THE SPECTROGRAPHIC SENSITIVITY OF MANGANESE, COBALT AND MAGNESIUM

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
John Arthur Crane
1946

This is to certify that the

thesis entitled

The Spectrographic Sensitivity of Manganese, Cobalt and Magnesium

presented by

John Arthur Crane

has been accepted towards fulfillment
of the requirements for

MS degree in Chemistry (Physical)

D. T. Ewing
Major professor

Date Aug. 8, 1946

M-795

THE SPECTROGRAPHIC SENSITIVITY
OF
MANGANESE, COBALT AND MAGNESIUM

By

John Arthur Crane

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1946

Acknowledgement

The writer wishes to express his appreciation to Dr. D. T. Ewing for his guidance and enthusiasm in the direction of this investigation.

Introduction

Spectrographic examinations of dilute solutions show that 30 milli-micrograms of manganese, 60 milli-micrograms of cobalt and 3 milli-micrograms of magnesium can be readily detected. This paper is largely a study of the various factors to be taken into consideration to show the presence of such small quantities of these three elements in various types of samples. Important factors necessary to consider in this investigation are purity of materials including electrodes, particular wave length of element under observation, excitation voltages and exposure times.

Cu
Cn

Two methods of excitation have been investigated. The preliminary work utilized a direct durrent arc source in which the solution was placed in the cavity of a carbon electrode, the solution evaporated and an arc struck between this and a second carbon rod. After the sensitivity of manganese was determined by this method, the condensed spark excitation was used. This consisted of evaporating the solution on pure copper electrodes and passing a high voltage spark between two copper electrodes.

This work has been concerned with the determination of the actual amounts of the elements present on the electrode and from these values, the concentration in the complete sample has been calculated.

Apparatus

The direct current arc source consists of a 220 volt direct current generator, a potential divider, and a series resistor by which the current through the circuit can be controlled. The circuit diagram is shown in Fig. 1.

The condensed spark apparatus is a little more complicated and is shown in Fig. 2. It is made up of a step-up transformer with 110 volt primary and a maximum secondary potential of 25,000 volts, and a .02 microfarad condenser with a maximum of 20,000 volts. A self inductance coil is placed in series with the spark in order to eliminate air lines from the spectrum. (1)

The electrodes used in this investigation are shown in Fig. 3. National Carbon spectrographic carbons were used in the arc method, and special purity copper electrodes were used in all spark work.

A Bausch and Lomb Littrow type spectrograph with a quartz optical system was used in making all the photographic plates in this investigation. The optical system of the instrument is shown in Fig. 4. Light enters the slit (S) and passes through a right angle prism (R) by which it is rotated 90° to pass through a columnating lens (L) before it enters the Littrow prism (P). This is a 30° prism, the back surface of which is coated with aluminum so that it will reflect ultraviolet and visible radiation without absorption bands. The light is then reflected by the prism through the same lens (L) which now

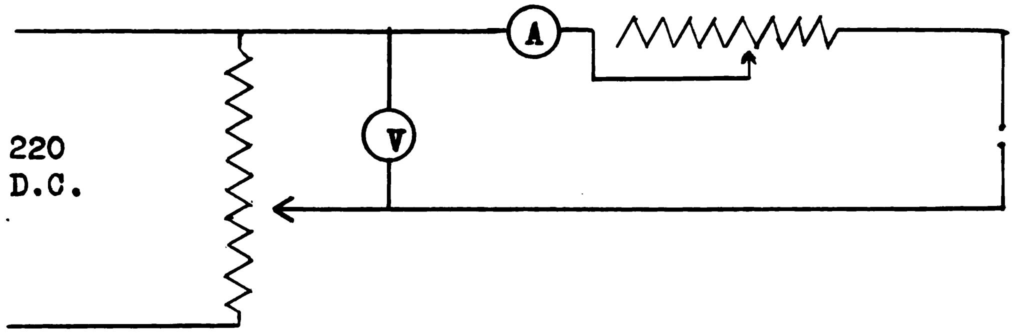

Fig. 1.- Direct current arc circuit .

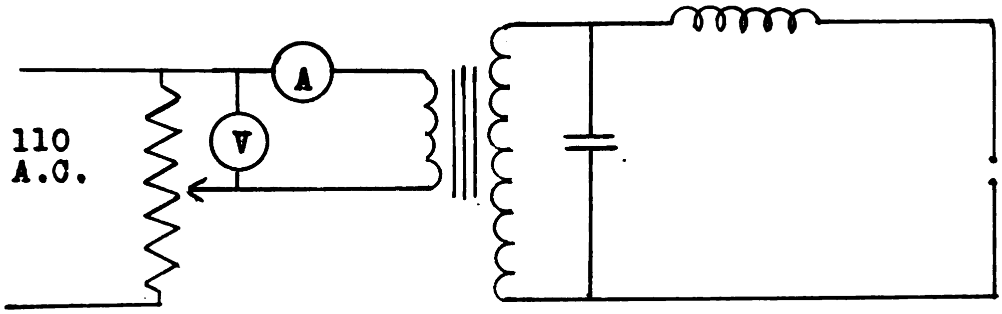

Fig. 2.- Condensed spark circuit .

acts as a focusing lens and serves to focus the energy on the photographic plate which is maintained at the correct curvature to keep the spectrum in focus. (1) (2) Instrument was adjusted to position VII (focus 157.5; tilt 210) which covers the range from 2327 to 2973 Angstroms.

Kodak Spectrum Analysis No. 1 plates were used in this investigation. They were processed in a constant temperature, 18°C., mechanically agitated developing tank using Kodak developer D-11. After the plate was dried, the density of the various lines was determined by means of a Hilger microphotometer. This instrument consists of a light source which is focused on the photographic plate by means of a series of lenses. The light which passes through the plate is picked up by a second series of lenses which focus the light on a photoelectric cell. The current which is generated in the photo cell is transmitted to a ballistic galvanometer. The galvanometer deflection is a measure of the relative amount of light incident on the photo cell. (2)

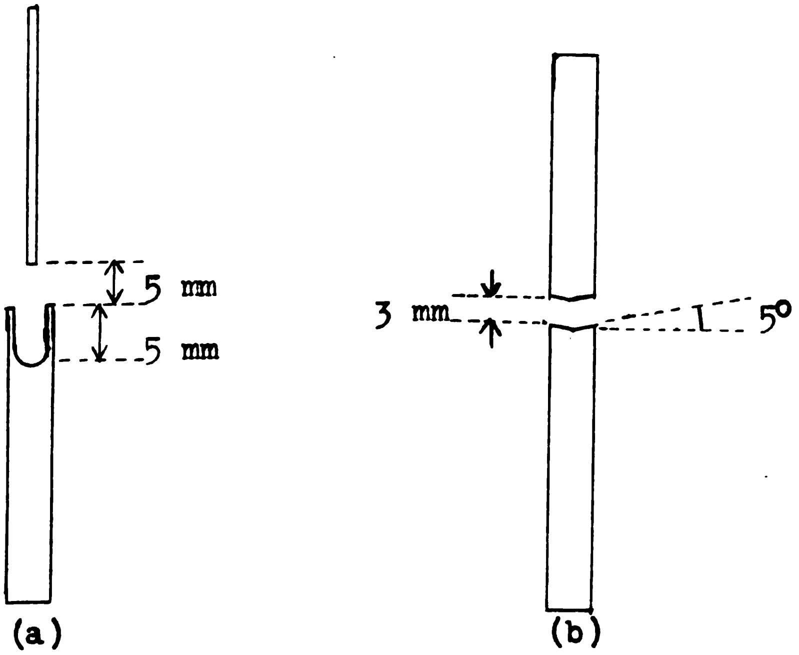

Fig. 3.- (a) carbon electrodes; (b) copper electrodes.

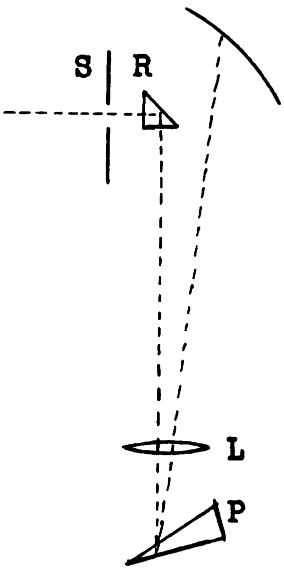

Fig. 4.- Optical diagram of the Littrow spectrograph.

The arc was used as a light source in the first part of this investigation. The anode electrodes were spectroscopic grade carbons $\frac{1}{4}$ inch in diameter and broken into approximately 2 inch lengths. A crater was bored in one end of the rod as shown in Fig. 3. The cathodes were of the same quality, but were 1/8 inch in diameter so as to prevent the arc from wandering out of focus. The carbons were arced 30 seconds at 60 volts and 6 amperes in order to remove any superficial impurities. The anodes were placed in a 120°C oven for 30 minutes after which the craters were filled with the samples. The electrodes were then air dried for 30 minutes followed by placing then in the oven for 15 minutes.

The arc can best be aligned by going through the following procedure. Remove the plate holder from the spectrograph and adjust the focus and tilt of the instrument so that the visible portion of the spectrum is in focus. Open the shutter and remove the Hartman diaphram completely. This will allow the entire length of the slit to be illuminated. Strike an arc between two carbon electrodes and by observing the spectrum with the aid of a magnifying eyepiece, adjust the lateral position of the electrodes so the spectrum is visible. Next, the horizontal position must be aligned so that the spectral lines are of constant intensity over their full length. When the adjustments have been completed, the position of the electrode iamge is marked on a permanently located test screen so that the electrodes can always be set at the same position.

The base solution was made up of .1% copper as $CuCl_2 \cdot 2H_2O$ in 4% hydrochloric acid to which 25 grams of ammonium chloride was added per liter of solution. Manganese was added to this solution as $MnCl_2 \cdot 4H_2O$ (.3675 gram contains 100 milligrams of manganese) and the volume made up to one liter. By dilution of this stock solution with the base solution, the concentration of the various samples was varied to cover the range from .1 to 10 milligrams per liter. By this method, it was possible to obtain solutions which contained definite concentrations of manganese, and each sample contained a constant amount of copper which served as an internal standard for the quantitative work. The ammonium chloride and hydrochloric acid were added to the solution in order to produce a more uniform arc. (3) The samples were placed in the crater by means of a calibrated pipette to be certain that .3ml. were used in all cases.

It was necessary to determine the optimum exposure time by observing the line density and background density of spectra produced by exposures covering the probable range of time. The results of this determination are shown in Table I. From the table, it will be seen that the maximum line density compared to the background density was obtained with an exposure of 180 seconds. It should also be noted that the background intensity increased sharply with exposures of more than 120 seconds. Since it was desirable to use lines of low density, it was deemed better to use an exposure of 120 seconds in order to obtain the most dense lines and the least possible background. The relation of background density to exposure time is shown in Fig. 5. The data presented here is taken from plate #23.

Table I

Effect of Exposure Time on Photographic Densities

Clear plate deflection = 30 cm.

Exposure Time	Deflection		Density (Log I_0/I)		
Seconds	Backgr.	Cu	Backgr.	Cu	Cu/Backgr.
30	27.6	12.8	.036	.370	.334
45	27.4	10.0	.039	.477	.438
60	27.3	9.4	.041	.504	.463
90	27.1	8.4	.044	.553	.509
120	27.0	7.7	.046	.591	.545
180	25.2	6.7	.076	.650	.584
240	23.9	6.4	.099	.671	.572
300	22.5	6.2	.125	.686	.561
360	21.9	6.0	.136	.700	.564

The developing process was also investigated in order to increase the sensitivity of this method. The original development time was four minutes at 18°C. with continuous agitation of the developer. By developing plates at various shorter periods, it was found that no appreciable change in the density of the line occured after two minutes in the developer if the background density was taken into consideration. The final procedure decided upon which gave

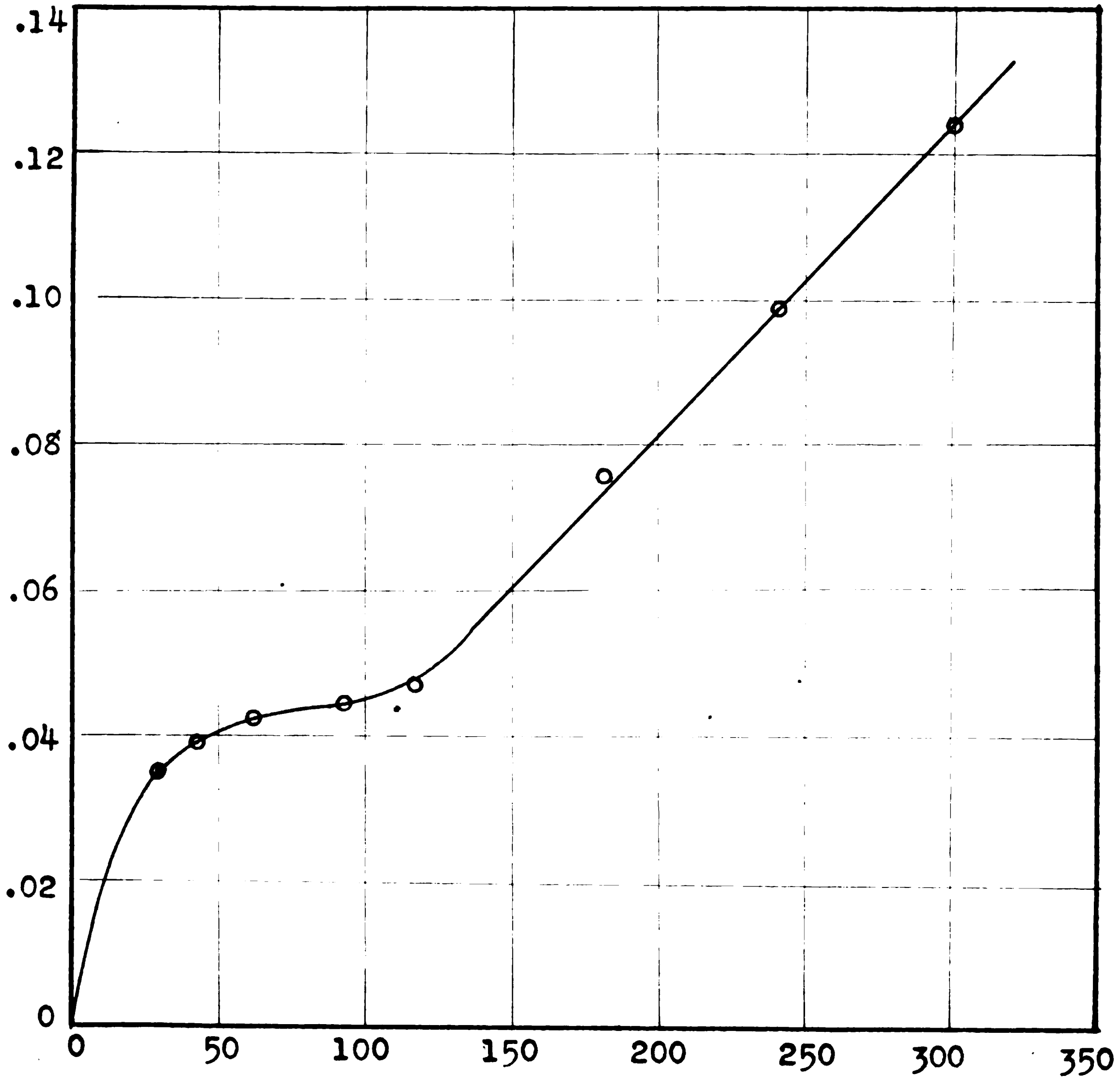

Fig. 5.- Relation of background density to exposure time.

the best results was to develop in D-11 at 18°C. for two minutes followed by fifteen seconds in a 5% acetic acid stop bath. The plate was fixed in the acid fixing bath for two minutes after which it was washed in running water for fifteen minutes, rinsed in distilled water, sponged and dried on an A.R.L.- Deitert plate drier.

After the plate had been dried, the lines to be examined were spotted on the plate and the densities determined by means of a Hilger microphotometer. This instrument must be turned on ten minutes before any readings are taken in order to allow the light source to attain equilibrium. The galvanometer deflection for total darkness on the photocell must be noted and should remain at zero. The galvanometer deflection was adjusted to a constant value for the background of each spectrum (I_0), and the deflection (I) was measured for each line being used. The Density was calculated from these values; $D = \text{Log } I_0/I$. (2) The various steps of the step sector spectrum were read in the same manner in order to obtain the plate calibration curve. In order to obtain any accurate results, an intensity calibration must be made of each photographic plate used. (4) This was done by removing the Hartman diaphram and using the motor driven rotating step sector, the seven steps of which are in a ratio of 1:1.5. The Density of the steps is plotted against the logrithm of the relative exposure (Log E) to obtain the calibration curve. The step sector was exposed by means of an iron arc at 50 volts and 6 amperes for four seconds. The Hartman diaphram was used in making the exposures of the samples. The shutter was opened before the arc was struck. The arc was run at 50 volts and 6 amperes for two minutes.

The most sensitive arc line of manganese is that line at 4030.8 International Angstroms, but this is in the range of the carbon bands so it, of course, could not be used. The next most sensitive line is at 2576.1 Angstroms and is the one which was used. (5) The density values of the manganese line and of the copper line at 2618.4 Angstroms was determined and by refering these values to the calibration curve, the Log relative intensity of the two lines was determined. This value was then plotted against the Log concentration to give the working curve. The copper line used for a reference line should be chosen such that its density lies on the straight portion of the calibration curve and should be a line of constant density.

A typical set of data used for obtaining the working curve for the determination of manganese by the arc method is given in Table II. The data for this table have been obtained from plate #33. Figs. 6 and 7 show the calibration curve and working curve respectively which were obtained from this data. It will be seen from the data that the extreme concentration of manganese which could be detected was .4 mg.1. Since the samples each contained .3 ml., the extreme amount of manganese which could be detected by this method was 120 milli-micrograms.

TABLE II

CALIBRATION AND WORKING CURVE DATA
FOR MANGANESE DETERMINATION
BY THE ARC METHOD

Sector Step	0	1	2	3	4	5	6	7
Galv. Read.	25.0	24.8	24.5	23.7	22.0	19.3	15.6	12.3
Density	.000	.003	.009	.022	.055	.113	.205	.308

Manganese Content	Galv. Reading		Density Log I_0/I		Log Intensity Mn 2576.1; Cu 2618.4		
g. x 10^{-9}	Mn	Cu	Mn	Cu	Mn	Cu	Mn/Cu
3000	19.8	20.8	.101	.080	4.78	4.48	.30
2400	20.0	19.7	.097	.103	4.74	4.83	-.09
1800	20.8	20.1	.080	.095	4.84	4.70	-.22
1200	21.5	19.6	.066	.105	4.23	4.86	-.63
900	22.8	20.7	.040	.082	3.69	4.50	-.91
300	24.2	20.5	.014	.086	2.45	4.56	-2.11
240	24.2	19.5	.014	.108	2.45	4.90	-2.45
180	24.5	19.2	.009	.115	2.00	5.01	-3.01
150	24.6	20.6	.007	.084	1.70	4.54	-2.84
120	24.6	19.7	.007	.103	1.70	4.83	-3.13
90	25.0	19.2	.000	.115	----	5.01	-----

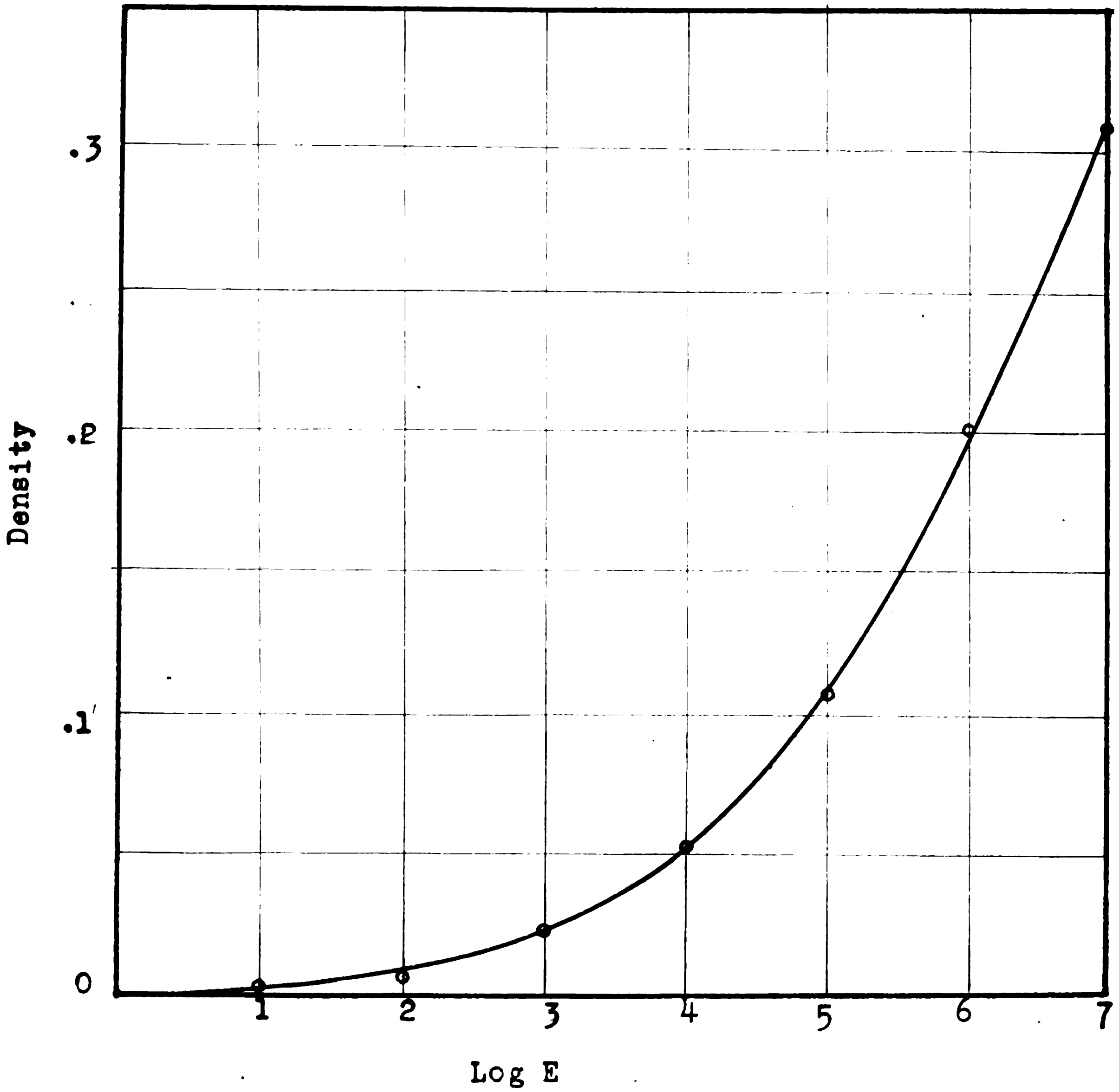

Fig. 6.- Plate calibration curve for D-11 developer.

✓

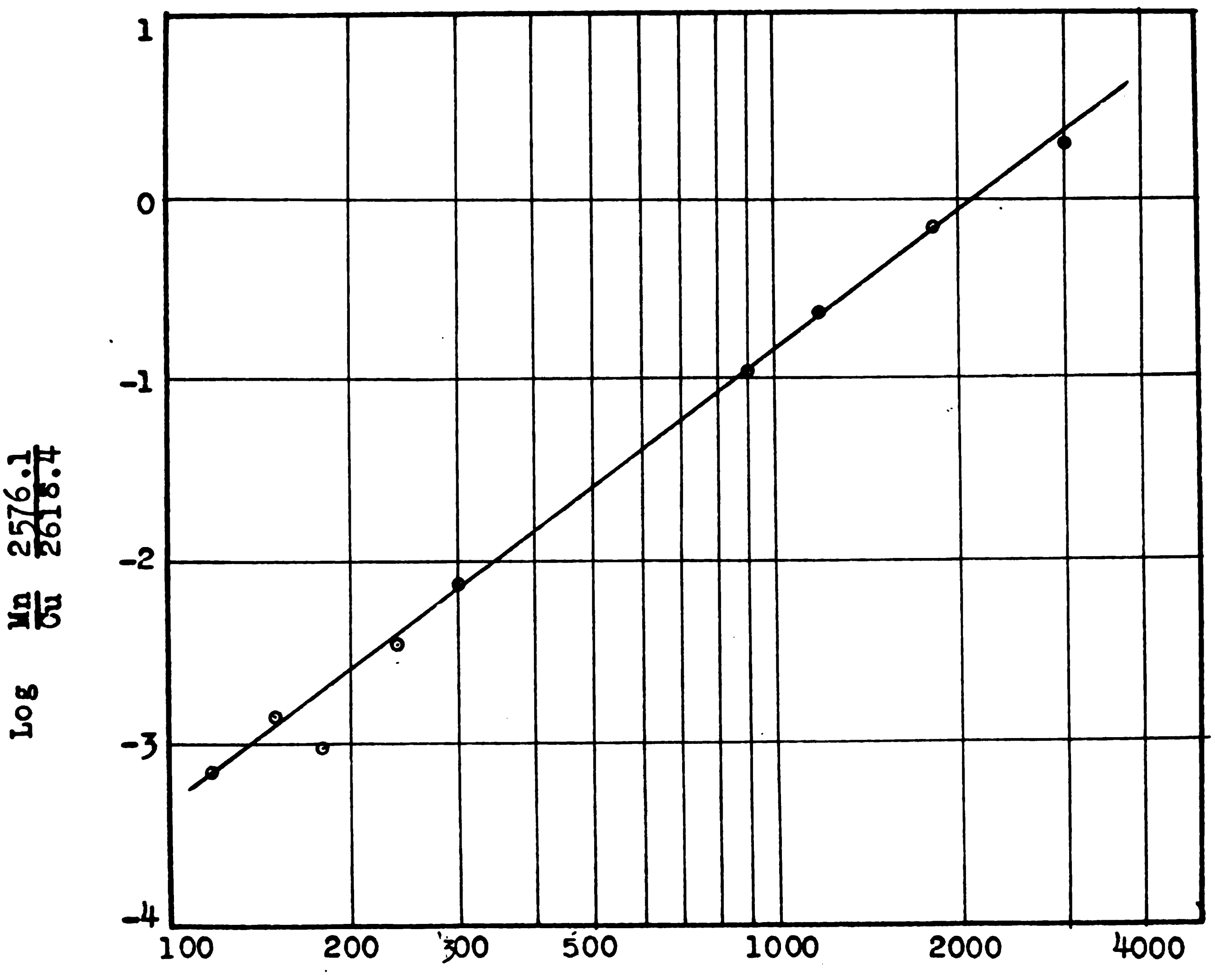

Fig. 7.- Working curve for the determination of manganese by the arc method.

In the spark excitation method, the electrodes used were special purity copper rods ¼ inch in diameter and about 3 inches long. The electrodes were machined level at first, but the drop tended to run off the sparking surface during the evaporation process. In order to correct this defect, various shapes were tried, and a 5° taper on each electrode was decided upon. The electrode on which the drop was placed was made concave and the other was made convex on the same taper in order to maintain a constant space between the electrode surfaces. The taper was held to a minimum so that the light would not be shielded from the spectrograph. The electrodes were machined before each exposure to remove the oxide coating formed by the spark. By removing .015 inch, a clean, fresh surface was obtained. Thus each pair of electrodes could be used for a large number of exposures.

The standard solutions were prepared by dissolving a weighed amount of $MnCl_2.4H_2O$ in distilled water. The copper in the electrodes served as the internal standard. No ammonium chloride or hydrochloric acid was added to these samples.

The electrodes were made ready for exposing by placing one drop from a calibrated pipette on the face of the concave electrode and evaporating the sample in an oven at 120° C. for thirty minutes. The exposures were made immediately after removal of the electrodes from the oven.

The spark gap was properly aligned according to the method previously used in this laboratory. (6) A spark is passed between two electrodes which have been set at approximately the correct position. The Hartman diaphram and step sector housing are removed from the optical path; the focusing lens is adjusted horizontally so as to produce a sharp image on the slit housing. The electrodes are shifted so that the image is vertically in line with the slit; then the lens is adjusted vertically so that the best possible illumination is obtained over the entire length of the slit. The alignment is checked by setting the spectrograph to the visible range and examining the spectrum with the aid of a magnifying eyepiece.

A primary potential of 55 volts with a current of 7 amperes was used for the spark excitation. The optimum exposure time was determined by making exposures of 15, 30, 45, 60, 75 and 90 seconds from which it was decided to use 45 seconds for exposing all the samples. The lines reached their maximum density in this time, and the background density was held to a minimum. The step sector was exposed under the same excitation conditions using iron electrodes for thirty seconds.

The plate development process and the microphotometer procedures were the same as those described in the section dealing with the arc excitation methods.

A typical set of data for the determination of manganese by the spark excitation method is given in Table III. The working curve from this data, which was taken from plates 59 and 60, is shown in Fig. 8. The curve has a tendency to level off at the lower concentrations, but this is to be expected due to the extremely low amount of manganese present in the spark gap.

TABLE III

WORKING CURVE DATA FOR MANGANESE DETERMINATION BY THE SPARK METHOD

Manganese in sample	Galv. Reading		Density Log I_0/I		Log Intensity Mn 2576.1; Cu 2482.3		
g. x 10^{-9}	Mn	Cu	Mn	Cu	Mn	Cu	Mn/Cu
300	22.9	24.2	.038	.014	2.64	2.45	1.19
240	21.0	22.8	.075	.040	4.39	3.69	.70
210	20.5	22.5	.086	.048	4.57	3.90	.67
180	20.3	21.6	.090	.064	4.63	4.21	.42
150	20.9	21.5	.078	.066	4.44	4.25	.19
120	23.0	22.6	.036	.044	3.56	3.81	-.25
100	23.1	21.6	.034	.064	3.53	4.22	-.69
60	24.2	22.2	.014	.044	2.03	3.81	-1.72
30	24.3	21.8	.012	.059	2.35	4.12	-1.77
24	25.0	23.2	----	.033	----	3.47	-----

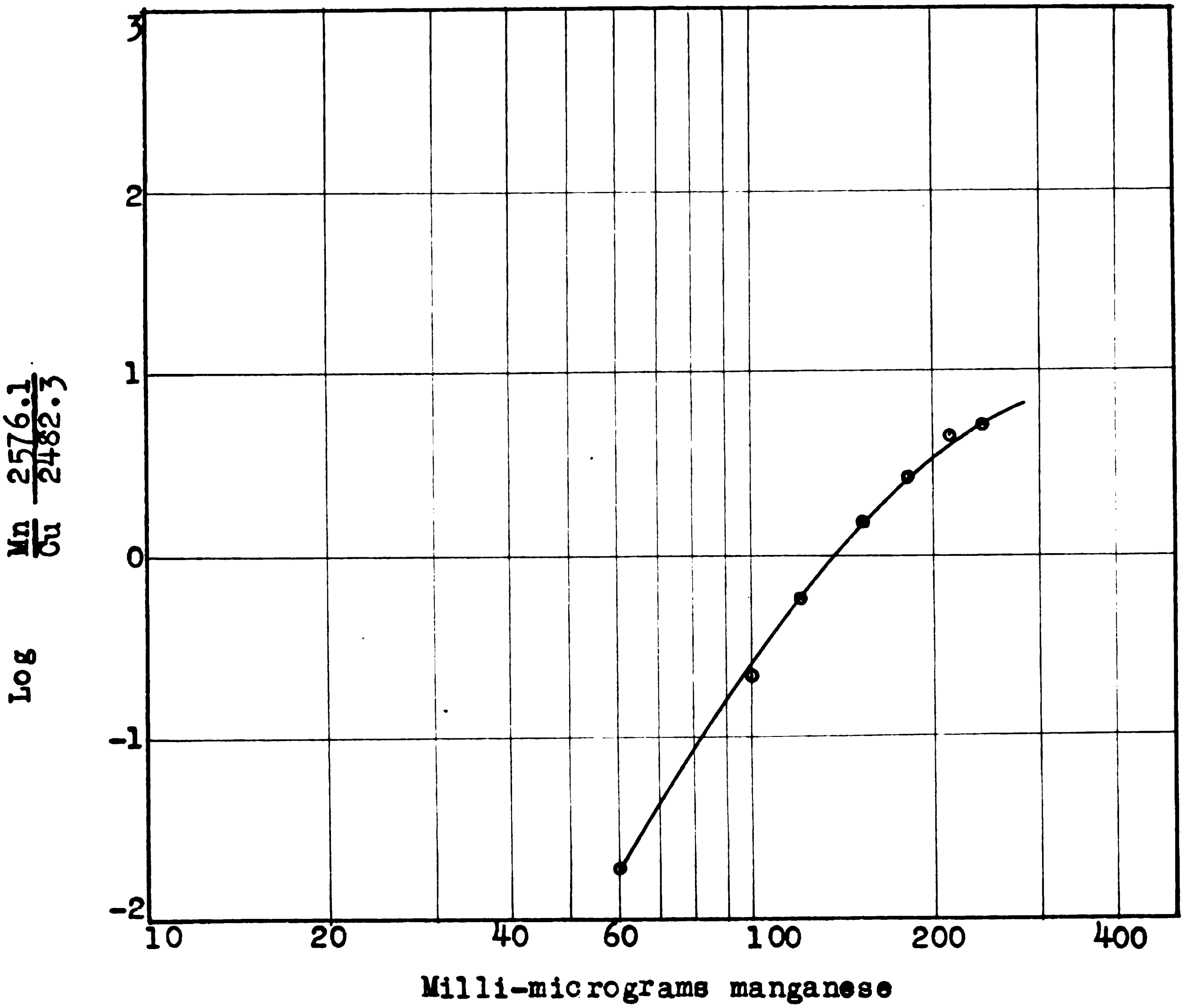

Fig. 8.- Working curve for the determination of manganese by the spark method.

Since it appeared possible to detect smaller amounts of manganese by the spark method as compared to the arc procedure used, other trace elements were investigated by the spark method. Cobalt was investigated using the line at 2582.2 Angstroms since this is the most sensitive spark line. (7) The solutions were prepared by dissolving $Co\ (NO_3)_2 \cdot 6H_2O$ in distilled water; .4938 grams of the salt contains 100 mg. of Cobalt. The same procedure as used in the spark determination of manganese was used in this case. The data obtained from making exposure of various concentrations of Cobalt are shown in Table IV. The working curve covering this low concentration of Cobalt is shown in Fig. 9.

TABLE IV

WORKING CURVE DATA FOR COBALT DETERMINATION BY THE SPARK METHOD

Cobalt in sample	Galv. Reading		Density Log I_0/I		Log Intensity Co 2582.2; Cu 2493.1		
g. x 10^{-9}	Co	Cu	Co	Cu	Co	Cu	Co/Cu
360	16.0	21.8	.194	.060	5.92	4.13	1.79
300	16.0	19.6	.194	.106	5.92	4.86	1.06
240	19.5	20.8	.108	.080	4.90	4.48	.42
180	19.4	19.8	.110	.101	4.93	5.02	.09
150	21.7	21.6	.061	.063	4.14	4.18	-.04
120	21.3	20.5	.069	.084	4.29	4.55	-.26
100	22.6	21.4	.044	.068	3.81	4.26	-.45
60	23.2	21.7	.033	.062	3.47	4.17	-.70

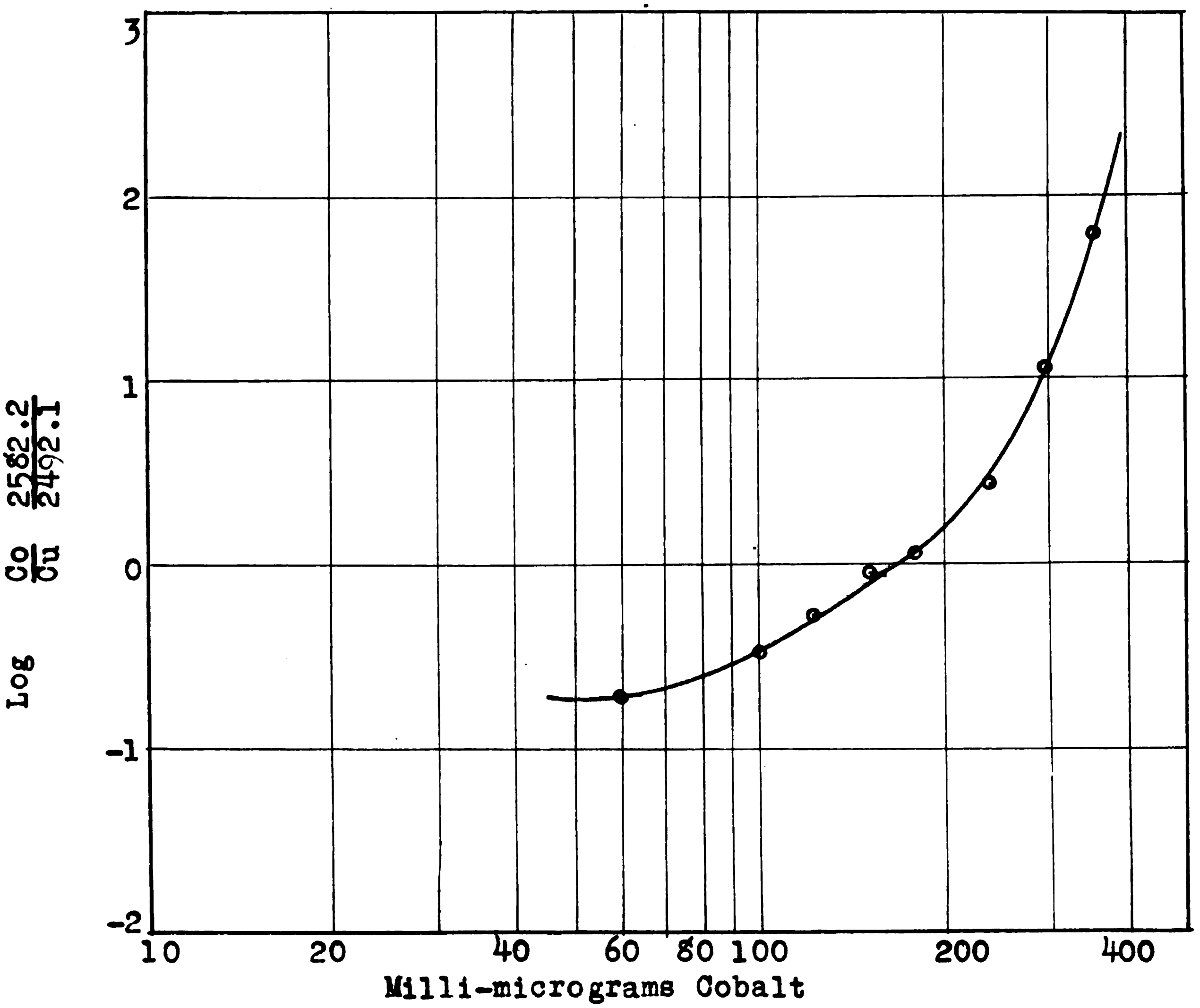

Fig. 9.- Working curve for the determination of Cobalt by the spark method.

In detecting the slightest amount of magnesium, some difficulty was encountered due to the limitations of the electrodes. Magnesium 2852.1 line could not be used in this work because there was enough magnesium present as impurity in the electrodes to bring this line into the spectrum when no sample was in the spark gap. The next most sensitive spark line, which occurs at 2795.5 Angstroms, was used. The effect of the electrodes on this line was noticeable, but not to the extent of the 2852.2 line. The standard solutions were prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$ in distilled water; 1.0549 grams of the salt contains 100 mg. of magnesium. The procedure used in preparation of the electrodes and making the exposure was the same as that used in determining the sensitivity of manganese. The date obtained from observation of the photographic plates used are given in Table V. The working curve for magnesium is presented in Fig. 10.

TABLE V

WORKING CURVE DATA FOR MAGNESIUM
DETERMINATION BY THE SPARK METHOD

Magnesium in sample	Galv. Reading		Density Log I_0/I		Log Intensity Mg 2795.5; Cu 2493.1		
g. x 10^{-9}	Mg	Cu	Mg	Cu	Mg	Cu	Mg/Cu
30.0	18.6	22.7	.128	.042	5.18	3.67	1.51
24.0	20.2	22.7	.093	.042	4.68	3.67	1.01
18.0	22.0	23.6	.056	.025	4.04	3.16	.88
15.0	22.2	23.3	.052	.030	3.97	3.35	.62
12.0	20.5	22.2	.086	.052	4.57	3.97	.60
10.0	21.1	21.8	.073	.059	4.36	4.12	.24
6.0	19.5	19.5	.108	.108	3.75	3.75	.00
3.0	22.4	21.8	.048	.059	3.91	4.12	-.21

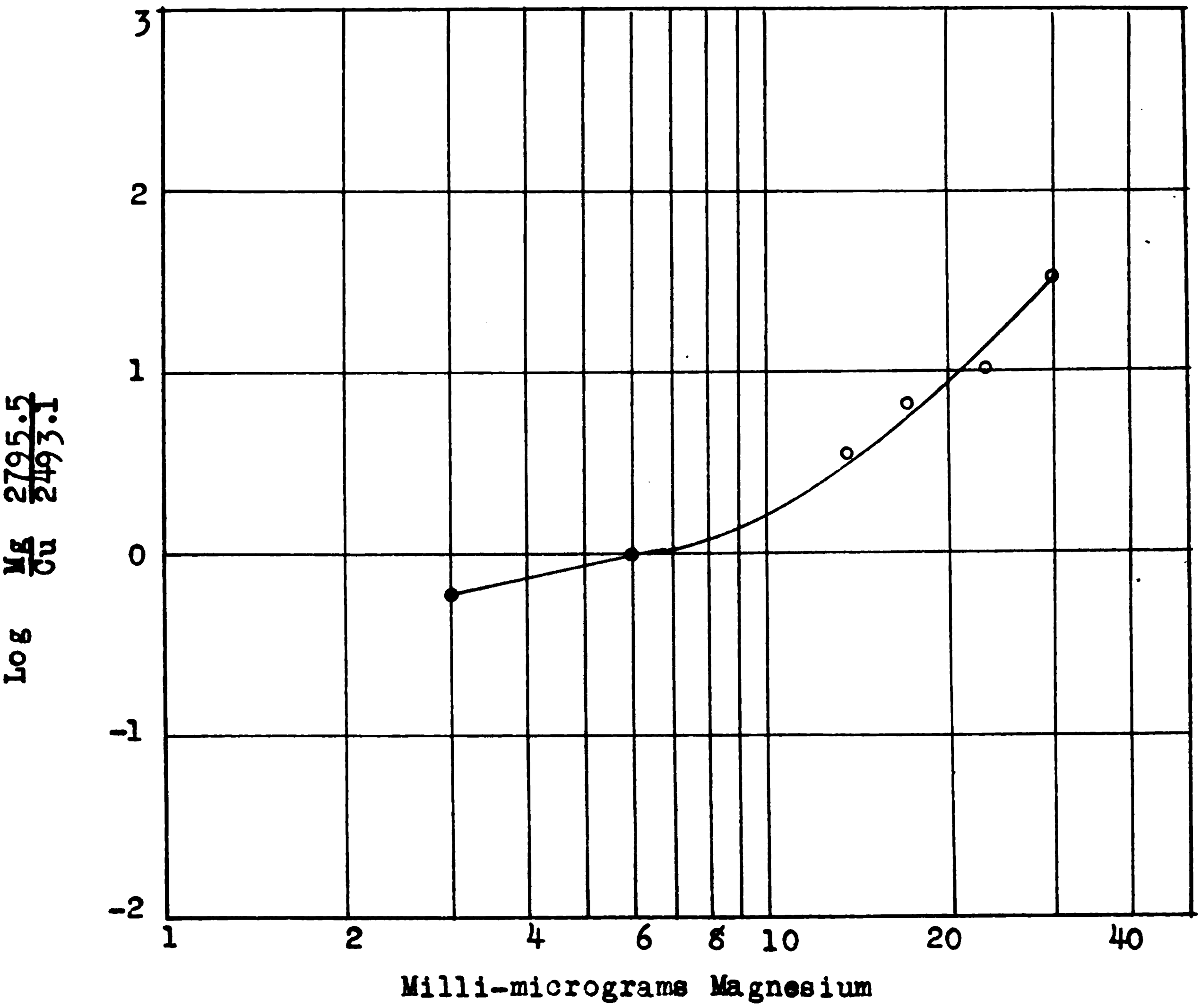

Fig. 10.- Working curve for the determination of magnesium by the spark method.

On the basis of the working curves obtained, a series of analyses was run on soils and organic matter. The results of the investigation of these samples are summarized in Table VI.

The soil samples were prepared for examination by digesting .1 gram of the sample in 10 ml. of concentrated hydrochloric acid for 24 hours at room temperature. After digestion, .03 ml. of the clear solution was evaporated on the copper electrodes, and the sample sparked under the standardized conditions.

The organic matter was treated according to the method suggested by Hess, Owens, and Reinhardt. (8) One-tenth gram samples were ashed after the addition of 1 ml. of concentrated sulphuric acid. When charring was nearly complete, concentrated nitric acid was added dropwise to the hot solution until a clear liquid was obtained. The solution was then evaporated almost to dryness, cooled, and taken up in .5 ml. of 2 N nitric acid. A constant volumne, .03 ml., of the solution was then evaporated on the electrodes and sparked after evaporation.

TABLE VI

SUMMARY OF DETERMINATIONS OF TRACE ELEMENTS

Sample	Manganese %	Cobalt %	Magnesium %	Others Found
Soil 1/0-4	.045	------	*	Fe, B, Zn, Ba.
1/6-12	.020	------	*	Same
8/0-7	.027	------	*	Same
8/8-16	.023	------	*	Same
9/0-7	.031	------	*	Same
9/8-14	.015	------	*	Same
Organic '3777'	----	------	*	Ni, Fe.

* Magnesium was present in all samples in amounts larger than those covered by the working curves.

The sensitivity of manganese as determined by the arc method is in good agreement with the work done in other laboratories. (8)(9) The minimum amount of manganese which could be detected by the arc method was 120 milli-micrograms.

It was possible to detect smaller amounts of manganese by using the spark excitation, so most of the interest was centered in this method. Amounts of manganese as small as 30 milli-micrograms could be detected by this method. Magnesium appears to be more easily detected than either manganese or cobalt. The actual minimum of Magnesium was not determined due to the presence of magnesium in the copper electrodes, but a working curve was obtained covering the range down to 3.0 milli-micrograms. The extreme leveling off of the magnesium working curve is due to the impurity of the electrodes. The determination of cobalt was possible to approximately the same extent as manganese; the least observable amount of cobalt being 60 milli-micrograms.

It was not possible to detect quantitatively the amount of magnesium in the presence of cobalt. The cobalt greatly increased the appearent concentration of magnesium. This was the only case of interference noted in this investigation. It was observed that high relative humidity while the plates were being exposed caused poor results in that the sensitivity of the elements was reduced.

Summary

1. The spectrographic sensitivity of manganese under direct current arc and alternating spark excitation has been determined.

2. The sensitivity of magnesium and cobalt by the spark excitation method has been observed.

3. Working curves for low concentrations of the three elements have been derived.

4. Methods of handling various types of samples have been presented.

References Cited

1. Bausch & Lomb, "Instruments for Spectrographic Analysis," Bausch & Lomb Optical Company, Rochester, N.Y., 1932, p. 42.
2. Brode, W.R., "Chemical Spectroscopy," 2nd Ed., John Wiley & Sons, Inc., New York, N.Y., 1943, p. 36, 115.
3. Ewing, D.T., Wilson, M.F., and Hibbard, R.P., *Ind. Eng. Chem.*, *Anal. Ed.*, *9*, 410 (1937)
4. Twyman, F., "The Practice of Spectrum Analysis with Hilger Instruments," 6th Ed., Adam Hilger, Ltd., London, Eng., p. 32.
5. Ryde, J.W., and Jenkins, H.G., "Sensitive Arc Lines of 50 Elements," A. Hilger, Ltd., London, Eng., 1944.
6. Brandt, S.M., "The Spectroscopic Working Curves for Magnesium and Other Elements in Aluminum Alloys," M.S. Thesis, Michigan State College, East Lansing, Michigan, 1943, p. 7.
7. Harrison, G.R., "M.I.T. Wave Length Tables," John Wiley & Sons, Inc., New York, N.Y., 1939, p. 382.
8. Hess, T.M., Owens, J.S., and Reinhardt, L.G., *Proceedings of the Seventh Summer Conference on Spectroscopy and its Applications*, 29 (1939)
9. Melvin, E.H., and O'Connor, R.T., *ibid*. 42 (1939)