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COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION

Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization

Topical Report

By
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Donald F. McMillen
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January 1992

Work Performed Under Contract No. AC22-89PC89883

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PROJECT ASSESSMENT

Introduction

Under subcontract to Consolidation Coal Co. (U.S. DOE Contract No. DE-AC22-89PC89883), SRI International evaluated two analytical methods for application to coal liquefaction. These included field ionization mass spectrometry (FIMS) and a technique employing iodotrimethylsilane for the derivatization of oxygen bound to alkyl carbon (alkyl ethers). The full report authored by the SRI researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the methods 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 provided a clear demonstration of the potential utility of field ionization mass spectrometry (FIMS) for the examination of distillation resid materials (b.pt. >850°F) derived from direct coal liquefaction. The technique can be used to determine the molecular weight profile of a resid sample and provide speciation of some components of the resid. A simple data analysis method which deconvolutes the mass profile into two groups was applied to the FIMS profiles generated in this study. Using this approach, quantified differences among the samples could be related to the various process conditions under which the samples were produced. It was also possible to make inferences from the FIMS data regarding resid reactivity. The FIMS technique, coupled with this or similar data analysis methods, therefore, can be considered a potentially useful technique for the process developer. Homologous series of various tetra- to hexacondensed aromatics (and naphthenoaromatics for which no corresponding fully aromatic structures exist) were identified in the samples. These compounds have been shown by others to be related to the reactivity of petroleum vacuum gas oil toward hydroprocessing. It appears that this is also true concerning the reactivity of coal-derived resids toward hydrocracking and that the presence of these compounds is related to the processing conditions that produced the samples. Further development of this analytical method as a process development tool is justified based on these results.

The use of iodotrimethylsilane to derivatize and subsequently quantitate the oxygen bound to alkyl carbon in coal liquefaction resids also was investigated in this study. The total amount of derivatizable oxygen was found to be less than 20% of the total oxygen for all samples. Experimental problems were encountered in the application of this method that prevented a more precise determination of the concentrations of alkyl carbon/oxygen bonds. Further development of this analytical method as a process development tool does not seem to be justified on the basis of these results.

Program Description

This report describes the work performed at SRI International under a subcontract to Consolidation Coal Co., 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 process development, and those which have not been fully demonstrated in this application. Consol is providing well-documented samples from different direct coal liquefaction process development 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.

Participant's Methodology

SRI used field ionization mass spectrometry (FIMS) to analyze distillation resids (850°F$^+$). These are solids at room temperature, and contain THF-soluble and insoluble organic material and mineral matter. The samples were produced at the Wilsonville pilot plant. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic or catalytic/catalytic). Samples from Wilsonville were taken from three locations: between the reactors, after the second-stage reactor, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. The majority of the Wilsonville samples were composites of samples taken over long periods of single runs. Two interstage samples were obtained from single run periods and were chosen to represent thermal vs. catalytic first-stage processing. The FIMS experimental procedure is described on pages 3-4 of the attached report.

The oxygen derivatization (iodotrimethylsilane analysis) technique was applied to whole process oils obtained from two facilities: the Wilsonville pilot plant and Hydrocarbon Research Inc. (HRI) bench unit. Feed coal rank was the major processing parameter which varied among the Wilsonville runs. Samples from HRI were chosen to represent production of material from runs utilizing a raw feed coal and a feed coal that had been pretreated to reduce its oxygen content. The experimental procedures utilized in these analyses are described on page 28 of the attached report.

Participant's Major Findings

FIMS

SRI reported the following principal observations for the application of FIMS to coal liquefaction materials. An expanded discussion can be found in the attached report, pages 4-28. Many of the FIMS spectra showed distinct bimodal distributions. Because of this, a simplified data analysis scheme was applied in which the mass profiles were mathematically deconvoluted into two curves with maxima at about 350 and 600 Da. The areas under these curves were assigned the names "Component A" and "Component B", respectively. Components A and B were quantified and used in a simple conversion model for the assumed production and consumption routes of the components. This model is described in Table 4 in the text. Relative changes in Components A and B could be observed in relation to process parameters such as feed coal, sampling point, reaction conditions, and yield structure. The SRI researchers noted that changes in Components A and B were consistent with changes in resid conversion and retrogression, as observed in the process yields.

Specific chemical structures could be assigned to prominent peaks in the 240 to 320 Da range of the FIMS spectrum. The compounds identified are either tetra- to hexacondensed aromatic hydrocarbons, or naphtheno-aromatic compounds that have no fully aromatic analog. Homologues of these compounds with molecular weights of up to 350 Da were observed. These structural assignments correspond closely to the compounds observed by Sullivan et al.[1] in hydroprocessed petroleum vacuum gas oils. Sullivan et al. implicated these compounds in decreased reactivity toward conversion, and increased coking and catalyst deactivation. SRI found the highest average concentration of these compounds in the resids from Wilsonville Run 259 (Pittsburgh seam coal), intermediate concentrations in the resids from Wilsonville Runs 257 (Ill. 6 coal) and 255 (Texas lignite), and the lowest concentrations in the resids from Wilsonville Runs 251-II (Wyodak coal) and 250 (Ill. 6 coal). In light of the work of Sullivan et al., the fact that the resids with the lowest apparent reactivity toward conversion (Run 259) contained the highest concentration of these compounds appears to be a significant finding regarding resid reactivity. SRI speculates that it is probably condensed aromatic structures such as these, not oxygenated structures, which are responsible for retrogressive reactions in highly processed coal liquefaction resids.

Derivatization

In an effort to quantify the oxygen bound to alkyl carbon in coal liquefaction resids, researchers at SRI used a derivatization technique which employs iodotrimethylsilane in an organic solvent. The extent of reaction of the iodosilane reagent with the resid is determined by measuring the amount of unreacted iodide in solution. Although the solvent of choice (acetonitrile) is a poor solvent for the resid, good solvents (e.g., pyridine, tetrahydrofuran) interfere with the iodotrimethylsilane reagent; therefore, chloroform, which is a moderately good solvent, was used. An attempt to use an ion-selective electrode to quantify the amount of iodide ion produced from unconverted iodotrimethylsilane was unsuccessful; ion-exchange chromatography was used instead. Unexpected background reactions with the chloroform were responsible for about a 10% loss of iodide ion in the analysis. Analysis of the data corrected for the 10% loss shows that less than approximately 20% of the total oxygen in the resids is bound to aliphatic carbon. Though this is not a precisely determined result, it is consistent with the known phenolic oxygen contents of these materials, which are about 50 to 75% of the total oxygen. Accuracy and precision of the method employed would need to be improved to improve the utility of the method. SRI notes that further development of this method should not be a high priority.

Consol Evaluation

The FIMS technique was shown to be potentially useful for the analysis of direct coal liquefaction resid samples in support of process development. The FIMS profile consists of a broad distribution of molecular weights ranging from 200 to 1000 Da. In many cases, the spectra had a distinctly bimodal distribution. The novel use of a simplifying two-component model to handle the complex FIMS profiles proved to be highly effective. The two pseudocomponents, centered at about 350 and 600 Da, were quantified by use of a non-linear regression routine that fitted an expression to the general forms of the peaks. Fitting parameters were derived from a few sample spectra. Although the function chosen may not provide the best fit for these data, it was sufficiently good for interpretive purposes. Differences in the relative weight percent of these components for different samples could be attributed to changes in process parameters. This simple scheme holds great potential for process development application. Another possible application of these easily derived values is their use in sophisticated numerical models of coal liquefaction processes.

The structural identification of some molecular components in the 240 to 320 Da range may provide important information regarding the fundamental chemistry involved in resid reactivity and coal processing. It is considered highly likely that the concentration of these compounds is related to the degree of difficulty in hydrocracking/hydrotreating the resids examined.

The FIMS method relies on volatilizing the sample under high vacuum. Although the percent of volatiles closely matched the tetrahydrofuran (THF) solubility of the sample, it did not correspond to the total organic content of the sample. It is likely that the FIMS analyses performed here did not include the highest molecular weight, least soluble portion of the distillation resid. This will have to be considered in the application of the method. The capital investment for FIMS equipment is approximately $250,000; cost for expendables is on the order of $40 per sample. It requires one-half hour for sample preparation and approximately one to two hours of instrument time to analyze one sample. The computer time and cost for the mathematical deconvolution and curve fitting technique are trivial.

Quantitation of the aliphatic oxygen in resids by derivatization with an iodosilane reagent showed that typically less than 20% of the total oxygen contained in these materials is bound to alkyl carbon atoms. Although the results obtained by this method are consistent with other available information, the accuracy and precision of the method are considered poor. The technique can not be considered rapid as applied here; i.e., with ion chromatographic, rather than ion-selective electrode, detection. The chromatographic method must be conducted by a skilled technician and it requires more manpower than the electrochemical technique originally attempted.

Further Development

There are a number of avenues for further development of the FIMS technique for analyzing coal liquefaction derived resids in support of process development. A better curve-fitting routine could be developed using a more sophisticated mathematical function. This may provide some further insight into the nuances of shifts in the molecular weight distributions attributable to processing conditions. Analyses of whole process stream samples, rather than of only resids, and evaluation of data on a mass-flow basis would aid in understanding the pseudocomponent reactions. Additional speciation of the compounds in the FIMS profile will provide a better picture of the fundamental chemistry of the coal-derived resids. Some attention should be given to better quantifying the completeness of volatilization of the samples.

Contractor's Statement of Work

Field Ionization Mass Spectrometry (FIMS) is a technique which has been used for a variety of applications relevant to coal liquefaction. It has not, however, been demonstrated widely for its ability to answer questions pertaining to the chemistry of coal conversion. As such, it fits well within the scope of the participants program.

The application of FIMS to a reasonably large sample set (17 samples) will allow a demonstration of the value of this technique. These samples have been selected (see Table 1 in the attached text) so that the utility of FIMS for addressing the issue of resid reactivity can be evaluated. The seventeen samples will be supplied to SRI with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^{1}H-NMR, resid reactivity data (calculated), and the full history of the sample (plant, process conditions, age, and storage conditions). All samples are non-distillable residual materials which may contain insoluble organic matter (IOM) and ash. Sample size will be at least 0.5 g. Most samples will be brittle pitch-like materials that will be supplied as approximately -8 mesh (2.4 mm) pieces.

The evolution of various compound types (for example, alkanes, phenols, dihydroxybenzenes, etc.) will be followed through the thermal program of the FIMS experiment. This FIMS profiling will be done for each sample. These data then will be used in a factor analysis for correlation of the FIMS data with other sample properties or attributes such as feed coal, operating conditions, chemical analyses, and resid reactivity.

The analysis of oxygen functional groups in coal-derived resids is of particular interest. A wet chemical technique in which trimethyl-iodosilane is used to derivatize the alkyl carbon-oxygen bond will be applied to resid-containing coal liquefaction oils. Alkyl carbon-oxygen bonds are quantified by measuring the reacted iodine. The reaction and analysis will be performed in pyridine solution. Six samples will be provided to SRI for derivatization. Four of these samples (those from Wilsonville) are whole oil composites comprised of samples taken over a large portion of a specific run. These materials may contain ash and THF insoluble organic material. The two samples from HRI are pressure filter liquids and as such contain only traces of insolubles. Each of these samples will be supplied with the following information: elemental analyses, ash content and ash elemental analysis (where appropriate), phenolic -OH concentration, calorific value, hydrogen classes by ^{1}H-NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Sample size will be at least 5 g.

SRI International

Final Report • November 1991

CHARACTERIZATION OF COAL LIQUIDS

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SRI Project No. 2177
Contract No. DE-AC22-89PC89883

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SUMMARY

SRI International has analyzed a series of coal-derived residual oils by field ionization mass spectrometry (FIMS) and explored the feasibility of using iodotrimethylsilane as an ether-cleavage reagent for determining the amounts of aliphatic carbons bearing oxygen in these resids. The general objective of this work is to understand how coal characteristics and/or variations in process configuration impact resid reactivity and ultimately to determine the chemical and physical differences in these resids responsible for the reactivity differences.

The FIMS analysis of 15 resid samples, taken from three sampling points in five close-coupled two-stage liquefaction runs at the Wilsonville facility, shows the samples to be very similar in some respects. This similarity was expected since these resids are constrained to appear similar by their complexity (which usually gives similar intensities for nearby nominal masses), by identical distillation processes, and by changes in process parameters that are typically made to keep product quality and operability within acceptable limits. Nevertheless, FIMS analysis of the whole resids provided spectra showing significant differences, easily apparent to the eye, in the overall spectral profiles.

Because the spectral profiles appeared as if they resulted from the superposition of two curves, with intensities peaking at about 350 and 600 Da, we mathematically deconvoluted the profiles into lumped Components A and B, respectively, and assigned these components places in a simple lumped conversion model. We then proceeded to test whether the changes in the two components with sampling point, coal type, and process conditions made a picture that was self-consistent and bore any relationship to the changes in yield structure with changes in these same variables. This test showed that the correspondence was surprisingly good, given the complexities and the simplifying assumptions. That is, the changes in the percent of low-mass and high-mass components were consistent with the ease or difficulty of resid conversion and retrogression, as observed in the yield structures.

In addition to differences in the overall profiles, FIMS analysis of resids also showed a substantial level of "structure" in the 240 to 350 Da range. This structure, seen as large ratios (5/1 or more) in the intensity of adjacent even masses, most certainly carries additional chemical information, but it requires great hubris to speculatively assign, without benefit of additional information, chemical structures to nominal masses in this range where the starting material was itself an unknown and exceedingly complex material. In view of this complexity, we were gratified to note that all of the prominent peaks in this range corresponded to PCAH species that

have previously been identified by Sullivan and Boduszynski and coworkers in petroleum vacuum gas oils (VGO), and implicated in increased coking, catalyst deactivation, and decreased process performance in VGO hydrotreatment.[1] Thus, while phenolics and other oxygenated structures have been implicated as the primary candidates for the retrogressive reactions limiting the initial conversion of coals during liquefaction or pyrolysis, it is probably PCAH structures such as these that are responsible for coking in these heavily processed resids.

The use of iodotrimethylsilane to quantitate the oxygen bound to alkyl carbon in the resids yielded the finding that the levels of such oxygen are quite low, typically less than 20% of the total oxygen. A background reaction of the iodotrimethylsilane with the solvent chloroform limited the accuracy of the determinations for these low levels of alkyl-O structures, and would need to be suppressed if accuracy and precision are to be improved. The finding of low levels of cleavable oxygen compounds may also carry information about the abundance of another class of oxygen structures, benzylic phenols. Such structures are potentially important as retrograde intermediates in the thermal conversion of virtually any phenolic feedstock, but specific information on their presence would require additional pure compound studies. On balance, we judge, from the low levels of total oxygen in these resids, from the small percentage in alkyl ether (i.e., thermally labile) structures, and from the recognition of prominent PCAH components in the resids that are likely coke precursors, that future efforts in oxygen speciation via iodotrimethylsilylation do not warrant first priority.

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INTRODUCTION

Under a subcontract from Consolidation Coal Company (Consol), SRI International analyzed a series of heavy oils by field ionization mass spectrometry (FIMS) and tested the feasibility of using a derivatization scheme using iodotrimethylsilane for determining the amount of aliphatic carbons bearing oxygens. This work was conducted under the Participants' Program of Consol's contract with the U.S. Department of Energy, Pittsburgh Energy Technology Center (PETC) on the characterization and evaluation of coal liquefaction process streams. One objective of Consol's program is to provide a bridge between direct coal liquefaction process development and analytical chemistry. More specifically, under this Participants Program Consol provides a range of well-documented samples obtained from process development units to various analytical researchers, who then apply their chosen methodology to determine the value of the method to process understanding and development. One goal of SRI's project was to help answer several questions relating to the chemistry of liquefaction and how to improve the overall process.

The technique of field ionization (FI) consists of passing the vapors of a material through a region of intense electric field to polarize and ultimately ionize the molecules. The ions are then mass analyzed using standard mass spectrometric techniques. For most organic compounds, this procedure causes minimal fragmentation and produces only the molecular ions. The resulting spectra are thus true representations of the molecular weight profiles of the volatilized materials. FIMS has been used for a variety of applications relevant to coal liquefaction. However, its ability to answer the very difficult questions pertaining to the chemistry of resid reactivity has not been demonstrated. The objective of the task on FIMS analysis was to evaluate the utility of FIMS for addressing the issue of resid reactivity by analyzing a reasonably large set of related samples. Table 1 lists the samples sent to SRI for analysis by FIMS and by the scheme using derivatization with iodotrimethylsilane.

The analysis of oxygen functional groups in coal-derived resids is of particular interest. SRI proposed a wet chemical technique in which iodotrimethylsilane is used to derivatize the alkyl carbon-oxygen bond. This technique was applied to resid-containing coal liquefaction oils. Iodotrimethylsilane converts C_{al}-O bonds into C_{al}-I bonds. Thus, dialkyl ethers, aryl alkyl ethers, and esters of aliphatic alcohols will consume iodotrimethylsilane and produce organic iodides. Other reactions of iodotrimethylsilane, such as hydrolysis and reduction of sulfoxides, ultimately produce inorganic iodide (I^-). The scheme consists of allowing a known amount of iodotrimethylsilane to react with a known amount of resid; following the reaction, the entire sample is quenched by aqueous workup, producing I$^-$ from unconverted iodotrimethylsilane. Thus, only that iodotrimethylsilane which produced R-I from aliphatic ethers will fail to generate I$^-$. By comparing the amounts of I$^-$ from samples with resids and controls, we can quantify alkyl carbon-oxygen bonds.

Table 1

SAMPLES FOR FIMS AND IODOTRIMETHYLSILANE ANALYSES

Sample	Coal Feed	Source/Conditions	Sample Point
FIMS analysis			
1	Illinois No. 6	W; Run 257 G; L/H	Interstage oil
2	Illinois No. 6	W; Run 257 F; H/L	Interstage oil
3	Illinois No. 6	W; Run 250; T/C	Product oil
4	Illinois No. 6	W; Run 250; T/C	Recycle oil
5	Illinois No. 6	W; Run 250; T/C	Interstage oil
6	Illinois No. 6	W; Run 257; C/C	Product oil
7	Illinois No. 6	W; Run 257; C/C	Recycle oil
8	Illinois No. 6	W; Run 257; C/C	Interstage oil
9	Wyodak	W; Run 251-II; T/C	Product oil
10	Wyodak	W; Run 251-II; T/C	Recycle oil
11	Wyodak	W; Run 251-II; T/C	Interstage oil
12	Lignite	W; Run 255; T/C	Product oil
13	Lignite	W; Run 255; T/C	Recycle oil
14	Lignite	W; Run 255; T/C	Interstage oil
15	Pittsburgh	W; Run 259; C/C	Product oil
16	Pittsburgh	W; Run 259; C/C	Recycle oil
17	Pittsburgh	W; Run 259; C/C	Interstage oil
Iodotrimethylsilane analysis			
18	Wyodak	W; Run 251-II	Recycle oil
19	Lignite	W; Run 255	Recycle oil
20	Illinois No. 6	W; Run 257	Recycle oil
21	Pittsburgh	W; Run 259	Recycle oil
22	Black Thunder	HRI; Run 227-57;P 14	PFL
23	Black Thunder	HRI; Run 227-62;P 16	PFL

NOTE: All samples for FIMS analysis are distillation resids. All samples for iodotrimethylsilane analyses are whole oils.

C/C = catalytic/catalytic; T/C = thermal/catalytic; H/L = high/low (first state/second stage) reactor temperature; L/H = low/high (first state/second state) reactor temperature; P = period; W = Wisonville; PFL = pressure filter liquid.

TASK 1. FIMS ANALYSIS OF RESIDS

EXPERIMENTAL PROCEDURES

The analyses were conducted using SRI's FIMS instrument, which consists of a foil-type field ionizer interfaced with a 60-degree magnetic-sector mass analyzer and a PDP 11/23 computer for instrument control, data acquisition, and report production. The spectrometer has a resolving power ($M/\Delta M$) of 1300, although it is capable of scanning up to 3000 Da. Typically, approximately 20 µg of the sample is taken in a melting point capillary and introduced into the spectrometer with a heatable direct insertion probe. The sample is heated at a fixed rate from ambient (or ~-67°C for samples with sufficiently high vapor pressure) to about 700°C. The pressure in the ion source chamber is generally in the 10^{-6} Torr, although the pressure in the capillary sample holder is considerably higher. We estimate the sample pressure to be around 10^{-4} Torr. Under these conditions materials with atmospheric equivalent boiling points (AEBP) up to about 1400°F are expected to vaporize completely, and those with AEBPs in between 1400° and 1600°F to vaporize at least partially. What often limits the vaporization of these high boiling materials are the coupling reactions with other species present in the sample. Hence the quoted limits should be regarded as a rough guide. (Similarly, other pyrolytic reactions can occur that produce volatile species not present at such in the original mixture.) The spectra of the evolving volatiles are continuously recorded, and at the end of a run, they are added to produce a "sum" spectrum of the total volatiles.

Sampling

The amount of sample analyzed is small, and there is a possibility of analyzing a non-representative sample. The samples received from Consol were composites of many periods during a run. They had been finely ground to homogenize them, although most of the samples contained a few large particles along with the fine particles. To minimize this risk of non-representative sampling, we normally use a procedure that tends to reject the few large particles and focuses on the fines. Typically, we would introduce about 30 fine and perhaps 100 ultrafine* particles into the capillary tube. Thus, to the extent that the bulk of each of the original samples from different periods in a run was ground to fine particles, this procedure should have resulted in analysis of a sample representative of the whole run.

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* Fine here is defined n ~50 - 120 µm; ultrafine as 5-50 µm.

Heating Regimen

The exact regimen used for analyzing the set of samples was arrived at by analyzing one sample from each of the four coal types and examining their vaporization behavior. We found that the samples generally evolved above 70°C. Given that these samples were vacuum resids, we did not expect any volatiles at ambient temperatures. However, we noticed that one sample (Sample No.6) gave volatiles even at very low temperatures and required cooling with liquid CO_2 to intercept all the volatiles. Therefore, we settled on a fixed regimen that called for initial cooling of the samples and then heating them at a rate of 5°C/min to 500°C. The heating rate was kept constant except when sample volatility dictated slowing down to avoid overloading the ion-counting electronics. This regimen allowed us to collect about 16 subspectra for each sample corresponding to different temperature ranges. To facilitate future comparison between different samples, we tried to collect subspectra over identical temperature ranges as far as practical.

RESULTS

Volatility and General Features

FI-mass spectra of all the samples together with their thermal evolution profiles are included in the Appendix. Figures 1 and 2 show the plots of the interstage oil from periods F and G of Run 257. These spectra are typical of the entire set. They consist of a broad distribution of molecular weights ranging from about 200 to 1000 Da. There is an additional group of peaks in the 50 to 120 Da range corresponding to small fragment ions. The total intensity of this low-mass group is typically extremely low compared to that of the main profile, reflecting the minimal ion fragmentation that is typical of most liquefaction product streams during FIMS analysis. Immediately apparent from these spectra are two profiles: a more intense profile for the even masses and the other (dark profile) corresponding to the odd masses. Peaks at odd masses generally arise due to ^{13}C, N, or fragmentation. Because FIMS does not cause much fragmentation and these spectra have been corrected for natural abundance of ^{13}C, the odd-mass profile arises mainly from compounds containing nitrogen.

Table 2 gives the fraction of the sample vaporized during the FIMS analysis. The volatility of the oils from the Illinois No. 6 and Pittsburgh coals was generally around 90%, while that from the lower rank coals was substantially less. The volatility of the resids appears to be largely governed by the amount of minerals present in the sample. In most cases the observed volatility corresponds to the THF-solubility determined at Consol. However, we recognize that there are

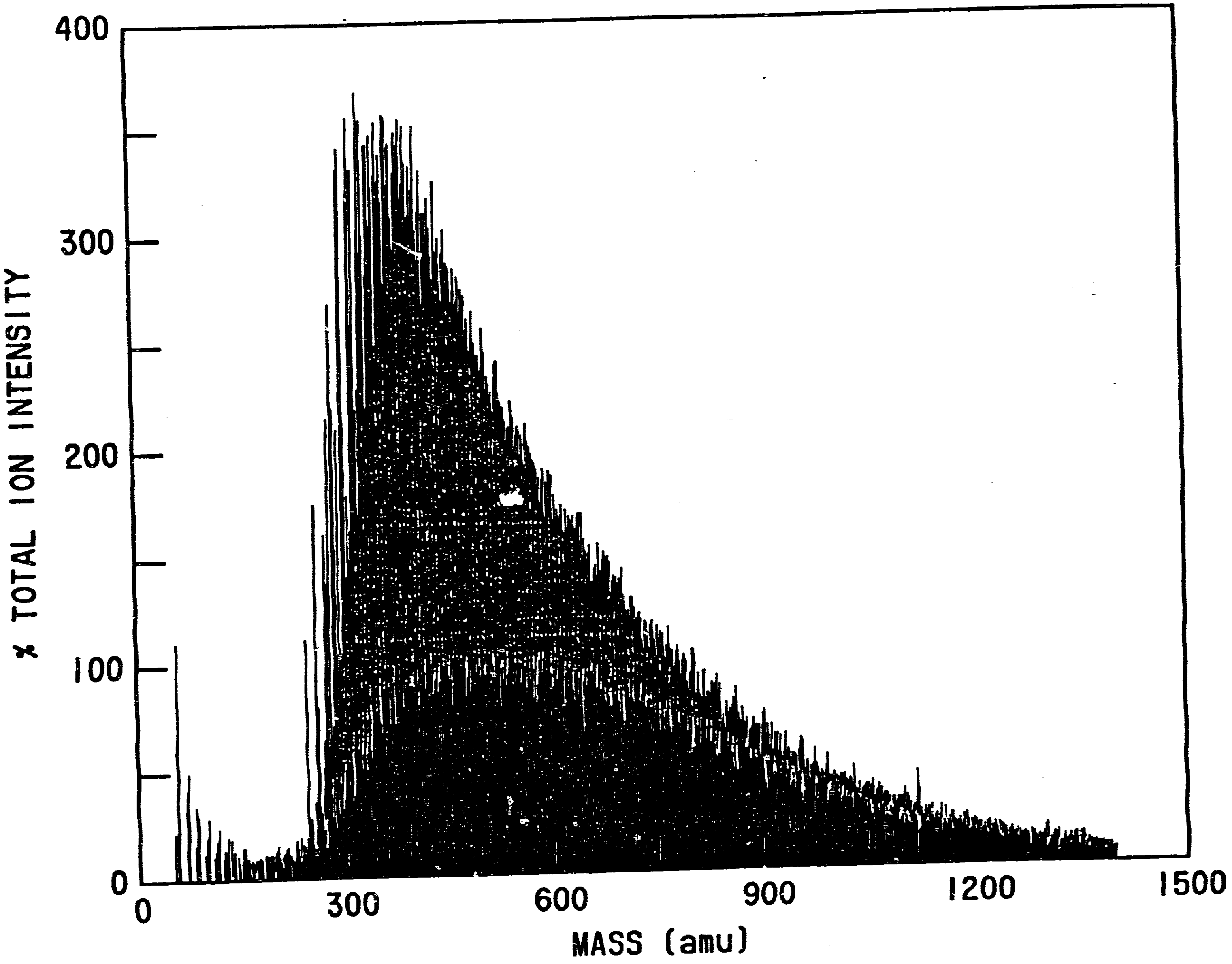

Figure 1. FIMS of interstage oil from Period G of Run 257

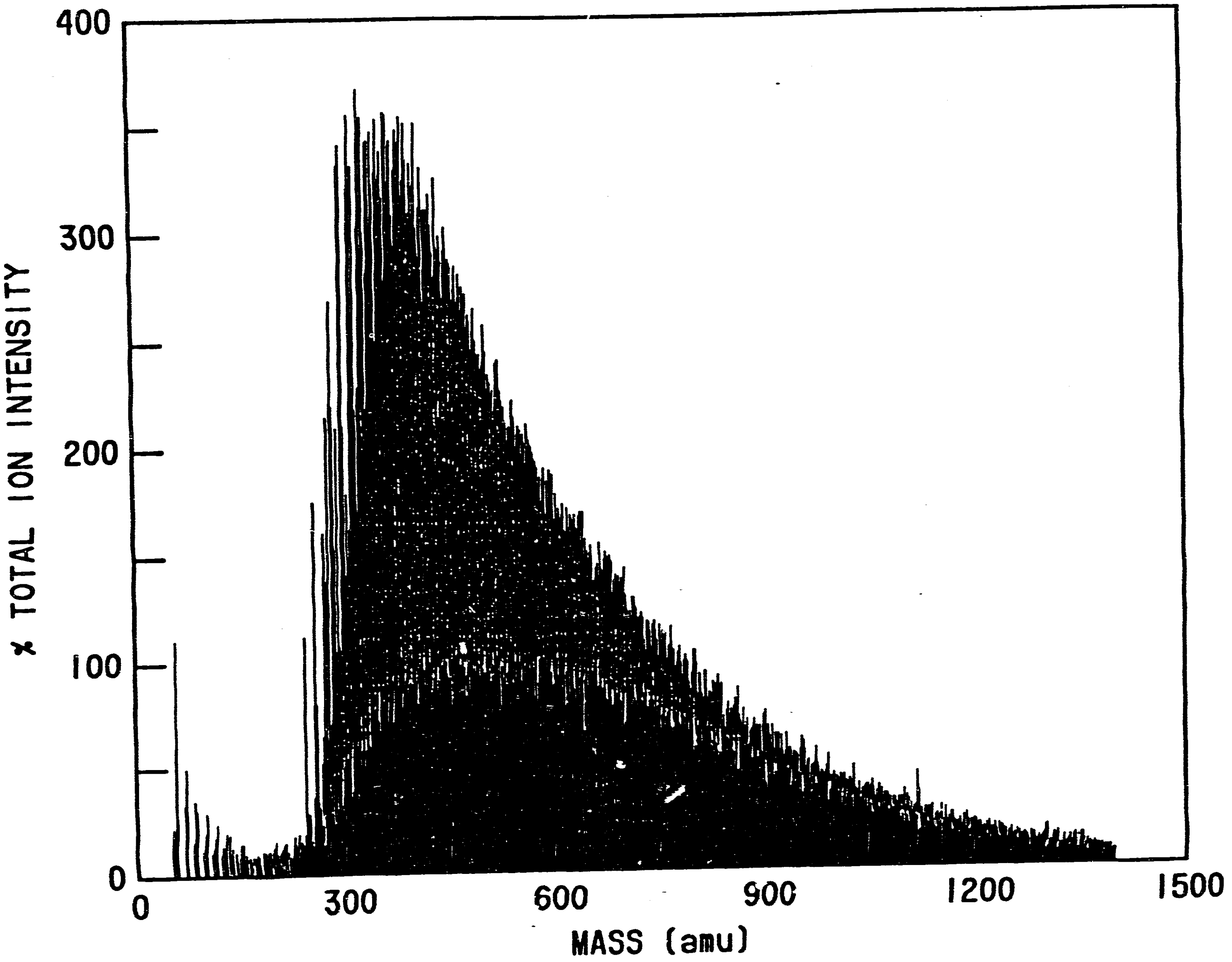

Figure 2. FIMS of interstage oil from Period F of Run 257

a few outliers. For example, the observed 100% vaporization of Sample Nos. 1, 2, 6, and 17 does not seem reasonable in view of the fact that they too contained substantial (~10 to 20%) ash. Furthermore, Samples 1, 2, and 8 are all interstage oils from Run 257, the first two being from periods G and F respectively and the third a composite sample. Yet, Samples 1 and 2 were found to be 100% volatile in the FIMS and Sample 8 to only 77%. Thus, either the sampling procedure was not always successful in obtaining a representative sample from the ground composite, or FIMS volatilities do not reliably correlate with the mineral or THF-insolubles content.

Table 2

PERCENTAGE OF VOLATILITY AND COMPONENT A IN THE RESID SAMPLES

Ref. No.	Coal, Run	Sample Point	FIMS Volatility (%)	THF-Solubility (%)[a]
1	Ill. No. 6, 257, G	Interstage Oil	100	72.6
2	Ill. No. 6, 257, F	Interstage Oil	100	75.5
3	Ill. No. 6, 250	Product Oil	75	84.6
4	Ill. No. 6, 250	Recycle Oil	75	99.6
5	Ill. No. 6, 250	Interstage Oil	90	89.2
6	Ill. No. 6, 257	Product Oil	100	65.2
7	Ill. No. 6, 257	Recycle Oil	90	75.9
8	Ill. No. 6, 257	Interstage Oil	77	66.2
9	Wyodak, 251	Product Oil	62	56.5
10	Wyodak, 251	Recycle Oil	57	59.6
11	Wyodak, 251	Interstage Oil	41	57.4
12	Lignite, 255	Product Oil	60	52.4
13	Lignite, 255	Recycle Oil	57	56.5
14	Lignite, 255	Interstage Oil	53	53.9
15	Pitts., 259	Product Oil	79	79.6
16	Pitts., 259	Recycle Oil	78	83.2
17	Pitts., 259	Interstage Oil	100	82.2

[a] Determined by Consol

At first glance, all the FI mass spectra in Figures 1 and 2, and those in the Appendix, look very similar. The similarity is reassuring because the following factors all tend to provide material of similar molecular weight range and polarity:

(1) Removal of material boiling at less than 850°F.

(2) Removal of some material rejected as insoluble by the ROSE-SR unit.

(3) The necessity for using a plant operating regimen in which process parameters are changed with a new feedstock to maintain operability (and therefore product quality) within certain limits.

Apart from being similar, the spectra also show that the resids are very complex mixtures. The bulk of the material in these samples falls in the 200-1200 molecular weight range and considering coal-origin and heteroatom content of the products, the "average" molecule at, say, m/z 600 would contain one oxygen, one nitrogen, and one-half sulfur. Therefore, most of the resid molecules are polyfunctional, and not classifiable, even in principle, according to simple chemical type or class.[2] For these reasons, we did not believe that an examination of the differences in the different resid samples in terms of individual molecular ion peaks should be the major focus of attention. Even when the differences in individual peaks were statistically significant, it would be nearly impossible, without additional information, to ascribe those differences to specific structural types. Thus, we focused primarily on clusters of peaks. We note here that there are a few peaks in the 240 to 340 Da range in each of the spectra that do stand out in all the spectra, and we examined them in some detail. However, before discussing this group of peaks, we first describe our attempt at a semi-quantitative.characterization the overall profiles.

In many instances, the spectra appear to be composed of two partially overlapping clusters of peaks: one such cluster, which we will call Component A, is centered around 350 Da and the other cluster, which we will call Component B, is centered around 600 Da. Relative to Component B, Component A appears to span a relatively narrower MW range. In other work, we had observed the somewhat bi-modal distribution of molecular weights in coal liquefaction resids. However, those observations were with isolated samples, and we were not sure if they were indicative of a general trend. Examination of seventeen related samples in this project confirmed the general nature of this distribution, and we felt encouraged to examine this distribution and see if the relative amounts of the two components can be correlated with some process-related parameters. Even visual inspection suggested that there were notable differences between the samples in the relative amounts of Components A and B. In the following section, we discuss how we quantified A and B, and the implications of the changes in their relative amounts with processing.

We also analyzed the spectra using SAS, a software package for statistical analysis. Our objective was to extract from the set of three spectra for each run a spectrum of the "invariant" component, the hypothesis being that the resids were composed of a relatively difficult-to-convert component ("invariant") and an easier-to-upgrade component ("residual"). However, this approach was not as successful as we had hoped. An easier way to examine the differences was to simply subtract the least common denominator. This latter exercise was extremely illustrative and highlighted the prominence of a light component (Component A, above) in the product oil of the Illinois No. 6 cat-cat run, as well as the double-humped nature of many of the profiles. However, the difficulty of attaching a direct meaning to the spectra obtained from this subtraction prompted us to to mathematically deconvolute the original spectra into two envelopes, and we subsequently directed most of our effort to examination of the deconvoluted spectra.

Analysis of Overall Profiles

Mathematical Deconvolution. Figures 3 and 4 show all the sum spectra laid out in two groups so that the overall nature of the profiles can be seen. All figures are shown to the same scale to aid direct visual comparison between spectra. In Figure 3, the spectra from the three thermal-catalytic runs are shown from left to right in order of increasing rank. In Figure 4, the two catalytic-catalytic runs with Illinois No. 6 and Pittsburgh coals are shown (center and right), and for comparison, the spectra from the thermal-catalytic Illinois No. 6 run are repeated (from Figure 3) on the left. In both figures, the spectra are arranged from top to bottom in order of increased level of processing (increased distance from the raw coal feed). The top row is the interstage oil (R1235, 1236, or 1258), the middle row is the product oil (second-stage reactor product, V1067), and the bottom row is the recycle oil (V131B). The process configurations were not identical for all runs; those differences most likely to be important will be considered in the discussion below.

As mentioned above, by simple visual inspection we can decompose both the odd-mass and the even-mass envelopes of the FI mass spectra into two components, a low-mass component, A, centered between 300 and 400 Da, and a broader, high-mass component, B, centered about 600 Da. Several steps are involved in deconvoluting the spectra and quantifying the amounts of A and B in any sample. First, we have to assign a general functional form to each of the component envelopes; second we perform a least-squares fit on a few selected samples to derive the parameters for the general formula describing the two components; third we fit the spectra using these expressions while varying only the relative amplitude factors, and finally, we integrate the product of mass with the fitted expressions over the mass range to obtain the relative *weight* fractions of the two components.

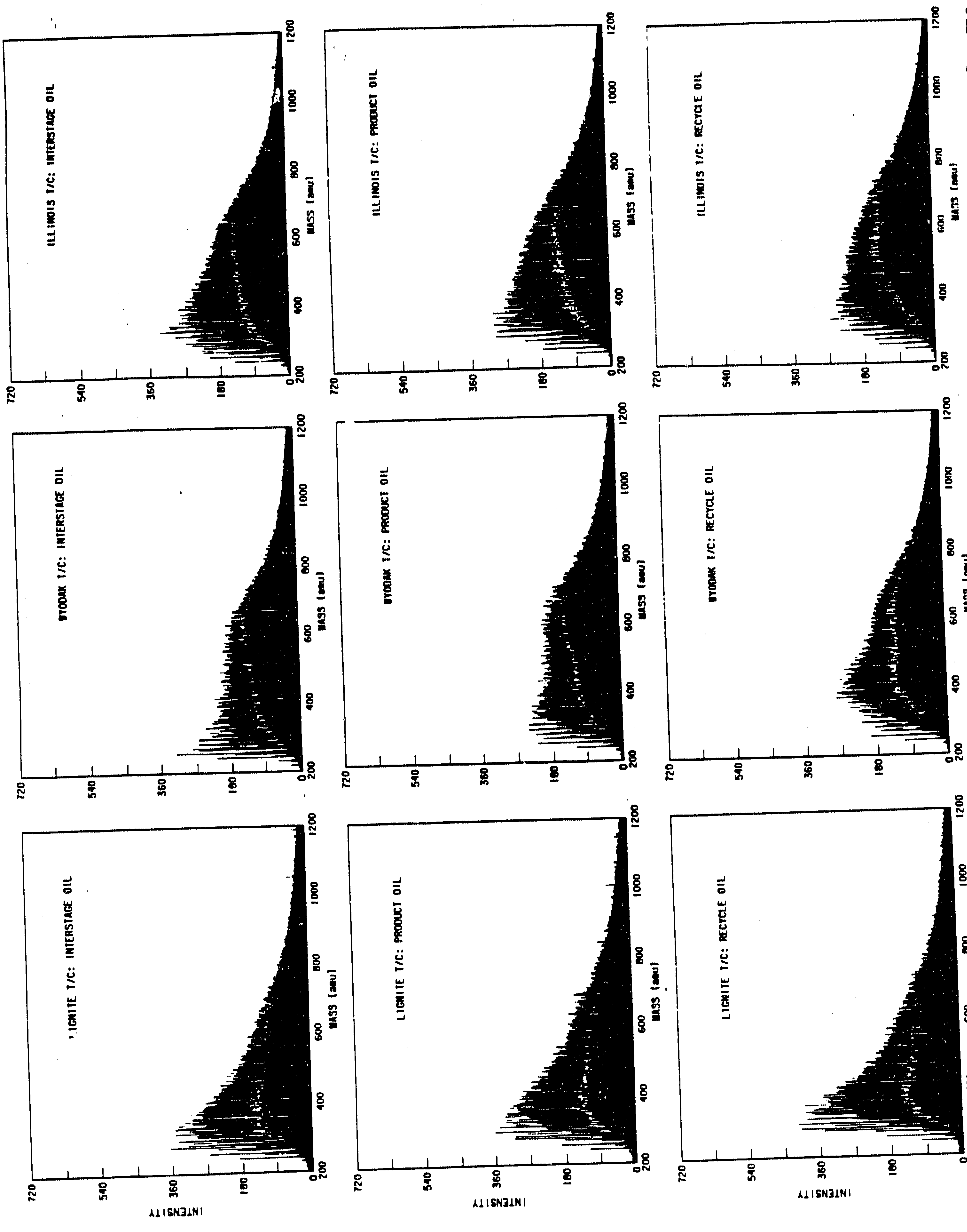

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Figure 3. FI-mass spectra of the resids from the therm-cat runs of Lignite, Wyodak, and Illinois No. 6 coals.

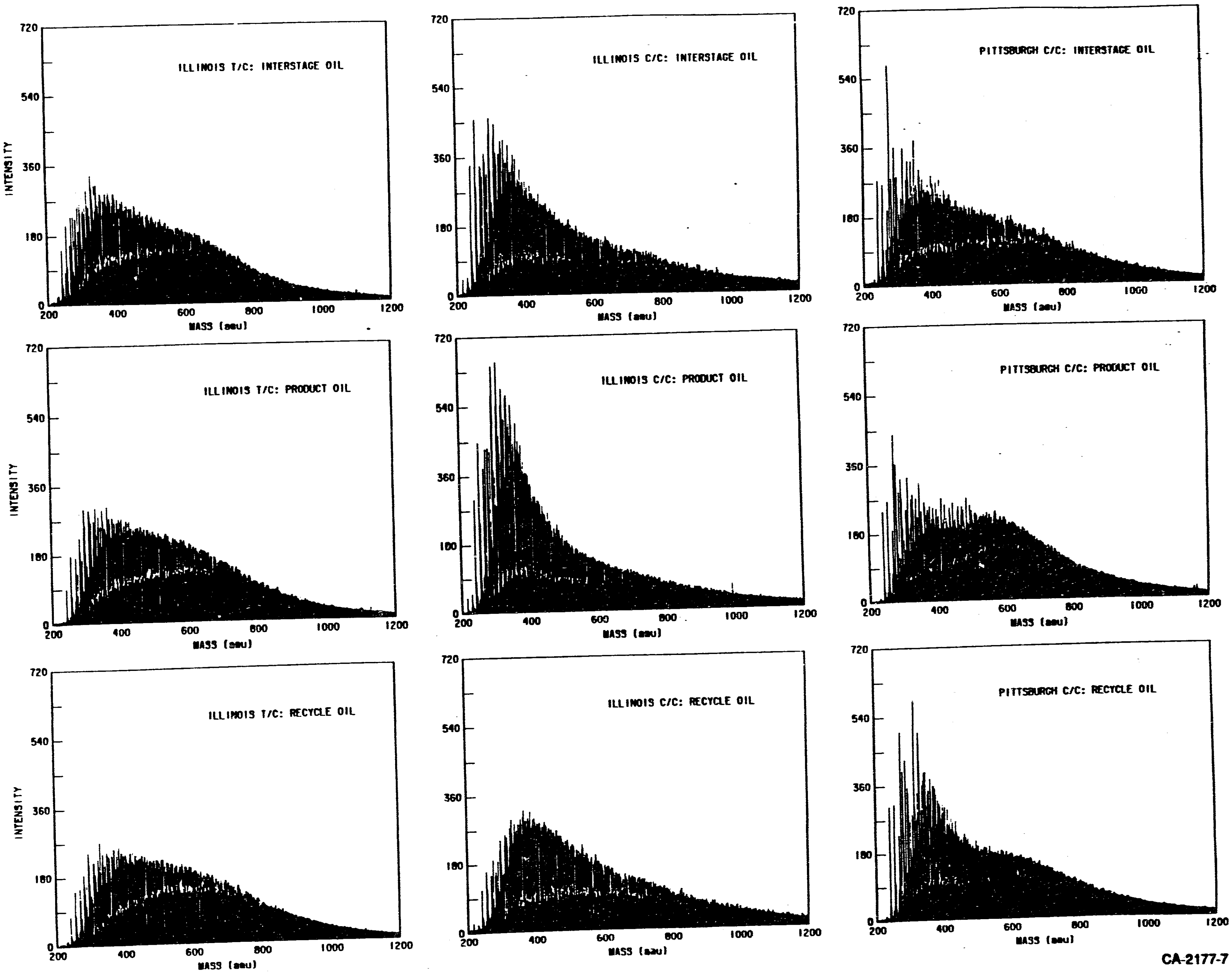

Figure 4. FI-mass spectra of the resids from the therm-cat and cat-cat runs of the illinois No. 6 coal and the cat-cat run of the Pittsburgh coal.

We chose to express the rising part of each envelope as a power function of the molecular weight (m^{α}) and the decline as an exponential ($e^{-\beta m}$). The parameters α and β were to be different for each of the two components, but the overall functional form was constrained to be the same. The following expression gives the intensity (I_m) at any mass:

$$I_m = Q_A m^{\alpha_A} e^{-\beta_A m} + Q_B m^{\alpha_B} e^{-\beta_B m}$$

Here Q_A and Q_B are the weighting factors for the two curves. The parameters α_A, β_A, α_B, and β_B were determined by a regression analysis. Rather than fit all of the spectra by regression, we decided that a more meaningful test would be to select for regression five of the most divergent looking spectra. Once the parameters α and β were determined, they were fixed and the remaining spectra were fitted by varying only the Q's.

Because the odd-mass profiles have lower intensity and slightly different shape, we at first performed the regression on them separately to provide two separate sets of shape parameters α and β. This resulted in deconvolution into four components (A_{even}, A_{odd}, B_{even}, and B_{odd}). However, given that this approach of deconvoluting the mass spectra had not been attempted before, and its value in explaining any trends resulting from process variations was uncertain, we decided to choose the simpler course and focus on the weight fractions of A and B determined by fitting the even-mass profiles, using parameters derived only from regression of five even-mass spectra. We also tried the other three combinations (even-profile parametrization applied to odd profiles, odd-profile parametrization applied to odd profiles, etc.). The use of even profiles with even-profile parametrization, however, gave the best fit, as indicated by the residuals, and was also the one that showed the largest range in the relative amounts of A and B. Accordingly, the %A and %B values (for the whole sample) are taken entirely from even profiles via the expression

$$\%A = \frac{100 \times \int Q_A m^{\alpha_A} e^{-\beta_A m} \cdot m \, dm}{\int Q_A m^{\alpha_A} e^{-\beta_A m} \cdot m \, dm + \int Q_B m^{\alpha_B} e^{-\beta_B m} \cdot m \, dm}$$

Figure 5 shows an example of the deconvolution. The dots are the data for the even masses in the FIMS of the recycle oil from the run with the Pittsburgh coal (Run 259). This spectrum was not among the ones used in the least-squares fit to obtain the parameters defining A and B. The continuous line through the data is the fit obtained by varying the amounts of A and B. The contributions of A and B components to the total fit are shown by the two dashed lines. The fit in this case is reasonably good over most of the mass range, except at high masses where the fit

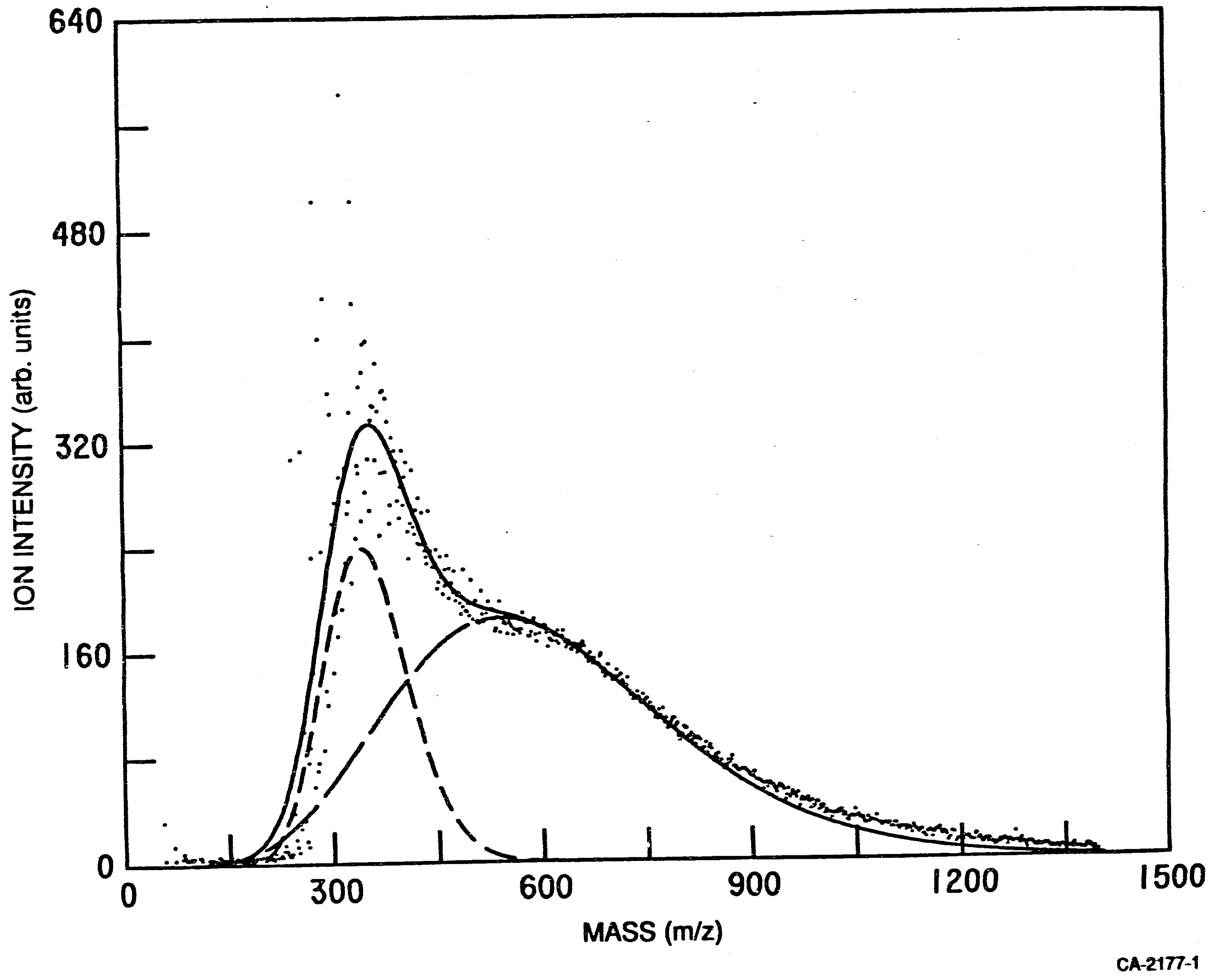

Figure 5. Deconvolution of FIMS of Pittsburgh (Run 259) recycle oil into Components A and B.

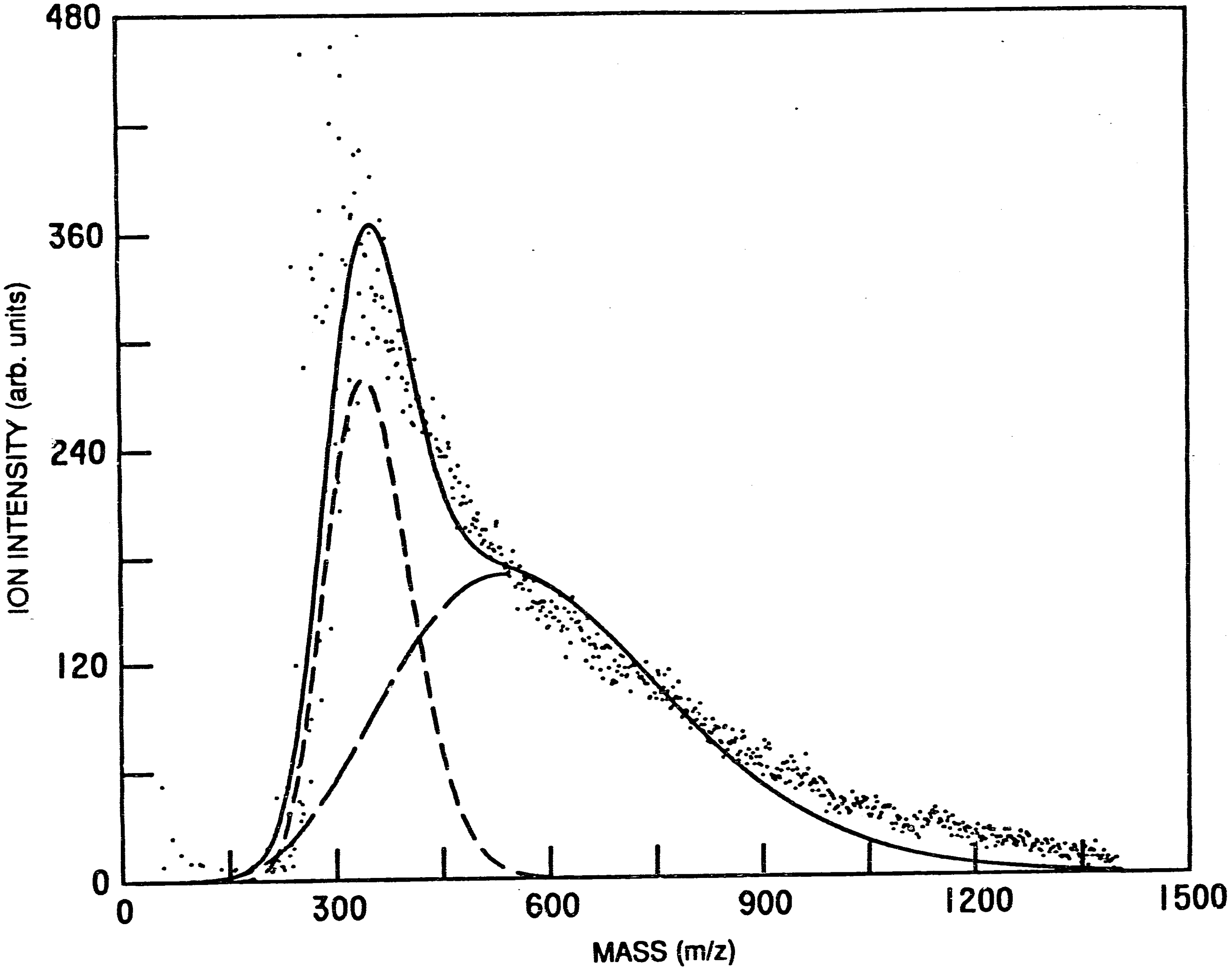

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Figure 6. Deconvolution of FIMS of Illinois No. 6 cat-cat (Run 257) interstage oil into Components A and B.

gives a lower intensity than the data. The break in the curve around 450 Da is well mimicked by the fit. However, the fit to spectra that did not show a clear break is not as good, as can be judged from Figure 6, which shows the results of deconvolution for the Interstage oil from the cat-cat run with the Illinois No. 6 coal. This lack of goodness suggests that the functional form chosen is not the best and could be improved. However, within the scope of the present contract we were not able to test other functions.*

The values for percent of Component A calculated from the deconvolution of both even- and odd-mass profiles are given in Table 3. In both cases the reported percent A values may appear to be less than those anticipated by simple visual inspection, but it should remembered that these are *weight* percentages, and therefore will be skewed in favor of the heavier component, B. The data in Table 3 for the different resids are arranged in two matrices that correspond to the location of the FI mass spectra of the different resids in Figures 3 and 4. When we used odd-mass profiles for regression and fitted the odd-mass spectra, the results gave substantially smaller percentages of Component A, typically 3-12% as compared to 9-20% for the even-profile-based fit. These smaller percentages for Component A are consistent with the result of visual inspection of the profiles in Figures 3 and 4: the even mass profiles are substantially "richer" in Component A. This difference means that the low molecular weight resid molecules that constitute Component A are defined as such (resids) because they consist of PCAH moieties that have inherently low volatility or of molecules having smaller aromatic systems that are substituted with polar oxygen functions (rather than of structures having nitrogen incorporation, which would give primarily odd-mass molecules).

The discussion in the following paragraphs of the variations in percent of Component A in the different product streams and runs is entirely in terms of the even-mass profile fitting. We note that while the absolute values of %A are quite different from the even-mass- and odd-mass fittings, the sample-to-sample changes in the odd-mass fittings tend to parallel those in the even-mass fittings.

Besides the composite sample for the Interstage oil from Run 257 (cat-cat, Illinois No. 6), we also received samples from periods F and G from this run. FI mass spectra of these samples (Figures 1 and 2) are nearly superimpossible. Not surprisingly, the deconvolution of these two spectra gave very similar quantities of Component A (15.8 and 16.0% respectively). In contrast, the composite spectrum (Figure 7) has a noticeably different profile, which is reflected in the somewhat larger amount of Component A (22.4%). Thus switching the temperature of the two stages appears to make less difference than other changes made during the course of Run 257.

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* It is apparent from the FIMS profiles that simple gaussian or gamma functions could not adequately fit the data either.

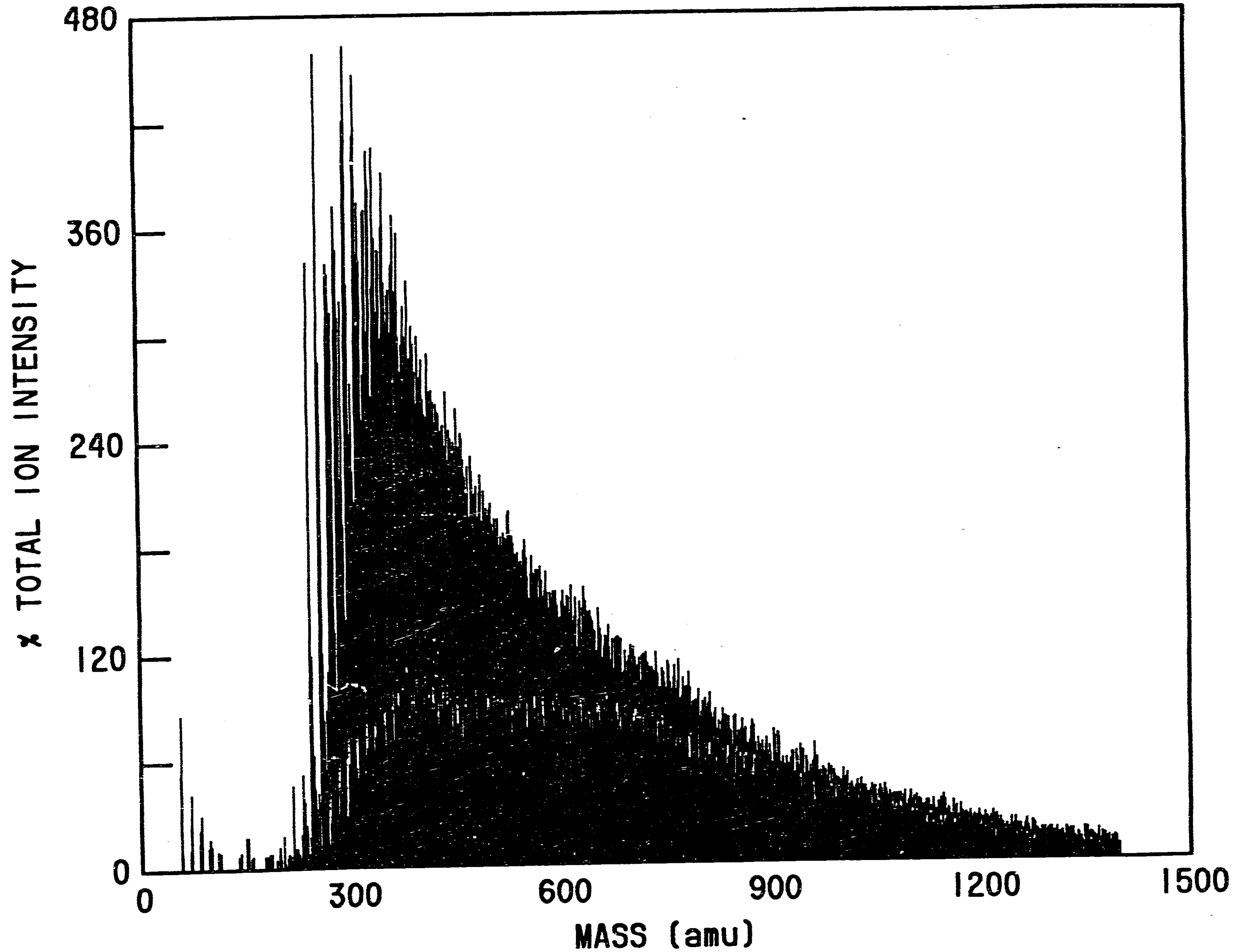

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Figure 7. FIMS of Illinois No. 6 cat-cat (Run 257) composite interstage oil.

Table 3

PERCENTAGE OF LOW-MOLECULAR WEIGHT COMPONENT A IN RESIDS TAKEN FROM DIFFERENT RUNS AND SAMPLING POINTS

Wt% A in the Sample Determined from Even-Mass Profile

Sample point	255 Lignite Therm--Cat	251-II Wyodak Therm--Cat	250 Illinois Therm--Cat	257 Illinois Cat-Cat	259 Pittsburgh Cat-Cat
Interstage oil	21.5	11.4	13.9	22.4[1]	13.7
Product oil	18.2	9.0	10.4	32.0	9.2
Recycle oil	21.6	10.0	8.6	13.1	18.5

Wt% A in the Sample Determined from Odd-Mass Profile

	255 Lignite Therm--Cat	251-II Wyodak Therm--Cat	250 Illinois Therm--Cat	257 Illinois Cat-Cat	259 Pittsburgh Cat-Cat
Interstage oil	12.9	5.9	5.5	7.9[2]	4.0
Product oil	10.5	3.6	2.9	12.9	2.2
Recycle oil	12.4	5.3	1.2	4.3	6.3

[1] Composite Sample; values for periods F and G are 15.8 and 16.0% respectively.

[2] Composite Sample; values for periods F and G are 5.6 and 6.3% respectively.

Processing Implications of Lumped Components. In an attempt to determine whether the changes in percents of lumped Components A and B make a consistent connection with the processing behavior of the four coals in these five runs, we have chosen a simple lumped conversion picture in the context of which we will discuss the changes in each run and from run to run. We do this realizing that "Component A" for one coal or process configuration is not truly identical to Component A for another. The main production and consumption pathways for the two components are given in the matrix below.

Table 4

ASSUMED PRODUCTION AND CONSUMPTION ROUTES FOR COMPONENTS A AND B

	Component A	Component B
Increases	Upgrading of "B"; dissolution of coal (w/cat)	Direct dissolution of coal; retrogression of "A"
Decreases	Retrogression to "B"; upgrading to distillate.	Formation of and/or rejection into IOM; upgrading to "A".

We begin by considering the most obvious differences among the 15 spectra themselves. At a glance, it is clear that the Illinois No. 6 catalytic-catalytic product oil (Figure 4) has a very pronounced low-mass intensity (200-400 Da), a difference that does not show up so strikingly in the weight-average molecular weight values. This low-mass grouping is somewhat less prominent in the "younger" interstage oil. Evidently, under the catalytic-catalytic conditions, high yields of material that is low molecular weight are produced from the coal or "fresh" resid in the first-stage reactor, and most noticeably, in the second-stage reactor. As defined by its boiling point, most of the low molecular weight product should have reported to the distillate fraction. However, the product oil sample for the Illinois No. 6 cat-cat run showed substantial volatility during FIMS analysis even at subambient temperatures. Thus, although all the samples were topped off using the same procedure, there could have been some variations in the amount of the volatiles (heavy VGO components) left in sample during the distillations, given substantial differences in amounts of these materials in the sampled streams.* In any event, it appears that the production, in the second-stage reactor, of low molecular weight products appearing at the distillate-resid "borderline" is much less for the Pittsburgh coal.

In significant contrast to the prominent low-mass intensity in the Run 257 product oil, the recycle oil (which nominally differs from the product oil only in that a portion of the stream has been split off, sent through a vacuum flash separator, and had the ash and insoluble organic matter removed in the ROSE-SR unit) has substantially less of the 200 to 400 Da intensity. Whereas one

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* Indeed, the spectrum obtained by adding the subspectra collected from 70°C and above (i.e., ignoring the first two subspectra) does not show the prominent cluster of peaks around 300 Da. We also note that onset of the full temperature-range sum spectrum of Run 257 product oil (Figure 4e) is at the same mass (~250 Da) as all the other resids.

expects some of the high molecular weight organic material visible with FIMS to be rejected along with the ash, and therefore for the *higher* end of the molecular weight profile to be trimmed in the recycle oil (as compared with the product oil), it is the *lower* end of the profile that has shrunk. We suggest, in accord with comments by Brandes and Winschel, that this observation is consistent with significant retrogression between V1067 and V131B, in other words, with the occurrence of significant coupling reactions when the high temperatures are maintained during the "physical" separation process or subsequently in the holding tanks, but in the absence of the catalyst or H_2 pressure.

Thus, with the Illinois No. 6 coal (under cat-cat conditions), the coal seems to come apart into small pieces fairly readily, but also undergoes retrograde reactions to go back together again quite readily. This scenario is entirely consistent with the aforementioned highly polar or PCAH nature of the low molecular weight components and the known proclivity of these structures for undergoing retrograde reactions. The scenario is, however, only a rationalization and should be tested for consistency by considering the other sets of spectra for the Illinois, Pittsburgh, and Wyodak coals and the Texas lignite.

The most direct comparison here is with the Pittsburgh coal, because it was used in the only other catalytic-catalytic run included in the set of resid samples. Here, as we move from the interstage oil to the product oil (Figure 4), we see that a bimodal distribution again appears, but that the Component B now dominates over Component A. In this case, the fresh resid seems to be much less readily converted (in the second-stage reactor) into A; the net change in fact is for the B to become *more* important as a result of reaction in the second stage. The differences between the Pittsburgh product oil and the recycle oil seem to reflect mainly removal of high molecular weight material, B. This is as would be expected, but is in contrast to the Illinois catalytic-catalytic case, where the effect of putting a side stream through the ROSE-SR unit (and the holding tanks) was curiously to *increase* the amount of B.

We can summarize the situation for the Illinois No. 6 and Pittsburgh catalytic-catalytic runs by saying that for Illinois No. 6, the second stage reactor produces (as seen in the product oil) much more Component A from an easily fragmentable fresh resid, but that Component A is drastically reduced by retrograde reactions during the at-temperature manipulations involved in splitting a stream off to the ROSE-SR unit to provide the partially deashed recycle stream. In contrast, for the Pittsburgh coal, passage through the second-stage reactor actually increases the amount of Component B, reflecting greater difficulty in reducing the molecular weight of the fresh Pittsburgh resid. When a stream is split off for deashing, however, Component A is significantly increased, as one would expect if the rejection of organic matter as insoluble is not overwhelmed by rapid retrograde reactions.

The next appropriate comparison is between the Illinois catalytic-catalytic run (Run 257), and the Illinois thermal-catalytic run (Run 250). Although these runs are separated substantially in time and are configured slightly differently (apart from the absence of first stage catalyst in Run 250), we will, for purposes of initial discussion, consider only the absence of catalyst in Stage 1 and the resulting differences in reactor temperature.

In Run 250, the level of Component A in the interstage oil is only about half that in Run 257, and passage through the Stage 2 reactor *decreases* Component A still further (rather than increasing it as in Run 257). We conclude (since Stage 2 is catalytic in both cases) that the product of the thermal first stage is less reactive. Apparently the "fresh" resid is more refractory because of the absence of catalyst and/or the slightly higher temperatures used during operation of a thermal first stage. This conclusion only reiterates that already reached by Winschel and others based on process yields; however, it is interesting that we quickly and independently arrived at the same conclusion about reactivity of the resids in the cat-cat and therm-cat runs simply by noting the amounts of two lumped components in the resids.

Another point of comparison is the change in going from product oil to recycle oil. The result here is qualitatively similar to the change seen in the cat-cat run (Run 257): a decrease in amount of Component A. Even though this decrease is smaller than the two-fold decrease seen in Run 257, it is nonetheless surprising, because in Run 250, 100% of the recycle stream has gone through the ROSE-SR unit, having its ash and part of its heavy organics rejected. Nevertheless, there is a decrease in the low molecular weight component. Thus, we conclude that even in the therm-cat Illinois No. 6 run, where Component A is not so prominent in the product oil, the thermal stress in the separation trains and downstream holding tanks causes retrogression of low molecular weight materials that outweighs removal of heavy materials as insoluble organic matter (IOM) in the ROSE-SR unit itself.

Moving to the two lower rank coal in this series, also processed in a therm-cat configuration, we see that for both the Wyodak coal and the lignite, second-stage reaction causes a decrease in the percentage of Component A — a change that is qualitatively similar to that seen for the Illinois therm-cat run (Run 250). With respect to changes between the product oil and the recycle stream, there is a slight increase in Component A for both the Wyodak and the lignite, whereas in Run 250 Component A decreased. Since we associated the decrease in Component A between the product and recycle streams for the Illinois No. 6 runs with a proclivity for retrogression, we would conclude from the slight *increase* in A that the Wyodak and lignite resids are actually less prone to retrograde reaction than the Illinois No. 6 resids. The observed increase in A supports the conclusion that PCAH species, which are expected to be less abundant in the lower rank coals and their products, are the primary candidates for retrogressive reactions in these highly processed resids. The observed increase in Component A is thus most likely due to a greater rejection of Component B as was observed with the Pittsburgh coal.

Finally, with respect to changes observed between the recycle oil and the interstage oil, we see that in some cases there is an increase and in some a decrease in the %A as a result of the addition of fresh coal and reaction in the first stage reactor. The most notable increase is in Run 257, where a highly reactive coal (Illinois No. 6) and a catalytically produced fresh resid combine to yield substantial component A "directly" from the coal. There is even an increase, albeit a smaller one, in the therm/cat run for the same coal. On the other hand, the Pittsburgh coal, in Run 259 shows a decrease in Component A, even though a catalytic first stage is being utilized. This result is consistent with our earlier observation that the upgrading of Pittsburgh resid (including the conversion of resid component A to resid component B) is rather difficult. In the case of the Wyodak, there is a slight increase in Component A (though smaller than for the Illinois No. 6 Therm/cat, Run 250). It is not clear whether this difference fits exactly with the generalization of harder-to-convert-but-easier-to upgrade for the Wyodak coal. For the lignite, there is a substantial decrease in Component A as a result of coal addition and first stage reaction. This decrease could be associated with ease of upgrading the lignite Component A to distillate, an expected behavior. However, we note that the Pittsburgh cat/cat run (Run 259) also shows a decrease in component A as a result of first stage reaction, and it was there ascribed to a *difficulty* in converting from Component B to Component A within the resid manifold.

In closing this discussion, we would say that while the correspondence is not perfect, the deconvolution of FIMS spectra into lumped components, A and B, leads to conclusions reasonably in concert with what is already recognized in low-rank coal liquefaction. It is satisfying to see so many observations about reactivity reiterated, not on the basis of yields, but on the basis of differences in molecular weight distribution of streams that are already constrained by process conditions and product fractionation to be as similar as possible.

Examination of Prominent Individual Peaks

While most of the FI-mass spectral profiles are basically quite smooth, with no prominent masses, it is noteworthy that at the low mass end (240 to 350 Da), there is substantial "structure" in the spectra. Moreover, the same peaks appear as prominent in spectra of all the fifteen resids. The six major series apparent in the spectra of these resids begin at m/z 242, 276, 282, 300, 308, and 316. As an example we show in Figure 8 the spectrum of the resid portion of the recycle oil

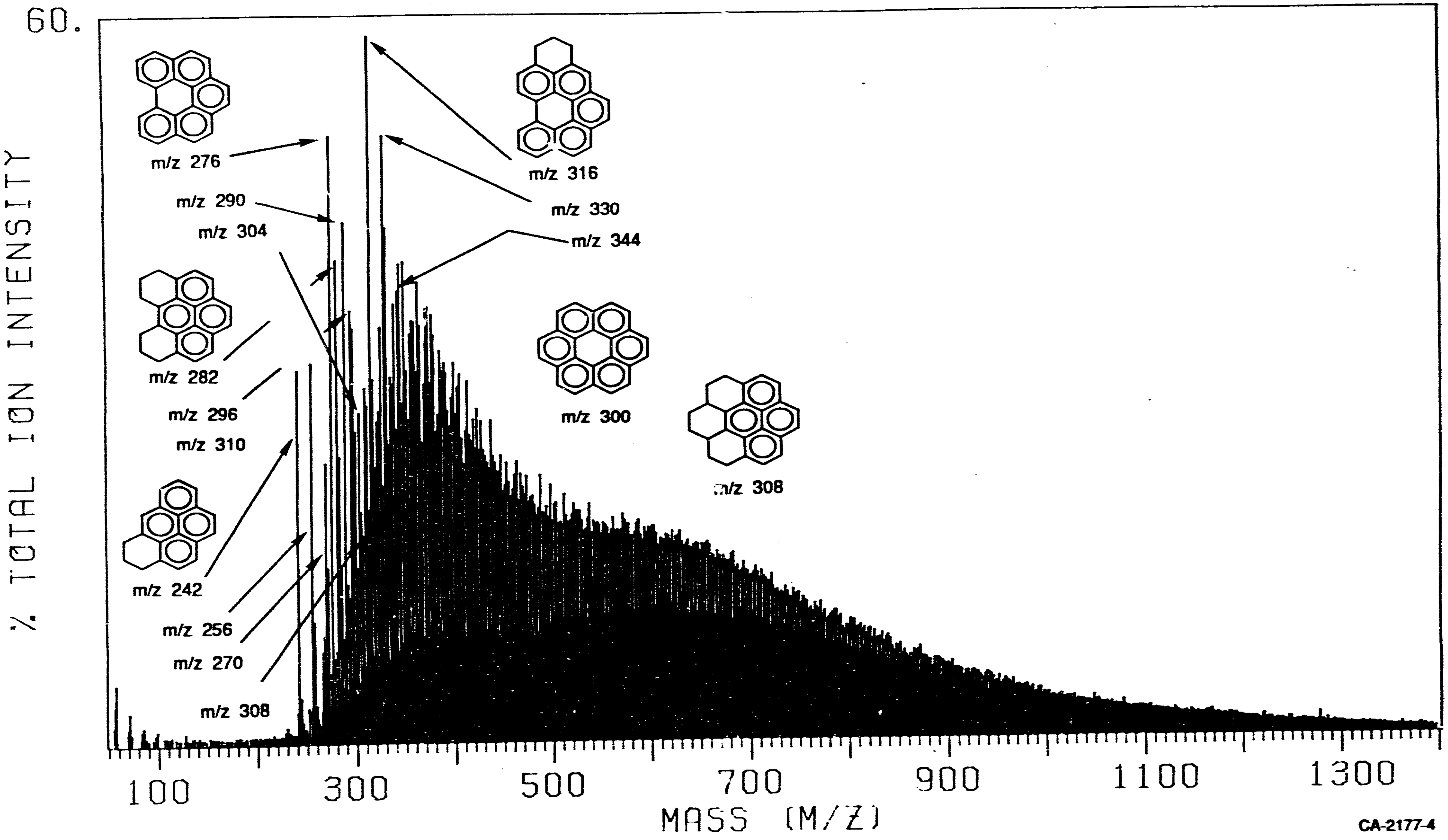


Figure 8. FIMS of the Pittsburgh (Run 259) recycle oil showing the prominent PCAH structures in the 200-350 Da range.

derived from the Pittsburgh coal (Run 259) with these prominent peaks labeled. Figure 9 shows, in the normal SRI tabular form, the intensities up to m/z 776 for this same spectrum. In this table the intensities of the different peaks are arranged in fourteen columns such that members of a homologous series fall one beneath the other. Thus, beno[ghi]perylene (mass 276) and its alkyl homologs (at masses 290, 304, and so on) lie in the same column and are quickly identified.

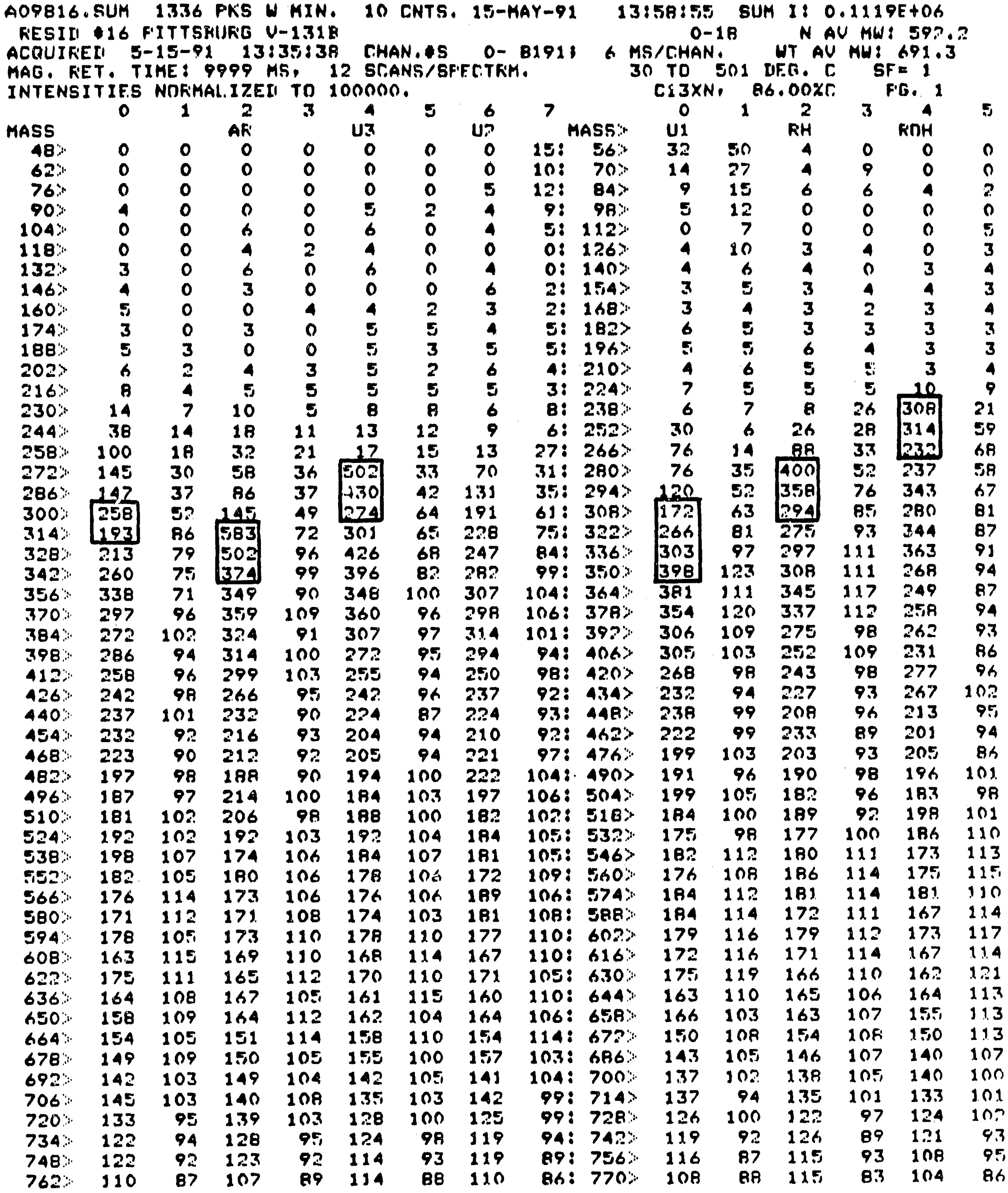
Curiously enough, the six major peaks apparent in these resid spectra are either the same as, or closely related to, those recently identified by Sullivan, Boduszynski, and Fetzer[1] as showing substantial increases during hydrotreating of petroleum vacuum gas oil fractions. While this correspondence does not promise an instant unraveling of the mysteries of resid behavior, it must be more than coincidence and clearly offers threads that should be followed through.

It should be noted that in the case of petroleum VGO, FIMS analysis of the whole oil did not allow specific series to stand out from the MS profiles, let alone to be identified on the basis of nominal mass. It was only after Boduzynski performed chromatographic separations based on the number of double bonds and eliminated the overlapping of various naphthenes with PCAH having the degree of unsaturation (i.e., being in the same Z-series), that it became possible to make definitive identification in the vacuum gas oils of the compound classes listed above.[3] It is fortuitous that these series stand out as much as they do in these coal-derived whole residual oils. This fortunate circumstance is presumably the result of distillation of most of the naphthenic series that overlap with (have the same Z number) with various PCAH series in this MW range.

The first general observation to be made about the six major series listed above is that they are all oxygen-free. This conclusion in not inconsistent with a level of oxygen in these resids that corresponds to an O/C ratio of about 1/80, so that on average there would be about one oxygen associated with, say, every third coronene (C_{24}) species. It also reiterates that it is the PCAH structures that are probably responsible for the coking and production of IOMs.

The major peak in Run 259 interstage oil is m/z 276. Benzo[ghi]perylene, m/z 276, was identified by Boduszynski as one of two peaks that increased markedly during resid desulfurization between the start of run (SOR) and end of run (EOR) as the catalyst degraded, and the temperature had to be increased in order to maintain a relatively constant level of desulfurization. Moreover, subsequent catalytic hydrocracking using EOR desulfurized VGO required higher temperatures and resulted in significantly higher hydrocracking (HCR) catalyst degradation rates. These increased difficulties were encountered even though the EOR desulfurized product actually had an overall *lower* aromatic content than the SOR product!

The intensity of the ion corresponding to the next step up from benzo[ghi]perylene, coronene (m/z 300), is considerably less than that of m/z 276, typically about half. Previously,



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ACQUIRED  5-15-91  13:35:38  CHAN.#S   0- 8191:  6 MS/CHAN.     WT AV MW: 691.3
MAG. RET. TIME: 9999 MS,  12 SCANS/SPECTRM.           30 TO  501 DEG. C   SF= 1
INTENSITIES NORMALIZED TO 100000.                      C13XN,  86.00%C     PG. 1
          0     1     2     3     4     5     6     7             0     1     2     3     4     5
MASS                 AR          U3          U2             MASS>    U1          RH         ROH
 48>      0     0     0     0     0     0     0    15:   56>    32    50     4     0     0     0
 62>      0     0     0     0     0     0     0    10:   70>    14    27     4     9     0     0
 76>      0     0     0     0     0     0     5    12:   84>     9    15     6     6     4     2
 90>      4     0     0     0     5     2     4     9:   98>     5    12     0     0     0     0
104>      0     0     6     0     6     0     4     5:  112>     0     7     0     0     0     5
118>      0     0     4     2     4     0     0     0:  126>     4    10     3     4     0     3
132>      3     0     6     0     6     0     4     0:  140>     4     6     4     0     3     4
146>      4     0     3     0     0     0     6     2:  154>     3     5     3     4     4     3
160>      5     0     0     4     4     2     3     2:  168>     3     4     3     2     3     4
174>      3     0     3     0     5     5     4     5:  182>     6     5     3     3     3     3
188>      5     3     0     0     5     3     5     5:  196>     5     5     6     4     3     3
202>      6     2     4     3     5     2     6     4:  210>     4     6     5     5     3     4
216>      8     4     5     5     5     5     5     3:  224>     7     5     5     5    10     9
230>     14     7    10     5     8     8     6     8:  238>     6     7     8    26   308    21
244>     38    14    18    11    13    12     9     6:  252>    30     6    26    28   314    59
258>    100    18    32    21    17    15    13    27:  266>    76    14    88    33   232    68
272>    145    30    58    36   502    33    70    31:  280>    76    35   400    52   237    58
286>    147    37    86    37   430    42   131    35:  294>   120    52   358    76   343    67
300>    258    52   145    49   274    64   191    61:  308>   172    63   294    85   280    81
314>    193    86   583    72   301    65   228    75:  322>   266    81   275    93   344    87
328>    213    79   502    96   426    68   247    84:  336>   303    97   297   111   363    91
342>    260    75   374    99   396    82   282    99:  350>   398   123   308   111   268    94
356>    338    71   349    90   348   100   307   104:  364>   381   111   345   117   249    87
370>    297    96   359   109   360    96   298   106:  378>   354   120   337   112   258    94
384>    272   102   324    91   307    97   314   101:  392>   306   109   275    98   262    93
398>    286    94   314   100   272    95   294    94:  406>   305   103   252   109   231    86
412>    258    96   299   103   255    94   250    98:  420>   268    98   243    98   277    96
426>    242    98   266    95   242    96   237    92:  434>   232    94   227    93   267   102
440>    237   101   232    90   224    87   224    93:  448>   238    99   208    96   213    95
454>    232    92   216    93   204    94   210    92:  462>   222    99   233    89   201    94
468>    223    90   212    92   205    94   221    97:  476>   199   103   203    93   205    86
482>    197    98   188    90   194   100   222   104:  490>   191    96   190    98   196   101
496>    187    97   214   100   184   103   197   106:  504>   199   105   182    96   183    98
510>    181   102   206    98   188   100   182   102:  518>   184   100   189    92   198   101
524>    192   102   192   103   192   104   184   105:  532>   175    98   177   100   186   110
538>    198   107   174   106   184   107   181   105:  546>   182   112   180   111   173   113
552>    182   105   180   106   178   106   172   109:  560>   176   108   186   114   175   115
566>    176   114   173   106   176   106   189   106:  574>   184   112   181   114   181   110
580>    171   112   171   108   174   103   181   108:  588>   184   114   172   111   167   114
594>    178   105   173   110   178   110   177   110:  602>   179   116   179   112   173   117
608>    163   115   169   110   168   114   167   110:  616>   172   116   171   114   167   114
622>    175   111   165   112   170   110   171   105:  630>   175   119   166   110   162   121
636>    164   108   167   105   161   115   160   110:  644>   163   110   165   106   164   113
650>    158   109   164   112   162   104   164   106:  658>   166   103   163   107   155   113
664>    154   105   151   114   158   110   154   114:  672>   150   108   154   108   150   113
678>    149   109   150   105   155   100   157   103:  686>   143   105   146   107   140   107
692>    142   103   149   104   142   105   141   104:  700>   137   102   138   105   140   100
706>    145   103   140   108   135   103   142    99:  714>   137    94   135   101   133   101
720>    133    95   139   103   128   100   125    99:  728>   126   100   122    97   124   102
734>    122    94   128    95   124    98   119    94:  742>   119    92   126    89   121    93
748>    122    92   123    92   114    93   119    89:  756>   116    87   115    93   108    95
762>    110    87   107    89   114    88   110    86:  770>   108    88   115    83   104    86
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CA-2177-5

Figure 9. Example of a pattern table showing the arrangement that places members of a homologous series in a single column. Example shown is for Pittsburgh (Run 259) recycle oil.

Clar had concluded[4] that the formation of a new ring by addition of a four-CH unit piece (ortho ring closure) was kinetically favored, but that formation of a new ring by closing a two-carbon bridge over a "bay" region was thermodynamically favored. This conclusion was also supported by subsequent estimates of the heats of formation of large PCAH by Stein.[5] Thus, the greater buildup of benzoperylene than coronene illustrates a bottleneck in the ring closure to form coronene. In any event, Sullivan et al.[1] were able to show that those RDS VGO streams that were more difficult to catalytically hydrocrack were precisely those that had 10 to 100 times more benzo[ghi]perylene and coronene in them than the original RDS feed.

Mass 242 is the first prominent peak in *all* of the spectra. Its prominence is partly a result of the cut point in removal of distillate, but once again, the identity of the major contributor goes beyond coincidence. The mononaphthenic pyrene of molecular weight 242 shown in Figure 8 is an odd-carbon molecule, which cannot form a stable fully aromatic species. Its abundance was noted by Sullivan et al. with some curiosity.[1] In their case, the most abundant member of the class was the unsubstituted m/z 242 itself (rather than a C_3 or C_4 derivative as is usually the case with even-carbon species), making m/z 242 look less like it was derived by breakdown of a larger molecule than by buildup from a smaller species. Regardless of which of these is the case, the abundance of mass 242 is undoubtedly connected with the fact that the odd radical species is fully aromatic and a member of the class of radicals homologous with phenyalenyl radical, $C_{13}H_9^{\bullet}$ which are extremely stable radicals and ubiquitous in thermally processed hydrocarbon streams and sooting flames. The intensity at mass 316 is probably accounted for largely by another odd-carbon molecule, the naphtholog of m/z 242.

Based on the evidence presented by Sullivan et al.[1] and the very striking correspondence between the major peaks seen here and some of those identified by them, we consider it to be very likely that most of the prominent peaks noted here are causally related to the difficulty of catalytic/thermal breakdown to smaller species (distillate) and to the buildup of more refractory resid and IOM. At present, it is difficult to make a more quantitative statement regarding the importance of these peaks. We report in Table 5 the intensity (as a percent of the total ion count) of the six ions discussed above for each of the fifteen composite resids, listed in the same order as the spectra are shown in Figures 3 and 4. A few of the trends that emerge from an initial examination are listed below.

Table 5

INTENSITIES OF THE DOMINANT PCAH AND HYDRO-PCAH PEAKS IN COMPOSITE RESID SAMPLES

Oil	m/z	LIGNITE Run 255	WYODAK Run 251-II	ILLINOIS Run 250	ILLINOIS Run 257	PITTSBURGH Run 259
Interstage Oil	242	0.19	0.22	0.15	0.34	0.28
	276	0.37	0.19	0.23	0.32	0.58
	282	0.33	0.27	0.23	0.37	0.29
	300	0.24	0.20	0.17	0.33	0.24
	308	0.29	0.23	0.24	0.21	0.18
	316	0.35	0.24	0.30	0.38	0.36
Product Oil	242	0.12	0.12	0.18	0.30	0.24
	276	0.31	0.14	0.14	0.43	0.44
	282	0.31	0.23	0.23	0.43	0.37
	300	0.23	0.17	0.19	0.38	0.20
	308	0.24	0.17	0.13	0.28	0.14
	316	0.31	0.21	0.27	0.47	0.33
Recycle Oil	242	0.11	0.12	0.08	0.13	0.31
	276	0.35	0.14	0.12	0.19	0.50
	282	0.41	0.19	0.19	0.15	0.40
	300	0.24	0.18	0.17	0.18	0.26
	308	0.28	0.14	0.12	0.16	0.17
	316	0.34	0.22	0.21	0.26	0.58

- Consistent with the fact that the Pittsburgh resid is the most difficult to upgrade, the intensities for m/z 276, benzo[ghi]perylene, observed for the Pittsburgh coal (Run 259) are generally higher than those for any ot the other samples. However, this relationship appears not to always hold. In the interstage and recycle oils for Run 259, the levels are 2 to 2.5 times higher than the respective samples for Run 257, the catalytic/catalytic Illinois No. 6 run, but for the product oil the levels are essentially equal.

- The cat/cat run with Illinois No. 6 coal (Run 257), produces more of m/z 276 by about a factor of two than the therm/cat run (Run 250), even though the resid produced in 250 was considered to have been more difficult to upgrade. If the large PCAH are produced in significant part by the cracking activity of the alumina-supported catalysts, we might rationalize that without the first stage catalyst, less benzo[ghi]perylene is formed. But if we accept this rationalization, we are then forced to say that the difficulty in upgrading the Illinois therm/cat fresh resid is not due to benzoperylenes, coronenes, etc., but is due instead to the fact that less cracking occurred in the first stage. Thus, it is apparent that the situation is complex and not susceptible to analysis by simple inspection.

- If instead of comparing the absolute levels, we compare the ratios of peaks at m/z 276 and 300 we find that in going from the recycle stream to the interstage oil the relative amount of benzo[ghi]perylene increases in the more difficult-to-process Runs 250 and 259, while it decreases in Run 257.

- Changes in the ratios of hydroaromatic/aromatic pairs as the resid moves through the system provide an additional point for comparison. We find that of Runs 250, 257 and 259, only Run 257 shows an increase in the ratios of hexahydrobenzo[ghi]perylene to benzo[ghi]perylene as well as of octahydrocoronene to coronene. Runs 250 and 257 show a decrease in these ratios as expected from the addition of the more "aromatic" coal to the recycle resid.

These trends do not extend to the entire set of runs. In other words we were not able to construct a consistent set of correlations between the most prominent homologous series and the processing behavior in the five runs. However we believe it is very likely that the difficulty in significant part is that the run-to-run comparisons attempted are anything but all-other-things-being-equal comparisons. A more careful examination of these data is warranted. One correction that ought to be included in this analysis is for the background intensity of all other components that might be present at these specific masses. The background could be adequately represented by the "fit" to the profile described in the previous section. The correction is small for peaks at 242 Da, but probably substantial for those at 300 Da. An alternative strategy would be to perform a factor analysis on this set of peaks and identify the major trends. We suggest that these tasks be undertaken in a future effort.

TASK 2. DERIVATIZATION ANALYSIS USING IODOTRIMETHYLSILANE

The objective of this task was to determine the concentration of oxygens attached to aliphatic carbons in coal liquids. Iodotrimethylsilane is known to react with such structures and produce alkyl iodides.[6] Our approach consists of treating samples with a known quantity of iodotrimethylsilane followed by an aqueous workup. Any unconverted iodosilane would be transformed to inorganic iodide ions during workup while iodosilane used to cleave ethers or esters will not produce inorganic iodide. Other reactions of iodosilane not involving C_{al}-O, such as reduction of sulfoxides to sulfides, also result in formation of iodide ions.[6] An estimation of the iodide ions by ion-selective electrodes or ion-exchange chromatography should therefore provide, by comparison with a control, an estimate of the C_{al}-O structures.

We prepared a calibration curve for the iodide-selective electrode and found a good linear response over the range of concentrations we expected to encounter in actual analyses. Control runs with iodosilane resulted in the expected concentration of iodide ions. However, we were puzzled to find that when iodosilane was allowed to react with several model structures such as benzyl phenyl ether and methyl benzoate, the resultant solutions gave readings corresponding to no consumption of iodide. We followed some of these reactions in an NMR tube and clearly observed the expected chemical reaction. Thus, either the resulting organic iodide is hydrolyzing very rapidly to give inorganic iodide (an unlikely scenario, but needs to be tested) or some other ions in the solution are interfering with the electrode.

By isolating organic iodides from the organic layer, we convinced ourselves that the organic iodides were not being hydrolyzed to inorganic iodide ions. Hence, the inability to detect any difference using ion-selective electrode must be due to interference from some other ion or combination of ions in the mixture. We therefore abandoned the ion-selective electrode approach and used ion-exchange chromatography to estimate the iodide ions.

Using this procedure, we were able to determine the amounts of C_{al}-O in standard solutions of benzyl phenyl ether in chloroform. The results validated the analysis scheme, but also showed a consistent loss of about 10% of the iodide even when no ether was present. We conducted the reaction of the six coal resids with iodosilane in duplicate. Following aqueous workup, the iodide content was determined by ion-exchange chromatography. The results are given in Table 6. The resulting deficit in iodide should correspond to the C_{al}-O content of the coal resid; however, as mentioned above there was also some (~10%) background reaction in the control. The observed deficits were corrected for the background reaction. The corrected deficits are also given in Table 6. They are very small, and sometimes negative, indicating that these processed oils do not contain any significant amount of C_{al}-O bonds. Thus, any oxygen other than phenols is present in diaryl ether structures such as benzofurans.

Table 6

IODOTRIMETHYLSILANE ANALYSIS OF COAL RESIDS

Expt. No.	CoalResid (mg)	Me_3SiI (mg)	I (mmol)	$[I^-]$ 100 mL	Δ^a (mmol)	wt% O-C(al)[b]	Corr. Δ^c (mmol)	Corr wt% O-C(al)
Blank	0	93.94	0.47	3.80^{-3}	0.09	--	--	--
18a W	89.79	143.46	0.72	5.60^{-3}	0.16	2.80	0.02	0.36
18b	55.87	73.04	0.37	2.90^{-3}	0.08	2.15	0.01	0.16
19a L	106.34	137.90	0.69	5.60^{-3}	0.13	1.95	0.00	-0.03
19b	55.38	68.39	0.34	2.90^{-3}	0.05	1.50	-0.01	-0.39
20a I	98.30	140.06	0.70	6.00^{-3}	0.10	1.63	-0.03	-0.54
20b	72.48	85.41	0.43	3.40^{-3}	0.09	1.92	0.01	0.12
21a P	100.66	129.40	0.65	5.00^{-3}	0.15	2.34	0.02	0.37
21b	85.96	104.64	0.52	3.90^{-3}	0.13	2.48	0.03	0.62
22a BT	99.53	144.10	0.72	6.10^{-3}	0.11	1.78	-0.03	-0.44
22b	83.83	101.78	0.51	3.70^{-3}	0.14	2.65	0.04	0.80
23a BT	109.93	145.10	0.73	6.00^{-3}	0.13	1.83	-0.01	-0.19
23b	90.21	101.54	0.51	4.00^{-3}	0.11	1.91	0.01	0.19

[a] Initial [I] -100 × $[I^-]$.
[b] 100 × {Δ × 16/(sample wt.)}
[c] Proportional to the amount of iodotrimethylsilane used in the run relative to blank.

Iodotrimethylsilane reactions are best conducted in acetonitrile solvent.[7] However, the coal resids were not appreciably soluble in acetonitrile. Tetrahydrofuran would be a good solvent for the resids, but not iodotrimethylsilane, which will convert it to diiodobutane. We conducted a few experiments in pyridine, but soon realized that the strongly nucleophilic solvent reacts with organic iodides, forming quaternary salts and liberating ionorganic iodide ions. Therefore, this solvent would not be suitable for our purpose. Hence, we settled on chloroform as the solvent. There appears to be some background reaction in this medium that consumes iodotrimethylsilane, and we could only correct for it. If we could suppress this reaction, we could have reliably estimated even smaller amounts of C_{al}-O linkages. In the presence of this background reaction, the precision of the method is compromised, and we can only conclude that the amount of C_{al}-O linkages is less than 20% of the oxygen.

The finding of only a small fraction of the oxygen in these liquids to be either ethers or esters of aliphatic alcohols is, in retrospect, not terribly surprising. The phenylO-Me bond strength in anisole (the strongest of phenyl-alkyl ethers) is 63.5 kcal/mol.[8] At 420°C (788°F) this translates to a homolysis half life of 7 hours, a value that can be taken as a reasonable upper limit for this class of bonds under the Wilsonville operating conditions. Given the expected electronic and steric effects of substituents on the phenyl ring[8] it would not be surprising to find most such bonds to be gone in the liquefaction products. However, this could not have been predicted with any certainty because of the expected variations in bond strengths, and because we know nothing that would preclude temporary re-formation of anisole-type ethers through radical recombination.

It is also possible that the current findings carry some implications about another class of oxygenated structures, benzylic phenols. These structures, even they are not ethers, are possibly subject, through nucleophilic attack on their respective keto forms, to cleavage by iodotrimethylsilane. Such coupled phenols, although themselves only moderately stable, are potential retrograde intermediates in the thermal reactions of virtually any phenolic substrates, since their formation has been shown to be very facile in mixtures of benzyl and phenoxy radicals.[9] Owing to the unexpected difficulties encountered in using ion-specific electrodes for I^- measurement, and the background reaction between iodotrimethylsilane and chloroform, we did not have the time to determine whether any such benyzylic phenol structures are reactive under the ether cleavage conditions used in this work. Such a determination may be worthwhile in the future, because information on their presence or absence of benzylic phenols in liquefaction product streams is relevant to the problem of understanding retrogressive reactions of phenolic structures during liquefaction.

Finally, the finding that alkyl oxygen is no more than about 20% of the oxygen (by difference) in these samples is not inconsistent with the fact that the hydroxyl oxygen analyses typically show levels that are half to three quarters of the nominal (i.e., by difference) oxygen in the composite resid samples.

ASSESSMENT AND RECOMMENDATIONS

Neither FIMS nor any other single analytical technique can provide a complete chemical description of vacuum resids; however, FIMS does provide, in a single measurement, substantial information about these materials. A very large fraction of the resids is vaporized and hence analyzed by FIMS. The fractional volatility during FIMS analysis corresponds closely to the THF-solubility of the sample; hence it is fair to say that essentially all of the THF-solubles are analyzed by FIMS. The FI-mass spectra of the set of resids analyzed in this project look very similar (as well they might since product fractionation and process conditions have been adjusted in order to make them similar). However, the accuracy and reproducibility of FIMS allows for distinctions to be made at several levels.between these superficially similar-looking spectra.

During this research effort we found that FIMS of many of the whole liquefaction resid samples exhibited a bimodal molecular weight distribution. This bimodal distribution can be considered to result from the superposition of two components having molecular weight distributions that peak at about 350 and 600 Da. The relative amounts of the low and high molecular weight components differ significantly from sample to sample, and simple mathematical deconvolution into Components A and B has revealed a correlation between the variations in A and B on the one hand and coal type, process condition, and process performance on the other.

Although the FI-mass spectral profiles are generally smooth and devoid of features, the low mass ends of the spectra exhibit substantial "structure" or evidence of homologous series. Moreover, the same peaks appear as prominent in spectra of all the fifteen resids. These homologous series clearly carry information on chemical structure, but useful speculative assignment of chemical structures to nominal masses in the 240-350 mass range, without benefit of additional information, is essentially impossible. However, recognition of some of the same prominent masses previously associated by Sullivan et al.[1] with increased difficulties in hydrotreating vacuum gas oils prompted us to seek correlations between processing variables the intensity of these peaks. Several trends were identified. Examples include the generally greater amount of benzo[ghi]perylenes and coronenes in the more difficult-to-convert Pittsburgh resids, and the smaller ratios of PCAH to corresponding hydroaromatic structures in the more easy-to-convert resids. However, these trends do not extend to the entire set of runs, and suggest that a more detailed examination of such data be undertaken. We believe that such an examination, coupled with the deconvolution into lumped low and high molecular weight components, will provide substantial independent information for cross-correlation with other resid properties and processing parameters.

The use of iodotrimethylsilane as an ether cleavage reagent revealed that the levels of oxygen bound to alkyl carbon in the resids are quite low, typically less than 20% of the total oxygen. An unexpected background reaction of the iodotrimethylsilane with the chloroform solvent limited the accuracy of the determinations for these low levels of alkyl-O structures, and control experiments were used to correct for this reaction. The observed scatter limits the accuracy of any single measurement, but the results taken together clearly indicate low levels of alkyl oxygen. Suppression of the background reaction might be worthwhile if it were found that iodotrimethylsilane could cleave benzylic phenols, a potentially important class of intermediate retrograde products.

FUTURE STUDIES

Two lines of investigation are suggested by the present work. We have seen that there is value to describing the FIMS profiles in terms of lumped components and that this effort needs to be refined and pursued further. Also, we have seen that the low mass end of FIMS of the resids that has a few prominent peaks corresponding to specific PCAH components. These components have previously been associated with processing difficulties. Our preliminary examination of their relative intensities suggests has revealed certain trends. We believe that a more detailed examination of these and similar data will lead to an understanding of how chemical composition of resids impacts processing.

Furthermore, even though the behavior of the resids is of primary interest here, we recommend that FIMS analyses of the vacuum distillate be performed in conjunction with the resid analyses. Analysis of distillates will help ascribe an apparent decrease in, say, Component A either to conversion to distillate material or retrogression to resid Component B.

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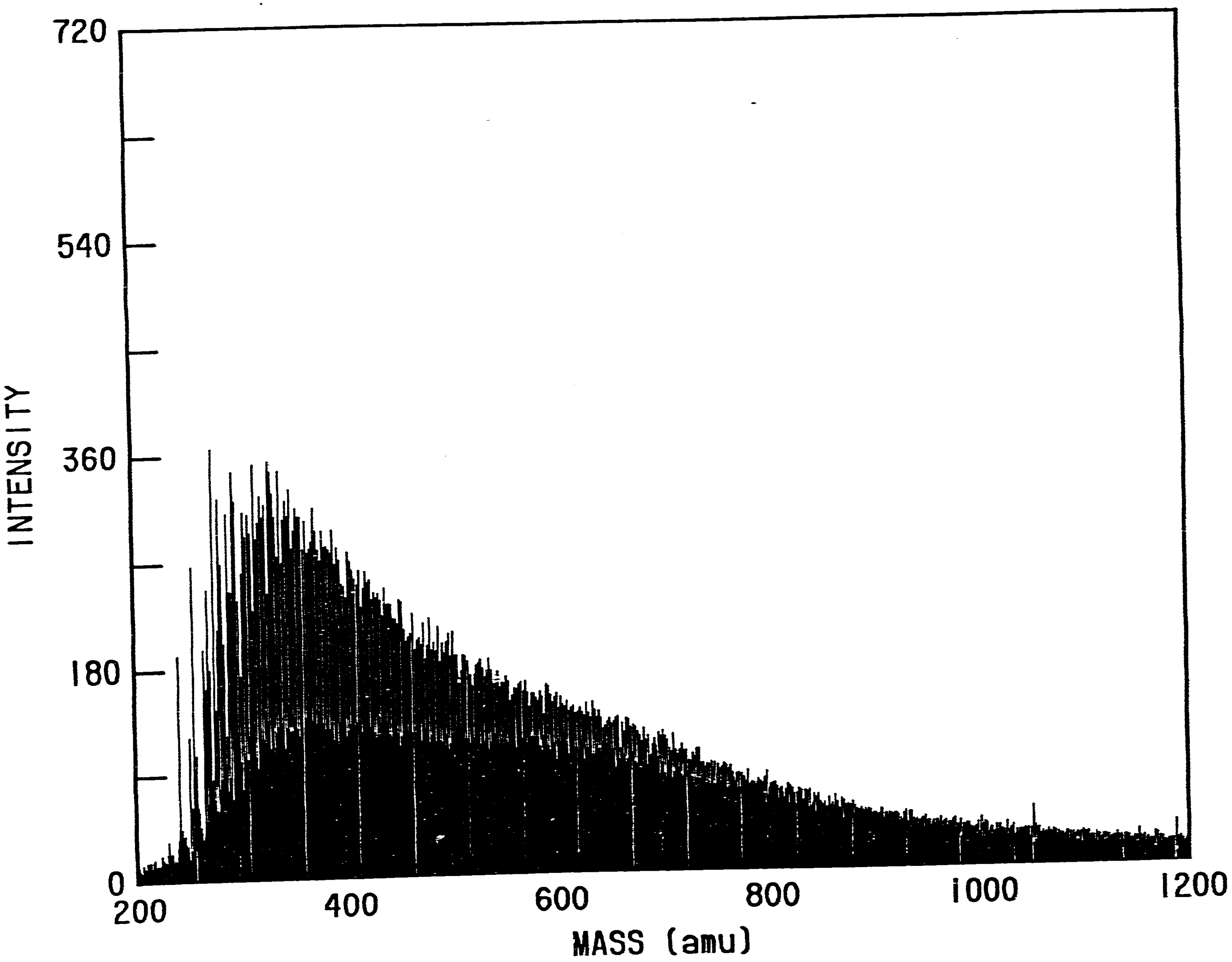
Appendix A

FI-MASS SPECTRA OF THE FIFTEEN COAL RESIDS



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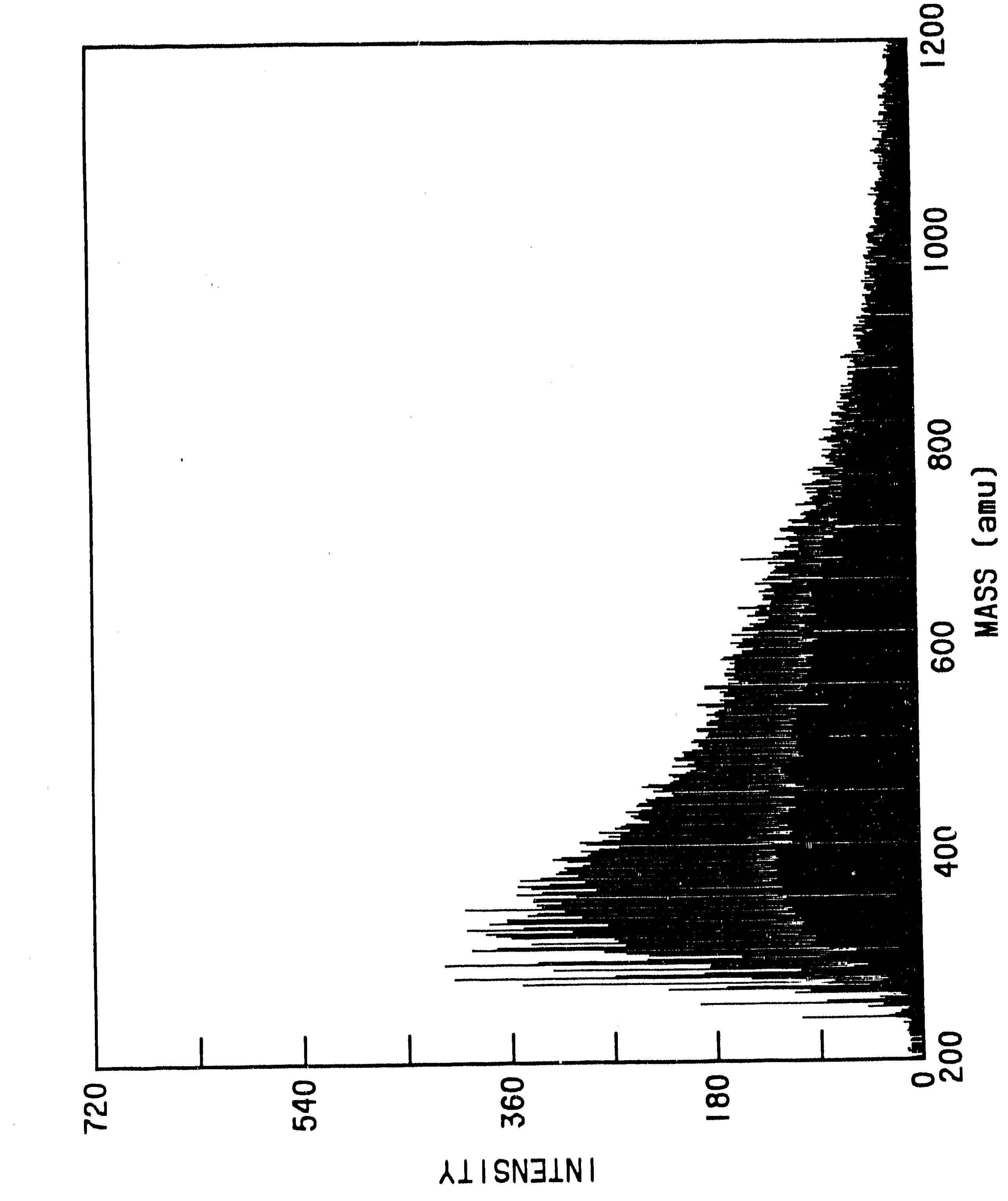

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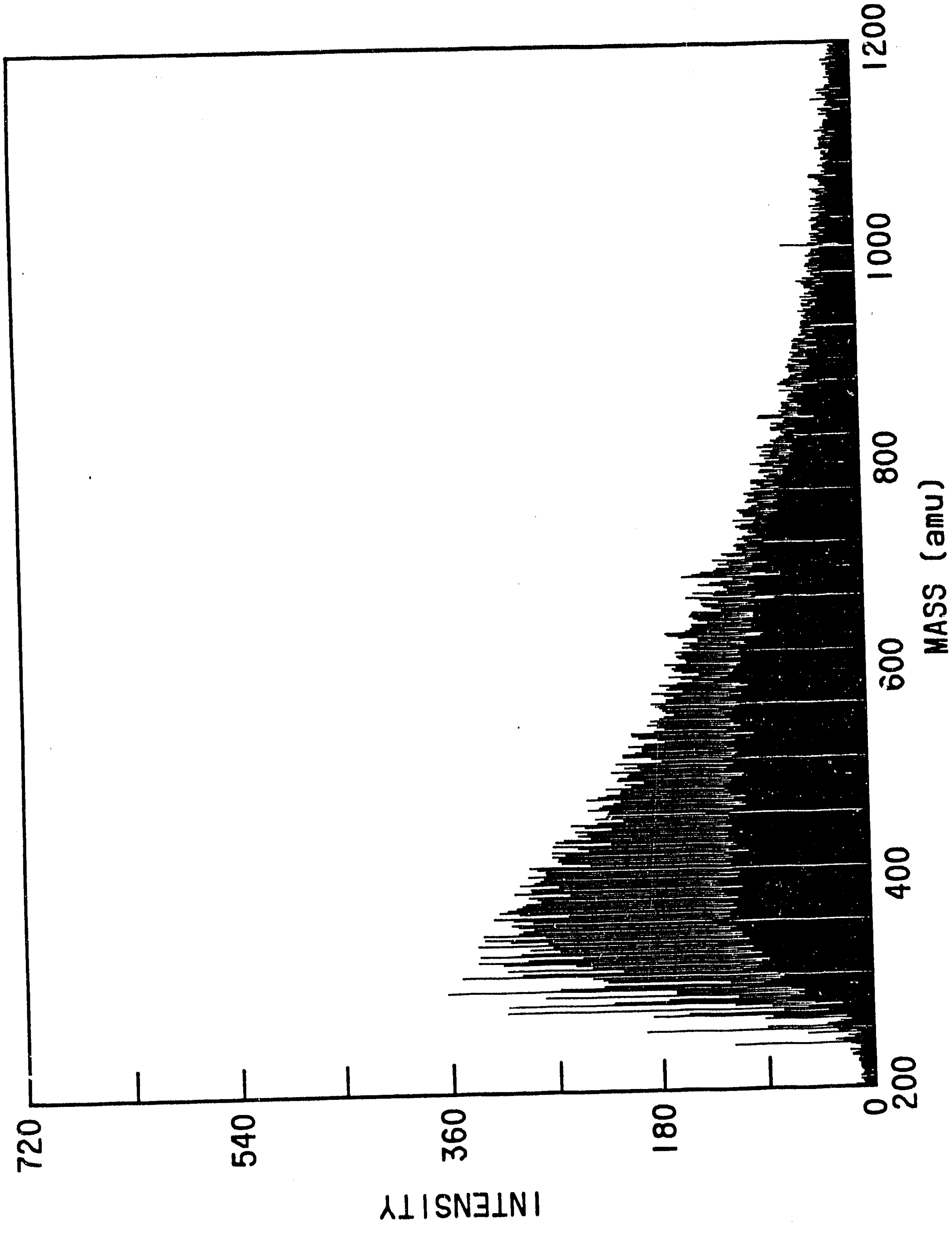

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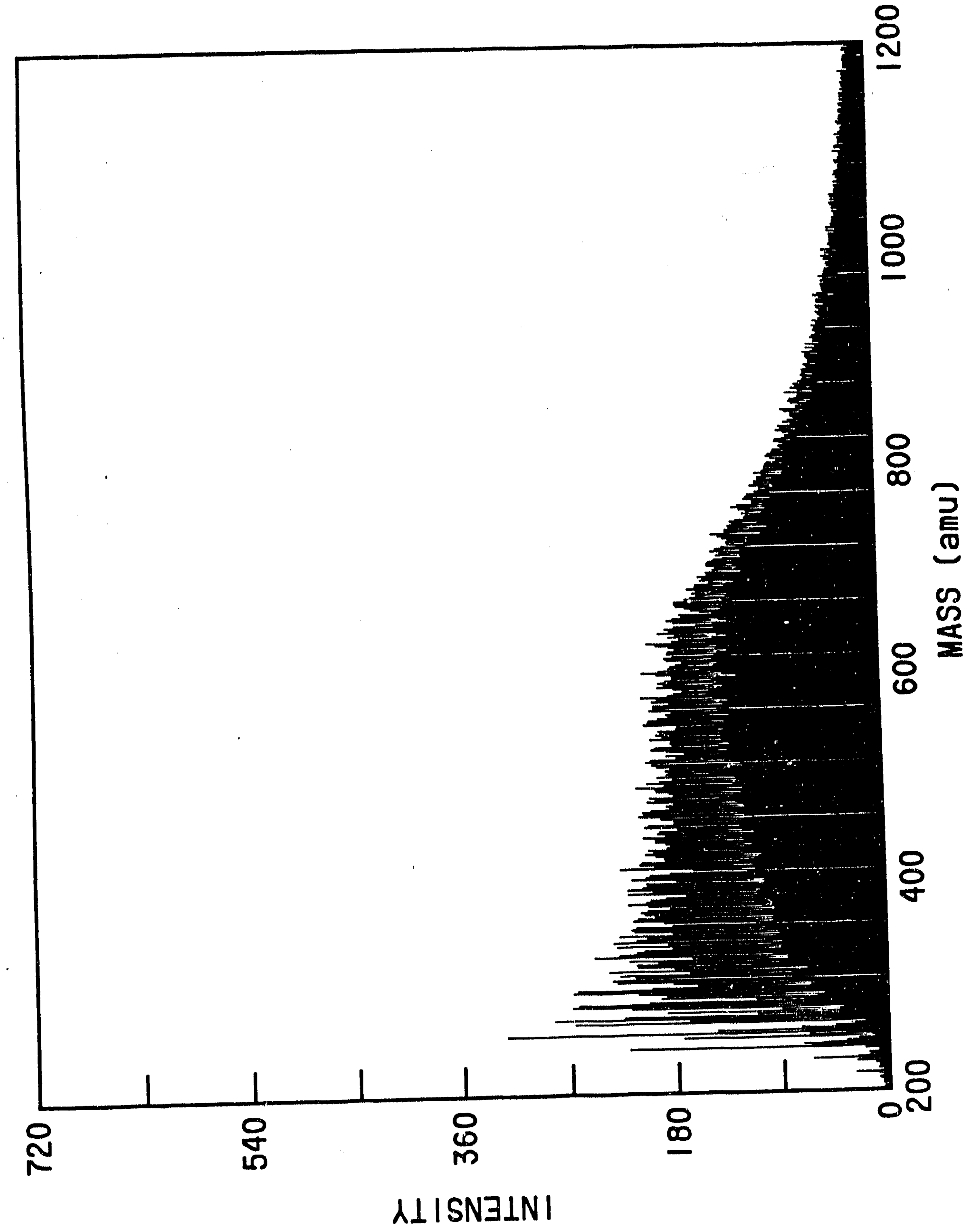

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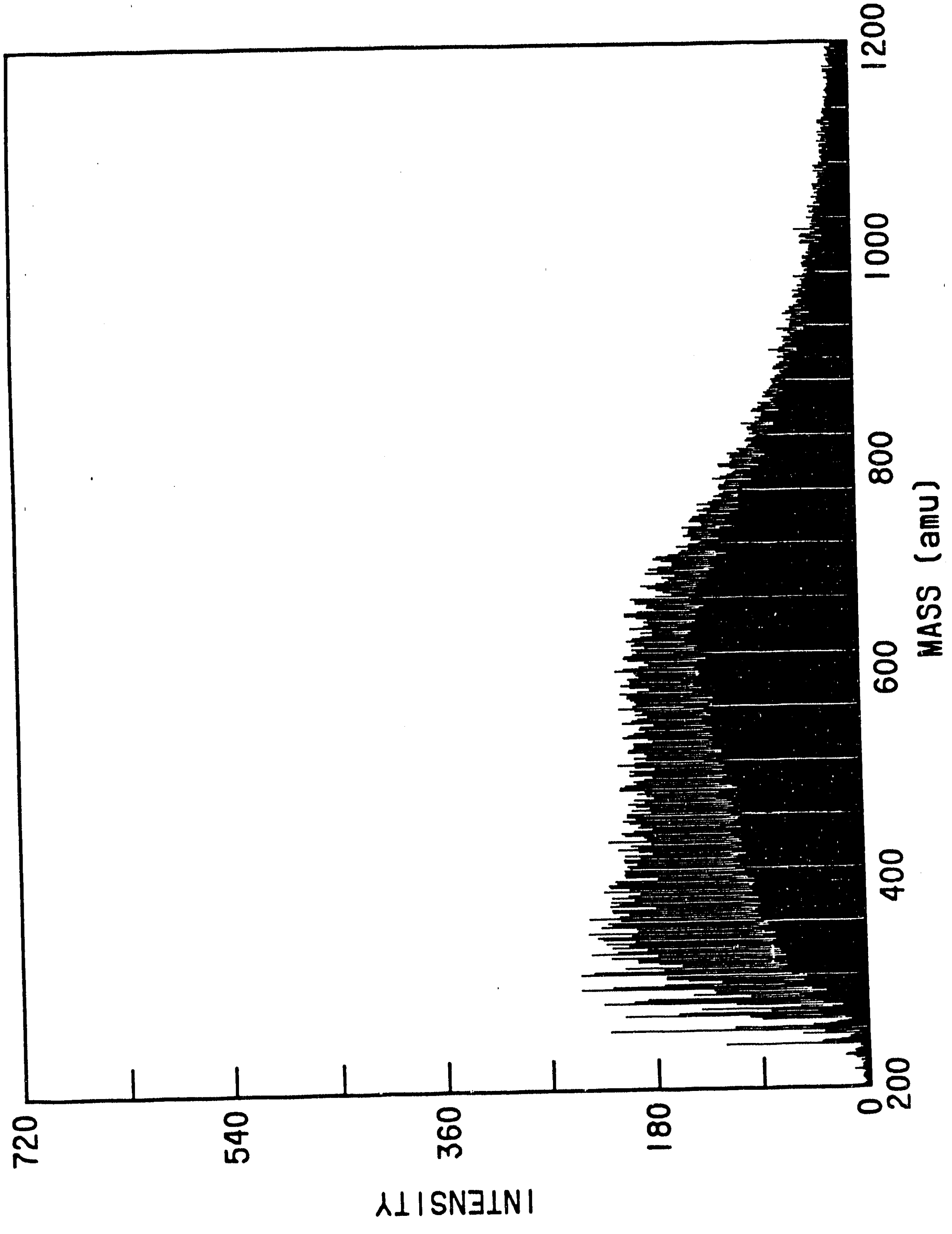

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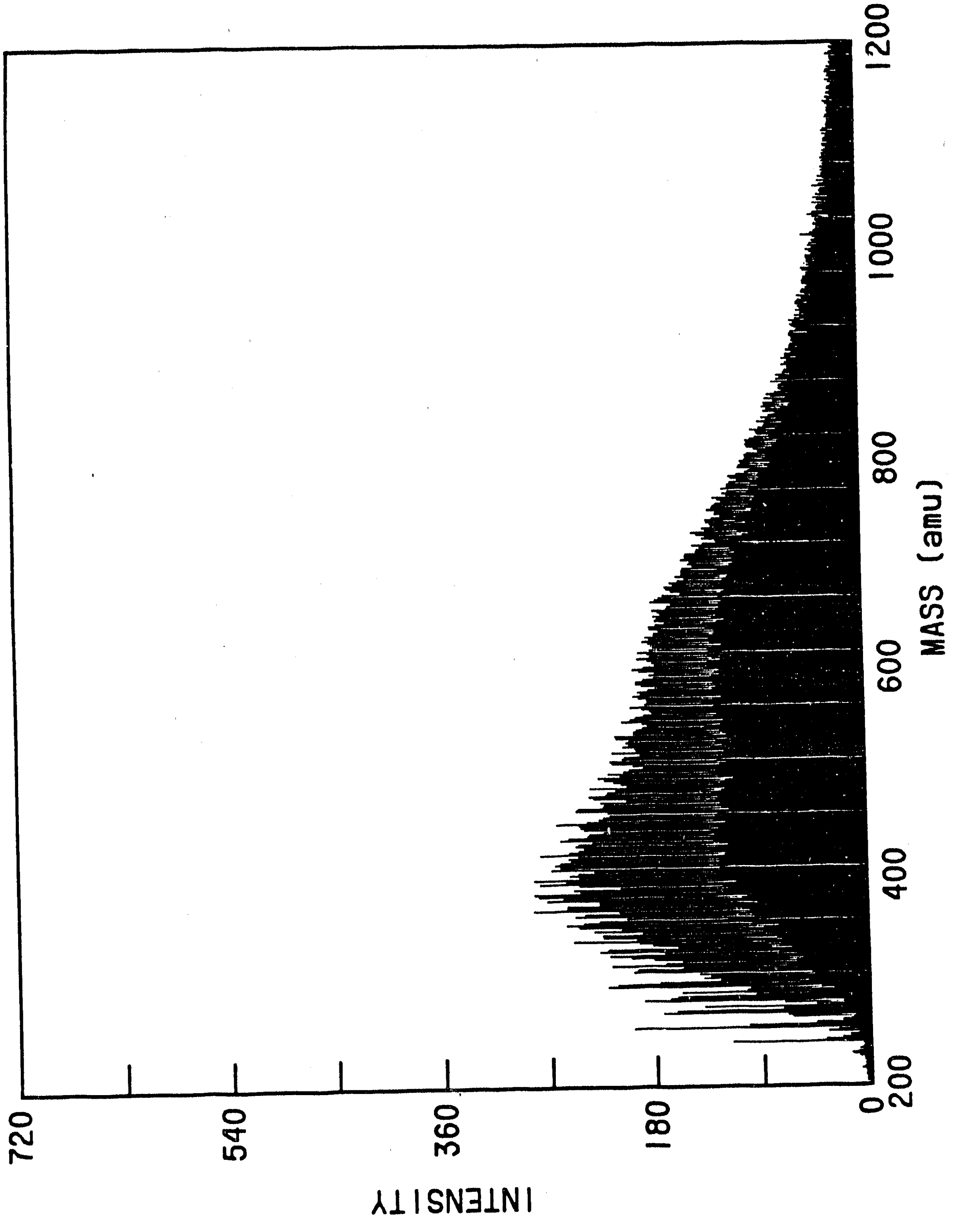

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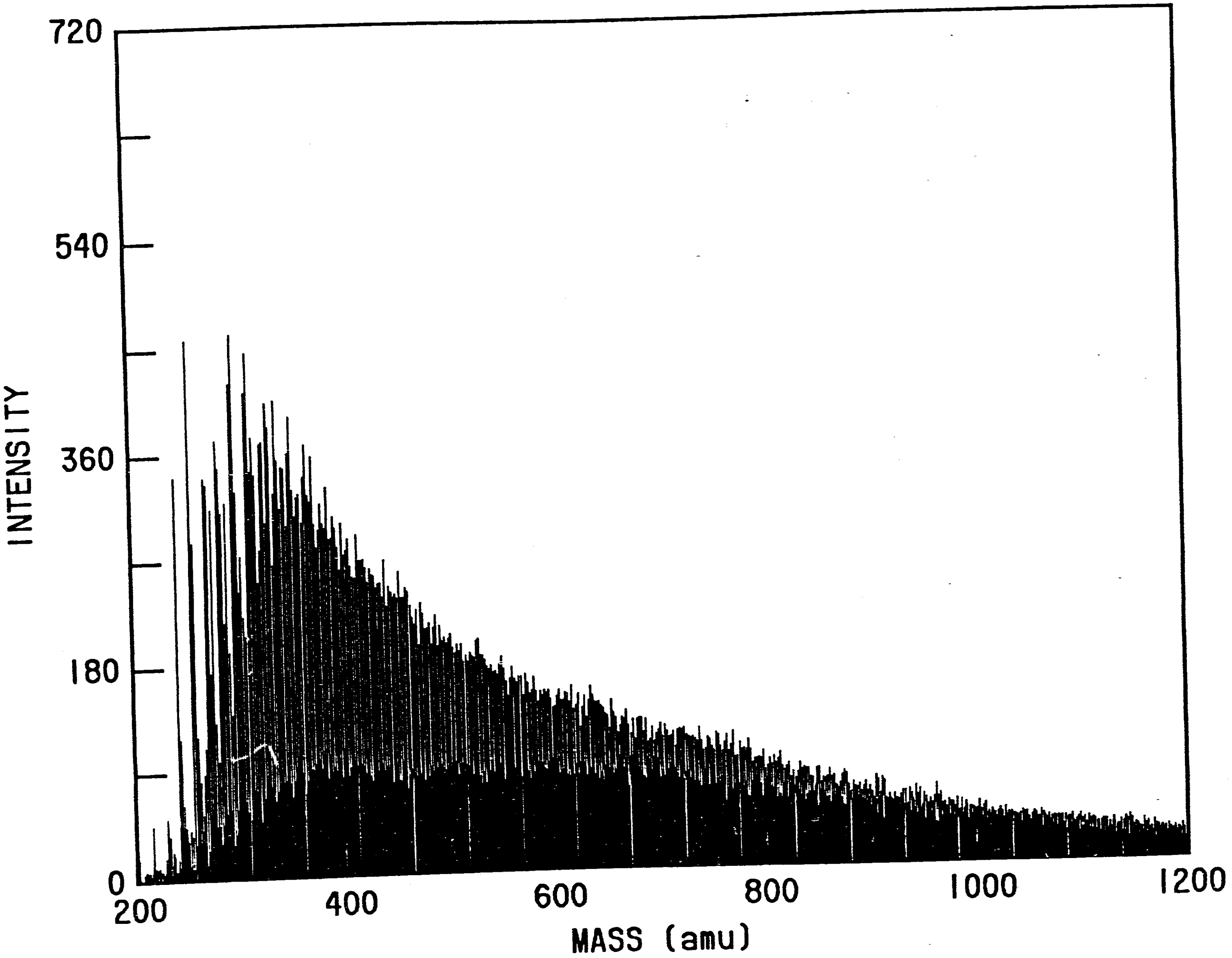

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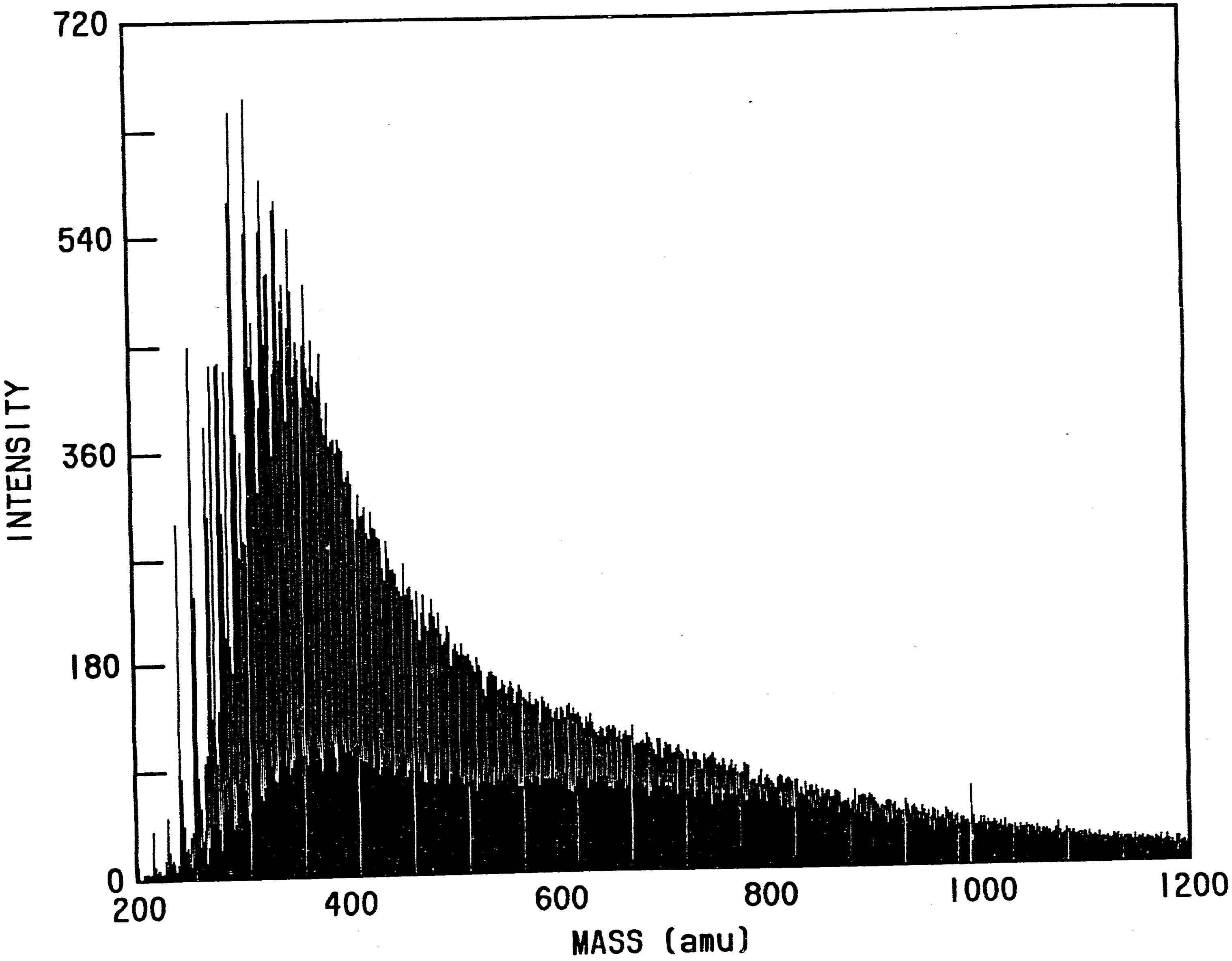

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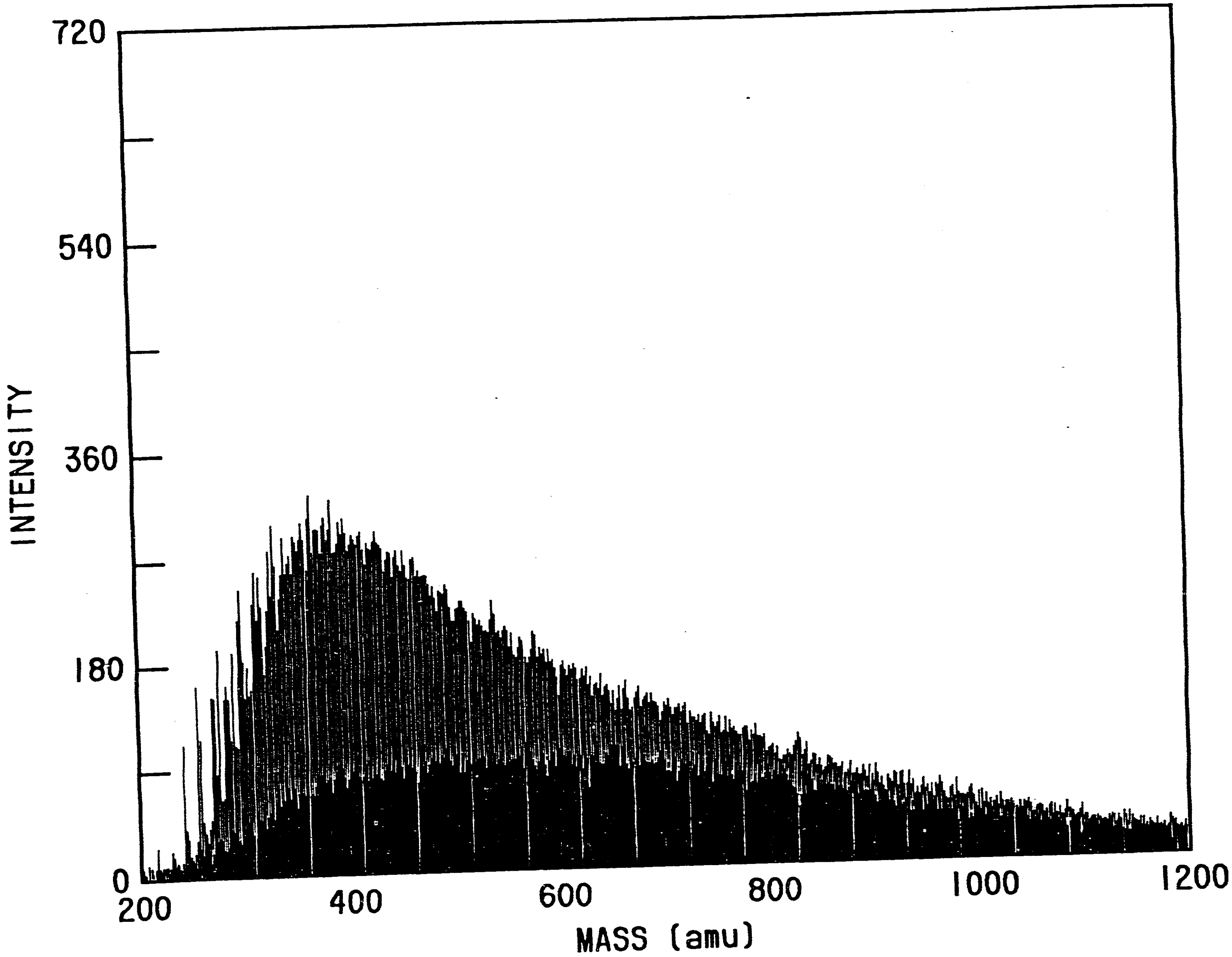

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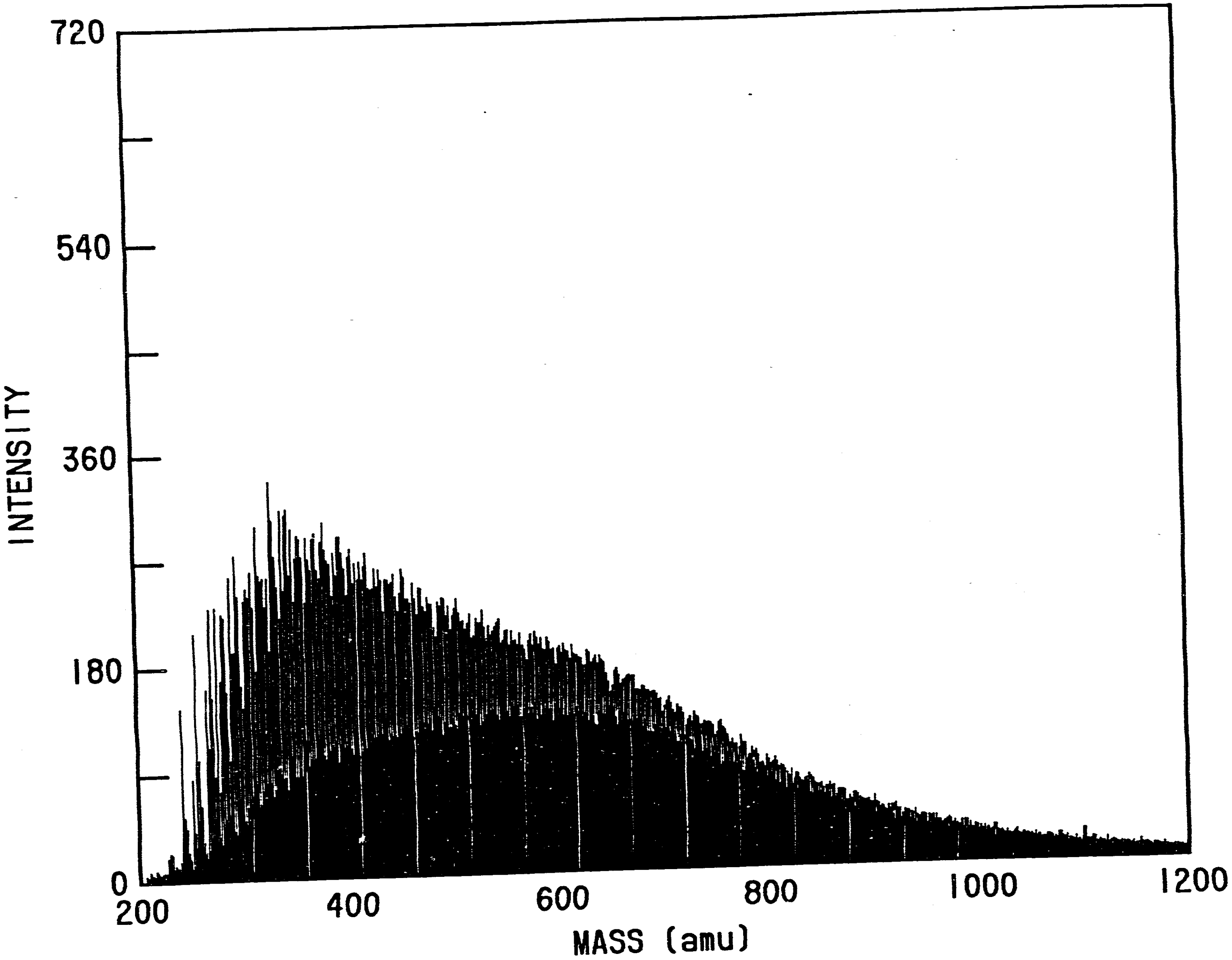

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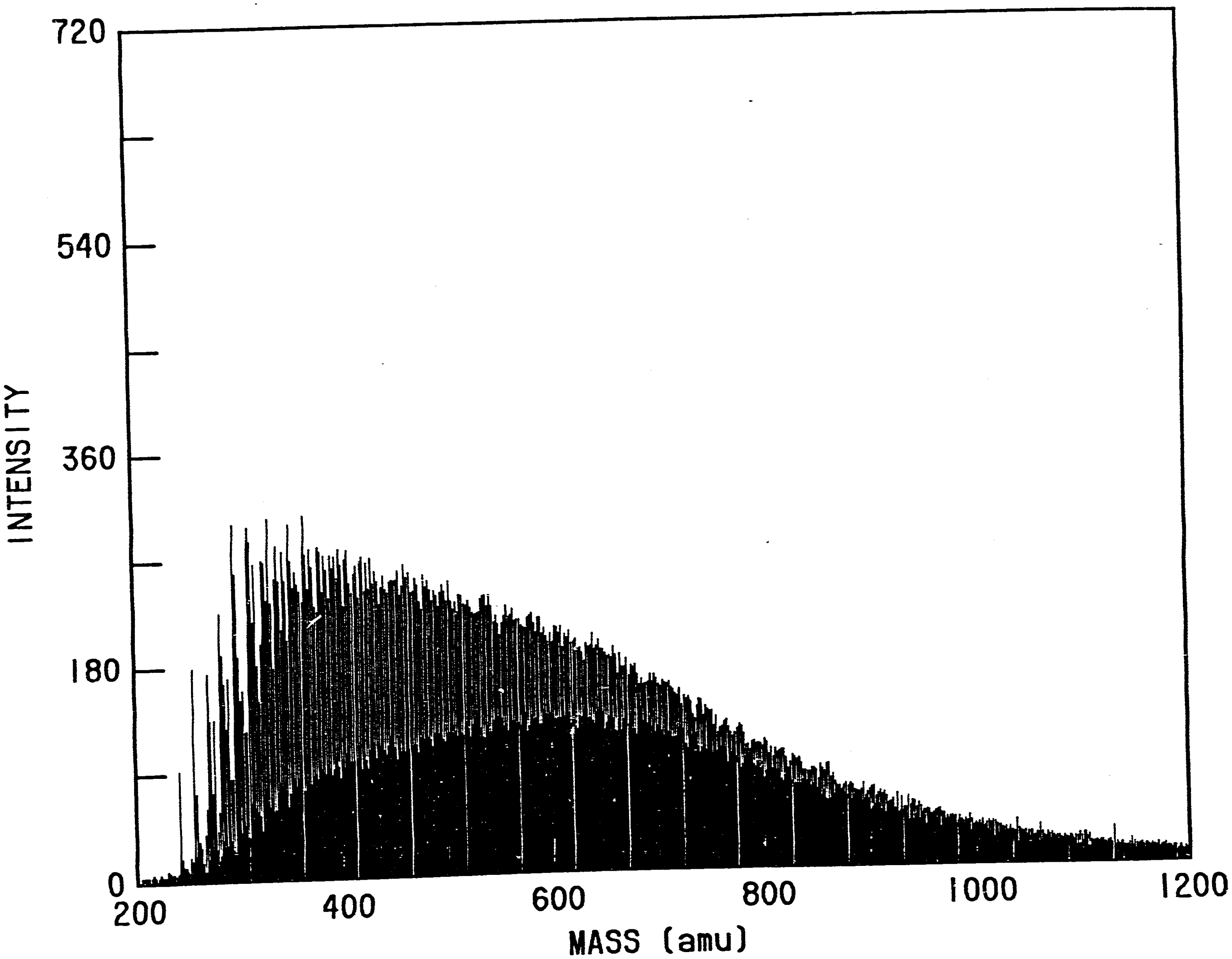

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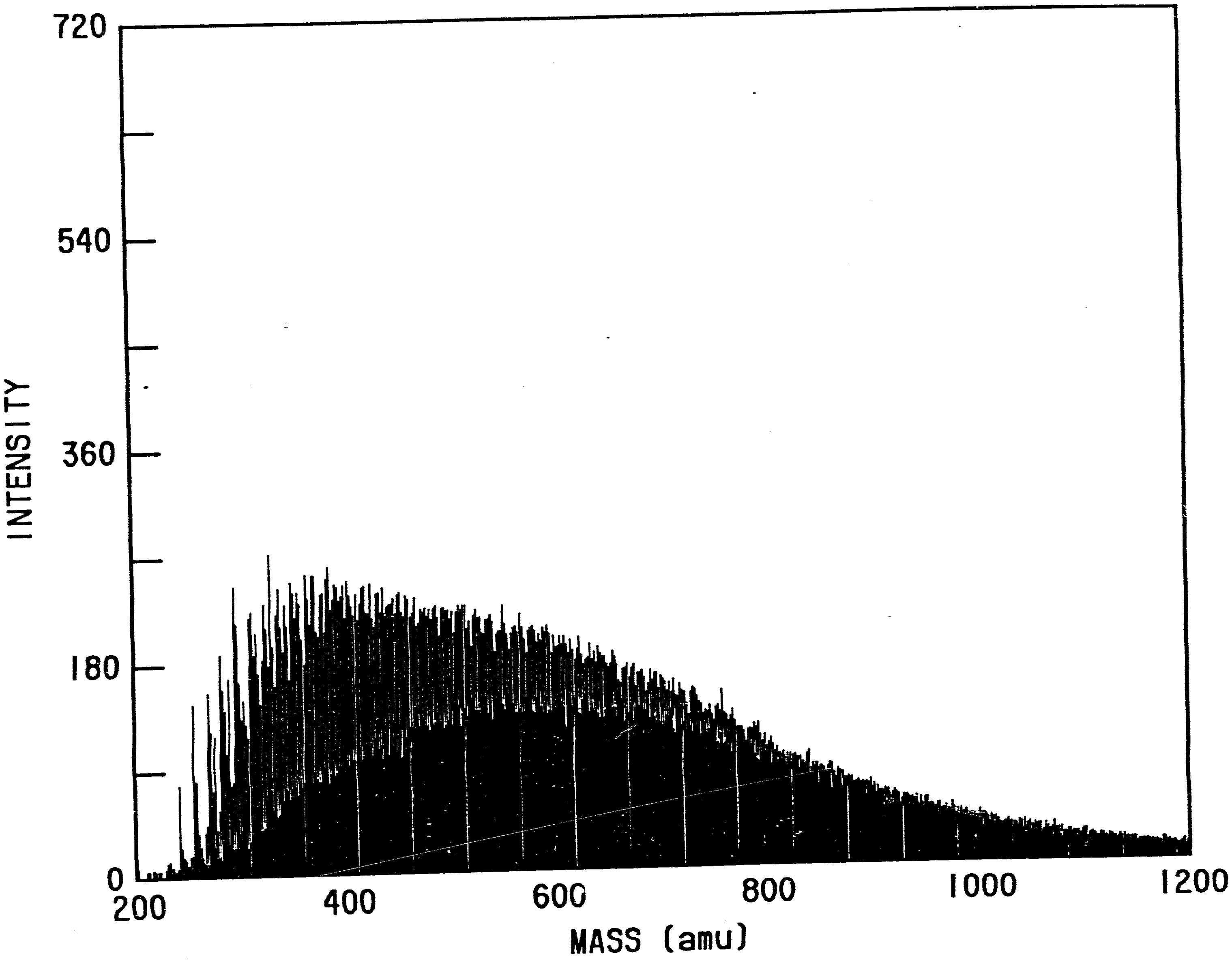

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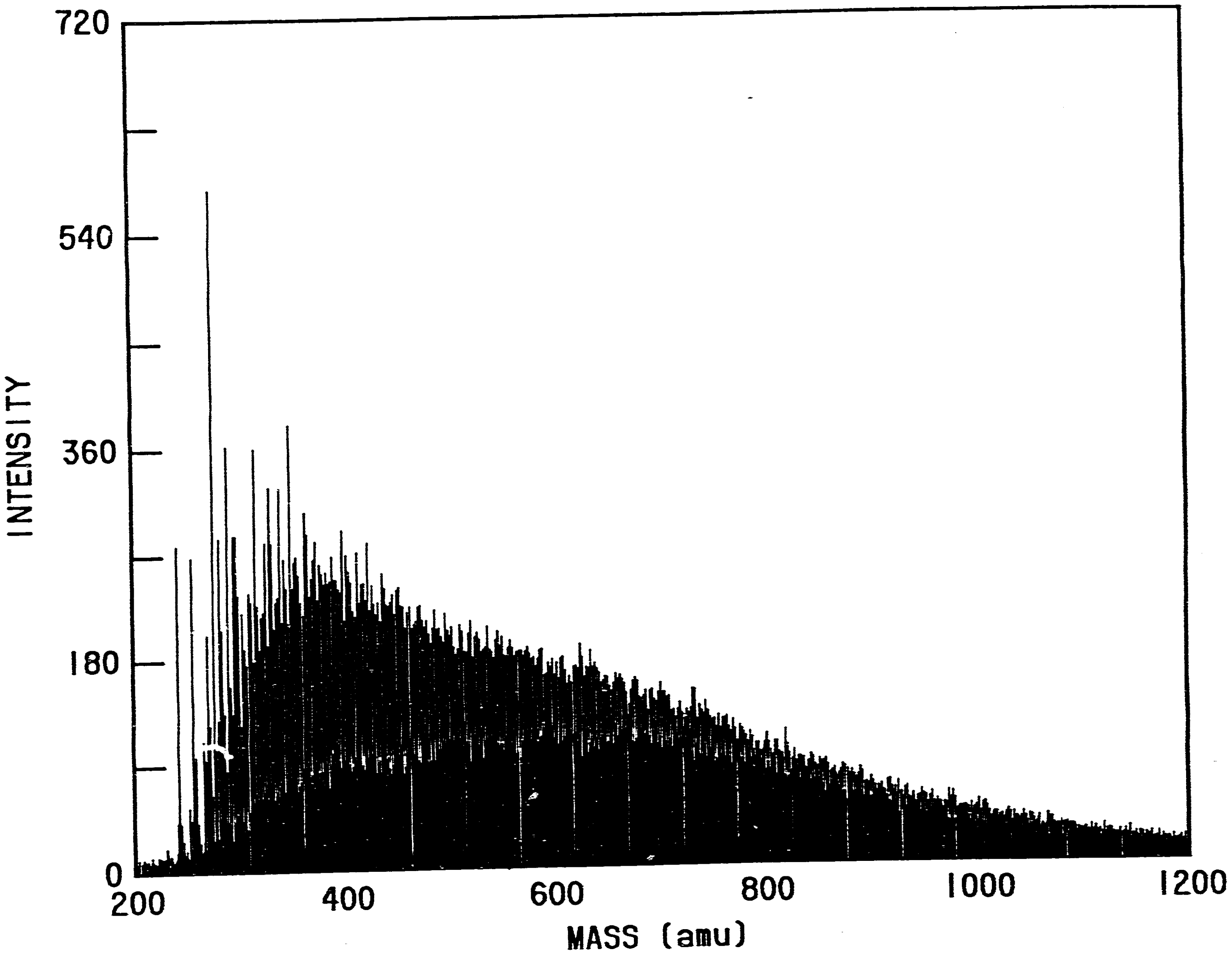
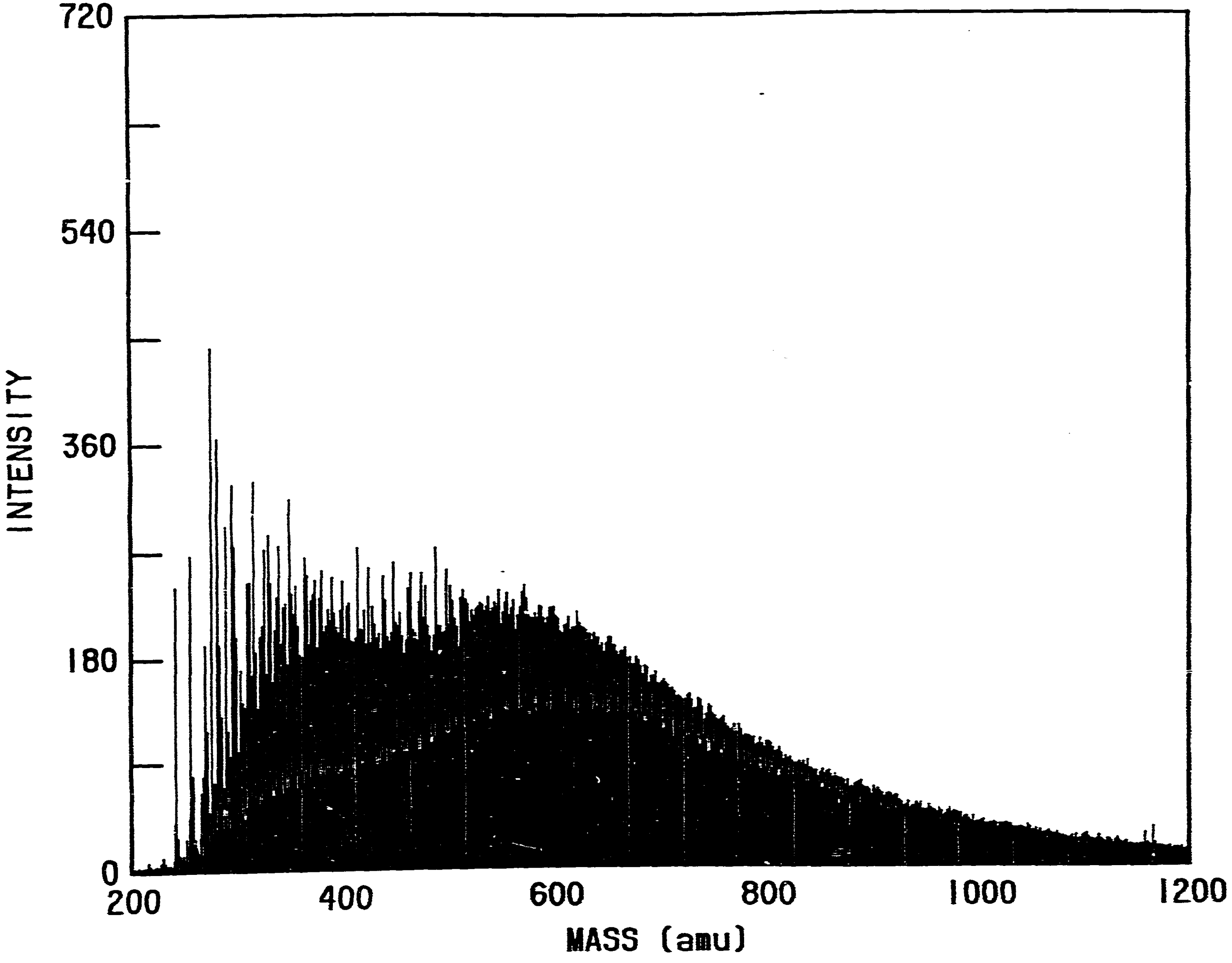
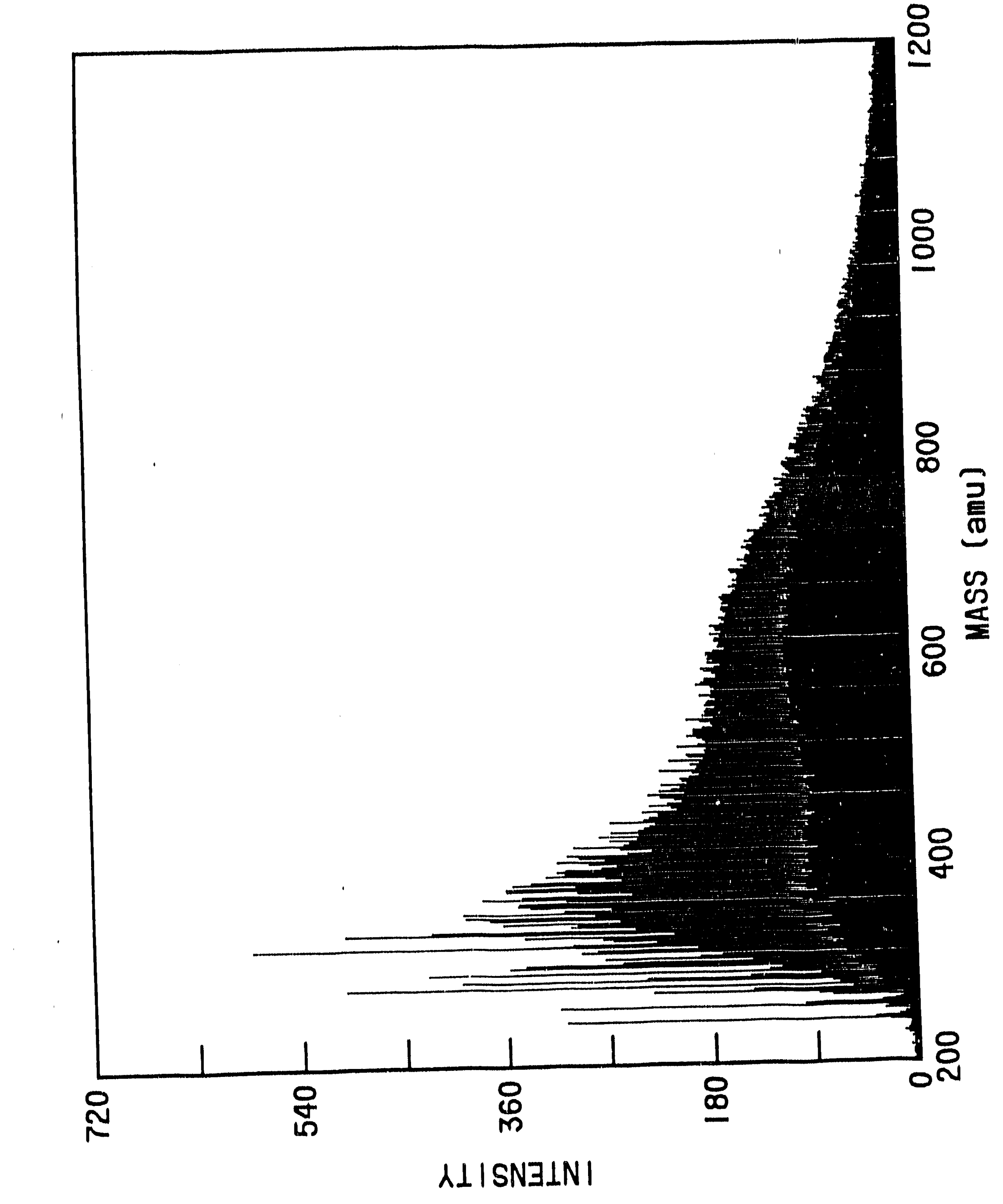


PITTSBURGH C/C: INTERSTAGE OIL



PITTSBURGH C/C: PRODUCT OiL



PITTSBURGH C/C: RECYCLE OIL

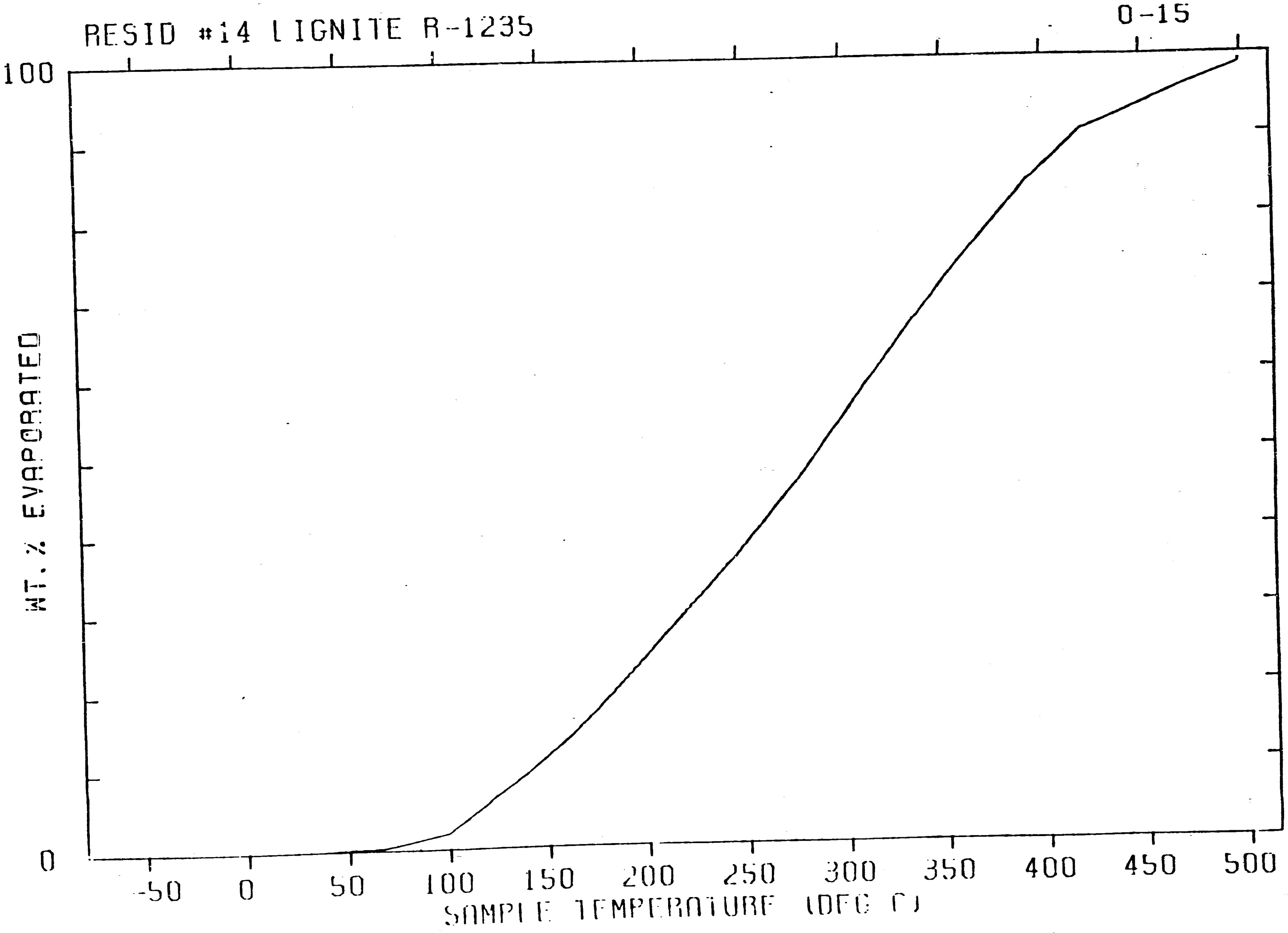
Appendix B

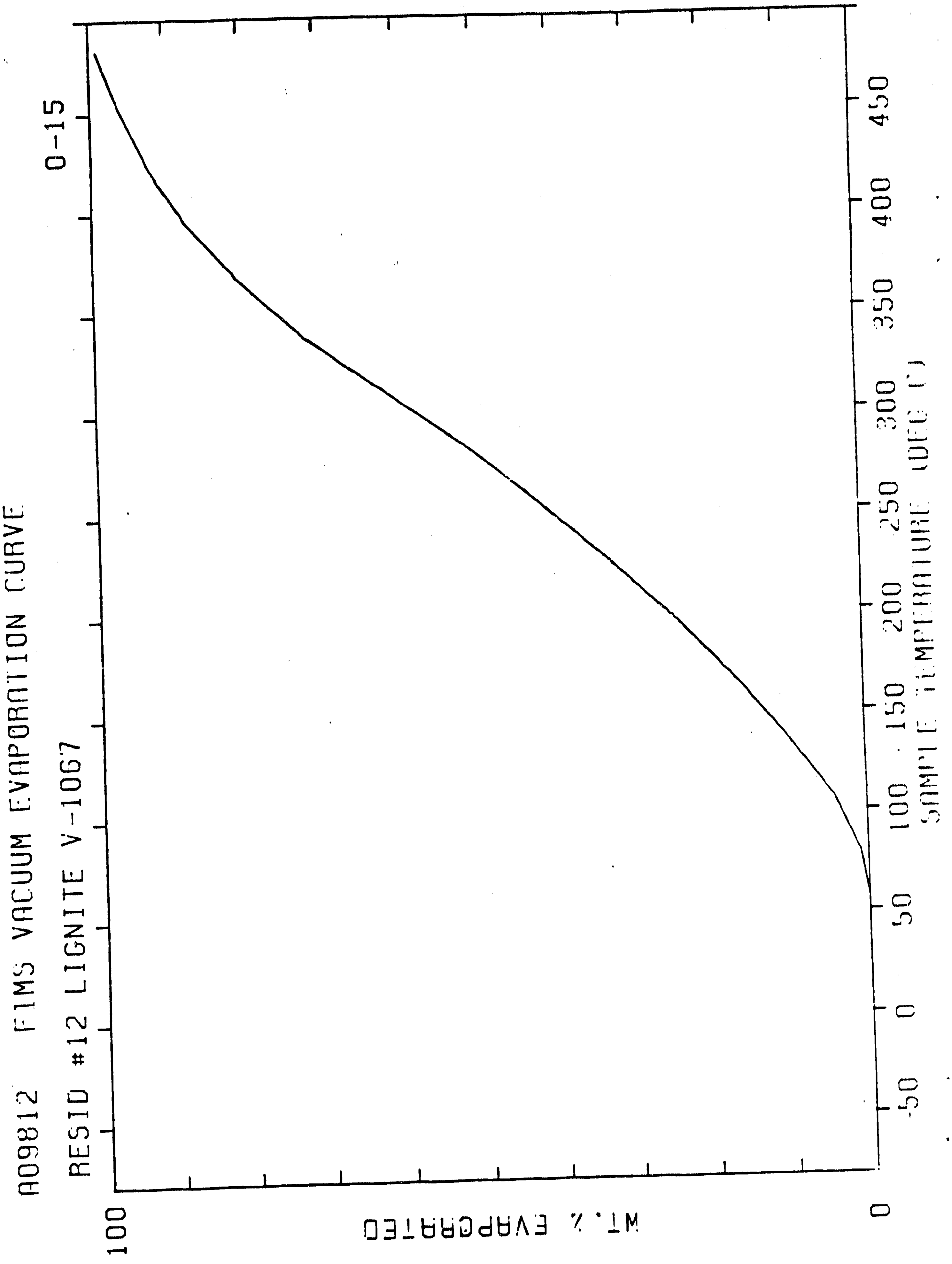
VACUUM EVAPORATION CURVES FOR COMPOSITE RESIDS

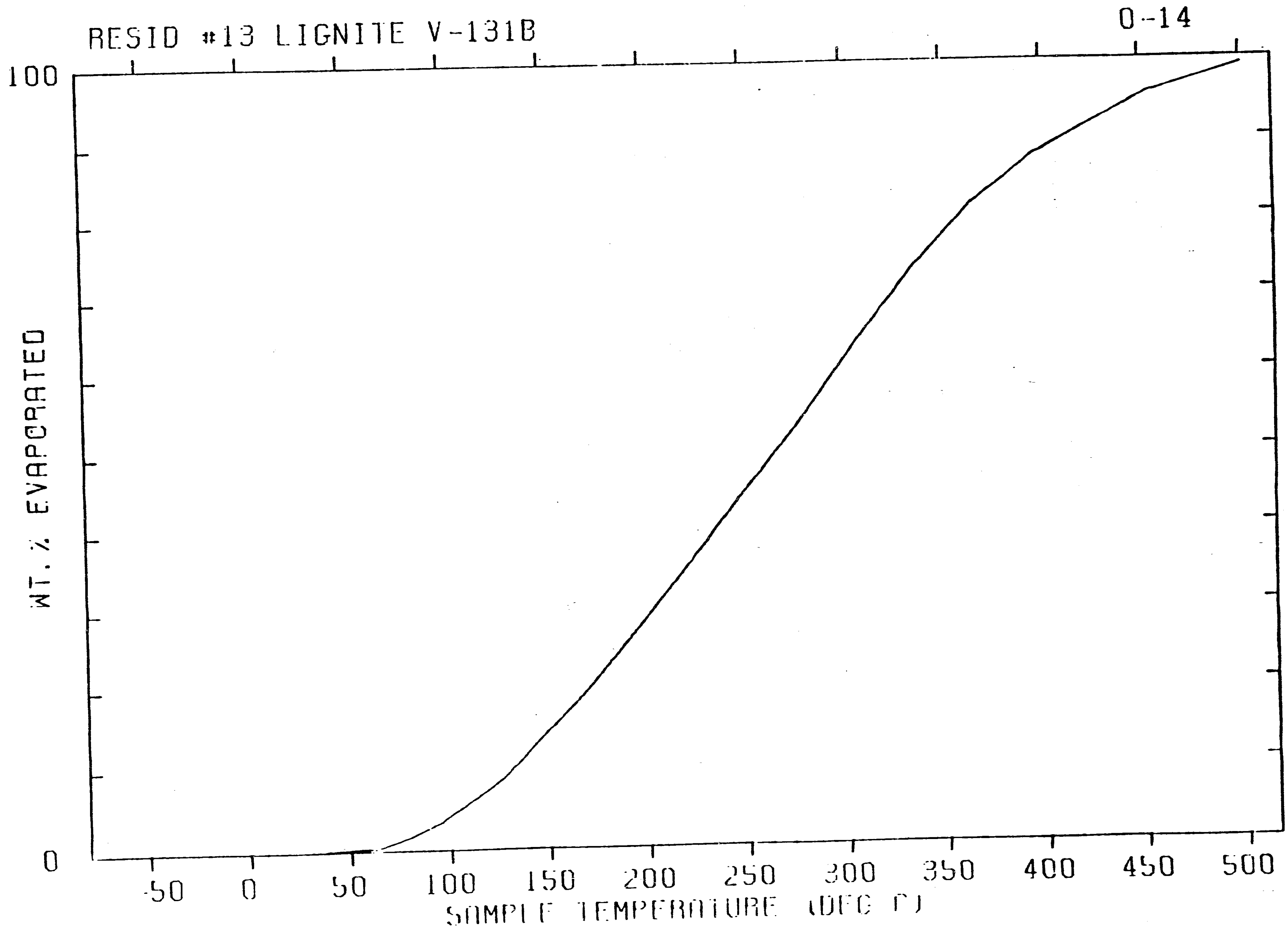
(Note that 100 on these curves is not 100% of sample, but 100% of that volatilized during analysis)

A09814 FIMS VACUUM EVAPORATION CURVE

RESID #14 LIGNITE R-1235

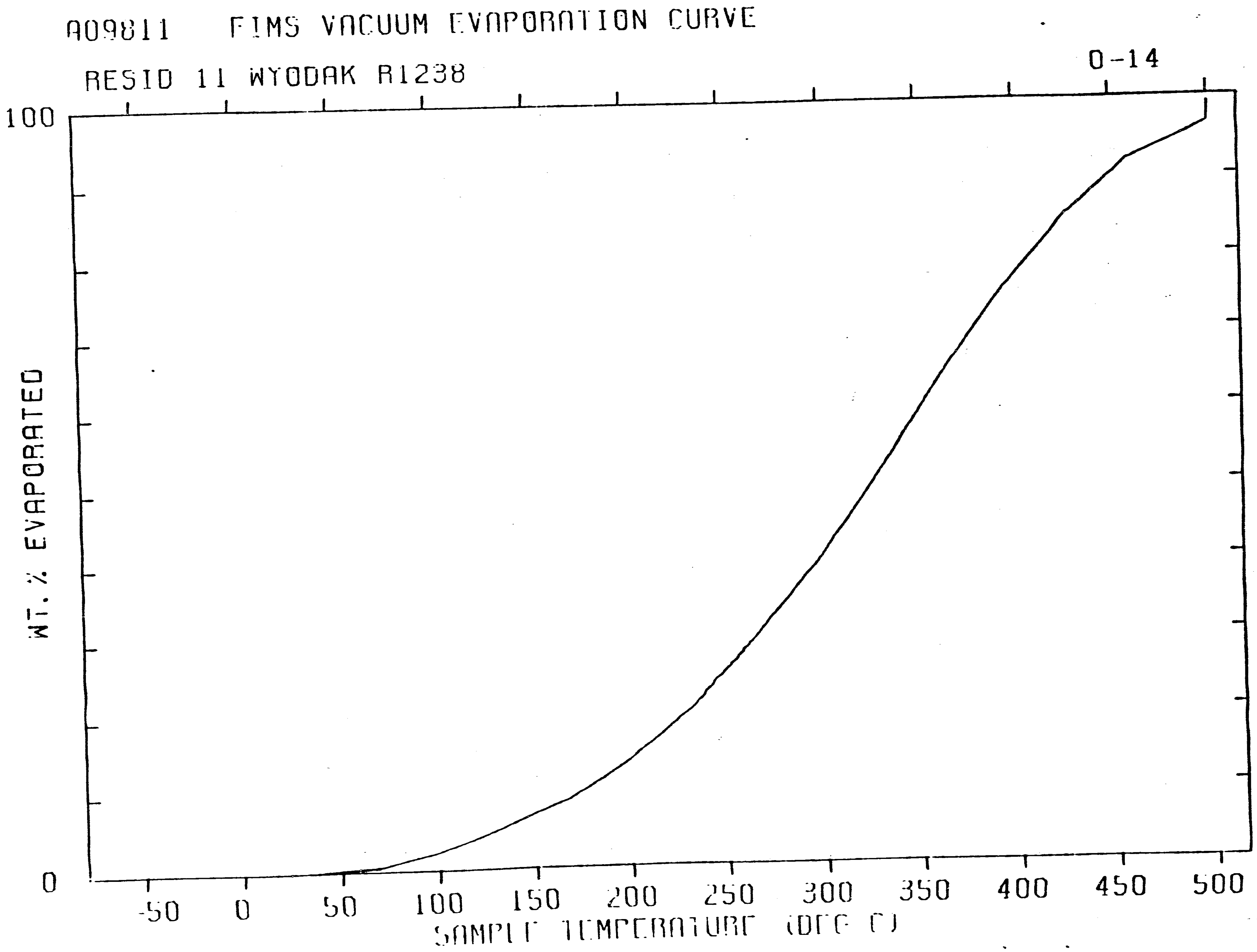


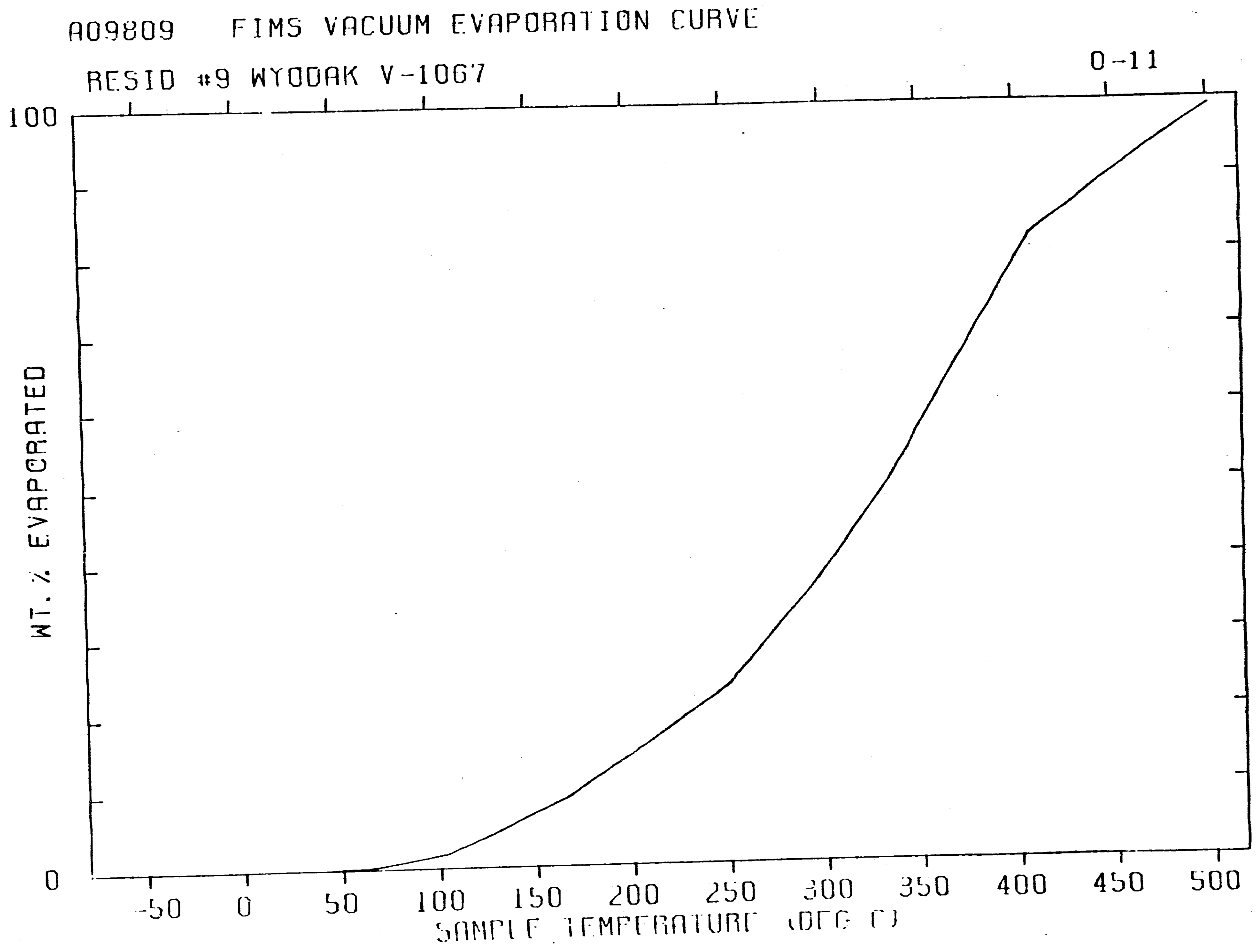

A09812 FIMS VACUUM EVAPORATION CURVE
RESID #12 LIGNITE V-1067
0-15
WT.% EVAPORATED
100
0
SAMPLE TEMPERATURE (DEG C)
-50
0
50
100
150
200
250
300
350
400
450



A09813 FIMS VACUUM EVAPORATION CURVE

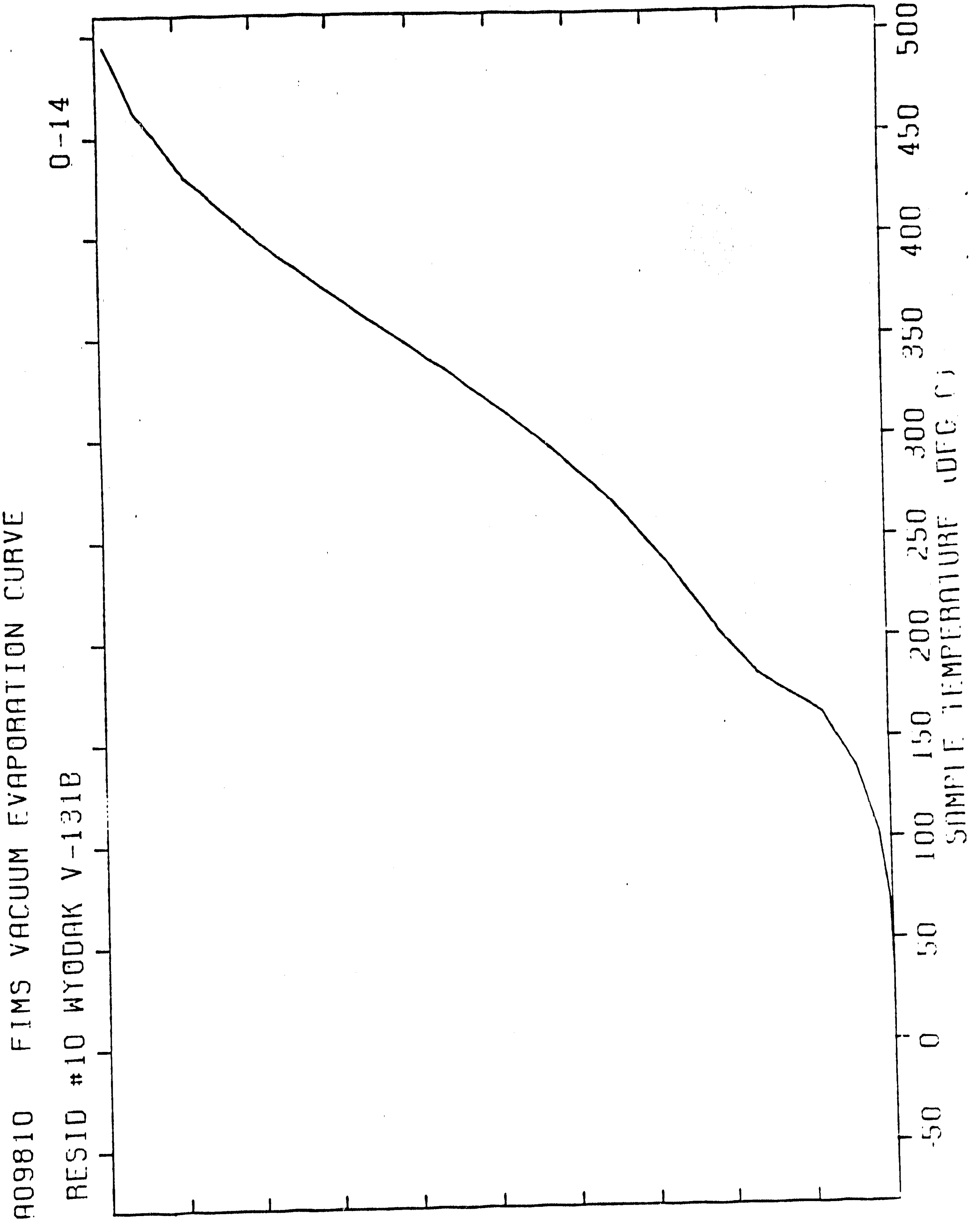
RESID #13 LIGNITE V-131B


A09811 FIMS VACUUM EVAPORATION CURVE
RESID 11 WYODAK R1238
0-14
100
0
WT.% EVAPORATED
-50
0
50
100
150
200
250
300
350
400
450
500
SAMPLE TEMPERATURE (DEG C)



A09809 FIMS VACUUM EVAPORATION CURVE

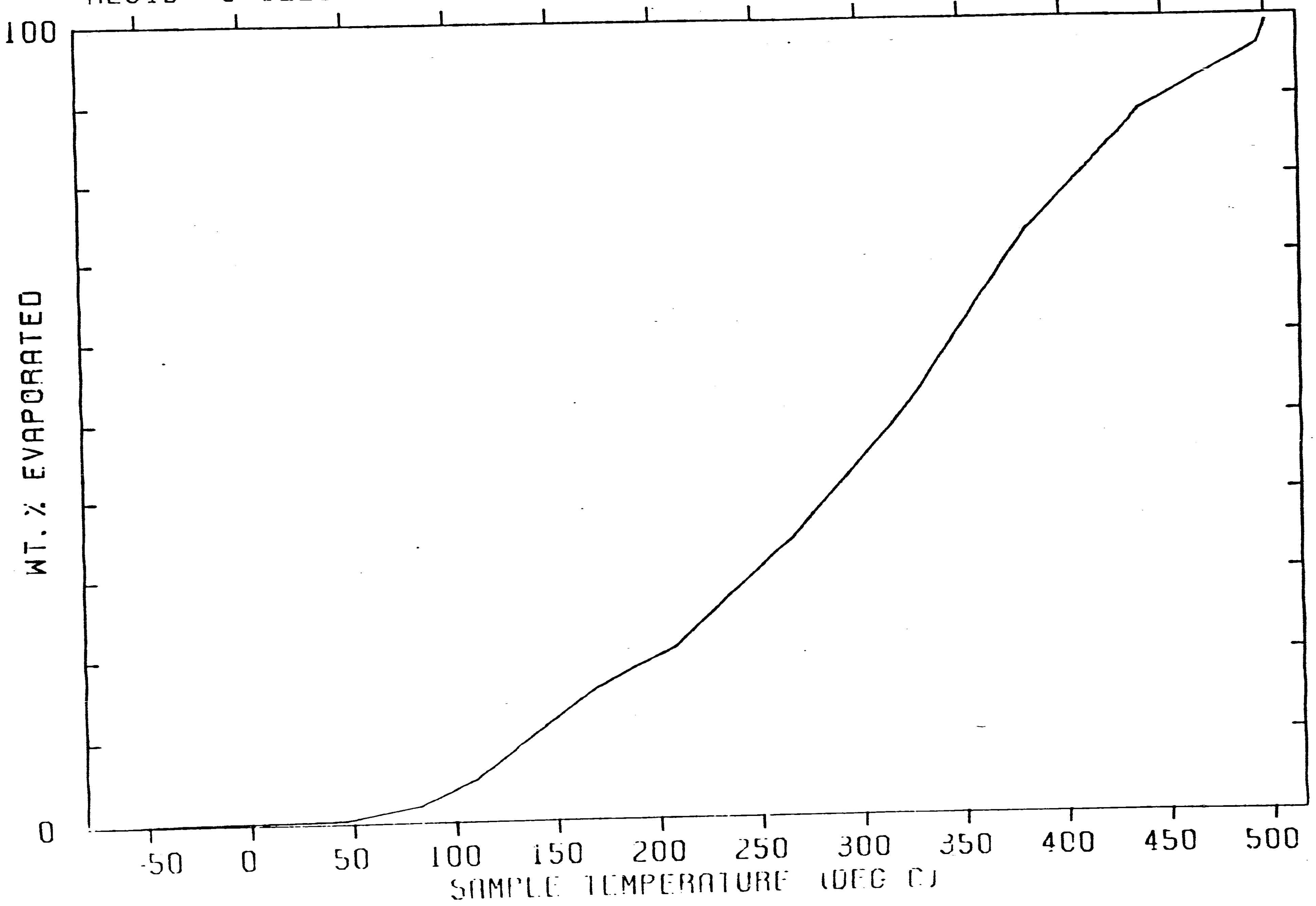
RESID #9 WYODAK V-1067


A09810 FIMS VACUUM EVAPORATION CURVE
RESID #10 WYODAK V-131B
O-14
WT.% EVAPORATED
100
0
SAMPLE TEMPERATURE (DEG C)
-50
0
50
100
150
200
250
300
350
400
450
500

A09805 FIMS VACUUM EVAPORATION CURVE

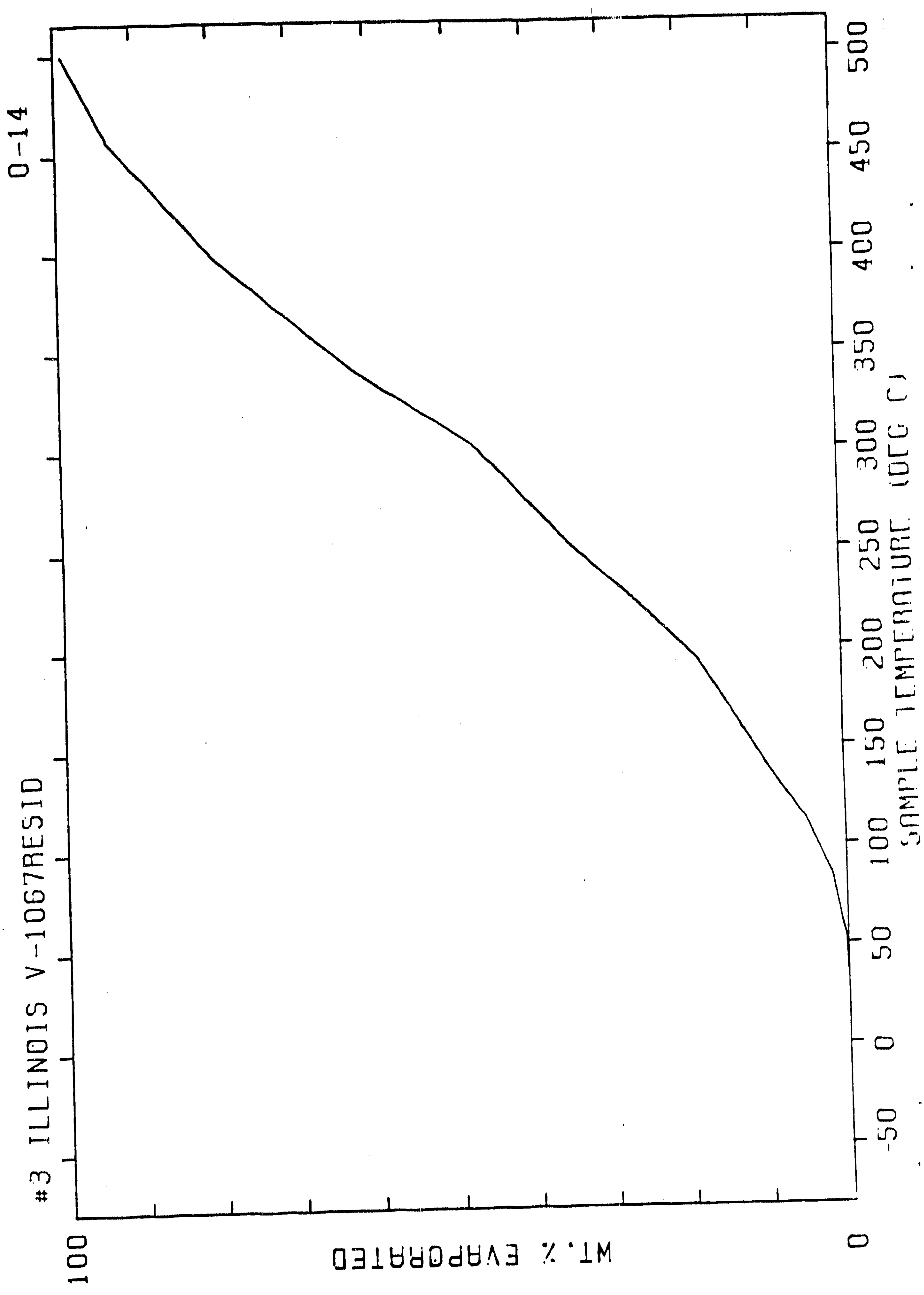
RESID #5 ILLINOIS R1235

0-11



A09803 FIMS VACUUM EVAPORATION CURVE

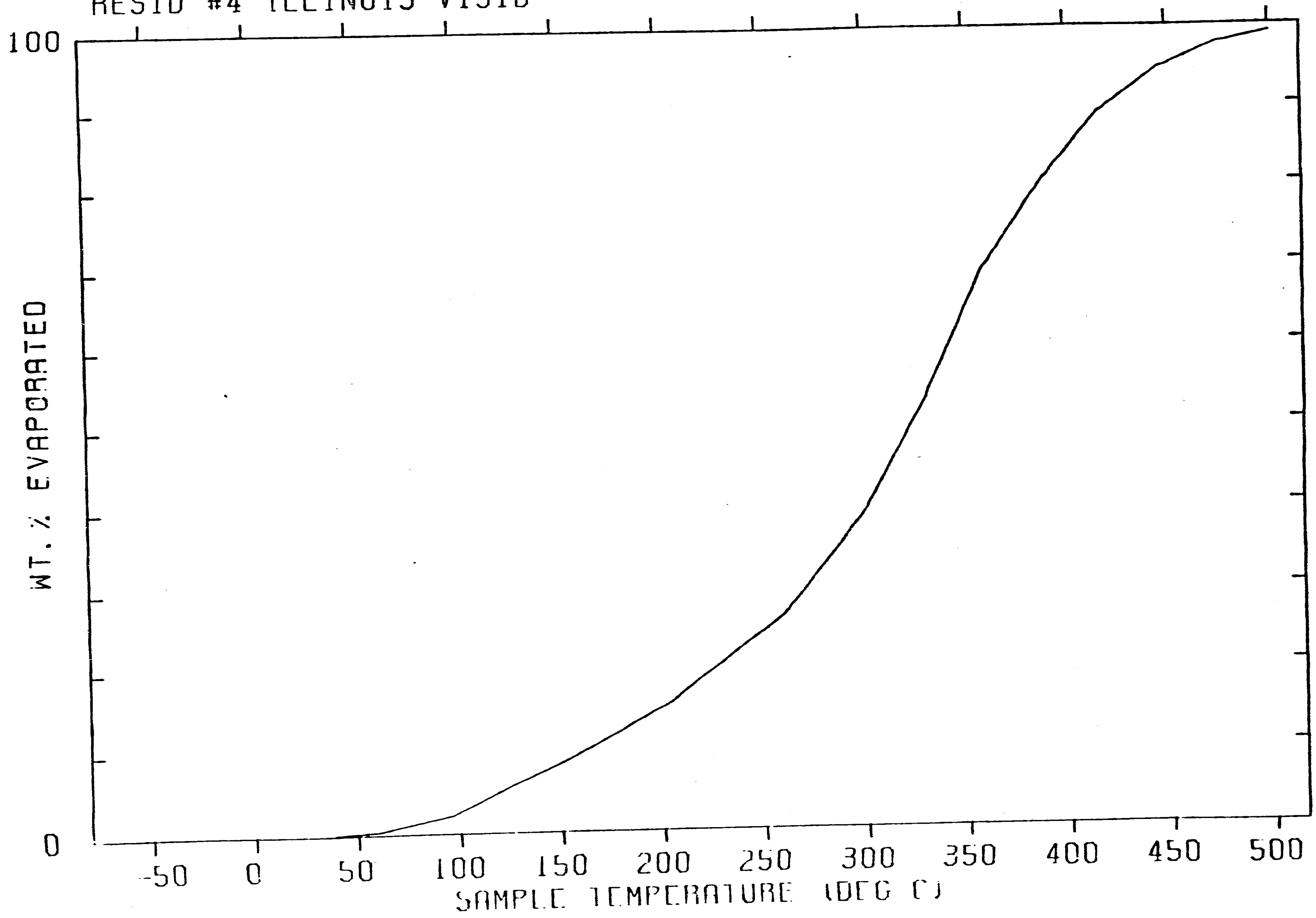
#3 ILLINOIS V-1067RESID



C09804 FIMS VACUUM EVAPORATION CURVE

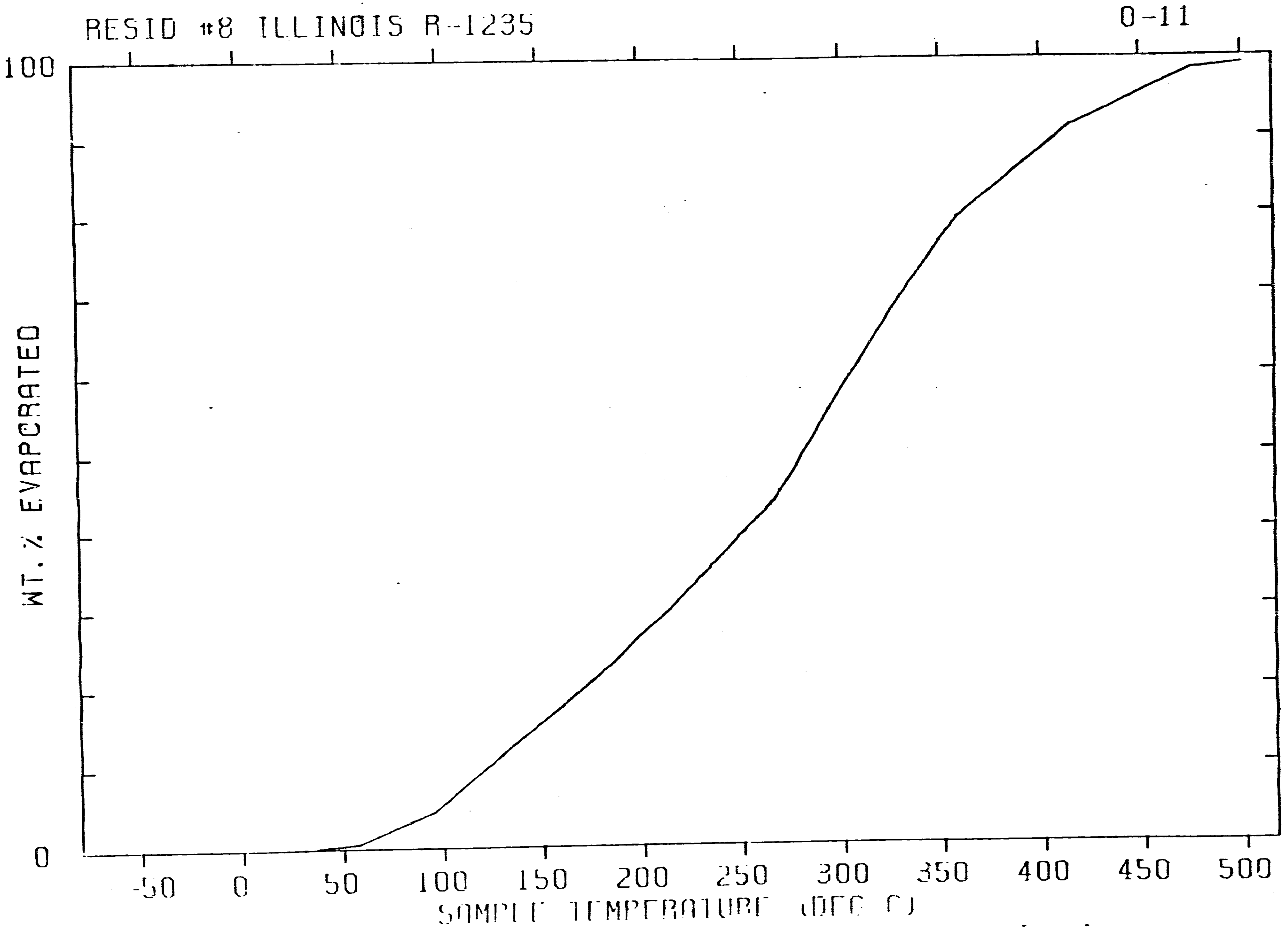
RESID #4 ILLINOIS V131B

0-13



C09808 FIMS VACUUM EVAPORATION CURVE

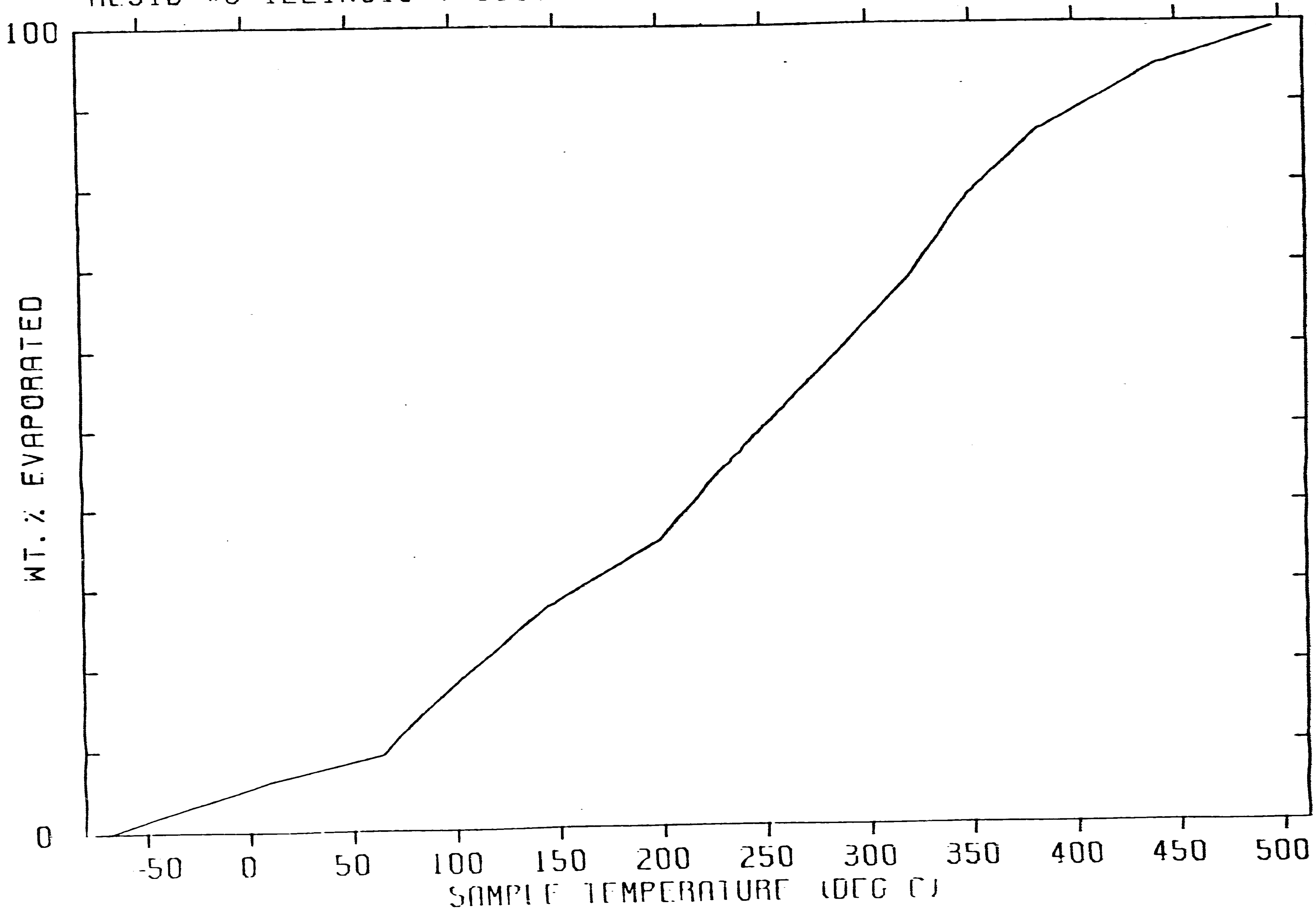
RESID #8 ILLINOIS R-1235

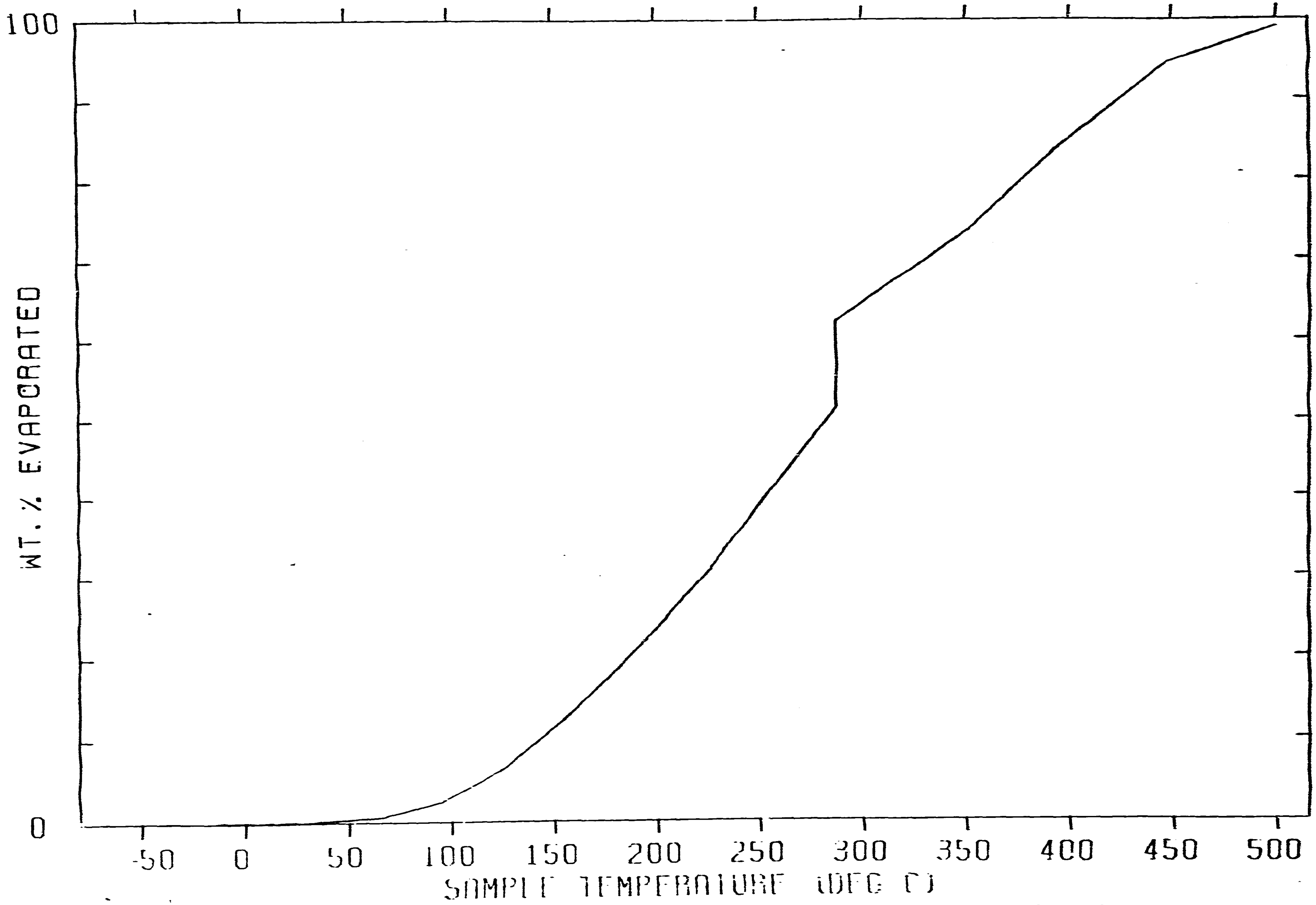


A09806 FIMS VACUUM EVAPORATION CURVE

RESID #G ILLINOIS V-1067

0-12

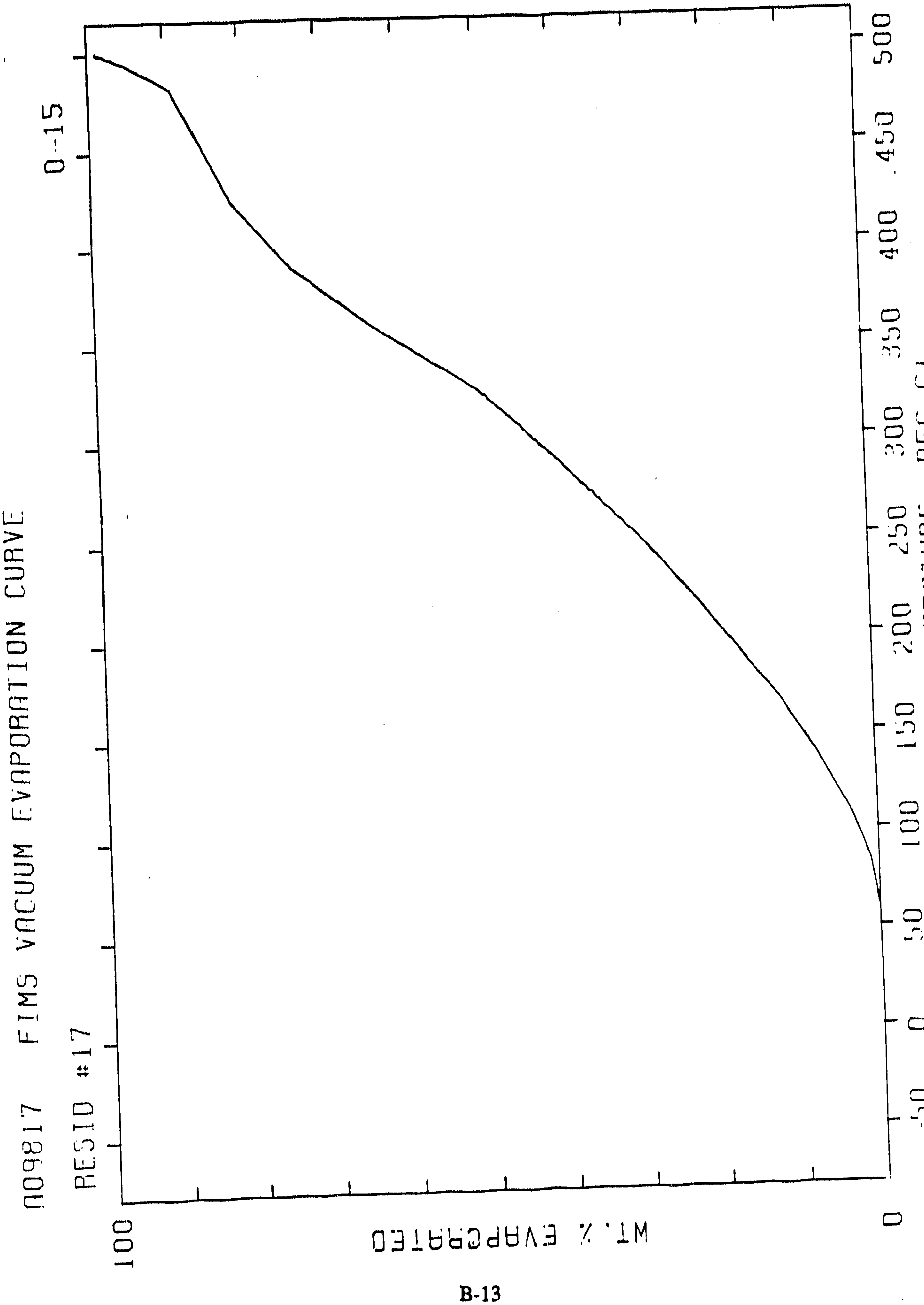


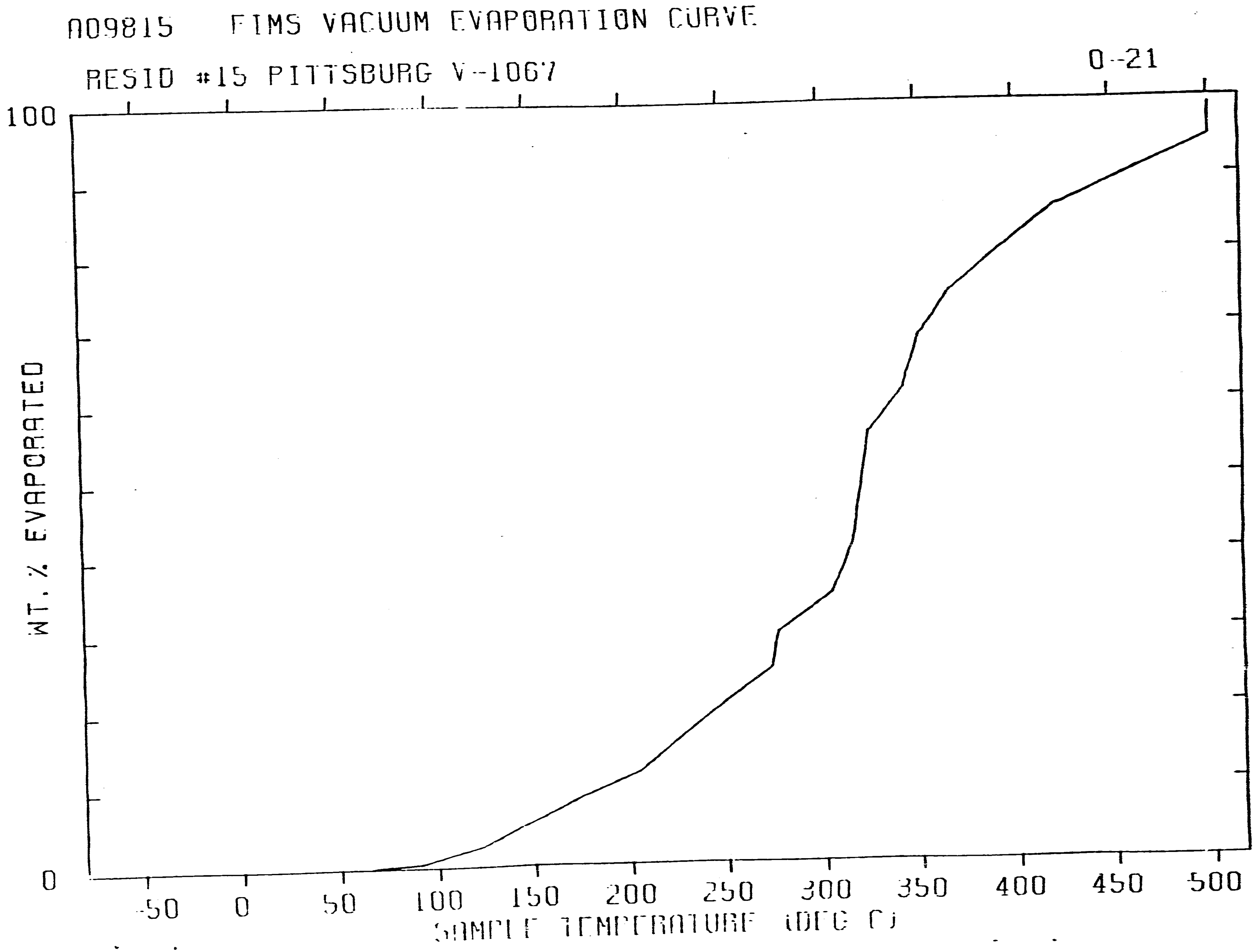


A09807 FIMS VACUUM EVAPORATION CURVE

RESID #7 ILLINOIS V-131B

0-13


A09817
RESID #17
FIMS VACUUM EVAPORATION CURVE
0-15
-50
0
50
100
150
200
250
300
350
400
450
500
SAMPLE TEMPERATURE (DEG C)
100
0
WT.% EVAPORATED

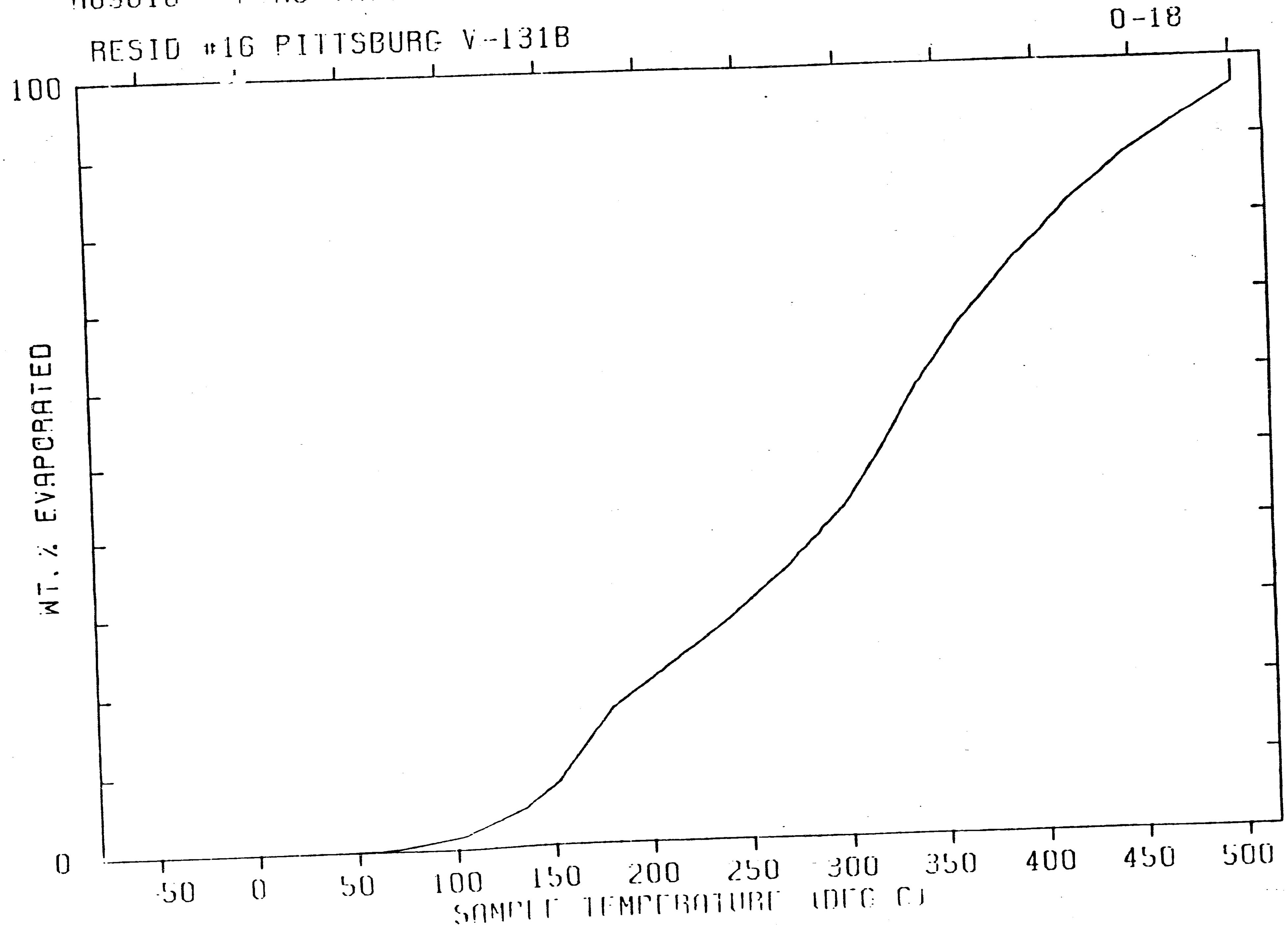


A09815 FIMS VACUUM EVAPORATION CURVE

RESID #15 PITTSBURG V-1067

009816 FIMS VACUUM EVAPORATION CURVE

RESID #16 PITTSBURG V-131B



END

DATE
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6/29/92