SPECTROCHEMICAL ANALYSIS OF SILICATES USING THE STALLWOOD JET

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ABSTRACT

The effects of irregular slit illumination, polar distribution of elements in the arc plasma and self-absorption are discussed in relation to the use of the Stallwood jet for D.C. analysis of minor elements in silicates. A general method for simultaneous determination of 19 elements, using a graphite matrix with Pd as internal standard is described. Precision and accuracy are discussed in terms of the standard samples G1 and W1.

INTRODUCTION

Among the wealth of improvements made in most instrumental methods of analysis over the last twenty years D.C. spectrochemical analytical methods have largely remained static until recently. Such improvements as were made involved few new principles and, although some progress was made towards achieving satisfactory precision and accuracy, the results of D.C. analysis are often regarded with suspicion by chemists. B. J. Stallwood's invention of the air-jet (1954) was a major contribution which permits reproducible results to be obtained in routine work by technicians. The principle of the air-jet is that the sample electrode is continually cooled during arcing by an annular current of air which, flowing upward, also stabilizes the arc and prevents irregular burning. These factors lead to improved precision and a reduction in selective volatilization is found to diminish matrix effects.

The purpose of the present paper is to give an account of some aspects of D.C. quantitative procedures which bear on precision and accuracy, and which were encountered during development of methods for analysis of silicates. They are particularly relevant to stigmatic spectrographs and mainly concern D.C. air-jet excitation. A Jarrell Ash 21-foot stigmatic grating spectrograph (Wadsworth mount) with 1st order dispersion of 5.2Å/mm. has been used throughout, recording spectra on two 4 by 10-inch plates.

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FACTORS INFLUENCING PLATE CALIBRATION

Slit Illumination

Since in later sections some irregularities will be described which could be explained by uneven slit illumination, this topic needs some discussion.

Where a step-filter or step-sector is to be used for plate calibration or intensity reduction it is necessary that the jaws of the slit be accurately parallel and that the light intensity along the length of the slit be regular. In addition the use of condensing lenses is generally necessary to improve sensitivity. The following condensing system was used (quartz lenses):

25 cm. focal length cylindrical lens (horizontal axis) at the slit
6.7 cm. focal length cylindrical lens (vertical axis) 16.1 cm. from the slit.
Adjustable diaphragm (aperture 5 mm.) 27.5 cm. from the slit
10 cm. focal length spherical lens 58.1 cm. from the slit
Arc-electrodes 72.5 cm. from the slit.

The arc was magnified about twofold to form an image on the diaphragm, which served as a secondary source.

Two factors should be borne in mind with regard to the optical train. Firstly, the vertical positions of all components must be carefully adjusted so that each is centred on the optical axis. If this is not done the optical axis will not pass through the centre of the slit and the top half of the slit will have a different light intensity distribution from the bottom half (see Fig. 1). Secondly, the system will only be in focus for a fairly narrow wavelength range. If the components are adjusted to be in focus in the visible region (as in the above arrangement) the infra-red and low ultraviolet images will not be in focus. The practical result appears to be that the intensity distribution will be less regular along the slit for out-of-

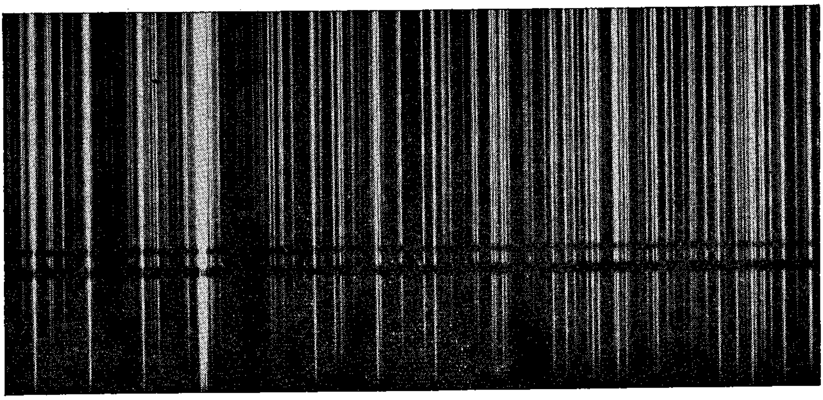

FIG. 1. Non-uniform slit illumination arising from incorrect vertical adjustment of a lens. The horizontal bars are caused by dust on the slit and should be disregarded. The whole slit length (20 mm.) is shown.

focus wavelengths. These factors influence data in Table 1, which are transmission values for a number of spectral lines, recorded using a long (13 mm.) slit with no step-sector. Each line has been measured in five places spaced equidistantly from top to bottom.

The data in Table 1 show firstly that only the central region of the slit shows regular illumination. They also show the optical axis to be displaced slightly above the middle of the slit (the image is inverted and the axis appears to be low). Thirdly, the data show the illumination to be rather more regular at wavelengths close to the visible, for which the optical components were focused. Figure 2 shows the intensity distribution

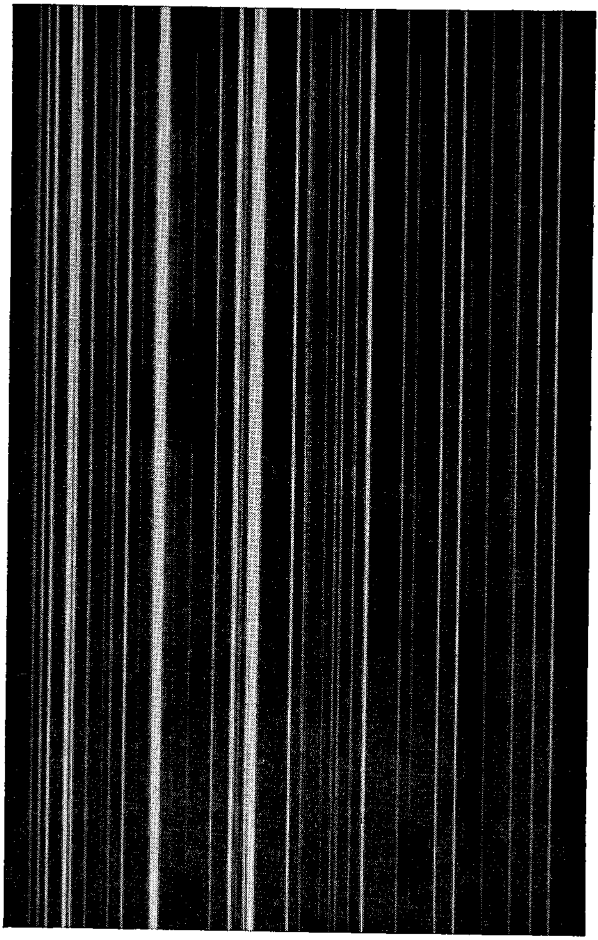

FIG. 2. A satisfactory slit intensity distribution, showing that the central region is evenly illuminated. The whole slit length (20 mm.) is shown.

TABLE 1. TRANSMISSION VALUES AT DIFFERENT POINTS ON LONG SPECTRAL LINE IMAGES

Line	Top 0 mm.	3 mm.	Middle 7 mm.	10 mm.	Bottom 13 mm.
Be 2348Å	1.5	0.7	0.5	0.5	0.7
Pd 2476	74	18.5	13.5	15.5	43
B 2497	3.6	1.2	0.9	1.0	1.9
Mg 2776	66	37	34	34	57
Ga 2943	1.6	1.1	1.0	1.1	2.2
Pd 3258	5.6	3.4	3.4	3.6	5.5
CN about 3680	61	48	45	43	49
CN about 3990	47	35	33	31	38
V 4379	23	15	13	12.5	18
Band line about 4600	81	61	56	45	65

for a long (20 mm.) slit exposure for which the optical arrangements were judged to be satisfactory.

It is clear from the foregoing that only the central region of the slit can be illuminated with enough regularity to permit a step-sector or filter to be placed near the slit for plate calibration. Using a seven or eight step-sector it is likely that readings from the top and bottom steps will be valueless with the optical arrangement described above. As far as possible readings should be restricted to the central steps.

Polar Effects

It is well-known that under certain conditions the concentration of elements may vary along the length of a D.C. arc. The cathodelayer (Glimmschicht) effect, in which trace constituents are concentrated near the cathode, was utilized by Mannkopf & Peters (1931) to obtain maximum sensitivity in the analysis of rocks and minerals in a method which has been widely used by geochemists and others. In many applications, however, a more regular elemental distribution in the arc-plasma is necessary to obtain higher precision, and for this purpose anode excitation is usually recommended.

When using the Stallwood jet it might be expected that the arc-column would be relatively homogeneous, since the arc becomes a narrow confined discharge and the customary flame-like features are eliminated by the upward-moving air flow. In this situation, using anode excitation, polar effects should be at a minimum. However polar effects will only be apparent of course if a stigmatic spectrograph is used where the line-image records the intensity-distribution along the slit. Polar effects of this kind were encountered in trying to adapt a method first used by Kvalheim (1947) and recently developed by Hawley & MacDonald (1956), in which $SrCO_3$ and graphite are used as a buffer for the analysis of silicates. Figure 3 shows three spectra: the top two record a 1:9 mixture of scapolite and graphite and the last is a 1:1:2 mixture of scapolite, $SrCO_3$ and graphite. Anode excitation with the Stallwood jet was used and a rotating step-sector was placed close to the slit. *In spite of the effect of the sector* it can be clearly seen that in the spectrum where $SrCO_3$ was used certain lines (Sr 2428, Al 2367, Al 2373, Si 2435) show marked polar effects. These are interpreted as showing a preferential concentration of these elements near the lower electrode (marked + on the figure). Where graphite alone was the buffer such effects are generally absent, although they have been detected for some lines of both major and trace elements. It should be stressed that an optical train was used (see previous section) which is designed to give even slit illumination.

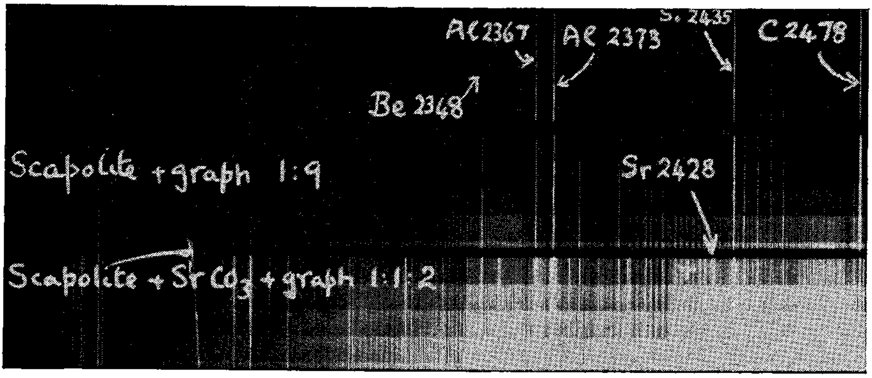

FIG. 3. Polar effects shown by several lines in the spectrum where $SrCO_3$ was used in the buffer (see text).

The practical consequences are two-fold. Firstly, it is necessary to choose lines for plate calibration which do not show a polar effect (the effect has also been detected in a pure iron arc). Secondly, a line showing a polar effect will be valueless for analysis, unless a very short slit is used. Slight effects of this kind may not be visible to the eye but are revealed by irregularities in plate calibration and working curves. Where good precision is required it has proved necessary to check every analysis line in a spectrum exposed with a long slit and no sector.

Self-Absorption

Self-absorption commonly occurs with any element when its concentration in the arc-plasma exceeds a certain limit. The limit depends on the character of the arc used, the element in question and various other factors but self-absorption is commonly encountered with many

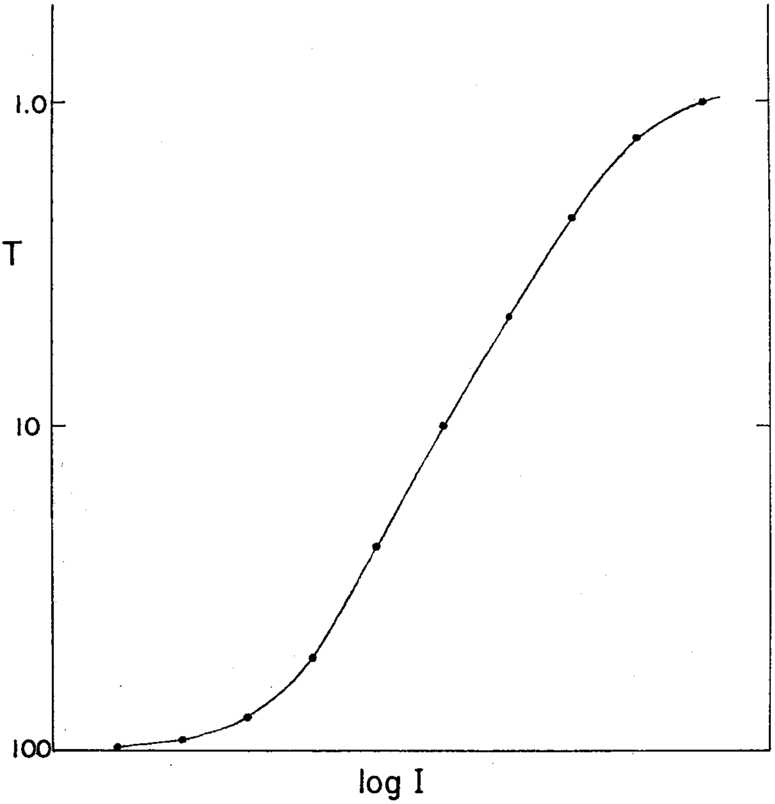

FIG. 4. Emulsion response for Be 3131, showing log transmission (*T*) plotted against log *I*. Note the self-absorption in dense line-images (low *T*-values).

elements when the concentration in the sample exceeds 0.1% and the persistent lines are used. By continually flushing the arc column with air, as in the Stallwood jet, self-absorption is substantially reduced but is not eliminated.

When the response of a photographic emulsion to light has been accurately related to exposure (plate calibration) it is usual to find a linear relation between density and log intensity continuing from densities of about 0.5 to 2.0 or more. Self-absorption in an analysis line is then revealed by the flattening of the working-curve slope at higher concentrations. When this situation arises it is frequently necessary to reject the analysis line as unsuitable and search for another. This is troublesome and, in the case of elements such as boron which have few sensitive lines, may be impossible. Moreover it is difficult to calibrate the emulsion accurately in any case (see later).

The writer accordingly adopted a different approach, using analysis lines for emulsion calibration, including some which show definite self-absorption in the flattening of the slope of the calibration curve at higher densities. The calibration curve, therefore, related line density to exposure *only for the particular line concerned in the method used* and was not a true emulsion calibration: this empirical approach gave a calibration curve flattened at the top for a self-absorbed element, but resulted in a linear working-curve even at fairly high concentrations (Figs. 4, 5).

Construction of Emulsion Calibration Curves

Two methods are commonly used for emulsion calibration in routine spectrographic procedures and require the diminution of spectral line intensity by either a rotating step-sector or a fixed step-filter: there are other and better methods but these are seldom practical in analytical laboratories.

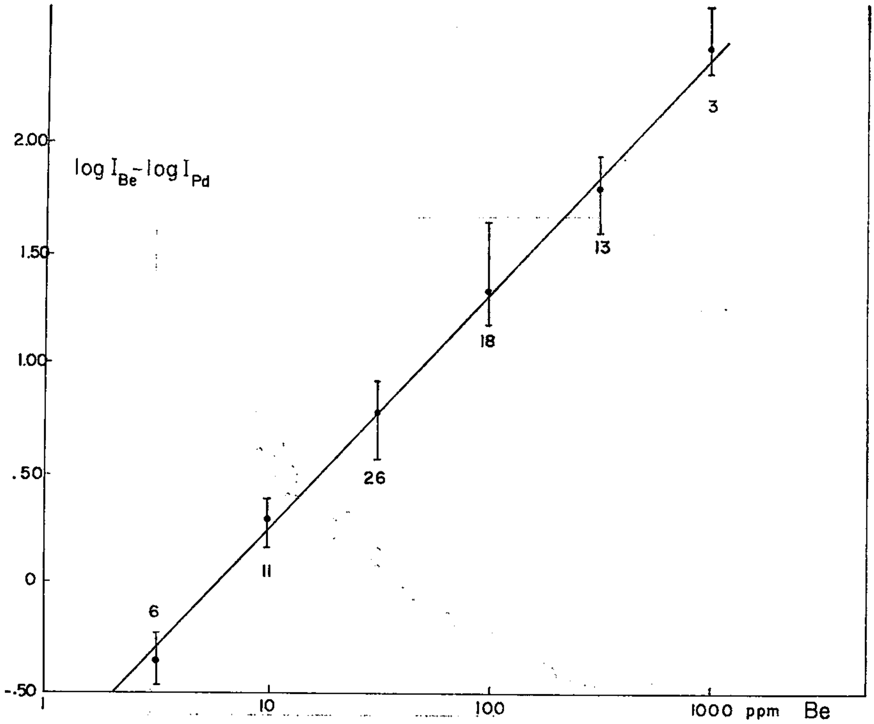

FIG. 5. Working curve showing the relation between log concentration and log I (Be 3131) minus log I (Pd 2476) for 77 artificial standards. The mean, range and number of points is shown for each concentration. By using the emulsion response curve given in Fig. 4 the working-curve shows no self-absorption in the range 1 to 1000 ppm.

In both these methods a prime requirement is that the slit (or line image) be evenly illuminated: for stigmatic instruments this is critical and where polar effects are likely only the central portion of the slit can be used. If, however, a long slit can be evenly illuminated then by using a 7 step-sector it is possible to construct a complete calibration curve from one line in one spectrum. This procedure was used for some time in the writer's laboratory with occasional anomalous results (which appear now to have been due to irregular slit illumination or undetected polar effects) and has been discontinued.

The 2-step method is the alternative procedure and is widely recommended (Harvey, 1950; Ahrens, 1950). In the manner in which it is customarily used a series of pairs of readings are obtained from a group of lines in a spectrum which has been exposed with a step-sector or filter. The pairs of readings are then plotted against each other to define a *preliminary curve* from which the *calibration curve* is readily obtained. The advantages of this method are that (*a*) only the central portion of the slit need be used, thus minimizing polar and uneven illumination effects, (*b*) the multiplicity of points on the preliminary curve should compensate for any errors in measurement or emulsion irregularities, and (*c*) the inherent weaknesses of basing the emulsion calibration on one line only are removed.

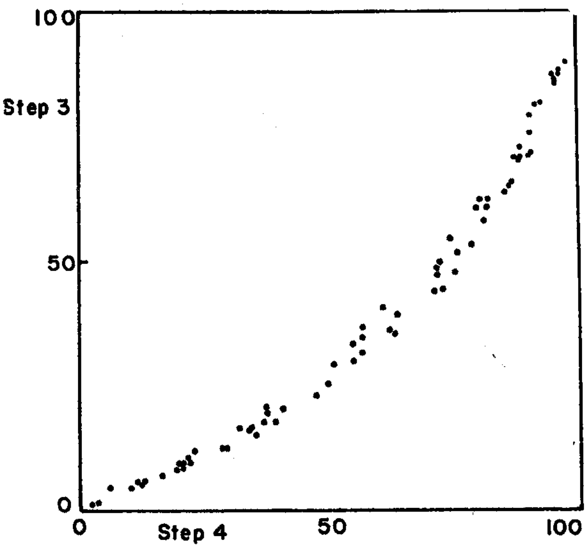

FIG. 6. Transmission values for steps 3 and 4 of numerous lines from a single Fe-arc spectrum in the region 2800–3000 Å.

The 2-step method has been used in this laboratory with (*a*) an iron arc using the electrode shape recommended by Harvey (1950, p. 70), (*b*) an iron arc obtained by arcing ferric oxide in a graphite electrode, and (*c*) using analysis lines in standards and samples for analysis. In all three cases difficulties have been encountered (by several operators over a period of years) resulting from a wide spread of points on the preliminary curve (Fig. 6): the transmission figures used were accurately reproducible and densitometer errors were negligible. It is likely that the spread of points was caused by varying degrees of self-absorption and polar effects: only lines with negligible background were used.

In the light of the previous remarks on self-absorption use of the iron arc was discontinued and it was decided to calibrate each analysis (and internal standard) line used. For this purpose many pairs of readings from different spectra on different plates taken over a period of several months were pooled on one preliminary curve for each line (they still showed considerable spread in some cases) and a series of calibration curves constructed. The subsequent success of this method (the same curves have been used for 18 months but are checked continually) bears out Harvey's remark (1950, p. 70) that ". . . a careful calibration periodically gives far more consistent results and is less time consuming than a hurried calibration of each film or plate." Processing is carefully controlled and is summarized later, and does not appear to have caused any of the difficulties referred to above. However, on most plates the clear plate reading (transmission 100%) varies across the plate and must be adjusted before every reading, in the vicinity of the spectrum.

INTERNAL STANDARDS AND THE USE OF THE STALLWOOD JET

The work reported in this paper emerged from the development of a method suitable for the determination of minor and some major elements in a wide variety of silicate materials in a single procedure. For this aim it was evident that some precision and sensitivity would have to be sacrificed and the choice of matrix and internal standard would be critical if one method were to be used for some 20 elements.

Several matrix substances were tested and particular attention was given to $SrCO_3$ and graphite. Owing to the polar effects and a loss of sensitivity encountered with $SrCO_2$ its use was discontinued but graphite appeared suitable. Using a 1:1 mixture of sample to graphite the sensitivity for most of the metals required is about 10 ppm and for a few (Be and Ag in particular) is less than 1 ppm, using lines in the region 2200 to 4800 Å. The admixture of an equal weight of graphite minimizes systematic errors due to varying sample composition. However CN band emission is intense, since the air-jet largely prevents selective volatilization, and a number of lines (e.g. Pb 4057) could not be used: this was later remedied by using an argon-oxygen mixture in place of air (Shaw, Wickremasinghe & Yip, 1958). Variation of the air-flow rate appears to have little effect on the results but was standardized at 1 litre/minute.

The use of Pd as internal standard has been recommended by Ahrens (1950, 1954). It proved satisfactory in the present method for elements as different as Ag and Zr and is of course at negligible concentrations in common silicates. Several aspects of the internal standardization procedure, however, differ from usual experience.

Certain conditions should ideally be satisfied in the choice of an internal standard: (*a*) the analysis and internal standard elements should have similar volatilization characteristics, commonly expressed by their ionization potentials, (*b*) analysis and internal standard lines should be chosen to have similar wavelengths and lie on the same plate, and should have similar excitation potentials; (*c*) the spectral lines used should not show self-absorption. In the present method these conditions were sedldom met, but the results, expressed in terms of the fit of points to working-curves and reproducibility of results, were satisfactory. With regard to condition (*a*) the ionization potential of Pd is 8.3 volts, whereas the extreme values for the elements determined are Ba, 5.19 and Be, 9.28 volts (Ahrens, 1950).

So far as the choice of Pd lines was concerned, this was again made on an empirical basis. Working-curves were constructed for each element using each of the lines Pd 3609, 3441, 3258, 3242 and 2476, and the best chosen: in every case this was either Pd 3258 or 2476. The lines used are listed in Table 2 and show that part of condition (*b*) was not satisfied: that is, all the lines on the III-F plate were successfully combined with Pd 3258 on the S.A.1 plate. Unfortunately excitation potentials for several lines were not available but the potentials listed in Table 2 indicate a considerable variation.

Condition (*c*), concerning lack of self-absorption in internal standard lines, is not applicable in view of the earlier discussion.

The foregoing paragraphs should not be taken as indicating that the customary conditions for choice of internal standard lines are invalid. With the improved excitation characteristics of the Stallwood jet, however, the choice is not as critical as with ordinary D.C. methods.

PHOTOMETRY AND CALCULATION METHODS

As a result of the relatively heavy background encountered when using the air-jet, a background correction must be applied to each line. The choice of the wavelength at which background should be measured is

TABLE 2. WAVELENGTHS AND OTHER DATA FOR SPECTRAL LINES USED

Spectral Line			Ionization potential of element (volts)	Excitation potential (volts)	Internal standard line used	Emulsion type
Pd	B	2476.418	8.3		—	S.A.1
Pd	A	3258.780			—	S.A.1
Ag		3280.683	7.54	3.75	A	S.A.1
B		2497.733	8.28	4.9	B	"
Ba		4554.042	5.19	2.73	A	III-F
Be		3131.072	9.28	3.94	B	S.A.1
Co		3453.505	8.5	4.00	A	"
Cr		4254.346	6.74	2.90	A	III-F
Cu		3273.962	7.68	3.77	A	S.A.1
Ga		2943.637	5.97	4.3	A	"
La		4333.734	5.59	3.02	A	III-F
Mg	A	2776.690	7.61		A	S.A.1
Mg	B	2781.417			A	"
Mn	A	2576.104	7.41	4.8	B	"
Mn	B	2801.064			A	"
Mn	C	3212.884			A	"
Mn	D	3258.413			A	"
Mo		3193.973			A	"
Ni		3414.765	7.606	3.64	A	"
Sc		4246.829	6.7	3.22	A	III-F
Sr		4607.331	5.67	2.68	A	"
Ti	A	3349.406	6.81	3.73	A	S.A.1
Ti	B	3354.635			A	"
Ti	C	3321.588			A	"
Ti	D	3346.728			A	"
V	A	3102.299	6.76		B	"
V	B	3185.396		3.94	A	"
Y	A	3216.682	6.5		A	"
Y	B	3242.280		3.99	A	"
Zr	A	3391.975	6.92	3.80	A	"
Zr	B	3388.299			A	"
Zr	C	3393.124			A	"

Different lines of one element are designated A, B, etc.

Wavelengths taken from Harrison (1939). Other data from Ahrens (1950) & Saidel, Prokofjew & Raiski (1955).

very critical for weak lines and was made on a sample of similar composition to the samples to be analyzed in which the element in question was absent.

Using an Applied Research densitometer reproducible figures were obtained for transmission readings between 90 and 1.0, estimating the first decimal for readings less than 10.0. Neither the extended range nor the refined measurements can be justified theoretically, when considered in relation to overall errors, but again the results gave some justification for the procedure, especially for weak lines where background corrections are considerable.

So far as possible lines were read on the central step to minimize polar effects (usually 3 or 4 steps were exposed), but for very strong or very weak lines the reading was taken on an adjacent step. The transmission readings were converted to arbitrary log intensity units (*Y*-values), taking zero log intensity for a line of transmission 10 (density = 1) on the 4th step, using a calculating-board of the type described by Honerjäger-Söhm & Kaiser (1944). The *Y*-values for analysis and internal standard lines were subsequently subtracted to give Δ *Y*-values which

TABLE 3. DETAILS OF THE AIR-JET METHOD USING A GRAPHITE MATRIX WITH PD AS INTERNAL STANDARD

Spectrograph	JACO 21-foot grating, Wadsworth mount, first order dispersion 5.2Å/mm.
Condensing optics	25 cm. focal length cylindrical lens (horizontal axis) at the slit; 6.7 cm. focal length cylindrical lens (vertical axis) 16.1 cm. from the slit; diaphragm with 5 mm. aperture 27.5 cm. from the slit; 10 cm. focal length spherical lens 58.1 cm. from the slit; arc located 72.5 cm. from the slit
Slit width	30 microns
Intensity control	7-step sector at the slit, log intensity ratio = 0.2; 1 mesh-screen for further reduction
Slit length	6 mm.; sector height adjusted for steps 3, 4, 5
Electrodes	National Carbon Co. graphite ("Special" grade): sample (anode), 1/8" rod, plain crater 1/16" x 3/8"; counter-electrode, 1/8" rod
Emulsions and range	Eastman Kodak Type S.A.1 plate, 2200–3550Å Eastman Kodak Type III-F plate, 3550–4900Å
Processing	3 minutes development in D19 developer at 20° C.; 15 seconds stop-bath; 20 minutes acid fix; 20 minutes wash
Voltage	220v. D.C. on open-circuit
Exposure	Completion; 80 to 90 seconds
Current	Started at 3 and raised to 6 1/2 amperes
Air-jet	1 c. litre/minute
Sample	1 part mineral to 1 part graphite powder containing 0.1% $PdCl_2$
Artificial standards	Prepared from Johnson-Matthey "Specpure" compounds; (*a*) SC series; matrix of: SiO_2, 45%: Al_2O_3, 23% : $CaCO_3$, 22%: NaCl, 9%: Fe_2O_3, 1%; to this matrix were added "Spex-mix" (Spex Industries Inc.) containing 43 metals at 1.34% concentration and Ga_2O_3, and standards were prepared by dilution to cover the range 3.16 to 10,000 ppm; some standards at higher concentrations were arced using 2 intensity-reduction screens; (*b*) SLY series; matrix of: SiO_2, 50%: Al_2O_3, 20%: $CaCO_3$, 15%: NaCl, 5%: Fe_2O_3, 5%: MgO, 5%; Sc_2O_3, Y_2O_3 and La_2O_3 were diluted with this matrix to give standards covering the range 10 to 1000 ppm; (*c*) ST series; matrix of: SiO_2, 60%: Al_2O_3, 25%: $CaCO_3$, 10%: NaCl, 5%; TiO_2, Mn_3O_4, ZrO_2, MgO and Fe_2O_3 were diluted with this matrix to give standards covering the range 0.1 to 3.16%
Photometry	ARL photodensitometer used; galvanometer readings between 1.0 and 95 were used and background corrections applied in all cases; clear-plate reading adjusted to 100 before each measurement; readings made on step 4 (steps numbered 0 to 8) where possible
Exposure sequence	At least one standard exposed on each sample plate in order to check calibration curves and minimize working-curve drift; samples analyzed in triplicate, one on each of three pairs of plates

TABLE 4. RELATIVE ERRORS FOR GRAPHITE MATRIX METHOD

Spectral line from Table 1	No. of standards	No. of sample replicates	Relative error (E) for triplicate analysis: Based on standards only	Relative error (E) for triplicate analysis: Based on standards plus sample replicates	Range
B	73	7		19.4%	3—1000 ppm
Be	77	7		14.0	<1—1000
Ga	83	8		12.4	3—1000
Cr	77	9		13.5	3—1000
Ti A	79	7		8.5	1—1000
Ti B	50	7		11.4	30—1000
Ti C	30	9		7.5	0.03—3%
Ti D	40	9		5.9	0.03—3%
Mg A	41	9		8.9	0.03—3%
Mg B	44	9		12.4	0.03—3%
V A	78	8		11.8	3—1000
V B	83	9		10.3	10—1000
Mo	83		11.6%		1—1000
Ni	79	9		8.4	1—1000
Co	80	9		9.0	1—1000
Cu	71	8		14.6	<1—1000
Zr A	81	8		13.6	10—1000
Zr B	27		7.6		0.03—1%
Zr C	30		9.7		0.03—3%
Mn A	92		Not calculated		10—1000
Mn B	90	7		11.1	3—1000
Mn C	41	9		8.5	0.03—3%
Mn D	37	9		10.0	0.03—3%
Sc	32	9		11.3	3—1000
Ag	90	7		11.6	<1—1000
Y A	36		12.7		3—1000
Y B	34		10.9		3—1000
Sr	66	9		13.2	3—1000
La	14		Not calculated		100—1000
Ba	91	9		12.6	1—1000

E calculated by the method given in Shaw & Bankier (1954). Thus s and y are the standard deviation and mean of log k and

$$E = \frac{100}{\sqrt{3}} \times \frac{\text{antilog}\,(\bar{y}+s) - \text{antilog}\,(\bar{y}-s)}{\text{antilog}\,\bar{y}}$$

were used for constructing (standards) or interpolating (unknown) on working-curves plotted against log concentration (k). The subtraction could be made on the board if desired, but by working out the Y-value for each internal standard any unusual intensity changes, which might be caused by a gross error or poor exposure, became obvious.

OTHER ASPECTS OF THE METHOD

Samples are usually mixed by hand in agate mortars. A mechanical mixer, such as the Wigle-Bug, is used in many laboratories but there is

TABLE 5. REPLICATE DETERMINATIONS ON CA-30, G1 AND W1[a]

	Replicate no.	1	2	3	4	5	6	7	8	9	Mean[b]
Scapolite CA-30	B	11	10.5	7.4	8.6	13	11.5	8.2			9.8
	Be	1.9	1.6	1.9	1.8	1.3	1.6	1.4			1.6
	Ga	16	15	11.5	10	12.5	14	15			12
	Ti-A	39	41	51	41	46	47	51			45
	Ti-B	49	51	69	72	47	46	56			55
	Mg-A	1250	1350	1050	1400	1350	1500	1250			1300
	Mg-B	1300	1300	1050	1200	1350	1500	1250			1250
	Mn-B	43	44	39	39	46	50	43			43
Granite G1	Ti-C	2000	1350	1450	1350	1600	1550	1500	1600		1500
	Ti-D	1700	1100	1200	1250	1300	1300	1350	1300		1300
	Cu	6.3	11.5	15.5	11	6.2	9.8	12	7.5		9.5
	Zr-A	155	135	150	150	105	155	160	150		145
	Mn-C	340	260	280	270	250	360	330	330		300
Diabase W1	Cr	88	78	82	98	110	84	130	130	115	100
	V-A	110	110	125	200	150	145	96	96	96	120
	Ni	55	48	56	54	60	52	56	55	53	54
	Co	35	32	37	33	38	33	39	38	36	35
	Mn-D	1000	1000	1200	1200	1300	1050	1250	1300	1250	1200
	Sc	13.5	11.5	14.5	15	15.5	16.5	21	22	20	17
	Sr	130	125	145	150	170	130	170	180	160	150
	Ba	95	84	110	130	140	155	125	125	120	120

[a] Spectral lines labelled as in Table 1.
[b] The mean value is obtained from the mean value of ΔY and is not the mean of the individual concentrations listed.

a tendency for fine powders to adhere to the walls of the plastic mixing vials and prevent thorough homogenization. Mixing can be improved to some extent by first shaking a little graphite alone to coat the vial and the mixing ball, but this is not always successful.

Working-curve drift is commonly experienced in routine laboratories where numerous samples are analyzed. For research projects, for which the present method was devised, usually a batch of thirty or forty analyses are required and two or three standards are included on each pair of plates. The results are calculated after all the exposures have been completed and the pooled standards are checked with the working-curves. No serious discrepancies have yet been encountered. Calibration curves are checked on each plate. The working-curves were all initially calculated by a linear regression method which has been described elsewhere (Shaw & Bankier, 1954).

A tabulation of the details of the method is given in Table 3 and the relative errors for triplicate analysis are given in Table 4. Some replicate analyses given in Table 5 illustrate the reproducibility in terms of analyses. Some results of numerous analyses of the well-known standard granite (G1) and diabase (W1) are compared with available estimates

TABLE 6. ANALYSIS RESULTS ON G1 AND W1 BY GRAPHITE MATRIX METHOD, USING 8 REPLICATES ON G1 AND 9 ON W1

	*G*1			*W*1		
Element	Results (ppm)	Range reported in Ahrens (1954)	Probably reliable estimate	Results (ppm)	Range reported in Ahrens (1954)	Probably reliable estimate
B	nd	nd		tr <10	nd–10	
Be	tr <1.4	nd– <15		nd	nd– <15	
Ga	16	15–20	20 (see below)	8	11–20	15 (see below)
Cr	tr <20	8–30		100	100–150	
Ti C	1500			5200		
Ti D	1300			5000		
Ti *	1450			5100		
TiO_2*	2420		2500 Fairbairn (1953)	8520		11000 Fairbairn (1953)
Mg A	2100			—		
Mg B	2100			—		
Mg *	2100					
MgO*	3500		3900 Fairbairn (1953)	—		66300 Fairbairn (1953)
V A	11.5			120		
V B	14			230		
V *	11.5	8–26		120	170–340	
Mo	tr <14	<4–14		nd	nd–5	
Ni	tr <3	nd–60		54	47–150	
Co	nd	nd–10		35	20–50	
Cu	9.5	5–20	9.5 (see below)	>47	44–140	112 (see below)
Zr	145	130–280	162 Degenhardt (1957)	86	50–150	85 Degenhardt (1957)
Mn B	200			—		
Mn C	300			780		
Mn D	nd			1200		
Mn *	250			990		
MnO*	320		270 Fairbairn (1953)	1280		1700 Fairbairn (1953)
Sc	<1	nd–4		17	15–51	
Sr	250	120–900	233 Herzog & Pinson (1955)	150	120–450	177 Herzog & Pinson (1955)
Ba	—	1100–3000		120	150–390	

1. * denotes recommended value: for some elements this is also given for the oxide.
2. Following elements sought but not detectable (sensitivity in ppm in parentheses): Ag(1), La(100), Li(100), Sn(10), Y(30). The Y lines were subject to interference by Fe and Ti.
3. "nd" below sensitivity and "–" higher than range of method.
4. Estimates of Ga, Cu in G1 and W1 chosen from a compilation of published and unpublished analyses made by M. Fleischer (personal communication).
5. V B is subject to interference from an unlisted Ca line (Shaw. 1958).

by other workers in Table 6. The comparisons show few serious discrepancies and the figures for V have been discussed elsewhere (Shaw, 1958).

Finally, a word should be said regarding a problem encountered by many analysts but especially common among spectrographers, that is the difficulty of adapting a published method to one's own laboratory. In the ideal case it should be possible to adapt a method which has been adequately described to comparable instruments available in any other laboratory. Unfortunately, this is seldom possible without exhaustive testing, which generally leads to extensive modification of the method. The fact of the matter is that instruments are not generally comparable and the procedure satisfactory with one spectrograph may not be suitable with another. Moreover each laboratory has preferred details of technique and procedure which are often believed to be too insignificant for publication, but which may be essential steps in a successful method.

The response of a photographic emulsion to light is a recurring problem with many aspects and the events which occur between arcing the sample and fixing the plate or film control the success or failure of the spectrograph as an analytical instrument.

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