Spectrochemical Analysis * in Communication Research

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The development of spectroscopy is traced through Newton, Fraunhofer and Kirchoff to Hartley, Pollock and Leonard, and De Gramont who, in the period 1880–1920, applied the spectroscope to chemical analysis. It is shown that modern quantitative spectrochemical analysis began with the comparison standard method of Meggers in 1922, and developments since that time are discussed. The organization and functioning of the spectrochemical unit of the analytical group at the Bell Telephone Laboratories is described, and a number of examples of applications to telephone problems are given.

The foundation of spectroscopy may be traced back to the year 1666 when Sir Isaac Newton discovered that sunlight is composed of the several colors, and that it could be separated into its components by refraction with a prism. Newton failed to note the discontinuous nature of the solar spectrum and it was reserved for Fraunhofer, more than a century later, to investigate the absorption lines and to point out their importance. Fraunhofer noticed that the *D* line absorption doublet in the solar spectrum was identical in position with the bright line doublet observed in a flame fed with sodium chloride. Finally in 1859 Kirchhoff formulated the modern concept of the composition of the sun based on the observed absorption lines in the solar spectrum.

As a result of Kirchhoff's theory much attention was at once turned to the examination and mapping of the emission spectra of terrestrial substances and testing for their presence in the solar atmosphere. Bunsen and Kirchhoff proved the presence of many terrestrial elements in the sun. Lockyer actually discovered one element, helium, in the sun almost thirty years before its discovery on the earth. Thus did qualitative spectral analysis enjoy a brilliant beginning.

In the years that followed Kirchhoff's work the spectroscope was properly credited with many triumphs in the field of physics, but applications to chemical analysis were extended very little beyond simple qualitative detection of the elements. In 1882, however, Hartley performed quantitative analyses by determining at what concentrations in solutions the various spectral lines of metals would disappear.

* Any process of chemical analysis by means of the emission spectrum will be called "spectrochemical analysis" in this paper. Absorption and fluorescence methods have also been used but these will not be considered here.

For example, in a 1 per cent solution of silver the spark spectrum contains forty-five lines, under the conditions of Hartley's experiments. In a 0.1 per cent solution of silver twenty-five lines remain; in a 0.01 per cent solution only nine lines remain; and at 0.001 per cent but one of these persists. Pollock and Leonard, following Hartley, also used solutions with an improved sparking cell and extended this method of quantitative analysis to most of the common metallic elements. Almost simultaneously De Gramont began his monumental work of determining the persistent and ultimate lines (*raies ultimes*) of all the known elements under the conditions of a condensed spark discharge.

In 1922 Meggers, Kiess and Stimson [1] published the first paper on what might be called the modern method of spectrochemical analysis. Their departure from previous methods was that they did not rely solely upon the presence or absence of certain lines as a measure of the amount of an element present in the sample. Taking cognizance of the fact that the concentration at which a line will just be visible depends upon a number of other factors besides the nature of the element, another means of standardization was adopted as follows: A graded series of standard samples was prepared with known amounts of impurity in the same base material as the alloy to be analyzed. This series of standards was sparked under the same conditions as the alloy in question and all spectra recorded on the same plate. This practically eliminated all variables of development and plate sensitivity and reduced the variables of excitation materially. The impurity content was determined by a visual comparison of the spectra of samples and standards.

The method of Meggers, Kiess and Stimson, known as the comparison standard method, is still used extensively. It is subject, however, to limitations as to reliability, sensitivity, and precision. It is not always possible to make up homogeneous alloys for standards, and since only a minute amount of sample is excited by the spark it may be difficult to excite a representative sample. This can be obviated by using solutions instead of alloys. Spark excitation is limited in its sensitivity and it is frequently necessary to analyze for smaller amounts than can be detected in the spark spectrum. The use of arc excitation usually overcomes this difficulty and furthermore the arc is somewhat more suitable for work with solutions, especially with small volumes. Visual comparison of sample with standard is limited in precision. In recent years, however, the use of the densitometer (*vide infra*) or of the logarithmic sector has increased the precision of comparison so that it is possible to make spectrochemical analyses with a precision of better

[1] Meggers, Kiess and Stimson, *U. S. Bureau of Standards Paper* No. 444 (1922).

than ± 5 per cent of the amount determined. In some cases a precision of ± 1–2 per cent has been claimed.

Having traced briefly the development of spectrochemical analysis, we shall now describe the functions of a modern spectrochemical laboratory and illustrate these functions by examples from the experience of the Bell Telephone Laboratories. At the outset it should be pointed out that this laboratory is confronted with an exceptionally wide variety of samples to be analyzed, due to the large number of materials used in the Bell System. Other spectrochemical laboratories, generally speaking, place a different emphasis on the various functions to be described. Furthermore, we work in cooperation with a resourceful and skillful analytical laboratory and a well organized microchemical laboratory,[2] both of which have developed methods for some materials covering the usual range of the spectrograph. As a result our functions have been limited in some directions but extended in others, so that again our experience may be somewhat different from that of other laboratories. On the other hand, the work of this laboratory illustrates the flexibility of the spectrochemical method by demonstrating that it can sometimes be even more useful in collaboration with other methods than in competition with them.

1. Qualitative Analysis for Metallic Impurities

This is probably the most common type of service performed. The spectrograph is admirably suited for such analyses since, although it utilizes only a small amount of sample, it can detect almost infinitesimal quantities of the metals and most of the metalloids. Furthermore, a complete qualitative analysis can be run in a few hours—if the spectrum is simple or the sample relatively pure one hour is usually sufficient. Thus in a relatively short time and using only a small portion of a completely unknown specimen a guide can be furnished for quantitative analysis by spectrochemical or other methods. As we shall see in the following section, it is possible also to obtain a fair idea of the quantities of each metal present from the same spectrogram.

Numerous examples could be cited but it will be sufficient to state that all "general unknowns" are first subjected to a spectrochemical qualitative examination before further analysis is attempted, and to give two typical cases. A silver contact was behaving abnormally in tarnish tests and was submitted for analysis. A qualitative test revealed that the silver contained thallium. Subsequent checks on the spools of silver wire from which contacts had been made showed

[2] Clarke and Hermance, "Microchemical and Special Methods of Analysis in Communication Research," *Bell Sys. Tech. Jour.*, *15*, 483 (1936).

that the wire on one spool also contained thallium and this wire was rejected for further use as contact material. Total time spent: three hours.

A lot of zinc straps for supporting aerial cables was rejected in the field because the straps were "brittle," i.e., when flexed they would crack rather than bend freely. Between areas which cracked there were areas which bent easily and showed no signs of breaking. Spectrochemical examination of the zinc at the point of fracture revealed the presence of mercury, while this element was absent in the flexible areas (Fig. 1). Time spent: two hours.

2. Quantitative Analysis by Estimation

The first question usually asked when a qualitative analysis shows the presence of an element is, "How much is present?" It is easy to to tell from a qualitative plate whether the element in question is present as a major component, a minor component, an impurity, or merely as a trace. This information is frequently the deciding factor as regards further analytical work. This is particularly important in diagnosing troubles in field complaints. Very often the spectrochemical evidence alone will settle the matter—if not it will almost invariably tell just what further analyses are necessary, thus promoting the greatest possible efficiency in reaching a final solution of the problem.

The method of making such a rough quantitative analysis is to rely upon the experience of the analyst in judging the percentage of the element necessary to give the observed density of the lines under the conditions used. While such a procedure is theoretically unsound, an experienced analyst can make a surprisingly accurate "guess" by this method as has been repeatedly demonstrated by subsequent quantitative analysis.

An excellent example of an application of this technique of estimation is the identification of contact materials. It is sometimes desirable to identify the material composing a contact without removing the apparatus from its mounting, without impairing the contact for further use, and sometimes without more than momentarily interrupting its operation. The method used is to rub the surface of the contact with a small piece of fine, especially pure abrasive paper and burn the paper in a graphite arc, photographing the resulting spectrum. From the lines appearing in this spectrum which do not appear in the spectrum of the abrasive paper alone the elements composing the contact can be identified and their proportions estimated (Fig. 2).

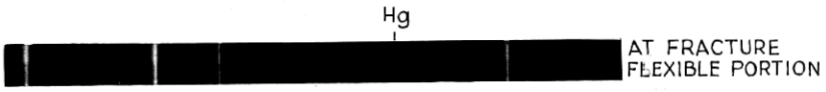

Fig. 1—Field complaint on failure of zinc straps for supporting aerial cables.

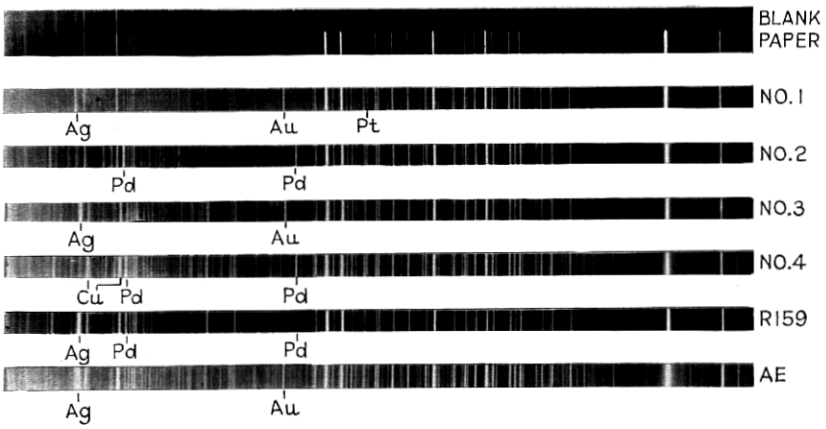

Fig. 2—Identification of contact alloys.

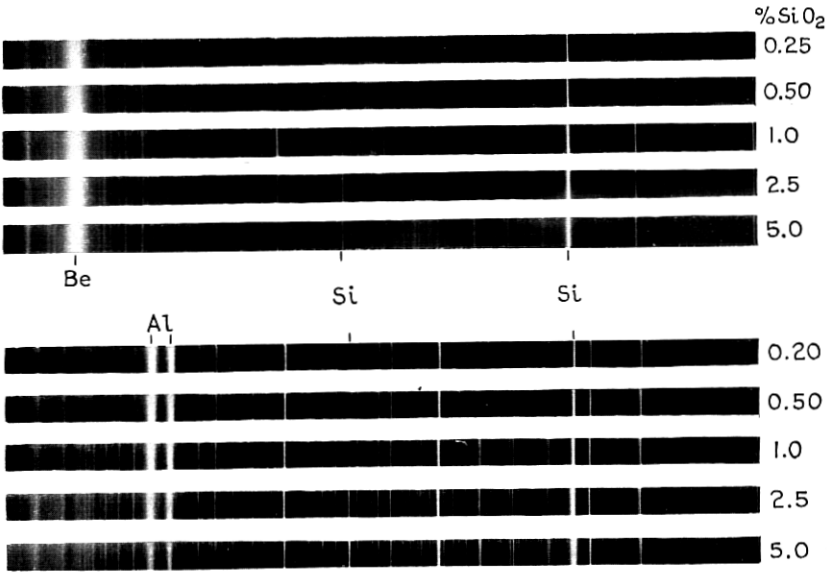

Fig. 3—Silica in beryllium oxide and aluminum oxide.

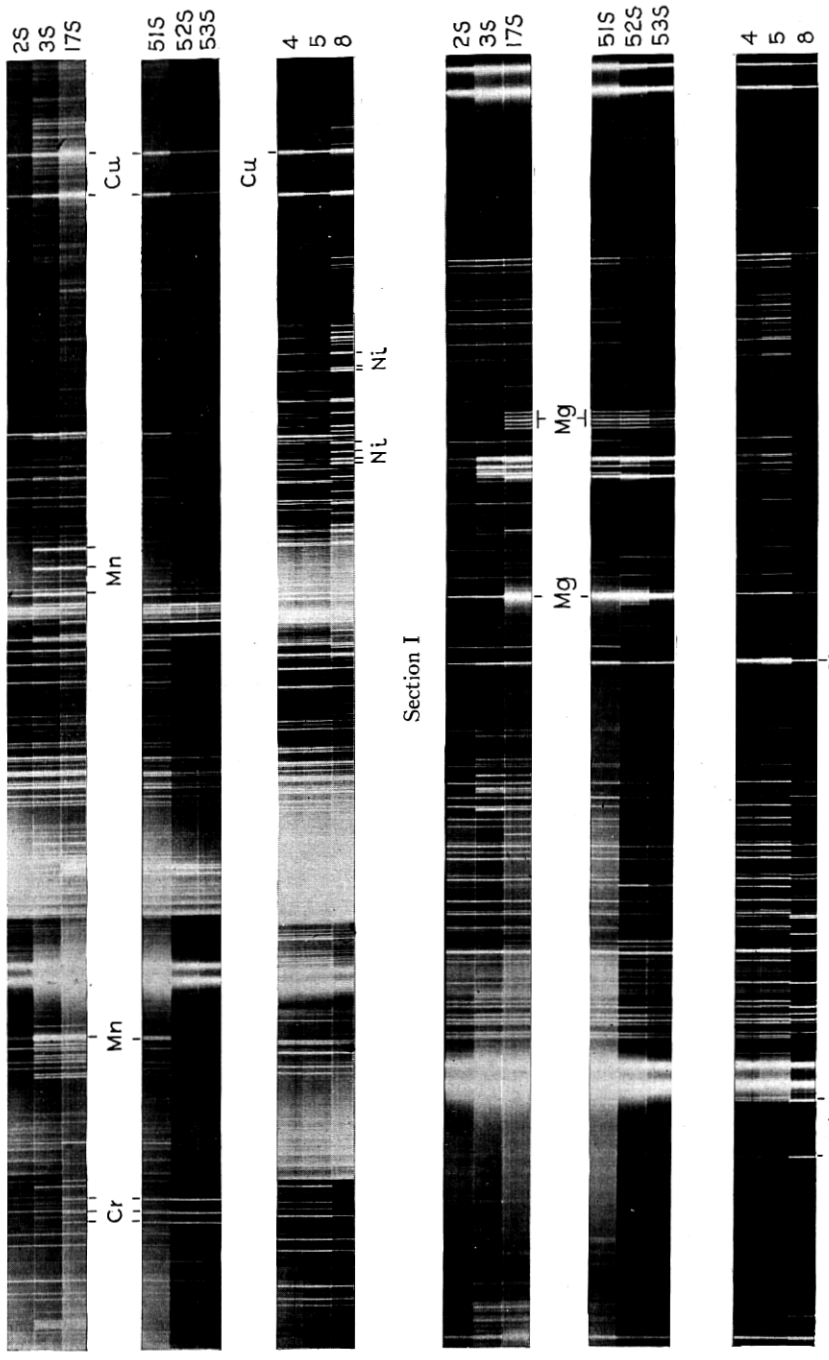

Fig. 4—Identification of aluminum alloys.

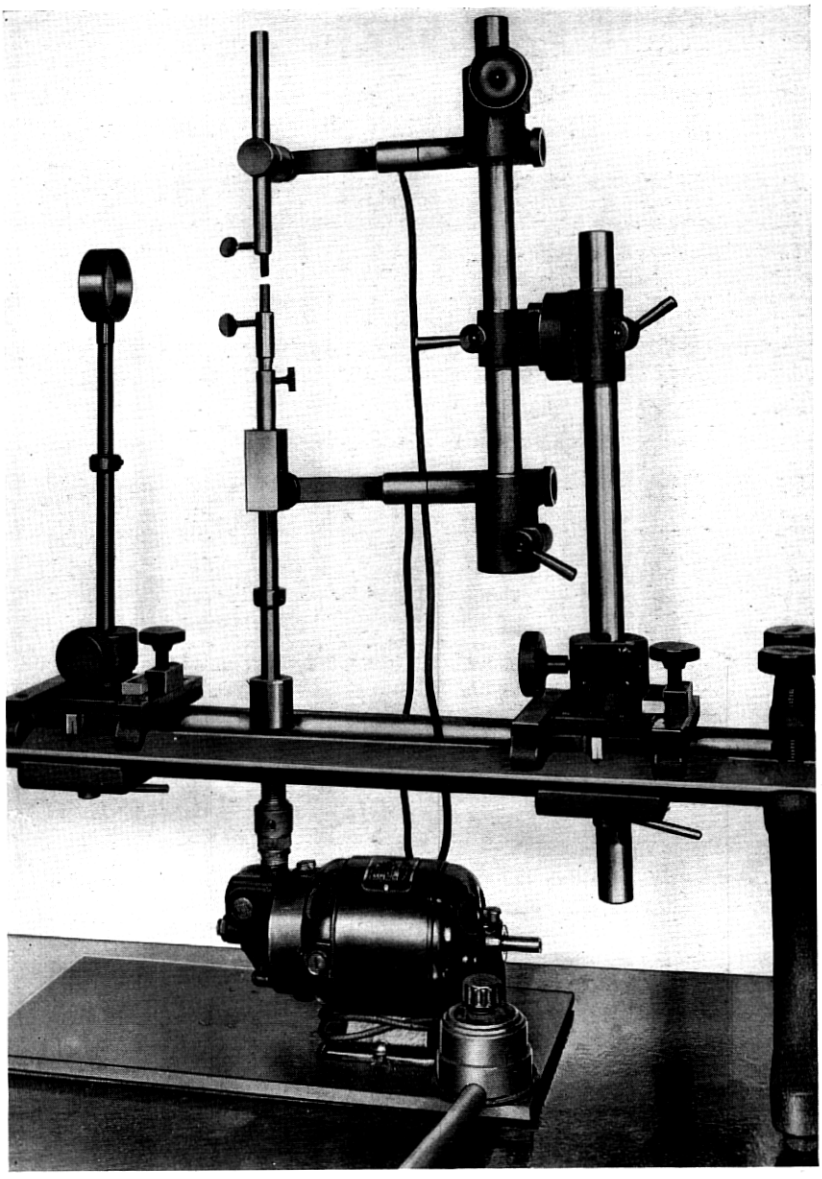

Fig. 5—Rotating electrode assembly adapted to De Gramont arc and spark stand.

Fig. 6—Step sector disk used for plate calibration.

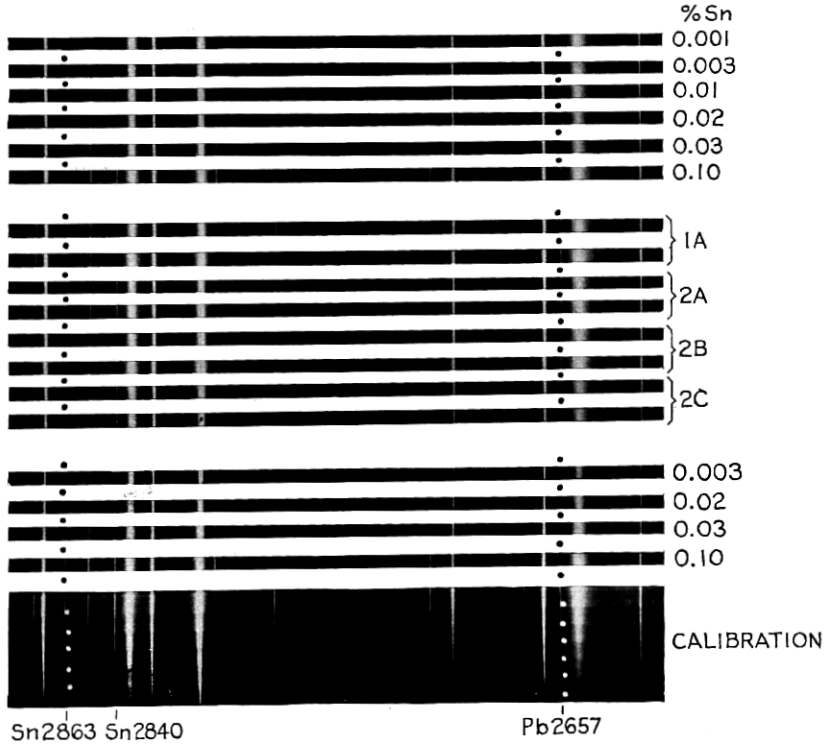

Fig. 7—Analysis of lead-antimony cable sheath for tin. An application of the internal standard method with plate calibration by the step sector.

Another example of this sort of analysis is the identification of aluminum alloys. It is a not uncommon occurrence for an alloy supposed to be of a certain composition to exhibit physical properties which would not be expected of such an alloy. Frequently it is important, therefore, to check the composition of the alloy and still preserve it for other tests. Now in the Bell System there are nine commonly used aluminum alloys, each of which contains different proportions of copper, manganese, magnesium, silicon, chromium and nickel. By examination of the spectrum obtained from a few grains of filings the analyst can easily tell by estimating the amounts of these minor components which of the nine alloys comprises the sample in question (Fig. 4).

3. Quantitative Analysis With High Speed and Moderate Precision

The greatest advantages of the spectrochemical method are speed, sensitivity, and flexibility of application. In many cases if a new material can be analyzed quickly only a moderate degree of precision is necessary. To fulfill such conditions an application of the method has been developed [3] which can be used for almost any material that can be dissolved in common solvents. The sample is first analyzed by method (1) or (2) above to find its approximate composition if that is not already known. Then a concentrated solution of the sample is prepared.

Another solution is prepared from pure specimens of the base materials present in the sample. To portions of this pure solution known amounts of the impurities present in the sample are added so that standard solutions are available for comparison with the sample. Spectra of the sample solution and the standard solutions are photographed on the same plate, using arc excitation on graphite electrodes, and the percentage of each impurity is estimated by comparison of line intensities. The method is capable of a precision of better than $\pm$ 10 per cent of the amount determined and can frequently be applied with little modification in cases where chemical methods would require considerable development work before they could be used. Furthermore the total sample needed for analysis is always very much less than is needed for a chemical analysis.

Since this is the quantitative method most widely applied in this laboratory numerous examples could be cited. To mention a few: aluminum, arsenic, tin and zinc in lead-base alloys, zinc in tin-base alloys, zinc in aluminum-base alloys, and cadmium, lead, tin, copper,

[3] Nitchie, C. C., *Indus. & Engg. Chem. (Anal. Ed.)*, *1*, 1 (1929).

iron, and magnesium in zinc-base alloys have been determined by this method.

4. Routine Analysis

In certain cases the spectrochemical method is superior to wet methods for routine quantitative analysis. In such cases dependence is placed on a set of solid standards whose composition is known, a set of standard solutions as in the foregoing section, or a standard working curve prepared by plotting the logarithm of the relative intensity of impurity lines as compared to lines of the base metal against the logarithm of the concentration of the impurity. In the latter case recourse is had to a photometric means of determining relative line intensity. The most common methods are the logarithmic sector method and the densitometer method (see next section). Both require considerable work to prepare the standard curve, but if many samples are to be analyzed periodically a saving in time results. The precision in such cases may be better than $\pm$ 5 per cent of the amount determined.

A few cases follow in which the spectrochemical method has proved superior for routine uses: (1) the analysis of zinc-base alloys, where it is more rapid; (2) the determination of zinc in tin-base alloys and in aluminum-base alloys, where no chemical or microchemical methods are available for the smaller amounts; (3) the determination of silicon in beryllium and aluminum oxides, where it is much more rapid (Fig. 3); (4) the determination of tin in lead-antimony cable sheath where it is more rapid; and (5) the determination of magnesium in nickel alloys where it is more economical of time and sample.

5. Quantitative Analysis with High Precision

Of recent years much of the published research on spectrochemical analysis has been concerned with attempts to improve the precision of the method. Applications of the densitometer and of the logarithmic sector have achieved something in this direction. Both of these devices have been used with some success in this laboratory. We have also developed a rotary electrode assembly (Fig. 5) which achieves a fairly steady mean position of the arc by causing it to vibrate rapidly about a point on the optical axis rather than to wander in a random manner over the electrode surface. The apparatus is applicable to the analysis of solutions in the graphite arc and to the analysis of alloys which can themselves be used as electrodes. Salts and other loose powders of course cannot be rotated at high speeds (600 R.P.M. is recommended).

The highest precision has been claimed by Duffendack and his

co-workers,[4] who use a "stepped diaphragm" to calibrate each plate with an intensity pattern in order to restrict their density measurements to the straight-line portion of the characteristic curve of the plate or to correct for deviations from the straight line portion. In this laboratory a step sector (Fig. 6) has recently been used to put the intensity pattern on each plate and the characteristic curve (Fig. 8) determined from this, using a photoelectric densitometer built in this laboratory. It is obvious from this curve that the measurement

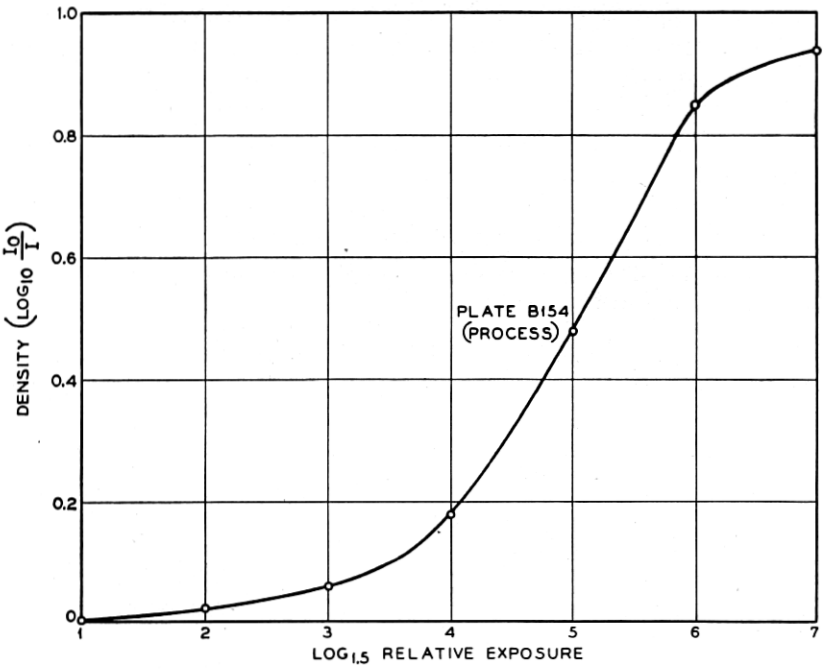

Fig. 8—A typical characteristic curve (exposure = intensity × time).

of the ratio of intensities of a given pair of lines varies with the densities of the lines as recorded on the plate. In this way errors of considerable magnitude may be introduced unless a calibration is made of the response of the plate to various levels of intensity of light of the wavelengths concerned. Results to date have shown an increased precision in all cases where plate calibration has been used, and a precision of better than ± 5 per cent of the amount determined is not uncommon. Examples from our experience include tin in lead-antimony cable sheath and other lead alloys (Fig. 7), magnesium in

[4] Duffendack, Wolfe, and Smith, *Indus. & Engg. Chem. (Anal. Ed.)*, *5*, 226 (1933) and others.

nickel filaments, and strontium-barium ratios in vacuum tube filament coatings.

6. Quantitative Analysis of Minute Traces

It has often been pointed out that spectrochemical methods can be used to assist classical and micromethods by establishing the purity of precipitates, checking the completeness of separation, demonstrating the presence or absence of interfering elements, etc. It has only infrequently been realized, however, that extremely minute concentrations of impurities can be determined by a combination of the two methods. In many cases a chemical separation can be made in which all of the impurities are removed from the bulk of the base material (it is not essential that *all* of the base material be separated as it is in chemical analyses) and can then be concentrated to fall within the spectrochemical range. In this way impurities can be determined by, say, method (3) above which could not be detected by direct excitation of the original sample. Scrupulous cleanliness and the carrying through of a reagents blank are, of course, essential when dealing with such small quantities.

7. As a Research Tool

Many times the spectrochemical method can be applied as a probe in obtaining important clues in a research project. This is particularly true when two presumably identical materials show unexpected differences in behavior. The research man may use nominally pure materials which are never really pure and thus introduce unsuspected impurities into his system which vary with different lots of materials. The spectrograph readily shows up differences in composition of the final product and thus often indicates the beneficial or detrimental effect of impurities.

In certain types of research on thin layers, the spectrochemical method is the only one of sufficient sensitivity to be used for quantitative analysis of the layers. Thus in thermionics it has been possible to measure the amounts of material on tungsten corresponding to changes in work function of the surface. Many other applications to thin films are possible and some are being worked on in this laboratory.

Thus it will be seen that chemical analysis by the emission spectrum is a powerful and versatile tool which enjoys and deserves an increasingly important role in communication research.

Acknowledgment

We are indebted to Mr. E. K. Jaycox for some of the method development as well as several of the spectrograms reproduced here.