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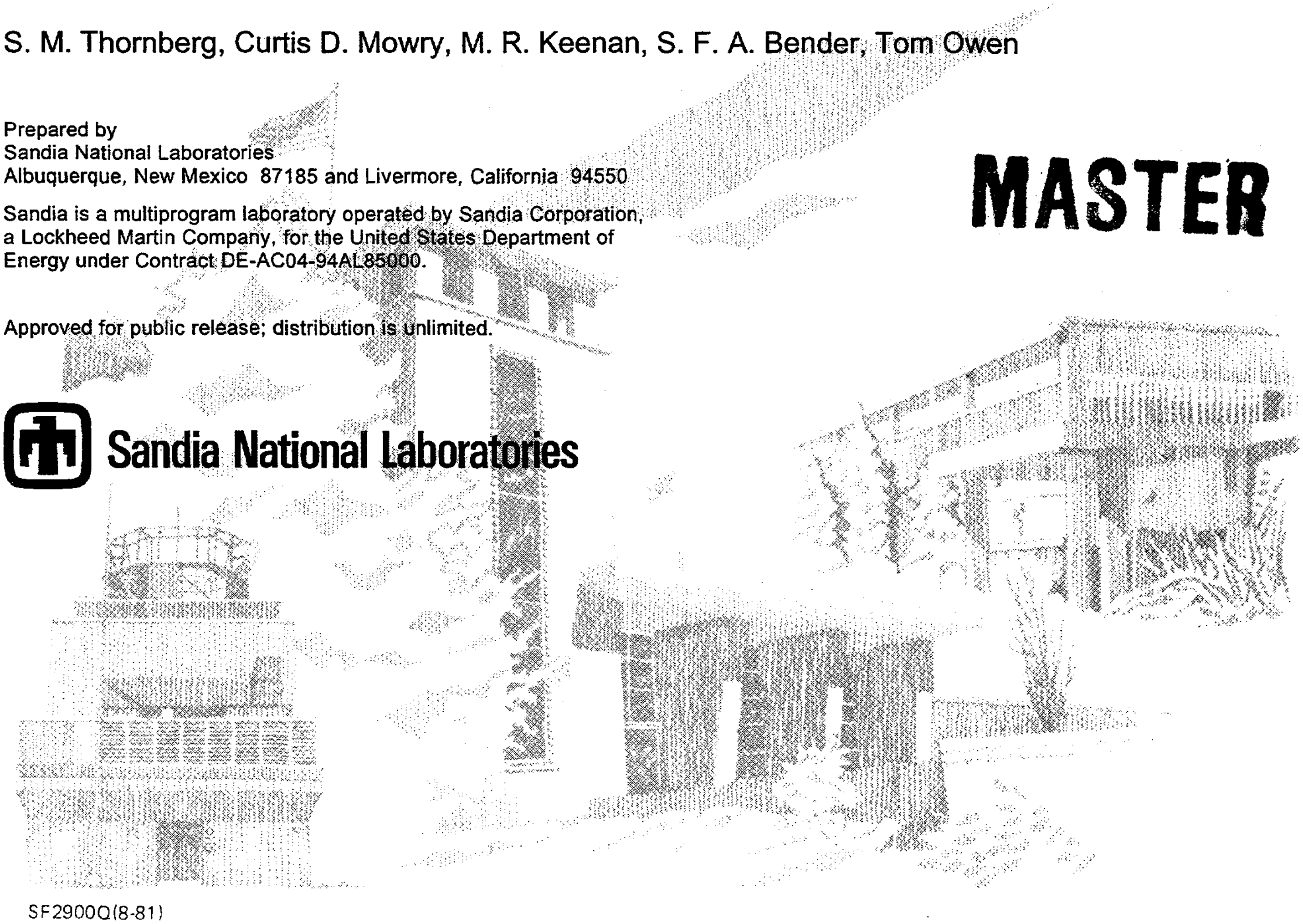
Real-Time Monitoring of Volatile Organic Compounds Using Chemical Ionization Mass Spectroscopy: Final Report

S. M. Thornberg, Curtis D. Mowry, M. R. Keenan, S. F. A. Bender, Tom Owen



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REAL-TIME MONITORING OF VOLATILE ORGANIC COMPOUNDS USING CHEMICAL IONIZATION MASS SPECTROSCOPY: FINAL REPORT

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ABSTRACT

Volatile organic compound (VOC) emission to the atmosphere is of great concern to semiconductor manufacturing industries, research laboratories, the public, and regulatory agencies. Some industries are seeking ways to reduce emissions by reducing VOCs at the point of use (or generation). This paper discusses the requirements, design, calibration, and use of a sampling inlet / quadrupole mass spectrometer system for monitoring VOCs in a semiconductor manufacturing production line. The system uses chemical ionization to monitor compounds typically found in the lithography processes used to manufacture semiconductor devices (e.g., acetone, photoresist). The system was designed to be transportable from tool to tool in the production line and to give the operator real-time feedback so the process(es) can be adjusted to minimize VOC emissions. Detection limits ranging from the high ppb range for acetone to the low ppm range for other lithography chemicals were achieved using chemical ionization mass spectroscopy at a data acquisition rate of approximately 1 mass spectral scan (30 to 200 daltons) per second. A demonstration of exhaust VOC monitoring was performed at a working semiconductor fabrication facility during actual wafer processing.

ACKNOWLEDGMENTS

The authors want to acknowledge the very helpful people at Intel (Graham Alcott, Scott Sibbett, and Leigh Gettier) who made the site demonstration a success. Thanks to Wu-Ching Chen (Department 6626, Sandia National Laboratories) for performing the market survey and to Art Verardo (Dept 6612, Sandia National Laboratories) and Mike Keenan for overall program management. The authors also appreciate Art Verardo for loaning the mass spectrometer to the Gas Analysis Laboratory.

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Acronyms

3D	three dimensional
atm cc/s	cubic centimeters per second at 1 atmosphere
CI	chemical ionization
CI/MS	chemical ionization/mass spectroscopy
CRADA	Cooperative Research and Development Agreement
EEP	ethyl-3-ethoxypropionate
EI	electron ionization
EPA	Environmental Protection Agency
FID	flame ionization detector
FTIR	fourier transform infrared spectroscopy
GC	gas chromatography
GC/MS	gas chromatography/mass spectroscopy
HMDS	hexamethyldisilazane
IPA	isopropyl alcohol
µGC	micro-gas chromatography
MS	mass spectroscopy
O.D.	outer diameter
ppb	parts per billion by volume
ppm	parts per million by volume
sccm	standard cubic centimeters per minute
SNL	Sandia National Laboratories
TIC	total ion count
VOC	volatile organic compound

MONITORING VOLATILE ORGANIC COMPOUNDS USING CHEMICAL IONIZATION MASS SPECTROSCOPY

Introduction

Volatile organic compound (VOC) emission to the atmosphere is a major concern of semiconductor manufacturing industries, research laboratories, the public, and regulatory agencies. Historically, focus has been on cleaning waste VOCs from the manufacturing plant's "air" emissions through the use of scrubbers and filters. Some industries are now seeking ways to reduce emissions by reducing VOCs at the point of use (or generation) to decrease the costs associated with removing VOCs from the air. For successful point of use reduction, VOC measurement methods must be developed for on-line process monitoring. These methods meet several performance specifications such as rapid response time, continuous detection, lower limit of detection, and speciation of the VOCs detected. Specie-specific information is needed since the chemicals used have different chemical properties as well as different levels at which they become a regulatory concern.

A variety of methods and instrumentation can be used to monitor airborne VOCs depending on the application and the equipment available. Reviews of methods and instrumentation including Environmental Protection Agency (EPA) methods and European methods are available.[1,2,3] Common methods may utilize gas chromatography (GC), mass spectroscopy (MS), fourier transform infrared spectroscopy (FTIR), chemical specific sensors, or hyphenated techniques including gas chromatography/mass spectroscopy (GC/MS). The EPA has developed many methods for monitoring airborne VOCs[4] and has reviewed field portable GCs.[5] Some rapid analysis GCs have the gas chromatographic column on an integrated circuit chip; this technique will be called micro-gas chromatography (μGC) in this paper. Infrared spectroscopy has also been used to monitor indoor volatile organic compounds.[6] Another method for measuring total organics in a gas stream, as demonstrated at Intel, is the flame ionization detector (FID).[7] This technique is very sensitive (ppb range) and has a rapid sampling rate for real-time profiling. However, concentration information for each organic compound in the gas stream could not be obtained since no separation was performed prior to the FID and since the FID is not a discriminating detector.

In this paper, a method developed for Intel to monitor the volatile organic emissions from a lithography tool will be presented. A list of analytical requirements was developed and various analytical methods were considered to see if they met these requirements. The analytical method selection rationale will be presented along with a description of the custom calibration/sampling manifold and calibrant vapor sources needed to meet those requirements. Instrument calibration, including linearity, detection limits, response times, and interferences for several analytes (acetone, hexamethyldisilazane (HMDS), isopropyl alcohol (IPA), and ethyl lactate), will be presented. These analytes are common in the semiconductor industry and provide a test matrix with a variety of volatilities, molecular weights, reactivities, and mass spectral behavior. This document also discusses some other factors to consider when applying the system described to other analytes present in semiconductor exhaust streams, and is intended to facilitate the transfer of this technology to other detection needs. Finally, the demonstration of the instrument in an operating wafer processing line on two different lithography tools using different chemicals and chemical dispense timings will be presented.

System Requirements and Method Selection

System Requirements

The system for gaseous VOC monitoring for the lithography process must meet several analytical and physical criteria in order to accurately characterize the emissions. In a typical lithography process, a wafer is unloaded from a carrier (processing rate: approximately 3 minutes/wafer) and placed on a chuck for spin coating (Figure 1). A series of chemicals are dispensed onto the surface of the spinning wafer. Centrifugal force spreads the chemicals across the wafer surface and any excess liquid is spun off. Excess liquids are collected for disposal and vapors are removed by the tool's ventilation system. These vapors, VOCs, in the ventilation system are the compounds measured by the instrument developed in this research. Therefore, the analytical requirements, based on the lithography process knowledge and limited FID data, include the ability to 1) detect the particular airborne VOCs used in lithography, 2) attain detection limits for these VOCs below 10 ppm by volume, 3) obtain concentration information for each analyte in the gas stream and 4) acquire at least 1 data scan per second.

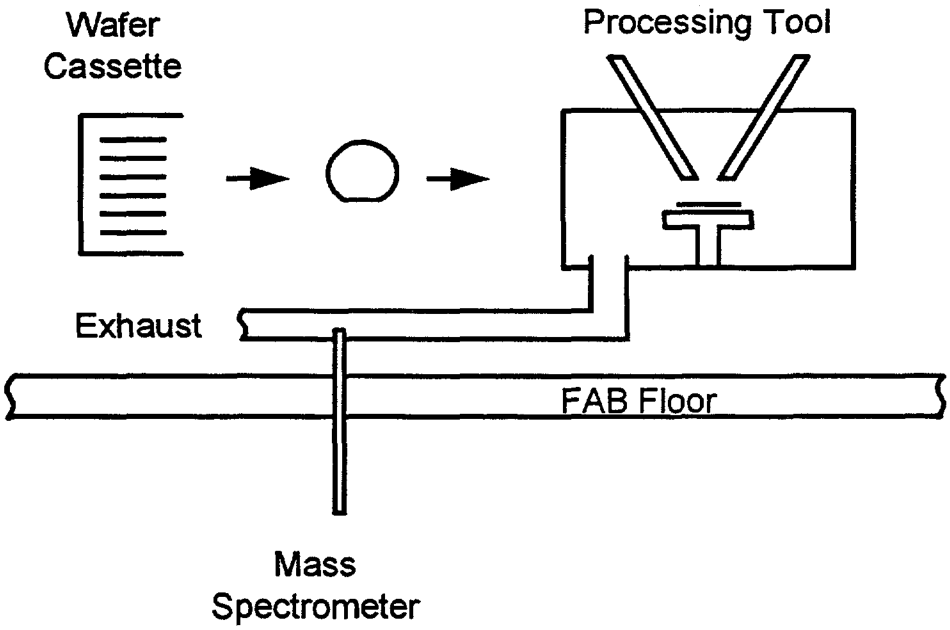


Figure 1. Wafers are transferred from the cassette to the tool for the application of lithography chemicals.

Physical requirements include the ability to be 1) easily transported on a cart, and 2) insensitive to electrical, vibration, and acoustical noise sources. In order to detect the onset of vapor emissions, the selected minimum concentration to be detected was approximately 2 orders of magnitude lower than the expected maximum concentration. This would allow detection of the concentration rise and fall of species whose maximum concentrations were estimated to be in the 1000 ppm range based on previous FID data.[7] A data acquisition rate of at least 1 data scan per second was needed to obtain a well resolved VOC emission profile. Any airborne VOC monitoring system should be flexible enough to analyze the exhaust from a variety of process tools, and a transportable system was required so that individual process tools could be adjusted to minimize VOC emissions. Finally, the system had to be insensitive to "noisy" environments since it was located in the "sub-fab", one floor beneath the cleanroom. This is the utility chase that houses equipment such as electrical transformers, breaker boxes, heating and air conditioning systems, vacuum pumps, ducts, etc.

Method Comparison

Several analytical techniques were examined to assess their ability to meet the requirements described above. Meeting the analytical requirements was the highest priority of the system requirements. The techniques evaluated were GC, GC/MS, μGC, FTIR, MS, and FID. Each technique is capable of detecting the lithography VOCs in the test matrix used here. Figure 2 plots these techniques versus detection limit and data acquisition rate. A vertical line indicates the required level. Only two techniques, MS and FID, met or exceeded both the detection limits and data acquisition rate requirements. However, FID could only meet the data acquisition rate requirement when used without chromatographic separation which does not allow for quantitation of individual analytes. While most of the techniques evaluated could meet one or two of the requirements, only mass spectroscopy met all the analytical and physical requirements. Further documentation supporting MS as the method of choice is contained in Appendix A.

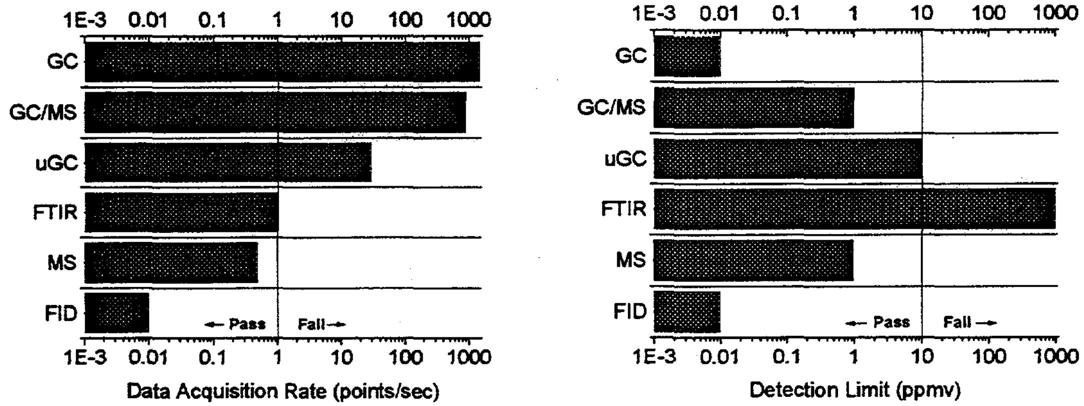


Figure 2. Comparison of detection limits and data acquisition rates for six techniques evaluated for on-line VOC detection. FID and MS are the only options with acceptable detection limits and data acquisition rates.

Chemical Ionization Mass Spectroscopy

Many mass spectrometers can be operated either in electron ionization (EI) or chemical ionization (CI) mode. In EI, electrons generated by a hot filament ionize and fragment the analyte molecules (Figure 3, top). The ionized molecules or fragments are then mass analyzed. Typically, electron ionization is a very energetic process which causes a high degree of fragmentation of the analyte molecules and leaves few, if any, molecular ions for detection. Identification and quantitation is performed using one or more of the fragment ions.

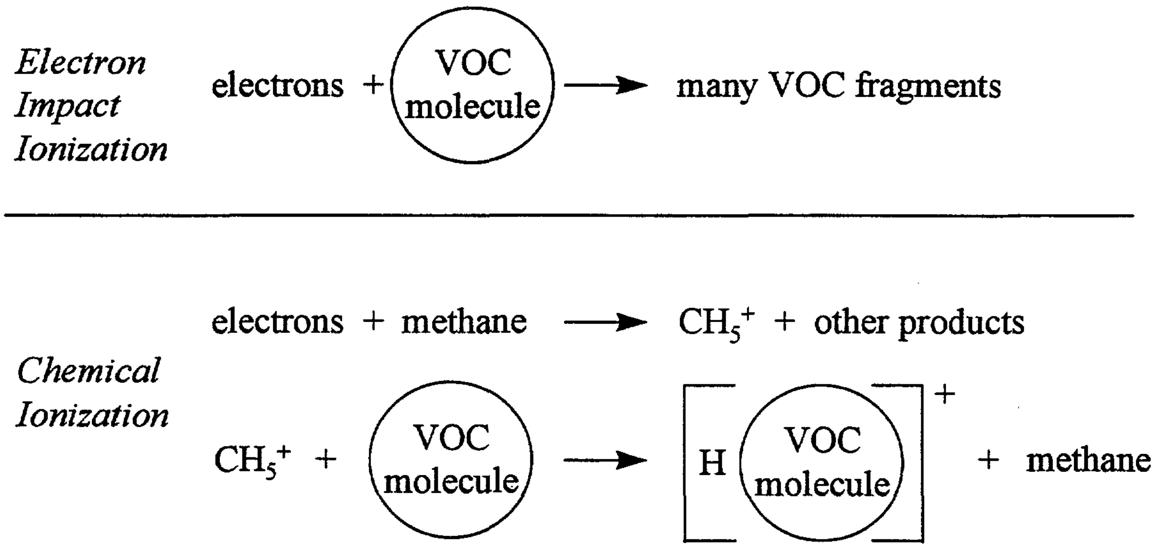


Figure 3. An illustration of electron (top) and chemical (bottom) ionization. Electron ionization is a one step process (ionization) generating many fragments, whereas chemical ionization is a two step process (generation of CH_5^+, and protonation) which generates a protonated VOC.

Chemical ionization differs from electron ionization in that reagent molecules (not electrons) ionize the analyte molecule.[8,9] In this work, methane CI (Figure 3, bottom) was used so the ionizing reagent molecule was CH_5^+. Methane gas is ionized by electrons and interacts with neutral methane molecules to form a number of products, one of which is CH_5^+. A proton is transferred from CH_5^+ to the sample molecule to form an $[M+H]^+$ ion where M is the molecular weight of the sample molecule. Therefore, the parent ion in chemical ionization appears in the mass spectrum at a mass which is 1 greater than the molecular weight of the neutral analyte molecule. Chemical ionization is much softer (less energetic) than electron ionization; this affords significant advantages for airborne VOC measurement when mixtures are present. In CI, analyte molecular ion signal is more intense and fewer fragment ions are produced which minimizes the mass spectral interferences and causes CI to be more sensitive than EI for many compounds. Consequently, the mass spectrum of a given analyte or a mixture of analytes contains fewer peaks. Figure 4 shows a comparison of EI and CI spectra for acetone. Fewer peaks in CI spectra has two effects: the spectra are easier to interpret, and there are fewer spectral interferences. These inferences can adversely affect the accuracy of quantitation in mixture analyses. Molecules which do not chemically ionize with methane (e.g., O_2, N_2)

will not be detected, further reducing the number of interference peaks in the mass spectrum.

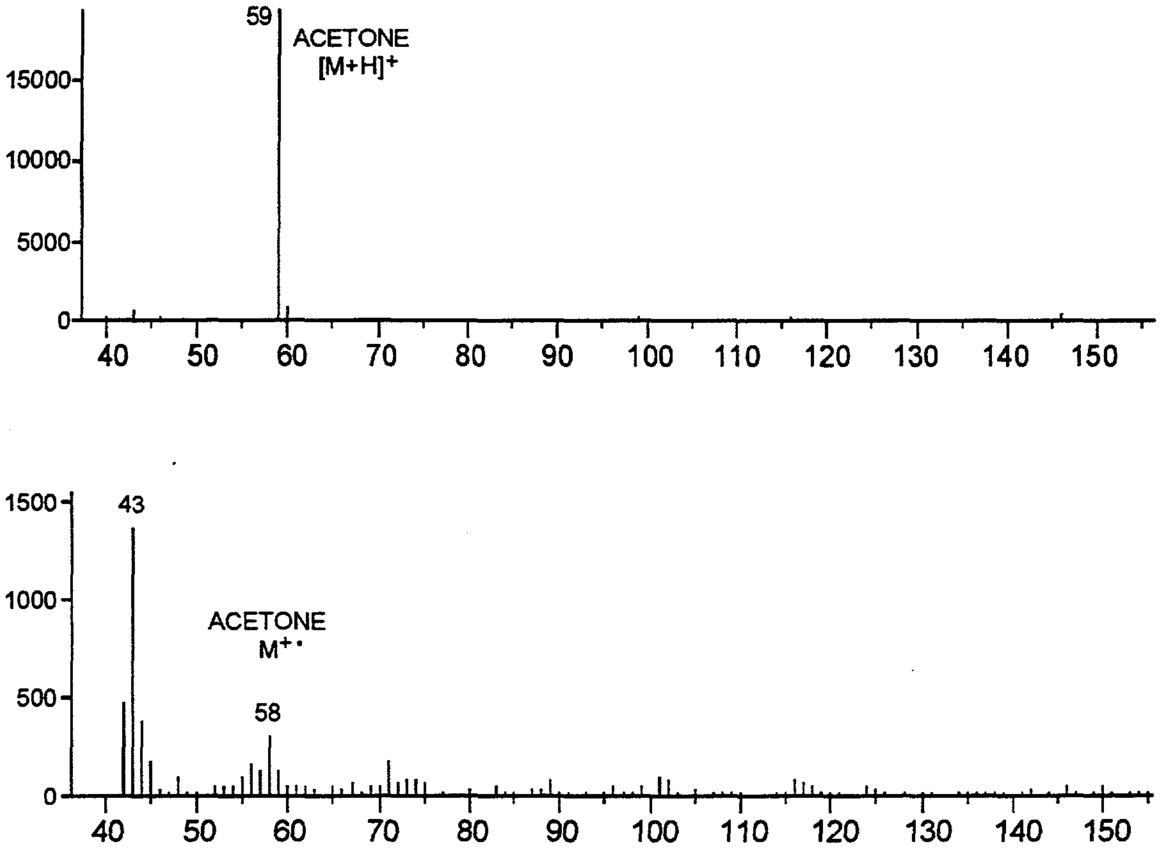


Figure 4. Chemical ionization and electron ionization mass spectra for acetone.

System description

Overview

System components included the quadrupole mass spectrometer (Finnigan Incos XL), mass spectrometer inlet, computer and printer, roughing pump, sample inlet, diaphragm pump, helium lecture bottle, methane lecture bottle, and the calibration manifold. All components were mounted on a two shelf cart for portability (Figure 5). The calibration manifold was used to introduce vapor from liquid sources of VOCs and the tool exhaust was sampled by drawing the gas through Teflon tubing by the diaphragm pump. Since this system was a prototype to demonstrate the capability to make lithography exhaust measurements, "off-the-shelf" components were used.

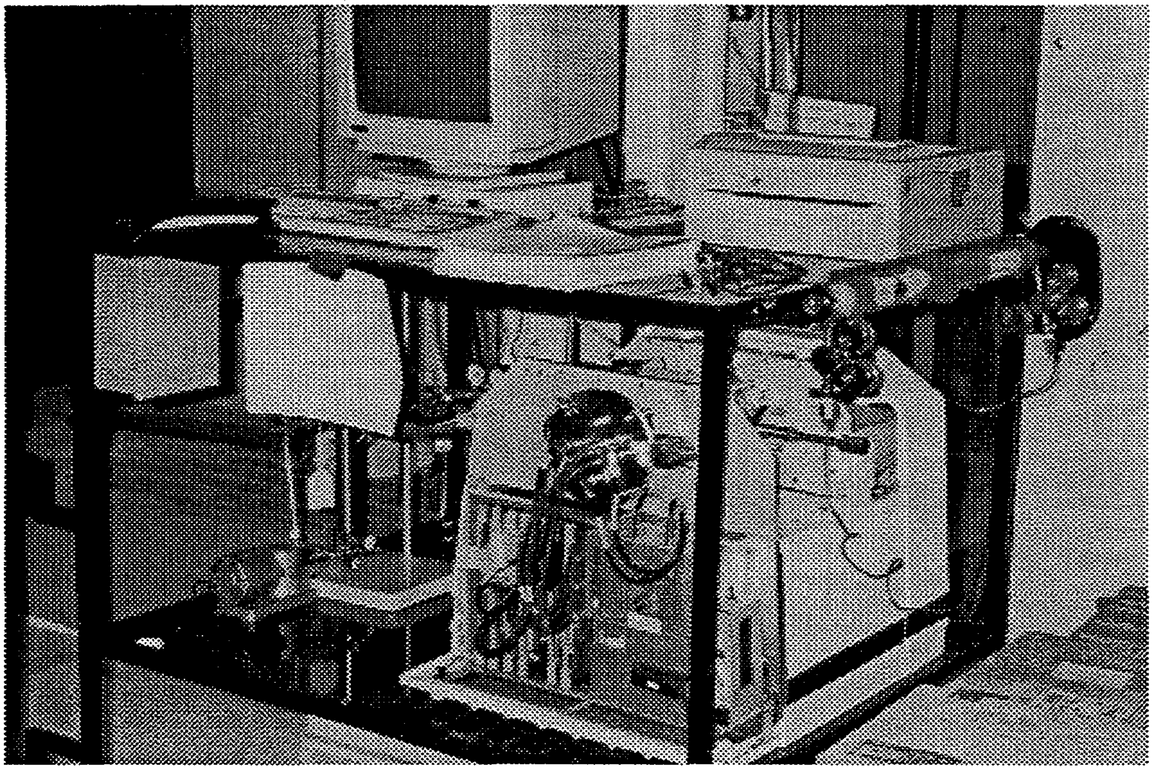


Figure 5. Photograph of the CI/MS system on the cart.

A schematic of the sampling/calibration manifold is shown in Figure 6. The mass spectrometer was operated in the chemical ionization mode using a scan range of 50-175 daltons (0.83 sec/scan) for calibration and a scan range of 30-200 daltons (0.96 sec/scan) for exhaust monitoring. The sampling/calibration manifold is used to create a gas stream consisting of either lithography tool exhaust air or calibration standard. This gas stream is drawn past a metering valve, and a small fraction passes through a length (less than 0.5 meters) of uncoated fused silica capillary tubing (0.25 mm dia.). Flow induced by the vacuum inside the mass spectrometer is introduced directly to the ion source region. A small flow of a buffer gas (helium) is also introduced into the ion source by using a fixed crimped tube leak (10^{-2} atm cc/s). The buffer gas, needed by the mass spectrometer ion source for proper operation, flows between the outside of the capillary tube and the inside of the 1/16 inch diameter stainless steel vacuum housing. The sample and buffer gases combine in the ion source region of the mass spectrometer.

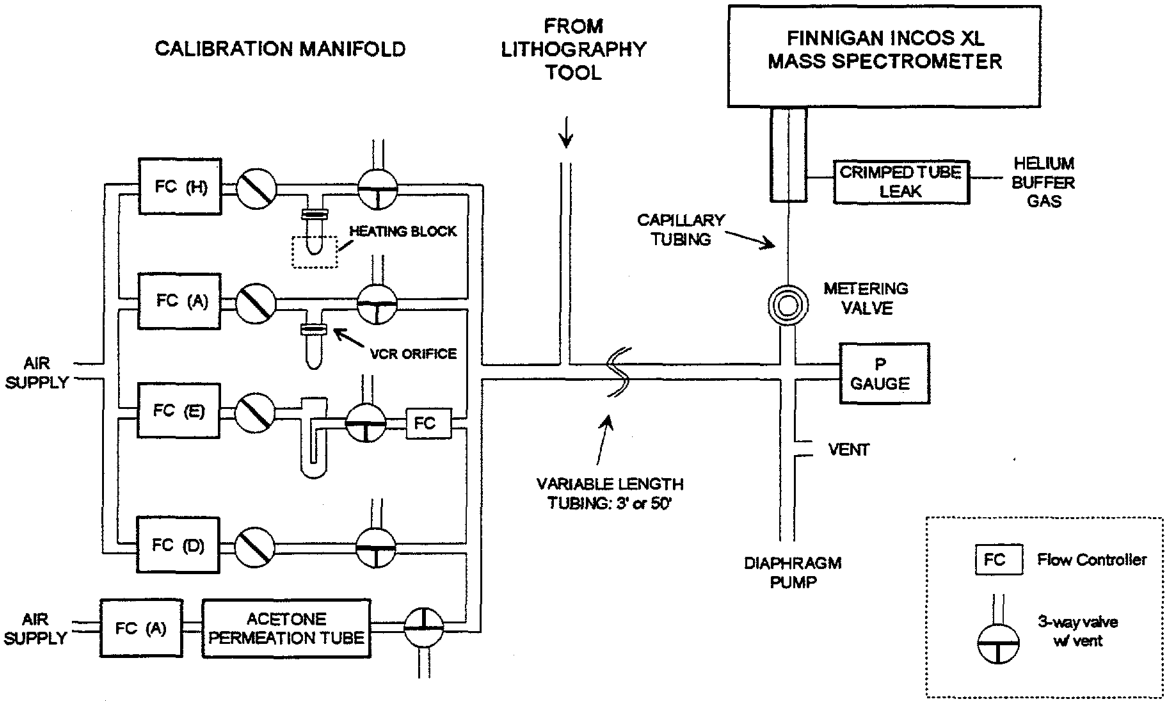


Figure 6. Schematic of the airborne VOC monitoring system. H- HMDS port, A- acetone port, E- ethyl lactate port, and D- diluent gas port.

Configurations in which sample flow was mixed with helium buffer gas before entering the capillary tube were all unsuccessful. Each configuration exhibited one or more undesirable properties including poor sensitivity (dilution effects) and slow response times (a "large" mixing volume). The configuration used overcame both of these limitations by eliminating buffer gas dilution and reducing the mixing volume to that of the ion source.

Calibration Manifold

The calibration manifold (Figure 6) was designed to generate single or multi-component gas streams with known concentrations of acetone, HMDS, IPA, and/or ethyl lactate. Individual compounds were calibrated by varying the diluent air flow (flow controller "D" in Figure 6) added to a constant (primary) flow passing across a calibrant source. The flow into the mass spectrometer, and therefore the pressure observed at the metering valve, must remain constant to achieve a reproducible signal. A high-conductance vent prevented pressure fluctuations due to variations in air flow, and the pressure at the metering valve remained at atmospheric pressure.

The air supply consisted of a laboratory air supply, zero air generator (Balston model 75-83, Haverhill, MA), mass-flow controllers (MKS model 1359C, Andover, MA), and controller readout (MKS model 247C, Andover, MA). The maximum total flow for the system was approximately 3000 sccm (standard cubic centimeters per minute) due to air supply limitations, and the minimum allowable flow was approximately 10 sccm. This minimum was determined experimentally for this system by placing a reservoir of acetone near the vent. Below 10 sccm the acetone was detected by the mass spectrometer because it was able to mix with the air in the vent and diffuse upstream to the metering valve.

Acetone (HPLC grade, Fisher Scientific, Pittsburgh, PA) IPA (HPLC grade, Fisher Scientific, Fair Field, NJ), and HMDS (supplied by Intel) were contained in separate glass tubes, each adapted to a VCR fitting equipped with a laser drilled orifice in a VCR gasket (Edmund Scientific, Barrington, NJ). The HMDS reservoir was kept in a temperature controlled heating block. Ethyl lactate (supplied by Intel) was placed in a glass bubbling tube (Fisher Scientific part #11-184, Pittsburgh, PA). A baratron gauge (MKS model 122AA-01000AB, readout PDR-C-2C) measured pressure at the metering valve (Negretti Valve, Southampton, Wales).

These conditions provided sufficient mass flow-rates as discussed below such that a calibration curve could be measured using the available range of air flow. Quantitation was performed by monitoring a single mass for each analyte. The signal intensity of the protonated molecular ion was monitored for acetone (m/z 59), isopropanol (m/z 61), and ethyl lactate (m/z 119); whereas the signal intensity of a fragment ion of HMDS (m/z 147) was monitored. Protonated HMDS was observed, but was far less abundant. Both ethyl lactate and HMDS produce fragment ions that should be considered if additional compounds are to be monitored since they may overlap with peaks of other compounds. For example, the fragment ion of HMDS appearing at m/z 73 creates an interference for any analyte whose protonated molecular ion would appear at the same mass. In mixture analysis the result could range from a small measurement bias to a false positive. In general, the less fragmentation present and the higher the m/z value monitored, the lower the probability of mass spectral interferences.

Calibrant Vapor Sources / Calculations

The concentrations for each calibrant had to be within the measurement range of the mass spectrometer. Many factors must be considered when sizing the mass flow of a calibrant source including the mass spectrometer response factor, diluent gas flow range, and the vapor pressure of the calibrant. Table 1 shows the vapor pressures of the analytes in this study.

Table 1. Vapor pressures of the compounds tested.

Compound	Vapor Pressure (Torr)
acetone	180 @ 20°C
IPA	40 @ 24°C
HMDS	20 @ 20°C
ethyl lactate	2.8 @ 20°C

Three types of calibrant source "leaks" supplied detectable mass-flow rates for the analytes presented: permeation tube, orifice reservoir, and reservoir. A constant gas flow was maintained through each source at all times using a 3-way valve to send calibrant flow to the mass spectrometer or divert it to the atmosphere. Acetone (ambient), IPA (ambient), and HMDS (72°C) reservoirs each with a 125 μm orifice and 10 sccm primary flow were used for their calibration. Additionally, a calibrated permeation tube of acetone (Vacuum Technology, Inc., Oak Ridge, TN) was used as a daily instrument check standard as well as a confirmatory calibration of the orifice source calibrations and calculations. Permeation tubes work best with volatile compounds that can easily permeate through the tube material. To calculate the concentration of the analyte when using a permeation tube, the calibrated analyte's permeation flow rate is divided by the total flow rate.

$$Concentration = \frac{Flow_{analyte}}{Flow_{total}}$$

Detectable mass-flow rates could not be obtained for HMDS nor ethyl lactate using permeation tube sources. This is probably a result of their lower vapor pressures and reduced permeability due to molecular size or structure. The mass-flow rate of orifice reservoir sources is dependent upon the vapor pressure, temperature and molecular weight of each analyte as well as the orifice diameter. The details of the calculation and parameters used are shown on the worksheets in Appendix C but the equation[10] used is

$$Q = 9.13 \cdot \left(\frac{P_1 - P_2}{760}\right) \cdot \frac{Area}{1 - \frac{P_2}{P_1}} \cdot \left(\frac{P_2}{P_1}\right)^{\frac{1}{g}} \cdot \left\{\frac{2 \cdot g}{g-1} \cdot \left(\frac{T}{M}\right) \cdot \left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{g-1}{g}}\right]\right\}^{\frac{1}{2}}$$

where Q is the flow rate (atm cc/s), P_1 is the upstream pressure (Torr), P_2 is the downstream pressure (Torr), *Area* is the area of the orifice, T is the gas temperature, M is the molecular weight of the gas, and g is a C_P/C_V (the ratio of the specific heat at constant pressure to that at a constant volume). This equation is valid if the mean free path of the molecules is much less than the diameter of the orifice (i.e., viscous flow regime) and the orifice has no thickness (i.e., behaves as an aperture). The nominal diameter from the orifice manufacturer was used to calculate the area, and the vapor pressure of the liquid at its temperature was used for P_1. The final parameter that needed to be determined was P_2, the downstream pressure for the analyte vapor. This parameter was determined by measuring the acetone permeation leak and the orifice type acetone source across the same concentration range and adjusting P_2 until the two calibration curves overlapped (Figure 7). The resultant value for the ratio P_1/P_2 was 2.5.

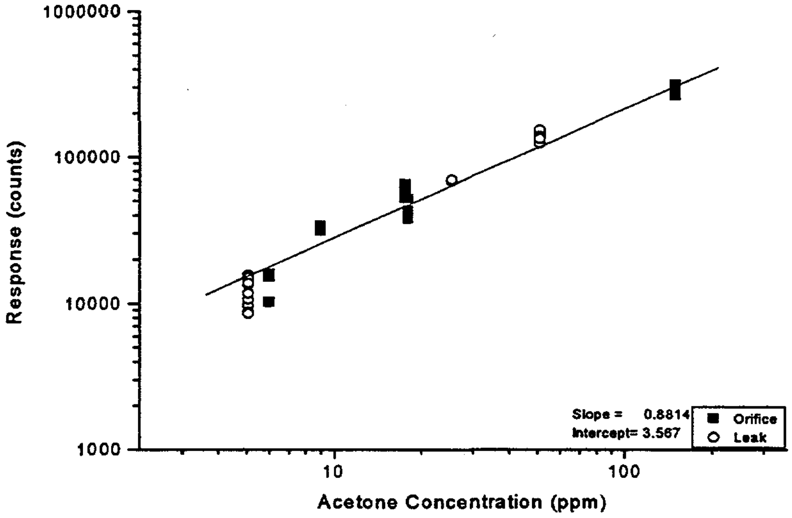


Figure 7. Calibration curve for acetone from approximately 5 ppm to 200 ppm.

Producing detectable ethyl lactate mass-flow from a heated reservoir / orifice type source was also unsuccessful due to the much lower vapor pressure of ethyl lactate. Equally unsuccessful was heating the reservoir to temperatures greater than 50°C to increase the mass flow because significant thermal decomposition of the ethyl lactate was observed. Therefore, ethyl lactate was placed in a room temperature bubbler, and flow from the bubbler was split using a second mass-flow controller. The mass flow was determined by measuring the mass loss of ethyl lactate in the tube per unit time given a constant flow through the bubbler.

The orifice-type source concentrations were calculated using the equation presented earlier using the respective vapor pressure and molecular weight of the calibrant and dividing the result by the total air flow. Finally, the ethyl lactate mass flow was calculated by measuring the mass loss of the ethyl lactate reservoir as a function of time under a constant air flow. This mass loss was converted to the equivalent gaseous volume and then divided by the total air flow to calculate the concentration.

Performance Evaluation

The calibration curves and estimated detection limits, the effect of tubing length and analyte concentration on instrument response times, and the magnitude of interactions between analytes during multi-analyte analyses are presented.

Instrumental characteristics and analyte quantitation data were derived from extracted ion plots similar to that shown in Figure 8 which plots the mass spectrometer's response at m/z 59 versus time to an acetone pulse of 12 ppm. The background is recorded first, the 3-way valve is opened to introduce acetone vapor to the mass spectrometer, and after a short delay, the acetone signal is stabilized. The net signal is calculated by subtracting the average background from the average height of the peak.

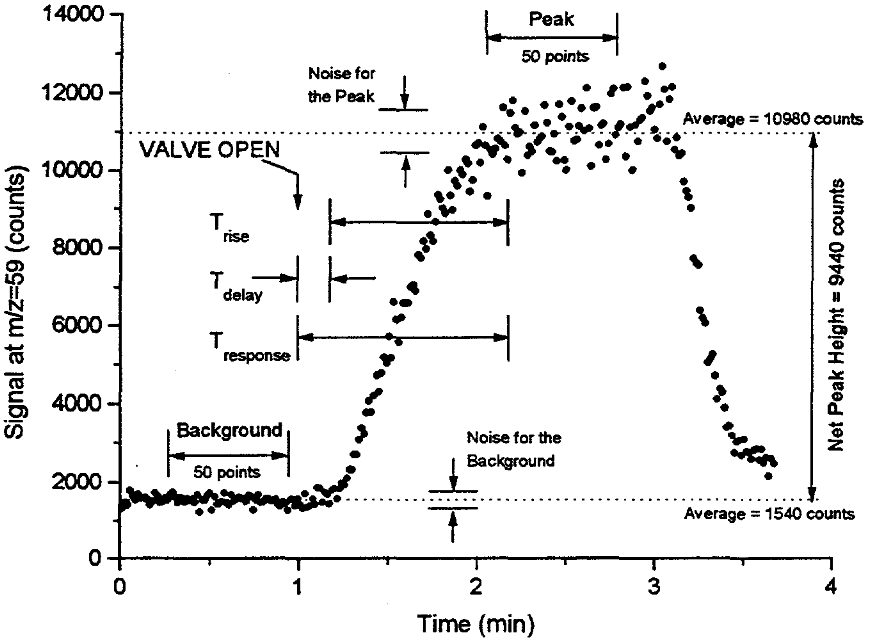


Figure 8. Extracted ion plot (m/z = 59 signal intensity versus time) showing the signal appearance and stabilization after the sample valve was opened to introduce 12 ppm acetone vapor into the manifold at a rate of 100 cc/min.

Calibration Curves and Detection Limits

Calibration curves were generated by varying the concentration of analyte flowing to the mass spectrometer and recording the steady-state signal of the indicative m/z for each analyte. Calibration curves for acetone, IPA, HMDS, and ethyl lactate are shown respectively in Figure 7, Figure 9, Figure 10, and Figure 11. The acetone calibration plot includes data from the calibrated permeation tube and an orifice reservoir sources of acetone from about 5 ppm to about 200 ppm. IPA, HMDS, and ethyl lactate exhibit good linearity over their calibration ranges. This demonstrates that linear calibrations can be achieved by monitoring a single mass per analyte.

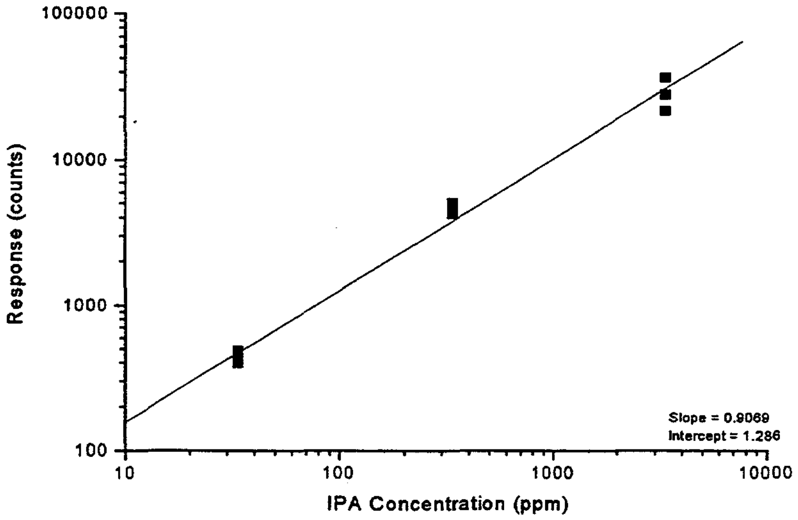


Figure 9. Calibration curve for isopropyl alcohol from approximately 30 ppm to 4,000 ppm.

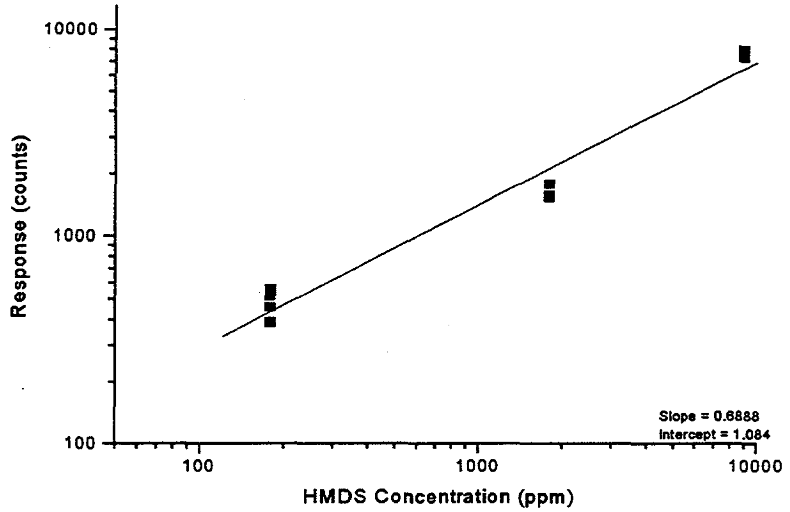


Figure 10. Calibration curve for HMDS from approximately 200 ppm to 7,000 ppm.

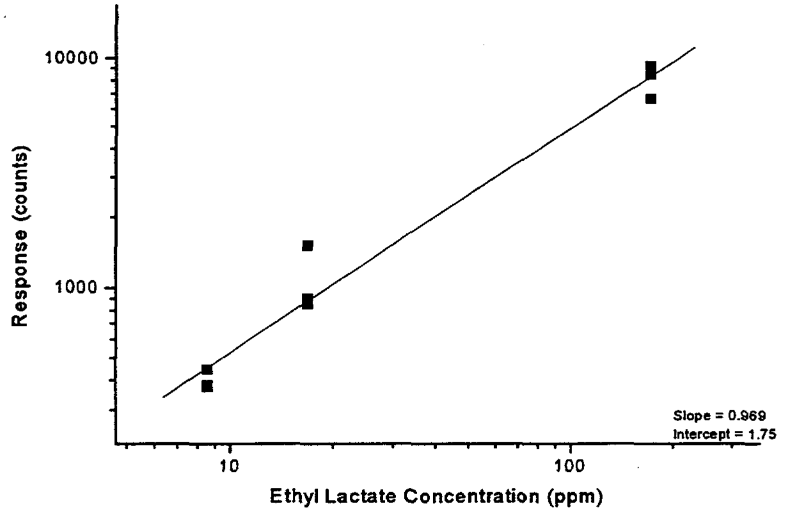


Figure 11. Calibration curve for ethyl lactate from approximately 8 ppm to 200 ppm.

Estimated detection limits were determined by calculating 3 times the standard deviation of the background at the mass characteristic for each analyte.[11] The detection limits are summarized in Table 2. These values are "estimated" since the detection limit was not experimentally determined by successively diluting standards but was calculated using the magnitude of noise recorded for the background.

Table 2. Summary of the estimated detection limit for each analyte.

Analyte	Demonstrated Calibration Range	Estimated Detection Limit
acetone	5-200 ppm	0.44 ppm
isopropyl alcohol	30-4,000 ppm	14 ppm
HMDS	200-7,000 ppm	11 ppm
ethyl lactate	8-200 ppm	1.5 ppm

The IPA and HMDS estimated detection limits are very close to the goal, 10 ppm, even without extreme measures to find the ultimate detection limit and could be easily lowered by taking some simple steps (e.g., averaging more points, cleaning and baking the ion source).

Analyte Interactions

In the preceding discussion, calibration curves were constructed by assuming that the mass spectrometer's response to any single chemical compound is independent of the concentration levels of any other chemical species that might be present in the sampled gas stream. This assumption will not always hold true, particularly in the presence of high concentrations. In fact, some evidence was obtained during the on-site demonstration that suggests that VOC measurement interactions may be observable in samples taken directly from a photolithography tool's exhaust. While it is beyond the scope of this report to thoroughly examine all possible analyte interactions, one method for evaluating such interactions will be illustrated below. The reader is then referred to any standard text on multivariate statistical techniques to learn how to account for these interactions while developing a calibration model for the instrument.

The discourse that follows will present a general relationship between typical univariate, pure compound calibration curves and a more complete model of instrument response that allows for analyte interactions. The steps that need to be followed to evaluate these interactions will then be explained and demonstrated by considering the specific case of an exhaust stream containing a mixture of three VOCs common to the photolithography process.

Assuming that the response of a measurement system to the concentration C_i of chemical compound i is independent of the presence of any other chemical species in the sample, the response can be described, typically, by:

$$R_i = a_{0i} + a_{1i}C_i$$

where a_{0i} and a_{1i} are the usual intercept and slope, respectively, of the standard calibration curve. If interactions among multiple analytes are present, however, this expression must be modified to account for the change in response to a given compound with the levels of the other constituents in the sample:

$$R_i = a_{0i} + a_{1i}C_i + \sum_{j \neq i}^{n} \frac{\partial R_i}{\partial C_j} C_j$$

A full first order model with interaction for a system containing *n* components will have, in general, 2^n parameters that need to be determined. In the specific case of a three component mixture, for example, the instrument response to analyte 1 can be given in terms of the three component concentrations as:

$$R_1 = a_{01} + a_{11}C_1 + a_{21}C_2 + a_{31}C_3 + a_{41}C_1C_2 + a_{51}C_1C_3 + a_{61}C_2C_3 + a_{71}C_1C_2C_3$$

with similar expressions for components 2 and 3. The eight coefficients a_{ij} that define the interaction model for component *j* can be determined by measuring the instrument responses to component *j* for eight independent combinations of analyte concentrations and solving the resulting set of simultaneous equations.

To illustrate the development of an instrument response model that includes analyte interactions, the simultaneous measurement of acetone, HMDS and ethyl lactate in a mixed gas stream was considered. The first step in the process is to define an experimental matrix that will provide the requisite data. In the present case, two concentration levels for each of the 3 analytes were chosen and were designated "Hi" and "Lo." The nominal concentrations corresponding to these levels are given in Table 3.

Table 3. Nominal concentrations associated with Lo and Hi levels for each analyte.

Analyte	Lo (ppm)	Hi (ppm)
Acetone	45	90
HMDS	260	950
Ethyl Lactate	60	220

The eight concentrations, the instrumental responses to which are needed to determine the model's coefficients, were then obtained as the $2^3 = 8$ ways that "Hi" and "Lo" concentrations can be independently selected for the three analytes. In order to guard against the effects of instrument drift or other time dependent phenomena, the eight concentration combinations were run in the randomized order shown in Table 4.

Table 4. Experimental matrix showing the analyte concentrations used to determine the coefficients of the first order interaction model describing the simultaneous measurement of acetone, HMDS and ethyl lactate.

Run Number	Acetone	HMDS	Ethyl Lactate
1	Lo	Hi	Hi
2	Hi	Lo	Hi
3	Hi	Hi	Lo
4	Lo	Lo	Lo
5	Hi	Lo	Lo
6	Lo	Hi	Lo
7	Lo	Lo	Hi
8	Hi	Hi	Hi

Using the apparatus shown in Figure 6, the analyses defined by the test matrix given in Table 4 were accomplished by independently varying the concentration of each analyte. Acetone and HMDS concentrations were controlled by utilizing either a 125 μm orifice

(“Hi”) or a 50 µm orifice (“Lo”) in each orifice reservoir's VCR fitting. The “Hi” and “Lo” ethyl lactate concentrations were produced by splitting a 10 sccm flow out of either a 500 sccm or 2000 sccm primary flow. Total flow was maintained at 50 sccm with the following individual flows: acetone 10 sccm, ethyl lactate 10 sccm, and HMDS 30 sccm.

Once the series of analyses have been performed, the next step is to screen the results for gross interactions that might suggest that a linear model will be inadequate, and to check the assumption that no time dependent phenomenon are present. Figure 12 shows the results of these analyses after individually normalizing the data for each given analyte/level combination to the average of the 4 measurements taken with that particular combination. No major interactions are observed as the data generally vary within a ± 20% window about the mean. In addition, no obvious time dependent effects are evident. It is interesting to note that in the case of the ethyl lactate measurements, 2 different ions were monitored. The results obtained from these two different ions are plotted in Figure 12 (circles and downward pointing triangles) and there is excellent agreement between the two. This suggests that alternative ions could be used to make measurements in the case that two different compounds have mass spectra that directly overlap on one or the other’s primary mass peak.

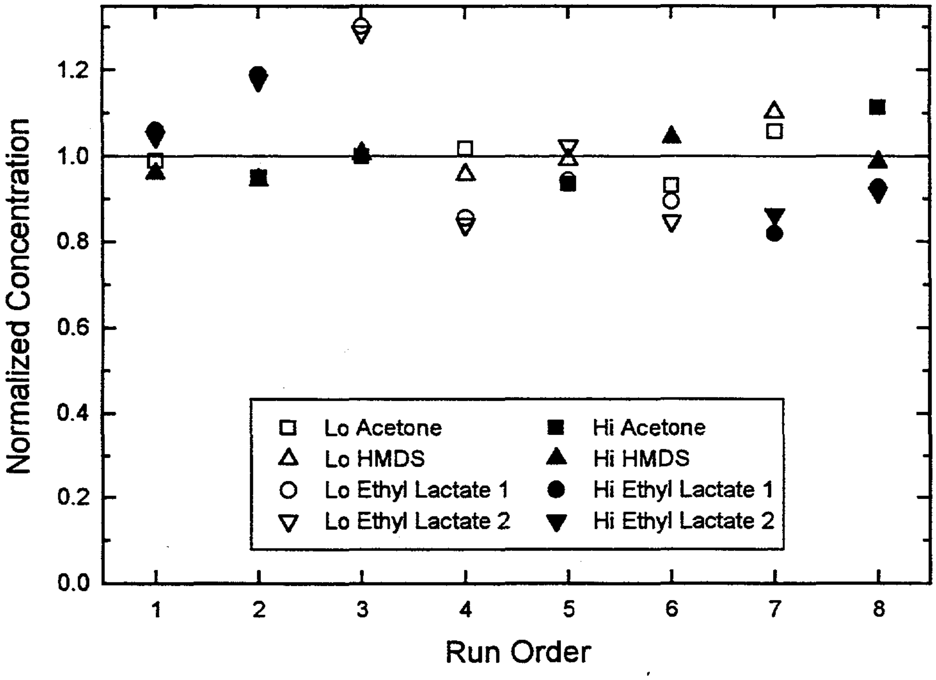
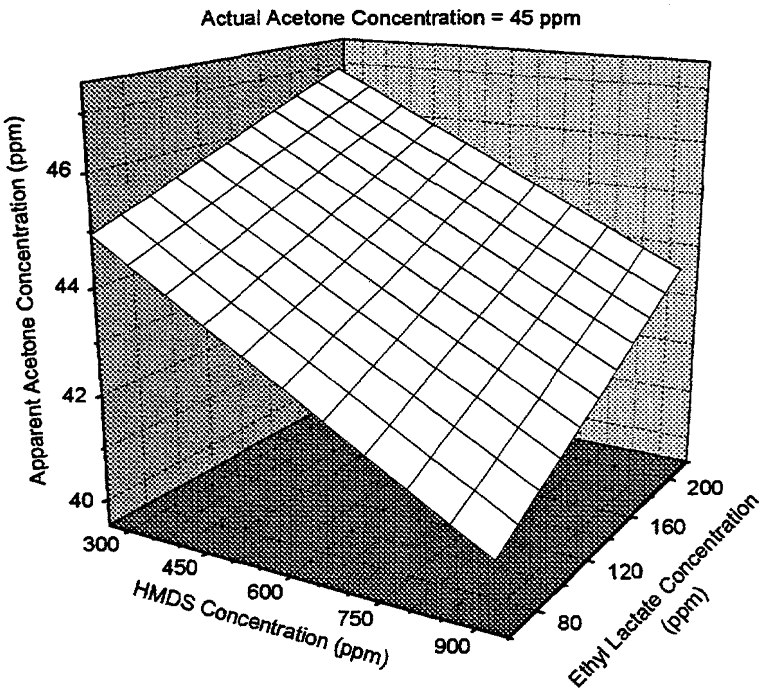


Figure 12. Summary of results for the analyte interaction study. The measured concentrations for each set of analyte/concentration levels have been normalized to their respective mean values.

The final step in defining the interaction model is to determine the unknown model coefficients. In the present case, instrument response was taken to be the apparent concentration, that is, the concentration calculated using pure-compound calibration curves. After solving the set of eight simultaneous equations for each of the three VOCs, the mathematical model can be used to predict the instrumental response given any combination of the three compounds within the concentration ranges investigated. When three compounds are present, a visual representation of the analyte interactions can be obtained by fixing the concentration of one analyte and using the model to predict the apparent concentration of that analyte that we would expect to observe in the presence of varying concentrations of the other two species. In general, these relationships can be plotted as surfaces in 3-dimensional space. Representative surface plots are shown in Figure 13-Figure 15 that correspond to the "Hi" and "Lo" levels for each of acetone, HMDS and ethyl lactate. While there are insufficient data to draw high precision conclusions about the interactions among these chemicals over the concentration ranges considered here, the plots do illustrate, in a qualitative sense, the variety of interaction behaviors that might be expected in a measurement of this type.



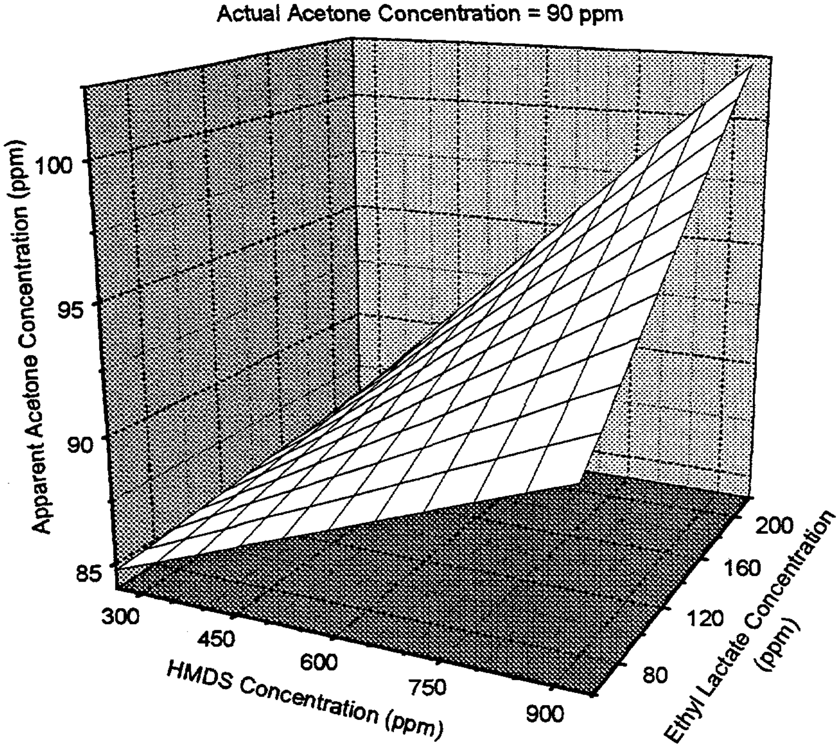


Figure 13. Variation of the measured acetone concentration as a function of actual acetone, HMDS and ethyl lactate concentrations.

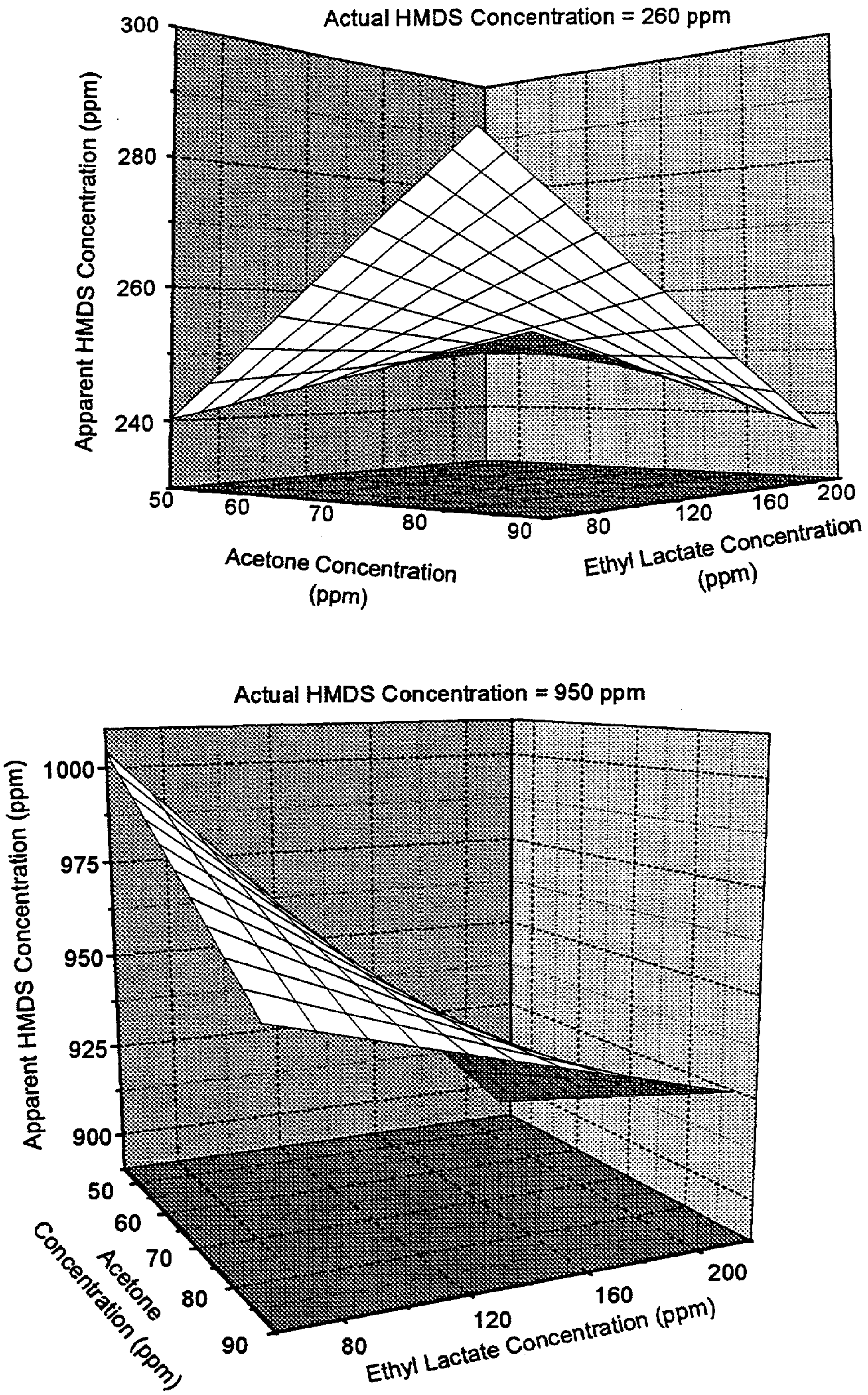
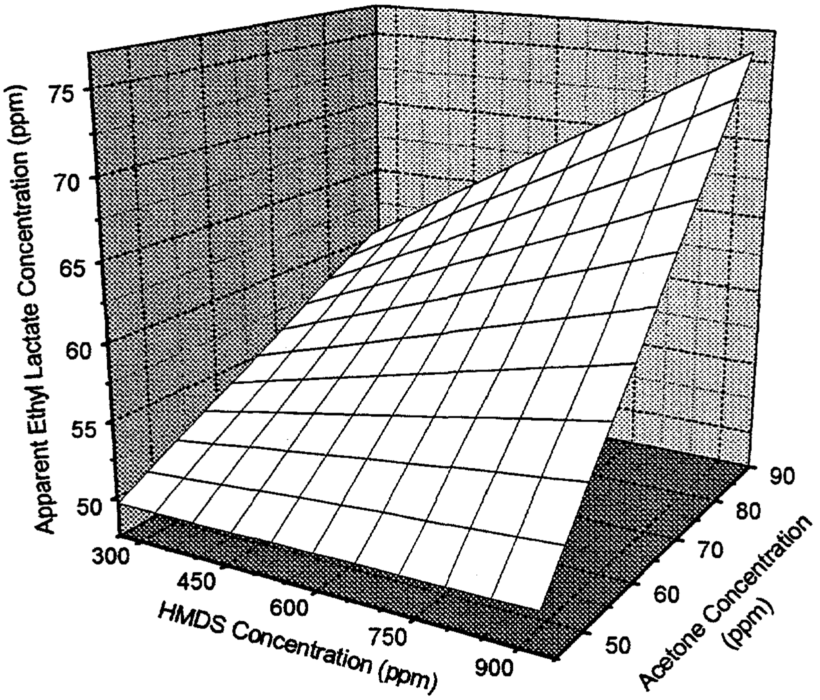


Figure 14. Variation of the measured HMDS concentration as a function of actual acetone, HMDS and ethyl lactate concentrations.

Actual Ethyl Lactate Concentration =60 ppm



Actual Ethyl Lactate Concentration = 220 ppm

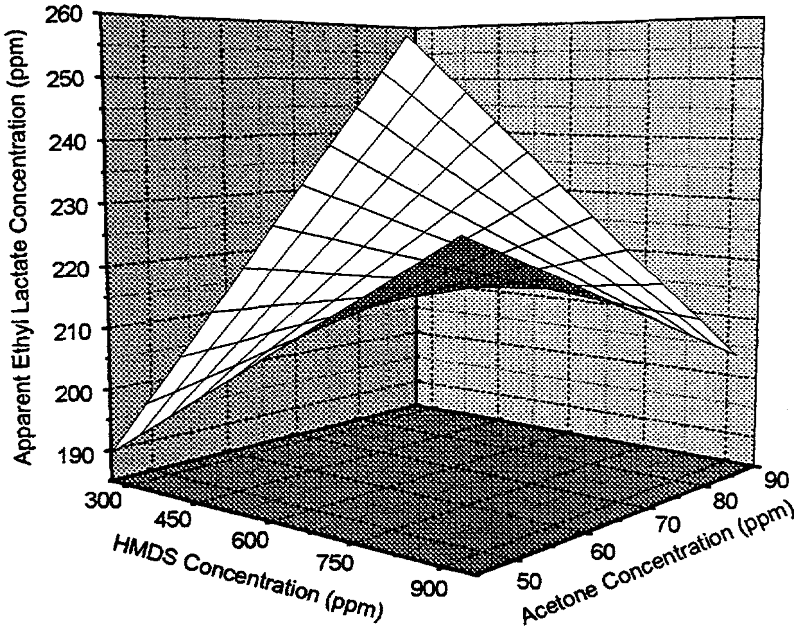


Figure 15. Variation of the measured ethyl lactate concentration as a function of actual acetone, HMDS and ethyl lactate concentrations

Response Times

To determine if the analyte measured is significantly delayed or if the rise time profile is significantly distorted by remote measurements through long tubing lengths, the effect of long lengths of tubing on response time must be determined. Acetone and HMDS were selected for these tests because there is a large difference between the volatility (vapor pressure for acetone is approximately ten times higher) and molecular structure. Two different lengths of Teflon tubing were alternately placed between the sampling/calibration manifold and the metering valve to the mass spectrometer as shown in Figure 6.

Figure 16 shows a plot of acetone signal (5 ppm peak concentration, 100 cc/min) versus time (minutes) for long (50 feet) and short (3 feet) tubing. Initially, the acetone mass flow is off, then opened for a period of time, and then shut off again. The "ON" arrow indicates the time at which acetone vapor was introduced to the sampling inlet/manifold. The delay time was measured from when the valve was opened ("ON") and when the signal reached approximately 90% of it's full value. The difference between the measured delay times for 50 feet and 3 feet was 70 seconds while the predicted delay for this flow was 78 sec. To test a less volatile compound, HMDS at approximately 50 ppm peak concentration was tested using the same tubing lengths and the results are shown in Figure 17 . These data also show no significant distortion to the curve shape was observed at these tubing lengths and analytes.

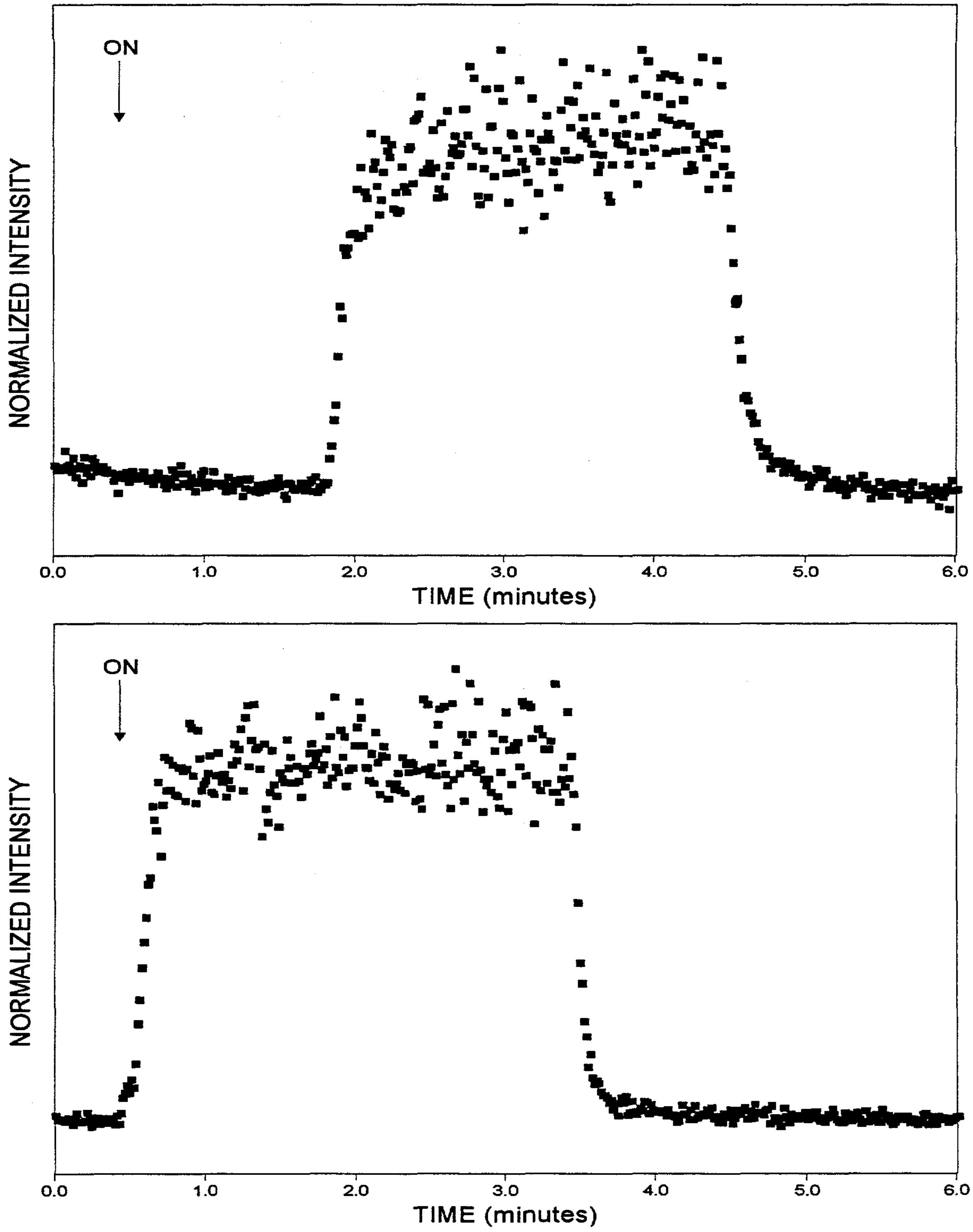


Figure 16. A plot of acetone signal (5 ppm peak concentration, 100 cc/min) versus time for 50 feet (top) and 3 feet tubing (bottom).

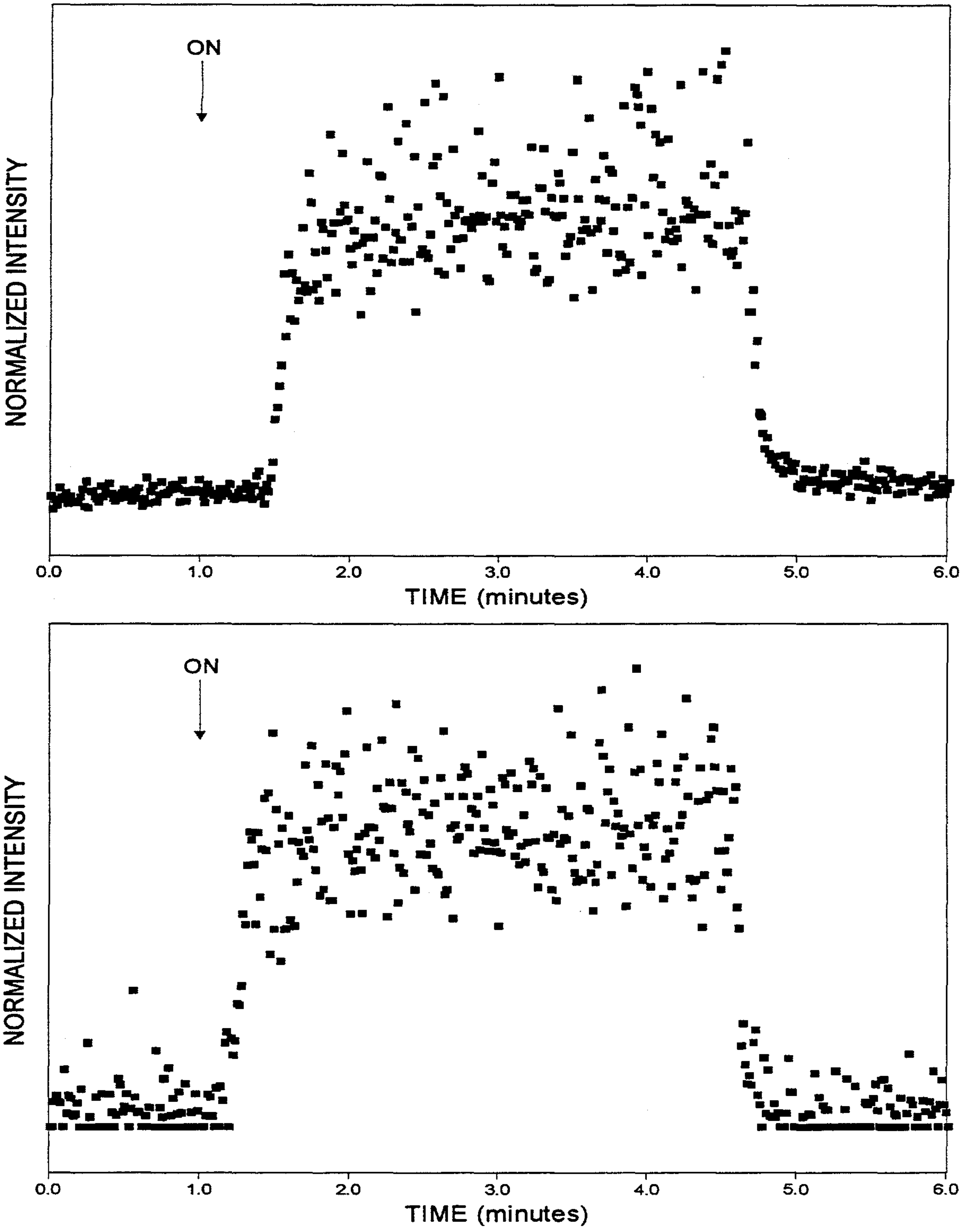


Figure 17. A plot of HMDS signal (50 ppm peak concentration, 250 cc/min) versus time for 50 feet (top) and 3 feet tubing (bottom).

On-site Demonstration at Intel, Rio Rancho, NM

The airborne VOC monitoring system measured exhaust gases from operating lithography tools at Intel in Rio Rancho, NM. The system was located in the utility chase (a hard hat area) beneath the cleanroom. During testing, many electrical controls as well as vacuum pumps were in operation around the system. At one point, welding operations occuring nearby showered sparks on the system during some experimental runs without affecting the data. The lithography tools (located in the cleanroom) were connected to the airborne VOC monitor via a sampling tube (50 feet, 0.25 inch O.D. Teflon) running through penetrations in the cleanroom floor and the lithography system exhaust duct. The gas flow rate through the sampling tube was approximately 2 liters/minute which equates to one tube volume of air flowing through the tube approximately every 8 seconds. The diaphragm pump operated continuously during the experiment; its only flow restriction was the conductance of the sampling tube and other manifold hardware.

The lithography tool was monitored during the processing of a cassette of 10 wafers. A peak was detected for each wafer as it was processed, illustrated in Figure 18, which plots total ion count (TIC) versus time which is normalized to the maximum signal. The TIC is the sum of all signals for the ions from 30 to 200 daltons. Three chemical dispense events occurred for each wafer: primer, photoresist, and edge bead removal. These events occurred within a short time and cannot be resolved using only the TIC plot. Total ion count data is similar to that expected if a non-selective detector (e.g., flame ionization detector or FID) was used to measure these airborne VOCs. This type of detection can be useful for "total" VOC measurement, yet without compound-specific information the contribution of each VOC cannot be determined. In mass spectroscopy, however, each data point represents a full mass spectrum, and by monitoring the appropriate masses the relative contribution of each VOC can be measured.

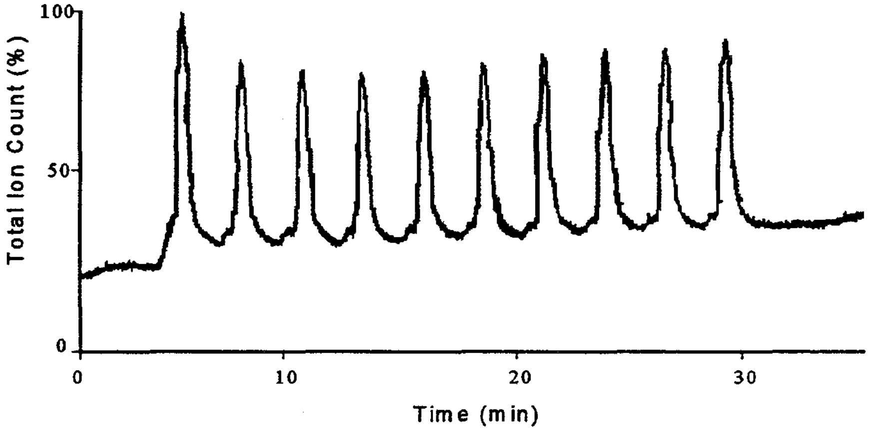


Figure 18. Total ion counts versus time of lithography tool exhaust using chemical ionization mass spectrometry. A cassette of ten wafers was processed during this time.

A second lithography tool, which processed wafers using a different group of chemicals that were dispensed onto the wafer at different time delays, was also monitored. Figure

19 demonstrates the multi-species monitoring capability of mass spectroscopy. Individual compounds in this lithography process were resolved using extracted ion plots. The signal of an ion unique to each compound as a function of time (Figure 19A-D) is shown. The TIC plot (Figure 19E) has a different appearance than that observed in Figure 18 since the chemicals used in this wafer processing tool were dispensed onto the wafer at different times. The "dips" observed in the ethyl-3-ethoxypropionate (EEP), resist, and HMDS plots coincided with a large flux of acetone, suggesting that the instrument's sensitivity was reduced due to a large population of ions in the source. The instrument's changing sensitivity will affect the response observed for each compound, including acetone, so steps must be taken to avoid this nonlinear region. The effect can be minimized by reducing the amount of sample entering the mass spectrometer, but the instrument should be recalibrated when the amount of sample entering the mass spectrometer has changed. By reducing the amount of sample, the sensitivity at higher concentrations will increase slightly as excess ions are avoided, but the detection limits may increase slightly depending on the magnitude of the sample reduction.

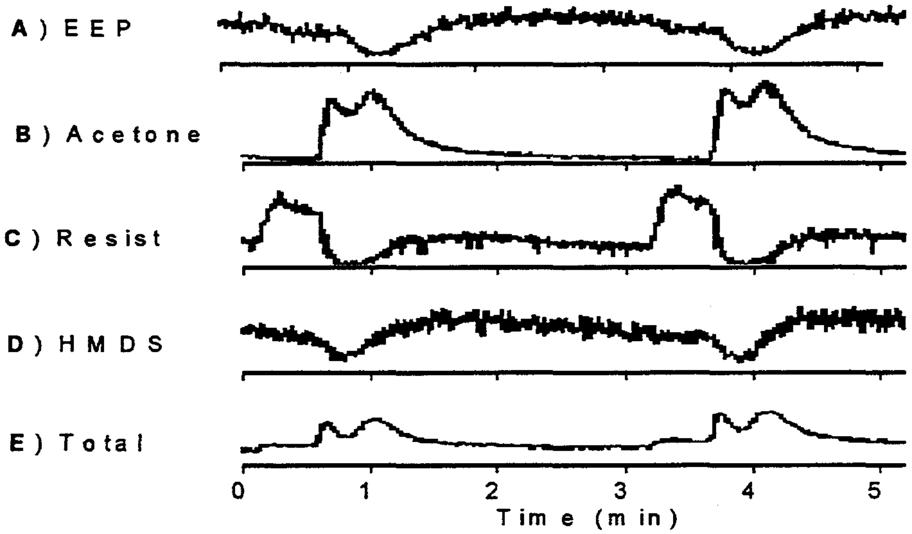


Figure 19. Extracted ion plots (A-D) and TIC plot (E) of the tool exhaust during the processing of two wafers using chemical ionization mass spectroscopy. The depressions observed in the signal for the less volatile compounds (e.g., HMDS and EEP) are probably due to a change in instrument sensitivity due to a large population of acetone ions.

The chemical composition of tool exhaust emissions can vary greatly as a function of time resulting from the varying volatility of the compounds, as seen in the extracted ion plots in Figure 20. The acetone concentration (Figure 20A, extracted ion plot m/z 59) rose and fell rapidly after it was dispensed onto each wafer. It also decreased to near background levels in the short time between wafers. Due to its volatility, it was not retained significantly in either the process tool or the sampling tube. On the other hand, the photoresist concentration (Figure 20B, extracted ion plot m/z 147) rose from a nominal baseline to a near steady-state level throughout processing of the full cassette, and returned gradually back toward background levels after the last wafer was processed. The slow response to the photoresist component was probably due to adsorption in the lithography tool. Before the cassette of wafers was processed, the acetone and photoresist signals were both very low (background levels). If only FID data were used, the precise background levels for each species would not be known and the additional information about the photoresist compound remaining elevated throughout the cassette would also not be known. CI/MS provides time dependent concentration information about each species.

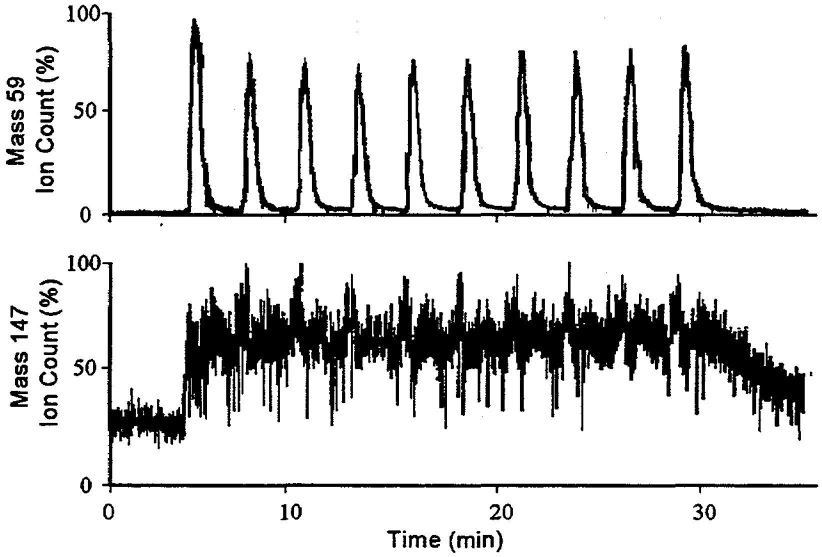


Figure 20. Extracted ion plots of acetone (top) and photoresist (bottom), showing the effect of volatility on compound concentration. The acetone plot shows large relative signals while each wafer was processed and near background levels in the interim. The photoresist rose to a steady state level and returned to a baseline value at some time after the last wafer was processed.

Figure 21 shows data collected during a lithography process during the processing of two wafers. For both chemical and electron ionization an extracted ion plot for acetone (top: m/z 59 for CI, m/z 58 for EI) and total ion count plots (bottom) are shown. All plots are normalized to 100% for the maximum signal. The CI plot shows a greater signal to noise ratio compared to that in the EI case. This illustrates the improved detection limits that CI provides through "soft" and selective ionization as discussed earlier by eliminating much of the background signal, or noise (other ionized species, e.g., air). Acetone was the primary exhaust component, yet for EI the relative signal change due to acetone was small. The TIC plots (Figure 21 bottom) demonstrate that chemical ionization also provides improved detection limits over electron ionization for measuring total organics.

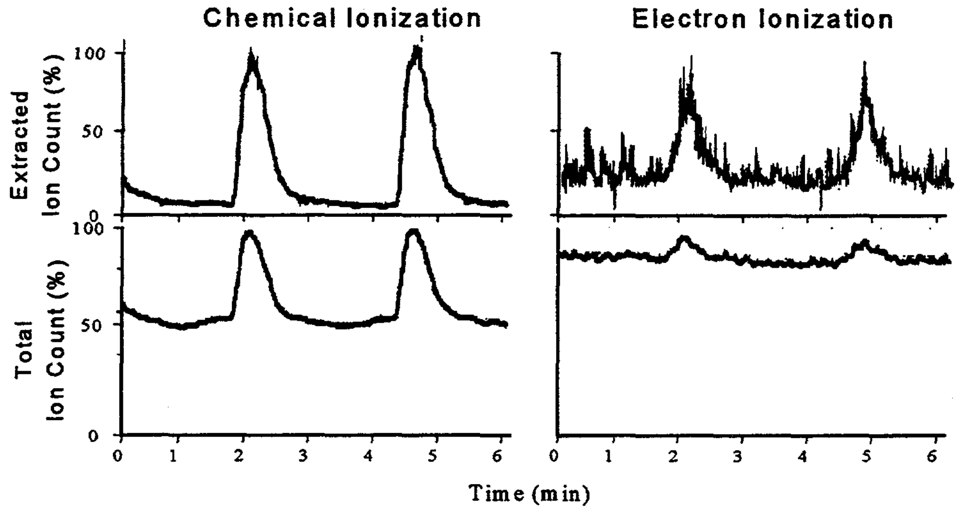


Figure 21. Extracted ion plots (top) and total ion count plots (bottom) for acetone in the exhaust from a lithography tool (m/z 59 in CI and m/z 58 in EI) using chemical ionization or electron ionization mass spectroscopy.

Summary

An airborne VOC monitoring system designed to measure volatile organics emitted from a variety of lithography process tools, using CI/MS, was calibrated in the laboratory and demonstrated at a working semiconductor manufacturing plant. All of the analytical and physical design goals (detect the particular airborne VOCs used in lithography, attain detection limits for these VOCs below 10 ppm by volume, obtain concentration information for each analyte in the gas stream, acquire at least 1 data scan per second, be easily transported on a cart, and be insensitive to electrical, vibration, and acoustical noise sources) were all met with the exception of the estimated detection limits for IPA and HMDS, which were 14 ppm and 11 ppm, respectively. The system measured multiple organic analytes present in the exhaust stream at Intel non-intrusively and in real time. Species-specific information as a function of time was extracted from the collected data. The use of chemical ionization mass spectroscopy improved detection limits, reduced chemical noise, and eliminated background interferences for the lithography chemicals detected. The airborne VOC monitoring system presented is potentially applicable to many areas where real-time monitoring for volatile organics in air is needed.

To apply the system towards other analytes, factors including calibration sources, calculations needed, and possible problems were discussed. Analytes (acetone, IPA, HMDS, and ethyl lactate) with a wide range of volatility and molecular weights were detected rapidly by monitoring either a molecular or fragment ion of each analyte. Using the same monitor mass, linear calibrations were demonstrated. Several methods for introducing the calibration compounds into the gas flow were explored and permeation tubes were effective for only very volatile compounds like acetone, orifice leak elements were effective for volatile to moderately volatile compounds like acetone, IPA and HMDS, and a bubbler tube was effective for the least volatile compound, ethyl lactate. A method for determining analyte interactions / interferences to quantitation was also demonstrated. Multiple-analyte calibration is a viable method for field calibration of these analytes. Instrument response time was not degraded by the use of longer sampling lines, simply postponed based on the length of tubing from the lithography tool to the VOC monitoring system.

An additional benefit for having the capability to measure the waste VOC concentrations in the exhaust from lithography tools is to have a process monitor which would alert the operator if chemicals were not dispensed on the wafer correctly. If the monitor detects the correct chemicals were not dispensed or incorrectly timed, the wafer, or wafers, could be automatically pulled from the production line before expensive post-dispense processing occurs. This process monitoring would result in a yield enhancement and a direct cost savings by not processing wafers which had improper chemical dispensing cycles.

Although the sampling rates were either 0.83 (150 daltons/scan) or 0.96 (170 daltons/scan) scans/second in these experiments, faster rates could be obtained by adjusting some instrument parameters. A "full" mass scan by the mass spectrometer was used in these experiments in order to detect any unexpected analyte interactions or background. In applications requiring shorter acquisition rates, most mass spectrometers can be set for smaller scan "windows". Only the mass range(s) containing useful information (i.e., 5 windows of 10 daltons/window = 50 daltons/scan total). Other functions available on newer mass spectrometers (Incos XL manufactured 1985) would greatly improve the utility of this system in a process environment. These functions include greater pressure control, alarm and log functions, and real-time signal display. Despite the limitations of the older Incos XL, the system was demonstrated successfully in a working semiconductor manufacturing plant.

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DRAFT

APPENDIX A: Market Survey for Potential MS Instruments

The information included in this section were compiled by Wu-Ching Cheng, Dept. 6626.

Market Survey of Capabilities of Commercially Available Instruments for Real-Time Monitoring of Volatile Organic Compounds

Intel/Sandia Cooperative Research and Development Agreement (CRADA)
Project E: Real-Time Speciation of Volatile Organic Compounds in Exhaust Streams, Phase I, Task B

August 11, 1994

Contents

1.0 Task Description

Intel Corporation and Sandia National Laboratories (SNL) have entered a Cooperative Research and Development Agreement (CRADA). Project E of the CRADA is Real Time Speciation of Volatile Organic Compounds in Exhaust Streams. Phase I of Project E is Development of Detailed Instrument Specifications, and Task B of Phase I is A Survey of Commercially Available Equipment.

Intel Corporation will be implementing on-line monitoring of effluent volatile organics from the photolithography operation. The operation consists of two steps. In the first step a photoresist coating is injected and spread over the top of a rotating disk. The photoresist is a volatile mixture and is present in the effluent air. In the second step, an edge bead remover solution is applied to the bottom of the rotating disk to remove any photoresist at the edge of the disk. The edge bead remover is also volatile and is present in the effluent air. The photoresist and edge bead remover appear in the effluent air as pulses of up to 10,000 ppm total organic carbon (TOC) within a time period of 10 to 20 seconds for each pulse. In order to provide definition of the pulse, it is required that the sampling/analysis time be less than 1 sec/sample. It is also required that each component of the photoresist and the edge bead remover in the effluent air be quantifiable down to the 10 ppm level. The composition of the photoresist and edge bead remover, along with the time and concentration requirements thus define the requirements of the analytical instrument.

Task B is the market survey for an instrument that will meet the requirements of the on-line monitoring objective. The instrument will be used for determining the effects of process changes such as changes in composition of the photoresist and/or edge bead remover on the concentrations of volatile organic compounds in the effluent air. It will not be used for the purposes of process control.

The type of instrument was reduced to mass spectrometers because:

- gas chromatography is not able to meet the quick response time requirement
- Flame Ionization Detectors (FID) are not able to meet the speciation requirement, although Intel has used FID to obtain total organic carbon (TOC) on a real-time basis.

The choice of mass spectrometers was later reduced to those that have capability for chemical ionization because chemical ionization does not fragment the molecule as much as the electron ionization technique.

In order to accomplish the market survey task, a list of vendors was compiled from:

- the Thomas Register
- the August edition of Analytical Chemistry Magazine
- users of mass spectrometers at Sandia National Laboratories (SNL)

2.0 Specifications

The list of compounds to be monitored is shown in Table 1, and the instrument requirements and specifications are summarized below:

- dynamic operating range, 10 to 10,000 ppm
- total sampling/data reduction time less than 1 second per sample
- precision and accuracy within 10%
- chemical ionization
- portable or cartable unit

The portability requirement is necessary for the purposes of monitoring various lines in the plant.

Table 1 Compounds to be Monitored

Compound	Common Name	Structure
Ethanol, 2-ethoxy acetate	Cellosolve Acetate	$C_2H_5O\text{-}(CH_2)_2\text{-}O\text{-}OC\text{-}CH_3$
Acetic acid butyl ester	n-Butyl Acetate	$C_4H_9\text{-}O\text{-}OC\text{-}CH_3$
Propionic acid, 3 -ethoxy, ethyl ester	Ethyl-3 Ethoxy Propionate(EEP)	$C_2H_5\text{-}O\text{-}CO\text{-}C_2H_4\text{-}O\text{-}C_2H_5$
2-Propanone	Acetone	$CH_3\text{-}CO\text{-}CH_3$
Disilazane, 1,1,1,3,3,3 hexamethyl	Hexamethyl Di-silazane (HMDS)	$(CH_3)_3\text{-}Si\text{-}N\text{-}Si\text{-}(CH_3)_3$
2-Propanol	Isopropyl Alcohol	$CH_3\text{-}CHOH\text{-}CH_3$
2-Hydroxy Propanoic Acid Ethyl Ester	Ethyl Lactate	$CH_3\text{-}CHOH\text{-}CO\text{-}OCH_2\text{-}CH_3$

3.0 Vendors Responses

A number of companies were contacted in regards to the requirements of the application. Several responded that their instruments were not able to fulfill the requirements of the application. The largest dividing requirement was the ability to do chemical ionization (CI). Table 2 summarizes the responses of the various companies with the upper tier occupied by those capable of providing CI instrumentation. Table A-1 in Appendix A gives more detailed comments by various vendors. Finnigan, Varian and VG Instruments appear to be the vendors of instruments most suited for this application. Varian uses an ion trap analyzer, VG uses a quadrupole and Finnigan has both an ion trap and a quadrupole available.

Pricing is similar for the Finnigan Magnum (ion trap) and the Varian Saturn III, from $60,000 to $66,000. Finnigan has recommended the Incos XL, a quadrupole system

Ta ,2

					Vendor Responses to Application Requirements							
			Summary of Vendors and Capabilities									
Vendor	Mode	CI Cust.	Analyzer	1 sec. Samp.	Quantify Mixture	Set-up, Training	Applic. Dev.	Will run Intel Sample	Cost	Dim. W*L*H	Wt. (lb)	Comments
A	EI/CI	-----	IT/Quad	Yes	Yes	Yes	Yes	Yes	63K	26x46x24	215	CI + available, CI - promised
												Several references of user experience
B	EI/CI	-----	IT	Yes	Yes	Yes	Yes	Yes	60-66K	22x43x22	220	Licences Ion Trap from Finnigan
C	EI	Yes	Quad	Yes	Yes	-----	Yes	Yes	80-85K	12x20.5x25	70	+ and - CI available
D	EI	Yes	Quad	No (1-2 sec.)	Yes	-----	-----	-----	-----	-----	-----	Suggest RGA/users Membrane Inlet
E	EI	No	Quad	No	-----	-----	-----	Yes	-----	-----	-----	Suggest using EI with < 40 eV
F	-----	-----	-----	No	-----	-----	-----	-----	-----	-----	-----	Cannot do application
G	EI	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	Cannot do application
H	EI	No	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
I	-----	-----	-----	No	-----	-----	-----	-----	-----	-----	-----	-----
J	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	Cannot do application
K	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	Cannot do application
L	-----	-----	Quad	-----	-----	-----	-----	-----	-----	-----	-----	No longer selling CI
M	EI	-----	Quad	-----	-----	-----	-----	-----	-----	-----	-----	Uses HP Core
List of vendors were obtained from Analytical Chemistry Journal August 15, 1993 under Chemical Ionization												
Mass Spectrometer and also from Thomas Register												
IT=Ion Trap												

which has CI with negative ion as well as positive ion detection capability, claiming significant resolution advantages; the cost is about $35,000 more. Finnigan now also has capability to add negative ion detection to the Magnum, again for an additional cost of $35,000. Thus, the total Finnigan cost with negative ionization is about $100,000. VG Instruments can provide an instrument for the application using a quadrupole meeting the full requirements with negative ionization as well; the cost is about $100,000. VG is willing to supply system and application development for a total cost of $180,000 to $200,000. The system would have a capillary inlet with continuous sample flow into the mass spectrometer.

Hewlett Packard, which also uses a quadrupole analyzer, has had experience with VOC's using a membrane inlet. However, a 1 to 2 second sampling time would be required. Perkin-Elmer cannot do the application, therefore no cost or equipment size data is provided. Of potential interest is Balzers High Vacuum which suggested operating with electron impact ionization (EI) at an energy of about 40 eV; traditional EI operates at 70 eV or 100 eV. With the lower ionization energy, fragmentation is decreased. However, tests would need to be done to determine if the softer ionization provided at lower ionization energy would be enough to significantly improve resolution for the application. Balzers is willing to do some testing as are Finnigan, Varian and VG.

4.0 User Responses

Vendors suggested that users of their equipment would be another source of information concerning the suitability of their instruments for the Intel application. Not included in the specifications for the application are such parameters as downtime and potential reasons for shutdown. It was hoped that the users would have some of this information. Table B-1 in Appendix B gives a full list of comments from various users of the equipment.

It is generally felt that Finnigan, VG and HP instruments are rugged, but may require maintenance several times a year. It is also generally felt that CI would achieve the required resolution and quantification in the specified operating range. There are reports of excessive oxidation from the air stream and excessive wear on the vacuum pump due to continuous on-line operation (Eckenrode, Viking Instruments, Dow Chemical).

5.0 Discussion

Table 3 gives a summary of EI spectra provided by the NIST library. Appendix B gives the complete EI spectra for each of the species. The numbers in the table represent abundances at the various m/z ratios. The maximum abundance on the scale was 10,000. Therefore, a reading of 9999 means that the abundance is off-scale. Abundances less than 1000 are not listed in order to simplify the table. From the EI spectra for the species of interest, there are a number of overlapping peaks. For example, the peaks for ethyl lactate (Propanoic acid, 2-hydroxyl ethyl ester) are at m/z of 45 and 29. But isopropyl alcohol has a large peak at m/z of 45 and EEP(Propanoic acid, 3-ethoxy ethyl ester) has a large peak at m/z of 29 and also a significant peak at m/z of 45. Likewise, three species have a large peak at m/z of 43; that is cellosolve acetate, n-butyl acetate and acetone.

Table 3 Summary of EI Spectra (NIST) for Species of Interest

		EI Spectra (NIST)																				
Species						m/z																
	15	26	27	29	31	43	44	45	56	58	59	61	71	72	73	89	101	102	117	130	146	147	Sum
2 Ethyoxyethyl acetate	1138	0	1096	0	3450	9999	2500	1220	0	0	3050	300	0	2799	335	0	0	0	0	0	0	0	25887
Acetic acid, butyl ester	0	0	1561	0	621	9999	290	120	3364	130	0	1011	110	0	1121	0	0	0	0	0	0	0	18327
Propanoic acid, 3-ethoxy ethyl ester	0	0	3422	8047	7274	0	0	3143	0	0	9999	0	4842	1661	2352	1521	3562	2421	3023	0	0	0	51267
Acetone	3412	676	894	463	0	9999	234	0	0	2338	80	0	0	0	0	0	0	0	0	0	0	0	18096
Silanamine, 1,1,1,-tri methyl-N-	0	0	0	0	0	0	0	926	0	0	737	0	0	0	1323	0	0	0	0	3495	9999	1878	18358
Isopropyl alcohol	0	0	800	400	400	1300	450	9999	0	100	550	0	0	0	0	0	0	0	0	0	0	0	13999
Propanoic acid, 2-hydoxyl ethyl ester	0	370	1762	2711	210	0	200	9999	0	40	0	0	0	0	0	0	0	0	0	0	0	0	15292
Note: readings of 9999 are off-scale																						

It is possible that deconvoluting an EI spectra could result in quantification of the species of interest. It is also possible that a softer EI (at a lower electron energy, such as 40 eV) would give less fragmentation and allow for adequate resolution of compounds while maintaining the required sensitivity. However, CI spectra such as those determined by Thornberg, Figures 1 through 4, and summarized in Table 4, would result in better resolution and quantification of the species.

Table 4 CI Analyses on Intel Sample
Thornberg

Species	Distinguishing CI Peaks
Ethyl Lactate	119
n-Butyl Acetate	117
xylene	107
Cellosolve Acetate	133
Acetone	59
EEP	147/101

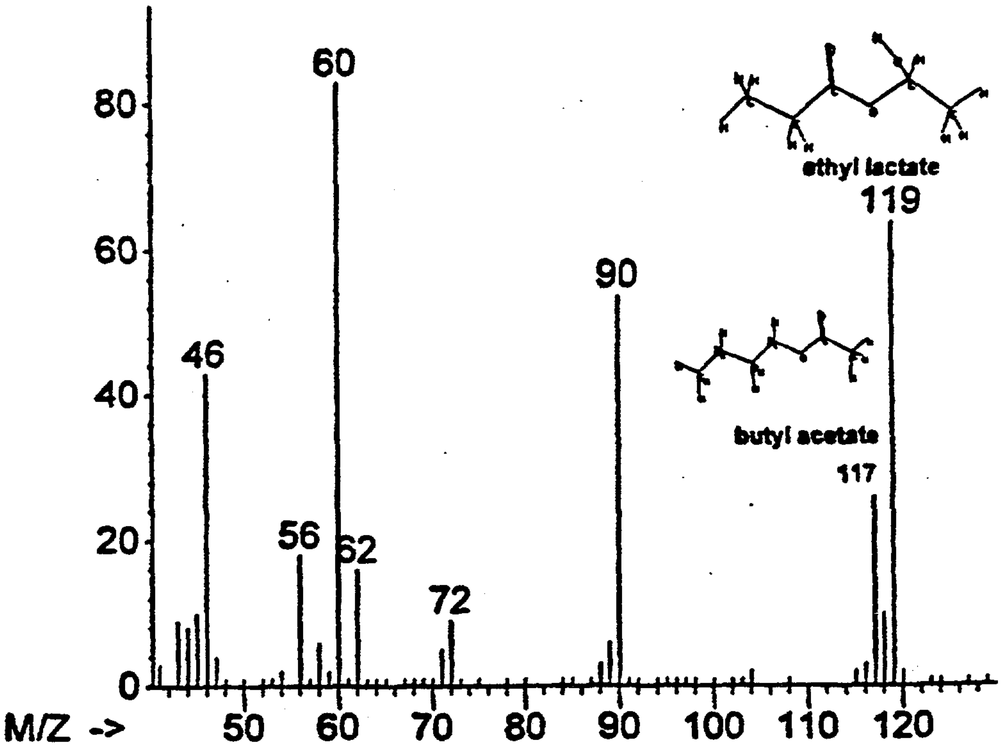

Figure 1 Chemical Ionization of Sample 1
Abundance: Average of 1.319 to 1.597 Minutes

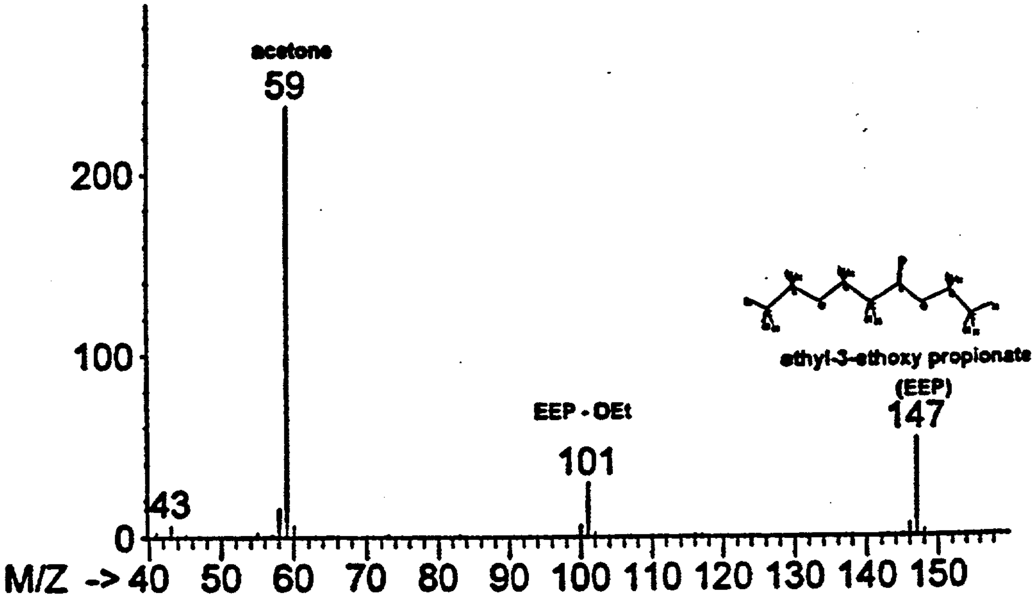

Figure 2 Chemical Ionization of Sample 2
Abundance: Average of 22.213 to 24.184 Minutes

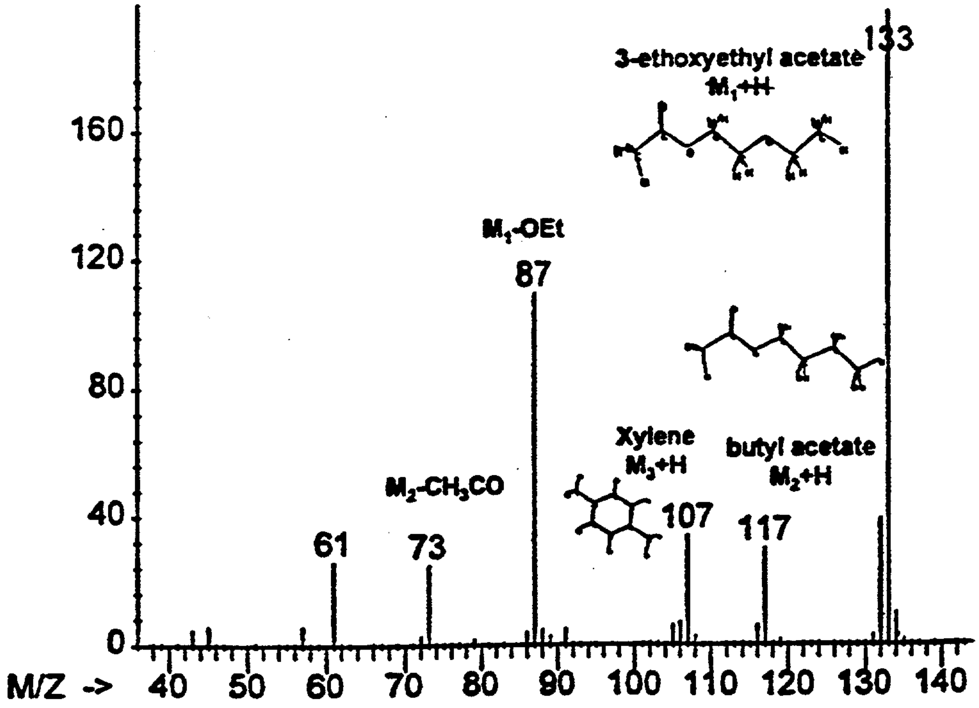

Figure 3 Chemical Ionization of Sample 3
Abundance: Average of 0.202 to 2.665 Minutes

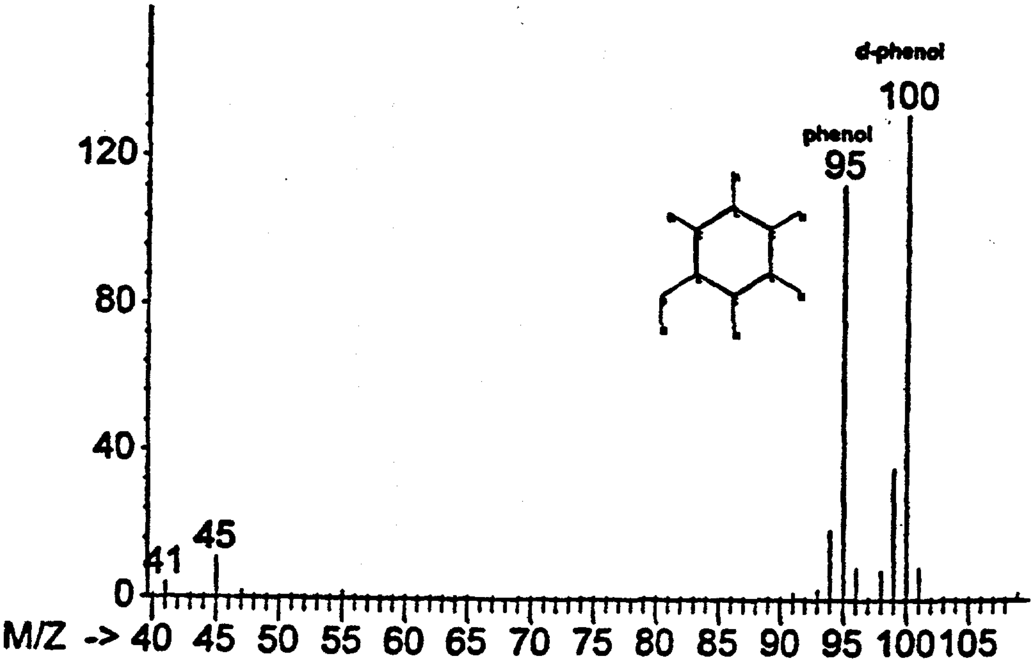

Figure 4 **Chemical Ionization of Sample 4**
Abundance: Average of 4.556 to 5.868 Minutes

6.0 Conclusions

The conclusions from the market survey are that:

- The three vendors Finnigan, Varian and VG Instruments have systems that have a good probability of fulfilling the requirements with CI and either a quadrupole or ion trap mass spectroscopy system
- System cost range from $60K to $85K
- The systems are portable on a cart
- With the addition of negative ion detection for CI, system cost is about $100K
- Application development is required and available in all cases
- There is a possibility that EI at a lower ionization energy may fulfill the application requirements

7.0 Appendices

Appendix A: Vendor Comments

Appendix A: Vendor Comments

Table A-1 Summary of Vendor Comments

Company/ Contact	Name/ Number	Comments
Balzers	Rick van Vorous 505-892-4166	• 1 second sampling/analysis time may be a problem • Perhaps EI with less than 40eV using quadrupole would give softer ionization and spectra that is easier to discriminate and quantify (standard spectra are at 70 and 100 eV) • Willing to analyze Intel samples
CMS (OI)	Tim Vrice 205-733-6916	• Can't meet rapid time requirement
Finnigan	Ann Hoffman 801-483-1097	• + ion and - ion CI available • several options for inlet • references of users: 1. Neil Arnold 2. Hank Butilar (Univ. of Utah) - inlet for specific ions 3. Gary Iceman (NMSU)-ITMS 4. Phil Hemberger (LANL) - three versions of ion traps 5. Diana Wilkins Univ. of Utah, Toxicology 6. Connie Sakashit, NW Toxicology • Perkin-Elmer ion trap is made by Finnigan • Believes Finnigan CI unit can do Intel's application
Fison (VG)	Peter Trynor 508-524-1222 Dave Pudvah 508-524-1307	• Feels their EI can decode Intel mixtures, but need 2 to 3 seconds per sample • Will do installation and training • Can custom-make CI system for Intel application
Hewlett Packard	Karen Malen 505-823-6107 John Hughs 510-460-1666 Jeff Christiansen 703-758-9339	• CI not standard, requires development work • Requires 1 to 2 sec. residence time in source. • CI would read most species. • Suggests RGA. • Concerned about condensation fouling by HMDS and cellosolve acetate. Suggest lines be heated, fused silica O.K. for HMDS. • Operation with CI more complicated, must regulate reagent gas. • Ref.: Steve Doherty Dow Chemical. • RGA good for close proximity - 3 ft. • Viking uses HP core
Perkin-Elmer	D. Schaff 505-271-2323	• Cannot do application
Varian (Finnigan)	Kevin Emery 602-461-3349	• Licenses ion trap patent from Finnigan. • Can do CI, also MS/MS • Feels ion trap is just as rugged as quadrupole • Offers demonstrated analysis, $1400/day at plant for about 1 week • Willing to analyze Intel samples
Viking	Jeff Christiansen Brian Eckenrode 703-758-9339	• Uses HP core • Selected ion monitoring (SIM) does 2000 amu/sec • Experience of Dow Chemical for on-line MS operation indicate excessive oxidation of filaments and overloading of vacuum pumps

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APPENDIX B: Mass Flow Calculations for Orifices (Apertures)

The following pages contain calculations used to determine mass flow rates for the various compounds using their vapor pressures.

Conductance Calculation

ACETONE

Initialization parameters: (they must be in cgs units)

Empirical Formula	**Orifice (microns)**	**Vapor Pressure (torr)**	**Temperature (K)**
$C := 3$	$d := 125$	$P := 184$	$T := 293$
$H := 6$			
$O := 1$			
$N := 0$			

End of Initialization parameters. Start of Calculations.

$r := \frac{d}{2} \cdot 10^{-4}$

$\text{Area} := 3.14159 \cdot r \cdot r$

$\text{Area} = 1.227 \cdot 10^{-4}$ cm²

$M := C \cdot 12 + H \cdot 1 + O \cdot 16 + N \cdot 14$

$M = 58$ g/mol

Upstream:

$P1 := P$

Downstream:

$P2 := \frac{P}{\text{Pratio}}$

Convert to cgs:

$cf := .7356$

$P2 := P2 \cdot cf$

$P1 := P1 \cdot cf$

$\text{Pratio} := 2.5$

$Cp := 18$

$Cv := \frac{3}{5} \cdot Cp$

$g := \frac{Cp}{Cv}$

For an ideal gas:

$g := \frac{5}{3}$

If the MFP for the molecule is much less than the orifice size, the viscous assumption is valid.

$\text{MeanFreePathForAir} := \frac{5 \cdot 10^{-3}}{630}$

$\text{MeanFreePathForAir} = 7.937 \cdot 10^{-6}$ cm

$r = 0.006$ cm

Equation for Viscous Flow:

$$\text{Cond} := 9.13 \cdot \frac{\text{Area}}{1 - \frac{P2}{P1}} \cdot \left(\frac{P2}{P1}\right)^{\frac{1}{g}} \cdot \left[\frac{2 \cdot g}{g - 1} \cdot \left(\frac{T}{M}\right) \cdot \left[1 - \left(\frac{P2}{P1}\right)^{\frac{g-1}{g}}\right]\right]^{\frac{1}{2}}$$

$\text{Cond} = 0.003$ cc/s

$Q := \text{Cond} \cdot \frac{P1 - P2}{760}$

$Q = 3.21 \cdot 10^{-4}$ $\text{atm} \frac{\text{cc}}{\text{s}}$

Conductance Calculation

HMDS

Initialization parameters: (they must be in cgs units)

Empirical Formula	Orifice (microns)	Vapor Pressure (torr)	Temperature (K)
$C := 6$	$d := 125$	$P := 20$	$T := 293$
$H := 19$			
$O := 0$			
$N := 1$			
$Si := 2$			

End of Initialization parameters. Start of Calculations.

$r := \frac{d}{2} \cdot 10^{-4}$

$\text{Area} := 3.14159 \cdot r \cdot r$

$\text{Area} = 1.227 \cdot 10^{-4}$ cm²

$M := C \cdot 12 + H \cdot 1 + O \cdot 16 + N \cdot 14 + Si \cdot 28$

$M = 161$ g/mol

Upstream:

$P1 := P$

Downstream:

$P2 := \frac{P}{\text{Pratio}}$

Convert to cgs:

$P2 := P2 \cdot cf$

$P1 := P1 \cdot cf$

$Cp := 18$

$Cv := \frac{3}{5} \cdot Cp$

$g := \frac{Cp}{Cv}$

For an ideal gas:

$g := \frac{5}{3}$

If the MFP for the molecule is much less than the orifice size, the viscous assumption is valid.

$\text{MeanFreePathForAir} := \frac{5 \cdot 10^{-3}}{630}$

$\text{MeanFreePathForAir} = 7.937 \cdot 10^{-6}$ $\qquad r = 0.006$ cm

Equation for Viscous Flow:

$$\text{Cond} := 9.13 \cdot \frac{\text{Area}}{1 - \frac{P2}{P1}} \cdot \left(\frac{P2}{P1}\right)^{\frac{1}{g}} \cdot \left[\frac{2 \cdot g}{g - 1} \cdot \left(\frac{T}{M}\right) \cdot \left[1 - \left(\frac{P2}{P1}\right)^{\frac{g-1}{g}} \right] \right]^{\frac{1}{2}}$$

$$Q := \text{Cond} \cdot \frac{P1 - P2}{760}$$

$\text{Cond} = 0.002$

$Q = 2.09 \cdot 10^{-5}$ $\quad \text{atm} \frac{cc}{s}$

Conductance Calculation Ethyl Lactate

Initialization parameters: (they must be in cgs units)

Empirical Formula	**Orifice (microns)**	**Vapor Pressure (torr)**	**Temperature (K)**
$C := 5$	$d := 125$	$P := 2.8$	$T := 293$
$H := 10$			
$O := 3$			
$N := 0$			

End of Initialization parameters. Start of Calculations.

$$r := \frac{d}{2} \cdot 10^{-4}$$

$$Area := 3.14159 \cdot r \cdot r$$

$$Area = 1.227 \cdot 10^{-4} \quad \text{cm}^2$$

$$M := C \cdot 12 + H \cdot 1 + O \cdot 16 + N \cdot 14$$

$$M = 118 \quad \text{g/mol}$$

Upstream:

$$P1 := P$$

Downstream:

$$P2 := \frac{P}{Pratio}$$

Convert to cgs:

$$P2 := P2 \cdot cf$$

$$P1 := P1 \cdot cf$$

$$Cp := 18$$

$$Cv := \frac{3}{5} \cdot Cp$$

$$g := \frac{Cp}{Cv}$$

For an ideal gas:

$$g := \frac{5}{3}$$

If the MFP for the molecule is much less than the orifice size, the viscous assumption is valid.

$$MeanFreePathForAir := \frac{5 \cdot 10^{-3}}{630}$$

$$MeanFreePathForAir = 7.937 \cdot 10^{-6} \qquad r = 0.006 \quad \text{cm}$$

Equation for Viscous Flow:

$$Cond := 9.13 \cdot \frac{Area}{1 - \frac{P2}{P1}} \cdot \left(\frac{P2}{P1}\right)^{\frac{1}{g}} \cdot \left[\frac{2 \cdot g}{g-1} \cdot \left(\frac{T}{M}\right) \cdot \left[1 - \left(\frac{P2}{P1}\right)^{\frac{g-1}{g}}\right]\right]^{\frac{1}{2}}$$

$$Q := Cond \cdot \frac{P1 - P2}{760}$$

$$Cond = 0.002$$

$$Q = 3.42 \cdot 10^{-6} \quad atm\ \frac{cc}{s}$$

Conductance Calculation — Isopropyl Alcohol

Initialization parameters: (they must be in cgs units)

Empirical Formula	Orifice (microns)	Vapor Pressure (torr)	Temperature (K)
$C := 3$	$d := 125$	$P := 33$	$T := 293$
$H := 8$			
$O := 1$			
$N := 0$			

End of Initialization parameters. Start of Calculations.

$$r := \frac{d}{2} \cdot 10^{-4}$$

$$Area := 3.14159 \cdot r \cdot r$$

$$Area = 1.227 \cdot 10^{-4} \quad \text{cm}^2$$

$$M := C \cdot 12 + H \cdot 1 + O \cdot 16 + N \cdot 14$$

$$M = 60 \quad \text{g/mol}$$

Upstream:

$$P1 := P$$

Downstream:

$$P2 := \frac{P}{Pratio}$$

Convert to cgs:

$$P2 := P2 \cdot cf$$

$$P1 := P1 \cdot cf$$

$$Cp := 18$$

$$Cv := \frac{3}{5} \cdot Cp$$

$$g := \frac{Cp}{Cv}$$

For an ideal gas:

$$g := \frac{5}{3}$$

If the MFP for the molecule is much less than the orifice size, the viscous assumption is valid.

$$MeanFreePathForAir :\square \frac{5 \cdot 10^{-3}}{630}$$

$$MeanFreePathForAir = 7.937 \cdot 10^{-6} \qquad r = 0.006 \quad \text{cm}$$

Equation for Viscous Flow:

$$Cond := 9.13 \cdot \frac{Area}{1 - \frac{P2}{P1}} \cdot \left(\frac{P2}{P1}\right)^{\frac{1}{g}} \cdot \left[\frac{2 \cdot g}{g - 1} \cdot \left(\frac{T}{M}\right) \cdot \left[1 - \left(\frac{P2}{P1}\right)^{\frac{g-1}{g}}\right]\right]^{\frac{1}{2}}$$

$$Q := Cond \cdot \frac{P1 - P2}{760} \qquad Cond = 0.003$$

$$Q = 5.65 \cdot 10^{-5} \quad \text{atm} \, \frac{\text{cc}}{\text{s}}$$

APPENDIX C: VOC Statement of Work for the 1994 Intel CRADA

The pages included in this section pertain to the VOC monitoring activity and have been copied from the full CRADA statement of work.

Sandia National Laboratories
Albuquerque, New Mexico 87185

date: March 3, 1994

to: Distribution

Michael R Keenan

from: M. R. Keenan, 1824, MS0342

subject: 1/26/94 Version of the Statement of Work

I have enclosed copies of the portion of the CRADA Appendix A: Statement of Work that is relevant to our working group (Project E) and of the entire Joint Work Statement. Information related to the real-time speciation of VOCs project is dispersed throughout the latter document. These documents are dated 1/26/94, and it is my understanding that these were the final versions that were submitted for approval.

distribution:

Angela R. Boggs
Intel Corporation
FB9-10
4100 Sara Road
Rio Rancho, NM 87124

Scott Sibbett
CFM Research Center
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MS0342 S. E. Dempster, 1824
MS0343 S. M. Thomberg, 1823
MS0755 A. E. Verardo, 6612
MS0720 W. Cheng, 6626
MS0342 M. R. Keenan, 1824
Dept 1824 File

Project E: Real Time Speciation of Volatile Organic Compounds in Exhaust Streams

Intel and Sandia will work together to develop a method to speciate and quantify volatile organic compounds (VOCs) found in effluent gasses at the New Mexico Intel plant. VOCs are emitted in the plant's exhaust streams after use in Intel's photolithography process. An instrument that can give accurate, real-time measurements of the quantity and species of VOCs would allow identification of emission sources, and ultimately aid in reduction of vapor emitted into the environment.

The technical objective of this project is to develop a portable device for monitoring VOCs used in Intel's photolithography process. At project end, a demonstration of the prototype will display the instrument's ability to specify VOC type and quantity in a production setting. This project, scheduled for nine months, is divided into four phases as defined below.

Phase I. Development of Detailed Instrument Specifications.

Objective. To determine required instrument specifications.

Discussion. Phase I is comprised of the following two tasks:

Task A. Sandia and Intel personnel will detail required instrument specifications. The chemicals to be analyzed, required sensitivity levels, speed of response, and operational environment parameters will be defined.

Task B. Sandia will take a survey of commercially available equipment that will meet requirements defined in Task A.

Responsibilities. Sandia and Intel will jointly define instrument specifications. Sandia will complete market survey of equipment.

Phase I Deliverables: A set of specifications for a portable VOC monitoring instrument will be prepared. A list of commercially available equipment that can meet those specifications will be identified.

Phase II. Prototype Instrument Development.

Objective. To develop, assemble, calibrate, and test the monitoring system for selected VOCs.

Discussion. Phase II is comprised of the following two tasks:

Task A. Sandia will develop a measurement protocol, assemble the measurement system, and calibrate the system for specific VOCs selected by Intel.

Task B. Sandia will develop an instrument test bed using Intel-supplied VOCs and existing Sandia equipment and facilities.

Responsibilities. Sandia will build and test system using Intel VOCs.

Phase II Deliverables: A tested prototype of a VOC monitoring system will be ready at the end of Phase II.

Phase III. Demonstration of Prototype at Intel NM Production Facility.

Objective. To install and demonstrate prototype instrument at Intel Production Facility.

Discussion. Phase III is comprised of the following two tasks:

Task A. The production facility ports will be selected and prepared for reception of the VOC measurement system.

Task B. The prototype instrument will be installed at the selected ports. The instrument's capabilities will be demonstrated.

Responsibilities. Sandia and Intel will work together to install and operate the new instrumentation.

Phase III Deliverables: The working VOC measurement system will be in place and ready for data collection.

Phase IV. Verification of Prototype Instrument Performance per Phase I Specifications.

Objective. Collect and analyze performance data from the operating VOC system.

Discussion. Data from the performance of the VOC system at the various Intel process ports will be collected. The system's real time operation will be compared to the performance specifications. A final report will be prepared including instrument specifications, data analysis, training information, and any recommendations for improvement.

Responsibilities. Sandia and Intel will jointly collect and analyze data. Sandia will be responsible for preparation of the final report.

Phase IV Deliverables: A report covering all aspects of the performance and operation of the VOC monitoring instrument will be completed.

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APPENDIX D: Pure Compound Spectra at Sandia (GC/MS, CI-MS)

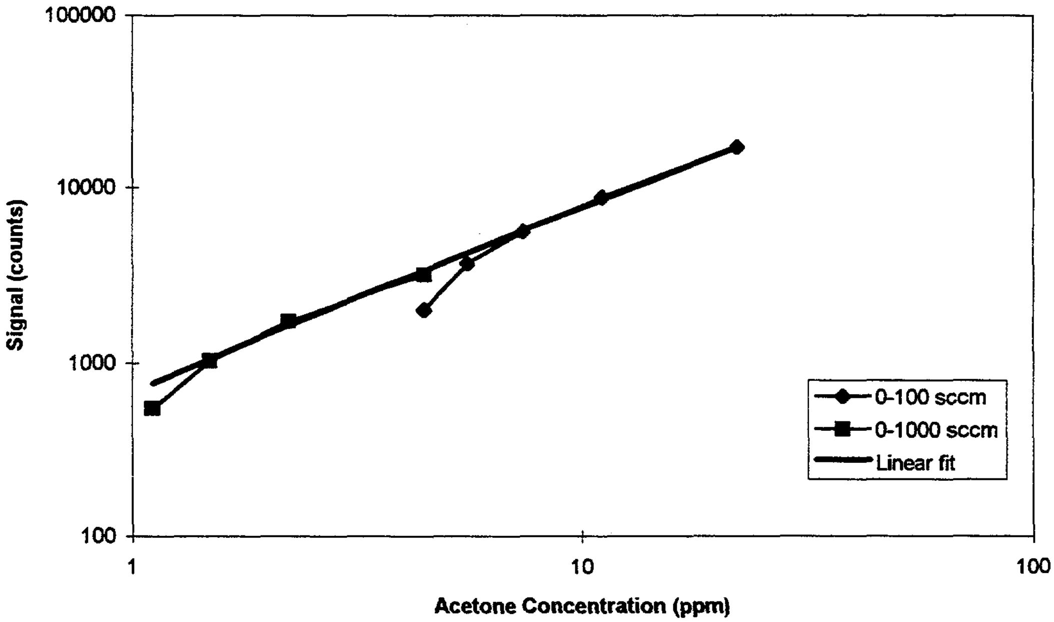
These data support the calibration curves, show the parent molecular peaks for EI and CI mass spectra, and also show the purity of the chemicals from the GC/MS runs.

Key to data files included:

File Name	Date	Scans	Conditions
ACE01	10/5/94	50-3000	Acetone permeation tube rise time measurements
ACE02	10/6/94	1-3900	Acetone permeation tube calibration curve: 20 - 100 sccm
ACE03	10/6/94	1-4075	Acetone permeation tube calibration curve: 100 - 500 sccm
INTEL_6		1-12 min	Ion trap mass spectrometer chemical ionization data for HMDS, photoresist EBR
_CI	4/12/94	mass scan	Ion trap mass spectrometer chemical ionization data for photoresist
_EI	4/12/94	mass scan	Ion trap mass spectrometer electron impact ionization data for photoresist
_CI2	4/12/94	mass scan	Ion trap mass spectrometer chemical ionization data for EBR
_EI3		mass scan	Ion trap mass spectrometer electron impact ionization data for EBR
_CI2		mass scan	Ion trap mass spectrometer chemical ionization data for resist
_EI1		mass scan	Ion trap mass spectrometer electron impact ionization data for resist
HMDS2	4/12/94	GC/MS	GC/MS run of HMDS to check chemical purity
	4/12/94	GC/MS	GC/MS run of resist to check chemical purity
	4/13/94	GC/MS	GC/MS run of photoresist to check chemical purity
	4/12/94	GC/MS	GC/MS run of EBR to check chemical purity

Chemical	**Compound**	**B. P.**	**Mol. Wt.**
Resist	Ethyl lactate	154	118
	n-butyl acetate	125	116
	xylene	140	106
	resins	na	na
	butyl acetate	125	116
	xylene	140	106
	ethylene glycol monoethylether acetate	156	132
HMDS	hexamethyldisilazane	?	146
	acetone	57	58
	ethyl-3-ethoxypropionate	?	146

	Acetone permeation std.						
Perm value:		7.40E-06	cc/s				
Serial no:		TP176					
Cal. Flow (cc/min)	Calc. Con (ppm)	Peak ht. (counts)	Linear fit				
20	22.2	17084	17167.67	Slope:	777.7742	22.2	17084
40	11.1	8794	8534.378	Intercept:	-98.9155	11.1	8794
60	7.4	5607	5656.614			7.4	5607
80	5.55	3679	4217.731			4.44	3175
100	4.44	2002	3354.402			2.22	1710
100	4.44	3175	3354.402			1.48	1023
200	2.22	1710	1627.743		Plug in		To
300	1.48	1023	1052.19		Counts:		calculate
400	1.11	549	764.4139		99328	=	127.8352
500	0.888	281	591.7481				ppm



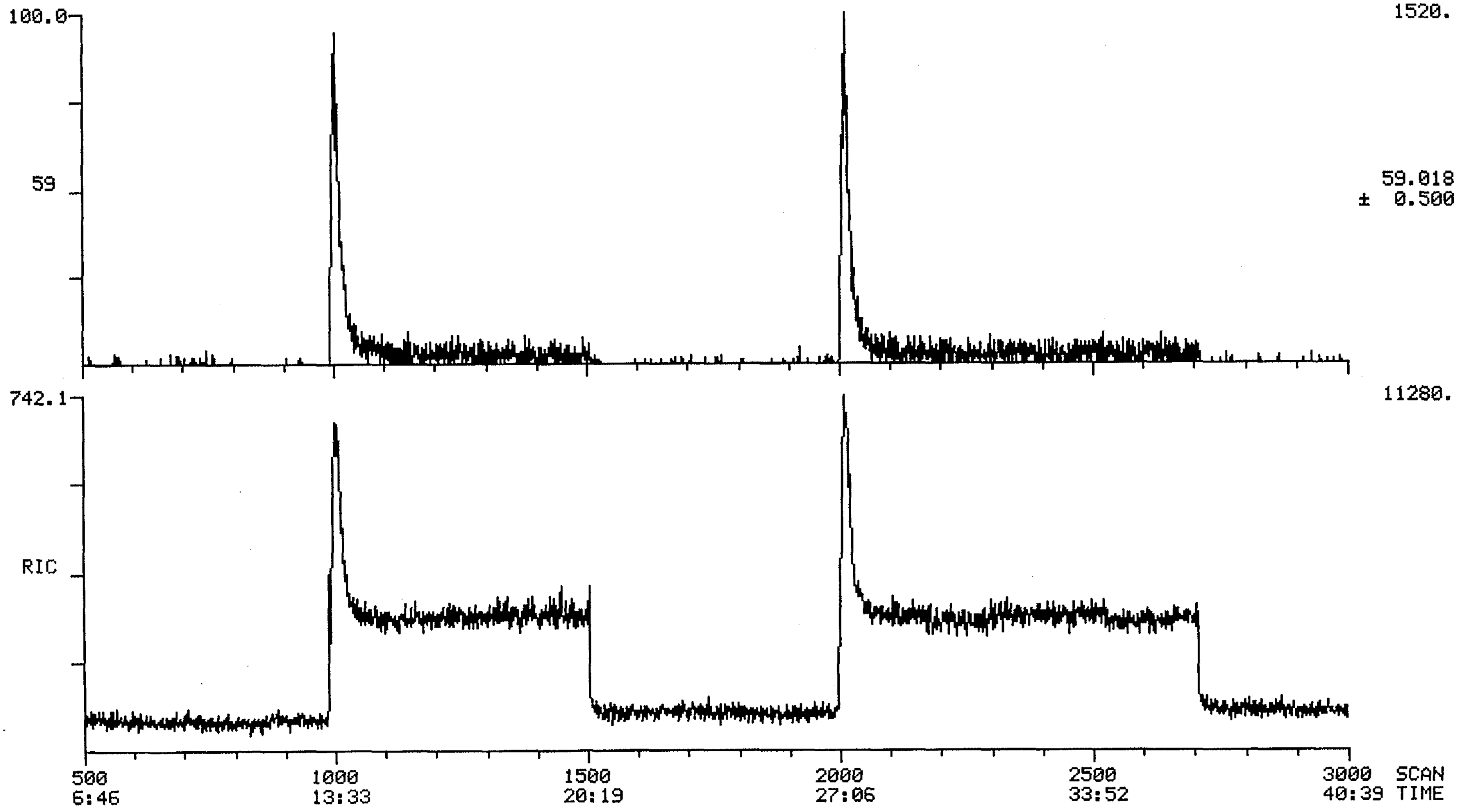
Linear equation fit to determine acetone equivalents:

ppm = 0.12857 * (counts) + .127178

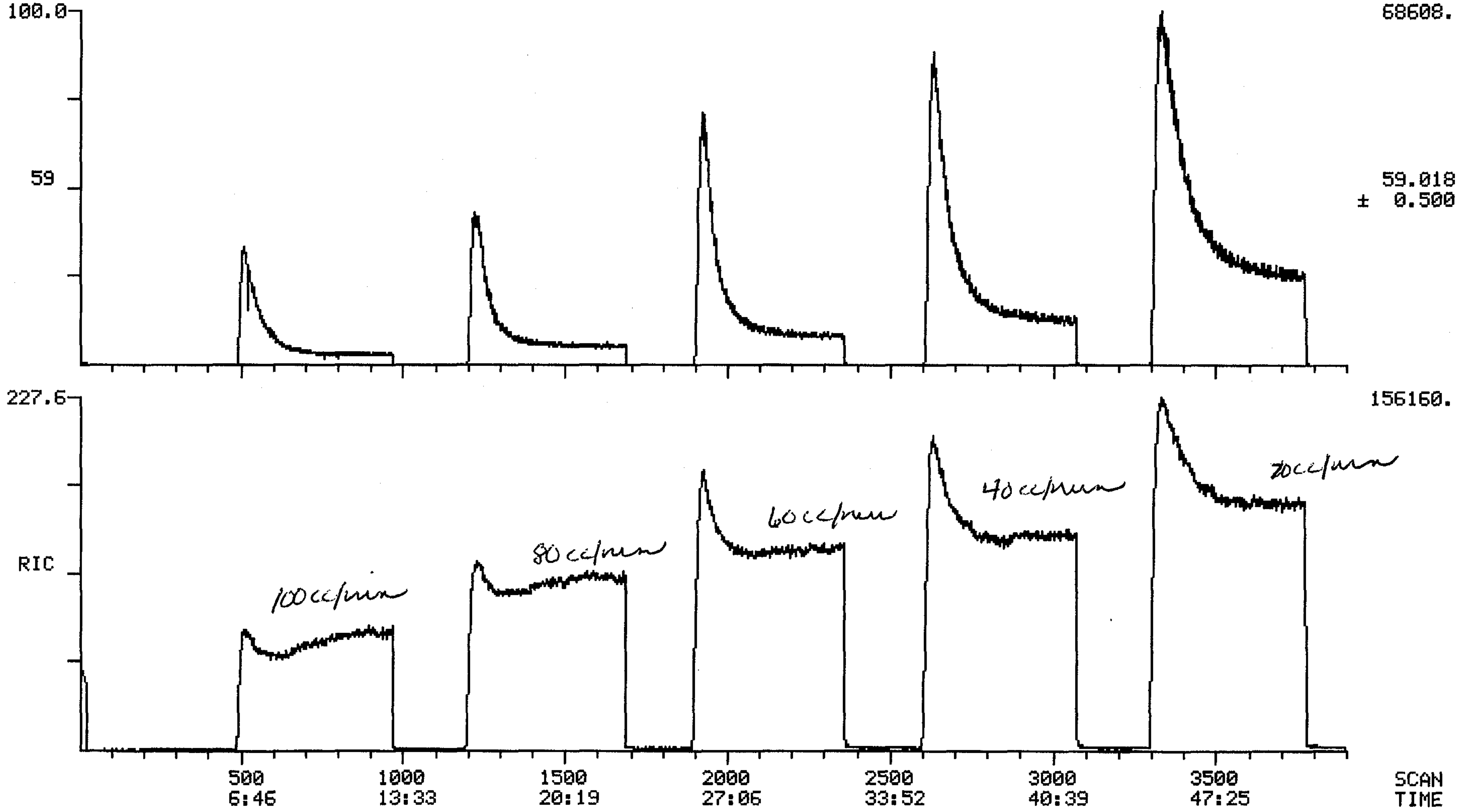
RIC+MASS CHROMATOGRAM
10/05/94 15:07:00
SAMPLE: ACETONE
CONDS.: 120 CI
RANGE: G 1,3080 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ACE01 #1
CALI: CALTAB #3

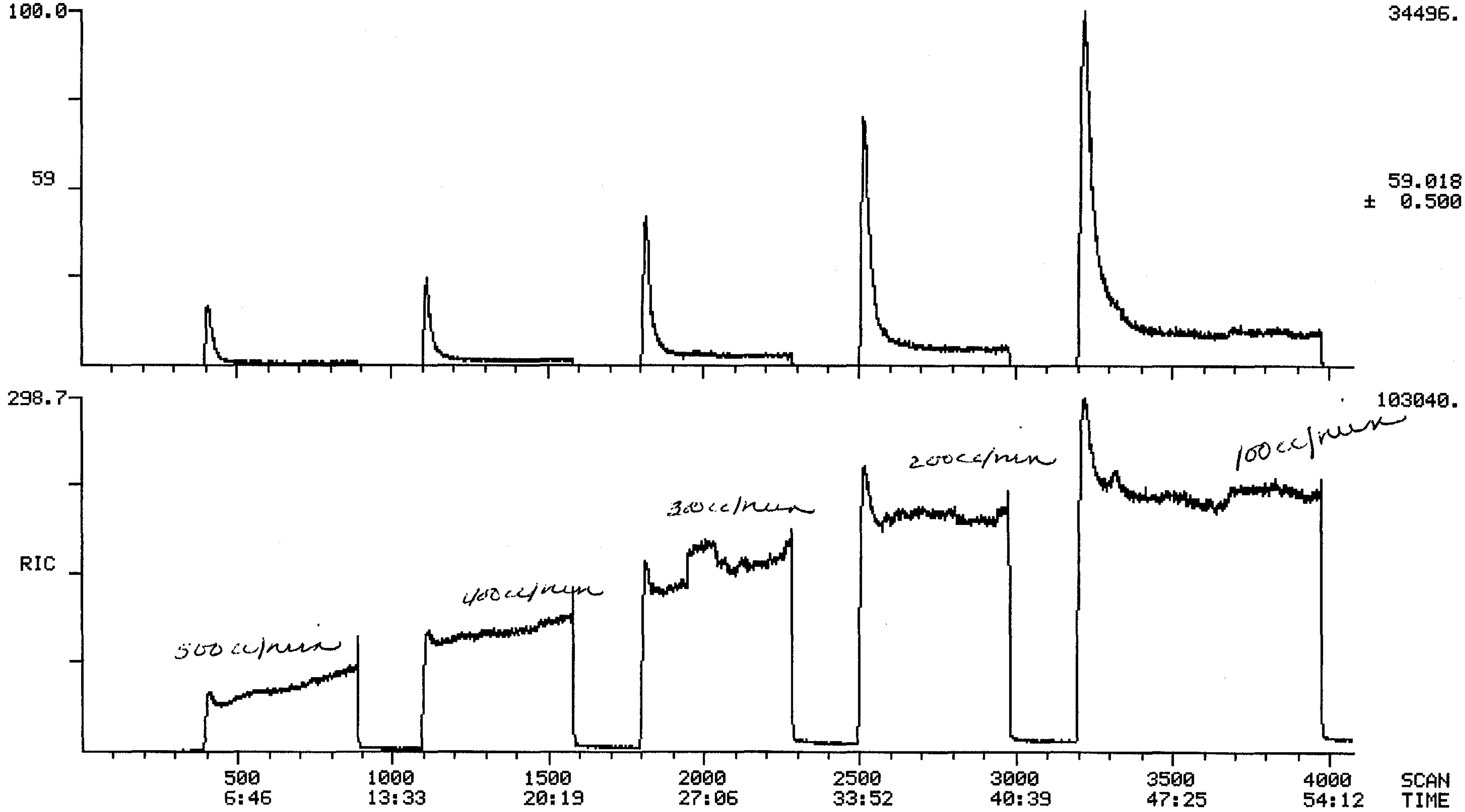
SCANS 500 TO 3000

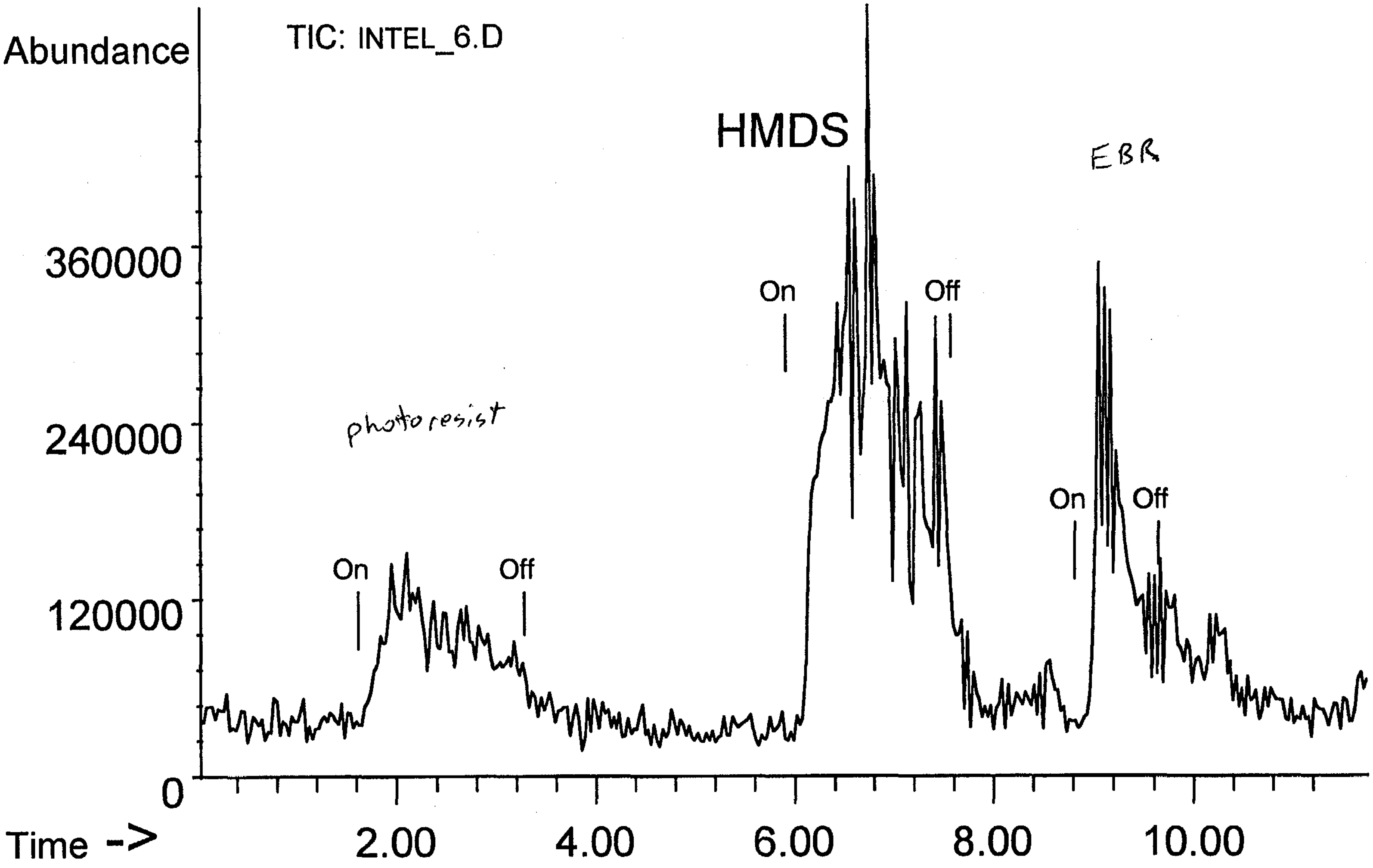


RIC+MASS CHROMATOGRAM　　DATA: ACE02 #1　　SCANS　1 TO 3900
10/06/94　9:01:00　　CALI: CALTAB #3
SAMPLE: ACETONE
CONDS.: 100CC/MIN TO 10CC/MIN
RANGE: G　1,4702　LABEL: N　0, 4.0　QUAN: A　0, 1.0 J　0　BASE: U 20,　3



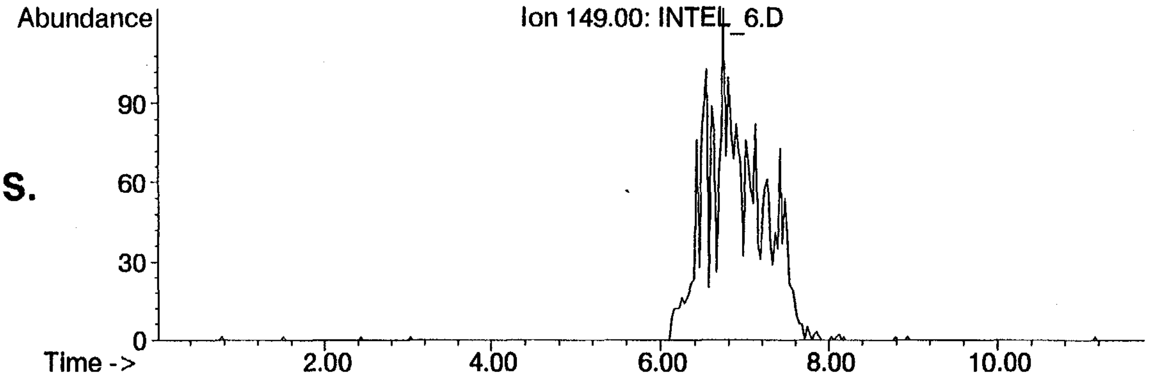
RIC+MASS CHROMATOGRAM DATA: ACE03 #1 SCANS 1 TO 4075
10/06/94 13:56:00 CALI: CALTAB #3
SAMPLE: ACETONE
CONDS.: 500CC/MIN TO 100CC/MIN
RANGE: G 1,4075 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



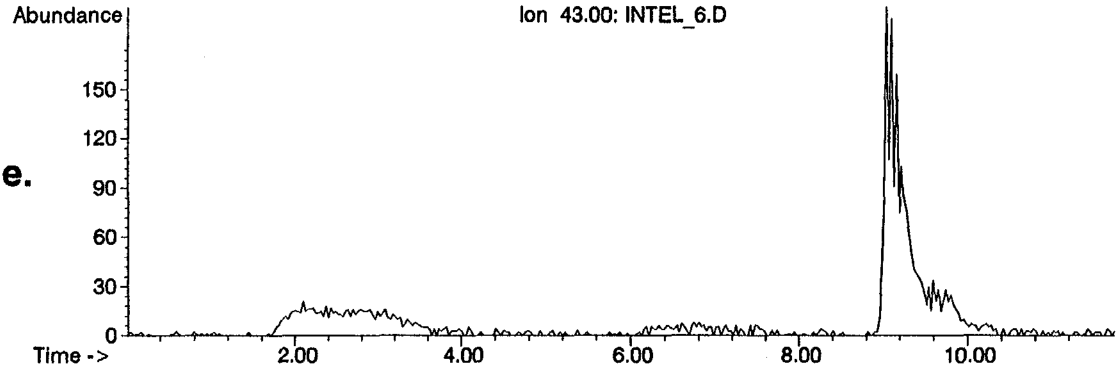


The headspace of vials used to store the chemicals was sampled. Gas was sampled through 50 feet of teflon tubing and all hardware maintained at ambient temperature. ITMS data.

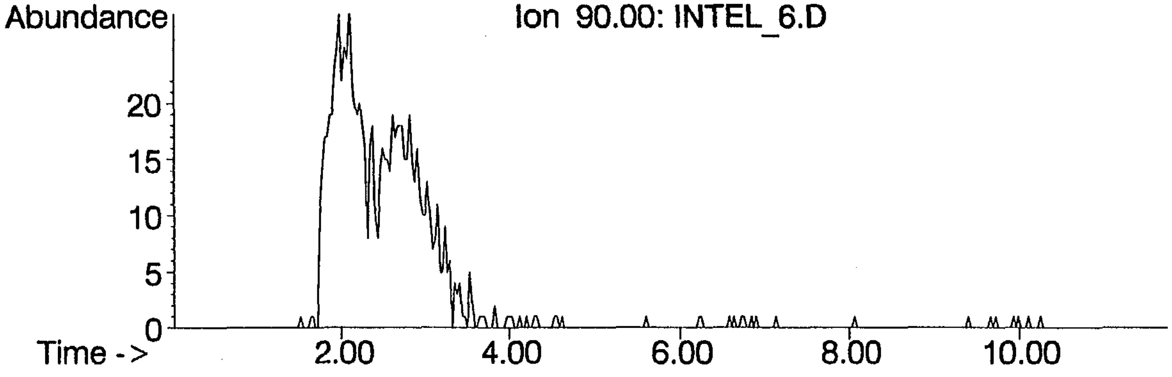
Extracted ion plot for HMDS.

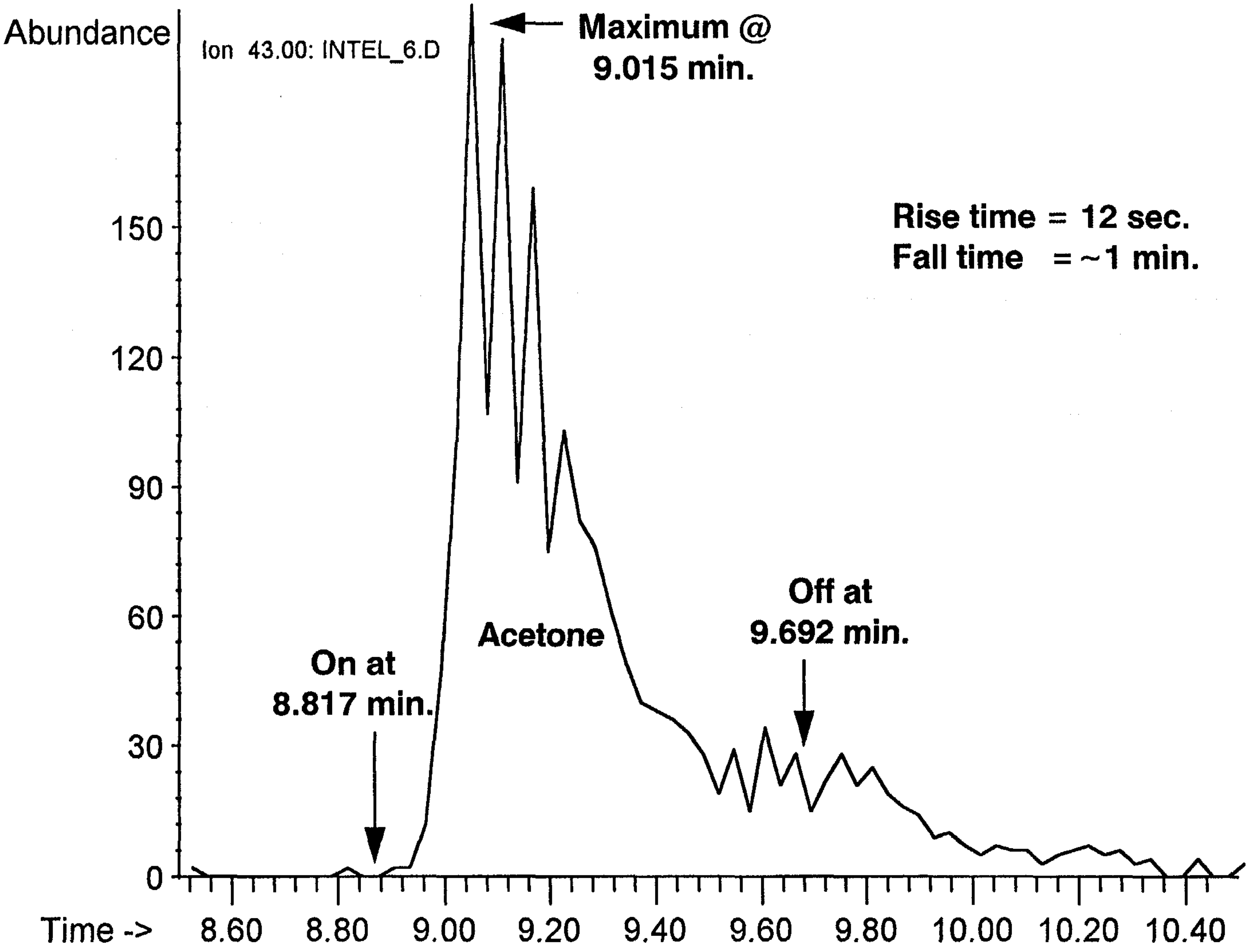


Extracted ion plot for acetone.

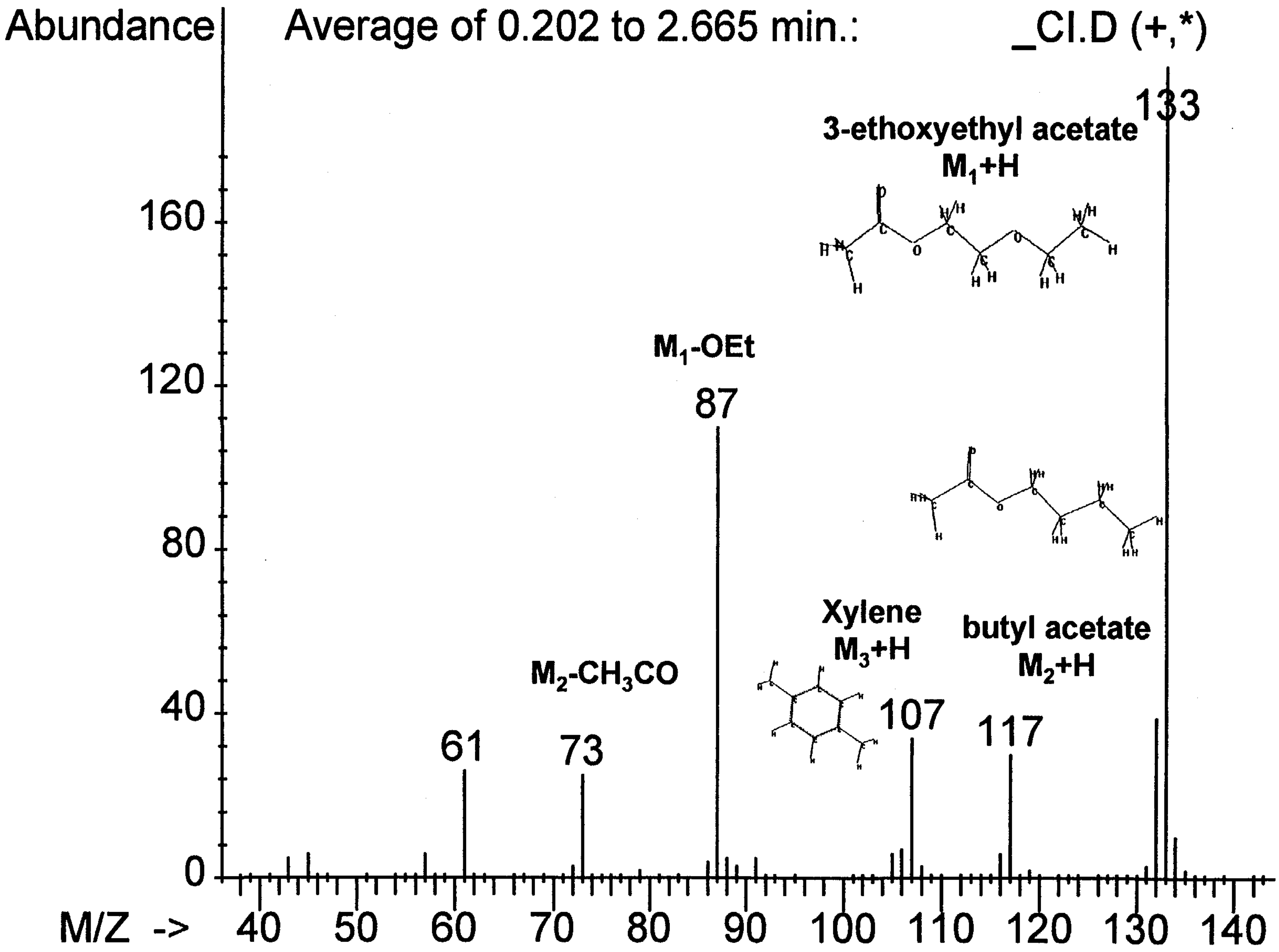


Extracted ion plot for 3-ethoxyethyl acetate.

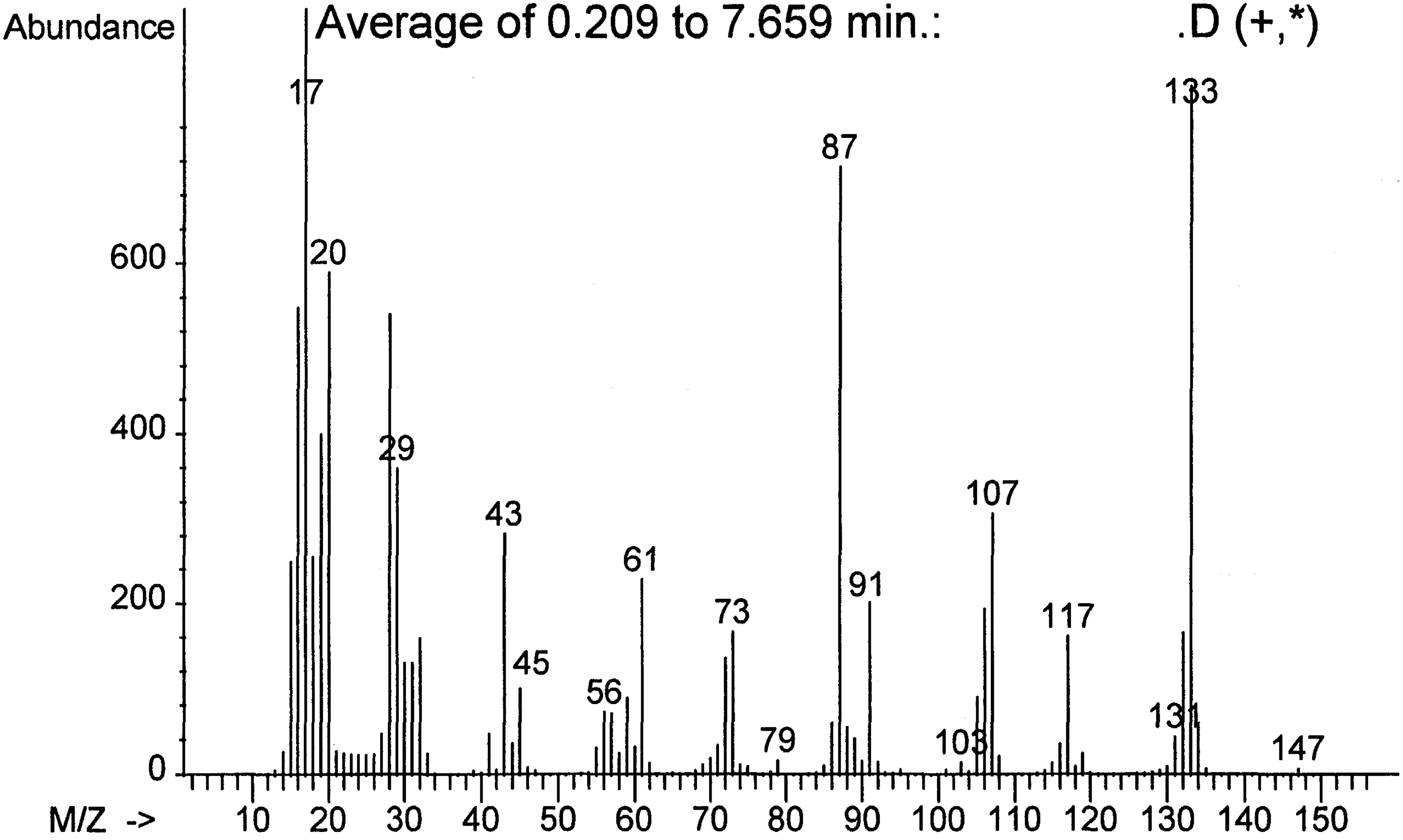




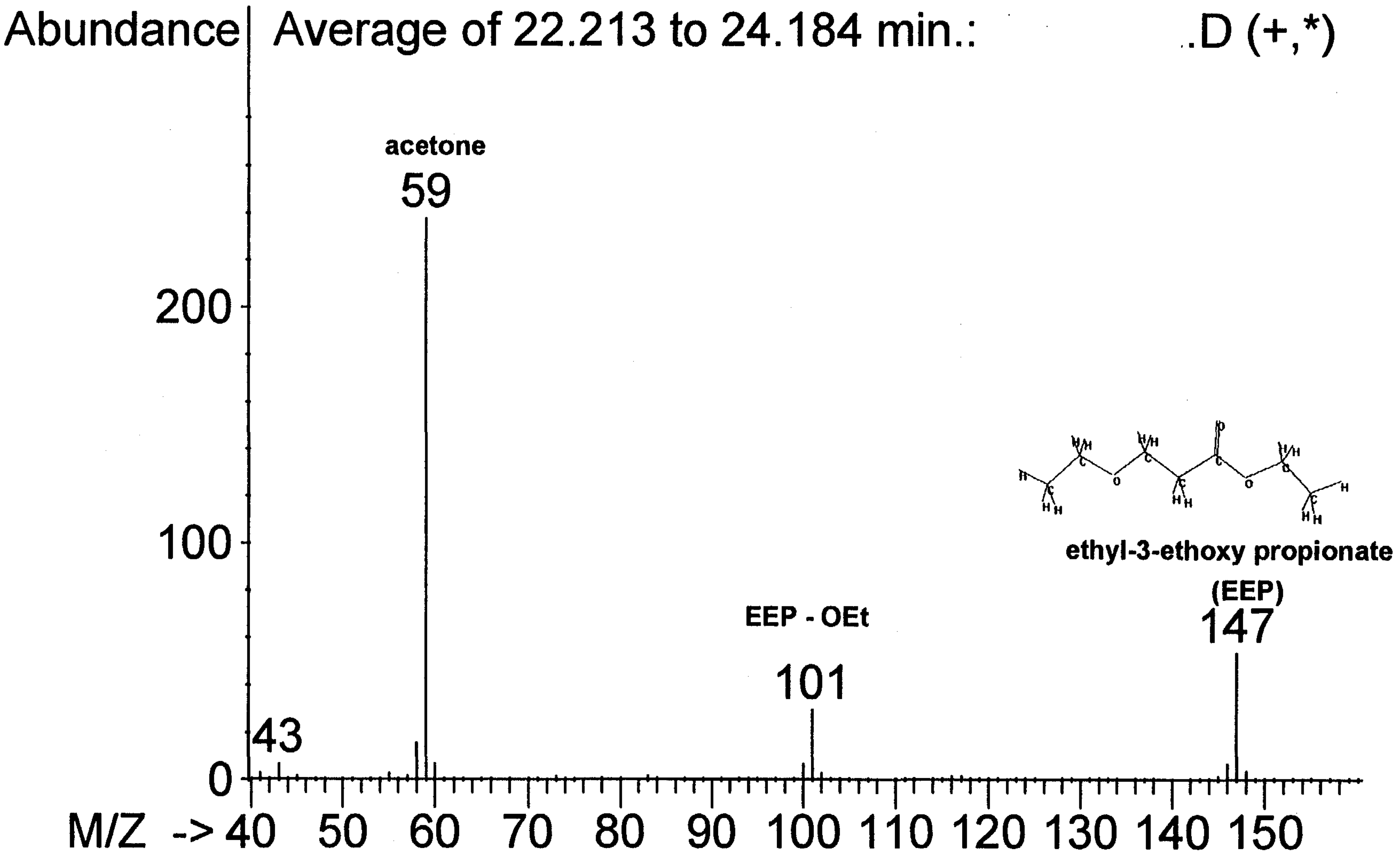
Sample was drawn through 50 ft. of teflon tubing (0.25▒ dia.) using a diaphragm pump.


Abundance
Average of 0.202 to 2.665 min.:
_CI.D (+,*)
160
120
80
40
0
M/Z ->
40
50
60
70
80
90
100
110
120
130
140
133
3-ethoxyethyl acetate
M_1+H
M_1-OEt
87
61
73
M_2-CH_3CO
Xylene
M_3+H
107
butyl acetate
M_2+H
117

EI

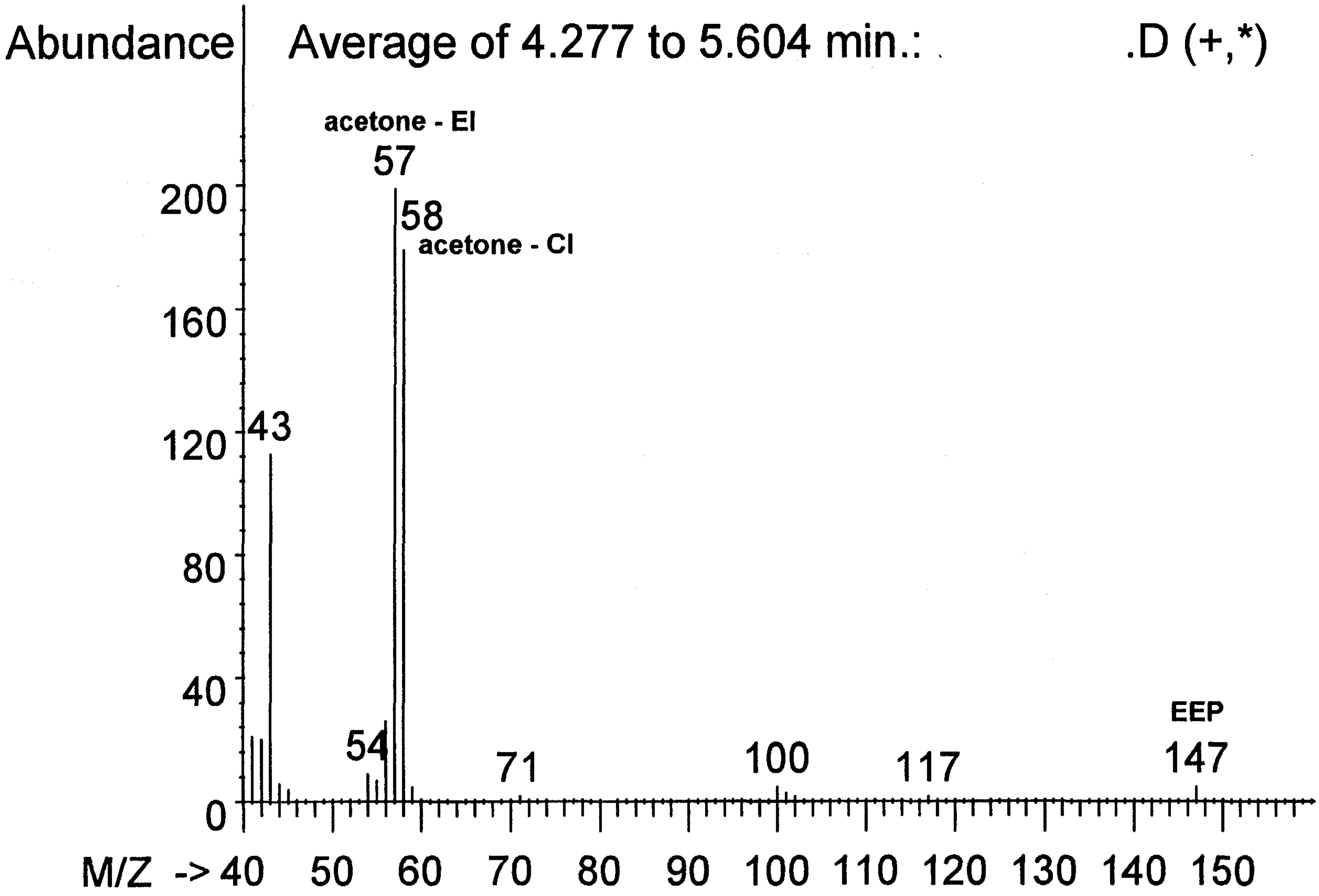

Average of 0.209 to 7.659 min.:
.D (+,*)
Abundance
600
400
200
0
M/Z ->
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
17
20
29
43
45
56
61
73
79
87
91
103
107
117
131
133
147

CI

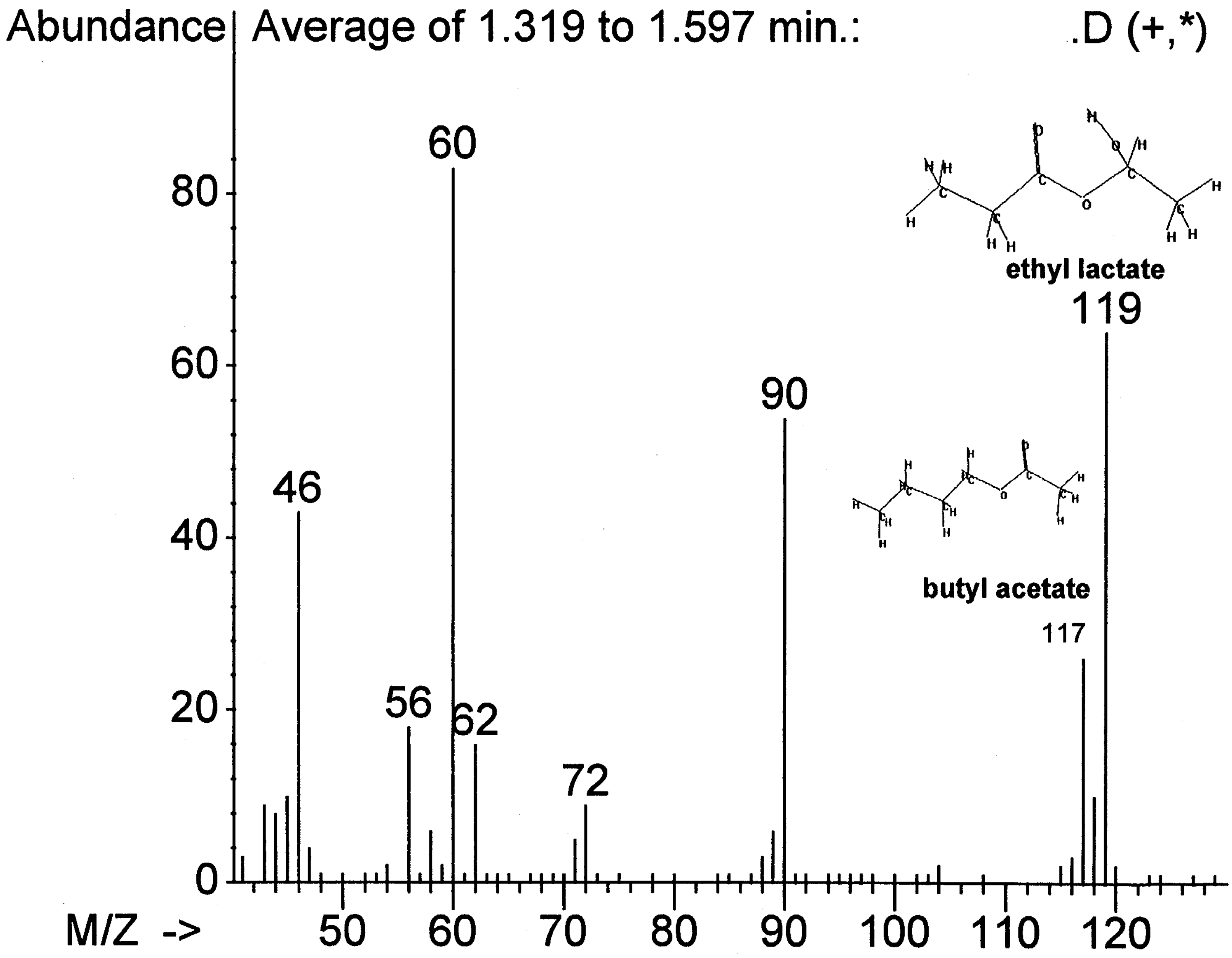


Abundance
Average of 22.213 to 24.184 min.:
.D (+,*)
acetone
59
EEP - OEt
101
ethyl-3-ethoxy propionate
(EEP)
147
43
0
100
200
M/Z -> 40
50
60
70
80
90
100
110
120
130
140
150

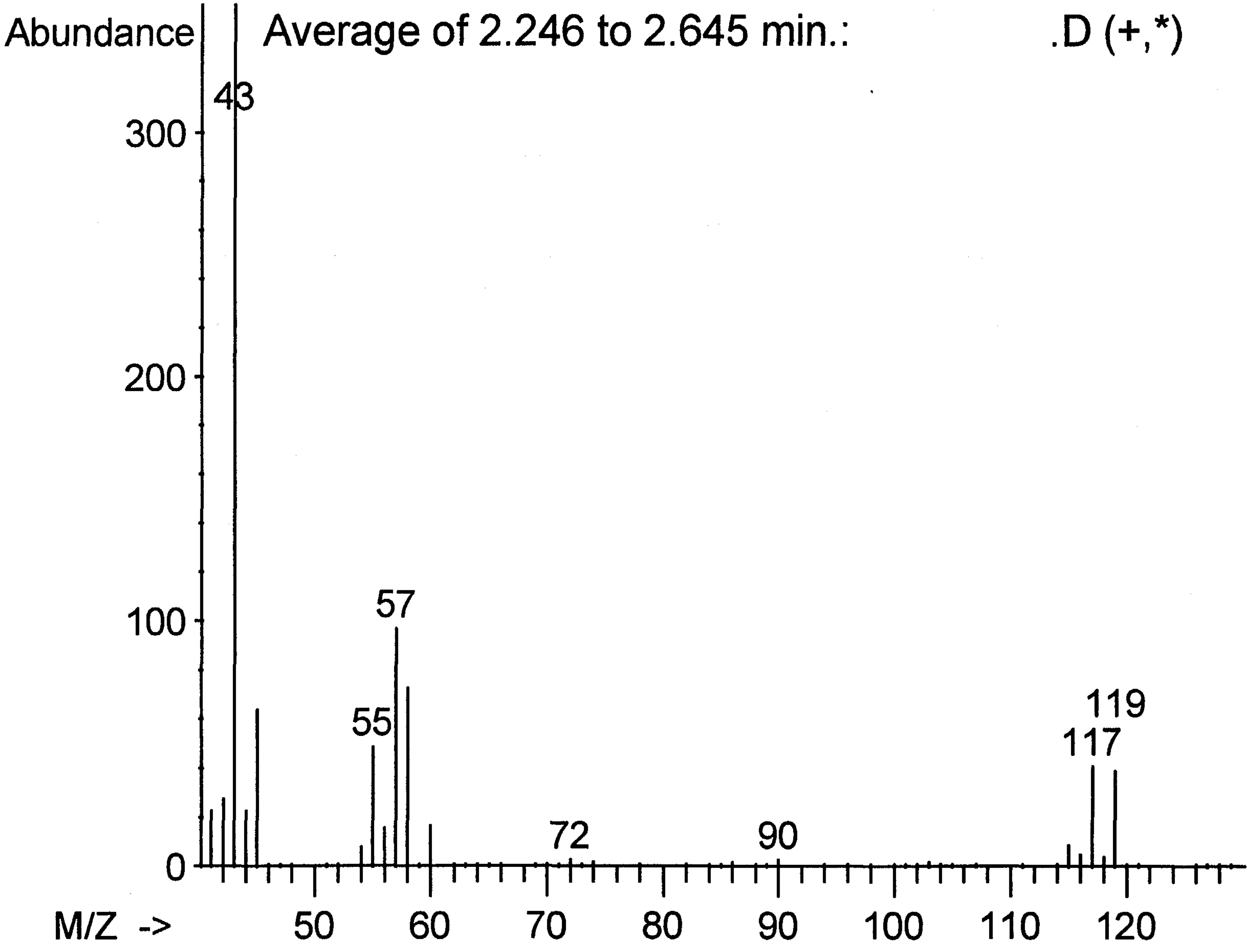
EI


Abundance
Average of 4.277 to 5.604 min.: .D (+,*)
acetone - EI
57
58
acetone - CI
43
54
71
100
117
EEP
147
200
160
120
80
40
0
M/Z -> 40
50
60
70
80
90
100
110
120
130
140
150

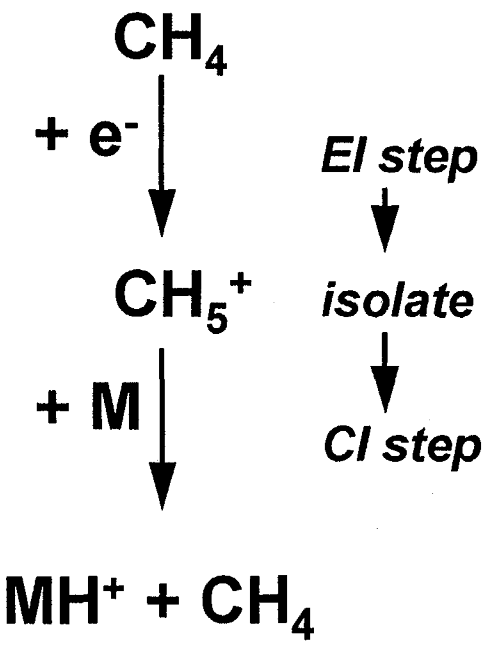
CI


Abundance
Average of 1.319 to 1.597 min.:
.D (+,*)
80
60
40
20
0
M/Z ->
50
60
70
80
90
100
110
120
46
56
60
62
72
90
117
119
ethyl lactate
butyl acetate

EI


Abundance
Average of 2.246 to 2.645 min.:
.D (+,*)
300
200
100
0
43
57
55
119
117
72
90
M/Z ->
50
60
70
80
90
100
110
120

Typical Chemical Ionization using Methane



CH_4

$+ e^-$

EI step

CH_5^+

isolate

$+ M$

CI step

$MH^+ + CH_4$

(M is the analyte molecule)

$$CH_4 + e^- \rightarrow \{CH_2^{+\cdot}, CH_3^+, CH_4^{+\cdot}\}$$

$$CH_4 + CH_4^{\cdot} \rightarrow CH_5^+ + CH_3^{\cdot}$$

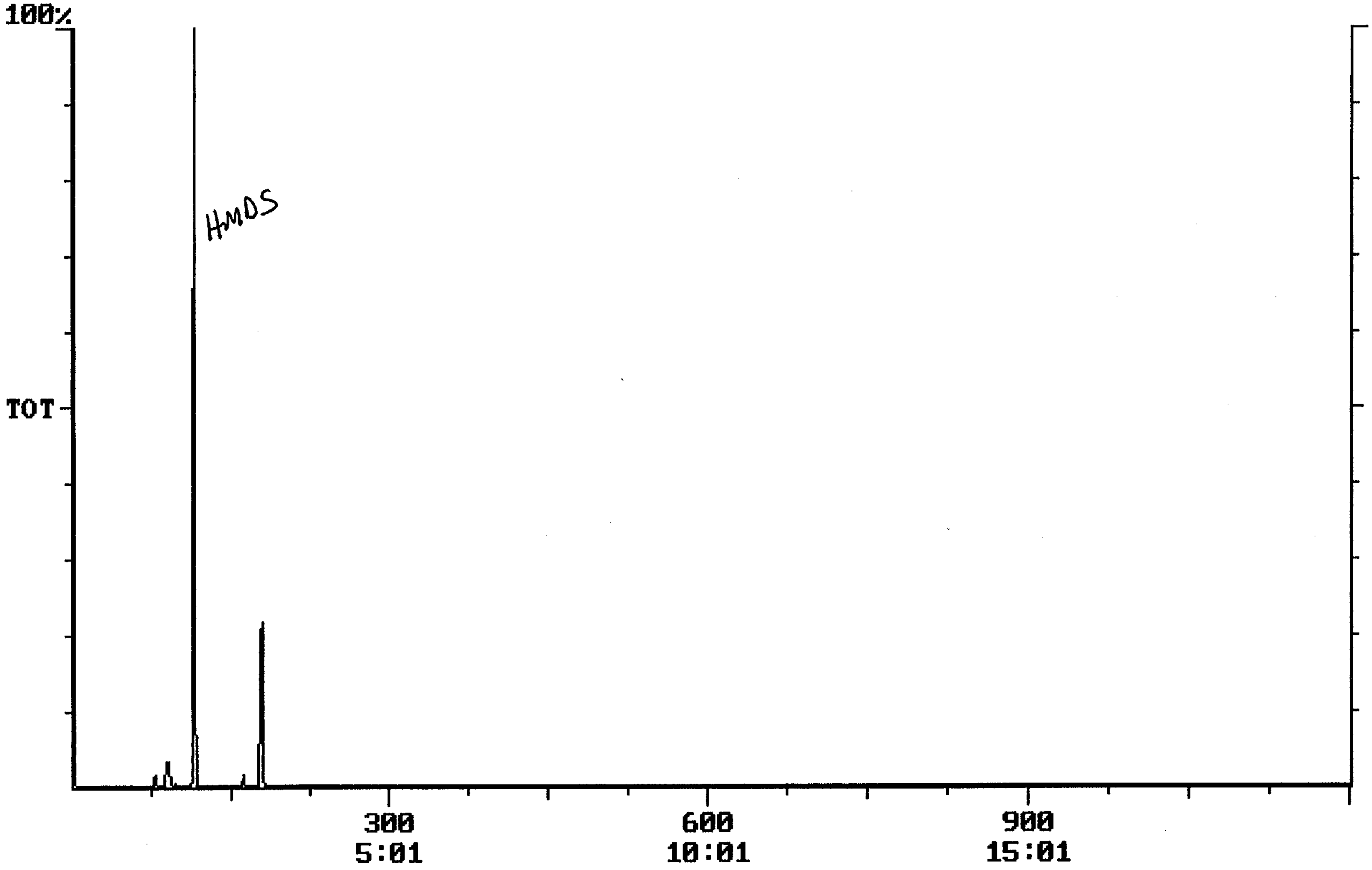
$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

$$CH_2^+ + CH_4 \rightarrow C_2H_4^{+\cdot} + H_2$$

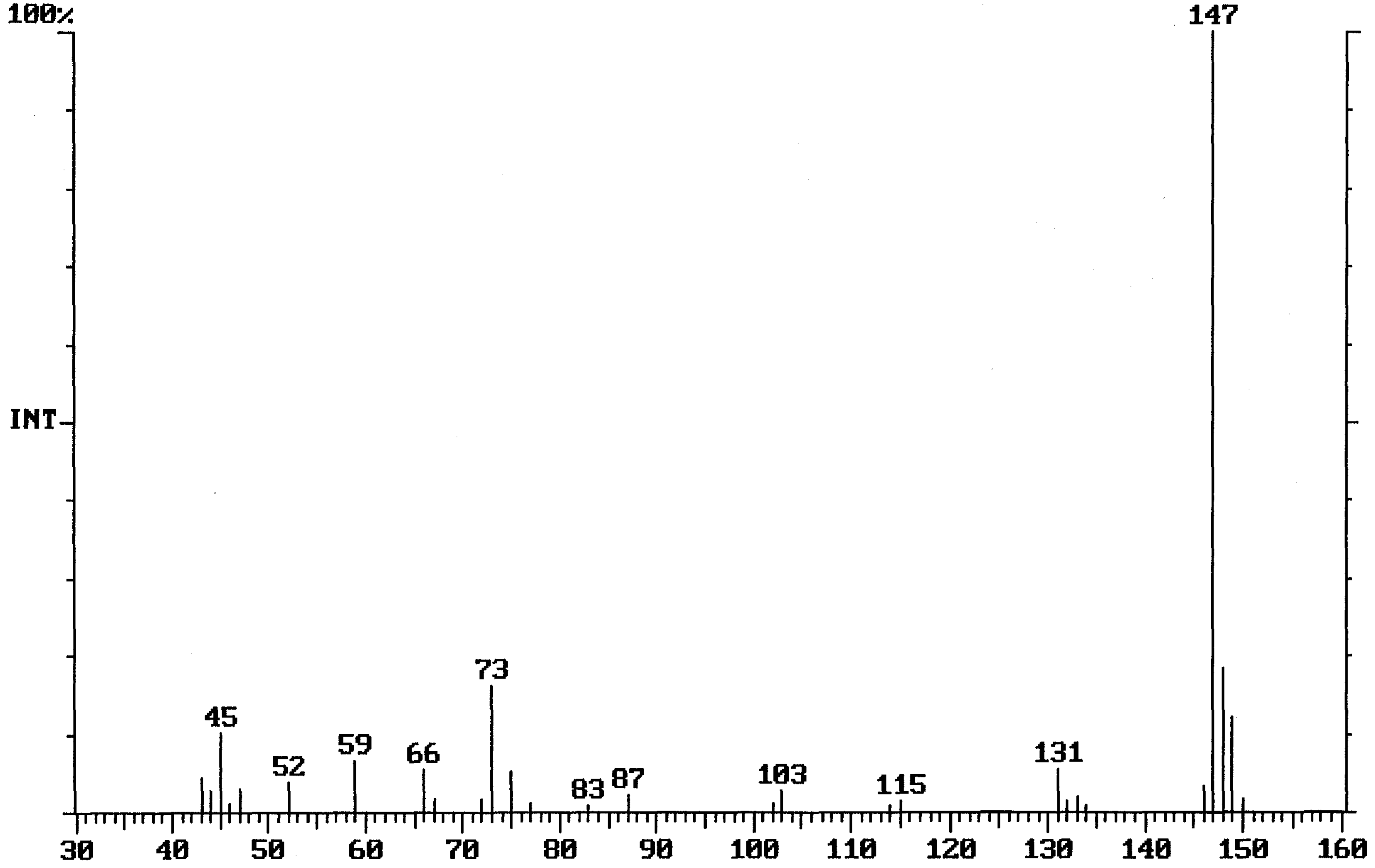
$$C_2H_4^{+\cdot} \rightarrow C_2H_3^+ + H^{\cdot}$$

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2$$

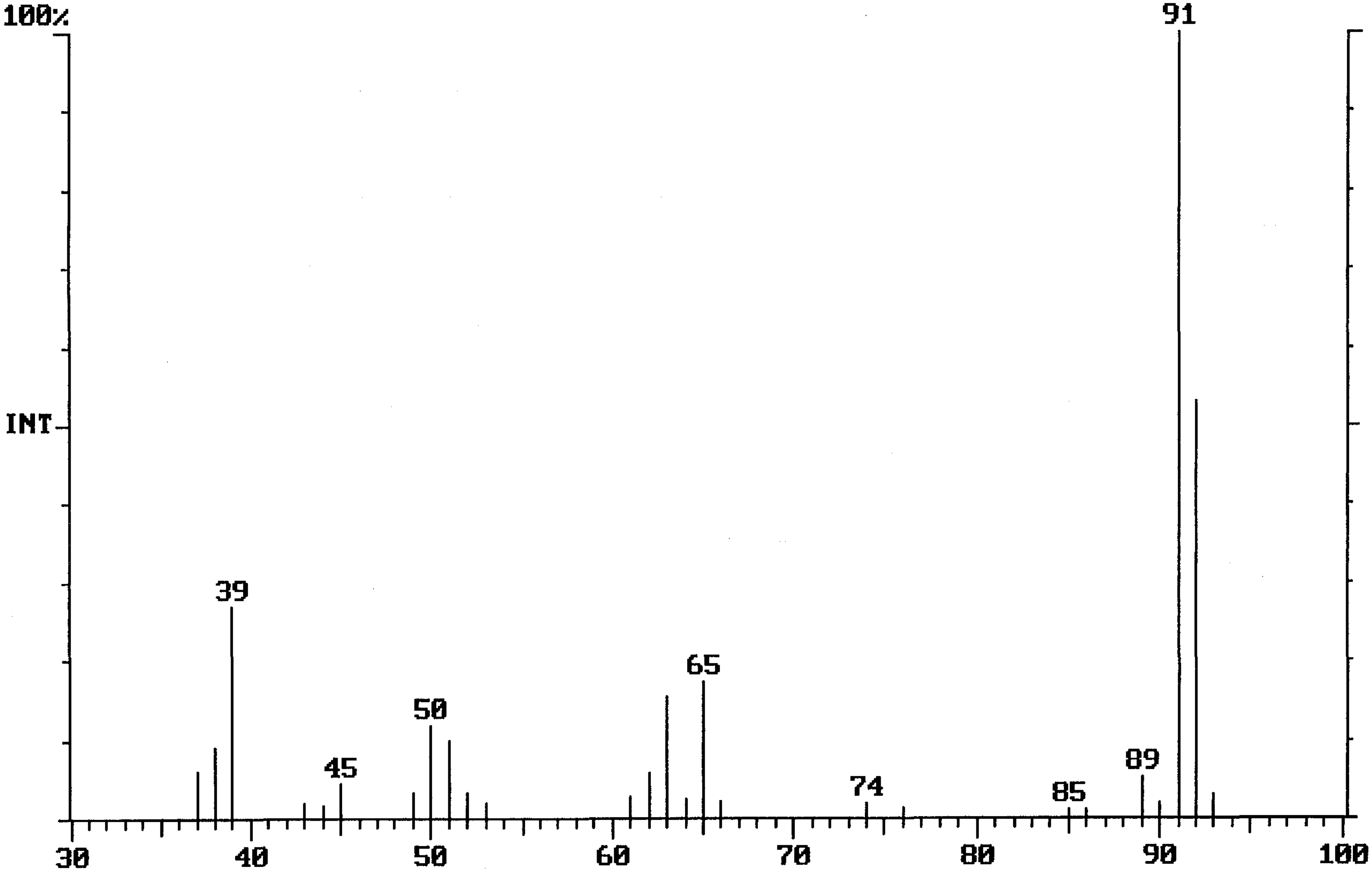
Chromatogram Plot File: C:\ITMS\HMDS2 Date: Apr-12-1994 12:35:06
Comment: INTEL PURE HMDS, 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5
Scan No: 1 Retention Time: 0:01 RIC: 1643 Mass Range: 36 - 91
Plotted: 1 to 1200 Range: 1 to 1800 100% = 9391757



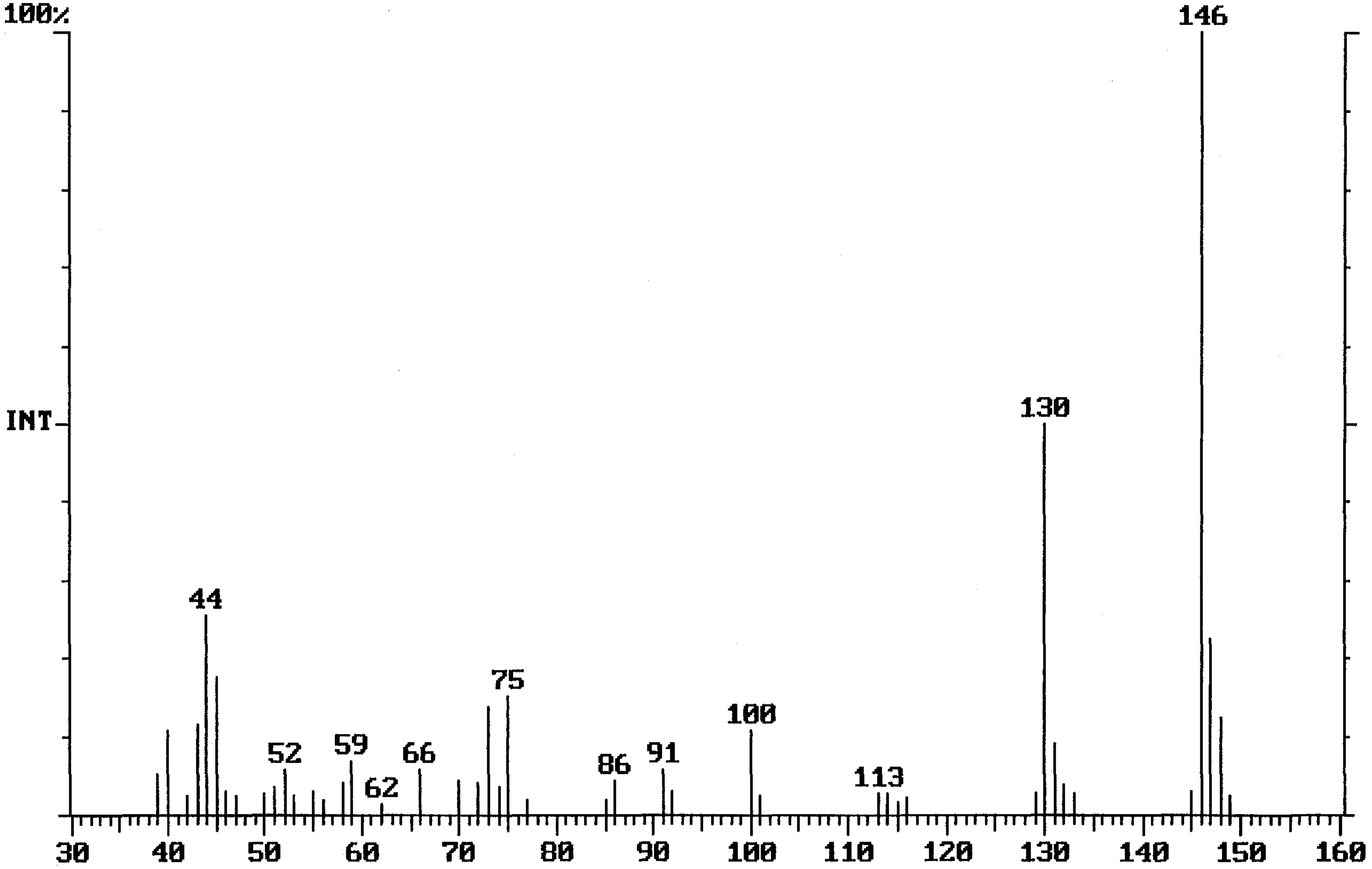
```
Spectrum Plot                       File: C:\ITMS\HMDS2   Date: Apr-12-1994  12:35:06
Comment: INTEL PURE HMDS, 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5
Scan No: 113       Retention Time: 1:54      RIC: 67353    Mass Range: 43 - 150
# Peaks: 28  Base Pk: 147  Ioniz: unknown  Int: 31434       100.00% = 31434
```



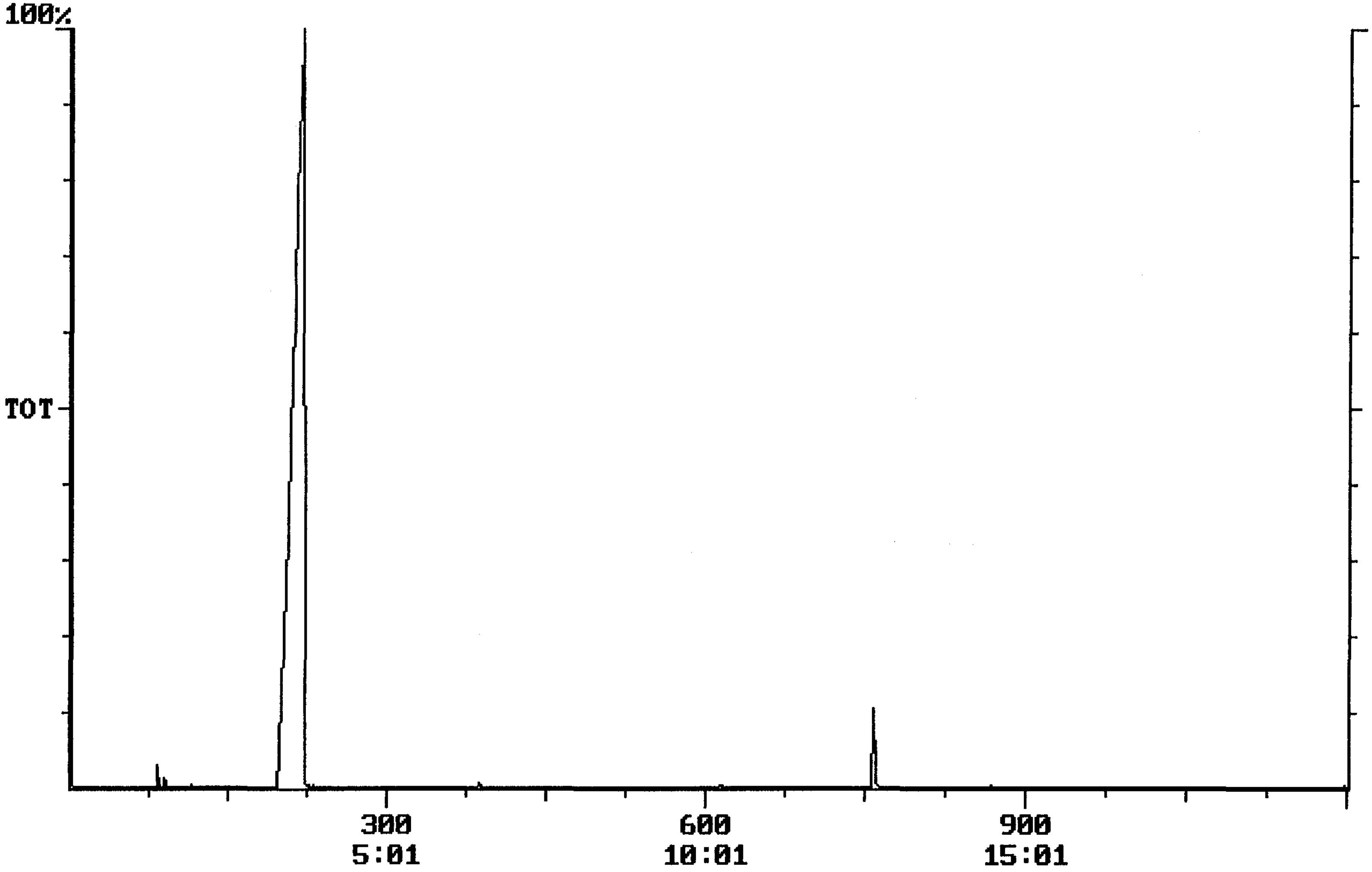
```
Spectrum Plot                     File: C:\ITMS\HMDS2   Date: Apr-12-1994  12:35:06
Comment: INTEL PURE HMDS, 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5
Scan No: 163      Retention Time: 2:44     RIC: 64784    Mass Range: 37 - 93
# Peaks: 26  Base Pk: 91   Ioniz: unknown  Int: 22176      100.00% = 22176
```



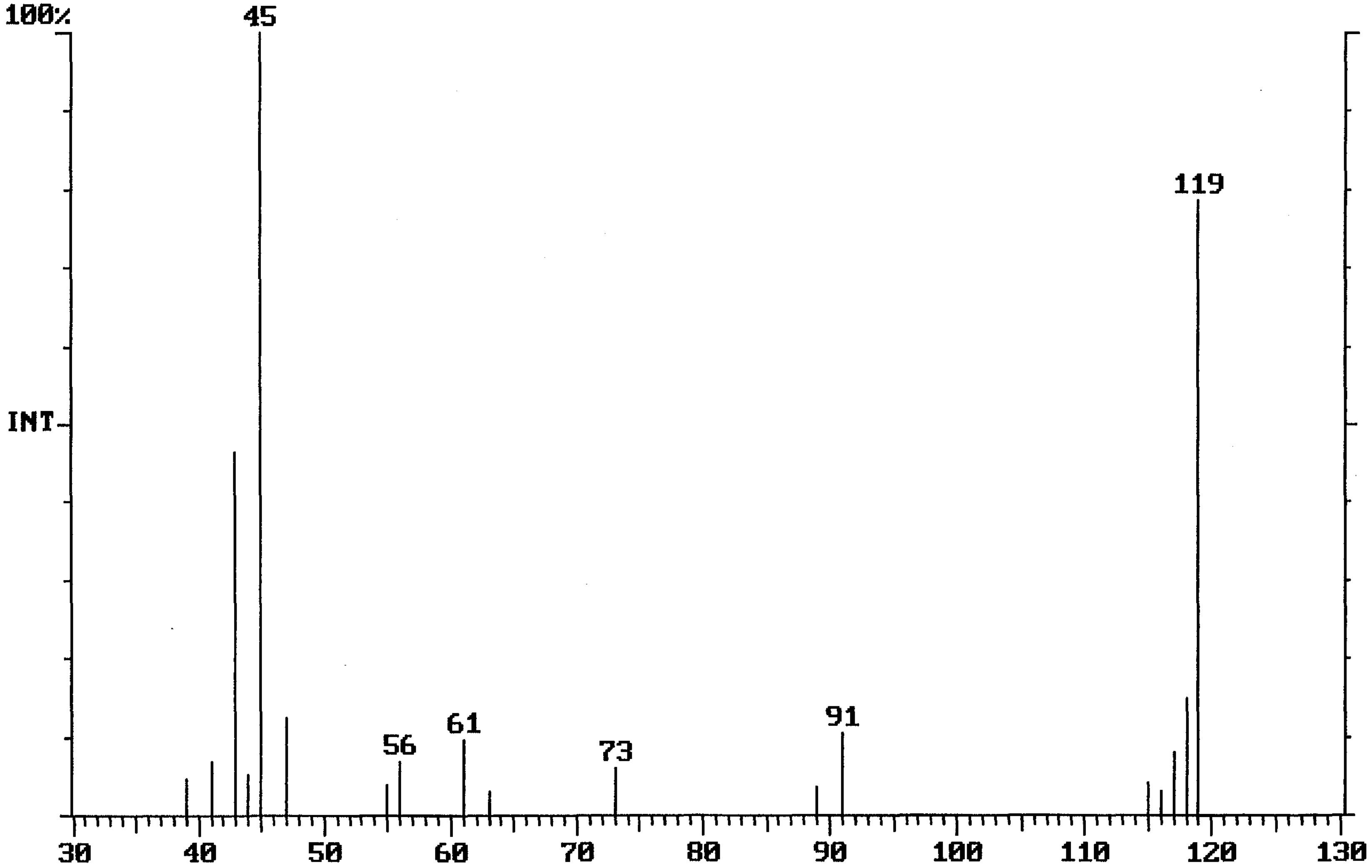
Spectrum Plot File: C:\ITMS\HMDS2 Date: Apr-12-1994 12:35:06
Comment: INTEL PURE HMDS, 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5
Scan No: 176 Retention Time: 2:57 RIC: 3402 Mass Range: 39 - 149
Peaks: 44 Base Pk: 146 Ioniz: unknown Int: 847 100.00% = 847



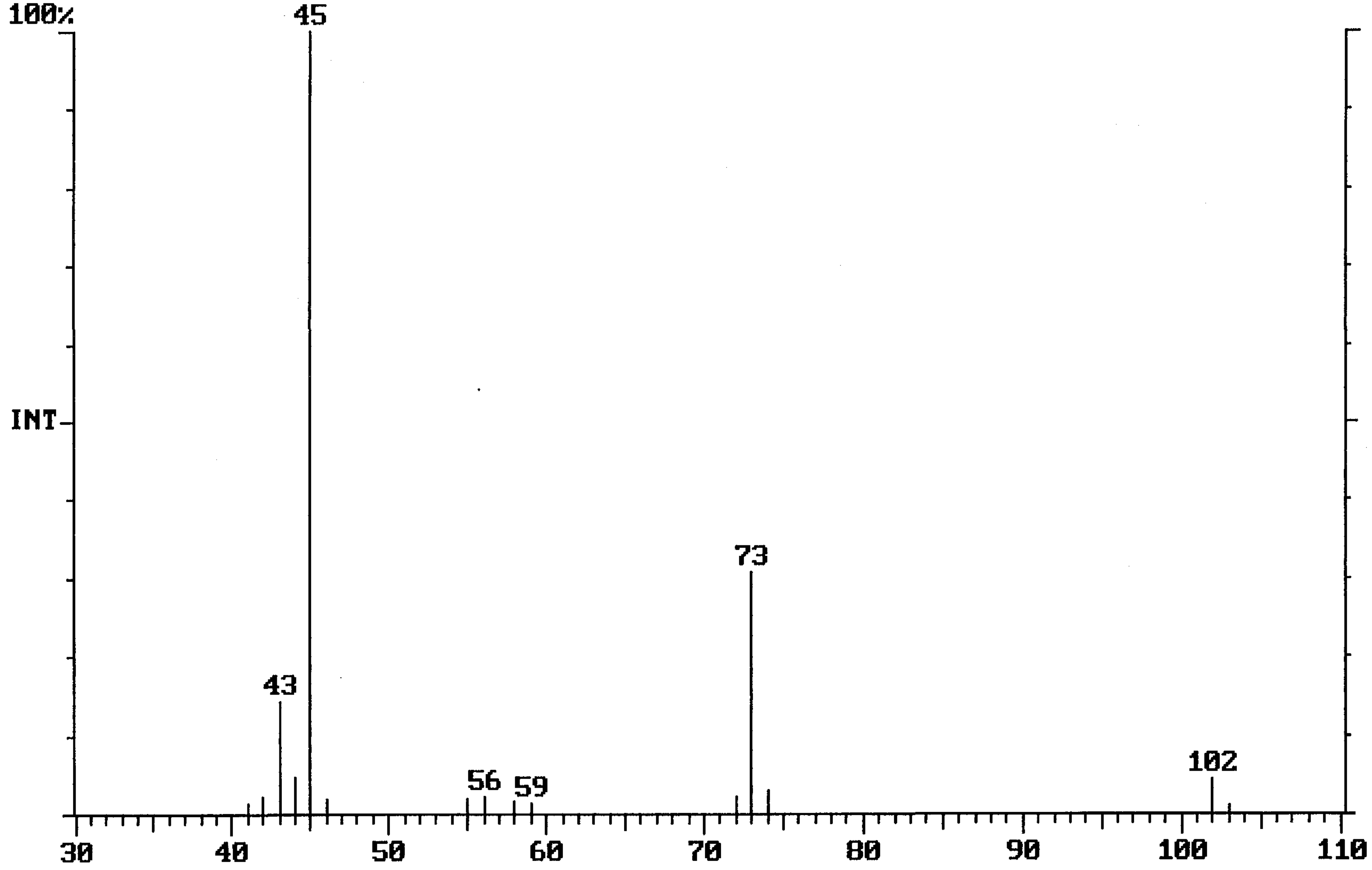
Chromatogram Plot File: C:\ITMS\ Date: Apr-12-1994 13:31:24
Comment: INTEL RESIST 50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 1 Retention Time: 0:01 RIC: 774 Mass Range: 36 - 207
Plotted: 1 to 1200 Range: 1 to 1210 100% = 4476445



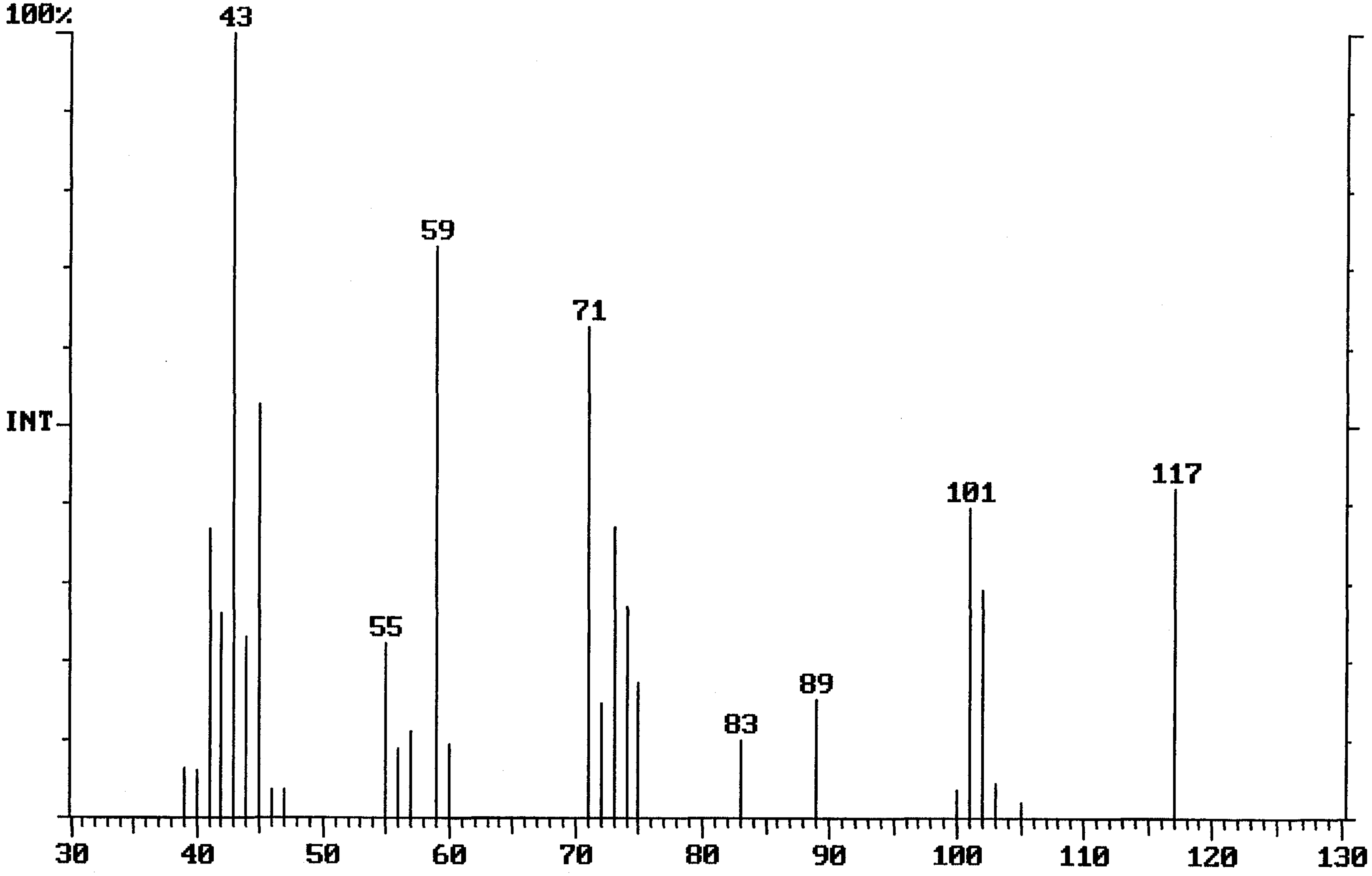
```
Spectrum Plot                    File: C:\ITMS\         Date: Apr-12-1994   13:31:24
Comment: INTEL               RESIST 50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 199      Retention Time: 3:20      RIC: 308611    Mass Range: 39 - 119
# Peaks: 18  Base Pk: 45    Ioniz: unknown   Int: 94795       100.00% = 94795
```



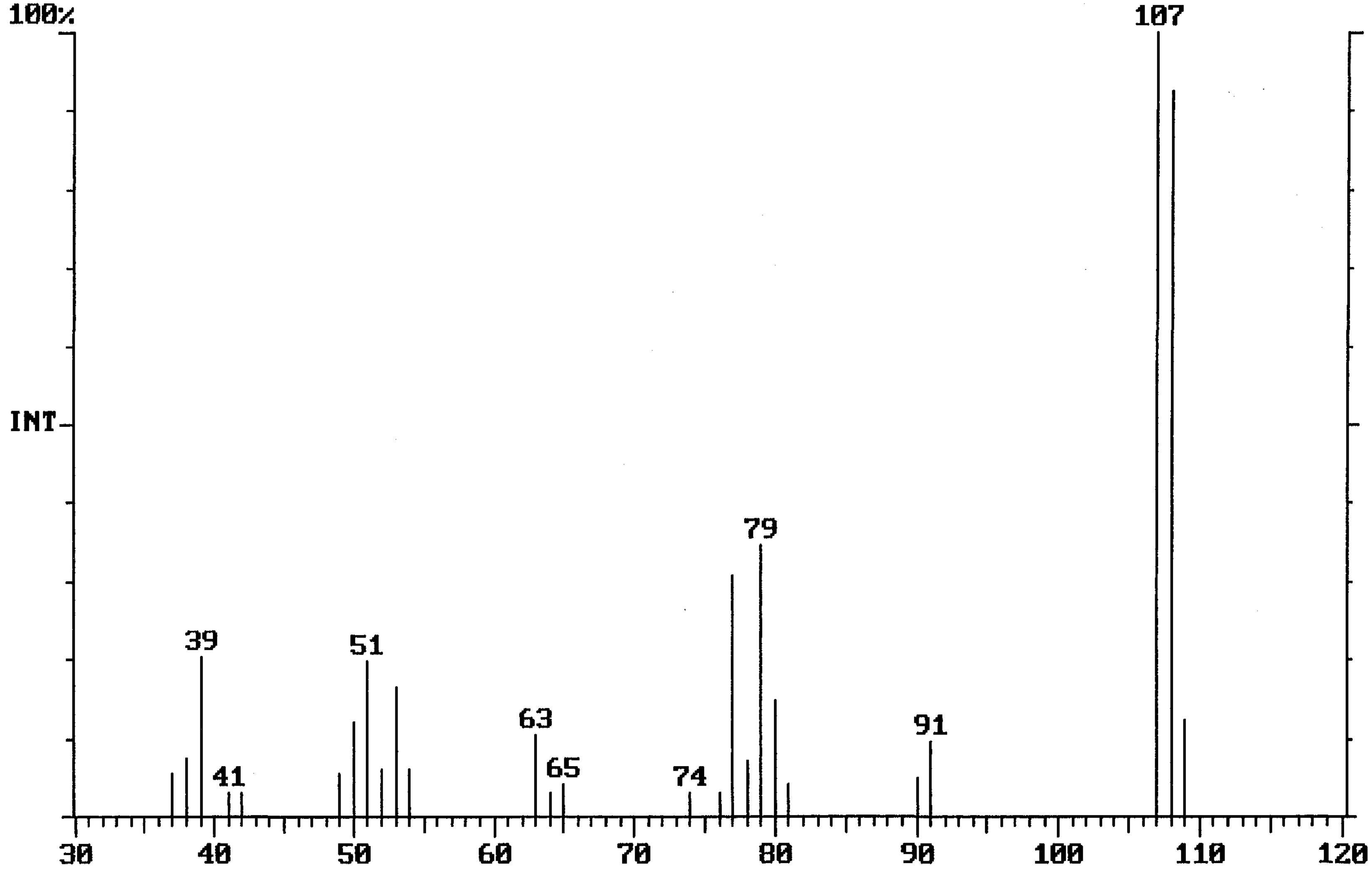
```
Spectrum Plot                    File: C:\ITMS\.        Date: Apr-12-1994   13:31:24
Comment: INTEL              RESIST 50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 389      Retention Time: 6:30     RIC: 21643     Mass Range: 41 - 103
# Peaks: 15   Base Pk: 45    Ioniz: unknown   Int: 12628       100.00% = 12628
```



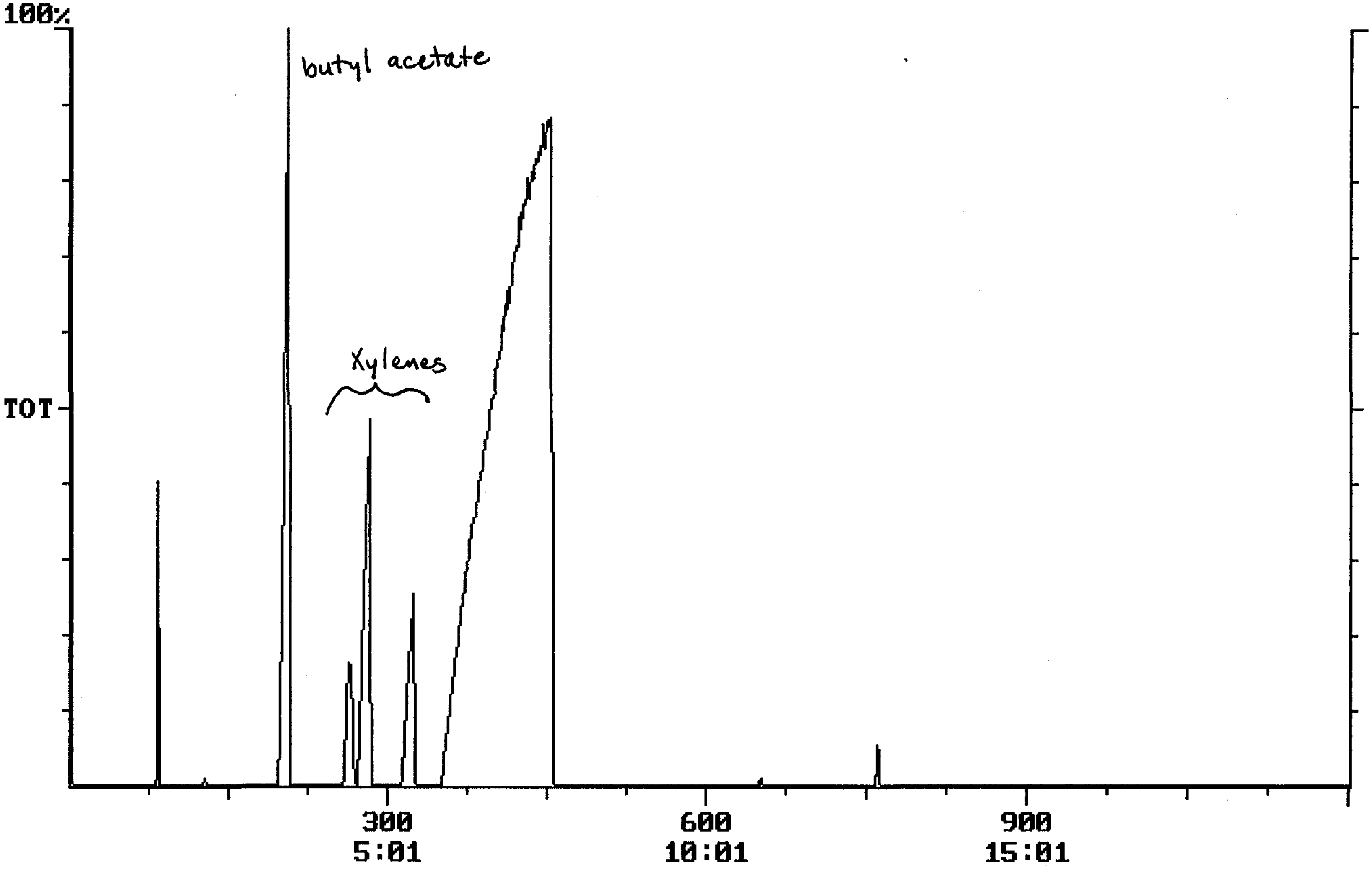
```
Spectrum Plot                      File: C:\ITMS\            Date: Apr-12-1994   13:31:24
Comment: INTEL                 RESIST 50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 615       Retention Time: 10:16     RIC: 17524     Mass Range: 39 - 117
# Peaks: 27  Base Pk: 43   Ionized: unknown  Int: 2556          100.00% = 2556
```



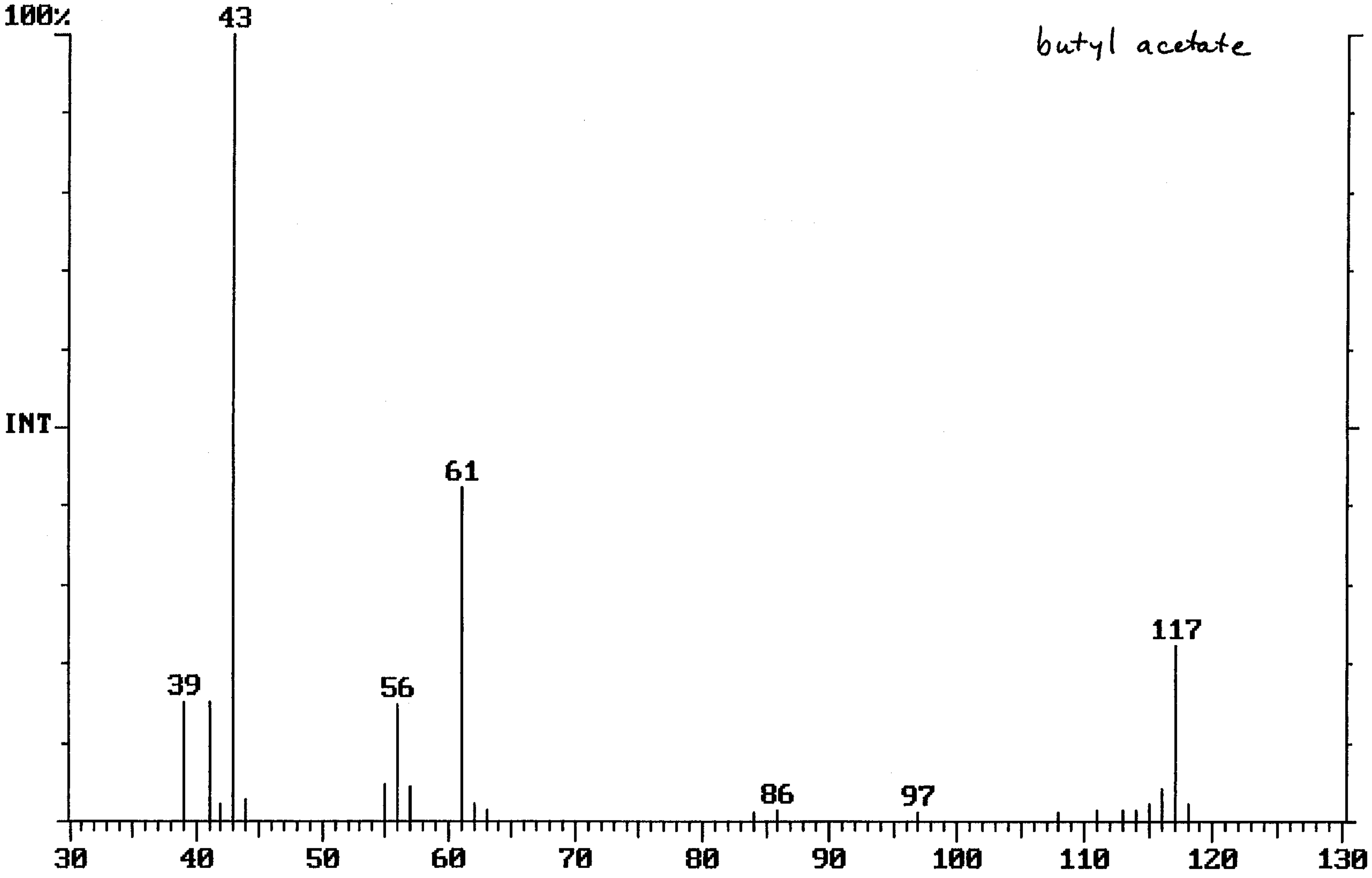
```
Spectrum Plot                    File: C:\ITMS\        Date: Apr-12-1994  13:31:24
Comment: INTEL              RESIST 50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 758      Retention Time: 12:39     RIC: 295921   Mass Range: 37 - 109
# Peaks: 26  Base Pk: 107  Ioniz: unknown  Int: 67543      100.00% = 67543
```



Chromatogram Plot File: C:\ITMS\ Date: Apr-13-1994 10:25:50
Comment: INTEL ,50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 1 Retention Time: 0:01 RIC: 769 Mass Range: 37 - 209
Plotted: 1 to 1200 Range: 1 to 1800 100% = 7989138

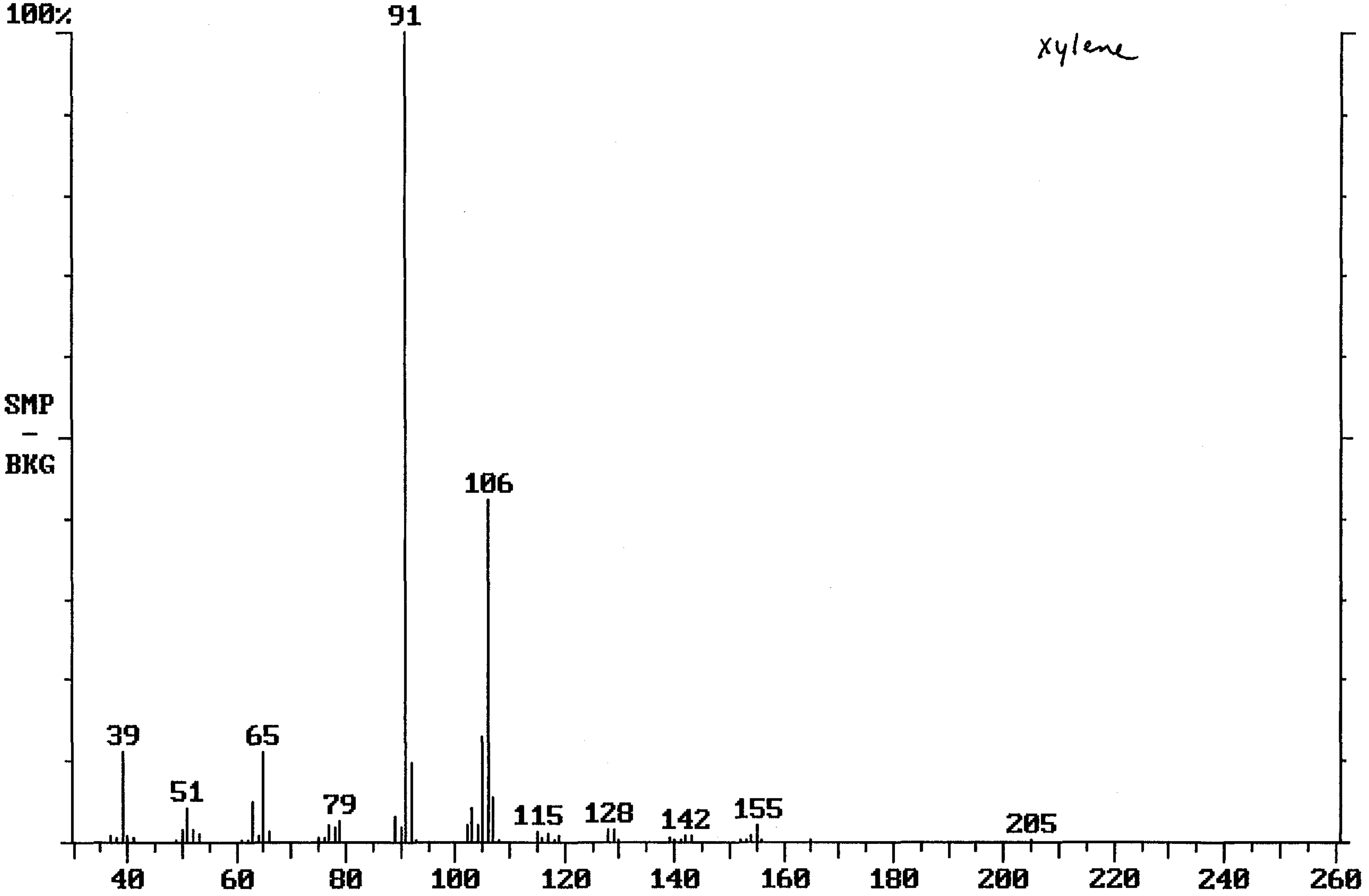


Spectrum Plot File: C:\ITMS\ Date: Apr-13-1994 10:25:50
Comment: INTEL ,50C 10 MIN 25C/MIN 250C 5 MIN
Scan No: 198 Retention Time: 3:19 RIC: 495802 Mass Range: 39 - 118
Peaks: 22 Base Pk: 43 Ioniz: unknown Int: 204854 100.00% = 204854



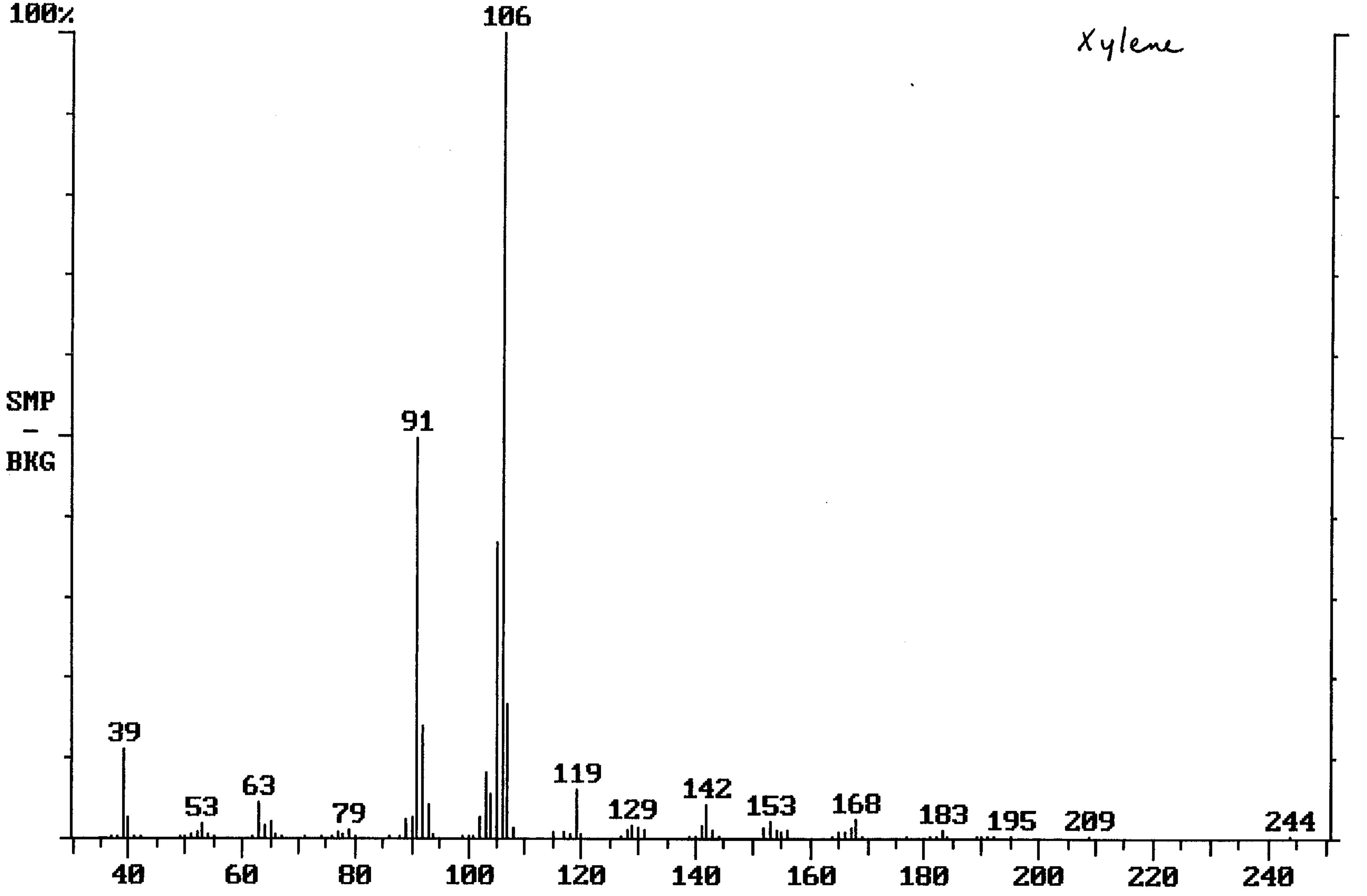
butyl acetate

Background Subtract File: C:\ITMS\ Date: Apr-13-1994 10:25:50
Comment: INTEL ,50C 10 MIN 25C/MIN 250C 5 MIN
Average of: 262 to 266 Minus: 245 to 249 100% = 482749



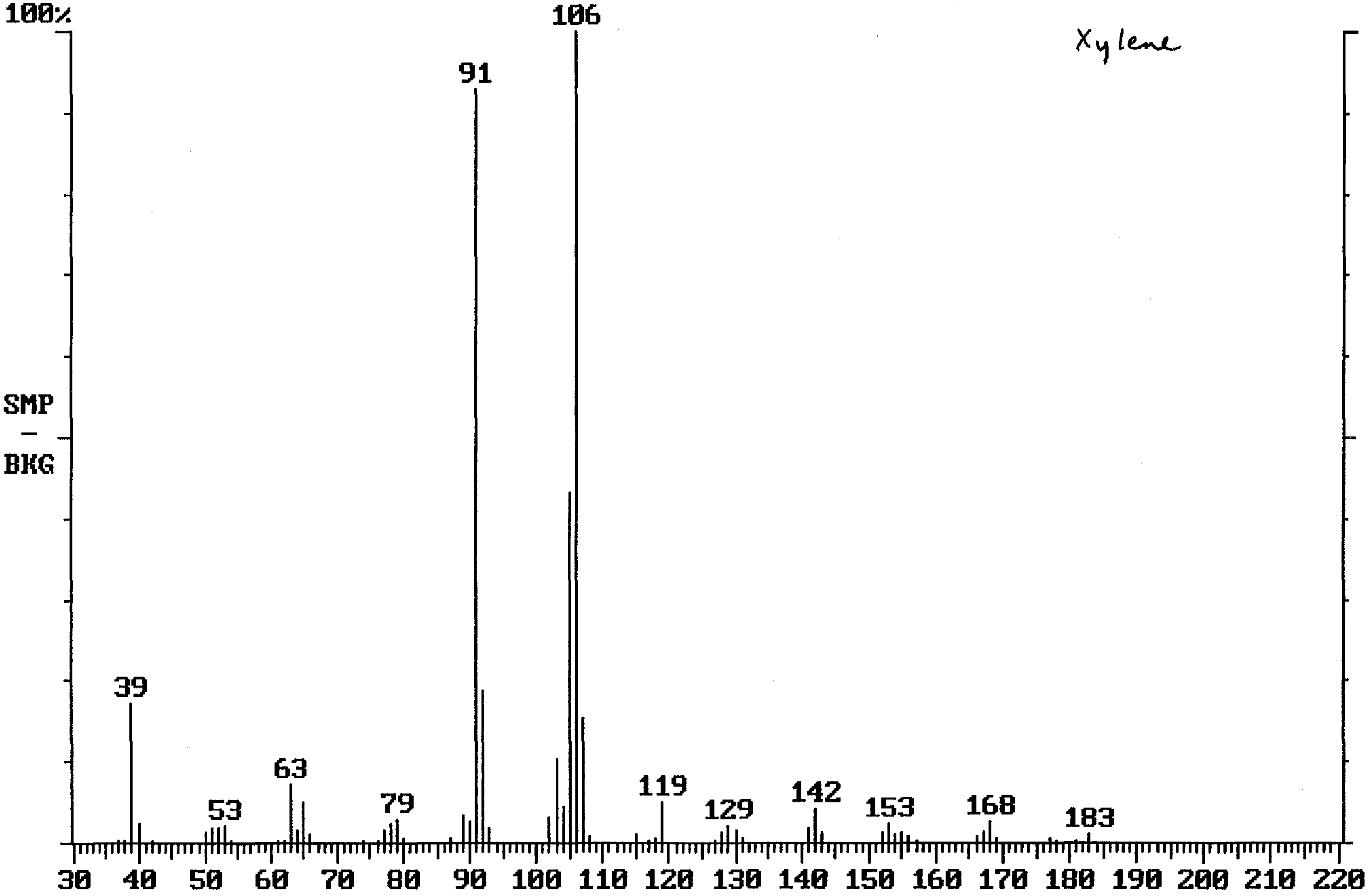
xylene

```
Background Subtract                  File: C:\ITMS\        Date: Apr-13-1994  10:25:50
Comment: INTEL                      50C 10 MIN 25C/MIN 250C 5 MIN
Average of: 282 to 286  Minus: 307 to 311                    100% = 824338
```



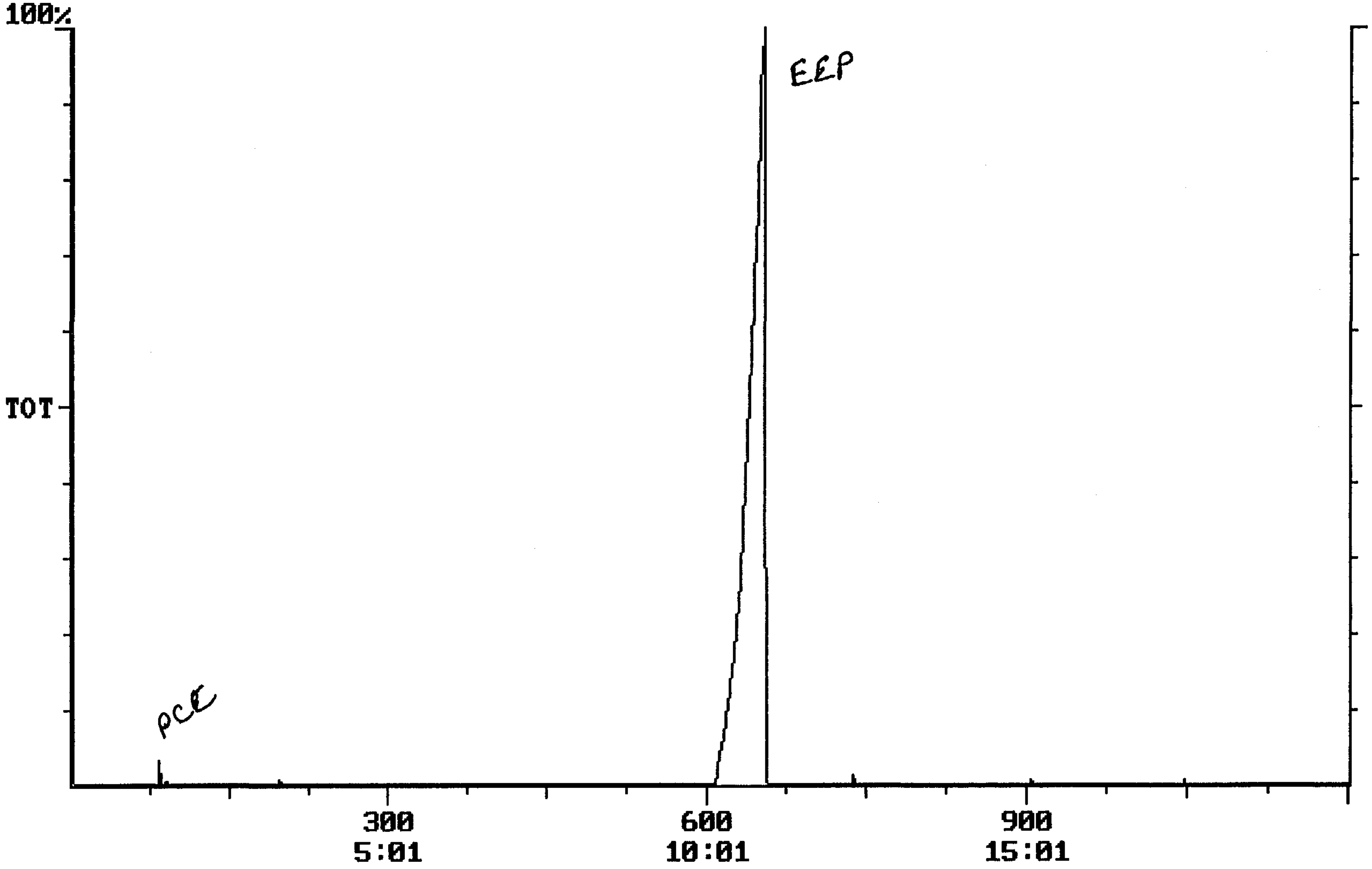
Xylene

Background Subtract File: C:\ITMS\ Date: Apr-13-1994 10:25:50
Comment: INTEL ,50C 10 MIN 25C/MIN 250C 5 MIN
Average of: 323 to 327 Minus: 345 to 349 100% = 304945

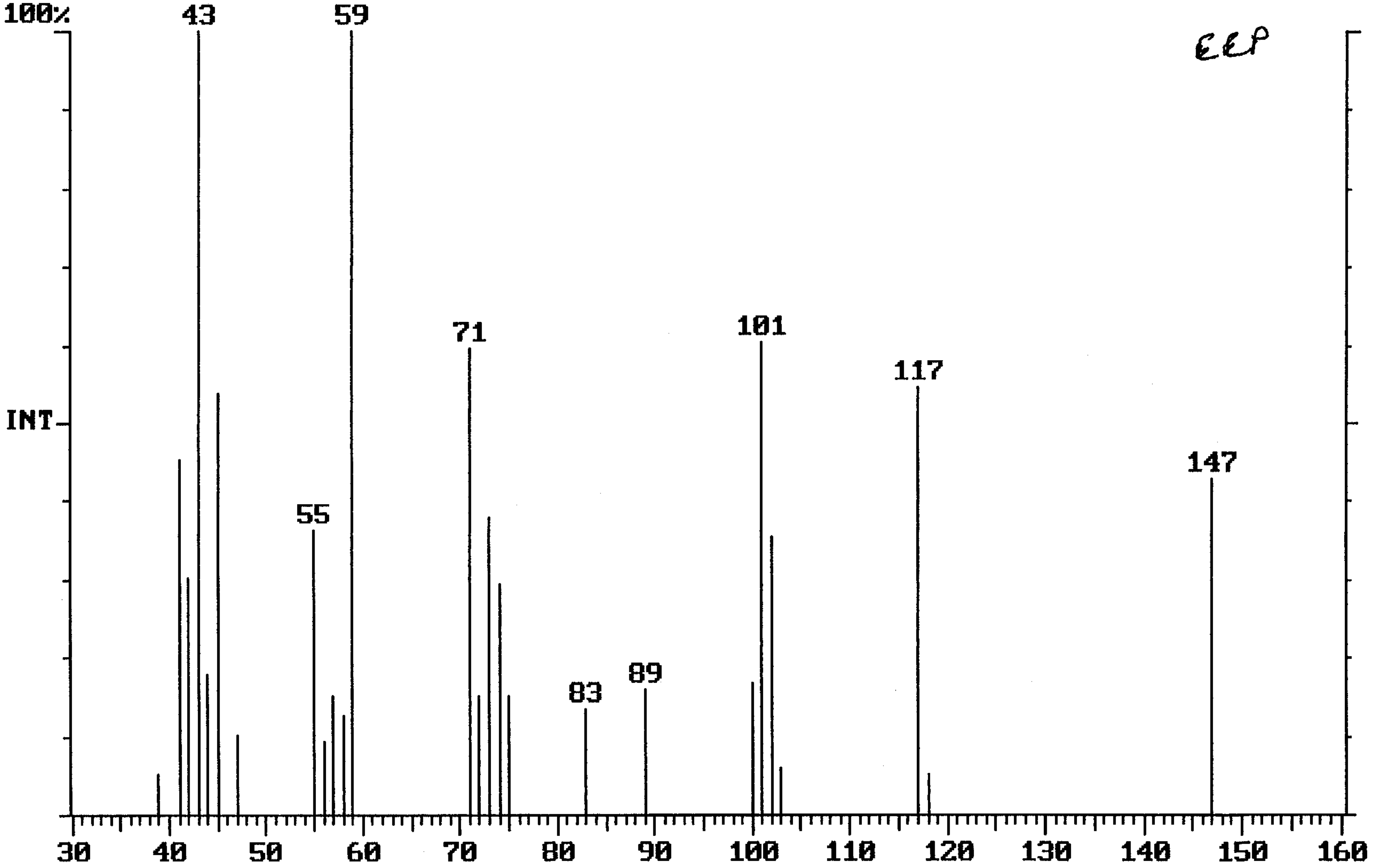


Xylene

```
Chromatogram Plot                File: C:\ITMS\         Date: Apr-12-1994  10:40:06
Comment: INTEL PURE     , 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5 M
Scan No: 1       Retention Time: 0:01      RIC: 586       Mass Range: 38 - 209
Plotted: 1 to 1200                       Range: 1 to 1722     100% = 3477232
```

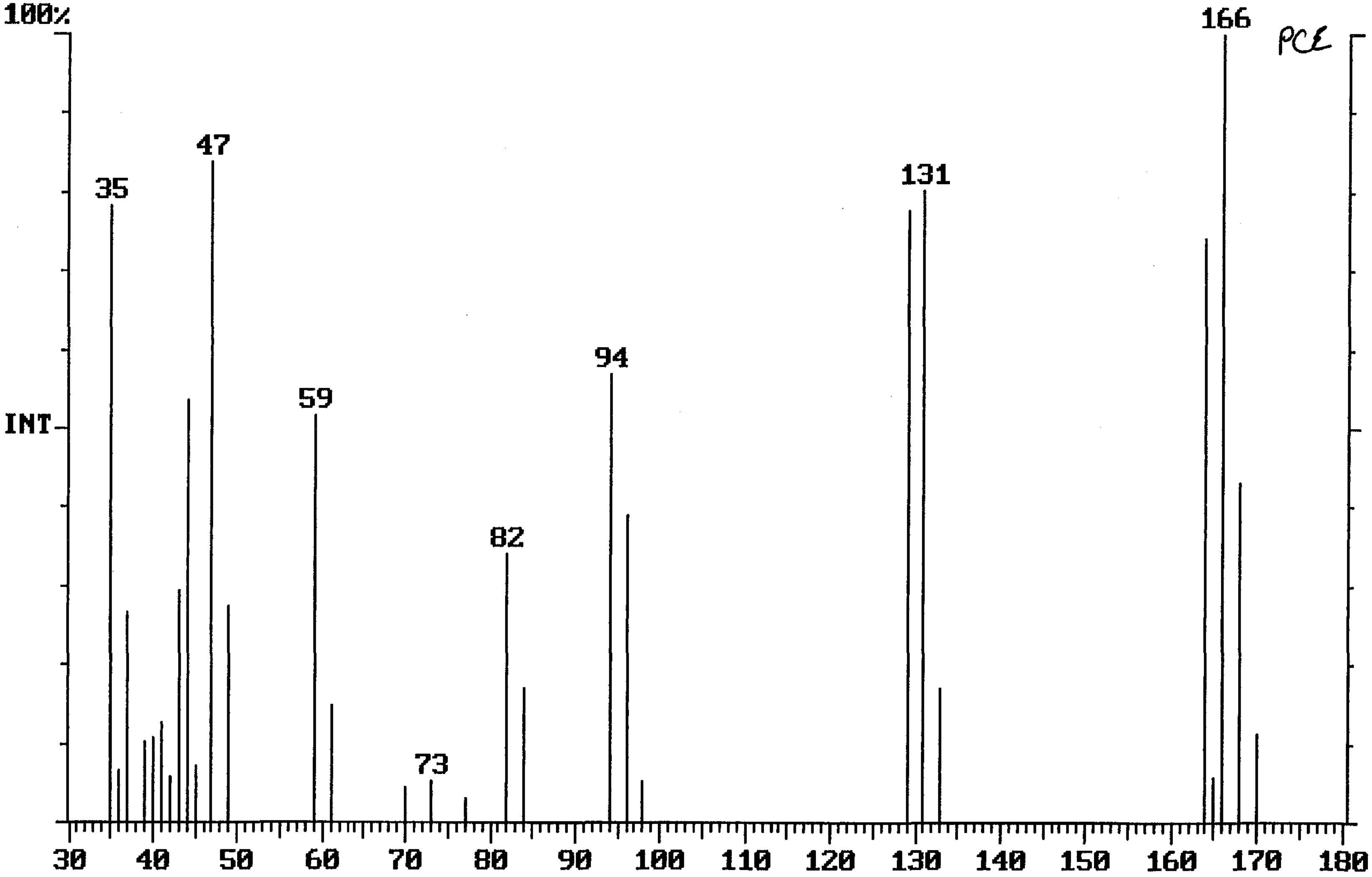


Spectrum Plot File: C:\ITMS\ Date: Apr-12-1994 10:40:06
Comment: INTEL PURE 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5 M
Scan No: 613 Retention Time: 10:14 RIC: 140858 Mass Range: 39 - 147
Peaks: 26 Base Pk: 43 Ioniz: unknown Int: 16712 100.00% = 16712



EEP

```
Spectrum Plot                    File: C:\ITMS\.        Date: Apr-12-1994  10:40:06
Comment: INTEL PURE    , 2 UL INJ,DESORB 100C,50C 10 MIN 25C/MIN 250C 5 M
Scan No: 196      Retention Time: 3:17      RIC: 3392      Mass Range: 35 - 170
# Peaks: 30  Base Pk: 166  Ioniz: unknown  Int: 341       100.00% = 341
```



PCE

APPENDIX E: CI/MS Data Taken at Intel (September, 1994)

All data in this section were taken during the three days the instrument and SNL personnel were on-site at Intel in Rio Rancho, NM (9/13-9/15/94).

Key for the data scans included:

File Name	Date	CI	EI	Scans	Conditions
ICI01	9/14/94	Y		0-200	Room air
				200-	SN 22, instrument slipped off tune during run, forepressure = .060
ICI02	9/14/94	Y		0-	SN 11, forepressure = .065
ICI05	9/15/94	Y		0-	SN 21, two peaks, then rising baseline
ICI06	9/15/94	Y		0-	SN22, SN21, SN13, SN11, HMDS,
ICI08	9/15/94	Y		0-	SN 22, startup of wafer batch, one complete cassette, foreP = .060
ICI09	9/15/94	Y		0-	SN 21, triplet peaks, transition between cassettes
IEI02	9/14/94		Y	0-500	Room air
				500-1000	methy ethyl ketone standard
				1000-1500	Room air
				1500-2000	methy ethyl ketone standard
				2000-2500	Room air
IEI03	9/14/94		Y	0-500	Room air
				500-1500	SN 11, foreP = .055
IEI04	9/14/94		Y	0-200	Room air
				200-	SN 11, foreP = .030
IEI05	9/14/94		Y	0-200	Room air
				200-	SN 11, foreP = .022
IEI06	9/14/94		Y	0-200	Room air
					SN 11, foreP = .035
IEI08	9/14/95		Y	0-200	Room air
				200-	SN 22

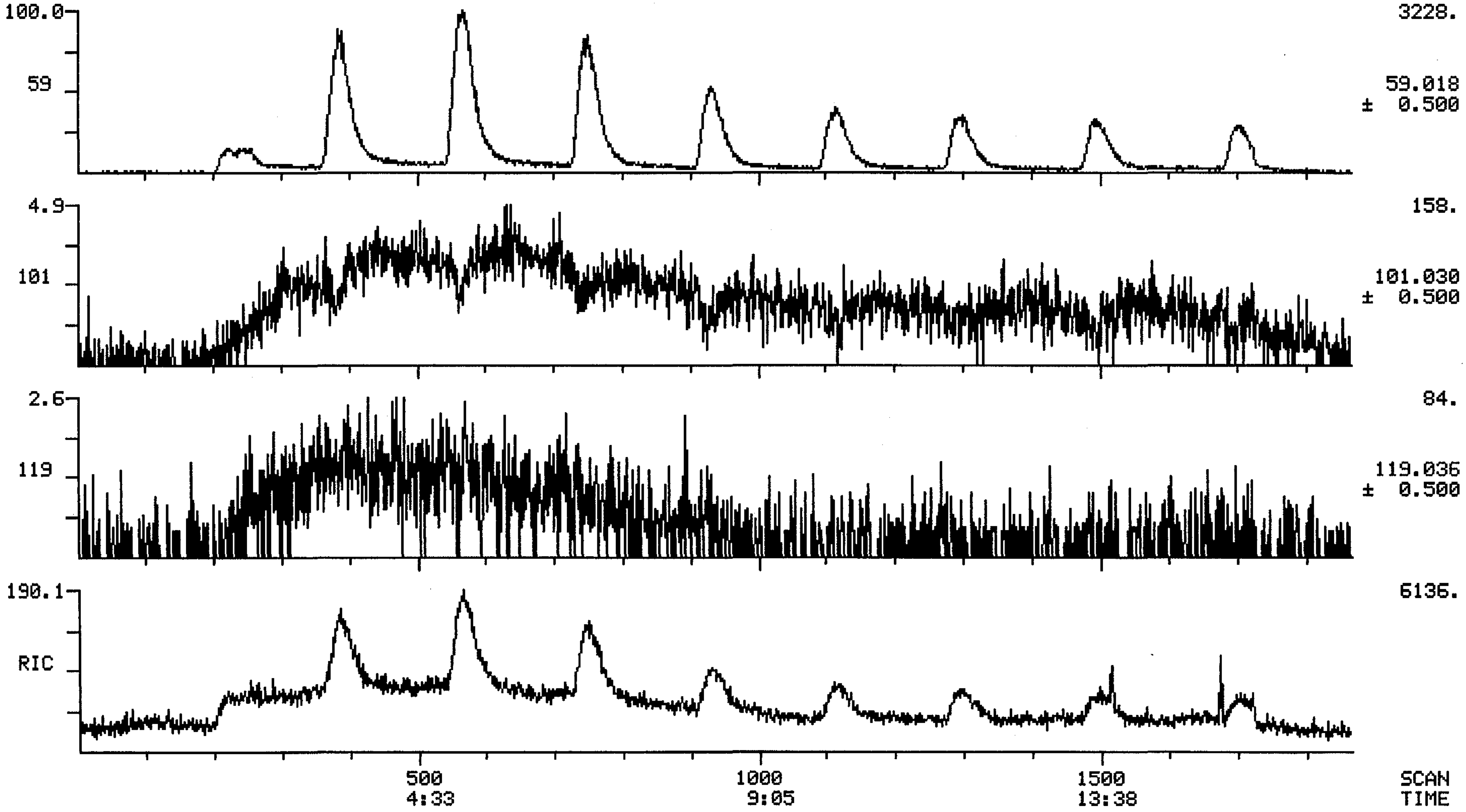
Key to lithography tools:

Tool ID	**Exhaust type**	**Chemicals**
SN 11	Combined coat & developer exhaust	cellusolve acetate HMDS Developer: tetramethyl ammonium hydroxide in DI H_2O
SN 13	Combined coat & developer exhaust	(instrument was out of order)
SN 21	Separated coat & developer exhaust	Ethyl lactate HMDS
SN 22	Combined coat & developer exhaust	Ethyl lactate HMDS Developer: tetramethyl ammonium hydroxide in DI H_2O

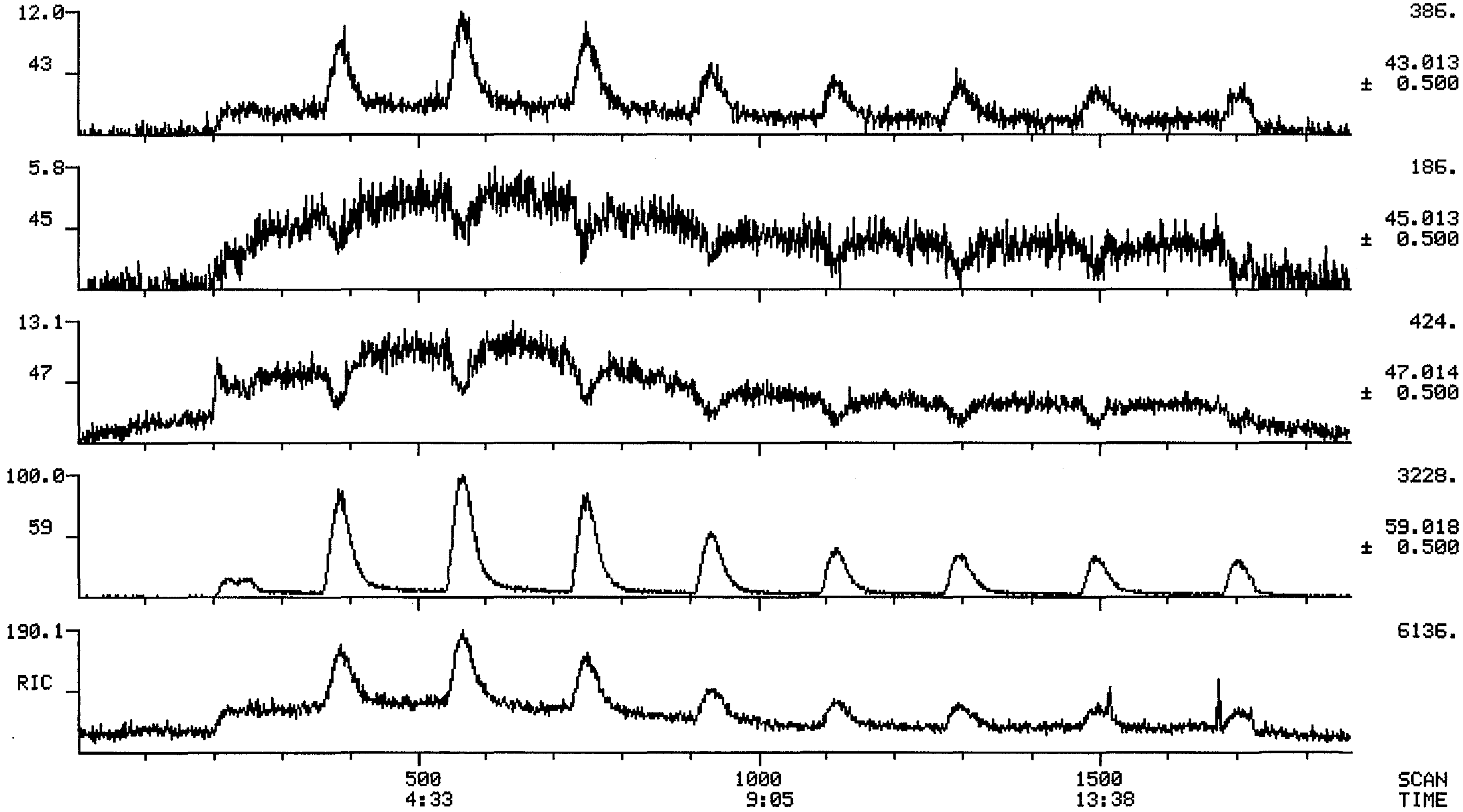
RIC+MASS CHROMATOGRAMS
09/14/94 16:34:00
SAMPLE: INTEL-SN 22
CONDS.: 180
RANGE: G 1,1865 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI01 #1
CALI: CALTAB #3

SCANS 1 TO 1865



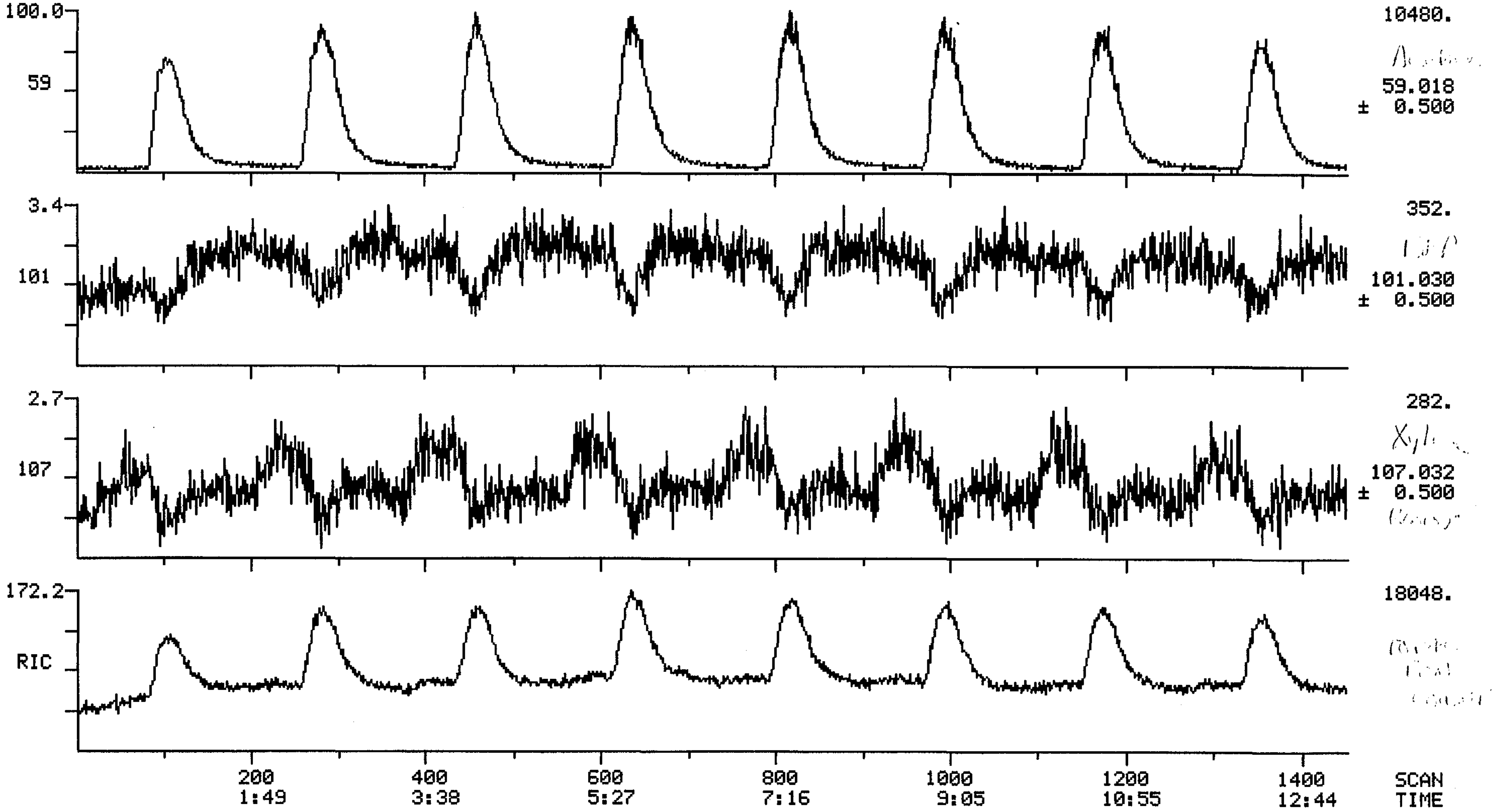
RIC+MASS CHROMATOGRAMS DATA: ICI01 #1 SCANS 1 TO 1865
09/14/94 16:34:00 CALI: CALTAB #3
SAMPLE: INTEL-SN 22
CONDS.: 180
RANGE: G 1,1865 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



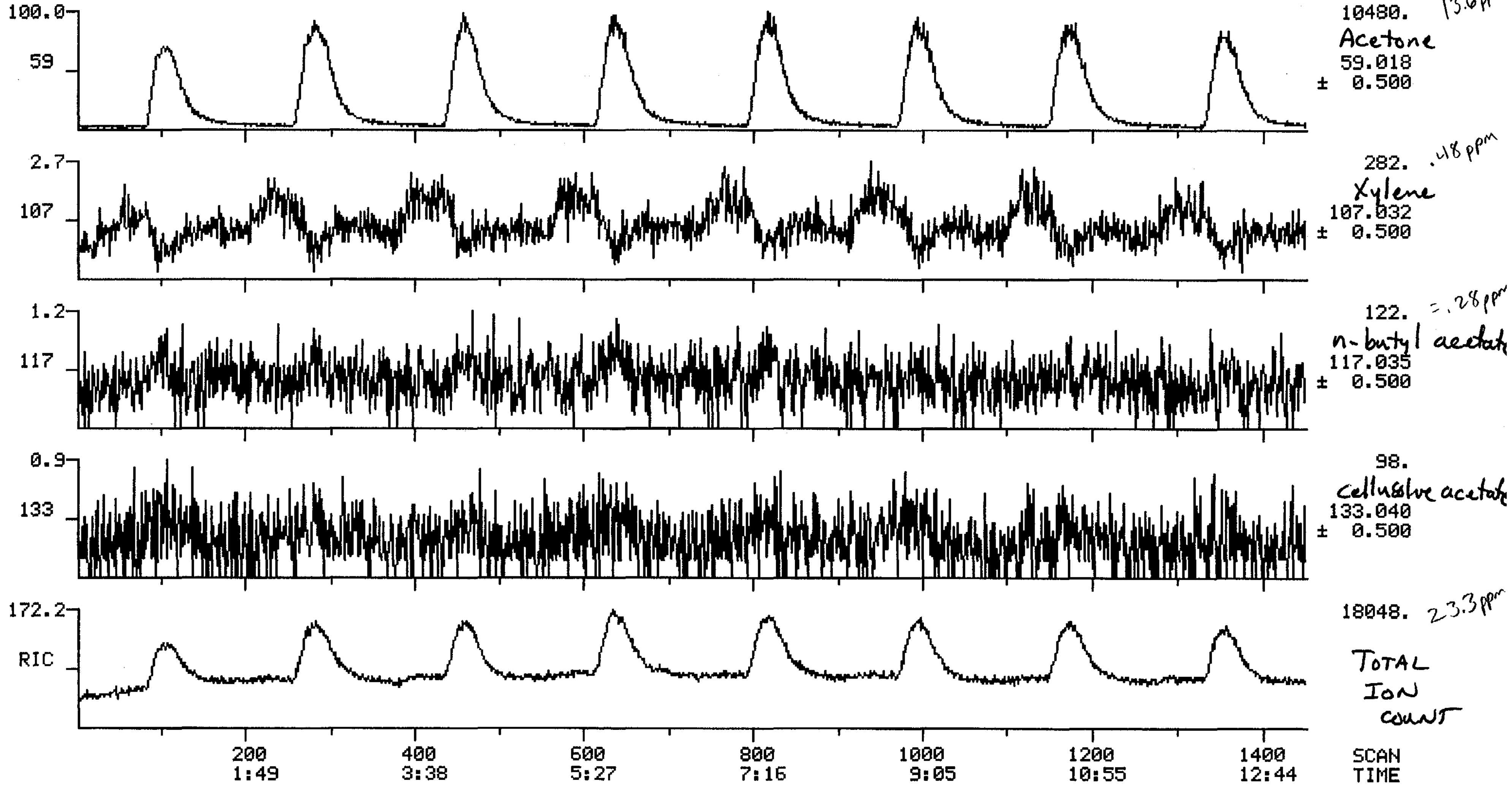
RIC+MASS CHROMATOGRAMS
09/14/94 16:59:00
SAMPLE: INTEL-SN 11
CONDS.: 120 CI
RANGE: G 1,1451 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI02 #1
CALI: CALTAB #3

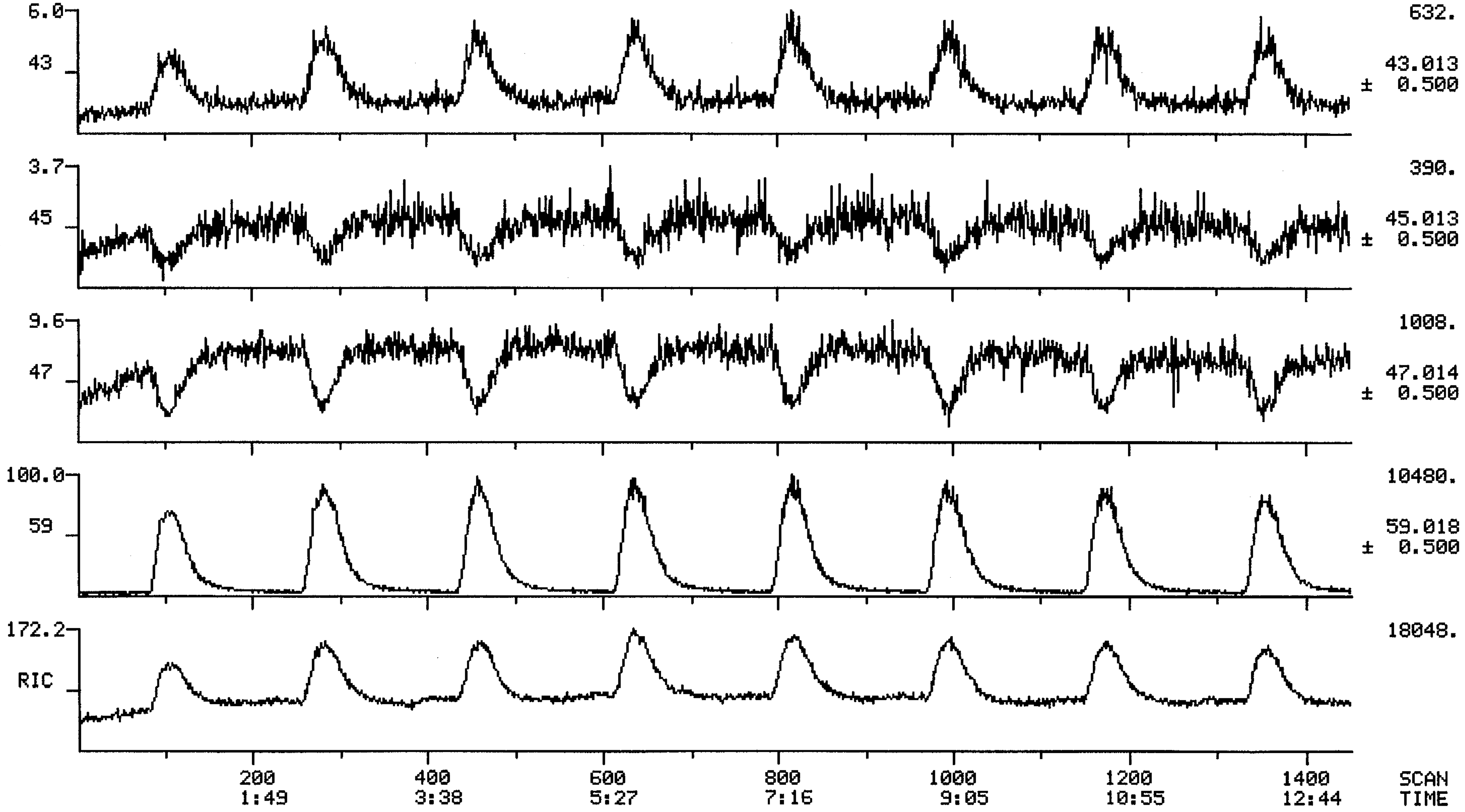
SCANS 1 TO 1451



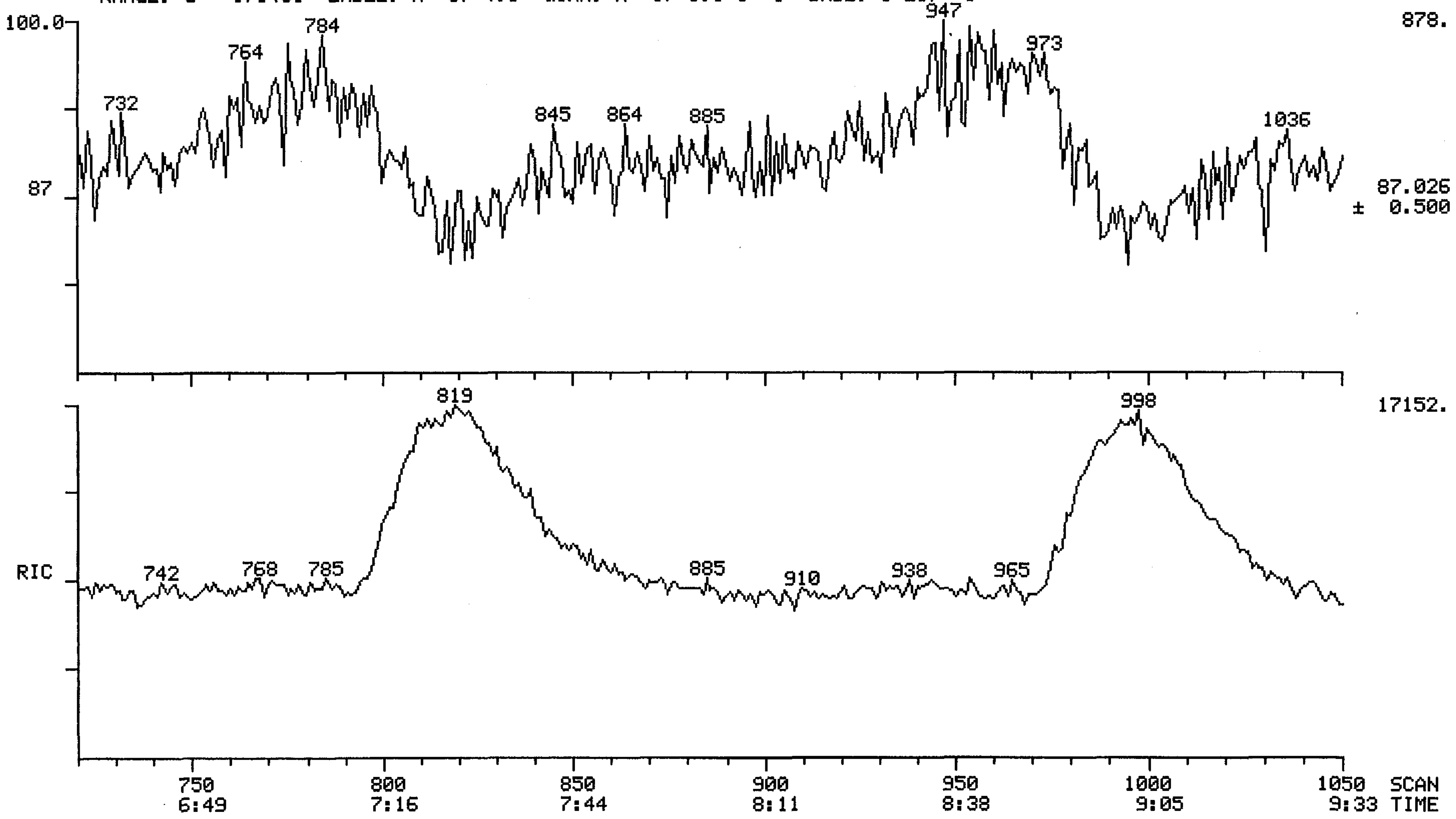
```
RIC+MASS CHROMATOGRAMS                      DATA: ICI02 #1          SCANS    1 TO 1451
09/14/94 16:59:00                           CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 120 CI
RANGE: G   1,1451   LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



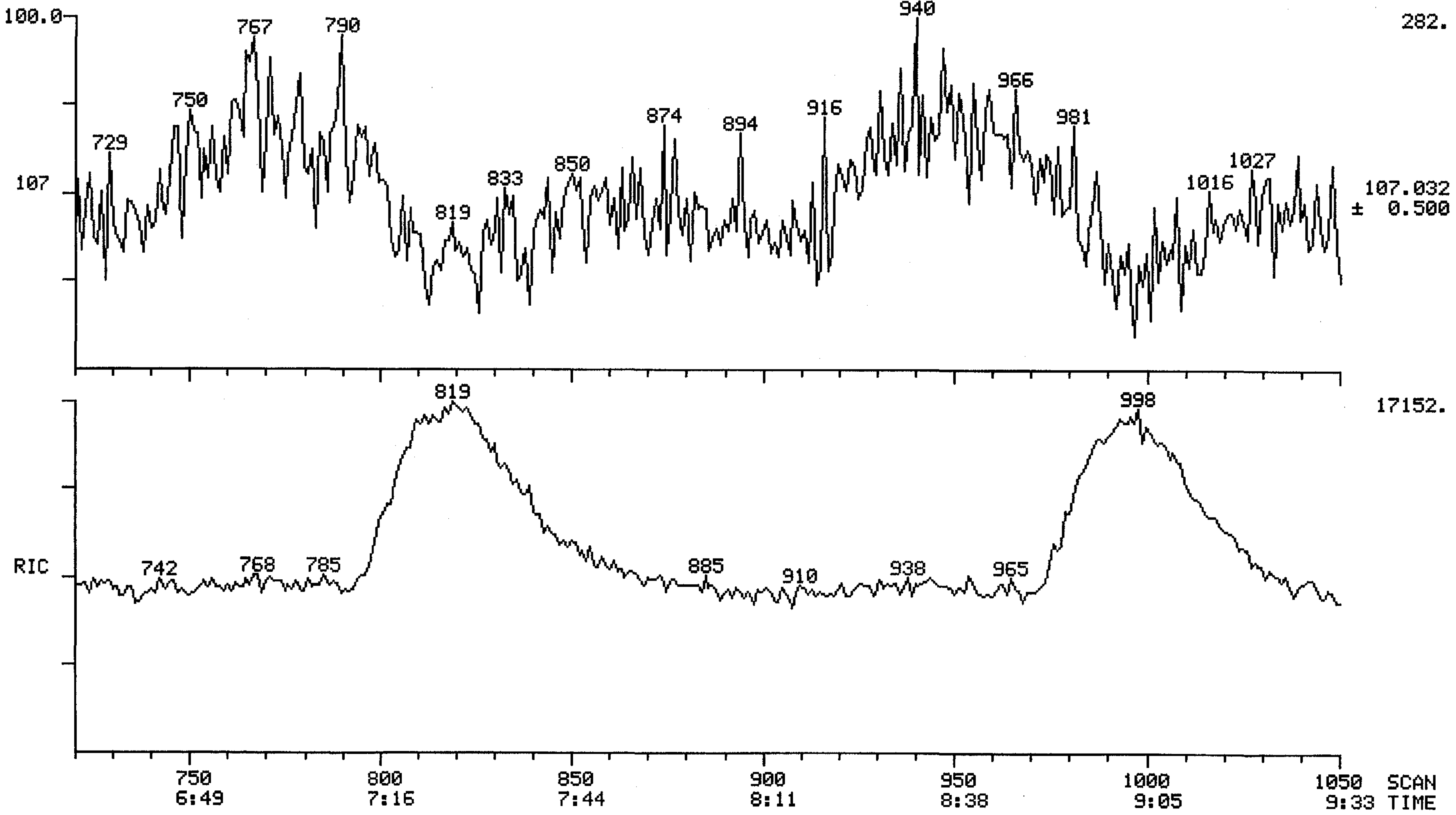
```
RIC+MASS CHROMATOGRAMS                          DATA: ICI02 #1         SCANS    1 TO 1451
09/14/94 16:59:00                               CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 120 CI
RANGE: G   1,1451  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



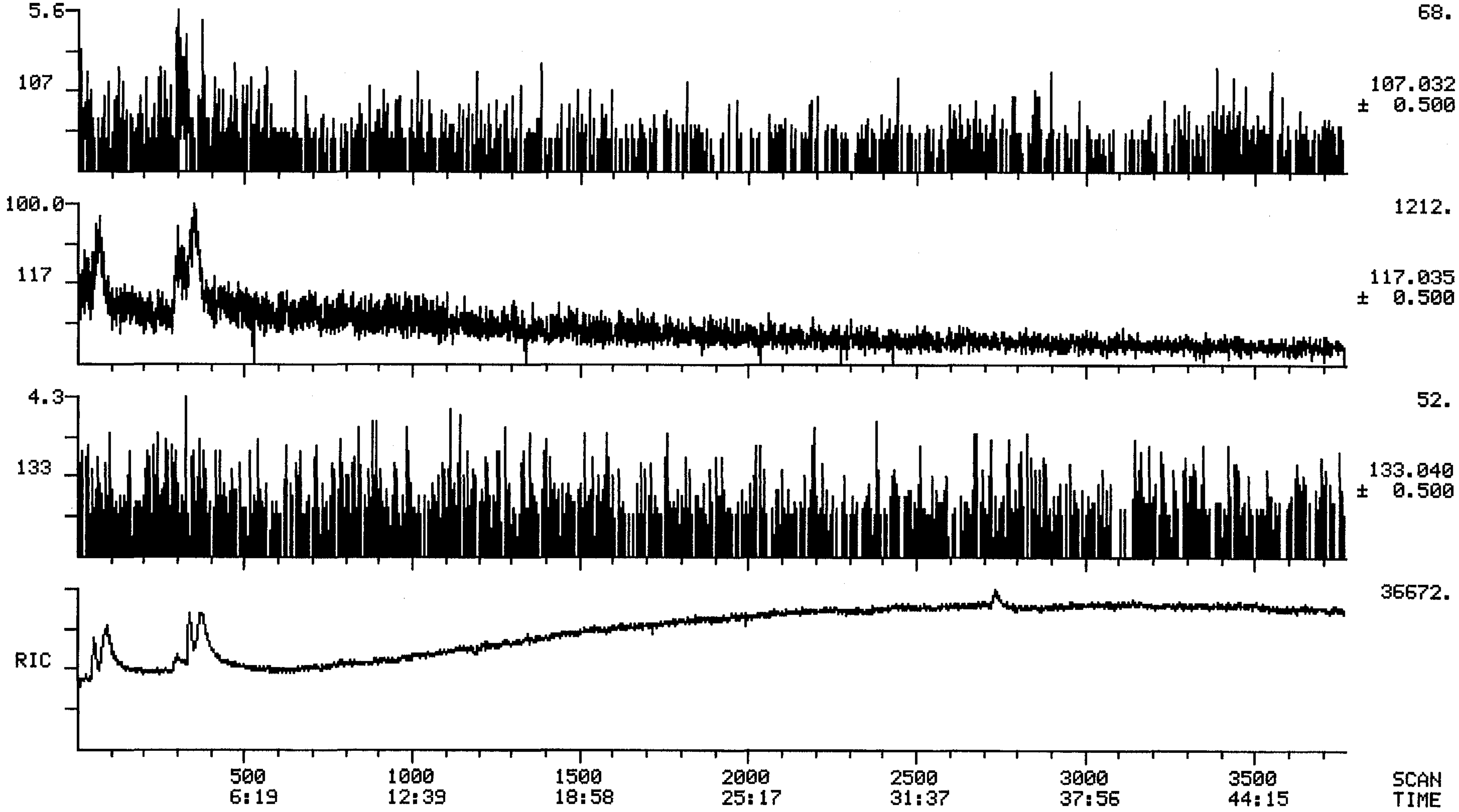
```
RIC+MASS CHROMATOGRAM              DATA: ICI02 #1        SCANS  720 TO 1050
09/14/94 16:59:00                  CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 120 CI
RANGE: G   1,1451  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



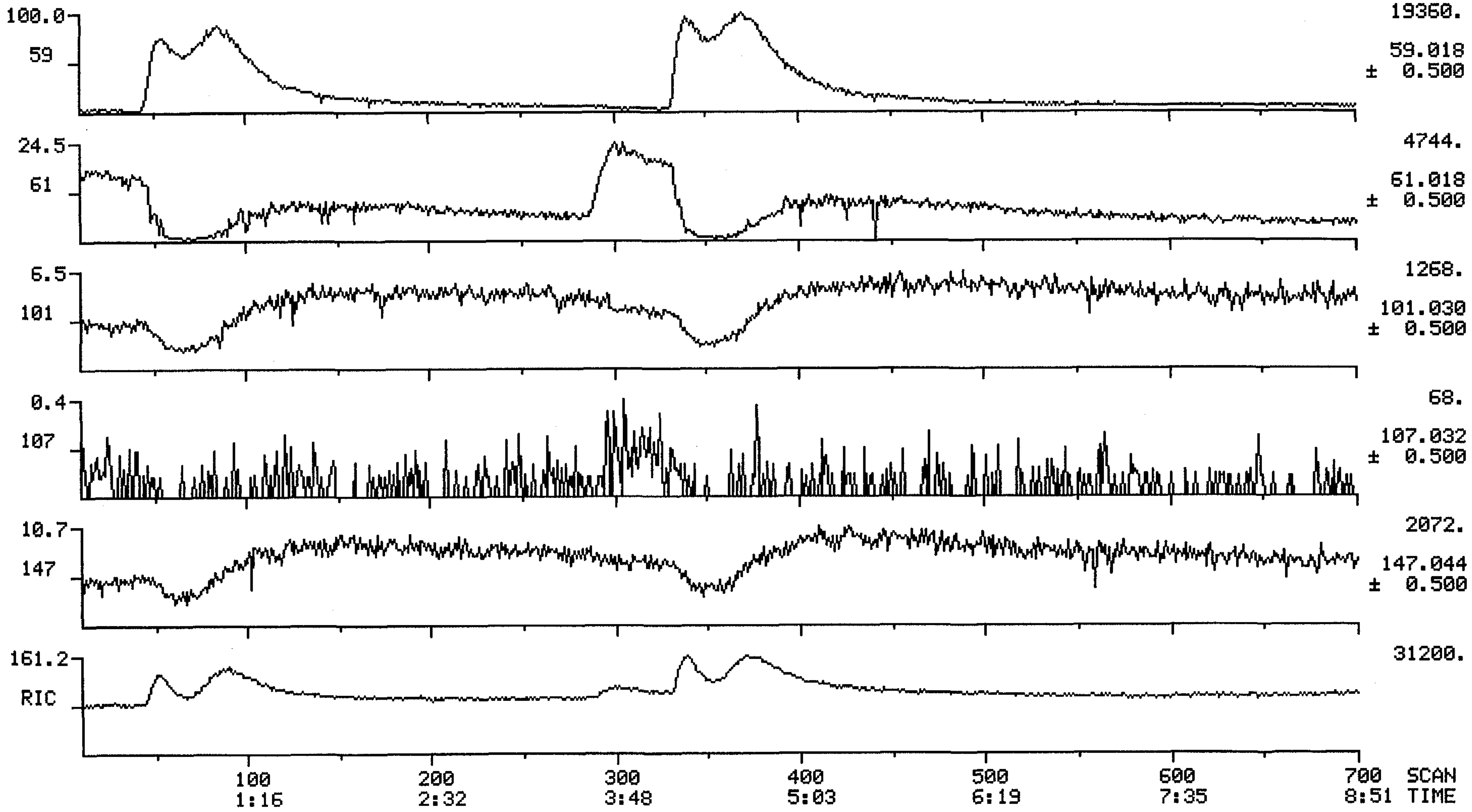
RIC+MASS CHROMATOGRAM DATA: ICI02 #1 SCANS 720 TO 1050
09/14/94 16:59:00 CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 120 CI
RANGE: G 1,1451 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



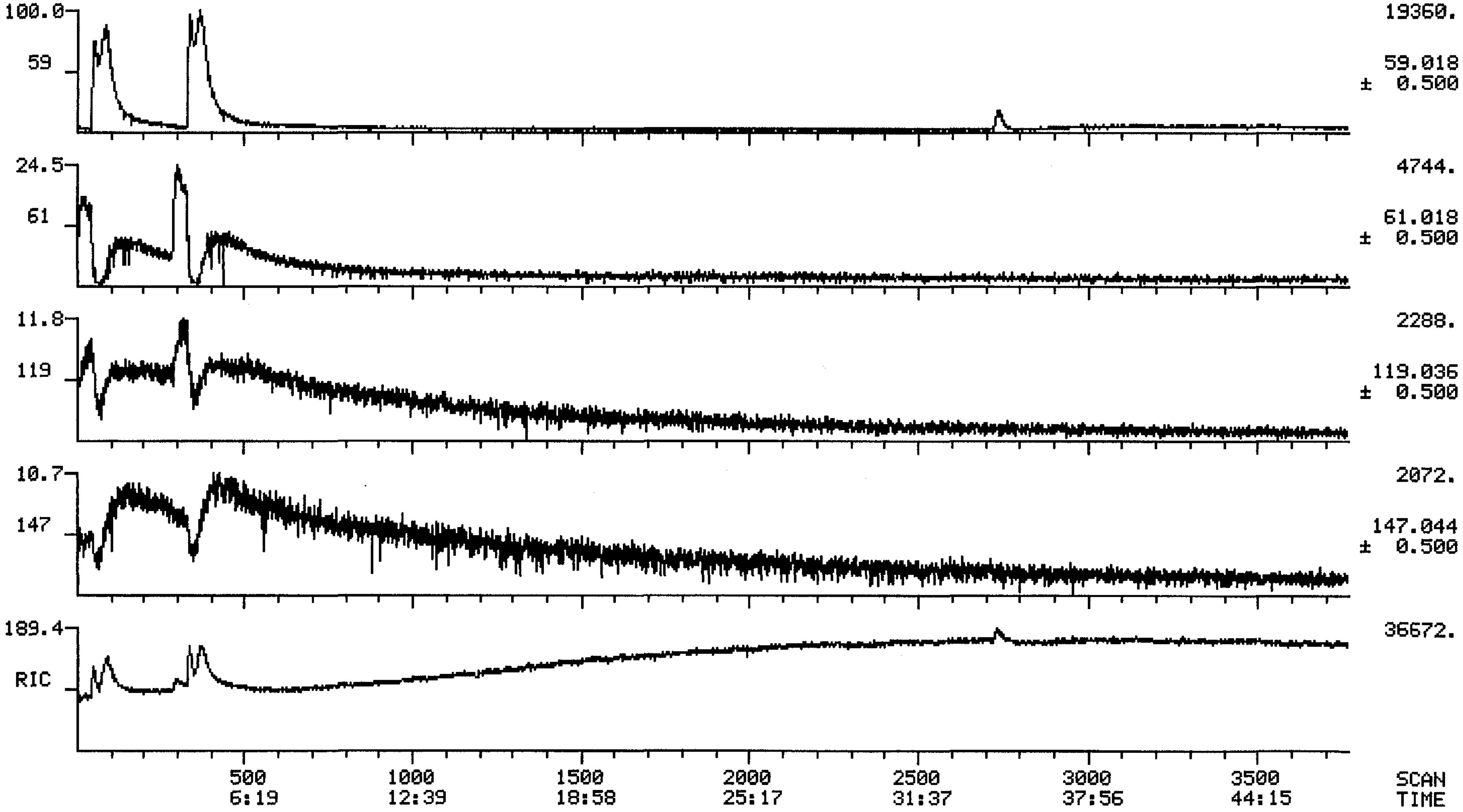
RIC+MASS CHROMATOGRAMS DATA: ICI05 #371 SCANS 1 TO 3767
09/15/94 9:04:00 CALI: CALTAB #3
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
RANGE: G 1,3767 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3



```
RIC+MASS CHROMATOGRAMS              DATA: ICI05 #371        SCANS   10 TO  700
09/15/94  9:04:00                   CALI: CALTAB #3
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
RANGE: G    1,3767  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



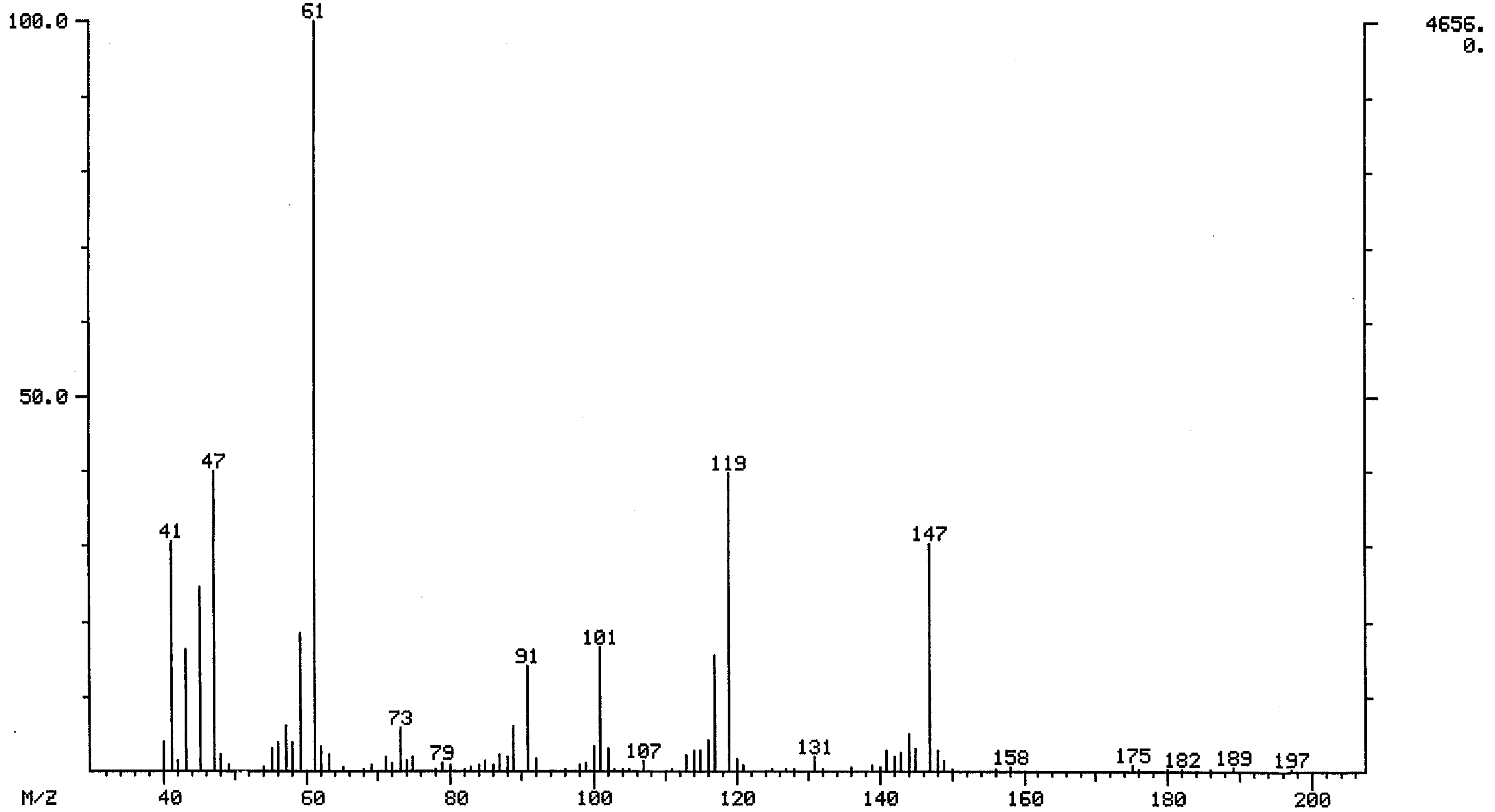
```
RIC+MASS CHROMATOGRAMS                  DATA: ICI05 #371        SCANS    1 TO 3767
09/15/94  9:04:00                       CALI: CALTAB #3
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
RANGE: G   1,3767  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



MASS SPECTRUM
09/15/94 9:04:00 + 3:48
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#300

DATA: ICI05 #300
CALI: CALTAB #3

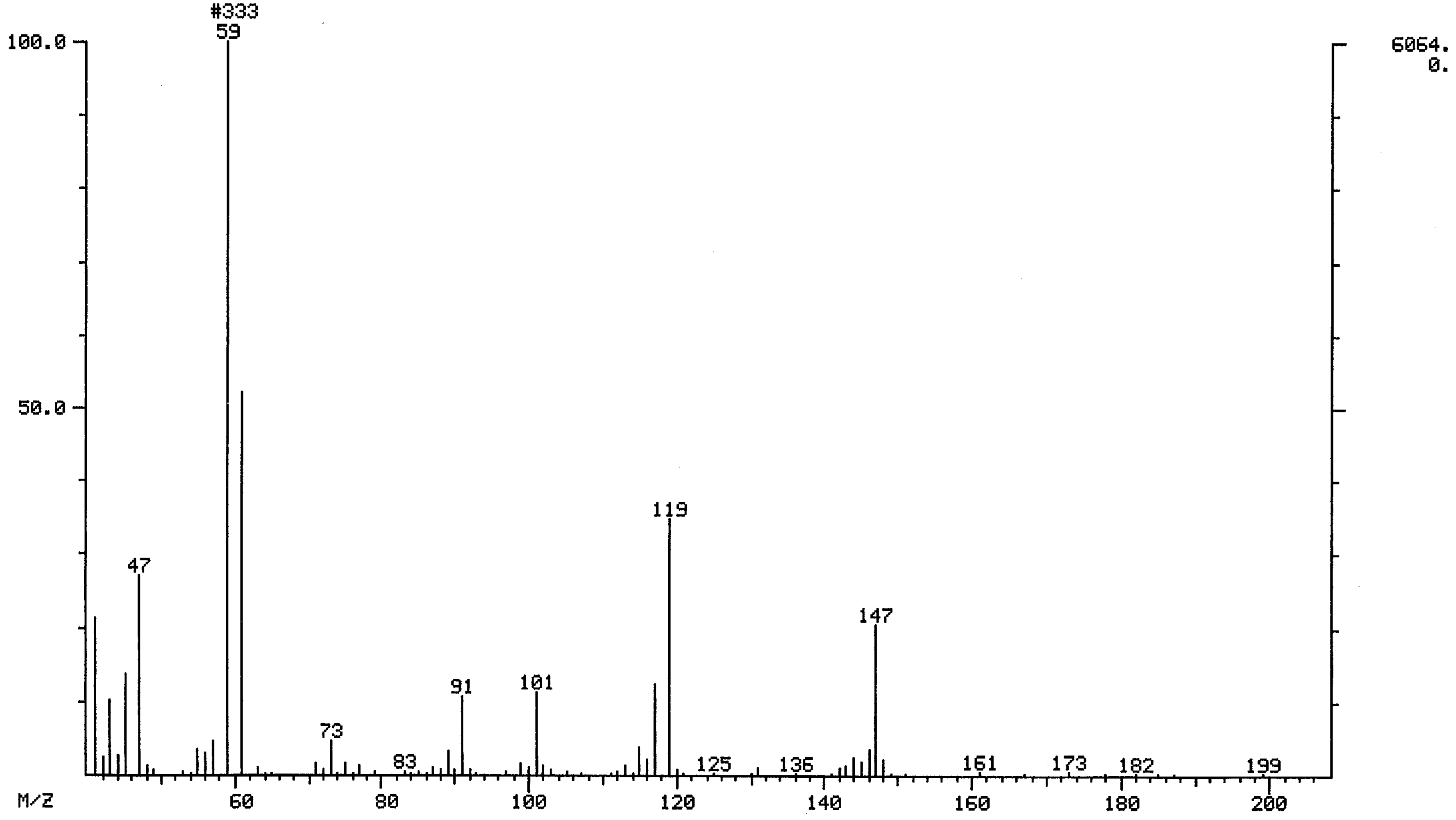
BASE M/Z: 61
RIC: 21632.



MASS SPECTRUM
09/15/94 9:04:00 + 4:13
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI05 #333
CALI: CALTAB #3

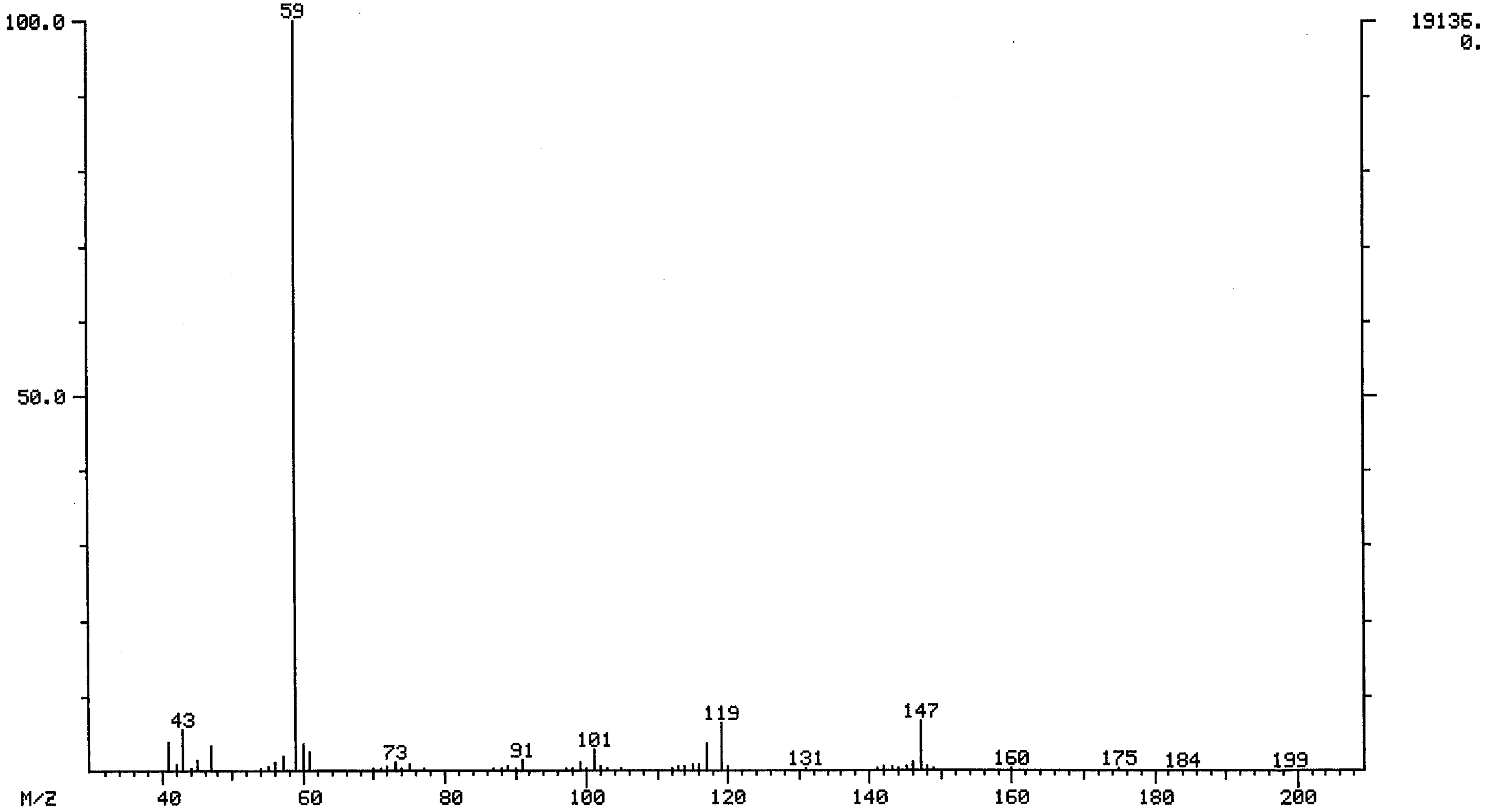
BASE M/Z: 59
RIC: 23840.



MASS SPECTRUM
09/15/94 9:04:00 + 4:41
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#371

DATA: ICI05 #371
CALI: CALTAB #3

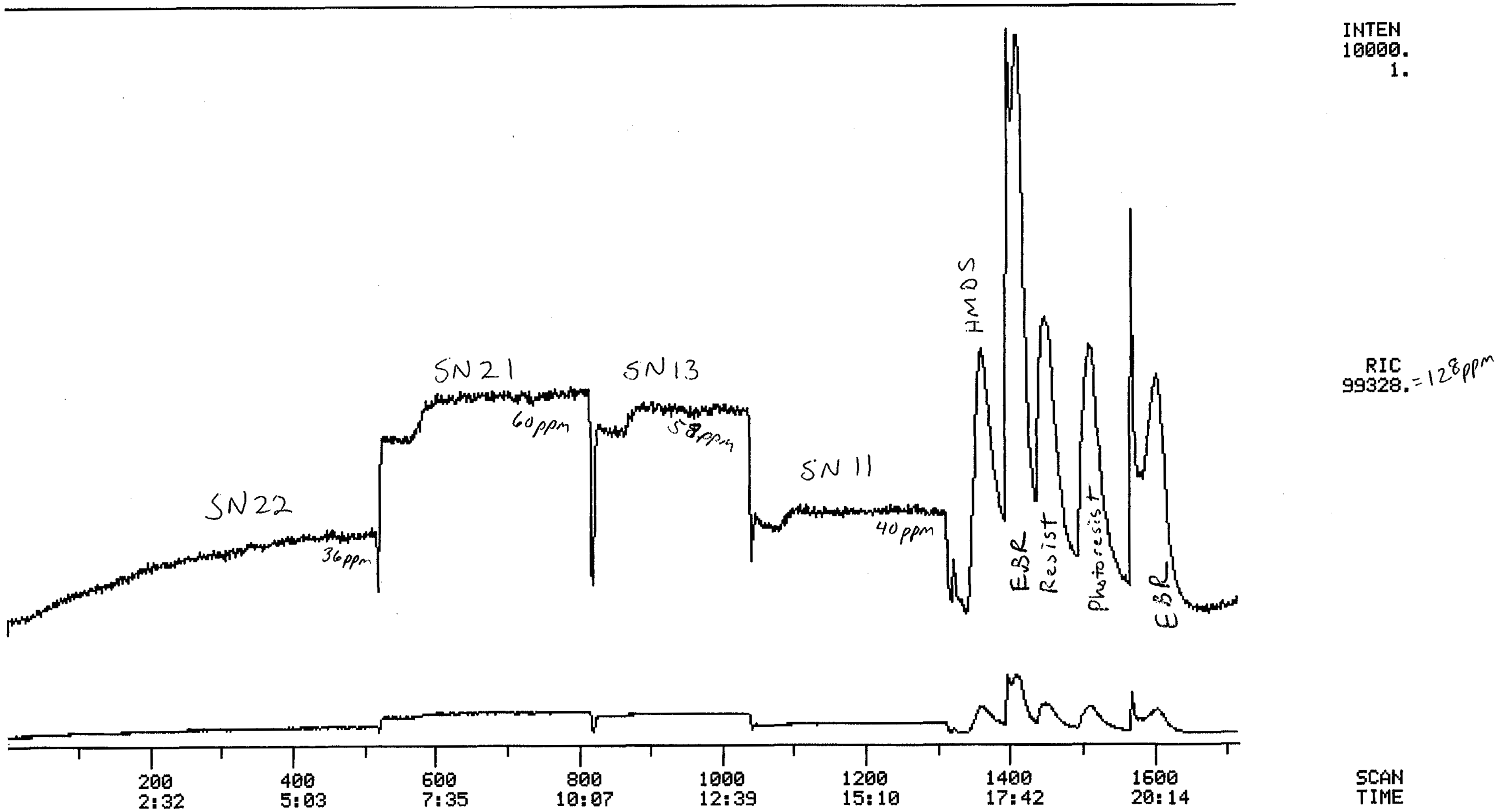
BASE M/Z: 59
RIC: 31392.



RIC
09/15/94 9:54:00
SAMPLE: INTEL-SN 21
CONDS.: 120 CI

DATA: ICI06 #1
CALI: CALTAB #3

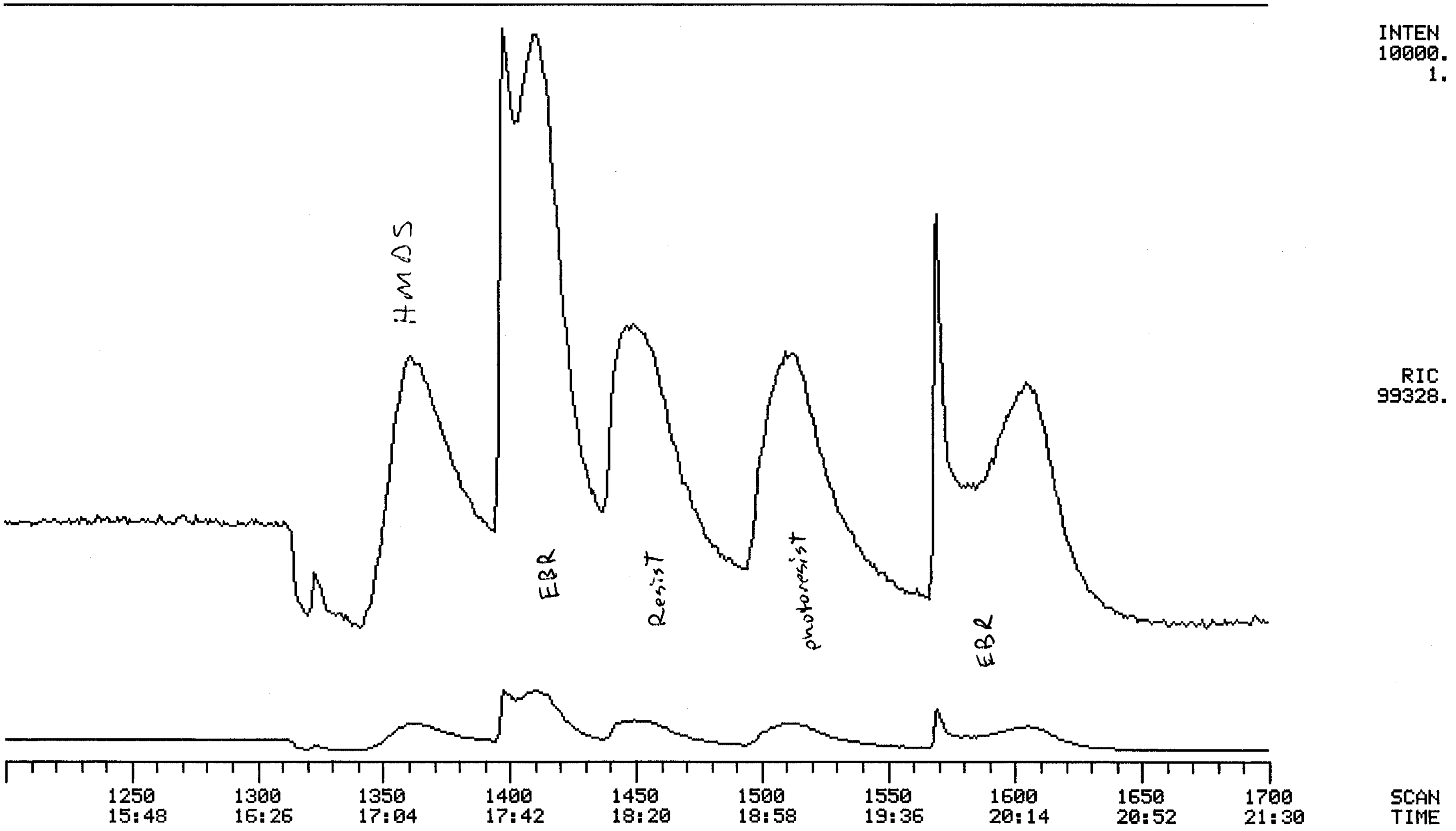
SCANS 1 TO 1716



RIC
09/15/94 9:54:00
SAMPLE: INTEL-SN 21
CONDS.: 120 CI

DATA: ICI06 #1606
CALI: CALTAB #3

SCANS 1200 TO 1700

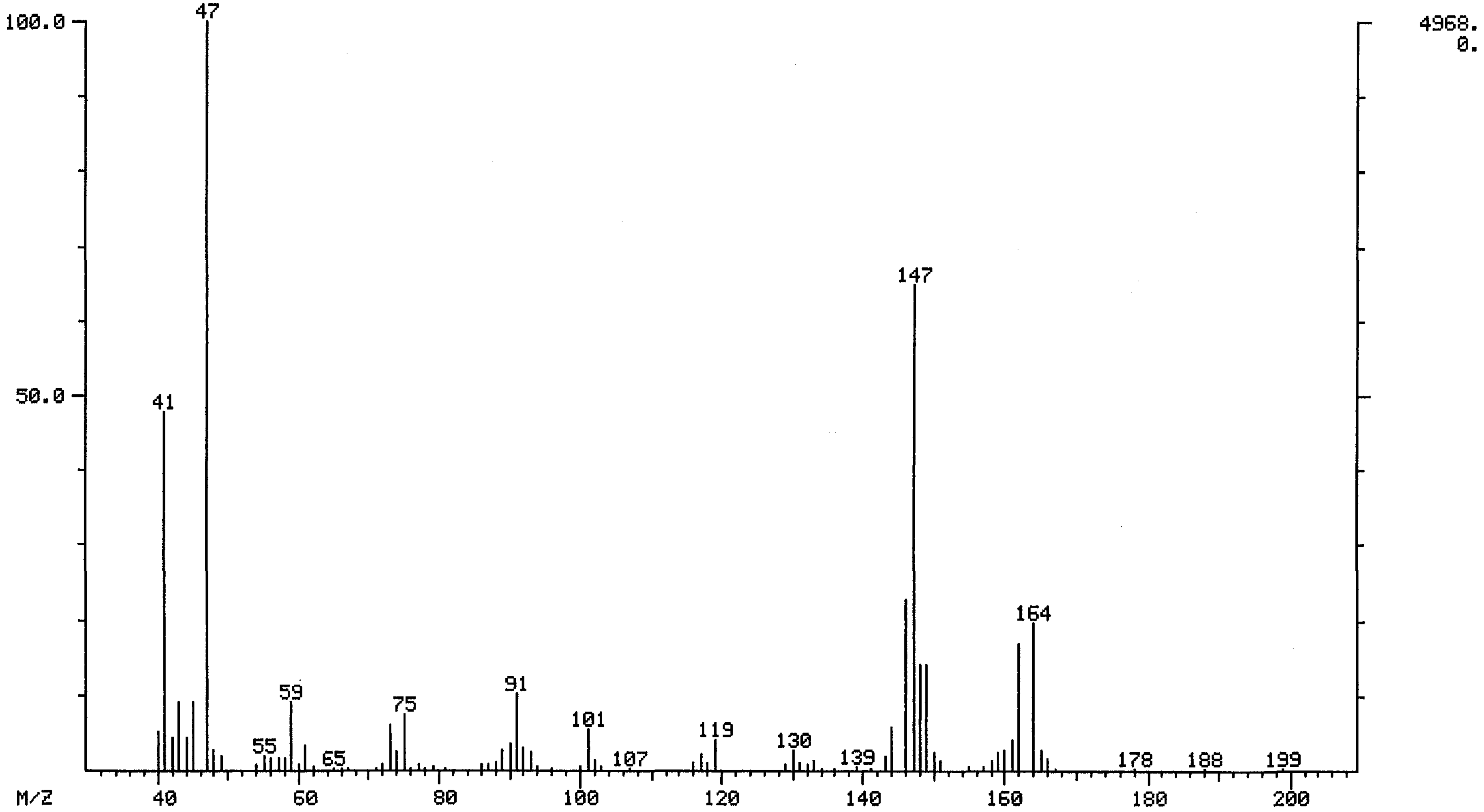


Small . ak

MASS SPECTRUM
09/15/94 9:54:00 + 16:45
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#1324

DATA: ICI06 #1324
CALI: CALTAB #3

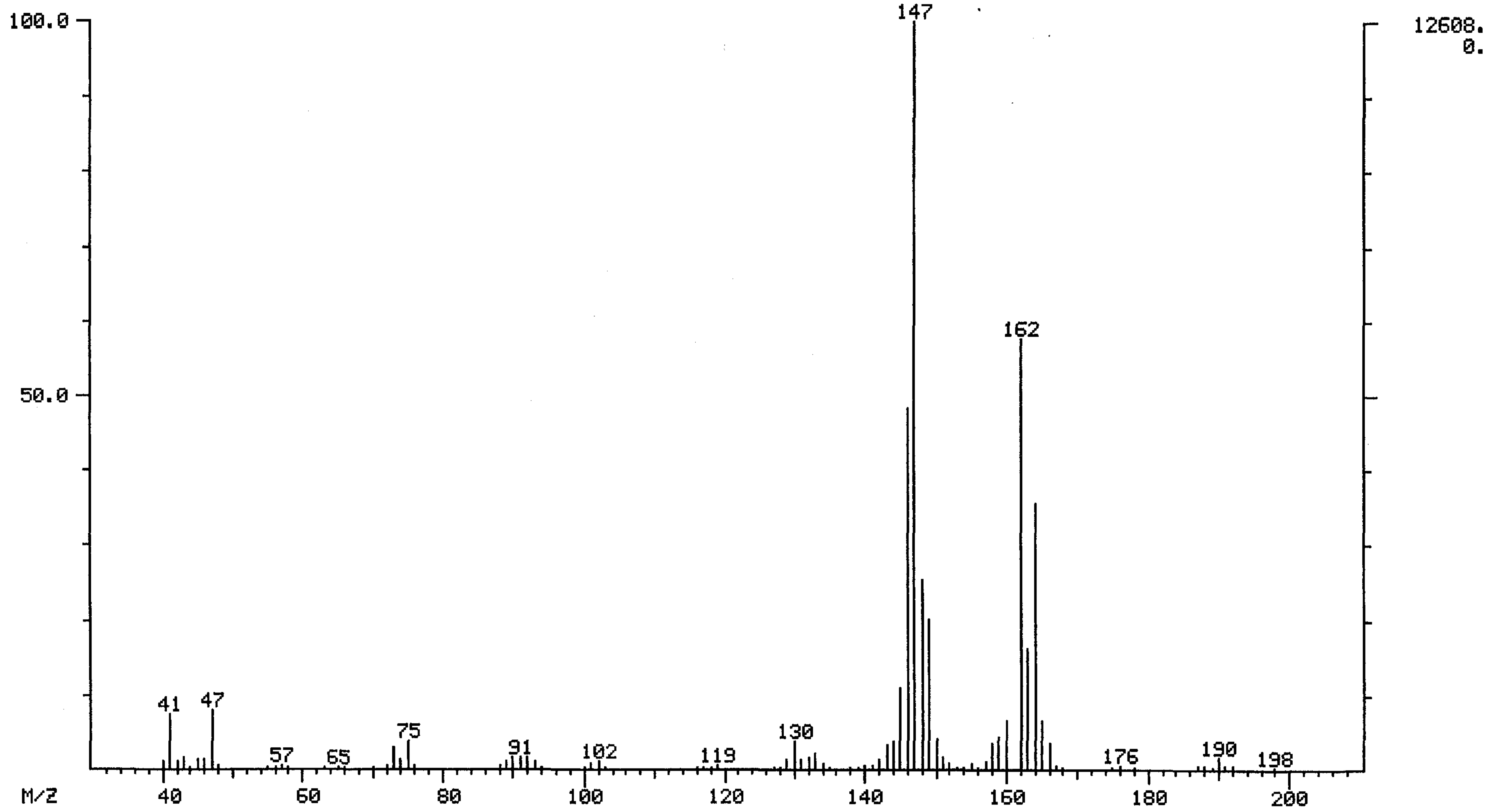
BASE M/Z: 47
RIC: 22880.



MASS SPECTRUM
09/15/94 9:54:00 + 17:13
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#1362

DATA: ICI06 #1362
CALI: CALTAB #3

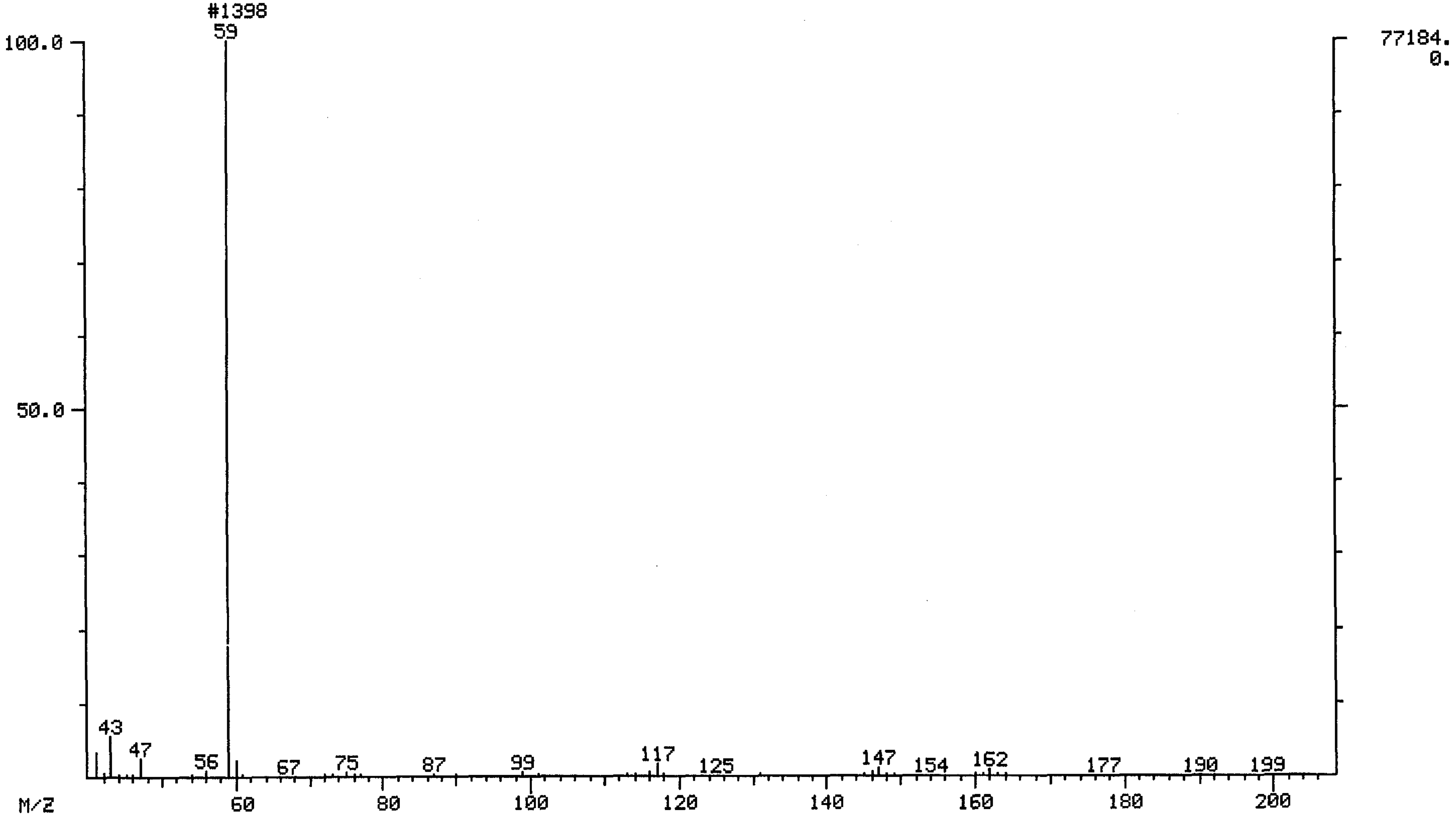
BASE M/Z: 147
RIC: 53312.



MASS SPECTRUM
09/15/94 9:54:00 + 17:41
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI06 #1398
CALI: CALTAB #3

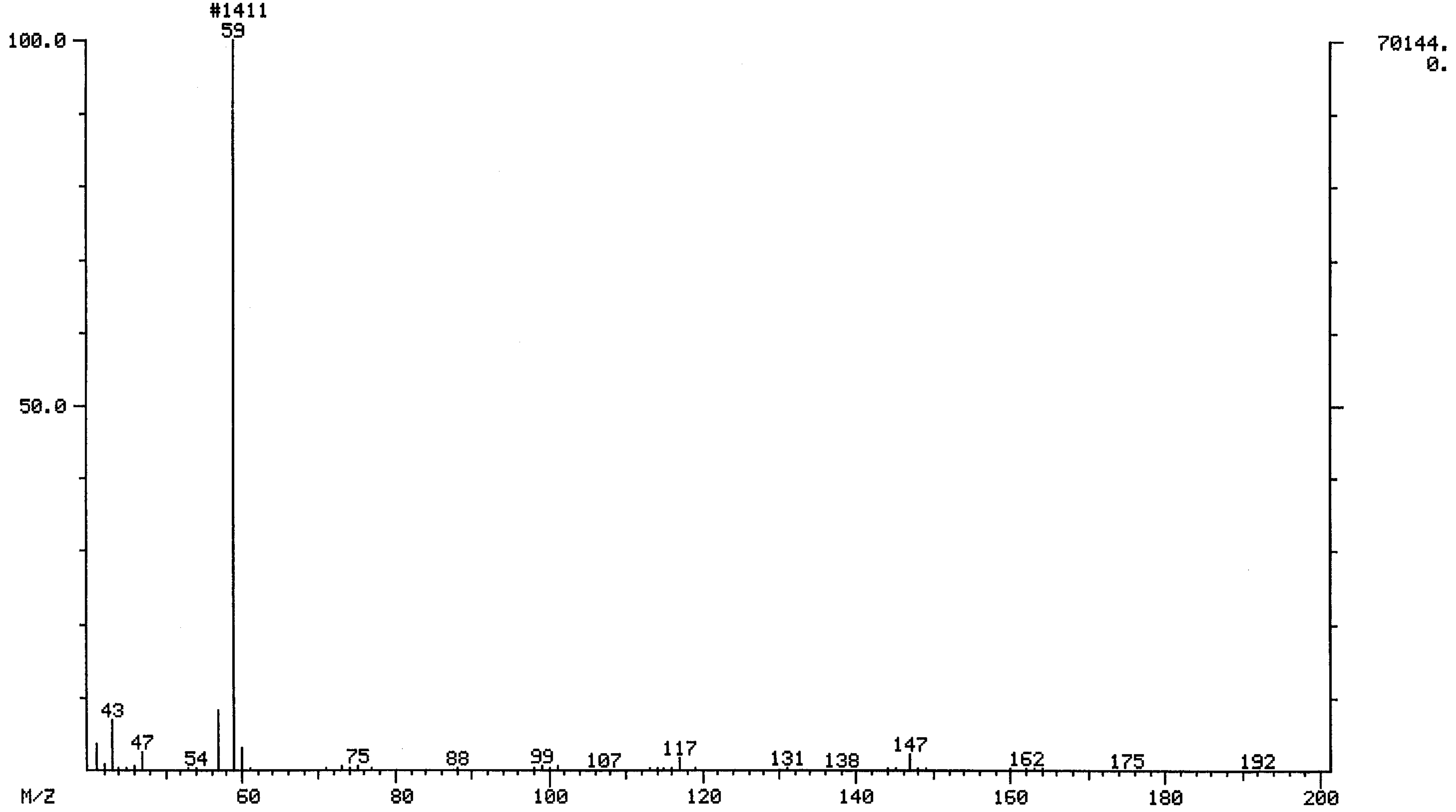
BASE M/Z: 59
RIC: 98816.



MASS SPECTRUM
09/15/94 9:54:00 + 17:51
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI06 #1411
CALI: CALTAB #3

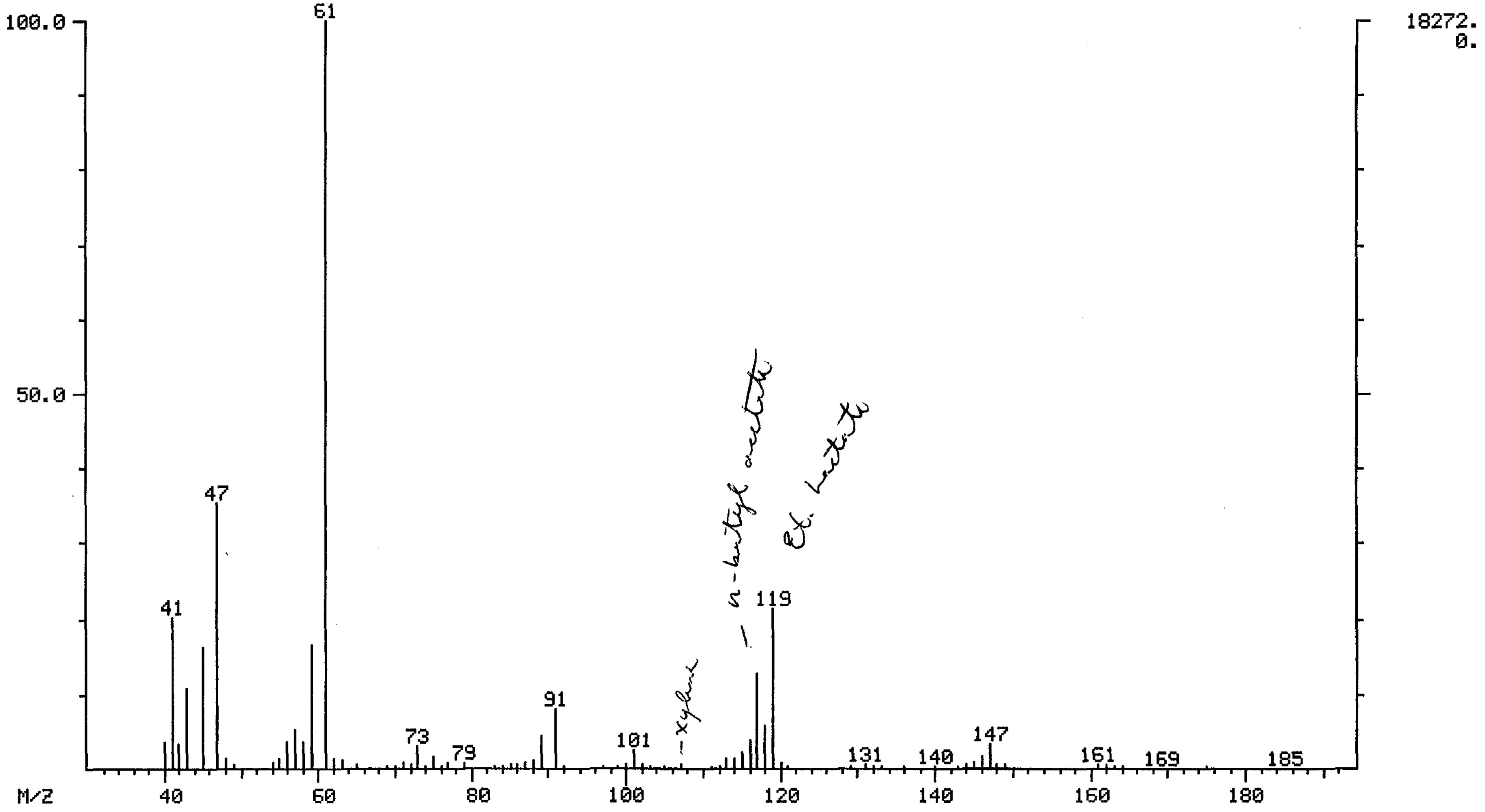
BASE M/Z: 59
RIC: 98304.



MASS SPECTRUM
09/15/94 9:54:00 + 18:20
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#1450

DATA: ICI06 #1450
CALI: CALTAB #3

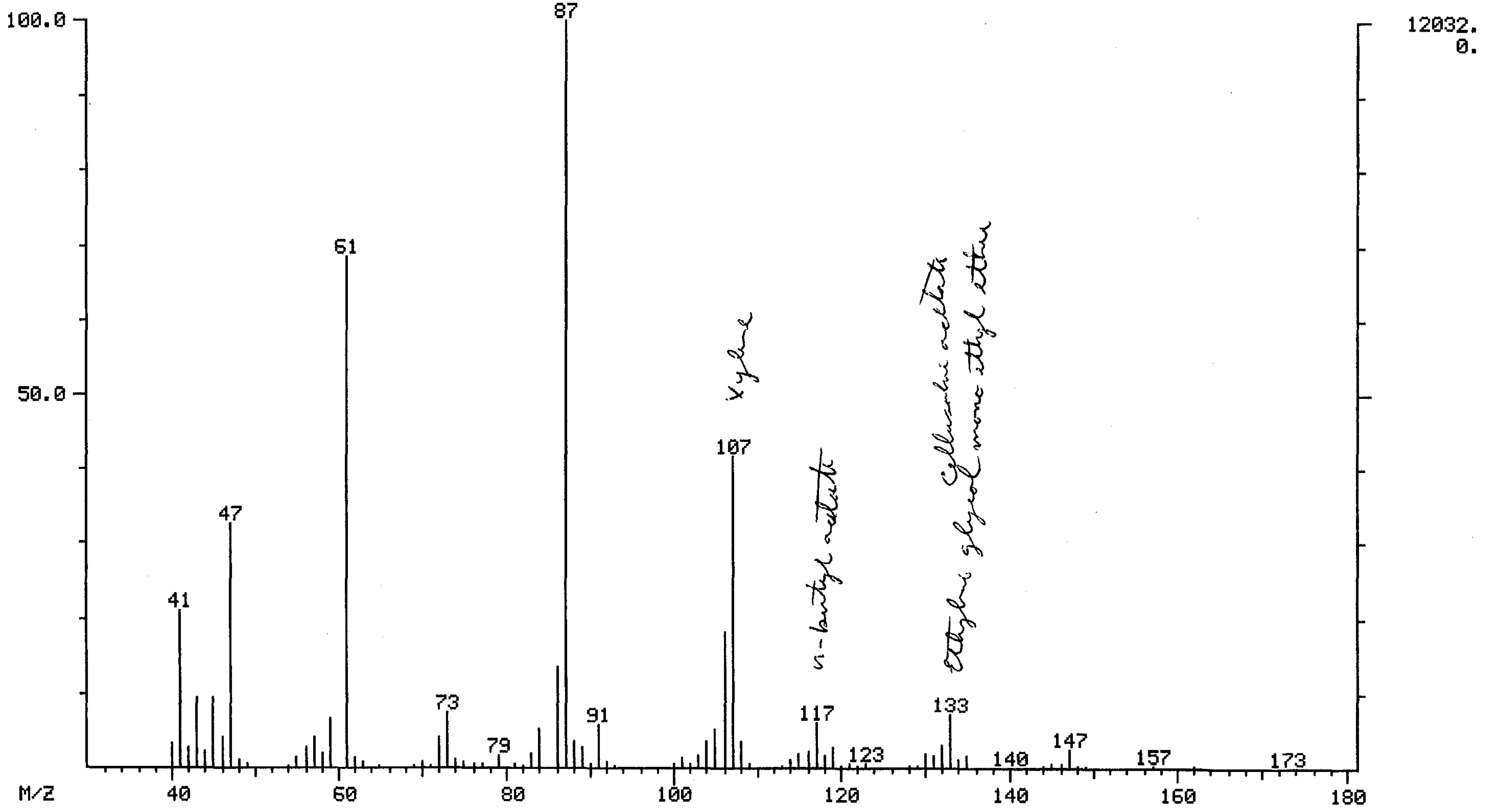
BASE M/Z: 61
RIC: 58048.



MASS SPECTRUM
09/15/94 9:54:00 + 19:07
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#1512

DATA: ICI06 #1512
CALI: CALTAB #3

BASE M/Z: 87
RIC: 53696.



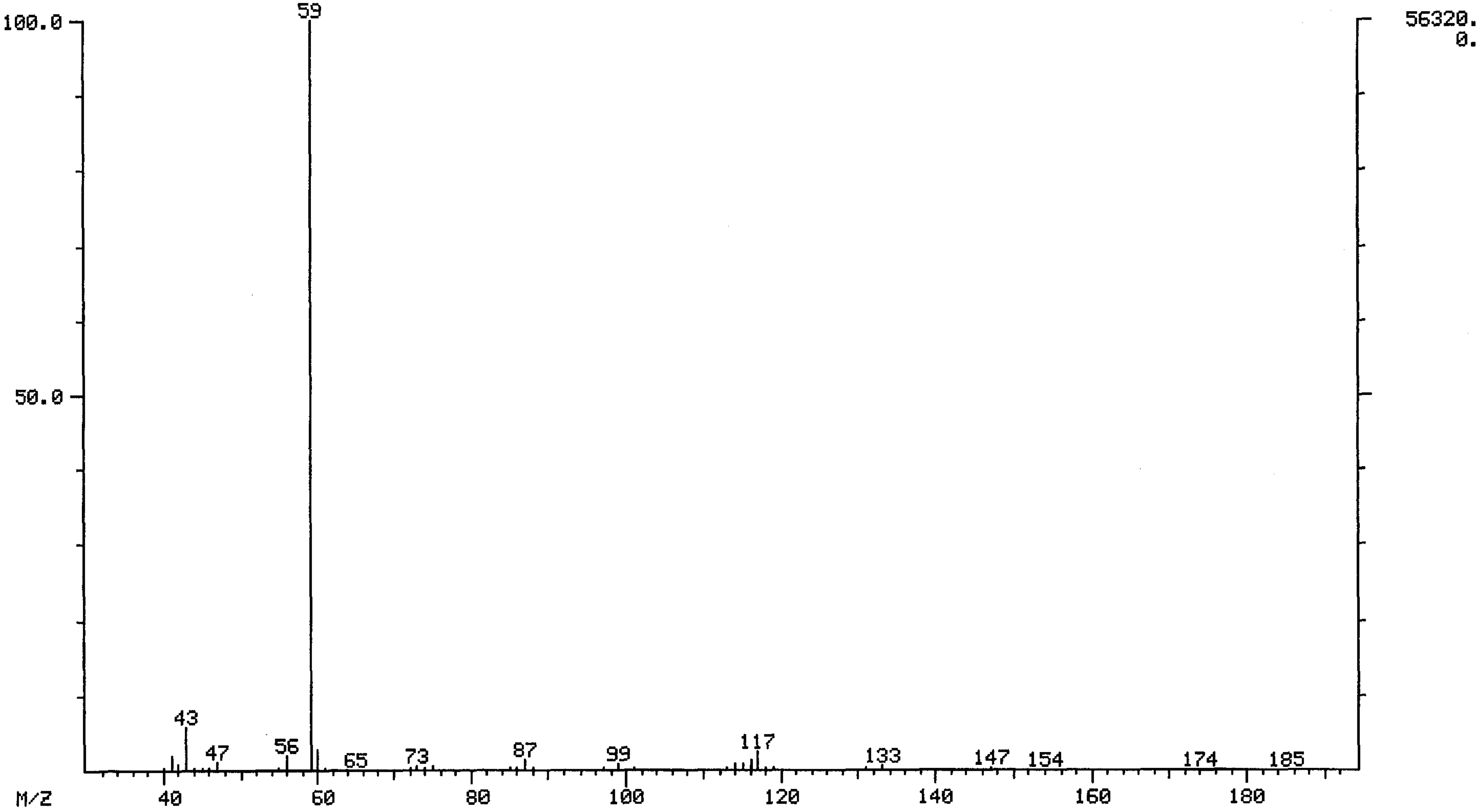
Xylene

n-butyl acetate

Cellosolve acetate

Ethylene glycol mono ethyl ether

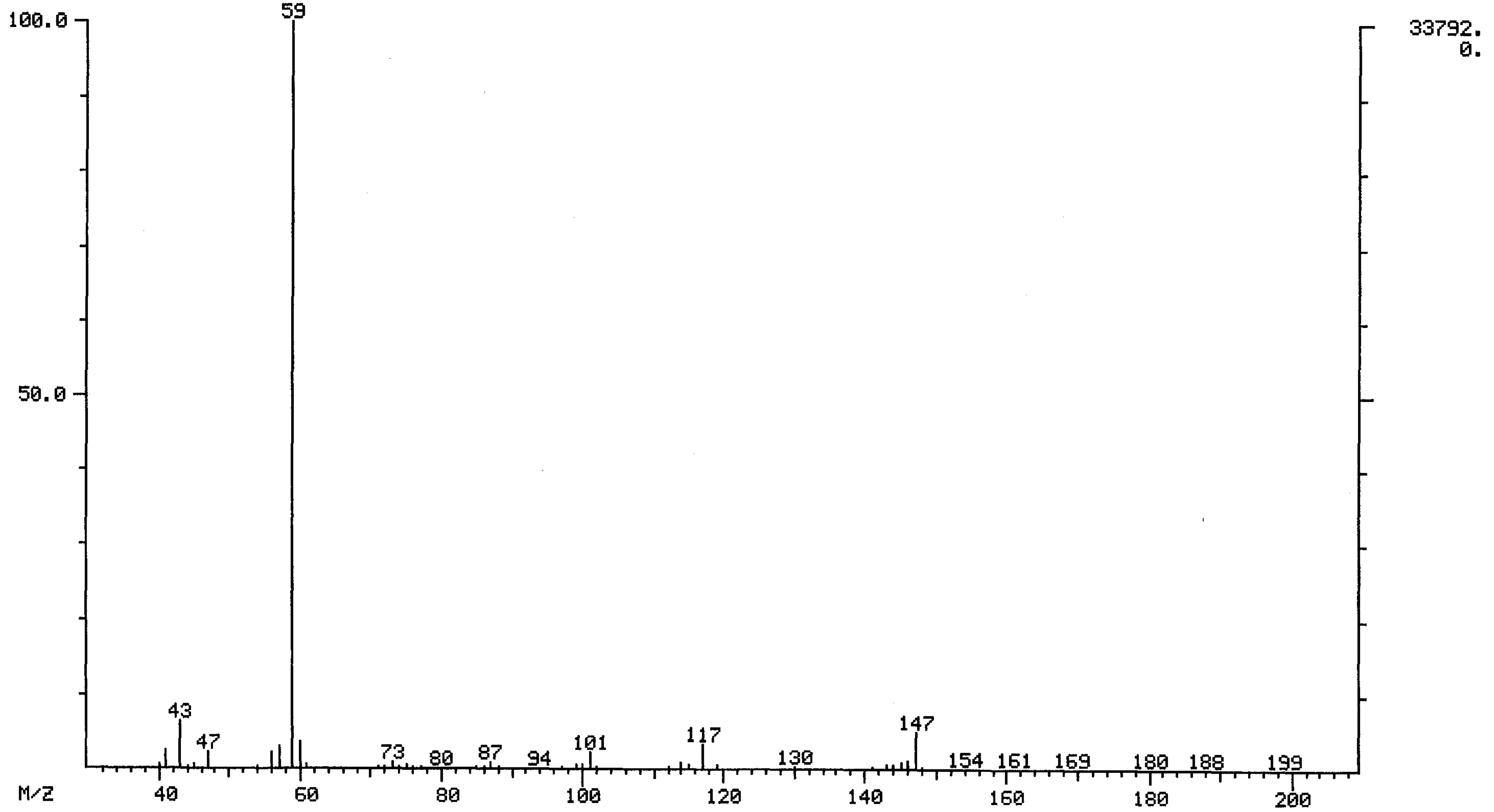
```
MASS SPECTRUM                                               DATA: ICI06 #1570           BASE M/Z:  59
09/15/94  9:54:00 + 19:51                                   CALI: CALTAB #3             RIC:    73472.
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP:    0 DEG. C
 #1570
```



MASS SPECTRUM
09/15/94 9:54:00 + 20:18
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#1606

DATA: ICI06 #1606
CALI: CALTAB #3

BASE M/Z: 59
RIC: 49600.

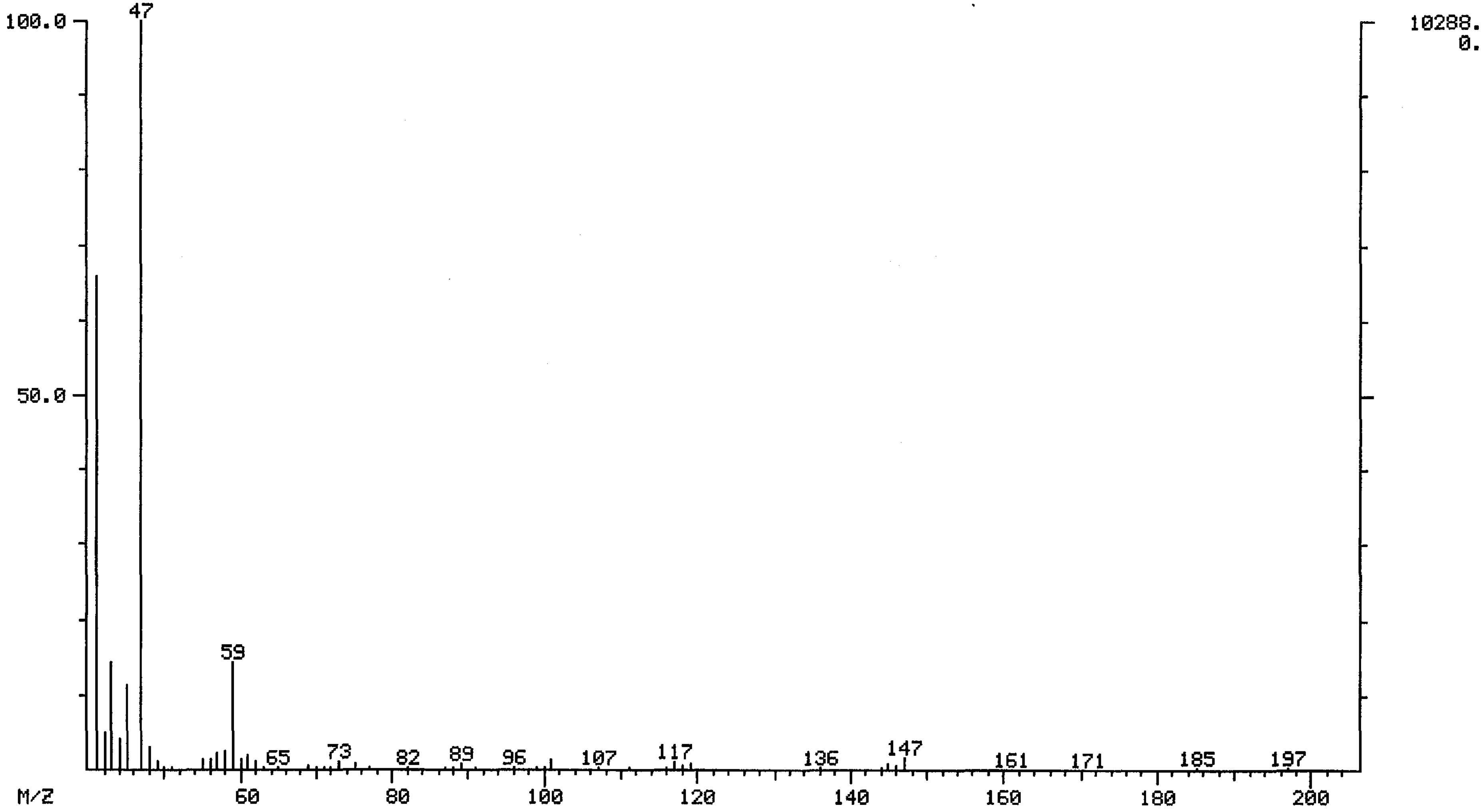


SN 22
BACKGROUND

MASS SPECTRUM
09/15/94 9:54:00 + 4:35
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#362

DATA: ICI06 #362
CALI: CALTAB #3

BASE M/Z: 47
RIC: 25408.

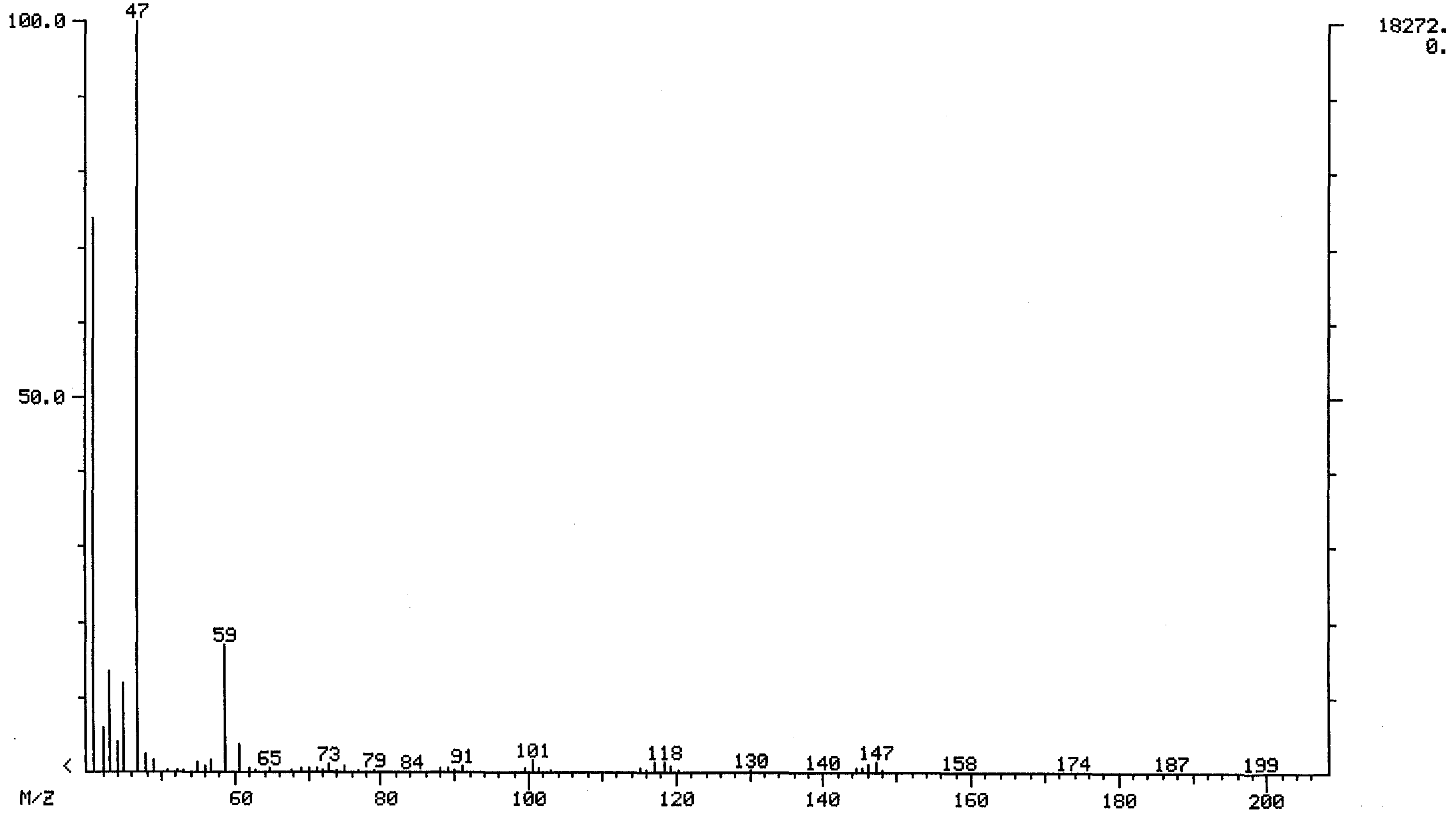


SN 21
Background

MASS SPECTRUM
09/15/94 9:54:00 + 8:51
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI06 #700
CALI: CALTAB #3

BASE M/Z: 47
RIC: 47232.

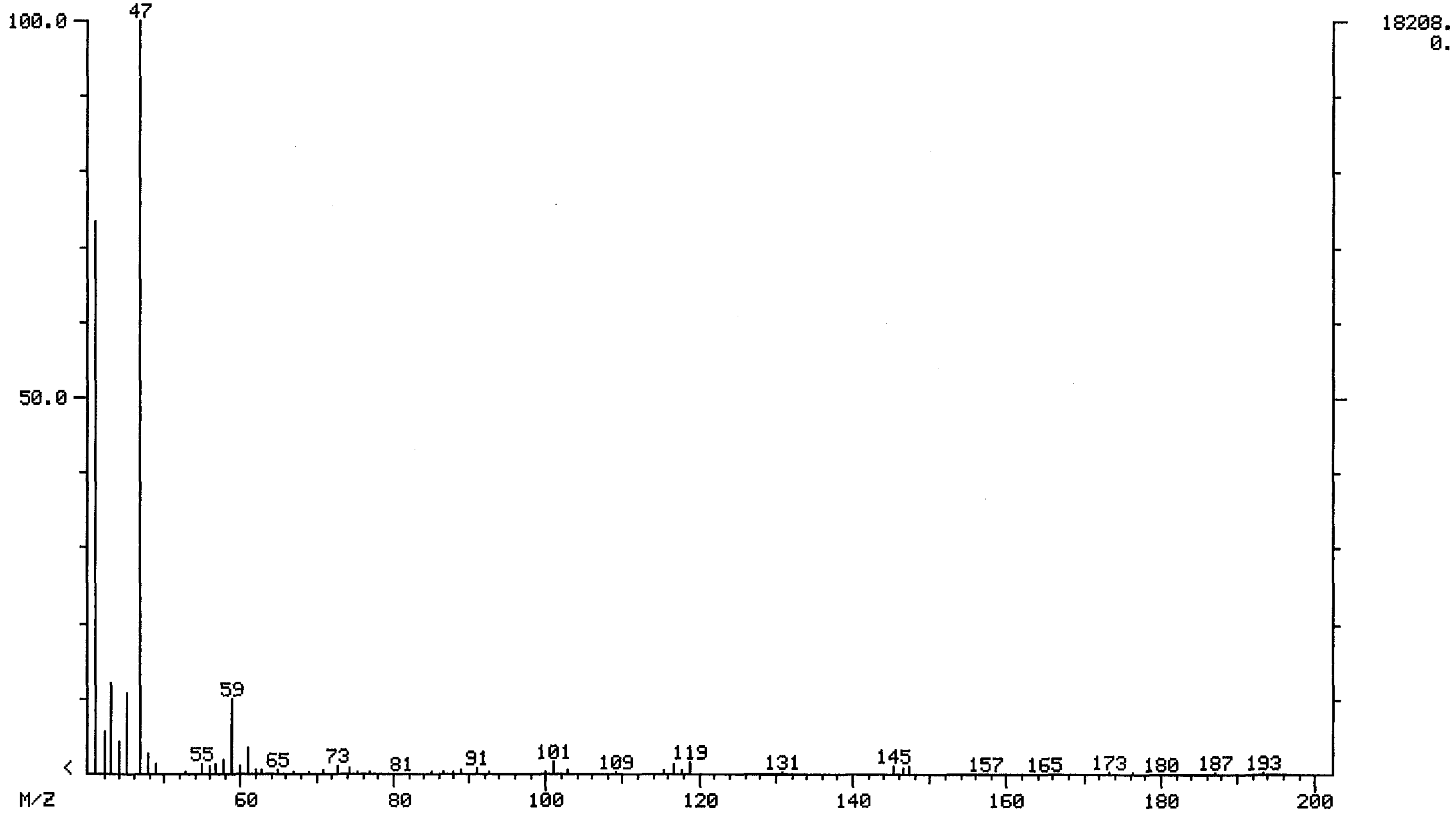


SN 13
BACKGROUND

MASS SPECTRUM
09/15/94 9:54:00 + 11:23
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI06 #900
CALI: CALTAB #3

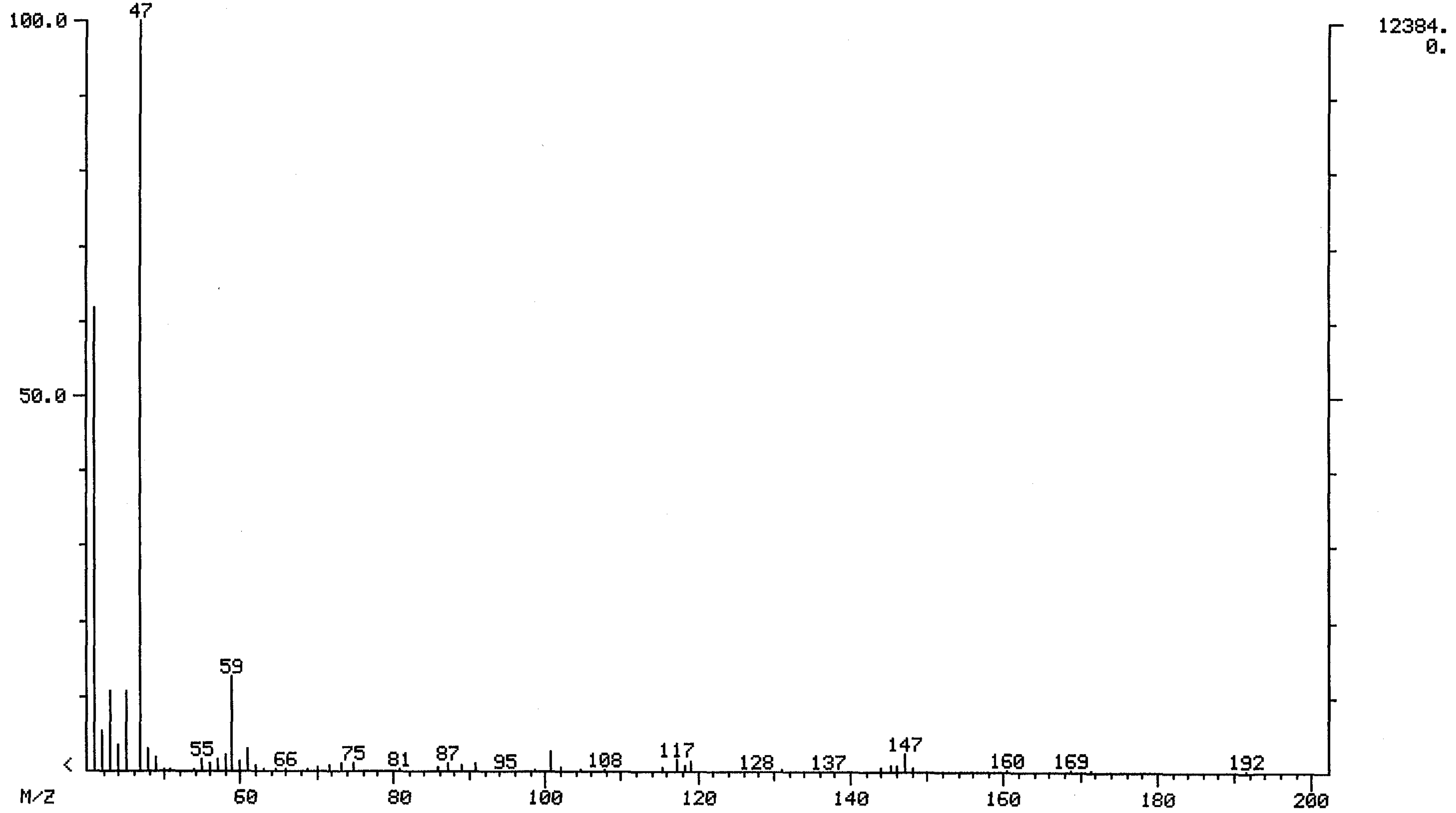
BASE M/Z: 47
RIC: 45376.



MASS SPECTRUM
09/15/94 9:54:00 + 15:10
SAMPLE: INTEL-SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI06 #1200
CALI: CALTAB #3

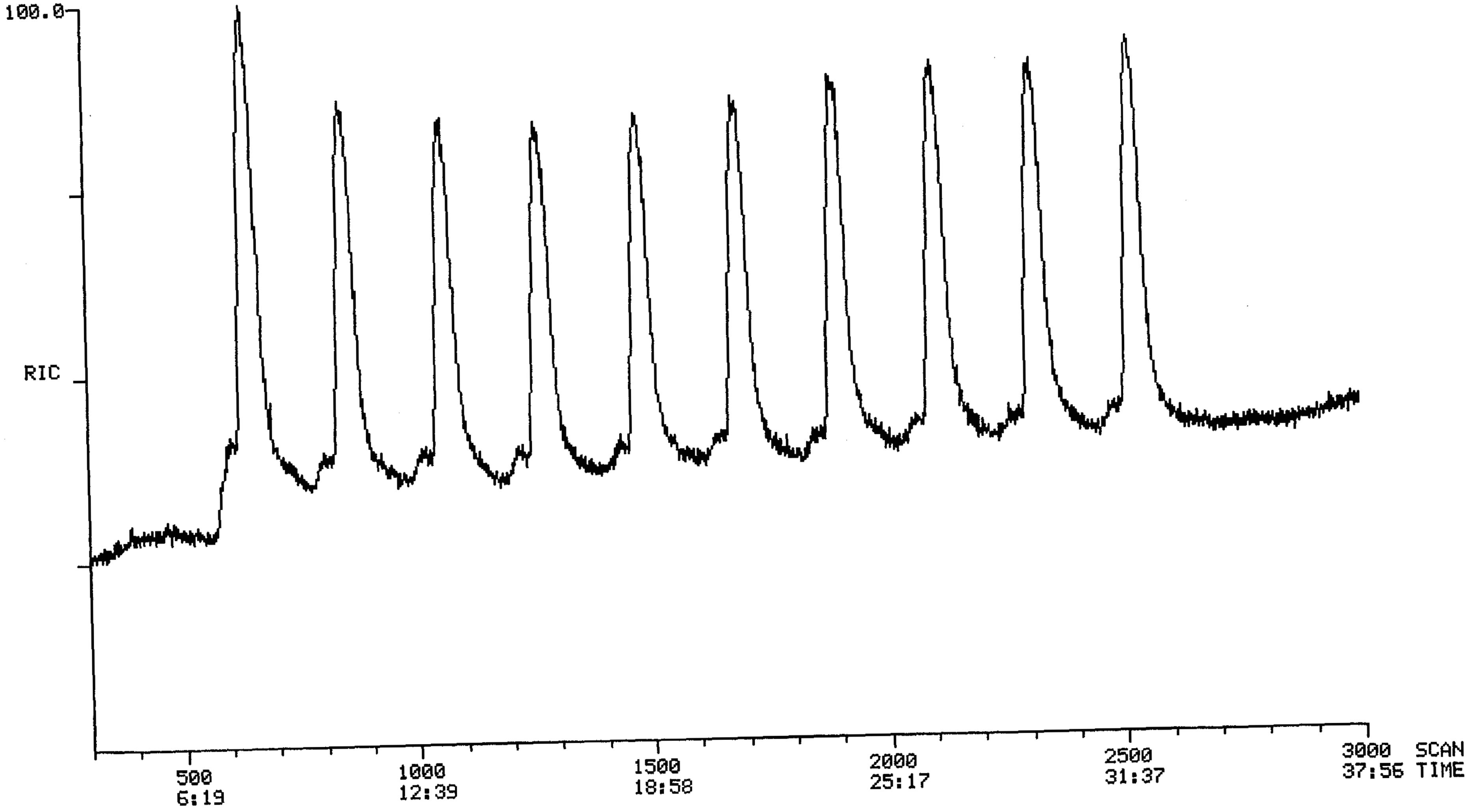
BASE M/Z: 47
RIC: 30720.



RIC
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

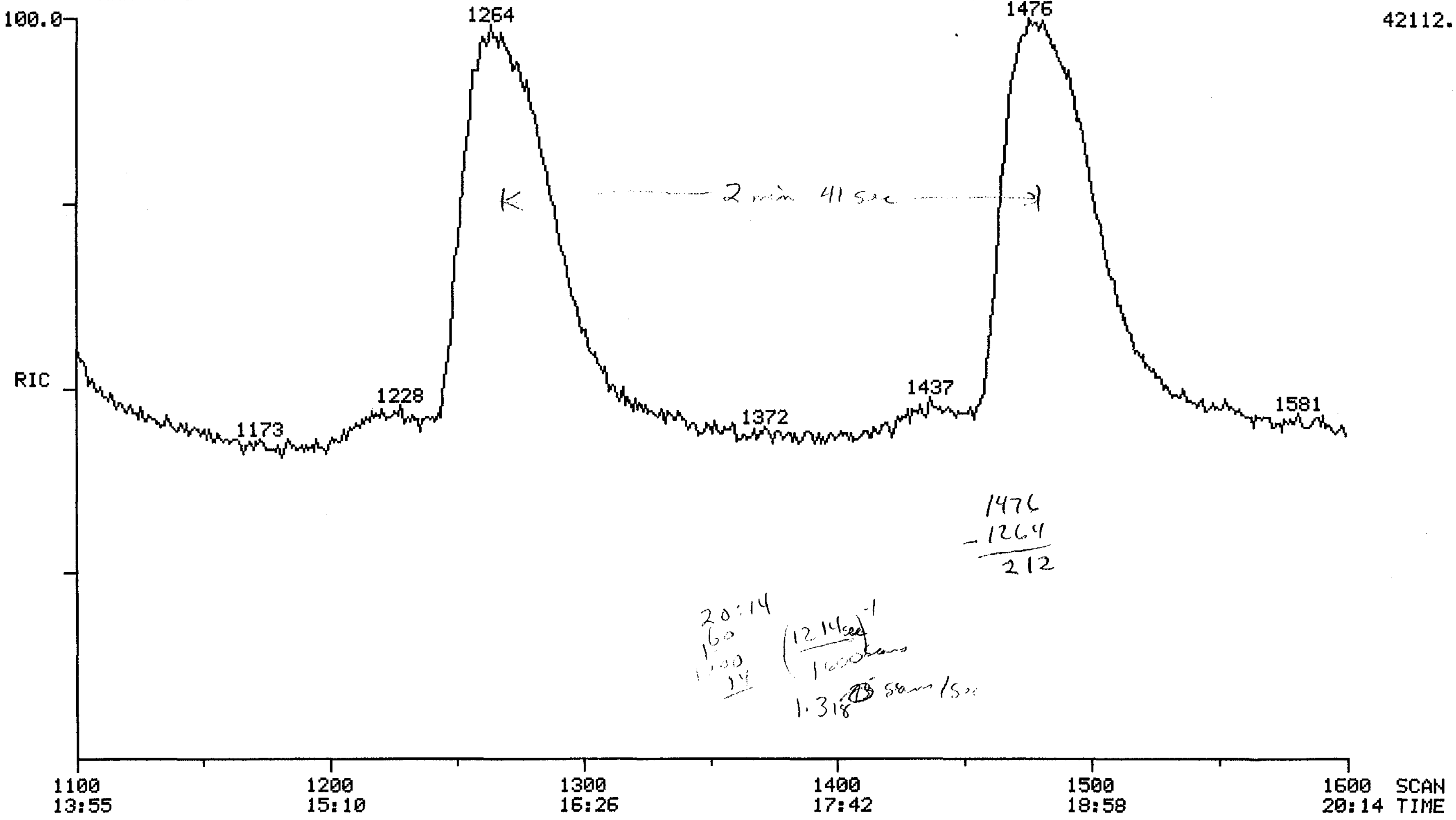
SCANS 300 TO 3000



RIC
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

SCANS 1100 TO 1600



K—— 2 min 41 sec ——→|

1476
-1264
212

20:14
160
1200
14

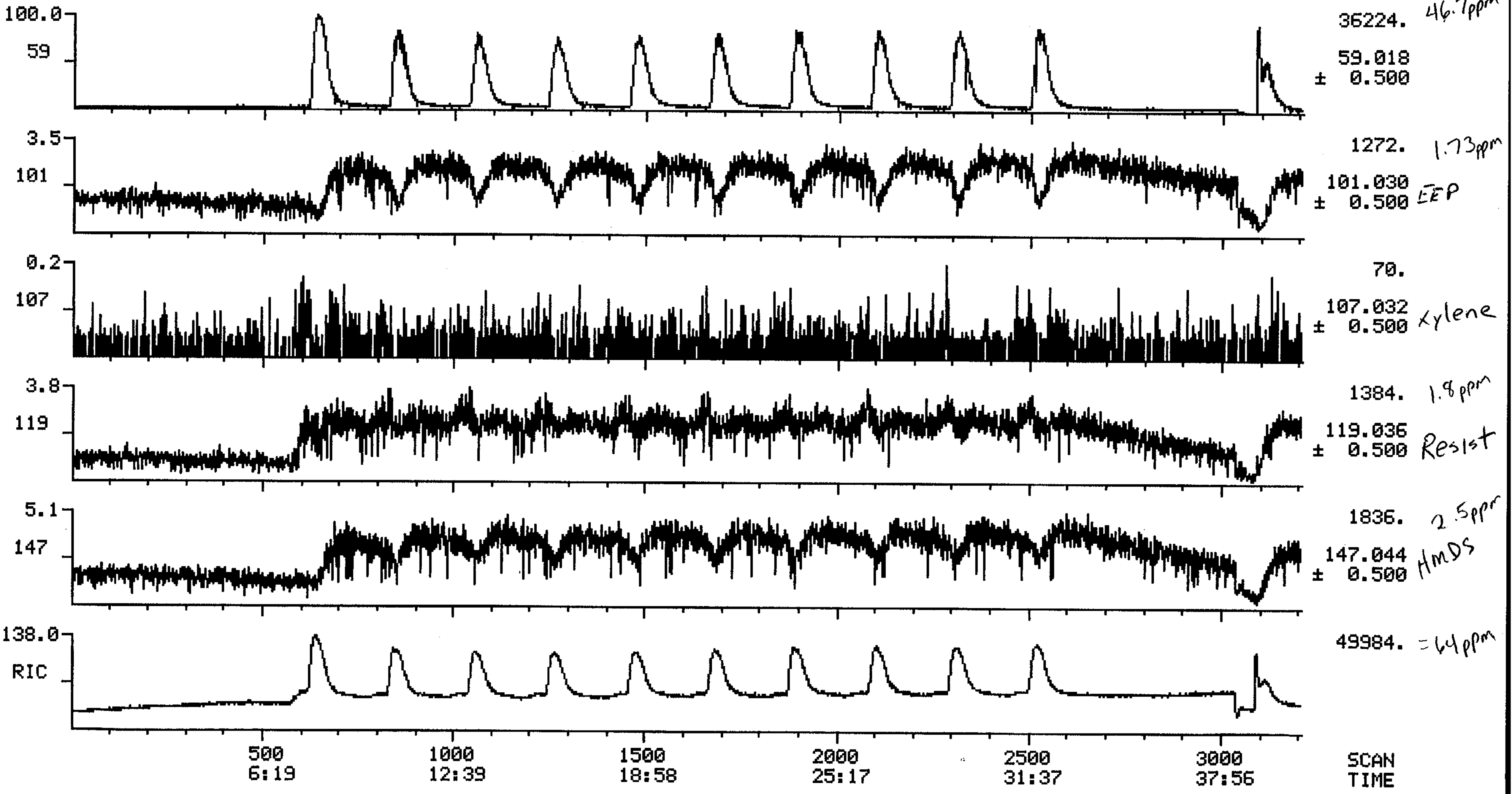
$\left(\frac{1214\text{sec}}{1600\text{scans}}\right)^{-1}$

1.318③ scans/sec

RIC+MASS CHROMATOGRAMS
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

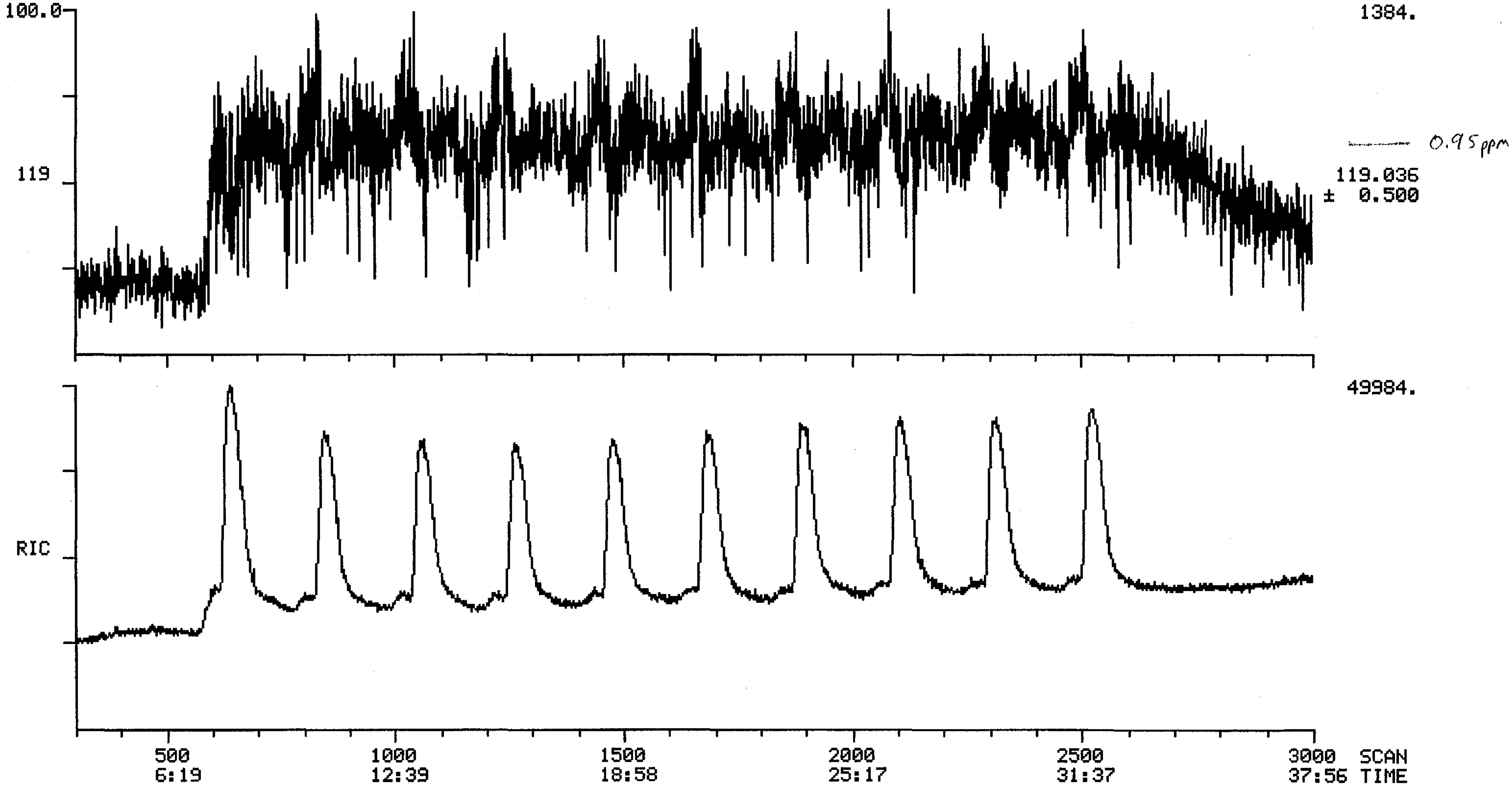
SCANS 1 TO 3209



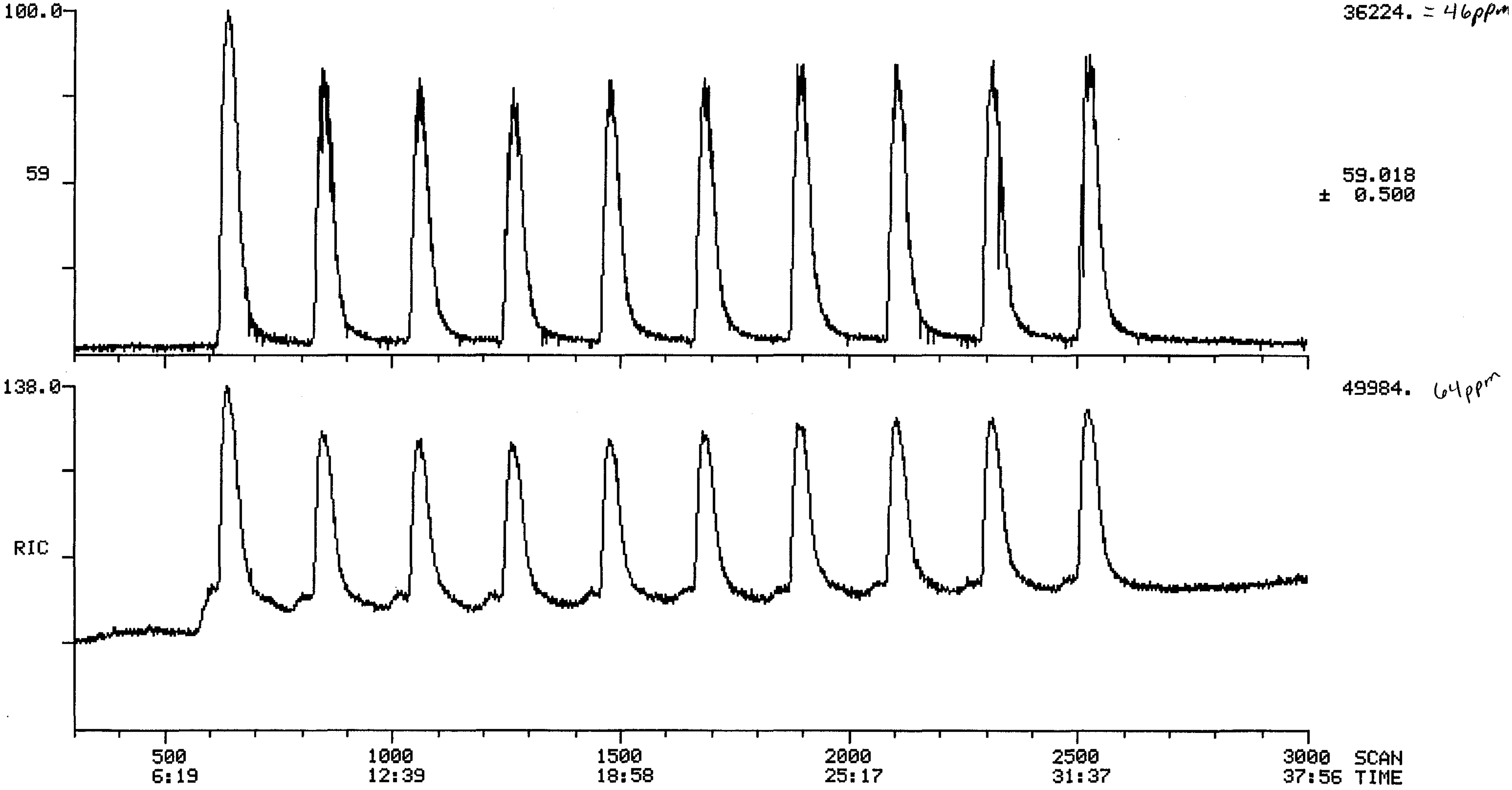
RIC+MASS CHROMATOGRAM
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

SCANS 300 TO 3000



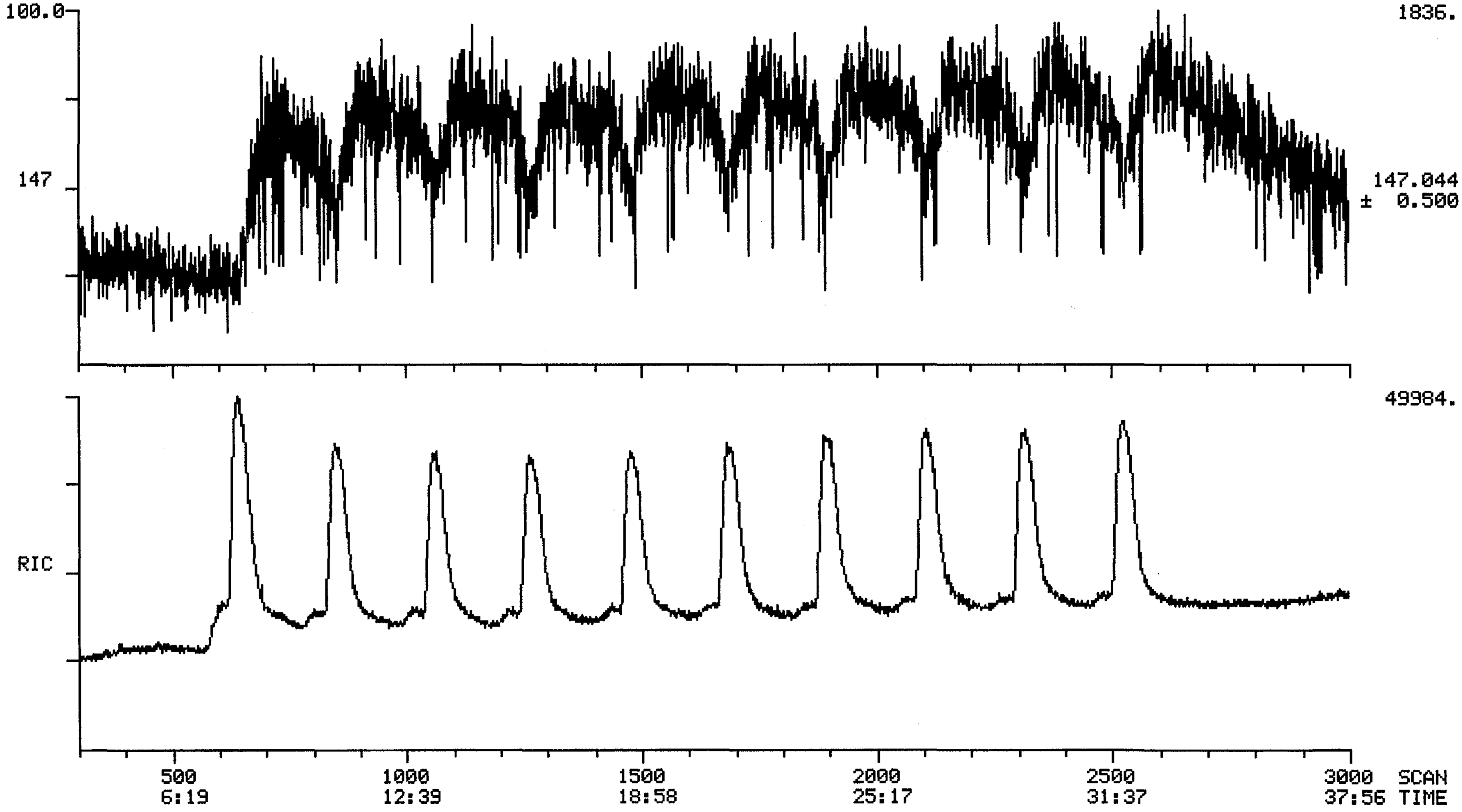
```
RIC+MASS CHROMATOGRAM                   DATA: ICI08 #1           SCANS  300 TO 3000
09/15/94 10:55:00                       CALI: CALTAB #3
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G   1,3209  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



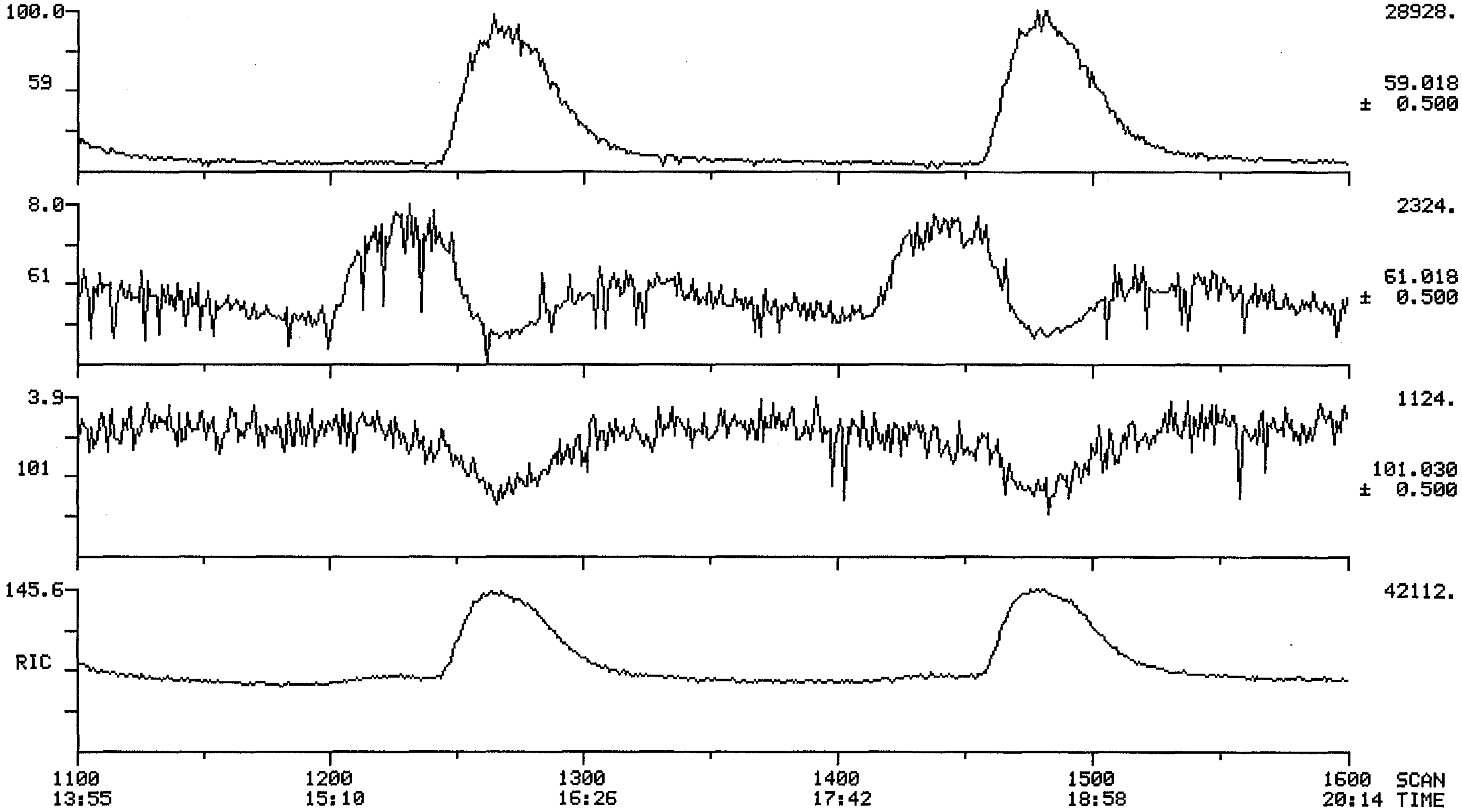
RIC+MASS CHROMATOGRAM
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

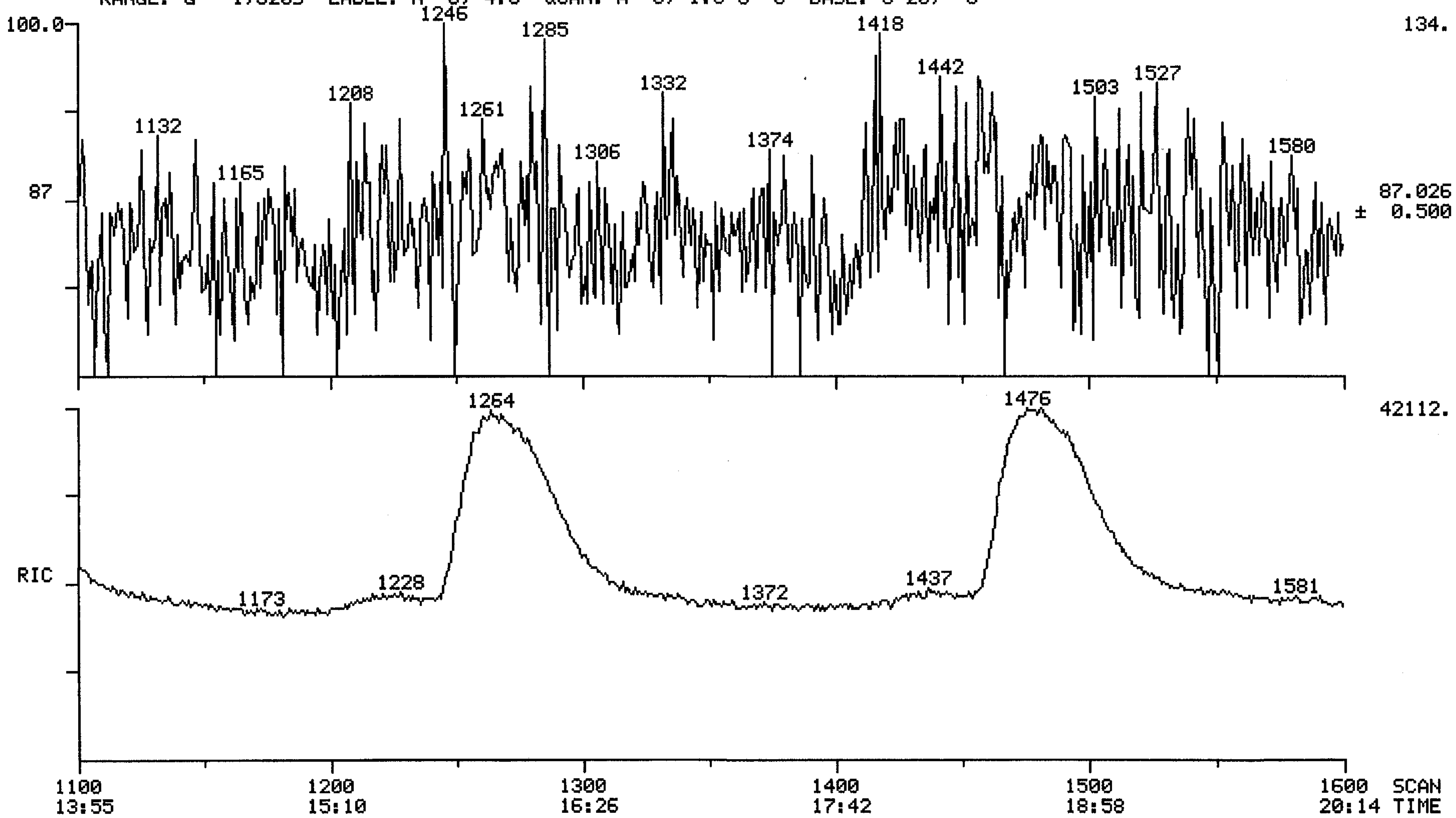
SCANS 300 TO 3000



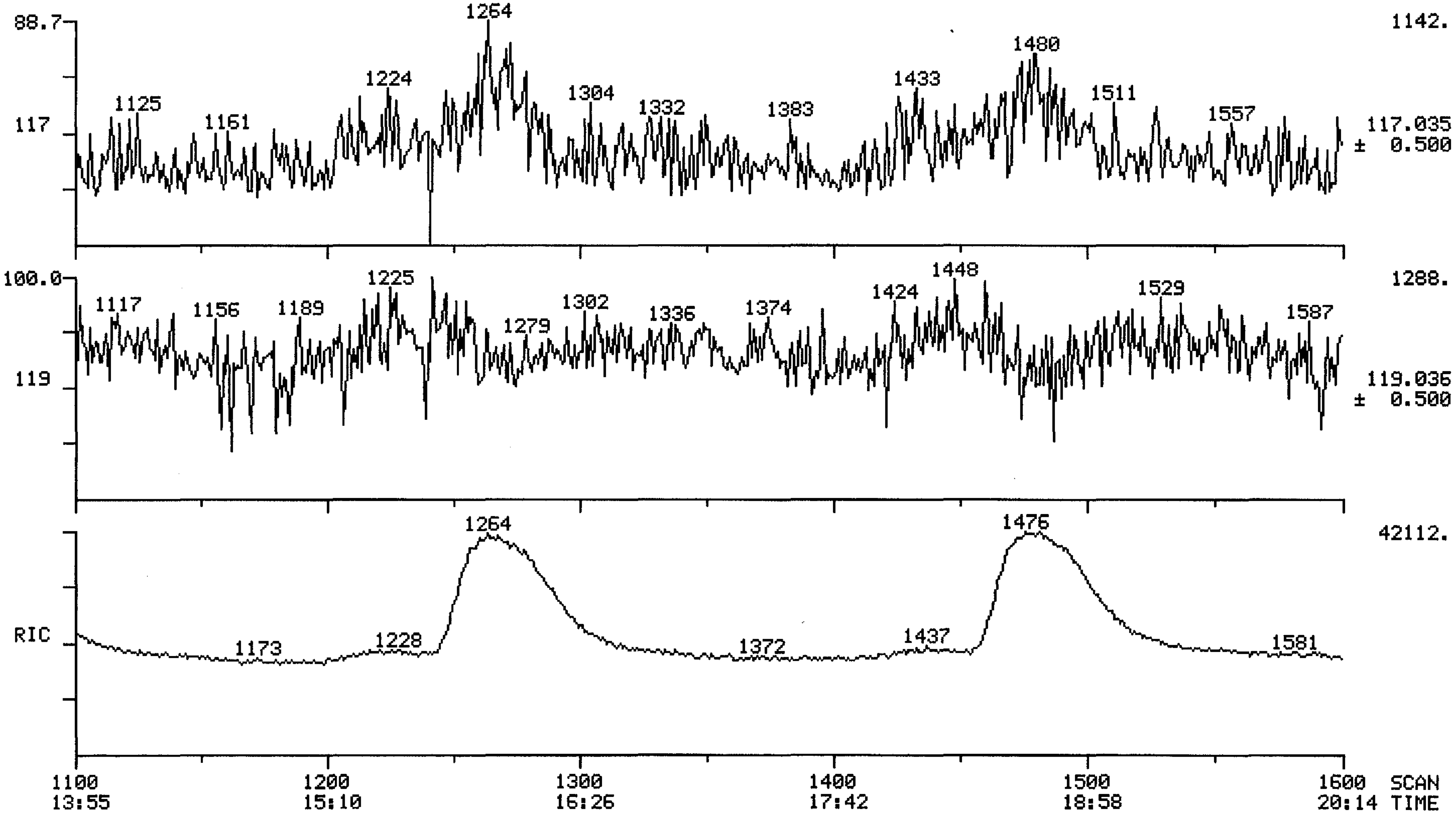
```
RIC+MASS CHROMATOGRAMS                DATA: ICI08 #1            SCANS 1100 TO 1600
09/15/94 10:55:00                     CALI: CALTAB #3
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G   1,3209  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



```
RIC+MASS CHROMATOGRAM                       DATA: ICI08 #1           SCANS 1100 TO 1600
09/15/94 10:55:00                           CALI: CALTAB #3
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G   1,3209  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



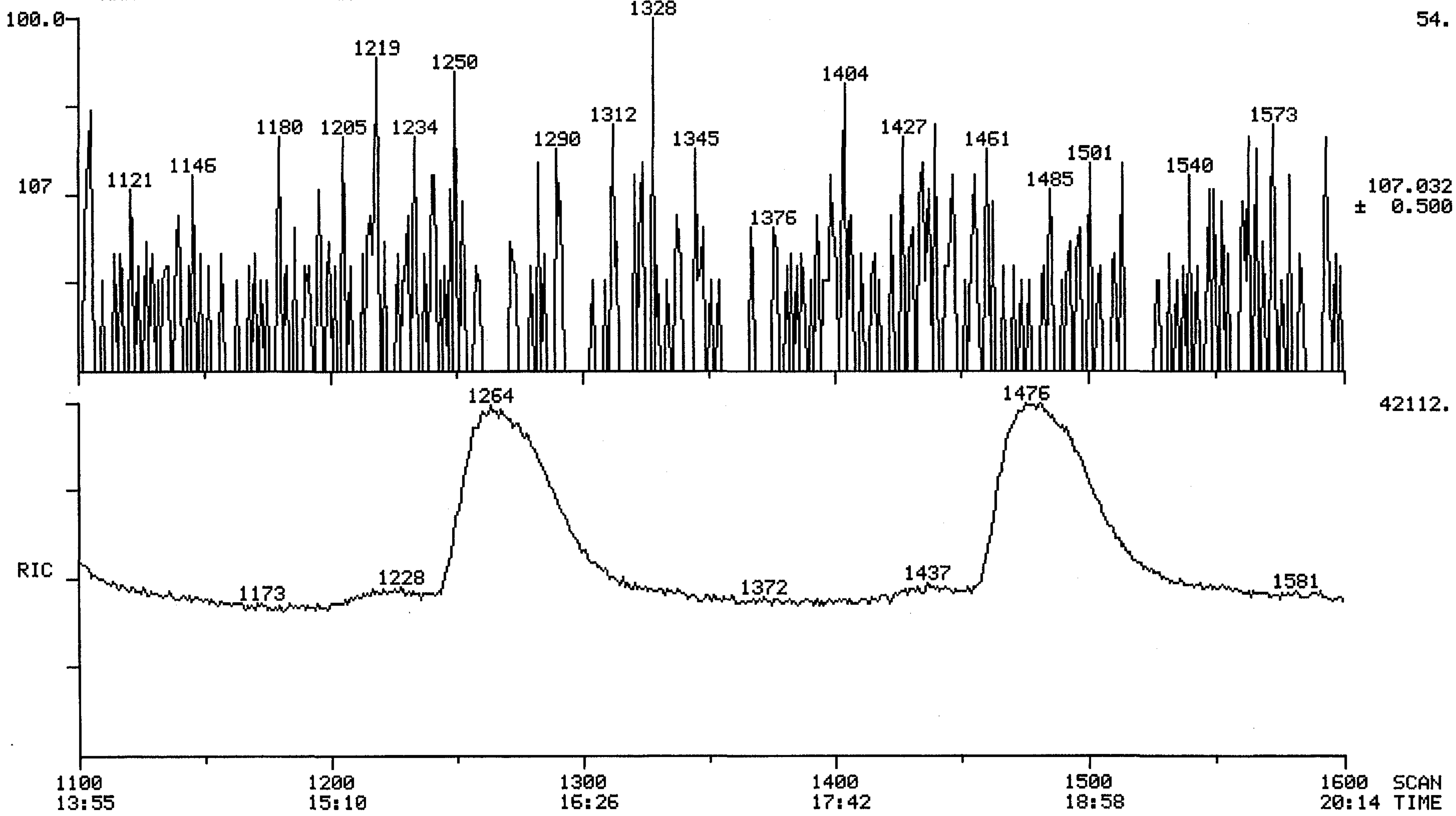
```
RIC+MASS CHROMATOGRAMS                DATA: ICI08 #1          SCANS 1100 TO 1600
09/15/94 10:55:00                     CALI: CALTAB #3
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G   1,3209  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



RIC+MASS CHROMATOGRAM
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

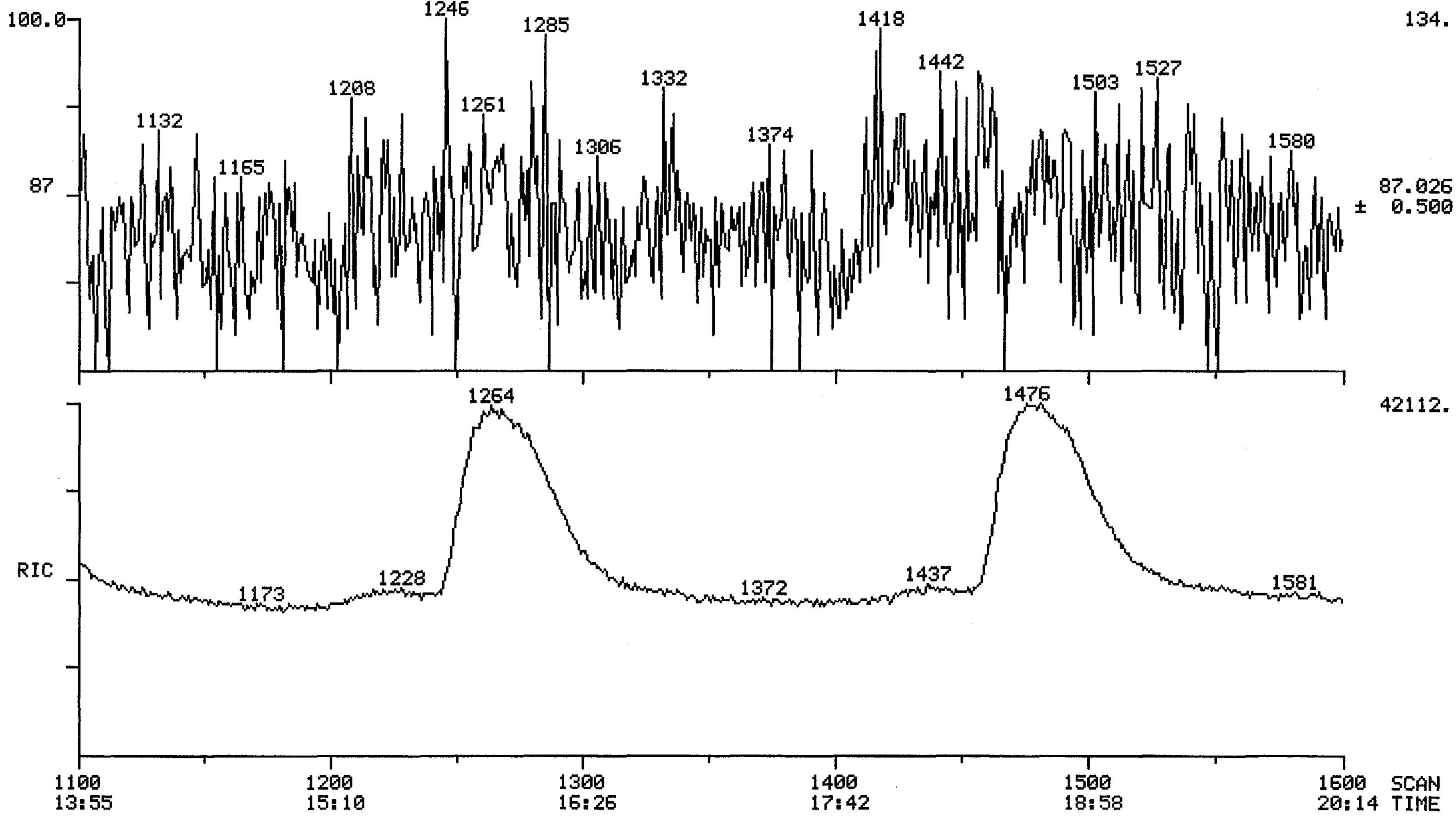
SCANS 1100 TO 1600



RIC+MASS CHROMATOGRAM
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

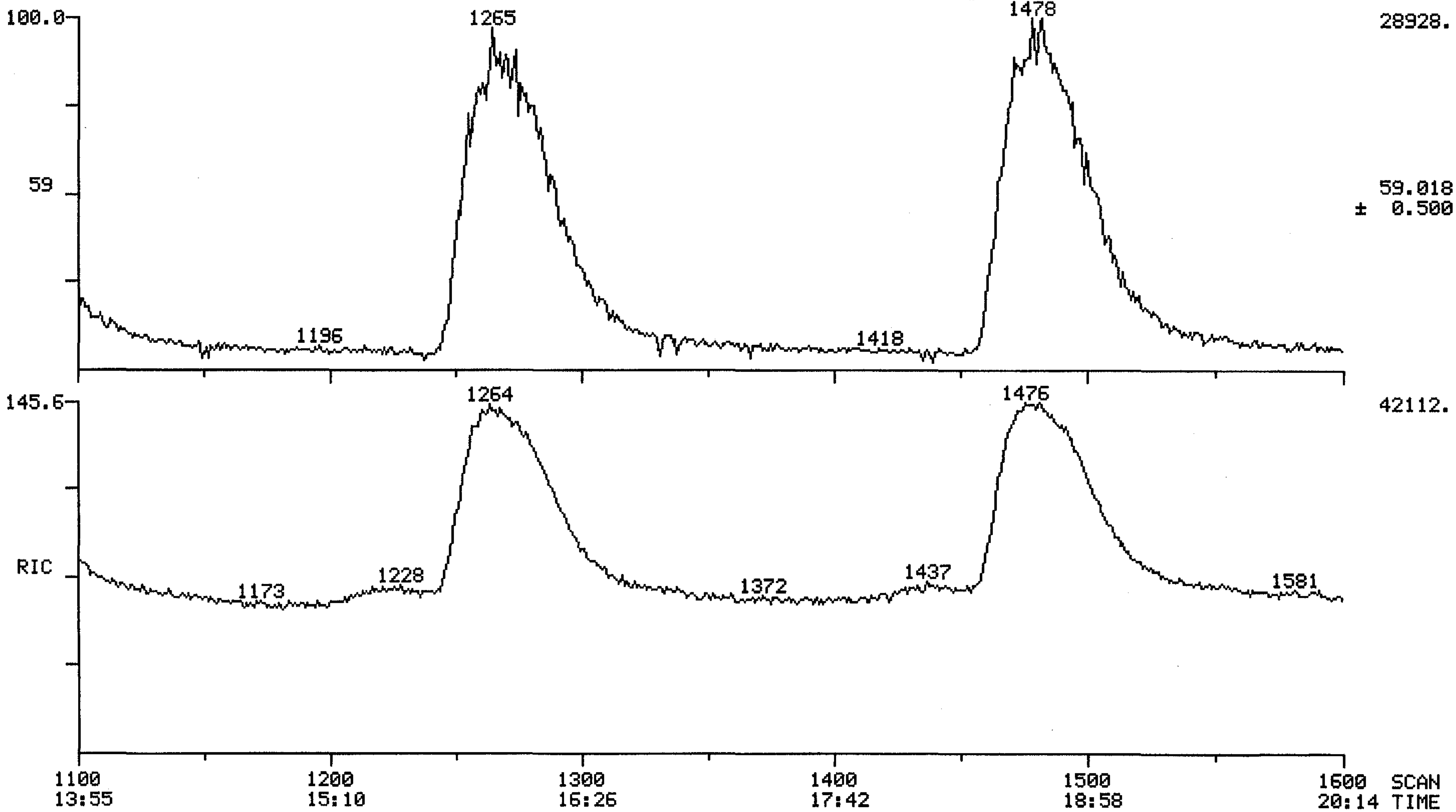
SCANS 1100 TO 1600



RIC+MASS CHROMATOGRAM
09/15/94 10:55:00
SAMPLE: INTEL-SN 22
CONDS.: 120 CI
RANGE: G 1,3209 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI08 #1
CALI: CALTAB #3

SCANS 1100 TO 1600

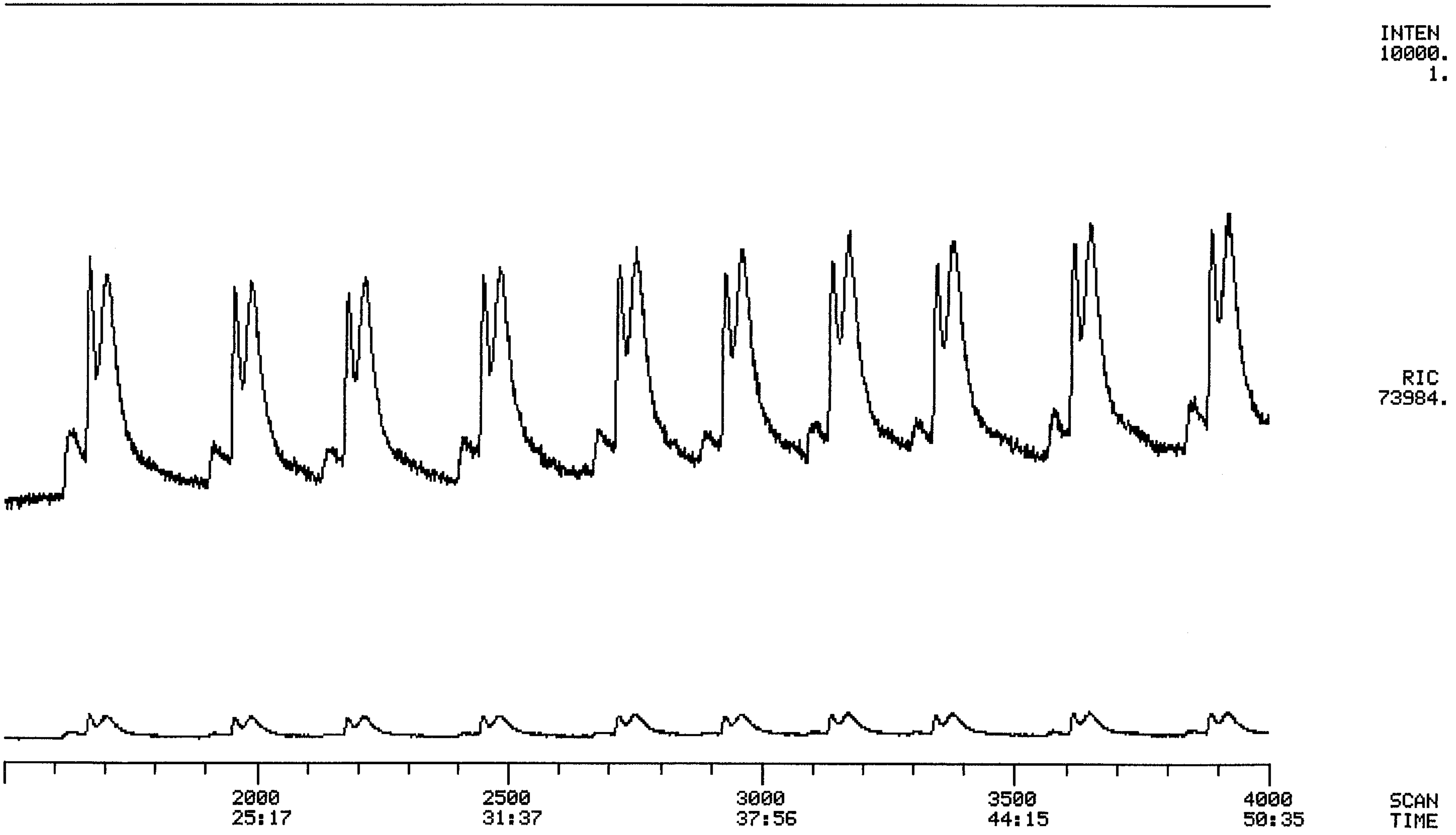


C
@ INTEL

RIC
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI

DATA: ICI09 #1
CALI: CALTAB #3

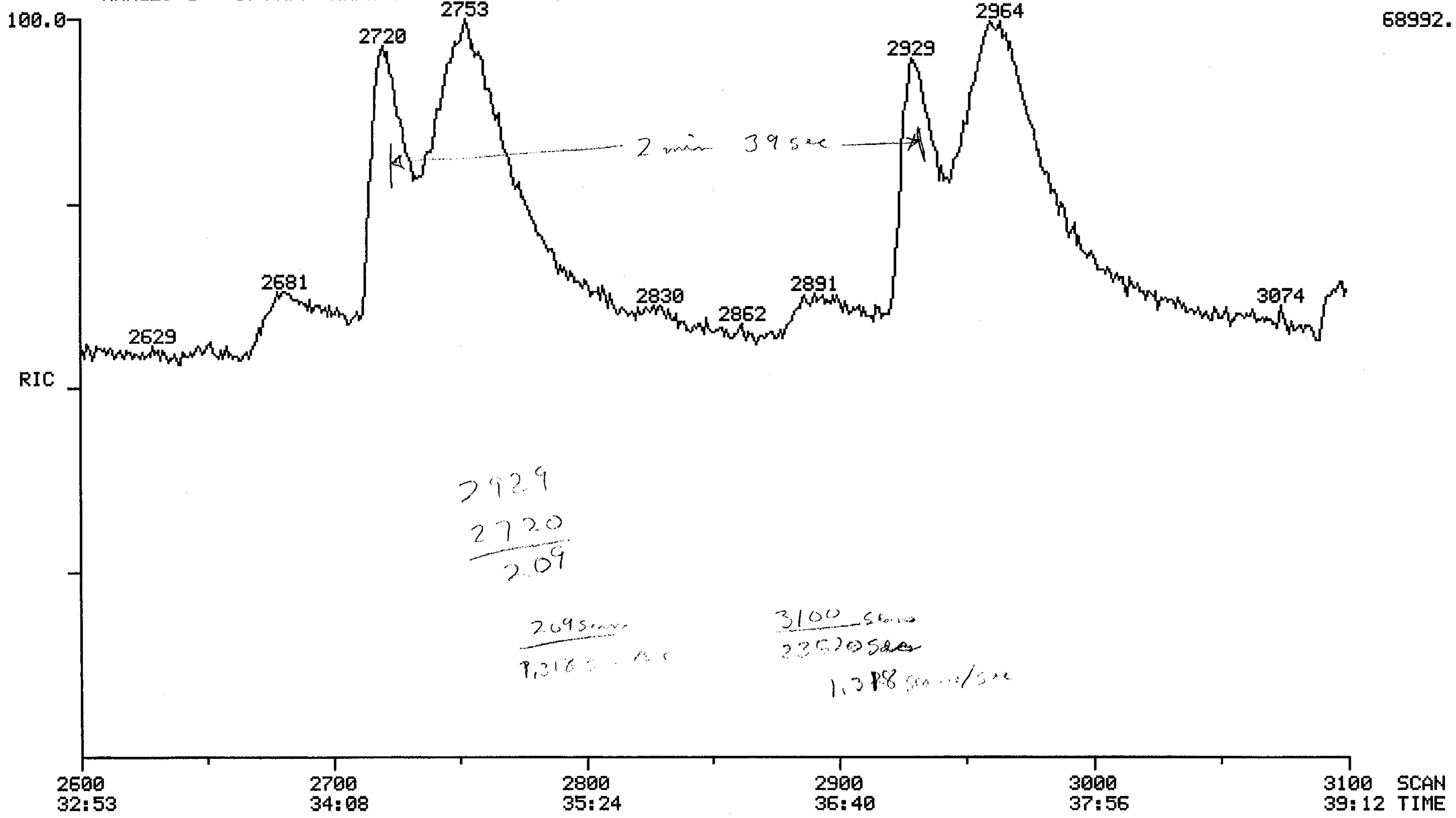
SCANS 1500 TO 4000



RIC
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI
RANGE: G 1,4484 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI09 #1
CALI: CALTAB #3

SCANS 2600 TO 3100



2 min 39 sec

2929
2720
209

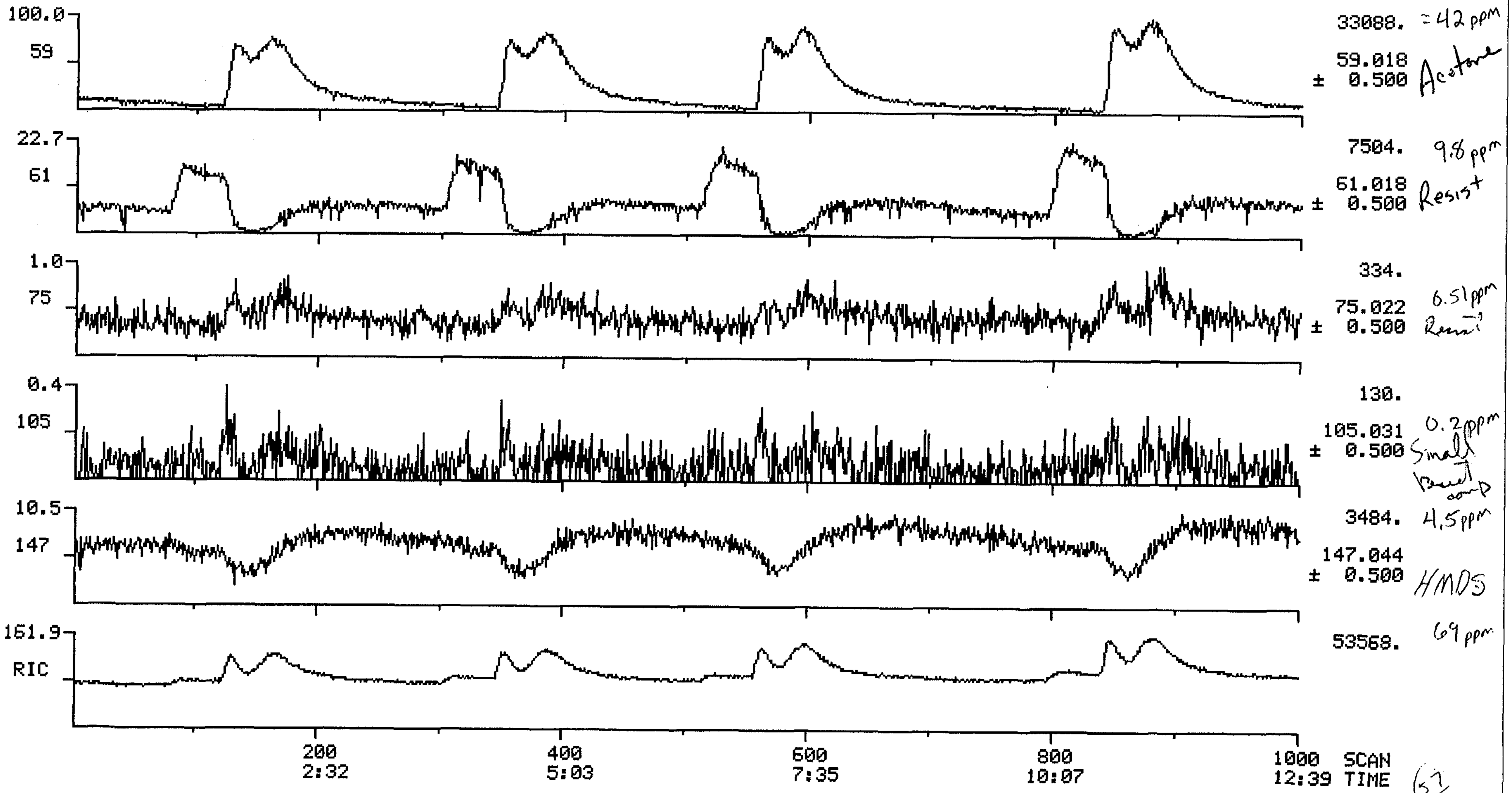
209 scans
1,316 s… sec

3100 scans
2352 secs
1,318 scans/sec

RIC+MASS CHROMATOGRAMS
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI
RANGE: G 1,4484 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI09 #1
CALI: CALTAB #3

SCANS 1 TO 1000

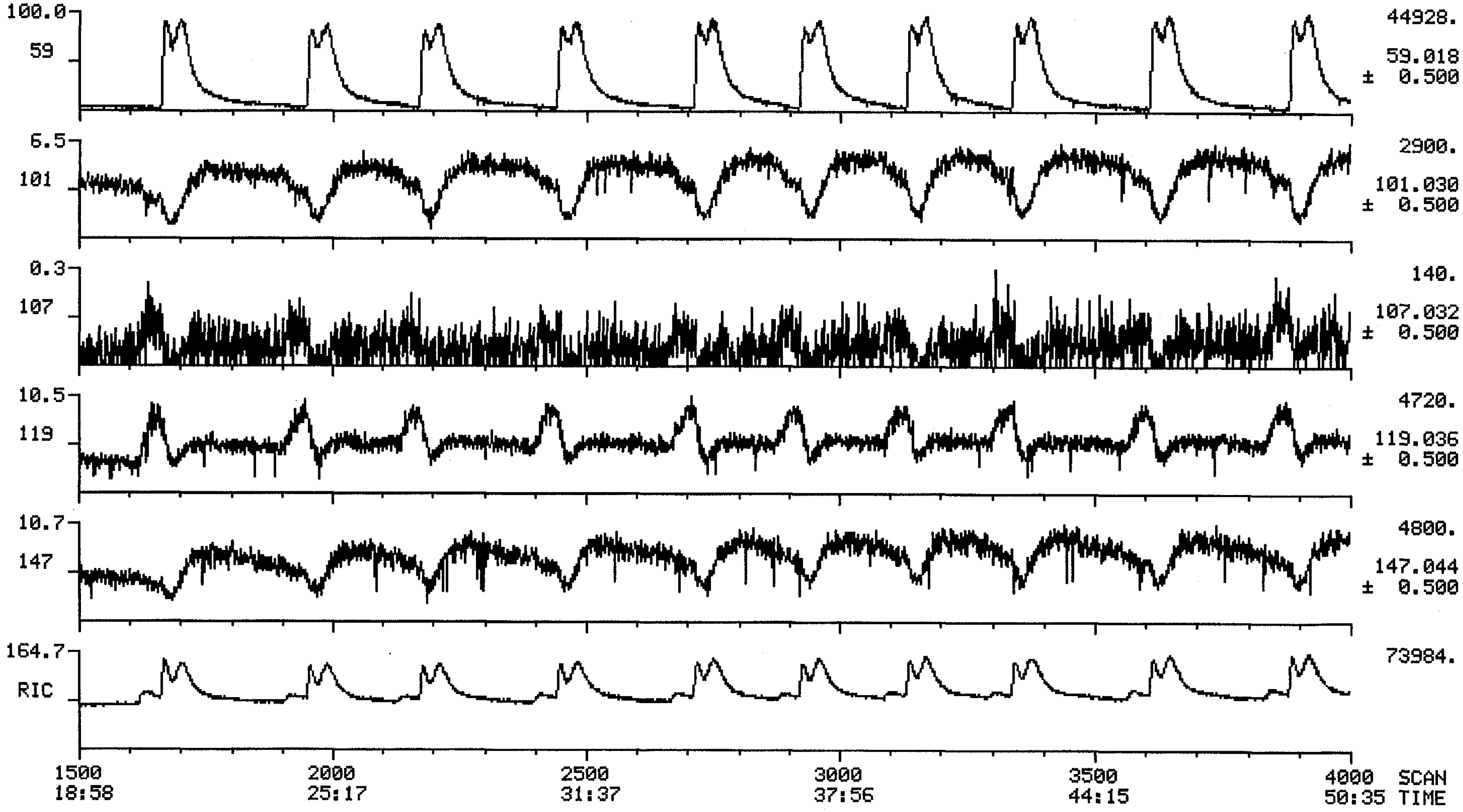


57/69

RIC+MASS CHROMATOGRAMS
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI
RANGE: G 1,4484 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI09 #1
CALI: CALTAB #3

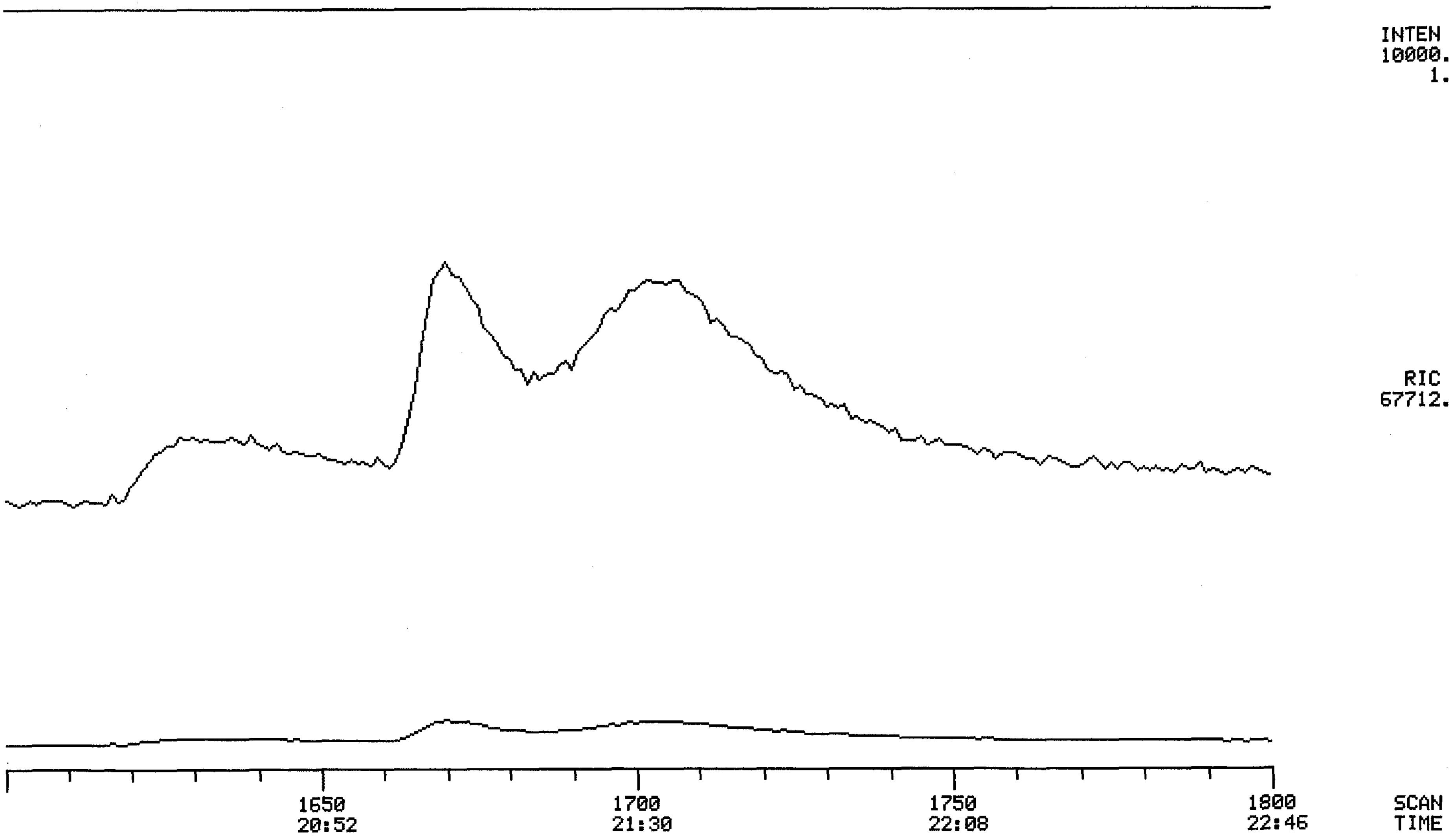
SCANS 1500 TO 4000



RIC
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI

DATA: ICI09 #1
CALI: CALTAB #3

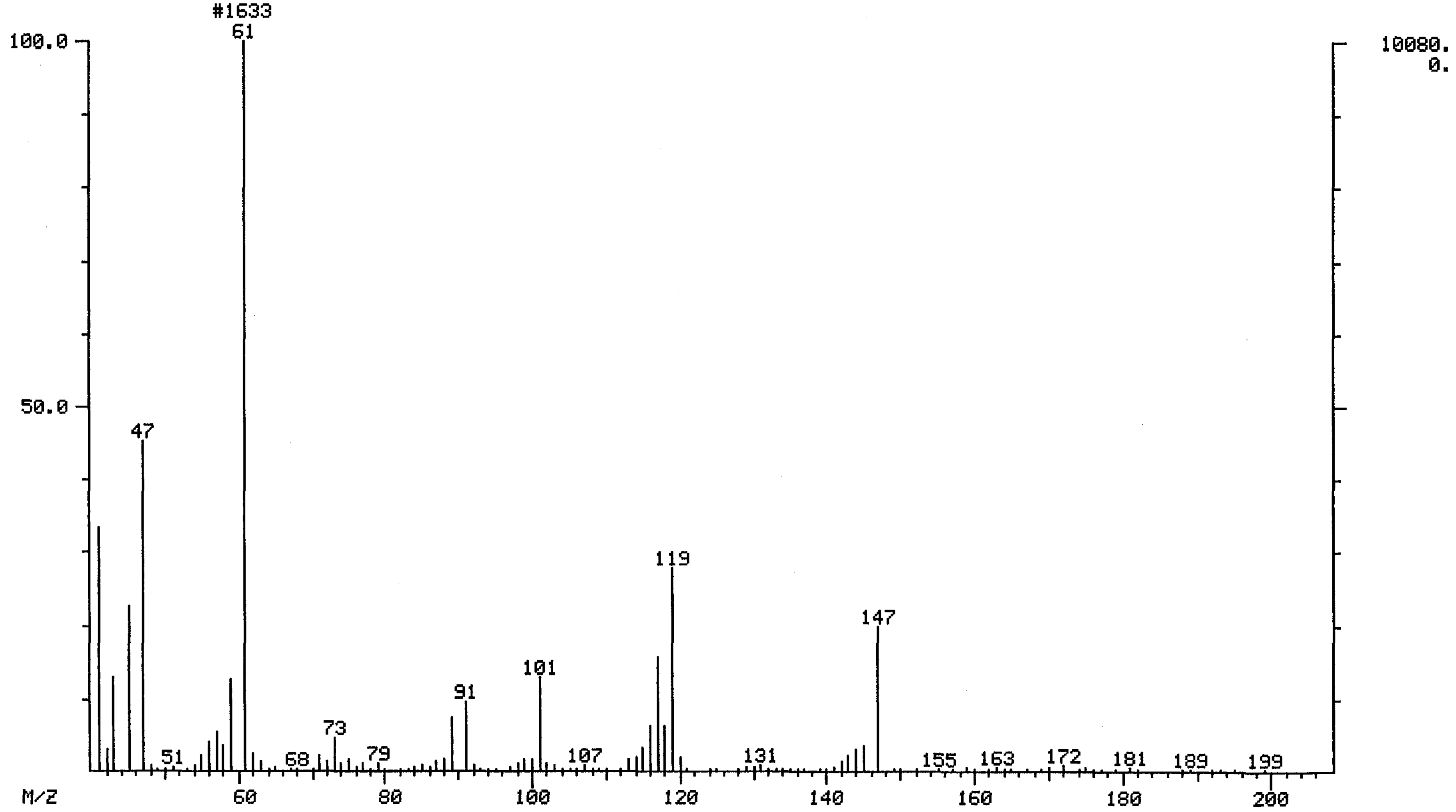
SCANS 1600 TO 1800



MASS SPECTRUM
09/15/94 11:34:00 + 20:39
SAMPLE: INTEL SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI09 #1633
CALI: CALTAB #3

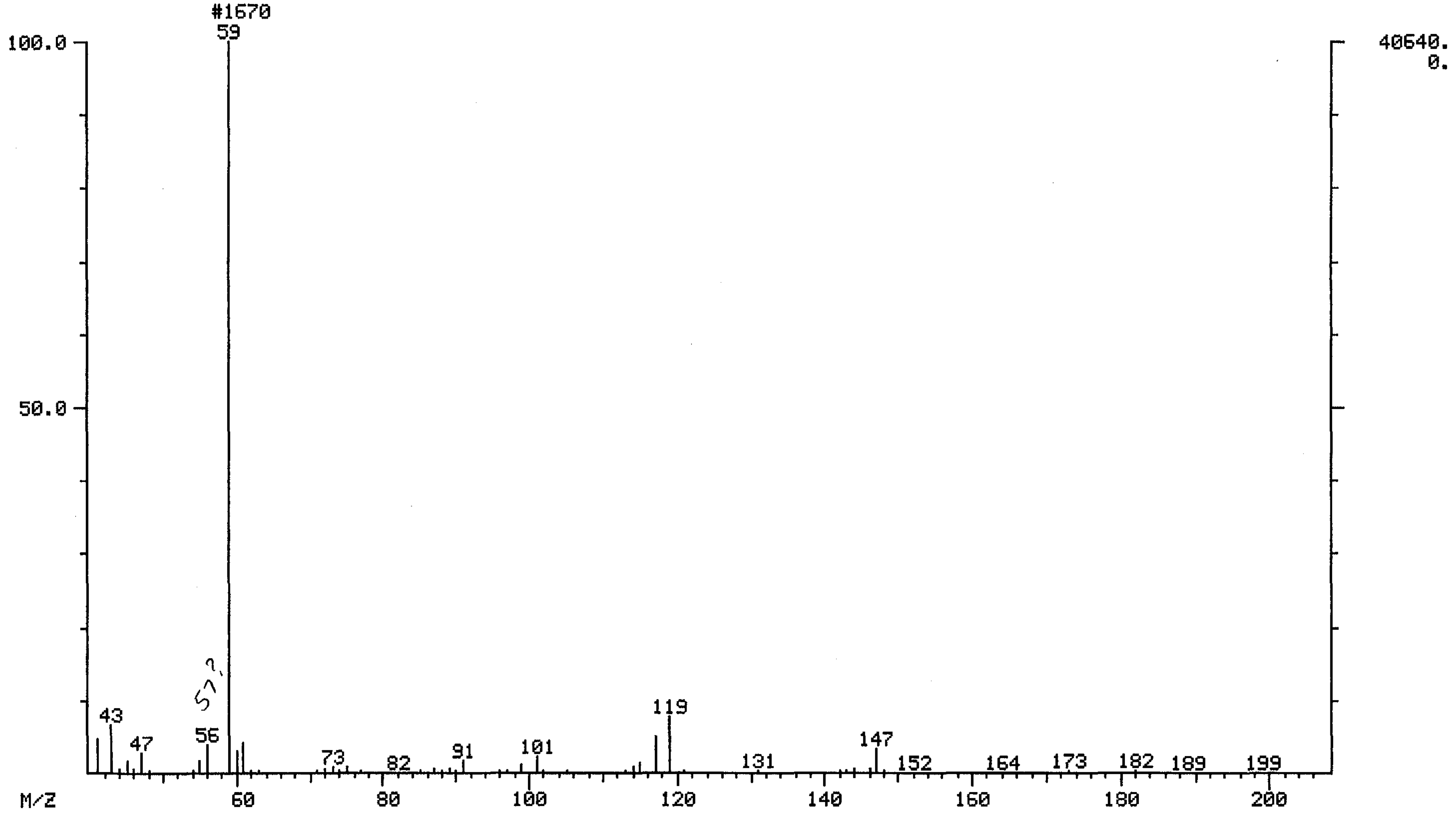
BASE M/Z: 61
RIC: 42688.



MASS SPECTRUM
09/15/94 11:34:00 + 21:07
SAMPLE: INTEL SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C

DATA: ICI09 #1670
CALI: CALTAB #3

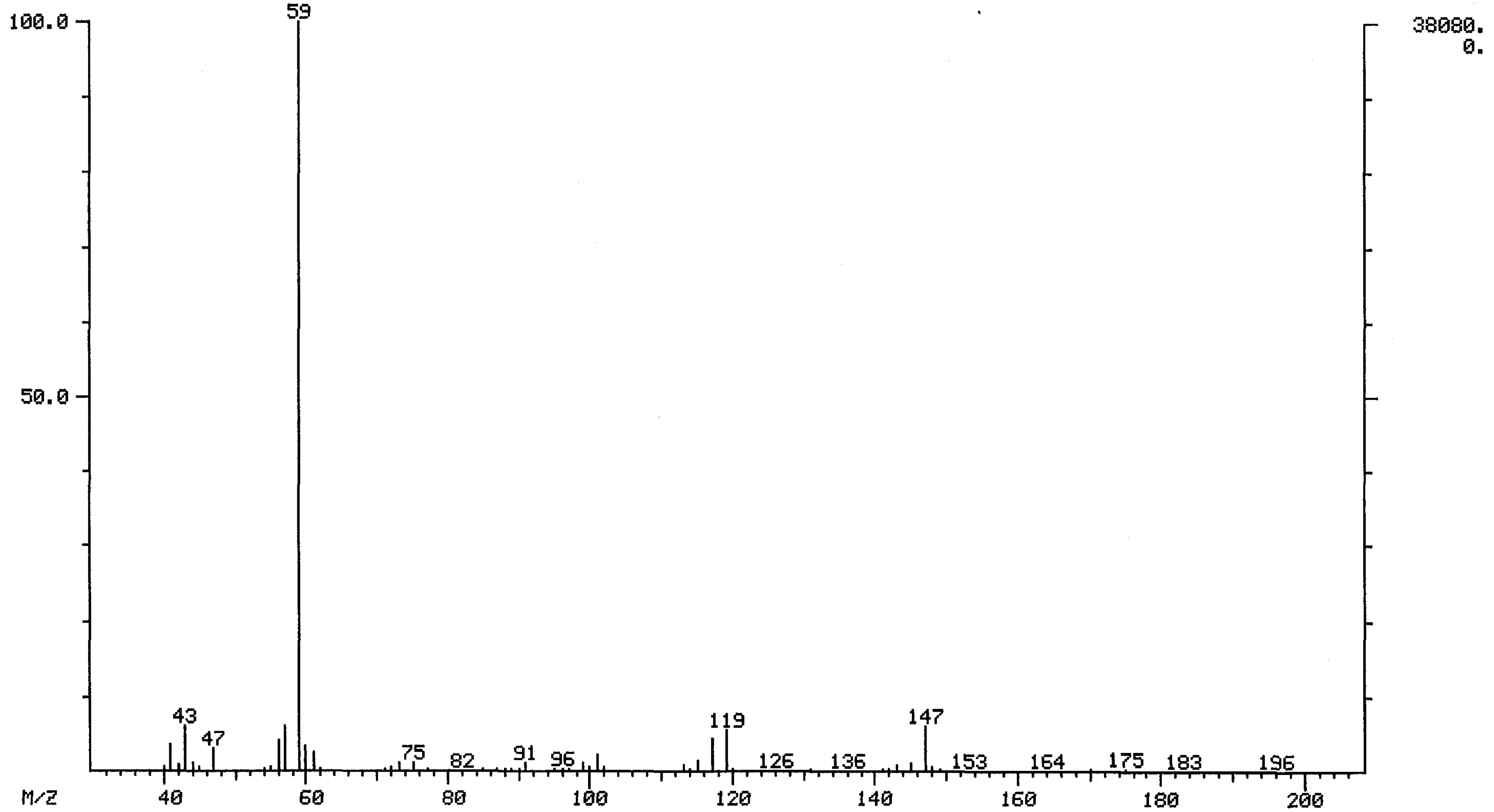
BASE M/Z: 59
RIC: 67200.



MASS SPECTRUM
09/15/94 11:34:00 + 21:33
SAMPLE: INTEL SN 21
CONDS.: 120 CI
TEMP: 0 DEG. C
#1704

DATA: ICI09 #1704
CALI: CALTAB #3

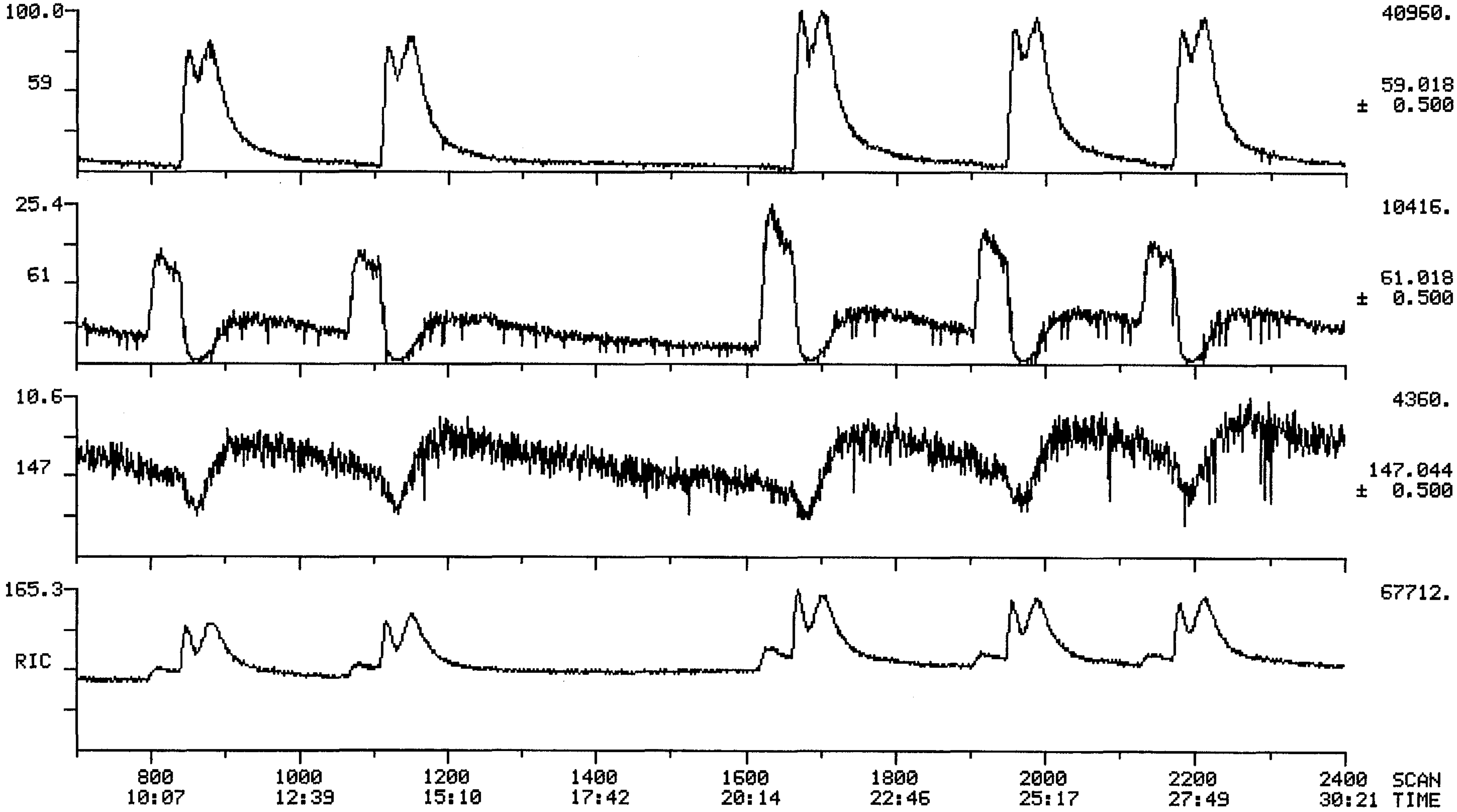
BASE M/Z: 59
RIC: 64832.



RIC+MASS CHROMATOGRAMS
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI
RANGE: G 1,4484 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI09 #1
CALI: CALTAB #3

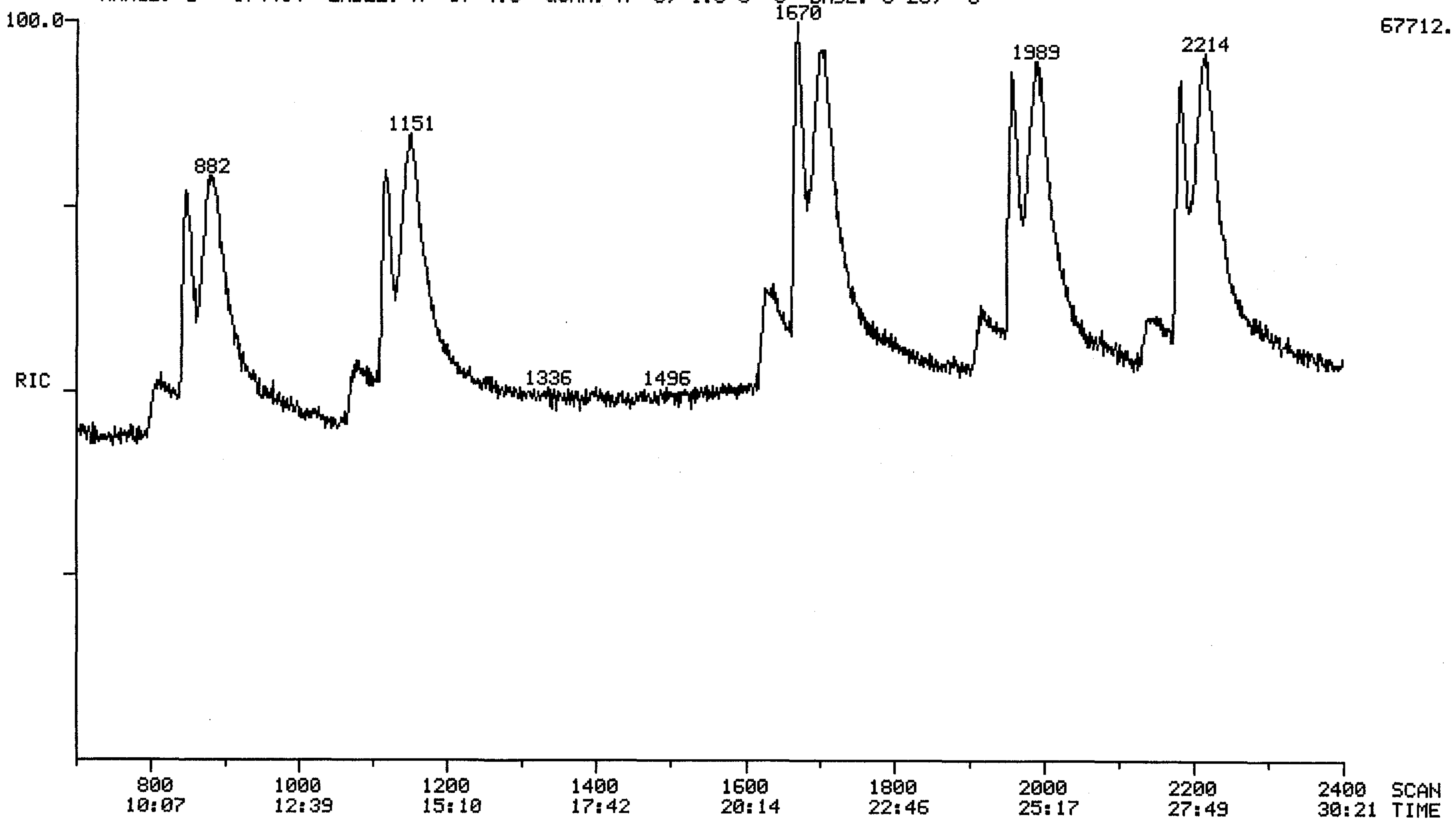
SCANS 700 TO 2400



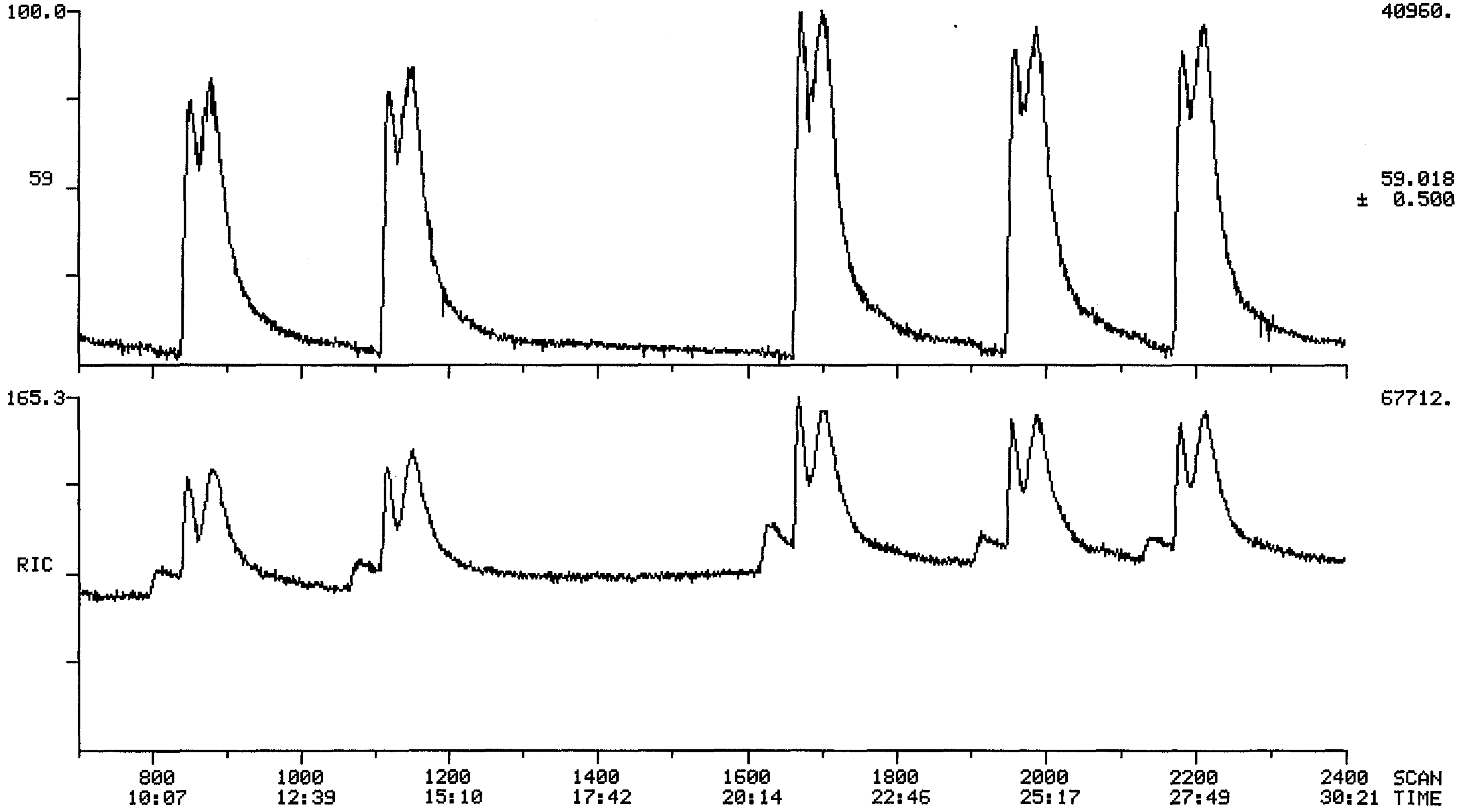
RIC
09/15/94 11:34:00
SAMPLE: INTEL SN 21
CONDS.: 120 CI
RANGE: G 1,4484 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: ICI09 #1
CALI: CALTAB #3

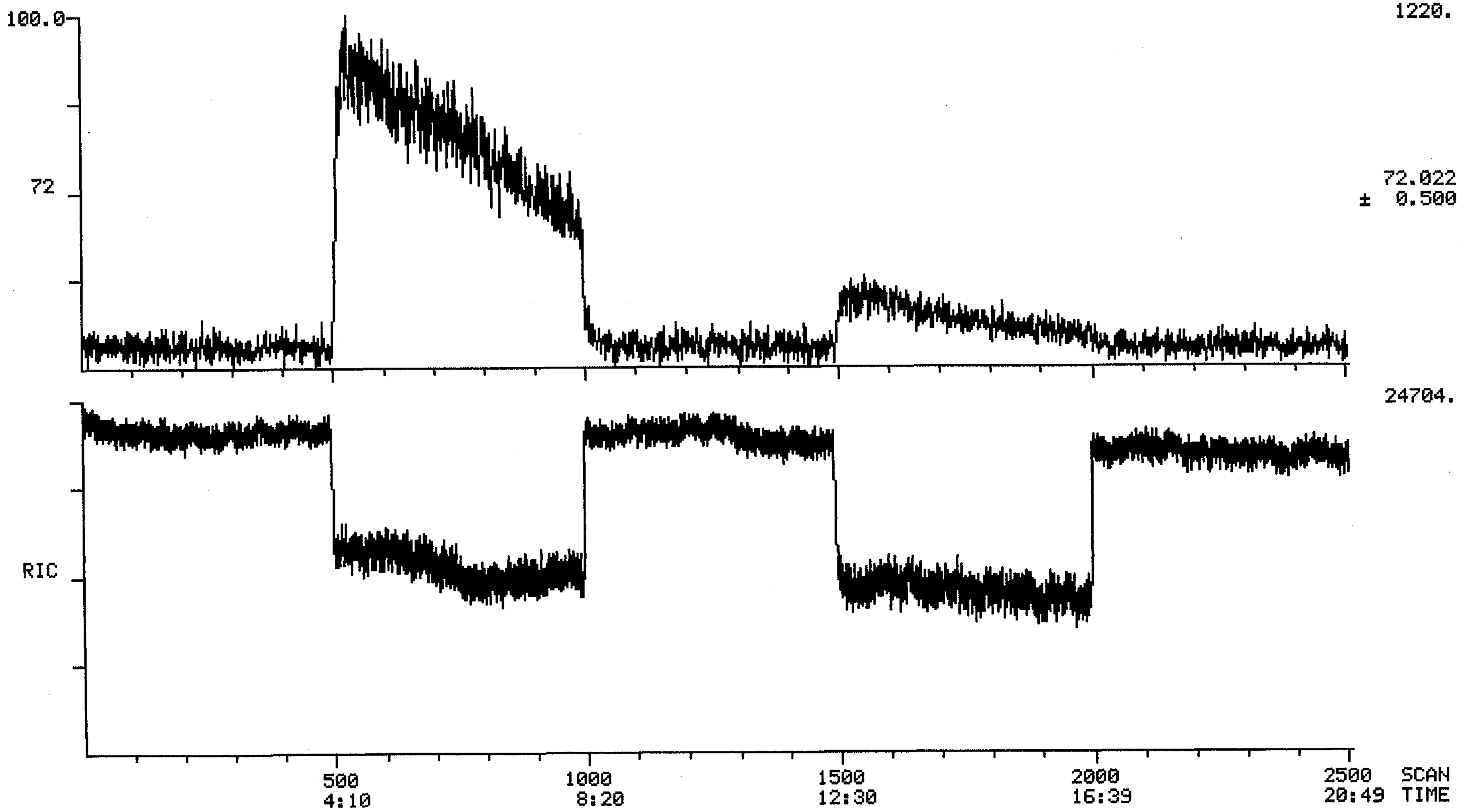
SCANS 700 TO 2400



```
RIC+MASS CHROMATOGRAM                    DATA: ICI09 #1          SCANS  700 TO 2400
09/15/94 11:34:00                        CALI: CALTAB #3
SAMPLE: INTEL SN 21
CONDS.: 120 CI
RANGE: G   1,4484  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

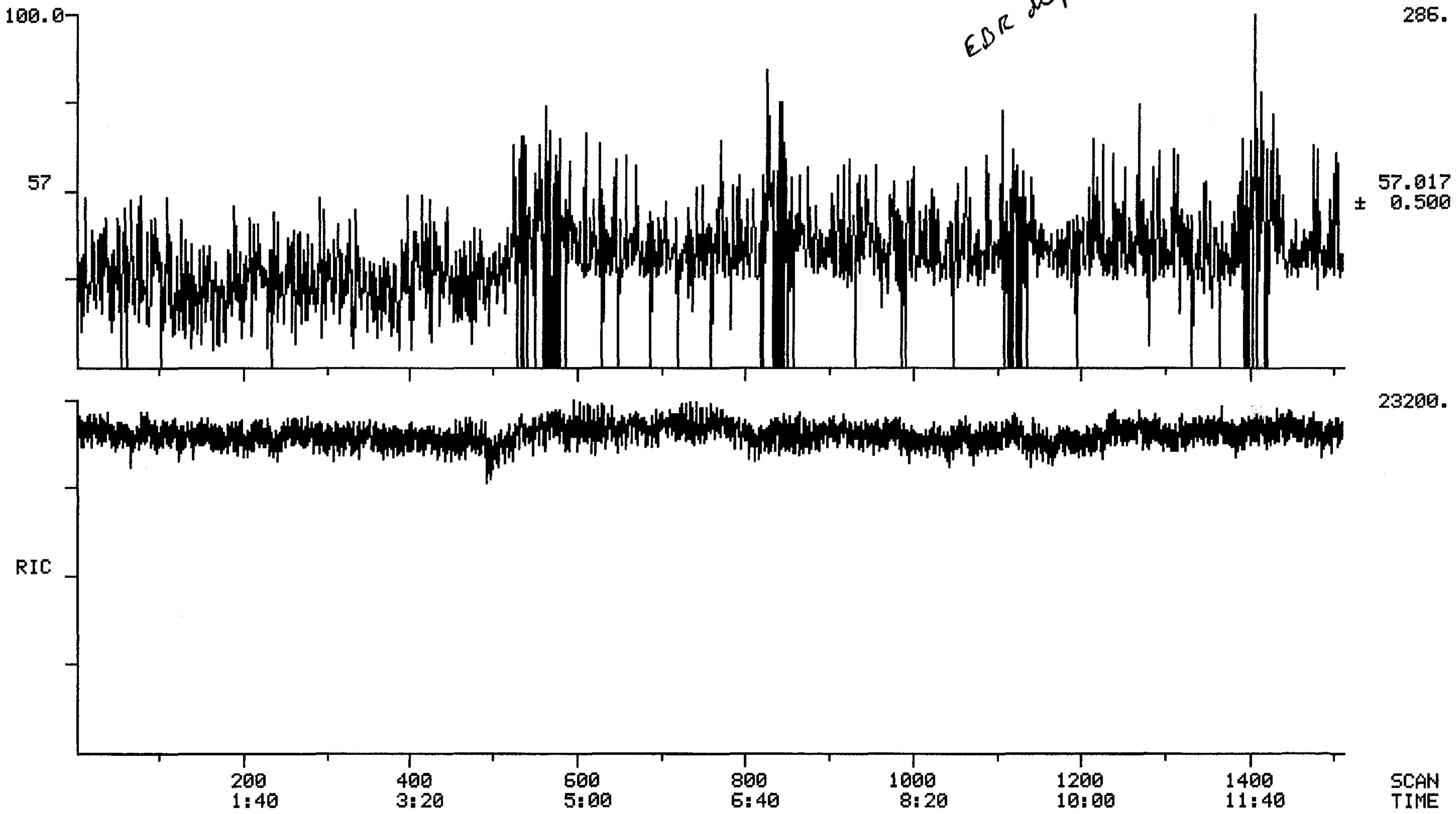


```
RIC+MASS CHROMATOGRAM                 DATA: IEI02 #1          SCANS    1 TO 2507
09/14/94 10:20:00                     CALI: CALTAB #3
SAMPLE: TRIAL RUN
CONDS.: 110
RANGE: G   1,2507  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



```
RIC+MASS CHROMATOGRAM                      DATA: IEI03 #1          SCANS    1 TO 1511
09/14/94 10:51:00                          CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G   1,1511  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

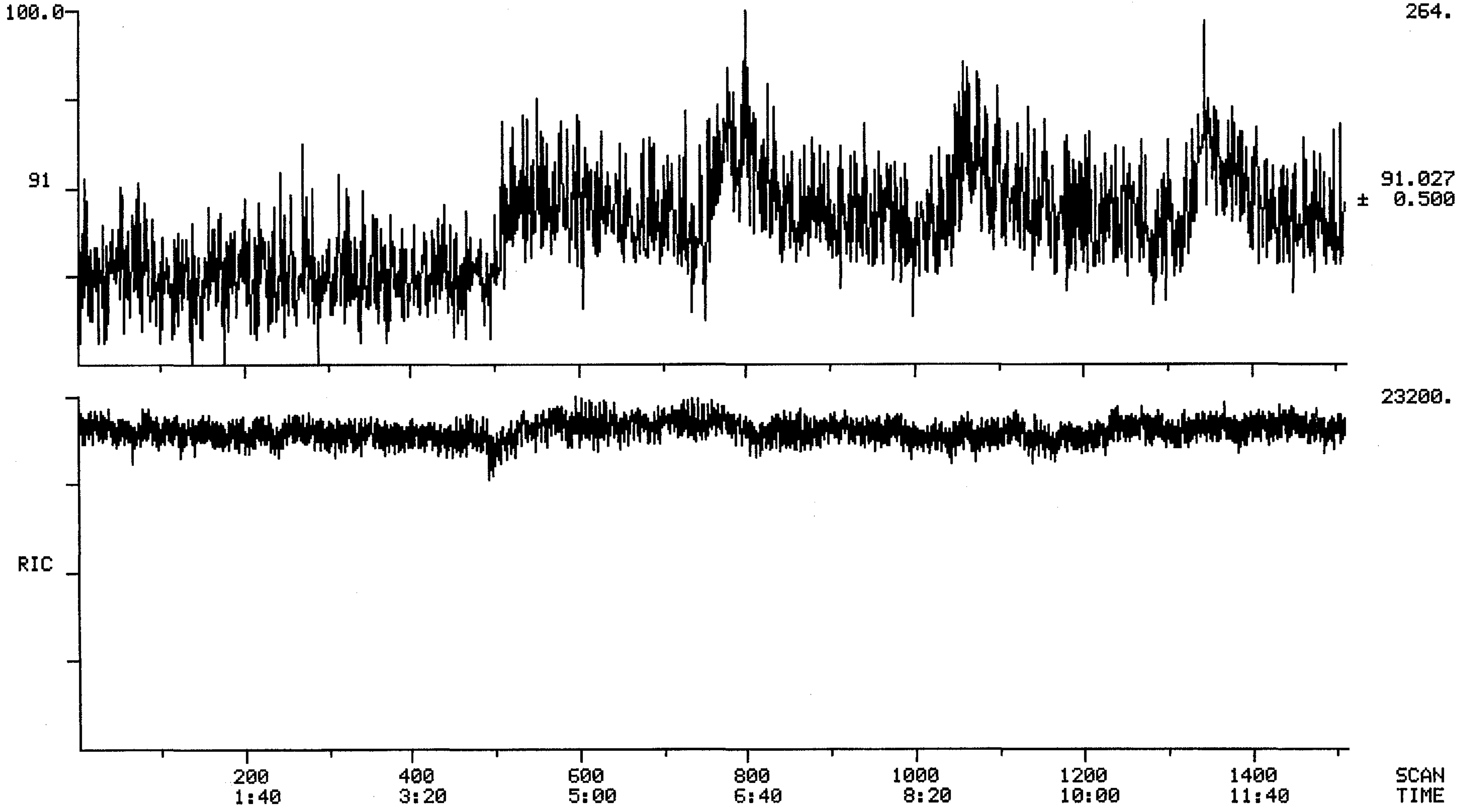
EDR dripped = 10 sec



RIC+MASS CHROMATOGRAM
09/14/94 10:51:00
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G 1,1511 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

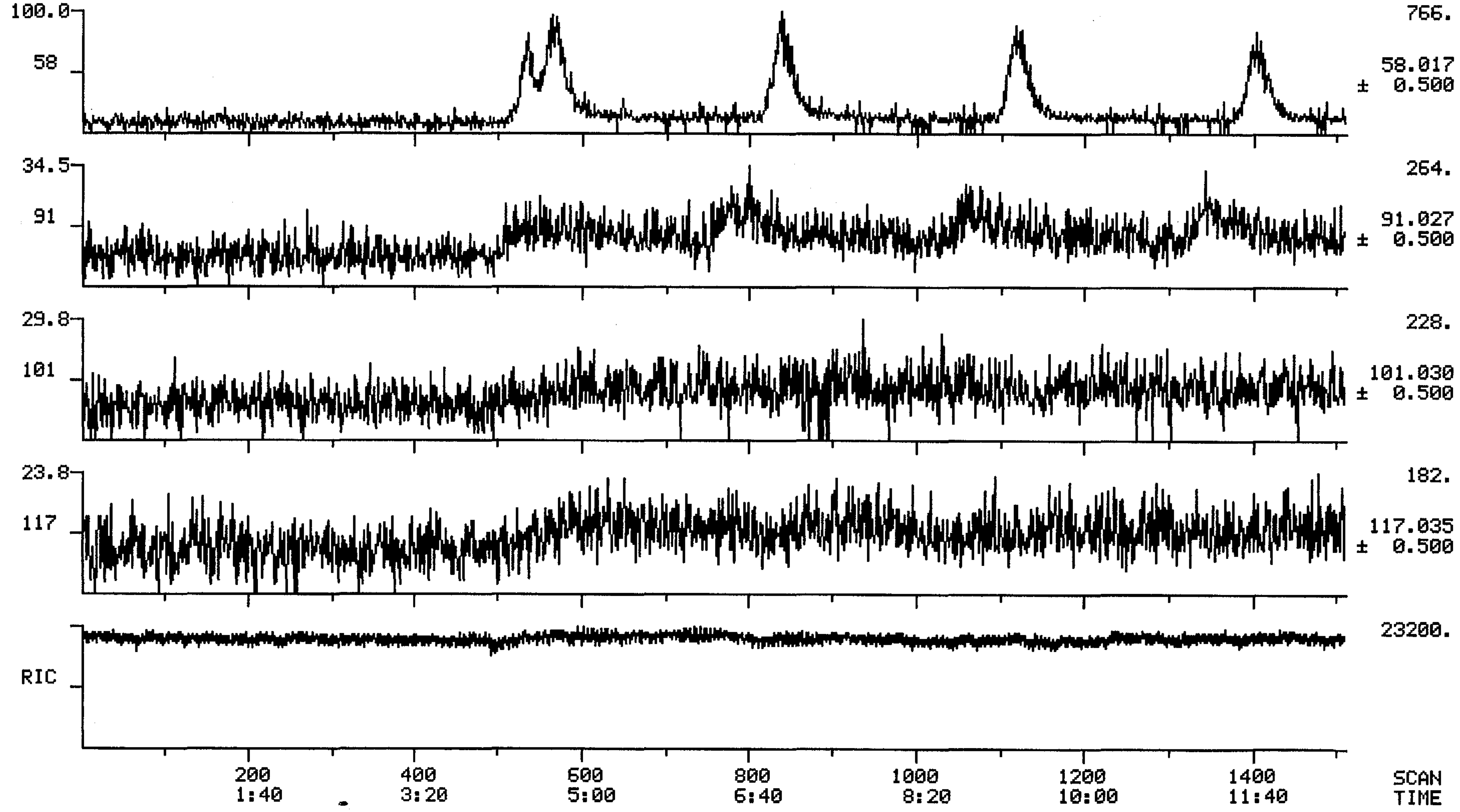
DATA: IEI03 #813
CALI: CALTAB #3

SCANS 1 TO 1511

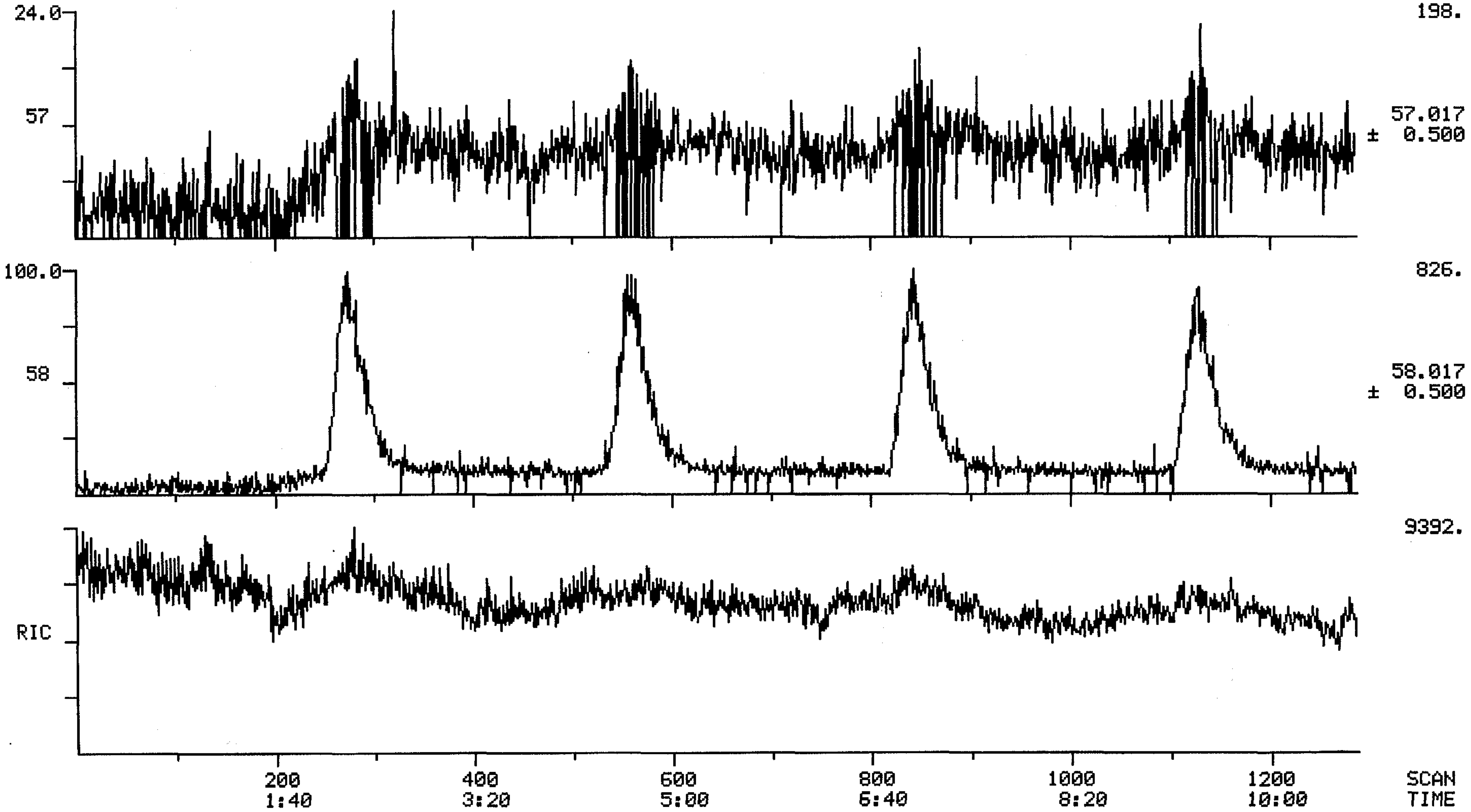


fou. $\rho \leq .057$

RIC+MASS CHROMATOGRAMS DATA: IEI03 #1 SCANS 1 TO 1511
09/14/94 10:51:00 CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G 1,1511 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

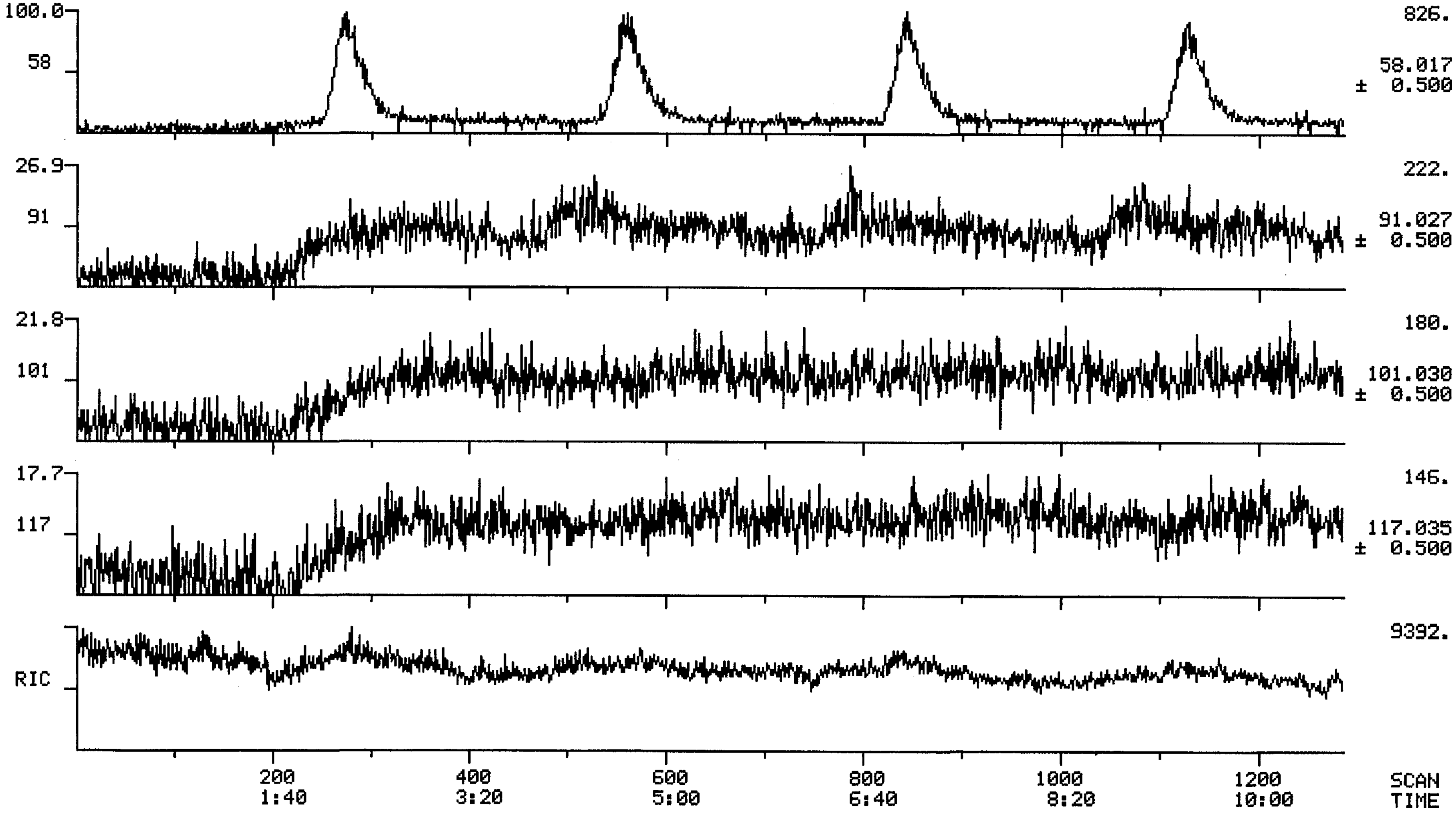


```
RIC+MASS CHROMATOGRAMS              DATA: IEI04 #760         SCANS    1 TO 1286
09/14/94 11:31:00                   CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G   1,1286  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

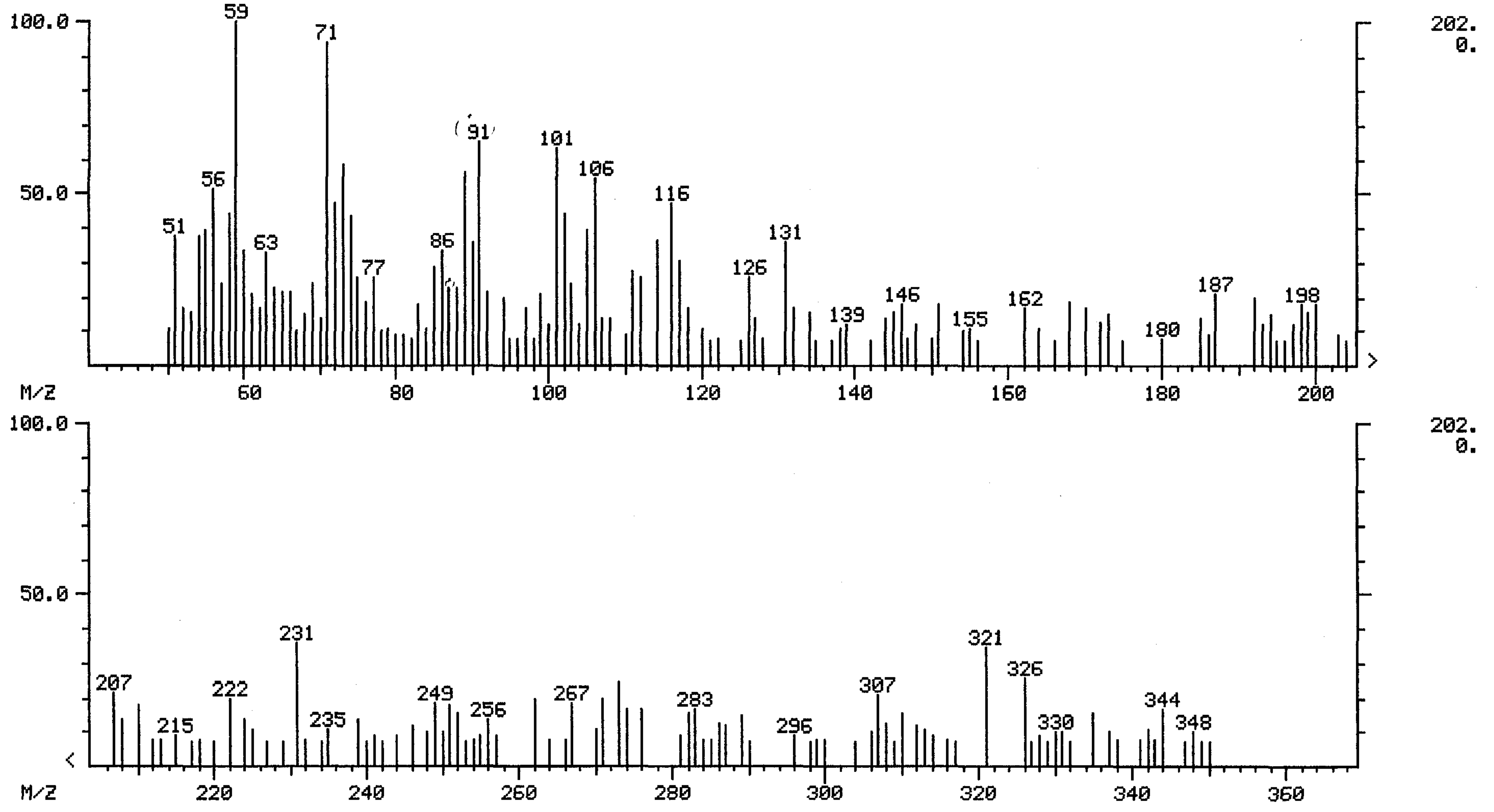


for P= ,030

```
RIC+MASS CHROMATOGRAMS                DATA: IEI04 #760        SCANS    1 TO 1286
09/14/94 11:31:00                     CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G   1,1286  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



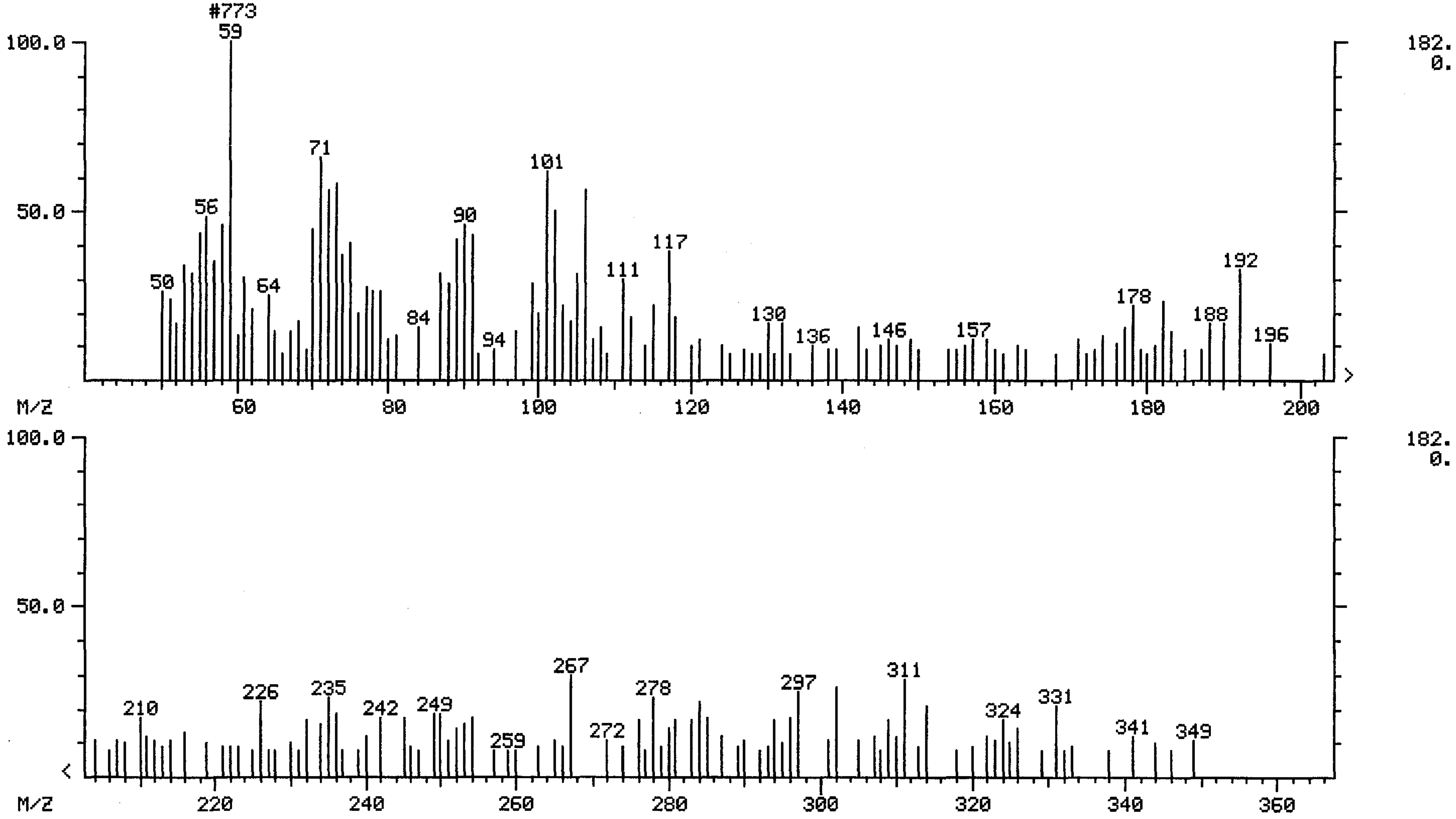
```
MASS SPECTRUM                                   DATA: IEI04 #802           BASE M/Z:  59
09/14/94 11:31:00 +  6:41                       CALI: CALTAB #3            RIC:       7152.
SAMPLE: INTEL-SN 11
CONDS.: 180
TEMP:    0 DEG. C
 #802
```



MASS SPECTRUM
09/14/94 11:31:00 + 6:26
SAMPLE: INTEL-SN 11
CONDS.: 180
TEMP: 0 DEG. C

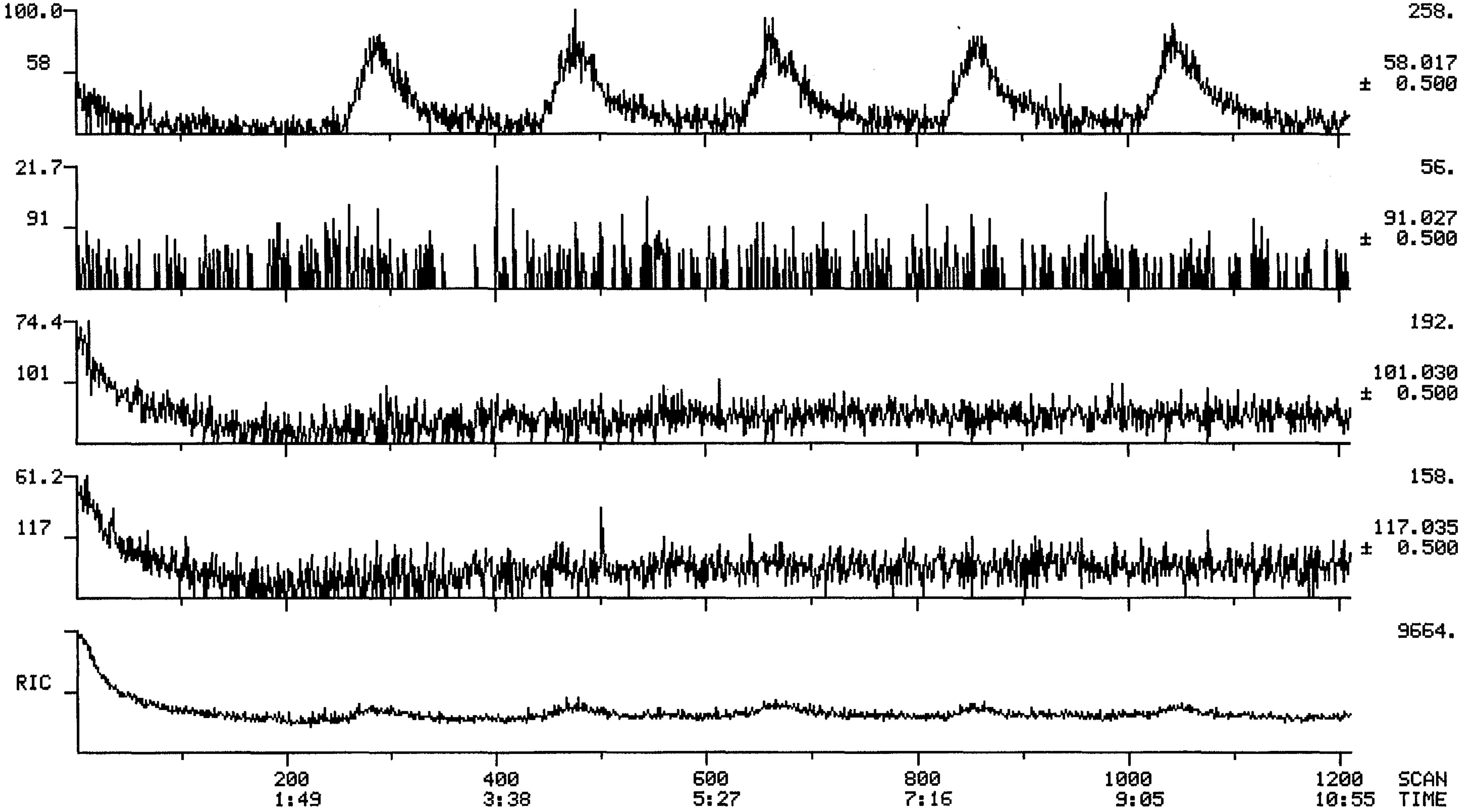
DATA: IEI04 #773
CALI: CALTAB #3

BASE M/Z: 59
RIC: 6392.

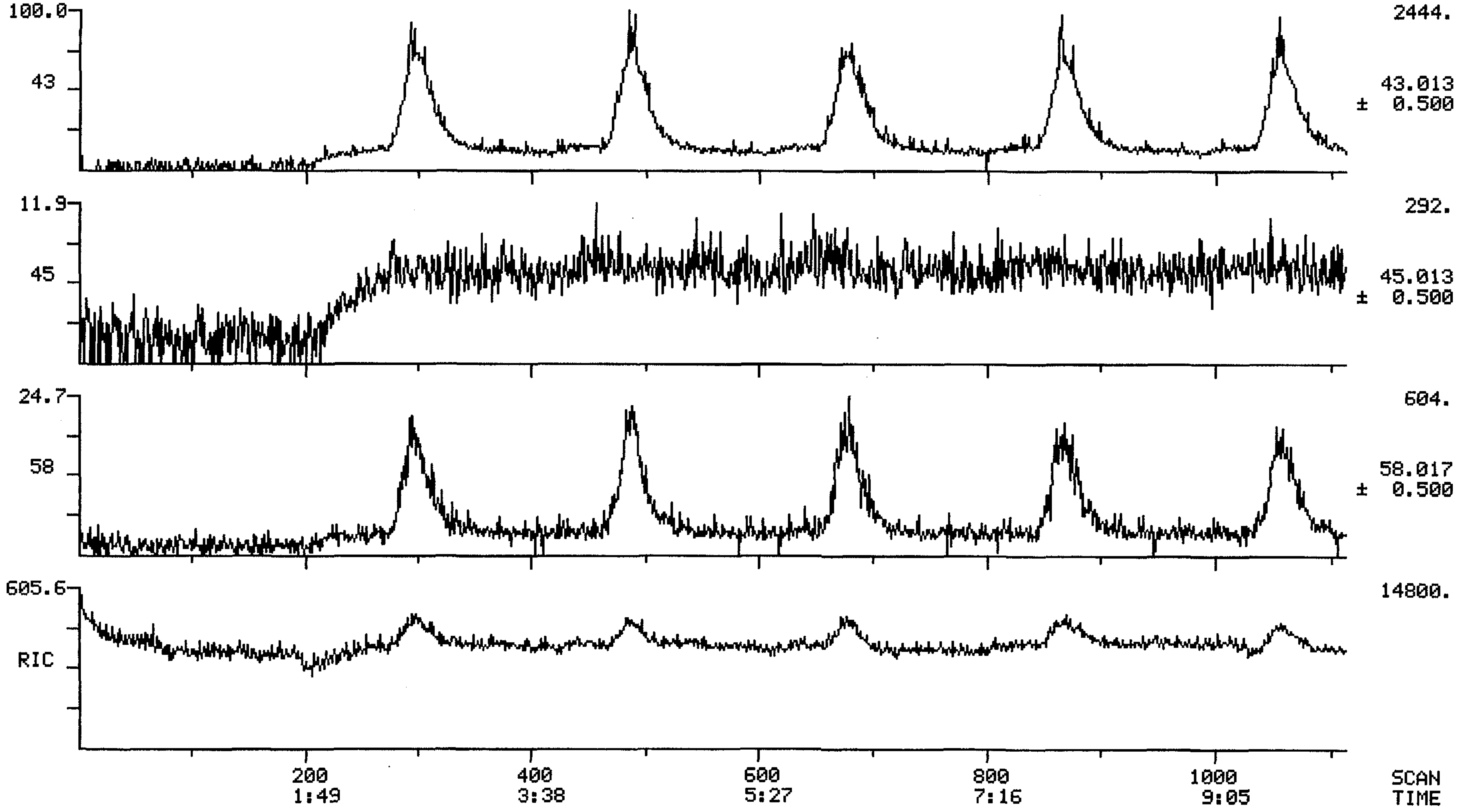


for P = .022

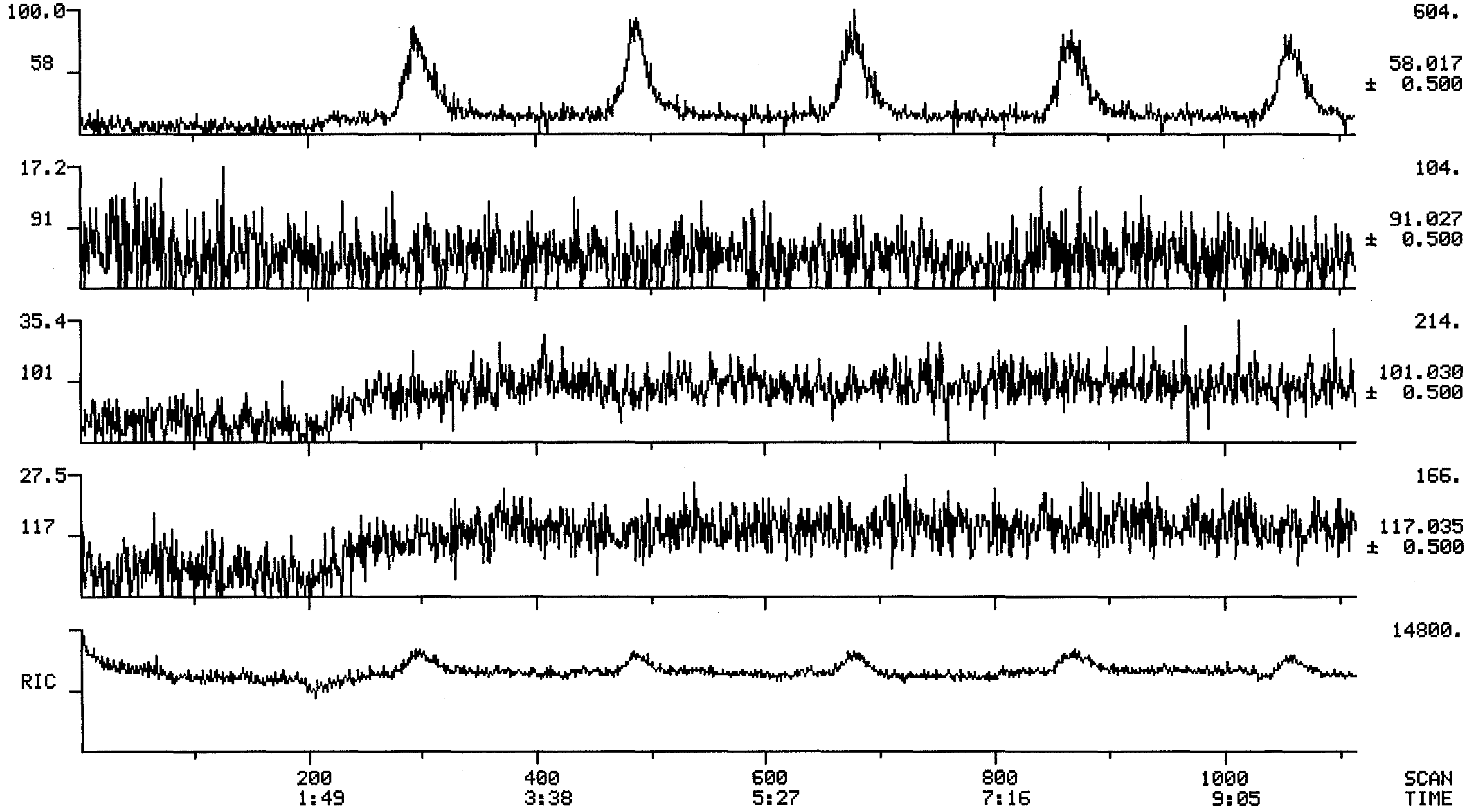
```
RIC+MASS CHROMATOGRAMS             DATA: IEI05 #1          SCANS    1 TO 1209
09/14/94 13:08:00                  CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G   1,1209  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



```
RIC+MASS CHROMATOGRAMS              DATA: IEI06 #1          SCANS    1 TO 1113
09/14/94 13:29:00                   CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G   1,1113  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



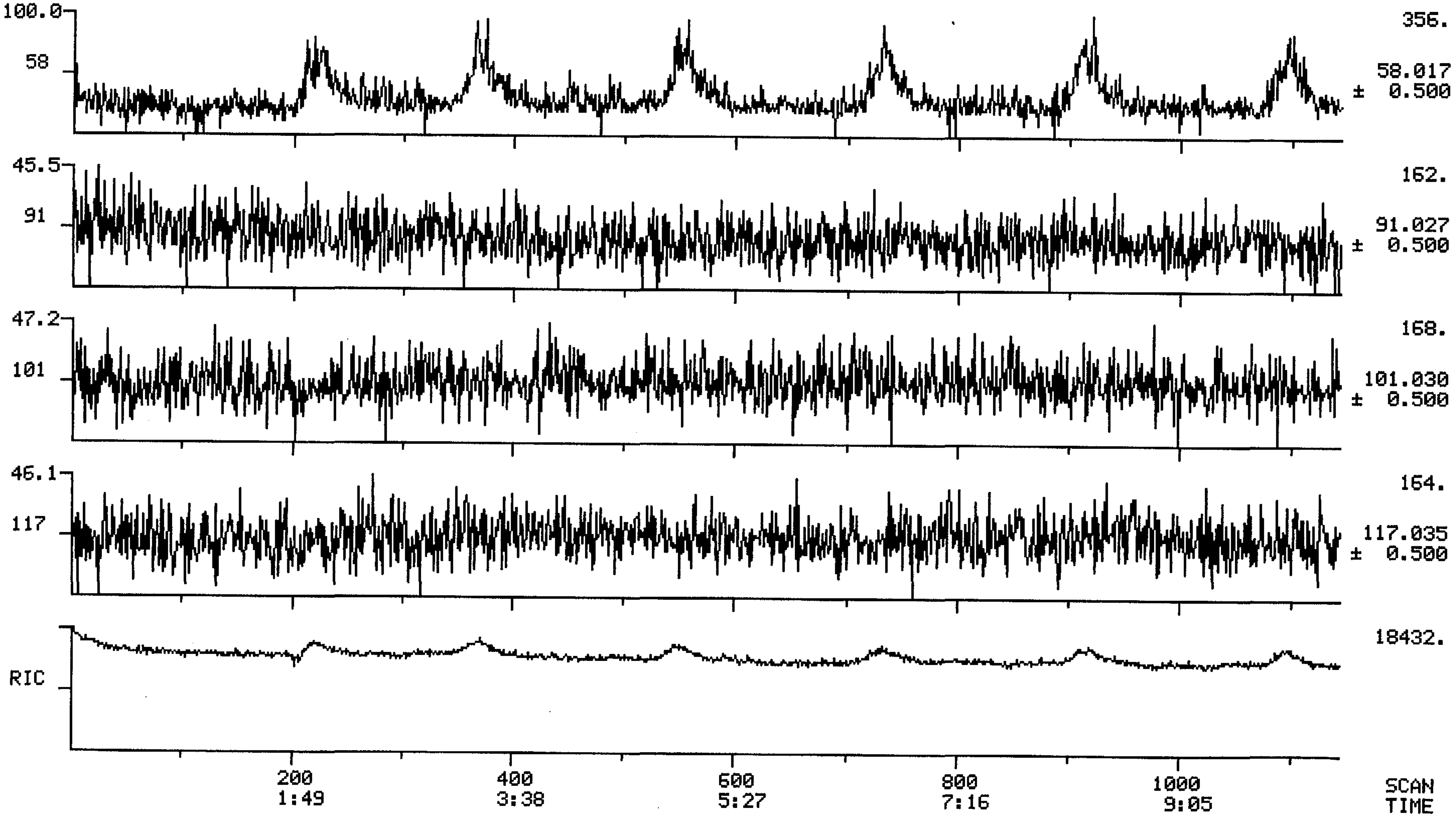
```
RIC+MASS CHROMATOGRAMS                DATA: IEI06 #1          SCANS    1 TO 1113
09/14/94 13:29:00                     CALI: CALTAB #3
SAMPLE: INTEL-SN 11
CONDS.: 180
RANGE: G   1,1113  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



RIC+MASS CHROMATOGRAMS
09/14/94 14:06:00
SAMPLE: INTEL-SN 22
CONDS.: 180
RANGE: G 1,1143 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: IEI08 #1
CALI: CALTAB #3

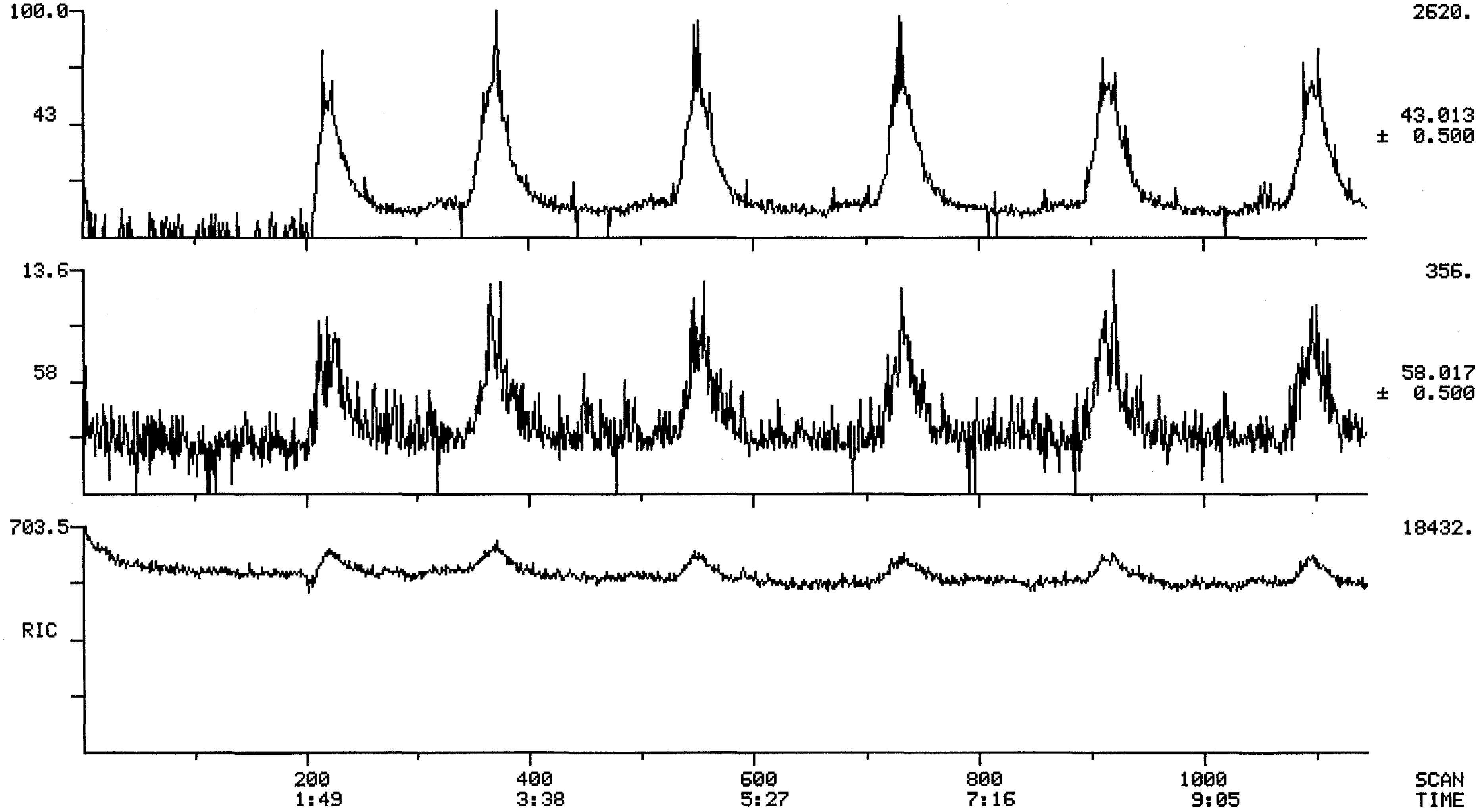
SCANS 1 TO 1143



RIC+MASS CHROMATOGRAMS
09/14/94 14:06:00
SAMPLE: INTEL-SN 22
CONDS.: 180
RANGE: G 1,1143 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: IEI08 #1
CALI: CALTAB #3

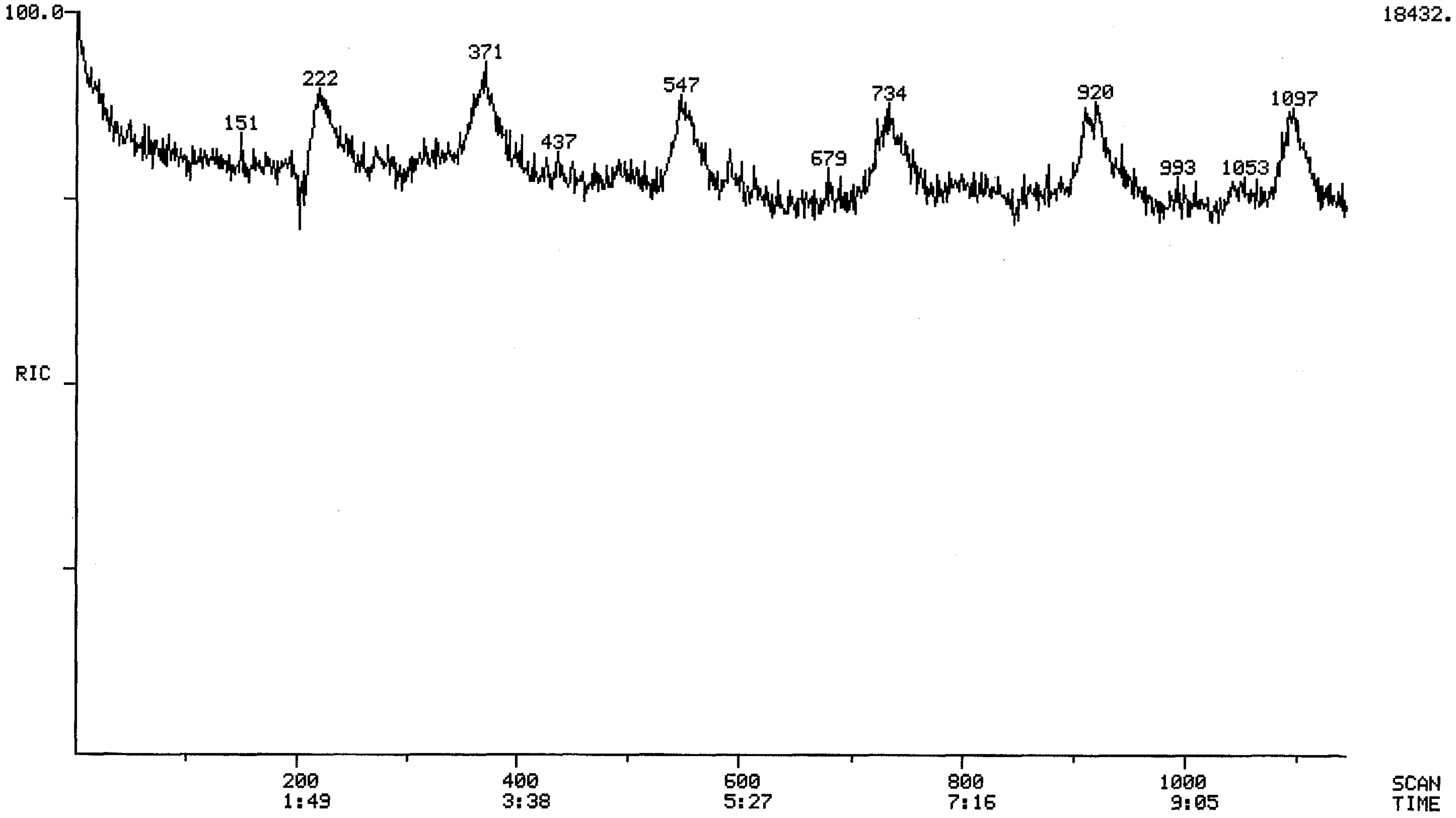
SCANS 1 TO 1143



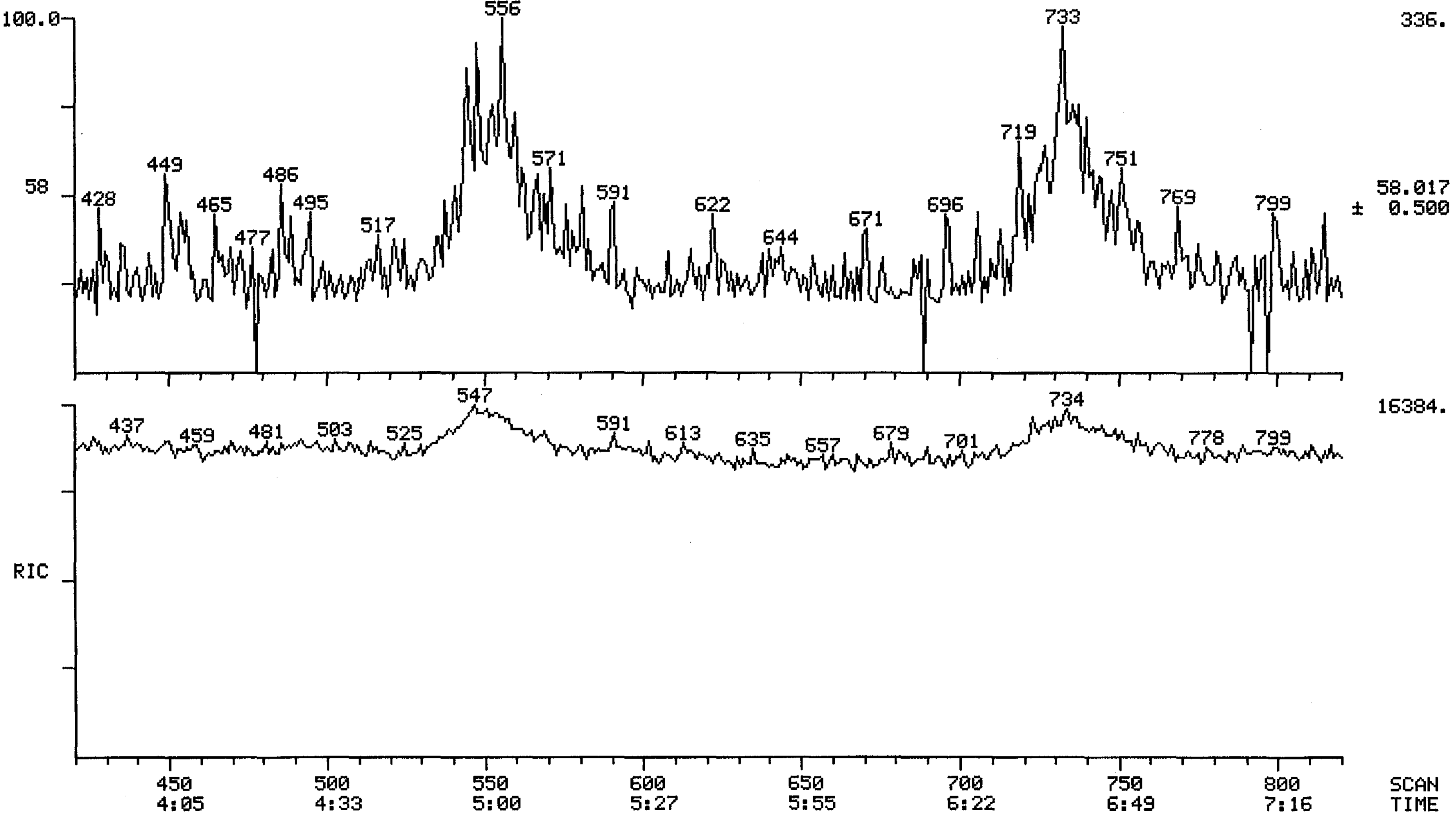
RIC
09/14/94 14:06:00
SAMPLE: INTEL-SN 22
CONDS.: 180
RANGE: G   1,1143 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: IEI08 #1
CALI: CALTAB #3

SCANS   1 TO 1143



```
RIC+MASS CHROMATOGRAM                        DATA: IEI08 #1            SCANS  420 TO  820
09/14/94 14:06:00                            CALI: CALTAB #3
SAMPLE: INTEL-SN 22
CONDS.: 180
RANGE: G   1,1143  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



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