ABSTRACT

Title of Thesis: X-RAY FLUORESCENCE SPECTROSCOPIC ANALYSIS OF COAL ASH
George Patrick Watson, Master of Science in Chemical Engineering

Thesis directed by: Dr. James M. Grow
Associate Professor
Department of Chemical Engineering
and Chemistry

Several coal ashes and prepared mixtures were analyzed by x-ray fluorescence spectroscopy. Various techniques were studied to determine the most reliable procedure for quantitatively estimating, from fluorescent peak intensities, the concentrations of seven major oxides typically present in the ash. These ashes were analyzed with only minimal sample preparation. In order to determine the self-consistency of the procedure, several mixtures of known composition were prepared containing the major elements present in an ash.

Because of inter-element absorption and enhancement effects, several computational techniques were used to calculate composition from spectrum peak intensities. The method that yielded the most accurate estimates of the mixtures was an empirical form devised by Criss and Burkes.

Comparison of the estimated coal ash compositions by this procedure did not agree with results obtained by atomic absorption analysis. However, it is believed that this is not because of the x-ray fluorescence procedure applied; inconsistent ash sampling and preparation and improper standards are the probable causes.

X-RAY FLUORESCENCE SPECTROSCOPIC ANALYSIS OF COAL ASH

by
George Patrick Watson

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APPROVAL SHEET

Title of Thesis: X-RAY FLUORESCENCE SPECTROSCOPIC ANALYSIS OF COAL ASH

Name of Candidate: George Patrick Watson
Master of Science in Chemical Engineering

Thesis and Abstract Approved: ______________________ 9/14/84
Dr. James Grow
Associate Professor
Department of Chemical
Engineering and Chemistry

______________________ ______
Dr. Joseph W. Bozzelli
Associate Professor
Department of Chemical
Engineering and Chemistry

______________________ 9/14/84
Dr. Barbara B. Kebbekus
Associate Professor
Department of Chemical
Engineering and Chemistry

VITA

Name: George Patrick Watson

Permanent address:

Degree and date to be conferred: M.S. ChE., 1984

Date of birth:

Place of birth:

Secondary Education: Essex Catholic High School 1977

Collegiate institutions attended	Date	Degree
New Jersey Institute of Technology	1984	M.S. ChE
New Jersey Institute of Technology	1981	B.S. ChE

Major: Chemical Engineering

Positions held:

1984 Process Engineer
Superior Air Products Co.
2001 Jernee Mill Rd.
Sayreville NJ

1981 Technical Representative
The Rolfite Co.
300 Broad St.
Stamford CT

DEDICATION

To my grandmothers, Mary Watson and Helen Ries

ACKNOWLEDGMENTS

I would like to acknowledge the help and guidance of my advisor Dr. James Grow who also first sparked my interest in quantum chemistry. I would also like to thank Sheila McCarthy for her help in proofreading and moral support. Finally, I would like to thank my parents, George F. and Joan A. Watson, for their support and patience while I completed my degree.

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I INTRODUCTION

The adverse effects of ash in modern boilers is a well recognized problem in the present day electric power industry. Coal-fired electric utility plants experience many special operating difficulties as well as other problems due to the amount and the characteristics of the inorganic material in coal. The ability to quickly and reliably identify the properties of coal ashes could improve power utility performance.

One of the most important of the operating problems is known as slagging. Slagging occurs when molten ash particles impinge and accumulate on the steam tubes and furnace wall of a boiler. Combustion gas flow can be severely restricted and heat transfer is hindered. Vannetti and Busch recently reviewed the problems associated with coal ash from the practical standpoint of utility boiler availability and efficiency (1). They emphasize that the degree of slagging or the significance of other problems is strongly related to the mineral composition of the coal ash.

Power plant personnel can prevent slagging to a large degree by changing operating parameters such as excess oxygen or combustion temperature (2). Coal pre-treatment, additives, and blending can also be used to control these problems. However the properties of the ash must first be determined so that the most suitable modification can be made.

Several experimental tests have been developed to indicate the physical characteristics of an ash. The most widely used of these is the ash fusion temperature test . This test, standardized by the American Society of Testing and Materials (ASTM) characterizes coal ash by four temperatures identified using the plastic properties of the ash. Ash is prepared from a coal sample by crushing it and oxidizing it in an oven until all volatile components materials are removed. The ash is then placed in an oven with a temperature that is increasing at a constant rate (typically about 4 degrees C per minute). The temperature is recorded at four conditions: when the cone first deforms (initial deformation temperature), the softening temperature (the point where the ash forms a bead), the hemispherical temperature, and the fluid temperature.

This test is time consuming, relatively expensive, and as pointed out by Huggins et. al., it has no direct physical significance (for instance, the fluid temperature is not the true liquidus temperature of the ash mixture) (3). Another important disadvantage is that no conclusions can be drawn about the properties of coal blends, based on fusion temperature data from the individual coals. Similarly, the effects of additives cannot be estimated from only the fusion test results of the coal.

An alternative approach is correlation of coal ash characteristics to the chemical composition of the ash. Given a reliable technique to determine the amount of major elements present, a straightforward calculation or a graph can yield information such as approximate fusion temperatures. It should be noted that the characteristics of coal blends and the effects of additives can be estimated without further experimental work.

Much work has been done in developing these correlations. Wiengartner and Rhodes collected the compositions and ash fusion temperatures of over 1200 different coals and regressed this information to obtain empirical correlations that could predict the fusion temperatures of various coals (4). Reid reviewed and examined several of these correlations to predict these and other properties such as slag vicosity (5). Others, such as Moza and Austin, have analyzed the properties of slags sticking on steel surfaces and the effect of composition (6). All of these works examined ash content in terms of the oxides of the following elements: sodium, magnesium, aluminum, silicon, sulfur, potassium, calcium, titanium, and iron - the most abundant ash components.

To use these correlations, a reliable method for quantitative analysis is needed. The ASTM describes a method to determine the relative amounts of the major ash components by atomic absorption spectroscopy (7). The coal must be ashed, the ash fused in lithium tetraborate at high temperature and then dissolved in acid. Standards of each element are prepared from stock solutions to create a calibration curve and the sample is analyzed. The procedure is accurate but time consuming. It may also be argued that because the results of such a test are used in correlations that are approximate and empirical in nature, the accuracy of this method is unnecessary.

To be of practical use to boiler designers and operators, a simple, fast, relatively inexpensive analytical procedure is required. The purpose of this paper is to report on the use of x-ray fluorescence spectroscopy as such a technique.

To make this method practical, sample preparation is to be kept to a minimum. Ashes are prepared from the coals by crushing and oxidizing in a furnace. The ashes are then to be analyzed as powders without further preparation. Seven important elements are considered: aluminum, silicon, sulfur, potassium, calcium, titanium, and iron. Two other elements normally considered in ash analyses, sodium and magnesium, are not included because their concentrations are not readily obtained from the available equipment.

Artificial standards will also be used to investigate the various quantitative analysis procedures that will convert spectroscopic data into concentrations. These standards can be prepared to contain as many or as few of the actual ash components as possible, therefore providing a way to examine simple cases and increase the mixture complexity in stages.

II THEORY

X-ray fluorescence spectroscopy (XRF) is based on measuring the wavelength of radiation emitted by an atom after it has interacted with an x-ray photon. The x-ray frees an electron from the atom as it passes though the material to be analyzed. The atom in turn emits fluorescent radiation as it rearranges itself to a more stable form.

The first step in the analytical scheme consists of generating an x-ray photon from a source - an x-ray tube or radioactive material such as cobalt-57. This photon, known as a primary x-ray, is then directed toward a sample to be analyzed. An x-ray tube creates these photons by accelerating an electron beam and directing them into a metal target. The electrons transfer their kinetic energy to electrons in the target atoms. The excited atomic electrons emit x-radiation as they return to their original state.

As it passes through the sample material, a primary x-ray interacts with an electron in an atom. The increase in energy enables the electron to escape from the atom. The resulting ion is now in an unstable form and several transitions are possible. In one case, an electron from an orbital with an energy higher than the escaped electron may "drop down" to fill in the gap. The difference in energy between the states is removed from the system by emitting a fluorescent x-ray.

The energy of this x-ray is precisely determined by the difference in energy between the two orbital states and is characteristic of a particular element. Not all orbital transitions are possible however. Aside from energy considerations, the conservation of angular momentum also restricts what electron can fill a vacant orbital. As an example, a transition from a 2S to a 1S state plus a photon is not allowed because the total spin and orbital angular momentum are not conserved. The probability that an allowed transition from one state to another will occur is called the fluorescent yield, which is found by experiment.

Fluorescent photons with energies in the x-ray region can only be produced by transitions of the inner core electrons - orbitals influenced very little by bonding or the states of valence and conducting electrons. The XRF energies are therefore to a large degree unaffected by the chemical form of the sample constituents. This fact also makes it possible to use absorption and transition properties of a pure element in calculations even when the element is chemically combined.

The fluorecent x-rays are labeled according to the name of the orbital that has the vacancy to be filled. For instance, an x-ray generated by the transition of a 2P-3/2 orbital electron to fill a vacancy in the 1S state is called a K-alpha-1 x-ray - named for the K or the inner-most shell. For the lower atomic number elements, such as the ones investigated in this paper, the most important emitted photons are the K-alpha x-rays.

On a macroscopic scale, the amount of primary x-ray photons absorbed by a very thin sample of an element i is proportional to the intensity of the incident radiation. This leads to an exponential decay in intensity as a beam passes through a thick sample

$$I \propto \mathrm{EXP}(-\mu \rho L)$$

where I is the beam intensity, ρ is the sample density, L is the thickness and μ is known as the mass absorption coefficient for the element at the particular x-ray energy. The overall mass absorption coefficient of a homgeneous mixture is the weighted average of each

$$\mu = \sum \mu_i \chi_i$$

the term χ is the mass fraction of element i. This fact is very important when the intensity of a fluorescent x-ray energy is to be related to the composition of a sample. The portion of primary x-rays absorbed by an element is a function not only of the weight percent of that element, but it is related to how many photons are absorbed by the other elements as well.

Inter-element effects, also known as matrix effects, which affect the relative intensities of the fluorescent x-rays of elements in a mixture are broken into two categories: absorption and enhancement. Absorption effects due to other elements in a sample reduce the available primary x-rays by absorbing the photons themselves. The observed fluorescent x-ray intensity of the element is reduced. Other elements may also absorb the fluorescent x-ray of an element before it can escape the sample and therefore reduce the observed intensity again.

Enhancement occurs when the fluorescent x-ray of a particular element is used as the primary x-ray of a second element. The second element emits more fluorescent radiation than it would had the enhancing element not been present. In particular, this is known as second order enhancement - higher order enhancements occur when a third element absorbs the x-rays of the second and emits more photons than normal, etc. Enhancement higher than second order is generally considered negligible (8).

Based on these principles, a relationship between observed intensities of a sample to be analyzed and the elemental composition can be derived as is shown in the next section.

III RELATED LITERATURE

There are many examples of the use of quantitative analysis procedures using X-ray fluorescence spectroscopy in literature, dealing with such diverse materials as cements and steel alloys. X-ray fluorescence spectra have been noted to be highly reproducible; however, the relationship between the composition of a sample and the intensities of the characteristic peaks of the elements in the sample spectrum is not straightforward. Since about 1955, several methods have been proposed to determine the composition from spectra. They may be divided into two categories: the fundamental parameters approach, and empirical methods.

The general form of the fundamental parameter approach was originally derived from first principles by Sherman and improved upon by Shiraiwa and Fujino (8). The intensity of fluorescent radiation emitted by an element is written as the sum of primary and enhancement effects, each of which depends on the composition (see table 1). In addition, each term is integrated with respect to the primary wavelength to include the effect of all the exciting x-ray energies.

To use this method, some basic properties of the components (the fundamental parameters) must be known. They include the mass absorption coefficients of each element as a function of incident x-ray wavelength, and the fraction of atoms that will emit a particular fluorescent x-ray when excited (the fluorescent yields).

Sherman's derivation was based on the following assumptions: the sample is homogeneous, and that none of the incident x-rays emerge from the other side of the sample (infinite thickness).

Criss and Burkes modified the fundamental parameter equation to a more practical form by replacing the integrals with summations to facilitate the use of tables of mass absorption coefficients and of the primary x-ray spectrum (9). In addition, they used actual spectra to describe the x-ray tube radiation instead of calculated intensities.

Using one standard of known composition to scale the intensities appropriately, the composition of unknown materials could be calculated. The form of the fundamental parameter equation solves for the intensity of a characteristic line - not the composition - explicitly. Therefore an iterative procedure is necessary to solve for the composition by using an initial estimate of the weight fractions of each element and using these values to find the expected x-ray intensity. This value is compared with the actual intensity and the composition assumption is adjusted appropriately. When the measured intensity equals the calculated intensity for each element, the iteration stops. Criss and Burkes used samples of stainless steel to evaluate the method. The results compared well with wet chemical analyses. Any discrepancies were attributed to the inaccuracy of the fundamental parameters that were used.

Another variation of the fundamental parameters method is that of Otvos, Wyld and Yao. A computer method called EXACT was developed which uses the same approach as that of Criss and Burkes but is based on the additional supposition that the primary x-ray source is monochromatic (10). The amount of information needed is considerably reduced. The calculations are also considerably simplified since the summation (integration) over the primary x-ray spectrum is unnecessary.

Several clays and stainless steels were analyzed by this method and the results were compared with certified wet chemical analysis results. To ensure that the primary beam is monochromatic, they used radioactive iron, cadmium, and americium as x-ray sources.

Recent literature describes computer programs that incorporate the Criss and Burkes fundamental parameter method. One such program is LAMA 1, written by Laguitton and Mantler, which relaxes the fundamental parameter restriction of an infinitely thick sample (11). Several steels with compositions and intensities found in other literature were used to test the program.

The second category of quantitative analysis methods, the empirical approach, have been and are presently being used instead of the fundamental parameters method for 2 basic reasons: the very large amount of data needed and the restrictions imposed by the assumptions in the more rigorous method.

Early empirical models were developed because of the lack of reliable parameters (such as jump ratios and mass absorption coefficients) that are necessary for a fundamental parameter approach. Lucas-Tooth and Pyne developed a simple linear relationship between composition and the peak intensities, loosely based on the fundamental parameter equation of Sherman (12). A set of analyzed standards are fit to equations with several coefficients by linear regression. For a seven component sample, eight standards are necessary. This fact reveals the advantage of the fundamental parameters approach; only one analyzed standard is needed. Lucas-Tooth and Pyne described the ratio of the mass fraction of component to the line intensity associated with it as a linear function of the mass fraction of each of the other components (see table 1 for definition of symbols). By approximating the mass fractions by a polynomial series in terms of intensities and truncating

$$\frac{C_i}{I_i} = K + \sum A_j I_j + \sum B_j I_j^2 + \cdots$$

The following form results

$$\frac{C_i}{I_i} = K + \sum_j A_j I_j$$

Criss and Burkes compared their fundamental parameter method with that of an empirical equation. This form sets the ratio of mass fraction to intensity to a linear function of the mass fractions of all of the components which is the Lucas-Tooth form without the further simplification to intensities (9). This is essentially the same form as that proposed by Beattie and Brissey (13). The coefficients, A, may be found by linear regression of data from standards as in the Lucas-Tooth method.

Rasberry and Hienrich in 1974 reviewed several empirical forms in the literature and re-wrote each one in a common notation (14). They found that many were identical and the others differed in only in minor respects. They proposed their own equation which differed from the others in that enhancement elements were contained in non-linear terms (the coefficients B are used for elements that enhance component i).

$$\frac{C_i}{R_i} = 1 + \sum_j A \ C_j + \sum_j \frac{B \ C_j}{1 + C_i}$$

The symbol R is the ratio of the intensity of component in a sample to the intensity of pure (see table 1). This ensures that the calculated composition is constrained to vary from 0 to 100% so that the coefficients may be used beyond the limits of the standard compositions with confidence. The coefficients were found by analyzing binary systems of each of the components. The composition of an unknown is calculated by successive substitution of guesses of composition.

A method that was not considered by Rasberry and Hienrich was that of Wheeler and Jacobus. An empirical equation was applied that was an extention of a simpler equation used by Andermann and Allen (15). The ratio of mass fraction to intensity is no longer a linear function of the other compositions or intensities:

$$\frac{C_i}{I_i} = A_{1i} + A_{2i}\,EXP\left(\sum_j B\,I_j\right)$$

The coefficients must be found by non-linear regression analysis (16).

Recent work has also been done in the development of semi-empirical or quasi-fundamental methods. Quinn describes a computer program that used the concept of an equivalent wavelength (17). This approach assumes that the polychromatic primary radiation may be characterized by a monochromatic source. With this assumption, a fundamental parameters method is applied analogous to the EXACT program of Otvos, Wyld and Yao. This significantly simplifies calculations. Quinn's program iteratively searches for the proper equivalent wavelength that yields a calculated total sample composition of 100%.

Two of the analysis methods described above have been applied to obtain the composition of the inorganic matter in coal. One is by Wheeler and Jacobus who looked specifically at coal ash in their x-ray fluorescence investigation. If N represents the number of elements to be analyzed, then at least N + 2 standards are necessary to calculate the coefficients. Since 12 standards were used to obtain coefficients for 10 elements, it is not surprising that the equations yielded estimates of composition that match the actual data well. However, they cite the results of only one analyzed ash that was not used as a standard. It is therefore not possible to infer the reliability of the method.

The effects of sample preparation on relative peak intensities were also studied. One important factor appeared to be the degree of grinding, which was also studied by Andermann and Allen (15 & 18). Ash samples were prepared by grinding them into a mixture of boric acid and sodium stearate and pressing them into a pellet.

The second method is work done by Prather, Guin, and Tarrer who reported the use of the EXACT procedure in determining coal ash composition (19). Using a National Bureau of Standards analyzed sample as the Exact standard, the relative amounts of many elements -ranging from aluminum to lead- were determined for several coals. No comparison was made between these results and those of another analytical method and therefore no conclusions can be drawn about the reliability of this method.

Recently Wheeler has reported the use of artificial standards in x-ray fluorescence quantitative analysis of coal ashes (20). Because accurately analyzed ashes are expensive and not easily obtained, Wheeler used several analyzed minerals and cements with similar compositions to ashes for standards. To extend the range of standards, some of these standards were mixed with pure oxides or other standards to simulate typical ash. Combinations such as brick and bauxite were fused in lithium tetra-borate in a furnace, ground in boric acid and sodium stearate and analyzed as discussed in Wheeler and Jacobus. The empirical approach outlined above was then used to analyze raw coal samples, but some correction factors were also used to account for the difference between the standard and coal ash characteristics.

TABLE 1

RELATIONSHIPS BETWEEN COMPOSITION AND FLUORESCENT X-RAY INTENSITIES

FUNDAMENTAL PARAMETER EQUATION:

$$I_K = \int \frac{J(\lambda)\cdot Q_K \cdot \mu_K(\lambda)}{\sum C_i \mu_i(\lambda) + \sum C_i \mu_i(\lambda_K)} d\lambda$$

$$+ \sum_{j=1}^{\eta} \left[\int \frac{J(\lambda)\cdot Q_K \cdot Q_j \cdot \mu_i(\lambda_j)\cdot \mu_j(\lambda)}{\sum C_i \mu_i(\lambda) + \sum C_i \mu_i(\lambda_K)} \right.$$

$$\left. \times \left(\frac{2\cdot Q}{\sum C_i \mu_i(\lambda_K)} \mathrm{LN}\left(1 + \frac{\sum C_i \mu_i(\lambda_K)}{\sum C_i \mu_i(\lambda_j)}\right)\right) d\lambda \right]$$

LUCAS-TOOTH AND PYNE EQUATION:

$$\frac{C_K}{I_K} = K_K + \sum_{i=1}^{\eta} A_{Ki} I_i$$

CRISS AND BURKE EQUATION:

$$\frac{C_K}{I_K} = K_K + \sum_{i=1}^{\eta} A_{Ki} I_i$$

RASBERRY AND HEINRICH EQUATION:

$$\frac{C_K}{R_K} = K_K + \underbrace{\sum_{i} A_{Ki} C_K}_{\text{ABSORB}} + \underbrace{\sum_{j} \frac{B_{Kj} C_j}{1 + C_j}}_{\text{ENHANCE}}$$

TABLE 1 (CONTINUED)

WHEELER AND JACOBUS EQUATION:

$$C_K = K_K + A_K \cdot I_K \cdot EXP\left(\sum_{i} B_{Ki} I_i\right)$$

Where

C_K	MASS FRACTION OF COMPONENT K
I_K	X-RAY INTENSITY OF COMPONENT K
$\mu_i(\lambda)$	MASS ABSORPTION COEFFICIENT OF COMPONENT AT WAVELENGTH λ
$J(\lambda)$	PRIMARY RADIATION INTENSITY AT WAVELENGTH λ
Q	COEFFICIENT RELATED TO FLUORESCENT YIELD AND SYSTEM GEOMETRY
K, A, B	EMPIRICAL COEFFICIENTS
R	RATIO OF INTENSITY OF COMPONENT K IN A SAMPLE AND THE INTENSITY PURE K

IV THE SPECTROMETER

The instrument used to analyze all samples was a Kevex Corporation 0700 spectrometer system controlled by a Digital Equipment Corporation PDP11 microcomputer. The spectrum being aquired or manipulated is displayed on a high resolution color monitor. Countrate data is printed on a Digital Equipment Corporation Decwriter.

The 0700 spectrometer contains a rhodium target x-ray tube that can support a potential difference from 7000 to 60,000 volts. The manufacturer recommends a minimum of 7000 volts because the x-ray emission intensity fluctuates significantly at smaller voltages. Power to the the tube is regulated to within 100 volts. The tube is cooled by a circulating system of anti-freeze.

The x-ray tube may directly irradiate the sample or it may be directed toward secondary targets. These secondary targets are polished surfaces of metals such as titanium, iron, and germanium. The x-rays emitted from the tube first hit the secondary and the flourescent radiation emitted is then directed at the sample.

The samples (up to 16) are held in a rotating tray. The fluorescent radiation emitted by the sample is absorbed by a silicon-lithium semiconductor detector that is cooled by a liquid nitrogen bath. The energy of the current emitted by the detector is proportional to the energy of the incident x-ray photon.

The instrument is also equipped with a vacuum pump to evacuate the air between the sample, tube and detector. Air not only scatters x-rays, but it also contains argon which creates its own fluorescent radiation.

The spectrometer is controlled by a computer system that can adjust x-ray tube voltage and current, select secondary targets, and move to new sample positions. Programs may be written so that a series of samples are analyzed and stored. Two 8 inch floppy disk drives are used to load software and to save spectra. Another microcomputer controls the crt display of a spectrum and manages the memory that accumulates the data.

The electrical energy from the detector is "shaped" by a pulse shaper that converts the energy pulse into a spike with an exponential decay. Longer time constants (such as 8 microseconds) facilitate accurate energy measurements but also increase the amount of time needed to process the pulse. More incoming x-rays must be rejected which slows down the aquiring process and also increases the chance of counting two x-rays as one. A compromise is necessary; in the experimental work that follows a pulse shape of 4 microseconds was used.

After pulse shaping, the energy is converted to a binary number by an analog to digital converter and stored in a multi-channel analyzer. The energy of a photon is in effect converted into a memory location address and the contents of that address is incremented by one. The spectrum is displayed as a graph of x-ray counts versus x-ray energy (in units of thousands of electron volts or KeV).

Because the detector, shaper, and converter ignore other x-rays if one pulse is currently being processed, the "dead-time" must be accounted for. The converter contains electronics that accounts for this by measuring the actual time that the equipment is available for counting. A spectrum that is acquired for 200 seconds is not measured in real time but in "live-time" and may actually take over twice as long.

After acquiring an XRF spectrum, the next step is to obtain the net peak intensities of the characteristic peaks of each element present. This has been done with the available Kevex software package, QUANTEX. The QUANTEX package is a group of Fortran subroutines that manipulate the data of the spectrum currently displayed.

The first step in manipulating the data is to remove what are known as escape peaks. These peaks are created when fluorescent x-rays interact with the silicon in the detector and create fluorescent silicon radiation. If this radiation is not re-absorbed (escapes), the incident x-ray will have a measured energy that is lower than the actual by exactly 1.74 KeV which is the energy of the silicon K-alpha x-ray. The QUANTEX subroutine called ESCAPE moves the escape peaks back to their proper position in the spectrum.

The next step is background removal. Background radiation is a continuous smear of x-rays that originate primarily from the primary radiation. Some of the primary x-rays are not absorbed by a sample but are scattered into a new direction without a change in energy. The Background can be thought of as a "reflection" of the x-ray tube spectrum. Background is removed by modelling the shape to a set of straight lines that are created by the user and then by subtracting this model from the spectrum. The QUANTEX commands are BKM or BacKground Model and BKS standing for BacKground Subtract.

The peaks of interest are then "painted" or marked and the QUANTEX command RESULTS is executed which regresses the marked regions to gaussian peak shapes. The position and width of each peak is set by the data appropriate to an element; the hieght is fitted to minimize the differences in the model and the data. The net peak intensities are then printed along with the estimated statisical error.

Figure 1 is a typical example of a raw spectrum before background removal. Figure 2 is the associated net peak intensity printout for that spectrum.

All of these commands may be executed interactively by the user or they may be stored in an automatically executable procedure file, called an ATO. Listings of the ATO's used in this work may be found in the appendix.

QUANTEX also contains a version of EXACT as described on page 12. Fluorescent yields and mass absorption coefficients are stored on disk for the first 92 elements. The peak intensities obtained from the RESULTS routine can be saved for the EXACT program so that spectra can be analyzed automatically.

Once a set of calibration coefficients are obtained by analyzing a standard of known composition, the concentrations of an unknown with similar characteristics can be obtained. The calibration coefficients (one for each element), or cc's, are functions of the system geometry and x-ray tube and detector characteristics. In principle, these cc's should be constant for all sample types; however the cc's must also account for sample surface variations and other conditions so that they are constant only when similar samples are considered.

The QUANTEX routine XRC calculates the cc's from peak intensities obtained from RESULTS and the composition of the standard. The composition of an unknown is calculated by obtaining the peak intensities from RESULTS and executing the routine XRF. This program is an extension of the EXACT method. One convenient option contained in it is the ability to obtain quantitative results of elements in weight percent on an oxide basis. The analysis results are printed out on the Decwriter unit, an example of which can be seen in figure 3.

All of these programs are described in detail in the QUANTEX users manual (21).

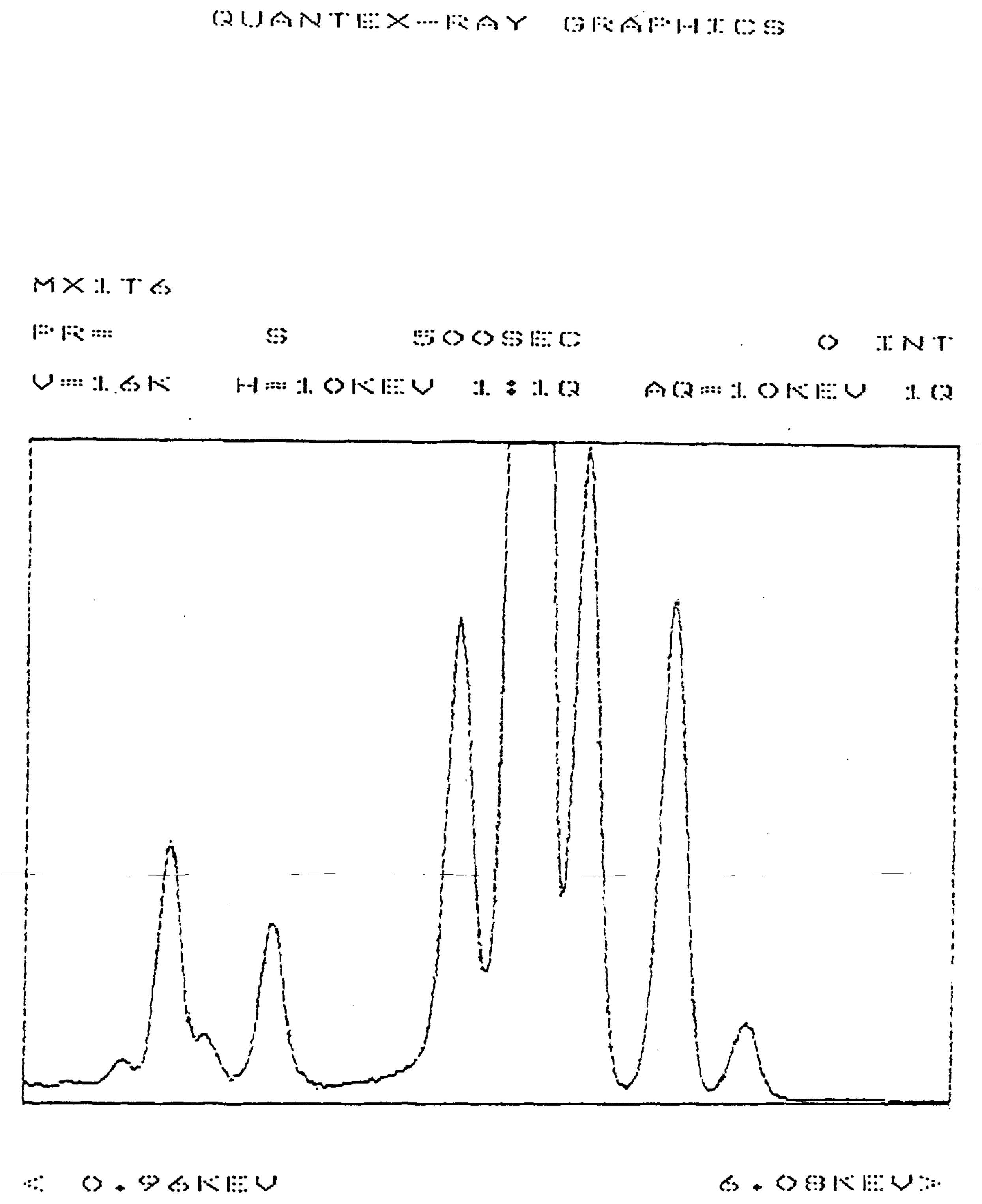
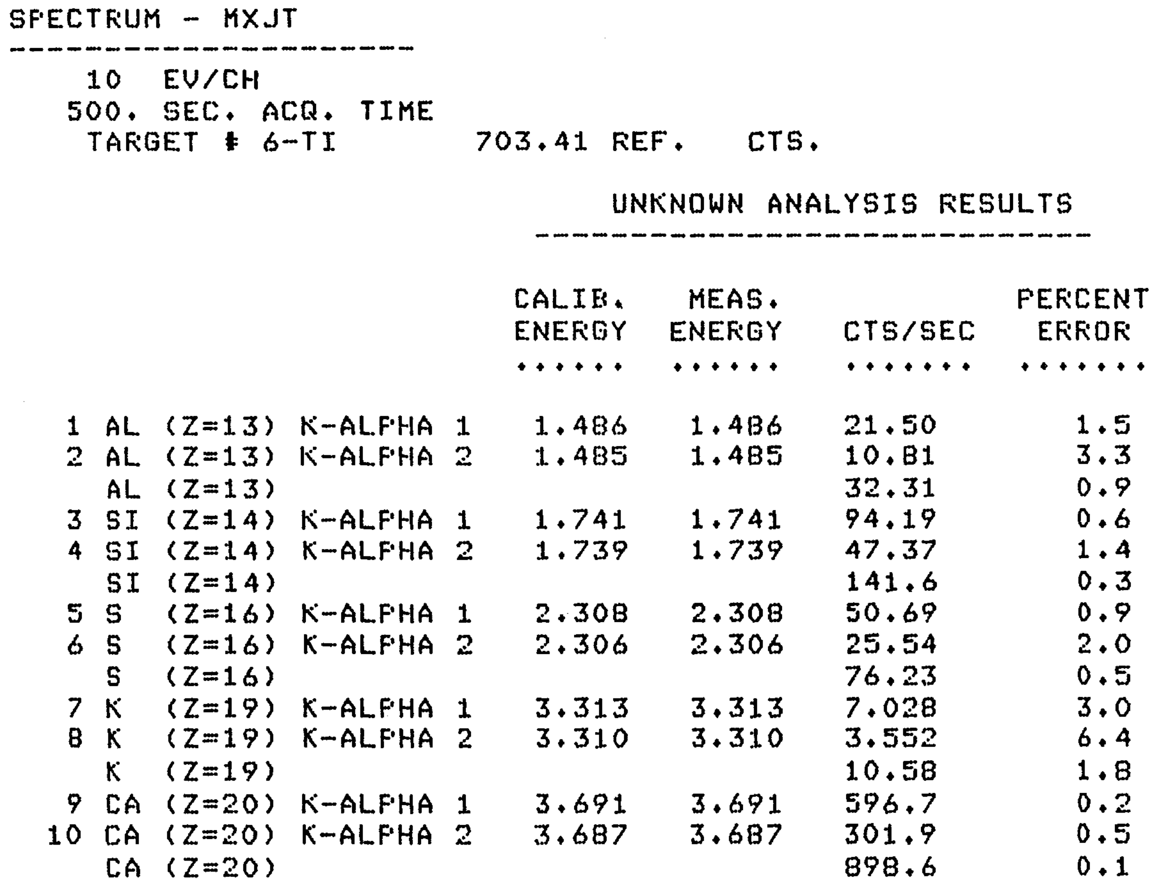


Figure 1
Example of XRF spectrum before background removal.



```
SPECTRUM - MXJT
---------------------
    10  EV/CH
   500. SEC. ACQ. TIME
    TARGET # 6-TI        703.41 REF.   CTS.

                                           UNKNOWN ANALYSIS RESULTS
                                       -----------------------------

                                      CALIB.   MEAS.             PERCENT
                                      ENERGY   ENERGY   CTS/SEC   ERROR
                                      ......   ......   .......  .......

   1 AL (Z=13) K-ALPHA 1   1.486    1.486   21.50       1.5
   2 AL (Z=13) K-ALPHA 2   1.485    1.485   10.81       3.3
     AL (Z=13)                              32.31       0.9
   3 SI (Z=14) K-ALPHA 1   1.741    1.741   94.19       0.6
   4 SI (Z=14) K-ALPHA 2   1.739    1.739   47.37       1.4
     SI (Z=14)                              141.6       0.3
   5 S  (Z=16) K-ALPHA 1   2.308    2.308   50.69       0.9
   6 S  (Z=16) K-ALPHA 2   2.306    2.306   25.54       2.0
     S  (Z=16)                              76.23       0.5
   7 K  (Z=19) K-ALPHA 1   3.313    3.313   7.028       3.0
   8 K  (Z=19) K-ALPHA 2   3.310    3.310   3.552       6.4
     K  (Z=19)                              10.58       1.8
   9 CA (Z=20) K-ALPHA 1   3.691    3.691   596.7       0.2
  10 CA (Z=20) K-ALPHA 2   3.687    3.687   301.9       0.5
     CA (Z=20)                              898.6       0.1
```

Figure 2
Example of printout from QUANTEX routine RESULTS.

```
                                              AUG.  9, 1983


                    ENERGY-DISPERSIVE X-RAY ANALYSIS



                                  D


                        STARTING DATA

  I Z TYPE TARGET CALIB.CONST. SEC    REF.CTS.  WT. %     CPS

  1 AL KA    6-TI   3.736E+05   200    328.77             15.13
  2 SI KA    6-TI   1.255E+06   200    328.77             201.7
  3 CA KA    6-TI   6.822E+06   200    328.77             1889.
  4 FE KA    4-GE   3.093E+05    50   3138.94             2677.
---------------------------------------------------------------
  5 O                                         O PPM
---------------------------------------------------------------


                               RESULTS

                  WEIGHT %   STD.DEV.         OXIDE %   STD.DEV.

          O        44.61
          AL        8.48      0.14     AL2O3    16.02      0.26
          SI       23.57      0.13     SIO2     50.43      0.28
          CA        5.126     0.008    CAO       7.172     0.011
          FE       19.01      0.02     FE2O3    27.17      0.03
        TOTAL     100.80
```

Figure 3

Example of printout from QUANTEX routine EXACT

V ANALYSIS PROCEDURE

The sample spectra were collected in groups of three or four at a time by an ATO called COLLECT (see appendix). After allowing for x-ray tube warm-up (30 to 60 minutes), the samples were placed in plastic cups with thin Mylar bottoms and set in the rotating sample holder. The sample region was the evacuated with a vacuum pump.

To account for fluctuations in x-ray tube output and detector variations, a reference countrate was obtained. By limiting the number of spectra collected to four per series, the reference could be constantly updated. The reference value was obtained by calculating the net peak intensity of a convenient region of the reference spectrum. After considerable experimentation, a polished disk of tungsten and cobalt was chosen as a reliable reference material.

The target and acquisition time is set and the spectrum of the first sample is obtained and saved on disk. The next sample is moved into place and the new spectrum is acquired and stored.

The targets and x-ray tube conditions were selected by trial and error. Direct primary x-ray excitation (designated by target 38 or T38) is the most efficient x-ray source and therfore can produce spectra in a relatively short time. Operating the tube at 10 kilovolts provided a primary spectrum that could excite all of the elements studied. The x-ray tube current was set to 0.02 milliamps to provide a reasonable countrate and about 50% deadtime. Spectra were acquired for 200 seconds.

To examine the performance of various primary source characteristics, two secondary targets were chosen to also acquire spectra. A titanium secondary (T6) was used to measure the countrates of aluminum, silicon, sulfur, potassium, and calcium. The tube voltage was set to the recommended level of 15 kilovolts and the current set to the maximum allowed of 2.0 milliamperes. Because the x-ray beam emitted by this secondary is relatively weak, the spectra were acquired for 500 seconds.

A germanium secondary target (T4) was used to acquire titanium and iron countrates since neither of these elements can be excited by titanium K-alpha x-rays emitted from T6. This target is more efficient than T6; only 200 seconds were required to obtain reasonably sized peaks. The x-ray tube was set to 15 kilovolts and 2.0 amperes.

The peak intensities of all of the elements are obtained from two spectra. This procedure takes at least three times longer than that of direct excitation (T38).

VI ASH ANALYSIS USING EXACT PROGRAM

Initial attempts were made to analyze several coal ashes using the available quantitative analysis software - the Kevex version of EXACT described on page 12 and on page 24 of this work. The ashes of six coals had been previously analyzed by atomic absorption spectroscopy by Dr. Sheih of the New Jersey Institute of Technnology Environmental Engineering Program as part of a Department of Energy grant to study the leaching and other properties of coal flyash. One other coal, analyzed by an independent laboratory, was made available through the Public Service Electric and Gas Company.

The ashes used in the present work were prepared from these coals by first crushing the raw coal in a rotary mill for about 5 minutes to ensure a small and uniform ash particle size. The coal powders were then oxidized in an oven at 600 degrees Celsius for 5 hours.

The ashes were analyzed using direct primary x-rays (Target 38) for 200 seconds. The PSE&G sample, labeled ID20783, was considered the ash with the most reliable analysis; it was therefore used as the standard to calculate the calibration coefficients (see page 24). The analyses of the other ashes are given as ranges (see table 2).

The results were discouraging. The estimated compositions poorly matched the atomic absorption compositions. In addition, the sum of the estimated mass fractions were in some cases far above a total of 1.0 . The discrepancies must be attributed the inapplicability of the EXACT method with the given sample and excitation conditions.

One basic assumption in the EXACT procedure is that the primary radiation source is monochromatic which is far from true in the above case. The x-ray source is characterized by the K-alpha radiation of chlorine (with an energy of 2.62 KeV). To produce fluorescence in iron at least x-rays of 6 KeV are necessary, indicating that since iron K-alpha peaks are prominent, much of the x-radiation has energies far above the chlorine energy. This problem can be alleviated simply by employing secondary targets. The spectrum emitted from a secondary is much "sharper" - mostly the K-alpha radiation of the secondary material. The titanium target of the Kevex spectrometer, the secondary with the lowest K-alpha wavelength, is useful in exciting low atomic number elements. The germanium secondary can be used to excite titanium and iron.

The same ashes were analyzed by using titanium and germanium secondary targets as described on page 30. Table 2 summarizes the EXACT results. While the secondary target approach yielded better results than that of direct excitation, there were still major discrepancies. Calcium and iron, which usually are important components in ash were poorly estimated. Aluminum and silicon had low deviations but their concentrations varied very little from sample to sample. Sulfur oxide had by far the largest deviations this will be discussed again later in section IX.

To discover the cause of these inaccuracies, it became necessary to reduce the number of variables in the systems studied. Standards were prepared from powders of pure compounds of the pertinent elements. The advantage of analyzing these mixtures is that as little or as many components can be studies as needed. Wider ranges with reliable concentrations could be created as well.

TABLE 2
COMPARISON BETWEEN AA AND EXACT RESULTS USING T4 &T6

WEIGHT FRACTIONS OF OXIDES

NAME	Al2O3	SiO2	SO3	K2O	CaO	TiO2	Fe2O3	
ID20783	.1624	.4039	.0728	.0223	.1652	.0072	.0921	AA
EXACT	.1624	.4039	.0728	.0223	.1652	.0072	.0921	EXACT
STANDARD *								
	0	0	0	0	0	0	0	DIFF.
ELLSWORTH	.22-.25	.45-.51	.027-.031	.019-.023	.046-.053	.012-.015	.17-.18	AA RANGE
	.24	.48	.029	.021	.050	.014	.18	AA AVG.
	.27	.49	.105	.014	.039	.007	.16	EXACT
	.03	.01	.076	-.007	-.011	-.007	-.02	DIFF.
DEEP HOLLOW	.23-.28	.49-.51	.034-.035	.021-.023	.016-.020	.017-.024	.17-.18	AA RANGE
	.26	.50	.035	.022	.018	.020	.18	AA AVG.
	.27	.50	.104	.014	.039	.010	.17	EXACT
	.01	0	.069	.006	.023	.010	-.01	DIFF.
BADGER	.27-.30	.46-.52	.021-.025	.015-.019	.028-.032	-	-	AA RANGE
	.29	.49	.023	.017	.030	.017	.16	AA AVG.
	.33	.49	.058	.014	.035	.011	.094	EXACT
	.04	0	.036	-.003	.005	-.006	-.07	DIFF.
KEYSTONE	.24-.26	-	.033-.050	.026-.032	-	-	-	AA RANGE
	.25	.50	.041	.029	.022	.013	.15	AA AVG.
	.26	.54	.056	.024	.031	.012	.089	EXACT
	.01	-.04	.015	-.025	.009	-.001	-.06	DIFF.
CONEMAUGH	-	-	.050-.054	-	-	-	-	AA RANGE
	.28	.48	.052	.021	.019	.014	.17	AA AVG.
	.32	.52	.075	.017	.031	.007	.14	EXACT
	.04	.04	.023	-.004	.011	.007	-.03	DIFF.
AVERAGE ABS. DEVIATION	.03	.02	.043	.009	.012	.06	.04	
AVERAGE ABS. % DEVIATION	10%	4%	140%	43%	50%	30%	24%	

* STANDARD WAS NOT INCLUDED IN AVERAGE DEVIATIONS

VII MIXTURE TESTS

The first test was to determine if the x-ray intensities were consistent indications of composition. If instrumental fluctuations or sample surface characteristics were also important then they would complicate analysis considerably.

Binary mixtures were chosen so that ideally a peak intensity is a function of only one independent variable (one mass fraction). The pure oxides of aluminum and iron were heated for several days above 100 degrees Celsius to drive off any moisture and then stored in a desiccator. Twelve mixtures were prepared by weighing the components to within 0.5 milligrams for a total mixture weight of 10 grams. The mixtures were then ground in a shatterbox for 5 minutes to ensure uniform particle size and complete mixing. Three binary mixtures of silicon and iron oxides were prepared by this procedure as well.

The mixtures were analyzed with the titanium and germanium secondary targets in the same manner as the ashes. The results, which are represented on the graph, figure 4, clearly show that the peak intensities of iron oxide is related only to concentration and not to other unmeasurable effects caused by the heterogeneous nature of the powders. Note that the curve is non-linear, which indicates that absorption effects are present and that straightforward linear calibration curves will not work in a multi-component system.

Four component mixtures were then prepared from of the most abundant oxides found in coal ashes: alumina, silica, calcium oxide, and iron oxide. Nine of them were analyzed with the two secondary targets. The sample labeled "D" was used as the EXACT standard to test this method on the mixtures. Table 3 contains the results of this test. Even for these simple mixtures, the procedure could not model the samples well, especially for aluminum and silicon content.

The problem appeared to be not because of parameters independent of composition but in the way that the intensities and composition are related. The EXACT method is based on the assumption that all elements of a sample are intimately mixed. However, heterogeneous mixtures of these elements should have different absorption and enhancement properties - especially if the size of a particle is large in comparison with the penetration depth of the primary x-rays into the sample.

Figure 5 is a plot similar to figure 4 for the four component mixtures. Note that there is no longer a smooth trend in weight percent iron oxide at various countrates. The peak intensity is a function of more than just the iron content alone.

The EXACT procedure is apparently too rigid to deal with heterogeneous mixtures (and ashes). Yet figure 5 indicates that interelement effects are present and must be included in calculations. Empirical methods offer an alternative where absorption and enhancement can be accounted for and the magnitude of these effects can be specified by a series of standards.

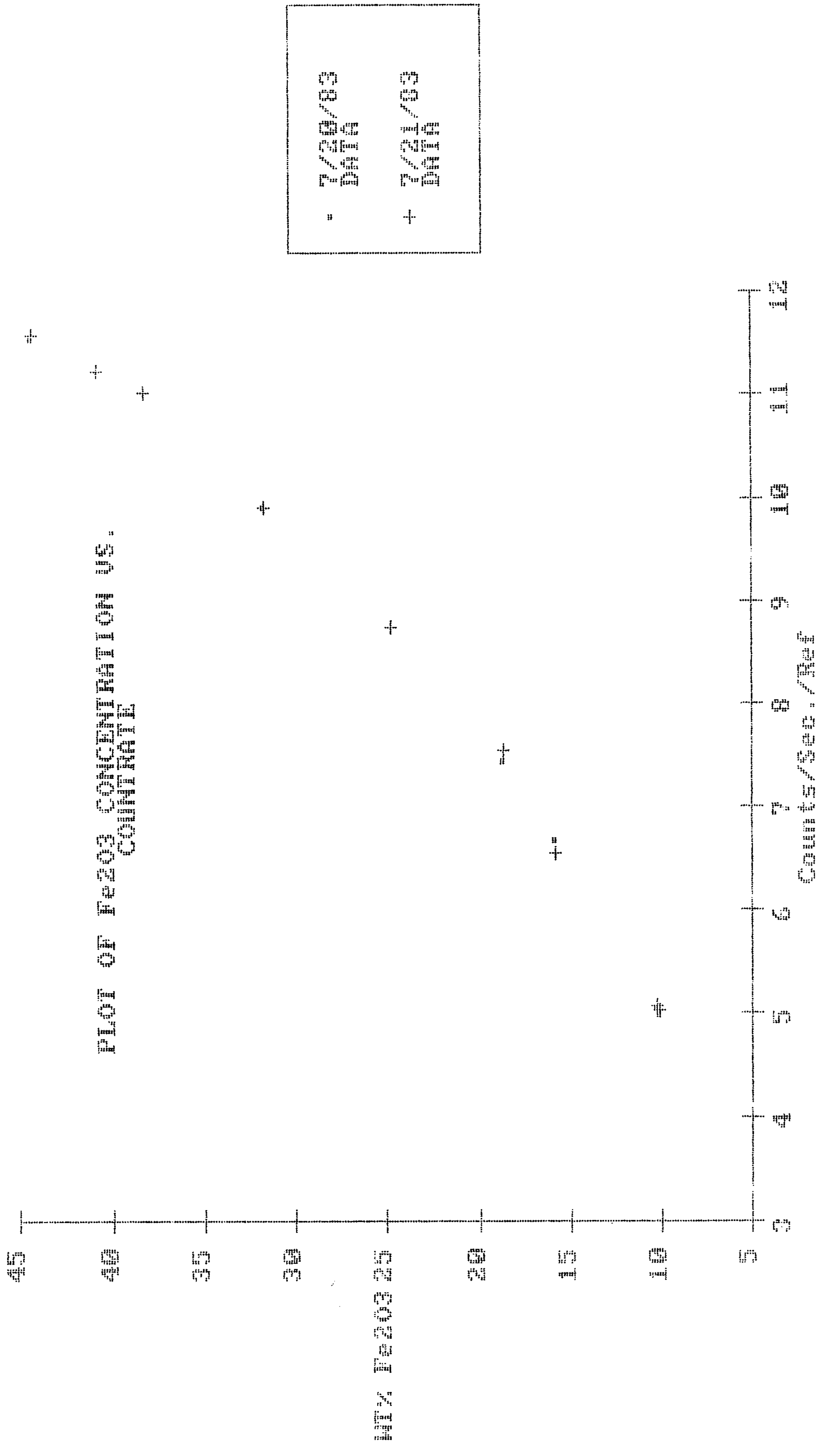

PLOT OF Fe2O3 CONCENTRATION VS.
COUNTRATE
· DATE 7/28/83
+ DATE 7/21/83
Wt% Fe2O3
5
10
15
20
25
30
35
40
45
Counts/Sec./Ref
3
4
5
6
7
8
9
10
11
12

Figure 4

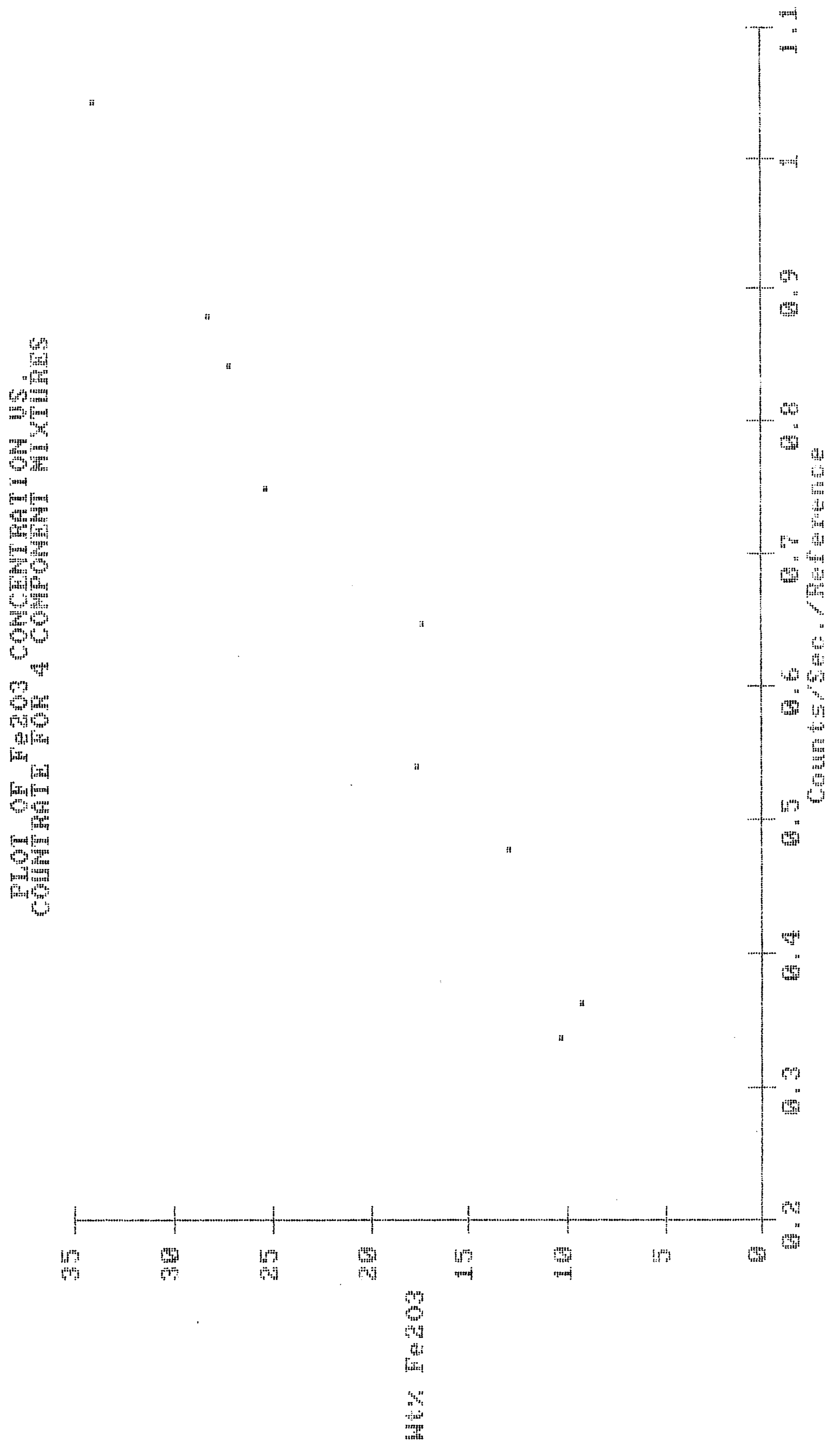

PLOT OF Fe203 CONCENTRATION VS.
COUNT RATE FOR 4 COMPONENT MIXTURES
Wt% Fe203
0
5
10
15
20
25
30
35
Counts/Sec./Reference
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1

Figure 5

TABLE 3
EXACT ANALYSIS RESULTS OF 4 COMPONENT MIXTURES USING T4 &T6

WEIGHT FRACTIONS OF COMPONENTS

NAME	Al_2O_3	SiO_2	CaO	Fe_2O_3	
D (STANDARD)*	.1593	.4985	.0709	.2714	ACTUAL
	.1607	.5027	.0712	.2721	EXACT
E	.2563	.5442	.0259	.0259	ACTUAL
	.2755	.5913	.0276	.1736	EXACT
F	.2055	.4797	.1397	.1751	ACTUAL
	.1827	.4716	.1395	.1801	EXACT
G	.2671	.5868	.0534	.0927	ACTUAL
	.2770	.6385	.0561	.0962	EXACT
H	.2568	.3891	.0726	.2815	ACTUAL
	.2049	.3967	.0706	.2811	EXACT
I	.1726	.5615	.1628	.1031	ACTUAL
	.1541	.5420	.1674	.1117	EXACT
J	.3084	.5115	.0515	.1286	ACTUAL
	.2807	.5324	.0518	.1307	EXACT
K	.2455	.4090	.0930	.2525	ACTUAL
	.1899	.4007	.0892	.2504	EXACT
L	.1849	.4520	.0230	.3401	ACTUAL
	.1652	.4825	.0233	.3240	EXACT
AVERAGE ABS. DEV.	.028	.024	.019	.005	
AVERAGE % DEV.	12%	5%	3%	3%	

* STANDARD WAS NOT INCLUDED IN AVERAGE DEVIATIONS

VIII EMPIRICAL METHODS

Three empirical methods were studied to determine a reliable quantitative analysis procedure. The methods chosen were the Rasberry and Hienrich, Criss and Burkes, and Wheeler and Jacobus equations along with modifications of each of these. The equations are listed in table 1. The following criteria were used to judge the relative accuracy of these methods:

> The accuracy in estimating the compositions of the standards characterized by the average absolute deviations of each component, and
>
> The accuracy in predicting concentrations in mixtures not used as standards.

Other points useful in the evaluations include the minimum number of standards needed to calculate the necessary coefficients and the simplicity of the calculations.

To examine the accuracy of the models, 13 mixtures were prepared that contained the 7 most abundant elements (excluding oxygen) in a typical coal ash: aluminum, silicon, sulfur, potassium, calcium, titanium and iron. The 3 elements S, K, and Ti are normally expressed as oxides in quantitative analysis results of ashes. Since it is not possible or convenient to handle these oxides, elemental sulfur and titanium, and potassium hydroxide were used. The preparation of the mixtures is identical to that of the binaries described on page 35. Nine of these mixtures were used as standards while the remaining 4 were analyzed as unknowns.

The sample spectra were obtained by both primary x-ray source techniques to determine whether the secondary target approach is necessary. The x-ray tube conditions have been discussed on page 29.

Since solving the necessary coefficients for all of the methods involves a multi-variable linear least squares regression, the same basic equations apply for all cases. The error, E, is defined by the difference between the actual independent variable value, Y, and the value of the equation that estimates it

$$E = Y - U - \sum_{i} V_i X_i$$

where the Xs are the N independent variables of the equation and U and the Vs are the coefficients to be determined. To evaluate the coefficients that will produce the minimum error squared for all input data, the partial derivative of the sum of all of the errors squared is taken with respect to each coefficient and set to zero to obtain the minima. This process leads to a set of linear simultaneous equations that can be represented as matrices. Solving the set of equations yields the optimum value of each coefficient. The equations and matrices that must be solved are shown in table 4 along with the relationships between the general linear equations and the variables of each empirical method.

The first equation tested was a modified version of the Rasberry and Hienrich model (hereafter refered to as R&H)

$$\frac{C_K}{R_K} = 1 + \sum A_i C_i + \sum B_j \frac{C_j}{1 + C_K}$$

The term R is the ratio of the peak intensity of component k in the sample to that of pure k. By moving the pure intensity term to the other side of the equation, the following form results:

$$\frac{C_K}{I_K} = K + \sum A_i C_i + \sum B_j \frac{C_j}{1 + C_K}$$

where A and B are redefined and K is the inverse of the pure component intensity. The advantage of this rearrangement is that the pure component count rate need not be known; it can be fitted by regression just as the A and B interaction coefficients are.

A Pascal program was written and implemented on an IBM Personal Computer, called FIT, a listing of which may be found in the appendix. Intensity and composition data of the standards and a list of the elements that enhance other components are read in from an input file. The summations are calculated and placed in the correct position in the matrices described in table 4. A Gauss-Jordan reduction routine is used to solve the simultaneous equations. Finally, the coefficients are printed out as well as saved on a floppy disk for later use. A typical printout of the coefficients is shown in figure 6.

These coefficients are then used by another Pascal program, QUANT, to calculate the composition of an unknown. QUANT follows the algorithm outlined by Rasberry and Hienrich in their paper (14). Since the mass fraction of an element cannot be separated from the enhancement terms, the set of equations relating composition to intensity cannot be solved directly. A successive substitution routine is employed where a first guess of composition is obtained by initially ignoring interaction effects. New estimates of the concentrations are calculated and the process is repeated until the total composition change from one iteration to the next is less than 0.01 percent. A listing of QUANT can be found in the appendix.

It was found that the above program did not consistently converge. Various schemes such as changing the initial guesses did not help. The modified R&H procedure was temporarily dropped and a similar method, the Criss and

Burkes equation (C&B) was examined.

The C&B procedure is essentially the same as the R&H except that both enhancement and absorption terms are identical; the C&B is a special case of the R&H equation.

The interaction coefficients may be solved by the XRFIT program without modification. All that must be done is to specify that no enhancement terms are to be used. The advantage of the C&B method is that an iterative procedure is not needed to solve for unknown concentrations. A sample composition may instead be computed by solving a set of simultaneous equations. Another Pascal program, QUANT3, was written to do this (see appendix). Table 5 states the analysis results and deviations from the actual mass fractions. Significant errors are evident, especially the estimates of mixtures not used in calculating the coefficients.

A modified form of the Wheeler and Jacobson (W&J) equation was also investigated. The authors apparently did not remove the spectra backgrounds before computing the peak intensities. The background is accounted for by the term A in their equation (see table 1). If however, background radiation is properly removed, this coefficient should be zero. The empirical equation may then be rearranged to a linear form:

$$\mathrm{LN}\left(\frac{C_K}{I_K}\right) = K + \sum_i A_i I_i$$

Solving for the K and A's is similar to the previous methods (see program FIT2 in the appendix). The solution of mass fractions is a straight-forward substitution of the spectrum intensities.

Just as with C&B, the estimates obtained from the W&J equation yielded poor results for unknowns outside of the range of the standards (see table 5). Evidently, just blindly regressing data will not produce results, especially when the number of standards is limited. The empirical methods in the forms used suffer from the lack of "structure" - the opposite reason for the problems incurred in using EXACT. A "structure" can be induced in the R&H method by using these equations as they were originally formed with the pure component count rates used to specify the intensity at 100%.

Each of the mixture components was crushed and analyzed by the same procedure employed for the mixtures themselves. The peak intensities of the pure form of each of the mixture components were obtained under the same conditions as the mixture analyses. FIT was modified so that the coefficients, K, were determined by the standards data instead of being calculated (called FIT3). As stated on page 14 the specification of the pure intensity countrate ensures that all computed mass fractions must lie between 0 and 1 .

The R&H method then converged within 20 iterations every time (the QUANT program did not have to be modified). Various enhancement combinations were studied but very little improvement was found in the overall estimates.

The C&B procedure (R&H with no enhancements) produced results very similar to those of R&H. The more complex form of the enhancement term did not increase the accuracy in predicting compositions. Without the R&H enhancement terms, the unknown analysis programs were greatly simplified (an iterative procedure would not be necessary).

XRF data obtained from both excitation methods were examined. The T4&T6 x-ray sources yielded slightly more accurate results than the T38 method.

The overall absolute deviations indicate that secondary targets T6 and T4 produce spectra that can be used to estimate composition better than direct excitation T38 spectra (see table 6).

Three conclusions were drawn from the work with mixtures:

> The restrictions imposed by the assumptions of which EXACT is based may prevent an accurate analysis of powdered samples.
>
> Of the three methods studied, the Criss and Burkes empirical quantitative analysis equation provides the most reliable results. This method is also the simple in that the concentrations in an unknown may be solved without an iterative procedure, such as R&H and EXACT. But the x-ray intensity of each component in the pure form must first be obtained to properly "scale" the equation.
>
> The secondary targets of titanium and germanium yield peak intensities (T4&T6) that are slightly easier to correlate with mass fractions than is possible with direct x-ray tube excitation.

TABLE 4

MULTI-VARIABLE LINEAR LEAST SQUARES ANALYSIS

THE FORM OF THE EQUATION AND THE ERROR OF POINT

$$Y = U + \sum_{i}^{\eta} V_i X_i$$

$$E_K = Y_K - U - \sum_{i}^{\eta} V_i X_{iK}$$

WHERE

Y IS THE DEPENDENT VARIABLE

X ARE THE η INDEPENDENT VARIABLES

U AND V ARE THE COEFFICIENTS TO BE OPTIMIZED BY MINIMIZING THE SUM OF THE SQUARES OF THE ERROR OF EACH POINT

THE COEFFICIENTS ARE CALCULATED BY SOLVING THE MATRIX EQUATION:

$$\begin{vmatrix} \sum_K Y_K \\ \sum_K Y_K X_{1\eta} \\ \vdots \\ \sum_K Y_K X_{\eta K} \end{vmatrix} = \begin{vmatrix} N & \sum X_{1K} & \cdots & \sum X_{\eta K} \\ \sum X_{1K} & \sum X_{1K} X_{1K} & \cdots & \\ \vdots & \vdots & & \\ \sum X_{\eta K} & & & \sum X_{\eta K} X_{\eta K} \end{vmatrix} \times \begin{vmatrix} U \\ V_1 \\ \vdots \\ V_\eta \end{vmatrix}$$

TABLE 4
(CONTINUED)

CORRESPONDENCE BETWEEN GENERALIZED VARIABLES AND EMPIRICAL EQUATIONS

R&H AND C&B:

$Y \rightarrow \frac{C}{R}$ $\quad$ $X \rightarrow C$ $\quad$ $\frac{C}{1 + C}$

ABSORB $\quad$ ENHANCE (R&H)

$U \rightarrow K$ $\quad$ $V \rightarrow A$ $\quad$ B

W&J:

$Y \rightarrow LN\left(\frac{C}{I}\right)$ $\quad$ $X \rightarrow I$

FIGURE 6

```
LEAST SQUARES FIT OF XRF DATA TO RASBERRY-HEINRICH MODEL


INPUT DATA :   *
MIX DATA 1-6,10-12    1/6/84 target 38

                  **
K RATIOS:
    3.4434    0.1303    0.0773    0.4157    0.7207    0.0523    0.1298
                    ***
COEFFICIENTS :
    0.0000   -4.3028   -7.0888    1.1488    3.0564   -2.4923    1.9548
    1.0317    0.0000    0.3539   -0.7447    1.1851    1.3042    0.9379
    0.0870   -0.0618    0.0000    0.1784    0.2193   -0.0243   -0.0634
    0.2416   -0.5481   -0.6650    0.0000   -0.3336    0.2276   -0.3132
   -0.2350   -0.8618   -1.1272    0.2254    0.0000   -0.6809   -0.7806
   -0.1313    0.0541    0.2190   -0.1352   -0.1008    0.0000    0.0177
   -0.1787   -0.0641    0.0618   -0.1657   -0.1599    0.0135    0.0000
                        ****
STORED IN RECORD 2
```

* NAME OF STANDARDS DATA

** RECIPROCAL OF INTENSITIES AT 100%

*** INTERACTION COEFFICIENTS. COLUMNS AND ROWS CORRESPOND TO ELEMENTS IN ORDER OF INCREASING ATOMIC NUMBER: Al, Si, S, K, Ca, Ti, Fe. NOTE THAT DIAGONALS (EG. Al-Al) ARE SET TO ZERO BY THE REQUIREMENTS OF THE MODEL.

**** RECORD NUMBER OF DISK FILE WHERE COEFFICIENTS ARE STORED.

TABLE 5
MASS FRACTIONS OF MIXTURE COMPONENTS ESTIMATED BY C&B AND W&J METHODS

NAME	Al2O3	SiO2	S	KOH	CaO	Ti	Fe2O3	
MX1	.148	.394	.031	.042	.160	.025	.199	ACTUAL
	.144	.396	.028	.040	.140	.028	.225	C&B
	.147	.398	.030	.042	.151	.026	.202	W&J
MX2	.151	.399	.017	.049	.040	.036	.308	ACTUAL
	.148	.401	.016	.047	.033	.038	.319	C&B
	.151	.397	.017	.049	.041	.036	.306	W&J
MX3	.146	.440	.064	.003	.140	.007	.201	ACTUAL
	.146	.438	.064	.003	.142	.007	.201	C&B
	.147	.437	.065	.003	.147	.006	.198	W&J
MX4	.152	.500	.017	.013	.100	.064	.153	ACTUAL
	.159	.496	.020	.013	.132	.058	.135	C&B
	.154	.493	.018	.014	.111	.062	.148	W&J
MX5	.197	.392	.099	.021	.102	.045	.146	ACTUAL
	.201	.389	.104	.022	.112	.041	.140	C&B
	.198	.390	.100	.022	.106	.042	.145	W&J
MX6	.153	.450	.060	.017	.109	.058	.153	ACTUAL
	.152	.463	.057	.018	.094	.059	.156	C&B
	.151	.461	.056	.017	.092	.061	.161	W&J
MX10	.192	.509	.059	.071	.020	.051	.099	ACTUAL
	.200	.508	.062	.078	.023	.048	.091	C&B
	.192	.507	.059	.071	.021	.051	.098	W&J

TABLE 5 CONTINUED
MASS FRACTIONS OF MIXTURE COMPONENTS
ESTIMATED BY C&B AND W&J METHODS

NAME	Al2O3	SiO2	S	KOH	CaO	Ti	Fe2O3	
MX11	.305	.588	.006	.006	.014	.007	.076	ACTUAL
	.316	.596	.006	.006	.015	.006	.067	C&B
	.304	.590	.005	.006	.013	.007	.077	W&J
MX12	.258	.561	.050	.020	.016	.042	.055	ACTUAL
	.237	.549	.045	.017	.014	.046	.065	C&B
	.258	.559	.050	.020	.016	.042	.054	W&J
MX13	.181	.523	.037	.056	.020	.082	.102	ACTUAL
	.185	.478	.040	.051	.027	.078	.102	C&B
	.223	.501	.063	.074	.056	.054	.064	W&J
MX14	.170	.585	.029	.007	.040	.019	.149	ACTUAL
	.150	.505	.017	.004	.049	.022	.189	C&B
	.238	.521	.046	.008	.346	.010	.070	W&J
MX15	.300	.497	.010	.004	.1258	.010	.053	ACTUAL
	.321	.557	.016	.005	.2305?	.003	.000?	C&B
	.339	.512	.030	.006	1.284	.004	.018	W&J
MX16	.296	.404	.005	.013	.0757	.006	.201	ACTUAL
	.266	.425	.009	.007	.2411?	.003	.059?	C&B
	.302	.424	.011	.007	.4193?	.004	.091?	W&J
ABS. DEV. ALL	.010	.019			.029		.029	
% DEV. ALL	4.5%	3.9%			34.6%		20.7%	
ABS. DEV. *	.019	.052			.071		.059	
% DEV. *	12.7%	10.0%			89.8%		49.4%	

* MIXTURES NOT USED AS STANDARDS
? LARGE DISCREPANCY

TABLE 6
MASS FRACTIONS OF MIXTURE COMPONENTS ESTIMATED BY C&B METHOD USING DIFFERENT EXCITATION CONDITIONS

NAME	Al_2O_3	SiO_2	S	KOH	CaO	Ti	Fe_2O_3	
MX1	.148	.394	.031	.042	.160	.025	.199	ACTUAL
	.140	.414	.035	.032	.135	.026	.197	T38
	.138	.412	.034	.031	.157	.026	.198	T4T6
MX2	.151	.399	.017	.049	.040	.036	.308	ACTUAL
	.149	.401	.017	.048	.042	.036	.307	T38
	.149	.404	.017	.048	.041	.037	.308	T4T6
MX3	.146	.440	.064	.003	.140	.007	.201	ACTUAL
	.153	.442	.056	.004	.140	.007	.198	T38
	.155	.431	.060	.004	.141	.006	.201	T4T6
MX4	.152	.500	.017	.013	.100	.064	.153	ACTUAL
	.159	.485	.019	.015	.100	.063	.153	T38
	.155	.481	.017	.015	.100	.064	.153	T4T6
MX5	.197	.392	.099	.021	.102	.045	.146	ACTUAL
	.199	.367	.092	.024	.101	.041	.149	T38
	.190	.385	.094	.022	.100	.042	.145	T4T6
MX6	.153	.450	.060	.017	.109	.058	.153	ACTUAL
	.151	.459	.060	.019	.107	.057	.153	T38
	.155	.461	.060	.020	.109	.058	.153	T4T6
MX10	.192	.509	.059	.071	.020	.051	.099	ACTUAL
	.210	.484	.056	.080	.020	.050	.101	T38
	.196	.493	.056	.066	.020	.050	.098	T4T6

TABLE 6 CONTINUED
MASS FRACTIONS OF MIXTURE COMPONENTS ESTIMATED BY C&B METHOD USING DIFFERENT EXCITATION CONDITIONS

NAME	Al2O3	SiO2	S	KOH	CaO	Ti	Fe2O3	
MX11	.305	.588	.006	.006	.014	.007	.076	ACTUAL
	.310	.566	.006	.007	.014	.007	.079	T38
	.323	.579	.006	.007	.013	.006	.074	T4T6
MX12	.258	.561	.050	.020	.016	.042	.055	ACTUAL
	.230	.615	.045	.011	.015	.043	.051	T38
	.224	.597	.052	.012	.016	.045	.056	T4T6
MX13	.181	.523	.037	.056	.020	.082	.102	ACTUAL
	.153	.560	.042	.046	.022	.086	.101	T38
	.153	.512	.014	.047	.021	.088	.101	T4T6
MX14	.170	.585	.029	.007	.040	.019	.149	ACTUAL
	.145	.599	.020	.008	.048	.022	.132	T38
	.161	.533	.019	.004	.055	.021	.140	T4T6
MX15	.300	.497	.010	.004	.126	.010	.053	ACTUAL
	.350	.474	.011	.012	.125	.009	.060	T38
	.307	.440	.007	.015	.116	.009	.054	T4T6
MX16	.296	.404	.005	.013	.076	.006	.201	ACTUAL
	.259	.428	.006	.012	.086	.009	.222	T38
	.271	.372	.003	.013	.089	.008	.210	T4T6
AVERAGE ABS. DEVIATION								
AVERAGE ABS. % DEVIATION								

IX ASH ANALYSIS BY EMPIRICAL METHODS

Based on the previous conclusions, a plan could now be formulated to analyze ashes and obtain reasonable results. The secondary targets of titanium and germanium were used in tandem to obtain spectra for 9 ashes, 7 of which were described earlier and 2 more ashes obtained from the Department of Environmental Protection project mentioned on page 31. The Criss and Burkes procedure was used with the interaction coefficients obtained from the 7 component mixtures. While the mass fractions of iron oxide and calcium oxide were reasonably well estimated, the alumina content was consistently too high and the silica was consistently underestimated (see table 7).

There are two possible explanations for the discrepancies. One is that the formula weights assumed for these oxides are incorrect; the silica used in the mixtures may not have had the exact ratio of two oxygen atoms to a silicon atom. If this is so, then not only will the aluminum and silicon contents be in error, but the estimates of the other components will be incorrect as well. Note that this would not affect the analysis to the mixtures since all of them would be in error by the same ratio.

Another explanation for the trends in table 7 can be explained by inspecting the chemical forms of the mineral matter occuring in coal and in the heterogeneous nature of the ash products. Gluskoter, Shimp, and Ruch discuss the various minerals present in coal and mention minerals containing silicon such as clays and silicates that also invariably contain aluminum chemically bound in the mineral (22). The iron however is usually in the form of iron sulfide or iron sulfate. Similarly, calcium is usually in the form of calcium sulfate or calcium carbonate. When ashed at a relatively low temperature (no melting), the iron and calcium minerals convert into independent iron oxide and calcium oxide particles. The aluminum and silicon are, however, bound into one particle.

The local environment of the silicon and aluminum in an ash is therefore much different from that of a mixture of pure oxide particles. The intimate mixing in the ash ensures that enhancement and absorption effects be more pronounced than in a heterogeneous mixture.

The results in table 7 indicate this. The aluminum content is apparently larger because the peak intensity is greater. This is in turn because the aluminum is enhanced by the absorbtion of silicon K-alpha radiation. The silicon content appears smaller because of the increased absorbtion by aluminum.

In either case the aluminum and silicon coefficients obtained from the mixtures are not appropriate for ash analysis. It should be noted that the coefficients are apparently valid for the other two major ash components. Figure 7 shows the results of calculations that show that if the given concentrations of a coal ash are used with the interaction coefficients found from the mixtures, the calcium content can be estimated to within 1% and iron to within 5%. However, this was found to be true for only the coal labeled ID20783 (with an accurately known composition); the other ashes did not yield such accuracy.

The interaction coefficients were recalculated using 7 ashes as standards. The interaction coefficients for sulfur were found to be very far from any previous values. An increase in interactions was expected for the same reason as the change in the aluminum and silicon interactions, but the quantities were an order of magnitude larger. It was suspected that the sulfur concentration data may not be valid. The ashes used in the atomic absorption measurements and in the XRF tests were derived from the same coal but may not have been ashed at the same conditions. Since the sulfur may have volatilized in different amounts, the concentration data may not be valid. Especially poor sulfur results were originally noted in the EXACT ash tests (page 33 and table 2).

The sulfur data was removed from the input file and the coefficients were computed for the remaining six components. The results of this test may be found in table 8. The first seven coal ashes listed in the table were used as standards. The four major component compositions were in most cases consistent with the atomic absorption results. Titanium and potassium concentrations however were far from accurate. Two other ashes were tested as unknowns. The ash labeled Militant yielded compositions far from the given atomic absorption concentrations.

TABLE 7
ASH ANALYSIS USING MIXTURE INTERELEMENT COEFFICIENTS OF C&B METHOD

WEIGHT FRACTIONS OF OXIDES

NAME	Al_2O_3	SiO_2	SO_3 *	K_2O *	CaO	TiO_2 *	Fe_2O_3	
ID20783	.162	.404	.073	.022	.165	.0072	.092	AA
	.299	.364	.027	.074	.144	.005	.082	C&B
ELLSWORTH	.24	.48	.029	.021	.050	.014	.18	AA
	.320	.416	.032	.042	.031	.008	.102	C&B
WELLMORE CACTUS I	.24	.49	.024	.037	.029	.013	.16	AA
	.299	.344	.025	.086	.027	.008	.135	C&B
DEEP HOLLOW	.26	.50	.35	.022	.018	.020	.18	AA
	.351	.389	.017	.059	.023	.011	.147	C&B
BADGER	.29	.49	.023	.017	.030	.017	.16	AA
	.423	.385	.015	.060	.027	.010	.084	C&B
KEYSTONE	.25	.50	.041	.029	.022	.013	.15	AA
	.328	.423	.015	.069	.022	.009	.082	C&B
CONEMAUGH	.28	.48	.052	.021	.019	.014	.17	AA
	.381	.410	.017	.062	.022	.009	.123	C&B

* CONVERSIONS WERE NECESSARY TO EXPRESS THESE COMPONENTS IN OXIDE FORM

FIGURE 7

CHECKING Fe AND Ca ESTIMATES OF AN ASH USING C&B MIXTURE COEFFICIENTS AND THE AA COMPOSITIONS OF OTHER COMPONENTS

COAL ASH ID20783

FOR Fe

COEFFICIENTS A

-.0267	-.0374	.0289	.0324	.0233	.0675	.0
Al	Si	S	K	Ca	Ti	Fe

K = .0565

$$\left[\frac{C}{I}\right]_{Fe} = K + \sum_{i}^{7} A_i C_i$$

THE Fe COMPOSITION IS ESTIMATED TO BE 0.087
COMPARED TO THE GIVEN 0.092 FROM AA RESULTS

FOR Ca

COEFFICIENTS A

-.0013	-.0261	.0627	-.0317	.0	.0189	.0062
Al	Si	S	K	Ca	Ti	Fe

K = .0484

THE Ca COMPOSITION IS ESTIMATED TO BE 0.1646
COMPARED TO THE GIVEN 0.165 FROM AA RESULTS

TABLE 8
ASH ANALYSIS USING MIXTURE INTERELEMENT COEFFICIENTS OBTAINED FROM ASHES THEMSELVES FOR C&B METHOD

WEIGHT FRACTIONS OF OXIDES

NAME	Al2O3	SiO2	K2O	CaO	TiO2	Fe2O3	
ID20783	.162	.404	.022	.165	.0072	.092	AA
	.161	.394	.020	.175	.007	.090	C&B
ELLSWORTH	.24	.48	.021	.050	.014	.18	AA
	.240	.494	.025	.032	.019	.17	C&B
WELLMORE CACTUS I	.24	.49	.037	.029	.013	.16	AA
	.24	.485	.036	.035	.016	.16	C&B
DEEP HOLLOW	.26	.50	.022	.018	.020	.18	AA
	.19	.47	0.0?	.010	.072	.20	C&B
BADGER	.29	.49	.017	.030	.017	.16	AA
	.28	.49	.016	.035	.020	.16	C&B
KEYSTONE	.25	.50	.029	.022	.013	.15	AA
	.25	.51	.033	.008	.005	.14	C&B
CONEMAUGH	.28	.48	.021	.019	.014	.17	AA
	.29	.48	.025	.005	.006	.17	C&B
NOT USED AS STANDARDS							
MILITANT	.28	.52	.022	.014	.015	.13	AA
	.17	.47	.052	.150	.008	.28	C&B
WELLMORE CACTUS II	.25	.52	.030	.029	.015	.12	AA
	.19	.47	.020	.085	.045	.17	C&B

X CONCLUSIONS

The empirical method of relating composition to x-ray fluorescent intensities due to Criss and Burkes is a reliable procedure for obtaining reasonably accurate (within 10%) compositions of multicomponent mixtures. The fluorescent x-ray intensity of the pure forms of the mixture components must first be determined to confine the empirical coefficients used to calculate unknown concentrations.

The approach is simple and straightforward to implement using a computer. An empirical method such as this one also has the advantage of the ability to use many standards to arrive at the model parameters. Linear least squares analysis calculates the "best" coefficients based on the data of many standards. This can not be done with the EXACT method in a simple manner.

The EXACT procedure, as with all fundamental parameter methods, uses only one standard to calculate necessary parameters. While this is useful when the availability of standards is limited, it relies on the accuracy of one sample analysis obtained from another source. The range of applicability is also limited to analyzing a range of concentrations similar to the standard.

It also appears that complicated or tedious sample preparation is not necessary to obtain reasonably accurate quantitative results from XRF. Mixtures ground to a fine powder in a mill can be analyzed quantitatively with an appropriate model.

Predicting ash compositions by any of the models studied proved to be disappointing. Results show that the interaction coefficients from artificially produced samples cannot be used for coal ashes. There also appears to be major discrepancies between the AA and XRF results that cannot be explained solely by the methods and models employed. The problem may be due to the differences in the samples used to compare the methods. While ashes of the same name were used in the AA and XRF procedures, this does not necessarily mean that they have the same composition. The given percentages of the ash components were given in ranges of values from several samplings. The large discrepancies in the sulfur analyses indicates that differences in sample preparation also may account for the poor predictions.

It should be noted, however, that the results of one coal ash that had been well characterized (ID20783 - the given concentrations were obtained from the analyses of several laboratories) did indicate that the Criss and Burkes method could be used to estimate the major ash components if more reliable ash standards could be obtained. Analysis procedures (such as AA and XRF) for coal ash, it is important to prepare the ash under identical conditions and if possible, from precisely the same source to ensure consistency.

APPENDIX

PROGRAM LISTINGS

Using UCSD p-System Pascal Implemented on an IBM Personal Computer

```
PROGRAM FIT;

{ This program fits XRF count data to the Rasberry-Heinrich }
{ model and stores the coefficients on disk (file pat:fit)  }
{ Ci/Ri = Ki + Sum[ Aij*Cj ] + Sum[ Bij*Cj/(1+Ci) ]         }
{          Written by Pat Watson around 1/84                }


CONST
     MAXLEN=10;

TYPE
     ONEDIM   = ARRAY[1..MAXLEN] OF REAL;
     MATRIX   = ARRAY[1..MAXLEN,1..MAXLEN] OF REAL;
     FITREC   = RECORD
       ENHANCE : ARRAY[1..MAXLEN,1..MAXLEN] OF BOOLEAN;
       COEFFICIENT : ARRAY[1..MAXLEN,0..MAXLEN] OF REAL;
       TITLE : STRING[80];
       NC : INTEGER
       END;

VAR
     FITDATA                    : FILE OF FITREC;
     C,NSTAND,NCOMP             : INTEGER;
     SUMY                       : REAL;
     SUMX,SUMXY,B               : ARRAY[1..MAXLEN] OF REAL;
     SUMXX,A,COUNT,COMP         : ARRAY[1..MAXLEN,1..MAXLEN] OF REAL;
     PROUT                           : TEXT;
     DATATITLE                       : STRING;


PROCEDURE OPENFILE;

  VAR  I,J : INTEGER;

  BEGIN
  (*$I-*)
  RESET(FITDATA,'PAT:FIT');
  (*$I+*)
  IF IORESULT<>0 THEN
    BEGIN
    WITH FITDATA^ DO
      BEGIN
      TITLE := ' '; NC := 0;
      FOR I := 1 TO MAXLEN DO
        BEGIN
        COEFFICIENT[I,0] := 0.0;
        FOR J := 1 TO MAXLEN DO
          BEGIN
          COEFFICIENT[I,J] := 0.0;
          ENHANCE[I,J] := FALSE
          END
        END
      END;
```

```
    REWRITE(FITDATA,'PAT:FIT');
    FOR I:=0 TO 20 DO
      BEGIN
      SEEK(FITDATA,I);
      PUT(FITDATA)
      END;
    END
  END;

PROCEDURE GETDATA;

  VAR
      I,J,LAST,Q          : INTEGER;
      NAME,LINE           : STRING;
      INDATA              : TEXT;

  BEGIN
  WRITELN(' ENTER INPUT DATA FILE:');
  READLN(NAME);
  NAME := CONCAT('PAT:',NAME,'.TEXT');
  RESET(INDATA,NAME);
  READLN(INDATA,DATATITLE);
  READLN(INDATA,NSTAND,NCOMP);
  FOR I := 1 TO NSTAND DO
    BEGIN
    FOR J := 1 TO NCOMP DO READ(INDATA,COMP[J,I]);
    FOR J := 1 TO NCOMP DO READ(INDATA,COUNT[J,I]);
    END;
  FOR I := 1 TO NCOMP DO
    FOR J := 1 TO NCOMP DO
      BEGIN
      READ(INDATA,Q);
      IF Q=1
        THEN FITDATA^.ENHANCE[I,J] := TRUE
        ELSE FITDATA^.ENHANCE[I,J] := FALSE;
      END;
  CLOSE(INDATA)
  END;

PROCEDURE SUM_EM_UP;

  VAR  I,J,K    :INTEGER;
       XJ,Y     :REAL;

  BEGIN
  SUMY:=0.0;
  FOR I:=1 TO NCOMP DO
    BEGIN
    SUMXY[I]:=0.0;
    SUMX[I]:=0.0;
    FOR J:=1 TO NCOMP DO
      SUMXX[I,J]:=0.0
    END;
```

```
  FOR I:= 1 TO NSTAND DO
    BEGIN
    Y:=COMP[C,I]/COUNT[C,I];
    SUMY:=SUMY+Y;
    FOR J:=1 TO NCOMP DO
      BEGIN
      IF FITDATA^.ENHANCE[C,J]
        THEN XJ:= COMP[J,I]/(1.0+ COMP[C,I])
        ELSE XJ:= COMP[J,I];
      SUMXY[J]:=SUMXY[J]+XJ*Y;
      SUMX[J]:= SUMX[J]+XJ;
      FOR K:=1 TO NCOMP DO
        IF FITDATA^.ENHANCE[C,K]
          THEN SUMXX[J,K]:= SUMXX[J,K]+XJ*COMP[K,I]/(1.0+COMP[C,I])
          ELSE SUMXX[J,K]:= SUMXX[J,K]+XJ*COMP[K,I]
      END
    END
  END;

PROCEDURE MAKEMATRIX;

  VAR I,I1,J,J1      : INTEGER;

  BEGIN
  A[1,1]:= NSTAND;
  B[1]:= SUMY;
  I1:= 1;
  FOR I:= 2 TO NCOMP DO
    BEGIN
    IF I1=C THEN I1:=I1+1;
    B[I]:= SUMXY[I1];
    A[1,I]:= SUMX[I1];
    A[I,1]:=A[1,I];
    J1:= 1;
    FOR J:= 2 TO NCOMP DO
      BEGIN
      IF J1=C THEN J1:=J1+1;
      A[I,J]:= SUMXX[I1,J1];
      J1:=J1+1
      END;
    I1:=I1+1
    END
  END;

PROCEDURE GAUSSJORDAN(VAR A:MATRIX; VAR B:ONEDIM; DEGREE: INTEGER);

  VAR
         I,J,K,L            :INTEGER;
         BIG,COEFF,TERM,TEMP:REAL;

  BEGIN
  FOR I:= 1 TO DEGREE-1 DO
    BEGIN
    BIG:=0.0;
    FOR K:= I TO DEGREE DO
```

```
   BEGIN
   TERM:=ABS(A[K,I]);
   IF TERM > BIG THEN
     BEGIN
     BIG:= TERM;
     L:= K
     END
    END;
  IF I <> L THEN
    BEGIN
    FOR J:= 1 TO DEGREE DO
      BEGIN
      TEMP:= A[I,J];
      A[I,J] := A[L,J];
      A[L,J] := TEMP;
      END;
    TEMP := B[I];
    B[I] := B[L];
    B[L] := TEMP
    END;
   FOR J := I+1 TO DEGREE DO
     BEGIN
     COEFF := A[J,I]/A[I,I];
     FOR K:= I TO DEGREE DO
       A[J,K] := A[J,K] - COEFF*A[I,
     B[J] := B[J] - COEFF*B[I]
     END
   END;
 FOR I:= DEGREE DOWNTO 1 DO
   BEGIN
   B[I] := B[I]/A[I,I];
   FOR J:= I-1 DOWNTO 1 DO
     B[J] := B[J] - A[J,I]*B[I]
   END
  END;

PROCEDURE STORIT;

  VAR    I,J              :INTEGER;

  BEGIN
  WITH FITDATA^ DO
    BEGIN
    J:=0;
    FOR I:=1 TO NCOMP DO
      BEGIN
      IF J=C THEN J:=J+1;
      COEFFICIENT[C,J] := B[I];
      J:=J+1
      END;
    COEFFICIENT[C,C]:= 0.0
    END
   END;
```

```
PROCEDURE PRINTIT;

  VAR      I,J    :INTEGER;

  BEGIN
  REWRITE(PROUT,'PRINTER:');
  WRITE(PROUT,'LEAST SQUARES FIT OF XRF DATA TO RASBERRY-HEINRICH');
  WRITELN(PROUT,' MODEL');
  WRITELN(PROUT); WRITELN(PROUT);
  WRITELN(PROUT,'INPUT DATA :   ');
  WRITELN(PROUT,DATATITLE);
  WRITELN(PROUT); WRITELN(PROUT);
  WITH FITDATA^ DO
    BEGIN
    WRITELN(PROUT,'K RATIOS:');
    FOR I := 1 TO NCOMP DO
      WRITE(PROUT,COEFFICIENT[I,0]:10:4);
    WRITELN(PROUT); WRITELN(PROUT);
    WRITELN(PROUT,'COEFFICIENTS :');
    FOR I := 1 TO NCOMP DO
      BEGIN
      FOR J := 1 TO NCOMP DO WRITE(PROUT,COEFFICIENT[I,J]:10:4);
      WRITELN(PROUT)
      END
    END;
  WRITELN(PROUT)
  END;

PROCEDURE SAVE_ON_DISK;

  VAR      RECNUM         :INTEGER;

  BEGIN
  WRITELN('ENTER RECORD NUMBER TO STORE DATA');
  READLN(RECNUM);
  IF RECNUM>20
    THEN WRITELN('DATA NOT STORED....ONLY 20 RECORDS ALLOWED.....')
    ELSE BEGIN
    FITDATA^.TITLE:=DATATITLE;
    FITDATA^.NC := NCOMP;
    SEEK(FITDATA,RECNUM);
    PUT(FITDATA);
    CLOSE(FITDATA,LOCK);
    WRITELN(PROUT,'STORED IN RECORD ',RECNUM)
    END
  END;
```

```
BEGIN (* MAIN *)
OPENFILE;
GETDATA;
FOR C := 1 TO NCOMP DO
  BEGIN
  SUM_EM_UP;
  MAKEMATRIX;
  GAUSSJORDAN(A,B,NCOMP);
  STORIT;
  END;
PRINTIT;
SAVE_ON_DISK
END.
```

```
PROGRAM FIT2;

  {THIS PROGRAM USES XRF COUNT DATA AND COEFFICIENTS   }
  { ON FILE FIT2 FOR THE WHEELER-JACOB MODEL           }

CONST
     MAXLEN=10;

TYPE
     ONEDIM   = ARRAY[1..MAXLEN] OF REAL;
     MATRIX   = ARRAY[1..MAXLEN,1..MAXLEN] OF REAL;
     FITREC   = RECORD
       COEFFICIENT : ARRAY[1..MAXLEN,0..MAXLEN] OF REAL;
       TITLE : STRING[80];
       NC : INTEGER
       END;

VAR
     FITDATA                  : FILE OF FITREC;
     C,NCOMP,NSAMPLE          : INTEGER;
     COUNT                    : ARRAY[1..20] OF ONEDIM;
     COMP                     : ONEDIM;
     PROUT                         : TEXT;
     DATATITLE                     : STRING;


PROCEDURE OPENFILE;

  VAR      RECNUM : INTEGER;

  BEGIN
  RESET(FITDATA,'PAT:FIT2');
  WRITELN('ENTER RECORD CONTAINING COEFFICIENTS:');
  READLN(RECNUM);
  SEEK(FITDATA,RECNUM);
  GET(FITDATA)
  END;
```

```
PROCEDURE GETDATA;

  VAR
      I,J                     : INTEGER;
      NAME                    : STRING;
      INDATA                  : TEXT;

  BEGIN
  WRITELN(' ENTER COUNT DATA FILE:');
  READLN(NAME);
  NAME := CONCAT('PAT:',NAME,'.TEXT');
  RESET(INDATA,NAME);
  READLN(INDATA,DATATITLE); WRITELN(DATATITLE);
  READLN(INDATA,NSAMPLE);
  FOR I := 1 TO NSAMPLE DO
    FOR J := 1 TO NCOMP DO READ(INDATA,COUNT[I,J]);
  CLOSE(INDATA)
  END;

PROCEDURE INITIALPRINT;

  BEGIN
  REWRITE(PROUT,'PRINTER:');
  WRITELN(PROUT,'QUANTITATIVE RESULTS OF XRF COUNT DATA USING
  WHEELER MODEL');
  WRITELN(PROUT); WRITELN(PROUT);
  WRITELN(PROUT,'INPUT DATA :  ');
  WRITELN(PROUT,DATATITLE);
  WRITELN(PROUT); WRITELN(PROUT);
  WRITELN(PROUT,'COEFFICIENT TITLE:');
  WRITELN(PROUT,FITDATA^.TITLE);
  WRITELN(PROUT); WRITELN(PROUT)
  END;

PROCEDURE CALCIT;

  VAR I,J         :INTEGER;

  BEGIN
  WITH FITDATA^ DO
    BEGIN
    FOR I := 1 TO NCOMP DO
      BEGIN
      COMP[I] := COEFFICIENT[I,0];
      FOR J := 1 TO NCOMP DO
        COMP[I] := COMP[I] + COEFFICIENT[I,J]*COUNT[C,J];
      COMP[I] := COUNT[C,I]*EXP(COMP[I])
      END
    END
  END;
```

```
PROCEDURE PRINTIT;

  VAR I          : INTEGER;

  BEGIN
  FOR I := 1 TO NCOMP DO WRITE(PROUT,COMP[I]:10:4);
  WRITELN(PROUT);
  WRITELN(PROUT)
  END;

BEGIN (* MAIN *)
OPENFILE;
NCOMP := FITDATA^.NC;
GETDATA;
INITIALPRINT;
FOR C := 1 TO NSAMPLE DO
  BEGIN
  CALCIT;
  PRINTIT
  END;
END.
```

```
PROGRAM FIT3;

{ This program fits XRF count data to the Rasberry-Heinrich }
{ model and stores the coefficients on disk (file pat:fit)   }
{ Ci/Ri = Ki + Sum[ Aij*Cj ] + Sum[ Bij*Cj/(1+Ci) ]          }
{        Written by Pat Watson around 1/84                   }


CONST
     MAXLEN=10;

TYPE
     ONEDIM   = ARRAY[1..MAXLEN] OF REAL;
     MATRIX   = ARRAY[1..MAXLEN,1..MAXLEN] OF REAL;
     FITREC   = RECORD
       ENHANCE : ARRAY[1..MAXLEN,1..MAXLEN] OF BOOLEAN;
       COEFFICIENT : ARRAY[1..MAXLEN,0..MAXLEN] OF REAL;
       TITLE : STRING[80];
       NC : INTEGER
       END;

VAR
     FITDATA                 : FILE OF FITREC;
     C,NSTAND,NCOMP          : INTEGER;
     SUMXY,B                 : ONEDIM;
     SUMXX,A                 : MATRIX;
     COUNT,COMP              : ARRAY[1..20] OF ONEDIM;
     PROUT                   : TEXT;
     DATATITLE               : STRING;


PROCEDURE OPENFILE;

  VAR  I,J : INTEGER;

  BEGIN
  (*$I-*)
  RESET(FITDATA,'PAT:FIT');
  (*$I+*)
  IF IORESULT<>0 THEN
    BEGIN
    WITH FITDATA^ DO
      BEGIN
      TITLE := ' '; NC := 0;
      FOR I := 1 TO MAXLEN DO
        BEGIN
        COEFFICIENT[I,0] := 0.0;
        FOR J := 1 TO MAXLEN DO
          BEGIN
          COEFFICIENT[I,J] := 0.0;
          ENHANCE[I,J] := FALSE
          END
        END
      END;
```

```
    REWRITE(FITDATA,'PAT:FIT');
    FOR I:=0 TO 20 DO
      BEGIN
      SEEK(FITDATA,I);
      PUT(FITDATA)
      END;
    END
  END;

PROCEDURE GETDATA;

  VAR
      I,J,LAST,Q          : INTEGER;
      NAME,LINE           : STRING;
      INDATA              : TEXT;

  BEGIN
  WRITELN(' ENTER INPUT DATA FILE:');
  READLN(NAME);
  NAME := CONCAT('PAT:',NAME,'.TEXT');
  RESET(INDATA,NAME);
  READLN(INDATA,DATATITLE);
  READLN(INDATA,NSTAND,NCOMP);
  FOR I := 1 TO NSTAND DO
    BEGIN
    FOR J := 1 TO NCOMP DO READ(INDATA,COMP[J,I]);
    FOR J := 1 TO NCOMP DO READ(INDATA,COUNT[J,I]);
    END;
  FOR I := 1 TO NCOMP DO
    FOR J := 1 TO NCOMP DO
      BEGIN
      READ(INDATA,Q);
      IF Q=1
        THEN FITDATA^.ENHANCE[I,J] := TRUE
        ELSE FITDATA^.ENHANCE[I,J] := FALSE;
      END;
  READLN(INDATA);
  FOR I := 1 TO NCOMP DO READ(INDATA,FITDATA^.COEFFICIENT[I,0]);
  CLOSE(INDATA)
  END;

PROCEDURE SUM_EM_UP;

  VAR  I,J,K    :INTEGER;
       XJ,Y     :REAL;

  BEGIN
  FOR I:=1 TO NCOMP DO
    BEGIN
    SUMXY[I]:=0.0;
    FOR J:=1 TO NCOMP DO
      SUMXX[I,J]:=0.0
    END;
```

```
  FOR I:= 1 TO NSTAND DO
    BEGIN
    Y:=COMP[C,I]/COUNT[C,I]-FITDATA^.COEFFICIENT[C,0];
    FOR J:=1 TO NCOMP DO
      BEGIN
      IF FITDATA^.ENHANCE[C,J]
        THEN XJ:= COMP[J,I]/(1.0+ COMP[C,I])
        ELSE XJ:= COMP[J,I];
      SUMXY[J]:=SUMXY[J]+XJ*Y;
      FOR K:=1 TO NCOMP DO
        IF FITDATA^.ENHANCE[C,K]
          THEN SUMXX[J,K]:= SUMXX[J,K]+XJ*COMP[K,I]/(1.0+COMP[C,I])
          ELSE SUMXX[J,K]:= SUMXX[J,K]+XJ*COMP[K,I]
      END
    END
  END;

PROCEDURE MAKEMATRIX;

  VAR I,I1,J,J1      : INTEGER;

  BEGIN
  I1:= 1;
  FOR I:= 1 TO NCOMP-1 DO
    BEGIN
    IF I1=C THEN I1:=I1+1;
    B[I]:=SUMXY[I1];
    J1:= 1;
    FOR J:= 1 TO NCOMP-1 DO
      BEGIN
      IF J1=C THEN J1:=J1+1;
      A[I,J]:= SUMXX[I1,J1];
      J1:=J1+1
      END;
    I1:=I1+1
    END
  END;

PROCEDURE GAUSSJORDAN(VAR A:MATRIX; VAR B:ONEDIM; DEGREE: INTEGER);

  VAR
         I,J,K,L               :INTEGER;
         BIG,COEFF,TERM,TEMP:REAL;

  BEGIN
  FOR I:= 1 TO DEGREE-1 DO
    BEGIN
    BIG:=0.0;
    FOR K:= I TO DEGREE DO
      BEGIN
      TERM:=ABS(A[K,I]);
```

```
     IF TERM > BIG THEN
       BEGIN
       BIG:= TERM;
       L:= K
       END
     END;
   IF I <> L THEN
     BEGIN
     FOR J:= 1 TO DEGREE DO
       BEGIN
       TEMP:= A[I,J];
       A[I,J] := A[L,J];
       A[L,J] := TEMP;
       END;
     TEMP := B[I];
     B[I] := B[L];
     B[L] := TEMP
     END;
   FOR J := I+1 TO DEGREE DO
     BEGIN
     COEFF := A[J,I]/A[I,I];
     FOR K:= I TO DEGREE DO
       A[J,K] := A[J,K] - COEFF*A[I,K];
     B[J] := B[J] - COEFF*B[I]
     END
   END;
  FOR I:= DEGREE DOWNTO 1 DO
    BEGIN
    B[I] := B[I]/A[I,I];
    FOR J:= I-1 DOWNTO 1 DO
      B[J] := B[J] - A[J,I]*B[I]
    END
  END;

PROCEDURE STORIT;

  VAR    I,J               :INTEGER;

  BEGIN
  WITH FITDATA^ DO
    BEGIN
    J:=1;
    FOR I:=1 TO NCOMP-1 DO
      BEGIN
      IF J=C THEN J:=J+1;
      COEFFICIENT[C,J] := B[I];
      J:=J+1
      END;
    COEFFICIENT[C,C]:= 0.0
    END
  END;
```

```
PROCEDURE PRINTIT;

  VAR     I,J   :INTEGER;

  BEGIN
  REWRITE(PROUT,'PRINTER:');
  WRITE(PROUT,'LEAST SQUARES FIT OF XRF DATA TO RASBERRY-HEINRICH');
  WRITELN(PROUT,' MODEL');
  WRITELN(PROUT,'USING PURE COMPONENT COUNTRATES FOR Ks');
  WRITELN(PROUT); WRITELN(PROUT);
  WRITELN(PROUT,'INPUT DATA :   ');
  WRITELN(PROUT,DATATITLE);
  WRITELN(PROUT); WRITELN(PROUT);
  WITH FITDATA^ DO
    BEGIN
    WRITELN(PROUT,'K RATIOS (GIVEN):');
    FOR I := 1 TO NCOMP DO
      WRITE(PROUT,COEFFICIENT[I,0]:10:4);
    WRITELN(PROUT); WRITELN(PROUT);
    WRITELN(PROUT,'COEFFICIENTS :');
    FOR I := 1 TO NCOMP DO
      BEGIN
      FOR J := 1 TO NCOMP DO WRITE(PROUT,COEFFICIENT[I,J]:10:4);
      WRITELN(PROUT)
      END
    END;
  WRITELN(PROUT)
  END;

PROCEDURE SAVE_ON_DISK;

  VAR     RECNUM        :INTEGER;

  BEGIN
  WRITELN('ENTER RECORD NUMBER TO STORE DATA');
  READLN(RECNUM);
  IF RECNUM>20
    THEN WRITELN('DATA NOT STORED....ONLY 20 RECORDS ALLOWED.....')
    ELSE BEGIN
    FITDATA^.TITLE:=DATATITLE;
    FITDATA^.NC := NCOMP;
    SEEK(FITDATA,RECNUM);
    PUT(FITDATA);
    CLOSE(FITDATA,LOCK);
    WRITELN(PROUT,'STORED IN RECORD ',RECNUM)
    END
  END;
```

```
BEGIN (* MAIN *)
OPENFILE;
GETDATA;
FOR C := 1 TO NCOMP DO
  BEGIN
  SUM_EM_UP;
  MAKEMATRIX;
  GAUSSJORDAN(A,B,NCOMP-1);
  STORIT;
  END;
PRINTIT;
SAVE_ON_DISK
END.
```

```
PROGRAM QUANT;

CONST    MAXLEN=10;

TYPE
     ONEDIM   = ARRAY[1..MAXLEN] OF REAL;
     MATRIX   = ARRAY[1..MAXLEN] OF ONEDIM;
     FITREC   = RECORD
       ENHANCE : ARRAY[1..MAXLEN,1..MAXLEN] OF BOOLEAN;
       COEFFICIENT : ARRAY[1..MAXLEN,0..MAXLEN] OF REAL;
       TITLE : STRING[80];
       NC : INTEGER
       END;

 VAR
     FITDATA                          : FILE OF FITREC;
     C,CNEW                           : ONEDIM;
     COUNT                            : MATRIX;
     ERROR                            : REAL;
     ITERATION,NSAMP,NCOMP,SAMPLE : INTEGER;
     TITLE                            : STRING[80];
     PROUT                            : TEXT;


 PROCEDURE GET_FIT_DATA;

   VAR RECNUM     : INTEGER;

   BEGIN
   RESET(FITDATA,'PAT:FIT');
   WRITELN('ENTER RECORD NUMBER');
   READLN(RECNUM);
   SEEK(FITDATA,RECNUM);
   GET(FITDATA)
   END;

 PROCEDURE GET_COUNT_DATA;

   VAR
     NAME          :STRING;
     INDATA        :TEXT;
     I,J           :INTEGER;

   BEGIN
   WRITELN('ENTER FILENAME FOR COUNT DATA');
   READLN(NAME);
   NAME:= CONCAT('PAT:',NAME,'.TEXT');
   RESET(INDATA,NAME);
   READLN(INDATA,TITLE);
   READLN(INDATA,NSAMP);
   FOR I := 1 TO NSAMP DO
```

```
    FOR J := 1 TO NCOMP DO
      READ(INDATA,COUNT[I,J])
  END;

PROCEDURE FIRSTGUESS;

  VAR  I        :INTEGER;

  BEGIN
  FOR I := 1 TO NCOMP DO
    BEGIN
    C[I] := COUNT[SAMPLE,I]*FITDATA^.COEFFICIENT[I,0];
    IF C[I] < 0.0 THEN C[I] := 0.05
    END
  END;

PROCEDURE CALCIT;

  VAR
       I,J      :INTEGER;
       X        :REAL;

  BEGIN
  WITH FITDATA^ DO
    BEGIN
    ITERATION := 0;
    REPEAT
      ERROR := 0.0;
      FOR I := 1 TO NCOMP DO
        BEGIN
        CNEW[I] := COEFFICIENT[I,0];
        FOR J := 1 TO NCOMP DO
          BEGIN
          IF ENHANCE[I,J]
            THEN X := C[J]/(1.0 + C[I])
            ELSE X := C[J];
          CNEW[I] := CNEW[I] + COEFFICIENT[I,J]*X
          END;
        CNEW[I] := CNEW[I]*COUNT[SAMPLE,I];
        ERROR := ERROR +ABS(C[I]-CNEW[I])
        END;
      FOR I := 1 TO NCOMP DO C[I] := CNEW[I];
      ITERATION := ITERATION +1;
      UNTIL (ERROR < 0.005) OR (ITERATION > 100)
      END
    END;
```

```
PROCEDURE PRINTIT;

  VAR  I         :INTEGER;

  BEGIN
  WRITELN(PROUT,ITERATION,' ITERATIONS ',' ERROR = ',ERROR);
  FOR I := 1 TO NCOMP DO WRITE(PROUT,C[I]:10:4);
  WRITELN(PROUT); WRITELN(PROUT)
  END;

PROCEDURE INITIAL_PRINT;

  BEGIN
  REWRITE(PROUT,'PRINTER:');
  WRITELN(PROUT,'CALCULATION OF COMPOSITION FROM XRF DATA');
  WRITELN(PROUT,'      USING RASBERRY-HEINRICH MODEL');
  WRITELN(PROUT);
  WRITELN(PROUT,'DATA :');
  WRITELN(PROUT,TITLE);
  WRITELN(PROUT);
  WRITELN(PROUT,'COEFFICIENTS USED :');
  WRITELN(PROUT,FITDATA^.TITLE);
  WRITELN(PROUT);
  WRITELN(PROUT)
  END;

BEGIN (*MAIN*)
GET_FIT_DATA;
NCOMP := FITDATA^.NC;
GET_COUNT_DATA;
INITIAL_PRINT;
FOR SAMPLE := 1 TO NSAMP DO
  BEGIN
  FIRSTGUESS;
  CALCIT;
  PRINTIT
  END
END.
```

```
PROGRAM QUANT3;

        {THIS PROG CALCS COMPOSITION FROM INTENSITIES }
        {USING THE CRISS AND BURKE MODEL    2/11/84   }

CONST    MAXLEN=10;

TYPE
     ONEDIM  = ARRAY[1..MAXLEN] OF REAL;
     MATRIX  = ARRAY[1..MAXLEN] OF ONEDIM;
     FITREC  = RECORD
       ENHANCE : ARRAY[1..MAXLEN,1..MAXLEN] OF BOOLEAN;
       COEFFICIENT : ARRAY[1..MAXLEN,0..MAXLEN] OF REAL;
       TITLE : STRING[80];
       NC : INTEGER
       END;

VAR
     FITDATA                        : FILE OF FITREC;
     B                              : ONEDIM;
     A                              : MATRIX;
     COUNT                          : ARRAY[1..20] OF ONEDIM;
     NSAMP,NCOMP,SAMPLE             : INTEGER;
     TITLE                          : STRING[80];
     PROUT                          : TEXT;


PROCEDURE GET_FIT_DATA;

  VAR RECNUM    : INTEGER;

  BEGIN
  RESET(FITDATA,'PAT:FIT');
  WRITELN('ENTER RECORD NUMBER');
  READLN(RECNUM);
  SEEK(FITDATA,RECNUM);
  GET(FITDATA)
  END;
```

```
PROCEDURE GET_COUNT_DATA;

  VAR
    NAME            :STRING;
    INDATA          :TEXT;
    I,J             :INTEGER;

  BEGIN
  WRITELN('ENTER FILENAME FOR COUNT DATA');
  READLN(NAME);
  NAME:= CONCAT('PAT:',NAME,'.TEXT');
  RESET(INDATA,NAME);
  READLN(INDATA,TITLE);
  READLN(INDATA,NSAMP);
  FOR I := 1 TO NSAMP DO
    FOR J := 1 TO NCOMP DO
      READ(INDATA,COUNT[I,J])
  END;

PROCEDURE PRINTIT;

  VAR  I           :INTEGER;
       TOTAL       :REAL;
  BEGIN
  WRITELN(PROUT);
  TOTAL:=0.0;
  FOR I:=1 TO NCOMP DO TOTAL:=TOTAL+B[I];
  WRITELN(PROUT,'FINAL COMPOSITION:');
  WRITELN(PROUT,'TOTAL =   ',TOTAL:7:4);
  FOR I := 1 TO NCOMP DO WRITE(PROUT,B[I]:10:4);
  WRITELN(PROUT);
  END;

PROCEDURE INITIAL_PRINT;

  BEGIN
  REWRITE(PROUT,'PRINTER:');
  WRITELN(PROUT,'CALCULATION OF COMPOSITION FROM XRF DATA');
  WRITELN(PROUT,'     USING CRISS AND BURKE MODEL');
  WRITELN(PROUT);
  WRITELN(PROUT,'DATA :');
  WRITELN(PROUT,TITLE);
  WRITELN(PROUT);
  WRITELN(PROUT,'COEFFICIENTS USED :');
  WRITELN(PROUT,FITDATA^.TITLE);
  WRITELN(PROUT);
  WRITELN(PROUT)
  END;
```

```
PROCEDURE MAKEMATRIX;

  VAR I,J           : INTEGER;

  BEGIN
  FOR I:= 1 TO NCOMP DO
    BEGIN
    FOR J := 1 TO NCOMP DO
      BEGIN
      A[I,J]:=FITDATA^.COEFFICIENT[I,J]
      END;
    B[I]:= -FITDATA^.COEFFICIENT[I,O];
    A[I,I]:=-1.0/COUNT[SAMPLE,I]
    END
  END;

PROCEDURE GAUSSJORDAN(VAR A:MATRIX; VAR B:ONEDIM; DEGREE: INTEGER);

   { THIS PROC SOLVES SIMULTANEOUS EQ.S AND RETURNS ANSWER IN B }

  VAR
         I,J,K,L            :INTEGER;
         BIG,COEFF,TERM,TEMP:REAL;

  BEGIN
  FOR I:= 1 TO DEGREE-1 DO
    BEGIN
    BIG:=0.0;
    FOR K:= I TO DEGREE DO
      BEGIN
      TERM:=ABS(A[K,I]);
      IF TERM > BIG THEN
        BEGIN
        BIG:= TERM;
        L:= K
        END
      END;
    IF I <> L THEN
      BEGIN
      FOR J:= 1 TO DEGREE DO
        BEGIN
        TEMP:= A[I,J];
        A[I,J] := A[L,J];
        A[L,J] := TEMP;
        END;
      TEMP := B[I];
      B[I] := B[L];
      B[L] := TEMP
      END;
```

```
      FOR J := I+1 TO DEGREE DO
        BEGIN
        COEFF := A[J,I]/A[I,I];
        FOR K:= I TO DEGREE DO
          A[J,K] := A[J,K] - COEFF*A[I,K];
        B[J] := B[J] - COEFF*B[I]
        END
      END;
    FOR I:= DEGREE DOWNTO 1 DO
      BEGIN
      B[I] := B[I]/A[I,I];
      FOR J:= I-1 DOWNTO 1 DO
        B[J] := B[J] - A[J,I]*B[I]
      END
    END;
  BEGIN (* MAIN *)
  GET_FIT_DATA;
  NCOMP := FITDATA^.NC;
  GET_COUNT_DATA;
  INITIAL_PRINT;
  FOR SAMPLE := 1 TO NSAMP DO
    BEGIN
    MAKEMATRIX;
    GAUSSJORDAN(A,B,NCOMP);
    PRINTIT
    END;
  END.
```

LITERATURE CITED

1) Vanetti, G.E., and C.F. Busch, "A Utility Perspective on the Significance of Mineral Analysis of Ash Data", Coal Testing Conference Proceedings, 1981, pp. 48-58

2) Reid, W. T., External Corrosion and Deposits American Elsevier Press, New York, 1971.

3) Huggins, F. E., D. A. Kosmacke, and G. A. Huffman, "Correlation Between Ash Fusion Temperature and Ternary Equilibrium Phase Diagrams" Fuel vol. 60 1981.

4) Winegartner, E. C., and B. T. Rhodes, "An Empirical Study of the Relationship of Chemical Properties of Ash Fusion Temperatures" Transactions of the A.S.M.E. Journal for Engineering Power, November 1974.

5) Reid, W. T., "Coal Ash - Its Effect on Combustion Systems" Chemistry of Coal Utilization, M. A. Elliot, Editor, John Wiley and Sons, New York, 1981.

6) Moza A. K., and L. G. Austin, "Studies on Slag Deposit Formation in Pulverized Coal Combustors" Fuel vol. 61 Feb. 1981 pp. 161-165.

7) American Society of Testing and Materials Standards D-3682-78, pp. 439-446.

8) Jenkins, R., An Introduction to X-ray Spectrometry Heyden and Son Ltd., London 1980.

9) Criss, J. W., and L. S. Birks, "Calculation Methods for Fluorescent X-ray Spectrometry", Analytical Chemistry, vol. 40 no. 7, June 1968 pp. 1080-1086.

10) Otvos, L. W., G. E. Wyld, and T. C. Yao, "Fundamental Parameter Method for Quantitative Analysis with Mono-Chromatic X-ray Sources", 25th Annual Denver X-ray Conference, 1976.

11) Laguitton, D. and M. Mantler, "Lama I - A General Fortran Program for Quantitative X-ray Fluorescence Analysis" Advances in X-ray Analysis, vol. 20 1977, pp. 515-528.

12) Lucas-Tooth, H. J., and C. Pyne, Advances in X-ray Analysis, vol. 7 1964, pp. 523-530.

13) Beatty, H. J., and R. M. Brissey, "Calibration Method

for X-ray Spectrometry" Analytical Chemistry, vol. 26 no. 6 June 1954.

14) Rasberry, S. D., and K. F. J. Heinrich, "Calibration for Inter-element Effects in X-ray Fluorescence Analysis" Analytical Chemistry vol. 46 no. 1 January 1974 pp. 81-89.

15) Andermann, G. and J. D. Allen, "X-ray Emmision Analysis of Finished Cements" Analytical Chemistry vol. 33 November 1961, pp. 1695-1699.

16) Wheeler, B. D., and N. C. Jacobus, "Quantitative Analysis of Coal and Coal Ash by Energy Dispersive X-ray Fluorescence" 1980.

17) Quinn, A. P., "Quasi-Fundamental Correction Methods Using Broad Band X-ray Excitation" Advances in X-ray Analysis, vol. 22 1979, pp. 293-302.

18) Prather, J. W., J. A. Guin, and A. R. Tarrer, "X-ray Fluorescence Analysis of Trace Elements in Coal and Solvent Refined Coal" Analytical Methods for Coal and Coal Products, vol. 3, 1979.

19) Andermann, G., "Improvements in the X-ray Emmision Analysis of Cement Raw Mix" Analytical Chemistry vol. 33 November 1961, pp. 1689-1695.

20) Wheeler, B. D., "Utilizing Artificial Standards in Chemical Analysis of Coal" CQ Spring 1983, pp.30-33.

21) Kevex XRF QUANTEX-RAY Software User's Manual Kevex Corporation, 1101 Chess Drive, Foster City, California.

22) Gluskoter, H. J., N. F. Shimp, and R. R. Ruch, "Coal Analyses, Trace Elements, and Mineral Matter" Chemistry of Coal Utilization, M. A. Elliot, Editor, John Wiley and Sons, New York, 1981.