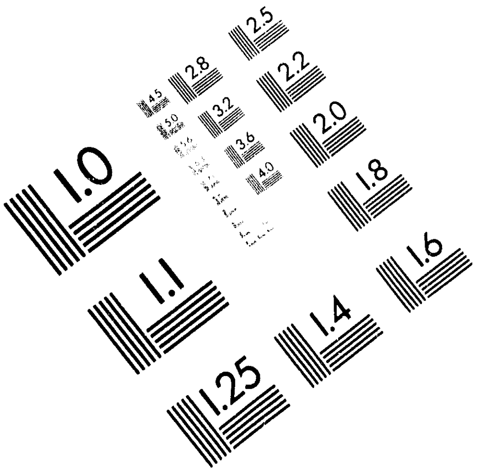

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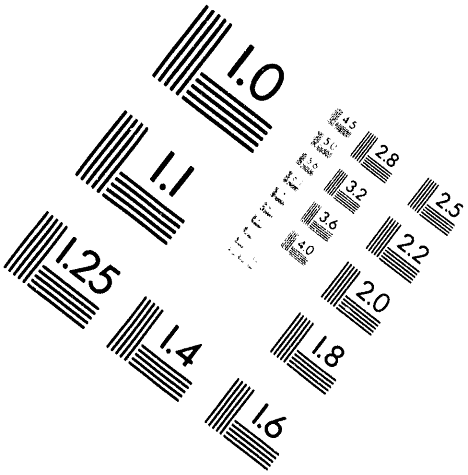

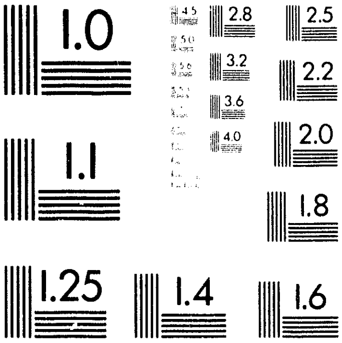

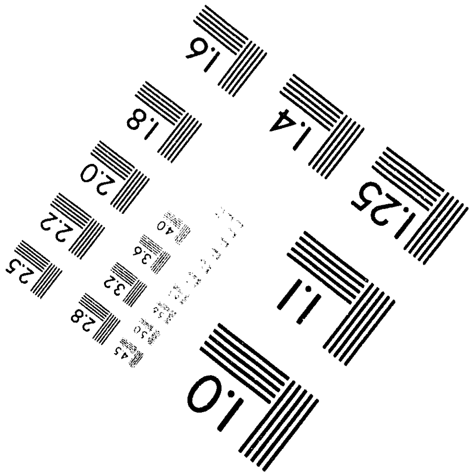

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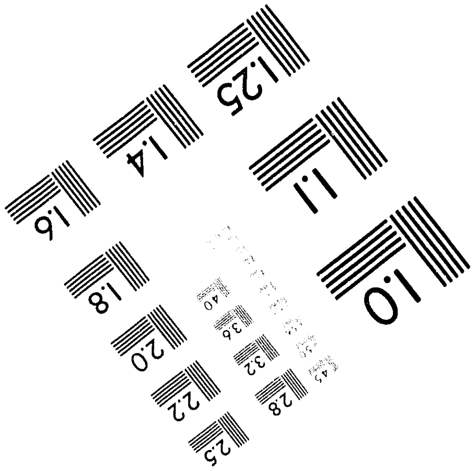

1 of 2

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Coal Liquefaction Process Streams Characterization and Evaluation

Analysis of Black Thunder Coal and Liquefaction Products from HRI Bench Unit Run CC-15

Topical Report

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PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The University of Utah applied the technique of ^{13}C-nuclear magnetic resonance (NMR) spectrometry to the analysis of selected, direct coal liquefaction-derived materials. The full report authored by the University of Utah researchers is presented here. The following assessment briefly highlights the major findings of the project, and describes the application of ^{13}C-NMR to provide information on the complex chemistry inherent in the conversion of coal to liquid products. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials and the potential impact of the use of these methods on process economics at the conclusion of this contract.

Summary

This study was designed to apply ^{13}C-nuclear magnetic resonance (NMR) spectrometry to the analysis of direct coal liquefaction process-stream materials. ^{13}C-NMR was shown to have a high potential for application to direct coal liquefaction-derived samples in Phase II of this program.[1] In this Phase III project, ^{13}C-NMR was applied to a set of samples derived from the HRI Inc. bench-scale liquefaction Run CC-15. The samples include the feed coal, net products and intermediate streams from three operating periods of the run. High-resolution ^{13}C-NMR data were obtained for the liquid samples and solid-state CP/MAS ^{13}C-NMR data were obtained for the coal and filter-cake samples. The ^{13}C-NMR technique is used to derive a set of twelve carbon structural parameters for each sample (CONSOL Table A). Average molecular structural descriptors can then be derived from these parameters (CONSOL Table B).

Program Description

This report describes the work performed at the University of Utah under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. The broad objective of this Participants Program is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed then is evaluated for its usefulness in analyzing direct coal liquefaction derived materials. Methods which demonstrate high potential for analysis of process stream samples and provide information which is potentially useful for process design or operation (thus, those which have the potential for immediate impact on process economics) are further tested by application to a comprehensive set of process-derived materials.

Participant's Methodology

The University of Utah used ^{13}C-NMR spectrometry to analyze one coal sample and a set of 12 process-stream samples from the HRI Inc. bench unit Run CC-15 (also known as HRI Run 227-75). The samples included the feed coal and the major products and intermediate process streams from three run conditions (2, 3, and 4) which include run periods 8, 11, and 14, respectively. Three samples are filtered process liquids (PFLs); three samples are viscous process streams, designated "Interstage", obtained from the first-stage internal recycle loop that contain ash and insoluble organic material (IOM); three samples are pressure filter cakes (PFCs) which contain approximately 50% ash and IOM; three samples are light distillates, produced by blending the atmospheric still overhead (ASOH) and separator overhead (SOH) materials; and one sample is the feed coal for Run CC-15, Wyodak and Anderson seam, Black Thunder mine, subbituminous coal. The thirteen samples were supplied to Utah with the following analytical information, as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, and hydrogen classes by ^{1}H-NMR.

High-resolution ^{13}C-NMR spectra were obtained for the liquid samples (using inversion-recovery and quantitative techniques) and solid-state cross-polarization/magic angle spinning (CP/MAS) ^{13}C-NMR spectra were obtained for the coal and filter-cake sample. Bloch decay experiments were attempted on one filter-cake sample. Distortionless-enhanced proton transfer (DEPT) ^{13}C-NMR and quantitative ^{1}H-NMR spectra also were obtained for one liquid sample. The ^{13}C-NMR spectrometry experimental procedures are described on pages 2-3 and 22-26 of the attached report.

Participant's Major Findings

The following principal observations from the application of ^{13}C-NMR spectrometry to coal liquefaction materials were reported by Utah. An expanded discussion can be found in the attached report, pages 3-8 and pages 26-27 (Appendix 1).

The molecular structural information, obtained from high resolution ^{13}C-NMR studies on the nine liquid samples, was used to identify three major structural reactions; ring protonation, ring opening and ring dealkylation. The aromaticity of the samples, degree of substitution, and the length of side chains for samples obtained from different locations in the liquefaction plant was obtained from the ^{13}C-NMR spectra and the derived parameters.

Analyses of the PFC samples proved to be problematic. These solid samples, under the conditions of the cross polarization (CP) analysis, released an oily component which could not be contained in the rotor spinning at 4100 Hz. This non-solid component could not be quantitatively detected in the CP experiment because of the occurrence of motional averaging of the dipolar interaction required for polarization. In a Bloch decay experiment on a single sample (Ref. No. 11) it was determined that this oily component of the PFC sample was more aliphatic in character than the remaining solid material. However, in the Bloch decay experiment there was a broad probe background which could not be suppressed. Because of the problems associated with the presence of the oily component in the PFC samples, ^{13}C-NMR data obtained on the PFC samples should be used only for qualitative purposes.

A low signal in the NMR spectral region associated with bridgehead carbon for the ASOH/SOH samples, led to the assumption that these materials contain structures with, on average, only one 6-membered aromatic ring. However, the average cluster size of the PFL and interstage samples (8-12 aromatic carbons per 100 carbons) is only slightly smaller than that of the starting coal (13 aromatic carbons per 100 carbons).

The carbon aromaticity (F_a') of the PFL samples increased as the run proceeded, presumably due to second-stage catalyst aging. The carbon aromaticity of the interstage samples increased slightly in the later run periods. Although the samples are slightly more aromatic, the ring carbons in the interstage samples are more protonated in the later run periods, indicating an increasing degree of hydrogenation. The PFL samples, while more aromatic in run period 11 (Ref. No. 6) than in run period 8 (Ref. No. 2) show a lower degree of aromatic carbon hydrogenation (F_a^H/F_a') in run period 11. This may indicate that in the absence of the dispersed iron oxide catalyst (run period 11) condensation reactions were more prominent in the second stage at the expense of hydrogenation reactions. The interstage samples show the reverse behavior in the percent of protonated aromatic C. In run period 11, they have a higher F_a^H/F_a' than in run period 8, indicating that in the absence of the iron oxide catalyst side chains are cleaved, the size of the clusters decreases, the number of aromatic carbons per cluster decreases, and hydrogenation of the ring occurs.

The number of carbons per side chain for the interstage samples is similar to the starting coal (on the order of two). The PFL samples early in the run (period 8) show a large increase from the feed coal in the number of carbons per side chain, which may be indicative of ring opening reactions. In later run periods this value was lower, possibly as a result of decreasing second-stage catalyst activity. The long side chains on the ASOH/SOH samples (5.0 ±0.5, 4.5 ±0.4, and 6.0 ±0.7 per side chain for Ref. Nos. 5, 9 and 13, respectively) are believed to arise from ring opening reactions.

CONSOL Evaluation

Utah presented the information obtained from the nine liquid process-stream samples by categorizing the samples by time and by sampling location (Figures 1-6). The combination of information available about the process conditions, process yield data, analytical data obtained from other analytical methods, and the data derived in this project allows for a cursory description of the chemical mechanisms of coal conversion in the liquefaction process.

Experimental problems associated with the PFC samples can be resolved in further work by washing the sample of the oily component and analyzing the soluble and insoluble fractions separately.

The precision of the two ^{13}C-NMR solution techniques (inversion-recovery and quantitative ^{13}C-NMR) used to analyze the nine liquid samples is high; measurements are highly reproducible. The inversion-recovery technique requires 48 hr acquisition time per sample and the quantitative ^{13}C-NMR method required 15-20 hr total acquisition time per sample. The four solid samples (three PFC's and the coal) were examined by solid-state ^{13}C-NMR techniques. The experimental time required for the solid sample is on the order of two days per sample to complete both the variable contact time and dipolar dephasing experiments. The 100 MHz instrument used for solid state experiments in this study costs approximately $200,000, the 500 MHz instrument used for the liquid samples costs about $500,000.

Further Application

Continued application of ^{13}C-NMR spectrometry to provide a set of carbon structural parameters and average molecular structural descriptors for process samples is recommended. Not only will additional data increase our chemical understanding of the nature of coal-derived materials, these data can be used to surmise the general mechanism of direct coal-liquefaction reactions. It is recommended that an expanded suite of coal liquefaction samples be examined by this method, including process stream samples and the corresponding feed coals. The structural parameters developed for the process samples can contribute to the development of a comprehensive model of coal liquefaction.

Participant's Statement of Work

The CP/MAS ^{13}C-NMR technique will be used to analyze one coal sample and three process-derived solid samples obtained from the HRI Inc. bench unit. From this analysis, the Utah researchers will derive a set of twelve carbon structural parameters for each sample. These twelve parameters will include: fraction of aromatic carbon, fraction of carbonyl carbon, fraction of protonated aromatic carbon, fraction of non-protonated aromatic carbon, etc. (see Solum et al.[1] for a full list of the twelve parameters). Average molecular structural descriptors will then be derived from these parameters. These descriptors will include: mole fraction of bridgehead carbons, aromatic carbons per cluster, number of attachments per cluster, molecular weight per cluster, etc. (see Solum et al.[1] for a full list of these eight descriptors). Nine liquid samples will be analyzed by four consecutive methods: quantitative ^{1}H-NMR, quantitative ^{13}C-NMR, a proton-carbon correlation experiment (HETCOR), and relaxation experiment. These four experiments will provide structural information (similar to the solid samples) for the liquid samples. The thirteen samples will be supplied to the University of Utah with the following information as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^{1}H-NMR. Sample size will be at least 5 g. Three samples will be filtered process streams, three samples will be viscous process streams which contain ash and insoluble organic material (IOM), three samples will be filter cakes which contain approximately 50% soluble organic material and 50% ash and IOM, three samples will be light distillates, one sample will be coal.

Reference

1. Solum, M. S.; Pugmire, R. J. "Coal Liquefaction Process Streams Characterization and Evaluation; ^{13}C-NMR Analysis of CONSOL THF-Soluble Residual Materials from the Wilsonville Coal Liquefaction Process, Topical Report" DOE/PC89883-65, November 1992.

CONSOL Evaluation Table A
Carbon Structural Parameters
Determined by ^{13}C-NMR

Symbol	Fractions of sp^2-hybridized Carbon	Symbol	Fractions of sp^3-hybridized Carbon
f_a	total carbon	f_{al}	total carbon
$f_{a'}$	in an aromatic ring	f_{al}^H	CH or CH_2
f_a^C	carbonyl	f_{al}^*	CH_3 or nonprotonated
f_a^H	protonated and aromatic	f_{al}^O	bonded to oxygen
f_a^N	nonprotonated and aromatic		
f_a^P	phenolic or phenolic ether		
f_a^S	alkylated aromatic		
f_a^B	aromatic bridgehead		

CONSOL Evaluation Table B
Average Molecular Structural Descriptors
(Lattice Parameters)
Determined by ^{13}C-NMR

Symbol	Description	Symbol	Description
χ_b	mole fraction of condensed carbons; $\chi_b = f_a^B/f_{a'}$	B.L	bridges and loops per cluster; $BL=(\sigma+1) \times P_O$
C	average aromatic cluster size	S.C	side chains per cluster; $SC=(\sigma+1)$-BL
$\sigma+1$	number of attachments per cluster	MW	total molecular weight; $MW=(Cx12.01)/(f_a x\%C/100)$
P_O	fraction of intact bridges; $P_O=\{f_a^P+f_a^S-f_{al}^*\}/\{f_a^P+f_a^S\}$	M_δ	average molecular weight per attachment

Analysis of Black Thunder Coal and Liquefaction Products from HRI Bench Unit Run CC-15

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UNIVERSITY OF UTAH SUBCONTRACT FROM CONSOL R&D UNDER
DOE CONTRACT NO. DE-AC22-89PC89883

Table of Contents

Experimental

Results and Discussion

Executive Summary

In an effort to gain insight into changes that occur at the molecular level in coal liquefaction, detailed ^{13}C NMR studies were carried out on a selected set of samples provided by CONSOL, INC. personnel. In an initial study conducted in 1992 a detailed solid state ^{13}C NMR study was conducted on a set of 11 THF soluble resid samples obtained from direct liquefaction processing streams at the Wilsonville facility[1]. Structural parameters were derived that were used to characterize the carbon skeletal structure and functional group distribution of the selected resid samples. In the context of our initial study and recommendations, CONSOL, INC. carefully selected a set of process products obtained from a single coal. The sample set consisted of the starting coal (Wyodak and Anderson seam, Black Thunder Mine, subbituminous), 3 filter cakes, and 9 coal derived liquid products. The liquids were collected at different stages of the process (HRI bench unit Run CC-15). High Resolution ^{13}C NMR data was obtained on the liquid samples and solid state NMR data was obtained for the parent coal and filter cake samples. A complex analysis of the liquid samples was made in order to extract as much information as possible from the rich set of data made available for this study.

The data obtained on the liquid samples studied provides a complex set of parameters. Three major types of structural reactions can be identified from the NMR data,ring protonation, ring opening, and ring dealkylation. It also appears that differences can be found in the rates of these reactions that occur in the two stages of the reactor. In the first processing stage, the interstage liquid samples exhibit a small increase in aromaticity (relative to the parent coal) but it is not evident that the catalyst used has any effect on the aromaticity. The pressure filter liquids, on the other hand exhibit marked differences in aromaticity that may be related to catalyst and aging effects. Changes in aromaticity can occur in two different ways; ring protonation or loss of sp^3 carbons by a wide variety of dealkylation or cracking mechanisms. The significant increase in the presence of protonated aromatic carbon observed in the PFL and INT samples can occur only if ring protonation reactions occur in both stages of the process. Data are obtained which suggest that both hydrogenation and dealkylation reactions have occurred in both stages of the process. From a consideration of data on the side chain length (with respect to the parent coal), it appears that extensive ring opening reactions have occurred in both stages of the process, particularly in the PFL liquids obtained down stream from the second stage of the reactor.

Introduction

In an effort to gain insight into changes that occur at the molecular level in coal liquefaction, we have carried out detailed ^{13}C NMR studies on a selected set of samples provided by CONSOL, INC. personnel. In an initial study conducted in 1992 we carried out a detailed solid state ^{13}C NMR analysis of a set of 11 THF soluble resid samples obtained from direct liquefaction processing streams at the Wilsonville facility[1]. Structural parameters were derived that were used to characterize the carbon skeletal structure and functional group distribution of the selected resid samples. These NMR data indicated that one can elucidate the major structural changes that occur in resid samples derived from different coals. From the data obtained it was concluded that the resids, on average, are similar to the cluster structure of the parent coal except that the resid cluster has been removed from the infinite coal lattice by breaking, on average, one cross link with the subsequent loss of some bridge mass. Furthermore, the data suggested that the similarities in the resids are more pronounced than the differences; there is much more similarity in the resids than is found in the parent coals.

From the initial study we concluded that..."It appears that carefully designed studies on the liquefaction behavior of coal would be feasible if an appropriate battery of analytical tools were used.....In order to maximize the information on structural changes that occur it would seem desirable to document the ^{13}C NMR and other analytical data on the actual starting coal and the unreacted char as well as the resid and coal derived liquids....The assemblage of [these data] would be a monumental undertaking but it would, for the first time, provide a complete data set for a detailed understanding of direct liquefaction processes."[1]

In the context of our initial study and recommendation, CONSOL, INC. carefully selected a set of process products obtained from a single coal. The sample set consisted of the starting coal (Wyodak and Anderson seam, Black Thunder Mine, subbituminous), 3 filter cakes, and 9 coal derived liquid products. The liquids were collected at different stages of the process (HRI bench unit Run CC-15). Three sets of samples were provided as follows:

1) Sample set I (iron oxide catalyst, FeOOH, impregnated in the feed coal in the first stage and supported catalyst, NiMo, Shell S-317, in the second stage).
    a) pressure filter cake (PFC), sample reference number 3.
    b) pressure filter liquid (PFL), sample reference number 2.
    c) interstage (INT), sample reference number 4.
    d) combined sample of separator overhead and atmospheric still overhead (SOH-ASOH), sample reference number 5.
2) Sample set II (no iron oxide catalyst in the first stage and supported catalyst in the second stage).
    a) pressure filter cake (PFC), sample reference number 7.
    b) pressure filter liquid (PFL), sample reference number 6.
    c) interstage (INT), sample reference number 8.
    d) combined sample of separator overhead and atmospheric still overhead (SOH-ASOH), sample reference number 9.
3) Sample set III (iron oxide catalyst, FeOOH, impregnated in the feed coal in the first stage and supported catalyst, NiMo, Shell S-317, in the second stage).
    a) pressure filter cake (PFC), sample reference number 11.
    b) pressure filter liquid (PFL), sample reference number 10.
    c) interstage (INT) sample reference number 12.
    d) combined sample of separator overhead and atmospheric still overhead (SOH-ASOH), sample reference number 13.

The starting coal and 3 pressure filter cake samples were studied using the standard ^{13}C CP/MAS prescription used in this laboratory.[2,3] The nine liquid samples were analyzed as described in the experimental section in order to obtain structural parameters similar to those obtained for solid samples.

Experimental

Sample preparation

Nine coal derived liquid samples were studied in this work: references-2, 4, 5, 6, 8, 9, 10,12 and 13. All samples were provided by CONSOL Inc. and they were obtained from the HRI bench unit Run CC-15 (sometimes referred to as 227-75).

1 g of sample was placed in a 10 mm NMR tube to which 7 ml of $CDCl_3$ (with a trace of TMS as reference) was added. As prepared, the solutions of sample-5, 9 and 13 were brown, transparent, clear solutions whereas the others were black, non-transparent solutions.

The coal sample and 3 filter cake solid samples were used as received. As described in the results section and Appendix 1 the filter cakes contained some heavy oils that were spun out during the high speed magic angle spinning experiments. No attempt was made to separate the heavy oils from other insoluble material in these three samples.

NMR Experiments

Two basic solution NMR techniques were used to analyze all 9 samples: inversion-recovery and quantitative ^{13}C experiments. ^1H NMR and DEPT experiments were performed for reference 5 to assess the feasibility of using these experiments to derive additional structural information. While the DEPT experiment does provide additional structural information in the aliphatic region of the spectrum, it was concluded that the additional time and effort required to obtain such data on all samples was not possible with the available resources. Furthermore, it was concluded that J-coupled spectra (Hetcor) would be too time consuming given the resources available for the project and no further attempts were made to obtain 500 MHz proton spectra. For the purposes of the remainder of the ^{13}C analysis, the low field proton NMR data supplied by CONSOL was adequate. A quantitative ^{13}C experiment with added relaxation reagent, $Cr(acac)_3$, was also performed on reference 5 to check the accuracy of the conventional quantitative ^{13}C technique.

The inversion-recovery technique[4,5] was used to measure the variation of magnetization of sp^2 hybridized carbons. Seventeen delay times ranging from 0.025 to 40 sec were used in acquiring the inversion recovery data. A total of 160 scans were accumulated for each FID and a 50 sec delay was used to allow full recovery of all carbons between successive scans. The total acquisition time for an inversion-recovery experiment was around 48 hours. (see Appendix 2). The data obtained were then processed by a nonlinear curve fitting procedure to yield the contribution of the sp^2 hybridized carbon to the total magnetization of the sample under investigation (see Appendices 3 and 4).

Quantitative ^{13}C spectra were obtained using a 90° pulse time of 14.0 ms and a pulse delay of 25 s with gated decoupling to suppress the nuclear Overhauser enhancement

(NOE). Up to 4000 scans were accumulated for each experiment and the total acquisition time for a spectrum was 15 -20 hours. (See the Appendix 5 and the experimental values of the integrated intensities).

All solid state ^{13}C NMR experiments were carried out on a Chemagnetics CMX-100. The liquid samples were run on a Varian VXR-500 spectrometer with a Nalorac 10 mm broad band probe. Liquid spectra were recorded at a temperature of 25^0 C with TMS as reference.

Results and Discussion

Solid Samples

The data obtained from the solid state ^{13}C NMR analysis were communicated previously and that report is contained in Appendix 1. The structural parameters derived from the NMR data are given in Table 1. The filter cake samples, references 3, 7, and 11, were found to contain a heavy oil which separated from the solid during the high speed magic angle spinning experiments. As stated in Appendix 1, the liquid phase may not be quantitatively detected in a cross polarization experiment because of the motional averaging that occurs in non crystalline materials. A series of Block decay or single pulse excitation experiments were run on reference 11 and the data obtained demonstrate that the aliphatic material in the sample is not fully detected in the cross polarization experiments. Hence, the data obtained on reference numbers 3, 7, and 11 should be used only for qualitative information. The solid state NMR data obtained from the starting coal is typical for that observed in subbituminous coals and is used as a reference point for the analysis of the remainder of the liquid samples.

Liquid Samples

The magnetization (intensities) of sp^2 carbons (chemical shift region 90-165 ppm) were measured for each sample (see corresponding spectra in Appendix 5) and the data were fit to the following five parameter polynomial equation:

$$M(t) = M_p[1-(1+\beta)\exp(-t/T_p)] + M_q[1-(1+\beta)\exp(-t/T_q)]$$

where M_p and M_q represent the magnetization contributions of the protonated and nonprotonated carbons, respectively, T_p and T_q are the corresponding relaxation time constants, and β is a scaling parameter used to compensate for incomplete inversion due to pulse imperfections. Actually, there are only 4 independent parameters in this equation as the sum of M_p and M_q is always normalized to unity. This nonlinear curve fitting permits separation of the contributions from protonated carbons (P) and nonprotonated carbons (Q) and, thus, the ratio of these two types of carbons is obtained as:

$$P/Q = M_p/M_q \text{ where } M_p + M_q = 1$$

This ratio, in turn, can be used to estimate the average ring size in complex polycyclic aromatic hydrocarbon mixtures such as the 9 samples under investigation.

The polynomial function fitting of inversion-recovery experimental data was carried out by using the computer program Igor modified by Shi Bai.[5] The results obtained from the curve fittings are summarized in Table 2. Supplementary material of the fitting processes and corresponding graphs are presented in Appendix 3 and Appendix 4, respectively.

Quantitative ^{13}C NMR spectra are collected in Appendix 5 together with the relative integration values (percentages) of different spectral regions. Each spectrum was broken down into the following region and integrals were taken for each region:

2 -22 ppm,
22-50 ppm,
50-60 ppm,
60-75 (74) ppm,
79-90 ppm,
90-135 ppm,
135-150 ppm,
150-165 ppm and
165-240 ppm.

A beak at 75-79 ppm was used to exclude the solvent peaks ($CDCl_3$) at 77 ppm. The measured relative intensities (in percent of total intensity) of individual spectral regions are presented in Table 3. It can be seen from this table that samples 5, 9 and 13 are quite similar to each other. Signals in the aliphatic region, 22 - 50 ppm, of these three samples dominate the spectra. The other six samples have much stronger signals in the aromatic region.

The data obtained from both experiments (Inversion-recovery and Quantitative ^{13}C) were initially analyzed according to the method used for analysis of solid coal spectra. It was concluded that the high resolution data offered the opportunity to expand this analysis due to the rich amount of data available in the aliphatic region of the spectra of the liquid samples. The following are the definitions of the parameters used in this analysis:

I_{90-150}	Relative intensity in the indicated chemical shift region (90-150 ppm in this case);
$f_a = I_{90-240}/I_{2-240}$	Fraction of total sp^2 carbon;
$f_{al} = 1-f_a$	Fraction of total sp^3 carbon; aliphatic carbon;
$f_a^C = f_a * I_{165-240}/I_{90-240}$	Carbonyl fraction;
$f_a' = f_a - f_a^C$	Aromatic fraction; aromaticity;
$f_a^H = f_a' * M_p$	Protonated aromatic fraction;
$f_a^N = f_a' - f_a^H$	Nonprotonated aromatic fraction;
$f_a^P = f_a' * I_{150-165}/I_{90-165}$	Phenolic substituted fraction;
$f_a^S = f_a' * I_{135-150}/I_{90-165}$	Alkyl substituted fraction;
$f_a^B = f_a^N - f_a^P - f_a^S$	Aromatic bridgehead fraction;

$f_{al}^* = f_{al} * (I_{2-22}+I_{50-60})/I_{2-90}$	methyl and methoxy carbon
$f_{al}^H = f_{al} - f_{al}^*$	CH, CH_2 carbon fraction;
$f_{al}^O = f_{al}*I_{50-90}/I_{2-90}$	Aliphatic carbons bonded to oxygen;
$\chi_b = f_a^B/ f_a'$	Mole fraction of bridgehead carbons;
AC/CL	Number of aromatic carbons per cluster;
f_a^H/f_a'	Fraction of aromatic carbons that are protonated;
$(f_a^s+f_a^P)/f_a'$	Fraction of aromatic carbons that have substituent groups;
$\sigma+1$	Coordination number, or number of attachments per cluster;
Bridges and Loops	Number of bridges and loops per cluster;
Molecular Weight	Average molecular weight per cluster;
Side chains	Average number of side chains per cluster;
δ_{mw}	Average molecular weight per side chain

The parameters obtained from analysis of the data are given in Tables 4-6. Several new structural parameters were added to those used previously in order to take advantage of the additional information available from high resolution NMR data. In attempting to characterize the average cluster size for the liquid samples a discrepancy was found for sample references 5, 9, and 13. The inversion recovery data predicted that these samples had larger ring cluster sizes than the PFL and INT samples. Careful inspection of the carbon 13 NMR spectra of these three samples indicated that there was only very small amounts of signal found in the normal chemical shift range for bridgehead carbons. It was assumed that polycyclic aromatic rings were not present to any significant extent in reference samples 5, 9, and 13 and, hence, the analysis of the data on these samples assumes the presence of only structures that contain, on average, one aromatic ring and all relevant data parameters for these 3 samples were treated according to this assumption. The data analysis on the remaining samples suggest an average cluster size slightly smaller than that of the starting coal.

In Table 4 two structural unit parameters are used that have not been previously defined. The ratio f_a^H/f_a' denotes the fraction of aromatic carbons that are protonated (as opposed to the parameter f_a^H which defines the fraction of total carbon that is aromatic and protonated). Likewise, the ratio $(f_a^s+f_a^P)/f_a'$ defines the fraction of aromatic carbons that have substituent groups attached either as carbon substituents (f_a^s) or oxygen substituents

(f_a^P). In Table 5 the number of side chains per 100 carbons is given as $f_a^S+f_a^P$. The number of carbons per side chain is obtained from the total number of aliphatic carbons divided by the number of side chains (all parameters are normalized to a basis of 100 carbons). The number of aromatic hydrogens, H_{aro} is taken as f_a^H. Total hydrogen is obtained from the elemental analysis of each sample. The number of methyl hydrogens is estimated as $3(f_{al}^*)$. The remainder of the hydrogen present as CH and CH_2, (H_{aliph}), is estimated as H_{total} - H_{aro} - $Methyl_H$. The H/C value in the CH and CH_2 carbons is estimated from the ratio H_{aliph}/f_{al}^H. It is clear from the values obtained that the side chains are not highly branched as the C/H ratio is approximately 2.

Table 6 contains the cluster parameters of the samples studied. The parent coal, with an average cluster size of 13 aromatic carbon atoms, has a coordination number of 5.1, has 3.3 bridges and loops, a molecular weight of approximately 346 daltons, and contains 1.8 side chains with an average mass of 37 daltons per side chain. The coordination number ($\sigma+1$) consists, on average, of 3.3 bridges and loops and 1.8 side chains. It is noted that all liquid samples have lower coordination numbers than the parent coal. This is to be expected since these materials have been detached from the macromolecular structure and dealkylation reactions have occurred which reduce the number of ring attachments. Hydrogenation reactions then increase the amount of protonated aromatic hydrogens, reduce the number of bridges and loops, and reduce the number of side chains. It is interesting to note that the mass of the average side chain is essentially constant in each sample. It should be pointed out that only the coordination number can be estimated for the overhead samples. The number of attachments on an aromatic ring is between 2 and 4 for the PFL and INT samples and is only slightly higher (4-5) for the SOH-ASOH samples. The number of carbons per side chain is between 2 and 4 for the PFL and INT samples and is 5-6 for the overhead still samples.

The data on the overhead still samples (i.e., a basic one aromatic ring structure with a relatively high number of ring attachments) suggest the presence of highly naphthenic structures (e.g. tetralin and other hydroaromatic types). When considered together with the number of carbons per side chain (5-6 carbons) these data suggest that these materials also contain relatively short side chain groups. Such structures would be expected to be derived from 2-3 ring aromatic structures if ring opening reactions occurred which did not lead to subsequent ring dealkylation at every site.

In order to more clearly portray the large amount of data obtained from the samples studied, the data has been grouped by collection point for comparison, e.g., separator still overhead and atmospheric still overhead (SOH-ASOH), reference numbers 5, 9, and 13; pressure filter liquids, reference numbers 2, 6, and 10; and interstage liquids, reference numbers 4, 8, and 12. Figure 1 displays the carbon aromaticity (f_a') for the overhead still samples (SOH-ASOH), the pressure filter liquids (PFL) and the interstage (INT) liquids. In each case the data is compared to that of the parent coal. It is clear that the different process conditions represented in reference numbers 5, 9, and 13 do not change the f_a values in these samples. The data for the PFL exhibit a significant change among samples 2, 6, and 10 suggesting effects due to catalyst type and aging effects in the second stage catalyst. The interstage samples (4, 8, and 12) exhibit slight increases with reference number with each sample having a higher f_a value than the parent coal.

Another probe of the changes that occur in the aromatic structure can be obtained by considering the number of protonated aromatic carbons (f_a^H) in each sample (Figure 2) and the fraction of aromatic carbons that are protonated (f_a^H/f_a', Figure 3). The f_a^H values in the SOH-ASOH samples are much lower than the value found for the parent coal while the f_a^H values for the PFL and INT samples are considerably higher than that of the parent coal. These data indicate that extensive ring protonation reactions have occurred in the materials collected at these two points. The variation of the parameter values among samples is probably due to the effects of the catalysts present in the different processing stages. The normalized aromatic carbon data (Figure 3) indicates that the fraction of aromatic carbons that are protonated in the overhead samples is comparable to that of the parent coal but a wide range of variation is noted.

In Figure 4 the normalized ring substituents indicate that the PFL and INT sample sets have a lower number of ring substituents than the parent coal while the opposite is found for the overhead samples. No significant variation is seen among the PFL samples but the overhead and INT samples exhibit variations that are significantly different. The PFL and INT data indicate the effects of ring dealkylation reactions that occur in both stages of the hydorgenation process. The overhead still samples exhibit large increases in the number of aromatic ring substituents when compared to the parent coal. Furthermore, the variation in this parameter among the three samples is quite significant.

Figure 5 displays the number of carbons per side chain. All three sample sets contain more carbons per side chain than the parent coal. These data suggest that ring opening reactions are not accompanied with side chain cracking reactions that would liberate large amounts of light gases. The PFL and INT samples all have comparable values but the side chain length is shorter in these samples than the values observed for the overhead samples. Little variation in this parameter is noted in the PFL liquids. Some variation is noted among the INT and SOH-ASOH sample sets that are significant and would reflect differences in catalytic affects in the various stages of the processing stream.

The techniques employed can be used to approximate the average cluster size in the liquid samples in a manner similar to that employed for solids.[2,3] As noted earlier, this method breaks down in the analysis of the SOH-ASOH samples. Based on a careful inspection of the NMR data it is clear that these samples consist primarily of single aromatic ring species. This conclusion has been independently corroborated by CONSOL personnel based on analytical results obtained by other analysis methods.[6] However, the cluster size approximation seems to be valid for the PFL and INT liquids since these materials contain polycondensed aromatic hydrocarbons.[6] While it is possible that these samples also contain some single ring aromatic species, the ^{13}C NMR data suggest that 2 and 3 ring aromatic moieties are the predominate structures present. Figure 6 contains the comparisons of the average aromatic cluster size in each of the three groups of samples compared to that of the parent coal. All SOH-ASOH samples are assumed to be single ring aromatic compounds. The estimated cluster sized of the PFL and INT liquids are between 12 and 8. The error in this parameter is ±2 carbons. The PFL liquids exhibit a variation in this parameter which may be significant with a value for Reference Number 10 at 8 aromatic carbons per cluster. The INT liquids, on the other hand display a monatonic decrease with Reference Number from 13 (the parent coal) to 9 for Reference Number 12. The significance of this trend in the INT liquids is not clear from the data available at the present time.

Conclusions

The data obtained on the liquid samples studied provides a complex set of parameters. Three major types of structural reactions can be identified from the NMR data, ring protonation, ring opening, and dealkylation. It also appears that differences can be found in the rates of these reactions that occur in the two stages of the reactor. In the first processing stage, the interstage liquid samples exhibit a small increase in aromaticity (relative to the parent coal) but it is not evident that the catalyst used has any affect on the aromaticity. The pressure filter liquids, on the other hand exhibit marked differences in aromaticity that may be related to catalyst and aging effects. Changes in aromaticity can occur in two different ways; ring protonation or loss of sp^3 carbons by a wide variety of dealkylation or cracking mechanisms. A significant increase in the presence of protonated aromatic carbon in the PFL and INT samples (Figures 2 and 3) will occur only if ring protonation reactions occur in both stages of the process. From Figures 3 and 4 it can be seen that both hydrogenation and dealkylation reactions have occurred in both stages of the process. Since the side chain length is greater (with respect to the parent coal) in all samples studied, it appears that extensive ring opening reactions have occurred in both stages of the process, particularly in the PFL liquids obtained down stream from the second stage of the reactor. The variation in the average aromatic cluster size occurs as expected but the trends in the PFL and INT liquids is not clear.

References

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TABLE 1. ^{13}C CP/MAS Data on Black Thunder Coal and Filter Cake Samples

MATERIAL	f_a	f_a'	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
REF#1	.68	.58	.10	.19	.39	.08	.15	.16	.32	.24	.08	.07
REF#3	.73	.65	.08	.26	.39	.07	.15	.17	.27	.18	.09	.08
REF#7	.73	.69	.04	.26	.43	.05	.15	.23	.27	.19	.08	.05
REF#11	.71	.64	.07	.25	.39	.07	.16	.16	.29	.20	.09	.08

MATERIAL	χ_b	C	$\sigma+1$	P_0[a]	B.L.	S.C.	MW	M_δ
REF#1	.276	13	5.1	.65	3.3	1.8	346	42
REF#3	.262	13	4.4	.59	2.6	1.8	282	28
REF#7	.333	16	4.7	.60	2.8	1.9	321	26
REF#11	.250	12	4.3	.61	2.6	1.7	259	26

a. P_0 is the fraction of intact bridges in a cluster structure. This value is calculated from the assumption that all substituents end in a methyl group and is defined as:

$$P_0 = ((\text{attachments}/100\ \text{carbons}) - f_{al}^*)/(\text{attachments}/100\ \text{carbons})$$

Table 2. Paramaters Obtained from Polynomial Fitting[a]

Sample	color	β	M_p	M_q	T_p, (s)	T_q, (s)	χ^2
Reference-2	Dark	0.6694	0.5076	0.4924	0.73	4.46	0.0045
Reference-4	Dark	0.6942	0.4405	0.5595	0.33	2.08	0.0167
Reference-5	Light brown	0.7416	0.2805	0.7195	2.55	7.01	0.0061
Reference-6	Dark	0.5784	0.4507	0.5493	0.38	1.47	0.0024
Reference-8	Dark	0.6600	0.5593	0.4407	0.95	7.84	0.0044
Reference-9	Clear Brown	0.6744	0.2395	0.7605	2.15	8.13	0.0107
Reference-10	Dark	0.6389	0.6300	0.3700	0.78	4.72	0.0031
Reference-12	Dark	0.6414	0.5678	0.4322	0.77	4.58	0.0071
Reference-13	Clear brown	0.6946	0.4256	0.5744	2.39	11.07	0.0057

a. $M(t) = M_p[1-(1+\beta)\exp(-t/T_p)]+M_q[1-(1+\beta)\exp(-t/T_q)]$, $M_p + M_q = 1$; χ^2, or chi-squared is a measure of the goodness of fit of the data to the model.

Table 3. Integrated Intensities of Quantitative ^{13}C NMR Spectra[a]

Sample	2-22 ppm	22-50 ppm	50-60 ppm	60-75 ppm	79-90 ppm	90-135 ppm	135-150 ppm	150-165 ppm	165-240 ppm
Reference-2	8.05	45.73	0.65	0.00	0.00	31.69	13.06	0.83	0.00
Reference-4	5.60	34.39	0.24	0.12	0.35	40.28	16.88	2.13	0.00
Reference-5	15.01	64.30	0.08	0.00	0.00	13.81	6.60	0.35	0.00
Reference-6	5.77	36.17	0.45	0.00	0.02	40.73	15.63	1.10	0.14
Reference-8	5.96	33.76	0.30	0.00	0.00	44.43	14.34	1.23	0.00
Reference-9	15.42	62.31	0.00	0.02	0.00	15.22	6.59	0.47	0.00
Reference-10	5.68	35.89	0.50	0.03	0.00	41.54	15.30	1.05	0.00
Reference-12	5.12	32.31	0.32	0.00	0.00	45.28	15.44	1.52	0.00
Reference-13	13.05	64.43	0.67	0.00	0.00	15.41	5.99	0.44	0.00

a. A break at 75-79 ppm was used in order to exclude the solvent, $CDCL_3$, peaks. Values for each sample have been normalized to 100.

Table 4. Aromatic and Aliphatic Structural Paramaters[a]

Sample	f_a'	f_a^C	f_a^H	f_a^S	f_a^P	f_a^N	f_a^B	f_a^H/f_a'	$(f_a^S+f_a^P)/f_a'$	f_{al}^H	f_{al}^*	f_{al}^O
Coal	58	0	19	15	8	39	16	0.33 ±0.01	0.40 ±0.06	24	8	7
#2	46	0	23	13	1	22	9	0.50 ±0.01	0.30 ±0.03	46	9	1
#4	59	0	26	17	2	33	14	0.44 ±0.01	0.32 ±0.03	34	6	0
#5	21	0	6	15	0	15	0	0.29 ±0.03	0.71 ±0.07	64	15	0
#6	57	0	26	16	1	32	15	0.46 ±0.01	0.30 ±0.02	36	6	0
#8	60	0	34	14	1	26	11	0.57 ±0.01	0.25 ±0.02	34	6	0
#9	22	0	5	17	0	17	0	0.23 ±0.03	0.77 ±0.07	62	15	0
#10	58	0	36	15	1	21	5	0.62 ±0.01	0.28 ±0.02	36	6	1
#12	62	0	35	15	2	27	10	0.56 ±0.01	0.27 ±0.02	31	5	0
#13	22	0	9	13	0	13	0	0.41 ±0.02	0.59 ±0.07	64	14	1

a. Normalized to value per 100 carbons. All data have been rounded to the nearest digit and the errors are ±1 unless otherwise noted.

Table 5. Hydrogen Distribution[a]

Sample	# of side chains ($f_a^s+f_a^p$)	# of C per side chain	H_{aro}	Total H	Meth H	H_{aliph}[b]	H/C (aliph)
Coal	23	1.4 ±0.1	19	88	24 ±2	45 ±4	1.9 ±0.3
#2	14	3.9 ±0.4	23	134	27 ±2	84 ±4	1.8 ±0.2
#4	19	2.1 ±0.1	26	117	18 ±2	73 ±4	2.1 ±0.2
#5	15	5.0 ±0.5	6	180	45 ±2	129 ±4	2.0 ±0.2
#6	17	2.5 ±0.2	26	121	18 ±2	77 ±4	2.1 ±0.2
#8	16	2.5 ±0.2	34	110	18 ±2	58 ±4	1.7 ±0.2
#9	17	4.5 ±0.4	5	176	45 ±2	126 ±4	2.0 ±0.2
#10	16	2.6 ±0.2	37	125	18 ±2	70 ±4	1.9 ±0.2
#12	17	2.2 ±0.1	35	110	15 ±2	60 ±4	1.9 ±0.2
#13	13	6.0 ±0.7	9	172	42 ±2	121 ±4	1.9 ±0.2

a. Normalized to value per 100 carbons. All data have been rounded to the nearest digit and the errors are ±1 unless otherwise noted.

b. $H_{aliph} = H_{total} - H_{aro} - H_{methyl}$.

Table 6. Cluster Parameters[a]

Sample	C_{aro}	$\sigma+1$	Bridges & Loops	Molecular weight	Sidechains	δ_{mw}[c]
Coal	13	5.1 ±1.1	3.3	346	1.8	37
#2	10	3.0 ±1.0	1.1	294	1.9	35
#4	12	3.9 ±1.0	2.7	275	1.2	34
#5	b	4.3 ±1.0	-	-	-	-
#6	12	3.6 ±1.0	2.3	282	1.3	38
#8	10	2.7 ±0.4	1.7	218	1.0	36
#9	b	4.6 ±1.1	-	-	-	-
#10	8	2.2 ±0.8	1.4	192	0.8	44
#12	9	2.5 ±0.8	1.8	195	0.7	35
#13	b	3.5 ±1.0	-	-	-	-

a. Parameters are on a per cluster basis.

b. These samples did not appear to contain a significant number of bridgehead carbons, hence, have been assumed to be composed principally of single aromatic ring compounds.

c. Average side chain mass in daltons

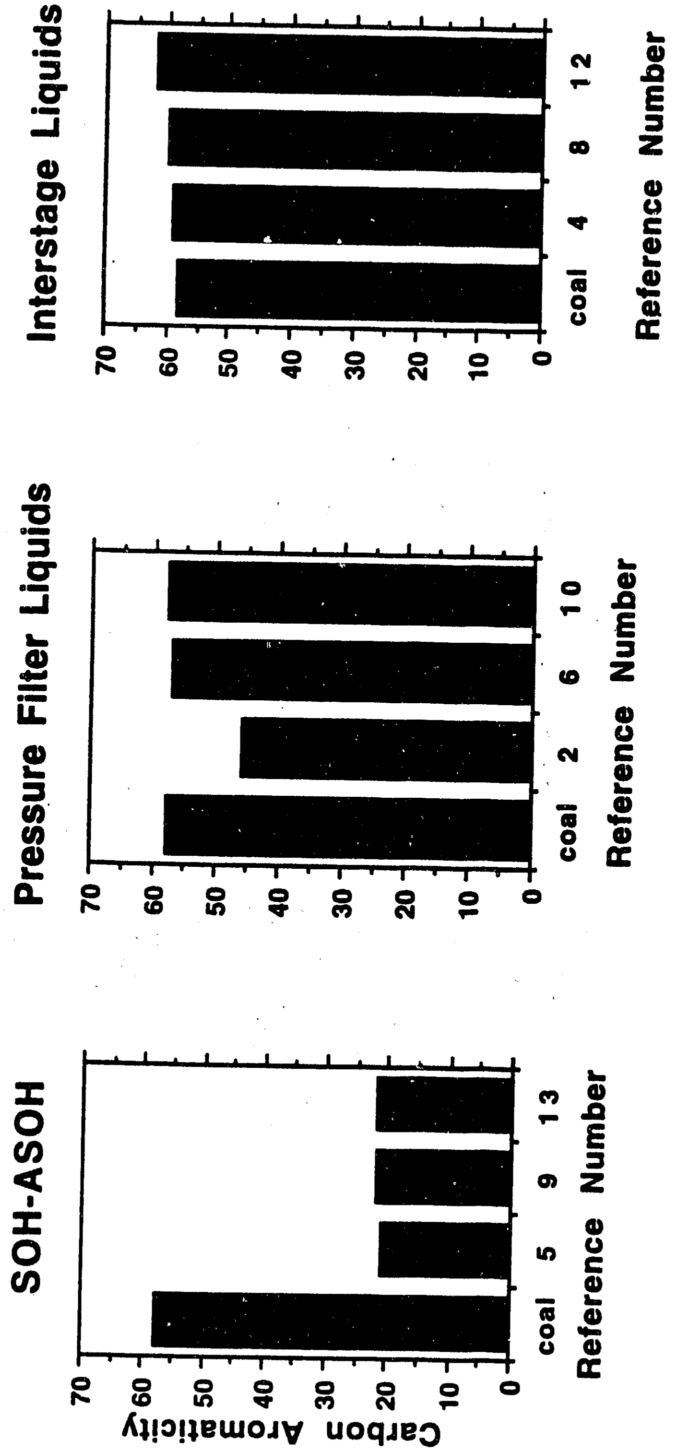

SOH-ASOH
Pressure Filter Liquids
Interstage Liquids
Carbon Aromaticity
70
60
50
40
30
20
10
0
coal
5
9
13
2
6
10
4
8
12
Reference Number

Figure 1

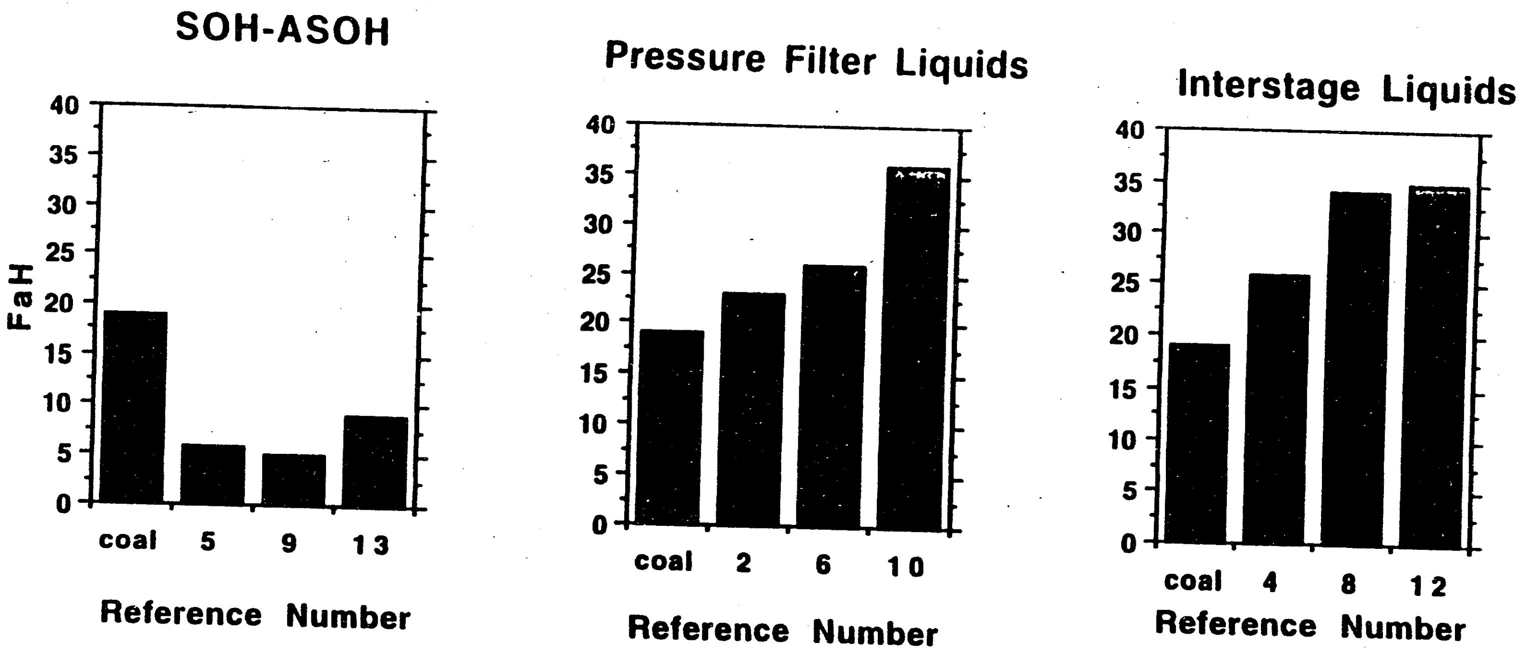
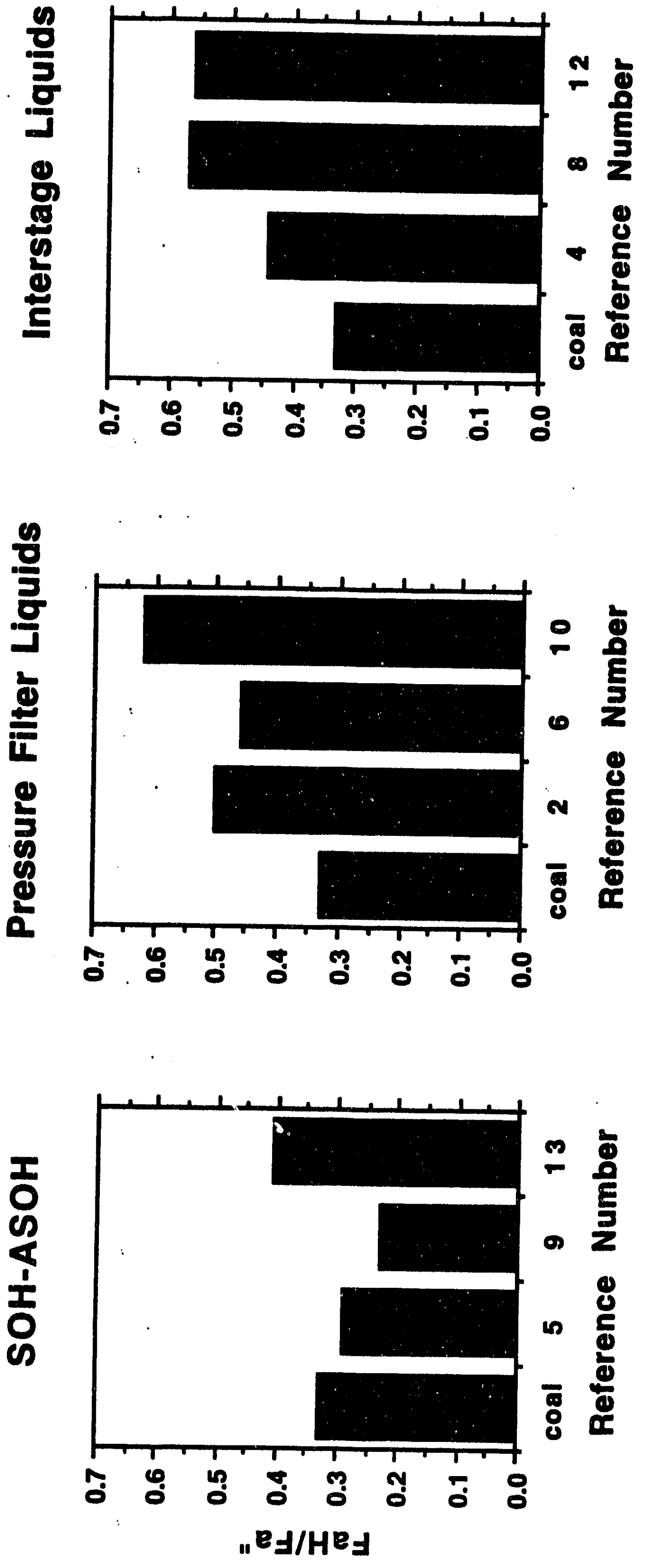

SOH-ASOH
Pressure Filter Liquids
Interstage Liquids
FaH
40
35
30
25
20
15
10
5
0
coal
5
9
13
2
6
10
4
8
12
Reference Number

Figure 2



Interstage Liquids
Pressure Filter Liquids
SOH-ASOH
FaH/Fa"
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
coal
4
8
12
2
6
10
5
9
13
Reference Number

Figure 3

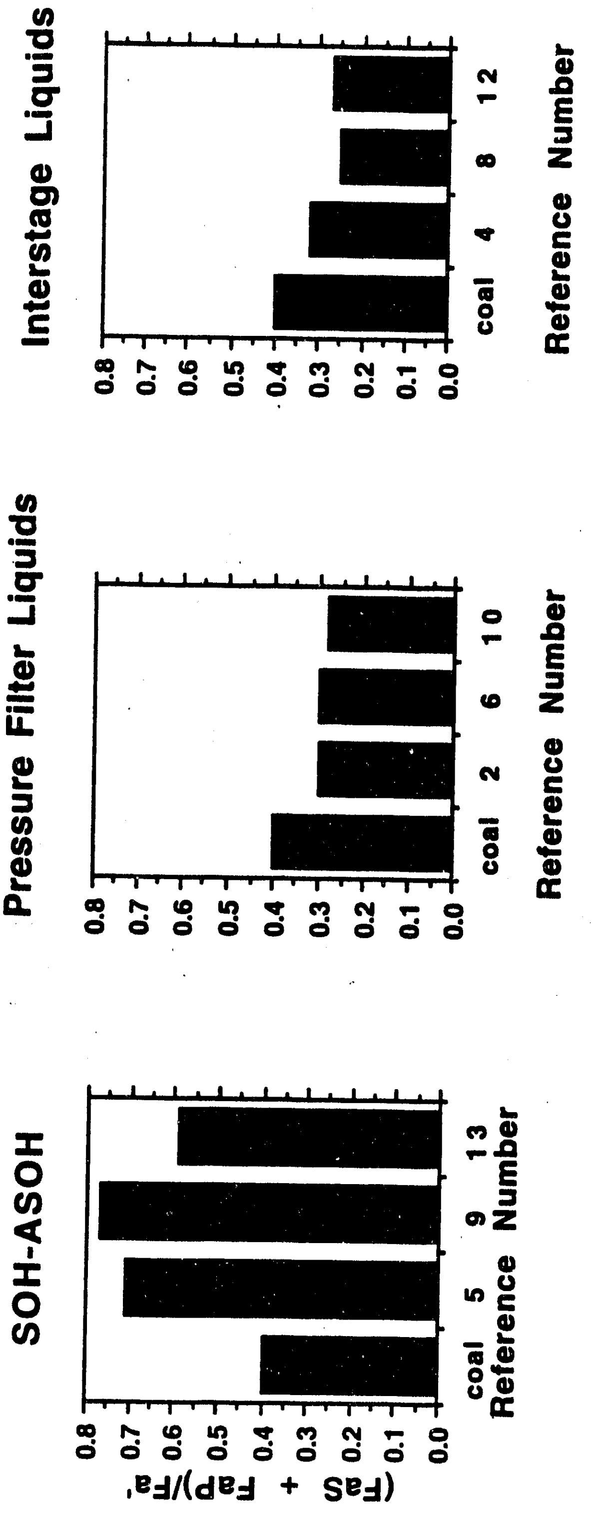

SOH-ASOH
Pressure Filter Liquids
Interstage Liquids
(FaS + FaP)/Fa'
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
coal
5
9
13
2
6
10
4
8
12
Reference Number

Figure 4

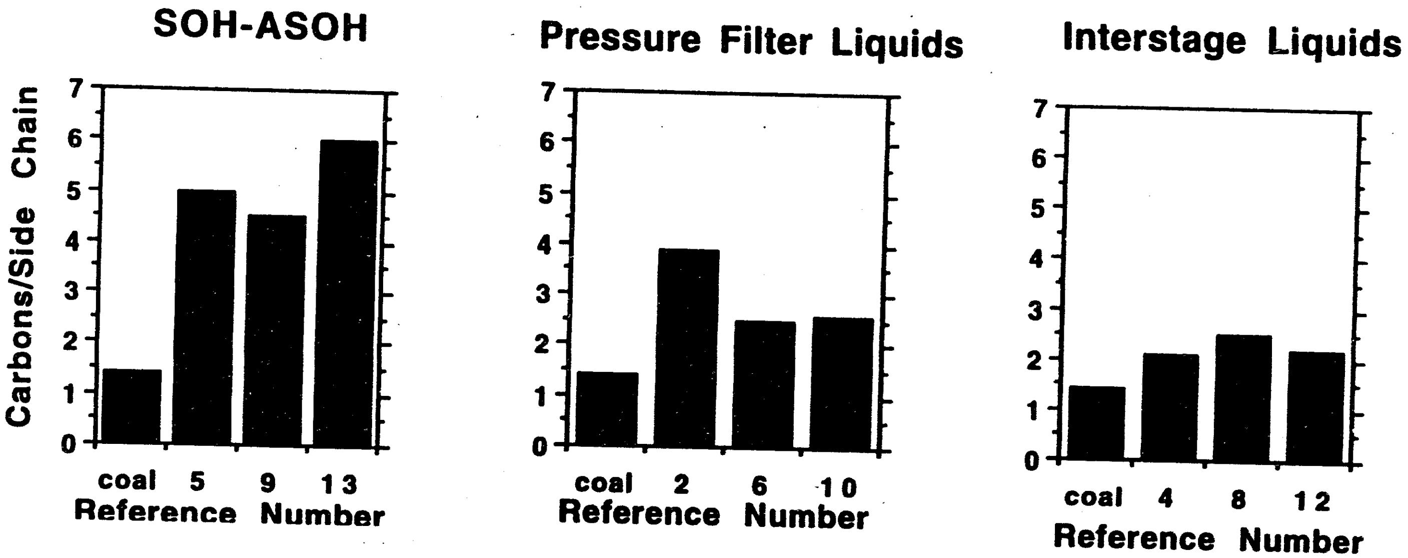

SOH-ASOH
Pressure Filter Liquids
Interstage Liquids
Carbons/Side Chain
0
1
2
3
4
5
6
7
coal
5
9
13
2
6
10
4
8
12
Reference Number

Figure 5

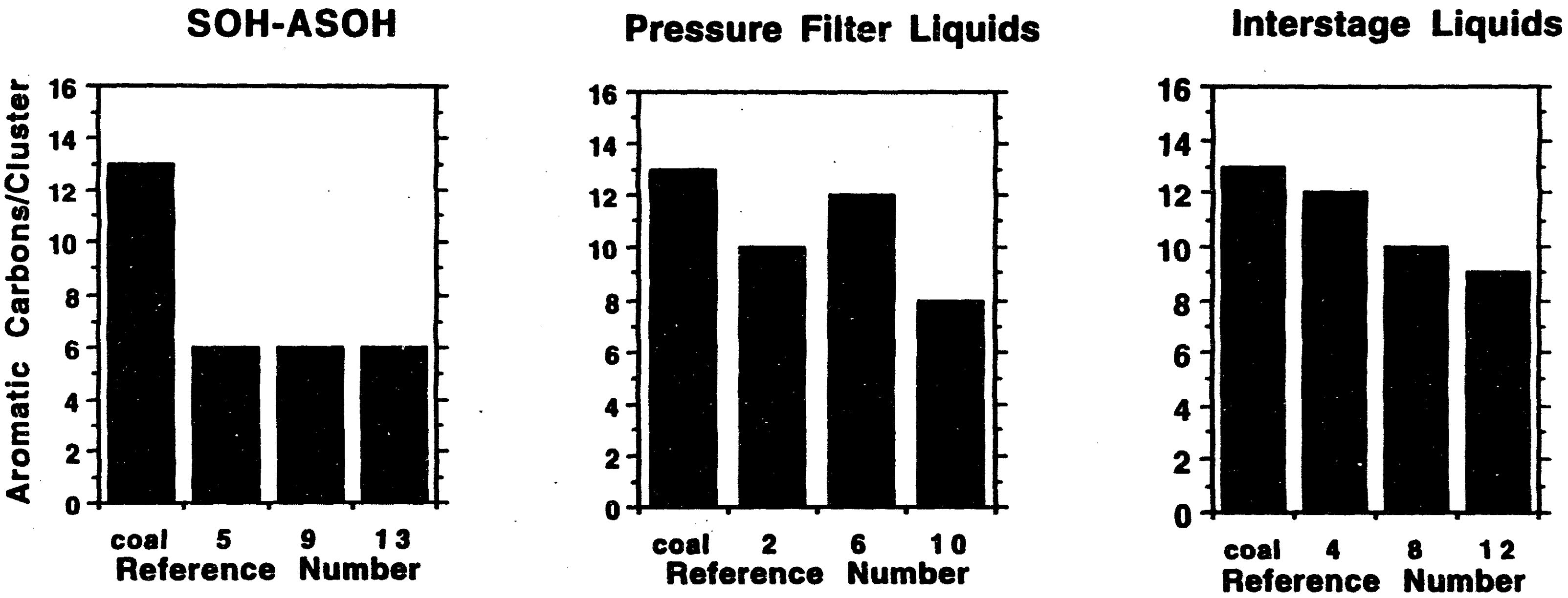

SOH-ASOH
Pressure Filter Liquids
Interstage Liquids
Aromatic Carbons/Cluster
0
2
4
6
8
10
12
14
16
coal
5
9
13
2
6
10
4
8
12
Reference Number

Figure 6

Appendix 1. Solid State ^{13}C NMR Analysis of CONSOL Coal and Processed Filter Cakes

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I. Experimental Methods

Two basic NMR experiments using ^{13}C CP/MAS techniques were performed on each of the samples in addition to a normal CP/MAS experiment with 10,000 scans and a 2 ms contact time from which integrations over selected ranges were taken. All of the experiments were run with a 1s recycle delay and a 20 kHz spectral width. The spectrometer is a Chemagnetics CMX-100 with a carbon frequency of 25.152 MHz and a proton frequency of 100.02 MHz and a decoupling field of about 56 kHz. The spinning speed was controled at 4100 +/- 5 Hz for the coal sample and set to 4100 Hz for the filter cake samples where the unregulated variation is about +/- 25 Hz. All three filter cake samples (ref 3,7 11) had a small amount of liquid come out of the roter even with the tightest rotor caps on and this liquid covered the optical detector and speed control regulation was not possible. In addition to the above experiments several Block decay (BD) experiments were done on sample Ref 11 with pulse delays of 3,60, 180 and 300 s and 100 scans each to compare with CP/MAS. A pulse delay of 180s was needed before the spectra stopped changing (at least noticeably within the low SN). There was a broad background from the probe in the BD experiment which made phasing the spectra difficult and may have distorted the spectra somewhat especially in the region downfield of 165 ppm so no integrations were done on these spectra.

The first basic experiment run was a variable contact time experiment where the contact time was varied in 21 times from 5 μs to 25 ms and 3000 to 3500 scans were recorded for each contact time. The nmr spectrum for each contact time was integrated from 240 to 90 ppm for the aromatic region and from 90 to 0 ppm for the aliphatic region. Each region was fit separately to the following five parameter equation to determine the magnetization for the region independent of relaxation effects.

$$M(t)=(M_G+M_L)\cdot\{\exp(-t/T^{H}_{1\rho})\}-M_L\cdot\exp(-t/T_{LCH})-M_G\cdot\exp(-0.5\cdot(t/T_{GCH})^2) \qquad (1)$$

In the above equation T_{GCH} is the time constant for the first stage polarization for carbons with directly attached protons, T_{LCH} is a composite time constant for the 2nd stage polarization for carbons with directly bonded protons and the polarization for carbons without protons. M_G and M_L are the respective magnetizations. $T_{1\rho}^{H}$ is the spin-lattice relaxation time constant in the rotating frame.

Using the total magnetizations (M_G+M_L) from the aromatic and aliphatic regions the aromaticity and aliphaticity are calculated as follows[1, 2]:

$$f_a = M_{Total}^{ar}/(M_{Total}^{al} + M_{Total}^{ar})$$

$$f_{al} = M_{Total}^{al}/(M_{Total}^{al} + M_{Total}^{ar}) \qquad (2)$$

and where the intensity from spinning sidebands has been included in the total magnetization for the aromatic region. Using integrals from the 2 ms spectrum the fractional amount of carbonyl and carboxyl groups, f_a^C, having chemical shifts between 240 and 165 ppm are subtracted from the aromaticity to give a corrected aromaticity as:

$$f_{a'} = f_a - f_a^C. \qquad (3)$$

The next step in the spectral deconvolution routine is to use dipolar dephasing experiment to separate those aromatic carbons with directly bonded protons from all the rest. This experiment was run with a contact time of 2 ms which in all cases had the highest intensity aromatic signal and the number of scans on each point was again between 3000- 3500. This experiment is similar to a normal CP experiment except for an interval after crosspolarization where there are no RF fields on and magnetization from protonated carbons decays quickly and the magnetization from nonprotonated carbons decays slowly. The dephasing interval was varied in 23 times from 2 μs to 200 μs and the data fit to the following four parameter equation:

$$M(t) = M_L^{dd}e^{-t/T_L^{dd}} + M_G^{dd}e^{-0.5(t/T_G^{dd})^2} \qquad (4)$$

where M_L^{dd}, T_L^{dd} are associated with nonprotonated carbons and M_G^{dd}, T_G^{dd} with protonated carbons.

Using dipolar dephasing results the corrected aromaticity is then subdivided as follows:

$$f_a^H = f_{a'} \times M_G^{dd} \tag{5}$$

and

$$f_a^N = f_{a'} \times M_L^{dd}. \tag{6}$$

Using chemical shift ranges from the 2 ms contact time spectrum two more aromatic parameters may be defined. They are, f_a^P, which represents aromatic carbon attached to oxygen and, f_a^S, the amount of aromatic carbon bonded to aliphatic carbon but also including biaryl linkages. The two shift ranges are 150-165 ppm and 135-150 ppm respectively. The amount of bridgehead or condensed carbon is then given as:

$$f_a^B = f_a^N - f_a^P - f_a^S. \tag{7}$$

The aliphatic region can also be subdivided by chemical shift ranges. From the 2 ms spectrum the fractional amount of methyls (0-22 ppm) and methoxy (50-60 ppm) are used to calculate the parameter, f_{al}^*, and the amount of other types of aliphatic carbon (almost all CH and CH_2) is then calculated as:

$$f_{al}^H = f_{al} - f_{al}^*. \tag{8}$$

One last parameter is also calculated, f_{al}^O, and represents the amount of aliphatic carbon bonded to oxygen and may include parts of both the other aliphatic parameters. This parameter is calculated from the fractional amount of the aliphatic signal between 50 and 90 ppm as integrated from the 2 ms contact time spectrum.

Using the above 12 structural parameters, our cluster size model[1] and an elemental analysis the lattice parameters including aromatic cluster size and the lattice coordination number may be obtained.

The aromatic cluster is estimated from the mole fraction of condensed carbons which is calculated as:

$$\chi_b = f_a^B/f_{a'} \tag{9}$$

and using this result and our model[1] the cluster size, C, estimated.

Using $f_a^P + f_a^S$ as the total number of attachments per 100 carbons, the corrected aromaticity and the cluster size, $\sigma+1$, the total number of attachments per cluster is calculated.

Another lattice parameter, P_0, the fraction of intact bridges in the lattice is roughly estimated, with the approximation that broken bridges end in a single methly group, as:

$$P_0 = (f_a^P + f_a^S - f_{al}^{*})/(f_a^P + f_a^S). \tag{10}$$

The number of attachments per cluster can now be divided in to two subgroups as, B.L., the number of bridges and loops per cluster and, S.C., the number of side chains per cluster. A loop is defined as a bridge back to the same cluster. They are calculated as:

$$\text{B.L.} = (\sigma+1)\times P_0 \tag{11}$$

and

$$\text{S.C.} = (\sigma+1) - \text{B.L.}. \tag{12}$$

Using the aromatic cluster size, C, the corrected aromaticity, $f_{a'}$, and the %C from an elemental analysis the total molecular weight, MW, of the cluster including all sidechains and half of the bridge materical can be calculated as:

$$MW = (C\times 12.01)/(f_{a'}\times \%C/100). \tag{13}$$

From dipolar dephasing results the number of protonated and nonprotonated aromatic carbons are known and the molecular weight from the aromatic carbons and any attached protons can be subtracted from the total molecular weight to get the total molecular weight of the aliphatic material. This weight when divided by (σ+1) gives, M_8, the average molecular weight per attachment.

II. Results and Discussion for Coal and Filter Cakes

After loading the filter cake samples in the rotor and spinning at 4100 Hz for a few hours it was noticed that the optical spinning speed detection was not working. After investigation it was found that liquid had leaked out of all three filter cake samples and it was impossible to contain all of the sample even with the tightest rotor caps. This implies that these samples consist of two phases. The liquid phase will not be detected or detected to the full extent in a crosspolarization experiment because of motional averaging of the dipolar interaction needed for crosspolarization.

Bloch decay experiments on Ref 11 show that there is aliphatic material that has too much motion to detect fully in CP based experiments but does show up in single pulse spectra, (compare spectra 1 and 5 in appendix). This is consistent with the CONSOL proton nmr results on the pyridine soluble fraction of the samples which show a high aliphatic content. Due to the broad probe background that could not be supressed this Bloch decay spectrum should be used only for qualitative information.

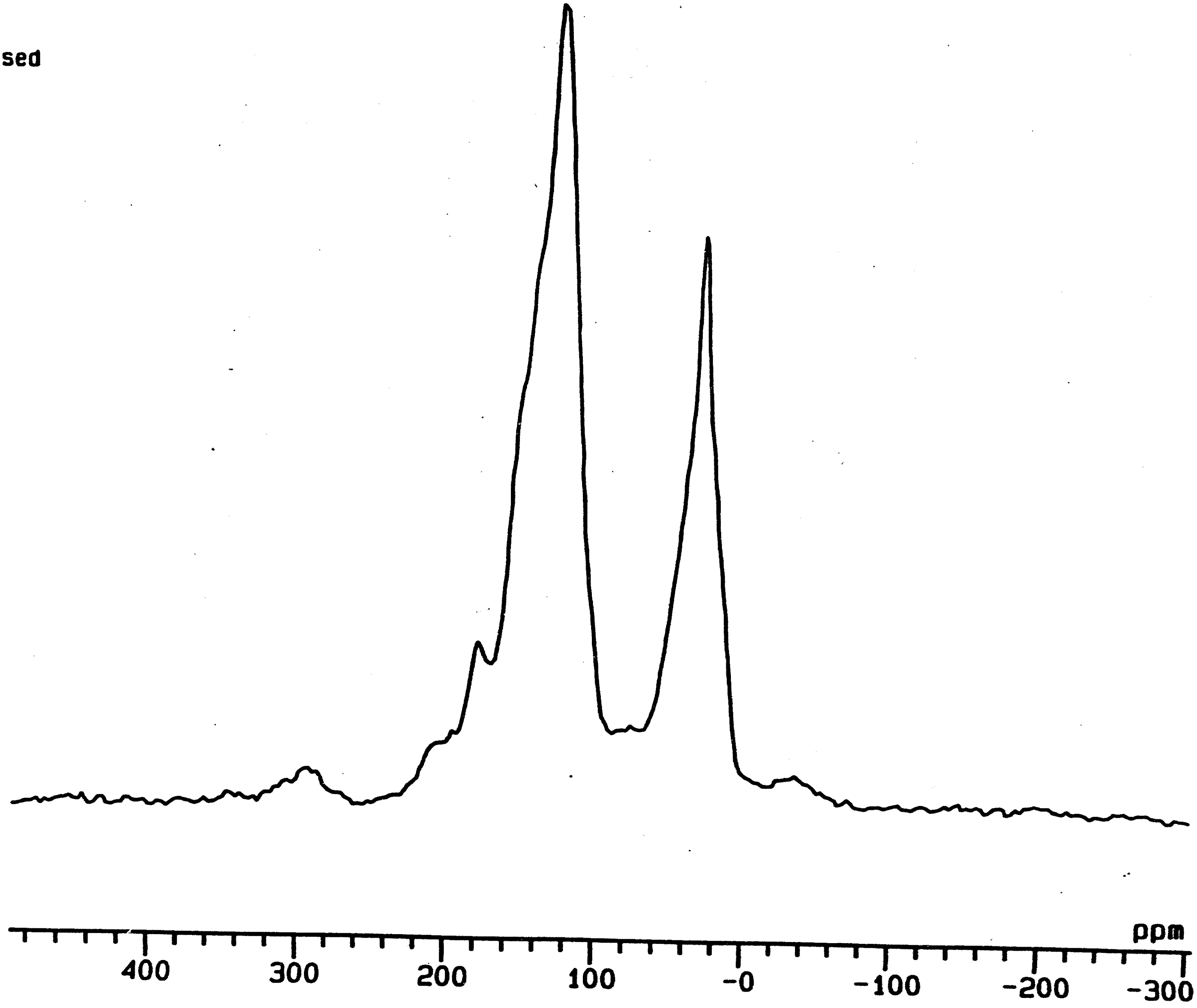
The NMR parameters form the VCT and DD fits are given in Tables 1 and 2 for the aromatic and aliphatic fits respectively. All of these parameters are in the normal ranges for fossil fuel samples with nothing unusual. The structural and lattice parameters are shown in Table 3 for the original coal and the filter cakes. This information is for the more rigid macromolecular phase of this two phase system for the filter cakes. Most of the structural and lattice parameters for the three samples are very similar. The aromatic cluster size on sample ref 7 with a value of 16 is slightly higher than the other samples and the coal with values of 12-13. If one compares the spectra (Apendix spectra 2-5) of the three filtercakes one sees that samples ref 3 and 11 are very similar in appearence and ref 7 somewhat different. Samples 3 and 11 have broad lineshapes with a broad band under the whole spectral range where as sample 7 has sharper features. This difference seems to correlate with the amount of Fe_2O_3 in the samples, as shown in Table 4, which is about two and a half times as large in samples 3 and 11 as in sample 7 and the original coal which also has sharper spectral features.

Another point of discussion is the amount of oxygen functional groups in the samples. The coal has from CONSOL'S elemental analysis 22 oxygen atoms per 100 carbon atoms. In looking at the structural parameters (f_a^C, f_a^P, and f_{al}^O) the sum of these is 25 with some possible double counting so these parameters correlate well with the elemental analysis. For the three filter cake samples as shown in Table 4 the oxygen atoms per 100 carbons are 2.5, 4 and 1 for samples ref 3, ref 7, and ref 11 respectively. The sum of the oxygen related structural parameters are 23, 14 and 22 respectively. This difference may be due to large line broadening from the iron in the samples which may add more intensity to those regions than there should be.

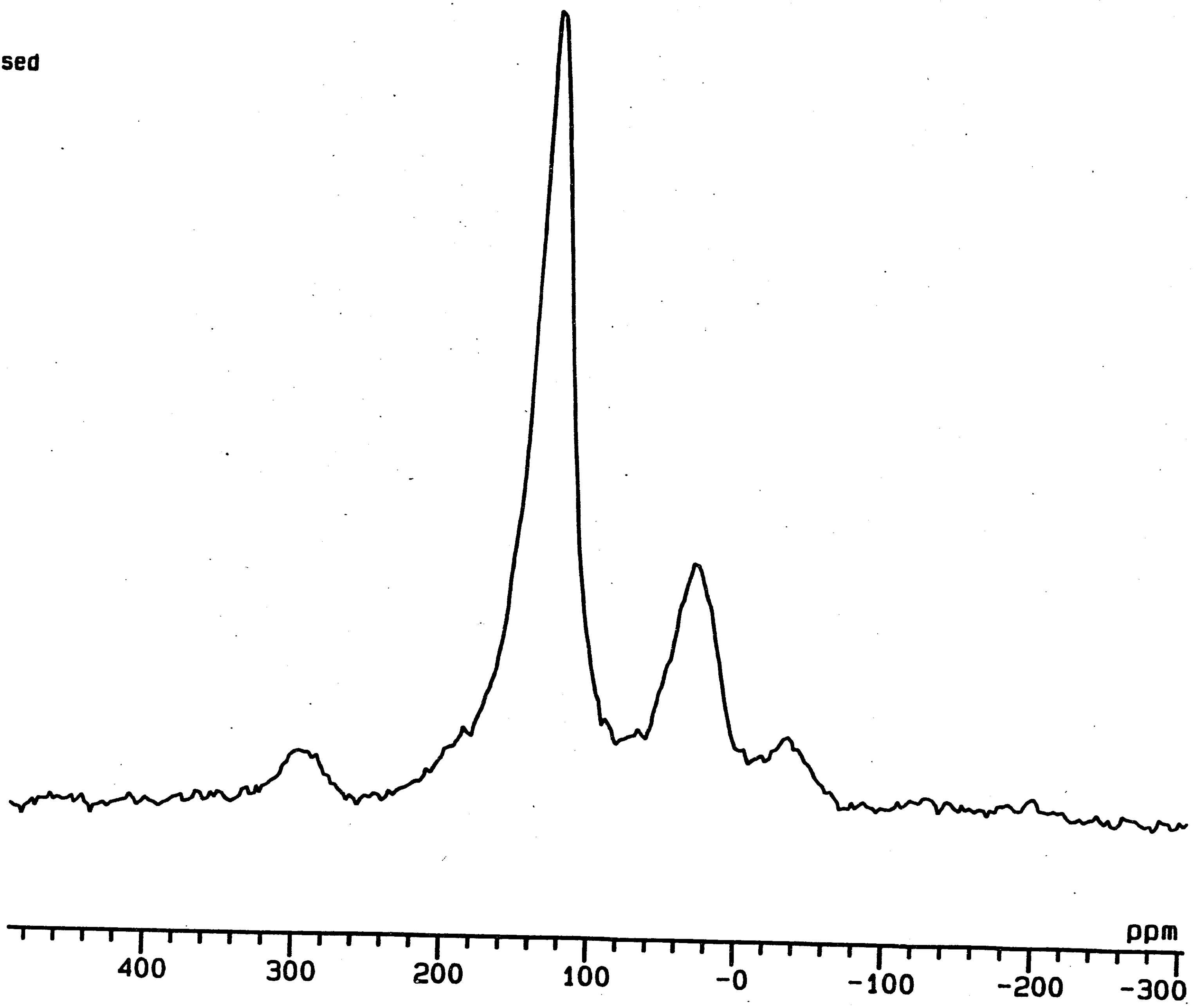
Because of the amount of iron in samples 3 and 11 and the two phase nature of these systems the CP/MAS results on these samples are of inferior quality to the previous sample set and the results should be considered only qualitative in nature.

A. Appendix of Spectra

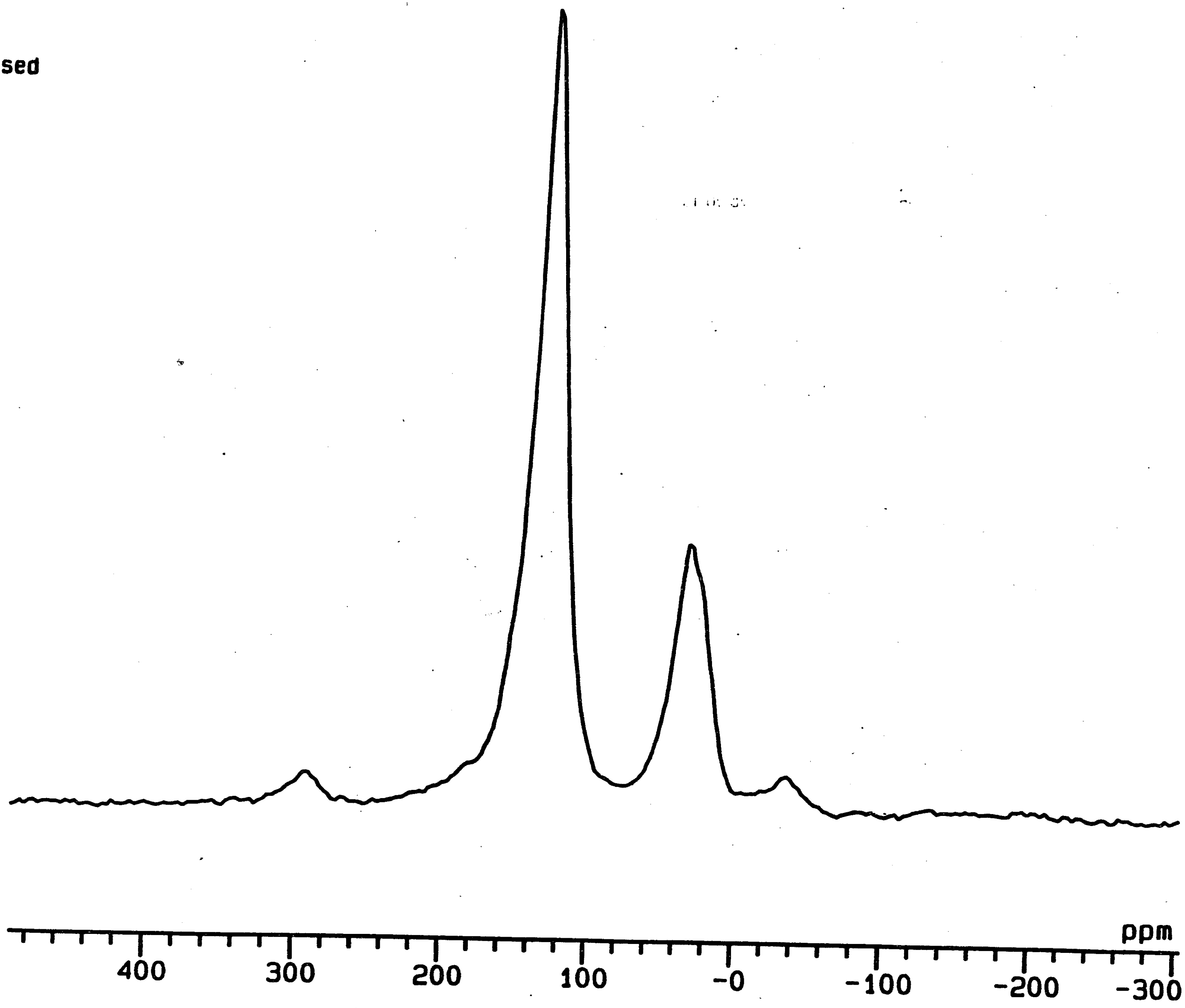
ref#1
ppfn=cpb
CP with bckg. suppressed
cfn=conref1cp
cdir=consol2
cfp=0
ac=10000 scns
tlb=50 Hz
sf1=25.152 MHz
sf2=100.0198 MHz
sw=20 KHz
rmv=17.6 ppm
rmp=0.594921 virt
fdsc=3205K
tph0=88.23 deg
tph1=319 deg
gain=354.813
a=255
a1=255
a2=255
a4=255
ad=5 usec
al=256 cplx
aqtm=12.801 msec
ct=2 msec
dw=50 usec
extm=1.0148 sec
p=160 deg
pd=1 sec
pw=4.3 usec
rd=25 usec
txduty=0.0166023
txon=16.848 msec



```
ref3
ppfn=cpb
CP with bckg. suppressed
cfn=conref3cp
cdir=consol2
cfp=0
ac=10000 scns
tlb=50 Hz
sf1=25.152 MHz
sf2=100.0198 MHz
sw=20 KHz
rmv=17.6 ppm
rmp=0.594736 virt
fdsc=1859K
tph0=92.23 deg
tph1=319 deg
gain=354.813
a=255
a1=255
a2=255
a4=255
ad=5 usec
al=256 cplx
aqtm=12.801 msec
ct=2 msec
dw=50 usec
extm=1.0148 sec
p=160 deg
pd=1 sec
pw=4.3 usec
rd=25 usec
txduty=0.0166023
txon=16.848 msec
```



ref7
ppfn=cpb
CP with bckg. suppressed
cfn=conref7cp
cdir=consol2
cip=0
ac=10000 scns
tlb=50 Hz
sf1=25.152 MHz
sf2=100.0198 MHz
sw=20 KHz
rmv=17.6 ppm
rmp=0.594736 virt
fdsc=4478K
tph0=90.23 deg
tph1=319 deg
gain=354.813
a=255
a1=255
a2=255
a4=255
ad=5 usec
al=256 cplx
aqtm=12.801 msec
ct=2 msec
dw=50 usec
extm=1.0148 sec
p=160 deg
pd=1 sec
pw=4.3 usec
rd=25 usec
txduty=0.0166023
txon=16.848 msec



```
ref#11
ppfn=cpb
CP with bckg. suppressed
cfn=conref11cp
cdir=consol2
cfp=0
ac=10000 scns
tlb=50 Hz
sf1=25.152 MHz
sf2=100.0198 MHz
sw=20 KHz
rmv=17.35 ppm
rmp=0.595043 virt
fdsc=2494K
tph0=90.23 deg
tph1=319 deg
gain=354.813
a=255
a1=255
a2=255
a4=255
ad=5 usec
al=256 cplx
aqtm=12.801 msec
ct=2 msec
dw=50 usec
extm=1.0148 sec
p=160 deg
pd=1 sec
pw=4.3 usec
rd=25 usec
txduty=0.0166023
txon=16.848 msec
```

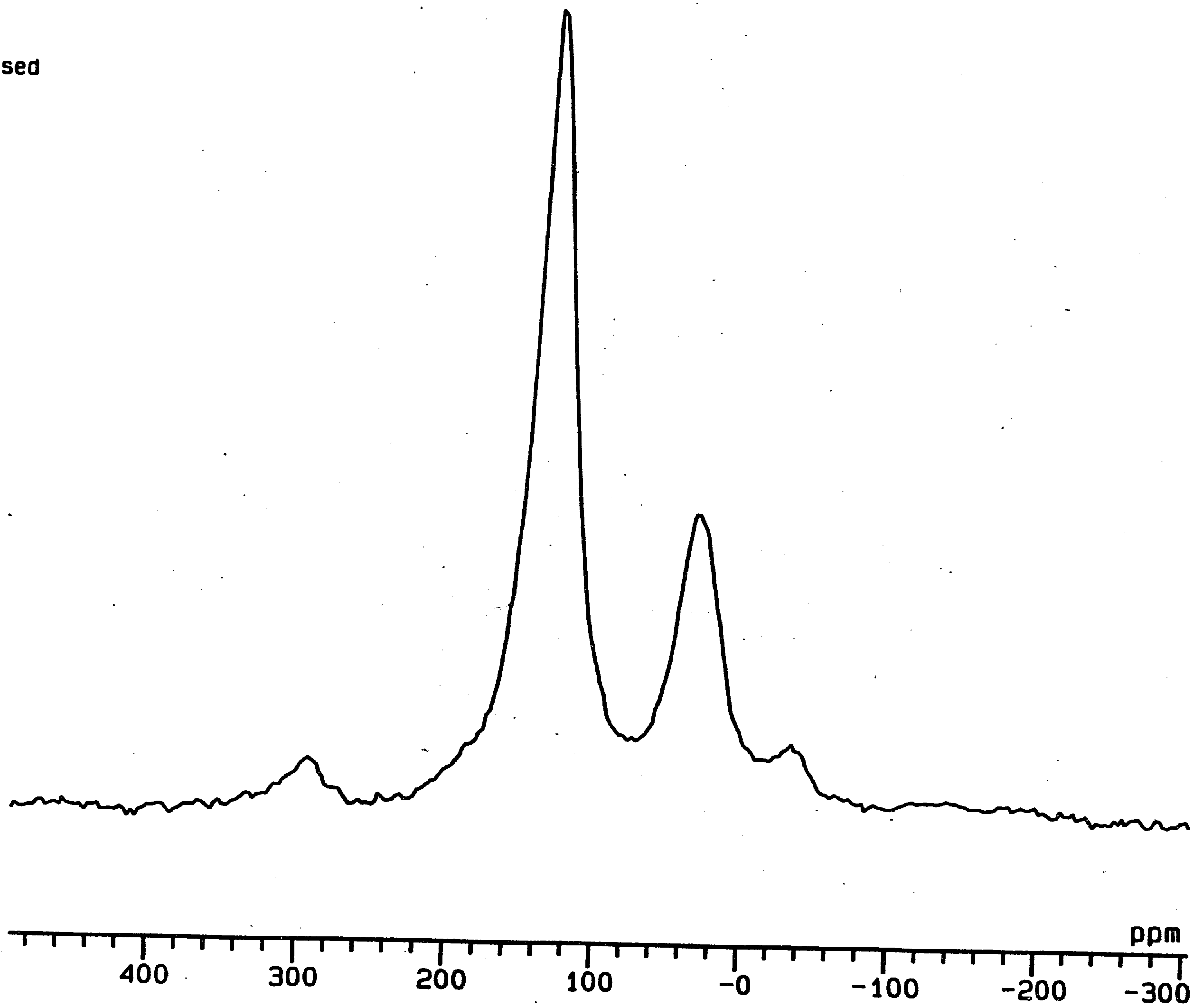


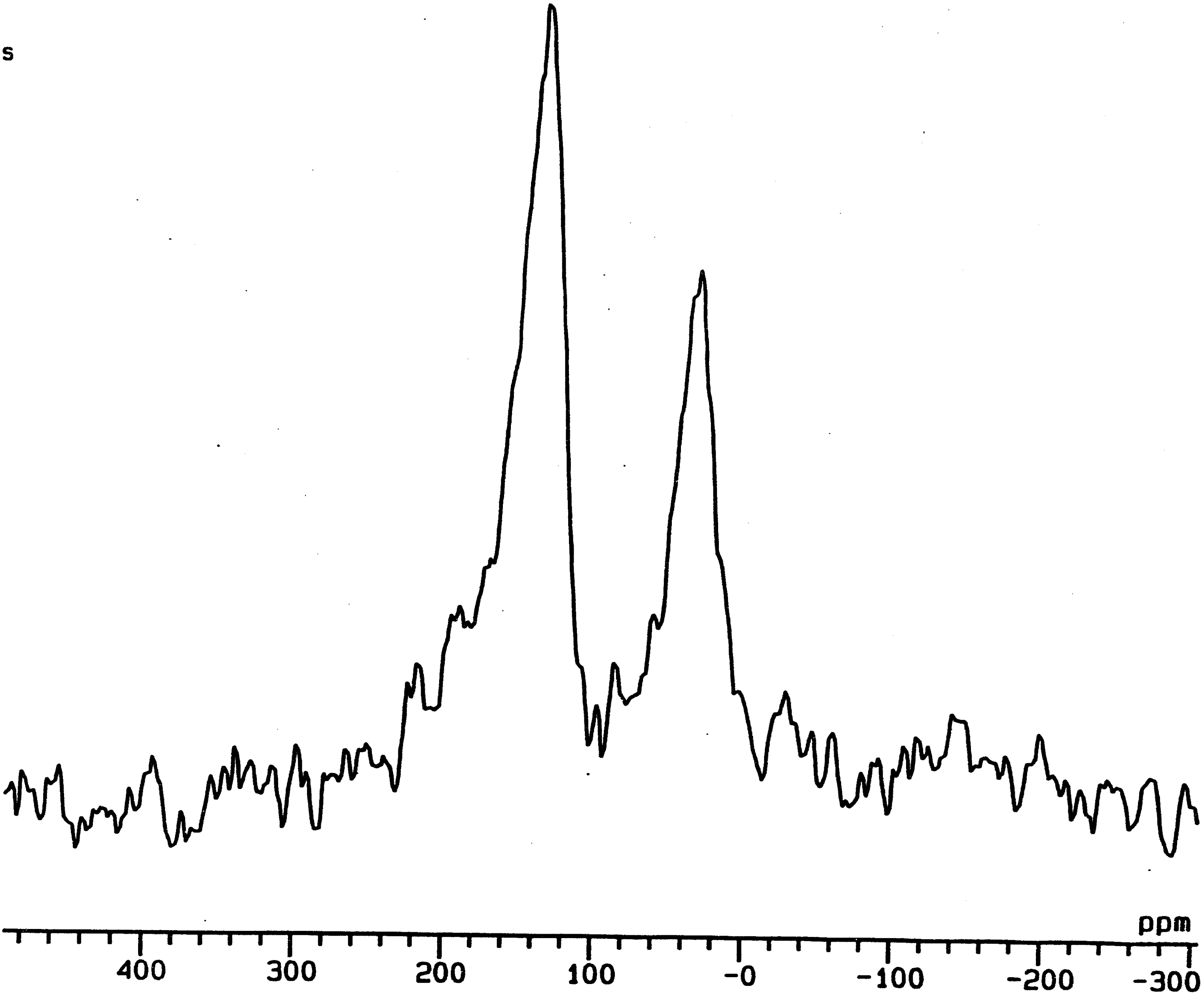
TABLE 1: NMR PARAMETERS

Aromatic	M_G^{CH}	M_{L1}^{CH}	M_{L2}^{CH}	$T_G^{CH}(\mu s)$	$T_{L1}^{CH}(\mu s)$	$T_{L2}^{CH}(ms)$	$M_{1\rho 1}$	$M_{1\rho 2}$	$T_{1\rho 1}(ms)$	$T_{1\rho 2}(ms)$	M_G^{dd}	M_L^{dd}	$T_G^{dd}(\mu s)$	$T_L^{dd}(\mu s)$
Ref 1	0.16	0.84	–	17	319	–	1.0	–	5.4	–	0.32	0.68	18	312
Ref 3	0.25	0.75	–	23	346	–	1.0	–	7.3	–	0.40	0.60	19	181
Ref 7	0.23	0.77	–	17	326	–	1.0	–	7.5	–	0.38	0.62	18	283
Ref 11	0.24	0.76	–	18	311	–	1.0	–	8.5	–	0.39	0.61	18	217

TABLE 2: NMR PARAMETERS

Aliphatic	M_G^{CH}	M_{L1}^{CH}	M_{L2}^{CH}	$T_G^{CH}(\mu s)$	$T_{L1}^{CH}(\mu s)$	$T_{L2}^{CH}(ms)$	$M_{1\rho 1}$	$M_{1\rho 2}$	$T_{1\rho 1}(ms)$	$T_{1\rho 2}(ms)$	M_G^{dd}	M_L^{dd}	$T_G^{dd}(\mu s)$	$T_L^{dd}(\mu s)$
Ref 1	0.40	0.60	-	13	116	-	1.0	-	5.0	-	-	-	-	-
Ref 3	0.43	0.57	-	19	181	-	1.0	-	5.0	-	-	-	-	-
Ref 7	0.38	0.62	-	13	127	-	1.0	-	7.5	-	-	-	-	-
Ref 11	0.36	0.64	-	15	139	-	1.0	-	6.8	-	-	-	-	-

consol2 ref11
ppfn=1pdb
4 - pulse bckg suppress
cfn=conref11bd180
cdir=consol2
cfp=0
ac=100 scns
tlb=100 Hz
sf1=25.152 MHz
sf2=100.0198 MHz
sw=20 KHz
rmv=17.35 ppm
rmp=0.594799 virt
fdsc=18.08K
tph0=296 deg
tph1=317 deg
gain=354.813
a1=255
a4=255
ad=5 usec
al=256 cplx
aqtm=12.801 msec
dw=50 usec
extm=180.01 sec
p=160 deg
pd=180 sec
psd=300 nsec
pw=4.7 usec
pw1=4.7 usec
rd=25 usec
txduty=7.13849e-05
txon=12.85 msec

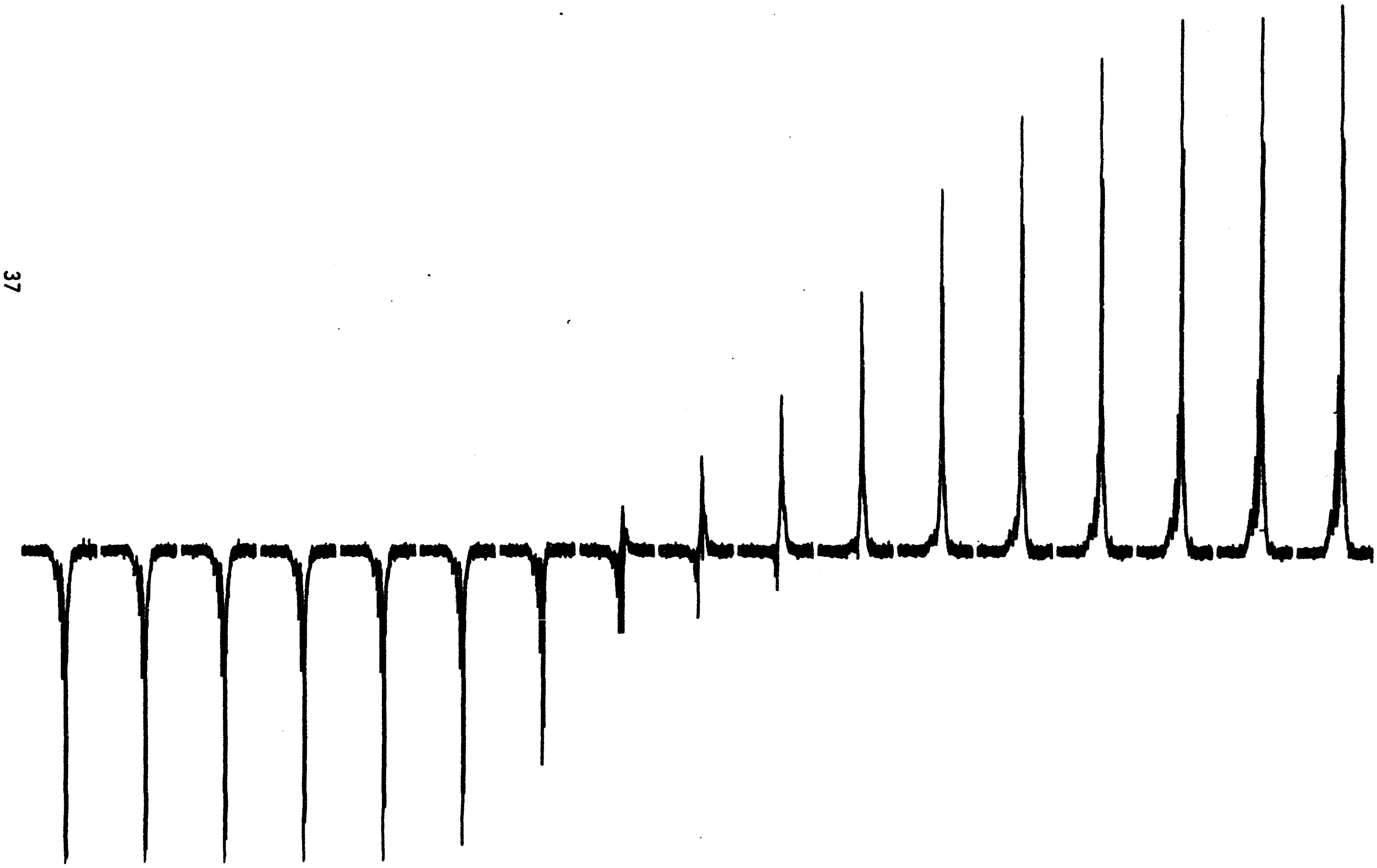


References

1. Solum, M. S.; Pugmire, R. J.; Grant, D. M. *Energy & Fuels*, **1989**, *3*, 187.
2. Orendt, A. M.; Solum, M. S.; Sethi, N. K.; Pugmire, R. J. ; Grant D.,M. In *ADVANCES IN COAL SPECTROSCOPY*; Meuzelaar, H., Ed.; Plenum Press: New York, 215, 1992.

Appendix 2. Spectra Obtained from Inversion Recovery Experiments

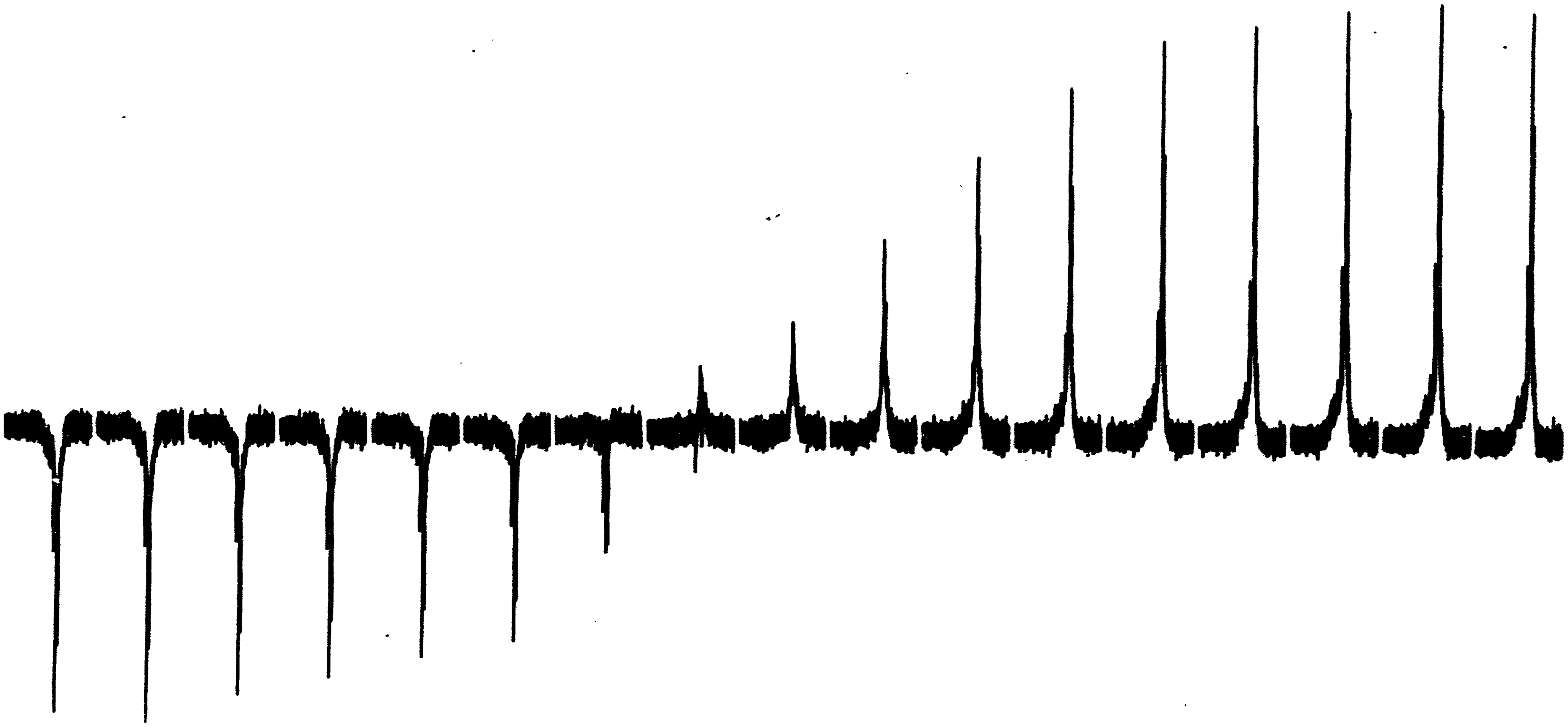
Inverse-Recovery experiment of coal sample-2 in $CDCl_3$, 10 mm tube,09/23/93 Sample 2



Sample 2

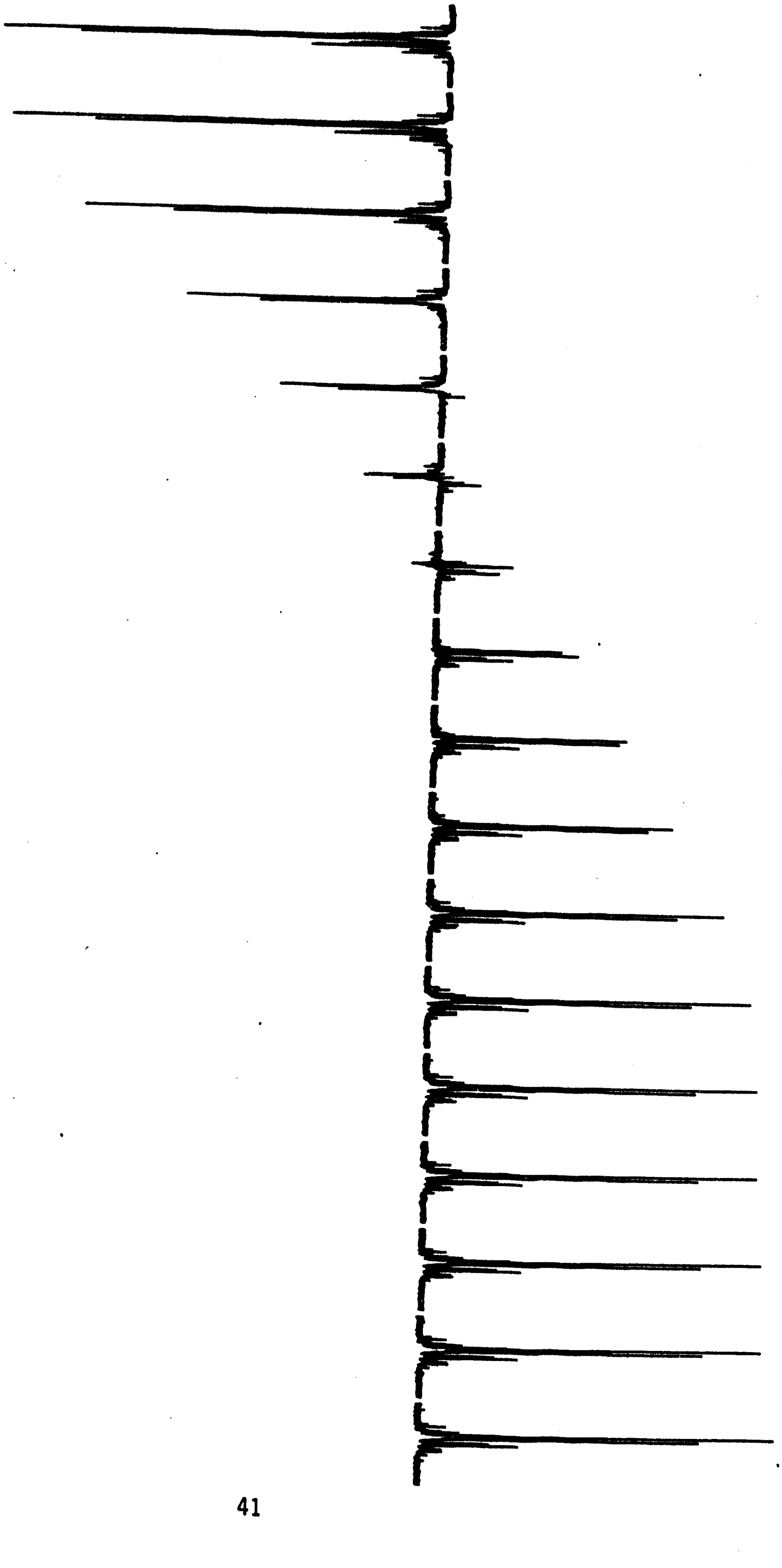
```
 17
 0.02500        -0.64597
 0.04000        -0.61805
 0.08000        -0.57392
 0.12000        -0.51604
 0.16000        -0.46071
 0.20000        -0.43817
 0.40000        -0.23404
 0.80000         0.01953
 1.20000         0.19762
 1.80000         0.36218
 2.80000         0.56302
 4.00000         0.68214
 5.60000         0.78782
 8.00000         0.87011
12.80000         0.93677
25.60000         0.97513
40.00000         0.99921
 17
 0.02500        -0.64625
 0.04000        -0.62364
 0.08000        -0.55851
 0.12000        -0.53446
 0.16000        -0.46967
 0.20000        -0.42169
 0.40000        -0.21940
 0.80000         0.02893
 1.20000         0.18600
 1.80000         0.36477
 2.80000         0.53599
 4.00000         0.70093
 5.60000         0.76455
 8.00000         0.85838
12.80000         0.92285
25.60000         0.98407
40.00000         0.99902
```

Inversion-Recovery of coal sample-4 in CDCl3, Oct. 12,1983 Sample 4



Sample 4

```
 17
 0.02500        -0.63821
 0.04000        -0.55816
 0.08000        -0.51039
 0.12000        -0.40218
 0.16000        -0.35775
 0.20000        -0.32060
 0.40000         0.03681
 0.80000         0.27808
 1.20000         0.46682
 1.80000         0.54886
 2.80000         0.76904
 4.00000         0.85079
 5.60000         0.96158
 8.00000         0.95917
12.80000         1.04370
25.60000         1.06390
40.00000         0.99733
```



Inverse recovery experiment of coal sample 5 in CDCL3. 08/13/93 Sample 5

Sample 5

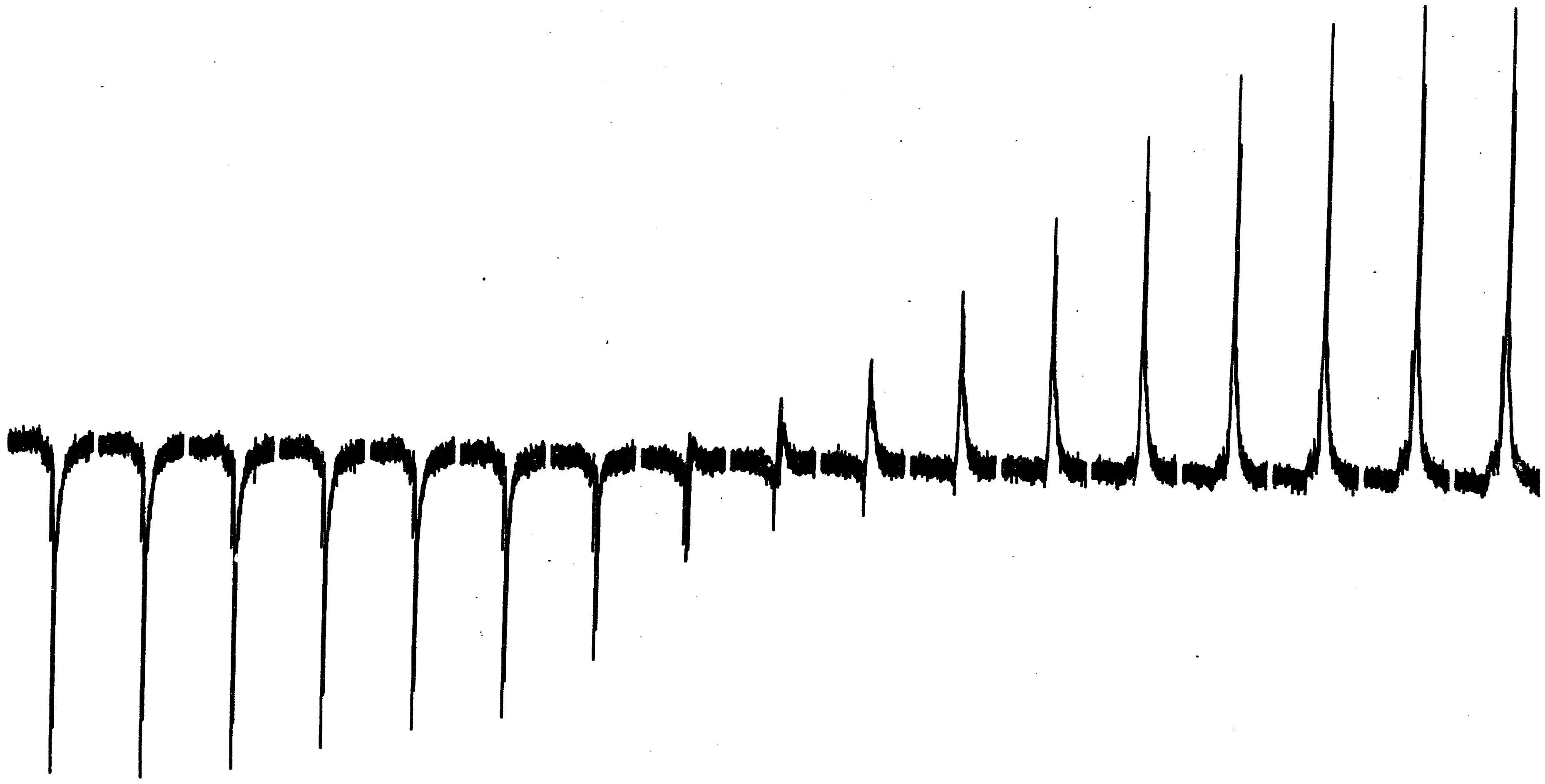
```
 17
 0.02500      -0.66384
 0.04000      -0.64297
 0.08000      -0.65417
 0.12000      -0.62275
 0.16000      -0.65187
 0.20000      -0.58438
 0.40000      -0.56650
 0.80000      -0.44107
 1.20000      -0.35125
 1.80000      -0.17380
 2.80000       0.00842
 4.00000       0.17437
 5.60000       0.33378
 8.00000       0.52723
12.80000       0.71401
25.60000       0.89109
40.00000       0.99449
```

Inverse-Recovery experiment of Sample-6 in $CDCl_3$,09/08/1993 Sample 6

Sample 6

```
17
0.02500      -0.50561
0.04000      -0.50159
0.08000      -0.40461
0.12000      -0.30928
0.16000      -0.24069
0.20000      -0.17073
0.40000       0.08929
0.80000       0.39817
1.20000       0.59711
1.80000       0.74110
2.80000       0.87313
4.00000       0.92942
5.60000       0.98188
8.00000       1.01629
12.80000      0.99567
25.60000      1.02872
40.00000      0.99920
```

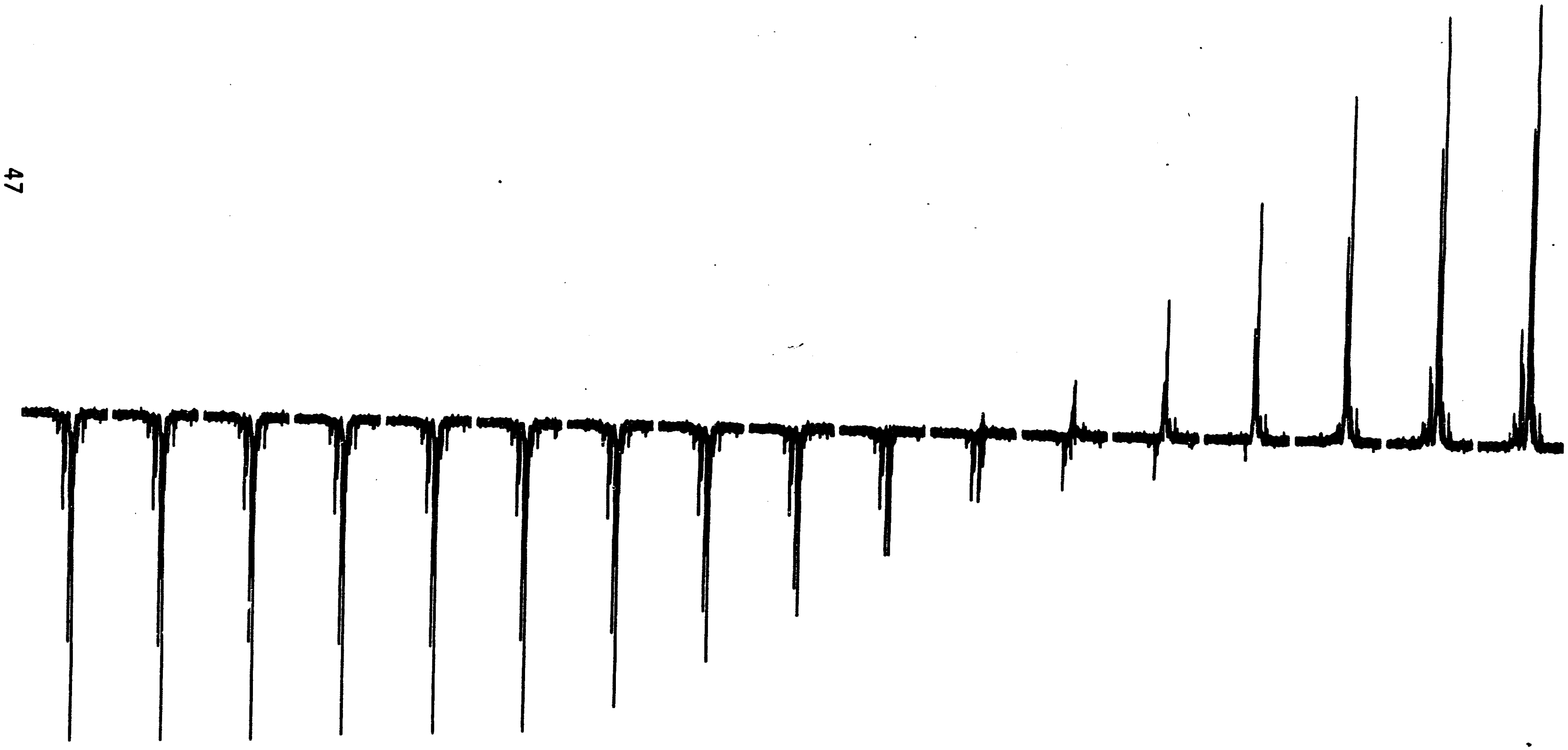
Inver-Recov of coal sample-8 in CDCl3,10/25/1993 Sample 8



Sample 8

```
 17
 0.02500        -0.66327
 0.04000        -0.62174
 0.08000        -0.59323
 0.12000        -0.53656
 0.16000        -0.46876
 0.20000        -0.44892
 0.40000        -0.28893
 0.80000        -0.06363
 1.20000         0.08963
 1.80000         0.26911
 2.80000         0.42796
 4.00000         0.56283
 5.60000         0.66053
 8.00000         0.72730
12.80000         0.84221
25.60000         0.97866
40.00000         1.00059
```

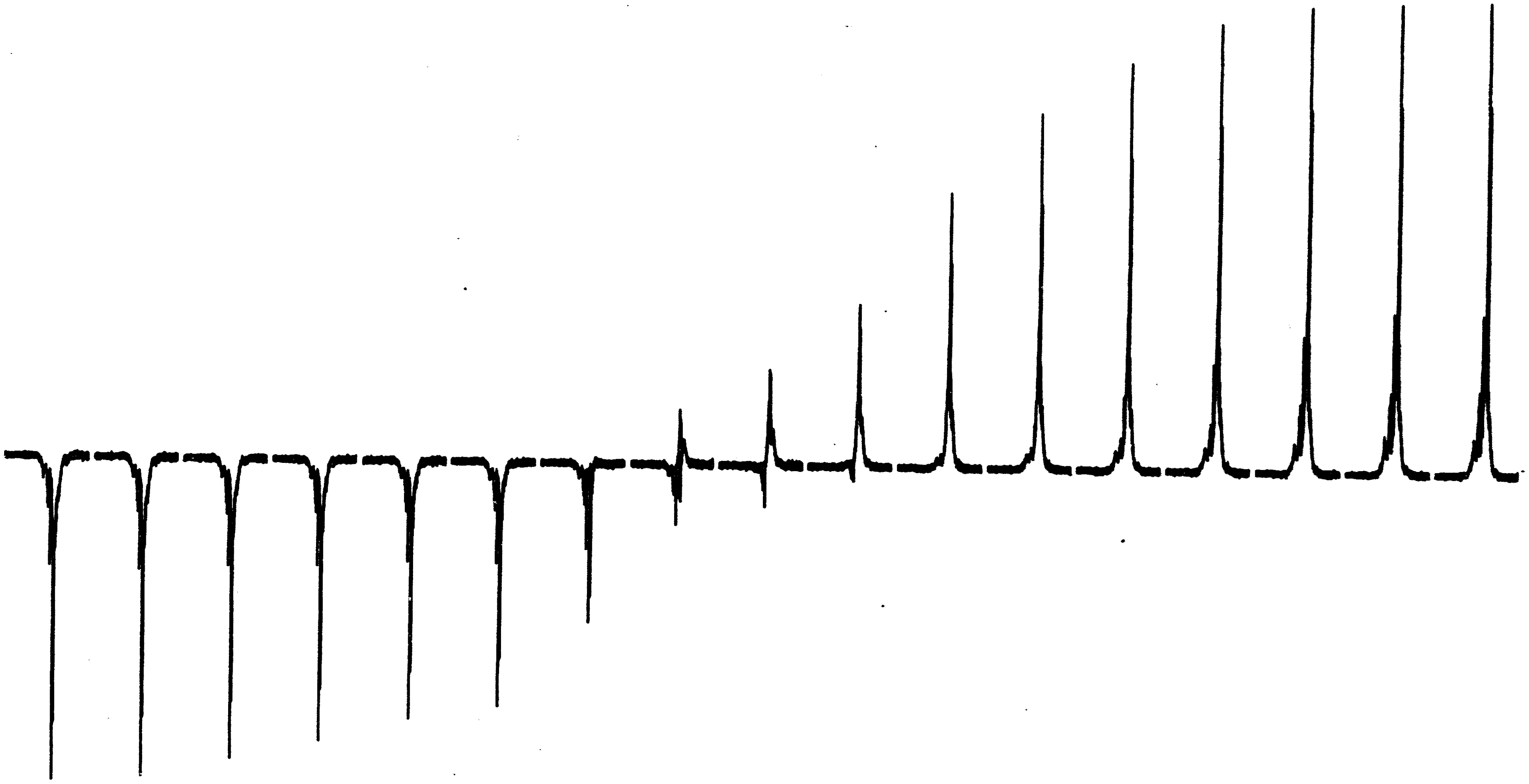
Inverse-recovery experiment of sample-9 in CDCl3, 10 mm tube, 08/17/93 Sample 9



Sample 9

```
 17
 0.02500        -0.67412
 0.04000        -0.62032
 0.08000        -0.63349
 0.12000        -0.62590
 0.16000        -0.61411
 0.20000        -0.65338
 0.40000        -0.55985
 0.80000        -0.47367
 1.20000        -0.29133
 1.80000        -0.20174
 2.80000         0.02837
 4.00000         0.14432
 5.60000         0.31336
 8.00000         0.50954
12.80000         0.75599
25.60000         0.92517
40.00000         1.00202
 17
 0.02500        -0.67810
 0.04000        -0.61829
 0.08000        -0.62670
 0.12000        -0.62786
 0.16000        -0.60873
 0.20000        -0.65981
 0.40000        -0.56061
 0.80000        -0.48264
 1.20000        -0.28449
 1.80000        -0.20389
 2.80000         0.03123
 4.00000         0.14591
 5.60000         0.31895
 8.00000         0.50991
12.80000         0.76401
25.60000         0.92784
40.00000         1.00028
```

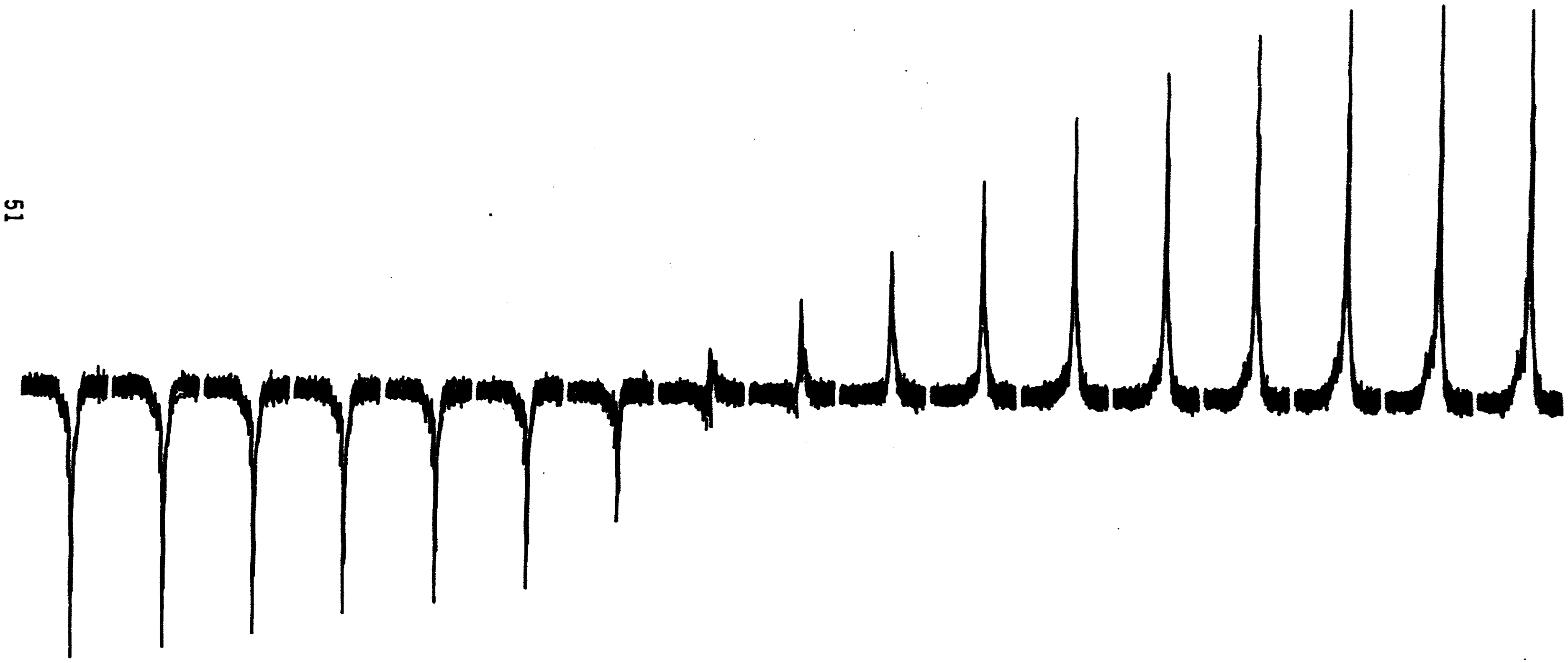
Inversion-Recovery of coal sample-10 in CDCl3, 10/15/1993 Sample 10



Sample 10

```
 17
 0.02500       -0.61707
 0.04000       -0.59485
 0.08000       -0.52959
 0.12000       -0.47313
 0.16000       -0.41039
 0.20000       -0.37955
 0.40000       -0.16921
 0.80000        0.12618
 1.20000        0.28848
 1.80000        0.47081
 2.80000        0.62864
 4.00000        0.75304
 5.60000        0.82070
 8.00000        0.89410
12.80000        0.92579
25.60000        0.98837
40.00000        1.00018
 17
 0.02500       -0.61569
 0.04000       -0.59183
 0.08000       -0.52880
 0.12000       -0.47306
 0.16000       -0.40931
 0.20000       -0.37919
 0.40000       -0.17087
 0.80000        0.12590
 1.20000        0.28819
 1.80000        0.47338
 2.80000        0.62900
 4.00000        0.75654
 5.60000        0.81983
 8.00000        0.89538
12.80000        0.92426
25.60000        0.98915
40.00000        1.00002
```

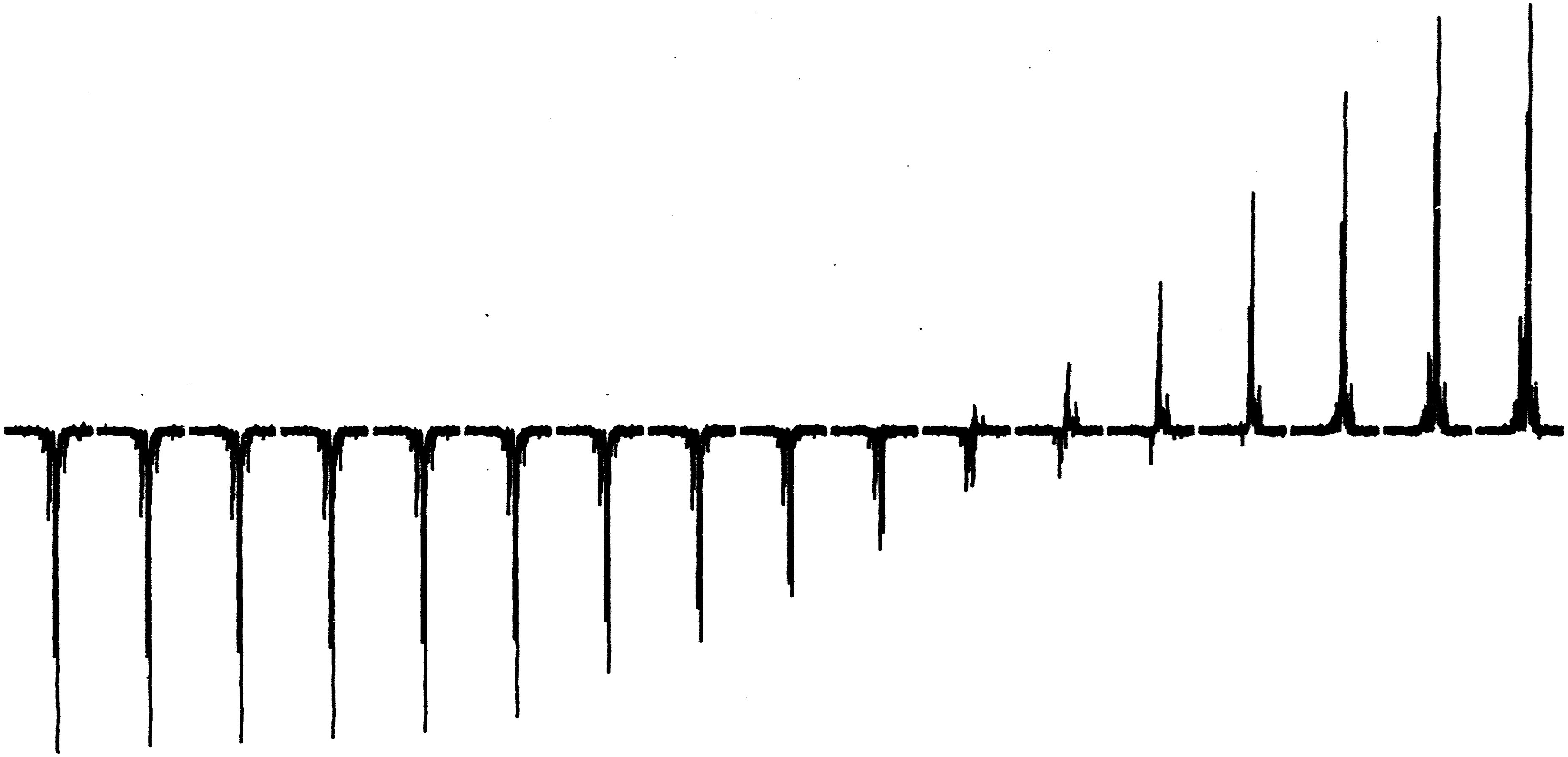
Inversion-Recovery of coal sample-12 in CDCl3, 10/18/83 Sample 12



Sample 12

```
 17
 0.02500      -0.61494
 0.04000      -0.59038
 0.08000      -0.55868
 0.12000      -0.49365
 0.16000      -0.44370
 0.20000      -0.36132
 0.40000      -0.19535
 0.80000       0.09330
 1.20000       0.21650
 1.80000       0.42480
 2.80000       0.58707
 4.00000       0.73286
 5.60000       0.78934
 8.00000       0.85121
12.80000       0.95437
25.60000       0.99005
40.00000       0.99979
 17
 0.02500      -0.60941
 0.04000      -0.58962
 0.08000      -0.56352
 0.12000      -0.49692
 0.16000      -0.44402
 0.20000      -0.35585
 0.40000      -0.19648
 0.80000       0.09437
 1.20000       0.21591
 1.80000       0.42452
 2.80000       0.58854
 4.00000       0.73858
 5.60000       0.78961
 8.00000       0.85077
12.80000       0.95677
25.60000       0.99465
40.00000       0.99990
```

Inverse-Recovery experiment of Sample-13, 1.2 ml in 5.0 ml CDCl3, 08/20/93 Sample 13



Sample 13

```
 17
 0.02500      -0.69011
 0.04000      -0.68959
 0.08000      -0.64359
 0.12000      -0.63864
 0.16000      -0.62787
 0.20000      -0.63306
 0.40000      -0.56045
 0.80000      -0.43784
 1.20000      -0.28518
 1.80000      -0.16515
 2.80000      -0.02101
 4.00000       0.19758
 5.60000       0.35098
 8.00000       0.50737
12.80000       0.68468
25.60000       0.89316
40.00000       1.00212
 17
 0.02500      -0.69128
 0.04000      -0.69054
 0.08000      -0.64298
 0.12000      -0.63547
 0.16000      -0.62664
 0.20000      -0.63718
 0.40000      -0.56217
 0.80000      -0.43644
 1.20000      -0.27241
 1.80000      -0.16053
 2.80000      -0.01927
 4.00000       0.19675
 5.60000       0.35454
 8.00000       0.50641
12.80000       0.68128
25.60000       0.89504
40.00000       1.00024
```

Appendix 3. Analysis of Inversion-Recovery Experiments on Coal Derived Liquids

Appendix 3. Analysis of Inverse-Recovery Experiments on Coal Derived Liquids

•Reference-2

```
FuncFit coal w C2 /X=t
Fit converged properly
y= coal(w,x)
 w={0.66938,0.50764.0.7345.4.4601}
```

β M_p T_p T_q

```
V_chisq= 0.00446417; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0115.0.045.0.082.0.417}
```

•Reference-4

```
FuncFit coal w C4 /X=t
Fit converged properly
y= coal(w,x)
 w={0.69423,0.44047.0.33425.2.0981}
V_chisq= 0.0166834; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0311.0.0764.0.079,0.3}
```

•Reference-5

```
FuncFit coal w C5 /X=t
Fit converged properly
y= coal(w,x)
 w={0.74159,0.28054.2.5483.7.008}
V_chisq= 0.00607073; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0097.0.253.1.25.1.35}
```

•Reference-6

```
FuncFit coal w C6 /X=t
Fit converged properly
y= coal(w,x)
 w={0.57836,0.45074.0.37949.1.4698}
V_chisq= 0.00235275; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0114.0.0722.0.0535,0.139}
```

•Reference-8

```
FuncFit coal w C8 /X=t
```

```
Fit converged properly
y= coal(w,x)
 w={0.65994,0.55927,0.95321,7.8427}
V_chisq= 0.00442137; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0103,0.0316,0.0786,0.743}
```

•Reference-9

```
FuncFit coal w C9 /X=t
Fit converged properly
y= coal(w,x)
 w={0.67441,0.2395,2.1493,8.1287}
V_chisq= 0.0106706; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0133,0.169,1.16,1.37}
```

•Reference-10

```
FuncFit coal w C10 /X=t
Fit converged properly
y= coal(w,x)
 w={0.63892,0.63002,0.7826,4.7215}
V_chisq= 0.00311678; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.00939,0.0396,0.0602,0.513}
```

•Reference-12

```
FuncFit coal w C12 /X=t
Fit converged properly
y= coal(w.x)
 w={0.6414,0.56777,0.77055,4.5763}
V_chisq= 0.00707083; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.0142,0.0599,0.0996,0.639}
```

•Reference-13

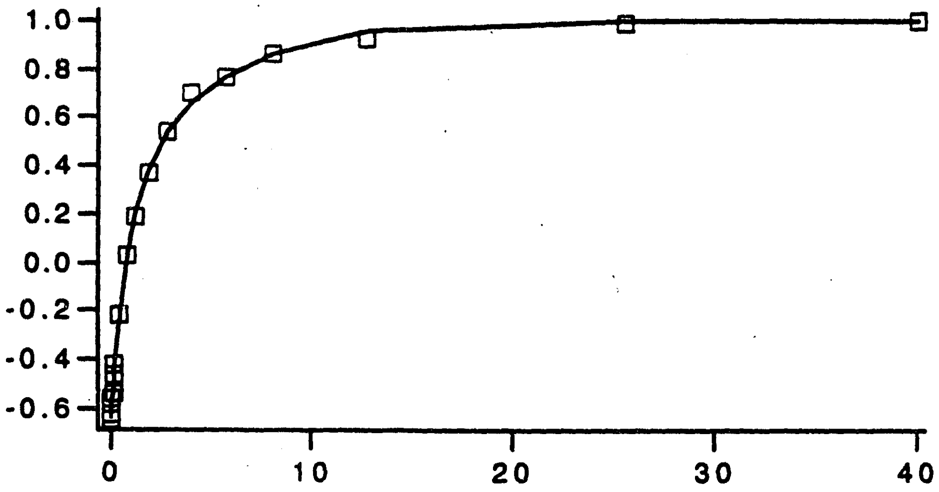
```
FuncFit coal w C13 /X=t
Fit converged properly
y= coal(w,x)
 w={0.69455,0.42565,2.3909,11.074}
V_chisq= 0.00569036; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
 W_sigma={0.00939,0.0776,0.396,1.35}
```

Appendix 4. Fitting Curves for Inversion-recovery Experiment Data on Coal Derived Liquids

Appendix 4. Fitting Curves for Inversion-recovery Experiment Data on Coal Derived Liquids

Reference-2

Polynomial function fitting of Inverse-recovery result

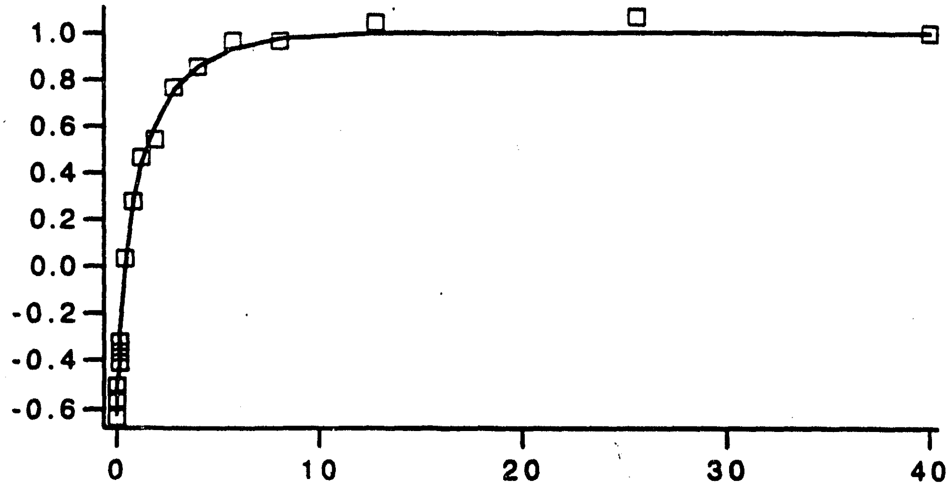


FuncFit coal w C2 /X=t
Fit converged properly
y= coal(w,x)
w={0.66938,0.50764,0.7345,4.4601}
V_chisq= 0.00446417; V_npnts= 17; V_numNaNs= 0; V_numINFs= 0;
W_sigma={0.0115,0.045,0.082,0.417}

$\beta = 0.66938$, $M_p = 0.50764$, $T_p = 0.7345$, $T_q = 4.4601$,
$M_q = 1 - M_p = 0.49236$.

Reference-4

Polynomial function fitting of Inverse-recovery result

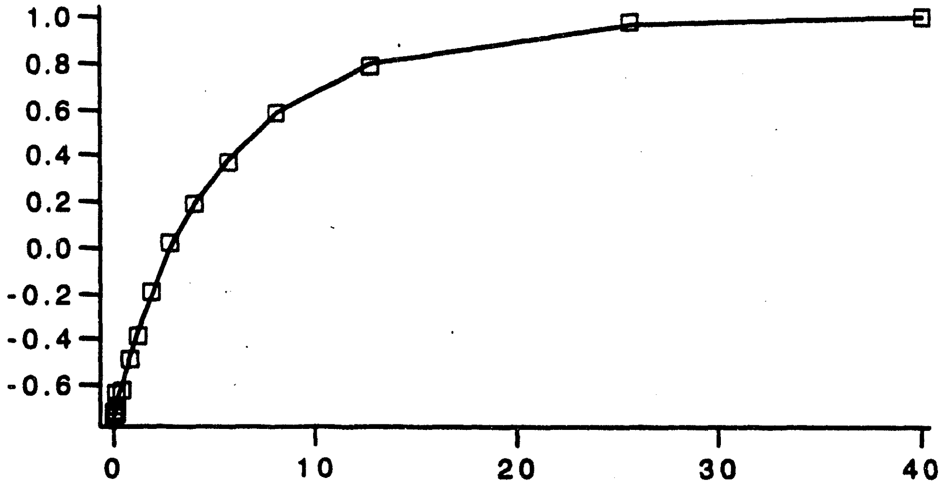


```
FuncFit coal w C4 /X=t
Fit converged properly
y= coal(w,x)
w={0.69423,0.44047.0.33425,2.0981}
V_chisq= 0.0166834; V_npnts= 17; V_numNaNs= 0;          V_numINFs= 0;
W_sigma={0.0311.0.0764,0.079,0.3}
```

$\beta = 0.69423$, $M_p = 0.44047$ $T_p = 0.33425$ $T_q = 2.081$,
$M_q = 1 - M_p = 0.55953$.

Reference-5

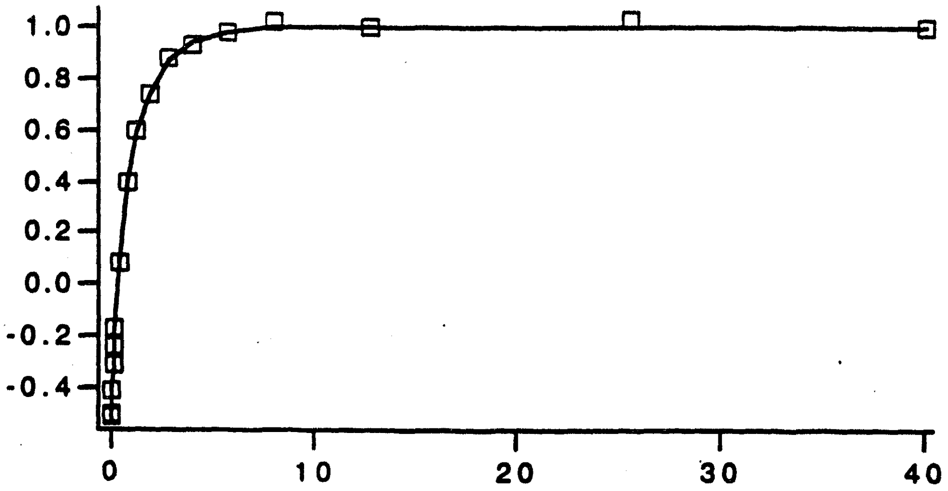
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C5 /X=t
  Fit converged properly
y= coal(w,x)
 w={0.74159,0.28054,2.5483,7.008}
V_chisq= 0.00607073; V_npnts= 17; V_numNaNs= 0;
 V_numINFs= 0;
  W_sigma={0.0097,0.253,1.25,1.35}
```

Reference-6

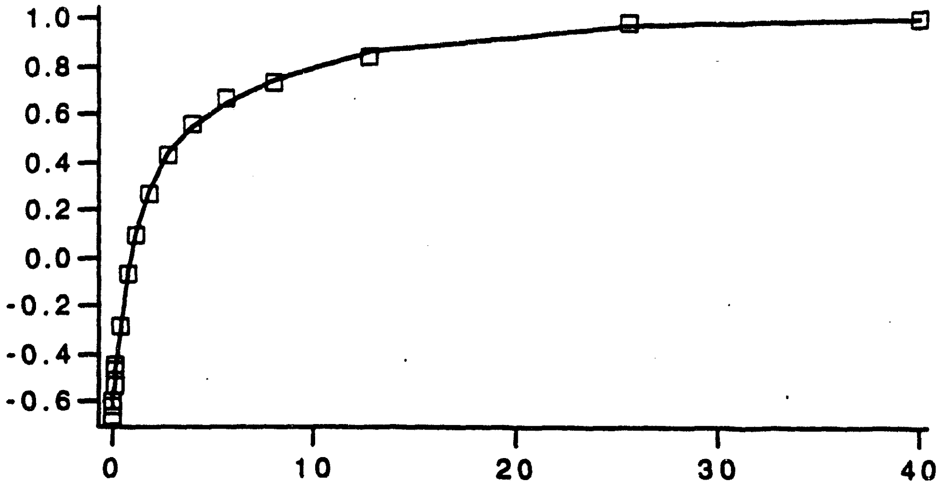
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C6 /X=t
Fit converged properly
y= coal(w,x)
w={0.57836,0.45074,0.37949,1.4698}
V_chisq= 0.00235275; V_npnts= 17; V_numNaNs= 0;        V_numINFs= 0;
 W_sigma={0.114, 0.0722, 0.0535, 0.139}
```

Reference-8

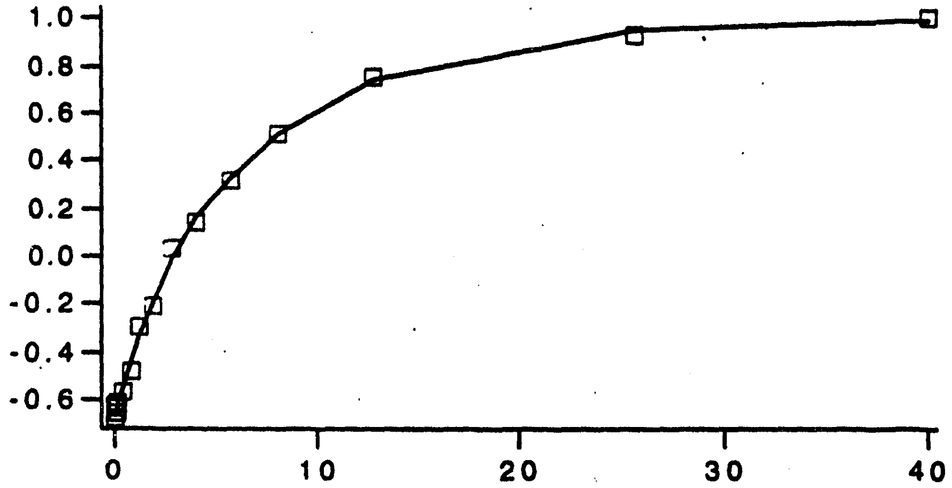
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C8 /X=t
Fit converged properly
y= coal(w,x)
w={0.65994,0.55927,0.95321,7.8427}
V_chisq= 0.00442137; V_npnts= 17; V_numNaNs= 0;
W_sigma={0.0103,0.0316,0.0786,0.743}
```

Reference-9

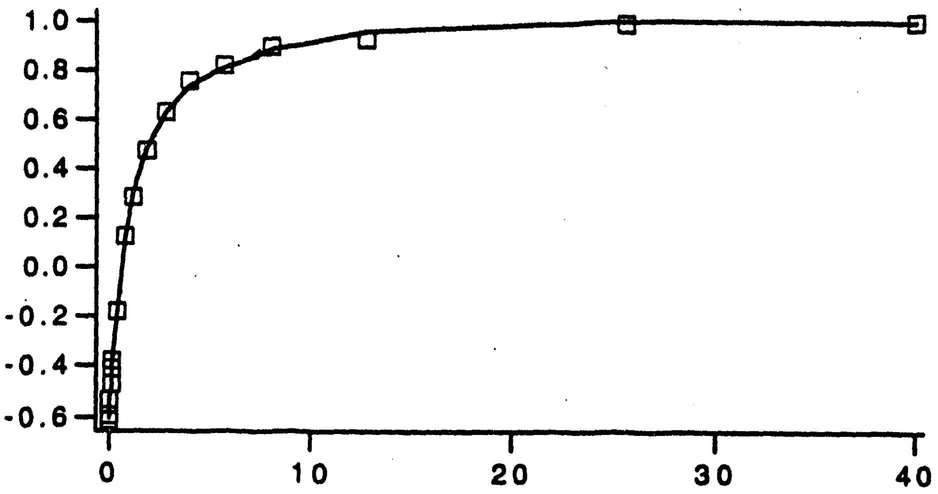
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C9 /X=t
Fit converged properly
y= coal(w,x)
w={0.67441,0.2395,2.1493,8.1287}
V_chisq= 0.0106706; V_npnts= 17; V_numNaNs= 0;          V_numINFs= 0;
W_sigma={0.0133,0.169,1.16,1.37}
```

Reference-10

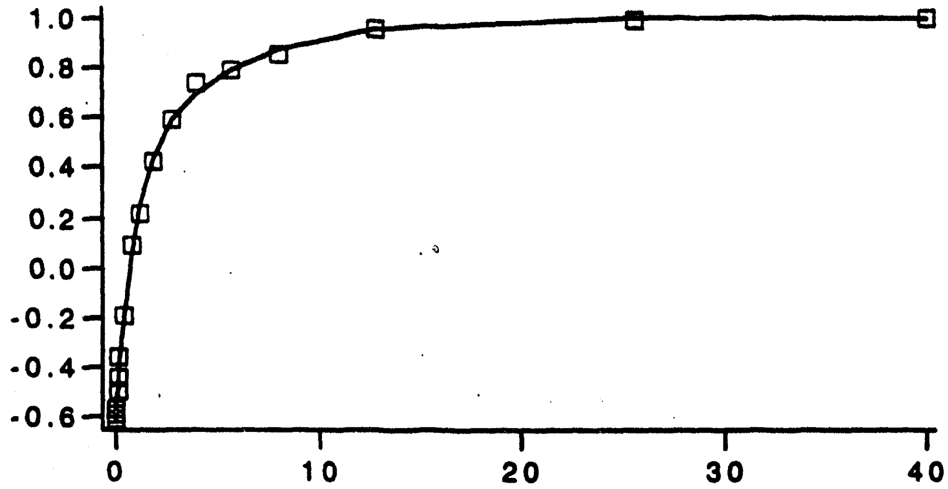
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C10 /X=t
Fit converged properly
y= coal(w,x)
w={0.63892,0.63002,0.7826,4.7215}
V_chisq= 0.00311678; V_npnts= 17; V_numNaNs= 0;        V_numINFs= 0;
W_sigma={0.00939, 0.0396, 0.0602, 0.513}
```

Reference-12

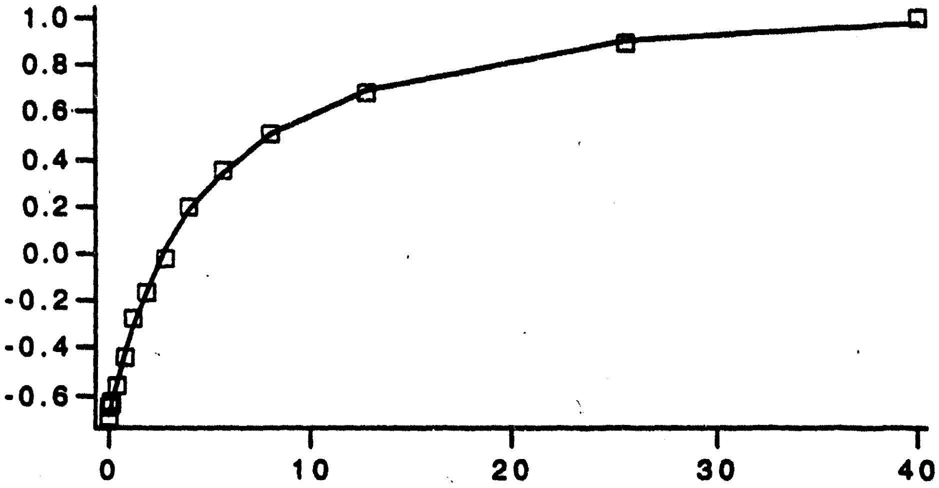
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C12 /X=t
Fit converged properly
y= coal(w,x)
w={0.6414,0.56777,0.77055,4.5763}
V_chisq= 0.00707083; V_npnts= 17; V_numNaNs= 0;        V_numINFs= 0;
W_sigma={0.0142,0.0599,0.0996,0.639}
```

Reference-13

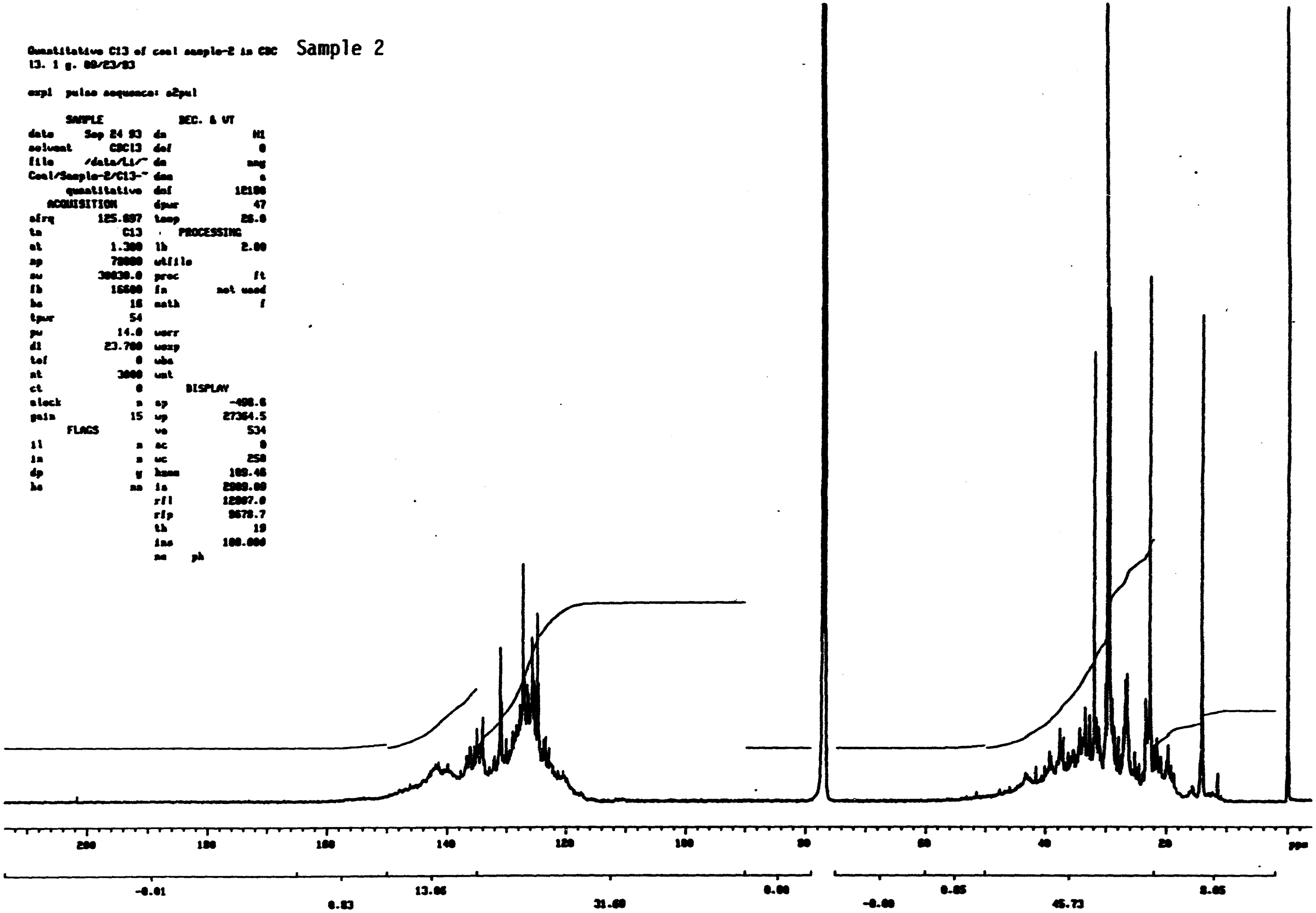
Polynomial function fitting of Inverse-recovery result



```
FuncFit coal w C13 /X=t
Fit converged properly
y= coal(w,x)
w={0.69455,0.42565,2.3909,11.074}
V_chisq= 0.00569036; V_npnts= 17; V_numNaNs= 0;        V_numINFs= 0;
W_sigma={0.00939,0.0776,0.396,1.35}
```

Appendix 5. Quantitative ^{13}C Spectra of Coal Derived Liquid Samples

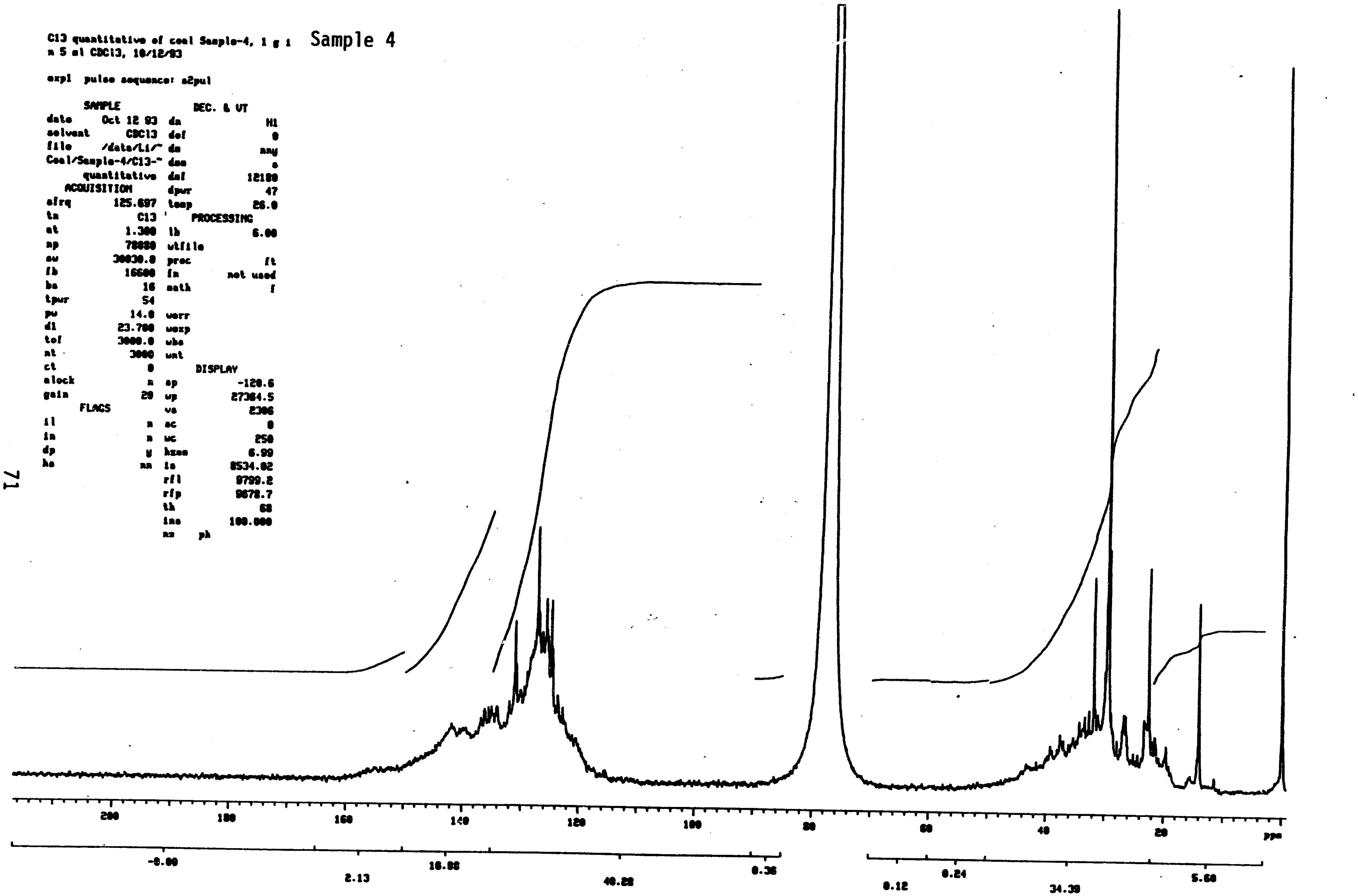
```
Quantitative C13 of coal sample-2 in CDC   Sample 2
13. 1 g. 09/23/93

exp1  pulse sequence: s2pul

     SAMPLE              DEC. & VT
date      Sep 24 93  dn            H1
solvent       CDCl3  dof            0
file     /data/Li/~  dm           nny
Coal/Sample-2/C13-~  dmm            s
       quantitative  dmf        12100
   ACQUISITION       dpwr          47
sfrq        125.697  temp        25.0
tn              C13   .  PROCESSING
at            1.300  lb          2.00
np            78000  wtfile
sw          30030.0  proc          ft
fb            16600  fn      not used
bs               16  math           f
tpwr             54
pw             14.0  werr
d1           23.700  wexp
tof               0  wbs
nt             3000  wnt
ct                0       DISPLAY
alock             n  sp        -498.6
gain             15  wp       27364.5
      FLAGS          vs           534
il                n  sc             0
in                n  wc           250
dp                y  hzmm      109.46
hs               nn  is       2000.00
                     rfl      12907.0
                     rfp       9678.7
                     th            19
                     ins      100.000
                     nm    ph
```



Sample 2

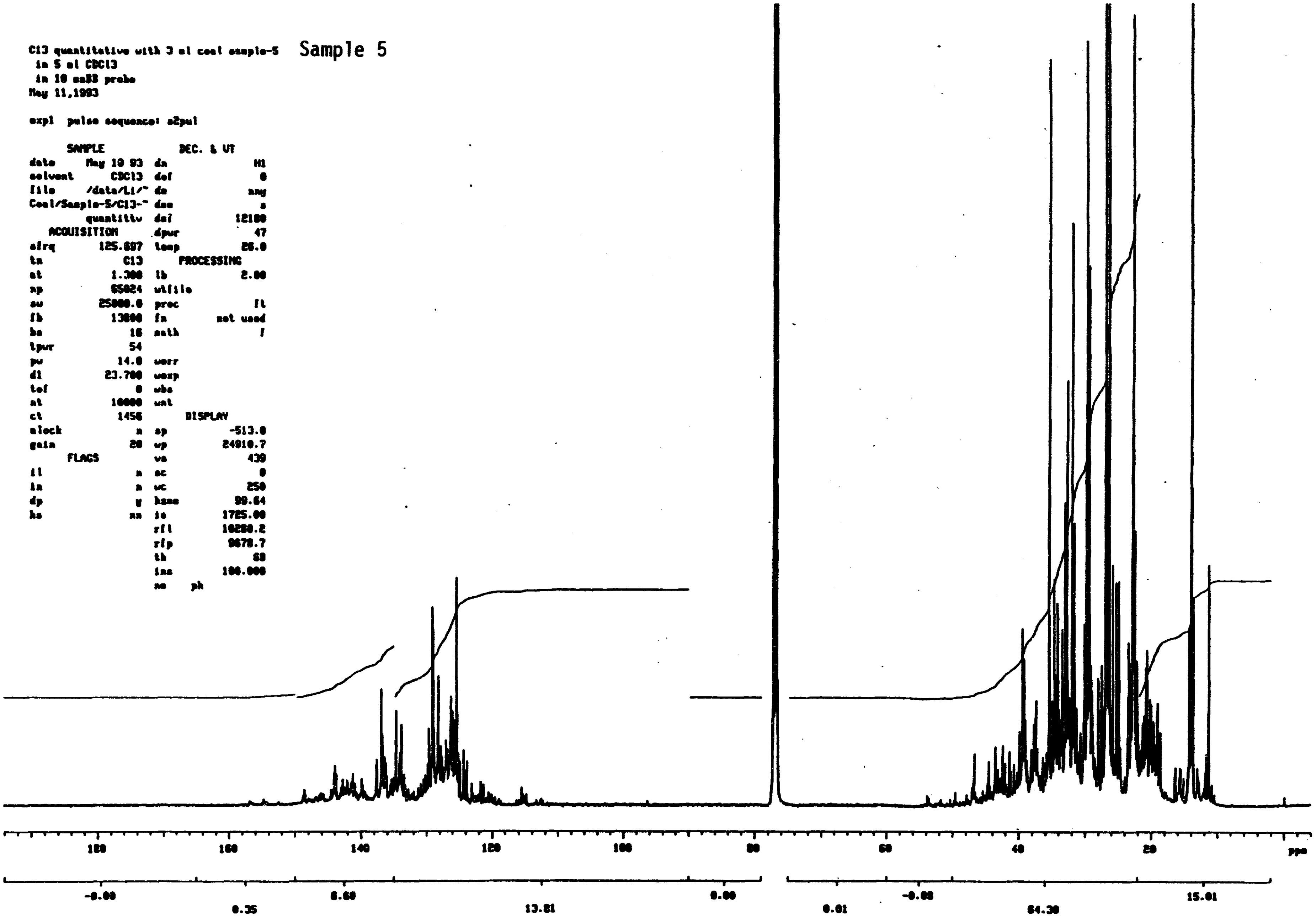
region	start	ppm	end	integral
1	213.736		165	-0.00700248
2	165		150	0.834088
3	150		135	13.0637
4	135		90	31.6854
5	90		79	0.0035155
6	75		60	-0.00145144
7	60		50	0.645092
8	50		22	45.7303
9	22		2	8.04642

```
C13 quantitative of coal Sample-4, 1 g i   Sample 4
n 5 ml CDCl3, 10/12/93

expl  pulse sequence: s2pul

      SAMPLE                 DEC. & VT
date     Oct 12 93  dn                 H1
solvent      CDCl3  dof                 0
file    /data/Li/~  dm                nny
Coal/Sample-4/C13-~ dmm                 c
       quantitative dmf             12100
   ACQUISITION      dpwr               47
sfrq       125.697  temp             26.0
tn             C13      PROCESSING
at           1.300  lb               6.00
np           78080  wtfile
sw         30030.0  proc               ft
fb           16600  fn           not used
bs              16  math                f
tpwr            54
pw            14.0  werr
d1          23.700  wexp
tof         3000.0  wbs
nt            3000  wnt
ct               0      DISPLAY
alock            n  sp             -120.6
gain            20  wp            27384.5
     FLAGS          vs               2306
il               n  sc                  0
in               n  wc                250
dp               y  hzmm             6.99
hs              nn  is            8534.02
                    rfl            9799.2
                    rfp            9678.7
                    th                 68
                    ins           100.000
                    nm    ph
```



Sample 4

region	start	ppm	end	integral
1	216.743		165	-0.000984644
2	165		150	2.12958
3	150		135	16.8781
4	135		90	40.2785
5	90		85	0.357046
6	70		60	0.117327
7	60		50	0.244783
8	50		22	34.391
9	22		3	5.6047

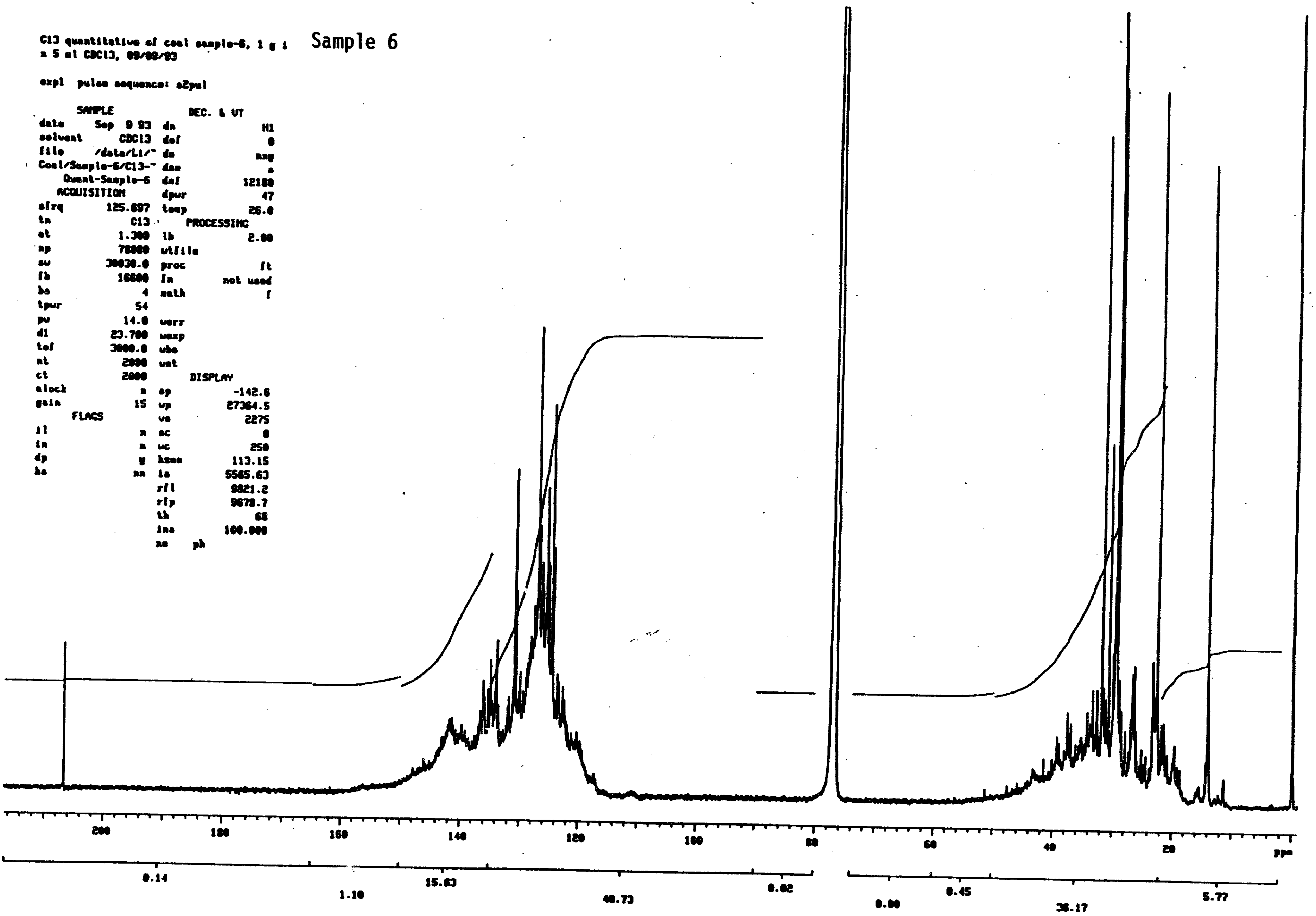


```
C13 quantitative with 3 ml coal sample-5
 in 5 ml CDCl3
 in 10 mmBB probe
May 11,1993

exp1  pulse sequence: s2pul

      SAMPLE               DEC. & VT
date      May 10 93  dn              H1
solvent       CDCl3  dof              0
file     /data/Li/~  dm             nny
Coal/Sample-5/C13-~  dmm              s
          quantitty  dmf          12100
   ACQUISITION       dpwr            47
sfrq        125.697  temp          26.0
tn              C13       PROCESSING
at            1.300  lb            2.00
np            65024  wtfile
sw          25000.0  proc            ft
fb            13800  fn        not used
bs               16  math             f
tpwr             54
pw             14.0  werr
d1           23.700  wexp
tof               0  wbs
nt            10000  wnt
ct             1456         DISPLAY
alock             n  sp          -513.0
gain             20  wp         24910.7
       FLAGS         vs             439
il                n  sc               0
in                n  wc             250
dp                y  hzmm         99.64
hs               nn  is         1725.00
                     rfl        10280.2
                     rfp         9678.7
                     th              60
                     ins        100.000
                     nm    ph
```

Sample 5

Sample 5

region	start	ppm	end	integral
1	194.1		165	-0.000669073
2	165		150	0.347977
3	150		135	6.60234
4	135		90	13.8129
5	90		79	0.00212249
6	75		60	0.00688387
7	60		50	-0.0814927
8	50		22	64.3046
9	22		2	15.0053



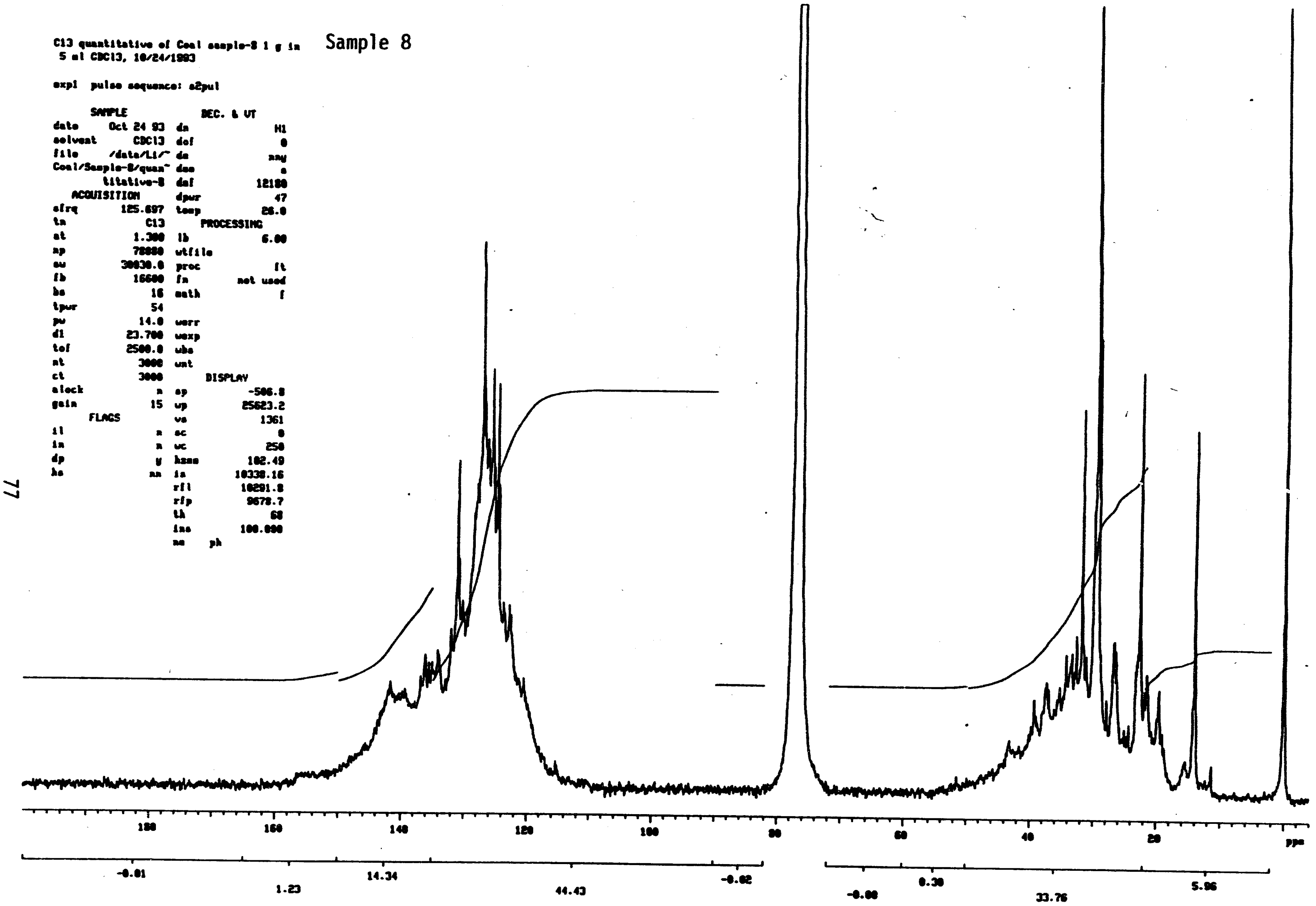
Sample 6

```
C13 quantitative of coal sample-6, 1 g in 5 ml CDCl3, 09/08/93

exp1  pulse sequence: s2pul

      SAMPLE                    DEC. & VT
date      Sep  9 93  dn                  H1
solvent       CDCl3  dof                  0
file     /data/Li/~  dm                 nny
Coal/Sample-6/C13-~  dmm                  s
   Quant-Sample-6    dmf              12100
   ACQUISITION       dpwr                47
sfrq        125.697  temp              26.0
tn              C13       PROCESSING
at            1.300  lb                2.00
np            78000  wtfile
sw          30030.0  proc                ft
fb            16600  fn            not used
bs                4  math                 f
tpwr             54
pw             14.0  werr
d1           23.700  wexp
tof          3000.0  wbs
nt             2000  wnt
ct             2000          DISPLAY
alock             n  sp              -142.6
gain             15  wp             27364.5
       FLAGS         vs                2275
il                n  sc                   0
in                n  wc                 250
dp                y  hzmm            113.15
hs               nn  is             5565.63
                     rfl             9821.2
                     rfp             9678.7
                     th                  68
                     ins            100.000
                     nm     ph
```

Sample 6

region	start	ppm	end	integral
1	216.568		165	0.136489
2	165		150	1.09523
3	150		135	15.6269
4	135		90	40.7331
5	90		80	0.0189852
6	74		60	0.00293721
7	60		50	0.4512
8	50		22	36.1691
9	22		2	5.76609

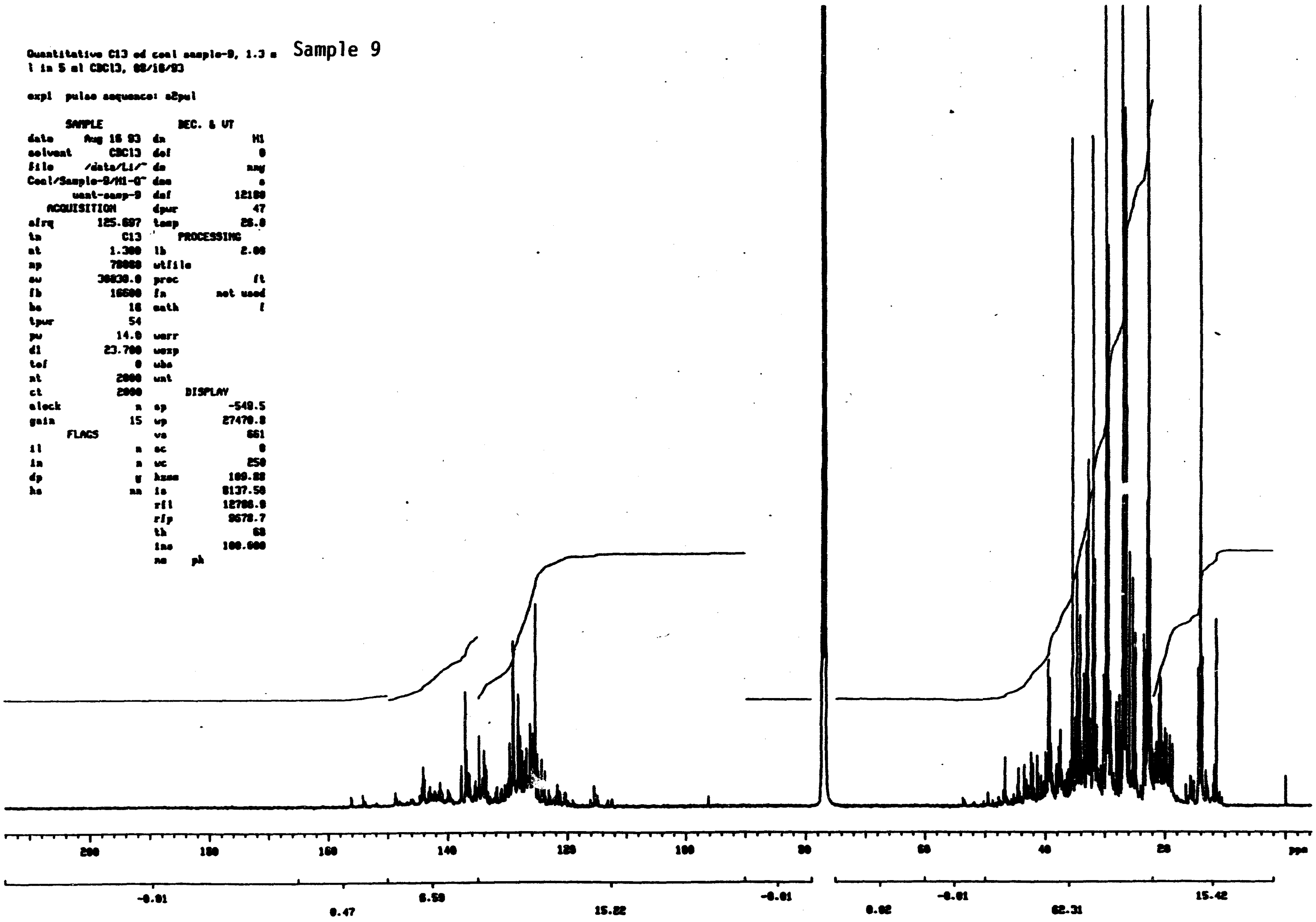
Sample 8



```
C13 quantitative of Coal sample-8 1 g in
 5 ml CDCl3, 10/24/1993

exp1  pulse sequence: s2pul

      SAMPLE              DEC. & VT
date      Oct 24 93  dn            H1
solvent       CDCl3  dof            0
file     /data/Li/~  dm           nny
Coal/Sample-8/quan~  dmm            w
        titative-8   dmf        12100
   ACQUISITION       dpwr          47
sfrq        125.697  temp        26.0
tn              C13      PROCESSING
at            1.300  lb          6.00
np            78080  wtfile
sw          30030.0  proc          ft
fb            16600  fn      not used
bs               16  math           f
tpwr             54
pw             14.0  werr
d1           23.700  wexp
tof          2500.0  wbs
nt             3000  wnt
ct             3000        DISPLAY
alock             n  sp        -506.8
gain             15  wp       25623.2
      FLAGS          vs          1361
il                n  sc             0
in                n  wc           250
dp                y  hzmm      102.49
hs               nn  is      10338.16
                     rfl      10291.8
                     rfp       9678.7
                     th            60
                     ins      100.000
                     nm    ph
```

Sample 8

region	start	ppm	end	integral
1	199.817		165	-0.0122612
2	165		150	1.23186
3	150		135	14.3445
4	135		90	44.4316
5	90		82	-0.0157656
6	72		60	-0.00127583
7	60		50	0.300412
8	50		22	33.7618
9	22		2	5.95917

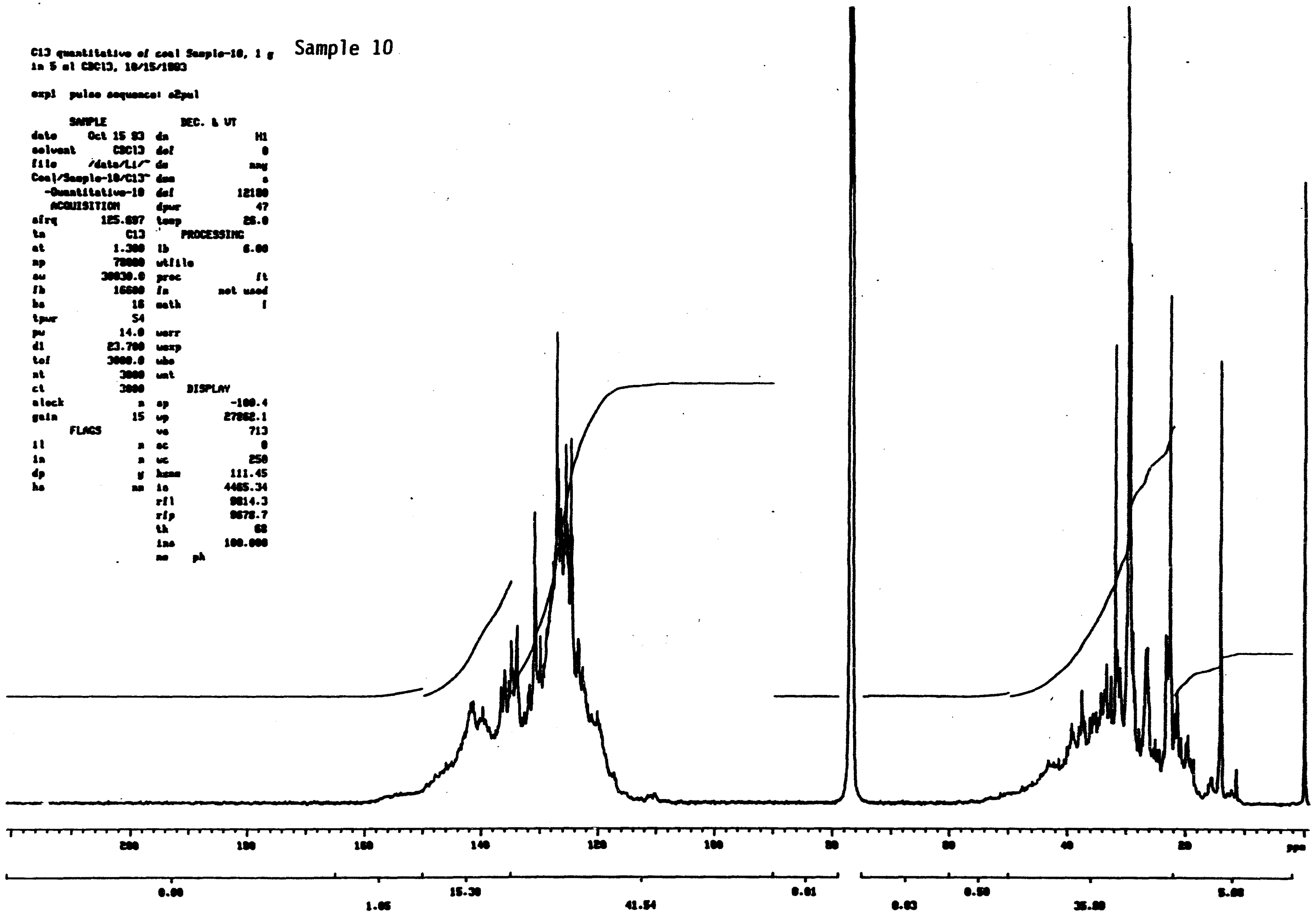


Sample 9

```
Quantitative C13 of coal sample-9, 1.3 g
l in 5 ml CDCl3, 08/16/93

exp1  pulse sequence: s2pul

      SAMPLE              DEC. & VT
date      Aug 16 93  dn              H1
solvent       CDCl3  dof              0
file     /data/Li/~  dm             nny
Coal/Sample-9/H1-Q~  dmm              s
        uant-samp-9  dmf          12100
   ACQUISITION       dpwr            47
sfrq        125.697  temp          25.0
tn              C13      PROCESSING
at            1.300  lb            2.00
np            78080  wtfile
sw          30030.0  proc            ft
fb            16600  fn        not used
bs               16  math             f
tpwr             54
pw             14.0  werr
d1           23.700  wexp
tof               0  wbs
nt             2000  wnt
ct             2000        DISPLAY
alock             n  sp          -549.5
gain             15  wp         27470.8
      FLAGS          vs             661
il                n  sc               0
in                n  wc             250
dp                y  hzmm        109.88
hs               nn  is         8137.50
                     rfl        12706.0
                     rfp         9678.7
                     th              60
                     ins        100.000
                     nm    ph
```

Sample 9

region	start	ppm	end	integral
1	214.177		165	-0.0071093
2	165		150	0.466073
3	150		135	6.59465
4	135		90	15.2243
5	90		79	-0.0137763
6	75		60	0.0162499
7	60		50	-0.0137194
8	50		22	62.3105
9	22		2	15.4228



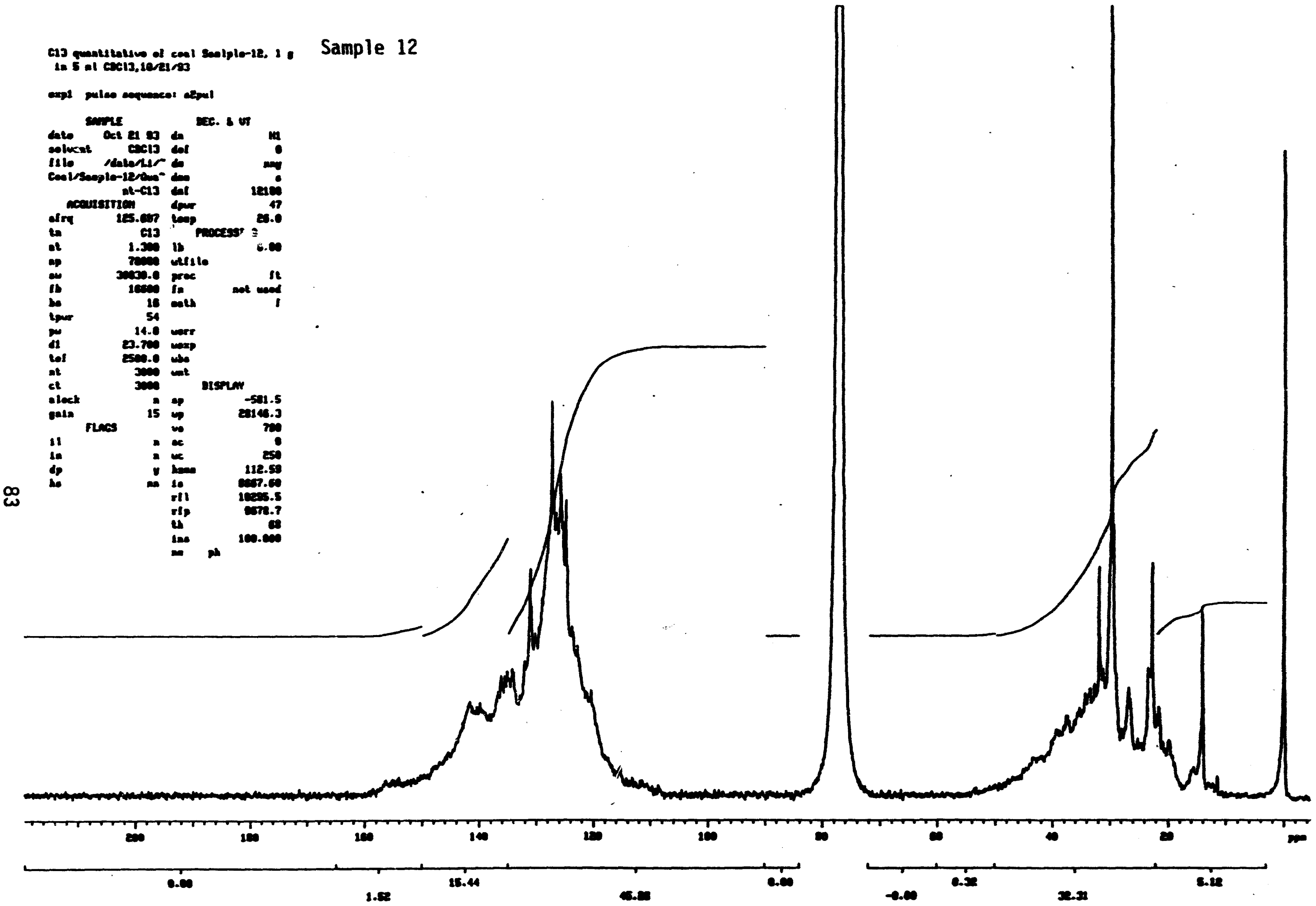
```
C13 quantitative of coal Sample-10, 1 g
in 5 ml CDCl3, 10/15/1993

exp1  pulse sequence: s2pul

      SAMPLE                 DEC. & VT
date      Oct 15 93  dn             H1
solvent       CDCl3  dof             0
file     /data/Li/~  dm            nny
Coal/Sample-10/C13~  dmm             s
  -Quantitative-10   dmf         12100
   ACQUISITION       dpwr           47
sfrq        125.697  temp         26.0
tn              C13      PROCESSING
at            1.300  lb           6.00
np            78000  wtfile
sw          30030.0  proc           ft
fb            16600  fn       not used
bs               16  math            f
tpwr             54
pw             14.0  werr
d1           23.700  wexp
tof          3000.0  wbs
nt             3000  wnt
ct             3000         DISPLAY
alock             n  sp         -100.4
gain             15  wp        27862.1
      FLAGS          vs            713
il                n  sc              0
in                n  wc            250
dp                y  hzmm       111.45
hs               nn  is        4465.34
                     rfl        9814.3
                     rfp        9678.7
                     th             68
                     ins       100.000
                     nm    ph
```

Sample 10

region	start	ppm	end	integral
1	220.863		165	0.00204018
2	165		150	1.04839
3	150		135	15.2953
4	135		90	41.5436
5	90		79	0.0063844
6	75		60	0.0322558
7	60		50	0.501937
8	50		22	35.8928
9	22		2	5.67732

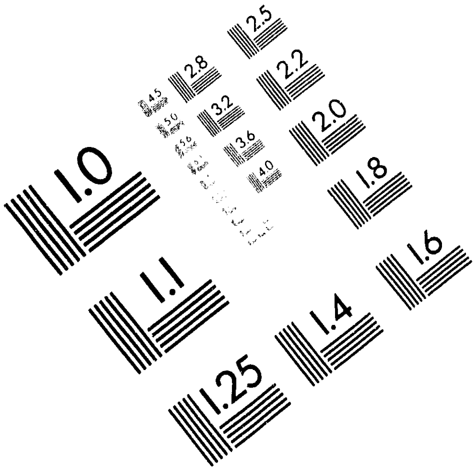
Sample 12

```
C13 quantitative of coal Sample-12, 1 g
 in 5 ml CDCl3,10/21/93

exp1  pulse sequence: s2pul

     SAMPLE            DEC. & VT
date     Oct 21 93  dn           H1
solvent      CDCl3  dof           0
file     /data/Li/~ dm          nny
Coal/Sample-12/Qua~ dmm           s
            nt-C13  dmf       12100
   ACQUISITION      dpwr         47
sfrq       125.697  temp       26.0
tn             C13       PROCESS
at           1.300  lb         6.00
np           78000  wtfile
sw         30030.0  proc         ft
fb           16000  fn     not used
bs              16  math          f
tpwr            54
pw            14.0  werr
d1          23.700  wexp
tof         2500.0  wbs
nt            3000  wnt
ct            3000       DISPLAY
alock            n  sp       -581.5
gain            15  wp      28146.3
     FLAGS          vs          700
il               n  sc            0
in               n  wc          250
dp               y  hzmm     112.59
hs              nn  is      8067.60
                    rfl     10295.5
                    rfp      9678.7
                    th           68
                    ins     100.000
                    nm    ph
```



Sample 12

region	start	ppm	end	integral
1	219.295		165	0.0022462
2	165		150	1.52213
3	150		135	15.4448
4	135		90	45.2762
5	90		84	0.00160499
6	72		60	-0.00250987
7	60		50	0.322531
8	50		22	32.31
9	22		3	5.12298



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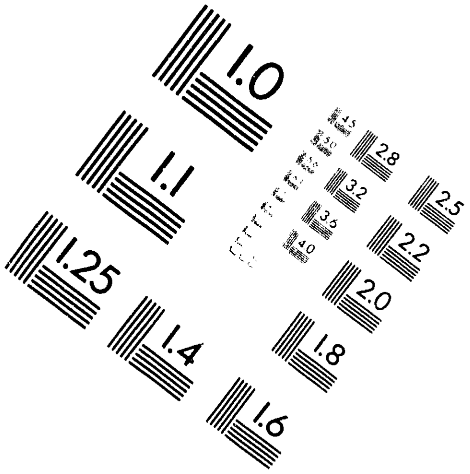

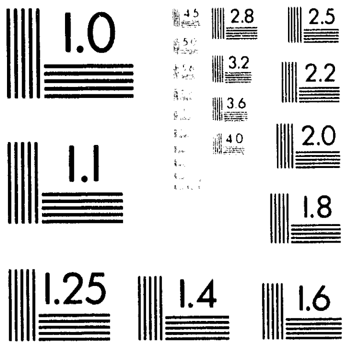

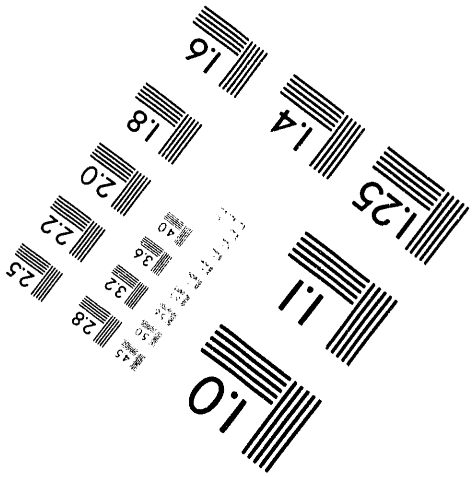

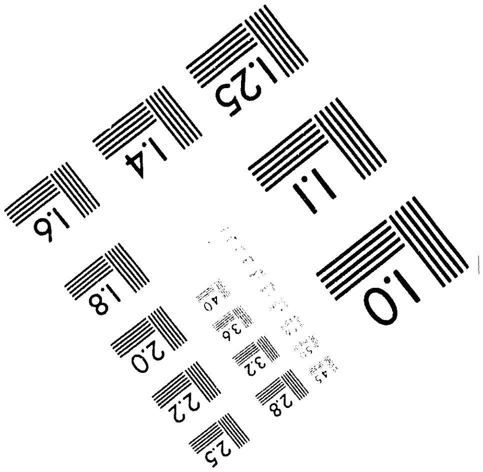

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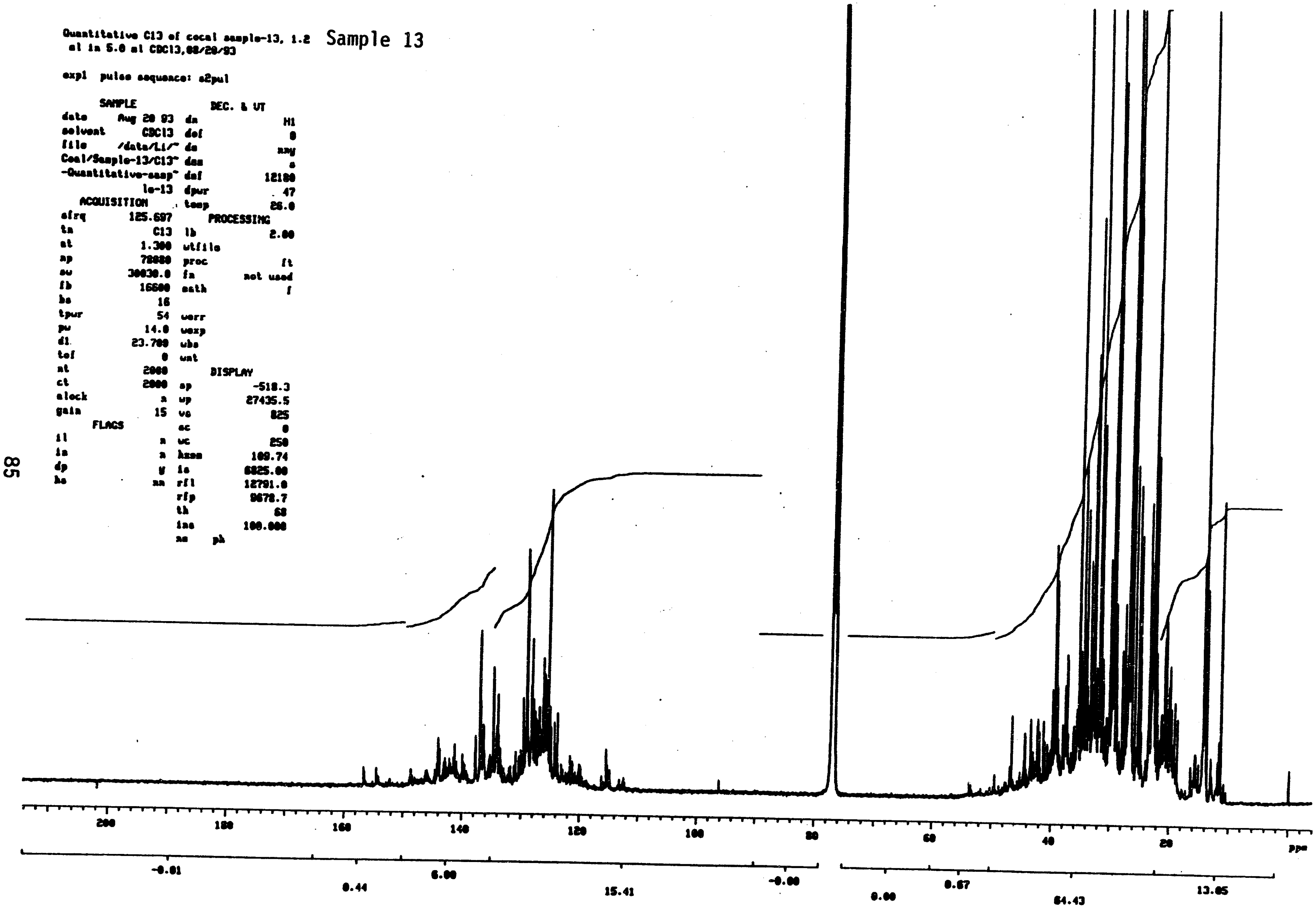
2 of 2

Sample 13

```
Quantitative C13 of cocal sample-13, 1.2
 ml in 5.0 ml CDCl3,08/20/93

exp1  pulse sequence: s2pul

      SAMPLE               DEC. & VT
date      Aug 20 93  dn              H1
solvent       CDCl3  dof              0
file     /data/Li/~  dm             nny
Coal/Sample-13/C13~  dmm              w
-Quantitative-samp~  dmf          12100
              le-13  dpwr            47
   ACQUISITION       temp          26.0
sfrq        125.697      PROCESSING
tn              C13  lb            2.00
at            1.300  wtfile
np            78080  proc            ft
sw          30030.0  fn        not used
fb            16600  math             f
bs               16
tpwr             54  werr
pw             14.0  wexp
d1           23.700  wbs
tof               0  wnt
nt             2000         DISPLAY
ct             2000  sp          -510.3
alock             n  wp         27435.5
gain             15  vs             825
      FLAGS          sc               0
il                n  wc             250
in                n  hzmm        109.74
dp                y  is         6825.00
hs               nn  rfl        12791.0
                     rfp         9678.7
                     th              60
                     ins        100.000
                     nm    ph
```



Sample 13

region	start	ppm	end	integral
1	214.144		165	-0.00643308
2	165		150	0.436183
3	150		135	5.99909
4	135		90	15.4132
5	90		79	-0.000153732
6	75		60	0.00364472
7	60		50	0.67035
8	50		22	64.43
9	22		2	13.0541

DATE FILMED

6/22/94

END