

DETERMINATION OF COLUMBIUM IN ORES BY X-RAY FLUORESCENCE¹

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ABSTRACT

Analyses for columbium in pyrochlore ores from North Bay, Ontario, have been made successfully by using *x*-ray fluorescence techniques. It was necessary to use, as in methods of optical spectroscopy, an internal standard for this work. The choice of a suitable internal standard for a particular metal in a specific mineral association or ore-type requires consideration of the characteristic *x*-ray spectrum and absorption edges not only of the metal to be analysed for but also of the metals with which it is associated. For these reasons, molybdenum was found to be a suitable internal standard for columbium in the analyses of these ores.

INTRODUCTION

X-ray spectroscopy has been used recently with very satisfactory results to supplement optical spectroscopy in the spectrochemical analysis of metals in ores and minerals.

Because of the current demand for columbium, research was started in April, 1953, in the *x*-ray laboratory of the Department of Geological Sciences of McGill University on methods of *x*-ray analysis for columbium in ores of the metal. A method using *x*-ray spectroscopy was set up and many routine analyses for columbium in ore samples were run during the following months with excellent results.

THEORY

Secondary x-radiation

X-ray spectroscopy involves an analysis of the secondary *x*-ray or fluorescence spectrum of an atom or element when that atom is subjected to primary *x*-radiations from a separate *x*-ray tube. Because each element possesses a characteristic emission spectrum, an analysis of its spectrum will serve to identify the element. The concentration of an element present in a sample is proportional to the intensity of the characteristic lines in its emission spectrum and therefore measurement of these intensities will give the percentage of the element present.

The emission spectrum of an element consists of characteristic wavelengths depending on its atomic structure. These wavelengths may be grouped into several series according to the electron-shells or energy

¹ EDITOR'S NOTE.—The 15th meeting of the International Union of Pure and Applied Chemistry, in 1949, agreed to use the name *niobium* instead of *columbium* for element 41. The element is still best known as columbium to mineralogists in North America, in future the newly accepted name should be used.

levels of the atom, but wave-lengths from only two, the *K* and the *L* series, are commonly used in *x*-ray spectroscopy, and within these series the characteristic wave-lengths or lines most commonly used are the $K\alpha_1$, $K\beta_1$ in the *K* series, and the $L\alpha_1$, $L\beta_1$, and $L\beta_2$ in the *L* series.

The analysis of a secondary *x*-ray emission spectrum of an element is made by the separation or dispersion and the identification of the characteristic wave-lengths present in the spectrum. This dispersion is accomplished by using the diffraction grating supplied by suitably spaced atomic planes of a crystal. For our present purposes, the most satisfactory planes were the $(33\bar{1})$ planes of a mica crystal. The diffracted wave-lengths are identified by their reflection angles as given by the Bragg equation $n\lambda = 2d \sin \theta$ in which *n* is the order of the reflection, λ the diffracted wave-length, *d* the spacing in Ångstrom units of the diffracting atomic planes, and θ is the spectrometrically measured angle of incidence of the *x*-rays on the diffracting planes.

A Geiger counter mounted on a goniometer is used to intercept and identify the wave-lengths in terms of the Bragg angle and also to measure the intensities of radiations for each wave-length, in terms of quanta of radiation per second. The Geiger counter does this by passing on the impulses received from the quanta to an electronic scaling and counting unit.

The proportionality constant of the intensity of a particular line of the element in relation to the percentage of the element present in a sample is determined by reference to intensity measurements made on the same line, the reference line, in standard samples containing known amounts of the element to be determined. In practice, a calibration curve giving percentage of element in terms of intensities for a specific line in the spectrum of that element is prepared by measuring line intensities on prepared samples. This proportionality relation depends not only on the percentage of that element but also on the kind and percentage of other elements present in the sample, *i.e.*, on the composition of the matrix. However, as long as the composition of the matrix of an unknown sample remains approximately the same as the matrix of the reference or standard sample, the proportionality between intensity of reference line and percentage of element will be constant. These conditions usually obtain in samples of steels and alloys, and standard samples with varying proportions of the same elements may be prepared and analysed and a calibration curve set up for a particular element on the standard.

Should the matrix of the unknown be different from that of the standard samples, as it usually is in ores and minerals, then the proportionality between the percentage of an element and the intensity of a reference

line of that element may be altered from what it is in the standard samples from which the calibration curve was prepared. This is so because, if a change is made in the concentration of some other element that possesses one or more lines that may have absorption or excitation effects on the particular reference line used in the intensity measurements, then the measure of the intensity of that line will also be changed and the proportionality of measured intensity to the amount of the element present also changed.

Internal standard

The disturbing effect of the matrix may be minimized in the analyses of ores and minerals by the use of an internal standard. In this method a known amount of an element, the internal standard, is added to the standard samples and the same amount to the unknown samples. If the internal standard contains an emission line whose wave-length is close to that of a line in the element to be analysed for, then the absorption or excitation of the two nearby lines by the matrix will be in very nearly the same ratio. The intensity ratios of these reference lines in the two elements, the internal standard and the element to be analysed, are then determined in standard samples prepared to contain different percentages of the one element and a constant percentage of the internal standard. In a sample of unknown composition to which the same percentage of the internal standard has been added, it is only necessary then to measure the intensities of the reference lines, calculate the intensity ratio, and by reference to the calibration curve prepared from the standard samples, determine the percentage of the sought-for element present.

The ores or minerals should not contain in abundance an element or elements that will either suppress by absorption or enhance by secondary radiation more of the one reference line than the other. Knowing what elements might be expected in a sample, reference is made to wave-length tables (von Hevesy, 1932, p. 148) of absorption edges and emission lines. From these it can be determined whether there are any edges with wave-lengths between those of the reference lines. If there is such an edge, there will be a greater absorption and suppression of the reference line with the shorter wave-length, and consequently a change, for a given amount of the internal standard, in the intensity ratio of the reference lines. For analogous reasons, the unknown sample should not contain elements with lines whose wave-lengths lie either between the absorption edges of the reference lines of the sought-for element and the internal standard, or on the short wave-length side of their absorption edges. Otherwise there will be an enhancing by excitation of one or the other of the reference lines and a change in the intensity ratio of the lines.

The possibilities of disturbing effects from lines of other elements in a sample can be minimized by the selection of an internal standard that possesses a reference line very close to a reference line in the sought-for element, and also possesses an absorption edge close to the absorption edge of that same line.

EQUIPMENT

In this investigation, a General Electric SPG Fluorescent X-ray Spectrometer was used, with an XRD-3 General Electric Spectrogoniometer and X-ray Detector. The primary x -radiation was obtained from tungsten-target Machlett AEG-50T tube and a sample area $\frac{3}{4}$ -inch square irradiated. The secondary x -ray or fluorescent radiation from the sample was diffracted through a bent mica crystal arranged for transmission with a d spacing of *ca* 1.5 Å, and detected by a Geiger-counter spectrometer. An electronic circuit provided for the chart recording (Fig. 1) of location and relative intensities of the lines in the emission spectrum of the sample.

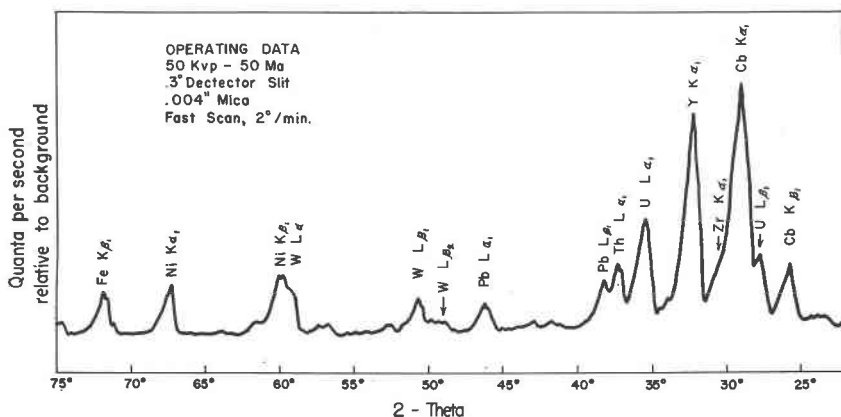


FIG. 1. Secondary x -ray spectrum from an ore-sample; scanning for qualitative analysis only.

Automatic scanning and the chart-recorder were used only for qualitative analyses of unknown samples. For quantitative work, the goniometer of the spectrometer was set at the 2-theta angle for each of the reference lines, one in the sought-for element and one in the internal standard. The time required for a pre-set number of counts or quanta from each setting was recorded by a timer; from this the total intensity determined as counts or quanta per second and intensity ratios calculated. Because the counts due to the effect of extraneous background are normally the same under similar operating conditions for the elements

in the unknown samples and for the elements in the standard samples, the net number of counts due to the element alone is not determined.

EXPERIMENTAL PROCEDURE

Mineralogy of the ore to be analysed

The problem undertaken was the development of an accurate and relatively rapid method of determining columbium in a complex columbium ore from North Bay, Ontario. This ore contained the following non-metallic minerals, listed in approximate order of decreasing abundance: calcite, orthoclase, quartz, apatite, biotite, garnet, sodic pyroxene, pyrochlore, fluorite, albite, scapolite, and small amounts of uraninite. The metallic minerals included small amounts of pyrite, magnetite, and hematite. Not all these minerals were necessarily present in all samples of the ore. It may be noted that no molybdenum minerals were present.

Choice of an internal standard

In choosing an internal standard, many samples were scanned to determine what elements might be expected to occur in troublesome amounts. From a study of the spectral charts so obtained and from tables of the principal x -ray spectral lines and of absorption edges, molybdenum was chosen as the internal standard, and the $K\alpha_1$ lines of this element and of columbium chosen as reference lines. Since molybdenum did not occur

TABLE 1. PRINCIPAL X-RAY SPECTRAL LINES OF THE ELEMENTS¹

Wave-length XU ²	Element	Line	Absorption Edge, XU
616	Rh	$K\alpha_2$	533
620	Mo	$K\beta_2$	618
630	Th	$L\gamma_2$	627
631	Mo	$K\beta_1$	618
642	Ru	$K\alpha_1$	558
646	Ru	$K\alpha_3$	558
652	Th	$L\gamma_1$	627
708	Mo	$K\alpha_1$	618
708	U	$L\beta_3$	569
712	Mo	$K\gamma_2$	618
718	U	$L\beta_1$	592
739	Y	$K\beta_1$	726
745	Cb	$K\alpha_1$	650

¹ von Hevesy, 1932, pp. 141-142.

² XU = X-ray wave-length unit; 1000 XU = 1kX = 1.00202 Å.

in the ores on which work was done, the amount present would always be only the amount added as the internal standard.

A study of the preceding Table will show the lines that come between the K absorption edges at 618XU and 650XU for molybdenum and columbium respectively. Not only are these intervening lines relatively weak lines, but the possible interfering elements, ruthenium and thorium, occur in the ores in no more than trace amounts.

Reference to a table of absorption edges (von Hevesy, 1932, p. 156) showed that the only edges between $K\alpha_1$ at 708XU for molybdenum and $K\alpha_1$ at 745XU for columbium were the L absorption edge for uranium at 721XU and the K absorption edge for yttrium at 726XU. Although uranium is present in the ores, the L absorption edge is weak; and although the K of yttrium edge is relatively strong, the amount of yttrium present is small. The effect of these elements on the $K\alpha_1$ intensity ratios of columbium and molybdenum would therefore be negligible. For these reasons, the $K\alpha_1$ line of molybdenum was chosen as a suitable reference line for the $K\alpha_1$ line of columbium in the North Bay ores, and standards using molybdenum as the internal standard for columbium were set up.

Technique

Standards were prepared to contain the same percentage (5%) of MoO_3 (C.P.) and the following percentages of Cb_2O_5 : 0.15, 0.30, 0.90, 1.00, 2.00, 2.50. This was the range expected in the material to be analysed, as previously determined from chemical analyses of selected typical samples.

Because of the abundance of orthoclase feldspar in the ore, feldspar, ground to pass 100-mesh, was used as a matrix for the mixtures of molybdenum and columbium oxides. However, runs were also made with other prepared samples using calcite and quartz as a matrix, and satisfactory checks were obtained.

To ensure getting samples as uniform as possible—uniform both as to particle size and as to the mixing of Cb_2O_5 and MoO_3 —each sample, after addition of the oxides, was ground the same length of time, ten minutes, in a mechanically operated agate mortar and pestle. A ten-minute grind of the powdered oxides into the 100-mesh feldspar matrix appeared to be the optimum to give reproducible results with a minimum amount of sample preparation.

From a 10-gram initial sample, a $2\frac{1}{2}$ -gram sample, enough to fill two sample trays, an original and a duplicate, was cut for analysis.

The sample trays consist of small rectangular blocks $2'' \times 1\frac{1}{4}'' \times \frac{3}{16}''$ into which a rectangular cavity $\frac{7}{8}''$ square $\times \frac{3}{32}''$ deep has been routed. The blocks were cut from a sheet of cold-setting plastic.¹ The area of the

cavity, $\frac{7}{8}$ -inch square, is a little larger than the opening, $\frac{3}{4}$ -inch square, for the irradiating x -rays, but this oversize ensures a constant area of irradiation for all samples. Data are lacking on the minimum thicknesses of powder in a sample tray that will produce maximum fluorescence under specified operating conditions. Other conditions being the same, a thickness less than the minimum will produce less intensity of a particular spectral line, but a greater thickness will not produce a greater intensity. For a metallic element Glucker (in Koh & Caugherty, 1952) has estimated this thickness to be in the order of 0.1 mm. Since there was no shortage of material for analysis, a convenient depth of $\frac{1}{32}$ -inch for the sample cavity was used, a depth well in excess of that necessary for maximum fluorescence yield.

The filled trays were packed lightly with the powdered sample and smoothed off with a glass slide. The trays, one at a time, are then placed in a holder where they are held at an angle of 30 degrees from the horizontal. The holder, with its sample, is so placed below the lower part of the x -ray tube that a vertical beam of x -rays irradiates the exposed surface of the sample and is reflected horizontally from this surface through the mica crystal to the Geiger tube. It is our experience that none of the sample is lost from the tray with this arrangement. The intensity of the radiations of the selected lines, $K\alpha_1$ in the emission spectra were then determined for columbium and molybdenum. This was done by setting the goniometer at the 2θ angles for the $K\alpha_1$ lines respectively of columbium and molybdenum and obtaining the time for a predetermined number of quanta from each of these two $K\alpha_1$ lines. Five time-counts were made on each line for each sample, the average time taken, and from this time, the intensity in terms of quanta per second determined for each line. The logarithm of the intensity ratio of these lines, $ICbK\alpha_1$ to $IMoK\alpha_1$ was then plotted against log per cent Cb_2O_5 , and the working curve (Fig. 2), with molybdenum as an internal standard, obtained.

In practice, all unknown samples for analysis are ground to pass 100-mesh, 5 per cent MoO_3 added to each sample, and, as with the standards, given a 10-minute mixing grind in a mechanical mortar and pestle. For each sample, the intensity ratio, $ICbK\alpha_1$ to $IMoK\alpha_1$, is determined and from this ratio the percentage of Cb_2O_5 present in the sample is read from the working curve.

Because of the low intensity of secondary radiations from amounts of Cb_2O_5 less than 0.1 per cent and resulting inaccuracy of results, no attempt was made to determine amounts of Cb_2O_5 less than this; that is, less than 0.07 per cent Cb. For the present investigation the upper limit

¹ Polyester Resin Laminac manufactured by American Cyanamid Co., N. Y.

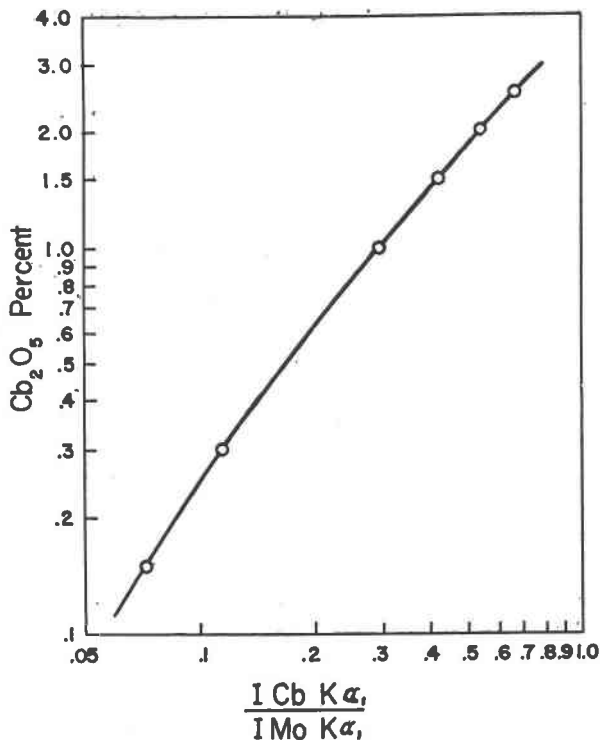


FIG. 2. Working or calibration curve for columbium using molybdenum as an internal standard.

for which standards were prepared was 2.5 per cent Cb_2O_5 .

Using the technique outlined above with molybdenum as the internal standard, about 2,500 ore-samples have been analysed for columbium in the University laboratory from May, 1953 to November, 1953, inclusive, and very consistent results have been obtained.

ACKNOWLEDGEMENTS

The writer gratefully acknowledges the helpful advice of Dr. S. C. Robinson and Mr. E. J. Brooker of the Geological Survey of Canada, during the initial stage of the development of this procedure. He also wishes to thank Professor J. E. Gill of McGill University for his critical reading of the manuscript.

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