PRACTICAL SPECTROGRAPHIC ANALYSIS.

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ABSTRACT.

A brief review of various methods which have been proposed for chemical analyses by means of the spectrum is followed by a detailed description of the principle, apparatus, and procedure employed in making quantitative analyses from the spectra of condensed sparks. The practical application of this method is illustrated by three examples taken from the work of the spectroscopy section of the Bureau of Standards and deals with the quantitative determination of impurities in various samples of tin, gold, and platinum. Other applications to problems in chemistry, metallurgy, mineralogy, physics, biology, etc., are suggested.

CONTENTS.

I. INTRODUCTION.

Many of the early scientists who laid the foundations of spectroscopy hoped to find in the new science simple and easy methods of making chemical analyses. Among these early investigators may be named Brewster, Herschell Talbot, Fraunhofer, Kirchhoff, and Bunsen. For a time this hope was strengthened and gave promise of actual realization as the methods of observing extended from flames to electrical arcs, sparks, and Plücker tubes; and several new members, discovered by means of the spectroscope, were added to the family of chemical elements. Although the spectroscope is occasionally referred to for advice by the chemists of to-day, it must be admitted that spectral methods have not fulfilled the early hopes that they could be universally used for both qualitative and quantitative analyses. With the exception of a few investigators, such as Lockyer, Hartley, Pollock, and de Gramont, who maintained interest in the applications of spectroscopy to chemical analysis, the development of the science has remained during the last half century almost entirely with the physicists and astronomers who naturally enough have directed its progress along lines suggested by physical and astronomical problems.

The extraordinary sensitiveness of the spectra of certain elements is perhaps the principal reason for the almost complete abandonment of spectral analysis by chemists. A quantity of sodium much smaller than balances can weigh is sufficient to cause two yellow rays (the D lines) to appear bright and strong in the Bunsen flame. Prof. Roscoe is authority for the statement that one three-millionth of a milligram of sodium, one one-hundred-thousandth of a milligram of lithium, and six one-hundred-thousandth of a milligram of strontium or calcium can easily be detected spectroscopically. Such indications were bewildering and disturbing when due to traces in which the chemists were not interested. Furthermore, a particular spectroscopic method may show extreme sensitiveness for some elements and none at all for others. For example, luminous vapors in a Bunsen flame may show the lines of the alkali metals with an intensity which apparently bears little or no relation to the quantity of material present while many elements, such as the halides and metalloids, may be present in large quantities and still show no spectrum under these conditions. It appeared that different classes of elements would require different methods of observation employing flames, electric arcs, high potential sparks, Plücker tubes, etc., each method being adapted only to certain elements. If this were inevitable, so much special apparatus and such a wide knowledge of special experimental facts would be required that chemists could scarcely be blamed for discarding spectral methods of analysis.

If one examines the spectra of flames, arcs, or sparks, either visually or photographically, it is seen that with the diminution of an element in a mixture its spectrum becomes simplified, more and more lines disappear, so that only a few of the most sensitive lines remain when a minute trace of the element is present. This fact led to many attempts to establish methods of quantitative spectral analysis but so far none of them has been entirely satisfactory or generally adopted by chemists. Such methods applied to flame spectra and based upon either the brightness or timed visibility of the lines have all miscarried for reasons which are now more or less obvious. Quantitative analyses with electrical spectra were first suggested by Lockyer[1] in 1874 who found that the lengths of spectral lines in arcs or sparks are sensitive to the quantities of metals in a mixture so that as the quantity of an element diminishes its spectral lines become shorter and shorter until all but the longest lines disappear. Although quantitative analyses are possible on this basis the results are so dependent on the strength of the current, the length of the arc or spark, and other observing conditions, that the method has never found favor among practical workers.

Hartley [2] introduced a new method of quantitative analysis in 1884, employing spark spectra of solutions. He found that the spectra of metals in solution were identical with those of the solid metals and that similar solutions (chlorides, sulphates, nitrates, carbonates) containing the same amounts of a metal give identical spectra. Sparks between graphite electrodes saturated with solutions of various concentrations were found to give "persistent lines" which could be correlated with amounts from 1 per cent to minute traces—1 part in 10, 000, 000, 000 in the case of magnesium. When a more powerful induction coil was used the sensitivity was increased 10, 000 fold. Similar investigations were carried on by Pollock and Leonard [3] who used gold electrodes, and it was demonstrated that the method based on persistent lines could be standardized to give quantitative results in certain cases. However, it seems that this method is too restricted in application and difficult in standardization to be of much practical service in chemical analysis.

The most successful method, and one which may really find wide application in practice, is that originated in 1895 by de Gramont [4] who for the past 27 years has labored industriously and consistently to perfect a method of practical spectrographic analysis which is sensitive for nearly all of the known chemical elements. The distinguishing feature of this method is the use of electrical condensers in the spark circuit so that conditions are more favorable for dissociation, ionization, and radiation in the luminous source. In principle the method is similar to those above mentioned. De Gramont studied the condensed spark spectra of minerals, definite alloys and mixtures representing different dilutions of a particular metal and found that certain lines vanish as the dilution progressively increases, and the last

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[1] Phil. Trans., 164, II, p. 479; 1874.

[2] Phil. Trans., 175, II, pp. 49, 325; 1884.

[3] Proc. Roy. Soc., Dublin (2), 11, pp. 217, 229, 257; 1908.

[4] Ann. de Chim. et de Phys. (8), 17, p. 437; 1909. Ann. de Chim., 3, p. 269; 1915.

to disappear, which he called "raies ultimes," represent a trace of the element. These sensitive lines coincide in many cases with Lockyer's "long lines" and with Hartley's "persistent lines."

The effects of capacity and self-inductance on spark spectra are of considerable practical importance and can be manipulated in ways which give the condensed spark method of analysis certain advantages over all other methods. In the first place, a spark with capacity in the circuit will bring out not only the lines of the conducting metals but also the lines of metalloids and halides if such elements are present. Some of these nonmetallic elements show no spectrum under any other conditions except in Plücker tubes or similar apparatus.

The ordinary spark consists of three stages: The initial discharge which gives only the spectrum of air, then some rapid oscillations producing the high temperature or short lines near the electrodes, and finally the aureole itself which furnishes the low temperature metallic lines. The oscillating spark produced by the introduction of self-inductance consists only of the aureole giving a lower temperature spectrum of the metal. If increasing amounts of self-inductance are placed in the discharge circuit the first effect is to reduce the spectrum of air; with a somewhat larger amount the spectra of the metalloids vanish, and the high temperature or "short lines" of Lockyer disappear with further increasing self-induction until the spark spectrum finally resembles that of the arc. These effects of self-inductance are of great assistance in simplifying the work of spectral analysis by removing the superposed air spectrum and by separating the metals from the metalloids.

For the past seven years the spectroscopic laboratory of the Bureau of Standards has been at work developing the method of quantitative analysis based on a study of the raies ultimes and sensitive lines which appear in the spectra of certain alloys. So far the work has been limited to alloys in which one element predominates. In other words, chemists and metallurgists, in seeking to prepare very pure materials, find it a difficult problem to determine the amounts and kinds of impurities present when they total 1 per cent or less of the whole, and it is in problems of this kind that the efforts of the Bureau of Standards have been successful and give promise of wider application as various new problems present themselves.

The object in this paper is, therefore, to describe in some detail the principle of this method of spectrographic analysis, the apparatus and experimental procedure involved, to illustrate it with examples from our experience and to suggest some of the possibilities and limitations of analytical work based upon modern spectroscopic knowledge.

II. THE CONDENSED SPARK METHOD OF SPECTROGRAPHIC ANALYSIS.

1. PRINCIPLE OF THE METHOD.

The general characteristics of raies ultimes are, according to de Gramont, as follows: 1. They are not necessarily the strongest or most brilliant spectral lines of the element to which they belong. 2. They persist even when strong self-induction (from 0.025 to 0.1 henry) is introduced in the condenser discharge circuit. 3. They are present in the arc spectrum. 4. When the spectrum of an element furnishes lines which are spontaneously reversed, the raies ultimes are found among these. 5. They are found also in the spectra of flames. 6. In spectra whose lines have been arranged in series, they find their place as important series lines. The raies ultimes of the condensed spark may be considered as those which persist as the temperature decreases or as the electrical energy of the luminous source diminishes. In other words, the diminution of concentration of an element modifies its spectrum in the same manner as a diminution in the vibratory energy of its atoms or electrons. Modern developments in the quantum theory of spectral line emission and recent experiments on atomic structure, the origin of radiation and the physical significance of spectral series have thrown much light on the subject of spectrographic analysis and indicate that there is a sound physical basis underlying the empirical methods which have been mentioned above. A discussion of this, however, is presented in another paper (Meggers, The Physical Basis for Spectrographic Analysis, B. S. Scientific Paper, forthcoming). For the present we will limit ourselves to the purely empirical facts upon which practical spectrographic analysis has thus far been based.

As stated before, the raies ultimes are the most sensitive spectral lines of an element and represent vanishing traces of its presence in a mixture or alloy. Many years of experimental search for such lines have resulted in their discovery for most of the known chemical elements and de Gramont[5] has recently collected in one table the most sensitive lines for 60 elements. Not only have the raies ultimes been recognized but in many cases the limiting concentrations which show them under particular experimental conditions have been determined. The spectral sensitivity of most metals is very great but certain of the metalloids which show no ordinary arc spectra are also relatively less sensitive in the condensed spark. Among these are fluorine, chlorine, bromine, iodine, oxygen, nitrogen, sulphur, and selenium. Other metalloids, such as phosphorus, arsenic, antimony, carbon, boron, silicon, and tellurium yield both arc and spark spectra but their raies ultimes do not approach the extreme sensitiveness of the metals.

If a graded series of alloys is carefully prepared; for example, tin containing zinc in the proportions 0.001, 0.01, 0.1, 1.0, and 10 per cent, and their spark spectra are obtained and compared under identical conditions, the following will be observed. The sample containing the smallest amount of zinc will show only the raies ultimes of this element and the complete spectrum of tin. The next alloy, with 0.01 per cent zinc, will show the raies ultimes with increased intensity and new sensitive lines will begin to appear. All these lines will appear stronger and in addition still more new sensitive lines present themselves as the concentration of zinc increases until the complete spectrum of this element is produced. These partial spectra and the relative intensities of their lines are readily correlated with the percentage composition of the alloys and this furnishes the key for the complete analysis of similar alloys of unknown composition. It is well to repeat and emphasize that the interpretation of quantitative results must be based upon standardized apparatus and observing conditions and upon the experience gained from studies of the spectra of carefully analyzed or prepared standards. There may be some who are inclined to believe that these essentials make all methods of spectral analysis impracticable, but we hope to prove that this is not the case. It would be as unreasonable to expect that a single spectroscopic fact or experience could apply to all chemical elements as it would be to continue the search for a universal solvent. Ordinary wet chemical methods also require definite and different procedure for each element or group of elements and in many cases the standard methods are complicated, tedious, wasteful, and even uncertain. There are practical

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[5] C. R., 171, p. 1106; 1920.

possibilities in spectral methods which recommend them as an aid to wet chemical analysis, especially where the chemical methods are inapplicable to small amounts or small samples and in cases of tedious routine.

2. THE APPARATUS.

The necessary apparatus is neither very complicated nor expensive and should be a part of the equipment of every large chemical laboratory. For the production of condensed sparks an electrical condenser charged to a high potential is required. Ordinary Leyden jars or tin foil separated by glass plates serve well as condensers. The capacity should be of the order of 0.005 mf or more. A Ruhmkorff coil or an alternating current transformer is necessary to raise the potential of the charging current and this potential may be from 10,000 to 50,000 volts. An induction coil, such as is used for X-ray tubes and giving a 10 cm spark in air, may be used, but the difficulties with interrupters and maintenance of constant operating conditions are resulting in the gradual displacement of Ruhmkorff coils by alternating current transformers. Such transformers are much more readily obtainable and more dependable that the induction coils and are extremely convenient and constant in operation. Commercial current of about 60 cycles and 100 to 120 volts is available in nearly all laboratories and when used with transformers in which the ratio of secondary to primary windings is 100 gives a satisfactory means for producing spark spectra for spectrographic analysis.

For reasons given above, it is desirable to have various quantities of self-induction for insertion in the spark circuit. These are easily constructed by winding the proper number of turns of insulated wire on a wooden or pasteboard cylinder of the proper diameter. Thus a coil of 50 to 100 turns of fine wire wound on a cylinder of 4 to 5 cm diameter will be found to be sufficient self-induction for the suppression of the superposed spectrum of the air which is otherwise strong and confusing. The range of self-inductance which is serviceable in practical spectroscopy is about from 0.00007 to 0.005 henry and suitable coils are readily designed by using the formula

$$L=4\pi n^2 lA\times 10^{-9}$$

where n is the number of turns per unit length, l, the length in centimeters, and A, the cross section of the solenoid in square centimeters.

Figure 1 is a diagram of the electrical circuit for the production of spark spectra. The primary of the transformer is connected through a resistance *R* with a line furnishing alternating current. In the secondary circuit or high potential side of the transformer *T*, the spark electrodes, *E*, the self-inductance *L*, and an ammeter *A* are placed in series. One or more condensers *C*, are connected in parallel with the spark electrodes, between which an oscillatory discharge takes place after the condenser has been charged to a higher potential than the spark gap can maintain.

Three different types of electrodes are essential for analyses of metals, salts, and liquids, respectively. Whenever solid metallic electrodes are available they should be used and as far as possible a standard size and shape should be adopted so that uniformity may be secured in the spectra. We have found cylindrical rods of 2 or 3 mm diameter and 10 to 20 mm length most suitable for our work. Soft and ductile metals and alloys, such as tin, may be worked into electrodes by casting or by hammering and drawing, while harder ones are sawed and filed or turned to proper shape and size. For the analyses of salts, precipitates, minerals, and nonconducting metals or mixtures in general the "sels fondus" method of de Gramont[6] is very well adapted. In this case the lower electrode consists of the material to be analyzed held in suspension in molten lithium or sodium carbonate contained in a small platinum cup. This electrode is heated in a Bunsen flame. The upper electrode is a heavy platinum wire.

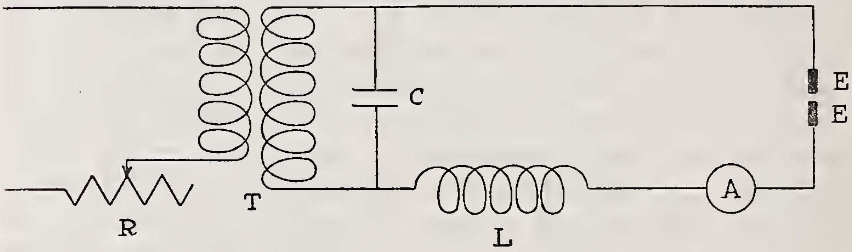

FIG. 1.—*Electrical circuit for spark spectra*

R=resistance in primary circuit of transformer *T*; *C*=condenser; *L*=self-inductance; *A*=ammeter; and *E*=spark electrodes

De Gramont[7] has also developed an apparatus for obtaining the spectrum of a liquid by passing the electrical spark between two drops of the liquid emerging from capillary tubes of quartz. Another way is to use a lower electrode consisting of a bundle of

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[6] de Gramont, C. R., **121**, 1895; **122**, 1896; **124**, **125**, 1897; **126**, 1898.

[7] de Gramont, C. R., **145**, p. 1170; 1907.

fine platinum wires held upright in the liquid, and a heavy platinum wire for the upper electrode. The solution is drawn to the top of the lower electrode by capillary forces and volatilized in the spark.

Since it has been found that the majority of sensitive spectral lines lie in the ultra-violet part of the spectrum it is necessary to use quartz, or concave grating spectrographs, because instruments containing glass are opaque to most of the ultra-violet light. The observations in this invisible region of the spectrum are made by photography and the photographic record, called a spectrogram, is then examined for the results. The photographic plate is a permanent record of the spectrographic analysis and on the same plate the spectra of a considerable number of unknown and standard samples may be obtained so that the results are strictly comparable and easily interpreted. The plan of a quartz spectrograph, which is very appropriate for spectroscopy of the ultra-violet, is shown in Figure 2.

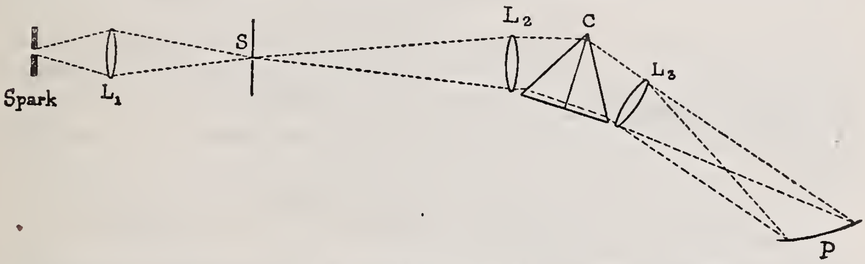

FIG. 2.—*Quartz spectrograph*

L_1, L_2, L_3=quartz lenses; C=Cornu quartz prism; S=slit; P=photographic plate

An image of the spark is projected on the slit S of the spectrograph by means of a quartz-condenser lens, L_1, and the spectrum produced by the prism C is focused on the photographic plate P, which on account of the lack of achromatism in the quartz lenses, L_2, L_3, must be slightly bent and set at an angle of about 27° with the optical axis of the camera. Quartz shows high transmission for ultra-violet light down to wave lengths shorter than 2000 A, but it has undesirable properties of double refraction. Even along the optic axis of the crystalline material light is circularly doubly refracted (left and right handed) thus producing two oppositely polarized images of the spectral lines. Fortunately nature has supplied both right and left-hand rotating quartz so that these effects may be compensated in the spectrograph. The collimator and camera lenses therefore consist of different kinds of quartz and the prism is the so-called Cornu type which consists of two prisms of 30° each, one of which is made of right-handed and the the other of left-handed quartz.

In some respects a concave grating on speculum metal is best suited for this kind of work. It gives a normal spectrum, in which wave lengths are directly proportional to distances measured along the spectrum, and this is an advantage for wave-length measurements or identifications. If a concave grating is used for practical spectrographic analysis, it is well to have it mounted with an auxiliary mirror so that the slit images are stigmatic.[8] This permits the use of an adjustable diaphragm in front of the slit so that various spectra can be recorded in juxtaposition for comparison and also gives more intense spectra than the Rowland type of mounting. A plan of the grating spectrograph recommended is given in Figure 3, in which *L* is a quartz lens, *S* represents the slit, *M* the mirror, *G* the grating, and *P* the photographic plate.

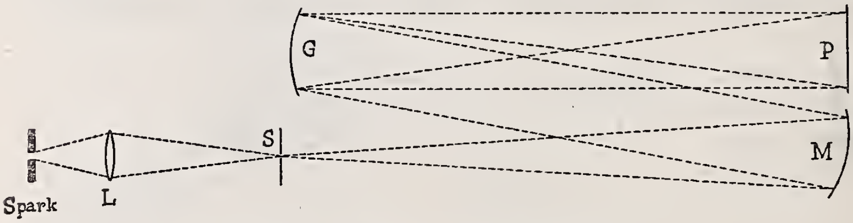

FIG. 3.—*Concave grating spectrograph*

L=quartz lens; *S*=slit; *M*=concave mirror; *G*=concave grating; *P*=photographic plate

For the exact identification of spectral lines it is sometimes necessary to measure wave lengths to one or two hundredths of an Angstrom unit. (1 Angstrom unit = 1 A = 10^{-7} mm.) The dimensions of the spectrographs should therefore be such that the dispersing and resolving powers permit this accuracy in wave-length determinations to be made if necessary.

III. PROCEDURE IN MAKING AN ANALYSIS.

As stated above, practical spectrographic analysis is based upon knowledge of sensitive spectral lines derived from preliminary studies of standard samples, synthetic alloys, or salts mixed in definite proportions. In the case of all the metals having melting points above 300 or 400° C. synthetic alloys of a pure metal with its common impurities are easily prepared in gas or electrical furnaces. For this purpose the Ajax-Northrup induction furnace

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[8] See Meggers and Burns, Spectroscopic Notes, B. S. Scientific Papers No. 441, p. 185; 1922.

is especially recommended, because the metals are then inductively mixed to make perfectly homogeneous alloys and contamination and losses from volatilization may be reduced to a minimum. This was the method pursued at the Bureau of Standards in preparing standard samples of gold alloyed with silver, copper, lead, and iron and also of pure platinum alloyed with rhodium, iridium, and palladium to serve as reference standards in the spectrographic analysis of these noble metals. An alloy of 1 per cent impurity and 99 per cent pure metal was first prepared. A portion of this was diluted in sufficient pure metal to reduce the impurity to one-tenth per cent. Similarly a portion of this is again diluted with pure metal to reduce the impurity to one one-hundredth per cent, then to one one-thousandth per cent, etc. Such a series may also be prepared by properly diluting small portions of the original 1 per cent alloy, and in some cases this is the better procedure.

In many cases, samples which have been carefully analyzed by chemical methods may be used to advantage in studying the partial spectra of elements present in relatively small quantities and thus obtain the correlation of spectrum and concentration. We have in this way examined many analyzed samples of tin and gold for the purpose of substantiating and extending the results obtained from synthentic alloys. The study of sensitive lines and partial spectra of substances, which are more or less infusible and nonconducting (silicates, minerals, precipitates, etc.), is facilitated by the method proposed by de Gramont of mixing them with fusible salts, such as sodium or lithium carbonates. The latter is especially recommended because of the simplicity of its spectrum, the low fusion point, and the superior power for dissociating silicates. Such mixtures can be prepared in definite proportions and a graded series again gives information as to raies ultimes and lines appearing with higher concentrations.

After a method of observing has been standardized and experience has been gained in the study of standard samples, the analysis of any unknown materials becomes a matter of simple routine. It is a good practice to photograph alongside the spectrum of the unknown the spectra of several standard samples. This simplifies the identification of the spectral lines or chemical elements and makes the quantitative determination a process of simple comparison or interpolation. Care must be exercised to obtain the spectra in good focus and to make equivalent exposures of different samples on the same photographic plate.

For determining the wave lengths which identify lines on spectrograms, a photomeasuring micrometer is employed. The one in use at the Bureau of Standards is illustrated in the accompanying Figure 4. For any particular region of the spectrum, standard micrometer settings may be calculated for known spectrum lines. The work of examining a spectrogram may therefore be reduced to a minimum by adjusting the spectrogram on the measuring engine so that a known line in the spectrum coincides with the micrometer filar when the scale has a predetermined setting. A table containing a list of raies ultimes of various elements expressed in terms of micrometer settings will allow an examination and analysis to be made as rapidly as the settings can be made.

For measuring the intensity of spectral lines a microphotometer is used. Several types of instruments are available but it is believed that a new type recently developed at the Bureau of Standards will prove more advantageous for the particular problem in question. This instrument[9] combines the work of the photomeasuring micrometer and photometer so that both operations may be made at once thereby reducing the amount of work necessary to completely interpret a spectrogram.

IV. EXAMPLES OF QUANTITATIVE SPECTROGRAPHIC ANALYSIS.

The practical application of the condensed-spark method of spectrographic analysis may be illustrated by three examples taken from the work of the spectroscopy section of the Bureau of Standards. These examples will deal in succession with the quantitative analysis of tin, gold, and platinum.

1. ANALYSIS OF TIN.

One problem in which the spectrographic method demonstrated its superiority over the ordinary chemical methods was furnished by the analysis of tin used as fusible safety plugs for steamboat boilers. For vessels under its jurisdiction the United States Steamboat Inspection Service requires, among other things, that the fusible plugs shall contain not less than 99.7 per cent tin and not more than 0.1 per cent each of lead and zinc. Another requirement of the plug is that its melting point be approximately 230° C. The common impurities occurring alloyed with tin are lead, zinc, antimony, copper, iron, arsenic, and bismuth, and more rarely, cadmium, manganese, nickel, cobalt, sulphur, and phos-

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[9] Meggers and Foote, B. S. Scientific Papers, **16**, p. 299; 1920.

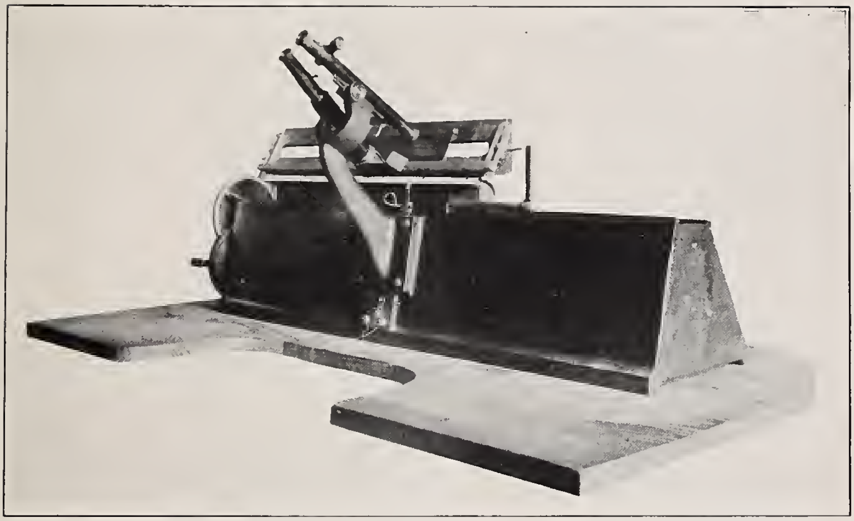

FIG. 4.—*Micrometer for spectrograms*

The spectrogram is mounted on a frame which is moved along ways by turning an accurately made screw so that successive spectral regions come into the field of view of the microscope. The second microscope is for reading the scales after a setting is made on a spectral line. Distances between spectral lines can be measured to 0.001 mm.

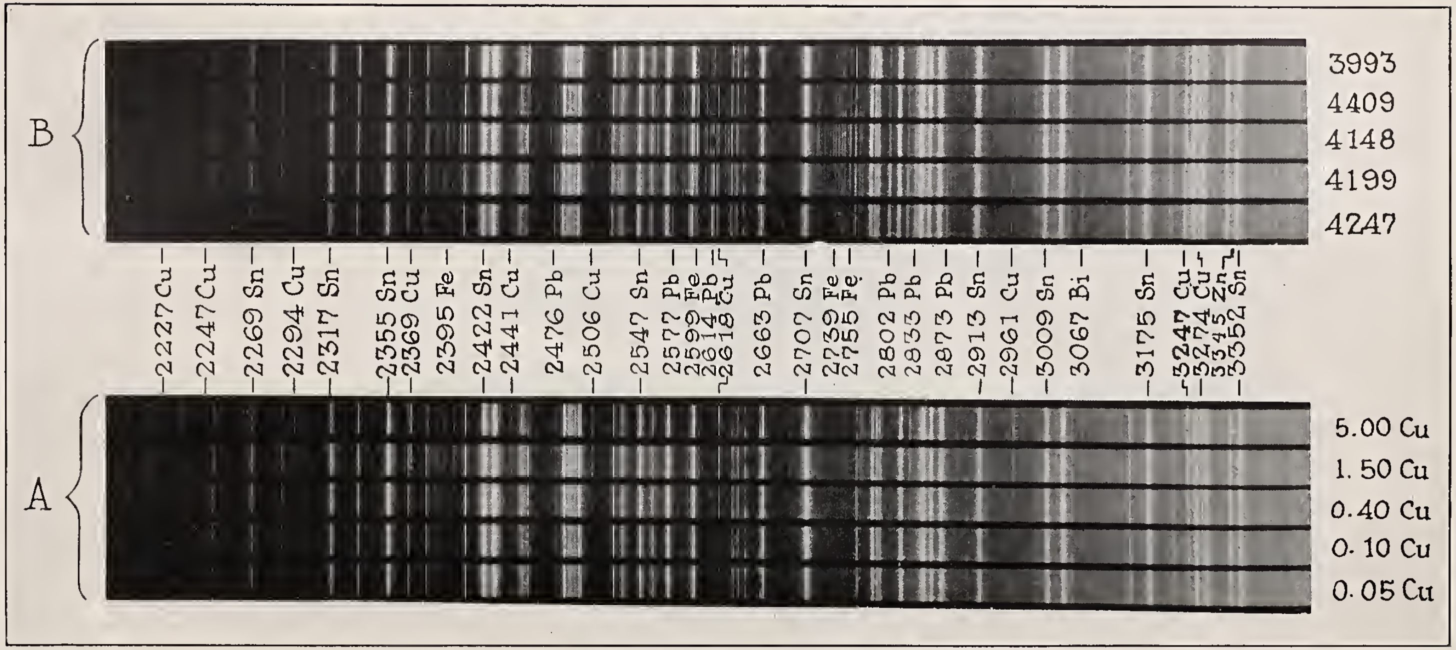

Fig. 5.—*Spark spectra of tin (ultra violet, 2200–3500 A)*

A=series of standard tin-copper alloys, containing 0.05, 0.10, 0.40, 1.50, 5.0 per cent of copper. The wave lengths of prominent tin lines and sensitive copper lines are marked on the margin of the spectrogram.

B=series of boiler plugs analyzed in Table 1. The raie ultime for copper is 3247.53 A, lead 4057.84, iron 2382.04, zinc 3344.99, bismuth 3067.69, silver 3280.66, nickel 2416.15. Some of these and other sensitive lines are marked.

The relative intensity variations in sensitive lines with differences in concentrations of the elements are readily observed.

phorus. The effect of lead, zinc, bismuth, cadmium, or copper is to lower the melting point of the alloy, whereas iron and antimony raise it. In addition to its effect on the melting point, zinc imparts a crystalline structure to the tin which permits its oxidation and thereby renders it useless as a safety plug. To some extent this is neutralized by the presence of lead. But the requirements that only minute quantities of the elements may be present in the metal used for plugs renders the chemical analysis difficult. When only small quantities of lead and zinc or bismuth and copper are present they both may respond to the same chemical test for one of them, thus giving a wrong analysis. No such confusion qualitatively is possible in the spectroscopic analysis, and from a study of the intensities of the raies ultimes and other sensitive lines appearing in the spectrum it is possible to determine very closely the quantity of each present in the alloy.

In Figure 5 are shown typical spectra of tin containing various impurities. These were obtained with a quartz spectrograph. The lower set of five samples represent standard alloys of tin with copper, the amounts of copper present being indicated at the right and identification of the principal lines being given above in terms of wave length in Angstrom units. Similar standards of tin with copper, lead, iron, and other impurities are prepared either separately or with all the impurities present in one set of samples. The upper set of five samples are typical boiler-plug tins which have been analyzed in terms of standard samples and also by the usual chemical methods. A comparison of the results is given in Table 1.

TABLE 1.—Analysis of Tin.

Sample.	Spectrographic.							Chemical.			
	Cu.	Pb.	Fe.	Zn.	Ni.	Ag.	Bi.	Cu.	Pb.	Fe.	Zn.
3993........	0.1	0.1	0.005	0.001	0.001	0	0	0.08	0.10	0.03	....
4409........	.6	.05	.1	.07	.001	0	0	.62	.04	.04	0.06
4148........	.4	.08	.07	.005	.001	0	0.001	.45	.10	.09	....
4199........	.8	.6	.02	.04	.01	0.001	.01	.76	.63	.02	....
4247........	.6	1.0	.01	.15	.01	.001	.01	.65	.98	.042	....

This demonstrates that the spectrographic method is capable of giving quantitative results with considerable precision. In fact, the precision probably surpasses that of the chemical gravimetric method in a case of this kind, for it is precisely for the small quantities for which weighing errors are large that the spectral methods show their greatest sensitiveness. The greatest economy, however, is in materials and time. Whereas a chemical analysis will require about 10 g of material, only a few milligrams are consumed to make a spark spectrum. A dozen samples carried along simultaneously require about two days for a chemical analysis. The same can be accomplished in two hours by spectral methods. There can be no doubt that for many such problems which are in the nature of routine tests spectrographic methods may be substituted for the relatively more tedious and wasteful chemical work.

2. ANALYSIS OF GOLD.

Another problem which will convey to the reader an idea of the practical value of spectrographic analysis is afforded by our work on gold. About two years ago John W. Pack, assayer of the U. S. Mint, San Francisco, asked the Bureau of Standards if it could furnish or develop for him more reliable or economical methods of analyzing the gold which went into the national coinage and reserve. The most persistent impurities to get rid of in purifying gold are silver, copper, lead, iron, nickel, and the platinum metals. In grading the gold product of electrolytic refineries the mint often has to decide whether the total impurity present is 0.01 per cent or 0.02 per cent (999.9 or 999.8 fine in gold) and individual fire assays may show a full 1,000 fine in gold. There are no strictly assaying methods for the determination of individual base metals in gold bullion, and such chemical analysis must of necessity be done by wet methods most carefully carried out on very large amounts of metal when only minute traces of the base metal are involved. At least 15 g of bullion are required in a test for 0.01 per cent of iron, and complete analysis by chemical methods is prohibitive on account of the cost in time and materials. Such analyses, however, are quite practical by spectrographic methods, for which only a few milligrams of material and an hour of time are required. The world's gold currency is estimated to be nearly $10,000,000,000 in value. If it is assumed that assays upon which this value is based are unable to detect 0.01 per cent of impurities, then $1,000,000 is base metal.

It was suggested that the key to the problem lay in comparing the spectra of unknown samples with those of standard samples containing known amounts of the expected impurities. For the preparation of these samples the mint supplied gold which was almost spectroscopically pure, the only impurity present being a trace of copper, revealed faintly by its raie ultime, the ultra-violet line whose wave length is 3247 A. This gold was regarded as 99.9999 per cent pure. With portions of this gold were alloyed known quantities of pure silver, copper, iron, and lead in percentages ranging from 1 to 0.001. For the careful preparation of these standard samples we are indebted to the Metallurgical Division of the Bureau of Standards. Figure 6 reproduces a portion of the ultra-violet spark spectra of gold and impurities, the spectra being produced by a concave grating spectrograph. The upper set of spectra represents a group of standard samples and the lower set shows five samples of mint gold for which the assay results and spectrographic analyses are compared in Table 2.

TABLE 2.—Analysis of Gold.

Sample.	Spectrographic.				Assay: Gold.
	Gold.	Silver.	Copper.	Iron.	
A	99.54	0.4	0.01	0.05	99.5+
B	99.40	.5	.05	.05	99.5—
C	99.44	.5	.01	.05	99.5
D	99.899	.09	.01	.001	99.9+
"1000"	99.997	.001	.001	.001	100.0

3. ANALYSIS OF PLATINUM.

For several years the Chemistry Division of the Bureau of Standards has been developing methods for the purification of elements in the platinum group,[10] and the spectroscopy section has cooperated by making spectrographic tests to indicate the progress of purification and to measure the amounts of impurities which still have physical significance. It is well known that certain physical properties of metals are extremely sensitive to traces of impurities which are not readily detected by chemical methods. This is of exceptional importance in the case of platinum, which finds such wide use in precision measurements of temperature. The melting point of pure platinum is one of the standard fixed points in the temperature scale, its thermal coefficient of electricial resistivity plays an important rôle in platinum-resistance thermometry, and the thermal electromotive forces generated between junctions of pure platinum and platinum alloys are extensively employed for temperature measurements with the aid of so-called thermocouples. In connection with the preparation of pure platinum metal the spectrograph showed that, when the

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[10] Wichers, J. Am. Chem. Soc., 43, p. 1268; 1921.

purest platinum sponge was fused on lime or magnesia, the metal was contaminated with traces of calcium or magnesium, but when fused on thoria no impurities could be detected. Metal was finally prepared which was probably 99.9999 per cent pure. This pure metal was then used in the preparation of definite alloys of platinum with other metals of the platinum group, so that the partial spectra of these added metals could be correlated with percentage concentration, and thus establish the empirical basis for quantitative analyses by spectrographic methods.

Spectra of platinum alloys with iridium are shown in the upper part of Figure 7, and similar spectra of platinum-rhodium alloys below. In either case the successive appearance of new lines and increasing intensity can be followed as the concentration of another element alloyed with platinum increases. The raie ultime for iridium in this portion of the spectrum is 3220.79 A and for rhodium 3434.97 A. Both are sensitive for less than 0.001 per cent. As a typical example of the partial spectra of an element which may be correlated with the part which this element forms of the entire alloy, Table 3 is presented to show the partial spectra of rhodium in platinum. The intensities are estimated relative to those of platinum lines, the faintest lines being designated as 1 and the strongest as intensity 10.

From information of this kind, quantitative estimates of the impurities present in any one of the metals of the platinum group are readily made from an examination of the spectrum, and the variations in physical properties of such metals can then be interpreted in so far as these variations are due to contaminating elements. For example, the relatively small amounts of calcium (several thousandths of 1 per cent) which may be introduced into platinum when the sponge is melted on lime may cause an electromotive force of 30 to 40 microvolts to be developed at a hot (1200° C.) junction of such metal and pure platinum. Most alloys of platinum with other platinum metals or the base metals which are present as impurities give a positive emf against platinum itself. Thermoelectric tests on the above-mentioned series of platinum-rhodium alloys showed that the emf developed is exactly proportional to the amount of rhodium present. The alloy containing only 0.01 per cent of rhodium still gave 20 microvolts positive to pure platinum at the copper point (1083° C.). As platinum of higher purity has been produced, the value determined for its thermal coefficient of resistivity (0 to 100° C.) has

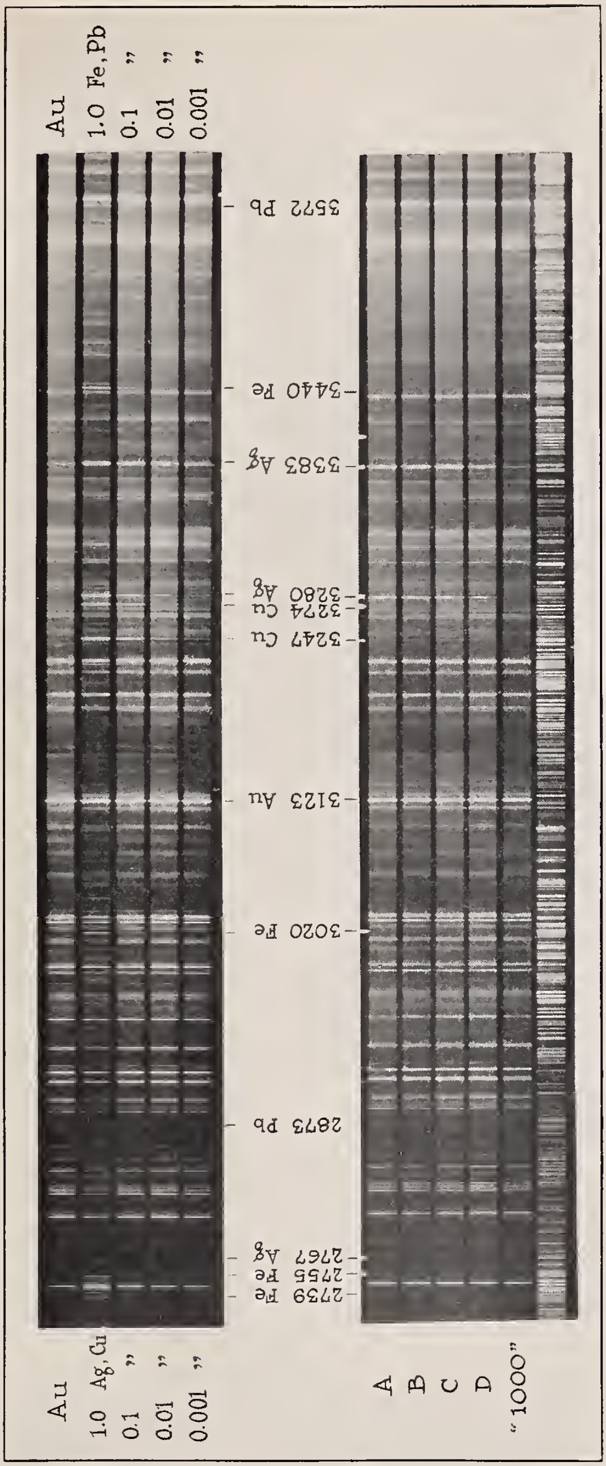

Fig. 6.—*Spark spectra of gold (ultra violet, 2700–3600 A)*

Upper group, reading down, pure gold and standard alloys containing 1.0, 0.1, 0.01, and 0.001 per cent each of silver, copper, iron, and lead. The wave lengths of some of the sensitive lines are marked on the margin of the spectrograms.

Lower group, reading down, mint samples of gold, *A*, *B*, *C*, *D*, “1000 fine,” analyzed in Table 2, spectrum of the iron arc furnishing the scale of wave lengths.

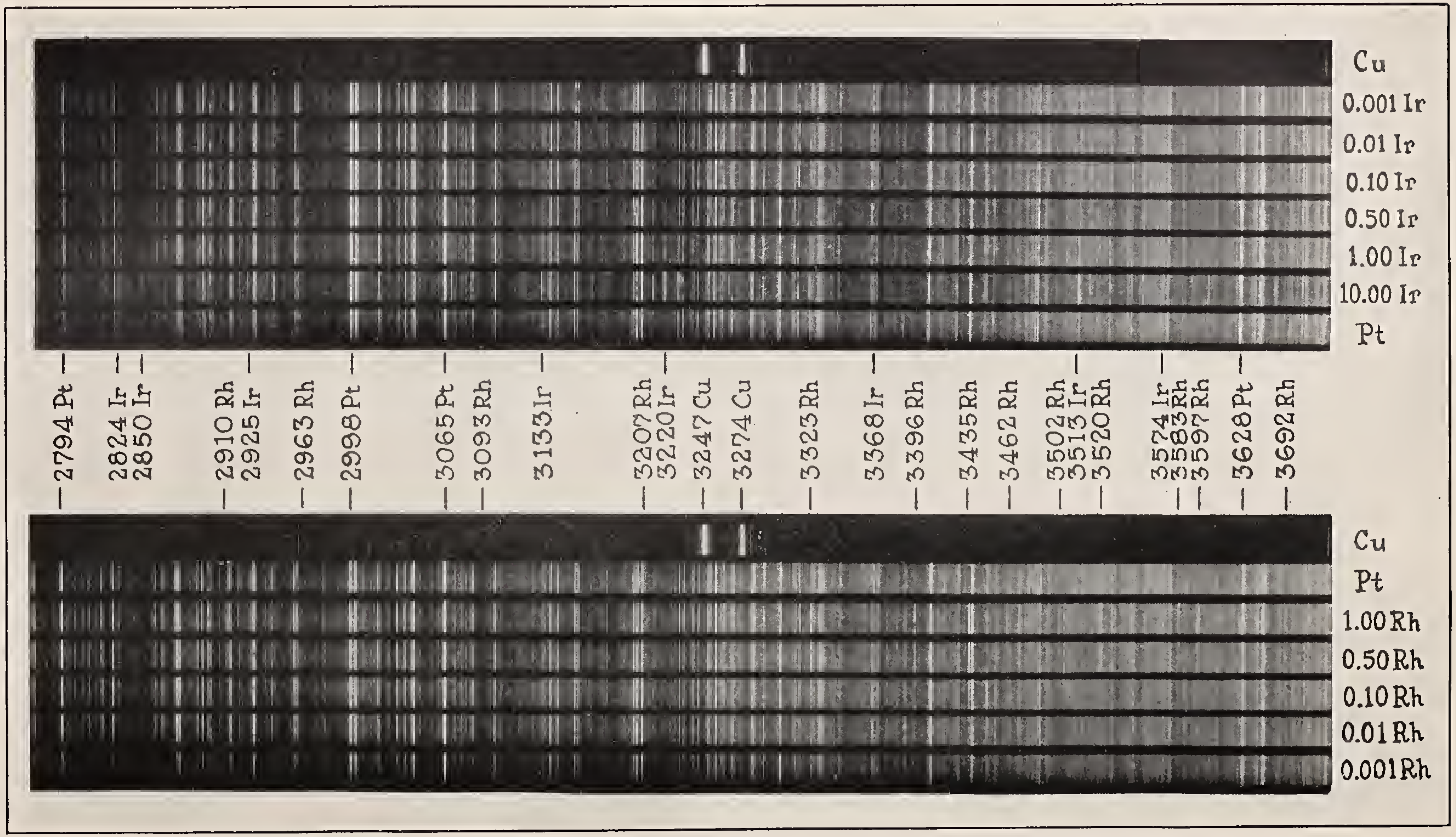

FIG. 7.—*Spark spectra of platinum alloys (ultra violet, 2700–3700 A)*

Upper group, reading down, copper arc spectrum for scale of wave lengths, platinum-iridium alloys containing 0.001, 0.01, 0.1, 0.5, 1.0, 10.0 per cent iridium, pure platinum. Lower group, reading down, copper arc spectrum, pure platinum, platinum-rhodium alloys containing 1.0, 0.5, 0.1, 0.01, and 0.001 per cent rhodium. Some of the sensitive iridium and rhodium lines are indicated by their wave length values.

also increased. In 1896 this constant was represented by 0.0037, in 1917 it was 0.003868; for the purest commercial platinum which we have recently examined it is 0.003912, while the best platinum produced by the Bureau of Standards has a coefficient of 0.003924.

TABLE 3.—Partial Spectra of Rhodium in Platinum: Estimated Relative Intensities.

Wave length.	Pt.	1 per cent Rh.	0.5 per cent Rh.	0.1 per cent Rh.	0.01 per cent Rh.	0.001 per cent Rh.
2819.24		1				
2830.28	7	7	7	7	7	7
2924.09		2	1			
2963.55		3	2	1		
2986.19		1				
2988.86		2	1			
2997.96	8	8	8	8	8	8
3019.78		2	1			
3048.89		2	1			
3093.47		2	1			
3178.99	5	5	5	5	5	5
3207.28		3	2	1		
3263.16		2	1			
3271.65		2	1			
3280.58		3	2	1		
3290.23	6	6	6	6	6	6
3307.37		1				
3323.13		6	4	2	1	
3368.38		2	1			
3372.26		5	4	2	1	
3396.85		6	5	4	2	1
3399.70		3	2	1		
3408.15	10	10	10	10	10	10
3412.31		3	2	1		
3421.25		2	1			
3434.97		8	6	5	3	2
3440.57		4	2	1		
3455.19		2	1			
3457.90		2	1			
3462.04		6	4	2	1	
3470.68		6	4	1		
3474.80		6	4	2		
3478.93		4	3	1		
3485.27	8	8	8	8	8	8
3498.76		2	1			
3502.56		6	4	3	2	1
3507.36		4	3	2		
3528.04		5	4	2		
3538.16		2	1			
3543.99		3	2	1		
3549.57		4	2	1		
3570.26		3	1			
3583.15		6	4	2		
3587.43	4	4	4	4	4	4
3596.20		5	4	2		
3597.18		6	4	2	1	
3605.87		1				

It is observed that the spectrum of platinum is extremely complex. The same is true for all the other metals of the platinum group, and it might be assumed that this would make the interpretation of the spectra difficult and cumbersome. The examination of any spectrogram is greatly facilitated by placing it on a photomeasuring micrometer for which scale readings corresponding to the positions of sensitive spectral lines have been calculated in advance. This can be done once for all during the preliminary study of standard samples. It is our practice to photograph on all spectrograms made for analysis the arc spectrum of copper which serves as a reference scale from which to determine wave lengths. The spectrogram is then adjusted on the measuring engine so as to bring the line 3247 A into coincidence with the filar of the microscope when the scale reads 300,000. Then, as rapidly as the carriage on which the plate rests can be moved, we have entering the field of view of the microscope all the positions occupied by sensitive lines according to their computed scale readings, and the absence or presence and relative intensities of these lines are noted. The relative intensities of the lines can, after some practice, be estimated visually with a high degree of exactness, so that the use of a microphotometer is required only for work of the utmost refinement. With these, and especially with simple types of spectra, a trained observer, who becomes familiar with the relative positions occupied by the sensitive lines, can entirely dispense with auxiliary apparatus and interpret the spectrogram quickly and accurately. Enough has been presented in connection with the analysis of tin, gold, and platinum to justify the conclusion that quantitative spectrographic analysis applied to problems of the kinds described above is a successful procedure and one that may be readily extended to many problems in chemistry, metallurgy, mineralogy, physics, biology, and other sciences.

V. GENERAL APPLICATIONS.

The methods of analysis described and illustrated above may be applied directly to minerals. In fact the principles of this method were worked out by de Gramont on this very problem and published as his thesis[11] in 1895. Since then he has described similar applications such as: Testing minerals for silver,[12] spectographic analysis of galenas and argyrites,[13] the presence of boron in certain minerals.[14] Analysis of zinc blendes by means of arc spectra has been described by Urbain.[15]

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[11] Analyse Spectrale directe des mineraux, Baudry, Paris, 1895. Also Bull. Soc. Chim. (3), **13**, p. 945, 1895. C. R., **118**, pp. 591, 746, 1894; **119**, p. 68, 1894; **120**, p. 778, 1895; **121**, p. 121, 1895; **126**, p. 1514, 1898.

[12] C. R., **147**, p. 307; 1908.

[13] C. R., **145**, p. 231; 1907.

[14] C. R., **168**, p. 857; 1919.

[15] C. R., **149**, p. 602; 1909.

Metallurgical problems, too, are frequently solved by reference to the spectrograph. It is now well recognized that minute quantities of impurities of foreign substances sometimes effect great changes in the physical properties of a metal. This fact is taken advantage of in the production of certain alloys in which a small amount of one element is intentionally mixed with another. Typical examples of metallurgical problems were presented above.

Additional examples are to be found among the works of de Gramont, e. g., researches on the spectrum of titanium [16] and its applications to metallurgy and mineralogy, the spectra of silicon and quantitative analysis of steels,[17] and expecially the summary of his technical applications of spectroscopy [18] during the war. Methods for economical analysis of scrap iron, tool steels, etc., may be of considerable importance to the iron and steel industries.

The analytical chemist surely can conceive of innumerable instances where spectral data would be of assistance in the solution of particular problems or perhaps offer the only mode of attack in some cases. In the first place, the extraordinary sensitivity of raies ultimes recommends this test for the purity of materials for atomic weight determinations.[19] Unfortunately, this test has not always been applied in such work. A preliminary qualitative analysis, made spectrographically, will reveal at once (with few exceptions) all of the chemical elements present in an unknown, and thus save much time which the wet chemical methods require for successive search for different elements in different chemical groups. Another advantage of this preliminary test is to demonstrate the absence of certain elements, or groups of elements, since this information is often of more value than evidence of slight impurities. For elements present as traces or small concentrations, sufficiently accurate quantitative estimates result from a simple inspection of the sensitive lines. When the material available for analysis is not more than a few milligrams the chemical methods are hopeless, but the spectrum is quite as easily produced with a microscopic particle as with a large mass. In the ordinary course of laboratory work the spectrogram, as a rule, can not only identify the elements but also detect the ten-thousandth part of 1 per cent present in complex mixtures, even if only a few milligrams of the material are available. Precipi-

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[16] C. R., 166, p. 94; 1918.

[17] C. R., 173, p. 13; 1921.

[18] Bull. Officiel de la Direction des Rescarches Scientific et Industrielles, et des Inventions, No. 9, p. 480; 1920.

[19] de Gramont, J. Ch. Phys., 14, p. 336; 1916.

tates, filtrates, electrolytes, etc., are oftentimes much more conveniently and quickly analyzed with a spectrograph than with the ordinary chemical methods.

Physicists are now interested chiefly in the theoretical side of spectroscopy because of the light it throws on atomic structure and the mechanism of radiation, but they should also realize that spectral analysis has important practical applications in their work. The effect of traces of impurities on physical properties of metals was illustrated above in the discussion of thermal emf variations in impure metals of the platinum group. Furthermore, many physicists have attempted to establish certain physical constants, such as melting points, latent heats, expansion coefficients, electrical resistances, with extreme precision and at the same time have worked with more or less pure materials and were ignorant of the amounts or effects of the impurities present.

One field in which spectrographic analysis might find useful application is in the study and control of glass production. Glass is usually a mixture of a large number of elements, it is difficult to analyze chemically, and in the case of optical glass in particular its most essential properties depend on its chemical constitution and homogeneity. Here is another example of the importance of minute quantities of metals in a mixture. A few hundredths of 1 per cent of iron in optical glass gives it a strong green color, which disqualifies the glass for most uses. Small quantities of cadmium, selenium, cobalt, manganese, etc., are intentionally added to glass for the production of different colored glasses.

Biology, physiology, and other sciences no doubt also have a practical interest in spectroscopy. In these days, when the influence of minute quantities is so widely recognized, the rôle played by the long-continued assimilation of the less familiar elements by the human system can not be regarded as insignificant. One of the earliest applications of spectroscopy by Bunsen, Kirchhoff, and others was to the investigation of natural waters, and in the course of this inquiry rubidium and caesium were discovered. Some of the recent spectrographic discoveries in these fields are the occurrence of boron in the majority of vegetable and animal substances and in most natural waters[20], and the discovery of de Gramont[21] that zinc is a constituent of all animal organisms. The spectroscope which aided in the discovery of the chemically inert gases has also assisted in establishing the fact that these

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[20] J. S. C., I, 1916, pp. 661–663.

[21] C. R., **170**, p. 1037; 1920.

gases are very widely distributed throughout the universe. Appreciable quantities of helium and argon have been found in the earth's atmosphere, in sea and river water, in gases evolved from mineral waters, in natural gas wells, in a large number of the older rocks and minerals, and in the case of helium, in the sun and other stars and in many nebulae.

Hartley[22] spectrographically analyzed the mineral constituents of dusty atmosphere in Dublin and found calcium, copper, iron, lead, nickel, manganese, magnesium, and carbon. A surprising fact was that ten times as much copper as calcium existed in that atmosphere, but this was finally accounted for by the repeated flashes on the overhead cables of tramcars which must yield a copper dust of extreme tenuity. It was pointed out that "as no atmosphere is free from dust, and that of cities is particularly dusty, these mineral constituents must be regarded as possible reagents in cases where there is evidence that very minute quantities of basic substances can initiate chemical reactions and isodynamic changes, such as have generally been considered as spontaneous, and in all cases where a solution in contact with air is liable to be affected."

WASHINGTON, April 7, 1922.

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[22] Proc. Roy. Soc., 85A, p. 271; 1910-11.

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