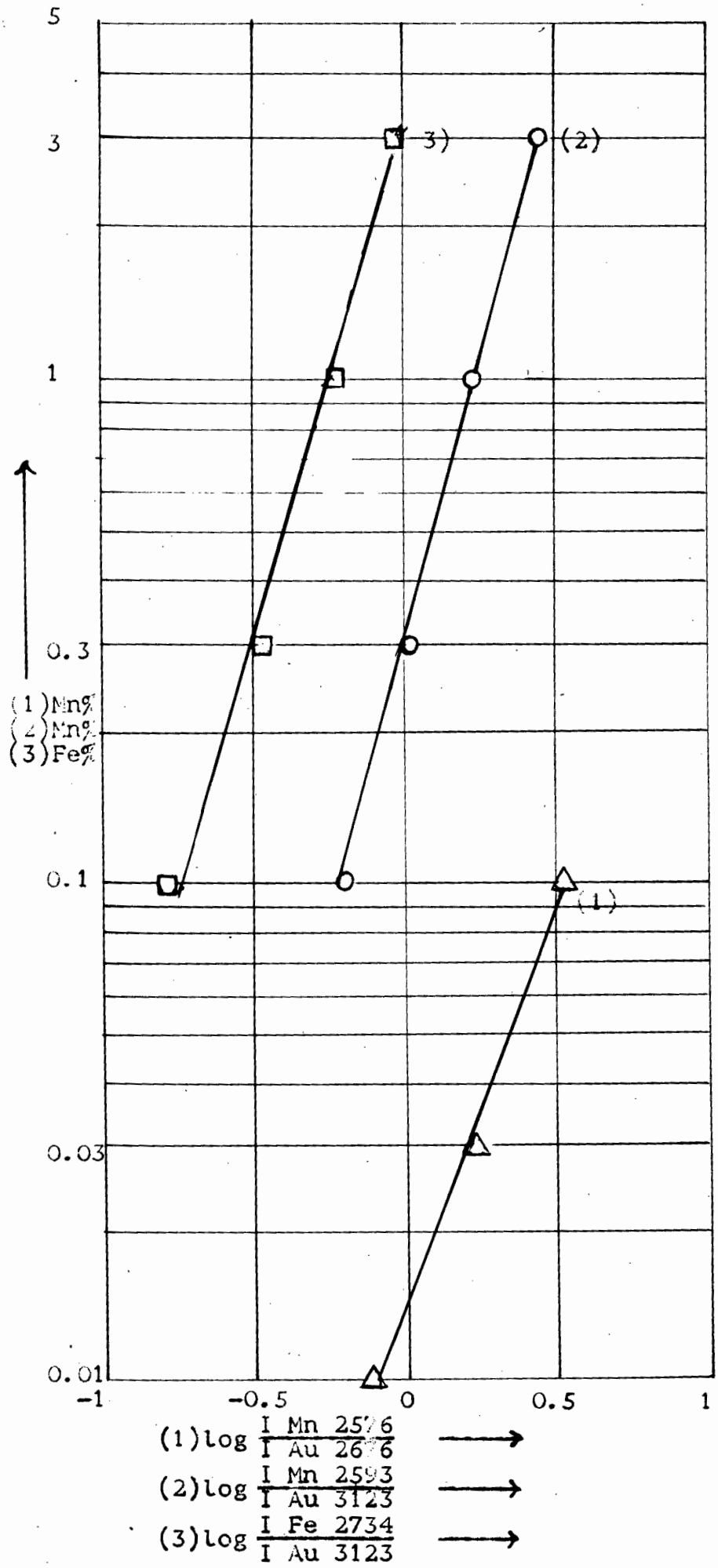
The samples and standards were mixed 1 : 1 with graphite containing 1% Au, as in method A., and the line pairs were Mn 2593 / Au3123, Mn 2576 / Au2676 and Fe 2734 / Au 3123. Au 3123 was chosen in preference to Au2676 for samples containing higher manganese concentrations, because these were concentrates of pyrochlore in calcite, and it was feared that Nb2675.9 (10) and Ta 2675.9 (150), might interfere with Au 2675.95. The lower Mn samples were plain calcites and dolomites, where interference was unlikely.

An accuracy of ± 10% was obtained for Mn, and ± 6% for Fe. The coefficients of variation, calculated from 25 sets of duplicate determinations, were 9% for Mn and 7% for Fe. The working curves are given in Figure 11, page 60.

Figure 11

The graph of (1) Mn%, (2) Mn% and (3) Fe% versus

(1) $\log \frac{I\ Mn\ 2576}{I\ Au\ 2676}$ (2) $\log \frac{I\ Mn\ 2593}{I\ Au\ 3123}$ (3) $\log \frac{I\ Fe\ 2734}{I\ Au\ 3123}$



3.12 Strontium.

Strontium has been determined in several media. Wilson and Fields[72] estimated the Sr content in CaO by adding sodium potassium tartrate, dissolving in HCl, evaporating the liquid on to a copper anode, and sparking. Comparisons of Sr 4607/ Ca 4300, Sr 4215 / Ca 4203 and Sr 4078 / Ca 4283 covered the range 0.025 - 1.2% Sr.

As Ca, Ba, and Sr are very similar chemically and spectrochemically, they are good internal standards for each other. The disadvantage of using them for this purpose is that they are likely to occur together. Turekian, Gast, and Kulp[73] in 1957 overcame this difficulty when analysing silicates, by mixing 1 : 1 with $CaCO_3$ which had previously been purified by ion-exchange. Sr4607 was then compared with the weaker Ca line, Ca 4578.

In 1943, Hybbinette[74] also used Ca as internal standard for the determination of traces of Sr in pegmatites. The samples were dissolved, an excess of Ca added as a carrier, and an oxalate precipitation made. Kulp, Turekian and Boyd[75] (1952) used calcium as an internal standard for the determination of Sr in limestone and fossils.

/Ba...

Ba was used as an internal standard by Goldsmith, Graf and Joensuu[76] in 1955, when studying the Sr content of magnesium calcites. Sr 4607 and Ba 4523 were used for the analysis of samples containing 0.05 - 1% Sr. Sr 4607 was also used by Strock[77] in 1942, when investigating the Sr content of mica.

Most workers investigating the spectrochemical determination of trace amounts of Sr have used the arc line Sr 4607, but, investigating lithium mica and other minerals, Ahrens[78] found it necessary to use the ion line Sr 4077 because of the excessive interference from Li 4603. Sr 4215 was also ruled out because of its coincidence with Rb 4215.

Heler and Taylor[33] (1959) used the Pd internal standard method already described for Ca and Ba, for the determination of Sr in alkali feldspars.

In the present investigation it was decided to use method A for Sr as the volatility of gold was far closer to that of Sr than that of Cd. Only six analysed dolomite samples were available to check the strontium method, as Sr is not generally considered of any great economic importance.

/The usual...

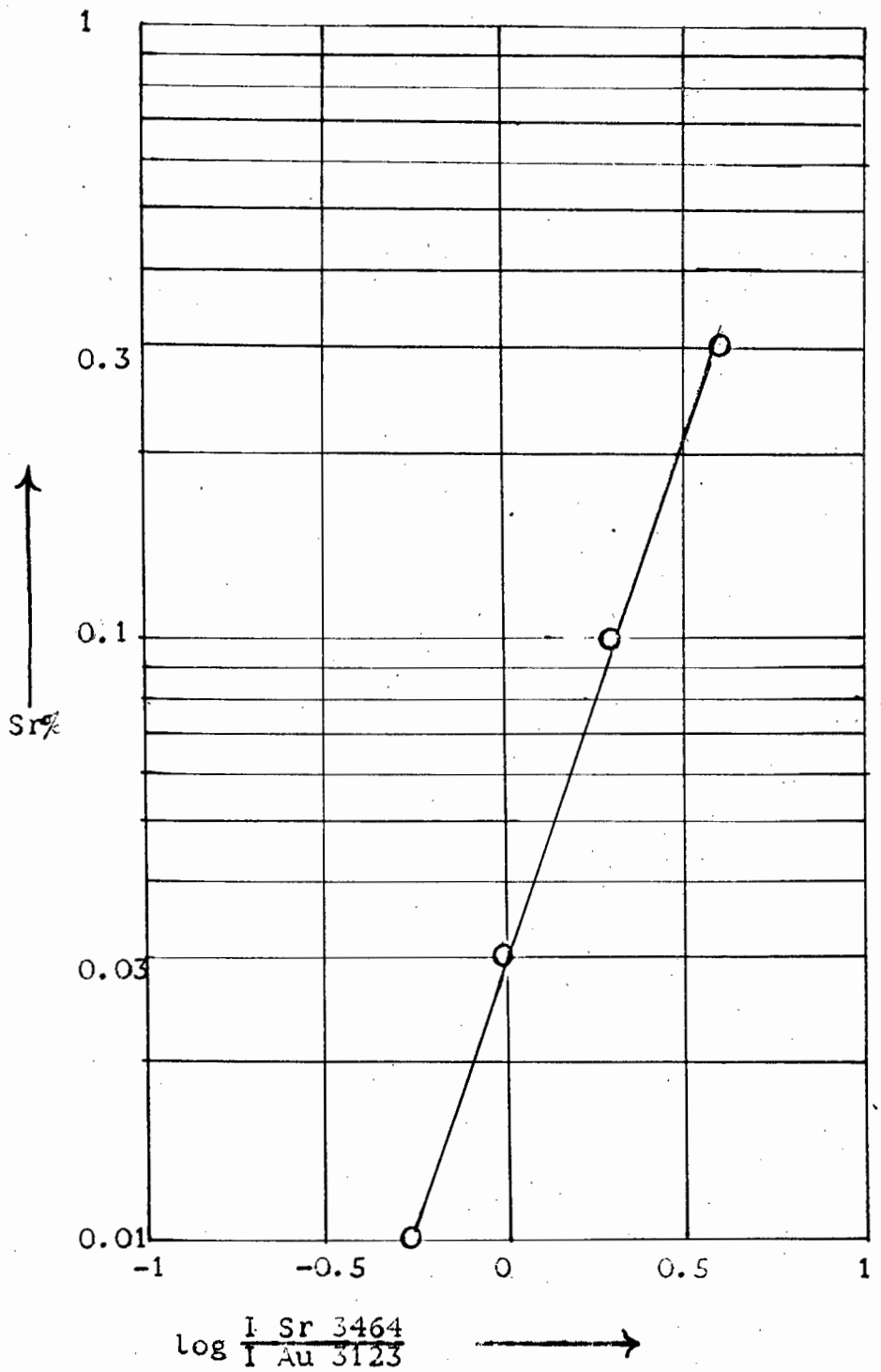
The usual Sr lines, 4607 and 4077 were not considered, as their wavelengths were outside the range generally employed in Method A, and great sensitivity was not needed. Sr 3464.1, although an ion line, was found to be suitable. The background, in the vicinity of this line, was rather high from the CN band, with head at 3590.4 and background readings were taken on both sides of the line and corrections made on the Respectra calculating board.

Equal steps of Sr 3464 and Au 3123 were compared, and the working curve obtained is given on page 64. Assuming the chemical results to be correct for the six samples (they were not chemical standards) an accuracy (mean deviation from the chemical figure) of ± 16% was obtained. The results are given on page 127. One sample was analysed spectrographically ten times, and a coefficient of variation of ± 11% was obtained.

averages?

Figure 12

The graph of Sr% versus log $\frac{\text{I Sr 3464}}{\text{I Au 3123}}$



3.13. Tin.

A tin deposit can be worth mining when as little as 0.05% Sn is present as finely ground, alluvial tin, but if the cassiterite is present in hard rock, it can be necessary for 0.5% Sn or more to be present before the deposit becomes of economic importance.

Tin has been detected in zincblende by Oftedal[79], together with several other elements, and by Strock[80]. The latter obtained quantitative results from stepped spectra, by comparing exposure - time ratio for equal densities on each pair of lines.

Tin was determined in silicate and sulphide minerals by Shilling[81] (1955). The sample was mixed with an equal amount of potassium antimonyl tartrate, placed in the crater of a graphite electrode, and excited by a 12 amp. d.c. arc. Sb 2489.5 and Sb 2426.4 were compared.

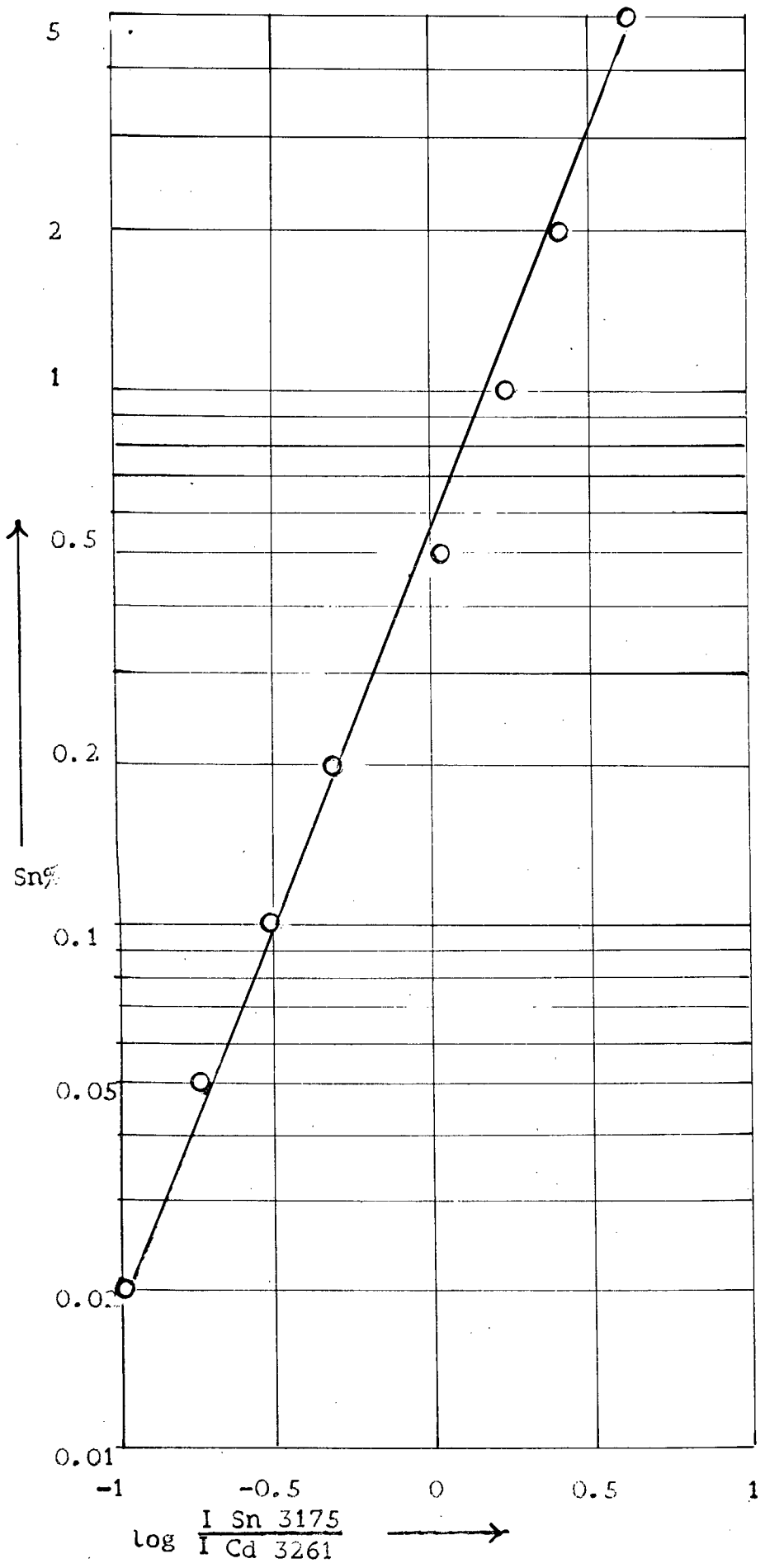
The methods of Hegemann and Leybold[70], and Hustler and Hammaker[35] were also applied to the determination of Sn in galena and sands respectively. Many of the general methods described in Section 1 have also been applied to tin.

Sn 3262.3 was used by Ahrens and Liebenberg[82] for the determination of Sn in mica, and Brooks, Ahrens, and Taylor[83] used an anion - enrichment procedure to determine Sn in most rocks.

/Concentrations...

Figure 13

The graph of Sn% versus log $\frac{\text{I Sn 3175}}{\text{I Cd 3261}}$.



In the case of the samples from Deposit B, as W was also required, it was decided to try the method that was in use for the involatile elements (see section 4). This method C was as follows:-

Samples and standards were mixed with graphite containing 0.1% Pt (using the calculated amount of ammonium chloro platinate) equal parts of sample and graphite mixture being used. The mixture was arced at 5 amp for 5 seconds followed by 15 amp. for 20 seconds. Approximately 20 mg of sample mixture were packed in U.P.C. 101L electrodes, and with the arcing conditions given above, nothing appeared to be left in the electrode after burning.

A suitable Pt line had been found to be Pt 2659, but this seemed somewhat too different in wavelength from Sn 3175. Sn 2840 is nearer, and only slightly weaker than Sn 3175, (an intensity of 300 as compared to 500) and also occurs in a clearer part of the spectrogram. Concentrations of less than 0.01% were not required, so it was decided to compare Sn 2840 and Pt 2659, the fifth step of Sn being compared with the third step of Pt. The working curve is given in Figure 14, and the results on page 128.

The samples analysed by this method were received for arbitration between two laboratories. As can be seen from the agreement between the two laboratories, the chemical results could not be considered as being accurate, so it was impossible to calculate the accuracy of the spectrographic method.

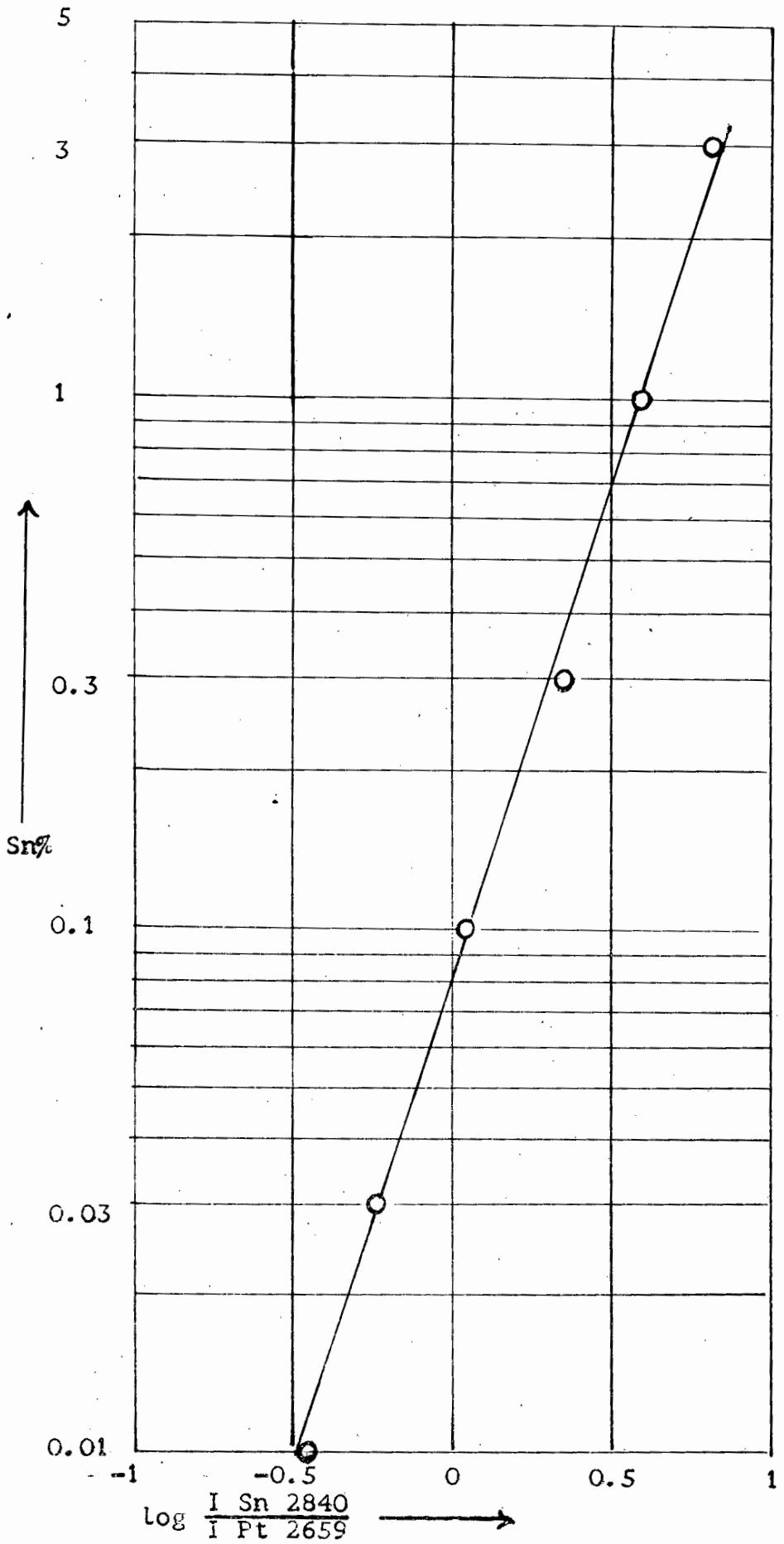
/It was...

It was however, found in the mineralogical experiment involved that the proportions of tin in the concentrates and tailings corresponded better with the original head value when the spectrographic results were used instead of the chemical figures. The higher samples had to be diluted with matrix before adding the graphite mixture.

One sample was analysed 15 times, and the coefficient of variation of $\pm$ 9% obtained.

Figure 14

The graph of Sn% versus log $\frac{\text{I Sn 2840}}{\text{I Pt 2659}}$.



Zn 2138.56. (800R) is the strongest Zn line available, but it can only be used when specially sensitized plates are employed. O' Connor[86] in 1941 used this line to determine Zn in fertilizers. He enhanced the sensitivity of the volatile Zn by using deep electrodes, and obtained a limit of detection of approximately 2 p.p.m.. Rogers[87] in 1935 also used this line for the determination of Zn in biological ash. The line suffers from self reversal, but Eve and Maskew[88] overcame this in the analysis of plant materials by using an air jet to remove the outer layers of the arc.

In general, at the present moment, a deposit of zinc is not considered of economic importance unless present at over the 1.5% level (30 lb/ton). However, the samples submitted for Zn analysis were part of a geochemical survey, where small traces were of interest. The possible cost of using specially sensitized plates in such a survey was formidable, so that the use of Zn 2138 was not considered. Specially sensitized plates are also less readily availabe than the normal varieties , and it was feared that considerable delays might be incurred in obtaining them.

/The fact...

The fact that thousands of samples might have to be analysed by people with little spectrographic experience, on a routine basis, made it seem wise to try to improve the sensitivity of Zn 3345.02, without resorting to special double arc techniques, such as that of Wedepohl[85], or Shaw, Joensuu and Ahrens[89] (1950)

It was originally intended to use the method of Schnopper and Adler[55] for the geochemical survey, and a mixture two parts Li_2CO_3 to one part graphite containing 2% Cd (added as CdO) was made. Samples and standards were mixed equally with this, and approximately 100 mg was packed into a large National Carbon L4018 lower electrode, and arced at 10 amp. to completion. It was found that under these conditions the limit of detection was approximately 1,000 p.p.m.. This was not satisfactory. The curve obtained is shown in (1) Figure 15.

It was thought that the high percentage of Li present in the internal standard mixture might be adversely affecting the sensitivity of Zn, so a mixture of 2% Cd in graphite was added in equal parts to the standards, and the working curve shown in (2) Figure 15 was obtained. All other conditions were kept as before. By this means the limit of detection was reduced to 300 p.p.m. and although this was still unsatisfactory, it was an improvement, so the new internal standard mixture was adopted.

/Up...

Up to this stage in the development of the method the "average" matrix had been used, but it had been noted that the samples were relatively free from calcium, whereas in the standards Ca 3344.51 was causing halation around the zinc line. It was therefore decided to continue investigations using a pure silica matrix, and by so doing the limit of detection in the standards was lowered to between 100 - 200 p.p.m..

As this was still unsatisfactory level of detection, it was decided to try to improve it by changing the arcing conditions to decrease the high background at the Zn line. The current was therefore started at 5 amp., as in Method B, and switched to 15 amp. after 5 sec.. A test plate was taken using the method given in 2.3, and it was found that all the Zn and Cd were volatilized within 15 seconds. The procedure was then adopted of arcing for 5 seconds at 5 amps (to prevent the sample 'exploding' out of the electrode) followed by 15 sec. at 15 amp.. By using this technique, the limit of detection was lowered to approximately 70 p.p.m..

/This...

This was considered satisfactory in the survey, as although all samples could not be assigned a Zn concentration more specific than 'less than 70 p.p.m.', there was enough sensitivity for the peaks to be plotted. It was fortunate that the samples were highly siliceous in nature, as otherwise sensitivity must have been lost.

Within a short period it became clear that the use of high purity electrodes was uneconomic, and a change was made to Spectro-Tech. graphite machined to the shape of L 4018. As was the case with the Cu, Co, Ni survey (see 3.15) no contamination was noted resulting from this change. The working curve is given in (3) Figure 15, on page 76.

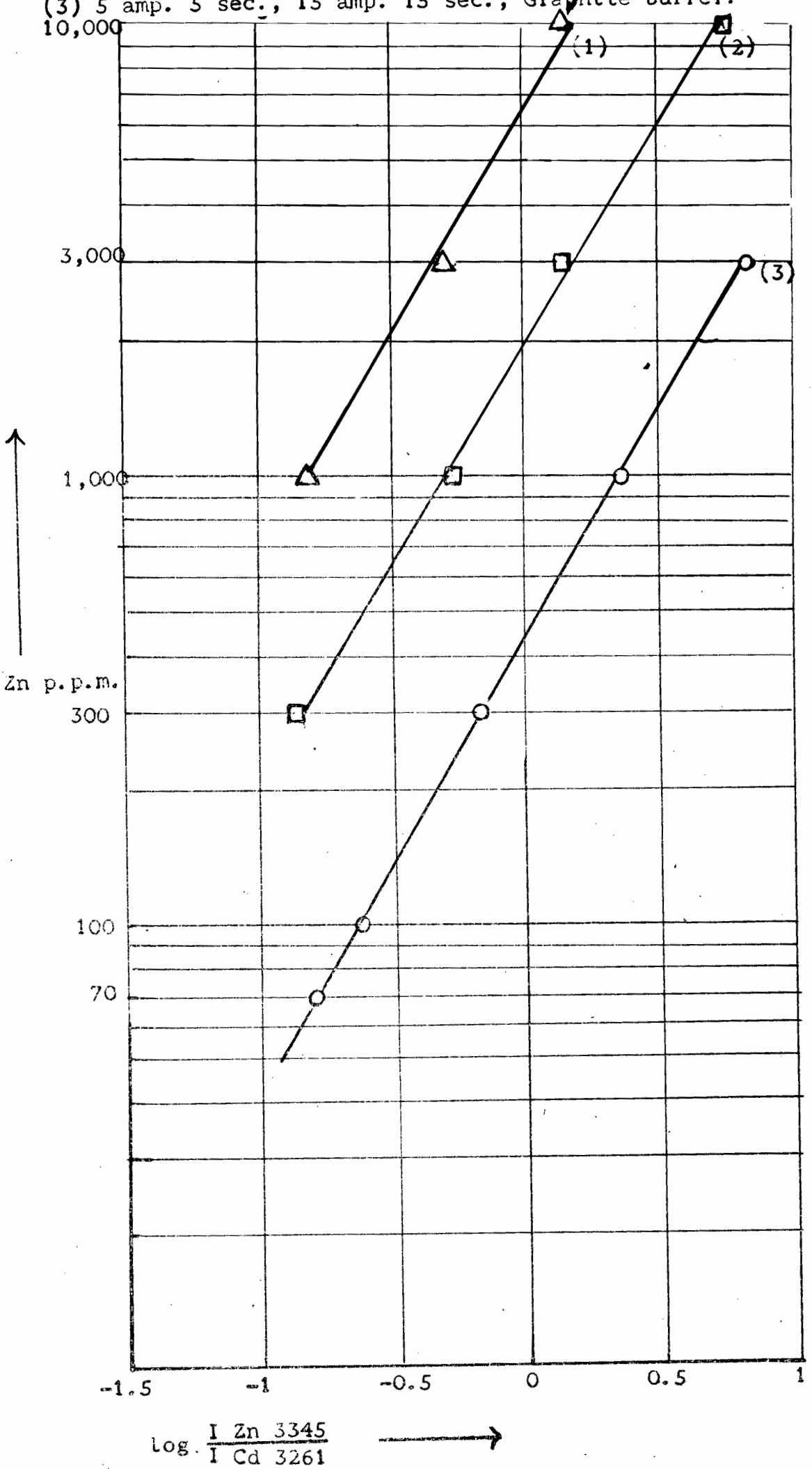
The first step of Zn 3345 was compared with the second step of Cd 3261. Background readings were taken immediately adjacent to both sides of both lines, and the mean backgrounds for each line used for background corrections on the Respectra calculating board.

Twenty samples were analysed chemically, as well as spectrographically, and an accuracy of 8.4% obtained. A coefficient of variation of 8.2% was obtained from fifty duplicate determinations.

Figute 15

The graph of Zn p.p.m. versus log $\frac{\text{I Zn 3345}}{\text{I Cd 3261}}$

(1) 10 amp., Li_2CO_3/Gr. buffer, (2) 10 amp. Gr. buffer
(3) 5 amp. 5 sec., 15 amp. 15 sec., Graphite buffer.



3.15 Cobalt, Copper and Nickel determinations in a geochemical survey.

During the course of the authors work at Goldfields Laboratories, the company decided to undertake a geochemical survey for copper, cobalt and nickel. The geologists took samples at known distances from a reference point, and at various depths. The samples were sieved, packed into small envelopes, and sent for analysis. The information as to position and depth was given on the envelope, e.g. AK 220', 5', the symbol A giving the direction from post K, the distance from this post being 220', and the depth at which the sample was taken 5'. The meaning of the symbols was known by the geologists at the company's head office, who correlated the data. With a few minor variations, it was decided to use the author's Method A on these samples. The work was done by a team of three or four people, depending on who was available in the laboratory, led by M.B. Forsyth, M.A. and the author. Between three and four thousand analyses were made during the course of the survey.

One important variation from Method A was dictated by the question of cost. It was felt that the use of the highest purity graphite electrodes would render the method more expensive than the corresponding chemical techniques.

/As...

As the geologists were only interested in the peaks shown by this survey, it was decided not to report accurately any figures of less than 50 p.p.m.. The symbol x was used when the element was detected at a level of less than 50 p.p.m. and — when it was not detected. Under these conditions it was found that the use of U.C.P. Spectrotech rods machined to the shape of National Carbon L400, and U.C.P. 101U electrodes, instead of purer carbons, did not affect the accuracy of the determinations.

With an arcing period of 5 sec. at 5 amps, followed by a burn at 15 amps, there was a tendency for the sample to be ejected from the electrode on increasing the current. The arcing conditions were therefore changed to 5 sec. at 5 amps, followed by 5 secs. at 10 amps, and then 15 amps to completion.

Samples and standards were treated as in Method A. The fourth step of gold was compared with the fourth steps of copper and cobalt, and the third step of nickel. The slit of the spectrograph was masked, so that only these steps were exposed, so as to cut the number of plates used, and consequent costs, and also to reduce the total time lost in developing. It may be of intesest to note that four was found to be the optimum number of workers; two at the balances, one at the spectrograph, and one combining the work at the microphotometer, and in the darkroom.

/Operators...

Operators changed positions at least four times a day to prevent undue tedium.

The lines chosen were Cu 3274.0, Co 3453.5, Ni 3002 and Au 3222.8, and one of the sets of working curves used is given on page 81. These were transcribed onto the concentration slides of the Respectra calculating board, and the results read off directly. The method was restandardised whenever a new batch of a dozen boxes of plates was opened, but the curves, however, varied very little. All plates were kept under refrigeration except the box in use, and one other. This spare box was kept at ambient temperature, so that when one box was finished there was no delay waiting for plates to achieve room temperature.

The method was used on approximately three thousand soil samples, and chemical checks were made on every fiftieth sample. In general these agreed to within 30%, although in some cases the variation was much greater. In the author's opinion these wide fluctuations were due to sampling errors, as the samples were of the order of -100 mesh, depending on the procedure adopted in the field, and indeed, in some cases, roots, and other organic matter were found. It was not considered economic to recrush the samples, as the sampling error in the field were held by those in charge of the investigaion, to be considerably higher than those encountered in the laboratory.

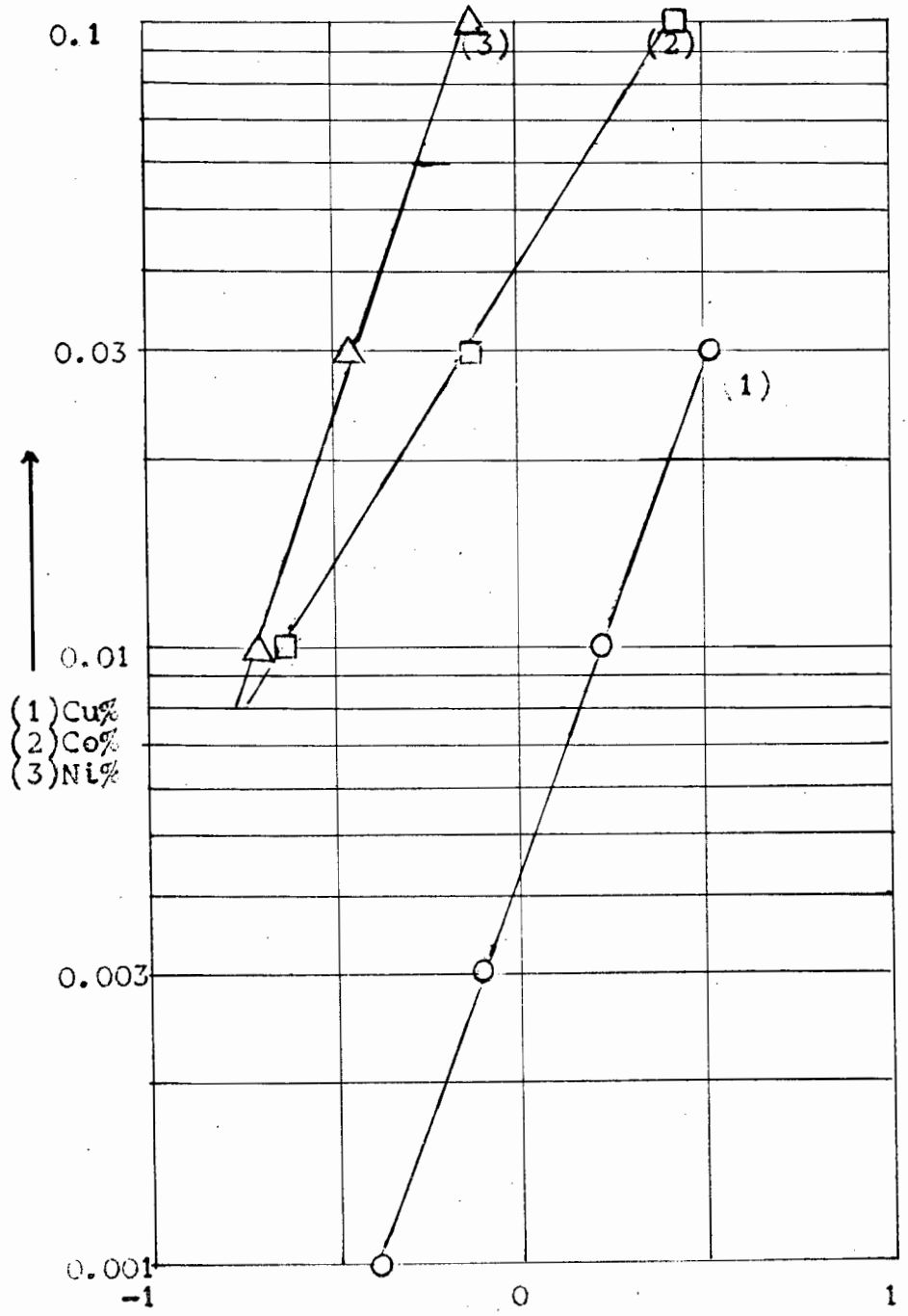
/When...

When a significant peak was obtained, another sample was taken in the laboratory, and replicate analyses were made.

The contour maps obtained from these analyses were satisfactory, and a deposit was discovered, though whether it was of economic significance or not was not disclosed.

Figure 16

The graph of (1) Cu%, (2) Co% and (3) Ni% versus
(1) $\log \frac{I\ Cu\ 3274}{I\ Au\ 3123}$ (2) $\log \frac{I\ Co\ 3453}{I\ Au\ 3123}$ and (3) $\log \frac{I\ Ni\ 3002}{I\ Au\ 3123}$



4. METHODS FOR INVOLATILE ELEMENTS.

4.1 General.

The involatiles of interest to the laboratory were Be, Ge, Mo, Nb, Ta, Ti, W and Z. The platinoids were not sought quantitatively, as they were rarely, if ever, detected in ores. Had they been detected quanlitatively, there would have been immediate investigation by chemical assay procedures, so there was little support for developing quantitative spectrochemical methods for these elements.

4.2 Choice of internal standard.

Hawley and MacDonald[13] (1956), using a Stallwood jet, determined Be, Mo, V, Zr, and other elements, using $SrCO_3$ as internal standard. Several ground state lines were used over wide concentration ranges, as the removal of the outer, flame-like, shell of the arc greatly reduced self - absorption. For the present method Sr was not, however, considered a very suitable internal standard, as it occured naturally in many of the samples received.

Ahrens[19] has used Pd as internal standard for the determination of several involatile elements, the samples being mixed with graphite containing the internal standard.

/A modification...

A modification of this procedure was used at the Department of Geology and Mineralogy, Oxford[19] where one part of sample was mixed with two parts of graphite containing 0.015% $(NH_4)_3Pd(NO_2)_6$. Pd 3421 was the internal standard line. Hirst and Nicholls[14] also used Pd as internal standard for the determination of V, Mo, Be, and several other elements in limestones.

Cyanogen band suppression can be effected by the addition of alkali metal salts to the arc. These, however, keep the temperature of the arc relatively low, so that many refractory materials are not excited until the alkali phase of the burn is finished. In the analysis of refractory elements, it can therefore be expected that the CN bands will tend to be dark when the element has been volatilised. /$CaCO_3$? For this reason analysis lines were chosen as far on the ultraviolet side of the CN band with head at 3590 A as possible. It was possible to find lines for all the elements, of sufficient sensitivity for the laboratory's requirements, and with wavelengths below 3200 A. Most workers using the Pd internal standard methods used Pd 3421, but in the present investigation this appeared to be in a part of the plate with a very high background, and it was decided to try to find another element, possibly less volatile than Pd, and with lines in a more suitable part of the spectrum for the analysis lines chosen.

/The other...

The other conditions governing the choice of internal standards, given in 2.1, had also to be considered, e.g. the possibility of mutual occurence in detectable, or at least significant concentrations.

Platinum seemed to be a suitable internal standard from most considerations. It had the same order of boiling point as the elements to be considered (as shown in Table 3), was unlikely to occur in detectable concentrations in the vast majority of samples, and had two suitable lines, Pt 2659.44 and Pt 3064.71.

The lines used, and some other data are given in Table 3 on page 85. Unfortunately it was not possible to find the excitation potentials of all the lines listed in standard reference works e.g. Saidel, Prokofjew and Raiski[90] but those available have been tabulated. In several cases (notably Be) the normal analysis lines have not been employed, because, in general they were too strong for the average sample received for analysis. These choices will be discussed under the subsections dealing with individual elements.

/Table 3...

Table 3.

Element	Boiling Pt °C	Line Å	Intensity	Excitation ptl, eV
Platinum*	4300	2659.44	2000R	4.6 *
		3064.71	2000R	4.05
Tungsten	5900	2662.83	15	5.06 *
WO_3	m. pt 1473			
Beryllium	2970	2650.47	100	7.40 *
BeO	ca. 3900			
Molybdenum	4800	2816.15	200	-
MoO_2	s.			
Germanium	(2700)	3039.06	1000	4.96 *
GeO_2	m. pt 1115			
Niobium	3700	2972.8	200	-
Nb_2O_5	m. pt 1520			
Tantalum	4100	2908.91	150	-
Ta_2O_5	m. pt 1470 d.			
Vanadium	3000	3185.40	500R	3.96
V_2O_5	1750 d.			
Titanium	5100	2956.13	125	4.24
TiO_2	m. pt 2130 d.			
Zirconium	5050	2571.39	300R	-
ZrO_2	4300			

* The boiling points of platinum oxides are not given, as they decompose into platinum and oxygen at low temperatures, and the platinum is not added to the internal standard mixture as an oxide

/Conditions...

4.3 Conditions of arcing.

Various mixtures were made of Pt in graphite, and, after arcing these, it was decided that by mixing the samples and standards in equal parts with graphite containing 0.1% Pt (using graphite mixed with the calculated amount of ammonium chloroplatinate) the Pt lines would be of suitable intensity.

As in section 3.3 an "exposure plate" was taken using 1% of the elements to be determined. It was found that using 20 mg of sample - internal standard mixture, the lines were of insignificant intensity (transmission of over 80%) after 5 sec. at 5 amp. followed by 25 sec. at 15 amp.. However, it must be remembered that if strong concentrations of alkali metals are present, these might take some time to be volatilised, without affecting the refractory elements and compounds. It was therefore decided to arc to completion, but this only took more than 30 - 35 sec. in the presence of high concentrations of alkali metals.

The electrodes used were United Carbon Products 101L and National Carbon L4036, as the shallower 101 L gave higher temperatures and faster exposures than the electrodes used in section 3. Otherwise the plates and developing procedures were the same.

/Tungsten...

4.4 Tungsten.

Scobie[91] (1943) determined tungsten in ores and alloys by dissolving the sample, adding a soluble aluminium salt, and coprecipitating with Na_2CO_3. The mixed oxides were burnt on graphite electrodes at 15 - 17 amp.. Visual comparison was then made with W 2896 in synthetic standards. A detection limit of 2 p.p.m. was obtained with this form of chemical enrichment.

Wilson and Fields[92] (1944) also pre-enriched the tungsten from schists by dissolving in an HF/H_2SO_4 solution, adding a soluble titanium salt as carrier, and precipitating with tannin, phenazone and cinchonine. The ignited residues were then made into pellets with $(NH_4)_2SO_4$, and arced on C electrodes. W 2948 was the analysis line used, and visual comparisons were made with synthetic standards. A detection limit of 0.7p.p.m. was reported.

Kaufman and Derderian[93] (1949) determined tungsten in low-grade ores, without chemical pre-enrichment. The samples were mixed with an equal weight of AgCl, and ignited to completion in the d.c. arc. A high dispersion grating spectrograph was used, and it was found that Fe4294.1 did not interfere with W 4294.6 unless the quantity of iron present was in excess of 50% Fe_2O_3.

/A detection...

A detection limit of as little as 5 p.p.m. was reported, and if the W was in excess of 500 p.p.m. SiO_2 had to be added to bring the concentration below this level.

Sergeev[94] (1947) employed tungsten's magnetic properties, to draw W atoms selectively into the arc. Horizontal electrodes were used, mounted over the powdered sample. When the arc was started the specimen melted, and a magnet placed above the arc axis caused the W atoms to diffuse upwards and become excited. The background was said to be negligible using this method, and a detection limit of 10 p.p.m. W in powdered rock samples was obtained.

Ahrens[95] (1943) used Si as an internal standard for determining W in highly siliceous ores. Although Si is comparitively volatile compared to W and its carbide, the method was successful, as the tungsten was present as WO_3 which is easily sublimed. 6 - 7 amp. anode excitation was used, and a coefficient of variation of ± 6% obtained.

The strongest W lines are W 4302.108 (60), W 4294.614 (50) and W 4008.753 (45).

/Using...

Using quartz the dispersion in this region is bad, and the background is somewhat high. W 4302 was affected by interference from Fe 4302.2(50), Ti 4301.9 (25), and background from Ca 4302.5, so this line could not be employed. W 4294.6 was practically masked by the strong iron line Fe 4294.128 (700), and W 4008.753 suffered interference from Ti 4008.928 (80). This last interference had already been noted by Brintzinger and Titzmann[96] (1948), when using W 4008.7 to determine W in slags. They stated that a spectrograph of high dispersion was necessary if this line were to be used. Unfortunately, during most of this work, only quartz optics were available, so that all the strongest W lines were impracticable.

Mixtures were made of 1% and 0.1% W in graphite, and, on inspecting the spectrogram, and checking the best available lines for interferences, W 2663.83 appeared to be the most suitable. A composite of the samples submitted for W analysis was analysed spectrographically, and it was found that the approximate matrix composition was 30% $CaCO_3$, 30% SiO_2, 30% MgO and 10% Fe_2O_3. An artificial matrix of this composition was then made. This mixture will hereafter be referred to as Matrix 3. Standards of 3, 1, 0.3, 0.1 and 0.03% were then made in this mixture, and Method C, which will be described below, was applied.

/Method C...

METHOD C.

Samples and standards were mixed 1 : 1 with graphite containing 0.1% Pt (made by using the calculated amount of ammonium chloroplatinate, and dry grinding with increasing quantities of graphite, until the correct amount has been added). Approximately 20 mg. of this mixture was packed into United Carbon Products 101L electrodes, and arced at 5 amp. for 5 sec. (to prevent sample ejection) and 15 amp. to completion. The total exposure rarely exceeded 30 - 35 sec, unless the sample contained high concentrations of alkali metals. The cathodes were National Carbon L4036 counter-electrodes. The other conditions (wavelength range, plates, developement, etc.) were the same as for Methods A and B.

The first step of W 2663 was compared with the third step of Pt 2659. Background readings were taken on the tungsten line, and the necessary corrections made on the Respectra calculating board. The working curve obtained is given in Figure 17 (1).

Surprise was felt at the composition of the composite sample, as most of the individual specimens were concentrates from an ore body containing Wolframite in a gangue mainly consisting of pegmatite.

/It was...

It was therefore decided to investigate the effect that might be produced if future samples should arrive containing a much higher silica content. Standards were therefore made in pure SiO_2, and arced using the same procedure. The working curve obtained is given in Figure 17 (2). It will be seen that the ratio is enhanced when $CaCO_3$ and MgO are present, and depressed when only silica is present. A watch was therefore kept on the SiO_2 content of the samples, but the matrix was not found to vary significantly from Matrix 3. This was possibly due to the concentration technique employed, or the samples might have been taken from the edge of the deposit where there were carbonitite intrusions.

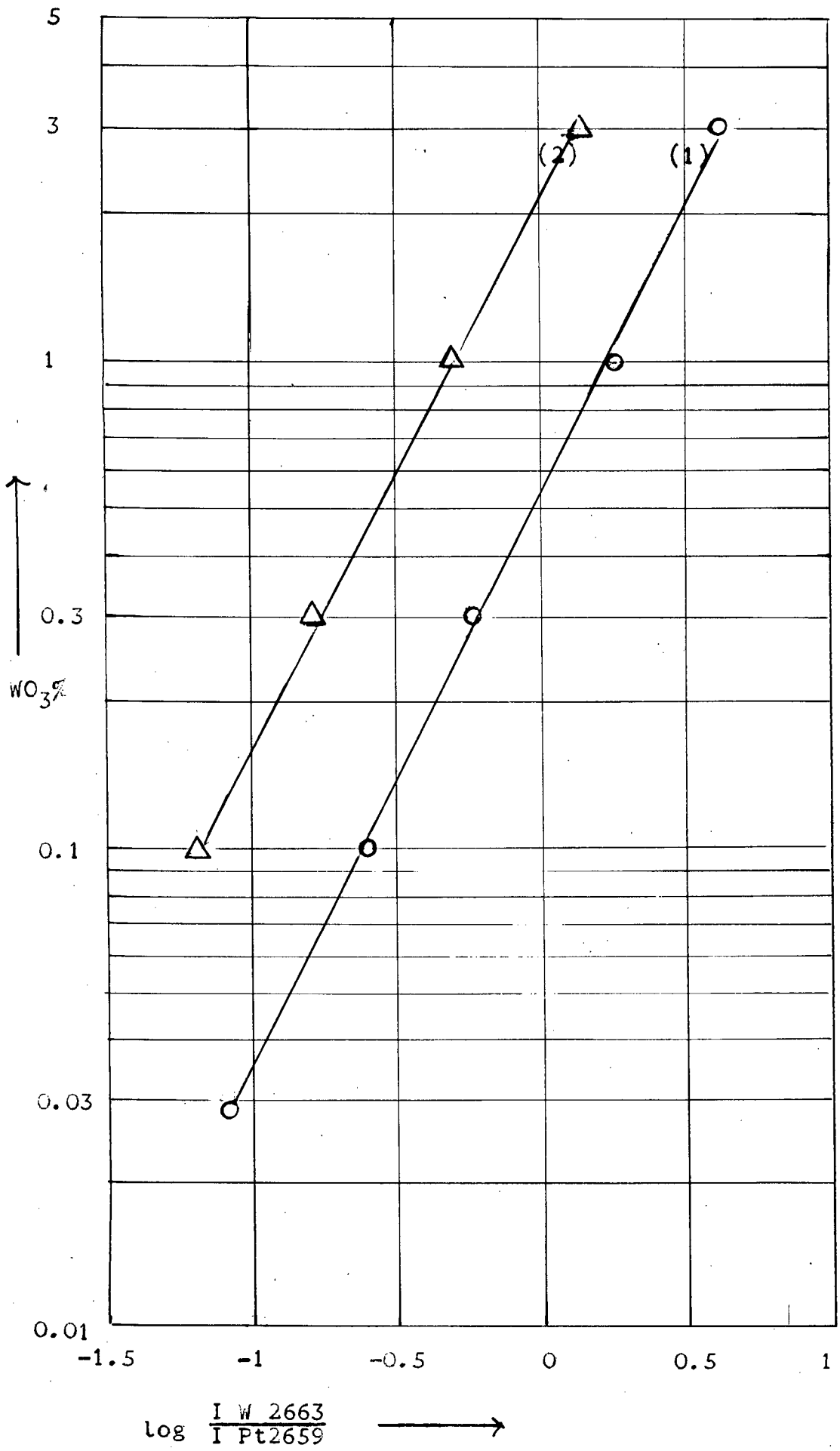
The results for the tungsten analyses are given on page 130. As was the case for tin, the samples received were for arbitration between two laboratories, and the chemical results could not be considered as accurate. It was therefore not possible to calculate the accuracy of the method. A better material balance was, however, obtained with the spectrographic results, than with the chemical figures, in the ore dressing experiment involved. Three samples were analysed ten times each, and the coefficient of variation was calculated to be ± 9%.

/Beryllium...

Figure 17

The graph of $WO_3\%$ versus log $\frac{I\ W\ 2663}{I\ Pt\ 2659}$

(1) in Matrix 3, (2) in silica.



4.5 Beryllium

Beryllium has lately become increasingly important in nuclear and other industries. The production of pure Be, however, entails very severe health hazards, and many papers have been written in recent years on the detection of traces of Be in air. Landis and Coons[97] (1954) ashed fine filter paper/air samples, added $BaCl_2$, and arced at 16 amp. for 2 sec. after the end of the Be volatilisation phase. Working on the same problem, Churchill and Gillieson[98] (1952) sucked the air to be sampled through a source chamber, in which a spark passed through Cu electrodes. The analysis line Be 3130.4 was measured by a photomultiplier cell, and the whole apparatus could be wheeled on a trolley. Concentrations down to 0.5 micrograms of Be per cubic meter could be detected.

Many papers also deal with the effect of the matrix on the determination of Be in ores. Fesefeldt[99], in 1929, found that Na_2CO_3 weakened the Be line intensity, whereas CaO had no effect. Kemula and Rygielski[100] (1933) found that there was an inverse correlation between the intensity of the Be lines and the ionization potential of the major matrix constituent.

/However...

However Marks and Jones[101] (1948) found that the intensity of Be 3321 was not affected by matrix variations. A mixture of $CaCO_3$ and graphite was used as a buffer, and the samples were arced to completion using a constant current arc, maintained by an automatic current regulator. Goldschmidt and Peters[102] (1932) also found that the intensity of Be 2348 remained constant in quartz, alumina and olivine, for the same Be concentration.

Be 2348.61 (2000R), Be 3321.343 (1000r), Be 3131.072 (200) and Be 3130.416 (200) are the most commonly employed lines for Be analysis. These lines were all too strong for the present investigation, as Be is of very little interest in the mining industry unless present in concentrations well in excess of 1000 p.p.m., by which level the strongest lines are very dense. Be 2650 was found to be of suitable intensity, and conveniently close to Pt 2659.

The beryllium samples were from two sources, both highly siliceous, but one batch containing considerably more calcium and iron than the other. It was therefore decided to make Be standards in three matrices.

/calcium...

(a) calcium carbonate

(b) Matrix 3 (see page 89)

(c) Silica.

These standards and the samples were then mixed 1 : 1 with graphite containing 0.1% Pt and Method C (p.90) was used.

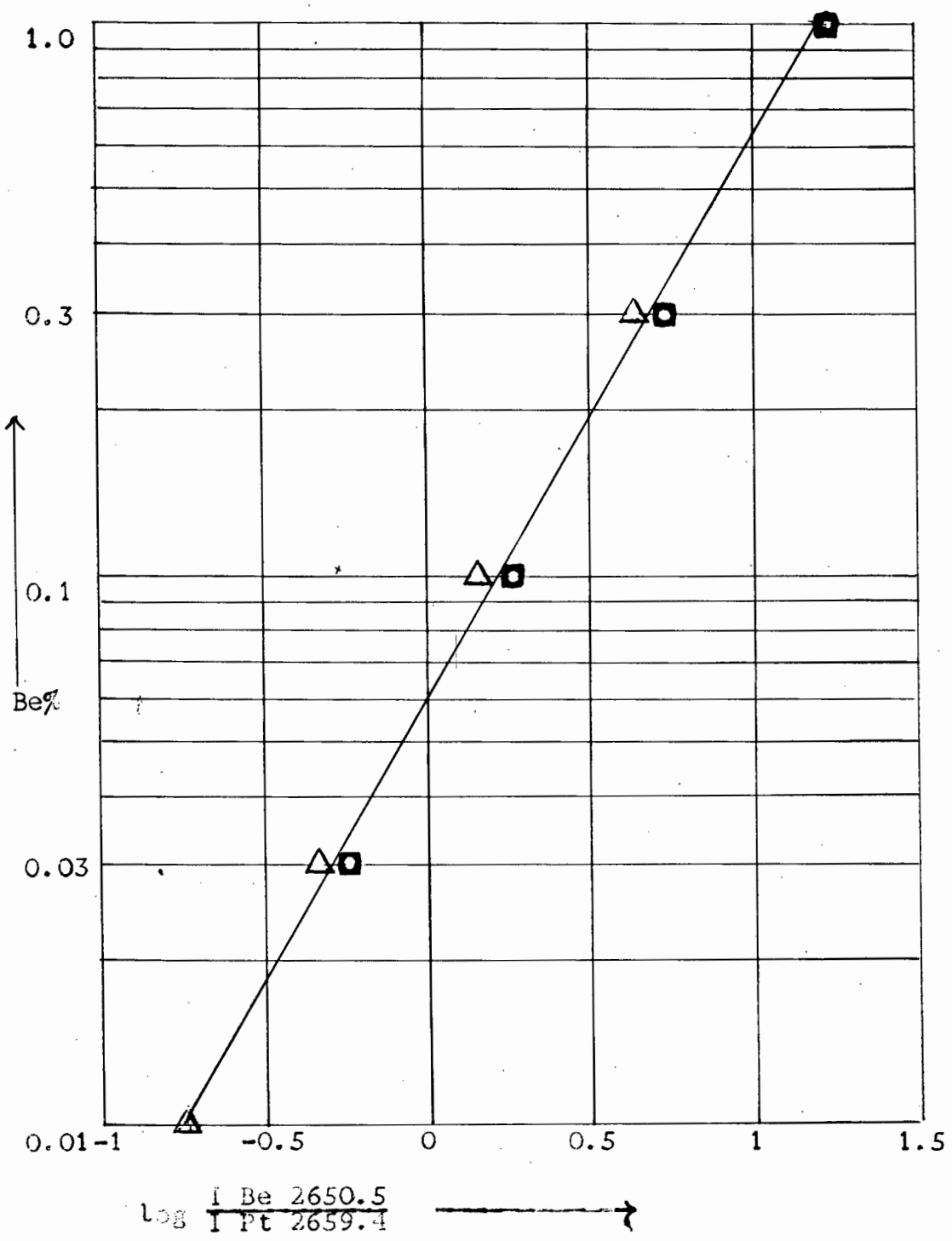
The working curves obtained are given on page 96, and it will be seen that the curves for the SiO_2 and $CaCO_3$ matrices were virtually identical. Matrix 3 seemed to slightly suppress the Be line, but the effect was very small. As Matrix 3 contained 10% Fe_2O_3, and the samples, while containing some iron, were not as high as this, it was decided to use the best curve for all three matrices, and this was the one drawn in Figure 18.

Equal steps of Be 2650.5 and Pt 2659.4 were compared, and it was found that at this region there was no necessity for background corrections. The samples available for checking the method were not chemical standards, but assuming them to be correct, the accuracy (mean deviation % from the chemical result) was ±12%. The reproducibility was calculated by arcing one sample 15 times, and the coefficient of variation was ± 10%

/Germanium...

Figure 18

The graph of Be% versus log. $\frac{I\ Be\ 2650.5}{I\ Pt\ 2659.4}$



4.6 Germanium.

While germanium is not involatile, it was always required in samples whose W, Mo, V, or Ti contents were also of interest. It was therefore decided to see if Method C could be applied for the determination of this element, so as to be able to make simultaneous determinations for whichever of the other elements was required.

When investigating the geochemistry of Ge, Goldschmidt and Peters[103] (1933) found that they could obtain a detection limit of approximately 1 p.p.m. with cathode layer excitation. Very large cathodes were employed, and the analysis line Ge 2651 was only recorded during the early period of arcing.

Britske and Varshavskaya[104] (1948) determined germanium in copper sulphide ores, using Ge 2709. It was found that Ge intensity increased with current, with an optimum at 17 amps. A detection limit of 5 - 10 p.p.m. was obtained, with a mean square error of 10 - 15%.

Saito (1951)[105] also obtained a detection limit of approximately 10 p.p.m. when investigating the Ge content of several minerals.

/The samples...

The samples were mixed with NaCl and applied to C electrodes. Using an intermittent d.c. arc, the most sensitive Ge lines were Ge 2651.1 and 3039.1.

Ge has also been determined in ores by Marks and Hall[106] (1946) using a $CaCO_3$ / graphite dilution method, and in meteorites by Lovering, Nichiporuk, Chodos, and Harrison Brown[52]. Coal and coal dust frequently contain Ge, and many workers have developed methods for Ge determination in this matrix.

To determine possible matrix effects in ores, standards were again made in three matrices:-

(a) calcium carbonate

(b) Matrix 3

(c) silica

as for Be, and Method C was applied. Equal steps of Pt 3065 and the strongest Ge line Ge 3039, were compared.

The working curves are given in Figure 19, and it will be seen that Ge is depressed by SiO_2 as compared with pure $CaCO_3$, but there is little difference whether 30% SiO_2 or 100% SiO_2 is present.

/The samples...

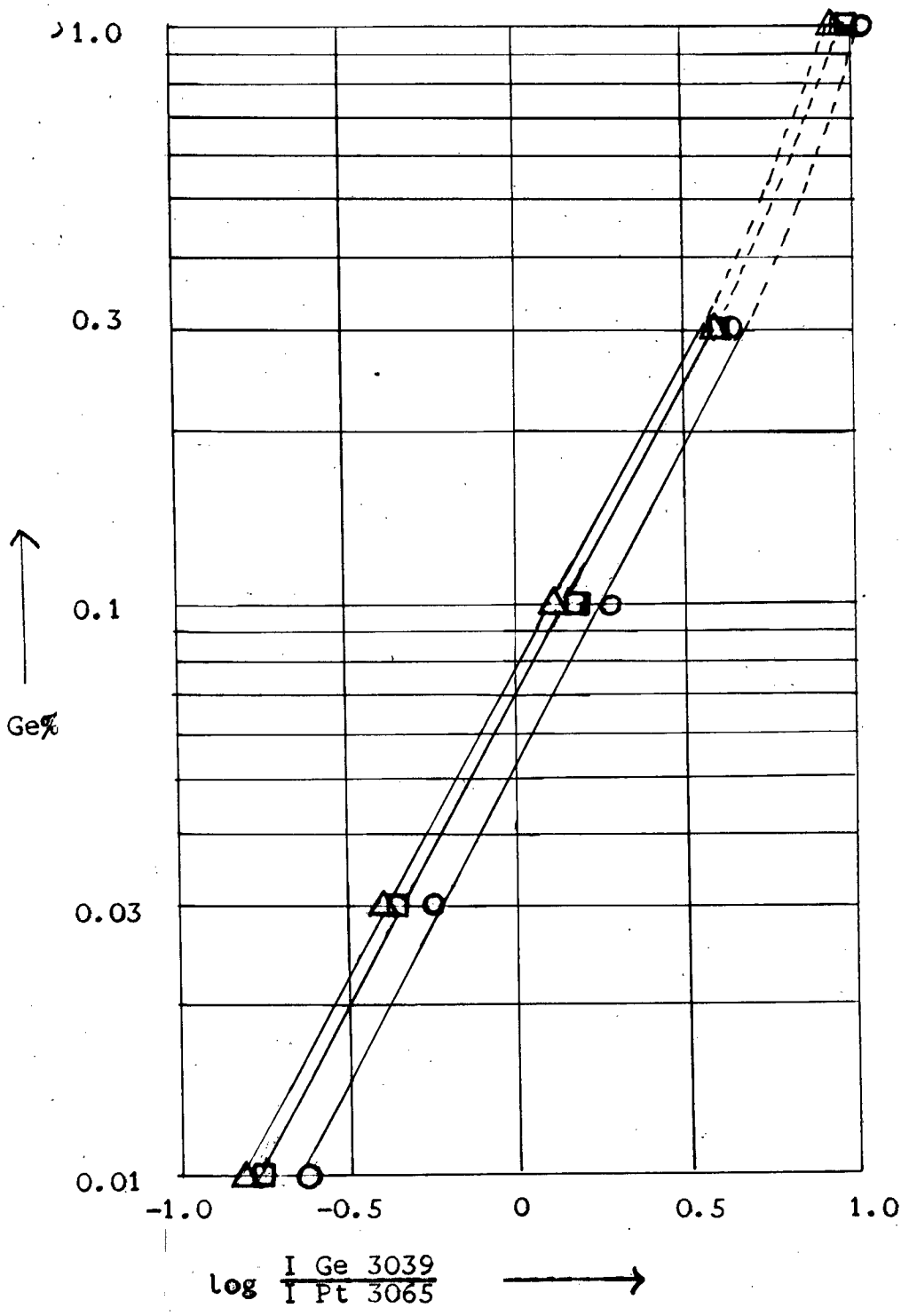
The samples available for checking the method consisted of two groups, Ge 1 - 5, had been chemically checked in duplicate, while the second set had been chemically analysed by triplicate determinations. Both sets of samples consisted of highly siliceous material. Assuming the chemical results to be correct, the spectrographic accuracy (mean deviation % from the chemical results) was ± 14% for the first set, and ± 7% for the second. The increase in accuracy is probably due to the higher level of Ge in the second set. The results are given on page 132. The overall accuracy for the 12 samples was ± 10%.

One sample (containing 0.18% Ge) was arced ten times and gave a coefficient of variation of ± 9%.

It will be seen from Figure 19, that self-absorption starts at Ge concentrations of over 0.3%. This is not surprising, as Ge 3039 is a ground state line.

Figure 19

The graph of Ge% versus log $\frac{\text{I Ge 3039}}{\text{I Pt 3065}}$



—O— in $CaCO_3$

—□— in Matrix 3

—△— in SiO_2

self absorption occuring.

4.7 Niobium and Tantalum.

Niobium was determined in igneous rocks, bauxites, and titanium minerals by Fleischer, Murata, Fletcher, and Narten[107] in 1952. The samples were mixed with either quartz, or a quartz - Na_2CO_3 mixture, and Nb 3163.40 and 3194.98 were the analysis lines. No internal standard was employed.

Nb was also determined in low grade ores by Thorne and Childs[108] in 1953. One part of sample was mixed with five parts each of TiO_2 and $(NH_4)_2SO_4$, and this mixture was pressed into a pellet. This was then arced at 9 amp. between Cu electrodes. Ti was used as internal standard, the analysis lines being Nb 4058.94 / Ti 4052.94 and Nb 4100.92/ Ti 4145.05. Nb 4100.9 can only be used if a relatively high dispersion spectrograph is available, as otherwise interference will occur with Fe 4100.7.

Another direct method for Nb determination was that of Rankama and Joensuu[109] (1946), who diluted samples with TiO_2, and mixed with a 4 : 1, C : NaCl buffer. After excitation by a cathode layer method, Nb 4058 was measured, and the limit of detection was 10 p.p.m..

/When...

When studying the geochemistry of niobium and tantalum, however, Rankama[110,111] found it necessary to employ a chemical enrichment technique.

Niobium and tantalum are becoming of increasing metallurgical interest, and many samples were submitted for analysis. These were mainly from a pyrochlore deposit, where the matrix consisted predominantly of carbonatites. Although the strongest Nb lines are Nb 4079.729 and Nb 4058.938, neither of these could be used. As only quartz optics were available, Nb 4079.7 could not be resolved from Fe 4079.8 or Ti 4079.7, and Nb 4058.9 was useless, as manganese was always present in the samples, causing interference with Mn 4058.9. It was, indeed, found that most of the more sensitive Nb lines suffered interference from either Ti, Mn, Fe, Ca or Mg, so that resort had to be made to the relatively insensitive Nb 2928. A Nb deposit is usually of economic significance when more than 0.5% pyrochlore is present, so that this line was not too weak to be considered, as it would be in a geochemical survey.

Analysis lines were also difficult to choose for Ta, as the strongest line Ta 3311.162 had an extremely high background from the CN band with head at 3590.4, and Ta 2714.674 was very close to the strong iron line Fe 2714.868.

/Under...

It was therefore decided to use Method C on all samples that burnt in the normal manner, but when the colour and nature of the burn indicated that large amounts of alkalies were present, the samples and standards were buffered with equal weights of Na_2CO_3. Fortunately very few samples were involved, as, in general, the deposit was uniformly composed of carbonatites.

The Nb and Ta results are given on pages 133 and 134. On the ten samples, an accuracy of ± 16% was obtained for Nb if Nb05a was included, and ± 10% if this result was excluded. As the samples were not chemical standards, a deviation of more than six times the mean of the other samples would seem to indicate that the chemical result of Nb 05a was suspect. For Ta the accuracy was ± 12%.

Reproducibilities were calculated from two samples that were each analysed ten times. The coefficient of variation for Nb was ± 10%, and for Ta ± 11%.

Figure 20

The graph of Nb% versus log $\frac{I\ Nb\ 2928}{I\ Pt\ 3065}$ for various matrices.

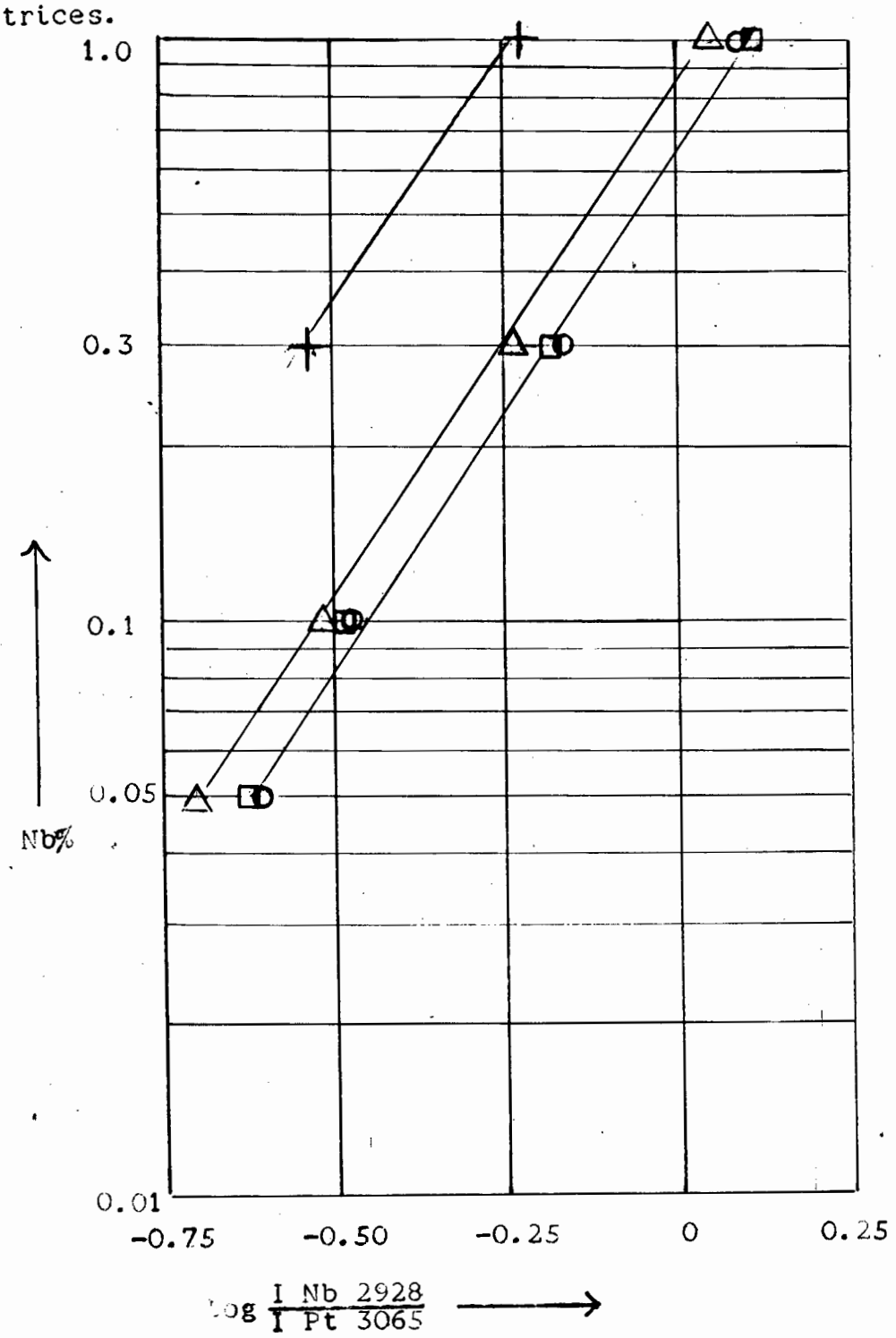
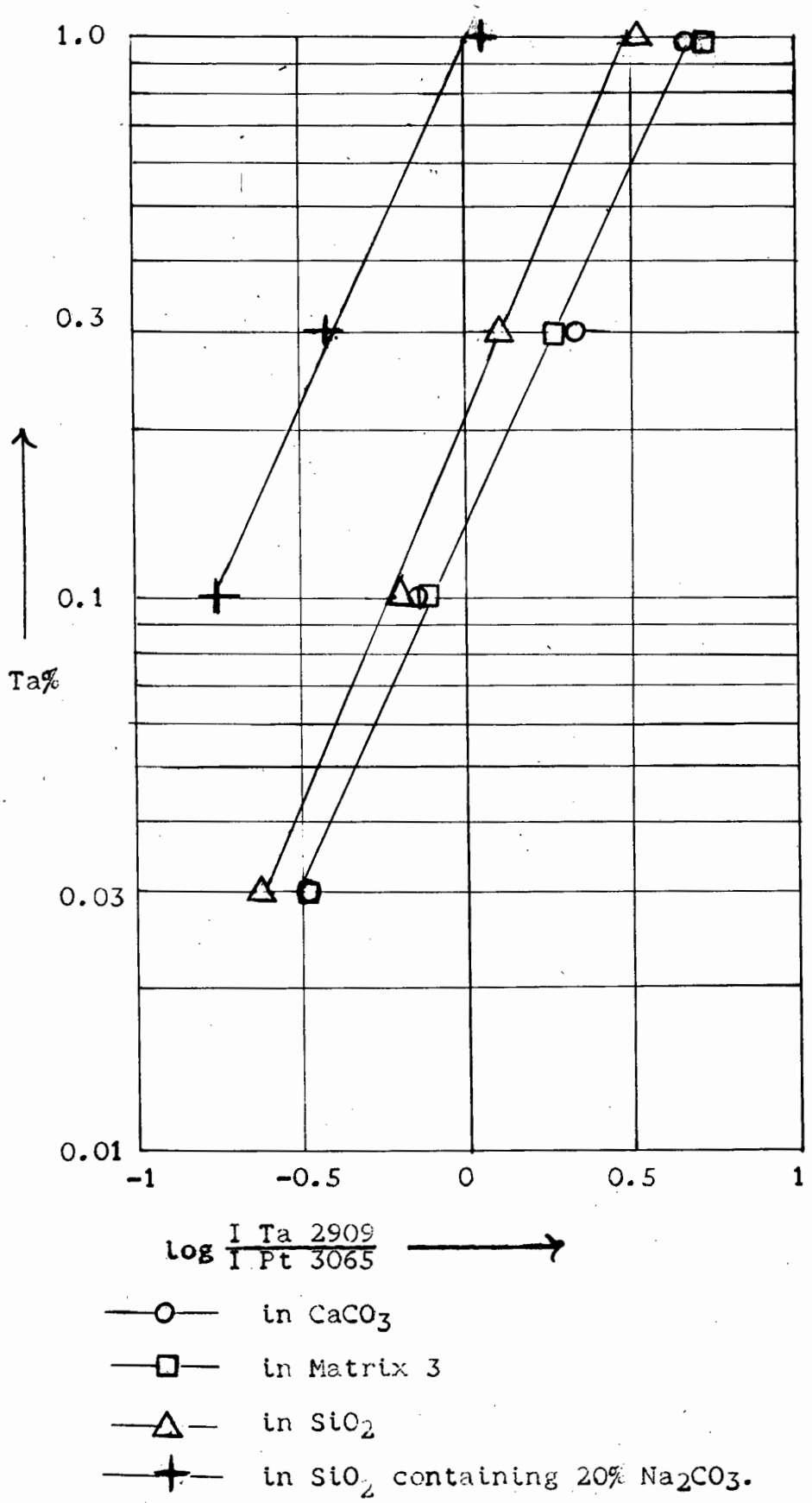


Figure 21

The graph of Ta% versus log $\frac{\text{I Ta 2909.91}}{\text{I Pt 3065.71}}$ for various matrices.



4.8 Molybdenum.

Many molybdenum deposits are discovered in granites, from which this element is freed by fine grinding and flotation. The spectrochemical determination of Mo has been studied by several workers. In 1943, Borovik[112] used Cr and Pt as internal standards in the determination of this element, and Carlsson[113] using an iron/potassium buffer determined Mo and W in ores.

The effect of matrix changes on the determination of Mo was studied by Vainstein, Pavlenko and Belyaev[114] (1957). Unfortunately the author has been unable to obtain either a copy of this publication, or a detailed abstract, so that no description of their findings can be given here.

The two strongest Mo lines, Mo 3902.963, and Mo 3798.252 cannot be used, unless special precautions are taken for the suppression of the cyanogen band with head at CN 3883. Mo deposits are rarely of economic importance if the Mo level is not considerably higher than 0.5% Mo. Mo 3170.347, which is frequently used, was very strong and in some concentrates interference was noted from Fe 3170.346 (10).

/A suitable...

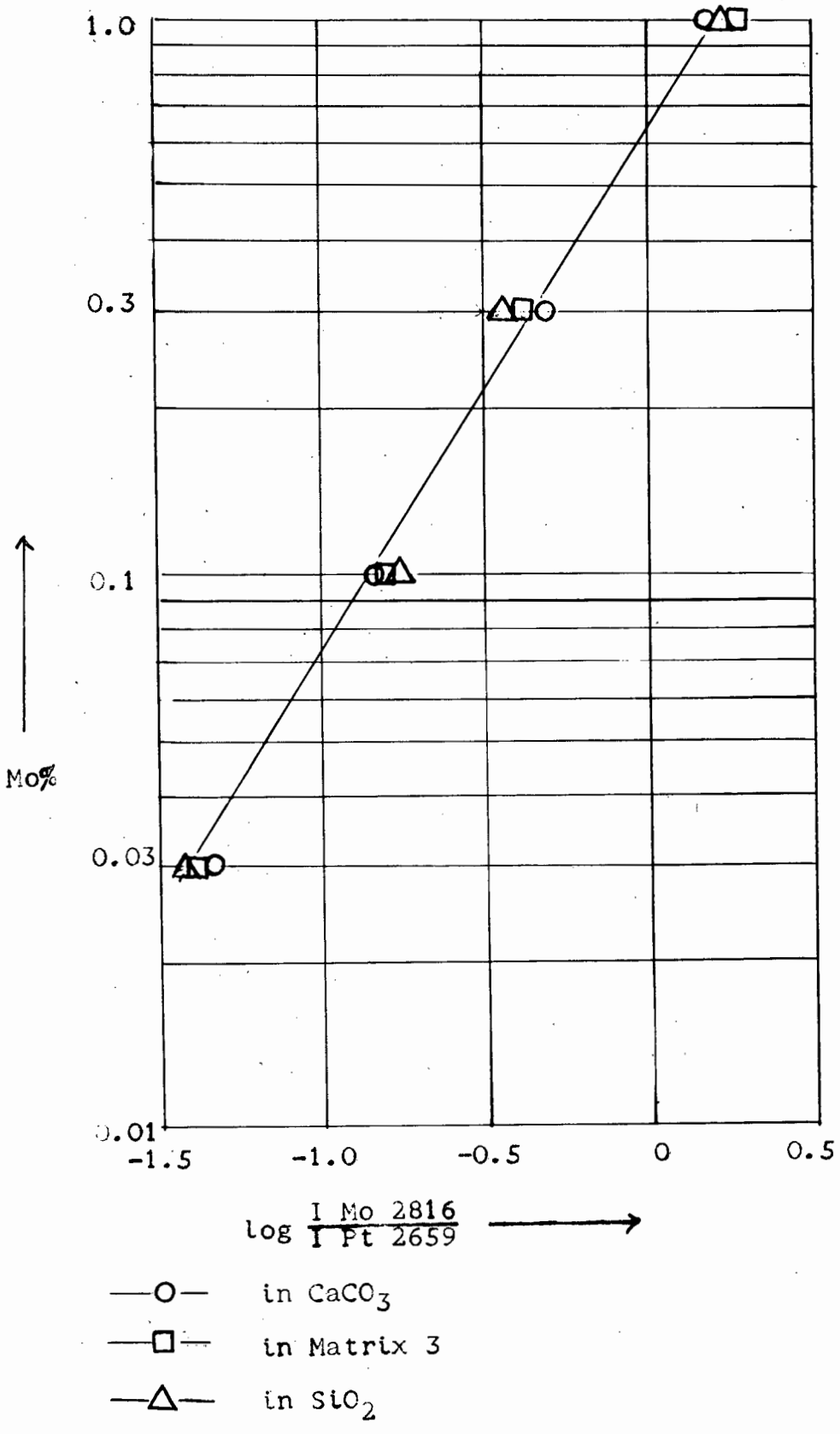
A suitable line pair for the determination of Mo was found to be Mo 2916 and Pt 2659. No appreciable difference was found in the characteristics of Ilford Thin Film Half Tone Plates over this range. The samples and standards were treated as in Method C, and standards were again made in three matrices, ($CaCO_3$, Matrix 3 and SiO_2). The working curve obtained is given in Figure 22, and it will be seen that there was no significant matrix effect. Equal steps of Mo and Pt were compared, and backgrounds were not measured, unless they were unusually heavy (less than 85% transmission).

The results are given in 5.20, and it will be noted that for high Mo values the results tended to be slightly less than the chemical figures. This could be due to either a slight error in the slope of the calibration curve, or a bias in the chemical method.

The accuracy found was ±13%. Two samples containing 0.19 and 0.077% Mo were analysed ten times each, and the coefficient of variation was ± 11%.

Figure 22

The graph of Mo% versus log $\frac{\text{I Mo 2816}}{\text{I Pt 2659}}$ in various matrices.



4.9 Vanadium, Titanium and Zirconium.

These three elements have been considered as a group, since vanadium is often recovered as a by-product from titanium minerals (e.g. the titaniferous ores of the Bushveldt complex) and zirconium is also obtained as a by - product in the recovery of ilmenite from river sands. Zr is also frequently found in rutile and sphene.

Preuss (1937)[115] determined V in waste ore using cathode layer excitation, with Fe as internal standard. The lines compared were V 3814 and Fe 3100, and an accuracy of approximately ± 7% was obtained. This method was also used for the determination of V in graphite.

V 3185 has frequently been used for analysis. Young[116] (1954) when investigating the V and Zr contents of sediments, used the line pairs V 3185 Pd 3421 and Zr 3391: Pd 3421. A relative deviation of ± 8.5% was obtained for V and ± 14% for Zr. V 3185 was also used in the present analysis, as, at the time of investigation, the author was not aware that Shaw[117] (1958) had discovered that this line suffers interference from Ca 3185.38. The apparent change of V intensity with increased Ca concentration is illustrated in Figure 23.

/Shaw...

The line pair chosen was Ti 3248 / Fe 3145. Roubault and Sinsou[66] compared Ti 3349 with Ni 3129 when estimating several trace elements in crystalline silicate rocks.

Sahāma[120] (1946) determined V and Zr in titanite, using the method of Rankama and Joensuu[109]. Zr is extremely difficult to volatilise, and Hamaguchi and Kuroda[121] found that the addition of $BaCl_2$ to silicates caused a more uniform entry of Zr into the arc. When the Ti content of the samples is known, Zr 3438 can also be compared with Ti 3242, and this procedure has been followed at the Department of Geology of Oxford University[122].

In the present work, the lines used were V 3185.40, Ti 2956.13 and Zr 2571.39. This Ti line was chosen instead of the more intense Ti 4981.7, 3653.5, 3361.2, 3349.4 and 3341.875 for several reasons. Ti 4981.7 was not very strong with quartz optics, and the other lines all had dark backgrounds from the CN bands with heads at 3883.4 and 3590.4. Furthermore, Ti is only of economic interest, when present as Ilmenite in river sands, if the concentration exceeds approximately 5%, so that there was no need to use the most sensitive lines.

/Zr...

Zr 2571.39 was chosen instead of Zr 4687.8, Zr 3438.2 and Zr 3391.9, as these lines suffered from the same disadvantages as the strongest Ti lines. Zirconium is frequently recovered as a by product from ilmenite, but it is of little economic importance unless approximately 0.5% Zircon is present, so that optimum sensitivity was not required.

Method C was used, and the standards were made in the same three matrices as before, ($CaCO_3$, Matrix 3 and SiO_2). Equal steps of V3185 and Ti 2956 were compared with Pt 3065, and the first step of Zr 2571 was compared with the second step of Pt 2659. It can be seen from the graphs (Figures 24 and 25) that Zr and Ti are depressed in a pure SiO_2 matrix. If the Ca content of the samples was low, they were mixed 1 : 1 with $CaCO_3$ before arcing, as with V determinations.

The results are given in pp 136-138. The accuracies were ±6.4% for Ti, ±10% for V, and ±6.8% for Zr.

/Two...

Two samples were arced ten times each for these elements, and the reproducibilities were calculated. The coefficients of variation were ± 6.9% for Ti, ± 9.5% for V and ± 6.5% for Zr.

Some of the samples in which Zr was determined were magnetic concentrates, so that it would appear that the presence of large quantities of iron does not affect the Zr method.

Figure 23

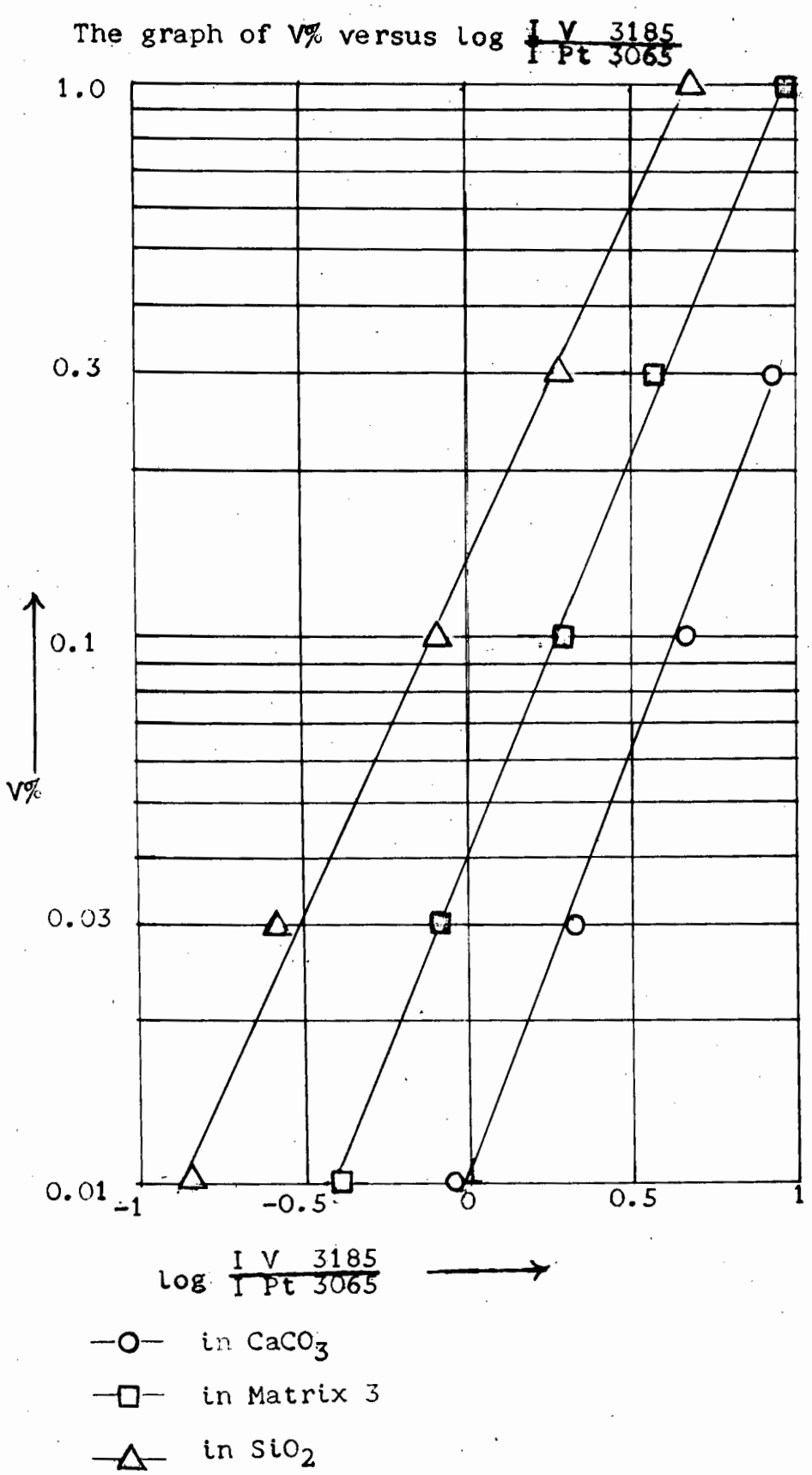

The graph of V% versus log I V 3185 / I Pt 3065
1.0
0.3
0.1
0.03
0.01
V%
-1
-0.5
0
0.5
1
log I V 3185 / I Pt 3065
in CaCO3
in Matrix 3
in SiO2

Figure 24

The graph of Zr% versus log $\frac{\text{I Zr 2571}}{\text{I Pt 2659}}$

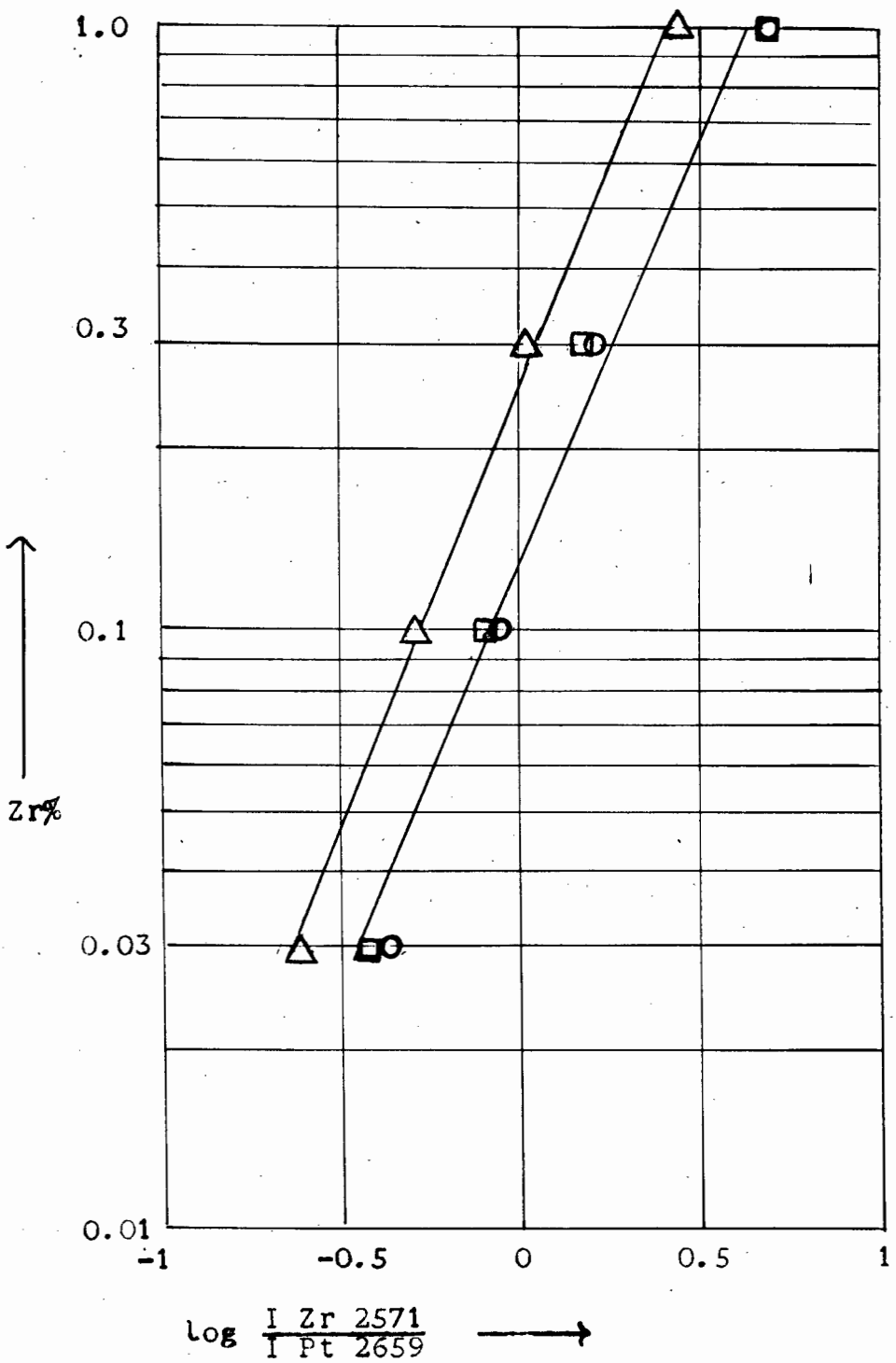
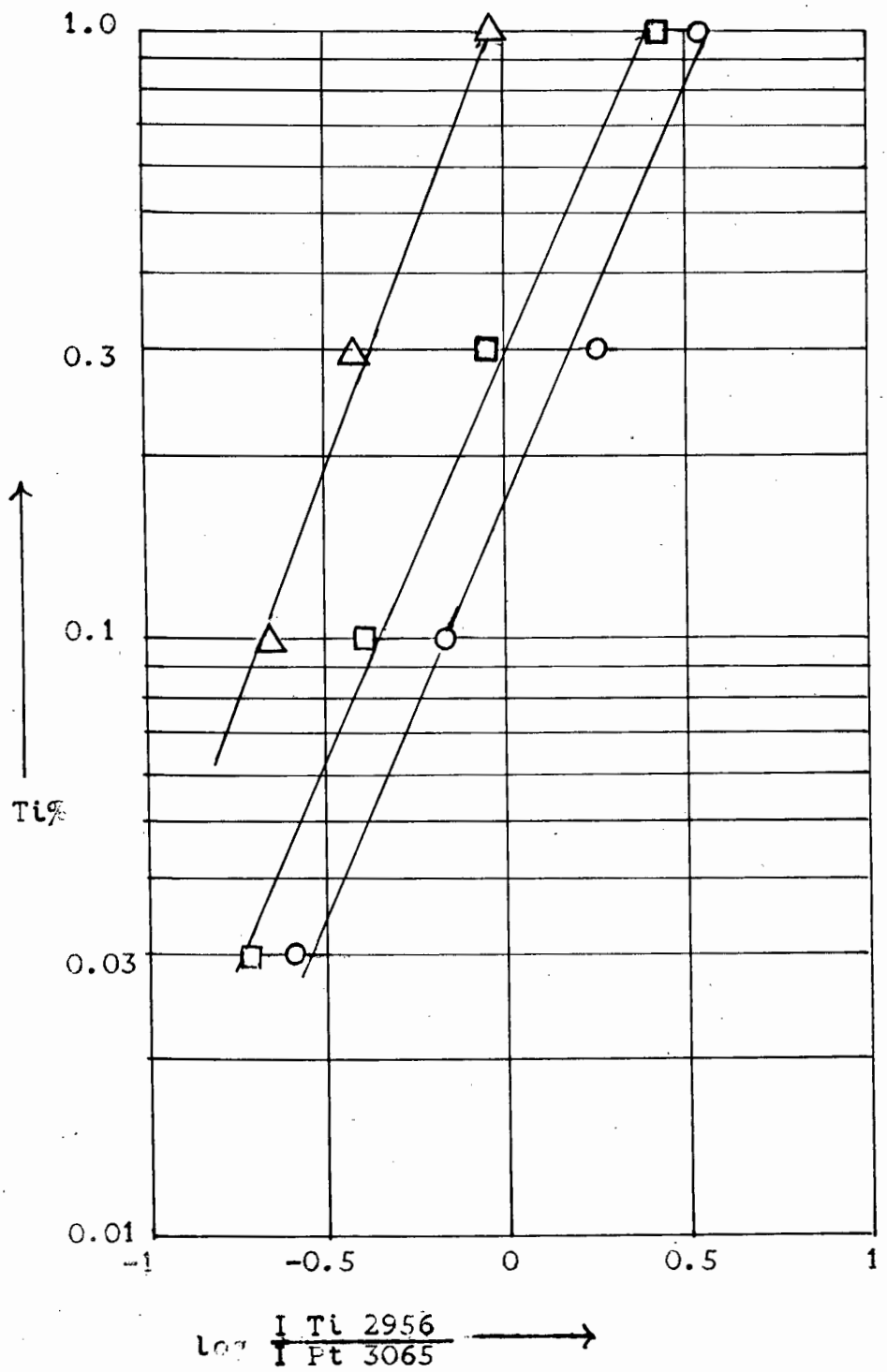


Figure 25

The graph of Ti% versus log $\frac{\text{I Ti 2956}}{\text{I Pt 3065}}$



5. RESULTS.

5.1 Arsenic.

Table 4.

Sample	Arsenic per cent		Deviation %
	Spectrographic	Chemical	
As 1	0.29	0.25	16
As 2	0.18	0.13	38
As 3	0.40	0.34	18
As 4	0.53	0.57	7
As 5	0.70	0.77	9
As 6*	0.52	0.40	30
As 7*	0.15	0.18	17
As 8*	0.14	0.21	33
As 9*	0.04	0.07	43
As 10*	0.19	0.18	6
As 11	0.07	0.08	13
As 12	0.30	0.26	15
As 13	0.41	0.45	9
As 14	0.78	0.86	9
As 15	1.10	0.95	16
As 16	0,30	0.25	20
As 17	0.21	0.17	24
As 18	0.42	0.39	8
As 19	0.51	0.51	0
As 20	0.67	0.63	6

/5.2 Antimony...

5.2 Antimony

Table 5.

Sample	Antimony per cent		Deviation %
	Spectrographic	Chemical	
Sb 1	4.5	5.6	20
Sb 2	44	47	7
Sb 3	32	30	7
Sb 4	27	24	13
Sb 5	0.65	0.72	10
Sb 6	0.63	0.53	19
Sb 7	0.47	0.45	4
Sb 8	0.93	0.89	4
Sb 9	0.15	0.22	32
Sb 10	1.7	1.5	13

A dilution technique was used for samples containing over 10% Sb.

/5.3 Phosphorus...

5.3 Phosphorus.

Table 6.

Sample	Phosphorus per cent		Deviation %
	Spectrographic	Chemical	
P 1	12	13	8
P 2	1.4	1.5	7
P 3	3.7	4.3	16
P 4	11	11	0
P 5	1.6	1.6	0
P 6	1.3	1.0	30
P 8	0.40	0.30	33
P 9	0.65	7.7	15
P 10	0.57	0.65	11
P 11	0.24	0.19	26
P 12	2.9	2.9	0
P 13	1.8	2.2	18
P 14	0.48	0.46	4
P 15	12	10	20
P 16	1.3	1.0	30
P 17	6.5	6.4	2
P 18	8.0	6.9	16
P 19	9.2	8.8	4
P 20	1.5	1.3	15

/5.4 Barium...

5.4 Barium

Table 7.

Sample	Barium per cent		Deviation %
	Spectrographic	Chemical	
Ba 1	0.52	0.62	15
Ba 2	0.21	0.17	24
Ba 3	0.046	0.050	8
Ba 4	0.079	0.099	20
Ba 5	0.14	0.11	27
Ba 6	0.82	0.70	17

5.5 Bismuth.

Table 8.

Sample	Bismuth per cent		Deviation %
	Spectrographic	Chemical	
Bi 1	0.15	0.20	25
Bi 2	0.091	0.086	6
Bi 3	0.074	0.085	13
Bi 4	0.053	0.061	11
Bi 5	0.032	0.022	9

/5.6 Boron...

5.6 Boron.

Table 9.

Sample	Boron per cent		Deviation %
	Spectrographic	Chemical	
B 1	0.34	0.36	6
B 2	0.14	0.18	22
B 3	0.46	0.40	16
B 4	0.60	0.45	33
B 5	0.19	0.17	12
B 6	0.24	0.23	5
B 7	0.27	0.29	7
B 8	0.81	0.80	1
B 9	0.77	0.80	4
B 10	0.13	0.15	13

The boron samples consisted of two batches, B 1 - 5 and B 6 - 10, which were analysed on different occasions. It will be seen that the accuracy for the second set is much better than for the first, the reason for this is unknown, as the samples seemed similar.

/5.7 Chromium...

5.7 Chromium

Table 10.

Sample	Chromium per cent		Deviation %
	Spectrographic	Chemical	
Cr 1	32	35	9
Cr 2	23	29	21
Cr 3	13	25	48
Cr 4	23	20	15
Cr 5	7.2	7.3	1
Cr 6	32	28	14
Cr 7	27	27	0
Cr 8	22	24	8
Cr 9	16	17	6
Cr 10	25	27	8
Cr 11	12	12	0
Cr 12	22	20	10
Cr 13	23	21	10
Cr 14	11	10	10
Cr 15	9.8	9.9	1
Cr 16	8.7	9.0	3
Cr 17	15	17	12
Cr 18	23	20	15
Cr 19	19	20	5
Cr 20	8.2	9.5	14

/5.8 Copper and Nickel...

5.8 Copper and Nickel.

Table 11.

Sample	Cu Spec %	Cu Chem. %	Ni Spec %	Ni Chem %
Cu 1	0.002	0.001		
Cu 2	0.001	0.002		
Cu 3	0.001	0.001		
Cu 4	0.005	0.005		
Cu 5	0.001	0.001		
Cu 6	0.001	0.005		
Cu 7	0.004	0.005		
Cu 8	0.003	0.003		
Cu 9	0.002	0.003		
Cu 10	0.003	0.002		
CuNi1	0.07	0.07	0.50	0.50
CuNi2	0.21	0.18	0.63	0.59
CuNi3	0.42	0.49	0.70	0.54
CuNi4	0.30	0.19	1.10	0.67
CuNi5	0.24	0.20	0.61	0.55
CuNi6	0.20	0.20	0.80	0.67
CuNi7	0.22	0.21	0.70	0.61
CuNi8	0.50	0.58	0.61	0.37
Ni 1			0.30	0.11
Ni 2			0.20	0.12
Ni 3			0.16	0.09
Ni 4			0.02	0.02
Ni 5			0.03	0.02
Ni 6			0.03	0.02
Ni 7			0.04	0.02

/5.9 Lead...

5.9 Lead.

Table 12.

Sample	Results (1)	Results (2)	Chemical Pb%	Devn %
Pb 1	0.0028	0.0071	0.0068	5
Pb 2	0.068	0.062	0.058	7
Pb 3	0.0012	0.0060	0.0067	10
Pb 4	0.021	0.11	0.11	0
Pb 5	0.0026	0.014	0.011	27
Pb 6	0.0027	0.0060	0.0048	25
Pb 7	0.0021	0.013	0.016	19
Pb 8	0.0028	0.025	0.024	4
Pb 9	0.0050	0.047	0.042	12

Result (1) were those obtained using an internal standard mixture of cadmium in graphite.

Results (2) were those obtained using an internal standard mixture of cadmium in 2 : 1 Li_2CO_3 : graphite.

/5.10 Calcium...

5.10 Calcium and Magnesium.

Table 13.

Sample	Ca Spec %	Ca Chem. %	Devn %	Mg Spec %	Mg Chem %	Devn. %
Ca1*	1.8	1.7	6	0.65	0.60	8
Ca2*	3.2	3.3	3	0.92	0.99	7
Ca3*	3.1	3.3	7	0.88	0.93	5
Ca4*	2.6	2.7	4	0.75	0.69	9
Ca5	5.3	5.0	6	1.7	1.9	11
Ca6	3.6	4.2	14	2.5	2.1	19
Ca7	7.1	6.6	8	3.0	3.2	8
Ca8	1.8	2.0	10	0.95	1.0	5
Ca9	2.1	1.8	17	0.97	0.89	9
Ca10	3.1	2.8	11	0.65	0.55	18
Ca11	2.7	2.4	13	0.86	0.70	23

*These samples were in a descloizite matrix.

/5.11 Iron...

5.11 Iron and Manganese.

Table 14.

Sample	Mn % Spec.	Mn % Chem.	Devn %	Fe % Spec.	Fe % Chem.	Devn. %
FeMn1	0.21	0.19	10	5.0	4.8	4
FeMn2	0.10	0.12	8	10	9.7	3
FeMn3	0.34	0.36	5	6.2	5.5	13
FeMn4	0.41	0.38	8	12	12.6	5
FeMn5	0.57	0.50	14	6.1	5.9	3
FeMn6	0.46	0.42	10	7.2	7.8	7
FeMn7	0.21	0.25	8	9.0	9.3	3
FeMn8	0.23	0.20	15	3.1	3.7	14
FeMn9	0.70	0.60	16	9.1	8.9	2
FeMn10	0.31	0.35	11	7.0	6.8	3
FeMn11	0.27	0.29	8	3.9	4.2	7
FeMn12	0.16	0.14	14	6.5	7.0	7

5.12 Strontium.

Table 15.

Sample	Sr % Spec.	Sr % Chemical	Deviation %
Sr 1	0.21	0.20	5
Sr 2	0.18	0.16	13
Sr 3	0.27	0.19	42
Sr 4	0.16	0.15	7
Sr 5	0.14	0.12	17
Sr 6	0.19	0.17	12

5.13.1 Tin. Method B.

Table 16.

Sample	Sn Spec. %	Sn Chem. %	Deviation %
Sn1	0.31	0.28	11
Sn2	0.040	0.032	25
Sn3	0.40	0.31	29
Sn4	0.36	0.46	22
Sn5	0.32	0.30	7
Sn6	0.78	0.72	8
Sn7	0.45	0.45	0

5.13.2 Tin. Method C.

Table 17.

Sample	Spec. Sn%	Lab. (1) Sn%	Lab. (2) Sn%
Sn1	0.17	0.19	less than 0.05
Sn2	0.12	0.08	less than 0.05
Sn3	0.30	0.36	0.12
Sn4	0.30	0.35	0.12
Sn5	0.24	0.16	0.10
Sn6	0.02	0.04	less than 0.05
Sn7	0.19	0.07	"
Sn8	0.04	0.08	"
Sn9	0.15	0.10	"
Sn10	0.12	0.10	"
Sn11	36	36.74	38.55
Sn12	24	26.76	26.11
Sn13	26	16.94	15.86
Sn14	40	40.60	40.49

/5.14 Zinc...

5.14 Zinc.

Table 18.

Sample	Zinc per cent		Deviation %
	Spectrographic	Chemical	
Zn 1	0.27	0.26	4
Zn 2	0.18	0.20	10
Zn 3	0.12	0.10	20
Zn 4	0.25	0.25	0
Zn 5	0.095	0.10	5
Zn 6	0.087	0.079	10
Zn 7	0.026	0.022	18
Zn 8	0.017	0.018	6
Zn 9	0.011	0.010	10
Zn 10	0.034	0.032	6
Zn 11	0.076	0.080	5
Zn 12	0.26	0.022	18
Zn 13	0.33	0.30	10
Zn 14	0.37	0.40	8
Zn 15	0.057	0.049	16
Zn 16	0.010	0.010	0
Zn 17	0.021	0.019	10
Zn 18	0.10	0.095	5
Zn 19	0.076	0.074	3
Zn 20	0.23	0.24	4

/5.15 Tungsten...

5.15 Tungsten.

Table 19.

Sample	Spec. WO_3%	Lab. (1) WO_3%	Lab. (2) WO_3%
W 1	11	11.96	13.1
W 2	9.0	9.09	10.0
W 3	19	17.80	20.7
W 4	17	15.54	18.7
W 5	18	16.55	13.1
W 6	34	28.41	23.6
W 7	10	8.76	9.3
W 8	8.0	11.00	12.6
W 9	11	14.98	12.1
W 10	24	20.96	23.0
W 11	22	28.47	13.4
W 12	6.1	5.42	5.0
W 13	10	11.77	9.4
W 14	16	18.63	12.3
W 15	10	17.63	19.2
W 16	29	27.00	32.4
W 17	15	13.82	14.9
W 18	0.15	0.14	0.033
W 19	0.07	0.06	0.026
W 20	0.06	0.10	0.053
W 21	0.35	0.16	0.064
W 22	0.10	0.20	0.096
W 23	0.25	0.40	0.13
W 24	0.04	0.04	0.022
W 25	0.13	0.07	0.036
W 26	0.11	0.10	0.066
W 27	0.15	0.15	0.037
W 28	0.11	0.12	0.075
W 29	0.06	0.03	0.015
W 30	0.17	0.14	0.10
W 31	0.09	0.04	0.027
W 32	0.09	0.12	0.037

5.16 Beryllium.

Table 20.

Sample	Beryllium per cent		Deviation %
	Spectrographic	Chemical	
Be 1	0.26	0.30	13
Be 2	0.24	0.25	4
Be 3	0.18	0.16	13
Be 4	0.15	0.20	25
Be 5	0.15	0.20	25
Be 6	0.48	0.50	4
Be 7	0.37	0.33	12
Be 8	0.60	0.50	20
Be 9	0.72	0.75	4
Be 10	0.80	0.72	11
Be 11	0.35	0.29	20
Be 12	0.27	0.27	0
Be 13	0.57	0.50	14

/5.17 Germanium..

5.17 Germanium.

Table 21.

Sample	Germanium per cent		Deviation %
	Spectrographic	Chemical	
Ge 1	0.051	0.060	15
Ge 2	0.026	0.023	13
Ge 3	0.034	0.041	17
Ge 4	0.017	0.020	15
Ge 5	0.046	0.036	28
Ge 6	0.10	0.092	9
Ge 7	0.23	0.25	8
Ge 8	0.37	0.33	12
Ge 9	0.54	0.45	20
Ge 10	0.61	0.62	2
Ge 11	0.50	0.50	0
Ge 12	0.89	0.88	1

/5.18 Niobium...

5.18 Niobium.

Table 22.

Sample	Niobium per cent		Deviation %
	Spectrographic	Chemical	
Nb01a	0.31	0.33	6
Nb02a	0.68	0.61	11
Nb03a	1.75	1.90	8
Nb04a	0.14	0.14	0
Nb05a	1.20	0.75	60
NbL1c	0.32	0.35	9
NbL2c	0.76	0.64	20
NbL3c	0.12	0.14	14
NbL4c	1.10	1.27	13
NbL5c	0.22	0.28	21

In this case the chemical results were obtained by paper chromatography, with one in three being checked by gravimetric methods.

/5.19 Tantalum...

5.19 Tantalum.

Table 24

Sample	Tantalum per cent		Deviation %
	Spectrographic	Chemical	
Ta 1	0.062	0.070	11
Ta 2	0.25	0.23	9
Ta 3	0.17	0.14	22
Ta 4	0.063	0.080	21
Ta 5	0.20	0.30	33
Ta 6	0.27	0.30	10
Ta 7	0.43	0.45	4
Ta 8	0.61	0.59	4
Ta 9	0.44	0.46	4
Ta 10	0.72	0.81	11
Ta 11	0.18	0.20	10
Ta 12	0.26	0.25	4
Ta 13	0.43	0.50	14
Ta 14	0.52	0.50	4
Ta 15	0.81	0.70	16
Ta 16	0.79	0.75	5
Ta 17	0.25	0.20	25

/5.20 Molybdenum...

5.20 Molybdenum.

Table 23.

Sample	Molybdenum per cent		Deviation %
	Spectrographic	Chemical	
Mo 1	0.025	0.023	9
Mo 2	0.039	0.042	7
Mo 3	0.20	0.24	16
Mo 4	0.21	0.24	13
Mo 5	0.59	0.69	14
Mo 6	0.063	0.071	11
Mo 7	0.30	0.38	21
Mo 8	0.14	0.16	13
Mo 9	0.048	0.056	14
Mo 10	0.44	0.46	5
Mo 11	0.21	0.22	5
Mo 12	0.074	0.062	20
Mo 13	0.024	0.018	33
Mo 14	0.009	0.009	0
Mo 15	0.013	0.015	13

/5.21 Titanium...

5.21 Titanium.

Table 25.

Sample	Titanium per cent		Deviation %
	Spectrographic	Chemical	
Ti 1	5.2	5.2	0
Ti 2	1.7	1.9	10
Ti 3	1.3	1.3	0
Ti 4	9.2	9.3	1
Ti 5	0.30	0.34	12
Ti 6	0.17	0.15	13
Ti 7	14	13	8
Ti 8	8.6	9.0	5
Ti 9	0.87	0.90	3
Ti 10	0.95	0.95	0
Ti 11	0.47	0.43	10
Ti 12	0.43	0.46	7
Ti 13	0.36	0.33	9
Ti 14	0.33	0.35	6
Ti 15	0.71	0.72	2
Ti 16	0.77	0.74	4
Ti 17	0.54	0.51	6
Ti 18	0.11	0.095	15
Ti 19	0.18	0.15	20

/5.22 Vanadium...

5.22 Vanadium.

Table 26.

Sample	Vanadium per cent		Deviation %
	Spectrographic	Chemical	
V 1	0.004	0.003	33
V 2	0.081	0.090	10
V 3	0.042	0.034	21
V 4	0.69	0.67	3
V 5	1.2	1.1	9
V 6	0.34	0.30	13
V 7	0.78	0.80	3
V 8	0.53	0.50	6
V 9	0.91	1.01	9
V 10	0.097	0.091	7
V 11	0.047	0.051	8
V 12	0.049	0.050	2
V 13	0.023	0.020	15
V 14	0.071	0.065	10
V 15	0.25	0.27	8
V 16	0.31	0.33	6
V 17	0.57	0.50	14
V 18	0.33	0.31	7
V 19	0.61	0.55	11
V 20	0.82	0.82	0

/5.23 Zirconium...

5.23 Zirconium.

Table 27.

Sample	Zirconium per cent		Deviation %
	Spectrographic	Chemical	
Zr 1	8.6	8.9	3
Zr 2	5.5	5.1	8
Zr 3	0.87	0.90	3
Zr 4	0.91	0.89	2
Zr 5	0.55	0.50	10
Zr 6	0.38	0.36	6
Zr 7	0.56	0.59	5
Zr 8	0.18	0.17	6
Zr 9	0.21	0.18	17
Zr 10	0.27	0.25	8
Zr 11	0.23	0.23	0
Zr 12	0.31	0.34	9
Zr 13	0.41	0.45	9
Zr 14	0.47	0.50	6
Zr 15	0.52	0.49	6
Zr 16	0.60	0.51	18
Zr 17	0.71	0.70	1
Zr 18	0.75	0.69	9
Zr 19	0.81	0.81	1
Zr 20	0.85	0.81	5
Zr 21	0.93	0.90	3
Zr 22	0.95	0.99	5
Zr 23	0.17	0.22	18
Zr 24	0.21	0.20	5
Zr 25	0.37	0.35	6

6. CONCLUSIONS.

Methods have been found for the spectrographic determination of P, As, Sb, Ba, Bi, B, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Sr, Sn, Zn, W, Be, Mo, Ge, Nb, Ta, V, Ti, and Zr in ores. Four internal standards are employed, Te, Cd, Au and Pt. Both accuracies and coefficients of variation are less than $\pm$ 15% for all elements except Ba, with an accuracy of $\pm$ 19%, and As, when present in highly siliceous material.

7. APPENDIX.

THE CALCULATION OF COEFFICIENTS OF VARIATION AND ACCURACIES.

(a) Coefficient of Variation.

When n determinations were made on one sample, the result for the i th determination being x_i , the standard deviation σ was calculated from the expression

$$\sigma = \sum_{i=1}^{n} \sqrt{\frac{(\bar{x} - x_i)^2}{n - 1}}$$

where $\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$.

The coefficient of variation was then expressed as $100 \frac{\sigma}{\bar{x}}$ %.

This is the standard method for calculating coefficients of variation, incorporating Bessel's correction for small samples. A description will be found in most text-books on statistics, e.g. Moroney [123] (1956).

When the coefficient of variation was calculated from a large number of sets of duplicate determinations on different samples, a procedure recommended by Professor Kerrich of the University of the Witwatersrand was adopted.

/The.....

The distribution of the range $R = x_N - x_I$, where x_N and x_I represent the largest and smallest values of a sample of n, has been investigated by Pearson and Hartley[124]. They tabulate the distribution of $\frac{R}{\sigma}$ for samples of size $2 \leq n \leq 20$ for a normal distribution with variance σ^2.

From the table of fractiles W_p of the distribution of range probabilities given by Hald[125] it can be calculated that the mean of the range, which will be called M(R), for two determinations will be given by $1.128\ \sigma_x$. The coefficient of variation is $\frac{100\ \sigma_x}{\bar{x}}\%$ as before, but will only be constant if σ_x is proportional to x. If x_1 and x_2 are the values of two duplicates, $|x_1 - x_2|$ is the range, and is proportional to $\sigma_{\frac{x_1+x_2}{2}}$, i.e. $\sigma_{\bar{x}}$.

Graphs were therefore plotted of $|x_1 - x_2|$ versus $\frac{x_1 + x_2}{2}$, and although there was considerable scatter, there appeared to be a straight line relationship between these variables. The best possible straight line was estimated graphically, as, with errors on each axis, the least squares method could not be rigorously employed. M(R) equals $1.128\sigma_x$, so $\frac{M(R)}{\bar{x}}$, the slope of the line, is equal to $1.128\ \frac{\sigma_x}{\bar{x}}$

The coefficient of variation, $100\ \sigma_x\%$ was therfore calculated from the slope of the graph.

(b) Accuracy

The accuracy was calculated by assuming the chemical results to be correct. If x_i^c and x_i^s are the chemical and spectrographic results respectively for sample i, the percentage deviation of the spectrographic from the chemical figure is given by

$$100 \left| \frac{x_i^c - x_i^s}{x_i^c} \right| \%.$$

As, in this case, there seemed to be no reason for using a geometric mean, the arithmetic mean of these deviations was used to express accuracy,

$$\text{i.e. } \frac{100}{n} \sum_{i=1}^{n} \left| \frac{x_i^c - x_i^s}{x_i^c} \right| \%.$$

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