

THE USE OF X-RAYS FOR THE DISCOVERY OF NEW ELEMENTS¹

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When Moseley started his researches on the spectroscopy of X-rays one of his immediate aims was to ascertain whether the regularity to be found would follow the sequence of the atomic weights or that of the atomic numbers, whether the sequence Fe, Ni, Co or Fe, Co, Ni would be found (1). The result of his efforts is well known, as well as the simple relation between wave length and atomic number which he discovered. Moseley entertained no doubt, that X-ray spectroscopy would prove to be of great use in the analysis of alloys and of minerals and specially in searching for missing elements. In fact, he carried out an investigation of a rare earth sample sent to him by Urbain which showed the optical "celtium lines." He could not detect the presence of other than known elements, namely those of the last members of the rare earth group. The later identification of the optical "celtium lines" with those of the element 71 (lutecium) in fairly pure state was in full accordance with Moseley's results. Apart from this single case, Moseley did not embark on chemical analysis but endeavoured to elucidate the K- and L-series of all the available elements. Moseley's work was continued by Siegbahn, and we owe to him and his collaborators great progress in elucidating the X-ray spectra of most of the chemical elements as well as the development of the technique of X-ray spectroscopy which made the X-ray method easily applicable to analytical purpose.

Working in Siegbahn's laboratory about eight years later Hadding (2) emphasized the use of X-ray analysis for the detection of elements in minerals and especially of the rare earth

¹ It is with very great pleasure the writer is following the request of the editor to write an article on the above topic.

elements, many of which are not distinguished by the usual analytical methods. Following up the suggestion of Hadding, who himself applied X-ray analysis to minerals containing rare earth elements, Goldschmidt and Thomassen (3) carried out a very exhaustive research and were thus enabled to give a rough estimate of the ratio of the rare earth elements present in practically every one of the more important rare earth minerals. We may add that the important results of Goldschmidt and Thomassen could hardly have been obtained in any other way. When Coster and the present writer (4) were faced at about the same time with the problem of detecting and estimating hafnium no other method could be used but X-ray analysis. They mixed a known amount of tantalum oxide with the sample to be investigated and measured the intensity of the corresponding tantalum and hafnium line, assuming that the effect of equivalent amounts of hafnium and tantalum on the photographic plate is about the same. Later when in possession of pure hafnium oxide this method was replaced by a somewhat different one (5). A known amount of the oxides of the elements 71 and 72 were mixed with ZrO_2 and the intensity ratio of the $Lu\beta_2$ and $Hf\beta_1$ lines determined at a known tube voltage. To estimate the hafnium content of a sample, the latter was turned into oxide and a known amount of Lu_2O_3 added. By comparing the intensities of the above mentioned two lines which lie very closely together on the photographic plate² and knowing the intensity ratio of the lines given by a sample containing equal quantities of HfO_2 and Lu_2O_3 the amount of hafnium present can easily be calculated. As the problem of the exact estimation of the elements by the X-ray method lies beyond the scope of this report, we shall not discuss this or similar methods further.

GENERAL CONSIDERATIONS OF X-RAY SPECTRA

The question may be put why the introduction of X-ray spectroscopy is to be considered a highly remarkable and in

² These lines are only 4x units apart, a circumstance which is very favorable to an accurate comparison of their intensities.

some respects quite fundamental step forward in analytical chemistry. The answer to this question can be summed up in the following points:

I. As X-ray spectra are connected with the temporary removal of electrons from inner electronic groups, while the optical spectra are connected with the removal of outer electrons, the X-ray spectra are necessarily less complex than optical spectra.

II. The appearance of the X-ray lines is practically independent whether the element is present in the free state or as any compound. Optical spectra are highly dependent on the state of the element; furthermore the presence of other elements may partly or entirely suppress the appearance of some lines.

III. The position of the X-ray lines can be calculated in advance, a fact which is of great importance in searching for missing elements.

We may further add that the ease with which the tube voltage and thus the excitation of the X-lines can be regulated is of great practical importance, since it allows the excitation or suppression of a given line at will. Any chemical element which lies between sodium and uranium in the periodic table can be identified by its K-lines, any between copper and uranium by its L-spectrum. Lines belonging to these groups are the ones generally used in recent analytical work and only exceptionally the M-lines of the heaviest elements. The possibility of the coincidence of a K-line with other lines is in general appreciably smaller than this possibility for an L-line and therefore the K-series is more useful for the identification of an element, especially, as we shall discuss more in detail later, if the element to be detected is present only at a low concentration. But on account of the much higher voltage, which the excitation of the K-series requires, the L-lines have hitherto been more frequently used for the determination of the heavier elements. We will in the following consider the detection of tantalum and discuss in connection with this example the general features and the possible errors of X-ray analysis.

THE DETECTION OF TANTALUM

To establish the presence of tantalum in a mineral we fix a small sample of the pulverised mineral on the anticathode and bombard this with cathode rays. $L_{-\alpha_1}$ being the strongest line of the L-series, the presence of this line will be first sought for, using a vacuum spectrograph.³ To excite the L_{α} line a minimum of 10,000 volts is necessary, but a higher one, for example 18,000 volts is more convenient. Let us assume, that on the photographic plate a line appears at the expected position 1518 X ($= 1,518 \text{ \AA}$) and ask whether the appearance of this line is conclusive evidence for the presence of tantalum. If the line is sufficiently strong and the experimenter sufficiently skilful to locate it with an accuracy of an X unit, we may answer in the affirmative. Should this not be the case the appearance of the line is far from being conclusive for the presence of tantalum. In the case of a faint line the error of measurement may amount to several X units and if an error of 3 X units is made the Dy $L_{-\gamma_5}$ line may be mistaken for the Ta $L_{-\alpha_1}$ line. We may decide which line we have observed in either of two ways. We may abandon the α_1 line and try to excite the $\beta_1, \beta_2, \alpha_2$ and other lines or we may ascertain the absence of the Dy α_1 line; if the latter is absent, the much weaker Dy γ_5 line can not be present. The first mentioned alternative is in general to be preferred. The next strong tantalum line has the wave length 1324 X, a line exactly coinciding with hafnium β_2 and differing only by 3X units from Pt α_2 . Tantalum β_2 exactly coincides with Zn β_2 and comes very near to W β_1 . If the sample contains 1 per cent or more of tantalum as well as the α_1 line, the α_2 line will be easily visible. The appearance of such a "doublet" composed of two lines of widely different intensities (10:1) is always reassuring for the X-ray spectrographer, though the possibility of queer coincidences may even in this case not quite be disregarded. But the expected intensity ratio of the lines is in general one of the most decisive proofs of the presence of the element sought for, considering that this constant ratio is known and very different for different rays.

³ A vacuum is necessary since the soft L-rays are absorbed by air.

Besides the possibility of the coincidence of the Dy_{γ_5} line with the Ta_{α_1} line the possibility of the coincidence of the second order $Bi L_{\gamma_4}$ with the latter must be faced. This possibility can be easily tested by lowering the voltage under 16,000 volts, the minimum voltage for the bismuth line. The use of very high voltages to produce the lines increases the intensity of lines, but increases at the same time the possibilities of coincidence of the line sought with secondary, tertiary and higher order of other elements so far as the L series is considered. When investigating the K line this disturbing effect of the use of very high voltages does not usually interfere, hence the advantages of the use of the K lines when the presence of very small amounts of an element has to be ascertained.

The behavior of tantalum as regards coincidence of its lines with those of other elements is by no means exceptional and the above example may suffice to show the unsafe ground on which we are moving when trying to identify an element on the basis of few very faint lines, as some investigators (6) claim to have done. We must further remember that such faint lines can not only be due to coincidency but can also be produced through an imperfection of the diffracting crystal. Besides the emission lines also the absorption edges have repeatedly been used to identify elements (7). The appearance of the K absorption edge at 183, 6 X is, for example, strictly characteristic for the presence of tantalum.

We will discuss in the following the use of X-ray analysis for discovery of missing elements.

THE ELEMENT 72

When searching for the element 72 in zirconium minerals Coster and the writer could see on the first plate exposed the L_{α_1} line for which they were searching (comp. figure 1). As the mineral investigated contained so much as about 2 per cent hafnium silicate the line was very distinct as may be seen on figure 1 which represents a photometric curve of the blackening of the photographic plate. To make the result obtained conclusive the investiga-

tion was continued simultaneously in two different directions. The attempt was made to excite the other lines of the L spectrum calculated by interpolation and to investigate the effect of chemical treatment on the intensity of the α_1 line, i.e., on the concentration of the element in the sample emitting this line. The mineral was fused with acid potassium fluoride and the melt

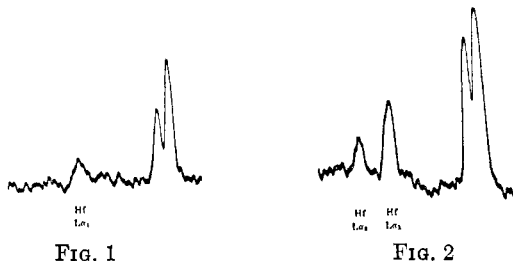


FIG. 1. PHOTOMETRIC CURVE OF THE FIRST ZIRCON INVESTIGATION
 FIG. 2. PHOTOMETRIC CURVE AFTER THE FIRST CHEMICAL CONCENTRATION OF HAFNIUM

extracted with hot water containing some hydrofluoric acid and crystallized a few times. The intensity of both the α_1 and the α_2 line increased very markedly as in the spectrum of the mother liquor obtained by this process shown by figure 2, thus clearly indicating that these lines are due to a substance which can be separated from zirconium.

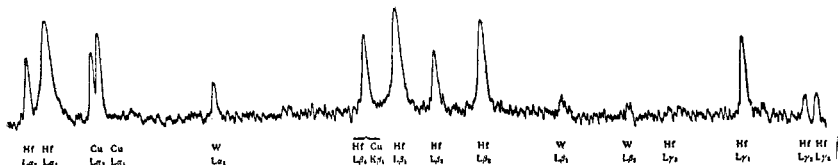


FIG. 3. PHOTOMETRIC CURVE OF THE X-RAY SPECTRUM OF PURE HAFNIUM

The X-ray method was not only found to be a unique analytical weapon in the discovery of the element 72, but also in the process of isolating hafnium, when the method was employed to check the result of every step of the prolonged process of separation. The complete L spectrum of hafnium taken by Coster (8) is shown by figure 3. It was obtained by using practically pure HfO_2 . It is of interest to note the rather peculiar coincidence

of the L_{α} doublet of hafnium with the second order K_{α} doublet of zirconium. This coincidence is somewhat disturbing, as hafnium always occurs together with zirconium. When using a voltage exceeding 18,000 we cannot distinguish the hafnium lines from zirconium lines. By lowering the voltage we can, however, suppress the ZrK_{α} doublet.

THE ELEMENTS 43 AND 75

While hafnium is sufficiently abundant to be detected by the X-ray method, in any mineral containing zirconium, elaborate trials to detect the presence of the apparently very rare elements 43 and 75 in minerals entirely failed. In 1925 Noddack, Tacke and Berg (9) announced the discovery of these elements in chemical preparations produced by very elaborate work from columbite and various other minerals and proposed for these elements the names of masurium and rhenium respectively. They estimate that the minute samples obtained contained a small per cent of the elements looked for. The following lines were observed:

| | 43 | | | 75 | | | | |
|-----------------|----------------|----------------|---------------|----------------|----------------|---------------|---------------|---------------|
| | K_{α_1} | K_{α_2} | K_{β_1} | L_{α_1} | L_{α_2} | L_{β_1} | L_{β_2} | L_{β_3} |
| Observed..... | 672. | 675. | 601. | 1429.9 | 1440.7 | 1235.0 | 1204.8 | 1216.0 |
| Calculated..... | 673.4 | 677.9 | 600.0 | 1430.6 | 1440.6 | 1235.5 | 1204.1 | 1216.9 |

Let us now consider the possible coincidences of other lines with lines of the element 75. The L_{α_1} line of 75 coincides with $Zn K_{\alpha_3}$, but $Zn K_{\alpha_3}$ is appreciably weaker than $Zn K_{\alpha_1}$, whilst the 75_{α_1} line is about of the same intensity as the $Zn K_{\alpha_1}$ line, also seen on the plate. The very weak L_{α_2} line of 75 does not coincide with any known line. The L_{β_1} line coincides with $W L_{\beta_3}$ but is, as Berg (10) remarks, stronger than we should expect it to appear from the intensity of the stronger tungsten lines seen on the plate. L_{β_2} coincides with Tl_{α_1} ; L_{β_3} with Tl_{α_2} . Berg emphasizes that the intensity ratio of the lines observed is the expected one. Later Heyrowsky and Dolejsek (11) reported the appearance of the L_{α_1} , L_{β_1} , L_{β_2} and L_{γ_2} of the element 75 in preparations

extracted from "pure" manganese compounds. The results of the X-ray examinations quoted above have not yet been corroborated by any chemical or optical evidence. We have also to mention, that similar experiments as the above described ones were recently carried out partly by Zvjaginstsev (12) and partly by Prandtl (13), both with negative result.

THE ELEMENT 61

In the case of the element 61, the last missing rare earth element, optical spectroscopy proved to be more sensitive than the X-ray method. It was with the aid of the former that Harris, Yntema and Hopkins (14) succeeded first in showing the presence of the element 61 (illinium) in fractions of rare earth preparations obtained after very elaborate chemical work. They were actually guided in their work by the observation of the absorption band spectra, but succeeded in showing the presence of a very faint L_{α_1} and L_{β_1} line in their most concentrated preparation after a very long exposure and intense bombardment of their sample with cathode rays. Simultaneously with Harris, Yntema and Hopkins, R. J. Meyer, Schumacher and Kotowski (15) were also successful in concentrating illinium sufficiently for it to be shown by an X-ray examination made by Dehlinger, Glocker and Kaup (16). In the latter investigation the use of the K-lines proved to be of great value, as very high voltages could be applied without the risk of coincidence of the lines observed with any line of higher order and because the possibility of a coincidence of primary lines in this short-wave region of the spectrum is much smaller than in the region of the L spectrum. One of the K lines of illinium, $61 K_{\beta}$, coincides, however, with TbK_{α_2} . The L lines of the element 61 coincide almost exactly with the following lines. $Il_{\alpha_1} + \alpha_2$ with La_{β_2} and Bi_{α_1} (second order); $Il_{\beta_1} + \beta_4$ with Pr_{β_7} ; Il_{β_2} with Sm_{β_3} ; Il_{γ_1} with Nd_{γ_2} , and so on. It is of interest to note that Meyer and his collaborators used the same method to concentrate 61 (James' bromate crystallization) as did Harris, Yntema and Hopkins. A somewhat different method was used

by Rolla and Fernandes (17). These investigations were carried out simultaneously with those previously mentioned and resulted in obtaining a concentration of element 61 sufficient to give optical absorption bands which are considered characteristic of this element as well as a very faint K absorption limit in the X-ray spectrum.

As to the two missing elements in the region between hydrogen and uranium, the elements 85 and 87, the general evidence tends to show that only radioactive isotopes of these elements are likely to be found.

A detailed description of the method of X-ray analysis and an exhaustive table of the known X-ray lines is to be found in the brilliant monograph of Siegbahn "The spectroscopy of X-rays," Oxford University Press 1925.

REFERENCES

- (1) Comp. HEVESY: Die Naturwissenschaften, **11**, 604 (1923).
- (2) HADDING: Proc. Acad. Science, Stockholm No. 11, 1922. Z. anorg. Chem. **122**, 195 (1923).
- (3) GOLDSCHMIDT AND THOMASSEN: Proc. Acad. Science, Oslo. No. 5, 1924.
- (4) COSTER AND HEVESY: Nature, **111**, 79 (1923). Coster, Chem. News, **127**, 65 (1923).
- (5) HEVESY: Proc. Copenhagen Acad. Science, No. 7, 1925. Chem. Rev. **2**, 27 (1925).
COSTER AND NISHINA: Chem. News, **130**, 149 (1925).
- (6) LORING AND DRUCE (Chem. News, October 30, November 6, 13, 20, and 27, 1925) claimed on such evidence the discovery of 4 missing elements (75, 85, 87 and 93) in a sample extracted from a manganese mineral, later reduced to two, the elements 75 and 87 (LORING: Nature **117**, 152 and 622 (1926)).
- (7) This method was chiefly used by de Broglie and his collaborators.
- (8) COSTER: Phil. Mag., **46**, 956 (1923).
- (9) NODDACK, TAKE AND BERG: Naturwiss., **13**, 567 (1925).
- (10) BERG: Z. tech. Physik. **6**, 599 (1925).
- (11) DOLEJSEK AND HEYROWSKY: Nature, **116**, 783 (1925).
- (12) ZVJAGINSTSEV: Nature, **118**, 262 (1926).
- (13) PRANDTL: Z. angew. Chem., **39**, 1049 (1926).
- (14) HARRIS, YNTEMA AND HOPKINS: Science, **63**, 575, (1926). J. Amer. Chem. Soc., **48**, 1594 (1926).
- (15) MEYER, SCHUMACHER AND KOTOWSKI: Naturwiss., **17**, 771 (1926).
- (16) DEHLINGER, GLOCKER UND KAUP: Naturwiss., **17**, 772 (1926).
- (17) ROLLA AND FERNANDES: Proc. Acad. Science Rome, **4**, 181 (1926). Chem. Gaz. Chim. Ital., **56**, 435 (1926).