EFFECT OF WEATHERING ON SOLVENT EXTRACTION OF COALS

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INTRODUCTION

Ambient temperature air oxidation of coal (weathering) is a problem in storage, utilization, and characterization. This work grew out of our observations that toluene insoluble, pyridine soluble (TIPS) fractions of Illinois coals isolated by conventional Soxhlet extraction differed in number average molecular weights, phenol contents, and elemental analyses from the TIPS fractions isolated by the slurry/centrifugation method. Several Soxhlet fractions would not completely redissolve in the extraction solvent and phenol and oxygen contents were unreproducible. The problems have been traced to oxidation during extraction and subsequent work-up, unremoved extraction solvents, and contamination of Soxhlet extracts by colloids. The procedure described below avoids these problems and gives reproducible yields of soluble extracts with good material balances. Sequential extraction of coal with toluene followed by THF, DMF, and pyridine shows that weathering lowers the total extract yield, shifts the distribution from polar soluble toward non-polar solubles, and increases the amount of colloids in the crude extracts.

EXPERIMENTAL PROCEDURES

Coal samples were stored in argon flushed desiccators and handled in nitrogen flushed glove bags as much as possible. Samples ground to -100 mesh in a nitrogen flushed ball mill were dried to constant weight at 100° C and 0.05 Torr ("standard conditions") in a large Abderhalden apparatus(1) before use. Soxhlet thimbles were washed with the solvents to be used and dried to constant weight under standard conditions. Solvents were dried and distilled under an Ar atmosphere before use.

Soxhlet extraction of an 8-10 g sample of the coals described in Table 1 with approximately 120 mL of Ar purged solvent, under an Ar atmosphere, was continued for two to seven days with each solvent (Scheme). Two, 3 L RB flasks were attached to the inert gas system as ballast tanks; otherwise when the Soxhlet apparatus cycled, air was sucked back into the system through the oil bubbler at the gas exit. The insoluble residue was washed free of solvents with two or three cycles of 80% methanol/water for three hours each in the Soxhlet apparatus, followed by drying of the residue in the thimble to constant weight under standard conditions.

Soluble fractions were filtered, under an Ar blanket, through a Nylon Millipore AP pre-filter and a 0.45 µm Millipore filter, followed by removal of bulk solvent on the rotary evaporator and drying to constant weight under standard conditions. Colloidal material collected on the filter was counted as part of the residue. DMF and pyridine soluble fractions were washed three or four times with 80% methanol/water and recovered by centrifugation at 2800 G prior to Abderhalden drying. Removal of solvents was monitored by the loss of sharp IR bands at 1661 and 1386 cm^{-1} for DMF and at 1537, 1485, 1253, 750, and 650 cm^{-1} for pyridine, Figure 1.

FT-IR spectra of coal fractions, as KBr pellets (3.0 mg/300 mg), were recorded on a Nicolet 20-DXB spectrometer at 2 cm^{-1} resolution. Argon purged pyridine solutions of coal fractions were spun for 5 - 12 hrs at 24,000 rpm in a Beckman L3-50 Ultracentrifuge using stainless steel sample tubes in the SW27 rotor. The clearing

factor (k) for this experiment was 136; average Relative Centrifugal Field (RCF) = 76,000 G; maximum RCF = 104,000 G.(2) GPC analyses of coal fractions at 6.0 mg/mL in pyridine were performed on a three-column train of ASI Ultragel size exclusion columns (100, 500, 1000 Å) using HPLC grade pyridine at 1.8 mL/min as mobile phase with Refractive Index detection. The system has an efficiency of 7,150 for toluene and is currently calibrated with polystyrene (linear in the 20,000 to 100 dalton region). A 'bootstrap' calibration using narrow molecular weight distribution coal fractions is in progress. MW_n values were determined on a Knauer Model 11.00 Vapor Pressure Osmometer using pyridine at 90° C. Experimental values at three or four concentrations were extrapolated to infinite dilution.

RESULTS AND DISCUSSION

Most coals and especially oxidized coals produce colloidal material upon Soxhlet extraction by polar solvents which can be removed by centrifugation or Millipore, but not ordinary, filtration. Failure to remove this material from extracts has the consequence of defining 'soluble' as anything which will pass through a Soxhlet thimble. For the unoxidized coals in Table 1, less than 0.5% by weight of colloidal material was usually recovered on the Millipore filter. Oxidized coals produced over 2% colloidal material which completely clogged Millipore filters unless the Nylon Pre-filters were used. The FT-IR spectrum of a colloid isolated from the THF extract of coal 701 is shown in Figure 2. The bands at 1723, 1385, and 1177 cm^{-1} suggest esters of fatty acids.(3) Painter and Davis have previously noted FT-IR evidence for aliphatic esters in oxidized coals.(4) The band at 1035 and shoulder at 1130 cm^{-1} have been observed in coal minerals, however sharp kaolinite bands near 3660 cm^{-1}, visible in spectra of coals and residues, are missing in the colloids.(5)

Pyridine and DMF cannot be completely removed from coal by vacuum drying, resulting in high nitrogen contents, but best demonstrated by solvent peaks in the FT-IR spectrum of a water-washed residue after drying to constant weight (Figure 1 and Ref. 6). Since the residue had been extracted with pyridine after the DMF, this shows that both are tightly bound to the coal and that pyridine will not displace or wash out the DMF. Large volumes of 10% HCl or 5% THF in water (6d) will remove pyridine, but not DMF, from residues and extracts. Some mineral matter is lost to the acidic solution. The most efficient washing procedure uses several small portions of 80% (v/v) methanol/water followed by drying to constant weight under standard conditions. The choice of this mixture follows from the high wetting rates of coal in methanol/water and the large heat of immersion of coal in methanol compared with a variety of other solvents.(7) That these considerations lead to removal of DMF under mild conditions suggests that the binding of DMF, and possibly pyridine, to coals and residues may be a surface effect. Unoxidized samples bind pyridine and DMF more tightly than do oxidized samples.

Sequential solvent extractions of coal were carried out as shown in the Scheme and are summarized in Table 2. Total material balances were 92-98% and were 94-105% for individual elements. Several experiments in which the solvent order was changed indicate that each solvent in the Scheme dissolves everything soluble in the previous solvents plus additional material made soluble by both the increasing solvent power (8) and coal swelling ability of the later solvent.(8a, 9) GPC traces of TIPS fractions lack the low molecular tails apparent in pyridine fractions from sequential extraction, Figures 3 - 6. TIPS is isolated by precipitation from the total pyridine extract with excess toluene so that all toluene solubles are removed. However, during sequential extraction some small molecules are not extracted by toluene or THF because coal is not swollen enough for efficient mass transport and this material remains to be extracted by DMF or pyridine. Re-extraction of residue

R600 (Table 2) with pyridine produced 0.8% new extract and 97% recovery of residue, suggesting that little soluble material remains after sequential extraction.

GPC analyses of each soluble fraction, redissolved in pyridine, are plotted together as a Molecular Size Profile, Figures 3 - 6. The solid vertical bars represent the fraction of total extract soluble in the indicated solvent. Although the molecular mass scale cannot yet be used for quantitative analysis of these coal fractions, the changes in molecular size with extraction solvent, coal rank, and oxidation are apparent. Weathered coal gives lower yields in sequential extraction (Table 2), or single solvent extraction.(10) After a pyridine solution of MW_n 1530 TIPS from coal 450 (13.7% total soluble, 8.4% TIPS) was exposed to air for 4 days, 86% by weight remained pyridine soluble. This material had a MW_n of 1498 and produced no further precipitate upon additional air exposure. Pyridine extracts of weathered coals are less prone to oxidation induced precipitation, as if oxidation causes cross-linking which renders a portion of the coal insoluble, either within the coal matrix before extraction, or in solutions of extracts later.

ACKNOWLEDGEMENT

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TABLE 1

ELEMENTAL ANALYSES (DAF) OF COALS STUDIED

COAL #	TYPE	FROM	%C	%H	%N	%S	%O(Diff)
0450	ILL 2	ISGS[a]	78.01	5.50	1.36	3.36	11.77
0500	ILL 5	ISGS	76.55	5.33	1.60	4.96	11.56
0501	OXID[b]	0500					
0600	ILL 6	ISGS	74.09	5.18	1.39	5.51	13.84
0700	ILL 6	ISGS	78.19	5.58	1.38	5.12	9.73
0701	OXID[b]	0700	76.55	5.45	1.39	4.99	11.59
0910	MVBit[c]	APCS	86[d]	5.3	1.9	2.8	4.0

a Illinois State Geological Survey
b Air oxidized, -100 mesh coal, room temperature, 6 months
c Upper Freeport, Agronne Premium Coal Sample # 1
d Approximate, final data not available from Argonne

TABLE 2

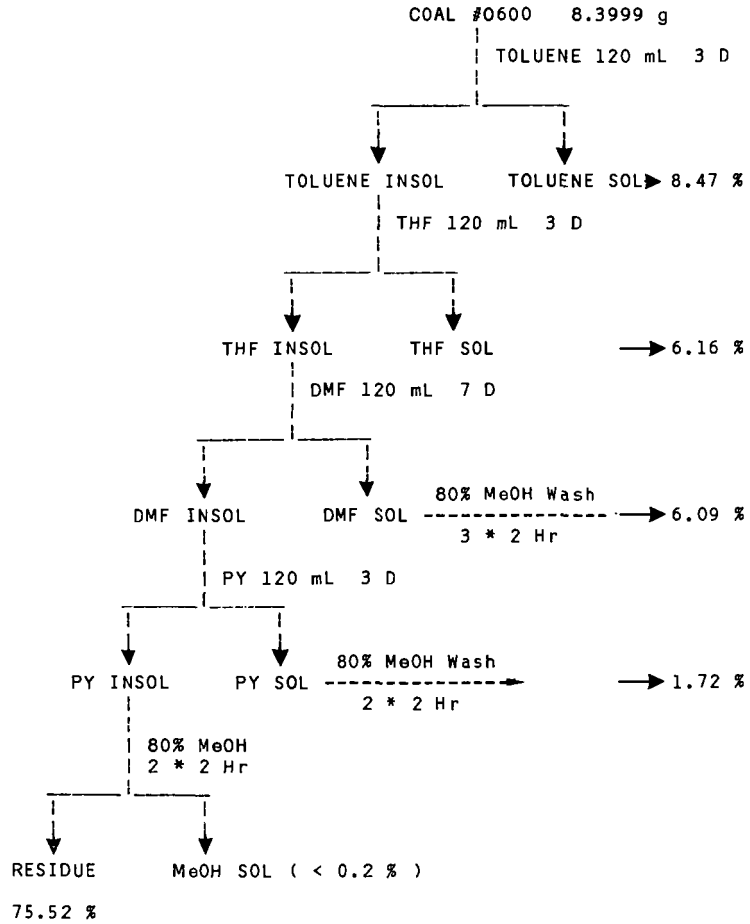
SEQUENTIAL SOXHLET EXTRACTION[a]

COAL #	% TOL SOL	% THF SOL	% DMF SOL	% PY SOL	TOTAL % SOL	% RESID	% Mat Bal
0500	0.82	7.33	5.94	1.42	15.5	75.77	91.3
0501	3.57	3.72	4.23	2.18	13.7	86.16	99.9
0600	8.47	6.16	6.09	1.72	22.4	75.52	98.0
R600[b]	0.18	0.01	0.43	22.17	22.8	74.85	97.6
0700	3.30	6.73	7.32	2.10	19.4	71.96	91.4
0701	6.54	5.69	4.70	1.81	18.7	72.39	91.4
0910	0.52	0.14	8.97	11.24	20.9	78.16	99.1

a Extraction order: Toluene, THF, DMF, Pyridine
b Extraction order: Pyridine, Toluene, THF, DMF

SCHEME

SEQUENTIAL SOXHLET EXTRACTION



TOTAL SOLUBLE: 22.44 %

TOTAL RECOVERED: 97.96 %

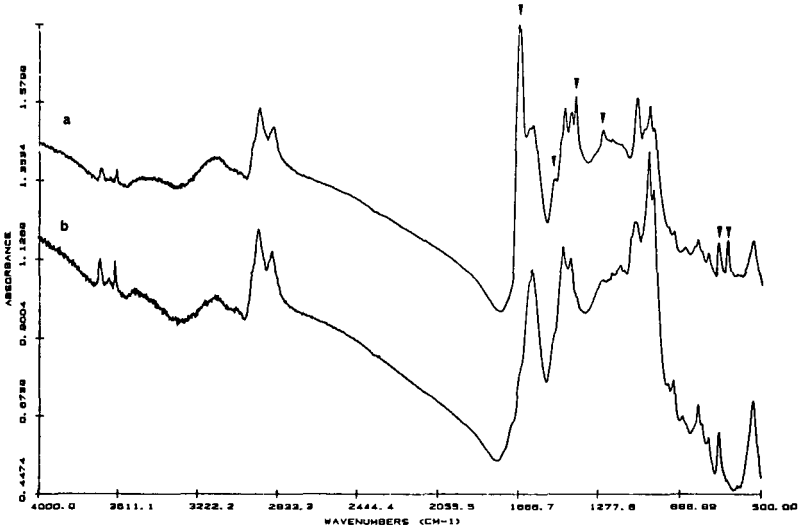


FIGURE 1. (a) FT-IR spectrum of residue from coal 0700 containing DMF and PY. ► = Solvent absorption bands. (b) Spectrum of same residue after 80% methanol/ water wash and standard drying.

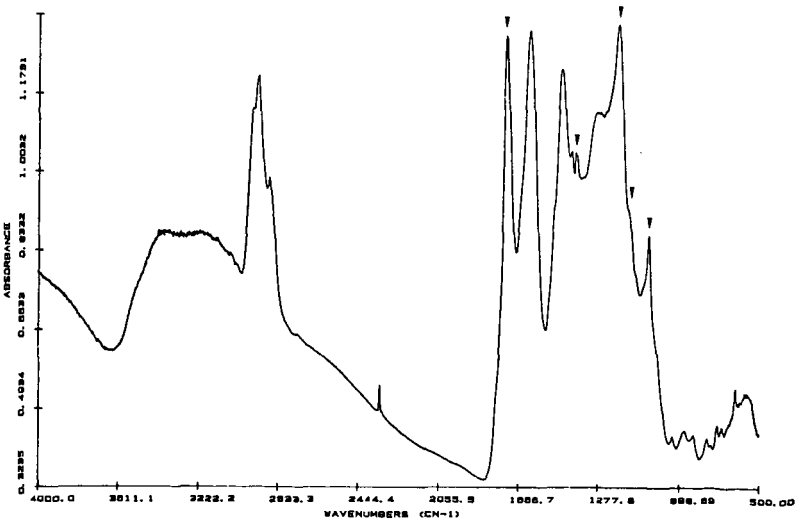


FIGURE 2. FT-IR spectrum of colloid isolated from Millipore filtration of THF extract from coal 0701. ► = Features discussed in text.

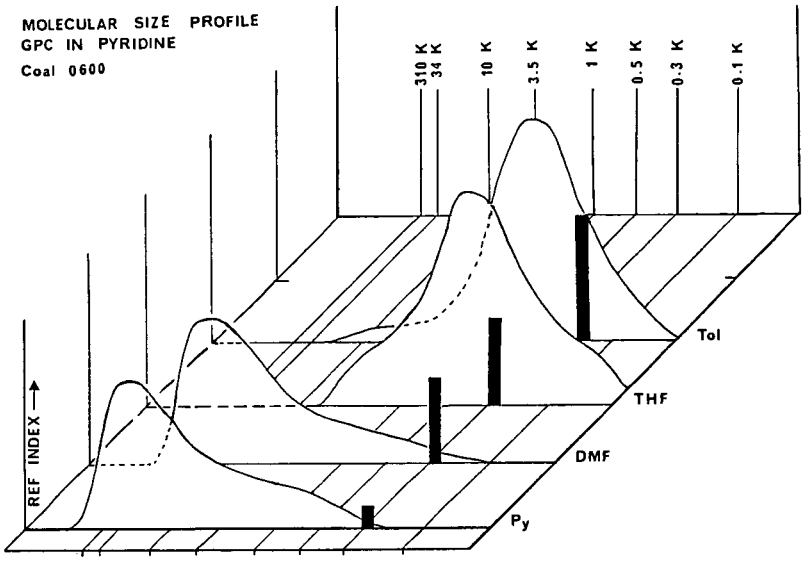


FIGURE 3. Combined GPC traces of sequential extracts from coal 0600 (Table 2). Concentration = 6.0 mg/mL in pyridine, flow rate 1.8 mL/min.

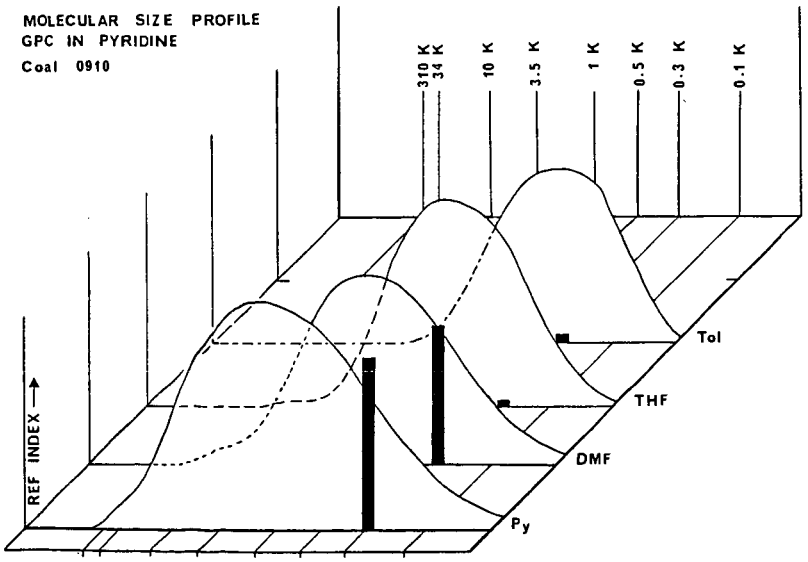


FIGURE 4. Combined GPC traces of sequential extracts from coal 0910 (Table 2). Concentration = 6.0 mg/mL in pyridine, flow rate 1.8 mL/min.

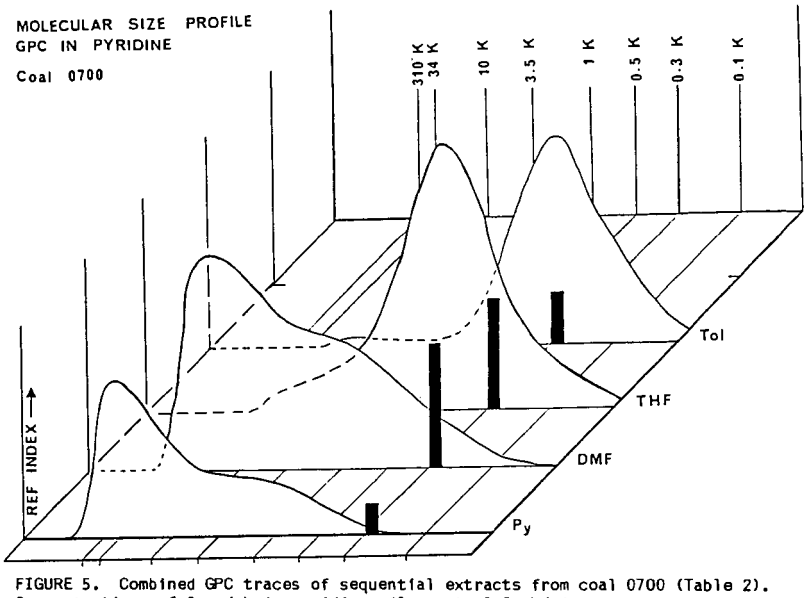


FIGURE 5. Combined GPC traces of sequential extracts from coal 0700 (Table 2). Concentration = 6.0 mg/mL in pyridine, flow rate 1.8 mL/min.

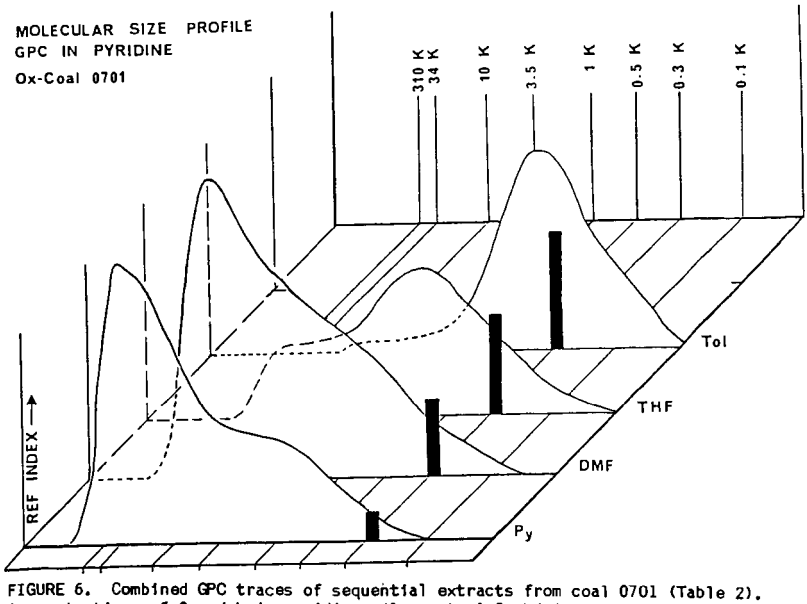


FIGURE 6. Combined GPC traces of sequential extracts from coal 0701 (Table 2). Concentration = 6.0 mg/mL in pyridine, flow rate 1.8 mL/min.