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The simultaneous determination of minor and trace elements in coal using instrumental neutron activation analysis

MASTER

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INTRODUCTION

Activation Analysis

Activation analysis is a nuclear method of analysis which has developed rapidly during the last twenty years and is now one of the most useful methods of trace analysis. The technique is particularly suited for the sensitive and accurate determination of a wide variety of elements which are not conveniently determined by standard methods of trace analysis. In contrast to conventional chemical analysis, the principal limitations of the technique arise from the nuclear properties of an element and not its chemistry.

The activation process involves the exposure of a sample to a source of particles or photons with sufficient energy to produce a nuclear transformation. The most common activation particle is the neutron with thermal energies, but fast neutrons, X-rays and other particles such as protons, deuterons, and alpha particles have been used successfully. The nuclear reactions brought about by thermal neutrons are of the (n,γ) type. A reaction of this kind produces an isotope of the irradiated element with the mass number increased by one. The resulting nuclide, a heavier isotope of the activated element will, in the majority of cases, be radioactive and decay by emitting a beta particle or gamma ray.

Elemental determinations using activation analysis techniques require a consideration of the laws governing the rate of growth and decay. Upon irradiation of a sample, the rate of growth of a particular radioactive species may be represented by equation 1.

$$R_G = \phi n \sigma = \frac{\phi m N^{o} f \sigma}{A} \qquad (1)$$

where n = the number of target atoms

ϕ = the neutron flux (n/cm^2-sec)

m = the mass of the trace element in the specimen (gm)

A = the Atomic weight of the trace element (gm/gm-atom)

f = the fractional isotopic abundance of the target nuclide

N^o = Avogadro's number (atoms/gm-atom)

σ = the reaction cross-section (cm^2/atom) or barn/atom.

The rate of decay of the radioactive species at any given time is given by equation 2.

$$R_o = \lambda N \tag{2}$$

where N = the number of atoms of the radioactive species present

λ = the decay constant of the nuclide.

Therefore the overall rate of formation of a given nuclide must take into consideration the rate of formation during irradiation and also its rate of decay. This formation rate may be represented by equation 3.

$$\frac{dN}{dT} = \text{Rate of growth} - \text{Rate of decay} \tag{3}$$

$$= \frac{\phi m N^o f \sigma}{A} - \lambda N \tag{4}$$

where upon integration yields

$$R_o = \frac{\phi m N^o f \sigma}{A} (1 - e^{-\lambda t_1}) \tag{5}$$

in which t_1 = the duration of the irradiation. Now the disintegration

rate, D, of the activated product at any time, t_2, after irradiation may be calculated using equation 6.

$$D = \frac{\emptyset m N^{o} f \sigma}{A} \left(1 - e^{-\lambda t_1}\right) e^{-\lambda t_2} \tag{6}$$

Absolute determinations using equation 6 are rarely used due to uncertainties in the values of $\emptyset$ and σ. To avoid these uncertainties a comparative technique is employed. In this technique a sample containing a known amount of the element of interest and the unknown sample are irradiated simultaneously for the same time in the same flux. Under ideal conditions, the specific activities (disintegration rate/weight of element) of both standard and unknown are the same. Therefore, equation 7 can be used to determine the amount of the element of interest in the unknown sample.

$$\frac{\text{Activity of unknown}}{\text{Weight of unknown}} = \frac{\text{Activity of standard}}{\text{Weight of standard}} \tag{7}$$

Due to the nuclear nature of the method, the neutron activation analysis technique is subject to few systematic sources of error compared to many chemical or physiocochemical methods of analysis. There are, however, several sources of error which are associated specifically with neutron activation analysis. These sources of error include neutron flux perturbation in samples and standards, neutron self-absorption during irradiation, interfering nuclear reactions on other elements which produce the nuclide of interest, and the measurement of the activities of the induced radionuclides.

For a discussion of all of the above sources of errors along with a more thorough discussion on activation analysis in theory and in practice, the reader is referred to several excellent books and monographs which have recently appeared in the literature.[1-6]

Purpose

The combustion of coal is a major source of air pollution, and in the ever-increasing concern regarding environmental contamination, the need has been recognized for versatile and reliable methods for the determination of trace elements in coal and their combustion products. Instrumental neutron activation analysis (INAA) with thermal neutrons is one of the most versatile analytical techniques for trace analysis. A comprehensive report by Block and Dams discussed the possibilities offered by this technique for trace analysis of coal, based on thermal neutron irradiation and a coaxial Ge(Li) detector. They were able to determine 43 elements in a large number of Belgian coal and coal ash samples.[7,8] Nadkarni determined 39 elements in coal and coal fly ash.[9] The INAA method used by Nadkarni has been described in detail elsewhere in its applications to biological,[10] geological and lunar,[11] and environmental samples.[12] Other investigators[13-15] have reported analyses of coal and fly ash by procedures similar to those of Block and Dams and Nadkarni.

The purpose of this project was to develop a procedure for determining minor and trace elements in coal using INAA, specifically elements which exposed to thermal neutrons would produce radioactive isotopes with short half-lives, mostly less than 10 minutes. Most of the published methods for applying INAA to coal analysis involve decay times of several hours,

and thus do not determine these elements. The nuclear properties of the elements considered for analysis are listed in Table 1.

Table 1. Nuclear properties of the elements considered for analysis

Element	Target Isotope	Isotopic Abundance	Product Nuclide	Half-Life	Thermal Neutron Cross Section	Measurement (KeV)
Al	^{27}Al	100	^{28}Al	2.31 m	0.24 b	1779
Br	^{79}Br	50.5	^{80}Br	17.6 m	8.5 b	617
Cl	^{37}Cl	24.5	^{38}Cl	37.3 m	0.4 b	1643
Cu	^{65}Cu	30.9	^{66}Cu	5.10 m	2.3 b	1039
Mg	^{26}Mg	11.2	^{27}Mg	9.45	0.027b	844[a] 1014
Mn	^{55}Mn	100	^{56}Mn	2.58 h	13.3 b	847[a] 1811
Ti	^{50}Ti	5.3	^{51}Ti	5.79 m	0.14 b	320
V	^{51}V	99.8	^{52}V	3.76 m	4.9 b	1434
Ca	^{48}Ca	0.18	^{49}Ca	8.8 m	1.1 b	3084

[a] γ energy not used in analysis.

EXPERIMENTAL

Irradiation Facilities and Detection Equipment

All coal samples were irradiated at the Ames Laboratory Research Reactor (ALRR). The ALRR was a heavy water moderated and cooled steady state reactor operated at 5 Megawatts (MW).

A pneumatic transfer system was used for rapid access to high neutron fluxes. For all irradiations, the system used was R5. Its irradiation position is located at the side of the reactor just below the core center line. The thermal neutron flux at this position when operating at 5 MW was 2.3×10^{13} neutrons/cm^2/sec with a cadmium ratio of approximately 20 to 1. The cadmium ratio is the ratio of the total neutron flux to that portion of the flux having neutron energies above the cadmium cut-off (approximately 0.6 electron volts). The R5 pneumatic system included an automatic timing system. This system was used to insure that the sample was irradiated, allowed to decay, and counted for the same period of time.

The detection system consisted of an Ortec Win Series Coaxial lithum-drifted germanium, Ge(Li), detector with the resolution of the system being 2.1 Kev measured at half maximum for a 1.33 Mev photopeak of ^{60}Co. The efficiency of the detector is warranted by the manufacturer to be 20% of a 3 x 3 inch sodium iodide detector. This detector is coupled to an Ortec preamplifier and a Cl Model 1417B Spectroscopy Amplifier which, in turn, is coupled to a Nuclear Data 50/50 Analyzer system. The Nuclear Data 50/50 Analyzer consists of a Series 50/50 Storage and Display Unit which has a 4096 Channel, 24-bit memory, display circuitry and the necessary circuitry for direct connection with input and output devices as well as

the PDP/8/L computer system. Also, a BNC Tail Pulse Generator Model RP-1 which was gated at 60 HZ by a RIDL Model 47-2 Pulser was input to the preamplifier during the collection of spectra. This was done to correct the spectra collection times for the analyzer dead time. All the spectra obtained from the detection system were transferred to 9-track magnetic tape via the associated PEC tape drive for temporary storage. Figure 1 shows a photograph of the detection equipment.

Samples and Sample Preparation

The coals analyzed in this study included the National Bureau of Standards (NBS) standard reference material 1632 along with eight different Iowa raw and clean coals. The NBS standard reference material 1632 is a blend of commercially available coals supplied by five electric power plants: Tennessee Valley Authority, Stevenson, Alabama; Commonwealth Edison, Chicago, Illinois; Baltimore Gas and Electric Company, Baltimore, Maryland; Carolina Light and Power Company, Roxboro, North Carolina; and Potomac Electric Power Company, Washington, D.C. These plants were specially selected to provide coals that covered a broad spectrum of the coal mining industry. Some of the coals required regrinding to obtain a fine particle size. The coals were then sieved and the portions passing through a 120 mesh sieve and retained on a 325 mesh sieve were taken. After sieving, the five coals were blended in a double-coned blender. After 1 hour the material was immediately removed and bottled. The raw Iowa coals were prepared for analysis by Steve Howe.[1] He used the American

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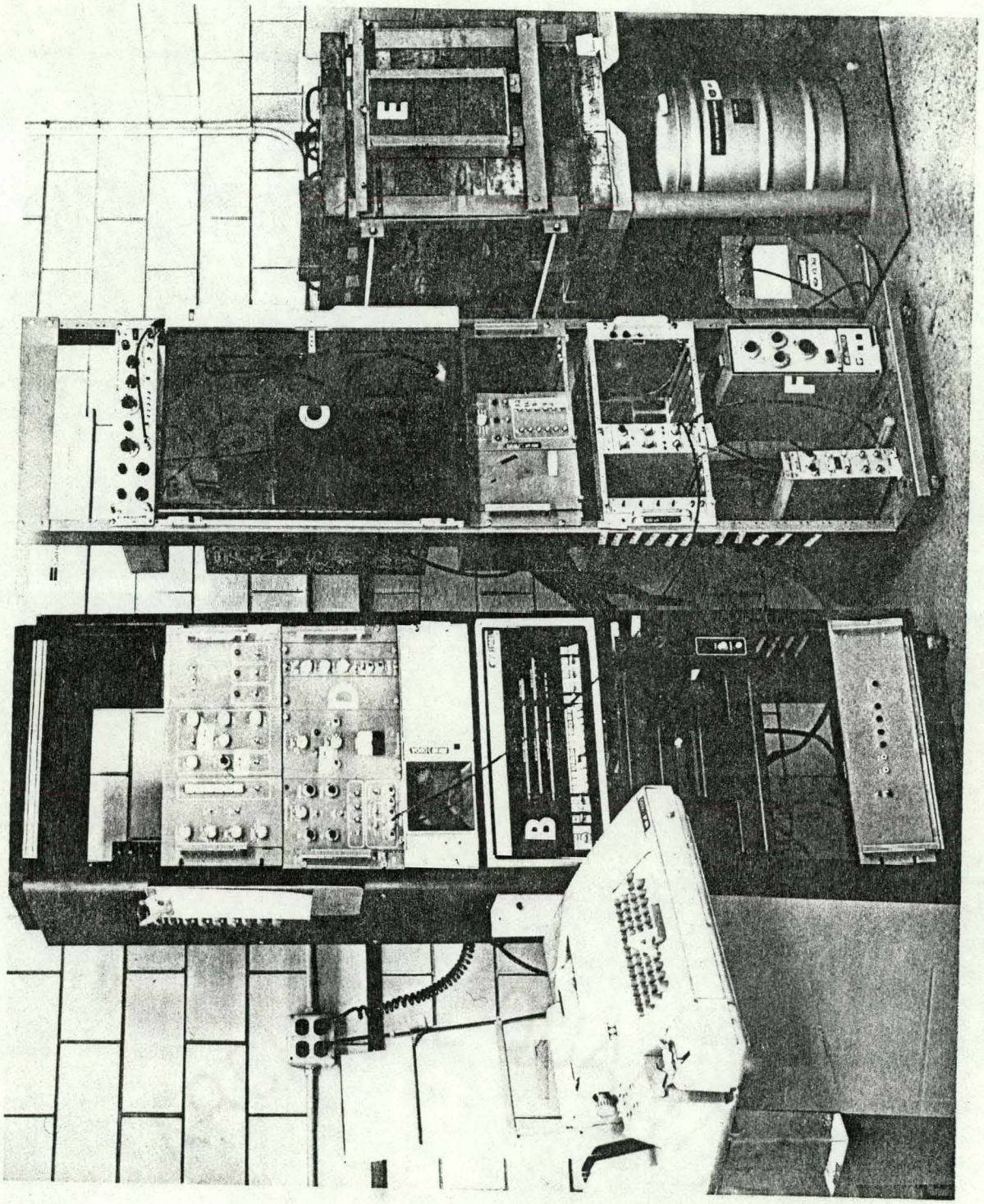
[1] Coal Preparation Technician.

Figure 1. A photograph of the detection system consisting of (a) teletype, (b) PDP/8/L computer, (c) PEC tape drive, (d) analyzer, (e) detector with a 2 inch lead shield, and (f) pulse generator.


E
C
F
D
B

Society for Testing and Materials (ASTM) method D22341-B-2 for collection of the gross samples. The Iowa cleaned coals were obtained from the Iowa State Coal Refining Plant. The methods used to clean the coals are (1) the float-sink (heavy media separation) technique in which raw coal is washed in a slurry which forces pure coal to float and non-combustible refuse to sink, and (2) the concentration table method, also a gravity separation. After the coals were cleaned, ASTM method D22341-B-2 was used to obtain samples for analysis.

The drying of the coal samples consisted of two 24 hour drying intervals. First, approximately 100 mg of coal was weighed and placed in a vacuum desiccator containing anhydrous $CaSO_4$ and dried for 24 hours. Then the sample was removed from the desiccator, reweighed, and dried for another 24 hours. In all cases the weight of the coal samples remained constant after the second 24 hour drying period. The samples were then bottled and placed in a desiccator containing $CaSO_4$ until analysis was performed. However, the NBS has two recommended procedures for drying coal samples. They are (1) drying for 24 hours using a cold trap at or below $-50^{o}C$ and a pressure not greater than 0.2 mm Hg and (2) drying in a desiccator over P_2O_5 or $Mg(ClO_4)_2$. The first procedure was not used due to the time involved in setting up a cold trap and keeping the pressure lower than 0.2 mm Hg. The second procedure was not used because it was very time consuming (>48 hours).

All samples, which ranged from 25 to 30 mg, were weighed into cleaned 2/5 dram polyethylene vials. These vials were placed in cleaned 4-dram polyethylene vials along with the titanium flux monitor. Each 4-dram

polyethylene vial was placed in a small "rabbit" for irradiation. The position of the 4-dram polyethylene vial within the rabbit was maintained in the desired geometry by styrofoam strip. It should be noted that in each irradiation the end of the rabbit containing the sample entered the reactor last. All 2/5 dram vials were sealed with a flame heated glass rod before irradiated.

Flux Monitor

In this work the samples and the standards were irradiated separately because of the short half-lives of the isotopes produced. Because of this it was necessary to use a flux monitor to determine the variations in the positioning of the sample within the pneumatic transfer system and the neutron flux. This flux monitor, a 10 μl solution of titanium, was irradiated simultaneously with each standard and sample. The titanium flux monitor was counted for one minute, five minutes after irradiation. From these counts a correction factor shown in equation 8 was derived for each irradiation.

$$CF_x = \frac{A_x P}{\sum_{i=1}^{P} A_i} \tag{8}$$

where CF_x = the correction factor for irradiation x

A_x = the activity of the flux monitor in irradiation x

P = the total number of irradiations

A_i = the activity of the flux monitor in irradiation i,

Post-irradiation Treatment

After the irradiation the sample was allowed to decay for 2 minutes and then immediately removed from the rabbit, rinsed, and counted 10 cm above the detector face.

Standard Solution

Stock sollutions were prepared containing milligram quantities for each of the following elements: Al, Br, Ca, Cl, Mg, Mn, Ti, and V. The reagents and solvents used to prepare these solutions are listed in Table 2.

Table 2. Reagents used to make standard solutions

Element	Reagent	
Al	Aluminum Foil	Dilute Nitric Acid containing 20 mg of copper metal
Br	Ammonium Bromide (NH_4Br)	Distilled-Deionized water
Ca	Calcium Carbonate ($CaCO_3$)	Dilute Nitric Acid
Cl	Ammonium Chloride (NH_4Cl)	Distilled-Deionized Water
Mg	Magnesium Metal	Dilute Nitric Acid
Mn	Manganese Metal	Dilute Nitric Acid
Ti	Titanium Metal	Dilute Hydrofluoric Acid and Dilute Nitric
V	Ammonium Vanadate (NH_4VO_3)	Dilute Nitric Acid

The standard solution, containing each of the elements listed in Table 2, was prepared from the stock solutions. Ten microliters of this

solution was then taken and pipetted into a 2/5 dram capsule and dried under an infrared lamp for 20 minutes.

Counting

The samples and standards were counted for 6 minutes, 9 minutes after irradiation. This counting scheme was used because immediately after the irradiation the intense ^{28}Al activity made the measurement of longer-lived isotopes difficult. Conversely, if a decay interval of 20 minutes is allowed before counting, while the ^{28}Al activity has decreased, the disintegration rates of other radionuclides such as ^{51}Ti, ^{52}V, and ^{27}Mg also have decayed to a point where detection is difficult. Figures 2 and 3 illustrate the necessity for choosing the appropriate decay interval. The spectra shows decay intervals of 3, 4, 6, and 9 min. The spectrum of the 9 min decay is expanded to clearly show the appearance of the ^{27}Mg peak. Also, special attention should be given to the low energy end of the spectra. It can be clearly seen that the area of the Ti peak increases as the decay interval increases. Figure 4, which was taken from a paper by Abel and Rancitelli,[13] illustrates the initial activities and their decay with time.

Calculations

All of the recorded spectra were processed by the Fortran-coded peak finding routine ICPXGT. This program detects photopeaks by an analysis of the smoothed second derivative of the spectrum. In the initial search all negative minima in the smoothed second derivative are considered to be peak locations if two rather liberal criteria are met. These are that

Figure 2. The spectra of NBS coal after decay interval of 3 and 4 minutes.

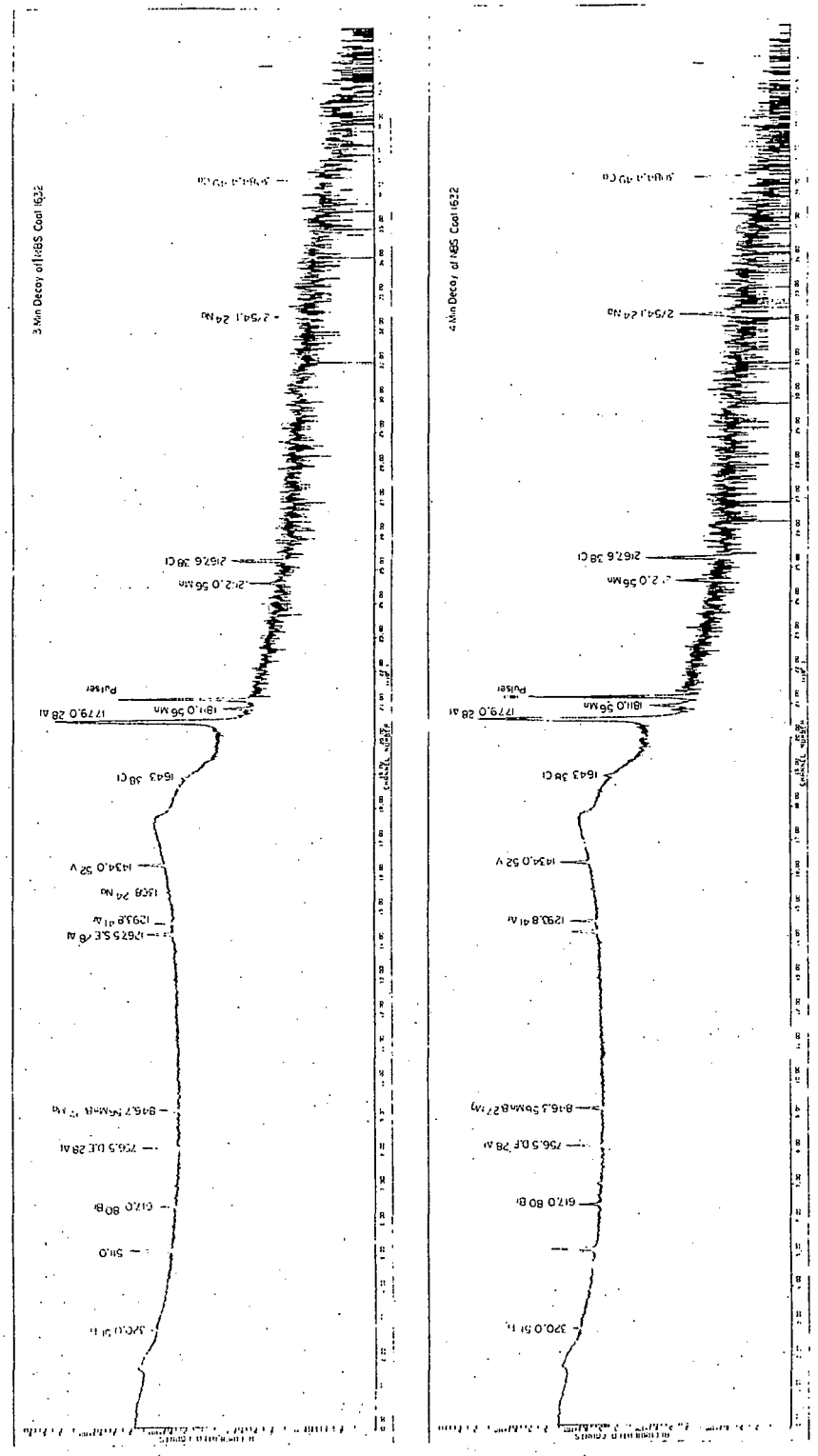

3 Min Decay of HBS Coal 1632
4 Min Decay of HBS Coal 1632
Pulser
Pulser

Figure 3. The spectra of NBS coal after decay interval of 6 and 9 minutes.

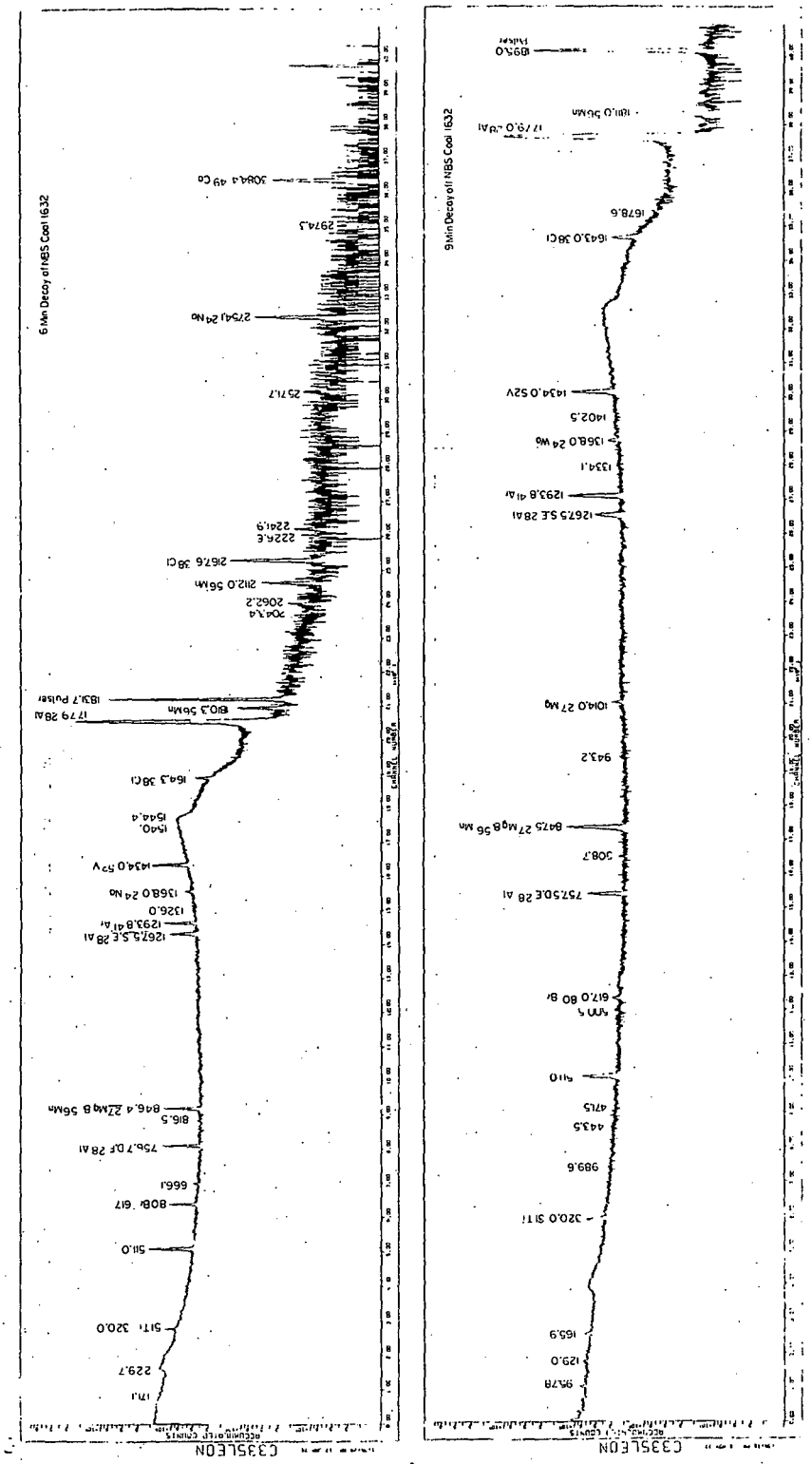
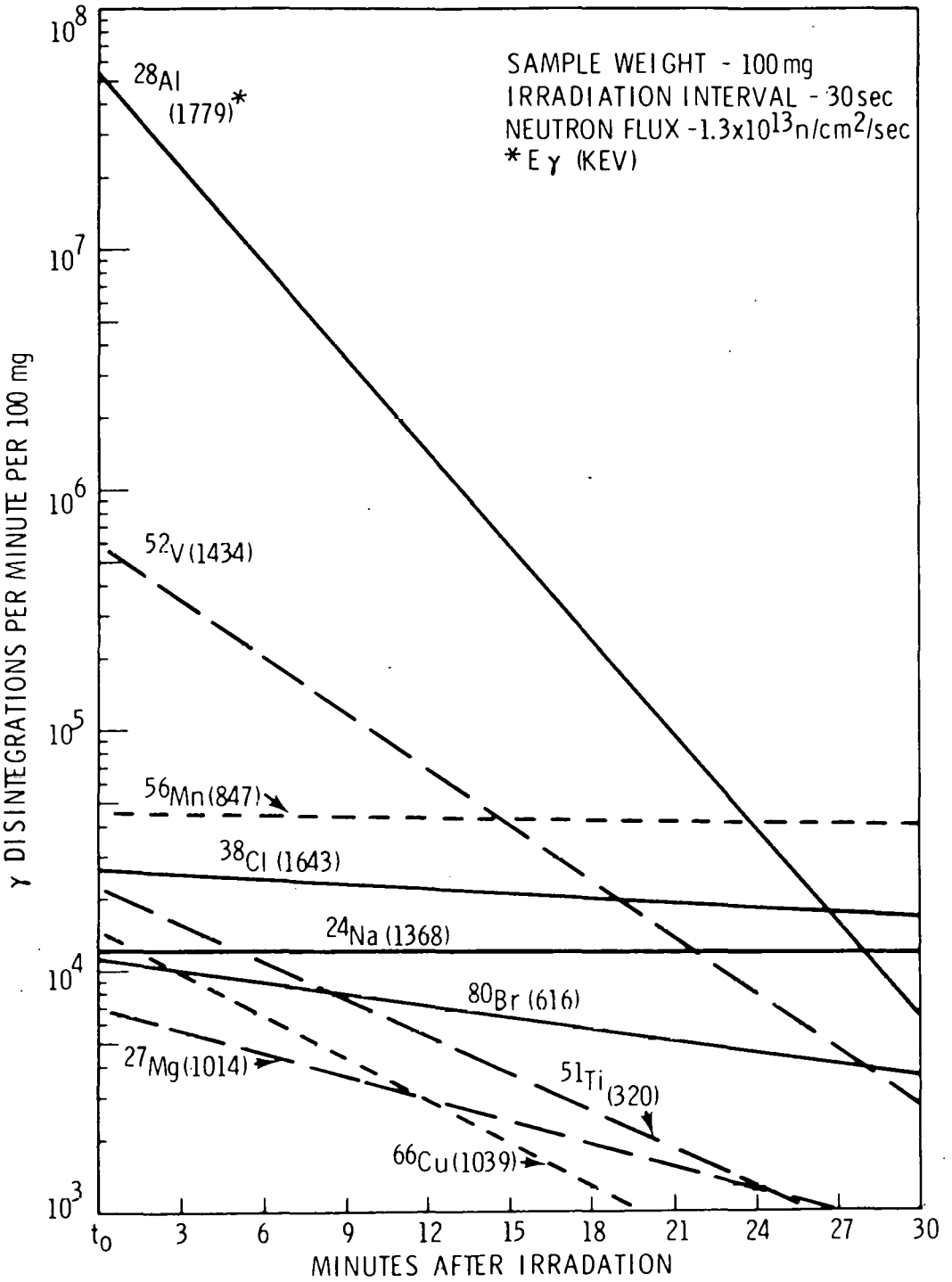

6 Min Decay of NBS Coal 1632
9 Min Decay of NBS Coal 1632
C33SLEON
C33SLEON

Figure 4. A graph that illustrates the activities of a few short-lived radionuclides produced during a 30 sec irradiation and their decay with time after irradiation.


SAMPLE WEIGHT - 100 mg
IRRADIATION INTERVAL - 30 sec
NEUTRON FLUX - 1.3x10^13 n/cm^2/sec
*E γ (KEV)
28Al (1779)*
52V (1434)
56Mn (847)
38Cl (1643)
24Na (1368)
80Br (616)
27Mg (1014)
51Ti (320)
66Cu (1039)
γ DISINTEGRATIONS PER MINUTE PER 100 mg
MINUTES AFTER IRRADATION
10^8
10^7
10^6
10^5
10^4
10^3
t0
3
6
9
12
15
18
21
24
27
30

the width of the peak must be between 3 and 15 channels, while the magnitude of the minimum must be at least 0.35 times its standard deviation.

If a peak with a width exceeding 15 channels is encountered during the initial search, a test is made to determine if there are other local minima present. If this is found to be the case, the peak is assumed to be a multiplet. In practice, the default values of 3 and 15 channels eliminate most artifacts caused by statistical fluctuations in the counts when the initial search is made.

After the preliminary search, an attempt is made to fit a Gaussian curve to each of the resultant potential peaks. The Gaussian fitting subroutine is essentially the one described by Heath et al. in AEC-Report IDO-17017. This procedure evaluates 3 parameters for the top 75 percent of the peak, a region which has been found empirically to consistently yield the best results by minimizing errors from such sources as poor background corrections, non-Gaussian peaks, etc.

Before the Gaussian fitting procedure is applied, the counts within the predetermined peak limits are corrected for underlying Compton and background events. This correction is made by fitting a least square straight line through 5 channels to the left and 5 channels to the right of the peak, and subtracting the result from the region to be fitted. The first point on each side is taken at a minimum of 1.5 times the peak width from the center of the peak.

Also, an energy calibration routine is included in the program. Energy calibration data may be read in with any spectrum, and the resultant

calibration may be used with as many succeeding spectra as desired. Both linear and quadratics fits are calculated for each set of calibration points. The print out for this program includes the exact location of the peak, standard deviation of the location, peak width, peak height, peak area, the standard deviation of these areas, the energy calculated from the quadratic calibration line and the spectrum number. In addition, the program will yield a semi-log plot of the spectrum on which each of the peaks is labeled with its approximate energy.

The activity of each element, which is essential in the use of the comparative method, can be calculated using equation 9.

$$\text{Activity} = \frac{\text{Area of the Element Peak} \times 3600}{\text{Area of the Pulser}} \tag{9}$$

where 3600 is a constant that gives the activity units of counts/min. Once the activity of a specific element is calculated and the correction factor applied, equation 7 is used to calculate the weight of the element in the sample. It should be noted that equation 7 only applies when the decay and counting intervals are the same. If they are not, then equation 10 is used to correct the calculated activity to the beginning of the counting period.

$$A_{corr} = \frac{A\lambda(t_2-t_1)}{e^{-\lambda t_1} - e^{-\lambda t_2}} \tag{10}$$

where A_{corr} = Activity at the beginning of counting period

A = Activity calculated by equation 7 (counts/min)

t_1 = Beginning of count period

t_2 = Ending of the count period.

Next the concentration of the element is determined using equation 11.

$$\text{Concentration} = \frac{\text{Weight of the Element}}{\text{Weight of the Sample}} \qquad (11)$$

If the weight of the element is expressed in micrograms and the weight of the sample in grams, the concentration is expressed in parts per million (PPM). The concentration can also be expressed in percent. This is done by dividing the quotient obtained from equation 11 by 10,000.

RESULTS AND DISCUSSION

NBS Coal 1632 Analyses

The results obtained from the analysis of the NBS coal 1632 are listed in Table 3 with results obtained by other investigators. The overall agreement is extremely good. However, the aluminum concentration is lower than most of the literature values except those of Sheibley.[16] Four of the investigators, Sheibley, Ondov et al.,[15] Nadkarni,[9] and Steinnes and Rowe[17] used INAA to determine the elements listed in Table 3. Chattopuday used instrumental photon activation analysis (IPAA) and the Illinois State Geological Survey (ISGS) used X-ray fluorescence.

The INAA methods of Sheibley and Ondov were modifications of techniques developed by Dams et al.[18] and Zoller and Gordon.[19] In their methods the samples were irradiated along with standards containing known amounts of each element at a flux of 10^{13} n/cm^2/sec. Irradiations of 30 sec duration were used for observation of species with half-lives $\leq$38 min; and 5 min irradiations for 38 min $< t_{\frac{1}{2}} \leq$ 15 hr. Standards containing each element to be determined in an irradiation were made by pipetting aliquots of standard solutions onto 5.5 cm diameter Whatman No. 1 filter material. These standards were irradiated simultaneously with the samples. For most elements, the standards were checked by irradiating them simultaneously with weighable amounts of the pure elements or their compounds. In their work two irradiation and two counting intervals were needed to determine the elements listed in Table 3. The bromine was determined using the ^{82}Br isotope which has a 35.3 hr half-life.

Nadkarni's procedure, which has been referred to earlier, was developed for analysis of biological, geological, and environmental samples. In this

Table 3. Elemental concentration in NBS coal (SRM1632). Comparison of present data with literature values

Element	Present work	Ondov et al.	Chattopaday and Jervis	ISGS
Al, %	1.51 ± 0.05	1.85 ± 0.13		2.21
Br, ppm	20.2 ± 0.05	19.3 ± 1.9		20.0
Ca, %	0.34 ± 0.04	0.43 ± 0.05		0.70
Cl, ppm	970 ± 20	890. ± 125		1000.0
Mg, %	0.165 ± 0.02	0.20 ± 0.05	0.16 ± 0.015	0.11
Mn, ppm	41.6 ± 0.91	43.0 ± 4.0	47.1 ± 4.1	39.0
Ti, ppm	966 ± 39.0	1040 ± 110.0	973.0 ± 50.0	1100.0
V, ppm.	35.4 ± 1.2	36.0 ± 3.0	33.9 ± 3.0	50.0

Nadkarni	Sheibley	Steinnes and Rowe	NBS certified value
1.76 ± 0.31	1.57 ± 0.15	1.74 ± 0.04	
15.2 ± 1.4	20.0 ± 3	19.5 ± 0.03	
0.43 ± 0.02	0.407 ± 0.056	0.35 ± 0.03	
945 ± 35.0	750 ± 75.0	844 ± 37.0	
0.15 ± 0.03	0.098 ± 0.025	0.17 ± 0.03	
40.3 ± 6.9	38.0 ± 2.6	41.1 ± 3.6	40.0 ± 3.0
839.0 ± 172.0	1312.0 ± 150.0	890.0 ± 50.0	
32.7 ± 3.4	36.0 ± 4.0	35.0 ± 2.9	35.0 ± 3.0

procedure the standards and the samples were irradiated simultaneously for 1-2 min at a flux of 1×10^{12} n/cm^2/sec. The samples were counted from immediately after irradiation up to 6 hours. The standards used in this work were U. S. Geological Survey Standard diabase rock W-1 or the NBS standard reference material Orchard Leaves 1571. In their work bromine and calcium were determined from longer-lived isotopes (^{82}Br and ^{47}Sc).

The procedure of Steinnes and Rowe[17] is not clearly described. The one thing that is really interesting about the work of Steinnes and Rowe is that the samples were allowed to decay 20 min before counting which seems to be too long for determining ^{52}V, ^{51}Ti, and ^{27}Mg. The results reported are, however, in good agreement with the ones obtained.

The X-ray fluorescence (XF) procedure used by ISGS is described by Kuhn et al.[20] In many cases the XF results obtained by this method are higher than those obtained by INAA and IPAA. The XF method when applied to whole coal has been severely handicapped by the lack of analyzed standards which made it necessary for the ISGS to prepare calibration curves from samples analyzed in their laboratories by other methods. The accuracy of the XF method is, therefore, dependent on the accuracy of the methods used to analyze the calibration standards. Also, because of the lack of standards, variations in analyses made by other methods, and errors caused by coal sampling problems, made it difficult to evaluate the need for X-ray matrix corrections and to select the best method for applying them when different whole coals were analyzed.

The IPAA procedure is described in detail by Chattopadhyay and Jervis.[21] This procedure is very time consuming and offers no real advantages over INAA for the elements listed in Table 3.

The NBS certified values were for 250 mg samples. Because of the activities induced by the neutron activation, it was necessary that the sample sizes be considerably below those recommended by the NBS. The sample size, however, did not affect the analytical results.

Iowa Raw and Cleaned Coal Analyses

The results for the analyses of the Iowa raw and cleaned coals are reported in Tables 4-10. In the cases of Al, Mn, Ti, and Ca it is clear that these elements are being removed by the cleaning process. However, V, Br, and Cl are removed from some Iowa coals but are not from others. The precision obtained for the concentration of these elements in the Iowa coals are not as good as for the NBS coal. This is probably due to inhomogeneous samples. Another probable cause of the low precision is the drying process used by Steve Howe. Once he obtained the coal samples they were placed in an oven and dried at a temperature exceeding $100^{o}C$ for 1-2 hours. Drying samples at this temperature for that period of time can cause the loss of volatile elements such as Br and Cl. It should be noted that the drying procedure described in the section "Samples and Sample Preparation" was applied to each sample before analysis was performed.

The accuracy of this procedure can not be evaluated because there are no other reported values for these elements in Iowa coals.

This procedure was checked by analyzing a NBS coal sample with each set of Iowa coals analyzed. Only two of the eight elements, V and Mn, were checked for the NBS coal. They were chosen because these were the only two elements with certified values that produced radioactive isotopes with relatively short half-lives.

Table 4. Al concentration in Iowa raw and cleaned coals

Iowa coal mine	Raw coal concentration %	Cleaned coal concentration %	% Element removed
Big Ben	0.288 ± 0.02	0.281 ± 0.02	2.29
Childers	0.91 ± 0.11	0.66 ± 0.05	27.6
Star	1.06 ± 0.03	0.78 ± 0.09	26.3
ISU	0.893 ± 0.02	0.806 ± 0.04	9.7
ICO	0.66 ± 0.06	0.478 ± 0.02	28.1
Jude	1.06 ± 0.02	0.99 ± 0.04	7.2
Mich	1.15 ± 0.04	0.967 ± 0.01	16.0
Scott	1.04 ± 0.04	0.74 ± 0.04	28.7

Table 5. Ca concentration in Iowa raw and cleaned coals

Iowa coal mine	Raw coal concentration %	Clean coal concentration %	% Element removed
Childers	0.923	0.578	37
Star	1.18	1.22	
ISU	1.84	0.400	78.2
Jude	3.85	0.845	78.0
Mich	2.46	2.12	14.0
Scott	0.943	0.515	45.4
Shinn	1.39	1.30	5.27

Table 6. V concentration in Iowa raw and cleaned coals

Iowa coal mine	Raw coal concentration in PPM	Cleaned coal concentration in PPM	% Element removed
Big Ben	16.3 ± 1.5	16.3 ± 1.3	
Childers	26.6 ± 3.3	21.7 ± 2.3	18.7
Star	17.0 ± 1.3	15.3 ± 1.8	10.1
ISU	27.0 ± 1.9	29.5 ± 1.0	
ICO	20.0 ± 2.1	14.3 ± 0.34	28.6
Jude	20.1 ± 0.05	22.0 ± 0.3	
Mich	29.9 ± 1.0	34.8 ± 0.8	
Scott	30.4	22.3	26.7

Table 7. Mn concentration in Iowa raw and cleaned coals

Iowa coal mine	Raw coal concentration in PPM	Cleaned coal concentration in PPM	% Removal
Big Ben	34 ± 7	32 ± 4	6.1
Childers	115 ± 8	67 ± 6	42.
Star	168 ± 11	121 ± 8	28.
ISU	205 ± 5	70 ± 5	66.
ICO	57 ± 5	53 ± 7	
Jude	492 ± 4	154 ± 32	69.
Mich	286 ± 68	191 ± 5	33.
Scott	164 ± 9	43 ± 7	73.

Table 8. Cl concentration in Iowa raw and cleaned coals

Iowa coal mine	Raw coal concentration in PPM	Cleaned coal concentration in PPM	% Element removed
Big Ben			
Childers	622 ± 68	429 ± 31	31
ISU	287 ± 73	116 ± 31	60
ICO	288 ± 5	190 ± 23	34
Jude	263	352 ± 32	
Mich	343 ± 6	321 ± 35	6.6
Scott	350	237 ± 47	32

Table 9. Br concentration in Iowa raw and cleaned coals

Iowa coal mine	Raw coal concentration in PPM	Cleaned coal concentration in PPM	% Element removed
Big Ben	37.5	32.9	12.1
Childers	21.6	26.3	
Star	21.8	33.2	
ISU	38.2	23.5	38.5
ICO	34.6	38.3	
Jude	36.2	30.3	16.3
Mich	43.3	39.4	8.98
Scott	30.8	29.5	4.29

Table 10. Ti concentration in Iowa raw and cleaned coals

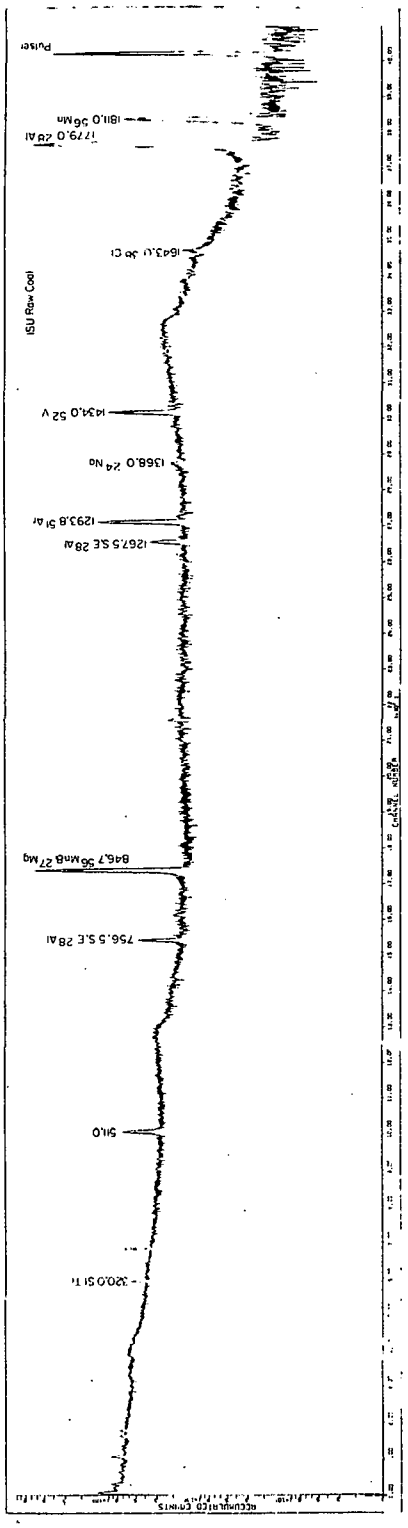
Iowa coal mine	Raw coal concentration in PPM	Cleaned coal concentration in PPM	% Removal
Big Ben	233 ± 31	204 ± 17	12.4
Childers	576 ± 36	335 ± 2	42
Star	540 ± 19	383 + 28	29
ISU	410 ± 29	366 ± 41	11
ICO	461 ± 51	386 ± 43	16
Jude	439 ± 29	357 ± 51	19
Mich	548 ± 51	432 ± 79	21
Scott	690 ± 39	387 ± 20	44

Magnesium was not detected in the Iowa coals which implies the concentration of the Mg was $\leq$445 ppm, the detection limit for Mg under these conditions. The concentrations of Cl in the Big Ben raw and clean coals were not reported because these coals were dried in a desiccator containing $Mg(ClO_4)_2$. Thus the Cl concentration was extremely high.

A possible cause of error in these determinations was nuclear interference. The two most probable nuclear interferences could be caused by (n,p) reactions taking place on adjacent elements in the periodic table, specifically $^{27}Al(n,p)^{27}Mg$ and $^{28}Si(n,p)^{28}Al$. These two possible interfering reactions were investigated and it was found that the (n,p) reaction produced less than 0.045% of the total activity of each of their elements.

Because of the close down of the ALRR this work was done with a six month time limit. As a result the concentrations reported for some elements, e.g. Br and Ca, are for single determinations. It was shown that all eight elements can be determined simultaneously in coal. Figures 5, 6, and 7 are spectra of Iowa raw and cleaned coals.

Figure 5. Spectra of Iowa raw and cleaned coals.


ISU Raw Coal
Pulser
1811.0 56Mn
1729.0 28Al
1643.0 35Cl
1434.0 52V
1368.0 24Mg
1293.8 51Va
1267.5 S.E 28Al
846.7 56MnB 27Mg
756.5 S.E 28Al
511.0
320.0 Si Ti
ACCUMULATED COUNTS

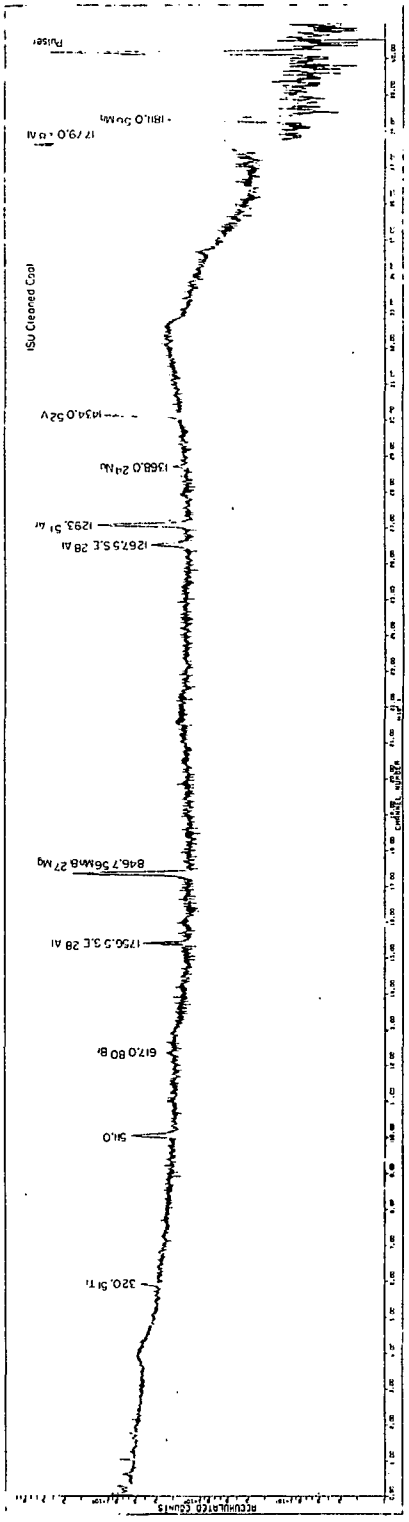
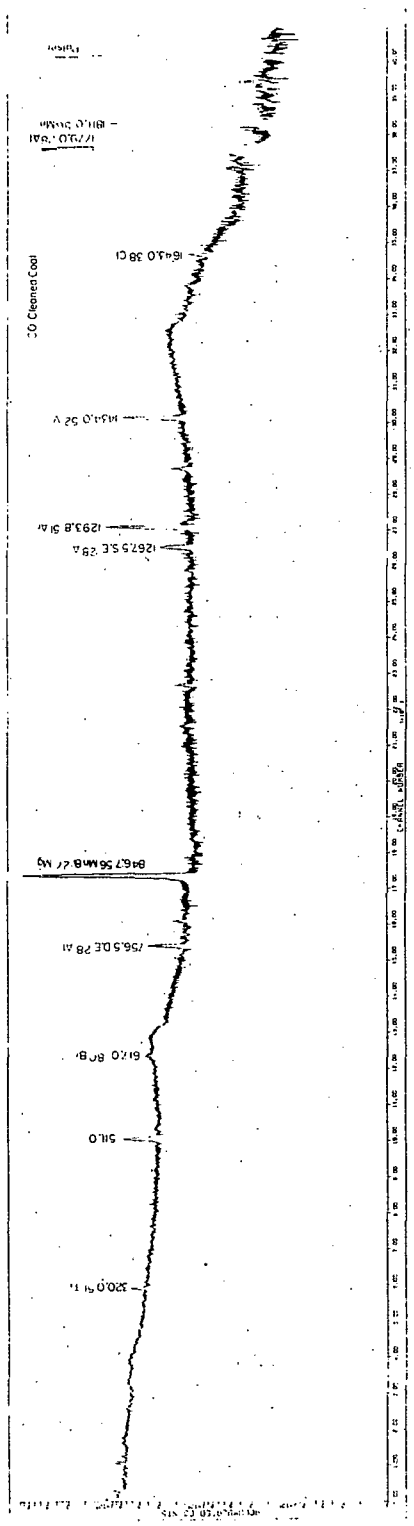

ISU Cleaned Coal
Pulser
1811.0 56Mn
1729.0 28Al
1434.0 52V
1368.0 24Mg
1293.5 51Va
1267.5 S.E 28Al
846.7 56MnB 27Mg
1756.5 S.E 28Al
617.0 80Br
511.0
320.0 Si Ti
ACCUMULATED COUNTS

Figure 6. Spectra of Iowa raw and cleaned coals.


(C) Cleaned Coal
1643.0 38 Cl
1293.8 81 Al
756.5 0.E 28 Al
320.0 91 Ti

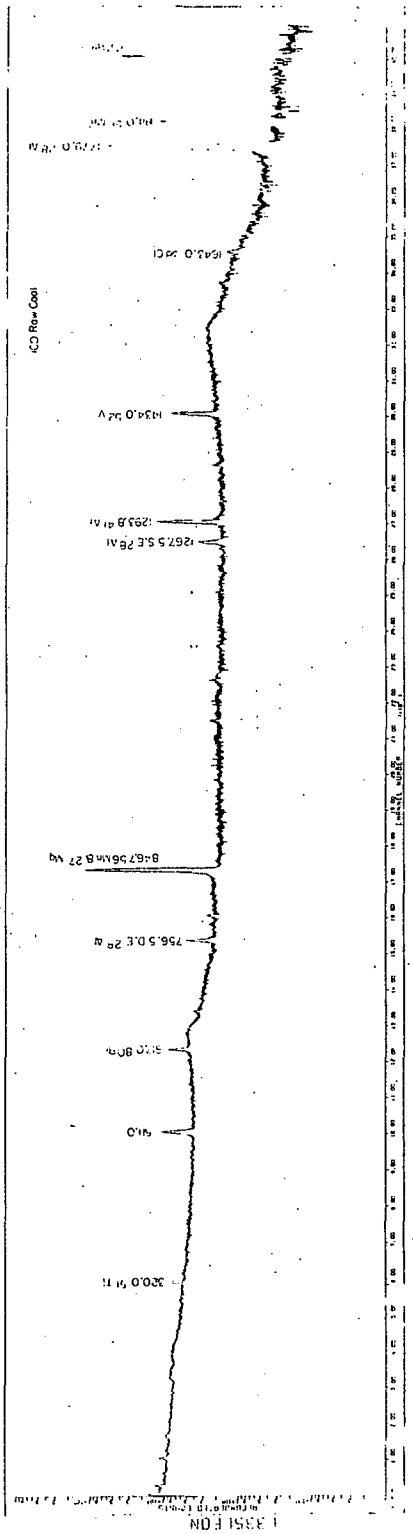
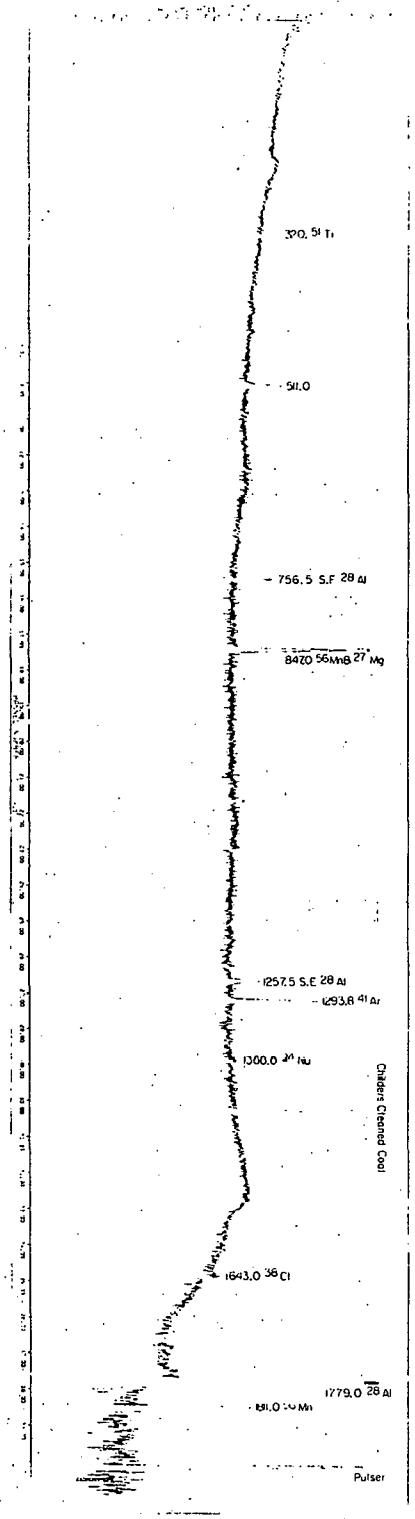
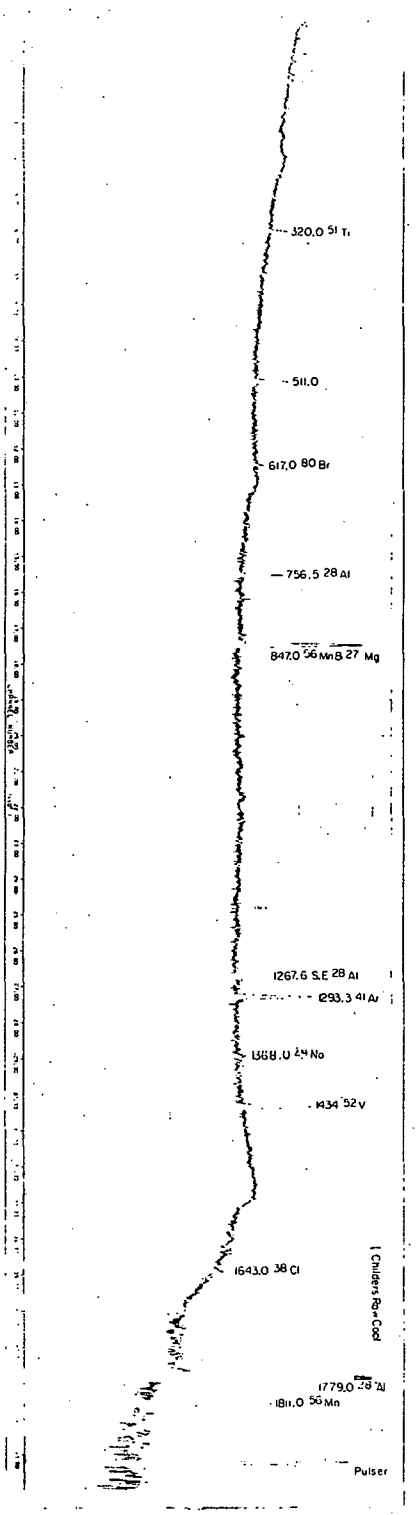

(C) Raw Coal
1643.0 38 Cl
1293.8 81 Al
756.5 0.E 28 Al
320.0 91 Ti

Figure 7. Spectra of Iowa raw and cleaned coals.


320. 51 Ti
511.0
756.5 S.F 28 Al
847.0 56Mn 8 27 Mg
1257.5 S.E 28 Al
1293.8 41 Ar
1368.0 24 Na
1643.0 38 Cl
1779.0 28 Al
1811.0 56 Mn
Pulser
Childers Cleaned Coal


320.0 51 Ti
511.0
617.0 80 Br
756.5 28 Al
847.0 56 Mn 8 27 Mg
1267.6 S.E 28 Al
1293.3 41 Ar
1368.0 24 Na
1434 52 V
1643.0 38 Cl
1779.0 28 Al
1811.0 56 Mn
Pulser
Childers Raw Coal

CONCLUSION

The INAA procedure developed in this work is a rapid, accurate, and precise method for determining minor and trace elements in coal. This procedure allows the determination of elements with half-lives <10 min which is not usually accomplished by other INAA techniques.

The results obtained for the NBS coal are in good agreement with the literature values. The accuracy and the precision is very good. However, the precision of the determinations of the Iowa coals was poor. This precision can probably be improved by using better collection, mixing, and drying techniques for the sample.

The cleaning procedure used by the ISU Coal Refining Plant appears to remove trace and minor elements as well as sulfur and iron from coal. However, the amount of the element removed seems to depend on the coal in which it is contained. This may be due to the way the element is chemically bound in the coal. However, before any conclusions are drawn, additional analyses should be made on samples taken from the coal and dried with greater care.

LITERATURE CITED

1. Kruger, P., "Principles of Activation Analysis," John Wiley, New York, N.Y., 1971.

2. DeSoete, D., R. Gijbels, and J. Hoste, "Neutron Activation Analysis," John Wiley, New York, N.Y., 1971.

3. Rakovic, M., "Activation Analysis," Iliffe Books Ltd., London, England, 1970.

4. Lyon, W. S., ed., "Guide to Activation Analysis," D. Van Nostrand Co., Princeton, N.J., 1964.

5. Adams, F. and R. Adams, "Applied Gamma-ray Spectrometry," Biddles Ltd., Great Britain, 1975.

6. Friedlander, G., J. W. Kennedy, and J. M. Miller, "Nuclear and Radiochemistry," John Wiley, New York, N.Y., 1964.

7. Block, C. and R. Dams, Anal. Chim. Acta, 11, 68 (1973).

8. Block, C. and R. Dams, Environ. Sci. Technol., 146, 9 (1975).

9. Nadkarni, R. A., Radiochem. Radioanal. Letters, 21, 161 (1975).

10. Nadkarni, R. A. and G. H. Morrison, Anal. Chem., 45, 1957 (1973).

11. Nadkarni, R. A. and G. H. Morrison, J. Radioanal. Chem., 18, 153 (1973).

12. Nadkarni, R. A. and G. H. Morrison, Environ. Letters, 6, 273 (1974).

13. Abel, K. H. and L. A. Rancitelli, Adv. Chem. Ser., 141, 118 (1975).

14. Tamura, N., Radiochem. Radioanal. Letters, 18, 135 (1974).

15. Ondov, J. M., W. H. Zoller, I. Omez, N. K. Aras, G. E. Gordon, L. A. Rancitelli, K. H. Abel, R. H. Felby, K. R. Shah and R. C. Tagaini, Anal. Chem., 47, 1102 (1975).

16. Sheibley, D. W., Adv. Chem. Ser., 141, 98 (1975).

17. Steinnes, E. and J. J. Rowe, Anal. Chim. Acta, 87, 451 (1976).

18. Dams, R., J. A. Robins, K. A. Rahn and J. W. Winchester, Anal. Chem., 42, 861 (1970).

19. Zoller, J. H. and G. E. Gordon, Anal. Chem., 42, 257 (1970).

20. Kuhn, J. K., W. F. Harfst and N. F. Shimp, Adv. Chem. Ser., 141, 66 (1975).

21. Chattopadhyay, A. and R. E. Jervis, Anal. Chem., 46, 1630 (1973).

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