Qualitative and Quantitative Chemical Analysis by Line Emission Spectra

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IT has been recognized for nearly a century that the spectrum emitted by an atom is characteristic of that atom and of its energy condition. There is no general agreement on the question of who should be credited with the discovery of this fact, but there is little doubt that the first important application of this fundamental principle of spectrum analysis was made by Kirchhoff and Bunsen. In 1860, in the course of a study of the spectra of the alkali metals, they observed in the spectra of some of their preparations spectral lines which they could not associate with any of the known alkalis. Correctly concluding that these lines indicated the presence of unidentified atoms, Kirchhoff and Bunsen undertook the separation of the suspected new elements, and in 1861 isolated the two new alkali metals, caesium and rubidium.

This striking demonstration of the power of the spectroscope, together with Kirchhoff's explanation of the Fraunhofer lines of the sun's spectrum (1859) and the use of these lines by Kirchhoff and Bunsen to demonstrate the presence of numerous metals in the sun, called the attention of the scientific world to the possibilities of qualitative analysis with the spectroscope. It is now well recognized that the study of line-emission spectra offers one of the most sensitive and rapid methods for the detection and quantitative estimation of many of the elements in solids, liquids and gases. Spectrographic methods are free from many of the sources of error and inaccuracy of chemical methods, but the practice of spectrum analysis requires a recognition of the limitations and possibilities of the method, as well as of the precautions to be observed in its application.

Although the presence of the spectral lines of an element are an indication of the presence of that element in the emitting light source, the positive identification of the spectral lines requires a consideration and elimination of the possibility of disturbing lines, i.e., lines of other elements very close to the position of the lines in question. And the converse statement, that the absence of the spectral lines of an element permits the conclusion that the element is absent from the emitting source, requires a knowledge of the excitation possibilities of the element in the source used, as well as some information on the excitation probabilities of its various spectral lines and on the sensitivity of the spectroscopic apparatus used.

That the question of disturbing lines may be very troublesome can be readily appreciated from the fact that the Harrison list[1] of the stronger spectral lines of the elements in the range 10,000A − 2000A contains 100,000 lines, or an average of about 12 lines per angstrom unit. Clearly, even if the precision of the lists and of the measurements of a qualitative determination were adequate, only the dispersion of a large grating could fix, with sufficient certainty, the wave-length and origin of a single line. Other criteria must be applied.

One such criterion is found in the lists and charts of the most sensitive lines of the elements, i.e. the lines which appear in the spectrum when only minimum amounts of the element are present in the source. Such charts are, for example, those of Bardet[2] for prismatic spectra, and of Crook[3] for grating spectra. Or one may prepare his own by marking the lines on a spectrogram recorded on his own equipment from a sample of the R.U. powder of A. Hilger, Ltd., which contains traces of fifty metallic elements.

Given an unknown specimen to investigate, the first step is to photograph its spectrum, using a light source and spectrograph adapted to the quantity and nature of the sample. It is usually desirable to record a reference spectrum beside

the unknown one, and iron is usually best, since it is so used in both charts mentioned. If the matrix, or major component, of the specimen is known or easily identified, good practice is to compare, if possible, the spectrum of a pure sample of this material, taken under identical conditions, with that of the specimen. Elimination of the common lines reduces the problem to that of the determination of the source of the remaining lines. A comparison may then be made with the reference chart of sensitive lines, and will doubtless reveal several close coincidences with lines of one or more elements. In many cases some knowledge of the sample under investigation will aid in deciding whether the presence of any or all of these elements is probable. In any case, further verification must be sought in the form of additional lines of the elements in question. Spectra of pure samples are of some use, but more helpful are lists or charts showing the order of disappearance, with diminishing amount, of the lines of the elements. Such a chart is that of Löwe,[4] showing spectra from a small quartz instrument of 1, .1, .01, and 0.001 percent of each of 44 elements, in solution on graphite electrodes; while tables with similar information are those of Twyman and Smith.[5] If all, or nearly all, of the lines which should accompany a tentatively identified line of an element are found with proper relative intensities, the presence of the element may be considered established. Similar corroborative evidence may often be gained from a consideration of the classification of the lines of a particular element. If all the lines of a multiplet or line group appear, or if the earlier members of a series are found accompanying tentatively identified lines which are higher members of the series of an element, again one may be confident of its presence.

Sometimes, however, the major constituent has a great number of lines, which obscure many of the corroborative lines sought, or it may be that there are traces of impurities in the element and it is difficult to find lines other than the most sensitive or persistent ones. Recourse must be had, then, to a process of eliminating other elements which might have radiated the lines in question. Consultation of tables of principal lines, such as the Harrison[1] or Kaiser-Ritschl[6] tables, with due consideration of the dispersion of the spectrogram, will reveal which elements have lines close enough to interfere. These elements must then be considered in turn, and their presence, or that of the one originally suspected, established. The consideration of interfering lines can be simplified by the use of the tables of Gerlach and Riedl,[7] which give, for each of the detection lines of fifty-seven elements, the interference lines which must be considered, and useful, decisive criteria for their identification.

The presence of lines of any suspected element in the spectrogram may be checked by the above procedure. The absence of the detection lines of an element indicates that it is not present in the sample in sufficient amount to be detected with the source used. It should be noted, however, that there are wide variations in the relative spectral sensitivity of different elements and of different light sources. Arcs are, in general, very much more sensitive than spark sources, and the spectra of metals much easier to excite than those of the metalloids. The gaseous elements cannot be ordinarily detected except in gas discharge tubes, and the sensitive lines of sulphur lie in the vacuum spectrograph region. Otherwise, practically every element is amenable to the ordinary methods of spectrographic analysis.

The intensity with which the spectrum of an element is excited depends, to a considerable extent, on the nature of the other elements in the sample. In general, an element of low boiling point, high vapor pressure, and low ionization potential will be excited at the expense of those of higher boiling points or ionization potentials, or of relatively lower vapor pressures at the electrode temperatures.

Under favorable conditions, the presence of an element in concentrations as low as one part in a million is readily detected. Owens[8] has reported, in the analysis of caustic liquors, an absolute sensitivity of 1×10^{-6} mg of test element on the electrodes and a relative sensitivity for manganese as low as 0.000002 percent. A rather unfavorable case, on the other hand, is that of tin in minerals, for which, having used as source the cathode layer of a d.c. arc and a glass spectrograph, v. Tongeren[9] reported a sensitivity of
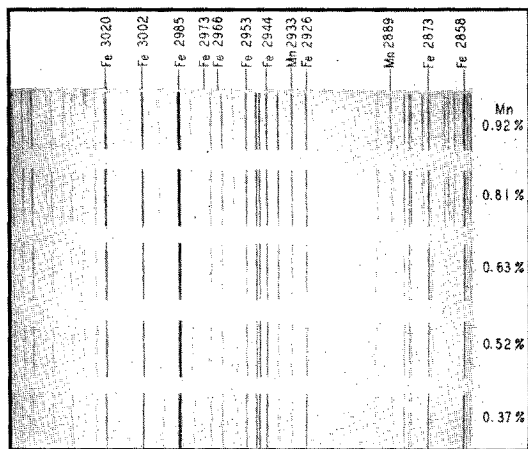
FIG. 1. Spectrograms of samples of iron, containing manganese in increasing amounts.

only 0.3 percent of SnO_2. The sensitivity in this case would have been much higher if the much more sensitive ultraviolet tin lines could have been used. Many other examples of the sensitivity of various elements in different sources are given by Owens and by v. Tongeren. Since the sensitivity of trace determination depends so much on the spectrograph, the photographic plate and the light source used, as well as on the other elements present in the sample, it is best, if previous experience in similar cases is lacking, to undertake some tests on samples of known and similar composition before reaching the conclusion that any element is lacking.

In general, under carefully selected working conditions, the sensitivity of trace analysis by the spectrograph is better than that of chemical gravimetric analysis, and as good as, or better than, colorimetric methods. The speed is usually greater, especially if suitable master charts or spectra are available. The specimens can ordinarily be used in their natural form: as solid electrodes; as liquid dried on the ends of graphite or silver electrodes; as powders or nonconductors packed in cavities in graphite electrodes. A few minutes suffice to expose and process a plate and the examination of not too complicated spectra is rapidly made.

While the qualitative examination of samples for traces of impurities is an important use of the spectrograph, no less important is the rapid spectrographic examination of samples of un-

known composition to determine what elements are present and which, if any, need to be determined by the more laborious chemical methods. In this connection we may mention the sorting of scrap steels as to alloy type in steel mills,[10] the classification of minerals,[11] and the detection of metallic poisons in criminal investigations.[12]

Examples of this sort could be multiplied, but those given will serve to show that the variety of such applications is as great, perhaps, as in qualitative chemical analysis. The great advantage of the spectrograph in this type of analysis lies in its speed and the wide variety of samples which can be handled with the same equipment and technique. An exposure can be made in about a minute after preparing the sample; the photographic plate can be processed and dried in from 5 to 15 minutes; and the examination can be made in a few minutes more. Much time may often be saved in later chemical analysis by the knowledge thus gained of what elements are present.

In the analyses just discussed, the great advantages of the spectrograph, as we have seen, are its speed and universality. In connection with the trace analyses, mentioned earlier, it was pointed out that the extreme sensitivity of spectrographic determinations permitted the detection of impurities difficult or impossible to demonstrate chemically. These applications of the spectrograph are the earliest and the best known. They are today still the commonest analytical uses of the spectroscope. Quantitative analysis with the spectrograph, however, is rapidly increasing and, with further development of the technique and wider appreciation of its possibilities, bids fair, in the future, to become the most important analytical use of the spectrograph.

Quantitative spectrochemical analysis rests on the observation that when an element is present in a matrix, or body of other materials, in small and decreasing amounts, its spectral lines grow gradually weaker and disappear in a definite order. An example of this effect of abundance on the strength of the spectrum of a substance present in small amounts is seen in Fig. 1, which shows a series of iron spectra containing small known percentages of manganese. It will be seen that different manganese lines disappear with

different rates and at different percentages in the sequence. The first systematic study of this effect was made by Hartley, at Dublin, in 1882. He laid the foundations of quantitative analysis by the spectrum, and he made the first quantitative analysis—that of beryllium in cerium compounds.

Hartley and his immediate successors, such as Pollock, at Dublin, and de Gramont, at Paris, made their analyses by comparing the spectra of their samples with those of a graded series of similar composition and choosing, visually, the known which best matched the unknown. As has been pointed out above, the intensity of the spectral lines of a minor or secondary component in a source are influenced, not only by the characteristics of the spectrographic equipment and photographic technique, but also by the nature and amount of other elements in the source and by random fluctuations in the operation of the source. Accordingly, methods of visual comparison, especially without careful selection and control of the source, can be expected to give results with only the roughest kind of accuracy— perhaps 10–25 percent.

Present practice in quantitative spectrochemical analysis attains, as we shall see, an accuracy comparable with that of chemical analysis and a speed much greater. Success has followed from a careful scrutiny of every step of the process, which has resulted in more consistent and controllable light sources, better photographic materials, more direct comparison methods, and, above all, precise photometry of spectral line intensities.

The ideal light source for analytical spectroscopy would be one in which the spectral lines of each element in the electrodes varied in intensity with concentration according to an invariable and definite law, regardless of what other elements were present. If such a source were available and its characteristics well enough known, it would be possible to set up an absolute, or nearly absolute, method of analysis. A calibration of the spectrographic apparatus and photographic materials used could be made for each element by the use of one sample containing a known amount of the element. With the constants of the equipment thus fixed, later analyses could be made by a determination of the intensity with which the analysis line of the element was radiated from any sample.

Absolute spectrochemical analysis is the ultimate goal of spectroscopists; recent improvements in light sources, and·photographic materials offer some hope that this goal is not unattainable. Few, however, have as yet undertaken analysis on this basis. A recent attempt is that of Preuss[13] in mineral analysis. The accuracy was quite rough but the principle may be useful when more precise methods are not applicable.

In all present spectroscopic sources, to a greater or less extent, the relative intensity of lines of any one element, and of lines of different elements, varies from instant to instant, for a variety of reasons. For example, fluctuations in discharge temperature, due largely in electrical discharges to current variation, result in fluctuation in the relative excitation of different lines because of their different excitation functions. The potential gradient in an electrical discharge depends on the ionization potential of the atoms present and so may be influenced by the kind and amount of atoms present other than those under analysis. Again, the rate and order in which different elements evaporate from the electrodes and appear in the radiation from the source depends on their relative vapor pressure and boiling points, as well as on the boiling point of the major constituent of the electrode, and is influenced by local variations in electrode temperature.[14]

The most successful quantitative spectrochemical analyses undertake to eliminate variations in the light source by the use of the "internal standard" principle of Gerlach.[15] Gerlach pointed out that many of the difficulties of source fluctuations, which are emphasized by using an "external reference standard" in another spectrum, are avoided when a chosen line of the element under analysis is compared with a line of a reference element in the same spectrum. Gerlach's original proposal was to choose, for each of several concentrations of the analysis element, a line pair made up of a line of·the analysis element and a line of the reference element which were equal in intensity at that concentration. Analysis consisted of selecting visually the pair of equal intensity and thus fixing the concentration of the element to be

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determined. Most modern procedures which aim at high precision use only one pair of lines. From experimental measurements a graph of the relative intensity of these lines is plotted against the concentration, and analysis is performed by reading from this analytical curve the concentration in the sample corresponding to the observed ratio of the analytical line pair.

A qualitative analysis involves the choice of a suitable light source, the selection of a spectrograph and a suitable analysis pair, and the development of a photometric technique for determining the line intensities. These three items are relatively independent of one another and so may be discussed in turn.

All spectrochemical light sources may, with scarcely an exception, be classified as flames, arcs or sparks, and each class is susceptible of more or less variation in experimental arrangement and use. The flame, as a source for quantitative spectroscopy, has been utilized chiefly by H. Lundegårdh.[16] Lundegårdh uses an acetylene-air flame into which, by means of an atomizer, the material to be analyzed is sprayed in solution. The method is especially suitable for biological analyses—such as analysis of soil, plants, and animal samples—and for readily soluble inorganic material. Lundegårdh has applied it to 34 of the commoner metallic elements. He finds a sensitivity of from 0.001 to 0.000001 mol per liter for the various elements. Higher concentrations can, of course, be handled by dilution of the solution. Suitable reference elements for the internal standard method are readily introduced into the solution. Lundegårdh states that if a photometer is used to determine the line intensities, the errors will never exceed 5 percent of the amount present and are often not more than 1–2 percent. These accuracies are as good as claimed for any other sources, but the method has not been widely adopted in this country, no doubt largely because arcs and sparks are somewhat more convenient, especially for solid samples.

The electric arc is, of all sources, the simplest in construction and operation. In essence, it requires only a connection to the direct source of potential, a regulating resistance and an arc stand to hold the samples. While its simplicity and sensitivity have made the direct-current arc popular for qualitative work, other sources tend to displace it for quantitative work because of the difficulty of obtaining an arc of steady and reproducible characteristics,[17] and because of the objectionable background usually found in the spectrograms. Some modifications of the arc are more promising. Gerlach[18] has made good use of the interrupted arc on 80 volts a.c. in which the electrodes are automatically brought together and separated. The arc is re-established at each contact; the electrodes are kept too cool for oxidization and resultant band spectra; and there is little of the wandering of the arc over the electrodes which results in erratic variations in electrode temperature and, hence, in differential evaporation of the various electrode components. A similar result is attained by Pfeilsticker,[19] who uses 220 volts a.c. across to a short gap and applies, at the peak of each cycle, a high Tesla voltage, which causes a spark to ionize the gap and permit a momentary arc flash.

An arc of analogous characteristics, but without mechanical complications, is attained by applying 1100 to 4400 volts a.c. to a gap of one millimeter or less. The voltage is sufficient to produce on each cycle an ionizing spark, which is succeeded immediately by an arc which persists until the gap voltage falls too low. The current is regulated by a large resistance or inductance in series with the arc. First introduced by Duffendack and Thomson[20] for biological analysis, it has been used by Duffendack and Wolfe[21] for caustic liquors, by Owens[8] for organic and heavy chemicals, and by Sawyer and Vincent[14] for steel. Samples may be solid metal electrodes, liquids dried on graphite electrodes or powdered material packed in cavities in graphite electrodes. Extremely sensitive, consuming a very small sample and capable of accuracy, under favorable conditions, of ±5 percent, this source seems destined for wider use.

The most sensitive type of arc is, perhaps, that developed by Mannkopff and Peters[22] at Gottingen. They found that the radiation from the region just above the cathode in a carbon arc reveals the lines of extremely minute amounts of metallic traces in powdered samples packed in a cavity in the carbon cathode. This method has been extensively used for analysis of geo-

logical[9] and other nonconducting samples. Among the most accurate results obtained with the cathode layer are those of Preuss,[13] but this method seems to excel more in sensitivity and in applicability to refractory material than in high precision.

For samples suitable to the technique, when too great sensitivity is not required, some type of spark is preferred by many operators, because of its greater adaptability and reliability. The spark consumes a very small amount of material and the heating is localized so that erratic and differential evaporation may be lessened. A spark source operates from a transformer or other high voltage supply, generally between 10,000 and 50,000 volts, which charges a suitable condenser. The available energy is fixed by the voltage and capacity. The condenser discharges through a spark circuit containing more or less inductance and resistance and the sample gap, with an oscillating and damped current. A certain amount of inductance is needed to eliminate air lines; as more is added the discharge tends to become more like an arc in nature. The capacity used is ordinarily in the range from 0.002 to 0.2 microfarad, with inductances of 50 to 5000 millihenries. The exact sizes will be fixed by the energy available and excitation desired.

The simple condensed spark circuit has been frequently used in analysis and, as in the case of the arc, many modifications have been introduced to meet specific needs or to give improved control in operation. W. Gerlach,[18] for analysis of biological samples, has used a unidirectional Tesla discharge between a point electrode and a metal plate on which was placed a glass slide carrying the liquid or solid specimen. A similar d.c. spark has been used in biological investigations by Foster[23] and his associates at McGill University. Instead of using a Tesla discharge, however, they supplied direct current at 10 kv to a condenser, which then discharged intermittently, two or three times a second, through an inductance and the spark gap. This method is very sensitive, uses only about $\frac{1}{10}$ cc of sample, and is said to be accurate to within 10 percent.

In an attempt to regularize the damping of the trains of discharges which occur at each spark, Feussner[24] placed a synchronous motor-driven, rotary gap in the spark circuit to permit
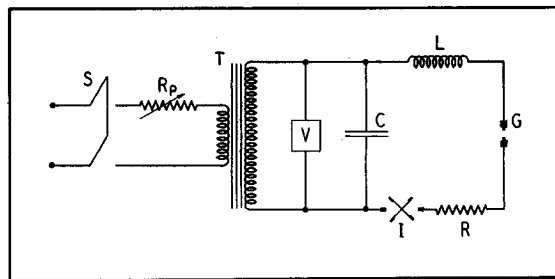

FIG. 2. Circuit diagram of condensed spark source, comprising S, line switch; Rp, adjustable primary resistor; T, high voltage transformer; V, electrostatic voltmeter; C, condenser; I, synchronous interrupter; R, resistor; G, sample gap; L, inductance.

sparking only at the peak voltage, and coupled inductively to the circuit a tuned circuit to absorb the energy, while a quenched gap in series also helped to damp the oscillations rapidly. Vincent and Sawyer[25] have achieved a similar result with a simpler circuit (Fig. 2) which utilizes a rotary gap but damps the oscillations by a resistance in the sparking circuit and an air blast on the spark gap. They found it possible, with this circuit, to carry out extremely rapid analyses of the composition of cast iron and steel with a probable error in a single determination of the order of 1.5–2.0 percent.

Kaiser and Wallraff,[26] in a noteworthy research on a sparking circuit of the above type, have shown the necessary conditions for reproducible sparks. Each train of sparks must die away before the next begins, so that the new series may begin always at a uniform voltage and so with the same energy available for vaporizing and exciting the electrode material, while the sparks must play over the electrode surface uniformly to avoid local effects or irregular heating. The necessary conditions for uniformity are most easily attained with circuits of the type just described, but the work of various investigators[27] has shown that excellent results may, in many cases at least, be obtained with the ordinary spark circuit.

That so many variations in light sources have been used for spectrochemical analysis is a clear indication that there is no universal source adaptable to all problems. Considerations of form and amount of sample, of sensitivity required, of speed and accuracy compel for

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each new application an investigation to determine the most satisfactory light source.

Similarly, there is no universal spectrograph for all analysis work. In most of the work to date, quartz prism spectrographs have been used, largely because of the large number of sensitive analysis lines in the ultraviolet region, and because of the relatively uniform sensitivity and contrast of photographic emulsions for much of the region. Glass spectrographs are usable, especially for those elements to the left and bottom of the periodic tables, which more often have sensitive lines in the longer wave-lengths. Grating spectrographs have been less used, chiefly because in the past the lack of adequate commercial supplies has raised questions as to ready replacement of gratings in case of accident or damage in cleaning. Recently, more models of grating spectrographs have become available, and their simplicity, together with their greater dispersion and resolving power in the longer wave-lengths, should lead to their wider use, if it can be assured that their surfaces, more delicate than prism surfaces, can be adequately protected and safely cleaned.

The spectrograph should have sufficient dispersion to separate the spectral lines of the samples, preferably with a slit of 20–50 micron width, since the wide lines lead to smaller microphotometer errors. Large dispersion also tends to decrease difficulties from spectrum background, since this continuous or unresolved band radiation is diluted by more dispersion, while the line widths are unchanged. Small spectrographs generally have higher speeds than large ones, as well as lower cost, and may be preferred for use with spectra which are not too complicated.

The photographic material used for recording the spectrum should have high contrast, to give good concentrational sensitivity, and small grain size, to reduce photometer errors, and it should have uniform sensitivity and contrast over a relatively wide spectral range. Emulsions with these characteristics are generally slow. Slow speed is not necessarily a disadvantage, since adequate illumination is often available in spectrographic light sources, and it is desirable to make the exposures long enough to consume a reasonable amount of the sample. Excellent examples of fine grained, high contrast plates are the Cramer Contrast and Eastman Spectrum Analysis No. 1, both, in addition, having thin emulsions which permit rapid processing. The Eastman Polychrome plate has been much used when somewhat faster plates are needed, and has, like the other two, a wide region of relatively uniform contrast.

Plate processing is best carried out in rocking trays to promote rapid, uniform results, and to avoid Eberhard effect. Vincent and Sawyer[28] have described a technique with rocking trays and forced washing and drying by which plates with thin emulsions can be completely processed ready for photometering in from three to four minutes. Since plate processing is generally the most time-consuming step in the analysis process, some such technique is highly desirable if much analysis work is to be done.

As was pointed out above, quantitative analysis is ordinarily done by measuring the ratio of intensities of a line of the analysis element and of a reference element, and interpolating the content from a plot of this ratio against concentration of the element to be determined. For rapid work, it is essential to make the intensity measurement with a microphotometer. Numerous models of microphotometers are available and their details need not be discussed here. Nonrecording or "spotting" instruments are to be preferred, since only a few lines are to be measured and a record both consumes time and introduces an additional source of error. It is essential that the instrument be quick in action (not over one or two seconds to reach a steady deflection), and that the clear-plate and dark readings be very permanent and stable. The plate carriage must be rigid and accessible, and both the plate mounting and motion must be convenient. The instrument should be able to photometer an area at least 3 to 5 millimeters in length and 25 to 50 microns wide, in order to reduce errors due to plate grain; plate grain errors, due to random location in the emulsion of individual grains, can hardly be kept as low as a mean error of 1 percent,[29] even with fine grained plates, unless an area that large is used. With the best modern light sources and techniques, even a 1 percent photometer error will limit the accuracy of analysis.
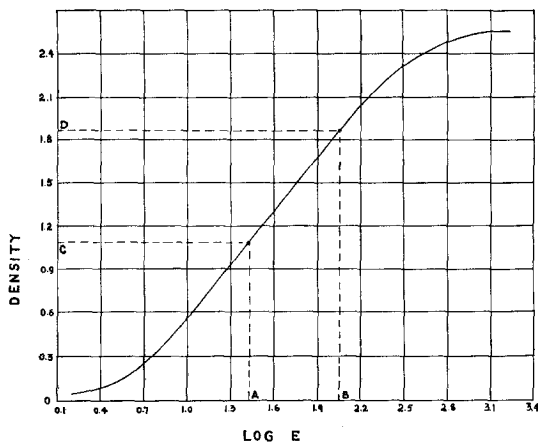
FIG. 3. Characteristic curve of a photographic plate, showing increase of density with exposure.

Numerous procedures have been developed for determining the intensity of the spectral radiations from the microphotometer readings.[30] All rest, of course, on the relationship, discovered by Hurter and Driffield, between the light exposure received by the photographic plate and the density of the developed image (Fig. 3). Since the slope of this characteristic curve of the emulsion varies from batch to batch of emulsion, as well as with age, development, and other factors, it is necessary to determine it for each plate, either directly or implicitly by determinations of intensity ratios of the analysis line pairs from spectrograms of two or more samples of known analysis recorded on the plate. Procedures which avoid direct calibration have been described by Twyman, Lothian and Dreblow[31] and by Ramb.[32]

Highest precision, however, certainly demands individual calibration and the time for such calibration need not be greater than that required by the precautions necessary in exposing and processing to avoid calibration, while the danger of error is greatly diminished. For calibration it is necessary to have on each plate a series of calibrating marks corresponding to known graded exposures. Numerous established procedures have been used to this end: Duffendack[33] replaced the spectrograph slit by a stepped slit illuminated by continuous radiation; Scheibe and Neuhäusser[34] obtained a number of graded steps of intensity in each spectral line by the use of a rotating logarithmic sector in front of the slit; Follett[35] attained the same end by an absorbing wedge before the slit. If the light source used is sufficiently uniform, a simple and time-saving method in routine work is to use several lines in the spectrum under analysis, whose relative intensities have been previously determined. This procedure has been used in steel analysis by Vincent and Sawyer.[17] In plotting the characteristic curve, some workers prefer to plot galvanometer deflection instead of density. The resulting characteristic curve is of similar general shape and usefulness.

From the characteristic curve may be read directly the exposure corresponding to the microphotometer reading or the density of any line. What is wanted, however, is the logarithm of the ratio of the exposures of the analysis and reference line. This log ratio can be obtained from the difference $A - B$, corresponding to the two galvanometer readings C and D (Fig. 3), since the difference of the logarithms is the logarithm of the ratio, and the difference is independent of the zero of either coordinate. A plot of the log concentration against log ratio for data obtained from spectrograms made under standard working conditions, from a series of samples of known graded composition, gives an analytical curve from which analyses of unknown samples may be read directly, as soon as their log ratio has been obtained from a spectrogram. Such an analytical curve for the determination of manganese in iron is shown in Fig. 4. It will be noted that the analytical curve is a straight line, as is generally the case over a considerable range of concentration. The curves, however, tend to bend over and reach a saturation as the concentration increases, thus decreasing the accuracy of determination and finally limiting the usefulness of analysis with the particular line pair. To go to higher percentages of concentration, a new line pair must be sought which saturates at higher concentration. In analysis the selection of suitable line pairs must, in fact, always be made after careful canvas of the possibilities.

Ideally, of course, the reference line should respond exactly as does the analysis line to all changes in the light source conditions; i.e., they should have the same excitation function. Actually, this ideal cannot be realized, but only more or less approximated. Experimental tests will show that some pairs of lines give results of much better accuracy than others, indicating

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better parity of the lines. Line pairs which are so found to behave similarly under varying source conditions have been called by Gerlach[15] homologous lines. If possible, the reference line should be near the analysis line; proximity in wave-length avoids variation in plate contrast, while proximity on the plate minimizes variations in sensitivity from point to point of the plate. The density of the reference line should preferably fall within the working range of the density of the analysis line—generally this density range will be from 0.3 to 1.0. In the case of liquid or powdered samples, the internal standard material may be added to the sample; accordingly, a wide range of choices exists, and it is often possible to select an element with ionization potential and boiling point near those of the analysis element. Such a choice is likely to result in a satisfactory reference line the intensity of which is easily controlled by varying the amount of material added. In the case of solid samples, an attempt must be made to find a satisfactory internal-standard reference line among the lines of those constituents of the matrix which are present in large enough concentrations to preclude any effect on their line intensities due to variations in the minor constituents. Many examples will be found, in the literature cited, of suitable choices of line pairs for analysis by earlier workers.

With proper choice of analysis line pairs and of light source, quantitative spectrochemical analysis is readily carried out for all the elements for which qualitative analysis is done with the spectrograph, and for a wide variety of substances and through wide ranges of concentration. Before quantitative work can be done on a new kind of substance or element, preliminary work with graded samples of known composition is required to establish the best operating conditions and to set up the analysis curve. Once this groundwork has been done, routine quantitative determinations are made with the expenditure of little more trouble or time than is required for qualitative examination. The concentrations covered may vary from quantitative trace analyses as low as 0.00001 percent[8] to alloy compositions of 10 percent or more. The upper limit is set chiefly by the difficulty of finding suitable analysis lines that do not reach a saturation in intensity at these higher per-

centages. Concentrations up to 4 or 5 percent are at present the ideal range.

Recent years have witnessed remarkable improvements in the accuracy and speed with which routine analysis can be done. With proper procedure, except in very unfavorable cases, the probable error of a single observation should not be over 10 percent. Much work is regularly done with an error of 5 percent, and in favorable cases mean errors have been reported as low as 1.1 percent[36] for antimony in lead, and 1.2 percent[37] for silicon in cast steel. The error may, of course, be reduced by averaging results from several spectra, and since these may be recorded on one plate, thus involving only one plate processing, the time of analysis is not greatly extended. It should be pointed out that the error in spectrographic determinations tends to be a nearly constant percentage, whether the amount analyzed for is large or small, while the error of gravimetric chemical methods is rather a constant absolute error. The spectrographic method thus has a marked advantage at low concentrations while the chemical method is advantageous at higher concentrations.

The spectrographic methods of analysis tend to exceed chemical methods in speed, often by large factors. Many cases have been reported in which a single observer can make from thirty to fifty analyses a day, each for several minor constituents in a sample. Owens,[27] in reporting on the results of one of the largest industrial
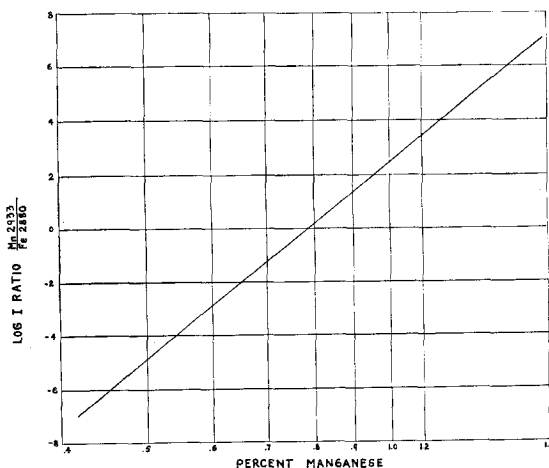

Fig. 4. Analytical curve for the determination of manganese in iron, showing increase of the logarithm of the ratio of the intensity of the manganese line, 2933A, to that of the iron line, 2880A, as the concentration of manganese increases.

spectrochemical laboratories, gives an average time required for one determination of only 7 man-minutes, while the same determinations in a chemical laboratory would take at least four times as long. Vincent and Sawyer[37] have described another large installation for iron and steel analysis in which a high precision analysis of a sample for as many as six minor constituents can be completed and reported in six minutes, and in which two crews of four operators each in a 16-hour day handle over 300 samples.

The recent progress in the development of spectrochemical analysis has led to a much greater interest and much wider application of the spectrograph to the analytical problems of biology, medicine, agriculture and industry. This increasing use of the spectrograph is strikingly shown in the rapid growth of publications in the field. In their *Index to Literature in Spectrochemical Analysis*,[38] Meggers and Scribner list the papers on the subject, by years. In the years 1920–1925 an average of 10.5 papers a year appeared, while the period 1932–37 produced an average of 107 papers a year. The art of spectrochemical analysis has reached a state where, in the ranges and for the elements and substances to which it is applicable, it can deliver routine analyses with adequate accuracy and much greater speed than the older chemical methods. There is every reason to anticipate that the active development work now being carried on will result, in the next few years, in even greater extension of the scope of the spectrograph as an analytical tool.

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