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Neutron-capture gamma-ray analysis of coal for sulfur, iron, silicon and moisture

David Allyn Fay
Iowa State University

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FOR SULFUR, IRON, SILICON AND MOISTURE.

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Neutron-capture gamma-ray analysis of coal for sulfur, iron, silicon and moisture

by

David Allyn Fay

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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I. INTRODUCTION

The increasing energy demands of this country have led to the increased use of coal as an energy source. Unfortunately, most coals contain substantial concentrations of mineral matter and trapped moisture, sufficient in some cases to make them unsuitable for use. The identification and quantitative determination of the constituents of coal is thus of major importance, primarily because some may have detrimental effects during the use of coal. This investigation centers on the determination of four undesirable constituents of coal: sulfur, iron, silicon and moisture.

Excess moisture in coal is a definite contaminant. Moisture in coal reduces the heating value of the coal, increases the freight costs and contributes to difficulty in handling and shipping (1). Sulfur, iron, silicon and moisture all contribute to lowering the quality of coal, especially coal used for special purposes, such as in the production of coke, briquettes and chemicals (1). Iron and silicon are major components in the mineral matter of coal and contribute to the ash after combustion of the coal. Sulfur in coal is considered a potential atmospheric pollutant and high concentrations of sulfur render much potentially useful coal unsuitable as fuel (e.g., most Iowa coals) since power plants burning high sulfur coal cannot meet the federal limits for emission of sulfur oxides.

Coal as an energy resource is very important and to take full advantage of existing coal reserves requires that both high and low quality coals be used to the fullest extent. To accomplish this, low quality coals (high sulfur and ash content) must be processed to improve their quality or else pollution and environmental standards have to be relaxed.

Coals of poor quality can be mechanically processed to partially remove sulfur-bearing minerals and other non-combustible constituents making the coal more acceptable. When necessary, this improved coal can be mixed with low sulfur content coal creating a blend which is suitable for conventional uses, such as fuel for coal fired power plants.

Quantitative analysis of the minor components (0.1 - 10 percent) of coal becomes an important aspect of product control in coal processing. Sulfur and iron determinations at the coal cleaning plant are necessary for control of the operating parameters of the cleaning process. At the power plant, sulfur determinations of the blended coal mixture are necessary to assure that the sulfur content of the blend does not exceed currently acceptable amounts. The ideal analytical system designed for these analyses should hold to certain important prerequisites. The analytical system must provide rapid results to permit corrective adjustments to be made. The results must be sufficiently accurate and be obtained from a meaningful sample size. Finally, the system should be reasonably simple, providing computer-instrument compatibility so that the analyses can be automated.

Currently accepted practice for monitoring the various components of coal involves periodic coal sample analyses using analytical methods prescribed by the American Society for Testing and Materials (ASTM). A brief description of selected ASTM standard tests for sulfur, iron and moisture can be found in the Appendix (2). ASTM standard testing methods are generally quite good, but unfortunately, do not always effectively lend themselves to monitoring an on-going process. The ASTM standard methods for testing coal must involve tedious sampling in order to obtain representative samples. Also, these methods require hours to complete so that results often lag far behind the coal cleaning or blending process.

The application of capture gamma-ray spectrometry to the analysis of coal has many advantages over ASTM analytical methods. This technique involves the detection of prompt capture gamma-rays from the elements in coal when the sample is irradiated with thermal neutrons. The high penetrating power of neutrons and of the ensuing gamma radiation provides the potential for use of very large sample sizes. When large coal samples are used, the problems of sample heterogeneity and representative sampling are much less serious. Also, minor changes in the mineral composition of the coal seldom affect the accuracy of the measurement, which is specific to the element composition and independent of compound make-up. Capture gamma-ray spectrometry is a nondestructive technique which uses a low neutron flux so that no significant radioactivity is produced in the coal. Most important is that capture gamma-ray spectrometry permits the simultaneous determination of various elements while providing instantaneous output of information upon neutron irradiation of the sample. The potential for simultaneous element determinations coupled with the instantaneous nature of the analyses makes capture gamma-ray spectrometry a likely technique for eventual use in many process control applications, particularly those applications which deal with coal monitoring.

In this work capture gamma-ray spectrometry is examined as a possible technique for the simultaneous determination of sulfur, iron, silicon and moisture in coal, elements important to monitoring coal quality.

II. THEORY

Neutrons produced during fission will typically have greater than 1 million electron volts (MeV) of kinetic energy. The energies of these fast neutrons can be reduced through a process of many successive collisions with nuclei. The lighter the nucleus with which a neutron collides, the greater the fraction of the neutron's kinetic energy that will be transferred. After neutrons are slowed to energies comparable to thermal agitation energies they may either lose or gain energy in collisions, and the result is a Maxwellian distribution of velocities with the mean energy approximately equal to that of gas molecules at room temperature (3), *i.e.*, about 0.025 electron volts (eV) (4). The probable fate of thermal neutrons is either capture by the nucleus of some atom or disintegration by β-decay.

The capture of a neutron by a nucleus leads to the formation of an excited nuclear state which immediately decays to a more stable state by the emission of one or more prompt particles or photons (5).

$$
\begin{array}{ll}
 & \longrightarrow {}^{28}\mathrm{Al} + \gamma \\
 & \longrightarrow {}^{27}\mathrm{Al} + {}^{1}\mathrm{n} \\
 & \longrightarrow {}^{27}\mathrm{Al}^{*} + {}^{1}\mathrm{n} \\
{}^{27}\mathrm{Al} + {}^{1}\mathrm{n} \longrightarrow [{}^{28}\mathrm{Al}]^{*} & \longrightarrow {}^{27}\mathrm{Mg} + {}^{1}\mathrm{H} \\
 & \longrightarrow {}^{24}\mathrm{Na} + {}^{4}\mathrm{He} \\
 & \longrightarrow {}^{26}\mathrm{Al} + 2\,{}^{1}\mathrm{n}
\end{array}
$$

With thermal neutrons as bombarding particles, the most probable mode of de-excitation for most elements is by means of gamma emission. This type of nuclear reaction is known as an (n,γ) reaction, and the emitted gamma-ray is called a prompt or a capture gamma-ray. Particle emission competes strongly in only a few cases (5). In the gamma-emission process the excited compound nucleus may decay via a single gamma-ray transition or a cascade of several gamma-rays through intermediate nuclear levels. The latter case appears to be the most probable with the de-excitations producing on the order of 4.4 gamma-rays per compound nucleus (5). These neutron capture gamma-rays are usually emitted in less than 10^{-12} seconds and their total energy is essentially the binding energy of the neutron to the original nucleus (6).

The range for prompt gamma-ray energies is approximately 1-10 MeV. A gamma-ray which has an energy of at least 1.022 MeV may interact with matter to create a positron-electron pair. This process is called pair production, and the probability of such an event occurring increases with increasing gamma-ray energy. Many capture gamma-rays have energies which lie well above 1.022 MeV and pair production becomes the predominant process by which they initially interact with the detector. This process is followed by annihilation of the positron, and one or both of the annihilation gamma-rays (0.511 MeV each) may escape the detector, thus complicating high energy gamma-ray spectra with the appearance of single and double escape peaks.

After the emission of prompt gamma-rays following thermal neutron capture, the compound nucleus which is produced may still be unstable and undergo additional radioactive decay by α, β or further gamma-ray emission. Any radioactive decay events which occur after a sample has been removed from the neutron flux are known as delayed radiations and will possess a characteristic decay half life. During capture gamma-ray analysis, the emission of delayed α or β particles is of little consequence because they cannot penetrate the heavy metal shielding which surrounds the gamma-ray detector. Simultaneous detection of capture and delayed gamma-rays may become a problem if the half life of the delayed gamma emitting isotope is less than or equal to the irradiation period over which capture gamma-ray data are collected. This problem is serious only when capture gamma-ray data are collected below approximately 2 MeV. This is due to the fact that most gamma-rays produced by delayed nuclear activity have energies below 2 MeV. In the event that data for capture gamma-ray analysis need be collected below 2 MeV, Isenhour and Morrison have developed a modulation technique using a neutron beam chopper to circumvent problems due to delayed gamma-ray emission (6,7). The technique of using delayed gamma-ray spectroscopy in analyzing for various elements is classically known as instrumental neutron activation analysis (INAA).

Neutron activation analysis can be described mathematically by the equation:

$$R = N\phi\sigma(1-\exp(-\lambda t_i))\exp(-\lambda t_d)$$

where, R = count rate in counts per second (cps),

N = total number of target nuclei,

ϕ = neutron flux in neutrons per square centimeter per second (n/cm^2/sec),

σ = capture cross section in square centimeters (cm^2),

λ = decay constant $(0.693/t_{1/2})$,

t_i = irradiation time,

t_d = decay time after irradiation period,

$t_{1/2}$ = half life.

In capture gamma-ray activation analysis, the half life for gamma-ray emission is less than 10^{-12} seconds, therefore, the decay constant is approximately 10^{12} seconds^{-1} and for an irradiation of practical duration, $(1-\exp(-\lambda t_i)) = 1$. Likewise, the decay exponential term of this equation equals one, since data for capture gamma-ray analysis must be collected during the irradiation period, i.e., $t_d = 0$ and $\exp(-\lambda t_d) = 1$. The equation now simplifies to,

$$\bar{R} = N\phi\sigma,$$

which points out that capture reactions proceed without the usual growth and decay phenomenon associated with activation analysis.

An efficiency factor, E, can be added to this equation to account for the response of the detector to the activity produced. The decrease in detector efficiency with increasing gamma-ray energy and the appropriate geometry factor are part of this term.

If two species, in a homogeneous mixture, are examined by capture gamma-ray analysis, their ratio of count rates is proportional to their ratio of concentrations. Therefore,

$$\frac{R}{R'} = \frac{N\phi\sigma E}{N'\phi'\sigma'E'} .$$

Canceling neutron flux, the equation can be put into a more useful form by realizing that,

$$N = WN_o/A,$$

where, W = the weight in grams,

N_o = Avogadro's number,

A = the atomic weight.

Substitution yields:

$$\frac{R}{R'} = \frac{WE\sigma/A}{W'E'\sigma'/A'}$$

The ratio of count rates also depends upon the gamma-ray yield for each species at the energy of the gamma-ray in question. This gamma-ray yield, I, is expressed as the number of photons emitted per 100 neutron captures. The final equation expressing the ratio of counts for two species in a homogeneous mixture becomes:

$$\frac{R}{R'} = \frac{WE\sigma I/A}{W'E'\sigma' I'/A}$$

The group of terms, σI/A, is known as the "relative sensitivity index" and was first introduced by El-Kady (8) and Duffey and coworkers (9). The list of relative sensitivity indexes compiled (8,9,10) can be used as a guide in predicting the level of success when capture gamma-ray analysis is applied to a particular matrix.

The major capture gamma-ray energies for various important elements in coal are found in Table 1. Table 1 also contains the corresponding relative sensitivity indexes for each gamma-ray listed. More complete listings of capture gamma-ray energies can be found in Orphan (11), or Duffey *et al*. (9) and Senftle *et al*. (10). For a partial list of capture gamma-ray energies below 200 KeV, refer to Henkelmann (12).

From an analytical standpoint, capture gamma-ray activation analysis has a greater inherent sensitivity than INAA for many elements. Isenhour and Morrison (6) have produced a table comparing the estimated sensitivity of delayed and capture gamma-ray activation analysis for 63 elements. A selected portion of their table appears in

Table 1. Capture gamma-rays used and potentially interfering

Element	Cross section σ, barns	Atomic Weight A	E_γ MeV	I_γ[a]	Relative Sensitivity Index[b]
H	0.33	1.008	2.223	100	32.7
C	0.0034	12.01	4.945	67.0	0.019
			3.684	31.8	0.009
Al	0.230	26.98	7.724	25.9	0.221
			7.695	5.10	0.043
			4.734	4.14	0.035
			4.259	4.82	0.041
Si	0.160	28.09	7.199	6.30	0.036
			6.380	11.1	0.063
			4.934	62.1	0.354
			3.539	70.0	0.399
			2.093	23.6	0.134
S	0.512	32.06	8.641	2.66	0.042
			7.800	3.91	0.062
			5.420	59.1	0.944
			4.870	11.5	0.184
			3.221	27.1	0.433
			2.931	22.3	0.356
			2.380	44.5	0.711
Fe	2.62	55.85	7.647	23.9	1.12
			7.632	29.3	1.37
			6.018	8.71	0.409
			5.920	8.94	0.419
			4.219	4.33	0.203

---

[a] Photons per 100 neutrons absorbed (11).

[b] Relative yield per unit weight, $\sigma I/A$ (9,10).

Table 2. The sensitivity factor, S, as defined by Isenhour and Morrison is the minimum detectable weight of an element at unit flux and 100 percent counting efficiency. Sensitivity factors for delayed gamma-ray activation analysis were calculated from the following equation:

$$S = \frac{AR}{N_o\theta\sigma(1-\exp(-\lambda t_i))\gamma}$$

where, R = count rate in counts per second (cps) (using Buchanan's criteria (13) for a one-hour irradiation with a count rate of 1000 counts per minute (cpm) for half lifes less than one minute; 100 cpm for half lifes from one minute to one hour; and 10 cpm for half lifes greater than one hour),

θ = the isotopic abundance,

t_i = irradiation time (one hour),

γ = fraction of gamma-rays produced at the specified energy.

This equation is a simple rearrangement of the equation used to describe the exponential growth of activity within a sample as it is irradiated, and where no decay has occurred.

The same formula applies to capture gamma-ray activation analysis when the exponential growth term $(1-\exp(-\lambda t_i))$ is omitted, since saturation activity is produced as soon as the

Table 2. Estimated sensitivity factors for delayed and capture gamma-ray activation analysis[a]

	Delayed Gamma				Capture Gamma			
Element	Product	$T_{1/2}$	E_γ (MeV)	S_D	Reaction	E_γ (MeV)	S_C	Log (S_D/S_C)
Al	Al^{28}	2.3 m	1.78	4×10^2	$Al^{27}(n,\gamma)$	7.73	1×10^2	0
C	---[b]	---	---	---	$C^{12}(n,\gamma)$	4.95	1×10^3	
Ca	Ca^{49}	8.8 m	3.10	6×10^2	$Ca^{40}(n,\gamma)$	6.42	3×10^1	+1
Cl	Cl^{38}	37 m	3.75	4×10^3	$Cl^{35}(n,\gamma)$	1.17	8×10^{-1}	+4
Fe	Fe^{59}	45 d	1.289	1×10^7	$Fe^{56}(n,\gamma)$	7.64	2×10^1	+6
H	---[b]	---	---	---	$H^1(n,\gamma)$	2.23	8×10^{-1}	
Hg	Hg^{197}	65 h	0.077	4×10^3	$Hg^{199}(n,\gamma)$	0.37	4×10^{-1}	+4
K	K^{42}	12.5 h	1.53	1×10^4	$K^{39}(n,\gamma)$	0.77	2×10^1	+3
Mg	Mg^{27}	9.4 m	0.843	3×10^4	$Mg^{24}(n,\gamma)$	3.92	2×10^2	+2
Mn	Mn^{56}	2.6 h	0.845	1×10^1	$Mn^{55}(n,\gamma)$	7.26	1×10^1	0

---

[a] Compiled by Isenhour and Morrison (6).

[b] No usable delayed gamma reaction known.

Table 2. (Continued)

Element	Delayed Gamma				Capture Gamma			Log (S_D/S_C)
	Product	$T_{1/2}$	E_γ (MeV)	S_D	Reaction	E_γ (MeV)	S_C	
Na	Na^{24}	15 h	2.75	3×10^2	$Na^{23}(n,\gamma)$	0.48	2×10^1	+1
Ni	Ni^{65}	2.6 h	1.48	2×10^4	$Ni^{58}(n,\gamma)$	9.00	1×10^1	+3
S	S^{37m}	5.0 m	3.09	5×10^6	$S^{32}(n,\gamma)$	5.44	4×10^1	+5
Si	Si^{31}	2.6 h	1.26	4×10^5	$Si^{28}(n,\gamma)$	4.93	1×10^2	+3
Ti	Ti^{51}	5.8 m	0.32	2×10^4	$Ti^{48}(n,\gamma)$	1.39	3×10^0	+4
V	V^{52}	3.8 m	1.43	3×10^1	$V^{51}(n,\gamma)$	6.51	2×10^1	0

sample irradiation begins. A count rate of 10 cps was used to calculate sensitivity factors for capture gamma-ray activation analysis.

The last column in Table 2 gives the logarithm of the ratio of the delayed gamma-ray sensitivity factor to the capture gamma-ray sensitivity factor for the same element. For example, in the case of sulfur, a value of +5 means that the sensitivity for capture gamma-ray analysis is five orders of magnitude better than that for delayed gamma-ray analysis at the same flux and detector efficiency.

The sensitivity factors compiled by Isenhour and Morrison (6) indicate that capture gamma-ray activation analysis would be far superior to delayed gamma-ray activation analysis if the same neutron flux and detector efficiency were available for each experiment. The realization of these two equalities is not possible at this time and hence delayed gamma-ray activation analysis remains the more useful tool for most elements. The neutron flux which is available for capture gamma-ray analysis is typically six orders of magnitude less than that encountered in delayed gamma-ray experiments, thereby drastically decreasing elemental capture gamma-ray sensitivities. The fact that many useful capture gamma-rays occur at energies which are much higher than those encountered in delayed gamma-ray analysis results in decreased detection efficiency. For these reasons, capture gamma-ray activation analysis cannot presently compete with conventional neutron activation analysis using delayed gamma-ray spectrometry unless there is a need for *in situ* or *in vivo* analysis or in cases where elements which have high cross sections for thermal neutrons do not produce good delayed products, as is the case for sulfur, carbon, and hydrogen.

III. LITERATURE REVIEW

A. General Analytical Applications

The use of capture gamma-ray spectrometry as an analytical tool has greatly increased since the late sixties. A good discussion of the general aspects of capture gamma-ray analysis as applied to analytical problems is presented by Henkelman and Born (14). Many applications involve some type of on-site or on-line analysis problem, while other applications are concerned with the analysis of elements with high capture cross sections which produce stable products following neutron capture. In either case, the technique of capture gamma-ray analysis has been extended to many elements in a wide variety of matrices.

The more popular neutron sources for capture gamma-ray research activities are nuclear reactors and isotopic sources of californium-252. With either neutron source, there are two possible sample irradiation geometries, internal and external (15). An external target arrangement is achieved by extracting a neutron beam from the source through its shielding materials. The sample is irradiated outside the biological shield and the detector is placed close to the sample. This arrangement is most common in reactor based facilities. An internal target arrangement involves placing the sample near the isotopic neutron source or inside the reactor thermal column. The gamma-rays which are produced are then viewed by a detector located outside the biological shield. The internal target arrangement is preferred for most applications of californium-252 since this arrangement provides a greater neutron flux at the sample position.

Designing a safe workable biological shield is essential for use of californium-252 as a neutron source for capture gamma-ray studies. Important design considerations include source size, target geometry, construction of gamma-ray or neutron beam collimators and selection of appropriate shielding materials. Hootman (16) has provided information useful for estimating source shielding requirements, while others have discussed target geometry and collimator design (15) or specific shielding facilities (17,18). Evans et al. (19) has examined the background produced by different materials which could be used for source encapsulation, and the best construction materials for a neutron capture gamma-ray facility have been reported by Senftle (20).

Two types of gamma-ray detectors are currently available for practical use in analytical applications of capture gamma-ray spectrometry. Thalium-activated sodium iodide (NaI(Tl)) detectors provide fair energy resolution with good detection efficiency while lithium-drifted germanium (Ge(Li)) detectors offer almost the opposite, high energy resolution coupled with poor detection efficiency. The choice of detector depends upon the specific application. Lombard and Isenhour (21), and Greenwood (22) have conducted studies to compare the performances of Ge(Li) detectors to NaI(Tl) detectors. Their findings indicated that Ge(Li) detectors are superior to NaI(Tl) detectors for most applications. However, NaI(Tl) detectors are more useful for applications which require a rugged detector, making them suitable for use in process control applications or remote monitoring facilities. Demidov et al. (23) have demonstrated the application of Ge(Li) detectors for capture gamma-ray studies by determining the relative elemental make-up of metal alloys and geological samples. Hall and Friggens (24) have evaluated plastic scintillators for detecting prompt gamma-rays in continuous analysis of bulk materials, and found them to be unsuitable for analysis of materials having a complex gamma-ray spectrum due to very poor energy resolution.

NaI(Tl) and Ge(Li) detectors can be used in combination with one another to provide additional detection selectivity. The additional selectivity of these multiple detector systems is achieved electronically using coincidence or anti-coincidence circuitry. The application of two detector coincidence techniques has been considered by Lussie and Brownlee (5). Anticoincident coupling of two detectors, one of which surrounds the other, has been used for suppression of Compton background (25,26). Three detectors, coupled by coincidence circuitry, can be used to reduce the triad of photopeaks normally observed for a high energy monoenergetic gamma-ray to one photopeak. A detector system of this sort is known as a pair spectrometer and is very useful for simplifying high energy gamma-ray spectra by eliminating superfluous photopeak information. Orphan and Rasmussen (27) have described a pair spectrometer for studying neutron capture gamma-rays which can also be used as a Compton suppression spectrometer at low energies. Pair spectrometers are not commonly used for analytical work because of their cost, electronic complexity and lower count rates.

Some of the earliest quantitative applications of capture gamma-ray spectrometry include analyses for elements with high capture cross sections, such as boron, cadmium and rare earth elements. Isenhour and Morrison (28) have determined boron in a synthetic mixture using a neutron beam modulation technique and samarium oxide as an internal standard. Garbrah and Whitley (29) investigated neutron attenuation effects in large boron samples and determined boron in boric acid and steel. These latter researchers extended their work to include determinations of boron in glass samples, hydrogen in organic materials and rare earth elements (samarium, gadolinium, dysprosium and erbium) in rocks (30). They determined the rare earth elements by collecting NaI(Tl) spectra of several sets of standards. These spectra were then combined by a computer program to form a synthetic spectrum which was compared to that of the sample to find the "best fit". Lombard and Isenhour (31) have determined samarium and gadolinium in four of the most common rare earth ores using a Ge(Li) detector for data collection and a high speed beam chopper for automatic background subtraction. More recent work has been done by Gladney, Jurney and Curtis (32) to measure trace quantities of boron and cadmium in industrial and standard materials. The cadmium determination was not sufficiently sensitive to provide a practical alternative to more conventional methods.

Heurtebise, Buenafama and Lubkowitz (33,34) have used capture gamma-ray spectrometry for the routine determination of cobalt, molybdenum, nickel and moisture in hydrodesulfurization catalysts. These alumina based catalysts are important in the petroleum industry and the concentrations of cobalt, molybdenum and nickel control the catalytic activity. These determinations were obtained using reactor neutrons and a Ge(Li) detector for data collection. Titanium oxide was used as an internal standard.

Kusaka and Tsuji (35) have investigated the possibility of using an Am-Be neutron source for capture gamma-ray analysis. Capture gamma-ray spectra of several elements were examined; although the neutron flux of their facility was very low and background activity high, prominent peaks were observed for boron, samarium, cadmium, cobalt, mercury and chlorine. As a practical demonstration of the method, the chlorine content of various organic compounds was determined. Chlorine has also been determined in salt and sea water by Wiggins and Athow (36) using a californium-252 source. The chlorine content is useful in measuring the salinity of sea water which is important to sonar applications and ocean current flow patterns.

Duffey, Balogna and Wiggins (37) have studied the mineral content of geothermal waters by capture gamma-ray spectrometry. This was done to assess the possibility of analyzing waters used by geothermal power plants. Analysis of these waters would assist in plant control, to monitor corrosion and solid deposition and possibly to recover byproduct minerals. The measurements include the use of a californium-252 source and a Ge(Li) detector for data collection; results indicate that chlorine, sodium, calcium and silicon can be determined in geothermal waters by this technique.

Tiwari, Bergman and Larsson (38) have examined the prospect of determining nitrogen in organic materials using an Am-Be neutron source. A neutron howitzer was fabricated to thermalize the neutrons and direct them toward the sample. Urea was chosen as sample material for analysis. Low flux necessitated a large sample size. This work laid the foundation for future feasibility studies into the development of a rapid capture gamma-ray technique for protein determination in grain samples with both Am-Be (39) and californium-252 (40) neutron sources.

Comar *et al.* (41,42) have used neutron capture gamma-ray spectrometry for the analysis of biological samples, both *in vitro* and *in vivo*. A high thermal neutron flux for these studies was made possible through use of a curved neutron guide built from nickel-coated glass bricks. The reactor thermal neutrons are propagated in this guide by total reflection on the nickel walls and are separated from fast neutrons and fission gamma-rays owing to the curvature of the channel. Chlorine, sodium, potassium and boron were detected in calcined blood samples, while powdered bone specimens displayed gamma-rays from calcium, phosphorus, chlorine and nitrogen. Sulfur and nitrogen were observed in hair, and hydrogen was seen in all samples. Samples of cabbage and algae were analyzed for boron, chlorine and hydrogen, and results agreed well with those from other techniques. *In vivo* measurements were performed on human hands and legs. These irradiations included measurements of sodium, calcium and chlorine mass ratios.

Rundo and Bunce (43) have estimated the total hydrogen content of the human body without exposing the subject to any of the usual neutron sources. Capture gamma-rays naturally occur in the body when fast neutrons produced by cosmic radiation are first moderated by, and then captured in, body tissues. Their experiment consisted of collecting gamma-ray spectra of a human body shielded by lead; four large NaI(Tl) detectors were necessary for data collection. The 2.23 MeV capture gamma-ray peak from hydrogen was the only well-defined photopeak in these spectra and was used for estimating the hydrogen content of human subjects. Calibration of the counting facility was accomplished through the use of polyethylene cylinders filled with water and arranged to simulate a human body.

The emission of 2.23 MeV gamma-rays following thermal neutron capture in hydrogen atoms provides an ideal non-destructive method for quantitative analysis of total hydrogen in sample materials. Unfortunately, most materials contain many hydrogen bearing compounds so that knowledge of the total hydrogen content does not always provide valuable information about the material. Therefore, determinations of total hydrogen are usually reserved for samples which contain only one principal source of hydrogen atoms, _e.g._, in pure hydrocarbon liquids and solids (44). This capture gamma-ray analysis technique is particularly useful for moisture measurements whenever the total hydrogen content is directly proportional to the moisture content of the sample material, e.g., in the analysis of hydrodesulfurization catalysts (34) or fresh concrete mixtures (45,46).

Capture gamma-ray spectrometry has potential for use in determining the elemental composition of celestial bodies. Early experiments to determine the feasibility of using capture gamma-ray spectrometry to analyze the lunar surface involved reactor studies of rock and meteorite materials (47), while later studies employed a pulsed 14 MeV neutron source (48,49). More recent studies have used californium-252 as a portable source for field studies of the elemental composition of the earth's crust, with eventual possible application to space flight geochemical analysis (50,51). Both qualitative and semiquantitative results were obtained; ratios of elemental abundances were determined by examining the ratio of photopeak intensities, but errors of about 30 to 40 percent were inherent in the calculated elemental ratios. Proper high energy calibration of the detector used in these studies is critical to obtaining meaningful qualitative results. This energy calibration was managed by temporarily placing a chromium metal sample near the californium-252 source (52).

The potential of capture gamma-ray analysis for identifying various elements in rocks and minerals was recognized in the early sixties. Early analytical studies of rocks and minerals by Aripov *et al.* (53) were restricted to reactor neutrons and NaI(Tl) detectors. These studies involved an investigation of gamma-ray spectra for samples of pyrrhotine ($Fe_{1-x}S$), scheelite ($CaWO_4$), rock salt (NaCl) and chalcopyrite ($CuFeS_2$). Also, results obtained for the determination of sulfur in sedimentary rocks and nickel in nickel ore showed promise of success for future quantitative applications of capture gamma-ray analysis.

Interest in using capture gamma-ray spectrometry for ore prospecting and analysis has gained considerable favor with the introduction of portable neutron sources, particularly californium-252. Ore prospecting applications involve *in situ* detection of various elements useful in evaluating mineral deposits. *In situ* analysis is often necessary where collection of sample material for chemical analysis is difficult or expensive, *e.g.*, in a borehole or on the ocean bottom. A good discussion of *in situ* mineral analysis by means of neutron capture gamma-ray techniques is provided by Fanger and Pepelnik (54). Ore analysis, after or during the mining operation, is useful for monitoring the ore quality or controlling ore beneficiation processes. A good discussion of the practical aspects of using californium-252 for capture gamma-ray analysis of ore process streams is presented by Duffey *et al*. (55)

Capture gamma-ray borehole logging with isotopic neutron sources other than californium-252 has been successful for identification of chlorine, silicon, calcium, hydrogen and iron in shales, sandstones and limestones (56), but the availability and lower cost of californium-252 has made it more attractive for future use (57). Nargolwalla (58) has field tested a californium-252 borehole sonde. In these field studies nickel, iron and silicon were simultaneously determined in a borehole drilled into a nickel ore body. Moxham, Senftle and Boynton (59) have conducted similar field tests on nickel and copper ore bodies. These researchers have combined delayed and capture gamma-ray techniques to expand the number of detectable elements. The delayed and capture gamma-ray spectra are collected simultaneously with a Ge(Li) detector and stored together in the same memory region of the multichannel analyzer. Aluminum, manganese, sodium, magnesium, copper and vanadium were activated and detected by the delayed method, while nickel, iron, silicon and hydrogen were detected by their respective capture gamma-rays.

An earlier investigation involving the combined use of delayed and capture gamma-ray techniques was performed by Eden (60). In this work, samples were irradiated with a partially thermalized neutron beam from a pulsed neutron generator. The spectra were stored in a multichannel analyzer system using two separate memory groups for the two types of gamma-rays. The pulsing unit synchronized the neutron irradiation with the appropriate part of the multichannel memory, according to which type of gamma radiation was being measured. The results indicated that semiquantitative determination of copper, aluminum and manganese was feasible with an overall error of 10-15 percent.

Researchers at the University of Maryland (61,62,63) have carried out capture gamma-ray experiments with californium-252 which are concerned with mineral exploration of the ocean floor for manganese and gold. The aim of these studies was to locate groups of interference free peaks which could serve as spectral signatures for identifying manganese and gold deposits on the ocean floor. This was accomplished by collecting Ge(Li) detector spectra of manganese nodules and gold ore which was placed in a laboratory simulated marine environment. These same researchers have analyzed low grade nickel ore for nickel (63,64), and titanium ore for titanium (65) using capture gamma-ray spectrometry and a californium-252 source. These experiments were later extended to the detection of the sought element (nickel or titanium) on artificially prepared ore surfaces and also in laboratory test boreholes.

Another application of capture gamma-ray spectrometry to mineral mining and processing involves the analysis of copper ore. Akalin (66) and Sandquist _et al_. (67) have conducted capture gamma-ray experiments using known ore composites and a series of three californium-252 sources situated around the ore sample. They have been reasonably successful at determining copper, iron, aluminum and silicon in copper ore but have had problems in dealing with variations in the moisture content of the ore. Large changes in the moisture content affect the thermal neutron flux because moisture acts to moderate neutrons from the californium-252 sources. These problems were overcome by monitoring the neutron flux (68). Duffey *et al*. have also performed capture gamma-ray experiments on copper mill materials (69). Their work uses only one californium-252 source and includes results and spectra for synthetic and actual copper ores, flotation concentrate and mine tailings.

Greenwood *et al*. (70) have tried to develop a rapid and accurate analysis of iron ore for iron, aluminum, silicon, calcium, magnesium and manganese using fast and thermal neutron activation analysis, as well as capture gamma-ray analysis. Capture gamma-ray analysis provided the quickest results for the iron content of the ore. However, the gamma-rays from the iron were so predominant that analysis for minor elements was impossible from a single spectrum. A sum-coincidence spectrometer (71) was employed to try and overcome this masking affect. The conclusion was that such an analysis of iron ore was not yet competitive with existing techniques. A more current feasibility study for utilizing capture gamma-ray analysis as a nondestructive technique for the identification and estimation of iron and gold in simulated ore mixtures has been conducted (72,73,8). This study was primarily concerned with qualitative analysis, identification of interferences and determination of sensitivities. Wiggins et al. (74,75) along with Duffey et al. (76,55) have studied process control applications of californium-252 to the ores of iron, nickel and copper. Recently, iron has been determined in its ore by using a low flux Am-Be neutron source (77). Holmes et al. (78) hold a patent for an apparatus designed to measure the concentration of water, iron and aluminum in iron ore which is moving on a conveyor belt. This device utilizes a collection of three detectors positioned at specific locations along the conveyor belt so that iron might be determined by capture gamma-ray analysis, water by a neutron moderation technique and aluminum by activation analysis.

Zwittlinger (79) has analyzed refined steel samples by capture gamma-ray analysis using reactor neutrons. Chromium, nickel and manganese were the principal elements determined in these samples, but iron, cobalt and tungsten were determined in some. All analyses were done with gamma-rays above 5 MeV, using a Ge(Li) detector for data collection. Analytical results agreed well with element concentrations determined previously by chemical methods. Najam et al. (80) have determined iron, chromium, nickel, manganese and boron in samples of stainless steel and iron ore using reactor neutrons. Low energy gamma-rays, ranging from 0.2 to 1.4 MeV, were used in these analyses. This reduced the time of analysis considerably since greater detection efficiency is realized at lower energies. The problem of congestion of peaks due to Compton continuum and escape peaks was overcome by using a Ge(Li) detector in conjunction with an anti-Compton NaI(Tl) annulus. The results obtained in this work agreed well with chemical analyses. Heurtebise and Lubkowitz (81) have researched the analytical problems of metal analysis in alloys using a reactor thermal neutron beam with the hopes of transferring the knowledge acquired to similar studies using californium-252 sources. They present a mathematical model for analysis of certain metals with an accuracy of 6 percent. Titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, silver, cadmium, gold and mercury are measured with good precision at the percent concentration level.

B. Applications to Coal Analysis

The ability to monitor the composition of a coal process stream is the goal of a number of analytical techniques. Continuous monitoring of coal streams would facilitate automatic quality control in coal cleaning plants and in coal utilization applications. Present methods for monitoring coal quality involve laborious and time-consuming sampling and chemical analysis, and are not adaptable for automatic process control. Nuclear analytical techniques are amenable to automation and provide potential for simultaneous multi-element determinations from very large samples.

The first serious applications of nuclear technology to monitoring a coal process stream began in the early sixties. These early coal analysis systems relied upon neutron generators as a source of 14 MeV neutrons. With a source of 14 MeV neutrons, fast neutron inelastic scattering and fast neutron activation analysis could be studied. Initial studies concentrated on demonstrating the feasibility of fast neutron techniques by analyzing small samples of coal in a laboratory setting where experimental conditions could be precisely controlled (82,83). Results from these initial studies indicated that carbon, oxygen, aluminum and silicon content of coal samples could be fairly accurately determined, semiquantitative analyses were possible for iron and order of magnitude estimates were possible for sulfur and hydrogen. By 1966, a fast neutron analysis system had been installed in a pilot plant (84,85). Continuous testing with a moving coal stream showed that a useful signal was obtained from silicon activation but not from aluminum activation. Neutron inelastic scattering (determination of carbon and oxygen) results were not obtained with moving samples since feasibility was marginal and the coal industry had lost interest.

Process control applications of (α,n) or (γ,n) neutron sources were found to be suitable for use in analyzing ore slurries for silicon, aluminum and fluorine (85). Unfortunately, in industrial on-stream analysis of bulk solids such as coal, where the sample presentation is by conveyor belt or similar method, the reduced geometrical efficiency of irradiation and counting rules out the use of sources with total output less than about 10^8 neutrons per second (n/sec) (85). Isotopic sources with such outputs were considered to be prohibitively expensive, therefore their use was dismissed.

Californium-252 has become a viable neutron source for industrial and experimental applications since the late sixties. This isotope of californium has a half life of 2.65 years and produces neutrons with an average energy of about 2 MeV but the most probable energy is about 1 MeV. These energies are well-suited for capture gamma-ray analysis but are low for most inelastic neutron scattering or fast neutron activation analyses. The increased availability of californium-252 sources at reasonable cost and high neutron flux has shifted interest toward the use of capture gamma-ray spectrometry as a means of analyzing coal for process control. In addition, capture gamma-ray analysis was expected to yield useful analytical results for sulfur and hydrogen in coal, which could not be provided by earlier fast neutron techniques.

Early reactor capture gamma-ray studies of coal were reported by Rasmussen and Hukai (86). These studies involved collecting spectra of coal with a Ge(Li) detector for 25 hours. Thirty prominent photopeaks were used to identify the presence of ten elements and semiquantitative results for these elements were calculated based upon calibration of the system with a coal sample whose chemical analysis was assumed correct. Sulfur, iron, silicon and hydrogen were among these ten elements. After this study, Rasmussen focused his attention on the possible use of californium-252 for on-line analysis of coal (87). This resulted in a feasibility study which involved placing coal in a 55-gallon drum and a californium-252 source at its center (88). Capture gamma-rays were observed with a Ge(Li) detector placed outside the drum and this assembly was calibrated using an analyzed coal sample assumed as a standard. Analysis of four different types of coal showed promising results for analysis of sulfur in coal and possibly the water content. Results for silicon analysis in the presence of iron did not look promising due to peak interferences and a generally poor signal-to-background ratio. Examination of spectra confirmed that analysis of coal would be possible even with the much poorer energy resolution of NaI(Tl) detectors.

At the same time as Rasmussen's feasibility study (c. 1971), Parsignault et al. (25) reported on an analysis system using a californium-252 neutron source and utilizing a NaI(Tl) detector surrounded by an anti-Compton shield of plastic scintillating material. This system was designed to measure capture gamma-rays from sulfur and other constituents of coal. These researchers found it necessary to apply corrections for variations in the bulk density of coal and for changes in the neutron thermalization rate due to changes in the moisture content of coal. A separate gamma-ray source and detector placed at opposite ends of the coal bin provided gamma-ray attenuation measurements which could be related to the bulk density of the coal sample. Thermalization rate corrections were obtained by monitoring the 2.23 MeV photopeak, a measure of total hydrogen.

A few years later (c. 1974), the Russian researchers Pak and Starchik (89) were experimenting with a Po-Be neutron source for determining iron in coal. They maintained that knowledge of the iron content of coals could provide an indirect means of monitoring sulfur since much of the sulfur is held in pyritic materials. Capture gamma-ray spectra of 40 kilogram coal samples were collected with a NaI(Tl) detector. The iron content of the sample was determined by measuring the ratio of counts in two energy ranges in the gamma-ray spectrum of coal. This ratio measurement was devised to exclude the influence of bulk density and ash content on the results of the iron determination, although aluminum was viewed as a potential source of interference.

Capture gamma-ray work closely related to previous studies with coal was done by Pouraghabagher and Profio (90). In their research (c. 1974), a small californium-252 source was immersed in a large volume of fuel oil and a NaI(Tl) detector collected the capture gamma-ray spectrum. Sulfur in the oil was determined by comparing the area of the 5.42 MeV photopeak in spectra of standards and sample. Standard sulfur mixtures were prepared by combining carbon disulfide and low sulfur content oil.

During this same time period, a company known as Nuclear Enterprises developed and marketed an instrument for the measurement of sulfur in hydrocarbons (91). Details about this instrument are limited but the basis for its operation centers around a preferential absorption (attenuation) of radiation from americium-241 by sulfur. Nuclear Enterprises also markets a device for measuring the moisture content of granular solids in hoppers and bins which is based on moderation of fast neutrons.

Some of the best known research into monitoring the constituents of coal has been conducted at the Morgantown Energy Research Center (MERC) in West Virginia. Early work by this group involved developing a neutron moisture meter for monitoring the moisture content of coal flowing through a bin at high tonnage flow rates (92,93). The moisture content of coal was determined by measuring the thermal neutrons produced due to moderation of fast neutrons from an Am-Be source. Additional work has involved the capture gamma-ray determination of carbon in coal (94). The feasibility of analysis for carbon was demonstrated in actual experiments, but was too slow to provide effective process control. More recent work by this group (c. 1974) has involved monitoring sulfur levels in a coal processing stream with a nuclear meter. At the pilot plant stage of operation (95), this nuclear sulfur meter consisted of a cone shaped bin with a californium-252 neutron source placed at its center. A conveyor belt system was used to recirculate coal through the bin thereby simulating an industrial system. This nuclear meter utilizes two single-channel analyzers to measure a ratio of counts accumulated in two overlapping regions within the capture gamma-ray spectrum of coal (96), and is intended to minimize the effects of other elements in coal (97,98). Interference effects from iron, aluminum, silicon and moisture were examined. These researchers suggested monitoring both sulfur and iron concentrations to obtain a rough distinction between organic and pyritic sulfur. After pilot plant testing of the nuclear sulfur meter proved successful, the meter was installed in a coal preparation plant (99,100). The meter was calibrated with a coal of known sulfur content and a cut of coal from the main coal transport conveyor was passed through the meter for sulfur analysis. The results were compared with conventional sampling and chemical analysis, and indicated that the precision of the meter was adequate for process control, but there was a need for improved coal handling equipment, because testing operations were often halted due to coal binding and void formation in the test bin.

In similar coal monitoring research by Duffey _et_ _al_. (_c_. 1976), a small californium-252 neutron source has been used to irradiate synthetic coals, mixtures of polystyrene beads (as a base), aluminum oxide, silica, sulfur, iron and other powders (101). Tests with synthetic coal were conducted because their make-up can be accurately controlled, unlike real coal, whose heterogeneity can lead to somewhat questionable analyses. Samples were placed in a 55-gallon drum which rested on the californium-252 storage shield. When measurements were to be made, the neutron source could be pulled up into the center of the sample drums. Capture gamma-ray spectra were collected for 100 hours by a Ge(Li) detector placed near the top of the sample drum and the hydrogen response at 2.23 MeV was used as an internal flux monitor. Later, these same researchers obtained fair quantitative results from iron, sulfur, silicon and chlorine in actual coal samples (102,103). These results were estimated by comparison of sample spectra to spectra of the synthetic coal mixtures.

Recent capture gamma-ray experiments with a californium-252 neutron source (c. 1977) by Gozani et al. have been designed to provide realistic accuracy limits for element determinations in coal (104). Sensitivities for sulfur and ash elements relative to carbon were estimated and the relative error was shown to be inversely proportional to the square root of the measuring time and directly proportional to the square root of the background area under the photopeak. Both Ge(Li) and NaI(Tl) detectors were used for collection of gamma-ray spectra. Spectra collected with the NaI(Tl) detector were unfolded and resolution enhanced using the MAZE code (105) and compared with the photopeak data from the Ge(Li) spectra.

Ghavi and Cogburn (106) (c. 1977) have determined sulfur in two different grades of coal using a californium-252 source and a large NaI(Tl) detector. These analyses were accomplished by adding known amounts of sulfur to pulverized coal. After counting each sample, the 5.42 MeV sulfur peak areas were plotted against the mass of sulfur added. A straight line extrapolation back to the sulfur axis indicated the sulfur content of the coal. Comparison of their results to sulfur analyses by X-ray fluorescence yielded a relative accuracy of 6 percent.

Jurney, Curtis and Gladney (26) (c. 1977) have determined sulfur in coal and other matrices by capture gamma-ray spectrometry using a small Ge(Li) detector surrounded with a NaI(Tl) anticoincidence annulus for suppression of background caused by the escape of Compton scattered photons from the detector. Unlike most other research groups, these researchers work with small sample sizes (300-600 mg) and sample irradiation is accomplished inside the thermal column of a reactor (107). Also, these researchers are the first to use lower energy sulfur capture gamma-rays (at 841 and 2380 KeV) for analytical purposes. These gamma-rays are usually not observed in capture gamma-ray spectra of coal because of Compton background, which was reduced in these experiments by use of more sophisticated counting equipment.

IV. MATERIALS AND METHODS

A. Irradiation Facility

All irradiations were carried out at the Ames Laboratory Research Reactor (ALRR), Ames, Iowa, administered by Iowa State University under contract with the Department of Energy. Since this study, financial difficulties have resulted in the shutdown of the ALRR. The facility was a large-scale enriched uranium-heavy water reactor designed for operation at power levels up to 10 megawatts (MW) but operated at 5 MW.

All capture gamma-ray studies took place at Face 1 of the ALRR, which allows access to the reactor's thermal column. Samples were irradiated in a collimated beam of thermal neutrons which emerged through a port in the graphite thermal column. The neutron flux as measured with gold foils was approximately 6 x 10^5 neutrons per square centimeter per second (n/cm^2/sec). The neutron beam was nearly 100 percent thermal as no counts above background could be found for gold foils encased in cadmium after a two-hour irradiation.

The neutron beam was well-collimated and approximately 4 centimeters (cm) in diameter at the surface of the sample. If scattering of the neutrons by the sample is neglected, this means that approximately 250 cm^3 are irradiated for a rotating sample packed in a cylindrical polyethylene irradiation container (height 16 cm, diameter 9 cm). The bulk density of a sample packed into a polyethylene container was about 0.8-1.0 grams per cubic centimeter (g/cm^3) for coal. Therefore, approximately 200-250 grams (g) of coal were irradiated with the neutron beam. Actually, scattering of neutrons tends to spread the neutron beam increasing the effective sample size.

The neutron flux was monitored during each irradiation with a uranium fission chamber, located in close proximity to the reactor face so as to minimize the possibility that gamma-rays from the fission of uranium in the chamber would reach the detector.

A boral shutter was used to control the intensity of the neutron beam so that instrument dead times could be kept at approximately 10 percent. This shutter could also be used to block the neutron beam making it safer to change samples and preventing the production of extraneous activities in the sample cavity.

A solid cylinder of bismuth was placed in the outermost end of the thermal column neutron port. Bismuth reduces both the neutron and gamma-ray fluxes as they exit the port, but the attenuation coefficients of bismuth for thermal neutrons and gamma-rays are 0.229 and 0.322 cm^{-1}, respectively, as measured by Lombard *et al.* (108). Therefore, the bismuth plug serves as a filter for improving the ratio of thermal neutrons to fission gamma-rays in the emergent beam.

During the course of capture gamma-ray studies, two slightly different facilities were developed for irradiating and counting samples. The two facilities had nearly identical geometries with respect to neutron beam-to-sample and sample-to-detector positions. The first facility was constructed by stacking concrete blocks upon one another until the desired shielding and height requirements were achieved. This facility was large and sometimes awkward to work with, so that after reasonable success had been demonstrated using this first facility, a second facility was designed for increased versatility.

Figure 1 is a schematic representation of the first irradiation facility. The schematic portrays an overhead view of the facility. The major parts include the sample irradiation cavity, the sample rotator, the beam catcher and the gamma-ray detector.

The sample cavity was lined with boral and made large to reduce background effects. Boral is used as a shielding material because boron-10 has a very high capture cross section for thermal neutrons and emits only lower energy capture gamma-rays (<1.8 MeV). Boral was available in 1/4 inch sheets as a composite material consisting of 35 percent boron carbide crystals in aluminum, with a cladding of commercially pure aluminum. Unfortunately, the aluminum in the boral can emit potentially interfering high-energy

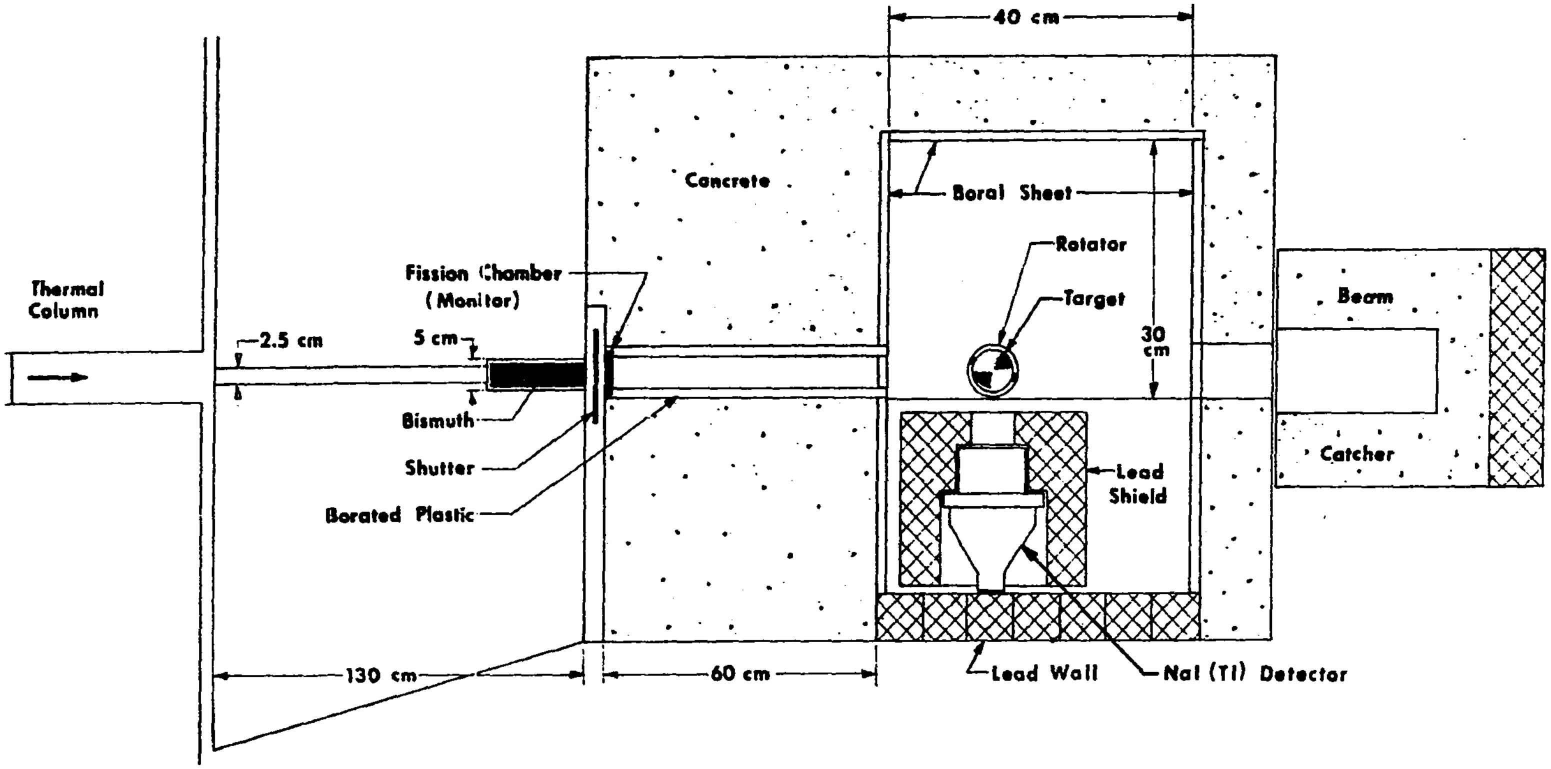


Figure 1. Overhead view of the first irradiation facility

capture gamma-rays after neutron capture (approximately 7.7 MeV). These as well as other gamma-rays emitted from neutron capture reactions at the walls of the cavity become a less significant source of background as the sample cavity size increases.

A rotating sample platform was mounted within the cavity which rotated the samples at 2 revolutions per minute (rpm) to provide a uniform average flux during the irradiation period. The time chosen was 40 minutes instrument live time using a thalium-activated sodium iodide (NaI(Tl)) detector, and 100 minutes instrument live time using a lithium-drifted germanium (Ge(Li)) detector.

A hole on the back side of the cavity allowed the neutron beam to leave the cavity and be stopped by a beam catcher.

In capture gamma-ray analysis, the gamma-rays are emitted instantaneously, necessitating an on-line counting arrangement. The detector used with this first irradiation facility was a 4x4 inch NaI(Tl) crystal located 90° to the beam direction at an experimentally determined optimal distance of 11.5 cm. This distance was chosen for maximum peak resolution and minimum background interference. A sheet of boral was placed between the detector and sample to prevent the activation of the NaI(Tl) crystal by scattered neutrons. The NaI(Tl) crystal and associated photomultiplier tube were fitted with a snug, cylindrical lead shield to reduce background radiation. A removable lead insert was placed at the face of the detector shield with a 2 inch hole cut through its center. This insert restricted the exposed face of the detector and provided a reasonable degree of collimation of incoming capture gamma-rays from the sample. The NaI(Tl) detector could be replaced with a small chicken-neck style Ge(Li) detector. When in use, the Ge(Li) crystal was surrounded by a cylindrical lead gamma-ray shield much like that of the NaI(Tl) detector.

Figure 2 is a schematic representation of the second irradiation facility. This figure portrays a side view of the facility. The major differences between this second facility and the first are the position of the gamma-ray detector, the method of sample rotation and the walls of the sample cavity. Figure 3 is a detailed side view for the sample cavity of the second irradiation facility.

The physical dimensions for the sample cavity were slightly larger than the dimensions of the cavity in the first facility, but the primary difference lay in the materials used to construct the cavity walls. The interior of the cavity walls were 1/2 inch thick lexan sheets. These sheets of lexan served as additional moderating material for any scattered fast neutrons inside the cavity, thus increasing the chances for thermalizing the neutrons before

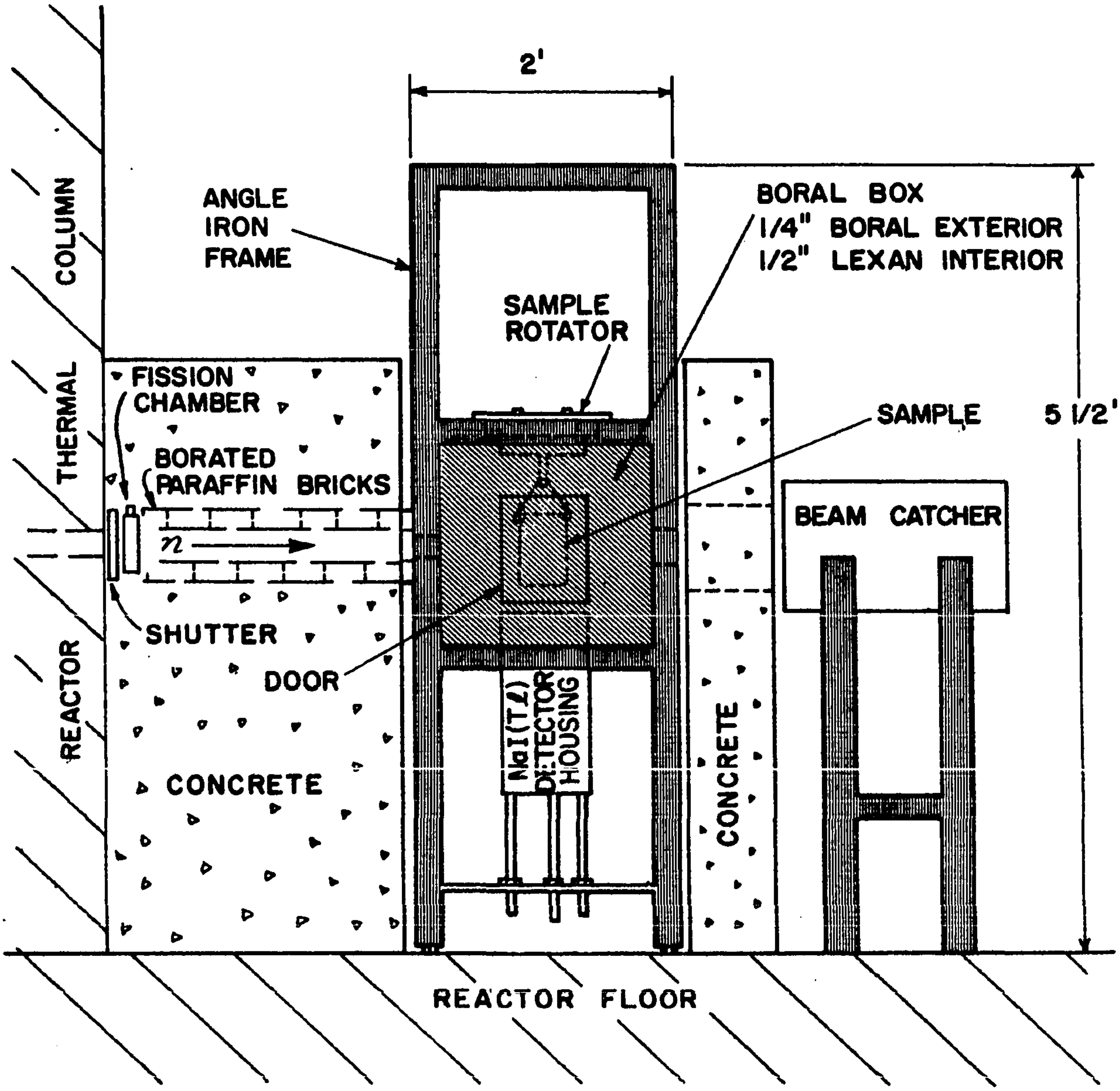


Figure 2. Side view of the second irradiation facility

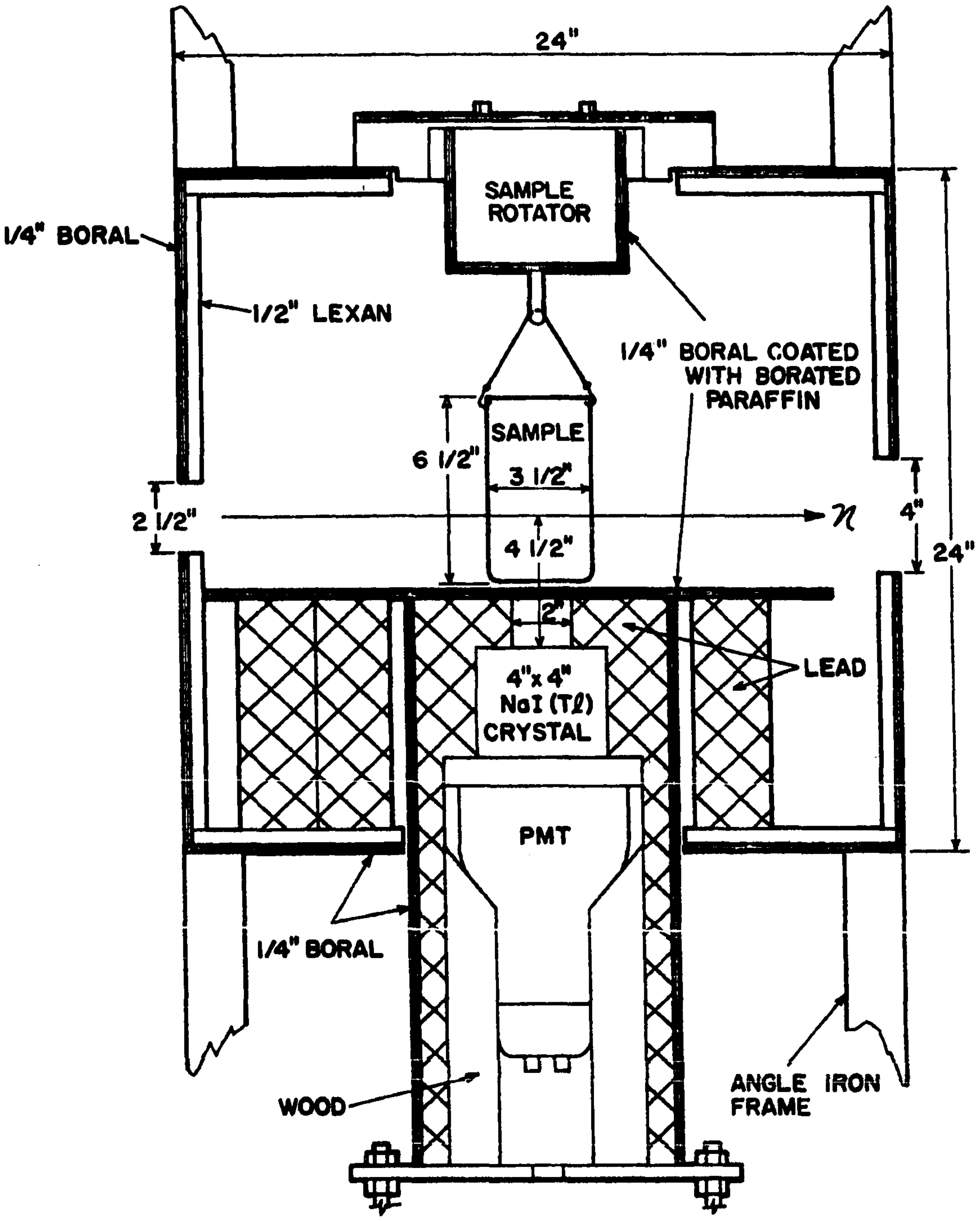


Figure 3. Detailed cross sectional view of the sample cavity of the second irradiation facility

they reached the boral exterior of the cavity walls. Between the 1/4 inch boral exterior and the 1/2 inch lexan interior was a sandwiched layer of borated paraffin. In fact, all boral surfaces on the interior walls of the cavity were coated with a 1/8 inch layer of borated paraffin. The purpose behind the borated paraffin was to reduce the background due to thermal neutron capture by aluminum in the boral.

In the second irradiation facility, the sample rotator was modified and positioned above the sample. The sample was hung from the protruding shaft of the motor by a fine piano wire (see Figure 3). The shaft of the motor ended in a small slotted bearing and the piano wire was flexible enough to permit the sample to center itself reproducibly above the detector.

The location of the NaI(Tl) detector in the second irradiation facility was changed from a horizontal to a vertical position, still at 90° to the neutron beam (see Figure 2). By placing the detector in a vertical position, operator mobility about the facility was increased because of the compactness of the facility. Also, the detector could now be moved in or out of the sample cavity more easily, since the detector was supported by three threaded rods. Adjustment of nuts on the threaded rods allowed adjustment of detector position.

The NaI(Tl) detector used with the second irradiation facility is the same detector that was used with the first facility except that its radiation shield was improved. The 4x4 inch NaI(Tl) crystal and associated photomultiplier tube were completely encased in a custom-fitted detector housing, consisting of a cylindrical exterior made of boral, and an interior of lead and wood. The lead shielded the NaI(Tl) crystal from background radiation while an inner wooden sleeve supported the detector in its vertical position. The face of the NaI(Tl) crystal was exposed to the sample through a 2 inch diameter hole cut in the center of the lead shielding. As before, a sheet of boral was placed between the detector housing and the sample to prevent scattered neutrons from activating the detector crystal. This protective boral sheet was supported by a number of additional lead bricks placed on the floor of the sample cavity and arranged around the hole in the floor of the cavity through which the detector housing protruded (see Figure 3). Lowering and removing the NaI(Tl) detector housing left ample room for a Ge(Li) detector and its floor-standing liquid nitrogen dewar. The arrangement of lead bricks topped by the boral sheet within the cavity provided an ideal background shield for a Ge(Li) detector.

The functioning parts of the second facility were rigidly fixed within an angle-iron frame. This allowed the whole facility to be moved or shifted with a minimum of disturbance to the more critical factors of the irradiation geometry. The four legs of the frame ended with a large nut and bolt assembly which allowed minor height adjustments to be easily completed.

An additional feature of the second irradiation facility was the easy access to the sample through a door in the sample cavity. The small dimensions of the door made it unlikely that the operator could place more than his hands into the sample cavity, thereby reducing operator exposure. This feature also served to protect the operator in the event that he should forget to close the boral neutron shutter. If such an event occurred, the operator would spend less time changing a sample because of easy sample access.

All other aspects of the second irradiation facility, such as the neutron shutter, beam catcher and fission chamber, were identical to the first irradiation facility discussed previously.

B. Instrumentation

The accumulation of capture gamma-ray spectra involved the use of either a thalium-activated sodium iodide (NaI(Tl)) or a lithium-drifted germanium (Ge(Li)) detector, accompanied by their respective conventional preamplifier and amplifier stages. The pulse height information from the amplifier stage was fed to a multichannel analyzer, complete with its own analog-to-digital converter (ADC). The ADC translated the pulse height information into digital form for temporary storage in the multichannel analyzer's memory. The X-Y output of the multichannel analyzer was connected to a display oscilloscope so that the accumulated spectrum could be examined. Once collected, the spectrum was transferred from the multichannel analyzer to punched paper tape for subsequent computer data reduction.

The NaI(Tl) detector used was a 4-inch-diameter by 4-inch-length Harshaw NaI(Tl) crystal (Harshaw Chemical Co., Cleveland, Ohio) coupled to a matching photomultiplier tube. This detector has a higher detection efficiency than the Ge(Li) detector for high energy gamma-rays and was used principally for quantitative purposes. The experimentally measured resolution of this detector was roughly 150 KeV full width at half maximum (FWHM) at 5 MeV.

A 30 cubic centimeter coaxial Ge(Li) detector was used for high resolution gamma-ray spectroscopy. This detector was used only with the second irradiation facility. Some quantitative work was done with this detector but it was used primarily for peak identification. The detector specifications include a measured resolution of 3.48 KeV FWHM for the 1.33 MeV photopeak of ^{60}Co, a peak-to-Compton ratio of 12 to 1, and an efficiency of 3.5 percent of a

3x3 inch NaI(Tl) detector at 1.33 MeV. At 5 MeV the experimentally measured resolution was approximately 25 KeV FWHM. A smaller less efficient chicken-neck style Ge(Li) detector was available for use with the first irradiation facility. With this style of detector, the cryostat and housing system for the Ge(Li) crystal are bent at 90° to the vertical enabling the detector to approach the experiment from the side. The manufacture's specifications were not available for this detector, but an experimentally observed resolution of about 40 KeV FWHM at 5 MeV was found. This detector was used only for peak identification.

The multichannel analyzer used was a Technical Measurement Corporation (North Haven, Connecticut) model 1001 pulse height analyzer with 1024 channels.

C. Samples

The samples used to demonstrate the effectiveness of a new analysis technique should be of varying kinds, but within the bounds of routine samples. This allows the experimenter to determine the limits of the technique, as to sample type, applicable concentration range, etc. To this purpose, five groups of permanent samples were prepared to evaluate the technique of capture gamma-ray spectrometry for sulfur and iron determination in coal. These samples are referred to as permanent because order of magnitude calculations indicate that it would take approximately 10^8 years to change the sulfur (or iron) concentration of a coal sample containing 1 percent sulfur-32 (or iron-56) by 1 percent. These concentration changes were assumed to have been caused by transmutation due to neutron irradiation, using a neutron flux of 10^6 n/cm^2/sec.

Three of these five groups of samples were prepared by adding known amounts of sulfur, or iron, or sulfur and iron, to a "base" coal, which was untreated, low-sulfur-content Wyoming coal. In the samples spiked with sulfur and iron, iron (as Fe_2O_3) was added in order to approximate pyritic sulfur.

The remaining coal samples consisted of ordinary run-of-mine (ROM) coal collected from various mine sites in Iowa. These ROM coal samples were split into two groups. The first group was collected in October, 1975, and tagged with the identification labels of 001 through 006. These six samples were used, along with the three sets of spiked samples, as standards to which the final group of ROM samples would be compared. This final group of ROM samples, which were to be treated as unknowns, were obtained in June, 1976, and tagged with the identification labels of SAM-1 through SAM-5.

Both spiked and real coal samples were used in these experiments to show that capture gamma-ray spectrometry is effective for simultaneous sulfur and iron determination over a wide range of sulfur-to-iron concentration ratios.

To establish the concentration of sulfur in the ROM coal samples to be used as standards, it was necessary to have them analyzed several times by an independent laboratory. These samples (001-006) were mixed in a ball mill and submitted for analysis four times from January to June, 1976. The first three times the samples were submitted to the Ames Laboratory Analytical Services group. The fourth time, the samples were submitted to Warner Laboratories, Inc. (Cresson, Pennsylvania). The sulfur concentrations of the remaining ROM coal samples (SAM-1 - SAM-5) were determined only once (by Warner Laboratories, Inc.) since they were to be treated as unknowns. As unknowns, the accuracy of their sulfur content was less critical, and additional expense was not warranted. The sulfur content of the base Wyoming coal used in preparing the spiked samples was known to be about 0.6 percent by weight. Therefore, the sulfur content of the spiked samples was already known with reasonable certainty. As a check on these values, the spiked samples were submitted once to Warner Laboratories, Inc. for sulfur analysis.

The iron content for all groups of samples was determined by the Ames Laboratory Analytical Services group. These results were combined with results obtained by instrumental neutron activation analysis using delayed gamma-ray spectroscopy.

The moisture content for some of the samples was determined by the Ames Laboratory Analytical Services group. The results could not be used in preparing any sort of calibration curve for moisture since the moisture content of coal is continually changing to achieve equilibrium with moisture in the ambient air. The results indicated a range of 2-10 percent moisture in the samples analyzed. This range in moisture content at any given time probably contributes substantially to the error associated with analysis of sulfur and/or iron in coal by capture gamma-ray spectrometry.

For the moisture measurement experiments, weighed amounts of water were added to dried Wyoming coal by spraying and mixing. The wetted sample was then placed into its sample container and the bulk density determined. A capture gamma-ray spectrum was collected immediately following the sample preparation.

The silicon content for all coal samples was determined by 14 MeV neutron activation analysis. The results were never used as capture gamma-ray spectrometry proved to be inadequate for silicon analysis.

Both the Ames Laboratory Analytical Services group and Warner Laboratories, Inc. used conventional ASTM methods for analysis of sulfur, iron, and moisture. These ASTM methods are briefly discussed in the Appendix.

The analysis of iron by instrumental neutron activation analysis involved an 8-hour irradiation of about 1/10 gram of coal in R-3. R-3 is the label given to a pneumatic transfer system which moves the samples to a location near the center of the reactor's core, where the neutron flux was 2.8×10^{13} n/cm^2/sec. A portion of the iron-58 (0.33 percent natural abundance) in the coal undergoes an (n,γ) reaction to produce iron-59 which has a 45-day half life. After a 10-day decay period following the irradiation, the 1095 and 1290 KeV iron-59 gamma-ray peaks were counted with a Ge(Li) detector and their respective peak areas were used for quantitative analysis of iron. National Bureau of Standards standard coal (SRM #1632) was used as the iron standard.

The analysis of silicon by 14 MeV neutron activation analysis involved a 2-minute irradiation of about 1/10 gram of coal in a fast neutron beam furnished by a neutron generator. The generator produces 14 MeV neutrons by the $^{3}H(d,n)^{4}He$ reaction. The facility has been described by Clark and Stensland (109). The presence of iron in the sample interferes with the silicon analysis. The important nuclear reactions of silicon and iron are $^{28}Si(n,p)^{28}Al$ and $^{56}Fe(n,p)^{56}Mn$, respectively. The sample is counted with a NaI(Tl) detector for 2 minutes immediately following the irradiation. The 1.78 MeV gamma-ray of aluminum-28 was used for quantitative analysis of silicon after it had been corrected for the interference contribution from the 1.81 MeV gamma-ray of manganese-56. The interference correction is made by use of a lower-energy manganese-56 peak (0.85 MeV), and amounted to approximately 10-15 percent of the original peak area. High purity Amercil quartz was used as the silicon standard.

Table 3 contains the combined results for sulfur, iron, and silicon analysis of all the coal samples, by the respective methods and laboratories mentioned above. Concentrations are given in total percent by weight. This table also contains the values for the bulk density of each coal sample as determined by the sample's volume displacement and weight. Bulk density measurements for all coal samples were necessary to correct for changes in the observed counting rate due to sample bulk density variations. The sensitivity of the counting rate to differences in the bulk density between similar samples was due to the fact that the sample size was large relative to the cross sectional area of the neutron beam. Therefore, the neutron beam passed through the sample and irradiated only a portion of the total sample; the actual amount of sample that was irradiated depends upon its bulk density since the sample was rigidly confined to the dimensions of the sample container.

The low neutron flux of the capture gamma-ray facility dictated that the sample size be large to compensate for

Table 3. Sample composition data

Sample	Bulk Density (g/cc)	% S	% Fe	% SiO_2
1) ROM COAL (Iowa Mine)				
001 (ICO)	0.894	6.22±0.10	3.01	4.02
002 (LOVILIA)	0.841	3.61±0.12	2.45	---
003 (LOVILIA)	0.843	4.70±0.49	3.09	2.21
004 (JUDE)	0.881	7.21±0.21	3.71	2.40
005 (OTLEY)	0.862	5.66±0.50	3.97	2.17
006 (SCOTT)	0.894	6.98±0.41	3.71	4.26
SAM-1 (LOVILIA)	0.871	4.74	3.96	3.06
SAM-2 (MICH)	0.883	5.69	---	---
SAM-3 (OTLEY)	0.907	7.23	5.15	4.04
SAM-4 (JUDE)	0.865	6.18	3.06	2.43
SAM-5 (ICO)	0.88	5.91	2.88	4.08
2) SPIKED COAL				
BASE Wyoming Coal	0.961	0.65	0.45	---
2% S	0.972	2.67	0.45	1.74
4% S	0.973	4.62	0.45	1.84
6% S	0.978	6.13	0.45	---
8% S	0.988	9.18	0.45	1.67
1% Fe	0.916	0.50	1.37	4.14
2% Fe	0.936	0.50	2.47	3.84
4% Fe	0.933	0.50	4.41	3.68
6% Fe	0.956	0.50	6.41	3.59
2% S/1.74% Fe	0.945	2.56	2.52	1.91
4% S/3.48% Fe	0.966	4.37	3.91	1.93
6% S/5.24% Fe	1.014	5.84	5.82	---
8% S/6.96% Fe	1.015	7.55	6.84	1.63

decreased elemental sensitivity. A large sample size has advantages when dealing with coal. Coal by nature is notoriously heterogeneous, and the use of a large sample will decrease the effects of sampling errors. The sample containers held a total of approximately 600 grams of coal while the neutron beam irradiated slightly more than 200-250 grams of that coal as it traversed the sample.

Homogeneous samples were obtained by mixing each coal sample in a ball mill for at least 12 hours. All coal samples were pulverized to the same particle size (60 mesh) and compacted in the irradiation containers with a hand operated hydraulic press. The containers were polyethylene, 9 cm in diameter and 16 cm high. The height to which coal is packed into its container is slightly important because the scattering of neutrons by the sample can make possible neutron capture reactions in the upper regions of the coal sample, even though the beam may be located an inch or more below the top surface of the sample. Variations in the packing height can therefore lead to small variations in the observed counting rate.

D. Gamma-Ray Spectra

Neutron capture spectra of pure sulfur, iron, carbon, silicon and aluminum were obtained under identical conditions for comparison with spectra of the coal samples, and to aid in determining possible overlapping peaks and their interferences. Peak identification was aided by spectra taken with a small Ge(Li) detector.

Figures 4 and 8 (Ge(Li)), and 5 and 6 (Na(Tl)) show details of the spectra. For two reasons these figures are useful only in a qualitative sense. First, the heights of the spectra above background were arbitrarily shifted to avoid overlap and hence are completely unrelated. Second, the exact amounts of material which the neutron beam irradiated are unknown, and the live times over which these spectra were accumulated varied. These four figures are useful for determining peak locations in different spectra and relative peak intensities in a given spectrum.

Examination of Figure 7 shows that double escape peak are more prominent than their corresponding single escape or full energy peaks when a small Ge(Li) detector is used. This figure also shows that with a 4x4 inch NaI(Tl) detector the full energy peak becomes the more prominent peak. For this reason, full energy peaks were selected for element determinations when a NaI(Tl) detector was used, and double escape peaks were used with a Ge(Li) detector.

Once spectra for the coal samples were collected, the net area under each peak (full energy, single escape or double escape peak) was obtained by assuming that the peak is superimposed on a linear background. The peak areas were

Figure 4. Neutron capture spectra (4.4-7.8 MeV) of the common elements in coal, taken with a Ge(Li) detector

From the top: coal, sulfur, iron, carbon, silicon, background (with empty polyethylene bottle). Aluminum peaks are from boral shielding. M, full energy peak; M', single escape peak; M", double escape peak. Energies in MeV. Vertical scale is logarithmic and displaced vertically to separate spectra

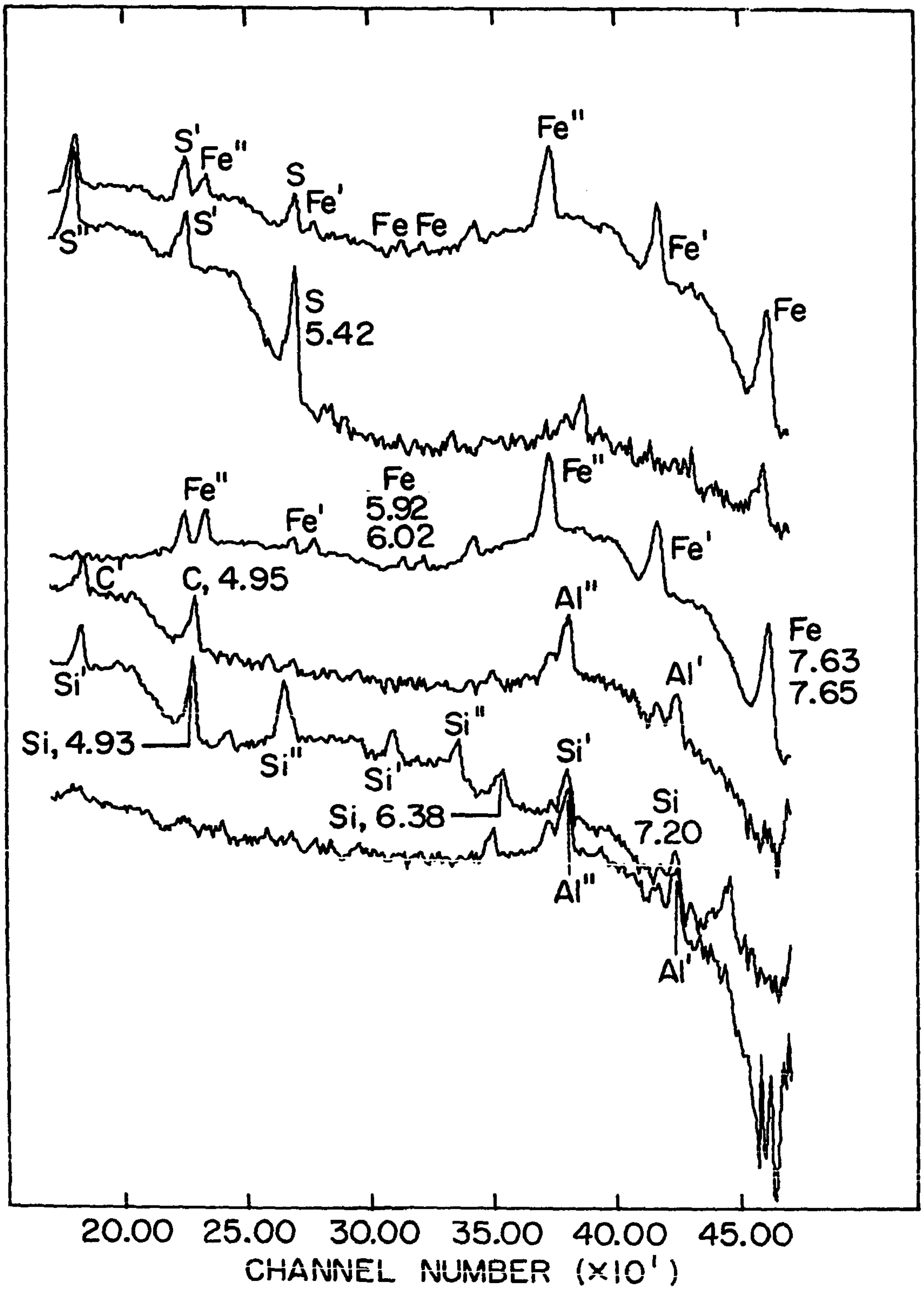

S'
Fe''
S
Fe'
Fe Fe
Fe''
S''
S'
Fe'
S
5.42
Fe
Fe''
Fe'
Fe
5.92
6.02
Fe''
Fe'
C'
C, 4.95
Al''
Fe
7.63
7.65
Si'
Al'
Si, 4.93
Si''
Si''
Si'
Si'
Si, 6.38
Si
7.20
Al''
Al'
20.00
25.00
30.00
35.00
40.00
45.00
CHANNEL NUMBER (×10')

Figure 5. Neutron capture spectra (4.4-7.8 MeV) of the common elements in coal, taken with a NaI(Tl) detector

From the top: sulfur, iron, carbon, silicon, aluminum, background (with empty polyethylene bottle). M, full energy peak; M', single escape peak; M", double escape peak. Energies in MeV. Vertical scale is logarithmic and displaced vertically to separate spectra

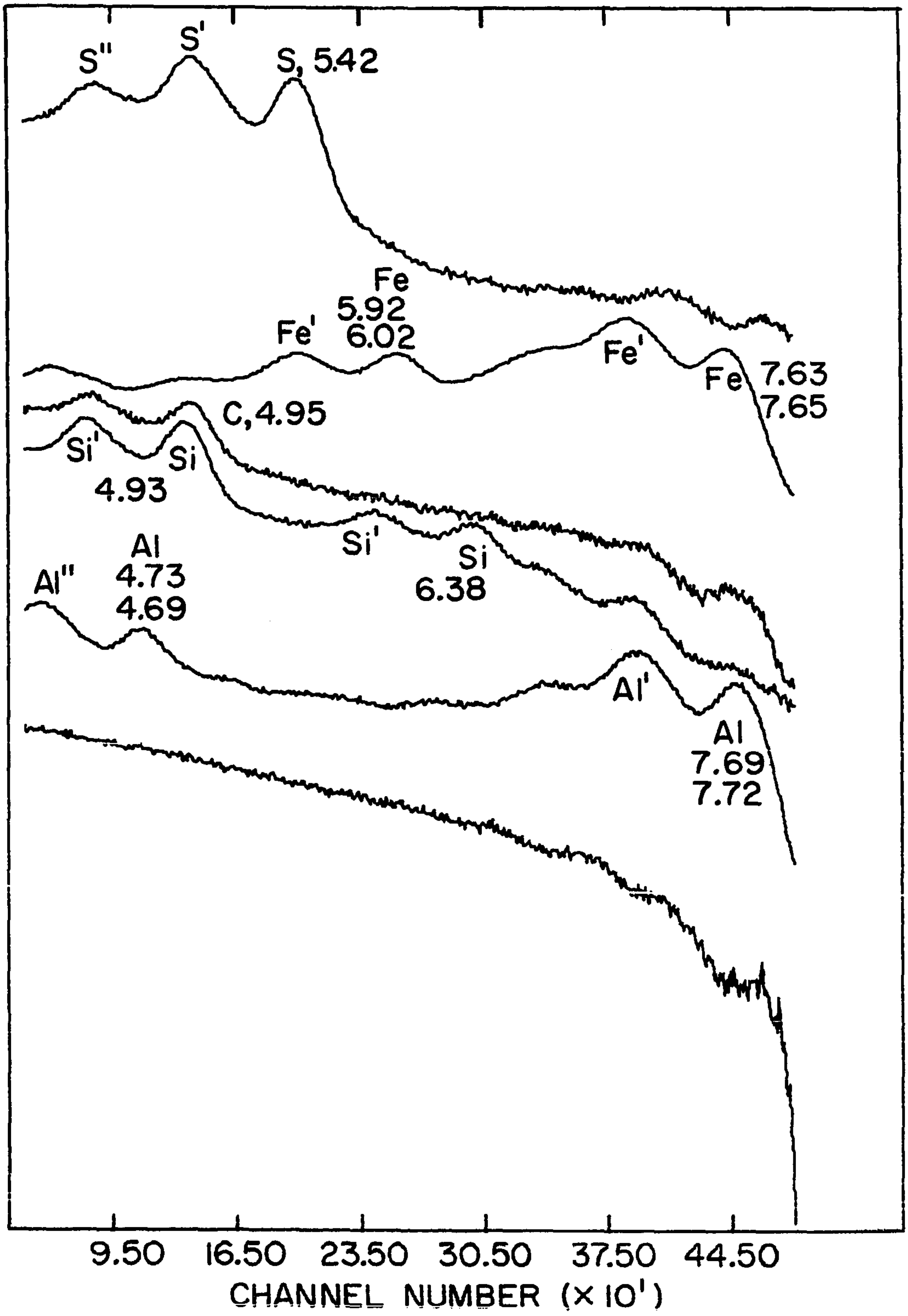

S''
S'
S, 5.42
Fe
5.92
6.02
Fe'
Fe'
Fe
7.63
7.65
C, 4.95
Si'
Si
4.93
Si'
Si
6.38
Al''
Al
4.73
4.69
Al'
Al
7.69
7.72
9.50
16.50
23.50
30.50
37.50
44.50
CHANNEL NUMBER (× 10')

Figure 6. Neutron capture spectra (2.6-5.1 MeV) of the common elements in coal, taken with a NaI(Tl) detector

From the top: silicon, sulfur, iron, aluminum, carbon, background (with empty polyethylene bottle). M, full energy peak; M', single escape peak; M", double escape peak. Energies in MeV. Vertical scale is logarithmic and displaced vertically to separate spectra

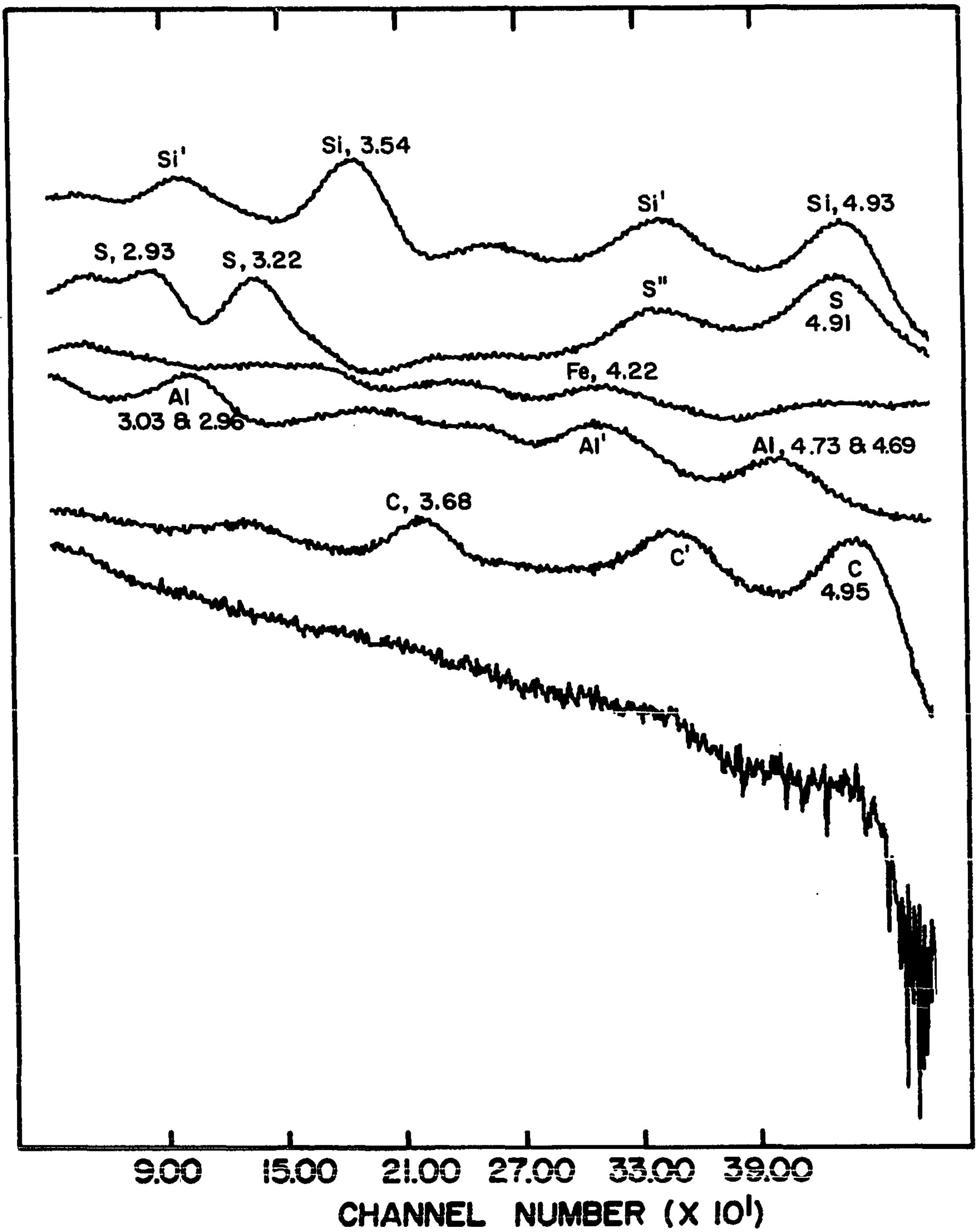

Si'
Si, 3.54
Si'
Si, 4.93
S, 2.93
S, 3.22
S"
S
4.91
Fe, 4.22
Al
3.03 & 2.96
Al'
Al, 4.73 & 4.69
C, 3.68
C'
C
4.95
9.00
15.00
21.00
27.00
33.00
39.00
CHANNEL NUMBER (X 10^1)

Figure 7. Capture gamma-ray spectra of coal: top, NaI(Tl); bottom, Ge(Li)

The gain settings used in accumulating these spectra were similar but not the same, as seen by examining the high energy region near the three major iron peaks

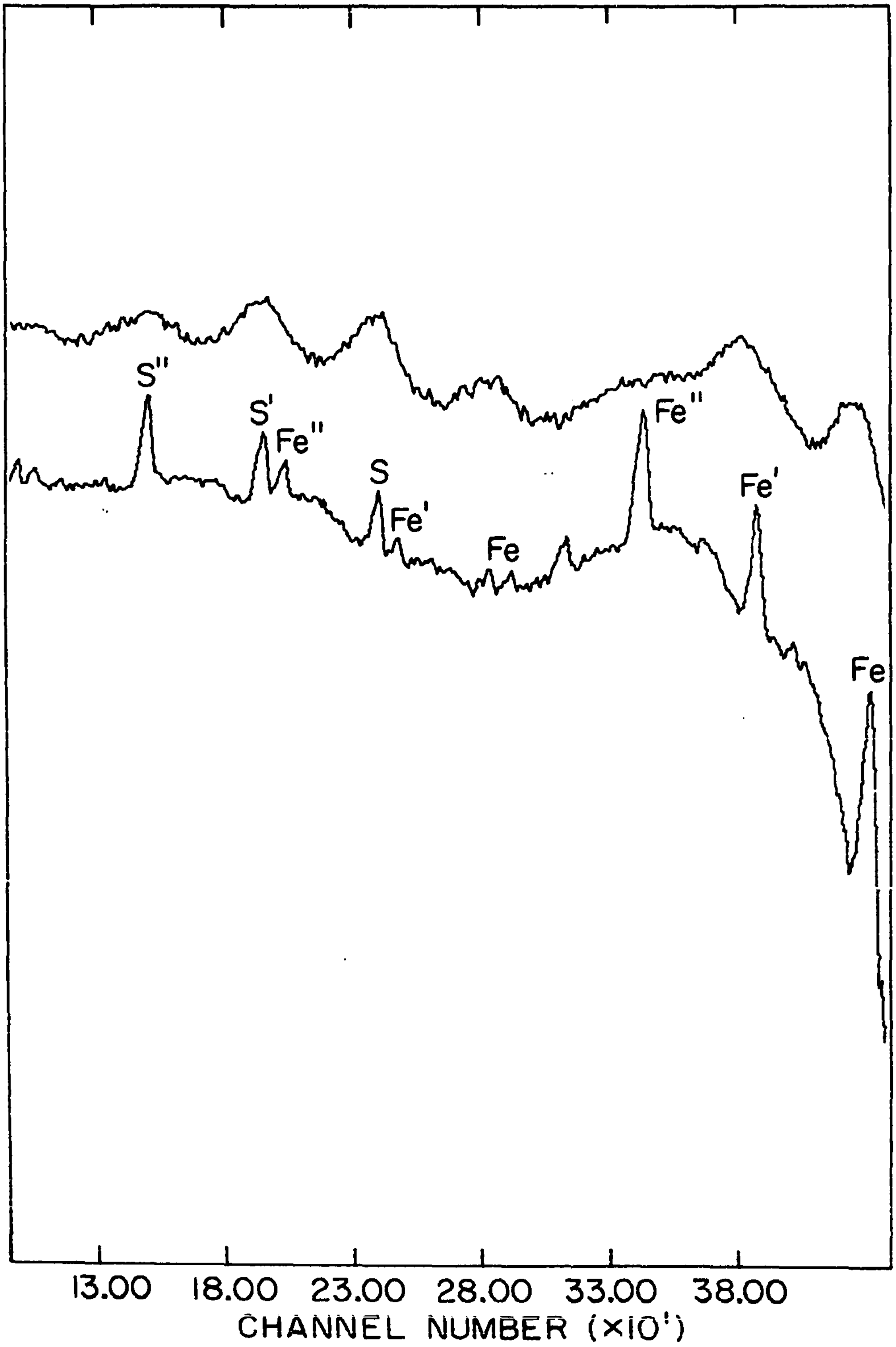
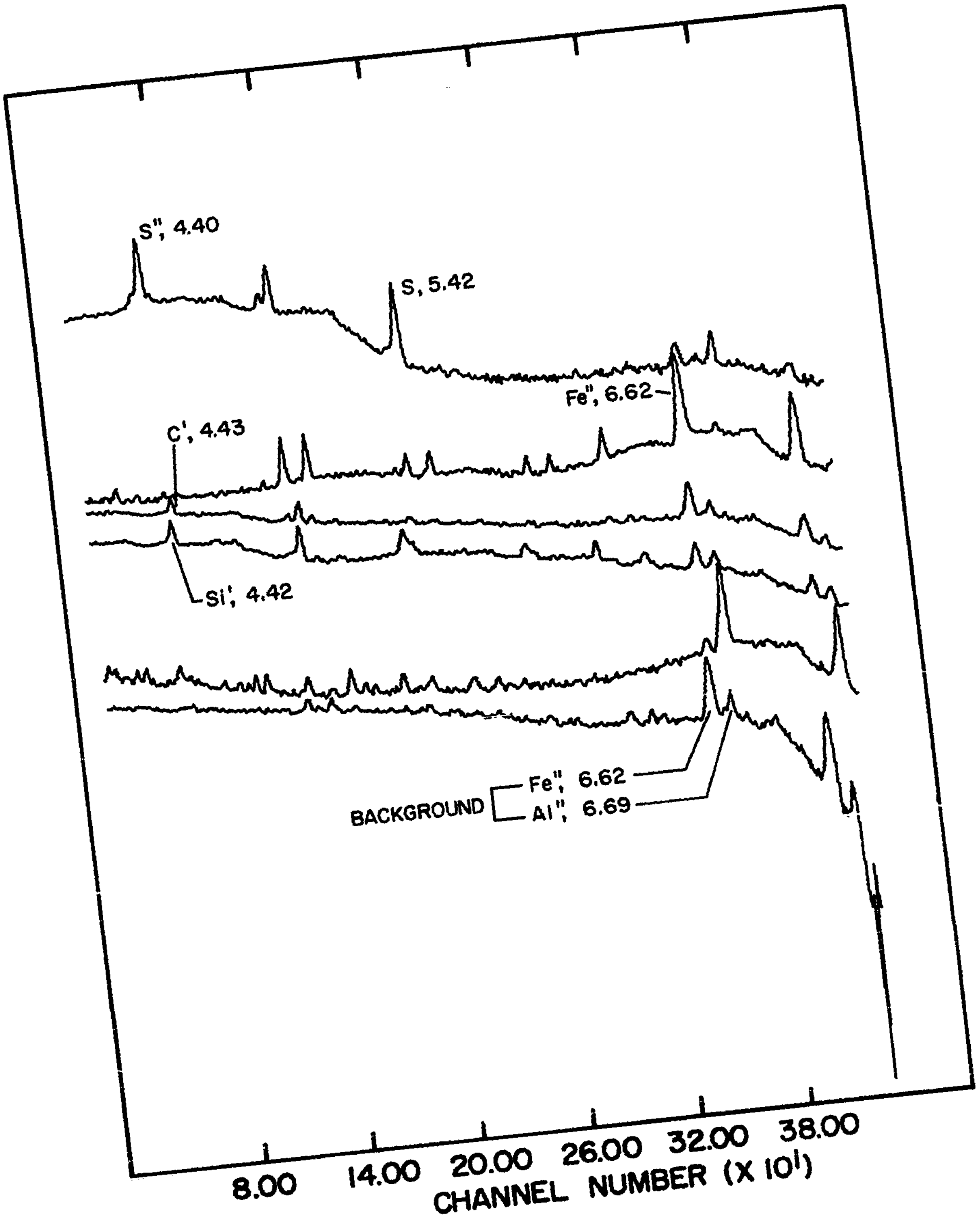

S''
S'
Fe''
S
Fe'
Fe
Fe''
Fe'
Fe
13.00
18.00
23.00
28.00
33.00
38.00
CHANNEL NUMBER ($\times 10^1$)

Figure 8. Neutron capture spectra (4.2-7.2 MeV) of the common elements in coal, taken with a Ge(Li) detector

From the top: sulfur, iron, carbon, silicon, aluminum, background (with empty polyethylene bottle). M, full energy peak; M', single escape peak; M", double escape peak. Energies in MeV. Vertical scale is logarithmic and displaced vertically to separate spectra


S", 4.40
S, 5.42
Fe", 6.62
C', 4.43
Si', 4.42
BACKGROUND
Fe", 6.62
Al", 6.69
8.00
14.00
20.00
26.00
32.00
38.00
CHANNEL NUMBER (X 10^1)

also corrected for variations in the neutron flux, live times of the multichannel analyzer, sample bulk density, and iron interferences when necessary. These corrected peak areas were plotted against previously known amounts of the respective elements of interest, sulfur, iron or hydrogen (as water added), to obtain calibration curves for these elements.

1. Sulfur determination using a NaI(Tl) detector

Spectra obtained with NaI(Tl) and Ge(Li) detectors, shown in Figure 7, were compared, and the 5.42 MeV gamma-ray was selected as the best capture gamma-ray for sulfur determination with a NaI(Tl) detector. The full energy peak at 5.42 MeV was chosen for routine use since it was more prominent in the NaI(Tl) spectra than the escape peaks at 4.91 and 4.40 MeV. Also, the only major interfering peak with a significantly varying peak area occurring near this peak is an iron single escape doublet at 5.41 and 5.51 MeV. The Ge(Li) spectra indicate that it should be possible to correct for this iron interference by using either the iron full energy peak at 5.92 MeV or another iron double escape peak at 6.62 MeV as a measure of the amount of iron present in the coal sample. Actual amounts of iron present in the coal samples need not be known in order to correct for the iron interference if the ratios of iron peak areas are used to make the corrections. With NaI(Tl) detectors, the two iron full energy peaks at 5.92 and 6.02 MeV are not resolved, but appear as a single peak. Together, their combined single escape peak interferes with the sulfur full energy peak at 5.42 MeV, but the peak area ratio method of correcting for this iron interference still applies.

A double escape peak from silicon at 5.36 MeV (from the 6.38 MeV gamma-ray) could interfere with the sulfur determination. However, a more intense silicon full energy peak at 3.54 MeV was not seen in the Ge(Li) spectra of coal samples and the possibility of silicon interference could thus be eliminated. By examining Figures 4 and 5, it also becomes apparent that double escape peaks are much less intense with a 4x4 inch NaI(Tl) detector than with a small Ge(Li) detector, providing an immediate advantage in the case of silicon interference. Figure 4 shows a double escape peak from silicon directly underneath the sulfur full energy peak at 5.42 MeV, while Figure 5 shows that this is absent in the NaI(Tl) spectra.

Carbon offers no interference to the sulfur full energy peak at 5.42 MeV. The only carbon peak readily observed in a Ge(Li) spectrum from coal (see Figure 7) is a double escape peak at 3.92 MeV. In NaI(Tl) spectra this peak becomes much broader and unresolvable from a weak sulfur double escape peak at a slightly lower energy. The full energy peak corresponding to this weak sulfur double escape peak occurs at 4.87 MeV, and appears as a shoulder on the low energy side of the sulfur single escape peak at 4.91 MeV. This shoulder is visible in the spectrum for pure sulfur shown in Figures 4 and 8.

By examining background spectra, it was found that no interference peaks from aluminum in the boral shielding occur in the 5.4 MeV region. The only discernible peaks in the background occur from two aluminum full energy peaks at 7.69 and 7.72 MeV.

2. Sulfur determination using a Ge(Li) detector

The 4.40 MeV double escape peak of sulfur was selected for sulfur determination when a Ge(Li) detector was used. This escape peak of sulfur is more prominent than the single escape or full energy peaks of sulfur at 4.91 and 5.42 MeV, respectively. Comparison of spectra in Figure 8 shows that both carbon and silicon yield potentially interfering peaks to the 4.40 MeV sulfur double escape peak, while iron and the background offer no interference. The interference due to silicon was considered negligible, since neither the silicon full energy peak at 3.54 MeV nor any evidence of its escape peaks could be found in Ge(Li) detector spectra of coal samples. The interfering carbon single escape peak occurs at 4.43 MeV, 30 KeV higher than the sulfur double escape peak. The peak area of the carbon single escape peak was significant but its contribution to the sulfur double escape peak can be removed if a Ge(Li) detector of sufficient resolution is employed. The resolution of the Ge(Li) detector (approximately 25 KeV FWHM) used for these experiments was adequate enough to resolve the sulfur double escape peak and the carbon single escape peak so that only the lower sides of each photopeak overlapped. With the use of a technique by Bevington involving computer assisted data reduction (110), a nonlinear least squares program was written to fit a Gaussian function to the sulfur double escape peak, thereby excluding the carbon single escape peak from area determinations of the sulfur peak.

3. Iron determination using a NaI(Tl) detector

The iron capture gamma-ray doublets at 5.9 and 7.6 MeV were chosen for the determination of iron when a NaI(Tl) detector was used. These doublets appear as single photopeaks because of the poor energy resolving characteristics of the NaI(Tl) detector. Examination of Figure 5 shows that only silicon could interfere with the 5.9 MeV iron doublet. As before, the interference due to silicon can be eliminated due to absence of any noticeable capture gamma-ray peaks for silicon in the Ge(Li) spectra of coal samples. Figure 5 also indicates that aluminum could interfere with the 7.6 MeV iron doublet. The importance of this interference was considered to be minimal since the relative sensitivity indexes for iron and aluminum capture gamma-rays at 7.6 MeV (see Table 1) indicate that capture gamma-ray analysis should be an order of magnitude more sensitive toward iron.

Both the 5.9 and 7.6 MeV iron capture gamma-ray peaks are subject to background interference due to iron capture reactions in the construction materials of the irradiation facility. This interference existed as a constant background and could be accurately measured and subtracted before processing iron peak area information. Actual background measurements indicated that the background interferences from iron in the construction materials was small, therefore no background subtraction was made.

4. Iron determination using a Ge(Li) detector

The 6.6 MeV double escape peak of iron was chosen for the determination of iron when a Ge(Li) detector was used. This double escape peak is a doublet which originates from the 7.63 and 7.65 MeV full energy capture gamma-rays of iron. Examination of Figures 4 and 8 shows that this iron photopeak was subject to interference from silicon but not from aluminum, since the detector resolution was sufficient to separate these two photopeaks (65 KeV separation between iron and aluminum photopeak centers). Interference from silicon could be dismissed due to the absence of any noticeable capture gamma-ray peaks of silicon in the Ge(Li) spectra of coal samples.

As mentioned earlier, iron capture reactions in the construction materials of the irradiation facility contribute a constant background to all iron photopeaks. The background due to iron was highest for the second irradiation facility. This background spectrum is shown in Figure 8 (the background spectrum of Figure 4 was collected for the first irradiation facility). The thickness of lead used to shield the Ge(Li) detector from background gamma radiation was approximately 2 inches less than that used to shield the NaI(Tl) detector. Consequently, it became necessary to accurately determine and subtract out this background contribution to the 6.6 MeV iron peak area before any data processing. This background correction amounted to 45 percent of the initial peak area for a coal sample containing 1 percent iron and 15 percent of the initial peak area for a coal sample containing 6 percent iron.

5. Silicon determination

The 3.54 MeV peak of silicon appeared to be the best capture gamma-ray for silicon determination. Examination of spectra in Figure 6 shows that none of the common elements in coal yield major capture gamma-rays which directly overlap the 3.54 MeV silicon full energy peak.

6. Moisture determination

For moisture measurements, the 2.23 MeV full energy peak of hydrogen was used. This peak is very intense and showed no dependence upon minor interfering elements.

V. RESULTS

The initial objective of this research was to develop a technique for the determination of sulfur in coal using capture gamma-ray spectrometry. The technique was to provide accurate results using simple equipment. The time between securing the sample and obtaining results was to be minimized so that the technique might be useful for monitoring a coal process stream. As this work progressed, the objectives were expanded to include the determination of iron, moisture and silicon in coal.

A. Sulfur Determination

1. Data collected with a NaI(Tl) detector

The prospect of sulfur analysis was first investigated using the spiked coal samples. It was apparent from Ge(Li) spectra collected on the Wyoming coal that this coal did not contain substantial amounts of iron or sulfur. The spiked coal samples, which were made from this Wyoming coal, were used to investigate the magnitude of the iron interference on sulfur determination. This was done by collecting NaI(Tl) spectra for the spiked Wyoming coal samples and comparing the increase in the sulfur full energy peak area (at 5.42 MeV) of the sulfur and iron spiked samples relative to the sulfur full energy peak area of the samples spiked with sulfur only. From these comparisons the ratio of areas for the iron single escapt peak doublet at 5.46 MeV to the full energy doublet at 5.97 MeV was found to be 1.27. In subsequent analysis, the product of this ratio and the measured peak area at 5.97 MeV was subtracted from the peak area at 5.42 MeV to provide the contribution due to sulfur alone. A typical correction for the interference from a high iron content coal was about 38 percent of the total 5.42 MeV peak. Once the 5.42 MeV peak had been corrected for iron contribution, it was then divided by the bulk density of the sample to account for varying amounts of coal which had been irradiated.

Capture gamma-ray spectra were collected for coal samples using both the first and second irradiation facilities. The corrected peak areas obtained from these spectra were used to construct sulfur calibration curves for the respective irradiation facilities. The calibration curve for the first irradiation facility is shown in Figure 9, and Figure 10 shows a similar calibration curve for the second irradiation facility.

2. Data collection with a Ge(Li) detector

The use of a high resolution Ge(Li) detector combined with the proper data reduction techniques for the determination of sulfur in coal had the advantage of being a direct sulfur determination, unlike the iron interference correction method involved with NaI(Tl) detector data. By using a

Figure 9. Sulfur calibration curve for the first irradiation facility. Percent total sulfur <u>versus</u> area of the sulfur full energy peak at 5.42 MeV (NaI(Tl) data).

+, ROM coal samples; O, Wyo. coal spiked with sulfur; Δ, Wyo. coal spiked with sulfur and iron

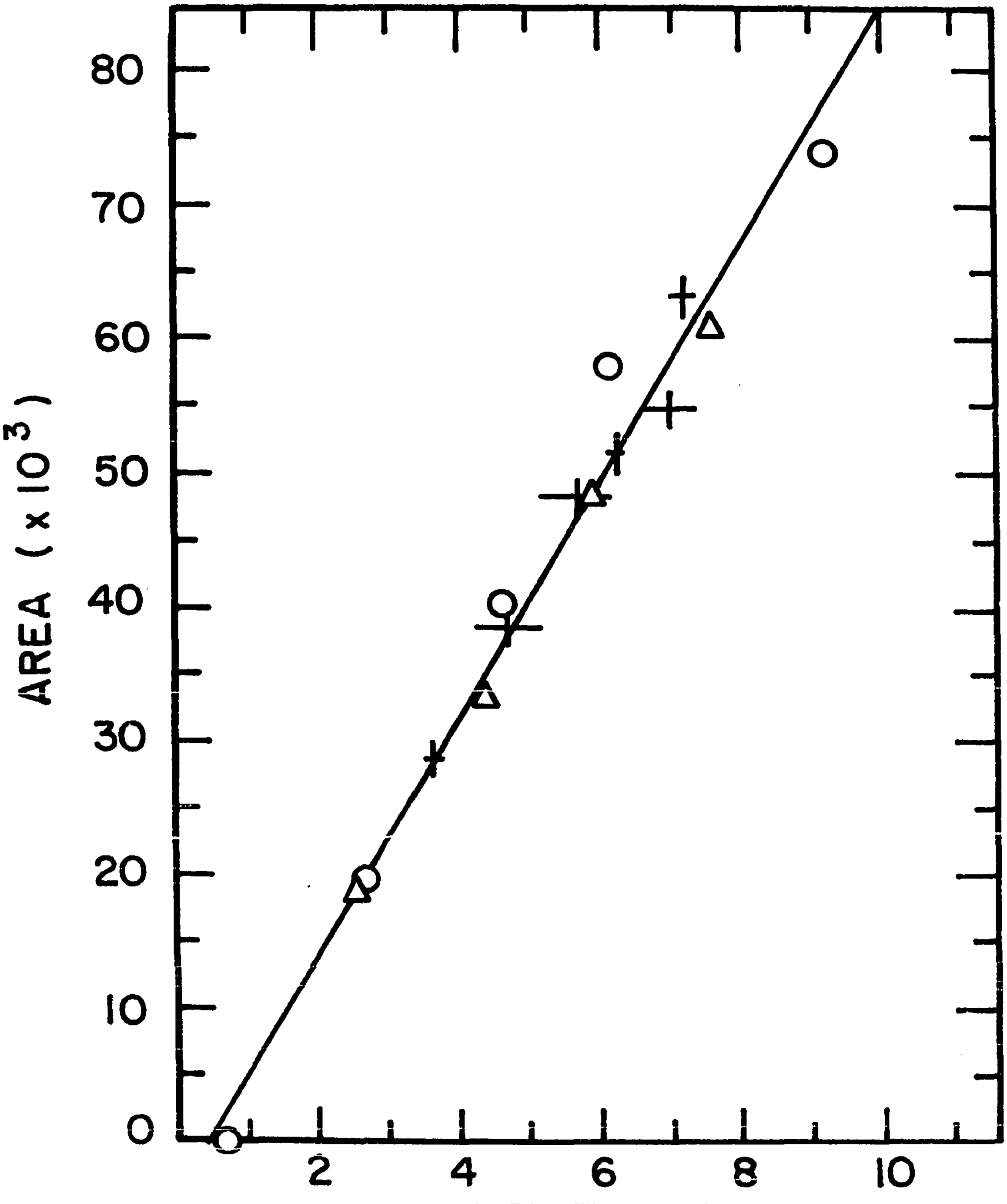
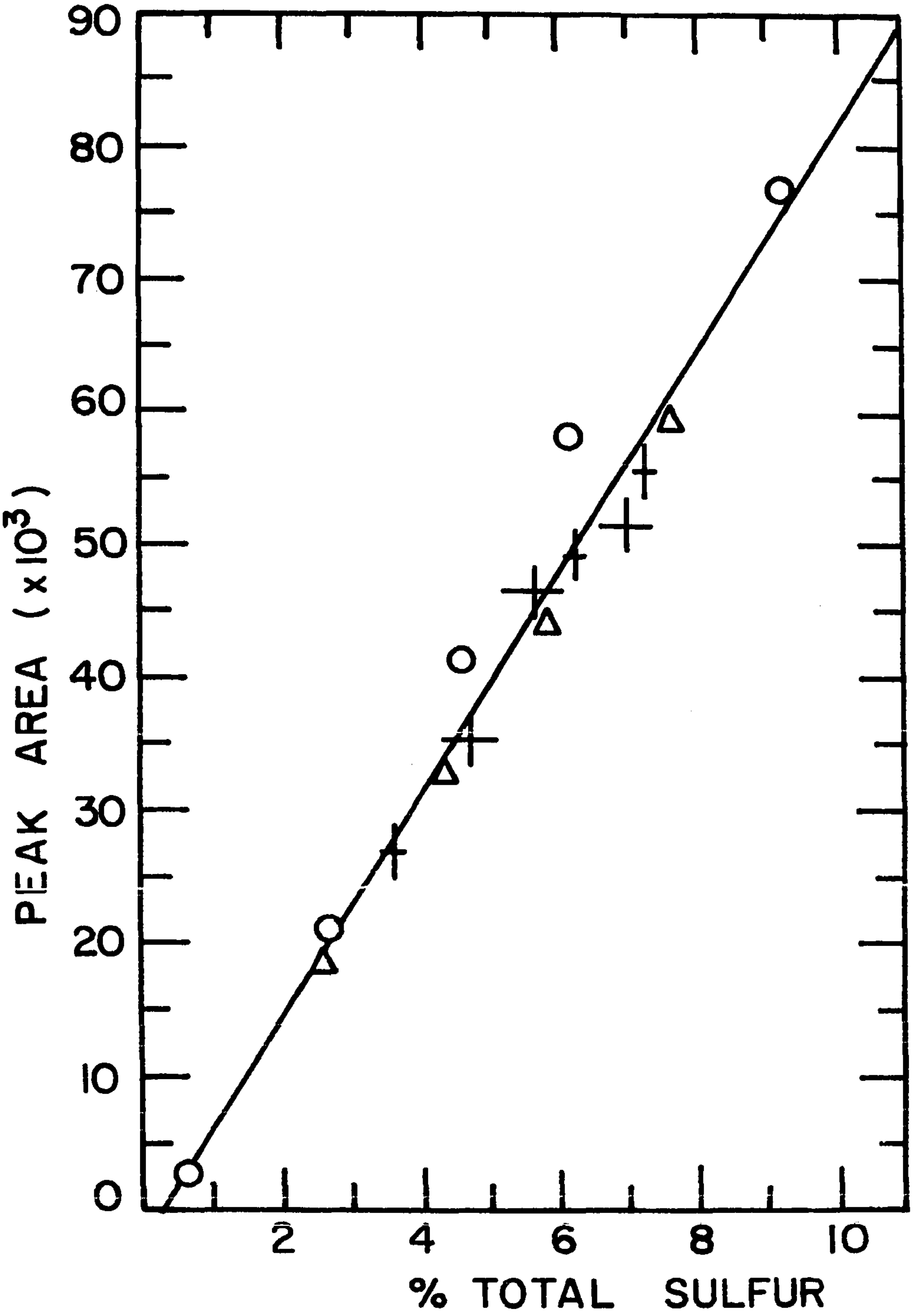

AREA (x 10^3)
80
70
60
50
40
30
20
10
0
2
4
6
8
10
% TOTAL SULFUR

Figure 10. Sulfur calibration curve for the second irradiation facility. Percent total sulfur *versus* area of the sulfur full energy peak at 5.42 MeV (NaI(Tl) data)

+, ROM coal samples; O, Wyo. coal spiked with sulfur; Δ, Wyo. coal spiked with sulfur and iron


90
80
70
60
50
40
30
20
10
0
PEAK AREA (x 10^3)
2
4
6
8
10
% TOTAL SULFUR

Ge(Li) detector, the 4.40 MeV sulfur double escape peak and a potentially interfering carbon peak were partially resolved. Further resolution of these two photopeaks was accomplished by using a computer to fit a Gaussian function to the upper 2/3 of the 4.40 MeV peak. The area of this fitted function, above a straight line background, was divided by the bulk density of the sample to obtain a specific peak area (area/g/cc) that could be used to construct a sulfur calibration curve. The background was determined by calculating a linear least squares line between two groups of background points, one group on either side of the 4.40 MeV photopeak.

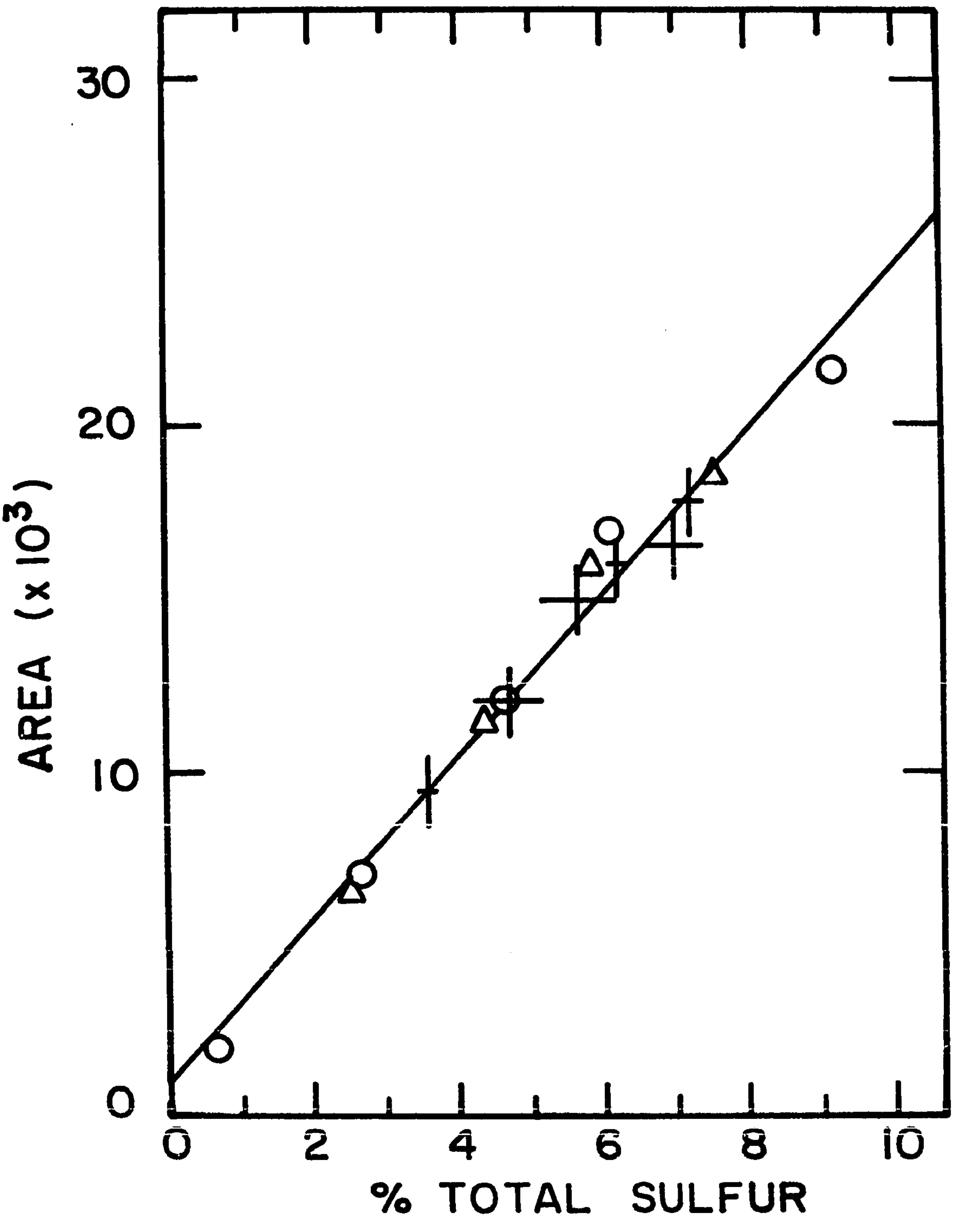
The second irradiation facility was the only facility used in collecting quantitative Ge(Li) spectra for the coal samples. Therefore, only one calibration curve for sulfur is available for Ge(Li) detector data. Figure 11 shows the sulfur calibration curve for the second irradiation facility.

3. Demonstration of sulfur determination

The determination of sulfur by capture gamma-ray spectrometry was demonstrated by analyzing five ROM samples of Iowa coal (SAM-1 - SAM-5) which had previously been analyzed by an independent laboratory. Analysis of these five samples by capture gamma-ray spectrometry was repeated five times. These five experiments spanned a time period from January to November, 1977. During each experiment,

Figure 11. Sulfur calibration curve for the second irradiation facility. Percent total sulfur _versus_ area of the sulfur double escape peak at 4.40 MeV (Ge(Li) data)

+, ROM coal samples; O, Wyo. coal spiked with sulfur; Δ, Wyo. coal spiked with sulfur and iron


30
20
10
0
AREA (x 10^3)
0
2
4
6
8
10
% TOTAL SULFUR

fifteen coal samples with known total percent sulfur content were treated as standards. For each experiment, the proper sulfur peak areas from the gamma-ray spectra for each of these standards were used to calculate a linear least squares line. This least squares equation was then used to calculate the sulfur content of the five unknown samples. The results from these experiments are summarized in Table 4.

The column containing the average of values for the four NaI(Tl) experiments shows good precision. The precision is about ±0.2 percent sulfur, while the accuracy is about 5-15 percent relative to the values obtained by Warner Laboratories. The average relative accuracy is 5.6 percent.

The last column of Table 4 shows the results obtained for capture gamma-ray analysis of coal using a Ge(Li) detector. These results indicate poorer accuracy than the NaI(Tl) results. The decreased accuracy results from poorer counting statistics for the Ge(Li) detector data.

The count rate observed for a particular experiment will depend upon which detector system and which gamma-ray are used. The relative response of the respective detectors for the particular sulfur gamma-ray can be determined using the slopes of the calibration lines for the NaI(Tl) and Ge(Li) detector data. The NaI(Tl) data was collected for 40 minutes while the Ge(Li) detector data were collected for 100 minutes.

Table 4. Sulfur determination results for the SAM-x coal samples

		NaI(Tl)					
Sample	%S (Warner)	Exp1	Exp2	Exp3	Exp4	Average (Std.Dev.)	Ge(Li)[a]
SAM-1	4.74	4.86	4.72	4.86	4.99	4.86±.11	5.50
SAM-2	5.69	5.70	5.99	5.90	5.61	5.80±.18	5.72
SAM-3	7.23	6.35	6.04	6.18	6.14	6.18±.13	6.67
SAM-4	6.18	6.62	6.48	6.77	6.38	6.56±.17	6.71
SAM-5	5.91	6.18	5.88	6.15	6.13	6.09±.14	6.44

[a] Using 4.4 MeV sulfur double escape peak.

NaI(Tl) 8500 counts/%S/40 min = 212.5 CPM/%S

Ge(Li) 2300 counts/%S/100 min = 23.0 CPM/%S

$$212.5/23.0 = 9.2$$

These calculations indicate that for equal counting times, the capture gamma-ray technique developed for use with a 4x4 inch NaI(Tl) detector is roughly one order of magnitude more sensitive toward sulfur than the technique developed for use with a small Ge(Li) detector.

B. Iron Determination

1. Data collected with a NaI(Tl) detector

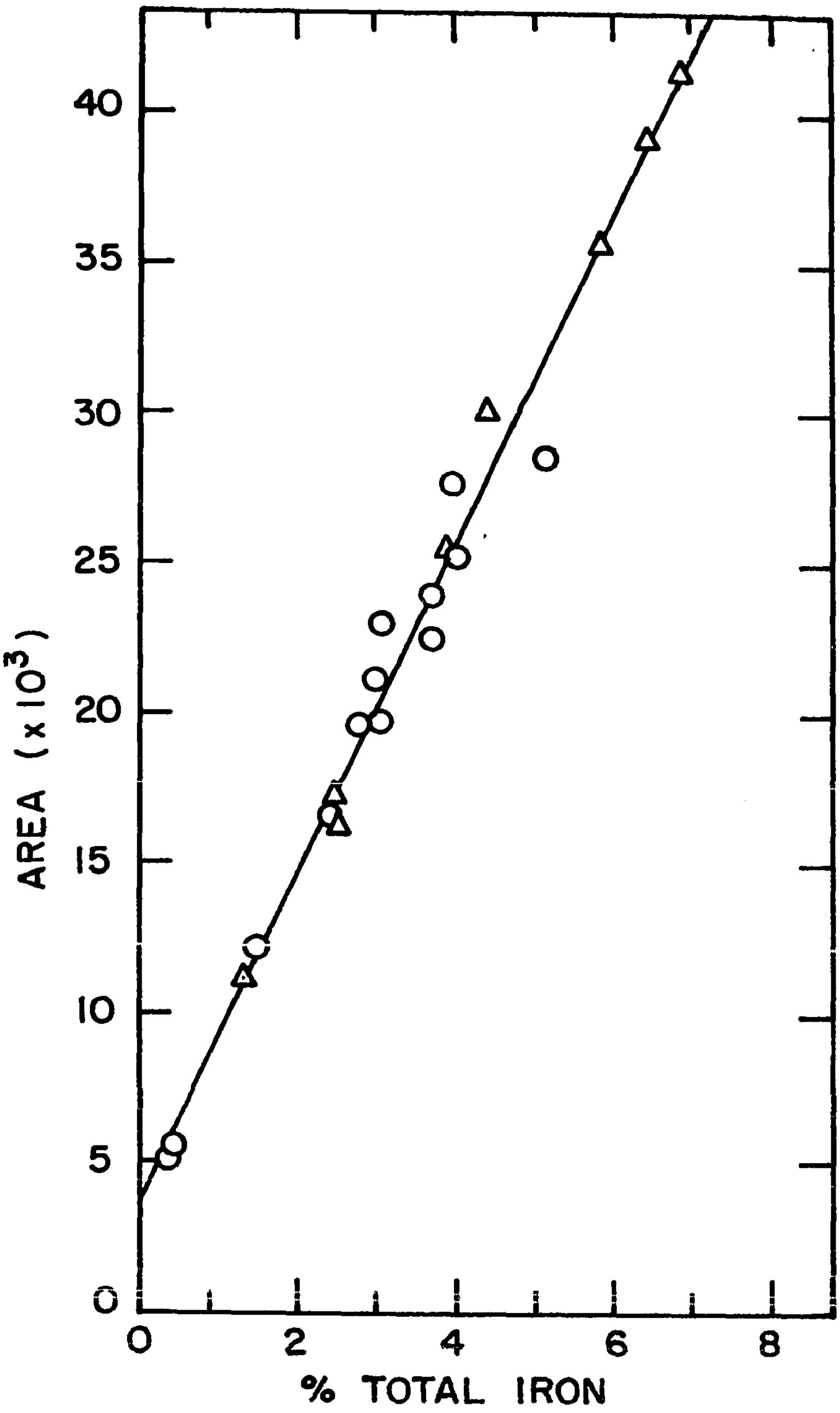
The prospect of iron analysis was investigated using both the 5.9 and 7.6 MeV iron full energy capture gamma-ray doublets. These two iron gamma-ray peaks had been determined to be free from any appreciable gamma-ray or background interference. Therefore, the respective peak areas were determined directly by assuming that the photopeaks were superimposed on a linear background. After taking the bulk density of the individual samples into consideration, these areas were used to plot calibration curves for both iron gamma-rays. Figures 12 and 13 show the calibration curves for the 5.9 and 7.6 MeV iron gamma-rays, respectively. These calibration curves are for the second irradiation facility; no quantitative information concerning iron analysis was collected with the first irradiation facility.

2. Data collection with a Ge(Li) detector

The collection of gamma-ray spectra and the treatment of data for the analysis of coal for iron, using a Ge(Li) detector, was nearly identical to the process described previously for iron determination with a NaI(Tl) detector. Two major differences, besides the use of a different detector and iron gamma-ray, existed between these two techniques. First, using the Ge(Li) detector required a longer data acquisition period because of low count rates. Second, a

Figure 12. Iron calibration curve for the second irradiation facility. Percent iron *versus* area of the iron full energy doublet at 5.9 MeV (NaI(Tl) data)

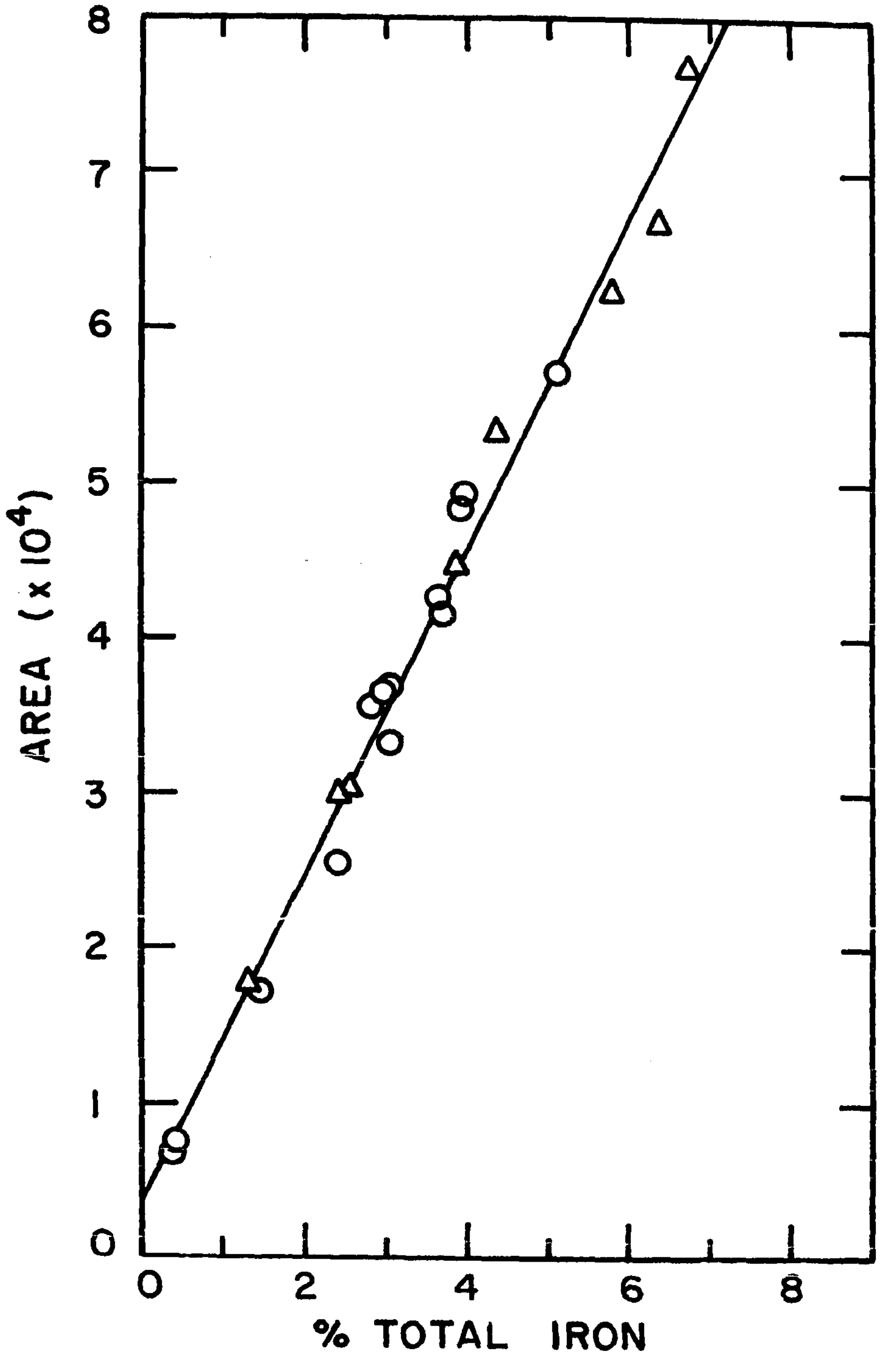
O, ROM coal samples; Δ, spiked coal samples



AREA ($\times 10^3$)
0
5
10
15
20
25
30
35
40
0
2
4
6
8
% TOTAL IRON

Figure 13. Iron calibration curve for the second irradiation facility. Percent iron *versus* area of the iron full energy doublet at 7.6 MeV (NaI(Tl) data)

O, ROM coal samples; Δ, spiked coal samples


AREA (x 10^4)
0
1
2
3
4
5
6
7
8
0
2
4
6
8
% TOTAL IRON

poorer gamma-ray background shield around the Ge(Li) detector made it necessary to subtract a substantial background contribution from the 6.6 MeV iron double escape peak. Corrected peak areas for the 6.6 MeV iron peak were used to construct the calibration curve for the second irradiation facility; this calibration curve is shown in Figure 14.

3. Demonstration of iron determination

Data for iron analysis was collected simultaneously with the data needed for démonstration of sulfur analysis. Analogous to the previously described sulfur analysis experiments, each iron analysis experiment involved the use of fifteen coal samples of known total percent iron concentrations as standards. Five other coal samples (SAM-1 - SAM-5), also of known iron content, were treated as unknown samples. Calculated iron concentrations for the five unknown samples were based upon the areas and calibration lines for the 5.9 and 7.6 MeV iron peaks collected with a NaI(Tl) detector and the 6.6 MeV iron peak collected with a Ge(Li) detector. The results from these experiments are summarized in Tables 5 and 6.

The NaI(Tl) results for both full energy iron capture gamma-rays show about the same precision and accuracy. The precision is about ±0.2 percent iron, and the accuracy is about 8-10 percent relative to the known iron concentration values.

Figure 14. Iron calibration curve for the second irradiation facility. Percent iron *versus* area of the iron double escape peak at 6.6 MeV (Ge(Li) data).

O, ROM coal samples; Δ, spiked coal samples

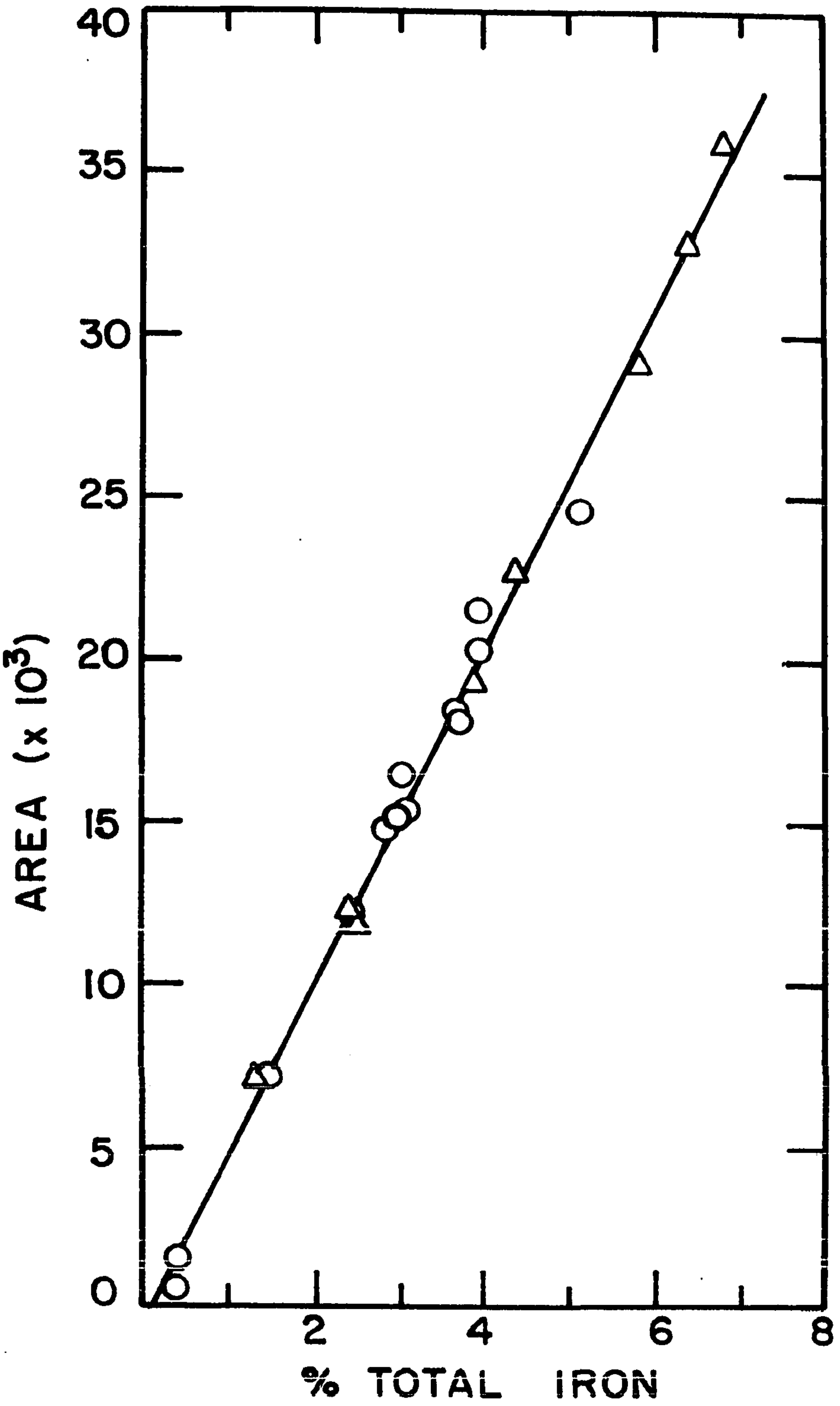

40
35
30
25
20
15
10
5
0
AREA (x 10^3)
2
4
6
8
% TOTAL IRON

Table 5. Iron determination results for the SAM-x coal samples, as determined by using the 5.9 MeV iron photopeak

Sample	%Fe[a]	NaI(Tl) Exp2	NaI(Tl) Exp3	NaI(Tl) Exp4	NaI(Tl) Average (Std.Dev.)	Ge(Li)[b]
SAM-1	3.96	4.30	4.33	4.15	4.26±.10	4.25
SAM-2	---	3.33	3.48	3.54	3.45±.11	3.97
SAM-3	5.15	4.67	4.49	4.67	4.61±.10	4.83
SAM-4	3.06	3.14	2.92	3.44	3.17±.26	3.29
SAM-5	2.88	2.95	2.90	2.80	2.88±.08	2.99

[a] Average of INAA and spectrophotometric results.

[b] Using 6.6 MeV iron double escape peak.

Table 6. Iron determination results for the SAM-x coal samples, as determined by using the 7.6 MeV iron photopeak

Sample	%Fe[a]	NaI(Tl) Exp2	NaI(Tl) Exp3	NaI(Tl) Exp4	NaI(Tl) Average (Std.Dev.)	Ge(Li)[b]
SAM-1	3.96	4.15	4.36	4.29	4.27±.11	4.25
SAM-2	---	3.89	3.91	4.17	3.99±.16	3.97
SAM-3	5.15	4.82	5.13	5.05	5.00±.16	4.83
SAM-4	3.06	3.14	3.19	3.20	3.18±.03	3.29
SAM-5	2.88	2.98	3.10	3.33	3.14±.18	2.99

[a] Average of INAA and spectrophotometric results.

[b] Using 6.6 MeV iron double escape peak.

The last column of Tables 5 and 6 are the same and show the results obtained for capture gamma-ray analysis of iron in coal using a small Ge(Li) detector. The agreement between NaI(Tl) and Ge(Li) detector results is slightly better for iron analysis than for sulfur analysis.

A comparison between the different experimental conditions (detector and gamma-ray used) can be made by examining the relative sensitivity of each set of conditions for iron. The sensitivity is obtained by dividing the slopes of the various calibration lines by the data collection times.

NaI(Tl), 5.9 MeV	5600 counts/%Fe/40 min = 140 CPM/%Fe
NaI(Tl), 7.6 MeV	10^4 counts/%Fe/40 min = 250 CPM/%Fe
Ge(Li)	5300 counts/%Fe/100 min = 53 CPM/%Fe

140/53 = 2.6   250/53 = 4.7   250/140 = 1.8

These calculations indicate that the 7.6 MeV iron photopeak-NaI(Tl) detector combination would be the more sensitive combination for capture gamma-ray analysis of iron.

C. Routine Sulfur and Iron Determination

The results presented in the previous two sections of this chapter indicate that capture gamma-ray spectrometry can be used for the determination of sulfur and iron in coal, with predictable precision and accuracy. To further demonstrate the application of this method, it was used for the analysis of two coal samples acquired through the Iowa Coal Project (ICP).

Part of the ICP involves the refining of coal at the Iowa State University (ISU) Coal Preparation Plant. Coal refining works on the principle of gravity separation, which allows pyritic materials as well as other noncombustible materials which become mixed with the coal during mining, to be separated from coal. Removal of pyritic sulfur from coal is particularly important for Iowa coals, since these coals contain a higher percentage of sulfur than is environmentally acceptable. The effectiveness of the ISU Coal Preparation Plant for removing sulfur from coal could be routinely monitored by using capture gamma-ray spectrometry for analysis of coal samples taken from the input and output streams of the plant (providing the Ames Lab Research Reactor was still in operation).

The two ICP coal samples analyzed by capture gamma-ray spectrometry were collected from the input and output streams of the ISU Coal Preparation Plant, and labeled "Plant Feed" and "Plant Clean", respectively. These samples were analyzed for total sulfur and total iron content using a NaI(Tl) detector for collection of gamma-ray spectra. The 5.42 and 7.60 MeV photopeaks were used for the analysis of sulfur and iron, respectively. Five additional coal samples of known sulfur and iron content were analyzed with these new samples to verify the irradiation facility calibration. The results of these analyses are listed below:

	% Sulfur	% Iron
Plant Feed	8.3	4.6
Plant Clean	6.4	2.4

These results indicate that the ISU Coal Preparation Plant removed 23 percent of the initial sulfur and 48 percent of the iron initially present in the feed coal. Assuming that the iron is present primarily as pyrite (FeS_2), the results for iron indicate that approximately half of the pyritic material originally in the feed coal was removed by the coal refining process used at the ISU Coal Preparation Plant.

The underlying purpose behind the analysis of the two ICP coal samples was not to provide a routine service but to gather information concerning the turn-around time for reliable analysis results. The turn-around time, starting from the time two bulk samples of coal are submitted to return of analysis results would require about 2 days, the greatest amount of time being required for sample preparation (crushing, mixing and compaction of the samples into the irradiation containers). The accumulation of a capture gamma-ray spectrum and reduction of the data require only about one and a half hours per sample, assuming a NaI(Tl) detector is used for data collection. Greater overall efficiency for routine analysis of coal samples could be realized if 4-5 samples were analyzed on a daily basis.

D. Silicon Determination

The prospect of determining silicon in coal was investigated by collecting capture gamma-ray spectra for eleven ROM coal samples, with known silicon content (expressed as SiO_2). These spectra were collected with NaI(Tl) and Ge(Li) detectors. Examination of these spectra failed to reveal any silicon capture gamma-ray peaks, particularly the most prominent 3.54 MeV silicon photopeak. Certainly, capture gamma-rays from silicon are produced during neutron irradiation of a coal sample, but the sample and experimental conditions were such that capture gamma-ray spectrometry lacked the necessary sensitivity for silicon analysis.

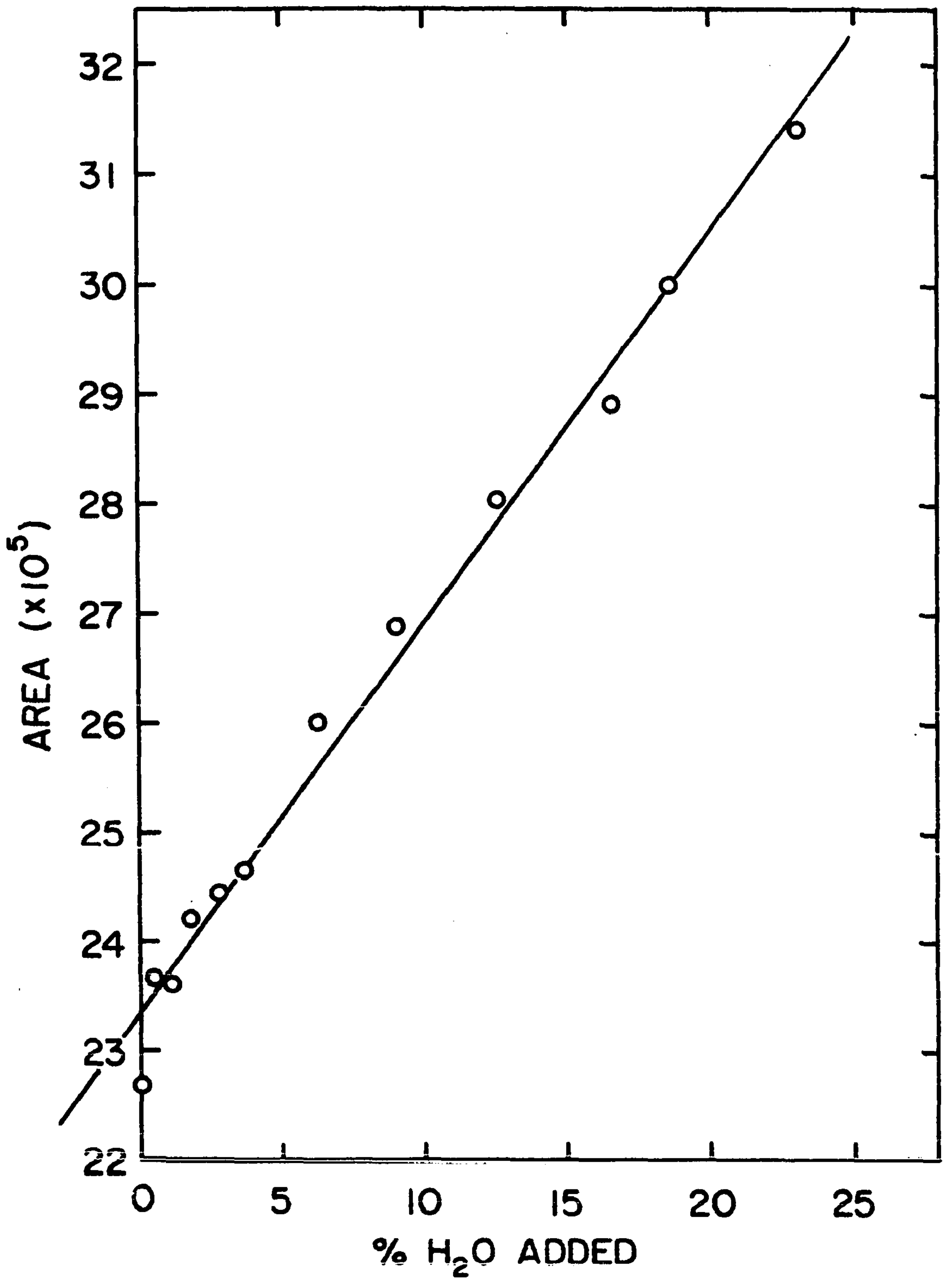
E. Moisture Determination

Moisture determination was studied by adding water to previously dried coal and measuring the area of the hydrogen peak at 2.23 MeV with a NaI(Tl) detector. This peak area is a measure of the total hydrogen content of the coal, moisture plus organically bound hydrogen.

The purpose of this work was to develop a technique which would be useful for analyzing bulk quantities of coal, and in particular for monitoring moisture in coal in a coal process stream. The size of coal particles following size gradation equipment in a process stream generally remains within a rather constant range, with the bulk density being dictated by free-fall packing of the coal as it moves through the process. In finely crushed coals, increases in the moisture content decrease the bulk density of the coal so that the bulk density of the sample becomes an important factor in measuring the relative moisture content of these coals. Conversely, the bulk density of large-size fractions of coal remain fairly constant with changing moisture content. Consequently, two size fractions of coal were used for these experiments to demonstrate the effect of coal particle size on moisture determination. The large-size coal fraction was between 0.1 and 0.5 inches, while the small-size fraction was made up of coal crushed to approximately 60 mesh (0.01 inch).

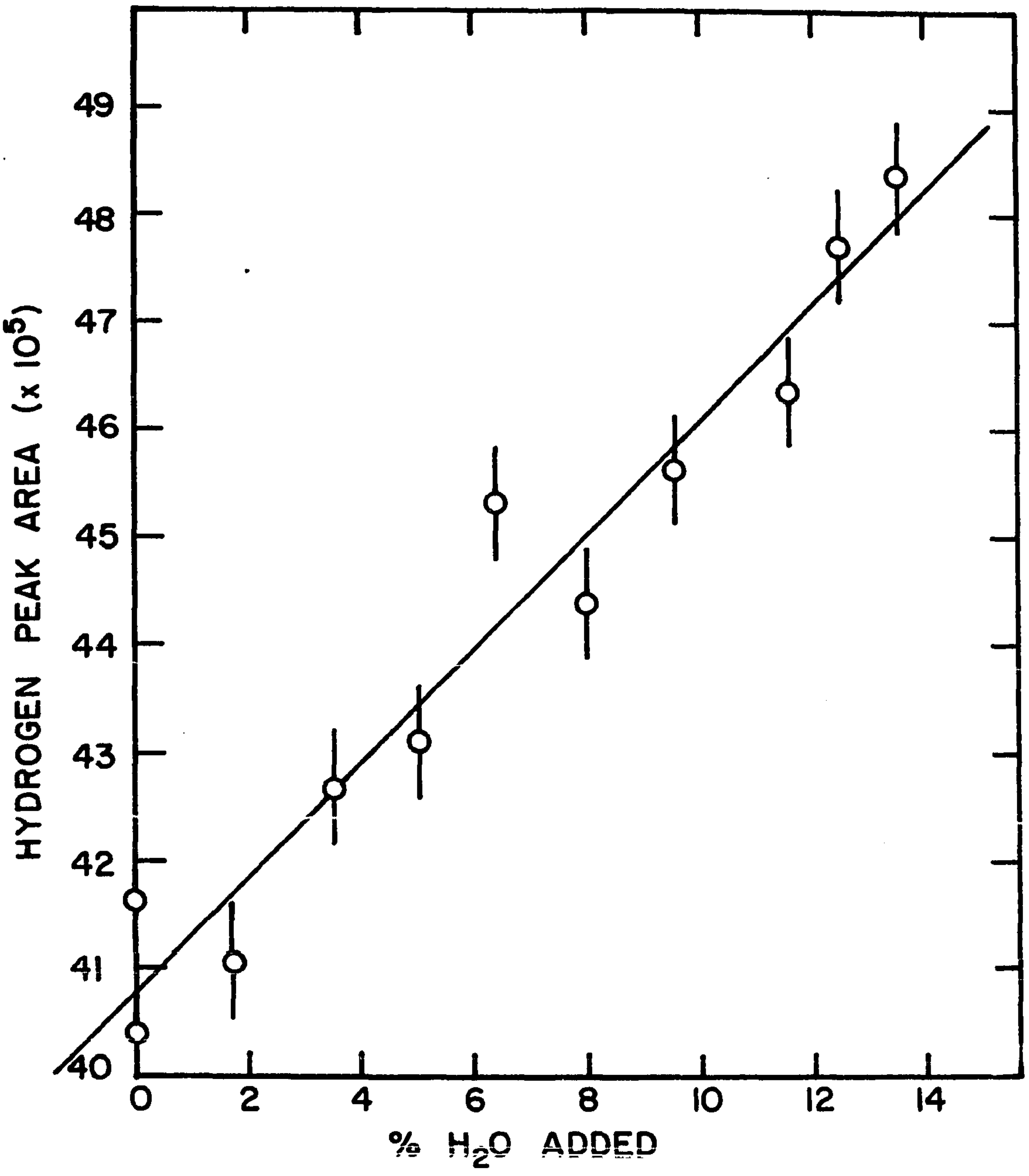
The linearity of the relation between the area of the peak at 2.23 MeV and moisture added to coal for the two different size fractions is shown in Figures 15 and 16. Figure 15 is for the large-size coal fraction and the plotted peak areas were not corrected for sample bulk density as this correction was not necessary. Figure 16 represents the

Figure 15. Area of the hydrogen capture gamma-ray peak at 2.23 MeV *versus* percentage of water added to 0.1-0.5 inch coal



AREA (x10^5)
32
31
30
29
28
27
26
25
24
23
22
0
5
10
15
20
25
% H2O ADDED

Figure 16. Area of the hydrogen capture gamma-ray peak at 2.23 MeV *versus* percentage of water added to 60 mesh coal


HYDROGEN PEAK AREA (x 10^5)
40
41
42
43
44
45
46
47
48
49
0
2
4
6
8
10
12
14
% H_2O ADDED

moisture addition data collected for 60 mesh coal. To obtain linear results for 60 mesh coal, it was necessary to take the changing bulk density of the sample into account. This was accomplished by dividing the measured peak area by the respective bulk density. The large vertical error bars of Figure 16 result from the uncertainty in the bulk density of the sample and not from counting statistics. The X-axes of Figures 15 and 16 are labeled as percent of water added to a previously dried coal sample. If the calibration lines of these figures are extrapolated back to zero peak area, the respective intercepts along the X-axes represent the amounts of hydrogen in the dried coal samples. These intercepts yield values of 7.2 and 8.5 percent bound hydrogen for Figures 15 and 16, respectively. These are reasonable values for bound hydrogen considering the extent of the extrapolation.

Since capture gamma-ray spectrometry is only capable of measuring the total hydrogen content of a sample, it becomes necessary to use both a "dried" and "as received" coal sample in order to obtain meaningful results for an actual moisture determination. In plant applications, a single measurement of a dried sample could suffice as the base for a number of routine determinations, but the dried coal sample must be taken from the same lot of coal for which routine determinations will be made. This necessity is due to the fact that the bound hydrogen in coal can cover a range roughly between 5 and 8 percent by weight, the actual percentage being dependent upon the type and quality of the coal. Since water is only 11 percent hydrogen by weight, this rough three percent range in bound hydrogen translates to a 27 percent range for moisture in coal, making the accurate determination of bound hydrogen critical.

Ironically, since it is necessary to dry a sample of the coal prior to determining its moisture content by capture gamma-ray spectrometry, it becomes quicker and easier to perform the moisture analysis on a lost weight basis. Clearly then, the best application for capture gamma-ray moisture analysis would be one of measuring the relative moisture content of coal in a process stream which consisted of large quantities of the same grade of coal. In this case, periodical weight loss experiments combined with capture gamma-ray spectrometry could establish the bound hydrogen content for the coal being processed.

VI. DISCUSSION

The results of this work show that the analysis of coal for total sulfur and iron is possible using thermal neutron capture gamma-rays. The simultaneous determination of these two elements in coal can be carried out on a routine basis provided that sufficiently large samples are available. Collection of gamma-ray spectra may involve the use of either NaI(Tl) or Ge(Li) detectors, each having specific advantages and disadvantages. A NaI(Tl) detector has poor energy resolving characteristics relative to a Ge(Li) detector, but is more sensitive to gamma-ray detection so that shorter data collection times may be adopted. The distribution of gamma-ray counts between full energy and escape peaks for a Ge(Li) detector favors the use of double escape peaks for analytical purposes, while full energy peaks are the first choice when a NaI(Tl) detector is employed. Therefore, the detector choice influences which photopeaks might be useful for element determinations since full energy and double escape peaks may be subject to different interference contributions (*e.g.*, sulfur determination in the presence of iron).

The determination of sulfur, free from iron interference, is possible if a Ge(Li) detector is used for collection of gamma-ray spectra and the area of the 4.40 MeV double escape peak of sulfur is used to represent the sulfur content of the sample. However, in the analysis for sulfur with a NaI(Tl) detector, it is necessary to correct the 5.42 MeV sulfur full energy peak for iron interference. This correction is obtained from the area of the iron full energy doublet at 5.9 MeV. A slight over-correction for this interference results in an intercept of approximately 0.5 percent total sulfur, rather than a zero percent intercept, for the sulfur calibration curves in Figures 9 and 10. This over-correction occurs because the correction factor (see page 79) is slightly large. The value of this experimentally determined correction factor remains large because it was optimized to yield the best results when applied to coal samples of known sulfur content. In the use of this correction factor, it is assumed that whatever produces a peak at 5.9 MeV will also contribute an area 1.27 times as large to the peak at 5.42 MeV. A potential problem could arise by applying this correction to coal samples of high and widely varying silicon content. Silicon has a single escape peak of moderate intensity at 5.87 MeV which would contribute to the full energy iron doublet at 5.9 MeV. However, the corresponding double escape peak for silicon at 5.36 MeV appears to be absent with a 4x4 inch NaI(Tl) detector (see Figure 5), thus violating the assumptions made in performing the iron correction.

Throughout the course of this work, it was recognized that certain photopeaks used in analyzing for both sulfur and iron were subject to potential silicon interferences. These interference contributions were considered negligible based upon the absence of any silicon photopeaks, particularly the 3.54 MeV peak, in capture gamma-ray Ge(Li) spectra of Iowa coals. Neglecting these silicon interferences may not be completely justified since other researchers have reported that weak silicon photopeaks can be found in Ge(Li) spectra of coals if a Ge(Li) detector with adequate resolution (7-10 KeV at 7 MeV) is employed (86,101,102). These same researchers have made use of the 4.93 MeV silicon peak for estimating the silicon content of high ash coals (5-25 percent SiO_2). Silicon was a minor constituent in the coal samples used in this work (1-4 percent SiO_2, see Table 3) and therefore may present a minor interference in the capture gamma-ray iron and sulfur analyses of these samples. Although no direct evidence of silicon interference appears in the results of this work, corrections for silicon interference may be necessary for coals with higher silicon content.

The intercepts of the iron calibration curves in Figures 12 and 13 indicate positive peak areas for zero percent iron. The indication of a peak area where none is expected is due to a small but constant iron gamma-ray background which was not subtracted from these results. This background results from neutron capture reactions occurring in the angle-iron frame of the second irradiation facility.

The routine determination of moisture in coal appears to be a difficult task, even though these results have demonstrated that a linear relation exists between the peak area of the hydrogen capture gamma-ray and the moisture content of coal. This apparent difficulty is due to the fact that the hydrogen capture gamma-ray peak area is a function not only of the moisture but also of the organically bound hydrogen in coal. Therefore, the accuracy of the determined moisture content relies heavily upon the ability to determine the bound hydrogen capture gamma-ray response of the coal. The best way to obtain this information is to irradiate a previously dried coal sample. Any practical application of capture gamma-ray spectrometry to moisture analysis of coal must involve large quantities of the same grade of coal so that periodic determinations of the bound hydrogen capture gamma-ray response can serve as the base for a number of routine moisture determinations. Even so, there is no guarantee that the bound hydrogen content within a large quantity of similar coal will remain constant. As little as a one-half percent increase in the bound hydrogen content results in a hydrogen capture gamma-ray peak area which would indicate a 4.5 percent increase in moisture based upon the bound hydrogen response measured prior to the one-half percent increase. With this limited information at hand, it would seem that monitoring the moisture content of coal could be better left to some technique other than capture gamma-ray spectrometry, although full scale plant application may prove otherwise.

The methods developed in this work for the simultaneous determination of sulfur and iron in coal could be improved through continued research. Future work should be directed toward applying these analytical methods to a wider variety of coals taken from different geographical regions. By applying these methods to a variety of coal ranks, the integrity of the iron interference correction could be checked and the potential for silicon to interfere with iron and sulfur determinations could be examined. Additional work might include improving the irradiation facility by replacing its metal framework with wood, concrete or plastic materials, thus reducing the gamma-ray background of the facility. One improvement which should be included is the development of a better sample irradiation vessel. The improved irradiation vessel should be designed to completely encase the sample and provide automatic sample compaction during sample preparation. The amount of compaction need only be great enough to hold the coal sample as a solid plug so that shifting or settling of the sample would not be possible. The automatic sample compaction could be accomplished with a snug fitting solid ram placed on top of the coal before screwing the top end-cap of the irradiation vessel into place. The ram would compress the coal as the top end-cap was tightened. After weighing the sealed irradiation vessel filled with coal, the bulk density of the sample to be irradiated could be easily and accurately calculated. Completely enclosing the sample in its irradiation container would permit easier development of automated sample changing equipment. Ultimately, the entire system could be interfaced with a minicomputer to control sample changing, collection of gamma-ray spectra and reduction of data.

Future work into the application of capture gamma-ray spectrometry for coal analyses should involve state-of-the-art instrumentation and detector systems. The results of this work have demonstrated adequate success using rather modest equipment. The major problems which had to be overcome generally dealt with spectral interferences due to photopeak overlap. The best way of eliminating these types of interferences would be to use a Ge(Li) detector with better energy resolving characteristics, such as those used by Ewan and Tavendale (111) or Rasmussen and Hukai (86). These researchers reported using Ge(Li) detectors with resolutions between 7-10 KeV FWHM at 7 MeV. The majority of the photopeak overlap interferences encountered during this work could have been eliminated if a Ge(Li) detector of similar resolution were available (see page 53).

VII. BIBLIOGRAPHY

1. J. W. Leonard and D. R. Mitchell, Eds., Coal Preparation, 3rd ed.,(American Institute of Mining, Metallurgical and Petroleum Engineers, 1968).

2. Gaseous Fuels; Coal and Coke; Atmospheric Analysis, 1974 Annual Book of ASTM Standards, Part 26 (American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa., 1974).

3. G. Friedlander, J. W. Kennedy and J. M. Miller, Nuclear and Radiochemistry, 2nd ed. (John Wiley and Sons, Inc., New York, 1964).

4. F. Adams and R. Dams, Applied Gamma-Ray Spectrometry, 2nd ed. (Pergamon Press, New York, 1970).

5. W. G. Lussie and J. L. Brownlee, Jr., in Proceedings of the 1965 International Conference on Modern Trends in Activation Analysis, College Station, Texas, 1965, p. 194.

6. T. L. Isenhour and G. H. Morrison, Anal. Chem. 38, 162 (1966).

7. S. M. Lombard, Ph.D. thesis, University of Washington, Seattle, Washington, 1969.

8. A. A. El-Kady, Ph.D. thesis, University of Maryland, College Park, Maryland, 1969.

9. D. Duffey, A. A. El-Kady and F. E. Senftle, Nucl. Instr. Meth. 80, 149 (1970).

10. F. E. Senftle, H. D. Moore, D. B. Leep, A. A. El-Kady and D. Duffey, Nucl. Instr. Meth. 93, 425 (1971).

11. V. J. Orphan, Line and Continuum Gamma-Ray Yields from Thermal Neutron Capture in 75 Elements, Report AD 717639, USNTIS, Springfield, Va., 1970.

12. R. Henkelmann, Z. Physik 258, 315 (1973).

13. J. D. Buchanan, in Proceedings of the 1961 International Conference on Modern Trends in Activation Analysis, College Station, Texas, 1961.

14. R. Henkelman and H. J. Born, J. Radioanal. Chem. *16*, 473 (1973).

15. R. C. Greenwood, in *Applications of Cf-252, Proc. Amer. Nucl. Soc. Meeting* Sept. 11-13, 1972, Austin, Texas, AEC Report CONF-720902.

16. H. E. Hootman, AEC Development Report 1232, 1970.

17. G. D. Atkinson, Jr., E. L. Draper, Jr., B. B. Tomlin and S. P. Nichols, in *Applications of Cf-252, Proc. Amer. Nucl. Soc. Meeting* Sept. 11-13, 1972, Austin, Texas, AEC Report CONF-720902.

18. L. W. Dahlke, in *Applications of Cf-252, Proc. Amer. Nucl. Soc. Meeting* Sept. 11-13, 1972, Austin, Texas, AEC Report CONF-720902.

19. A. G. Evans, F. E. Senftle, P. F. Wiggins and D. Duffey, Trans. Am. Nucl. Soc. *13*, 488 (1970).

20. F. E. Senftle, Nucl. Appl. and Tech. *10*, 204 (1971).

21. S. M. Lombard and T. L. Isenhour, Anal. Chem. *40*, 1990 (1968).

22. R. C. Greenwood, Trans. Am. Nucl. Soc. *10*, 28 (1967).

23. A. M. Demidov, L. I. Govor and V. A. Ivanov, Sov. At. Energy *28*, 145 (1970).

24. A. W. Hall and G. R. Friggens, U.S. Bureau of Mines Report of Investigations 7920, 1974.

25. D. R. Parsignault, H. H. Wilson, R. Mineski and S. L. Blatt, in *Neutron Sources and Applications, Proc. Amer. Nucl. Soc. Meeting* April 19-21, 1971, Augusta, Ga., AEC Report CONF-710402.

26. E. T. Jurney, D. B. Curtis and E. S. Gladney, Anal. Chem. *49*, 1741 (1977).

27. V. J. Orphan and N. C. Rasmussen, Nucl. Instr. Meth. *48*, 282 (1967).

28. T. L. Isenhour and G. H. Morrison, Anal. Chem. *38*, 167 (1966).

29. B. W. Garbrah and J. E. Whitley, Anal. Chem. *39*, 345 (1967).

30. B. W. Garbrah and J. E. Whitley, Intern. J. Applied Rad. Isotopes **19**, 605 (1968).

31. S. M. Lombard and T. L. Isenhour, Anal. Chem. **41**, 1113 (1969).

32. E. S. Gladney, E. T. Jurney and D. B. Curtis, Anal. Chem. **48**, 2139 (1976).

33. M. Heurtebise, H. Buenafama and J. A. Lubkowitz, Anal. Chem. **48**, 1969 (1976).

34. M. Heurtebise and J. A. Lubkowitz, Anal. Chem. **48**, 2143 (1976).

35. Y. Kusaka and H. Tsuji, J. Radioanal. Chem. **5**, 359 (1970).

36. P. F. Wiggins and K. Athow, Trans. Am. Nucl. Soc. **14**, 129 (1971).

37. D. Duffey, J. P. Balogna and P. F. Wiggins, Nucl. Tech. **27**, 488 (1975).

38. P. N. Tiwari, R. Bergman and B. Larsson, Intern. J. Applied Rad. Isotopes **22**, 587 (1971).

39. P. N. Tiwari, Radiochem. Radioanal. Lett. **6**, 363 (1971).

40. T. C. Roberts, Jr. and N. D. Eckhoff, Feedstuffs **45**, 30 (April 30, 1973).

41. D. Comar, Trans. Am. Nucl. Soc. **12**, 503 (1969).

42. D. Comar, C. Crouzel, M. Chasteland, R. Rivier and C. Kellershohn, in *Proceedings of the 1969 International Conference on Modern Trends in Activation Analysis*, Vol. I, Gaithersburg, Maryland, 1969.

43. J. Rundo and L. J. Bunce, Nature **210**, 1023 (1966).

44. D. Ishii, Y. Hirose and H. Mori, Japan Analyst **15**, 601 (1966) (in Japanese).

45. M. C. Taylor, Anal. Instrum. **12**, 165 (1974).

46. M. C. Taylor, J. R. Rhodes and D. L. Bernard, NBS Special Publication 425, 496 (1975).

47. R. C. Greenwood, J. H. Reed, R. D. Kolar and C. W. Terrell, Trans. Am. Nucl. Soc. **6**, 179 (1963).

48. J. H. Reed, J. W. Mandler and C. W. Terrell, Trans. Am. Nucl. Soc. 10, 27 (1967).

49. J. W. Mandler and J. H. Reed, Trans. Am. Nucl. Soc. 12, 471 (1969).

50. J. I. Trombka, F. Senftle and R. Schmadebeck, Nucl. Instr. Meth. 87, 37 (1970).

51. J. I. Trombka, E. L. Eller, J. T. Gerard, F. Senftle and P. Philbin, Trans. Am. Nucl. Soc. 14, 932 (1971).

52. J. I. Trombka, E. L. Eller, K. J. King and I. T. Fine, Trans. Am. Nucl. Soc. 13, 490 (1970).

53. G. Aripov, B. E. Krylov, E. M. Lobanov, N. S. Matveev, and M. M. Romanov, A. A. Khaidarov, Technical Report No. AEC-TR-6639, 1962.

54. U. Fanger and R. Pepelnik, in Second International Symposium on Neutron Chapter Gamma-Ray Spectroscopy and Related Topics Sept. 2-6, 1974, Petten, The Netherlands.

55. D. Duffey, P. F. Wiggins and F. E. Senftle, Trans. Soc. Mining Eng., AIME 254, 113 (1973).

56. R. L. Caldwell, W. F. Baldwin, J. D. Bargainer, J. E. Berry, G. N. Salaita and R. W. Sloan, Geophysics 28, 617 (1963).

57. H. J. Paap and H. D. Scott, in Neutron Sources and Applications. Proc. Amer. Nucl. Soc. Meeting April 19-21, 1971, Augusta, Ga., AEC Report CONF-710402.

58. S. S. Nargolwalla, Trans. Am. Nucl. Soc. 21, 107 (1975).

59. R. M. Moxham, F. E. Senftle and G. R. Boynton, Econ. Geo. 67, 579 (1972).

60. Y. Eden, J. Radioanal. Chem. 6, 165 (1970).

61. F. E. Senftle, D. Duffey and P. F. Wiggins, Marine Tech. Soc. Journ. 3, 9 (1969).

62. P. F. Wiggins, F. E. Senftle and D. Duffey, Trans. Am. Nucl. Soc. 13, 60 (1970).

63. P. F. Wiggins, Ph.D. thesis, University of Maryland, College Park, Maryland, 1970.

64. F. E. Senftle, P. F. Wiggins, D. Duffey and P. Philbin, Econ. Geo. 66, 583 (1971).

65. P. F. Wiggins, D. Duffey and F. E. Senftle, Trans. Am. Nucl. Soc. 13, 490 (1970).

66. O. Akalin, Ph.D. thesis, University of Utah, Salt Lake City, Utah, 1974.

67. G. M. Sandquist, O. Akalin, V. C. Rogers and T. A. Linn, Trans. Am. Nucl. Soc. 18, 65 (1974).

68. G. M. Sandquist, O. Akalin, V. C. Rogers and J. M. Byrne, Trans. Am. Nucl. Soc. 19, 77 (1974).

69. D. Duffey, J. P. Balogna, P. F. Wiggins and A. A. El-Kady, Anal. Chim. Acta 79, 149 (1975).

70. R. C. Greenwood, J. H. Reed and C. A. Stone, Trans. Am. Nucl. Soc. 4, 245 (1961).

71. R. C. Greenwood, J. H. Reed and C. A. Stone, Trans. Am. Nucl. Soc. 4, 127 (1961).

72. A. A. El-Kady and D. Duffey, Trans. Am. Nucl. Soc. 12, 42 (1969).

73. A. A. El-Kady, D. Duffey and P. F. Wiggins, Anal. Chim. Acta 54, 97 (1971).

74. P. F. Wiggins, D. Duffey and F. E. Senftle, Trans. Am. Nucl. Soc. 14, 518 (1971).

75. P. F. Wiggins, D. Duffey, F. E. Senftle and A. A. El-Kady, in *Applications of Cf-252, Proc. Amer. Nucl. Soc. Meeting* Sept. 11-13, 1972, Austin, Texas, AEC Report CONF-720902.

76. D. Duffey, P. F. Wiggins and F. E. Senftle, in *Neutron Sources and Applications, Proc. Amer. Nucl. Soc. Meeting* April 19-21, 1971, Augusta, Ga., AEC Report CONF-710402.

77. R. Zaghloul, M. Obeid, and R. Henkelmann, Radiochem. Radioanal. Lett. 17, 7 (1974).

78. R. J. Holmes, A. W. Wylie, and K. G. McCracken, U.S. Pat. 3,889,112, June 10, 1975.

79. H. Zwittlinger, J. Radioanal. Chem. 14, 147 (1973).

80. M. R. Najam, M. Anwar-Ul-Islam, A. F. M. Ishaq, J. A. Mirza, A. M. Khan and I. H. Qureshi, J. Radioanal. Chem. 27, 115 (1975).

81. M. Heurtebise and J. A. Lubkowitz, Trans. Am. Nucl. Soc. 21, 60 (1975).

82. T. C. Martin, S. C. Mathur and I. L. Morgan, in The Application of Nuclear Techniques in Coal Analysis Interim Technical Report No. 2, October 24, 1963, Texas Nuclear Corp., Austin, Texas, AEC Report CONF-313-2.

83. T. C. Martin, I. L. Morgan and J. D. Hall, in Proceedings of the 1965 International Conference on Modern Trends in Activation Analysis, College Station, Texas, 1965, p. 71.

84. C. V. Parker, Jr., T. C. Martin and I. L. Morgan, Trans. Am. Nucl. Soc. 9, 109 (1966).

85. J. R. Rhodes, P. F. Berry and R. D. Sieberg, AEC Report CRO-2980-18, 1968.

86. N. C. Rasmussen and Y. Hukai, Trans. Am. Nucl. Soc. 10, 29 (1967).

87. N. C. Rasmussen, Anal. Instrum. 7, 186 (1969).

88. N. C. Rasmussen, Trans. Am. Nucl. Soc. 14, 931 (1971).

89. Y. N. Pak and L. P. Starchik, Coke & Chem. 11, 12 (1974).

90. A. R. Pouraghabagher and A. E. Profio, Anal. Chem. 46, 1223 (1974).

91. A. Bond, Process Engineering, March 1975, p. 62.

92. R. F. Stewart, A. W. Hall and J. L. Konchesky, Coal Age 75, 85 (1970).

93. A. W. Hall, J. L. Konchesky and R. F. Stewart, U.S. Bureau of Mines Report of Investigations 7807, 1973.

94. R. F. Stewart, in Proceedings of the 17th National ISA Conference on Instrumentation for Iron and Steel Industry, March 15-16, 1967; Trans. ISA 6, 200 (1967).

95. R. F. Stewart, A. W. Hall, J. W. Martin, W. L. Farrior and A. M. Poston, U.S. Bureau of Mines Technical Progress Report 74, 1974.

96. G. F. Fasching and G. H. Patton, U.S. Pat. 3,868,509, Feb. 25, 1975.

97. A. B. Tanner, R. C. Bhargava, F. E. Senftle and J. M. Brinkerhoff, Nucl. Instr. Meth. 102, 61 (1972).

98. J. W. Martin and A. W. Hall, ERDA Report MERC/RI-76/4, Morgantown Energy Research Center, Morgantown, West Virginia, 1976.

99. A. W. Hall, J. W. Martin, R. F. Stewart and A. M. Poston, U.S. Bureau of Mines Report of Investigations 8038, 1975.

100. D. F. Summers, Coal Age 82, 82 (1977).

101. D. Duffey, N. O'Fallon, K. G. Porges and P. F. Wiggins, Trans. Am. Nucl. Soc. 24, 117 (1976).

102. D. Duffey, N. O'Fallon, K. G. Porges, R. J. Armani and P. F. Wiggins, Trans. Am. Nucl. Soc. 26, 161 (1977).

103. O. L. Herzenberg, N. M. O'Fallon, C. E. Cohn, K. G. Porges and D. Duffey, in Third International Conference on Nucl. Meth. in Env. En. Res., Univ. of Missouri, Columbia, Mo., 1977 (unpublished).

104. T. Gozani, E. Evans, V. Orphan, J. Reed and D. Shreve, Trans. Am. Nucl. Soc. 26, 160 (1977).

105. M. Sperling, SAI-72-574-LJ-Defense Nuclear Agency Report INA 2990F, Science Applications, Inc. (1972).

106. M. R. Ghavi and C. O. Cogburn, in Third International Conference on Nucl. Meth. in Env. En. Res., Univ. of Missouri, Columbia, Mo., 1977 (unpublished).

107. E. T. Jurney, H. T. Motz and S. H. Vegors, Jr., Nucl. Phys. A 94, 351 (1967).

108. S. M. Lombard, T. L. Isenhour, P. H. Heintz, G. L. Woodruff and W. E. Wilson, Intern. J. Applied Rad. Isotopes 19, 15 (1968).

109. R. G. Clark and W. A. Stensland, J. Radioanal. Chem. 4, 366 (1970).

110. P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences (McGraw Hill, Inc., New York, 1969).

111. G. T. Ewan and A. J. Tavendale, Nucl. Instr. Meth. 26, 183 (1964).

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IX. APPENDIX: SELECTED ASTM STANDARD METHODS

Standard methods for testing coal for sulfur, iron and moisture are described and are briefly discussed. A detailed account of each method can be found in the Annual Book of ASTM Standard Methods for the analysis of Gaseous Fuels, Coal and Coke, and the Atmosphere (2). These ASTM tests were used by the Ames Laboratory Analytical Services group and Warner Laboratories, Inc. for determining total sulfur, iron and moisture in the coal samples used in this work.

A. Total Sulfur

The preferred method for determining total sulfur in coal is called the Eschka method (D 3177). In the Eschka method, a sample of finely crushed coal (approximately one gram) mixed with magnesium oxide and sodium carbonate (Eschka mixture) is ignited in a muffle furnace. This is done by placing a crucible containing the sample into a cold muffle furnace and gradually raising the temperature to 800°C. This temperature is maintained for approximately one and a half hours. After the ignition is complete, the residue is digested with hot water, and nondissolved solids are removed by filtration. Sulfur in the filtrate is completely oxidized to sulfate which is precipitated as barium sulfate with an excess of barium chloride solution.

The barium sulfate is filtered out using ashless filter paper and the filter paper is smoked off gradually in a crucible held over a burner. Finally, the dry weight of the barium sulfate is used to calculate the sulfur content of the coal sample.

B. Iron

Determining iron in coal (D 2795) begins by ashing a 3-5 gram coal sample taken from coal crushed to 60 mesh. The sample is spread in a layer on a porcelain roasting dish, placed in a cold muffle furnace and heated gradually so that the temperature reaches 500°C in one hour (decomposition of pyrites) and 750°C in two hours (decomposition of carbonates). After cooling, the ash is crushed to 100 mesh in an agate mortar and reignited at 750°C for one hour. After cooling, a solution is prepared by dissolving a weighed portion of the ash with sulfuric, hydrofluoric and nitric acids. Iron is finally determined by a spectrophotometric procedure which involves treating the solution with solutions of hydroxylamine hydrochloride, orthophenanthroline and sodium citrate and measuring the absorbance at 510 nanometers. Comparison of the measured absorbance to the absorbance of a similarly treated standard iron solution allows the concentration of iron in the coal sample to be calculated.

C. Moisture

The determination of moisture in coal (D 3173) involves measuring the weight loss of the coal sample (approximately one gram) after it has been heated under rigidly controlled conditions. The coal sample in a porcelain boat is placed in a preheated oven which has a current of dry air passing through it. The sample is heated for one hour at 104 to 110°C. Finally, the hot sample is cooled in a desiccator and weighed when cold to determine the moisture loss.