APPLICATION OF THE SOLUTION METHOD OF SPARK EXCITATION
TO THE SPECTROGRAPHIC ANALYSIS OF
MAGNESIUM IN PLANT MATERIAL

by

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INTRODUCTION

In recent years much emphasis has been placed upon the mineral content of agricultural products. In particular, studies are constantly being carried out to determine the effect of various minerals, or combinations of minerals, upon the nutritional value of plant matter. This type of research demands that methods be available for the determination of many elements in a large number of samples of complex substances. It has been found, in many cases, that the established methods for the determination of a number of these elements lack adaptability to wide variations in composition. This is often the case in analyzing a heterogeneous group of such substances.

For this reason many agricultural chemists have adopted physical methods of analysis which are not as restricted to composition as many of their chemical counterparts. However, one of the most important advantages of physical analysis, compared to the same chemical method, is the relative amount of time required for a complete analysis. With these circumstances in mind, this research began as a problem of applying the a. c. spark as a spectrographic source for the analysis of agricultural products. Due to the limitation of time, however, attention was centered upon the direct determination of magnesium from solution, and with simultaneous determination of other elements within the same sensitivity range.

SURVEY OF THE LITERATURE

Many methods have been proposed for the determination of magnesium. The greater number of these have been modifications of the thiazole yellow colorimetric method. These modifications have been, for the most part, attempts to stabilize the color formed, or to remove or account for interfering ions. Mikkelson and Toth (19) tested 130 compounds as color producing agents for magnesium, and found thiazole yellow to be the most satisfactory. They found, however, that calcium, iron and aluminum had to be removed previous to analysis.

Reitemeir (22) reported a method for the analysis of soils in which only calcium was removed before magnesium was determined. Sterges and MacIntire (26), and also Wolf (30), developed methods for the determination of magnesium in plants on a micro scale. In these methods no interfering ions were removed, since their concentrations were very low in the range studied.

The stability of the color formed in the thiazole yellow method has been the subject of much study. Results from these studies have shown that hydroxylamine acts as a color stabilizer (9) after removal of iron, calcium, phosphorous, and aluminum. Polyvinyl alcohol along with hydroxylamine and a compensating solution, which contained all interfering ions, has been reported as being satisfactory (31), but all of these solutions, with the exception of the compensating solution, were not stable over long periods of time.

Other methods for magnesium determination, that do not utilize thiazole yellow, have been reported. In these methods 8-hydroxy-quinoline has been used as the color producing agent. The method reported by Weeks and Todd (28), requires the previous removal of interfering ions. The method developed by Willson (29) minimized the effect of extraneous ions since it is used on micro scale.

These methods have certain faults or limitations that are common to all, such as instability of the color, or color agent, the necessity of removing interfering ions, or a critical pH range over which the method is sensitive. All of these factors indicate that a workable spectrographic procedure for the determination of magnesium in plants is desirable.

Magnesium has been determined spectrographically, using the d. c. arc, but this method has not proven too satisfactory in this laboratory. Since the method chosen for this research involves the excitation of solutions by means of the high-voltage a. c. spark, only the various techniques of solution excitation were considered in this literature search.

Of the methods described for solution excitation, only a few seemed simple enough to justify their use as routine procedures. Among the more elaborate methods are the ones used by Jolibois and Bossuet (12) and by Duffendack et al. (4). In these methods, the sample is placed in a constant level bulb and allowed to flow through a capillary tube into a chamber

which contained a platinum electrode. The spark would be struck across this electrode and another situated above the container. The solution is allowed to flow over the top of the lower electrode and thus enter the analysis gap. This type of apparatus necessitates a thorough washing of the complete system between samples and therefore appears to be time consuming.

Kiers and Englis (13) made use of a small pipette which is inserted into an upper electrode of carbon, and allows the solution to drop through the hollow electrode into the analysis gap. Although this method is much simpler than those mentioned above, it still requires washing between samples. It was found also that the rate of flow from such a pipette is very difficult to control.

Lamb (14) has described an atomizer arrangement in which the solutions are caused to be vaporized across the analytical gap. Lamb (14) stated that this method requires only washing of the electrodes between samples, and that the same electrodes may be used for all samples. This method has the fault common to all atomizers. The atomizer becomes clogged and thus necessitates the removal of all solid material from the solution. The rotating disk electrode is one of the newer sources for spark excitation. It has been used by Jacobson and Meyers (11) to determine minerals in biological fluids, and was reported to be satisfactory. This type of apparatus was not available for this research so a similar one was constructed. The finished unit proved

to be too erratic to permit reproducibility, so it was given up
in favor of a simpler method.

A simpler method of solution excitation was followed in the
work of Mathis (18). The lower electrode was drilled out partial-
ly, the carbon replaced, and the solution added to this absorptive
receptacle. The solution was then immediately sparked. A very
similar technique was used by Sloviter and Sitkin (24). They pre-
heated carbon electrodes to make them absorptive, added the solu-
tion, and then began the excitation.

The method introduced by Feldman (6,7) seemed adaptable to
rapid, simple, and yet accurate analysis. Delany and Owens (5)
have reported favorably upon this method as a means of deter-
mining many impurities in bismuth matrices. Since this method
was adopted for our research, it will be described in greater
detail in the following sections.

<div style="text-align:center">EXPERIMENTAL</div>

<div style="text-align:center">Description of Apparatus</div>

The spectrograph used in this research was a Bausch and Lomb,
large, Littrow-type instrument with interchangeable glass or
quartz optics. The quartz optics, which allow the selection of
wave lengths between 2100 and 8000 Å, were used for the method
described here. Position five, which covers the range from
2600 to 3350 Å was used, and attained by setting the focus at

108 with the plate tilt at 242.

The spectrograph has an optical path of 1827 mm, and a linear dispersion of 3.15 Å per mm at a wave length of 2780 Å. The prism is 57 mm high, and has a refracting face of 95 mm.

Energy from the source was focused with a condensing lens upon a cylindrical lens which focused it upon the slit itself. The use of this cylindrical lens enhanced the illumination and made shorter exposures possible.

The power 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 0.45 KVA output furnished a secondary voltage of 15,000 volts a. c. from a primary voltage of 115 volts.

Preparation of a Calibration Curve

Since a prism does not give constant dispersion, it was necessary to prepare a calibration curve for position five by plotting wave length versus scale reading of the plate. This was accomplished by sparking an iron spectrum and, just below it, on the same plate, a spectrum of one of the standards used for the determination.

An approximate curve was constructed from a few of the iron lines as compared to the iron spectra given by Brode (1). From this approximate curve, wave lengths of strong, known lines were

found and corrected to true values. The original curve was then re-drawn to fit. Figure 1 is a graph of the curve thus prepared.

Selection of Magnesium Line for Analysis

Magnesium exhibits many strong spectral lines which are adaptable to spectrographic analysis. Many substances, however, are contaminated with magnesium and purification of standards and apparatus is tedious. For this reason it appeared desirable to select one of the less intense lines for this research. The five magnesium lines which lie between 2777 and 2783 $\overset{\text{o}}{\text{A}}$ appeared to offer the characteristics demanded of them. Of these five lines, however, only the first and third were used because they were adaptable to extreme concentration changes. It was found later than in actual determinations the third line of the group (2779.8 $\overset{\text{o}}{\text{A}}$) gave the most consistent agreement with the chemical determinations, and was used therefore for the remainder of the analyses. Brode (1) lists no interfering ions for this line, and this was found to be true in all concentrations studied.

Selection of the Internal Standard

The use of internal standards in spectrochemical analysis was first introduced by Gerlach and Schweitzer (8) and has been used advantageously by many workers in the field. In selecting

an internal standard for the purpose of measuring the relative exposure for any given sample, an attempt is made to utilize some element whose properties are such that it will respond to excitation in the same manner as the test element.

In order to meet these requirements, the internal standard should, (a) have the same ionization potential as the test element, (b) be of nearly equal mass as the test element, (c) have nearly the same boiling point as the test element, and (d) have the same distribution modulus as the test element. These are the basic qualifications set forth by Langstroth and McRae (16,17) in their studies of the nature of the excitation source.

Many elements have been used as internal standards for magnesium. Among these, Jacobson and Meyers (11) tried lithium, cadmium, copper, and nickel. They reported best results with lithium. It was found, however, to be unsatisfactory for the magnesium line at 2780 Å since lithium has no strong lines in this region of the spectrum.

Duffendack et al. (4) used the cadmium line at 3261 Å as a control line for the magnesium line at 2852 Å. This line was undesirable also since the hydroxyl bands, which begin at about 3000 Å, would cause varying background on the photographic plate.

Clements (3) reported good results with tin as an internal standard for phosphorous, and Smith et al. (25) reported that it was favorable for boron. These reports suggested that these elements might be determined simultaneously or, perhaps, under different conditions, with the same set of samples.

Examination of the properties of tin and magnesium showed that they compared favorably with respect to ionization potentials. Their potentials are 7.3 and 7.6 volts respectively, and their energy distribution, given by Langstroth and McRae (16) are of the same order. Excluding the boiling points of the elements, which was not considered as critical in this type of excitation, the only unfavorable feature which tin exhibited was its much larger mass. Tin was chosen as the internal standard since it seemed to offer more favorable than unfavorable characteristics.
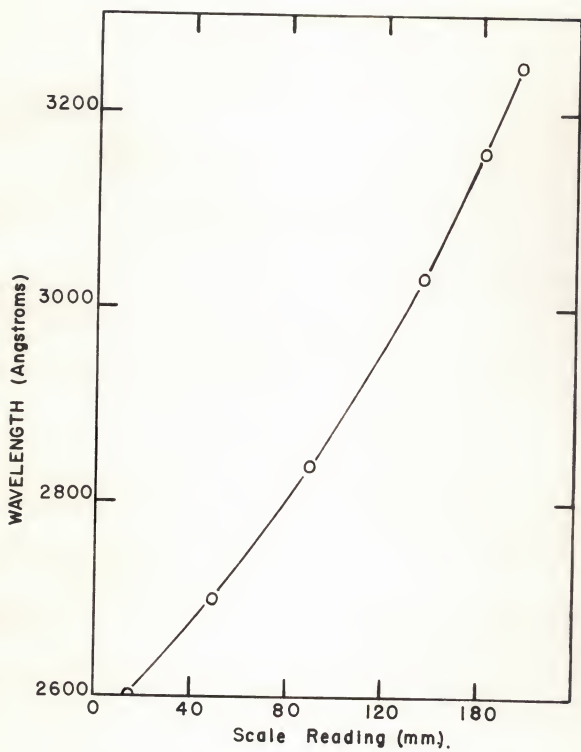
FIG. I. CALIBRATION CURVE FOR POSITION 5.

Selection of the Spectrographic Buffer

It has been generally accepted that in the analysis of com-
plex materials where extraneous ions of low ionization potential
or high concentration are present, the intensities of the test
elements or internal standard will be affected by the foreign
ions. To minimize this effect, it is common practice to employ
an ion of low ionization potential as a spectrographic buffer.

In the high voltage a. c. spark it was considered that most
particular attention should be given the transport mechanism of
the ions present. According to Langstroth and McRae (17), ions
of varying size and ionization potential have different energy
distributions along the axis of the discharge. The introduction
of an element of lower ionization potential than the test element
into the discharge will cause the distribution of the test element
to fall off more sharply toward the unloaded electrode. The pur-
pose, then, of the buffer element is to effect a more even energy
distribution throughout the spark gap.

The buffer solution should contain an ion of low potential
and of small mass. It should not have a very complex spectrum,
and should not interfere with the test element. Some of those
that have been suggested are, aluminum chloride, sodium chloride,
potassium-aluminum sulfate, lithium chloride, and lithium tar-
trate.

In the use of an element for an internal standard in the
analysis of solutions, one need not be concerned with the

hygroscopicity, or boiling point of that element. These are two important factors to be considered in the analysis of solids. Since only the ionization potential, mass, and complexity of spectrum were to be considered here, lithium chloride, which has been reported as a satisfactory buffer (25), was selected. For all analyses in this research, lithium chloride was used as a buffer to the extent of 8 mg per ml of sample solution.

In order to determine if lithium had any undesirable effect on either the magnesium or tin lines, a set of test solutions was made up containing varying amounts of lithium chloride. Figure 2 represents the data obtained from these solutions. These data show that, aside from the slight depression in the intensity of the magnesium line with the initial addition of lithium, the amount of buffer added to any one sample is not critical as far as interference is concerned. The working curves in Figure 3 show the linearity of the plotted ratios and indicate that no ions are interfering.

Influence of Extraneous Ions

The influence of extraneous ions has been investigated by several workers and most of them have agreed that when foreign ions were present in large quantities, compared with the test element, an alteration in intensity of the lines of the test element occurred. Brode (1) reported a case where one Mg/Pb
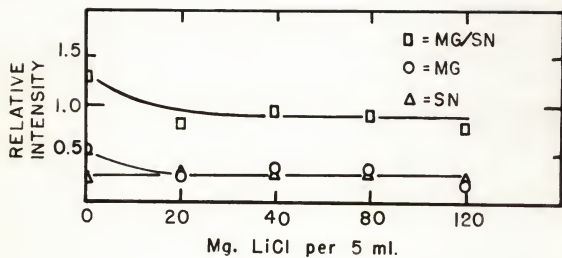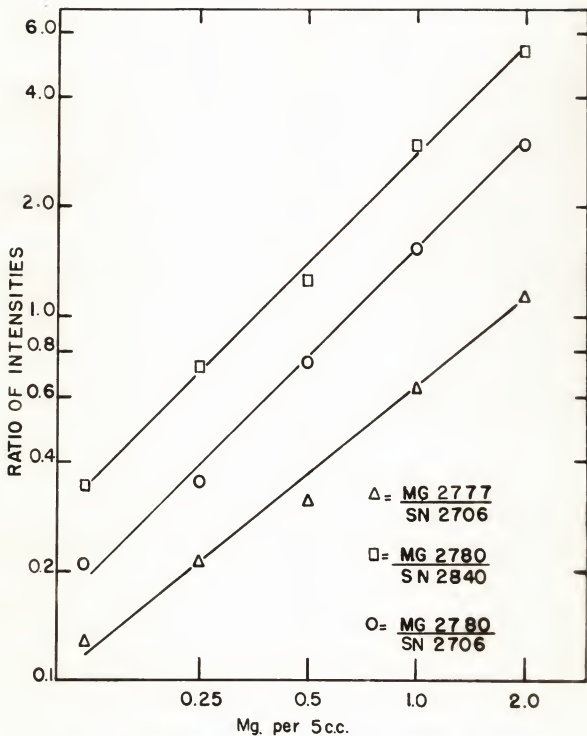
FIG. 2. EFFECT OF LITHIUM ON THE MG/SN RATIO.

FIG. 3. WORKING CURVES FOR MAGNESIUM ANALYSIS

ratio increased while another Mg/Pb ratio decreased due to the presence of the same ion. Brode and Timma (2) have devised a mathematical relationship which describes the magnitude of the effect of the extraneous ion on the intensity of the test element. Clements (3) found that the effect of calcium and potassium on the lines of phosphorous could be minimized through the use of a suitable buffer ion.

Duffendack et al. (4) reported an enhancement of the magnesium 2852 Å line upon the addition of calcium to the solutions tested. The internal control line used was the cadmium 3261 Å line. Scribner (23), however, found that a cadmium electrode acted as a stabilizer for the Mg/Al ratio throughout a series of samples of varying composition. This difference in behavior was probably due to the differences in the quantity of cadmium present in each case.

All authors whose papers have been studied agree that the selection of a suitable buffer solution minimizes the effect of extraneous ions when they are present. In order to establish the reliability of lithium chloride as a spectrographic buffer, the elements calcium, potassium, and phosphorous, all of which occur in large and varying quantities in plant material, were added to solutions containing only tin, magnesium, and lithium ions. All elements were in the form of their chlorides. Figures 4, 5, and 6 show the effect of these elements on the line intensities and on the intensity ratios. The relative concentrations of the elements used are given in Table 1. The wide intensity

changes which occurred with the addition of these elements were not attributed solely to the presence of the specific ions present, but also to the variations which occur in the current and to the fact that a variation of total concentration of ions seemed to influence the intensities of the individual lines.

Calcium produced slight variations in the intensities of the tin and magnesium lines. The variations are considered as having negligible influence on the working curves. Phosphorous caused general suppression of the line intensities, and the ratio of the lines showed a decrease which was found to be minimized in the working curves prepared with the standards given in Table 4. The addition of potassium seemed to give no troublesome error in line intensities or ratios with exception of the first addition. This first point appeared to be in error but, since it could not be redetermined, it was retained in the figure but was not considered in drawing the curves.

From the data obtained in these studies, and from the marked enhancement of the tin line which occurred during an unsuccessful determination in which the standards employed had no foreign ions present, it was assumed that the effect of total ions concentration was of much greater magnitude than extraneous ions and demanded more attention.[1]

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[1] The average density of the Sn 2706 Å line was 0.250 in the standard solutions, while it was 0.921 in the samples. The density of this line showed a continuous increase with increasing concentration of magnesium in the standard solutions.
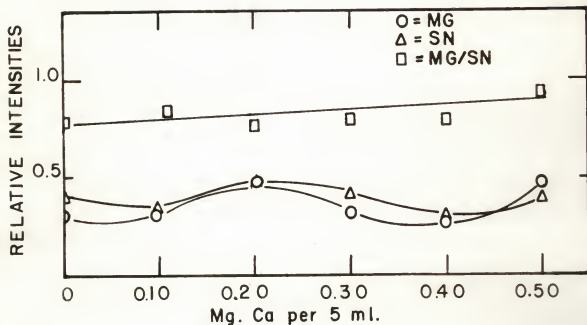
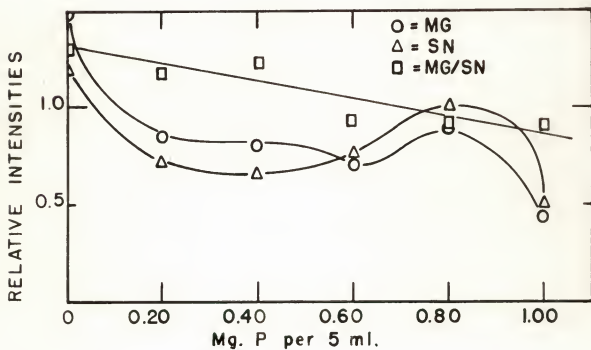FIG. 4. EFFECT OF CALCIUM ON THE MG/SN RATIO.

FIG. 5. EFFECT OF PHOSPHOROUS ON THE MG/SN RATIO.

Mg. K per 5 ml.
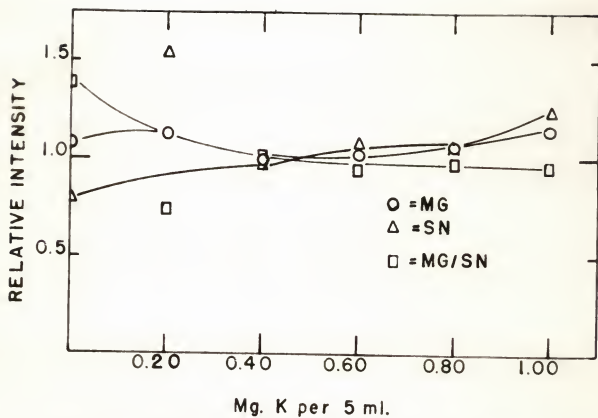
FIG. 6   EFFECT OF POTASSIUM ON THE MG/SN RATIO.

Table 1. Composition of solutions used to study the effect of
extraneous ions.

Extraneous ion	Conc. of ion mg/ml	Conc. Mg mg/ml	Conc. Sn mg/ml	Conc. LiCl mg/ml
Calcium				
1.	0.00	0.10	0.20	8.00
2.	0.02	"	"	"
3.	0.04	"	"	"
4.	0.06	"	"	"
5.	0.08	"	"	"
6.	0.10	"	"	"
Potassium				
1.	0.00	"	"	"
2.	0.04	"	"	"
3.	0.08	"	"	"
4.	0.12	"	"	"
5.	0.16	"	"	"
6.	0.20	"	"	"
Phosphorus				
1.	0.00	"	"	"
2.	0.04	"	"	"
3.	0.08	"	"	"
4.	0.12	"	"	"
5.	0.16	"	"	"
6.	0.20	"	"	"

Stability of the Magnesium:Tin Ratio

The most important criterion to be met by any line pair used
in quantitative spectrographic analysis is that the lines chosen
for investigation should give reproducible ratios. In a study
of the stability of the Mg/Sn ratio, several solutions were made
up to contain constant amounts of the two elements. Several

exposures of these solutions were made and the constancy of the
ratios noted. In solutions which contained only tin and mag-
nesium the line intensities varied considerably, but in the solu-
tions containing lithium this variation was less noticeable.
This is shown in Table 2. The effect of the lithium ion on the
ratios of the lines is quite pronounced. For this study each
electrode was refilled and three consecutive exposures were
made. The electrode was then discarded and replaced with a new
one. It should be noticed that the optical density of the lines
increased as each electrode was re-used. If no lithium chloride
was present, however, there was a decrease.

Why the intensity ratio should increase in this manner with
successive sparking of any one electrode is not known. It was
noticed, however, that, in solutions which contained all of the
ions present in plant ash, this increase was more marked. Lang-
stroth and Brown (15) found that a similar increase in intensity
occurred with increasing concentration of magnesium, and de-
scribed it as being due to absorption of energy in the lower con-
centrations. It was found in this research, however, that the
initial sparking of a sample gave results which compared most
favorably with the chemical analysis.

Since no explanation for the behavior of the line intensities
was readily available, and would have constituted a research pro-
ject in itself, each sample was given only one exposure on each
electrode. Duplicate exposures were made with different elec-
trodes and very little trouble was encountered.

Table 2. The stability of the Mg/Sn ratio, and the effect of the buffer solution.

	Without buffer				With buffer			
No. :	Mg den.	: Sn : den. :	Mg/Sn:	:Percent: dev. :	Mg den.	: Sn : den.:	Mg/Sn :	:Percent dev.
1.	.594	.594	1.00	20.6	.244	.301	.811	7.0
2.	.409	.268	1.52	20.6	.297	.367	.810	6.9
3.	.438	.292	1.50	19.0	.332	.432	.770	1.6
4.	.553	.602	0.92	27.0	.204	.260	.785	3.6
5.	.516	.450	1.15	8.7	.276	.357	.775	5.0
6.	.516	.482	1.07	15.1	.319	.444	.720	5.3
7.	.602	.509	1.18	6.4	.201	.252	.798	5.3
8.	.426	.357	1.19	5.6	.264	.409	.645	14.9
9.	.409	.284	1.43	13.5	.337	.469	.718	5.3
10.	.538	.426	1.26	0.0	.211	.237	.890	17.4
11.	.314	.233	1.35	7.2	.337	.469	.718	5.3
12.	.305	.201	1.52	20.6				
Mean.			1.26	13.8			.844	6.1

Preparation of the Electrodes

The electrodes used in this research were commercial grade graphite from the National Carbon Company. The graphite rods were cut in to 1¼ inch lengths for both the upper and lower electrodes. The porous cup electrode, which served as the upper electrode, was prepared by placing the cut rods into an especially built jig quite similar to the one described by Feldman (7), and drilling through the center, along the axis, to within approximately 0.5 mm of the bottom. The drilling was done on an ordinary drill press, and uniform floor-thickness was maintained through use of a slightly tapered spacer which could

be slipped under the drill on one corner but not on the other.

A 5/32 inch drill was used to prepare the porous cup electrodes which were 5/16 inch outside diameter; the counter electrodes were 3/16 inch in diameter. This arrangement of electrodes insured adequate spark area and yet limited the discharge to the sample area. Figure 7 shows the porous cup electrode in cross section and the counter electrode in place.

Preparation of the Standards

A standard stock solution very similar to that used by Morris et al. (20) was prepared and portions of this solution were used in making up the standards for the determinations. Tables 3 and 4 give the composition of the standards and stock solution. To prepare a standard from the stock solution, an equivalent amount of the stock was measured into a small glass vial and evaporated to dryness. The remaining salts were then redissolved in five ml of the buffer solution which contained the internal standard.

Table 3. Composition of the standard solutions.

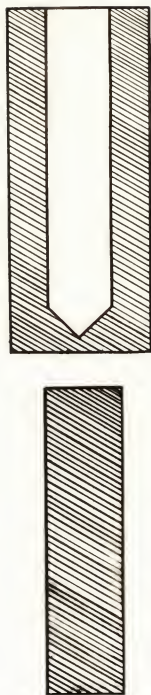| Standard number	:	Stock sol. ml	:	Buffer sol. ml	:	Mg/5ml mg	:	Sn/5ml mg
1.		0.05		5.00		0.125		2.00
2.		0.10		"		0.250		"
3.		0.20		"		0.500		"
4.		0.40		"		1.000		"
5.		0.80		"		2.000		"

FIG. 7.   THE POROUS CUP ELECTRODE; WITH
          THE COUNTER ELECTRODE.

Table 4. Composition of the stock solution (one liter).

Element	Weighed as	Grams of salt	Grams of element
K	KH_2PO_4	21.8500	6.284
P			5.000
Mg	$MgSO_4 \cdot 7H_2O$	25.4409	2.500
Mn	$MnSO_4 \cdot H_2O$	0.0924	0.030
Al	Al_2O_3	0.1899	0.100
Na	NaCl	3.1711	1.250
B	H_3BO_3	0.0572	0.010
Cu	$CuCl_2 \cdot 2H_2O$	0.0536	0.020
Ca	$CaCO_3$	1.3880	0.500
Fe	$Fe(NH_4)_2SO_4 \cdot 6H_2O$	1.4230	0.100

Spectrographic Procedure

A one-gram sample of plant material was dried in an air oven
overnight at 100° C., and the amount of moisture was calculated.
The moisture-free sample was then ashed in a muffle furnace over-
night at 650° C. The per cent of ash was found and a weighed
portion of the ash was placed in a small glass vial. For most
samples 15 mg of ash proved to be adequate. Two ml of 1:1
hydrochloric acid were added to the ash, and the vial was placed
on a hot plate to evaporate the solution to dryness at medium

heat. It was found that better solution of the residue could be accomplished if the sample was removed immediately after complete evaporation of the liquid.

When the sample had cooled to room temperature, five ml of the buffer solution containing 0.4 mg of tin per ml and 8.0 mg of lithium chloride per ml were added. The vial was then stoppered tightly and shaken vigorously to insure solution of all salts. After all insoluble matter had settled out, the sample was ready for analysis.

A portion of the sample was injected into the upper electrode with a long-nosed dropper which was inserted into the electrode until it touched the bottom, and withdrawn as the solution was dispensed. This precaution avoided trapping any air bubbles in the cup.

No prespark period was given the sample, as the solution entered the analysis gap at a maximum of three seconds after ignition. For most samples, the time necessary to feed into the gap was less than one second. The dropper was washed in distilled water at least five times between samples and then rinsed in the next solution to be run.

All samples were given a 60 second exposure at a slit width of 50 microns, and a spark gap of 2.5 mm. Slit height was maintained at one mm, thus limiting the exposure to the center of the spark image and allowing as many as 40 exposures on one 4x10 inch plate. Eastman type 33 plates were used. The spark

gap was adjusted to proper dimension with a leaf-spacer which consisted of strips of stainless steel of different thicknesses which were mounted about a fixed shaft. The leaves were held in a plane parallel to the optical bench by a compressed spring and spacers. The shaft upon which the spacer was mounted was clamped onto the optical bench and could be raised or lowered to adjust the heighth of the electrodes for focusing.

For the alignment of the electrodes during operation, the following procedure was followed. The spacer was swung into place and the lower electrode was raised until contact was made with the spacer. The upper electrode was then lowered until it rested upon the spacer without impairing movement of the spacer. The spacer was then pivoted away from the electrodes and the sparking begun.

A set of standards was exposed on each plate to insure proper calibration of the working curve. The exposed plate was developed for five minutes at 68° F. in X-ray developer that was diluted with two parts of water. It was then given a short rinse in a short stop which contained approximately one-half ml of acetic acid, and fixed in X-ray fixer for at least ten minutes. This entire operation was carried out in a constant temperature, constant agitation developing tank.

The plates were washed for at least 20 minutes, and dried on a warm air drier. Line intensities were read on an ARL-Dietert densitometer and a working curve was prepared for each plate.

Comparison With Chemical Method

In order to compare the spectrographic method with an accepted chemical method, eighteen samples were analyzed by the proposed method and results were compared with those obtained on the same samples by the thiazole yellow method. A modification of the thiazole yellow method described by Wolf (30) was used for the colorimetric analysis. Results of these analyses are presented in Table 5.

For the colorimetric procedure, 20 mg of ash was dissolved and made up to 50 ml with Morgan's universal extracting solution (21). This was designated as "sample". The sample was allowed to stand overnight to insure solution of all magnesium. A one-ml portion of the sample was withdrawn, and placed in a colorimeter tube. This was then made up to 20 ml with the extracting solution, and then one ml of thiazole yellow reagent (0.2 gm/400 ml 50 per cent methyl alcohol), and exactly 3.5 ml of 15 per cent sodium hydroxide were added.

The per cent transmittancy was read exactly five minutes after addition of the sodium hydroxide. A standard curve was prepared by making a series of solutions to contain from one to five ppm. of magnesium. The standards were treated in the same manner as were the samples. A blank was made to contain all reagents used in the samples, and the galvonometer was set so that this blank gave a 90 per cent transmittancy. The color measurements were made on an Evelyn colorimeter with the green 515 m filter.

Samples 1 through 11 were alfalfa ash which ranged from 1.39 per cent magnesium to 2.00 per cent. The remainder of the samples, which were determined by an independent worker, were sorghum ash and ranged from 1.58 to 2.86 per cent magnesium.

Table 5. Comparison of the spectrographic method with the thiazole yellow method.

Sample number	Per cent Mg in ash		Difference	Per cent difference
	Spec.	Thiazole yel.		
1.	1.34	1.51	0.17	11.3
2.	1.37	1.50	0.13	8.6
3.	1.77	2.00	0.23	11.5
4.	1.36	1.51	0.15	9.9
5.	1.83	2.00	0.17	8.5
6.	1.42	1.43	0.01	0.7
7.	1.40	1.52	0.12	7.9
8.	1.18	1.39	0.21	15.1
9.	1.37	1.79	0.42	23.4
10.	1.43	1.54	0.11	7.2
11.	1.35	1.44	0.09	6.2
12.	1.77	1.58	0.19	12.0
13.	1.47	1.71	0.24	14.0
14.	1.67	1.64	0.03	1.8
15.	1.90	1.96	0.06	3.3
16.	2.20	2.34	0.14	6.0
17.	2.27	2.44	0.17	6.9
18.	3.20	2.86	0.34	11.9
Mean				9.2

While there seems to be rather large percentage differences in some of the values listed above, and absolute error is small in most cases. Sample no. 9 for example shows only a 0.063 mg error in a 15 mg sample of ash.

Precision of the Method

Acceptance of a method demands as its primary criterion
precision within the method itself. In order to judge this pro-
cedure for precision, a series of determinations were made on
two samples, and the values obtained are compared in Tables
6 and 7. The per cent probable error obtained in the alfalfa
analysis was 2.36, with a standard error of 3.38 per cent. In
the case of the sorghum sample, fewer determinations were made
but due to the higher concentration, better precision was attain-
ed with a standard error of 2.80 per cent and a probable error
of 1.95 per cent. This is believed to be acceptable precision
and compares favorably with other determinations (25).

Table 6. Precision obtained in the spectrographic determina-
tion of magnesium in alfalfa.

Determina- tion no.	Mg/15 mg ash mg	Per cent Mg/ash	D.	$D^2 \times 10^{-4}$
1.	0.199	1.33	0.02	4
2.	0.210	1.40	0.05	25
3.	0.195	1.30	0.05	25
4.	0.195	1.30	0.05	25
5.	0.220	1.46	0.11	121
6.	0.220	1.46	0.11	121
7.	0.240	1.60	0.25	625
8.	0.165	1.10	0.25	625
9.	0.196	1.31	0.04	16
10.	0.171	1.13	0.22	484
11.	0.212	1.41	0.06	36
Totals	2.223	14.80	1.21	2107
Mean	0.202	1.35	0.11	

Table 6 (concl.).

Determina- tion no.	Mg/15 mg ash mg	Per cent Mg/ash	D.	$D^2 \times 10^{-4}$

Standard deviation (s) = $(D^2)^{\frac{1}{2}}/(n-1)^{\frac{1}{2}} = (2107 \times 10^{-4})^{\frac{1}{2}}/(10)^{\frac{1}{2}} =$
0.144

Standard error = $s/(n)^{\frac{1}{2}} = 0.144/(3.16)^{\frac{1}{2}} = 0.0456 = 3.38\%$

Probable error = $0.0456 \times 0.7 = 0.0319 = 2.36\%$

Table 7. Precision obtained in the spectrographic determination of magnesium in sorghum.

Determina- tion no.	Mg/15 mg ash mg	Per cent Mg/ash	D.	$D^2 \times 10^{-4}$
1.	0.325	2.16	0.21	421
2.	0.400	2.66	0.29	841
3.	0.360	2.40	0.03	9
4.	0.350	2.35	0.03	9
5.	0.330	2.20	0.17	279
6.	0.380	2.54	0.17	279
7.	0.350	2.33	0.04	16
Totals	2.495	16.63	0.94	1854
Mean	0.356	2.37	0.13	

Standard deviation (s) = $(D^2)^{\frac{1}{2}}/(n-1)^{\frac{1}{2}} = (1854 \times 10^{-4})^{\frac{1}{2}}/(6)^{\frac{1}{2}} =$
0.175

Standard error = $s/(n)^{\frac{1}{2}} = 0.175/(7)^{\frac{1}{2}} = 0.066 = 2.80\%$

Probable error = $0.066 \times 0.7 = 0.046 = 1.95\%$

Estimation of Other Elements

In the spectrographic determination of magnesium, some use
has been made of the flame source (10) as a means of excitation.
While this method gives good results, it has nothing to offer to-
ward an estimation of the relative concentrations of other ele-
ments present in the sample. Although this method was developed
primarily for the determination of magnesium, it was found that
other elements whose lines are sensitive to spark excitation in
the concentration used gave fair working curves when the tin
line at 2706 Å was used as a reference. No attempt was made to
check the reliability of these curves but it was felt that they
offer valuable information concerning the approximate concentra-
tions of these other elements.

Figure 8 illustrates typical working curves for the simul-
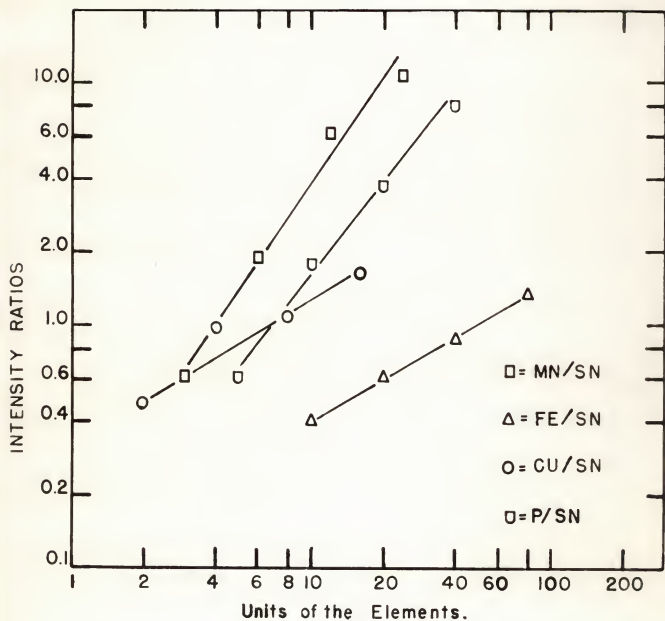taneous estimation of phosphorous, iron, manganese, and copper.

FIG. 8. WORKING CURVES FOR ESTIMATION OF OTHER
ELEMENTS.

CONCLUSIONS

A spectrographic method for the determination of magnesium
in plant material has been developed. The method employs the
porous cup electrode for direct spark excitation of solutions.
Lithium chloride was used as a buffer solution to minimize the
fluctuations which occurred in the excitation source, and tin
was used as an internal standard.

The proposed method gave fair comparison with the thiazole
yellow method for magnesium determination, and gave an average
standard error of 3.06 per cent with an average probable error
of 2.15 per cent in the analysis of plant material. Magnesium
was determined successfully in alfalfa and sorghum ash with a
minimum amount of preparation.

It was found that calcium, phosphorous, and potassium had
little effect on the working of the internal standard principle
within the concentration ranges studied. It was found, however,
that a great increase in the total ion content of any solution
gave marked enhancement of the tin line.

The proposed method also allows a simultaneous estimation
of iron, copper, potassium, and phosphorous from the same set
of exposures. It is felt that this method has much to offer
toward this type of analysis and that a further study of its
application should be made.

ACKNOWLEDGMENTS

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APPLICATION OF THE SOLUTION METHOD OF SPARK EXCITATION
TO THE SPECTROGRAPHIC ANALYSIS OF
MAGNESIUM IN PLANT MATERIAL

by

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The purpose of this research was to study the application of the high voltage a. c. spark to the excitation of solutions for spectrographic analysis of plant material. The spectrograph used was a Bausch and Lomb, large, Littrow-type instrument, and the source was a Bausch and Lomb condensed spark unit.

Lithium chloride was used as a spectrographic buffer, and tin was used as an internal standard. The influence of calcium, potassium, and phosphorous on the line intensities was studied and it was found that these three elements caused some variations, but that these variations were not pronounced enough to be considered important. It was found that solutions containing high concentrations of ions caused considerable variation in the line intensities. When a standard solution containing most ions present in the samples was used this variation was minimized.

An attempt to make duplicate runs on one electrode was unsuccessful. Line intensities increased with each successive exposure. The ratios of the lines also increased in the same manner. This behavior was not accounted for, but was found to be suppressed when lithium chloride was present.

All determinations were made with 15 mg samples of plant ash. This ash was digested in dilute hydrochloric acid before it was taken up into the buffer solution. Samples were made up to 5 ml. Portions of the sample solution were introduced into the porous cup electrode with a long-nosed pipette. Exposures

were 60 seconds at a slit width of 50 microns and a slit length
of one mm.

Exposures were made on Eastman type 33 plates which were
developed for 5 minutes in dilute X-ray developer and fixed in
X-ray fixer. Line intensities were read on an ARL densito-
meter. A set of standards was exposed on each plate, and a
standard curve was prepared from these standards.

The proposed method was compared to an adaptation of the
thiazole yellow method on a series of 18 samples. The average
difference between these two determinations was 9.2 per cent.
The maximum difference amounted to 0.063 mg of Mg in 15 mg of
ash. Eleven alfalfa analyses showed a standard deviation of
0.144, a standard error of 3.38 per cent, and a probable error
of 2.36 per cent. These same figures for seven sorghum analyses
were 0.175, 2.80 per cent, and 1.93 per cent respectively.

This procedure allows the simultaneous estimation of copper,
iron, manganese, and phosphorous.