

**MINTEK**

# **REPORT**

**No. M131**

THE DETERMINATION OF COPPER AND NICKEL IN IRON- AND CHROMIUM-BEARING  
MATERIALS BY A PRESSED-POWDER TECHNIQUE AND  
X-RAY-FLUORESCENCE SPECTROMETRY

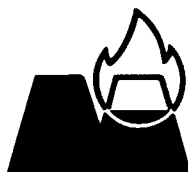
by

A.M.E. Balaes and K. Dixon

30th May, 1984

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**COUNCIL FOR MINERAL TECHNOLOGY**  
200 Hans Strijdom Road  
RANDBURG  
South Africa



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**(ANALYTICAL SCIENCE DIVISION)**

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## SYNOPSIS

A method was developed that is suitable for the determination of copper and nickel in ores such as those from the Merensky and UG-2 Reefs.

The sample was ground finely and diluted with river sand so that matrix variations were avoided as much as possible. After the addition of a wax-polystyrene binder, the material was pelletized. The matrix effects of iron and chromium, and the effects of their mutual interferences on the determination of copper and nickel, were then investigated.

Equations were derived for the corrected copper and nickel  $K\alpha$  intensities, and were applied to the analyses of head, concentrate, middling, and tailing samples. Comparative values obtained by atomic-absorption spectrophotometry were found to be in reasonable agreement with the X-ray values; the average deviation was +0,3 per cent for copper and -1,6 per cent for nickel relative to the AAS values.

The limits of detection of the method for copper and nickel are 31 and 40  $\mu\text{g/g}$  respectively; the limit of determination for copper is 92  $\mu\text{g/g}$  and for nickel is 119  $\mu\text{g/g}$ . The relative standard deviation at 900 and 2400  $\mu\text{g}$  of copper and nickel per gram is 0,02.

## SAMEVATTING

Daar is 'n metode ontwikkel wat geskik is vir die bepaling van koper en nikkell in ertse soos dié afkomstig van die Merensky- en UG2-rif.

Die monster is fyn gemaal en met riviersand verdun om matriksvariasies so ver moontlik te vermy. Na die byvoeging van 'n was-polistireenbindmiddel is die materiaal gepastilleer. Vervolgens is die matriks-uitwerkings van yster en chroom en die uitwerking van hul onderlinge steuring op die bepaling van koper en nikkell ondersoek.

Daar is vergelykings vir die gekorrigeerde koper- en nikkell- $K\alpha$ -intensiteit afgelei en toegepas op toevoer-, konsentraat-, middelskot- en uitskotmonsters. Vergelykende waardes wat deur atoomabsorpsiespektrofotometrie verkry is, het geblyk redelik met die X-straalwaardes ooreen te stem; die gemiddelde afwyking was +0,3 persent vir koper en -1,6 persent vir nikkell relatief tot die AAS-waardes.

Die opspooringsgrens van die metode vir koper en nikkell is onderskeidelik 31 en 40  $\mu\text{g/g}$  en die bepalingsgrens vir koper is 92  $\mu\text{g/g}$  en vir nikkell 119  $\mu\text{g/g}$ . Die relatiewe standaardafwyking by 900 en 2400  $\mu\text{g}$  koper en nikkell per gram is 0,02.

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## 1. INTRODUCTION

At the Council for Mineral Technology (Mintek), consideration was given to the determination of copper and nickel as a means of monitoring the distribution of platinum-group metals during the beneficiation of ores from the Merensky and UG-2 Reefs. Analysis for this purpose would need to be rapid and would need to complement the use of the Lab-X radio-isotope system for the rapid determination of higher concentrations of these metals. The method of analysis selected was X-ray-fluorescence spectrometry used with a pressed-pellet technique, in which the only preparation required is grinding and pelletization of the sample.

The establishment of a suitable method called for an assessment of the mutual interferences between copper and nickel, the interferences from substantial amounts of iron and chromium present as chromite, and the matrix effects caused by these elements, together with a determination of appropriate influence factors.

## 2. EXPERIMENTAL METHODS

### 2.1. Instrumental Parameters

All the measurements were made with a fully automatic sequential Siemens SRS X-ray-fluorescence spectrometer. The spectrometer is interfaced to a Data General Nova IV minicomputer through a Siemens LC200 logic controller. The spectrometer is also coupled to a loader that has eighty sample positions. The instrumental parameters are shown in Table 1 and, including the  $2\theta$  angles, are all controlled by the Nova IV mini-computer. Alternatively, these parameters can be stored in the memory of the LC200 logic controller.

TABLE 1

*Instrumental parameters*

Tube	Rhodium at 40 mA 60 kV
Detector	Scintillation counter
Counting time	40 s
Collimator	0,15° (fine)
Bragg crystal	LiF (220) cut

Element	Cu	Ni	Fe	Cr
Analytical line	K $\alpha$	K $\alpha$	K $\beta$	K $\beta$
Wavelength, Å	1,541 84	1,659 19	1,756 61	2,084 87
Goniometer setting, $2\theta$ angle				
(a) Peak	65,55°	71,26°	76,16°	94,12°
(b) Background	68,40°	73,71°	81,00°	97,00°

### 2.2. Reagents

The various components used in the preparation of pellets for the analysis of copper and nickel are given below.

(1) *Mixture of Copper and Nickel Oxides*

An amount of 0,400 g of each oxide was added to 9,2 g of river sand and mixed in a tungsten carbide Siebtechnik bowl for 5 minutes.

(2) *Iron and Chromium Oxides*

Must be of analytical reagent grade.

(3) *River Sand*

Must be clean and free from copper and nickel.

(4) *Binder*

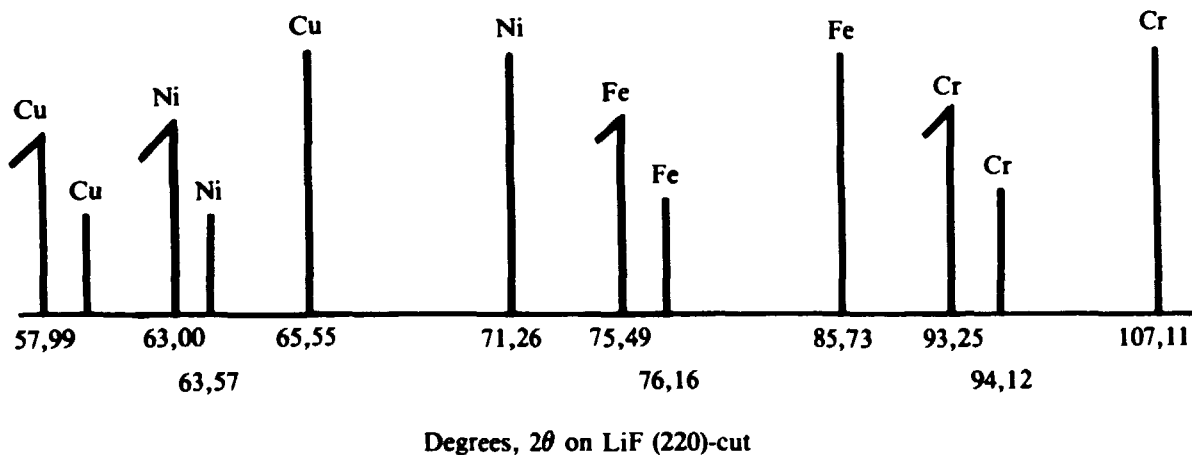
A mixture of 1 part of Sasolwax N3 and 9 parts of a polystyrene copolymer (EMU120FD, a powder with a particle size of less than 10  $\mu$ m supplied by the Badische Anilin- und Soda-Fabrik A.D.)

### 2.3. Interferences

From tables of X-ray wavelengths, the elements that could give interference on the copper and nickel K $\alpha$  and on the iron and chromium K $\beta$  spectral lines are essentially the rare-earth elements. As the

concentration of these elements in the ores from the Merensky and UG-2 Reefs is low, no significant spectral overlap can be expected. Wavelength scans for typical samples confirm this, but indicate that significant matrix problems occur.

Figure 1 shows the  $2\theta$  angles of the spectral lines and absorption edges for all four elements; from this information the instrumental parameters and the angles of the analyte spectral line and background angles were deduced (Table 1). It was concluded that consideration would have to be given to the mutual matrix effects of copper and nickel, to the mutual matrix effects of chromium and iron, and to the matrix effects of these first two elements on copper and nickel.



Not to scale

Key: The straight long lines represent the  $K\alpha$  lines, and the straight short lines the  $K\beta$  lines. The hooked lines represent the K-absorption edges

FIGURE 1. The K-spectral lines and absorption edges of copper, nickel, iron, and chromium

2.4. A Mathematical Model for the Determination of Copper and Nickel

The following factors must be taken into account when copper and nickel concentrations are calculated from the intensities of the Cu  $K\alpha$  and Ni  $K\alpha$  analytical lines:

- (1) the factors for background correction in the determination of copper, nickel, iron, and chromium, i.e. the factors to be applied to the measurements made at the background  $2\theta$  angle for them to be related to the background at the  $2\theta$  angle of the analyte spectral line,
- (2) the influence of chromium in the matrix on the Ni  $K\alpha$ , Cu  $K\alpha$ , and Fe  $K\alpha$  analytical lines (absorption),
- (3) the influence of iron in the matrix on the Cu  $K\alpha$ , Ni  $K\alpha$ , and Cr  $K\beta$  lines (which results in an enhancement of the Cr  $K\beta$  intensity and an absorption of the Cu  $K\alpha$  and Ni  $K\alpha$  intensities), and
- (4) the influence of copper in the matrix on the Ni  $K\alpha$  (enhancement) and of nickel in the matrix on the Cu  $K\alpha$  (absorption) analytical line.

2.4.1. Correction for Background Intensities

The background measurements for copper and nickel are corrected as follows. The background and the analyte peak of a blank sample are measured at the  $2\theta$  angles, and the background factor is calculated according to equation (1):

$$f = \frac{I_i}{I_b}, \dots\dots\dots(1)$$

where  $I_i$  and  $I_b$  are the intensities at the analyte and background  $2\theta$  angles respectively.

The background factors for copper, nickel, and iron are high because of leakage from copper and iron in the tube, the leakage radiation for copper affecting the background intensity for nickel.

2.4.2. *The Mutual Interference of Copper and Nickel*

Two series of pellets were made: one with a constant concentration of copper oxide in the final pellet and varying nickel oxide content, and the other with a constant concentration of nickel and varying copper oxide content (Table 2).

TABLE 2

*Mutual interference of copper and nickel: composition of pellets*

Condition:

Binder: 1,0 g

Concentration in pellet, $\mu\text{g/g}$		Mass of oxides, g		Matrix† g
CuO	NiO	CuO	NiO	
2000	-	0,5000	-	8,5
2000	1000	0,5000	0,2500	8,25
2000	2000	0,5000	0,5000	8,00
2000	4000	0,5000	1,000	7,50
2000	6000	0,5000	1,500	7,00
2000	8000	0,5000	2,000	6,50
-	2000	-	0,500	8,5
1000	2000	0,2500	0,500	8,25
2000	2000	0,5000	0,500	8,00
4000	2000	1,000	0,500	7,50
6000	2000	1,500	0,500	7,00
8000	2000	2,000	0,500	6,50

† River sand

After the appropriate  $2\theta$  angles had been measured and the net peak intensities for the Cu  $K\alpha$  and Ni  $K\alpha$  lines calculated, no change in the Cu  $K\alpha$  intensity was observed with varying concentrations of nickel oxide; similarly, the Ni  $K\alpha$  intensity was not affected by varying concentrations of copper oxide.

2.4.3. *The Effect of Chromium in the Matrix on the Fe  $K\beta$  Analytical Line*

Several pellets containing a constant concentration of iron and varying amounts of chromium in a matrix of river sand were prepared (Table 3), and the intensities were measured at the  $2\theta$  angles given in Table 1. Equation (2) can be applied to the measured intensities:

TABLE 3

*Determination of the influence of chromium on iron:  
composition of pellets*

Conditions:

Binder 1,0 g

CuO-NiO 0,25 g

(contains 10,000  $\mu\text{g}$  of each oxide)

CuO-NiO* g	Cr <sub>2</sub> O <sub>3</sub>		Fe <sub>2</sub> O <sub>3</sub>		Matrix† g
	mg	%	mg	%	
-	-	-	-	-	9
0,25	-	-	100	10	8,4
0,25	50	5	100	10	8,35
0,25	100	10	100	10	8,3
0,25	200	20	100	10	8,2
0,25	300	30	100	10	8,1

\* % based on a sample of 1 g

† River sand



$$[\text{Fe}] = \frac{I_{\text{Fe } K\beta}}{m_{\text{Fe } K\beta}} \{1 + \alpha_{\text{Cr } K\beta/\text{Fe } K\beta} \times I_{\text{Cr } K\beta}\}, \dots\dots\dots (2)$$

where  $[\text{Fe}]$  is the concentration of the analyte in micrograms per gram,  
 $I_{\text{Fe } K\beta}$  is the net intensity of the Fe  $K\beta$  analytical line in counts per second,  
 $\alpha_{\text{Cr } K\beta/\text{Fe } K\beta}$  is the matrix effect of the chromium on the iron,  
 $I_{\text{Cr } K\beta}$  is the net intensity of the Cr  $K\beta$  analytical line in counts per second, and

$m_{\text{Fe } K\beta} = \frac{I_{\text{Fe } K\beta}}{[\text{Fe}]}$  is the sensitivity of the iron when no chromium is present, or the Fe  $K\beta$  intensity per microgram of iron per gram in the absence of chromium.

Rearrangement of equation (2) gives equation (3), which is in the form of a straight line ( $y = mx + c$ ):

$$\frac{m_{\text{Fe } K\beta} \times [\text{Fe}]}{I_{\text{Fe } K\beta}} = 1 + \alpha_{\text{Cr } K\beta/\text{Fe } K\beta} \times I_{\text{Cr } K\beta} \dots\dots\dots (3)$$

A plot of  $m_{\text{Fe } K\beta} \times [\text{Fe}]$  versus  $I_{\text{Cr } K\beta}$  is substantially linear and has a slope of  $\alpha_{\text{Cr } K\beta/\text{Fe } K\beta}$ .

The application of equation (3) to all the intensity data that were obtained from the measurements of the pellets gives a slope of 7,6001E-04 and an intercept of 1,0092.

Equation (4) therefore expresses the correction for the matrix effects due to the influence of chromium on iron:

$$[\text{Fe}] = \frac{I_{\text{Fe } K\beta}}{m_{\text{Fe } K\beta}} (1 + 7,6001 \times 10^{-4} \times I_{\text{Cr } K\beta}). \dots\dots\dots (4)$$

Equation (4) can now be expressed as

$$I_{\text{Fe } K\beta \text{ cor}} = I_{\text{Fe } K\beta} (1 + 7,6001 \times 10^{-4} \times I_{\text{Cr } K\beta}), \dots\dots\dots (5)$$

where  $I_{\text{Fe } K\beta \text{ cor}}$  is the net intensity,  $I_{\text{Fe } K\beta}$ , in counts per second corrected for the influence of the chromium present in the matrix.

**2.4.4. The Effect of Iron in the Matrix on the Cr  $K\beta$  Analytical Line**

Pellets containing a constant concentration of chromium oxide (10 per cent  $\text{Cr}_2\text{O}_3$ ) and varying concentrations of iron oxide (2, 4, 8, and 10 per cent  $\text{Fe}_3\text{O}_4$ ) in a matrix of river sand were prepared (Table 4), and the intensities were measured at the  $2\theta$  angles given in Table 1.

After the net Cr  $K\beta$  intensity had been calculated, the change in intensity with increases in iron concentration was found to be negligible, i.e. within experimental error.

**2.4.5. The Effects of Chromium in the Matrix on the Ni  $K\alpha$  and Cu  $K\alpha$  Analytical Lines**

Pellets containing a constant concentration of copper and nickel oxides (2000  $\mu\text{g/g}$ ) and varied concentrations of chromium oxide (0 to 30 per cent  $\text{Cr}_2\text{O}_3$ ) were prepared (Table 5) and the intensities measured at the different  $2\theta$  angles given in Table 1.

Equation (3) can now be written with either copper or nickel as the analyte and chromium as the interfering element:

$$\frac{m_{\text{Ni } K\alpha} \times [\text{Ni}]}{I_{\text{Ni } K\alpha}} = 1 + \alpha_{\text{Cr } K\beta/\text{Ni } K\alpha} \times I_{\text{Cr } K\beta}, \dots\dots\dots (6)$$

or

TABLE 4

Determination of the influence of iron on chromium: composition of pellets

Conditions:

Binder 1,0 g  
 CuO-NiO 0,25 g  
 (contains 10,000 µg of each oxide)  
 Cr<sub>2</sub>O<sub>3</sub>: 100 mg (10%)\*

Fe <sub>2</sub> O <sub>3</sub>		Matrix† g
mg	%	
-	-	9
-	-	8,4
20	2	8,38
40	4	8,36
80	8	8,32
100	10	8,30

\* % based on a sample of 1 g  
 † River sand

TABLE 5

Effect of chromium or iron on the peak intensities of the Ni Kα and Cu Kα lines: composition of pellets

Conditions:

NiO-CuO 0,25 g  
 Binder 1,0 g

Cr <sub>2</sub> O <sub>3</sub> or Fe <sub>2</sub> O <sub>3</sub>				Matrix† g
mg	%	mg	%	
-	-	-	-	9
-	-	-	-	8,5
50	5	20	2	8,43
100	10	40	4	8,36
150	15	60	6	8,29
200	20	80	8	8,22
250	25	100	10	8,15
300	30	150	15	8,05

† River sand

$$\frac{m_{Cu\ K\alpha} \times [Cu]}{I_{Cu\ K\alpha}} = 1 + \alpha_{Cr\ K\beta/Cu\ K\alpha} \times I_{Cr\ K\beta} \dots\dots\dots (7)$$

where  $m_{Ni\ K\alpha}$  and  $m_{Cu\ K\alpha}$  are the sensitivities for nickel and copper respectively, when no chromium is present,

[Ni] and [Cu] are the concentrations of the analytes in micrograms per gram,

$I_{Ni\ K\alpha}$  is the net intensity of the Ni Kα analytical line in counts per second,

$I_{Cu\ K\alpha}$  is the net intensity of the Cu Kα analytical line in counts per second,

$\alpha_{Cr\ K\beta/Ni\ K\alpha}$  is the matrix effect of the chromium on the nickel, and

$\alpha_{Cr\ K\beta/Cu\ K\alpha}$  is the matrix effect of the chromium on the copper.

Both equations (6) and (7) are again in the form of a straight line ( $y = mx + c$ ).

A linear regression analysis of the intensity data obtained from the pellets containing the constant amount of nickel oxide-copper oxide mixture and varying amounts of Cr<sub>2</sub>O<sub>3</sub> gives a slope of 6,0829E-4 and an intercept of 1,0983 in the case of the Ni Kα line, and a slope of 4,9096E-4 and an intercept of 0,9982 in the case of the Cu Kα line.

Equations (6) and (7) therefore express the correction for matrix effects due to the influence of chromium on nickel and copper and can be written as follows:-

$$[Ni] = \frac{I_{Ni\ K\alpha}}{m_{Ni\ K\alpha}} (1 + 6,0829 \times 10^{-4} \times I_{Cr\ K\beta}), \dots\dots\dots (8)$$

$$[Cu] = \frac{I_{Cu\ K\alpha}}{m_{Cu\ K\alpha}} (1 + 4,9096 \times 10^{-4} \times I_{Cr\ K\beta}); \dots\dots\dots (9)$$

or as

$$I_{Ni\ K\alpha\ cor} = I_{Ni\ K\alpha} (1 + 6,0829 \times 10^{-4} \times I_{Cr\ K\beta}), \dots\dots\dots (10)$$

$$I_{Cu\ K\alpha_{cor}} = I_{Cu\ K\alpha}(1 + 4,9096 \times 10^{-4} \times I_{Cr\ K\beta}), \dots\dots\dots (11)$$

where  $I_{Ni\ K\alpha_{cor}}$  is the net intensity,  $I_{Ni\ K\alpha}$ , corrected for the influence of chromium, and  
 $I_{Cu\ K\alpha_{cor}}$  is the net intensity,  $I_{Cu\ K\alpha}$ , corrected for the influence of chromium.

**2.4.6. The Effects of Iron in the Matrix on the Ni K $\alpha$  and Cu K $\alpha$  Analytical Lines**

Pellets containing a constant concentration of 2000  $\mu$ g of copper oxide and 2000  $\mu$ g of nickel oxide per gram, and varying concentrations of iron oxide (0 to 20 per cent Fe<sub>2</sub>O<sub>3</sub>) were prepared (Table 5), and the intensities were measured at the different 2 $\theta$  angles given in Table 1.

Equation (3) can now be rewritten with either copper or nickel as the analyte and iron as the interfering element.

$$\frac{m'_{Ni\ K\alpha} \times [Ni]}{I_{Ni\ K\alpha}} = 1 + \alpha_{Fe\ K\beta/Ni\ K\alpha} \times I_{Fe\ K\beta}, \dots\dots\dots (12)$$

$$\frac{m'_{Cu\ K\alpha} \times [Cu]}{I_{Cu\ K\alpha}} = 1 + \alpha_{Fe\ K\beta/Cu\ K\alpha} \times I_{Fe\ K\beta}, \dots\dots\dots (13)$$

where  $\alpha_{Fe\ K\beta/Ni\ K\alpha}$  is the matrix effect of iron on nickel,  
 $\alpha_{Fe\ K\beta/Cu\ K\alpha}$  is the matrix effect of iron on copper,  
 $m'_{Ni\ K\alpha}$  is the sensitivity of nickel K $\alpha$  when no iron is present, or the Ni K $\alpha$  intensity per 1% nickel in the absence of iron, and  
 $m'_{Cu\ K\alpha}$  is the sensitivity of copper K $\alpha$  when no iron is present.

Equations (12) and (13) are in the form of a straight line. A linear regression analysis of the data obtained by application of the intensity measurements for the specially prepared pellets to equations (12) and (13) gives a slope of 2,7131E-4 and an intercept of 1,002 94 in the case of the Ni K $\alpha$  line, and a slope of 2,0419E-4 and an intercept of 1,003 92 in the case of the Cu K $\alpha$  line.

Equations (12) and (13) therefore express the correction for matrix effects due to the influence of iron on nickel and copper, and can be written as follows:

$$[Ni] = \frac{I_{Ni\ K\alpha}}{m'_{Ni\ K\alpha}} (1 + 2,7131 \times 10^{-4} \times I_{Fe\ K\beta}), \dots\dots\dots (14)$$

$$[Cu] = \frac{I_{Cu\ K\alpha}}{m'_{Cu\ K\alpha}} (1 + 2,0419 \times 10^{-4} \times I_{Fe\ K\beta}); \dots\dots\dots (15)$$

or as

$$I'_{Ni\ K\alpha_{cor}} = I'_{Ni\ K\alpha}(1 + 2,7131 \times 10^{-4} \times I_{Fe\ K\beta}), \dots\dots\dots (16)$$

$$I'_{Cu\ K\alpha_{cor}} = I'_{Cu\ K\alpha}(1 + 2,0419 \times 10^{-4} \times I_{Fe\ K\beta}), \dots\dots\dots (17)$$

where  $I'_{Ni\ K\alpha_{cor}}$  is the net intensity,  $I'_{Ni\ K\alpha}$ , corrected for the influence of iron, and  
 $I'_{Cu\ K\alpha_{cor}}$  is the net intensity,  $I'_{Cu\ K\alpha}$ , corrected for the influence of iron.

**2.4.7. The Relationship between Concentration and Intensity for Copper and Nickel in a Matrix Rich in Iron and Chromium**

Samples from the Merensky and UG-2 Reefs can contain high concentrations of iron and chromium in the form of chromite. The matrix effects of both iron and chromium on the determination of copper and nickel can be considerable, and the necessary corrections for matrix effect must therefore be applied to the copper and nickel intensities.

DETERMINATION OF COPPER AND NICKEL

By a combination of the different factors for matrix influence (Table 6) as calculated in equations (10), (11), (16), and (17), the corrected net intensities in counts per second for the Cu K $\alpha$  and Ni K $\alpha$  analytical lines can now be deduced.

TABLE 6

*Factors for the determination of copper and nickel*

Background factors	influence factors
$f_{Cr}$ 1,143	$\alpha_{Cr K\beta/Fe K\beta}$ $7,60 \times 10^{-4}$
$f_{Cu}$ 3,928	$\alpha_{Cr K\beta/Ni K\alpha}$ $6,08 \times 10^{-4}$
$f_{Ni}$ 3,774	$\alpha_{Cr K\beta/Cu K\alpha}$ $4,91 \times 10^{-4}$
$f_{Fe}$ 4,758	$\alpha_{Fe K\beta/Ni K\alpha}$ $2,71 \times 10^{-4}$
	$\alpha_{Fe K\beta/Cu K\alpha}$ $2,04 \times 10^{-4}$

$$I_{Cu K\alpha_{cor}} = I_{Cu K\alpha}(1 + \alpha_{Fe K\beta/Cu K\alpha} \times I_{Fe K\beta_{cor}} + \alpha_{Cr K\beta/Cu K\alpha} \times I_{Cr K\beta}) \dots\dots\dots (18)$$

Because of the matrix influence of chromium on iron, the corrected value arrived at in the equations must be substituted for  $I_{Fe K\beta_{cor}}$  when

$$I_{Cu K\alpha_{cor}} = I_{Cu K\alpha} [1 + \alpha_{Fe K\beta/Cu K\alpha} \times I_{Fe K\beta}(1 + \alpha_{Cr K\beta/Fe K\beta} \times I_{Cr K\beta}) + \alpha_{Cr K\beta/Cu K\alpha} \times I_{Cr K\beta}]; (19)$$

or, in specific terms (Table 6),

$$I_{Cu K\alpha_{cor}} = I_{Cu K\alpha} [1 + 2,0419 \times 10^{-4} \times I_{Fe K\beta}(1 + 7,6001 \times 10^{-4} \times I_{Cr K\beta}) + 4,9096 \times 10^{-4} \times I_{Cr K\beta}] \dots\dots\dots (19a)$$

Similarly,

$$I_{Ni K\alpha_{cor}} = I_{Ni K\alpha} [1 + \alpha_{Fe K\beta/Ni K\alpha} \times I_{Fe K\beta}(1 + \alpha_{Cr K\beta/Fe K\beta} \times I_{Cr K\beta}) + \alpha_{Cr K\beta/Ni K\alpha} \times I_{Cr K\beta}]; (20)$$

or, in specific terms,

$$I_{Ni K\alpha_{cor}} = I_{Ni K\alpha} [1 + 2,7137 \times 10^{-4} \times I_{Fe K\beta}(1 + 7,6001 \times 10^{-4} \times I_{Cr K\beta}) + 6,0829 \times 10^{-4} \times I_{Cr K\beta}] \dots\dots\dots (20a)$$

2.5. Calibration

The calibration standards (Table 7) were measured by use of the instrumental parameters given in Table 1. The measured intensities were first corrected for background intensities by use of equation (1). The net intensities were then corrected for the influence of chromium and iron in the matrix by use of equations (19) and (20) and the influence factors given in Table 6.

When the corrected nickel and copper intensities were plotted against concentration, linear calibrations were obtained (Figures 2 and 3).

TABLE 7

Calibration standards

Conditions:

Binder 1,0 g

CuO-NiO 0,8 g of each + 19,2 g of river sand = 40 000 µg/g of oxide

CuO mixt. g	NiO mixt. g	Matrix† g	Concentration in pellet, µg/g	
			CuO	NiO
0,0125	0,2500	8,7375	50	1000
0,0250	0,0500	8,9250	100	200
0,0500	0,6250	8,3250	200	2500
0,1250	0,3750	8,5000	500	1500
0,2500	0,2500	8,5000	1000	100
0,3750	0,0125	8,6125	1500	50
0,6250	0,1250	8,2500	2500	500
-	-	9,000	-	-

† River sand

$$I_{Ni\ K\alpha_{cor}} = m_{Ni\ K\alpha} \times [Ni] + c, \dots\dots\dots (21)$$

$$[Ni] = \frac{I_{Ni\ K\alpha_{cor}} - c}{m_{Ni\ K\alpha}}, \text{ and } \dots\dots\dots (22)$$

$$[Cu] = \frac{I_{Cu\ K\alpha_{cor}} - c}{m_{Cu\ K\alpha}}, \dots\dots\dots (23)$$

where [Cu] and [Ni] are the concentrations of copper and nickel,  
 $I_{Ni\ K\alpha_{cor}}$  and  $I_{Cu\ K\alpha_{cor}}$  are the net Ni Kα and Cu Kα intensities respectively, corrected for the influence of chromium and iron in the matrix,  
 $m_{Ni\ K\alpha}$  and  $m_{Cu\ K\alpha}$  are the sensitivities for copper and nickel respectively in the presence of chromium and iron in the samples.

3. SENSITIVITY AND LOWER LIMITS OF DETECTION

The sensitivity, lower limits of detection, and lower limits of determination for copper and nickel in samples from the Merensky and UG-2 Reefs were calculated for the experimental conditions given in Table 1, and are listed in Table 8. The values given in Table 8 are specific to the X-ray-fluorescence spectrometer at Mintek, which is equipped with a rhodium tube.

TABLE 8

Sensitivity, lower limits of detection, and lower limits of determination

Element	Sensitivity (S <sub>i</sub> ) (count/s)/(µg/g)	Lower limit of detection (c <sub>L</sub> ) µg/g	Lower limit of determination µg/g
Cu	0,9475	30,8	92
Ni	0,6336	39,7	119

DETERMINATION OF COPPER AND NICKEL

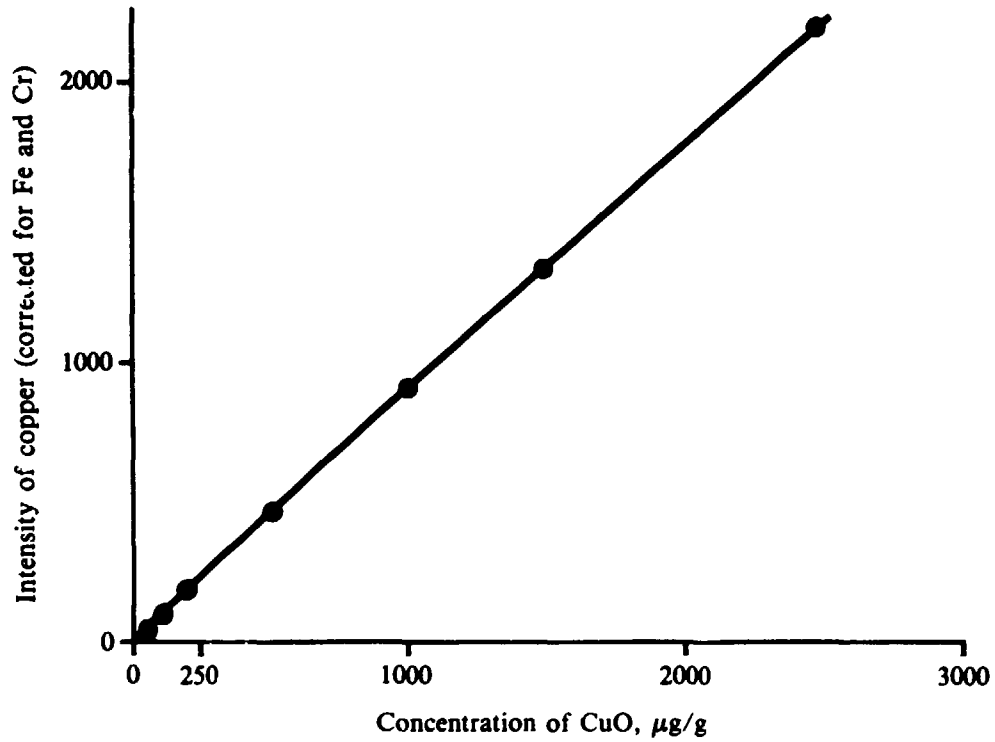


FIGURE 2. Calibration for copper oxide

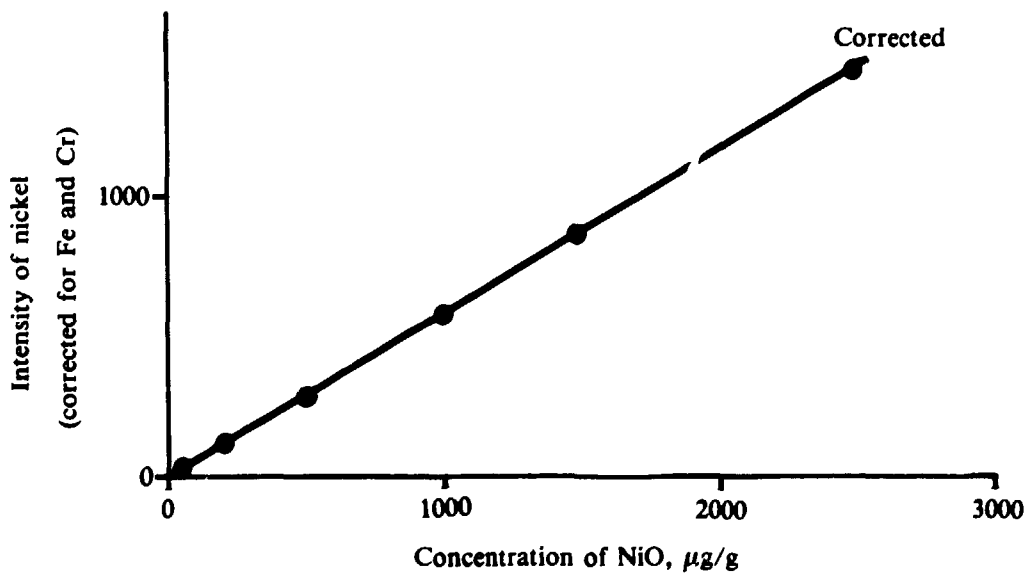


FIGURE 3. Calibration for nickel oxide

The sensitivity is given by

$$I_{i\text{cor}} = S_i C_i, \dots\dots\dots (24)$$

where  $S_i$  is the slope of the calibration curve of the sensitivity expressed in counts per second per unit of concentration of element  $i$ ,  
 $C_i$  is the concentration of analyte  $i$ , and  
 $I_{i\text{cor}}$  is the net intensity (corrected for matrix effects) of element  $i$ .

DETERMINATION OF COPPER AND NICKEL

The lower limit of detection (LLD or  $c_L$ ) was calculated according to the formula given by Jenkins and De Vries<sup>1</sup>:

$$c_L = \frac{2\sqrt{2}}{S_i\sqrt{T}} \sqrt{R_b} \dots\dots\dots (25)$$

where  $c_L$  is the lower limit of detection,  
 $R_b$  is the counting rate at the background  $2\theta$  angle, and  
 $T$  is the total counting time.

From equation (25) it is evident that, when longer counting times are used, the lower limit of detection becomes smaller for a given background intensity and a given sensitivity. For practical purposes, the counting time for the copper and nickel determinations in ore from the Merensky and UG-2 Reefs was kept at 40 seconds for the intensity measurements at the background and 40 seconds for those at the analytical line.

For quantitative analysis, the lower limit of determination is taken as three times the lower limit of detection.

4. RESULTS

Pellets were prepared from a suite of samples containing varying concentrations of copper, nickel, iron, and chromium. The appropriate masses of sample, inert diluent, and binder are given in Table 9. The peak intensities were measured by use of the operating parameters given in Table 1, and the concentrations were calculated from equations (19) and (21). These concentrations are compared in Table 10 with those obtained by atomic-absorption spectrophotometry.

The reproducibility of the method was determined from replicate analyses of an 'in-house' reference material, the analytical data relating to this sample being given in Table 11. The relative standard deviation for both elements is approximately 0,02.

TABLE 9  
*Variation of sample mass and diluent with concentration*

Condition:  
 Mass of binder 1,0g

Estimated concentration of Cu and Ni $\mu\text{g/g}$	Mass of sample g	Mass of diluent g
0 to 2 000	9	-
2 000 to 4 000	4,5	4,5
8 000 to 10 000	2,0	7
10 000 to 20 000	1,0	8

TABLE 10  
*Comparative values for copper and nickel*

Total copper, $\mu\text{g/g}$		Relative deviation of XRFS to AAS (%)	Total nickel, $\mu\text{g/g}$		Relative deviation of XRFS to AAS (%)
AAS*	XRFS†		AAS*	XRFS†	
870	883	+ 1,5	2175	2193	+ 0,8
210	223	+ 6,2	1320	1328	+ 0,6
2630	2617	- 0,5	5040	4701	- 6,7
2300	2412	+ 4,8	4500	4390	- 2,4
1370	1401	+ 2,3	3270	3286	+ 0,5
710	674	- 5,1	1460	1523	+ 4,3
50	67	+ 34,0	990	857	- 11,4
312	292	- 6,4	1600	1644	+ 2,7
548	552	+ 0,7	1395	1375	- 1,4
Average deviation		+ 0,3	Average deviation		- 1,6

\* Atomic-absorption spectrophotometry

† X-ray-fluorescence spectrometry

TABLE 11

*Precision of analysis*

In-house reference material	Accepted value $\mu\text{g/g}$		XRFS mean value $\mu\text{g/g}$		Relative standard deviation, $s_r$		No of results
	Copper	Nickel	Copper	Nickel	Copper	Nickel	
53/71	950	2400	902	2446	0,017	0,0022	4

The deviation between the values obtained by X-ray-fluorescence spectrometry and by atomic-absorption spectrometry are, with one exception, within 7 per cent for both elements, with average deviations of +0,3 and -1,6 per cent (relative to the atomic-absorption values) for copper and nickel respectively. The largest deviations occur at the lower concentrations of copper and nickel, where minimal dilutions have to be made for reasonable atomic-absorption measurements to be made. Under these conditions spike recoveries ranged from 86 to 93 per cent, and the corrected results therefore have this level of uncertainty.

## 5. DISCUSSION

Where the total concentrations of copper and of nickel have to be determined, the X-ray method is relatively rapid: 10 samples can be analysed in 2,5 hours. Fusion of the sample is difficult with samples such as those from the UG-2 Reef, which contains spinels that are extremely refractory. The analysis time is therefore much longer (15 to 20 hours) if the sample has to be completely dissolved as required in atomic-absorption spectrophotometry.

Mutual-interference factors are incorporated in the on-line or off-line calculations for the X-ray-fluorescence procedure, and automatically compensate for the effect of one element on another. Adequate compensation for these effects by atomic-absorption spectrometry, particularly at low concentrations, would necessitate a spike recovery over a range of concentrations, thus increasing the time for analysis.

The X-ray-fluorescence method is most advantageous when the total concentrations of copper and of nickel are required. It has little advantage when the concentration of soluble copper or nickel is required since the sample-preparation times are then similar to those for atomic-absorption spectrometry and inductively-coupled plasma optical emission spectroscopy, and there is little difference in the measurement times.

## 6. CONCLUSIONS

By the rapid X-ray-fluorescence method developed for the determination of copper and nickel in samples of varying iron and chromium content, the analysis range is 100 to 4000  $\mu\text{g/g}$  for each element, and the relative standard deviation of the determinations is approximately 0,02.

Calibration is effected with synthetic mixtures of oxides, and corrections are made for the matrix effects of chromium and iron by on-line computation.

## 7. REFERENCE

- JENKINS, R., and DE VRIES, J.L. Worked samples in X-ray analysis. London, MacMillan, 1978.



## APPENDIX

THE DETERMINATION OF COPPER AND NICKEL IN IRON- AND CHROMIUM-BEARING MATERIALS  
BY A PRESSED-POWDER TECHNIQUE AND X-RAY-FLUORESCENCE SPECTROMETRY  
LABORATORY METHOD No. 29/15

## 1. OUTLINE

Finely ground sample material is mixed with varying amounts of diluent (river sand), depending on the concentrations of copper and nickel to be determined, to give a total mass of 9 g for each sample, to which is added 1 g of wax binder. A pellet is pressed, and the net peaks are determined after corrections have been made for the interference by iron and chromium (from the matrix) on the spectral lines for copper and nickel, and for the interference by chromium on the line for iron. The net peak corrected for matrix interferences is plotted against concentration.

## 2. APPLICATION

The method is applicable to the determination of copper and nickel in such material as the head samples, concentrates, middlings, and tailings of ore from the Merensky and UG-2 Reefs in concentrations greater than 100  $\mu\text{g/g}$  of copper and 120  $\mu\text{g/g}$  of nickel per gram. The matrix effects are limited by fine grinding and dilution.

The limits of determination are 100 and 120  $\mu\text{g/g}$  for copper and nickel respectively, with detection limits of 30 and 40  $\mu\text{g/g}$ . The relative standard deviation for both elements is 0,02 at 900  $\mu\text{g/g}$  (copper) and 2400  $\mu\text{g/g}$  (nickel).

## 3. SAMPLE MASS

The mass of sample, diluent (river sand), and binder relative to the concentrations to be determined are given in Table I-1.

TABLE I-1

*Variation of sample mass and diluent with concentration*

*Condition:*

Mass of binder 1,0g

Estimated concentration of Cu and Ni $\mu\text{g/g}$	Mass of sample g	Mass of diluent g
0 to 2 000	9	-
2 000 to 4 000	4,5	4,5
8 000 to 10 000	2,0	7
10 000 to 20 000	1,0	8

## 4. REAGENTS

*(1) Inert Diluent*

Must be river sand that is free of copper and nickel.

*(2) Wax Binder*

A mixture of 1 part of Sasolwax N3 and 9 parts of polystyrene copolymer EMU 120FD (supplied by the Badische Anilin- und Soda-Fabrik A.D.).

*(3) Metal Oxides (CuO, NiO)*

These must be of analytical reagent grade.

## 5. EQUIPMENT

*(1) Herzog Press*

Dies must give a pellet 40 mm in diameter.

## DETERMINATION OF COPPER AND NICKEL

**(2) SRS200 Siemens Sequential Spectrometer**

Must be fully automatic with an 80-position sample loader.

**(3) A Desk-top Computer**

Such as an HP85 computer, or the Nova IV Data General minicomputer.

### 6. PROCEDURE

#### 6.1. Preparation of Samples

- a. Weigh the required masses of sample, diluent, and binder into a beaker.
- b. Mix well with a spatula and transfer to a pelletizing die (40 mm diameter).
- c. Apply pressure at 5 t for 2 minutes and label the pellets.

#### 6.2. Measurement of Samples

- a. Load the copper and nickel standards, control standards, blanks, and samples into the sample holders, and load the holders into the sample trays of the automatic sample loader.
- b. Set the logic controller LC200 for control of the spectrometer by external control mode.
- c. Using the nickel-copper stringfile, measure all the samples and standards at the appropriate wavelength positions (see Table I-2), and send the data to the nickel-copper data file.
- d. Calculate the results with a desk-top computer, or the Nova IV (for on-line calculations).
- e. Print out the results and the report.

### 7. OPERATING PARAMETERS

The instrumental parameters, analytical lines, and background positions are given in Table I-2.

TABLE I-2

*Operating parameters*

Spectrometer	Siemens SRS200 and LC200
Voltage	60 kV
Current	40 mA
Tube	Rh target
Detector	Scintillation
Radiation path	Air
Collimator	150 μm
Bragg crystal	LiF 220
Discriminator	Window to include 99% of energy of Ni Kα and Cu Kα pulses
Counting time	40 seconds
Analytical lines	Ni Kα 71,26° 2θ, Fe Kβ 76,16° 2θ, Cu Kα 65,55° 2θ, Cr Kβ 94,12° 2θ
Background positions	68,40° 2θ, 73,71° 2θ, 81,00° 2θ, 97,00° 2θ

### 8. CALCULATION

The corrected intensities for copper and nickel are given by the following equations, which incorporate corrections for the interference of chromium and iron on the spectral lines for copper and nickel, and the interference of chromium on the spectral line for iron:

$$I_{Cu\ K\alpha_{cor}} = I_{Cu\ K\alpha} [1 + \alpha_{Fe\ K\beta/Cu\ K\alpha} \times I_{Fe\ K\beta} (1 + \alpha_{Cr\ K\beta/Fe\ K\beta} \times I_{Cr\ K\beta}) + \alpha_{Cr\ K\beta/Cu\ K\alpha} \times I_{Cr\ K\beta}], \quad (I-1)$$

and

$$I_{Ni\ K\alpha_{cor}} = I_{Ni\ K\alpha} [1 + \alpha_{Fe\ K\beta/Ni\ K\alpha} \times I_{Fe\ K\beta} (1 + \alpha_{Cr\ K\beta/Fe\ K\beta} \times I_{Cr\ K\beta}) + \alpha_{Cr\ K\beta/Ni\ K\alpha} \times I_{Cr\ K\beta}], \quad (I-2)$$

## DETERMINATION OF COPPER AND NICKEL

where  $I_{\text{Cu } K\alpha}$ ,  $I_{\text{Fe } K\beta}$ ,  $I_{\text{Cr } K\beta}$  and  $I_{\text{Ni } K\alpha}$  are the intensities for the respective analytical lines,  
 $\alpha_{\text{Fe } K\beta/\text{Cu } K\alpha}$  is the matrix effect of iron on copper,  
 $\alpha_{\text{Cr } K\beta/\text{Fe } K\alpha}$  is the matrix effect of chromium on iron,  
 $\alpha_{\text{Cr } K\beta/\text{Cu } K\alpha}$  is the matrix effect of chromium on copper,  
 $\alpha_{\text{Fe } K\beta/\text{Ni } K\alpha}$  is the matrix effect of iron on nickel, and  
 $\alpha_{\text{Cr } K\beta/\text{Ni } K\alpha}$  is the matrix effect of chromium on nickel.