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## Practical experiences with automated radioisotope energy-dispersive X-ray fluorescence analysis of exploration geochemistry samples

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**Practical Experiences  
with Automated  
Radioisotope  
Energy-Dispersive X-Ray  
Fluorescence Analysis of  
Exploration  
Geochemistry Samples**

DK7900132

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**Risø National Laboratory, DK-4000 Roskilde, Denmark  
June 1979**

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**PRACTICAL EXPERIENCES WITH AUTOMATED RADIOISOTOPE ENERGY-  
DISPERSIVE X-RAY FLUORESCENCE ANALYSIS OF EXPLORATION  
GEOCHEMISTRY SAMPLES**

**H. Kunzendorf**

**Abstract.** Energy-dispersive X-ray fluorescence (EDX) equipment with radioisotope excitation and sample changer for the analysis of stream sediments, soils and rocks is described. Spectrum data handling and matrix corrections for the system with a  $^{238}\text{Pu}$  source are outlined briefly. Characteristic parameters for the analytical method are evaluated. A comparison of the analyses of V, Cu, Zn and Pb in about 160 stream sediment samples with those obtained by atomic absorption spectrophotometry (AA) is given. Reasonably good agreement between EDX and AA analyses is obtained for Cu, Zn and Pb.

**INIS descriptors**

**COPPER, EXPERIMENTAL DATA, EXPLORATION, GEOCHEMISTRY, LEAD, MULTI-ELEMENT ANALYSIS, PLUTONIUM 238, QUANTITATIVE CHEMICAL ANALYSIS, ROCKS, SAMPLE CHANGERS, SEDIMENTS, SOILS, TABLES, VANADIUM, X-RAY FLUORESCENCE ANALYSIS, X-RAY SPECTRA, ZINC.**

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## INTRODUCTION

A widely used routine analytical method in geochemical exploration is atomic absorption spectrophotometry (AA). The popularity of AA among exploration geochemists is largely due to the availability of inexpensive, compact and efficient equipment, and to the presence of well-established analytical procedures for a large number of elements of the Periodic Table. According to Levinson (1974) about 70% of all analyses made in exploration geochemistry in the United States and Canada were by AA. However, time consuming sample decomposition procedures and the fact that simultaneous multielement analysis seldom is achieved are drawbacks of the method. Also, regarding stream sediments and soils, low detection limits at the ppb-level associated with AA are not necessary for certain economic metals.

A development of conventional X-ray fluorescence (XRF) attracting increasing interest is energy-dispersive X-ray fluorescence, EDX (Bowman et al., 1966, Kunzendorf and Wollenberg, 1970, Woldseth, 1973). The method is also applicable to exploration geochemistry (Kunzendorf, 1972). Characteristic X-rays from the sample are ordered in energy units in EDX displays and qualitative identification of elements in a sample is therefore very simple, a fact often underestimated when comparing EDX with XRF. Although X-ray tube excitation may be applied in connection with EDX equipment (Giauque et al., 1977), a compact and stable-emission radioisotope as exciter yields satisfactory results, comparable to tube excitation (Spatz and Lieser, 1977). Radioisotopes commonly used are  $^{55}\text{Fe}$  (analysis of K through Cr),  $^{238}\text{Pu}$  (analysis of K through Se),  $^{109}\text{Cd}$  (analysis of Rb through Mo), and  $^{241}\text{Am}$  (analysis of Cs through Tm), partly because of a sufficiently long half-life (> 1 year). Modern matrix correction methods can be applied to EDX methods (Rasberry and Heinrich, 1974, Nielsson, 1977). Routine analysis of geochemical samples by EDX is possible (Hansel and Martell, 1977, Clayton and Packer, 1977, Kunzendorf et al., 1978). EDX equipment available uses minicomputers for both data recording and X-ray spectrum data reduction. Compact EDX apparatus with built-

in computing facilities can be used, even under field conditions, and experiences with EDX systems, therefore should be of interest to the exploration geochemist.

A radioisotope EDX system coupled to a sample changer is described in this paper. Calibration procedures typical for EDX analysis using a  $^{238}\text{Pu}$  source for excitation of elements with atomic numbers  $Z > 19$  are outlined and discussed. A comparison of the technique with AA is given.

#### INSTRUMENTATION

Typically, EDX equipment consists of a cooled Si(Li) or Ge(Li) detector, a detector - radioisotope - sample arrangement, and a minicomputer for recording and storage of the spectra and for handling the data. Compact instrumentation is commercially available.

The EDX system used in this investigation was described by Kundendorf (1971). A  $30 \text{ mm}^2$  Si(Li) detector with energy resolution of about 200 eV for Mn  $K_{\alpha}$  X-rays is coupled to a sample changer with capacity of 48 samples (Fig. 1). X-ray spectra are automatically recorded by a multichannel analyser and stored on paper tape. Although the EDX equipment has electronic pulse pile-up rejection to prevent X-ray spectrum distortion at high count rates, count rates were generally kept low. The EDX system is stable, even over long periods of time, so that zero shift and gain stability of electronic units are negligible.

In general, the sample is poured into a sample container the bottom of which is a very thin mylar foil. The sample container is stored on a perspex plate with space for 48 containers. For analysis the plate is adjusted to the sample changer wheel. Radioisotope source, sample and detector are arranged in back-scatter geometry, but the disc source irradiates the sample from



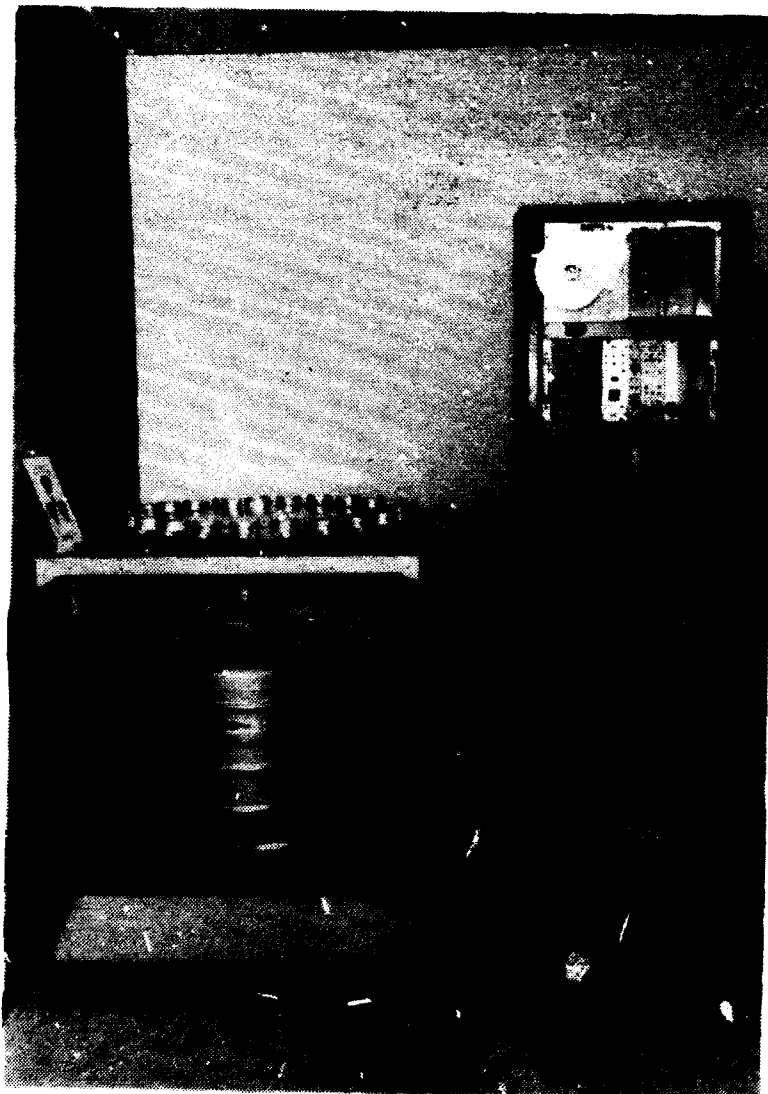
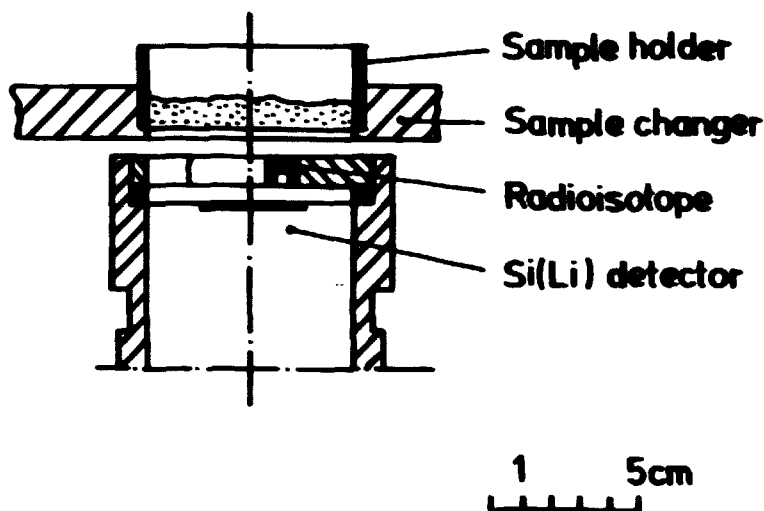


Fig. 1. Photograph of the EDX instrumentation with sample changer.

a point off the detector-sample axis (Fig. 2). A large area ( $\approx 38 \text{ cm}^2$ ) sample container is used, partly to enhance the flux of characteristic X-radiation from the sample. "Infinitely thick" samples are analysed, i.e. 20 to 30 g of geological sample material is necessary for analysis. Radioisotopes used routinely include 30 mCi  $^{238}\text{Pu}$  and 10 mCi  $^{109}\text{Cd}$ .

X-ray spectra recording times are 2000 and 1000 seconds, respectively. In this way, about 300 samples per week can be analysed. Four standard rock samples are used in each EDX run to control the stability of the EDX system. Analytical data



**Fig. 2.** Arrangement of sample, radioisotope and detector for the EDX instrumentation.

from the system are stored on the disc memory of the central computer and can be used directly for geochemical evaluations.

#### X-RAY SPECTRUM TREATMENT

##### General considerations

The X-ray spectrum emitted from the  $^{238}\text{Pu}$  source is shown in Fig. 3. The source with half-life of 86.4 years emits mainly uranium L X-rays with energies between 12 and 20 keV.

When source X-rays hit an infinitely thick geological sample simulated by an admixture of 80%  $\text{SiO}_2$  and 20%  $\text{Al}_2\text{O}_3$ , the X-rays are scattered both inelastically (Compton effect) and elastically (Rayleigh scattering). Owing to the use of backscatter geometry a strong Compton backscatter peak occurs for each of the source L X-rays (Fig. 3). Its intensity, in part, is a function of the average atomic number  $Z_{\text{ave}}$  of the sample. For normal rocks  $Z_{\text{ave}}$  varies between 11 (granitic composition) and

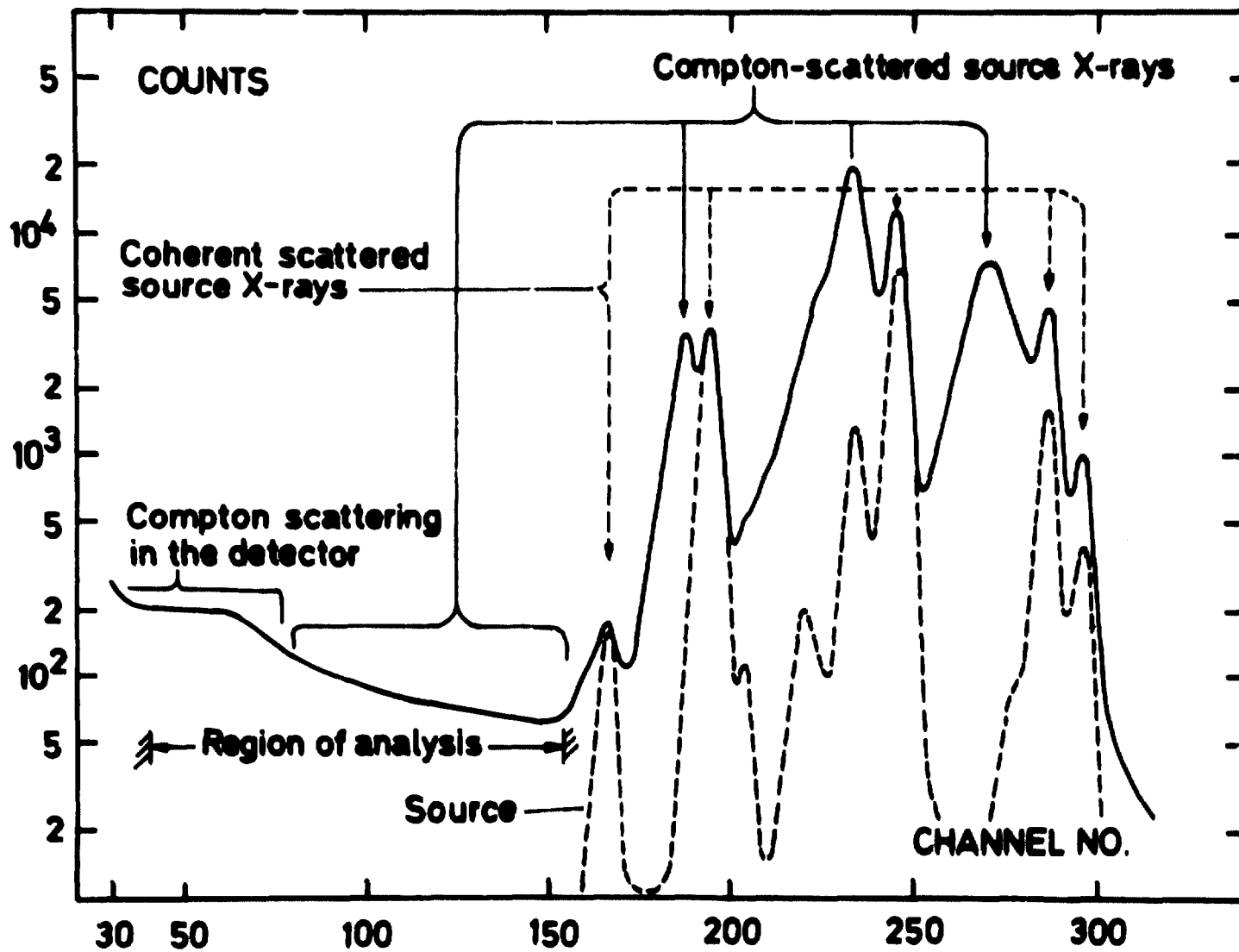


Fig. 3. X-ray spectrum emitted by the <sup>238</sup>Pu source (dotted line) and the X-ray spectrum from a siliceous matrix exposed to source X-rays.

about 13 (basalt), depending mainly on the iron content present. The intensity of this backscatter peak then is a most important parameter concerning the sample composition and may in turn be used to correct characteristic X-ray intensities (Anderman and Kemp, 1958).

In the region of interest for X-ray analysis (Fig. 4) the background is due to mainly Compton scattered X-rays. A granodiorite sample GSP-1, supplied as -200 mesh standard rock powder by the U.S. Geological Survey yields in the region of interest characteristic K X-rays of the elements K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, and Pb L X-rays after irradiation with the  $^{238}\text{Pu}$  source. Two other elements must always be taken into consideration: gold L X-rays from the detector material, and tungsten L X-rays from contamination of tungsten carbide grinding equipment. Generally, characteristic X-rays of much less intensity may also be generated by the scattered primary radiation. Also, characteristic X-rays may be scattered before leaving the sample and therefore increase the background intensity. Although the X-ray spectra emitted by other radioisotopes are somewhat different similar considerations than for  $^{238}\text{Pu}$  are valid.

#### Data reduction

In the region of X-ray analysis a complex spectrum of characteristic X-rays has to be treated properly to yield true intensity figures. X-ray intensities then have to be converted into metal contents. Evaluation methods in EDX analysis were recently reviewed by Gardner et al. (1978). A possible data reduction method somewhat different and exemplified by sample GSP-1 is given below.

Before any spectrum unfolding method for overlapping X-ray peaks can be applied the proper background for the sample has to be subtracted. As mentioned earlier, the background is mainly Compton scattered radiation and depends greatly on the sample's composition. The shape of the background spectrum however does not change for a fixed analytical geometry. The X-ray spectrum of the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  mixture (Fig. 3) with its amplitude normalised

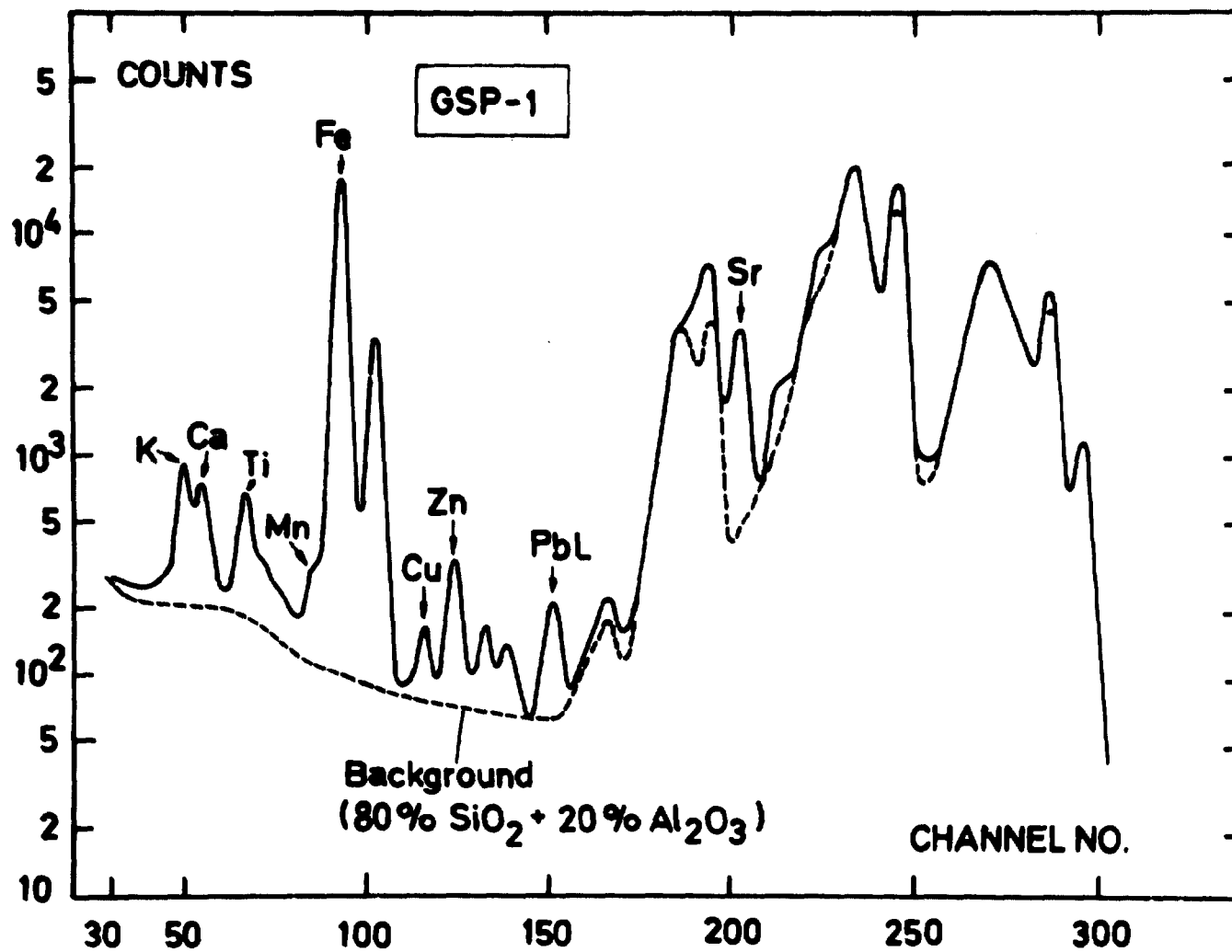


Fig. 4. Typical X-ray spectra of a siliceous matrix used as background spectrum (dotted line) and of a U.S.G.S. standard rock sample GSP - 1.

to the amplitude of the backscatter peak of the sample may be used for background subtraction. The backscatter based background subtraction does not apply to the low energy part of the region of analysis because it comprises radiation scattered in the detector only (see Fig. 3). A fixed background subtraction is therefore recommended in the energy region of K, Ca and Ti K X-rays.

After subtraction of the proper background standard one-element X-ray spectra (K or L X-rays) stored in a computer memory can be fitted to the measured X-ray spectrum of the sample by least-squares fitting techniques. In most cases the software of the minicomputer of EDX instrumentation has stored single element X-ray spectra generated from pure metals. In this case however, it has to be considered that intensity ratios for  $K_{\alpha}$  and  $K_{\beta}$  X-rays of pure single elements are different to the ratios obtained from single elements in a rock matrix.

Another possibility of least-squares fitting involves the construction of a X-ray spectrum with Gaussian-shaped X-ray peaks using experimentally determined detector resolution as a function of X-ray energy, and empirical X-ray intensity ratios. The dependence of the energy resolution vs. X-ray energy is shown in Fig. 5. Regression analysis yields a slightly increasing curve for the energy resolution expressed as FWHM (full width at half maximum) with X-ray energy. A good approximation for the FWHM in the range of X-rays for elements K through Ga would be a constant value of 4.5 channels (equivalent to about 310 eV). K X-ray intensity ratios for these elements may be determined experimentally. X-ray spectra of elements at the 1% (by weight) level in a siliceous matrix are recorded for this purpose. Pure elemental oxides should not be used for these elements because increased absorption of K X-rays occurs in the oxide. For example, the measured  $K_{\beta}/K_{\alpha}$  intensity ratio of a high grade copper plate ( $Z_{ave} = 29$ ) is 0.159, that of CuO ( $Z_{ave} = 24.8$ ) is 0.163, and that of about 2% CuO in the siliceous matrix ( $Z_{ave} = 11$ ) is 0.187, about 20% greater than for the copper plate.

A simplified theoretical K X-ray spectrum for the elements potassium through selenium can be constructed. The X-ray spec-

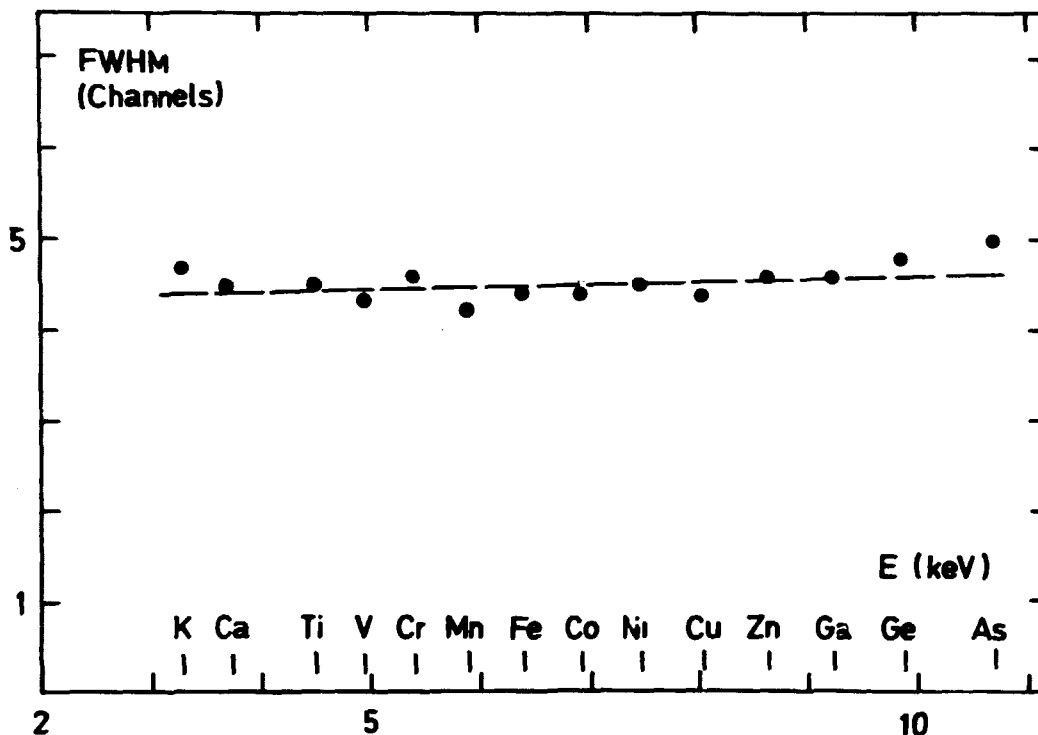


Fig. 5. Energy resolution of the EDX system as a function of X-ray energy in the range for X-ray analysis, between 3 and 11 keV. The energy resolution is expressed as full width at half-maximum (FWHM).

trum of a single element with  $j$  X-rays (e.g.  $K_{\alpha 1}$ ,  $K_{\alpha 2}$ ,  $K_{\beta 1}$  and  $K_{\beta 2}$  X-rays) can be written as sum of Gaussian functions in the region of analysis, between channels  $x_0$  and  $x_N$

$$G_1(x)_{\text{theo}} = \sum_{i=x_0}^{i=x_N} \left( \sum_{j=1}^{j=4} a_j \cdot \exp - \left\{ \frac{(x_i - x_j)^2}{2\sigma^2} \right\} \right) \quad (1)$$

where  $a_j$  and  $x_j$  are the relative intensity and energy (converted into channels) of the  $j$ -th X-ray, respectively, and  $\sigma$  is the energy resolution of the EDX system ( $\sigma = \text{FWHM}/2.354$ ). For  $p$  elements the constructed X-ray spectrum is

$$G_p(x)_{\text{theo}} = \sum_{k=1}^{k=p} \left( \sum_{i=x_0}^{i=x_N} \left( \sum_{j=1}^{j=4} a_{k,j} \cdot \exp - \left\{ \frac{(x_i - x_{k,j})^2}{2\sigma^2} \right\} \right) \right) \quad (2)$$

with  $C_k$  as the fractional intensity of the element  $k$  in the complex X-ray spectrum. From the least-squares expression

$$\{G(x)_{\text{meas}} - G_p(x)_{\text{theo}}\}^2 = \text{minimum} \quad (3)$$

with  $G(x)_{\text{meas}}$  as the measured (background subtracted) X-ray spectrum of the sample, the fractional intensities  $C_k$  of the  $p$  elements in the sample can be calculated. The mathematical procedures involved with least-squares fitting were reviewed by Trombka and Schmadebeck (1968). The measured and the fitted X-ray spectrum for sample GSP-1 using calculated  $C_k$ 's are plotted in Fig. 6.

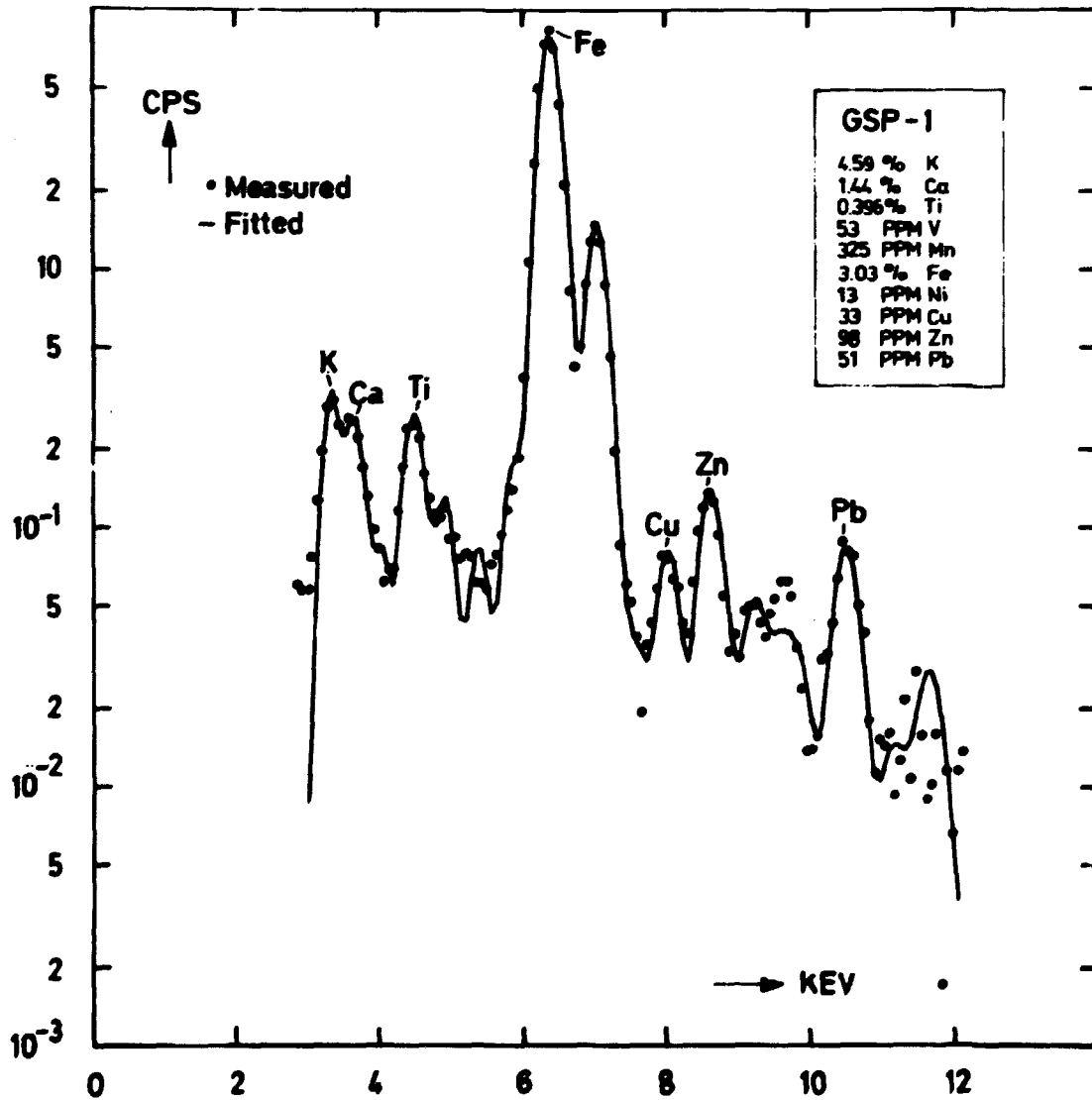


Fig. 6. Measured and fitted X-ray spectrum of U.S.G.S. standard GSP - 1.



Escape of Si K X-rays from the detector is a minor effect to be considered. However, high Fe contents in geological samples suggest escape peak correction for this element. Escape peak intensities as fractions of respective K X-ray intensities of elements (concentrations 1% by weight) in a siliceous matrix are given in Fig. 7.

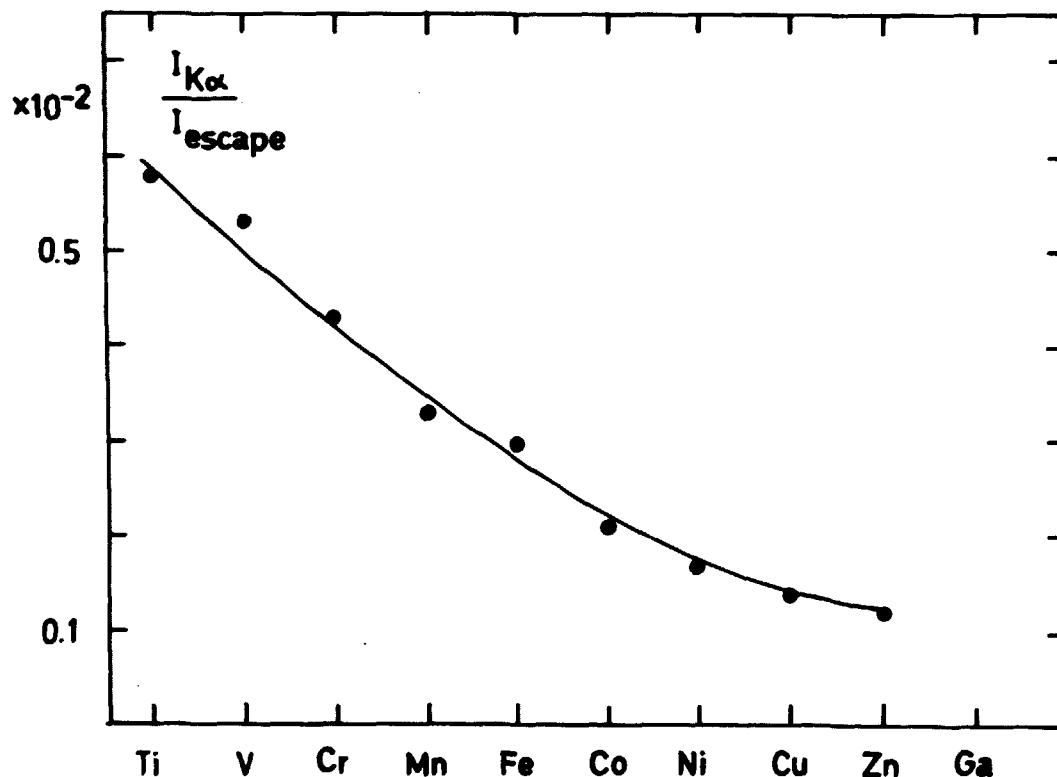


Fig. 7. Si escape peak intensity expressed as the fraction of the K X-ray intensity plotted for elements of interest.

#### Calibration of the EDX system

Calculated fractional X-ray intensities of the elements K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Sr and Pb in standard rock samples are used to calibrate the EDX system with <sup>238</sup>Pu excitation. U.S. Geological Survey standards G-2, GSP-1, AGV-1, BCR-1, DTS-1, W-1, and PCC-1 (Flanagan, 1972) elemental contents are compiled in table 1.

When plotting fractional X-ray intensities derived from the least-squares expressions directly vs. elemental contents linear

Table 1. Pertinent data of U.S. Geological Survey standard rock samples used for the calibration of the EDX system.

Element content	Range in the stand.rocks	G - 2	GSP - 1	AGV - 1	BCR - 1	DTS - 1	W - 1	PCC - 1
K (%)	0 - 5	3.74	4.59	2.40	1.41	0.001	0.53	0.003
Ca (%)	0 - 8	1.39	1.44	3.50	4.95	0.107	7.83	0.36
Ti (%)	0 - 1.5	0.300	0.396	0.623	1.319	0.008	0.641	0.009
V (ppm)	0 - 400	35	53	125	399	10	264	30
Cr (ppm)	0 - 4000	7	13	12	18	4000	114	2730
Mn (ppm)	0 - 1500	265	325	751	1394	852	1317	930
Fe (%)	0 - 10	1.85	3.03	4.73	9.37	6.04	7.76	5.84
Ni (ppm)	0 - 2500	5	13	19	16	2269	76	2339
Cu (ppm)	0 - 200	12	33	60	18	7	110	11
Zn (ppm)	0 - 150	85	98	84	120	45	86	36
Ga (ppm)	0 - 50	23	22	21	20	0.2	16	0.4
Sr (ppm)	0 - 1000	479	233	657	210	0.35	190	0.41
Pb (ppm)	0 - 100	31	51	35	18	14	8	13
Z <sub>average</sub>		11.5	11.8	11.9	12.8	11.6	12.6	11.5

dependence is seldom obtained for several reasons: standard rock samples vary in matrix composition and characteristic X-rays therefore are absorbed differently before leaving the sample; high Fe contents in some rocks (e.g. basalts) yield secondary X-ray fluorescence, particularly from K, Ca, Ti, V and Cr. Different matrix composition can be accounted for in a first approximation by using the correction method proposed by Anderman and Kemp (1958). Information on X-ray interaction data for X-ray fluorescence analysis of geological samples was compiled by Gwozdz et al. (1973). A powerful and simple matrix correction is the normalisation of fractional X-ray intensities to a backscatter count rate, e.g. in our system this is accomplished by normalising the fractional X-ray intensities to the count rate in the backscatter peak between channels 225 and 240. The effect of normalisation is exemplified in Fig. 8, where least-squares derived fractional X-ray intensities and normalised intensities are plotted vs. the Fe content. Although the average atomic numbers for samples DTS-1 and PCC-1 are close to the values in the other standards, very high Mg contents in both samples (MgO>40%) yield lower absorption for the Fe K X-rays and therefore fractional X-ray intensities which are too high. By normalising the intensities to a backscatter count rate a linear regression line for 0 to 10% Fe in rocks can be calculated.

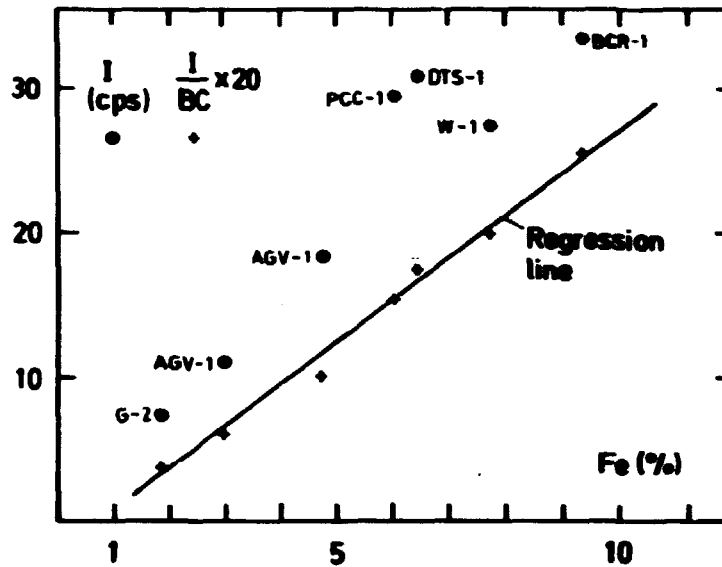


Fig. 2. Calibration curves for Fe. A linear regression line is given for backscatter corrected Fe K X-ray intensities.

Varying Fe contents in the rock samples are accounted for by experimentally determined correction factors. For example, iron K X-rays enhance potassium K X-ray intensities by a constant factor which value is about 0.3% of the fractional Fe K X-ray intensity. After this correction a linear expression for the K content can be established.

A factor of influence is the grain size and its distribution within the sample. Our system was calibrated for U.S.G.S. standard rock powders with grain sizes of less than 0.074 mm (-200 mesh). Many of the exploration geochemistry samples are analysed as -0.177 mm (-80 mesh) fractions. To check the influence of grinding on 5 stream sediments a grinding experiment was carried out. The results for one of these samples are shown in table 2. By grinding the sample to grain size class -0.074 mm a significant change of elemental contents is observed. However, because shorter grinding to grain sizes of -0.149 mm (-100 mesh) does not change the analytical results significantly, and because the Fe content remains nearly constant during grinding steps, the change of analytical results of the finest fraction sample may be due to contamination from the ball mill. The grain size influence may be more pronounced for other types of

**Table 2.** Results of a grinding experiment of a stream sediment sample

Element	-80-mesh fract.	-100-mesh fract.	-200-mesh fract.	$\Delta$ (80-200) (%)
K (%)	3.14	3.23	2.75	-12.4
Ca (%)	2.97	2.93	2.47	-16.8
Ti (%)	0.317	0.325	0.260	-15.5
V (ppm)	11	1	0	-
Cr (ppm)	0	0	0	-
Mn (ppm)	340	325	267	-21.5
Fe (%)	2.26	2.34	2.21	-2.2
Ni (ppm)	0	0	0	-
Cu (ppm)	9	11	5	-44.4
Zn (ppm)	49	54	69	40.8
Ga (ppm)	7	6	10	42.8
Sr (ppm)	135	136	136	0.7
Pb (ppm)	30	32	34	13.3

geological samples. In routine geochemical prospecting, however, analytical results on -0.177 mm fractions only are interpreted, and systematic errors like those exemplified in table 2 have only limited influence on the validity of the results of the prospecting program.

#### Performance of the EDX system

The EDX system described was used for several years. Each analytical run with the sample changer includes analysis of 4 of the 7 U.S.G.S. standards. The analytical results on these standards are used to calculate performance parameters for EDX analysis.

Precision values expressed as the relative standard deviation of 5 repeated measurements of the standard AGV-1 are compiled for 11 elements in table 3. The measurements were carried out within one month. Long-term stability over a period of about 1.5 years are judged from 36 analyses of this standard. Generally, the precision of the EDX analyses is of the order of 10%. The exceptions are the analyses of V, partly because vanadium K X-rays are not excited effectively by the <sup>238</sup>Pu source and the V content of AGV-1 is rather low.

**Table 3.** Precision values for 11 elements in the rock sample AGV-1. The values were derived from repeated measurements within one month (N = 5) and over a period of about 1.5 years (N = 36). The values are given in per cent.

	K	Ca	Ti	V	Mn	Fe	Cu	Zn	Ga	Sr	Pb
N = 5	5.0	2.6	3.2	32.8	14.0	0.4	9.1	3.9	14.3	2.7	4.9
N = 36	9.1	7.8	9.4	43.4	13.8	7.7	9.8	6.8	22.8	2.3	12.2

A possibility of calculation of the accuracy A of EDX analyses is by the following formula

$$A = t_{n-2} \left\{ \sum_{i=1}^n \frac{(x_{O,i} - x_i)^2}{n-2} \right\}^{\frac{1}{2}}$$

where  $x_{O,i}$  is the recommended elemental content and  $x_i$  the measured content of sample i, n is the number of standards and  $t_{n-2}$  is the appropriate Student's t distribution value. However, the A estimate is of little value for elements with large concentration range and if the recommended elemental contents have poor accuracies. An estimate of accuracies obtained with the system described may be obtained by a run of the U.S.G.S. after calibration of the system (table 4). Generally the accuracy of EDX measurements is about 50 ppm for V, Cr and Ni, and about 10 ppm for Cu, Zn, Sr and Pb.

**Table 4.** Accuracy of EDX analyses for some selected elements calculated from measurements on U.S.G.S. standard samples. All values are given in ppm, except for Ti.

	Ti (%)	V	Cr	Mn	Ni	Cu	Zn	Ga	Sr	Pb
Accuracy	0.07	66	224	250	127	17	11	8	17	12
Average cont. in standards	0.47	131	985	833	677	36	79	15	270	24

It is difficult to determine detection limits for each element analysed by the EDX system for several reasons. Firstly, the concept of taking 2 times the standard deviation of the background count rate as basis for detection limit calculations is not applicable because the background varies according to the sample composition. Secondly, intensity calculations in EDX

analysis involve both subtraction (background) and normalisation (backscatter count rate) steps which may be sources of considerable error. Detection limits for the elements analysed with the EDX system were therefore not evaluated. However, an indication of the order of magnitude of the detection limits to be expected with our system are the accuracies given in table 4.

#### Comparison with AA

Splits of the -0.177 mm fractions of about 160 stream sediments and soils collected in East Greenland were analysed both by EDX and AA for the metals V, Cu, Zn and Pb (Koenigler, 1976). The results of these analyses are plotted in Fig. 9 and a summary of these data is given in table 5.

Table 5. Regression data for the comparison of EDX and AA of about 160 stream sediment samples (-80 mesh fraction). N = number of analyses, A = intercept with the Y axis (in ppm), B = slope of the regression line, r = correlation coefficient.

	N	A	B	r
V	163	43.56	0.254	0.561
Cu	165	4.29	0.964	0.896
Zn	165	-15.32	0.995	0.960
Pb	165	4.61	0.752	0.803

Reasonably good agreement of the data of both methods is obtained, except for V. For this element on the other hand, even with considerable deviation of EDX data from the AA data, a significant positive correlation coefficient is calculated. Assuming that AA data represent the true V concentrations of the samples EDX data could still be used for geochemical interpretations by applying a correction expressed by the regression constants A and B (table 5). The large spread of V data at low elemental contents also suggests detection limits of greater than 50 ppm for this element. For Zn a constant deviation of EDX data from AA data is observed. However, it is made clear through Fig. 9 that detection limits of the EDX method for elements Cu, Zn and Pb are expected to be close to 10 ppm.

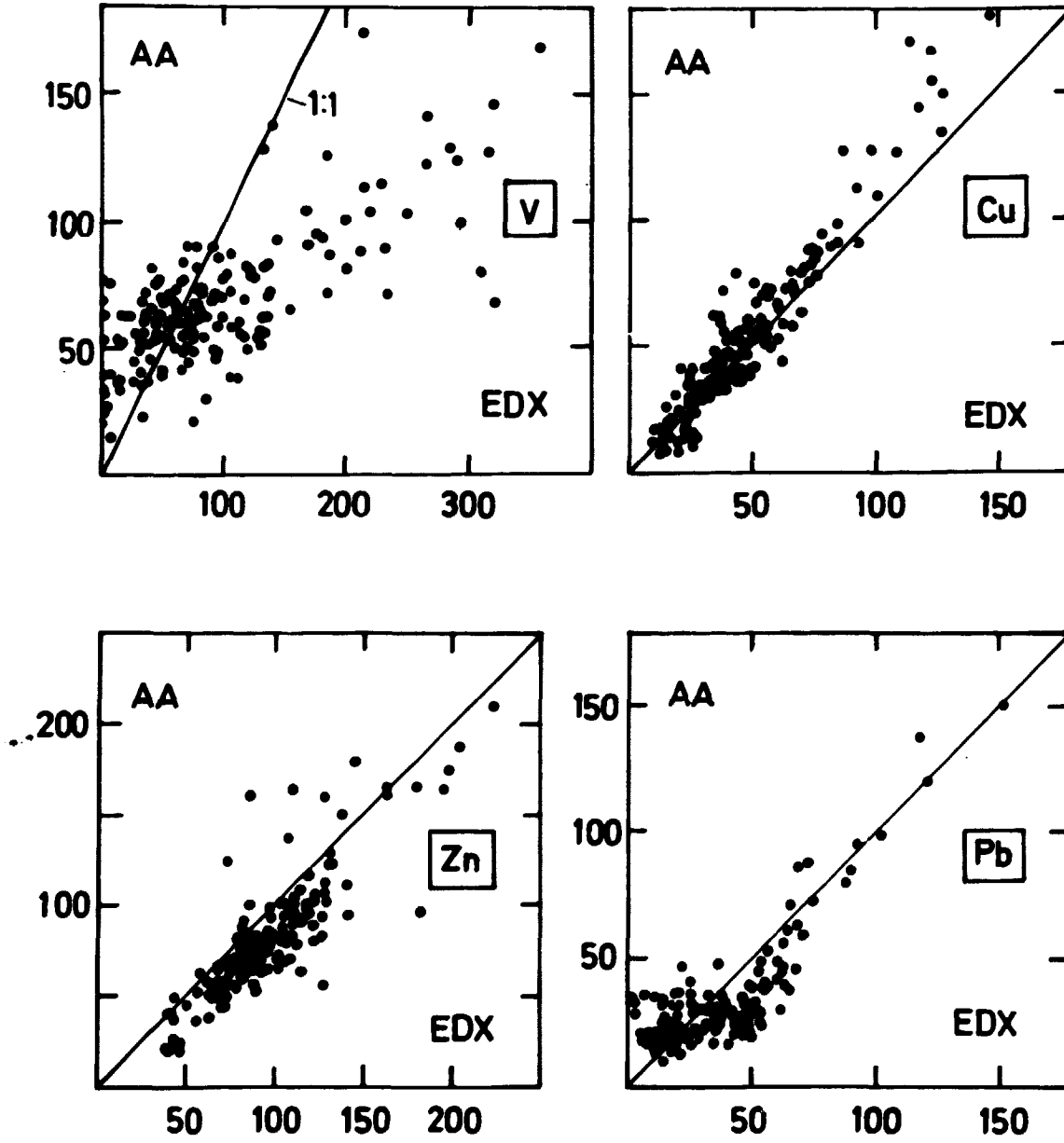


Fig. 9. Comparison of EDX and AA data for about 160 stream sediment samples.

## CONCLUSIONS

Typical EDX instrumentation for analysis of exploration geochemistry samples is described in this paper. Methods of X-ray data reduction and matrix correction are discussed shortly.

Although commercially available EDX equipment differs somewhat from the instrumentation described here as regards computing facilities, the following can be concluded from this investigation:

1. Simultaneous analysis of V and Cr, and Ni, Cu, Zn and Pb is possible at the 50 and 10 ppm levels, respectively, using one radioisotope source ( $^{238}\text{Pu}$ ).
2. Some major elements (K, Ca, Ti, Mn and Fe) are recorded simultaneously and valuable information about the geological environment of the sample therefore exists.
3. Automated EDX analyses can be carried out on -0.177 fractions directly and may be repeated easily at any time.
4. Throughputs of several hundreds of samples per week are possible.
5. Metal identification in anomalous samples is very easy.

A major drawback of the analytical EDX system is the requirement for cooling of the semiconductor detector system. Even with large dewars for liquid nitrogen field application of this kind of equipment is still limited in remote areas. However, development of detectors operated at room temperature or cooled by Peltier effect devices can be expected in the future.

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