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# Assay of Powdered Metallic Ores by Means of a Portable X-Ray Fluorescence Analyser

by H. Kunzendorf, L. Løvborg and H. Wollenberg

November 1971

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Abstract

Radioisotope X-ray fluorescence analysis of powdered metallic ores has been carried out by means of a portable instrument. Description of and experience with this instrument are included. Elements investigated were Cr, Ni, Cu, Zn, Zr, Nb, Mo, La plus Ce, and Pb. Typical powdered ore minerals of these elements were mixed with powdered material of granitic or gabbroic composition, and calibration curves were established by plotting the difference count rates obtained by means of the portable X-ray fluorescence analyser against the contents of the elements in the mixtures. Regression analysis of the lower linear part of these curves yielded detection limits and accuracies, both of the order of 0.1%.

**Statens trykningskontor**

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## 1. INTRODUCTION

A method of rapid semiquantitative elemental analysis has become available to the geologist through the technique of radioisotope-excited X-ray fluorescence (IXRF). Replacing the cooled X-ray tube applied in conventional X-ray fluorescence by a radioactive source, using the well-known balanced X-ray filter technique<sup>1)</sup> and a non-dispersive X-ray detection system, British scientists introduced the first portable IXRF system in 1965<sup>2)</sup>. These instruments are now commercially available.

With appropriate calibrations the method can be used on in-situ rock surfaces, on flat surfaces of hand specimens, and on powdered samples. Calibrations and on-the-outcrop analyses of Zr, Nb, and La plus Ce by portable IXRF instruments have recently been described by Wollenberg et al.<sup>3)</sup>; earlier, Bohse et al.<sup>4)</sup> reported field determinations of Zr and Nb by IXRF in a systematic study of the kakortokites of the Ilímaussaq intrusion, South Greenland. Gallagher<sup>5)</sup> and Bowie<sup>6)</sup> described IXRF examinations of powdered metallic ore samples.

In IXRF X- or Y-rays, emitted by a radioactive source, whose strength is usually a few millicuries, excite X-rays in the sample. These X-rays pass through X-ray filters and reach the detector.

The technique of balanced X-ray filters provides the high resolution necessary to detect characteristic K or L X-rays from a sample. The thicknesses of the filters are adjusted to accommodate specific X-ray pass bands. They are produced from materials which contain elements whose X-ray absorption edges bracket the  $K_{\alpha}$  or  $L_{\alpha}$  X-ray energies characteristic of the element being sought (fig. 4). Thus, in most cases the difference in counting rates between exposures with each of the filters in position, is proportional to the abundance of the target element.

In this report we emphasize the use of portable IXRF instrumentation (EKCO Mineral Analyser) in the analyses of powdered samples of metallic and rare elements which, presently or in the future, might be sought in economic geologic exploration in Greenland. We shall point out the usefulness of the method, describe the instrumentation and its operation, discuss the limitations of the instrumentation in a field geochemical study, and shall furnish calibration curves, relating Cr, Ni, Cu, Zn, Zr, Nb, Mo, La plus Ce, and Pb abundances to instrument counting rates.



## 2. INSTRUMENTATION<sup>x</sup>

The EKCO Mineral Analyser consists of three units: a measuring head (probe), the analyser unit, and a battery pack. It is transported in a carrying case with shoulder strap. The overall weight of the instrument is approx. 8 kg. Fig. 1 is a photograph of the Mineral Analyser.

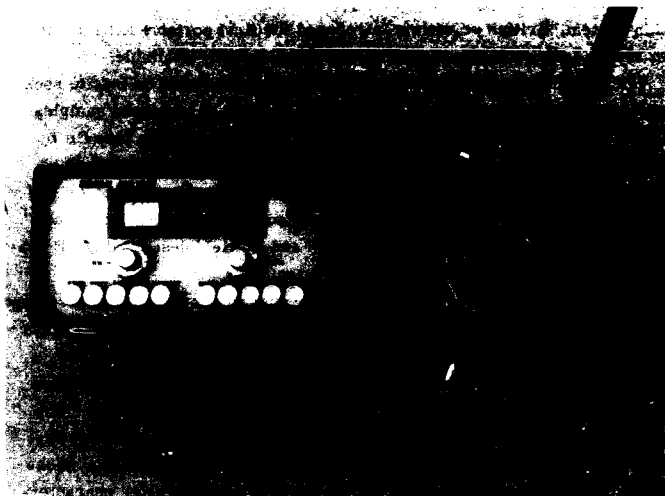


Fig. 1. Photograph of the Mineral Analyser and the experimental set-up (top view). The powdered sample is placed on the front of the probe.

As a supplement to the supplier's description of the instrument, we present here short explanations of the three units, and also include brief descriptions of our experience with it.

### 2.1. The Probe

The probe unit contains an encapsulated radioactive source and an X-ray filter set, both chosen for the determination of one single element in a powder sample; a 2 mm thick NaI(Tl) scintillation crystal, a photomultiplier, and a preamplifier. Its approx. weight is 1.6 kg.

<sup>x</sup>) available from: EKCO Instruments Ltd., Southend-on-Sea, Essex, England

By means of four fast release screws it is possible to separate the probe unit into two parts: the section which comprises the source and the section on which the X-ray filter set and the detector system are mounted.

The back of the radioactive source is strongly shielded, and photons are only emitted from the front. When not in use the source is covered with a lead shutter which shields the user from radiation.

Under working conditions the shutter is removed by means of a trigger outside the probe. In this position, as schematically shown in fig. 2, the radiation from the source reaches the sample through a thin melinex foil, covering the front opening of the probe. This foil protects the X-ray filter set and the detector from moisture and dirt; excited characteristic X-rays from the sample reach the scintillation detector through this melinex foil and a thin beryllium window in front of the detector.

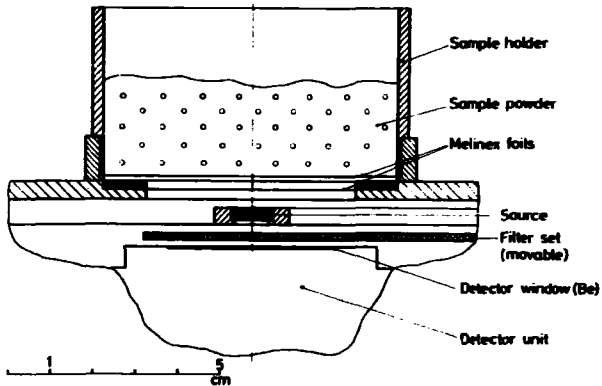


Fig. 2. Sketch of the experimental set-up.

To change the source three small screws on the source section have to be removed. Owing to their small size, these screws can easily be lost during the changing operation. Since no spare sets of screws are provided with the probe unit, it is recommended to change the source with care.

Change of the filter set is a safer operation because of the greater size of the screw which fixes the set onto the probe section. However, also here no spare has been provided; it should be ordered as an additional accessory.

A special sample holder for the measurement of rock powders is available. It consists of a 76 mm dia. x 2 mm x 38 mm aluminium cylinder and a 79 mm dia. x 3 mm x 11 mm press ring; a thin melinex foil is stretched between them and fastened to the cylinder by the ring. The sample is then poured into the cylinder. It is recommended to change the foil for each analysis because fine-grained powder from the previous sample adheres to the foil.

In the laboratory the probe is mounted in a normal retort stand and the sample holder with the rock powder in it placed on the front opening of the probe.

## 2.2. The Analyser Unit

The approximate weight of this unit is 3.7 kg.

Its components comprise a pulse height analyser, a timer/scaler unit, and a high voltage power supply.

On the front panel of the analyser we find:

- (a) the battery check display, operated in connection with the push button marked BATT;
- (b) the display of the counting results by four indicator tubes giving the four most significant counting decades of a six-decade scaler;
- (c) two ten-turn potentiometers with protective covers; one marked HV for regulation of the detector high voltage between +725 V and +550 V; the other marked DISC for continuous variation of the upper level of the discriminator between approximately 1.0 V and 6.5 V;
- (d) ten push buttons, divided into a row of instrument-checking or instrument-setting buttons on the right side of the instrument panel, and a row of buttons regulating the counting procedure on the left side. Ten- or one hundred-second counting intervals can be chosen by pushing the respective buttons.

## 2.3. The Battery Pack

The DC voltage necessary to operate the electronic components of the analyser unit is provided by the battery pack.

Twenty DEAC DKz and four DEAC SD4 rechargeable cells give 24 V and 5 V over the operation time of approximately 5 hours.

Power consumption of the display indicator tubes is usually high, which in turn shortens the life time of the 5 V battery. It is therefore necessary to switch the instrument off whenever long periods between measurements occur.

The battery pack weighs approximately 2.9 kg. It is connected to the analyser unit by means of two screws and an attachment band; the DC connection is obtained by a multipin connector.

After a 5-hour working day we found it troublesome to disconnect analyser and battery pack. We therefore modified the connecting mechanism by two clamps. As an additional accessory a battery charger/power unit is available. It has the same size as the battery pack and may be connected to the analyser unit in the same manner.

Recharging the DEAC batteries is carried out by connecting battery pack and battery charger with a multipin connector and setting the functional selective plug of the battery charger in the BATT position. For empty batteries a charging time of 16 hours is sufficient.

If 110 or 220 VAC are available in the field laboratory, the battery charger may be operated as the DC power unit instead of the battery pack. In this case it is only necessary to set the functional selective plug of the unit in the POWER position.

### 3. PROCEDURES

#### 3.1. Instrument Adjustment and Counting

After choosing an appropriate filter set and a source for analysis of one element in a sample, we must determine the optimum settings for the high voltage applied to the detector and optimum window width of the single channel analyser. This operation is more complicated than in a conventional sliding channel analyser because of the fixed lower discriminator level of the Mineral Analyser.

The following procedure is recommended:

1. Choose a powder sample which contains a large concentration of the element to be analysed.
2. Adjust to a fixed small DISC value.
3. Set the HV potentiometer at 0.
4. Bring the filter set in the position "1" on the probe; count in the

ADD mode for 10 SEC; switch the filter set in the "2" position and count in the SUBTRACT mode for another 10 sec.

5. Note the resulting difference count rate and the HV setting.
6. Increase the HV by another step and repeat procedures 4 and 5.
7. Adjust to a new DISC value and repeat procedures 4 to 6.

A typical result of a channel setting procedure is shown in fig. 3.

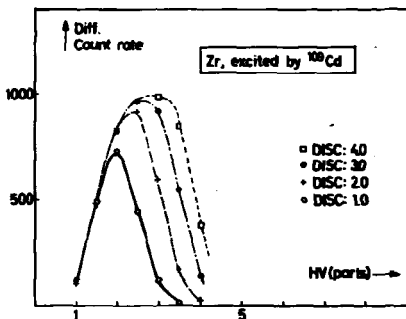


Fig. 3. Curves obtained in the adjustment procedure in the case of Zr assessment.

Optimum settings for the elements Cr, Ni, Cu, Zn, Zr, Nb, Mo, La, Ce, and Pb are given in table 1. They are only valid for our instrument and have to be adjusted when another Mineral Analyser is used.

Table 1

Characteristic X-ray energies, excitation sources, filters and instrument settings  
for Cr, Ni, Cu, Zn, Zr, Nb, Mo, La plus Ce, and Pb

Z	El- ement	K X-ray energy (keV)	Excitation source	Source strength (mCi)	Source energy (keV)	Half- life (years)	Filter pair	EKCO settings	
								HV	DISC (parts)
24	Cr	5.4	} $^{238}\text{Pu}$	10	12-17	86.4	Tl/V	4.5	3.0
28	Ni	7.47					Fe/Co	4.0	3.5
29	Cu	8.04					Co/Ni	3.75	4.0
30	Zn	8.62					Ni/Cu	3.75	4.0
40	Zr	15.75	} $^{109}\text{Cd}$	1	22.1	1.3	Rb/Sr	2.5	2.5
41	Nb	16.58					Sr/Y	2.5	2.5
42	Mo	17.44					Y/Zr	2.0	2.0
57	La	} 34.08					$^{241}\text{Am}$	3	59.5
58	Ce								
82	Pb	74.24	$^{57}\text{Co}$	0.5	122.136	0.7	Ir/Re	0	2.25

Table 2

Description of calibration materials and methods of chemical analysis

Element	Material and provider	Method of chemical analysis and analyst
Pb	Galena (86.3% Pb), vein at Blyklippen area, East Greenland; N.	Concentration of Pb, followed by polarography; A. Thorboe, Risø Chemistry Department
La plus Ce	Monazite (21.1% Ce, 9.8% La), beach sand concentrate, Malaya; G. Asmund, Risø Chemistry Department	Ce by mass spectrometry; E. Larsen, Risø Chem. Dep.; La from Ce/La ratio by isotope-excited X-ray fluorescence spectrometry by the authors (HK, HW)
Mo	Powder sample series of molybdenite ore from Malmbjerg, East Greenland; N.	Wet chemical analysis; N.
Nb	Kakortokite sample series from Kangerdluarssuk area, Ilímaussaq intrusion, South Greenland; Authors and D.	Colorimetry; A. Jensen, D.
Zr	do.	Wet chemical analysis (cupferron); S. A. Markland, Risø Chem. Dep.
Zn	Spalerite (67% Zn), vein at Blyklippen area, East Greenland; N.	Concentration of Zn followed by polarography; A. Thorboe, Risø Chem. Dep.
Cu	Bornite (21.5% Cu), vein in Skærgaard intrusion, East Greenland; N.	Dilution in HNO <sub>3</sub> , followed by electrolysis of Cu; A. Thorboe, Risø Chem. Dep.
Ni	Chemical reagent NiSO <sub>4</sub> · 6H <sub>2</sub> O (22.3% Ni); E. Merck A/S.	-
Ni	Rammelsbergite (3.2% Ni), Riechelsdorf, Hessen, Germany; Prof. G. Friedrich, TH Aachen.	Atomic absorption; A. Thorboe, Risø Chem. Dep.
Cr	Chromite ore (12% Cr), Fiskenæsset area, West Greenland; M. Ghisler, Institut for almen geologi, Copenhagen University.	Atomic absorption; A. Thorboe, Risø Chem. Dep.

N. Nordisk Mineselskab A/S, Copenhagen

D. Dansk Svovlsyre og Superphosphat Fabrik A/S, Copenhagen

### 3. 2. Preparation of Calibration Materials

To provide calibration curves from which detection limits and accuracies for the various elements could be derived, we obtained or made sets of standards containing known amounts of the elements. A description of the calibration materials, and methods of their chemical analyses are given in table 2. In the cases of Mo, Nb, and Zr, the calibration series consisted of crushed (minus 100 mesh) chemically analyzed wholerock samples, chosen initially for their varying counting rates as measured in the field.

For the other six elements studied, we prepared sets of calibration standards by successively diluting minus 100 mesh powders of chemically analyzed ores with material whose average atomic number is similar to that which might be encountered in nature. For Pb, La plus Ce, Zn, Zr, and Cu, we diluted appropriate ore minerals with powdered granite. Chromium and nickel ores, usually associated with more mafic rock types, were successively diluted with gabbro. This procedure provided sequences of 9 to 12 100 g samples, 50 g of which were diluted with 50 g of matrix material for each successive counting step. Thus, a 50 g aliquot, representing each counting step was permanently retained.

The weight of the rock powder necessary for optimum X-ray response to isotope excitation is difficult to calculate. However, its order of magnitude can be estimated using mass-absorption coefficients of the characteristic X-rays and the law of absorption of electromagnetic radiation in matter.

Mass-absorption coefficients, critical penetration depths, and critical sample weight at the 90% absorption level for  $K\alpha$  X-radiation of the elements Cr, Ni, Cu, Zn, Zr, Nb, Mo, La plus Ce, and Pb in a granitic matrix are given in table 3. It appears that only in the cases of La plus Ce and Pb determinations, our sample weight of 50 g is somewhat insufficient for optimum X-ray response. We would, however, expect no influence on the calibration curves of these elements because of the use of a fixed sample weight (50 g).

The necessary sample weight for Ni in gabbro determined experimentally appears in fig. 4 as the plateau value of the curves and is in good agreement with the theoretical considerations.



Table 3

Mass-absorption coefficients, critical penetration depth, and critical sample weight  $W_{90\%}$   
for the K X-radiation of the elements Cr, Ni, Cu, Zn, Zr, Nb, Mo, La plus Ce, and Pb

Element	Mass-absorption coefficient $\mu/\rho$ (cm <sup>2</sup> /g)	$x_{\text{critical}}$ (mm) absorption					$W_{90\%}$ (g)
		99%	95%	90%	75%	50%	
Cr	103	0.165	0.107	0.083	0.049	0.024	0.86
Ni	57	0.298	0.194	0.150	0.089	0.044	1.56
Cu	48	0.355	0.230	0.179	0.106	0.053	1.86
Zn	39	0.436	0.284	0.220	0.131	0.065	2.28
Zr	6.6	1.58	1.68	1.31	0.78	0.39	13.6
Nb	5.8	2.94	1.91	1.49	0.88	0.44	15.4
Mo	5.0	3.41	2.22	1.72	1.03	0.51	17.9
La+ Ce	0.87	19.6	16.6	9.90	5.90	2.90	103
Pb	0.24	71.1	46.3	35.9	21.4	10.7	373

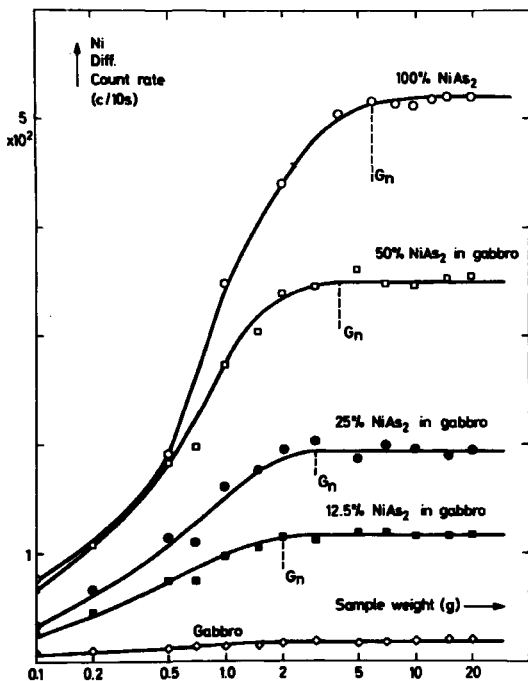


Fig. 4. Experimentally determined, necessary sample weight ( $G_n$ ) for rammelsbergite ( $NiAs_2$ ) in gabbro.

### 3. 3. Counting

In most cases the counting steps consisted of three successive 20-second runs, 10 seconds for each filter. The samples were remixed between every run to minimize effects of inhomogeneities. Where very low positive or negative difference count rates resulted, runs were lengthened to 100 seconds to improve counting statistics. The relative error (precision) of such countings is  $\sqrt{(N_1 + N_2)/(N_2 - N_1)}$ , where  $N_1$  and  $N_2$  are the counts obtained with each filter.

#### 4. MATRIX EFFECT CONSIDERATIONS

As in conventional X-ray fluorescence analysis certain effects might influence the analytical result and must therefore also be considered in radioisotope X-ray fluorescence. These are X-ray interactions with the elements composing the sample and physical effects. They are usually combined under the name matrix effect<sup>7)</sup>.

In our examples of measurements we assume that X-ray interaction phenomena predominate over the physical effects.

The interactions include absorption of primary and secondary X-rays in the sample; the degree of absorption is characterised by the mass absorption coefficient of the sample material  $\mu$  ( $\text{cm}^2/\text{g}$ ), since this value is a function of the average atomic number  $Z$  ( $\mu \sim Z^4$ ). This means that the intensity of the characteristic X-radiation of an element is strongly dependent on the  $Z$  value of the sample material. In the case of normal rocks  $Z$  varies only from 10 to 14 in the sequence from granitic to ultrabasic rocks. Any estimation of absorption corrections is therefore relatively simple. However, if the concentrations of metals to be determined are greater than 5 to 10%, it will become more complicated to account for absorption, because the sample may then have a much higher  $Z$  value than normal rocks. Corrections in this case have to be found empirically for each element.

Enhancement may also occur in radioisotope X-ray fluorescence. Its magnitude is dependent, too, on mass absorption considerations. The effect may be exemplified by the association of Fe/Ni in a sample. The K X-absorption edge of Fe (7.1 keV) is close to the energy of Ni K $\alpha$  X-rays (7.45 keV). This means that Ni K $\alpha$  X-rays are strongly absorbed by Fe in a sample, and in turn the intensity of Fe K $\alpha$  X-rays is enhanced.

The energy-absorption behaviour around the characteristic X-ray energies of some elements examined by us with the Mineral Analyser is shown in fig. 5. From this figure it appears that enhancement has to be expected for the following element associations: Cr/Ti, Ni/Fe, Cu/Co, Zn/Ni, Zr/Rb, Nb/Sr, Mo/Y, La plus Ce/L, and Pb/Re, Os.

In the case of our present study, only Zn/Ni may be affected by enhancement. Rb, Sr, Y, Re, and Os are usually present only in small amounts in the rock types we are dealing with, and therefore have no effect on our measurements; also there is no appreciable iodine.

The physical effect which most strongly influences our measurements of rock powders is particle size. Our samples were all finer than -100 mesh; calibration curves of the elements represented here apply to this

grain size samples with other grain sizes require new calibrations with the Mineral Analyser.

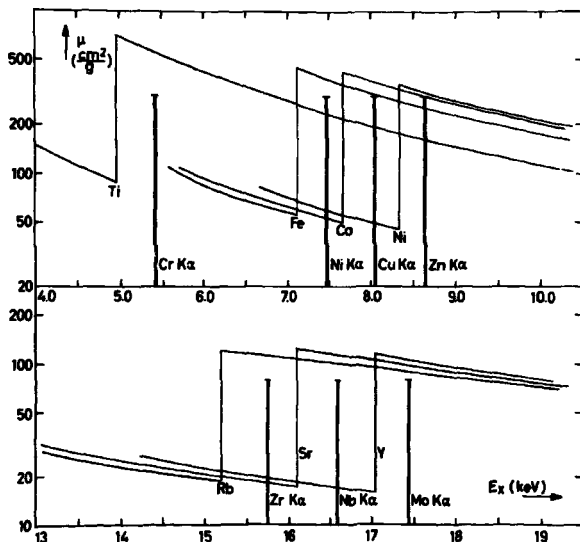


Fig. 5. Energy-absorption behaviour around the characteristic X-ray energies of Cr, Ni, Cu, Zn, Zr, Nb, and Mo.

## 5. RESULTS AND DISCUSSION

Linear regression analyses were made for the lower straight-line portions of the calibration curves relating difference count rates to element contents. Resulting data were used for estimation of accuracies and detection limits, which together with their associated difference count rates are listed in table 4.

Detection limits were obtained directly from regression analysis. Since they have the mean elemental content of the calibration series as basis they tend to increase with increasing mean contents. Therefore, detection limits

Table 4

Results of regression analysis of the lower linear parts  
of the calibration curves

Material	Element	Range of element content (%)	Mean content (%)	Detection limit (%)	Count rate at det. lim. (c/30s)	Accuracy	Sensitivity (counts/%)
Chromite ore, success.dilut. with gabbro	Cr	0-12	4.21	0.21	64	0.08	13.4
NiSO <sub>4</sub> · 6H <sub>2</sub> O, success.dilut. with gabbro	Ni	0-5.58	1.38	0.19	23	0.18	45.3
Rammelsbergite, success.dilut. with gabbro	Ni	0-1.6	0.45	0.06	23	0.03	473.2
Bornite, success.dilut. with granite	Cu	0-5.38	1.51	0.14	-18	0.17	35.6
Spalerite, success.dilut. with granite	Zn	0-4.2	1.18	0.14	-58	0.25	67.0
Kakortokite sample series	Zr	0.7-2.77	1.76	0.21	103	0.19	330.0
Kakortokite, success.dilut. with granite	Zr	0-0.99	0.22	0.04	43	0.02	473.2
Kakortokite sample series	Nb	0-0.29	0.19	0.07	19	0.02	190.4
Molybdenyte sample series	Mo	0-0.17	0.12	0.03	194	0.03	918.4
Monazite, success.dilut. with granite	La plus Ce	0-0.49	0.19	0.02	865	0.01	472.6
Galena, success.dilut. with granite	Pb	0-2.7	0.88	0.10	280	0.14	147.5

for the elements Cr, Ni, Cu, Zn, Zr and Pb are rather pessimistic values compared to those given by EKCO, who define a detection limit based on two standard deviations above the background count rate.

Also listed are sensitivities (the slopes of the regression lines, expressed as counts/% element) which vary by nearly a factor of 100, from 13.4 for Cr to 918 for Mo. These values are only thought to be a guide because they are strongly influenced by such parameters as range of elemental content, matrix material and radiation energy of the source.

A brief discussion of the calibration for each element and its calibration curve (fig. 6 to 13) is given below.

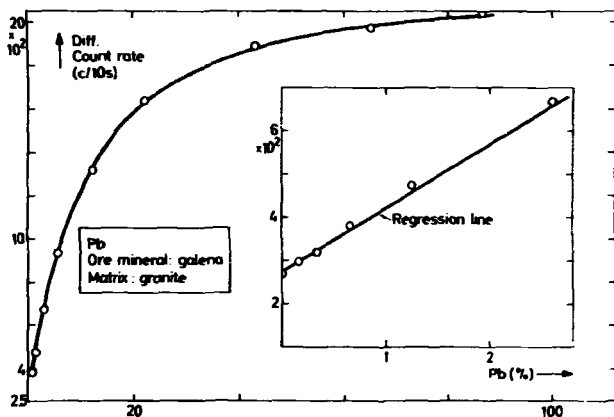


Fig. 6. Calibration curve for Pb in granite. The regression line is drawn for the lower linear part of the calibration curve.

### 5.1. Lead

The calibration for galena successively diluted with granite (fig. 6) covers the range 0 to 87% Pb. The nearly linear lower portion of the curve, 0 to 2.6%, was treated by regression analysis. Contents of Pb greater than 2.6% tend to bend the curve to the right, reflecting the effects of self-absorption of X-rays in the more Pb-rich samples. However, other linear portions of the calibration curve can be found and treated similarly.

Relatively high positive intercept values of the regression line indicate that also for lead minerals in a heavier matrix positive intercept values are to be expected.

### 5.2. Lanthanum plus Cerium

The calibration series, based on monazite successively diluted with granite, covers the range 0.03 to 31% La plus Ce, with linear regression analysis from 0.03 to 0.48%. The IXRF system is quite sensitive to comparatively low contents of these elements (detection limit 0.02%), though the difference count rate at the zero intercept of the calibration line (fig. 7) is rather high.

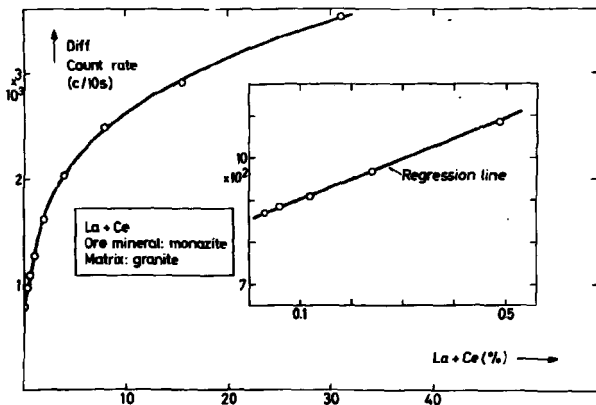


Fig. 7. Calibration curve for La plus Ce in granite. The regression line is drawn for the lower linear part of the calibration curve.

A second almost linear calibration interval can be used for element contents from 0.5 to 2% Ce plus La.

Self-absorption of X-rays in the sample, also for these elements, is characteristic of the high-content part of the regression line.

The validity of the calibration curve is based on a constant Ce/La ratio.

### 5.3. Molybdenum

Chemically analyzed drill samples, containing varying amounts of molybdenite from the Malmbjerg occurrence, East Greenland, were used for the Mo calibration. The host rock is alkali granite (Bearth, 1959)<sup>8</sup>). The contents spanned a range from 0.04 to 0.18% Mo, and formed a linear relationship between the element and difference count rate (fig. 8). Of the elements studied the sensitivity of our IXRF system was found to be greatest for Mo. Regression analysis indicates an apparent detection limit of 0.03%.

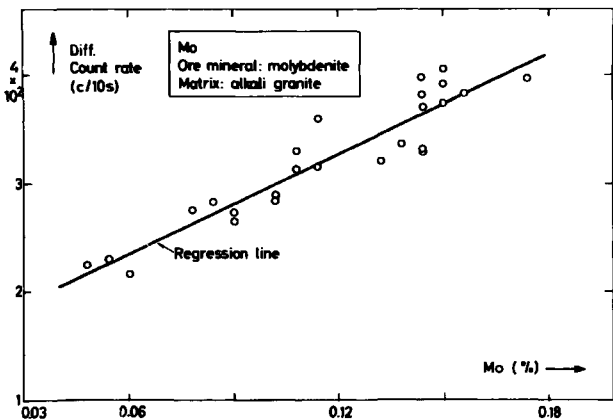


Fig. 8. Calibration curve for Mo in an alkali granite series.

We expected a low detection limit because 22.1 keV photons emitted by the <sup>109</sup>Cd source are very close to the binding energy of K-electrons (20.0 keV) in the Mo atom and therefore excite it very easily.

### 5.4. Niobium

Five samples of kakortokite from the Ilimaussaq intrusion show good linearity over the range 0.09 to 0.29% Nb (fig. 9). The Nb content is governed by the abundance of eudialyte. The good response of the system to Nb is exemplified by the strong linearity at relatively low difference count rates, and the apparent low detection limit, 0.07%.



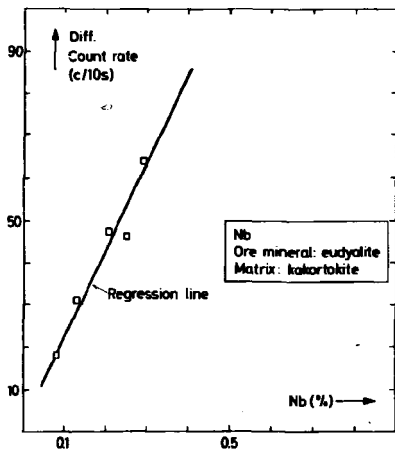


Fig. 9. Calibration curve for Nb in a kakortokite sample series.

### 5.5. Zirconium

The kakortokite samples used for Nb also furnished the Zr calibration (fig. 10). As with Nb, the eudyalite content of these rocks controls Zr; Zr abundances are roughly an order of magnitude greater than those of Nb. We expect that in kakortokite samples the calibration curve for Zr would lose linearity beginning in the range 5 to 10%. The apparent detection limit stated in table 4, 0.21%, is artificially high, because of the abundant Zr in the kakortokite samples. We expected that the true detection limit of the system for Zr would be more like that of Nb.

Therefore, an eudyalite rich sample (7.94%) has been successively diluted with granite. Regression analysis of the lower linear part (0 - 1% Zr) of the calibration curve (fig. 11) yielded a detection limit of 0.04% Zr.

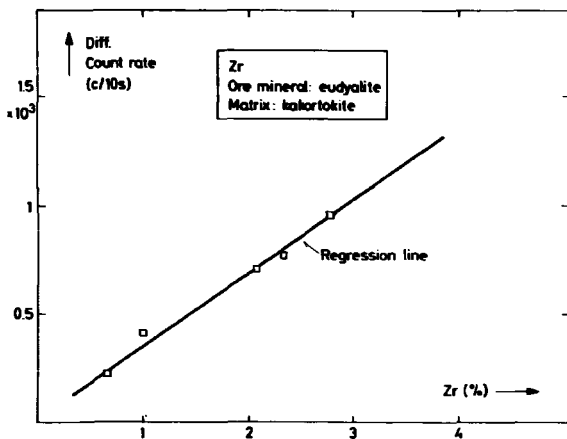


Fig. 10. Calibration curve for Zr in a kakortokite sample series.

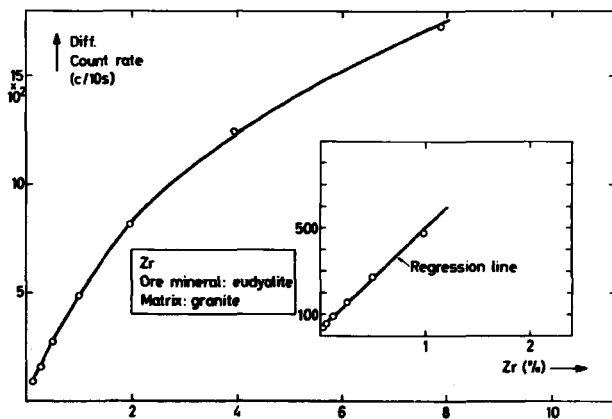


Fig. 11. Calibration curve for Zr in granite. The regression line is drawn for the lower linear part of the calibration curve.

### 5.6. Zinc

The calibration curve for Zn (fig. 12), based on successive dilution by granite, is linear over the range 0 to 4.2%. In the figure we show that there is only a slight difference between lines obtained for two different HV and DISC settings of the Mineral Analyser. Most notable are the strong negative difference count rates associated with Zn contents less than 1.2%. These are valid numbers, indicating that one must consider negative as well as positive count rates in measurements for some elements depending on the performance of the balanced filters. The detection limit based on the mean Zn content of the samples used for regression analysis is 0.14% Zn. It is approximately three times as high as the value given by EKCO.

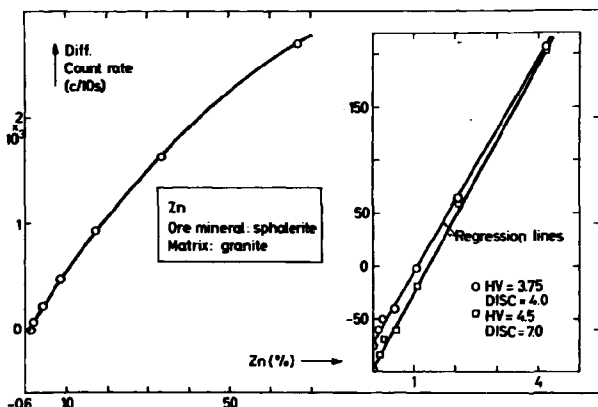


Fig. 12. Calibration curve for Zn in granite. The regression lines are drawn for two different instrument settings.

### 5.7. Copper

To test the effects of matrix materials we successively diluted bornite with two different rock types: granite and gabbro. The resulting calibration curves are shown in fig. 13. Bornite in granite, the somewhat lighter matrix, gives a significantly different regression line than bornite in gabbro. The latter mixture has a greater negative difference count rate associated with a sample containing no Cu. The calibration curves for both mixtures are linear over ranges from 0 to 5.5% Cu.

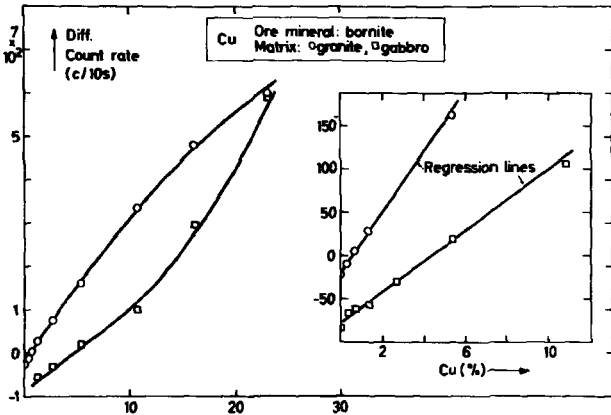


Fig. 13. Calibration curves for Cu in gabbro and in granite. The regression lines are drawn for the lower linear parts of the curves.

### 5.8. Nickel

Initially, for lack of a nickel sulfide ore, we used a nickel sulfate reagent  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , successively diluted with gabbro to furnish a calibration curve (fig. 14). In this mixture linearity exists over a range 0 to 5.5% Ni. This is comparable with a calibration made later by dilution of a nickel sulfide ore (rammelsbergite), also with gabbro, with a linear range from 0 - 1.6% Ni (fig. 15). Estimated detection limits were 0.19% Ni and 0.06% Ni, respectively.

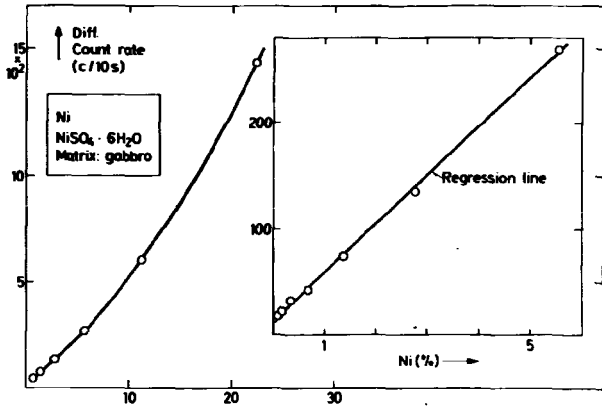


Fig. 14. Calibration curve for nickel sulfate in gabbro. The regression line is drawn for the lower linear part of the calibration curve.

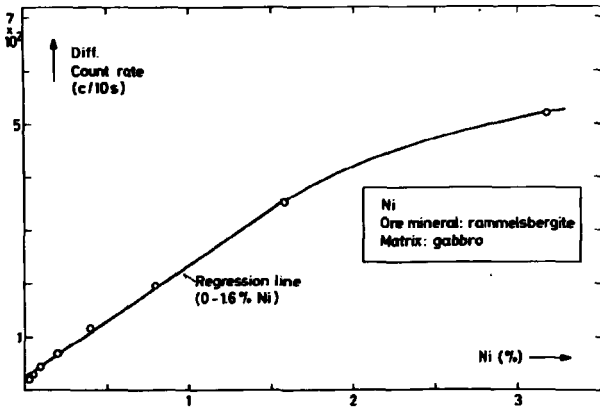


Fig. 15. Calibration curve for Ni in gabbro. The regression line is drawn for 0 to 1.6% Ni.

### 5.9. Chromium

Because of its more general association with basic rocks, chromite was successively diluted with gabbro to furnish the calibration curve for Cr (fig. 16). Linearity is evident over a broad range, 0 to 12%, but with a rather flat slope to the calibration line. The apparently high detection limit based on the regression analysis, 0.21%, is partly due to this broad range, incorporating relatively high Cr contents.

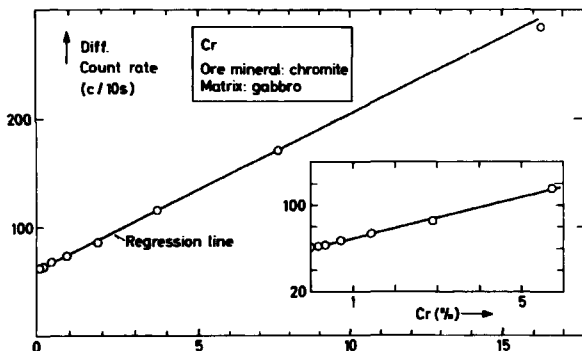


Fig. 16. Calibration curve for Cr in gabbro.

## 6. CONCLUSIONS

We have shown that a portable radioisotope X-ray fluorescence analyser may be applied successfully for the analysis of Cr, Ni, Cu, Zn, Zr, Nb, Mo, La plus Ce, and Pb in powdered metallic ores.

For most of these elements it appears that calibration curves obtained from difference count readings of successively diluted ore minerals with typical ore matrix material can be divided into linear parts; we have only treated the lowest linear part by regression analysis. With the exception of Cr in gabbro and Zr in kakortokite, detection limits are less than 0.1%.

The effective time of measurement for one sample is less than one minute. The procedure is essentially non-destructive, the instrumentation compact, of low weight and easy to operate. Provided a rock crusher can

be made available a portable X-ray fluorescence analyser can be used for ore grade assessment in the field camp. We shall therefore recommend the use of the following procedure of analysis in field conditions:

- (a) quick petrological estimation of the host rock (matrix) of the ore (e. g. granite);
- (b) measurement of the difference counts of the metals sought for in the powdered ore sample with a radioisotope X-ray fluorescence analyser;
- (c) calculation of the metal content from the calibration curve which has been established by the method proposed by us;
- (d) selection of a few samples which should be analysed by other methods.

It would be worthwhile to extend the number of elements covered by our examinations to such economically important metals as Ti, Mn, Co, Sn, and W.

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