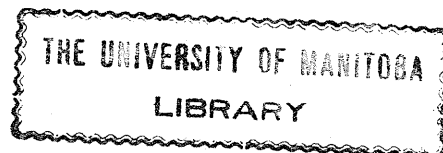


THE INFLUENCE OF SAMPLE
COMPOSITION ON THE INTENSITY
RATIO OF LINE PAIRS OF
VARIOUS ELEMENTS.

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of line pairs of various elements.

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The influence of sample
composition on the intensity
ratio of line pairs of
various elements.

(1) INTRODUCTION.

Methods of quantitative spectrographic analysis consist in introducing the sample into an appropriate source and exciting the atoms to radiate their characteristic spectra. Determinations of the intensity ratio of the selected line pair arising from the test and internal standard elements, permits the concentration of the former to be read off from a previously determined "working curve". This procedure assumes that the intensity ratio of a chosen line pair is a function only of the concentrations of the elements involved, and is independent of other factors which may vary from sample to sample. Accordingly the accuracy of analytic results depends to a large extent on the degree to which this condition is fulfilled. Numerous workers have observed a dependence of the intensities ratios on the general composition of the sample (1,2,3,4,5,6,7,8). Although procedures have been designed to minimize this dependence under specific sets of conditions, there has been no extensive systematic investigation of the general problem; the factors responsible for the dependence remain unknown.

G.O.Langstroth and K.B.Newbound (8) made a preliminary study of the variations which occur in the relative intensities of certain magnesium, lead, and cadmium line pairs, when

various foreign salts are added to standard samples excited in a condensed spark source. This thesis describes an extension of their work. The behaviour of the relative intensities of various line pairs on addition of chosen substances to standard samples has been investigated for eleven elements. It was hoped that a critical analysis of ^{these} this more extensive data would permit some inference regarding the characteristics which two elements must possess if the intensity ratio of a line pair is to exhibit a minimum variation. The solution of the problem is desirable from an immediately practical viewpoint, viz., as a guide to the selection of an appropriate internal standard element.

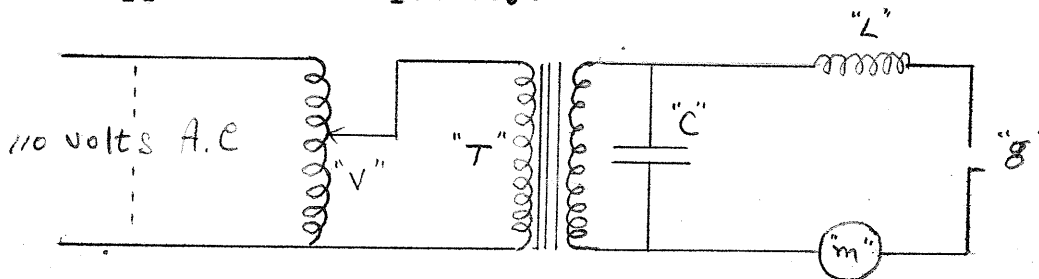
As will appear later, the choice of elements to be investigated was based on consideration of their atomic characteristics. In general several lines were examined for each element. Four different substances were used as extraneous additions, and both buffered and unbuffered standard samples were used. Furthermore a study was made of the effects of varying certain control conditions.

It was found that the change in the intensity ratio of a line pair depends on the composition of the standard sample, on the extraneous material added, and on the line pair chosen for the investigation. Under certain cases ^{In} these

changes could be kept at a minimum by the correct choice of the line pair. There is no ^{obvious} correlation between the changes in the intensity ratios and either the excitation potentials of the lines or the ionization potentials and the atomic masses of the elements. By operating the source at a constant current or steadying the discharge by illuminating it with ultra violet light, yields ^{essentially} the same results as obtained from the source operated at the minimum breakdown potential. Buffering the standard sample with potassium acetate did not always reduce the effects of the extraneous materials. This supports the results of G.O.Langstroth and K.B.Newbound. [The form in which the element is introduced into the source is immaterial.] No generalization regarding the choice of the internal standard element or the line pair can be made. The method of correlation, proposed by Levy (9), for making corrections in intensity ratios due to changes caused by extraneous materials, is inapplicable to this type of analysis. Information on a single discharge of the spark source is desirable.

(II) APPARATUS AND TECHNIQUE.

Plate I illustrates the apparatus used for the first portion of this work. The source used was a condensed A.C. spark. "T" (fig., 1) is a Thordarson transformer rated to give 20,000 volts on open circuit when 110 volts 60 cycle A.C., is applied to the primary.



A "variac" control "v" , was placed in the primary circuit of the transformer to vary the applied voltage. The .014 microfarad condenser "c" was built from glass plates with alternate sheets of aluminium foil, boiled in wax to ensure adequate insulation. The 30 microhenry inductance "l" was made of 37 turns of heavy copper wire wound on a $1\frac{3}{4}$ inch diameter cardboard cylinder. The inductance was placed on the pointer electrode side of the spark gap since it was found that for a given sample "plate background" was noticeably less with it in this position. The spark gap "g" consisted of a fixed point electrode and a

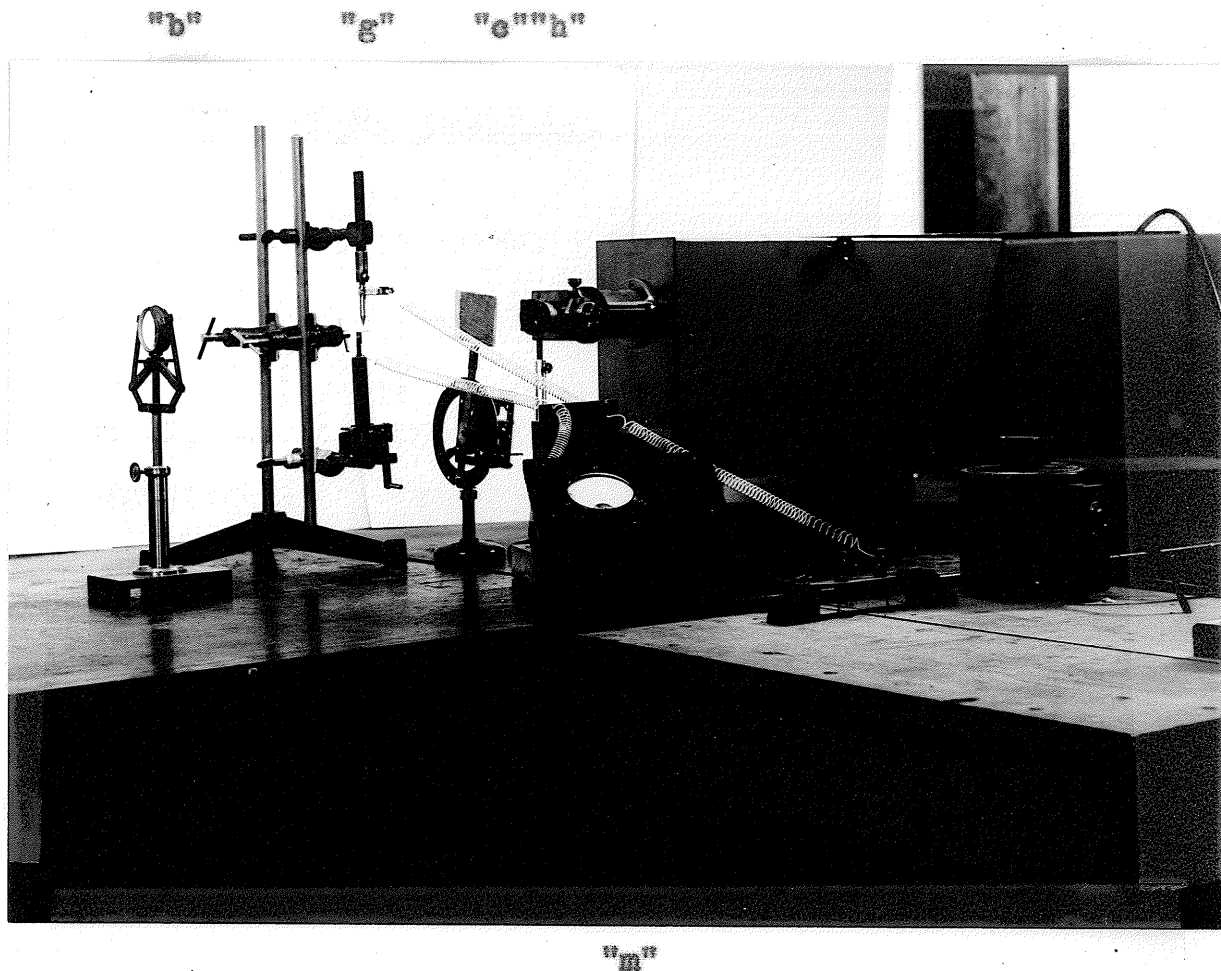


Plate I. General view of apparatus.

"b" lens to aid the replacement of the electrodes.

"g" spark gap.

"e" screens.

"h" quartz lens.

"m" thermocouple ammeter.

(1×1.2) cm^2 ., copper plate capable of motion in a horizontal plane. The spark gap separation was 3.1 mm., throughout the experiment. The image of the spark gap was focussed on the collimating lens of the spectrograph by means of a quartz lens "h" (focal length 15cm.,, speed f:4) placed at the slit. Consequently light from every portion of the spark~~g~~ entered the spectrograph. Hence the results obtained were space- and time- integrated over the whole of the source. This arrangement was used in order to obtain satisfactorily uniform line contours.

The spectrograph employed was built in the University of Manitoba and is equivalent to a commercial "medium quartz" instrument. The spectral range is from 2100A to 6000 A. The spectra were recorded on Eastman 40 photographic plates. A slit separation of 45 microns was used throughout the work.

The spark gap was always kept on the optical axis of the spectrograph by refocussing its image through lens "b" on a screen not shown on plate I. This permitted removal of the point electrode for cleaning after each exposure and replacement in its original position. Wire screens were used to cut down the intensity of the light from the source. The screens were kept in motion during the time of the exposure

by means of clockwork "c". That the use of screens as neutral intensity weakeners is permissible under such conditions was shown by Harrison (10).

In certain instances (i.e. in the study of complex salts) it was necessary to use an antimony weakener⁽¹¹⁾ placed directly before the spectrograph slit and covering about half the slit length. This arrangement permitted changes in the intensity ratios of strong to weak lines to be studied. It was not necessary to know the absorption coefficient of the weakener since the results were required only in terms of the ratios for the sample with no extraneous addition.

To study the effect of strongly illuminating the spark gap with ultra violet light, the image of an iron arc was focussed on the plate electrode in a region just below the point of the upper electrode , plate II. Two quartz lenses "w" (focal lengthsth 15 and 10 cm., speed f:4) were used for this purpose. The arc "a" was placed on the optic axis of these lenses which formed an angle^{of} θ about 35 degrees with the normal to the plane electrode. The iron arc was operated with a standard electrode separation of 1/8 inch and a current of 4 amperes. It was placed 34 cm., from the plate electrode. The magnification was one. Calibration marks were placed on every plate by means of the arc and step sector method (12).

"a"

"w"

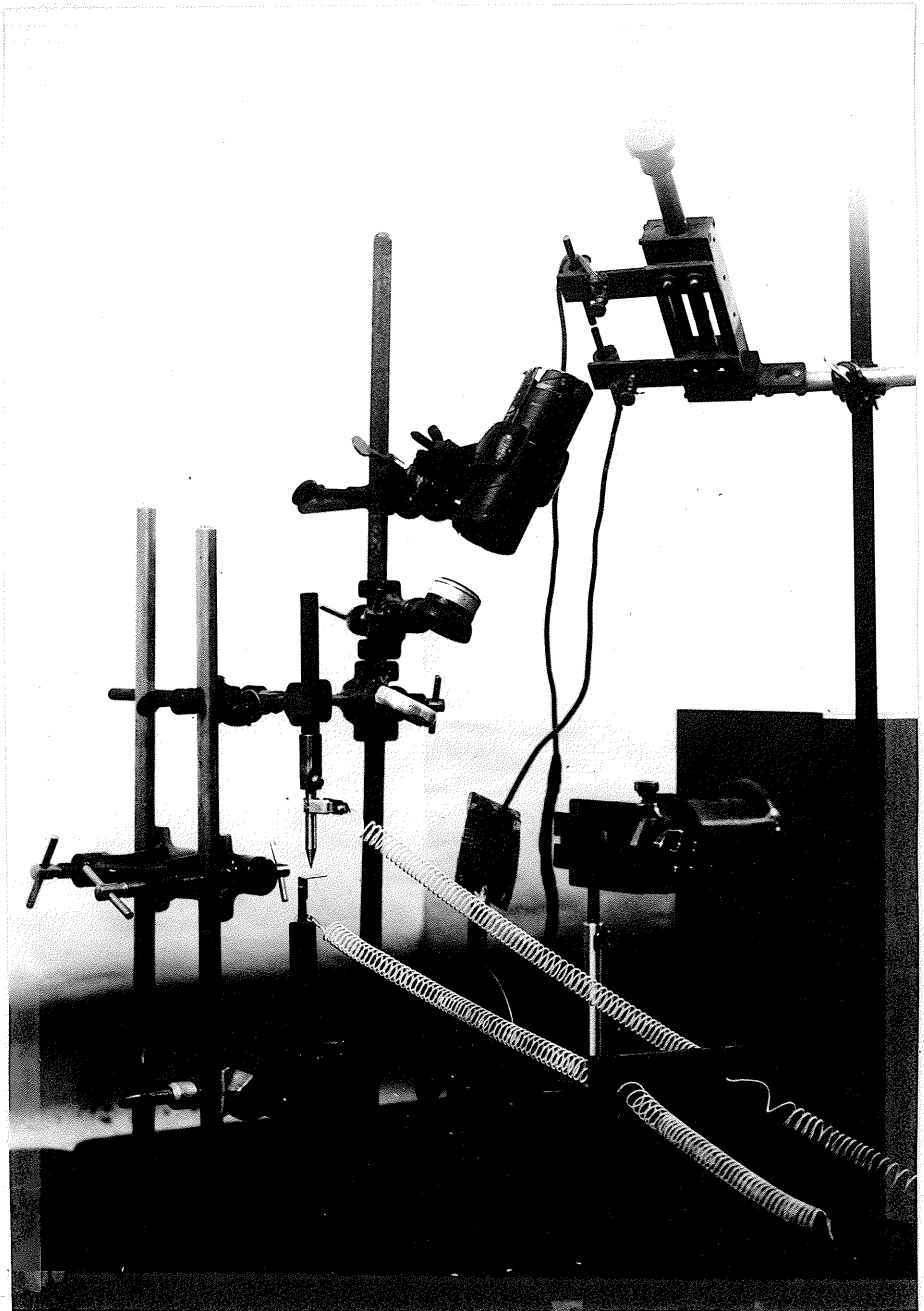


Plate II Arc and lenses for ultra violet illumination.

"a" iron arc

"w" quartz lenses

A brass arc "e" was placed at a distance of 120 cm., from the slit of the spectrograph. It was operated at a current of 3 amperes and an electrode separation of 1/8 inch. The step sector "f" was placed at the slit of the spectrograph and rotated at a speed greater than 20 revolutions per second to eliminate the intermittency effect. Calibration marks in steps of 100, 75, 50, 32, 19, 13, and 6 percent of the total intensity (corresponding to the relative angular openings of the sector) were obtained. An exposure time of 5 seconds was used. A photograph of the apparatus used for producing the calibration spectra is shown in plate III.

The intensity of the spectral lines were measured by means of the microphotometer built in the University of Manitoba (13), using the standard method (cf. 12).

(a) Loading the electrodes.

The electrodes were cleaned by washing for a few seconds in concentrated nitric acid, and rinsing with distilled water. The electrodes were dried by blowing the excess moisture off and placing in the flame of a pyrex glass burner. Care was taken that the electrode was not kept too long in the nitric acid or the flame otherwise a thin film of oxide formed on the surface of the electrode and the loaded sample collected

"e"

"f"

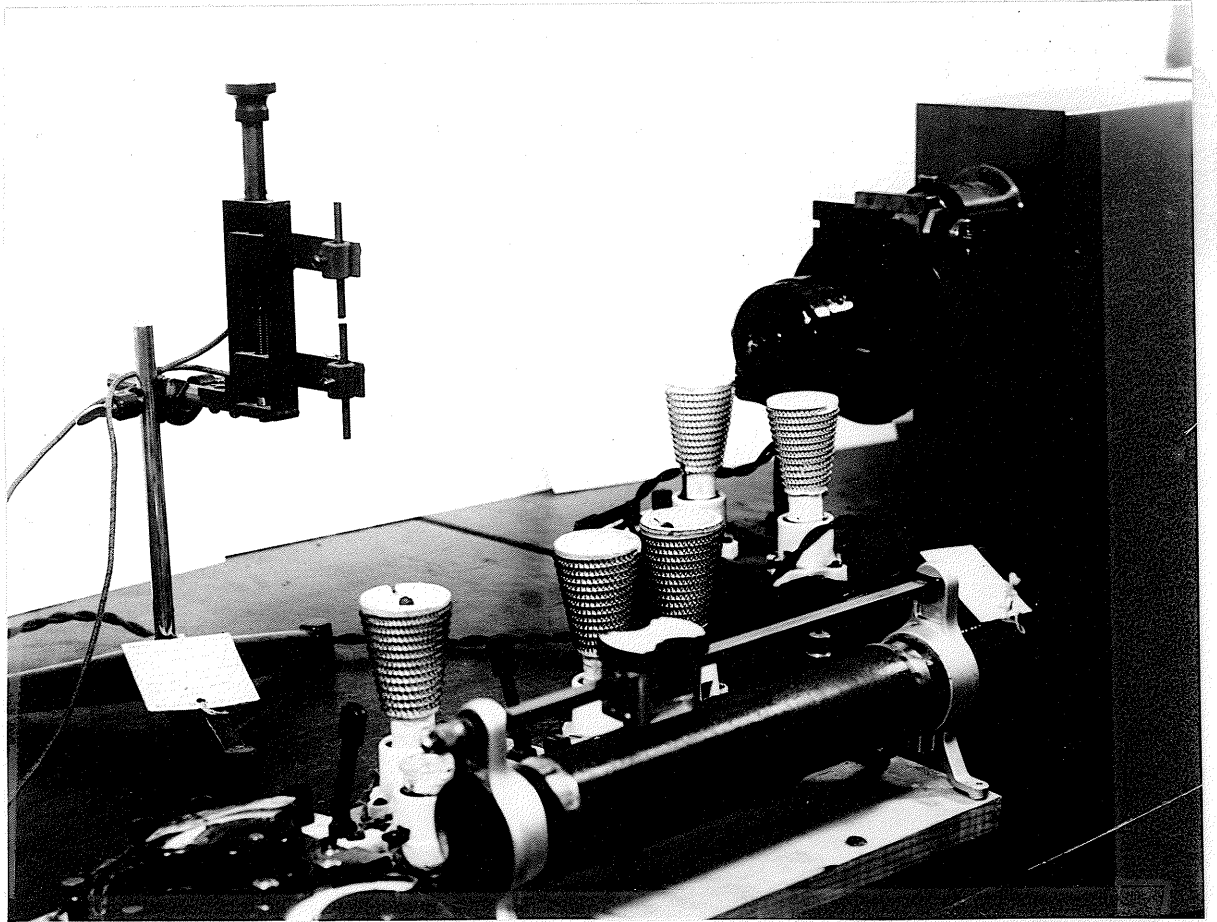


Plate III Apparatus for obtaining calibration spectra.

"e" brass arc

"f" step sector

in droplets instead of spreading uniformly over the entire surface of the plane . The samples to be analysed were loaded with .050 c.c. pipettes calibrated to within 2% . The electrodes were dried under reduced pressure. In general it was found that the electrodes thus dried exhibited ^athicker ring of the material around the edges. This uneven distribution causes a reduction of the reproducibility . It was found that if the electrodes were dried intermittently to complete dryness, and if each time the remaining moisture was spread over the entire electrode by blowing through a pipette, more uniform distribution of the material took place provided the sample did not contain salts which form colloidal suspensions, e.g. tin chloride.

(b) The exposure.

When sparking the sample the lower plate electrode was kept in motion in a horizontal plane by means of a crank so that its whole surface was covered by the spark during an exposure of 60 seconds. The same exposure time was used throughout these experiments. In this way by tracing a multiple "W" pattern on the plate electrode, a fresh surface of the sample was continuously being sparked. When the spark was operated at minimum breakdown potential, the Variac control on the primary of the transformer was adjusted until the spark was on

the point of stopping. This caused the spark to occur every other half cycle of the line voltage. It is important to note that allowing the spark to occur every cycle is partially equivalent to doubling the exposure time and ~~part~~ partially to resparking the same electrode. [This may result in a reduction of reproducibility.]

When the spark was operated at a constant current in the oscillatory circuit, the value of the current was controlled by means of the Variac and read on the thermocouple ammeter (m) plate II.

(c) Processing.

The spectra were photographed on Eastman 40 plates. These were processed by developing in D-61 developer for four minutes, washing in water for two minutes, fixing in an acid hardening fixing bath F-5 for at least twenty minutes, and finally washing in running tap water for at least one half hour. The plates were then rinsed in distilled water and dried.

(d) General precautions.

(1) More electrodes of each sample were prepared

than were used in order that a selection for uniformity of drying could be made. Those electrodes which dried unevenly were rejected.

(2) The spectra for a complete set of data were photographed on a single plate. In all cases the spectrum of the sample containing no extraneous material was photographed along with the spectra of the samples containing the different extraneous materials on the same plate and at least two spectra of the same kind of sample were recorded. This eliminated the errors which may be introduced from plate to plate for all the results were given in terms of the same arc spectrum.

(3) The microphotometer was allowed at least ten minutes to reach a steady state before any readings were taken. The zero and the clear plate deflections were checked ^{measurements on} after each spectra.

(4) In the determination of the intensity ratios several calibration curves were used for each plate to cover the wavelength range of the lines under investigation, since in general the slopes of the calibration curves are different for different wavelengths. It was not necessary to know the

relative intensities of the different brass arc lines in terms of which the intensities of the investigated lines were given, since each plate contained a complete set of data (see 2 above) and only the changes in the intensity ratios are of interest here. See plate IV,

(e) Choice of elements.

In choosing the elements for the standard samples consideration of their ionization potentials and atomic masses played an important role. In addition to the expectation on general grounds that these factors might play an important part in determining the behaviour of the elements in the discharge, there is evidence that they are significant factors in determining the intensity distribution along the discharge axis (14). The spark was operated at the minimum breakdown potential. In addition these samples were tried with a constant amount of potassium acetate added to act as ^aspectroscopic buffer.

Table 1 gives the composition of the different samples. The first column gives the elements composing the standard sample. The second and the third columns give the atomic ^{mass} and the ionization potentials of the elements respectively. The

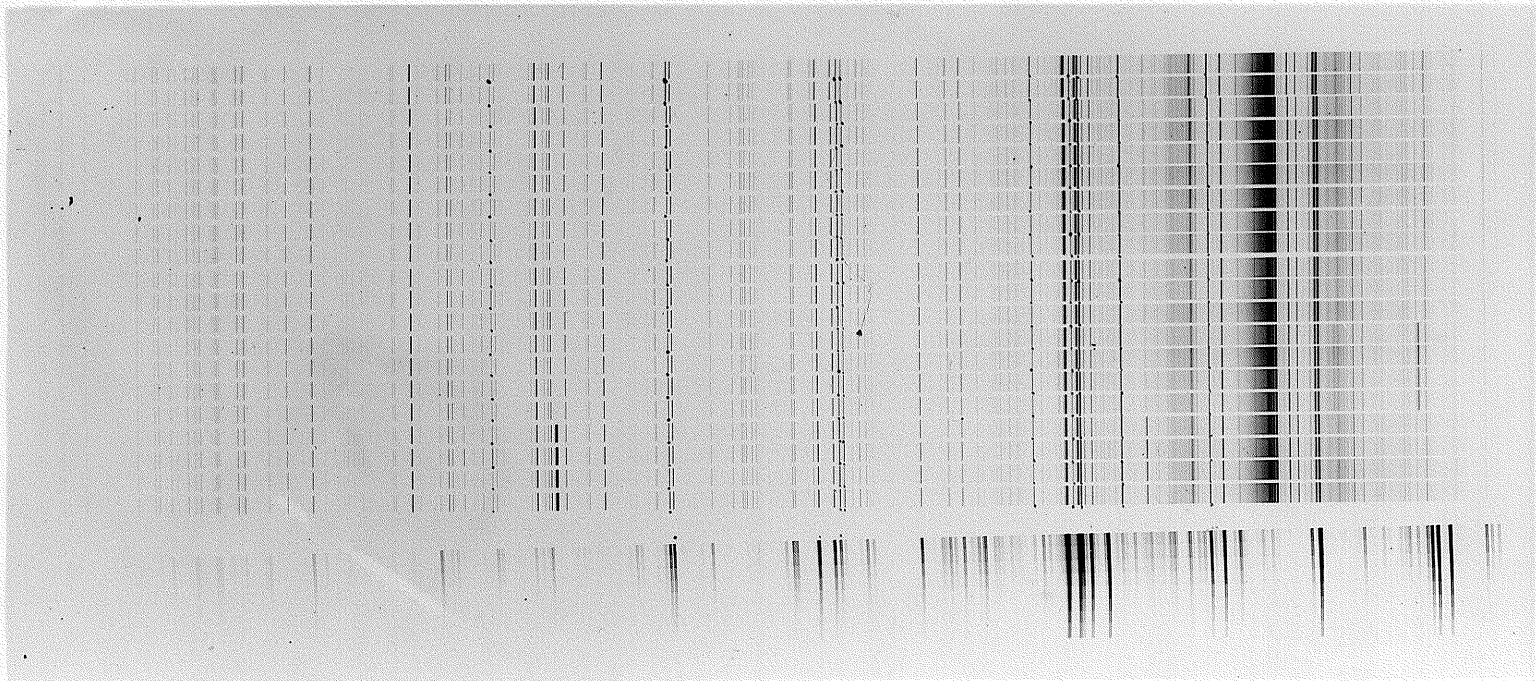


Plate IV
A typical spectrogram.

Key to plate IV.

Characteristic of source. (Constant current.)

Cu electrode / sample #2 , Buffered

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" " " " " "
" " " " " "

Cu electrode / sample #2, containing KCl, Buffered.

" " " " " " "
" " " " " " "
" " " " " " "

Cu electrode / sample #2, containing NH₄Cl, Buffered.

" " " " " " "
" " " " " " "
" " " " " " "

Cu electrode / sample #2, containing LiCl , Buffered.

" " " " " " "
" " " " " " "
" " " " " " "

Cu electrode / sample #2, containing H₃BO₃, Buffered.

" " " " " " "
" " " " " " "
" " " " " " "

Brass arc, step sector rotated at the slit(Calibration marks.)

Note the dots above the calibration spectrum
which indicate the spectral lines used to obtain the different
calibration curves to cover the range of the wavelengths
studied.

fourth column gives the form in which the elements were introduced into the sample but it does not follow that that was the final form the elements assumed since reactions with other salts present in the sample might have taken place. The last column gives the amounts of salt in each sample. The amount of salt to be used was determined by trial in such a manner that the lines investigated were of the same order of intensity in the pure standard sample.

In all the samples given in table 1, the elements were dissolved in the same solution except in the case of samples #1 and # 2, where the silver was loaded separately. To observe whether the order of loading had any effect on the intensity ratios, a few samples were tried reversing the order of loading; *No effect was detected. for the lead-tin ratio, and table 17 shows that although there was a detectable effect for the silver addition of lithium chloride altered the ratio in the same sense in both instances.*

Table 2 gives the extraneous materials and buffer that were added to each one of the standard samples in table 1. The first column gives the composition, the second the amount, The third and fourth give the buffer and its amount,

To observe to what extent the effects of the extraneous materials used in the above table are representative of the effects produced by different amounts, sample #4 was sparked using the following amounts of boric acid only; 0.00; 1.06; 2.13; 4.24; 6.02; 8.24 and 10.3×10^{-3} gm., / c.c. of solution. The spark was operated at minimum breakdown potential.

Table 1

Standard Sample	Elements	Atomic Mass (mass units)	Ion., Pot'l (volts)	Form introduced	Amount used (gm., salt/c.c. of solution)
#1	Ag	108	7.5	AgNO ₃	.194 x10 ⁻³
	Sn	118	7.4	SnCl ₂ ·6H ₂ O	.94 "
	Mg	24	7.6	MgCl ₂ ·6H ₂ O	1.05 "
#2	Ag	108	7.5	AgNO ₃	.194 "
	Sn	118	7.4	SnCl ₂ ·6H ₂ O	.94 "
	Pb	207	7.4	PbNO ₃	2.00 "
#3	Mn	55	7.4	MnCl ₂ ·4H ₂ O	1.50 "
	Ni	59	7.6	NiCl ₂ ·6H ₂ O	1.00 "
	Mg	24	7.6	MgCl ₂ ·6H ₂ O	1.05 "
#4	Ni	59	7.6	NiCl ₂ ·6H ₂ O	1.00 "
	Sn	118	7.4	SnCl ₂ ·6H ₂ O	.94 "
	Mg	24	7.6	MgCl ₂ ·6H ₂ O	1.05 "
#5	Ba	137	5.2	BaCl ₂ ·2H ₂ O	8.00 "
	Sn	118	7.4	SnCl ₂ ·6H ₂ O	.94 "
	Cd	112	9.0	CdCl ₂ ·2H ₂ O	4.00 "
#6	Mg	24	7.6	MgCl ₂ ·6H ₂ O	1.05 "
	Sr	87	5.7	SrCl ₂ ·6H ₂ O	12.00 "
	Al	27	6.0	AlCl ₃ ·6H ₂ O	1.00 "
#7	Zn	65	9.4	ZnCl ₂	1.60 "
	Ni	59	7.6	NiCl ₂ ·6H ₂ O	3.00 "
	Sr	87	5.7	SrCl ₂ ·6H ₂ O	10.0 "

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Table 2

Extraneous material	Amount gm./c.c.	Buffer	Amount used gm./c.c.
KCl	6.00 x10 ⁻³	potassium acetate	50.0 x10 ⁻³
NH ₄ Cl	1.00 "		
LiCl	3.60 "		
H ₃ BO ₃	10.3 "		

.....

(f) effects of current variation:

In the previous work it was observed that the addition of the extraneous material to the standard sample caused a change in the oscillatory current of the inductive capacitative circuit. Sample #4 with the addition of lithium chloride was sparked for three different values of current to observe what change on the intensity ratio would be produced. Samples #1 and #2 were sparked using a constant current, to observe the effects on the changes in the intensity ratio due to the presence of the extraneous material. Both buffered and unbuffered samples were used. The current was maintained constant by means of the Variac control; its value was read on the thermocouple ammeter "m" plate I.

(g) Effects of illuminating the electrodes with ultra violet light.

In the above work it was observed that for such samples as containing^{ed} boric acid, [the spark would not breakdown unless] the current value^{were} was large. In order to lower the breakdown potential of the spark for such samples the spark gap was illuminated with ultra violet light from an arc. The photoelectrons emitted caused a lowering of the breakdown potential and insured that the spark broke down every half cycle of the line voltage. The ultra violet light

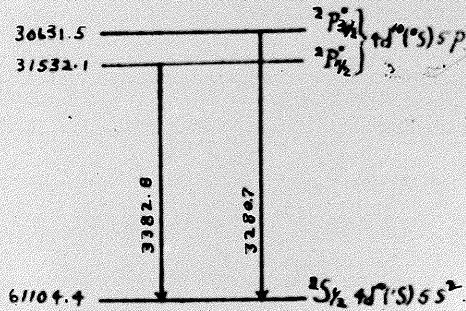
caused a steadier operation of the spark . It is probably as effective if not more so than the interrupter described by Feussner (15). The capacities "c"~~plate~~ fig., 1 were .014 and .026 microfarads. Sample #1 buffered and unbuffered were used.

(h) Complex salt.

The sample for this portion of the work was made from potassium aluminium sulphate, 4.00×10^{-3} gm., /cc. of solution, and 4.00×10^{-3} gm., / cc. of magnesium sulphate. The extraneous materials were: cadmium sulphate 12×10^{-3} gm/cc.; ammonium sulphate 30×10^{-3} gm., /cc.; sodium sulphate 15×10^{-3} gm., /cc., and zinc sulphate 15×10^{-3} gm.,/cc., of solution. The spark was operated at the minimum breakdown potential.

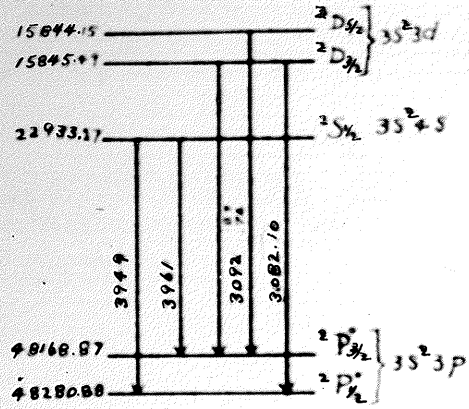
Plates V, VI, VII, give the energy level diagrams of the elements. The term classifications and values are given as in Bacher and Goudsmit (16). The information is limited to those lines studied in these experiments. The wavelengths were taken from the M.I. T. Wavelength Tables.

ion pot'l - 7.54 v



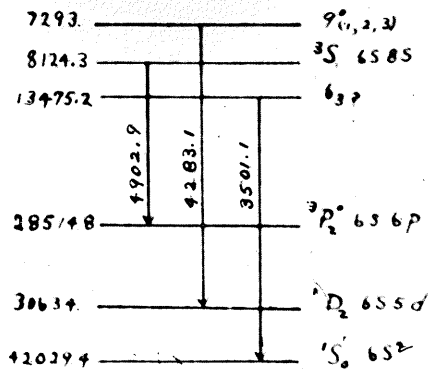
Ag I

ion pot'l - 5.96 v



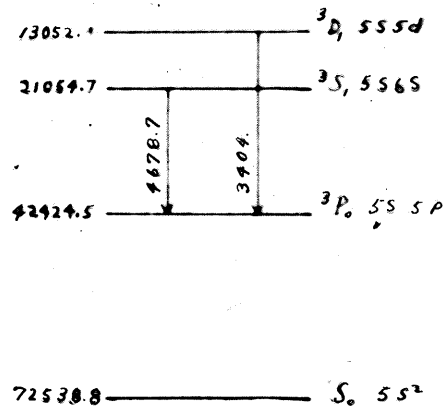
Al I

ion pot'l - 5.19 v



Ba I

ion pot'l - 8.96 v



Cd I

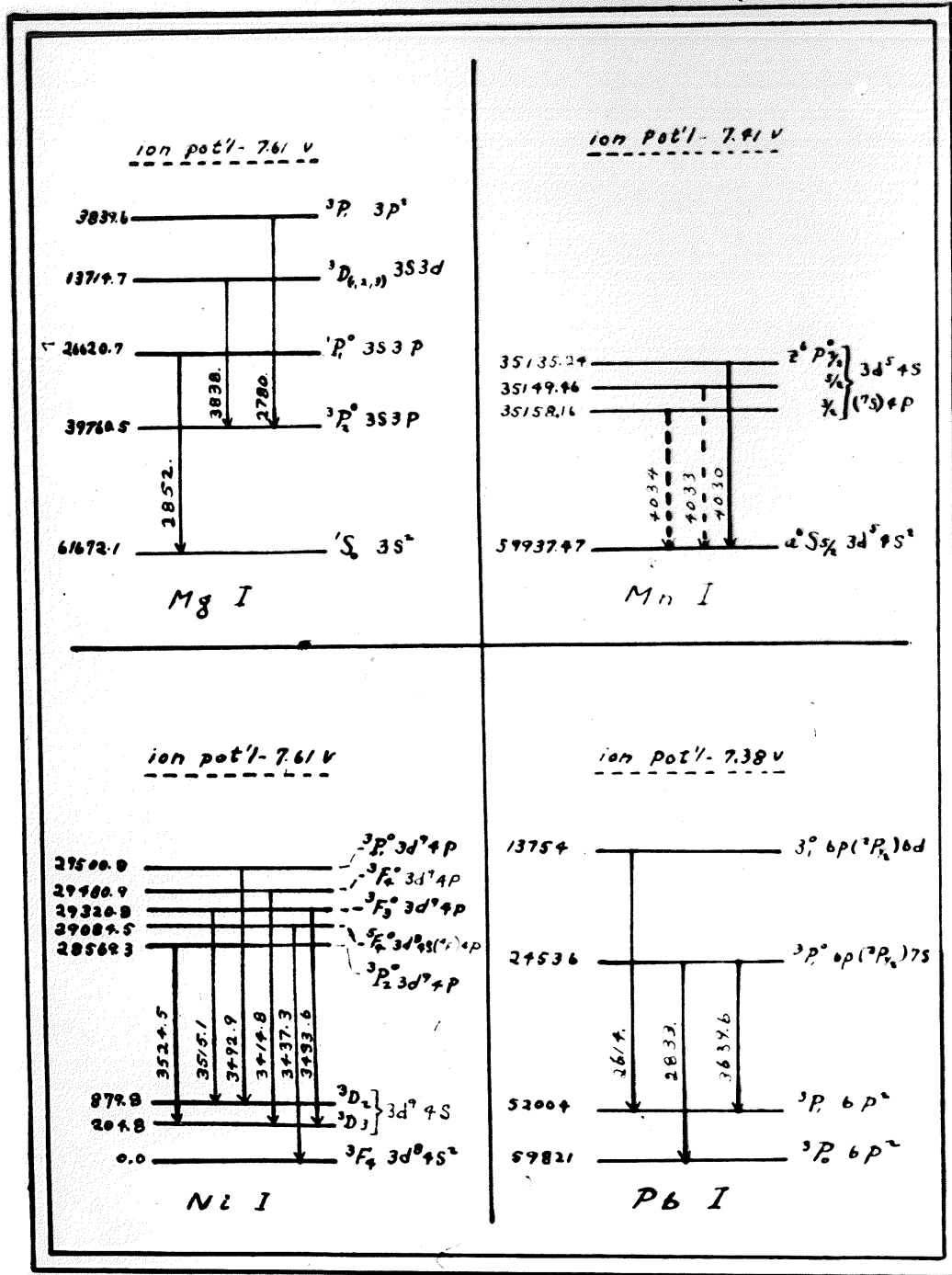


Plate VI

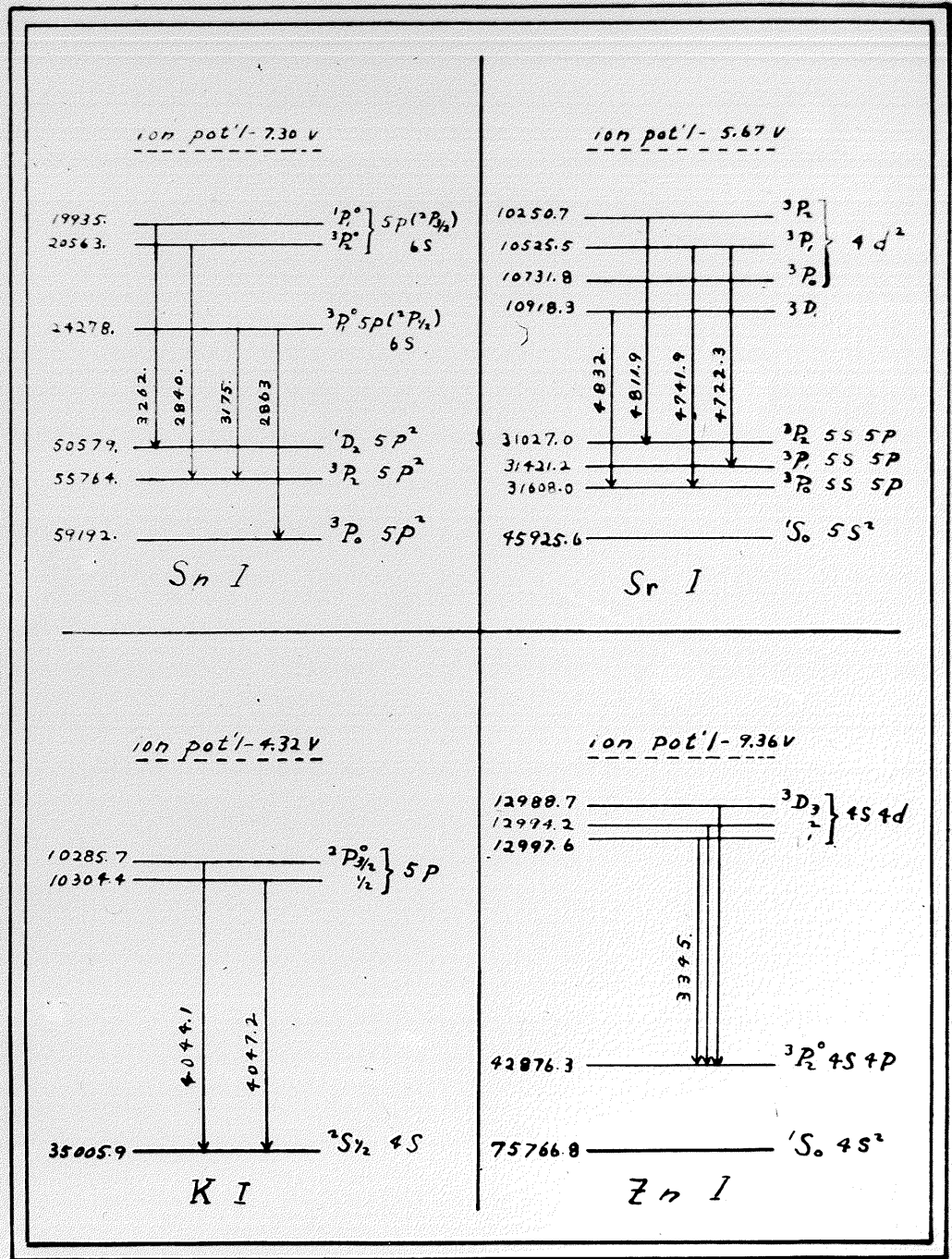


Plate VII

(III) RESULTS.

The data ^{are} ~~is~~ presented in the form of tables. All the ratios are given in terms of the ratios obtained ^{with} ~~upon~~ no addition to the standard sample. The ratio values are accurate to within two significant figures. Graphs were used where it was found convenient.

(a) Results with minimum breakdown potential.

Table 3

Standard sample:	#1				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Ag:Sn					
3382:3262	1.0	.97	.99	1.37	1.27
3280:3175	1.0	1.02	.98	1.21	1.24
3382:3175	1.0	1.00	.95	1.16	1.15
3280:3262	1.0	1.04	.98	1.24	1.41
Sn:Mg					
3262:2852	1.0	.98	1.11	1.08	1.60
3175:2852	1.0	.98	1.17	1.07	1.75
3262:3838	1.0	.94	.94	1.37	2.70
3175:3838	1.0	.90	.97	1.36	2.83
Ag:Mg					
3382:2852	1.0	.97	1.09	1.43	2.00
3280:2852	1.0	1.01	1.16	1.31	2.16
3382:3838	1.0	.92	.93	1.67	3.31
3280:3838	1.0	.92	.95	1.69	3.73

(Each determination is a mean of 9 readings.)

Table 4

Standard sample:	#1 buffered with potassium acetate				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Ag:Sn					
3382:3262	1.0	1.06	1.05	1.42	1.68
3280:3175	1.0	1.16	1.07	1.41	1.55
3382:3175	1.0	1.09	1.04	1.39	1.58
3280:3262	1.0	1.08	1.08	1.43	1.65
Sn:Mg					
3262:2852	1.0	1.02	.95	.86	.79
3175:2852	1.0	1.01	.95	.87	.89
3175:3838	1.0	1.03	1.04	1.55	1.39
3262:3838	1.0	1.05	1.04	1.55	1.31
Ag:Mg					
3382:2852	1.0	1.10	1.00	1.21	1.33
3280:2852	1.0	1.12	1.03	1.23	1.35
3382:3838	1.0	1.12	1.10	2.16	2.20
3280:3838	1.0	1.15	1.13	2.21	2.19

(Each determination is a mean of 9 readings.)

Table 5

Standard sample:	#2				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Ag:Sn					
3382:3262	1.0	1.03	1.16	1.41	1.67
3280:3175	1.0	1.05	1.19	1.28	1.42
3382:3175	1.0	1.09	1.16	1.37	1.53
3280:3262	1.0	1.00	1.19	1.36	1.52
Ag:Pb					
3382:3640	1.0	1.11	1.28	1.47	2.14
3382:2833	1.0	1.20	1.38	1.24	1.87
3382:2614	1.0	1.36	1.35	1.64	2.15
3280:3640	1.0	1.07	1.29	1.42	1.99
3280:2833	1.0	1.16	1.41	1.20	1.74
3280:2614	1.0	1.32	1.38	1.58	2.02

(Table 5 cont'd.)

Sn:Pb					
3262:3640	1.0	1.00	1.02	1.00	
3262:2833	1.0	1.16	1.18	.87	1.15
3262:2614	1.0	1.34	1.18	1.19	1.37
3175:3640	1.0	1.02	1.04	1.08	1.40
3175:2833	1.0	1.09	1.19	.89	1.22
3175:2614	1.0	1.26	1.18	1.20	1.42

(Each determination is a mean of 4 readings.)

Table 6

Standard sample: #2 buffered with potassium acetate.

Extraneous material: none KCl NH₄Cl LiCl H₃BO₃

<u>Line ratio</u>	<u>none</u>	<u>KCl</u>	<u>NH₄Cl</u>	<u>LiCl</u>	<u>H₃BO₃</u>
Ag:Sn					
3382:3262	1.0	1.32	1.45	1.36	1.55
3280:3175	1.0	1.17	1.25		1.35
3382:3175	1.0	1.14	1.20	1.19	1.28
3280:3262	1.0	1.23	1.47	1.27	1.64
Ag:Pb					
3382:3640	1.0	.78	.68	1.23	1.20
3383:2833	1.0	.76	.69	1.09	.95
3382:2614	1.0	.78	.71	1.16	1.00
3280:3640	1.0	.78	.70	1.22	1.12
3280:2833	1.0	.77	.72	1.12	1.03
3280:2614	1.0	.78	.73	1.16	1.17
Sn:Pb					
3262:3640	1.0	.58	.48		
3262:2833	1.0	.58	.48		
3262:2614	1.0	.58	.49	.89	.72
3175:3640	1.0	.67	.57	1.11	.89
3175:2833	1.0	.69	.58	1.00	.86
3175:2614	1.0	.69	.60	1.06	

(Each determination is a mean of 4 readings.)

Table 7

Standard sample: # 3

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
<u>Mn:Ni</u>					
4030:3515	1.0	1.35	1.24	1.38	1.21
4030:3415	1.0	1.34	1.19	1.31	.96
2610:3415	1.0	.37	.61	.29	.55
2610:3515	1.0	.36	.60	.30	.71
2632:3515	1.0	.35	.56	.28	.70
2632:3415	1.0	.35	.61	.28	.54
<u>Ni:Mg</u>					
3515:2852	1.0	.90	.97	.93	.91
3415:2852	1.0	.90	.97	.98	1.19
3515:3838	1.0	.91	1.07	1.24	
3415:3838	1.0-	.90	1.30		
<u>Mn:Mg</u>					
2632:2852	1.0	.52	.61	.26	.63
4030:2852	1.0	1.23	1.20	1.28	1.15

(Each determination is a mean of 4 readings.)

Table 8

Standard sample: # 3 buffered with potassium acetate.

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
<u>Mn:Ni</u>					
4030:3515	1.0	.98	1.12	1.01	1.14
4030:3415	1.0	1.00	1.20	1.09	1.18
2610:3415	1.0	.95	.85	1.01	.97
2610:3515	1.0	.92	.79	.90	.93
<u>Ni:Mg</u>					
3515:2852	1.0	1.06	.97	.95	.92
3415:2852	1.0	1.04	.92	.87	.89
3515:3838	1.0	1.10	1.02	1.67	1.16
3415:3838	1.0	1.08	.96	1.51	1.11

(Table 8 cont'd.)

Mn:Mg					
4030:2852	1.0	1.05	1.10	.95	1.05
2610:2852	1.0	.97	.79	.88	.87
4030:3838	1.0	1.09	1.17	1.67	1.34
2610:3838	1.0	1.04	.83	1.55	1.10

(Each determination is a mean of 4 readings.)

Table 9

Standard sample: #4

Extraneous material: none KCl NH₄Cl LiCl H₃BO₃

Line ratio

Sn:Mg					
3262:2852	1.0	.84	1.08	.89	1.18
3175:2852	1.0	.84	1.09	.92	1.25
3262:3838	1.0	.91	1.30	1.06	2.29
3175:3838	1.0	.88	1.27	1.06	2.36

Ni:Mg					
3515:2852	1.0	1.03	1.03	1.04	.96
3415:2852	1.0	.87	1.01	.92	1.11
3515:3838	1.0	1.05	1.17	1.24	1.81
3492:2852	1.0	1.05	.96	.99	.93
3524:2852	1.0	.96	1.03	1.02	1.11
3492:3838	1.0	.99	1.13	1.18	1.75
3524:3838	1.0	1.01	1.18	1.21	2.12

Ni:Sn					
3524:3175	1.0	1.21	.93	1.13	.90
3515:3175	1.0	1.19	.92	1.15	.77
3493:3175	1.0	1.14	.90	1.10	.74
3415:3175	1.0	1.05	.94	1.01	.90
3524:3262	1.0	1.14	.92	1.16	.95
3515:3262	1.0	1.18	.92	1.19	1.09
3493:3262	1.0	1.14	.89	1.14	.78

(Each determination is a mean of 4 readings.)

Table 10

Standard sample: #4 buffered with potassium acetate

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Sn:Mg					
3262:2852	1.0	.98	1.06	.74	.75
3175:2852	1.0	1.02	1.05	.80	.80
3262:3838	1.0	1.04	1.16	1.17	1.17
3175:3838	1.0	1.09	1.15	1.28	1.24
Ni:Mg					
3515:2852	1.0	.93	.87	.87	.80
3414:2852	1.0	1.00	.93	.91	.86
3515:3838	1.0	1.00	.95	1.39	1.25
3415:3838	1.0	1.06	1.02	1.49	1.35
3492:2852	1.0	.94	.88	.85	.82
3524:2852	1.0	.95	.93	.96	.91
3493:3838	1.0	1.00	.96	1.35	1.22
Ni:Sn					
3524:3175	1.0	.98	.91	1.20	1.17
3515:3175	1.0	.92	.84	1.08	1.02
3493:3175	1.0	.93	.86	1.05	.99
3415:3175	1.0	.96	.90	1.16	1.11
3524:3262	1.0	1.02	.90	1.30	1.23
3515:3262	1.0	.92	.80	1.13	1.04
3493:3262	1.0	.98	.85	1.15	1.09

(Each determination is a mean of 4 determinations.)

Table 11

Standard sample: # 5

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Ba:Ca					
4903:4679	1.0	.84	.69	.55	.51
4903:3403	1.0	.93	.78	.64	.55
4283:4679	1.0	1.12	1.13	1.27	.47
4283:3403	1.0	1.23	1.30	1.50	.52
3501:4679	1.0	1.00	1.13	1.20	.48
3501:3403	1.0	1.10	1.29	1.42	.53
Ba:Sn					
4903:3175	1.0	.97	.72	.43	.45
4903:2863	1.0	.99	.65	.45	.48

(Table 11 cont'd)

Ba:Sn					
4903:2840	1.0	1.01	.65	.46	.48
4283:3175	1.0	1.31	1.03	1.02	.43
4283:2863	1.0	1.32	1.02	1.06	.46
4283:2840	1.0	1.34	1.07	1.08	.45
3501:3175	1.0	1.17	1.04	.97	.44
3501:2863	1.0	1.16	1.02	1.01	.46
3501:2840	1.0	1.19	1.08	1.03	.45
Cd:Sn					
4678:3175	1.0	1.15	.94	.80	.84
4678:2863	1.0	1.19	.94	.85	.95
4678L2840	1.0	1.20	.97	.85	.94
3404:3175	1.0	1.05	.84	.69	.83
3404:2863	1.0	1.08	.84	.72	.88
3404:2840	1.0	1.09	.85	.72	.86

(Each determination is a mean of 2 readings.)

Table 12

Standard sample: #5 buffered with potassium acetate.

Extraneous material: none KCl NH₄Cl LiCl H₃BO₃

Line ratio

	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
Ba:Ca					
4903:4679	1.0	1.02	1.18	.93	1.20
4903:3403	1.0	1.02	1.17	.90	1.22
4283:4678	1.0	1.07	1.03	.89	1.18
4283:3403	1.0	1.08	1.02	.87	1.23
3501:4679	1.0	1.05	1.07	.94	1.20
3501:3404	1.0	1.05	1.05	.92	1.25
Ba:Sn					
4903:3175	1.0	.78	1.37	.95	1.07
4903:2863	1.0	.77	1.46	.94	1.10
4903:2840	1.0	.82	1.41	.95	1.09
4283:3175	1.0	.83	1.18	.91	1.07
4283:2863	1.0	.82	1.28	.90	1.10
4283:2840	1.0	.86	1.21	.91	1.08
3501:3175	1.0	.81	1.22	.97	1.08
3501:2840	1.0	.79	1.30	.94	1.10
3501:2840	1.0	.83	1.23	.96	1.09

(Table 12 cont'd.)

Cd:Sn						
4678:3175	1.0	.78	1.17	1.03	.91	
4678:2863	1.0	.76	1.24	1.02	.92	
4678:2840	1.0	.81	1.18	1.02	.91	
3404:3175	1.0	.76	1.17	1.06	.88	
3404:2863	1.0	.76	1.25	1.03	.89	
3404:2840	1.0	.78	1.18	1.04	.86	

(Each determination is a mean of 2 readings.)

Table 13

Standard sample: # 6

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Al:Mg					
3962:3838	1.0	.97	1.10	.98	1.14
3962:2852	1.0	.96	1.01	.82	.63
3944:3838	1.0	1.05	1.14	1.02	1.20
3944:2852	1.0	1.06	1.05	.82	.66
3082:3838	1.0	1.04	1.06	.85	1.05
3082:2852	1.0	1.06	.99	.72	.58
3093:3838	1.0	1.03	1.01	.87	.98
3093:2852	1.0	1.05	.95	.75	.54
Sr:Mg					
4832:3838	1.0	1.60	.99	1.02	.69
4832:2852	1.0	1.61	.93	.85	.37
4812:3838	1.0	1.58	1.02	1.06	1.16
4812:2852	1.0	1.54	.93	.86	.62
4742:3838	1.0	1.63	.94	.97	.69
4742:2852	1.0	1.66	.88	.82	.38
4722:3838	1.0	1.65	.98	1.01	.75
4722:2852	1.0	1.66	.91	.85	.41
Sr:Al					
4832:3962	1.0	1.68	.92	1.04	.60
4832:3944	1.0	1.52	.86	1.03	.56
4832:3092	1.0	1.56	.99	1.16	.70
4832:3082	1.0	1.53	.94	1.20	.65
4742:3962	1.0	1.73	.87	.99	.61
4742:3944	1.0	1.58	.83	.99	.67
4742:3093	1.0	1.60	.94	1.10	.71
4742:3083	1.0	1.58	.89	1.14	.66

(Table 13 cont'd.)

4722:3962	1.0	1.73	.90	1.04	.65
4722:3944	1.0	1.56	.86	1.02	.65
4722:3093	1.0	1.60	.96	1.15	.78
4722:3082	1.0	1.58	.92	1.20	.71
4812:3962	1.0	1.67	.95	1.08	1.01
4812:3044	1.0	1.50	.89	1.08	.95
4812:3092	1.0	1.52	1.01	1.18	1.17
4812:3083	1.0	1.52	.97	1.24	1.09

(Each determination is a mean of 2 readings.)

Table 14

Standard sample: # 6 buffered with potassium acetate.

Extraneous material: none KCl NH₄Cl LiCl H₃BO₃

Line ratio

		KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
Al:Mg					
3962:3838	1.0	1.01	1.07	1.10	.94
3962:2852	1.0	.97	1.08	.94	.86
3944:3838	1.0	1.05	1.02	1.11	.89
3944:2852	1.0	.94	1.00	.94	.82
3082:3838	1.0	1.12	1.02	1.10	.90
3082:2852	1.0	1.00	1.03	.94	.84
3093:3838	1.0	1.11	1.05	1.16	.94
3093:2852	1.0	.98	1.04	.98	.86

Sr:Mg					
4832:3838	1.0	.89	.98	.95	.90
4832:2852	1.0	.80	.98	.80	.82
4812:3838	1.0	.98	1.05	1.03	.93
4812:2852	1.0	.88	1.06	.88	.87
4742:3838	1.0	.88	1.03	.95	1.07
4742:2852	1.0	.79	1.01	.79	.98
4722:3838	1.0	.89	1.06	.99	1.04
4722:2852	1.0	.81	1.06	.84	.97

Sr:Al					
4832:3962	1.0	.82	.91	.85	.95
4832:3944	1.0	.84	.97	.85	1.01
4832:3092	1.0	.82	.93	.83	.95
4832:3082	1.0	.80	.94	.84	.97
4742:3962	1.0	.80	.94	.85	1.12
4742:3944	1.0	.82	.99	.83	1.19

(Table 14 cont'd.)

4742:3093	1.0	.80	.95	.81	1.12
4742:3083	1.0	.78	.96	.83	1.14
4722:3962	1.0	.82	.98	.88	1.11
4722:3944	1.0	.85	1.04	.88	1.18
4722:3092	1.0	.81	1.00	.85	1.12
4722:3082	1.0	.80	1.02	.88	1.14
4812:3962	1.0	.90	.98	.92	1.00
4812:3944	1.0	.93	1.03	.91	1.06
4812:3092	1.0	.90	.99	.88	.99
4812:3083	1.0	.88	1.02	.92	1.03

(Each determination is a mean of 2 readings.)

Table 15

Standard sample: # 7					
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Sr:Ni					
4832:3524	1.0	2.40	1.01	1.26	.17
4832:3515	1.0	2.38	1.08	1.38	.22
4832:3492	1.0	2.40	1.12	1.37	.21
4832:3415	1.0	2.35	1.03	1.26	.18
4742:3524	1.0	2.06	.98	1.18	.22
4742:3515	1.0	2.07	1.05	1.29	.29
4742:3492	1.0	2.07	1.06	1.28	.30
4742:3415	1.0	2.04	.99	1.17	.52
Sr:Zn					
4832:3345	1.0	2.74	.98	1.98	.29
4742:3345	1.0	2.40	.95	1.85	.40
Zn:Ni					
3345:3524	1.0	.87	1.02	.65	.57
3345:3515	1.0	.88	1.09	.71	.72
3345:3492	1.0	.88	1.16	.70	.73
3345:3415	1.0	.85	1.04	.64	.62

(Each determination is a mean of 2 readings.)

Table 16

Standard sample: # 7 buffered with potassium acetate

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Sr:Ni					
4832:3524	1.0	1.00	.89	.92	.58
4832:3515	1.0	.97	.89	.92	.58
4832:3492	1.0	1.03	.93	.96	.59
4832:3415	1.0	1.05	.96	.98	.66
4742:3524	1.0	.97	.93	.98	.52
4742:3515	1.0	.96	.94	.99	.52
4742:3492	1.0	1.01	.97	1.02	.52
4742:3415	1.0	1.04	1.00	1.04	.54
Sr:Zn					
4832:3345	1.0	.99	.94	.97	.49
4742:3345	1.0	.97	.98	1.03	.45
Zn:Ni					
3345:3524	1.0	1.01	.95	.95	1.18
3345:3515	1.0	.97	.94	.94	1.17
3345:3492	1.0	1.05	1.00	1.00	1.19
3345:3415	1.0	1.07	1.02	1.01	1.22

(Each determination is a mean of 2 readings.)

(a') Results for reversing the order of loading.

Table 17

Standard sample: # 2

Order of loading	AgNO ₃ first	AgNO ₃ last
Extraneous material:	none LiCl	none LiCl
<u>Line ratio</u>		
Sn3175:Pb2833	.94 .80	.93 .80
Ag3281:Sn3175	3.95 4.49	3.30 5.00

(b) Results with various additions of boric acid.

Table 18

Standard sample: # 4

Boric acid (gm.x10⁻³/cc.) 0.00 1.06 2.13 4.24 6.02 8.24 10.3

Line ratio

	0.00	1.06	2.13	4.24	6.02	8.24	10.3
Ni:Mg							
3524:3838	1.00	1.38	1.44	1.86	2.08	2.65	2.60
3524:2852	1.00	1.05	1.10	1.04	1.11	1.01	.82
3515:3838	1.00	1.16	1.27	1.40	1.52	1.74	2.07
3515:2780	1.00	.90	.93	.93	1.08	1.03	1.03
3427:2852	1.00	.92	.98	.90	.98	.98	1.08
3415:2852	1.00	.99	1.00	.98	1.02	.92	.92

Ni:Sn							
3524:2863	1.00	.92	.90	.90	1.06	.92	.64
3515:2863	1.00	.78	.79	.69	.78	.62	.51
3437:3262	1.00	.75	.74	.77	.97	1.05	1.17
3415:3262	1.00	.80	.75	.83	1.00	.98	.98

Sn:Mg							
3262:3838	1.00	1.57	1.73	2.07	1.90	2.52	3.00
3262:2852	1.00	1.22	1.32	1.18	1.02	.95	.93
3175:3838	1.00	1.54	1.70	2.17	2.17	3.13	4.25
3175:2852	1.00	1.18	1.31	1.24	1.15	1.24	1.31
2863:2852	1.00	1.14	1.22	1.15	1.04	1.10	1.25

(Each determination is amean of 2 readings.)

(c) Effects of current variation.

Table 19

Standard sample: #4 /LiCl, Buffered # 4 / LiCl

Current (amp,) 1.3 1.8 2.2 1.5 2.0

Line ratio

Ni:Mg					
3515:2852	1.0	.81	.70	1.0	.82
3415:2852	1.0	.84	.75	1.0	.91
3524:2852	1.0	.83	.75	1.0	.91
3415:3838	1.0	.93	.97	1.0	1.00

(Table 19 cont'd.)

Sn:Mg						
3175:2852	1.0	.81	.70	1.0	. 82 .91	
3262:2852	1.0	.80	.70	1.0	.92	
2840:3838	1.0	1.01	1.05	1.0	1.14	
Ni:Sn						
3524:3175	1.0	1.00	1.00	1.0	1.00	
3524:3262	1.0	1.04	1.08	1.0	1.01	
3515:3175	1.0	.97	.94	1.0	.91	

(d) Results with constant current (2.3 amps.).

Table 20

Standard sample:	# 1				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Ag:Sn					
3382:3262	1.0	1.05	.96	1.42	1.33
3280:3175	1.0	.91	.88	1.23	1.18
3382:3175	1.0	1.04	.92	1.37	1.24
3280:3262	1.0	.80	.93	1.28	1.21
3383:2840	1.0	1.24	1.06	1.52	1.18
3281:2840	1.0	1.08	1.02	1.38	1.16
Ag:Mg					
3382:2852	1.0	1.33	1.20	1.66	1.61
3280:2852	1.0	1.15	1.16	1.50	1.57
3382:3838	1.0	1.44	1.06	2.44	2.25
3280:3838	1.0	1.26	1.03	2.19	2.19
Sn:Mg					
3262:2852	1.0	1.26	1.25	1.18	1.21
3175:2852	1.0	1.28	1.30	1.22	1.31
3262:3838	1.0	1.37	1.11	1.74	1.70
3175:3838	1.0	1.40	1.18	1.80	1.85
2840:2852	1.0	1.07	1.14	1.08	1.36
2840:3838	1.0	1.17	.99	1.60	1.89

Table 21

Standard sample:	#1 buffered with potassium acetate.				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Ag:Sn					
3382:3262	1.0	1.03	1.13	1.28	1.18
3280:3175	1.0	1.08	1.02	1.28	1.12
3382:3175	1.0	1.02	1.08	1.30	1.18
3280:3262	1.0	1.02	1.07	1.27	1.17
3383:2840	1.0	1.09	1.16	1.36	1.09
3281:2840	1.0	1.07	1.10	1.38	1.16
Ag:Mg					
3382:2852	1.0	1.01	1.04	1.01	1.05
3280:2852	1.0	1.00	.98	1.02	1.04
3382:3838	1.0	1.09	.99	1.14	1.12
3280:3838	1.0	1.08	.95	1.16	1.13
Sn:Mg					
3262:2852	1.0	1.00	.92	.79	.90
3175:2852	1.0	.99	.97	.80	.92
3262:3838	1.0	1.07	.88	.89	1.24
3175:3838	1.0	1.06	.90	.90	.97
2840:2852	1.0	.95	.90	.75	.90
2840:3838	1.0	1.02	.86	.83	.96

(Each determination is a mean of 4 readings.)

Table 22

Standard sample:	#2				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Ag:Sn					
3382:3262	1.0	1.22	1.25	1.57	1.31
3280:3175	1.0	1.06	1.15	1.37	1.24
3383:3175	1.0	1.25	1.18	1.45	1.26
3280:3262	1.0	1.05	1.22	1.50	1.30
3383:2840	1.0	1.30	1.25	1.62	1.35
3280:2840	1.0	1.11	1.24	1.57	1.34

(Table 22 cont'd.)

Ag:Pb					
3383:3640	1.0	1.01	1.07	1.26	1.70
3383:2833	1.0	1.28	1.28	1.27	1.61
3383:2614	1.0	1.62	1.34	1.89	1.82
3280:3640	1.0	1.02	1.05	1.20	1.67
3280:2833	1.0	1.10	1.26	1.21	1.60
3280:2614	1.0	1.38	1.31	1.77	1.79

Sn:Pb					
3262:3640	1.0	.99	.86	.81	1.29
3262:2833	1.0	1.05	1.03	.82	1.23
262					
3262:2614	1.0	1.32	1.10	1.22	1.38
3175:2640	1.0	.97	.92	.89	1.35
3175:2833	1.0	1.04	1.09	.90	1.19
3175:2614	1.0	1.30	1.14	1.29	1.20
2840:2833	1.0	1.01	1.03	.77	1.18
2840:3640	1.0	.93	.86	.77	1.25

(Each determination is a mean of 4 readings.)

Table 23

Standard sample: #2 buffered with potassium acetate.

Extraneous material: none KCl NH₄Cl LiCl H₃BO₃

Line ratio

Ag:Sn					
3382:3262	1.0	1.12	1.02	1.10	1.07
3280:3175	1.0	1.13	.97	1.12	1.09
3383:3175	1.0	1.10	1.02	1.06	1.06
3280:3262	1.0	1.21	.99	.97	1.13
3383:2840	1.0	1.13	1.03	1.10	1.11
3280:2840	1.0	1.15	.97	1.16	1.15

Ag:Pb					
3383:3640	1.0	1.16	1.07	1.44	1.06
3383:2833	1.0	1.16	1.10	1.22	.99
3383:2614	1.0	1.20	1.16	1.27	.94
3280:3640	1.0	1.19	1.17	1.48	1.09
3280:2833	1.0	1.16	1.06	1.25	1.03
3280:2614	1.0	1.20	1.14	1.31	1.10

(Table 23 cont'd.)

Sn:Pb					
3262:3640	1.0	1.02	1.21	1.35	1.29
3262:2833	1.0	1.00	1.10	1.15	.95
3262:2614	1.0	1.04	1.15	1.20	1.01
3175:3640	1.0	1.06	1.24	1.37	1.01
3175:2833	1.0	1.03	1.10	1.16	.95
3175:2614	1.0	1.07	1.42	1.21	1.02
2840:2833	1.0	1.01	1.10	1.14	.91
2840:3640	1.0	1.04	1.22	1.35	.97
2840:2614	1.0	1.05	1.16	1.20	#07 .97

(Each determination is a mean of 4 readings.)

(e) Results for the spark gap illuminated with ultra violet light.

Table 24

Standard sample:	# 1				
Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Ag:Sn					
3382:3262	1.0	.86	.90	1.12	1.65
3280:3175	1.0	.88	.84	1.20	1.50
3382:3175	1.0	.86	.87	1.10	1.47
3280:3262	1.0	.86	.88	1.19	1.70
Sn:Mg					
3262:2852	1.0	1.06	1.31	.91	1.22
3262:3838	1.0	1.02	1.31	1.04	1.64
3175:3838	1.0	.99	1.35	1.04	1.86
Ag:Mg					
3280:2852	1.0	.90	1.13	1.07	2.06
3382:3838	1.0	.85	1.17	1.10	2.70
3280:3838	1.0	.92	1.14	1.22	2.80

(Each determination is a mean of 2 readings.)

(f) Results with increased capacity in the discharge circuit
and ultra violet light illumination of the spark gap.

Table 25

Standard sample: # 1

Extraneous material: none KCl NH₄Cl LiCl H₃BO₃

Line ratio

	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
Ag:Sn					
3382:3262	1.0	.85	.81	1.12	1.31
3280:3175	1.0	.93	.95	1.22	1.37
3382:3175	1.0	.87	.86	1.12	1.25
3280:3262	1.0	.90	.91	1.22	1.44
3382:2840	1.0	.91	.86	1.19	1.26
3280:2840	1.0	1.00	.97	1.30	1.40

Sn:Mg					
3262:2852	1.0	1.02	1.49	1.12	1.38
3175:2852	1.0	1.01	1.44	1.13	1.49
3262:3838	1.0	.81	1.20	1.17	2.64
3175:3838	1.0	.80	1.15	1.20	2.83
3262:2780	1.0	.93	1.20	1.27	2.00
3175:2780	1.0	.90	1.15	1.27	2.10
2840:2780	1.0	.84	1.13	1.18	2.04
2840:2852	1.0	.94	1.40	1.04	1.43
2840:3838	1.0	.74	1.12	1.10	2.72

Ag:Mg					
3382:2852	1.0	.86	1.21	1.24	1.81
3280:2852	1.0	.92	1.35	1.35	1.99
3382:3838	1.0	.68	.97	1.32	3.50
3280:3838	1.0	.73	1.08	1.43	3.80
3382:2780	1.0	.77	.98	1.35	2.50
3280:2780	1.0	.83	1.09	1.54	2.85

(Each determination is a mean of 2 readings.)

Table 26

Standard sample: # 1 buffered with potassium acetate.

Extraneous material:	none	KCl	NH ₄ Cl	LiCl	H ₃ BO ₃
<u>Line ratio</u>					
Ag:Sn					
3382:3262	1.0	1.18	.86	2.10	1.38
3280:3175	1.0	1.08	.84	1.86	1.32
3382:3175	1.0	1.22	.93	2.03	1.42
3280:3262	1.0	1.04	.82	1.93	1.28
3382:2840	1.0	1.13	1.01	2.05	1.36
3281:2840	1.0	1.01	.97	1.90	1.24
Sn:Mg					
3262:2852	1.0	.96	1.59	.63	1.56
3175:2852	1.0	.94	1.48	.65	1.52
3262:3838	1.0	1.26	2.28	1.15	2.98
3175:3838	1.0	1.21	2.11	1.20	2.92
3262:2780	1.0	1.10	1.63	1.05	1.88
3175:2780	1.0	1.07	1.52	1.01	1.71
2840:2780	1.0	1.15	1.40	1.00	1.92
2840:2852	1.0	1.00	1.36	.64	1.60
2840:3838	1.0	1.30	1.95	3.56	3.05
Ag:Mg					
3382:2852	1.0	1.14	1.38	1.33	2.17
3280:2852	1.0	1.01	1.31	1.22	2.02
3382:3838	1.0	1.48	1.95	2.48	4.10
3280:3838	1.0	1.32	1.89	2.27	3.74
3382:2780	1.0	1.37	1.48	2.17	2.73
3280:2780	1.0	1.18	1.34	1.88	2.43

(Each determination is a mean of 2 readings.)

(g) Data on complex salt.

Table 27

Standard sample: Complex salt.

Extraneous material:	none	CaSO ₄	NH ₄ SO ₄	Na ₂ SO ₄	ZnSO ₄
<u>Line ratio</u>					
K:Al					
3047:3961	1.0	2.04	4.46	.55	1.79
3047:3944	1.0	2.12	4.96	.51	2.02
3047:3098	1.0	2.24	3.41	.53	1.78
3047:3082	1.0	2.13	4.14	.57	1.87
K:Mg					
3047:3838	1.0	1.99	2.86	.68	1.95

(Table 27 cont'd.)

3047:2852	1.0	1.99	2.86	.68	1.95
3047:2780	1.0	2.05	3.37	.85	2.08
Al:Mg					
3962:3838	1.0	1.10	.75	1.44	1.04
3962:2852	1.0	.95	.64	1.22	1.07
3962:2780	1.0	.96	.88	1.49	1.13
3944:3838	1.0	1.07	.64	1.37	.90
3944:2852	1.0	.93	.55	1.16	.92
3944:2780	1.0	.96	.81	1.46	1.20
3082:3838	1.0	1.11	.73	1.34	1.00
3082:2852	1.0	.97	.64	1.16	1.03
3082:2780	1.0	1.00	.89	1.46	1.11

(Each determination is a mean of 3 readings.)

(IV) DISCUSSION.

Results given in the Tables are averages of at least 2 determinations; in many the results are averages of 4 and in certain instances of 9 determinations. The mean error calculated for 200 readings chosen at random over the results of several plates is 5.5 % with a standard deviation of 3.5 %.

(a) Results obtained with minimum breakdown potential.

The tables of section III (a) confirm and considerably extend the results of the previous investigators (8). They show that additions of extraneous material to standard samples commonly cause marked changes in the intensity ratios of investigated line pairs. Furthermore, the nature of the intensity changes depends on the kind of substances added, the elements giving rise to the line pair investigated, and the particular lines considered. For example, in the standard sample #2 (Sn, Ag and Pb) Table 5 the line ratio Ag3280:Pb3640 increased by 7% on the addition of potassium chloride, but Ag3280:Pb2614 increased by 32% under exactly the same conditions. However when boric acid was used instead of potassium chloride, these same ratios increased by 99% and 102% respectively. The same type of behaviour occurred for Ni3524:Mg2852 and Ni3515:Mg3838 in standard sample #4 Table 9 , to Ba4283:Cd3404 and Ba3501:Cd4679 in standard sample #5 table 11.

The data indicate that this dependence of the intensity ratio on the general sample composition may be a serious matter in certain types of analyses if high accuracy is desired.

In the attempt to obtain some knowledge concerning the factors responsible for this dependence, the elements for the standard sample were chosen with respect to the ionization potentials and the atomic masses. In order to correlate the changes in the line intensity ratios and the characteristics of the elements, the data ^{were} ~~was~~ arranged as in table (28).

The first column gives the elements; the second column gives the line ratios; the third column gives the ratios of the excitation potentials of these lines; the fourth column gives the classifications of the lines and the fifth the average deviation "d" from unity produced by the extraneous material on the buffered and the unbuffered samples. For example: for the Ni3524:Mg2852 line intensity ratio the mean deviation from unity for the four extraneous materials in table 9 is

$$\frac{.04 \neq .03 \neq .02 \neq .11}{4} = .05 \text{ and for table 10 it is}$$

$$\frac{.05 \neq .07 \neq .04 \neq .09}{4} = .07\%. \text{ The mean of these two is } .06\%.$$

This is the value for "d" for this line intensity ratio in table (28). Similarly for all the other ratios. The table is arranged in ascending values of "d".

Table 28

<u>Elements</u>	<u>Ratio</u>	<u>Exc't Pot'l</u>	<u>Classification</u>	<u>"d"</u>
Ni:Mg	3524:2852	28569:25051	D-P:S-P	.06
Ni:Mg	3515:2852	29321:35051	D-F:S-P	.07
Al:Mg	3093:3838	32437:47957	P-D:P-D	.07
Al:Mg	3962:3838	25348:47957	P-S:P-D	.07
Ni:Sn	3415:3175	29481:34914	D-F:P-P	.08
Al:Mg	3082:3838	32436:47957	P-D:P-D	.08
Ni:Mg	3493:2852	29501:35051	D-P:S-P	.09
Al:Mg	3944:3838	25348:47957	P-S:P-D	.09
Ni:Sn	3493:3175	29501:34914D	D-P:P-P	.11
Mn:Mg	2610:2852			.12
Al:Mg	3962:2852	25348:35051	P-S:S-P	.12
Al:Mg	3944:2852	25348:35051	P-S:S-P	.12
Al:Mg	3082:2852	32436:35051	P-D:S-P	.12
Sr:Mg	4812:3838	35675:47957		.12
Cd:Sn	4678:3175	51484:34914	P-S-P-P	.12
Sn:Mg	3175:2852	34914:35051	P-P:S-P	.12
Ni:Sn	3493:3262	29501:39257	D-P:D-P	.13
Ni:Sn	3515:3262	29321:39257	D-F:D-P	.13
Ni:Sn	3524:3175	28569:34914	D-P:P-P	.13
Al:Mg	3093:2852	32437:35051	P-D:S-P	.13
Sr:Al	4812:3962	35675:25348		.13
Sr:Al	4812:3944	35675:25348		.13
Cd:Sn	4678:2863	51484:34914	P-S:P-P	.13
Ni:Sn	3524:3262	28569:39257	D-P:D-P	.14
Mn:Mg	4030:2852	24802:35051	P-S:S-P	.14
Sn:Mg	3262:2852	39257:35051	D-P:S-P	.14
Sr:Mg	4722:3838	35400:47957		.14
Zn:Ni	3345:3515	74478:29321	P-D:D-F	.14
Zn:Ni	3345:3492	74478:29501	P-D:D-P	.14
Zn:Ni	3345:3524	74478:28569	P-D:D-P	.15
Zn:Ni	3345:3415	74478:29481	P-D:D/F	.15
Ba:Cd	3501:4679	28554:51484		.15
Cd:Sn	3403:3175	59487:34914	P-D:P-P	.15
Cd:Sn	3403:2863	59487:34914	P-D:P-P	.15
Cd:Sn	3403:2840	59487:38629	P-D:P-P	.15
Ba:Sn	3501:3175	28554:34914		.16
Sr:Mg	4832:3838	35194:47957	P-D:P-D	.16
Mn:Ni	4030:3415	24802:29481	S-P:D-F	.17
Ni:Mg	3515:3838	29321:47957	D-F:P-D	.17
Sr:Mg	4722:3838	35400:47957		.17
Ni:Mg	3415:3838	29481:47957	D-F:P-D	.18
Sr:Al	4722:3093	35400:32437		.18
Ba:Cd	4903:3403	33905:59487	P-S:P-D	.18
Ba:Cd	4283:4679	34736:51484		.18
Ba:Sn	3501:2863	28554:34914		.18
Ba:Sn	3501:2840	28554:38629		.18
Mn:Ni	4030:3515	24802:29321	S-P:D-F	.19
Sn:Pb	3175:2833	34194:35285		.19

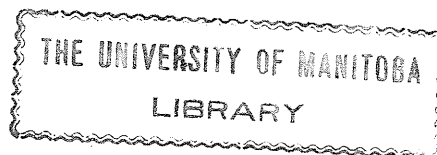
(Table 28 cont'd.)

Sr:Al	4832:3944	35194:25348	P-D:P-S	.19
Sr:Al	4832:3092	35194:32439	P-D:P-D	.19
Sn:Pb	3175:3640	34914:35285	D-P:P-P	.20
Sr:Al	4722:3944	35400:25348	P-P:P-S	.20
Sr:Al	4832:3962	35194:25348	P-D:P-S	.20
Sr:Mg	4812:2852	35675:35051	P-P:S-P	.20
Ba:Sn	4283:3175	34726:34914		.20
Ba:Sn	4283:2840	34736:38629		.20
Ni:Mg	3493:3838	29501:47957	D-P:P-D	.21
Ag:Sn	3382:3175	29552:34914	S-P:P-P	.21
Sr:Al	4722:3082	35400:32436	P-P:P-D	.21
Sr:Al	4722:3962	35400:25348	P-P:P-S	.21
Sr:Al	4742:3083	35400:32436	P-P:P-D	.21
Sr:Al	4742:3944	35400:25348	P-P:P-S	.21
Mn:Mg	2610:3838			.22
Sr:Al	4742:3093	35400:32437	P-P:P-D	.22
Sr:Al	4742:3962	35400:25348	P-P:P-S	.22
Ba:Cd	3501:3404	28554:59487		.22
Ba:Sn	4283:2863	34736:34914		.22
Mn:Mg	4030:3838	2480:47957	S-P:P-D	.23
Ag:Sn	3280:3175	30472:34914	S-P:P-P	.23
Sn:Pb	3262:3640	39257:35285		.24
Sr:Al	4832:3082	35194:32436	P-D:P-D	.24
Sr:Mg	4722:2852	35400:35051	P-P:S-P	.24
Ba:Cd	4903:4679	33805:51484	P-S:P-S	.24
Ba:Cd	4283:3403	34736:59487		.25
Ba:Sn	4903:3175	33905:34914	P-S:P-P	.25
Sn:Pb	3175:2614	34914:46327		.26
Sr:Mg	4742:2852	35400:35051	P-P:S-P	.26
Sr:Mg	4832:2852	35194:35051	P-D:S-P	.26
Ba:Sn	4903:2840	33905:39629	P-S:P-P	.27
Ag:Pb	3280:2833	30472:35285	S-P:P-P	.28
Ag:Mg	3382:2852	29552:35051	S-P:S-P	.28
Ag:Sn	3280:3262	30472:39257	S-E:D-P	.29
Ba:Sn	4903:2863	33905:34914	P-S:P-P	.29
Ag:Pb	3383:2833	29552:35285	S-P:P-P	.30
Ag:Sn	3382:3262	29552:39257	S-P:D-P	.30
Sn:Pb	3262:2614	39257:46327	D-P:P-	.30
Ag:Mg	3280:2852	30472:35051	S-P:S-P	.30
Sn:Mg	3262:3838	39257:47957	D-P:P-D	.31
Mn:Ni	2610:3415			.31
Mn:Ni	2610:3515			.32
Sn:Pb	3262:2833	39257:35285	D-P:P-P	.32
Sr:Ni	4742:3415	35400:29481	P-P:D-F	.32
Ag:Pb	3280:3640	30472:35285	S-P:P-P	.33
Sr:Ni	4742:3492	35400:29501	P-P:D-P	.33
Sr:Ni	4742:3524	35400:28669	P-P:D-P	.33
Sr:Ni	35400:29321	4742:3515	P-P:D-F	.34
Sr:Ni	4832:3415	35194:29481	P-D:D-F	.36
Sn:Mg	3175:3838	34914:47957	P-P:P-D	.37

(Table 28 cont'd.)

Ag:Pb	3382:3640	29552:35285	S-P:P-P	.37
Ni:Mg	3524:3838	28569:47957	D-P:P-D	.38
Sr:Ni	4832:3524	35194:28569	P-D:D-P	.39
Ag:Pb	3383:2614	29552:46327		.40
Ag:Pb	3280:2614	30472:46327		.40
Sr:Ni	4832:3515	35194:29321	P-D:D-F	.40
Sr:Ni	4832:3492	35194:29501	P-D:D-P	.40
Sr:Zn	4742:3345	35400:74478	P-D:P-D	.44
Sr:Zn	4832:3345	35194:74478	P-D:P-D	.50
Mn:Ni	2632:3515			.53
Mn:Ni	2632:3415			.56
Mn:Mg	2632:2852			.55
Ag:Mg	3382:3838	29552:47957	S-P:P-D	.72
Ag:Mg	3280:3838	30472:47957	S-P:P-D	.78

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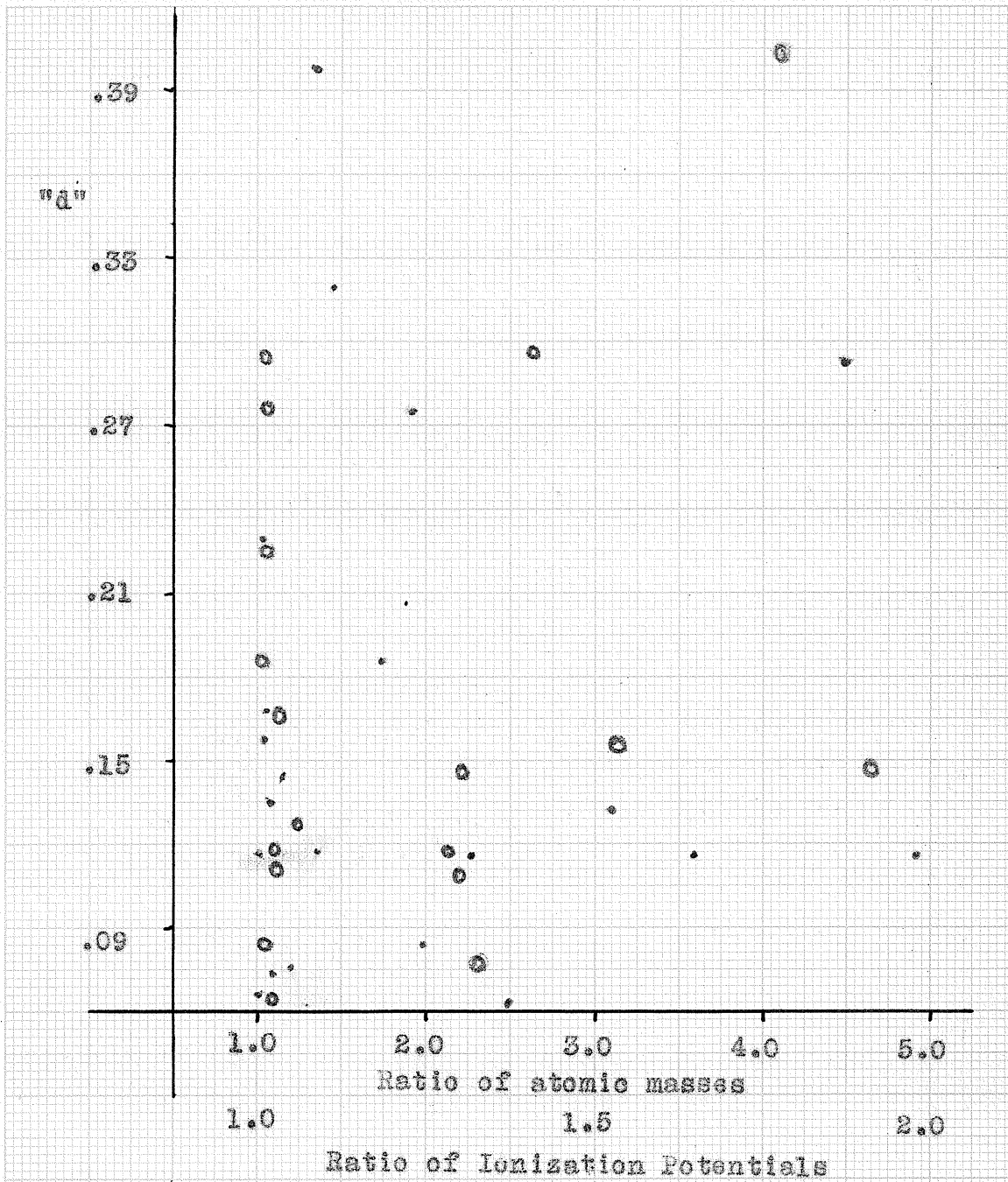


(i.e. ionization po
or atomic cm

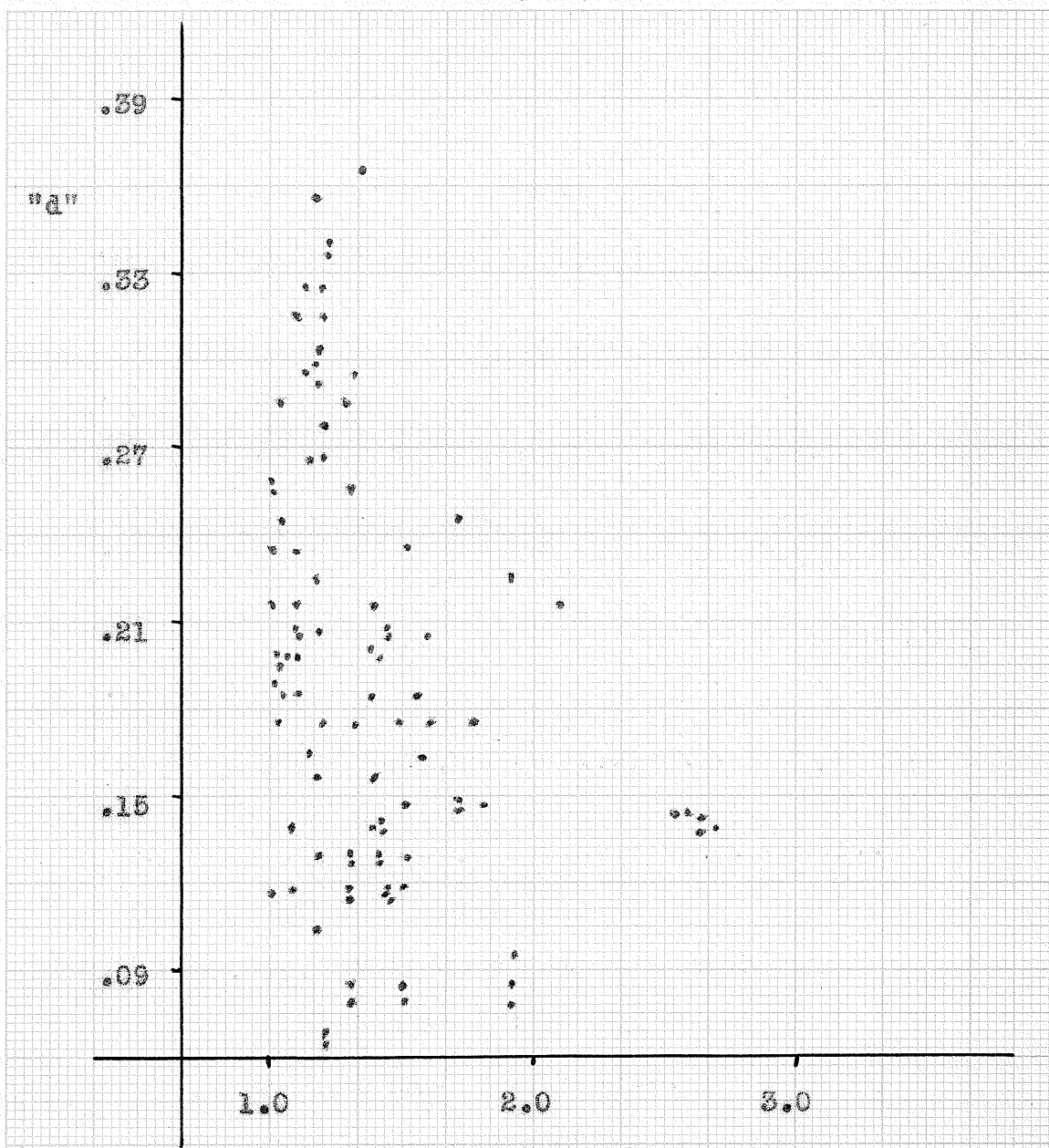
An analysis of the data shows that neither of these factors is of marked importance over the range of the experiments (see graph 1).

Furthermore there appears to be no correlation between the stability of an intensity ratio and the excitation potentials of the two lines involved (graph 2). An examination will show that line pairs belonging to the same classifications (Sharp, Diffuse, etc.) in their respective atoms occur just as frequently at the beginning and the end of table (28), suggesting that they are not associated with the stability of an intensity ratio.

The population of the final levels associated with a line pair (which in part determines the self reversal and the self absorption of the lines) could not be correlated in any way with the changes in the intensity ratios. In calculating the relative final level populations of the lines, it was assumed that the "effective" discharge temperature was 8000°K ; this represents the magnitude of the temperature usually found (17), and G.O.Langstroth and W.W.Brown (18) have shown that lines ending on levels near the ground state exhibit self-reversal but no appreciable self-absorption. The relative populations were calculated from the Boltzmann expression:



Graph #1. Correlation between the mean deviation "d" in intensity ratio due to the additions of extraneous material and (a) Atomic mass of elements (b) Ion., Pot'l of elements using the best intensity ratios of the element pairs.



Graph #2. Correlation between the mean deviation "a" due to the additions of extraneous material and the excitation potentials of the line pair.

$$N_i = \frac{(2j_i + 1)}{(2j_0 + 1)} N_0 e^{-E_{i0}/kT}$$

where: N_i is the population of the i th., level; E_{i0} the excitation energy of the i th., level; j_i the inner quantum number of the i th., level; k is Boltzmann's constant; T is the "effective" temperature; etc.

No obvious correlation has as yet been found between the stability of the ratios and other physical characteristics of the elements involved. As will appear later, line pairs arising from two elements of the complex salt are subjected to marked relative intensity variations on additions of extraneous material.

While the data ^{have} has not yet been subjected to searching analysis ^{lack of} because of ⁱ time, they appear to present at present no apparent criteria for the choice of two elements which may be expected to behave ⁱⁿ nearly the same way in the discharge viz. for the choice of "internal standard" elements.

(b) Buffering the samples.

Adding potassium acetate as a spectroscopic buffer does not eliminate the changes in the line intensity ratio due to the additions of the extraneous material to the standard sample.

but always did reduce any extreme variations. This is evident from an inspection of any of the data. In particular, a reduction in the changes in the line intensity ratio due to the presence of potassium as extraneous material would have been expected upon buffering with potassium, since this is the "method of excess" suggested by Duffendack, ^{W.C.} ~~Wiley~~ and Owens (7). However it did not always take place. For example in table 15, the strontium to nickel line intensity ratios increased to an average value of 2.20 upon the addition of potassium chloride to the standard sample. In table 16 however the standard sample was buffered with potassium acetate and the same strontium to nickel line intensity ratios were not significantly affected by the addition of potassium chloride. On the other hand, in table 13, the strontium to aluminium line intensity ratios increased to an average value of 1.60 upon the addition of potassium chloride to the ^{an} standard sample. In table 14, the same standard sample was buffered with potassium acetate and the strontium to aluminium line intensity ratio decreased to an average value of .85 upon the addition of potassium chloride; in this case buffering with potassium did not eliminate the influence of potassium chloride upon the intensity ratio. There is no apparent reason for these two types of behavior^{or}.

(c) Thermal equilibrium in the source.

From the changes in the intra spectrum ratios of an atom it ^[might be thought to be possible] is possible to calculate the changes in the "effective" temperature of the source. Assuming (17) a Maxwell-Boltzmann distribution of the atoms among the energy levels, a change in temperature dT can be calculated from the equation :

$$dT = \frac{-kT^2 dI_{in}}{\Delta E_{in} I_{in}} \quad \text{----- (1)}$$

which is derived from:

$$I_{in} = P_{in} e^{-\Delta E_{in}/kT} \quad \text{----- (2)}$$

where $P_{in} = \frac{v_{in}^4}{v_n^4} \cdot \frac{p_i(2j_i+1)}{p_n(2j_n+1)} ;$

I_{in} is the intensity ratio of the i th., ^{to} ~~and~~ the n th., lines; v_i is the frequency of the i th., line ; p_i is the transition probability; j_i is the inner quantum number of the initial level of the i th., line; ΔE is the difference in energies

between the initial levels of the i th., and the n th., lines; k is Boltzmanns constant; T is the "effective" temperature and dT is the temperature change corresponding dI_{in} , the change in the intensity ratio of the two lines.

From the data which gave rise to table (9), it was found that the Sn3175:Sn3262 line intensity ratio did not change upon the addition of boric acid to the standard sample, but for the Mg2852:Mg3838 line pair the intensity ratio changed from 2.20 to 4.24 under exactly the same conditions. Hence, ^(as suggested by Levy 191) if the tin lines had been used as the "control ratio", no corrections are to be applied to the intensity ratios of line pairs of any elements in samples containing boric acid, and so in analyses no correction is to be applied to the corresponding relative concentrations of the two elements. An inspection of table 9 will show that boric acid did cause a change in intensity ratios of a considerable number of line pairs.

On the other hand, if the magnesium lines were used as the "control ratio", a ΔT corresponding to the change ΔI_{in} of equation 2 of the magnesium lines has to be applied to the tin lines. A change in the intensity ratios of the tin lines due to the addition of boric acid would result. Data shows that no such change took place. A similar type of behaviour was found in the data for table 11.

For this reason the method of correction of the intensity ratios for the effects of extraneous material, proposed by Levy (9), and based on the assumption that the effects were due entirely to temperature changes, has not been found applicable to this method of analysis and probably to others as well.

(d) Results with various amounts of boric acid.

The curves in graph #3 further illustrate that the change in the intensity ratio depends on the line pair used as well as on the amount of boric added to the standard sample.

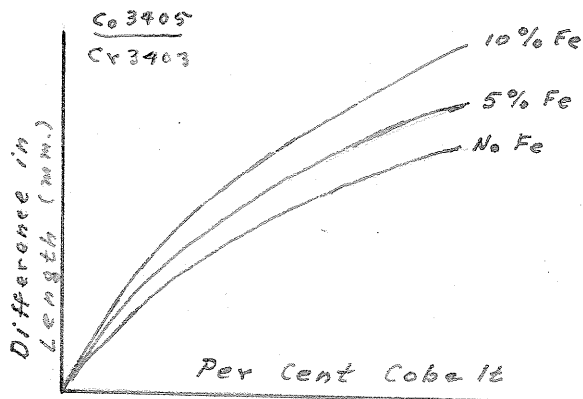
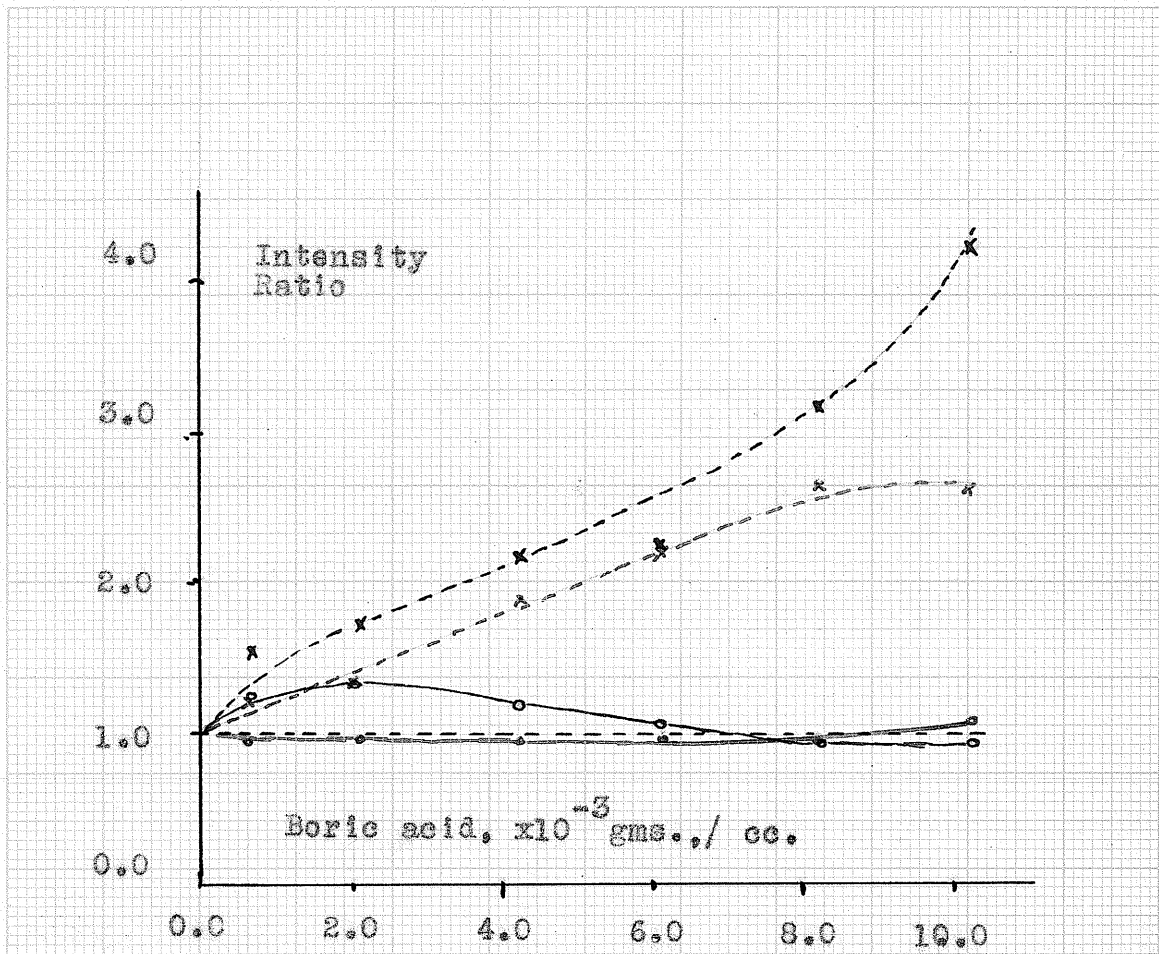


Fig. 2. Influence of iron on working curve of Cobalt (4).

For example, the intensity ratio Ni3437:Mg2852 was not appreciably changed whereas Ni5437:Mg2852 was. A similar change occurred for the tin to magnesium line intensity ratios. If the standard samples used throughout these experiment had been composed from different relative amounts of the same elements, it

is assumed that the results so far obtained would still have



Graph #3. Variation of intensity ratios upon the addition of boric acid to standard sample #4.

Ni3937 o ——— o
Mg2852

Sn3175 x - - - - x
Mg3838

Ni3524 x - - - - x
Mg3838

Sn3262 o ——— o
Mg2852

been of the same nature. This ^{is} will be borne out by an examination of figure 2 which was taken from the work of Twyman and Hitchen (4). The addition of 5% of iron to the standard sample of cobalt and chromium caused an upward shift of the whole "working curve", that is for any concentration of cobalt relative to chromium. The addition of 10% of iron caused only a still further shift. This shift corresponds to the variation of the intensity ratio in graph #3. Hence the effects of the extraneous materials may be minimized by the correct choice of element and line pairs provided the variation in the extraneous material is not too great.

(e) Results for different methods of excitation.

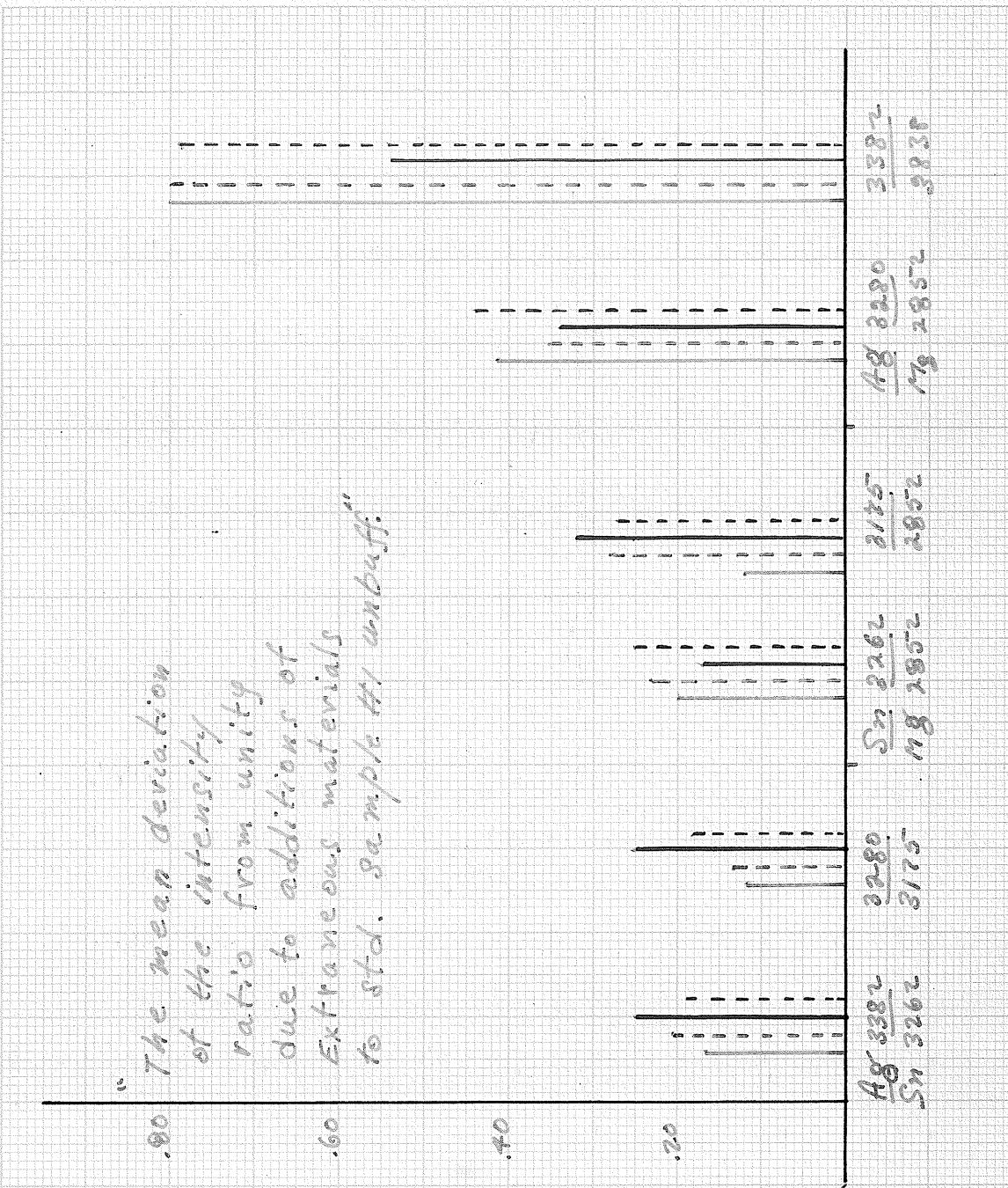
Graph #4 was prepared

^ From the data in section III. [graph #4 was prepared.]

It reveals that the effects due to the additions of extraneous material could not ^{in general} be reduced by changing the method of excitation. Apparently the changes due to extraneous material are not associated with the current in the discharge column otherwise the intensity ratios in table III (d) would have remained constant. Steadying the discharge with ultra violet illumination improves reproducibility.

(f) Results for the complex salt.

The standard sample composed of the complex salt was



Graph #4. Showing the effects of the different methods of excitation on the mean deviations of the intensity ratios from unity due to the additions of the four extraneous materials to std., sample #1, unbuffered.

min. break. pot'l. /-----|
 current const. & 2.3 amp.-----|
 ultra violet illumination -----|
 2 condensrs & ultra violet -----|

chosen with the expectation that the potassium to aluminium line intensity ratio would be unaffected by the presence of the extraneous material. The results show that the variations in the intensity ratios are not wholly due to the changes in the release from the electrode, therefore it does not matter in what form the elements occur in the standard sample.]

(V) CONCLUSIONS.

The following conclusions are drawn from the results of these experiments on the influence of sample composition on the intensity ratio of line of various elements.

Variations
(1) ~~The presence~~ of extraneous materials in the standard sample will in general cause a variation in the intensity ratios of line pairs and will as a result affect the accuracy of the spectrographic methods of analyses.

(2) These variations depend upon the composition of the standard sample, upon the type and the amount of the extraneous material, and on the line pairs ^{chosen for} of the investigated ^{ion} elements.

There is no obvious correlation between
(3) ^t The stability of a line pair ~~(does not depend upon)~~ and the ionization potentials or the atomic masses of the elements, nor the excitation potentials or the classifications of the selected line pairs.

(4) The influence of the extraneous material is present whether the source is operated at a minimum breakdown potential, or at a constant current, or whether the discharge is steadied with ultra violet illumination. It is not associated with the current value of the discharge.

(5) Buffering the standard sample with potassium acetate does not in general eliminate the influence of the extraneous material on the intensity ratios of a line pair.

(6) The results are time- and space- integrated over the whole of the source. It is desirable to examine each single discharge of ~~each~~ which the spark is composed.

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