

Lawrence Berkeley National Laboratory

Recent Work

Title

JULY MONTHLY PROGRESS REPORT - ENVIRONMENTAL EFFECT AND CONTROLS FOR COAL-WATER SYSTEMS

Permalink

<https://escholarship.org/uc/item/9gn3x322>

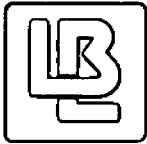
Authors

Newton, Amos

Fox, Phyllis.

Publication Date

1980-08-01



Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT
DIVISION

For Reference
Not to be taken from this room



RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUL 22 1980

LIBRARY AND
DOCUMENTS SECTION

LBID-261 c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

August 22, 1980

TO: Charles Grua
FROM: Amos Newton and Phyllis Fox
RE: July Monthly Progress Report
Environmental Effect and Controls for
Coal-Water Systems
LBID-261

PHENOLIC COMPOUNDS IN COAL SLURRY WATER

Of the possible organic compounds which might be found in coal slurry water, phenolic compounds are the most likely candidates. The high solubility of phenolic compounds in water and the difficulty of extracting such compounds from water suggests that if phenolics occur in coal they will be partially extracted into the water phase.

Experiments previously described have shown that phenol can be recovered from water by methylation with dimethyl sulfate and extraction of the resulting anisole (methyl phenyl ether). Yields of 40 to 80% were found for the determination of phenol and deuterophenol in water at the part per billion concentration level by this method.

The sensitivity of anisole and 2,3,4,5,6-deuteroanisole in the GC/MS is such that 0.25 ng of either compound shows a good response at the parent ion of each respective compound ($M/z = 108$ for anisole and $M/z = 113$ for 2,3,4,5,6-deuteroanisole). No interference has been observed at $M/z = 108$ or $M/z = 113$ within a wide window on each side of the anisole emergence time in the reconstructed gas chromatogram of any phenolic sample from coal slurry water.

In order to check if other phenolic compounds are methylated and recovered with phenol and perdeuterophenol, a solution containing 100 ng each of perdeuterophenol, phenol, o-cresol, and resorcinol in 500 ml of 1.0 N NaOH was methylated by stirring overnight at 2⁰C with 50 ml of dimethyl sulfate. The products were extracted with hexane and the hexane solution concentrated to 10 ml. The results are shown in Table 1. Each compound shows excellent recovery and adequate sensitivity at the parent M/z to demonstrate the fact that they should be detected at a concentration of 0.5 ppb. The ratio of parent ion intensity to the total ion intensity for each compound is very nearly 1/3.

TABLE 1

GC/MS Results of Methylating Phenolic Compounds

Compound	Parent Ion M/z	Parent Ion Mass Chromatogram Peak Area	Peak Area Compound Peak Area for $C_6D_5OCH_3$
$C_6D_5OCH_3$	113	17800	1.00
$C_6H_5OCH_3$	108	20500	1.15
$CH_3(C_6H_4)OCH_3$	122	22800	1.28
$C_6H_4(OCH_3)_2$	138	13600	0.76

Measurements of mass chromatograms M/z = 108, 113, 122, and 138 represent a relative measure of the occurrence of each respective compound in the coal slurry water.

When Wyodak coal is slurried with water, phenol is found in the water at a concentration of about 5 ppb. Values from 1 to 10 ppb have been observed. The use of perdeuterophenol as an internal standard by addition of a known amount of perdeuterophenol to the coal slurry water after centrifugation should act as a standard for the behavior of ordinary phenol without regard for losses in the methylation, extraction, and concentration procedures. The relative areas of the mass chromatograms at M/z = 113 and M/z = 108 should directly represent the relative concentrations of deuterophenol and phenol in the coal slurry water.

$$\frac{A (M/z = 113)}{A (M/z = 108)} = \frac{\text{Conc } (C_6D_5OD)}{\text{Conc } (C_6H_5OH)} \quad (1)$$

If chromatographic peaks are observed from resorcinol (M/z = 138) or cresol (M/z = 122), these concentrations can be calculated by use of the appropriate mass chromatographic area. No mass 122 or mass 138 peaks were

observed in the chromatograms of any coal slurry water. If cresols or resorcinol type compounds occur in coal slurry water from Wyodak coal, the concentration must be less than 0.5 ppb. The concentration of phenol in coal slurry water in experiments in which a deuterophenol internal standard was added are shown in Table 2.

TABLE 2
Concentration of Phenol in Coal Slurry Water

Expt. No.	Conc C_6D_5OD added ppb	Mass Chromatograms		Conc. Phenol ppb
		Peak Area M/z = 113	Peak Area M/z - 108	
1	100	24083	1291	5.36
2	5	108	246	11.4
3	5	435	108	1.2

The results in Table 2 show more scatter than expected when an internal standard is used. The factor of 10 difference in experiments 2 and 3 are outside experimental errors expected with the method. It does not appear reasonable that the deviation can be attributed to differences in the kilogram samples of coal used in each respective experiment. Further experiments with known solutions of phenol in water need to be done to further evaluate the GC/MS performance of samples with added internal standards.

ABSORPTION OF PHENOL BY COAL

The addition of perdeuterophenol and/or phenol to makeup water before coal is added in the slurry mode should result in the same phenol concentration in the water as is found with no phenol added. This conclusion is based on the assumption that the concentration of phenol in the water is the result of a distribution of phenol between water and coal and that this equilibrium distribution is reached from both directions, i.e., coal to water or water to coal.

Perdeuterophenol was added to the starting water at a concentration of 100 ppb (100 µg/liter). One kg of Wyodak coal was slurried with 4 l of this water. The water was separated by centrifugation and the phenols separated by methylation and extraction with hexane. The hexane was concentrated to 10 ml and one microliter of this was injected into the GC/MS. In a second experiment, ordinary phenol was added to the starting water at 100 ppb concentration, and in a third experiment both perdeuterophenol and ordinary phenol were added to the starting water, each at a concentration of 100 ppb. In none of these experiments was an internal standard added after centrifugation. Therefore quantification is based on the response to known solutions of phenol and deuterophenol in water, methylated, extracted, and concentrated by the same method.

The results are shown in Table 3. They show that phenols are absorbed from water by coal and that the final concentrations of phenols in water is very close to the concentration found in water from phenol leaching out of coal. The fact that perdeuterated phenol is at a lower concentration than phenol in those samples to which perdeuterated phenol was added shows there to be a reservoir of phenol in the coal which is exchangeable with the perdeuterophenol.

TABLE 3
Effect of Adding Phenol and Perdeuterophenol
to the Starting Water for Coal Slurry Formation

Sample	Conc. of Phenol in Water		
	ppb C ₆ D ₅ OCH ₃	ppb C ₆ H ₅ OCH ₃	ppb total phenols
1. 100 ppb C ₆ D ₅ OD added	1.0	2.5	3.5
2. 100 ppb C ₆ H ₅ OH added	---	8.5	8.5
3. 100 ppb C ₆ D ₅ OD and 100 ppb C ₆ H ₅ OH added	7.9	17.5	25.4

In experiment 3 the total amounts of phenols added are greater, and they appear to be less fully absorbed, though this difference in absorption

needs to be checked. In principle, from the total concentration of phenols added, the volume of water, the weight of coal, and the ratio of perdeuterated phenol in the water to ordinary phenol in the water, one could calculate the reservoir of easily exchangeable phenol in the coal. This has not been done because it has not been established that the perdeuterophenol was reduced to a steady state in any of the experiments.

FUTURE PLANS

The absorption by coal of phenolic compounds other than phenol will be investigated. The addition of such compounds as o-cresol; 2,6, dimethylphenol; 1-naphthol; and 2-phenylphenol to the starting water will be made. Similar experiments will be done with other classes of compounds and other coals.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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