CHEMICAL ANALYSIS OF CERAMIC MATERIALS BY MEANS OF THE EMISSION SPECTRUM

BY

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INTRODUCTION

The object of this investigation is to determine qualitatively and quantitatively the principle chemical constituents and associated impurities in ten ceramic materials which were obtained from regions in the state of Virginia. These materials are all intended for the glass industry, and may be accepted or rejected for this purpose depending upon the presence or absence of certain impurities which would render them useless to the industry. In some cases a minumum percentage of an impurity is acceptable in a material which, if it were present in any greater amount, would render it useless.

The foundation upon which qualitative analysis by the emission spectrum is based is the fact that an element which has been rendered luminous will emit spectrum lines of frequencies which are peculiar to that element. Based on the theory that the atom is composed of a positively charged nucleus surrounded by a number of electrons depending upon the element, with each electron traveling its own orbit, it is seen that by an electrical discharge through the material atoms are continually raised from the normal into excited states. In such a case the atom has received sufficient energy to cause an electron in the outermost orbit to change from its particular energy shell to one farther from the nucleus, depending upon the amount of energy gained by the electron.

In Figure 1, the energy shells, or energy levels, of a sodium atom have been indicated by horizontal lines. The spacing between any two levels is proportional (1) to the amount of energy in ~~volts~~ volt-electrons which must be imparted to an ~~atom~~ electron in order that it may shift from the lower of the two levels to the upper level, and (2) to the reciprocal of the wave length, that is, the number of waves per centimeter of the electromagnetic radiation emitted during the downward shift of the electron back to its normal level.

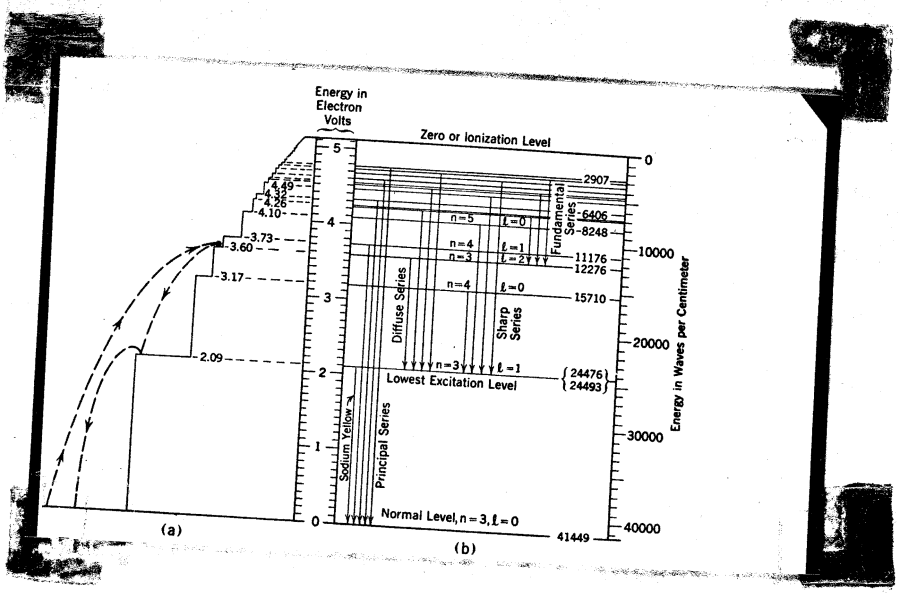


Fig. 1

The electron's return to the normal state may take place in a number of ways: a single transition may occur, or the electron may take several "jumps" to reach the normal level as is indicated on the left side of Figure 1. The transitions which do occur are called permitted transitions. In figure 1, permitted transitions are indicated by vertical lines between levels. The spectrum of sodium vapor contains a spectral line for each one of the vertical lines because energy is emitted by a particular transition equal to a constant times the frequency of the corresponding spectral line. The constant, known as Planck's universal constant, has the value 6.542×10^{-27} erg-seconds. This energy will be referred to as a "photon" or "light quantum". Therefore, a material which has been vaporized will emit photons of frequencies which are peculiar to the material.[2] These frequencies influence the appearance of a luminous vapor to the extent that the principle color is due to the greatest number of photons emitted of that frequency, i.e.; the yellow color of a sodium vapor lamp can be attributed to the intensity of the two principle lines of sodium of wave length 5890 A. and 5896 A. However, photons of many frequencies are also emitted at the same time but at a lesser intensity which can be seen when

the light is passed through a prism or grating. Suppose the spectrum of not one element but several elements were viewed by passing the light from the luminous vapor of several elements in combination through a prism or grating. There would be no difficulty in recognizing the lines of each element as though it had been viewed alone. However, the spectral lines of the other elements will be intermingled in their respective positions. The problem of the observer, then, is to determine the wave length of each of these lines and thereby ascertain the element which emitted it. In the case of an alloy or a compound, the chemical composition could be readily recognized by its emission spectrum. This constitutes chemical spectrum analysis.

In whatever form it may take, spectrum analysis was based on the investigations of Robert W. Bunson and Gustav Kirchhoff[3] in 1857. Their work, in turn, utilized the results of observers as far back as 1832, who left documents describing the spectra of colored flames and the conclusions they came to as to the origin of these colors. The great service spectroscopy has rendered in the study of the behaviour of the electron has received abundant recognition, and prior to twenty years ago was used only for that purpose and to identify small percentages of elements in composition or mixture with other elements. Since that time investigators have worked on methods for making quantitative determinations of an element occuring in more or less pronounced proportions in another element. It is a problem

upon which many investigators have worked, among these being Hartley, de Gramont, Leonard, and Pollok.[3] It is this phase of chemical analysis, referred to as quantitative analysis, with which the principal part of the next section of this paper is concerned.

II REVIEW OF LITERATURE

Uses of the Spectrograph

Available literature on spectrum analysis as applied to chemical determinations is not abundant, because spectroscopy has but recently been used in this manner. Its most important function until recent years was in studying atomic structures and the behaviour of the electron, and in detecting small amounts of impurities in a supposedly pure element.

The many advantages which spectrographic analysis display over chemical analysis serve to promote its importance in industry.[4] Often chemical analysis for certain substances are difficult to make with accuracy and rapidity. Two important uses of qualitative analysis to industry are (1) the quickness and relative ease with which contamination may be detected in a metal being refined and the excellent check it offers at each step during a complicated process, and (2) an accurate method of ascertaining the cause of imperfections in a faulty product which has been returned. An examination of a break in a metal product at the exact point of breakage is possible with a spectrograph and will reveal the cause of the fault due to an excess of a constituent or an impurity that could not be recognized by chemical analysis under the same conditions.

Spectrographic analysis has been used at the Dow Chemical Company, Midland, Michigan, since 1925.[5] Its applications have increased because of experience and improved technique from purely qualitative analysis and visual estimations of small

amounts of impurities in materials, to accurate quantitative analysis which have, in many cases, replaced chemical methods.

The value of spectroscopic methods in the production of such commercially important metals as platinum is unquestioned. The high value of the metal leads to constant recovering of all forms of scrap from all sources. The scrap metal must be accurately analyzed with the minimum of material destroyed in testing. Because of the chemical inertness of the platinum group, methods of analysis employing solutions have been replaced by the less arduous spectroscopic determinations.

Many papers and complete descriptions of procedures have been written on the spectral analysis of iron and its alloys, copper, lead, tin, and silver. Although quantitative methods have been questioned again and again, and while the process is still in a formative stage, excellent results have been obtained in the production and development of these metals.

Qualitative Analysis

Qualitative analysis is the determination of the elements present in a mixture or compound by the presence of their characteristic spectral lines on a spectrum, either visible or recorded on a photographic plate. Where the spectrum is composed of lines, it is concluded that atoms are present in the vapor; if the spectrum is composed of bands the vapor contains molecules. This distinction in itself is a chemical analysis of the simplest kind. The bands of the molecular spectra are in themselves

groups of very numerous lines, made up of the spectral lines due to the "energy jumps" within the atom and to the energies of the vibrations which the atoms of the molecule execute relative to one another. Such problems as proving that the vapor of bismuth or antimony is composed of molecules is easily sloved by viewing the band spectra, but the same proof would be exceedingly difficult by vapour density tests.

If a qualitative analysis is to be made of a compound, the first necessary condition is that excitation should be such as to dissociate chemical combinations. It has just been seen that the spectrum of molecules, which would be the case of a compound, is one of bands and cannot be used to identify ~~spectral lines~~ elements.[6] The atoms that result from the dissociation must be made luminous under similar conditions. The presence of ~~an chemic l~~ inert element in a compound may be entirely unsuspected in the spectrum, and will only be ~~seen~~ detected when concentrations are present millions of times greater than that necessary, say, for sodium to give its distinct yellow color to a flame. The excitation necessary for a particular line in the spectrum of an element is as characteristic as the wave length of that line. However, in the usual analysis of metals, except the alkali metals, the conditions of excitation differ very little from one another, so that a spectrum of an alloy generally includes all the elements of the compound.

Quantitative Analysis

The purpose of a quantitative analysis is to ascertain the atomic concentration of small amounts of materials, such as impurities, in the primary constituent of the compound to be analyzed. From one or two per cent to several thousanths of a per cent of an impurity is the optimum range of investigation. The practice of quantitative analysis in any of its various forms is based on the work of Lockyer,[5] one of the early investigators, who estimated the abundance of an element in the electrodes of an arc by observing the strength of the spectral lines.

Until recently all the methods of quantitative analysis were merely rough estimations. Even these were of great value to experimental research and as an aid to the chemist. Although Lockyer obtained a relative estimate of the amount of an element, which shall be called an "admixture," found in the composition of the primary substance, the photographic "blacking" due to a spectral line is not a measure of the intensity of emission as one would ordinarily think. The obvious supposition would be that a line of a given blackness would be invariably a definite measure of the intensity of the radiation which produced it. The case is, however, that it is as much dependant upon arc or spark discharge conditions, the type of photographic plate used, and the time of exposure as the intensity of the source. The number of spectrum lines of the admixture which will appear at

certain concentrations is dependant upon these conditions. Thus, two direct measures would be valid only when the conditions just stated are absolutely constant. This is practically impossible because of uncontrollable factors which will be discussed later.

If it is desired to verify whether an alloy meets the requirements of a specified composition, or if it is required to know whether a prescribed purity of a substance has been reached or exceeded, the method of comparison spectra[3] is the simplest and most direct. In either case the per cent of the admixture in the primary substance must be found. This is done by preparing a number of samples containing the primary substance in constant amounts and the admixture in known concentrations within the range of the mixture being analyzed. The number of these samples will depend upon the degree of exactness required. Spectra of these samples are then photographed in order with a spectrum of the unknown mixture lying between each pair of known composition. Thus, the developed plate will present a spectrum of, say, highest concentration at the top, then an unknown, etc. Throughout this procedure the conditions of discharge and exposure should be kept as constant as possible. An examination of the spectra will produce that pair of spectra of the standard, or known, substance and the unknown specimen whose lines of the primary constituent are nearest to equal intensity and the admixture lines nearest to equality. This, of course, will be the percentage of the admixture in the primary. In the case that

the unknown lies between two standards, interpolation may be necessary to approximate the percentage, or more standards may be made within that range.

A method similar to this but more exact is that called the "Absolute Method of Homologous Lines."[3] With the aid of a magnifying eyepiece, the observer may make a comparison of the degree of blackening of an A-line, admixture line, with a P-line, of the primary substance, which lies near it and on a similar background. Thus, the required ratio of the quantities of A and P is determined from the ratio of the intensities of the observed A and P lines, as measured with a microphotometer. In such a case, if the time of exposure is varied or the plate under or over developed, the ratio of the lines will remain constant. However, any change in the discharge conditions, or the presence of any other element will alter this ratio. Since the latter conditions are as difficult to be kept constant as the former, it was necessary to find a criterion for maintaining constant conditions throughout the analysis. In view of the fact that the conditions of luminosity were directly dependant upon the conditions of the discharge, the problem resolved itself into finding the correct conditions of luminosity and assumming that the conditions of discharge in each case were constant. This is done by preparing two samples of varying known amounts of A in P as in the comparison method and photographing their spectra. The pairs of lines of A and P whose intensities are the same should be sought and their wave lengths

determined. These pairs must consist of either spark or arc lines, but not a combination of the two. Then samples are prepared whose concentrations lie between the two samples just photographed, and a pair of lines whose intensities are exactly equal are noted. The contentration may be determined by comparison with the spectrograms of varying amounts of A in P and whose fixation pair are always equal in intensity. When the influence of the discharge conditions is eliminated the homologous pair will exhibit lines of equal intensity independent of other admixtures in the material.

In the event that no suitable P lines or P lines may be found in the region under consideration, the number of P lines or A lines, whichever is deficient, may be artificially increased by photographing an additional spectrum of an element just above the spectrum in question in which there may be found suitable lines. Comparison is then made of the A lines

and the substituted P lines in exactly the same manner. This is known as the "Method of Substitution."[3] This method was made use of in the quantitative analysis made in this investigation.

An entirely different method of quantitative analysis was adopted by G. Scheibe in 1928, using the logarithmic sector of Hamburger and Holst.[3] Ordinarily in photographing a spectrum for analysis, the slit of the spectrograph is uniformly illuminated throughout. In this method, the intensity of the illumination is varied intentionally from point to point along the slit. The best means of obtaining a uniform variation is the rotating disc in front of the slit, devised by Hamburger and Holst.

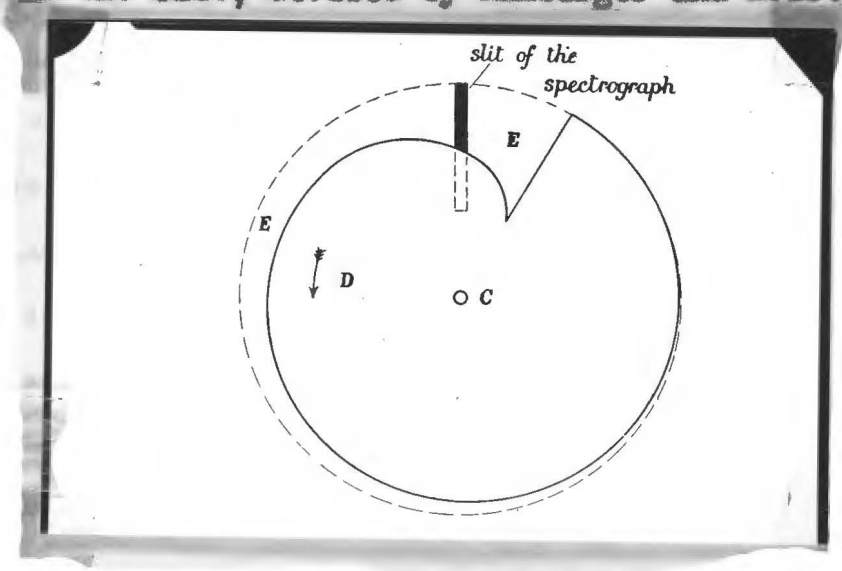


fig. 2

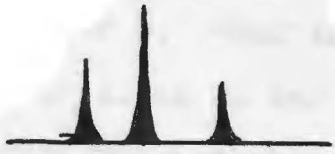


fig. 3

In figure 2, the slit of the spectrograph is indicated by the broad black line at the top of the circle. The rotating sector, or disc, is set up between the slit and the source of light. If the sector is slowly rotated in the direction indicated, the upper portion of the slit will receive illumination over a longer period of time than the lower portion. Consequently the intensity will vary along the slit with respect to time. When the spectrum is developed using the sector rotating through one revolution, it will appear as in Figure 3. Since the photographic density varies as the logarithm of the amount of light, and the time of exposure at different points along the spectrum line is made to vary logarithmically with the length of the slit exposed, the difference in lengths of the two lines in the spectrum will be proportional to the logarithm of the ratio of the intensities of these two lines.[7] This method can used for establishing fixation points of the homologous pairs of lines and can be used for analysis of concentrations. As applied to the latter, a series of spectra of standards containing varied and known percentages of the impurity 'a' in P, is photographed on the same plate with the sample containing the unknown amount of 'a' in P. A working curve is plotted using the difference in lengths of a selected pair of 'a' in P lines of the standards, and the percentage of 'a' in P. From the measured difference in length of the same pair of lines in the sample containing the unknown percentage of 'a', the actual percentage may be read from the curve.

or the ratio of the concentrations.* When one concentration is known many others may similarly be found.

* Gerlach, W., and Schweitzer, E.; Chemical Analysis by the Emission Spectrum, page 111.

III THE INVESTIGATION

Object

The spectroscopic methods outlined in the last section are not supposed to replace the chemical analysis of a similar nature, but rather to supplement it. In ascertaining the composition of an unknown compound which has two or more primary constituents, the usual quanitative chemical analysis cannot be improved upon by a spectrograph. Its function lies in the range of 5 per cent or less which usually implies that the element is an impurity or a prescribed constituent in an alloy. It would be impossible to show the presence of elements at that low concentration in a mixture by purely chemical means, much less the amounts of these impurities in the total mixture. Generally, it may be said that the usual chemical analysis operates most effectively in the range above 5 per cent while a spectrographic analysis is suited to the range of 5 to 0.001 percent. In the event that one or two "persistent" lines of an element may be found on a spectrogram but that a quantitative analysis for the element is impossible due to the faintness of the lines, the element shall be called a "trace." By "persistent" lines is meant those lines which are the last to disappear when the concentration of one element in another is decreased to zero. In a handbook[8] which lists the wavelengths of the line spectrum of an element, these lines are marked with a capital "P."

Specifically, the object of this investigation is to identify all the impurities and traces of elements found in ten ceramic sands and to determine for ~~three~~ one of the important sands, the concentration of these impurities in the mixture. In the case in which the chemical formula specified the percentage of an element in the mixture, a quantitative analysis was not made.

Methods of Procedure

The qualitative analysis consisted of photographing the spectra of the ten materials and determining the wave length of the lines in the spectra. The materials were placed in recessed carbon electrodes which had been purified and subjected to a potential of 120 volts at 8 amperes for 30 seconds. The electrode which contained the sample was made positive with respect to the electrode above it. The electrodes were placed three to five millimeters apart. Thus, the ~~potential gradient~~ fall in potential across the arc never exceeded eight or ten volts which is more than the ionizing potential of any element present. The spectra of each pair of electrodes were photographed along with the sample so that those lines due to impurities in the carbon might be rejected. Carbon electrodes were used for two reasons, (1) because the temperature due to the arc was very much greater for carbon than, say, copper, and complete volatilization was insured, and (2) because the samples were free of carbon.

In order to measure the wave lengths of the lines on the photographic plate, one line must necessarily be known. The two principle copper lines, 3274 A and 3247 A, invariably appeared as an impurity in the carbon electrodes. Measurements were made by means of a calibrated eye-piece from this known line out to any line in question. This distance was multiplied by the dispersion factor and added if the wave length were in the increasing direction, or subtracted if decreasing, from the known wave length. This new wave length was then identified in the "Tabelle Der Hauptlinien Der Liniemspektra Aller Elemente" by Kayser, and labeled on the plate. The chief difficulty encountered was the fact that from eight to ten different elements might lie within one angstrom of the position measured and the inaccuracy of the measurement might involve 1/10 angstrom. In many instances the observer was completely mystified as to which element a certain line belonged. This difficulty was overcome to a great extent by using an instrument of greater accuracy for measuring questionable lines. As mentioned before, if an element is present in very low concentrations, only the persistent lines were sought. If these were not present or if the persistent lines were much fainter than that of the line in question, the choice of the element to which it belonged was erroneous, and the process was repeated. About three hundred and fifty lines were measured and identified by this process.

The quantitative analysis was a much more involved process. The method of Homologous Pairs as described in the last section was used. One sample was of particular interest due to its greenish color which could not be accounted for by any chemical analysis. Geologists have wondered for many years why this particular feldspar is green when another feldspar, which gives exactly the same chemical analysis, is white. Upon examining the spectrum of this sample, it was found that four impurities not listed in any chemical analysis were present in an abundance considerably more than a trace. Compounds of these four elements were procured and solutions made up that would give a certain percentage of the element in one drop. Fortunately, one sample was completely free of the impurities being analized. This sample was used as the standard to which various percentages of the "impurity" elements were added. Such precautions as testing the electrodes for impurities and finding the correct amount of material which would be completely destroyed in the arc after 30 seconds were taken before preparing the standards. The samples were powdered and the solutions of the impurity elements were dropped onto the material in the recessed electrode. Each electrode was baked until thoroughly dry after each application of a solution. This was necessary be cause of the fact that the solution would have boiled away immediately if it had been placed directly in the arc. The spectra of the standards were photographed, the plates developed, washed and dried. Upon examination it was found that the elements were in considerably greater proportions than the first

estimated range. The entire process was repeated which gave the desired results. Since an arc was used, whose potential drop is constant compared to a spark, fixation lines were not necessary. In searching for homologous pairs it was found that there was a lack of primary lines in those regions in which the impurities showed up to an advantage. Therefore, copper, which is rich in lines, was substituted in a known amount as a means of comparison. With this aid, homologous pairs were found which gave the correct concentrations. The results of this process are described in the following section.

Apparatus and Materials used

The instrument used in this work was a grating spectrograph. The grating was of aluminized speculum metal having 14,428 lines per inch ruled* on the concave spherical surface whose radius of curvature was 6 feet. The most important feature of a good grating spectrograph is its grating. The validity of a spectrogram is more dependent upon this one factor than any other. One of the earliest gratings was that used by Wallaston and Fraunhofer which consisted of two screws set vertically a small distance apart wound with very fine wire. This was a "transmission" type grating; that is, the spectrum of the source fell beyond the grating. With this type grating the two "D" lines of sodium, 5890 A and 5896 A, were measured.

* Ruled by J. A. Anderson at Johns Hopkins University

The type grating used in this investigation is a "reflection" grating. The light is broken into its spectrum and reflected from the grating. The number of ruled lines per inch, the total number of ruled lines, and the radius of curvature of the grating are the best measures of its worth. Many different mountings have been described for the position of the slit, grating, and plate with respect to one another, for these three comprise the essential parts of the spectrograph. The mounting proposed by Rowland is used in the construction of the apparatus for this experiment. The focal length of the grating is due to its curvature. Rowland showed that if a spherical mirror had lines ruled on it at distances apart the same as lines ruled equally along its chord, that this grating would also serve to focus the diffracted light into the several orders. A grating has the property of giving spectra on each side of the central image which are called spectra of different "orders". This is not true of a prism;

a prism has only one order. The presence of orders in a spectrograph is a disadvantage in some situations because the orders overlap. Thus, the observer might endeavor to identify a line which belonged to an adjacent order. In the region around 3200 A there is less overlapping of orders than elsewhere. The spectrograms of the samples were all taken at that range.

Rowland based the principles of his mounting upon the fact that if a slit and grating are set up at any two points on the circumference of a circle whose diameter is the radius of curvature of the grating, the different orders of the spectra are all in focus on the circumference of this circle.

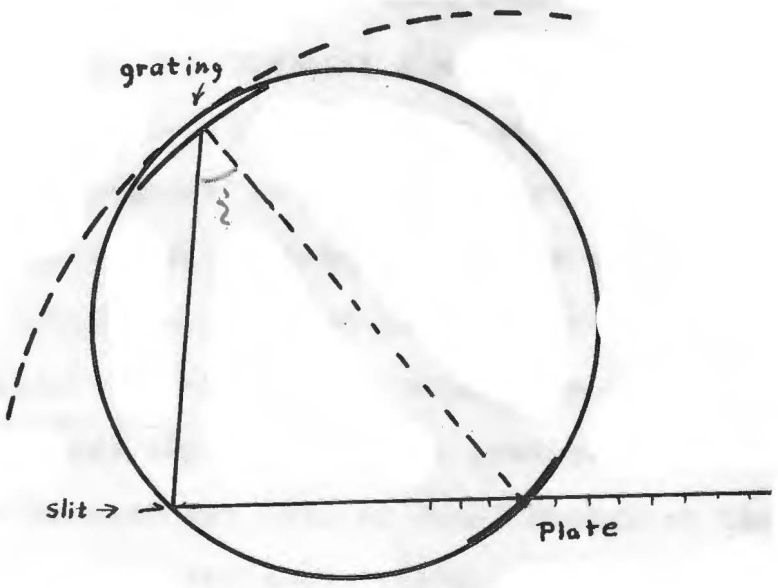
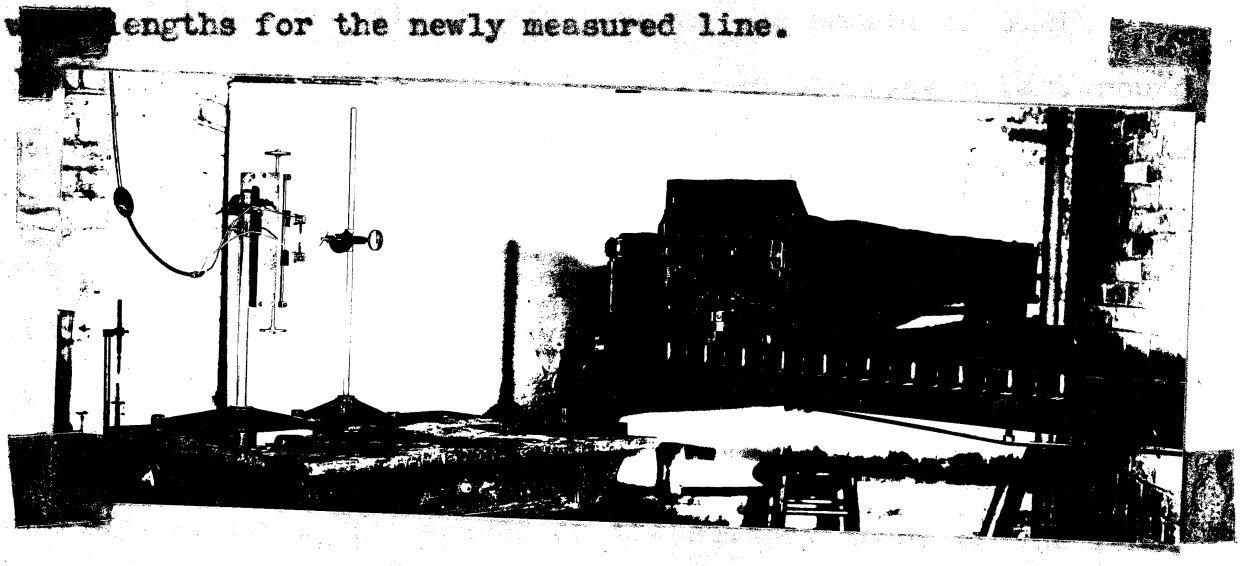


fig. 4

It is seen from Figure 4 that the grating is mounted with its axis normal to the center of the photographic plate. The grating and plate holder move together over tracks set at right angles. The slit is placed at the intersection of the tracks. As the grating is moved along the track, the angle of incidence of the light beam from the source will vary. The angle between lines drawn from the center of the grating to the center of the plate, and to any given spectral line, called θ, is equal to the ratio of the distance from the given spectral line from the center of the plate and the distance from the plate to the grating. By using the instrument as a spectroscope, viewing the spectrum through an eyepiece set at the center of the plate, θ will equal zero. Increasing the angle of incidence by moving the plate holder along the track, the observer will note spectral lines passing from right to left of increasing wavelength. Used in this manner, the distance moved will always be directly proportional to the wave length of the line in view. This is the only known instrument to which a direct reading linear wavelength scale may be attached. Used as a spectrograph, the image will no longer be a single line, but a series of all wave lengths which appear in the source over a distance of ten inches will comprise the image on the photographic plate. θ will no longer be zero but will be small enough so that a constant may be calculated for that small range. This constant is known as the "dispersion factor" and is numerically equal to the rate

of change of the distance along the photographic plate holder ~~track~~ with respect to the corresponding change in wave length. Actually the reciprocal of this value, called the "plate dispersion" is used in calculating wave lengths. It was found by taking the difference in the wave lengths of the two principal copper lines, 3274 A and 3247 A, and dividing by the distance between the two lines in millimeters. The value was 9.43 angstroms per millimeter. It was found to be practically constant over the range of ten inches. Any inconsistency of the plate dispersion was overcome by taking as small distances as possible between lines and using the corrected value found in the tables of wave lengths for the newly measured line.



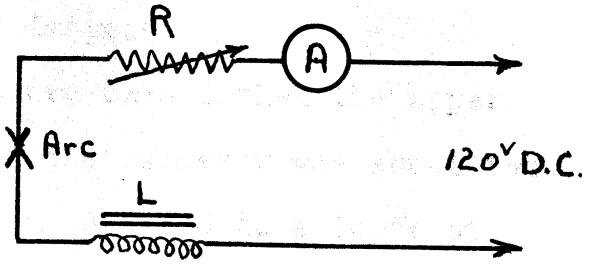


Fig. 5

The source of light was that given off by the excited atoms of the material in question which had been placed in a recessed carbon electrode. This electrode and the one above it were held in place on an arc board as can be seen in Figure 5. The apparatus was connected as shown in the diagram. The direct current potential could be applied by a switch in any one of the lines. A series resistance governed the magnitude of the current. The arc was struck by means of a carbon rod which was kept clean by sandpapering it after each material had been vaporized. The light from the arc was focused by means of a quartz lens, used because quartz transmits the ultra-violet, on a slit which governs the amount of light received by the grating. If the slit is too wide a background of the band spectrum with wide lines superimposed upon it can be seen. The slit was narrowed until a minimum of background with sharp lines upon it was visible. This was done in the visible region at about 5200 A. Before using the instrument, it was lined up, which is a process of adjusting the light source until the light falls exactly in the middle of the grating, focusing the source on the slit by means of the lens, and adjusting the slit for a sharp image.

The carbon electrodes were turned on a lathe, the upper electrode smoothed and shaped until its diameter was about two millimeters. The lower electrode was drilled to a depth of

about half an inch and a diameter equal to the upper electrode. The outer region was shaped until as narrow a wall as possible was obtained. Into this thin cup the sample was to be placed. These electrodes were purified by burning them in an arc of 120 volts at 6 amperes for one minute.

The samples were received from the Ceramics Department of the Virginia Polytechnic Institute with their approximate chemical quantitative analysis. The primary constituent in seven of the sands was silicon ~~oxide~~ dioxide which constituted 98 per cent or more of the total mixture. Aluminum was found in varying amount, as was calcium, zirconium, iron, and magnesium. In two of the sands for which but one approximate analysis was given, two primary substances were present; ~~oxide of silicon~~ silicon dioxide and ~~oxide of calcium~~ Calcium Oxide. Upon careful examination of the spectra of both sands, this observer came to the conclusion that the two were exactly the same to the last trace of an impurity. The remaining sand was composed chiefly of oxide of calcium, quite an abundance of zirconium, potassium, sodium, and magnesium. The spectrum of the latter was entirely different from any of the others. The physical properties of the sands were similar in that ~~much~~ of them were near white while one was distinctly green, and another had a slightly brownish cast due to less than one per cent of iron oxide. The sands ranged from a coarse granular consistency to a finely powdered form. While only a

few grams of the sample was available, the supply was much more than sufficient as only the small amount of 20 milligrams was used for each spectrum. Compared to a chemical analysis this is a great saving of material being used.

The spectra were recorded on thin Eastman Process glass plates, and developed for six minutes in developer 61-a.

IV RESULTS

In this section are recorded the wave lengths of all lines which identified elements in each sample. The chemical analysis is also included for each sample.

Number 1.

"Clinch Mountain" (First)*

Chemical Analysis:

SiO_2	98.900%
$Al_2O_3 + Zr_2O_3$	0.629%
Fe_2O_3	0.091%
CaO	0.060%
MgO	0.090%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg
2506	3443	3968	2969	2852
2514	3092	4934	3099	2802
2516	3082	4226		2795
2519	3944			
2524				
2528			Impurities	
2631				
2881		Ti	Cu	Fe
2981				
3905		3361	3274	3020
		3349	3247	
		3341		

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* Notations used to identify samples are the same as given by the Ceramics Department of V. P. I.

Number 2.

"Clinch Mountain" (Second)

Chemical Analysis:

SiO_2	99.440%
$Al_2O_3 + Zr_2O_3$	0.370%
Fe_2O_3	0.034%
CaO	0.020%
MgO	0.060%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg
2506	3443	3968	2969	2852
2514	3092	3934	3099	2802
2516	3082	4226		2795
2519	3944			
2524	2575			
2528	2567			
2631	3934			
2881				
2981				
3905				

Impurities

Ti	Cu	Fe
3361	3274	3020
3349	3247	
3341		

Number 3.

"Clinch Mountain" (Third)

Chemical Analysis:

SiO_2	99.310%
$Al_2O_3 + Zr_2O_3$	0.390%
Fe_2O_3	0.017%
CaO	0.030%
MgO	0.060%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg
2435	2567	3934	2964	2795
2506	2575	3968	3099	2802
2514	3082	4226		2852
2516	3092			
2519	3443			
2524	3944			
2528				
2631				
2881				
2981				
3905				
2927				

Impurities

Ti	Fe
3341	3020
3349	
3361	

Number 4.

"Clinch Mountain" (Fourth)

Chemical Analysis:

SiO_2	98.500%
$Al_2O_3 + Zr_2O_3$	0.780%
Fe_2O_3	0.149%
CaO	0.010%
MgO	0.170%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg
2435	2567	3934	2969	2852
2506	2575	3968	3099	2795
2514	3082	4226		2802
2516	3092			
2519	3443			
2524	3944			
2528	3961			
2631				
2881				
2981				
3905				
2927				

Impurities

Ti	Fe
3341	3020
3349	
3361	

Number 5.

"Barker Sandstone"

Chemical Analysis:

SiO_2	99.050%
$Al_2O_3 + Zr_2O_3$ . .	0.610%
Fe_2O_3	0.022%
CaO	0.040%
MgO	0.100%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg
2435	3443	3934	3099	2852
2506	3082	3968	2969	2802
2514	3092	4226		2795
2516	3944			
2519	3961			
2524				
2528				
2631				
2881				
2981				
3905				
2927				

Impurities

Ti	Cu	Fe
3341	3274	3020
3349	3247	3719
3361		3722

Number 6 and 7.

Apelite

Chemical Analysis:

SiO_2	60.38%
$Al_2O_3 + Zr_2O_3$ . .	23.58%
Fe_2O_3	0.236%
CaO	5.88%
Na_2O	6.49%
K_2O	3.07%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg	Na	K
2435	2373	3934	3099	2795	3303	3449
2506	2567	3968	2969	2802		4044
2514	2575	4226		2852		4047
2516	2652					
2519	2660					
2524	3082					
2528	3092					
2631	3443					
2881	3944					
2981	3961					
3905						
2927						

Impurities

Ti	Ga	Cu	Rb	Fe
3341	4172	3274	4215	3020
3350	4033	3247	4201	3719
3361	2943			3722
				3727
				3737
				3745

Number 8.

Mendota Limestone

Chemical Analysis:

SiO_2	0.62%
$Al_2O_3 + Zr_2O_3 + Fe_2O_3$ . . .	3.50%
CaO	52.66%
MgO	0.76%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg
2506	3737	3736	3099	2795
2514	3443	3934	2969	2802
2516	3092	3968		2852
2519	3082			
2524	2567			
2528	2575			
2435				
2631				
2881				
3905				

Impurities

Cu	Fe
3247	3020
3274	3719
	3722
	3727
	3737
	3734
	3745

Number 10.

Chemical Analysis:

SiO_2	99.810%
Al_2O_3 + Zr_2O_3 . . .	0.170%
Fe_2O_3	0.014%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Zr	Ca
2435	3443	3099	3934
2506	3082		3968
2514	3092		4226
2516	3944		
2519	3961		
2524			
2528			
2631			
2881			
2981			
3905			
2927			

Impurity
Fe
3020

Number 9.

Green Feldspar

Chemical Analysis:

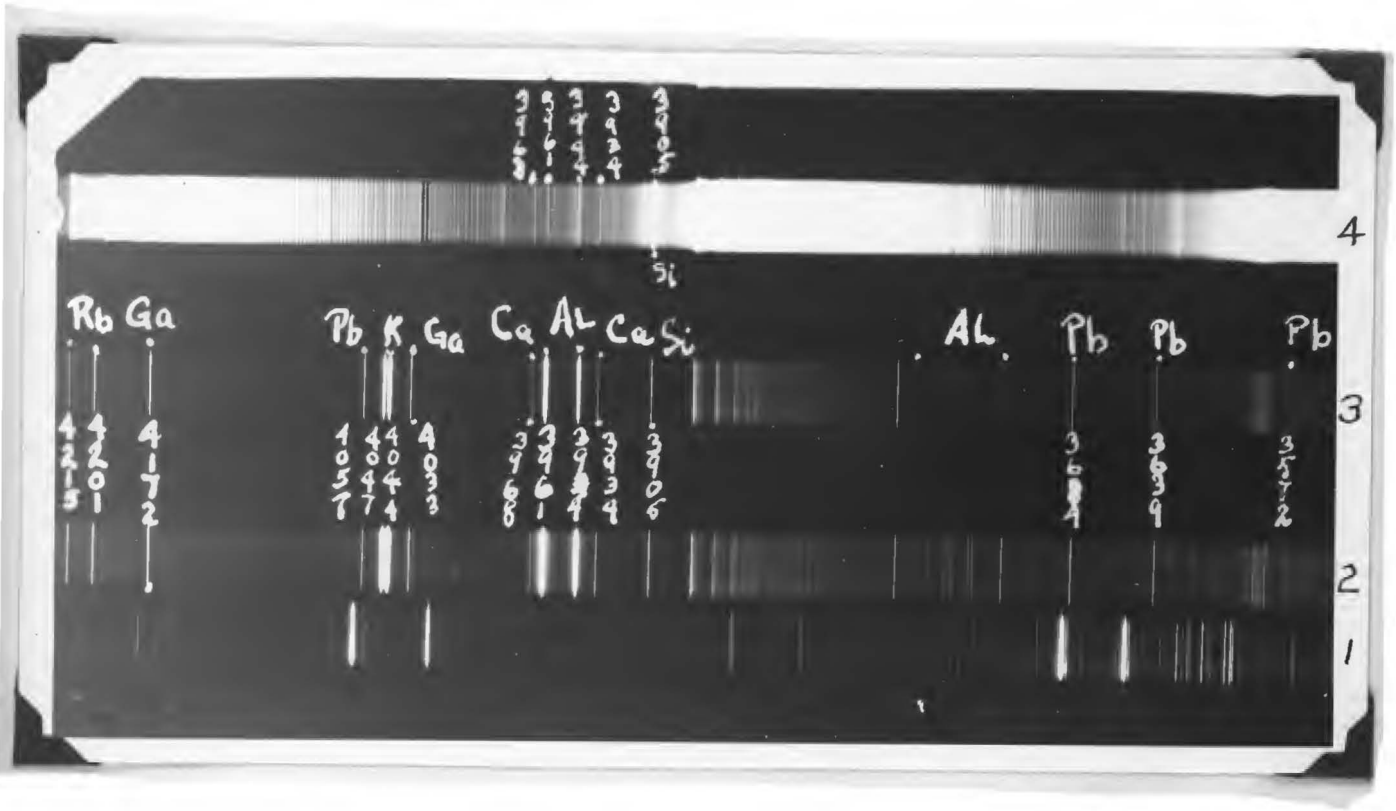
SiO_2	65.02%
$Al_2O_3 + Zr_2O_3$ . . .	18.74%
Fe_2O_3	0.01%
CaO	0.08%
Na_2O	2.04%
K_2O	14.00%

Spectrographic Qualitative Analysis (wave lengths of identified lines in angstroms):

Si	Al	Ca	Zr	Mg	Na	K
2435	2373	3934	3099	2795	3303	3449
2506	2567	3968	2969	2802		4044
2514	2575			2852		4047
2516	2652					
2519	2660					
2524	3082					
2528	3092					
2631	3443					
2881	3944					
2981	3961					
3905						
2927						

Impurities

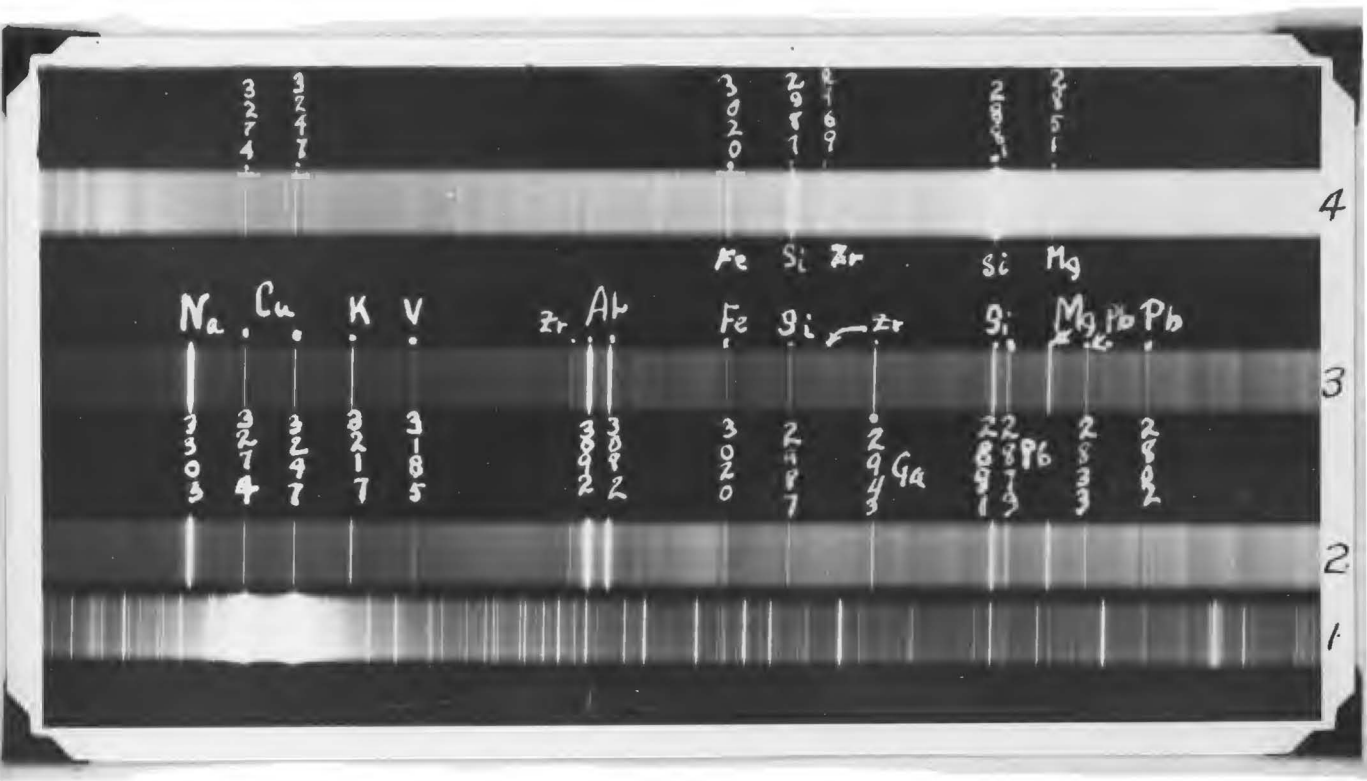
Ti	Ga	V	Rb	Fe
3341	4172	3183.42	4215	3020
3350	4033	3183.99	4201	
3361	2943	3185.41		
	2944			



Number 9.

Green Feldspar

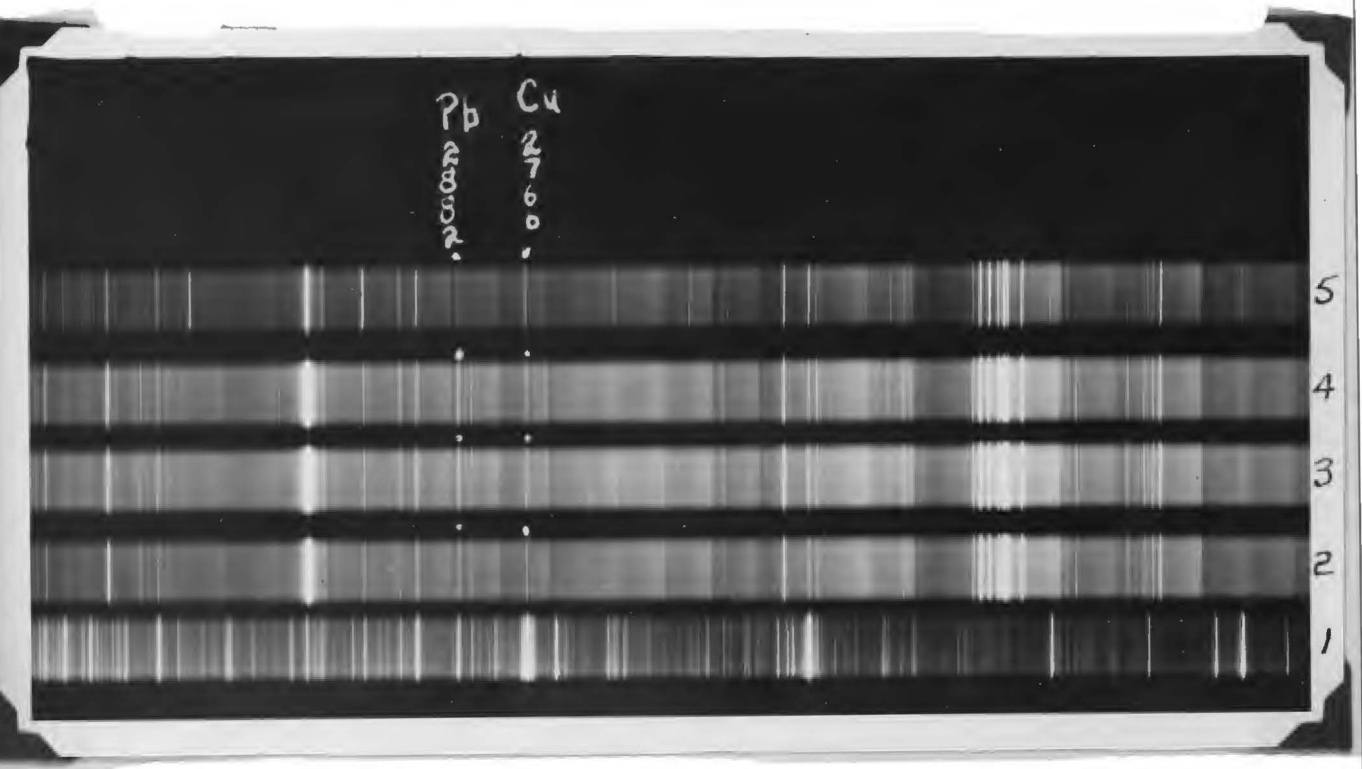
This photograph and the one on the following page constitute the spectrum of the green feldspar sample. The first spectrum is that of copper for reference use; the second and third are spectra of the feldspar; the fourth spectrum is that of the carbon electrodes in which the sample was burned.



Number 9.

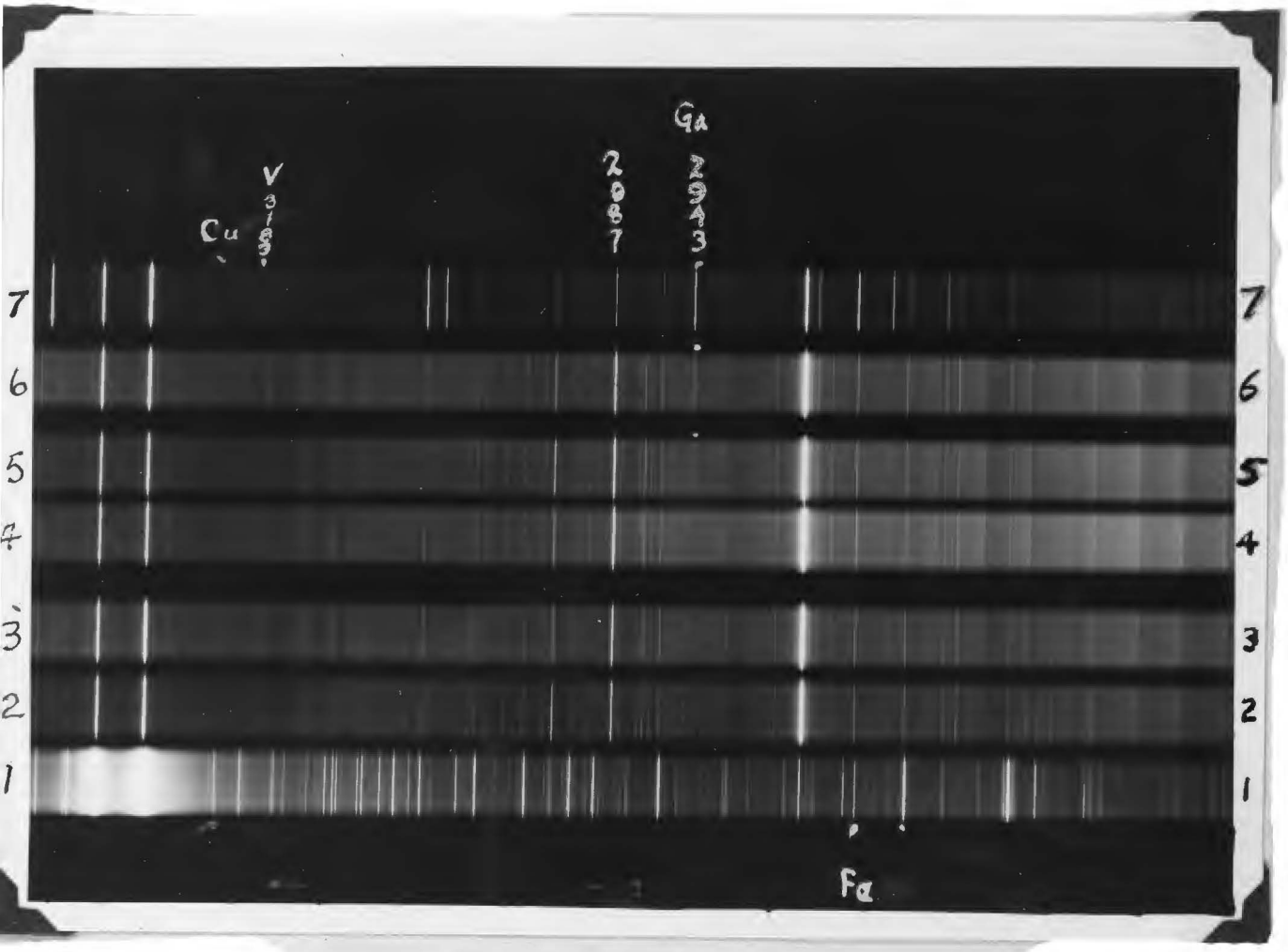
Green Feldspar

The short wave length half of the spectrum of feldspar is shown above. The three principal lines of vanadium appear at 3185Å. The double line of gallium is visible at 2943Å.



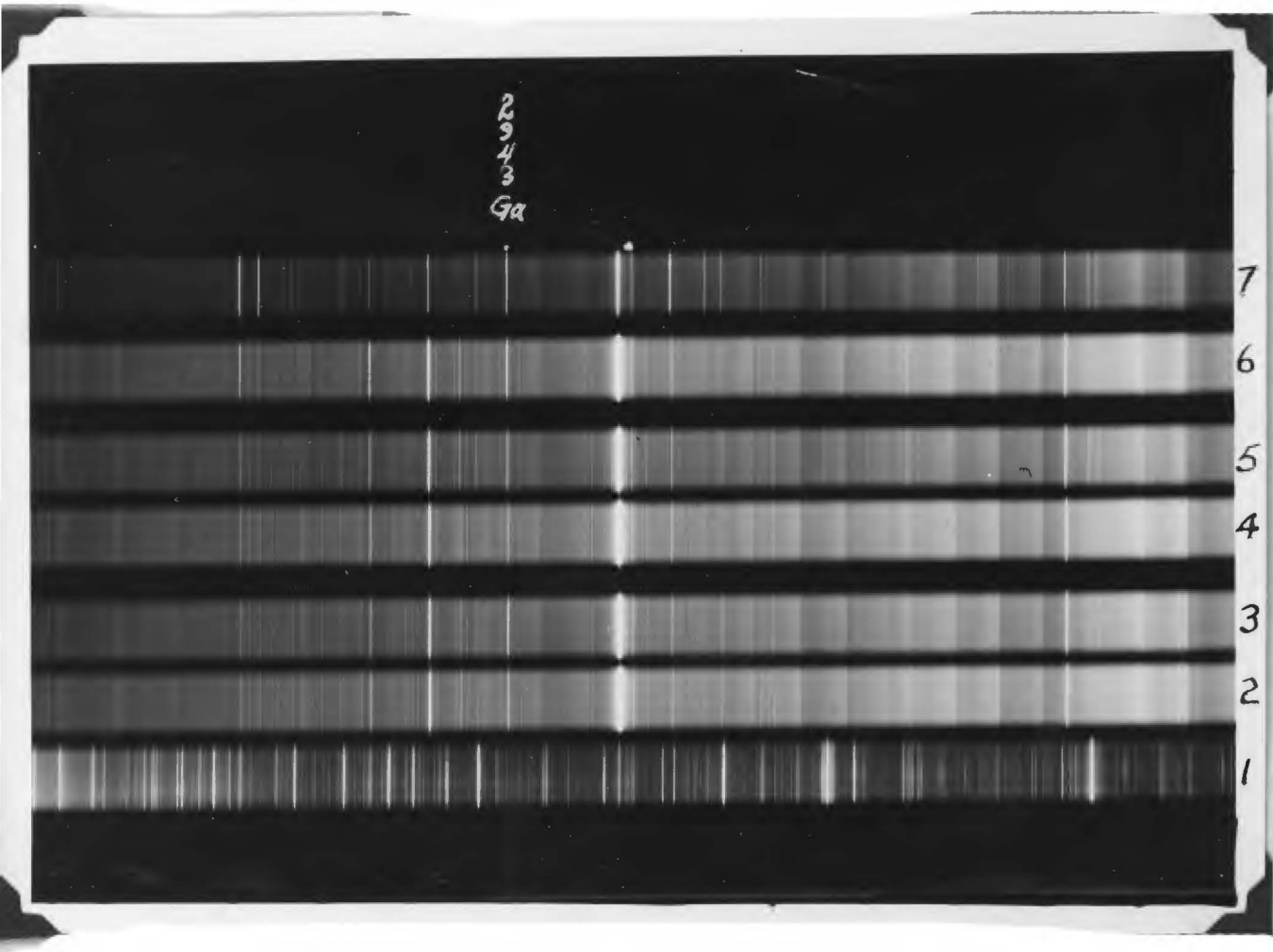
Determination of Lead Concentration

The fifth spectrum is that of feldspar, Number 8, showing the homologous pair of lead and copper lines. Directly below are the three samples containing 0.43% lead, 0.47% lead, and 0.50% lead, respectively. The first spectrum is that of copper. The two lines that match in intensity are those in the fourth spectrum indicating a concentration of 0.50% lead.



Determination of Vanadium Concentration

The three lines of vanadium in sample Number 9 are difficult to see in the fourth, third, and second spectra on the above plate at 3183 angstroms. These concentrations are 0.047%, 0.045%, and 0.043% of vanadium, respectively. The homologous pair is seen in the seventh spectrum and appear at equal intensities in the second spectrum indicating a concentration of 0.043%.



Determination of Gallium Concentration

Spectrum number 7 is that of sample number 9 showing the double line of gallium at 2943 angstroms. Spectra six through two are standards ranging from 2.25% to 1.25% gallium. The first spectrum is that of copper. By comparison of intensities the gallium of the sample appears to match the line of gallium in spectrum number 5 whose concentration is 2.00%. Due to a shortage of the rare metal, closer estimates were not possible.

V Discussion of Results

The first five samples, labeled "Clinch Mountain" were very similar in composition and were associated with the same impurities. While the number of lines that an element exhibits on a spectrogram is not a valid method of measuring its abundance, a comparison of concentrations may be drawn. That all the samples are rich in silicon and aluminum is evident from the number of lines displayed. This is particularly true of aluminum, which is in greater abundance in the second Clinch Mountain sample and shows more lines. The impurities associated with these first five samples were mainly titanium, iron, and a slight trace of copper. Of the three, titanium was most concentrated, iron second, and copper last. The lines of iron are of a very low intensity and are very numerous, and, unfortunately, the persistent lines lie close to the carbon bands. These factors tend to reduce the chances of identifying all of the iron lines.

Samples Number 6 and 7, the two apelite sands, were found to be identical. As can be seen in the tables of wave lengths for these samples, the abundance of aluminum was greatest for this sand. This sand contained both sodium and potassium and a much greater percentage of iron than any of the other sands. Titanium was present along with the rare metals, gallium and rubidium. These rare metals seem to be associated with those sands which have a high concentration of aluminum and which contain sodium and potassium. The presence of the last two

elements in any sample tends to reduce the carbon bands and increases the chance of suppressing an element present because of their extremely low ionization potentials.

Sample Number 8 was noted to contain a much greater concentration of calcium than any of the other sands by the broad calcium lines on the spectrogram. While these lines were very heavy, few additional lines of calcium were identified at this concentration, proving that the number of lines was not a measure of abundance. This sample was free of the rare metals listed for numbers 6 and 7, but contained traces of titanium and iron.

Sample ten was by far the purest sand and contained none of the rare metals. Only a trace of iron was found.

Sample number 9 was green feldspar which has puzzled geologists for a number of years as to why it exhibits this particular color. The white feldspar gives a chemical analysis which is identical with the green feldspar. The spectrogram of the green feldspar contained lines of vanadium, gallium, rubidium, and lead, as well as all of the elements listed in the chemical analysis. In order to determine which element was responsible for the coloring, the percentages of concentration of lead, gallium, and vanadium were determined. Lead was found to be present in concentration of one half of one per cent, vanadium at 0.043 per cent, and gallium approximately 2.00 per cent. The presence of the latter element in such high concentration is probably the cause of the coloration. The sulfide of this element is distinctly green.

VI CONCLUSIONS

1. All samples contained impurities as listed below:

   Number 1. Titanium, iron, trace of copper.

   Number 2. Titanium, iron, trace of copper.

   Number 3. Titanium, iron.

   Number 4. Titanium, iron, trace of copper.

   Number 5. Titanium, iron, trace of copper.

   Number 6. Titanium, gallium, rubidium, iron, copper.

   Number 7. Titanium, gallium, rubidium, iron, copper.

   Number 8. Copper, iron.

   Number 9. Titanium, gallium, rubidium, vanadium, iron.

   Number 10. Iron.

2. Samples Number 6 and 7 are identical.

3. Sample Number 9, green feldspar, contained the following concentrations:

   Lead 0.5%

   Vanadium . . . 0.043%

   Gallium . . . 2% (approximately)

4. The green color of sample Number 9 is probably due to the relatively large concentration of gallium.

VII Acknowledgments

The author wishes to acknowledge gratefully the constant assistance and supervision of Professor H. D. Ussery and all of the members of the Department of Physics; also to express appreciation to the Ceramics Department and the Chemistry Department for the samples and rare earth metals used in this investigation.

Since the completion of this investigation, Mr. H. D. Ussery while working at the National Bureau of Standards, in July, 1939, made a determination of the gallium in the green feldspar, and found that there is 0.2% gallium in this mineral. The explanation of the difference in these two determinations lies in the way in which the standards were prepared. In the work described in the thesis the standard samples were made up by adding dilute solutions to the matrix material after being placed in the carbon electrodes. In the case of gallium, very dilute solutions were used, no concentrated solutions being available, and a large percentage of the solution must have been absorbed by the electrodes at the expence of the matrix. Since the boiling temperature of gallium is very nearly 2000 C, it is entirely possible that much of it remained in the electrodes and was never vaporized.

VIII BIBLIOGRAPHY

1. Dow, G. W.; Fundamentals of Engineering Electronics; John Wiley & Sons, Inc., New York; 1937.

2. Foote, P. D. and Mohler, F. L.; The Origin of Spectra; The Chemical Catalog Co., Inc., New York; 1922.

3. Gerlach, W., and Schweitzer, E.; Foundations and Methods of Chemical Analysis by the Emission Spectrum; Adam Hilger, Limited, London; 1929.

4. A. S. T. M.: Methods of Chemical Analysis of Metals.

5. A. S. T. M.: Symposium on Spectrographic Analysis, 1935.

6. Twyman, F., and Allsopp, C. B.; The Practice of Spectrophotometry; Adam Hilger, Limited, London; 1934.

7. Smith, D. M.; Metallurgical Analysis by the Spectrograph; British Non-ferrous Metals Research Association, London; 1933.

8. Handbook of Chemistry and Physics; Chemical Rubber Publishing Company, Cleveland, Ohio; 1935.