Quantitative Chemical Analysis by X-rays and its Application.¹

By Prof. G. HEVESY, Freiburg im Breisgau.

THE late H. J. G. Moseley was convinced that his discovery of X-ray spectroscopy would prove to be of value to analytical chemistry. He had chiefly the analysis of alloys in mind, and his well-known photograph of the brass spectrum, showing the stronger copper and weaker zinc lines, can be considered as the first application of X-ray spectroscopy in the field of analytical chemistry. His untimely death prevented him from attacking any other problem than the connexion between atomic number and X-ray spectra. The result of his endeavour is well known; it led him to discover the fundamental law governing X-ray spectra.

The first application of X-ray spectroscopy to the analysis of minerals was made in 1922 by Hadding in Siegbahn's laboratory. Shortly afterwards, Goldschmidt and Thomassen made a very exhaustive examination of the relative abundance of rare earth elements in a great number of different minerals. By comparing the intensity of the X-ray lines, they concluded that very marked differences exist in the relative abundance of neighbouring even and odd elements, and confirmed the generalisation put forward by Harkins and Oddo.

The important problem studied by Goldschmidt and Thomassen could be most satisfactorily solved without a strictly quantitative analysis, the differences between the abundance of neighbouring elements being very marked. The necessity for a strictly quantitative application of X-ray spectroscopy was, however, apparent when in the same year Coster and myself had to face the problem of the separation of hafnium from zirconium. The two elements being so similar, it was necessary when testing the efficiency of a separation method to determine small differences in the hafnium-zirconium ratio. We added to the sample to be investigated just sufficient tantalum oxide to make the hafnium La_1 and tantalum La_1 lines appear in equal intensity on the photographic plate, and concluded that in this case the unknown number of hafnium atoms present equalled the known number of tantalum atoms. Later, tantalum oxide was replaced by lutecium oxide and the intensity of the hafnium- $L\beta_1$ and lutecium- β_2 lines compared. The wave-length difference of two lines amounts in the latter case to four X-units only, corresponding to $\frac{1}{5}$ mm. on the photographic plate. Closeness of the wave-length of the lines to be compared is of great advantage. The intensity ratio of these lines was determined experimentally and was found to be 2.55. Similar considerations to those which led to the choice of lutecium as the reference substance for the determination of hafnium induced us to take erbium as a reference substance when estimating tantalum, the lines to be compared being in this case tantalum- La_1 (1518.3 X units) and erbium- $L\beta_2$ (1510.6 X units), to use niobium or thorium when estimating zirconium, and so on.

The investigation of cases like those above mentioned, where a mixture of a few refractory oxides is to be analysed, can easily be carried out. In other cases, however, we encounter appreciable difficulties.

SOURCES OF ERROR AND THEIR ELIMINATION.

(a) Error is due to the fact that the initial ratio of the unknown element to the reference element in the surface layer of the sample, which alone is accessible to the exciting action of the cathode rays, changes during the experiment. (The half-value depth for β -particles, for example, accelerated by 20,000 volts is, in zirconium oxide, only 2×10^{-5} cm.) This change, chiefly investigated by Coster and Nishina, is due to the effect of cathode rays on the sample; under the action of the latter, chemical reaction or melting of the sample can occur, which may lead to a partial separation or shift of one of the two elements to a deeper part of the sample which is inaccessible to the cathode rays. Their action may in the same way lead to evaporation or electrostatic repulsion of one or both components.

(b) The presence in the sample of other substances than the element to be estimated and the reference substance, which we shall for the sake of brevity call 'impurities', though they may constitute the larger part of the mixture, may influence the intensity ratio of the two lines. First, one of the two lines may be absorbed more strongly by the impurity than the other; and secondly, the X-rays emitted by the impurity may excite the two lines to be compared by secondary action and increase their intensity. This excitation can be a selective one, and can lead to a false intensity ratio due to the presence of the impurity.

The errors due to causes discussed under (a) can be eliminated by avoiding the use of cathode rays for the excitation of the X-ray spectrum of the sample to be investigated. Not the sample itself, but a target of tungsten is bombarded by cathode rays, and the X-rays thus produced are used to excite the spectrum of the sample to be investigated. This method of X-ray analysis, where the secondary radiation is analysed, will be denoted as the secondary method, and the usual method, where the spectrum is excited by cathode rays, as the primary method. The secondary method has been used in several cases in recent years both by Glocker in Stuttgart and in my laboratory, and has been found to work very satisfactorily. In my laboratory an electronic tube constructed by Coster, and admirably suited for this purpose, is used. By using 40 k.w. and 10 milliamp., a fairly strong copper- $K\alpha$ line can be obtained in the course of three minutes. The energy necessary to produce a secondary line is very appreciably greater than that for a primary line of equal intensity, but in the case of the secondary method a much larger current can be used—up to 100 milliamp. and still higher.

¹ Paper read at a joint discussion between Sections A and B of the British Association at Johannesburg on Aug. 1.

This is due to the fact that in the latter case the energy is distributed over the large surface, whereas in the former case it has to be focused on a comparatively small surface of the sample.

Besides the above-mentioned advantages, a further advantage should be emphasised. When determining elements present only in minute amounts in the sample, it is often necessary to expose the plate for a long time to the action of the X-rays: in the case of the primary method, the time of exposure is limited by the fact that the continuous radiation emitted by the anticathode darkens the plate and covers the weak lines. In the case of the secondary method, the continuous radiation reaching the plate being negligible, the exposure can be continued for a very long time.

The curve on the left of Fig. 1 shows the analysis of cyrtolithe obtained by the secondary method; while that on the right shows the analysis obtained by the primary method. From the former the hafnium oxide content works out to be 11.1 per cent, in good agreement with the value obtained by analysing the zirconium oxide plus hafnium oxide extracted from the mineral (11.3 per cent), while the primary method gives an entirely false result.

While the errors due to the effect of cathode rays can be successfully eliminated by using the secondary X-ray method, as mentioned above, we may still encounter those discussed under (b). Selective absorption will occur when the absorption edge of an impurity, present in large quantities, is situated between the two lines to be compared. In this case a selective absorption of the line of the shorter wave-length can occur; for example, between nickel- $K\alpha_1$ (1655 X-units) and cobalt- $K\alpha_1$ (1785 X-units) the iron- K edge (1740 X-units) is situated. The presence of large amounts of iron

FIG. 1.—Photometer curves of cyrtolithe excited by X-rays (left) and by cathode rays (right).

in the sample can accordingly influence the intensity ratio. The most general remedy for such an error is to use very closely situated lines: when the wave-length difference is very small, the probability that an absorption edge will be situated between the two lines is only minute.

An example of the other case, in which strong lines of impurities are situated between the edges

of the two elements to be compared, is the presence of large amounts of zinc in a mixture of tantalum and erbium. The strongest lines of the K spectrum of zinc (α_1 ; α_2 ; β_1) are situated between the edges of the latter elements. The zinc lines can thus excite erbium but not tantalum, and are bound to shift the equal intensity ratio in favour of erbium.

FIG. 2.—Photometer curves of equal intensity mixture of tantalum and erbium alone (on left), and of the same mixture with the addition of five atoms of zinc for each atom of erbium (right).

On the left-hand side of Fig. 2 is seen the photometer curve of the equal intensity ratio of an erbium-tantalum mixture, and on the right-hand side the same with five atoms of zinc present for each atom of erbium. The equal intensity ratio is altered by 20 per cent owing to the presence of the large amounts of zinc. In the not very probable case that tantalum should have to be determined in the presence of a large excess of zinc, a corrected equal intensity ratio would be necessary, or the erbium abandoned as reference substance and replaced by, for example, iridium.

A third case of disturbance is encountered when the absorption edge of the impurity is situated between the absorption edges of the two lines to be compared. This has, again, a weakening effect on the intensity of the line of the element with the absorption edge with the shorter wave-length.

The most general remedy for the disturbances we have just mentioned is the use of reference lines with closely situated edges. We mentioned previously as a remedy for other selective absorption errors the use of reference elements with closely situated lines; as both requirements—closely situated lines and edges—can only be found in a limited number of cases (about twenty), the X-ray analyst finds himself compelled to compromise between these two requirements. To be able to carry out accurate quantitative analysis of minerals or alloys with a great number of constituents, it is necessary to ascertain if large amounts of disturbing impurities are present and choose the reference lines suitable to the special case. If only an approximately quantitative method of determination is needed, these precautions are not necessary, nor are they necessary if an accurate analysis of a mixture of a few refractory oxides, for example, $ZrO_2 + HfO_2$ or $TiO_2 + Ta_2O_5 + Nb_2O_5$ is to be carried out.

Full tables containing suitable reference lines for elements between sodium and uranium will be published shortly.

APPLICATIONS OF THE ANALYTICAL X-RAY METHOD.

The chief field of application of the method of quantitative X-ray analysis is the determination of rare elements in minerals and alloys, but it can be applied to practically any element.

Minerals.—The determination of hafnium, which can only conveniently be done by the X-ray method, has already been mentioned. A further example of X-ray spectroscopy as applied to minerals is the case of tantalum and niobium. These can be separated by different chemical methods, but it is scarcely possible to effect a separation, or even to show the presence of the elements, when only traces are present in the mineral. For example, the presence of tantalum or niobium in the most important titanium minerals, such as ilmenite, titanite, rutile (apart from ilmeno-rutile and struverite, which are rich in tantalum and niobium), was not known before the application of X-ray analysis, in spite of the fact that the largest amounts of tantalum or niobium in the earth's crust are actually to be found in titanium minerals. This is due to the fact that niobium and tantalum generally accompany titanium in laboratory separations, and have likewise been deposited together by geochemical processes. They show conspicuously the phenomenon of a comparatively rare element being masked by a very similar abundant one, a phenomenon investigated by Goldschmidt and named by him 'camouflage'.

Tantalum and niobium being in many cases only present in a concentration of 1 in 1,000,000, it is necessary before applying the X-ray method to increase the concentration by a chemical one. Such a combination of chemical and X-ray methods proves in several cases to be very useful, especially in determining the abundance of the rarer elements in the lithosphere or in meteorites. While exhaustive data are available on the abundance of the more common elements, as shown by the well-known work of Clark and Washington, before X-ray methods were introduced, scarcely any data were available on the abundance of many of the rarer elements, though these constitute the majority. To determine the abundance of the latter in the lithosphere, the following method proved very useful. A large number of samples of igneous rocks were taken, in the same proportion as they occur in the earth's crust, and the mixture of the samples analysed by combined chemical and X-ray methods.

Alloys.—The method of quantitative X-ray analysis is very useful in investigating both common metals, such as commercial samples of iron, and also alloys of precious metals such as platinum. In the former case, minute amounts of vanadium, chromium, and so on, can also be determined by other than X-ray methods, for example, by the recently highly developed method of electro-analytical titration, but in this case it is necessary to dissolve the alloy, whereas in the X-ray investi-

gation this is not necessary so long as the proportion of the metal present is not less than one in ten thousand. The X-ray method has greater advantages in the case of the platinum metals, where chemical analysis is very tedious.

Soil Samples.—The analysis of soil samples should be quoted as a third case. The phosphorus content, for example, can be determined conveniently and quickly by adding zirconium oxide to the sample and comparing the intensity of the phosphorus- $K\alpha_1$ and zirconium- $L\beta_1$ lines.

We have discussed so far the use of X-ray emission spectra for analytical purposes. An entirely different method of X-ray analysis makes use of the selective absorption by the sample containing the element to be determined. This method, worked out by Glocker, can be used where one heavy element is present in large excess over several light ones, but in general it is preferable to use the emission method.

We may refer in passing to the great progress made in quantitative optical spectroscopy. This progress is due to a great extent to the fact that the principle which was found very useful in the domain of X-ray spectroscopy, namely, the addition of a reference substance to the sample to be investigated, has also been introduced into optical spectroscopy. In the case of elements such as lead, zinc, cadmium, or the alkali metals, the optical method can be used with equal advantage, or in some special cases even more successfully than the X-ray method, but in the case of elements forming refractory compounds, such as the titanium group, the vanadium group, the rare earths, and so on, the optical method encounters serious difficulties which do not occur in the X-ray method.

SUMMARY.

Quantitative analysis by X-rays is best carried out by first mixing the substance to be determined very thoroughly with a suitable reference substance. The intensity ratio of the reference line and the line to be determined is determined empirically beforehand. To avoid the disturbing effect of cathode rays, the sample is bombarded by X-rays, and the secondary spectrum investigated. As the presence of large amounts of certain impurities can influence the intensity ratio of the lines to be compared, it is necessary to know for each element under which conditions an exact determination is possible, and to choose the reference line accordingly. In the case of an approximate determination, and also in several cases of exact determination, this precaution is not necessary. The chief application of the method is the determination of rare elements present only in small amounts, where chemical methods more or less fail and the advantages of the X-ray method are most pronounced. Very promising also is the combination of the chemical and X-ray methods, as this allows, for example, a determination of all the rarer elements in the earth's crust and in meteorites. The analysis of soil samples (determination of the phosphorus content, etc.) and of alloys are further important applications.