THE INFLUENCE OF EXTRANEOUS ELEMENTS ON
LINE INTENSITIES IN THE A.C. SPARK AND THE D.C. ARC

by

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INTRODUCTION

During the past few years considerable attention has been directed toward the influence of extraneous elements on line intensities in spectrochemical work. This constitutes a major problem in trace mineral investigations, since these influences are more pronounced if the elements under consideration are in low concentrations. These influences have been investigated by numerous scientists (4,6,7,8,9,14,15,17).

In this research the influence of calcium upon the intensity of magnesium both in the a.c. spark and the d.c. arc was investigated. The procedure was then reversed to study the influence of magnesium upon calcium in the two sources. These two elements are present as minerals in plants, so it was thought advisable to use concentrations approximating those present in the common forage plants. It is well known that the effect of extraneous elements can be decreased or eliminated through the use of spectrographic buffers. Therefore, the same procedures were repeated except that a buffer was added to the samples being investigated.

The investigators listed above have studied many sequences of elements under varying conditions. Some of the elements which have been studied are: Na, V, Pb, Sn, Mn, Fe, Al, Bi, Ca, Cu, Zn, Ti, P, K, Li, Cd, Rb, Si, Cr, Ni, Zr, La, Ag, Mo, Ga, C, and B. However, there has been little work done on correlating the effects of different excitation sources on the influences of

extraneous elements. The results obtained by these workers have
not always been in close agreement. The combination of elements
investigated in this research has not been reported by other
workers. If the effect of one element upon another can be deter-
mined and nullified, it would lead to higher accuracy in trace
mineral analyses by spectrochemical means.

SURVEY OF LITERATURE

Brode and Silverthorn (8) through their study on the effects
of impurities on line intensities of Cd and Zn in quantitative
spectrochemical analysis have shown the following results. Cop-
per and bismuth had an appreciable effect on the relative inten-
sities of the cadmium and zinc lines. The effects were in oppo-
site directions for in the presence of copper, the intensity of
the zinc lines was reduced as compared to cadmium, and bismuth
reduced the intensity of the cadmium line compared with zinc
lines.

The intensities of spectral lines of vanadium have been in-
creased through the addition of sodium chloride (4). This en-
hancement was noticeable for lines of both the neutral and ion-
ized atom. However, potassium chloride intensified the lines
of the neutral atom and decreased the intensity of the lines of
the ionized atom.

Wada (16) investigated the reciprocal effects of the alkali
metals on their detection in the electric arc. The following

conclusions were drawn from his study: (a) the presence of po-
tassium increased the sensitivity of the sodium test; (b) the
test for potassium was not affected by the presence of sodium
and lithium, but it increased the sensitivity of tests for all
other alkalies. The results of his work were illustrated by
plotted curves.

Waldbauer and Means (17) have shown that the intensity of
the spectral lines of calcium increased with an increase in the
percentage of the alkali metal present. However, at higher con-
centrations the line enhancement tended to be decreased.

Brode and Hodge (7), and Brode and Bournique (6) investi-
gated the influence of extraneous anions on line intensities.
They concluded that in a given series of compounds of different
anions but with common cations, the line intensity of the cation
is greatest for those compounds having the lower boiling point.

Duffendack, Wiley, and Owens (10) concluded that the in-
fluence of the extraneous element on the ratios of the inten-
sity of the element under investigation to the internal standard
reached a maximum value. This maximum influence was attained
through the addition of a large amount of the extraneous element
to the standard solutions and unknowns.

It has been indicated, through the work of Brode and Timma
(9), that the effect of the extraneous element varies with the
amount of the extraneous element, but not in a simple linear
fashion. They were able to arrange a sequence of elements

based on their boiling points and excitation potentials in which
the intensities of the elements above a given one were enhanced
and those below were decreased. This sequence agreed closely
with a mathematical expression which included the boiling point
and excitation potential of the element. However, if such an
arrangement of elements were studied, it would require a strict
reproducibility of the excitation sources used in their work.

Marked variations have been observed in the relative inten-
sities of magnesium, cadmium, and lead lines when amounts of
foreign substances were added to standard samples and excited
in a condensed spark source (13). The changes in the inter-
spectra intensity ratios depended on the nature and amount of
the added substances, as well as, on the elements under con-
sideration.

Langstroth and McRae (12) stated in their work that unless
appropriate precautions were taken, the intensity ratios and
therefore the determined concentrations, varied with variations
in the extraneous composition of the samples, even though the
amounts of the internal standard and the investigated element
present remained constant. The authors indicated the necessity
for the use of a spectroscopic buffer and provided certain
criteria for the choice of the buffer and internal standard
elements.

The effect of changing the conditions of the excitation
source upon the influence of extraneous materials in spectro-
chemical analysis has been studied by Andrychuck and

McMullen (2). They reported that the extraneous material affected the mechanism of volatilization more than the mechanism of excitation. Operating the excitation source at a temperature above the boiling points of the constituents of the sample and at high excitation energies as obtained from a low inductance spark source reduced the influence of extraneous materials.

Schrenk and Clements (15) have shown that potassium and calcium decreased the line intensity of phosphorus. Also, when cobalt was used as an internal standard, increasing amounts of calcium tended to enhance the cobalt line. It was noted that phosphorus increased the intensity of the cobalt line. Through the use of a lithium tartrate buffer, they were able to minimize these extraneous element effects.

EXPERIMENTAL PROCEDURE

Instruments Used

A Bausch and Lomb, large, Littrow spectrograph was used throughout this investigation. The instrument is provided with interchangeable quartz and glass optical systems, and in this research the quartz system was used. The quartz prism has a height of 57 mm and a refracting face of 95 mm, which utilizes the full aperature of the lens. The lens is 70 mm in diameter and has a focal length of 1827 mm.

Two positions were used in this investigation, position

five which covers the range of 2600 to 3350 Å, and position
three which covers the range of 2900 to 4800 Å. These differ-
ent positions are obtained by rotation of the prism, movement
of the prism and lens to a new focus, and a change in the tilt
of the photographic plate. The first two adjustments are co-
ordinated by means of a cam, which causes the prism to rotate
as it is moved forward or backward during focusing. The plate
tilt is adjusted directly through a screw and recording scale.
The dispersion of the instrument is 3.15 Å per mm at 2780 Å
and 5.15 Å per mm at 3160 Å. The light from the source was
focused with a condensing lens upon a cylindrical lens which
then focused it upon the slit. A rotating adjustable sector
on a motor mount was secured just ahead of the cylindrical lens.
This sector was used to adjust exposure conditions for the dif-
ferent sources. It was also possible, through the use of this
sector, to expose for sufficient time to make certain that all
the sample was volatilized.

Two energy sources were used in conducting this research.
The first source employed was a Bausch and Lomb condensed spark
unit which had a fixed capacitance of 0.005 micro-farads and six
stops for selection of inductance in the circuit. The inductance
could be varied from zero to 20.56 micro-henrys. A transformer
with a 0.45 KVA output furnished a secondary voltage of 15,000
volts a.c. from a primary voltage of 115 volts. The second source
of excitation was a direct current generator maintained at a po-
tential of 125 volts and a current of eight to ten amperes.

The following conditions were maintained constant: slit width, 60 microns; slit height, 1.0 mm; electrode separation, 2.5 mm; and exposure time, 60 seconds. When the a.c. spark excitation source was used the rotating sector was set at three-fourths, and when the direct current source was used the sector was set at one-eighth.

Kodak Number 33 photographic plates were found to give good results for the magnesium and calcium under investigation. All plates were developed four minutes at 20° C. in Kodak X-ray developer diluted with two parts of water. The plates were then placed in a fixing bath for ten minutes after which they were washed for thirty minutes in running water, and dried for eight minutes on a warm air drier. The transmittancies of the lines were measured with a projection type Allied Research Laboratories - Dietert densitometer. It was possible to obtain check readings of the transmittancies within a fraction of one percent.

Choice of the Calcium and Magnesium Lines

Calcium exhibits numerous spectral lines which may be adaptable to spectrochemical use. The line chosen for this research was the one having a wavelength of 3158.9 Å. According to Brode's Tables (5) this is a first ionization state line, having a spark intensity of 300 and an arc intensity of 100. The line is also relatively free of interference lines from other elements. Ahrens (1) states that the detection limit for calcium is

approximately 0.00005 percent. In using solutions compounded
from analytical grade reagents, interfering elements were not
a factor in the selection of the spectral line.

The element magnesium is extremely sensitive for spectro-
graphic analyses. Using the most sensitive line of magnesium
(2852.1 Å), concentrations as low as 0.0001 percent are usually
detectable (1). The line utilized in the magnesium investiga-
tion was the one having a wave length of 2779.8 Å. Brode (5)
lists this line as having a spark intensity of 50, an arc in-
tensity of 40, and arising from a first ionization state. There
are no interfering lines listed in Brode's Tables for this wave
length.

Preparation of Samples

Analytical grade calcium carbonate was dissolved in a small
portion of dilute hydrochloric acid and made up to volume with
distilled water, so that the concentration of calcium was 2000
ppm. For magnesium analyses, stock solutions containing 2000 ppm
of magnesium were made from analytical grade magnesium nitrate
hexahydrate dissolved in water and made to volume. Table 1 shows
the composition of the solutions used for the analyses.

For the buffered solutions, two ml of a lithium tartrate
solution containing 81,000 ppm of lithium tartrate were added
to each of the solutions mentioned in Table 1. The concentra-
tion of the buffer in the sample was then approximately 3860 ppm.

Table 1. Formulation of samples for analysis from stock
          solutions.

Solution number	ml stock Ca solution	ml stock Mg solution	ml H$_2$O	ppm Ca	ppm Mg
1	5	0	35	250	0
2	5	2	33	250	100
3	5	4	31	250	200
4	5	10	25	250	500
5	5	20	15	250	1000
1	0	5	35	0	250
2	2	5	33	100	250
3	4	5	31	200	250
4	10	5	25	500	250
5	20	5	15	1000	250

Preparation of Electrodes

Porous cup type electrodes are required when the a.c.
spark excitation source is used. This type electrode was pre-
pared from the standard 5/16 inch diameter carbons supplied by
the National Carbon Company. The 5/16 inch diameter rods were
cut into 1¼ inch lengths. These cut rods were then placed in a
jig similar to the one described by Feldman (11) and drilled with
a 5/32 inch drill through the center, along the axis, to within
approximately 0.5 mm of the bottom. This gave a uniform thick-
ness to the porous cup electrodes and the sample feed rate ap-
peared to be constant throughout. The porous cup electrode
served as the upper electrode and a 3/16 inch diameter carbon
rob served as the counter electrode. Figure 1 shows a cross
section of the porous cup electrode and also the counter elec-
trode space indicated.

In utilizing the d.c. arc source, cupped type electrodes
were used. The 5/16 inch diameter rods were cut into 1¼ inch
lengths. The ends of the anode were crater shaped 1.5 mm deep.
The cathodes, of the same diameter, were bullet shaped. On the
end of the blunt nose of the cathode there was a cylindrically
shaped projection 1 mm in diameter and 6 mm long. This projec-
tion tended to prevent wandering of the arc and also allowed a
60 second exposure without the electrode being consumed. The
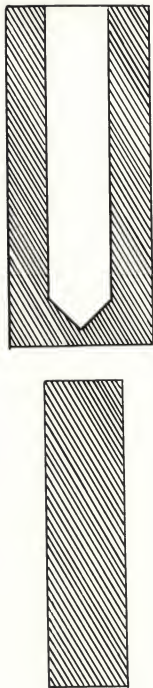anode craters were filled with a saturated solution of carnauba

Fig. 1. The Porous Cup Electrode; with
the Counter Electrode

wax in carbon tetrachloride and dried for 45 minutes at 100° C.
in an oven. Figure 2 shows the electrodes used in the d.c. arc.

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Introduction of Samples into the Porous
Cup Electrodes and onto the Cratered Electrodes

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The porous cup electrodes were pre-sparked for 120 seconds
when being used with an unbuffered solution. When calcium was
being investigated, a 60 second pre-spark period was recorded on
the photographic plate, and the intensity of the calcium line
from the electrode was utilized as a correction factor for the
calcium line of the sample. Pre-sparking was required for the
solution to pass through the electrode uniformly. The solution
samples were placed in the porous cup electrodes by means of a
long, slender nosed dropper inserted to the bottom. The dropper
was slowly removed as the electrode filled. This procedure of
filling was necessary in order to prevent air from being trapped
in the bottom of the electrode. After each sample was sparked,
the dropper was rinsed at least five times with distilled water
and twice with the next sample before loading another electrode.
When working with a buffered solution in the a.c. spark, the solu-
tion would not pass through the electrode if it had been pre-
sparked as indicated. However, the solution would pass through
if the electrode had been pre-arced for twenty-five seconds. When
calcium was under consideration, two pre-arced electrodes were
sparked for sixty seconds on each plate to determine the calcium
correction factor for the electrodes.
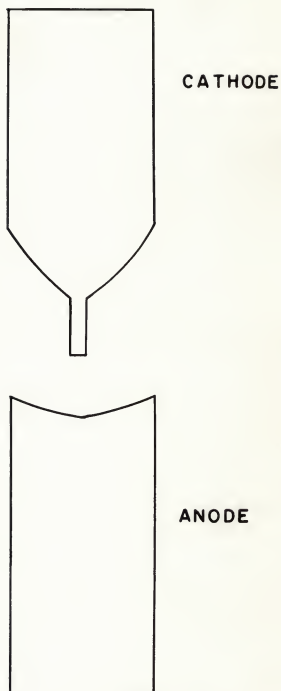
CATHODE

ANODE

Fig. 2. Cupped and Bullet Shaped Electrodes
used in the D. C. Arc

In the d.c. arc source, the cratered electrodes were used. A 0.1 ml volume of the sample was placed in the crater by means of an Applied Research Laboratories semi-automatic pipette. Each sample was run in triplicate. After the craters were filled, the electrodes were placed in an air oven at 80° C. for one hour and then the temperature was increased to 100° C. for at least five hours. This period of time insured complete drying of the samples on the electrodes. Each electrode was removed from the oven just before being arced, and in this manner there was little possibility of picking up moisture from the air. The solutions which were buffered with lithium tartrate did not form a smooth crust as did the unbuffered solutions. Instead they tended to form a small round ball of residue.

EXPERIMENTAL RESULTS

Effect of Magnesium Upon Intensity of Calcium in the A.C. Spark

The first series of determinations were made to determine the effect of magnesium upon the intensity of calcium in the a.c. spark using unbuffered solutions. The porous cup electrodes were pre-sparked and filled as previously described. The electrodes were then placed in the holders and the electrode spacing adjusted to 2.5 mm with a stainless steel leaf spacer (14). This spacer was mounted on an adjustable shaft so that it could be

moved into place for electrode alignment and then moved back for
sparking. The samples were run in duplicate and exposed for
sixty seconds. Five plates were exposed giving a total of ten
determinations for each sample. After processing the plate,
transmittancies were read on the ARL densitometer and the optical
density of the calcium line calculated, corrected for calcium in
the electrode, and converted to a 0.5 density basis. This cor-
rection and conversion was carried out as follows: The optical
density of the calcium line in the blank electrode was subtract-
ed from the optical density of the calcium line in the sample.
The optical density of the calcium line with no magnesium present
was set equal to 0.5, then the optical density of the calcium
line when magnesium was present was calculated by means of the
ratio, $\frac{\text{O.D. of Ca line} + \text{Mg}}{\text{O.D. pure Ca line}} = \frac{X}{0.5}$ where X is the optical den-
sity of the calcium line containing magnesium converted to the
0.5 basis. It is probable that the most erratic results, which
in some cases were eliminated, were due to variations in feed
rate caused by unequal electrode thickness. These results are
shown in Table 2 and Fig. 3.

Effect of Calcium Upon Intensity of Magnesium in the A.C. Spark

The next series of runs were made to determine the effect
of calcium upon the intensity of the magnesium line in the a.c.
spark using unbuffered solutions. The procedure as given above

Table 2. The effect of magnesium upon the intensity of calcium (3158.9 Å) in the a.c. spark.

Solution	Optical density*					Av.	Standard deviation	Density corrected to 0.5 basis
	Plate number							
	22	23	25	26	27			
Ca 250 ppm	0.650	0.760	0.755	0.751	0.648	0.704	0.0528	0.500
	0.729	0.736	0.614	0.674	0.726			
Ca 250 ppm	0.629	0.630	0.653	0.886	0.607	0.710	0.0935	0.504
Mg 100 ppm	0.729	0.673	0.710	0.845	0.741			
Ca 250 ppm	0.686	0.608	0.678	0.593	0.723	0.684	0.0521	0.486
Mg 200 ppm	0.720	0.696	0.722	0.660	0.757			
Ca 250 ppm	0.753	0.657	0.616	0.643	0.655	0.668	0.0456	0.475
Mg 500 ppm	0.720	0.601	0.663	0.681	0.690			
Ca 250 ppm	0.736	0.632	0.626	0.587	0.658	0.630	0.0635	0.448
Mg 1000 ppm	0.668	0.488	0.649	0.641	0.612			

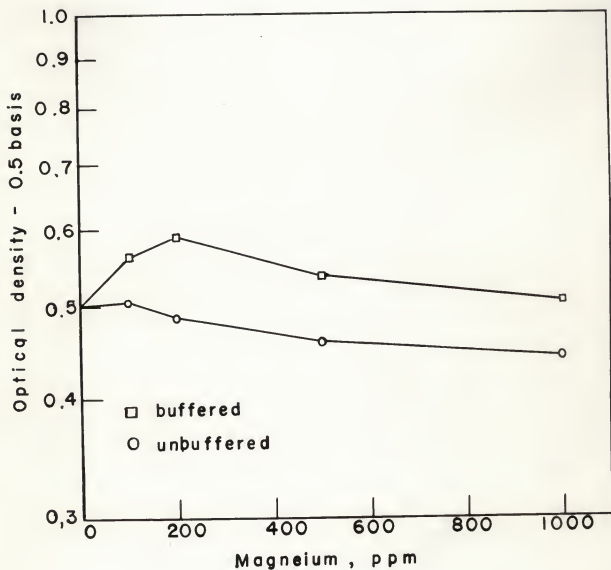*All densities have been corrected for electrode impurity.

Fig. 3. The Effect of Magnesium upon the Intensity of Calcium (3158.9 Å) in the A.C. Spark.

was followed except that no electrode correction was necessary for the magnesium lines since magnesium was not present as an impurity in the electrodes. The samples were run in triplicate and six plates were exposed giving a total of eighteen analyses on each sample. These results are shown in Table 3 and Fig. 4.

A series of samples were run using the National Carbon Company High Purity Electrodes in order to determine if the electrode impurities had any effect on the calcium and magnesium lines under consideration. The results obtained from these samples indicated that the impurities present in the standard electrodes were not affecting the intensities of the calcium and magnesium spectral lines.

Effect of Calcium Upon Intensity of Magnesium in the D.C. Arc

The effect of calcium upon the intensity of the magnesium line was next determined in the d.c. arc. For this investigation the rotating sector was changed to one-eighth in order that a sixty second exposure could be utilized. This length of exposure was necessary to insure complete consumption of the sample. The results of this series are shown in Table 4 and Fig. 5. Doubtful data were eliminated since occasionally small flakes of the sample were lost in the arc.

Table 3. The effect of calcium upon the intensity of magnesium (2779.8 Å) in the a.c. spark.

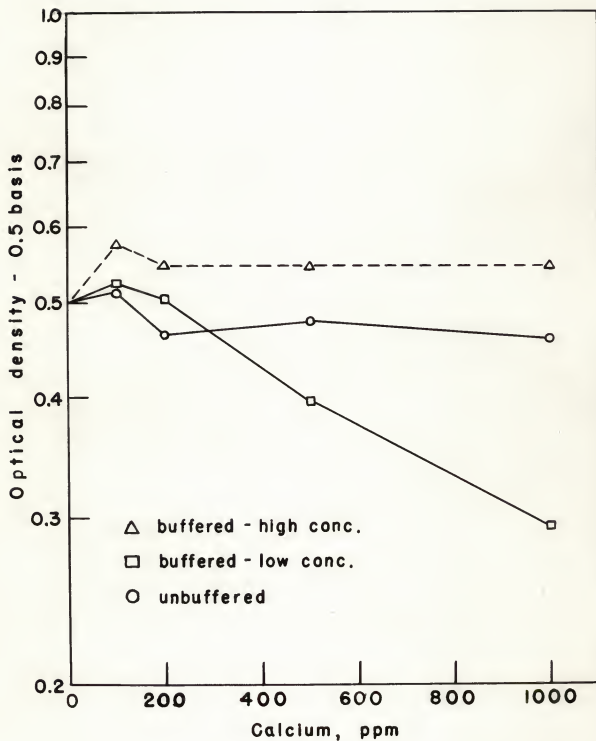| Solution	Optical density Plate number						Av.	Standard deviation	Density corrected to 0.5 basis
	29	30	31	32	33	34			
Mg 250 ppm	0.528	0.662	0.656	0.411	0.634	0.609	0.591	0.1035	0.500
	0.546	0.688	0.714	0.430	0.648	0.611			
	0.428	0.722	0.686	0.456	0.573	0.585			
Mg 250 ppm	0.524	0.417	0.682	---	0.444	0.668	0.614	0.1146	0.519
Ca 100 ppm	0.656	0.666	0.594	0.428	0.620	0.629			
	0.569	0.832	0.796	0.577	0.660	0.668			
Mg 250 ppm	0.757	0.450	0.639	0.488	0.370	0.516	0.549	0.1242	0.464
Ca 200 ppm	0.482	0.572	0.830	0.496	0.395	0.558			
	0.596	0.573	---	0.438	0.387	0.492			
Mg 250 ppm	0.620	0.432	0.531	0.376	0.552	---	0.564	0.1079	0.477
Ca 500 ppm	0.629	0.502	0.678	0.459	0.512	0.606			
	0.745	0.671	0.478	0.660	0.450	0.682			
Mg 250 ppm	0.722	---	0.546	0.372	0.500	0.409	0.539	0.1251	0.457
Ca 1000 ppm	0.460	0.476	0.688	---	0.504	0.593			
	0.734	0.503	0.733	0.438	0.366	0.577			

Fig. 4. The Effect of Calcium upon the Intensity of
Magnesium (2779.8 Å) in the A.C. Spark.

Table 4. The effect of calcium upon the intensity of magnesium (2779.8 Å) in the d.c. arc.

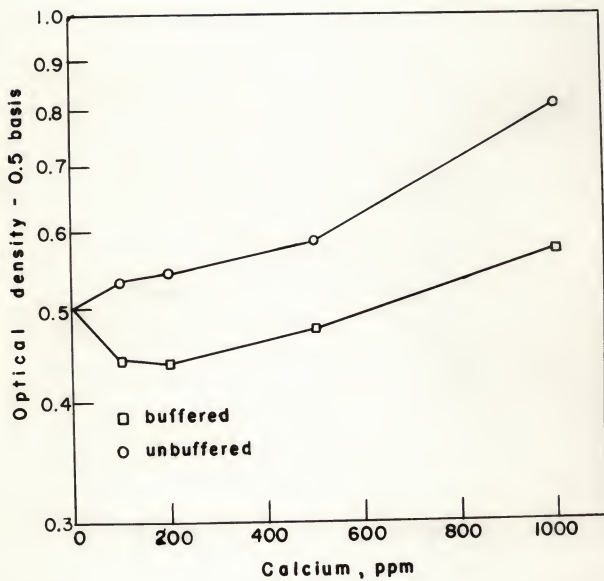| Solution	Optical density Plate number				Av.	Standard deviation	Density corrected to 0.5 basis
	41	42	43	44			
Mg 250 ppm	0.306 0.454 0.408	0.436 0.446 0.388	0.416 0.404 0.420	0.436 0.412 0.456	0.415	0.0403	0.500
Mg 250 ppm Ca 100 ppm	0.346 0.404 0.410	0.456 0.330 0.476	0.462 0.435 0.546	0.502 0.465 0.469	0.442	0.0614	0.532
Mg 250 ppm Ca 200 ppm	0.513 0.317 0.294	0.432 0.392 0.594	0.492 0.584 0.449	0.502 0.395 0.434	0.450	0.0935	0.542
Mg 250 ppm Ca 500 ppm	0.445 0.464 0.300	0.442 0.564 0.569	0.569 0.543 0.406	0.318 0.569 0.659	0.487	0.0991	0.587
Mg 250 ppm Ca 1000 ppm	0.584 0.660 0.770	0.658 0.594 0.600	0.780 0.693 0.710	0.748 0.568 0.722	0.674	0.0749	0.812

Fig. 5. The Effect of Calcium upon the Intensity of
Magnesium (2779.8 Å) in the D.C. Arc

Effect of Magnesium Upon Intensity of
Calcium in the D.C. Arc

The d.c. arc source was next utilized to determine the effect of magnesium upon the intensity of the calcium line. The procedure previously described was utilized also in this series. These results are given in Table 5 and Fig. 6.

Selection of Spectroscopic Buffer

In attempting to select a suitable spectroscopic buffer for use with calcium and magnesium, the works of Schrenk and Clements (15) and Langstroth and McRae (12) were considered.

Schrenk and Clements have used lithium tartrate with a good deal of success in this laboratory. The buffer has been used on solutions containing phosphorus, calcium, and potassium. The use of this buffer caused practically complete cancellation of the repression of the phosphorus line by potassium and calcium.

The work of Langstroth and McRae on the transport phenomena of materials in the condensed d.c. spark indicates that a buffer should contain an element of low ionization potential. When such an element is present in sufficient amount it will alter the transport phenomena to such an extent that the extraneous element will not affect it.

An excellent buffer requires that it will form a uniform, tenacious film on the surface of the electrode. This requirement

Table 5. The effect of magnesium upon the intensity of calcium (3158.9 °A) in the d.c. arc.

| Solution | Optical density Plate number | | | | | Av. | Standard deviation:0.5 basis | Density corrected to 0.5 basis |
	48	49	50	66	67			
Ca 250 ppm	0.372 0.384 ---	0.392 0.473 0.344	0.475 0.512 0.490	0.620 0.577 0.602	0.578 0.699 0.585	0.515	0.1151	0.500
Ca 250 ppm Mg 100 ppm	0.365 --- 0.390	0.469 0.342 0.384	0.444 0.406 0.450	0.620 0.648 0.545	0.699 0.620 0.545	0.495	0.1170	0.481
Ca 250 ppm Mg 200 ppm	0.324 0.398 0.404	0.404 0.319 0.340	0.490 0.421 0.426	0.450 0.553 0.745	0.658 0.561 0.668	0.477	0.1221	0.463
Ca 250 ppm Mg 500 ppm	0.389 0.429 0.464	0.437 --- 0.437	0.510 0.584 0.389	0.585 0.594 0.569	0.658 0.648 0.553	0.518	0.0929	0.503
Ca 250 ppm Mg 1000 ppm	0.268 0.234 0.276	0.298 0.278 0.289	0.456 0.446 0.502	0.523 0.585 0.594	0.530 0.620 0.426	0.422	0.1361	0.410
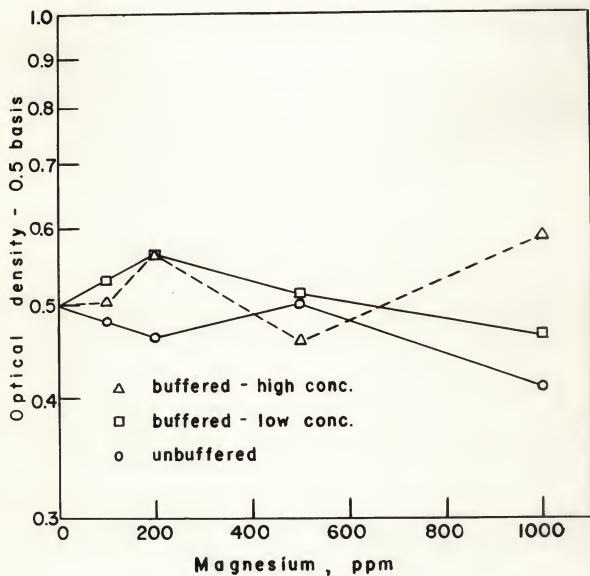
Fig. 6. The Effect of Magnesium upon the Intensity of
Calcium (3158.9 Å) in the D.C. Arc

was realized in the case of low concentrations (250 ppm) of sample, but in the higher range (500 to 1000 ppm) the layer was not uniform.

A stock buffer solution containing 81,000 ppm of lithium tartrate was used in compounding the buffered samples for this work. The composition of these samples is shown in Table 1. Two ml of the stock buffer solution were added to each sample of the series for analysis. The concentration of the lithium tartrate in the solutions was approximately 3,860 ppm.

When the buffered samples were used with the porous cup electrodes in the a.c. spark, considerable difficulty was encountered in the passage of the solution through the electrode into the spark. These electrodes had been prepared and treated at the same time as those used with the unbuffered solutions. It was then noted that Ayres and Berg (3) had used pre-arced porous cup electrodes and were able to obtain good results. A twenty-five second pre-arc was then applied to the blank electrodes before filling. In this manner the porosity of the electrodes was increased and the samples passed through readily. However, this pre-arcing may influence the determinations since the pre-arcing seemed to enhance the feed rate much more than the pre-sparking.

Table 6 and Fig. 3 show that an enhancement of the calcium line in the a.c. spark occurred when the buffered solutions were used as compared to a repression with the unbuffered solutions. The same phenomenon is true in the d.c. arc as shown in Fig. 6

Table 6. The effect of magnesium upon the intensity of calcium (3158.9 $\overset{\circ}{A}$) in the a.c. spark. (Solutions buffered with lithium tartrate).

Solution	Plate number 51	52	53	Av.	Standard deviation	Density corrected to 0.5 basis
Ca 250 ppm	0.509	0.472	0.490	0.552	0.1428	0.500
	0.840	0.472	0.529			
Ca 250 ppm	0.820	0.671	0.430	0.620	0.1370	0.562
Mg 100 ppm	0.685	0.594	0.519			
Ca 250 ppm	0.618	0.699	0.582	0.651	0.0933	0.590
Mg 200 ppm	0.820	0.606	0.582			
Ca 250 ppm	0.399	0.560	0.529	0.560	0.0914	0.535
Mg 500 ppm	0.631	0.657	0.582			
Ca 250 ppm	0.631	0.455	0.472	0.556	0.0825	0.504
Mg 1000 ppm	0.657	0.582	0.539			

*All densities have been corrected for electrode impurity.

which was plotted from the data tabulated in Table 7.

The effect of the buffer upon the slight repression of the calcium line due to magnesium in the a.c. spark was erratic. The result of a series of three runs in duplicate is shown in Table 8 and Fig. 4.

The enhancement of the magnesium line due to the presence of calcium in the d.c. arc was nullified through the use of the spectroscopic buffer. These results are shown in Table 9 and Fig. 5.

DISCUSSION

Magnesium, when it occurred as an extraneous element, caused a slight depression of the calcium line in the a.c. spark. The average standard deviation over the range of samples studied was approximately 9 percent. The effect of magnesium upon the intensity of calcium is shown in Fig. 3. Buffering the solution with lithium tartrate decreased the slight effect of magnesium upon calcium in the a.c. spark. The standard deviation was 18.7 percent for the buffered solution. When the d.c. arc was employed as an excitation source, the effect of magnesium upon calcium was approximately the same as in the a.c. spark. However, the average standard deviation (24.7 percent) for this series was considerably higher than in the a.c. spark. The spectrographic buffer reacted in the same manner in the d.c. arc as it did in the a.c. spark, except that the standard deviation also was higher (26.7 percent). When the buffer concentration was

Table 7. The effect of magnesium upon the intensity of calcium (3158.9 Å) in the d.c. arc. (Solutions buffered with lithium tartrate).

Solution	Optical density Plate number			Av.	Standard deviation	Density corrected to 0.5 basis
	68	69	70			
Ca 250 ppm	0.444 0.332 ----	0.289 0.332 0.426	0.420 0.372 0.244 0.204	0.340	0.0837	0.500
Ca 250 ppm Mg 100 ppm	0.319 0.354 0.516	0.260 0.347 0.495	---- 0.377 0.357 0.237	0.362	0.0934	0.532
Ca 250 ppm Mg 200 ppm	0.367 0.382 0.502	0.538 ---- 0.362	0.367 0.409 0.456 0.409	0.421	0.0638	0.618
Ca 250 ppm Mg 500 ppm	0.403 0.420 0.409	0.462 0.420 0.272	0.377 0.292 0.218 0.222	0.350	0.0898	0.514
Ca 250 ppm Mg 1000 ppm	0.260 ---- 0.444	0.292 0.248 0.420	0.146 0.314 0.561 0.174	0.318	0.1345	0.467

Table 8. The effect of calcium upon the intensity of magnesium (2779.8 Å) in the a.c. spark. (Solutions buffered with lithium tartrate).

Solution	Plate number 60	Plate number 61	Plate number 62	Av.	Standard deviation	Density corrected to 0.5 basis
Mg 250 ppm	---	0.297	0.268	0.313	0.0424	0.500
	0.332	0.292	0.377			
Mg 250 ppm	0.409	0.280	0.357	0.330	0.0497	0.527
Ca 100 ppm	0.337	0.280	0.314			
Mg 250 ppm	0.332	0.252	0.264	0.317	0.0538	0.507
Ca 200 ppm	0.398	0.342	0.314			
Mg 250 ppm	0.264	0.280	0.244	0.249	0.0264	0.398
Ca 500 ppm	0.211	0.229	0.268			
Mg 250 ppm	0.208	0.158	0.155	0.183	0.0215	0.293
Ca 1000 ppm	0.208	0.184	---			

Table 9. The effect of calcium upon the intensity of magnesium (2779.8 Å) in the d.c. arc. (Solutions buffered with lithium tartrate).

Solution	Optical density			Av.	Standard deviation	Density corrected to 0.5 basis
	Plate number					
	63	64	65			
Mg 250 ppm	0.903 0.782 ---	0.854 --- 0.638	0.721 0.757 ---	0.776	0.0945	0.500
Mg 250 ppm Ca 100 ppm	0.502 --- 0.569	0.699 0.382 ---	0.824 1.097 0.733	0.687	0.2355	0.442
Mg 250 ppm Ca 200 ppm	0.594 0.810	0.553 0.668 0.721	0.530 0.854 0.710	0.680	0.1170	0.438
Mg 250 ppm Ca 500 ppm	0.824 0.538 ---	0.745 --- 0.629	0.668 0.903 0.870	0.740	0.1347	0.477
Mg 250 ppm Ca 1000 ppm	0.733 0.838 0.903	0.979 1.000 0.838	0.699 1.022 1.022	0.893	0.1293	0.574

increased by a factor of ten, the influence of magnesium on the intensity of the calcium line was not altered appreciably as shown in Fig. 6. Inspection of Fig. 6 also indicates that considerable variation of results was obtained with both concentrations of buffer. The loss of sample during excitation was probably responsible for these variations. Due to the relatively high standard deviations, both in the a.c. spark and the d.c. arc, it is probable that magnesium has very little effect upon the intensity of calcium in either source of excitation.

The intensity of the magnesium line in the a.c. spark decreased slightly when calcium was present as the extraneous element. The decrease in intensity apparently reached a maximum at a concentration of 200 ppm of the extraneous element. The average standard deviation was 20.2 percent for the series. When the spectrographic buffer was added to the solution, the slight decrease in the intensity of the magnesium line was eliminated at low concentrations of the extraneous element. However, when the extraneous element was present at higher concentrations, a marked decrease in the intensity of the magnesium line occurred in the buffered solution. It is probable that this phenomenon may be explained in the following manner: (a) At low concentrations of the extraneous element, the buffer may be present in sufficient quantity to minimize the effect of the extraneous element. (b) At higher concentrations of the extraneous element, the buffer may not be sufficiently concentrated to offset the influence of the extraneous element. For these buffered

solutions the average standard deviation was 13.6 percent. An examination of Fig. 4 would indicate that when an extraneous element is present, a higher concentration of buffer may be required to stabilize the intensity of the magnesium line in the a.c. spark. Therefore, a tenfold increase in buffer was utilized to determine if the influence of calcium upon the intensity of magnesium could be eliminated. The effectiveness of these solutions is shown in Fig. 4 and indicates that it may be possible to obtain a higher precision in determining magnesium under such conditions. The intensity of magnesium was considerably enhanced by calcium when the d.c. arc was used as a source of excitation. When the solution was buffered, the enhancement appeared to be minimized as shown in Fig. 5. The average standard deviations for the unbuffered and buffered solutions were 15.2 percent and 19.3 percent respectively. The data therefore indicate that calcium had very little effect upon the intensity of magnesium in the a.c. spark, but show a considerable enhancement of the same line in the d.c. arc.

Brode and Timma (9) developed an equation which relates the boiling point and excitation potential of an element to the intensity of its spectral line. When the intensities of the calcium and magnesium lines were calculated using the equation proposed by Brode and Timma, the values obtained for the two lines were similar. The difference between these calculated intensities was approximately fifteen percent, which may indicate that the elements should have relatively little effect upon

each other. It is possible that the magnesium and calcium may be converted to their oxides at the temperature obtained in the d.c. arc. If this is true, the energy required to vaporize the oxides would be greater than that of the original material. In the a.c. spark, where the solution is fed directly into the spark gap, it is improbable that the magnesium and calcium would be converted to their oxides. Therefore, the effect of one element upon another should be different in the two sources of excitation, and the results of this research has shown this to be true.

CONCLUSIONS

It has been shown that calcium and magnesium can influence each other in both the a.c. spark and the d.c. arc. These effects are summarized as follows: (a) The presence of magnesium will cause a decrease in the intensity of the calcium line in the a.c. spark and also in the d.c. arc. The results in the a.c. spark tend to be more uniform than those obtained in the d.c. arc; (b) When calcium is present as an extraneous element in the determination of magnesium, there will be a slight repression of the magnesium line in the a.c. spark and a considerable enhancement in the d.c. arc.

The effects stated above have been eliminated somewhat through the use of lithium tartrate as a spectrographic buffer. This buffer minimized the effect of magnesium upon calcium. The results were erratic when a low concentration of buffer was used

to eliminate the effect of calcium upon magnesium. However, higher concentrations of buffer have minimized the effect of calcium upon the intensity of the magnesium line.

The standard deviations as indicated in Tables 2 through 9 are high. This would tend to indicate several sources of error, which in all probability, could be partially eliminated through a more comprehensive study of the effects of these elements upon each other.

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THE INFLUENCE OF EXTRANEOUS ELEMENTS ON
LINE INTENSITIES IN THE A.C. SPARK AND THE D.C. ARC

by

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This research was conducted to study the influence of extraneous elements on line intensities in the a.c. spark and the d.c. arc. Calcium and magnesium were the investigated elements. A Bausch and Lomb, large, Littrow spectrograph with quartz optics was used throughout the research.

Kodak Number 33 photographic plates were found to give good results when calcium and magnesium were investigated. All plates were developed four minutes in dilute Kodak X-ray developer and fixed in X-ray fixer. The transmittancies of the lines were measured with a projection type Allied Research Laboratories - Dietert densitometer.

The concentration of the element being investigated was held constant at 250 ppm. The extraneous element was varied as follows: 0; 100; 200; 500; and 1000 ppm. Lithium tartrate was used as a spectrographic buffer to minimize the influence of the extraneous elements. When a high concentration of buffer was employed, the concentration of the element under investigation was 125 ppm.

Results indicated that the presence of magnesium will cause a decrease in the intensity of the calcium line in the a.c. spark and also in the d.c. arc. When calcium is present as an extraneous element in the determination of magnesium, there will be a slight repression of the magnesium line in the a.c. spark and a considerable enhancement in the d.c. arc. These effects have been eliminated somewhat through the use of lithium tartrate as a spectrographic buffer. This buffer minimized the effect of

magnesium upon calcium. Erratic results were obtained when a
low concentration of buffer was used to eliminate the effect
of calcium upon magnesium. However, higher concentrations of
buffer have minimized the effect of calcium upon the intensity
of the magnesium line in the a.c. spark.

Date Due