

A QUANTITATIVE AND QUALITATIVE INVESTIGATION
OF BRITISH COLUMBIA COAL USING ENERGY
DISPERSIVE X-RAY FLUORESCENCE

by

Cynthia L. Nichols

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APPROVAL

Name: Cynthia Nichols

Degree: Master of Science

Title of Thesis: A Quantitative and Qualitative Investigation
of British Columbia Coal Using Energy
Dispersive X-ray Fluorescence

Examining Committee:

Chairperson: C.H.W. Jones

J.M. D'Auria
Senior Supervisor

A.C. Oeschlager
Professor

L.K. Peterson
Professor

W.M. Johnson
External Examiner
Ministry of Energy, Mines and
Resources
Victoria, B.C.

Date Approved: Sept. 16, 1980

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Investigation of British Columbia Coal

Using Energy Dispersive X-Ray Fluorescence

Author: _____

(signature)

CYNTHIA NICHOLS

(name)

Dec. 17/80

(date)

ABSTRACT

Energy dispersive x-ray fluorescence spectroscopy with a Mo secondary target was used to quantitatively and qualitatively assess the trace elements in British Columbia coals. The aims of the study were: 1) to develop a method whereby multielement analysis of coal could be performed rapidly and accurately to the parts per million level, 2) to determine if the relative values for the trace elements could be used to distinguish between either a) individual coal seams or b) coals from different locations.

A total of 50 samples were obtained from 3 locations in the Hat Creek coal field and 4 locations in the Crowsnest coal field. Thirty-seven of the samples from the Crowsnest coal field (Sparwood Ridge) were classified according to the individual seams from which they were obtained.

Optimum sample preparation and operating conditions were established. Analysis of the data was aided by the computer program GAMANAL. Calibration curves using the National Bureau of Standards Coal (NBS 1632) were generated

for the elements K,Ca,Ti,Fe,Ni,Cu,As,Br,Rb and Sr. Calculated values gave concentrations which agreed favourably with those obtained using NAA, AA, spark source mass spectrometry and an independent XRF study. Errors ranged from 2% to as high as 30%.

None of the elements studied appeared to be present in greater concentration than is present in the environment naturally. However, ashing the coal samples indicated that Br is depleted while most of the other elements become more concentrated.

Using the Compton normalized peak areas for the elements K,Ca,Ti,Fe,Cu,Ni,Zn,As,Cr,Rb,Br and Sr, interelement correlations were investigated. Outliers were eliminated and the linearity of the relationships checked. Stepwise discriminant analysis using a maximum Rao's V statistic as the inclusion criterion was applied to the Sparwood Ridge samples. Six discriminant functions were generated. Reclassification of the samples using the discriminant coefficients indicated that the samples could be discriminated according to the seams from which they were obtained with 80% success.

A similar analysis was applied to the coal samples from different locations. Of the 6 canonical variates generated, the first three accounted for 99% of the variation. In the case of the discrimination by location, 93% of the samples were successfully classified.

In summary, results indicate that while the trace elements can be used to distinguish between coal seams in a particular location, the discrimination is more successful in the case of non-adjacent seams. The greatest degree of discrimination occurs between samples of coal from different locations in B.C.

for
Alan and Sean

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1. INTRODUCTION

1.1 Background

Energy has emerged as an issue of concern for the 80's. As oil supplies dwindle and energy demands increase, all indications point to the fact that our interests must focus on alternative energy sources. Among those considered, coal has become increasingly attractive.

In light of the recommendations made in the National Energy Plan in the United States (1) it is predicted that many smaller power plants in the U.S. will convert from oil and gas to coal. Similar trends might reasonably be expected in Canada as well (2).

Estimates of coal reserves in Canada indicate that there are 42 billion tons of indicated and measured coal reserves and a further 165 billion tons of inferred resources. Of these, 99% are located in Western Canada (i.e. B.C., Alberta and Saskatchewan).

At present, the domestic and export demands for coal are 20.1 Mtce (million tons of coal equivalent) annually and comprise 9% of Canada's energy needs. The most conservative projections to the year 2000 give an estimate of these demands to increase to 71 Mtce. This figure reflects the estimate that coal will comprise about 12% of Canada's future energy needs (3).

These figures may be gross underestimates since they are based on the rather unrealistic assumptions that coal will retain its relative cost with respect to oil and gas and that the role of coal as an energy source will be exclusively as the primary fuel as opposed to using it in liquefaction or some other process.

As interest shifts away from oil and gas toward coal and other energy sources, it becomes increasingly important to investigate some of the environmental and economic aspects of coal mining and use.

One of the more important areas of concern focusses on the environmental impact of trace elements present in whole coal and coal ash (4,5,6). In the draft environmental impact statement for the Coal Research, Development and Demonstration Program, the Energy Research and Development Administration addressed the question of the probable water quality problem associated with the increased utilization of coal in the U.S.(7). The general water quality objectives as outlined by the Pollution Control Board is given in table I (8). ERDA stated that potential concerns revolve about: 1) the presence of potentially toxic and carcinogenic compounds in coal residue and products and, 2) the potential presence of trace metal pollutants in coal products and by-products. They concluded that little is known about these subjects and that further study is warranted.

The increased role played by coal in the economy requires that more information about coal reserves and quality in general be available. Similarly, the question of environmental impact must be faced. Much interest has recently centred about the potential effects of the trace elements resulting from mining, stockpiling and burning coal (9,10,11,12).

Table I. Water quality objectives for the discharge of trace elements into marine and fresh waters.

Parameter		Concentration
Aluminum	dissolved mg/l Al	0.2
Antimony	dissolved mg/l Sb	5.0
Arsenic	dissolved mg/l As	1.0
Cadmium	dissolved mg/l Cd	0.02
Chromium, hexavalent and trivalent	dissolved mg/l Cr	0.15
Cobalt	dissolved mg/l Co	1.0
Copper	dissolved mg/l Cu	0.10
Cyanide	total mg/l CN	0.50
Fluoride	dissolved mg/l F	5.0
Iron	dissolved mg/l Fe	0.5
Lead	dissolved mg/l Pb	0.20
Manganese	dissolved mg/l Mn	1.0
Mercury	dissolved mg/l Hg	0.005
Molybdenum	dissolved mg/l Mo	10.0
Nickel	dissolved mg/l Ni	1.0
Selenium	dissolved mg/l Se	0.20
Silver	dissolved mg/l Ag	0.05
Tin	dissolved mg/l Sn	2.0
Zinc	dissolved mg/l Zn	0.3

1.2 Research Outline

Until recently, there were no readily available methods by which the question of pollution at low levels could be investigated. As such, very little information is available on the trace element content or distribution in B.C. coals from either the economic or environmental viewpoints.

The aim of the research reported here was to use energy dispersive x-ray fluorescence to develop a means by which the trace elements in coal could be quickly and easily studied. This led to two major areas of interest:

The first was to quantitatively determine the levels of some of the trace elements present and to investigate these values in light of their potential effects. More specifically, once the trace element concentrations were determined for a selection of elements in coal obtained from various areas in B.C., attention could turn to the question of two possible mechanisms through which these metals could be released into the environment. The first was through

climatic effects on stockpiled coal such as leaching processes which might occur when coal is stored. Secondly, it was of concern to consider the fate of any trace element when combustion occurs.

The second major area of interest was a qualitative investigation of the trace elements in particular coal seams and in particular coal locations. Specifically, this was carried out to determine if the trace elements in an individual sample could be used as a means of identification of a particular coal seam or location.

Geologists have long sought a method by which seams can be identified (13,14). Such a procedure is desirable from both a geological and an economic point of view. Because of factors such as the relatively rapid changes in the thickness of the seams, the interval between the seams and other geological problems, difficulty has invariably been experienced in the mapping of coal seams. A dependable correlation method would result in stratigraphic and structural studies of great value. Furthermore, one of the problems facing geologists lies in the valuation of coal

rank (i.e. quality) (15,16). Since the thermal and export worth of a coal is greatly influenced by its rank, a dependable method for such a determination has been long sought. At present several classification schemes exist. The particular method used varies from one area to another, and indeed from one coal field to another. The most frequently used scheme in North America is based, to a large extent, on microscopic observation of the coal and as such is highly subjective.

It was recognized that if the trace element distribution could be used to distinguish between various coal seams, then this could potentially lead to a more quantitative classification method. Furthermore since coal represents sediments accumulating in various aquatic environments, geochemical studies on the succession of strata might also be expected to clarify an interrelationship between the geochemistry of a deposit and its condition of formation.

1.3 Coal Formation and Trace Element Distribution

An understanding of the trace metals present and their distribution requires some knowledge of the coal formation process.

Coal is the result of shallow water swamp sediments which generally accumulate in acid water and terminate in the formation of peat. Other external processes result in solidification of the peat and coal morphosis. The origins of coal involve biochemical and metamorphic stages in the sequence: peat to lignite to bituminous and finally to anthracite coal (17). General analyses have shown that numerous and varied elements are enriched in coal relative to the average content in the earth's crust. Any enrichment which occurs has generally been attributed to three possible mechanisms: a) accumulation of an element by the primary plant material during growth, possibly followed by further concentration during selective decay of the materials, b) accumulation of an element from the surrounding ground water by absorption or chemical reaction during coalification, c) concentration of the element in the mineral matter deposited along with the plant material in pre-coal accumulation (13,18,19).

If the interelement association in a seam is the result of the primary biological concentration or of the sorption during early stages of peat accumulation, the content of the element in a coal sample will be independent of the sample position in the seam. Samples from any position in the seam could then be used for identification.

If however, the trace elements result from a sorption process after coalification, it is expected that concentration would have occurred at seam margins. This would require a more careful selection of coal samples for identification purposes.

In a survey of coals from various sources, Nicholls (13) found that elements such as B, Ni, Cu and Ge tend to be evenly distributed throughout the seam whereas Pb and V show seam margin enrichment.

In general, the distribution of the trace elements will be related to the rate and area of accumulation of the organic matter. If the availability of the trace elements from a source area remains constant, then the concentrations

that will result in the organic matter will be inversely proportional to the rate of accumulation. In addition, if the areal extent of the deposition is large, then low concentrations of trace elements will result. This is why generally thick, widespread coal beds would be expected to have lower trace element concentrations and conversely, why thinly bedded coal could be expected to have higher concentrations (20).

The average concentration of an element in the earth's crust is termed the 'clarke' value. Attempts have been made recently to compare the trace element concentrations in coals from different areas with their clarke value, thereby estimating the degree, if any, to which the various elements are enriched. In an extensive study of coal from three major producing areas of the U.S. (Illinois Basin, Western U.S. and Eastern U.S.), Ruch, Kuhn et al (21,22,23) found that, on the average, very few elements were significantly concentrated in the coal. They did point out, however, that enrichment tended to depend on the locality of the specific coal field, and hence generalizations were difficult.

Although it is generally accepted that there is a wide variation between coals from different regions, the extent to which trace elements can be used to classify coal samples has largely been unexplored. Newmarch (24) attempted to use trace elements to classify coal seams. His study, however, was greatly hampered by a lack of suitable means to quickly analyze the sample and to handle the resulting data. Gluskoter (23) attempted to investigate the relationship between the trace elements, done as an element by element correlation. Although some interesting relationships were found, no patterns emerged and no generalizations or conclusions in terms of the overall distribution of trace elements from one seam or one location to another could be made.

In a study of the trace elements in New Zealand coals, Sim and Lewin (25) found there was a wide variation in composition of the ashes of coals from different regions. This observation was not followed up by an evaluation of these differences.

1.4 Quantitative Studies

As previously indicated, one of the major tasks in the research undertaken was to devise a method whereby a quantitative evaluation of the trace elements in coal could be quickly and easily assessed. Prior to 1970, analyses were conducted by high temperature ashing of the coal followed by either wet chemical or instrumental methods which could only be used for single elements. These procedures left much room for error as well as being slow and relatively inefficient. With the development of x-ray fluorescence, a rapid, non-destructive, sensitive, multielement technique has become available. This permits the simultaneous determination of a number of elements with a minimum of sample preparation hence eliminating the need to ash the coal first.

In the case of B.C. and Alberta coal, the published studies have mainly dealt with the general content and the physical properties of various samples (26). While such investigations are useful for estimating the gross characteristics they do not reliably measure the full spectrum of trace elements or their fate under various conditions.

In the study carried out by the Illinois Geological Survey (23), x-ray fluorescence was used to analyze 101 coal samples. This study served to provide a number of coal 'standards' for trace element analysis and as such to provide information on the trace element content of Illinois coal.

A number of researchers have recently become concerned over the trace element behaviour as a result of coal combustion. Billings (27) estimated that the mercury liberated during the combustion of a 700Mw coal fired electrical generating station is in the order of 2.5 kg per day. Natusch (10) classified many of the trace elements and oxides according to their carcinogenicity and reactivity with special emphasis given to those present in or produced from fossil fuels. He estimated that fossil fueled power plants contribute approximately 25% of the anthropogenic particulate matter emitted to the atmosphere in the U.S. In an earlier study (28), he had reported that there was a preferential concentration of the trace elements As, Sb, Cd, Cr, Pb, Ni, Se, Tl and Zn in the smallest of the particulates emitted from coal fired power plants. These

particulates are not trapped by the stack filtering devices and find their way into the atmosphere.

In subsequent studies, Lyon (29,30) and Koakenin (31) have investigated the concentrations of trace elements at various sampling positions in coal fired power plants. Through a mass balance study, the latter of these investigators found that enrichment occurs in the case of Cu, Zn, As, Mo, Sb, Se, and Po.

Very little work has been done in the area of the effects of water on coal stockpiles. In general, any studies conducted have not managed to develop a standardized dependable method for investigating the coal pile leaching. Davis and Boagly (32) reviewed the research conducted on coal storage pile leachates and concluded that what little research that had been conducted in this area consisted mainly of individual 'grab' samples on a number of different coals of different composition rather than sustained or controlled testing. While a full scale study of coal pile leachates was not the purpose of the research undertaken, concern over the fate of the trace elements in whole coal naturally leads to consideration of such a question.

2. EXPERIMENTAL

2.1 XRF Theory

The basic principle of x-ray fluorescence is not complicated. When a source of primary radiation impinges upon an atom, a vacancy may be created in one of the atomic shells. Electrons from higher energy orbitals fill these vacancies thereby releasing photoelectrons whose energy is characteristic of the energy difference between the outer and inner orbital. The detection and observation of these emitted photoelectrons, which are characteristic of the element in question, results in a fluorescence spectrum. Although the theory has been well developed and may be found in detail elsewhere (33,34,35) a few of the more important features merit discussion.

In theory, a vacancy may be created in any of the atomic shells and similarly, filling may occur as a result of an energy loss by any electron possessing more energy.

In fact, however, the proper choice of conditions will favour K-shell vacancies with the result that the most frequent transition (80%) will be the $L \rightarrow K$, resulting in K_{α} x-rays. In accordance with the selection rules for allowed transitions, other transitions also commonly occur and some can be detected with various intensities.

One of the more important considerations in XRF is the nature of the primary radiation. Although it may be either electromagnetic radiation or a charged particle beam, only the first of these is widely used and understood (36).

In order for an electron to be ejected from its orbital, it is necessary that the impinging radiation exceed the electron binding energy for that element. The minimum energy required to expel a given electron from its orbital is referred to as the absorption edge. This is also related to the mass absorption coefficient, that is, the 'stopping power' of an element. If several elements are to be detected, it follows that the energy of the primary radiation must exceed the absorption edge of all the elements of interest. This however, is not the only

condition that must be met. If the energy of the primary radiation is too great, the photons may be too energetic to be efficiently absorbed or, if they are, penetration may be so deep that the resulting x-rays are unable to escape. In the case of multielement detection, the requirement for a monochromatic source is desirable so that the energy continuum produced by the sample is minimized, since scatter from the sample would result in a high background. From the above considerations, it is found that the optimum conditions for creating K shell vacancies occur when the primary radiation is such that it is a monochromatic source with energy which just slightly exceeds the absorption edge of the highest atomic weight element to be detected.

Not every x-ray produced is detected. Three major processes occur which reduce the sensitivity of the resulting spectrum. These are the production of auger electrons, compton scattering and rayleigh scattering.

The first of these involves the reabsorption of an x-ray such that it results in the formation of an extra vacancy in a higher energy level. Thus two higher level

vacancies are created. This is a significant phenomenon which can be numerically represented by the fluorescent yield, ω ; where ω equals the ratio of the number of emitted x-rays to the number of vacancies created. Typically, the fluorescent yield ranges from 1% for low Z elements to about 10% for higher Z elements (33,37).

Compton (inelastic or incoherent) scatter results when an x-ray interacts with a loosely bound outer electron from another atom. In accordance with the conservation of energy and momentum, the x-ray is deflected at an angle θ and with energy $E(\text{scat}) < E(\text{init})$. The energy of the recoiling photon, therefore, will be a function of the initial energy and of the scattering angle. It is evident that the more loosely bound the electrons present (higher Z), the greater the probability for this process to occur. Thus the Compton scatter, which manifests itself as a broad peak in the spectrum, is a reflection of the average atomic mass of the target. For the same reason, it is also the major source of background 'noise' from the sample.

Rayleigh (elastic or coherent) scatter is the third process which contributes to the overall absorption effects. This involves the interaction of an incident x-ray with tightly bound electrons of a neighbouring atom. In such a situation the electrons are not dislodged and the x-ray is scattered without any resultant loss of energy. This process thus results in a peak which reflects the overall resolution of the spectrometer. It can be considered that tightly bound inner electrons are those associated with the heavier elements and as such the coherent scattering process will be more important for the higher Z elements. This process will predominate when the binding energy of the orbital electrons exceeds the incident x-ray energy. Thus the rayleigh scattering peak should also reflect the average atomic mass of the sample (38,39).

Consideration of the rayleigh/compton ratio reveals that it should give an indication of the nature of the sample and of the system. That is, the R/C value should increase as: 1. the incident x-ray energy is decreased (more elastic processes occur), 2. the atomic number increases (rayleigh scattering $\propto Z^2$ whereas compton

scattering $\propto Z$), 3. the angle of incoherent scatter decreases (fewer Compton scattered x-rays will be detected since most detectors are perpendicular to the primary beam).

An investigation of this ratio using the Simon Fraser University system showed values of 0.520 for CaCO_3 which is a low Z substance to 3.02 for the higher Z substance, $\text{Pb}(\text{NO}_3)_2$.

Absorption and enhancement effects also influence the XRF process in samples consisting of more than one element and arise from the following phenomena:

1. The absorption coefficient of the matrix may be such that the primary, exciting x-rays are preferentially absorbed. Thus the elements of interest are not efficiently detected.

2. The absorption coefficient of the matrix may be such that those x-rays emitted by the element of interest are absorbed. Thus, the elements of interest are not efficiently detected.

3. The absorption coefficient of the element of interest may be such that the x-rays emitted by the matrix will be of sufficient energy that they will act as a primary x-ray source for that element, thus enhancing its effect.

It is primarily consideration of the features discussed above that dictate the instrument operating conditions and sample analysis techniques.

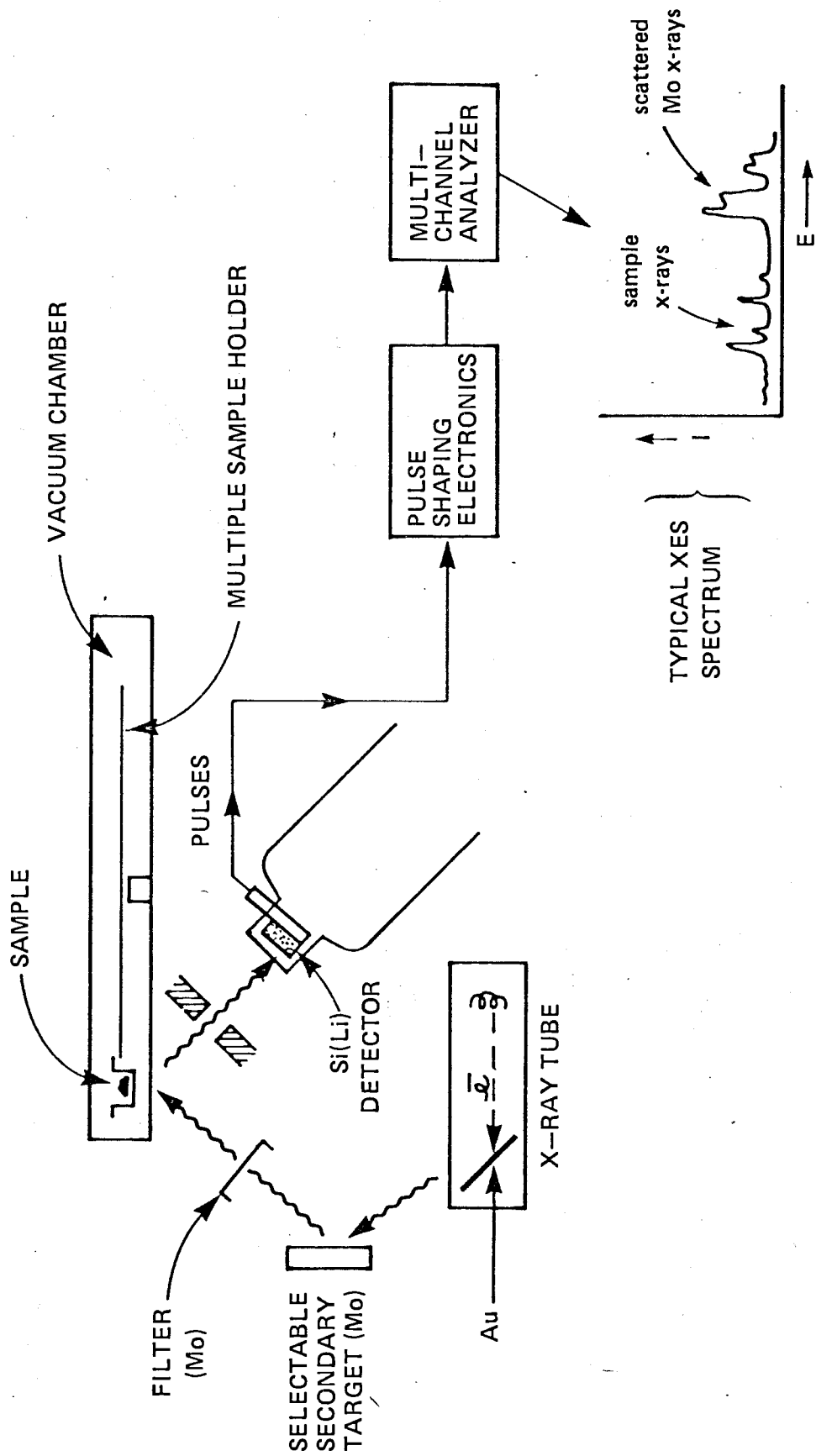
2.2 Instrumentation

In general, two basic types of x-ray fluorescence spectrometers are in common use; wavelength dispersive, in which the resulting x-rays are detected by measuring their wavelengths and energy dispersive, in which the energy of the resulting x-ray is measured. The latter of these is a more recent innovation made possible by the development of efficient semiconductor detectors.

The instrument used in this study was an energy dispersive system manufactured by the Kevex Corporation. A schematic is shown in figure 1. A few of the more salient features bear discussion.

Figure 1

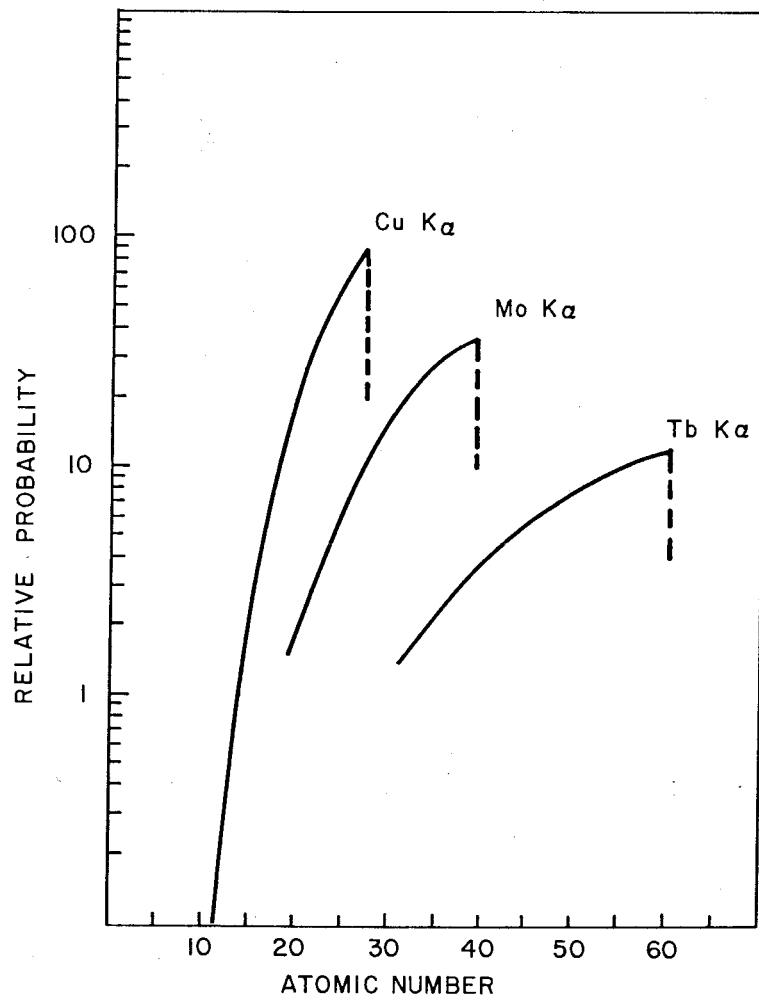
A Schematic Representation of the Secondary Target
X-ray Fluorescence System.



In order for fluorescence to occur, vacancies must be created in the inner orbitals of an atom. As discussed in the previous section, the most commonly used technique is to use electromagnetic radiation. This may be accomplished by using a primary radiation source directly or by means of a secondary excitation system. The secondary excitation system has definite advantages (40) and was the method employed for this study.

A Au target x-ray tube was used as the primary radiation source. This produces an energy continuum and, for reasons discussed, is not suitable as a fluorescent source for the sample. In order to produce nearly monochromatic radiation, the beam is directed to a secondary target. This results in excitation of the target material and the production of an energy spectrum characteristic of this material. Figure 2 shows plots of the relative probability of excitation of different elements for three secondary targets. From these it is evident that the secondary target must be chosen with the elements of interest in mind in order to obtain the greatest degree of sensitivity. A secondary Mo target was selected for all analyses in this study since it was found that a significant number of trace elements in coal were excited by the K (α and β) x-rays of Mo.

Figure 2
Relative Probability for Characteristic X-ray
Production by Mono-energetic Photons.



A Mo foil was used to filter out the bremsstrahlung radiation at higher energy than the secondary target $K\alpha$ x-rays. This is possible due to the fact that an element will strongly absorb energy greater than its absorption edge but is fairly transparent to lower energy photons. The resulting nearly monochromatic radiation impinges upon the sample where characteristic x-rays are produced. A sampling time of twenty minutes (real time) was used throughout this study.

The x-rays produced are detected using a Si(Li) semiconductor detector. In such a system, the detector receives all the excited x-rays of the sample at once. Separate pulses are then generated based on the energy of the incoming signals. Thus the sample x-rays are dispersed on the basis of their energy. Such a system offers the capability of being able to measure the energies of the incident x-rays over a wide energy range in a truly multielement fashion.

The energy resolution of the system determines its ability to separate x-rays from adjacent elements in the periodic table, and also affects the detection limit for analysis of elements in the presence of a background. The resolution is dependent upon both the basic processes occurring in the detector and on the signal/noise ratio of the associated pulse processing electronics.

Analysis using energy dispersion differs somewhat from the older, more conventional system in which the x-rays are separated on the basis of wavelength by rotating a crystal through successive angles. As a result, the characteristic x-rays for each element are detected sequentially.

In the present study, the resultant spectrum is accumulated in 400 channel groups in a Victoreen Scipp Model 104TP multichannel analyzer. From here it is transferred to magnetic tape and processed using the IBM 370 computer at SFU. A typical coal spectrum is shown in figure 3. A table of absorption edge and transition energies for selected elements is given in table II.

Figure 3

Typical XRF Spectrum of NBS 1632 Coal.

NBS COAL STANDARD 1632

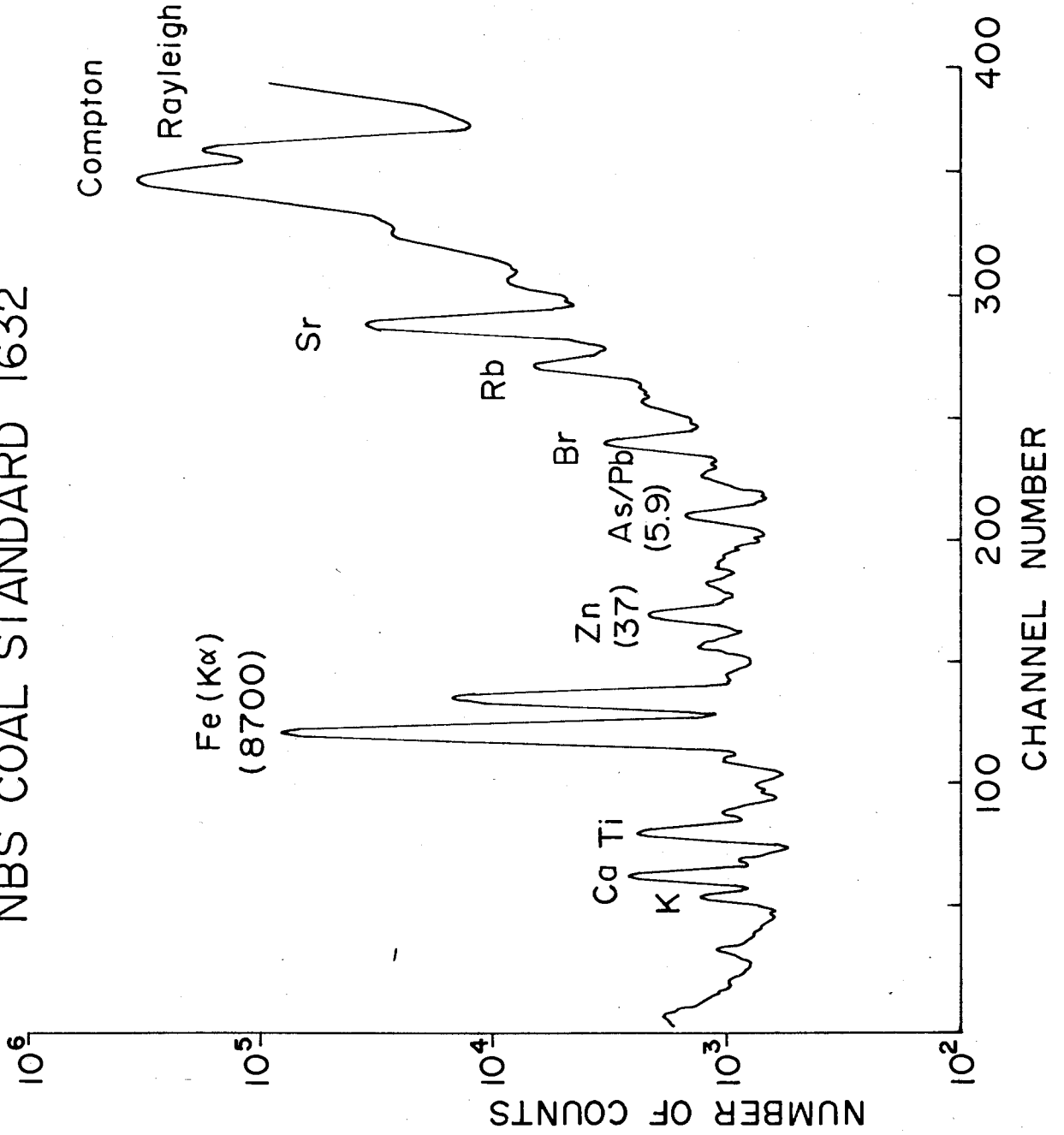


Table II. Absorption edge and transition energies for selected elements.

Element	Line (KeV)				
	K(ab)	$K\alpha_1$	$K\beta$	$L\alpha$	$L\beta$
Si	1.838	1.74	1.83	—	—
K	3.607	3.31	3.59	—	—
Ca	4.038	3.69	4.01	0.34	0.34
Ti	4.965	4.51	4.93	0.45	0.46
Cr	5.989	5.41	5.95	0.57	0.58
Fe	7.112	6.40	7.06	0.70	0.72
Ni	8.333	7.48	8.26	0.85	0.87
Cu	8.979	8.05	8.90	0.93	0.95
Zn	9.659	8.64	9.57	1.01	1.03
As	11.87	10.54	11.72	1.28	1.31
Se	12.66	11.22	12.49	1.38	1.42
Br	13.47	11.92	13.29	1.48	1.53
Rb	15.20	13.39	14.96	1.69	1.75
Sr	16.10	14.16	15.83	1.81	1.87
Mo	20.00	17.48	19.60	2.29	2.39

A summary of the XRF operating conditions is given below.

X-ray tube setting: 40 KeV; 30 mA

Secondary target and filter: Mo with Mo foil

Counting time: 20 minutes (no dead time correction)

Detector resolution: 446 eV. at 4.06 KeV

2.3 Sample Location and Collection

In order to obtain a representative sampling of coals, samples were obtained from a number of different sources. The majority provided by the B.C. Ministry of Energy, Mines and Petroleum Resources were taken from the southeastern corner of B.C. as shown in figure 4. A great deal of geologic and mining survey work has been done in this area. Thus, a large number of samples along with some relevant information could be obtained as necessary. A total of forty-six samples were obtained from this region. These came from five different location sites (figure 5). The thirty six samples taken from the Sparwood Ridge area were further classified according to the coal seams from

Figure 4

General Location of Crowsnest and Hat Creek Coalfields
in British Columbia.

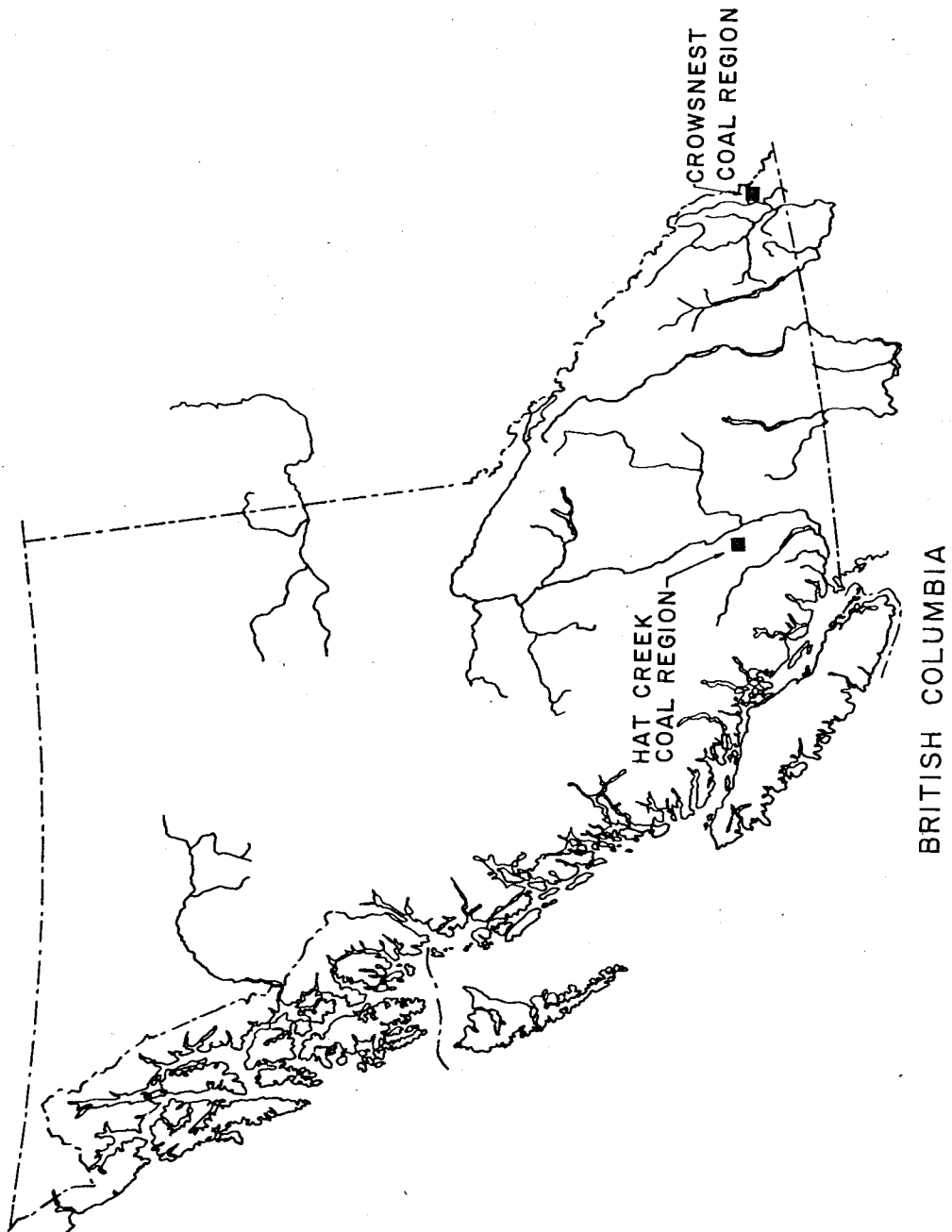
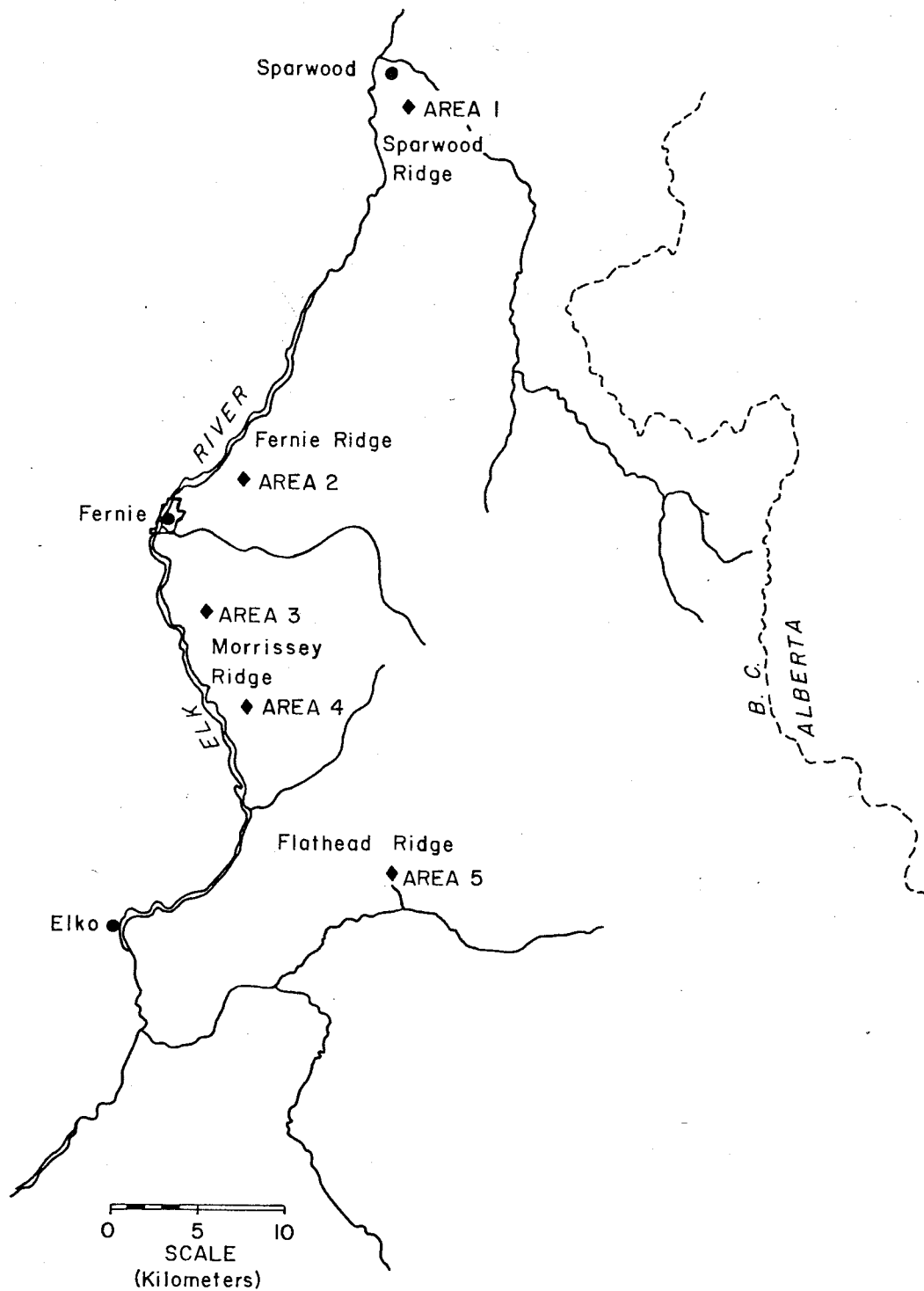


Figure 5

Locations of Five Sampling Areas in the Crowsnest
Coalfield.

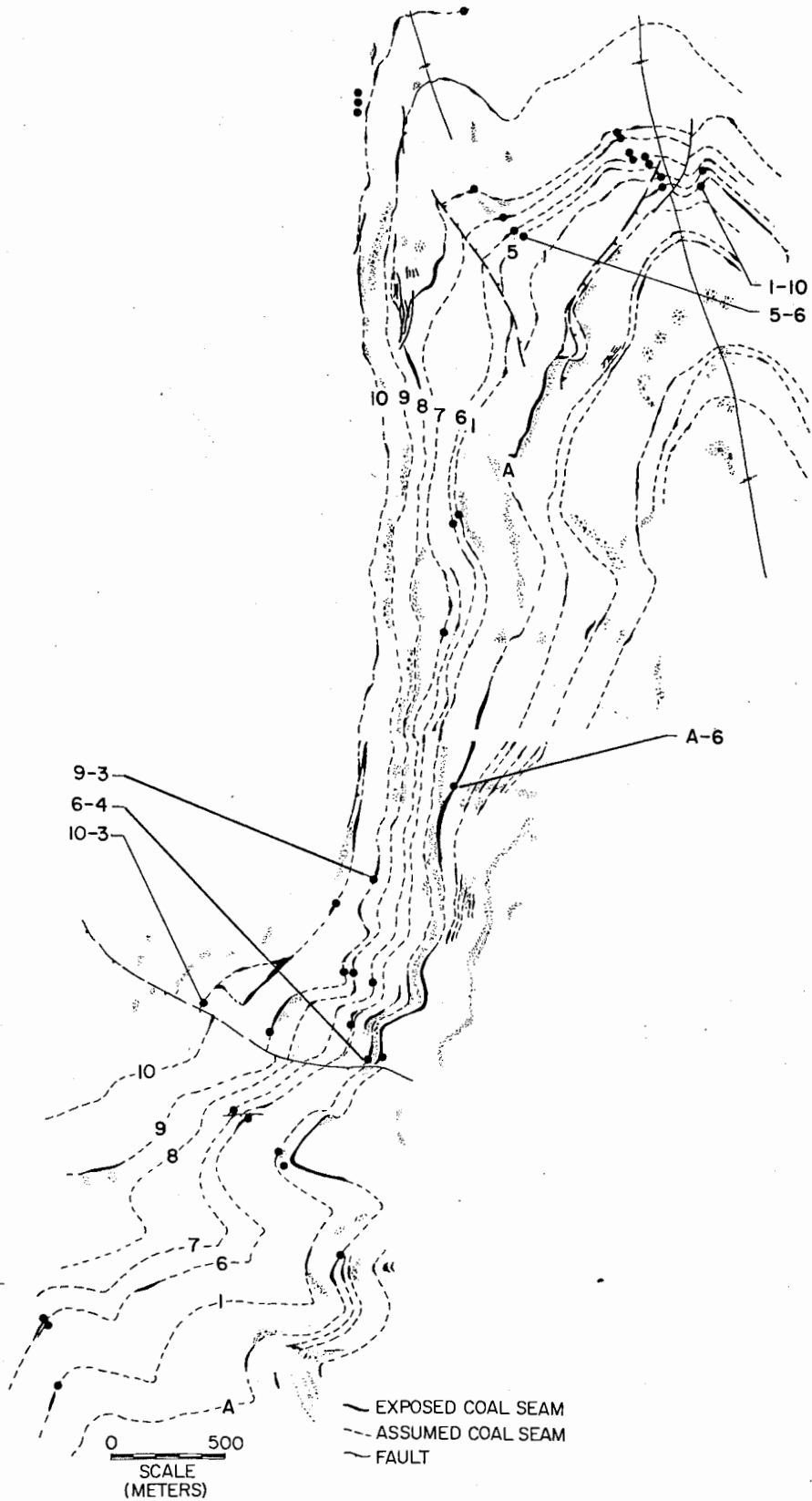


which they came. Actual sample locations for this area are shown in figure 6 and represent an area of approximately 20 square km. The labelling of the sample identifies the seam from which it was taken followed by an identification number. The seam numbers were qualitatively assigned by the Ministry on the basis of geological field studies. The identification number is arbitrarily assigned, in that it is assigned sequentially to samples as they are collected. The numbers given here correspond to those used at the Ministry so that additional information can be obtained if required. Gaps in either the seam number or the identification number are not, therefore, significant, reflecting only those samples chosen to be studied.

The samples obtained from the other four sites in the Crowsnest Region come from different coal outcrops and were used to represent different coal collection locations. In fact, while sites 3 and 4 are from separate outcroppings, survey work indicates that the two sites are geologically connected. The numbering system used to identify the samples other than those from the Sparwood Ridge area is completely arbitrary.

Figure 6

Detailed Map of Sparwood Ridge Area Showing Seams and
Sampling Locations With Selected Sample Sites Labelled.



SPARWOOD RIDGE
COAL SEAMS AND SAMPLE LOCATIONS

All coal samples from the Crowsnest Coalfield were collected as channel samples along the entire depth of freshly exposed seams. This was done by chipping away about 30 cm of the weathered surface with a spade. The sample was then collected as a continuous channel of about 4 cm wide and 2 cm deep from the newly opened surface. The chips were quartered and crushed to -70 mesh. The screened coal was requartered to provide a representative sample from a particular sampling site. From this representative sample, about 10 grams was scooped into a clean labelled bottle to be used as the analysis sample for this study. This was the form in which it was obtained from the Ministry of Energy, Mines and Petroleum Resources.

Since Hat Creek has become an economically important coal source in B.C., it was decided to use this coal as an additional sample source. Three samples were obtained from the Hat Creek coal reserve west of Cache Creek, B.C., (figure 4). These represent three individual sample sites separated by approximately 1 km. These samples were originally collected as diamond drill core samples rather than as channel samples. The cores were washed then cut

with a diamond saw. One half of the core was crushed to -100 mesh, mixed and quartered. Approximately 100 grams of the treated coal was obtained for analysis.

The collection method used for the Hat Creek coal results in a sample which may be a composite of more than one seam. The three samples therefore, were taken to represent three distinct coal locations rather than individual seams.

Two additional sets of samples were used in this study. Recently, the National Bureau of Standards has certified three coal standards. (At the outset of this project, only one of these was available.) The National Bureau of Standards ASTM coal 1632 formed the basis of the quantitative analysis for the trace elements.

An extensive study carried out in Illinois resulted in the characterization of the trace elements in a large number of samples from various areas in the United States. Five of the coal samples were obtained along with documentation of their trace element content for 45

elements. Although these samples are not true certified samples, they served as a check of the accuracy of the quantitative determinations performed in this study. Approximately 5 grams of pulverized coal was obtained for each of the five samples.

2.4 Sample Preparation

X-ray fluorescence spectrometry has a distinct advantage over many other analytical techniques in that qualitative information can be obtained quickly with little or no sample preparation. However, if meaningful quantitative information is to be obtained, preparation and standardization of the samples is necessary. In fact, the nature of the sample greatly affects the spectrometric determinations. The major considerations with regard to the sample itself are composition, thickness and, for solid samples, particle size.

As previously discussed, a number of processes can lead to absorption and scatter of incident photons within the sample itself. This implies that the intensity of a

given spectral peak will vary as a function of the average Z of the matrix. That is, it will be affected by all of the elements which go into the makeup of the sample. This becomes an especially important consideration for multielement quantitative studies.

Although it is theoretically possible to determine the concentration of a given element directly from peak intensities, this also requires prior knowledge of the elements present and their mass absorption coefficients. Practically, however, determination of the amount of an element present normally requires the comparison with a standard of known composition. Three approaches are possible:

1. If the samples and standard have very different matrices, a correction factor can be applied to compensate for the different absorption effects. This method has been widely investigated with varying degrees of success (41,42,43,44). For the most part, this approach requires a knowledge of the distribution of trace elements through the samples as well as a knowledge of the values relating absorption-enhancement effects, geometry, detector efficiency, fluorescence yield and other processes.

2. A strongly absorbing substance can be used to dilute the sample (45). The matrix effects due to the diluting substance should be large enough so that fluctuations in the weight fractions of the major constituent elements has little total effect. This approach has its own obvious disadvantages in terms of trace element analysis.

3. Whenever possible, the matrix of all samples and the standard should be the same. Then, since the samples used have essentially the same composition, the matrix effects should also be the same. The slight fluctuation in total concentration should not be enough to significantly alter the nature of the sample insofar as absorption and enhancement effects are concerned. This can be demonstrated if a reasonably constant R/C ratio is obtained for all samples used.

The third method was the one used for this study. The R/C ratio ranged from .46-.70 which represents a minor overall change in view of the range observed between CaCO_3 and $\text{Pb}(\text{NO}_3)_2$.

For quantitative and semi-quantitative analysis, advantage can also be made of the fact that the intensity of the spectral background varies linearly with the Compton scatter radiation. This peak can be used as an internal correction standard to compensate for any matrix absorption effects which occur as well as to eliminate such factors as instrument and detector noise, sample positioning and x-ray tube current fluctuations.

This approach was taken in this study. The area of the Compton peak for each sample was estimated by adding together the counts in a five channel band taken about the peak maximum. This procedure was used in view of the fact that the Compton peak is Gaussian in shape and constitutes the majority of the pulses making up the spectrum. Typically a single channel at the peak maximum contains 10 counts in contrast to a typical trace element in which the net peak area may be in the order of 10^2 . As such, a five channel band is proportional to the total peak area while giving values which are not too unwieldy. The peak area of each element of interest was then systematically normalized by dividing the total number of counts in the peak by the number of counts in the Compton peak.

With regard to the preparation of the sample itself, consideration must be given to the grain size of the solid particles, surface texture of the prepared sample and to the amount of material (thickness) used. These three factors also influence the enhancement-absorption effects and thus the overall performance of the analysis.

Grain size and surface effects have been studied extensively (46,47). The volume of sample which contributes to the measured radiation is dependent upon the penetration depth of the exciting radiation. This depth will vary with the energy of the incident x-rays and the matrix of the sample. This requires that the specimen to be analyzed be completely homogeneous since, if compositional variations in depth are present, the measured count will not be truly representative of the sample. Consequently, the particle size of the sample should be reduced to less than one-fifth the effective penetration depth (48). For lower atomic weight elements, this generally requires pulverizing to 5-50 μm (-300 mesh).

Although solid samples can be analysed in the form of finely ground powders, problems encountered with uneven surfaces must be considered. The uneven texture in a sample will result in a shielding effect such that, in some cases, the exciting radiation may be obstructed from reaching certain points in the sample while in others the characteristic x-ray from an element may be blocked from leaving the matrix. One method of eliminating such an effect is to press a weighed amount of material into an even surfaced pellet. This has the added advantage of providing an easily handled uniform sample. As a result, sample orientation errors should be at a minimum.

The last factor which bears consideration is the thickness of the sample. For a sample of constant composition, the intensity of a characteristic x-ray will vary with the sample thickness. The spectral x-ray intensities will increase with thickness until a saturation occurs at which point further increase in thickness has no effect on the line intensities. This is referred to as the critical or infinite thickness of the sample. The infinite thickness can be expressed as

$$I_t/I_\infty = 1 - \exp [-(\mu/\rho)\rho t] \quad \dots(1)$$

where:

I_t = analyte line intensity from a film of thickness t (cm)

I_∞ = analyte intensity from a film of infinite thickness (cm)

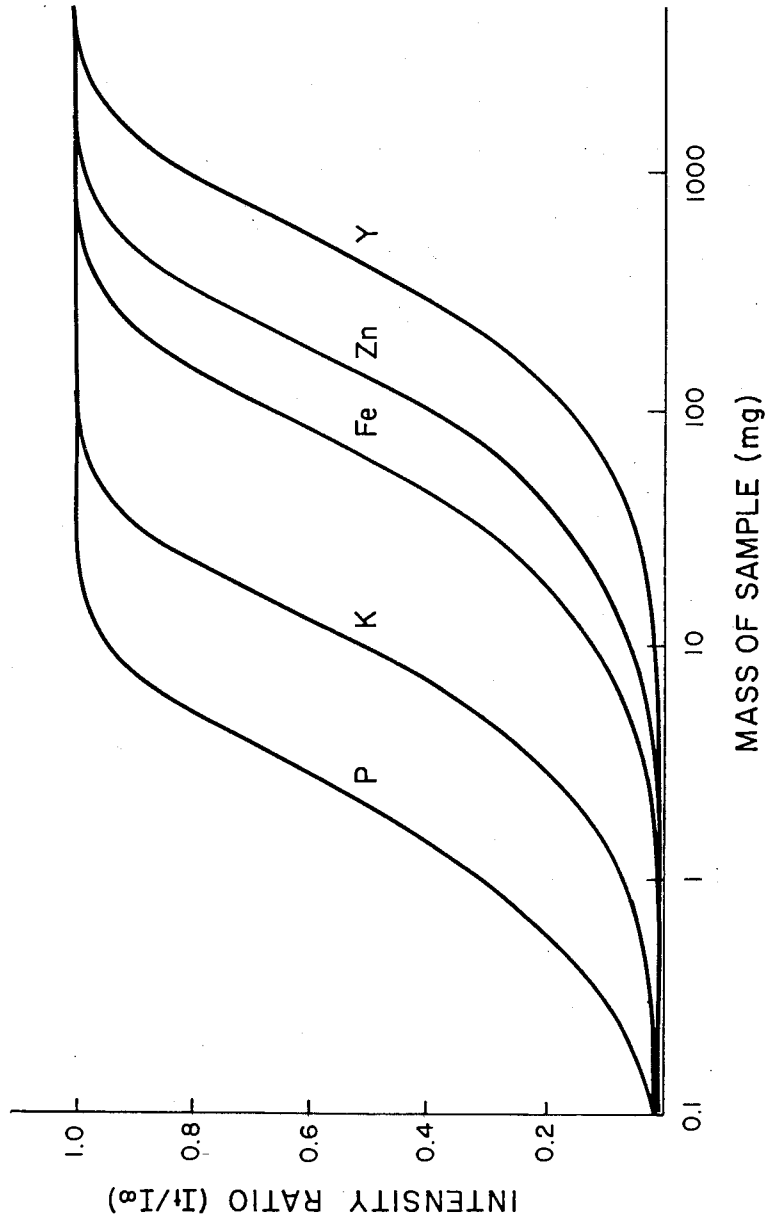
μ/ρ = the total mass absorption coefficient (cm /g)

ρ = density (g/cm)

t = thickness of film (cm)

Since the mass absorption coefficient is a function of the Z of an element, it follows that the infinite thickness is different for each element. A plot of I_t/I_∞ versus mass is shown in figure 7. Moreover, as thickness increases, so do enhancement- absorption effects. That is, sensitivity decreases as infinite thickness is approached. It follows, therefore, that no advantage is gained by having samples greater than the critical thickness.

Figure 7
Relationship Between the Intensity Ratio and
Sample Mass.



Absorption-enhancement effects all but disappear as the thickness of the sample approaches a film. This means that for very thin samples, x-ray line intensities vary linearly with concentration (33,49,50). This however poses additional problems in that very thin samples are difficult to handle and, as well, the actual amount of various trace elements can be reduced to below the detection limit. As a result, choice of an optimum sample size requires a compromise between the various factors and is found somewhere in the midrange.

In this study, a preliminary investigation was carried out to determine the optimum sample preparation techniques. The first step in the procedure was to reduce the grain size of the samples to $< 50 \mu\text{m}$. Several grinding units were available; stainless steel, plastic vials with a glass grinding ball and an alumina-silica vial. The first two of these proved unsatisfactory.

Stainless steel was found to contaminate the samples. The plastic vials had the advantage of being clean. They were also disposable which meant that a new

vial could be used for each sample and also provide the storage container for the ground coal. However, these containers are not physically very strong. As a result particles become embedded in the walls of the container during the grinding process. It was feared that some inhomogeneity could result from this. Furthermore, since coal can be very hard, the plastic grinding vials proved to be rather inefficient requiring long grinding times in order to achieve the desired results.

The alumina-silica vial with a ceramic ball proved to be most satisfactory. The main disadvantage was that only two vials were available. This meant that the samples could not be stored in the vial. Instead, after grinding, they had to be transferred to clean plastic storage containers and the alumina-silica grinder thoroughly cleaned. Several methods for cleaning the vials were attempted but the coal, being rather inert, was difficult to remove. The method devised was to first remove all loose powdered coal. The disassembled pieces were then soaked in concentrated nitric acid for a minimum of one hour, rinsed with distilled water and placed in a muffle furnace at 500 C. until all traces

of organics disappeared (that is, a minimum of two hours). The cooled vial was then ready for the next sample.

Rather than sieve each ground sample and thereby increase the possibility of contamination, it was decided to standardize the grinding process. Approximately one gram each of three randomly selected coal samples was individually ground until it would pass through a 300 mesh sieve. The time taken to achieve this degree of fineness was noted and all remaining samples were ground for the preset period of time. Using this approach, approximately one gram of each coal sample was ground for 40 minutes.

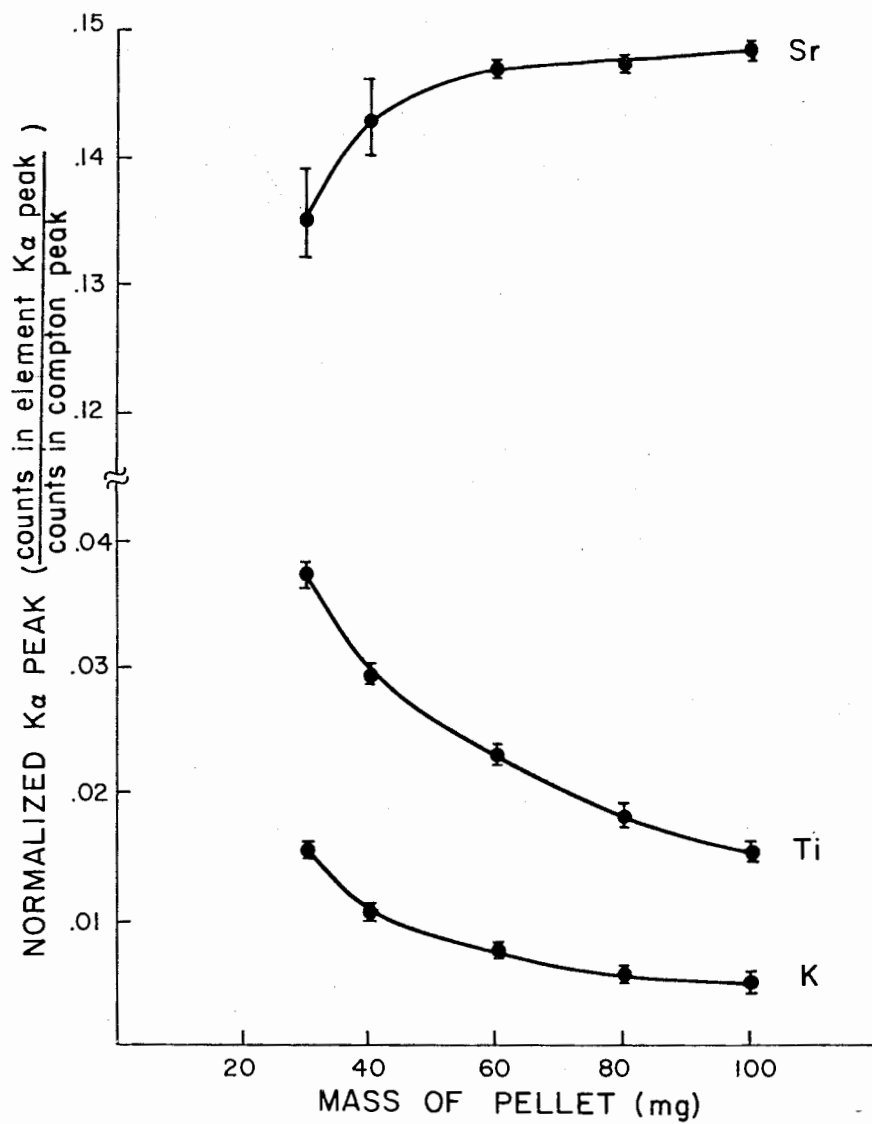
Initially, it was feared that there might be enough variation in the coal matrix from one sample to another to affect the absorption-enhancement effects. It was decided to try mixing the coal with enough of a strongly absorbing material to stabilize the matrix. Both sulphur and graphite were tried. A number of pellets of varying size and with varying amounts of absorbing material were made. This did not prove worthwhile for two reasons. The trace element concentration was diluted enough to make detection difficult and no significant improvement in sensitivity was realized.

It was decided to use the ground coal 'as is'. Fortunately, coal has good binding characteristics thus the pellets made were physically strong and easily handled without the need to add any binding material. It was found that smooth surfaced, good quality pellets were obtained using a pressure of 7.5 tons (104 Mpa). All pellets were made using a 13 mm diameter pellet press.

As previously discussed, the thickness of the pellet is critical. A number of pellets of NBS coal with masses 25,40,60, 80 and 100 mg were analyzed. Plots of the normalized peak areas of a selection of elements versus the mass is shown in figure 8. A mass of 40 mg was chosen as optimum for all analyses. In order to best evaluate the precision and the errors involved in the study, ten 40 mg pellets of each of the samples were made. The briquetted samples were placed in an aluminum cup sample holder with a thin mylar film stretched over one end to support the sample. The mylar was replaced after each analysis. A slight tap at the side of the sample cup permitted centering of the sample. At no time during the sample preparation was handling of the pellet necessary.

Figure 8

Relationship Between Normalized Peak Area and
Sample Mass for the Elements K, Ti and Sr.



2.5 Sensitivity, Background and Errors

The most widely accepted definition of detection limit or sensitivity is that amount of trace element that gives a net line intensity equal to three times the square root of the background intensity for a specific counting time (47,51). That is,

$$LLD = 3(N_b)^{1/2}c/N_e \quad \dots (2)$$

where:

N_b = counts from background

c = concentration of trace element

N_e = counts from element

The above equation indicates that the detection limit can be minimized by reducing the number of background counts. Since the background results from such factors as the scattering processes, it can, to some extent, be controlled but not eliminated by optimizing operating conditions. As indicated earlier, the approach taken to minimize the background effects was to normalize to the

compton peak. Lower limits of detection were evaluated for each of the elements of interest and are given in table III. An analytical study using any method requires a critical evaluation of the errors involved. This is especially true in trace element analysis where peak intensities very near the detection limit are to be determined. As such, it is imperative that random errors be kept to a minimum. If the errors are assumed to be independent and random, then the total error can be calculated as the sum of the various contributions (52):

$$\epsilon_T^2 = \epsilon_N^2 + \epsilon_O^2 + \epsilon_P^2 + \epsilon_I^2 + \epsilon_{Pt}^2 \quad \dots(3)$$

where:

- ϵ_T^2 = total error
- ϵ_N^2 = counting error
- ϵ_O^2 = operational error due to drift
- ϵ_P^2 = placement error
- ϵ_I^2 = homogeneity error
- ϵ_{Pt}^2 = preparation error

Table III. Lower limit of detection for elements in whole coal.

Element	LLD (ppm)	1 σ
K	125	12
Ca	60	5
Ti	21	1
Cr	6.6	0.7
Fe	5.9	0.4
Ni	2.7	0.4
Cu	2.1	0.1
Zn	2.3	0.6
As	0.64	0.19
Se	0.86	0.18
Br	1.3	0.5
Rb	1.4	0.1
Sr	1.5	0.2

Choice of the counting time was made on the basis of convenience as well as the counting error. For a single measurement of N counts accumulated in a time t , the relative counting error is given by:

$$\epsilon_N = \frac{1}{\sqrt{N}} = \frac{1}{\sqrt{It}} \quad \dots (4)$$

where:

- N = accumulated counts in a peak
- I = intensity of a peak (counts/s)
- t = time of counting (s)

From the above equation, it is evident that the counting error decreases as the number of counts increases and, in principle, may be made negligibly small for sufficiently long counting times. This however, is impractical leading to excessively long analyses with no concomitant gain. For example, doubling the number of counts in a particular peak from 5×10^5 to 10^6 results in a drop in error from 0.14% to 0.10% (at the 68.3% confidence level) (33,46). A counting time of 20 minutes (with no dead

time correction) was chosen. This generally gives approximately 1000 counts in the NBS copper peak with a resulting 2.2 % error at the 68.3% confidence level and 4.5% at the 95.4% confidence level.

An estimate of the operational error was made by analysing a single 40 mg pellet of NBS standard coal ten consecutive times. No adjustments were made in either the operating conditions (other than to ensure that they remained constant) or in the sample placement. The operational error was then estimated by determining the precision of analysis using two trace elements: Fe and Cu. The results of ten determinations showed an error of .24% for the normalized Fe peak and an error of 2.1% for the Cu peak.

Specimen placement error was also investigated. As above, a single 40 mg pellet was analysed ten times. However, between each analysis, the sample was removed from the sample holder and reloaded thereby changing the orientation and precise placement in the cup. The precision of the analyses was again calculated on the basis of the Fe

and Cu peak intensities. The errors obtained for the normalized peak areas were 2.8% and 10.9% for Fe and Cu respectively. The values take into consideration a correction for the counting errors and operational errors discussed above according to equation 3.

As outlined in the sample preparation section, much care was given to ensure as consistent and homogeneous a sample as possible. This is estimated to be the greatest source of individual error in that some of the variation must arise from the fact that when dealing with trace quantities of elements it is not physically possible for them to be distributed completely homogeneously throughout the sample. Evaluation of sample errors was made by preparing and analyzing ten 40 mg pellets of each of the coal samples. Throughout this report, all errors are given at one standard deviation based on ten replicated determinations (except where otherwise indicated).

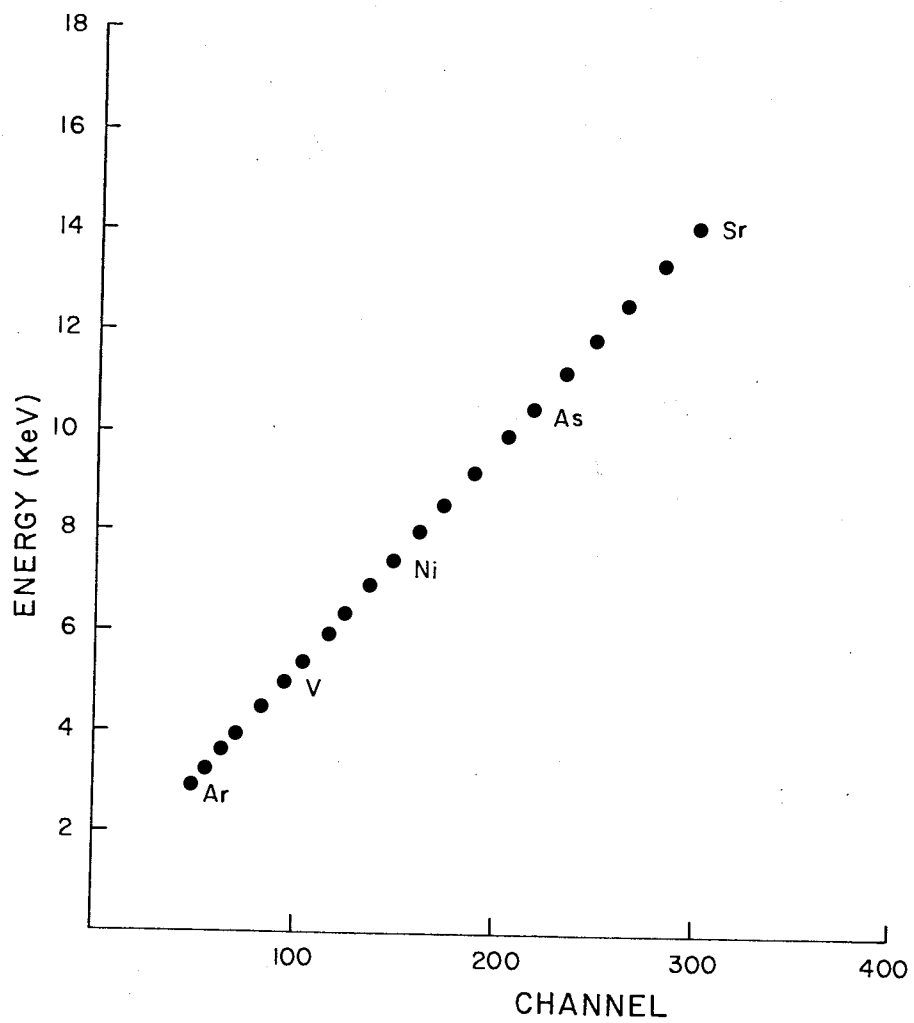
2.6 Spectral Analysis

The spectral information, in digital form, was transferred from the multichannel analyser to magnetic tape and processed using an IBM 370 computer. Figure 9 shows that there is a linear relationship between the energy of the detected pulses and the channel in which they are stored. Thus peak identification is not normally a difficult task.

Many approaches have been taken to best reduce the data in order to obtain values corresponding to the peak intensities. The simplest is to merely count the number of pulses over a set number of channels centred about a peak maximum and subtract a background value estimated by a straight line fit between peak minima. This method generally results in fairly large errors, especially in the case where peaks are weak or ill defined as is often the case in trace element determinations.

Figure 9

Relationship Between Energy of K_{α} Peak and the Stored Channel Under Normal Operating Conditions.



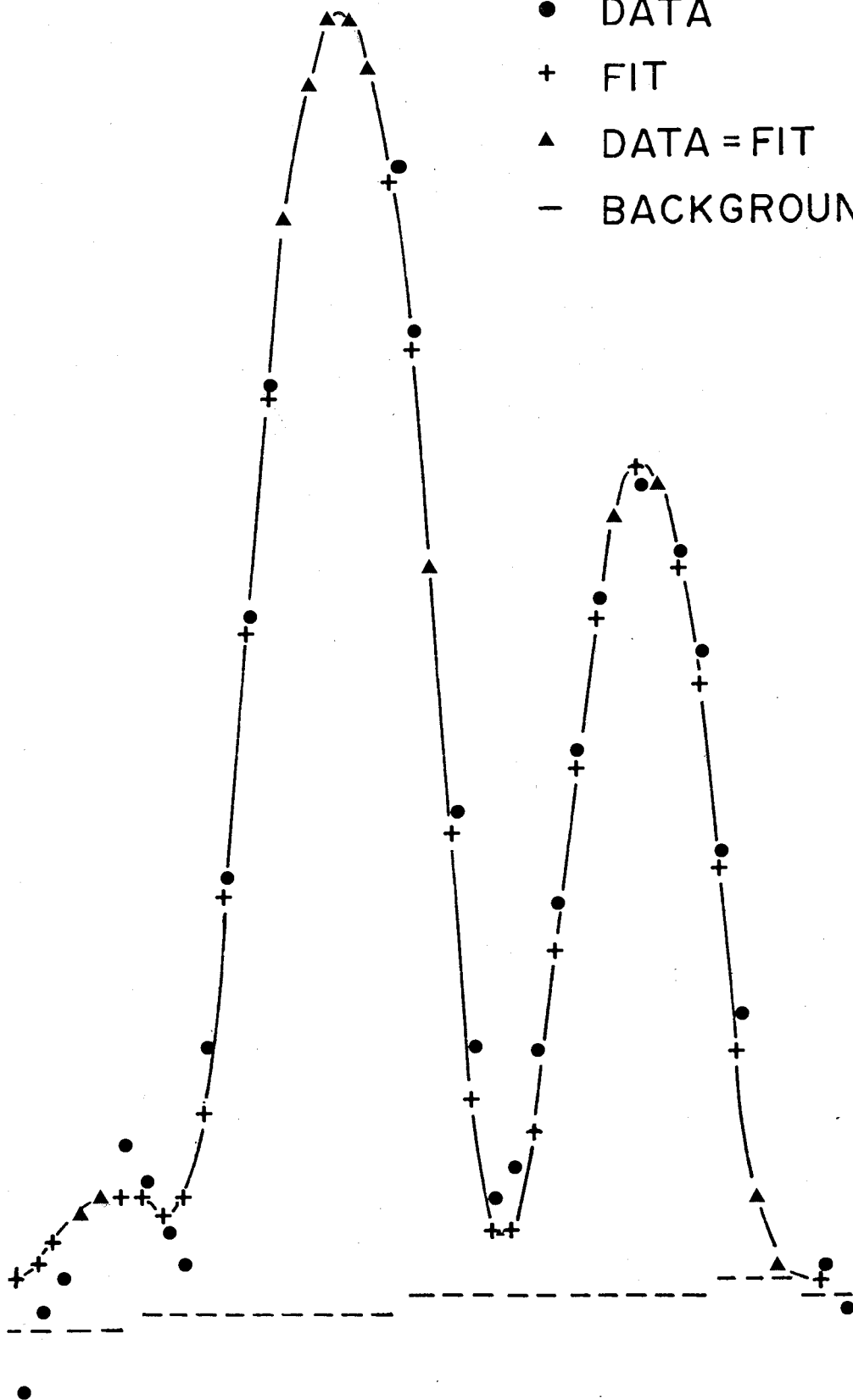
A number of elaborate computer programs exist for spectrum stripping. The program GAMANAL (53) was used for the analysis of all spectra obtained in this study. This code was originally designed to be applied to gamma-ray spectra. However, through a judicious choice of the various parameters it was found to successfully handle x-ray fluorescence spectral data.

The advantages of this program lie in the way backgrounds are estimated and multiple peaks are handled. Background estimations are made in a series of stages in which the entire spectrum is smoothed. Then the background under a peak is estimated using a smoothed step function. Peaks are located by examining both the deviation in the actual number of counts from the background and the first and second derivatives in a peak region. A fit to a peak is estimated by considering it to be the sum of a gaussian function and a trailing term. Multiplets are taken to be linear combinations of more than one such peak. A typical fit showing the actual counts and the fitted counts as well as the background estimation are shown in figure 10. Normally, the GAMANAL program fitted approximately 35 peaks to a spectrum of which 12 were used for further investigations.

Figure 10

Fit of GAMANAL Program to Actual Data for a Typical
Peak.

- DATA
- + FIT
- ▲ DATA = FIT
- BACKGROUND FIT



One area of difficulty was encountered when trying to fit x-ray fluorescence data. The Compton peak, in general, is too broad to be fitted within the bounds of the allowed parameters. As a result, this peak was generally 'seen' as a multiplet comprised of up to ten peaks. Thus, fitted peak values reported for the Compton 'multiplet' were not used. Rather, the Compton scatter peak was evaluated as previously described, that is, as a five channel window taken at the peak maximum. This practice was not thought to affect the accuracy or precision of any of the results.

2.7 Quantitative Analysis

2.7.1 Whole Coal Studies

When quantitative analysis is to be done using XRF, use is often made of the fact that for a thin film sample, the concentration of an element is directly proportional to the intensity of the peak (54,55). This means that thin film standards can be made from the pure elements of interest. The concentrations in an unknown sample can be determined by comparison with the standards. If the unknown

is not a thin film sample, a suitable matrix correction factor is applied. Unfortunately, this implies that there is some prior knowledge about the composition of the sample.

The other approach requires comparison of the intensity of an element peak in a sample with a well characterized standard. In view of the foregoing discussion on matrix effects, it is evident that it is necessary for the standard to have as nearly an identical composition as possible to the sample. The standard chosen for this study was the NBS 1632 coal standard. Table IV gives the certified values for this material (56). It must be noted that in some cases, certified values were not available. However, the figures reported are the average values obtained when this coal sample was subjected to a specially conducted 'round-robin' analysis at four independent laboratories (57).

Although it is possible to directly compare the peak intensities for a given element between the sample and the standard, this is a highly suspect procedure. This assumes that the peak intensity is a strictly linear function of the

Table IV. Elemental concentrations in NBS coal 1632.

Element	Concentration ($\mu\text{g/g}$)
K	$2800 \pm 300^{\text{a}}$
Ca	$4300 \pm 500^{\text{a}}$
Ti	$1040 \pm 110^{\text{a}}$
Cr	20.2 ± 0.5
Fe	8700 ± 300
Ni	15 ± 1
Cu	18 ± 2
Zn	37 ± 4
As	5.9 ± 0.6
Se	2.9 ± 0.3
Br	$19.3 \pm 1.9^{\text{a}}$
Rb	$21 \pm 2^{\text{a}}$
Sr	$161 \pm 16^{\text{a}}$

^aAverage result of a minimum of 20 determinations from four laboratories

concentration which is not always the case. Unless the two compared intensities are very close, errors can result. As a check on the linearity of the concentration versus peak intensity, calibration curves must be generated. In the case of coal, it was necessary that this procedure be followed with care.

In general, it is considered that NBS materials, if possible, be used only as a check on the analysis. However, since this was the only material available, it was decided to use the NBS coal as the standard. In the course of the study, two other certified coals were issued. This was then used to check certain of the results.

Since coal is a solid material, if calibration curves are to be generated, it is necessary to 'dilute' the standard with some material which would not interfere with the analysis and also would have the same matrix properties as the coal itself. Careful mixing of the standard and the diluting material was necessary to produce a completely homogenous and representative standard.

Two 'diluting' materials were considered; graphite and somar (an organic based binding agent distributed by Kevex Corp.). Although both worked adequately, less variation in the R/C ratio and physically more desirable pellets were produced using the somar. Five grams of each of 25.0% coal, 50.0% coal, 66.6% coal and 80.0% coal were prepared using the NBS standard and the somar material. The preparations were thoroughly mixed (25 min) in an alumina-silica vial using the procedure previously described. Ten 40 mg pellets of each of the mixtures and of pure NBS coal were made and subsequently analysed. The net peak intensities for ten of the elements were then normalized to the compton. These values permitted the establishment of standard calibration curves of normalized peak intensity versus concentration for each element of interest. The error associated with the normalized areas reflects the homogeneity of the sample and thus the success of the mixing process. A linear regression was applied to each plot resulting in an expression :

$$I_p = mC + I_R \quad \dots (5)$$

where:

I_p = normalized peak intensity of an element

m = slope of the calibration curve

C = concentration of the element

I_R = residual background

The standard calibration curves for Fe and Br are shown in figure 11. The linear regression equations for each element are given in table V.

Multiplets occur when two detected x-rays (eg. Ca $K\alpha$ and K $K\beta$, As $K\alpha$ and Pb $L\beta$, and Br $K\beta$ and Rb $K\alpha$) are very close in energy. In order to determine the peak intensity due only to the element of interest, it is therefore necessary to either use another characteristic peak or apply a correction factor to the $K\alpha$ peak intensity. The second of these was used here.

Figure 11
Standard Calibration Curves for Bromine and Iron Using
NBS 1632 Coal.

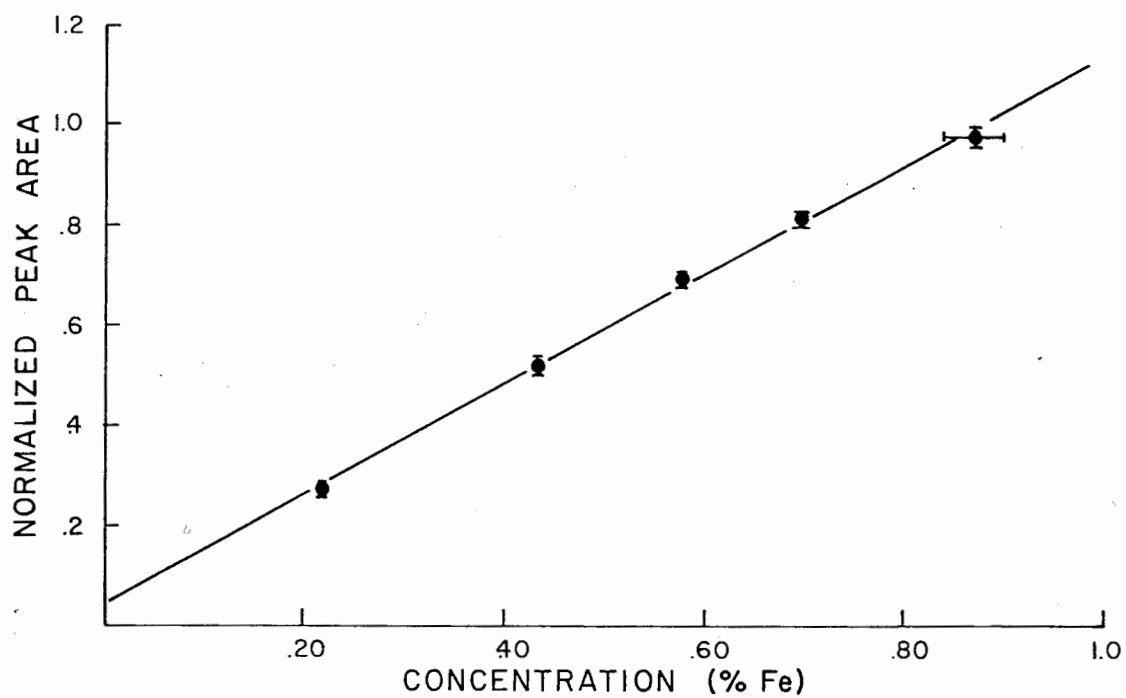
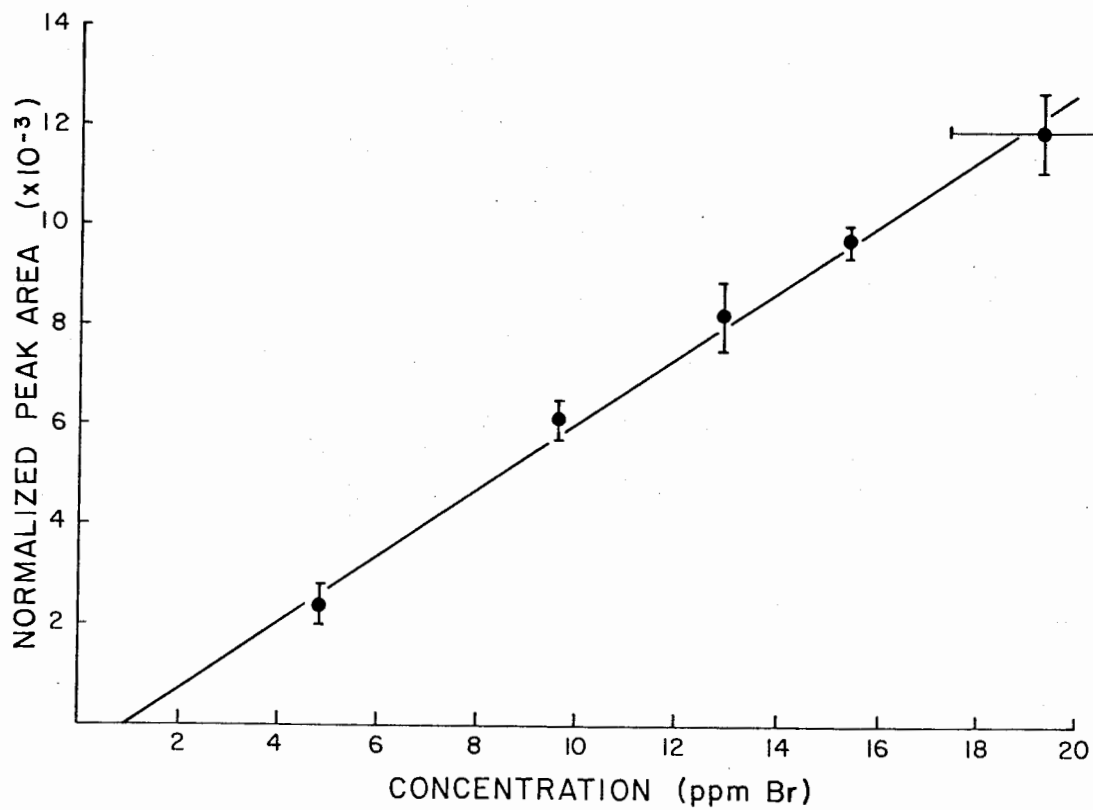


Table V. Calibration curves for elements obtained by least squares analysis.

Element	Line	Slope (m)	Intercept (I _R)
K	K _α	3.56×10^{-6}	0.0010
Ca	K _α	7.94×10^{-6}	0.0028
Ti	K _α	2.75×10^{-5}	0.0016
Fe	K _α	1.04×10^{-4}	0.050
Ni	K _α	1.14×10^{-4}	0.0011
Cu	K _α	2.03×10^{-4}	0.0015
As	K _α	1.15×10^{-3}	-0.0009
Br	K _α	6.54×10^{-4}	0.00047
Rb	K _α	9.11×10^{-4}	0.0021
Sr	K _α	8.34×10^{-4}	0.00054

$$m = \frac{\text{area of element } K_{\alpha}}{\text{area of compton}} \cdot \text{concentration of NBS } (\mu\text{g/g})$$

$$I_R = \frac{\text{area of element } K_{\alpha}}{\text{area of compton}}$$

Since the absorption qualities of different matrices vary, the determination of a correction factor is best done experimentally. A small amount of the pure chemical containing the interfering element was thoroughly mixed with somar and a 40 mg pellet made. In this study, three such pellets were made in the approximate ratio 1:10- KHCO_3 plus somar, $\text{Pb}(\text{NO}_3)_2$ plus somar and NaBr plus somar. For potassium, the $K_\alpha : K_\beta$ ratio was determined. This factor was then used throughout the study to determine the true Ca peak intensity:

$$I_{\text{Ca } K_\alpha} = I_M - \left(\frac{K \text{ } K_\beta}{K \text{ } K_\alpha} \cdot I_{K \text{ } K_\alpha} \right) \quad \dots (6)$$

where:

$I_{\text{Ca } K_\alpha}$ = intensity of Ca K_α peak

I_M = intensity of multiple peak: $K \text{ } K_\beta + \text{Ca } K_\alpha$

$I_{K \text{ } K_\alpha}$ = intensity of K K_α peak

$K \text{ } K_\beta / K \text{ } K_\alpha$ = correction factor = 0.111

In the case of Pb, two L x-rays are in the energy range of the analysis: Pb L_α (10.55 KeV) and Pb L_β (12.61 KeV). Hence, the true As K peak intensity can be determined:

$$I_{As\ K\alpha} = I_M - \left(\frac{Pb\ L\beta}{Pb\ L\alpha} \cdot I_{Pb\ L\alpha} \right) \quad \dots(7)$$

where:

$I_{As\ K\alpha}$ =intensity of As $K\alpha$ peak

$I_{Pb\ L\alpha}$ =intensity of Pb $L\alpha$ peak

I_M = intensity of the multiple peak

$Pb\ L\beta / Pb\ L\alpha$ = correction factor = 0.231

Similarly, since Br $K\beta$ (13.29 KeV) interferes with Rb $K\alpha$ (13.39 KeV), a correction factor of .150 was applied to the Rb peak since it was found that $Br\ K\beta / K\alpha = .1504$.

The corrections were performed automatically as part of the data reduction procedure using the program AREAS. In many cases the correction intensities proved to be too small to be significant.

Care must be observed when applying the standard calibration equations to a sample. The sample concentration should be, if possible, in the same range as the standard.

2.7.2 pH Studies

A selection of three coals was made to investigate how the trace elements are affected by a variation in pH. Two procedures were tried. The first involved buffered solutions in which coal samples were soaked. However, it was recognized that this would not represent a realistic situation. The three coals were retested using various concentrations of H_2SO_4 .

Procedure A:

Approximately 1 gram samples of each of NBS coal, a Hat Creek coal and a Sparwood ridge coal were placed in a 15 ml beaker. Ten ml of Fisher buffer solution was added to each and the mixture thoroughly stirred to ensure complete wetting of the samples. Each beaker was covered to prevent evaporation and left to stand for 24 hours. After soaking, the coal was suction filtered onto a fritted glass disc and allowed to air dry. The dried coal was reground and pressed into 40 mg pellets for analysis. This procedure was carried out using the buffered solutions : pH 2, 4, 6 and 8

Procedure B:

Three acidic solutions were prepared using H_2SO_4 in distilled water: pH 2.1, 4.0, 5.4. Approximately one gram of the appropriate coal was placed in a sintered glass filtering funnel. Ten ml of the acid solution was slowly poured over the coal. Suction was applied to the funnel allowing the solution to filter through at a rate of about 2 ml/min. When all the acid had been used, the coal was allowed to air dry. Since this tended to cause caking of the coal, the dried coal was reground and pressed into 40 mg pellets. This procedure was repeated for each of the three coal samples using each of the acid solutions plus distilled water. A reading of the pH of the filtrate was taken after each of these leaching experiments. The filtrate, however, was not saved. No total recovery analysis was performed.

2.7.3 Ashing Studies

Four coals were selected to determine the characteristics of coal under various temperature conditions. One or two grams of a powdered coal sample was

weighed out into a clean ceramic crucible. The samples were then placed in a muffle furnace under the following conditions:

1. All were heated for precisely one hour at 250°C.
2. The crucibles were placed in a 250°C oven for 15 minutes. The temperature was then raised to 500°C. The total ashing time was 90 minutes.
3. The crucibles were placed in a 500°C oven. The temperature was immediately increased to 750°C for a total time of 60 minutes. The samples were removed, stirred and returned to the 750°C oven for a further 30 minutes.

The treated samples were then weighed to determine the ash content.

It was found that such ashed samples lost all their binding qualities, thus they were mixed with 50% by weight of somar. The mixture was blended well by placing in the shaker for 10 min and 40 mg pellets made. The resulting

pellets still proved to be extremely fragile and great care had to be exercised in analyzing them.

Analysis of these samples was done semi-quantitatively only. Since the ashing procedure significantly changes the sample matrix, the established calibration curves could not be used to apply to these samples. An NBS fly ash standard does exist. However, the certified elements are limited and do not cover the elements of interest in this study. An entirely new set of procedures would be required to obtain quantitative results on these samples. This was beyond the intent of the present study.

2.7.4 Verification

Neutron activation analysis is an analytical technique whereby radioactive isotopes are produced in a sample by irradiation with thermal and/or fast neutrons. The γ -rays emitted by these isotopes are detected and their energy measured. Generally, the sample plus a standard is irradiated for a selected period of time. After irradiation

and appropriate radioactive decay, a gamma-ray spectrum is obtained. Quantitative determinations are made by comparing the number of characteristic γ -rays produced in the unknown with the number resulting from the standard. A detailed account of the process can be found elsewhere (58,59,60).

Ten samples were selected for analysis using the neutron activation analysis facility at TRIUMF. Due to the limited supply and relatively high cost of NBS standard coal, it was decided to use a method of secondary standards for the analyses. That is, one arbitrary coal sample was selected and analyzed using the certified coal as the standard. This unknown then became the secondary standard and samples of this coal were then included with all other unknowns for irradiation. Unfortunately, the coal selected to serve as the secondary standard contained very low concentrations of most of the trace elements of interest. As a result, comparison between the secondary standard and the unknown was difficult.

NAA is generally not as susceptible to contamination as most other analytical techniques, nevertheless precautions must be taken to ensure that cleanliness is maintained.

Polyethylene snap-cap vials were used as sample containers. These were soaked in a solution of 50:50 nitric acid overnight and then rinsed thoroughly with distilled deionized water. The clean vials were then dried in a warm (50° C) oven. Exactly one gram of ground material (-70 mesh) was introduced into each of the small vials (10x20 mm) and the cap heat sealed using a clean soldering iron. An identification mark was etched into the polyethylene. One vial containing the standard followed by one vial containing an unknown were then placed in a larger polyethylene vial. The cap was heat sealed and identified. The prepared samples were then transported to the TRIUMF facility for analysis.

2.8 Discriminant Analysis

Discriminant analysis is a mathematical method in which a set of variables is transformed in such a manner that group differences are established. The procedure is statistical in nature and requires the application of a few basic principles. A brief account of some of these is given in appendix I.

Although a complete description of the mathematics is beyond the scope of this study and can be found elsewhere (61,62,63), some of the more important concepts, as they apply to this work, are given here.

Discriminant analysis is applied when there exists a set of observations for p variates in which a number of either experimentally or naturally defined groups exist. In principle, the procedure is a test of the null hypothesis: $H_0: \mu_1 = \mu_2 = \mu_3 = \dots$, that is, that the group means of all sets of observations are identical. A rejection of H_0 implies that significant differences do exist and that a transformation can be found which will better define the separation. Using the set of p variates for each of the n groups, a set of transformed, discriminant variables, are constructed in such a way that the F-ratio (between groups variation/ within groups variation) for each of the variables is maximized. If more than one discriminant function is constructed, the additional criterion is applied that they must all be linearly independent, that is, orthogonal to one another. The maximum number of functions necessary to describe all of the between group variation is equal to either the number of variables or one less than the number of groups; whichever is smaller, i.e. $s = \min(n-1, p)$.

More specifically, if the group means on all the variates is expressed as the vector \tilde{y} , then the discriminant analysis problem is to determine the weights to apply to each \tilde{y} to form the \tilde{z} variates having the described properties. Thus we require

$$\tilde{z}_i = \alpha_i' \tilde{y} \quad \dots (8)$$

where:

\tilde{y} = the vector of the group means for p variates.

\tilde{z}_i = the transformed vector.

α_i = vector weights. The elements of $\tilde{\alpha}$ are the discriminant function coefficients.

For a matrix of between groups sum of squares and cross products, \tilde{A} the corresponding between groups function for \tilde{z}_i is given by $\tilde{\alpha}_i' \tilde{A} \tilde{\alpha}_i$. Similarly for a matrix of within groups sum of squares and cross products, \tilde{W} , the corresponding function for \tilde{z}_i is $\tilde{\alpha}_i' \tilde{W} \tilde{\alpha}_i$.

This means that the ratio to be maximized is

$$\lambda_i = \frac{\sum \tilde{\alpha}_i' \tilde{A} \tilde{\alpha}_i}{\sum \tilde{\alpha}_i' \tilde{W} \tilde{\alpha}_i} \quad \dots(9)$$

subject to the restriction that the within groups variance of \tilde{Z} be unity:

$$\frac{1}{n_e} \sum \tilde{\alpha}_i' \tilde{W} \tilde{\alpha}_i = 1 \quad \dots(10)$$

For more than one discriminant function, the additional constraint that all functions be orthogonal requires

$$\sum \tilde{\alpha}_i' \tilde{W} \tilde{\alpha}_j = 0 \quad \dots(11)$$

The value which maximizes the resulting function given in equation 9 is the eigenvalue, or the canonical variance, and is a measure of the between groups variation. Thus larger values indicate a greater disparity between the group means on any given discriminant variable. In a stepwise discriminant analysis, all p of the variates are

not used at once. Rather, it is recognized that some variables may be better discriminators than others, or alternatively, that there may be a dependence between one or more of the variables thus rendering some of them redundant. Various criteria can be used to determine which variable has the best discriminating power, followed by the next best and so forth. This process continues until the discrimination process does not produce significantly better results if more of the variables are considered.

A number of criteria are available for such a decision making process. Rao's V (63,64) is a generalized distance measure. The variable selected is the one which contributes to the largest increase in V when added to the previous variables. This amounts to the greatest overall separation of the groups. For a large number of cases, Rao's V statistic approaches a χ^2 distribution.

In this study, use was made of the SPSS (Statistical Package for the Social Sciences) program for discriminant analysis (65). The input for this program requires that the specific variables to be considered be entered as a vector

for each group member. It was not necessary that actual concentration values for each element be entered, thus, normalized relative peak areas were utilized.

The analysis of the spectral data using the GAMANAL program resulted in the energies, net areas and other related statistics for each peak appearing in the spectrum being printed. A computer program AREAS was written to select the peaks of interest, normalize them to the Compton peak, average the values from the ten replicates and output them in a form readily acceptable by the SPSS program.

A stepwise discriminant analysis was used. Several criteria were tried for the stepwise procedure but it was found that the best results were obtained when the Rao's V statistic was applied.

3 RESULTS

3.1 Quantitative Analysis

3.1.1 Whole Coal Samples

Normalized peak areas were obtained for 12 elements: K, Ca, Ti, Cr, Fe, Ni, Cu, Zn, As, Br, Rb and Sr.

Table VI shows typical normalized areas and errors (1 standard deviation) for a representative sample from each seam. A complete table of the normalized peak areas and errors for all of the coal samples analyzed is given in Appendix II. The total error, which includes those previously discussed (i.e. counting error, sample preparation, etc) for the ten replicate samples ranges from about 2% for elements present in significant amounts eg. Fe, to 30% for elements in low concentration eg Cr.

The linear regression equations obtained from the calibration procedure were applied to each of the Hat Creek and Crowsnest Coalfield samples. This resulted in absolute concentration values for the trace elements and minor constituents. Since Cr has large errors associated with it,

Table VI. Mean values for the normalized peak areas μ for the trace elements in selected samples.

$$\frac{\text{area}}{\text{compton}} \times 10^2$$

(% error at 1 S.D.)

Sample I.D.	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn	As	Br	Rb	Sr	R/C ratio
1-10	0.39 (7)	1.4 (5)	2.6 (1)	0.14 (15)	13 (1)	0.55 (6)	0.41 (12)	0.68 (8)	0.21 (19)	0.29 (16)	0.59 (8)	17 (2)	47 (0.5)
5-8	0.90 (9)	3.6 (4)	4.4 (4)	0.17 (3)	18 (3)	0.17 (22)	0.36 (10)	0.68 (9)	0.15 (12)	0.16 (17)	0.64 (10)	26 (1)	45 (0.7)
6-1	1.2 (4)	5.7 (4)	5.2 (4)	0.22 (23)	96 (4)	0.19 (13)	0.47 (9)	0.71 (11)	0.18 (6)	—	1.9 (5)	22 (4)	59 (0.4)
7-1	0.71 (6)	6.4 (5)	4.8 (6)	0.15 (16)	52 (5)	0.15 (14)	0.58 (6)	0.59 (13)	0.20 (11)	—	1.3 (13)	22 (4)	56 (1)
9-3	0.45 (5)	12.4 (1)	2.8 (2)	—	50 (2)	—	0.30 (17)	0.27 (16)	0.11 (16)	0.14 (15)	0.46 (18)	4.5 (4)	50 (0.8)
10-3	0.56 (14)	11.8 (3)	2.8 (5)	—	91 (4)	0.55 (12)	0.44 (14)	0.15 (7)	0.48 (5)	0.19 (34)	0.79 (11)	17 (2)	53 (0.5)
A-6	0.11 (5)	4.0 (5)	4.4 (3)	0.20 (13)	11 (2)	0.24 (16)	0.43 (17)	0.76 (9)	0.16 (19)	0.16 (14)	0.84 (6)	28 (2)	48 (0.8)
H.C.	0.87 (2)	4.5 (2)	7.3 (3)	0.49 (6.7)	296 (3)	0.84 (8)	1.7 (5)	2.3 (6)	0.90 (9)	2.7 (3)	2.0 (7)	25 (2)	78 (1)
NBS (1632)	1.1 (10)	3.6 (6)	3.0 (3)	0.18 (28)	98 (2)	0.30 (20)	0.52 (10)	1.1 (22)	0.59 (29)	1.2 (2)	1.8 (5)	1.4 (2)	49 (8)

and is present in quantities which are very near the detection limit, concentrations of this element could not be accurately determined. Similarly, a non-linear calibration curve was obtained for Zn. While this, in itself, would not prevent the calculation of the concentration values, the errors associated with the determinations were such that no meaningful results could be obtained. The absolute concentration values for the remaining elements in a selection of samples are given in table VII along with the calculated errors.

Using the method previously described, ten coal samples were analyzed using neutron activation analysis. The resulting concentrations for these samples are shown in table VIII.

The three Hat Creek samples had been analysed by three independent laboratories prior to the analysis done in this study. These laboratory analyses were conducted, in one instance, by spark source mass spectrometry and in the other instances by atomic absorption. In all cases, elaborate sample preparation was required involving either a digestion procedure or ashing, with a correction factor

Table VII. Concentration of the trace elements in Hat Creek and selected Crownsnest coals.

Sample	concentration $\mu\text{g/g}$ (error at 1 S.D.)										
	K	Ca	Ti	Fe	Ni	Cu	As	Br	Rb	Sr	
A-6	1520 (150)	4700 (260)	1550 (50)	9500 (150)	8.8 (3.0)	17 (6)	2.2 (0.3)	1.7 (0.9)	9.9 (1.0)	300 (7)	
1-10	803 (80)	1470 (100)	900 (10)	770 (20)	38 (3)	17 (3)	2.6 (0.4)	3.7 (0.7)	5.8 (0.5)	512 (2)	
5-8	2240 (200)	4100 (250)	1500 (70)	1200 (40)	5.3 (2.0)	14 (2)	2.1 (0.2)	1.7 (0.4)	7.4 (1.2)	287 (3)	
6-1	3160 (150)	6800 (300)	1830 (75)	8300 (400)	6.8 (2.2)	20 (3)	2.5 (0.4)	0.81 (0.05)	22.6 (1.1)	240 (10)	
7-1	1700 (130)	7600 (250)	1650 (70)	4300 (250)	1.8 (3.1)	21 (2)	2.6 (0.2)	—	14.8 (1.9)	240 (11)	
9-3	940 (50)	1200 (200)	960 (20)	4100 (100)	—	7 (2)	1.7 (0.2)	1.3 (0.5)	4.7 (1.1)	48 (2)	
10-3	1270 (200)	14600 (450)	950 (50)	7900 (300)	38 (5.7)	16 (7)	5.0 (0.2)	2.6 (1.0)	8.8 (1.0)	186 (4)	
HC 1	2800 (200)	4600 (150)	2300 (50)	31000 (2000)	47 (4)	60 (4)	6.8 (0.3)	6.0 (1)	20.2 (2.1)	249 (4)	
HC 2	610 (120)	3100 (300)	1300 (50)	6900 (300)	19 (4)	36 (4)	4.3 (0.5)	25 (1)	7.3 (1.1)	44 (5)	
HC 3	2200 (100)	5300 (170)	2600 (50)	28000 (500)	64 (6)	76 (4)	8.6 (0.7)	43 (1)	24.6 (1.3)	280 (10)	

Table VIII. Comparison of concentration values for Fe, Sr and As using XRF and NAA.

Sample	Element	Method	
		XRF (present study)	NAA (TRIUMF)
A-5	Fe	1700 ± 200	<8000
	Sr	124 ± 12	95 ± 15
	As	2.6 ± 0.6	0.9 ± 0.2
1-1	Fe	3050 ± 90	4600 ± 2800
	Sr	154 ± 3	135 ± 15
	As	3.1 ± 0.3	2.1 ± 0.4
1-2	Fe	3900 ± 100	<9100
	Sr	420 ± 7	310 ± 30
	As	2.4 ± 0.4	0.90 ± 0.30
1-5	Fe	4400 ± 100	4100 ± 2000
	Sr	562 ± 9	420 ± 40
	As	2.3 ± 1.0	0.4 ± 0.1
1-10	Fe	775 ± 25	<6600
	Sr	512 ± 3	175 ± 20
	As	2.6 ± 0.4	1.0 ± 0.3
1-12	Fe	3000 ± 200	4700 ± 2200
	Sr	156 ± 20	245 ± 30
	As	3.0 ± 0.5	1.4 ± 0.4
7-1	Fe	4300 ± 250	6100 ± 2800
	Sr	240 ± 11	230 ± 30
	As	2.6 ± 0.3	1.3 ± 0.3
6-1	Fe	8300 ± 400	10200 ± 3600
	Sr	240 ± 10	230 ± 30
	As	2.5 ± 0.4	0.8 ± 0.2
9-1	Fe	1500 ± 50	5100 ± 2500
	Sr	41 ± 2	42 ± 8
	As	2.3 ± 0.5	0.5 ± 0.2
10-3	Fe	7900 ± 350	6700 ± 2500
	Sr	186 ± 4	175 ± 20
	As	5.0 ± 0.2	8.9 ± 0.9

All values reported as µg/g.

applied to relate the resulting concentration values to a whole coal value. Results from these analyses along with those obtained in this study are shown in table IX.

As an additional check on the accuracy of the results obtained in this study, comparisons were made with the results obtained on the five U.S. coal samples. The analyses performed by the IGS employed x-ray fluorescence as well as neutron activation analysis and optical emission spectrochemical analysis. These values are shown in table X.

3.1.2 Ashing and Leaching Results

Each of the samples responded slightly differently to the ashing procedure. The characteristics of these samples after the ashing procedure as well as the percent weight loss under the various conditions is given in table XI.

Although absolute concentration values were not obtained for the ashed samples, trends relating the relative concentration versus ashing temperature are shown in figure 12 for one of the Hat Creek samples.

Table IX. Concentration values from various analyses of Hat Creek coal ⁸⁶ samples.

<u>Hat Creek 1</u>					
Element	Analysis method		Spark source Mass spectrometry (Lab 1)	AA (Lab 2)	AA (Lab 3)
	XRF (present study)	NAA (TRIUMF)			
K	2800 ± 200 ^b		MCA ^a		
Ca	4600 ± 150		MC		
Ti	2300 ± 50		MC		
Fe	31000 ± 500	29100 ± 8400	MC		
Ni	47 ± 4		13,10,18		
Cu	60 ± 4		48,68,33	40	49
As	6.8 ± 0.3	10.8 ± 1.2	4,6,5	6	12,12,18
Br	6.0 ± 1		5,1,4		
Rb	20 ± 2		15,24,21		
Sr	249 ± 4	450 ± 100	250,250,180	170,175	222,218
<u>Hat Creek 2</u>					
K	610 ± 120		MC		
Ca	3100 ± 300		MC		
Ti	1300 ± 50		MC		
Fe	6900 ± 300	5700 ± 2700	MC		
Ni	19 ± 4		7,8,10		
Cu	36 ± 4		38,27,29	28	60,58
As	4.3 ± 0.5		3,5,5		20,18,24
Br	25 ± 1		2,2,3		
Rb	7.3 ± 1.1		4,4,8		
Sr	44 ± 5		50,38,39	70	192,189
<u>Hat Creek 3</u>					
K	2200 ± 100		MC		
Ca	5399 ± 170		MC		
Ti	2600 ± 50		MC		
Fe	28000 ± 500	26400 ± 7600	MC		
Ni	64 ± 6		8,11,84		
Cu	76 ± 4		25,21,44	66,64	57,62,61
As	8.6 ± 0.7	14.2 ± 1.5	4,5,8	10	17,18,22
Br	43 ± 1		2,5,7		
Rb	24.6 ± 1.3		9,7,16		
Sr	280 ± 10	260 ± 50	99,250,100		175,170

^aMC = Major Constituent

^bAll values are given in µg/g.

Table X. Concentration values ($\mu\text{g/g}$) for trace elements in five Illinois coal samples.

Sample	Analysis	Element										
		K	Ca	Ti	Fe	Ni	Cu	As	Br	Rb	Sr	
1 ^b (18446)	SFU	<125	7800 (250) ^a	500 (50)	1300 (100)	<2.7	7.6 (1.8)	<0.6	<1.3	<1.4	395 (5)	
	Illinois	100	15000	400	3000	1.6	9.4	0.34	1.4	<1.0	400	
2 (17309)	SFU	<125	9800 (1000)	460 (50)	2800 (450)	<2.7	15 (10)	1.8 (0.2)	1.1 (0.5)	1.3 (0.5)	175 (20)	
	Illinois	200	24700	500	5500	5	22	1.3	4.0	—	—	
3 (18844)	SFU	1000 (125)	3500 (100)	700 (50)	9500 (250)	4.5 (2.0)	16 (7)	6.8 (0.5)	16 (1)	9.1 (1.0)	115 (5)	
	Illinois	1300	5500	800	11000	6.4	15	15	18	10	130	
4 (18463)	SFU	3000 (200)	8100 (200)	790 (30)	8800 (250)	10 (3)	23 (4)	5.2 (0.5)	<1.3	22.5 (2)	240 (10)	
	Illinois	3200	13000	700	10000	9.5	18	7.2	0.5	29	470	
5 (18437)	SFU	400 (80)	16700 (900)	250 (20)	3000 (125)	<2.7	6 (3)	4.4 (0.5)	<1.3	1.3 (0.5)	420 (10)	
	Illinois	700	29000	300	5000	5.3	4.8	9.8	1.9	1.9	380	

^aError on XRF analysis— $\mu\text{g/g}$ for 1 standard deviation.

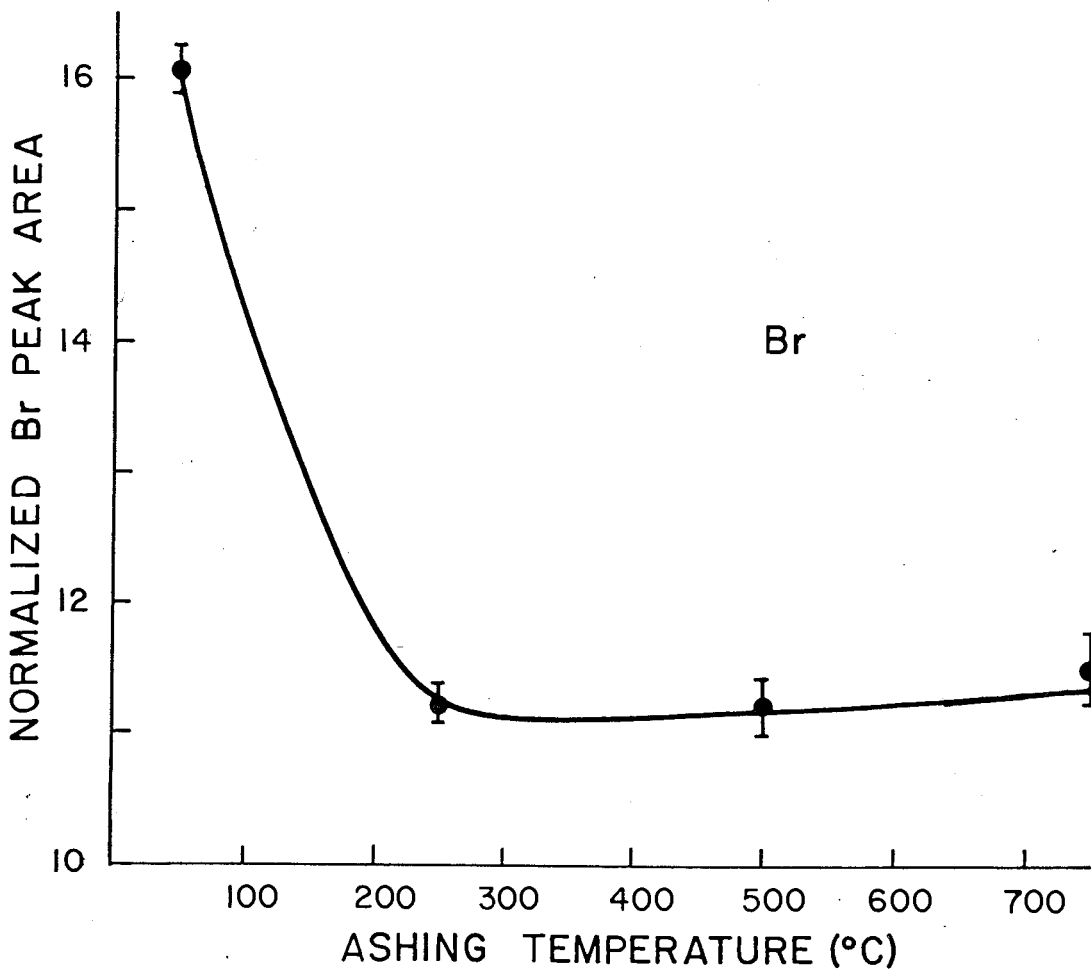
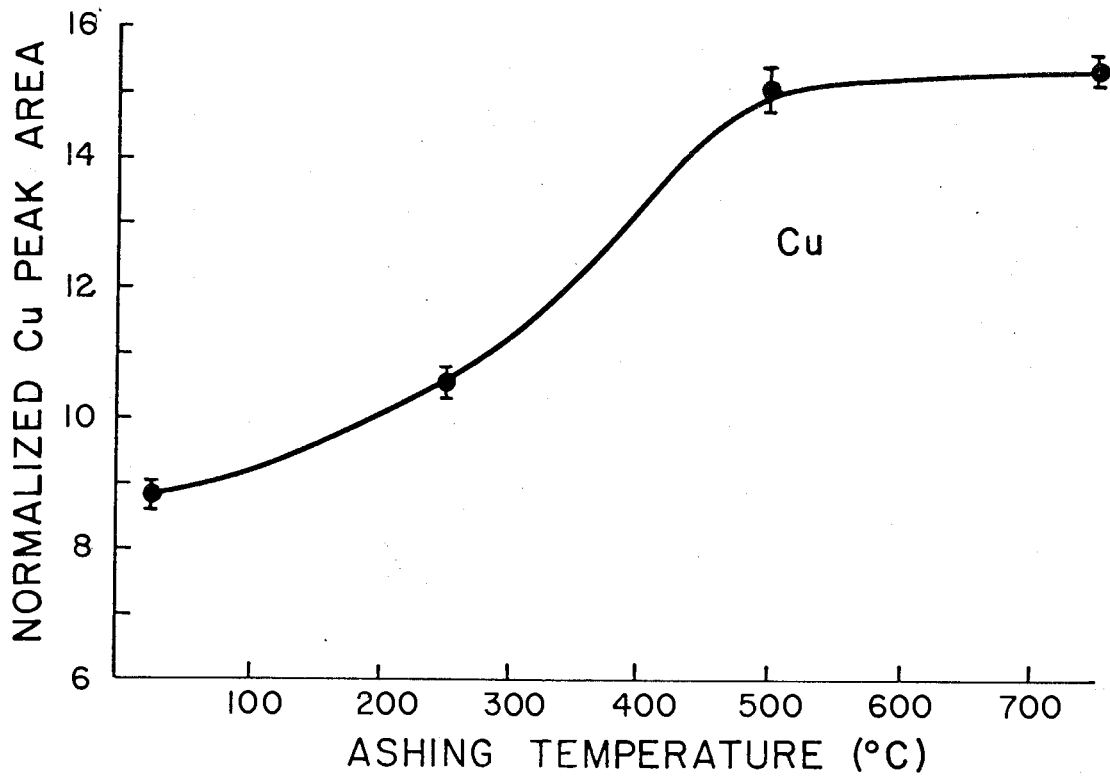
^bNumber represents Illinois identification number.

Table XI. Characteristics of ashed samples.

Sample	Ashing condition	Characteristics of ash	% weight loss
Hat Creek 2	1 hr at 250 C	medium grey	34%
	1.5 hr at 500 C	light grey-tan, powdery	80%
	1.5 hr at 750 C	charred surface light tan ash	74%
5-1	1 hr at 250 C	dark grey	55%
	1.5 hr at 500 C	medium grey, powdery	86%
	1.5 hr at 750 C	grey to white	88%
A-6	1 hr at 250 C	black	11%
	1.5 hr at 500 C	dark grey	77%
	1.5 hr at 750 C	light brown; much remained black	61%
NBS	1 hr at 250 C	black	20%
	1.5 hr at 500 C	medium grey	80%
	1.5 hr at 750 C	light tan, bottom caked black	63%

Figure 12

Relationship Between Normalized Peak Area and Ashing
Temperature for Cu and Br in an Ashed Hat Creek Sample.



Results of the leaching experiments are shown in figures 13 and 14. These graphs show the concentration of Ca and Sr as a function of the pH of the leaching solution under the two experimental conditions as described previously. Absolute concentration values for the elements in the three samples subjected to the leaching procedure are given in table XII.

3.2 Qualitative Analysis.

The relative normalized peak areas for the 13 elements K, Ti, Ca, Cr, Fe, Ti, Ni, Cu, Zn, As, Br, Rb, and Sr and the Rayleigh scatter peak were used in the discriminant analysis.

A correlation matrix generated for the normalized areas is presented in table XIII. As a check on the linearity of the relationships and hence the validity of the correlation matrix used to perform the discriminant analysis, scattergrams were plotted for each pair of variables. One of these is shown in figure 15. Since extreme observations, or outliers, can substantially affect

Figure 13

Relationship Between Remaining Ca in a Leached Sample
and the pH of the Solution for NBS Coal and Hat Creek
Coal Under Leaching Conditions A and B.

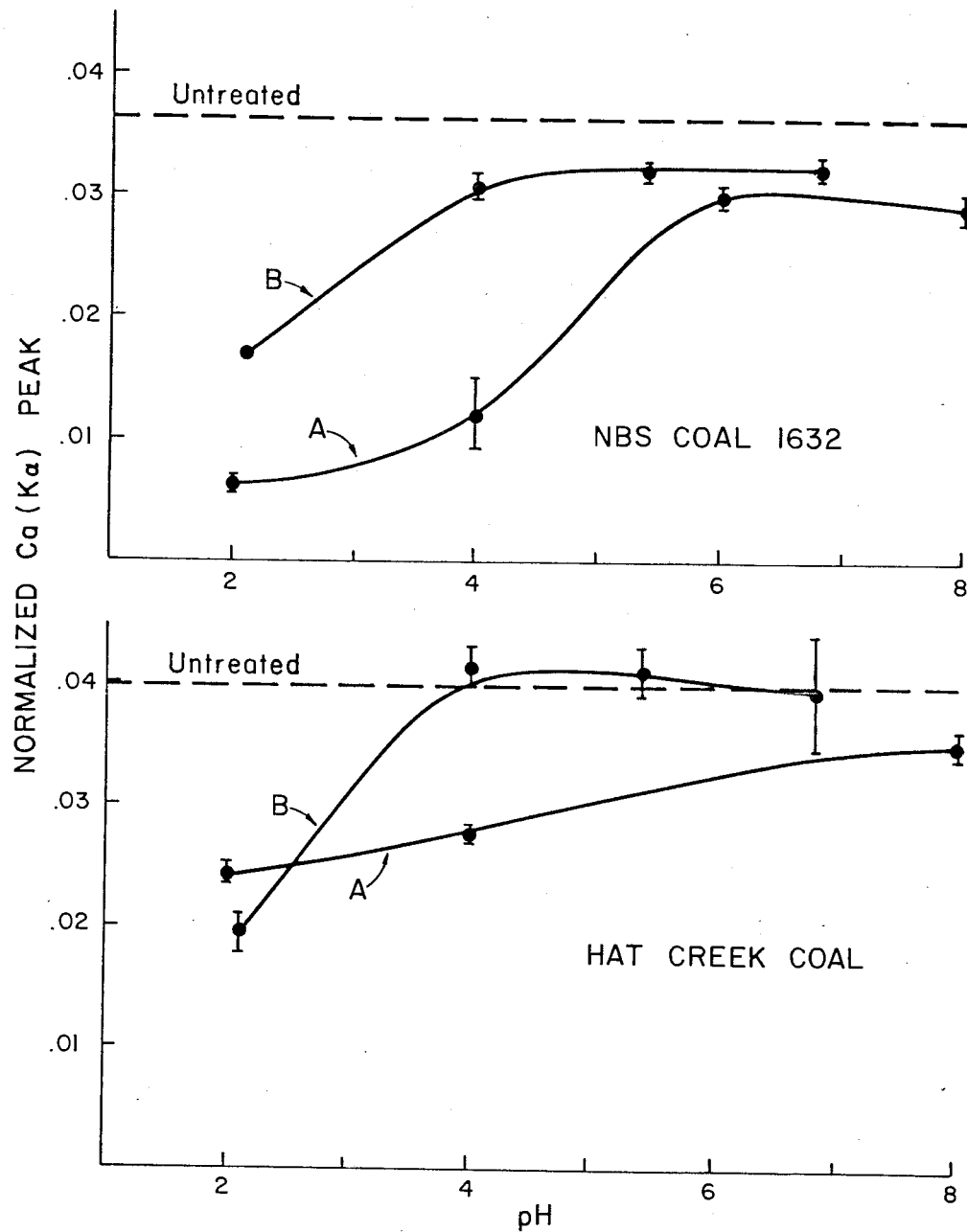


Figure 14

Relationship Between Remaining Sr in a Leached Sample
and the pH of the Solution for NBS Coal and Hat Creek
Coal Under Leaching Conditions A and B.

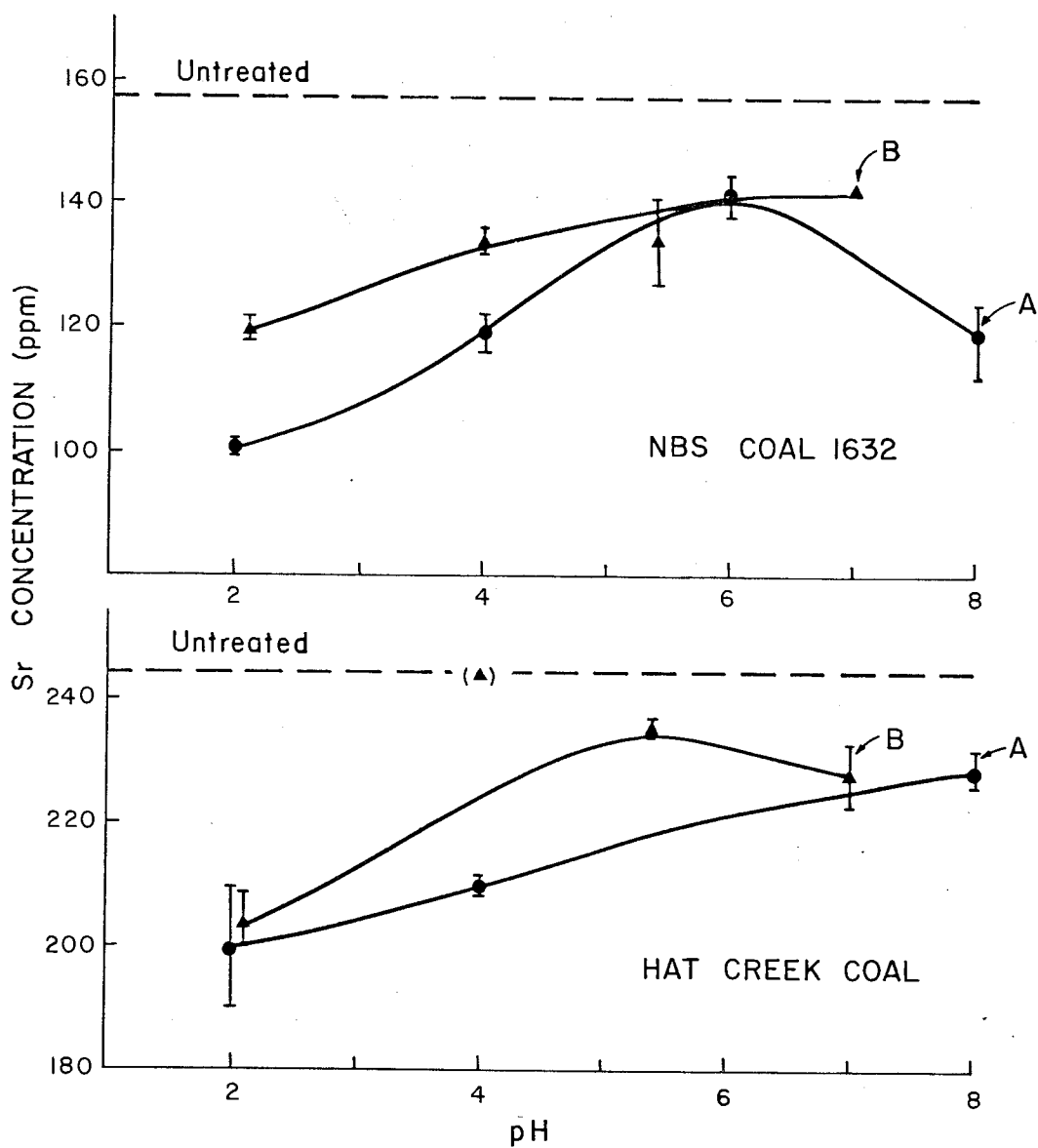


Table XII. (cont'd)

Sample	Conditions	Element										
		K	Ca	Ti	Fe	Cu	As	Br	Rb	Sr		
NBS	pH 2.1 (B)	3075	1800	1100	7800	13	4.0	17.8	19	120.		
									(1)			
	pH 4 (B)	2900	3550	1040 (25)	8800 (300)	19 (3)	1.7 (0.4)	15.6 (2)	21 (1)	135 (3)		
	pH 5.4 (B)	3050	3700	1060 (50)	8600 (300)	19 (2)	4.8 (0.5)	19.3 (2)	21 (1)	135 (7)		
	distilled H ₂ O (B)	2950	3725	1070	8900	23	4.9 (0.2)	—	22	142		
9-1	untreated	2340 (50)	5200 (100)	1350 (100)	1450 (50)	12 (2)	2.3 (0.4)	<1.3	4.8 (0.7)	42 (1)		
	pH 2 (A)	—	4750 (50)	1250 (100)	1400 (50)	12 (2)	2.4 (0.4)	—	4.2 (0.2)	36 (1)		
	pH 4 (A)	—	6700 (100)	1250 (50)	1470 (100)	—	2.2 (0.2)	—	4.4 (0.7)	41 (1)		
	pH 6 (A)	—	7600 (150)	1100 (50)	1250 (50)	8.3 (2)	2.3 (0.4)	—	5.5 (1.9)	38 (2)		
9-1	pH 2.1 (B)	790 (50)	—	1250 (200)	1600 (100)	20 (5)	—	—	3.9 (0.2)	37 (5)		
	pH 4 (B)	1200 (250)	8300 (1000)	970 (300)	1500 (100)	—	—	—	—	41 (3)		
	pH 5.4 (B)	1200 (250)	9300 (400)	1300 (100)	1550 (100)	18 (3)	2.3 (0.2)	—	3.9 (0.2)	43 (1)		
	distilled H ₂ O (B)	1050 (200)	9000 (300)	1300 (150)	1700 (50)	15 (2)	2.1 (0.2)	—	4.3 (0.6)	42 (1)		

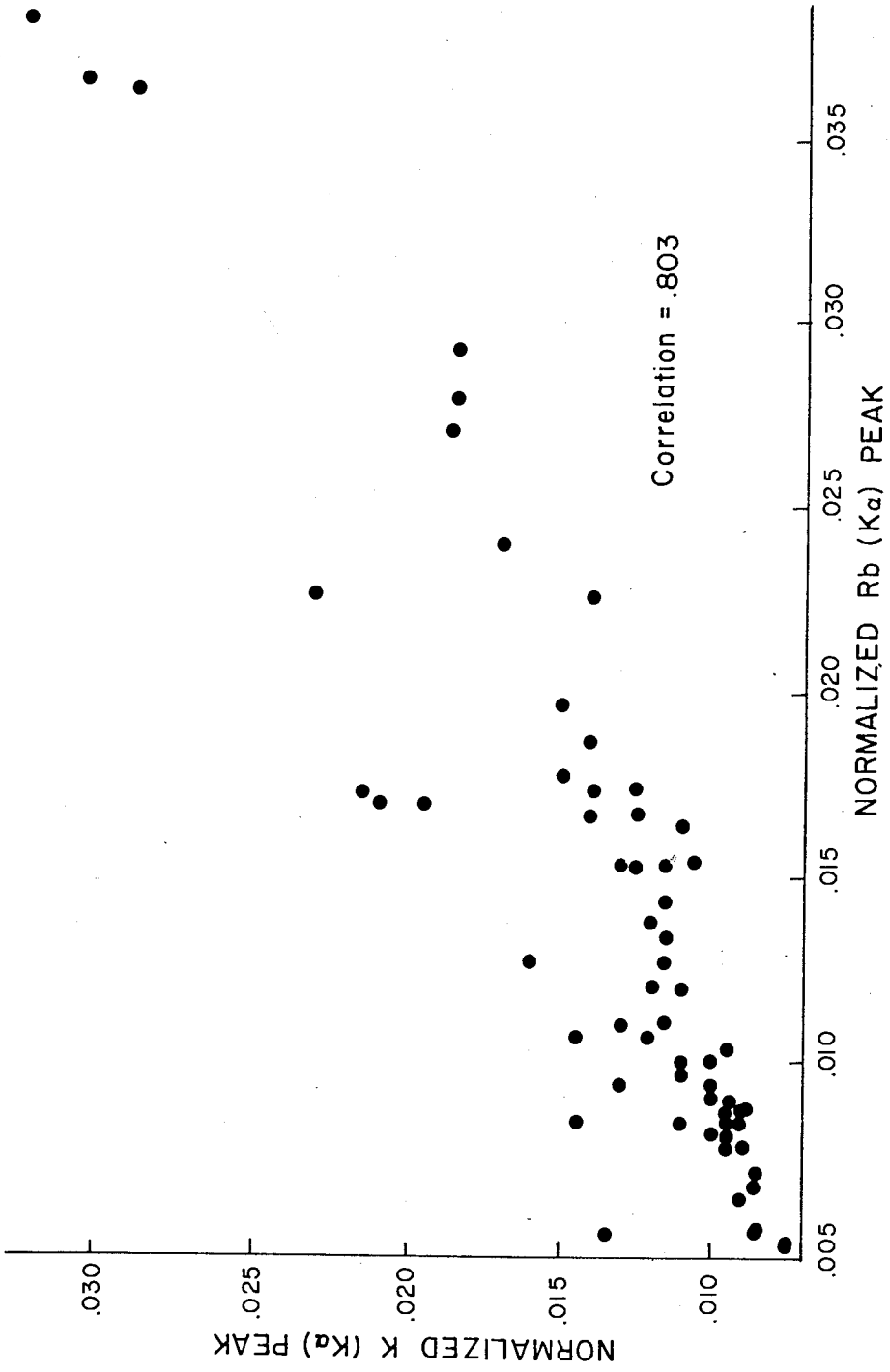
aLeaching experiments performed according to procedure A.
 bBleaching experiments performed according to procedure B.
 cErrors in µg/g for 1 standard deviation.

Table XIII. Coefficients of correlation between elements from the Crowsnest coal region.

	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn	As	Br	Rb	Sr	ratio
K	1.0	0.220	0.444	0.668	0.232	0.359	0.401	0.405	0.278	-0.075	0.803	0.171	0.439
Ca		1.0	0.264	0.243	0.114	0.411	0.082	0.058	0.024	0.186	0.198	0.214	0.361
Ti			1.0	0.570	0.359	0.270	0.662	0.268	0.363	-0.094	0.585	0.480	0.340
Cr				1.0	0.186	0.400	0.520	0.530	0.339	-0.154	0.594	0.271	0.386
Fe					1.0	0.062	0.272	0.081	0.420	-0.140	0.197	0.087	0.359
Ni						1.0	0.489	0.769	0.246	0.168	0.289	0.488	0.136
Cu							1.0	0.530	0.477	0.011	0.572	0.236	0.450
Zn								1.0	0.381	0.065	0.389	0.322	0.312
As									1.0	0.122	0.381	0.086	0.629
Br										1.0	-0.002	-0.104	-0.069
Rb											1.0	0.289	0.454
Sr												1.0	0.220
ratio													1.0

Figure 15

Scattergram Showing Relationship Between K and Rb in
Crowsnest Coal Samples.



the value of the mean and hence give an unreliable estimate of the calculated parameters, all such values were eliminated from the analysis by inspection of the individual scattergrams. Only obviously deviant values were eliminated.

A stepwise discriminant analysis was then applied to the 37 Sparwood Ridge samples. These coal samples were classified according to the particular coal seam from which they came on the basis of their trace element distributions. The descending order of discrimination by the variables meeting the F statistic criterion was Br, Sr, R/C ratio, Rb, Ni and Ti. Since the 7 seams were involved in the analysis, six discriminant functions were generated of which the first three accounted for 97% of the discriminating power. The statistics generated for the discrimination along with the levels of significance are shown in table XIV. Also included are both the standardized and unstandardized discriminant function coefficients for the six discriminant functions.

Table XIV. Statistics resulting from discriminant analysis on 37 Sparwood 98 Ridge seam samples.

Unstandardized discriminant function coefficients						
Element	Canonical function					
	1	2	3	4	5	6
K	-3.39	26.1	-8.85	20.8	-11.4	11.1
Ca	0.353	3.91	-14.9	4.73	-6.48	-9.45
Ti	35.8	105	18.9	9.31	18.1	-50.8
Cr	-441	550	-1314	254	553	16.3
Ni	-188	91.9	30.7	152	-192	-76.1
Br	-1173	-375	-125	-168	804	-254
Rb	-91.8	-128	61.0	-88.0	-43.8	-17.5
Sr	-6.62	8.45	9.36	0.230	0.129	6.29
ratio	20.5	-13.8	10.5	10.0	3.14	2.27
constant	-6.81	4.89	-4.99	-6.15	-2.51	0.796

Standardized discriminant function coefficients						
Element	Canonical function					
	1	2	3	4	5	6
K	-0.109	0.842	-0.285	0.673	-0.367	0.357
Ca	0.0246	0.273	-1.04	0.331	-0.453	-0.661
Ti	0.570	1.67	0.302	0.148	0.288	0.809
Cr	-0.536	0.668	-1.59	0.310	0.672	0.0198
Ni	-0.430	0.210	0.0703	0.347	0.439	-0.174
Br	-0.917	-0.293	-0.0981	-0.131	0.629	-0.199
Rb	-0.822	-1.15	0.546	-0.788	-0.392	-0.157
Sr	-0.819	-1.05	1.16	-0.0285	0.0160	0.779
ratio	1.22	-0.820	0.624	0.596	0.187	0.135

Table XIV. (cont'd)

Function	Eigenvalue	% of Variance	canonical correlation squared	Chi-squared	significance
1	5.675	65.2	0.850	110	0
2	1.380	15.9	0.580	58	0.029
3	0.880	10.1	0.468	35	0.165
4	0.367	4.22	0.268	18	0.448
5	0.276	3.19	0.217	10	0.469
6	0.120	1.38	0.107	3	0.547

Wilks' Lambda

0.0171

0.114

0.272

0.511

0.699

0.893

As a visual aid of the discrimination, the discriminant scores for the samples were computed and a plot of these using the first two discriminant functions was generated. A group mean was determined for each of the functions by averaging the scores for the samples within a particular group. The group means of all the functions resulted in a group centroid. Such a plot, for the first two discriminant functions, showing the individual samples as well as the group centroids for the Sparwood ridge samples is shown in figure 16.

As a test of the discrimination, the standardized coefficients were reapplied to each of the samples, treating them as unknowns. A classification score was computed for each of the samples. Under the assumption that the classification scores conform to a multivariate normal distribution, these scores were converted into probabilities of group membership. Thus when treated as unknowns each of the coal samples could be grouped according to the seam to which it had the highest probability of belonging. A summary of this reclassification for the Sparwood Ridge samples is given in table XV. It was found that, based on the derived discriminant functions, 80% of the samples were correctly classified.

Figure 16

Plot of the First Two Discriminant Functions for the
Sparwood Ridge Seam Samples.

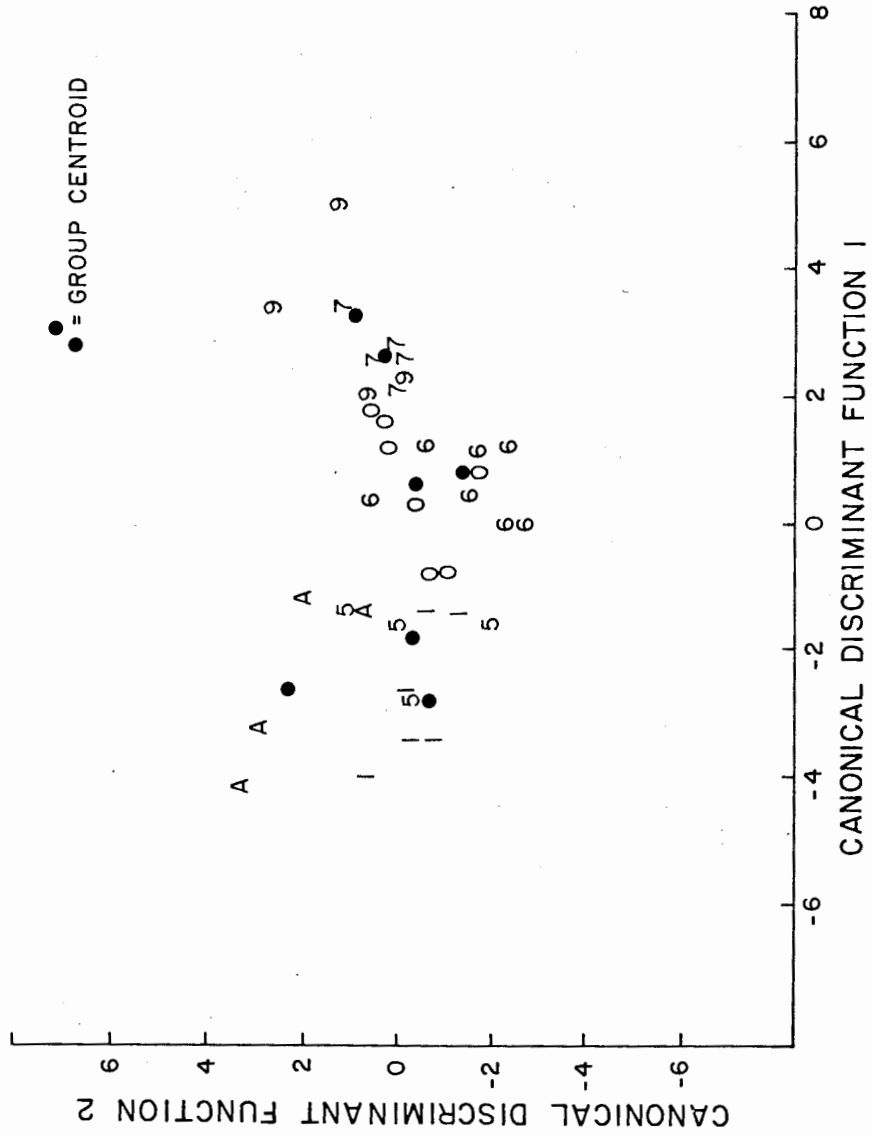


Table XV. Summary of reclassification of Sparwood Ridge seam samples.

Actual seam	Predicted seam						
	1	5	6	7	9	10	A
1	4 (66.7%)	1 (16.7%)	—	—	—	1 (16.7%)	—
5	1 (25%)	3 (75%)	—	—	—	—	—
6	—	—	5 (83%)	—	—	1 (17%)	—
7	—	—	—	5 (100%)	—	—	—
9	—	—	—	—	3 (75%)	1 (25%)	—
10	—	—	1 (14.3%)	—	6 (86%)	—	—
A	—	1 (25%)	—	—	—	—	3 (75%)

A second discriminant analysis was applied to the samples from Sparwood Ridge, Hat Creek and areas 2-5 as identified in figures 4 and 5. In this instance, the samples were grouped according to location with no consideration given to the seam from which they came. The order of inclusion of trace elements in the stepwise procedure was Br, Ti, Zn, Cu, As, Sr and Ca. The purpose of such an analysis was to determine if the between location variation was greater than the pooled within location variation. A set of discriminating functions was generated which maximized the differences. The discriminant functions along with the related statistics for the analysis are given in table XVI. A plot of the sample discriminant scores using the first two discriminant functions is shown in figure 17 and the result of the reclassification in which the samples were treated as unknowns is given in table XVII. Based on the reclassification, it was found that 93% of the samples were correctly placed.

Table XVI. Statistics resulting from discriminant analysis by location of ¹⁰⁴Crowsnest and Hat Creek samples.

Unstandardized discriminant function coefficients						
Element	Canonical function					
	1	2	3	4	5	6
K	221	153	-21.9	-224	103	181
Ca	-4.53	-4.27	5.75	-6.59	14.4	-20.1
Ti	-1.00	4.14	-3.03	-7.80	-10.4	-9.38
Fe	-1.86	-2.02	-2.15	0.512	0.270	0.306
Ni	68.4	129	-290	-220	-87.2	-148
Cu	-248	169	-92.7	-106	-20.8	-157
Zn	6.71	-57.3	42.8	97.9	-57.0	48.8
Br	-691	821	-106	-3.47	43.9	67.8
Rb	-211	-138	60.6	73.4	-45.6	-31.3
Sr	0.336	-0.668	-0.264	6.56	2.99	1.00
ratio	29.0	20.4	-14.4	-0.578	-1.19	0.591
constant	-0.97	-10.1	8.51	1.16	-0.124	0.570

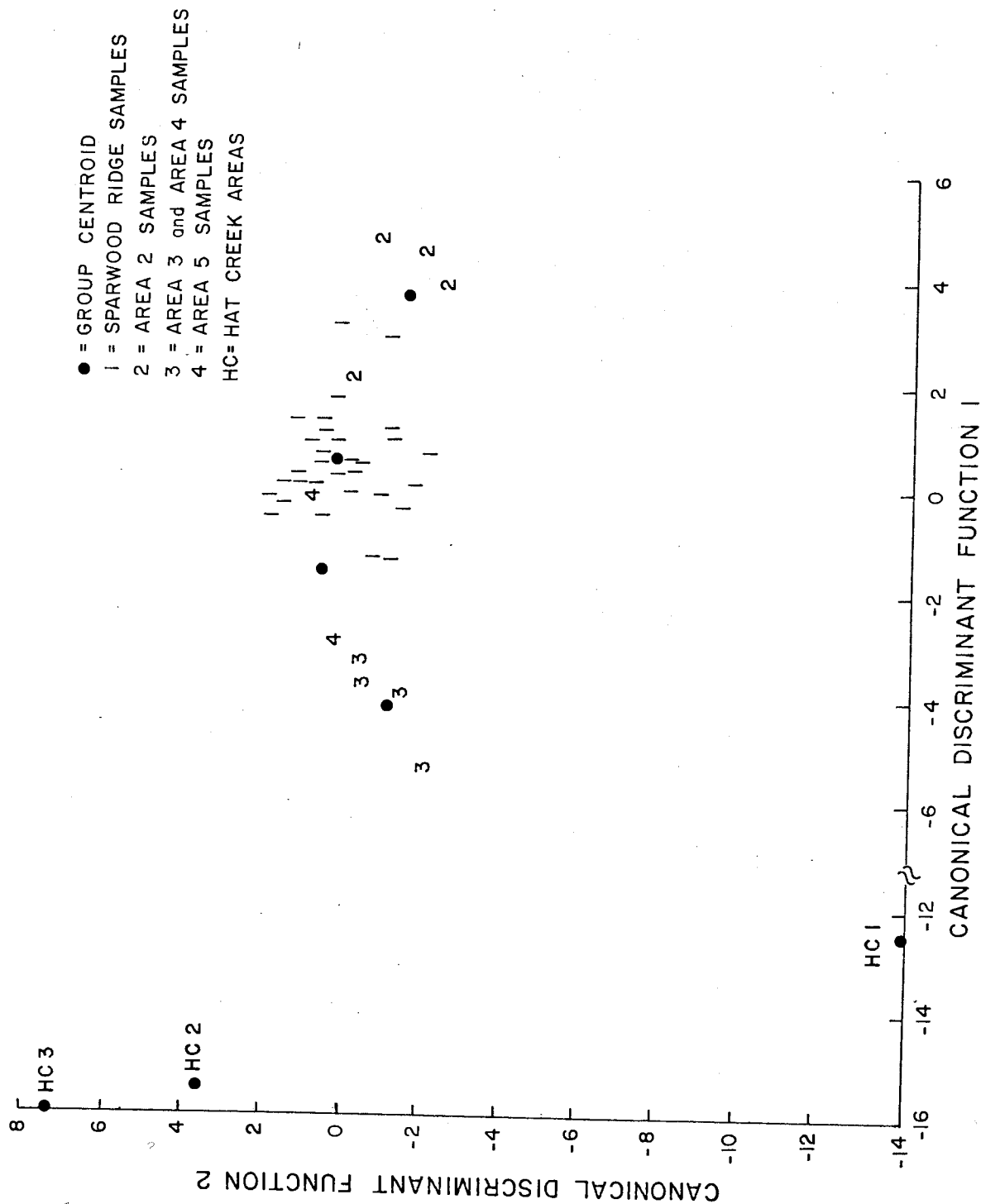
Standardized discriminant function coefficients						
Element	Canonical function					
	1	2	3	4	5	6
K	1.23	0.851	-0.122	-1.25	0.575	1.01
Ca	-0.191	-0.180	0.242	-0.278	0.607	-0.847
Ti	-0.0486	0.201	-0.147	-0.378	-0.506	-0.454
Fe	-0.564	-0.614	-0.654	0.0155	0.0821	0.0931
Ni	-0.135	0.253	-0.572	-0.434	-0.172	-0.291
Cu	-0.454	0.309	-0.169	-0.194	-0.0381	-0.288
Zn	0.0613	-0.523	0.390	0.894	-0.520	0.455
Br	-0.710	0.844	-0.109	-0.00357	0.0451	0.0697
Rb	-1.88	-1.23	0.540	0.654	-0.406	-0.279
Sr	0.00415	-0.0825	-0.0326	0.810	0.369	0.123
ratio	1.44	1.02	-0.717	-0.0288	-0.0595	0.0295

Table XVI. (cont'd)

Function	Eigenvalue	% of Variance	Canonical correlation squared	Chi-squared	Significance	Wilks' Lambda
1	266	86.1	0.996	733	0	0.00001
2	38.6	12.5	0.975	375	0	0.0028
3	3.57	1.16	0.781	140	0	0.111
4	0.339	0.11	0.253	43.2	0.0094	0.510
5	0.234	0.08	0.190	24.5	0.040	0.682
6	0.188	0.06	0.158	11.0	0.087	0.841

Figure 17

Plot of the First Two Discriminant Functions for
the Samples From the Five Crowsnest Coalfield Areas
and the Hat Creek Area.



4. DISCUSSION OF RESULTS

4.1 Quantitative Analysis

4.1.1 Whole Coal Samples

The trace element concentrations were calculated using the calibration curves generated from the compton normalized areas on the NBS coal standard as described in section 2.7.1. Inspection of these curves (figure 11) shows that a small non-zero intercept resulted in each case. This was attributed to the presence of some residual background not accounted for by the normalization process.

A check on the linearity of the regression curve fit to the calibration data showed that the linear model was appropriate. Two of the curves, K and Ti showed some evidence of 'levelling off' at higher concentrations. However the linear fit was still within the error limits of the calibration values. Such deviations from a perfect fit are the result of the errors previously discussed, The largest being any deviation from homogeneity within the

samples. The agreement of the predicted trace element concentration values with those values obtained using other methods confirms the propriety of the linear fit.

The trace element concentration values obtained in this study for the Hat Creek coal samples are in general agreement with those obtained using other techniques, particularly spark source mass spectrometry. It is noted that the limited range of elements that can be analyzed as well as the limited concentration range obtained using the various methods points out the difficulty in obtaining reliable concentration values on whole coal.

In general, it appears as though NAA is the least successful of the methods. The reason for the lack of success in using this method to verify the results obtained in this study are varied.

1. These tests were conducted at the TRIUMF facility in Vancouver and represent the first set of analyses performed there. As such, it is highly probable that the conditions under which the analysis was made were not properly established. Since the analysis was not conducted by the author, no check over these could be made.

2. The analysis was conducted under relatively poor neutron flux conditions resulting in questionable results.

3. Only a few elements could be analyzed for due to the long irradiation times which would be required for some of the elements of interest.

4. A method of secondary standards was employed. The sample chosen as the secondary standard had much lower trace element concentrations than the unknown samples of interest and thus errors resulted when comparisons and extrapolations were made.

The table of results gives an indication of the limited range of elements that could be successfully analyzed using atomic absorption. While the results, in general, appear to be in line with those obtained in this study and with those from the SSMS analysis, atomic absorption suffers from the fact that it is a single element technique. An additional difficulty is the fact that the sample must be in an easily volatilized form. In the case of coal this is a particularly difficult task since it is necessary to ash the coal and then digest it using aqua

regia and hydrofluoric acid. This feature also proves to be the major disadvantage of the SSMS method. When analysis is performed using either of these techniques, a correction factor must be applied to the resulting values to relate them back to a whole coal value. Such a procedure relies upon the assumption that none of the trace elements are lost in the ashing procedure. While this appears to be the case for most of the elements present, it is not possible to be certain that no volatilization of a particular element has occurred. This may contribute to the fact that in some cases, such as for bromine, the results obtained using these techniques appeared to be consistently lower than those obtained in the reported research. Furthermore, the complex preparation required in the case of AA and SSMS increase the chances of error due to either contamination or loss.

Table X gives the calculated concentrations of trace elements in the five Illinois samples. The analyses performed by the Illinois Geological Survey on the coal samples were done using both XRF and Instrumental Neutron Activation Analysis. In some cases, optical emission spectroscopy was employed. Again, close agreement is seen

between the values obtained in this study and those obtained by the IGS. Since no indication of the size of the errors were given for the concentrations obtained in the Illinois study, it is difficult to evaluate discrepancies such as for Fe in samples 1, 2 and 6 or As in sample 3. It is interesting to note the large discrepancy in the Ca values. In almost all cases, the values obtained in this study were lower by a factor of approximately two. Since Ca was not analyzed in any of the other verification studies, no check on the accuracy of the Ca analysis, in general, could be made. Furthermore, since no indication of the errors involved in the IGS study was reported, an evaluation of the resulting differences is difficult. No explanation could be found for such deviations.

Table XVIII shows the average concentration of elements in the earth's crust (Clarke values) (13,66). A comparison of these values with the concentrations of the elements in coal gives an indication of the effectiveness of the total coal forming processes in fixing various elements in coal. Such a comparison indicates that very few elements are found to be concentrated in these coals relative to the

Table XVIII. Average contents of trace elements
in the earth's crust ($\mu\text{g/g}$).

Ag	0.7	Cu	55	Ni	75
As	1.8	Fe	5630	Pb	12.5
Ba	425	Ga	15	Rb	90
Be	2.8	Ge	1.5	Se	0.05
Br	2.5	K	2090	Sr	375
Ca	4150	Li	20	Ti	570
Co	25	Mn	950	V	135
Cr	100	Mo	1.5	Zn	70

clarke values. In fact, only As shows an enrichment, in some cases, by a factor of more than two. In general, As is associated with the sulfide-rich fraction of the coal and most likely is in solid solution in the ferrous disulfides in coal (23).

In all of the coals studied, most of the elemental concentrations are lower than the clarke, with elements such as Cr, Ni, Cu and Zn being depleted by a factor of at least two.

4.1.2 Ashing and Leaching Experiments

Since the effects of a trace element can only be realized when it is released or in some other way comes into contact with the environment, it is necessary to consider the effects of the ashing and leaching processes on the coal samples.

A number of difficulties were encountered in attempting to ash the samples and establish the relative concentrations of the trace elements. One of the problems

revolved about the difficulty in the preparation of stable pellets. The necessity of using the somar binding agent required that the amount of ash used in each sample be reduced in order to avoid preparing too large a pellet. Hence, the chance of errors in the analysis was greatly increased. The second difficulty encountered was the change in matrix that occurred with the elimination of the organics from the coal. This means that while some qualitative estimate of the trend in the trace elements can be inferred from the results, no conclusions can be drawn about the actual concentration values. Nevertheless, consideration of the normalized peak areas as a function of increased temperature of the ashing process tends to show a definite increase in the level of the elements present, as shown for Cu in figure 12. Such an observation appears to be true for all elements with the exception of bromine. (figure 12). This is an indication of the nature of bromine in the coal and is consistent with the findings of Ting and Manahan (67) who observed that this is generally true for all halides. Such a result would tend to indicate that bromine is associated with the organic fraction of coal.

The observed trend in the levels of trace elements indicates that while the concentrations are below the Clarke values in whole coal, such is most definitely not the case in the ash. Elements such as As, already enriched in coal, may well be at unacceptable levels in the ash. Concentration of the trace elements naturally leads to concern over the emission of fly ash into the atmosphere (28). The levels of trace elements relative to their toxicity would require a knowledge of their actual concentrations.

Consideration of the plot for Cu as a function of temperature shows a levelling off near 500°C. The same trend was observed for K, Ca, Ti, Fe, Ni, As, Sr and Rb. Although such a levelling off is to be expected at an elevated temperature, the actual result obtained here may be misleading since observations tended to indicate that the samples at 750°C had not completely ashed properly. A 'crust' of insulating ash formed and prevented the uniform ashing of the sample. Attempts at stirring the sample did not alleviate the situation. Since more detailed investigation of the ashing properties were beyond the scope of this study, no further experiments were attempted.

The leaching characteristics of the coal samples indicate that some of the elements show a definite dependence on the pH of the leachate. For example, a plot of the concentration of Ca remaining in the sample shows that most of the element is leached out at low pH and reaches a minimum at approximately pH 4-5. This is consistent with the assumption that Ca is present in coal as either the carbonate or the sulphate. Inspection of table XII indicates that each of the elements responded differently to the leaching procedures. For example, little or no effect was noticed for Fe, Rb or Ti whereas each of the other elements showed varying degrees of pH dependence. It is noted that Cu and As both showed a definite pH dependence when subjected to procedure B. However, procedure A had little or no effect. Such a result indicates the importance of the method under which such a study is conducted. A more detailed study of the effects could give more insight into the actual chemical form of the trace elements in the coal. It should be further noted that no K values are reported for procedure A due to the fact that the buffer solution contained a potassium salt. As such, meaningless values resulted for this element.

Although the relative amounts of the elements per unit of coal is small, the total absolute amount of each available in a large coal storage pile could have important consequences in water, soil or air quality. Similarly, coal leachate effects may be subtle in that although an individual element may not be at toxic levels, it may have a synergistic effect (eg. Cu is more toxic when Zn or Cd are present). Concentrating effects may occur as an element moves through the food chain. The actual toxicity arising from such processes can only be evaluated in light of the actual concentration of a particular element that is leached out of a sample and into the environment (9,68). Such an evaluation would require a mass balance study and a control of the volumes of leachate produced. Such an evaluation was beyond the scope of this study.

4.2 Qualitative Analysis

4.2.1 Correlations

The elemental correlations indicate a number of interesting tendencies. The correlation matrix shown in table XIII is made up of samples from the Crowsnest coal field. Close study of this matrix shows that strong positive

correlations exist between a number of elements, for example K and Rb, K and Cr and Ti and Rb while in most cases relatively low correlations are present. A few of these warrant closer examination.

1. The highest value of a positive correlation coefficient is between K and Rb (0.803). This is not surprising in view of the fact that both these elements are group 1A metals and hence exhibit similar chemical properties. The tendency for both K and Rb to be relatively unaffected by the action of acid or water indicates these elements are probably not present as soluble salts or hydroxides. This could possibly indicate the presence of the oxide or insoluble complex formation such as $[(K,Rb)_2Al_2Si_6O_{16}]$ (69).

2. Both Ti and K have a tendency to form alumino-silicates (lithophile elements) and hence tend to be associated in coal. The positive correlation (.444) is an indication of this tendency. While not as high as some of the other correlations, this value is nevertheless statistically significant.

3. Rubidium shows high correlations with a number of elements besides K with values of .585, .594, and .572 with Ti, Cr, and Cu respectively. The Rb-Ti correlation would be the result of alumino-silicate compounds. No explanation for the Rb-Cu value can be found since these elements do not form any interelement complexes.

4. Other high correlations may also be the result of chemical similarities (Cu and Zn) or the correlations may, in part, be an artifact of the analysis. Such may well be the situation in the case of the high correlations seen between Cr and a number of the other elements. As indicated previously, Cr has associated with it large errors which may in turn contribute to falsely high correlations.

5. It is interesting to note the generally low correlation between the rayleigh/compton ratio and the various elements. There does not appear to be a tendency toward higher correlations with higher atomic number as might be expected. This illustrates the complex nature of the R/C ratio and indicates that a number of other factors are involved with this value. Such an apparent lack of correlation points to the fact that the interdependence of all the elements in the matrix must be considered.

A similar correlational analysis conducted by IGS on the coal from the Illinois Basin tended to show many of the same trends. That is, high correlations occurred between K and Rb, K and Ti, Rb and Cr and between As and Ni while in most other cases low, non-significant correlations were seen between elements. A few significant differences did show up. For example, whereas a high correlation is seen in table XIII between Zn and Cu and between Rb and Cu, in Illinois these associations were non significant. This may be attributed to the differing conditions in environment at the time of coal formation.

4.2.2 Discriminant Analysis of Coal Seams

Table XIV show the relevant statistics generated when the discriminant analysis was applied to the coal samples which were grouped according to particular seams. The six discriminant functions are given, corresponding to the $(n-1)$ groups present. Not all of these functions are significant or useful. As previously indicated, the eigenvalues and their associated canonical correlations denote the relative ability of each function to separate the

groups. In particular, the eigenvalue is a measure of the relative importance of the discriminant functions while the sum is a measure of the total variance existing in the discriminating variables. From the table, we find that of the six functions generated, the first three account for 91% of the variance. Thus the fourth and subsequent functions appear to be of little value. The canonical correlations provide a further measure of the importance of the individual functions. These values measure how well each of the functions is correlated with those remaining. Furthermore, the value of the square of the canonical correlation is the proportion of variance in a particular discriminant function which can be accounted for by the groups present. Hence, in the case of the first function, 85.0% of its variance can be attributed to group differences. This drops to 26.8% in the case of the fourth function and lower still for the remaining two.

As an additional measure of the importance of the discriminating functions, a value for Wilks' lambda is computed. This is an inverse measure of the discriminating power in the original variables which has not yet been

removed by the discriminant functions. That is, since the discrimination is based on the variability of each of the trace elements within the sample, the aim of the analysis is to be able to account for all of this variation. Thus the larger the value of Λ , the less the unaccounted for information remaining. In order to determine the significance of the Wilks' Λ value, a Chi squared statistic was computed along with its level of significance. From table XIV, it can be seen that the probability of obtaining a value of 0.171 or less is effectively 0, while the probability of obtaining, by chance, a value of 0.5112 or smaller is 44.8%. This again, indicates that only the first three discriminant functions are significant.

Both the standardized and unstandardized discriminant coefficients are of analytical importance. The absolute value of each standardized coefficient represents the relative contribution of a particular element to the overall score. Thus, for the first discriminant function, Br, Rb, Sr and the R/C ratio all make the greatest contribution, whereas Ca is of the least importance. In the second function, Ti contributes most highly while Ni and Sr

are of least importance. The standardized discriminant coefficients can also be used to compute a discriminant score. This however requires that the values corresponding to the trace element values be in standard normal form. The discriminant score obtained by multiplying the transformed trace element value by the appropriate standardized coefficient results in a normalized discriminant score which has an overall mean of zero and a standard deviation of one. Thus a particular normalized score will represent the number of standard deviations that sample is away from the mean for all cases for a given discriminant function.

The unstandardized discriminant coefficients can be applied in a more functional sense. These values do not require that the variables be in standard normal form. These are multiplied by the raw values of the variables to give a discriminant score. As such, the coefficients themselves do not have the same statistical interpretation as standardized coefficients. Nevertheless, the final discriminant score obtained using the unstandardized values is identical to that obtained in the standardized case. This means that a set of discriminant scores for truly unknown samples can be determined. A significance test can be applied to determine the probability of an unknown belonging to one of the pre-classified groups.

Figure 16 shows a plot of the first two discriminating functions as applied to each of the samples. Although a complete picture would require a plot of all six discrimination functions and as such a six dimensional space. As indicated previously, a plot of the first two accounts for much of the variability. Examination of this figure shows that there is some overlap between the groups. Some of the groups are not clearly separated even though the discrimination is statistically significant. The reclassification routine was able to correctly identify 80% of the cases as members of the group to which they actually belong. Closer examination clearly shows an overlap of the groups marked 1 and 5, corresponding to seams 1 and 5. Reference to the map in figure 6 shows that these are adjacent to one another. A similar overlap is noticeable between seams 7 and 9. Due to a fault plane, these seams are closely related. Attempts to identify particular samples which were incorrectly identified showed that in many instances errors occurred where the seams tend to 'narrow' in together. The samples identified as 5-6, 1-10, and 10-3 in figure 6 for example, were classified as belonging to seams 1, 5, and 9 respectively. Reasons for such results may be attributed to a number of possibilities:

1. a continuum with respect to the trace element concentration may exist in some cases such that, under certain conditions, there is no sharp demarkation between seams;
2. contamination of some samples with coal from a neighbouring seam occurred;
3. the seams from which the samples were taken were incorrectly identified. Since seams are currently identified from inferential geological formations and qualitative information, field errors can result.

4.2.3 Discriminant Analysis of Coal Locations

The discriminant analysis, as applied to coal locations generated five discriminant functions. In this instance, examination of the eigenvalues show that the first three accounted for 99.75% of the total variance. Similarly, the square of the canonical correlations indicate that while 99.6% of the variance for the first discriminant function can be attributed to group differences, this drops to 25.4% for the fourth discriminant function.

Consideration of the value of Wilks' Λ shows that the probability of obtaining a χ^2 value of 0.111 or less is effectively 0. This value increases for each of the remaining discriminant functions. These values all give an indication of the success of the discriminant analysis.

The plot of the first two discriminant functions shows that while there is some overlap between the Crowsnest coal field samples, these, as a group, are quite distinct from the Hat Creek samples. It is also significant to note that no overlap occurs between the Hat Creek locations. It must be pointed out that the number of Hat Creek samples is very small. However, it appears that the variability between different locations is quite pronounced. The reclassification of samples from these locations proved 93.2% successful.

It is interesting to note that while six locations are indicated in figure 5, application of a discriminant analysis program, when run originally, failed to discriminate between samples from locations 3 and 4. Further investigation of these locations give evidence that these are two outcrops of the same coal seams and as such were combined for the final analysis.

It must be emphasized that the reclassification success is in fact based on 'unknowns' which were in fact used in the original analysis. As such, while the percentages give a fair indication of how successful the discrimination is, they tend to be optimistically high.

Considering the two analyses performed, the results indicate that location discrimination is the more successful. The success of both of these however, cannot be ignored. While the discrimination by seams would be more important both economically and geologically, it must be emphasized that while it may not be possible to absolutely discriminate between coal seams using the trace elements, the method outlined here has possibilities as a valuable aid in such a procedure.

The success of the discriminant analysis tends to imply two applications:

1. given a coal sample, it is possible to give a probability that it belongs to one of a number of pre-classified seams;

2. given a coal sample, it is possible to give a probability that it belongs to a particular pre-classified seam.

Comparison of the two discriminant procedures shows that, using the stepwise procedure, the order of trace element inclusion when discrimination by seams was attempted was Br, Sr, R/C ratio, Rb, Ni, and Ti. When applied to coal locations, the order of inclusion was Br, Ti, Zn, Cu, As, Sr and Ca. Thus, depending upon the specific application, and presumably the specific samples under investigation, the importance of an element as a discriminator may change. This points to the fact that the number of variables included in an analysis may play an important role in the success. The added advantage that may result, however, must be weighed against the added complexity of the problem as well as the time involved in generating such values.

In general, it is felt that the main disadvantage of using discriminant analysis in the application outline in this study lies in the large amount of data required to initially set up the discrimination parameters.

5. DISCUSSION

5.1 X-ray Fluorescence: Sample Preparation and Analysis

XRF is an efficient and accurate means by which to both quantitatively and qualitatively study the trace elements in coal.

Certain factors must be considered before attempting to determine the concentration levels of various elements. As with any analytical technique, the most important considerations are accuracy, reduction of errors and lower limit of detection. As such, in this study, emphasis was given to the establishment of a reliable sample preparation technique and optimum operating conditions.

It was found that, due to the inertness and binding qualities of coal, pellets of whole raw coal could be used for the analysis. This required the grinding of a coal sample to a uniform grain size then pressing it into smooth surfaced 13 mm diameter pellets. Such a procedure probably

contributed to the greatest single source of error in the analysis. The grain size requirement of 5-50 μ m is not easily obtainable. It is felt that the alumina silica grinding vial produced the desired results. However, at best, this was inconvenient to use since elaborate cleaning procedures were required and, due to the cost of such an apparatus, only one was available. As well, relatively long grinding times were required.

The error resulting from the analysis of a single pellet run ten times after removal and replacement in the instrument gives an indication of the homogeneity of the sample. The relatively large error associated with Cu indicates that even the grinding method used did not produce a completely homogeneous sample. This may be, in part, a reflection of the fact that by virtue of their chemical composition, the elements cannot be completely evenly distributed. As such, it was felt that analyzing ten pellets from each sample helped to minimize the effects generated from the non-homogeneity.

Although longer counting times could perhaps increase the efficiency of the counting statistics, it is felt that the increase in time required to make this worthwhile would not be warranted.

The spectrum stripping routine used for the evaluation of the peak areas was the computer program GAMANAL. While other routines were available and have been used, the best results were obtained with this program. As discussed previously, for a variety of reasons the Compton peak could not be reliably evaluated using this program. This value had to be computed from the raw data for each case. While reliable results were obtained using this procedure, manipulation of the data was cumbersome. In the case of the qualitative analysis, a separate program was written to perform such a manipulation. While this worked well for this study, it is felt that a more efficient data reduction procedure would be desirable.

In order to calculate the absolute values of the trace elements, standard curves were established for each of the trace elements of interest. These related the concentration of the trace element in a sample of NBS coal to the Compton normalized peak area. As indicated in section 2.7.1, this had the disadvantage of requiring the NBS coal sample to act as a standard rather than as a check on the accuracy of the results. However, the necessity of using a standard with the same matrix characteristics as the sample has been emphasized. As with the preparation of the sample pellets, the greatest difficulty in preparing the standards for the analysis arises from the necessity of mixing the diluting agent (Somar) homogeneously with the ground coal. The resulting agreement between the results of this study and those from other sources gives a measure of the relative success of this procedure.

5.2 Qualitative Analysis: Sample Collection and Preparation

It must be emphasized, in view of the work by Nicholls and Zubovic (13,20) on coal seam formation and trace element enrichment, that sample collection methods are of utmost importance if discriminant analysis is to be applied.

The samples that are prepared for analysis must be representative of the entire coal seam. It was for this reason as well as those discussed above that the grinding and mixing procedures be as thorough as possible.

The use of the discriminant analysis program (SPSS) is a rather novel approach to evaluating the trace element distribution in a sample. The method was originally developed for use in the social sciences. However, with judicious application of the parameters, it proved highly successful in this area. Care must be exercised in utilizing such a technique in that outliers must be eliminated and errors should conform to a multivariate normal distribution.

5.3 Recommendations For Further Work

Recommendations for further research fall into two general areas:

1. investigations related to coal,
2. investigations related to x-ray fluorescence.

In the course of the studies conducted here on the trace element concentrations and especially the leaching experiments, it became clear that little is known about the chemical form of the elements in coal. Although in a few instances inferences could be drawn, it is felt that investigations such as leaching experiments supplemented with wet chemical analysis could give some interesting and valuable information in this regard. This would allow a more rigorous evaluation of the potential hazards or uses of coal under various conditions.

As previously indicated, a full study of the leaching properties of coal was beyond the scope of the study presented here. The results obtained were merely an indication that pH dependent processes do occur when coal is in contact with various media. A complete study would require an evaluation of the total mass balance and leaching conditions as well as characteristics of the coal, leaching solution and leachate.

The discriminant analysis proved reasonably successful. However, from an economic point of view, one of the benefits of performing such an analysis was to be able to relate the coal to its coking properties. As such, it would seem reasonable to determine if there is an association between the trace elements and the rank of a coal. Such an investigation would be more general than that undertaken here. The rank is related to the organic fraction of the coal and classified as exinite (derived from pollen, spores and leaf epidermis), vitrinite (derived mainly from original woody tissue of trees) and inertinite (derived from fungal remains, charcoal and charred wood) (15,70). Since there appears to be definite compositional differences between the three, it would be of interest to investigate if these are related to the trace elements in the coal.

At present the major problem with XRF lies in the area of handling complex solids and performing matrix corrections. In the study performed here, the method of using the NBS coal sample to prepare calibration curves worked primarily because of the fact that the coal matrix

remained relatively constant for all samples. On the other hand, determination of the trace element concentrations in the ash would require the establishment of new calibration curves. This would prove particularly difficult. Instances where there is a lack of standards and where the matrix changes significantly from one sample to the next, along with the requirement for homogeneity all lead to problems. Work is currently being done in this area (42), although there is, at present no satisfactory way of handling such cases. More research is needed on such problems and would require an intimate knowledge of the processes which occur in XRF as well as the instrumentation.

The above point out some of the possible areas in which further work is needed. While each area may not, in itself, comprise a major study, these suggestions are meant to indicate some of the concerns worth incorporating into future projects.

6. CONCLUSIONS

Energy dispersive x-ray fluorescence was used to measure the concentrations of K, Ca, Ti, Fe, Cu, Ni, As, Br, Rb and Sr in whole coal from the Crowsnest coal field and the Hat Creek coal field.

Sample preparation methods and operating conditions were established taking into consideration factors such as grain size and sample thickness. The lower limits of detection were determined and found to range from 125 $\mu\text{g/g}$ for K to 0.64 $\mu\text{g/g}$ for As. Homogeneity of the samples proved to be the largest single source of error. Errors on the normalized peak areas for ten replicate samples ranged from 2% in elements in large concentration to 30% in elements near the detection limit.

The concentrations of the trace elements, calculated from calibration with the NBS coal standard 1632, gave good agreement when compared with values obtained using neutron activation analysis, spark source mass spectrometry and atomic absorption. A verification study conducted using Illinois coal samples also gave good agreement for all elements except Ca.

These comparisons indicate that XRF is a practical, relatively sensitive method for quantitatively analyzing coal. The main strength of x-ray fluorescence lies in its multielement capability.

Results of ashing experiments indicate that most of the elements tended to be concentrated in the ash. Bromine, however, was depleted. Absolute concentrations were not calculated.

Results showed that the leaching of some elements from coal is pH dependent. The concentrations of the trace elements under two different leaching conditions were calculated. The nature of the leaching solution and conditions under which the experiment is conducted are important. In the case of three elements, percolating H_2SO_4 over a sample seemed to have a greater effect than prolonged soaking in a buffer solution.

Correlational analysis of the trace elements show that many elements are positively correlated. The most highly correlated is K:Rb ($r=0.803$). Other significant relationships were observed between Ti and K, and between Ti and Rb which form alumino silicate complexes.

The Compton normalized peak areas for K, Ca, Ti, Cr, Fe, Zn, Cu, Ni, As, Br, Rb, Sr and the Rayleigh scatter peak were used as variables in two discriminant analysis procedures.

Using the trace elements as variables to discriminate between seams in the Sparwood Ridge area was 80% successful. Most errors in reclassification occurred between adjacent seams or where a number of seams narrowed together. Discrimination between various locations proved 93% successful.

While discriminant analysis using the trace elements cannot be used as the sole method for distinguishing between coal seams or locations, it can provide a useful tool when care is exercised in collecting samples.

Thus results of the discrimination indicate that while the trace elements can be used to distinguish between coal seams in a particular location, the discrimination is more successful in the case of two non-adjacent seams. The greatest degree of discrimination occurs between samples from different coal locations.

APPENDIX I

MULTIVARIATE STATISTICS- WITHIN GROUP AND BETWEEN
GROUP MATRICES

The random variable is given by an observation vector comprised of p (>1) distinct random variables $\tilde{y}_i = (\tilde{y}_{i1}, \tilde{y}_{i2}, \dots, \tilde{y}_{ip})$. Thus for n samples, a data matrix can be constructed:

$$\tilde{Y} = \begin{bmatrix} Y_{11} & Y_{12} & \cdot & \cdot & \cdot & Y_{1p} \\ Y_{21} & Y_{22} & \cdot & \cdot & \cdot & Y_{2p} \\ \cdot & \cdot & & & & \cdot \\ \cdot & \cdot & & & & \cdot \\ \cdot & \cdot & & & & \cdot \\ Y_{n1} & Y_{n2} & & & & Y_{np} \end{bmatrix} = \begin{bmatrix} \tilde{y}_1^2 \\ \tilde{y}_2^2 \\ \cdot \\ \cdot \\ \cdot \\ \tilde{y}_n^2 \end{bmatrix}$$

The matrix product of each observational vector y and its transpose is the $p \times p$ symmetric matrix of squares and cross products of each of the elements:

$$\tilde{Y}_i \tilde{Y}_i' = \begin{bmatrix} Y_{i1}^2 & Y_{i1}Y_{i2} & \cdot & \cdot & \cdot & Y_{i1}Y_{ip} \\ Y_{i2}Y_{i1} & Y_{i2}^2 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ Y_{ip}Y_{i1} & \cdot & \cdot & \cdot & \cdot & Y_{ip}^2 \end{bmatrix}$$

Summing n of these matrices corresponding to all of the samples produces the total sum of squares and cross products matrix

$$S_T^2 = \sum_{i=1}^n \tilde{Y}_i \tilde{Y}_i' = \tilde{Y} \tilde{Y}' \quad \dots (1)$$

If the centroid or vector of means for a single variable over the n samples is given by

$$\tilde{m} = \frac{1}{n} \sum_{i=1}^n \tilde{Y}_i \quad \dots (2)$$

where:

\tilde{m} = vector of means

n = number of samples

then the \hat{S}_T matrix can be adjusted to give the sum of squares and cross products of mean deviations

$$\begin{aligned}\hat{W} &= \sum_{i=1}^n (\hat{Y}_i - \hat{m})(\hat{Y}_i - \hat{m})' \\ &= \hat{S}_T - n \hat{m} \hat{m}' \quad \dots (3)\end{aligned}$$

where:

\hat{W} = matrix of the sum of products of mean deviation scores

\hat{S}_T = total sum of squares and cross product matrix

n = number of samples

If the samples fall into defined groups \hat{W} must be computed for each of the j subgroups. Thus \hat{W}_j is the sum of products matrix adjusted to the group mean, or the within group sum of products matrix.

A variance-covariance matrix can be obtained for each group:

$$\hat{V}_{wj} = \frac{1}{(n_j - 1)} \hat{W}_j \quad \dots (4)$$

and hence a group correlation matrix:

$$\hat{R}_{wj} = \hat{D}_{wj}^{-1/2} \hat{V}_{wj} \hat{D}_{wj}^{-1/2} \quad \dots (5)$$

where:

\hat{R}_{wj} = the group correlation matrix

\hat{D}_{wj} = the diagonal matrix of \hat{V}_{wj}

\hat{V}_{wj} = the group variance-covariance matrix

To obtain a single estimate of the variance-covariance or correlation matrices, the \hat{W}_j 's must be combined to give a pooled within group sum of products:

$$\begin{aligned} \hat{W} &= \sum_j \hat{W}_j \\ &= \hat{Y}' \hat{Y} - \hat{M}' \hat{D} \hat{M} \end{aligned}$$

giving:

$$\hat{V}_w = \frac{1}{(n-j)} \hat{W} \quad \text{and:} \quad \hat{R}_w = \hat{D}_w^{-1/2} \hat{V}_w \hat{D}_w^{-1/2} \quad \dots (6)$$

where:

\hat{V}_w = the pooled within group variance-covariance matrix

\hat{R}_w = the pooled within group correlation matrix

\hat{D}_w = the pooled within group standard deviation matrix

\hat{M} = the matrix of group means

for the variance-covariance and correlation matrices respectively. The pooled within group correlation matrix uses weighted averages of the variance-covariance for the separate groups. It reflects the degree of association between specific variables.

A between group sum of squared deviation matrix can also be defined in which the sum of squared deviations apply to the p variables.

$$\tilde{A} = (\tilde{Y} - \tilde{Y})(\tilde{Y} - \tilde{Y}) \dots (7)$$

where:

\tilde{Y} = nxp matrix of group means on p variates

\tilde{Y} = nxp matrix of grand means on p variates

F-RATIO

The F-ratio is used to test the significance of the overall difference among several group means on a single variable. When there are k groups with a total of n samples, the F-ratio is given by:

$$F = \frac{S_b / (k-1)}{S_w / (n-k)} = \frac{S_b (n-k)}{S_w (k-1)} \quad \dots (8)$$

where:

S_b = sum of squared deviations between groups

S_w = sum of squared deviations within groups

k = number of groups

n = number of observations

This ratio, with $(n-k)(k-1)$ degrees of freedom, is a test of the null hypothesis that the population means of the groups are not significantly different. To test the hypothesis of equality of k group means at a given (α) significance level requires the comparison of the calculated F-ratio with tabulated $F_{(n-k)(k-1)(\alpha)}$ values. This assumes that the populations from which the samples are drawn are normal. Rejection of H_0 arises if the calculated F is too large.

λ - MAX

Maximizing an equation of the form:

$$\frac{\sum \tilde{x}' \tilde{B} \tilde{x}}{\sum \tilde{x}' \tilde{A} \tilde{x}} = \lambda \quad \dots (9)$$

requires setting the first derivative equal to zero.

Thus:

$$\frac{\partial \lambda}{\partial \mathbf{x}} = \frac{(\tilde{\mathbf{x}}^T \tilde{\mathbf{A}} \tilde{\mathbf{x}}) (2 \tilde{\mathbf{B}} \tilde{\mathbf{x}}) - (\tilde{\mathbf{x}}^T \tilde{\mathbf{B}} \tilde{\mathbf{x}}) (2 \tilde{\mathbf{A}} \tilde{\mathbf{x}})}{(\tilde{\mathbf{x}}^T \tilde{\mathbf{A}} \tilde{\mathbf{x}})^2} \quad \dots (10)$$

Substituting equation (9) into equation (10) gives

$$\frac{2 (\tilde{\mathbf{B}} \tilde{\mathbf{x}} - \lambda \tilde{\mathbf{A}} \tilde{\mathbf{x}})}{\tilde{\mathbf{x}}^T \tilde{\mathbf{A}} \tilde{\mathbf{x}}} = 0 \quad \dots (11a)$$

$$\text{or} \quad (\tilde{\mathbf{B}} - \lambda \tilde{\mathbf{A}}) \tilde{\mathbf{x}} = 0 \quad \dots (11b)$$

If we assume $\tilde{\mathbf{A}}$ exists and is non-singular then multiplying through by $\tilde{\mathbf{A}}$ gives:

$$(\tilde{\mathbf{A}}^{-1} \tilde{\mathbf{B}} - \tilde{\mathbf{I}}) \tilde{\mathbf{x}} = 0 \quad \dots (12)$$

or letting $\tilde{\mathbf{A}}^{-1} \tilde{\mathbf{B}} = \tilde{\mathbf{C}}$ gives:

$$(\tilde{\mathbf{C}} - \lambda \tilde{\mathbf{I}}) \tilde{\mathbf{x}} = 0 \quad \dots (13)$$

Solutions require that $x \neq 0$, hence:

$$(\hat{C} - \lambda \hat{I}) \hat{x} = 0 \quad \dots(14)$$

is the eigenvalue of \hat{C} and \hat{x} is the eigenvector. This means that λ and \hat{x} are maximized in the expression given in equation (13).

Normalized peak areas and errors for the Crowsnest Coal Region samples

$$\frac{\text{area}}{\text{compton}} \times 10^2.$$

(% error at 1 S.D.)

Sample I.D.	K	Ca ^a	Ti	Cr	Fe	Ni	Cu	Zn	As ^b	Br ^c	Rb	Sr	R/C ratio
A-6	0.11 (5)	4.0 (5)	4.4 (3)	0.20 (13)	11 (2)	0.24 (16)	0.43 (17)	0.76 (9)	0.16 (19)	0.16 (14)	0.84 (6)	28 (2)	48 (0.8)
A-5	0.14 (8)	1.3 (10)	4.2 (8)	0.13 (30)	24 (9)	0.15 (20)	0.36 (30)	0.40 (30)	0.20 (30)	0.12 (15)	1.2 (14)	12 (9)	44 (1.4)
1-10	0.39 (7)	14 (5)	2.6 (1)	0.11 (35)	13 (2)	0.55 (6)	0.49 (30)	0.68 (8)	0.21 (19)	0.29 (16)	0.54 (9)	47 (1)	47 (0.5)
1-11	1.6 (15)	16 (20)	5.1 (20)	0.33 (42)	61 (1)	0.66 (23)	0.76 (18)	5.0 (12)	0.33 (26)	0.28 (25)	1.1 (2)	34 (2)	54 (1)
1-12	1.9 (2)	3.0 (5)	1.1 (16)	0.19 (42)	37 (5)	0.38 (30)	0.55 (21)	1.6 (11)	0.26 (13)	0.22 (4)	2.9 (11)	14 (12)	56 (1.7)
5-6	0.19 (6)	9.9 (5)	4.5 (8)	0.31 (19)	74 (3)	0.49 (6)	0.60 (21)	1.7 (6)	0.20 (18)	0.19 (21)	1.8 (9)	32 (3)	52 (1.4)
1-5	0.75 (5)	14 (3)	4.4 (1)	0.28 (19)	53 (2)	0.63 (8)	0.45 (14)	0.74 (1)	0.17 (25)	0.17 (34)	0.56 (1)	51 (2)	48 (1.2)
5-7	0.87 (4)	2.6 (2)	3.7 (2)	1.6 (3)	25 (1)	0.11 (25)	0.38 (10)	0.71 (6)	0.15 (22)	0.20 (33)	1.2 (9)	31 (1)	51 (0.8)
5-8	0.90 (9)	3.5 (4)	4.4 (4)	0.17 (3)	18 (3)	0.17 (22)	0.36 (10)	0.67 (9)	0.15 (12)	0.16 (17)	0.67 (15)	26 (1)	45 (0.7)
5-9	0.54 (5)	2.5 (2)	2.7 (1)	0.15 (15)	14 (1)	0.43 (23)	0.39 (29)	0.85 (7)	0.13 (23)	0.20 (20)	0.63 (10)	15 (1)	46 (0.4)
6-1	1.2 (4)	5.7 (4)	5.2 (4)	0.22 (23)	96 (4)	0.19 (13)	0.47 (9)	0.71 (11)	0.19 (24)	-	1.9 (5)	22 (4)	59 (0.4)

Sample I.D.	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn	As	Br	Rb	Sr	R/C ratio
6-4	0.25 (2)	5.4 (5)	3.5 (5)	-	26 (2)	0.19 (6)	0.35 (33)	0.80 (5)	0.11 (32)	0.14 (31)	0.30 (22)	18 (2)	52 (2.8)
6-5	0.99 (6)	16 (5)	4.8 (4)	0.24 (12)	17 (2)	0.34 (19)	0.51 (13)	2.4 (2)	0.26 (1)	0.18 (2)	1.5 (1)	41 (1)	63 (0.7)
6-6	0.64 (9)	27 (3)	2.5 (5)	-	13 (2)	0.22 (17)	0.23 (36)	0.61 (10)	0.13 (23)	0.18 (30)	0.67 (14)	22 (1)	57 (0.7)
6-13	1.3 (5)	13 (3)	5.2 (3)	0.27 (22)	11 (2)	0.28 (14)	0.86 (10)	1.4 (4)	0.72 (8)	0.23 (32)	2.3 (5)	28 (2)	66 (1.4)
6-14	1.0 (11)	17 (9)	3.3 (8)	0.23 (33)	25 (4)	0.16 (25)	0.42 (6)	0.56 (10)	0.21 (16)	0.14 (27)	1.3 (8)	18 (2)	58 (0.9)
7-1	0.71 (7)	6.3 (3)	4.7 (4)	0.15 (20)	52 (5)	0.13 (26)	0.59 (7)	0.56 (17)	0.20 (11)	-	1.2 (13)	22 (5)	56 (1.3)
7-3	0.86 (6)	6.5 (5)	4.9 (5)	0.20 (33)	66 (5)	0.16 (23)	0.58 (27)	0.49 (9)	0.32 (9)	-	1.4 (12)	19 (2)	56 (1.0)
7-4	0.87 (5)	8.1 (2)	5.7 (2)	0.23 (19)	134 (4)	0.17 (10)	0.75 (17)	0.59 (12)	0.21 (12)	-	1.8 (6)	29 (2)	60 (0.7)
7-11	0.61 (6)	3.3 (4)	3.2 (2)	0.11 (30)	21 (2)	0.16 (15)	0.42 (27)	0.96 (6)	0.19 (14)	-	0.92 (8)	13 (2)	50 (1.3)
7-12	0.26 (7)	2.6 (4)	4.3 (2)	-	98 (2)	0.37 (8)	0.46 (17)	0.77 (15)	0.18 (22)	-	0.18 (30)	14 (2)	51 (1.0)
9-1	0.93 (22)	0.44 (5)	1.1 (3)	-	21 (2)	0.13 (17)	0.40 (10)	0.41 (5)	0.17 (34)	-	0.45 (13)	4.0 (3)	52 (0.8)
9-2	0.52 (4)	1.2 (4)	4.4 (3)	0.11 (17)	13 (1)	0.12 (17)	0.54 (33)	0.44 (22)	0.18 (20)	0.08 (35)	0.60 (10)	4.5 (1)	49 (0.8)
9-10	0.26 (3)	8.3 (4)	5.0 (5)	0.48 (15)	63 (3)	0.32 (18)	0.75 (11)	1.7 (4)	0.48 (10)	-	0.60 (3)	2.4 (2)	73 (0.8)
9-3	0.44 (4)	12 (1)	2.8 (2)	0.09 (35)	50 (2)	0.43 (35)	0.30 (17)	0.28 (17)	0.11 (16)	0.13 (25)	0.44 (21)	4.5 (3)	50 (0.9)

Sample I.D.	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn	As	Br	Rb	Sr	R/C ratio
10-4	0.25 (7)	9.7 (3)	2.4 (3)	-	11 (6)	0.09 (31)	0.22 (15)	0.28 (27)	0.08 (29)	0.12 (35)	0.20 (27)	5.1 (5)	47 (1.2)
10-3	0.55 (14)	11 (3)	2.8 (5)	0.10 (35)	91 (4)	0.54 (12)	0.47 (25)	0.15 (7)	0.48 (5)	0.22 (3)	0.79 (11)	17 (2)	53 (0.5)
10-5	0.77 (6)	28 (4)	2.4 (2)	-	41 (14)	0.13 (30)	0.49 (29)	0.15 (15)	0.49 (29)	0.22 (20)	0.79 (6)	17 (1)	57 (0.7)
10-25	0.15 (6)	9.0 (3)	0.91 (7)	0.06 (31)	7.2 (3)	0.13 (15)	0.20 (10)	0.09 (18)	0.09 (25)	0.14 (30)	0.13 (35)	2.3 (4)	45 (0.8)
10-26	0.83 (12)	1.6 (3)	0.15 (24)	0.06 (21)	2.7 (9)	0.06 (39)	0.17 (11)	0.30 (25)	-	0.16 (11)	0.14 (30)	4.8 (10)	40 (0.9)
10-27	0.15 (17)	4.7 (8)	1.4 (3)	0.06 (21)	11 (2)	0.10 (27)	0.52 (10)	0.18 (21)	0.09 (5)	-	0.15 (5)	1.6 (6)	43 (0.6)
10-1	0.29 (22)	5.2 (22)	6.1 (20)	0.37 (22)	16 (2)	0.27 (26)	0.69 (20)	0.14 (13)	0.30 (5)	-	3.2 (15)	2.0 (11)	60 (0.8)
1-2	1.6 (3)	14 (4)	3.2 (3)	0.21 (20)	47 (2)	0.70 (3)	0.61 (18)	2.8 (4)	0.19 (9)	-	1.3 (6)	39 (2)	50 (1.4)
1-1	2.7 (6)	19 (5)	4.1 (5)	0.24 (12)	38 (2)	0.38 (5)	0.53 (9)	1.7 (4)	0.26 (8)	0.16 (20)	3.1 (4)	14 (2)	56 (0.5)
A-2	1.1 (12)	6.8 (10)	4.4 (6)	0.25 (33)	47 (2)	0.34 (19)	0.50 (20)	0.98 (21)	0.16 (17)	-	1.1 (7)	26 (2)	48 (1.0)
A-3	0.52 (10)	1.9 (10)	4.3 (5)	0.24 (20)	139 (3)	0.31 (12)	0.42 (23)	0.90 (11)	0.17 (11)	0.17 (31)	0.48 (2)	19 (3)	47 (1.2)
1-4	1.5 (4)	13 (12)	3.4 (11)	0.22 (28)	45 (3)	0.54 (10)	0.57 (17)	1.5 (16)	0.29 (8)	0.20 (20)	1.7 (6)	42 (3)	49 (1.2)

Sample I.D.	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn	As	Br	Rb	Sr	R/C ratio
area 2 1	0.35 (23)	4.2 (11)	2.7 (13)	0.17 (11)	29 (2)	0.24 (35)	0.19 (31)	0.50 (8)	0.12 (17)	-	0.38 (12)	7.2 (2)	54 (2.1)
area 2 2	0.33 (6)	4.3 (3)	3.6 (2)	-	75 (2)	-	0.32 (7)	0.56 (6)	0.49 (2)	-	0.48 (3)	11 (2)	49 (1.5)
area 3 1	0.13 (2)	1.2 (3)	3.1 (1)	0.31 (3)	42 (0.5)	0.84 (6)	0.73 (5)	0.30 (2)	0.33 (10)	0.37 (13)	2.3 (7)	21 (4)	57 (1.2)
area 3 2	0.41 (7)	4.7 (2)	5.1 (2)	0.10 (31)	32 (3)	0.15 (7)	0.59 (9)	0.33 (12)	0.24 (6)	0.42 (4)	0.60 (10)	4.6 (1)	51 (0.9)
area 4 1	0.78 (10)	2.1 (5)	3.4 (4)	0.25 (11)	53 (8)	0.20 (10)	0.54 (4)	0.59 (12)	0.26 (6)	0.37 (9)	1.2 (8)	19 (1)	51 (1.1)
area 4 2	0.31 (13)	3.6 (3)	4.6 (2)	0.26 (8)	20 (0.8)	0.14 (27)	0.68 (2)	0.32 (22)	0.26 (18)	0.43 (1)	0.48 (6)	6.9 (2)	50 (0.8)
area 5 1	0.60 (7)	13.7 (2)	4.1 (1)	-	31 (2)	0.25 (16)	0.69 (4)	0.94 (6)	0.56 (7)	0.33 (7)	0.79 (10)	20.4 (3)	53 (0.9)
area 5 2	0.35 (8)	15 (2)	2.1 (2)	-	19 (3)	0.34 (7)	0.33 (9)	0.48 (12)	0.11 (6)	0.23 (4)	0.41 (10)	40 (1)	51 (1.3)
area 2 3	0.53 (9)	3.0 (2)	5.2 (1)	0.32 (14)	27 (3)	0.80 (7)	0.81 (2)	0.53 (1)	0.27 (5)	-	11 (6)	19 (1)	53 (1.0)
area 2 4	0.65 (10)	9.9 (4)	4.3 (5)	-	122 (0.5)	0.17 (31)	0.58 (8)	0.62 (12)	0.22 (4)	-	1.0 (8)	13 (2)	55 (1.3)

^aRepresents normalized areas which have been corrected for K K β interference.

^bRepresents normalized areas which have been corrected for Pb La interference.

^cRepresents normalized areas which have been corrected for Br Ka interference.

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