Lincoln University Digital Thesis

SOIL SULPHUR ANALYSIS

BY X-RAY FLUORESCENCE

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A thesis

submitted in partial fulfilment

of the requirements for the degree

of

Master of Agricultural Science

in the

University of Canterbury

by

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Lincoln College

1973

PREFACE

X-ray fluorescence spectrometry is widely accepted as a highly versatile and potentially accurate method of instrumental analysis.

The occurence of sulphur deficiencies in many areas has led to increased research on the role of sulphur as a plant nutrient.

To carry out such research effectively, convienent and accurate analytical methods for determining amounts of sulphur are necessary.

This study involves the setting into operation of the newly installed X-ray fluorescence plant at Lincoln College, and the formulation of an analytical procedure for the rapid determination of total sulphur in soil material. The resultant procedure is applied to analysis for total sulphur in the Reefton chrono-sequence of soils currently under study in the Soil Science Department.

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CHAPTER I

INTRODUCTION

I. THE INVESTIGATION

X-ray fluorescence is produced when a primary X-ray beam, with rays of sufficient energy interact with an atom causing re-emission of X-rays of a lower energy. These characteristic radiations can be used to identify and estimate the concentrations of elements in samples. Chemical methods for determining soil sulphur are usually slow, destructive and depend on the complete-ness of chemical reactions. Among the advantages of X-ray fluorescence spectrometry are speed, non destructive character, and applicability to both element and all its compounds. However elemental interactions with the wide variety of other soil con-stitutents, difficulties in sample preparation, the need for vacuum transmission, together with the minor amounts of sulphur present in soil samples, cause considerable difficulty in obtain-ing accurate results.

This investigation covers the analysis for total sulphur in whole soil samples using the minimum of sample preparation. The complete X-ray fluorescent analytical procedure is coupled to computer processing of data, thus making available mathematical processes uneconomical to attempt by hand. Using computing pro-cedures the accuracy of the concentration is obtained quickly by evaluation of counting errors, random and systematic equipment

variations, and calibration data scatter. Variations in sample composition and elemental interactions are investigated and corrections based on ignition loss are used to provide better results. The computing procedure demonstrated, successfully removes the uncertainty associated with the estimation of accuracy as well as providing a basis for processing fluorescence data for other elements.

II. LITERATURE REVIEW

Although X-ray fluorescence spectrometry is widely used in rock and soil mineralogical analyses, references to the use of the method for determining sulphur are few. With the development of chromium anode X-ray tubes, high reflectivity analysing crystals, and vacuum path spectrometers, the method can be used successfully for the detection and determination of sulphur in, for example, plant material (Alexander 1965, Mitcham et al 1965, Souty et al 1967). A recent report by Fields and Furkert (1971), using thin film techniques for sulphur analyses in plant material, obtained agreement within 3% of the chemically measured value. However the levels of sulphur in soil material (0.005% to 0.05%) are much lower than in plant material (0.2% to 0.5%) resulting in greatly decreased count-rates and accuracy. Further, plant matrices are more uniform and much more consistent from sample to sample. It is perhaps the wide variability in the properties of soil mater- ials that restricts the use of the method, rather than the diff- iculties associated with the detection of small amounts of

radiation.   Variable physical properties, and to a much greater extent, variation in chemical composition of the soil matrix, are major limiting factors in the present study.

Roberts and Koehler (1968) describe a procedure for the preparation of soil extracts for analysis by X-ray emission spectrometry.   Water soluble sulphate, extracted from the soil using $MgCl_2$ is fixed on Mylar film as a dry residue and stretch-mounted on the sample holder for irradiation.   The X-ray absorbing characteristics of interfering cations in the soil extracts are decreased by introducing H^+ ions and LiCl, leaving the sulphur present as Li_2SO_4.   Although the mounting technique and irradiation processes are rapid, the necessary chemical extractions and treatments lengthen analysis times considerably.   The precision of their measurements ranged from 2% to 10% of the amount of sulphur present in the extracts, from soil samples having a range of from 0.5 to 14 ppm extractable sulphur.   The method is not readily adaptable to the measurement of total soil sulphur.

The only report found on the successful determination of sulphur by use of X-ray fluorescence spectrometry for whole soil samples is by Brown and Kanaris-Sotiriou (1969).   Although failures are not usually reported, Brown and Kanaris-Sotiriou refer to at least one investigation (Takijima 1963) in which the method was concluded to be insensitive.   However taking less than 4 minutes per sample machine time, and having a limit of detection

of less than 10 ppm of sulphur, their average relative error was about 7%. In their work they regarded soils as a two component system of organic and mineral material and made a correction for absorption effects based on this division. Considerable inspiration for the present study comes from the reports of Brown and Kanaris-Sotiriou, whose efforts are seen to be verified.

A review discussion of the literature on one or two specialised topics in X-ray spectrometry are included as the topics arise in the text. These topics are considered in their context rather than in a general discussion because a review of even the use of X-ray fluorescence in the field of soil analyses only, would be much too voluminous and barely applicable. Many such reviews have been published, one of the more recent being that of Carr-Brion and Payne (1970). Mitchell (1968) reviews the role of the digital computer in the analytical laboratory together with the use of general statistical techniques in the evaluation of X-ray data and the use of specific computerized statistical-mathematical techniques in quantitative X-ray analysis.

CHAPTER II

ANALYTICAL PROCEDURE

I. USE OF COMPUTER

An objective of this study is to execute all calculations
automatically by computer, from the raw counting data punched into
cards to the printout of the sulphur content and its accuracy.
The computer analysis is in two parts.   The first of two main
programs processes the data from chemically analysed standards.
The second program uses the resulting mathematical parameters to
find unknown sulphur concentrations.

II. SAMPLE PREPARATION

A fusion dilution technique, usually the best preparation for
soil and silicate samples is not suitable for sulphur analyses.
Norrish and Hutton (1969) report that although sulphate is not
lost, some other forms of sulphur may not be completely retained.
Even with the addition of extra oxidising agents such as ammonium
nitrate some sulphur may be lost before it is incorporated into
the melt.   Sulphur is lost completely when fusions are made in
graphite crucibles.   Thus it seems probable when analysing soils
containing organic matter that during the fusion process with
reactive carbon present, volatile sulphur compounds could also be
lost.

The minimum of preparation required for pressed powder

samples makes the method attractive for rapid soil analysis.
However particle size effects, especially for long wavelength
sulphur radiation, limit the usefulness of the technique.
Dilution is not possible because of the already low sulphur
concentrations.   In this study there is little choice left other
than powdered samples.

The pressing procedure and equipment as described by Norrish
and Chappell (1967) produces pelleted samples with a boric acid
backing and edge, designed to fit into standard Philips sample
holders.   Soil samples are air dried and crushed in an agate
mortar to pass a 100 mesh (152 μm) sieve.   The backing is
required to prevent scoring of the die walls by quartz and other
hard minerals.   The samples (2g per pellet) are pressed to 10
tons beyond which pressure the boric acid starts to fracture.
Rock samples are ground in a tungsten carbide ball mill for
periods ranging from 5 seconds to several minutes depending on
hardness.   Pellets produced in this way are quite robust and are
easily identified by writing on the boric acid backing.   Each
disk is conviently stored in a small clear plastic bag for future
reference.   For continuous operation, from powders in containers
to labelled pellets in plastic bags, sample preparation should
average less than 3 minutes per sample including cleaning of the
necessary die parts.   A discussion on the significance of part-
icle size is found in Chapter III.   Another discussion on the
significance of moisture contained in the sample and backing is

found in Chapter IV. The small error caused by this moisture is eliminated by the use of a freeze drying procedure.

III. USE OF STANDARDS

X-ray fluorescence analyses require chemically analysed standards to use as references with the unknown concentrations found using ratios of count-rates. The count-rates from analysed samples are plotted against concentration and a calibration curve is used for subsequent unknowns. One of the major problems in detecting small amounts of radiation is the evaluation of errors due to instrumental drift. To minimise counting errors small counting rates necessitate large counting times, which in turn require stricter control of equipment drift. A common technique is to use an analysed standard sample in the batch of samples and correct each sample count-rate according to the value obtained for the standard.

(1) Standards for Sulphur

In the case of soil sulphur, the levels of sulphur in chemically analysed standard soils and the unknowns are much the same. Both levels are low requiring large counting times and risk of instrumental drift. Considerable advantage is gained if it can be arranged that the standard sample in each batch of unknowns has a high sulphur count-rate. The time required to record sufficient quanta to minimise the statistical counting error for the standard is greatly reduced, the probability of instrumental drift is decreased and the standard count-rate can be determined with

sufficient accuracy to calculate the drift with a minimum of uncertainity.

For example, in the four sample chamber (three unknowns plus one standard), using a 10,000 c/s sulphur count-rate instead of a fourth 50 c/s analysed standard, the total batch counting time is reduced from say 40 s to 31 s while the corresponding increase in accuracy for the adjusted sample count-rate is from 6.4% to 4.6%. In each case 4.5% of the error comes from the counting error of the sample but the added uncertainity in relating the samples to the reference has decreased from 1.9% to 0.1%. Note however that count-rates of the order of 10,000 c/s come only from very high sulphur containing compounds.

(2) Intermediate Standards

The procedure outlined in this study uses a high count-rate intermediate standard between the analysed samples and the unknowns. This reference substance may be any compound with a high but not necessarily known, sulphur content. A known sulphur content is of no use unless detailed data concerning mass absorption coefficients are also known, but such an exercise is not required. This substance is quickly counted for each batch of samples, both standard analysed samples and unknown samples and each sample count-rate is adjusted to the same arbitrarily specified count-rate for the intermediate substance. It is the count-rate which is specified, not the sulphur content although the two are connected by mass absorption coefficients. It is reasonable to

specify the arbitrary count-rate as that obtained with all equipment in good order. Each sample is thus corrected for variations in performance of the equipment. In theory there is no limit to the equipment variations that this procedure will correct for, as a factor affecting one count-rate will have a similiar effect on the other. In practice this is true only if the counting times are chopped into small intervals and divided alternatively thus eliminating time dependent factors. The reference substance count-rate serves as a useful check during counting operations of any drift as it occurs.

It is not necessary to re-calibrate equipment between periods of use and variations in operator settings such as pulse height analyser are allowed. Samples from different batches can be compared and there is no reason why a separate laboratory cannot carry out analyses without reference to analysed samples but with reference only to the intermediate substance during each batch.

The use of such a procedure immediately introduces extra calculations, particularly in correcting high count-rates for counter dead time, working out and applying drift corrections and evaluating the levels of accuracy. However with the use of computer processing of data this presents no real difficulty.

(3) Choice of Reference Substance

The choice of a suitable intermediate reference for sulphur is limited. Pure sulphur giving the highest possible count-rate

is ruled out because of the excessively high rate which overloads the present counting equipment. The count-rate could be reduced by lowering the X-ray tube operating power but altering the tube kV or mA settings during counting operations proved both time-consuming and annoying. Diluting elemental sulphur with the inert base $CaCO_3$ proved unseccessful due to difficulties in obtaining thorough mixing and in making identical standards. Good agreement between successive mixings could not be obtained.

Pure crystalline K_2SO_4 also proved unsuccessful. This salt was chosen because it is anhydrous and of good stability but the counting rate was still excessively high, even though the mass absorption coefficients for potassium (410) and oxygen (415) are considerably larger than for sulphur itself (240). Further difficulties were encountered in grinding the crystals to a sufficiently small size to overcome surface effects and also in duplicating the grinding process.

Covering of the reference sample with a 15 µm Mylar film seemed to have certain advantages. This was achieved by placing the disk in a sample holder fitted with a window. The high sulphur count-rate was reduced to a suitable value, any contamination by vacuum pump oil vapours supposedly decreased, and the risk of contamination of the vacuum chamber by high sulphur-containing salts was eliminated. However the Mylar window in the holder would not withstand the continual primary irradiation

without buckling and eventual cracking and rupture.   As the
cracks appeared the count-rate slowly increased and as the life of
the film seemed to depend on the mounting tension which was diff-
icult to control the idea was abandoned.

The final choice of reference standard was pure Ba SO_4.
The advantages of using this salt are (i) it is usually prepared
by precipitation and this gives both a uniform and suitable
particle size; (ii) it has no water of crystallisation and is
stable; (iii) the high mass absorption coefficient of barium
(1300) is sufficient in itself to reduce the count-rate to a
reasonable value, eliminating any mixing operations and the need
for any film; (iv) it is easily made into pellets, although
pressure cannot exceed about 2 tons without fracture.   A series
of $BaSO_4$ standards were tested against a single sample, the only
differences detected being fully accounted for by instrumental
drift and counting error.

IV.   COUNTING ROUTINE

There are two methods of determining the peak counting rate,
either by measuring the time required to collect a fixed number of
counts or by measuring the number of counts in a selected time.
The actual choice depends to a large extent upon the particular
circumstances, but in general, fixed time is used in this study
although it makes no difference to the computer programs.   For
sulphur determination in soil material, the background intensit-

ies and scattering are too large to be ignored (e.g. with pulse height analysis, a 4:1 peak to background ratio for 250 ppm). A rather complex treatment of peak to background counting rates is used in order to ascertain the error in the net intensity. In a given total time, the standard devia tion of the net intensity is least if the times taken to measure peak and background counts are split according to the relationship; $t_p/t_b = (R_p/R_b)^{\frac{1}{2}}$ where R_p and R_b are the respective count-rates. At low concentrations where R_p tends to R_b, the times become equal. However all calculations from the basic time and number of quanta data, are done automatically by computer, including a check on the optimum use of time. Because of the relatively long counting times, a chopping procedure is used to count alternatively on sample and reference.

V. INSTRUMENTATION AND EQUIPMENT

The fluorescence installation now consists of a standard Philips PW 1540 vacuum spectrograph, 2000 Watt (50 kV, 40 mA) chromium anode tube, 1 μm window gas flow proportional counter with full pulse height analysis, pentaerythritol (PE) analysing crystal, with coarse collimation and sample rotation. Although most of the investigation was carried out on the originally installed 1000 Watt tube and 5 μm window, all results given are with the newer equipment.

A slight modification to the X-ray tube was found necessary.

The lead shield over the Be window of the tube is removed and replaced by another, cut to allow only the 2.5 cm diameter center of the sample pellet to be irradiated. This eliminates scattered or secondary radiation from the sample holder and more important, from any sample accidently spilled onto the boric acid edge of the pellet during making. The area of sample irradiated is easily obtained by irradiating a sample of K_2SO_4 for a few seconds. The orientation of the sample is obtained by stopping any accidental rotation of the sample holder with cellotape around the sliding edge, and maintaining the same orientation as the sample is lifted out. The area of K_2SO_4 exposed to the X-ray beam turns purple. In this way irradiation area, depth of tube penetration into the housing, and correct orientation of the tube angle can be obtained. This procedure is more satisfactory than the recommended one of simply rotating the X-ray tube until maximum counts are obtained.

The Fortran programs are run on a standard IBM 1130 computer installed at the College. The programs will operate with 8k memory core but with an extra 8k recently added to the computer they run easier and faster.

CHAPTER III

MATRIX EFFECTS

Two absorption coefficients, a linear absorption coefficient μ_x, and a mass absorption coefficient μ_m, are used to express the diminution of intensity of an X-ray beam passing through matter. The first of these coefficients is defined by the relation,

$$I = I_o \cdot e^{-\mu_x L} \qquad (3.1)$$

and the second by,

$$I = I_o \cdot e^{-\mu_m M} \qquad (3.2)$$

where I_o and I are the incident and diminished intensities respectively, L is the path difference travelled by the X-ray through the sample, M is the mass (per unit area) of the sample the rays have passed through. Also, $\mu_m = \mu_x / (\text{sample density})$. Both μ_m and μ_x are wavelength dependent. Atoms in a compound absorb radiation independently of one another and the total absorption can be related to the individual atomic absorptions by the equation,

$$\mu = \sum_i^n (\mu_i p_i) \qquad (3.3)$$

where μ_i is the atomic mass absorption coefficient for each atomic species i, and p_i is the mass (weight) fraction of each atomic species i, and n is the number of species present.

The two main sources of error due to the nature of the sample matrix are particle size effects and elemental interactions, both of which can depend on absorption coefficients. Both can vary from being negligible to making nonsense of experimental results. A third matrix effect discussed briefly is that of the chemical state of the element together with the chemical composition of

the grains containing the element.

I. PARTICLE SIZE

For a true analysis the primary radiation must penetrate a representative distance into the sample. Also the specimen must be sufficiently homogeneous so that the depth of sample effectively contributing to the secondary characteristic radiation is uniform in composition. The intensity of a characteristic line emitted by a thin layer of material increases as the thickness is increased up to a value defined as "infinite" thickness. For any particular material this thickness can be calculated using equation 3.1 . For typical soil material and sulphur K_α radiation, μ_x approximately equals 2000 cm^{-1} so that 90% of the radiation is absorbed after a path distance of about 12 μm and 99% absorbed after 24 μm. The true infinite thickness value depends on the different absorption coefficients for the incident and fluorescent radiations and on the angles of incidence and take off from the sample. Using typical values the infinite thickness value for a soil sample for sulphur is about 10 μm. If the particle sizes are reduced sufficiently, which is to a linear dimension much less than the infinite thickness value, then intensities from individual components become relatively stable.

Bernstein (1961) considered the relationships between X-ray intensity and particle size for powder samples. It was shown that the fluorescent intensity from a pure material increased as

the particle size of the material was decreased. He also showed the general effects of particle size distributions in two-component systems, the intensities of both components becoming stable when the particle size was reduced sufficiently. A further study by Bernstein (1962) involved the relationship between intensity and particle size of a minor constituent in a powder sample. He showed that the relative intensity of the minor constituent in a mixture was a function of both the particle size and absorption coefficient of the matrix material. The relationship between intensity and particle size of the minor constituent in the mixture showed a levelling off at two different size ranges, firstly relatively large particles (approximately ten times the infinite thickness value), and secondly at relatively small particle sizes (approximately one-tenth of the infinite thickness value). For the small particle sizes the relative intensity calculated from the effects of linear absorption, increased to about 4 times that at infinite thickness particle size, while at the large sizes it dropped to about one-tenth of the infinite thickness value. Working with artificial mixtures, Bernstein obtained reasonable agreement between the theoretical curves and actual measurements.

Claisse and Samson (1961) give a fundamental mathematical study of heterogeneity effects in X-ray analysis. Working with a two component system, they derived an equation which gives the fluorescent intensity emitted by a unit surface of a two-phase

sample as a function of the relative proportions of the two
phases, the concentration of the fluorescent element, the grain
size, and the absorption characteristics of the two compounds.
They predicted that particle size effects would appear in a
limited region only of grain sizes, these effects depending on the
wavelength of the primary radiation and the nature of the com-
pounds in the mixture. However the study also concluded that for
low atomic number elements with their high absorption coefficients
the grain size scale is so low that it is impossible to grind
sufficiently and that in such cases the sample should be ground
just enough to have a sufficiently representative and reproducible
sample surface.

Although much particle size behaviour can be attributed to
the relative absorption coefficients of the materials there must
also be considered the effect of shielding due to surface finish,
particularly in the range of particle sizes which are around
infinite thickness value. In general, the longer the wavelength
of the measured element and/or the larger the mass absorption
coefficient of the matrix, the more critical is the required
surface finish.

In applying particle size effects to soil sulphur analyses,
an estimate of the distribution of sulphur in soil must be
attempted. Soil particles from a 100 mesh sieve have a range
of sizes from fine sand to very fine clay, and also each type of

soil has a different distribution of these particle sizes. To
achieve a uniform sample in terms of a particle size of one-tenth
infinite thickness would involve reducing all the particles to
half clay size or smaller, no small task in terms of grinding
procedures. In the majority of soils likely to be studied,
sulphur is found either as inorganic sulphate or in an organic
form. The inorganic sulphate is probably distributed around ion
exchange sites most of which will be associated with the clay
fractions. The amount of sulphate present probably represents
only a few ppm, a small fraction of the total content and is
probably distributed as discrete radicals roughly in proportion to
the reactive surface area of the particles. Thus the sulphate
fraction does not have a particle size of its own right but assumes
a uniform distribution associated with the finer soil fractions.
Organic matter sulphur is mainly found in protein and derived
organic complexes, all of which are fairly evenly distributed
throughout the organic material. The particle size of organic
sulphur thus becomes a problem of particle size and distribution
of organic matter. The plant residue portion of the total
organic matter varies with the sample but probably contains less
than 10% of the total and is represented by fairly large particles
up to the limit of the sieve size. The humus fraction on the
other hand is probably very finely divided, at least to fine clay
size or smaller. Much of the humus forms organic-mineral com-
plexes, iron or calcium humates etc., and is probably represented
more by coatings and clay derivatives rather than by particles.

The point to be made is, that sulphur is not distributed throughout soil in a particle size fashion but it predominates in the finer fractions of the soil material. The two-particle size analogy does not fit this situation very well as both mineral and organic material vary from say 15 times infinite thickness particle size to at least a couple of orders smaller than infinite thickness size. This range covers both situations outlined by Bernstein where the intensity levels off, with a continuous gradation between them. A possible model is that of larger particles coated with and with intersites filled with sulphur containing material, but a mathematical solution after the fashion of Claisse and Samson is much too complex. Add to the problem the variety of sizes to be found in the "larger" fraction and the cementing effects of iron and aluminium and one has a very complex system. The sensible practical solution is to point out the extreme complexity and hope that the grinding done is sufficient to ensure adequate uniformity within the thin surface layer to be irradiated.

A point of interest is that during the spiking of soil material with sulphur compounds to produce standards (see Figure VIII) it was observed that the particle size of the added sulphur compound markedly affected the count-rate, with the count-rate increasing with increasing size. The count-rate for soils indicated a very small sulphur particle size which was not quite reached even with tedious grinding and mixing of sublimed sulphur.

II. ABSORPTION COEFFICIENT

In X-ray fluorescence analysis the characteristic radiation from the element must travel through some thickness of the surrounding material before it reaches the surface of the sample. Because of scattering and absorption, the radiation intensity decreases during passage in accordance with equation 3.2 . The absorption coefficient μ which is the constant in the equation, varies with radiation energy and hence the particular element being analysed. With a single value of radiation energy the absorption coefficient also varies for each element encountered. If the ratios of the other elements in the sample change, then the combined absorption coefficient of the sample matrix alters and the calculated concentration is incorrect. For a particular characteristic radiation, the severity of the error depends on the difference in the magnitudes of the coefficients for each element.

The concentration of an element in a sample is usually given by the familiar "intensity" versus "concentration" line of calibration, $C = k.R.\mu$ (3.4)
where k is a proportionality constant depending on experimental conditions, μ is the mass absorption coefficient of the sample for the secondary characteristic radiation, R is the intensity (count-rate) of the characteristic radiation.

In the derivation of equation 3.4 (see for example Norrish and Chappell 1967), there are a number of conditions which must be

approximated. One of interest in the case of soils is that there must be no major elements in the sample with absorption edges between the wavelengths of the primary radiation effective in producing the fluorescent sulphur K_α radiation, and the wavelength of the sulphur radiation itself. The elements of interest in the case of sulphur with chromium excitation, are $Z = 17$ to $Z = 23$ (Cl, A, K, Ca, Sc, Ti, V). If these elements are present in major amounts the linear calibration is invalidated. However if an emperically derived correction is used for the secondary absorption, it nearly always corrects for the primary absorption as well.

(1) Variation of Soil Matrix

A variation in the mass absorption coefficient for the secondary radiation from sample to sample also invalidates equation 3.4 . The mass absorption coefficients for elements most likely to be found in organic matter are much smaller than the coefficients for many of the elements found in typical soil mineral material. The error resulting from a variation in the ratio of these two groups is reasonably serious but knowing the respective absorption coefficients the error can be virtually eliminated by mathematical procedures. This is made possible by the consistency in effective composition of these two fractions and although a variation in the composition of the mineral or organic fractions introduces a further variation, the effect of this second error is much less than that of the two fractions themselves.

This consideration led Brown and Kanaris-Sotiriou (1969) to suggest that the mass absorption coefficient of a soil for sulphur radiation could be regarded as the sum of an organic component and a mineral component, $\mu = \mu_m(1 - p) + \mu_o p$ (3.5)

where μ_m and μ_o are the mass absorption coefficients of the mineral and organic fractions respectively, and p is the mass (weight) fraction of the organic matter.   Equation 3.5 is a grouping application of the general equation 3.3 .   They then combined equations 3.4 and 3.5 to get their calibration equation,

$$C = k'.R(a(1 - p) + b.p) \qquad (3.6)$$

where a is the ratio of the mass absorption coefficient of mineral material to that of the sample, and b is the ratio of the mass absorption coefficient of organic material to that of the sample. Also Kanaris-Sotiriou and Brown (1969) oven-dried their material before grinding but it is not stated if they continued to keep the sample isolated from the atmosphere throughout the whole procedure.

In this study it was first proposed if possible to work on air dry samples and also to check the validity of the corrections by mathematical analyses.   However the effect of vacuum drying of the sample becomes a problem and is discussed more fully under errors arising from the vacuum system.   Most of the standards used had a moisture loss on oven drying of 1% to 4%.   Assuming all this moisture is lost under vacuum introduces an error on air dry samples of $\pm$ 2% of sulphur content.   In many situations this extra error may be quite acceptable.   However in samples

with very high content of allophane, montmorillonite or organic
matter, an extreme moisture loss of say 10% introduces a further
enhancement of about +15%.   This extra is not taken into account
during the analysis but if required a manual adjustment can be made
to the final result (see Figure IV).

The standard analyses were done firstly on an air dry basis
with satisfactory results which did not differ significantly from
those on an oven dry basis.   However because a few of the soils
to be analysed in the Reefton sequence have very high moisture
losses and because a completely oven dry basis is the more correct
procedure, the standards and all results given in this study are
on an oven dry basis.   If one wishes to work on air dry samples,
the implications of doing so are included in the following treat-
ment which covers both situations.   Also note that oven drying
does not remove structural water which varies from sample to
sample and thus the dual treatment is still necessary to allow for
the remaining water and hydroxyls.

Equation 3.5 is modified to include an extra term for water
content, $\mu = \mu_m(1 - p_o - p_w) + \mu_o p_o + \mu_w p_w$ (3.7)
Equation 3.7 is simplified as follows to enable it to be put in a
form for easy computation and to check the values of the coeffic-
ients. $\mu = \mu_m + p_o(\mu_o - \mu_m) + p_w(\mu_w - \mu_m)$

$$= \mu_m\left[1 + p_o((\mu_o-\mu_m)/\mu_m) + p_w((\mu_w - \mu_m)/\mu_m)\right] \quad (3.8)$$

The values μ_m, μ_o and μ_w can be evaluated as in the next section.

(2) Evaluation of Mass Absorption Coefficients

Using typical values for the concentrations of the major elements found in soils, the resultant mass absorption coefficients for the groups of elements are calculated from equation 3.3 . The wavelength of sulphur radiation is $K_\alpha = 5.373 \cdot 10^{-10}$m and each of the specified μ_i are for this wavelength and are obtained from standard tables (Jenkins and de Vries 1970a). The calculations of μ_m, μ_o and μ_w are given in Tables I and II. Note that considerable isomorphous replacement of cations in mineral material can be tolerated for little effect on μ_m due to the similarity of many μ_i values (Table III). The possible exceptions involve replacements in Ca and K but in typical soils these contribute in a minor way only. Table IV shows the error resulting from variations in soil mineral composition. Inspection of the range of cations given in data from Soils of New Zealand, Part 3 (1968), showed that in most cases μ_m deviated by less than 2% and a variation of more than 4% was rare. The coefficient for water is of course constant and typical compositions for organic material vary little, carbon and oxygen being the only major contributors (Table II). The values for organic and mineral material mass absorption coefficients quoted by Brown and Kanaris-Sotiriou are 220 and 1100 respectively giving a slightly greater relative magnitude and hence greater theoretical interference.

From the values given in Tables I and II the coefficients of p_o and p_w in equation 3.8 can be calculated. The mass absorption

TABLE I   Sulphur K_α Mass Absorption Coefficient

for Typical Mineral Material

Element	μ_i	Typical p_i	$\mu_i p_i$
O	415	49%	203
Na	995	1.5%	15
Mg	1280	1.0%	13
Al	1550	10%	155
Si	1900	31%	591
P	2120	0.1%	2
K	410	1.0%	4
Ca	465	1.0%	5
Ti	625	0.4%	3
Mn	905	0.1%	1
Fe	1030	5.0%	51
		100%	$\mu_m = 1043$

TABLE II   Sulphur K_α Mass Absorption Coefficient

for Typical Organic Material

and Water

Element	μ_i	Typical p_i	$\mu_i p_i$
H	2.3	4%	–
C	171	60%	103
N	280	5%	14
O	415	30%	125
P	2120	0.5%	11
S	240	0.5%	1
		100%	μ_o = 254
H	2.3	11%	–
O	415	89%	370
			μ_w = 370

TABLE III. Sulphur K_α Mass Absorption Coefficient

for Soil Oxides

Oxide	μ_i	Typical p_i	$\mu_i p_i$
SiO_2	1107	66.8%	738
Al_2O_3	1015	18.9%	192
Fe_2O_3	846	7.1%	60
MgO	934	1.7%	16
CaO	461	1.4%	6
Na_2O	846	2.0%	17
K_2O	412	1.2%	5
MnO_2	726	0.2%	14
TiO_2	542	0.7%	4
		100%	1052

TABLE IV

Error in Calibration Line Gradient Resulting

from Variations in Soil Mineral

Composition

SiO_2	Al_2O_3 + Fe_2O_3	Others	Ratio Al_2O_3 : Fe_2O_3				
			6:1	4:1	3:1	2:1	1:1
40%	48%	12%	+3.2%	+3.7%	+3.9%	+4.7%	+6.0%
50%	40%	10%	+1.7%	+2.0%	+2.3%	+2.9%	+3.9%
60%	32%	8%	0.0%	+0.4%	+0.6%	+1.0%	+2.0%
70%	24%	6%	-1.4%	-1.2%	-1.0%	-0.6%	0.0%
80%	16%	4%	-3.0%	-2.9%	-2.8%	-2.5%	-2.0%
90%	8%	2%	-4.6%	-4.5%	-4.5%	-4.3%	-4.1%

coefficient for the sample then becomes,

$$\mu = \mu_m(1 + (-0.76)p_o + (-0.64)p_w) \qquad (3.9)$$

The negative sign indicates an enhancement effect with increase in content. Water and organic matter have rather similiar enhancement effects, so in the actual analyses the two factors may be combined as follows into one term based on a loss in weight when heated. Note, the following takes into account the water remaining in the sample, any water lost from the sample under vacuum is treated later.

Including water remaining in the sample along with the organic matter term, the multiplier for p_o increases by +0.01 for each 10% of water in the total loss. Values of weight loss from air dry to 110^oC and from 110^oC to 550^oC were processed for about 75 soil samples to find the apparent relative amounts of water and organic matter. OA and A horizons gave a figure of 15% to 20% moisture in the total loss, B and C horizons varied from 25% to 30% and Dr horizons ranged from 20% to 40% in the total loss. It is better to make the adjustment most accurate for the upper organic matter rich horizons, therefore by using the value of 20% leads to the equation,

$$\mu = \mu_m(1 + (-0.0074)L) \qquad (3.9a)$$

where L is the percentage weight loss determined by heating the sample to 550^oC, by which temperature all organic matter and water should be driven off together with most of the structural hydroxyls. Using the actual values of organic matter and

water found in the samples, calculations showed that by includ-
ing both together and by using the value of -0.74, in no case
was the error introduced greater than 1.0% and in most cases
was less than 0.4%.

(3) Calibration Equation

Incorporating the above considerations, the calibration
equation 3.6 then becomes, $C = K.R(1 + B.L)$ (3.10)
where K is a new constant (given by $\mu_m k'$), R is the net intensity
as before, B is the enhancement factor, approximately -0.0074, and
L is the percentage weight loss on heating to $550^{\circ}C$.

Using the value of $B = -0.0074 \pm 0.00037$ (5.0%), Figure I
shows the theoretical apparent increase in sulphur content with
organic matter content. The error in the value for B corresponds
to a variation in μ_m of $\pm 3\%$ (see Table IV). Assuming that a
sample contains no organic matter, then for a given count-rate,
$C_1 = K.R.\mu_m$ which is an overestimation if organic matter is
present. If the sample does contain organic matter the true
concentration of sulphur is, $C_2 = K.R.\mu_m(1 + p_o((\mu_o - \mu_m)/\mu_m))$.
The percentage relative increase in the apparent sulphur content
is given by, $D = (C_1 - C_2)/C_2 \times 100\% = -B.p_o/(1 + B.p_o) \%$
In Figure I, D is plotted against p_o. This graph shows the same
shape of curve as that of a light element incorporated in a heavy
matrix. When p_o is zero then the enhancement is zero. When p_o
is unity (100%) then the enhancement is 285%. Most soils have
a p_o value in the 5% to 25% range.

FIGURE I   31

EFFECT OF ORGANIC MATERIAL ON APPARENT

SULPHUR CONTENT

% Organic Material in Sample
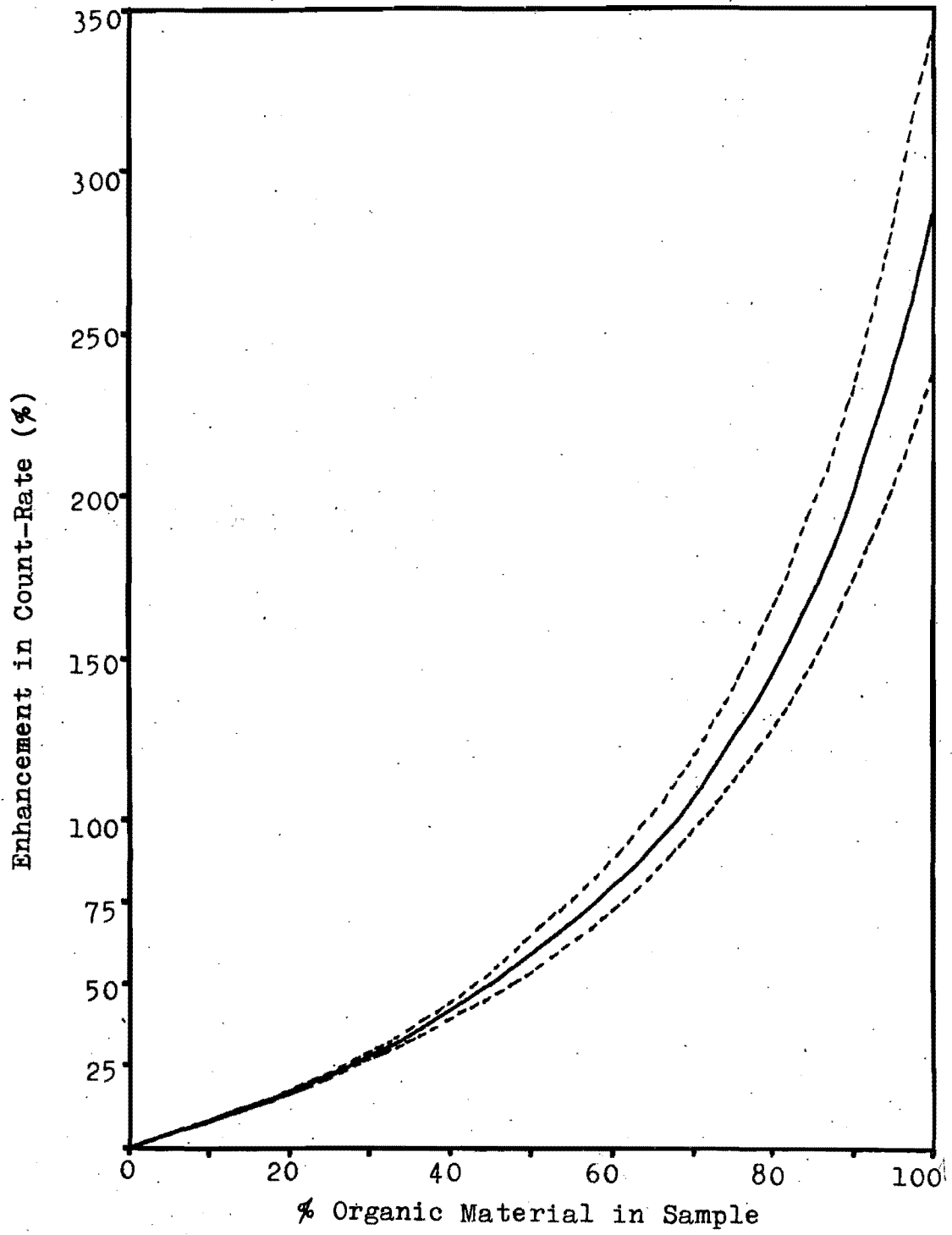
Thus to fit a mathematical expression to soil sulphur fluorescence data, the following equation should be used.

$$R' = R(1 + B.L) = m.C + c \qquad (3.11)$$

where m is the gradient of the calibration line in (c/s)/ppm.

C is the sulphur content in ppm.

c is the axis intercept in c/s to allow for systematic errors

R is the net measured count-rate

R' is the count-rate corrected for enhancement

L is the percentage loss determined by heating

B is the mass absorption correction factor.

Although this treatment may seem to presume that zero organic matter in the soil is the normal situation, this is of no consequence as the same results can be obtained by assuming 100% organic material as the normal and incrementing the mineral content.

III. CHEMICAL STATE

(1) Oxidation Number

As characteristic radiation arises from transfer of electrons from outer to inner orbitals, wavelengths alter slightly if the outer orbital is concerned with valency. Sulphur has a wide range of oxidation states from sulphide to sulphate. Using pure compounds it was found that the instrumental resolution was insufficient to resolve the difference in wavelength, although the difference could just be detected. Hence the shift in wavelength

is no problem in this study. Another aspect is any shift in
the relative intensities of the alpha and beta radiation with
oxidation state. Although the effect is expected to be negligible
it is somewhat of an unknown quantity in this study.

(2) Local Absorption

Of more consequence in soil samples is the problem of local
absorption. This heterogeneity effect is found if the composit-
ion of the grains containing the element to be determined changes
even if this change has a negligible effect on the overall
absorption coefficients of the material. If a sulphur atom is
surrounded by heavy absorber atoms then the characteristic
intensity penetrating the screen is less than if the sulphur atom
is surrounded by say oxygen atoms.

Sulphur in organic material is surrounded by light absorbers,
as is sulphate surrounded by oxygens. However sulphur incorp-
orated into a silicate matrix, or sulphides, may be surrounded by
heavy absorbers with a consequently lowered countrate. Although
it has been considered generally that such effects have a maximum
error of 5% (Jenkins and de Vries 1970a), the analyses of say fresh
rocks containing high concentrations of sulphides should be treated
with caution until more is known about the specific application
of sulphur in soils.

CHAPTER IV

ERRORS

As an element concentration is calculated as some function of the characteristic radiation intensity, any variation that produces some deviation in that intensity must be considered. The errors in quantitative X-ray fluorescence fall into three main classes. (a) Errors associated with the sample. (b) Random and systematic equipment variations. (c) Calibration and counting statistics. The errors associated with the sample matrix have been discussed in the previous Chapter.

The object is to find an analytical procedure which attempts to either overcome each source of variation or evaluate the resultant uncertainity in elemental concentration due to the variation. The basis of a suitable procedure is to reduce all variations from (a) and (b) above to counting or data processing errors and perform statistical calculations under the headings in (c). This is done by expressing both standard and unknown samples in terms of the intermediate reference count-rate which is governed by the operating conditions and settings of the X-ray installation. Any residual particle size and random inter-elemental effects that have not been corrected for, add to the standard errors when fitting a calibration function to the standard samples and are thus taken into account.

I. EQUIPMENT VARIATIONS

The basic operation and stability of the physical plant is primarily the concern of the equipment manufacturer. The experimental procedure must be designed to obtain the best results possible. The main sources of variation are electronic drift, geometrical settings, radiation detection and the vacuum system. Each variation in the above may have several possible causes, resulting in either a random variation, a systematic variation, or both. If a systematic error can be evaluated the precision of the measurement may decrease only slightly but a random error always increases the uncertainity in a result.

(1) Electronic Drift

Caused by ageing of components, temperature change or power flucuations, any drift is reflected similarly in the count-rates of both the reference substance and the samples and is evaluated in the processing of data. With the high stability power generator, variation in the X-ray tube intensity is of the order of 0.1% with at least as much again contributed by other electronics so there is little gain in trying to reduce other errors to much below this figure.

(2) Geometrical Settings

When the goniometer is initially aligned and calibrated with the correct settings, the main source of variation is in the positioning of the counter arm at the angle of the diffracted radiation, together with backlash in the screw threads. The first is an

operator systematic error and the second should be eliminated by
correct procedure.   If the initial alignment is upset, a system-
atic error results which can be rather difficult to trace.
Pentaerythritol (PE) analysing crystals have a rather high thermal
coefficient of expansion causing a slight shift in detection angle
of about 0.02° $2\theta/^{\circ}C$ for S K_{α}.   As with electronic drift, any
variation is evaluated during the processing of data.

(3) Radiation Detection

Other than electronic factors affecting the amplification
and counter dead time between pulses, the main variations are in
gas purity, cleanliness of the counter anode wire and the settings
of the pulse height analyser.   Variation in the rate of gas flow
seemed to have little influence provided there were no leaks in
the counter window.   As the voltage of the pulse from the counter
is proportional to the energy of the incident photon, an efficiency
figure of merit or "resolution" is defined as the half height
width of the pulse distribution curve.   The theoretical value of
the resolution for a given energy E is, $R = 38.3 \ K/E^{\frac{1}{2}}$
where K is a factor taking a value between 1.0 and 1.5 depending
upon the cleanliness of the counter.   The resolution can be
measured for any particular element in a few minutes and decreases
as the counter becomes dirty.   As the resolution of the counter
decreases, the settings of the pulse height analyser must be
adjusted to accomodate the new pulse distribution.

A frequent cause of decrease in count-rate, is the shift for

one reason or another, of the pulses out of the tightly specified

pulse height window.   The rigid settings are necessary to $\land$ back-

(decrease, inserted above)

ground from the low count-rates and a frequent check must be made

to ensure the counter tube voltage is correctly adjusted for the

counts to fall in the window.

Figure II shows the effect of pulse height analysis for a

typical soil sample containing 275 ppm of sulphur.   The first

order sulphur K_α line (75.85°) is sandwiched between a second

order Ti K_α line (77.97°) and a third order Fe K_β line (74.16°).

The first order sulphur K_β line (70.29°) is superimposed upon the

second order Ti K_β line (70.22°), together with any second order

V K_α line (69.93°) if this element is present.   The top trace (A)

is a scan with no pulse height selection except a threshold step

to eliminate circuit noise.   The height of the Ti K_β (n=2) peak

which is chopped off, is 42 cm on the same scale as drawn, and the

corresponding height for the Ti K_α (n=2) peak is 220 cm.   However

the difference in photon energies makes the pulse height analysis

removal of these lines relatively simple as shown in scans B, C

and D.   Scan B has too wide a window, scan C suitable, and scan

D too narrow a window with a loss of some of the already scarce

sulphur counts and no allowance for any small drift.   From the

scans it can be seen that suitable angles to estimate background

intensities are about 1.0° to 1.2° above and below peak value.

The use of pulse height analysis is invaluable in separating the

small sulphur peak from the soil spectrum.

FIGURE II 38

EFFECT OF PULSE HEIGHT ANALYSIS
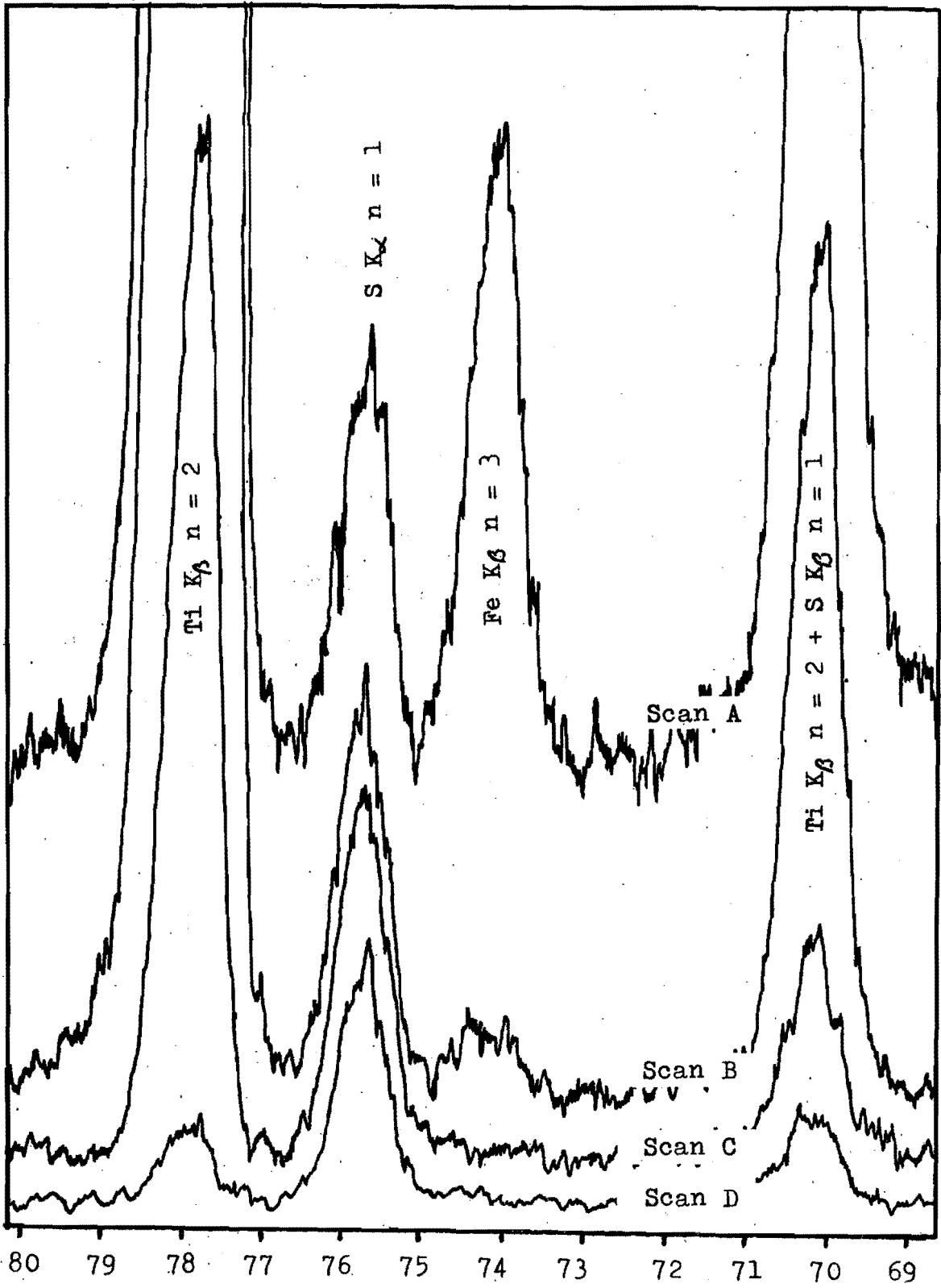
FIGURE III   39

EFFECT OF COUNTER VOLTAGE ON

COUNT-RATE

No Drift

1.0% Drift

2.0% Drift
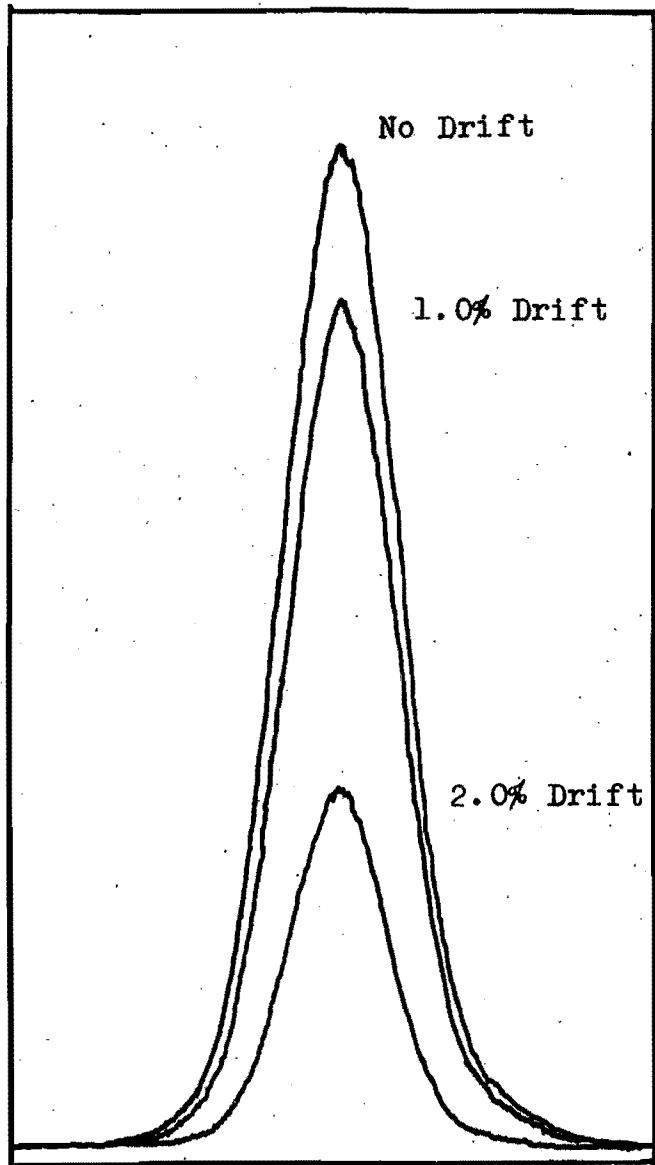
Figure III shows the effect on a sulphur count-rate of a slight drift in counting tube voltage, using optimum pulse height settings. The bottom two scans show the effect of the counter voltage differing by 1.0% and 2.0% respectively from the top scan value required to put all the pulses into the window. In practice it is easier to set the window and then correct for any drift by adjusting the counter voltage.

(4) Vacuum System

In measuring concentrations of elements with low atomic number, a vacuum path is necessary to decrease absorption of soft X-rays. This vacuum must reach a constant value within a short time as it is released with each change of samples. Small random variations have little effect, but variation in vacuum with pump oil temperature can produce a small systematic error as will any leak in the vacuum system. The vacuum pump must be warmed up with the rest of the system electronics.

(i) Contamination

As the mean free path of a molecule is greatly increased in the vacuum, there is always the possibility of sample contamination by surface absorption from the back streaming of vapours derived from the pump oil. Such contamination is very difficult to eliminate. Kanaris-Sotiriou and Brown (1969) describe a method which greatly decreased their contamination, by preparing powder specimens with a thin plastic film over the surface to be irradiated. They decreased the sulphur contamination from

235 ppm/hour to about 2 ppm/hour. As a suitable film material was not available during the present study it was decided to use a standard analytical procedure to decrease the effect. The barium sulphate intermediate reference has 14% sulphur so any contamination is negligible. If contamination is present, the fitted calibration line does not pass through the origin but gives a residual count-rate for no sulphur content. This intercept should remove the systematic error, provided that the contamination is constant after evacuation, the counting times are the same for both analysed and unknown samples, and the reference substance is in the exposed position during evacuation.

(ii) Vacuum Drying

The effect of water evaporating off the sample surface under vacuum is considered in two parts.

(1) Loss of water results in a void, concentrating the sulphur in the rest of the sample. The apparent enhancement due to concentration when a fraction p_w of moisture is lost is given by, $D_1 = p_w/(1 - p_w)$ .100% .

(2) Loss of water alters the mass absorption coefficient of the sample, the space the water occupied going from that of water (370) to that of space (zero). If there is no loss of water then (from equations 3.4 and 3.7),

$$C_1 = K((1 - p_o - p_w)\mu_m + p_o\mu_o + p_w\mu_w)$$ which is an over-estimation if some water is in fact lost. The true concentration is then given by, $C_2 = K((1 - p_o - p_w)\mu_m + p_o\mu_o)$.

The apparent enhancement due to change in absorption coefficient is

given by, $D_2 = (C_1 - C_2)/C_2 \cdot 100\%$.

The total enhancement $(D_1 + D_2)$, is plotted against water lost in Figure IV for several values of organic matter content.

It is not known how quickly the moisture is lost from the depth of sample (10 μm) contributing to the sulphur radiation. Weighing a sample after a series of vacuum and exposure times established that the sample lost about four times the weight of water contained in the 10 μm depth within the time taken to evacuate the chamber. A similiar amount of moisture was lost on exposure to the primary beam for 40 s. Although some of this moisture comes from deeper in the sample and some from the backing material, it would seem reasonable to assume that much of the surface moisture leaves the sample before or soon after counting begins.

Note that moisture loss and sulphur contamination both produce an enhancement effect. One wonders if some of the contamination reported by Kanaris-Sotiriou and Brown may in fact have been loss of surface moisture re-absorbed during sample preparation. Their subsequent use of plastic film over the surface may merely have prevented its evaporation. The results later in this study show that by using freeze dried samples virtually no increase in sulphur count-rate was observed and the axis intercept amounted to about 10 ppm. Using air dry samples

FIGURE IV   43

ENHANCEMENT FROM VACUUM DRYING

$$D = \frac{p_w \mu_w}{(1 - p_o - p_w)\mu_m + p_o \mu_o} + \frac{p_w}{1 - p_w} \cdot 100\%$$

Line 1, $p_o = 0.0$ Line 2, $p_o = 0.2$

Line 3, $p_o = 0.4$ Line 4, $p_o = 0.6$
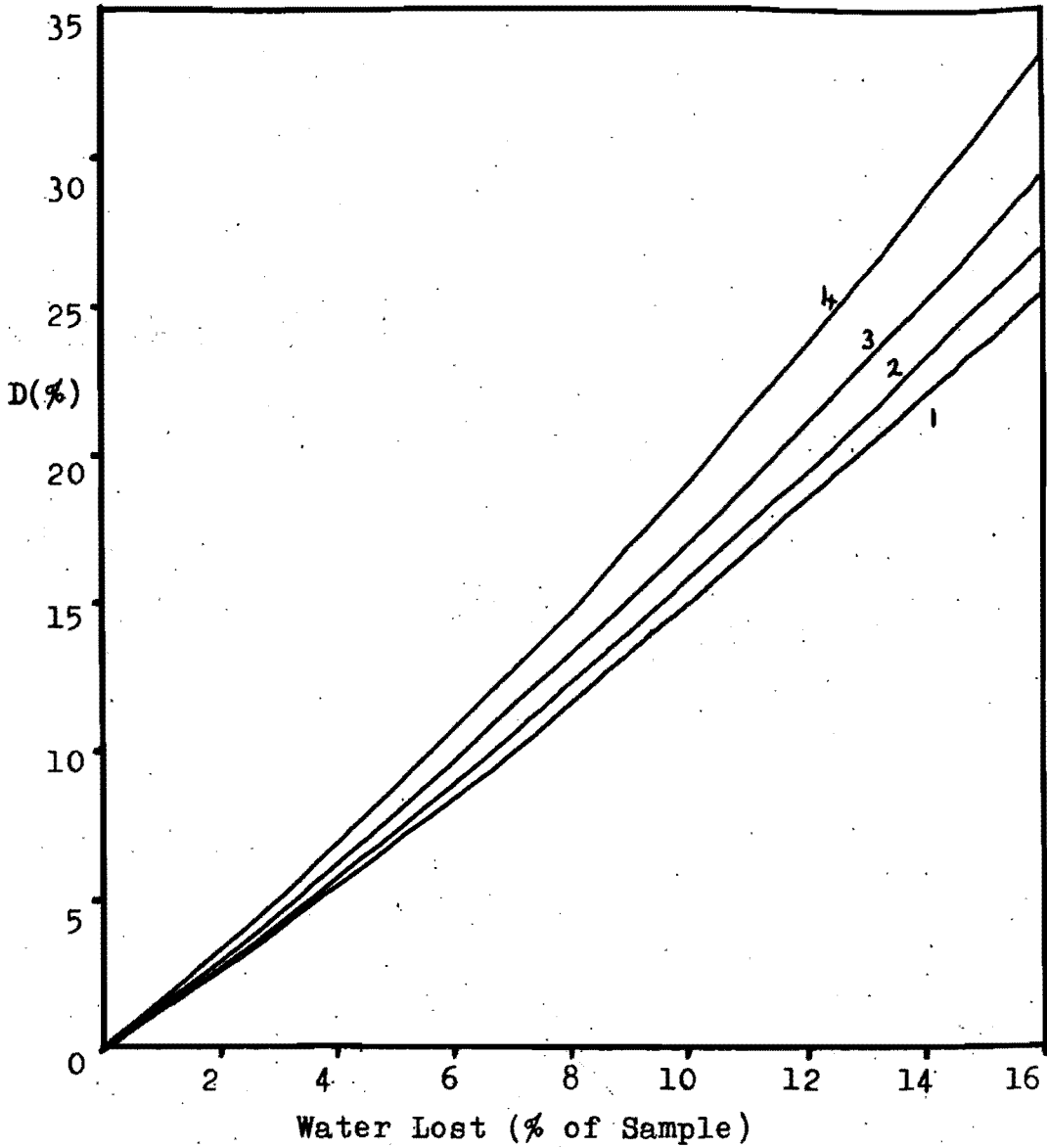
the count-rate increased during counting, producing an intercept
several times greater.   If vacuum pump oil was a source of contam-
ination then the vacuum pump on the freeze drier should also have
contributed during the 24 hour stay of the samples in the drier,
but no large scale contamination was evident.   It is concluded
for the present, that dryness of the samples is more important
than vacuum pump oil contamination.

When working on an air dry basis, the computing procedure
averages the enhancements in the standard samples and adds the
enhancement value to the axis intercept of the calibration line.
The scatter of enhancements about this average is included in the
random error term.   Thus for a group of samples with a water
loss of 1% to 4%, a 3.5% enhancement would be allowed for in the
sulphur contents, with a resulting scatter of 2%.   If the moist-
ure is known to be outside the range of standards then the add-
itional correction can be calculated from Figure IV.   When working
on an oven dry basis, hopefully all free moisture is removed by
freeze drying.

II. STATISTICAL ERRORS

The error formulae for processing raw data can all be derived
from standard statistics and are given in Appendix 4.   The part-
icular stages where these apply in quantitative analyses are;
(i) Basic counting errors (ii) Uncertainity in mathematical
corrections (iii) Fitting a line or other function to the data.

Provided the sources of variation are random, a strict statistical treatment will give the resultant error probability. When no other evidence is available, one has to assume the errors are random and independent.

Although the random distribution of X-ray photons follows the Poisson distribution for random events, when a large number of observations is made, the distribution approximates a Gaussian distribution. The standard deviation of the distribution is given by $s = N^{\frac{1}{2}}$ where N is the number of observations (or quanta). When determining the error in a count-rate, time is taken as accurate, but it must be long enough to obtain sufficient counts to ensure a suitable error value. Although the basic error in collecting 10,000 counts is 1.0%, it can be seen by inspecting the results, that to obtain 1.0% overall counting accuracy in the net sample count-rate, involves collecting about 26,000 counts.

Mathematical corrections arise from relating the sample to a standard, adjusting for effects such as counter dead time, and eliminating elemental interactions. In each case the errors must be combined using standard rules. Methods of finding the line of best fit and the standard errors in such constants as gradient and intercept are fairly well established. What is required is that one find a suitable computing procedure, apply it to the data, and combine the errors as outlined in Appendix 4. Source material

for many of the statistical equations is found in Jenkins and
de Vries (1970b), Weatherburn (1962) and Topping (1963).

Statistical and other mathematical manipulations are not a
substitute for good analytical technique and do not reveal any-
thing which is not already in the data. Statistical procedures
are simply tools used in X-ray spectrometry to get the most out of
an experiment.

CHAPTER V

COMPUTER PROCESSING OF RESULTS

I. HANDLING OF DATA

With a computer, the handling of data and hence human error is reduced. Counting data in the form of number of counts and counting times are transferred from visual machine display to a data sheet from which cards are punched and verified. The data sheet also includes any additional information such as chemical content for standard samples or ignition loss for the calculation of matrix corrections. Space on the card is reserved for sample identification, batch number, date, or other information not required for the analysis. The formal setting out of the card data is detailed in Appendix 3. A possible human error that is not necessarily detected by the present program is in the ordering of the data card deck into batches of samples. However if the (four) samples in a batch are given a specific batch number then it is easily checked by examination of the cards or printout, that the batch reference card immediately precedes the sample cards with that batch number.

II. EXPERIMENTAL ROUTINE

A rigid experimental routine must be formulated which consequently reduces the variation due to difference in technique of various operators. This routine can be used for future analyses without reference to analysed samples. The original data,

punched into cards, are the only information required for recal-
culation of the equation coefficients and the consequent calcul-
ation of unknown compositions. By storing the equation coeff-
icients in a lasting disk file, unknown samples can be evaluated
by a second program without reference to the original program
which processed the standard sample cards. One very useful
feature is, that as the pool of calibration data is extended by
the addition of analysed samples, the equation coefficients can
be up-dated in a few minutes by re-running the calibration
program including both new data and the old.

III. CALCULATIONS

The counting data are processed using the more or less stan-
dard equations found in Appendix 4. Each count-rate is corrected
for counter dead time and the errors are combined using partial
derivatives to obtain the standard error in the net count-rate.
When a reference card is encountered a drift factor is calculated
and the subsequent count-rates in that batch are corrected for
the systematic errors this factor involves. The drift factor
should approximate unity and is printed as a percentage deviation
from unity. A figure of merit Q, is given as a check for optimum
counting time on peak and background positions. Q is the quotient
of the actual peak to background time ratio, and the optimal peak
to background time ratio. If Q is less than unity, more time is
required on the background position but if Q is greater than unity
more time may be used to count on the peak position.

In the treatment of analysed sample data, both count-rate and error are stored as primary data for the regression analysis. It is required to solve equation 3.11 to find a linear relationship between the sulphur count-rates and the chemical values for sulphur concentration. This equation is rewritten as,

$$R_i' = R_i(1 + B.L_i) = m.C_i + c \qquad (5.1)$$

where i represents the value for the i-th sample and there are n such equations, where n is the number of samples. A weighted linear regression of R' on C is done for the n points using the method of least squares. Having found the constants B, m and c then, $\qquad C = (R(1 + B.L) - c)/m \qquad (5.2)$

where C is any unknown concentration, R is the net count-rate.

A quadratic equation is fitted to the corrected count-rates as a check for final linearity. Whenever a regression is performed, the sum of squares or correlation is given to show goodness or improvement in fit. When found, the constants and their errors are stored on disk file ready for application by the second program to unknown samples.

IV. CORRECTION FOR MASS ABSORPTION COEFFICIENTS

The object of the analysis is to determine the parameters B, m and c from equation 5.1 for a set of standard analysed samples. However from the derivation of this equation, the gradient m in these equations is the gradient of the line for samples containing zero organic matter. To solve these

equations, a more general form of equation 5.1 must be used,

$$R_i' = R_i(A + B.L_i) = m.C_i + c \qquad (5.3)$$

with A tending to unity and B tending to $(\mu_o - \mu_m)/\mu_m$ as the gradient tends to that for zero organic matter.

The parameter A cannot be specified initially as unity because A and B depend on the value of m and m is initially unknown. Rewriting equation 5.3, the values of A and B are found by the weighted simultaneous solution of the following linear equations, $A + B.L_i = (m.C_i + c)/R_i \qquad (5.4)$ where m is found by an iteration procedure such that A converges to unity. For the first approximation of gradient and intercept, a weighted line of regression of R on C using least squares is fitted to the raw data points (C_i, R_i), such that,

$$R_i = m_1.C_i + c_1 \qquad (5.5)$$

The values of C_i are taken as accurate and the weight assigned each pair (C_i, R_i) is $w_i = 1/L_i^4$. The values of A and B are then found by substituting m_1 and c_1 from equations 5.5 into equations 5.4 and solving.

However if these values of A and B are then substituted into equation 5.2 to calculate the corrected count-rates R_i' and a line of regression of R' on C using least squares is fitted to the points (C_i, R_i'), such that, $R_i' = m'.C_i + c'$ then it is found that m' falls somewhat short of the target gradient m_1. A second iteration procedure is necessary to obtain

the values of A and B which exactly satisfy equations 5.4 for m_1.
When this condition is obtained, the value of A is tested, the
value of m_1 is corrected to m_2 and the process repeated until A is
within a specified tolerance of unity.

Thus the constants A, B, m and c are obtained with the stan-
dard error in each case, and with A approximately unity and m
approximately the gradient for zero organic matter.   Then the
value of B can be compared with that calculated from theoretical
considerations.

V.   TREATMENT OF ERRORS

Considerable care is taken in the programs to include every
statistical error.   The formulae are given in Appendix 4.   The
only quantities for which no error exists are the chemically
determined sulphur content and the value for loss on ignition.
These two values must be taken as accurate for the purposes of the
analyses.   Of particular interest is the standard error in the
gradient and intercept of the regression line.   These two errors
reflect the scatter of data points around the line and give a
picture of the residual random errors in the whole analytical
procedure.

For the error in compound quantities, the standard errors
are combined using the particular special case of the general
partial derivative equation for $y = f(x_i)$ i = 1 to n.

The standard error for independent variables is given by,

$$S_y{}^2 = \sum_{i}^{n} ((\partial f/\partial x_i)^2 \cdot S_{x_i}{}^2)$$

In the calibration program, by back substitution of the original counting data, a comparison is made of the chemical and simulated sulphur concentrations. The form of this comparison is to express the difference in the two values as the number of calculated standard errors separating the two concentrations. From mean value theorem considerations, if there are no systematic errors in the calculated concentrations and the calculated error is a reasonable estimation of the error probability in the calculated concentration, then the difference values are a normal distribution with mean zero and standard deviation unity.

VI. DESCRIPTION OF PROGRAMS

Printouts and program listings appear in Appendices 1, 2 and 5. Program HXRAY processes the data from analysed samples and performs all the operations outlined in the previous sections of this Chapter. Program HXSUL calculates the net count-rate from cards and master references as described for HXRAY. The unknown concentration in the sample is then calculated from equation 5.2 using the parameters from HXRAY previously stored on the disk file. Figure V and Figure VI show the pathways within the programs.

FIGURE V 53

PROGRAM HXRAY

FIGURE VI   54

PROGRAM HXSUL

```
┌──────┐      ┌─────────────────────┐
│ LOAD │─────▶2│ READ PARAMETERS     │◀──────────────
└──────┘       │ FROM DISK           │
               └─────────────────────┘
                         │
                         ▼
               ┌─────────────────────┐
               │ INITIALISE          │
               └─────────────────────┘
                         │
                         ▼
        ──────▶24│ READ CARD │◀──────────────────────
               └───────────┘
                         │
                         ▼
   ◀──YES─│ LAST CARD? │─NO─▶  ┌──────────────┐
                               │ CALCULATE    │ 6
                               │ COUNT-RATE   │
                               └──────────────┘

        ◀──YES─│ REFERENCE │─NO─▶
               │ CARD ?    │
                                    ┌──────────────────┐
                                 10 │ DRIFT FACTOR     │─NO─
11 │ FIRST REF. CARD? │─NO─         │ MASTER COUNT     │
        │                          │ CALCULATED?      │
       YES                          └──────────────────┘
                                           YES
12 │ STORE MASTER │  13 │ STORE DRIFT │  ┌──────────────┐
   │ COUNT-RATE   │     │ FACTOR      │ 35 │ TOO MANY    │─YES─
                                        │ SAMPLES IN  │
                                        │ BATCH ?     │
                                          └──────────────┘
                                               NO
98 │ PRINT NET DATA │◀───YES─│ STORAGE │ 20
                              │ FULL ?  │
                                  NO
   ┌──────────────┐            ┌──────────────┐
   │ CALCULATE    │         30 │ CORRECT AND  │
   │ CORRECTED    │            │ STORE NET    │───▶
   │ COUNT-RATES  │            │ DATA         │
   └──────────────┘            └──────────────┘

   ┌──────────────┐
   │ CALCULATE    │─────▶99│ PAUSE │◀──────
   │ SULPHUR      │
   │ CONTENT      │
   └──────────────┘

   ◀──YES─│ INT REQ? │─NO─▶

   │ END │            ┌──────────────────┐
                      │ CONTINUE WITH    │
                      │ NEW SET OF DATA  │
                      └──────────────────┘
```

Disk data file HXDAT contains the analysis parameters and it must be referenced by a FILES record at each execution of HXRAY or HXSUL. If a special file is required for special parameters simply create another calling it a different name. Subroutine subprogram HXREG performs a weighted linear regression. It is used a number of times in the iteration procedures of HXRAY. Subroutine subprogram HXLIN finds the solution of a number of linear equations and is specifically used to find the solution of equations 5.4. This step may be required a number of times. Subroutine subprogram HXCUB performs a quadratic regression and is used to check the linearity of the final calibration line.

CHAPTER VI

RESULTS AND DISCUSSION

Both the X-ray fluorescence procedure and the computer pro-
grams perform as outlined in the appropiate text.   What remains
is to discuss the accuracy and applicability of the analysis with
reference to the samples analysed.

I. CHEMICAL SULPHUR VALUES

Chemically determined sulphur values were obtained for about
45 samples ranging from top soils to fresh rocks and representing
a wide range and variety of chemical and physical properties.
The chemical results quoted were those determined by the method of
Johnson and Nishita (1952) using the variation of Deans (1966) and
the fusion oxidation method of Steinbergs (1962).   Twenty five of
these samples were those used to set up this chemical method in
the Soils Laboratory at Lincoln.   The values given for sulphur
content for these samples were from 6 or more replicates, but some-
times the first two or so of these may have been discarded.   Of
the 25 samples, 10 were below 50 ppm of sulphur and although
giving a reasonable fluorescence result, these were left out of
the final calibration.   A further 20 chemically analyses samples
were obtained from runs of samples put through the chemical
procedure during its subsequent operation.   About half of these
were quadruplet determinations or better and the other half
duplicate determinations.   With experience gained in the chemical

procedure, duplicates return almost exactly the same value.

Most of these samples went through the X-ray procedure many times while the method was being perfected and the equipment modified. One of the final modifications to the equipment was the installation of a 2 kW X-ray tube which greatly increased the potential accuracy of the fluorescence procedure. The results quoted here are measured with the new tube although they do not differ significantly from those gained previously. The final X-ray analyses were replicated 3 or 4 times although the counting data for each pellet are grouped together for calibration purposes as it is the total number of quanta that is required. Once a sample is prepared the count-rate from that sample is virtually constant, but some variation can arise during sample preparation. An idea of the total variation can be gained from a Hurunui silt loam A horizon which was prepared 7 times with an average value of 685 ppm. This sample was one of the more difficult to prepare and the individual variations were -28, +5, +30, 0, -9, +2, +1 ppm respecively, which is a maximum variation of 4.4%. For the majority of samples there was virtually no difference between replicates. As the samples were counted in a fairly random order and mixed up in different batches, each sample has a separate drift factor, whereas normally for a single determination, three samples share the same drift factor.

It became obvious during the analysis that all the samples

were not going to lie on a straight line, no matter how many
duplications, iterations or mass absorption corrections were
applied. As an aid to see what was going on, the computer
program was modified to include a step which forced the mass
absorption correction to take the theoretical values and hence
put all the samples on a common base mass-absorption-wise.
The results are shown in Figure VII. The circles represent the
initial chemically analysed samples and the triangles those
samples analysed during subsequent operation of the chemical
setup. An immediate observation is the poor correlation. The
second result is that the samples more carefully analysed during
the initial setting up tend to the higher values of sulphur
content for a given count-rate and that these samples form not
too bad a line with the exception of the two highest sulphur
content samples. These two samples were fresh rocks containing
a high proportion of sulphides so for the reasons given in
Chapter III (3) they were temporarily ignored. Also the hardness
of the rock made them very difficult to grind and prepare.

As all the possible variations in the X-ray procedure had
been checked as far as was able, it was decided to repeat the
chemical determinations even though they had replicated well.
As before it was found that the duplicate determinations agreed
even better, but however, a systematic error of some sort produced
a new value in a number of samples. The results of some repeat
chemical analyses are set out in Table V.

FIGURE VII   59

CORRECTED COUNT-RATE AND CHEMICAL

SULPHUR CONTENT
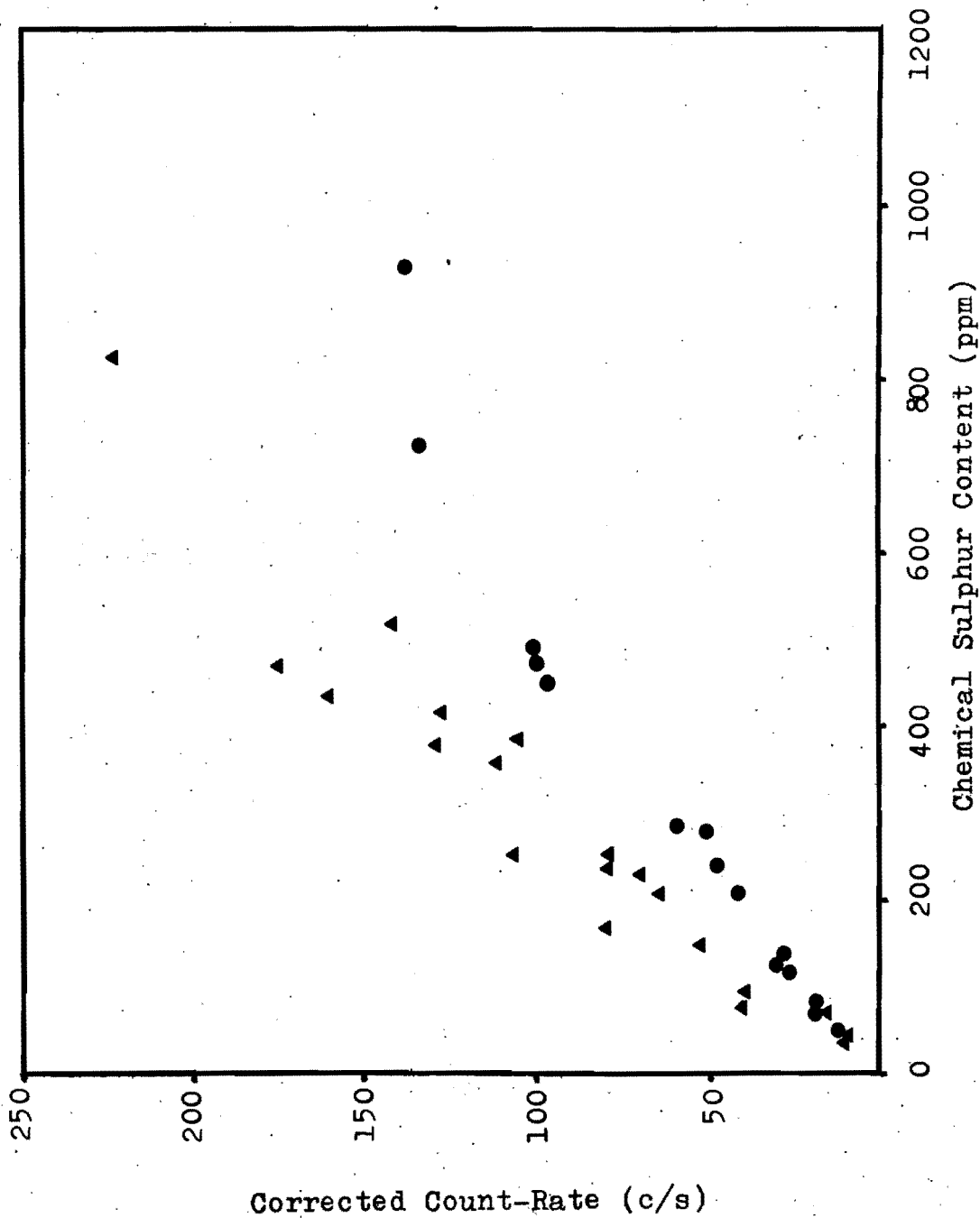
TABLE V

Variation in Chemical Values

Sample No.	Chemical Value (ppm)	No. of Reps.	Est. Std. Error	Repeat Chemical Values			Difference %
1	432	6	11	434	434		+0.5%
2	273	6	8	281	293		+5.5%
3	718	6	26	713	690		-2.2%
4	922	6	45	972	952		+4.3%
5	204	6	8	241	241		+18%
6	402	2	-	474	482		+20%
7	78	2	-	133	136		+73%
8	421	4	20	570	578		+37%
9	167	2	-	193	193		+16%
10	789	6	36	703	693	693	-12%

The first 5 of these samples were originally used to set up the apparatus and in general agree satisfactorily. For the next 5 samples one concludes that the chemical method as subsequently carried out, although precise in replication, is not sufficiently accurate for use in calibrating X-ray fluorescence equipment.

From the knowledge gained in helping to repeat the chemical values the author, who makes no claims at being an analytical

chemist, noted the following possible reasons for the discrepency. The chemical method is virtually a closed system except for the initial fusion-oxidation step. In the light of what was said about fusion in Chapter II under X-ray Sample Preparation, the fusion step is the first one suspect. A loss of some of the sulphur as a gaseous compound could explain the difference. It was noted that: (a) The fusion mixture must be very intimately mixed with the sample. For the original values on the last five samples this may not have been the case as on a batch basis they tended to be mixed rather quickly. (b) On the same five samples different size crucibles were used exposing a different surface area. (c) For sample 7 and possibly 5, twice as much sample was used for the repeat chemical values to bring them further up the chemical calibration curve. This is standard practice, but it also greatly reduced the relative surface area. (d) It had been noticed that samples nearer the door of the furnace may have a slightly different colour. The repeat values for the three replicates of sample 10 were nearest the door. (e) Crucible lids and guard layers of fusion mixture are not used. None of these factors influence replication of a normal run of samples but they may produce a difference for subsequent runs.

It was noticed that the samples from which least sulphur had been extracted for a given X-ray count-rate often contained large amounts of organic material. As the overall mass absorption coefficient had already been corrected, we are left with either a

local absorption effect as discussed in Chapter III (3) or a preference for loss when organic matter is high. The former could not possibly account for all the difference and the later would make sense if such a loss were mainly oxidizable organic sulphur compounds combining with reactive carbon during fusion, and depending to a certain degree on the points listed above. On re-examination of the work of Brown and Kanaris-Sotiriou (1969) it is found that they used highly accurate analysed samples, some of which were those used by Jenkinson (1968) in publishing his method for sulphur determination. However the method of Jenkinson and that of Bloomfield (1962) have not been set up yet for use as for large numbers of samples they are rather lengthy procedures.

II. SPIKED STANDARDS

Because of the difficulty in obtaining agreement between chemical concentration and fluorescent count-rate it was decided to try spiking samples with known quantities of sulphur. However considerable difficulty was encountered in getting a thorough mixing at the very low concentrations required, the process taking up to several hours per satisfactory standard.

A series of artificial standards was produced by mixing silica sand, Al_2O_3, Fe_2O_3, MgO and $CaCO_3$ in approximate proportions to produce a matrix with the same mass absorption coefficient as soil mineral material and then spiking with K_2SO_4. Celluose, urea, benzoic acid and KH_2PO_4 were mixed to produce an

artificial mixture behaving like organic matter. From an X-ray
mass absorption point of view these mixtures were identical to
the average found in soils. A series of 15 samples was prepared,
5 at zero "organic" level, 5 at 10% and 5 at 20%. These mixtures
behaved exactly as anticipated with the presence of "organic"
material enhancing the count-rates as calculated. The results
are summarised by line 1 in Figure VIII where the samples have
been corrected by the program for "organic" content. The signif-
icance of the actual gradient of this line is discussed later.

A second series of standards was prepared by mixing 7 of the
soils for which the chemical value was best known to produce a
matrix typical of an "average" soil sample. The mixture included
two A horizons, one B horizon, two very weathered, one partly
weathered and one fresh rock. This mixture was then spiked with
$BaSO_4$ and the result shown by line 2 of Figure VIII. A third
series of standards was prepared from the same mixture of soils
but instead was spiked with sublimed sulphur, requiring extreme
care and fanatical mixing. These results are given as line 3.

Figure VIII shows the effect of the particle size of the
sulphur-containing compound on the count-rate. Included as
line 4 is the line for sulphur as it occured in the best chemically
analysed samples. Line 1 for K_2SO_4 depicts the difficulty in
grinding the crystalline solid fine enough. The line for $BaSO_4$
shows a much finer particle size as the $BaSO_4$ was prepared by

FIGURE VIII   64

EFFECT OF SPIKING WITH VARIOUS
SULPHUR COMPOUNDS

o Line 1   Crystalline K_2SO_4
▲ Line 2   Precipitated $BaSO_4$
■ Line 3   Sublimed Sulphur
● Line 4   Soil Standards
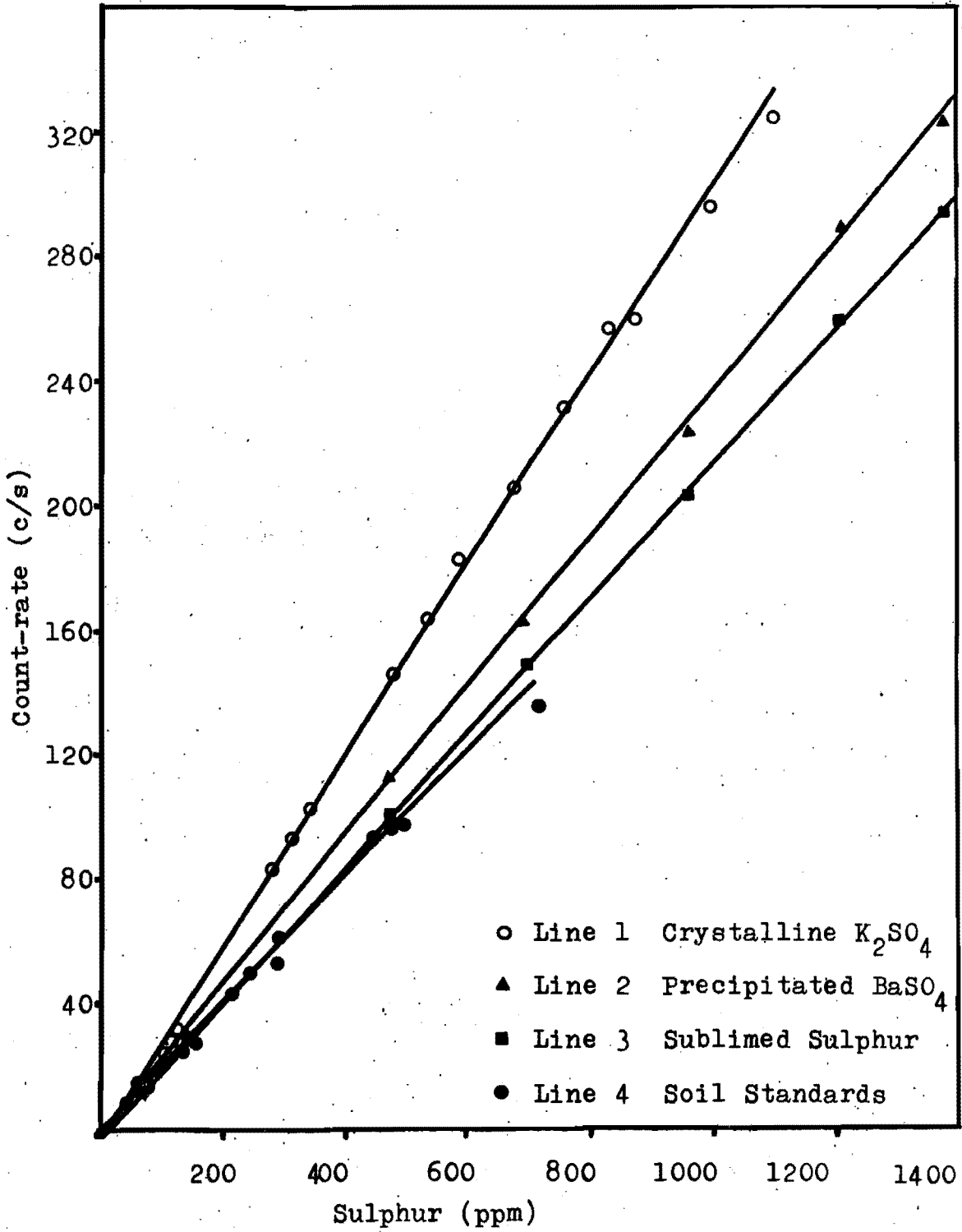
precipitation. The line for sublimed sulphur best approaches the gradient of the unspiked samples.

The obvious result is that one must spike in such a way as to approximate the natural distribution of sulphur in the soil, which is most likely to be atoms scattered uniformly throughout the finer fraction of soil material. More important is the observation that the gradients of the spiked samples indicate that not all of the sulphur is being detected all the time by the routine chemical setup, with many chemical values being well above the lines.

III. CALIBRATION DATA

The following three pages of computer printout (Table VI) summarise the best calibration available. The counting data are included in Appendix 2. The samples are 5 soils spiked with sublimed sulphur and 13 samples originally used to set up the chemical procedure. To be noted from the printout: (a) The magnitude of B (beta) which agrees exactly with the theoretical mass absorption correction. (b) The low third order coefficients. (c) The samples include the spiked soils which lie on a straight line anyway, so that the actual improvement in sums of residuals and correlation of the other unspiked soils is masked. (d) When unspiked soils only are used for calibration the differences as recorded in Table VIb are much smaller because there are not two slightly differing gradients involved.

TABLE VIa

X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM A   DETERMINATION OF EQUATION PARAMETERS

REGRESSION ANALYSIS

NET C/S VS CONC

GRADIENT ((C/S)/PPM)	0.216819 + 0.002959	(1.36)
INTERCEPT (C/S)	0.368 + 1.726	(*****)
CORRELATION COEFFICIENT	0.998514	
SUM OF RESIDUALS SQUARED	392.2	

INITIALISATION OF ITERATION

WEIGHTED 1/(LOSS ON HEATING)**4

GRADIENT ((C/S)/PPM)	0.201643 + 0.004358	(2.16)
INTERCEPT (C/S)	2.566 + 1.260	(49.13)
CORRELATION COEFFICIENT	0.996284	
SUM OF RESIDUALS SQUARED	7.4	

APPROXIMATION 1/1

ALPHA	0.98312 + 0.0015	(0.16)
BETA	-0.00727 + 0.00018	(2.48)
GRADIENT ((C/S)/PPM)	0.200136 + 0.002190	(1.09)
INTERCEPT (C/S)	0.740 + 1.278	(*****)
CORRELATION COEFFICIENT	0.999042	
SUM OF RESIDUALS SQUARED	214.9	

APPROXIMATION 1/2

ALPHA	0.99059 + 0.0016	(0.16)
BETA	-0.00733 + 0.00018	(2.50)
GRADIENT ((C/S)/PPM)	0.201641 + 0.002207	(1.09)
INTERCEPT (C/S)	0.746 + 1.287	(*****)

TABLE VIa Cont

CORRELATION COEFFICIENT   0.999043
SUM OF RESIDUALS SQUARED   218.2
NEW GRADIENT   0.203557

APPROXIMATION 2/1
ALPHA   0.99268 +   0.0016 (0.16)
BETA   -0.00735 +   0.00018(2.51)
GRADIENT ((C/S)/PPM)   0.202052 + 0.002211 (1.09)
INTERCEPT (C/S)   0.748   + 1.290   (*****)
CORRELATION COEFFICIENT   0.999042
SUM OF RESIDUALS SQUARED   219.0

APPROXIMATION 2/2
ALPHA   0.99992 +   0.0016 (0.16)
BETA   -0.00740 +   0.00018(2.53)
GRADIENT ((C/S)/PPM)   0.203539 + 0.002228 (1.09)
INTERCEPT (C/S)   0.753   + 1.299   (*****)
CORRELATION COEFFICIENT   0.999042
SUM OF RESIDUALS SQUARED   222.3

SECOND ORDER COEFFICIENTS

A (C/S)   3.6665   + 1.7149 (46.77)
B ((C/S)/PPM)   0.187657 + 0.007189(3.83)
C ((C/S)(C/S)/PPM)   0.000011 + 0.000005(43.52)
INDEX OF CORRELATION   0.999291
SUM OF RESIDUALS SQUARED   164.4

LINEAR COEFFICIENTS

GRADIENT (PPM/(C/S))   4.913 +   0.053 (1.09)
INTERCEPT (PPM)   -3.701 +   6.386 (*****)

TABLE VIb

PROGRAM A   DETERMINATION OF EQUATION PARAMETERS

SIMULATED AND CHEMICAL CONTENT	COMPUTED PPM			CHEM	DIFF
MIXTURE OF 7 SOILS	421.2 +	9.6(	2.28)	440	-1.94
SPIKED MIXTURE 1	672.2 +	12.8(	1.91)	695	-1.77
SPIKED MIXTURE 2	928.3 +	16.0(	1.73)	949	-1.28
SPIKED MIXTURE 3	1213.6 +	19.8(	1.63)	1207	0.33
SPIKED MIXTURE 4	1477.1 +	23.6(	1.59)	1456	0.89
RANGIORA SILT CLAY LOAM A HOR	468.7 +	10.5(	2.26)	447	2.05
RANGIORA SILT CLAY LOAM B HOR	282.7 +	8.1(	2.89)	282	0.09
RANGIORA ROCK (WEATHERED 4M)	236.7 +	8.0(	3.40)	281	-5.48
RANGIORA ROCK (WEATHERED 11M)	132.0 +	7.1(	5.42)	126	0.84
RANGIORA ROCK (WEATHERED 17M)	92.9 +	7.1(	7.70)	69	3.34
RED WEATHERED ARGILLITE	227.4 +	8.2(	3.62)	238	-1.28
FRESH SANDWACKE (1) 16M	476.8 +	9.8(	2.05)	471	0.59
FRESH SANDWACKE (2) 9M	196.8 +	7.6(	3.86)	205	-1.06
SILTY ARGILLITE (SOIL A HOR)	138.0 +	7.6(	5.54)	134	0.52
SILTY ARGILLITE 2.5M	132.3 +	7.6(	5.76)	124	1.08
SILTY ARGILLITE 5.5M	89.2 +	7.4(	8.31)	79	1.38
SILTY ARGILLITE (FRESH)	488.2 +	9.9(	2.04)	481	0.72
ARGILLITE (SOIL 75CM)	65.0 +	7.3(	11.25)	56	1.23

MEAN OF DIFFERENCES   0.0161
STANDARD DEVIATION   1.9446

TO REPEAT HXRAY PUSH PROGRAM START
OTHERWISE PUSH INT REQ

It was decided that for calibration purposes;

(a) The error value of B (beta) should be increased to the theoretical value of 5%.

(b) The line gradient should be that of the unspiked samples only and have an error of at least 3%, the theoretical variation.

Hence HXDAT, the file of parameters for use with unknown samples was loaded with these values and these values are the ones used in the following Chapter. Using this calibration produces a minimum error of ± 10 ppm or 4% whichever is greater. The parameters as used are listed at the beginning of Appendix 5.

CHAPTER VII

TOTAL SULPHUR IN THE REEFTON CHRONOSEQUENCE SOILS

Several studies on a chronosequence of terrace soils near Reefton have been completed or are in progress within the Soil Science Department at Lincoln College. The concepts of chrono-sequence studies, the history of the terraces and description of the soils found on them are already documented (e.g. Tan 1971, A.S. Campbell in preparation). This chapter is devoted simply to reporting the values of total sulphur found in these soils, primarily as an example of the application of the X-ray fluorescence technique. The samples were taken at one site only for each soil and therefore before reliable conclusions can be drawn, much more work needs to be done.

The original results for the six main sequence sites are given in Appendix 5 as the program printout for program HXSUL. Included are four other sites from the Ahaura terrace which were taken on a transect a few meters long to establish the effect of beech vegetation on soil properties. The results are given again in Figure IX expressed as g/m^2 per constant depth (64 cm of profile) and as g/m^2 per constant weight (96 g/cm^2 of profile) so as to overcome differences in bulk densities.

Notable features of the results are:
(a) The build up and decline of total sulphur with increasing soil development.

FIGURE IX   71

SULPHUR IN THE REEFTON SOILS
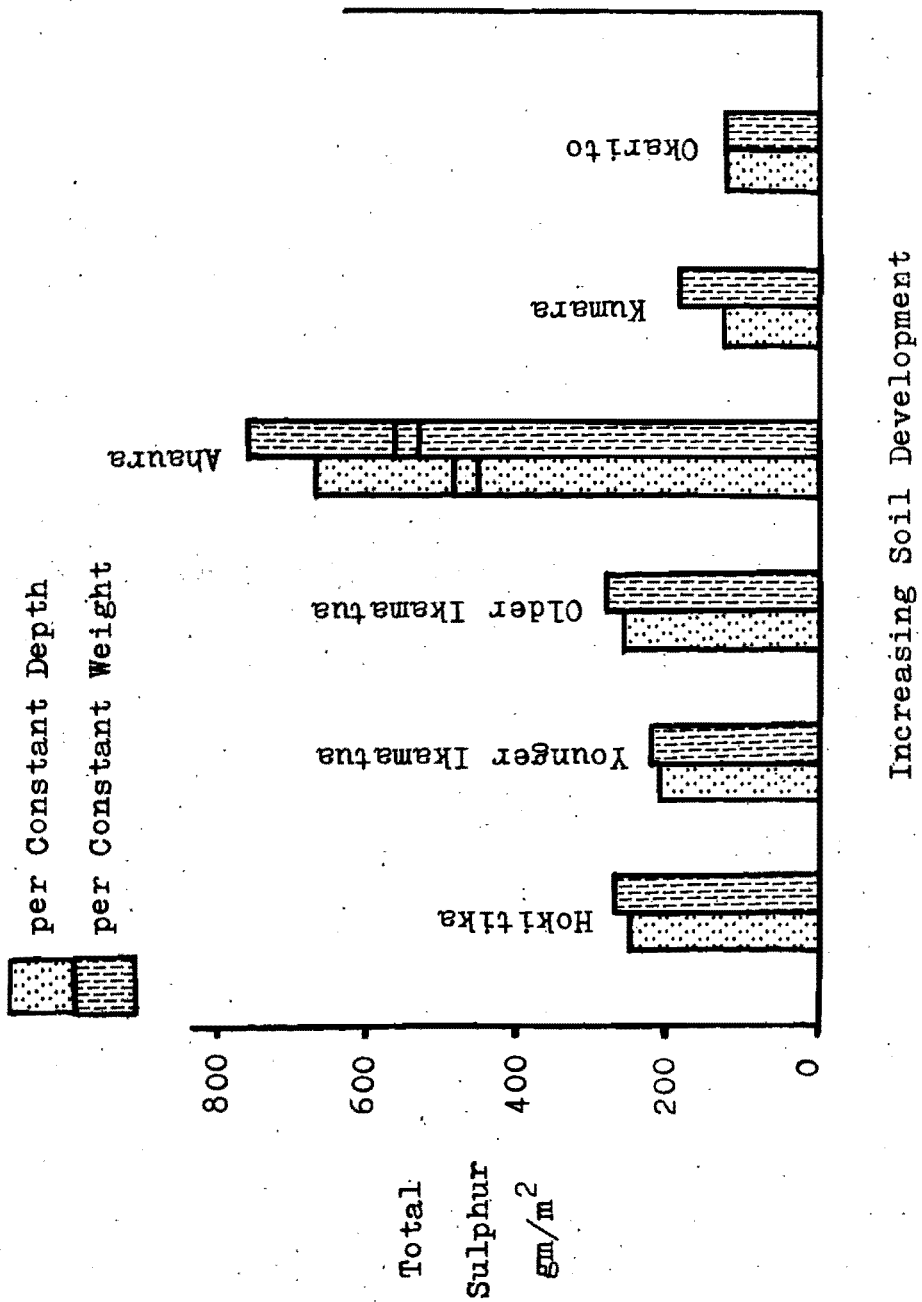
(b)   The slightly higher value for the Hokitika soil. It was observed that this site was under a grass cover whereas the others were under forest.

(c)   The very high value for the Ahaura soil.   Firstly this site was under an open canopy, but it must also be noted that the B horizon contains abnormally large amounts of sulphur.   A. S. Campbell (per comm) has found large amounts of amorphous material in some of these Ahaura sites and it would be interesting to know if this large value is associated with sulphate held by the amorphous constituent.

(d)   Also shown for the Ahaura terrace are the sulphur values for two sites a few meters from the first showing the variability of this surface.

Hence are raised several aspects of sulphur in the sequence of soils which would be well worth looking into, particularly if a rapid X-ray fluorescence method of analysing for sulphate alone could be developed.

CHAPTER VIII

SUMMARY

I. USE OF THE PROCEDURE

To use the procedure, the following steps need to be taken.
(a) Prepare the pelleted samples as outlined.   Time required,
about 3 minutes per pellet.

(b) Measure the fluorescence count-rate as outlined.   A novice
operator would require about a day to master the necessary equip-
ment techniques.   Time required, about 4 minutes depending on
the required accuracy and content.   Much of this time is spent
in waiting so there is ample time for documentation etc.

(c) Measure the weight loss of the sample on heating.   Time
required about 2 minutes for weighing on a batch basis.   In
many investigations this value is already required for other
purposes.

(d) Punch the data into cards as outlined in Appendix 3 and using
the appropiate program, obtain the sulphur content.   Total
computer time is only a matter of minutes for 80 samples.
Punching time depends very much on who does the punching.

Starting with a dry ground sample, total analysis time is
about 8 minutes per sample plus 2 minutes to determine weight
loss on heating.

Use of the analysis procedure requires no specialised knowledge of either computing or X-ray fluorescence.

II. GENERAL

(1) The analytical procedure described performs well and gives reasonable results.

(2) The reliance of X-ray fluorescence spectrometry upon good chemical analysis is emphasised as well as its usefulness in providing a clue to any chemical analysis difficulties. The rapidity of X-ray fluorescence spectrometry when compared with analytical chemistry makes perseverance with the method worthwhile.

(3) Aspects of the X-ray method which should be investigated further to ensure reliability are: (a) the effect of properties and distribution of organic material within a soil, particularly that of the particle size of organic matter. (b) measurement of the local absorption effect of organic material.

(4) Because X-ray analyses can be only as good as standards, an alternative chemical procedure should be set up to measure a few samples very accurately.

(5) The use of the computer greatly relieves the tedium of mathematical calculations. The mass absorption coefficient

calculations can be checked and even with the present data it can be seen that the measured values are reasonably close to the theoretical.

(6) Coupled with some well analysed plant material as standards, the method as outlined can be adapted easily to analyse the complete range from all plant material to all mineral soil.

(7) By leaching sulphate from the soil, it may also be possible to develop a similiar X-ray fluorescence method to measure sulphate alone using a repeat analysis. However as this depends on a difference value, the accuracy of chemical standards and X-ray absorption must come under extra scrutiny.

ACKNOWLEDGEMENTS

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APPENDIX I

FORTRAN PROGRAM LISTINGS

PAGE   1

// JOB

LOG DRIVE   CART SPEC   CART AVAIL   PHY DRIVE
  0000   0060   0060   0000

V2 M11   ACTUAL 16K   CONFIG 16K

// DUP

*DELETE   HXRAY
CART ID 0060   DB ADDR 1F10   DB CNT   008E

// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*IOCS(1132PRINTER)
*IOCS(CARD)
*IOCS(DISK)
*IOCS(TYPEWRITER)


```
C       PROGRAM HXRAY ANALYSES SULPHUR X-RAY FLUORESCENCE DATA
C       FROM SAMPLES OF KNOWN CONTENT TO FIND EQUATION
C       PARAMETERS TO APPLY TO UNKNOWN SAMPLES

        REAL L(40)
        DIMENSION NAME(15,40),INAME(15),S(40),R(40),E(40),A(40)
        DIMENSION B(40),F(9)
        COMMON NUM
        DEFINE FILE 1(10,3,U,NEXT)
        EQUIVALENCE(F(1),ALPHA),(F(2),EX),(F(3),BETA),(F(4),EY)
        EQUIVALENCE (F(5),GRAD),(F(6),EG),(F(7),CEPT),(F(8),EC)
        EQUIVALENCE (F(9),STD)
    2   STD=-1.0
        NUM=0
        NREF=0
        WRITE(3,27)
   27   FORMAT('1X-RAY FLUORESCENCE SULPHUR ANALYSIS',/,
       136('-'),/,
       2'OPROGRAM A      DETERMINATION OF EQUATION PARAMETERS',
       3/10('-'))
        WRITE(3,70)
   70   FORMAT('0COUNTING DATA',23X,'PEAK       BACKGROUND',/,
       114('-'),23X,'----',6X,10('-'),/33X,
       2'COUNTS TIME  COUNTS TIME    P/B',/,33X,11('-'),2X,
       311('-'),'    ---')

C       READ COUNTING DATA ONE CARD AT A TIME

   24   READ(2,3)ICODE,PEAK,TIME,BACK,SEC,ORGAN,SULP,INAME
    3   FORMAT(I1,F9.0,F5.0,F10.0,F5.0,F10.1,F9.0,1X,15A2)
        SEC=SEC+1.E-2
        BACK=BACK+1.E-6
        GO TO(6,6,98),ICODE

C       CALCULATE COUNTRATE
```

```
PAGE   2
     6 CP=PEAK/TIME
       CB=BACK/SEC
       CP=CP/(1.0-CP*2.E-6)
       CB=CB/(1.0-CB*2.E-6)
       COUNT=CP-CB
       FIG=(CP/CB)**0.5*SEC/TIME
       PLUS=(CP/TIME+CB/SEC)**0.5
       GO TO(10,11),ICODE
C      DATA CARD IS REFERENCE CARD
    11 NBAT=0
       NREF=NREF+1
       IF(STD)12,12,13
    12 STD=COUNT
       NSEC=1
       WRITE(3,23)INAME,COUNT,NSEC
       GO TO 24
    13 FAC=COUNT/STD
       FACER=PLUS/STD
       PFAC=(COUNT-STD)/STD*100.0
       WRITE(3,16)PFAC
    16 FORMAT('ODRIFT FACTOR (PERCENT) ',F7.3)
       GO TO 24
C      DATA CARD IS SAMPLE CARD
    10 NBAT=NBAT+1
       NUM=NUM+1
       IF(NREF-2)34,35,35
    34 WRITE(3,36)
    36 FORMAT('OINITIAL REFERENCE CARD MISSING')
       GO TO 99
    35 IF(NBAT-3)20,20,21
    21 WRITE(3,22)
    22 FORMAT('OMORE THAN 4 SAMPLES PER BATCH')
       GO TO 99
    20 IF(NUM-40)30,30,32
    32 WRITE(3,33)
    33 FORMAT('OSTORAGE LIMIT OF 40 SAMPLES')
       NUM=40
       GO TO 98
    30 PLUS=(PLUS/FAC*PLUS/FAC+(COUNT/FAC*FACER/FAC)**2)**0.5
       COUNT=COUNT/FAC
       DO 31 I=1,15
    31 NAME(I,NUM)=INAME(I)
       R(NUM)=COUNT
       E(NUM)=PLUS
       L(NUM)=ORGAN
       S(NUM)=SULP
       A(NUM)=1.0
       B(NUM)=1.0/ORGAN**4
       NTIME=IFIX(TIME)
       NSEC=IFIX(SEC)
       WRITE(3,23)INAME,PEAK,NTIME,BACK,NSEC,FIG
    23 FORMAT('0',15A2,F9.0,I4,F8.0,I4,3X,F4.2)
       GO TO 24
```

PAGE   3
```
C       PRINT COUNTRATES

   98 WRITE(3,27)
      WRITE(3,71)
   71 FORMAT('OANALYSIS DATA',19X,
     1'NET C/S      ERROR  LOSS  PPM',/14('-'),19X,
     219('-'),'  ----   ---')
      DO 72 I=1,NUM
      COUNT=R(I)
      PLUS=E(I)
      ORGAN=L(I)
      NSEC=IFIX(S(I))
      DEV=PLUS*100.0/COUNT
   72 WRITE(3,73)(NAME(J,I),J=1,15),COUNT,PLUS,DEV,ORGAN,NSEC
   73 FORMAT('0',15A2,F7.2,' +',F5.2,'(',F5.2,')',F6.1,I5)
      IF(NUM-3)57,58,58
   57 WRITE(3,59)
   59 FORMAT('0INSUFFICIENT NUMBER OF SAMPLES')
      GO TO 99
   58 WRITE(3,27)
      WRITE(3,1)
    1 FORMAT('0REGRESSION ANALYSIS',/,20('-'),/,/,
     1'0NET C/S VS CONC',/,16('-'))
      CALL HXREG(A,R,S,GRAD,EG,CEPT,EC)

C       INITIALISE ITERATION CYCLE
C       DATA SWITCH ZERO UP ON CONSOLE PUTS BETA = -0.74

      WRITE(1,60)
   60 FORMAT(' CHECK SWITCH ZERO, UP FOR BETA = -0.74',/,
     1' PUSH PROGRAM START')
      PAUSE
      CALL DATSW(0,NONE)
      GO TO (51,52),NONE
   51 ALPHA=1.0
      EX=0.001
      BETA=-0.0074
      EY=0.00037
      WRITE(3,53)
   53 FORMAT('0ALPHA = 1.0   BETA = -0.00740 + 0.00037 (5.0)')
      GO TO 54
   52 WRITE(3,9)
    9 FORMAT(/'0INITIALISATION OF ITERATION',/28('-'),
     1/'0WEIGHTED 1/(LOSS ON HEATING)**4')
      NREF=0
      CALL HXREG(B,R,S,BGRAD,BEG,CEPT,EC)
   47 GRAD=BGRAD
      EG=BEG
      NREF=NREF+1
      NBAT=0
      TOLL=BGRAD*5.0E-3

C       ITERATION CYCLE

    8 NBAT=NBAT+1
      WRITE(3,44)NREF,NBAT
   44 FORMAT(/'0APPROXIMATION ',I1,'/',I1)
      CEPT=0.0
```

```
       TGRAD=GRAD
       DO 18 I=1,NUM
       A(I)=(GRAD*S(I)+CEPT)/R(I)
       B(I)=(S(I)/R(I)*EG)**2+(A(I)/R(I)*E(I))**2+(EC/R(I))**2
   18  B(I)=1.0/B(I)
       CALL HXLIN (L,A,B,ALPHA,EX,BETA,EY)
   54  DO 41 I=1,NUM
       B(I)=R(I)*(ALPHA+BETA*L(I))
   41  A(I)=1.0
       CALL HXREG(A,B,S,GRAD,EG,CEPT,EC)
       GO TO (45,55),NONE
   55  IF(BGRAD-GRAD-TOLL)14,14,15
   14  IF(BGRAD-GRAD+TOLL)15,66,66
   15  GRAD=TGRAD+BGRAD-GRAD
       EG=GRAD*BEG/BGRAD
       GO TO 8

C   CHECK VALUE OF ALPHA

   66  IF(ALPHA-1.001)43,43,46
   43  IF(ALPHA-0.999)46,45,45
   46  BGRAD=BGRAD/ALPHA
       BEG=BEG/ALPHA
       WRITE(3,48)BGRAD
   48  FORMAT('ONEW GRADIENT ',F15.6)
       GO TO 47

C   CHECK LINEARITY OF REGRESSION

   45  CALL HXCUB(B,S)

C   BACK SUBSTITUTE PARAMETERS TO ORIGINAL DATA

       EGG=EG/GRAD/GRAD
       ECC=((EC/GRAD)**2+EGG*EGG)**0.5
       CEPTT=-CEPT/GRAD
       GRADD=1.0/GRAD
       DEV=100.0*EGG/GRADD
       FIG=100.0*ECC/CEPTT
       IF(FIG)77,78,78
   77  FIG=-FIG
   78  WRITE(3,75)
   75  FORMAT(/,/'OLINEAR COEFFICIENTS',/20('-'))
       WRITE(3,76)GRADD,EGG,DEV,CEPTT,ECC,FIG
   76  FORMAT('OGRADIENT (PPM/(C/S)) ',F10.3,' + ',F7.3,' (',
      1F5.2,')',/'OINTERCEPT (PPM) ',F15.3,' + ',F7.3,' (',
      2F5.2,')')
       WRITE(3,27)
       WRITE(3,40)
   40  FORMAT('OCORRECTED COUNT RATES',12X,
      1'CORRECTED C/S    ERROR      PPM',/22('-'),12X,21('-'),
      2'   ---')

C   CALCULATE AND PRINT CORRECTED COUNTRATES

       DO 74 I=1,NUM
       NSEC=IFIX(S(I))
       A(I)=ALPHA+BETA*L(I)
```

```
PAGE    5
        ER=((R(I)*(EX+L(I)*EY))**2+(E(I)*A(I))**2)**0.5
        ERROR=100.0*ER/B(I)
     74 WRITE(3,50)(NAME(J,I),J=1,15),B(I),ER,ERROR,NSEC
     50 FORMAT('0',15A2,F8.2,' + ',F5.2,' (',F5.2,')',I7)
        WRITE(3,27)
        WRITE(3,91)
     91 FORMAT('0SIMULATED AND CHEMICAL CONTENT',5X,
       1'COMPUTED PPM    CHEM  DIFF',/31('-'),5X,12('-'),
        25X,'----  ----')

C       CALCULATE AND PRINT SIMULATED CONCENTRATIONS

        SUM=0.0
        EG=EGG
        EC=ECC
        CEPT=CEPTT
        GRAD=GRADD
        DO 93 I=1,NUM
        SULP=GRAD*B(I)+CEPT
        ERROR=A(I)*EG+GRAD*(EX+L(I)*EY)
        ERROR=((E(I)*GRAD*A(I))**2+(R(I)*ERROR)**2+EC*EC)**0.5
        DEV=100.0*ERROR/SULP
        CORR=(SULP-S(I))/ERROR
        NSEC=IFIX(S(I))
        SUM=SUM+CORR
        B(I)=CORR
     93 WRITE(3,92)(NAME(J,I),J=1,15),SULP,ERROR,DEV,NSEC,CORR
     92 FORMAT('0',15A2,F7.1,' + ',F4.1,'(',F5.2,')',I5,F6.2)
        AVER=SUM/NUM
        SUM=0.0
        DO 94 I=1,NUM
     94 SUM=SUM+(AVER-B(I))**2
        SUM=(SUM/(NUM-1))**0.5
        WRITE(3,95)AVER,SUM
     95 FORMAT(/,/'0MEAN OF DIFFERENCES',F8.4,/,
       1'0STANDARD DEVIATION',F9.4)

C       STORE PARAMETERS ON DISK FILE

        WRITE(1'1)F
     99 WRITE(3,79)
     79 FORMAT(/,/'0TO REPEAT HXRAY PUSH PROGRAM START',/,
       1'0OTHERWISE PUSH INT REQ')
        PAUSE
        GO TO 2
        END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CORE REQUIREMENTS FOR
 COMMON      2  VARIABLES    1194  PROGRAM    2050

END OF COMPILATION

// DUP
```

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*STORE   WS   UA   HXRAY
CART ID 0060   DB ADDR   1FE1   DB CNT   008E

*DELETE   HXREG
CART ID 0060   DB ADDR   1F10   DB CNT   0022

```
// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS


C        SUBROUTINE HXREG PREFORMS A LINEAR REGRESSION OF R ON S
C        ACCORDING TO THE EQUATION   R = GRAD*S + CEPT   WHERE
C        ARRAY S IS CHEMICAL SULPHUR CONTENT TAKEN AS ACCURATE
C        ARRAY R IS FLUORESCENCE COUNTRATE
C        ARRAY A IS WEIGHT ASSIGNED TO EACH PAIR OF (S,R)

         SUBROUTINE HXREG(A,R,S,GRAD,EG,CEPT,EC)
         DIMENSION A(1),R(1),S(1)
         COMMON NUM

         W=0.0
         WX=0.0
         WY=0.0
         WXX=0.0
         WXY=0.0
         WYY=0.0
         WDD=0.0
         DO 2 I=1,NUM
         W=W+A(I)
         WY=WY+A(I)*R(I)
         WX=WX+A(I)*S(I)
         WYY=WYY+A(I)*R(I)*R(I)
         WXY=WXY+A(I)*R(I)*S(I)
     2   WXX=WXX+S(I)*S(I)*A(I)
         DELTA=W*WXX-WX*WX
         GRAD=(W*WXY-WX*WY)/DELTA
         CEPT=(WY*WXX-WX*WXY)/DELTA
         DO 4 I=1,NUM
         D= GRAD*S(I)+CEPT-R(I)
     4   WDD=WDD+A(I)*D*D
         SUM=WDD
         WDD=WDD/(NUM-2)
         EG =(W*WDD/DELTA)**0.5
         EC =(WXX*WDD/DELTA)**0.5
         CORR=((WXX-WX*WX/W)*(WYY-WY*WY/W))**0.5
         CORR=(WXY-WX*WY/W)/CORR
         WX=EG*100.0/GRAD
         WY=EC*100.0/CEPT
         IF(WY)60,61,61
    60   WY=-WY
    61   WRITE(3,5)GRAD,EG,WX,CEPT,EC,WY,CORR,SUM
     5   FORMAT('0GRADIENT ((C/S)/PPM) ',F13.6 ' + ' F8.6 ' (',
        1F5.2,')',/'0INTERCEPT (C/S) ',F15.3,4X,'+',F6.3,4X,'(',
        2F5.2,')',/,'0CORRELATION COEFFICIENT ',F10.6,
        3/'0SUM OF RESIDUALS SQUARED',F10.1)
         RETURN
         END
```

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FEATURES SUPPORTED
 ONE WORD INTEGERS

CORE REQUIREMENTS FOR HXREG
  COMMON   2   VARIABLES   26   PROGRAM   442

RELATIVE ENTRY POINT ADDRESS IS 0070 (HEX)

END OF COMPILATION

// DUP

*STORE   WS UA HXREG
CART ID 0060   DB ADDR 204D   DB CNT   0022

*DELETE   HXLIN
CART ID 0060   DB ADDR 1F10   DB CNT   0019

// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS


```
C     SUBROUTINE HXLIN SOLVES THE LINEAR EQUATIONS GIVEN BY
C     ALPHA + BETA*L = A   WHERE
C     ARRAY L IS LOSS ON HEATING TAKEN AS ACCURATE
C     ARRAY A IS THE EQUATION CONSTANTS
C     ARRAY B IS WEIGHT ASSIGNED TO EACH EQUATION

      SUBROUTINE HXLIN (L,A,B,ALPHA,EX,BETA,EY)
      REAL L(1)
      DIMENSION A(1),B(1)
      COMMON NUM

      AA=0.0
      BB=0.0
      AB=0.0
      AK=0.0
      BK=0.0
      DD=0.0
      DO 51 I=1,NUM
      AA=AA+B(I)
      BB=BB+L(I)*L(I)*B(I)
      AB=AB+L(I)*B(I)
      AK=AK+A(I)*B(I)
   51 BK=BK+L(I)*A(I)*B(I)
      DELTA=AA*BB-AB*AB
      ALPHA=(AK*BB-BK*AB)/DELTA
      BETA=(AA*BK-AB*AK)/DELTA
      DO 52 I=1,NUM
   52 DD=DD+(ALPHA+BETA*L(I)-A(I))**2
      DD=DD/(NUM-2)
      EX=(BB*DD/DELTA)**0.5
      EY=(AA*DD/DELTA)**0.5
      AA=EX*100.0/ALPHA
      BB=EY*100.0/BETA
      IF(BB)62,63,63
```

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```
   62 BB=-BB
   63 WRITE(3,53)ALPHA,EX,AA,BETA,EY,BB
   53 FORMAT('0ALPHA',18X,F10.5,'   + ',F8.4,' (',F5.2,')',/,
      1'0BETA',17X,F12.5,'   + ',F9.5,'(',F5.2,')')
      RETURN
      END
```

FEATURES SUPPORTED
 ONE WORD INTEGERS

CORE REQUIREMENTS FOR HXLIN
  COMMON   2 VARIABLES   18   PROGRAM   324

RELATIVE ENTRY POINT ADDRESS IS 003B (HEX)

END OF COMPILATION

// DUP

*STORE   WS   UA   HXLIN
CART ID 0060   DB ADDR 2056   DB CNT   0019

*DELETE   HXCUB
CART ID 0060   DB ADDR 1F10   DB CNT   0039

// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS


```
C     SUBROUTINE HXCUB FITS A CUBIC TO THE VALUES OF R AND S
C     ARRAY S IS CHEMICAL SULPHUR CONTENT TAKEN AS ACCURATE
C     ARRAY R IS FLUORESCENCE COUNTRATE

      SUBROUTINE HXCUB(R,S)
      DIMENSION R(1),S(1)
      COMMON NUM

      X=0.0
      XX=0.0
      XXX=0.0
      XXXX=0.0
      XY=0.0
      XXY=0.0
      Y=0.0
      YY=0.0
      DD=0.0
      DO 43 I=1,NUM
      X=X+S(I)
      XX=XX+S(I)**2
      XXX=XXX+S(I)**3
      XXXX=XXXX+S(I)**4
      Y=Y+R(I)
      YY=YY+R(I)**2
      XY=XY+S(I)*R(I)
   43 XXY=XXY+S(I)*S(I)*R(I)
      DELTA=NUM*(XX*XXXX-XXX*XXX)-X*(X*XXXX-XXX*XX)+XX*(X*XXX
      1-XX*XX)
```

```
      AA= Y*(XX*XXXX-XXX*XXX)-XY*(X*XXXX-XXX*XX)+XXY*(X*XXX
     1-XX*XX)
      AA=AA/DELTA
      BB= NUM*(XY*XXXX-XXY*XXX)-X*(Y*XXXX-XXY*XX)+XX*(Y*XXX
     1-XY*XX)
      BB=BB/DELTA
      CC= NUM*(XX*XXY-XXX*XY)-X*(X*XXY-XXX*Y)+XX*(X*XY-XX*Y)
      CC=CC/DELTA
      DO 44 I=1,NUM
   44 DD=DD+(AA+BB*S(I)+CC*S(I)*S(I)-R(I))**2
      SUM=DD
      DDD=DD/NUM
      DD=DD/(NUM-3)
      AAE=((XX*XXXX-XXX*XXX)*DD/DELTA)**0.5
      BBE=((NUM*XXXX-XX*XX)*DD/DELTA)**0.5
      CCE=((NUM*XX-X*X)*DD/DELTA)**0.5
      SS=(YY-Y*Y/NUM)/NUM
      CORR=(1.0-DDD/SS)**0.5
      X=AAE*100.0/AA
      XX=BBE*100.0/BB
      XXX=CCE*100.0/CC
      WRITE(3,45)AA,AAE,X,BB,BBE,XX,CC,CCE,XXX,CORR,SUM
   45 FORMAT(/,/,'0SECOND ORDER COEFFICIENTS',/26('-')
     1/'0A (C/S)',15X,F10.4,  '    +',F8.4,   '   (',F6.2,')',
     2/'0B ((C/S)/PPM)',9X,F12.6,  '  +',F10.6,    '(',F6.2,')',
     3/'0C ((C/S)(C/S)/PPM)',F16.6,  '  +',F10.6,'(',F6.2,')',
     4/'0INDEX OF CORRELATION',F14.6,
     5/'0SUM OF RESIDUALS SQUARED',F10.1)
      RETURN
      END
```

FEATURES SUPPORTED
 ONE WORD INTEGERS

CORE REQUIREMENTS FOR HXCUB
 COMMON   2 VARIABLES   54 PROGRAM   726

RELATIVE ENTRY POINT ADDRESS IS 00B0 (HEX)

END OF COMPILATION

// DUP

*STORE   WS UA HXCUB
CART ID 0060   DB ADDR 2036   DB CNT   0039

*DELETE   HXSUL
CART ID 0060   DB ADDR 1F10   DB CNT   005D

// FOR
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*IOCS(1132PRINTER)
*IOCS(CARD)
*IOCS(DISK)

```
C     PROGRAM HXSUL CALCULATES UNKNOWN SULPHUR CONCENTRATIONS
C     ACCORDING TO THE EQUATION
C     S=GRAD*(ALPHA+BETA*L)*R+CEPT

      REAL L(50)
      DIMENSION NAME(15,50),INAME(15),R(50),E(50),F(9)
      DEFINE FILE 1(10,3,U,NEXT)
      EQUIVALENCE(F(1),ALPHA),(F(2),EX),(F(3),BETA),(F(4),EY)
      EQUIVALENCE(F(5),GRAD),(F(6),EG),(F(7),CEPT),(F(8),EC)
      EQUIVALENCE(F(9),STD)

   2  NUM=0
      NREF=0
      WRITE(3,27)
  27  FORMAT('1X-RAY FLUORESCENCE SULPHUR ANALYSIS',/36('-'),
     1/'0PROGRAM B   EVALUATION OF UNKNOWN CONCENTRATIONS',
     2/10('-'))
      WRITE(3,1)
   1  FORMAT('0PARAMETERS USED',/16('-'))

C     READ PARAMETERS FROM DISK FILE

      READ(1'1)F
      CB=100.0*EX/ALPHA
      CP=100.0*EY/BETA
      IF(CP)60,61,61
  60  CP=-CP
  61  WRITE(3,8)ALPHA,EX,CB,BETA,EY,CP
   8  FORMAT('0ALPHA',F28.4,'   +',F8.4,'  (',F5.2,')',
     1/'0BETA',F31.6,'  +',F10.6,'  (',F5.2,')')
      CB=100.0*EG/GRAD
      CP=100.0*EC/CEPT
      IF(CP)62,63,63
  62  CP=-CP
  63  WRITE(3,4)GRAD,EG,CB,CEPT,EC,CP,STD
   4  FORMAT('0GRADIENT (PPM/(C/S))',F13.4,'   +',F8.4,
     1'   (',F5.2,')',/'0INTERCEPT (PPM)',F17.3,'    +',
     2F8.3,'   (',F5.2,')',/'0REFERENCE COUNTRATE',F12.2,/)
      WRITE(3,70)
  70  FORMAT('0COUNTING DATA',23X,'PEAK        BACKGROUND',/,
     114('-'),23X,'----',6X,10('-'),/33X,
     2'COUNTS TIME   COUNTS TIME    P/B',/33X,11('-'),2X,
     311('-'),'    ---')
      STD=-1.0

C     READ COUNTING DATA ONE CARD AT A TIME

  24  READ(2,3)ICODE,PEAK,TIME,BACK,SEC,ORGAN,INAME
   3  FORMAT(I1,F9.0,F5.0,F10.0,F5.0,F10.1,10X,15A2)
      BACK=BACK+1.E-6
      SEC=SEC+1.E-2
      GO TO(6,6,98),ICODE

C     CALCULATE COUNTRATE

   6  CP=PEAK/TIME
      CB=BACK/SEC
      CP=CP/(1.0-CP*2.E-6)
```

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```
      CB=CB/(1.0-CB*2.E-6)
      COUNT=CP-CB
      FIG=(CP/CB)**0.5*SEC/TIME
      PLUS=(CP/TIME+CB/SEC)**0.5
      GO TO(10,11),ICODE
C     DATA CARD IS REFERENCE CARD

   11 NBAT=0
      NREF=NREF+1
      IF(STD)12,12,13
   12 STD=COUNT
      NSEC=1
      WRITE(3,23)INAME,COUNT,NSEC
      GO TO 24
   13 FAC=COUNT/STD
      FACER=PLUS/STD
      PFAC=(COUNT-STD)/STD*100.0
      WRITE(3,16)PFAC
   16 FORMAT('ODRIFT FACTOR (PERCENT) ',F7.3)
      GO TO 24
C     DATA CARD IS SAMPLE CARD

   10 NBAT=NBAT+1
      NUM=NUM+1
      IF(NREF-2)34,35,35
   34 WRITE(3,36)
   36 FORMAT('OINITIAL REFERENCE CARD MISSING')
      GO TO 99
   35 IF(NBAT-3)20,20,21
   21 WRITE(3,22)
   22 FORMAT('OMORE THAN 4 SAMPLES PER BATCH')
      GO TO 99
   20 IF(NUM-50)30,30,32
   32 WRITE(3,33)
   33 FORMAT('OSTORAGE LIMIT OF 50 SAMPLES')
      NUM=50
      GO TO 98
   30 PLUS=(PLUS/FAC*PLUS/FAC+(COUNT/FAC*FACER/FAC)**2)**0.5
      COUNT=COUNT/FAC
      DO 31 I=1,15
   31 NAME(I,NUM)=INAME(I)
      R(NUM)=COUNT
      E(NUM)=PLUS
      L(NUM)=ORGAN
      NTIME=IFIX(TIME)
      NSEC=IFIX(SEC)
      WRITE(3,23)INAME,PEAK,NTIME,BACK,NSEC,FIG
   23 FORMAT('0',15A2,F9.0,I4,F8.0,I4,3X,F4.2)
      GO TO 24
C     PRINT MEASURED COUNTRATES

   98 WRITE(3,27)
      WRITE(3,71)
   71 FORMAT('OSAMPLE DATA',22X,'NET C/S',9X,'ERROR       LOSS',
     1/12('-'),22X,21('-'),4X,'----')
```

APPENDIX 2

HXRAY PRINTOUT

CONTAINING REFERENCE DATA

X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM A   DETERMINATION OF EQUATION PARAMETERS

| COUNTING DATA | PEAK | | BACKGROUND | | |
	COUNTS	TIME	COUNTS	TIME	P/B
BARIUM SULPHATE REFERENCE	19962.	1			
DRIFT FACTOR (PERCENT) 1.004					
MIXTURE OF 7 SOILS	27998.	240	2848.	120	1.10
DRIFT FACTOR (PERCENT) 1.219					
SPIKED MIXTURE 1	27916.	160	2111.	80	1.28
SPIKED MIXTURE 2	37089.	160	2210.	80	1.44
SPIKED MIXTURE 3	46926.	160	2130.	80	1.66
DRIFT FACTOR (PERCENT) 0.826					
SPIKED MIXTURE 4	56079.	160	2194.	80	1.78
DRIFT FACTOR (PERCENT) 0.104					
RANGIORA SILT CLAY LOAM A HOR	43312.	320	4070.	160	1.15
DRIFT FACTOR (PERCENT) 0.594					
RANGIORA SILT CLAY LOAM B HOR	27470.	320	3658.	160	0.96
DRIFT FACTOR (PERCENT) -0.444					
RANGIORA ROCK (WEATHERED 4M)	19059.	240	3256.	120	0.85
DRIFT FACTOR (PERCENT) -0.121					
RANGIORA ROCK (WEATHERED 11M)	16940.	320	3820.	160	0.74
DRIFT FACTOR (PERCENT) -0.126					
RANGIORA ROCK (WEATHERED 17M)	10466.	240	2850.	120	0.67
DRIFT FACTOR (PERCENT) 2.130					
RED WEATHERED ARGILLITE	12138.	160	2022.	80	0.86
DRIFT FACTOR (PERCENT) 1.369					
FRESH SANDWACKE (1) 16M	29739.	240	2849.	120	1.14
DRIFT FACTOR (PERCENT) 2.096					
FRESH SANDWACKE (2) 9M	15604.	240	2756.	120	0.84

```
DRIFT FACTOR (PERCENT)    0.975
SILTY ARGILLITE (SOIL A HOR)        8957. 160    1966.  80   0.75
DRIFT FACTOR (PERCENT)    0.729
SILTY ARGILLITE 2.5M                8617. 160    1958.  80   0.74
DRIFT FACTOR (PERCENT)    0.469
SILTY ARGILLITE 5.5M                7084. 160    1943.  80   0.67
DRIFT FACTOR (PERCENT)    0.804
SILTY ARGILLITE (FRESH)            30454. 240    2890. 120   1.14
DRIFT FACTOR (PERCENT)    1.259
ARGILLITE (SOIL 75CM)               6230. 160    1937.  80   0.63
```

X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM A   DETERMINATION OF EQUATION PARAMETERS

ANALYSIS DATA	NET C/S	ERROR	LOSS	PPM
MIXTURE OF 7 SOILS	92.02 + 0.82(	0.90)	8.1	440
SPIKED MIXTURE 1	146.36 + 1.20(	0.82)	8.1	695
SPIKED MIXTURE 2	201.82 + 1.37(	0.67)	8.1	949
SPIKED MIXTURE 3	263.62 + 1.52(	0.57)	8.1	1207
SPIKED MIXTURE 4	320.66 + 1.77(	0.55)	8.1	1456
RANGIORA SILT CLAY LOAM A HOR	109.83 + 0.77(	0.70)	16.8	447
RANGIORA SILT CLAY LOAM B HOR	62.62 + 0.64(	1.03)	9.3	282
RANGIORA ROCK (WEATHERED 4M)	52.52 + 0.75(	1.43)	9.2	281
RANGIORA ROCK (WEATHERED 11M)	29.10 + 0.56(	1.93)	6.8	126
RANGIORA ROCK (WEATHERED 17M)	19.88 + 0.61(	3.10)	1.4	69
RED WEATHERED ARGILLITE	49.54 + 0.87(	1.76)	6.8	238
FRESH SANDWACKE (1) 16M	98.84 + 0.85(	0.86)	1.4	471
FRESH SANDWACKE (2) 9M	41.19 + 0.66(	1.62)	1.2	205
SILTY ARGILLITE (SOIL A HOR)	31.11 + 0.80(	2.58)	9.8	134
SILTY ARGILLITE 2.5M	29.17 + 0.79(	2.73)	6.9	124
SILTY ARGILLITE 5.5M	19.89 + 0.75(	3.81)	6.6	79
SILTY ARGILLITE (FRESH)	102.02 + 0.86(	0.84)	2.5	481
ARGILLITE (SOIL 75CM)	14.54 + 0.73(	5.01)	5.2	56

X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM A   DETERMINATION OF EQUATION PARAMETERS

CORRECTED COUNT RATES	CORRECTED C/S	ERROR	PPM
MIXTURE OF 7 SOILS	86.50 + 0.83	(0.96)	440
SPIKED MIXTURE 1	137.57 + 1.22	(0.89)	695
SPIKED MIXTURE 2	189.70 + 1.43	(0.75)	949
SPIKED MIXTURE 3	247.78 + 1.66	(0.67)	1207
SPIKED MIXTURE 4	301.40 + 1.95	(0.64)	1456
RANGIORA SILT CLAY LOAM A HOR	96.16 + 0.86	(0.89)	447
RANGIORA SILT CLAY LOAM B HOR	58.30 + 0.63	(1.09)	282
RANGIORA ROCK (WEATHERED 4M)	48.94 + 0.72	(1.48)	281
RANGIORA ROCK (WEATHERED 11M)	27.63 + 0.54	(1.95)	126
RANGIORA ROCK (WEATHERED 17M)	19.68 + 0.61	(3.11)	69
RED WEATHERED ARGILLITE	47.04 + 0.84	(1.79)	238
FRESH SANDWACKE (1) 16M	97.81 + 0.86	(0.88)	471
FRESH SANDWACKE (2) 9M	40.82 + 0.66	(1.63)	205
SILTY ARGILLITE (SOIL A HOR)	28.85 + 0.75	(2.61)	134
SILTY ARGILLITE 2.5M	27.68 + 0.76	(2.75)	124
SILTY ARGILLITE 5.5M	18.92 + 0.72	(3.82)	79
SILTY ARGILLITE (FRESH)	100.12 + 0.87	(0.87)	481
ARGILLITE (SOIL 75CM)	13.98 + 0.70	(5.02)	56

APPENDIX 3

NOTES ON THE USE OF PROGRAMS

1. Card format for data cards.

(a) Col 1   Card identification number: 1 for sample,

2 for reference, 3 for last card

(b) Col 4-10 C_p Total quanta on peak

(c) Col 13-15 T_p Total time on peak (seconds)

(d) Col 19-25 C_b Total quanta on background

(e) Col 28-30 T_b Total time on background (seconds)

(f) Col 37-40   Percentage loss on heating (point in Col 39)

(g) Col 44-49   Chemical sulphur content (ppm)

(h) Col 51-80   Any sample identification, batch number etc.

Note that the use of a "program punch card" makes punching very

simple by automatically placing all numbers in their correct Cols.

2. Necessary infromation to be supplied on each card.

(i) Master count-rate card; a, b and c (from above).

(ii) Batch reference card; a, b and c.

(iii) Sample card; Standards a, b, c, f and g.

Unknowns a, b, c and f.

If no background count-rate d and e is supplied, the peak count

is taken as the sample count. The loss f may be zero.

3. Order of data cards in deck.

(1) Master count-rate reference card

(2) Batch reference card

(3) Sample card(s) Maximum of 3.

(4) Groups of (2) + (3) as required

(5) Last card with "3" in column 1.

An error message is printed if:

(a) The master count-rate card is not first.

(b) A sample card comes before a batch reference card.

(c) There are more than three sample cards following each batch reference card.

4. Program Capacities.

(a) HXRAY Maximum of 40 sample cards. (Could be expanded).

(b) HXSUL Maximum of 80 sample cards per run.

(c) Size of subprograms automatically adjusted.

An error message is printed in both programs if (i) More than the maximum allowable number of sample cards. (ii) In HXRAY, if less than 3 sample cards (minimum necessary to make sense of the analysis).

5. Core Loading.

The program HXRAY must have three subroutine subprograms, HXREG, HXLIN and HXCUB. The disk data file containing analysis parameters HXDAT must be referenced by a FILES record at each execution of HXRAY or HXSUL. Both HXRAY and HXSUL are re-cycled so as to be able to process a new series of data without having to reload the program.

APPENDIX 4

I. EQUATIONS USED IN PROGRAMS HXRAY AND HXSUL

1. Peak count-rate $R_p = C_p/T_p$ where C_p = total quanta detected on the peak position and T_p = total peak position counting time.

2. Background count-rate $R_b = C_b/T_b$ where C_b and T_b correspond to the above.

3. Correction for counter dead time (t), $R' = R/(1 - R.t)$ where t is specified as $2.(10^{-6})$ seconds.

4. Net count-rate $R_n = R_p' - R_b'$

5. Drift factor calculated as

    D = (batch reference count-rate)/(master count-rate).

6. Net count-rate corrected for drift $R = R_n/D$

7. The standard error in the un-corrected count-rate

$$s_R = \sqrt{R_p/T_p + R_b/T_b}$$

8. The standard error in the quotient $R = (R_n \pm s_R)/(D \pm s_D)$ is given by $s = \sqrt{s_R^2/D^2 + R_n^2.s_D^2/D^4}$

9. The coefficient of variation in a count-rate $e = 100.s/R_n$ %

10. The figure of merit for optimum counting time on peak and background positions is derived as follows. Optimum peak to background time ratio $= (R_p/R_b)^{\frac{1}{2}}$. Actual ratio is T_p/T_b. Therefore

$$1/Q^2 = (T_p^2/T_b^2)/(R_p/R_b). = (T_p^3.C_b)/(T_b^3.C_p)$$

$$Q = \sqrt{(T_b^3.C_p)/(T_p^3.C_b)} \qquad \text{using the values corrected}$$

for counter dead time.

II. EQUATIONS USED IN SUBROUTINE HXREG

A weighted linear regression of R on C for n points, with each (C_i, R_i) weighted w_i. Using the method of least squares such that, $\sum_i^n (m.C_i + c - R_i)^2$ is a minimum, then m and c are obtained from the simultaneous solution of the following two equations.

$$m. \sum_i^n (w_i.C_i^2) + c. \sum_i^n (w_i.C_i) = \sum_i^n (w_i.C_i.R_i)$$

$$m. \sum_i^n (w_i.C_i) + c. \sum_i^n (w_i) = \sum_i^n (w_i.R_i)$$

Denoting sums of products $\sum_i^n (w_i.C_i^2)$ as wCC etc., then,

$$m = \begin{vmatrix} wCR & wC \\ wR & w \end{vmatrix} \Big/ \begin{vmatrix} wCC & wC \\ wC & w \end{vmatrix} \quad \text{and} \quad c = \begin{vmatrix} wCC & wCR \\ wC & wR \end{vmatrix} \Big/ \begin{vmatrix} wCC & wC \\ wC & w \end{vmatrix}$$

If the residual for each pair of (C_i, R_i) is given as,

$d_i = m.C_i + c - R_i$ then denoting sums of products $\sum_i^n w_i.d_i^2$ as wdd etc., the mean square error in any expression,

$m.C_i + c - R_i$ is given by, $s = \sqrt{wdd/(n - 2)}$

The standard error in m, $s_m = \sqrt{w.s^2/D}$

The standard error in c, $s_c = \sqrt{wCC.s^2/D}$ where $D = \begin{vmatrix} w & wC \\ wC & wCC \end{vmatrix}$

The coefficient of correlation is given by $r = (wCR - wC.wR/w)/Z$

where $Z = \sqrt{(wCC - wC.wC/w).(wRR - wR.wR/w)}$

III. EQUATIONS USED IN SUBROUTINE HXLIN

To solve n linear equations $a_i.A + b_i.B = k_i$ where each equation is weighted w_i. However if each equation is multiplied by the square root of its weight then A and B are found by the

simultaneous solution of the following equations.

$$A. \sum_{i}^{n} (a_i^2) \quad + \quad B. \sum_{i}^{n} (a_i \cdot b_i) \quad = \quad \sum_{i}^{n} (a_i \cdot k_i)$$

$$A. \sum_{i}^{n} (a_i \cdot b_i) \quad + \quad B. \sum_{i}^{n} (b_i^2) \quad = \quad \sum_{i}^{n} (b_i \cdot k_i)$$

Denoting sums of products $\sum_{i}^{n} (a_i \cdot k_i)$ as ak etc., then,

$$A = \begin{vmatrix} ak & ab \\ bk & bb \end{vmatrix} \Big/ \begin{vmatrix} aa & ab \\ ab & bb \end{vmatrix} \quad \text{and} \quad B = \begin{vmatrix} aa & ak \\ ab & bk \end{vmatrix} \Big/ \begin{vmatrix} aa & ab \\ ab & bb \end{vmatrix}$$

If the residual for each equation is given as ,

$d_i = a_i \cdot A + b_i \cdot B - k_i$ then denoting sums of products $\sum_{i}^{n} (d_i^2)$

as dd etc., the standard error in any expression

$a_i \cdot A + b_i \cdot B - k_i$ is given by, $\quad s = \sqrt{dd/(n-2)}$

The standard error in A, $\quad s_A = \sqrt{bb \cdot s^2/D}$

The standard error in B, $\quad s_B = \sqrt{aa \cdot s^2/D}$ where $D = \begin{vmatrix} aa & ab \\ ab & bb \end{vmatrix}$

IV. EQUATIONS USED IN SUBROUTINE HXCUB

Quadratic regression of R on C of n points (C_i, R_i) using
the method of least squares such that,

$$\sum_{i}^{n} (a + b \cdot C_i + c \cdot C_i^2 - R_i)^2 \quad \text{is a minimum.} \quad \text{Then by}$$

considering simultaneous solutions of three linear equations (not
listed out) the coefficients are found as follows. Denoting
sums of products $\sum_{i}^{n} (C_i^2 \cdot R_i)$ as CCR etc., using the usual
vector notation, then a, b and c are given by the solution of,

$$\begin{vmatrix} a \\ b \\ c \end{vmatrix} \cdot \begin{vmatrix} n & C & CC \\ C & CC & CCC \\ CC & CCC & CCCC \end{vmatrix} = \begin{vmatrix} R \\ CR \\ CCR \end{vmatrix}$$

That is: $a = \begin{vmatrix} R & C & CC \\ CR & CC & CCC \\ CCR & CCC & CCCC \end{vmatrix} / D \qquad b = \begin{vmatrix} n & R & CC \\ C & CR & CCC \\ CC & CCR & CCCC \end{vmatrix} / D$

and $c = \begin{vmatrix} n & C & R \\ C & CC & CR \\ CC & CCC & CCR \end{vmatrix} / D \qquad$ where $D = \begin{vmatrix} n & C & CC \\ C & CC & CCC \\ CC & CCC & CCCC \end{vmatrix}$

If the residual for each pair of (C_i, R_i) is given as

$d_i = a + b.C_i + c.C_i^2 - R_i$ then denoting sums of products $\sum_i d_i^2$

as dd etc., the mean square error in any expression

$a + b.C_i + c.C_i^2 - R_i$ is given by $s = \sqrt{dd/(n-3)}$

The standard error in a, $\quad s_a = s^2.\sqrt{\begin{vmatrix} CC & CCC \\ CCC & CCCC \end{vmatrix} / D}$

The standard error in b, $\quad s_b = s^2.\sqrt{\begin{vmatrix} n & CC \\ CC & CCCC \end{vmatrix} / D}$

The standard error in c, $\quad s_c = s^2.\sqrt{\begin{vmatrix} n & C \\ C & CC \end{vmatrix} / D}$

The index of correlation $\quad r = \sqrt{1 - dd/(n.s_p^2)}$

where $\quad s_p = \sqrt{(RR - R.R/n)/n}$

APPENDIX 5

HXSUL PRINTOUT

OF REEFTON SOILS DATA

X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM B   EVALUATION OF UNKNOWN CONCENTRATIONS

PARAMETERS USED

ALPHA	1.0000	+ 0.0010	(0.09)
BETA	-0.007400	+ 0.000370	(5.00)
GRADIENT (PPM/(C/S))	4.9656	+ 0.1668	(3.35)
INTERCEPT (PPM)	-8.905	+ 9.195	(*****)
REFERENCE COUNTRATE	19962.35		

COUNTING DATA		PEAK		BACKGROUND		
		COUNTS	TIME	COUNTS	TIME	P/B
BARIUM SULPHATE REFERENCE		19962.	1			
DRIFT FACTOR (PERCENT)	0.080					
HOKITIKA A11		17215.	80	1095.	40	1.40
DRIFT FACTOR (PERCENT)	1.239					
HOKITIKA A12		10654.	80	919.	40	1.20
HOKITIKA C		3023.	80	899.	40	0.64
DRIFT FACTOR (PERCENT)	1.371					
IKAMATUA (YOUNGER) OA		85119.	80	1898.	40	2.37
DRIFT FACTOR (PERCENT)	1.264					
IKAMATUA (YOUNGER) A		12829.	80	1004.	40	1.26
DRIFT FACTOR (PERCENT)	1.325					
IKAMATUA (YOUNGER) AB		9271.	80	964.	40	1.09
DRIFT FACTOR (PERCENT)	1.079					
IKAMATUA (YOUNGER) B		7247.	80	993.	40	0.95
DRIFT FACTOR (PERCENT)	0.281					
IKAMATUA (YOUNGER) C		7220.	80	958.	40	0.97
DRIFT FACTOR (PERCENT)	1.229					
IKAMATUA (YOUNGER) DR		2419.	80	872.	40	0.58

```
DRIFT FACTOR (PERCENT)   -0.334
IKAMATUA (OLDER) OA                    37903.  80    1280.  40   1.92
IKAMATUA (OLDER) A                     17442.  80    1033.  40   1.45
DRIFT FACTOR (PERCENT)    1.325
IKAMATUA (OLDER) B2                    12009.  80     921.  40   1.27
DRIFT FACTOR (PERCENT)    0.710
IKAMATUA (OLDER) B3                    10307.  80    1002.  40   1.13
DRIFT FACTOR (PERCENT)    0.080
IKAMATUA (OLDER) C                      5815.  80     908.  40   0.89
DRIFT FACTOR (PERCENT)   -0.334
IKAMATUA (OLDER) DR                     3026.  80     904.  40   0.64
DRIFT FACTOR (PERCENT)    0.988
IKAMATUA (OLDER, PODSOL) A2            20367.  80    1230.  40   1.43
DRIFT FACTOR (PERCENT)    1.371
IKAMATUA (OLDER, WETTER) OA            35210.  80    1300.  40   1.84
DRIFT FACTOR (PERCENT)    1.326
IKAMATUA (OLDER, WETTER) A2H           17992.  80    1137.  40   1.40
DRIFT FACTOR (PERCENT)    1.229
IKAMATUA (OLDER, WETTER) A3BH          12827.  80    1076.  40   1.22
DRIFT FACTOR (PERCENT)    1.326
IKAMATUA (OLDER, WETTER) B2             5571.  80     925.  40   0.86
DRIFT FACTOR (PERCENT)    1.683
IKAMATUA (OLDER, WETTER) B3             5199.  80     939.  40   0.83
DRIFT FACTOR (PERCENT)    1.229
IKAMATUA (OLDER, WETTER) 2DR            4645.  80     895.  40   0.80
DRIFT FACTOR (PERCENT)    1.371
IKAMATUA (OLDER, WETTER) 3DR            4646.  80     873.  40   0.81
DRIFT FACTOR (PERCENT)    1.264
AHAURA (SITE 1) A                      22789.  80    1139.  40   1.58
DRIFT FACTOR (PERCENT)    0.281
AHAURA (SITE 1) AB                     16529.  80    1063.  40   1.39
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AHAURA (SITE 1) B2.1	22043.	80	1026.	40	1.63
DRIFT FACTOR (PERCENT) 1.683					
AHAURA (SITE 1) B2.2	25468.	80	1040.	40	1.75
AHAURA (SITE 1) B3	18924.	80	1044.	40	1.50
DRIFT FACTOR (PERCENT) 1.079					
AHAURA (SITE 1) C	8838.	80	944.	40	1.08
AHAURA (SITE 1) DR	4884.	80	843.	40	0.85
DRIFT FACTOR (PERCENT) 1.321					
AHAURA (SITE 2) A	23401.	80	1072.	40	1.65
AHAURA (SITE 2) AB	14589.	80	986.	40	1.36
AHAURA (SITE 2) B2	13632.	80	1039.	40	1.28
DRIFT FACTOR (PERCENT) 1.148					
AHAURA (SITE 3) A11	25355.	80	1162.	40	1.65
AHAURA (SITE 3) A12	20385.	80	1107.	40	1.51
AHAURA (SITE 3) B2	11038.	80	1023.	40	1.16
DRIFT FACTOR (PERCENT) 1.418					
AHAURA (SITE 4) OA	49030.	80	1450.	40	2.05
AHAURA (SITE 4) A2	17982.	80	1078.	40	1.44
AHAURA (SITE 4) B2	14900.	80	989.	40	1.37
DRIFT FACTOR (PERCENT) 0.794					
AHAURA (SITE 5) A2.1H	8230.	80	1091.	40	0.97
AHAURA (SITE 5) A2.2H	15683.	80	1232.	40	1.26
DRIFT FACTOR (PERCENT) 1.326					
AHAURA (SITE 5) B2	14083.	80	991.	40	1.33
DRIFT FACTOR (PERCENT) 0.988					
KUMARA A	11658.	80	1038.	40	1.18
DRIFT FACTOR (PERCENT) 0.587					
KUMARA AG	5850.	80	976.	40	0.86
DRIFT FACTOR (PERCENT) 0.710					
KUMARA G	4546.	80	973.	40	0.76
DRIFT FACTOR (PERCENT) 0.988					

KUMARA BH   7958. 80   1074. 40   0.96
DRIFT FACTOR (PERCENT)   0.710
KUMARA B3G   4634. 80   926. 40   0.79
DRIFT FACTOR (PERCENT)   0.587
KUMARA CG   3557. 80   981. 40   0.67
DRIFT FACTOR (PERCENT)   1.325
KUMARA DR   6055. 80   998. 40   0.87
DRIFT FACTOR (PERCENT)   0.080
OKARITO A   10664. 80   1035. 40   1.13
DRIFT FACTOR (PERCENT)   1.239
OKARITO AG   5331. 80   964. 40   0.83
DRIFT FACTOR (PERCENT)   1.264
OKARITA G   3217. 80   1002. 40   0.63
DRIFT FACTOR (PERCENT)   0.476
OKARITO BG   3087. 80   984. 40   0.62
OKARITO CG   2514. 80   927. 40   0.58
DRIFT FACTOR (PERCENT)   0.587
OKARITO DR   2802. 80   909. 40   0.62

X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM B   EVALUATION OF UNKNOWN CONCENTRATIONS

SAMPLE DATA	NET C/S			ERROR	LOSS
HOKITIKA A11	187.75	+	1.89	(1.01)	11.0
HOKITIKA A12	108.89	+	1.50	(1.38)	6.0
HOKITIKA C	15.13	+	1.00	(6.64)	1.2
IKAMATUA (YOUNGER) OA	1005.03	+	4.53	(0.45)	76.3
IKAMATUA (YOUNGER) A	133.62	+	1.63	(1.22)	15.4
IKAMATUA (YOUNGER) AB	90.61	+	1.43	(1.58)	9.0
IKAMATUA (YOUNGER) B	65.08	+	1.32	(2.02)	5.7
IKAMATUA (YOUNGER) C	66.13	+	1.32	(1.99)	3.5
IKAMATUA (YOUNGER) DR	8.34	+	0.94	(11.37)	1.0
IKAMATUA (OLDER) OA	443.72	+	2.84	(0.64)	49.8
IKAMATUA (OLDER) A	192.94	+	1.90	(0.98)	21.3
IKAMATUA (OLDER) B2	125.47	+	1.57	(1.25)	13.2
IKAMATUA (OLDER) B3	103.09	+	1.50	(1.46)	6.6
IKAMATUA (OLDER) C	49.96	+	1.22	(2.44)	2.7
IKAMATUA (OLDER) DR	15.28	+	1.02	(6.69)	1.2
IKAMATUA (OLDER, PODSOL) A2	221.78	+	2.04	(0.92)	31.2
IKAMATUA (OLDER, WETTER) OA	402.49	+	2.68	(0.66)	42.1
IKAMATUA (OLDER, WETTER) A2H	194.00	+	1.91	(0.98)	21.6
IKAMATUA (OLDER, WETTER) A3BH	131.87	+	1.65	(1.25)	13.9
IKAMATUA (OLDER, WETTER) B2	45.91	+	1.19	(2.59)	5.2
IKAMATUA (OLDER, WETTER) B3	40.83	+	1.16	(2.85)	4.2
IKAMATUA (OLDER, WETTER) 2DR	35.26	+	1.12	(3.18)	2.0
IKAMATUA (OLDER, WETTER) 3DR	35.77	+	1.11	(3.11)	2.7
AHAURA (SITE 1) A	253.35	+	2.14	(0.84)	27.6
AHAURA (SITE 1) AB	179.62	+	1.85	(1.03)	17.6
AHAURA (SITE 1) B2.1	249.34	+	2.11	(0.84)	10.1

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AHAURA (SITE 1) B2.2        287.71 +  2.23 ( 0.77)      6.0
AHAURA (SITE 1) B3          207.08 +  1.94 ( 0.93)      5.5
AHAURA (SITE 1) C            85.97 +  1.40 ( 1.63)      4.4
AHAURA (SITE 1) DR           39.55 +  1.12 ( 2.85)      2.3
AHAURA (SITE 2) A           262.42 +  2.15 ( 0.82)     28.4
AHAURA (SITE 2) AB          155.72 +  1.72 ( 1.10)     21.4
AHAURA (SITE 2) B2          142.60 +  1.68 ( 1.18)      8.7
AHAURA (SITE 3) A11         284.82 +  2.25 ( 0.79)     34.6
AHAURA (SITE 3) A12         224.69 +  2.02 ( 0.90)     27.8
AHAURA (SITE 3) B2          111.16 +  1.54 ( 1.39)     13.8
AHAURA (SITE 4) OA          569.30 +  3.22 ( 0.56)     65.2
AHAURA (SITE 4) A2          195.16 +  1.90 ( 0.97)     25.7
AHAURA (SITE 4) B2          159.33 +  1.74 ( 1.09)     12.8
AHAURA (SITE 5) A2.1H        75.03 +  1.40 ( 1.87)     13.7
AHAURA (SITE 5) A2.2H       164.01 +  1.82 ( 1.11)     23.3
AHAURA (SITE 5) B2          149.34 +  1.70 ( 1.13)     13.8
KUMARA A                    118.65 +  1.58 ( 1.33)     12.8
KUMARA AG                    48.45 +  1.23 ( 2.54)      6.5
KUMARA G                     32.28 +  1.14 ( 3.54)      4.7
KUMARA BH                    71.93 +  1.38 ( 1.92)      8.4
KUMARA B3G                   34.54 +  1.13 ( 3.29)      3.6
KUMARA CG                    19.82 +  1.07 ( 5.42)      2.5
KUMARA DR                    50.08 +  1.24 ( 2.48)      5.3
OKARITO A                   107.37 +  1.54 ( 1.43)     12.6
OKARITO AG                   42.03 +  1.18 ( 2.82)      6.5
OKARITA G                    14.98 +  1.04 ( 7.00)      2.0
OKARITO BG                   13.92 +  1.04 ( 7.48)      2.7
OKARITO CG                    8.21 +  0.98 (11.94)      1.5
OKARITO DR                   12.23 +  0.99 ( 8.15)      1.6
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X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM B   EVALUATION OF UNKNOWN CONCENTRATIONS

CORRECTED COUNT RATES	CORRECTED C/S	ERROR
HOKITIKA A11	172.47 + 1.91	(1.10)
HOKITIKA A12	104.05 + 1.46	(1.40)
HOKITIKA C	14.99 + 0.99	(6.64)
IKAMATUA (YOUNGER) OA	437.57 + 28.45	(6.50)
IKAMATUA (YOUNGER) A	118.40 + 1.64	(1.38)
IKAMATUA (YOUNGER) AB	84.58 + 1.37	(1.62)
IKAMATUA (YOUNGER) B	62.33 + 1.27	(2.04)
IKAMATUA (YOUNGER) C	64.42 + 1.29	(2.00)
IKAMATUA (YOUNGER) DR	8.27 + 0.94	(11.37)
IKAMATUA (OLDER) OA	280.20 + 8.38	(2.99)
IKAMATUA (OLDER) A	162.53 + 2.22	(1.36)
IKAMATUA (OLDER) B2	113.21 + 1.55	(1.37)
IKAMATUA (OLDER) B3	98.05 + 1.46	(1.48)
IKAMATUA (OLDER) C	48.96 + 1.19	(2.44)
IKAMATUA (OLDER) DR	15.14 + 1.01	(6.69)
IKAMATUA (OLDER, PODSOL) A2	170.57 + 3.01	(1.76)
IKAMATUA (OLDER, WETTER) OA	277.10 + 6.54	(2.36)
IKAMATUA (OLDER, WETTER) A2H	162.99 + 2.24	(1.37)
IKAMATUA (OLDER, WETTER) A3BH	118.30 + 1.63	(1.38)
IKAMATUA (OLDER, WETTER) B2	44.15 + 1.15	(2.60)
IKAMATUA (OLDER, WETTER) B3	39.56 + 1.13	(2.86)
IKAMATUA (OLDER, WETTER) 2DR	34.74 + 1.10	(3.18)
IKAMATUA (OLDER, WETTER) 3DR	35.05 + 1.09	(3.12)
AHAURA (SITE 1) A	201.60 + 3.10	(1.54)
AHAURA (SITE 1) AB	156.22 + 2.00	(1.28)
AHAURA (SITE 1) B2.1	230.70 + 2.18	(0.94)

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AHAURA (SITE 1) B2.2        274.94 +  2.25 ( 0.81)
AHAURA (SITE 1) B3          198.65 +  1.92 ( 0.96)
AHAURA (SITE 1) C            83.17 +  1.37 ( 1.64)
AHAURA (SITE 1) DR           38.88 +  1.11 ( 2.85)
AHAURA (SITE 2) A           207.27 +  3.25 ( 1.56)
AHAURA (SITE 2) AB          131.06 +  1.91 ( 1.45)
AHAURA (SITE 2) B2          133.42 +  1.64 ( 1.23)
AHAURA (SITE 3) A11         211.89 +  4.02 ( 1.89)
AHAURA (SITE 3) A12         178.46 +  2.82 ( 1.58)
AHAURA (SITE 3) B2           99.81 +  1.50 ( 1.50)
AHAURA (SITE 4) OA          294.62 + 13.84 ( 4.69)
AHAURA (SITE 4) A2          158.04 +  2.42 ( 1.53)
AHAURA (SITE 4) B2          144.24 +  1.75 ( 1.21)
AHAURA (SITE 5) A2.1H        67.42 +  1.32 ( 1.95)
AHAURA (SITE 5) A2.2H       135.73 +  2.07 ( 1.53)
AHAURA (SITE 5) B2          134.09 +  1.71 ( 1.27)
KUMARA A                    107.41 +  1.54 ( 1.43)
KUMARA AG                    46.12 +  1.18 ( 2.56)
KUMARA G                     31.15 +  1.10 ( 3.54)
KUMARA BH                    67.46 +  1.31 ( 1.95)
KUMARA B3G                   33.62 +  1.10 ( 3.29)
KUMARA CG                    19.46 +  1.05 ( 5.42)
KUMARA DR                    48.12 +  1.19 ( 2.49)
OKARITO A                    97.36 +  1.49 ( 1.53)
OKARITO AG                   40.00 +  1.13 ( 2.84)
OKARITA G                    14.75 +  1.03 ( 7.00)
OKARITO BG                   13.65 +  1.02 ( 7.48)
OKARITO CG                    8.12 +  0.97 (11.94)
OKARITO DR                   12.09 +  0.98 ( 8.15)
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X-RAY FLUORESCENCE SULPHUR ANALYSIS

PROGRAM B   EVALUATION OF UNKNOWN CONCENTRATIONS

COMPUTED SULPHUR CONTENT	COMPUTED PPM		ERROR
HOKITIKA A11	847.5 +	31.6	(3.73)
HOKITIKA A12	507.7 +	20.9	(4.12)
HOKITIKA C	65.5 +	10.7	(16.37)
IKAMATUA (YOUNGER) OA	2163.9 +	159.3	(7.36)
IKAMATUA (YOUNGER) A	579.0 +	23.2	(4.01)
IKAMATUA (YOUNGER) AB	411.0 +	18.1	(4.41)
IKAMATUA (YOUNGER) B	300.6 +	15.2	(5.07)
IKAMATUA (YOUNGER) C	310.9 +	15.5	(4.99)
IKAMATUA (YOUNGER) DR	32.2 +	10.4	(32.31)
IKAMATUA (OLDER) OA	1382.4 +	63.2	(4.57)
IKAMATUA (OLDER) A	798.1 +	30.6	(3.84)
IKAMATUA (OLDER) B2	553.2 +	22.3	(4.04)
IKAMATUA (OLDER) B3	478.0 +	20.1	(4.20)
IKAMATUA (OLDER) C	234.2 +	13.6	(5.83)
IKAMATUA (OLDER) DR	66.3 +	10.7	(16.26)
IKAMATUA (OLDER, PODSOL) A2	838.1 +	33.4	(3.99)
IKAMATUA (OLDER, WETTER) OA	1367.0 +	57.2	(4.18)
IKAMATUA (OLDER, WETTER) A2H	800.4 +	30.7	(3.84)
IKAMATUA (OLDER, WETTER) A3BH	578.5 +	23.2	(4.01)
IKAMATUA (OLDER, WETTER) B2	210.3 +	13.0	(6.22)
IKAMATUA (OLDER, WETTER) B3	187.5 +	12.6	(6.74)
IKAMATUA (OLDER, WETTER) 2DR	163.6 +	12.1	(7.44)
IKAMATUA (OLDER, WETTER) 3DR	165.1 +	12.1	(7.37)
AHAURA (SITE 1) A	992.1 +	38.1	(3.84)
AHAURA (SITE 1) AB	766.8 +	29.3	(3.82)
AHAURA (SITE 1) B2.1	1136.6 +	41.0	(3.60)

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AHAURA (SITE 1) B2.2         1356.3 +   48.0 ( 3.54)
AHAURA (SITE 1) B3            977.5 +   35.6 ( 3.65)
AHAURA (SITE 1) C             404.1 +   17.9 ( 4.44)
AHAURA (SITE 1) DR            184.1 +   12.5 ( 6.80)
AHAURA (SITE 2) A            1020.3 +   39.2 ( 3.84)
AHAURA (SITE 2) AB            641.9 +   25.5 ( 3.98)
AHAURA (SITE 2) B2            653.6 +   25.4 ( 3.89)
AHAURA (SITE 3) A11          1043.2 +   41.6 ( 3.99)
AHAURA (SITE 3) A12           877.3 +   34.1 ( 3.89)
AHAURA (SITE 3) B2            486.7 +   20.4 ( 4.19)
AHAURA (SITE 4) OA           1454.1 +   85.0 ( 5.84)
AHAURA (SITE 4) A2            775.8 +   30.4 ( 3.91)
AHAURA (SITE 4) B2            707.3 +   27.1 ( 3.84)
AHAURA (SITE 5) A2.1H         325.8 +   15.9 ( 4.89)
AHAURA (SITE 5) A2.2H         665.1 +   26.5 ( 3.98)
AHAURA (SITE 5) B2            656.9 +   25.6 ( 3.90)
KUMARA A                      524.4 +   21.5 ( 4.10)
KUMARA AG                     220.1 +   13.3 ( 6.06)
KUMARA G                      145.8 +   11.9 ( 8.16)
KUMARA BH                     326.1 +   15.9 ( 4.88)
KUMARA B3G                    158.0 +   12.0 ( 7.65)
KUMARA CG                      87.7 +   11.0 (12.62)
KUMARA DR                     230.0 +   13.5 ( 5.90)
OKARITO A                     474.5 +   20.0 ( 4.23)
OKARITO AG                    189.7 +   12.6 ( 6.68)
OKARITA G                      64.3 +   10.8 (16.80)
OKARITO BG                     58.8 +   10.7 (18.25)
OKARITO CG                     31.4 +   10.4 (33.29)
OKARITO DR                     51.1 +   10.6 (20.75)
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