United States Patent

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[72] Inventors **Colin Geoffrey Clayton**
Abingdon, England;
Bohdan Wladyslaw, Krakow, Poland

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[73] Assignee **United Kingdom Atomic Energy Authority**
London, England
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[33] **Great Britain**
[31] **19,833/67**

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[54] **METHOD OF X-RAY FLUORESCENCE ANALYSIS OF MATERIALS CONTAINING AN INTERFERING ELEMENT**
4 Claims, 5 Drawing Figs.

[52] **U.S. Cl.** **250/51.5**
[51] **Int. Cl.** **G01n 23/22**
[50] **Field of Search** 250/51.5

[56] **References Cited**

UNITED STATES PATENTS

3,270,200	8/1966	Rhodes	250/51.5 X
3,448,264	6/1969	Rhodes	250/51.5

OTHER REFERENCES

" Scattered X-Rays as Internal Standards in X-Ray Emission Spectroscopy," by G. Andermann et al., from Analytical Chemistry, Vol. 30, No. 8, Aug., 1958, pages 1,306– 1,309.

Primary Examiner—William F. Lindquist
Attorney—Larson, Taylor and Hinds

ABSTRACT: The invention discloses a method of analysis of a mixture containing a wanted element, an interfering element and a base rock designed to compensate for the effects of the interfering element and the base rock composition. In accordance with the invention the mixture is subjected to ionizing radiation and separate determinations are made, using balanced filters, of the intensity of the backscattered or fluorescent radiation:

a. at the characteristic energy of the wanted element,

b. at the characteristic energy of the interfering element, and

c. over an energy band intermediate between the above two energies.

A nomogram is plotted of the ratios a/c and b/c.

Fig. 1.

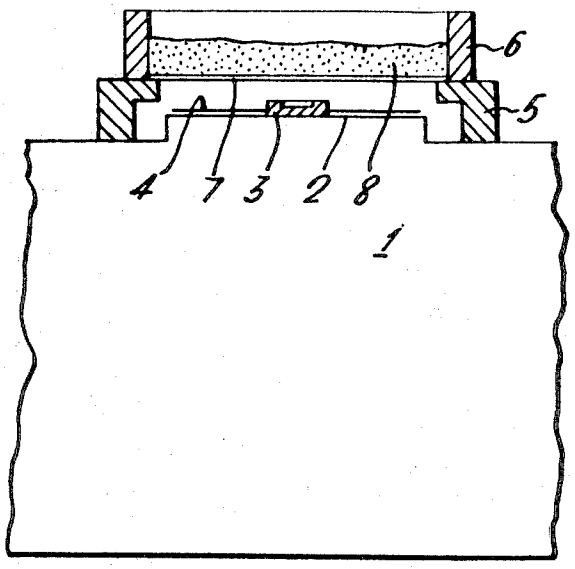

6
5
4
7
3
2
8
1

Fig. 2.

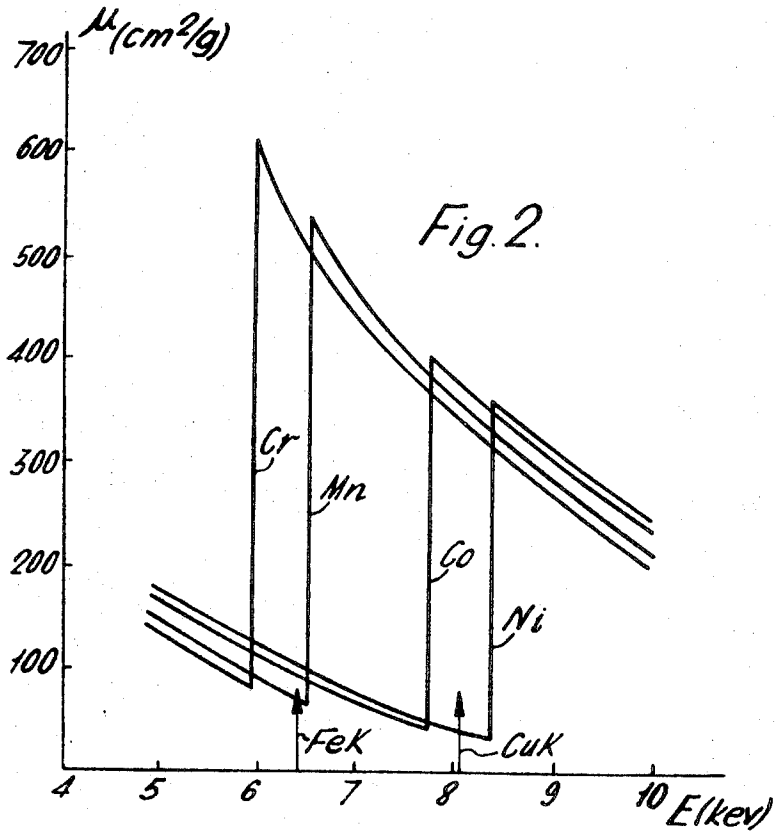

μ(cm²/g)
700
600
500
400
300
200
100
Cr
Mn
Co
Ni
FeK
CuK
4
5
6
7
8
9
10
E(kev)

Fig. 3.

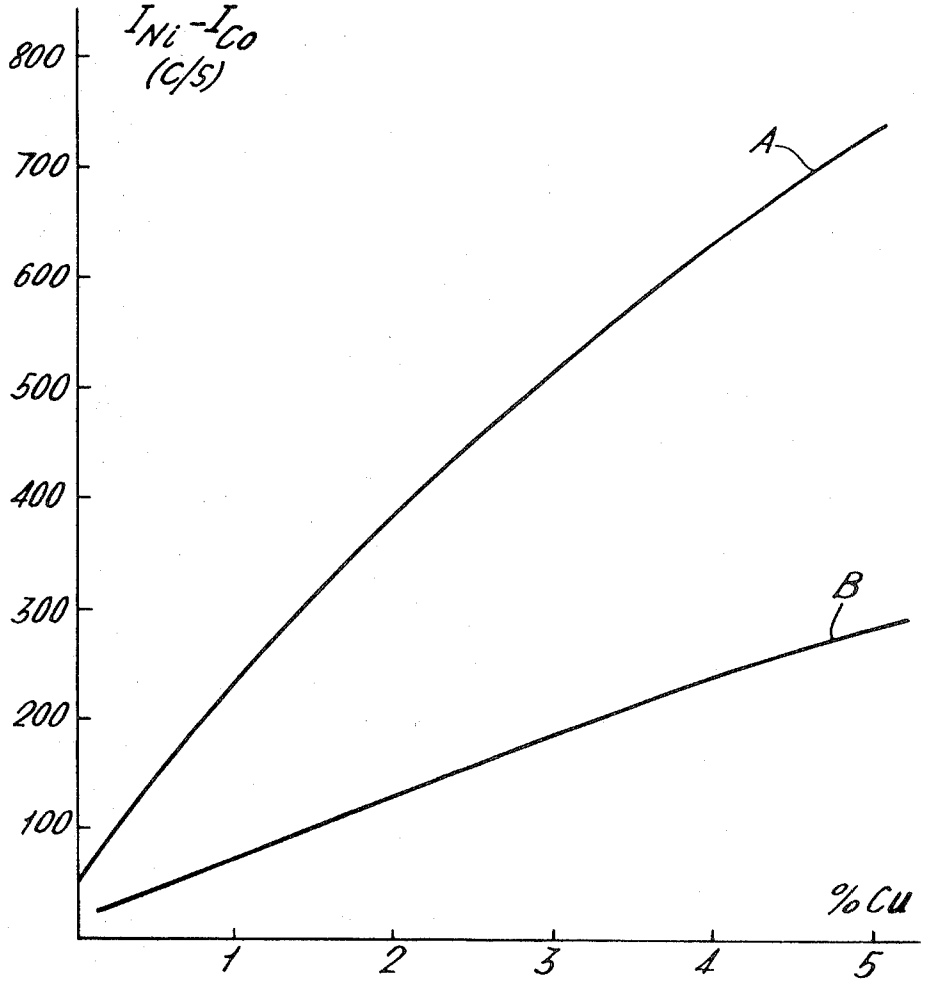


Fig. 4.

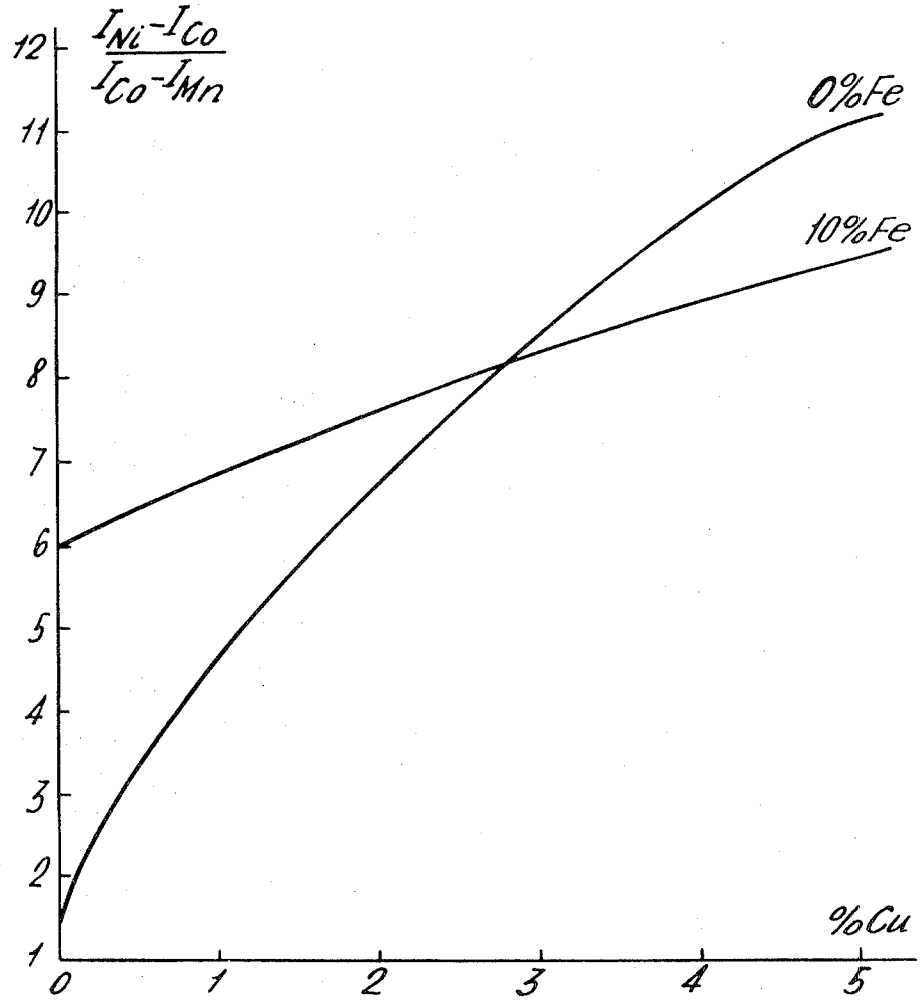
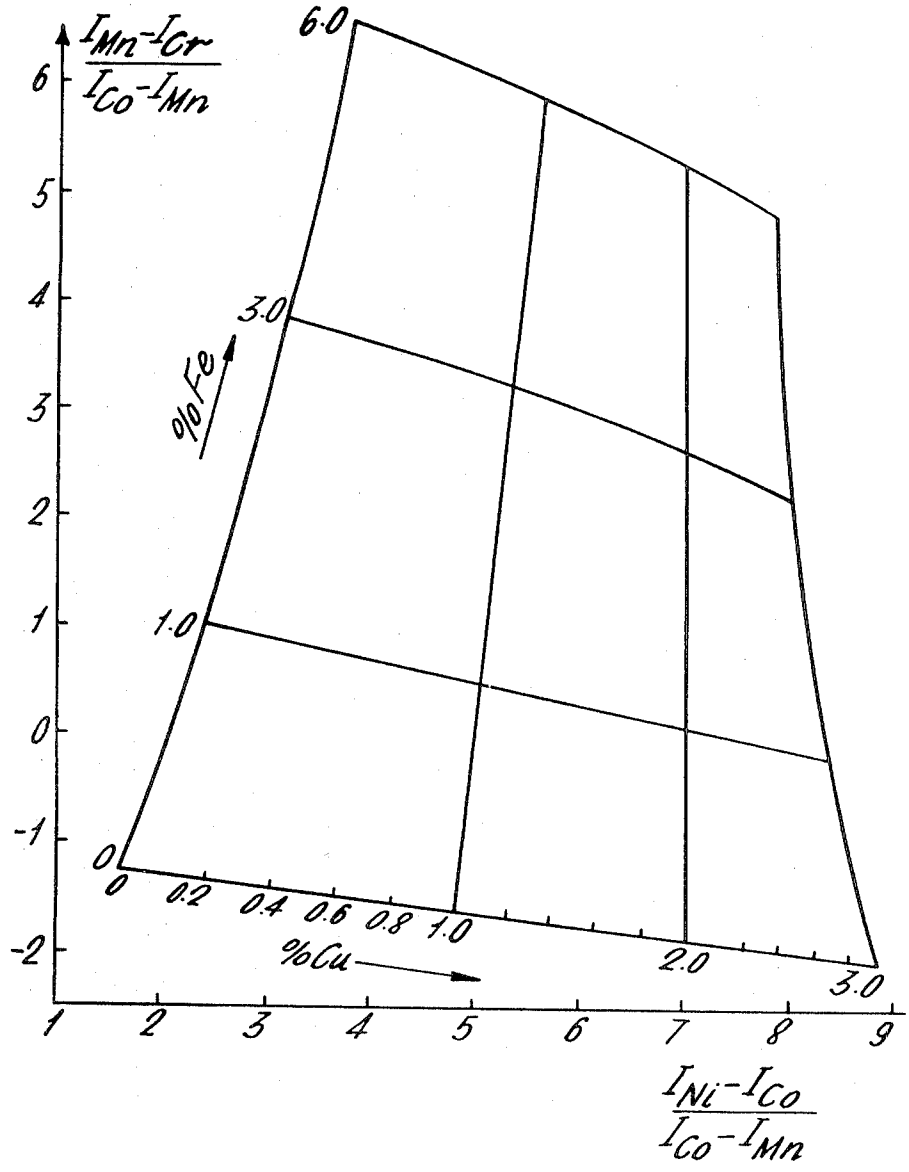


Fig. 5.


$\frac{I_{Mn}-I_{Cr}}{I_{Co}-I_{Mn}}$
6
5
4
3
2
1
0
-1
-2
6.0
3.0
1.0
0
%Fe
0 0.2 0.4 0.6 0.8 1.0 2.0 3.0
%Cu
1 2 3 4 5 6 7 8 9
$\frac{I_{Ni}-I_{Co}}{I_{Co}-I_{Mn}}$

METHOD OF X-RAY FLUORESCENCE ANALYSIS OF MATERIALS CONTAINING AN INTERFERING ELEMENT

BACKGROUND OF THE INVENTION

The present invention relates to the analysis of materials and in particular mineral ores using the well-known method of subjecting the material to ionizing radiation thereby to excite fluorescent X-rays.

More specifically the present invention relates to the technique of analysis using natural or artificial radioisotope sources as the origin of the radiation which excites fluorescence. As is known the fluorescent X-rays have an energy characteristic of the element emitting them and, after energy selection by an appropriate method, the intensity of these X-rays is measured. In this specification, the term "the wanted element" is used to define that element which is the subject of the analysis and the term "base rock" is used to define the gangue or other matrix (usually a calcium or magnesium compound) in which the wanted element is dispersed.

Unfortunately if the ore also contains "an interfering element" that is to say an element which has an atomic number close to, but less than, the atomic number of the wanted element difficulties are caused as the characteristic radiation emitted by the wanted element is to some extent absorbed by the interfering element and is reemitted as the characteristic radiation of the interfering element. Several different techniques designed to overcome this difficulty, known as the "matrix effect," have been described. In practice however, the problem is much more complicated as there may be several interfering elements. Moreover, the base rock of the ore may be of variable composition and may give rise to spurious results.

It is an object of the present invention to provide a method for the analysis of a material which takes into account the above difficulty.

SUMMARY OF THE INVENTION

According to the present invention there is provided a method of analysis of a mixture containing a wanted element, an interfering element and a base rock, comprising subjecting the mixture to ionizing radiation and determining separately:

a. the intensity, I_w, of the fluorescent radiation at the characteristic fluorescent energy, E_w, of the wanted element;

b. the intensity, I_i, of the fluorescent radiation at the characteristic fluorescent energy, E_i, of the interfering element;

c. the intensity, I_b, of the backscattered radiation over an energy band which is intermediate between, but does not contain, the characteristic fluorescent energies of the wanted and interfering elements.

Very desirably the source of ionizing radiation is an artificial or natural radioisotope. The power of such a source is limited and therefore the radiation intensity determinations are conveniently made using a pair of balanced filters for each determination.

It will be well known that the technique of using balanced filters depends upon the fact that two elements of adjacent atomic number have their K absorption edges spaced by certain energy and it is normally possible to select two elements having K absorption edges which bracket the energy of the fluorescent radiation of the wanted or interfering element as the case may be. Thus, the use of a pair of such balanced filters will give a measure of the energy emitted by the sample over a specific but narrow energy range. In practice it may only be necessary to use a total of four filters, two to bracket the characteristic energy of the radiation of the wanted element and two to bracket the characteristic energy of the radiation of the interfering element, while the intensity of the backscattered radiation is measured using the appropriate pair of filters selected from the four already provided.

The principle of the method depends upon the fact that the intensity of both characteristic and scattered radiation in the same energy region vary with the attenuation coefficient of the base rock in a similar manner. It follows that by determining the ratio of characteristic to backscattered intensity at adjacent energies the effect of the base rock can be minimized. Since the effect of the interfering element is also dependent upon the base rock, then a similar compensation can be made.

In practice, having obtained the above measurements, the quantity of the wanted element and indeed the quantity of the interfering element can both be determined from a calibration nomogram obtained by plotting:

$$I_i/I_b \text{ against } I_w/I_b$$

wherein:

I_i is the intensity of the radiation at the characteristic energy E_i of the interfering element:

I_w is the intensity of the radiation at the characteristic energy E_w of the wanted element; and

I_b is the intensity of the backscattered radiation.

If there is a second major interfering element, it is necessary also to determine the intensity of the fluorescent radiation at the characteristic fluorescent energy of this second interfering element and use a three-dimensional nomogram obtained by plotting:

$$I_{i1}/I_b \text{ vs. } I_{i2}/I_b \text{ vs. } I_w/I_b$$

wherein:

I_{i1} and I_{i2} are the intensities of the radiation at the characteristic energies of the first and second interfering elements.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the present invention may be more readily understood, one embodiment of the same will now be described with reference to the accompanying drawings, wherein:

FIG. 1 is a diagrammatic illustration of the counter arrangements,

FIG. 2 is energy diagram illustrating the function of the filters,

FIG. 3 is a graph showing the effect of base rock composition,

FIG. 4 is a graph showing the effect of ion content and

FIG. 5 is nomogram constructed in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In this embodiment the mixture is a copper ore where it is desired to measure the concentration of copper (wanted element), the primary interfering element is iron and the base rock may be either gypsum or basic artenite.

Referring now to the drawings and in particular to FIG. 1, it will be seen that the geometry is the conventional backscatter geometry and a detector which may, for example, be a scintillation or proportional counter, has a window 2 which surrounds a source 3 and around which source annular filters may be placed as desired. A stand 5 carries a sample holder 6 having a window 7 adjacent to the source 3 and above which window a sample 8 of powdered material is carried. This arrangement is conventional.

FIG. 2 shows a portion of the conventional absorption versus energy curves and shows the K absorption edges of the elements chromium, manganese, cobalt and nickel. It also shows the K fluorescent energies of iron and copper and it will be observed that chromium and manganese form a suitable pair of filters for iron radiation, while cobalt and nickel form a suitable pair for copper radiation.

If one takes two artificial copper ores containing no iron but based upon basic artenite and gypsum and measures the copper content using a pair of balanced nickel and cobalt filters in the conventional way, and plots the differential count through the two filters against copper content, curves A and B of FIG. 3 will be obtained, thereby illustrating the dependence of this classical method on the base rock composition.

In order to compensate for the effect of the base rock composition, it is necessary to measure the contribution of the base rock which is done by measuring the backscattered radiation over an energy band (FIG. 2) adjacent to the copper fluorescent energy and this is done by using cobalt and manganese as a pair of balanced filters which will accept a passband of energies at the appropriate level. In order to provide this compensation, the count rate due to the copper is divided by the count rate due to the base rock and is plotted against copper content as shown in FIG. 4 in which each line corresponds to two superimposed curves and refer to different base rocks which also contain iron in concentrations of zero and 10 percent.

Thus FIG. 4 plots

$$I_i/I_b \text{ vs. [Cu]}$$

In practice this is determined by the plot

$$\frac{I_{Ni}-I_{Co}}{I_{Co}-I_{Mn}} \text{ vs [Cu]}$$

It will be seen that although the FIG. 4 arrangement provides adequate compensation for base rock effects, the presence of iron as an interfering element still gives a considerable distortion to the results.

In accordance with the present invention the copper content free of the effect of iron is therefore determined by plotting the ordinate of FIG. 4 as the abscissa in FIG. 5 and plotting, as the ordinate in FIG. 5, a similar function in respect of iron. Therefore, FIG. 5 plots:

$$i_i/I_b \text{ vs. } I_w/I_b$$

In practice this is determined by plotting:

$$\frac{I_{Ni}-I_{Co}}{I_{Co}-I_{Mn}} \text{ vs } \frac{I_{Mn}-I_{Cr}}{I_{Co}-I_{Mn}}$$

As is conventional, it is necessary to use known samples in order to provide the calibration curve.

We claim:

1. In a method of analysis of a mineral mixture containing a wanted element, an interfering element and a base rock, wherein the mixture is subjected to ionizing radiation of an energy sufficient to excite X-ray fluorescence in the wanted element and the intensity of the combined backscattered X-ray and fluorescent X-radiation is measured: the improvement comprising the steps of,

a. detecting the intensity I_w at the characteristic X-ray fluorescent energy E_w of the wanted element;

b. separately detecting the intensity I_i at the characteristic X-ray fluorescent energy E_i of the interfering element;

c. separately detecting the intensity I_b of backscattered X-radiation over an X-ray energy band intermediate between but excluding E_w and E_i;

d. determining the ratios I_i/I_b and I_w/I_b; and

e. comparing said ratios with a suitable calibration nomogram which plots the ratio I_i/I_b versus the ratio I_w/I_b to determine the concentration of the wanted element.

2. A method according to claim 1, wherein the source of ionizing radiation is a radioisotope and the measurements are made using a pair of balanced filters for each determination.

3. A method according to claim 2, wherein the pair of balanced filters used in determining the intensity of the radiation over said intermediate band comprises one filter from each of the other two pairs of balanced filters, whereby only four counts need to be made.

4. In a method of analysis of a mineral mixture containing a wanted element, first and second interfering elements and a base rock wherein the mixture is subjected to ionizing radiation of an energy sufficient to excite X-ray fluorescence in the wanted element and the intensity of the combined backscattered X-ray and fluorescent X-radiation is measured: the improvement comprising the steps of,

a. detecting the intensity I_w at the characteristic X-ray fluorescent energy E_w of the wanted element;

b. separately detecting the intensity I_{i1} at the characteristic fluorescent energy E_{i1} of the first interfering element;

c. separately detecting the intensity I_{i2} at the characteristic fluorescent energy E_{i2} of the second interfering element;

d. separately detecting the intensity I_b of backscattered X-radiation over an X-ray energy band intermediate between but excluding E_w, E_{i1} and E_{i2};

e. determining the ratios I_{i1}/I_b, I_{i2}/I_b and I_w/I_b; and

f. comparing said ratios with a suitable three-dimensional calibration nomogram which plots the ratio I_{i1}/I_b versus the ratio I_2/I_b versus the ratio I_w/I_b to determine the concentration of the wanted element.

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