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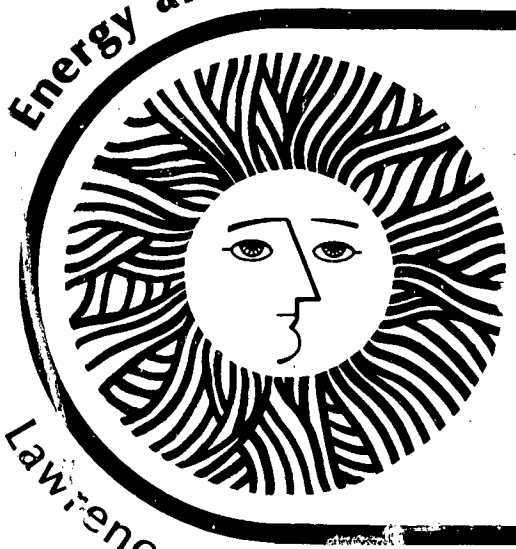

Extraction of Phenols from Coal Conversion Process Condensate Waters

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(M.S. Thesis)

June 1979

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Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48

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ABSTRACT

Condensate water samples from two typical coal-conversion processes were analyzed for phenols by gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC). Significant amounts of phenol, dihydroxybenzenes and the trihydroxybenzene phloroglucinol were found. The presence of a trihydroxybenzene is particularly important as trihydroxybenzenes are extremely resistant to biological oxidation.

The effects of water-phase pH on the extraction equilibria of the weakly acidic phenols were studied in a series of pH-controlled batch extractions of phenol, resorcinol, and hydroquinone into diisopropyl ether (DIPE) and hydroquinone into methyl isobutyl ketone (MIBK). The equilibrium distribution coefficient K_D decreased sharply in the pH range typical of condensate waters, 8.7-9.8, which is also the range of the pK_a's of the phenols. A simple model combining the acid ionization and the phase distribution equilibria fit the data well.

Batch extractions of di- and trihydroxybenzenes into MIBK and DIPE showed MIBK to be clearly a better solvent than DIPE. The distribution coefficients in MIBK were an order of magnitude greater than those in DIPE, some of which were much less than unity. DIPE is currently used in the Phenosolvan process to extract phenol from coke-oven and coal-conversion effluent waters. With the K_D's measured in this work, calculations showed that the Phenosolvan process, as currently run, will not remove polyhydroxybenzenes from alkaline water solution to the levels required for further treatment, recycle or discharge of the condensate waters.

Acknowledgements

I would like to express my appreciation to my Research Director, Professor C. J. King, for his guidance, interest and advice during the past year and one half. I have learned much and enjoyed working for him.

I would also like to thank Professor S. Lynn for his advice and interest in my work and for reviewing my thesis. I would also like to thank Professor S. D. Brown for his time and effort in reviewing my thesis. I am grateful to Dr. A. Newton for his condensate water analyses.

I would like to thank my good friends and co-workers Larry Ricker, Steve Lubic, and Ed Pittman for their assistance and advice. I greatly appreciate the time and effort Nancy Bell spent in proofreading the final draft, and the time Don Mohr spent in helping to assemble it. Finally, I would like to thank Stephanie Choy for efficient typing of the final draft.

My work was supported by the Lawrence Berkeley Laboratory and by HEW, through a Domestic Mining & Mineral Fuel Conservation Fellowship.

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Chapter I. Introduction

Securing adequate energy supplies for the future is becoming more difficult. Dwindling supplies of domestic oil and natural gas necessitate large imports of foreign oil and natural gas, damaging the balance of payments and subjecting the economy of the United States to the vagaries of international politics.

Coal conversion is one way of dealing with this problem. The United States has a major share of the world coal reserves. This coal can be converted to the liquid and gaseous fuels and petrochemical feedstocks in high demand. Sulfur, nitrogen, and ash are simultaneously removed, providing environmentally acceptable fuels. A major problem, however, is water use in coal conversion.

A. Foul Water Sources in Coal Conversion

Coal conversion both consumes and produces large quantities of water. A large portion of the water produced is process-condensate water, which is highly contaminated with organics, ammonia, and hydrogen sulfide. The other water streams produced are cleaner. The water produced during methanation in the production of substitute natural gas (SNG) can be used directly as boiler-feed water. However, the process condensate water must be treated before it can be released. In the arid western states, where large deposits of low-sulfur coal are located, the contaminated waters must be cleaned enough for recycle into the process.

For example, a 250$\overline{M}$ SCFD (9.79×10^9 BTU/hr) Lurgi SNG plant, the size proposed for the Four Corners Area, would produce 2700 GPM of this process-condensate water (1).

Similarly, a Solvent Refined Coal (SRC) plant producing 10,000 ton/day (13.3×10^9 BTU/hr) of SRC would produce process-condensate water at the

rate of 700 GPM (2, p. 106).

In a typical gasifier, shown in Figure 1-1, process-condensate water is obtained from the gas quench step where the hot gas from the gasifier is quenched and scrubbed with water to remove most of the ammonia, hydrogen sulfide and organics. Additional condensate comes from the H_2-CO shift reactor prior to methanation. In coal liquefication, water produced in the high-pressure liquefaction reactor and contained as moisture in the feed coal is flashed overhead along with ammonia, hydrogen sulfide, carbon dioxide and the light organics when the pressure on the reactor effluent is let down.

Water Purification Associates has detailed water requirements for gasification and liquefaction plants planned for the western United States (2). Water is needed for ash control and disposal, coal slurrying and revegetation of the mines, but the major uses are boiler-feed water and cooling tower make-up, both requiring quite clean water. Excessive levels of dissolved solids would cause scaling and fouling in the boilers and heat exchangers. Any water-recycle process must avoid the addition of dissolved solids to the condensate waters, as subsequent removal to produce high quality water would be expensive.

B. Condensate Water Analyses

Tables 1-1 and 1-2 list typical water analyses for condensate waters from Synthane gasification and SRC liquefaction processes, respectively (2, pp. 265 and 267). The high levels of ammonia make the waters alkaline, and, with the dissolved carbon dioxide, buffer the waters so that pH adjustment in a water treatment process would require large amounts of chemicals.

The figures listed in Tables 1-1 and 1-2 do not adequately reflect

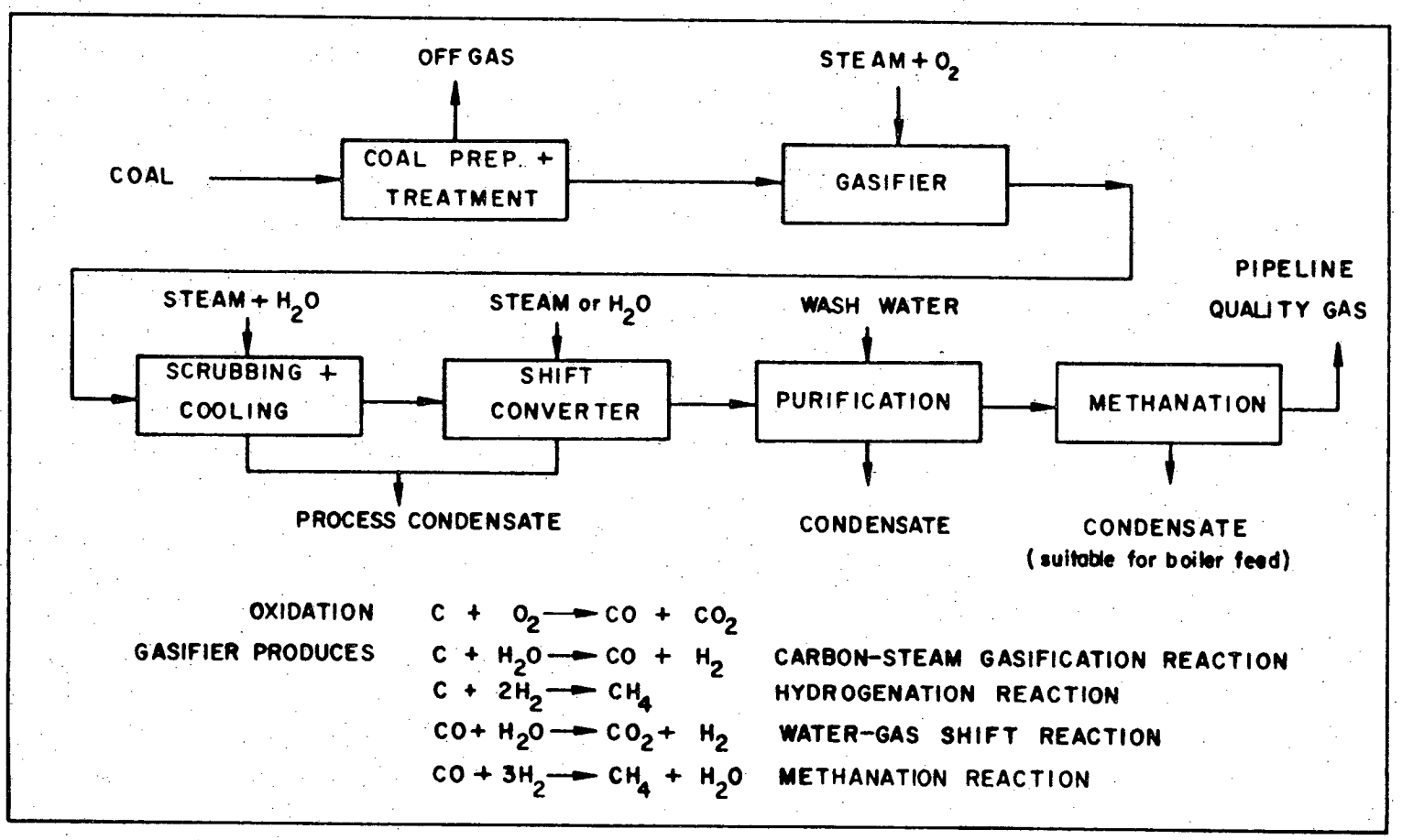

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Figure 1-1. Schematic of Coal Gasification Process

[adapted from Pittman, (13)]

Table 1-1. Standard Analyses of Synthane Gasification Process Condensate Water[a]

(All values in ppm except pH)

	Illinois No. 6 Coal	Wyoming Subbituminous Coal
pH	8.6	8.7
suspended solids	600	140
phenols (as phenol)	2600	6000
COD[b]	15,000	43,000
thiocyanate	152	23
cyanide	0.6	0.23
ammonia	8100	9520
chloride	500	-
carbonate	6000	-
bicarbonate	11,000	-
total sulfur	1400	-

[a] after Forney, et al., (3), as reported in (2)

[b] chemical oxygen demand

Table 1-2. Standard Analyses of Solvent Refined Coal Process Condensate Water[a]

(all values ppm except pH)

Coal	Kentucky
pH	8.6
total carbon	9000
total organic carbon	6600
inorganic carbon	2400
COD	43,600
phenols (as phenol)	5000
total Kjeldahl N	8300
total ammonia as N	7900
cyanide as CN	10
total sulfur as S	10,500

[a] values derived from (2)

the water quality, because of analytical shortcomings. In particular, the phenol concentrations were measured via a colorometric method involving reaction of phenols with 4-aminoantipyrene and potassium ferricyanide, a standard analysis for phenol in water (4). However, this method is highly approximate for substituted phenols, as different phenols will form differently colored dyes, and some of the para-substituted phenols will not react at all (4). No specific mention is made of the reactivity of polyhydroxybenzenes in the despcription of this test, but similar behavior should be expected. A few other sources give a more detailed breakdown of the organic contaminants in the waters. Table 1-3 shows the results of an early mass spectrometric analysis of a coal gasification wastewater [after Schmidt, et al, (5), as reported in (2), p. 264]. Later work by Ho, et al (6, 1976), presented in Table 1-4, does not show any dihydroxybenzenes in Synthane water. However, this could be due to the analytical methods used. It was found in the present work that analysis by gas chromatography, with conditions similar to those used by Ho, et al, and the same Tenox-GC column packing, failed to elute dihydroxybenzenes at all, while substituted monohydroxybenzenes did elute reasonably well.

Researchers at Exxon, developing the Exxon Donor Solvent (EDS) liquefaction process do report large concentrations of dihydroxybenzenes (7); their results are presented in Table 1-5.

The great differences in reported condensate water composition stem from a number of factors. The pilot plants supplying the water samples are experimental units, so that operating conditions are being varied, producing condensate waters that could also vary in composition. The samples may have been taken before steady-state operation was achieved. Different coals have different compositions, so that even when converted by the same process under the same conditions, different condensate waters

Table 1-3. Component Analysis of Process Condensate Water from the Synthane Gasification Process[a]

(All values in ppm)

	Illinois No. 6 Coal	Wyoming Subbituminous Coal
phenol	3400	4050
cresols	2840	2090
C_2 - phenols	1090	440
C_3 - phenols	110	50
dihydric phenols	250	530
benzofuranols	70	100
acetophenones	150	110
hydroxybenzaldehydes	60	60
naphthols	160	80
indenols	90	60
biphenols	40	40
benzothiophenol	110	20
pyridines	-	120
indoles	-	20

[a] after Schmidt et al, (5), as reported in (2)

Table 1-4. Major Organic Constituents of Synthane Process Condensate Water[a]

Component	Concentration (ppm)
Phenols	
phenol	2100
m-, p-cresol	1800
o-cresol	670
2,5-dimethylphenol	250
3,5-dimethylphenol	230
3,4-dimethylphenol	100
2.6-dimethylphenol	40
2,3-dimethylphenol	30
o-ethylphenol	30
β-naphthol	30
α-naphthol	10
Carboxylic Acids	
acetic acid	620
propanoic acid	60
n-butanoic acid	20
n-pentanoic acid	10
n-hexanoic acid	20

[a] values derived from (6, p. 489)

Table 1-5. Major Organic Constituents of Exxon Dover Solvent (EDS) Liquefaction Condensate Water[a]

Component	Concentration (ppm) Average[b]	Range
propanol	230	137-349
acetone	770	590-1070
MEK	160	114-221
acetic acid	2130	5049-10,019
propanoic acid	2790	1970-3737
isobutyric acid	300	230-412
n-butyric acid	840	576-1141
pentanoic (valeric) acid	420	233-663
phenol	2130	1638-2390
o-cresol	135	93-216
m-, p-cresol	1320	944-1579
C_2+ phenols	1310	696-1977
resorcinol	3830	2674-4366
others[c]	5600	3905-7006
total organics	26,900	22,775-34,056

[a] values from (7, p. 153)

[b] average of 4 analyses

[c] predominantly substituted dihydroxybenzenes

will be produced. Also, low-temperature liquefaction and gasification processes with short residence times tend to produce dirtier waters than high-temperature gasifiers (2, pg. 259). In addition to actual changes in water composition, the analytical methods used also contribute to the confusion surrounding the concentrations and identities of the phenols present in coal-conversion condensate waters.

C. Current Treatment Technology

Biological oxidation is the standard method of wastewater treatment. However, the high concentration of phenols in coal-conversion process condensate waters requires high dilution, even with phenol-adapted bacteria, to prevent the death of the bacteria. The high concentration of ammonia also presents a toxicity problem, requiring either ammonia-stripping pretreatment or dilution. Accompanying the high dilution are high capital requirements and operating costs, and in arid areas, the lack of dilution water.

These facters, along with a phenol product credit, make recovery processes attractive. The Phenosolvan process, a proprietary German process developed in the 1940's, is used commercially to treat coke oven wastewaters and is used on some operating gasifiers (8). Coke oven waters are similar to the coal-conversion condensate waters except that the latter are produced at a much higher rate and contain more phenols and large amounts of dissolved carbon dioxide. Because of their smaller water output, and because coke ovens are not usually located in arid areas, lime can be added to the coke oven wastewaters to release ammonia for more complete stripping without producing a dissolved-solids problem.

Figure 1-2 is a flowsheet of the Phenosolvan process (1,8). The gravel bed filter removes a large share of the tar and particulates,

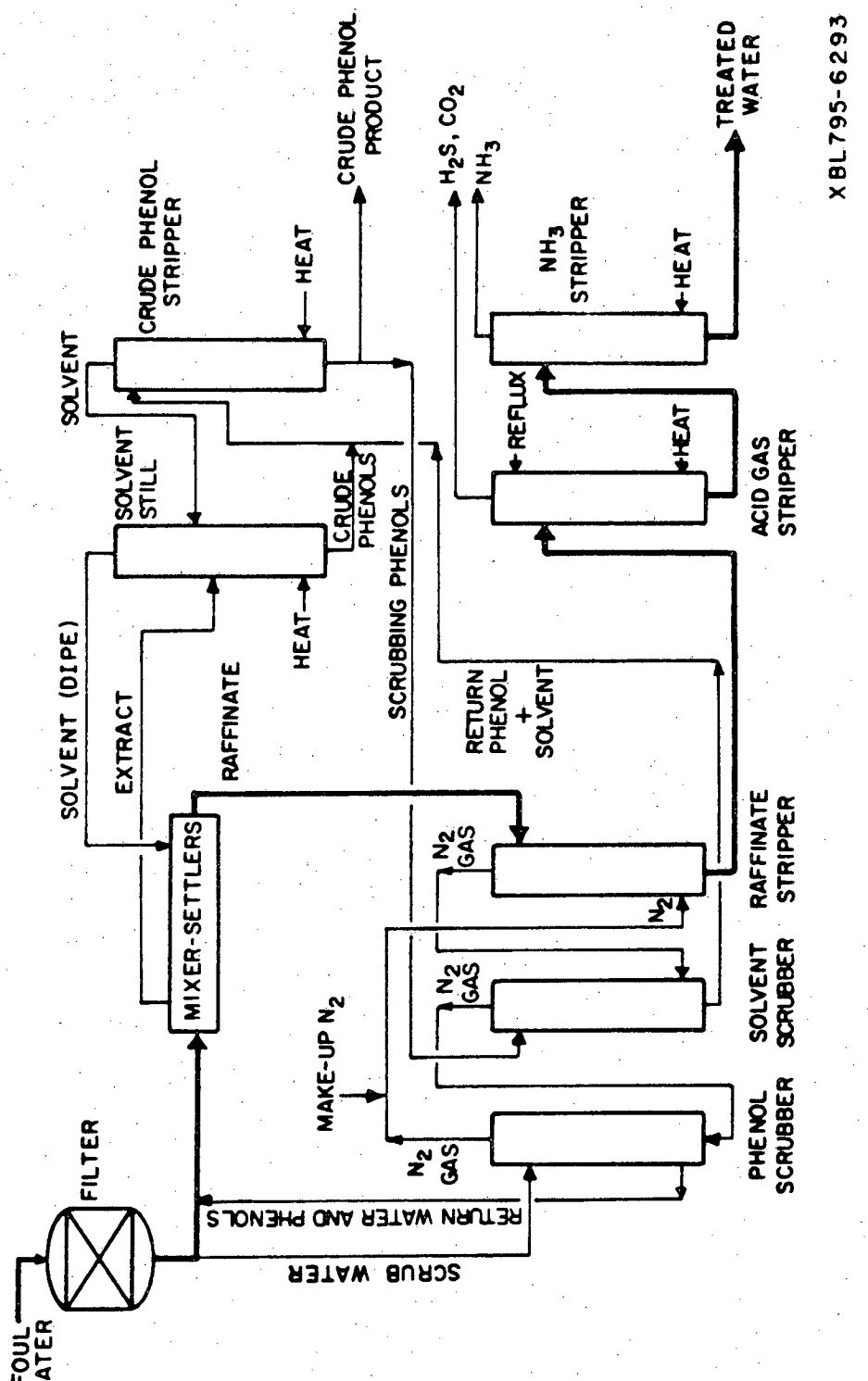


Figure 1-2. Phenosolvan Process Flow Diagram [after (1),(8)]

but the process must still be shut down every six months to remove tars and particulates from the heat exchangers and distillation columns (9). Diisopropyl ether (DIPE) extracts phenol from the water in a series of mixer-settlers. The solvent is recovered from the extract by distillation with the crude phenol product further stripped to remove residual DIPE. The raffinate is nitrogen-stripped to remove residual DIPE in a complex three-column system, with the nitrogen then phenol-scrubbed to remove the DIPE and then scrubbed with the feed water to remove the crude phenol, before being returned to the raffinate stripper. After nitrogen-stripping, the raffinate then proceeds to the acid gas and ammonia stripping operations.

Values of the equilibrium distribution coefficient K_D, which is defined as $\frac{\text{weight fraction solute in organic phase}}{\text{weight fraction solute in water phase}}$, for phenol and the dihydroxybenzenes between DIPE and water (10), presented in Table 1-6, raise doubts as to the ability of DIPE to extract dihydroxybenzenes adequately in plants designed to extract phenol. After treatment with the Phenosolvan process, the waters must normally be treated biologically to remove the last traces of the phenols. However, trihydroxybenzenes are known to be extremely resistant to biological oxidation (11), and, if present in the condensate waters, could prove very difficult to remove since their K_D's should be even lower than those for the dihydroxybenzenes.

D. Objectives of this Work

From the questions surrounding the condensate water compositions, the first objective of this work was formulated: to analyze representative coal-conversion process condensate waters for phenols, particularly the hydroxybenzenes. This would require the development of an analytical method to measure the concentrations of phenols in water solution directly.

Table 1-6. Equilibrium Distribution Coefficients (K_D) of Hydroxybenzenes Between DIPE and Water at 293°K[a]

Solute	K_D
phenol	28.9±1.7
catechol	4.2±0.2
resorcinol	1.9±0.1
hydroquinone	1.6±0.2

[a] from (9). Based on measurement of water phrase concentrations only, before and after equilibrium

The analytical method should also be suitable for routine analysis of single-solute phenolic solutions from the extraction studies to be performed in the second part of this work.

From the questions concerning polyhydroxybenzenes and the Phenosolvan Process, the second objective was formulated: to study the extraction of the various phenols themselves. Since phenols are weak acids, extraction from water should involve acid-base as well as distribution equilibria, and the effects of ionization of the phenols could be important in the alkaline condensate waters. Thus it was decided to measure the K_D's of some representative phenols in DIPE as a function of pH to develop an understanding of these two equilibria. DIPE was studied since any process developed must compete with the Phenosolvan process, which uses a DIPE solvent. Additional extraction experiments would then be made to find a better solvent than DIPE for recovery of phenols from water.

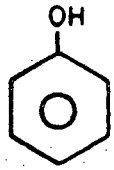
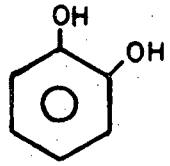
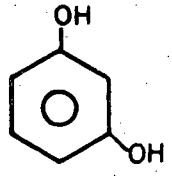
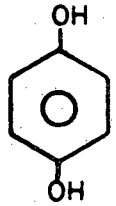
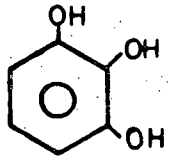
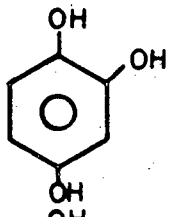
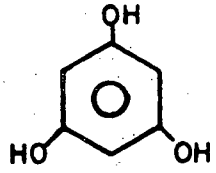
Among the phenols, interest centered about the polyhydroxybenzenes because of the questions about their biodegradability and extractability raised in the previous section. Also, data reported by Won (12), listed in Table 1-7, show that K_D's for methyl-substituted phenols are significantly higher than that of the parent phenol. The analytical-methods development and the solvent selection were directed towards the polyhydroxybenzenes, as they would be more polar and harder to extract. Table 1-8 lists the hydroxybenzenes studied and their structural formulas.

Table 1-7. Distribution Coefficients (K_D) for Phenols Between Water and Two Organic Solvents at High Dilution at 298.15°K[a]

Solute	Butyl Acetate	MIBK
3,5-dimethyl phenol	540	814
m-cresol	153	264
phenol	65	110
catechol	13.2	20.3
resorcinol	9.9	15.2

[a] values derived from (11)

Table 1-8. Common and IUPAC Names and Structural Formulas for Various Hydroxybenzenes

Common Name	IUPAC Name	Structural Formula
phenol	hydroxybenene	
catechol	1,2-dihydroxybenzene	
resorcinol	1,3-dihydroxybenzene	
hydroquinone	1,4-dihydroxybenzene	
pyrogallol	1,2,3-trihydroxybenzene	
hydroxyquinol	1,2,4-trihydroxybenzene	
phloroglucinol	1,3,5-trihydroxybenzene	

Chapter II. Experimental Procedure

A. Methods Development

A major problem with the process condensates was finding a reliable analytical method for the individual phenols. For the extraction studies, an analytical method was needed that did not require elaborate sample preparation, as each step increases the chance of error and lengthens the time required for analysis. Characterization of the process condensates could use more elaborate procedures, as fewer samples needed to be analyzed.

A.1. Gas Chromatography

Because of instrument availability and operating experience, gas chromatography was investigated first. Porapak^{R} porous polymeric packings, available from Varian, of Sunnyvale, California, were designed to separate polar organic compounds in water solution. Porapak Q, the least polar of the series, worked well for phenol itself and the methyl-substituted monohydroxybenzenes. But even when it was used at 240°C, near its temperature limit of 250°C, the dihydroxybenzenes eluted very poorly, giving a very low peak that tailed for hours. The column temperature of 240°C is still less than the boiling points of the dihydroxybenzenes, which range around 280°C.

Tenax-GC,^{R} also available from Varian, another porous polymeric packing similar to the Porapak packings but with a much higher temperature limit (375°C), was tried next. It behaved differently, retaining polar compounds less than Porapak Q. Compounds seem to be retained strongly until certain threshold temperatures are reached. This makes Tenax-GC better suited to separations using temperature programming than isothermal operation. This packing did not elute the dihydroxybenzenes at all, even at 350°C.

The dihydroxybenzenes did not elute, but the corresponding

dimethoxybenzenes eluted well. For qualitative analysis of the condensate waters, the methyl ether derivatives of the dihydroxybenzenes were made using dimethylsulfate. This procedure met with varying degrees of success. It did allow identification of the methyl ether derivatives of catechol (1,2-dihydroxybenzene) and 1,5-dihydroxy-2,3-dimethylbenzene using a gas chromatograph-mass spectometer (GC-MS). The methods used are described more fully in section B.1.

A.2. Liquid Chromatography

It was apparent that derivatization, followed by gas chromatography, would not be useful as a routine method of analysis. High-performance liquid chromatography (HPLC), however, is well suited to separations of nonvolatile materials. Separation is achieved by making use of the differences between the molecular interactions of the solutes within two immiscible liquid phases, one mobile and one affixed to a solid support.

The most basic HPLC instrument consists of a single high-pressure pump that pumps a constant-composition mobile phase through a chromatographic column and then a detector. Samples are injected into the mobile phase at the column inlet. This is known as an isocratic (constant mobile-phase composition) system.

A more useful system involves gradient elution. Two pumps pumping different miscible mobile phases are controlled to give a mixed mobile phase whose composition varies according to the program used by the solvent programmer. Gradient elution gives the same control over peak shape and retention time that temperature programming does in gas chromatography.

An isocratic system was used in this work, consisting of a Spectra Physics injection valve and Model 740 pump, a Waters Associates Model 27324 reverse-phase μBondapak^{R} C_{18} column 300 mm long and 3.9 mm in

diameter, and a Waters Associates Model 440 Ultraviolet Absorbance Detector operating at 254 nm.

There are two types of liquid-liquid chromatography. Normal-phase chromatography is when the fixed phase is polar and the mobile phase is nonpolar. In reverse-phase chromatography, the fixed phase is nonpolar and the mobile phase polar. The fixed-phase liquid can be either coated on the solid support or chemically bonded to it. The chemically bonded packings have the advantage that contaminants can be removed by solvent washes that would strip the fixed phase from a coated support.

Normal-phase HPLC is used to separate nonpolar compounds. The highly polar fixed phase accentuates the small differences in the polarity of the solutes. Nonpolar or slightly polar solvents like isooctane or dichloromethane are commonly used.

Reverse-phase HPLC is used to separate polar compounds. Here the fixed phase is nonpolar. Strongly polar solutes have higher affinities for the polar mobile phase than weakly polar or nonpolar solutes do, and have lower affinities for the nonpolar fixed phase than the weakly polar or nonpolar solutes do, and thereby elute first. Polar-solvent systems like methanol/water or acetonitrile/water are commonly used. If a polar column were used to try to separate polar solutes, the fixed phase-solute interactions would be so strong that the retention times would be too long.

With these ideas in mind, a Waters Associates μBondapak C_{18} bonded reverse phase column was selected to separate the phenols. The C_{18} columns are versatile reverse-phase columns and have been previously used to separate polynuclear aromatic hydrocarbons (PAH) (29) as well as phenols.

In HPLC, the nature of the mobile phase plays a much more important role than in GC. Instead of changing temperatures and columns to alter separations, as in GC, the mobile-phase composition is changed. In this work, the methanol/water system was chosen as the mobile phase to achieve separation on the reversed-phase column as methanol was more readily available, less expensive and less toxic than acetonitrile, which is often used because its mixtures with water possess a lower viscosity. The water portion of the mobile phase was processed by a Milli Q^R system, manufactured by Waters Associates, to remove particulates, organic and inorganic solutes by depth filtration, carbon adsorption and ion exchange, respectively. The spectral-grade methanol used was obtained from Matheson, Coleman & Bell, and was used as received.

Modern liquid chromatography has achieved high levels of performance through the use of small-size packing particles, typically 10 μm in diameter. Theoretical plate counts can be as high as 9000 theoretical plates per meter. Unlike some operating regimes of gas chromatography, the apparent plate counts of the peaks do not decrease with increasing mobile-phase flowrate, being only a weak function of flowrate. Higher flowrates will give faster analyses, but because of the small packing particle size result in high pressure drops which increase pump wear, pressure drops should be kept below about 200 atm. For trace analysis, slower flows are used which allow more time for detector response.

Care should be taken to keep the efficiency high and the pressure drop low. The column is packed at less than maximum density. Pressure surges can compress the packing, causing channelling and thereby irreversibly reducing column efficiency. Therefore mobile phase rates should not be changed at rates greater than 1 $ml \cdot min^{-2}$.

Similarly, mobile-phase composition should not be changed too quickly. Heat-of-mixing effects could cause the packing to shift, resulting in channelling. When one is changing mobile phases, a 50/50 mixture of the two should be used to flush the pump and then be pumped through the column until breakthrough occurs. For gradient-elution systems, a two-minute linear gradient would be sufficient .

Because of the small packing particle size, all samples and mobile phases had to be filtered to prevent column plugging. The mobile phases were degassed while being vacuum filtered. Degassing prevents bubble formation in the pump, which would stop mobile-phase flow, and bubble formation in the detector cell, which would cause an extremely noisy signal. Cellulose acetate filters with a 0.5 μm pore size were used to filter the aqueous mobile phases. As cellulose acetate is soluble in methanol and other organic solvents, all organic mobile phases were filtered with 0.5 μm fluorocarbon filters.

Samples were filtered through 0.5 μm fluorocarbon filters. Water does not wet fluorocarbon filters, so they had to be wetted first with methanol before the water samples would pass through the filters.

Solutes not eluted by the mobile phase would build up on the column when condensate water or pure-component samples were injected. These contaminants would degrade the separations. Column contamination was measured by its effect on the plate counts of the peaks and by changes in peak shape. Residence times were not greatly affected. If the peaks started tailing or became broader, the theoretical plate count was checked to see if it had decreased. Appendix B gives a sample calculation of the plate count using the 5 σ method.

The contaminants were removed from the column after each series

of analyses by a number of washing methods. First, to avoid sudden mobile-phase composition changes and to flush corrosive buffer solutions out of the pump, a 50 vol. % solution of methanol in water was pumped through the system. This was followed by a 100% methanol mobile phase that eluted most of the contaminants. If further washing was desired, four or five 2 ml injections of dimethylsulfoxide (DMSO) could be made into the pump suction while pumping methanol at 2 ml/min. The DMSO would remove polar contaminants from the column. The last DMSO injection was followed by a 50 ml methanol wash to remove the last traces of DMSO.

A number of precautions have to be observed when using DMSO. First, DMSO is rapidly absorbed through the skin, taking anything dissolved in it directly into the bloodstream. All of these phenols are toxic and the PAH's are carcinogenic so any DMSO already used to remove column contaminants could be hazardous. Second, DMSO has a high viscosity. If too large a slug is injected or the 2 ml portions are injected too close to one another, column pressure could surge, compressing the column packing and causing channelling.

Another method was used to remove the nonpolar contaminants. Following a series of analyses, the column was washed with an elutropic series of mobile phases, at flow rates of 2-3 ml/min. Mobile phases of different polarity could be added to the series, and different amounts of mobile phase might be needed, but the following series worked well to restore column efficiency: first 50 ml of water, followed by 100 ml of methanol, then 100 ml of dichloromethane, followed by 100 ml of n-heptane, and then back to methanol with 50 ml of dichloromethane followed by 50 ml of methanol. One thing to remember when washing with an elutropic series is that adjacent mobile phases must be completely miscible, with 50/50

mixtures used in between.

The importance and presence of the column contaminants was learned after a column had been irreparably damaged when the accumulated contaminants from a series of wastewater analyses remained on the column for a long time. Apparently enough oxygen was present in the mobile phase to allow oxidation of the phenols, producing an insoluble product that destroyed column efficiency and increased column pressure drop tremendously. The contamination could not be removed with DMSO or an elutropic mobile-phase wash.

The column is normally stored with a methanol mobile phase. If the column will not be used for an extended period of time, it should be removed from the instrument and stored as it was shipped, with a small bellows of methanol/water mobile phase attached to keep the column wet. If the column dries out, it will be ruined. The methanol/water mobile phase also prevents bacterial growth.

Several different detectors are currently available for HPLC use. Refractive index detectors will respond to almost any solute but are not as sensitive as ultraviolet (UV) absorbance detectors. These can be either fixed-wavelength or variable-wavelength. Most of the polyhydroxybenzenes have absorbance maxima near 280 nm, which is a fixed wavelength available with the Waters model 440 detector when the proper parts are installed. The wavelength used in the analyses for this work was 254 nm. The phenols absorbed sufficiently at 254 nm for the experiments performed. A variable-wavelength detector would be extremely useful, as interfering peaks could be removed by operating at different wavelengths.

Fluorescence detectors are also available. These are an order of magnitude more sensitive than the absorbance detectors, and are

useful in the analysis of PAH's, expected to be present in only trace quantities in the condensate waters.

Further information concerning column and mobile-phase selection and analytical techniques can be obtained elsewhere (14).

B. Condensate Water Analysis

Detailed experimental conditions and equipment used in the analysis of Synthane gasification and SRC liquefaction condensate waters are described in this section. The condensate waters were kept in cold storage at 4°C, away from light.

B.1. Analysis by Gas Chromatograph - Mass Spectrometer

As the phenols would not elute directly using gas chromatography, methyl ether derivatives were made using dimethyl sulfate $(CH_3)_2SO_4$ and NaOH by the procedure described for the synthesis of anisole (methyoxybenzene)(15). Because the phenols will oxidize under basic conditions in the presence of oxygen, the condensate water samples were nitrogen-sparged to remove dissolved oxygen before the NaOH was added. After reagent addition, the reaction mixture was refluxed overnight. Ammonia and low molecular weight amines were released from the condensate water samples by this procedure, as evidenced by a fishy smell and the high pH indicated by dampened pH test paper placed at the outlet of the reflux condenser (16).

After reaction, the mixture was extracted with ethyl ether to concentrate the methoxybenzenes. The ether extracts were analyzed on a Finnegan Model 4033 GC-MS (17) using a 10 m x 6.35 mm OV-101 column operated with a linear temperature program of 50°C for two minutes, 50° - 200°C at a rate of 5°C/min and then 200°C for 20 minutes. Peak identification was performed with the system's minicomputer.

An attempt was made to quantify the results by derivatizing pure-component water solutions of the phenols to get reaction yield. A GC equipped with a flame ionization detector was used, with external standardization.

B.2. Analysis by Liquid Chromatograph

Before filtration, 10 ml condensate-water samples were passed through C_{18} Sep-pak^{R} cartridges, available from Waters Associates, to remove nonpolar contaminants like grease and oil. Any hydroxybenzenes retained by the Sep-pak were eluted with 2 ml of water.

By trial and error, a mobile phase of 25 vol % methanol in water was found to separate the dihydroxybenzenes. The water was buffered to pH 3 with 0.005 M H_3PO_4 and 0.04 M KH_2PO_4 before addition of the methanol. This suppressed the ionization of the phenols and reduced peak tailing.

The trihydroxybenzenes were not adequately separated by this mobile phase, as shown in Figure 2-1. At this composition, pyrogallol (1,2,4-trihydroxybenzene) and hydroquinone (1,4-dihydroxybenzene) co-eluted. Pure water buffered to pH 3 did spearate the three trihydroxy-benzenes with some overlap of the phloroglucinol and hydroquinone peaks. At this composition, though, the remaining two dihydroxybenzenes co-eluted, as shown in Figure 2-2.

Short-chain organic acids are also found in these condensate waters (18,6). These have UV absorbance maxima near 208 nm. In an effort to separate the acids from the trihydroxybenzenes also expected to be present in the waters, a pH 7 buffered water mobile phase was tried. The pK_a's of the acids are around 4.5 to 5 while those of the phenols range from 9.8 to 10.3. At pH 7 the ionization of the phenols would be suppressed and that of the acids promoted, thereby

increasing the polarity difference of the compounds and their separation. It was found that the separation between phloroglucinol and hydroquinone suffered at pH 7 and that the organic acids did not absorb at the 254 nm wavelength used.

C. Equilibrium Measurements

C.1. Batch Extractions

Equilibrium distribution coefficients (K_D) were measured for polyhydroxybenzenes distributing between water and diisopropyl ether (DIPE), and between water and methyl isobutyl ketone (MIBK), in a series of pure-component batch extractions at 25°C. The effects of pH on these equilibria were studied by controlling the water phase pH with KOH.

As it was observed that basic water solutions of the phenols would darken and form precipitates when exposed to air, the extractions were performed under nitrogen in magnetically-stirred glass bottles sealed with serum stoppers. The water and the solvent were nitrogen-sparged to remove dissolved oxygen and saturated with each other before the solutes were added. Syringes were used to transfer feed solutions into the nitrogen-purged extractor bottles and to withdraw samples for analysis.

Acidic water solutions of phenols did not darken and degrade, except for the trihydroxybenzenes, which did, albeit slowly. As a result, extractions performed at low pH, except for the trihydroxybenzenes, were not performed under nitrogen. Water-phase samples of the higher pH extractions and those from the trihydroxybenzene extractions were acid-preserved with the addition of a few drops of 6 M HCl.

After extraction, three samples were taken: organic-phase and water-phase samples, both for solute concentration measurement, and a water-phase sample for pH measurement. The 10 ml pH sample was diluted

with 20 ml of distilled water for ease of measurement on a Corning Model 12 Research pH Meter previously calibrated in the expected pH range of the sample with standard buffer solutions. The change in pH with dilution was small in most cases, as shown by calculations in Appendix C. Corrected pH's are reported in this work. The other samples were diluted for ease of measurement or acid preservation of the sample.

The feed concentrations, along with the equilibrium phase concentrations, were measured and used to calculate a solute material-balance closure error that gave an indication of the accuracy of the results. As both phases were saturated with each other before solute addition, the difference in total phase weight before and after extraction due to changes in solvent-water mutual solubility caused by the solute were minimized, making the material balance calculation more accurate. The details of this calculation are described more fully in Appendix A.

The solvents used in the extractions were purified before use. DIPE was distilled to remove peroxides and a heavy, UV-absorbing oxidation inhibitor, most likely hydroquinone. The distilled DIPE was stored at 4°C over water to help prevent peroxide formation. For the phenol extractions, 1000 ppm of hydroquinone was added to the DIPE as an inhibitor. For the polyhydroxybenzene extractions, it was found that storage at 4°C over water was sufficient by itself to prevent peroxide formation. Peroxides would be a problem as they would oxidize the polyhydroxybenzenes as well as presenting a safety hazard.

After distillation, the DIPE was extracted with water to remove the light impurities, mostly 2-propanol. Water extraction was also used to remove the light components from the MIBK. After these treatments, the solvents were analyzed by GC and estimated to be about 99.9 wt. % pure.

C.2. Phenol Equilibria for DIPE/Water

For phenol distributing between DIPE and water, a K_d of approximately 40 was expected (12). For the first few extractions, a synthetic wastewater containing about 10,000 ppm phenol was extracted. To leave a phenol concentration in the water phase high enough to be easily measurable and be near the level found in the coal-conversion process condensates, 40 ml of water was extracted by 10 ml of DIPE. Later extractions had the phenol dissolved in the DIPE feed, as less solute was transferred between phases, and measurement errors were reduced by dealing with more concentrated solutions.

The samples were analyzed with a Varian 1740 gas chromatograph, equipped with a flame ionization detector (FID) and a 2.4m x 3.175 mm column packed with Porapak Q. The column temperature was maintained at 240°C. The helium carrier gas and hydrogen flows were set at 25 ml/min, with air flow at 250 ml/min.

The samples were collected in tared bottles containing a weighed amount of 95% ethanol. The ethanol reduced the volatility of the DIPE dissolved in the water phase enough to prevent loss. In the DIPE phase, the ethanol diluted the phenol concentration to a level easier to measure, Water-phase samples were preserved with HCl.

Concentrations were calculated from the peak areas using the methods of internal standardization as described elsewhere (19,13). Experimentally determined FID factors for phenol (1.42), DIPE (1.14) and the internal standard MIBK (1.20), based on an assumed FID factor of 0.99 for methyl ethyl ketone, were used in the analysis.

C.3. Polyhydroxybenzene Equilibria for DIPE/Water and MIBK/Water

The polyhydroxybenzenes, being of low volatility, were analyzed by

liquid chromatography. The procedures used differed for the two solvents studied, DIPE and MIBK. In both cases, however, external standards were used and the sample concentrations were calculated using peak areas and Beer's Law, shown to be valid for the solutes experimentally. All samples were filtered and were acid preserved, except for the samples from the low-pH dihydroxybenzene extractions.

The differences between the DIPE and MIBK extractions center around the organic-phase analysis. In liquid chromatography the samples must be miscible with the mobile phase. In the MIBK extractions this was achieved by diluting the organic-phase sample by a factor of about 20 by weight into a 50 vol. % solution of methanol in water. However, for the DIPE extractions, the K_d's were low enough that a diluted sample would be too dilute to be measured. Also, the water solubility of DIPE is lower than that of MIBK, making dilution more difficult.

The DIPE samples were injected directly. Good repeatability was observed. A separate ether-solution standard of the solute had to be used as the absorbance of the solutes depended on the sample solvent. The ether absorbances were lower. This bathochromic shift is probably due to increased association with water molecules in the water-phase samples. The ether-phase peaks tailed more also, but this was not a problem.

The mobile phase used in the extraction analyses consisted of a 25 vol. % solution of methanol in pH 3 buffered water. A H_3PO_4/KH_2PO_4 buffering system was used, with concentrations of 0.005 M and 0.04 M respectively. This mobile phase composition would effectively separate all the dihydroxybenzenes from each other but would not separate the trihydroxybenzenes. This was not a problem as the extractions were carried out in single-solute systems, and resulted in fast analyses.

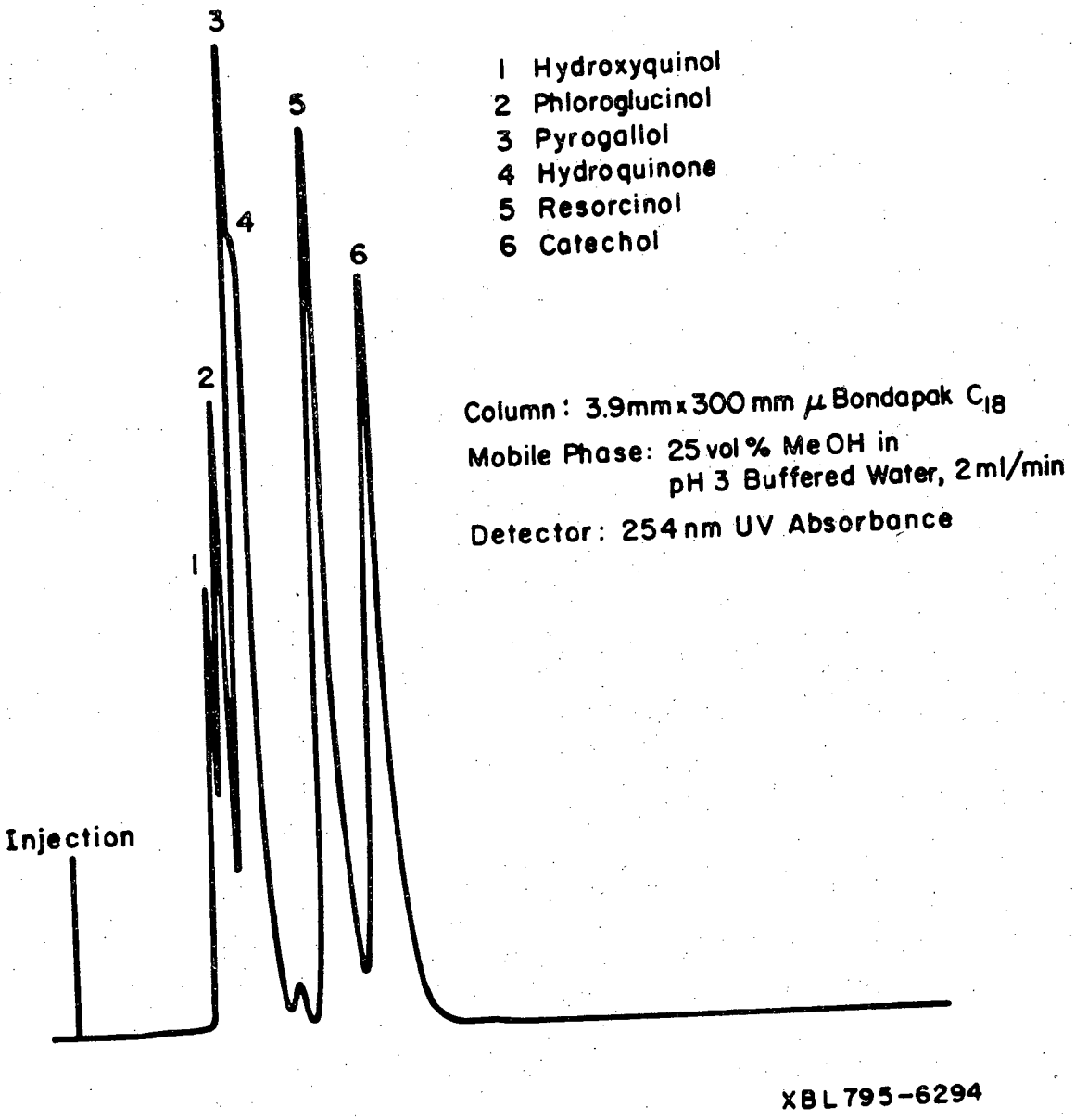


Figure 2-1. Liquid Chromatogram of Polyhydroxybenzene Mixture, Methanol/Water Mobile Phase

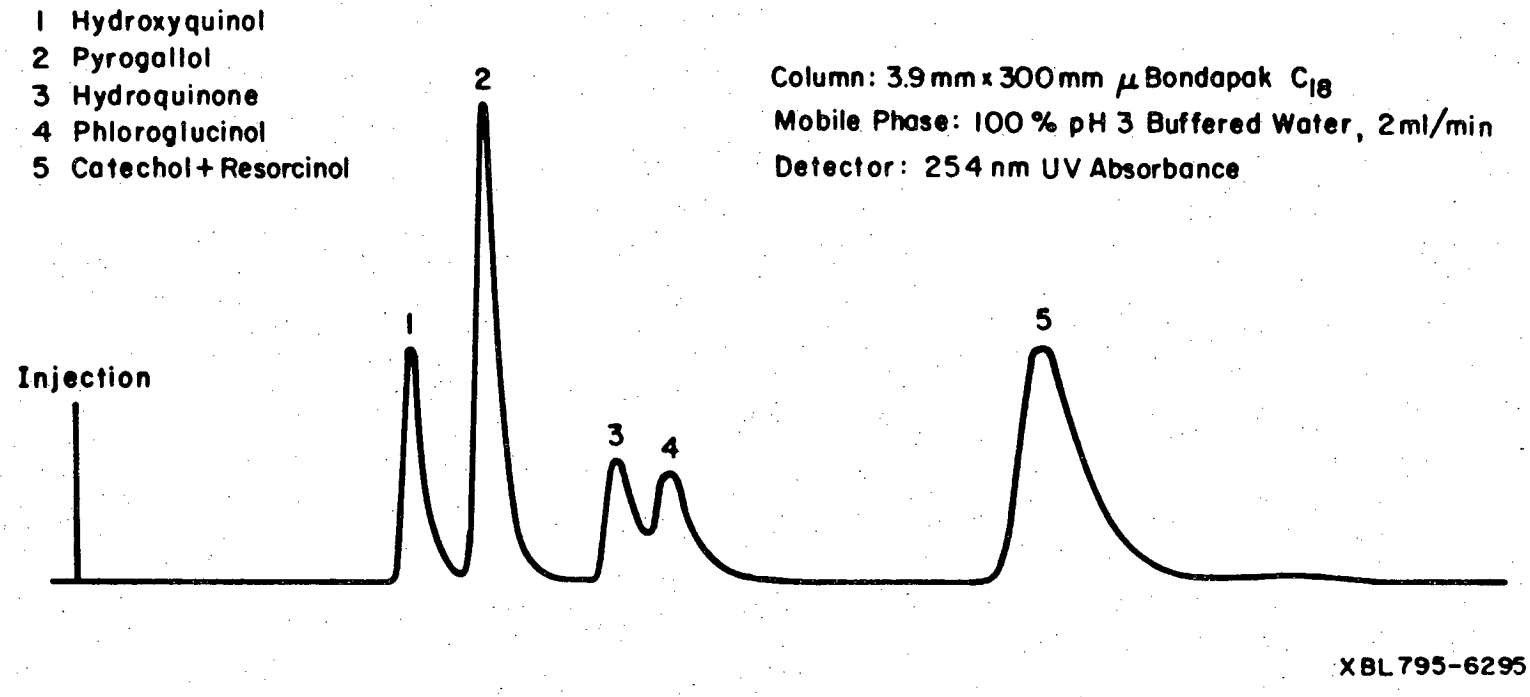


Figure 2-2. Liquid Chromatogram of Polyhydroxybenzene Mixture, 100% Water Mobile Phase

Chapter III. Water Analysis and Discussion

In this chapter the analyses of two coal-conversion process condensate waters for phenols will be presented.

A. Water Sample Sources and Ages

A condensate water sample from the Synthane gasification process being developed by the Department of Energy (DOE) at the Pittsburgh Energy Technology Center (PETC) was chosen as typical of the lower-temperature gasifiers which tend to produce highly contaminated waters. As typical of the liquefaction processes, water samples from the Solvent Refined Coal (SRC) process were obtained from the pilot plant in Ft. Lewis, Washington. SRC is being developed jointly by the Pittsburgh and Midway Coal Company and DOE.

To help prevent degradation, the samples were kept in cold storage at 4°C, away from light and air. The Synthane water sample, from run #40-CHMP-317, was received on December 12, 1977, after approximately one month in transit. The analysis of the sample by GC-MS was performed on March 10, 1978, when the sample was about four months old.

The SRC water, Sample #1003, from the Recycle Process Water Tank, was taken on November 17, 1977. It was analyzed by GC-MS on March 30, 1978, when the sample was about four and one-half months old. Analysis for dihydroxybenzenes by HPLC was performed on August 17, 1978, when the sample was nine months old. On March 19, 1979, the sample was analyzed by HPLC for trihydroxybenzenes. The sample was sixteen months old at that point.

B. Gas Chromatographic - Mass Spectrometric (GC-MS) Analysis

As described in Chapter 2, the condensate water samples were derivatized

and analyzed by GC-MS. Samples of the computer output for a methylated Synthane water are presented in Figures 3-1 and 3-2 and Table 3-1. The reconstructed gas chromatogram in Figure 3-1 is useful in locating peaks for comparison with chromatograms from other GC's with different detectors. This was important for quantification of the results, as the quadrupole mass analyzer in the MS used does not give quantitative information. The peak sizes on the reconstructed chromatograms did give a rough idea of the relative abundance of the components.

Table 3-1 shows the results for the largest peak in Figure 3-1. The five compounds in the library whose spectra best fit the spectrum of the peak are listed. The numbers in the columns under PURITY, FIT and RFIT are statistical measures of the fit between the compound listed and the peak. The closer all three numbers are to one thousand, the better the fit.

Figure 3-2 shows the mass spectrum of the same peak compared with the spectrum of the most likely fit, 1,2-dimethoxybenzene, the methyl ether derivative of catechol. Note that the peaks in the plot of the algebraic difference of the two spectra are small, indicating a good fit.

The other major peaks in the methylated Synthane condensate water were identified similarly, and are listed in Table 3-2. Results for the methylated SRC condensate water are listed in Table 3-3. The reconstructed chromatograms and statistical fit data are contained in Appendix D.

The results listed in the two Tables 3-2 and 3-3 have an important qualifier: the mass spectra of some of the structural isomers of the methoxybenzenes are quite similar. Indentification of the class of compound is definite, but its exact identity is not. For example, the

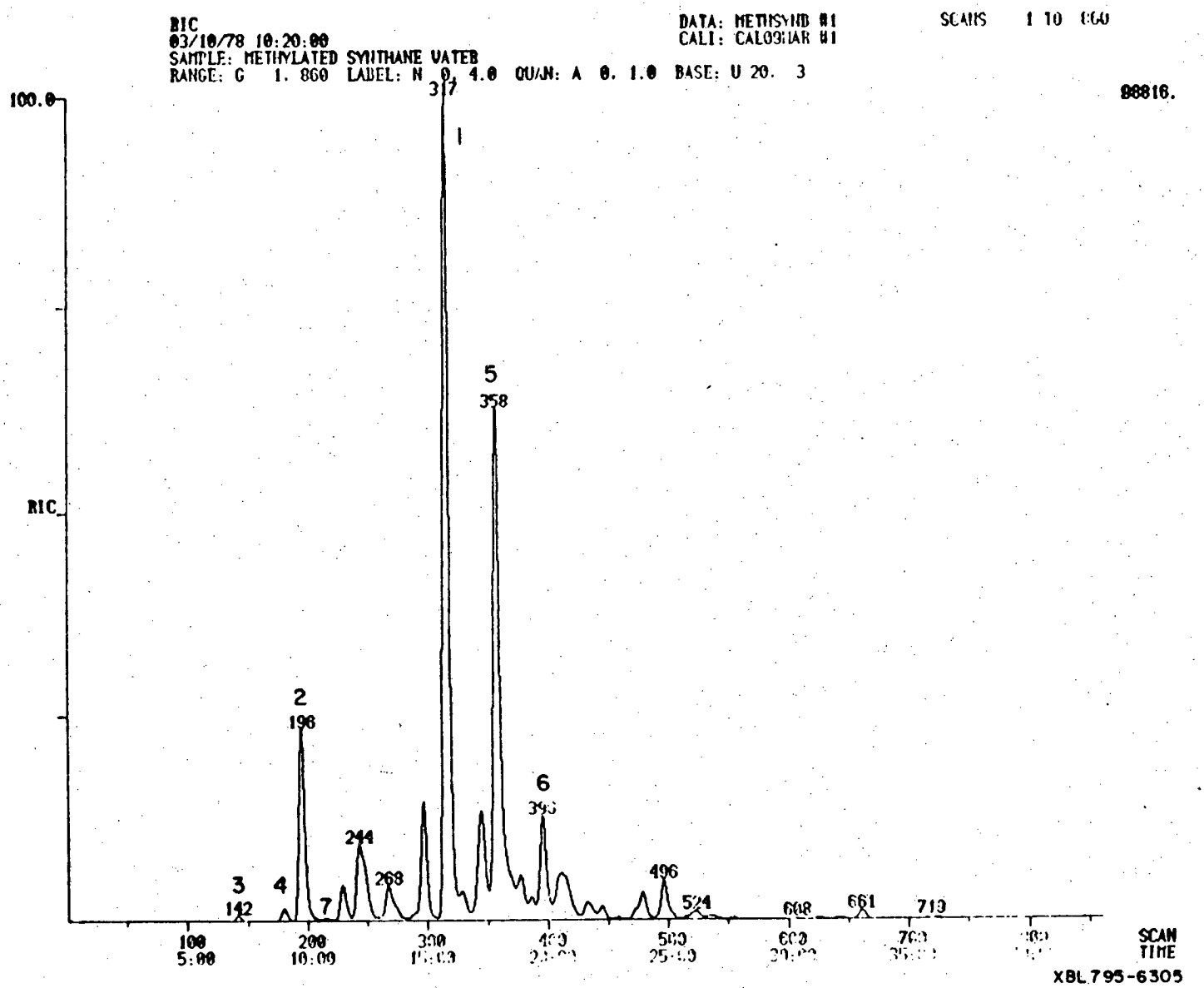


Figure 3-1. Computer-Reconstructed Gas Chromatogram of Methylated Synthane Water (see Table 3-2 for explanation of peak numbers)

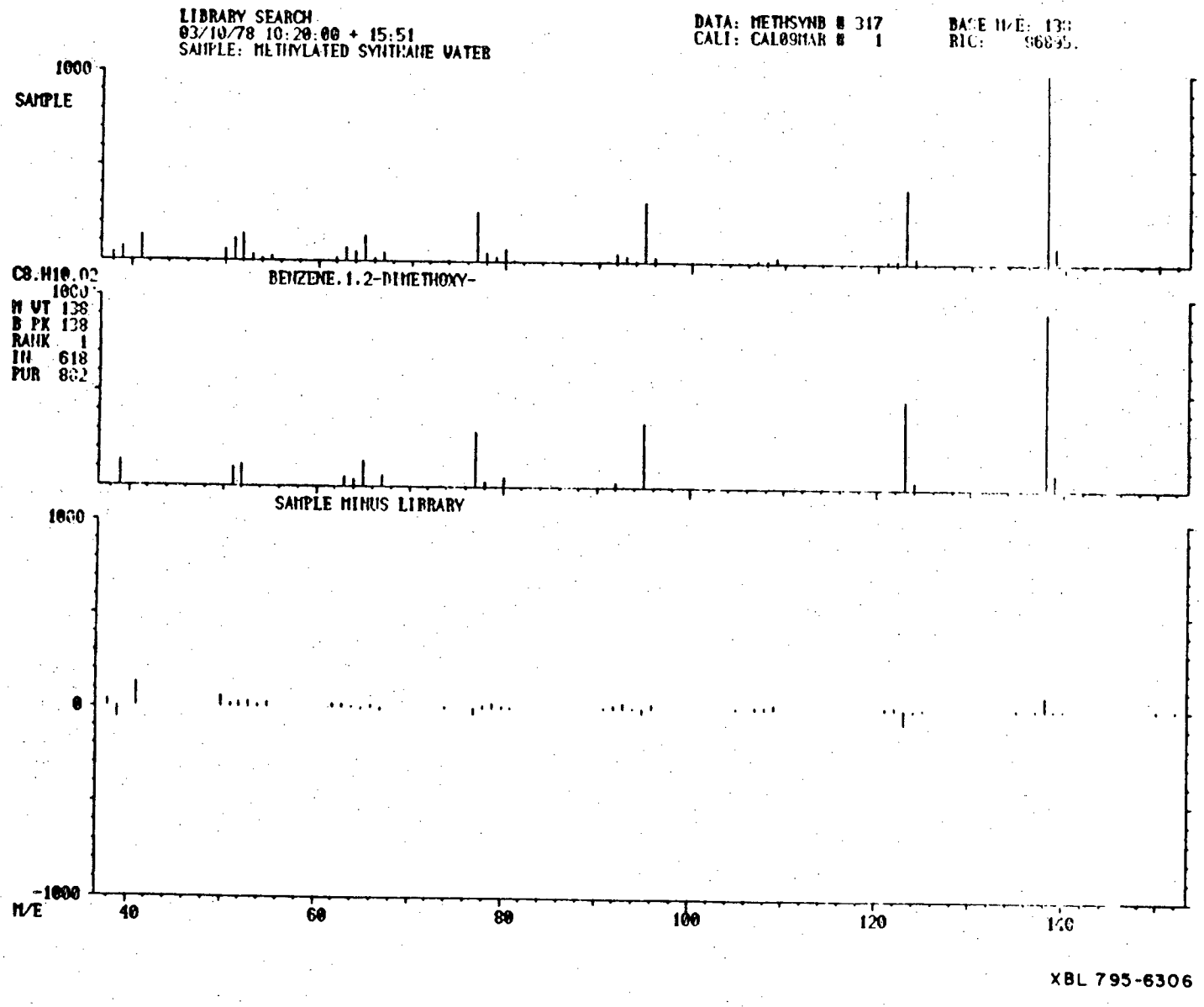


Figure 3-2. Mass Spectra Comparison: 1,2-Dimethoxybenzene and Methylated Synthane Water Peak #317

Table 3-1. Mass Spectra Comparison: Methylated Synthane Water Peak #317 with Five Best Statistical Fits

LIBRARY SEARCH DATA: METHSYNB • 317 BASE M/E: 138
03/10/78 10:20:00 + 15:51 CALI: CAL0[illegible]MAR • 1 RIC: 96895.
SAMPLE: METHYLATED SYNTHANE WATER

25409 SPECTRA IN LIBRARY[illegible]B SEARCHED FOR MAXIMUM PURITY
129 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	IN[illegible]	NAME
1	61[illegible]	BENZENE,1,2-DIMETHOXY-
2	1789	BENZENE,1,4-DIMETHOXY-
3	4272	2-[illegible]ONE,1-[illegible]YLIDENE-
4	1791	BENZENE,1,3-DIMETHOXY-
5	24[illegible]	[illegible]

RANK	FORMULA	M.WT	B.PK	PURITY[a]	FIT[a]	RFIT[a]
1	C8.H10.O2	[illegible]	[illegible]	[illegible]	934	682
2	C8.H10.O2	[illegible]	123	835	908	806
3	C9.H1[illegible].O	[illegible]	[illegible]	5[illegible]	853	741
4	C8.H10.O2	[illegible]	139	665	908	665
5	C10.H18	138	138	664	834	690

MASS	INTEN[b]	1[c]	2[c]	3[c]	4[c]	5[c]
38	37					
39	71	139		95		65
41	133		173	82		123
43				308		
50	56					
51	113	93	58			
52	140	114	81		89	
53	34		56	46		37
54	12					
55	28			77		65
62	17					
63	70	51	93		60	
64	40	39	92		49	
65	132	134	80		68	
66	13					
67	45	59		110		53
68						25
69						21
74	9					
77	257	208	52	51	56	23
78	41	27			121	
79	26		30	117	45	33
80	63	48	50	279	43	
81	8			101		191
82						51
91	3					
92	41	25	50		51	
93	31				46	
94	8					26
95	313	336	311	262	170	303
96	22					66
105	4					
107	15				43	
108	12				105	
109	26			90	173	
110				63		
121	14					
122	17					
123	397	452	767	455		387
124	31	36	60			
125	2					
135	6					
136	0					
137	4					
138	1000	927	537	839	972	446
139	80	84	45	111	115	49
140	6					
150	3					
152	2					

[a] statistical fit parameters

[b] peak intensities of unknown

[c] peak intensities of library compounds

Table 3-2. Qualitative Analysis of Methylated Synthane Water by GC-MS

Peak Number[a]	Compound	Parent Phenol	Certainty of Fit
1	1,2-dimethoxybenzene	catechol	good
2	1-methoxy-4-methylbenzene or 1-methoxy-3-methylbenzene	p-cresol m-cresol	both fix well, p-cresol slightly better
3	methoxybenzene	phenol	good
4	1-methoxy-2-methylbenzene	o-cresol	good
5	5-methoxy-2,3 dimethylphenol	1,5-dihydroxy-2,3-dimethylbenzene (dimethyl resorcinol)	fair
6	3-methoxy-2,4,6-trimethylphenol	1,3-dihydroxy-2,4,6-trimethylbenzene (trimethyl resorcinol)	fair
7		2-ethyl-5-methyl phenol	fair

[a] corresponds to peak numbers on Figure 3-1.

Table 3-3. Qualitative Analysis of Methylated SRC Water by GC-MS

Compound	Parent Phenol	Certainty of Fit
1,2-dimethoxybenzene	catchol	good
1-methoxy-1-methylbenzene	p-cresol	good
methoxybenzene	phenol	good
5-methoxy-2,3-dimethylphenol	1,5-dihydroxy-2,3-dimethyl benzene	fair

methyl ether derivatives of all three of the cresols make a good match to the peak reported as the methylation product of p-cresol in Table 3-2, yet the fit to the methyl ether derivative of p-cresol is a little better than the others.

Attempts were made to quantify the results listed in Tables 3-2 and 3-3. To obtain yields for the methylation reaction, pure, single-component water solutions were methylated and analyzed by GC. However, the yields in the complex condensate waters were not consistent with those in pure solution. In particular, the yield for the reaction producing anisole from phenol was very low in condensate water, yet very high in the single-component solutions. In the condensate waters, the dimethoxybenzene peaks were much larger than the anisole peak, yet of the phenols, phenol itself was present in the highest concentration, as shown by direct GC injection of the condensate water (phenol will elute) and by HPLC analysis presented in section C of this chapter. Although direct methylation of the condensate waters did not allow quantitation of the phenolic constituents, it did give qualitative identification very useful in confirming the results presented in the next section.

C. High-Performance Liquid Chromatographic (HPLC) Analysis

After the GC-MS analysis of the methylated condensate waters had been completed, the repeated exposure to air had degraded the Synthane water sample to the point where it was no longer useful. While the dark coloration could be caused by a small percentage of the solutes degrading to highly-colored compounds, large amounts of a dark precipitate formed also. This occurred, even with cold storage of the sample, by the time the Synthane sample was eight months old.

The degradation of the process condensate waters with increasing age

is most likely by reaction with atmospheric oxygen. The high concentrations of ammonia and phenols would be toxic to the bacteria necessary for biological oxidation. The polyhydroxybenzenes are not likely to be oxidation products of the other phenols. The dihydroxybenzenes catechol and hydroquinone are easily oxidized to o- and p-quinones, respectively. The other phenols also react via a free-radical mechanism to form highly conjugated, colored compounds (27, 28), observed here to have limited water solubility.

The SRC water, however, had not darkened, but appeared to be stable even when not kept cold. The SRC water was also fouler than the Synthane water, having a higher hydrogen sulfide content and a higher pH. HPLC confirmation and quantitation of the results obtained from the GC-MS proceeded with the SRC condensate water.

Initially the water was analyzed only for the dihydroxybenzenes. The dihydroxybenzene, phenol and cresol peaks were identified by matching retention times with a standard solution of the pure compounds. Concentrations were calculated from the peak areas of the sample and the standard using Beer's law.

There were a few problems with this initial analysis. The peak for catechol overlapped with others, preventing positive identification and quantification. Resorcinol was found in the SRC water by HPLC, yet the methyl ether derivative of resorcinol was not found in either methylated water. This could be due to a yield problem in the methylation of resorcinol by dimethyl sulfate, similar to the problem with phenol. The three cresol isomers were not resolved by the mobile phase used, 25 vol. % methanol in water, so an approximate concentration could be assigned to them by assuming them to be present in the same ratio as in the

standard and reporting the results as total cresols. As was explained in Chapter 1, as the cresols are less polar than phenol, they will be more easily extracted and therefore were of less interest in this work.

After the presence of the dihydroxybenzenes in the condensate waters had been confirmed and their extraction behavior studied, the SRC water was then analyzed for trihydroxybenzenes. The trihydroxybenzenes oxidize even more rapidly than the dihydroxybenzenes when in basic solution and exposed to oxygen. One would expect that their half-lives in the condensate waters might be very short, leaving nothing to analyze in an old sample. However, the same could be said for the dihydroxybenzenes with respect to phenol, yet the SRC water appeared stable. Thus it was decided to analyze the SRC water for trihydroxybenzenes. The concentrations found might not reflect those in a fresh sample, but the fact that they were present at all would be important.

One problem with the analysis for dihydroxybenzenes was not apparent until later when the SRC water was analyzed for trihydroxybenzenes. The mobile phase first used, 25 vol. % methanol in water, would not separate hydroquinone from phloroglucinol. The later analysis used a 100% water mobile phase which did resolve these peaks, revealing that a peak earlier identified as hydroquinone was in fact phloroglucinol, confirmed by spiking and matching retention times. The other trihydroxybenzenes were not observed.

Figures 3-3 and 3-4 are sample chromatograms of the SRC water. The quantitative results of the analysis are presented in Table 3-4. The phenol concentration is in line with that reported for SRC condensate in Table 1-2. The presence of the trihydroxybenzene phloroglucinol is quite

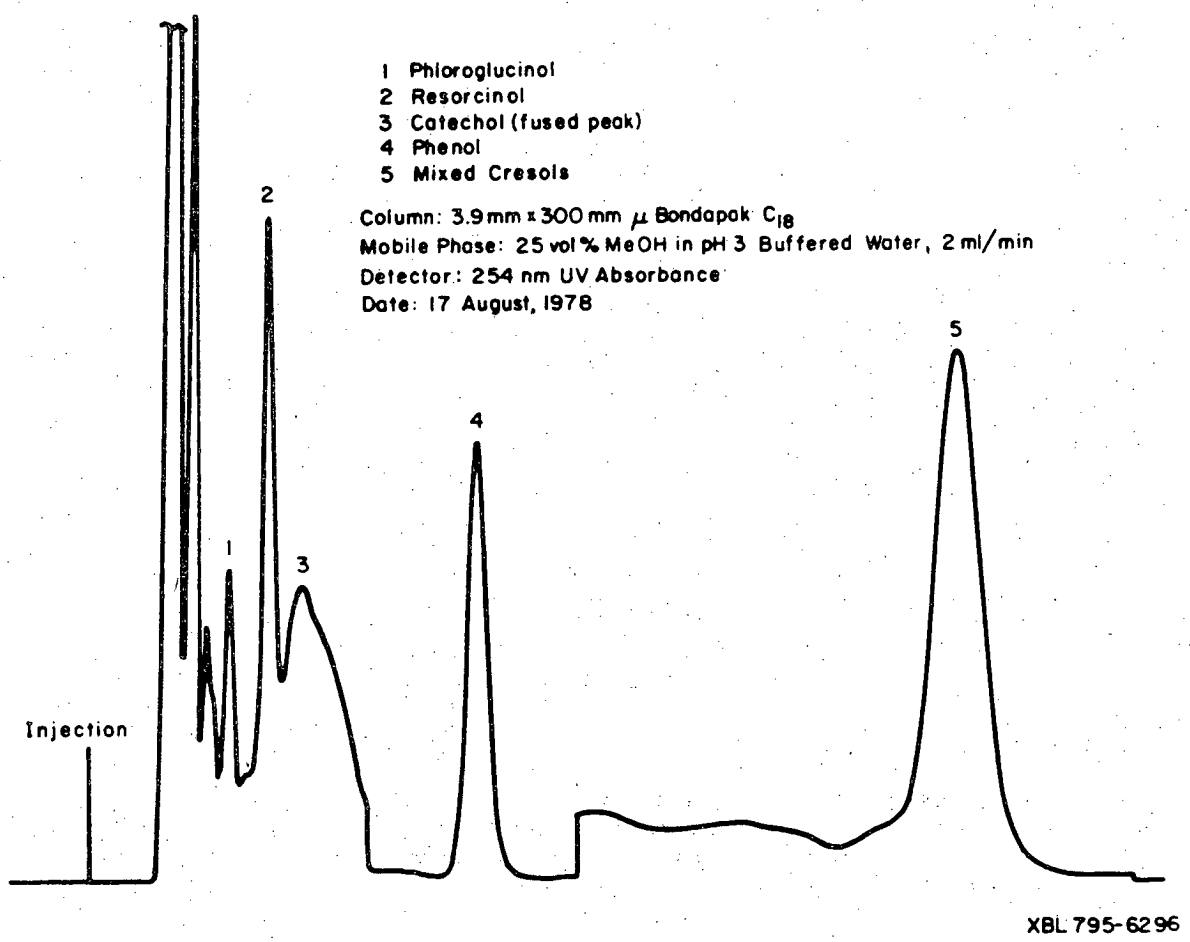


Figure 3-3. Liquid Chromatogram of SRC Condensate Water, Methanol/Water Mobile Phase

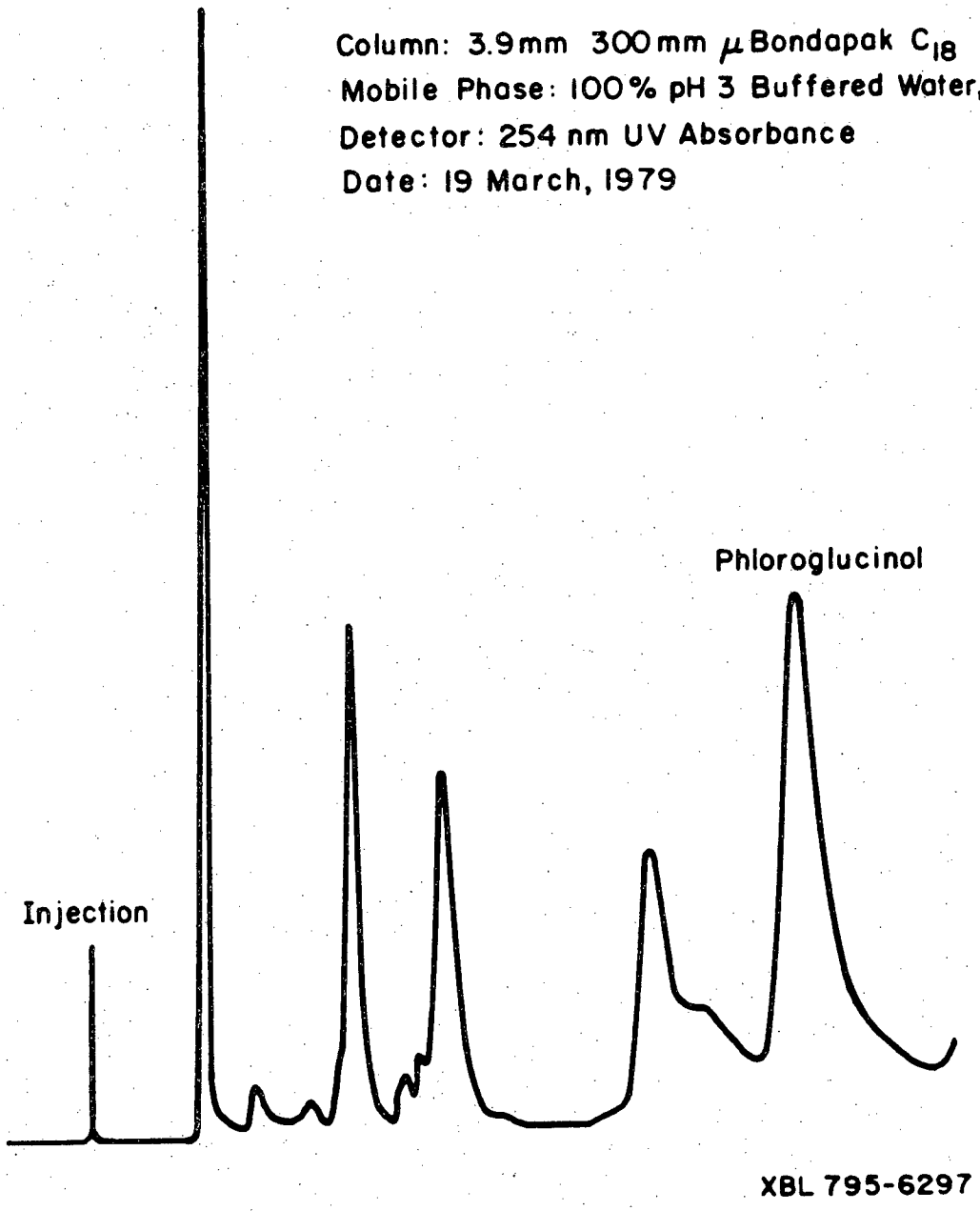


Figure 3-4. Liquid Chromatogram of SRC Condensate Water, 100% Water Mobile Phase

Table 3-4. Quantitative Analysis of SRC Condensate Water by HPLC

Compound	Concentration, ppm
phenol	6700
cresols	2850
resorcinol	2360
phloroglucinol	610[a]

[a] analysis five months later than others

important, as previous works (2,3,5,6,7) had made no mention of trihydroxybenzenes, except to note their strong resistance to biological oxidation (10). The presence of trihydroxybenzenes makes a strong case for solvent extraction or some other recovery process to remove the phenols from the condensate waters, as other destructive removal methods such as ozonation have yet to be proven and are expensive.

With the presence of one of the dihydroxybenzenes and one of the trihydroxybenzenes confirmed, one would expect to find the other isomeric polyhydroxybenzenes present also. The fact that the analyses performed did not detect the other polyhydroxybenzenes does not necessarily imply their absence in the condensate waters. With the GC-MS analysis of the methylated waters, reaction yield problems probably occurred in the methylation of the phenols by dimethyl sulfate, similar to the problem with phenol, preventing methyl ether formation and subsequent identification by GC-MS. With the direct HPLC analysis of the SRC water, the samples had aged to the point where phenols present initially could have oxidized significantly, preventing their identification or reducing the levels found. The SRC water had not darkened, but did have a yellow color similar to that of an oxidized solution of hydroquinone, which could be one reason why no hydroquinone was found by HPLC. With the complex chemistry of these process condensate waters, speculation about reasons for the absence of certain phenols and the presence of others is very difficult. Now that suitable analytical methods have been developed, the problem of the condensate water compositions can be more thoroughly investigated with the freshest possible samples.

Chapter IV. Batch Extraction Results and Discussion

A. Extraction Model

Phenols are weak acids. Extraction of phenols from water solution will therefore involve two equilibria: one in the water phase between ionized and nonionized phenol, and the other between the nonionized phenol in both liquid phases. Ionization constants at high dilution for the hydroxybenzenes of interest are listed in Table 4-1. No data were found for hydroxyquinol. As the available data did not include values at 25°C for all of the hydroxybenzenes, some values were interpolated using the van't Hoff equation:

$$\frac{d \ln K_a}{d(1/T)} = \frac{-\Delta H_r}{R} \qquad (4\text{-}1)$$

The second equilibrium is described by the distribution coefficient K_D. The two equilibria combine to give the following result (30):

$$K_D, \text{ apparent} = \frac{K_D, \text{ true}}{\frac{K_a}{[H^+]} + 1} \qquad (4\text{-}2)$$

At low pH, where the phenol is essentially completely nonionized, the apparent K_D is equal to the true K_D. As the pH increases, the effects of ionization will become more important. Near the pK_a of the phenol, K_D, apparent will be decreased to half that of the low pH value, and at higher pH will approach zero.

This behavior is significant, as the pH of the coal-conversion process condensate waters is near the pK_a's of the phenols, due to dissolved, ammonia. Because of the large amounts of carbon dioxide also dissolved, the waters are highly buffered, so unless the waters are first stripped to remove the dissolved gases, the pH cannot be altered without the

Table 4-1. Weak-acid Equilibria of Hydroxybenzenes at High Dilution[a]

Compound	T°C	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}
phenol	25	1.05×10^{-10}	9.98		
catechol	20	1.41×10^{-10}	9.85		
	25 [b]	3.31×10^{-10}	9.48		
	30	7.50×10^{-10}	9.12	8.37×10^{-13}	12.1
resorcinol	20 [b]	1.55×10^{-10}	9.81		
	25 [b]	3.36×10^{-10}	9.47		
	30	7.11×10^{-10}	9.15	4.78×10^{-12}	11.3
hydroquinone	20 [b]	4.47×10^{-11}	10.3		
	25 [b]	7.45×10^{-11}	10.1		
	30	1.22×10^{-10}	9.91	9.18×10^{-13}	12.0
pyrogallol	25	9.67×10^{-10}	9.01	2.30×10^{-12}	11.6
phloroglucinol	25	3.56×10^{-9}	8.44	1.32×10^{-9}	8.88

[a] from (20).

[b] interpolated (see text)

addition of large volumes of chemicals at great expense. For example, a 10 ml sample of SRC condensate water required one gram of hydrogen chloride to change the pH from an initial value of 9.1 to 5, the endpoint where the carbonate evolved as carbon dioxide. At a current bulk anhydrous hydrogen chloride price of $0.17/kg (21), this corresponds to an acid cost of $17/m^3 ($65/1000 gal) of condensate water. Less expensive sulfuric acid, at $0.064/kg in bulk, (21) gives an acid cost of $8.70/m^3 ($33/1000 gal) of condensate water, and generates a sludge disposal problem in the subsequent lime treatment step prior to ammonia stripping. As a general rule, the chemical cost for wastewater treatment should not exceed 10% of the total treatment cost. The cost of these acids alone far exceeds the total cost for a reasonable condensate water treatment process. Aside from the high chemicals cost, addition of ions to control pH must be discouraged as it would compound the dissolved-solids removal problem for both recycle and effluent waters.

B. Controlled-pH Extraction Results and Discussion

Figures 4-1, 4-2, 4-3, and 4-4 present the results of the four extraction series where the water-phase pH was varied. Aside from a few spurious data points in the phenol extractions, all of the data fall close to the curves predicted by Equation 4-2, when the equation is fit to the K_D measured at low pH and K_a is taken from Table 4-1. The effects of activity coefficients known to be different from unity in ionic solutions are ignored in this simple model. This does not introduce error into the results of the controlled-pH extractions as the ionic strengths of the water phase were low enough that the small effects of activity coefficient could not be detected with the analytical methods used. There could also be a cancellation in the weak-acid equilibrium

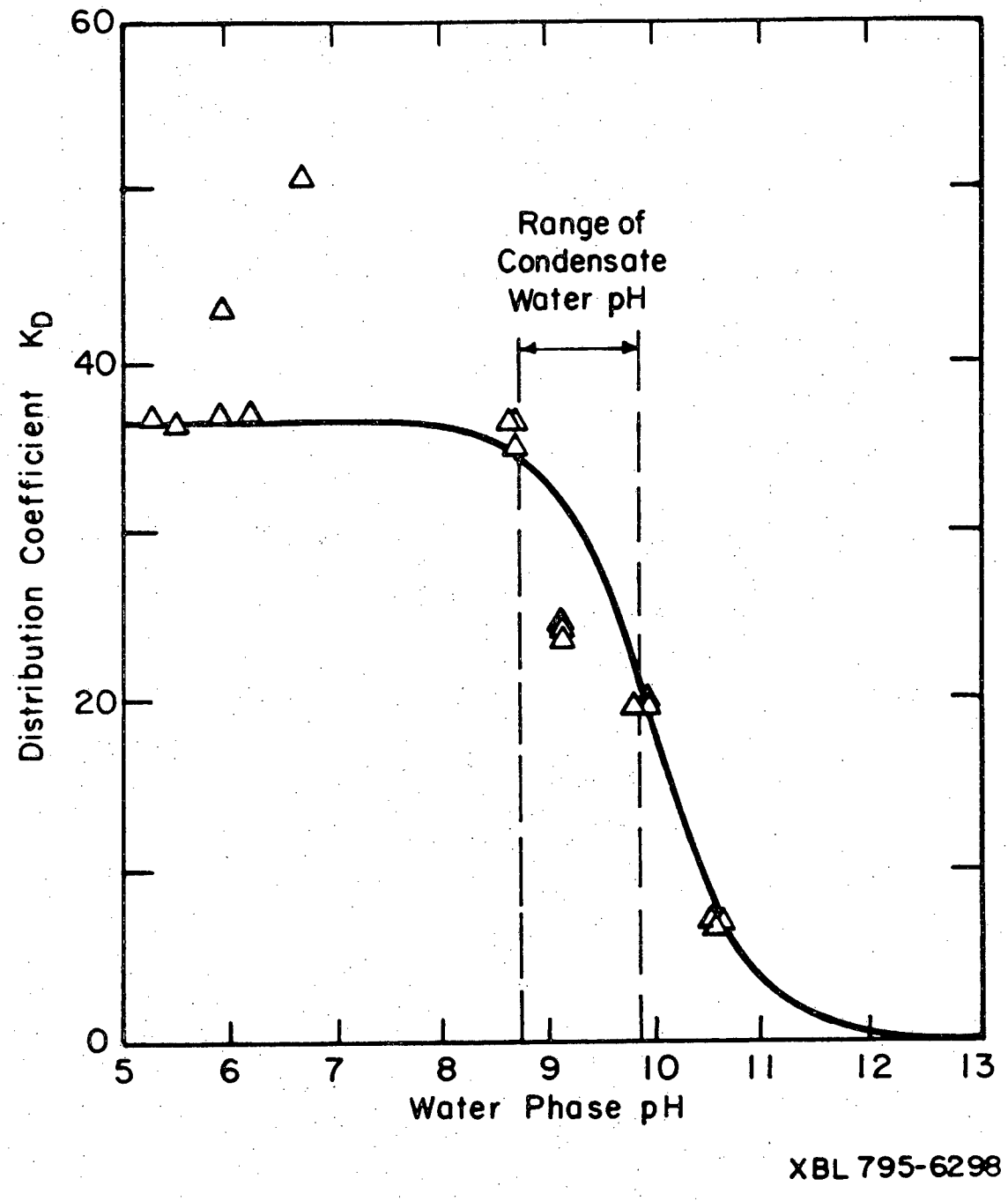


Figure 4-1. Distribution Coefficient for Phenol Between Diisopropyl Ether and Water as a Function of pH at 298°K. Curve from Equation 4-2 with K_D=36.5, K_a=1.05x10^{-10}.

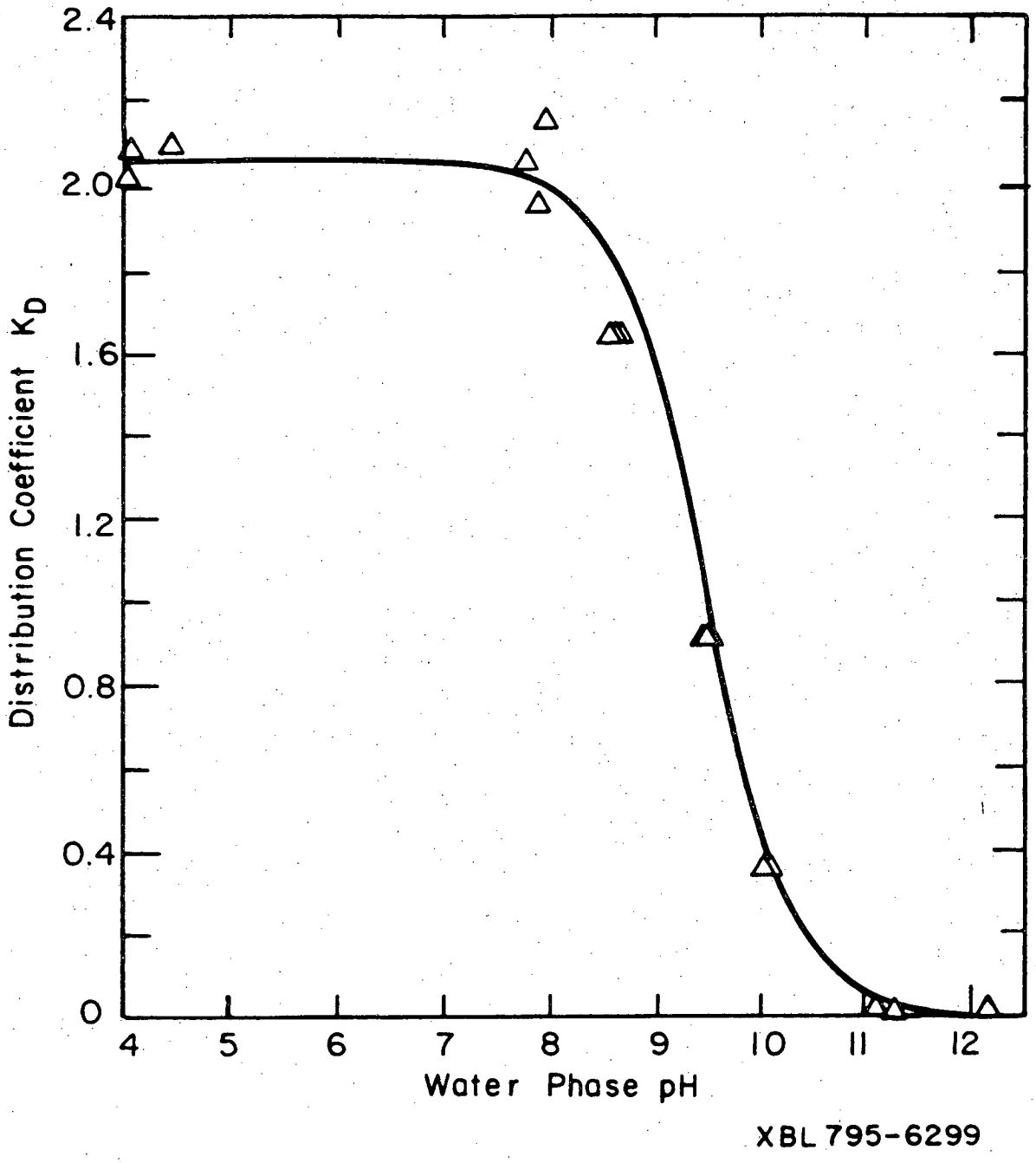


Figure 4-2. Distribution Coefficient for Resorcinol Between Diisopropyl Ether and Water as a Function of pH at 298°K. Curve from Equation 4-2 with K_D=2.06, K_a=3.36x10^{-10}.

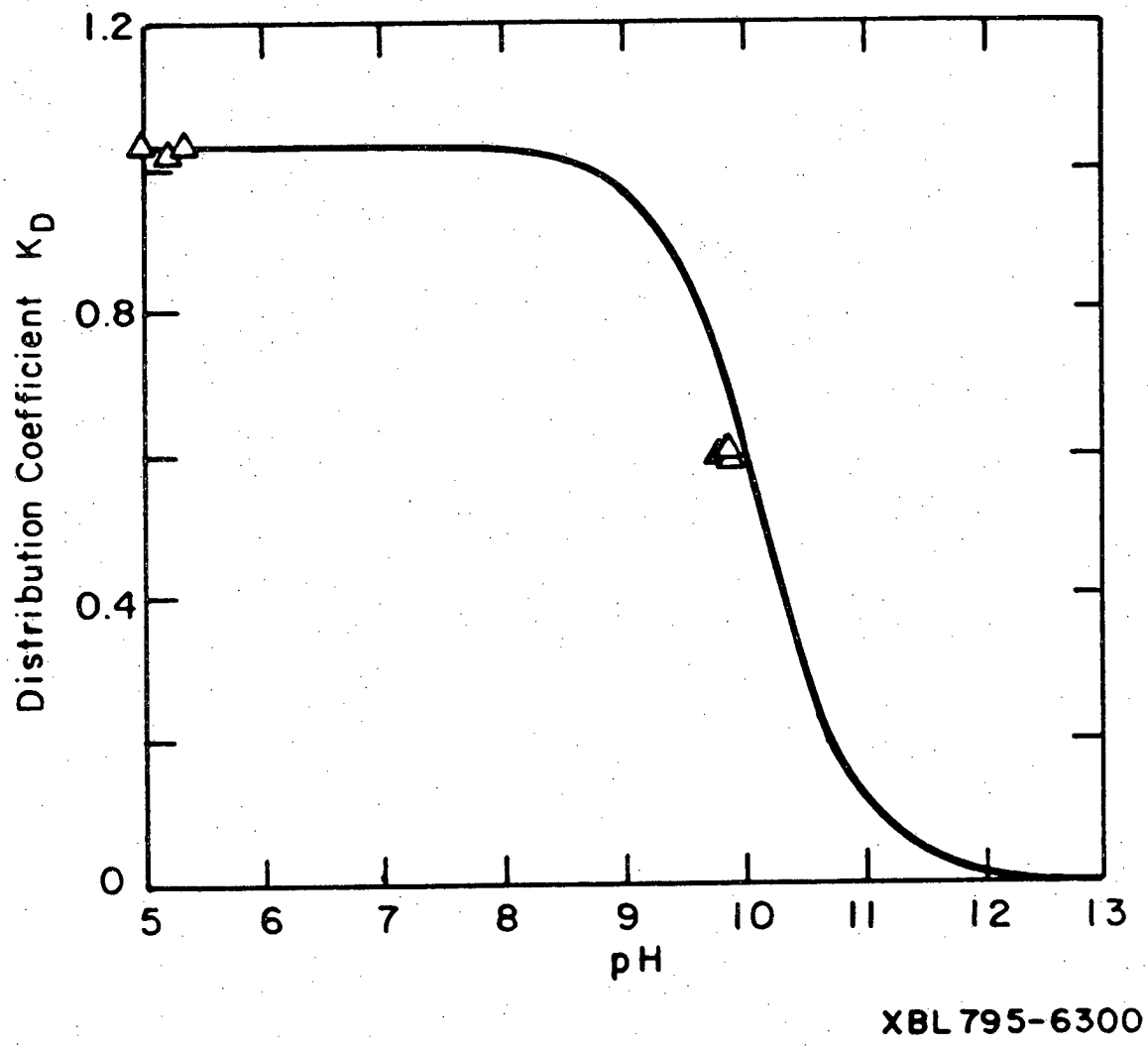


Figure 4-3. Distribution Coefficient for Hydroquinone Between Diisopropyl Ether and Water as a Function of pH at 298°K. Curve from Equation 4-2, with K_D=1.03, K_a=7.45x10^{-11}.

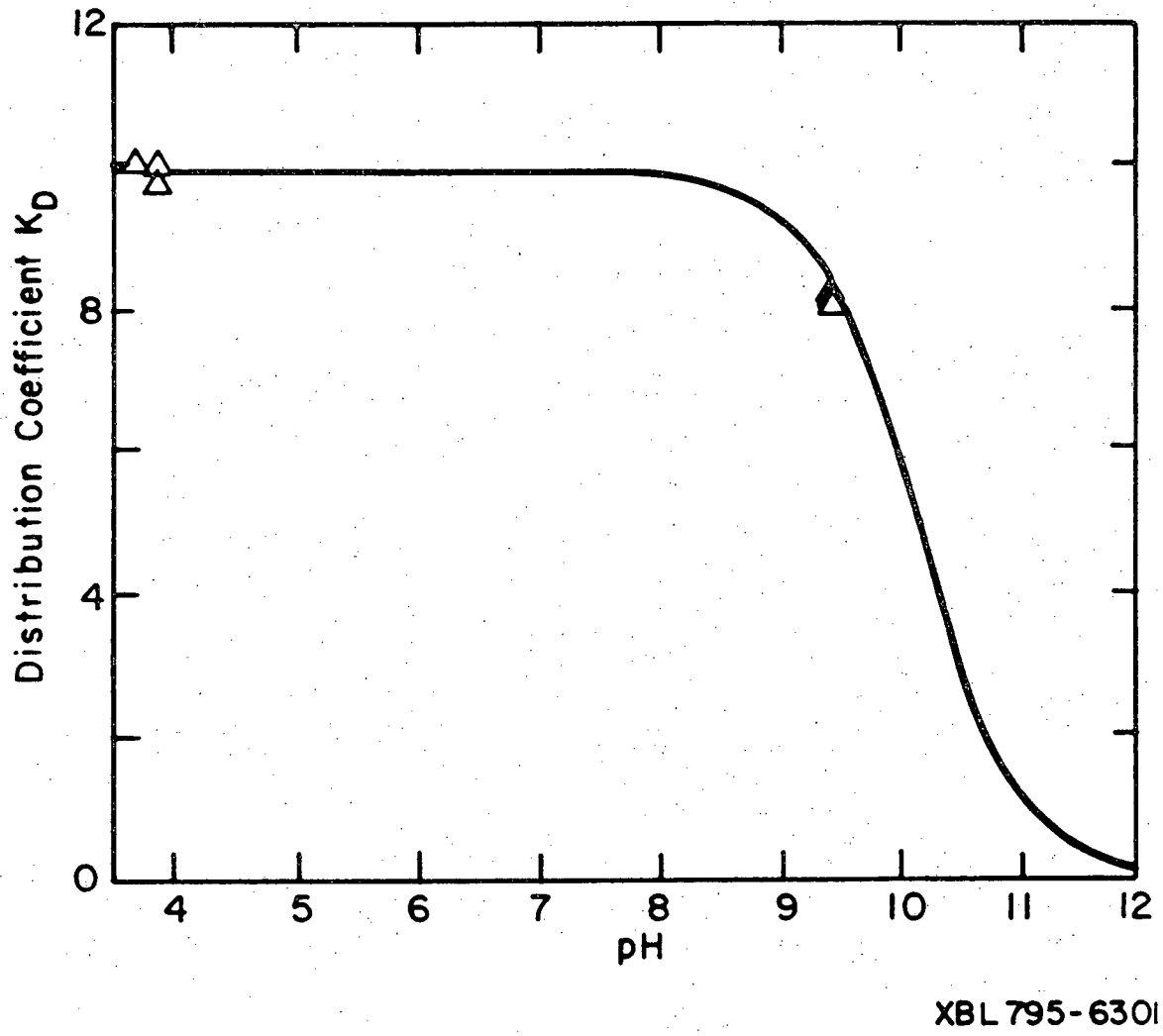


Figure 4-4. Distribution Coefficient for Hydroquinone Between Methyl Isobutyl Ketone and Water as a Function of pH at 298°K. Curve from Equation 4-2, with K_D=9.92, K_a 7.45×10^{-11}.

expression Eq. 4.3:

$$K_a = \frac{\gamma \pm [H^+][A^-]}{\gamma_{HA}[HA]} \qquad (4\text{-}3)$$

where the mean ionic activity coefficient $\gamma \pm$, unity at infinite dilution and less than unity in most ionic solutions below concentrations of 6 molal, is about equal to the activity coefficient of the free aqueous phenol, normalized in reference to an ideal solution at infinite dilution. As the true K_D is already a ratio of activity coefficients, as shown in Appendix C, unless the ionic environment changes drastically, the true K_D should remain fairly constant at low water-phase phenolic-solute concentration. The net result is a good fit of the model to the experimental data.

The range of condensate water pH is also plotted on Figure 4-1, the phenol-DIPE extraction results. Significant decreases in the overall K_D occur in this range. Because the amount of dissolved NH_4HCO_3 in the condensate waters is larger than the amount of KOH used for pH control in the single-solute extractions, the effects of ionic strength on the extraction equilibria would be more important in the condensate waters than in the single-component extractions. The higher ionic strength would decrease $\gamma \pm$, and, by a salting-out effect, would increase γ_{HA}. Both of these changes would increase the apparent K_a, shifting the curves predicted by Equation 4-2 in Figures 4-1 through 4-4 to the left.

The Phenosolvan process, currently operated commercially to process coke oven and coal gasifier condensate waters, uses DIPE to extract the phenols. Beychok (1) describes the Phenosolvan process with some calculations using the Kremser equation (22):

$$\frac{X_{in}}{X_{out}} = \frac{\left(\frac{K_D \cdot S}{W}\right)^{N+1} - 1}{\left(\frac{K_D \cdot S}{W}\right) - 1} \qquad (4\text{-}4)$$

where X_{in} and X_{out} refer to water phase concentrations, N is the number of stages, S and W refer to the solvent and water flow rates, respectively. The incoming solvent is assumed to be pure. Phenol and catechol, representative of the polyhydroxybenzenes, were assumed to be extracted from a Lurgi gasifier condensate. Using a solvent-to-feed ratio of 1:10 and a K_D for phenol of 20, 99.9% removal was calculated for 9 equilibrium stages. The K_D of 20 selected by Beychok accurately reflects the decrease due to water phase ionization of the phenol and corresponds to a pH of 9.8. But the K_D of 7.0 used for catechol is much too high. Table 4-2 lists the hydroxybenzene K_D's measured in this work, both for DIPE/Water and MIBK/Water systems. In DIPE, catechol has the highest K_D of the polyhydroxybenzenes, but even at low pH it is only 4.86. Using the model, K_D for catechol is 1.57 at a pH of 9.8. Instead of the catechol removal of 70% quoted by Beychok for a solvent-to-feed ratio of 1:10 and nine stages, the removal would only be 15.7%. Removals of the other polyhydroxybenzenes would be even lower, so the 60% removal for the polyhydroxybenzenes quoted by Beychok is unrealistic. It is clear that a better solvent for the polyhydroxybenzenes is required.

C. Solvent Selection

Burns (23) has measured K_D's for phenol distributing between MIBK and water at various temperatures, and found that K_D decreased with increasing temperature. At 30°C, the K_D of 60 is significantly higher than that for DIPE as a solvent. Burns also shows that significant energy savings can be realized using MIBK to extract phenol from coal-

Table 4-2. Distribution Coefficients for Hydroxybenzenes in DIPE/Water and MIBK/Water Systems at Low pH and 298°K

Solvent	Solute	pH	K_D	Water Phase Concentration, ppm	Material Balance Closure Error
DIPE	phenol	5.56	36.5	1350	+6.2%
	catechol	5.88	4.86	2060	-0.55%
	resorcinol	4.16	2.06	1990	+2.1%
	hydroquinone	5.17	1.03	2790	-1.0%
	hydroxyquinol	4.64[c]	0.181	2680	-6.0%
MIBK	phenol[a]	--	60	~2000	--
	catechol	4.18	18.7	2290	-0.66%
	resorcinol	4.21	17.9	1800	+0.72%
	hydroquinone	3.88	9.92	2490	+0.27%
	hydroxyquinol	4.24[c]	5.01	3000	+1.4%
	phloroglucinol	4.53[c]	3.92	~1500[b]	+9.2%
	pyrogallol	4.52	3.58	3050	+4.1%

[a] at 303°K, from (23).

[b] no external standard used. Based on feed solution concentration K_D

[c] not connected for sample dilution

conversion condensate waters instead of the DIPE used by the Phenosolvan process. The physical properties of MIBK are such that residual MIBK can be vacuum steam stripped from the raffinate using waste heat from the feed water, simultaneously cooling the feed water to give a higher K_D for extraction. DIPE is not suitable for vacuum steam stripping, and the Phenosolvan process uses a complicated three-column inert gas stripping system that increases internal recycle streams and distillation column loads greatly. Figure 4-5 is a diagram of Burns' proposed process. With this in mind, it was decided to investigate further the extraction of phenols from water with MIBK.

Referring again to Table 4-2, it is apparent that the K_D's for the hydroxybenzenes in MIBK are significantly higher than those in DIPE. This can be explained in a number of ways. First, MIBK, being a ketone, is more polar than DIPE, an ether. As the polyhydroxybenzenes are quite polar, they would have stronger dipole-dipole interactions with MIBK than DIPE. Second, the oxygen in the carbonyl group makes stronger hydrogen bonds than the ether oxygen does. The carbonyl C-O double bond donates electrons to the oxygen more readily than the C-O single bonds in the ether, making the carbonyl oxygen more negative than the ether oxygen and thereby increasing its hydrogen bonding ability. Also, hydrogen bonding is less sterically hindered in the ketone, as the hydrocarbon side chains are not attached to the oxygen, as in the ether, but to the carbonyl carbon.

It is interesting to note that for both solvents, the K_D's decrease by about one order of magnitude with the addition of each hydroxyl group, but that the K_D's for the polyhydroxybenzenes with MIBK are about one order of magnitude higher than for DIPE. The fact that the

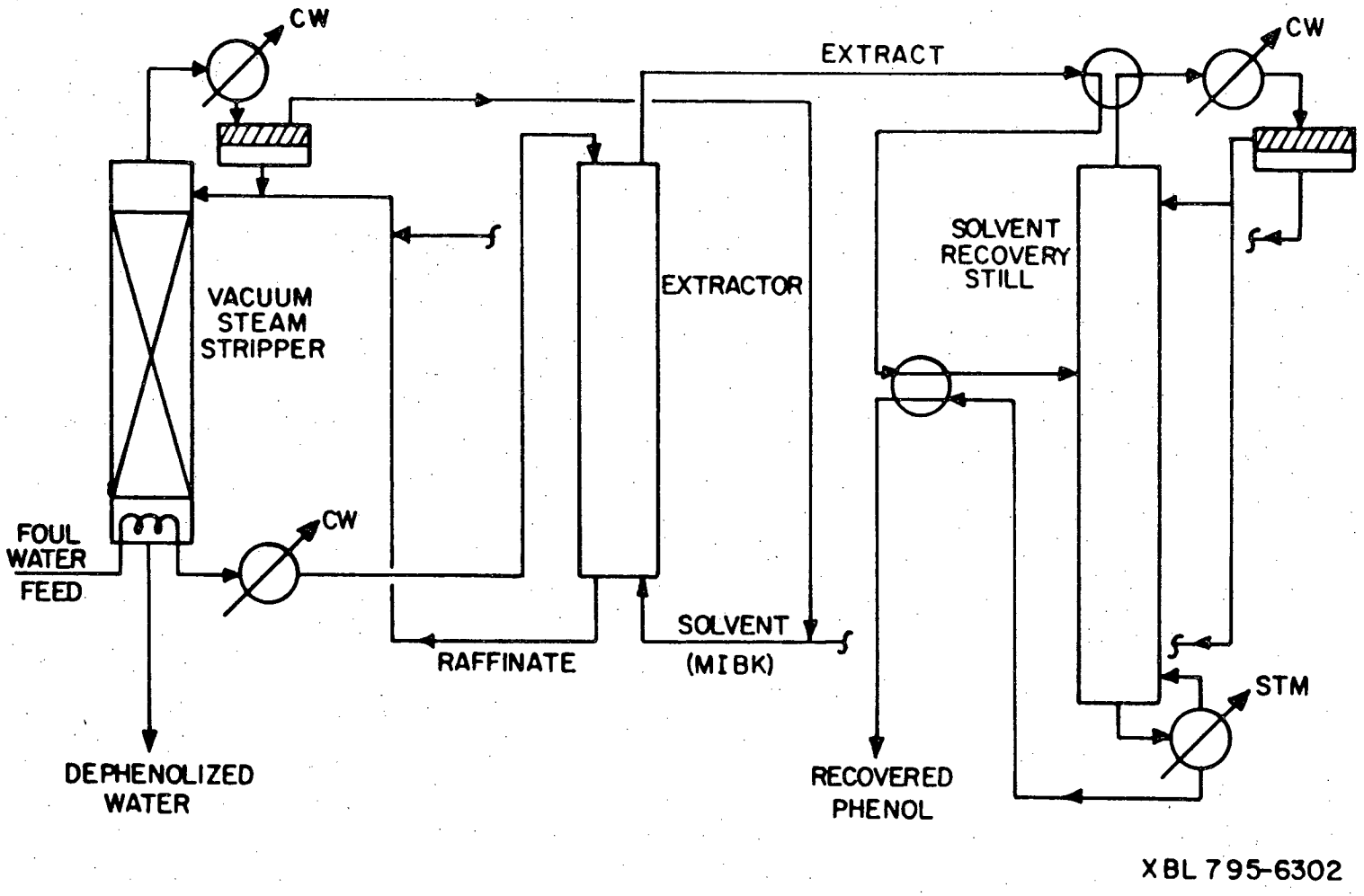


Figure 4-5. Energy-Efficient Phenol Extraction Process [after Burns, (23)]

K_D variation among the dihydroxybenzenes in DIPE is greater than that in MIBK again reflects the directional hydrogen bonding ability of MIBK, as the steric differences of the dihydroxybenzenes are minimized.

The ordering of the K_D's for the dihydroxybenzenes can be similarly explained. As water is a very polar solvent, polar solutes would be expected to have lower activity coefficients than nonpolar solutes. The three dihydroxybenzenes, arranged in the order of increasing polarity, are hydroquinone, resorcinol and then catechol. On this basis, one would expect the same order when the dihydroxybenzenes are arranged in the order of decreasing K_D, with the most polar compound having the lowest K_D. But this is not the case.

Water solubilities give a better indication of the water phase activity coefficients. The water solubilities, in parts per 100 parts water, by weight, are as follows (24): catechol, 45.1 at 20°C; resorcinol, 147 at 12°C; and hydroquinone, 6 at 15°C. One would expect the least soluble material to have the highest K_D, giving, in the order of increasing K_D: catechol, resorcinol, hydroquinone. However, this is not the case either.

The answer probably is a combination of both ideas, albeit it is still a conjectural argument. Catechol is the most polar, but hydrogen bonding between catechol and water is more sterically hindered than in the other dihydroxybenzenes. Catechol tends to hydrogen bond to itself. Even though resorcinol is less polar, the lack of steric hinderance in hydrogen bonding makes its water solubility higher than that of catechol. As would then be expected, catechol is more easily extracted from water than resorcinol.

Contrasted with this, hydroquinone has no dipole moment, only a quadrupole moment. Even though hydrogen bonding is the least sterically

hindered compared to the other dihydroxybenzenes, the lack of a dipole moment makes hydrogen bonding with water weaker, as is reflected in its water solubility, the lowest of the three dihydroxybenzenes. One would then expect hydroquinone to have the highest K_D. But organic phase effects are important also. Hydroquinone, being nonpolar, lacks the dipolar interactions that catechol and resorcinol have in solutions of DIPE and MIBK. Consequently, it has the highest activity coefficient in the organic phase. The net effect is to give hydroquinone the lowest K_D.

The increased polarity and the directional hydrogen bonding ability of MIBK made it a better solvent than DIPE for extraction of the polyhydroxybenzenes. Additional increases in polarity through the use of different functional groups or increased numbers of functional groups is likely to prove counterproductive in attempting to find a better solvent than MIBK. Water solubility would increase also, increasing the cost of solvent recovery. If the hydrocarbon side chains were increased to lower the water solubility, the polarity would drop, negating the gain in K_D. Separation of the solvent from the crude phenols would become more difficult as the boiling point of the solvent would be getting closer to that of phenol. The atmospheric boiling points of MIBK and phenol are 116.9°C and 181.8°C respectively. Additionally, the more complicated solvent molecule that would result from the attempt to get a better solvent would probably be more expensive. Thus, MIBK appears to be the best physically-interacting solvent for the extraction of phenols from water.

Chapter V. Summary

This work was divided into two parts. The first was analysis of representative coal-conversion process condensate waters for phenols, particularly the unsubstituted hydroxybenzenes. The second was investigation of the ionization and phase-distribution equilibria in the extraction of the weakly acidic phenols from water solution. Solvent extraction is the method currently used to remove phenols from coke-oven water effluents and some coal-gasifier process condensate waters.

Phenol, cresols, non- and methyl- substituted dihydroxybenzenes were identified as methyl ether derivatives by gas chromatography-mass spectrometry, confirming earlier work (3,5,6,7). These analyses could not be quantified because of methylation-reaction yield inconsistencies.

The Synthane water sample degraded, even with careful storage, before the analytical method using high-performance liquid chromatography (HPLC) was developed, so work continued with the SRC condensate water, which appeared stable. Initial HPLC analysis of the SRC condensate water revealed 6700 ppm of phenol, 2900 ppm of mixed cresols, 2400 ppm of resorcinol, and a peak identified in later analyses as 610 ppm of phloroglucinol.

Sample aging could have led to the total loss of some components and reductions in the amounts of the others. Fresh condensate water samples from the Synthane and SRC processes, along with samples from other processes, should be analyzed for phenols by HPLC so that the removals necessary for compliance with effluent- or recycled-water standards can be determined.

The presence of the trihydroxybenzene phloroglucinol is most important, as trihydroxybenzenes air-oxidize easily, which would cause severe

color problems for effluent water. Trihydroxybenzenes are also extremely resistant to biological oxidation (11), dictating removal by other means.

Batch extractions of phenol, resorcinol and hydroquinone into diisopropyl ether (DIPE), and of hydroquinone into methyl isobutyl ketone (MIBK), from water at different pH's showed that the water phase pH has a major influence on the distribution coefficient K_D of a weakly acidic phenol. This effect is accurately described by a simple model combining the weak acid ionization equilibrium in the water phase, having the equilibrium constant K_a, with the phase distribution equilibrium between the nonionized aqueous phenol and the organic phase phenol:

$$K_D, \text{ apparent} = \frac{K_D, \text{ true}}{\frac{K_a}{[H^+]} + 1} \qquad (4\text{-}2)$$

At the buffered high pH of the coal-conversion condensate waters, caused by large amounts of dissolved ammonia and carbon dioxide, the resultant reduction in the apparent K_D should cause problems in the extraction of the phenols. Postulation of optimistically high low-pH values for polyhydroxybenzenes has led to exaggerated projections of polyhydroxybenzene removal from coal-conversion condensate waters by the Phenosolvan process, a proprietary process that uses DIPE to extract phenols from effluent waters. Beychok (1) used a reasonable K_D of 20 for phenol, corresponding to a pH of 9.8, and with a solvent-to-feed ratio of 1:10 and nine equilibrium stages, calculated a phenol removal of 99.9%, and with a K_D of 7.0, calculated a catechol removal of 70% under the same conditions. Actual catechol removal under these conditions would be only 16%, based on a true K_D of 1.6 at a pH of 9.8. Removals of the other polyhydroxybenzenes will be even lower, as catechol has the highest K_D between DIPE and water of the polyhydroxybenzenes. With the

polyhydroxybenzenes present at levels in excess of 2000 ppm, the Phenosolvan process, as run, will not extract the process condensate waters to the degree necessary as a precursor to biological oxidation.

The batch extractions performed in this work show MIBK to be clearly a better solvent than DIPE for the extraction of phenols from water. The K_D's for polyhydroxybenzenes with MIBK are an order of magnitude higher than with DIPE. In the case of the trihydroxybenzenes, at low pH the K_D for DIPE extraction was around 0.2, but for MIBK extraction was around 0.4. In addition, Burns (23) describes energy savings achieved by using MIBK instead of DIPE for phenol extraction from water solution.

MIBK is probably the best physical solvent for the extraction of phenols from coal-conversion condensate waters in terms of cost, energy efficiency and its lack of reactivity, but more work needs to be done. Process condensate waters will emerge from coal-conversion processes at temperatures in excess of 70°C. The K_D for phenol between MIBK and water decreases as the temperature increases (23), and the polyhydroxybenzenes are likely to exhibit the same behavior. Not much of a penalty for higher temperature operation can be tolerated as the polyhydroxybenzene K_D's are not extremely high even at low pH. As the extraction model is sensitve to the value of pK_a used, extrapolation from the available data to higher temperature could be risky, so experimental determination of the pK_a's of the phenols at higher temperatures should be considered along with the distribution coefficient measurements.

Integration of the phenol recovery into the total water treatment stategy must also be investigated. The ammonia and acid gas stripping operations could occur before or after the phenol removal. The effects that the organics would have on these operations is presently unknown.

Also, methods of performing these separations without using mineral acids and bases to adjust the water pH (25), releasing the acid gases and ammonia, respectively, must be investigated. Tar is another problem, as it accumulates in the Phenosolvan process, requiring semi-annual or more frequent shut-downs for equipment cleaning (9). All of these problems must be addressed in a total water treatment process.

Appendix A: Batch Extraction Data

Tables A-1 through A-4 present the raw data for the batch extractions done in this work. Material balance nonclosures for Extractions 1b through 1f were calculated taking advantage of the organic solvent concentrations that could be measured in the water feed and water phase solutions by gas chromatography. A zero loss of water and DIPE was assumed. The phenol in the DIPE phase was assumed to have no effect on the water solubility in DIPE, which in turn implies that the water content of the DIPE phase did not change during the extraction. Therefore, all the water in the water feed was assumed to appear in the raffinate. On this basis, the raffinate and extract phase masses were calculated as follows, for a water feed of 1:

$$\text{Raffinate} = \frac{\text{mass of water in water feed (no loss to solvent phase, as evaporation)}}{\text{concentration of water in raffinate (by difference)}}$$

$$R = \frac{1 - W_{ao}^{\beta}}{1 - W_{bf}^{\beta} - W_{af}^{\beta}} \qquad \text{(A-1)}$$

$$\text{Extract} = \frac{\left(\begin{matrix}\text{mass of solvent and dissolved}\\ \text{water in solvent feed}\end{matrix}\right) - \left(\begin{matrix}\text{mass of solvent transferred}\\ \text{to water phase during}\\ \text{extraction}\end{matrix}\right)}{\text{concentration of solvent and water in extract (by difference)}}$$

$$E = \frac{S(1 - W_{bo}^{\alpha}) - [R \cdot W_{af}^{\beta} - W_{ao}^{\beta}]}{1 - W_{bf}^{\alpha}} \qquad \text{(A-2)}$$

$$\text{Material Balance Nonclosure (\%)} = \frac{-S \cdot W_{bo}^{\alpha} + R \cdot W_{bf}^{\alpha} + E \cdot W_{bf}^{\alpha}}{S \cdot W_{bo}^{\alpha}} \cdot 100 \qquad \text{(A-3)}$$

Table A-1. K_D as a Function of pH for Phenol in a DIPE/Water System at 298°K

Extraction	pH	K_D	Water Phase Concentrations Phenol (ppm)	Water Phase Concentrations DIPE (ppm)	DIPE Phase Phenol (ppm)	DIPE in Water Feed (ppm)	Phenol in DIPE Feed (ppm)	Phenol Material Balance Non-closure, %	Solvent/ Water Phase Ratio, by Weight[b]
1a	5.90	36.6	1360	9450	49800	---	9800[a]	+7.6	0.185:1
	5.28	36.6	1350	9460	49400	---	9800	+5.4	0.182:1
	5.50	36.3	1340	9560	48600	---	9800	+5.6	0.185:1
1b	6.18	36.8	1560	9040	57400	5330	64500	-0.42	0.185:1
	6.67	51.3	1120	8870	57400	5330	64500	-4.1	0.186:1
	5.91	43.1	1340	9170	57800	5330	64500	-1.9	0.188:1
1c	8.68	34.8	1740	9420	60600	5470	67700	+0.96	0.182:1
	8.69	36.1	1700	9330	61300	5470	67700	+1.9	0.185:1
	8.68	36.2	1690	9300	61100	5470	67700	+1.2	0.184:1
1d	9.14	24.2	2590	9470	62600	2650	68500	+7.4	0.190:1
	9.12	23.6	2620	9360	61900	2650	68500	+6.5	0.192:1
	9.14	24.6	2610	9360	64100	2650	68500	+9.2	0.198:1
1e	9.79	19.6	2510	9430	49300	8530	60800	+1.5	0.190:1
	9.92	19.8	2510	9420	49800	8530	60800	+2.5	0.188:1
	9.94	19.3	2540	9450	49000	8530	60800	+2.1	0.182:1
1f	10.58	6.72	5000	9150	33600	8530	60800	+0.36	0.176:1
	10.56	6.41	5210	9310	33400	8530	60800	+1.2	0.181:1
	10.59	6.44	5260	9380	33900	8530	60800	+1.8	0.179:1

[a] water phase phenol feed

[b] approximately 1:4 by volume

Table A-2. K_D as a Function of pH for Resorcinol in a DIPE/Water System at 298°K

Extraction	pH	K_D	Water Phase Concentration (ppm)	DIPE Phase Concentration (ppm)	Resorcinol in DIPE Feed (ppm)	Resorcinol Material Balance Non-closure, (%)	Solvent/ Water Phase Ratio, by Weight[a]
2a	4.43	2.09	2000	4179	6710	+2.2	0.746:1
	4.02	2.07	2000	4147	6710	+2.5	0.733:1
	4.02	2.02	1970	3987	6710	-0.45	0.731:1
2b	7.88	1.95	2100	4100	6940	+0.38	0.728:1
	7.91	2.15	2000	4290	6940	+1.2	0.732:1
	7.78	2.05	2090	4290	6940	+2.4	0.723:1
2c	8.59	1.63	2080	3380	6280	+2.9	0.674:1
	8.61	1.63	2130	3480	6280	+2.6	0.717:1
	8.65	1.62	2130	3450	6280	+2.9	0.707:1
2d	9.50	0.902	2970	2680	6700	+1.5	0.721:1
	9.50	0.906	2970	2690	6700	+0.99	0.729:1
	9.48	0.912	2940	2680	6700	+0.87	0.721:1
2e	10.05	0.354	3960	1400	6700	+1.4	0.734:1
	10.09	0.351	3880	1360	6700	+2.1	0.708:1
	10.11	0.351	3900	1370	6700	+3.0	0.706:1
2f	12.13	0.00970	7070	68.6	10300	-1.2	0.700:1
	11.14	0.0106	7350	77.7	10300	-0.20	0.720:1
	11.07	0.0114	7510	85.8	10300	+0.30	0.733:1

[a] approximately 1:1 by volume

Table A-3. K_D for Polyhydroxybenzenes in a DIPE/Water System at 298°K

Extraction	Solute	pH	K_D	Water Phase Concentration (ppm)	DIPE Phase Concentration (ppm)	Feed Solution Concentration (ppm)	Solute Material Balance Non-closure (%)	Solute/ Water Phase Ratio by Weight[c]
3	catechol	5.86	4.86	2030	9865	12930[a]	-2.3	0.735:1
		5.87	4.87	2080	10130	12930	+0.37	0.730:1
		5.91	4.87	2070	10090	12930	+0.31	0.719:1
4a	hydroquinone	5.33	1.03	2760	2820	6590[a]	-0.041	0.733:1
		4.98	1.03	2730	2800	6590	-1.1	0.734:1
		5.20	1.02	2710	2760	6590	-1.9	0.731:1
4b	hydroquinone	9.89	0.593	2360	1400	3360[b]	+0.90	0.729:1
		9.78	0.597	2360	1410	3360	+1.2	0.732:1
		9.85	0.604	2350	1420	3360	+0.58	0.718:1
5	hydroxyquinol	4.61[d]	0.180	2650	476	3230[b]	-6.9	0.748:1
		4.67[d]	0.182	2710	494	3230	-5.0	0.725:1

[a] solute in DIPE feed

[b] solute in water feed

[c] approximately 1:1 by volume

[d] not corrected for dilution of sample

Table A-4. K_D for Polyhydroxybenzenes in a MIBK/Water System at 298°K

Extraction	Solute	pH	K_D	Water Phase Concentration (ppm)	MIBK Phase Concentration (ppm)	MIBK Feed Concentration (ppm)	Solute Material Balance Non-closure (%)	Solute/ Water Phase Ratio by Weight[a]
6	Resorcinol	4.28	17.9	1810	32400	34200	+1.1	0.827.1
		4.19	17.9	1780	31800	34200	-0.76	0.831:1
		4.17	17.8	1820	32400	34200	+1.1	0.831:1
7	Catechol	4.19	18.4	2320	42700	45800	-0.60	0.822:1
		4.19	18.8	2290	43000	45800	+0.0090	0.817:1
		4.17	18.8	2250	42400	45800	-1.4	0.815:1
8a	Hydroquinone	3.88	10.0	2470	24800	27700	+0.40	0.820:1
		3.86	9.76	2500	24400	27700	-0.89	0.818:1
		3.90	10.0	2490	25000	27700	+1.3	0.816:1
8b	Hydroquinone	9.41	8.16	1790	14600	16700	+0.37	0.828:1
		9.45	8.14	1770	14400	16700	-1.1	0.833:1
		9.43	8.24	1820	15000	16700	+3.0	0.828:1
9	Hydroxyquinol	4.20[c]	4.90	3020	14800	18400	+0.051	0.837:1
		4.27[c]	5.15	2970	15300	18400	+2.8	0.823:1
10	Pyrogallol	4.54	3.63	3030	11000	14100	+4.7	0.806:1
		4.50	3.53	3060	10800	14100	+3.5	0.807:1
11	Phloroglucinol	4.55[c]	4.08	116[b]	473[b]	556[b]	+12.	0.763:1
		4.51[c]	3.75	114[b]	428[b]	556[b]	+6.0	0.707:1

[a] approximately 1:1 by volume

[b] standard area of peak. Solute was impure and a standard could not be made

[c] not corrected for sample dilution

where:

W is a mass fraction, 10^{-6} x ppm

α,β are superscripts denoting organic and water phases, respectively

a,b are subscripts denoting DIPE and phenol solutes, respectively

o,f are subscripts denoting before (feed) and after equilibrium, respectively

S is the solvent-to-water mass ratio

The material-balance nonclosures were calculated more simply in the polyhydroxybenzene extractions by assuming the raffinate and extract masses to be equal to the water and solvent feed masses, respectively. This assumption was made because the detector on the LC used is not sensitive to DIPE, so that for the DIPE extractions, the water phase samples would also have had to be analyzed by GC to get the solvent concentrations. This assumption causes less error for the polyhydroxybenzene extractions than it would for the phenol extractions. For the DIPE extractions, the polyhydroxybenzene K_D's had a value nearer one than phenol did, so the effect of the solute on the water-phase DIPE solubility would be much smaller for the polyhydroxybenzenes than for phenol. The change in the water-phase DIPE solubility would also have a larger effect in the phenol extractions because the solvent-to-water mass feed ration was about four times lower than in the polyhydroxybenzene extractions.

For the case in which the solute was fed in the organic solvent:

$$\text{Material Balance Nonclosure (\%)} = \frac{-S\cdot W_o^{\alpha} + S\cdot W_f^{\alpha} + W_f^{\beta}}{S\cdot W_o^{\alpha}} \cdot 100 \qquad \text{(A-4a)}$$

For the case in which the solute was fed in the water phase:

$$\text{Material Balance Nonclosure (\%)} = \frac{-W_o^{\beta} + S \cdot W_f^{\alpha} + W_f^{\beta}}{W_o^{\beta}} \cdot 100 \qquad \text{(A-4b)}$$

All mass fractions in Equations A-4a and A-4b refer to the phenolic solute, with the other notation remaining as in Equations A-1 through A-3.

For a comparison of the two methods, the material-balance nonclosure for the first point in extraction #1b is-0.42%, using Equations A-1, A-2 and A-3. Using Equation A-4a, the nonclosure is +2.1%.

Appendix B: Theoretical Plate Count Calculation

Column efficiency is most often measured in terms of the theoretical plate count of the column for a peak of interest. Column condition can be monitored numerically and appropriate column cleaning procedures instituted when contamination is indicated by a decrease in efficiency.

The method used most commonly is the tangent method. The theoretical plate count N is given by (26):

$$N = 16\left(\frac{R_t}{W}\right)^2 \qquad \text{(B-1)}$$

where R_t is the retention time in seconds of the peak and W is the peak width in seconds obtained by drawing tangents from the sides of the peak to the baseline. The peak is assumed to be symmetrical.

However, peaks are often not symmetrical. Tailing of peaks will not be reflected in a plate count based on an extrapolation from the middle of a peak, and column contamination first manifests itself as an increase in peak tailing. A more accurate method uses a peak width five times larger than the standard deviation (σ) of the curve, rather than the 4σ width used in the tangent method. The 5σ width is measured at 4.4% of the peak height and is used in the following equation for N (1):

$$N = 25\left(\frac{R_t}{W}\right)^2 \qquad \text{(B-2)}$$

Figure B-1 shows how these two methods can differ radically for a tailing peak, the tailing making $N_{5\sigma}$ less than $N_{4\sigma}$.

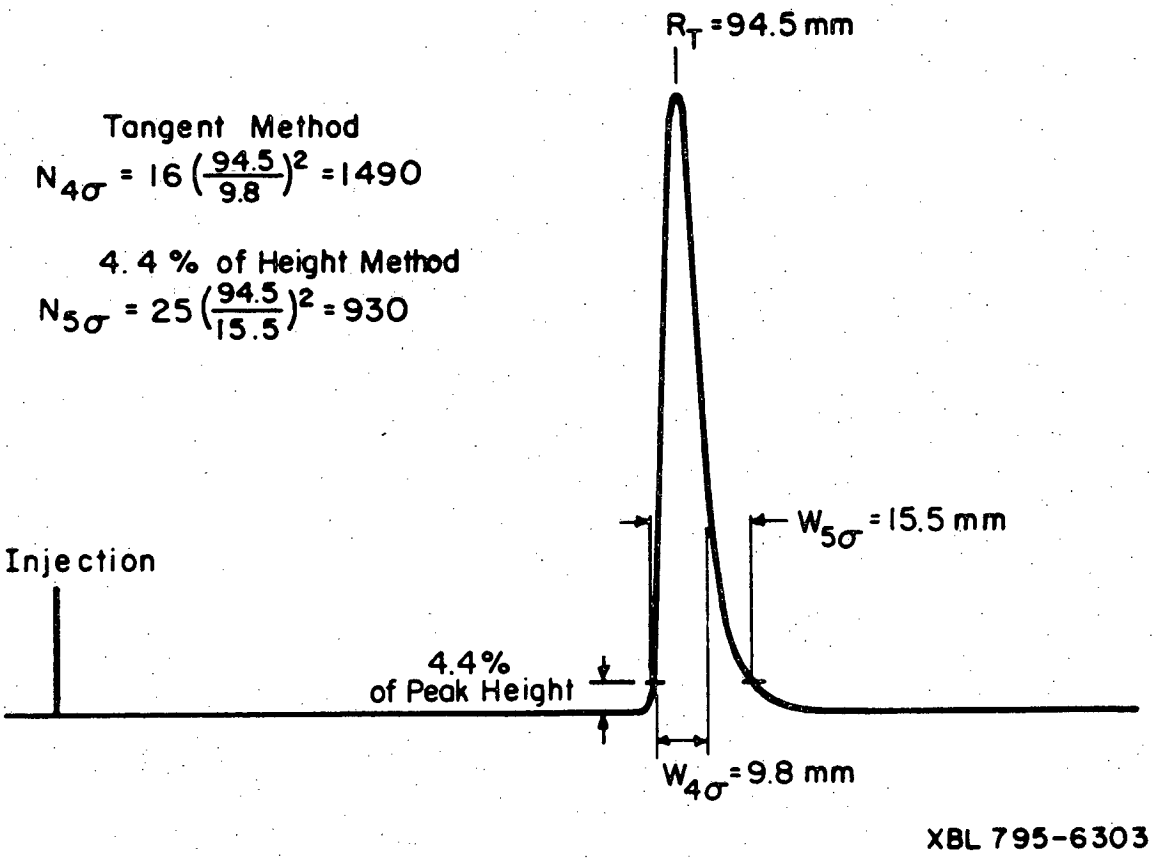


Figure B-1. Plate Count Calculation Methods

Appendix C: Sample pH - Correction Calculation

In the extractions, a 10 ml water-phase sample was diluted to 30 ml before pH measurement. The pH of the original water phase was calculated as follows, with the calculation here done for the second data point in Extraction 1a (Table A-1):

concentrated solution: phenol = 1350 ppm = 1.44×10^{-2}M

dilute solution: phenol = 1.44×10^{-2}M/3 = 4.80×10^{-3}M

pH = 5.72, $[H^+] = 1.91\times10^{-6}$M

for phenol at 25°C: $K_a = 1.05\times10^{-10}$

Calculating the concentration of ionized phenol in the dilute solution using the ionization equilibrium:

$$1.05\times10^{-10} = \frac{(1.91\times10^{-6})(X)}{(4.80\times10^{-3} - X)}$$

$$X = 2.64\times10^{-7}\text{M}$$

Concentrations of the ions and free phenol before equilibration in the more concentrated solution:

$[H^+] = 3\cdot1.91\times10^{-6} = 5.73\times10^{-6}$

$[PhO^-] = 3\cdot2.64\times10^{-7} = 7.92\times10^{-7}$

$[PhOH] = 3\cdot4.80\times10^{-3} = 1.44\times10^{-2}$

Calculating the change caused by the concentration and re-equilibration:

$$1.05\times10^{-10} = \frac{[5.73\times10^{-6}-X][7.92\times10^{-7}-X]}{[1.44\times10^{-2}+X]}$$

Neglecting X in the denominator and solving for X:

$X = 5.2\times10^{-7}$M

For the concentrated solution: $[H^+] = 5.73\times10^{-6} - 5.2\times10^{-7} = 5.21\times10^{-6}$M

pH = 5.28

In the pH range 8-10, the buffering action of the phenols prevented pH change upon dilution.

Appendix D: Gas Chromatograph - Mass Spectrometer (GC-MS) Data

Peak identification for the methylated condensate waters was performed by comparison of the mass spectra of the unknown peaks with a library of spectra, using the integral minicomputer of the Finnegan GC-MS. The computer-reconstructed gas chromatograms and the statistical comparisons for the peaks identified are contained in this appendix. Footnotes to Table D-1 explain the format of the computer output.

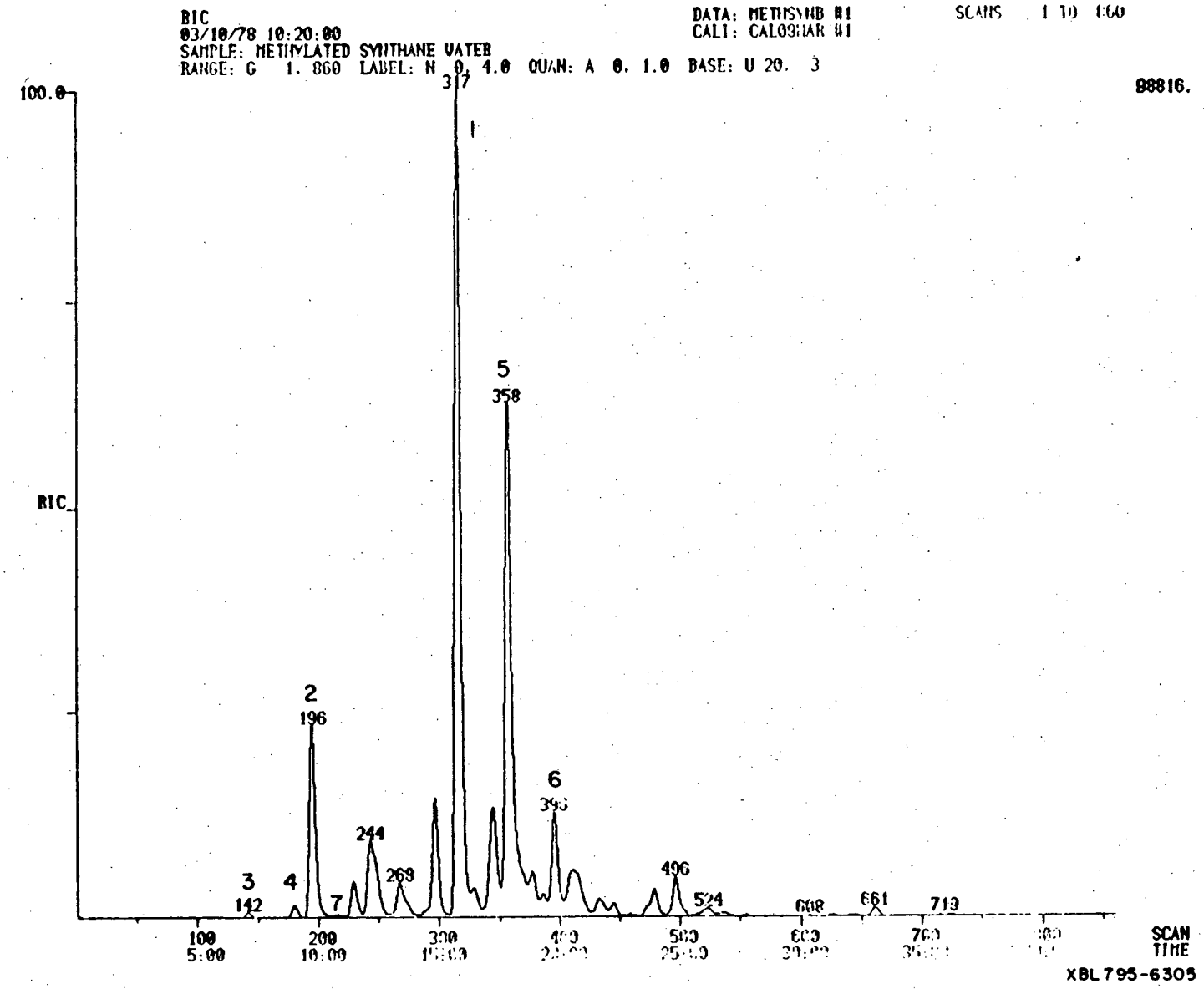


Figure D-1. Computer-Reconstructed Gas Chromatogram of Methylated Synthane Water

Table D-1. Methoxybenzene Identification in Methylated Synthane Water

LIBRARY SEARCH   DATA: METHSYNB ● 142   BASE M/E: 108
[illegible]/10/78 10:20:00 + 7:06   CALI: CALO9MAR ● 1   RIC: 517.
SAMPLE: METHYLATED SYNTHANE WATER

[illegible]5423 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
470 MATCHED AT LEAST 2 OF THE 4 LARGEST PEAKS IN THE UNKNOWN

RANK	IND	NAME
1	901	BENZENE,METHOXY-
2	898	HYDRAZINE,PHENYL-
3	104[illegible]1	CARBONICACID,METHYLPHENYLESTER
4	15919	PYRIDINIUM,1-AMINO-2-METHYL-,HYDROXIDE,INNERSALT
5	17492	PYRIDINIUM,1-AMINO-2-METHYL-,CHLORIDE

RANK	FORMULA	M.WT	B.PK	PURITY[a]	FIT[a]	RFIT[a]
1	C7.H8.O	108	[illegible]	8[illegible]0	830	999
2	C6.H8.N2	1[illegible]8	108	592	552	995
3	C8.H8.O3	152	10[illegible]	599	603	971
4	C6.H9.N2	10[illegible]	108	491	494	950
5	C6.H9.N2.CL	144	108	464	547	849

MASS	INTEN[b]	1	2	3	4	5
38		19				
39	79	76	76			
44				12		
50		25	89	28	31	
51		46	149	37	64	
52		12	99		41	
53					51	
59				59		
63		26	29	34		
64		15	23	14		
65	199	218	127	252	[illegible]	199
66		14	29	17	111	60
67					39	3
74		10				
77		67	145	90	51	
78	240	223	298	155	63	
79		46	42	42	39	
80					77	48
81					33	21
91			97			
92			2[illegible]4		629	598
93			172	24[illegible]	[illegible]	240
94				[illegible]		[illegible]
105			110			
107		26				[illegible]
108	1000	1000	1000	1000	1000	1000
109		77			[illegible]	71
152				255		
153				14		

[a] statistical fit parameters

[b] peak intensities of unknown

[c] peak intensities of library compounds

Table D-2. 1-Methoxy-2-Methylbenzene Identification in Methylated Synthane Water

LIBRARY SEARCH DATA: METHSYNB • 188 BASE M/E: 122
03/10/78 18:20:00 + 9:00 CALI: CAL09MAR • 1 RIC: 1381.
SAMPLE: METHYLATED SYNTHANE WATER

25409 SPECTRA IN LIBSRSYNB SEARCHED FOR MAXIMUM PURITY
127 MATCHED AT LEAST 5 OF THE 9 LARGEST PEAKS IN THE UNKNOWN

RANK	IND	NAME
1	3002	BENZENE,1-METHOXY-2-METHYL-
2	1022	BENZENE,1-METHOXY-4-METHYL-
3	735	PHENOL,2,5-DIMETHYL-
4	1045	PHENOL,2,4-DIMETHYL-
5	2674	PHENOL,2,3-DIMETHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C8.H10.O	122	122	893	883	978
2	C8.H10.O	122	122	878	878	935
3	C8.H10.O	122	122	847	847	937
4	C8.H10.O	122	122	815	815	914
5	C8.H10.O	122	107	813	813	922

MASS	INTEN	1	2	3	4	5
39	12	52	12	12	159	177
51		42	13	12	105	114
52			26			
53			26	39	87	71
63		21	17		45	
65		52	24	35	54	44
77	193	148	162	184	189	188
78	4	31	35	61	65	68
79	48	74	117	184	97	113
89		43				
90		53				
91	178	268	178	77	184	97
92		56	64			
93				21		
94						38
103				41	38	53
104				46	26	48
105				23		
107	475	398	264	576	573	694
108		40	22	46	47	56
121	127	171	361	286	330	225
122	1000	927	815	661	680	837
123	36	65	72	60	53	55

Table D-3. 1-Methoxy-4-Methylbenzene Identification in Methylated Synthane Water

LIBRARY SEARCH DATA: METHSYNB • 196 BASE M/E: 122
03/10/78 10:20:00 + 9:48 CAL: CAL09MAR • 1 RIC: 23135.
SAMPLE: METHYLATED SYNTHANE WATER

25489 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
60 MATCHED AT LEAST 7 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	IND	NAME
1	1022	BENZENE,1-METHOXY-4-METHYL-
2	913	BENZENE,1-METHOXY-3-METHYL-
3	3002	BENZENE,1-METHOXY-2-METHYL-
4	1045	PHENOL,2,4-DIMETHYL-
5	726	PHENOL,3,4-DIMETHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C8.H10.O	122	122	959	987	959
2	C8.H10.O	122	122	955	981	955
3	C8.H10.O	122	122	931	960	931
4	C8.H10.O	122	122	833	887	855
5	C8.H10.O	122	107	831	874	831

MASS	INTEN	1	2	3	4	5
38	10					
39	58	47	69	56	69	71
40	6					
41	4					
50	25					26
51	54	50	49	32	48	51
52	28	29	35			31
53	28	29	37		52	50
61	1					
62	7					
63	26	27	37	28	38	37
64	4					
65	32	35	38	61	50	46
74	3					
77	196	234	178	187	196	282
78	48	50	54	41	68	57
79	123	166	147	99	110	84
80	4					
89	16			36		
90	7			43		
91	250	152	236	216	73	57
92	81	57	186	46		
93	19		28			
96	1					
103					30	
104					27	
105	1					
107	207	288	172	353	567	641
108	13	23		42	47	49
120	1					
121	321	391	152	163	316	293
122	1000	881	1000	884	574	457
123	57	76	98	62	57	41

Table D-4. 2-Ethyl-5-Methylphenol Identification in Methylated Synthane Water

LIBRARY SEARCH DATA: METHSYNB • 215 BASE M/E: 121
7/10/78 10:22:00 • 10:45 CALI: CAL09MAR • 1 RIC: 351.
SAMPLE: METHYLATED SYNTHANE WATER

25409 SPECTRA IN LIBRARYN2 SEARCHED FOR MAXIMUM PURITY
194 MATCHED AT LEAST 3 OF THE 4 LARGEST PEAKS IN THE UNKNOWN

RANK	IND	NAME
1	5449	PHENOL,2-ETHYL-5-METHYL-
2	3911	PHENOL,3-ETHYL-5-METHYL-
3	861	PHENOL,4-(1-METHYLETHYL)-
4	568	PHENOL,2-(1-METHYLETHYL)-
5	6076	PHENOL,4-ETHYL-2-METHYL-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C9.H12.O	136	121	733	733	973
2	C9.H12.O	136	121	707	707	962
3	C9.H12.O	136	121	706	706	972
4	C9.H12.O	136	121	691	691	974
5	C9.H12.O	136	121	670	670	981

MASS	INTEN	1	2	3	4	5
39		179	78	62	61	171
41				31		
51		104	48	36	50	126
53		73				83
63		53				57
65		76	46	58	46	74
67			111			
77		308	327	418	441	396
78		76				106
79			75			142
91	335	335	335	335	335	335
93		64	60	120	117	
94				50		
102					19	
103			34	147	247	
104					23	
107		32	86	33	33	149
108						86
115		39	19		26	
119				23		
120				25	15	
121	1000	1182	947	1169	1169	1203
122	259	107	82	107	105	152
135		32	57	16		37
136	410	364	572	356	379	318
137		37	54	29	38	37

Table D-5. 1,2-Dimethoxybenzene Identification in Methylated Synthane Water

```
LIBRARY SEARCH                   DATA: METHSYNB # 317      BASE M/E:  138
03/10/78 10:28:00 + 15:51          CALI: CAL09MAR # 1        RIC:      96895.
SAMPLE: METHYLATED SYNTHANE WATER

25409 SPECTRA IN LIBRARY B SEARCHED FOR MAXIMUM PURITY
  129 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IND NAME
1    619  BENZENE,1,2-DIMETHOXY-
2   1789  BENZE[illegible],1,[illegible]-DI[illegible]-
3   4272  2-[illegible],1-CYC[illegible]IDENE-
4   1791  [illegible],1,2-DIMETHO[illegible]-
5   24[illegible]  [illegible]
```

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C8.H10.O2	[illegible]	[illegible]	[illegible]	934	682
2	C8.H10.O2	[illegible]	123	835	908	806
3	C9.H1[illegible].O	13[illegible]	13[illegible]	[illegible]	853	741
4	C8.H10.O2	13[illegible]	139	665	908	665
5	C10.H18	138	138	664	834	698

MASS	INTEN	1	2	3	4	5
38	37					
39	71	139		95		65
41	133		173	[illegible]		123
43				308		
50	56					
51	113	93	58			
52	140	114	81		89	
53	34		56	46		37
54	12					
55	28			77		65
62	17					
63	70	51	93		68	
64	48	39	92		49	
65	132	134	88		88	
66	13					
67	45	59		110		53
68						25
69						21
74	9					
77	257	208	52	51	56	23
78	41	27			121	
79	26		30	117	45	33
80	63	48	50	279	43	
81	8			101		191
82						51
91	3					
92	41	25	58		51	
93	31				46	
94	8					26
95	313	336	311	262	178	303
96	22					66
105	4					
107	15				43	
108	12				105	
109	26			90	173	
110				63		
121	14					
122	17					
123	397	462	767	455		387
124	31	36	68			
125	2					
135	6					
136	0					
137	4					
138	1000	927	537	839	972	446
139	88	84	45	111	115	49
140	6					
150	3					
152	2					

Table D-6. 5-Methoxy-2,3-Dimethylphenol Identification in Methylated Synthane Water

```
LIBRARY SEARCH                DATA: METHSYNB% ● 358     BASE M/E:  152
05/10/78 10:20:00 + 17:54     ENHANCED (S 348 2N 0T)    RIC:     56511.
SAMPLE: METHYLATED SYNTHANE WATER

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  186 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IND NAME
1 17680  PHENOL,5-METHOXY-2,3-DIMETHYL-
2  2209  1-CYCLOHEXENE-1-CARBOXALDEHYDE,2,6,6-TRIMETHYL-
3  3454  BENZENE,1-(ETHYLTHIO)-4-METHYL-
4  2836  2-CYCLOPENTEN-1-ONE,4-HYDROXY-3-METHYL-2-(2-PROPENYL)-
5 17643  BENZENE,1-(ETHYLTHIO)-3-METHYL-

RANK  FORMULA                          M.WT E.PK  PURITY  FIT  RFIT
1 C9.H12.O2                             152  152     747  993   754
2 C10.H16.O                             152  152     641  850   641
3 C9.H12.S                              152  152     636  852   708
4 C9.H12.O2                             152  152     630  850   678
5 C9.H12.S                              152  152     628  651   704

MASS   INTEN     1     2     3     4     5
  39    102   109           91    85    85
  40     47
  41     30           30           75
  43     19           26          159
  45                       211          156
  50     30
  51     64    69
  52     33
  53     52    26                 98
  55     23
  63     31                 66          78
  64     10
  65     29    31           82          92
  66     87
  67     12           112               89
  69           44           40          31
  76      8
  77    134   198           66    74    63
  78     47   151           26
  75     97    36    51     47   157    36
  80      7
  81     55          155           95
  89     15
  91    172    65    65    249   101   237
  92     10                 33          34
  93     17           50    22          22
  94     89           55
  95     13           73           57
 105     31                        34
 106     10
 107     67    86    70
 108     16
 109    221    77   191          236
 110     14
 111                              81
 119      3           61                38
 121     21    42    54    49          45
 122      2
 123     19    62   272   141    85    54
 124                      177    75   210
 133     10
 135     16
 136     19
 137    374   439   605   453   373   404
 138     39    58    69    43          47
 139      2
 149      4
 151     33   294
 152   1000   889   634   902   552   902
 153     96    89           97          80
 154      5                 44          43
 166     44
 167      3
```

Table D-7. 3-Methoxy-2,4,6-Trimethylphenol Identification in Methylated Synthane Water

LIBRARY SEARCH DATA: METHSYNB$ ● 396 BASE M/E: 151
03/10/78 19:28:00 + 19:48 ENHANCED (S 349 2N 8T) RIC: 10975.
SAMPLE: METHYLATED SYNTHANE WATER

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
55 MATCHED AT LEAST 6 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IND NAME
1 17684 PHENOL,3-METHOXY-2,4,6-TRIMETHYL-
2 17662 PHENOL,3-METHOXY-2,5,6-TRIMETHYL-
3 2841 ETHANONE,1-(2-HYDROXY-4-METHOXYPHENYL)-
4 17681 PHENOL,5-METHOXY-2,3,4-TRIMETHYL-
5 809 1,2-BENZENEDIOL,4-(1,1-DIMETHYLETHYL)-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C10.H14.O2	166	166	779	991	808
2	C10.H14.O2	166	166	774	875	817
3	C9.H10.O3	166	151	770	925	814
4	C10.H14.O2	166	166	765	878	811
5	C10.H14.O2	166	151	764	890	816

MASS	INTEN	1	2	3	4	5
39	45	45	58	44	40	45
40	11					
41	7	66			42	63
43			45	142		
50	8					
51	40		30	36	34	42
52	12			31		
53	22		40		40	
55	9	66				
63	16			21		
65	40		40	36	35	49
67		56	39		43	
69		55		26	55	
77	98	73	82		83	91
78	35					
79	64	55	72		73	49
80	9			31		
89	6					
90	6					
91	100	135	100		84	
92	9	57				
93	3					44
94				13		
95	102			97		
99						28
103	20					
105	53	27	32			70
106	19					
107	49	35	36	13	37	39
108	72			104		65
109				14		41
110						25
111						35
119	12					
120	1					
121	23	26	46		43	
122			25		17	
123	35	57	50	26	47	107
131	16					
135	64	137	132		97	77
136	19					
137		37	76		75	50
138				22		
147	20					
149				13		
150	10					43
151	1000	539	518	1100	567	1153
152	119	75	55	116	53	121
153				13		
162	20					
165	39	76	142	15	157	
166	569	851	788	410	753	349
167	57	85	87	43	83	42

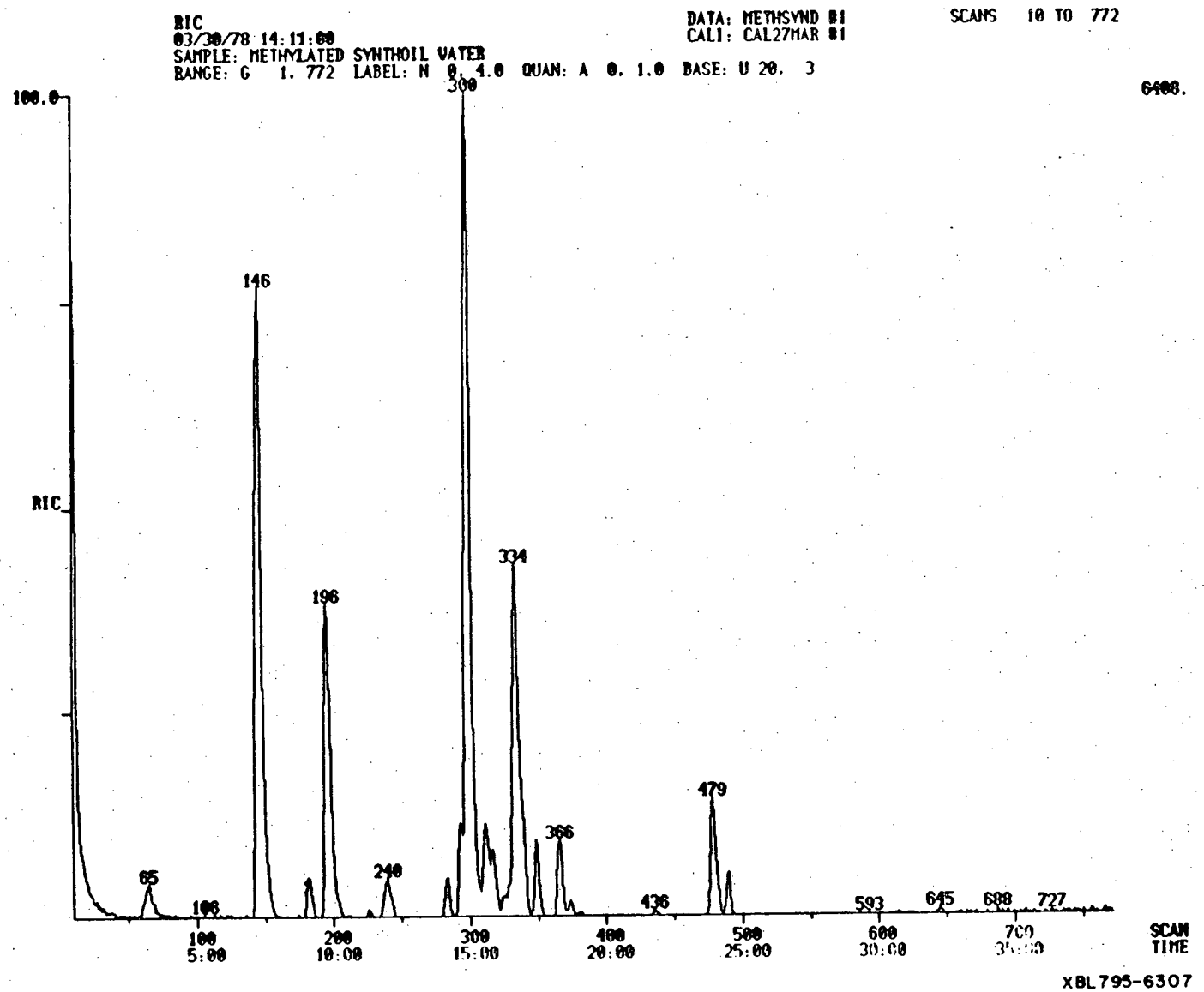


Figure D-2. Computer-Reconstructed Gas Chromatogram of Methylated SRC Water

Table D-8. Methoxybenzene Identification in Methylated SRC Water

```
LIBRARY SEARCH                  DATA: METHSYND • 146      BASE M/E:  108
03/30/78 14:11:00 + 7:18        CALI: CAL27MAR •   1      RIC:      4919.
SAMPLE: METHYLATED SYNTHOIL WATER

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  139 MATCHED AT LEAST 5 OF THE 13 LARGEST PEAKS IN THE UNKNOWN

RANK IND NAME
1   901  BENZENE,METHOXY-
2   898  HYDRAZINE,PHENYL-
3 10431  CARBONICACID,METHYLPHENYLESTER
4 19819  PYRIDINIUM,1-AMINO-2-METHYL-,HYDROXIDE,INNERSALT
5  2462  BENZOFURAN,4,5,6,7-TETRAHYDRO-3,3-DIMETHYL-

RANK  FORMULA                                  M.WT B.PK  PURITY   FIT   RFIT
1 C7.H8.O                                       108  109     910   939    948
2 C6.H8.N2                                      108  108     727   737    915
3 C8.H8.O2                                      152  108     679   725    895
4 C6.H8.N2                                      108  108     580   618    658
5 C10.H14.O                                     150  108     530   549    785

MASS   INTEN     1     2     3     4     5
  38     17    31
  39    258   128   106                 258
  41                                     162
  43      6
  44                        23
  50     22    47   130    39    53
  51     75    88   215    74   111
  52           22   101          75
  53                              78
  59                        90
  63     18    43    39    52
  64           25    37    21
  65    487   342   160   434   497    26
  66           22    36    26   170
  67                              59
  74           15
  77     90   100   106   150    66    61
  78    369   357   373   236   109    23
  79     61    77    52    64    51   114
  80                              101   26
  81                              43
  91                      80           56
  92                     202          548
  93     63           142   176   248    24
  94                        27
 105                                    27
 106                      85
 107           24
 108   1000   924   726   667   815  1024
 109     16    71                 82    90
 121                                    24
 135                                    23
 149                                    17
 150                                   282
 151                                    31
 152                        246
 153                         13
```

Table D-9. 1-Methoxy-4-Methylbenzene Identification in Methylated SRC Water

```
LIBRARY SEARCH                  DATA: METHSYND • 196      BASE M/E:  122
03/30/78 14:11:00 + 9:48        CAL1: CAL27MAR •   1      RIC:      2451.
SAMPLE: METHYLATED SYNTHOIL WATER

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  103 MATCHED AT LEAST 5 OF THE  8 LARGEST PEAKS IN THE UNKNOWN

RANK IND NAME
1  1022  BENZENE,1-METHOXY-4-METHYL-
2  3002  BENZENE,1-METHOXY-2-METHYL-
3   913  BENZENE,1-METHOXY-3-METHYL-
4   735  PHENOL,2,5-DIMETHYL-
5  2744  BENZENE,(METHOXYMETHYL)-

RANK  FORMULA                          M.WT B.PK  PURITY   FIT   RFIT
1 C8.H10.O                              122  122     878   878    963
2 C8.H10.O                              122  122     841   841    956
3 C8.H10.O                              122  122     828   828    953
4 C8.H10.O                              122  122     745   747    875
5 C8.H10.O                              122  122     720   778    834

MASS   INTEN     1     2     3     4     5
  39     14    14    14   177    14    84
  51           15    11   122    14    39
  52           24          46         114
  53           24          46    37
  63           18    21    32
  64                                    53
  65           25    54    32    35
  66                                    47
  77    179   175   149   144   195    77
  78          37    33    45    65    13
  79     63   125    79   128   111    33
  89                27                 18
  90                33                 11
  91    189   112   159   187    39   271
  92      8    41    34    84         57
  93                      23    11
 103                            36
 104                            40
 105                            20    40
 107    143   254   358   168   497
 108          21    36          40
 121    245   343   150   141   251   537
 122   1000   773   815  1030   560   605
 123          68    76    91    51    52
```

Table D-10. 1,2-Dimethoxybenzene Identification in Methylate SRC Water

LIBRARY SEARCH DATA: METHSYND ● 300 BASE M/E: 138
03/30/78 14:11:00 + 15:00 CALI: CAL27MAR ● 1 RIC: 6415.
SAMPLE: METHYLATED SYNTHOIL WATER

25489 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
95 MATCHED AT LEAST 5 OF THE 15 LARGEST PEAKS IN THE UNKNOWN

RANK	IND	NAME
1	618	BENZENE,1,2-DIMETHOXY-
2	1789	BENZENE,1,4-DIMETHOXY-
3	3446	BENZENE,(ETHYLTHIO)-
4	2678	1,3-BENZENEDIOL,4,5-DIMETHYL-
5	1791	BENZENE,1,3-DIMETHOXY-

RANK	FORMULA	M.WT	B.PK	PURITY	FIT	RFIT
1	C8.H10.O2	138	138	942	958	960
2	C8.H10.O2	138	123	885	814	848
3	C8.H10.S	138	138	671	754	836
4	C8.H10.O2	138	138	649	665	983
5	C8.H10.O2	138	138	642	778	772

MASS	INTEN	1	2	3	4	5
39	11	46		29		
41	39		77		52	
43					43	
45				56		
50	8			20		
51	31	33	26	40	35	
52	59	42	51			61
53			35		49	
55					46	
63	12	18	58			60
64		14	57			49
65	45	46	50	64	50	87
66				52		
67		20			40	
69				47	86	
77	103	129	37	59	98	51
78		12				116
79			22			43
80	5	21	37			41
84				29		
91					106	
92		12	37			64
93						58
95	194	165	232		95	223
107						39
108						95
109	16			94	23	156
110				263		
111				24		
120					31	
121					35	
123	260	407	646	471	537	
124	19	32	51	40	58	
137					301	
138	1000	814	452	726	601	937
139	57	73	38	69	54	111
140				34		

Table D-11. 5-Methoxy-2,3-Dimethylphenol Identification in Methylated SRC Water

```
LIBRARY SEARCH                    DATA: METHSYND • 334      BASE M/E:  152
03/30/78 14:11:00 + 16:42         CAL I: CAL271AR •   1     RIC:      2763.
SAMPLE: METHYLATED SYNTHOIL WATER

25489 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
   74 MATCHED AT LEAST 5 OF THE 12 LARGEST PEAKS IN THE UNKNOWN

RANK IND NAME
1  3454  BENZENE,1-(ETHYLTHIO)-4-METHYL-
2 19650  2-CYCLOPENTEN-1-ONE,4-ACETYL-1,2,3,5,5-PENTAMETHYL-
3 17680  PHENOL,5-METHOXY-2,3-DIMETHYL-
4 17643  BENZENE,1-(ETHYLTHIO)-3-METHYL-
5   583  ETHANONE,1-(2,4-DIHYDROXY-3,5-DIMETHYL)-

RANK  FORMULA                          M.WT B.PK  PURITY   FIT   RFIT
1 C9.H12.S                              152  152     738   768    869
2 C12.H18.O2                            194  152     728   843    829
3 C9.H12.O2                             152  152     720   721    916
4 C9.H12.S                              152  152     713   742    865
5 C8.H8.O3                              152  137     648   665    715

MASS   INTEN     1     2     3     4     5
  39     20    84           83   110    20
  43                                     38
  45          100                 163
  51                       47           17
  52                                     11
  53                 73    41           20
  55                 73
  63          19                 21     10
  65     6    23           47    27
  67                 25
  69          20           19    17     54
  77     33   33           85    33
  78          13           67
  79     10   24           18    19
  81                 72                 65
  91     24  131    58     55   131
  92          17                 19
  93          12    44           12
  94      6
  95                 39
 107                       80
 108                                    26
 109     84          25    71           84
 119                                 32
 121          37           37    37
 123    117  100   189     55    69      6
 124         135                 100
 137    257  409   376    442   435    757
 138    203   39          58    41     62
 139                                     7
 151                       269
 152   1000  823   771    815   815    296
 153     13   89          82    80     28
 154         41                 39
 166                 10
 179                  6
 194                  9
```

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Extraction of Phenols from Coal Conversion Process Condensate Waters

By

Douglas Carl Greminger

B.S.E. (University of Michigan) 1976

THESIS

Submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

in

Chemical Engineering

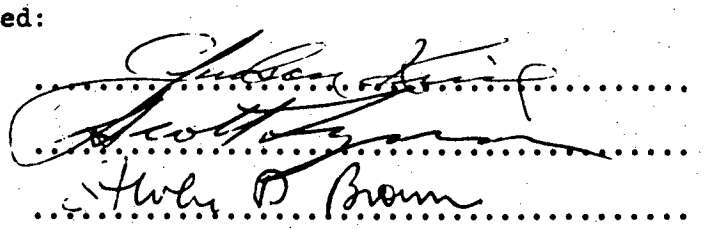
in the

GRADUATE DIVISION

of the

UNIVERSITY OF CALIFORNIA, BERKELEY

Approved:



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