D DOE/PC/89883--65

Distributi DE93 007943

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

Prepared by:

University of Utah
Departments of Chemistry and Fuels Engineering
Salt Lake City, UT 84112

M. S. Solum
R. J. Pugmire

Prepared for:

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

F. P. Burke
R. A. Winschel
S. D. Brandes

November 1992

Under Contract to:

United States Department of Energy
Contract No. DE-AC22-89PC89883

U.S. DOE Patent Clearance was provided by
Chicago Operations Office on November 12, 1992.

DOE/PC 89883-65

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

Prepared by:

University of Utah
Departments of Chemistry and Fuels Engineering
Salt Lake City, UT 84112

M. S. Solum
R. J. Pugmire

Prepared for:

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

F. P. Burke
R. A. Winschel
S. D. Brandes

November 1992

Under Contract to:

United States Department of Energy
Contract No. DE-AC22-89PC89883

U.S. DOE Patent Clearance was provided by
Chicago Operations Office on November 12, 1992.

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Utah studied the use of solid-state cross-polarization/magic angle spinning (CP/MAS) ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy to provide data from which a set of carbon structural parameters and molecular structural descriptors can be derived for the characterization of coal liquefaction resids. The full report authored by the University of Utah is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal-derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using CP/MAS ^{13}C-NMR spectroscopy for the chemical structural examination of distillation resid materials derived from direct coal liquefaction. A set of twelve carbon skeletal-structure parameters and eight molecular structural descriptors were derived from the NMR data. The technique was used previously to determine these parameters for coal and char, and in the construction of a coal pyrolysis model. The method was applied successfully to the tetrahydrofuran (THF)-soluble portion of eleven 850°F$^+$ distillation resids and one 850°F$^+$ distillation resid which contained ash and insoluble organic material (IOM). The results of this study demonstrate that this analytical method can provide data for construction of a model of direct coal liquefaction. Its further development and use is justified based on these results.

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. This Participants Program has two main objectives. The broad objective 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 is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Utah used CP/MAS ^{13}C-NMR spectroscopy to derive carbon structural parameters and molecular descriptors for the tetrahydrofuran (THF)-soluble portion of eleven 850°F^{+} distillation resids, and one resid which contained ash and insoluble organic material (IOM). The solid-state single pulse Bloch-decay method was determined to provide no additional information with these samples. The samples were produced at the Wilsonville pilot plant. Samples were taken from three locations: between the first- and second-stage reactors, after the second-stage reactor, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. The samples are composites of samples taken over long periods of individual processing runs. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic vs. catalytic/catalytic). The CP/MAS ^{13}C-NMR experimental procedures and the derivation of the carbon structural parameters and molecular descriptors are described on pages 2 through 6 of the attached report.

Participant's Major Findings

The following principal observations for the application of CP/MAS ^{13}C-NMR spectroscopy to coal liquefaction materials were reported by the University of Utah. An expanded discussion can be found in the attached report, pages 6 through 12.

Structural parameters derived from the NMR data were used to compare the coal-derived resids with coals similar to the coals from which they were produced. The coals were obtained from the Argonne Premium Coal Program and the Advanced Combustion Engineering Research Center. In most cases, the resids were found to have approximately the same aromatic cluster size (approximately three aromatic rings) as the respective coal. However, the average molecular weight (MW) of the clusters and the average mass per attachment (M_δ) is smaller for the resids than the coals ($MW_{resid} \approx 258$ vs $MW_{coal} \approx 329$, and $M_{\delta resid} \approx 26$ vs $M_{\delta coal} \approx 34$). In addition, the number of bridges and loops per cluster is smaller for the resids. The number of side chains per cluster was found to be smaller for certain resids for which it was concluded that the bridges or side chains were replaced in the liquefaction process by hydrogen. In the case of the resids produced from subbituminous Wyodak coal, the resids have a higher aromaticity and approximately 50% fewer and shorter side chains than the parent coal.

Some comparison was made of samples obtained from different locations in the Wilsonville plant from the same processing run. It was observed that for most of the samples, the resids had similar structural and lattice parameters. Similarities were more pronounced that differences; the resids are more similar to one another than are the coals. However, these parameters differed from the coal most similar to the feed coal used in the run, as was noted above. In only one case were significant differences noted between samples taken at different points from a single run. Utah reports that their data suggest that the structural changes that occur in the resid are almost complete after the first stage of the two-stage liquefaction process; no significant change was observed in resids obtained from other sampling points in the plant. The one notable exception to these findings was in the samples obtained from a thermal/catalytic run with Illinois No. 6 coal. In this case, there was a significant difference in the interstage and recycle samples. The interstage sample had a higher aromaticity ($f_{a'}$ = 0.72 vs 0.63, ±0.01), and had a smaller aromatic cluster size (C = 11 vs 14, ±2.5).

Proton aromaticities obtained indirectly by ^{13}C-NMR correlated well (R^2 = 0.94) with the direct ^{1}H-NMR and elemental analyses measurements of CONSOL on the same samples.

CONSOL Evaluation

The CP/MAS ^{13}C-NMR techniques were shown to be applicable to the analysis of direct coal liquefaction resid samples. Structural parameters were obtained for the THF-soluble resids and one whole resid which contained ash and IOM. Comparison of the structural parameters for the resids with coals comparable to the feed coals used in the processing runs showed structural changes, including removal of the clusters from the infinite lattice by breaking cross links, loss of bridge mass and hydrogenation. Among the resid samples, the similarities were more pronounced than the differences.

The precision of the CP/MAS ^{13}C-NMR techniques is high; measurements are highly reproducible. Sample preparation time is minimal, requiring only that the solid sample be uniformly ground and packed into the NMR tube. The experimental time required is on the order of 2 to 3 days per sample. The 100 MHz instrument used in this study costs approximately $300,000.

Further Development

The CP/MAS ^{13}C-NMR technique was shown to be a powerful tool for the elucidation of structural parameters in coal liquefaction derived resids. It was demonstrated that resid samples which contained ash and IOM could be examined without further preparation. It is recommended that an expanded suite of samples be examined by this method, including whole resids (or perhaps full-range liquids) from various points in the liquefaction process and the corresponding feed coals. The structural parameters developed for the resids (or full-range liquids) and coals could form the basis for a comprehensive model of coal liquefaction.

Participant's Statement of Work

Solid-state cross-polarization/magic angle spinning (CP/MAS) ^{13}C-nuclear magnetic resonance (NMR) spectroscopy has been used to examine fossil fuel materials. These analyses have provided a set of parameters from which molecular structure descriptors of materials such as coals and coal pyrolysis tars can be obtained. This technique has not been demonstrated with process-derived direct coal liquefaction materials, or investigated for its ability to answer questions pertaining to the chemistry of direct coal liquefaction. As such, it fits well within the scope of the participants program.

The University of Utah will examine ten direct coal liquefaction derived distillation resid materials by CP/MAS ^{13}C-NMR. From the NMR analysis, the Utah researchers will derive a set of twelve carbon structural parameters for each resid; 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. Average molecular structural descriptors then will be derived from these parameters; these descriptors will include: mole fraction of bridgehead carbons, aromatic carbons per cluster, number of attachments per cluster and molecular weight per cluster. Samples have been selected (see attached list) so that the resulting information may be applicable to the understanding of resid reactivity in the direct coal liquefaction process.

The samples will be supplied to the University of Utah with the following information, as available: elemental analyses, ash content, ash elemental analyses, phenolic -OH concentration by FTIR, calorific value, hydrogen classes by ^{1}H-NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). The ten samples are 850°F^{+} distillation residual materials. Sample size will be at least 3 g. The ten resid samples will be brittle pitch-like materials that will be supplied as approximately minus 60 mesh powder.

^{13}C NMR ANALYSIS OF CONSOL THF SOLUBLE RESIDUAL MATERIALS FROM THE WILSONVILLE COAL LIQUEFACTION PROCESS

Mark S. Solum and Ronald J. Pugmire*

Departments of Chemistry and Fuels Engineering*
University of Utah
Salt Lake City, Utah 84112

Table of Contents

I. Executive Summary

Solid state ^{13}C NMR spectroscopy experiments have been used to study a set of 11 THF soluble resid samples obtained from direct liquefaction processing streams at the Wilsonville facility. Structural parameters are derived from the NMR data that characterize the carbon skeletal structure and functional group distribution of the resid samples. These data are compared to similar data obtained on a set of coals of similar type and coal region. Elemental analyses, proton NMR data, and phenolic OH content of each sample were provided by CONSOL and employed in the analysis of the ^{13}C NMR data.

The ^{13}C NMR data indicate that one can elucidate the major structural changes that occur in resid samples derived from different coals. Several structural parameters of the resids are similar to those of comparable "parent" coals. No significant reduction in aromatic cluster size was noted in comparing the resid data with the parent coals. However, it is noted that the number of bridges and loops per cluster is lower in the resids than in the parent coals. The number of side chains per cluster is also lower in the resids derived from subbituminous coals (compared to the "parent" coals) and in the Illinois #6 resids obtained in the catalytic/catalytic mode (i.e., samples #4, 5, and 6). These results suggest that the resids bear some similarities to the "parent" coals in terms of cluster size but exhibit significant changes in other structural parameters such as number of bridges and loops and, in the case of the subbituminous coal, side chains per cluster. From these data one could argue that the resids are, on average, 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 indicate 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.

II. Experimental Methods

In this work, two basic NMR experiments using ^{13}C CP/MAS techniques were performed on each of the resids; a variable contact time (VCT) experiment and a dipolar dephasing (DD) experiment. In addition, a normal CP/MAS experiment was performed with a 2 ms contact time from which integrations over selected chemical shift ranges were taken. All of the experiments were run with a 1s recycle delay, 20 KHz spectral width and a spinning speed of 4100 Hz. The spectrometer used is a Chemagnetics CMX with a carbon frequency of 25.152 MHz, a proton frequency of 100.02 MHz, and a proton decoupling field of approximately 54 KHz.

The first experiment run on each sample is a variable contact time experiment where the contact time was varied by 21 time increments from 5 μs to 25 ms. The total number of scans recorded for each contact time increment were the same for each increment in any given sample and this number was in the range of 3,000 to 3,500 scans for any given sample. The NMR spectrum for each contact time increment was integrated from 240 to 90 ppm for the aromatic region and from 90 to 0 ppm for the aliphatic region. The magnetization for each spectral region was fit separately to the following five parameter equations to determine the total magnetization for the region independent of relaxation effects.

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

In the above equation T_{GCH} is the gaussian time constant for the first stage polarization for carbons with directly attached protons, T_{LCH} is a composite lorentzian time constant for the 2nd stage polarization for carbons with directly bonded protons and the polarization for nonprotonated carbons. M_G and M_L are the respective gaussian and lorentzian magnetizations. $T_{1\rho}{}^{H}$ is the spin lattice relaxation time for protons in the rotating frame. In all samples studied, the data could be adequately fit with a single value of $T_{1\rho}^{H}$. Example data for sample #1 are shown in Figure 1. All of the data fits for all samples were of similar quality.

Using the total magnetizations (M_G+M_L) from the aromatic and aliphatic regions the aromaticity (f_a) and aliphaticity (f_{al}) are calculated as follows[1,2].

$$f_a=M^{ar}_{Total}/(M^{al}_{Total}+M^{ar}_{Total});\quad f_{al}=M^{al}_{Total}/(M^{al}_{Total}+M^{ar}_{Total}) \tag{2}$$

The intensity from spinning sidebands has been included in the total magnetization for the aromatic region. Using integrals from the 2 ms CP/MAS 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:

$$f_{a'}=f_a-f_a^C. \tag{3}$$

The second step in the spectral deconvolution routine is to use a dipolar dephasing experiment to separate those aromatic carbons with directly bonded protons from all other carbons. This experiment was run with a contact time of 2 ms which in all cases is the point of maximum intensity in the aromatic signal. This experiment is similar to a normal CP experiment except for an interval after cross polarization where all RF fields are switched off and magnetization from protonated carbons decays quickly while the magnetization from nonprotonated carbons exhibits a much longer time constant for decay (see Table I). The dephasing interval was varied in 23 time increments from 2 μs to 200 μs and the data fit to the following four parameter equation:

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

where M_L^{dd}, T_L^{dd} are associated with nonprotonated carbons and M_G^{dd} and T_G^{dd} with protonated carbons. A typical set of data from sample #1 is shown in Figure 2.

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

$$f_a^H=f_a x M_G^{dd} \tag{5}$$

and

$$f_a^N=f_a x M_L^{dd}. \tag{6}$$

where f_a^N is the fraction of total carbons that are nonprotonated aromatics and f_a^H is the fraction of total carbons that are protonated aromatics.

Using chemical shift ranges from the 2 ms CP/MAS 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 or to another aromatic carbon via biaryl linkages. The two shift ranges are 150-165 ppm and 135-150 ppm respectively. The amount of bridgehead or condensed carbon, f_a^B, is then approximated 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 CP/MAS spectrum the fractional amount of methyl (0-22 ppm) and methoxy (50-60 ppm) groups 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:

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

The parameter f_{al}^{O}, represents the amount of aliphatic carbon bonded to oxygen and may include parts of both of 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, the cluster size model[1], and elemental analysis of the sample, a number of parameters including aromatic cluster size and the coordination number may be obtained.

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

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

Using only this result together with the cluster size model[1] (no other data is required) the average aromatic cluster size, C, is estimated. Using $f_a^P + f_a^S$ as an approximation to the total number of attachments per 100 carbons, together with the corrected aromaticity and the cluster size, the total number of attachments per cluster, or coordination number, $\sigma+1$, is calculated[2].

P_0 is defined as the fraction of intact bridges in the cluster and this parameter is estimated with the assumption that broken bridges end in a single methyl group. Hence,

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

The number of attachments per cluster can now be divided into two subgroups as, BL, the number of bridges and loops per cluster and SC, the number of side chains per cluster. A loop is defined as an aliphatic bridge back to the same cluster (i.e., tetralin type structures) and is calculated as:

$$BL=(\sigma+1)\times P_0 \tag{11}$$

while side chains per cluster are the difference between total attachments and bridges and loops.

$$SC=(\sigma+1)-BL \tag{12}$$

Using the aromatic cluster size, C, the corrected aromaticity, $f_{a'}$, and the % carbon, %C, from elemental analysis data, the total molecular weight, MW, of the cluster including all side chains and half of the bridge and loop material can be calculated as:

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

From the dipolar dephasing data the number of protonated and nonprotonated aromatic carbons are known and the molecular weight from the aromatic carbons and attached protons can be subtracted from the total molecular weight to obtain the total molecular weight of the aliphatic material. This weight, when divided by $(\sigma+1)$, gives M_δ, the average molecular weight per attachment.

III. NMR Data for Resids

The data from variable contact time (VCT) and dipolar dephasing (DD) experiments for the aromatic region are summarized in Table I and for VCT experiments for the aliphatic region in Table II. The gaussian and lorentzian time constants from these two experiments are very similar to coals run in this laboratory.[1,3] However, the proton relaxation time constant in the rotating field, $T_{1\rho}^H$, in both regions of all samples is longer (10-19 ms vs

3-7 ms) than is usually found in coals (other than anthracites) that have been exposed to air. These $T_{1\rho}{}^{H}$ values are even slightly longer than the Argonne coals that had not been exposed to air[1] which suggests that the free radical content of the resids is lower than that found in well preserved and oxygen free coals. It has been found[4] that a one to two order of magnitude decrease in the free radical content will significantly increase $T_{1\rho}{}^{H}$. This reduction in free radical content would be expected due to addition of hydrogen in the liquefaction process. The resid data can be fit with only a single $T_{1\rho}{}^{H}$ parameter (as opposed to many coals where 2 or 3 time constants are observed[3]). The proton $T_{1\rho}$ values are identical (within 2 standard deviations) in both the aromatic and aliphatic regions of each spectra. These data demonstrate that there are no apparent large multiple domains which have been evident in some of the coal and char samples studied in our laboratory[3] and in those reported by dela Rosa et al.[5] In coal samples one frequently finds multiple proton T_1 and $T_{1\rho}$ values. Such results indicate that proton spin diffusion is not capable of averaging out the differences in relaxation that may exist between large segregated domains of protons which are probably manifestations of the heterogeneous nature of the coal or char. The single exponentiality of the proton $T_{1\rho}$ data in these resids indicates that large isolated proton domains are probably not present. One may also note that the three samples (4,5,6) with the largest number of protons also have the three shortest $T_{1\rho}{}^{H}$'s values in both the aromatic and aliphatic regions. This observation suggests that relaxation may be dominated by proton dipolar-dipolar interactions in these samples.

One additional parameter that exhibits a significant difference from the large number of coal samples studied, including the Argonne Premium Coal Sample (APCS) set, is the relative amount of protonated aromatic carbons ($f_a{}^H/f_{a'}$). In coals previously run[1] this parameter falls in the range 0.30 - 0.40 except in the case of the APCS Zap sample. In the resid samples studied, this parameter falls in the range 0.40 - 0.49 and indicates that the aromatic rings bear more protons (e.g., the number of ring substituents is lower) than one finds in the parent coals.

The structural parameters for the twelve resid samples are given in Table III and these can be compared with the eleven (including the eight Argonne coals) ACERC coals given in Table IV. The especially relevant coals are: Illinois #6, Pittsburgh #8, Wyodak, PSOC-1443 (Texas lignite) and PSOC-1488 (Dietz). Table V contains the molecular formulas (C, H, N, O, rounded to the nearest atom) calculated from elemental analysis data together with H_a, the number of aromatic protons calculated from the total number of protons and ^1H NMR data supplied by CONSOL. For comparison purposes, the parameter obtained from f_a^H is included from Table IV. The aliphatic proton distribution has also been included in Table V.

IV. Discussion

The structures observed in the resid samples can be discussed from two different perspectives: 1) how the resid parameters compare, in a general way, to those same parameters in the comparison sample set (the coals studied by the Advanced Combustion Engineering Research Center, ACERC) tabulated in Table IV; specifically how the resid from a certain feed coal type compares to the coal of similar rank and coal region (i.e., Texas Lignite, PSOC-1443; Wyodak, Dietz, PSOC-1488; Illinois #6; and Pittsburgh) in the comparison set; 2) a comparison of the resids based on sampling point in the process stream.

In a general comparison of the resid structural and proton distribution data summarized in Tables III, IV and V, one can see that most of the resid parameters are within the ranges of the relevant ACERC coals of similar rank. The corrected aromaticities (f_a') for the resid samples span the range 0.57-0.76 whereas the five "comparable parent" ACERC coals span similar range (0.55-0.72). The aromatic cluster size of the resids was found to be essentially the same, within experimental error (the error is estimated to be about 2.5 carbons per cluster), and these values are generally the same as those found in the "parent" coals. This average size of about three aromatic rings is consistent with the

CONSOL proton NMR data which estimates the presence of much larger amounts of condensed systems compared to single ring systems for all samples.

One may also compare the average cluster coordination number, $\sigma+1$, between the resid samples and the five "parent" coals. For the resids the average is 3.8 as compared to 4.9 for the "parent" coals. When one partitions $\sigma+1$ into side chains, SC, and bridges and loops, BL, one finds that most of the difference is in BL where the average is 1.9 for the resids and 2.9 for the five coals whereas the SC parameter is 1.9 for the resids and 2.0 for the coals. These data would suggest that in the processing, one bridge on average is replaced on each cluster by a hydrogen. One should note that P_0 used in the partitioning of $\sigma+1$ could have errors as high as 25% in coal samples due to assumptions in its definition. This definition assumes all side chains terminate in a single methyl group and neglects other terminating groups such as OH (a constant of only 1 per 100 carbons in the resid samples) and multiple methyl groups (i.e., isopropyl, t-butyl, etc.). The P_0 parameter is used in modeling of coal devolatilization experiments.[6,8,9].

Two other parameters which exhibit some differences between the resids and the "parent" coals are the molecular weight per cluster, MW, and the average mass per attachment, M_δ. Both of these parameters are smaller in the resid samples (258, 26) than in the parent coals (329, 34). It appears that the molecular weight is lower in the resids for two reasons. First, the resids generally have one less attachment per cluster than is found in the parent coals. Second, the oxygen content of the resids is much lower compared to the coals which may explain the lower mass per side chain. One should note that it was not possible to exactly balance the oxygen count from the carbon ^{13}C NMR parameters, f_a^C, f_a^P, and f_{al}^O with the elemental analysis. The latter indicates that only 1 or 2 oxygens are present per 100 carbons. Even if one includes double counting of oxygen (i.e., an oxygen in a methoxy group attached to an aromatic ring would be counted also in f_a^P) the oxygen containing functional groups observed in the NMR spectra are slightly larger than the oxygen content obtained from elemental analysis. However, since elemental oxygen is obtained by difference in the ultimate analysis procedure, this result is not surprising as all the analysis errors are accumulated in this one parameter.

An interesting comparison can be made of the resid data as an internal consistency check, i.e., the number of protons per 100 carbons. It is interesting to note that Hanna et al.[7] have studied a large suite of Australian coals and compared the proton aromaticities as determined by both CRAMPS (combined rotation and multiple pulse spectroscopy) and DD techniques. This direct vs. indirect comparison is of value for the present study since Hanna has demonstrated a high degree of correlation (r^2 =0.94) between the two techniques suggesting that the values derived from indirect measurement (DD) of H_a are comparable to those obtained from the direct determination (CRAMPS). In the present study the proton aromaticity, H_a , is determined from the elemental analysis and CONSOL's proton NMR data while f_a^H is determined from DD experiments on each sample. As one can see in Figure 3, an excellent correlation exists between the two sets of data. (The correlation coefficient, r^2, of both sets of data are nearly identical). However, an offset of about 2 protonated carbons is noted in the DD data. The reason for this offset is unknown but could arise from several factors: the choice of one contact time (2 ms) for the DD experiment could underestimate slowly polarizing nonprotonated carbons; relaxation effects in both types of NMR experiments; functional groups such as alkenes in the selected aromatic chemical shift ranges; or incomplete dissolution of the THF soluble fractions. It is well known that if coal extracts and coal derived liquids are not carefully handled in an inert environment polymerization often occurs. Since the samples are opaque, the spectroscopist may not be aware that colloidal dispersions exist and, hence, the proton NMR data may not be representative of the total sample. The proton aromaticity values appear to have a systematic offset. The overall correlation coefficient of the data (.938) is almost identical to that reported by Hanna (.94). At present, it is not possible to rationalize the source of this error.

In analyzing the data it would be desirable to compare a given resid with its parent coal. Such is not possible in the sample sets analyzed and, hence, only rough approximations can be made. In order to compare sample #3, the lignite, with a starting coal, the best comparison coal is PSOC-1443, the Texas lignite. The biggest difference between the resid and the coal is in the amount of oxygen functional groups (f_a^C, f_a^P, and f_{al}^O) where the resid has a much lower oxygen content. In addition, the corrected aromaticity in the resid is about 10 units higher than in the lignite.

Samples #9, #10, and 10a are derived from the Pittsburgh seam and, as noted in Table III, these three samples exhibit almost identical structural and lattice parameters. If one compares these two resids to the parent Argonne Pittsburgh coal, many of the parameters are quite similar. The largest differences between these three products and the "parent coal" appears in the two parameters f_a^P and f_{al}^O which are two and four times as large in the coal. Another parameter, H_{al}/f_{al}^H (Table V), which represents the average number of protons on a nonmethyl aliphatic carbon, is related to the amount of branching in the aliphatic material. In general, as can be seen from the last entry in Table V, this number is higher for the resid samples than for the coals. For the Pittsburgh samples, the two resids have approximately 50% more protons on the aliphatic carbons than is noted for the comparable coal. These data lead one to the logical conclusion that very little chain branching occurs in these resids. It would seem that whatever structural changes occur in the resid, these changes are almost complete after the first stage and no significant changes are observed in the NMR data for the other two modes of processing this coal.

The two samples with the highest aromaticity ($f_a = 0.76$) are samples #7 and #8 derived from the subbituminous mix and run in the thermal/catalytic mode. In fact, most of the lattice and structural parameters for the two resids are quite similar but sample #7, the recycle product, exhibits a higher value of bridges and loops and, hence, a slightly higher molecular weight even though both samples have identical values of M_δ. In comparison with the two "parent" coals, Wyodak and PSOC-1488 (Dietz), the aromaticity of the resids is about 20 units higher. However, the number of side chains observed in samples # 7 and #8 are approximately 50% lower than are found in the two subbituminous coals. These changes could be rationalized by extensive dealkylation wherein apaproximately 50% of the alkyl substituents were removed without aromatic ring reduction (i.e., the observed aromaticities are the weighted averages one would expect through a 50% decrease in the number of aliphatic side chains if no concominant aromatic ring reduction occurred).

The last group of samples to be discussed are the six from the Illinois #6 coal. The first two, samples #1 and #2, which were run in the thermal/catalytic mode, were the only samples that displayed significant differences as a function of the sampling point in the processing stream. Sample #2, the interstage product, has a corrected aromaticity of 0.72 that is identical to the "parent" coal whereas the f_a' value for sample #1 (recycle), is significantly lower (0.63). The average aromatic cluster size is 14 and 11 aromatic carbons and these sample pairs represent the only case in which the cluster size difference exceeds the experimental error for determining this parameter. The cluster molecular weight in sample #1 is approximately 100 Daltons larger than for sample #2 due to the larger cluster size, one additional attachment per cluster (2.2 vs. 1.2) and a slightly higher mass per attachment. Sample No. 11 was included in the sample set in order to compare a deashed sample (#1) with one in which the mineral matter had not been removed. As can be seen in Table III, no significant differences were noted in the structural and lattice parameters of the two samples.

The three Illinois #6 samples (#4, #5, #6) run in the catalytic/catalytic mode exhibit structural parameters that were almost identical within experimental error. The corrected aromaticity for these samples ranged from 0.57 to 0.59 which is somewhat lower than those observed in the samples run in the thermal/catalytic mode. In the case of the Illinois coal the major structural changes seem to occur in the catalytic mode of process operation.

V. Summary Assessment

In summary, it has been demonstrated that ^{13}C NMR data can elucidate the major structural and major functional group changes that occur in resid samples derived from different coals. It is significant to note that several of the structural parameters of the resids are similar to those of comparable "parent" coals. No significant reduction in aromatic cluster size was noted in comparing the resid data with the parent coals. However, it is noted that the number of bridges and loops per cluster is lower in the resids than in the parent coals. The number of side chains per cluster is also lower in the resids derived from subbutiminous coals (compared to the "parent" coals) and in the Illinois #6 resids obtained in the catalytic/catalytic mode (i.e., samples #4, 5, and 6). These results suggest that the resids bear some similarities to the "parent" coals in terms of cluster size but exhibit significant changes in other structural parameters such as number of bridges and loops and, in the case of the subbituminous coal, side chains per cluster. From these data one could argue that the resids are, on average, 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 crosslink with the subsequent loss of some bridge mass. In addition, the data demonstrate that the resid has, in fact, undergone some hydrogenation. As expected in a hydrotreatment process, the oxygen functional groups have been significantly reduced. In only one case (Illinois #6, samples #1 and #2) were there significant structural changes noted in samples taken at different points in the process stream.

VI. Recommendation

It appears that carefully designed studies on the liquefaction behavior of coal would be feasible if an appropriate battery of analytical procedures were used. The resid samples studied demonstrated the similarities as well as the differences in the structure of this material that can occur in coal liquefaction processes. 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 assembly of a wide range of analytical data (such as that obtained by CONSOL for the resids studied) could provide a very detailed molecular picture of the changes that occur in the liquefaction process and, perhaps, provide important additional information about key reaction processes. The assemblage of FTIR, elemental analysis, mass spectroscopy, EPR, and NMR data on a common set of coals, resids, chars, and coal derived liquids 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.

REFERENCES

1. Solum, M.S.; Pugmire, R.J.; Grant, D.M. *Energy & Fuels*, **1989**, 3, 187.

2. The cluster coordination number, $\sigma+1$, is defined as

$$\sigma+1 = \text{number of attachments per cluster}$$

$$\sigma+1 = \frac{\text{Number of attachments/100 carbons}}{\text{number of clusters/100 carbons}}$$

$$\text{Number of attachments/100 carbons} = 100\,(f_a^P + f_a^S)$$

$$C = \text{Number of aromatic carbons/clusters}$$

This number is obtained from χ_b and the cluster model as discussed in Reference 1.

$$f_a' \times 100/C = \text{number of clusters/100 carbons}$$

3. 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.

4. Botto, R.E.; Wilson, R.; Winans, R.W. *Energy & Fuel*, **1987**, 1, 173.

5. dela Rosa, L.; Pruski, M.; Lang, D.; Gerstein, B.; and Solomon P., "Characterization of the Argonne Premium Coals by Using ^{1}H and ^{13}C NMR and FT-IR Spectroscopies," *Energy & Fuels*, **1992**, 6, 460.

6. Grant, D.M.; Pugmire, R.J.; Fletcher, T.H.; and Kerstein, A.R. "A Chemical Model of Coal Devolatilization Using Percolation Lattice Statistics, *Energy & Fuels*, **1989**, 3, 175.

7. Hanna, J.V.; Vassallo, A.M.; and Wilson, M.A., CRAMPS Determined Proton Aromaticities of Australian Coals: A Comparison with Dipolar Dephasing, *Energy & Fuels*, **1992**, 6, 28.

8. Fletcher, T.H.; Kerstein, A.R.; Pugmire, R.J.; and Grant, D.M. ""A Chemical Percolation Model for Devolatilization: 3. Chemical Structure as a Function of Coal Type", *Energy & Fuels*, accepted for publication.

9. Fletcher, T.H.; Solum, M.S.; Grant, D.M.; and Pugmire, R.J. "Chemical Structure of Char in the Transition from Devolatilization to Combustion", *Energy & Fuels*, accepted for publication

Table I: NMR Parameters from DD and VCT Experiments on the Aromatic Region.

MATERIAL	M_G^{vct}	T_G^{vct}(μs)	M_L^{vct}	T_L^{vct}(μs)	$T_{1\rho}^{Hvct}$(ms)	M_G^{dd}	T_G^{dd}(μs)	M_L^{dd}	T_L^{dd}(μs)
1-IL-R-250	.25	19	.75	413	15.4	.42	17	.58	231
2-IL-I-250	.28	18	.72	398	17.9	.47	17	.53	257
3-TX-I-255	.28	21	.72	489	16.9	.45	17	.55	267
4-IL-R-257	.26	19	.74	432	11.0	.42	17	.58	254
5-IL-I-257	.29	18	.71	409	12.5	.40	17	.60	268
6-IL-2-257	.34	23	.66	408	13.3	.41	17	.59	251
7-SB-R-258	.27	19	.73	429	19.2	.45	17	.55	293
8-SB-I-258	.32	17	.68	431	18.9	.49	17	.51	257
9-PT-R-259	.26	19	.74	410	17.5	.44	17	.56	278
10-PT-2-259	.27	18	.73	410	18.8	.44	17	.56	261
10a-PT-I-259	.30	20	.70	450	16.9	.45	18	.55	287
11-IL-R-250	.29	17	.71	463	19.8	.42	17	.58	247

ERRORS:

$M_G^{vct}\pm0.02$

$M_L^{vct}\pm0.02$

$T_G^{vct}\pm1\mu s$

$T_L^{vct}\pm6\%$

$T_{1\rho}^{Hvct}\pm3\%$

$M_G^{dd}\pm0.02$

$M_L^{dd}\pm0.02$

$T_G^{dd}\pm1\mu s$

$T_L^{dd}\pm6\%$

Table II: NMR Parameters from VCT Experiments on the Aliphatic Region.

MATERIAL	M_G^{vct}	$T_G^{vct}(\mu s)$	M_L^{vct}	$T_L^{vct}(\mu s)$	$T_{1\rho}^{Hvct}(ms)$
1-IL-R-250	.49	15	.51	123	14.7
2-IL-I-250	.38	14	.62	84	15.6
3-TX-I-255	.41	15	.59	98	15.9
4-IL-R-257	.49	15	.51	113	9.9
5-IL-I-257	.48	14	.52	100	11.0
6-IL-2-257	.42	14	.58	96	11.8
7-SB-R-258	.48	16	.52	104	16.8
8-SB-I-258	.47	14	.53	87	18.0
9-PT-R-259	.48	15	.52	120	15.6
10-PT-2-259	.44	14	.56	97	17.3
10a-PT-I-259	.40	15	.60	94	15.1
11-IL-R-250	.49	14	.51	106	19.3

ERRORS:

$M_G^{vct} \pm 0.04$

$M_L^{vct} \pm 0.04$

$T_G^{vct} \pm 1 \mu s$

$T_L^{vct} \pm 10\%$

$T_{1\rho}^{Hvct} \pm 3\%$

Table III: Structural and Lattice Parameters for CONSOL Resid 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
#1 Ill6 Recycle	.66	.63	.03	.26	.37	.03	.16	.18	.34	.24	.10	.02
#2 Ill6 Interstage	.74	.72	.02	.34	.38	.05	.16	.17	.26	.18	.08	.02
#3 Tex (l) Interstage	.68	.66	.02	.30	.36	.03	.16	.17	.32	.23	.09	.02
#4 Ill6 Recycle	.61	.58	.03	.24	.34	.03	.16	.15	.39	.28	.11	.03
#5 Ill6 Interstage	.61	.57	.04	.23	.34	.04	.16	.14	.39	.29	.10	.03
#6 Ill6 2nd Stg. Prod.	.61	.59	.02	.24	.35	.03	.15	.17	.39	.27	.12	.02
#7 SB Recycle	.78	.76	.02	.34	.42	.03	.17	.22	.22	.15	.07	.01
#8 SB Interstage	.77	.76	.01	.37	.39	.03	.17	.19	.23	.14	.09	.02
#9 Pitt Recycle	.72	.71	.01	.31	.40	.03	.16	.21	.28	.20	.08	.01
#10 Pitt 2nd Stg. Prod.	.73	.72	.01	.32	.40	.03	.17	.20	.27	.18	.09	.01
#10a Pitt Interstage	.72	.71	.01	.32	.39	.03	.15	.21	.28	.19	.09	.01
#11 Ill6 Recycle	.66	.63	.03	.26	.37	.04	.17	.16	.34	.25	.09	.02

MATERIAL	χ_b	C	$\sigma+1$	P_0	B.L.	S.C.	MW	M_δ
#1 Ill6 Recycle	.29	14	4.2	.47	2.0	2.2	299	30
#2 Ill6 Interstage	.24	11	3.2	.62	2.0	1.2	205	21
#3 Tex (l) Interstage	.26	12	3.5	.53	1.9	1.6	245	27
#4 Ill6 Recycle	.26	12	4.0	.42	1.7	2.3	280	33
#5 Ill6 Interstage	.25	12	4.2	.50	2.1	2.1	267	28
#6 Ill6 2nd Stg. Proc.	.29	14	4.3	.33	1.4	2.9	323	35
#7 SB Recycle	.29	14	3.7	.65	2.4	1.3	244	19
#8 SB Interstage	.25	12	3.2	.55	1.8	1.4	210	19
#9 Pitt Recycle	.30	14	3.7	.58	2.1	1.6	262	24
#10 Pitt 2nd Stg. Prod.	.28	13	3.6	.55	2.0	1.6	242	22
#10a Pitt Interstage	.30	14	3.5	.50	1.7_5	1.7_5	264	26
#11 Ill6 Recycle	.25	12	4.0	.57	2.3	1.7	255	27

Table III: Error Estimate for Structural and Lattice Parameters for Consol Samples.
(CONTINUED)

Structural Parameters

$f_a = 0.01$

$f_a^C = 0.01$

$f_{a'} = 0.01$

$f_a^H = 0.01$

$f_a^N = 0.01$

$f_a^P = 0.01$

$f_a^S = 0.01$

$f_a^B = 0.02$

$f_{al} = 0.01$

$f_{al}^H = 0.01$

$f_{al}^* = 0.01$

$f_{al}^O = 0.02$

Lattice Parameters

$\chi_b = 0.03$
$C = 2.5$
$\sigma+1 = 0.8$
$P_0 = .11$
B.L. = .6
S.C. = 1.0
MW = unknown error in elemental analysis, so not calculated.
M_δ = unknown error in elemental analysis, so not calculated.

All values rounded to nearest .01 for structural parmeters.

Table IV: Structural and Lattice Parameters for the ACERC Coals.

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
NORTH DAKOTA[a] (L)	.65	.55	.10	.22	.33	.09	.15	.09	.35	.26	.09	.11
WYODAK (SB)	.63	.55	.08	.17	.38	.08	.14	.16	.37	.27	.10	.10
BLIND CANYON[a] (HVB)	$.62_5$	$.60_5$	.02	$.21_5$	.39	$.06_5$	.14	$.18_5$	$.37_5$	.27	$.10_5$	.05
ILLINOIS #6 (HVB)	.72	.72	.00	.26	.46	.06	.18	.22	.28	.19	.09	.05
PITTSBURGH #8[a] (HVB)	.71	.70	.01	.27	.43	.06	.15	.22	.29	.21	.08	.04
STOCKTON SEAM (HVB)	.75	.75	.00	.27	.48	.05	.21	.22	.25	.17	.08	.04
UPPER FREEPORT (MVB)	.81	.81	.00	.28	.53	.04	.20	.29	.19	.11	.08	.02
POCAHONTAS (LVB)	.86	.86	.00	.33	.53	.02	.17	.34	.14	.09	.05	.01
PSOC-1443 TX (L)	.63	.56	.07	.17	.39	.10	.17	.12	.37	.26	.11	.08
PSOC-1488 (SB)	.64	.56	.08	.19	.37	.09	.15	.13	.36	.25	.11	.05
PSOC-1468 (A)	.95	.94	.01	.24	.70	.01	.08	.61	.05	.04	.01	.03

MATERIAL	χ_b	C	$\sigma+1$	P_0	B.L.	S.C.	MW	M_δ
NORTH DAKOTA[a] (L)	.16	9	3.9	.63	2.5	1.4	269	40
WYODAK (SB)	.29	14	5.6	.55	3.1	2.5	408	42
BLIND CAYNON[a] (HVB)	.31	15	5.1	.49	2.5	2.6	368	36
ILLINOIS #6 (HVB)	.31	15	5.0	.63	3.2	1.8	321	27
PITTSBURGH #8[a] (HVB)	.31	15	4.5	.62	2.9	1.6	310	28
STOCKTON (HVB)	.29	14	4.8	.69	3.3	1.5	270	20
UPPER FREEPORT (MVB)	.36	18	5.3	.67	3.6	1.7	310	17
POCAHONTAS #3 (LVB)	.40	20	4.4	.74	3.3	1.1	307	13
PSOC-1443 (L)	.21	10	4.8	.59	2.8	2.0	297	36
PSOC-1488 (SB)	.23	11	4.7	.54	2.5	2.2	310	37
PSOC-1468 (A)	.65	49	4.7	.89	4.2	0.5	656	12

a) Averaged over two or more vials.

Table V: Other Parameters per 100 Carbon Atoms.[a–f]

SAMPLE	C	H	O	N	H_a	f_a^H	OH	H_{me}	H_{al}	H_{al}/f_{al}^H
1-IL-R-250	100	99	2	1	25	26	1.0	30	43(42)	1.8(1.8)
2-IL-I-250	100	87	2	1	31	34	1.4	24	31(28)	1.7(1.6)
3-TX-I-255	100	88	2	1	28	30	1.4	27	32(30)	1.4(1.3)
4-IL-R-257	100	109	1	1	23	24	0.7	33	52(51)	1.9(1.8)
5-IL-I-257	100	108	2	1	24	23	0.9	30	53(54)	1.8(1.9)
6-IL-2-257	100	110	2	1	23	24	0.8	36	50(49)	1.9(1.8)
7-SB-R-258	100	81	2	1	31	34	1.1	21	28(25)	1.9(1.7)
8-SB-I-258	100	81	2	1	32	37	1.4	27	21(16)	1.5(1.1)
9-PT-R-259	100	88	1	1	27	31	0.9	24	36(32)	1.8(1.6)
10-PT-2-259	100	90	2	1	29	32	0.9	27	33(30)	1.8(1.7)
10a-PT-I-259	100	86	2	1	28	32	1.2	27	30(26)	1.6(1.4)
11-IL-R-250	100	99	1	1	26	26	1.0	27	45(45)	1.8(1.8)
NORTH DAKOTA (L)	100	79	19	1	-	22	-	27	30	1.2
WYODAK (SB)	100	85	17	1	-	17	-	30	38	1.4
BLIND CAYNON (HVB)	100	85	10	2	-	22	-	32	31	1.1
ILLINOIS #6 (HVB)	100	77	9	1	-	26	-	27	24	1.3
PITTSBURGH (HVB)	100	76	6	2	-	27	-	24	25	1.2
STOCKTON (HVB)	100	76	6	2	-	27	-	24	25	1.5
UPPER FREEPORT (HVB)	100	65	4	2	-	28	-	24	13	1.2
POCAHONTAS #3 (HVB)	100	58	1	1	-	33	-	15	10	1.1
PSOC-1443 (L)	100	86	21	2	-	17	-	33	36	1.4
PSOC-1488 (SB)	100	81	17	1	-	19	-	33	29	1.2
PSOC-1468 (A)	100	24	3	<1	-	24	-	3	--	--

a) All structural parameters listed here from other tables have been multiplied by 100.

b) Rounded to nearest atom except for CONSOL's OH data.

c) The comparison Argonne Illinois coal had 1 atom of sulfur, all other samples rounded to zero atoms.

d) H_a = (Condensed+Uncondensed aromatics)/100 × $(H - OH_{\text{if available}})$.

e) $H_{me} = 300 \times f_{al}^{*}$

f) $H_{al} = H - OH - H_a - H_{me}$. The numbers in parenthese were derived using f_a^H obtained from the DD experiment; H is from elemental analysis data; OH is from FTIR data; H_{me} is derived from ^{13}C NMR data in Table III.

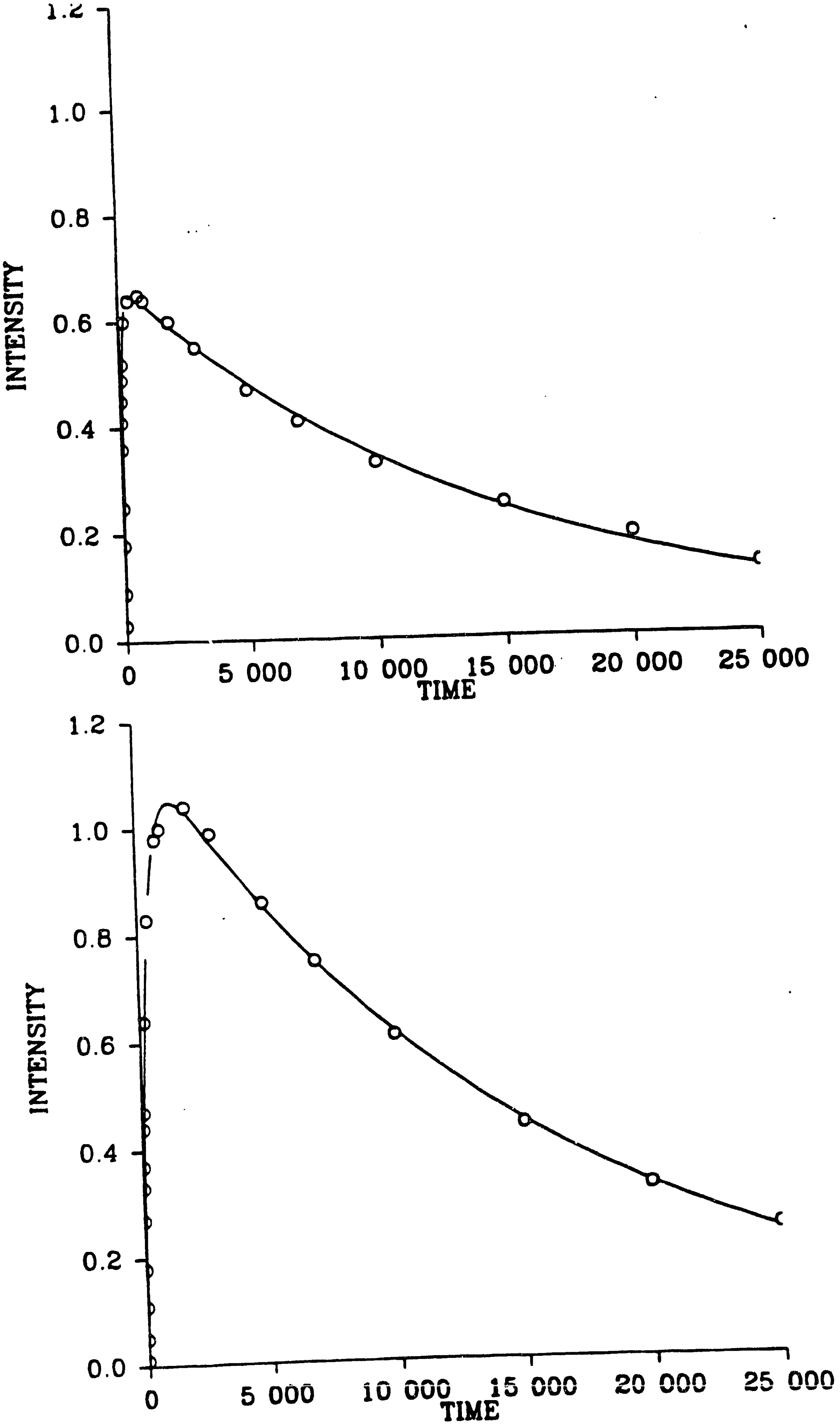


Figure 1. VCT fits for sample #1, time in μs: top) the aliphatic region, bottom) the aromatic region.

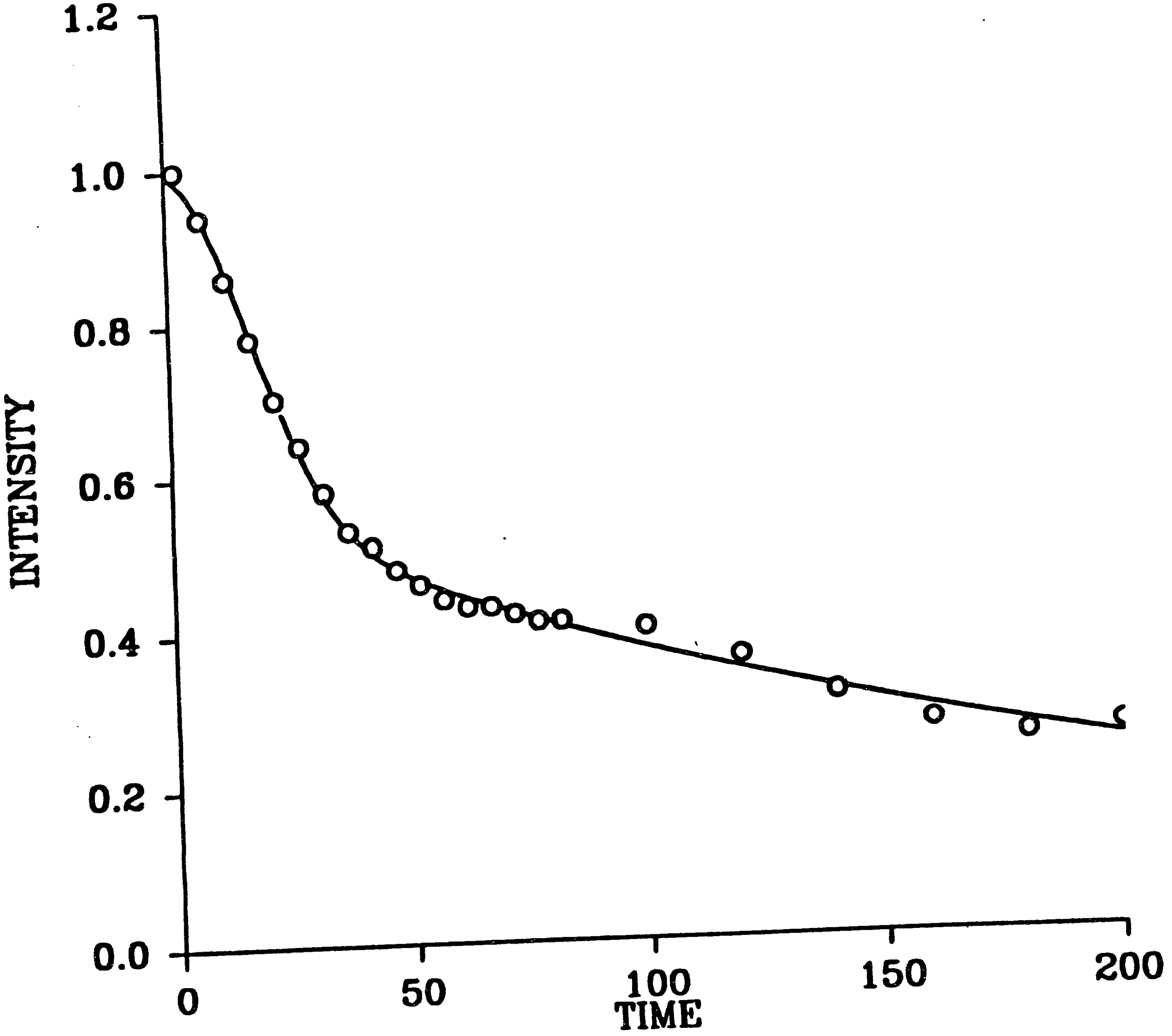


Figure 2. Diplar Dephasing fit for the aromatic region for sample #1. The time scale is in μs.

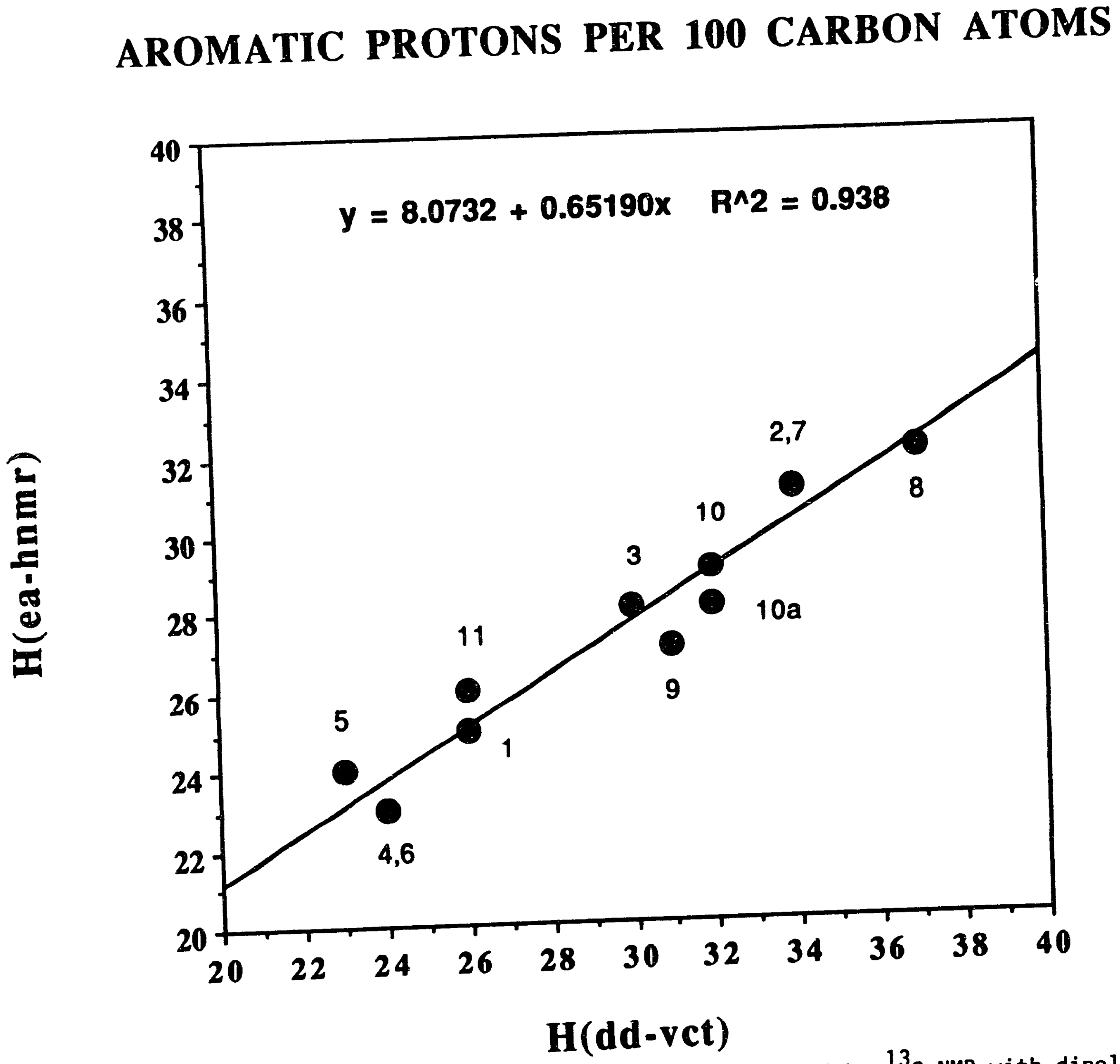


Figure 3. The number of aromatic protons as calculated by ^{13}C NMR with dipolar dephasing vs. a combination of elemental analysis and proton NMR data.

APPENDIX

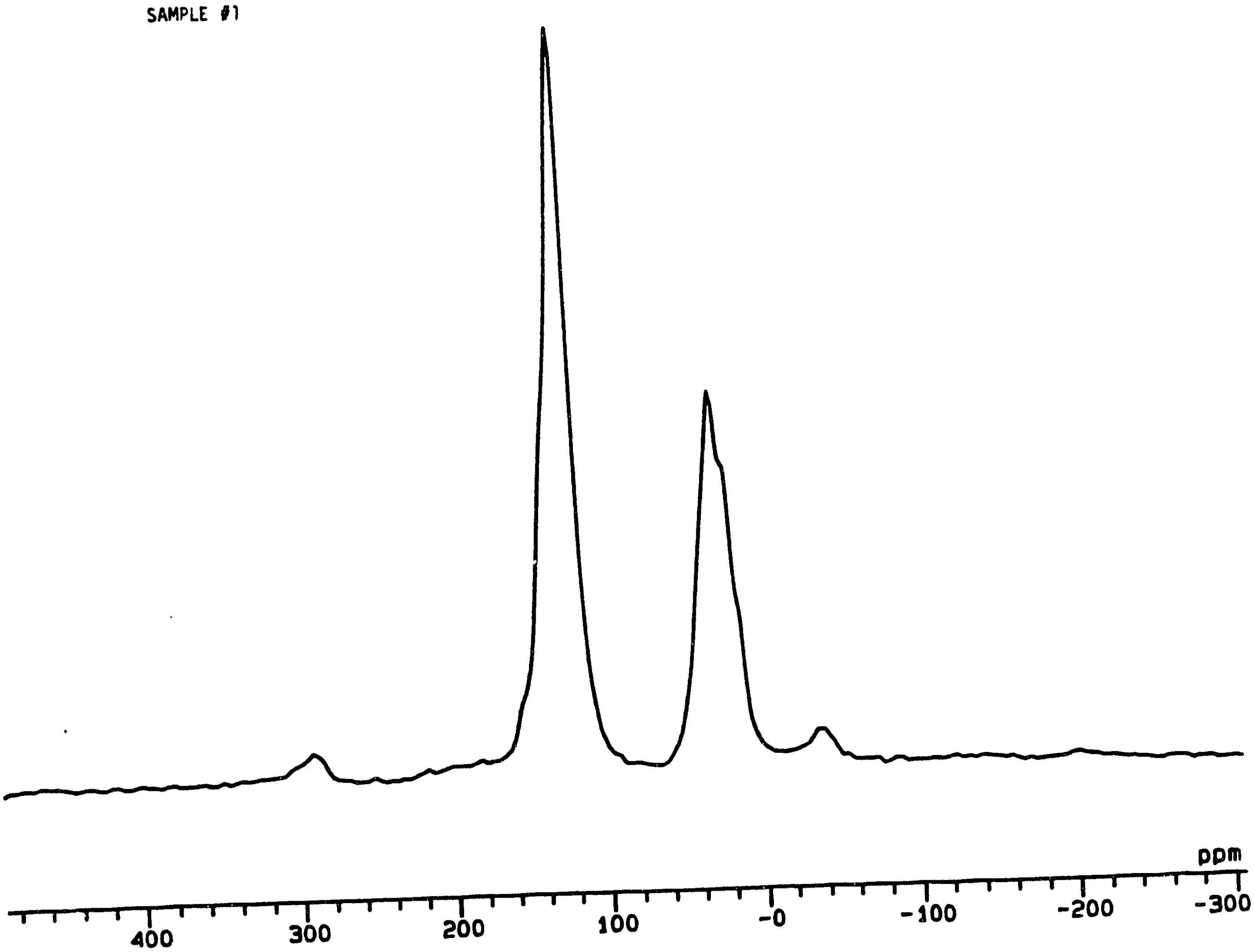
SPECTRA

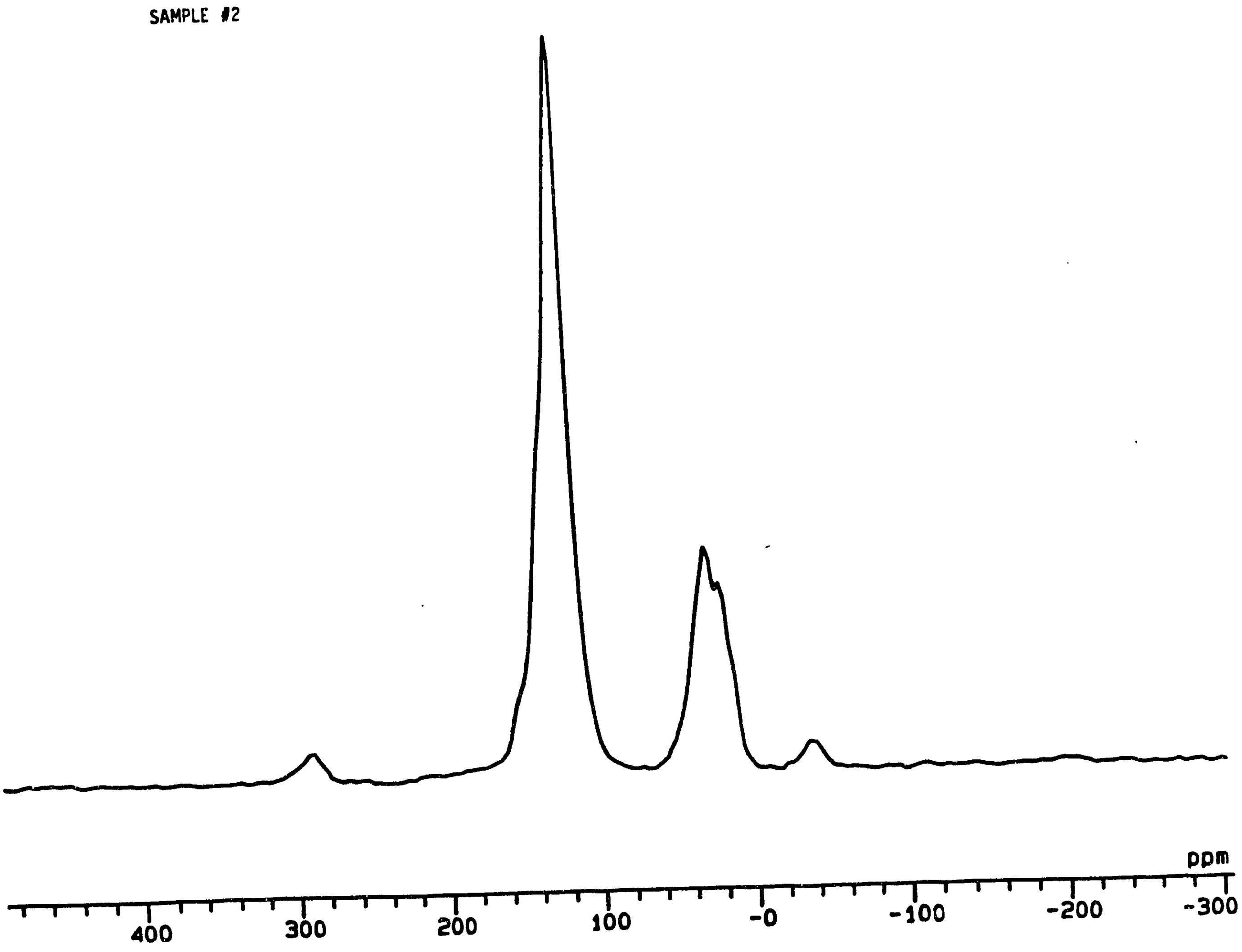
FOR

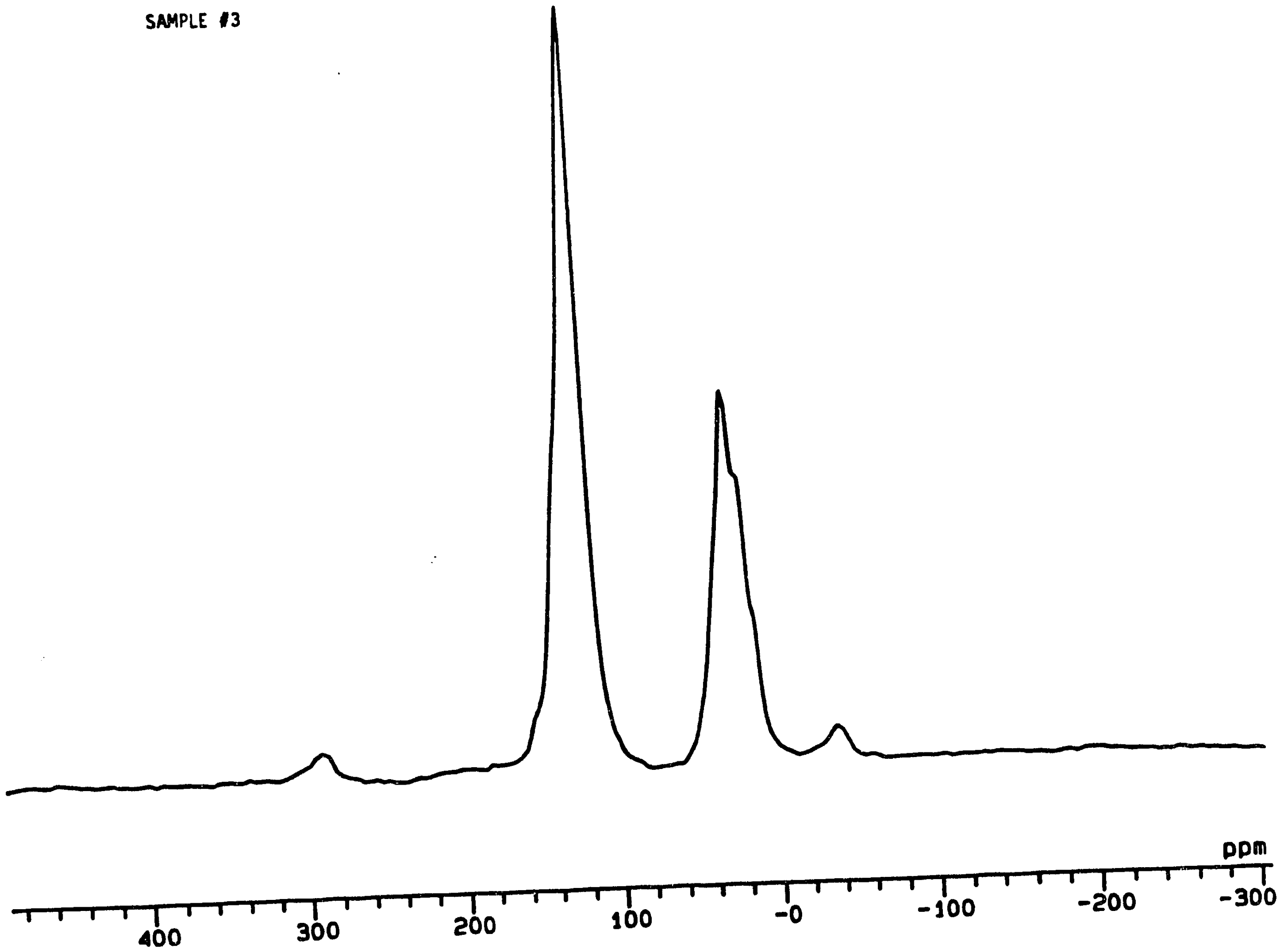
12

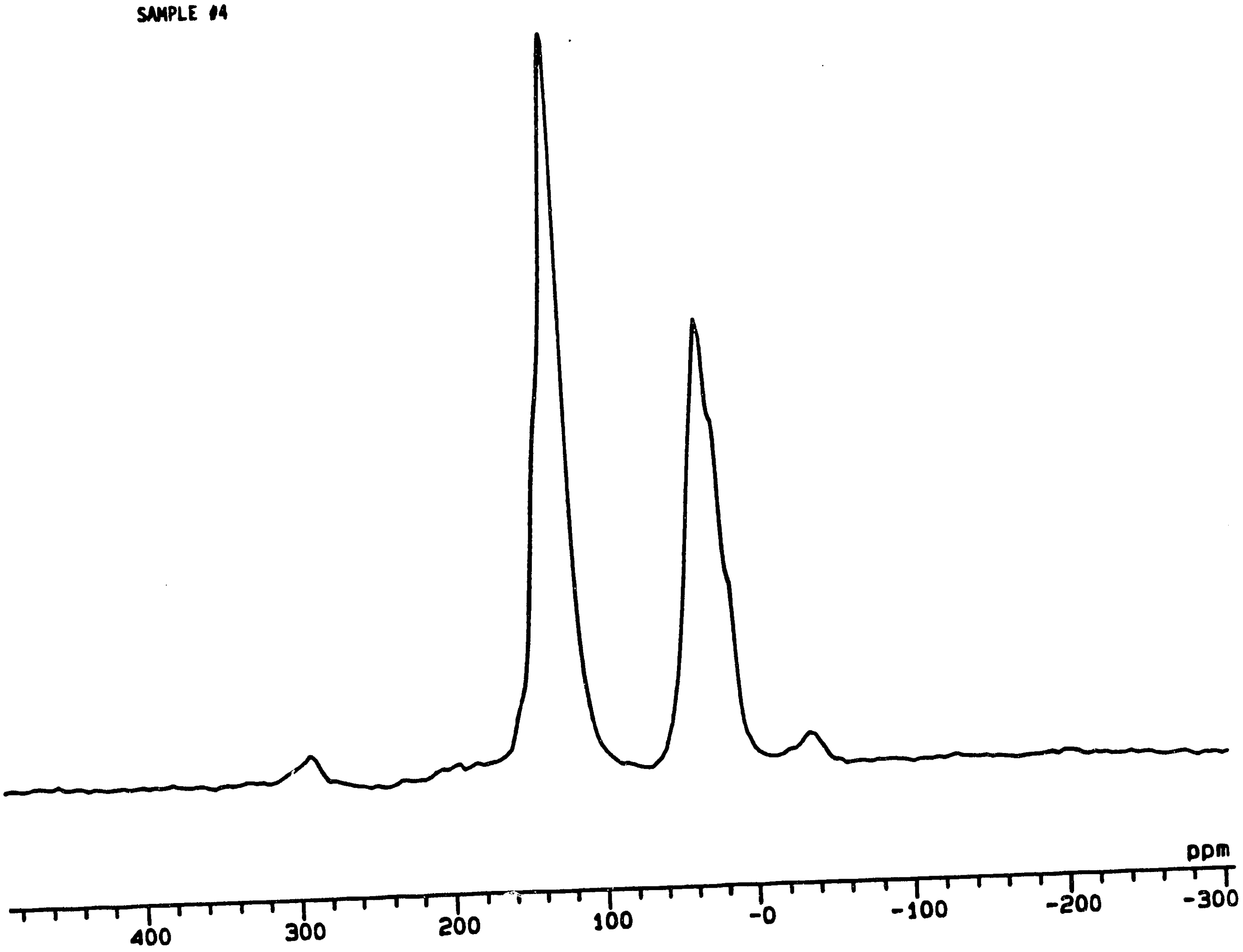
RESID

SAMPLES

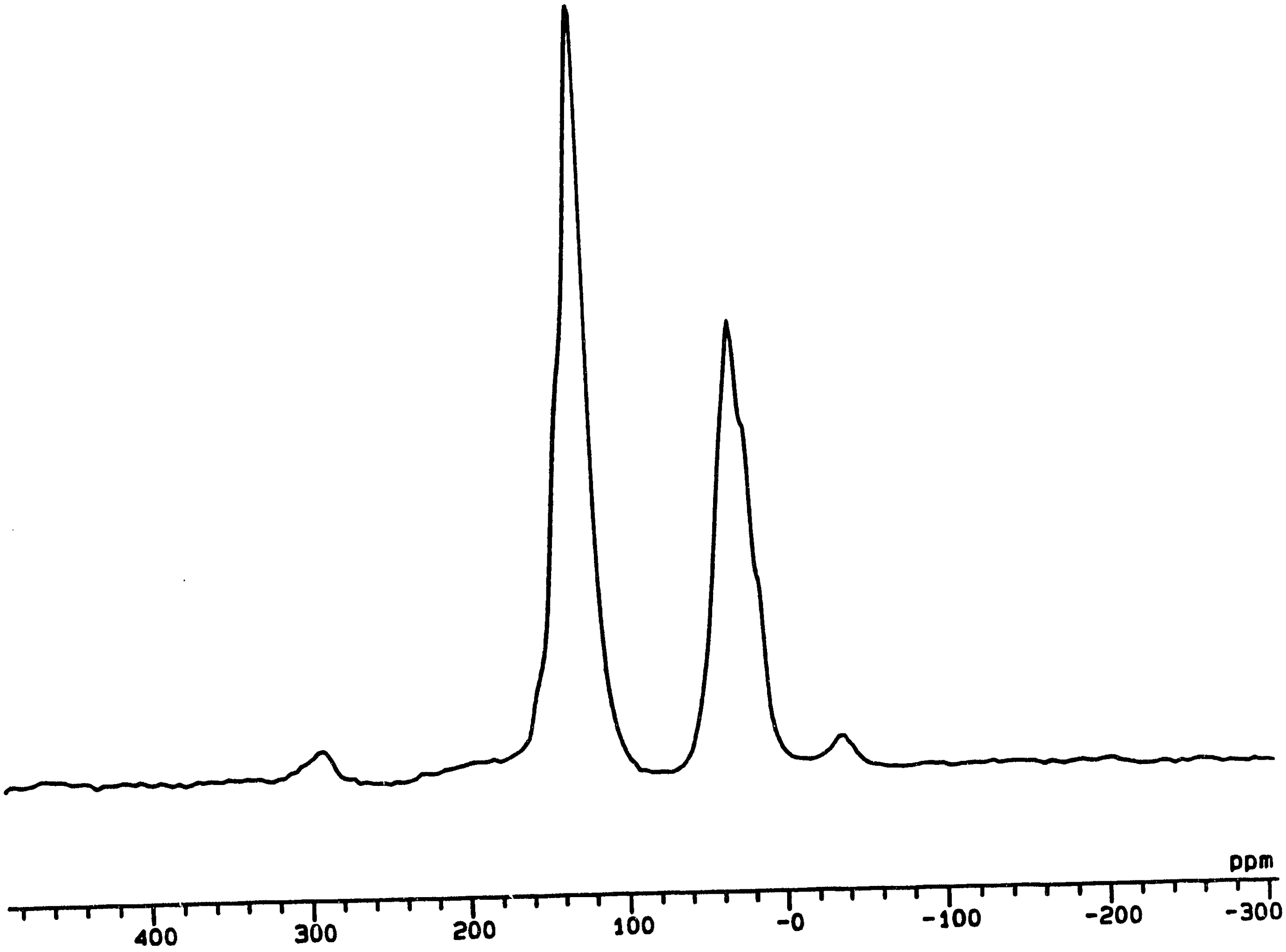

SAMPLE #1
ppm
400
300
200
100
-0
-100
-200
-300

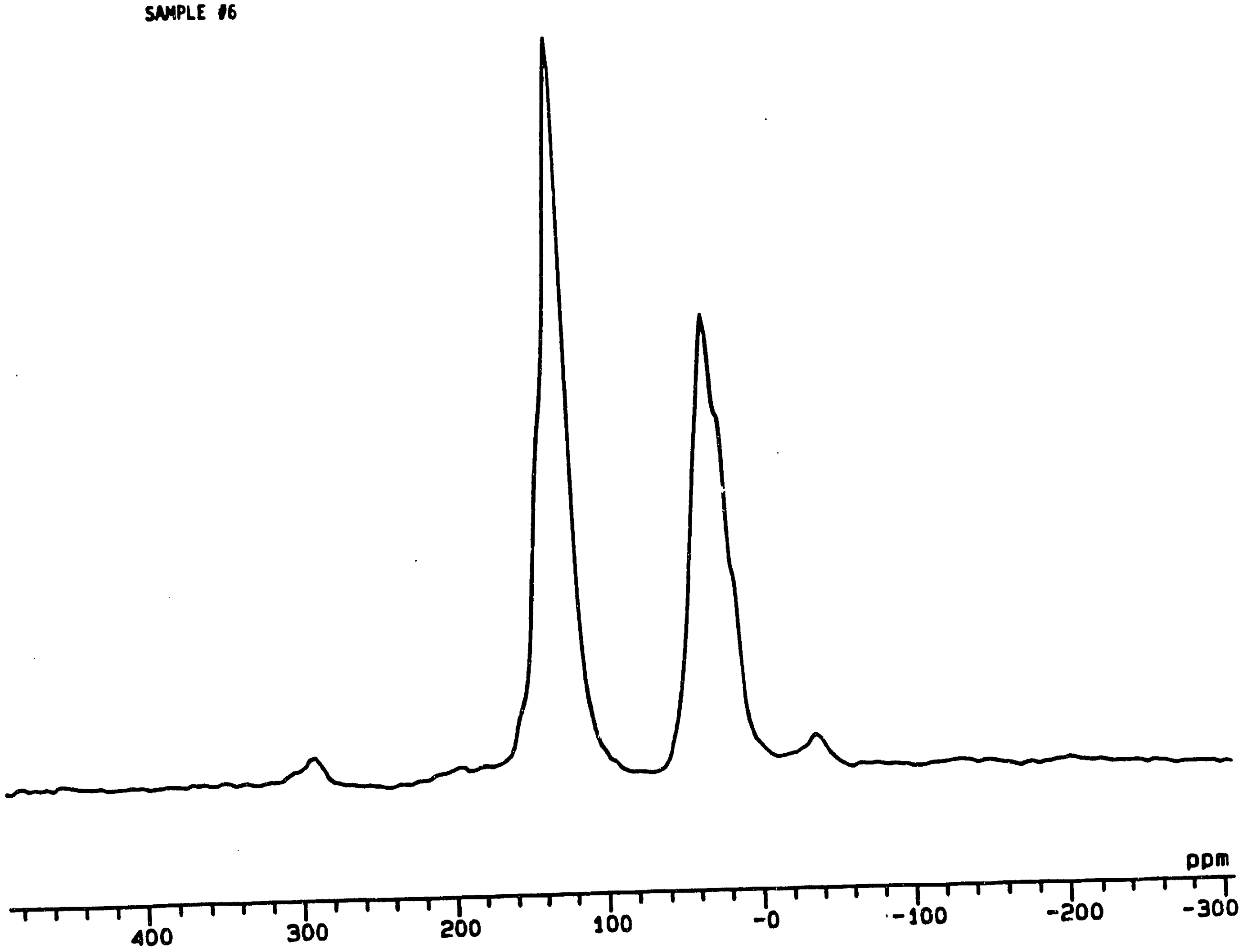

SAMPLE #2
ppm
400
300
200
100
-0
-100
-200
-300

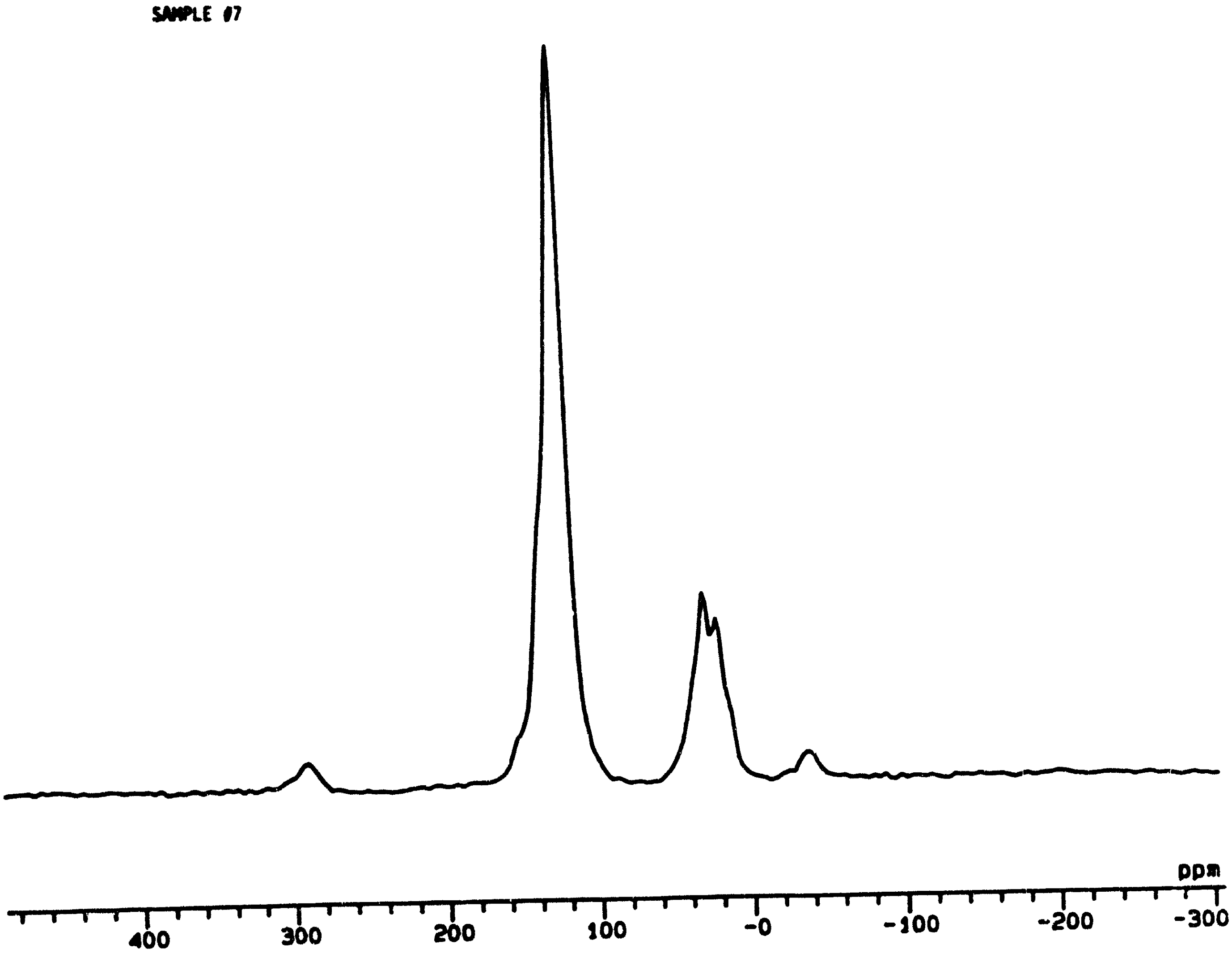

SAMPLE #3
ppm
400
300
200
100
-0
-100
-200
-300

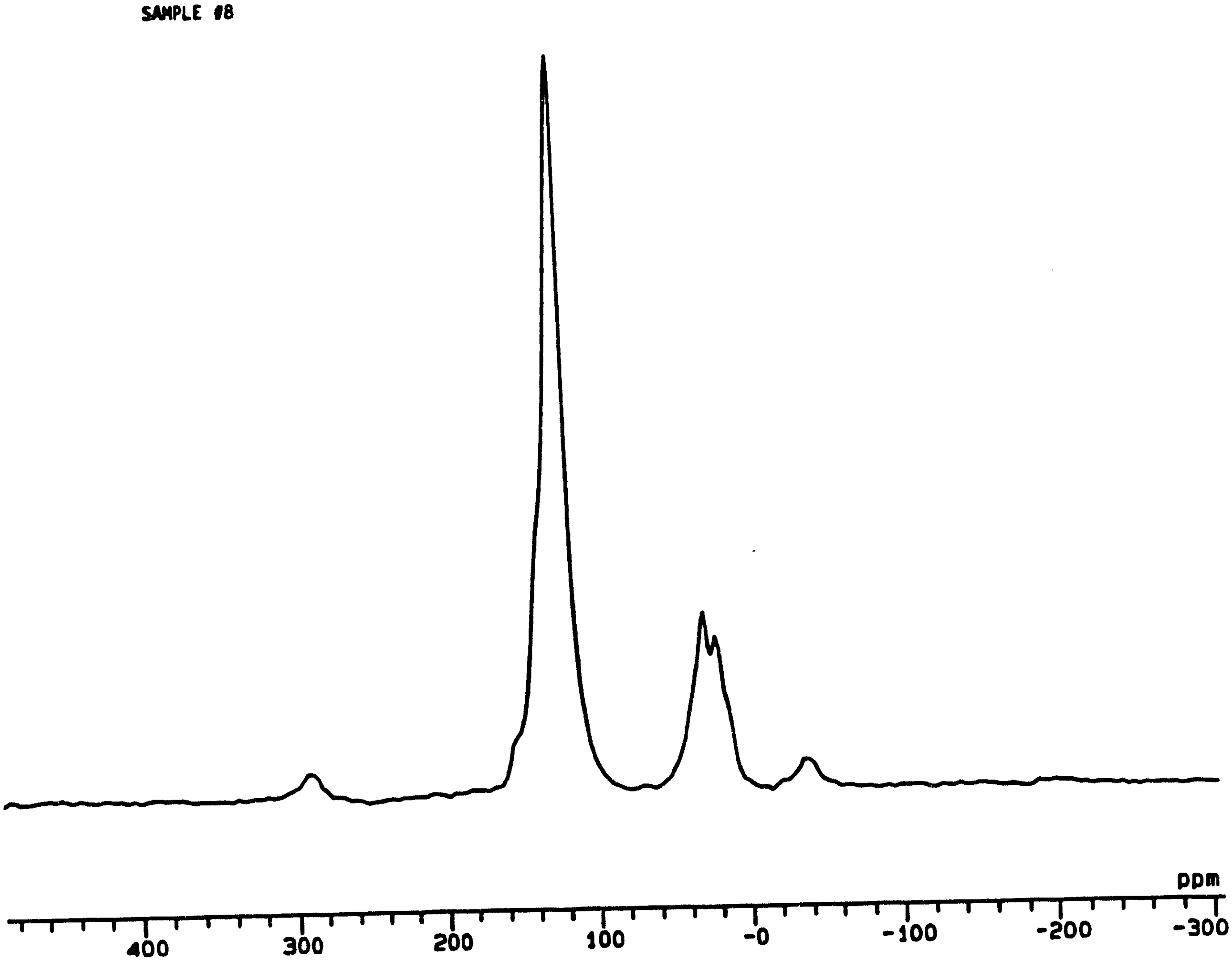

SAMPLE #4
ppm
400
300
200
100
-0
-100
-200
-300

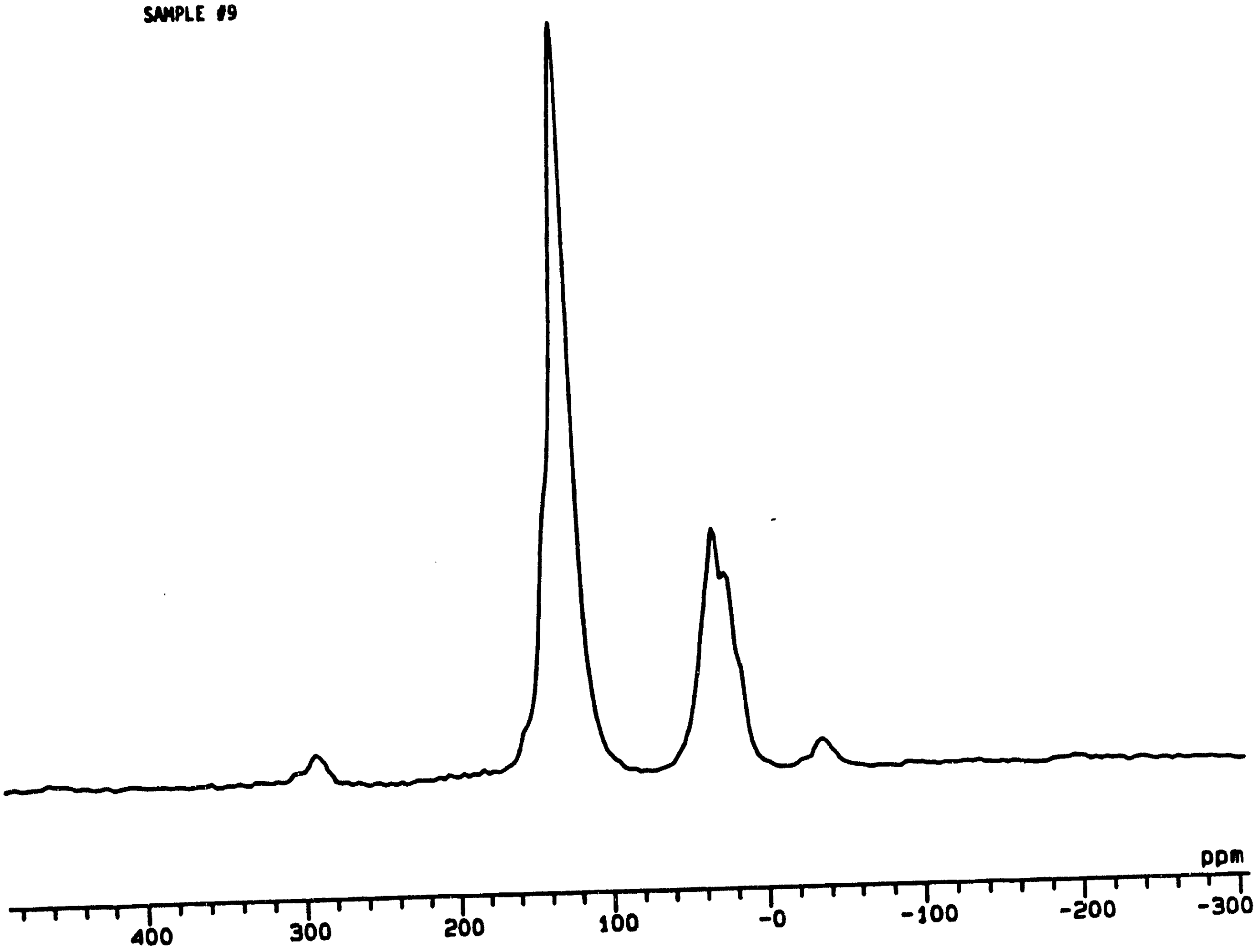
SAMPLE #5

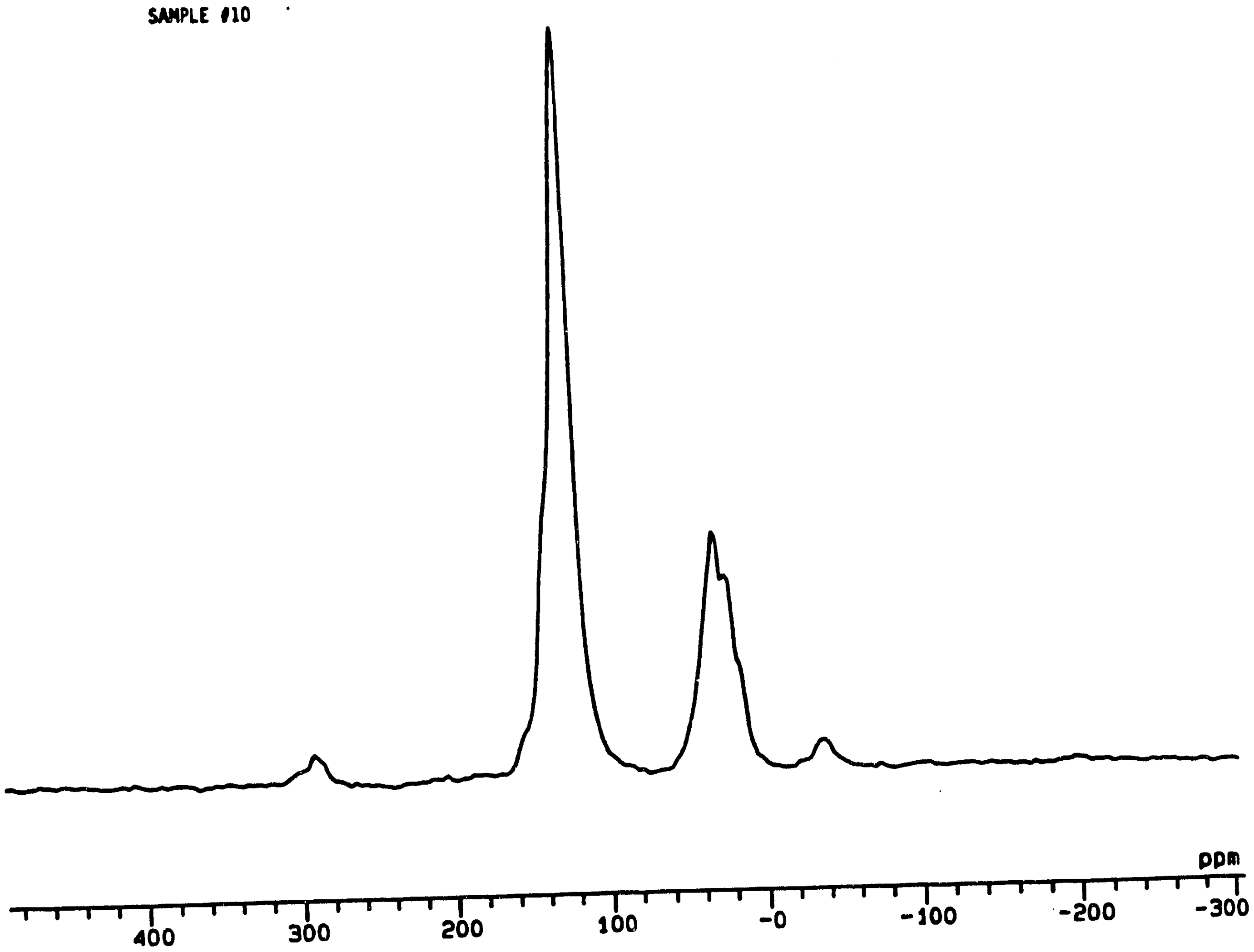


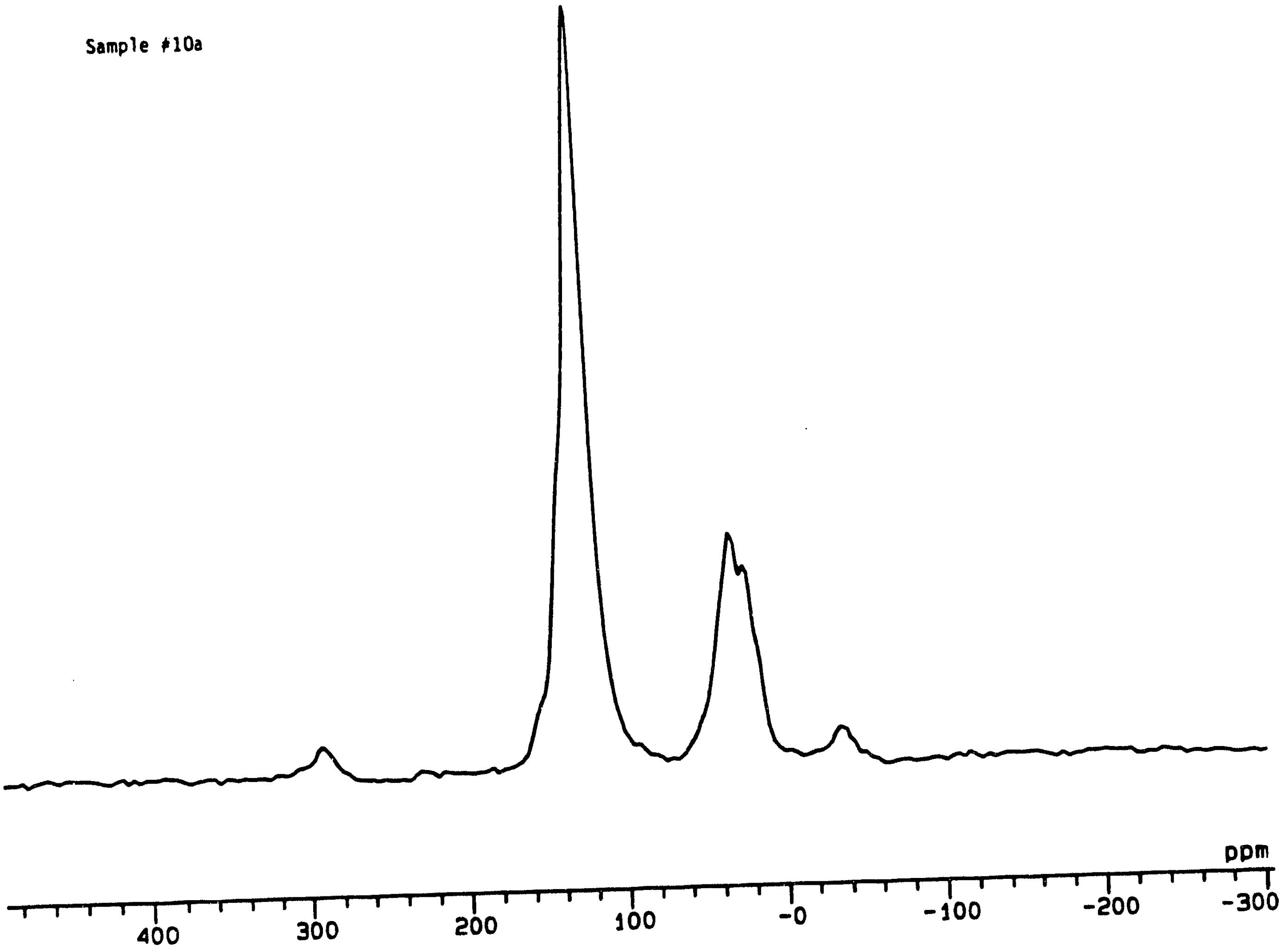

SAMPLE #6
ppm
400
300
200
100
-0
-100
-200
-300

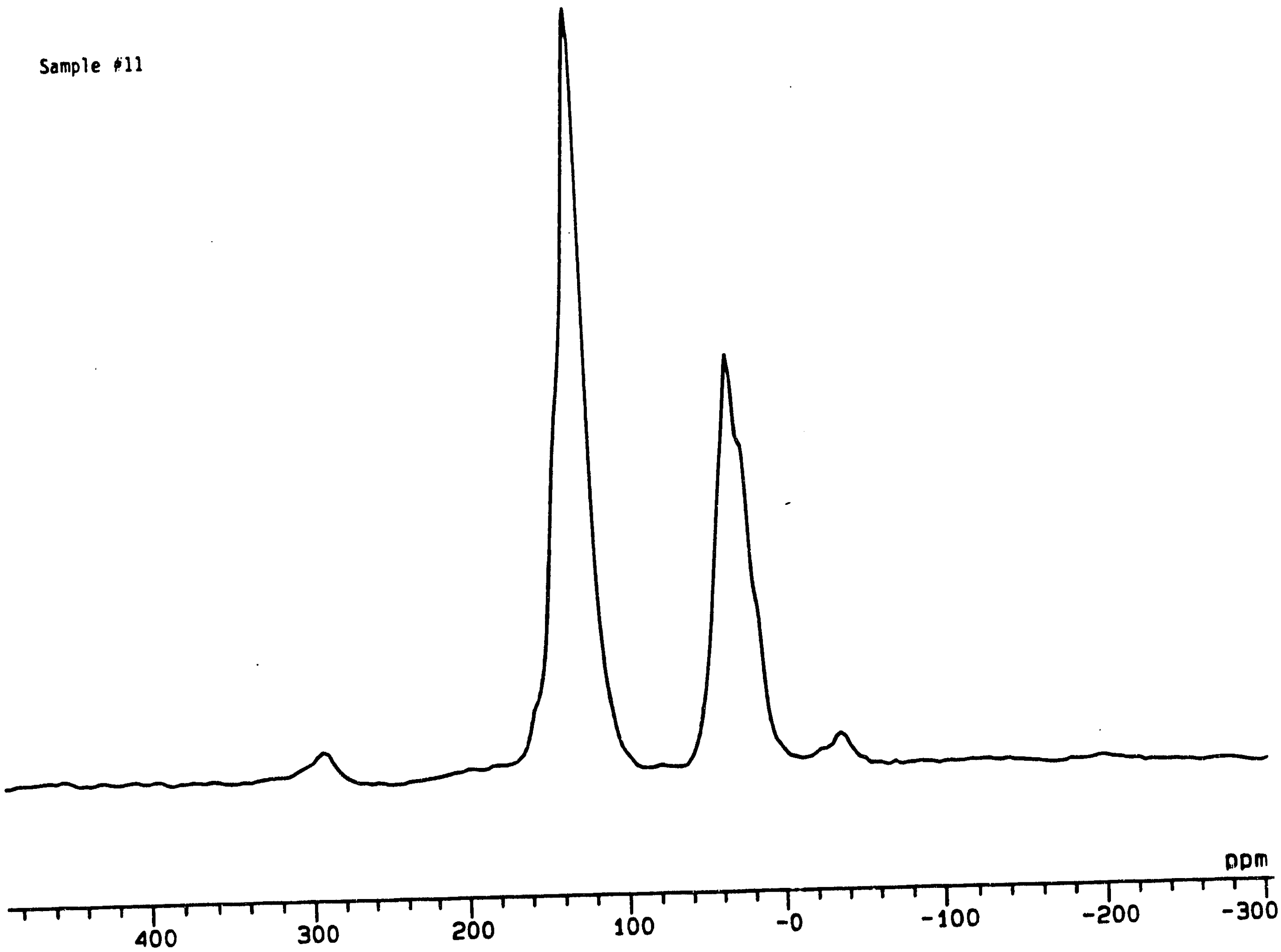

SAMPLE #7
ppm
400
300
200
100
-0
-100
-200
-300


SAMPLE #8
ppm
400
300
200
100
-0
-100
-200
-300


SAMPLE #9
ppm
400
300
200
100
-0
-100
-200
-300


SAMPLE #10
ppm
400
300
200
100
-0
-100
-200
-300


Sample #10a
ppm
400
300
200
100
-0
-100
-200
-300


Sample #11
ppm
400
300
200
100
-0
-100
-200
-300

END

DATE FILMED

3/31/93