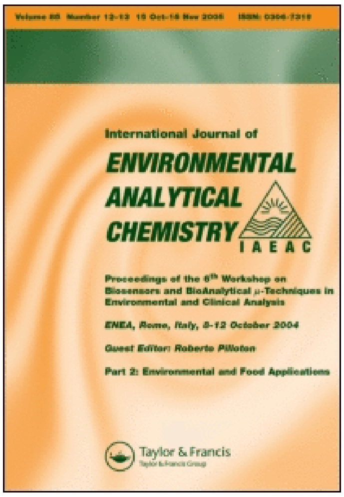

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Patrick J. Clark[a]; Ralph A. Zingaro[a]; Kurt J. Irgolic[a]; Ann N. McGinley[a]
[a] Department of Chemistry, Texas A&M University, College Station, Texas

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Arsenic and Selenium in Texas Lignite

PATRICK J. CLARK, RALPH A. ZINGARO,† KURT J. IRGOLIC and ANN N. McGINLEY
Department of Chemistry, Texas A&M University, College Station, Texas 77843

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Texas lignite samples were analyzed for arsenic and selenium utilizing hydride generation-dc helium emission spectrometry and gas chromatography-microwave plasma emission spectrometry. Arsenic and selenium were present in the samples at levels ranging from 1.0 to 5.5 ppm and 3.9 to 22.9 ppm, respectively. The arsenic concentrations vary slightly whereas the selenium levels fluctuate strongly as a function of depth in the lignite deposit. Analysis of specific gravity fractions of mined lignite indicated that arsenic and selenium are primarily associated with the lower density fractions and therefore probably in organic combination.

Knowledge of the chemical nature of the arsenic and selenium in coals is necessary in order to select the most appropriate chemical and physical treatment methods to control emission of these toxic elements to the atmosphere during direct combustion and to prevent catalyst deactivation during fuel conversion processes. Elements associated with the heavier mineral fractions can be partially removed by washing techniques. However, elements chemically bound to the organic fraction can be separated only during or after combustion, during chemical conversion processes, or possibly by chemical extraction processes. Limited success was achieved in arsenic and selenium removal from raw lignite utilizing non-aqueous solvent extraction with dimethyl sulfoxide.

INTRODUCTION

Lignite is a major energy resource in Texas with deposits estimated to be 10 billion tons within 200 feet of the earth's surface (available through conventional strip mining) and another 100 billion tons at depths of 200 to 5000 feet.[1] This abundance and accessibility make lignite an attractive source of electrical power. It has been estimated that annual lignite production will rise to 25 million tons by 1980, placing Texas among the

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†Author to whom all correspondence should be addressed.

top 10 coal-producing states of the nation.[1] As a result consideration must be given to the environmental impact resulting from the high consumption of this material.

It is firmly established that a number of potentially hazardous elements, including arsenic and selenium, are transferred to the atmosphere during combustion of coal. It has been estimated that 10% of the arsenic content[2] and 30% of the selenium content[3] of coal are released into the atmosphere either in the vapor form or deposited on fine particulate matter which may escape collection by the pollution abatement equipment utilized. In addition, elemental selenium present in the flue gases interferes with the Wellman–Lord process used to remove sulfur dioxide from flue gases.[4] In view of the increasing consumption of coal and lignite to meet the nation's energy requirements, the potential environmental hazard from these elements is significant since they are known to be toxic to plant and animal life.

Utilization of Texas lignite for production of synthesis gases, liquid fuels, and chemical feedstock raises concern about the possibility of trace elements causing catalyst poisoning in certain coal gasification and liquefaction processes. It has been reported that the presence of arsenic causes deactivation of the catalyst in the pressure hydrogenation of tar produced by low temperature carbonization of coal.[5,6]

Rapid and reliable analytical procedures for the determination of submicrogram amounts of arsenic and selenium in lignite and coal are described in this work. Application of these procedures to Texas lignite provided information on the amount, distribution, and mode of occurrence of arsenic and selenium in lignite. This information will aid in assessing the potential for the transfer of these elements into the products of lignite gasification and liquefaction. It will also be useful in assessing the feasibility of lignite pretreatment, such as froth flotation, in order to lower the concentrations of these volatile toxic elements to acceptable levels prior to direct combustion or conversion processes.

EXPERIMENTAL

Acid digestion procedure

Prior to analysis all lignite samples were wet ashed using the following nitric-perchloric acid digestion procedure. The sample (~0.5 g) was accurately weighed into a 125-ml Erlenmeyer flask. Concentrated nitric acid (20 ml) was added and the mixture heated on a hot plate (surface temperature 200°) with occasional swirling until the reaction had subsided and little or no reddish-brown nitrogen oxide vapor was being evolved

(1/2–2 hours). Concentrated perchloric acid (5 ml) was then added and the mixture heated at 250–270° until the appearance of dense white fumes. The mixture was then heated for another five minutes and allowed to cool before addition of 1 ml of concentrated hydrochloric acid and 10 ml of distilled water. The solution was purged with nitrogen for 10 minutes to remove chlorine and oxides of chlorine and then diluted volumetrically to 50 ml with distilled water. The final solution of the digested sample was filtered prior to analysis to remove undissolved silicate minerals.

Standards

Standard arsenate solutions were prepared from Merck & Co. Reagent Grade sodium arsenate. A stock solution of 1000 ppm was prepared in distilled water from which dilute standard solutions were prepared fresh daily. Standard selenium solutions were prepared in 0.1 N HCl utilizing selenous acid stock solution (1000 ppm) obtained from Alfa Products.

Arsenic determination

Instrumentation. The determination of total arsenic in lignite samples involved the conversion of arsenic to arsine, AsH_3, at pH 1 using sodium borohydride. The arsine generation system (Figure 1) was constructed using Pyrex glass, Teflon and stainless steel tubing (1/8 inch o.d.), stainless steel Swagelock connectors with Teflon front ferrules, glass O-ring joints (5 mm-i.d.), and stainless steel Whitey 3-way ball valves. The drying chamber and the reaction chamber were constructed from glass O-ring joints (25-mm i.d. and 30-mm i.d., respectively), the latter having a side arm constructed from a 15-mm i.d. O-ring joint through which the sample was introduced. Sodium borohydride solution was injected at the rate of 4 ml/minute into the reaction chamber through a 0.25-inch o.d. capillary tube using a syringe infusion pump.

Water vapor and carbon dioxide carried from the reaction chamber by the helium stripper gas along with the arsine during the reduction process were quantitatively removed by powdered sodium hydroxide and anhydrous magnesium perchlorate contained in the drying chamber. The arsine was collected in a liquid nitrogen cooled U-trap (15 inches in length, 0.25-inch o.d.) which had one leg packed with 100-mesh glass beads. The glass beads and any glass wool present in the arsine generation system should be silanized to prevent adsorption of arsine. Silanization of the glass was readily achieved by allowing a 5% solution of dimethyldichlorosilane in anhydrous diethyl ether to remain in contact with the glass surface for five minutes followed by a thorough rinsing with anhydrous methanol.

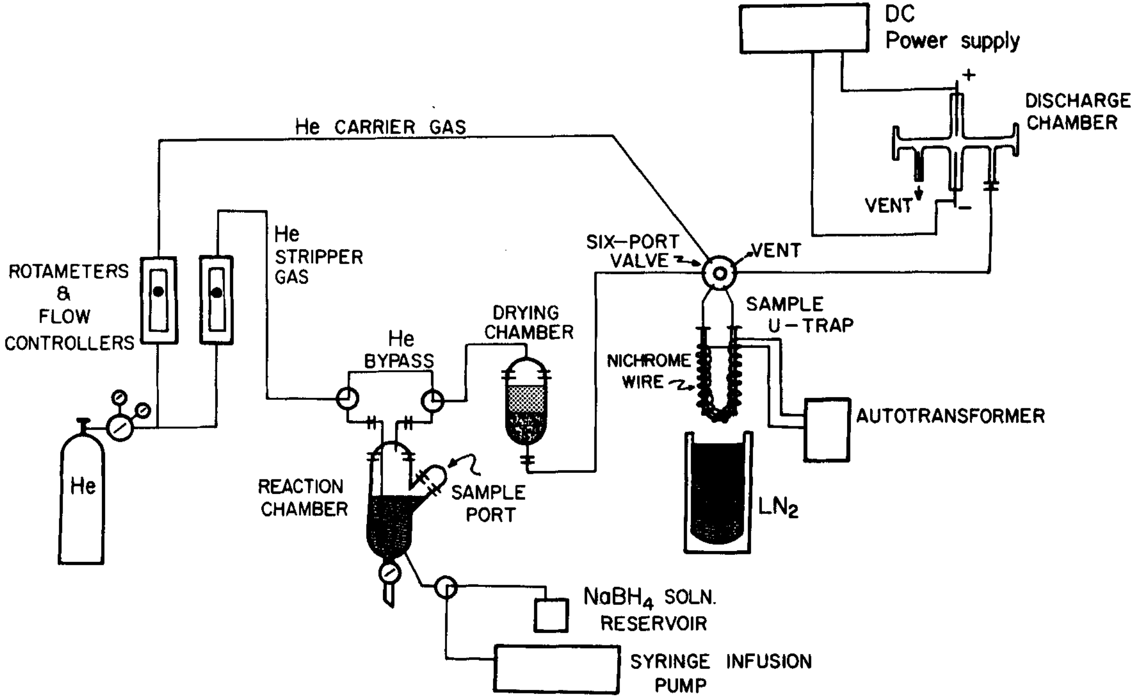


FIGURE 1 Arsine generation system.

A six-port valve located between the drying chamber and the sample trap allowed either the stripper gas from the reaction chamber (arsine collection) or carrier gas (arsine determination) to flow through the sample trap. This permitted selection of a helium carrier flow rate which was optimum for emission sensitivity rather than for stripping the arsine from the reaction solution. The six-port valve was coupled directly to the emission chamber.

Rapid volatilization of the arsine into the dc helium discharge was achieved by electrically heating the sample trap which was wound with B&S gage 24 Nichrome V resistance wire connected to an autotransformer.

The emission chamber, similar to that described by Feldman and Batistoni,[7] was constructed of 6-mm o.d. borosilicate glass tubing with vertical side arms 50 mm in length. Helium-arc welding electrodes (1/16-inch diameter), composed of tungsten-2% thorium oxide, were utilized as the electrodes. Each pointed electrode was held securely in position inside the vertical side arm of the chamber by means of a Nylon Swagelock reducing union whose internal orifice was enlarged sufficiently to accept the electrode.

The dc high voltage power supply for the helium discharge delivered an initial breakdown voltage of 1100 V dc. The operating voltage across the electrode gap was approximately 400 V dc with the current maintained at 40 mA (current regulation ± 0.1 %).

Radiation from the dc discharge passed through a fused quartz window of the chamber and was focused by means of a fused quartz plano-convex lens onto the entrance slit of a Jarrell-Ash Model 82-020 half-meter Ebert mounting scanning monochromator. Maximum sensitivity in the ultraviolet region was obtained by selection of a diffraction grating blazed at 1900 Å and by monitoring the 228.8 nm arsenic emission line with an EMI 9783B photomultiplier tube having a fused quartz window. The amplified signal was displayed on a strip chart recorder.

Procedure. After acid digestion, all arsenic in the sample was present in the pentavalent state which is reduced quantitatively by sodium borohydride at pH 1. A 10 ml volume of 10% oxalic acid and 0–10 ml of distilled water were introduced into the reaction chamber. The volume of water was varied to provide a total volume of 20 ml after sample addition. The sample, 5 μl to 10 ml volume, was then added and the chamber sealed. Helium stripper gas (flow rate 150 ml/min) was passed through the sample for four minutes to flush atmospheric gases from the sample, after which the sample trap was immersed in liquid nitrogen and the six-port valve turned to allow the stripper gas to flow through the sample trap.

Sodium borohydride solution (2% by weight in 0.2% NaOH) was injected into the reaction solution in four 2-ml aliquots at the rate of 4 ml/min for 30 seconds at 30 second intervals. The reaction solution was swept with helium for an additional two minutes. The helium flow was then routed around the reaction chamber and the sample trap was purged of residual reaction gases for an additional minute. During this time the reaction chamber was drained and rinsed in preparation for the next sample. The dc helium discharge was turned on and allowed to warm up for one minute. The six-port valve was then turned to allow the helium carrier gas (flow rate 300 ml/min) to flow through the sample trap. The liquid nitrogen was removed from the sample trap and sufficient voltage applied to the resistance wire to ensure rapid volatilization of the collected arsine which was swept into the discharge chamber by the helium carrier gas. After the arsenic emission peak was recorded, the discharge was extinguished while heating of the sample trap continued for an additional minute in order to remove any moisture which may have accumulated.

Selenium determination

Instrumentation. The determination of selenium involved the formation of 5-nitrobenzoselenadiazol by reaction of selenium(IV) with 4-nitro-*o*-phenylene-diamine at pH 1 utilizing the procedure described by Talmi and Andren.[8] The selenadiazol was extracted into toluene, an aliquot of which was injected into a Tracor Model 222 gas chromatograph utilizing a column packed with 4% SE-30 on 80/100 mesh Chromosorb G(HP). The injector temperature was 250°, the column temperature 230°, and the argon carrier gas flow rate 80 ml/min. The column effluent passed directly into a microwave plasma operated at atmospheric pressure. Microwave energy, 20 watts at 2450 MHz, was generated by a Kiva Instrument Corp. Model MPG-4 power supply and coupled to the effluent stream by means of an Evenson quarter-wave cavity (McCarroll version) supplied by the Opthos Instrument Corp. The effluent stream and resulting plasma were contained in a fused quartz tube (1/8 inch o.d., 3/32 inch i.d.). The 196.0 nm selenium emission line was monitored by the monochromator system described above.

Procedure. The 4-nitro-*o*-phenylenediamine (PD) solution was prepared by dissolving 0.5 g of the reagent in 1 N HCl and diluting to 50 ml with acid to form a 1% solution (by weight). This solution was extracted twice with 20 ml portions of toluene to remove any organic impurities. Although reported to be stable for one week, a fresh solution was prepared as required for each day's work.

A 25 ml aliquot of acid digested sample was introduced into a separatory funnel along with 1 ml of concentrated hydrochloric acid. After the addition of 2 ml of the PD solution, the mixture was allowed to stand for 40 minutes. The selenadiazol complex was then extracted with 1 ml of toluene by shaking for 5 minutes. The toluene layer was dried over anhydrous sodium sulfate and a 1 to 10 μl aliquot injected into the gas chromatograph. The microwave plasma was turned on only after the solvent peak had passed, complete resolution being obtained under the operating conditions described above. It was found that this procedure greatly reduced the formation of deposits on the walls of the quartz tube during plasma operation.

Determination of total arsenic and selenium in lignite cores

Numerous test borings were made by a commercial drilling company at a lignite deposit in Freestone County, Texas to ascertain the location, quality, and quantity of the deposit. Samples from two of these test cores, designated as Well 2 and Well 3 at the drilling sites, were made available to this laboratory for determination of arsenic and selenium distribution as a function of depth of the deposit.

This deposit forms part of the Wilcox group (lower Eocene). The beds vary in thickness from 5 to 12 feet at depths of 20 to 300 feet. The test borings (2-inch diameter drill cores) were sealed in plastic bags at the drill site to reduce air-oxidation and contamination. The samples (approximately 25 g each) had been removed at representative intervals and the depth below the surface in feet and inches of each sample was recorded. These were air-dried, ground to a fine powder using a mortar and pestle, oven-dried at 35° to constant weight, and a representative portion of each sample analyzed for total arsenic and selenium.

Determination of total arsenic and selenium in lignite fractions obtained by specific gravity separation

Determination of arsenic and selenium distribution in lignite fractionated according to specific gravity required a greater quantity of homogeneous material than was available from the test cores. Therefore, a bulk sample of mined Texas lignite, also from the Wilcox group, was utilized.

The bulk sample (12 Kg), crushed in a jaw crusher and sieved, yielded the following sieve fractions (as per cent of total sample): 7.4 % + 12-mesh, 5.2 % − 12/ + 14-mesh, 38.5 % − 14/ + 28-mesh, 44.8 % − 28/ + 100-mesh, 3.7 % − 100/ + 200-mesh, and 0.4 % − 200-mesh. The sieve fractions were analyzed for selenium and arsenic and the results were as follows: Se, As ppm (sieve size): 11.5±0.1, 4.9±0.5 (+12); 14.4±0.2, 4.5±0.1 (−12/+14); 12.0±20.1, 4.1±0.9 (−14/+28); 11.1±1.1, 3.0±0.1 (−28/+100); 10.8±0.1, 4.8±0.5 (−100/+200); 11.3±0.4, 6.1±0.5 (−200). These results indicate that there is no significant variation in concentration of these elements (varying particle size) among the sieve fractions. The −28/+100-mesh fraction was selected for further separation.

A representative portion of the −28/+100-mesh fraction was oven-dried at 35° to constant weight prior to fractionation. Separation according to specific gravity was achieved using solutions containing 1,1,2,2-tetrabromoethane (specific gravity 2.96 g/ml) and petroleum ether (boiling range 65–100°, specific gravity 0.70 g/ml). A 150 ml solution of the desired density was placed in a 250-ml separatory funnel and a 30 g sample of lignite was added. The standard "float-sink" or "washability" procedure[9] was followed. The heaviest fraction was separated first and the procedure repeated using successively lower density solutions until the desired degree of fractionation was achieved. Each fraction was washed with petroleum ether to remove traces of tetrabromoethane and oven-dried at 35° to constant weight before analysis.

RESULTS/DISCUSSION

Arsenic and selenium determinations

Selection of an analytical technique for the determination of total arsenic and selenium in Texas lignite was influenced by the desire for the future capability of determining the chemical form of the elements. Several methods of speciation have been reported,[3,10,11,12] all of which are based upon isolation of the species from the sample matrix followed by separation of the species from one another and quantitative measurement of the separated species. The analytical techniques utilized in this work combine the excellent separation capabilities of gas chromatography with the highly sensitive and element selective detection provided by both dc helium emission and microwave plasma emission spectrometry. The species to be determined is introduced into the emission detector where fragmentation and excitation of the species permits detection by observation of the atomic optical emission spectrum.

The quantitation of the emission peaks of arsenic and selenium was accomplished by preparing instrument calibration curves using separate standard solutions of known arsenic and selenium content. Due to the sharpness of the emission peak, the peak height was used for the arsenic determination. The selenium determination was made using peak area because the gas chromatograph peaks were typically broader. It was essential to analyze a reagent blank treated in the same manner as the samples to safeguard against possible contamination from the acids used in digestion.

It has been established that no arsenic or selenium is lost during digestion of the samples with the nitric-perchloric acid mixtures providing that heating is gradual and no charring of the sample occurs.[13] Standard solutions which were carried through the acid digestion procedure resulted in a calibration curve identical to that obtained directly from unaltered standard solutions. This was the case for both arsenic and selenium.

Complete dissolution of selenium from coal, slag, and fly ash samples utilizing nitric-perchloric acid digestion has been verified using neutron activation analysis[3] and using radioactive ^{75}Se tracer.[8] Total recovery of arsenic from coal and slag samples utilizing this acid digestion procedure has been verified using radioactive ^{74}As tracer.[14]

The absolute detection limit for arsenic by our method was 0.1 ng. Using a 10 ml aliquot of the acid digested sample, detection of 1 ppb arsenic in a 0.5 g sample of lignite was possible. The precision of four determinations performed on the same solution of an acid digested sample was ±5% (relative) over the 1–20 ng range used for analysis. The precision of four analyses performed on the $-28/+100$ mesh lignite was ±9% (relative). The precision of multiple analyses of all lignite samples ranged from ±3% to ±26% (relative) with an average of ±14%, which compares favorably with the ±10% relative standard deviation reported for arsenic in the NBS SRM 1632 (*Trace Elements in Coal*).

The absolute detection limit for selenium was 0.2 ng. Using a 10 μl aliquot of the toluene extract, detection of 80 ppb selenium in a 0.5 g sample of lignite was possible. The precision of four determinations performed on the same solution of an acid digested sample was ±5% (relative) over the 1–10 ng range used for analysis. The precision of four analyses performed on the $-28/+100$ mesh lignite was ±18% (relative). The precision of multiple analyses of all lignite samples ranged from ±0.4 to ±33% (relative) with an average of ±8%, which compares favorably with the ±10% relative standard deviation reported for selenium in the NBS SRM 632 (*Trace Elements in Coal*).

Reliability of measurements

The validity of the arsenic and selenium determinations utilizing the methods previously described was checked by having three lignite samples analyzed by outside laboratories. Analysis for arsenic was performed by Oak Ridge National Laboratory utilizing dc helium discharge spectrometry.[7] Selenium was determined using instrumental neutron activation analysis, performed by The Center for Trace Characterization, Texas A&M University. The results of these analyses are shown in Table I.

TABLE I
Comparison of arsenic and selenium concentrations using various analytical methods

	Arsenic concentration[a]		Selenium concentration[a]	
Sample	This work	ORNL	This work	Neutron activation
1	1.6 ± 0.4(3)[b]	1.3 ± 0.1(2)	11.2 ± 0.4(3)	11.5 ± 1.7(1)[c]
2	2.2 ± 0.4(3)	2.4 ± 0.2(2)	17.8 ± 1.3(3)	20.3 ± 3.0(1)
3	3.6 ± 0.4(3)	3.2 ± 0.5(2)	2.7 ± 0.9(3)	3.0 ± 0.5(1)

[a] All concentrations in μg/g.
[b] Number of analyses.
[c] Statistical error in analyses derived from standard deviation.

In a further effort to determine the degree of confidence with which analyses could be made, aliquots of the National Bureau of Standards SRM 1632 (*Trace Elements in Coal*) were analyzed for arsenic and selenium by the procedures described previously. The standard coal was dried in a desiccator over anhydrous magnesium perchlorate to a constant weight prior to acid digestion. Results from three determinations for arsenic and selenium were 5.0 ± 0.6 and 3.0 ± 0.3 ppm, respectively. National Bureau of Standards certified values are 5.9 ± 0.6 and 2.9 ± 0.3 ppm. Average results from an interlaboratory study[15] were 6.5 ± 1.4 and 3.4 ± 0.2 ppm for arsenic and selenium, respectively.

Analysis of lignite test cores

The concentrations of arsenic and selenium in the two lignite test cores, Well 2 and Well 3, are shown in Figure 2 as a function of the depth of the deposit from which each sample was obtained. The average arsenic concentrations in Well 2 and Well 3 are 1.9 and 2.0 ppm, respectively. There is very little variation of arsenic concentration with depth for either of the cores with the exceptions of the narrow region at 277 feet and the extreme top and bottom samples of Well 2. The average selenium concentrations in Well 2 and Well 3 are 8.5 and 9.2 ppm, respectively. In contrast with arsenic, the selenium concentration fluctuates widely with depth throughout both cores, ranging from 3.9 to 22.9 ppm.

The test cores were analyzed for moisture, ash, volatile matter, fixed carbon (by difference), and total sulfur by Core Laboratories, Incorporated (Tyler, Texas). Considerable fluctuation in the percent volatile matter and percent ash was observed in the test core samples, as shown in Figure 2. The volatile material is composed of the thermal decomposition products formed during heating of the sample at 950° for 7 minutes and includes the lower molecular weight organic compounds and the organic sulfur compounds.

The forms of sulfur present in the core samples were determined using the procedures described in ASTM D2492. The amount of sulfate sulfur was found to be negligible in the samples except at the extreme top and bottom of both deposits where it comprised 5 to 10% of the total sulfur. The pyritic sulfur concentrations, which fluctuated between 5 to 20% of the total sulfur present in the samples, and the organic sulfur concentrations, determined by difference, are shown in Figure 2 as a function of sample depth. The experimental error of the analytical procedure used to determine pyritic sulfur in coal is 0.05% (at sulfur levels $<2\%$). The variations in pyritic sulfur concentration with depth are within this experimental error for both test cores, with the exception of several points in Well 2. The variations in organic sulfur concentration with depth, identical to the relative variations of total sulfur with depth, do not indicate any observable trend.

Both arsenic and selenium are classified as chalcophile elements,[16] meaning that geochemically they are generally associated with sulfur-containing minerals. A portion of the mineral matter in lignite may be classified as inherent, that is, the inorganic elements are chemically combined with the organic matter of the coal, as is the case with organic sulfur. The mineral matter may also be extraneous, arising from inclusions of sand, shale, clay, or other materials present as distinct grains within the lignite or as partings between lignite layers.

No boring logs were obtainable for the test cores and therefore the identity of the soil and rocks associated with lignite deposits is unknown. Since information concerning exact location of the test cores was not available, the arsenic and selenium content of soils and rocks in that area could not be determined. The distribution of arsenic and selenium in the types of sedimentary rocks typically found in the region of the deposit has been reported as: shales—13 ppm As, 0.6 ppm Se; sandstones—1 ppm As, 0.05 ppm Se; carbonates—1 ppm As, 0.08 ppm Se.[17]

Based on the arsenic content of these sedimentary rocks, it is possible that a portion of the arsenic in lignite could be accounted for by the extraneous mineral content. Referring to Figure 2a, as the percent ash in Well 2 increases at the extreme top and bottom of the deposit, the arsenic content also increases, possibly as the result of an increase in the

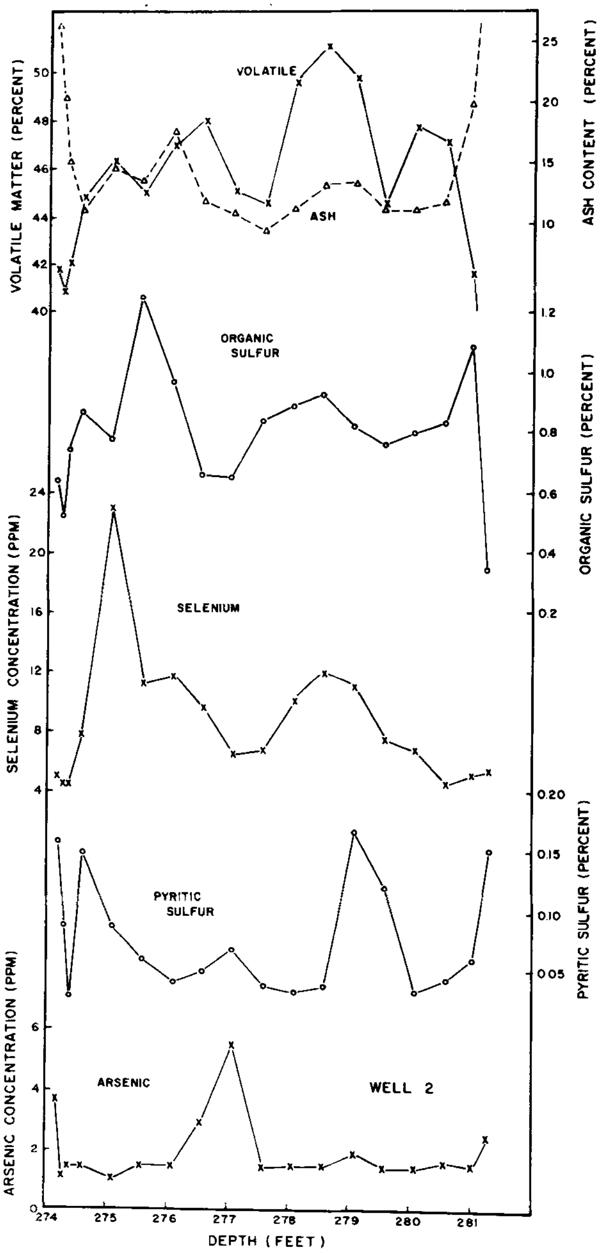

VOLATILE
ASH
VOLATILE MATTER (PERCENT)
50
48
46
44
42
40
ASH CONTENT (PERCENT)
25
20
15
10
ORGANIC SULFUR
ORGANIC SULFUR (PERCENT)
1.2
1.0
0.8
0.6
0.4
0.2
SELENIUM
SELENIUM CONCENTRATION (PPM)
24
20
16
12
8
4
PYRITIC SULFUR
PYRITIC SULFUR (PERCENT)
0.20
0.15
0.10
0.05
ARSENIC
WELL 2
ARSENIC CONCENTRATION (PPM)
6
4
2
0
274
275
276
277
278
279
280
281
DEPTH (FEET)

Fig. 2(a)

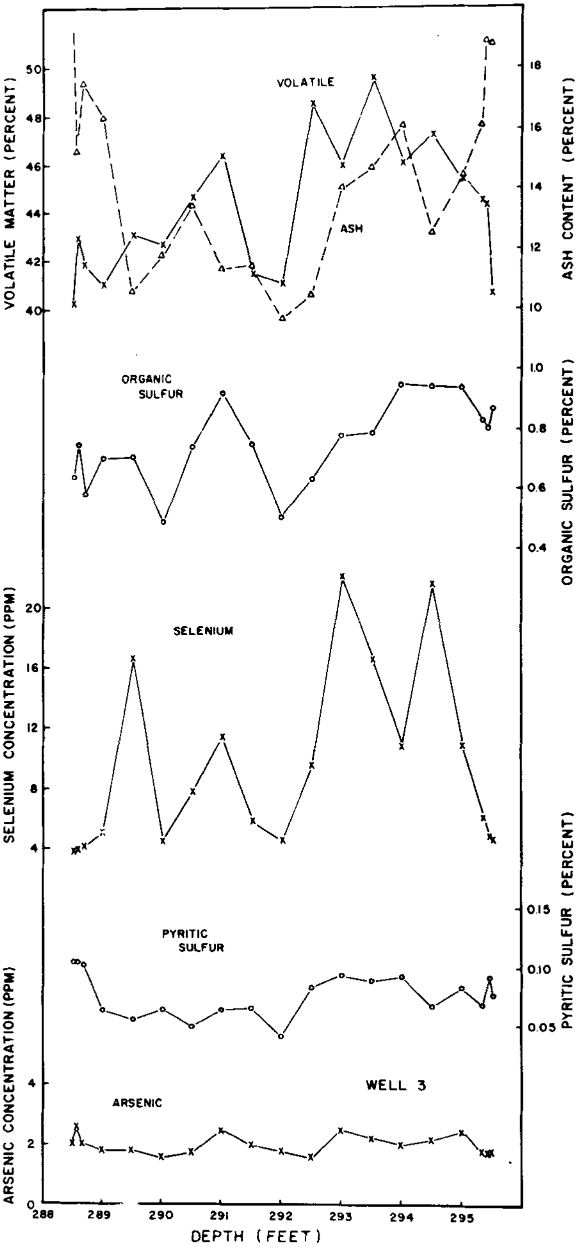


Fig. 2(b)

FIGURE 2 Distribution of arsenic, selenium, pyritic sulfur, organic sulfur, volatile matter, and ash in a lignite deposit as a function of sample depth below the surface for two test borings (a) Well 2 and (b) Well 3.

extraneous mineral matter associated with the lignite sample. However, there is no corresponding increase in arsenic content with increased ash content for Well 3. From this data it is not possible to state whether arsenic in lignite is associated predominantly with the organic matter or with the mineral matter.

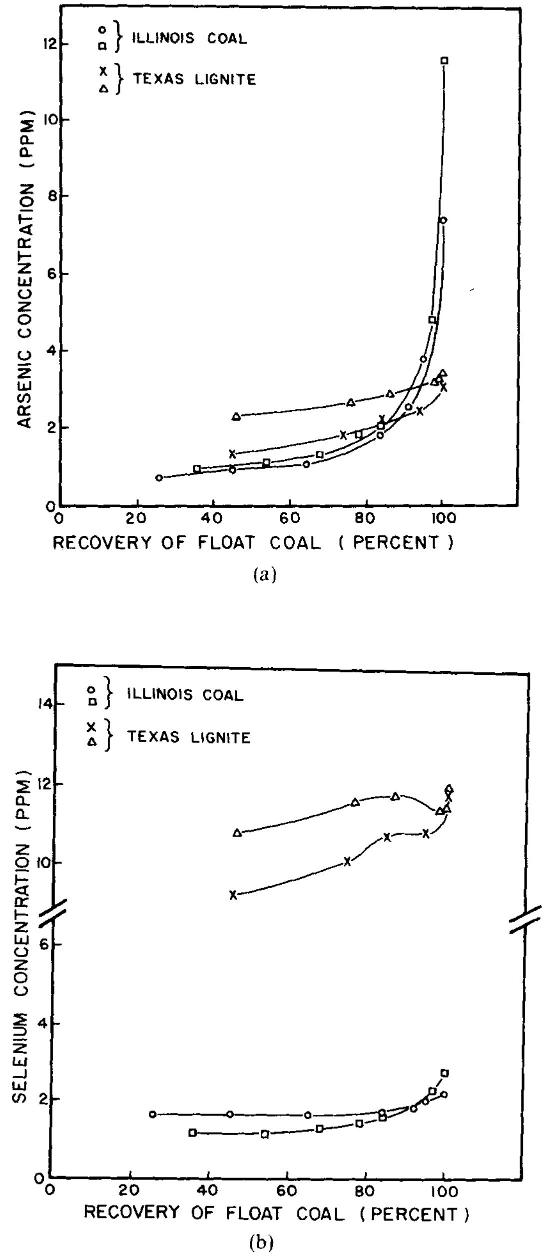
Since the selenium content of soils and rocks is generally quite low, it is unlikely that the selenium content in lignite can be attributed solely to the extraneous minerals. There appears to be some correlation between the variation in selenium concentrations with sample depth and the variations in percent volatile matter and percent ash for both Well 2 and Well 3 (Figure 2). In addition, there is a possible correlation between the variation in selenium concentration with sample depth and that of the organic sulfur concentrations for both test cores. However, it is not possible to state whether the selenium present in these lignite samples is predominantly organically or inorganically associated.

Specific gravity fractionation of bulk lignite

In order to determine whether arsenic and selenium are predominantly associated with the organic or inorganic components in Texas lignite, the distribution of these elements was investigated in various specific gravity fractions of lignite. The highest density fractions are composed primarily of mineral matter whereas the fractions of lowest density contain mainly organic material. The arsenic and selenium concentrations in the fractions obtained from $-28/+100$-mesh mined lignite are shown in Figure 3a and 3b, respectively, as "washability" curves.

The washability curve is a cumulative curve from which the concentration of an element in the float material can be ascertained for a particular percent of recovery of the coal. The total element concentration in the raw coal is that at 100 percent recovery and the concentration in the "cleanest" coal, i.e., most mineral free, is found at the low recovery end of the curve.[18] These data should be applicable irrespective of the medium in which the separation is conducted and assist in determining the effectiveness of upgrading or cleaning a coal by specific gravity or washing techniques, such as froth flotation. In addition to demonstrating which elements can be removed and to what extent, analysis of specific gravity fractions also indicates the mode of occurrence of an element in the coal, i.e., whether it is in organic or inorganic combination and if inorganic, with which group of minerals it is likely to be associated.

A negative slope of the washability curve would indicate that the element is more prominent in the lower density or organic fractions of the



(a)

(b)

FIGURE 3 Washability curves for Texas lignite and Illinois coal indicating the concentration of (a) arsenic and (b) selenium as a function of float coal recovery rate.

coal. A positive slope of the curve indicates that the element is concentrated in the heavier density or mineral fractions. This latter situation is pronounced for arsenic in several Illinois coals[18] (Figure 3a). The fraction having a density $>2.90\,\text{g/cm}^3$ comprises only 3–4% by weight of the raw coal, but contains 50–60% of the total arsenic present in the coal.[18] This degree of concentration in the heavy mineral portion is not evident in the case of Texas lignite. The fraction with a density $>2.59\,\text{g/cm}^3$ comprises 2% by weight of the raw lignite, but contains only 7% of the total arsenic present. The high percentage of the total arsenic content in the low and medium density fractions of lignite is illustrated in Figure 4.

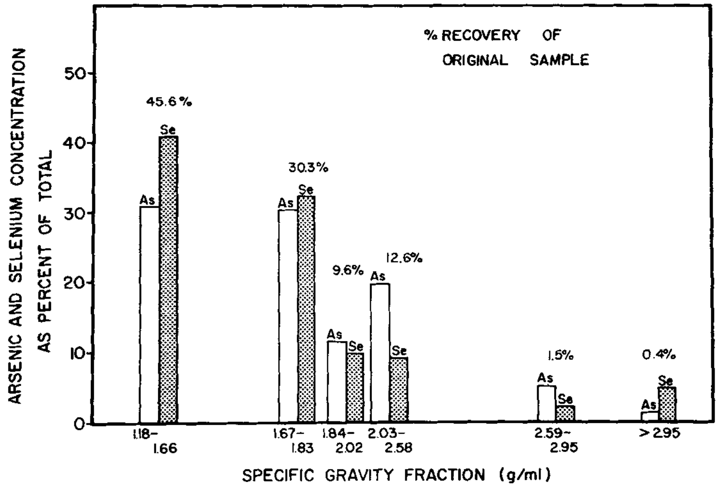


FIGURE 4 Distribution of arsenic and selenium in specific gravity fractions of Texas lignite as a function of fraction density.

The washability curves for selenium in Illinois coal (Figure 3b) resemble those for arsenic in Texas lignite. Although these curves have a positive slope, selenium is not as concentrated in the higher density fractions as was the case for arsenic. The fraction with a density $>2.90\,\text{g/cm}^3$ contains only 15–20% of the total selenium present in the coal.[18] For Texas lignite, the fraction with a density $>2.59\,\text{g/cm}^3$ contains only 7% of the total selenium present. The lowest density fractions ($<1.83\,\text{g/cm}^3$) contain 74% of the total selenium, slightly higher than in the case of arsenic (Figure 4).

Arsenic and selenium are found in the form of arsenides, selenides, and sulfides of such heavy metals as iron, copper, nickel, and cobalt. Arsenopyrite (FeAsS) is the most abundant and widespread mineral of arsenic. One of the more frequently encountered selenium minerals is ferroselite ($FeSe_2$). In addition, selenium may isomorphously replace sulfur in a number of minerals and is often found in association with both arsenopyrite and pyrite.[16] Selenium levels range from 1 to 140 ppm in arsenopyrite and as high as 3% in pyrite.[19] Although it appears that the majority of the arsenic and selenium in Texas lignite is organically combined, as much as 10% of these elements may be associated with minerals, e.g., clays, shales, and pyrites.

The organic matter of coal is quite complex, but it is known that lignite has a much higher percentage of aliphatic compounds and a higher oxygen content than the coals of higher rank. A large portion of the total oxygen in lignite is present in organic functional groups, probably associated with aliphatic side chains. These functional groups, widely thought to be constituents of the humic acids, include carboxyl (COOH), methoxy (OCH_3), phenolic and alcoholic hydroxyl (OH), and carbonyl (C=O). Lignites generally contain (by weight) 10% hydroxyl, 6–9% carboxyl, 3–6% methoxy, and 4% carbonyl groups.[20] These groups are known to form stable complexes and of these groups, the hydroxyl is most likely to complex with arsenic. The high organic association of arsenic in Texas lignite could be due to complexes of this nature.

All the nitrogen and the non-inorganic sulfur in coal are generally considered to be part of heterocyclic organic compounds, such as pyrrole, indole, pyridine, and similar sulfur derivatives.[20] These compounds may also be constituents of the humic acids. The organic sulfur content of coal is generally believed to be derived from the original sulfur-containing compounds in the coal-forming plants.[21] Since a number of plants are known to be highly efficient in concentrating selenium,[22] it is possible that the organic selenium in Texas lignite originated from the coal-forming plants as well. It is known that selenium forms stable heterocyclic compounds which are analogs of the previously mentioned heterocyclic compounds. Additional studies which deal with the identification of these organic sulfur, selenium and arsenic compounds in Texas lignite are planned in this laboratory.

Solvent extraction of lignite utilizing dimethyl sulfoxide and liquid sulfur dioxide

Upgrading or cleaning the type of Texas lignite encountered in this work by removal of the heavy mineral fraction using specific gravity techniques would not significantly reduce trace element levels. If the arsenic and selenium are chemically bound to the organic fraction, i.e., present as inherent mineral matter or organometallic compounds, removal is possible only during or after combustion, during chemical conversion processes, or possibly, by chemical extraction. Several non-aqueous solvents were investigated as potential extractants for arsenic and selenium from the −28/+100-mesh mined lignite.

Extraction of the lignite with dimethyl sulfoxide (DMSO) was carried out by refluxing the sample with solvent for six hours. Only 15.9% of the lignite was extracted into the DMSO, but this fraction contained 45% of the total arsenic and 35% of the selenium initially present in the raw lignite (Table II). DMSO is capable of dissolving a wide variety of both organic and inorganic compounds.

TABLE II

Concentrations[a] of arsenic and selenium obtained by solvent extraction of lignite

Materials analyzed		DMSO extraction of lignite[b]
Raw Material	As	4.4 ± 0.4(4)[c]
	Se	12.4 ± 2.2(4)
Soluble Fraction	As	15.3 ± 4.0(2)
	Se	29.1 ± 4.6(2)
	As	3.5 ± 0.9(2)
Insoluble Fraction	Se	10.6 ± 0.7(2)

[a] All concentrations in μg/g.

[b] The soluble and insoluble fractions of the lignite sample comprise 15.9 and 84.1%, respectively.

[c] Number of analyses.

Extraction of the lignite with liquid sulfur dioxide at −11° succeeded in dissolving only 1% of the sample. The insoluble fraction was analyzed for arsenic and selenium and contained 6.1 ± 0.5 ppm and 9.6 ± 0.5 ppm, respectively, compared to 4.4 ± 0.4 ppm and 12.4 ± 2.2 ppm, respectively, in the original sample. The mass balance for this extraction indicates that liquid sulfur dioxide had very little effect on the arsenic and selenium levels of the lignite.

Contamination studies

In order to determine whether arsenic and selenium contamination of the lignite test cores could occur from drilling fluids, a sample representative of commonly used drilling fluids was analyzed for arsenic and selenium. The material, National Premium Bentonite (200 mesh) supplied under the name Aquagel, was obtained from Baroid Petroleum Services Division, NL Industries Incorporated. The arsenic content was 5.1 ± 0.3 ppm and the selenium content 0.07 ± 0.01 ppm. The problem of potential arsenic contamination of test cores from the drilling fluid does exist but could be minimized by rinsing the freshly drilled cores with a minimum amount of water either before sealing in plastic for shipment or before sampling the cores.

The dimethyl sulfoxide used for the non-aqueous solvent extraction and the organic solvents used for the specific gravity fractionations were analyzed for arsenic and selenium. These elements were not present in detectable levels using our techniques.

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