MAINTENANCE OF THE COAL SAMPLE BANK AND DATABASE

Quarterly Technical Progress Report

Reporting Period: 1/01/97 - 3/31/97

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Contract Number DE-AC22-93PC93051

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DISCLAIMER

ABSTRACT

This project provides coal samples and accompanying analytical data for research by DOE contractors and others. All 56 samples have been purged with argon before storage, and the 33 samples in the DECS series are heat-sealed in foil laminate bags and stored under refrigeration. Eleven DECS samples have been collected under the current contract.

The program of organic geochemical analyses for the contract was completed during the quarter, and its results (pyrolysis - GC/MS, and NMR spectroscopy by CPMAS and DDMAS) on 21 samples as well as standardized liquefaction results on 28 samples are summarized in this report. Samples and data continue to be distributed from the DOE Coal Sample Bank and Database to other DOE contractors.

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EXECUTIVE SUMMARY

Maintenance of the Coal Sample Bank and Database

Quarterly Technical Progress Report 1/01/97 - 3/31/97

The mission of the DOE Coal Sample Bank and Database is to provide a variety of well-characterized, high-quality coal samples for public and private coal research. Eleven coal samples collected under the current contract and 45 from previous contracts, along with analytical data, are distributed on a continuing basis to DOE contractors and others performing coal research. Additional analyses of liquefaction behavior and organic geochemical characteristics are performed under the contract. The samples are stored to minimize deterioration, and 10 samples are analyzed annually to monitor the effectiveness of the storage methods.

This report reflects the level of effort described in the revised work statement submitted to DOE on September 5, 1996, setting out a reduction in effort following a cut in the level of funding of the project.

Sample collection, basic analysis, liquefaction analysis and organic geochemistry analysis specified under the contract have been completed. This report includes tabulations of numerical results from liquefaction and organic geochemical analyses.

INTRODUCTION

This five year project is intended to ensure the availability of well-characterized, high-quality coal samples for public and private coal research. It continues support of the DOE Coal Sample Bank and Database at The Pennsylvania State University. Eleven coal samples in the DECS- series have been collected, processed, packaged, and analyzed under the contract, and a resulting database is being maintained. These samples and data, as well as 45 samples collected under previous contracts, are distributed on a continuing basis to DOE contractors and others performing coal research.

Samples were chosen to maintain a sample bank of 56 coals representing the major U.S. coal fields and a variety of coal ranks and compositions. In addition to standard analyses, liquefaction tests have been performed, and organic geochemical analyses are being performed and are nearly completed. The samples are stored to minimize deterioration, and 10 samples are monitored annually by proximate, sulfur forms, and gaseous oxygen analysis to evaluate their condition.

RESULTS AND DISCUSSION

Task 1B. Storage and Inventory of Samples

All samples supported by the contract are stored in containers purged with argon before sealing; container locations are tracked by a computer inventory program. PSOC-series samples are stored in drums or buckets at the Coal Sample Bank building, or in cans in the Coal and Organic Petrology Laboratories. All DECS-series samples are stored under refrigeration in foil laminate bags.

During the quarter, samples were distributed and inventory records were updated. Storage and inventory of sample containers is expected to continue routinely through the next quarter.

Task 1C. Monitoring of Sample Quality

It was planned that one 300 g (2/3 lb) bag of each DECS sample would be analyzed annually to monitor sample condition. This Task has been reduced in scope, to 10 samples per year, because of reduction in funding. Effort in the related study of liquefaction behavior (under Task 1F) over time has also been reduced.

Task 1D. Collection and Processing of Replacement Samples

Collection and processing of 11 samples, as described in the Revised Statement of Work (Sept. 6, 1996) has been completed. Portions of samples collected under a previous contract are being processed to minus 0.25 mm (minus 60 mesh).

Task 1E. Basic Characterization of Coal Samples

All basic characterization of samples planned for collection under the contract has been

completed.

Task 1F. Liquefaction Testing

In this Task, appropriate samples will be subjected to a standardized liquefaction test using tetralin (1:1 coal:tetralin, 1000 psig H_2, 350°C, 30 min) and subsequent product workup. Work in this Task has been completed, although the total number of samples tested was reduced following a cut in the level of funding. Table 1 summarizes the results from this Task.

Task 1G. Investigation of Changes in Surface Chemistry During Storage

This Task has been discontinued.

Task 1H. Organic Geochemistry

Pyrolysis - Gas Chromatography - Mass Spectrometry

Measurements on the final set of samples have been completed. Runs were performed at a flash pyrolysis temperature of 610°C with a heating rate of 10°C/ms and a pyrolysis time of 10 s (for further discussion see the Quarterly Technical Progress Report for 7/01/94-9/30/94). Tables 2 and 3 summarize results from all such analyses performed under the contract. Results for samples DECS-2, 24, 26, 28 and 33 are reported here for the first time; the Appendix shows the total ion chromatograms of the pyrolyzates.

Nuclear Magnetic Resonance (NMR) Spectroscopy

Dried powdered samples of coal were placed in the bullet-type rotor of a Chemagnetics, Inc. M-100 NMR spectrometer and analyzed according to the cross-polarization, magic-angle spinning (CPMAS) and dipolar dephasing with magic angle spinning (DDMAS) procedures outlined by Hatcher (1988). Approximately 10,000 transients having a contact time of 1 ms and a cycle time of 1 s were acquired in 0.5K of data, zero-filled to 4K. The chemical shifts were referenced to hexamethylbenzene. For DDMAS, approximately 8000 transients with a cycle time of 1 s were used at each of 10 dephasing times.

CPMAS analyses planned for this contract have been completed; preliminary results are summarized in Table 4.

DDMAS measurements on the final set of samples were completed during the quarter. Table 5 shows structural parameters determined from DDMAS measurements, namely the fractions of protonated aromatic carbon and mobile methyl and quaternary aliphatic carbon, for all such analyses performed under the contract. Results for samples DECS-19, 29, 30, 31, 32 and 33 are reported here for the first time.

Bloch decay experiments planned for this contract have been completed. Bloch decay experiments were performed as described by Hatcher et al. (1992), principally to verify the spectra obtained by conventional CPMAS (presented in the last two quarterly progress reports). Approximately 2500 transients with a cycle time of 80 s were collected. The spectra have been presented in previous reports.

Table 1. Conversion of DECS samples in a standardized liquefaction test using tetralin (1:1 coal:tetralin, 1000 psig H_2, 350°C, 30 min), with detailed gas composition (average of two runs, except gas components based on one run).

sample			conversion, percent of dry ash-free coal												
number	rank	St	total	asph.	pre-asph.	oil	gas	gas composition							
								c1	c2	c3	c4	c5	c1-c5	other
DECS-1	subC	TX	66.3	12.5	9.2	8.9	35.7	8.5	4.0	1.6			14.1	21.6
DECS-2	hvCb	IL	62.7	9.1	32.7	8.1	12.8	6.5	1.6	1.1			9.2	3.6
DECS-4	hvCb	NM	48.5	6.1	11.7	7.6	23.1	0.5	0.4	0.2			1.1	22.0
DECS-5	hvCb	UT	45.0	6.9	27.2	6.8	4.1	0.5	0.4	0.1			1.0	3.1
DECS-6	hvAb	UT	30.1	7.9	7.7	7.0	7.5	0.5	0.2	0.1			0.8	6.7
DECS-7	hvCb	WY	44.6	8.3	4.9	10.3	21.1	1.1	0.6	0.2			1.9	19.2
DECS-8	subC	WY	60.2	6.6	10.9	11.8	30.9	9.3	4.8	1.2			15.3	15.6
DECS-9	subB	MT	35.0	6.1	9.1	4.2	15.6	0.6	0.4	0.1			1.1	14.5
DECS-10	subB	MT	35.5	7.2	8.6	4.7	15.0	0.7	0.3	0.2			1.2	13.8
DECS-11	ligA	ND	29.5	7.7	4.9	7.8	9.1	2.4	1.1	0.4			3.9	5.2
DECS-12	hvAb	PA	30.6	1.2	14.9	6.7	7.8	2.8	0.9	0.4	0.2	0.2	4.5	3.3
DECS-14	hvAb	WV	44.9	7.4	15.7	7.7	14.1	1.4	0.9	0.2			2.5	11.6
DECS-15	hvAb	UT	43.5	7.8	18.7	8.6	8.4	1.1	0.5	0.1			1.7	6.7
DECS-16	hvAb	UT	51.9	19.2	9.8	13.2	9.7	1.5	0.8	0.3			2.6	7.1
DECS-17	hvAb	UT	54.6	11.4	9.4	15.0	18.8	3.6	1.8	1.1			6.5	12.3
DECS-18	hvBb	KY	31.9	4.6	16.2	7.3	3.8	0.2	0.1	0.1			0.4	3.4
DECS-20	hvAb	KY	29.0	5.9	11.9	6.2	5.0	0.9	0.5	0.2			1.6	3.4
DECS-22	hvAb	PA	42.0	8.2	14.7	8.9	10.2	1.2	0.8	0.2			2.2	8.0
DECS-23	hvAb	PA	64.8	7.2	30.9	8.5	18.2	7.6	1.8	1.5	0.3		11.2	7.0
DECS-24	hvCb	IL	62.5	6.9	35.0	8.8	11.8	6.3	2.7	0.6			9.6	2.2
DECS-25	ligA	MT	53.6	3.9	7.4	6.4	35.9	0.5	0.1				0.6	35.3
DECS-26	subB	WY	54.6	5.3	10.1	6.8	32.4	0.5	0.1				0.6	31.8
DECS-27	subA	WY	48.2	13.9	14.0	7.2	13.1	6.0	1.6	0.5			8.1	5.0
DECS-28*	hvCb	AZ	42.2	10.4	15.0	6.2	10.6	7.1	1.6	0.7			9.4	1.2
DECS-29	hvAb	VA	22.1	3.3	7.7	6.3	4.8	0.6	0.2	0.1			0.9	3.9
DECS-31	hvAb	KY	36.4	15.7	3.2	7.4	10.1	0.5	0.1				0.6	9.5
DECS-32	hvAb	WV	29.8	4.6	16.3	6.6	2.3	0.3	0.1	0.1			0.5	1.8
DECS-33	hvBb	OH	62.8	27.3	20.4	12.2	2.9	0.7	0.4	0.3	0.1		1.5	1.4

* based on one run; second run failed

Table 2. Structural parameters determined by py/gc/ms, flash pyrolysis temperature of 610°C, heating rate 10°C/ms, pyrolysis time 10 s (percent of total gc-amenable products). Results of preliminary identification of peaks.

sample				n-alkanes and alkenes	phenols	non-oxygenated aromatic hydrocarbons	unident-ified
number	seam	rank	state				
DECS-1	Bottom	subC	TX	39.2	8.3	37.1	15.4
DECS-2	Illinois #6	hvCb	IL	26.7	21.5	35.6	16.2
DECS-8	Smith-Roland	subC	WY	27.2	15.6	14.3	42.9
DECS-9	Dietz	subB	MT	34.9	17.3	6.7	41.1
DECS-11	Beulah	lig	ND	37.3	17.8	27.9	17.0
DECS-12	Pittsburgh	hvAb	PA	14.6	11.5	15.1	58.8
DECS-13	Sewell	mvb	WV	33.9	16.8	6.9	42.4
DECS-17	Blind Canyon	hvAb	UT	24.3	5.4	5.5	64.8
DECS-18	Kentucky #9	hvBb	KY	41.5	22.3	7.6	28.6
DECS-19	Pocahontas #3	lvb	VA	16.0	18.9	9.6	55.5
DECS-23	Pittsburgh	hvAb	PA	39.3	38.5	9.0	13.2
DECS-24	Illinois #6	hvCb	IL	27.4	27.5	27.8	17.4
DECS-25	Pust	ligA	MT	19.9	8.8	1.6	69.7
DECS-26	Wyodak	subB	WY	34.8	26.6	27.2	11.4
DECS-27	Deadman	subA	WY	29.4	11.6	8.5	50.5
DECS-28	Green	hvCb	AZ	36.5	25.6	27.2	10.6
DECS-29	Upper Banner #3	hvAb	VA	21.8	3.5	10.7	64.0
DECS-30	Splash Dam	mvb	VA	28.0	3.6	4.3	64.1
DECS-31	Pond Creek	hvAb	KY	17.9	15.4	4.5	62.2
DECS-32	Stockton-Lewiston	hvAb	WV	15.3	20.1	10.3	53.5
DECS-33	Ohio #4A	hvBb	OH	32.2	19.1	34.7	14.0

Table 3. Structural parameters determined by py/gc/ms, flash pyrolysis temperature of 610°C, heating rate 10°C/ms, pyrolysis time 10 s (percent of identified products). Results of preliminary identification of peaks.

sample				n-alkanes and alkenes	phenols	non-oxygenated aromatic hydrocarbons
number	seam	rank	state			
DECS-1	Bottom	subC	TX	46.3	9.8	43.9
DECS-2	Illinois #6	hvCb	IL	31.9	25.6	42.5
DECS-8	Smith-Roland	subC	WY	47.6	27.4	25.0
DECS-9	Dietz	subB	MT	59.3	29.4	11.3
DECS-11	Beulah	lig	ND	44.9	21.4	33.7
DECS-12	Pittsburgh	hvAb	PA	35.4	27.9	36.7
DECS-13	Sewell	mvb	WV	58.8	29.2	12.0
DECS-17	Blind Canyon	hvAb	UT	69.1	15.3	15.6
DECS-18	Kentucky #9	hvBb	KY	58.2	31.2	10.6
DECS-19	Pocahontas #3	lvb	VA	36.0	42.4	21.6
DECS-23	Pittsburgh	hvAb	PA	45.3	44.3	10.4
DECS-24	Illinois #6	hvCb	IL	33.1	33.3	33.6
DECS-25	Pust	lig	MT	65.7	29.0	5.3
DECS-26	Wyodak	subB	WY	39.3	30.0	30.7
DECS-27	Deadman	subA	WY	59.4	23.4	17.2
DECS-28	Green	hvCb	AZ	40.9	28.7	30.4
DECS-29	Upper Banner #3	hvAb	VA	60.6	9.7	29.7
DECS-30	Splash Dam	mvb	VA	78.0	10.0	12.0
DECS-31	Pond Creek	hvAb	KY	47.4	11.9	40.7
DECS-32	Stockton-Lewiston	hvAb	WV	32.9	22.2	44.9
DECS-33	Ohio #4A	hvBb	OH	37.5	22.2	40.3

Table 4. Structural parameters of DECS coals determined by CPMAS measurements

sample				carbon aromaticity	(aromatic + carbonyl + carboxyl) / total carbons	phenolics/ total carbons	(carboxyl+ carbonyl)/ total carbons	oxygenated aliphatic carbons / total carbons
DECS-	seam	rank	St					
1	Bottom	subC	TX	0.45	0.52	0.14	0.07	0.050
2	Illinois #6	hvCb	IL	0.64	0.73	0.19	0.09	0.040
8	Smith-Roland	subC	WY	0.51	0.62	0.21	0.11	0.050
9	Dietz	subB	MT	0.59	0.68	0.20	0.09	0.030
11	Beulah	ligA	ND	0.60	0.71	0.20	0.11	0.020
12	Pittsburgh	hvAb	PA	0.69	0.76	0.16	0.07	0.023
13	Sewell	mvb	WV	0.79	0.80	0.14	0.01	0.010
17	Blind Canyon	hvAb	UT	0.54	0.60	0.18	0.06	0.040
18	Kentucky #9	hvBb	KY	0.63	0.66	0.15	0.03	0.020
19	Pocahontas #3	lvb	VA	0.80	0.81	0.13	0.01	0.010
23	Pittsburgh	hvAb	PA	0.67	0.75	0.17	0.08	0.024
24	Illinois #6	hvCb	IL	0.65	0.72	0.20	0.07	0.017
25	Pust	ligA	MT	0.60	0.72	0.21	0.12	0.037
26	Wyodak	subB	WY	0.56	0.68	0.20	0.12	0.022
27	Deadman	subA	WY	0.63	0.75	0.20	0.12	0.020
28	Green	hvCb	AZ	0.57	0.63	0.18	0.07	0.020
29	U. Banner #3	hvAb	VA	0.72	0.74	0.11	0.02	0.007
30	Splash Dam	mvb	VA	0.76	0.78	0.11	0.02	0.002
31	Pond Creek	hvAb	KY	0.70	0.72	0.13	0.02	0.009
32	Stockton-Lew.	hvAb	WV	0.73	0.75	0.15	0.02	0.002
33	Ohio #4A	hvBb	OH	0.75	0.80	0.15	0.05	0.019

Definitions:

carbon aromaticity* $fa' = I_{100\text{-}165\ ppm} / I_{total}$

(aromatic + carbonyl + carboxyl) / total carbons $fa = I_{100\text{-}220\ ppm} / I_{total}$

phenolics* / total carbons $fp = I_{140\text{-}165\ ppm} / I_{total}$

(carboxyl + carbonyl) / total carbons $fc = I_{165\text{-}220\ ppm} / I_{total}$

oxygenated aliphatic carbons / total carbons $fo = I_{60\text{-}90\ ppm} / I_{total}$

where:

I = area within the indicated chemical shift ranges in a CPMAS spectrum

I_{total} = 1 - 220 ppm

* corrected for contributions from spinning sidebands of aromatic carbons

Table 5. Structural Parameters of DECS coals determined by DDMAS measurements

sample				aromatic protonated C	mobile CH_3 and quaternary aliphatic C
number	seam	rank	St		
DECS-1	Bottom	subC	TX	0.30	0.15
DECS-2	Illinois #6	hvCb	IL	0.55	0.48
DECS-8	Smith-Roland	subC	WY	0.28	0.35
DECS-9	Dietz	subB	MT	0.34	0.19
DECS-11	Beulah	ligA	ND	0.45	0.22
DECS-12	Pittsburgh	hvAb	PA	0.49	0.29
DECS-13	Sewell	mvb	WV	0.37	0.19
DECS-17	Blind Canyon	hvAb	UT	0.40	0.14
DECS-18	Kentucky #9	hvBb	KY	0.20	0.34
DECS-19	Pocahontas #3	lvb	VA	0.25	0.34
DECS-23	Pittsburgh	hvAb	PA	0.39	0.58
DECS-24	Illinois #6	hvCb	IL	0.15	0.39
DECS-25	Pust	ligA	MT	0.43	0.14
DECS-26	Wyodak	subB	WY	0.56	0.15
DECS-27	Deadman	subA	WY	0.37	0.16
DECS-28	Green	hvCb	AZ	0.25	0.35
DECS-29	Upper Banner #3	hvAb	VA	0.29	0.49
DECS-30	Splash Dam	mvb	VA	0.21	0.72
DECS-31	Pond Creek	hvAb	KY	0.27	0.25
DECS-32	Stockton-Lewiston	hvAb	WV	0.19	0.53
DECS-33	Ohio #4A	hvBb	OH	0.17	0.65

Task 1I. Distribution of Coal Samples to Users

During the period 1/01/97 - 3/31/97 a total of 31 samples (25 DOE Sample Bank samples and 6 other Penn State samples) of various sizes in 34 containers were distributed. See Task 2C for a list of sample and data recipients. This task will continue in the same manner through the next quarter.

Task 2A. Programming

Only minor programming was undertaken during the quarter. See also the discussion of the world wide web site under 'Distribution of Data to Users.'

Task 2B. Data Entry

Entry of basic characterization data for the 11 samples collected under the contract has been completed.

Task 2C. Distribution of Data to Users

During the quarter a total of 177 data printouts were distributed. In addition, 10 special data requests were filled by database searches and printed output or creation of a data disk, resulting in distribution of information on 2117 samples. Requests for Sample Bank and Database information have been filled. This task will continue in the same manner through the next quarter.

Organizations supplied with coal samples and/or data include:

Battelle
Central Research Institute for the Electric Power Industry (CRIEPI), Japan (3)
Combustion Components Associates
Consortium for Fossil Fuel Liquefaction Science
CSIRO Division of Coal and Energy, Australia
Geneva Steel Corporation
Hokkaido University, Faculty of Engineering, Japan
Illinois State Geological Survey
Internal Revenue Service
NIST
Pennsylvania State University, Polymer Science Department
Pennsylvania State University, Fuel Science Department (3)
Pennsylvania State University, Geosciences Department
University of Cincinnati, Civil and Environmental Engineering Department (2)
University of Delaware, Chemical Engineering Department
U.S. Geological Survey

The numbers in parentheses represent multiple requests which were separately processed.

Additional clients have received information via a world wide web site (http://www.ems.psu.edu/COPL/).

CONCLUSIONS

The coal samples and data supported under this project are being used on an ongoing basis by DOE contractors and others performing coal research. Samples collected under the current contract are stored in argon under refrigeration in multilaminate bags which have demonstrated an ability to preserve the properties of the fresh coal. Samples and data continue to be distributed from the DOE Coal Sample Bank and Database to other DOE contractors.

All liquefaction and organic geochemical (pyrolysis - GC/MS, and NMR spectroscopy by CPMAS and DDMAS) analyses for the contract have been completed, and numerical results are tabulated in this report. These results will be evaluated in a future report.

REFERENCES

Hatcher, P.G., 1988. Dipolar-dephasing ^{13}C NMR studies of decomposed wood and coalified xylem tissue: evidence for chemical structural changes associated with defunctionalization of lignin structural units during coalification. Energy & Fuels, v. 2, pp 40-58.

Hatcher, P.G., Faulon, J.-L., Wenzel, K.A., and Cody, G.D., 1992. A structural Model for Lignin-Derived Vitrinite from High-Volatile Bituminous Coal (Coalified Wood). Energy & Fuels, v. 6, pp 813-820.

APPENDIX. Total ion chromatograms of pyrolyzates

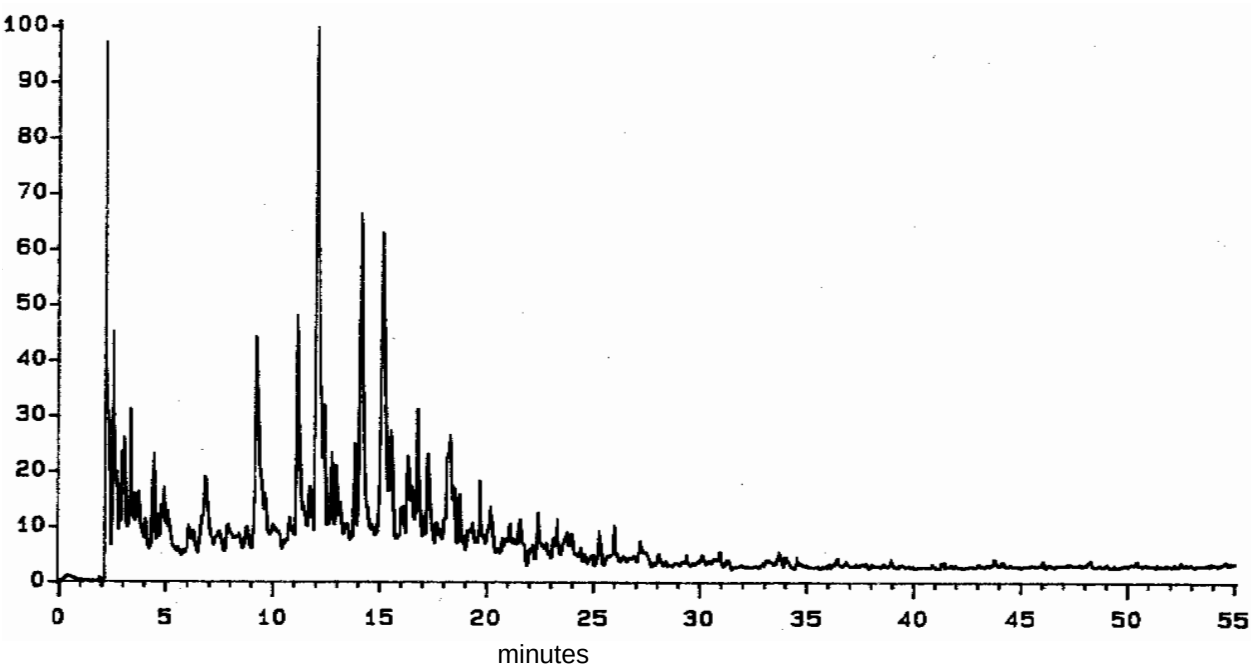

Figure 1. Total ion chromatogram of pyrolyzates from DECS-2, hvCb Illinois #6 seam, IL.

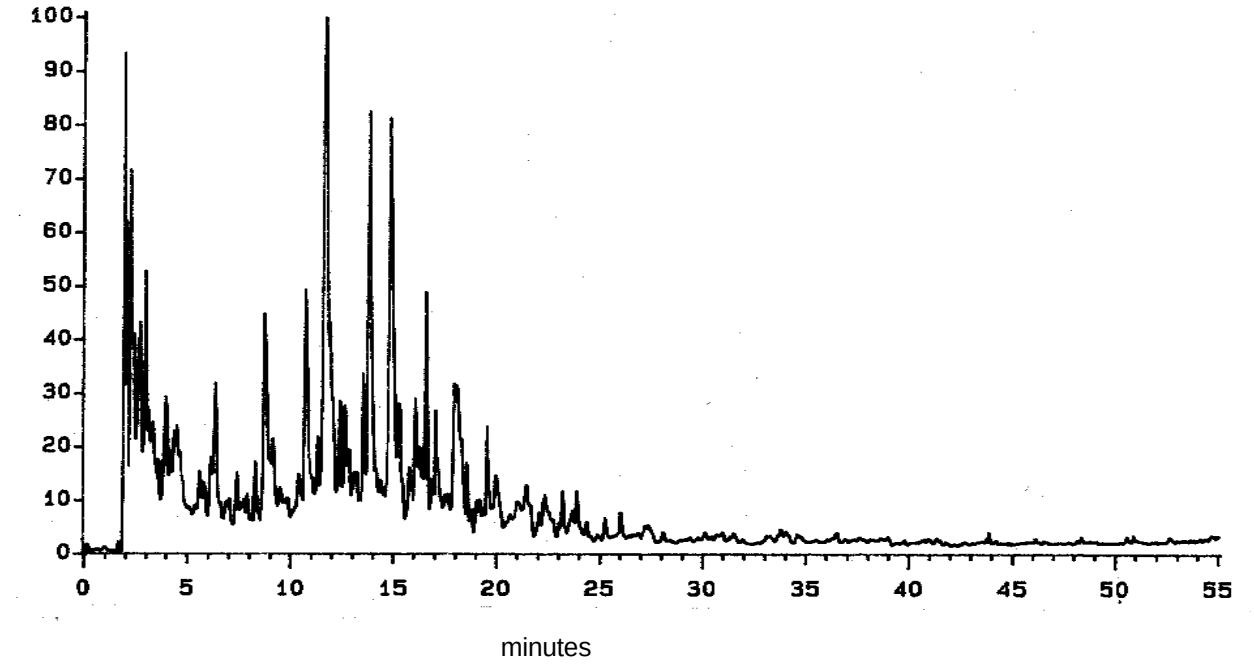

Figure 2. Total ion chromatogram of pyrolyzates from DECS-24, hvCb Illinois #6 seam, IL.

APPENDIX. Total ion chromatograms of pyrolyzates

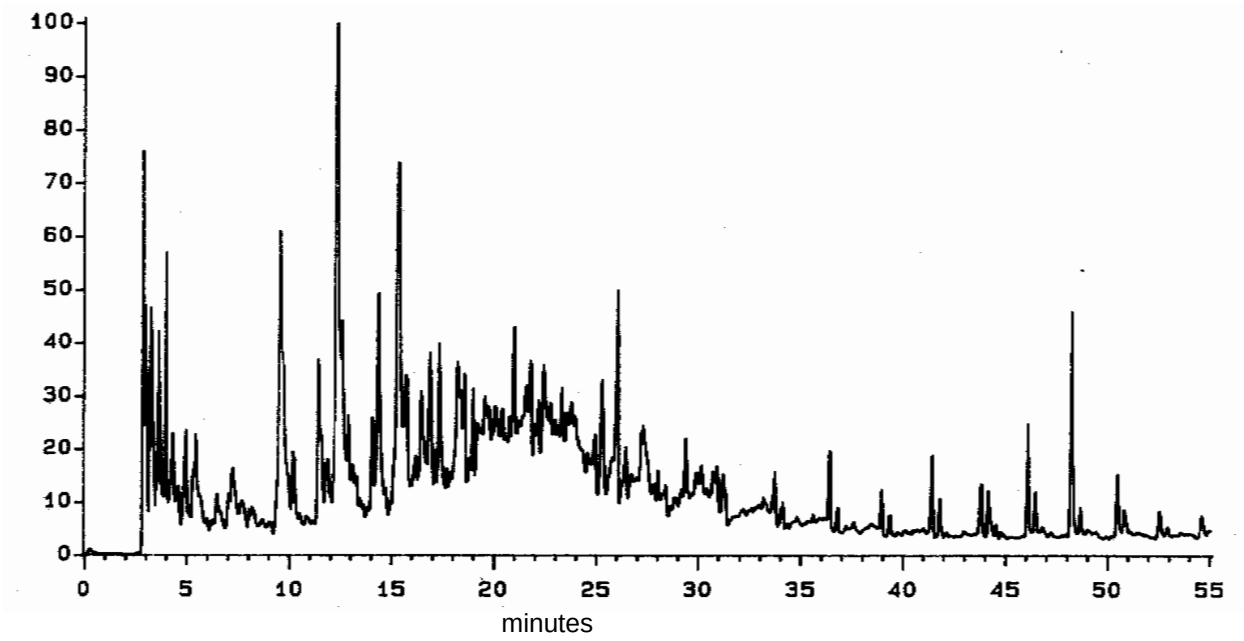

Figure 3. Total ion chromatogram of pyrolyzates from DECS-26, subB Wyodak seam, WY.

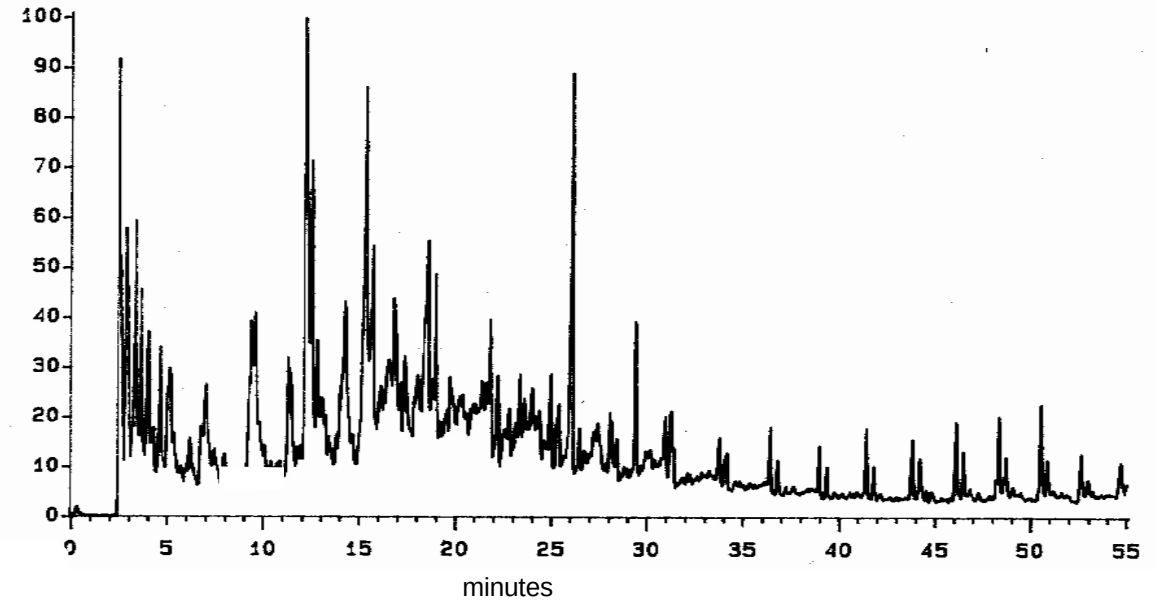

Figure 4. Total ion chromatogram of pyrolyzates from DECS-28, hvCb Green seam, AZ.

APPENDIX. Total ion chromatograms of pyrolyzates

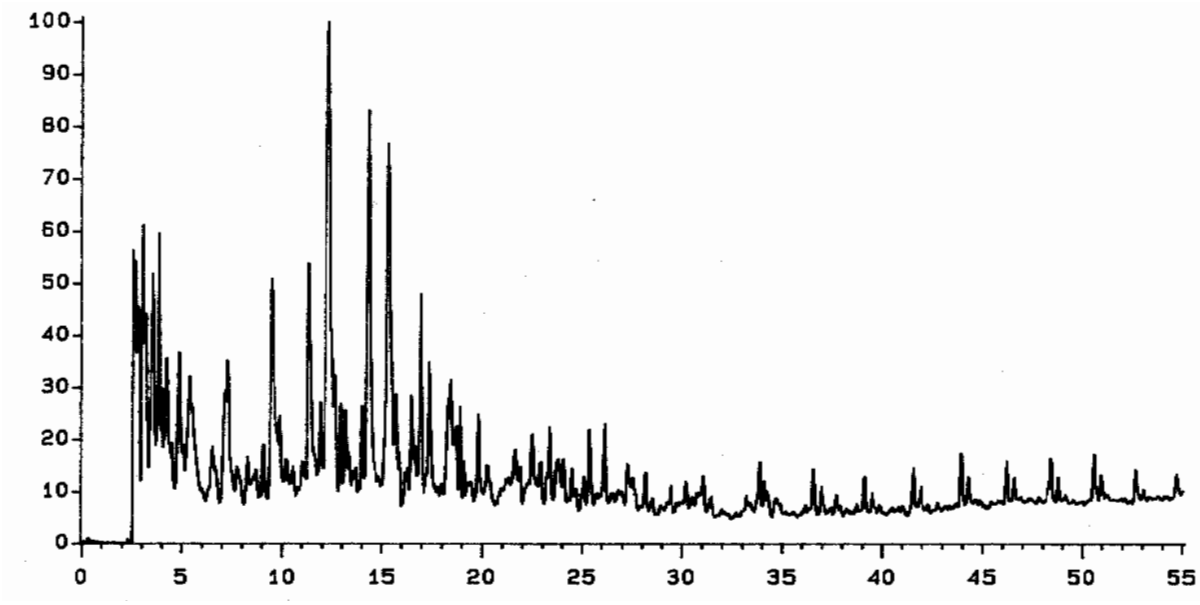

Figure 5. Total ion chromatogram of pyrolyzates from DECS-33, hvBb Ohio #4A seam, OH.