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TO: Charles Grua

FROM: Amos Newton and Phyllis Fox

RE: September Monthly Progress Report
Environmental Effect and Controls for
Coal-Water Systems
LBID-301

QUANTIFICATION OF GC/MS RESULTS

The use of deuterated internal standards for quantification of organics in coal slurry waters using the Finnigan 4023 GC/MS has been extended. Previously, results were described using internal standards mixed with the sample in the injection syringe. We have now made mixtures of anisole and 2,3,4,5,6 deuteroanisoles in varying ratios and concentrations. It has been shown that the respective parent ion peaks of M/Z=108 for anisole and M/Z=113 for deuteroanisole each represent very close to 33% of the total intensity of all peaks in the mass spectrum of each respective compound, and that these mass peaks can be used to quantify the relative amounts of the two compounds.

Various concentrations were made by volumetric mixing and diluting of standard solutions in hexane of anisole and deuteroanisole. The errors in mixing the solutions should be negligible and the ratio of anisole to deuteroanisole should be consistent for the various dilutions. The response of the GC/MS to each of the components can be measured by the intensity of the GC peak at each mass number (peak height) or the area of the GC/MS peak at each mass number. Both have been calculated in Table 1.

The data in Table 1 show that, contrary to expectations, the use of peak intensities yield more consistent results than do peak areas. Owing to the extreme narrowness of the GC peaks, too few scan points are available to give a good measure of the area. Using peak heights and an added amount of internal standard within a factor of 10 of the unknown amount of anisole present, the error should not exceed ± 10%.

Table 1. Test results of quantitation of anisoles.

Sample No.	Conc. in ppm		Ratio	Peak heights		Peak areas	
	D_5Anisole	Anisole	Anisole/ D_5Anisole	Ratio	Deviation %	Ratio	Deviation %
1	20.0	180.0	9.00	9.03	+0.3	9.71	+8
2	20.0	100.0	5.00	4.70	-6.0	5.50	+10
3	2.0	50.0	25.00	20.30	-19.0	32.00	+28
4	0.5	50.0	100.00	79.00	-21.0	171.00	+71
5	20.0	20.0	1.00	0.94	-6.0	1.09	+9
6	2.0	10.0	5.00	4.50	-10.0	6.40	+28
7	0.5	5.0	10.00	9.70	-3.0	20.40	+104
8	5.0	0.5	0.10	0.097	-13.0	0.05	-50
9	2.0	2.0	1.00	0.95	-5.0	1.09	+9
10	0.5	2.0	4.00	3.80	-5.0	6.80	+7
11	0.5	10.0	20.00	18.00	-10.0	37.10	+85

Because internal standards are so necessary for many projects, the factors which lead to errors in the results obtained by use of such standards will be evaluated in this and other methods.

PHENOLS IN COAL SLURRY WATER

Work has continued on the behavior of phenols in coal slurry water. A slurry of coal with water initially containing 100 ppb each of phenol, O-cresol, resorcinol, 1-napthol, 4-phenyl phenol and 2,6 dimethyl phenol was prepared. Slurry was centrifuged and perdeuterophenol added to a concentration of 5 ppb. The solution was made basic and methylated with dimethyl sulfate. The only methylated products observed were anisole and the internal standard, 2,3,4,5,6 deuteroanisole. The phenol concentration observed was 12 ppb which is in agreement with an average value from three previous experiments of 8 ppb. The concentration of each of the other phenols (none observed) in the coal slurry water was less than 0.1 ppb.

NITROGEN COMPOUNDS IN COAL SLURRY WATER

Some representative nitrogen containing compounds which might be formed from coal were added to water at a concentration of 100 ppb before a coal slurry of Wyodak coal was made. The slurry was centrifuged and the resulting water extracted with hexane. The hexane was examined for the component species by GC/MS and the results compared to an extract from water which had not been slurried with coal. One added component, pyrolle, did not appear in the GC/MS trace of the extract of either the slurry water or the water solution. Only quinoline was observed in the extract of the coal slurry water at a concentration of 1.5% of that added. The concentrations of pyridine, aniline, and diphenyl methane were each below the detectability levels under the conditions of the experiment. More than 99.7% of each of these added compounds was absorbed by the Wyodak coal (Table 2).

Table 2. The effect of coal on added nitrogen compounds.

Compound added	Conc. added ppb	Conc. found ppb	% absorbed
pyridine	100	< 0.2	> 99.8
aniline	100	< 0.3	> 99.7
quinoline	100	1.5	98.5
diphenyl methane	< 100	< 0.2	> 99.8

GENERAL PROPERTIES OF COAL SLURRY WATER

The pH of coal slurry water from Wyodak coal was found to be 6.5. The total organic carbon content of the water was 20 ppm. The water had a slight yellow color. The total organic carbon found may be caused by humic acids extracted from the sub-bituminous coal and/or very fine particles not completely removed by the centrifuge. This water is difficult to clarify and two hours of centrifuging at $2^{o}C$ and 7500 RPM are required for clarification.

FUTURE PLANS

Work has started on other types of coal but definitive results for them are not available. Coal slurry waters from a bituminous coal, Illinois No. 6, are under investigation. Further studies with deuterated PNA's are in progress to determine the extent of scavenging each of several PNA's from water by the slurried coal. The scavenging by each type of coal will be studied.

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