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Author
Newton, A.S.

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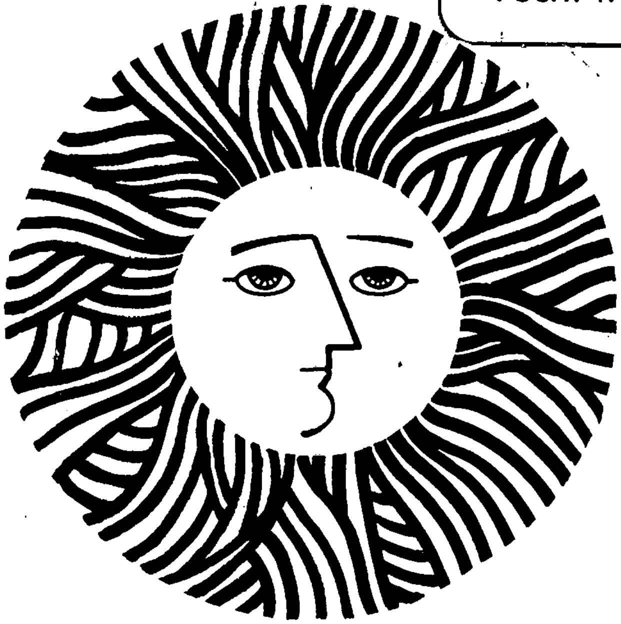

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Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Organic Compounds in Coal Slurry Pipeline Waters

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Abstract

Organic compounds in the water separated from coal pipeline slurry has been investigated on a laboratory basis for the slurry with each of three subbituminous coals: Wyodak, Illinois No. 6 and Black Mesa. The results are compared with results from the Black Mesa Pipeline slurry. Compounds such as aryl hydrocarbons, nitrogenous bases, aryl thiophenes and aryl ethers are all more than 99.9% adsorbed when added to water before slurry formation and are undetectable in the resulting slurry waters. Phenols occur in slurry waters and their identification and quantification using methylation with perdeutero phenol as an internal standard for capillary column GC/MS of the methyl ethers is described. Phenol, O-cresol, P-cresol, 2,6-dimethyl phenol, O-ethyl phenol and 3,5-dimethyl phenol were identified and quantified in all slurry waters from each coal. laboratory results on slurry waters from Black Mesa coal are in agreement with the results for these phenols in the clari-flocculator overflow water at the Mohave Generating Station.

Introduction

The transportation of coal by slurry pipeline is an established methodology. The Black Mesa Pipeline from Kayenta, Arizona to the Mohave Generating Station on the Colorado River near Laughlin, Nevada has operated since 1970. Some 5 million tons of coal per year have been transported as a 50-50 coal-water slurry from the mine in Arizona to the power station, a distance of 273 miles. This is the only coal slurry pipeline operating in the U.S. at the present time. An earlier line from Cody, Ohio to Eastlake, Ohio operated for some six years before being closed by economic considerations. The success of the Black Mesa pipeline and the economies of pipeline transportation vs. surface overland transportation ensure that further pipelines will be constructed as soon as water and property easement rights have been obtained for each particular planned project (Wasp, 1980; Gillaspie, 1980; Arlidge, 1980; Anon, 1980). Some of the proposed pipelines are shown in Figure 1. It is estimated that 5 to 9% of all coal will be transported by pipeline by 1990. Operating and proposed coal slurry pipelines are shown in Figure 1.

Pipeline transport is a clean method of moving coal (Dina, 1976; Montfort, 1980). The Black Mesa pipeline is completely buried except at pumping stations for its whole 273 mile length, though this is done to prevent freezing rather than for esthetic considerations. Coal is carried from the Peabody mine to the slurry preparation plant by conveyer belt. Once this coal is dumped into the supply hoppers for the plant, it is not directly exposed to the atmosphere again until it is prepared for the furnaces at the Mohave generating station. The initial dry grinding to pea size coal is performed in a closed system and all dust is collected and recycled. The coal is fed into one of three large (4 meters diameter by 5.5 meters long) rod mills by a continuous belt and an equal weight of water added. The rods in the mill are 10 cm diameter x 5.5 meters long cold rolled steel. Slurry is removed continuously. The average particle of coal is in the rod mill for about 10 minutes. The slurry is pumped from the rod mills to stirred storage tanks and from there into the pipeline for the 3-day trip to the Mohave generating station.

At the generating station the slurry is temporarily stored in tanks. For use, the bulk water is separated in continuous centrifuges, leading to a moist cake and a centrate containing 3 to 5% coal solids. The moist cake is further dried on a conveyer belt using waste heat from the boilers. The dry cake is repowdered and blown into the boiler furnaces as fuel. The centrate is separated in a clariflocculator into an almost clear overflow and a dense muddy underflow. Some proprietary additives are used to affect this separation. The underflow is sometimes burned but its direct use greatly reduces the power output of the plant. It is usually pumped to lined evaporation ponds and when dry it is scraped up, ground and burned as fuel in the boilers. Some troubles have occurred in the evaporation of such underflow ponds to a dry cake even in the desert location of the Mohave Generating station. The ponds form an impenetrable crust and the underlayers remain very muddy. The underflow problem has not been solved.

The overflow water containing 5 to 100 ppm of very fine coal is used at Mohave as make-up water in the cooling towers. All water is used and none is released to the aquatic environment. Ground water from wells between the plant and the Colorado River is monitored and no contamination has been observed.

The situation at the Mohave Generating Station is fairly unique in that it is located in a desert environment and all water can be utilized in house. A power plant located in an area with more available water might find it economic to discharge this water and use local water for the purpose or, alternately, the coal may be separated at dockside for shipment to other areas where it is to be burned for power. In these latter cases, the separated slurry water may be disposed into the local aquatic environment. Certainly the environmental consequences of such disposal should be known or predictable from the amounts of various impurities in the separated slurry water.

Water quality of slurry water has been the subject of several investigations (Anderson et al., 1978; Sanguanruang, 1977; Moore, 1979; Moore, 1980; Moore 1981). These have been mainly concerned with the usual inorganic water quality parameters and the effect on water quality with western (Wyoming) coals is not dramatic (Moore 1979), but with eastern coals, water quality deterioration in slurry transportation in regard to total solids, sulfates, chlorides and sodium are much more pronounced. With all coals the occurrence of organic compounds in slurry water is stated to be undetectable by extraction and gas chromatographic analysis (Moore, 1981). The COD (chemical oxygen demand) and BOD (biochemical oxygen demand) measured for slurry waters from various coals were found to be highly dependent on the source of coal and the contact time during coal-water milling and transport.

Other studies have been made on coal water interactions with respect to organic matter in the water. Shannon and Silveston, 1968, have studied the use of coal for adsorption of a synthetic sewage and found many types of organic material to be adsorbed by the coal. Highly polar materials such as sugars and phosphates were not adsorbed. Godwin and Manahan, 1979, studied the interchange of metals and organic matter between water and subbituminous coal and lignite and report titratable weak acids to be leached into the water. Humic acids are said to make up the major part of the COD of a coal slurry water. Humic acids are also suggested as agents which might complex and solubilize metallic elements from the coal. Dalton and Campbell, 1978, and Zubkova et al, 1974, found that phenols are adsorbed by coal. At a phenol concentration of 600 ppm they found a distribution coefficient between coal and water, K_o, equal to 40. Harlan, Green and Manahan, 1974, have studied coal humates and found that humic acids of unknown structure are solubilized from coal by partial surface oxidation on exposure to air at room temperature.

Several studies have shown coal to be an adsorbent for various organic compounds in water, El'bert and Bugrov, 1977, studied the adsorption on coal of organic compounds in various effluent streams. Koganovskii and Levchenko, 1978, used activated anthracite coal as a final purification of waste water. Humenick and Mattox, 1978, Mattox and Humenick, 1980, and Humenick, Britton and Mattox, 1982, studied the organic compounds in water from underground coal gasification and their adsorption by residual coal beds.

None of these studies apply directly to organics in coal slurry pipeline water under operating conditions. For coal slurry formation, the coal is ground to pea size in air, but the formation of the slurry in the rod mill is made under reducing conditions. The production of hydrogen by reaction of water with the fresh iron surface of the rods rapidly depletes all oxygen in the system and produces a reducing system. The fresh iron surfaces are formed by abrasion and have no overvoltage, hence reaction with water to form H_2 is favored with a reaction potential of about -0.03 V. The reducing character of the system will be maintained throughout the pipeline by abrasion of the pipe and reaction with water.

Coal Slurry Preparation:

A laboratory rod mill was designed and constructed which models both the mechanical actions and the chemical environment of the industrial rod mills used in the Black Mesa Slurry preparation plant at Kayenta, Arizona. The industrial mill and the laboratory mill differ in size, retention time in the mill, and continuous vs. batch operation.

The laboratory mill shown in Figures 2 and 3, was made from a 9-inch long piece of 8-inch O.D. seamless steel pipe. Inside were welded 1/2 x 1/2 inch steel bars parallel to the length and distributed uniformly around the circumference. These carry the rods and provide good grinding action. One end of the mill is welded shut. The other end has a flange, a cover sealed with an "O" ring, and a mechanism for holding the cover tightly in place with a center hold-down bolt. The cover also contains a valve, flush with the inside surface when closed, through which gas samples can be removed from the rod mill. The rod mill was driven on a jar mill drive, Fisher Scientific Co., Model 753 RM. This drive was modified to reduce the rotational speed of the rod mill to 28 RPM by the addition of an added 4:1 reduction pulley system. Five one-inch diameter cold rolled steel rods are sufficient to operate the system. Before use, the system was cleaned with trichlorethylene, hexane, alcohol, and steam. It was then oven dried for 48 hours. Two coal samples were ground in the mill before any data was taken. After each use, the mill was operated with clean water. It was never washed with solvents or detergents owing to the impossibility of removing all traces of coal from the surfaces and from crevices in the walls. These would carry contamination by any washing aids added.

The free volume of the rod mill is 5700 ml and 5000 ml of slurry can be processed at one time. Because the de-ionized water available is contaminated with phthalate esters at the part per billion level, tap water supplied by the East Bay Municipal Utility District was used to make up the slurry.

It was early apparent that the difficulties of centrifuging a slurry made with 50% water and 50% coal on a batch basis are formidable. The coal content of the slurry was reduced to 20% and the problem of obtaining at least two liters of water from each slurry batch was made much easier.

Processing of slurry was done using a Beckman Model J-H Centrifuge. Four 250 ml polycarbonates centrifuge bottles could be used at one time. Centrifuging at $0^{o}C$ for 1 hour at 7500 RPM yielded a clear centrate which could be readily decanted from the underlying coal. Slurries made from coals from different mines differed in their behavior in the centrifuge. Centrates were stored in 2 liter Pyrex bottles. As produced, the centrates were reducing, but on standing, ferric hydroxide precipitated from the centrate. Illinois No. 6 coal gave clearest slurry centrate but precipitated the most $Fe(OH)_3$ as the reduced iron oxidized.

Coal Preparation

The coals studied included two western subbituminous coals, Roland seam coal from the Wyodak mine at Gillette, Wyoming and Black Mesa coal from the Black Mesa mine of the Peabody Coal Co. at Kayenta, Arizona. Both these coals are low-sulfur western coals. A high sulfur eastern coal, Illinois No. 6 was also studied.

The coal samples were obtained directly from the mines by sending a clean steel drum to each respective mine with the request that it be filled with clean lumps of coal. The new steel drums were steam cleaned before shipment to the respective coal companies for filling. The clean steel of the inside of these drums did rust and some of this rust contaminated the lumps of coal. For use, a lump of coal was picked up by forceps and any rust present was displaced from the surface by impact on another lump of coal in the drum. The lump was then broken into smaller pieces in a clean steel container using a clean steel tamper. The pieces less than 1.5 cm in size were weighed in a clean beaker and poured into the laboratory rod mill. The coal pulverizing container consisted of a piece of steel pipe 8 in. O.D. x 8 in. long with 3/8" walls slipped onto a steel base 7 1/4 in. in diameter which was bolted to a 3/4 in. aluminum plate. The tamper was a 1 1/2 in. long section of 3 1/2 in. diameter steel rod mounted on a 10 inch long handle. Each piece of the container or tamper could be separately wiped clean after each use.

Contamination Precautions

Efforts were made to reduce contamination to a minimum. Contamination of the coal, or the rodmill, or the water from which the slurry was made is not a problem except for phenolic compounds, an unlikely contaminant. However, contamination of the centrate after separation was a problem in as much as parts per trillion contamination by putting the centrate in a bottle, separatory funnel or other container contaminated with hexane soluble organic compounds leads to the appearance of these compounds in the GC/MS analysis. By using perdeuterated compounds as spikes in the slurry makeup water, the fate of these compounds in the slurry water centrate could be followed independent of possible contamination after separation. To avoid messy chromatograms all glassware used in the handling, extraction, and concentration of the extract was washed with chromic acid, oven dried, and possible contamination entrances covered with aluminum foil. Blanks were run through the procedure on each bottle of hexane and for the methylation reagents, NaOH and dimethyl sulfate. One bottle of dimethyl sulfate was dark in color and methylation with it showed severe contamination with several unidentified compounds. The bottle was not used. The hexane extracts were dried with sodium sulfate and concentrated using a rotary evaporator to a volume of 1 to 2 ml. If further concentration was necessary it was done by evaporation the sample, contained in a small vial with a tapered V bottom, with a stream of dry nitrogen gas to the desired final volume.

Separation of Organic Constituents

The first experiments with slurry water showed two results. First in working at the part per billion level, extreme care must be used to prevent contamination. The most ubiquitous contaminants are the phthalate esters, octyl phthalate and butyl phthalate, which are leached from polyvinyl chloride tubing. Next is squalene which arises from fingerprints, third are the C20 to C30 n-alkanes, possibly from transfer of traces of lubricating oil via fingerprints. With due care it can be shown that these compounds are not derived from the coal slurry. The second result was that by straight extraction of the slurry water with nanograde hexane and further concentration by vacuum evaporation of the hexane, no organic components were observed at the 0.01 ppb level. It was therefore, decided to add organic compounds to the water before slurry formation and check their fate. In order to prevent any question in regard to contamination, when available, the compounds added were perdeutero compounds which do not occur in nature. Therefore, to check a group of compounds for their existence in coal slurry water, each liter of water was spiked with 1 ml of a 100 ppm solution in acetone or alcohol of each compound to be tested. After separation of the coal slurry water, internal standards were added to the extent of 1 part per billion. For most organic compounds this internal standard was normal anthracene which was shown not to appear in the slurry water.

Treatment of Phenols in Slurry Water

Phenols represent a separate class. Chriswell, Chang and Fritz, 1975, discuss methods for the determination of phenols in water. They are expected to be found in waters in contact with coal and they are not readily extracted by direct extraction with hexane. Usually no standards were added for phenols before slurry formation. To the clear slurry water centrate, perdeutero phenol was added as an internal standard for methylation, extraction, and GC/MS quantitation (Nowicki, Devine and Kieda, 1978).

Methylation of Phenols

Methods of methylating phenols which involve evaporation of the water to dryness are too slow and cumbersome for the determinations of phenols at the part per billion level. Methods which can be used in water solution usually do not work well at very low concentrations. Dimethyl sulfate methylates sodium phenolate quite rapidly, but at a level of 100 ppb in water, the yield of methyl-phenyl ether is usually very low. The methylation reactions in basic solution (1 N NaOH) are shown.

$$C_6H_5O^- + (CH_3)_2SO_4 \rightarrow C_6H_5OCH_3 + CH_3SO_4^- \tag{1}$$

$$(CH_3)_2SO_4 + OH^- \rightarrow CH_3SO_4^- + CH_3OH \tag{2}$$

$$CH_3SO^- + OH^- \rightarrow SO_4^= + CH_3OH \tag{3}$$

Reaction 2, the hydrolysis of dimethyl sulfate, is pseudo-first order in water solution, while the phenol methylation is second order and the rate is directly proportional to the concentration of phenol as well as the concentration of dimethyl sulfate.

As ordinarily performed with a small excess of dimethyl sulfate at room temperature, the hydrolysis, reaction 2, is so rapid that the low concentrations of phenols in coal slurry waters have no chance to react before the disappearance of the reagent dimethyl sulfate. Because dimethyl sulfate is only slightly soluble in water, if a large excess of dimethyl sulfate is used and the rate of hydrolysis is reduced by cooling the water and reagent to near 0^{o}, a respectable 40-80% yield of the methyl phenyl ether can be achieved at the part per billion concentration level of phenol. In Table 1 the results of some experiments are presented showing that some 50 to 150 ml of neat dimethyl sulfate added to a liter of 0^{o} water containing 10 - 1000 ppb phenol at a sodium hydroxide concentration of 1N is sufficient to give a respectable 40% yield of anisole. As shown in Table 2, anisole is readily extracted from water with several solvents with an extraction coefficient of about 16.

The following procedure was used to determine phenols in coal slurry water. A measured volume (near one liter) of clear centrifuged coal slurry water was added to a 2 l round bottom flask. 0.1 ml of a 100 ppm solution of perdeuterophenol in water was added. The concentration of the perdeuterophenol internal standard was 10 ppb in the slurry water. The solution was made near 1 N NaOH by the addition of 100 ml of 10 N NaOH. The basic solution was extracted with 3 x 100 ml of nano-grade hexane. The hexane extract was dried over Na_2SO_4, evaporated to about 2 ml on a rotary evaporator, further reduced to about 0.1 ml by blowing with N_2 gas, and analyzed for neutral and basic species on the GC/MS.

The basic water phase was cooled to $0^{o}C$, 70 ml of dimethyl sulfate and a Teflon coated stirring bar were added. The mixture was stirred overnight in an ice bath. In 16 hours the dimethyl sulfate was hydrolyzed. The solution was tested for pH and found to be still basic (if not some dimethyl sulfate may remain). The methyl-phenyl ethers were collected by extraction with 3 x 100 ml of nano-grade hexane. The extract was dried with anhydrous sodium sulfate and then evaporated on a rotary evaporator to a volume of 1 to 5 ml. This volume was measured when the hexane solution was transferred to 5 ml graduated cylinder. One microliter of this solution was injected into the GC/MS using the splitless method of injection with the split and spectum sweep turned off for 2 minutes.

For slurry waters from Wyodak and Black Mesa coals it was not necessary to pre-extract the basic water before methylation. Waters from slurries with Illinois No. 6 coal which were not extracted prior to methylation gave zero yield of methyl-phenyl ethers. It was observed that even at 0°C, the dimethyl sulfate hydrolyzed in a few minutes. With pre-extraction, the methylation proceeded normally. The component which catalyzed the hydrolysis of dimethyl sulfate and which was removed by extraction from the basic slurry water from Illinois No. 6 coal, was not detected in the extract hence was not identified.

GC/MS Operation

The extracts from coal slurry waters were analyzed on a Finnigan Model 4023 gas chromatograph/mass spectrometer/data system combination. This instrument consists of a Finnigan Model 9610 gas chromatograph equipped with a Grob type splitless injection system and a capillary column leading directly into the mass spectrometer ion source. The injector can be operated in the splitless or split mode as desired. In this investigation all samples were run in the splitless mode. The columns were 30 m. WCOT (wall coated open tube) glass columns coated with OV-101 or in the later runs, a 30 m quartz WCOT DB-5 (J. and W. Scientific) column. Both columns gave similar separations. The quartz DB-5 column was found to be more stable.

The gas chromatograph for splitless injections using hexane as a solvent was programmed as follows. The column was cooled to 45°C. At zero time the GC program and the computer program were started. At 6 seconds the helium flow to the septum sweep and sample split were cut off, and the only helium flowing through the injector went into the column. At 18 seconds the sample was injected. At two minutes the split and septum sweep Helium flows were restarted. At three minutes the column temperature program was started, 4^{o} per minute to $270^{o}C$ with a temperature hold at $270^{o}C$ for 30 minutes.

During the GC run, mass spectra were collected at one scan per second from mass 36 to mass 536. The mass spectrometer was a Finnigan Model 4000 quadripole instrument equipped with a Nova-3 computer (Data General Corporation) and Wangco. dual disk drives. Mass spectral data was stored on disks and processed using interactive software in the Incos 3.1 data system.

Results and Discussion

The quantitative determination trace quantities of organic materials using a GC/MS is subject to a number of errors. This is especially true for quadripole instruments in which the ion source potentials are very low (usually less than 20 volts) and so called contact potentials of even a few tenths of a volt can cause a change in ion collection efficiency and ion transmission efficiency through the quadripole analyzer. Thus a small chromatographic peak following a large one in a gas chromatogram might be recorded at a reduced sensitivity owing to the polarization of the ion source by the preceding large chromatographic peak. Equally important for small chromotographic peaks is the accurate setting of the true system zero, and the possible drift of this zero during the chromatographic run. Such effects are insignificant for large chromatographic peaks but are very important for small peaks where one may measure only the tops of the peaks if the zero is set too high in order to decrease unwanted noise in the data collection. If the zero is set too low, much noise is recorded and it is possible to fill completely a data disk in the chromatographic run of a single sample. Other factors are the minimum peak width recorded and the minimum counts in the analog to digital converter recorded; e.g., if M=10, digital counts below 10 will be recorded as zero, but those counts above 10 will be recorded as the correct number. In addition there are the statistical errors in A/D conversion of small signals which affect small chromatographic peak intensities, but have little effect on peaks of large intensities. These factors affect the intensity of each mass recorded since the peak intensity and peak mass are determined by the sum and centroid of some 10 to 20 (depending on scan parameters) samples across each mass peak. If the low shoulders on a mass peak are discarded because of the adjustable parameters in the data system, then the integrated intensity will be low. The small chromatographic peak, which is the result of a number of mass scans, will thus be affected by these considerations with the scans intensities on the sides of the chromatographic peak being more affected than those in the center of the chromatographic peak. As shown in Table 3, in the Finnigan system as adjusted for our use, low intensity chromatographic peaks are more reliably quantitated by using peak intensities rather than peak areas. For large chromatographic peaks either method will suffice with peak areas being slightly favored. Peak height measurements show a maximum of 20% variation in sensitivity with a factor of 100 variation in concentration, while sensitivities using peak areas differ by a factor of almost two when the component is at low concentration. Therefore, for low intensity chromatographic peaks, maximum intensities rather than peak areas were used to quantitate the chromatograms.

Larger gas chromatographic peaks are adequately quantitated by peak area. This result is shown in Table 4. One liter of a mixture of phenols of concentration 100 ppb each was methylated, extracted with hexane and the hexane concentrated to 5 ml. A one microliter sample of this concentrate was injected (corresponding to 20 ng each of the original phenols. The results in Table 4 show that the phenolic compounds listed have about the same sensitivity at the parent mass peak for each respective compound. Sensitivities are listed in peak areas on the mass chromatogram of the parent mass of each phenol. The parent mass intensity is near 30% of the total ion intensity in the mass spectrum of each of the respective methylated phenols. In Figure 4 is shown the GC/MS/data system separation of the methylated phenol parent ion at M/z = 108, the methylated perdeuterophenol parent ion at M/z = 113 as compared to the RIC (reconstructed ion chromatogram) of the injected sample. On capillary GC columns, perdeutero compounds are consistently eluted a few seconds earlier than normal hydrogen containing compounds. This is the reverse of expected elutions considering translational energy and temperatures are too low for vibrational excitation, so the increased electron velocity of perdeutero compounds must be ascribed to rotational and/or zero point energy differences.

The GC/MS sensitivity of various perdeutero polynuclear aromatic hydrocarbons (PNA's) was determined by injection of a 1 ml of a solution in ethanol containing 100 ppm of each of the hydrocarbons listed. The results shown in Table 5 demonstrate that except for perylene-d_{12} the sensitivity of the parent ion mass peak of each compound is roughly constant at 12000 to 17000 counts per 100 ng injected. This drop-off in sensitivity for high boiling compounds, perylene has a listed boiling point of $500^{o}C$, is similar to that observed in a standard solution of n-alkanes in which those alkanes larger than n-$C_{28}H_{58}$ are recorded at lower sensitivities than are the lighter n-alkanes, by the counts in the total RIC (reconstructed ion chromatogram) if the eluted GC alkane peak. This is attributed to the loss of high boiling compounds in the injection part of the gas chromatograph, i.e., high boiling compounds do not get into the capillary chromatographic column with the same efficiency as do lower boiling compounds.

Table 5 is shown the relative sensitivity of a variety of polycyclic compounds. These sensitivities are those found on a given day with a given ion source and a specific ion source tuning. For quantitation at another time with the GC/MS, a standard mixture was run to establish a sensitivity level, or better, an internal standard was added to the water before extraction and concentration but after separation from the coal. for the type of compounds shown in Table 5, normal anthracene, $C_{14}H_{10}$, as added as an internal standard.

The recovery of various compounds from water by extraction and concentration is shown in Table 6. Various types of compounds of differing polarity were added at 100 parts per trillion to a separated coal slurry water. The water was then extracted with hexane, the hexane dried with anhydrous Na_2SO_4 and the resulting extract concentrated in a rotary evaporator. The results shown in Table 6 show excellent recovery at the 100 ppt (parts per trillion) concentration level and show the method to be valid for the investigation of organics in water in the part per trillion level.

The adsorption of organic compounds by coal during and after slurry formation is illustrated in Table 7, the same compounds used in Table 6 to demonstrated recovery from coal slurry water have been added to water at a concentration of 100 ppb and the water used to make a 20% coal slurry. All compounds are adsorbed by the coal. Only adamantane was detected in the coal slurry water. The others are below the limit of detection for the sensitivity of each compound and the degree of concentration of the extract. The differing degrees of adsorption of adamantane in the three coals is suggestive that either the coals differ widely in adsorption capacity for adamantane or that the coals differ in the rate at which adamantane is adsorbed.

Some general observations of coal slurries from the three types of coals can be made. In Table 8 are given the measured gross properties of slurry waters from each of the three respective coals when made with 20% coal and 80% water, a system easily separated by centrifugation at 7500 RPM and near zero degrees to yield a clear centrate from each respective coal slurry. Slurry waters from Illinois No. 6 coal were clarified with the least centrifugation. Soon after centrifugation and exposure to air, a heavy red precipitate of ferric hydroxide formed in this slurry water. Black Mesa coal required longer centrifugation at 7500 RPM than did either of the other two coals.

As shown in Table 8, the coal slurry waters do not differ greatly in gross properties. The Black Mesa coal produced a slurry of highest inorganic carbon content. It also showed the highest pH of the three slurry waters. The slurry from Illinois No. 6 had the least total organic carbon at about 11 ppm compared to 18 ppm for the other two coals. This coal also had the most iron (not quantified) as shown by the largest by far amount of $Fe(OH)_3$ which precipitates on standing. The Black Mesa coal contained the lowest total solids as determined by simple evaporation, while the Wyodak coal showed the highest concentration of total solids.

The lack of non-polar organic compounds in coal slurry water is shown by the adsorption by coal of compounds added to the water before coal slurry formation. As shown in Tables 7, 9, and 10 the addition to the water of a variety of organic compounds which, from the assumed structure of coal (Wiser, 1975) (Anderson, et al., 1978) might be expected in coal slurry water results in the adsorption of greater than 99.9% of these compounds and the final concentration in the slurry water is less than .01 to .05 ppb, the lower limit being set by the GC/MS sensitivity of the compound and concentration factor of the extract. The upper limit is the solubility of the compound in water. May, 1980, has determined the solubility of many polycyclic aromatic hydrocarbons in water. In all cases an internal standard (usually 1 ppb of normal anthracene) was added to the coal slurry water after centrifugation and before extraction. The recovery of the standard was in all cases greater than 90%. It is also significant that in those solutions to which non-polar perdeuterated compounds were added to the water, not only were these compounds adsorbed, but no compounds were observed other than the spike of anthracene which were not attributable to random impurities introduced in the interaction and processing. Butyl and octyl phthalates, C_{20} to C_{30} alkanes, squalene and in the case of one of us (ASN) working with the samples, palmitic acid, were frequently observed at the concentration level of about 1 ppb. The phthalate esters acid from contact of equipment with polyvinyl chloride plastic, the squalene arises from fingerprints as do the traces of lubricating oil. The palmitic acid arises from the use of a medicinal hand cream by one of the principal investigators.

With extreme care all of these could be eliminated, and in many samples the concentrated extract contained no organic compounds other than the internal standard spike.

There is however, a rate effect in the adsorption, of organic compounds in the case of slurries prepared with Black Mesa Coal. If the slurry water is centrifuged immediately after the two hour period allowed for slurry formation, traces of some of the added compounds, are found in the slurry water. If the slurry water is kept for 3 days or 30 days with occasional stirring by running the rod mill for a few revolutions, all added neutral and basic compounds disappear to the 0.01 ppb level of detection. The results shown in Tables 9 and 10 are for slurry water which were in contact with the respective slurries for at least 3 days.

One compound which is formed in slurry formation of coal with water is hydrogen gas. While a systematic study of the production of hydrogen was not made, several experiments showed that in our apparatus H_2 was produced at the rate of 6 millimoles gas equivalent per hour. No hydrogen initially appears in the gas phase but oxygen in the closed rodmill disappears with time of slurry formation. After two hours of slurry formation the gas phase consists of a small amount of H_2, zero O_2, and N_2, Ar and CO_2 in the ratios normally observed in air. No methane or ethane was observed in the gas phase by mass spectrometer analysis (CEC model 21-103 mass spectrometer). An amount of CH_4 of 0.05 millimoles in the total gas would have been observed in the mass spectrometer analysis.

Hydrogen production ceases when the rod mill stops turning even though the coal is still in contact with the water and rods. The H_2 must therefore, be formed from the interaction of water with the freshly exposed surfaces of the rods and rod mill case caused by the grinding action of the hard components in the coal. This freshly exposed iron surface will have zero overvoltage and react immediately with water or oxygen. The mechanism is not important. The net result is that as long as oxygen is present, O_2 gas disappears. When the oxygen is gone, H_2 is produced. The O_2 could disappear through reaction with nascent hydrogen or by direct action of O_2 on the clean iron surface. The latter would happen if the reaction of dissolved oxygen with a fresh iron surface is faster than the reaction of liquid water in contact with that same surface.

Phenols

A most probable group of organic compounds to be found in coal slurry water are the phenols. Indeed these are found in coal slurry water as determined by methylation and extraction of the methyl-phenyl ethers. As shown in Table 11, phenol does occur in coal slurry water at the 5-10 ppb level. If perdeutero phenol is added to water at the 100 ppb level and slurry formed with this water, about the same amount of phenol is found in the water as was found with no perdeuterophenol addition. The phenol found was largely normal phenol with only a trace of perdeutero phenol being left in the water. In principle, if it were established that a steady state was reached, from the ratio of perdeuterated phenol to ordinary phenol in the water, one could calculate the total amount of exchangeable phenol in the coal.

Phenols in coal slurry water determined by the addition of 10 ppb perdeutero phenol internal standard to the centrate from coal slurry are shown in Table 12. Also in Table 12 are shown phenols determined in a centrifuged sample of the clariflocculator overflow from the Mohave Generating plant. All the coals show phenols to be present in the coal slurry water in the concentration range 1 to 50 ppm. Wyodak coal shows the lowest concentration of phenols and Black Mesa coal the highest. A comparison of the concentration of phenols in laboratory slurry water from Black Mesa coal shows a good agreement with the results from the slurry water from the Mohave Generating station.

The basic hexane extract from the Mohave generating station clariflocculator overflow water showed no hexane extractable compounds which could be attributed to the leaching of organic compounds from the coal into the slurry water. In Table 13 are shown some unusual the compounds observed in fractional ppb quantities in the clear centrifuged centrate as determined by hexane extraction. The result is an odd mixture of compounds, none of which appear likely to arise from coal. The low concentrations of camphor, vanillan and di-t-butylbenzoquinone may be components of the proprietary flocculants added, but their source was not established.

Conclusions

The investigation of possible organic contaminant in coal slurry water has shown that when completely separated from all coal fines, the water is remarkably free of organic material. Of the types of compounds likely to be considered damaging to the water quality, only a few phenols in the concentration range 1-50 ppb, with most centered around 10 ppb in concentration, were found. Other neutral and basic compounds are not produced or are adsorbed on coal to a concentration of less than 0.01 ppb. A total organic carbon content of the water of some 10 ppm is not accounted for by the phenols present. This excess organic carbon is assumed to be due to humic acids though this has not been demonstrated owing to the lack of a suitable method to identify and quantify to use for most purposes, humic or fulvic acids. The water should be safe, but if this water were to be chlorinated directly, chlorinated phenols in undesirable amounts (detectable by taste or odor) might be produced. There should be no restrictions on the use of clear coal slurry water for agricultural purposes, and its disposal to an area which might contaminate a public water supply is limited only by the phenol content which must be reduced below the taste or odor level. In practice, at the Mohave Generating station the cleanest water, the clariflocculator overflow water contains coal fines which detract from its appearance and usefulness outside the plant. The conversion of the clariflocculator overflow water to a clear centrate is an engineering problem which was not addressed in the present study.

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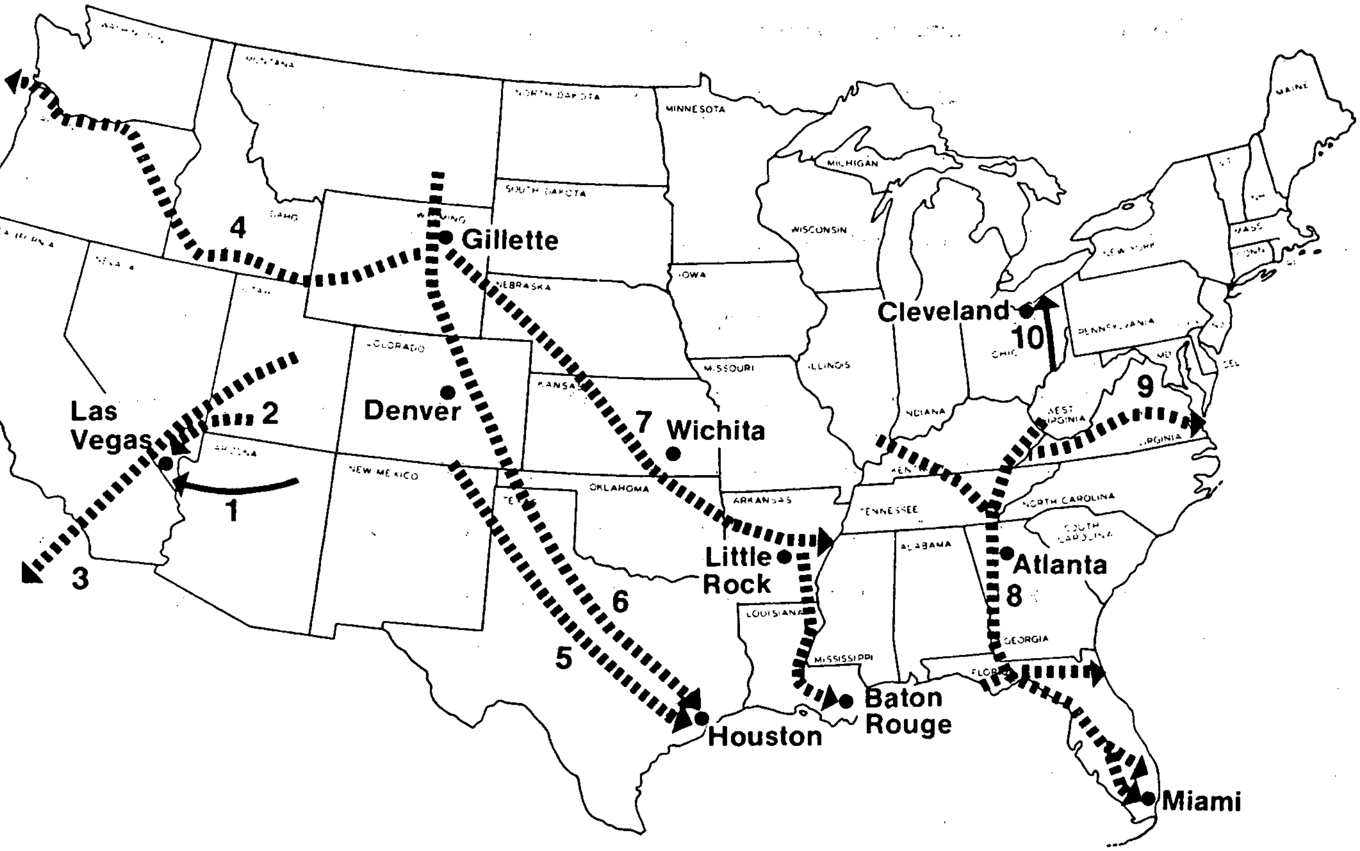
Figure Captions

Figure 1 Map showing operating and proposed coal slurry pipelines in the United States. Source: Slurry Transport Association, Washington, DC.

Figure 2 Exploded view of laboratory rod mill.

Figure 3 Assembled laboratory rod mill and its drive.

Figure 4 Separation by mass chromatography of the parent ions in the mass spectra of methylated perdeutero phenol (M/z = 113) and methylated normal phenol (M/z = 108). A comparison of the separated peaks and the RIC (reconstructed ion chromatogram) are shown.



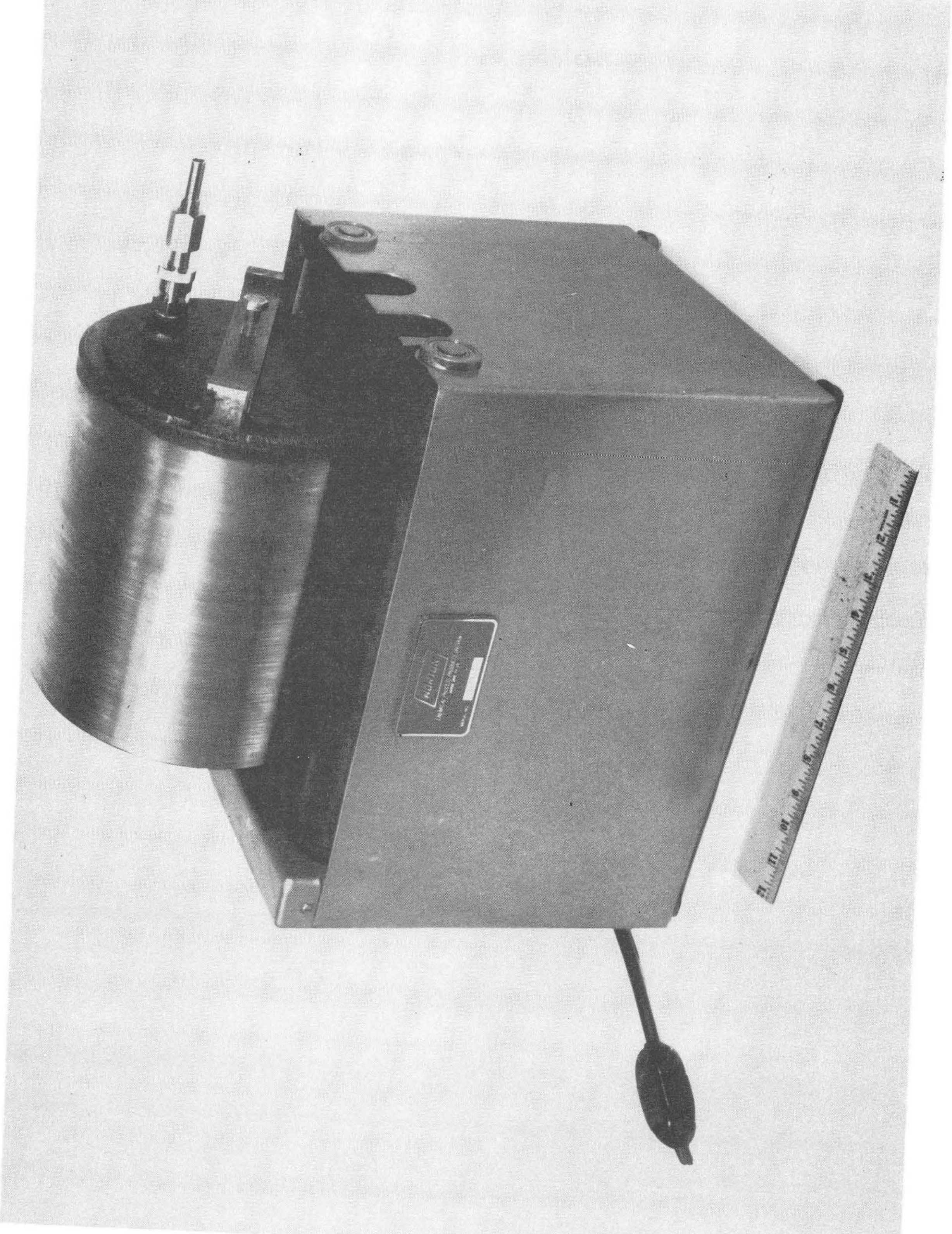
Existing Pipelines ▬▬▬▬▬▬▬▬▬▬

Planned/Proposed Pipelines ▮▮▮▮▮▮▮▮▮▮▮▮

Pipeline System	Length	Annual Capacity
1. Black Mesa	273 miles	4,800,000 tons
2. Allen-Warner Valley Energy System	183 miles	11,600,000 tons
3. Pacific Bulk Transportation System	650 miles	10,000,000 tons
4. Nices	1,100 miles	25,000,000 tons
5. San Marco	900 miles	15,000,000 tons
6. Texas Eastern	1,260 miles	22,000,000 tons
7. ETSI	1,378 miles	25,000,000 tons
8. Continental	1,500 miles	15-45,000,000 tons
9. VEPCO	350 miles	5,000,000 tons
10. Ohio	108 miles	1,300,000 tons

U.S Coal Slurry Pipeline Systems

XBB 790-15386



XBB 790-15385

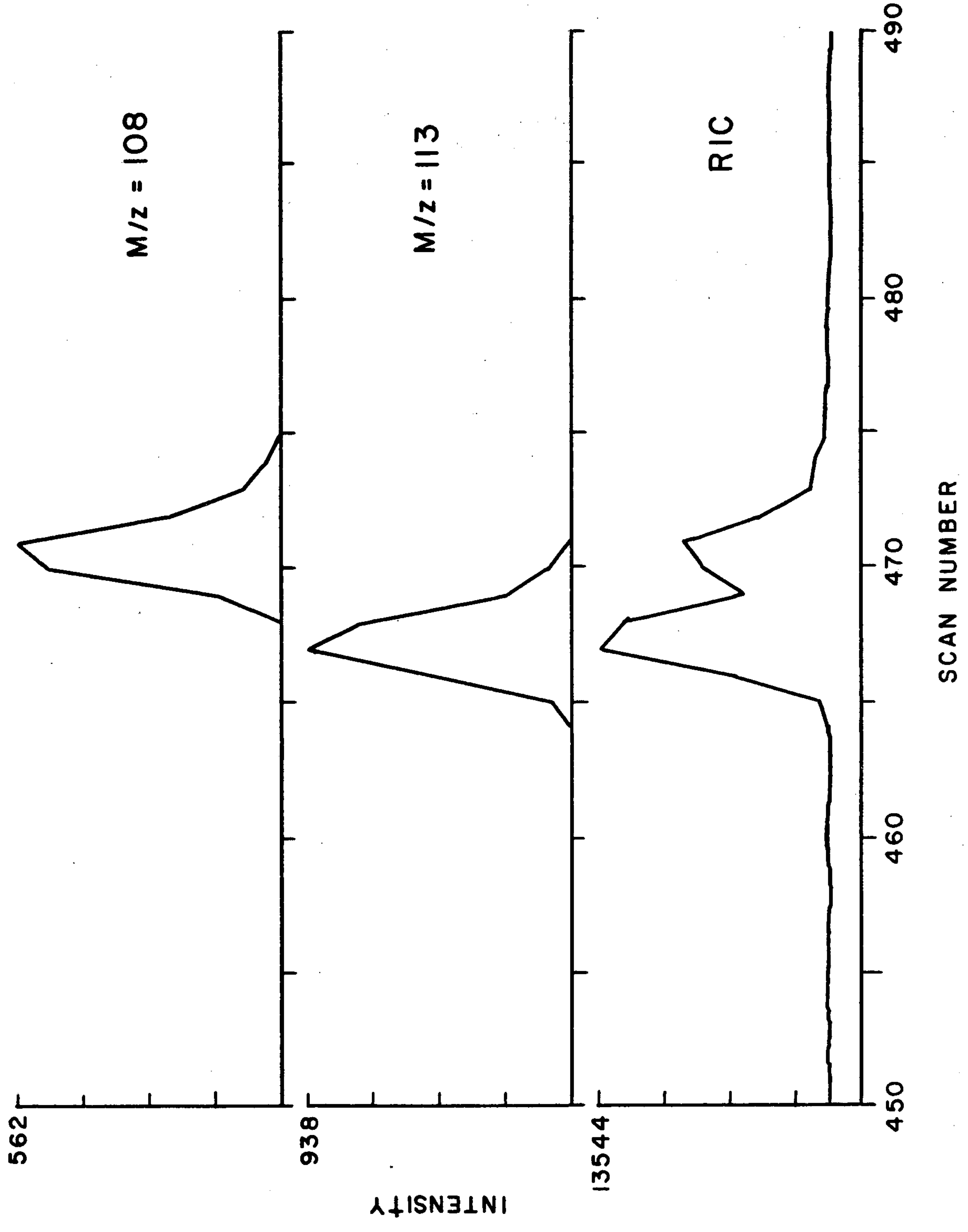

M/z = 108
M/z = 113
RIC
562
938
13544
INTENSITY
450
460
470
480
490
SCAN NUMBER

Table 1

Summary of Some Experimental Results in the Methylation of Phenol

Expt. No.	Phenol (Mg phenol/liter)	Dimethyl/Sulfate ml per liter	NaOH (Normality)	Temp (°C)	Yield Anisole (%)
1	1000	15	2	24	22
2	1000	15	2	24	17
3	1	15	2	24	4.3
4	500	15	2	24	4.3
5	100	50	1	26	43
6	10	150	0.5	26	39
7	110	150	1	2	82
8	2	50	1	10	36
9	10	150	0.1	2	0[a]
10	10	150	0.5	2	20
11	10	150	1	2	39

[a] No anisole detected, dimethyl sulfate present.

Table 2

Distribution Coefficients between Water and Various Organic Solvents for Anisole at 25°C

Solvent	$K = \frac{\text{concentration anisole in solvent}}{\text{concentration anisole in water}}$
Benzene	16.8
Diethyl ether	15.2
Methylene chloride	15.0
n-Hexane	17.5

Table 3

The Relative Sensitivities of Anisole and 2,3,4,5,6-Deuteroanisole in the GC/MS at Various Absolute and Relative Concentration Levels

Nanograms of Compound Added			Anisole/Deuteroanisole Sensitivity*	
			Sensitivity	
Anisole	Deuteroanisole	Weight Ratio	by Peak Height	by Peak Area
120	110	1.09	1.14	1.07
81	9.0	9.0	1.00	1.08
50	10	5	0.94	1.10
50	2	25	0.81	1.28
50	0.5	100	0.79	1.71
10	2	5	1.00	1.28
10.5	0.52	20	0.90	1.86
1.90	1.90	1.0	0.95	1.09
2.10	0.52	4	0.95	1.70
0.475	4.75	0.10	0.87	0.50

* Sensitivity is in digital counts per nanogram.

Table 4

GC/MS Characteristics of Methylated Phenols

Compound	Parent Mass	Ratio $\frac{\text{Parent Mass}}{\text{Total RIC}}$	Relative Sensitivity of Parent Mass
Phenol	108	0.305	100
0-Cresol	122	.286	116
2-6-Dimethylphenol	136	.260	113
Resorinol	138	.317	101
1-Naphthol	158	.347	95

Table 5

GC/MS Sensitivities for Some Perdeutero Polycyclic Aromatic Hydrocarbons

Compound	M/z Molecular Ion	Emergence Time in Seconds[a]	Ion Intensity[b] for 100 ng Injected
Acenaphthene-d_{10}	164	2191	16000
Phenanthrene-d_{10}	188	2730	17500
Pyrene-d_{10}	212	2750	16000
p-terphenyl-d_{14}	244	3325	12300
1,2-benzanthracene-d_{12}	240	3610	12500
Chrysene-d_{12}	240	3625	13000
Perylene-d_{12}	264	4325	3400

[a] OV-101 WCOT capillary column.

[b] Intensity in arbitrary units of peak height.

Table 6

GC/MS Sensitivities of Test Compounds and Recovery When Added to Coal Slurry Water

Compound	M/z Molecular Ion	Sensitivity Counts/ng	ng/liter Added	ng/liter Found
Adamantane	136	282	100	95
Dibenzothiophene	184	374	100	81
Carbazole	167	124	100	97
Benz(a)anthracene-7,12-dione	258	30.9	100	88

Table 7

Concentration in Coal Slurry Waters of Compounds Added to Water Before Slurry Formation

Compound	Concentration in ppb in Slurry Water From Coal[a]		
	Wyodak	Illinois No. 6	Black Mesa
Adamantane	0.008	0.030	0.135
Dibenzothiophene	<0.005[b]	<0.005	<0.005
Carbazole	<0.013	<0.012	<0.012
Benz(a)anthracene-7,12-dione	<0.055	<0.050	<0.050

[a] The initial concentration of each compound in water before slurry formation was 100 ppb.

[b] None detected in slurry water. Given is the concentration level at which the compound would have been detected at a signal/noise = 2.

Table 8

Total Carbon, Inorganic Carbon, Total Solids Content, and pH of Slurry Waters from Three Types of Coal

Water Property[a]	Coal Type		
	Black Mesa	Wyodak	Illinois No. 6
pH	7.83	6.57	6.78
Total Carbon (ppm)	56.6	23.1	32.1
Inorganic Carbon (ppm)	38.2	5.0	20.6
Organic Carbon (ppm) (Indirect)	18.4	18.1	11.5
Organic Carbon (ppm) (Direct)	19.8	17.9	10.5
Total Solids ppm	700	1820	1320

[a] Measurements made on centrate from a slurry of 20% coal content.

Table 9

The Adsorption of Nitrogenous Compounds From Water During Coal Slurry Preparation

	ppb of Compound in Slurry Water from:		
Compound[a]	Wyodak Coal	Illinois #6	Black Mesa
Pyrrole	<0.01	<0.01	<0.01
Pyridine	<0.01	<0.01	<0.01
Aniline	<0.01	<0.01	<0.01
Quinoline	<0.01	<0.01	<0.01
Diphenylamine	<0.01	<0.01	<0.01

[a] The initial concentration of each compound was 100 ppb.

Table 10

Adsorption of Added Perdeuterated Neutral Organic Compounds from Waters During Slurry Formation with Various Coals

Compound[a]	ppb of Compound in Coal Slurry Water from:[b]		
	Wyodak Coal	Illinois No. 6 Coal	Black Mesa Coal
Acenaphthene-D_{10}	<0.009	<0.013	<0.013
1,2-Diphenylethane-D_{14}	<0.005	<0.007	<0.007
Phenanthrene-D_{10}	<0.005	<0.010	<0.010
Pyrene-D_{10}	<0.003	<0.010	<0.010
p-Terphenyl-D_{50}	<0.003	<0.013	<0.013
n-Tetracosane-D_{50}	<0.01	<0.02	<0.02
1,2-Benzanthracene-D_{12}	<0.003	<0.015	<0.015
Chrysene-D_{12}	<0.003	<0.015	<0.015
Perylene-D_{12}	<0.008	<0.02	<0.02

[a] The compounds are listed in their order of emergence from a 25 m, J&W DB-3 bonded quartz column. The perdeuterated compounds were added to the water before slurry formation to a concentration of 100 ppb.

[b] The water was in contact with the coal for 3 days after slurry formation. The concentrations given are all maxima, the values depending on final volume of the hexane extract and the GC/MS sensitivity of an added internal standard.

Table 11

Phenol in Coal Slurry Waters Made With and Without Phenol in Water Before Slurry Preparation

Type Coal	ppb Phenol in Slurry Water[c]	
	by Extraction[a]	by Adsorption[b]
Wyodak	9.0 ± 2	11.0 ± 3
Illinois No. 6	<2.0	4.5
Black Mesa	1.2	12.9

[a] Nothing added to water before slurry formation.

[b] 100 ppb phenol added to water before slurry formation.

[c] Slurry centrate was separated immediately after slurry formation.

Table 12

Phenolic Compounds Found in Coal Slurry Waters

Compound[a]	Concentration of Phenolic in ppb in Coal Slurry Water			
	Wyodak Coal	Illinois No. 6 Coal	Black Mesa Coal	Mohave Clariflocculator Overflow
Phenol	4.2	8.3	13.2	8.5
O-Cresol	5.7	13.2	11.5	10.1
P-Cresol	6.8	15.7	27.2	14.2
2,6-Dimethylphenol	2.6	3.4	7.1	2.9
O-Ethyl Phenol	6.5	17.6	18.4	54
P-Ethyl Phenol	2.4	10.1	4.6	6.8
3,5-Dimethyl Phenol	0.3	1.2	2.1	1.0
C_3-Phenol[b]	<0.01	<0.04	2.9	1.5

[a] Phenols are listed in the order of the emergence of their methyl ethers from a 25 m, J&W DB-5 bonded quartz capillary column.

[b] The C_3-isomer is unidentified except by molecular weight.

Table 13

Miscellaneous Organic Compounds Observed in Hexane Extract of Centrifuged Mohave Generating Station Clariflocculator Over-Flow Water[a]

Compound	Concentration ppb
Camphor	0.3
Vanillan	0.4
di-t-Butyl-p-Benzoquinone	0.8
phenanthrene-d_{10}(a)	1.5

[a] Perdeutero phenanthrene was added to the centrate as an internal standard.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720