

Sulfur Species in Perchloroethylene and Other Coal Extracts

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INTRODUCTION

Earlier work (1,2,3) has indicated that elemental sulfur can be removed from coal by the use of perchloroethylene (tetrachloroethylene). The unique ability to remove the elemental form of the sulfur has led to considerable interest in the process and mechanism of action. Under joint CRSC-EPRI sponsorship, an effort has been made to understand the species that can be removed by extraction with perchloroethylene (PCE). The effort involved the extraction of a set of coals at Eastern Illinois University by Prof. David Buchanan and coworkers, and the related effort to identify the species in the extract by the use of gas chromatography-mass spectrometry at the Argonne National Laboratory (ANL). This paper reports on the analytical work on the extracts.

EXPERIMENTAL

Extracts were prepared and sent in glass vials to ANL. The contents of the vials were dissolved in solvents and studied in one of two systems.

The first system was a gas chromatograph equipped with a Hall Effect Conductivity Detector (HECD). This detector was selected because it can be made to be sensitive to sulfur-containing species and will permit establishing the number of species in very dilute concentrations. The HECD was mounted on a Tracor Model 540 gas chromatograph, and attached to a strip chart recorder. A J&W DB-5 column (30 m, .25 mm id) was used. The typical run started at 85 C for 4 minutes and then the temperature was increased at 10 C/minute to 320 C and held there for up to 30 minutes before cooling. The attenuator on the recorder was reset as needed to keep the peaks on the chart. The settings were recorded on the chart. A series of standards was run to provide retention time values for comparison with the observed peaks.

The HECD measures the conductivity of a sample which has been oxidized (in this case to SO_2) and introduced into a stream of purified methanol. This can be calibrated with standards of varying concentration to obtain quantitative data. The instrument is extremely sensitive to contamination from halogen containing-materials.

The system was calibrated for the amount of sulfur in the individual species by preparing different concentrations of thiophenol and making several runs to establish the response in terms of peak height per unit of mass of sulfur in the compound. The response was 5×10^{-12} grams of sulfur per one millivolt peak.

The second system was a Hewlett Packard GC/MS, model 5970B, which was set up using the same type of J&W DB-5 column used in the Tracor instrument. The same time-temperature profile used with the HECD system was employed to be able to compare the results on a common basis. At the beginning of each day the autotune procedure was used to assure that the instrument was performing to meet the manufacturer's specifications. A blank run was then carried out to check on performance of the chromatograph system and to check on the cleanliness of the solvent.

In a typical run, the chromatogram was displayed, data were saved, and analyzed later. The portion of the chromatogram to study was selected and the characteristics of the peaks to be included were specified. A macro was developed to analyze the mass spectral data for use with the Hewlett Packard computer system. Then for each peak the relative abundance for each mass was tabulated. The data were then checked against the library of about 133,000 spectra for the best matches. A graphical representation of the 4 best matches was printed together with a table of the 20 best matches. A numerical value of the "quality" of the match was included. A standard algorithm for this quality, developed earlier by McClafferty and coworkers, was used.

Initially the gas chromatograph was programmed to have a temperature increase of 10 C/minute for data acquisition. It became evident from the GC/MS results that a number of extracts contained many constituents. A precision temperature profile which used a 4 C/minute heating rate was then used to provide for better resolution of the peaks and improved identification of the species.

The coals used and samples derived from them included

Series 9391, 7107, 7111 and 7112

These extracts were prepared from Illinois #6 samples of the Argonne Premium Coal Sample Program (APCS) and the isotopically labelled sulfur sample of the Illinois Basin Coal Sample Program (IBCSP).

APCS #3, pristine, PCE extract, EIU #9391
IBCSP #7, oxidized, PCE extract, EIU #7107
IBCSP #7, light organics from EIU 7107, EIU #7111
IBCSP #7, heavy organics from EIU 7107, EIU #7112

Series 9395 and 9397

These samples were prepared from APCS #3, a pristine starting material.

Tetrahydrofuran extracts and fractionated on an alumina column to give the following EIU sample numbers

EIU # 9395 AHC Aliphatic hydrocarbons
EIU # 9395 PAC Neutral polycyclic aromatic hydrocarbons
EIU # 9395 N-PAC Nitrogen polycyclic aromatic hydrocarbons
EIU # 9395 HPAH Hydroxy polycyclic aromatic compounds
EIU # 9395 Py Pyridine eluent
EIU # 9395 MeOH Methanol eluent

Perchloroethylene extracts

EIU # 9397 AHC
EIU # 9397 PAC
EIU # 9397 N-PAC
EIU # 9397 HPAH
EIU # 9397 Py

Series 6320

These samples were prepared from IBCSP #5, unoxidized. These samples came from the same block of coal used for APCS #3.

These samples were extracted with THF and fractionated on an alumina column to give the following EIU sample numbers:

6320 AHC
6320 PAC
6320 N-PAC
6320 HPAH
6320 Py

The 6320 PAC fraction was further separated on a silica gel/PdCl₂ column to give:

6320 PAH
6320 PASH
6320 S-PAC, passed over a silica column.

Sample 6269

A PCE extract of oxidized IBCSP #5 was given the sample number 6269.

Sample 6201-38

IBCSP #5, oxidized, PCE extract was sample number 6201-38.
6201-38 untreated with NiCl₂
6201-38 treated with NiCl₂

Sample 5618

A THF extract of oxidized Ohio 5/6 coal is 5618. The sulfatic sulfur = 0.38%.

In addition to the extracts a number of standard compounds have been run in both instruments. For the HECD, this provided a set of retention times for checking the identity of compounds. For the GC/MS this provided a means of checking the mass spectra as well as retention times.

RESULTS AND DISCUSSION

A number of species were found with the HECD in the extracts. Retention times and peak heights were noted such that comparisons could be made later with GC/MS data.

Calibration data with thiophenol indicated that a peak of 1 mv was equivalent to an injection of one microliter containing 5×10^{-12} grams of sulfur. From this the percent of sulfur in the original extract due to these peaks has been calculated.

The data obtained with the HECD indicate that there are many sulfur species in the extracts. Peaks of retention times close to those for sulfur and dibenzothiophene have been observed. The number of sulfur species observed with this detector significantly exceeds the number that have been identified with the GC/MS. However the concentration of these species is so small, that their peaks are lost in the background of the GC/MS traces. The effort to quantify the peaks gave an indication of the amount of sulfur species that were present in the extracts examined with the HECD. The concentration of sulfur species identified in the extracts is usually such that they would account for at most 0.014% S in the sample extract. The organic sulfur content of the samples is at least 2%.

The GC/MS work indicates that the peaks observed are typical of the aliphatic (n-alkanes) and aromatic (substituted naphthalenes) species present in coal samples. In addition a number of substituted thiophenes, benzothiophenes, dibenzothiophene, thiazoles, benzothiazoles and elemental sulfur have been observed

in different samples. The most frequently observed and most abundant is dibenzothiophene. These data are consistent with the observations of Winans et al (10) on the existence of a number of heteroatom containing species in this sample.

In the HECD studies, the 9397 aliphatic hydrocarbon (AHC) extract contained two peaks close to those for sulfur in a total of 11 peaks. Elemental sulfur does elute with this fraction.

According to earlier reports elemental sulfur is not found in extracts of pristine coal samples (4). The results of this study are consistent with the earlier work. Elemental sulfur was seen in a PCE extract of an oxidized coal. This sample showed three forms of elemental sulfur differing in their molecular weights as the hexamer, heptamer and octamer. As expected the retention times increased with the molecular weight. Each comes off of the column at a reproducible retention time, and has a mass spectrum consistent with the particular polymer size. It is significant that the elemental sulfur is found in the oxidized sample which was later extracted with PCE, but not in the pristine samples.

The PCE does extract a series of species which on fractionation are typical of the fractions from better solvents. A range of n-alkanes was seen in the 9397 AHC fraction in addition to the tetramethyl longer chain hydrocarbons. The ability of PCE to remove some organic sulfur compounds from pristine samples is seen in the compounds identified from 9397 PAC. These compounds included three different substituted benzothiophenes and dibenzothiophene. The nitrogen-containing polycyclic fraction also had dibenzothiophene in it along with a possible isothiazole. The hydroxy polycyclic aromatic fraction had a small number of peaks, but they included substituted derivatives of benzenethiol, thiophene, benzothiazole and benzothiophene. In the latter case the quality of the matches were all low, but represent best choices from the available data.

The extracts which were analyzed without fractionation seemed to have too low a concentration of sulfur species for them to be observed. After fractionation, with the associated concentration of these species, the sulfur species were observed. The 9391 was a whole coal extract of pristine APCS #3 and showed almost no indication of a sulfur compound. The 9397 extract fractions showed evidence of sulfur compounds in three of the fractions (PAC, N-PAC and H-PAH). There were 10 peaks in the three fractions representing 9 compounds.

The THF fractions from the same pristine APCS #3 (9395 series) with sulfur compounds in them were essentially the same with the addition of the MeOH eluent. However there were fewer peaks observed (5) representing only 4 compounds. By comparison the PCE was more effective in solubilizing sulfur species. Only one was observed in both series (dibenzothiophene). The other compounds were different in the two series.

Those fractions with more sulfur species in the 9397 series were also observed to have more sulfur species peaks in the HECD studies than the other fractions. The PAC fraction in 9397 had 4 compounds while the HECD showed 53 peaks, and the N-PAC fraction had two compounds while the HECD showed 12 peaks.

Some species were identified which are associated with solvents as preservatives (2-6 bis(1,1dimethylethyl)4 phenol and its oxidation product (1,1 dimethylethyl) 4 methoxy phenol. PCE extracts sometimes had hexachlorobutadiene in them as a product of reaction of two PCE molecules. Others are associated with pump oils such as 1,2 benzenedicarboxylic acid and its esters.

A number of isomers exist for some common compounds in these samples. A number of dimethyl naphthalene isomers were indicated. The difference in quality for these is too small to assign a retention time to a specific isomer. In several cases the compound has simply been listed as dimethyl naphthalene. Since these are not sulfur compounds, the specific identification of these species was not crucial to the study.

CONCLUSIONS

1. Small quantities of a number of organic sulfur compounds are extracted from Illinois Basin coals by both perchloroethylene and THF. The amounts are much less than the total organic sulfur in the coal.
2. Elemental sulfur is found in some of the extracts. These extracts are from oxidized coal samples.
3. The elemental sulfur is found in the form of three oligomers with six, seven or eight atoms per molecule.
4. The organic sulfur compounds identified include substituted thiophenes, benzothiophenes, dibenzothiophene, thiazoles, benzothiazoles and possibly others in concentrations lower than were detected with the GC/MS.

5. The concentrations of sulfur species in whole coal extracts was too low to be observed with the GC/MS, but the concentration in the various chromatographic fractions did permit identification of sulfur species in some of the fractions.

6. The PCE extracted different sulfur compounds than the THF did, and extracted a larger number of them.

7. The fractions (PAC, N-PAC, HPAH) which contained sulfur compounds from PCE extractions also contained these types of compounds in the THF extractions.

8. The PCE and THF extracts contained a range of aliphatic and aromatic compounds common to Illinois #6 coal.

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