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<https://doi.org/10.18297/etd/1807>

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UNIVERSITY OF LOUISVILLE

AN INVESTIGATION OF METHODS FOR QUANTITATIVE
SPECTROGRAPHIC ANALYSIS

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

By

Frederick Bertram Johnston

1939

Frederick Bertram Johnston

AN INVESTIGATION OF METHODS FOR QUANTITATIVE
SPECTROGRAPHIC ANALYSIS

Approved by Examination Committee

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Approved for English

June 6, 1939

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LIST OF DEFINITIONS

Factor	Significance
Rem.	100 % - % Varied Constituent in the Standard Mixture.
F	$\frac{\text{Remainder in Standard Mixture}}{\text{Remainder in Average Ash}} ; \% \text{ Oxide in}$ $\text{Average Ash} \times F = \% \text{ Oxide in Standard Mixture.}$
X	$\frac{\text{Equivalent Weight of Reagent}}{\text{Equivalent Weight of Oxide}} ; \text{The term}$ "equivalent weight" used here signifies grams per gram atom of the element.
Y	Reciprocal of the number of ml. of solution containing 0.1 gram of an oxide.
ΔL	Difference of lengths of spectral lines in a "line pair". Units $= 1/32$ inch on film.
*	Indicates a secondary source of reference.

The author of this thesis
acknowledges the kind aid
and helpful suggestions of
Dr. E.E. Litkenhous,
who directed this research.

INTRODUCTION

During the past few years the spectrograph has become recognized as an excellent means for quantitative analysis. Its most useful application has been the rapid determination of minute quantities of certain constituents and impurities which determine the physical and chemical properties of various materials. The minor constituents of metals, alloys, soils, precipitates, solutions, and plant and animal tissues have been estimated by quantitative spectral analysis. Very little emphasis, however, has been placed upon estimation of the major components of any substance by this means.

A rapid, economical, and fairly accurate means for determination of predominant mineral elements of raw materials would be very desirable in the processing industries. The practical importance of such a method has been discussed by Shipman (25) in a study of the effect of inorganic compounds in grain fermentations.

It is the primary purpose of this research to investigate methods for quantitative spectrographic analysis. The secondary objective is to investigate the applicability of these methods to the quantitative spectral analysis of the major mineral constituents of grain. These are potassium, sodium, magnesium, calcium, iron, silicon, and phosphorus.

HISTORICAL

Sir Isaac Newton might truly be called the father of spectroscopy. Although the law of refraction was discovered by Snell in 1621, the fact that different wavelengths of light are refracted by different amounts was unnoticed until 1666. It was in that year Newton found that white light incident upon a prism is dispersed into a colored spectrum. Later he used a slit in his experiments, but it was Fraunhofer who developed the complete spectroscope when he introduced the use of the telescope for visual examination.

Fraunhofer observed the phenomenon of the absorption lines characteristic of the solar spectrum, and in 1814 published results mapping 700 of them. Shortly afterwards, it was learned that these absorption lines appear at wave-lengths corresponding to spectral emission lines of known elements. Bunsen and Kirchhoff pioneered an investigation to establish the constituent elements of the sun, and laid a foundation for the entire science of spectroscopic analysis. These men were probably the first to establish the fact that each element has its own distinctive spectrum. A few years later Huggens and Miller commenced similar work on the stars.

The first true efforts to use the spectrometer for quantitative analysis were made by Hartley (20)*(26)*,

who attempted to utilize the progressive disappearance of spectral lines of elements with decrease of their concentrations in the source. By 1882 he had investigated the proportions of certain metals which would be evidenced in compounds by the presence of their lines in the spectrum. Pollok and Leonard (26)*, using the condensed spark spectra of metallic salt solutions, continued Hartley's work. With a quartz spectrograph they were able to show the degree of persistence of the spectral lines as the quantity of a metal in the sample was reduced.

Thus Hartley and his co-workers laid the basis for a method of approximate quantitative spectral analysis which has been frequently used to the present time in mineralogical and other analyses.

Working on the spark spectra of solids such as minerals, alloys, and fused salts, de Gramont (20)* found that the persistent lines were not always the strongest in the spectrum of a metal, that they are actually arc lines, but are present in the spectra of hot flames. The methods in most common use today are modifications of that of de Gramont, consisting of the visual comparison of a spectrogram of the specimen with a series of spectrograms previously prepared from standards of known composition.

Hitchie (20) eliminated the objection of duplicating the so-called standard conditions by photographing the spectra of the standards in juxtaposition to the spectrum of the unknown for each determination. This overcame variations in exposure and development.

Another great advance has been described by Gerlach and Schweitzer in "Foundations and Methods of Chemical Analysis by the Emission Spectrum ". This was a simple method devised to eliminate small deviations in routine and fluctuations of the source. The intensity of the spectral lines of the unknown was equated or compared for various percentage compositions with lines of the base substance, or some foreign substance purposely introduced in known amount. This is now generally known as the "Internal Standard Method " of Gerlach.

Brownson and van Someren (26)* employed the method of Gerlach in estimation of aluminum, iron, nickel, lead, manganese, and tin in brass, and similar minor constituents in lead alloys. A comprehensive survey of their application of the spectrograph to this field of analysis was published in 1931. At the same time, Ramage (26)* and his collaborators used the methods of de Gramont for semi-quantitative analysis of elements in animal tissue.

The difficulty of finding suitably spaced "homologous-" or "comparison lines" when using the internal standard method was neatly overcome by Scheibe and Neuhauser (26)* in 1928. Their method involved use of the logarithmic wedge sector to measure the relative intensities of the two homologous lines, rather than merely noting their equality. Twyman and Simeon (31) made subsequent modifications and improvement on this method, and Twyman and Fitch (31)* introduced the ocular micrometer for measurement of the lengths of lines in a homologous pair.

Twyman and Harvey (26)* have successfully employed the sector for estimation of chromium, manganese, and nickel in steels, using an arc between two specimens of the test sample. In England, Smith (26)* has performed extensive investigations for application of these methods to the testing of commercial products for conformity to specifications.

During the past ten years, literature has disclosed the development of a great number of other methods for quantitative spectral analysis, but these have simply been modifications or combinations of those already described. The trend has been for the applications of spectrographic analysis to become more numerous and diverse, and toward improved technique to secure greater accuracy.

THEORY

When a substance is sufficiently excited, or brought to a very high energy level by volatilization in an electric arc, there results a characteristic emission spectrum. The discontinuous spectrum of the arc proper, arising from the luminous flame containing vapors of carbon and its compounds, is visible, and a number of narrow lines caused by vapors of the metals present appear. Violet bands are produced by cyanogen, formed by combination of the carbon and nitrogen of the air, and give the arc its characteristic color. In the arc, all the metals and carbon, silicon, boron, phosphorus, and arsenic yield characteristic spectra.

If a pure element or mixture is arced to produce a spectrum, a number of lines of varied intensity appear. If that element is diluted with other elements or materials, the original spectrum lines decrease in both intensity and number. Upon further dilution the weakest lines disappear, the stronger lines grow weaker, and at the lowest concentration at which the element can be detected there remain only the raies ultimes or persistent lines. Since under like conditions of excitation and observation a given concentration of an element yields the same intensity for the same lines, quantitative analyses can be made by comparing the number and intensities of the lines of

those elements being determined with a series of reference standards.

Thus the basis of quantitative spectral analysis is that under the same conditions of experiment the intensities of the spectral lines of an element in a substance are functions of its quantity in that substance. The modifying conditions are the method of excitation, -whether flame, spark, or arc, the intensity of that excitation, the electrical potential, and the influence of other constituent elements. There are also the factors introduced in the photographic process, such as the optical system used, the type of film employed, the width of the spectrographic slit, and method and time of development.

Although it is impossible to predict the line intensity which will correspond to a given concentration of an element in a material, for any fixed set of conditions, reliable correlations can be obtained between intensities of lines of several constituents and their percentages. This is most fully realized when these factors are taken in relation to those of a dominant element.

The lines to be compared should be chosen close together in the spectrum, and if a number of elements are to be estimated from a single spectrogram, all the selected lines, including those of the standard, should lie in a

region of constant or slowly varying contrast of the photographic film. This is determined practically by a visual appraisal of a film on which is recorded a fairly continuous spectrum, such as that of iron.

Plate background offers some difficulty, and few corrections seem reliable, so that it is better to arrange the exposure to minimize its amount. Some experimenters have maintained that a certain amount of background is desirable to bring the fainter lines over the "threshold of sensitivity" of the film. Also it is important to time the exposures so that blackenings of the more intense lines do not exceed the maximum blackening obtainable on the film.

When an element occurs in considerable amounts in the sample, there is apt to be reversal of some of its lines, so that those lines which are not readily absorbed should be chosen. It is possible for this reversal to produce a weakening of the whole line when the absorption is insufficient to produce complete reversal. Therefore lines can be found for an element present in high concentration which appear weaker than in the spectrum of the same element at considerably lower concentration.

In the usual analysis, a mixture of several elements is being examined, and the relative intensities of the lines frequently show wide variations because some lines

are strongly affected by the presence of even small amounts of another. The lines chosen should be tested for such effects. All estimates should be based on the weakest lines that are clearly defined, and on those which vary most rapidly with change in concentration of the element.

There is no limit to the concentration at which elements can be determined spectrographically, but the errors of estimation are proportionally large.

The ratio of line intensities changes quite slowly with change in arc current above a certain amount, and the ratio becomes insensitive to such fluctuations as exist in a normal arc.

The arc is preferable to the spark because it is quicker, more convenient, and is fairly accurate. It possesses greater sensitivity because of the high temperatures of the electrodes, and the resultant density and concentration of the vapors evolved.

The types of specimens tested are widely variant. In metallurgical analysis, pieces of metals to be tested have served as the electrodes, and a current of 3 amperes has proved sufficient to produce an arc revealing all of the constituents present. Very small pieces of metal or other samples, such as powders, precipitates, or residues from solutions can be examined by arcing them in the

cavity of a lower carbon electrode. Refractory materials such as soils must be volatilized by use of high amperage, which increases the sensitivity of the arc. It is sometimes convenient to dissolve the sample and to spectrograph the solution, either as a residue formed by evaporating a few drops of it on a hot electrode, or as a spray blown between the carbons. However, this latter is permissible only with the spark.

Plant and animal tissues can be sparked for spectral analysis, but the general practice has been to reduce these to an ash. A vegetable ash contains carbonates, chlorides, phosphates, and silicates in unknown proportions, the ratio of these varying according to the method of ashing the particular sample. However, the relative amounts of the minor metallic constituents and some major element will remain unchanged regardless of the treatment.

In order to avoid volatilization of phosphorus, arsenic, tin, and other elements during the ashing, the sample must be moistened with concentrated nitric acid, and as the organic material burns off, it must be cooled and renitrated. It is desirable to eliminate all carbon before spectrographing. When this is completed, the addition of a slight excess of sulfuric acid serves to reduce all of the metallic constituents to the common basis of

the sulfate. Thus, after the excess sulfuric acid has been driven off by evaporation and gentle ignition, the mass is in a condition approximating normal sulfates, homogeneously mixed with pre-existing phosphates, silica, and chlorides. If this ash is then mixed with an equal weight of spectroscopically pure ammonium sulfate, there is supplied in effect a constant amount of sulfuric acid, the mass is rendered more porous, and the action of the arc is more regularized.

Some success has attended the preparation of small electrodes of plant materials by compression, followed by carbonization.

The question of the effect of the anions present in a sample immediately arises. Tourtellette and Rask (30) have determined that the number and intensity of aluminum lines are due entirely to the concentration of that element in the spectral source and is independent of the attached radicals. Duffendack, Wiley, and Owens (6) found, however, that the sulfates and phosphate radicals decreased the relative intensities of the lines of all the elements studied (Na, K, Mg, and Ca) with respect to those of cadmium, and that the chloride ion enhanced the intensities of those lines without appreciably changing their relative intensities.

Sodium, potassium, and magnesium have been found to decrease the relative intensities of the spectral lines of each other with respect to those of cadmium (6). The amount of these effects increases with increase in concentration of the disturbing element, but reaches an approximately constant value at relatively high concentrations.

Chlorides give low temperature arcs because of their comparatively high volatility, and as a consequence the arcs are not very sensitive. Nitrates are unstable in the arc. Sulfates are the most desirable form as they give a high temperature arc, are easily prepared, and since they do not absorb atmospheric moisture, may easily be handled in the powdered form.

Finally, the various factors involved in the photographic process should be considered.

The sharpness of the end-points of the lines can be enhanced by adjusting the spectrograph to critical focus, developing the plates to maximum contrast without fog, and placing the arc as far from the slit as possible and the sector disk as close as possible. The density of the background is made negligible in comparison with that of the spectral lines in the same operation.

Graphite electrodes are preferable to copper because of the greater sensitivity resulting partly from the

higher temperature attained and partly from their greater reducing power. Carbon electrodes are generally chosen because of their lower price, ease of coring and washing after use, comparatively steady burning, and extremely sensitive spectrum evolved.

CONSIDERATION OF METHODS OF OTHER INVESTIGATORS

In the development of the method of spectral analysis used in this research, all previous methods were given critical consideration.

It has been previously mentioned that the intensities of the spectral lines of elements are approximately proportional to the respective amounts of those elements in the sample. The determination of the amount of any element, then, has depended upon the measurement of the intensities of those lines, in comparison with standards of known and controllable intensities. The comparison has been effected in a number of ways.

De Gramont simply compared the spectrum of the sample with a series of spectra previously prepared from similar samples of known but varying content. An approximate estimation of the amount of any constituent in the specimen was then made by matching the sample spectra with respect to the intensities of the lines of the elements in question.

A refinement of this method was introduced by Nitchie (20). Differences caused by variation in photographic material and development were largely eliminated by photographing the spectrum of the unknown in juxtaposi-

tion to the spectra of the standards. These were a graded series of mixtures of composition similar to that expected in the unknown. To avoid unnecessary expenditure of time, the particular standards to be used with the sample were selected by a preliminary test. The approximately correct value was then found by comparison with three successive standards. Of these, one contained the amount of the element predicted from the preliminary test, another slightly more than that concentration, and a third slightly less than that amount. Nitchie emphasized the importance of using the weakest lines that are clearly defined, to avoid possible error caused by reversal. He began the practice of using complex standards for the purpose of determining several constituents simultaneously.

Probably the best technique yet developed was that of the internal standard method of Gerlach and Schweitzer. The lines to be determined were compared with the lines of another constituent in the same spectrum. This reference element was present in known or at least controllable amounts in every sample. The particular advantage gained was that, if for uncontrollable reasons a variation of conditions occurred, both the lines of the constituent to be determined and the lines of the reference standard were affected to the same extent and their ratios remained

essentially the same. Naturally a preliminary calibration was requisite, based on similar measurements of spectra from the series of standard samples.

Thus all of the constituents present in smaller amounts were determined relative to the main constituent. A hypothetical example would be the determination of iron, aluminum, magnesium, and copper in water. If a mineral residue were obtained by evaporation of a given volume of water, stirred the while to insure homogeneity of the sample, all those elements could be determined relative to the calcium present. This would then be easily determinable chemically as parts per million of the water.

Duffendack and Wolfe (7) obtained excellent results in the analysis of caustic liquors for traces of metallic impurities, using as the internal standard a small amount of sodium molybdate. The molybdenum furnished spectral lines sufficiently close to those of the test elements to serve as the internal control for all, and the lines selected were such that analysis could be made for all the test elements from a single exposure.

Similarly, an accurate means for the determination of magnesium, calcium, sodium, and potassium relative to cadmium has been developed for urinalysis (6). To eliminate mutual errors introduced by these elements, the

investigators employed the "method of excess". This involved separation of the solution into four portions, and addition of an excess amount of the disturbing elements to each portion tested. In any one of the four, an addition of 2% eliminated variation produced by any single element. This led to the idea that an analysis could be conducted on mixtures in which the concentration of interfering elements was sufficiently large that the effect on the intensity of all the other elements remained constant.

For the determination of minor constituents in plant ash, such as rubidium or zinc, the practice has been to introduce a small amount of some element foreign to that material, such as tellurium (23) or cadmium (16). In metallographic spectral analysis, a main constituent usually served as the internal standard, relative to which minor constituents or impurities were determined (26).

The necessity of finding suitably spaced homologous lines for the internal standard method was removed by Scheibe and Neuhausser (26)*, who measured the relative intensities of the two lines rather than noting their equality. This was accomplished by use of the logarithmic sector - a thin metal disk, the edge of which had been cut away in a logarithmic curve. When this was rotated before the slit of the spectrograph, an intermittent variable

exposure along the length of the slit was secured. The upper portion of the slit received the most, and the lower portion the least exposure to the radiation, independently of the rate of rotation.

If there were a practically stigmatic image of the slit on the film- that is, if each element of the slit had a corresponding element of the spectrum line on the plate of film, then the photographic blackening of the spectrum line along its length exhibited the same variations as the intensity of illumination along the slit. It was known that the photographic density of a film is nearly a logarithmic function of the quantity of incident light or duration of exposure.

The sector was appropriately given such a form that the time of exposure varied logarithmically from point to point of the slit. Therefore, the differences of lengths of two spectrographic lines were proportional to the logarithms of the ratios of the intensities of those lines and hence a function of the relative amounts of the corresponding elements. In practice, the working or operating curves were obtained by plotting the differences in lengths of a given pair of lines against the corresponding ratios of the amounts of the two elements. Providing that the intensity of radiation of each element were directly

proportional to its amount in the sample, the relationship was a straight line. For any two elements, the resultant curves of this function have been found to be different for the different line-pairs used.

Since the exposure was variable along the length of the slit, a gradual tapering-off of the intensity of the lines occurred, and each had the appearance of a long wedge. The determining factor with regard to the accuracy obtainable has been the accuracy with which it was possible to measure the lengths of those lines. This method has been applied in a variety of analyses. Slavin (26) and Sullivan (27) independently adapted the use of the sector disk to quantitative determination of cadmium, lead, and other constituents in zinc. The former measured the differences in lengths of lines by an ocular micrometer, and the latter with a small eyepiece and scale. The theory of the logarithmic sector and its application to quantitative spectral analysis have been discussed by Twyman and Simeon (31) and Nultgren (15).

Of most recent development has been the Ratio Quantitative system of Judd Lewis (17). This was simply a modification of the internal standard method, and involved use of specially prepared standards. All the constituents were determined in relation to a single con-

stituent, which was preferably a major one, and which could be determined by chemical means. The standards were of like composition to the specimen, so that modifying effects of component chemicals upon other elements were produced in both. The spectra were therefore strictly comparable as long as the conditions of excitation were maintained constant. An agricultural base, for example, has been devised to make more normal comparisons with vegetable ashes.

This base contains the elements Calcium 10, Magnesium 10, Potassium 35, Sodium 5, Phosphate 35, and Silica 5 in the proportions given. This can be further modified with small quantities of other elements such as iron, manganese, aluminum, or zinc. The lines of any one of the elements calcium, magnesium, potassium, or sodium could be used as the standards for comparison.

Milbourn (19) has recently published a paper on the spectrographic analysis of soil and plant materials using this method.

APPARATUS

The entire apparatus is shown in Figures 2 and 3, pages 27 and 29, and is described with reference to these illustrations in the following discussion.

The instrument proper consisted of a light-tight triangular metal body, supported on three legs. Two of these fitted into a grooved board, onto which the optical bench was bolted, the third leg being free, but supported on a base of equal height. A loose fitting cover allowed immediate access to all parts. Baffles and screens within the housing prevented extraneous light from reaching the screen.

The slit, grating, and camera were arranged to give a first order spectrum in a "fixed" Rowland mounting. As shown in Figure 1, the camera and grating were at opposite ends of a diameter of the Rowland circle, and the slit was at the 90° vertex of a right triangle inscribed in the semi-circle.

The slit was made of stainless steel jaws, of which one was movable. One knurled screw outside the body controlled the width of the slit, and the other effected the rotation of the slit about a line which might be imagined to exist between the center of the slit and the grating. By this second adjustment the slit opening was made parallel to the lines of the grating.

Fig. 1 Spectrograph and Rowland Circle

Figure 2. Spectrograph and Logarithmic Sector

- C Hinged Cover
- D Sector Disk
- H Film Holder
- P Pinion
- M Slotted Mask

A Wallace concave reflecting replica grating of 106 cm. focal length and 15,000 lines per inch was used to produce the spectrum. Its radius of curvature was the diameter of the Rowland circle. Since the film holder, H, was curved to coincide with the circle, as shown in Figure 1, all the spectrum lines were approximately in focus upon it.

The length of the spectrum exposed was 25 cm., and the dispersion of the grating was such that a range of 4000 Angstrom units ($\text{\AA}$) was covered. The region from 2800 $\text{\AA}$ to 6800 $\text{\AA}$ was obtained when the grating was normal at 4800 $\text{\AA}$. Normal dispersion with very slight deviation at the ends of the range was obtained.

The grating was mounted in the Grating Holder. This device rested on a track normal to the center of the film holder. The distance of the grating from the film could be adjusted by sliding the assembly along this track, and a lock screw held it in the final position. The grating could be rotated about its optical axis by two vertically counter-acting set-screws. A set-screw at the rear of the holder tilted the grating about a horizontal axis through its surface, so that the spectrum was displaced in a vertical direction. Another set-screw rotated the grating about a vertical axis, so that the spectrum range was displaced along the Rowland circle.

Figure 3. Optical System and Arc

B	D.C.Switch-Box	L_1	Quartz Lens
C	Hinged Cover	L_2	Quartz Lens
D	Sector Disk	P	Pinion
H	Film Holder	T	A.C.-D.C. Switch

A micrometer screw, passed through a threaded bushing fixed to the rear face of the housing, provided a sensitive means for adjusting the position of the grating.

The film holder, H, was a frame device, slotted on one side to receive a metal slide, and having a hinged cover, C, on the other. This holder was removable, and the entire assembly could be shifted vertically by means of a rack and pinion, P. This permitted exposure of adjacent areas when a series of spectrograms was desired on a single film. Slotted masks of metal, such as M, of different sizes, could be fitted into the camera opening, so that the width and number of exposures could be chosen. A maximum number of thirteen spectrograms could be taken on a single film, using a sixteenth-inch slotted mask.

The hinged cover, C, attached to the back of the film holder facilitated introduction and removal of the films. A strip of celluloid buffed to translucence with emery paper served as an excellent viewing screen. To the right of the film holder was a scale, and a pointer attached to the assembly indicated its vertical position.

The arc and optical system was supported in proper alignment with the spectrograph by means of the lathe type optical track or bench, B, as shown in Figure 5. One end of this was supported by a leveling screw,

and the other is linked to an instrument leg by an adjustable arm, shown quite clearly in Figure 2.

The arc support consisted of a single rod on which two clamps were mounted for holding the upper and lower electrodes in a vertical position. The support rod was clamped onto a non-tilting carriage, which could be moved along the track to any desired position. An indicator rod or alignment pointer (22), mounted on the arc support between the two electrode clamps, made possible exact resetting of the arc position preliminary to each exposure. The ends of the electrode clamps, the electrodes, and the alignment pointer are visible just outside the edges of the light shield.

The semi-cylindrical light shield, S, was mounted indirectly to a fixed support by means of two right-angle clamps and a short rod, shown well in Figure 3. This produced in effect an adjustable universal coupling by which the shield could be easily tilted out of position when arc adjustments were being made, and by which it could be shifted in any one of three directions.

The electrical circuit for the arc has been shown diagrammatically in Figure 4. An electrical potential of 250 volts direct current was supplied by two 125 volt generators in the Electrical Engineering Laboratory.

Alternators at the panel board controlled the output voltage of each generator, which was set by the individual field rheostats. Behind the panel was the 30 ohm resistor, which provided a constant and major portion of the circuit load. This was followed in series by a transformer primary coil, which acted as an inductance, of about 1 henry capacity, and added a resistance of approximately 4 ohms.

At the termination of the conduit was the switch-box and outlet terminals. The negative lead passed to a 12.5 ohm rheostat, of 8 ampere capacity, by which the arc current could be varied, thence through the ammeter shunt to the upper electrode. The switch-box, voltmeter, rheostat, shunt-plug, and ammeter are all shown in the upper portion of Figure 3. The positive lead passed through a double-pole-double-throw switch, T, to the lower arc electrode. The outer terminals of this switch gave access to 110 volt alternating current for general alignment work.

Two cylindrical quartz lenses, designated in Figure 3 by L_1 and L_2 , were used. The first, L_1 , of 11.5 cm. (4.5 inch) focal length, was located 14 cm. from the arc, with the plane face toward the arc, and its principal axis horizontal. The function of this lens was to form an

Fig.4 Electrical Circuit

enlarged image of the arc flame on the slit, and consequently on the grating. The second, L_2 , of 35.5 cm. (14 inch) focal length, was clamped at exactly that distance from the slit, plane face toward the arc, but principal axis vertical. This lens served to concentrate a portion of the radiation emergent from the first as a vertical beam, convergent on the slit.

The logarithmic sector, D, and motor were mounted on the track next to the spectrograph body, so that the sector disk was almost flush with the face plate. This position is shown in Figure 2. In Figure 3, the sector and motor are shown displaced from the correct position, in order that an oblique front view is obtained. The adjustment of this device will be described under the method of procedure.

A strip of paper on which a centimeter scale had been printed was attached to the side of the optical bench, the zero point falling directly in the vertical plane of the slit. An end of this scale is visible at the bottom of each photograph of the instrument. The positions of all the components of the complete optical system were then measurable relative to the plane of the slit.

Both lenses were held in special clamps, and these were mounted on hinged carriages so that either

could be temporarily and conveniently removed from the system. Quartz lenses were necessary to obtain the spectrum in the ultraviolet region.

For qualitative and quantitative work solid spectrographic carbons of low ash and impurity content were used. These were originally 6 inches in length, and $3/16$ inch in diameter. For ordinary alignment work and experimental work, inexpensive carbons of the ordinary type were employed. These latter operated on alternating current, whereas the better type required direct current.

A viewing box allowed convenient examination of the finished negatives, either wet or dry. This had an inclined window on which the film was placed, and diffuse indirect light provided illumination from beneath.

A scale, divided into fortieth parts of an inch, and printed on Bristol board, was used to measure the wave-lengths of the spectral lines. Since the dispersion of the spectrograph was 4000 Angstrom units over 10 inches, or $400 \text{ \AA}^\circ$ per inch, each of these divisions was equivalent to $10 \text{ \AA}^\circ$.

An ordinary print box was enlarged for making prints from the ten inch negatives. A red bulb maintained continuous illumination, and a white bulb was operated by a plunger when the felted lid was closed. At the side

window was a guide into which a Wratten No. 3 Green Filter was inserted.

The type of film used was Eastman Commercial , J- 38, a nitrate particularly sensitive in the violet and ultraviolet regions. The dimensions were $2\frac{3}{16}$ inch by $11\frac{1}{4}$ inch. Eastman Supersensitive Panchromatic film of the same dimensions was used for the infra-red photography. DK-50 developer, "hypo" (sodium thiosulfate), and Azo F, No. 4, single weight, glossy finish print paper were also used in the photographic processes.

Masks having slots of $\frac{1}{4}$ and $\frac{3}{8}$ inch depths served for qualitative and quantitative exposures.

PROCEDURE

A specially grooved support board was prepared to insure rigid alignment of the spectrograph and optical system. Two of the spectrograph legs were fitted into rubber cups between the two runners forming the edges of the groove, and the third was supported on a small base of equal height. The optical bench was connected to the instrument leg, and securely strapped and bolted to the guide board. These details are shown quite well in the two photographic plates.

The arc system was installed at the extreme end of the optical track, with the light shield directly before it. The first quartz lens was mounted about 14 cm. from the arc, as previously described. With the arc operating on a wide gap between the electrodes, the height and position of the lens were varied until a clear image of the arc flame was obtained across the slit. This was an enlarged image of the inner flame of the arc, and had the appearance of a horizontal lavender band, flanked by the brilliant narrow white bands of the hot electrode tips.

Using the maximum arc gap that could be maintained between pure electrodes at the currents employed, a more refined adjustment of the lens was made, so that the depth of this band was about 1 inch. The arc gap, the shield opening, and the lens were then elevated to corres-

pond to the height of the center portion of the slit.

The slit and grating were next brought into proper adjustment. The slit was widened and by means of a small white card, the path of the entering beam of light was followed back to the grating. The position of the arc relative to the center line of the optical system was altered sufficiently that the narrow vertical image of the slit appeared directly across the center of the grating. Next, the elevation of the lens and arc were varied slightly until the image of the slit was symmetrical with the grating in a vertical respect.

To focus the grating this procedure was followed: The mounting of the grating was tilted about a horizontal axis until the arc spectrum appeared through a wide slotted mask on the viewing screen. Almost any metallic salt in the cavity of the lower electrode produced an excellent spectrum for this purpose. The mounting was further tilted until the line formed by the ends of the spectral lines was visible. The grating was then rotated about its optical axis by the opposing set-screws above it until that line of extreme ends of the spectral lines was parallel to the slot of the mask. The lines of the grating were then at right angles to the length of the camera holder.

With the slotted mask removed, the slit was

rotated about its axis until the spectral lines became vertical.

The desired range of operation was between $2300\text{\AA}$ and $6500\text{\AA}$. A mercury arc not being available, the spectrum of mercury, produced by volatilizing the oxide in the arc, was successfully used. The green line at $5461\text{\AA}$ was identified by its relation to other lines in the same spectrum, and the grating rotated about its vertical axis until this line was in a position about 2.1 inches or $840\text{\AA}$ from the left edge of the screen. This adjustment was verified by checking the position of the sodium "D" lines at $5890\text{--}5896\text{\AA}$.

The spectrum was then brought into sharp focus by sliding the grating holder along its track by means of the micrometer screw. The optimum position was selected by close observation of the various lines on the translucent screen through a reading lens, and this was later checked by direct observation with a small eyepiece. The assembly was then secured in position by tightening the lock screw.

The second lens was next placed in position, and slid back and forth on the track until the spectrum appeared brightest. A check of its position showed it to be at exactly its focal length of 35.5 cm. from the slit. This caused the entire surface of the grating to be illuminated,

and at the same time the intensity of illumination was increased. The intensity of the lines was enhanced, apparently without increasing the background.

The width of the slit was then gradually decreased until the point was reached at which a further narrowing of the aperture did not change the apparent width of the lines in the eyepiece, but only reduced their intensity. Observation of the sodium D-lines showed the pair to be resolved into the two components. At this point the lines were sharp and clearly defined, and good resolution had been obtained.

The logarithmic sector was finally mounted directly before the instrument, with the sector disk parallel to the front face, and as close as possible. Its elevation was then so adjusted that at maximum masking position there remained only a very narrow band of the spectrum across the bottom of the mask slot. The adjustment of the entire optical system was then such that the lengths of the lines varied apparently just between the edges of the mask slot or exposed strip, as the sector turned. The slot was $13/32$ inch in depth.

Two precautions had to be observed. First, great care had to be exercised not to shut or jam the jaws of the slit, and secondly, care was necessary to avoid touching

the surface of the grating or tightening of the holder to such an extent that the grating surface would be distorted.

A number of samples were prepared corresponding to an average ash. The "average ash" was computed from the mean of the upper and lower limits of the percentages of the constituents K_2O , Na_2O , CaO , MgO , Fe_2O_3 , SiO_2 , and P_2O_5 determined in the ash of samples of twelve different representative grains. Table I on the following page gives the "expected range of analysis", as the limits of these analyses were called. Table II shows the percentage composition of the "average ash", on the basis of a total of 100 %. Thirty-six standard mixtures were prepared. Of these there were six series, in each of which one of the constituents occurred in a different amount for each of the six mixtures in that series, varying by arbitrary amounts between the expected lower and upper limits of that particular oxide.

The remainder of each sample, or the portion exclusive of the desired oxide, retained the composition of the average ash. In this manner it was possible to maintain approximately constant the effects of other elements present on the intensity of that varied, and at the same time, in a series of six, to determine the effect of variation in amounts of the first on the line intensities

TABLE I.

Expected Range of Grain Ash Analysis

Constituent	%	
K_2O	20	35
Na_2O	6	10
CaO	2	6
MgO	8	18
Fe_2O_3	0.3	5
P_2O_5	30	42
SiO_2	1	25

TABLE II.

Composition of the " Average Ash "

Constituent	%
K_2O	26.40
Na_2O	7.69
CaO	3.84
MgO	12.49
Fe_2O_3	2.54
P_2O_5	34.55
SiO_2	12.49

of all the others. The percentage compositions of the various standard mixtures are given in Table III.

A convenient method for calculating the percentage of any oxide in the standard mixture is as follows: The desired percentage of the constituent being varied is subtracted from 100, and the percentage of that same constituent in the average ash is subtracted from 100. The remainder from the first operation divided by the remainder resulting in the second case gives a factor, F , by which the percentage of any oxide in the average ash can be multiplied to give the percentage of that oxide in the corresponding standard mixture. The value of the factor, F , for each standard mixture appears at the bottom of the data column for the compositions.

A study of the relative merits of the internal standard method and the ratio quantitative system was undertaken. The relative amounts of the constituent oxides was easily calculable from the data of the composition of the standard mixtures, so that a study of the second method was directly possible. For the first, molybdenum was selected as the best available internal standard, and was added to the samples to the extent of 2 % with respect to the total oxides.

The standards were prepared volumetrically.

Solutions were prepared of ammonium, potassium, magnesium, and iron sulfates, and of calcium nitrate and ammonium phosphate in such concentrations that average volumes of 20 to 30 ml. of each solution would be necessary in the synthesis of each mixture. Silica was added gravimetrically in the form of silicic acid, the silica content of which had been established by ignition. The ammonium molybdate solution was pipetted into each mixture. A volume of 10 ml. was convenient, and the solution was prepared of such concentration that this volume would contain 0.2 gram of molybdenum. This calculation is shown in Table V.

Sufficient reagents were used that in each case there would result 10 gm. of oxide. For an average sulfate ash, the total weight would be twice that of the oxides alone, as shown in Table V. Therefore 20 grams of ammonium sulfate was added to each mixture. This established then a constant ratio between the weights of molybdenum, ammonium sulfate, and the total oxides.

These mixtures were evaporated in beakers in a water bath. Continual stirring and mixing insured homogeneity, and residue on the walls of the beakers was washed down by a fine stream of water containing a trace of sulfuric acid. The dry residues were transferred to a clean mortar and ground to fineness before being stored in clean

labelled test tubes. A great deal of care was necessary to prevent contamination of these samples, and all the equipment used was first cleaned with concentrated sulfuric acid and rinsed well with distilled water.

A half bushel of corn was reduced to about 200 grams of ash for the spectrographic and chemical analyses. Evaporating dishes were filled with the grain and 50 cc. each of dilute nitric and dilute sulfuric acids added. The mixture was then **fired** in the gas furnace, and ignited until most of the carbon had been burned off. The residues were collected in a single dish, moistened with a slight amount of sulfuric acid, and reignited. All the final ashes were carefully mixed and ground to homogeneity.

A representative sample of 10 grams was then removed and ground well with an equal weight of ammonium sulfate and sufficient ammonium molybdate to furnish 0.10 gram of molybdenum.

Holes were drilled to a depth of about $3/16$ inch in the ends of the carbon rods to be used for lower electrodes with a $3/32$ inch drill, and the ends carefully ground conical in an ordinary pencil sharpener. To introduce and compress the specimens into these cavities the ends of the electrodes were pushed firmly into the mass of the samples.

Qualitative spectrograms were first taken to determine the lines of each element that could be easily identified or were suitable for quantitative work. The spectrograph room had been equipped as a dark-room, and the film could be loaded directly without the necessity of removing the film holder. This was covered with a black cloth to protect the edges of the film from chance stray light. The shutter was closed and the metal slide removed.

By means of the alignment pointer, the lower carbon containing the sample was clamped into the correct position. One operator then struck the arc and immediately widened the gap so that the white lines of the incandescent pole tips appeared beyond the ends of the slit. At the same time the second operator opened the shutter, and began timing a 45 second exposure. During this time, the shunt plug was removed and the current checked. All exposures were conducted at 6 amperes. At the expiration of the exposure time the shutter was released and the main switch thrown off.

The film holder was then lowered two notches for the quarter-inch slotted mask, the hot electrode dropped into a container, and the new carbon with its sample was clamped into position. When this procedure was followed for the seven exposures, a total time of less than ten minutes

Figure 5. Qualitative Spectrograms

was required.

The film was removed in the darkened room and developed in DK-50 developer at 15-16°C. The optimum time for physical development in a tray was found to be three minutes. This was timed by stop-watch. The progress of development could be observed briefly from time to time in the illumination from the dark green Wratten Filter.

After exactly three minutes the film was rinsed in a running stream of cold water for about a minute, and then placed in a tray of saturated "hypo" fixing solution. Fifteen minutes was allowed for this process, and the negative was then washed for twenty minutes before being hung to dry.

The order of appearance of the spectrograms on the film was inverse to that of the exposures. Predominant reference lines were established for the spectrum of each element, and by use of the measuring scale, the presence of lesser lines determined. Particular attention was directed to those lines recommended in the literature for quantitative work (3)(5)(6)(7)(10)(18)(19) .

A similar program was followed in obtaining the quantitative spectrograms. First, however, the smaller mask was replaced by the 3/8 inch slotted mask. This permitted only three exposures of each film, at pointer settings of

3 , 7, and 11.

The electrodes were handled waresfully to avoid contamination of the tips. Exposures were exactly timed as before, and were begun immediately that the arc was struck, so that the spectrum of the more volatile constituents would not be lost. The sector disk was operated continuously.

Two horizontal chalk lines marked the ends of the exposed length of the slit. By proper setting of the upper electrode, the white pole bands of both carbons were made to coincide with these marks. This insured a constant arc gap width and at the same time avoided the entrance of light from the "pole spots" through the slit. The upper electrode was scraped to a fresh surface following each use.

The same method of development was used. The developing solution was held at 15-16°C to prevent breaking or sliding of the gelatine film. During the development time one operator reloaded the film holder. The optimum times of development and exposure were determined experimentally, and were timed by stop-watch. The effect of these variables is shown in Figure .

The dried film was marked at approximately 200 Angstrom unit intervals (0.5 inch each) with reference

Figure 6. Representative Quantitative Spectrogram

to known lines. The film was then clamped between two plates of glass, and an enlarged image of it formed on the wall by means of a lantern slide projector. A magnification of 8 X resulted, so that the dispersion was $50 \text{ \AA}^\circ$ per inch.

A wave-length scale of this magnitude was prepared on a sheet of white paper, covering $200 \text{ \AA}^\circ$ (8 inches). When the end marks of this screen were made coincident with the numbered wave-length marks on the negatives, lines of any wave-length could easily be identified. The lengths of the lines desired were measured from the base line in units 0.25 inch in length. These corresponded to lengths of $1/32$ inch on the original film.

The lines measured were those of molybdenum, calcium, magnesium, and those of the variant constituent. The differences in lengths of the lines of the latter and one of the first three were computed for all possible combinations.

For these data, curves were plotted to determine the relationship between percentage amounts of each "variant" constituent and the differences in lengths of the line pairs corresponding to these amounts. Only those curves which followed approximately straight lines or appeared to be consistent functions were retained. The

values of the coordinates of the curves obtained are given in Table VII.

" Analytical Curves" were drawn showing the relation of the differences in lengths of line pairs, of which molybdenum was a component, and the corresponding percentages of the oxides of the other element. "Ratio Quantitative Curves" were obtained by plotting the differences in lengths of line pairs of the variant constituent and magnesium or calcium against the ratios of the percentages of the oxides of the elements of those line pairs.

The ash sample was photographed in duplicate, and the lengths of all lines used in the other determinations measured. From the so-called operating curves the analysis of the ash was established.

Three separate analyses were calculated, based upon the molybdenum, calcium, and magnesium. The SiO_2 was computed by difference in each case. In the case of Mg, the amount determined from the Mo was assumed to be correct. For the Ca, the amount was assumed to be that required to give a total of constituents, exclusive of silica, equal to the average of the totals in the other two cases.

Much experimental work was performed to develop the accessory equipment and to determine the operating characteristics of the spectrograph and film.

DATA

In the following table are given the compositions of the thirty-six standard mixtures prepared for obtaining the operating curves for the analysis of grain ash. The compositions are based upon the "average ash", the range of analysis of which has been shown in Table I.

For each series of six mixtures, one constituent oxide varies in concentration between the lower and upper expected limits of analysis. The range was slightly extended for some oxides. The particular oxide under consideration is designated as the "variant constituent". The remainder of the sample has the composition of the average ash. By this means the effect of the other constituents on the line intensities of the first is held approximately constant. Also, the spectra of the synthetic ash and those of the actual ash will be strictly comparable if the conditions of excitation are the same.

If the percentage of the varied constituent is subtracted from 100 in the standard mixture and in the average ash, the ratio of the remainder in the first case to that resulting in the second gives a factor F . Multiplied by this factor, the percentage of any oxide in the average ash gives the amount of that oxide in the standard mixture.

TABLE III.

Composition of Standard Mixtures
K₂O Varied

Number of Sample	1	2	3	4	5	6
%						
K ₂ O	16.00	20.00	24.00	28.00	32.00	36.00
Na ₂ O	8.77	8.33	7.94	7.53	7.10	6.68
CaO	4.38	4.17	3.97	3.76	3.54	3.34
MgO	14.27	13.60	12.90	12.23	11.55	10.87
Fe ₂ O ₃	2.90	2.76	2.62	2.49	2.35	2.21
P ₂ O ₅	39.45	37.55	35.77	33.85	31.93	30.03
SiO ₂	14.27	13.60	12.90	12.23	11.54	10.87
Total	100.06	100.03	100.03	100.09	100.01	100.00
% K ₂ O	16.00	20.00	24.00	28.00	32.00	36.00
Rem.	84.00	80.00	76.00	72.00	68.00	64.00
F	1.142	1.088	1.033	0.979	0.924	0.870

TABLE III.

Composition of Standard Mixtures

Na₂O Varied

Number of Sample	7	8	9	10	11	12
%						
Na ₂ O	2.00	4.00	6.00	8.00	10.00	12.00
MgO	13.26	12.98	12.70	12.43	12.17	11.90
SiO ₂	13.26	12.98	12.70	12.43	12.17	11.90
Fe ₂ O ₃	2.70	2.64	2.58	2.53	2.48	2.42
K ₂ O	28.03	27.43	26.87	26.30	25.70	25.17
P ₂ O ₅	36.65	35.90	35.15	34.40	33.65	32.93
CaO	4.08	3.99	3.90	3.88	3.74	3.66
Total	99.98	99.92	99.90	99.97	99.91	99.98
% Na ₂ O	2.00	4.00	6.00	8.00	10.00	12.00
Rem.	98.00	96.00	94.00	92.00	90.00	88.00
F	1.061	1.040	1.017	0.996	0.974	0.953

TABLE III.

Composition of Standard Mixtures

CaO Varied

Number of Sample	13	14	15	16	17	18
%						
CaO	1.00	2.00	3.00	5.00	7.00	10.00
MgO	12.87	12.73	12.60	12.35	12.09	11.70
SiO ₂	12.87	12.73	12.60	12.35	12.09	11.70
Fe ₂ O ₃	2.62	2.59	2.56	2.51	2.46	2.38
K ₂ O	27.20	26.93	26.63	26.10	25.55	24.73
P ₂ O ₅	35.60	35.20	34.86	34.15	33.45	32.35
Na ₂ O	7.91	7.84	7.75	7.60	7.43	7.19
Total	100.07	100.02	100.00	100.06	100.07	100.05
CaO	1.00	2.00	3.00	5.00	7.00	10.00
Rem.	99.00	98.00	97.00	95.00	93.00	90.00
F	1.030	1.020	1.009	0.989	0.968	0.937

TABLE III.

Composition of Standard Mixtures

MgO Varied

Number of Sample	19	20	21	22	23	24
MgO	2.00	6.00	10.00	14.00	16.00	20.00
SiO ₂	13.99	13.41	12.85	12.28	12.00	11.42
Fe ₂ O ₃	2.84	2.73	2.61	2.50	2.44	2.32
K ₂ O	29.55	28.35	27.16	25.95	25.35	24.15
P ₂ O ₅	38.67	37.10	35.55	33.95	33.15	31.60
CaO	4.30	4.12	3.95	3.78	3.68	3.51
Na ₂ O	8.60	8.25	7.90	7.55	7.37	7.03
Total	99.95	99.96	100.02	100.01	99.99	100.03
% MgO	2.00	6.00	10.00	14.00	16.00	20.00
Rem.	98.00	94.00	90.00	86.00	84.00	80.00
F	1.120	1.073	1.028	0.9825	0.960	0.915

TABLE III.

Composition of Standard Mixtures

 Fe_2O_3 Varied

Number of Sample	25	26	27	28	29	30
%						
Fe_2O_3	0.20	0.50	1.00	3.00	5.00	7.00
SiO_2	12.80	12.75	12.68	12.42	12.18	11.91
MgO	12.80	12.75	12.68	12.42	12.18	11.91
K_2O	27.05	26.95	26.80	26.27	25.73	25.20
P_2O_5	35.40	35.25	35.07	34.40	33.66	32.95
CaO	3.93	3.92	3.90	3.82	3.74	3.66
Na_2O	7.87	7.83	7.80	7.65	7.49	7.33
Total	100.05	99.95	99.93	99.98	99.98	99.96
% Fe_2O_3	0.20	0.50	1.00	3.00	5.00	7.00
Rem.	99.80	99.50	99.00	97.00	95.00	93.00
F	1.024	1.020	1.015	0.995	0.975	0.953

TABLE III.

Composition of Standard Mixtures						
P ₂ O ₅ Varied						
Number of Sample	31	32	33	34	35	36
%						
P ₂ O ₅	20.00	24.00	28.00	32.00	36.00	40.00
SiO ₂	15.27	14.50	13.73	12.97	12.20	11.45
MgO	15.27	14.50	13.73	12.97	12.20	11.45
Fe ₂ O ₃	3.10	2.94	2.80	2.64	2.48	2.33
K ₂ O	32.25	30.60	29.03	27.43	25.80	24.20
CaO	4.69	4.46	4.23	3.99	3.76	3.52
Na ₂ O	9.38	8.92	8.45	7.98	7.52	7.04
Total	99.96	99.92	99.97	99.98	99.96	99.99
% P ₂ O ₅	20.00	24.00	28.00	32.00	36.00	40.00
Rem.	80.00	76.00	72.00	68.00	64.00	60.00
F	1.221	1.160	1.100	1.038	0.978	0.917

In the preparation of the standard mixtures, it was desirable to use volumes of reagent solutions of the order of 20 to 30 ml. Also, for the purpose of convenience in calculation, it was advantageous that the concentration of each solution be such that each ml. represented some definite fraction of a gram of the corresponding oxide.

In the table on the following page are shown the factors used to calculate the weight of reagents used in preparing the solutions, and those for conversion of percent oxides in the tables of composition of standard mixtures to ml. of solutions.

The equivalent weights of oxide and reagent signify the weight of substance in grams equivalent to a gram atom of the element under consideration. Factor X is the ratio of the equivalent weight of the reagent to that of the corresponding oxide. Y is the reciprocal of the number of ml. containing 0.1 gram of oxide. The number of grams of reagent per liter is then determined by multiplying X by 100 Y. For ml. of solution to be used in preparation of the standard mixtures, the percentage amounts are multiplied by the factor $1/Y$.

The total weight of oxides resulting in each mixture is 10.00 grams.

TABLE IV.

Gravimetric and Volumetric Factors

Oxide	Equivalent Weight	Reagent	Equivalent Weight
K_2O	47.1	K_2SO_4	87.13
Na_2O	35.0	Na_2SO_4	71.02
CaO	56.07	$Ca(NO_3)_2$	164.10
MgO	40.32	$MgSO_4$	120.38
Fe_2O_3	79.84	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	392.54
P_2O_5	71.02	$(NH_4)_2HPO_4$	132.11
SiO_2	60.06	$H_2Si_3O_7$	60.06/0.911

Reagent	Factor X	Factor Y	Grams/Liter
K_2SO_4	1.85	1/2	92.50
Na_2SO_4	2.29	1/3	76.33
$Ca(NO_3)_2$	2.93	1/6	48.80
$MgSO_4$	2.985	1/2	149.25
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	4.92	1/10	49.20
$(NH_4)_2HPO_4$	1.86	1/1	186.00
$H_2Si_3O_7$	1.10	1/1	.....

TABLE V.

Amounts of Internal Standard and Diluent Substance
Added to Standard Mixtures

$$\frac{1000 \text{ ml.} \times 10 \text{ gm. oxide} \times 0.02 \text{ gm. Mo / gm. oxide}}{10 \text{ ml.}}$$

$$= 20 \text{ gm. Mo / Liter}$$

$$\frac{1236.32}{7 \times 96.7} \times 20 = 36.8 \text{ gm. (NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{ H}_2\text{O / Liter}$$

Oxide	Grams Oxide in 10 Grams of Average Ash	X	Grams of Reagent
K ₂ O	2.60	1.85	4.8
Na ₂ O	0.77	2.29	1.76
CaO	0.384	2.93	1.11
MgO	1.25	2.99	3.74
Fe ₂ O ₃	0.25	4.92	1.23
P ₂ O ₅	3.46	1.86	6.43
SiO ₂	1.25	1.10	1.37
Total	10.00		20.44

Amount (NH₄)₂SO₄ diluent = 20.00 gm./10 gm. oxide

In the following Table are listed spectral lines of the elements studied in this research, which were recommended in the literature. The bibliography numbers of the reference articles from which each was taken are given.

In addition to those listed it was necessary to select several lines from the qualitative spectrograms.

In Table VIII, the coordinates of the operating curves are tabulated. The values listed are those of ΔL , in units of $1/4$ inch on the enlarged image, or $1/32$ inch on the negatives. These values were obtained as the differences in lengths of members of line pairs, these being designated in the table. The columns fall under percentages of the constituent for analytical curves, and under ratios of the varied constituent and MgO or CaO for the ratio quantitative curves.

From that table have been excluded in a few cases points which did not agree with the general trend of the various curves. However, no point was rejected unless there were at least four others which did fall into an approximately straight line. In that case, the point not in agreement was assumed to be in error. Not all possible combinations of line pairs resulted in smooth curves, and only those giving straight lines or consistent functions were retained.

TABLE VI.

Spectrum Lines Recommended in the Literature
for Quantitative Analysis

K	Na	Mo
7665 (19)	3302 (5)(6)	2816 (7)
3447 (10)	5890 (18)(19)	3123 (19)
4044 (5)	5896 (18)	3158 (7)
4046 (6)		3903 (7)
Ca	Fe	Mg
3159 (10)	2483 (19)	2777 (10)
3179 (10)	2599 (10)	2780 (10)
3247 (5)	2698 (10)	2795 (7)
3934 (18)	2719 (3)	2852 (3)(5)
3969 (18)	3020 (3)(7)	3074 (3)(19)
4226 (5)(6)		3832 (3)
(7)(19)		
P		
2536 (10)		

TABLE VII.

Coordinates of Operating Curves

Oxide	Percent Oxide in Standard				
Line Pairs	Values of ΔL				
K_2O	16		20		36
aa K 3447 - Mo 2660	5.0		0.5		4.0
bb K 3447 - Mo 2816	1.0		-2.0		2.0
cc K 3447 - Mo 3122	2.5		0.0		4.0
Na_2O	2	6	8	10	12
aa Na 3281 - Mo 2816	4.0	—	2.5	—	1.0
bb Na 3281 - Mo 3158	6.5	—	3.5	5.0	2.0
cc Na 5209 - Mo 2816	-4.5	-3.0	-2.0	—	—
dd Na 5890 - Mo 2660	-4.5	-3.0	—	—	5.5
ee Na 5890 - Mo 2816	-7.0	-4.0	—	—	1.5
ff Na 5890 - Mo 3122	-5.0	-3.0	—	—	1.5
gg Na 5890 - Mo 3158	-4.5	-3.0	—	—	2.5
hh Na 5896 - Mo 2816	5.0	3.0	3.0	—	-1.0
CaO	1	2	3	7	10
aa Ca 3179 - Mo 2816	-3.5	1.5	2.5	4.0	—
bb Ca 3179 - Mo 3122	-1.5	2.0	2.5	6.5	—
cc Ca 4226 - Mo 2660	-2.0	2.5	—	3.5	4.25

TABLE VII.

Coordinates of Operating Curves

Oxide		Percent Oxide in Standard				
Line Pairs		Value of ΔL				
CaO		1	2	3	7	10
dd	Ca 4226 - Mo 2816	-2.5	1.0	6.0	—	—
ee	Ca 4226 - Mo 3122	-0.5	1.5	—	4.0	4.25
ff	Ca 4226 - Mo 3158	-3.0	—	0.5	—	-2.75
MgO		2	6	14	16	20
aa	Mg 2777 - Mo 3122	-2.0	0.5	—	2.0	2.5
bb	Mg 3030 - Mo 2660	—	7.25	1.5	0.0	—
cc	Mg 3030 - Mo 2816	—	—	-5.25	-3.0	0.0
dd	Mg 3030 - Mo 3122	-1.25	—	-0.25	1.0	4.5
ee	Mg 3077 - Mo 2660	7.5	5.25	—	2.25	—
ff	Mg 3077 - Mo 3122	-0.5	-0.5	—	3.25	6.5
Fe ₂ O ₃		0.2		0.5		1.0
aa	Fe 2483 - Mo 2660	0.5		3.0		1.0
bb	Fe 2483 - Mo 2816	-2.0		0.0		-1.0
cc	Fe 2599 - Mo 2816	-1.5		1.0		0.0
dd	Fe 2698 - Mo 2660	-1.5		-2.0		-1.0
ee	Fe 2698 - Mo 2816	-4.0		-5.0		-3.0

TABLE VII.

Coordinates of Operating Curves

Oxide	Percent Oxide in Standard				
Line Pairs	Value of ΔL				
Fe_2O_3	0.2		0.5		1.0
ff Fe 3020 - Mo 2660	7.0		10.5		7.0
gg Fe 3020 - Mo 2816	4.5		7.5		5.0
P_2O_5	20	24	28	32	36
aa P 2534 - Mo 2816	-0.5	-0.25	1.0	4.0	—
bb P 2553 - Mo 2816	—	-2.25	0.5	2.5	—
cc P 2644 - Mo 2816	-4.5	-3.75	3.0	6.5	—
dd P 2725 - Mo 2816	—	-2.25	3.5	6.5	—
ee P 2644 - Mo 2660	-1.5	-0.5	—	1.0	5.0
ff P 2725 - Mo 2660	—	1.0	5.5	7.0	—
gg P 2884 - Mo 2660	—	1.5	6.0	7.0	—
hh P 2896 - Mo 2660	3.0	1.0	0.5	—	-1.0
ii P 2644 - Mo 3122	-2.5	—	-1.5	0.0	2.0
jj P 2725 - Mo 3122	—	3.0	5.5	9.0	—
kk P 2884 - Mo 3122	—	3.5	6.0	9.0	—
ll P 3425 - Mo 3122	3.5	5.0	—	8.0	—

TABLE VII.

Coordinates of Operating Curves

Oxide Ratio		Quantitative Ratio		
Line Pairs		Value of ΔL		
K_2O / CaO		3.66	4.80	10.76
aa K 3447 - Ca 3179		3.5	-0.5	-2.25
bb K 3447 - Ca 3934		0.5	-0.5	-1.0
cc K 3447 - Ca 4578		1.0	1.5	2.0
K_2O / MgO		1.12	1.47	3.31
aa K 3446 - Mg 3030		4.5	-2.5	0.0
Na_2O / CaO		0.49	1.54	2.06
aa Na 3781 - Ca 3179		7.0	—	2.5
bb Na 5209 - Ca 3215		-4.0	-6.0	-7.0
cc Na 5896 - Ca 3179		6.0	2.5	—
dd Na 5896 - Ca 3215		3.5	0.0	-2.0
Na_2O / MgO		0.151	0.473	0.657
aa Na 5209 - Mg 2777		-5.0	-3.5	-1.0
bb Na 5209 - Mg 3077		-8.0	-6.25	-5.5
cc Na 5890 - Mg 2777		-7.5	-4.5	—
dd Na 5890 - Mg 3077		-10.5	-7.25	—
ee Na 5896 - Mg 3077		0.5	-0.25	-0.5

TABLE VII.

Coordinates of Operating Curves

Oxide Ratio		Quantitative Ratio				
Line Pairs		Value of ΔL				
CaO / MgO		0.0777	0.157	0.238	0.58	0.855
aa Ca 3179 - Mg 3030		-5.5	0.0	1.5	3.0	—
bb Ca 3215 - Mg 3077		—	-1.5	-0.5	—	1.0
cc Ca 3934 - Mg 2777		—	3.0	1.5	—	-3.0
dd Ca 3934 - Mg 3077		—	—	1.0	-0.5	-3.0
ee Ca 4226 - Mg 3030		-2.5	-0.5	5.0	—	—
ff Ca 4226 - Mg 3077		—	-2.5	—	-1.5	0.0
MgO / CaO		0.465	1.46	3.70	4.35	5.70
aa Mg 2777 - Ca 3215		—	5.0	2.0	0.0	-4.5
bb Mg 2777 - Ca 3247		-5.0	-4.0	-1.0	-2.0	-5.5
cc Mg 3077 - Ca 3215		—	4.0	2.0	1.25	-0.5
dd Mg 3077 - Ca 4578		—	-4.0	—	0.25	2.5
Fe ₂ O ₃ / MgO		0.0156		0.0392		0.079
aa Fe 2483 - Mg 3030		-2.0		-3.0		-4.0
bb Fe 3020 - Mg 3077		3.75		3.0		-1.0

TABLE VII.

Coordinates of Operating Curves				
Oxide Ratio		Quantitative Ratio		
Line Pairs		Value of ΔL		
$\text{Fe}_2\text{O}_3 / \text{CaO}$		0.051	0.128	0.256
aa	Fe 2483 - Ca 3179	-9.0	-7.0	-3.0
bb	Fe 2483 - Ca 3247	-5.0	-3.5	-4.0
cc	Fe 2483 - Ca 3934	-2.5	-1.0	-3.0
dd	Fe 2483 - Ca 4226	0.5	4.0	-1.5
ee	Fe 2599 - Ca 3179	-9.0	-6.0	-5.0
ff	Fe 2599 - Ca 3247	-5.0	-1.5	-3.0
gg	Fe 2599 - Ca 3934	-2.5	0.5	-2.0
hh	Fe 2698 - Ca 3179	-11.0	-12.0	-8.0
ii	Fe 2698 - Ca 3215	-4.5	-5.5	-3.0
jj	Fe 2698 - Ca 3247	-7.0	-8.5	-5.5
kk	Fe 2698 - Ca 3934	-4.5	-6.0	-5.0
ll	Fe 2698 - Ca 4226	-1.5	-1.0	-0.5
mm	Fe 3020 - Ca 3215	4.0	7.0	4.0
nn	Fe 3020 - Ca 3247	0.5	4.0	2.0
oo	Fe 3020 - Ca 3934	4.0	7.0	3.0
pp	Fe 3020 - Ca 4226	7.0	11.5	7.5

TABLE VII.

Coordinates of Operating Curves

Oxide Ratio		Quantitative Ratio				
Line	Pairs	Value of ΔL				
	P_2O_5 / CaO	0.62	0.785	0.965	1.17	1.395
aa	P 2534 - Ca 3934	-0.5	0.0	1.0	3.5	—
bb	P 2534 - Ca 4578	5.0	4.0	—	6.5	—
cc	P 2553 - Ca 3179	—	-6.0	-1.0	2.0	4.0
dd	P 2553 - Ca 3934	—	-2.0	-0.5	2.0	5.5
ee	P 2664 - Ca 3179	—	-7.5	-4.5	-3.0	1.0
ff	P 2725 - Ca 3179	—	-6.0	2.5	6.0	—
gg	P 2884 - Ca 3179	—	-5.5	3.5	6.0	—
hh	P 2884 - Ca 3934	—	-1.5	4.0	6.0	—
ii	P 2884 - Ca 4226	—	0.5	3.5	4.0	—
jj	P 3245 - Ca 3179	—	-4.0	0.0	5.0	—
kk	P 2896 - Ca 3247	-2.0	-3.0	—	-5.0	-6.0
	P_2O_5 / MgO	1.31	1.66	2.04	2.47	2.95
aa	P 2534 - Mg 2777	1.5	—	0.0	—	-2.0
bb	P 2896 - Mg 2777	1.5	1.0	—	-1.0	-3.0

TABLE VIII.

Results of Spectrographic Analysis of Corn Ash

Oxide or Oxide Ratio	Curve	ΔL	% Oxide	Oxide Ratio	Average
K_2O	aa	7.5	15.0		
	bb	4.5	15.0		
	cc	6.0	15.0		15.0 %
K_2O / CaO	aa	7.0		5.4	
	bb	4.0		5.3	3.35
K_2O / MgO	aa	2.5		1.1	1.1
Na_2O	dd	0.0	9.7		
	ee	-3.0	7.3		
	ff	-1.5	8.3		8.22 %
Na_2O / CaO	cc	-2.0		5.0	
	dd	-4.0		2.6	2.8
Na_2O / MgO	dd	0.5		1.10	
	ee	-5.5		1.08	1.09
CaO	aa	1.0	1.7		
	bb	2.5	2.7		
	cc	2.0	1.7		

TABLE VIII.

Results of Spectrographic Analysis of Corn Ash

Oxide or Oxide Ratio	Curve	ΔL	% Oxide	Oxide Ratio	Average
CaO	dd	2.0	2.0		
	ff	-0.5	3.2		2.5 %
CaO / MgO	aa	-1.0		0.17	
	bb	-1.0		0.19	
	cc	0.0		0.18	0.18
MgO	bb	1.5	14.0		
	dd	0.0	14.2		
	ff	2.5	15.0		14.4 %
MgO / CaO	cc	1.0		4.5	4.5
Fe_2O_3	aa	1.0	1.0		
	bb	-2.0	1.2		
	ff	7.5	0.98		
	gg	4.5	1.05		1.06
Fe_2O_3 / CaO	aa	-3.0		0.29	
	cc	-2.5		0.243	
	dd	-4.0		0.277	
	gg	-3.0		0.277	

TABLE VIII.

Results of Spectrographic Analysis of Corn Ash

Oxide or Oxide Ratio	Curve	ΔL	% Oxide	Oxide Ratio	Average
Fe_2O_3 / CaO	mm	5.5		0.222	
	oo	4.0		0.236	0.253
Fe_2O_3 / MgO	bb	-1.5		0.08	0.08
P_2O_5	aa	0.5	26.6		
	bb	-2.5	23.7		
	cc	-0.5	24.2		
	dd	0.5	25.2		
	ff	3.5	25.4		
	jj	2.0	22.8		
	ll	2.0	22.1		24.3 %
P_2O_5 / CaO	cc	-3.5		8.6	
	dd	-3.0		8.7	
	ff	-0.5		8.8	
	jj	-0.5		9.0	
	kk	-3.5		9.3	
	ll	-0.5		9.2	8.9
P_2O_5 / MgO	aa	0.5		1.80	
	bb	1.0		1.75	1.75

In Table VIII are tabulated the data secured from the spectrograms of the grain ash. The constituent or quantitative ratio is given, letter designation of the line pairs used in determination of the percentages or ratios from the operating curves are indicated, the corresponding values of ΔL for those line pairs, and the determined values and their averages.

A summation of these results appears in Table IX.

RESULTS

Direct current was found to be preferable to alternating current (110 volts) for excitation of the arc. Although the alternating current was convenient for adjustment and test operations, the arc was difficult to maintain and material was lost from the sample by sputtering. By use of the direct current a steady and easily burning arc was formed, and the spectrum produced was much more intense and showed finer structure. Furthermore, the spectrographically pure carbons would operate only on direct current.

It was found that the voltage drop across the arc was most nearly constant when it represented but a small portion of the potential drop of the circuit. For this reason the generators were operated at maximum voltage delivery, and a total resistance of about 35 ohms incorporated in the circuit, exclusive of the arc. The voltage drop across the arc gap at maximum width was about 60 volts and the current was 6 to 8 amperes.

The arc showed a marked tendency to wander about the pole tips, causing a variation in voltage drop across the gap and at the same time producing undesirable fluctuations in current. This was substantially reduced in several ways. First, by use of a wide arc gap the ability of the arc to wander was greatly diminished. Second, the

lower pole tips were ground carefully to an even edge about the periphery of the crater, and the upper electrode was pointed and carefully centered over the lower one. Finally, an inductance of about 1 henry was obtained in the circuit by adding a primary coil of a transformer in series.

Slight variations in the position of the arc flame continued to cause the image to shift across the face of the grating. A diffusing reflector was tried with success. This was a polished steel plate, burnished in parallel vertical lines. Placed on the optical axis at a large angle of incidence, it served to reflect diffused light from the arc indirectly to the optical system. However when a second lens was employed to project a long horizontal image of the arc flame across the slit, the slight wandering of the flame was of no significance.

Early in the experimental stage the operators discovered that the focal length of the replica grating varied considerably with appreciable change of room temperature or humidity. The micrometer screw, previously described, afforded a convenient means for accurately adjusting the position of the grating.

A number of modifications of the optical system were tested. The method for obtaining the combination of conditions found to be optimum has been described under the

method of procedure. The arrangement of the component parts of the system is shown in Figure 3.

The optical axis was 23 cm. above the track, corresponding to the center of the portion of the slit opening employed. The arc gap, shield window, and both lenses were centered upon it. The distances of the arc and lenses from the slit were 65, 51, and 35.5 cm. respectively.

As previously described, the same width of arc gap was obtained for each exposure by aligning the bright line of the pole spots in coincidence with the chalk lines drawn on the face of the instrument housing.

Results of tests made to determine the optimum conditions for duration of exposure and time of development are shown on the following page. An exposure of 30 seconds duration did not give sufficient detail, whereas a minute's exposure was satisfactory in this respect, but showed increasing background. Maximum density of the lines was desirable, but fogging is indicated beyond a developing time of 3.5 minutes. A combination of 45 seconds exposure and 3 minutes development time was selected.

From an observation of the figure this selection might appear doubtful, but the prints for that set of conditions were from the infra-red region of the photographic film, and actually show comparatively good results.

Fig. 7 Effect of Duration of Exposure and Development Time
on Quality of Spectrograms

It was learned that a developer temperature of 15-16°C was necessary to prevent sliding or breaking of the emulsion. Also, addition of small amounts of acetic acid to the hypo fixing bath had a desirable hardening effect on the gelatine.

Of the thirty-six standard mixtures, several were unavoidably lost in the preparation and could not be replaced. Spectrograms were made of those completed. A typical quantitative spectrogram is shown in Figure 6. Because the print is reversed from the negative, the wave-lengths decrease in magnitude from left to right. The wedge shaped appearance of the lines may be observed, and also the tendency of the lines to continue from the apparent point of termination completely across the spectrogram strip.

The narrow band of continuous exposure allowed in setting the elevation of the logarithmic sector is quite plain at the bottom of each spectrogram. The lengths of the lines were measured from the very bottom of the spectrogram and the differences computed. The continuous bright white bands are caused by cyanogen, and occur in the violet portion of the spectrum.

Upon enlargement with a projector, the lines of the spectrograms were easily identified, and the lengths were measured in units of 1/4 inch. This corresponded to

1/32 inch on the film. The grating was of good quality, and adjustments used gave excellent resolution of the lines.

Analytical curves are shown in the following six figures. The ordinates are values of the differences of lengths of particular line pairs, the wave-lengths of which are tabulated below the figures. The abscissae represent the ratios of the amounts of the oxides of the particular element and the Mo. Since the molybdenum is present in the mixture in constant amount, the percentage of the particular oxide, or varied constituent, was plotted directly.

It has been customary to represent line pairs as a ratio. For example, K 3446 / Mo 2660 . ΔL is the difference in lengths of these two lines, and will depend upon the amount of K_2O in the mixture or sample spectrographed. Actually, as explained in the theory, ΔL is a function of the relative amounts of the two substances, hence the representation as a ratio.

Some of the curves, such as those of K, are based upon lines which are easily reversed. Potassium lines in the arc spectrum which do not show reversal are rare, and it was necessary to attempt use of the others.

Assuming that the lengths of the molybdenum lines remained constant, it would be obvious, then, that the lengths of the potassium lines, or the intensity of the

radiation of potassium in the arc, decreased to a minimum at a concentration of about 25 % and rose again to a higher value.

Obviously a difficulty arises if these curves retrace their ordinate range symmetrically. It might be possible in the analysis of an ash sample to find differences in lengths for line pairs such that two sets of values are found for the percentage of one component. If the values for each set checked, the analyst might find it necessary to further dilute the sample and respectrograph it.

Actually such a case did occur twice. However, by reference to the ratio quantitative curves, and thereby indirect reference to the amounts of CaO and MgO determined without difficulty from straight line functions, the correct set of values was established.

For the coordinate system used, it should be proper for each curve to proceed upward toward the right. However, some of the lines display a negative slope. This may be partly explained by weakening of the line intensity caused by partial reversal.

Fig. 8

$$aa = \frac{K \ 3446}{M_o \ 2660}$$

$$bb = \frac{K \ 3446}{M_o \ 2816}$$

$$cc = \frac{K \ 3446}{M_o \ 3122}$$

Fig. 9

ANALYTICAL CURVES

 $\Delta L = Na - Mo$

$$aa = \frac{Na \ 3281}{Mo \ 2816}$$

$$cc = \frac{Na \ 5209}{Mo \ 2816}$$

$$ee = \frac{Na \ 5890}{Mo \ 2816}$$

$$gg = \frac{Na \ 5890}{Mo \ 3158}$$

$$bb = \frac{Na \ 3281}{Mo \ 3158}$$

$$dd = \frac{Na \ 5890}{Mo \ 2660}$$

$$ff = \frac{Na \ 5890}{Mo \ 3122}$$

$$hh = \frac{Na \ 5896}{Mo \ 2816}$$

Fig. 10

ANALYTICAL CURVES

$$aa = \frac{Ca \ 3179}{Mo \ 2816}$$

$$bb = \frac{Ca \ 3179}{Mo \ 3122}$$

$$cc = \frac{Ca \ 4226}{Mo \ 2660}$$

$$dd = \frac{Ca \ 4226}{Mo \ 2816}$$

$$ee = \frac{Ca \ 4226}{Mo \ 3122}$$

$$ff = \frac{Ca \ 4226}{Mo \ 3158}$$

Fig. 11

$$aa = \frac{M_g 2777}{M_o 3122}$$

$$dd = \frac{M_g 3030}{M_o 3122}$$

$$bb = \frac{M_g 3030}{M_o 2660}$$

$$ee = \frac{M_g 3077}{M_o 2660}$$

$$cc = \frac{M_g 3030}{M_o 2816}$$

$$ff = \frac{M_g 3077}{M_o 3122}$$

$$aa = \frac{\text{Fe } 2483}{\text{Mo } 2660}$$

$$dd = \frac{\text{Fe } 2698}{\text{Mo } 2660}$$

$$bb = \frac{\text{Fe } 2483}{\text{Mo } 2816}$$

$$ee = \frac{\text{Fe } 2698}{\text{Mo } 2816}$$

$$cc = \frac{\text{Fe } 2599}{\text{Mo } 2816}$$

$$ff = \frac{\text{Fe } 3020}{\text{Mo } 2660}$$

$$gg = \frac{\text{Fe } 3020}{\text{Mo } 2816}$$

$$aa = \frac{P \ 2534}{Mo \ 2816}$$

$$bb = \frac{P \ 2553}{Mo \ 2816}$$

$$cc = \frac{P \ 2644}{Mo \ 2816}$$

$$dd = \frac{P \ 2725}{Mo \ 2816}$$

$$ee = \frac{P \ 2644}{Mo \ 2660}$$

$$ff = \frac{P \ 2725}{Mo \ 2660}$$

$$gg = \frac{P \ 2884}{Mo \ 2660}$$

$$hh = \frac{P \ 2896}{Mo \ 2660}$$

$$ii = \frac{P \ 2644}{Mo \ 3122}$$

$$jj = \frac{P \ 2725}{Mo \ 3122}$$

$$kk = \frac{P \ 2884}{Mo \ 3122}$$

$$ll = \frac{P \ 3425}{Mo \ 3122}$$

In the following figures appear the ratio quantitative curves. Of each line pair indicated, one component was a spectral line of the varied constituent and the other a line of either magnesium or calcium. L designated the magnitude of the differences of lengths of the two lines.

The abscissae are the ratios of the concentrations of oxides of the varied constituents to those of MgO or CaO . Since both are variable, the percentage of the varied oxide could not be plotted directly. These ratios were calculated from the data tables for the composition of the standard mixtures.

Actually there was no absolute method of determining which of these lines or curves might have arisen from error or chance, although agreement of values in analysis of the grain ash gave some clue to this.

For determining the amount of an oxide or the ratio quantitative value of that oxide in the spectrographed ash, the L for the given line pair was obtained from the data for the ash spectrogram, and the abscissae determined. A few values were not in agreement with those obtained from the majority of the curves, and these were rejected as being due either to error in measurement of the length of a line in that pair, or to an erroneous curve.

Fig. 14

$$aa = \frac{K \ 3446}{Ca \ 3179}$$

$$bb = \frac{K \ 3446}{Ca \ 3934}$$

$$cc = \frac{K \ 3446}{Ca \ 4578}$$

Fig.15

$$aa = \frac{K \ 3446}{Mg \ 3030}$$

Fig. 16

RATIO QUANTITATIVE CURVES

 $\text{Na}_2\text{O}/\text{CaO}$
 $\Delta L = \text{Na} - \text{Ca}$

$$aa = \frac{\text{Na } 3781}{\text{Ca } 3179}$$

$$cc = \frac{\text{Na } 5896}{\text{Ca } 3179}$$

$$bb = \frac{\text{Na } 5209}{\text{Ca } 3215}$$

$$dd = \frac{\text{Na } 5896}{\text{Ca } 3215}$$

Fig.17

RATIO QUANTITATIVE
CURVES $\text{Na}_2\text{O}/\text{MgO}$ $\Delta L = \text{Na} - \text{Mg}$

$$\begin{array}{l} aa = \frac{\text{Na } 5209}{\text{Mg } 2777} \end{array}$$

$$\begin{array}{l} bb = \frac{\text{Na } 5209}{\text{Mg } 3077} \end{array}$$

$$\begin{array}{l} cc = \frac{\text{Na } 5890}{\text{Mg } 2777} \end{array}$$

$$\begin{array}{l} dd = \frac{\text{Na } 5890}{\text{Mg } 3077} \end{array}$$

$$\begin{array}{l} ee = \frac{\text{Na } 5896}{\text{Mg } 3077} \end{array}$$

Fig. 18

$$aa = \frac{\text{Ca } 3179}{\text{Mg } 3030}$$

$$dd = \frac{\text{Ca } 3934}{\text{Mg } 3077}$$

$$bb = \frac{\text{Ca } 3215}{\text{Mg } 3077}$$

$$ee = \frac{\text{Ca } 4226}{\text{Mg } 3030}$$

$$cc = \frac{\text{Ca } 3934}{\text{Mg } 2777}$$

$$ff = \frac{\text{Ca } 4226}{\text{Mg } 3077}$$

Fig. 19

RATIO QUANTITATIVE CURVES MgO/CaO

 $\Delta L = Mg - Ca$

$$aa = \frac{Mg}{Ca} \frac{2777}{3215}$$

$$cc = \frac{Mg}{Ca} \frac{3077}{3215}$$

$$bb = \frac{Mg}{Ca} \frac{2777}{3247}$$

$$dd = \frac{Mg}{Ca} \frac{3077}{4578}$$

$\% Fe_2O_3 / \% CaO$

$\bar{a}a = Fe\ 2483$	$\bar{e}e = Fe\ 2599$	$\bar{i}i = Fe\ 2698$	$\bar{m}m = Fe\ 3020$
$Ca\ 3179$	$Ca\ 3179$	$Ca\ 3215$	$Ca\ 3215$
$\bar{h}b = Fe\ 2483$	$\bar{f}f = Fe\ 2599$	$\bar{j}j = Fe\ 2698$	$\bar{n}n = Fe\ 3020$
$Ca\ 3247$	$Ca\ 3247$	$Ca\ 3247$	$Ca\ 3247$
$\bar{c}c = Fe\ 2483$	$\bar{g}g = Fe\ 2599$	$\bar{k}k = Fe\ 2698$	$\bar{o}o = Fe\ 3020$
$Ca\ 3934$	$Ca\ 3934$	$Ca\ 3934$	$Ca\ 3934$
$\bar{d}d = Fe\ 2483$	$\bar{h}h = Fe\ 2698$	$\bar{l}l = Fe\ 2698$	$\bar{p}p = Fe\ 3020$
$Ca\ 4226$	$Ca\ 3179$	$Ca\ 4226$	$Ca\ 4226$

Fig. 21

RATIO QUANTITATIVE CURVES

 $\text{Fe}_2\text{O}_3/\text{MgO}$
 $\Delta L = \text{Fe} - \text{Mg}$

$$aa = \frac{\text{Fe } 2483}{\text{Mg } 3030}$$

$$bb = \frac{\text{Fe } 3020}{\text{Mg } 3077}$$

Fig. 22

RATIO QUANTITATIVE

CURVES

$\Delta L = P - Mg$

$$aa = \frac{P \ 2534}{Mg \ 2777}$$

$$bb = \frac{P \ 2896}{Mg \ 2777}$$

Fig. 23

RATIO QUANTITATIVE

CURVES

 P_2O_5 / CaO $\Delta L = P - Ca$

$$aa = \frac{P}{Ca} \frac{2534}{3934}$$

$$ee = \frac{P}{Ca} \frac{2644}{3179}$$

$$ii = \frac{P}{Ca} \frac{2884}{4226}$$

$$bb = \frac{P}{Ca} \frac{2534}{4578}$$

$$ff = \frac{P}{Ca} \frac{2725}{3179}$$

$$jj = \frac{P}{Ca} \frac{3425}{3179}$$

$$cc = \frac{P}{Ca} \frac{2553}{3179}$$

$$gg = \frac{P}{Ca} \frac{2884}{3179}$$

$$kk = \frac{P}{Ca} \frac{2896}{3247}$$

$$dd = \frac{P}{Ca} \frac{2553}{3934}$$

$$hh = \frac{P}{Ca} \frac{2884}{3934}$$

$$ll = \frac{P}{Ca} \frac{2725}{3179}$$

The results of the spectrographic analysis of the corn ash sample prepared are shown in the table on the following page. The ash sample was photographed in duplicate, but photographic difficulties in obtaining the second spectrogram rendered some of the lines indeterminate.

The values of ΔL and the corresponding values of percentages of the oxide constituents and the quantitative ratios are given in Table VIII.

For the ratio quantitative system based upon MgO , the value of MgO determined on the basis of Mo (14.4 %) was assumed to be correct. For that based upon CaO , a value of 3.5 % CaO was assumed to be correct. This gave a total oxide content, exclusive of SiO_2 , equal to the average of the like contents of the other two determinations.

The percentage values based upon Mo and MgO showed excellent agreement, but those based upon CaO differed from the others appreciably. In almost every set of values for an individual percent, however, the values showed excellent agreement with their average.

TABLE IX.

Calculated Composition of Corn Ash

Oxide	X MgO	X CaO
K ₂ O	1.10	3.35
Na ₂ O	1.09	2.8
MgO	1.00	4.5
CaO	0.18	1.0
Fe ₂ O ₃	0.08	0.253
P ₂ O ₅	1.75	8.9
SiO ₂		

Oxide	% (Mo 2.0%)	% (MgO 14.4%)	% (CaO 3.5%)
K ₂ O	15.0	15.8	11.9
Na ₂ O	15.5	15.7	9.8
MgO	14.4	14.4	15.9
CaO	2.3	2.6	3.5
Fe ₂ O ₃	1.06	1.10	0.99
P ₂ O ₅	24.3	25.2	31.5
SiO ₂	27.44	25.2	26.3

SUMMARY

A Cenco Replica Grating Spectrograph was assembled, and accessory equipment added for convenience and accuracy in adjustment and operation.

A direct current arc between spectrographically pure carbons produced an emission spectrum of any substance placed in a cavity in the lower electrode. The current required was 6 to 8 amperes. An arc gap of 0.5 cm. was employed, and an enlarged image of the arc flame was produced on the slit and grating by means of a quartz lens. A portion of this beam of light was converged at the slit by a second lens, so that the entire surface of the grating was covered. Use of quartz lenses permitted photography in the ultraviolet region.

The slit width was adjusted to give maximum sharpness and resolution of the spectral lines, with minimum background, without decreasing the intensity of the lines. With the slit adjustment used, the optimum duration of exposure and time of development were found to be 45 seconds and 3 minutes respectively.

A number of synthetic ash standards were prepared, corresponding in composition to an "average ash". This was the average of the mineral analyses of twelve different representative grains, reduced to the basis of a total of 100 %. The constituents of the oxide ash were K_2O , Na_2O ,

MgO, CaO, Fe₂O₃, P₂O₅, and SiO₂. For each of the oxides except the last there was a series of six mixtures, in which the amount of the particular oxides varied between the lower and upper limits of the expected range of analysis.

The standard mixtures were prepared volumetrically from sulfates of the constituents, except Ca and Si, and an amount of ammonium sulfate added equal to the weight of the sulfate residue. Two percent of molybdenum, relative to the total oxides, was added in the form of ammonium molybdate solution, to serve as the internal standard. The molybdenum furnished lines sufficiently close to those of the test elements to serve as an internal standard for all, and at the same time of such intensity that one spectrogram served for analysis of all those elements. The solutions were evaporated to dryness, being stirred the while to insure homogeneity, and the residues ground to fineness.

Ground corn was ashed in the presence of nitric acid and an excess of sulfuric acid to reduce the mineral content to a condition approximating normal sulfates, homogeneously mixed with pre-existing silicates and phosphates.

A representative ash sample was mixed with an equal weight of ammonium sulfate and the correct amount of ammonium molybdate for spectrographing.

The samples for spectrographing were compressed into cavities drilled in the ends of the lower carbon electrodes. Exposure was begun immediately when the arc was struck, and the amount of sample used was such that during the time of exposure it was almost completely, if not entirely volatilized. Thus the complete record of every constituent of the sample was obtained.

A study was made of the Internal Standard method of Gerlach, and of the Ratio Quantitative system devised by Lewis. In the first method, the molybdenum served as a reference standard, and in the second, the oxide constituents were determined relative to the MgO and CaO present.

A rotating logarithmic sector disk was used before the slit opening, by virtue of which the lengths of the spectral lines of the various elements were a function of the logarithm of the ratio of their intensities, and consequently a direct function of their relative amounts.

Lines recommended in the literature or chosen from qualitative spectrograms were used. An enlarged image of each spectrogram was projected onto a screen, the proper lines identified, and their lengths measured.

Operating curves were then established for each line pair, showing the relation between differences of lengths of the two lines and the corresponding relative

amounts of the two constituents represented. In cases in which molybdenum was the reference element, since its amount was constant, the concentration of the other element could be plotted directly as percent oxide in the synthetic oxide ash. Such a curve has been designated as an Analytical Curve.

Ratio Quantitative Curves were established on coordinates of differences of lengths of line pairs consisting of some element and either Mg or Ca, and the corresponding ratios of the oxide of that element to MgO or CaO. For any two elements there were a number of possible line pairs. Only those curves which were straight lines or appeared to be consistent functions were retained.

Some curves showed symmetrical retrace of ordinate range, so that two sets of values for percentage of a constituent oxide could be obtained for a single set of values for L . This has been explained as the result of the reversal of lines of the particular constituent. However, when such a condition was encountered, by reference to the quantitative ratio curves, the amount of CaO and MgO having been established without doubt from straight line curves, the correct set of values was established.

No study was made of the effect of variation of the main constituent on the line intensities of the other

elements because of the complexity of that problem. The method of excess was used. This signifies that the concentrations of all the elements in the sample were of such an amount that the effect of each on the line intensities of all the others remained constant.

The replica grating showed fairly accurate dispersion, and good resolution was obtained for the lines. The determination of the end points of the lines was purely a matter of personal estimation, but the differences of lengths of two lines determined by different persons were in excellent agreement.

Line measurements were made of the corn ash spectrogram, and by reference to the operating curves the following analysis was obtained (based on Mo) :

Oxide	%
K ₂ O	15.0
Na ₂ O	15.5
MgO	14.4
CaO	2.3
Fe ₂ O ₃	1.06
P ₂ O ₅	24.3
SiO ₂	27.44

It was observed that the internal standard method

and the ratio quantitative system based on MgO gave results which were in excellent agreement. The analysis based on CaO did not agree well with those of the other methods. Both systems are recommended for quantitative spectral analysis.

By use of the methods employed, of the same times of exposure and development, and of like conditions of preparation of samples, it should be possible at any future time for investigators to determine these major mineral constituents of ash samples by means of the established operating curves.

The author wishes to
express his appreciation
for the aid and suggestions of
Mr. J.F.Hertweck,
Dr. R. A. Loring,
and
Prof. J.A. Ayers.

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* Indicates a secondary source of reference.

Mg.

Plate of Spectra

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