

**The Institution of Post Office Electrical Engineers.**

**Recent Applications of the Quartz and X-Ray  
Spectrographs to Post Office Problems**

R. TAYLOR, M.A., Ph.D., B.Sc.

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The object of this paper is to describe the developments in the uses of the Quartz Spectrograph and the X-Ray Spectrograph since the papers on these subjects read before the Institution by Mr. F. O. Barralet<sup>1</sup> in 1925 and by Dr. W. G. Radley<sup>2</sup> in 1929. Such repetition as there may be is felt to be necessary in order to make the developments clear.

## Chemical Analysis with the Quartz Spectrograph.

The growth in the interest and importance of this subject can be illustrated in several ways. In 1925, the year of Mr. Barralet's paper, eight papers were published relating to chemical analysis by means of atomic emission spectra: in 1939, and again in 1940, there were about one hundred.

Since 1933 there has been an annual conference on "Spectroscopy and its Applications" held at the Massachusetts Institute of Technology. In July, 1940, thirty-one papers were presented and discussed. A book, "Spectrographic Analysis in Great Britain,"<sup>3</sup> published in 1939, contains twenty-five contributions from scientific and industrial laboratories in this country in which applications of spectrographic methods to the analysis of metals, glasses, paints, fabrics, soils and plants are described. That these applications are not confined to the common uses of these materials is shown by contributions discussing their use in the technology of art, in archæology and in forensic science.

This recent, rapid, development is the more remarkable since it was as far back as 1860 that Bunsen and Kirchoff published a paper entitled "Chemical Analysis by Means of Spectral Observations." However, fifty years later, H. Kayser, author of the monumental "Handbuch der Spektroskopie," expressed these opinions: "Under these circumstances there is little prospect that in the future qualitative analysis will apply spectroscopic methods to a large extent," and "I come to the conclusion that quantitative spectroscopic analysis has shown itself as impractical." Yet the greater number of the recent papers is concerned with the apparatus and methods developed for quantitative analysis. It is due to the faith and perseverance of experimenters like W. N. Hartley and A. de Gramont that foundations were laid on which, during the past twenty years, following a period of neglect, there has been and still is being built an imposing edifice.

Everyone is familiar with the production of a spectrum, even if it only be by the refraction of a sunbeam in the prism of a chandelier. The prism analyzes the light emitted by the sun into its component colours, but "any atom or molecule will emit light if it be struck a hard atomic blow and all light originates from atoms which have thus been stimulated by heat or electricity."<sup>4</sup> The fundamental property

which makes spectrographic analysis possible is that each kind of atom emits a characteristic light, and the analysis of a given source of light into a spectrum by a prism or a diffraction grating shows which kind of atoms are present in that source.

The modern theory of spectra is closely linked with the modern theory of the atom. It was in 1913 that the Danish physicist, Niels Bohr, working with the late Lord Rutherford, was able to explain an empirical relationship between the wave-lengths of a series of lines in the hydrogen spectrum (Balmer Series), by combining Rutherford's result that the atom appeared to be composed of a central positively charged nucleus surrounded by a cluster of negatively charged electrons, with the quantum theory. Bohr postulated, first, that an atomic system possesses a number of stationary states in which the electrons can move without the emission of energy radiation taking place, although such emission is to be expected on the basis of classical electrodynamics, and, second, that any emission or absorption of energy radiation will correspond to the transition of an electron between two stationary states, such radiation being homogeneous and having a frequency  $\nu$  given by the expression

$$h\nu = A_1 - A_2$$

where  $A_1$  and  $A_2$  are amounts of energy associated with the two stationary states and  $h$  is Planck's constant. The rules determining the various possible stationary states and governing the transitions between them need not be considered here. It is sufficient that an atom be considered to possess a number of stationary states at different levels of energy, some occupied by electrons and others empty. It is only the outer electrons that are easily excited. "Stimulation by heat or electricity" raises some of these electrons to levels of higher energy, and light of the appropriate frequency is radiated when these gaps are subsequently filled. The amount of energy associated with one such transition is very minute—for a wave-length in the visible spectrum it is of the order of  $10^{-12}$  ergs. or one thousand million millionth of the energy required to light a 100-watt lamp for a second—but as millions of atoms are simultaneously affected the result becomes observable. The amount of the stimulation has an important effect on the spectrum that is obtainable: the comparatively mild disturbance of a flame or low voltage electric arc excites the atom to a limited extent and may just suffice to raise an electron to the next highest energy level. The spectral line or lines emitted on reversion to the normal state in this case are the most sensitive or persistent lines of the element, which de Gramont called the "raies ultimes." If the energy is sufficient to displace the electron completely from the atom, then all the permitted lines corresponding to the stationary states of the neutral atom can be emitted—the complete arc spectrum is obtained. The more violent disturbance caused by an electric spark produces some extra lines because some atoms which have already lost one electron become further excited before they have a chance of returning to their normal state; these lines correspond to stationary states of an ionised atom and are known as "spark lines." The most

<sup>1</sup> "Some Applications of Optical Methods to the Examination of Engineering Materials." Printed Paper No. 108.

<sup>2</sup> "X-Rays, and the Structure of some Engineering Materials." Printed Paper No. 121.

<sup>3</sup> Edited by A. C. Candler. London: Adam Hilger, Ltd.

<sup>4</sup> "Atoms in Action," by G. R. Harrison, p. 156.

violent disturbance is caused when the atoms are bombarded by high speed electrons. These are able to penetrate the outer layers of electrons and excite those near the nucleus. When the energy is sufficient to expel one of these electrons from the atom, the resulting gap is filled by an electron from a higher energy level in the atom, and as the energy difference  $A_1 - A_2$  is large near the nucleus where the electrostatic attraction is great, high frequency radiation is produced ( $10^{18}$  vibrations per sec.). This radiation is known as X-rays.

Thus, the Rutherford-Bohr atom gives a qualitative explanation of both optical and X-ray spectra, but it is from accurate spectroscopic measurements that many of the finer details of atomic structure have been filled in.

The quartz spectrograph in use at the Post Office Research Station is shown, with its cover off, in Fig. 1. It is one of the earliest of the large models made by Messrs. Adam Hilger Limited, and was described in detail by Mr. F. O. Barralet.<sup>5</sup> Quartz is used for the prism and lens instead of glass in order that the ultra-violet region of the spectrum may be examined. Fig. 2 shows some typical spectra taken with the instrument: they have a varied degree of complexity, related qualitatively to the element's Group in the Periodic Table. The arc and spark spectra of copper are also shown, produced respectively by a 50-volt, 1-ampere arc and a 5000-volt spark. In the days before the black-out mercury and sodium vapour lamps were becoming familiar sources of street light-

<sup>5</sup> Loc. cit., p. 28.

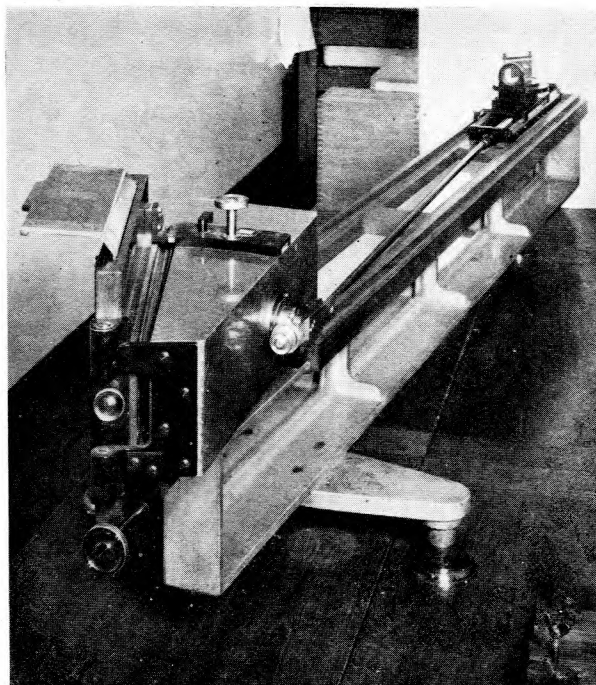


FIG. 1.—QUARTZ SPECTROGRAPH.

ing: the spectra of these elements show that the distinctive colour of the former is due to the combination of the characteristic green, blue and violet lines, and of the latter to the strong pair of yellow lines.

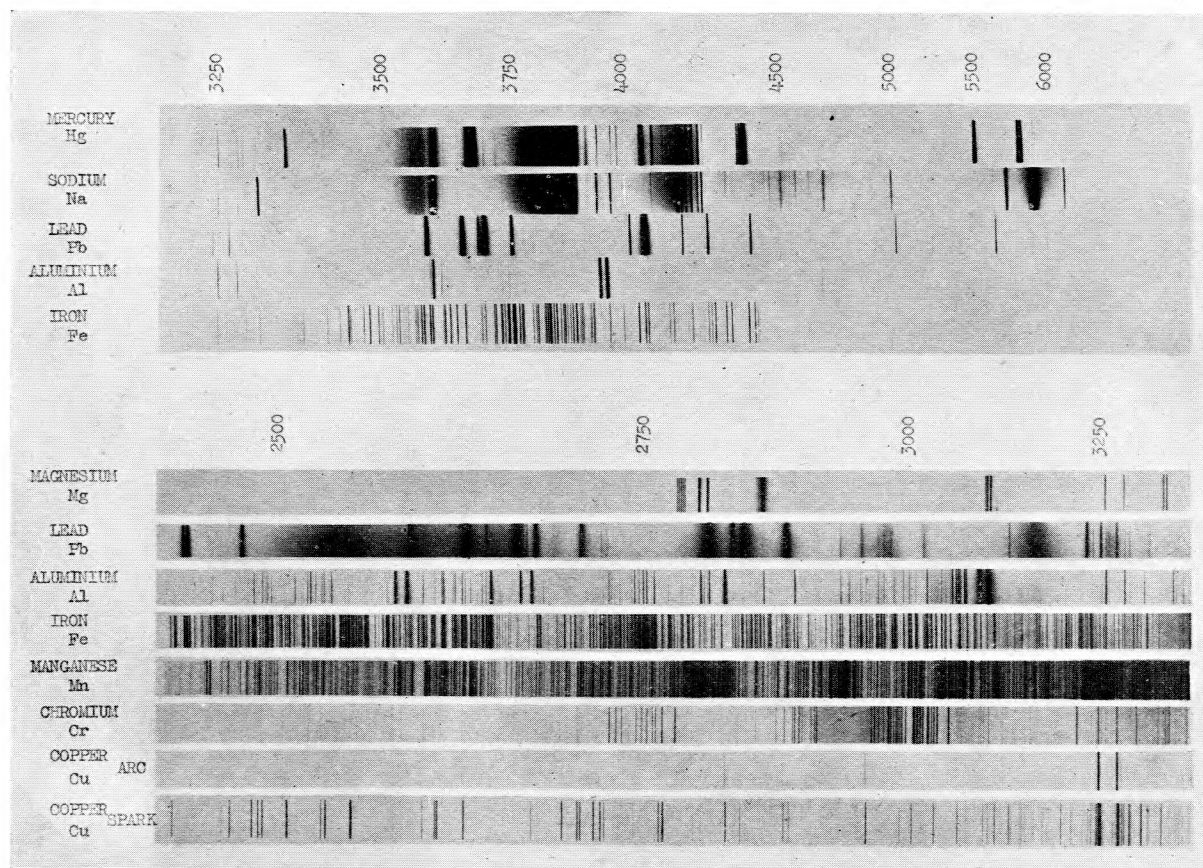


FIG. 2.

The heavy bands common to these spectra are due to the graphite electrodes which were used.

In qualitative analysis the spectrum of the material is obtained by suitable means—from arc or spark excitation—and either it is compared with spectra of the elements suspected to be present or the wave-lengths of the most intense lines are determined from their relation to those of a standard iron spectrum, photographed on the same plate. The elements present may then be identified with the aid of tables of wave-lengths: subsequently it may be necessary to check that the remaining lines are produced by these elements. When searching for small quantities of an element the most sensitive lines, the "raies ultimes," are looked for. It is convenient to have a set of reference plates containing the spectra of the more common elements in the ranges used on the instrument, so that identification is possible by superposition on the appropriate standard plate and matching the spectra. Alternatively the spectrum of R.U. ("raies ultimes") powder may be photographed on the same plate. This powder mixture, developed by J. W. Ryde and H. G. Jenkins, gives the sensitive lines of fifty elements and an indexed set of enlargements of its spectrum is provided. Inspection of the two spectra for common lines leads to the identification of the elements in the material. Another useful device, particularly when information is required about the impurities present in a sample, is to photograph the spectrum of the pure major constituent immediately above or below that of the sample, so that only the additional lines in the latter, those due to the impurities, remain to be identified. An example of this is shown in Fig. 3(a).

sample; solders from different sources; the cadmium plating on certain articles, where small amounts of mercury and zinc were in different proportions in two samples; certain light aluminium alloys, some of which contained nickel; fuse metals and lead accumulator plates.

The detection of contamination of, for example, rectifier plates by mercury vapour, a vacuum-deposited aluminium film by tungsten, and accumulator positive plates by antimony from the negative plates, is a further application. But perhaps the most useful and important application is simple identification, particularly when only a small quantity of material is available or the component must not be destroyed. Typical examples are metal films sputtered on ceramic bases and contacts of all kinds. In this latter category, such diverse materials as silver, tungsten, platinum, palladium-copper and silver-plated brass have been identified at one time or another. Some examples are illustrated in Mr. Barralet's paper (p. 30).

The spectrograph also affords a rapid method of distinguishing between copper, cadmium-copper and bronze overhead line-wires which may have been recovered after damage. (Fig. 3(a)). On several occasions another kind of "recovered" wire has been examined to determine whether, on the basis of its composition, the Post Office could disclaim ownership of wire which had been found during the post mortem examination of a cow.

It should be emphasised that negative results are frequently as valuable as positive, and the sensitivity of spectrographic methods is admirably suited to checking the purity of materials. Harrison wrote<sup>6</sup>—

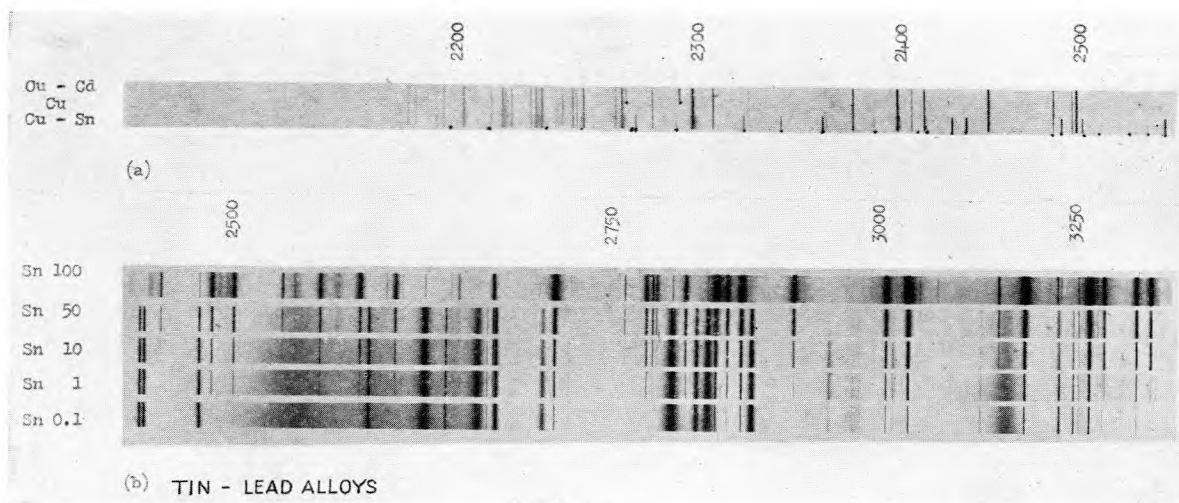


FIG. 3

Related to this last method is one which helps to solve a type of problem frequently met in the Post Office Research Station—that of two similar materials which behave differently in practice. By photographing the two spectra side by side it can be seen at a glance whether a difference in composition may account for the different behaviour. Examples of this have occurred with phosphor-bronze springs, where a good sample was shown to contain more lead and phosphorous and less zinc and silver than a poor

"the chemist finds that a tiny pinch of salt needs more than a bath-tub full of water in which to hide from the ferreting eye of the spectroscopist. . . . So bright is the light which the atoms in a small speck of metal can emit, that a piece of brass the size of a pinhead will serve for the complete determination of the presence or absence of seventy of the chemical elements, and none will be overlooked which is present

<sup>6</sup> "Atoms in Action," by G. R. Harrison, pp. 156-157.

in an amount as great as one-millionth part of the whole." At the Post Office Research Station some accumulator negative plates were analysed to determine whether the possible contamination with an aluminium salt had actually occurred and, in another case, galvanized wires, suspected of being produced in a bath containing aluminium, were tested and shown to be free from that metal.

These examples of qualitative analysis are, however, recent applications of old-established methods, but it is in quantitative analysis that the most progress has been made and in which a widely increased field of application may be looked for.

Fig. 3(b) shows the spectra of a series of tin-lead alloys. It has been arranged that the lines due to lead are of about the same intensity in all the spectra, and it is to be noted how the intensity and number of the tin lines decrease as the concentration diminishes. The problem for quantitative analysis is "What is the relation between the number of lines or their intensities and the quantity of the element?" Although some earlier workers based their analysis on the number of lines or, what is equivalent, on the appearance or disappearance of certain lines, such a method has obvious disadvantages, and methods based on intensities appear more promising. It is not, however, possible yet to photograph a spectrum of the material and to look at a particular line and be able to say how much of the constituent is present. In some way the spectrum has to be referred to a known standard, or some form of calibration curve has to be used. For example, results obtained from the spectra of a series of standard alloys may be plotted against the corresponding compositions to give a reference curve; or, if the concentrations of certain minor constituents or impurities in an alloy are required by specification to be within certain limits, the spectra of standard alloys containing respectively the maximum and minimum quantities allowed may be recorded on the same plate as those of the alloys under test.

The following are some of the factors which influence the appearance of the spectrum and its use for quantitative work:—

- (a) The source of light.
- (b) The condition of the electrodes.
- (c) The technique of producing the spectrum.
- (d) The recording of the spectrum and its standardisation.
- (e) The existence of suitable lines in the spectrum.

(a) The influence of flame, arc or spark excitation on the spectrum produced has already been discussed. The use of flame spectra in quantitative analysis is comparatively rare, though Lundegårdh in Germany, and a few workers in this country, have developed methods for giving a constant source with acetylene-air and oxy-hydrogen flames, the material being fed steadily in the form of spray or of a deposit on filter paper. The main application is in the estimation of the alkali and alkaline earth metals in biological materials and soils.

In the production of arc spectra, voltages of 50-250v. and currents of one to fifteen amperes are commonly used, control being effected by means of a variable resistance. Although arc methods are very sensitive—the high temperature developed vaporizing considerable quantities of the material—it is difficult

to keep the arc from wandering and, generally, to maintain the intensity of illumination constant. Gerlach uses an interrupted arc, in which the electrodes are repeatedly brought into contact and separated: this tends to reduce the continuous background of the spectrum by keeping the electrodes cooler, and to improve the stability of the light source. The Pfeilsticker method avoids mechanical movement by the use of high-frequency excitation. Recently, in America, a high-voltage alternating current arc has been recommended.

Spark methods, which involve a higher atomic temperature but a lower electrode temperature than arc methods, are found to give the most reproducible results. An A.C. transformer with capacitance and inductance is the most common type of sparking circuit. The values of the circuit elements used at the Post Office Research Station are 5000 volts, 0.015 or 0.005  $\mu$ F and 0.25 mH, the first capacitance being used in qualitative, the second in quantitative analysis. The conditions have a marked effect on the brightness and stability of the spark. For example, a reduction in the amount of inductance produces an increase in the brightness and noise of the spark and, it may be because of the greater mass of material volatilized, the minimum possible inductance is frequently recommended for obtaining greater accuracy in the analysis of certain aluminium alloys. With this type of circuit a number of separate flashes are produced for each period of the primary frequency, those after the first depending on the ionisation of the gap. To isolate the first discharge the method of the interrupted spark was developed independently by Feussner and at the Post Office Research Station. At the latter, the basic idea was to obtain the frequent natural discharge of a condenser charged to a specified voltage. Two metal sectors (Fig. 4), 90° and 180° respectively, are con-

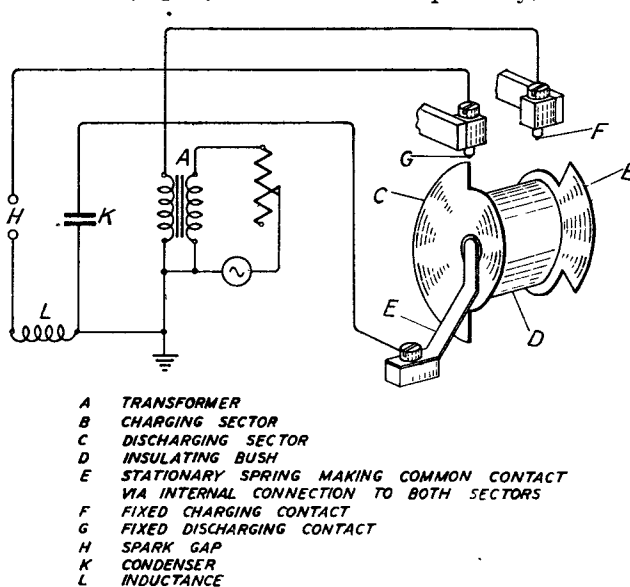


FIG. 4.—SPARK INTERRUPTER.

nected electrically and fixed concentrically, but out of phase, on an ebonite bush attached to the shaft of a 3000 r.p.m. synchronous motor. The common contact is connected to the condenser, and the two fixed contacts, past which the sectors rotate, to the transformer and electrode respectively. The fixed contacts

are so placed that the forward corner of the smaller (charging) sector is opposite the contact at the instant the voltage is zero. Thus the condenser is charged during a quarter of the alternating cycle to approximately the peak voltage developed by the transformer, and is then discharged during some part of the rest of the cycle. The result is a series of steady sparks occurring fifty times per second.<sup>7</sup> It is considered in many quarters that this refinement is not needed and that the same degree of accuracy is attainable with the simple sparking circuit.

(b) The shape and size of the electrodes, which are important factors in obtaining reproducibility, are to some extent dependent on the form of the material available. Where possible, cylindrical rods are used, but there is a difference of opinion as to whether they should be cut off flat, rounded off, pointed, or made wedge-shaped. In the case of lead or lead alloy cable sheathing, narrow ( $\frac{1}{4}$ -inch) strips are cut from the flattened sheath and filed to a blunt wedge: alternatively the opened sheath is rolled to a definite thickness and cut off square. When the shape of the material supplied is very awkward it may be necessary to dissolve it in a suitable solvent and to analyse the solution. Specially purified graphite rods are available in which a small cup can be drilled to take a drop or two of the solution (to facilitate the retention of the material in the cup and to make the subsequent discharge steadier, the cup is filled with some graphite chips). After drying, this electrode is matched against a solid graphite rod, which may or may not be sharpened to a point. A cup in a graphite rod can also be used for powders, but some workers prefer to form these into pellets to be placed on the lower electrode of a metal (copper or silver) arc.

It will be realised that with metal electrodes, and particularly with spark excitation, very little material is used, so that there may be a danger that a representative sample is not obtained, particularly from a heterogeneous alloy. Tests have been made in which one electrode with a large surface is moved relatively to the second electrode during an exposure. Some tests were also carried out at the Government Laboratory with a rotating electrode device—two discs moving at different speeds—which was developed at the Post Office Research Station. This device gives a sparking surface some fifteen times the normal electrode surface. The results for iron in "pure" aluminium and for copper in solder, where segregation might well occur, showed that the normal electrode presents a surface which is a good average of the bulk metal. Where heterogeneity is known or its presence is suspected an "average" spectrum may be taken by superimposing the spectra obtained by sparking to two or three different parts of the surface.

Recently it has been discovered that the state of an alloy—cast, wrought or annealed—affects the intensities of some of the lines in the spectrum, so that care has to be taken that standard samples are in the same condition as the unknown samples.

(c) In producing spectra with such an instrument as that at the Post Office Research Station it is necessary first of all to decide which section of the spectrum is required, and then to make the appro-

prate adjustments. The width of slit and the method of illuminating it remain to be decided. The resolution required and the amount of light available determine the former, and widths of 0.005 mm. to 0.05 mm. have been used in different circumstances. Some workers illuminate the slit directly with the source, others use a condensing lens. A spherocylindrical lens produces an elongated image and gives good intensity, but the image is not uniform enough along its length for accurate quantitative work, and for this a spherical condensing lens is used. By forming the image of the light source at the spectrograph lens, the required uniform illumination is obtained.

(d) Attempts have been made to measure the intensities of the spectral lines directly, using devices incorporating photoelectric cells, but it is more usual to photograph the spectrum and to assess the lines obtained on the photographic plate. For quantitative work at the Post Office Research Station, Ilford Ordinary plates are used, and Ilford Zenith plates for qualitative analysis. The plates are developed and fixed normally, although for quantitative work care is taken to standardize the conditions.

Unfortunately, however carefully the conditions of producing and recording the spectrum are standardized, the result is not absolutely invariable. By some means therefore the spectra on each plate have to be standardized. There are two distinct types of methods. In the first a reference line is found in the spectrum itself, in the second the plate is calibrated independently. One of the earliest and most used methods of the first type is to choose one or more lines of the base metal as a standard of reference. The variation in the content of this main constituent in the alloy, due to small changes in the quantities of impurities or minor constituents, is inappreciable and experience justifies the assumption that the spectrum of the main constituent remains unchanged. Suitable lines due to the minor constituents are selected and a table is prepared showing the compositions at which their intensities are equal to those of the standard lines, as judged by visual comparison (Fig. 5). With the methods of measuring intensities now available, this scheme may be expanded to include relative intensities differing from unity. Two such methods have been used at the Research Station. In the earlier method a logarithmic sector was used in the production of the spectra, in the present method a photoelectric microphotometer is used to measure the blackening of uniform spectral lines.

When the logarithmic sector—a disc, the periphery of which is cut in the form of a logarithmic spiral—is rotated in front of the slit of the spectrograph the lines of the spectrum recorded on the plate vary in intensity along their length, the less intense lines fading out. It has been shown that the difference in length of two lines is a measure of the ratio of their intensities in the source. By suitable selection of one line produced by the base metal and a second by the minor constituent, a figure can be obtained for that particular concentration. The method of analysis consists in obtaining the differences in length of this pair of lines for a series of alloys of known composition and plotting a "working" curve. It is found that the differences are a linear function of the logarithm of the composition over a moderate range of composition. The corresponding difference in length is obtained for

<sup>7</sup> This description is taken from the Post Office Research Station contribution to "Spectrographic Analysis in Great Britain."

Tin Lines.	2335.	2355.	2381.	2422.	2572.	2594.	2707.	2840.	3021.	3175.	3801.
<i>T<sub>in</sub></i>											
Per Cent.											
0-002								b.v.			
0-004								b.v.			
0-006								< Pb			
0-01								> 2657			
0-02								< Pb			
0-05		b.v.		b.v.				> 2717	b.v.		
0-1								< Pb			
0-2								> 3044			
0-25	b.v.							< Pb			
0-3		< Pb			b.v.			> 2628			
0-4		> 2332		< Pb	< Pb						
0-6		> 2389		> 2389	> 2657						
0-8			b.v.			b.v.					
1-2											
1-6											
2-0											
2-5											
3-0											
4-0											
5-0											
7-0											
9-0											

from J. Inst Metals

FIG. 5.—TIN IN LEAD AND LEAD ALLOYS.

the unknown alloy and its composition is then read from the curve.<sup>8</sup> One of the serious difficulties in this method is the determination of the end of a line which gradually fades out, though it is probably true that if a worker is using the method frequently on a routine test he will produce consistent results. A modification of this method is to use a step-sector which breaks the spectral lines into a number of steps of graduated intensity. Photometric measurement of the intensity of a step on one line and comparison with the intensities of the next weaker and stronger steps on the second line is a further improvement, which is extensively used by Breckpot and the Louvain school in Belgium.

The photoelectric microphotometer is illustrated in Fig. 6. A constant source of light from a lamp with a straight filament is brought to a focus on the emulsion side of the photographic plate and an enlarged image (ten times) is projected on the slit of the box containing a rectifier type photoelectric cell. The cell is connected through variable shunt and fixed series resistances to the galvanometer. The plate-holder can be moved in two directions at right angles, the motion parallel to the spectrum being controlled for short distances (2 cm.) by a screw and a slow-motion worm gear. An auxiliary lens enables a portion of the spectrum to be seen on the face of the cell box so that the lines to be measured can be set to the right position. With an unexposed portion of the plate in the beam, the shunt resistance is adjusted to give a standard deflexion of the galvanometer—50 cm. The image of the spectral line to be measured is then brought near the slit and by the slow motion made to traverse it. The minimum deflexion of the galvanometer, corresponding to the maximum blackness of the line, is noted. The densities of the other lines are determined similarly.

It is not necessary here to discuss the theoretical basis of the relationship between the intensity of the spectral line in the light source and the galvanometer deflexion obtained as above. For lines that are not

too intense nor too faint, the density of the line (I) is given by the expression

$$I = \log d_0 - \log d$$

where  $d$  is the galvanometer deflexion for the line and  $d_0$  for the unexposed portion of the plate. The difference in density of two lines (1,2) is thus equal to the logarithm of the inverse ratio of the deflexions.

$$I_1 - I_2 = \log d_2 - \log d_1 = \log \frac{d_2}{d_1}$$

The differences in density of a line of the base metal and one of the minor constituent are obtained for a series of compositions, and the working curve is obtained by plotting the results against the logarithm of the composition.

For the independent calibration of the plate, it is necessary that it be exposed to a set of radiations of known relative intensities. The methods adopted include the use of a slit with varying widths in known steps, a stepped sector (Breckpot's method) and a platinised plate of stepped densities. In all these cases the relative blackening of the different steps can be related to the relative intensities producing them and then the blackening of suitable spectral lines can be matched to these standards. It has been established that equal intensities on a photographic plate are not affected by slight variations in technique as unequal intensities may be.

(e) All the factors which have been discussed above depend finally upon the presence of suitable spectral lines. The response of photographic plates is a function of the wave-length of the incident light so that in the first place the lines chosen should not be too far apart: this was more necessary when visual comparison of intensities was used, and it is less necessary now that the plate may be calibrated for several wave-lengths in the range photographed. It is also necessary that the chosen lines should not be masked by others: the minimum permissible difference in wave-length allowed depends on the instrument, on the intensity of the lines and on the part of the spectrum. The excitation of the lines has to be considered; some lines are produced with comparatively

<sup>8</sup> For further details, see "The Quantitative Spectrographic Analysis of Lead Cable-Sheath Alloys," by G. H. Metson. *P.O.E.E. Journal*, 1932, Vol. XXV, p. 143.



little stimulation while others are very difficult to produce. Gerlach early recommended the use of lines whose intensities relative to one another do not vary with even widely varying electrical conditions. He was concerned with lines of equal intensity and, while the modern methods of measuring intensities permit of less severe restriction in this respect, it is still advisable to adhere to the first suggestion and, in general,

The problems of quantitative spectrographic analysis and the methods of dealing with them have been discussed—what of the results obtained? One point of interest is the agreement between the result of the spectrographic determination and that of a chemical analysis of the same material: a further point, equally important in deciding on the validity of the method, is the agreement between successive spectrographic

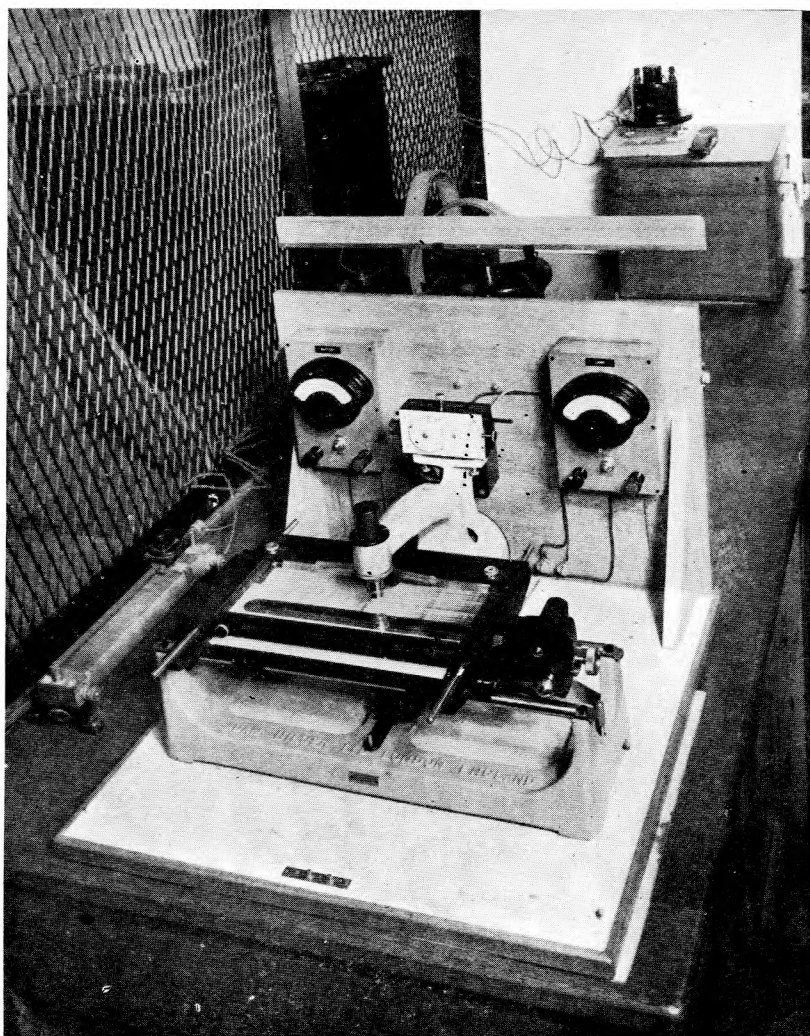


FIG. 6.—PHOTOELECTRIC MICROPHOTOMETER.

to compare arc lines with arc lines and spark with spark. The comparison of an arc line with a spark line in the spectrum of the base metal is often used as a check that the electrical conditions have been correctly reproduced, since this relationship is sensitive to changes.

Even when the base metal can provide no suitable line for comparison with that of the minor constituent in conformity with the above conditions, the spectroscopist is not beaten, for it is sometimes possible to use an auxiliary spectrum containing suitable lines. This may be done by using the auxiliary element as the second electrode or, in the powder or solution method, by the addition of a definite quantity of another element.

analyses. In a series of sixty-three determinations of an antimony-lead alloy, H. Kaiser found that all but three of his results were within 2.64 per cent. of the mean result with an average deviation of 1.1 per cent. With favourable materials, other workers have obtained similarly good reproducibility. Compared with chemical analysis, as a general statement, an accuracy of  $\pm 10$  per cent. of the amount of the minor constituent can be claimed for visual methods and  $\pm 5$  per cent. as an average figure for microphotometric methods. In particularly favourable circumstances, using a solution method, O. S. Duffendack obtained results consistent to  $1\frac{1}{2}$  per cent. In a number of cases, chemical analysis is insufficiently accurate fully to realise the accuracy of modern

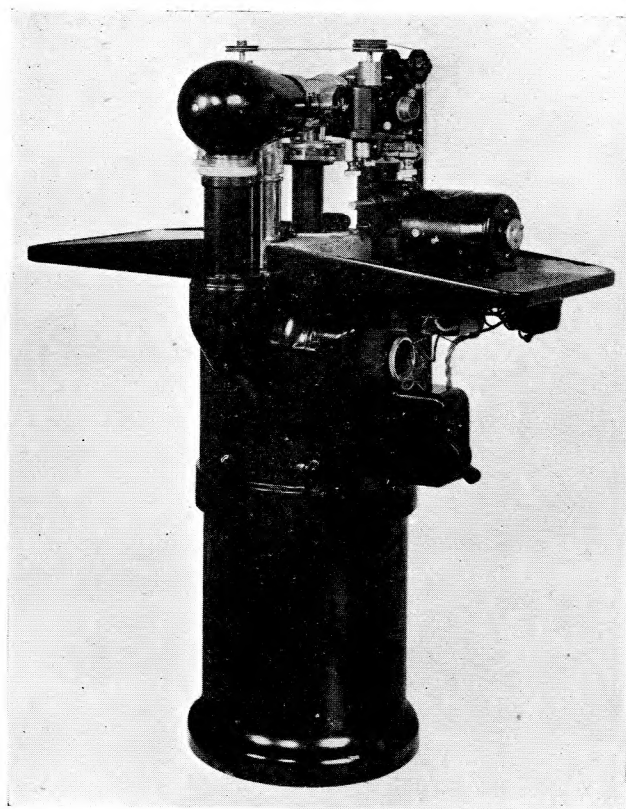


FIG. 7.—X-RAY SPECTROGRAPH.

methods of spectrographic analysis. It must be emphasised, though, that chemical and spectrochemical methods are complementary. For some analyses, particularly where the quantity is small or the chemical separation difficult, the latter is to be preferred; for others, and always for the major constituents, the chemical methods are necessary.

### X-Ray Spectrograph.

Dr. Radley has described the phenomenon of the diffraction of X-rays so thoroughly in his paper that only recent developments in its applications are dealt with here. It is necessary to make quite clear that the difference between the quartz and X-ray spectrographs is not simply a difference of wave-lengths, although, as mentioned earlier, the chemical elements have characteristic X-ray line spectra, the wave-lengths of whose lines may be measured with the aid of a diffraction grating spectrograph. In the type of X-ray spectrograph to be described, the crystal, which is the equivalent of the diffraction grating is the unknown and the source of radiation, characteristic of a particular metal, is known. The diffraction pattern or spectrum is related to characteristics of the crystal, rather than to the X-rays, although a change in the X-ray wave-length would modify the positions of the lines of the pattern. Thus unknown materials may be identified by analysis of the pattern or by a comparison of it with the patterns of known compounds. Some patterns and the arrangement of the atoms producing them were shown in a recent issue of the P.O.E.E. Journal.<sup>9</sup>

<sup>9</sup> July, 1940, Vol. XXXIII, p. 56.

In his paper, Dr. Radley stated that some of the patterns he obtained required exposures of several hours: in the apparatus shown in Fig. 7 this time is reduced to 20-45 minutes, and recent developments in X-ray tubes and the focussing of the beam make even shorter exposures possible. The apparatus at present used at the Post Office Research Station is self-contained. The high-tension transformer and the fan for cooling the anti-cathode are in the base and the X-ray tube is so arranged that strong beams of radiation emerge on both sides, so that two photographs can be taken simultaneously. The cameras, which are demountable, fit securely on rotating arms so that they can be set to receive the radiation from the target at a grazing angle, thus giving a point or line source, the beam being further defined by a long diaphragm fitted into the camera. The camera is essentially a cylindrical brass box, with the diaphragm directed towards the axis and with a hole at the opposite end of the diameter: the film is fitted round the inside of the box. The specimen may be mounted either on the axis (Debye-Scherrer method) or on the circumference opposite the diaphragm (Seemann-Bohlin method): in the former case the specimen is usually rotated. The camera supports can be removed and the outfit is then available as a source of X-rays for use with other types of camera or other apparatus. Such a use is illustrated in Fig. 8, where the diffracted

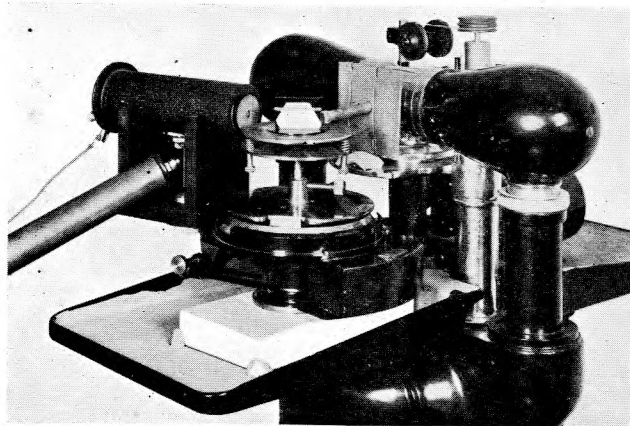


FIG. 8.—ARRANGEMENT OF X-RAY SOURCE, CRYSTAL AND IONISATION CHAMBER.

beams were detected with the aid of an ionisation chamber.

One of the most valuable uses of this method of analysis from the Post Office point of view is in the identification of the corrosion products often—too often—formed on the sheaths of lead-covered cables. Only a very small quantity of material is required, enough to cover a wire or glass fibre a few hundredths of an inch in diameter for a length of a quarter of an inch, and that material is not destroyed. It is unfortunate that lead absorbs X-rays so readily and that the patterns of the more complex lead compounds contain so many lines, but even so it has been possible in the greater number of samples examined to identify the compound with some degree of certainty by a comparison method. Among the other problems solved have been the identification of a black deposit on mirrors as finely divided aluminium, of the filling in Stabol as talc and of a jewel mounting as an agate.

Mixtures of Oppanol and Polythene have been shown to give the diffraction patterns of both constituents, indicating that they are not mutually soluble to any appreciable extent. On the other hand, some powders produced by the decomposition of a mixture of iron and nickel carbonyls and subsequently heat-treated, have been shown to be alloys (Fig. 9). The evidence

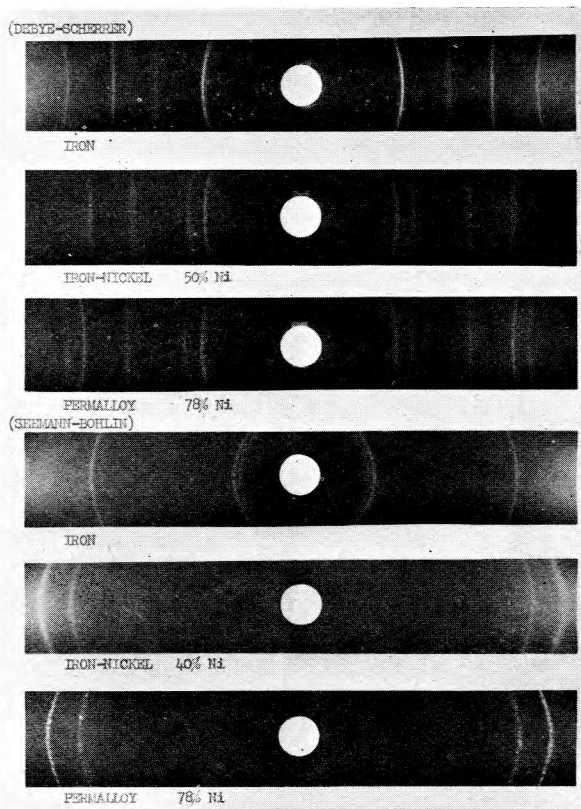


FIG. 9.—X-RAY PATTERNS OF IRON AND IRON-NICKEL ALLOYS.

for this is that there is no trace of the iron pattern in those of the alloys. The different distances apart of corresponding pairs of lines in the patterns of Permalloy and of alloys containing 40 and 50% nickel respectively indicate a difference in the spacing of the atoms. The "spottiness" of the Seemann-Bohlin pattern of Permalloy is caused by a grain size greater than  $10^{-3}$  cm., that of the other samples being  $10^{-3} - 10^{-5}$  cm.

The small camera (diameter  $5\frac{1}{2}$  cm.) at present in use does not permit of the characteristics of the crystals—the distance apart of the planes of atoms—being determined with a high degree of accuracy, but

by using other forms of camera in conjunction with the X-ray outfit some of the applications described below, which are comparatively recent developments in the use of X-rays, are possible. 19 cm. cameras are frequently used, and a 35 cm. camera has been used for very special work. As an indication of the accuracy obtainable by some precision methods, the distance apart of two atoms in a metal, if measured to one part in 100,000, is known to within  $10^{-13}$  inch.

Metals of all kinds are very widely used in the Post Office, and in many of the applications an X-ray crystal analysis would give valuable information. The radiographic aspects, such as the detection of flaws in metal castings are not included in this survey, but the finer study of the condition of the actual crystals in the material, whether they are too big or too small to perform their task to perfection. An estimate of the grain size can be made from an X-ray photograph. It can also tell if the material is in a heavily strained condition due to severe stressing in the forming operations or if the strains have been removed by annealing. Preferred orientation, due to the method of rolling, which may cause weaknesses in particular directions in a metal, is detectable by X-rays. A considerable volume of published work refers to the correlation of X-ray photographs with the fatigue properties of metals and alloys, in an attempt to determine whether the difference between a safe and an unsafe range of stress can be detected at an early stage; this problem must be considered as still in process of solution, though some satisfactory results have been claimed for specific tests on specific materials.

X-rays are also useful in examining the effect of alloying one metal with another, indicating whether the atoms of the added metal merely displace those on the base metal lattice and expand it so that they can fit more comfortably or whether they cause such strain that the original lattice breaks down and a new phase is formed. It may be considered that this can be solved by metallographic methods and so it can, but the X-ray method is frequently more convenient and quicker. The two methods are complementary. On the academic side, where X-rays have been used to determine the limits of composition between which different alloy phases can exist under equilibrium conditions, the results of the best work agree well with those of the best microscopic work.

This in outline indicates some of the types of problem in the solution of which the X-ray spectrograph can play a part, and there are probably many other applications.

It is evident that the usefulness of the Quartz and X-ray spectrographs to the work of the Post Office in the examination, control, and testing of materials is only just beginning.