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SLOPES OF WORKING CURVES IN EMISSION
SPECTROMETRIC ANALYSIS OF CERTAIN
SILICATES

by

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Slopes of Working Curves in Emission Spectrometric Analysis of Certain Silicates†

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Abstracts

In the emission spectrometric analysis of silicates, Strock recently reported large deviations from unity of the working curve slopes. He suggested that these abnormal slopes resulted from collisions of the second kind occurring in the direct-current arc discharge. These experiments were repeated, and data were treated statistically. Deviations from a slope of unity in nearly every case were satisfactorily explained by the experimental errors inherent in the method or by self-absorption.

Introduction

Recently, Strock (1,2) investigated the emission spectra of three sets of silicates that were intermediate compositions of pseudo-Wollastonite ($\text{CaO}\cdot\text{SiO}_2$), Diopside ($\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$), and Anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$). He observed that the slopes of working curves plotted on a logarithmic basis deviate radically from unity and suggested that these deviations were evidence of collisions of the second kind occurring in a direct-current arc discharge.

When the working curve is plotted so that the logarithm of the intensity ratio is the ordinate, low slopes may be observed if (a) the analytical-spectral-line-to-background intensity ratio is low, (b) unknown contamination of the sample occurs which introduces significant quantities of the elements whose concentrations are desired, (c) an unresolved interfering spectral line of another element is present or (d) the analytical spectral lines is self-absorbed. The same factors affecting the internal standard spectral line may produce a high slope if the concentration of the internal standard element is not constant or nearly so. Gillis and Eeckhout (3) have shown that high or low slopes may be observed in an addition method where the combined form of the added element is different than the form naturally present in the sample. In this situation, changes in slope are attributed to the volatilisation characteristics of the samples and added materials rather than to any collision processes in the discharge. However, none of these factors except self-absorption of the analytical spectral lines are expected to be important in this particular problem.

The most reliable work on collisions of the second kind has been done under carefully controlled conditions in discharge tubes at low pressures. (4,5). However, similar experiments have been performed by Baker, Adelstein and Vallee (6) and Stuart (7) at or near atmospheric pressures which have demonstrated the effects of this type of collision on spectral line intensities. A collision of the second kind may happen if the energy to be given up by one atom or ion is equal or nearly equal to the energy required to raise the second atom or ion from one energy level to another. The probability of this occurrence is greatly increased if the life-times of the atoms in the energy levels before the collision are long, i.e., the energy levels are the ground state or metastable. These conditions are most easily satisfied if one of the species has a high first excitation potential. To observe a change in slope of the working curve, both species must undergo a change in concentration from sample to sample in some regular fashion. If the concentration of one element is constant, the working curve for the other element will be shifted by a constant amount without a change in slope. If the concentrations of both elements do not change in a regular manner, an abnormally greater scatter in experimental points from which the working curve is drawn will be observed. In the silicates studied by Strock, calcium, silicon, magnesium, and aluminum vary in a regular manner with one another. In fact, the concentrations of each may be expressed as a straight line relationship with the concentrations of the other elements. However, there are no metastable states (8) in the atomic structures of the four species of atoms or the corresponding ions that could be involved in a collision of the second kind to affect the slopes of the working curves considered by Strock. It therefore appears highly unlikely that his observations can be explained by this process.

Addink (9) has commented on Strock's investigation, indicating that the low slopes are caused by self-absorption and the high slopes are caused by the regular variation in sample composition resulting in a corresponding change in arc temperature. These possible explanations are supported partially by Strock's observations, but there are a number of results which cannot be explained in this way. For example, no variation in arc temperature would be expected because the sample, which contains no elements of very low ionisation potential, is mixed with germanium metal in the ratio of 1:9. The effect of variation in sample composition would be negligible. Secondly, self-absorption does not

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explain the observed very low slope of the Mg II 2798.06 working curve in the pseudo-Wollastonite: Diopside system because the lower energy level of the transition which gives rise to this spectral line is 4.41 electron volts above the ground state and is not metastable.

In view of the above comments and since large deviations of working curve slopes from unity are rare, it was desirable to repeat Strock's experiments on the same system of silicates.

Materials and Experimental Work

The standards were prepared by fusing appropriate mixtures of pure silica, lime, alumina and magnesia and grinding the resultant product to 200 mesh. Since it was the experience of the laboratory that negligible losses of these refractory compounds occurred in the fusion process, no chemical analyses were made. The compositions of the standards are given in Table I. Standards No. 10, 20 and 30 correspond to the compositions of Diopside, Anorthite and pseudo-Wollastonite respectively. Hence the groups of standards corresponding to intermediate compositions of pseudo-Wollastonite: Diopside, Diopside: Anorthite and Anorthite: pseudo-Wollastonite are 30, 1-10; 10-20; and 20-30 respectively.

TABLE I. COMPOSITION OF THE STANDARDS

Standard No.	MgO per cent/wt.	CaO per cent/wt.	Al ₂ O ₃ per cent/wt.	SiO ₂ per cent/wt.
1	1.00	47.07		51.93
2	1.38	46.61		52.01
3	1.91	45.97		52.12
4	2.66	45.07		52.27
5	3.68	43.85		52.47
6	5.09	42.15		52.76
7	7.03	39.83		53.14
8	9.70	36.62		53.68
9	13.40	32.18		54.42
10	18.62	25.90		55.48
11	18.11	25.74	1.00	55.14
12	17.53	25.56	2.14	54.76
13	16.34	25.19	4.50	53.97
14	13.69	24.38	9.70	52.22
15	8.15	22.67	20.61	48.57
16	4.82	21.65	27.17	46.37
17	2.86	21.04	31.02	45.07
18	1.70	20.69	33.30	44.51
19	1.00	20.47	34.68	43.85
20		20.16	36.65	43.19
21		29.64	24.30	46.06
22		35.78	16.30	47.92
23		39.84	11.00	49.15
24		42.65	7.35	50.00
25		44.50	4.93	50.56
26		45.75	3.31	50.94
27		46.58	2.22	51.20
28		47.14	1.49	51.37
29		47.52	1.00	51.48
30		48.29		51.71

The germanium metal had been obtained from Dr. Strock's laboratory at Saratoga several years ago in connection with the development of a general semi-quantitative method for the analysis of rocks and minerals at the Mines Branch. This work culminated in the Stallwood air-jet procedure (10). The average particle size was found to be approximately 150 mesh by passing the material through a set of sieves. Qualitative spectrometric analysis revealed that the germanium contained silicon, aluminum, and magnesium. To determine if the concentrations of these elements were sufficiently high to constitute a serious blank correction in the subsequent work, a sample of the germanium was chemically analysed. This material was found

TABLE II. SPECTROSCOPIC CONDITIONS

Spectrograph	—Hilger large quartz and glass
Wavelength Region	—2450 - 3500 Å
Slit Width	—0.015 mm
Analytical Gap to Slit Distance	—38 cm
Quartz Condensing Lens to Slit Distance	—2 cm to form an image of the discharge on the collimating lens
Spark Gap	—5 mm
Source Conditions	—6 amp, 300 volts, direct-current arc obtained from an Applied Research Laboratories, Inc., Multisource unit
Upper Electrode, Negative	—high purity graphite rod, 2 inches long and 3/16 inches diameter, shaped to a 28 degree cone with a hemispherical tip of 1/32 inches radius of curvature
Lower Electrode, Positive	—high purity graphite rod, 2 inches long and 3/16 diameter, with a hole 4 mm deep and 7/64 inches diameter drilled into one end
Exposure Time	—4 min. which was the time to ensure burning to completion
Emulsion	—Kodak Spectrum Analysis No. 1
Photographic Processing	—(1) 3 min at 68°F in D-19 developer (2) 30 sec in SB-5 stop bath (3) 5 min. in F-5 fixer (4) washed in running water for 30 min (5) excess water removed with a cellulose sponge and dried in an Applied Research Laboratories, Inc. plate drier
Microphotometer	—Hilger non-recording.

to contain 0.02 per cent silicon and less than 0.01 per cent each of aluminum and magnesium. These concentrations would have negligible effect on the slopes of the silicon working curves and might decrease the slopes of the working curves for aluminum and magnesium by not more than five per cent. Since it was expected that far greater deviations in slope might be observed, no correction for the aluminum, magnesium, and silicon content in the germanium metal was made. The graphite powder used in this investigation was high purity material with a particle size of 200 mesh.

Each standard, the germanium metal and the graphite powder, were weighed and mixed in the proportion of 1:9:20 using a Sauter Ultra-matic semi-microbalance and a Wig-L-Bug electric mixer. During these operations and for subsequent storage, the materials were placed in a polystyrene vial, one inch by one half inch in diameter, with a polyethylene cap. A polymethylmethacrylate ball pestle was also placed in the vial to promote mixing. A weight of 18 mg of each mixed standard was placed in the electrode crater (Table II) and a drop of collodion placed on the top of each electrode to prevent the sample charge from being ejected from the electrode at the beginning of the discharge. The loading of each electrode was facilitated through the use of an electrode vibrator similar in design to that described by White and Champ (11).

Table II summarizes the spectroscopic conditions. The spectrum of each standard was recorded in triplicate. Emulsion calibration was performed by means of an eight-step rotating sector that had a step intensity ratio of 1.585:1. The spectral lines used for preparing working curves and emulsion calibration curves are listed in Table III.

Results and Discussion

The spectral line pairs and the slopes of the working curves are listed in Table IV. The slopes were calculated by the method of least squares. The data also provided the standard deviations in these estimates of the slopes. The 't' test revealed that the slopes of all of the magnesium and

TABLE III. SPECTRAL LINES AND ENERGY LEVELS

Analytical Spectral Line ^{1,2}	Energy Levels ⁸		Internal Standard Spectral Line ^{1,2}	Energy Levels ⁸		Emulsion Calibration Spectral Line ^{1,2}
	Upper	Lower		Upper	Lower	
	eV	eV		eV	eV	
Ca I 3006.858	1.89	6.00	Ge I 3067.007	2.02	6.04	Ge I 3067.007
Ca II 3181.275	3.14	7.02	Ge I 3067.007	2.02	6.04	Ge I 3067.007
Ca II 3179.332	3.14	7.02	Ge I 3067.007	2.02	6.04	Ge I 3067.007
Al I 3082.155	0.00	4.00	Ge I 3067.007	2.02	6.04	Ge I 3067.007
Al I 2575.100	0.01	4.81	Ge I 2533.229	0.07	4.94	Si I 2631.310
Mg I 2852.129	0.00	4.33	Ge I 2793.938	2.02	6.44	Ge I 2829.011
Mg II 2798.06	4.41	8.83	Ge I 2793.938	2.02	6.44	Ge I 2829.011
Mg II 2795.53	0.00	4.41	Ge I 2793.938	2.02	6.44	Ge I 2829.011
Mg I 2779.834	2.70	7.14	Ge I 2793.938	2.02	6.44	Ge I 2829.011
Mg I 2776.690	2.70	7.14	Ge I 2793.938	2.02	6.44	Ge I 2829.011
Si I 2987.648	0.78	4.91	Ge I 3067.007	2.02	6.04	Ge I 3067.007
Si I 2881.578	0.78	5.06	Ge I 2793.938	2.02	6.44	Ge I 2829.011
Si I 2631.310	1.90	6.59	Ge I 2533.229	0.07	4.94	Si I 2631.310
Si I 2528.516	0.03	4.91	Ge I 2533.229	0.07	4.94	Si I 2631.310
Si I 2514.331	0.00	4.91	Ge I 2533.229	0.07	4.94	Si I 2631.310

aluminum working curves differed significantly from unity. It should be noted that all of these slopes are less than unity. In spite of the wide range in slopes for silicon and calcium, the experimental errors account for these differences from unity. It may be argued that the silicon working curves in the pseudo-Wollastonite: Diopside system should have no correlation with silicon content since the atomic percentage of silicon in this system is fixed at 20 per cent. However, in the internal standard method, the spectral line intensity ratio is related to the atomic per cent ratio of silicon to germanium (13). But the atomic per cent ratio is proportional to the per cent by weight ratio (14), and since the germanium content on a weight basis is fixed in this investigation, the silicon working curves must have the expected correlation with silicon content. However, since the range of silicon is very low in these systems and the errors are particularly large for silicon, it is not surprising that large deviations in slope are observed.

Magnesium and aluminum working curves exhibit low slopes in every case. Those spectral lines that are emitted during transitions that end on the ground state or a metastable state of the atom or ion (Table III) can be self-absorbed and therefore produce working curves that have the lowest slopes. The working curves for Mg II 2798.06, contrary to Strock's observations, had the highest slopes, but still were significantly less than unity. The lower level of the transition that gives rise to this spectral line is

the upper level of the transition that causes the emission of Mg II 2795.53. Therefore, self-absorption is not possible in this case. Also, there are no other atoms or ions that have metastable states with the correct energy to indicate the likelihood of collisions of the second kind. Therefore, some other phenomenon such as different rates of vaporization from sample to sample because of the broad composition change may explain this low slope. It was noted during the preliminary work that the time to burn to completion consistently varied with the sample from 3.5 to 4 minutes. Mg I 2779.834 and Mg I 2776.690 each arise from two variations which have lower energy levels $3p^3P^{\circ}_2$ and $3p^3P^{\circ}_1$; and $3p^3P^{\circ}_1$ and $3p^3P^{\circ}_0$ respectively. $3p^3P^{\circ}_1$ is the upper energy level for the transition which gives rise to the weak spectral line Mg I 4571.1. The other two energy levels are metastable. Hence, there is a strong possibility that Mg I 2779.834 and Mg I 2776.690 will be self-absorbed. Oxygen has a metastable state, $2p^4\ ^1S_0$, 4.17 electron volts above the ground state of the neutral atom. Oxygen atoms in this state could take part in a collision of the second kind with aluminum atoms in the ground state. However, the oxygen content in the discharge column is essentially constant regardless of the sample used in these experiments, and referring to the discussion in the Introduction, no change in slope should be observed. For slopes less than unity, self-absorption adequately accounts for the observations recorded here.

TABLE IV. SLOPES OF THE WORKING CURVES

Spectral Line Pair A	Pseudo-Wollastonite: Diopside		Diopside: Anorthite		Anorthite: Pseudo-Wollastonite	
	Slope	Standard Deviation	Slope	Standard Deviation	Slope	Standard Deviation
		of the Slope		of the Slope		of the Slope
Ca I 3006.858/Ge I 3067.007	1.18	0.32	1.42	0.35	1.20	0.23
Ca II 3181.275/Ge I 3067.007	1.14	0.27	1.52	0.42	1.31	0.28
Ca II 3179.332/Ge I 3067.007	0.98	0.23	1.56	0.41	1.13	0.32
Al I 3082.155/Ge I 3067.007	—	—	0.65 ^a	0.034	0.58 ^a	0.027
Al I 2575.100/Ge I 2533.229	—	—	0.75 ^a	0.043	0.63 ^a	0.085
Mg I 2852.129/Ge I 2793.938	0.039 ^a	0.064	0.081 ^a	0.052	—	—
Mg II 2798.06 /Ge I 2793.938	0.75 ^a	0.058	0.86 ^a	0.045	—	—
Mg II 2795.53 /Ge I 2793.938	0.30 ^a	0.048	0.29 ^a	0.029	—	—
Mg I 2779.834/Ge I 2793.938	0.70 ^a	0.063	0.72 ^a	0.040	—	—
Mg I 2776.690/Ge I 2793.938	0.62 ^a	0.059	0.79 ^a	0.063	—	—
Si I 2987.648/Ge I 3067.007	0.89	0.88	1.62	0.36	2.13	1.06
Si I 2881.578/Ge I 2793.938	0.57	2.41	1.28	0.31	1.18	1.49
Si I 2631.310/Ge I 2533.229	0.057	2.63	1.17	2.12	2.04	1.21
Si I 2528.516/Ge I 2533.229	1.03	1.88	0.88	0.17	1.58	0.68
Si I 2514.331/Ge I 2533.229	-0.69	2.06	0.91	0.27	1.71	0.82

^aSlope is significantly different from unity using the 't' test at a 5 per cent probability level.

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