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**Evaluation of the Ion Trap Mass
Spectrometer for Potential
Application in the Space Station**

Gary L. Glish
Scott A. McLuckey

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Analytical Chemistry Division

**EVALUATION OF THE ION TRAP MASS SPECTROMETER FOR
POTENTIAL APPLICATION IN THE SPACE STATION**

by

Gary L. Glish and Scott A. McLuckey

Date Published: April 1988

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EVALUATION OF THE ION TRAP MASS SPECTROMETER FOR
POTENTIAL APPLICATION IN THE SPACE STATION

Gary L. Glish and Scott A. McLuckey

Abstract

This report describes preliminary experiments with an ion trap mass spectrometer, which were done to evaluate its potential for use in the environmental monitoring system of the proposed space station. The first section of the report describes various modes of operation of the instrument, discusses some of the present limitations, and discusses some of the potential solutions to these limitations. The next section discusses the experimental results obtained on sixteen compounds with particular emphasis on comparing these data to that expected from a standard mass spectrometer. The last section consists of a conclusion and comments on suggested future work.

I. Principles of operation

A schematic of the ion trap mass spectrometer (ITMS) is shown in Figure 1. It consists of a hyperbolic ring electrode (doughnut shape) and two hyperbolic end caps. The radius of the device is 1.0 cm. The electric fields generated from this arrangement are the same as in a quadrupole mass filter except that they act on the ion in all three dimensions instead of just the two of a regular quadrupole. Thus, the ITMS is a three dimensional quadrupole and the effect of its fields on the motions of ions is analogous to a conventional quadrupole mass filter.

The ITMS operates with a background pressure of He of $\sim 10^{-3}$ torr. The He acts as a buffer gas to damp the trajectories of the ions down toward the center of the ion trap. This provides better resolution and sensitivity. The ring electrode operates at a fixed rf frequency of 1.1 MHz and the voltage and frequency on the end caps is dependent upon the experiment being done (vide infra).

A. Ionization

Unlike conventional mass spectrometers, the ITMS does not have an ion source. The ions are formed in the ITMS by one of two methods, electron ionization (EI) and chemical ionization (CI). In EI, electrons are formed in the conventional manner by resistive heating of a tungsten wire. The electron beam is then gated into the ITMS through one of the end caps. The electrons are typically pulsed into the ITMS for a period of 0.1 to 10 milliseconds, or more. Ionization occurs by the normal inelastic collision of the electron with sample molecules. The rf voltage on the ring electrode affects the energy of the electrons and thus this energy cannot be well defined like it is with conventional EI sources. Thus, one purpose of this work was to determine how closely the EI mass spectra obtained on the ITMS resemble standard reference EI mass spectra and to determine the reproducibility of the mass spectra. During the ionization pulse, the ITMS is usually held at an rf level that traps all ions with mass-to-charge ratios greater than 20.

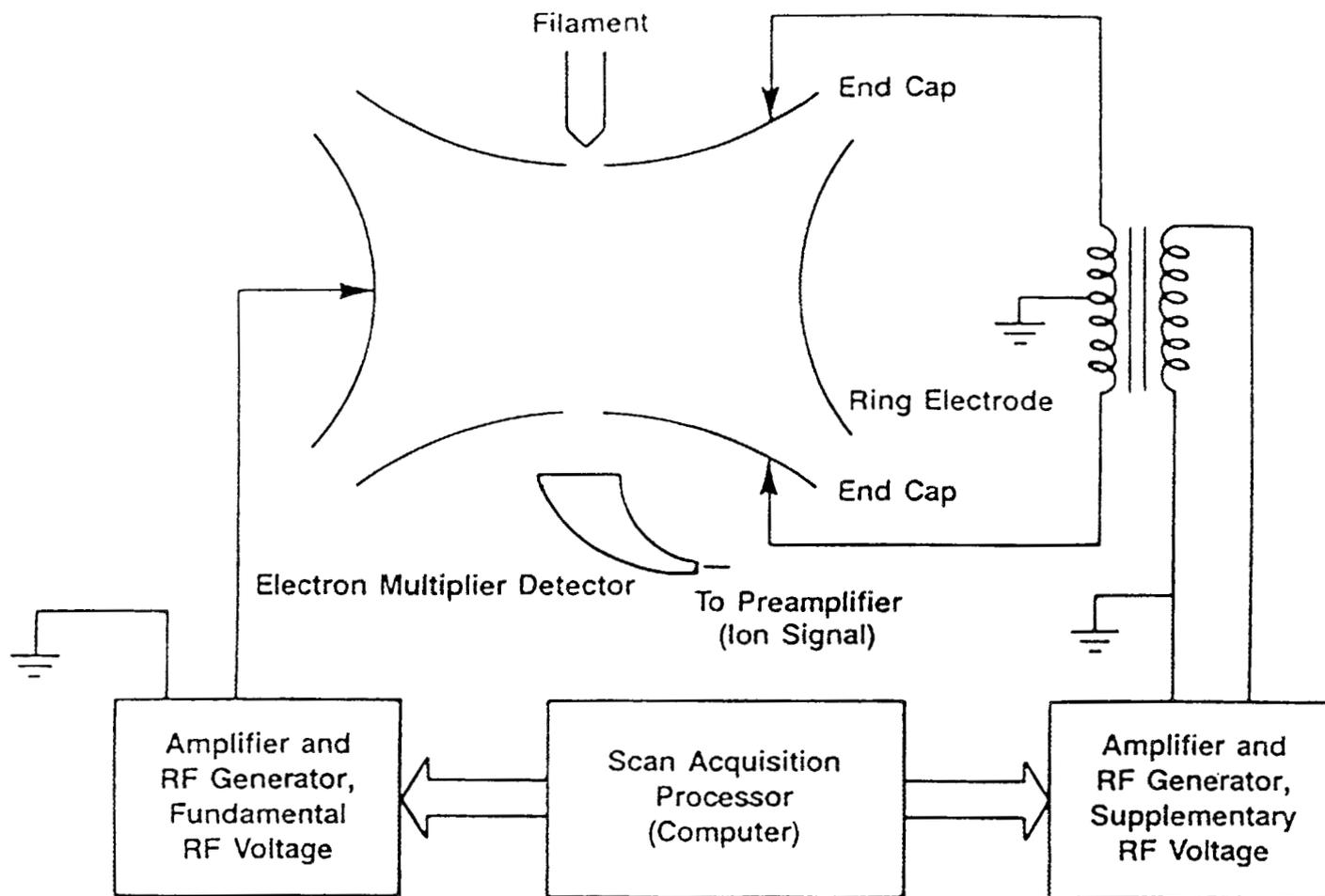


Fig. 1 Block Diagram of the Ion Trap Mass Spectrometer

To perform chemical ionization, a reagent gas (e.g. methane) is admitted to the ion trap at a pressure of $\sim 4 \times 10^{-5}$ torr. This reagent gas is then ionized by the pulse of electrons from the electron filament. The length of the pulse is usually 0.1 milliseconds. The rf level of the ring electrode is at a level where ions above m/z 4.5 are trapped. At the conclusion of the electron pulse, the rf level on the ring electrode is raised to allow trapping of all ions formed above m/z 15. A delay time of 10 to 100 hundred milliseconds then allows time for the reagent ions that have been formed to react with the sample in the ITMS, generally forming MH^+ ions. While the reagent gas pressure in the ITMS experiments is several of orders of magnitude less than in conventional CI sources, the long reaction time relative to the conventional sources provides for similar numbers of collisions and thus similar reactions. Thus, it is expected that ITMS chemical ionization spectra should be similar to CI spectra obtained with conventional instruments. However, there are not standard reference spectra available with which to compare.

B. Obtaining mass spectra

The ITMS differs from conventional mass spectrometers in that all stages of the experiment occur in the same region. The ionization and analysis occur in discrete time frames and not continuously as in conventional mass spectrometers where the ion source is independent of the mass analyzer(s). To obtain a mass spectrum with the ITMS, there is first an ionization period where the sample is ionized, followed by a scan of the ion trap to detect the ions trapped. The time required for this sequence of events is typically 30 to 50 milliseconds (the scan rate is 180 microseconds/dalton) and can be repeated numerous times to signal average the data. A schematic of this is shown in Figure 2.

For this experiment, the end caps are at ground potential and the ring electrode's rf amplitude is scanned. Since only an rf voltage is being used, this mode of operation can be described as that of an rf-only quadrupole mass filter. In the rf-only mode, a quadrupole mass filter acts as a "high-pass filter," transmitting all ions above a certain mass. The cut-off mass is determined by the amplitude of the rf

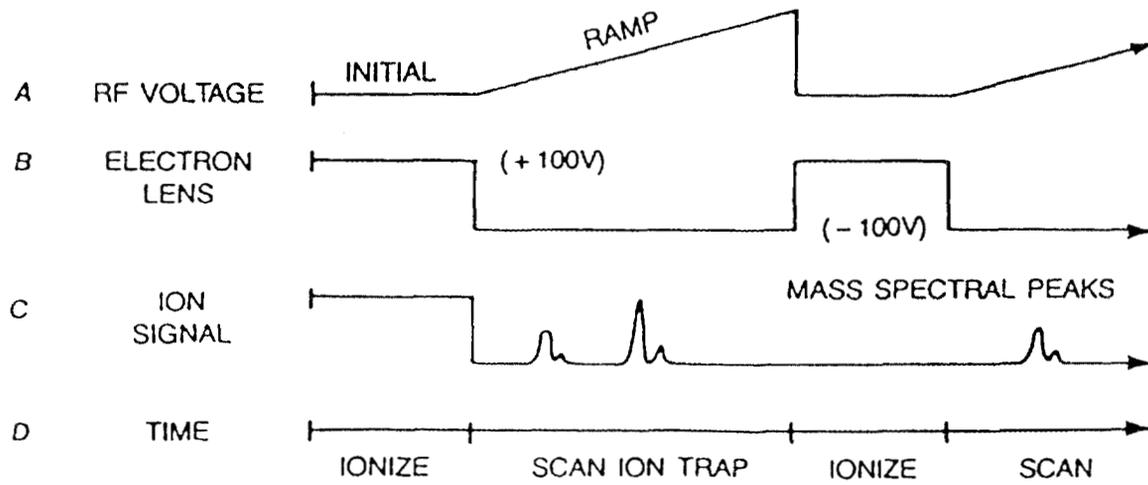


Fig. 2 Schematic Representation of the Operation of the Ion Trap Mass Spectrometer to Obtain a Mass Spectrum

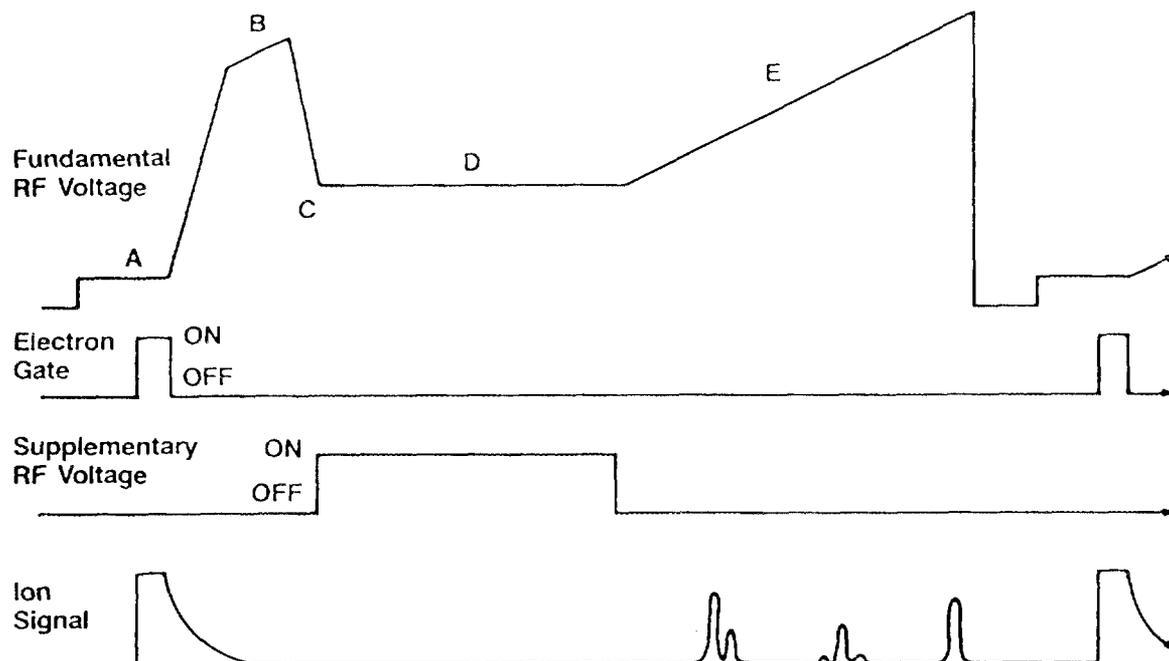
voltage. Thus, in the ITMS, rf-only operation traps all masses above the cut-off mass. As the rf amplitude is increased (scanned), ions of greater and greater mass acquire trajectories between the end caps greater than the distance between the end caps and are thus "ejected" out of the ITMS. These ejected ions are then detected by an electron multiplier.

C. Obtaining MS/MS spectra

Again, since the entire experiment is done within the volume of the ITMS, an MS/MS experiment requires several additional steps in the experimental sequence. After ionization, the ring rf amplitude is ramped, but only to a level just below the cut-off amplitude for the desired parent ion. This ramp ejects all the ions of m/z lower than the parent ion. After this first ramp is completed, the rf amplitude is lowered to a level suitable to trap daughter ions formed from the parent ion. A rf voltage is then applied to the end caps at the secular frequency of the parent ion, typically for 10 milliseconds. (At a given ring electrode rf level, the parent ion will have a specific secular frequency, β_z , the frequency of its oscillations along the axis of the end caps.) The parent ion absorbs power and undergoes collisions at increased kinetic energy with the background He gas. These collisions cause fragmentation (collision-induced dissociation (CID)) and the daughter ions so formed are trapped in the ITMS if their m/z is greater than that corresponding to the rf cut-off level of the ring electrode. After this "collision" pulse, the ITMS is scanned in the normal manner to obtain a mass spectrum, but due to the sequence of events, the data obtained is an MS/MS spectrum. Figure 3 shows a schematic of the event sequence.

There are three main parameters in the MS/MS experiment, all related to "collision" pulse. These are: the ring electrode rf level, which determines the secular frequency; the amplitude of the rf signal on the end caps; and the duration of this signal. Typically, the higher the ring rf level, the more efficient the CID process. However, daughter ion masses lower than the cut-off level will not be trapped and therefore

Ion Trap MS/MS Daughter Scan



- A Ionize and Store Mass Range of Interest
- B Select Low Mass Cut-Off (Select Parent)
- C Select Low Mass Cut-Off for Daughter Spectrum and β_z Value to Resonate Parent Mass
- D CID Parent and Store Daughters
- E Scan Resultant Mass Spectrum

Fig. 3 Schematic Representation of the Operation of the Ion Trap Mass Spectrometer to Obtain an MS/MS Spectrum

will not be detected. Another way to increase the efficiency of the CID process is to increase the amplitude of the end cap rf pulse; but at higher values the parent ions maybe ejected from the ITMS before they fragment and daughter ions may be formed farther from the center of the trap and therefore may be trapped less efficiently. Increasing the duration of the end cap rf pulse has the same effect as increasing the amplitude. Thus, to do CID MS/MS experiments in an ITMS, these parameters need to be optimized as a set and controlled closely for reproducible results.

D. Limitations of the ITMS

As with any device, the ITMS has some performance limitations. A few of the more prominent ones are discussed below along with some potential ways to reduce or alleviate them. One limitation is space charge effects that result if too many ions are contained in the ion trapping volume. Two related consequences of excessive space charge are degraded mass resolution and reduced sensitivity. Since most of these ions are subsequently ejected in the MS/MS experiment, it might be assumed that this should not be a problem. However, that is not the case. There seems to be a "memory" effect and even though the number of ions in the ITMS is substantially reduced prior to the "collision" pulse in an MS/MS experiment, the resolution of the resulting MS/MS spectrum still remains poor.

This space charge effect can be overcome by one of several methods for MS/MS experiments, although only one is available on the present ITMS system. If there are more than enough parent ions to perform an MS/MS experiment, the ionization time can be reduced, which will reduce the total number of ions formed in the trapping volume. Alternatively, Finnigan Mat has developed a proprietary method for restoring resolution that occurs prior to the "collision" pulse in the MS/MS event sequence.

Another limitation, related to space charge, is the dynamic range. Since only a limited number of ions can be trapped, a trace component may form too few ions to be detected. An estimate on the dynamic range is on the order of 10^3 . However, by operating the ITMS as a mass selecting

quadrupole (i.e., adding a d.c. voltage component to the ring electrode), only a selected mass (or range of masses) will be trapped. By applying this d.c. voltage only during the ionization pulse, ions from a trace component can be selectively trapped while ions from major components will be ejected from the ITMS as soon as they are formed (unless they have the same mass as the trace component). This mode of operation will increase the dynamic range by about three orders of magnitude when using EI. This particular mode will not work for chemical ionization since not only does the analyte mass of interest need to be trapped but also the reagent ion(s), so that they will ionize the analyte. However, one should be able to use a fourier transform technique developed by Prof. Alan Marshall at Ohio State University to selectively eject all of the ions out of the ion trap except those of interest. This would require repeating the ionization sequence several times to "build up" the ion intensity prior to doing the rest of the experiment.

Another potential problem with the ITMS is the possibility of unwanted ion/molecule reactions occurring. Since the whole experiment is done in the same region of space, neutral sample molecules are present throughout the analysis sequence and can react with ions in the ITMS. Evidence of this has been observed in at least one case in this study as will be discussed later. A possible solution to this problem would be the introduction of the sample through a pulsed valve instead of continuously, as is normally done. A positive aspect of the ion/molecule reactions is that often these provide additional information, such as isomer differentiation. Therefore, in many cases, they might be used advantageously.

For MS/MS experiments, the present ITMS system can only eject masses lower than the parent ion; any ions formed with masses higher are present during the entire course of the experiment. This has two possible drawbacks. Firstly, these higher mass ions could fragment spontaneously (they have different β_2 s so they are not kinetically excited and therefore don't undergo CID like the parent ion). Such spontaneous fragmentations may give artifact ions in the MS/MS spectrum. Secondly, the higher mass ions could react via ion/molecule reactions to form

artifact ions in the MS/MS spectrum. These higher mass ions can be eliminated by at least two methods. The first is the mass-selective trapping described earlier. The second is by ejecting them with the appropriate secular frequency applied to the end caps during the ejection of the ions of mass lower than the parent ion. Newer versions of the ITMS will certainly include some means for doing this ejection.

The inability to control the electron energy in EI experiments is an inherent limitation to the ITMS. However, it appears that most compounds give spectra reasonably close to the reference library spectra. Additionally, for a limited number of compounds such as for the application of interest in this work, an ITMS reference spectra library could readily be generated. The real limitation of not being able to control the electron energy is the inability to do low energy EI.

Another limitation that does not seem to have a solution at this point in time is the need to set the daughter ion cut-off level at a minimum of 25% of the parent ion mass for CID experiments. At lower values, the CID process is inefficient. Thus, low mass ions will not be detected in MS/MS experiments; but, in the vast majority of cases, these ions are not very informative. In many cases no daughter ions less than 25% of the mass of the parent ion will be formed. An alternative method to cause the ions to fragment can be used, such as photodissociation, but this makes the experiment more complicated.

Two other general limitations to the ion trap are the mass range (up to m/z 650) and the resolution (unit). By scanning β_z , it may be possible to analyze higher masses, but the resolution of such a method is not known. The unit mass resolution of the ITMS is typical of all types of quadrupoles. Neither of these limitations would appear to be important for the application of interest in this work.

II. Results

A. Experimental

The experiments were run on a standard Finnigan Mat Ion Trap Mass Spectrometer. The only change to the system was the addition of a vapor inlet line through which vapors from liquid samples could be introduced. All samples were used as obtained, either from the vendor or Martin Marietta Denver Aerospace. Samples were degassed by two freeze-pump-thaw cycles prior to being introduced into the vacuum system. The first experiments used a NuPro leak valve to introduce the sample into the ITMS system. Later a second NuPro leak valve was added to the inlet line, in series with the first, to give better control over the sample pressure. For EI experiments, the ionization time was from 0.1 to several milliseconds, while for CI experiments the electron beam was gated on for 0.1 ms and then a 10-100 millisecond reaction time was used. All chemical ionization experiments were performed with methane as the reagent gas.

MS/MS experiments were performed with a 10 ms "collision" pulse and a daughter ion trapping level of ~25% of the parent ion m/z. The amplitude of the end cap rf pulse was empirically determined to maximize the daughter ion yield. This value was usually in the range of 100 to 300 millivolts.

All experiments were performed with He as a bath gas at a pressure of $\sim 1 \times 10^{-3}$ torr. All spectra were acquired at a scan rate of 180 microseconds/dalton.

B. Electron Ionization

The 16 compounds listed in Table 1 were analyzed on the ITMS as representative samples from the various compound classes of interest. The list indicates whether, by visual inspection, the electron ionization mass spectra from the ITMS match with reference spectra available from the "Registry of Mass Spectral Data" (E. Stenhagen, S. Abrahamsson and F. W. McLafferty, eds., John Wiley & Sons, 1974). The ITMS spectra all showed a moderate to good match with all fourteen available reference

Table 1

<u>Compound</u>	<u>MW</u>	<u>EI</u>	<u>CI</u>	<u>CI/EI</u> ¹
Ethanol	46	M	G	0.92
Methylethylketone	72	G	M	7.15
Butanol	74	M	M	-
Ethylformate	74	M	G	1750
Diethylether	74	G	G	82.6
Propionic Acid	74	M	G	3.11
Carbon Disulfide	76	M	G	0.25
Nitrogen Tetroxide	92	NA	NA	-
Indole	117	G	G	1.92
n-propylbenzene	120	M	G	3.46
Cumene	120	G	G	3.48
Trichloroethylene	130	G	G	2.26
Freon 113	186	G	G ²	-
Tetradecane	198	G	G	17.1
Stearic Anhydride	550	NA	NA	-
Perfluorokerosene	>650	G	-	-

G = Good, M = Moderate, NA = Not Available, - = no data obtained;

¹comparison of the abundance most abundant ion in the molecular ion region of the mass spectrum; ²no MH⁺ observed but data similar to that obtained on our ZAB mass spectrometer using chemical ionization

spectra (stearic anhydride and nitrogen tetroxide are not in the reference data set). Figure 4 shows an example of a good match between the reference spectrum and ITMS data for tetradecane.

Four of the six that were deemed to be moderate matches were not good matches because there was too much "self chemical ionization" occurring (i.e. the ions and molecules were reacting in the ITMS to give MH⁺ ions in the mass spectra). Figure 5 shows an example of this for ethylformate. The lower portion of the spectra are quite similar but the large 75 ion is due to "self" CI and the 56 ion is a fragment ion from 75 (determined by an MS/MS experiment). All the species that underwent "self" CI were oxygen containing species. This is a fairly well known phenomena and occurs in conventional mass spectrometers at high sample

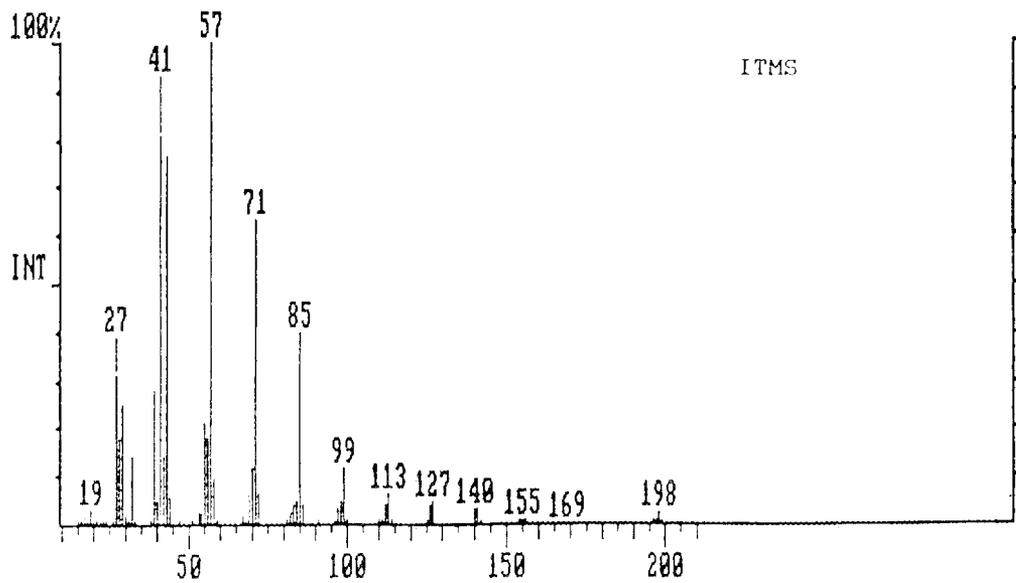
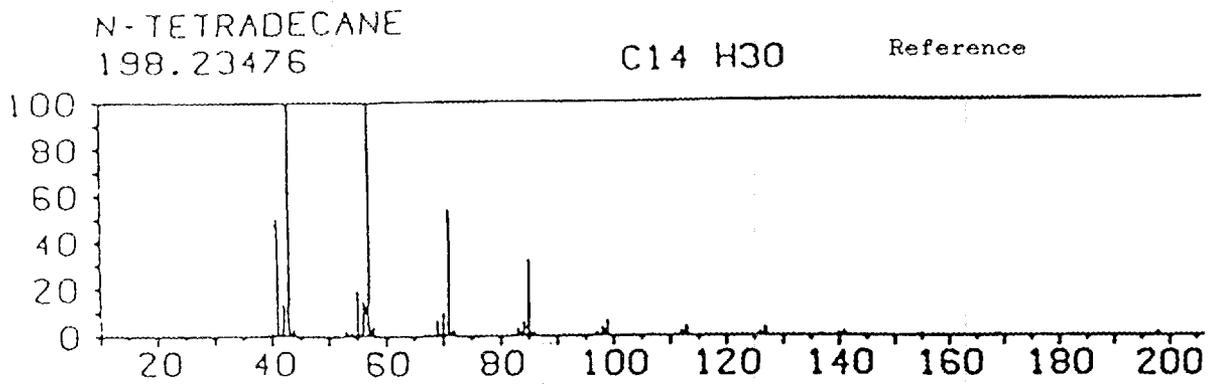


Fig. 4 The Literature EI Mass Spectrum (top) of Tetradecane and the EI Mass Spectrum Obtained with the ITMS (bottom)

ETHYL FORMATE
74.03678 C3 H6 O2

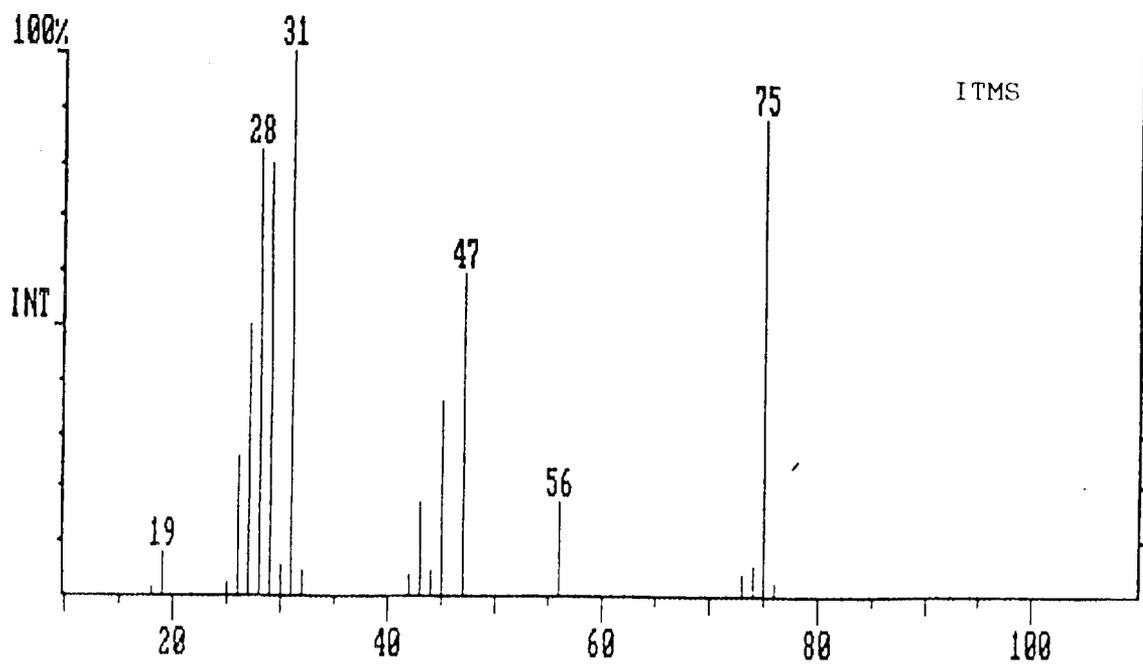
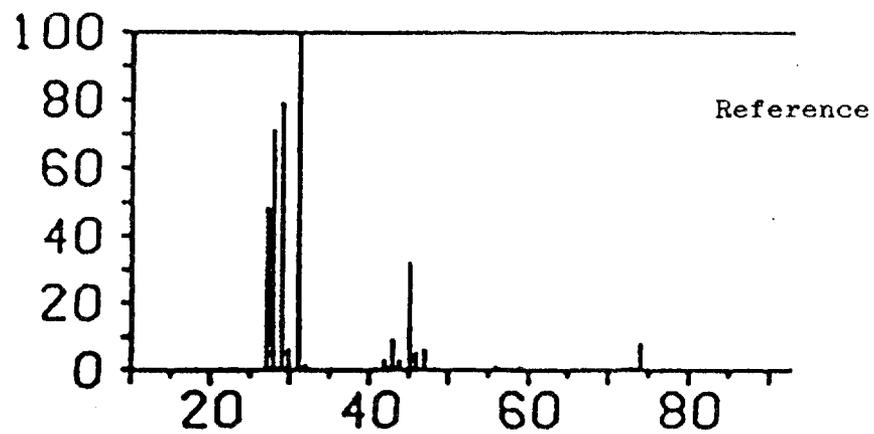


Fig. 5 The Literature EI Mass Spectrum (top) of Ethylformate and the EI Mass Spectrum Obtained with the ITMS (bottom)

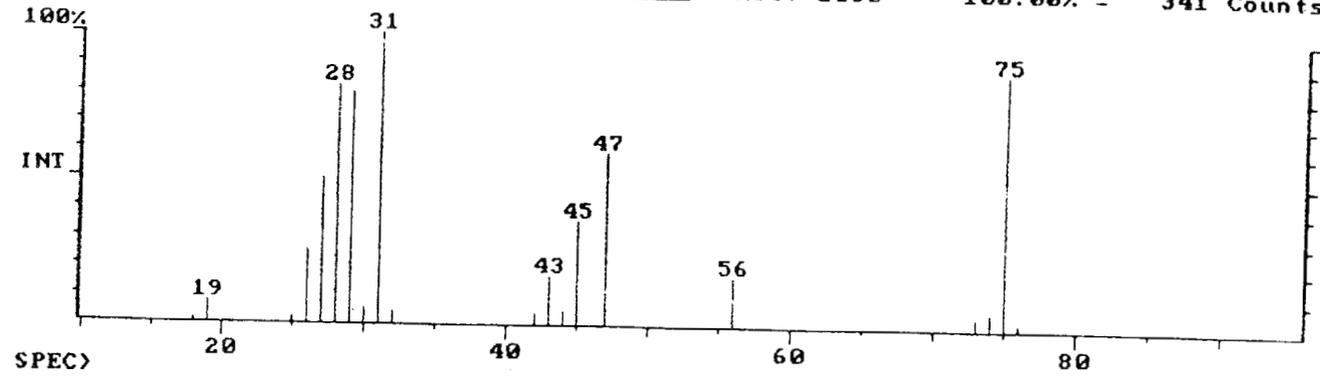
pressures. While the sample pressures were not what is considered unusually high in these experiments, the relatively long time-scale of the experiment allows the "self" CI to occur. Since a supposed advantage of the ion trap is the ability to have the CI reagent gas present during EI operation, EI operational mode spectra were acquired with and without the methane in the ITMS to see if that was responsible for the MH^+ ions. As can be seen in Figure 6 for ethylformate, the mass spectrum with methane present is almost identical to the one obtained without methane. This shows that indeed the ITMS can operate in an EI mode with the CI reagent gas present and that the MH^+ ions are a result of "self" CI.

The two other samples whose ITMS mass spectra showed a moderate match with the reference spectra had most of the appropriate ions in the spectra but at different relative abundances than the reference spectra. This is shown for n-propylbenzene in Figure 7. The EI mass spectrum of nitrogen tetroxide is similar to the reference spectrum for nitrogen dioxide, which is reasonable considering that those two species are in equilibrium with each other in the gas phase. The EI mass spectrum of stearic anhydride looks to be fundamentally like what would be expected from that compound, the main high mass ions being due to cleavages between the bridging oxygen and adjacent carbon atoms.

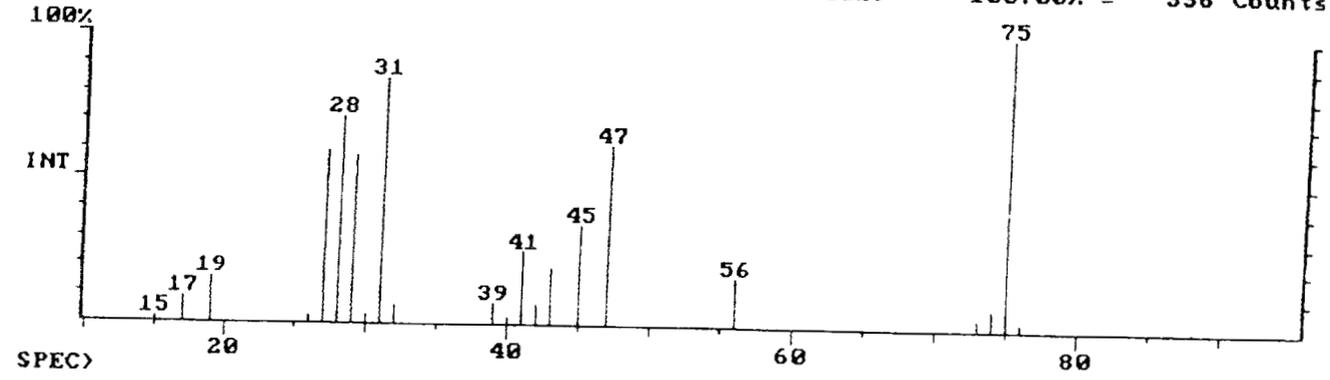
C. Chemical Ionization

The chemical ionization mass spectra obtained on the ITMS, with methane as the reagent gas, were generally quite good. There are not CI reference spectra available to compare these spectra with so they were judged mainly by whether or not the spectra contained a prominent MH^+ species. (Tetradecane gives a $(M-H)^+$ and not a MH^+ ion, but this is typical for saturated hydrocarbons under in CI.) While methylethylketone and butanol did not have prominent MH^+ ions, their spectra were similar to what would be expected. Use of a less acidic reagent gas, such as ammonia, most likely would lead to prominent MH^+ ions for these two compounds. The ions observed in the CI mass spectra of stearic anhydride suggest that this may also be true for this compound. The CI mass spectrum of nitrogen tetroxide suggest that fragmentation and

Spectrum # 9 Datafile: EFRMT1 Acquired: Jan-28-1987 10:23:49 + 0:05
 Comment: EIMS OF ETHYL FORMATE W/O METHANE
 Base Pk: 31 Int: 341 Range: 10 - 90 RIC: 2060 100.00% = 341 Counts



Spectrum # 17 Datafile: EFRMT2 Acquired: Jan-28-1987 10:25:54 + 0:09
 Comment: EIMS OF ETHYL FORMATE W/ METHANE
 Base Pk: 75 Int: 336 Range: 10 - 90 RIC: 2029 100.00% = 336 Counts



top- without methane
 bottom with methane

Fig. 6 The EI Mass Spectra of Ethylformate Obtained with and without Methane Present in the System

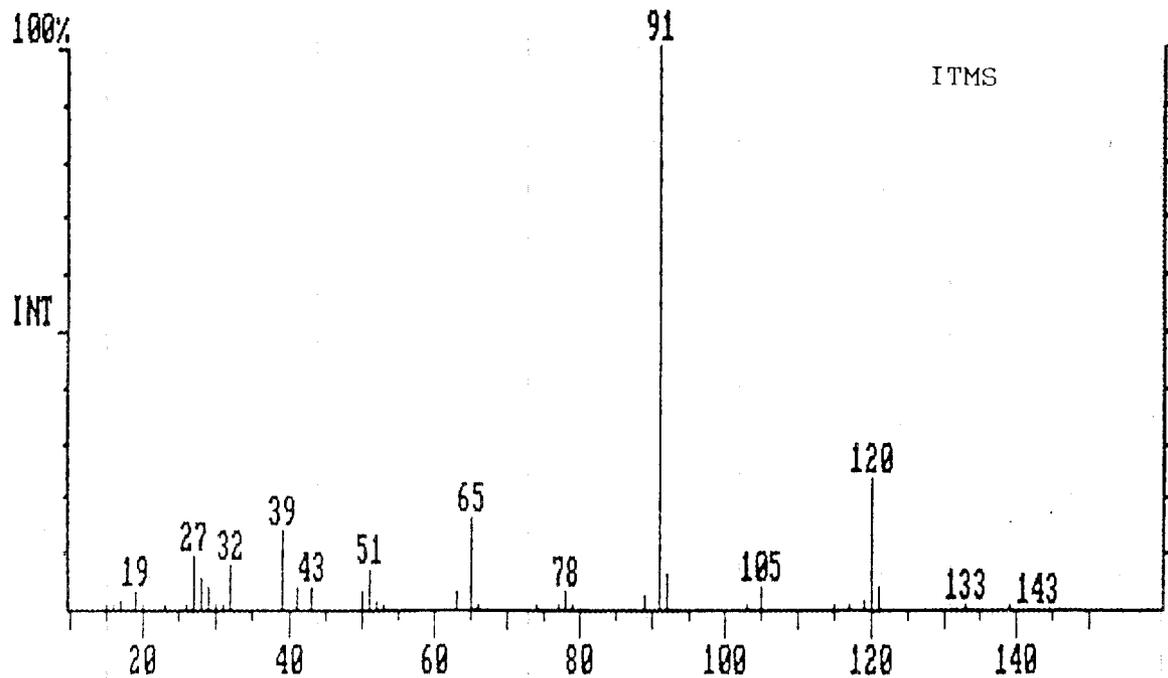
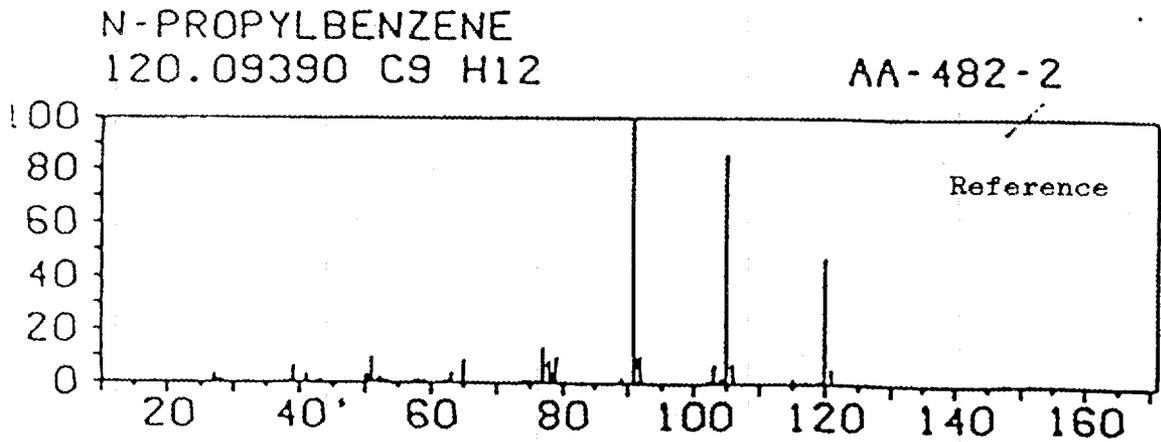


Fig. 7 The Literature EI Mass Spectrum (top) of n-propylbenzene and the EI Mass Spectrum Obtained with the ITMS (bottom)

reduction are occurring as the major high mass ion that is attributable to the sample corresponds to nitrogen dioxide plus two hydrogens.

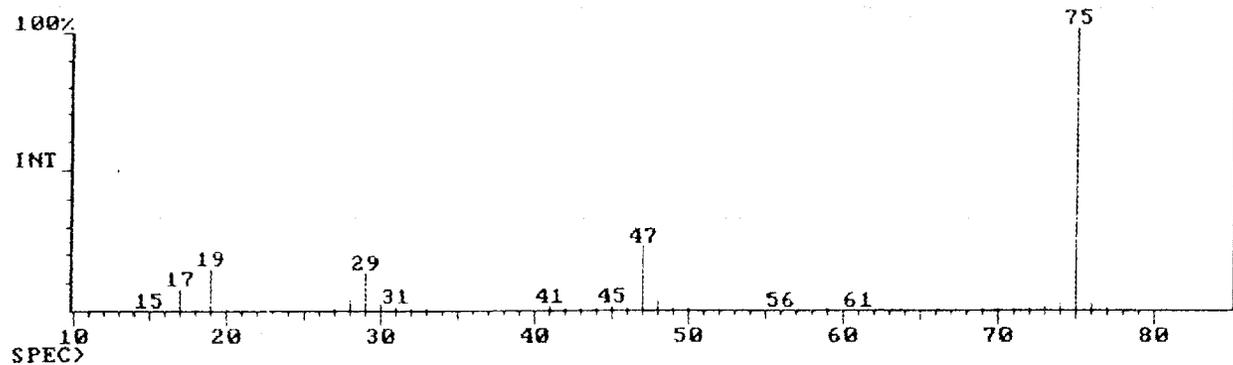
The last column in the Table gives a ratio of the most intense ion in the molecule region of the CI mass spectrum (generally MH^+) to the ratio of the most intense ion in the molecular ion region of the EI mass spectrum (typically M^+). As can be seen, CI is generally somewhat more sensitive and in some cases drastically so. However, these ratios are dependant upon the experimental conditions, viz. the ionization time. For example, Figure 8 shows the CI mass spectra for ethylformate obtained with 10 ms and 50 ms reaction times. The m/z 75 ion is almost ten times greater in abundance in the 50 ms reaction time spectrum. This is the spectrum used for the comparison in Table 1 and thus, if the 10ms reaction time was used the ratio would be 175 instead of 1750. Generally though, CI has less fragmentation and therefore more ions representative of the molecular weight of the sample compound.

D. MS/MS Spectra

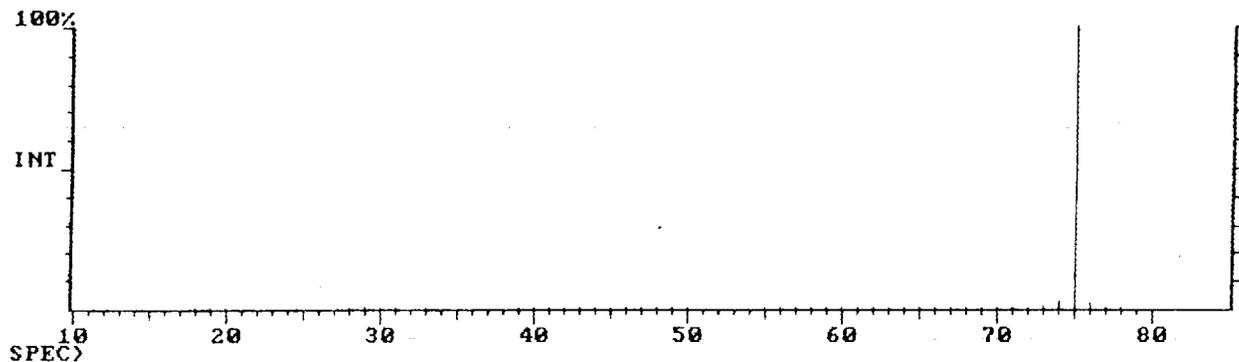
As stated in the first part of this report, the MS/MS spectra obtained with the ITMS are dependent upon the operating parameters, in particular the rf trapping level on the ring electrode, the rf amplitude on the end caps used for exciting the parent ion, and the duration of the "collision" pulse. The latter was always kept at 10 ms for these experiments. In most cases the end cap rf amplitude was optimized for each MS/MS experiment for a given rf level on the ring electrode. Thus, while we believe that the results obtained in this study are "typical," other operating conditions may give somewhat different results, as is the case with any technique.

The MS/MS spectra obtained in this study can be found in the appendix to this report. In general, the MS/MS spectra of parent ions formed by both EI and CI are consistent with expected fragmentations. A common feature of most of the MS/MS spectra is the limited number of different m/z daughter ions formed. For ions formed by EI, the average number of different mass daughter ions is about two, while for ions formed by CI it is one. These daughter ions are formed by what would be

Spectrum # 12 Datafile: E1FRM14 Acquired: Jan-28-1987 10:59:46 + 0:06
Comment: CIMS OF ETHYL FORMATE 10 MSEC REACTION TIME
Base Pk: 75 Int: 4835 Range: 10 - 80 RIC: 9445 100.00% = 4835 Counts



Spectrum # 7 Datafile: E1FRM15 Acquired: Jan-28-1987 11:03:25 + 0:07
Comment: CIMS OF ETHYL FORMATE 50 MSEC REACTION TIME
Base Pk: 75 Int: 41248 Range: 10 - 80 RIC: 49375 100.00% = 41248 Counts



top: 10 ms Cl reaction time

bottom: 50 ms Cl reaction time

Fig. 8 The Cl Mass Spectra of Ethylformate Obtained at Reaction Times of 10 and 50 Milliseconds

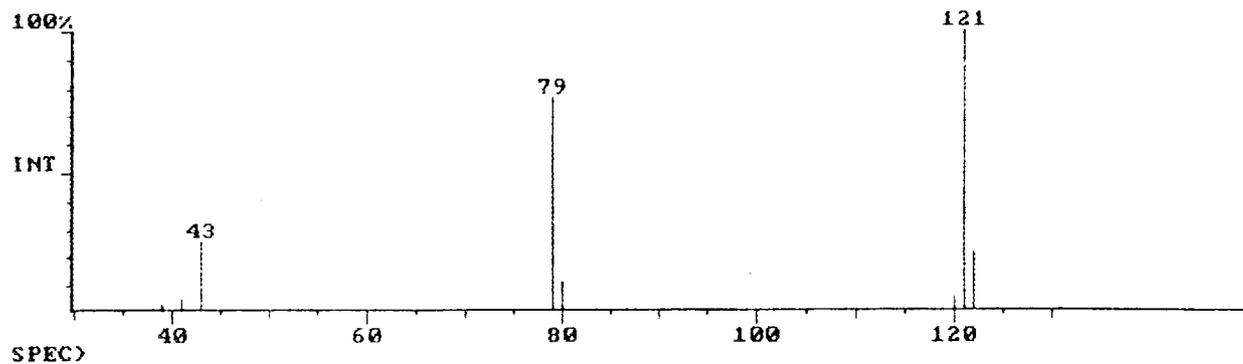
expected to be low activation energy processes (losses of small neutral species and simple radicals), which is consistent with a small amount of internal energy being deposited into the parent ion during the "collision" pulse. In general, the EIMS/MS spectra are more structure specific than the CIMS/MS spectra. This is due to the greater number of daughter ions found in the EIMS/MS spectra and also to the fact that the radical ions formed in EI tend to fragment by simple cleavages whereas the even-electron ions formed by CI usually fragment by rearrangement processes. These latter fragmentations are thus less indicative of the parent ion structure.

The overall collection efficiency in the MS/MS experiment (i.e. the sum of the ion intensity in the MS/MS spectrum divided by the intensity of the parent ion when no "collision" pulse is applied) is quite high, averaging around 70% for EI and 80% for CI generated ions. This efficiency can be very dependent upon the end cap rf amplitude. For example at a rf amplitude of 100 millivolts, the MS/MS of MH^+ from cumene had a collection efficiency of 80% but at an amplitude of 200 millivolts the collection efficiency was 20%. However, there was only a small difference in the absolute abundance of the fragment ions; the main difference was apparently an increased trapping efficiency for the parent ion in the 100 mV experiment. Conversely, for the isomer of cumene, n-propylbenzene, the change of the end cap rf amplitude from 100 to 200 millivolts resulted in little change in collection efficiency. Here though, the parent ion was fragmented much more efficiently as can be seen in Figure 9.

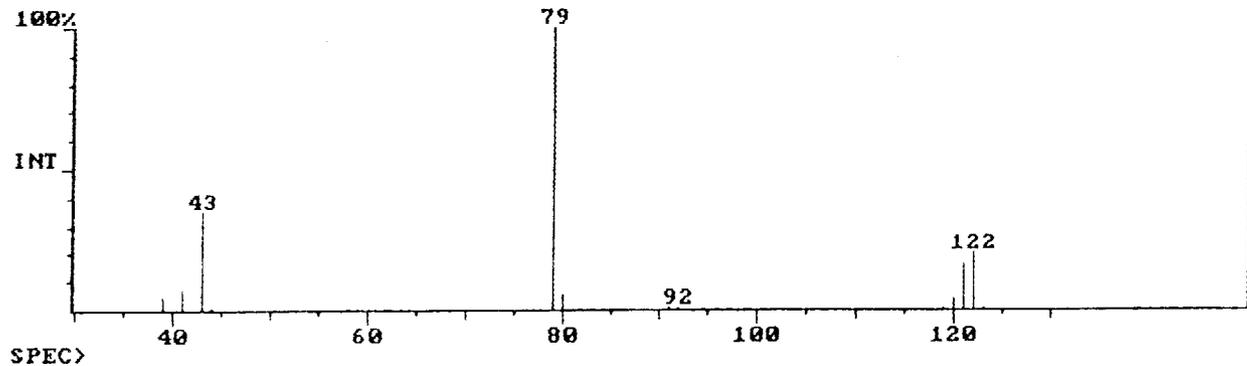
The effect of the rf level on the ring electrode on collection efficiency was studied using the M^+ ion from n-propylbenzene. At an rf level corresponding to 20 amu, the collection efficiency was 50%, while at an rf level corresponding to 30 amu it increased to 95%. As can be seen in Figure 10, the MS/MS spectra at the two trapping levels are very similar. This suggests that the reduced collection efficiency is due to losses of parent ions before fragmentation.

Figure 11 shows the MS/MS spectra of M^+ from n-propylbenzene obtained at different ion densities in the ITMS. The different ion

Spectrum # 11 Datafile: NPRBZ7 Acquired: Feb-25-1987 14:12:06 + 0:07
 Comment: CIMS/MS OF 121 FROM N-PROPYLBENZENE TA=100 @RF30
 Base Pk: 121 Int: 1098 Range: 39 - 122 RIC: 2741 100.00% = 1098 Counts



Spectrum # 11 Datafile: NPRBZ8 Acquired: Feb-25-1987 14:14:56 + 0:07
 Comment: CIMS/MS OF 121 FROM N-PROPYLBENZENE TA=200 @RF30
 Base Pk: 79 Int: 1295 Range: 39 - 123 RIC: 2593 100.00% = 1295 Counts

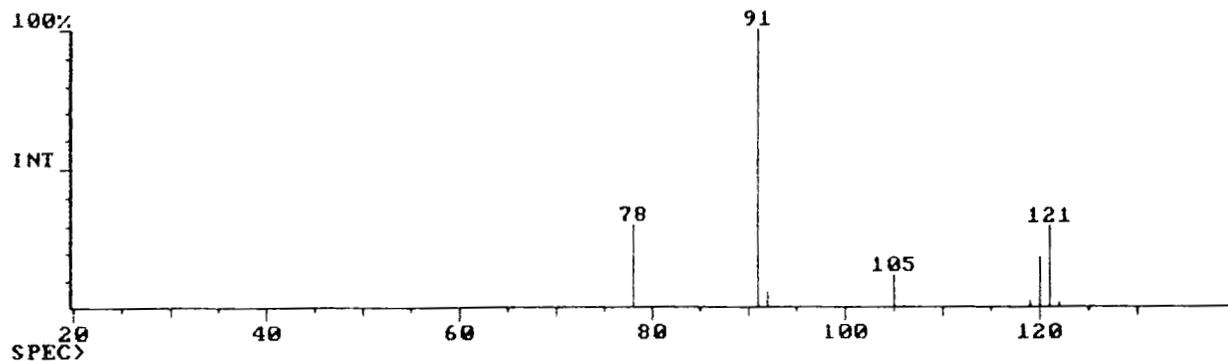


Top end cap rf amplitude = 100 mV

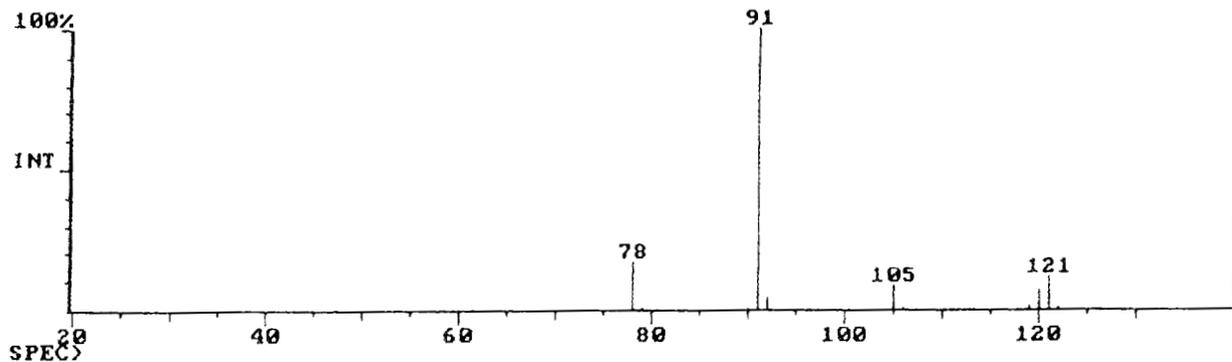
Bottom end cap rf amplitude = 200 mV

Fig. 9 The MS/MS Spectra of the Protonated Molecule (m/z 121) of n-propylbenzene Obtained with Supplementary rf Voltages of 100 and 200 Millivolts

Spectrum # 6 Datafile: NPRBZ2 Acquired: Feb-25-1987 13:36:54 + 0:02
Comment: EIMS/MS OF 120 FROM N-PROPYLBENZENE IA=200
Base Pk: 91 Int: 1402 Range: 20 - 130 RIC: 2819 100.00% = 1402 Counts



Spectrum # 16 Datafile: NPRBZ3 Acquired: Feb-25-1987 13:42:22 + 0:07
Comment: EIMS/MS OF 120 FROM N-PROPYLBENZENE IA=200 @RF30
Base Pk: 91 Int: 3940 Range: 20 - 130 RIC: 6088 100.00% = 3940 Counts

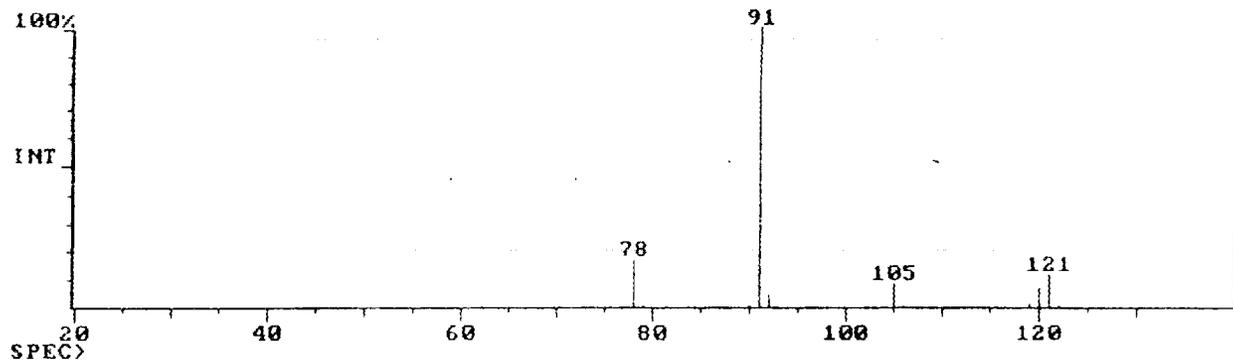


top trapping level = 20 amu

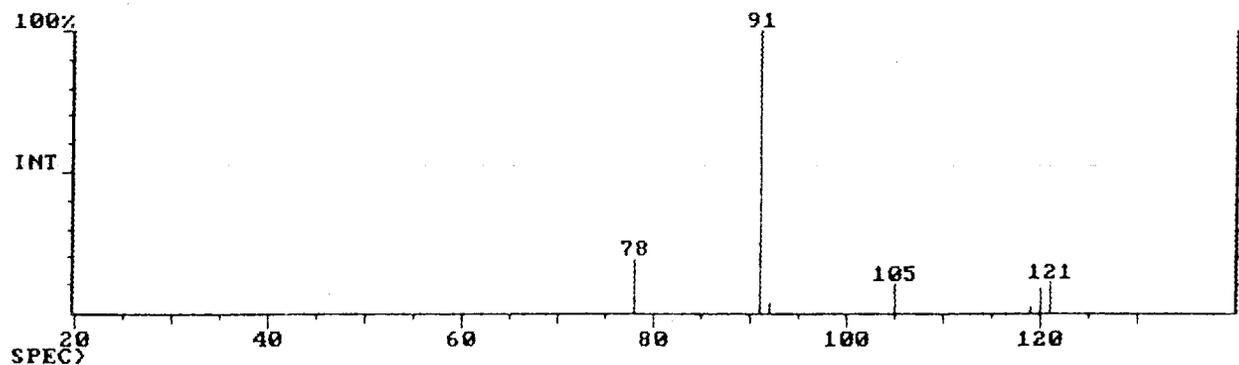
bottom trapping level = 30 amu

Fig. 10 The MS/MS Spectra of the Molecular Ion (m/z 121) of n-propylbenzene Obtained at Trapping Levels of 20 and 30 amu

Spectrum # 16 Datafile: NPRBZ3 Acquired: Feb-25-1987 13:42:22 + 0:07
Comment: EIMS/MS OF 120 FROM N-PROPYLBENZENE TA=200 GRF30
Base Pk: 91 Int: 3940 Range: 20 - 130 RIC: 6088 100.00% = 3940 Counts



Spectrum # 8 Datafile: NPRBZ4 Acquired: Feb-25-1987 13:51:16 + 0:03
Comment: EIMS/MS OF 120 FROM N-PROPYLBENZENE TA=200 GRF30 IONZ/10
Base Pk: 91 Int: 500 Range: 20 - 130 RIC: 789 100.00% = 500 Counts



top: ionization time = 1 ms

bottom: ionization time = 0.1 ms

Fig. 11 The MS/MS Spectra of the Molecular Ion (m/z 120) of n-propylbenzene Obtained with Ionization Times of 0.1 and 1.0 Milleseconds

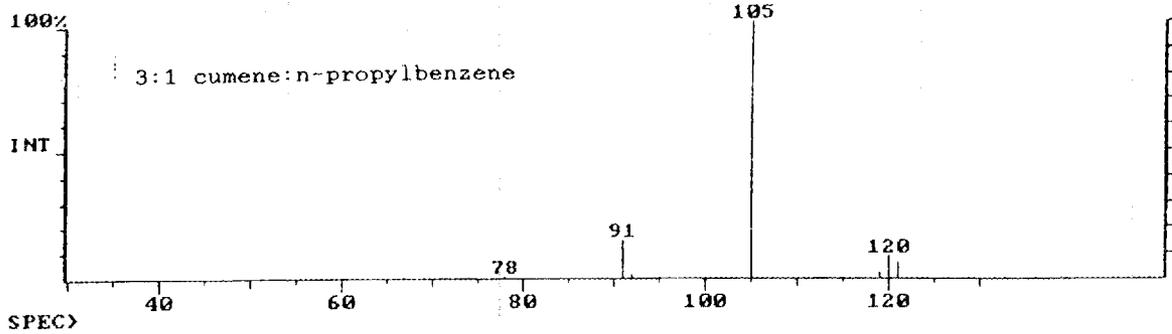
densities were obtained by changing the ionization time by a factor of ten. This changed the total number of ions detected by just under a factor of eight, and therefore, we assume also the ion density. Here the spectra are very similar indicating that, at least at this level of ion density, there is no effect on the MS/MS spectra with ion density.

E. Mixture Analysis

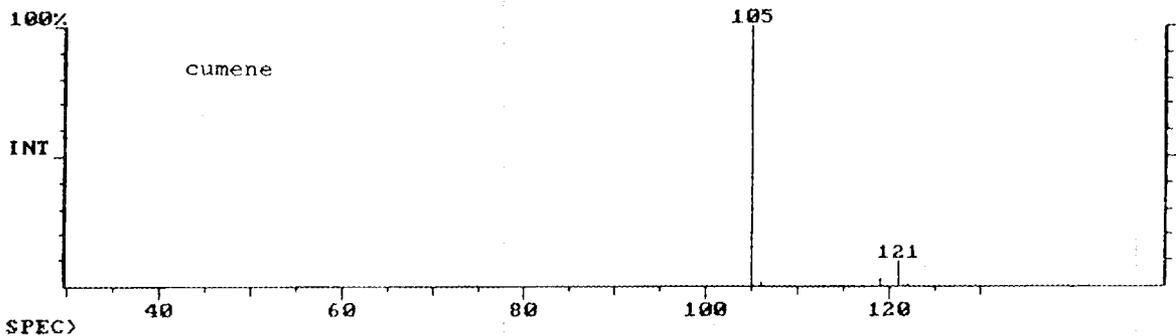
1. Propylbenzene isomers

Due to the different vapor pressures of the propylbenzene isomers and the crude inlet system available on the ITMS, a mixture could not be made up and introduced through a common line. Therefore, cumene was introduced through one inlet and n-propylbenzene through another. Because of different leak valves in these inlet lines, cumene had to be at a higher pressure. The partial pressures were adjusted to give approximately a 3:1 ratio of cumene:n-propylbenzene. The EIMS/MS spectrum of m/z 120 that was obtained is shown in Figure 12, along with the EIMS/MS spectra of the individual compounds. The presence of both compounds in the mixture is readily apparent, m/z 91 being due to n-propylbenzene and most of m/z 105 being due to cumene. (The contribution of n-propylbenzene to the peak at m/z 105 should be about 10% of the intensity of m/z 91; therefore, ~98.5% of the m/z 105 should be due to cumene.) The ratio of the 91 to 105 is ~ 1:6. The fact that it is not the same as the concentration of the two components, 1:3, could be a result of one or more of several factors. These include the possibility of different ionization efficiencies and/or different collisional activation cross-sections. More detailed experiments need to be done to determine the cause of this discrepancy. However, once these factors are determined, it should be possible to correct any data for these influences.

Spectrum # 8 Datafile: PRBZMIX1 Acquired: Mar-17-1987 15:44:08 + 0:03
 Comment: EIMS/MS OF 120 FROM PROPYL BENZENES TA=200 I/N = 2
 Base Pk: 105 Int: 1468 Range: 80 - 120 RIC: 2007 100.00% = 1468 Counts



Spectrum # 10 Datafile: IPRBZ3 Acquired: Mar-17-1987 14:53:36 + 0:05
 Comment: EIMS/MS OF 120 FROM I-PROPYLBENZENE TA=200
 Base Pk: 105 Int: 410 Range: 80 - 120 RIC: 480 100.00% = 410 Counts



Spectrum # 16 Datafile: NPRBZ3 Acquired: Feb-25-1987 13:42:22 + 0:07
 Comment: EIMS/MS OF 120 FROM N-PROPYLBENZENE TA=200 PRF30
 Base Pk: 91 Int: 3940 Range: 80 - 120 RIC: 6088 100.00% = 3940 Counts

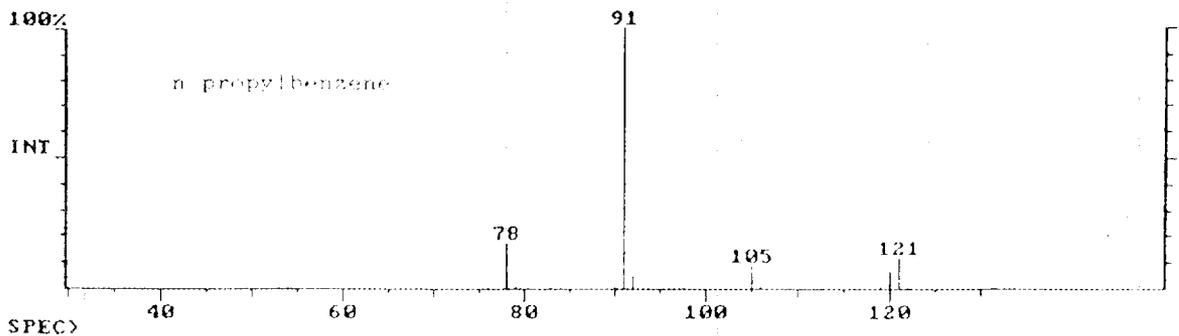


Fig. 12 The MS/MS Spectrum of a Binary Mixture of Propylbenzene Isomers (top) and the MS/MS Spectra of the Individual Isomers (middle and bottom)

2. Butanol, Diethylether, Ethylformate, and Propionic Acid

The compounds discussed in this section all have a nominal molecular weight of 74 daltons. Table 2 summarizes the individual MS/MS spectra of

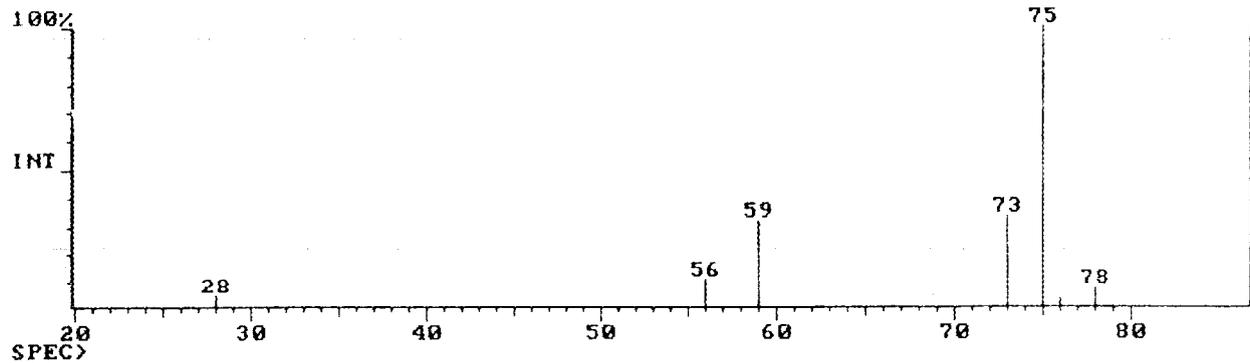
Table 2

<u>Compound</u>	<u>Mode</u>	IonizationParentDaughter ¹	
		<u>Ion</u>	<u>Ions</u>
Butanol	EI	73	55(10), 45(1)
		CI	7557
Diethylether	EI	74	73(1), 59(1)
		EI	7345
		CI	7547(25), 29(1)
Ethylformate	EI	74	56(2), 28(1)
		EI	7355
		CI	7547
Propionic Acid	EI	74	56(10), 57(4), 28(1)
		CI	7557(20), 47(1), 29(1)

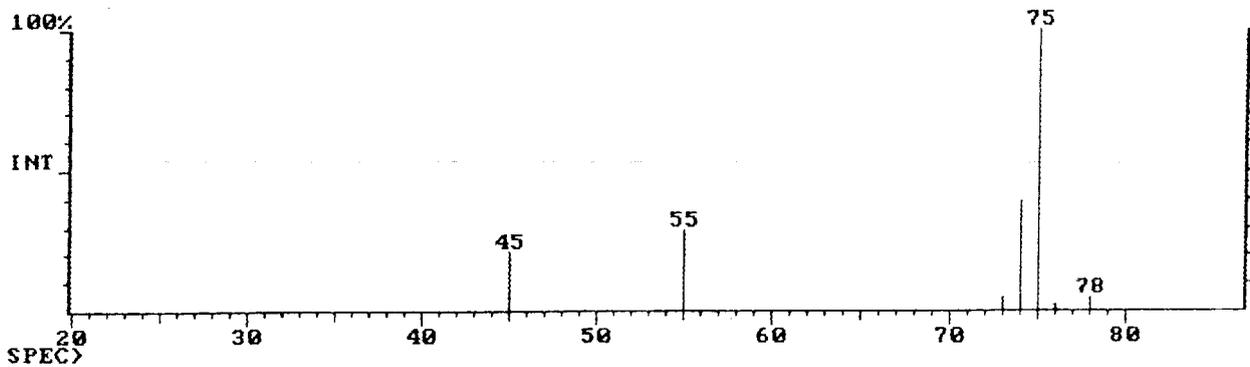
¹The numbers in parentheses are the relative abundances.

various ions formed from these compounds. These data indicate that it should be possible to distinguish the various isomers/isobars via one or a combination of MS/MS spectra. Again, as with the propylbenzenes, a liquid mixture of the compounds could not be introduced into the ITMS due to the wide range in volatility. Therefore, two different inlet lines were used to introduce diethylether together with each of the other compounds to form binary mixtures in the ITMS. Figure 13 shows EIMS/MS spectra for m/z 74 and 73 for a mixture of diethylether and ethylformate at approximately equal vapor pressures. In the MS/MS spectrum of m/z 74, the ions at m/z 73 and 59 are indicative of diethylether while those at m/z 56 and 28 are from ethylformate. For the MS/MS spectrum of m/z 73, m/z 45 is from diethylether and m/z 55 is from ethylformate. As in the propylbenzene case, the ratio of the fragment ions differs from the sample concentration due to the reasons discussed above. In fact, the diethylether daughter ions are more abundant in the MS/MS spectrum of 74, while the ethylformate daughter ion is slightly more abundant in the

Spectrum # 30 Datafile: MIX743-1 Acquired: Mar-03-1987 15:31:26 + 0:15
Comment: EIMS/MS OF 74 FROM MIX74-3 IA=300
Base Pk: 75 Int: 314 Range: 20 - 80 RIC: 601 100.00% = 314 Counts



Spectrum # 26 Datafile: MIX743-2 Acquired: Mar-03-1987 15:37:38 + 0:13
Comment: EIMS/MS OF 73 FROM MIX74-3 IA=300
Base Pk: 75 Int: 448 Range: 20 - 80 RIC: 909 100.00% = 448 Counts



top- MS/MS of 74

bottom- MS/MS of 73

Fig. 13 MS/MS Spectra of m/z 74 (top) and m/z 73 (bottom) from a 1:1 Binary Mixture of Isobars Diethylether and Ethylformate

MS/MS spectrum of m/z 73. It seems likely that this behavior would be helpful in attempts to quantitate the measurements since there should be some internal consistency in the measurements if the system behaves properly. From Table 2 it can be seen that the CIMS/MS spectra would not allow differentiation of a mixture of these compounds since the only difference in their MS/MS spectra is a very minor peak at m/z 29.

Figure 14 shows the CIMS/MS spectrum of a mixture of butanol and diethylether at approximately equal vapor pressures. The ion at m/z 57 is due to butanol and those at m/z 47 and 29 are due to diethylether. Figure 15 shows the CIMS/MS spectrum of a mixture of diethylether and propionic acid. This spectrum was obtained from background contamination several days after the individual samples had been run. The ion at m/z 57 is due to propionic acid while that at m/z 47 is from diethylether. The m/z 29 ion is not seen do to the extremely low signal levels. (The total background pressure was 5×10^{-8} torr.) The ions at m/z 77, 78, and 79 are other background contaminants.

F. MS/MS Sensitivity Experiments

The above example demonstrates the sensitivity of the ITMS. The base pressure in the instrument was 5×10^{-8} torr so the partial pressure of each of the species was less than that, but exactly what is unknown. To get a more quantitative measurement, trichloroethylene was used as the sample compound. Figure 16 shows the EIMS/MS spectra obtained at a sample pressure of 5×10^{-8} torr. (This was the lowest pressure at which we could satisfactorily introduce the sample.) At the 100°C operating temperature of the ITMS, this corresponds to 2.8×10^{-7} g/m^3 of trichloroethylene. (It should be noted that while the spectrum from the data system looks very clean, the signal-to-noise in the raw data is not this good. Thus, the ultimate detection limit in this particular experimental arrangement would not be much less than the quantity used here.)

Spectrum # 12 Datafile: BUTANOL6 Acquired: Feb-12-1987 16:15:40 + 0:09
Comment: CIMS/MS OF 75 FROM BUTANOL + MIX74 TA=300
Base Pk: 47 Int: 1699 Range: ~~20-80~~ RIC: 5401 100.00% = 1699 Counts

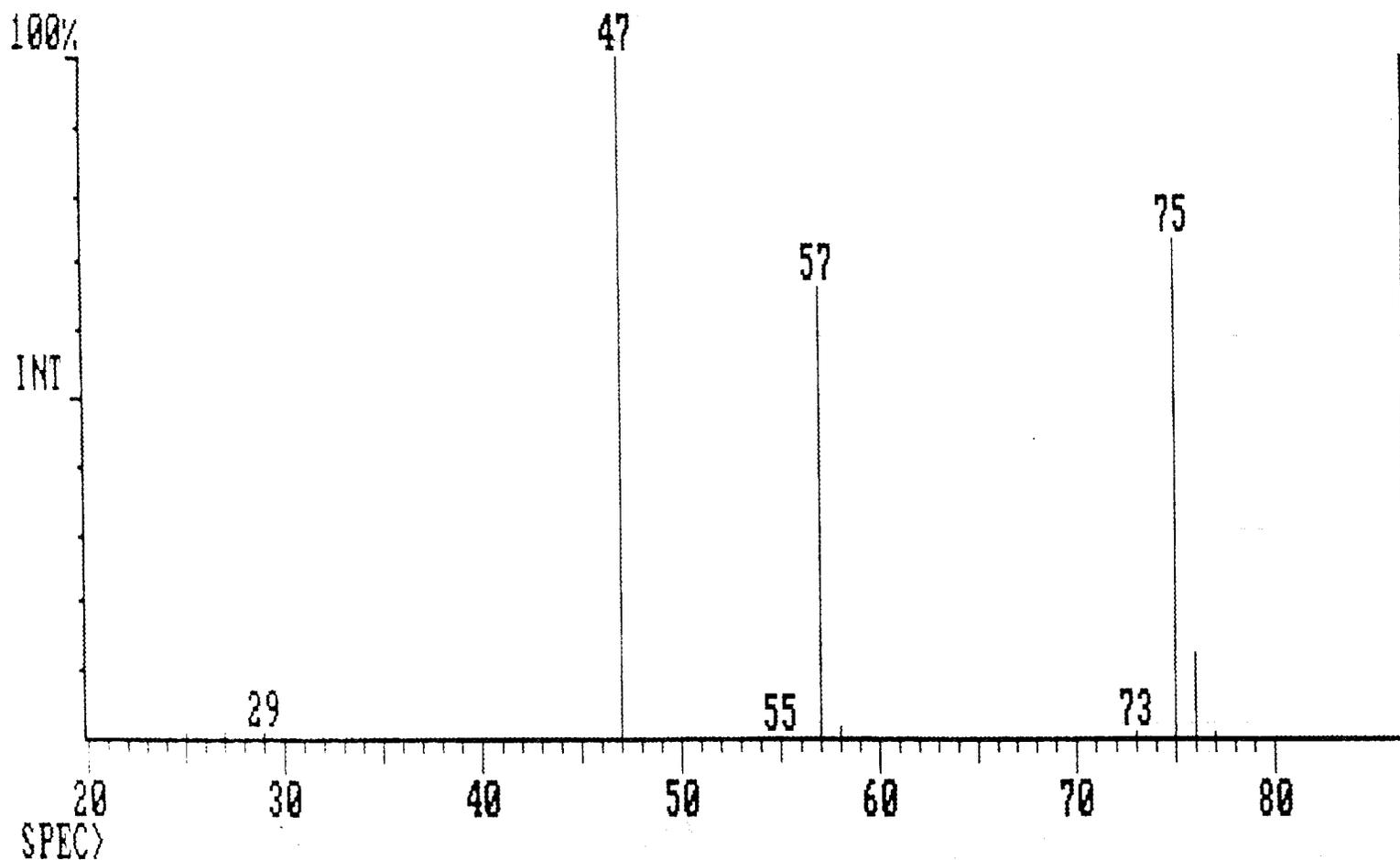


Fig. 14 CI MS/MS Spectrum of m/z 75 of a 1:1 Binary Mixture of Isomers Butanol and Diethylether

Spectrum # 3 Datafile: BKGD3 Acquired: Feb-04-1987 15:50:22 + 0:19
Comment: CIMS/MS OF 75 FROM BACKGROUND SAMPLE TOGGLE VALUE CLOSED TA=200
Base Pk: 77 Int: 34 Range: 40 - 80 RIC: 107 100.00% = 34 Counts

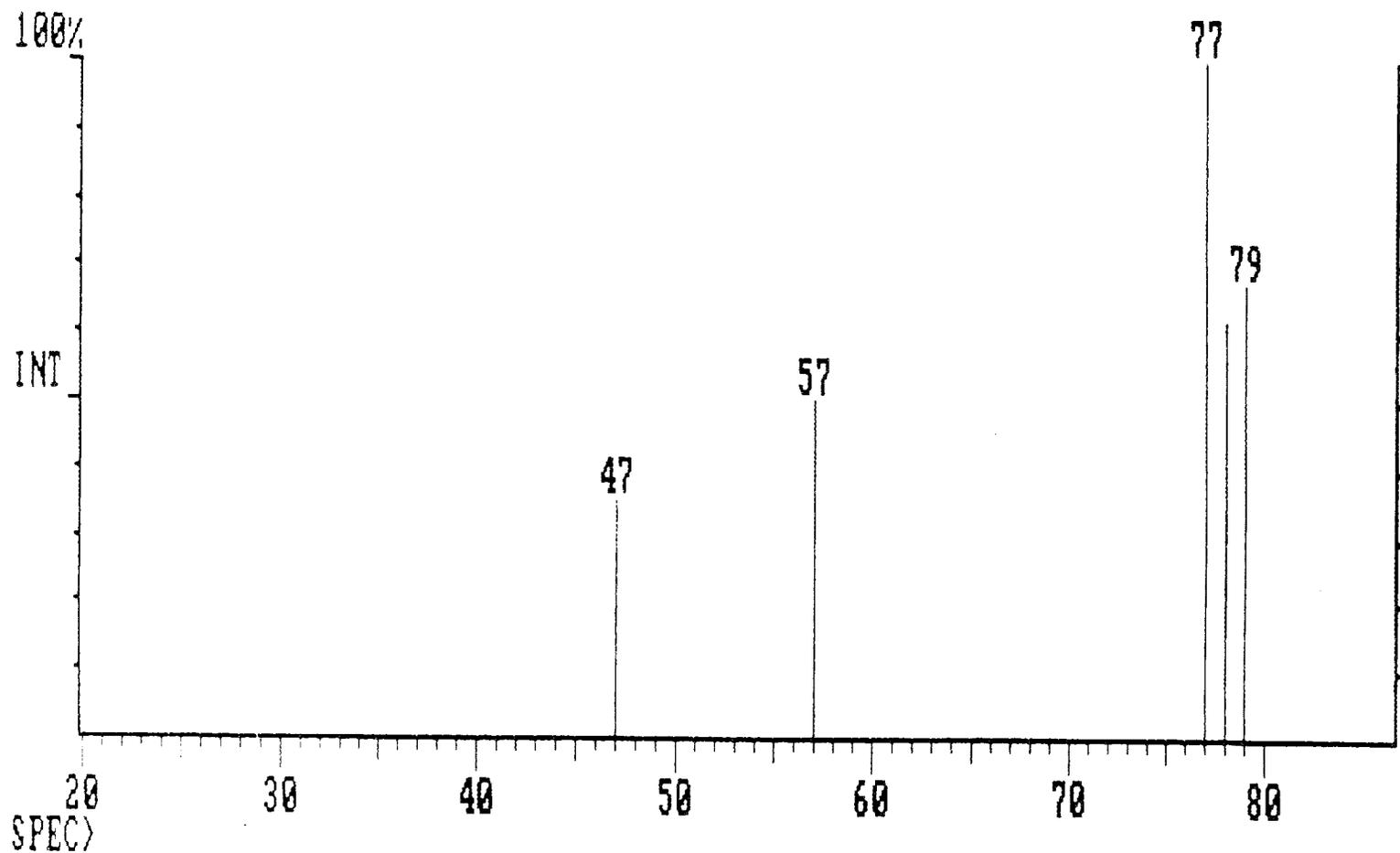


Fig. 15 CI MS/MS Spectrum of m/z 75 of a Binary Mixture of Isobars Diethylether and Propionic Acid

Spectrum # 4 Datafile: CL3ET3 Acquired: Mar-25-1987 16:35:53 + 0:11
Comment: EIMS/MS OF 130 FROM TRICHLOROETHYLENE P=9.0E-8 TA=400 RF=50
Base Pk: 130 Int: 48 Range: 95 - 131 RIC: 97 100.00% = 48 Counts

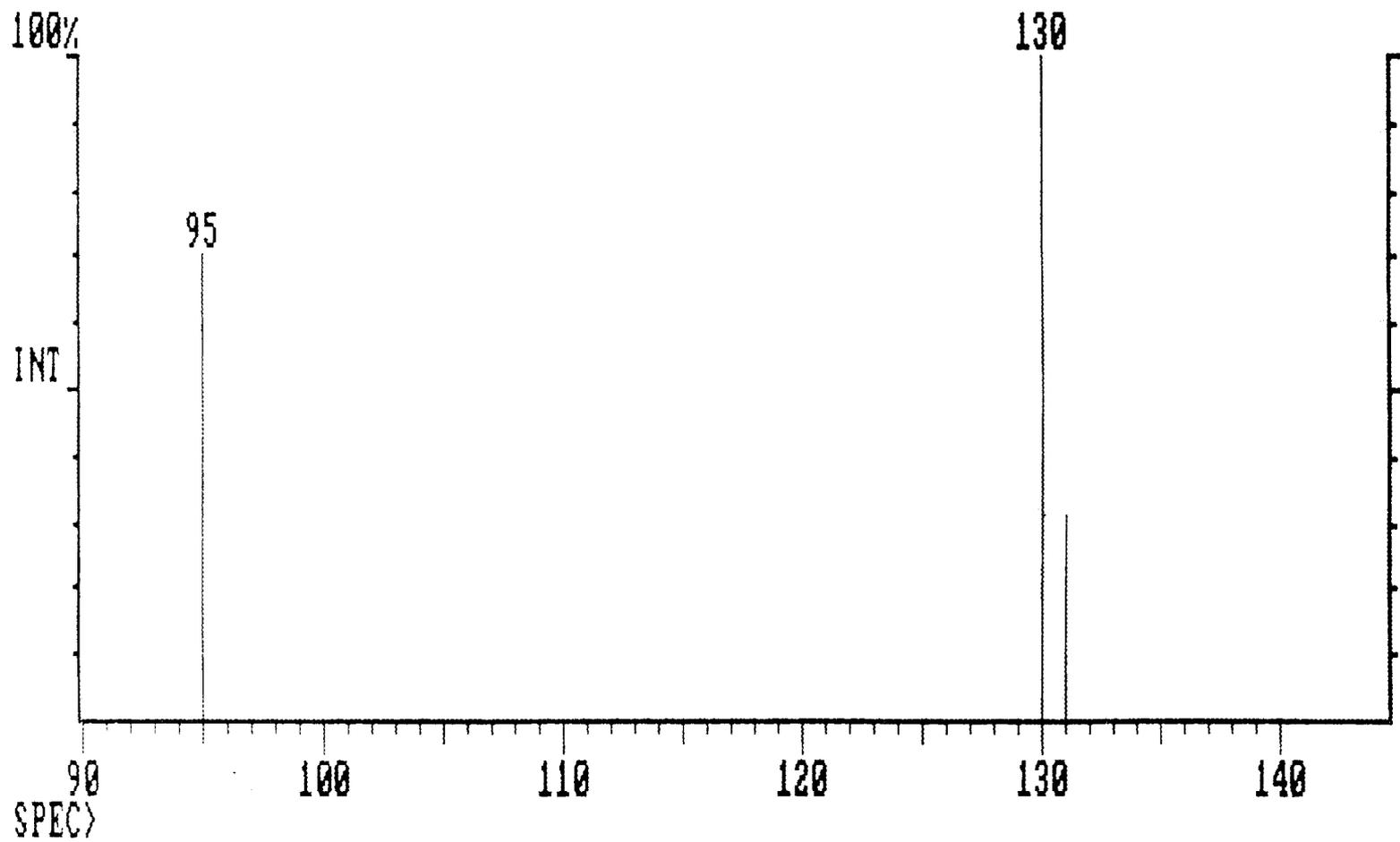


Fig. 16 MS/MS Spectrum of the Molecular Ion (m/z 130) of Trichloroethylene at a Pressure of 6.7×10^{-8} mbar

III. Conclusion and Future Areas of Study

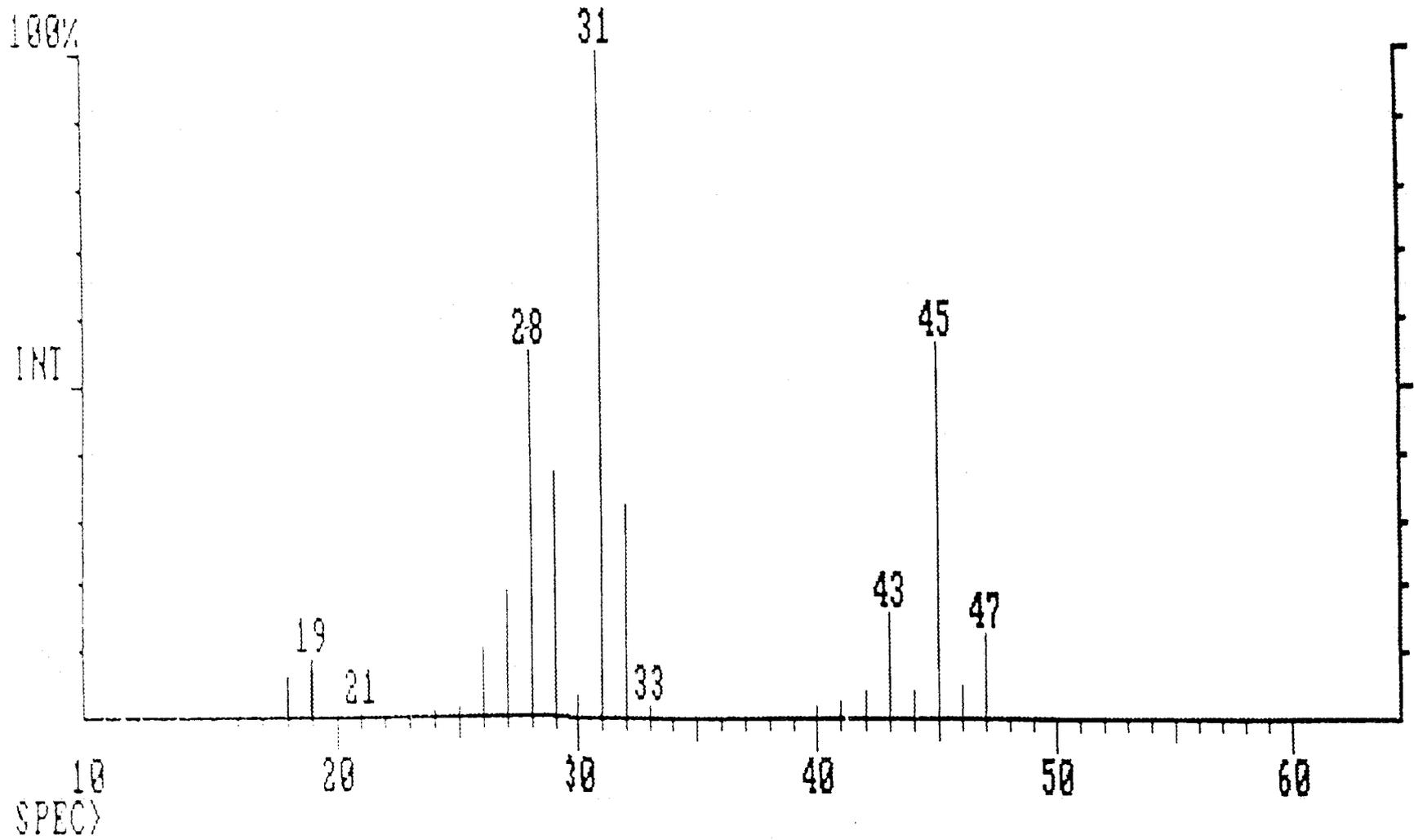
From this work we believe that the ITMS has very good potential as an analytical mass spectrometer and should be strongly considered further as part of the environmental monitoring system for the proposed space station. There are some aspects that should be addressed by further study before a final decision is made. Advances have been made with this instrument over its predecessor, the ion trap detector (ITD), that have alleviated many of the problems with the ITD. These have been discussed in section 1. From the data obtained in this study, the most important question to be addressed is whether the MS/MS spectra are specific enough, given the limited number of daughter ions that are typically produced. When answering this question, the full capabilities of the ITMS need to be explored. In particular, the limited number of daughter ions and high collection efficiency suggest that MS/MS/MS and maybe MS/MS/MS/MS experiments can be done to give high specificity. In addition, MS/MS spectra of fragment ions can be obtained to provide further specificity.

Another area of concern is the ion/molecule reactions that can occur in the ITMS. This needs to be studied and evaluated in conjunction with the type of ionization used. While a very powerful feature of the ITMS is the ability to always have the CI reagent gas present and thus switch from EI to CI via software, for the space station application it may be better to try to form the ions externally in an atmospheric sampling ion source and inject them into the ITMS for analysis. (Work on injecting ions into an ion trap is being done or planned in several labs.) In either case though, the background species that will get into the vacuum system must be considered as to how they might react with ions in the ITMS.

Appendix A

EI mass spectra from the ITMS

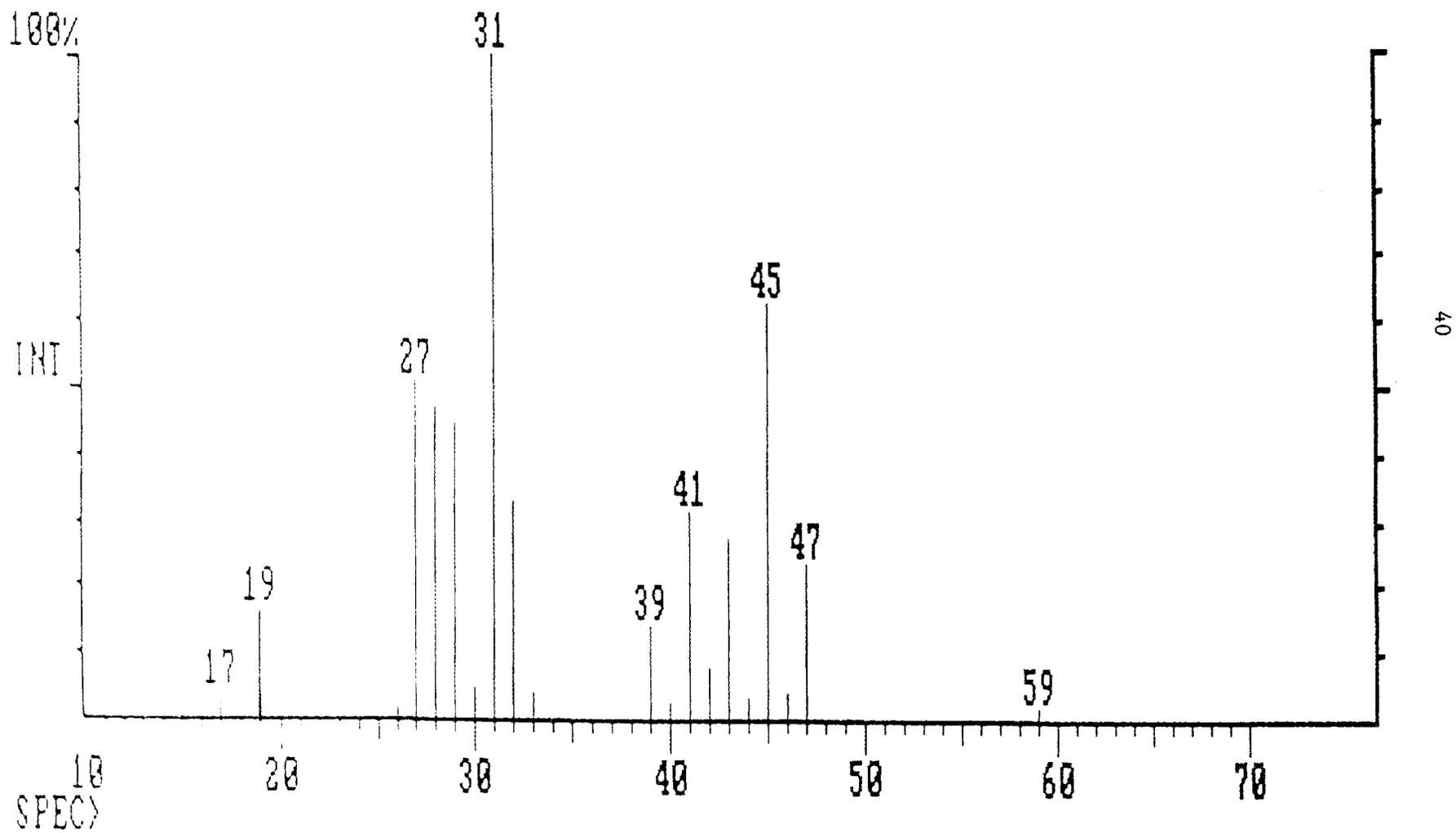
COMPOUND: ETHANOL
EI MASS SPECTRUM
(WITHOUT METHANE)



COMPOUND: ETHANOL

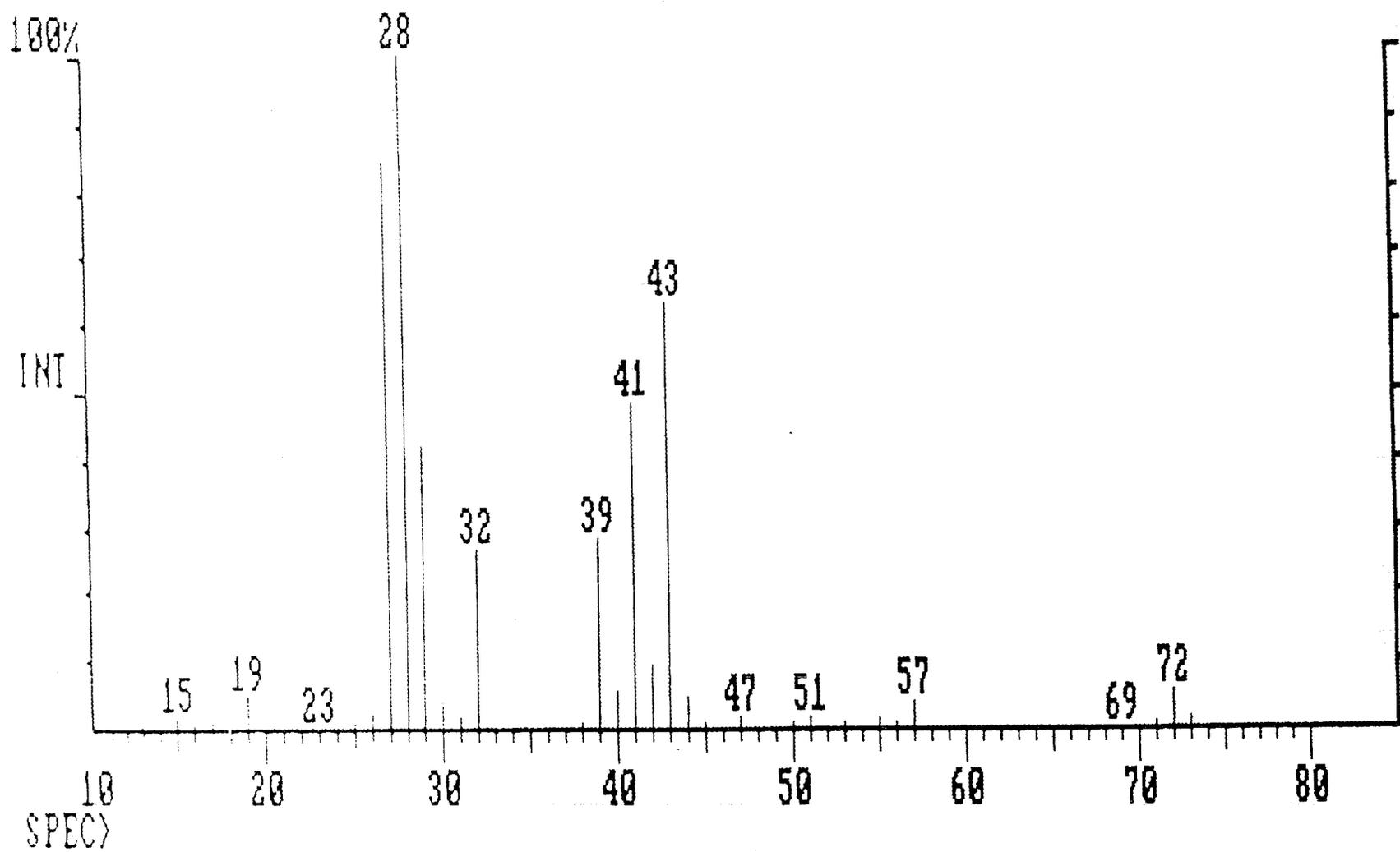
EI MASS SPECTRUM

(WITH METHANE)



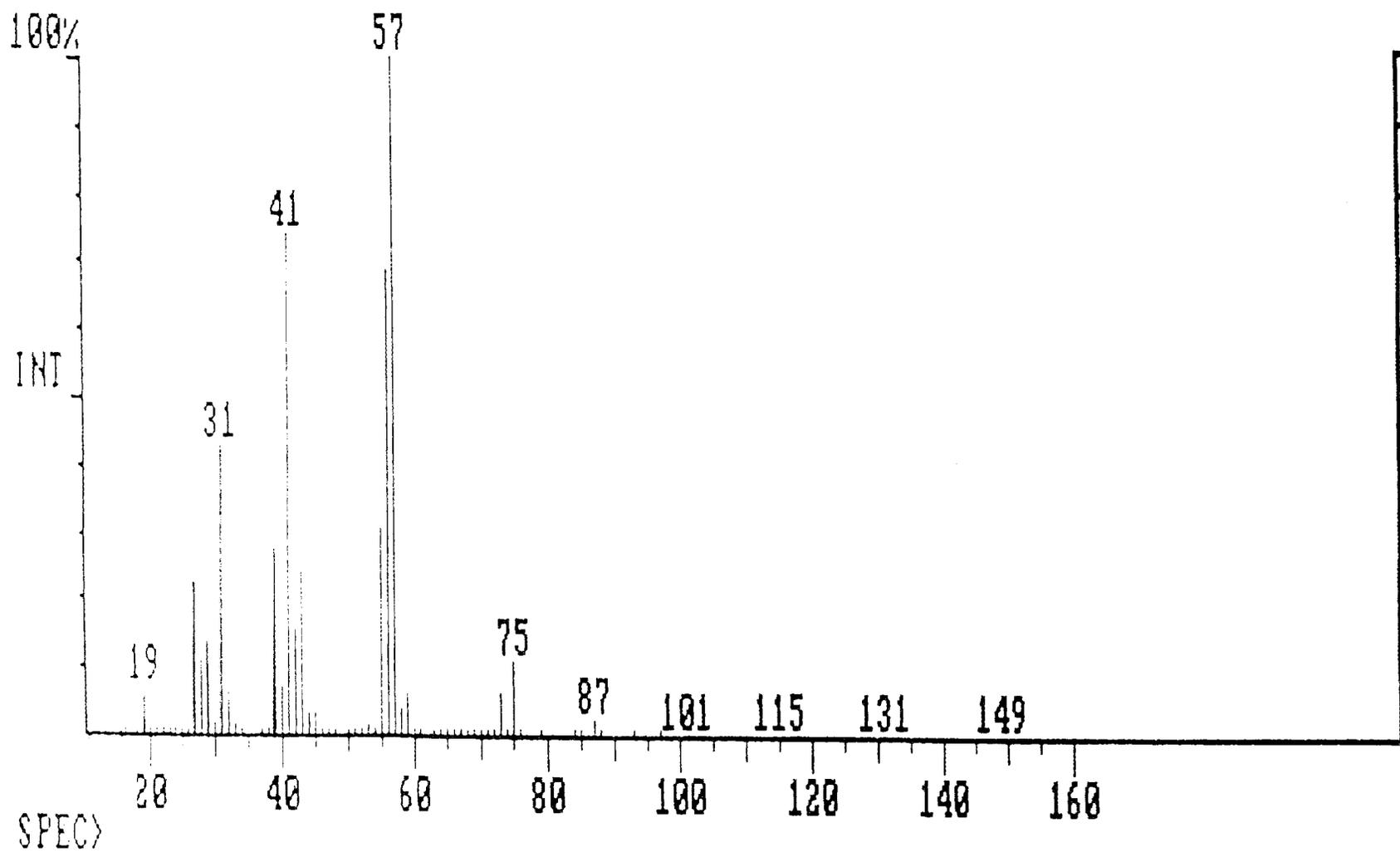
COMPOUND: METHYLETHYLKETONE

EI MASS SPECTRUM



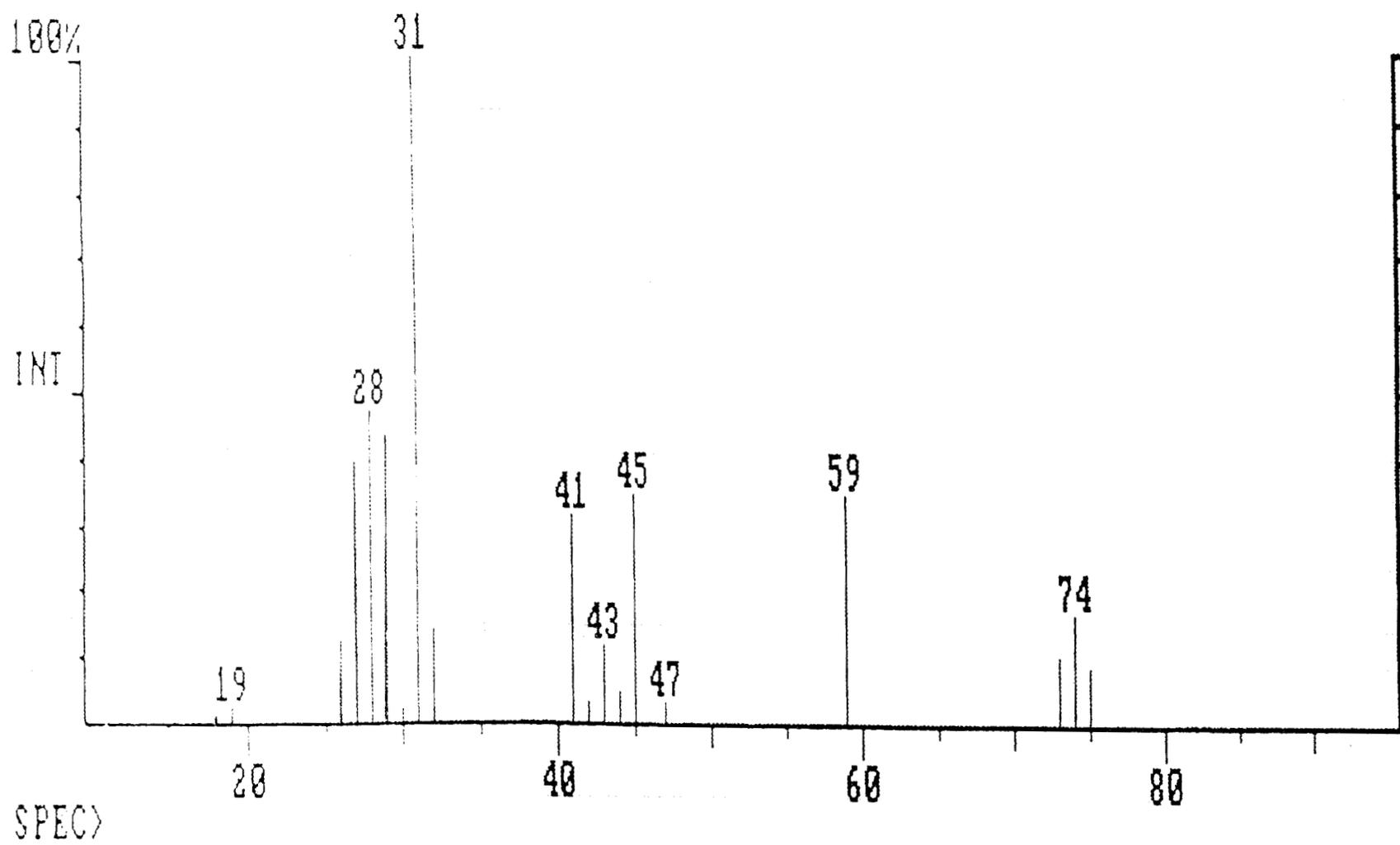
COMPOUND: BUTANOL

EI MASS SPECTRUM



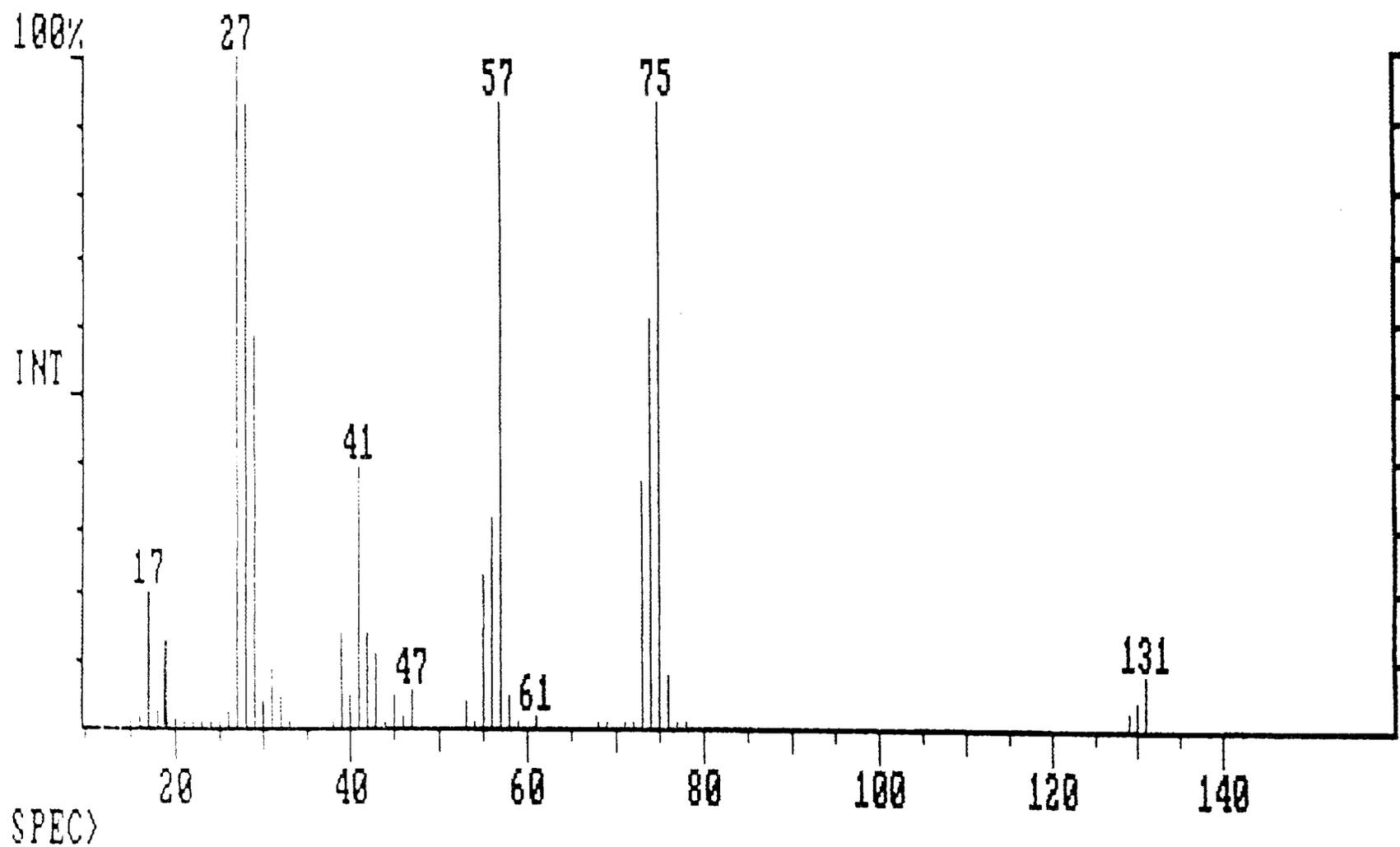
COMPOUND: DIETHYLETHER

EI MASS SPECTRUM

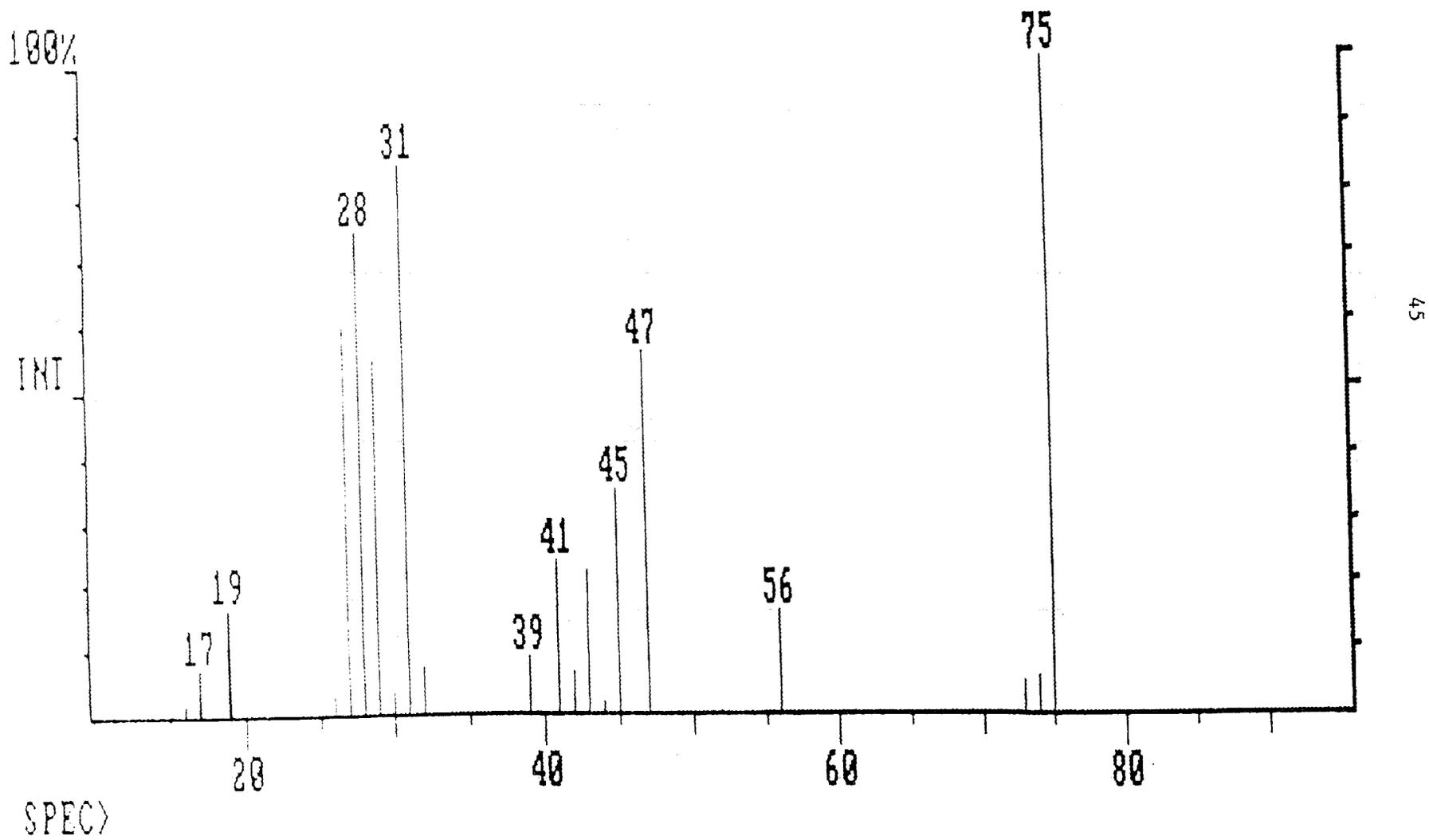


COMPOUND: PROPIONIC ACID

EI MASS SPECTRUM



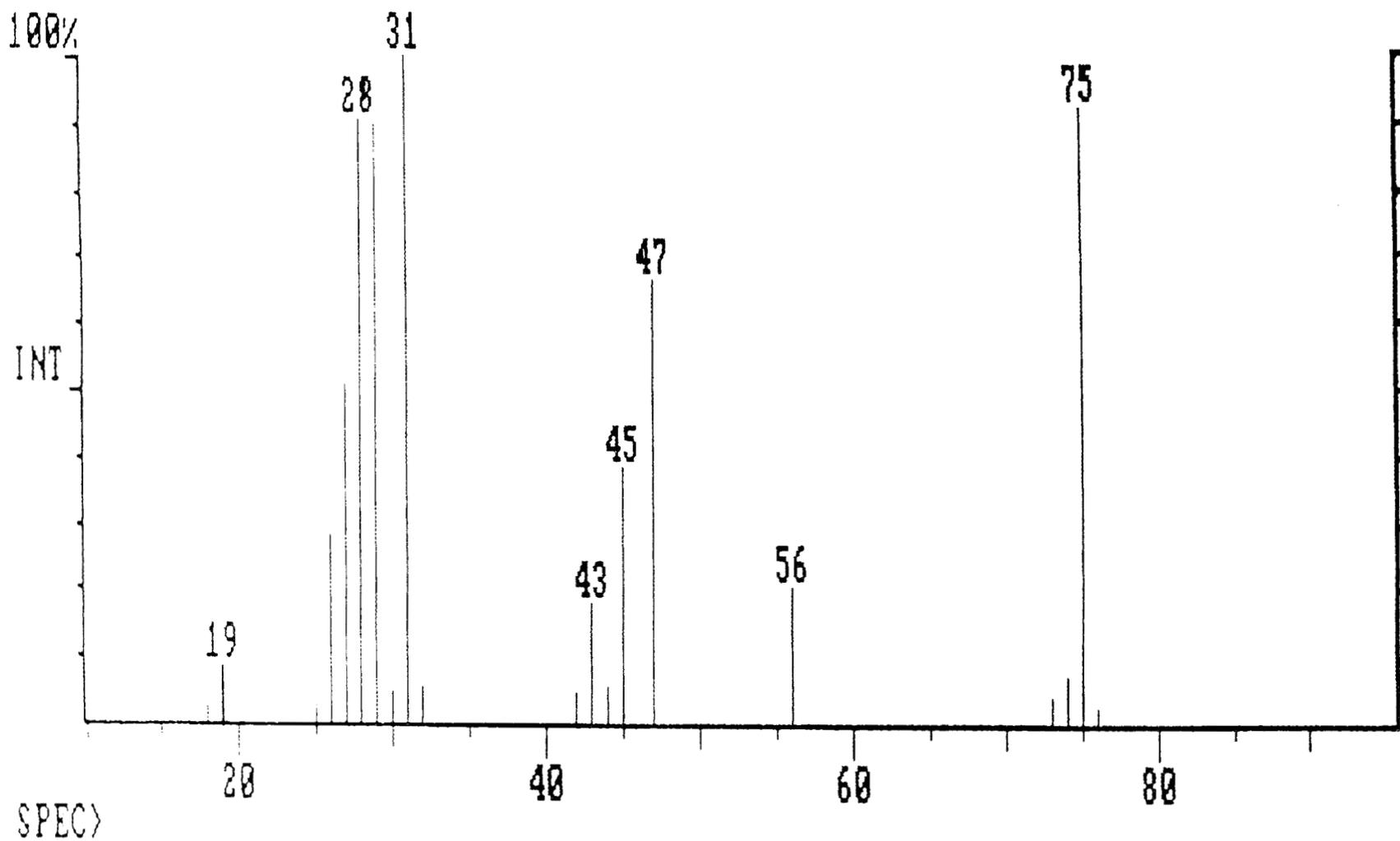
COMPOUND: ETHYLFORMATE
EI MASS SPECTRUM
(WITH METHANE)



COMPOUND: ETHYLFORMATE

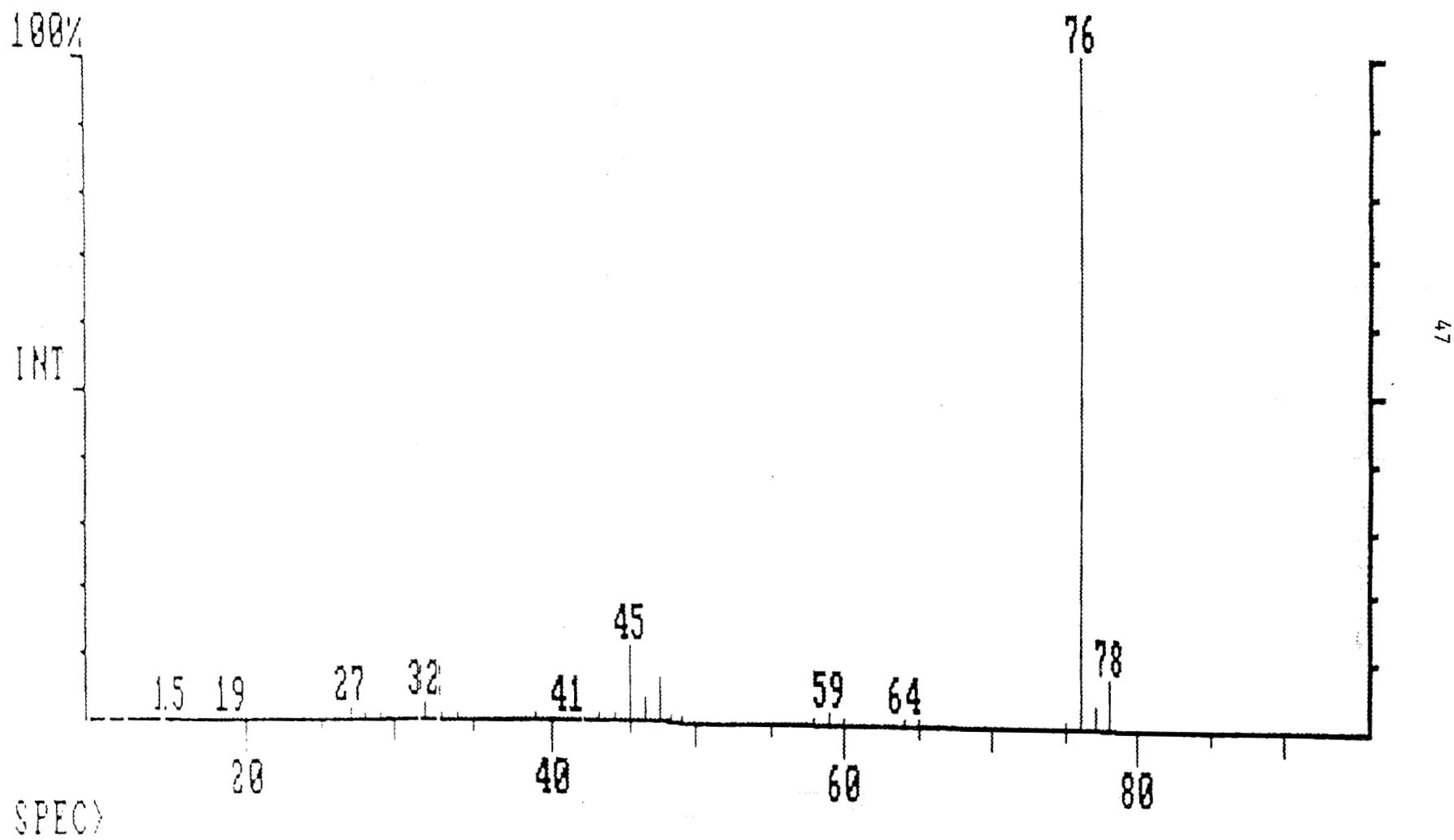
EI MASS SPECTRUM

(WITHOUT METHANE)

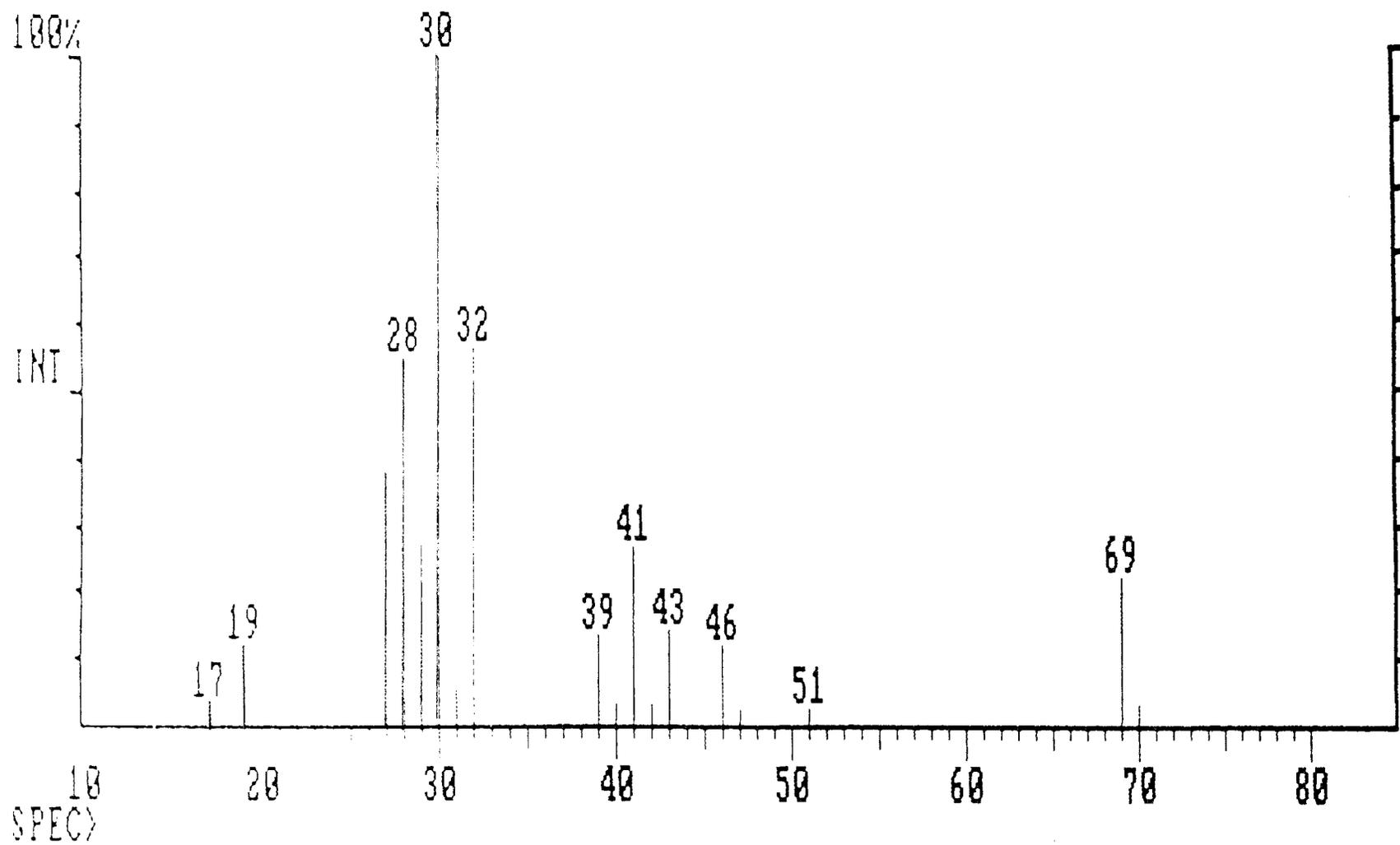


COMPOUND: CARBON DISULFIDE

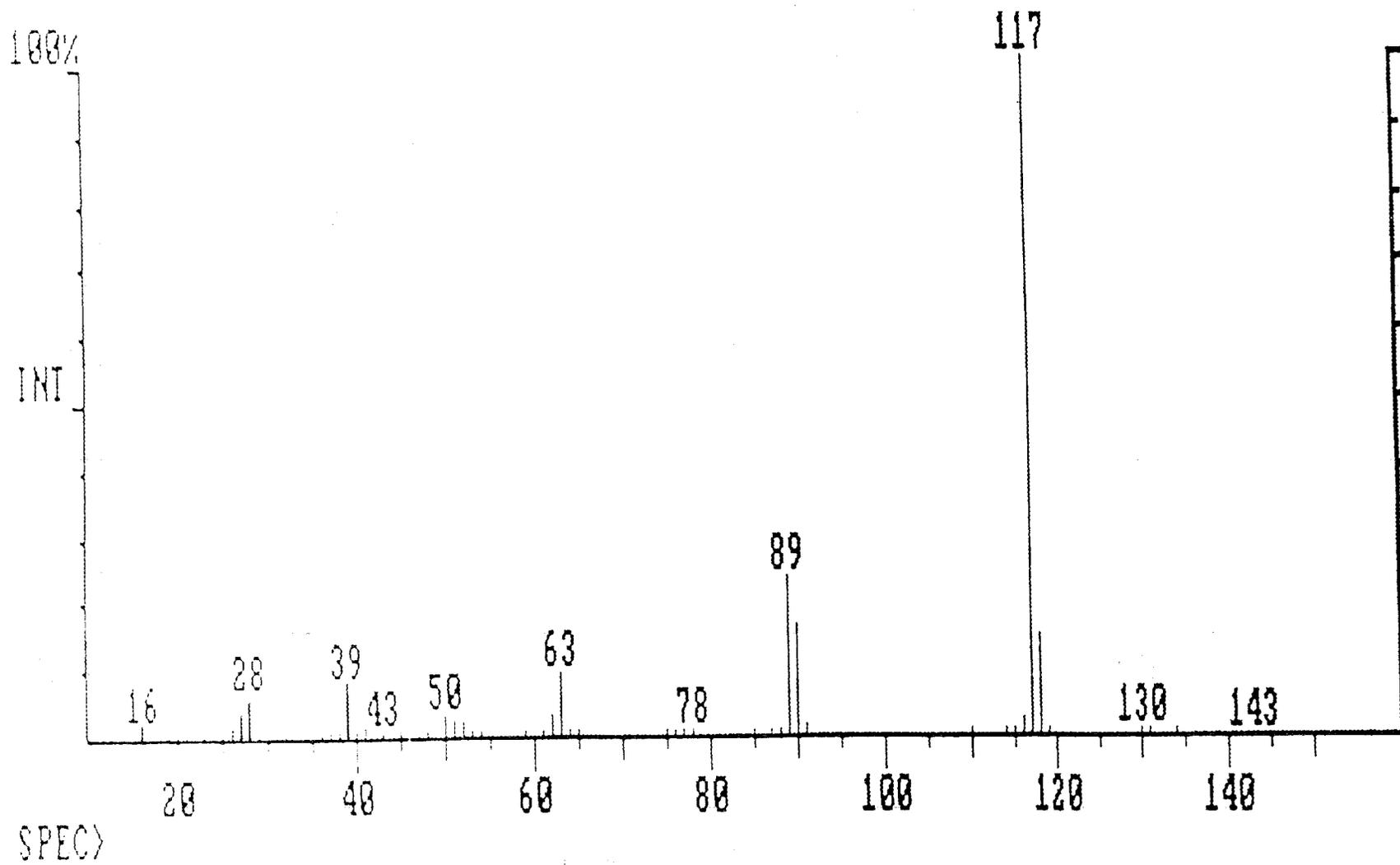
EI MASS SPECTRUM



COMPOUND: NITROGEN TETRAOXIDE
EI MASS SPECTRUM

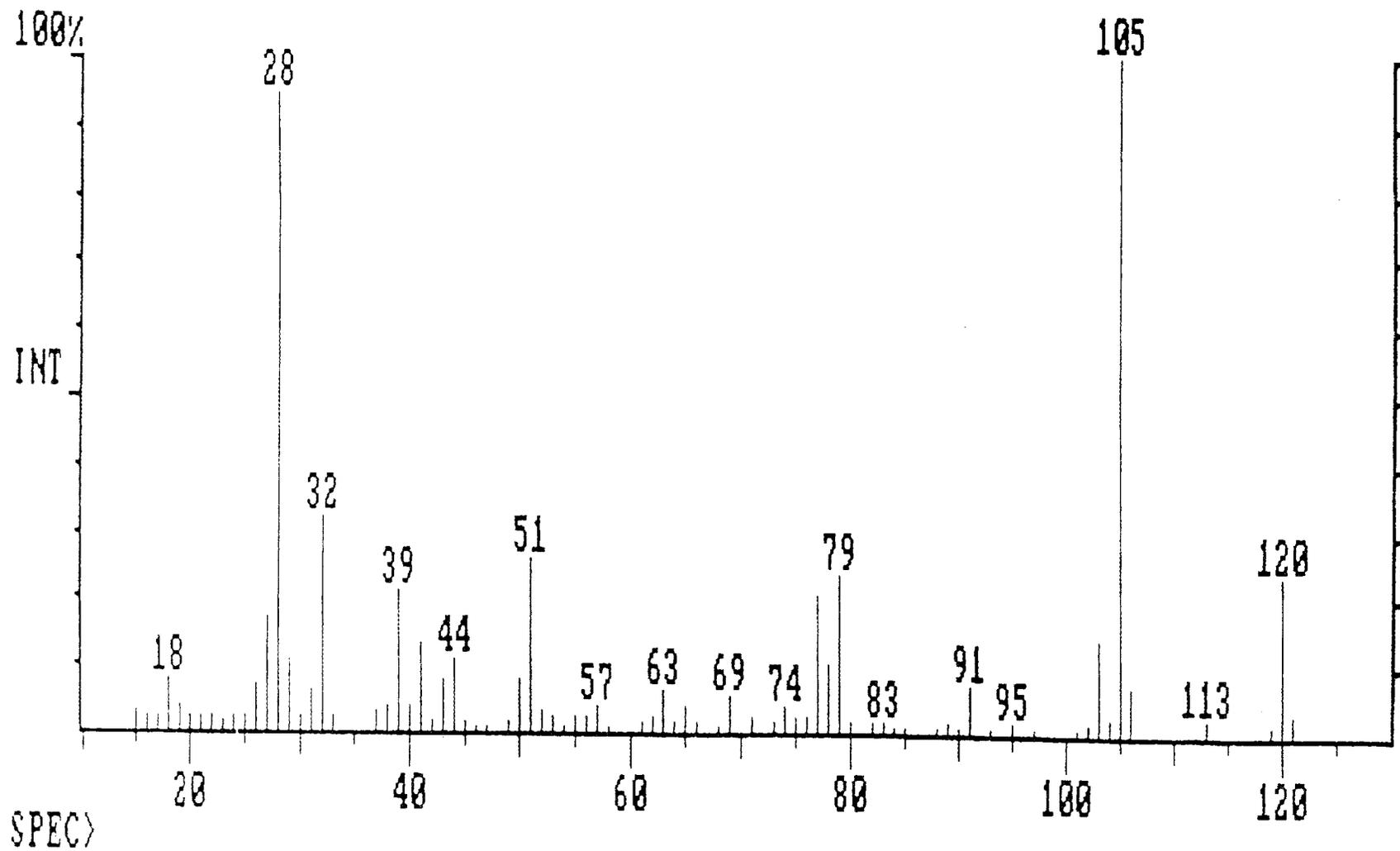


COMPOUND: INDOLE
EI MASS SPECTRUM



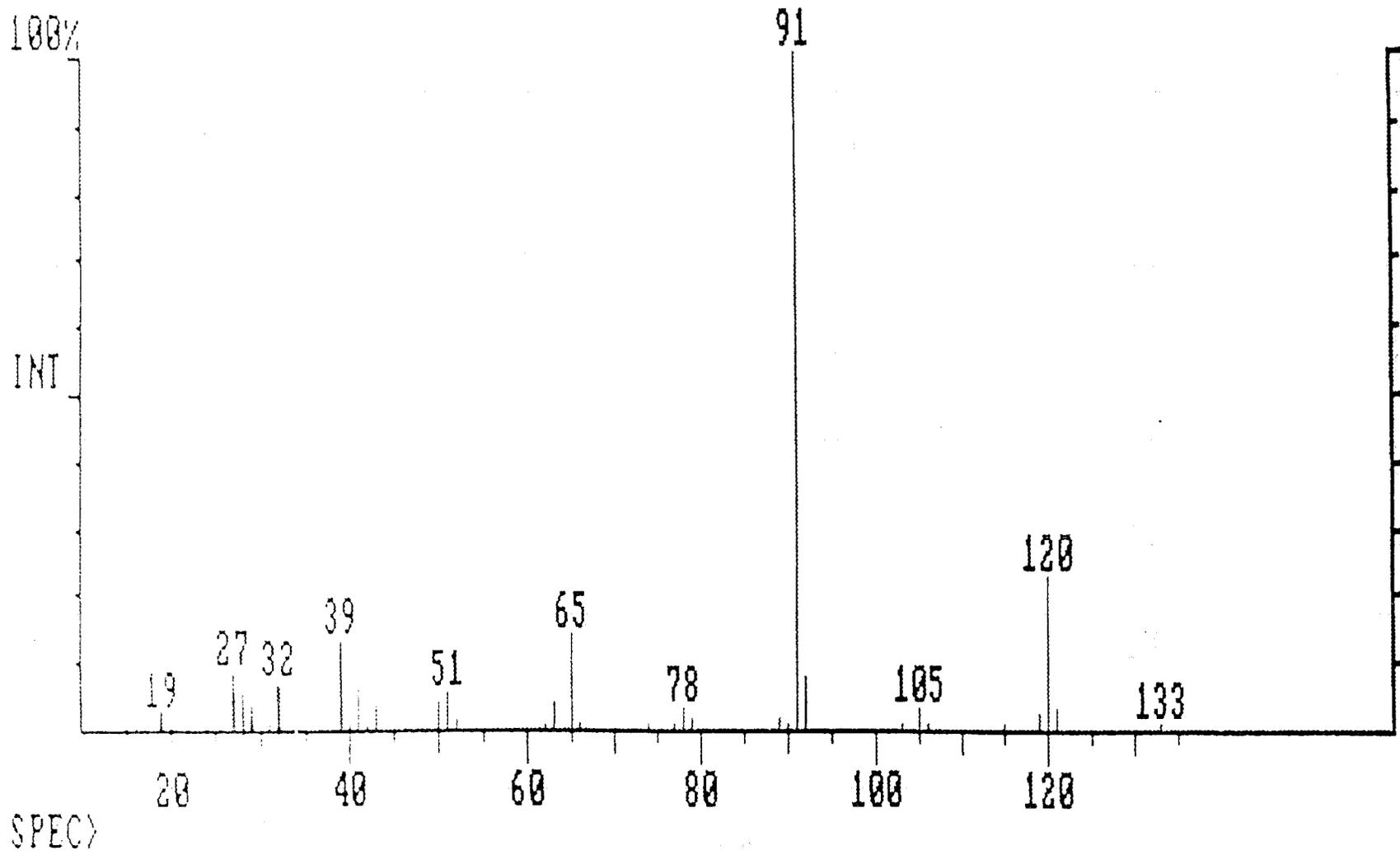
COMPOUND: LUMENE

EI MASS SPECTRUM



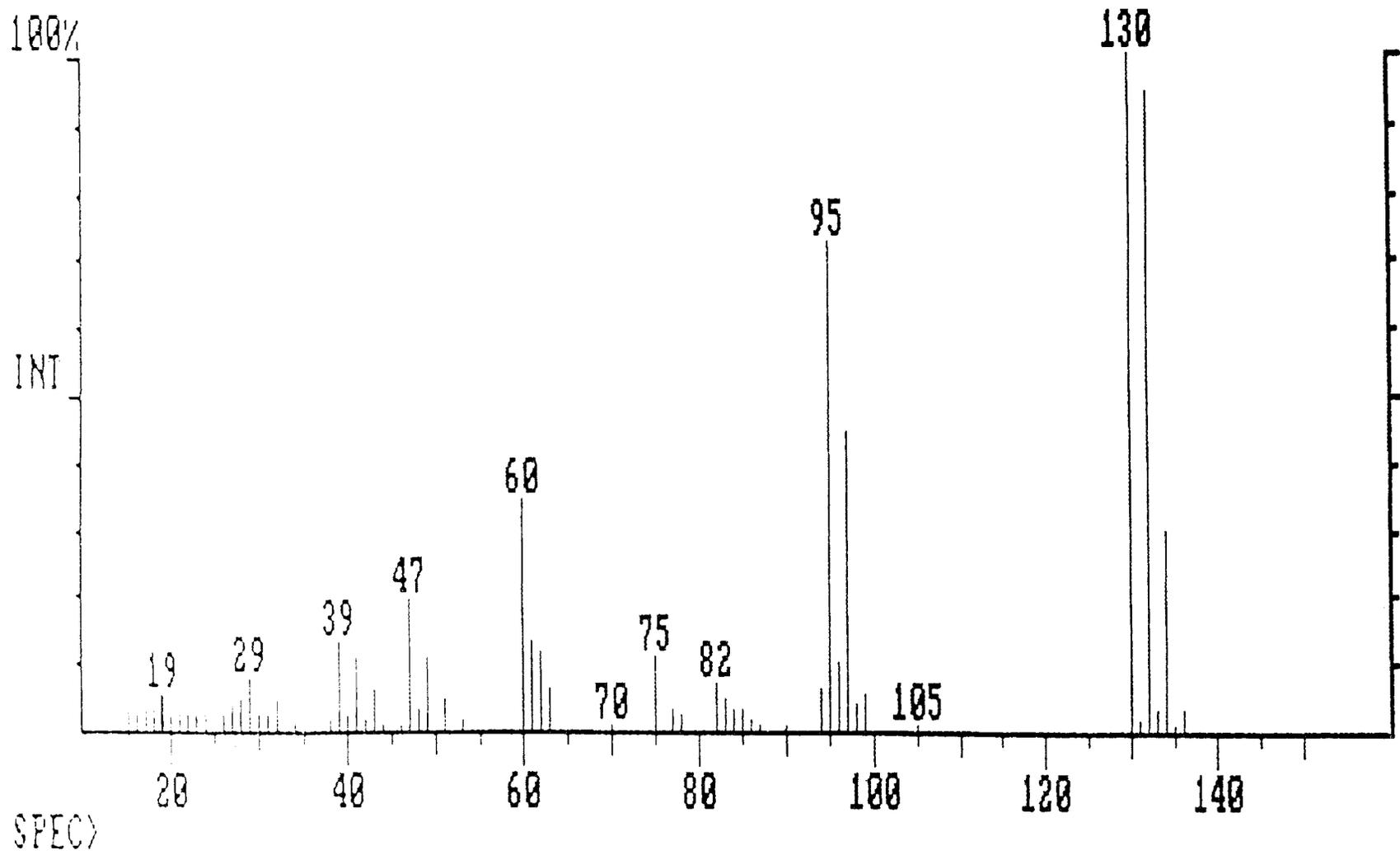
COMPOUND: N-PROPYLBENZENE

EI MASS SPECTRUM



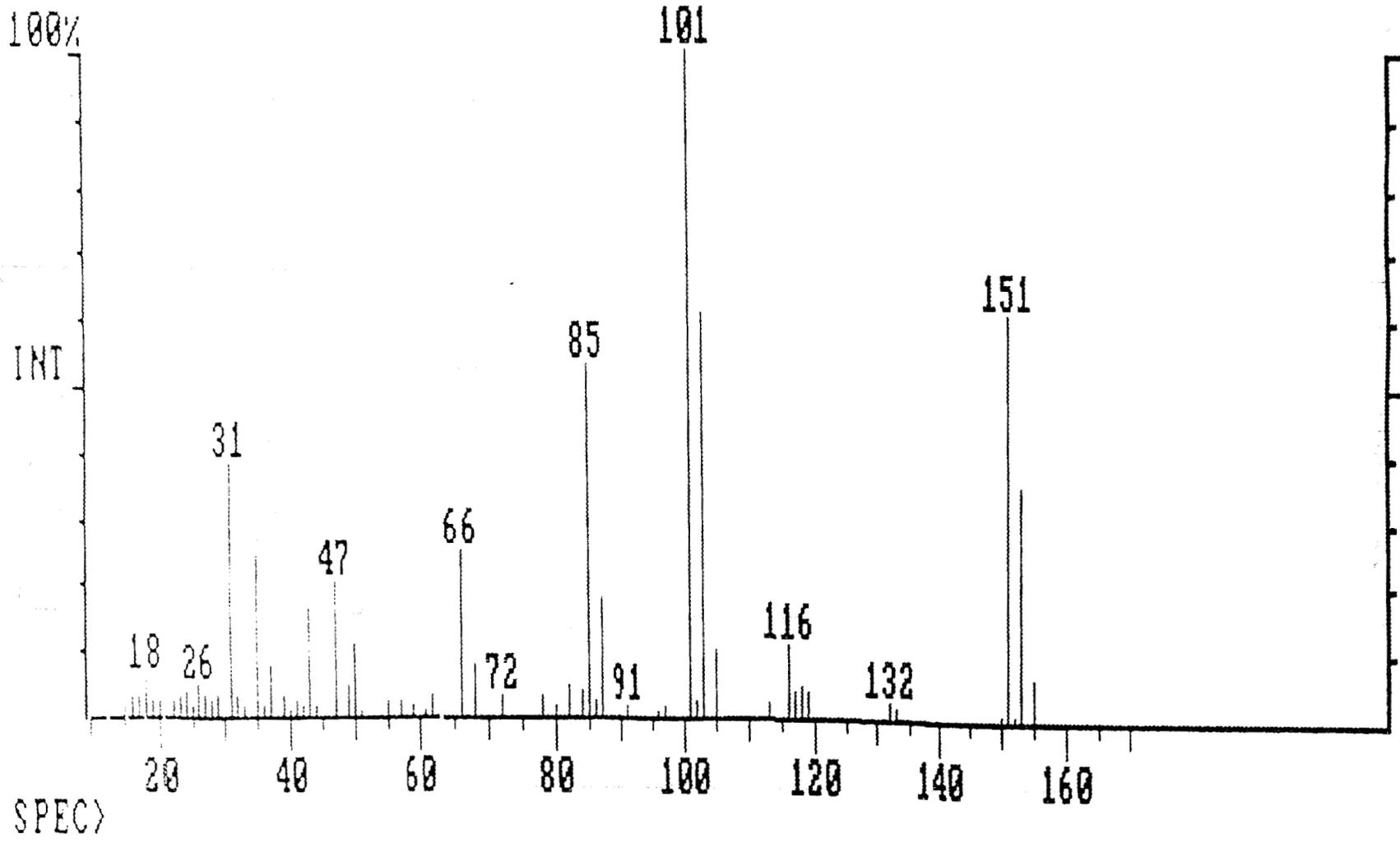
COMPOUND: TRICHLOROETHYLENE

EI MASS SPECTRUM



COMPOUND: FREON 113

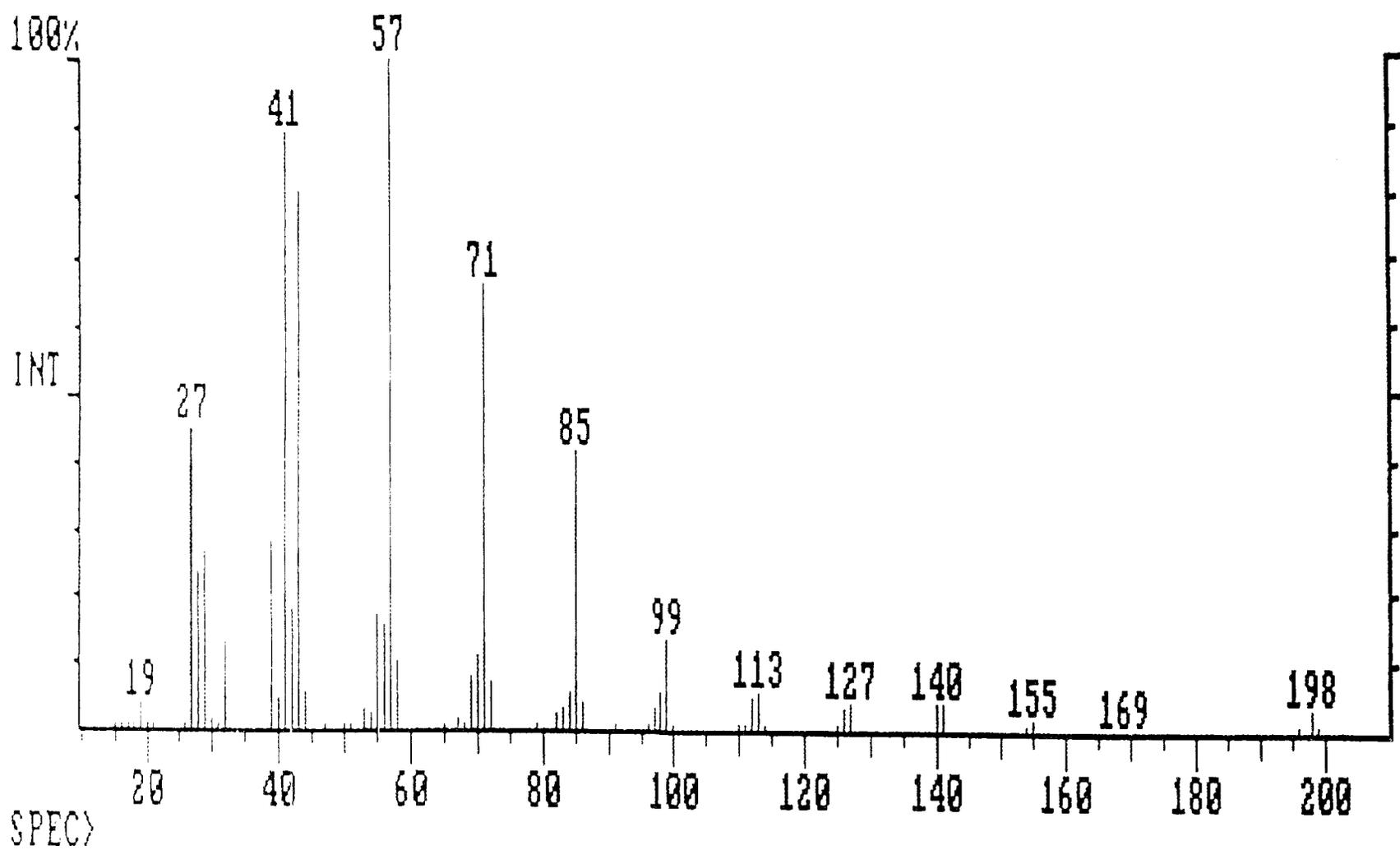
EI MASS SPECTRUM



COMPOUND: TETRADECANE

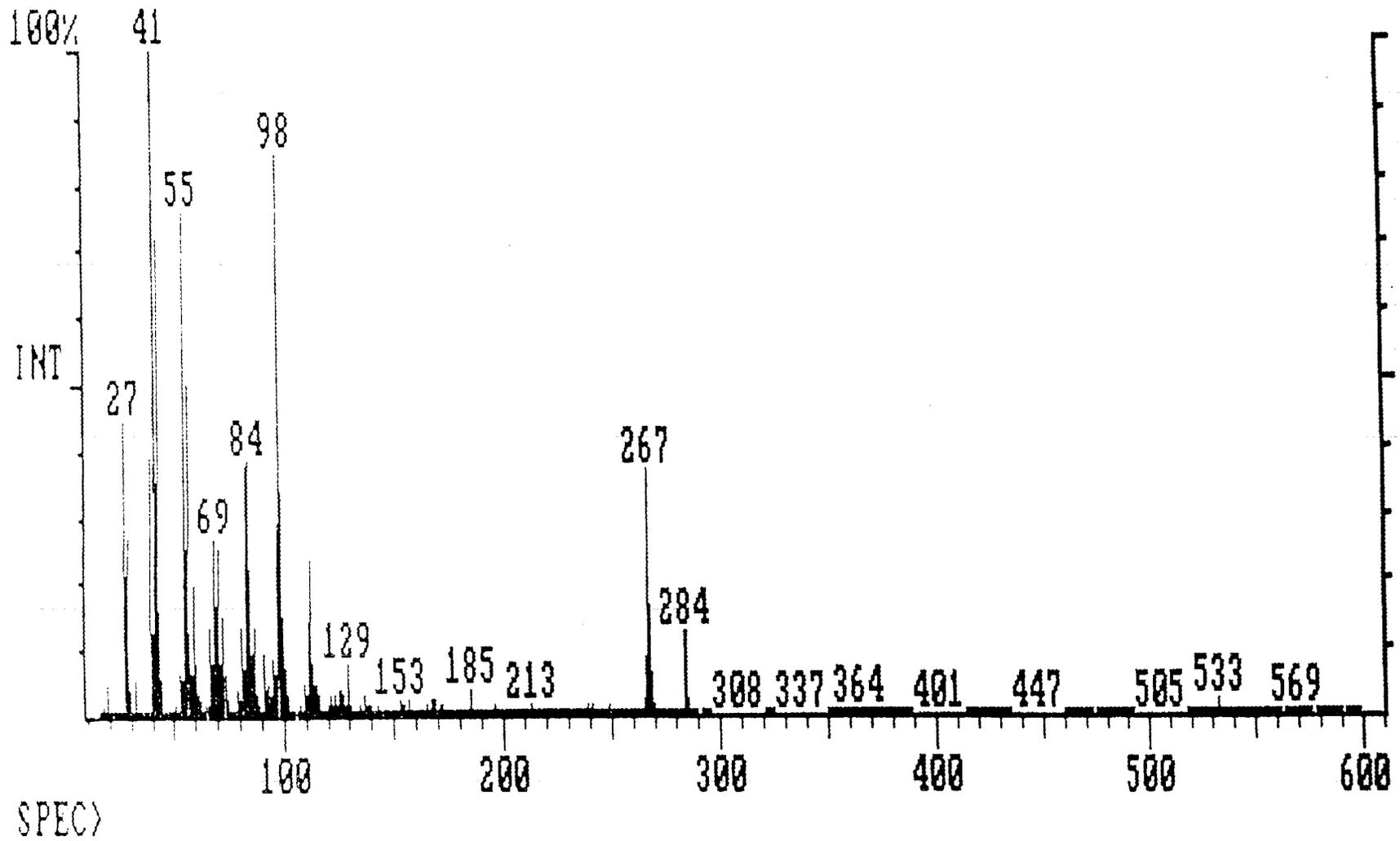
EI MASS SPECTRUM

(WITH METHANE)



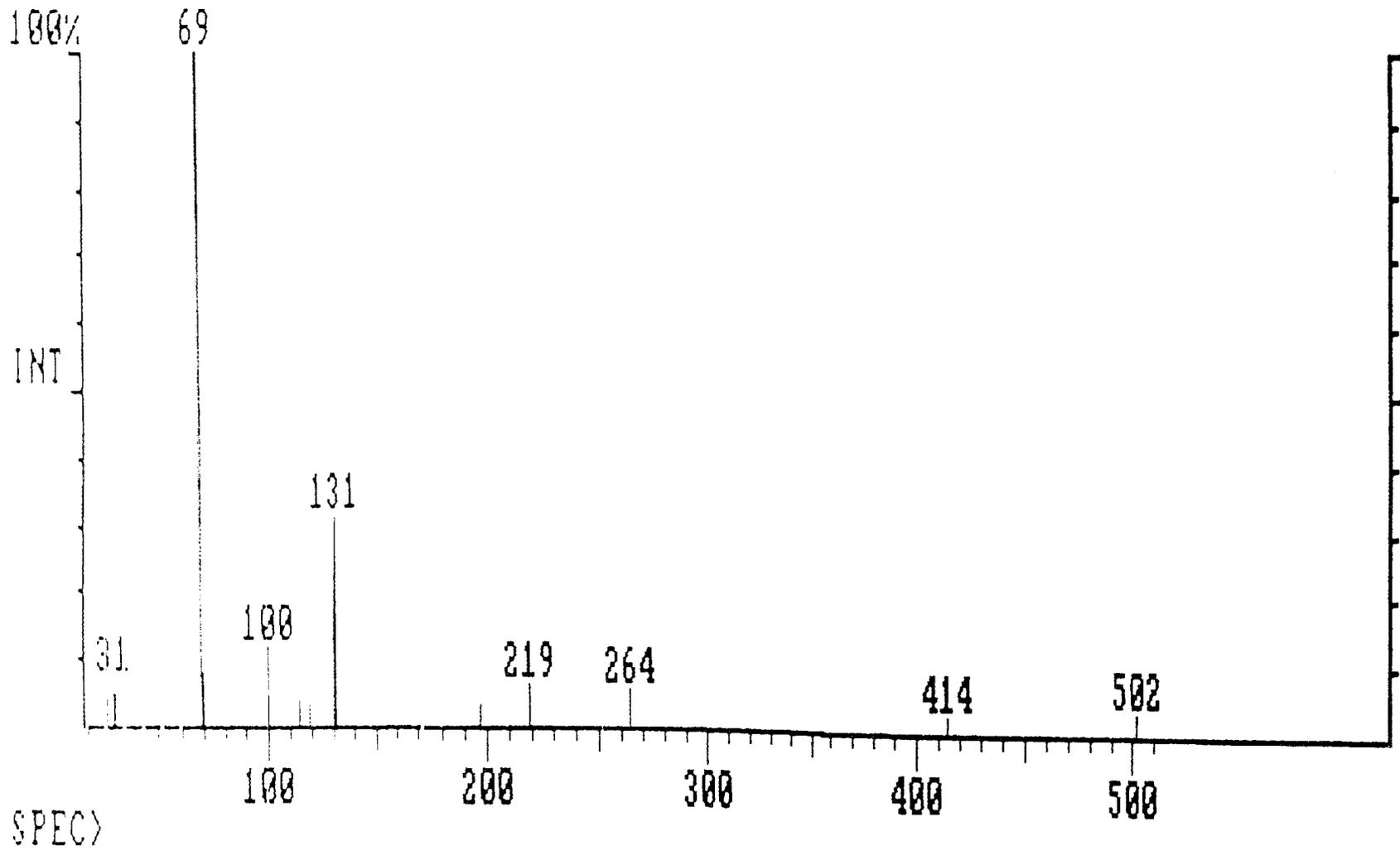
COMPOUND: STEARIC ANHYDRIDE

EI MASS SPECTRUM

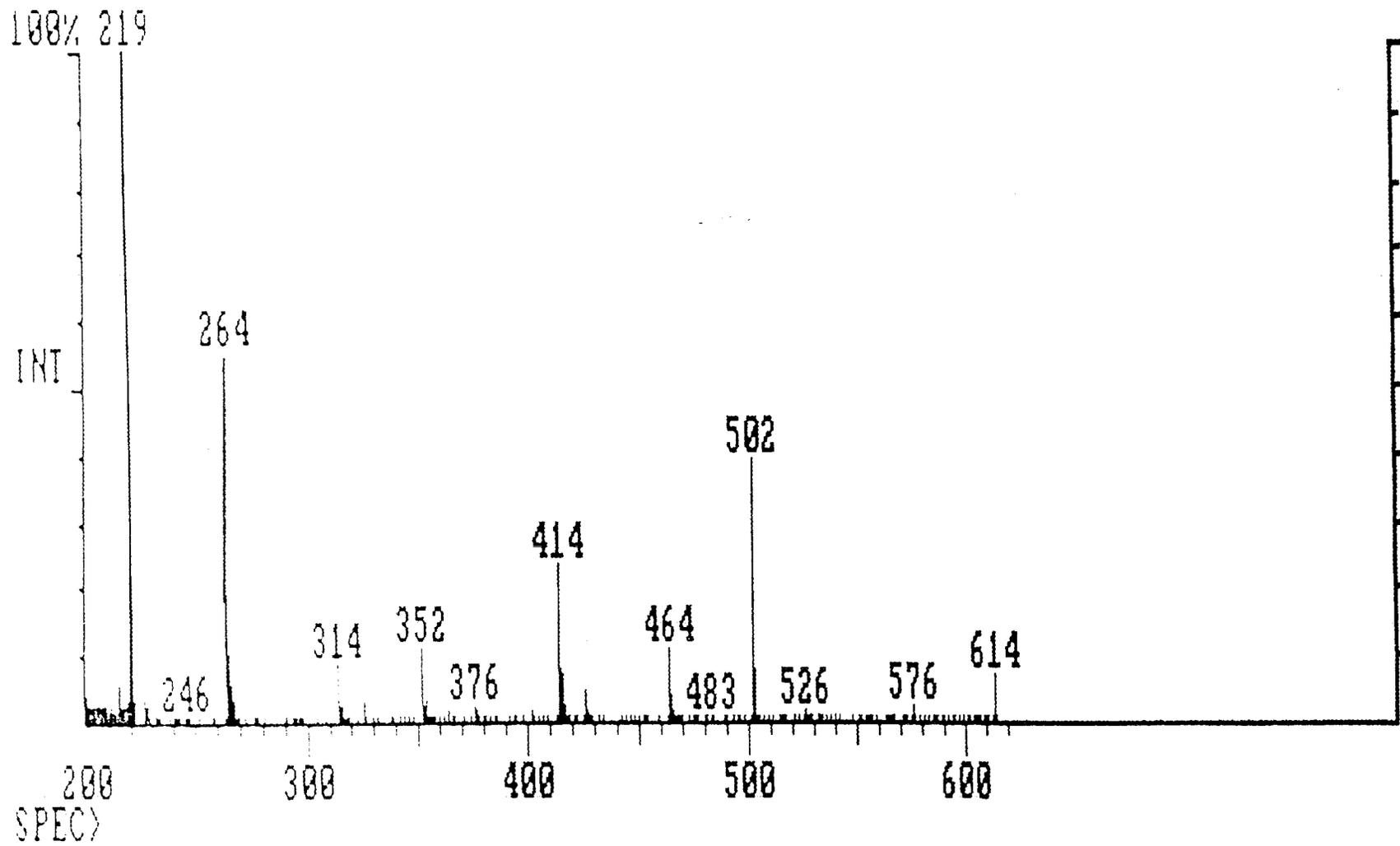


COMPOUND: PERFLUOROKEROSENE

EI MASS SPECTRUM



COMPOUND: PERFLUOROKEROSENE
EI MASS SPECTRUM

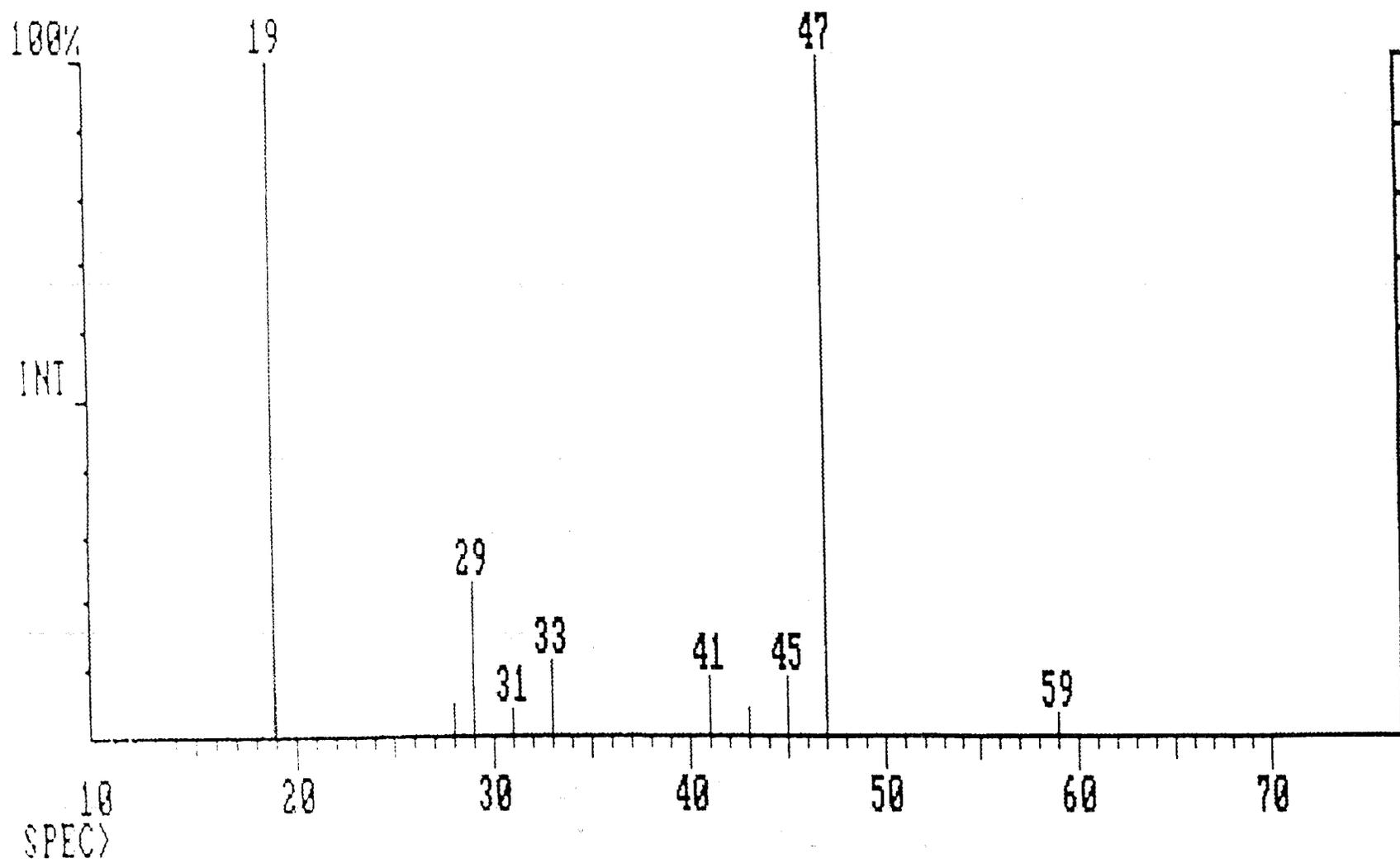


Appendix B

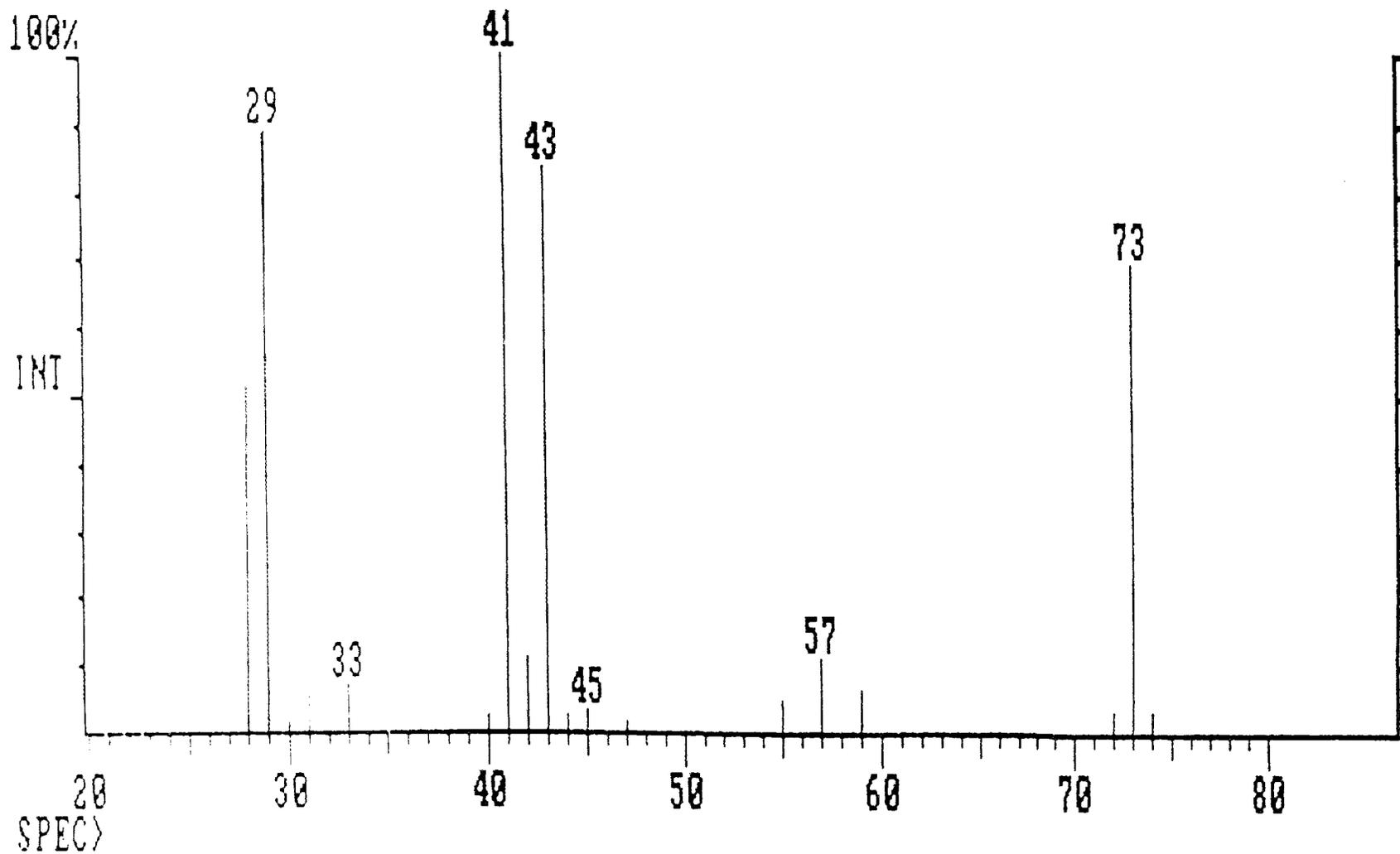
CI mass spectra from the ITMS

COMPOUND: ETHANOL

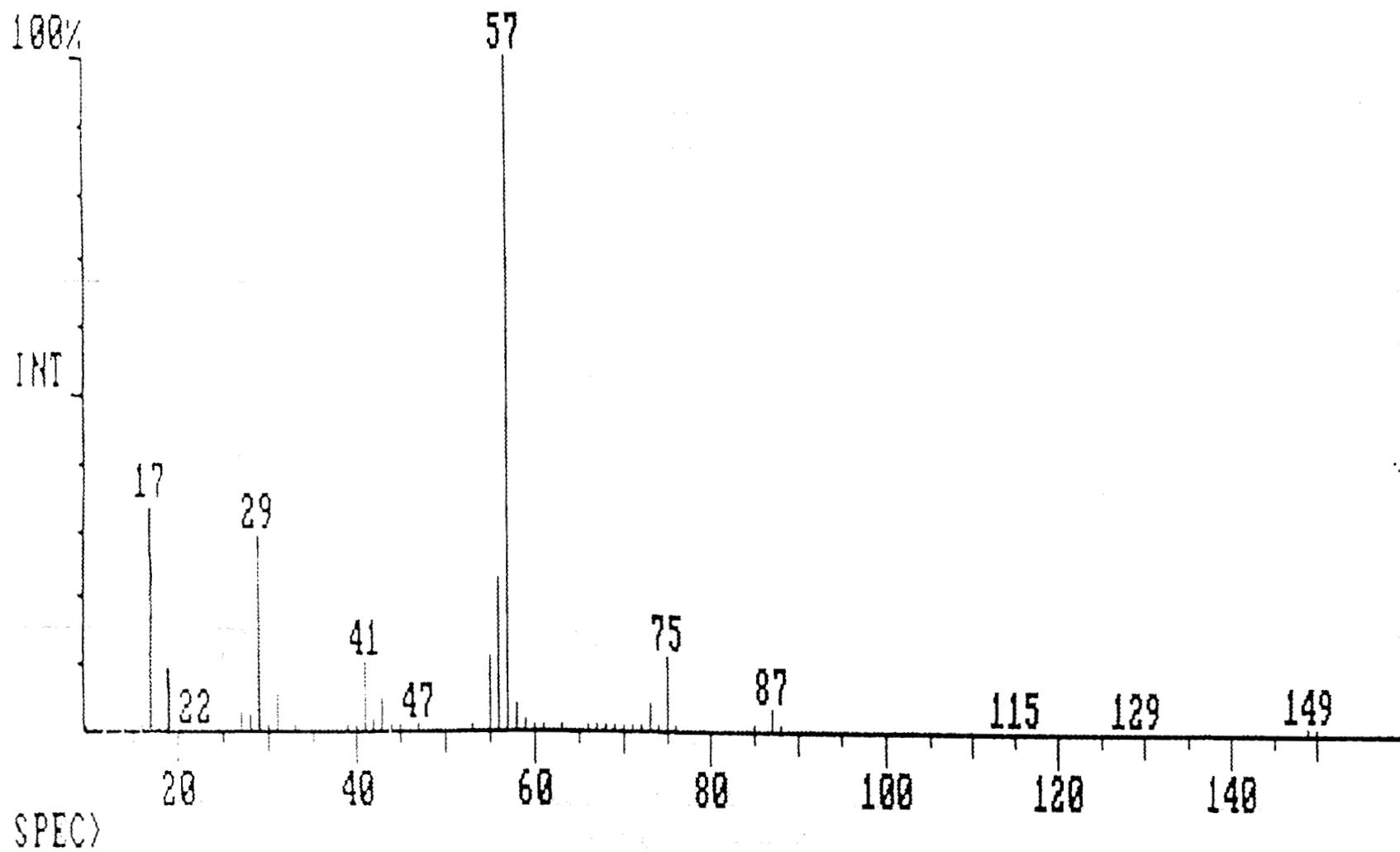
CI MASS SPECTRUM



COMPOUND: METHYLETHYLKETONE
CI MASS SPECTRUM

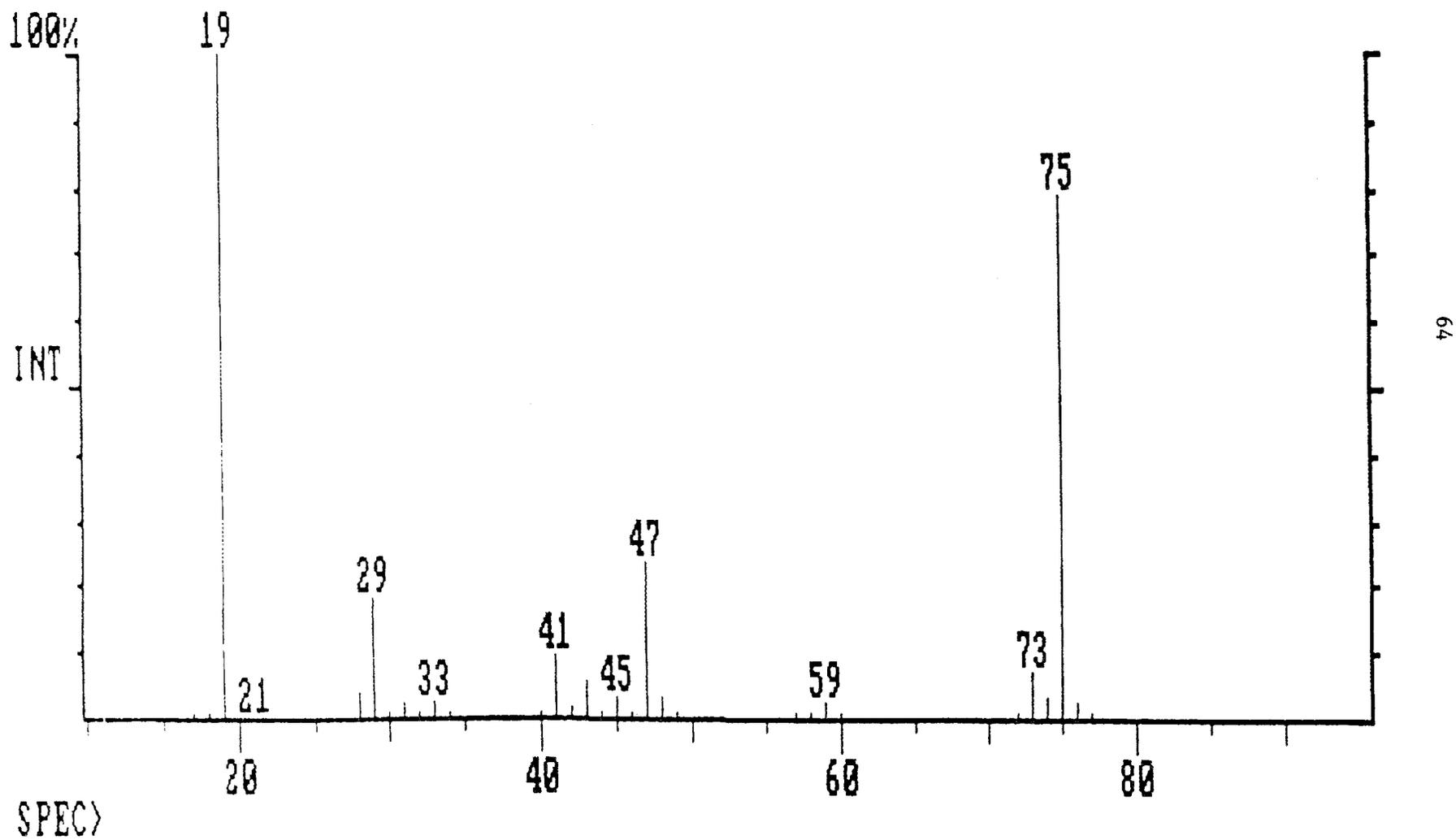


COMPOUND: BUTANOL
CI MASS SPECTRUM



COMPOUND: DIETHYLETHER

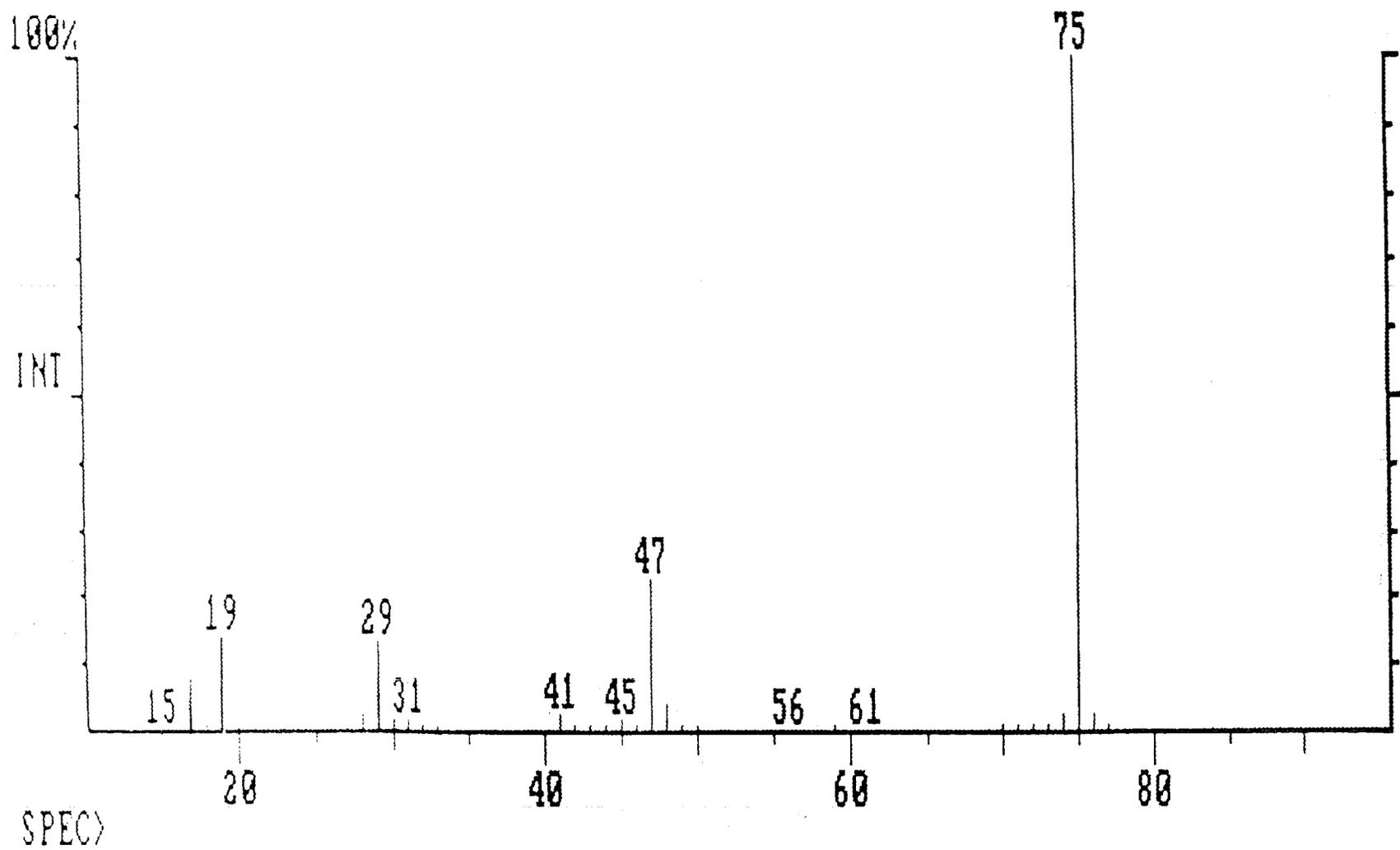
CI MASS SPECTRUM



COMPOUND: ETHYLFORMATE

CI MASS SPECTRUM

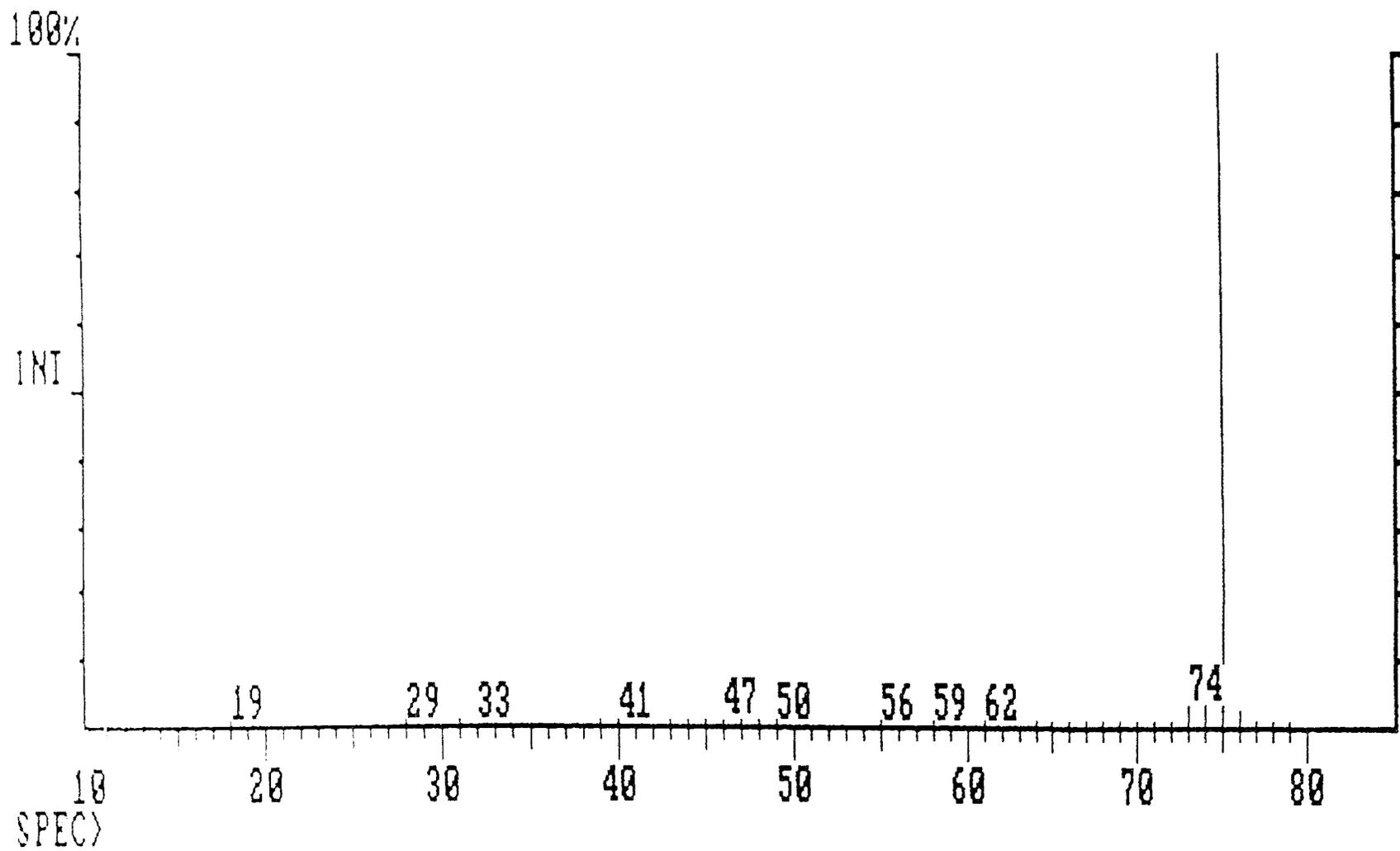
(10 MSEC REACTION TIME)



COMPOUND: ETHYLFORMATE

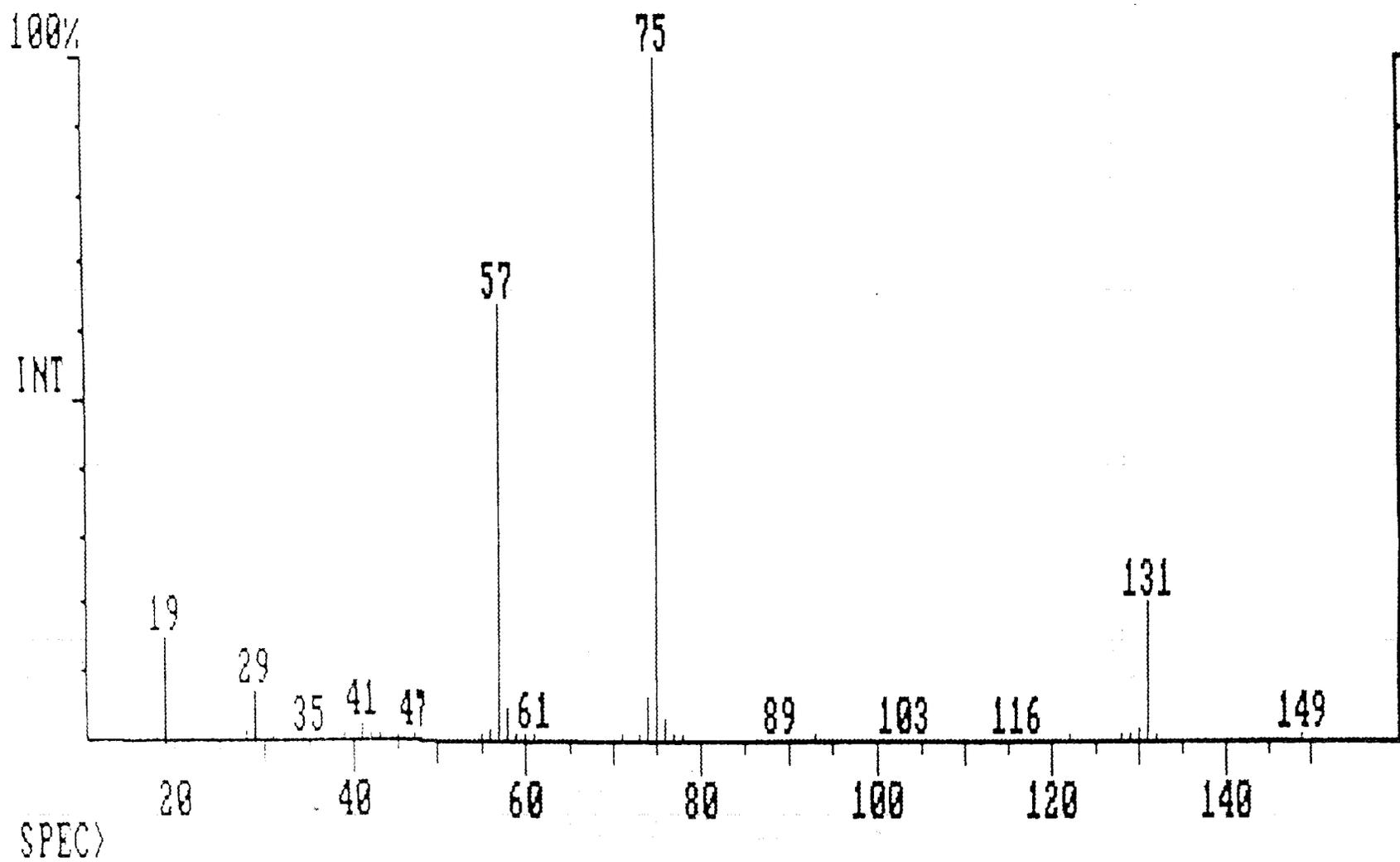
CI MASS SPECTRUM

(50 MSEC REACTION TIME)

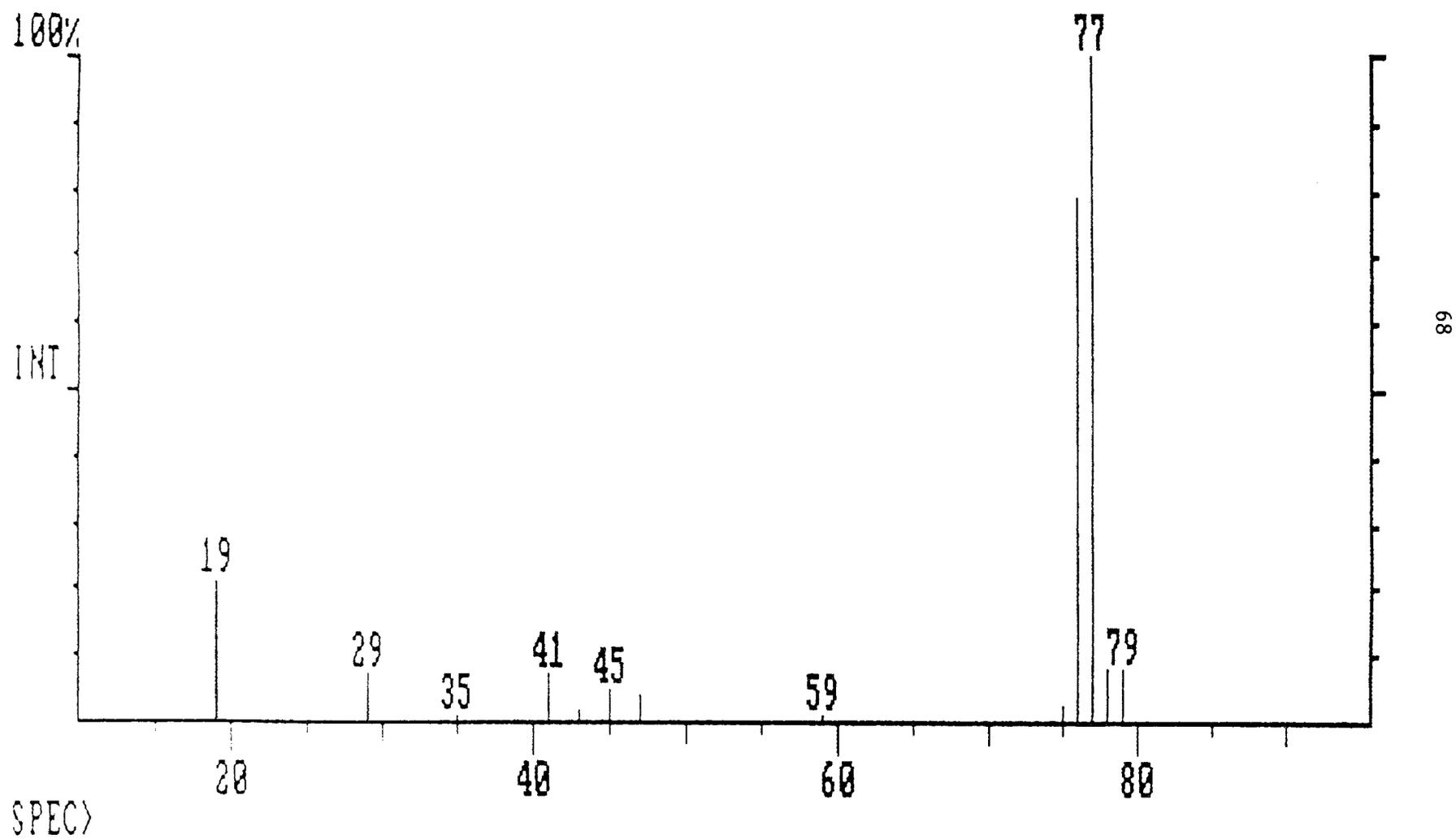


COMPOUND: PROPIONIC ACID

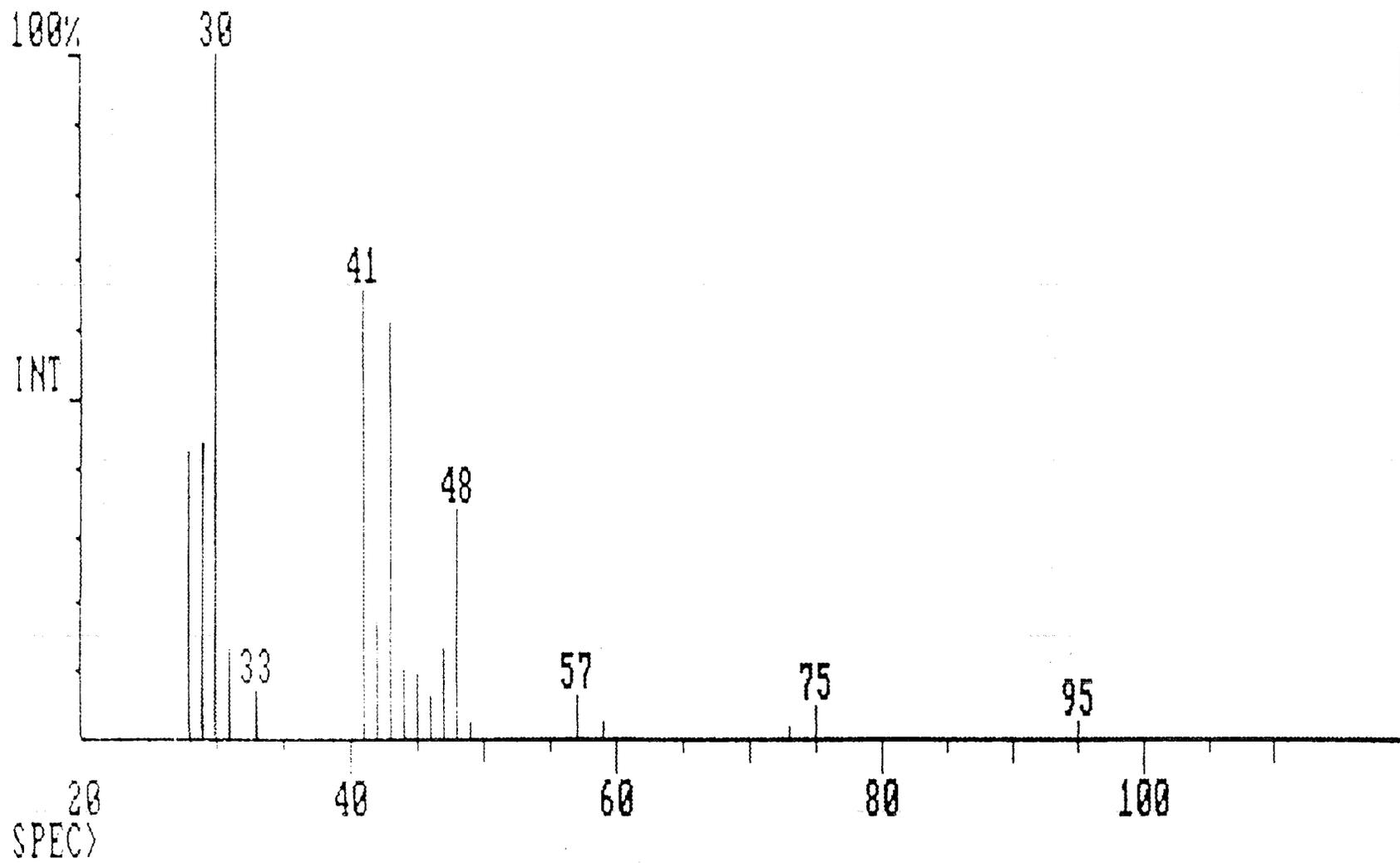
CI MASS SPECTRUM



COMPOUND: CARBON DISULFIDE
CI MASS SPECTRUM

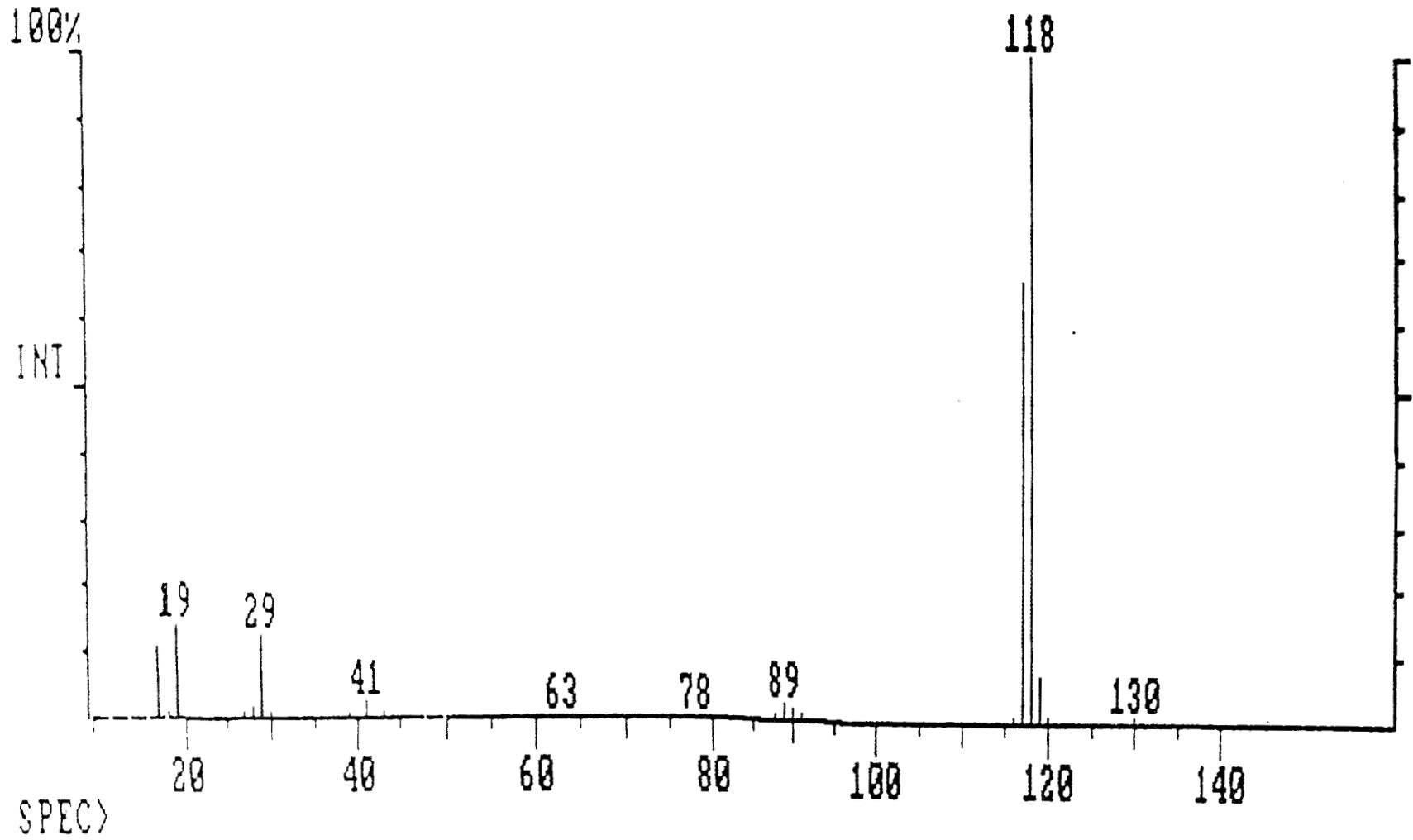


COMPOUND: NITROGEN TETRAOXIDE
CI MASS SPECTRUM



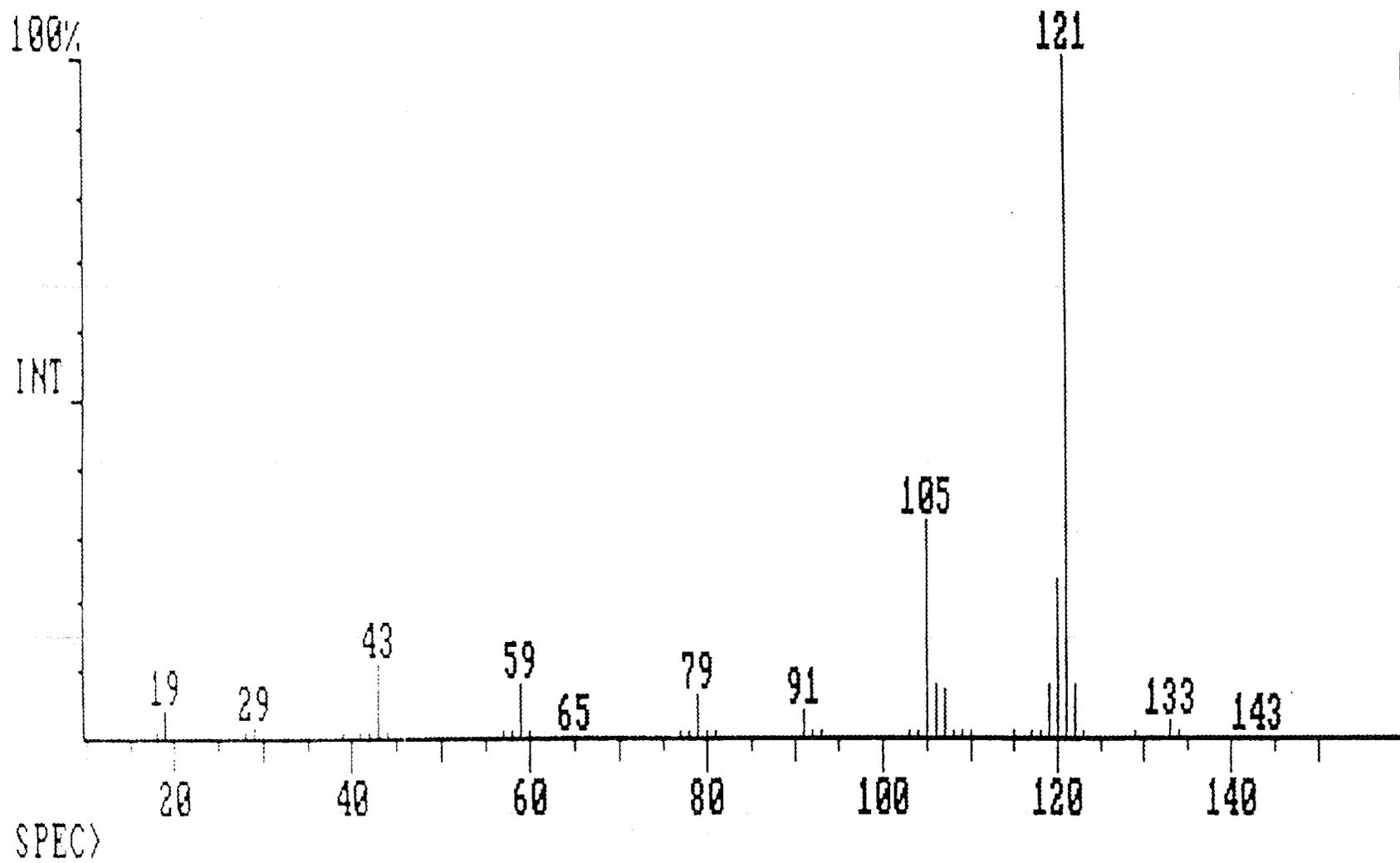
COMPOUND: INDOLE

CI MASS SPECTRUM



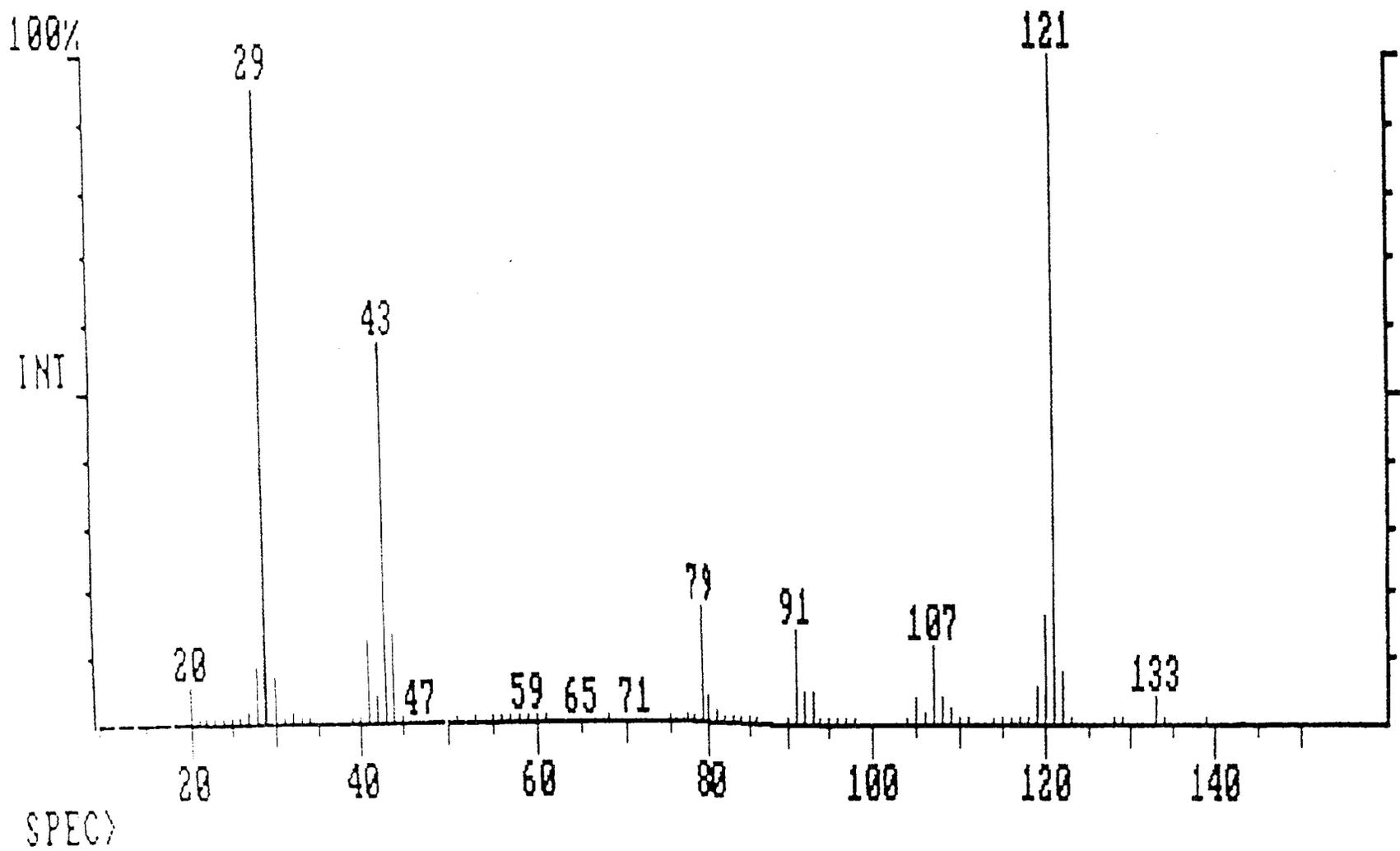
70

COMPOUND: CUMENE
CI MASS SPECTRUM



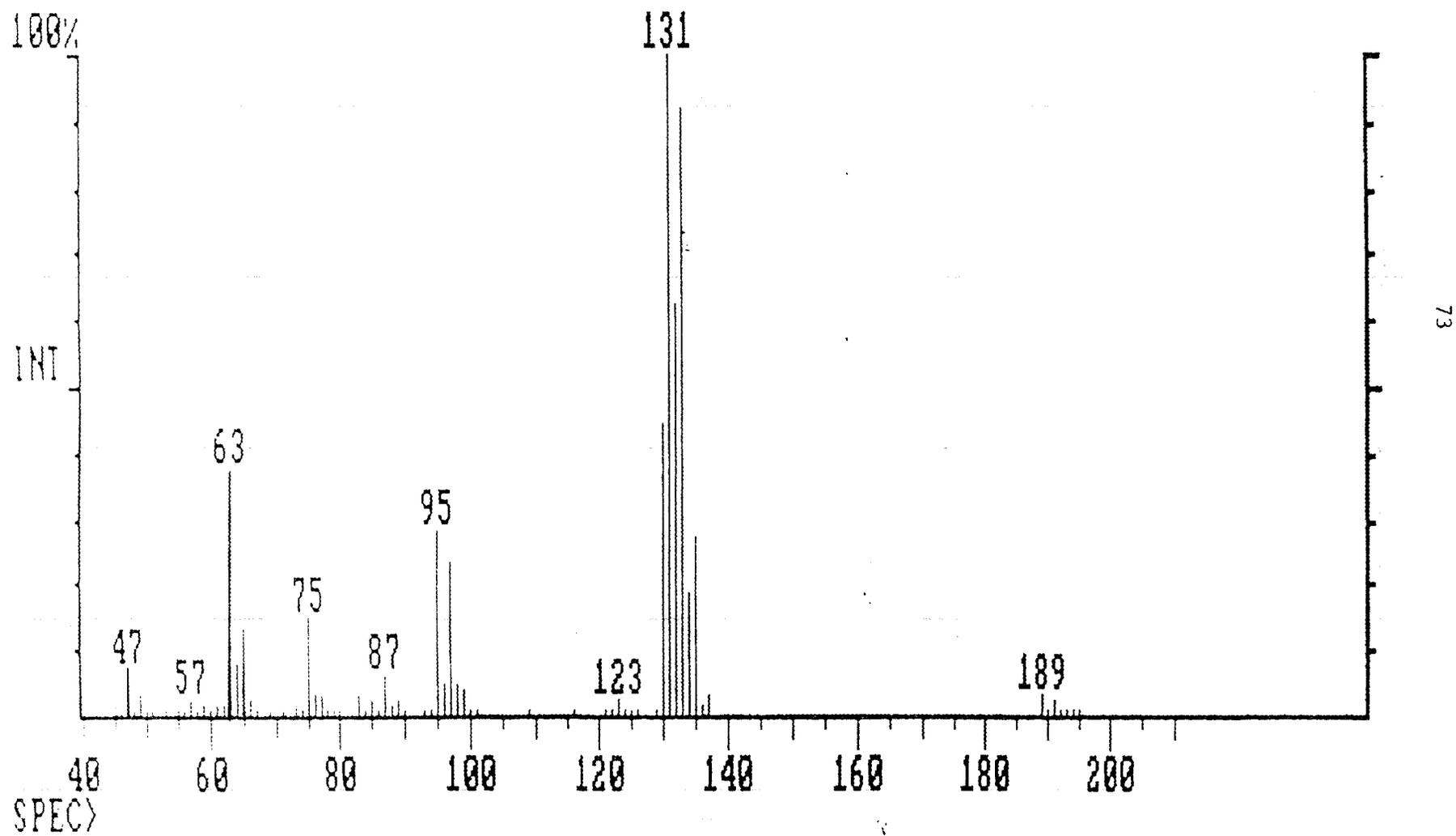
COMPOUND: N-PROPYLBENZENE

CI MASS SPECTRUM



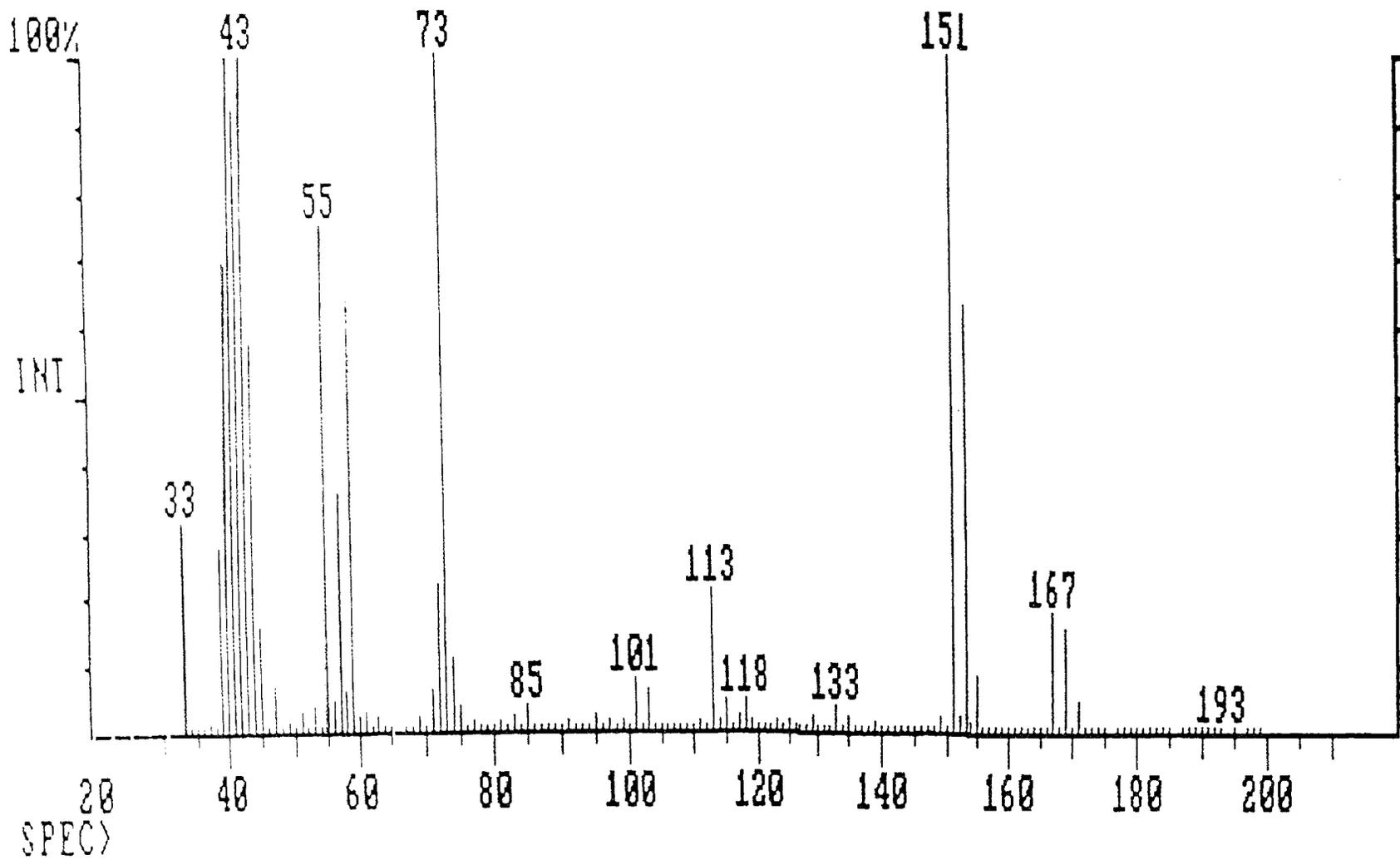
COMPOUND: TRICHLOROETHYLENE

CI MASS SPECTRUM



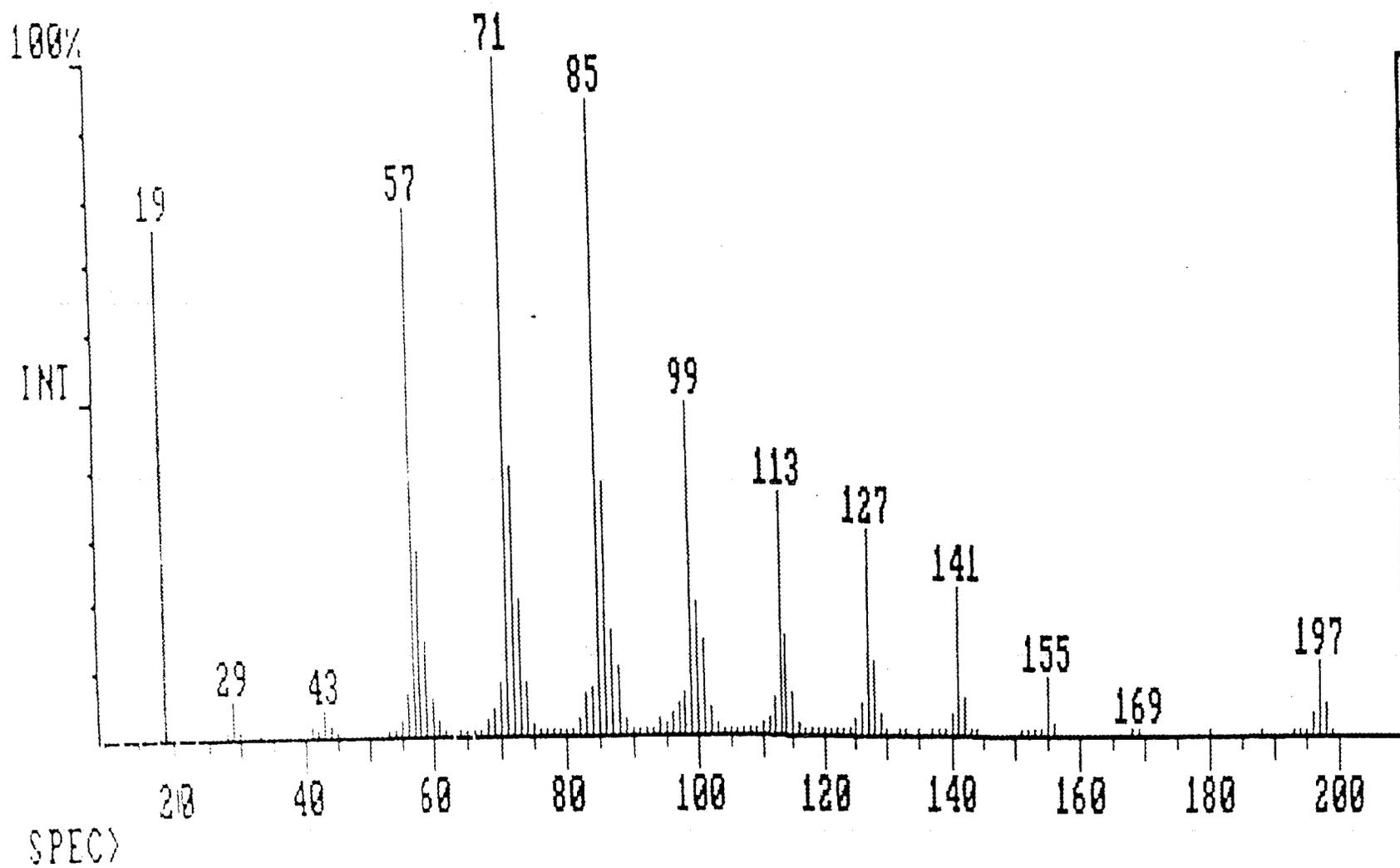
COMPOUND: FREON 113

CI MASS SPECTRUM



COMPOUND: TETRADECANE

CI MASS SPECTRUM



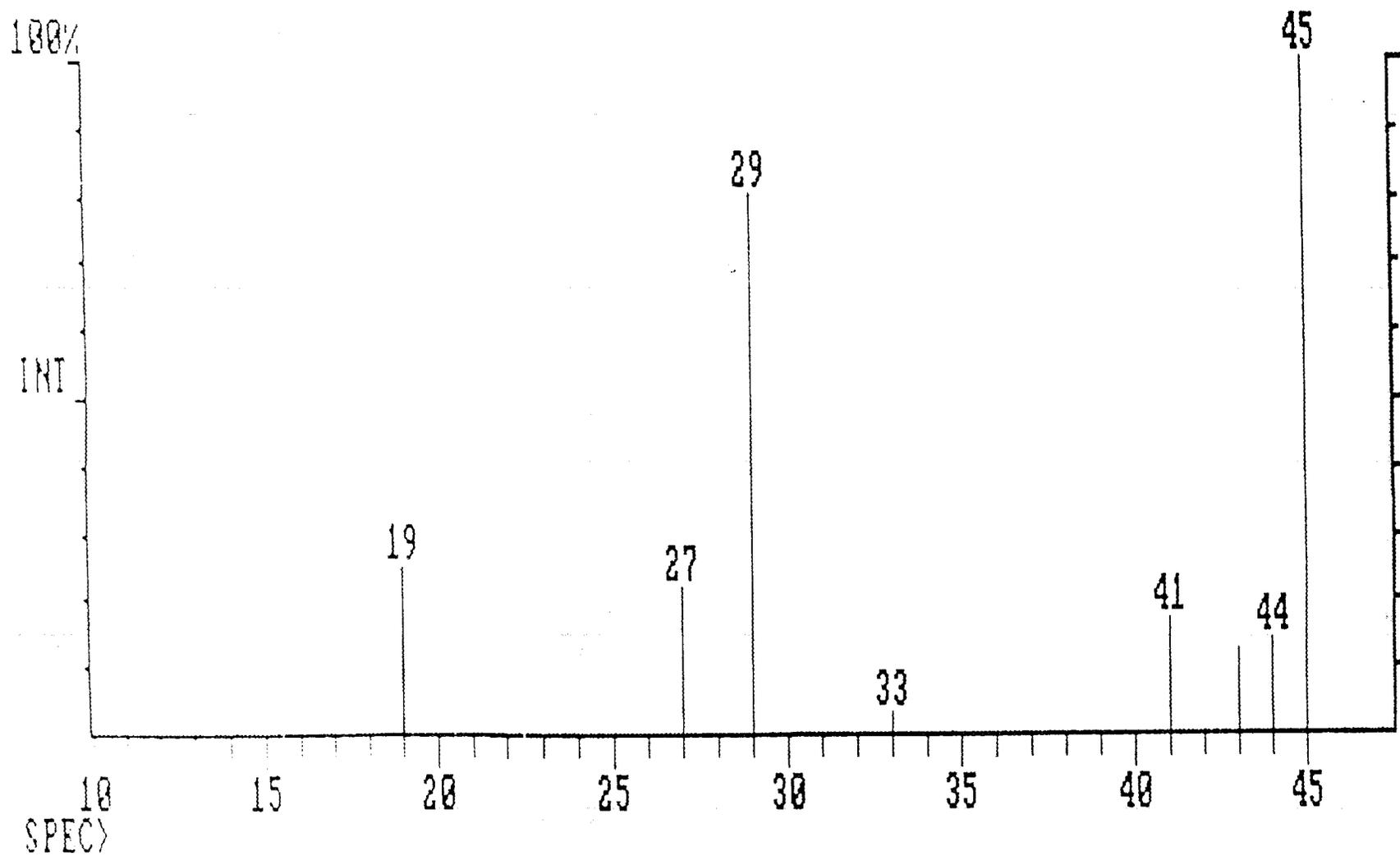
Appendix C

EI MS/MS spectra from the ITMS

COMPOUND: ETHANOL

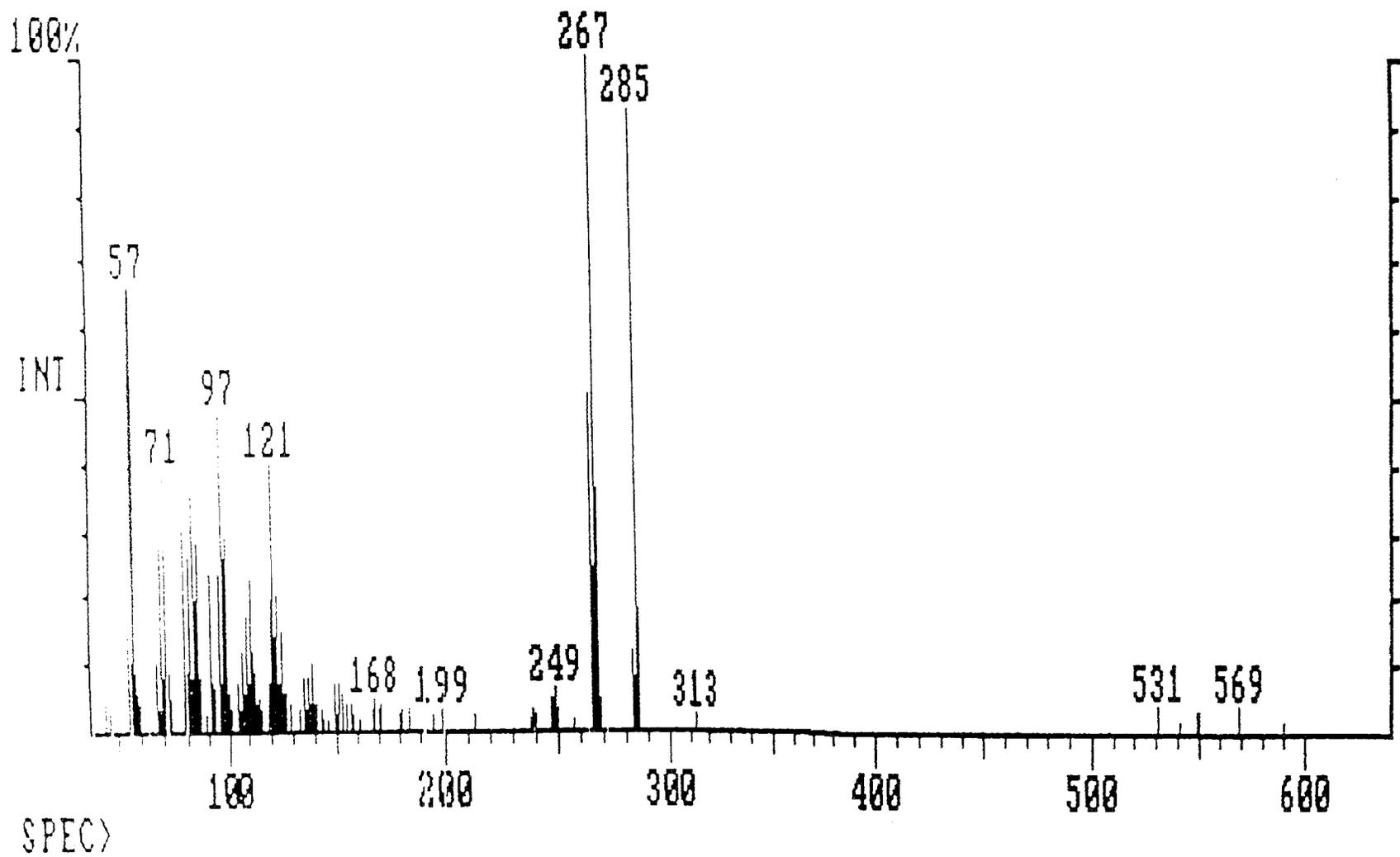
EI MS/MS SPECTRUM OF M/Z 45

(WITH METHANE)

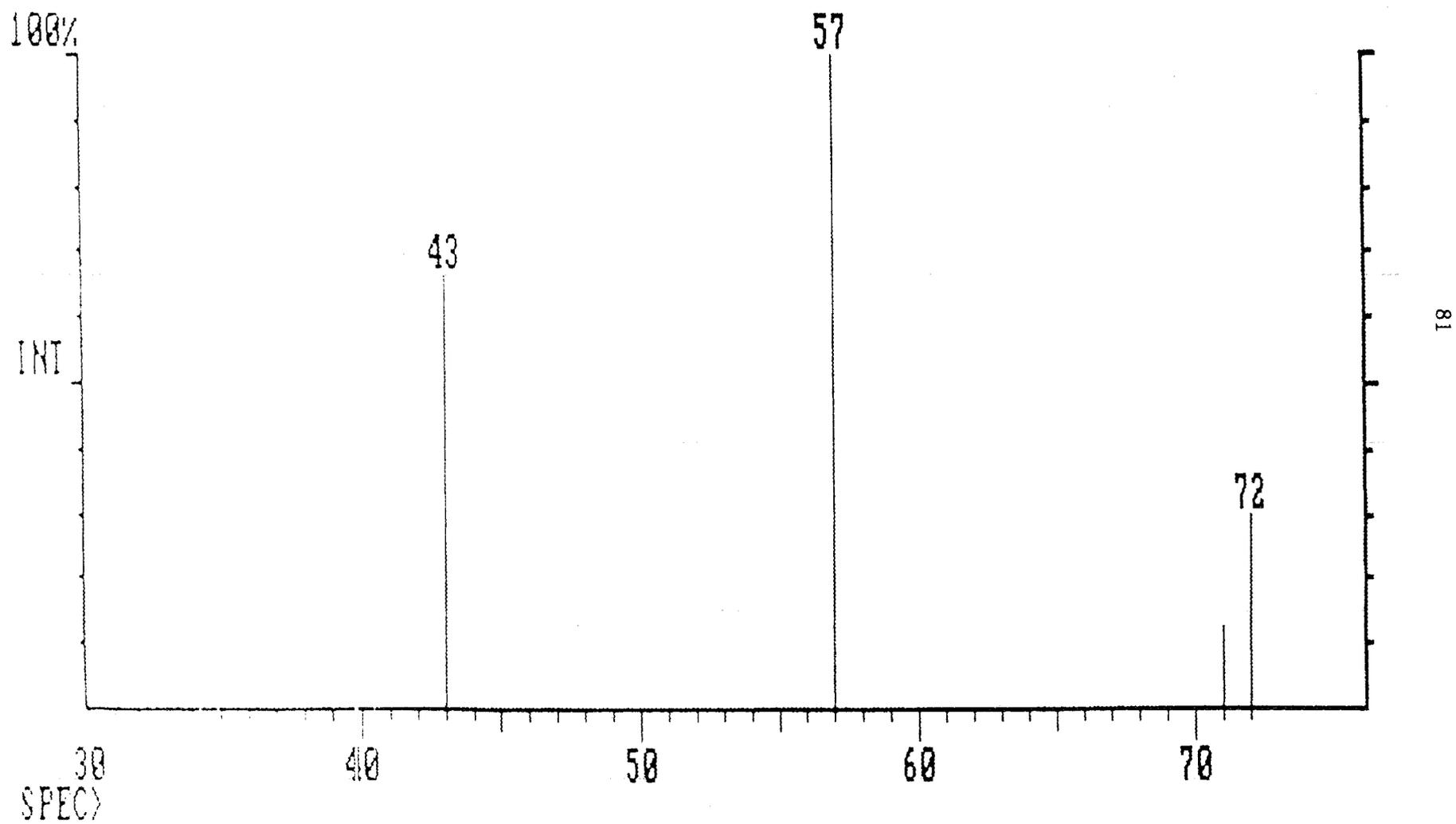


COMPOUND: STEARIC ANHYDRIDE

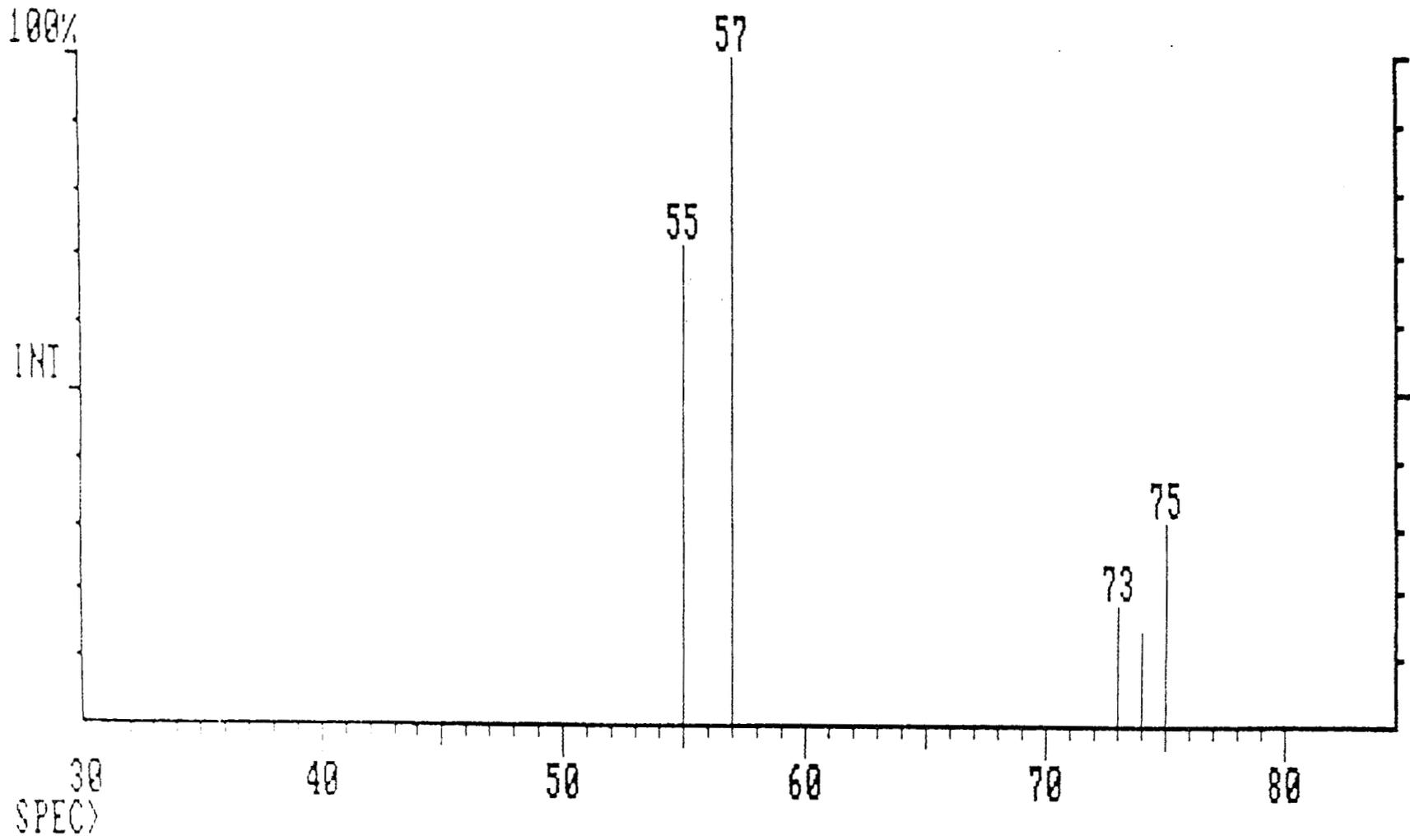
CI MASS SPECTRUM



COMPOUND: METHYLETHYLKETONE
EI MS/MS SPECTRUM OF M/Z 72

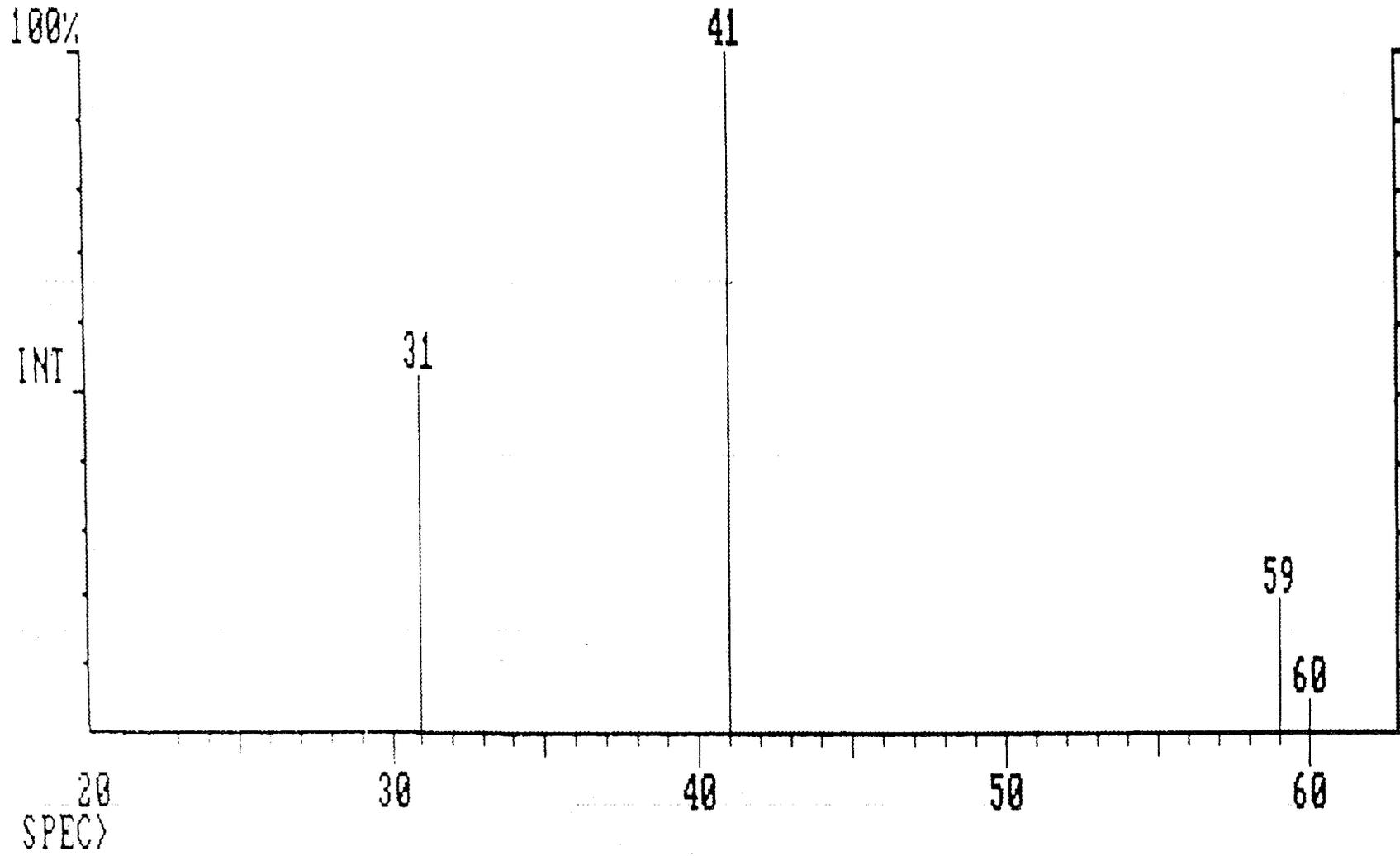


COMPOUND: BUTANOL
EI MS/MS SPECTRUM OF M/Z 73

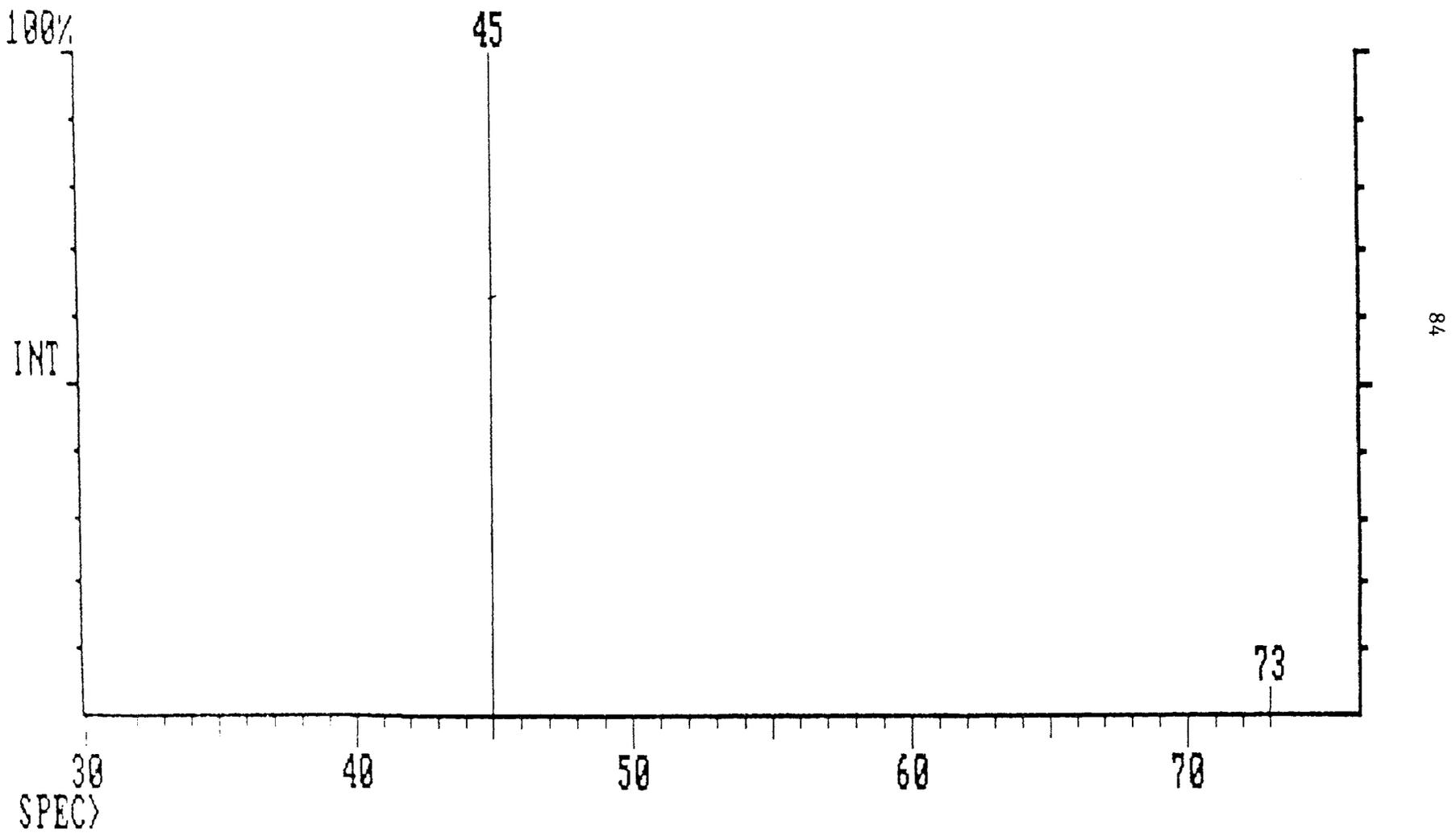


COMPOUND: DIETHYLETHER

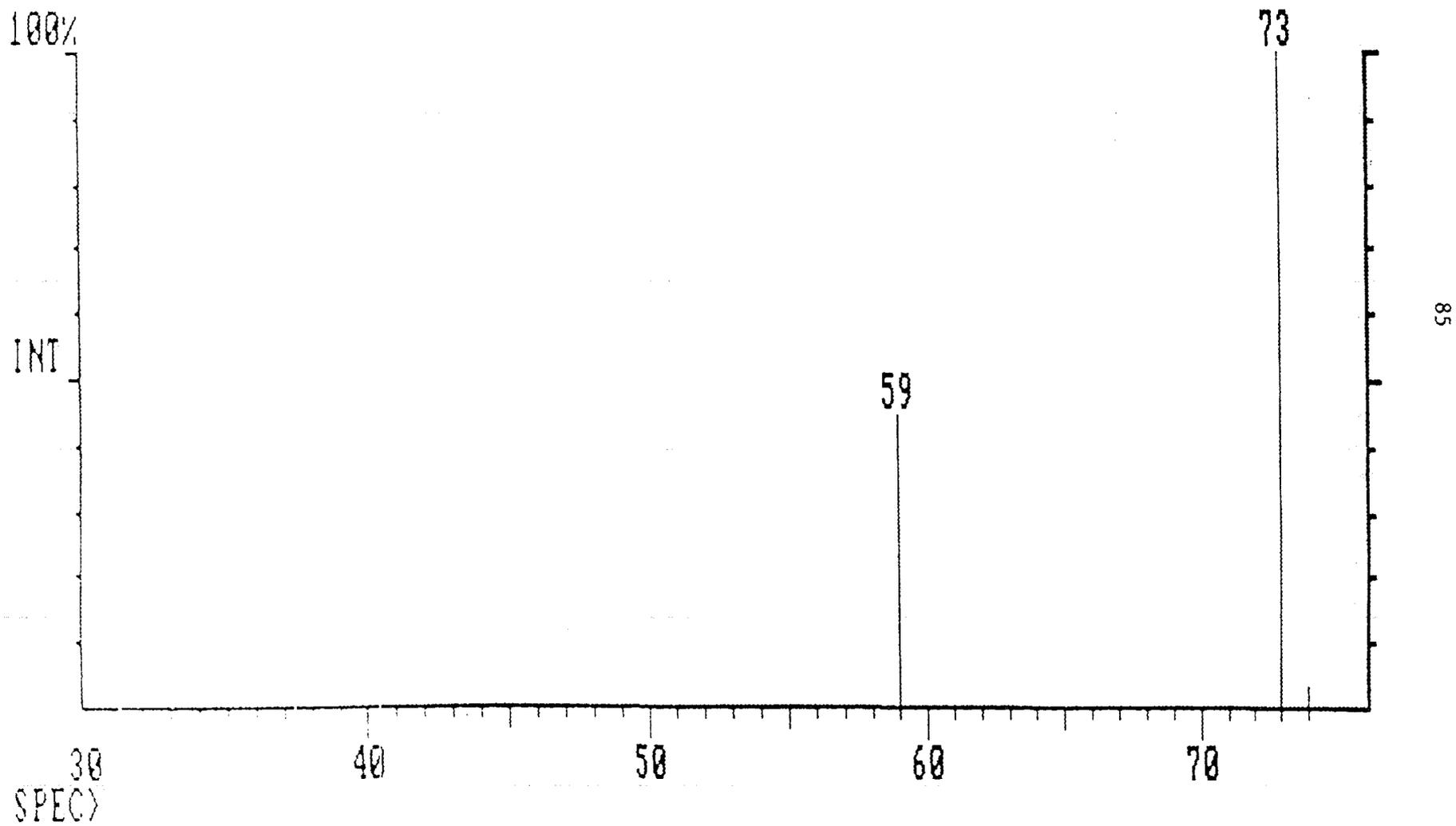
EI MS/MS SPECTRUM OF M/Z 59



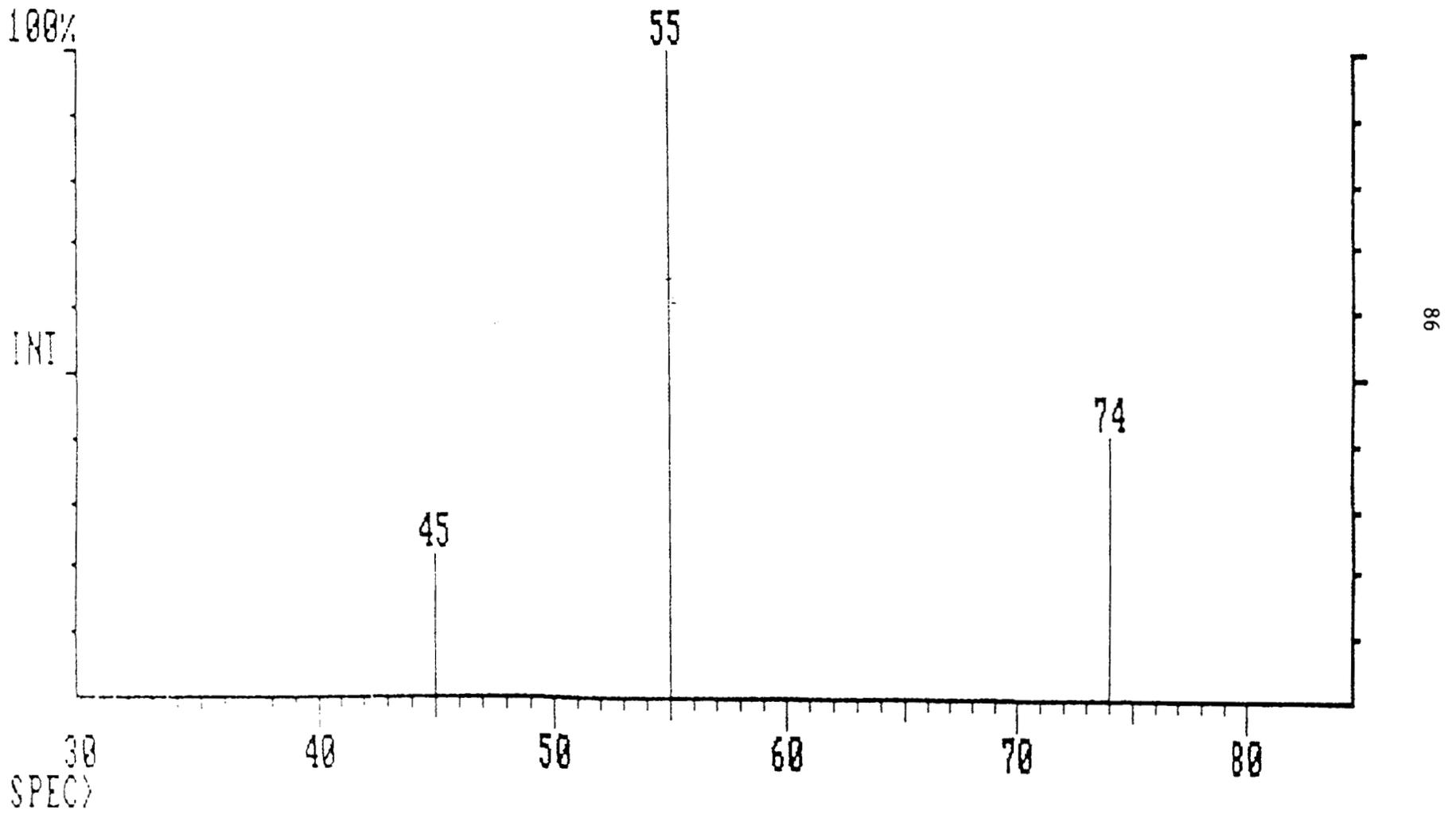
COMPOUND: DIETHYLETHER
EI MS/MS SPECTRUM OF M/Z 73



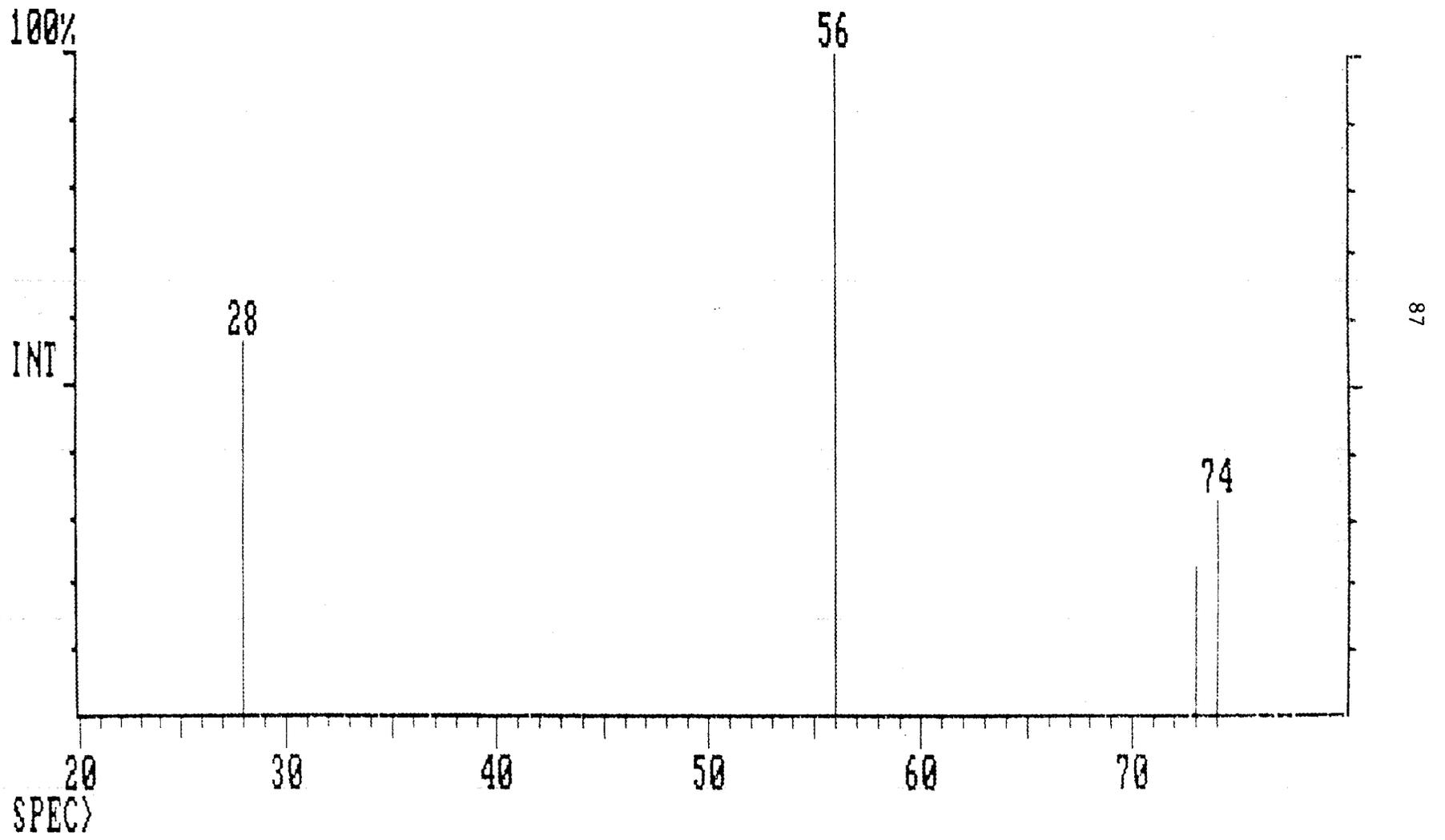
COMPOUND: DIETHYLETHER
EI MS/MS SPECTRUM OF m/z 74



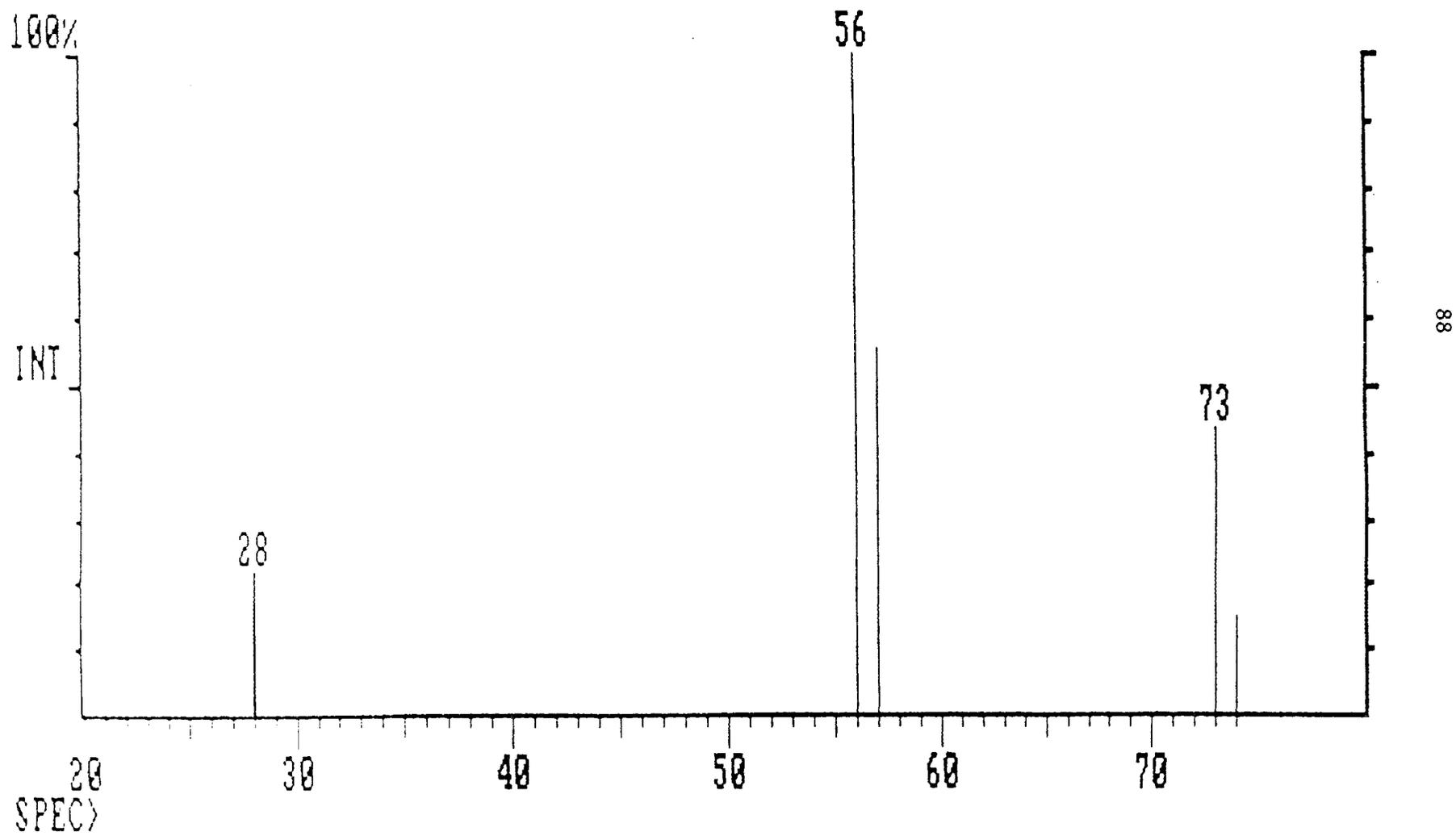
COMPOUND: ETHYLFORMATE
EI MS/MS SPECTRUM OF M/Z 73



COMPOUND: ETHYLFORMATE
EI MS/MS OF M/Z 74

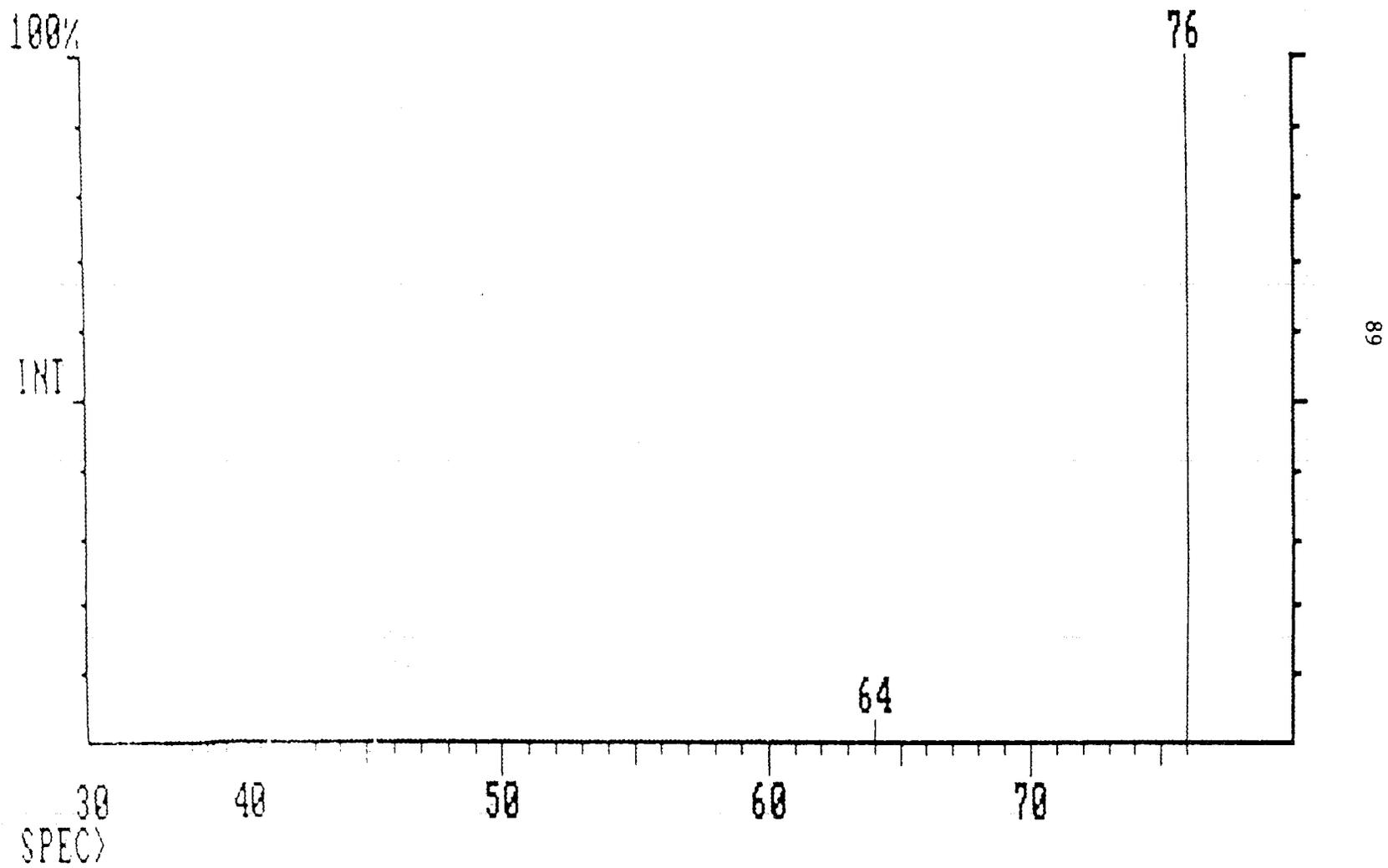


COMPOUND: PROPIONIC ACID
EI MS/MS SPECTRUM OF M/Z 74



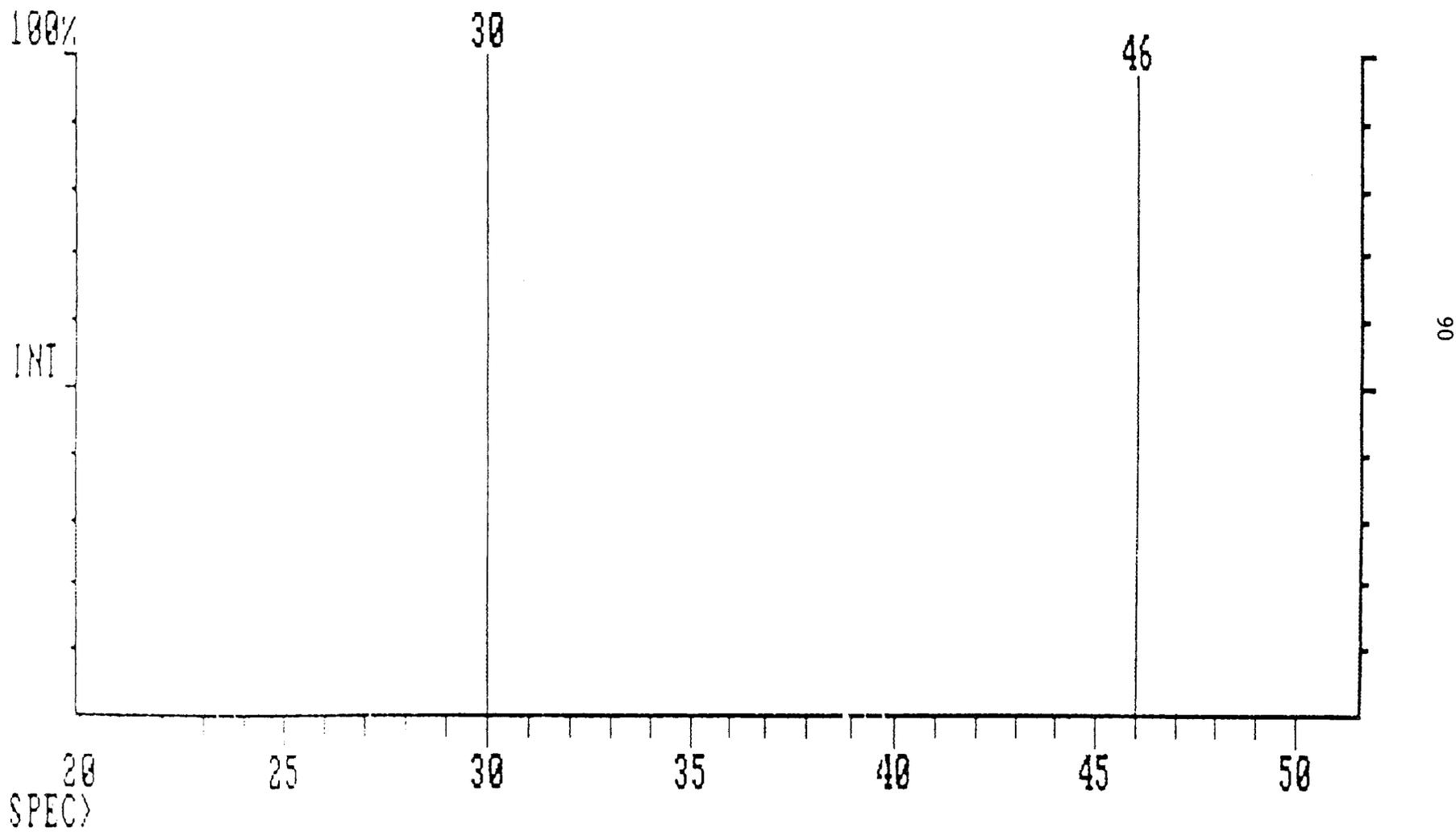
COMPOUND: CARBON DISULFIDE

EI MS/MS SPECTRUM OF M/Z 76



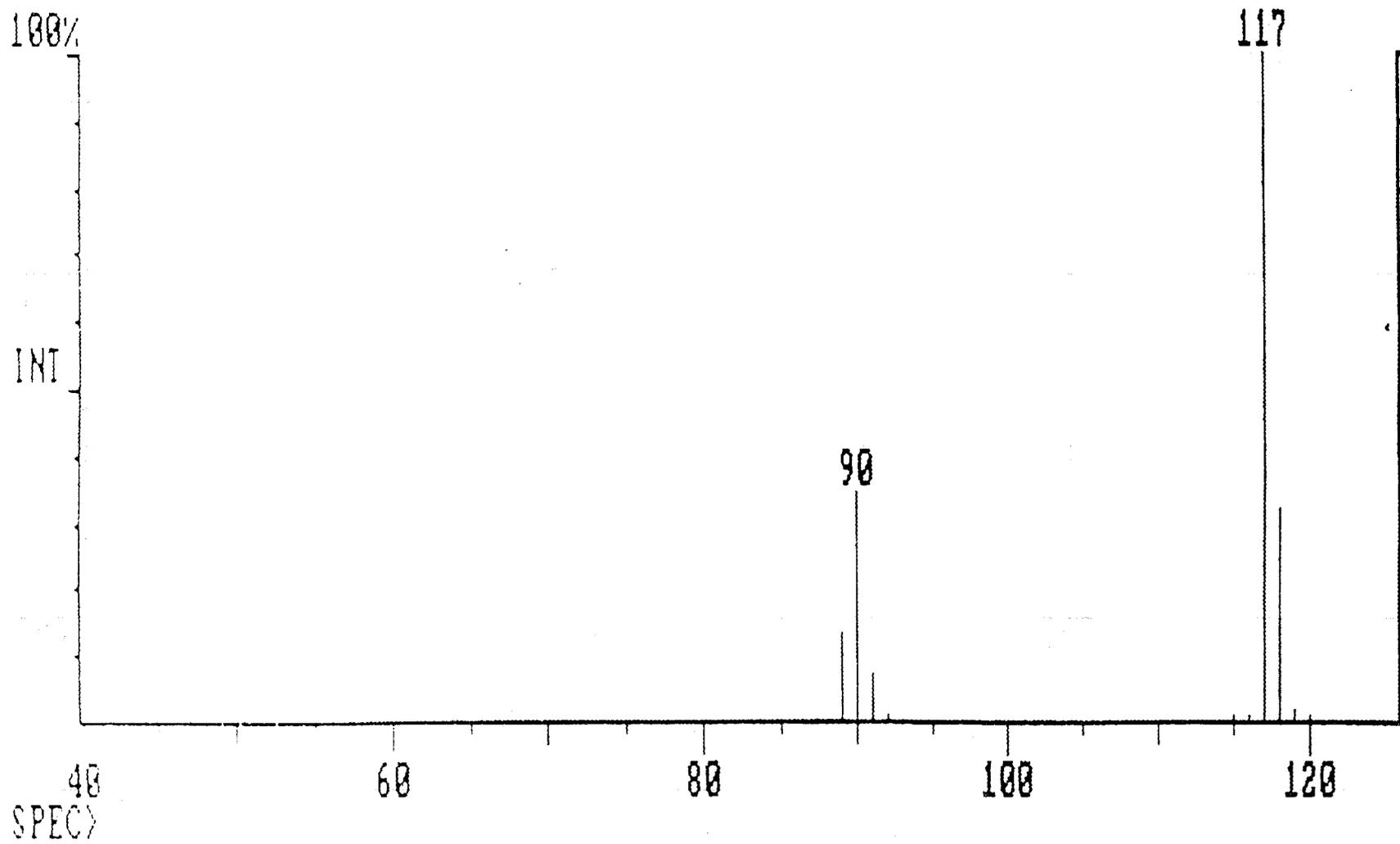
COMPOUND: NITROGEN TETRAOXIDE

EI MS/MS SPECTRUM OF M/Z 46



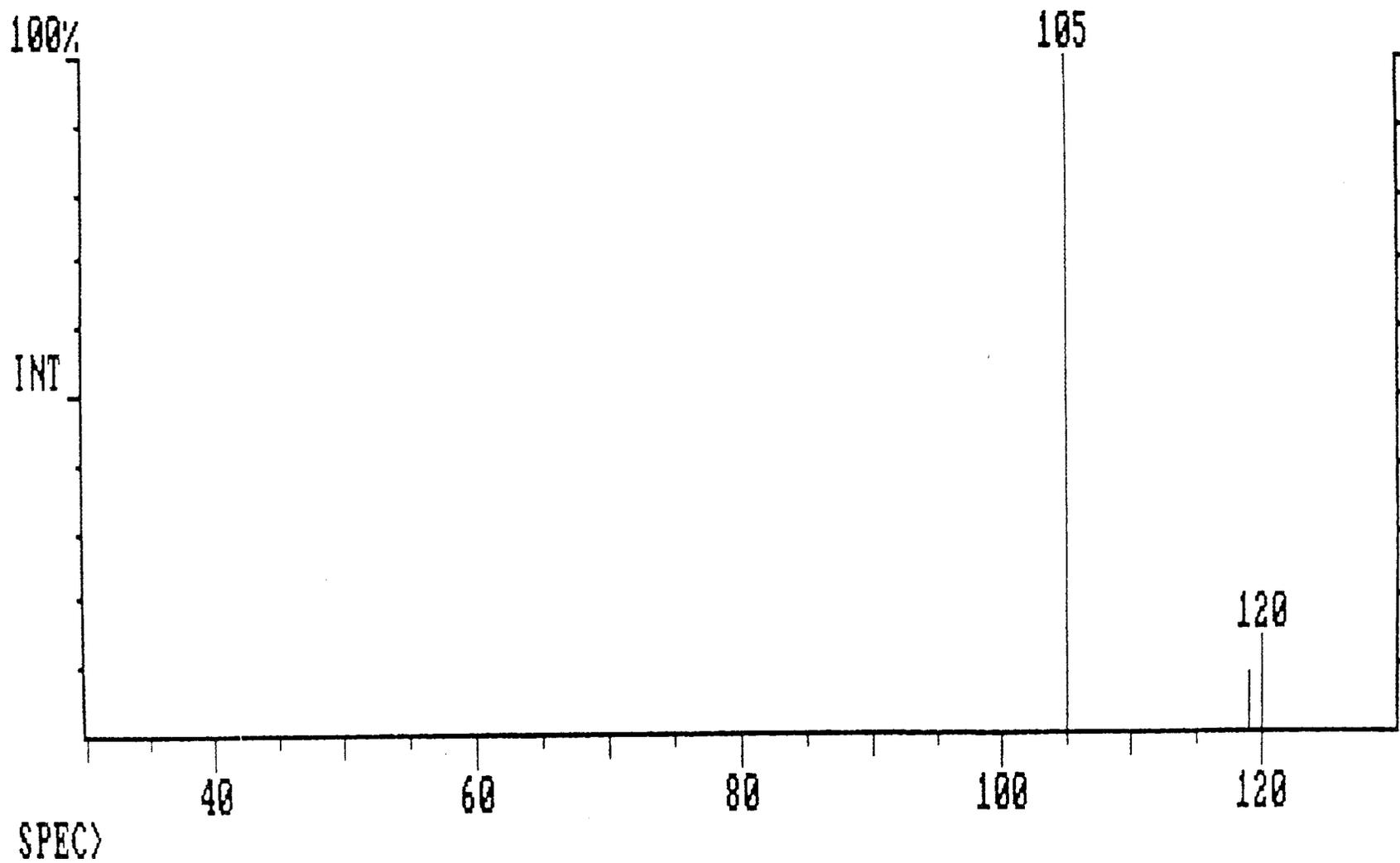
COMPOUND: INDOLE

EI MS/MS SPECTRUM OF M/Z 117

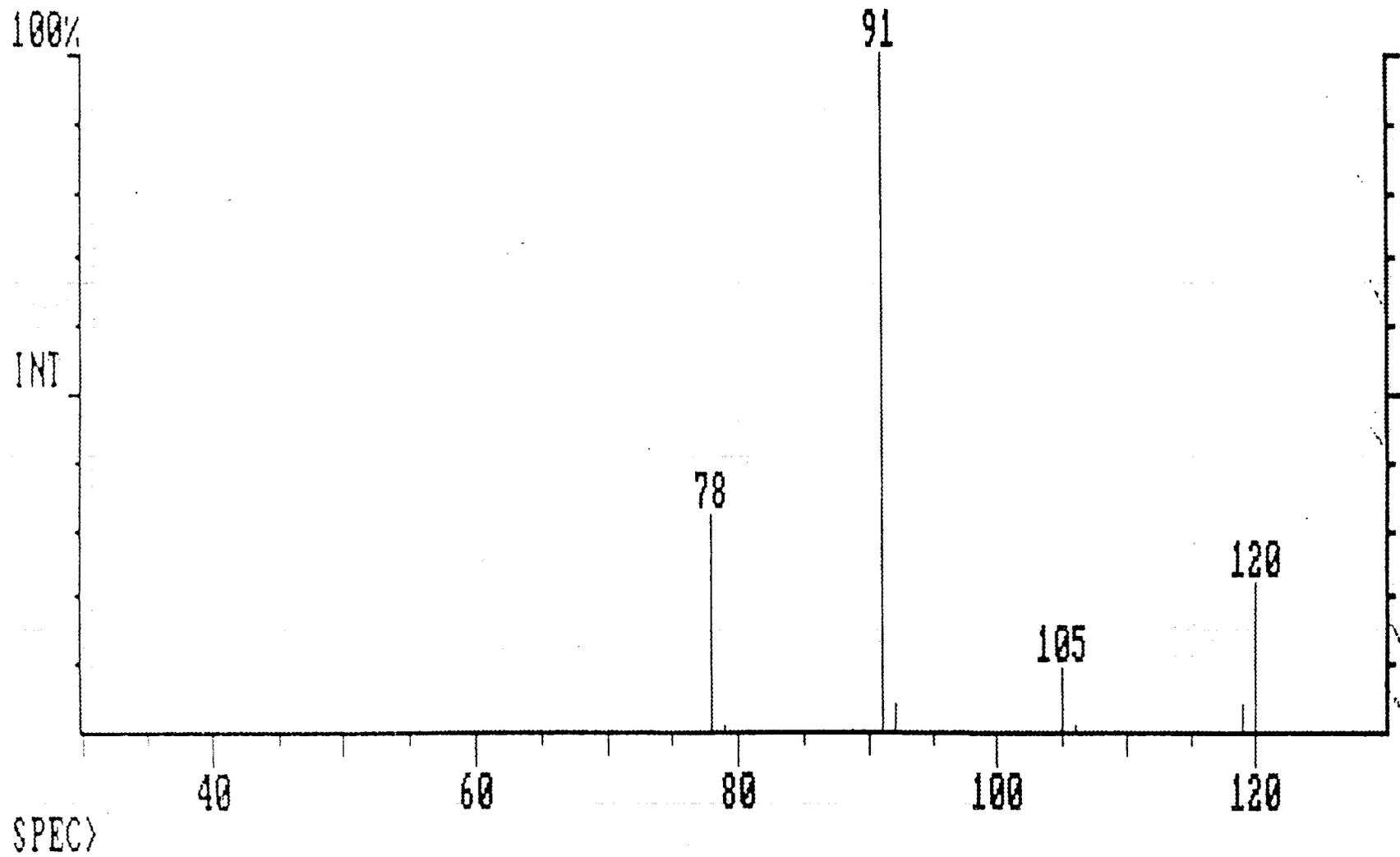


COMPOUND: CUMENE

EI MS/MS SPECTRUM OF M/Z 120

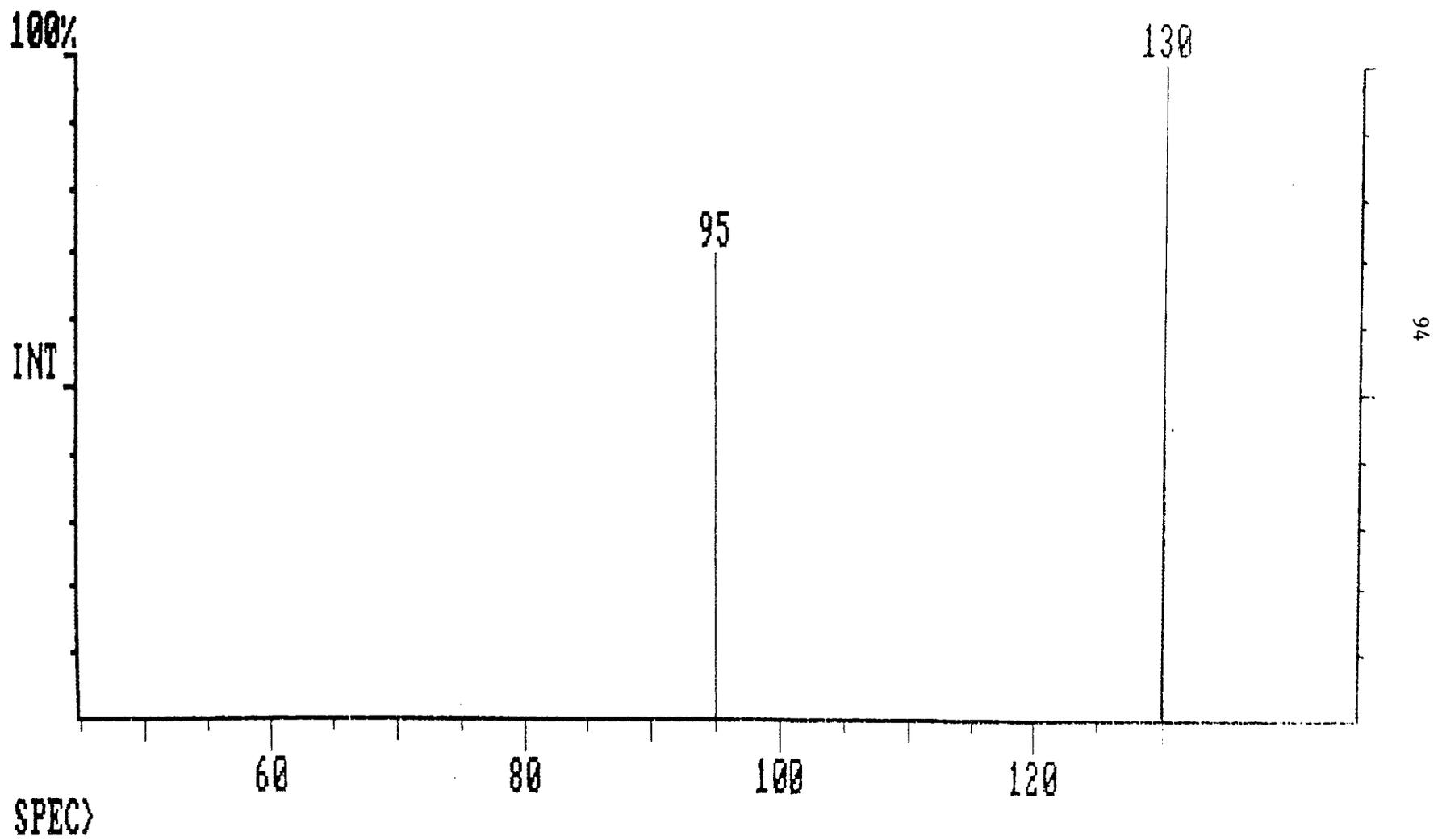


COMPOUND: N-PROPYLBENZENE
EI MS/MS SPECTRUM OF M/Z 120



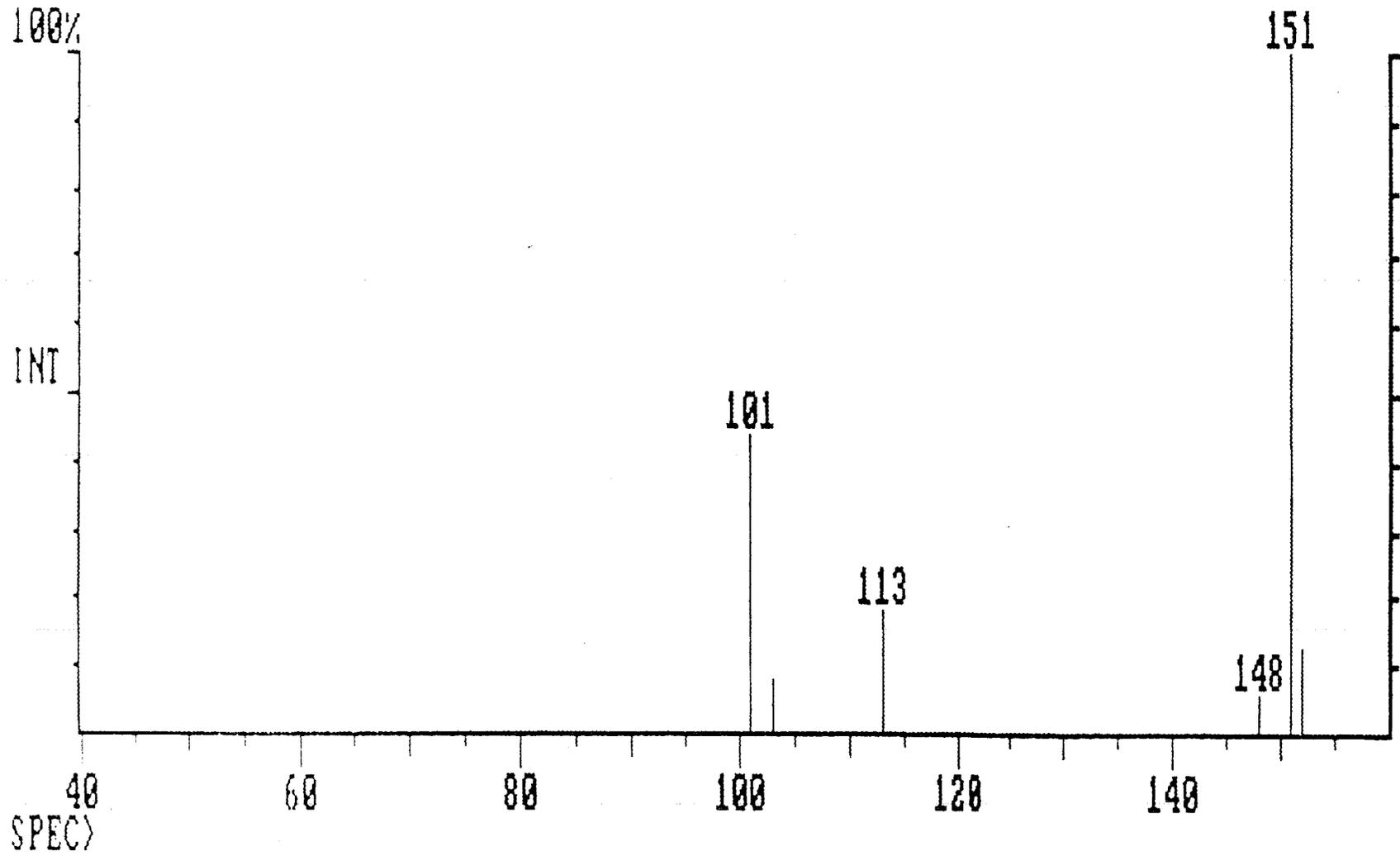
COMPOUND: TRICHLOROETHYLENE

EI MS/MS OF M/Z 130



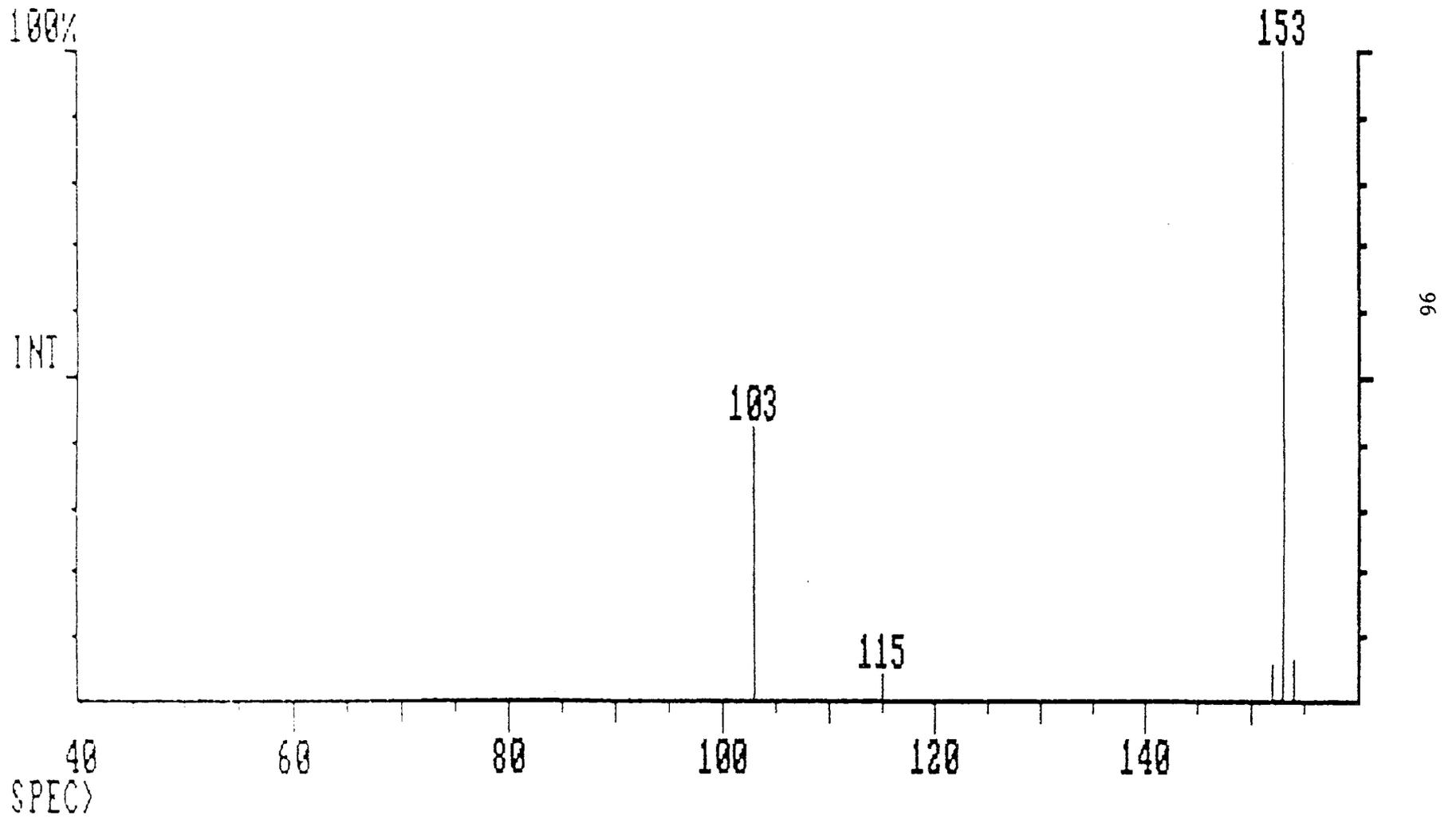
COMPOUND: FREON 113

EI MS/MS SPECTRUM OF M/Z 151

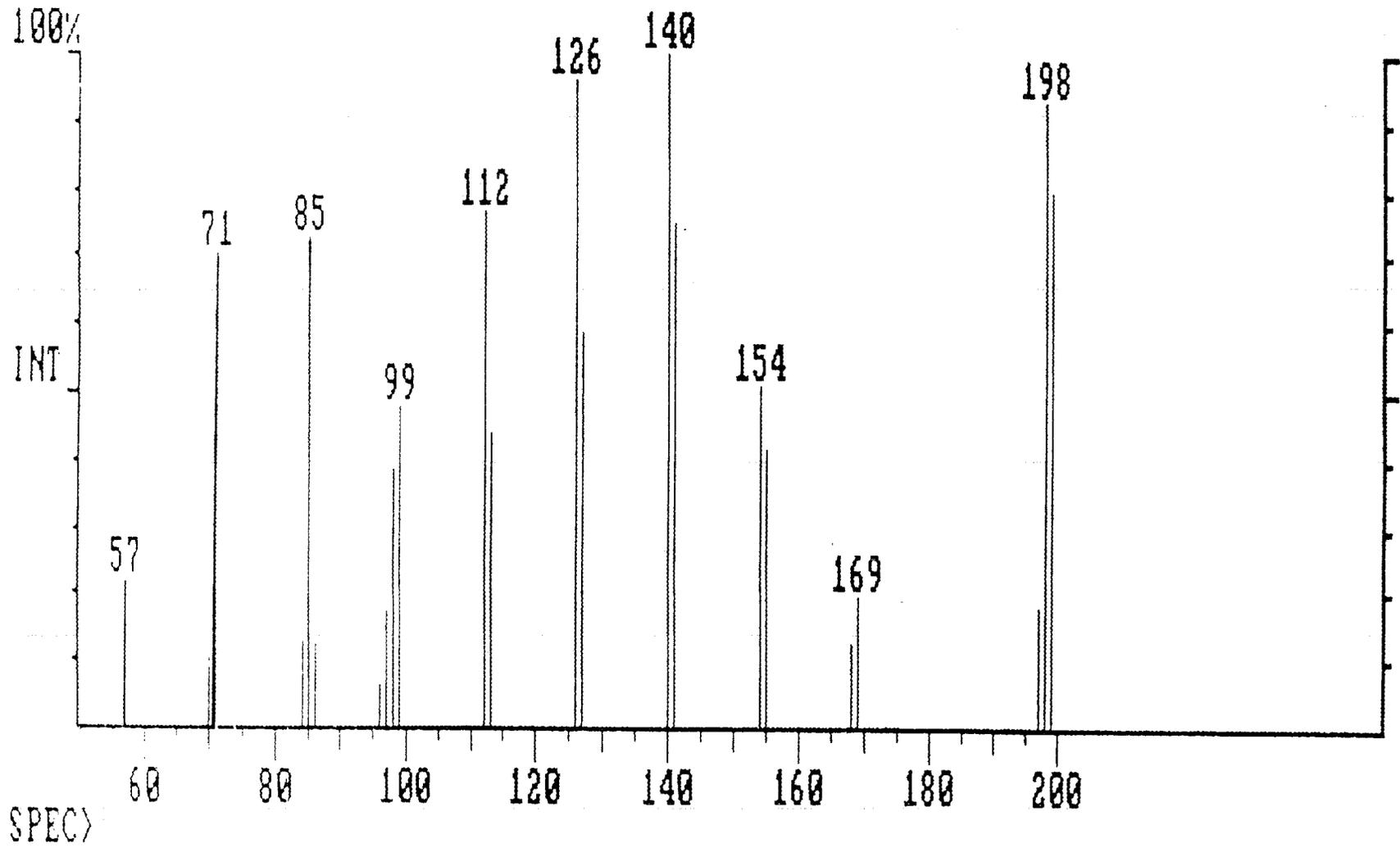


COMPOUND: FREON 113

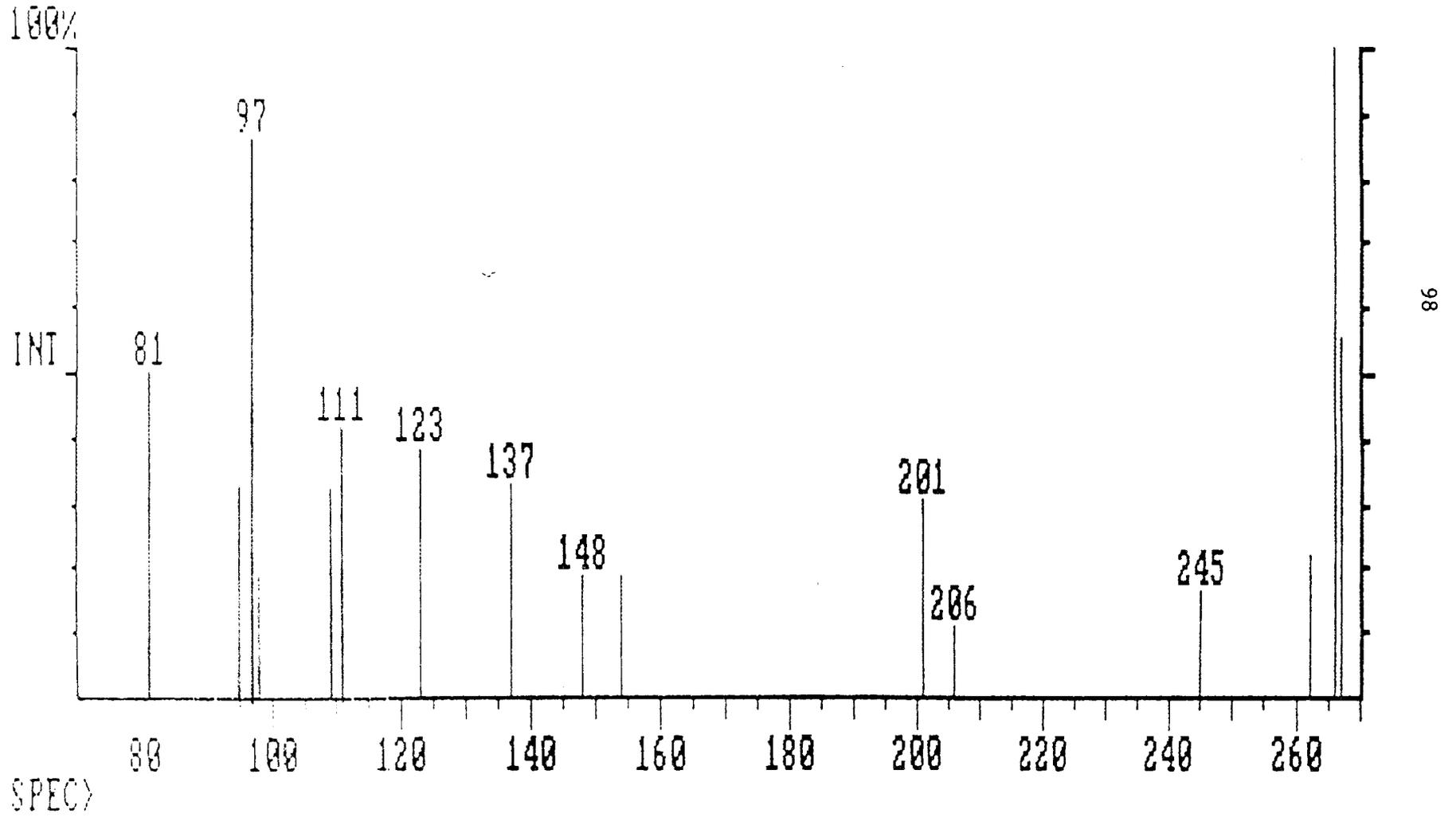
EI MS/MS SPECTRUM OF M/Z 153



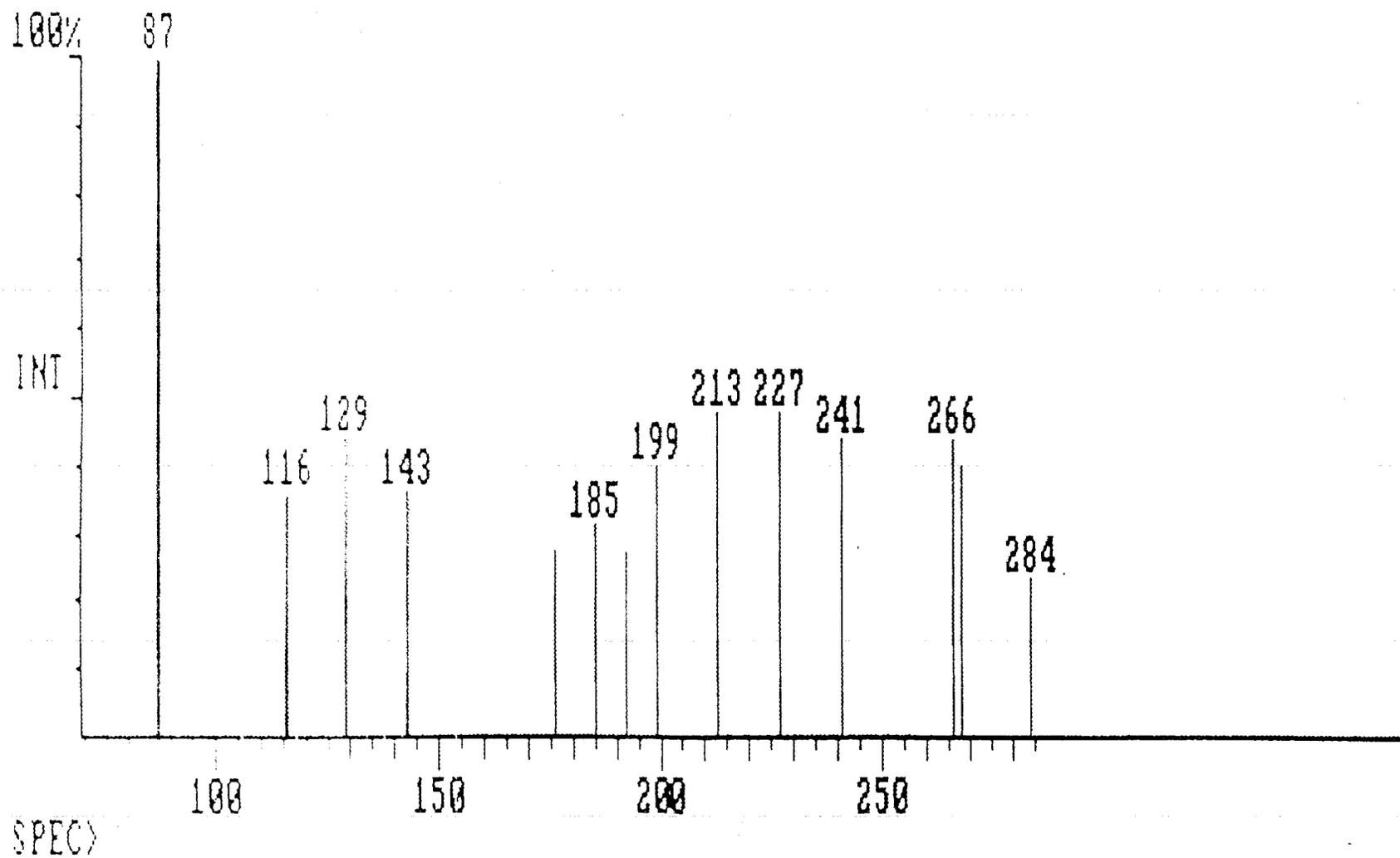
COMPOUND: TETRADECANE
EI MS/MS SPECTRUM OF m/z 198
(WITH METHANE)



COMPOUND: STEARIC ANHYDRIDE
EI MS/MS SPECTRUM OF M/Z 267

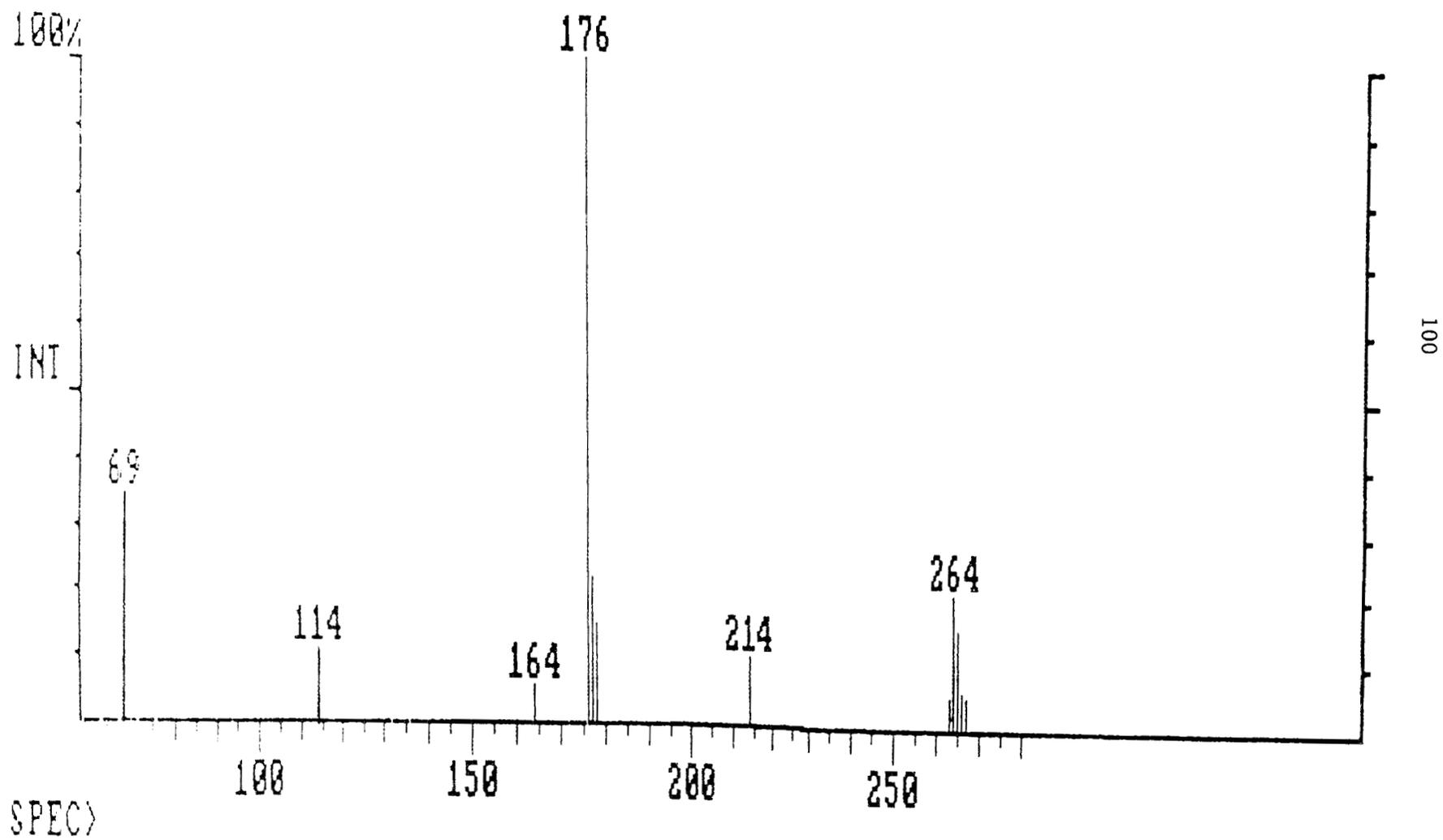


COMPOUND: STEARIC ANHYDRIDE
EI MS/MS SPECTRUM OF M/Z 284



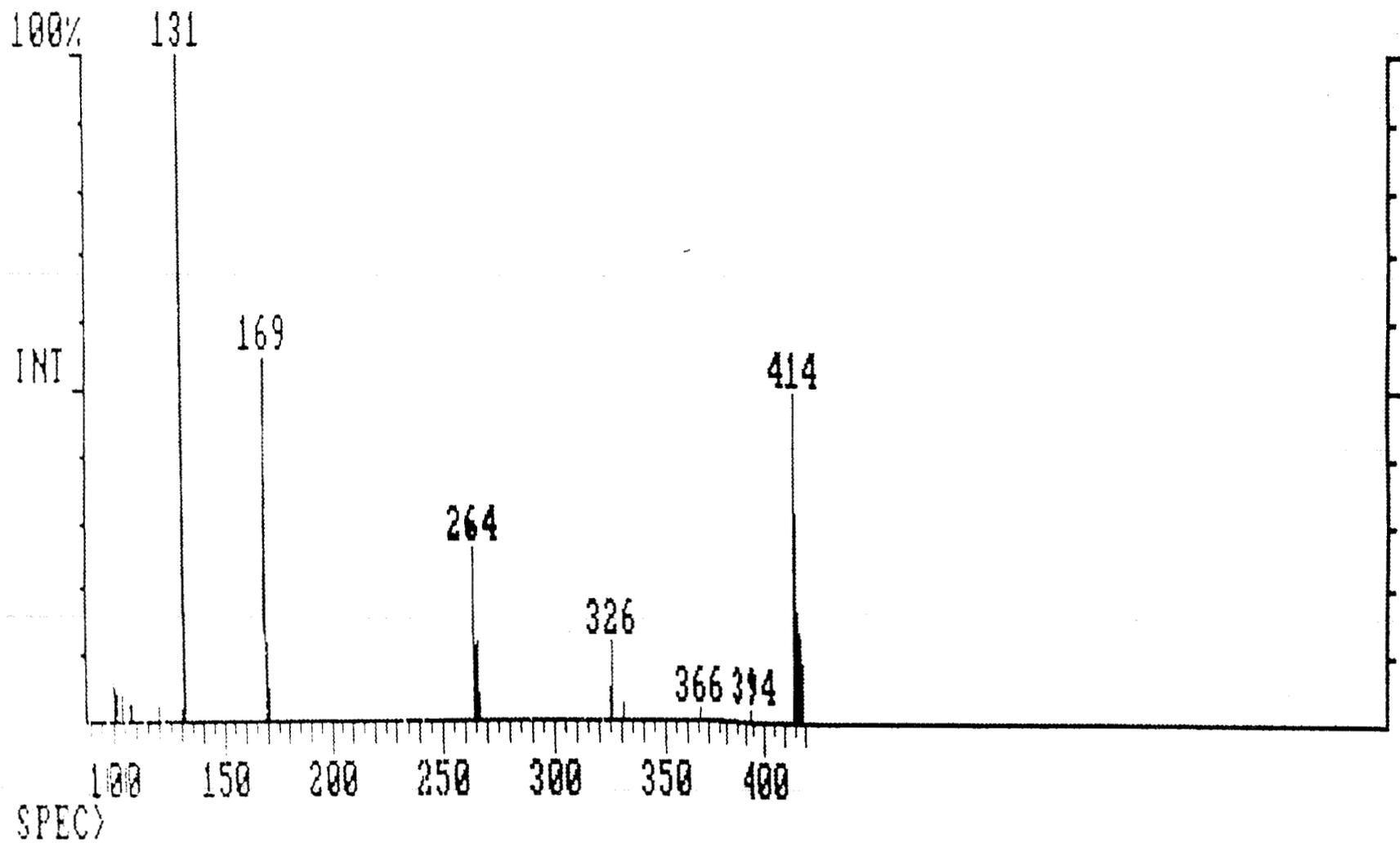
COMPOUND: PERFLUOROKEROSENE

EI MS/MS SPECTRUM OF M/Z 264



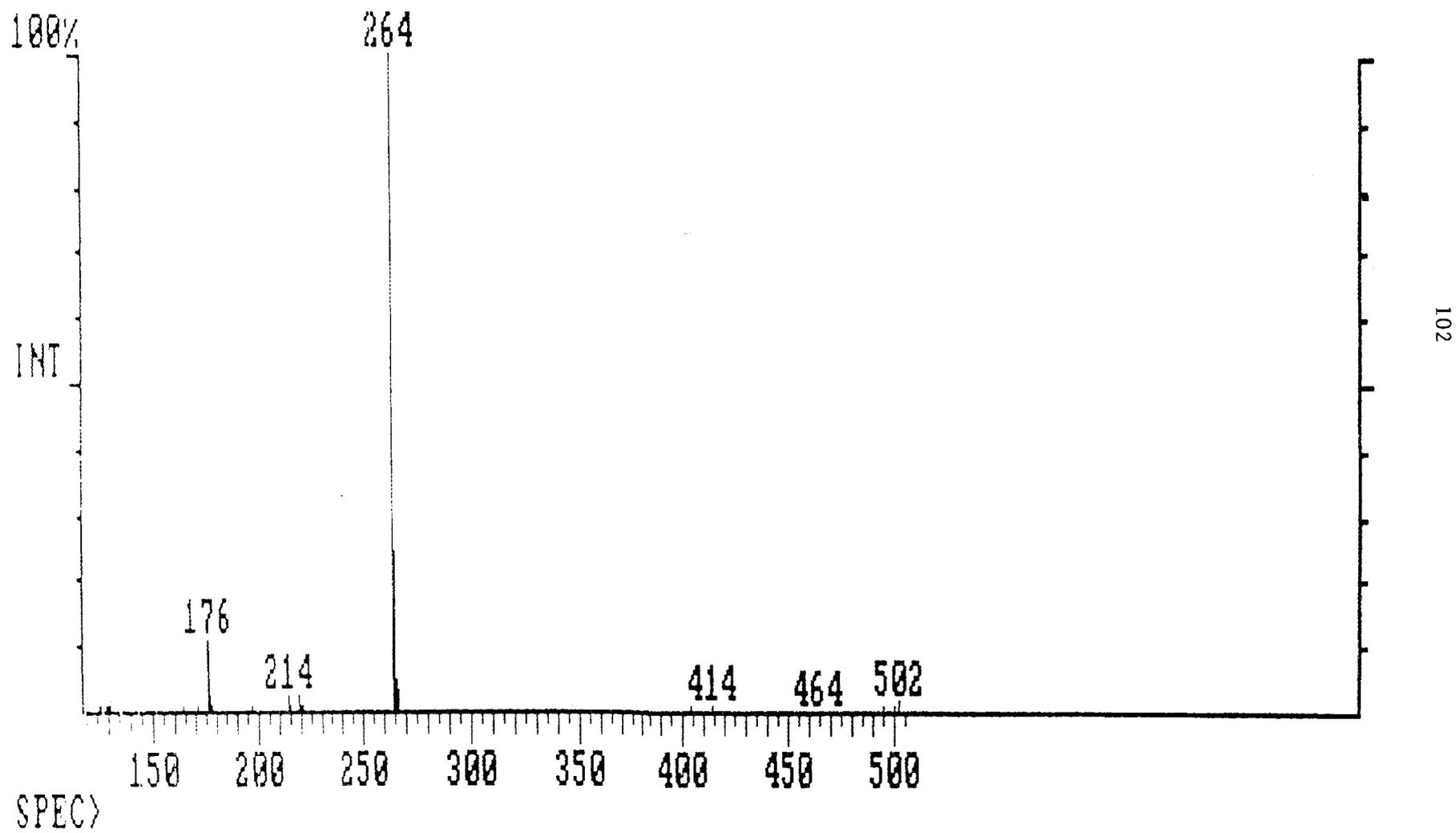
COMPOUND: PERFLUOROKEROSENE

EI MS/MS SPECTRUM OF M/Z 414



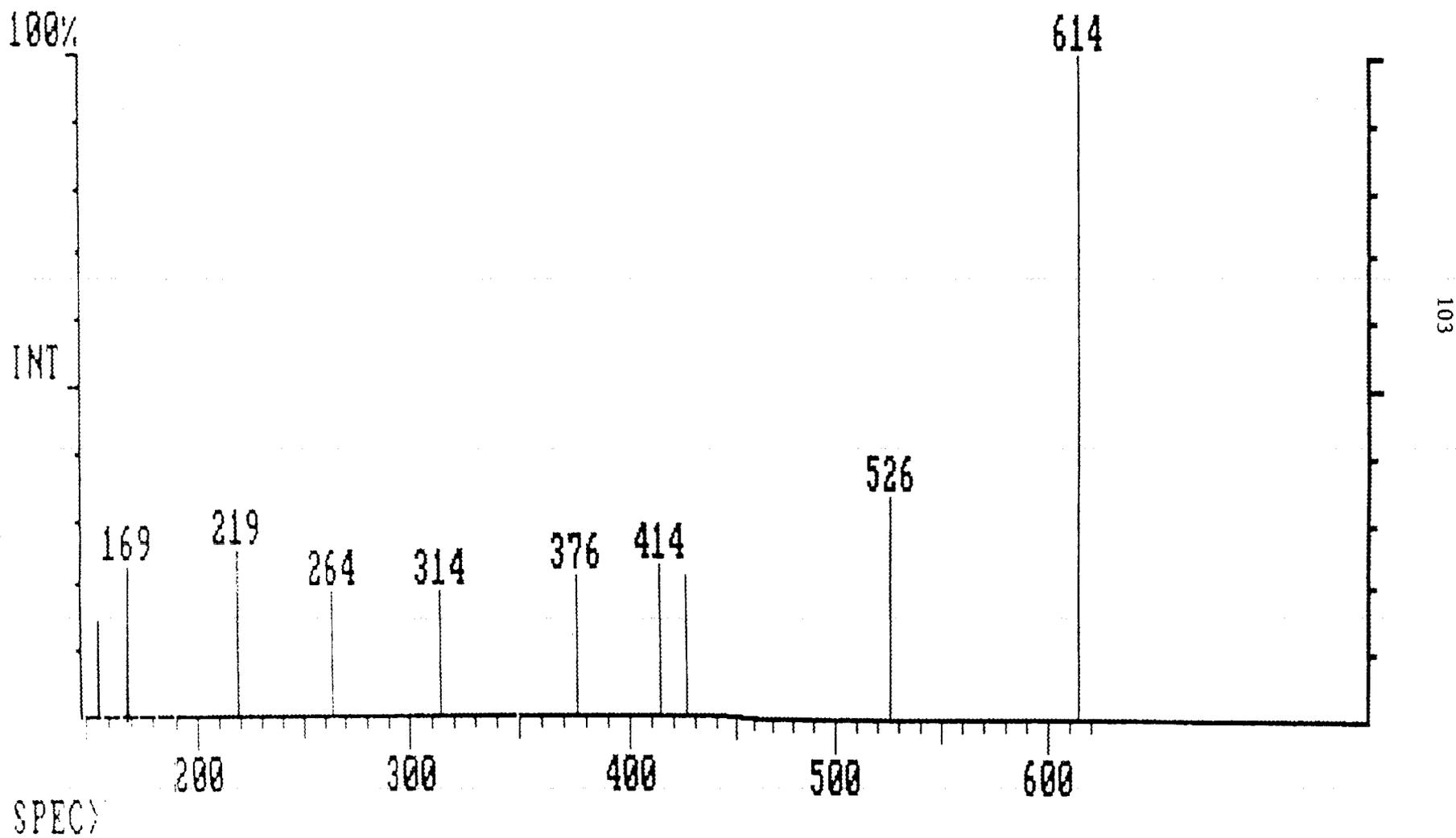
COMPOUND: PERFLUOROKEROSENE

EI MS/MS SPECTRUM OF M/Z 502



COMPOUND: PERFLUOROKEROSENE

EI MS/MS SPECTRUM OF M/Z 614

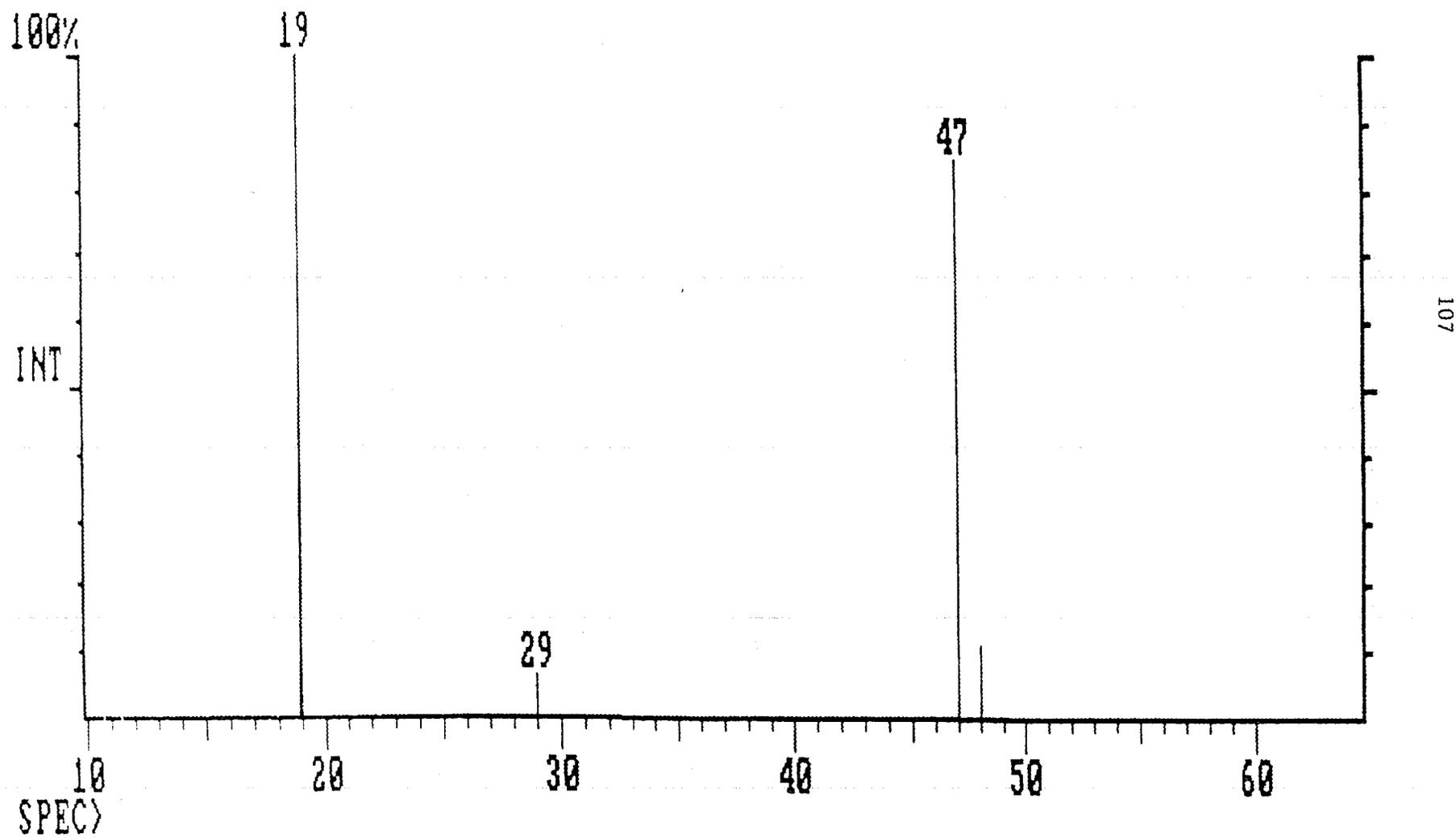


Appendix D

CI MS/MS spectra from the ITMS

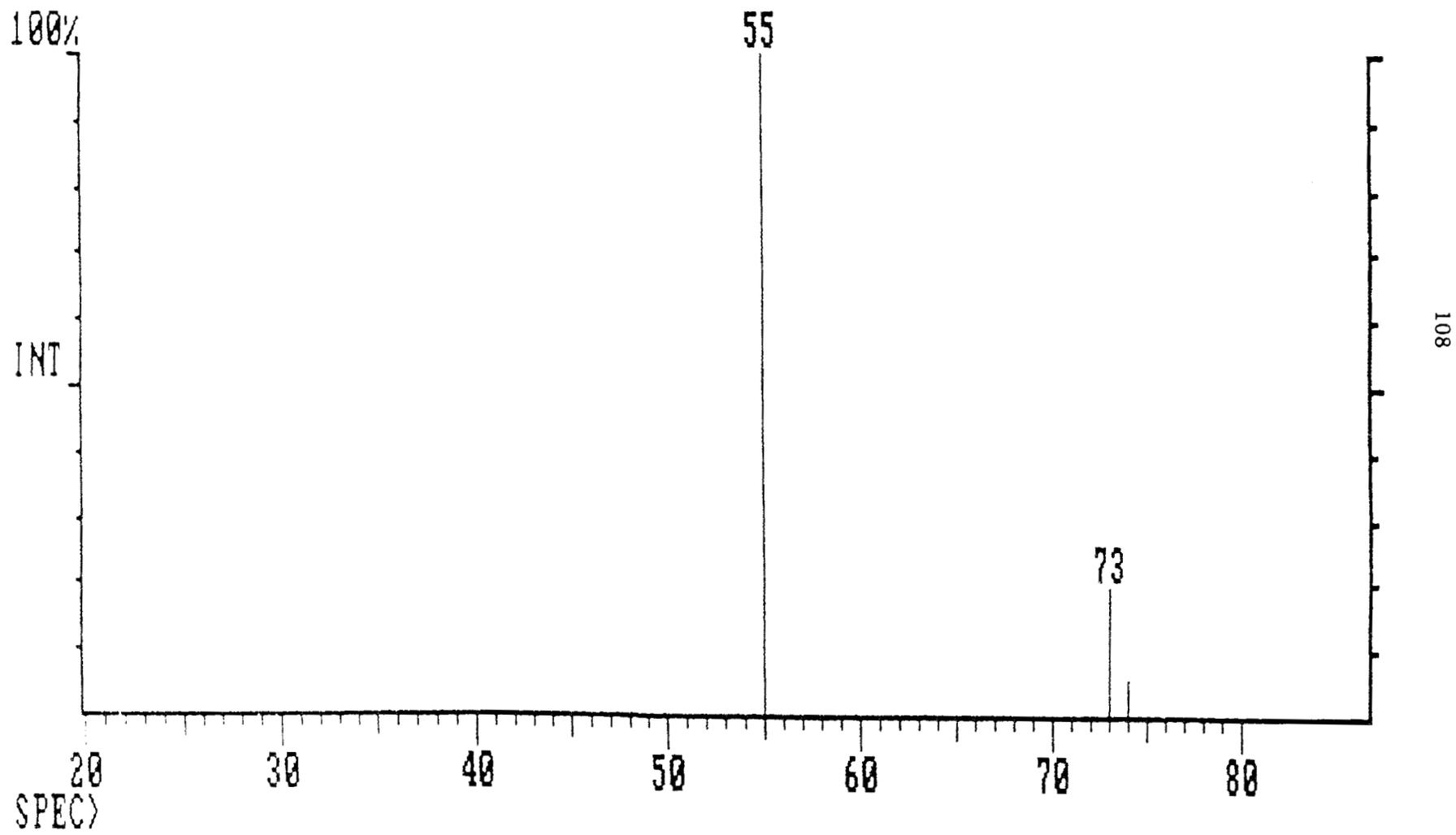
COMPOUND: ETHANOL

CI MS/MS SPECTRUM OF M/Z 47



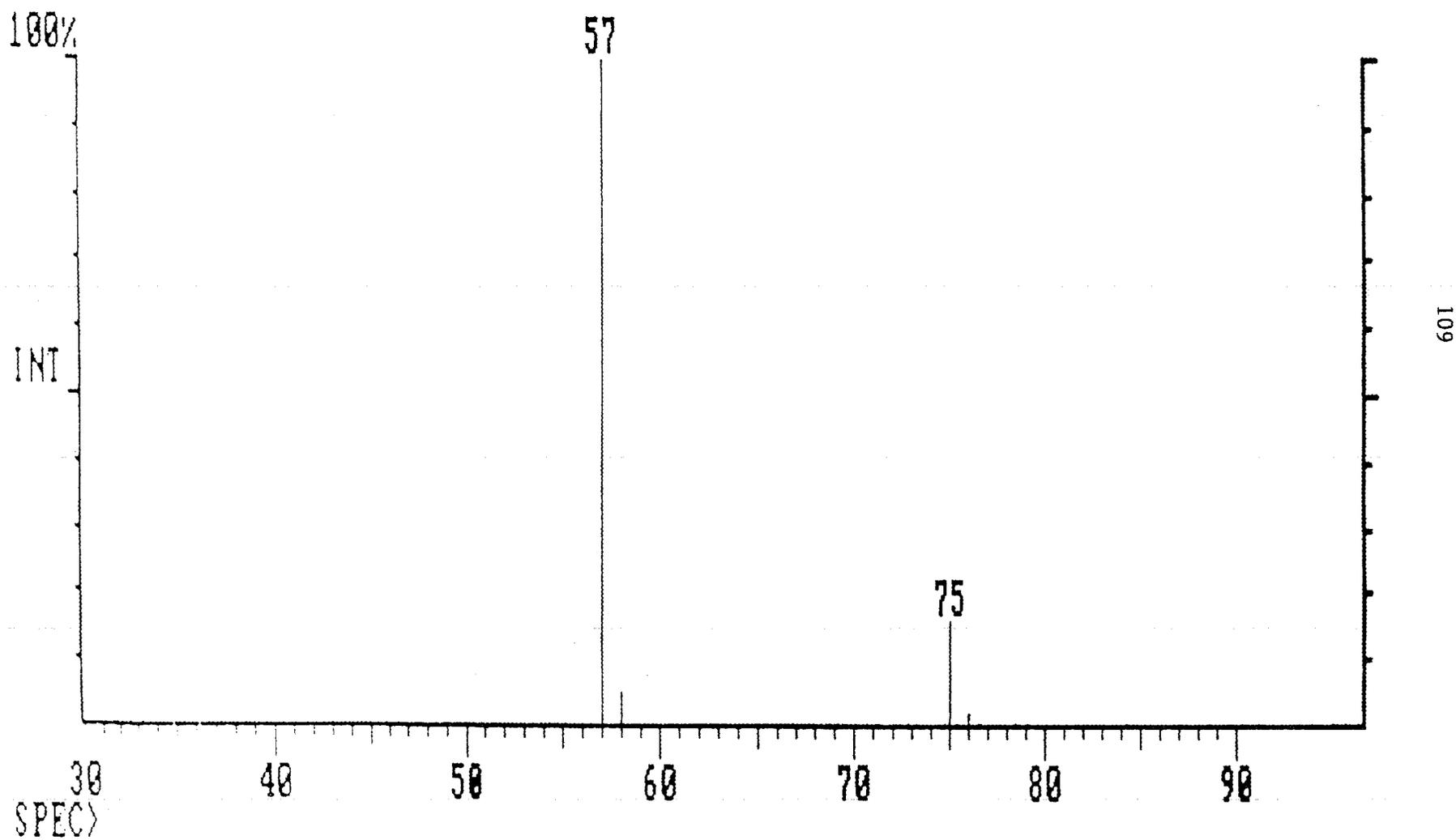
COMPOUND: METHYLETHYLKETONE

CI MS/MS SPECTRUM OF m/z 73



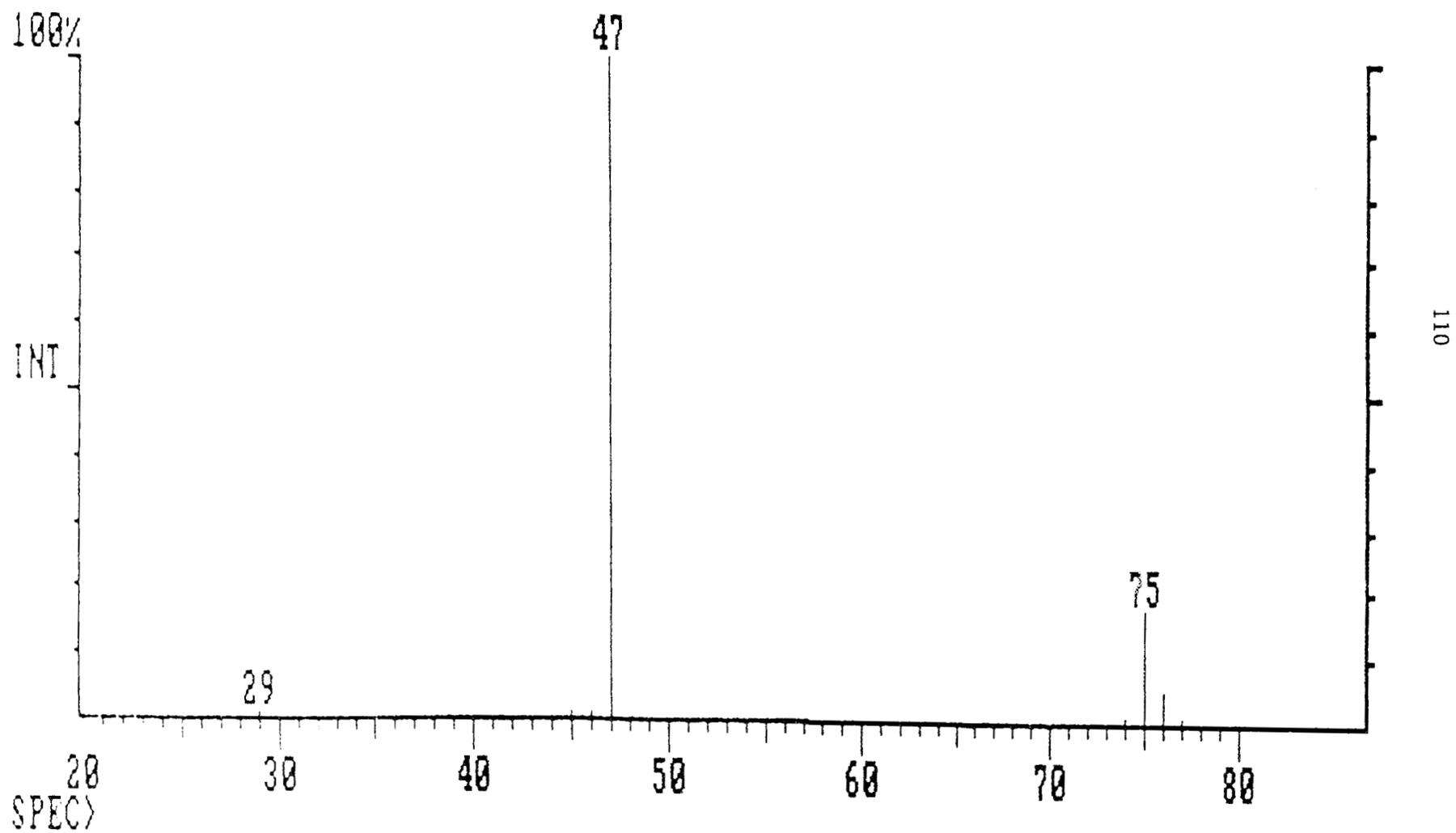
COMPOUND: BUTANOL

CI MS/MS SPECTRUM OF M/Z 75



COMPOUND: DIETHYLETHER

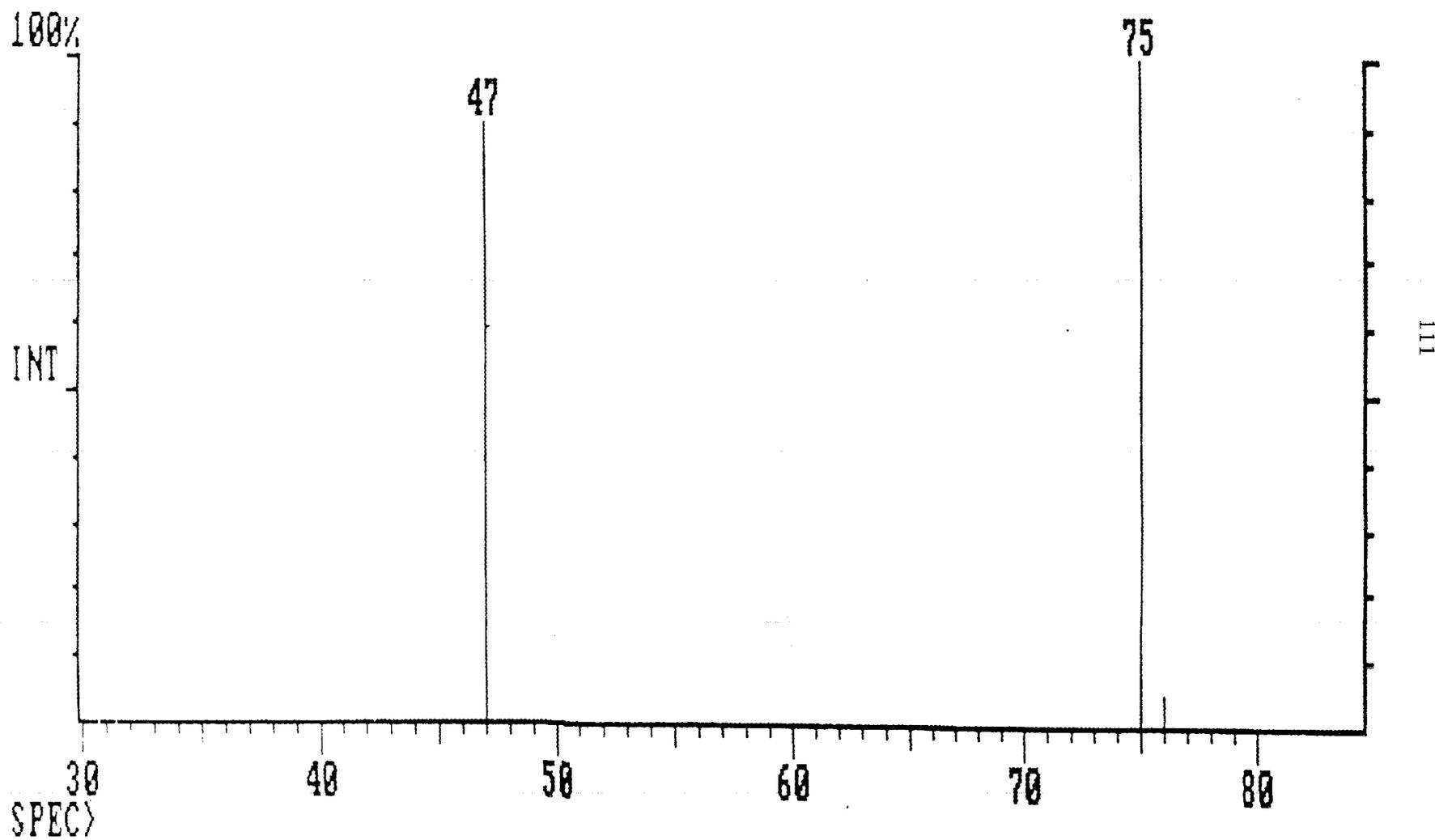
CI MS/MS SPECTRUM OF M/Z 75



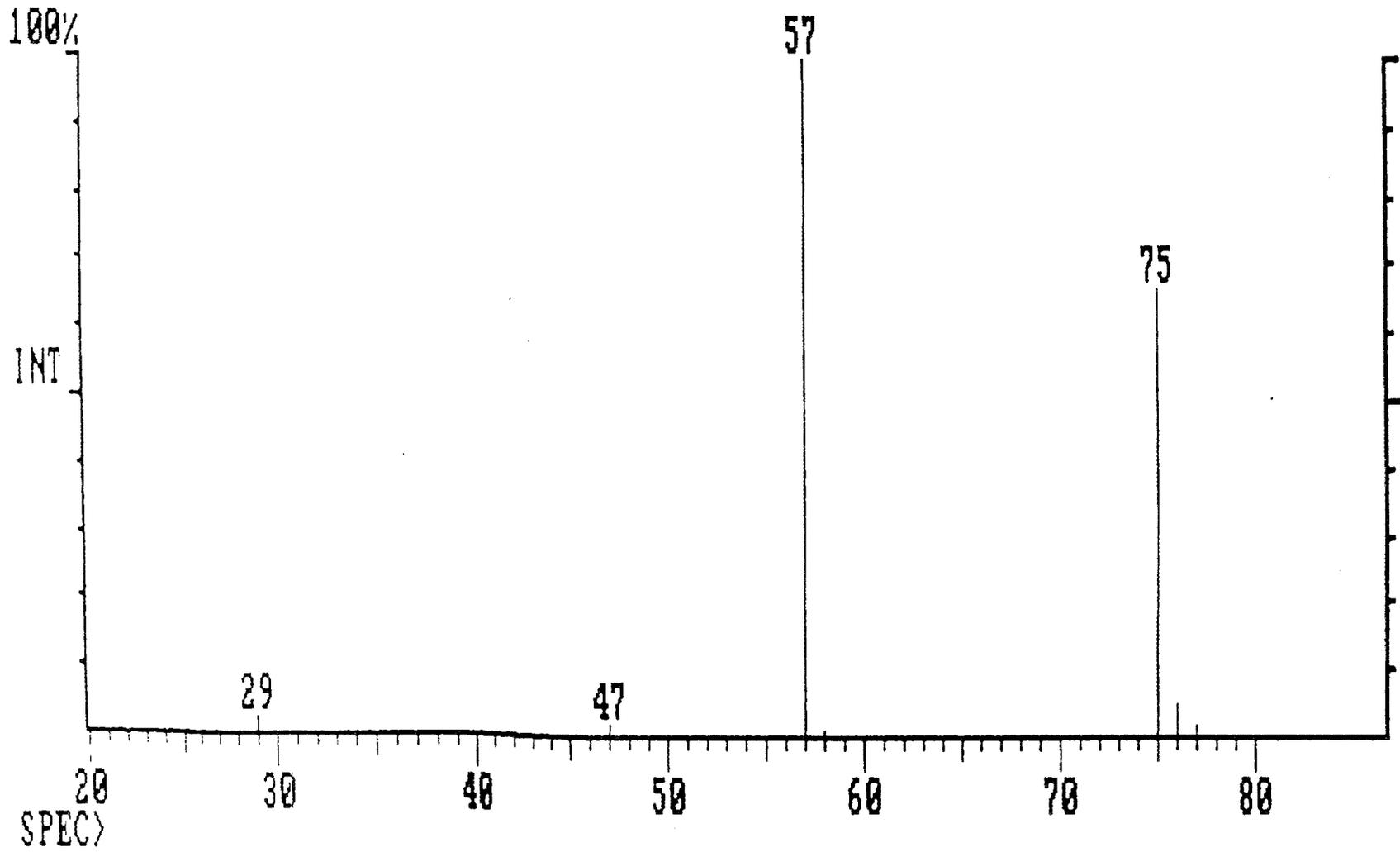
COMPOUND: ETHYLFORMATE

CI MS/MS SPECTRUM OF M/Z 75

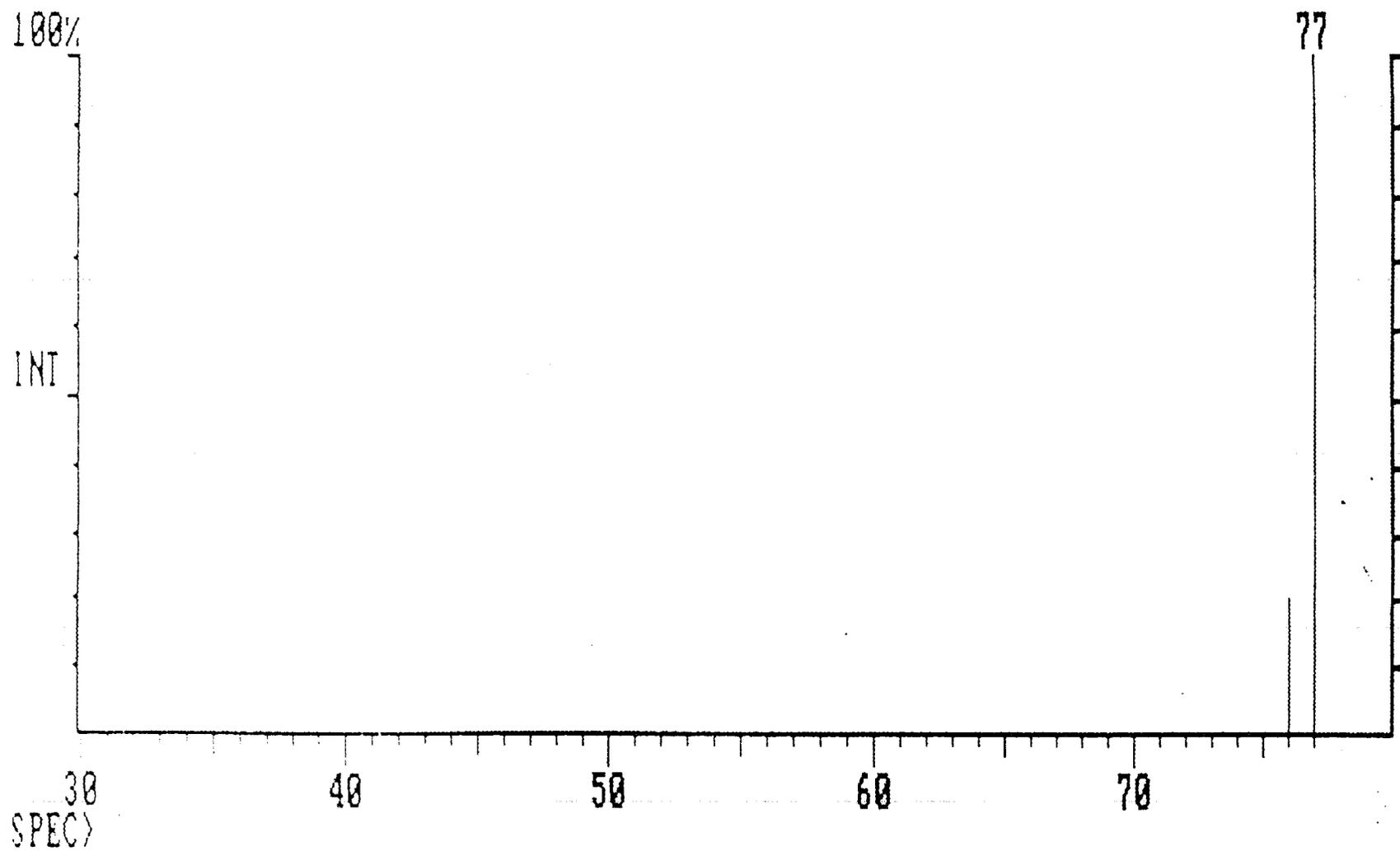
(50 MSEC REACTION TIME)



COMPOUND: PROPIONIC ACID
CI MS/MS SPECTRUM OF M/Z 75

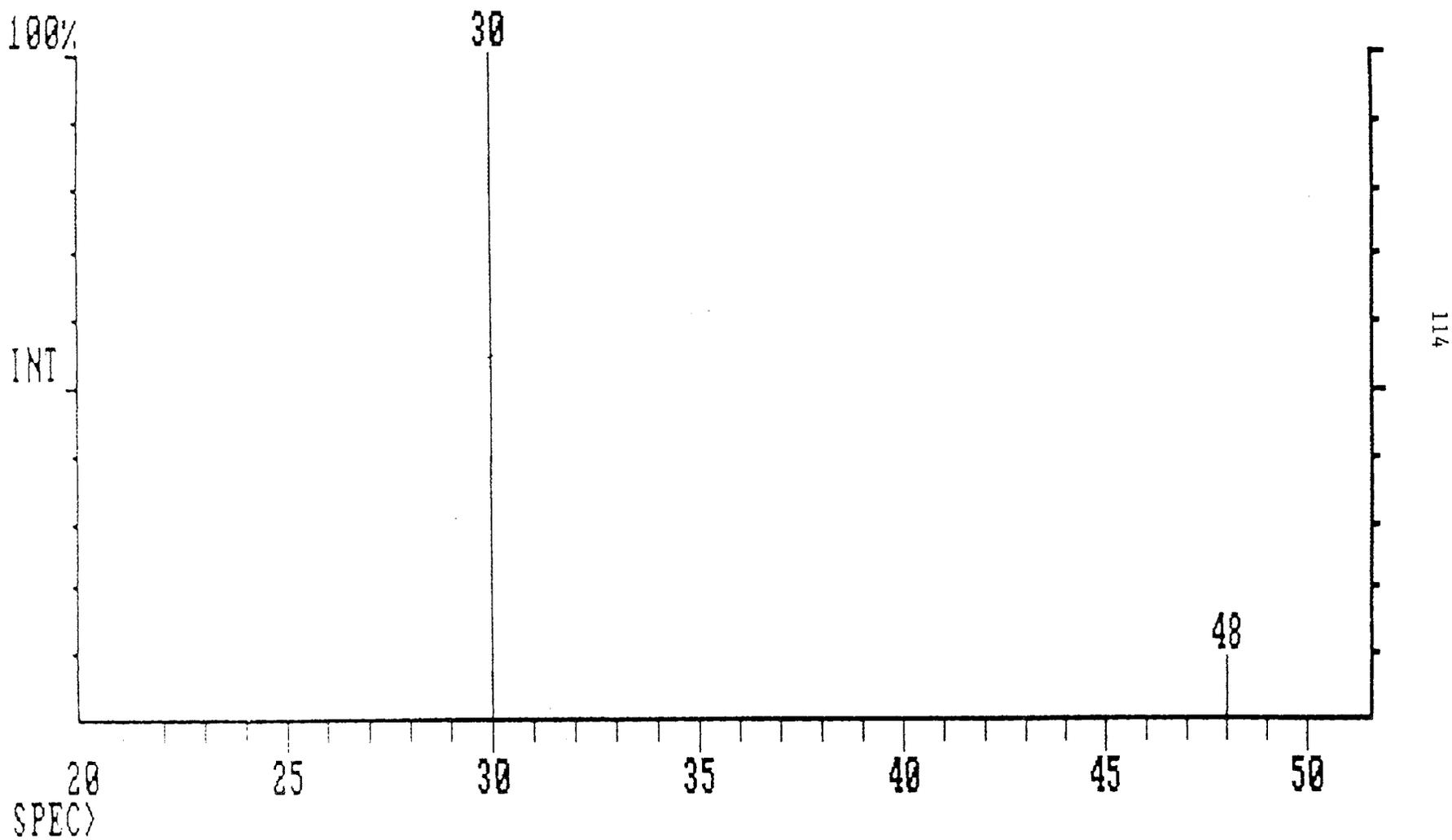


COMPOUND: CARBON DISULFIDE
CI MS/MS SPECTRUM OF M/Z 77



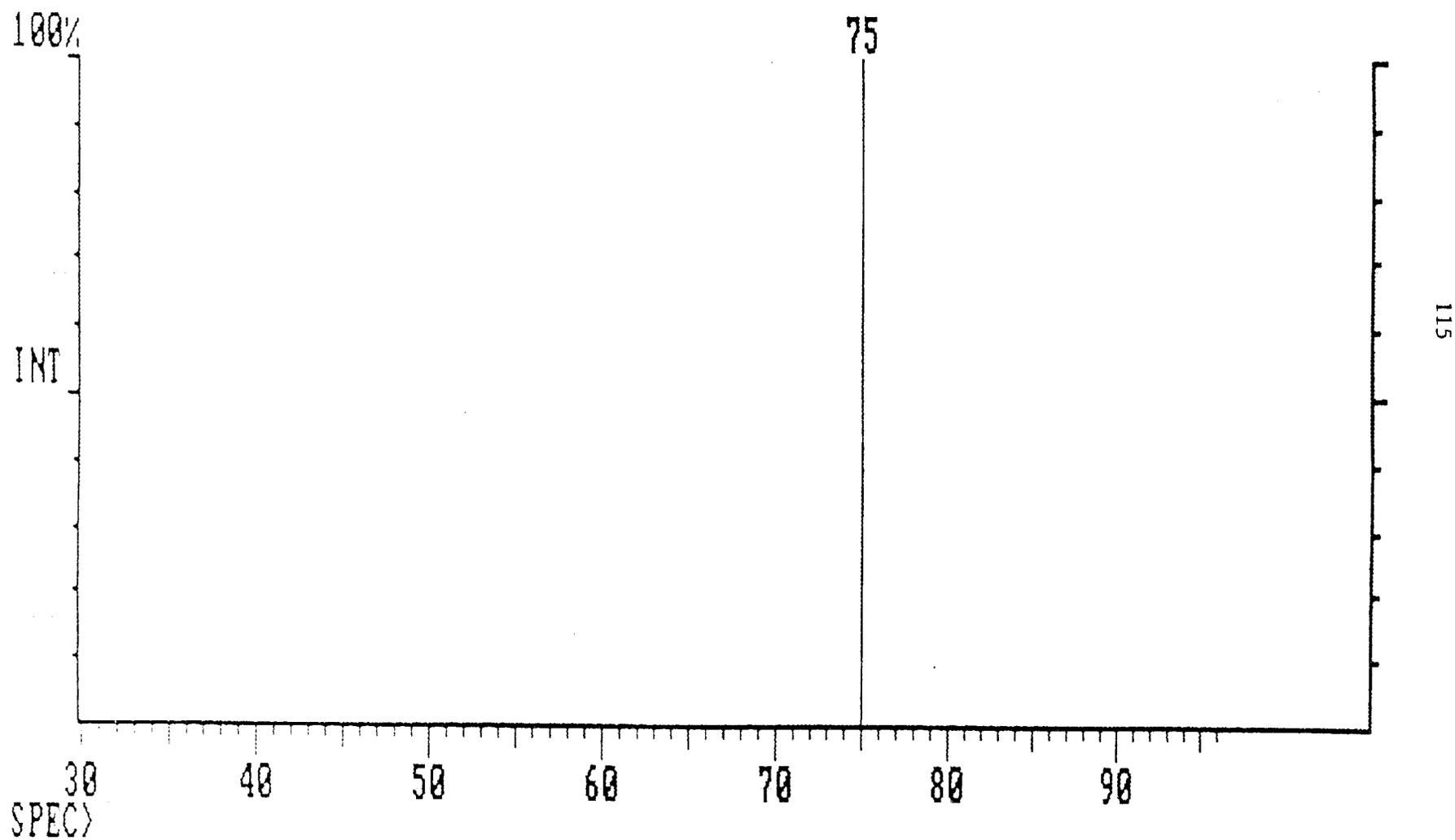
COMPOUND: NITROGEN TETRAOXIDE

CI MS/MS SPECTRUM OF M/Z 48



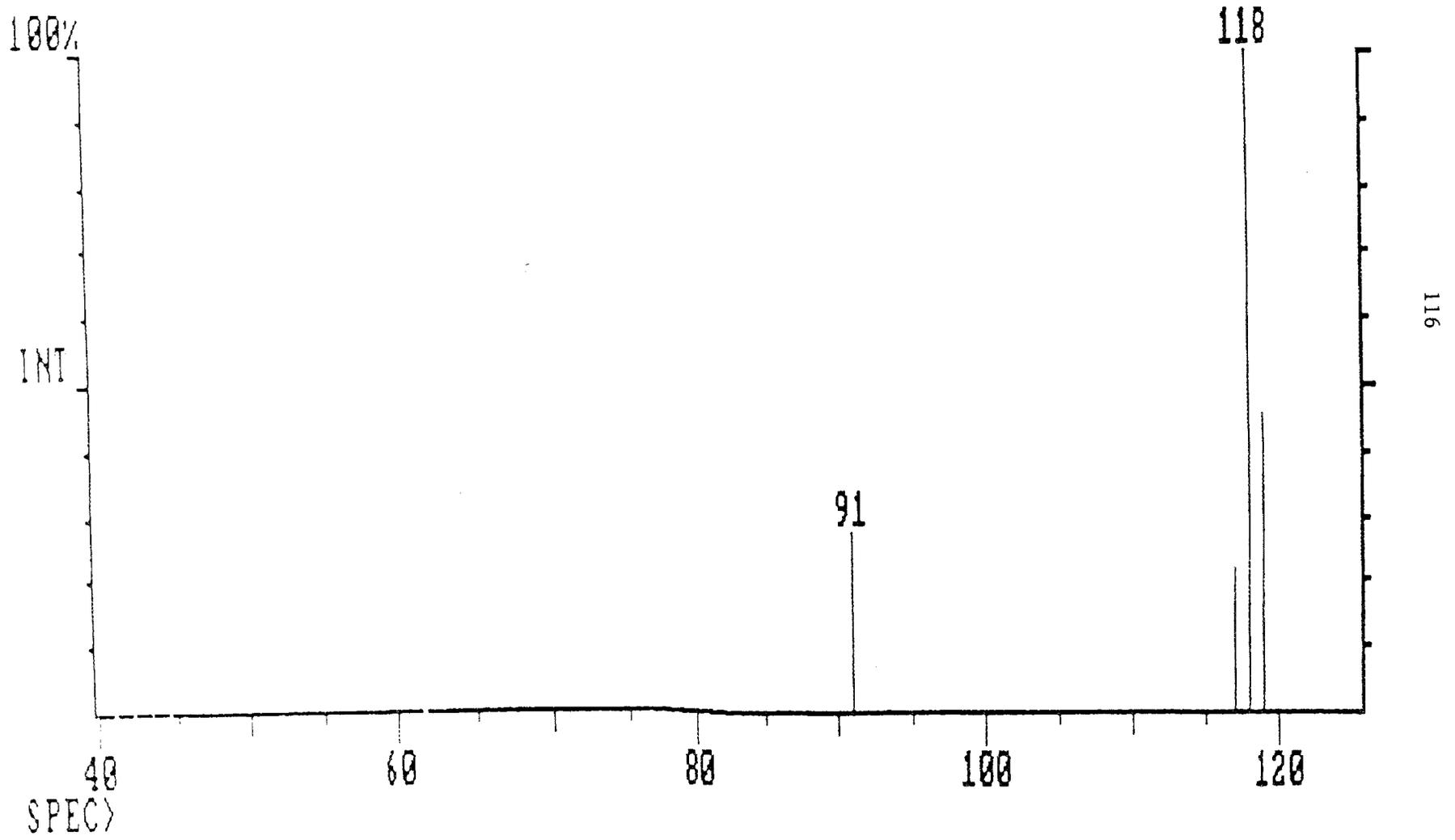
COMPOUND: NITROGEN TETRAOXIDE

CI MS/MS SPECTRUM OF M/Z 95



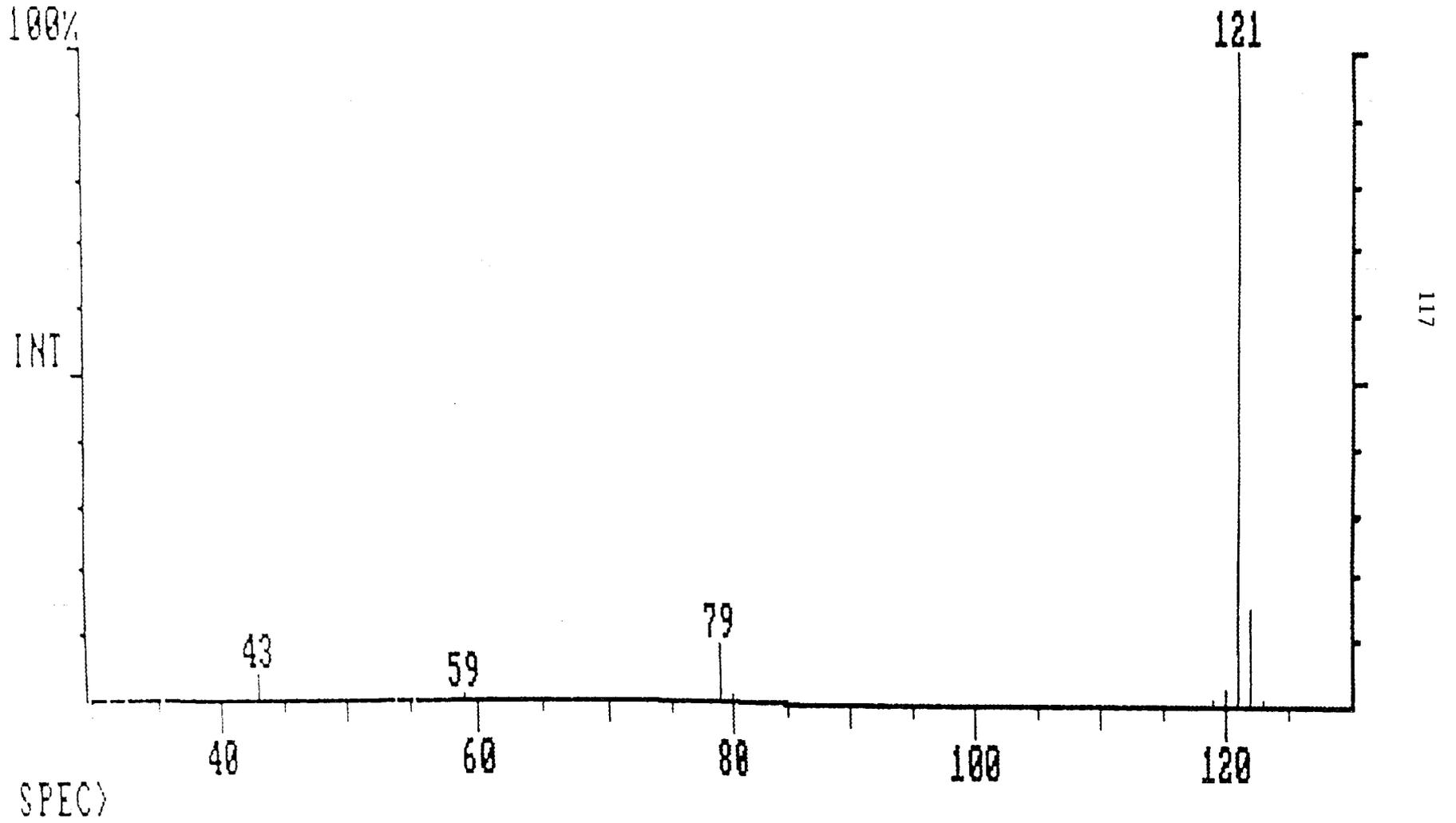
COMPOUND: INDOLE

CI MS/MS SPECTRUM OF M/Z 118

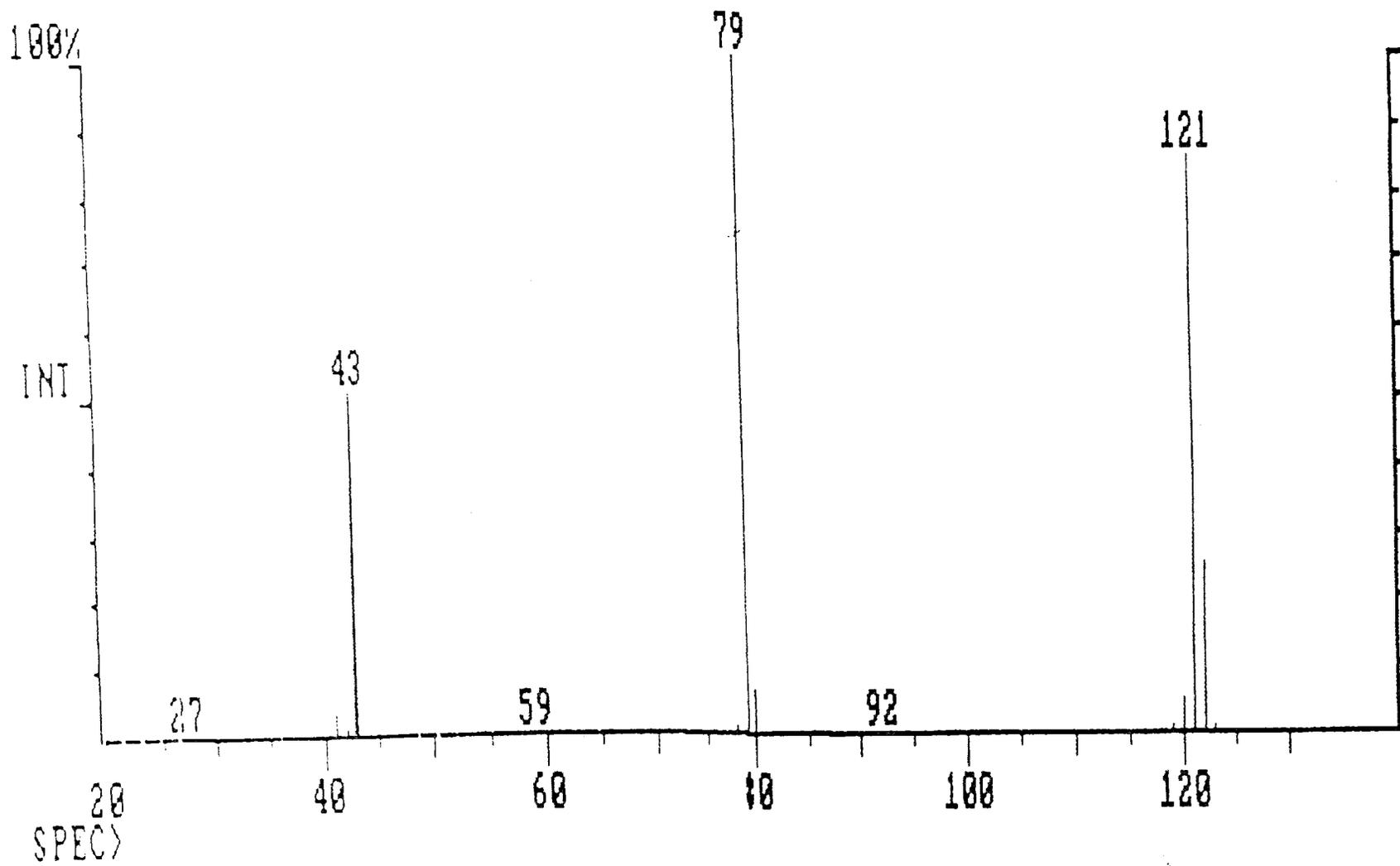


COMPOUND : CUMENE

CI MS/MS SPECTRUM OF M/Z 121

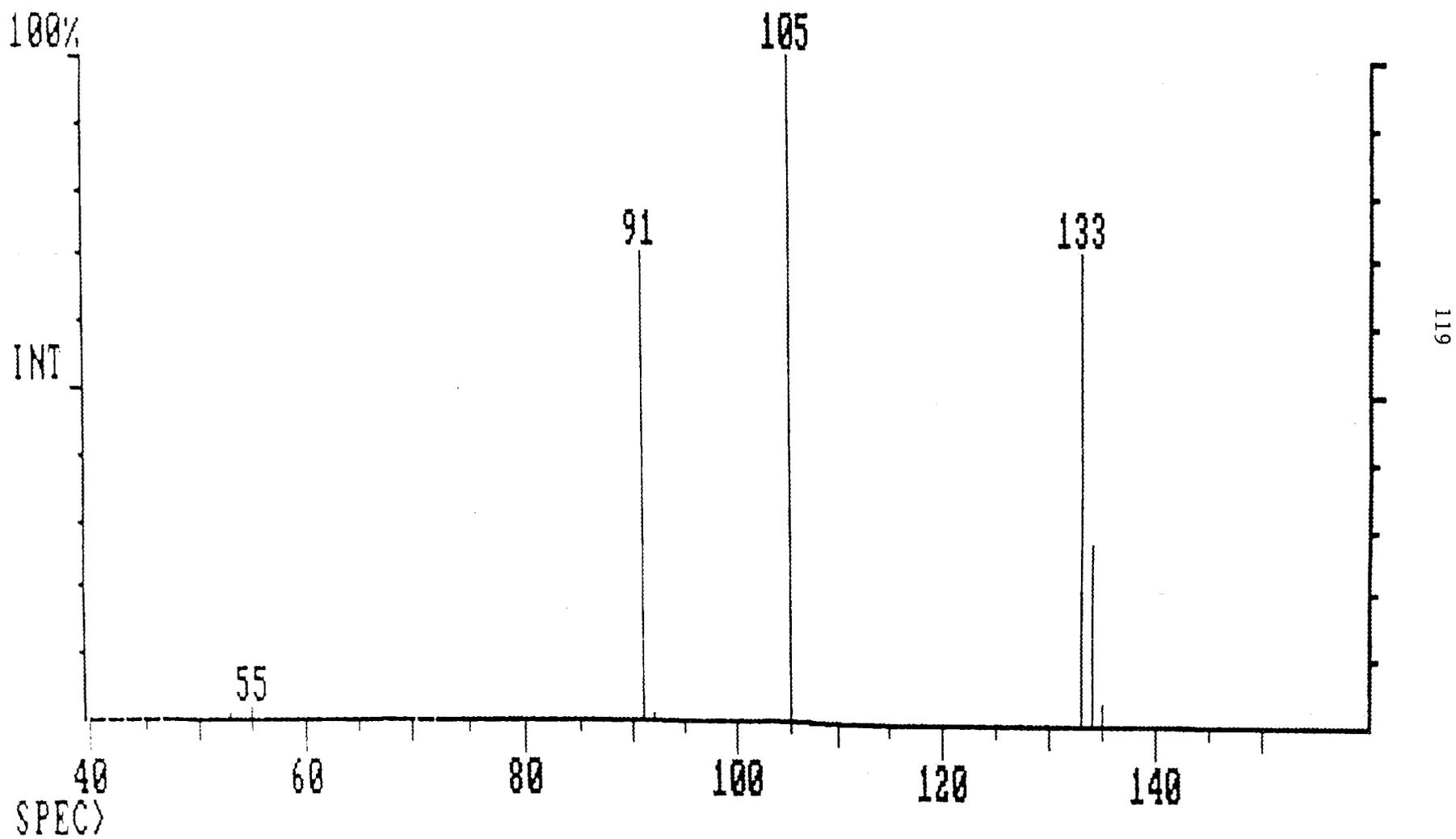


COMPOUND: N-PROPYLBENZENE
CI MS/MS SPECTRUM OF M/Z 121

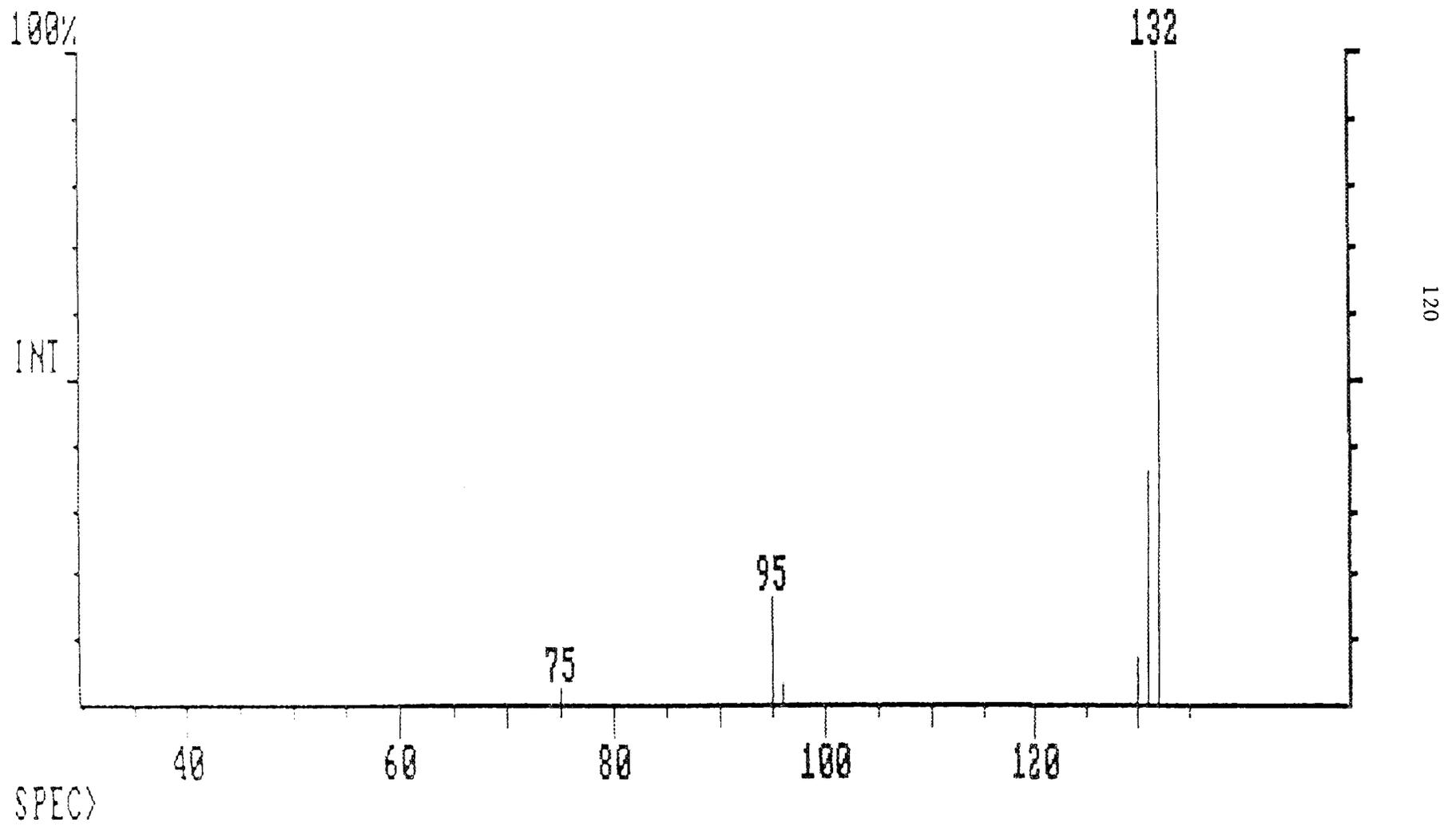


COMPOUND: N-PROPYLBENZENE

CI-MS/MS SPECTRUM OF M/Z 133

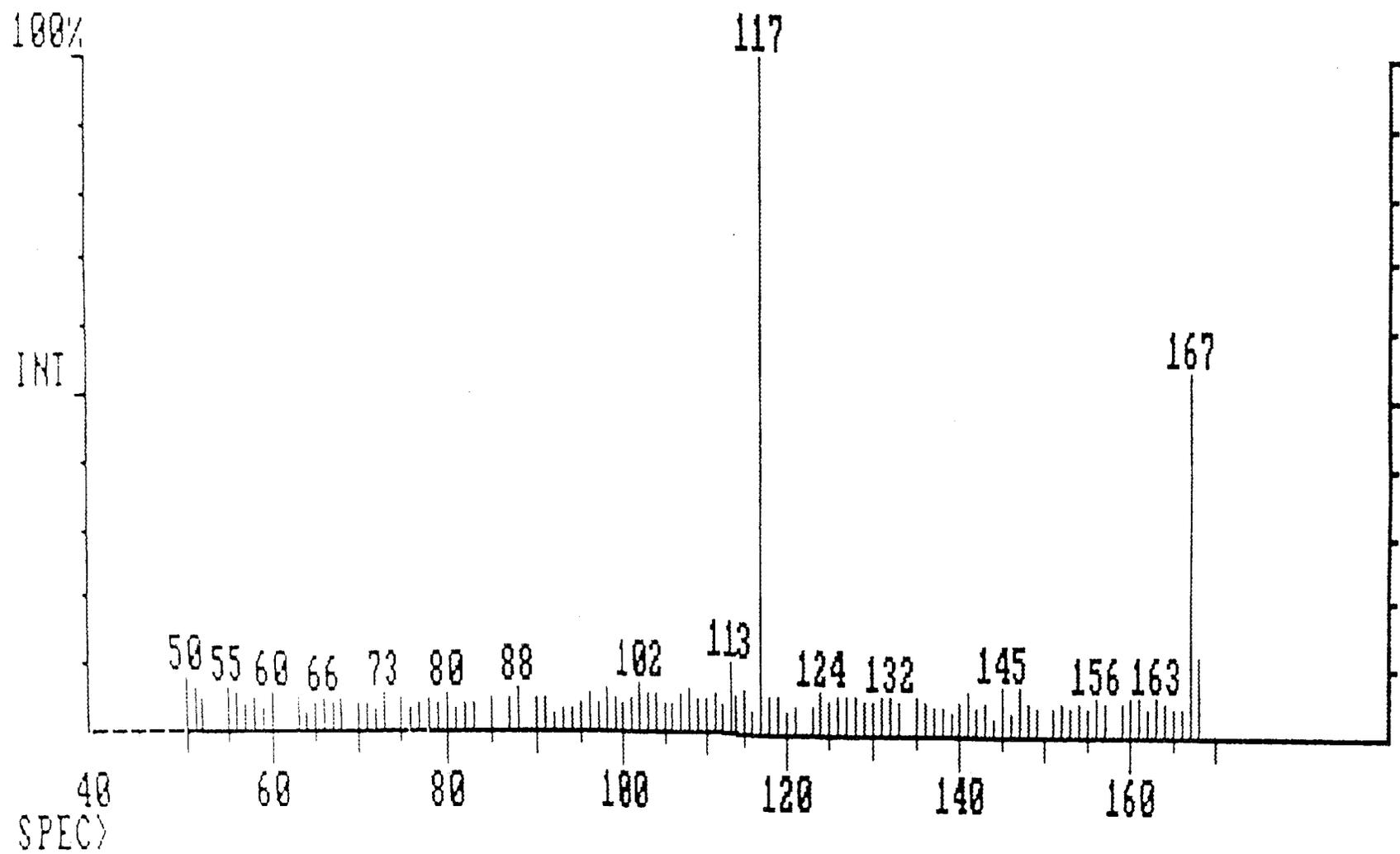


COMPOUND: TRICHLOROETHYLENE
CI MS/MS SPECTRUM OF M/Z 131



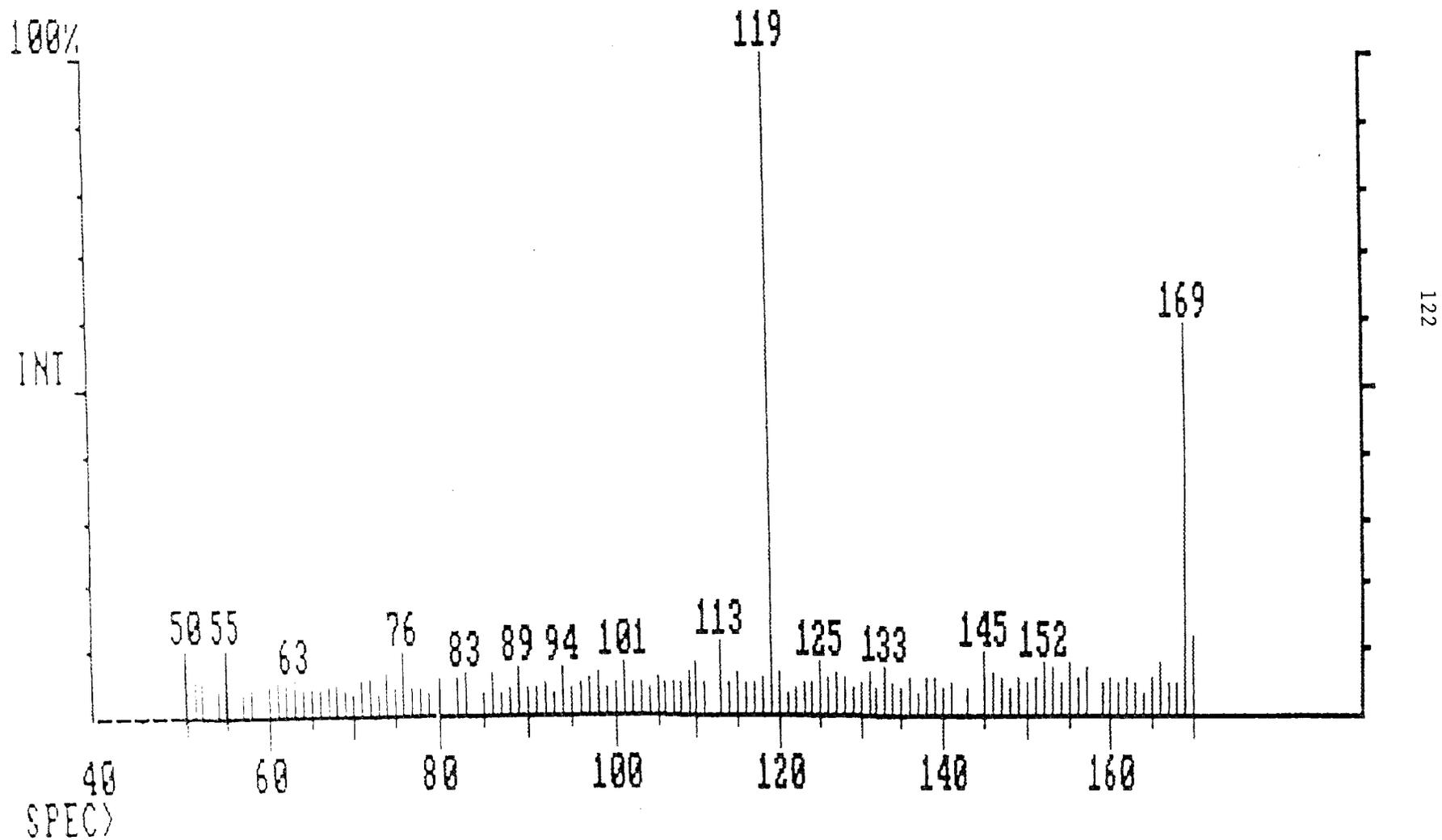
COMPOUND: FREON 113

CI MS/MS SPECTRUM OF M/Z 167



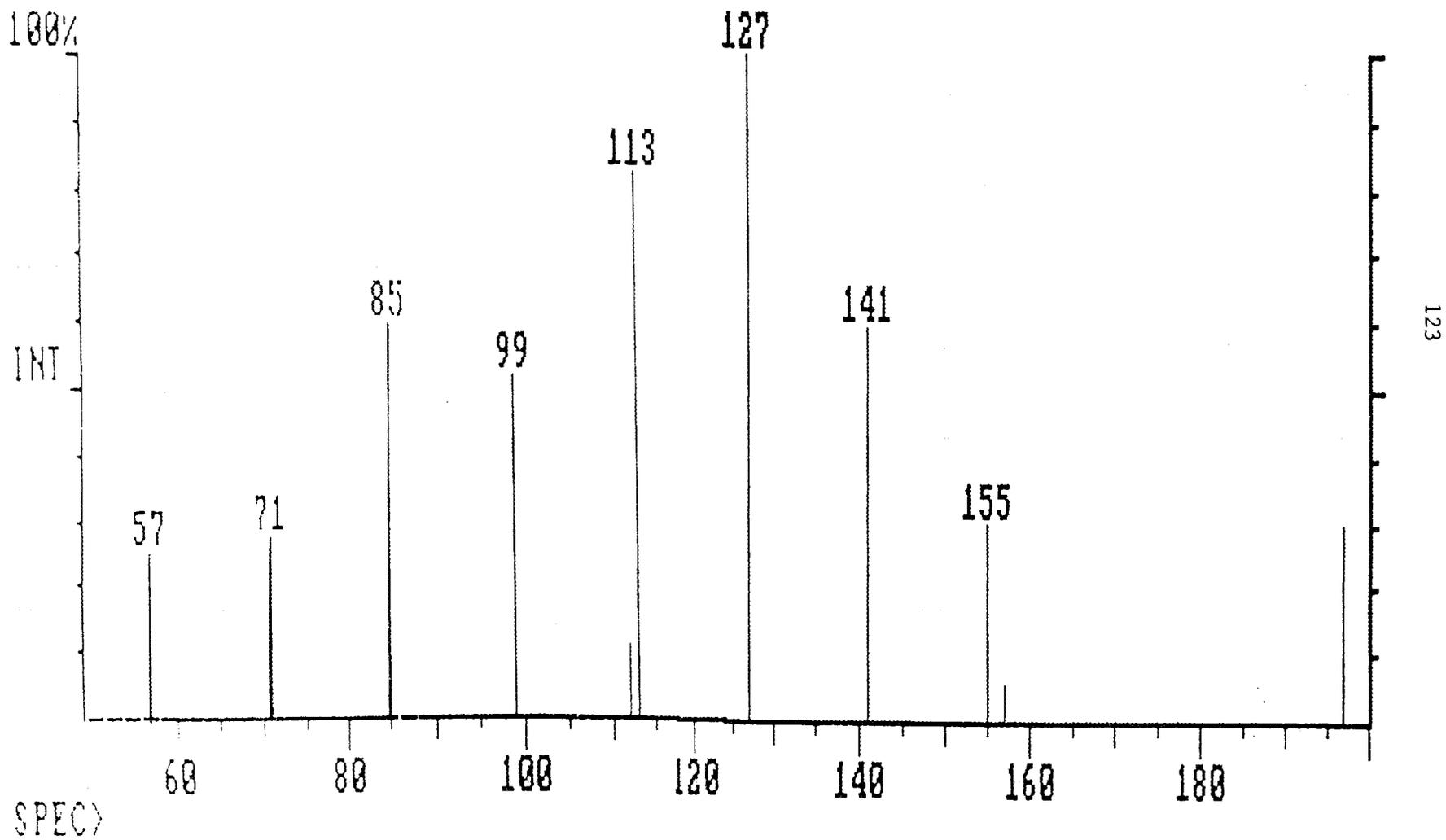
COMPOUND: FREON 113

CI MS/MS SPECTRUM OF M/Z 169



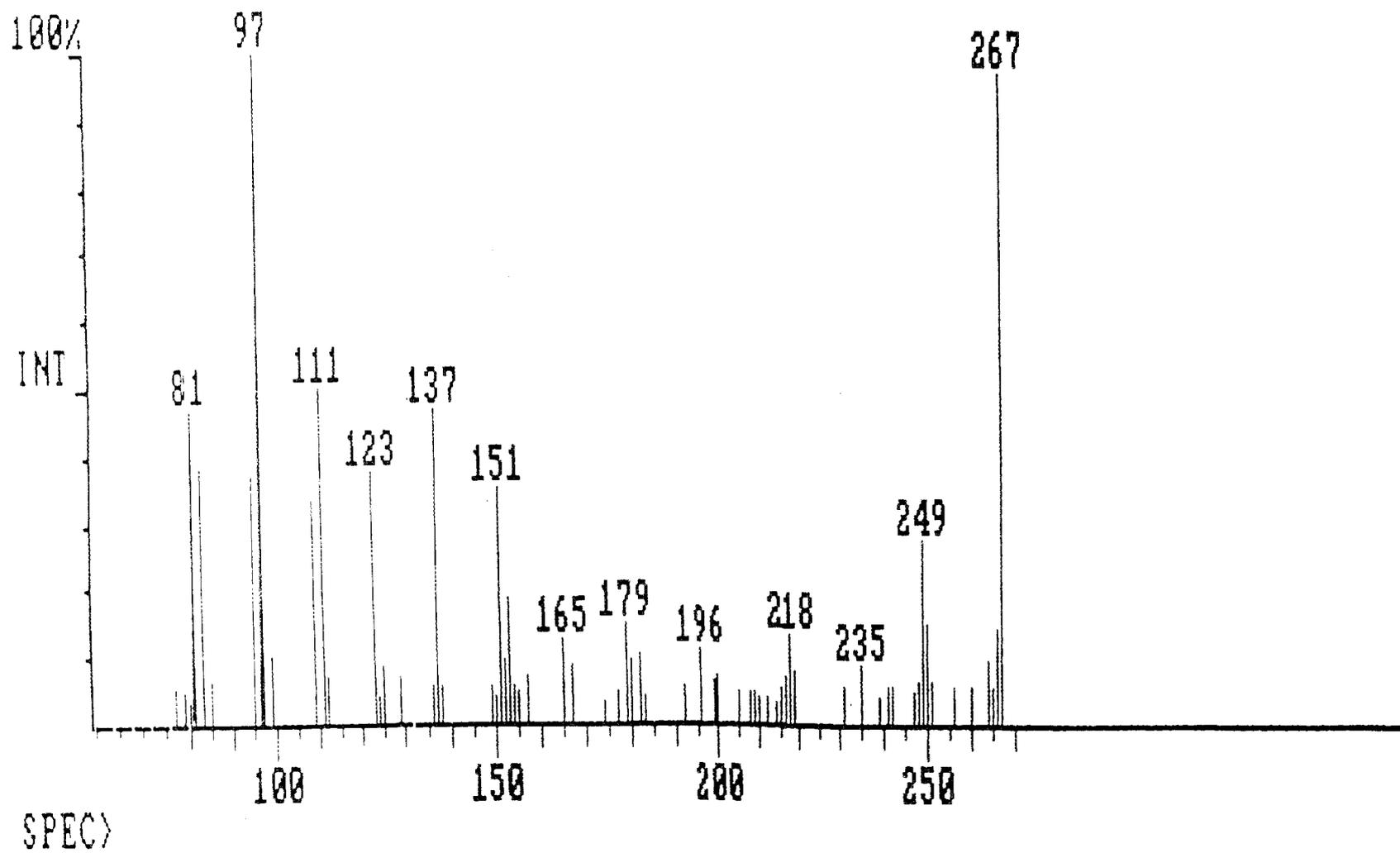
COMPOUND: TETRADECANE

CI MS/MS SPECTRUM OF M/Z 197



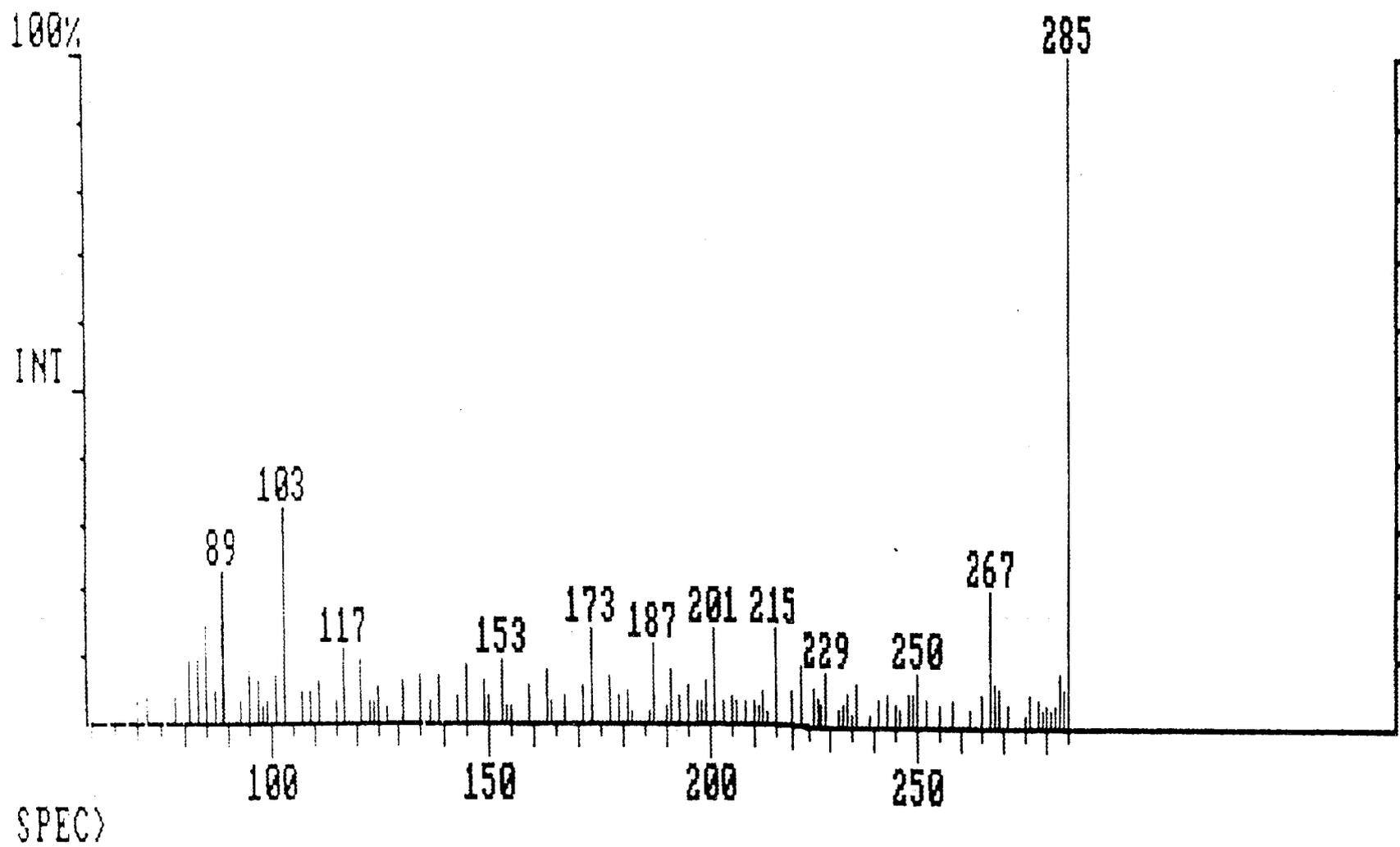
COMPOUND: STEARIC ANHYDRIDE

CI MS/MS SPECTRUM OF M/Z 267

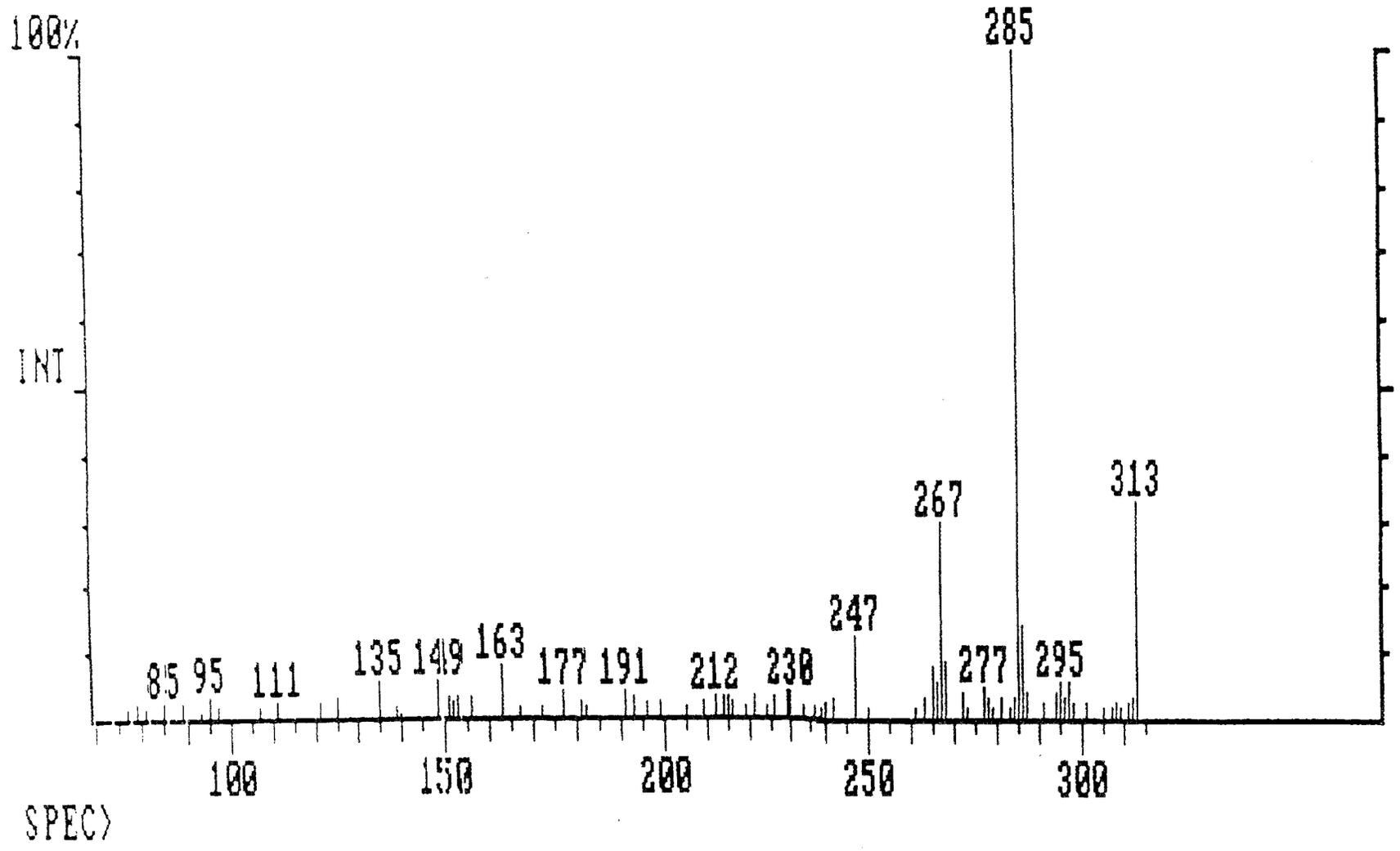


COMPOUND: STEARIC ANHYDRIDE

CI MS/MS SPECTRUM OF M/Z 285



COMPOUND: STEARIC ANHYDRIDE
CI MS/MS SPECTRUM OF M/Z 313

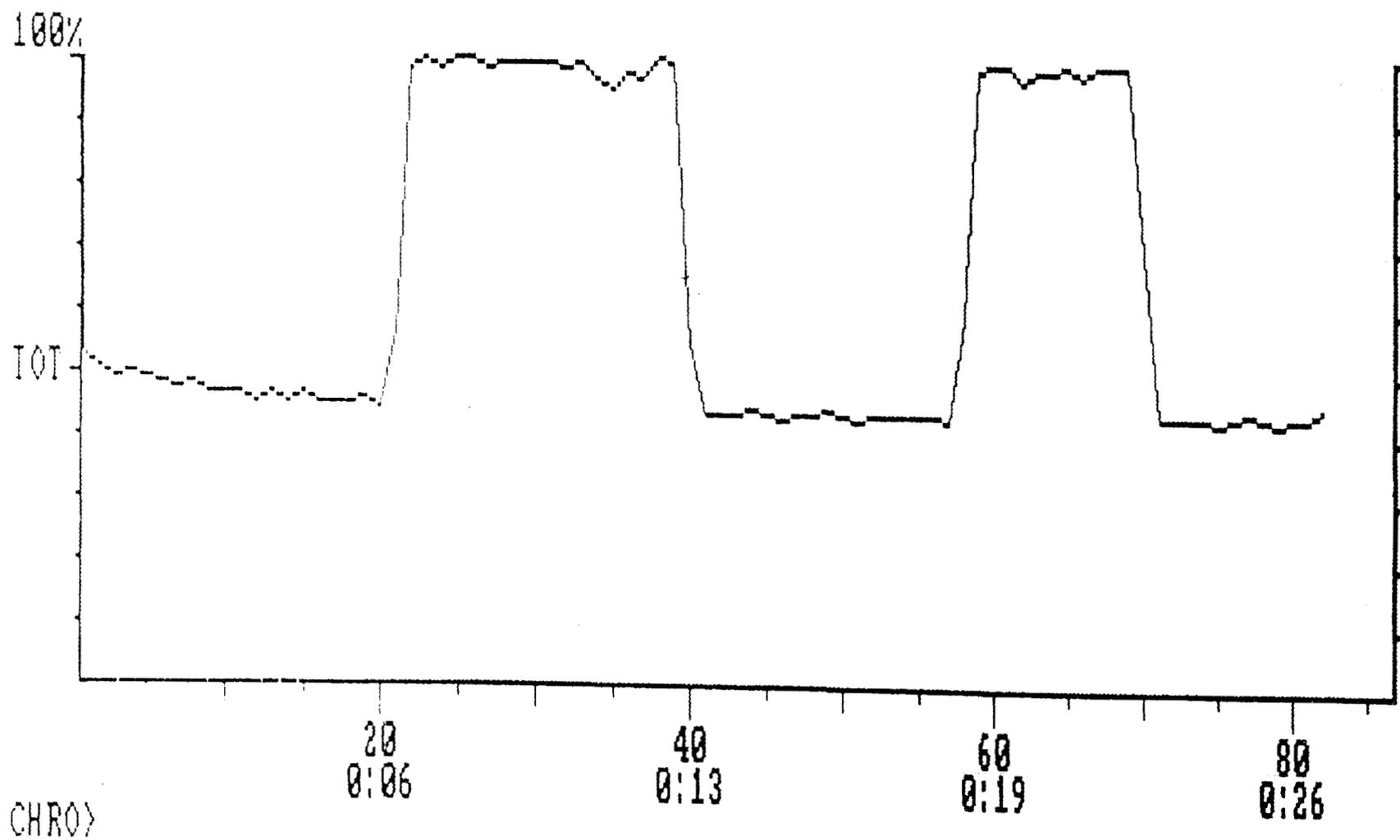


Appendix E

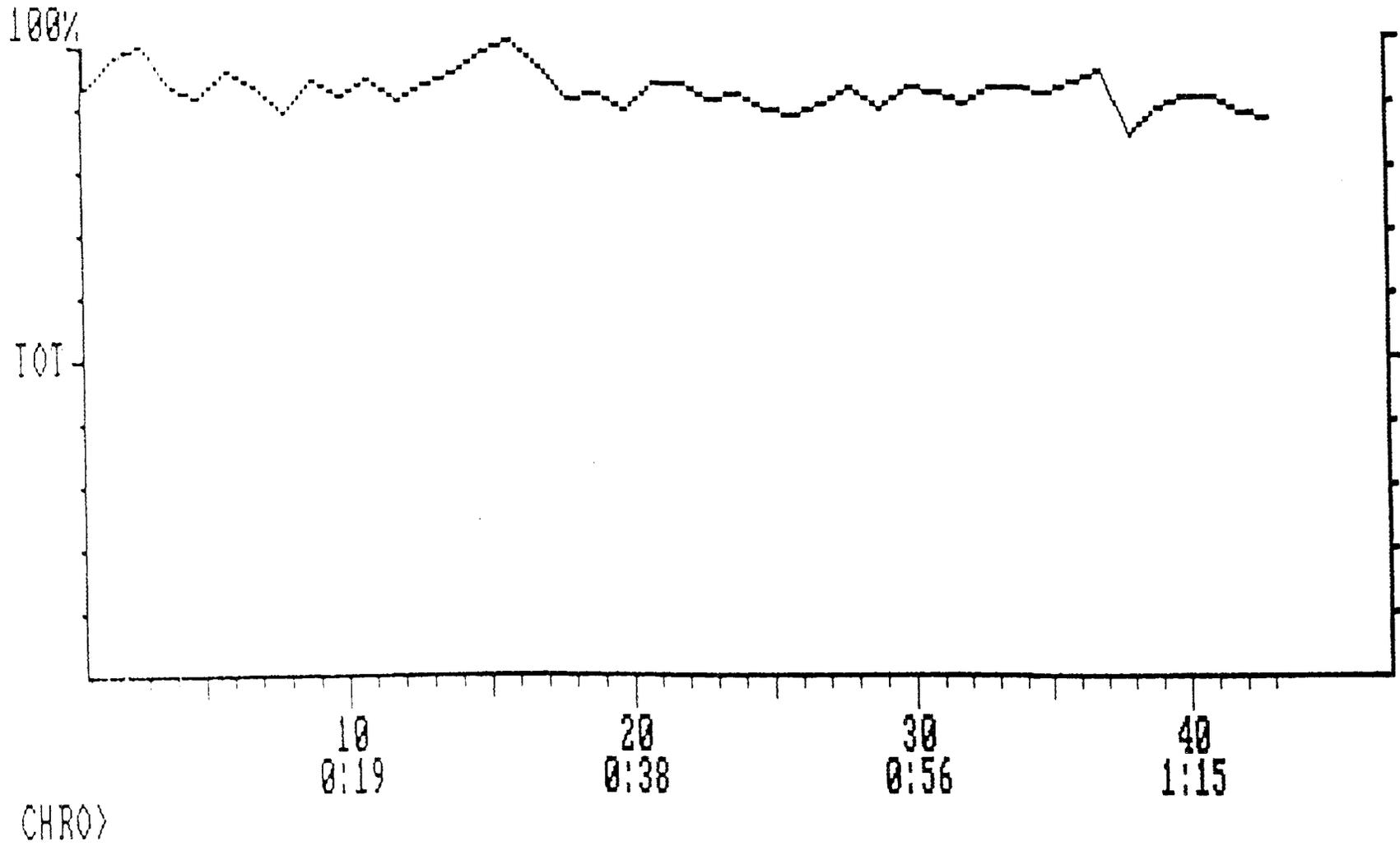
CAD Efficiency of the ITMS

These are plots of the total ion current with the "collision" pulse being applied for several scans and then being turned off for several scans. In most cases the "collision" pulse was cycled on, off, on, off and back on. The CAD efficiency is determined by dividing the average ion current during the off cycle by the average ion current during the on cycle.

COMPOUND: ETHANOL
CAD EFFICIENCY FOR EI MS/MS OF m/z 45
(WITH METHANE)

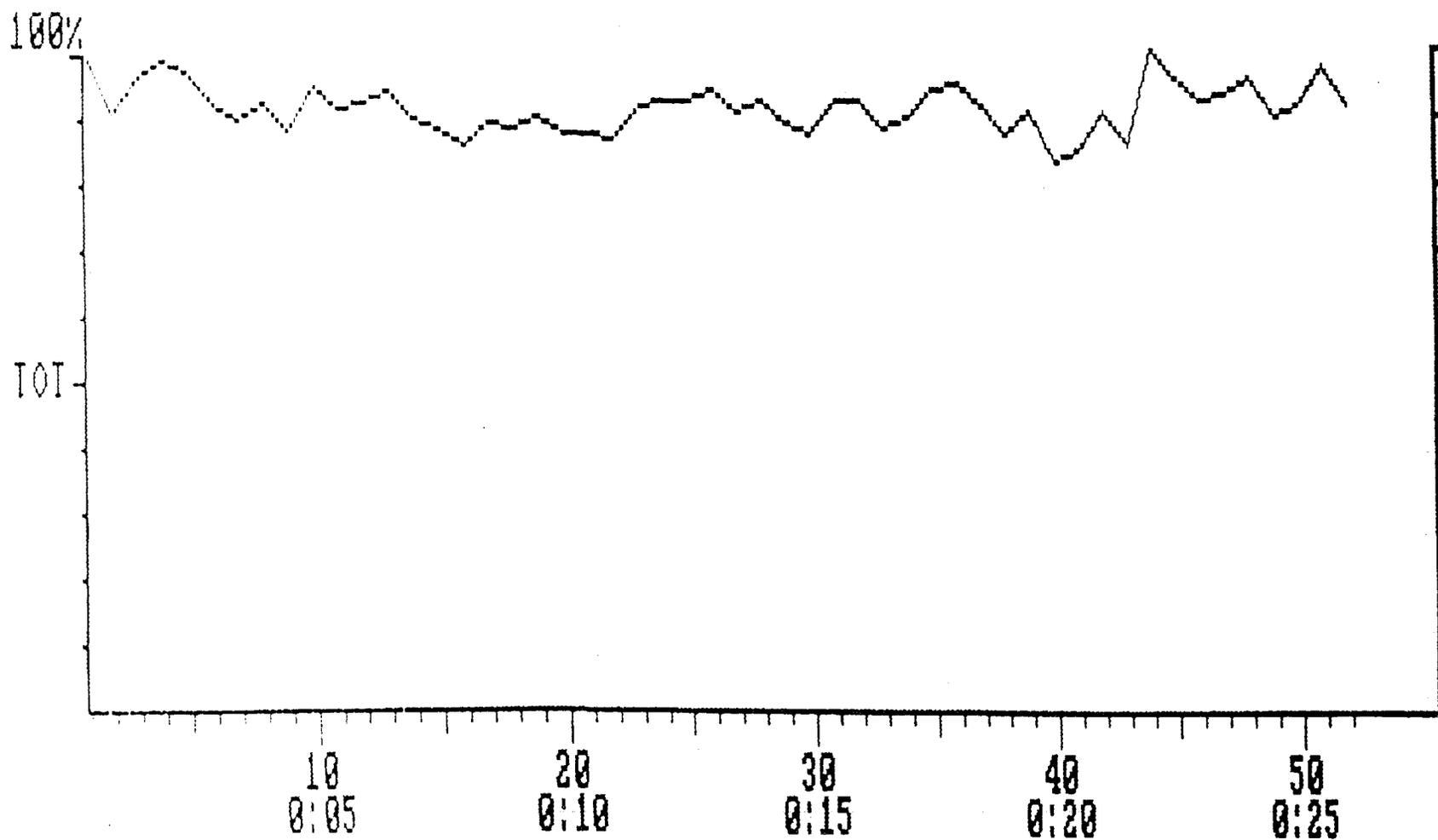


COMPOUND: METHYLETHYLKETONE
CAD EFFICIENCY FOR EI MS/MS OF M/Z 72



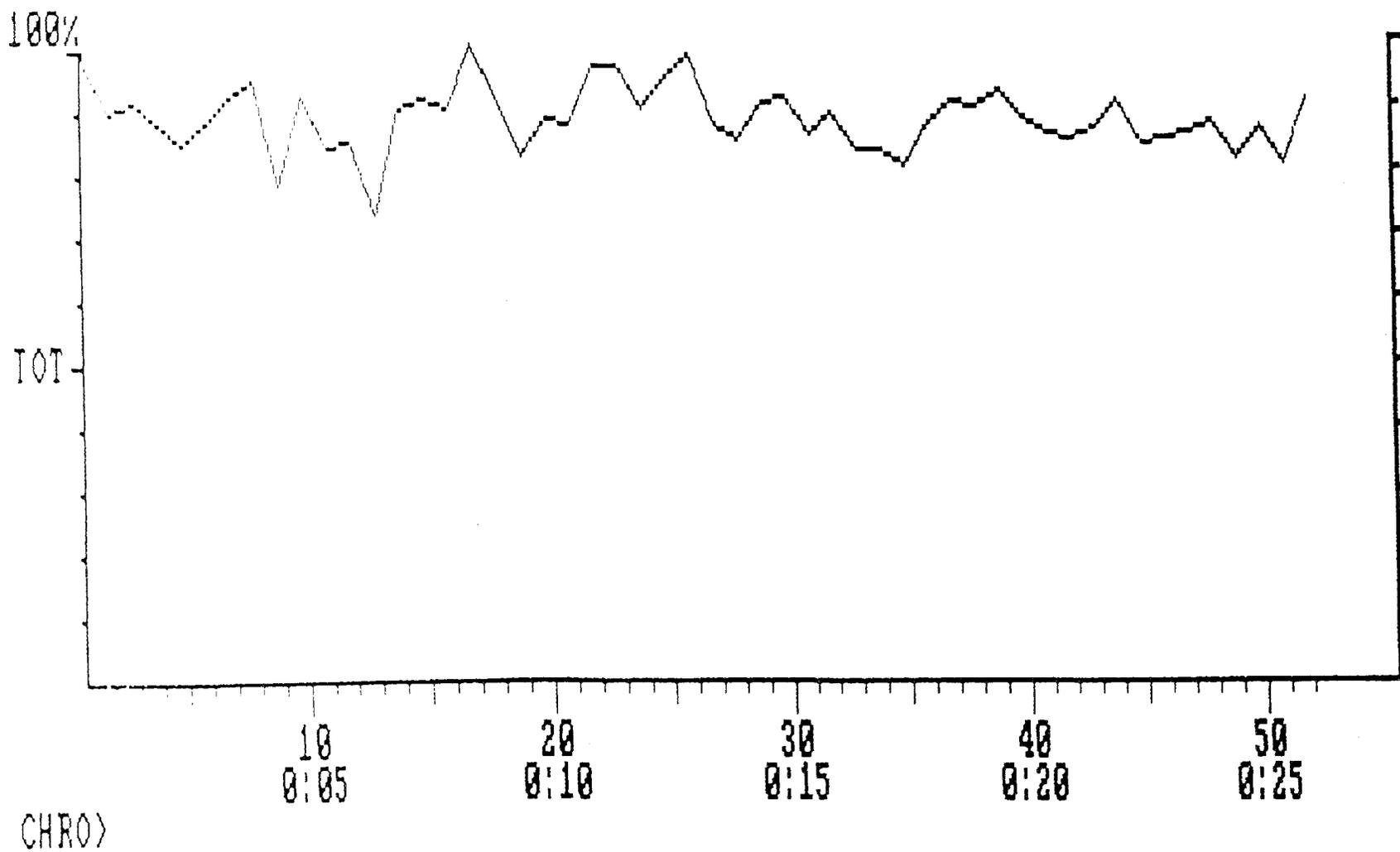
COMPOUND: BUTANOL

CAD EFFICIENCY FOR EI MS/MS OF M/Z 73



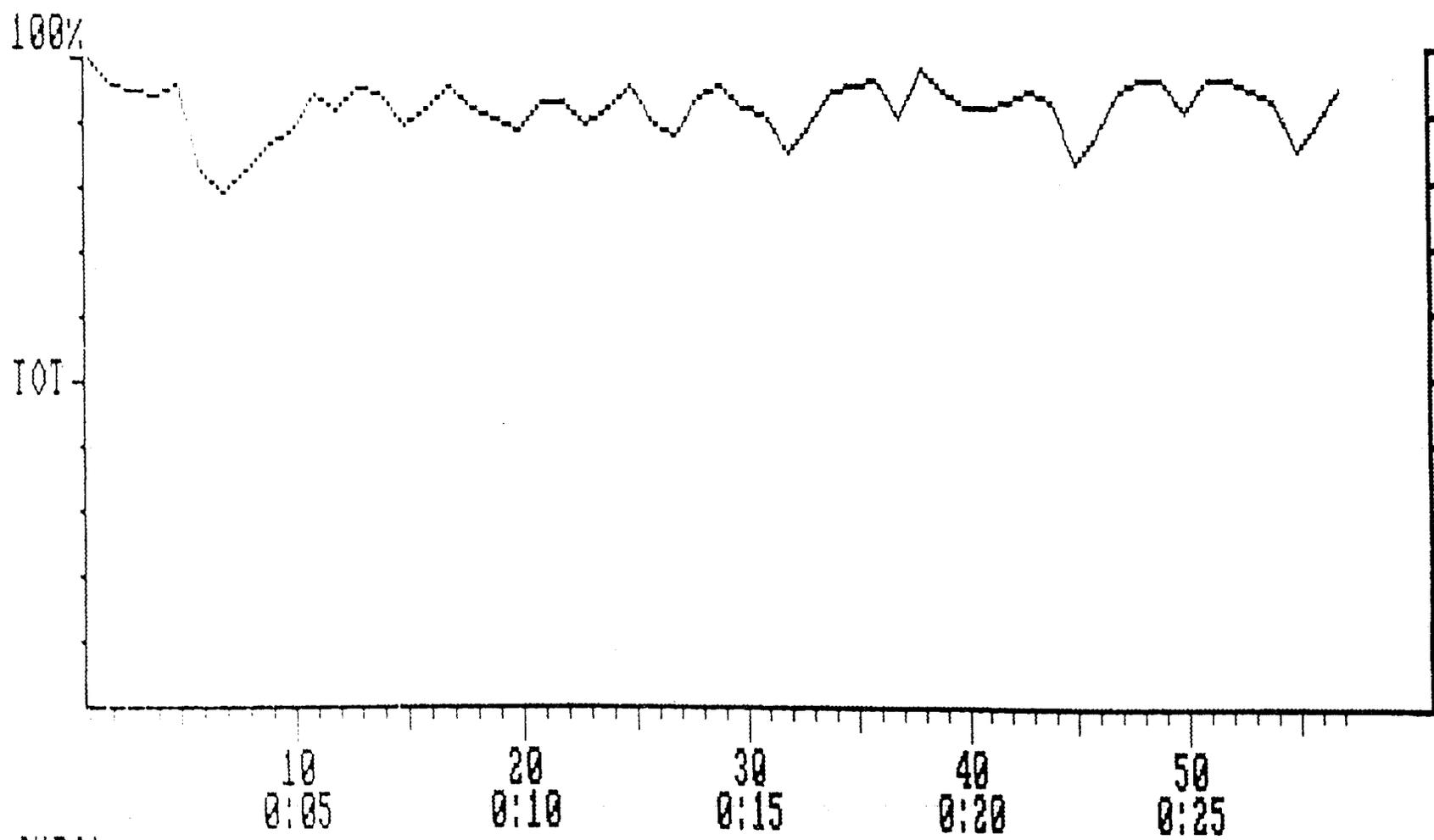
CHRO>

COMPOUND: DIETHYLETHER
CAD EFFICIENCY FOR EI MS/MS OF M/Z 59



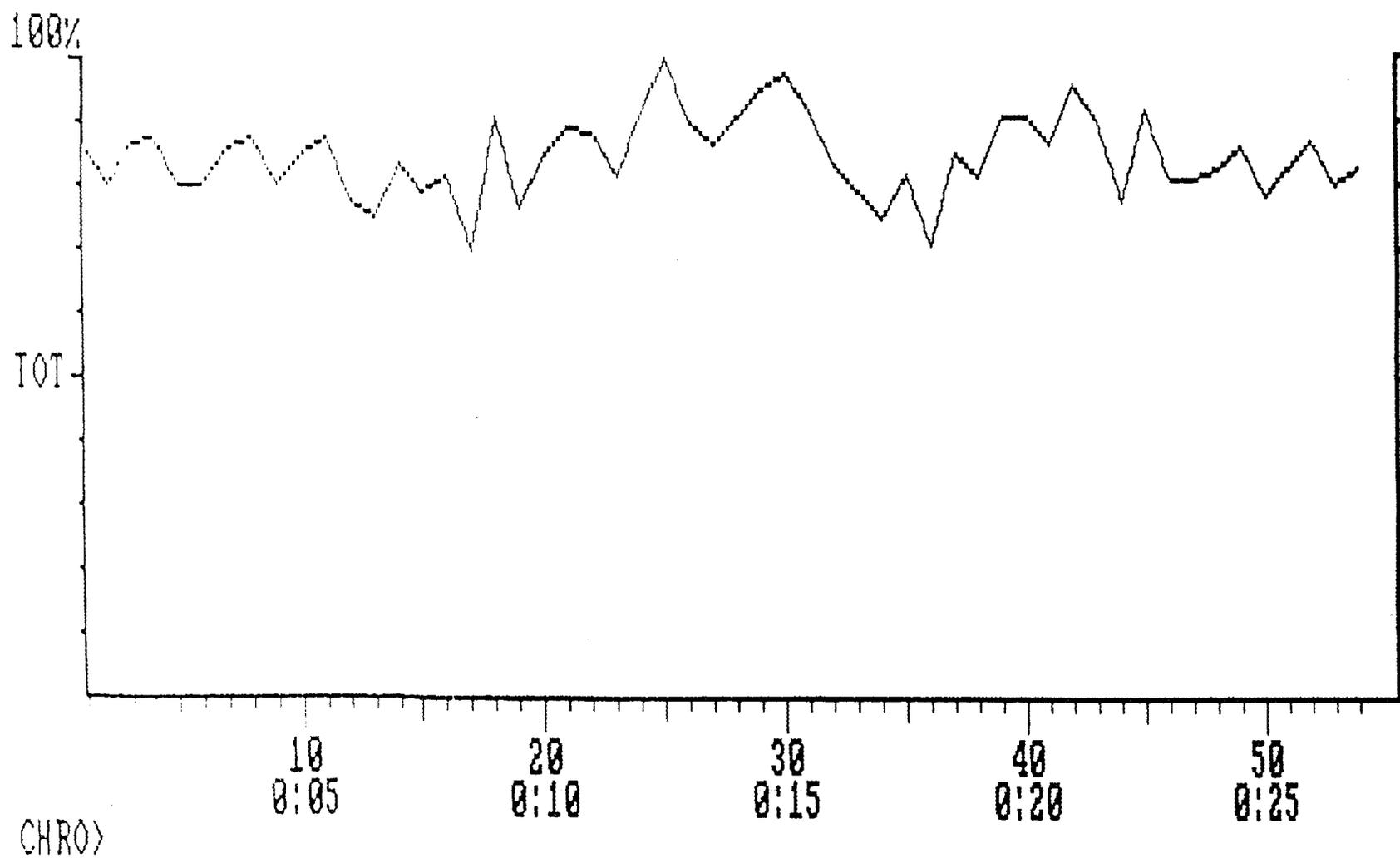
COMPOUND: DIETHYLETHER

CAD EFFICIENCY FOR EI MS/MS OF m/z 73



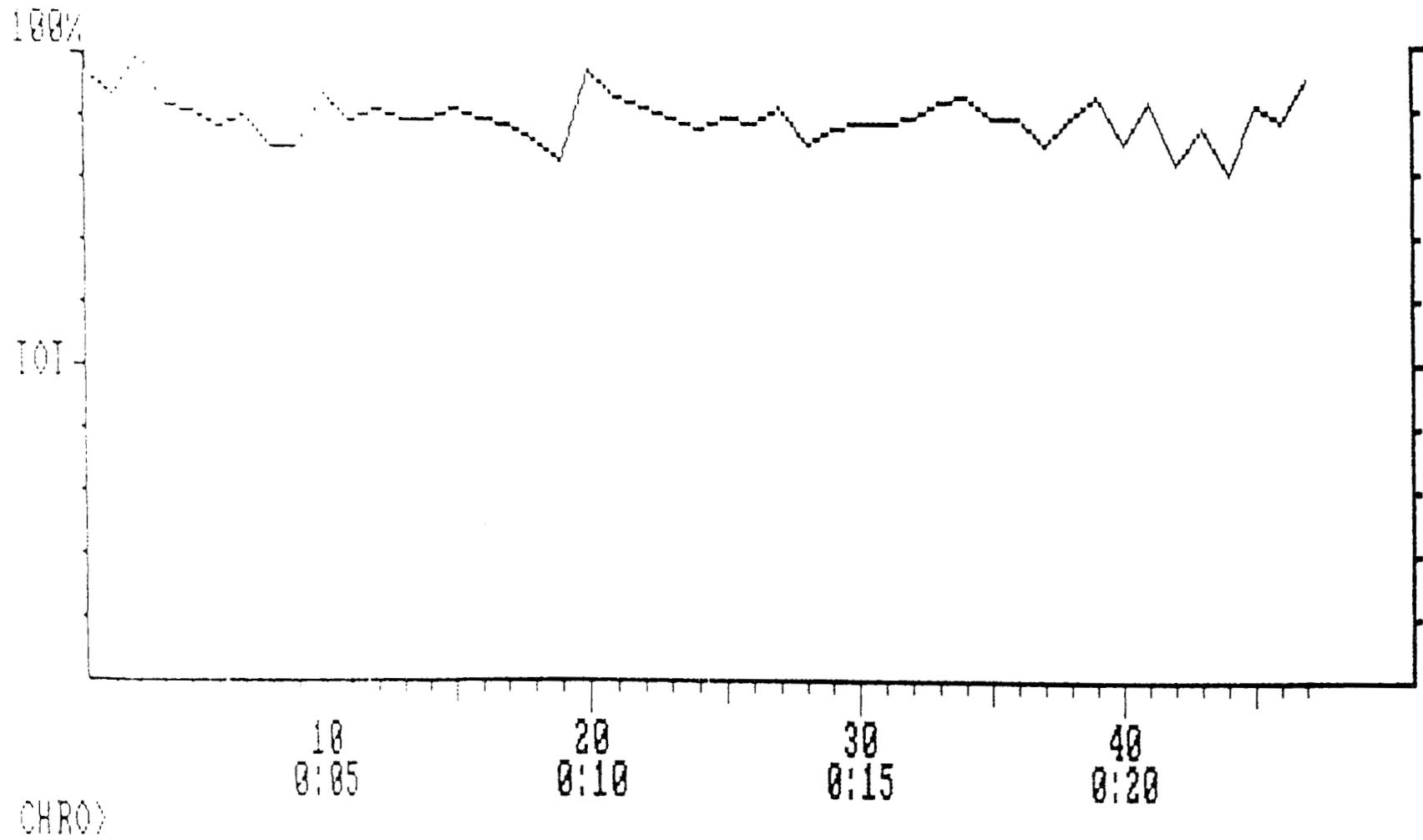
COMPOUND: ETHYLFORMATE

CAD EFFICIENCY FOR EI MS/MS OF M/Z 73

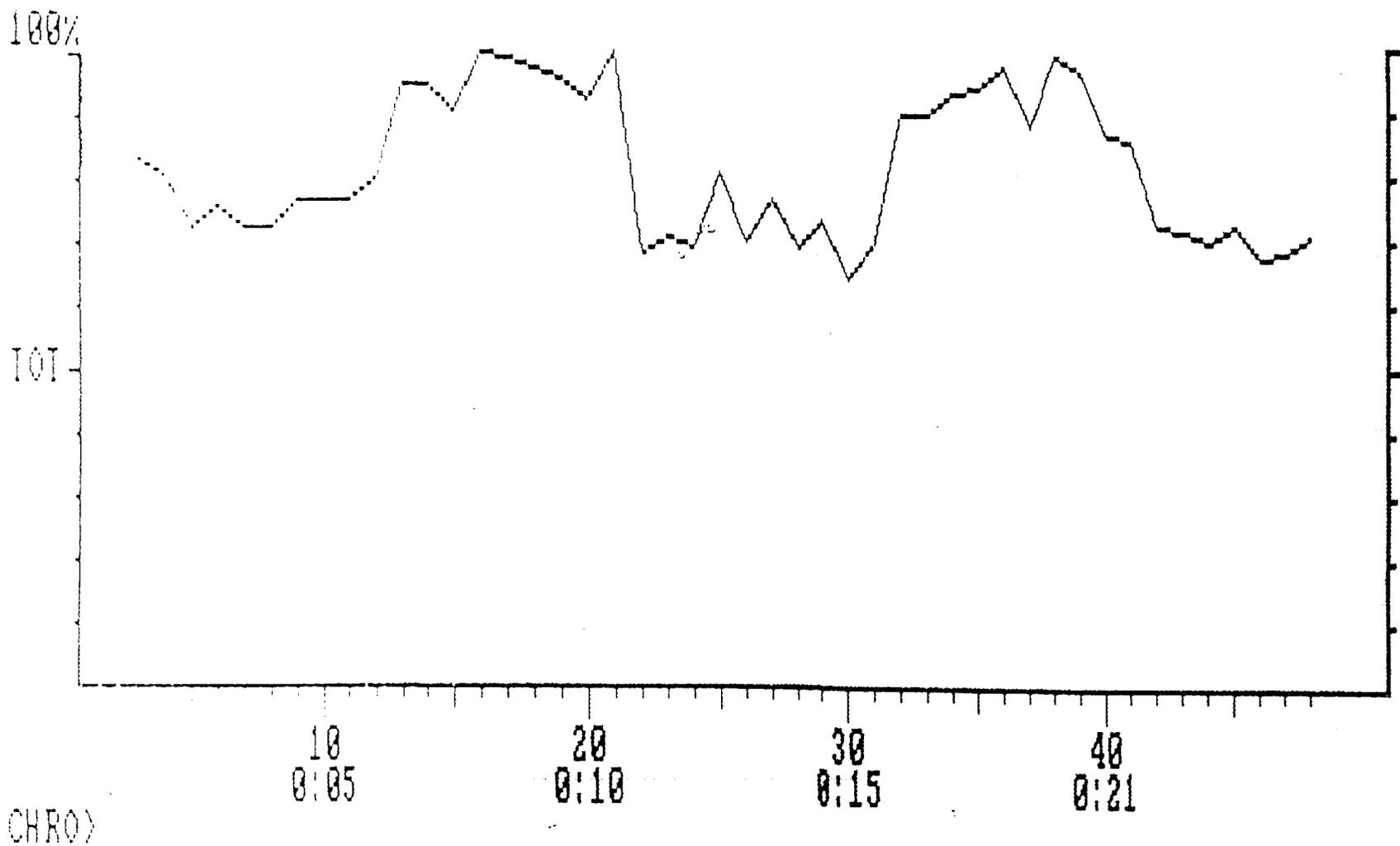


COMPOUND: ETHYLFORMATE

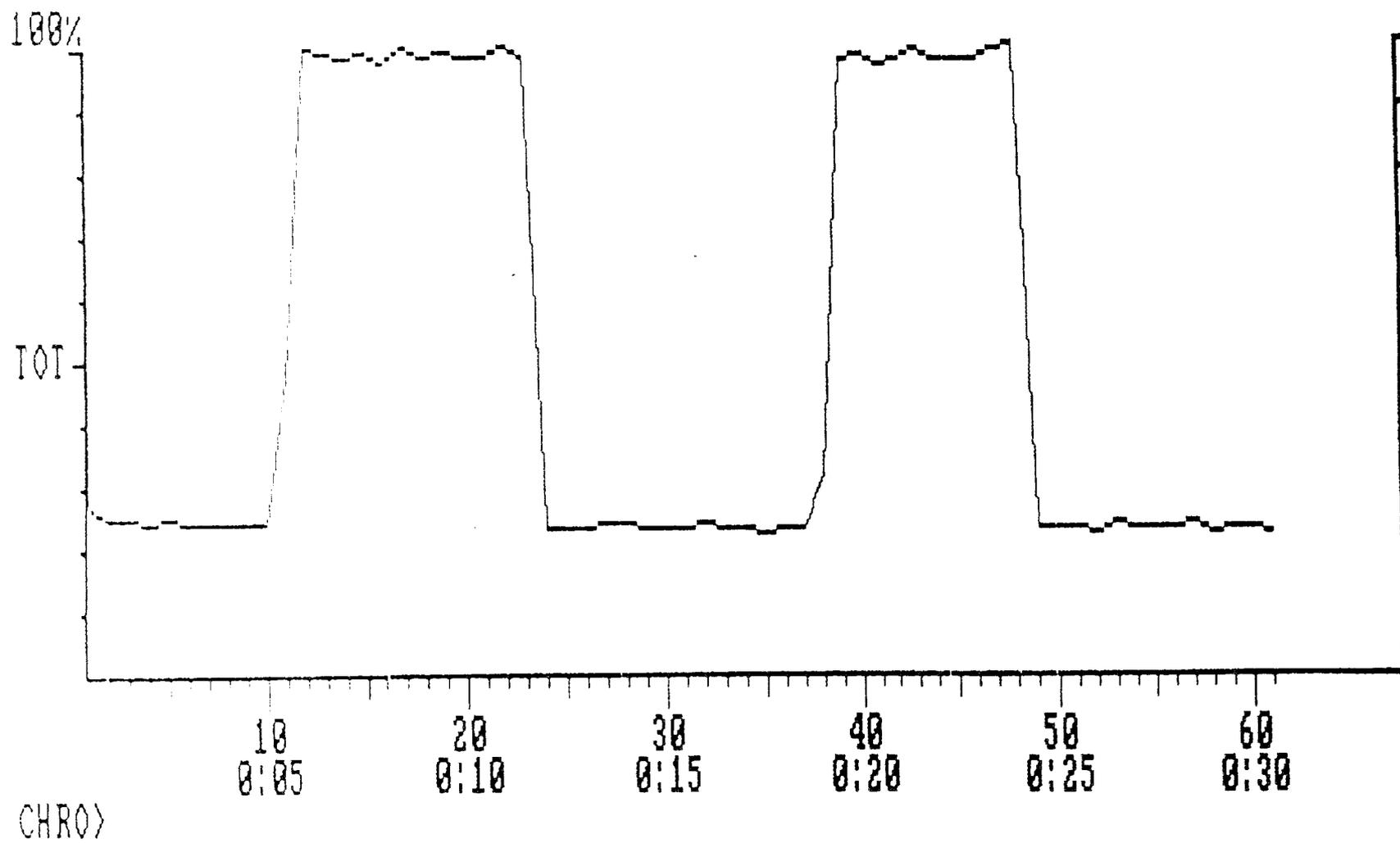
CAD EFFICIENCY FOR EI MS/MS OF M/Z 74



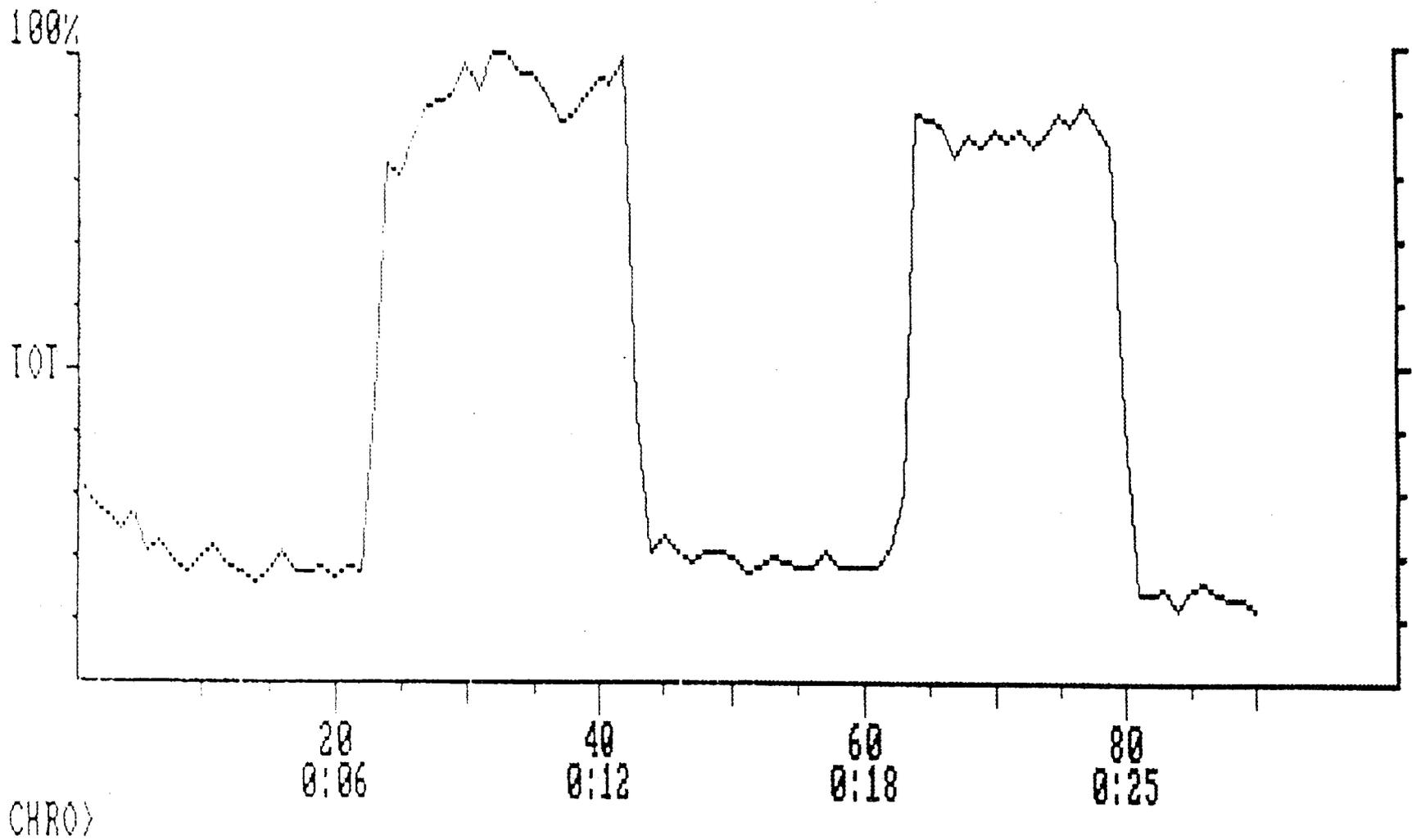
COMPOUND: PROPIONIC ACID
CAD EFFICIENCY FOR EI MS/MS OF M/Z 74



COMPOUND: CARBON DISULFIDE
CAD EFFICIENCY FOR EI MS/MS OF M/Z 76

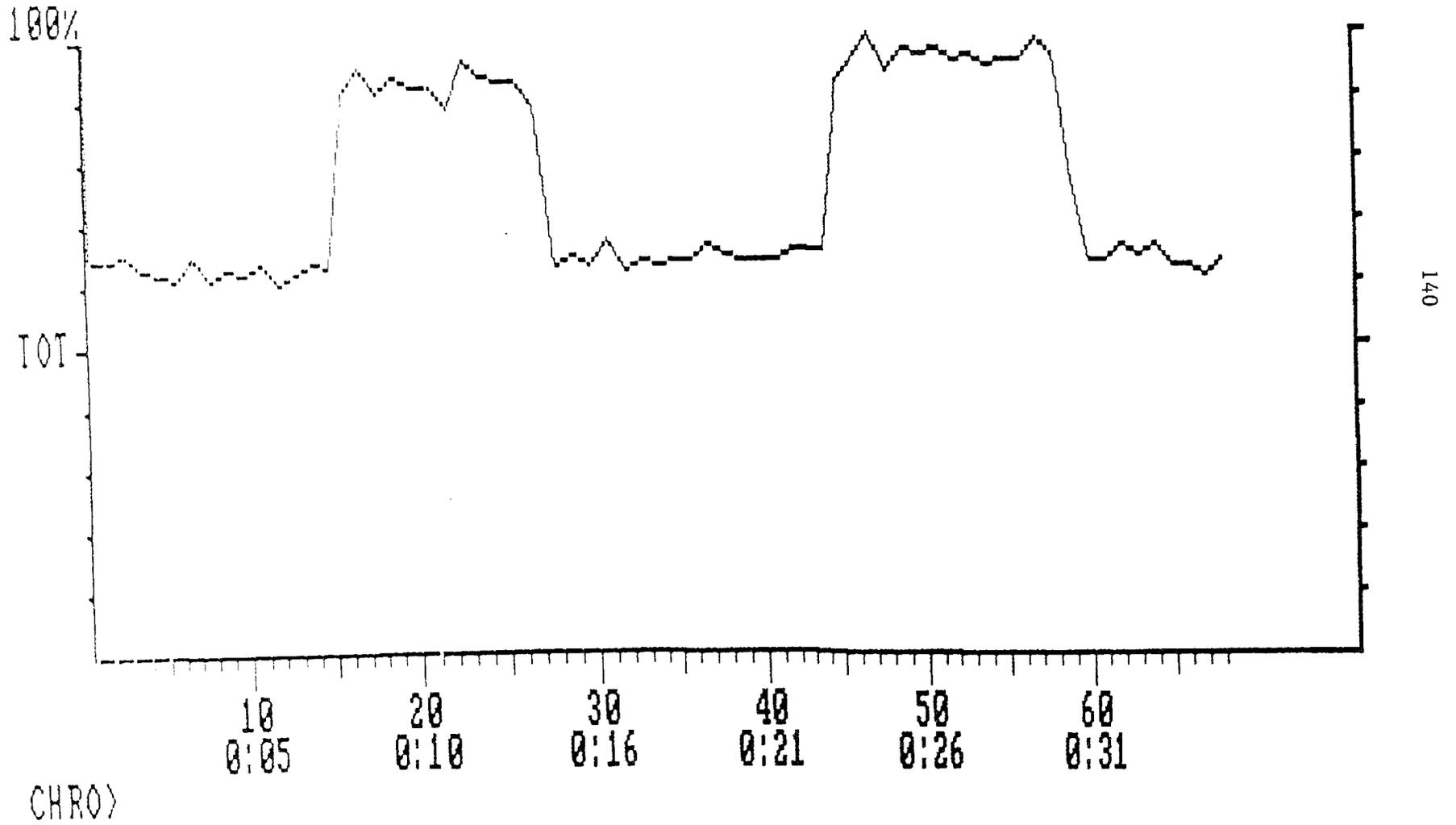


COMPOUND: NITROGEN TETRAOXIDE
CAD EFFICIENCY FOR EI MS/MS OF m/z 46



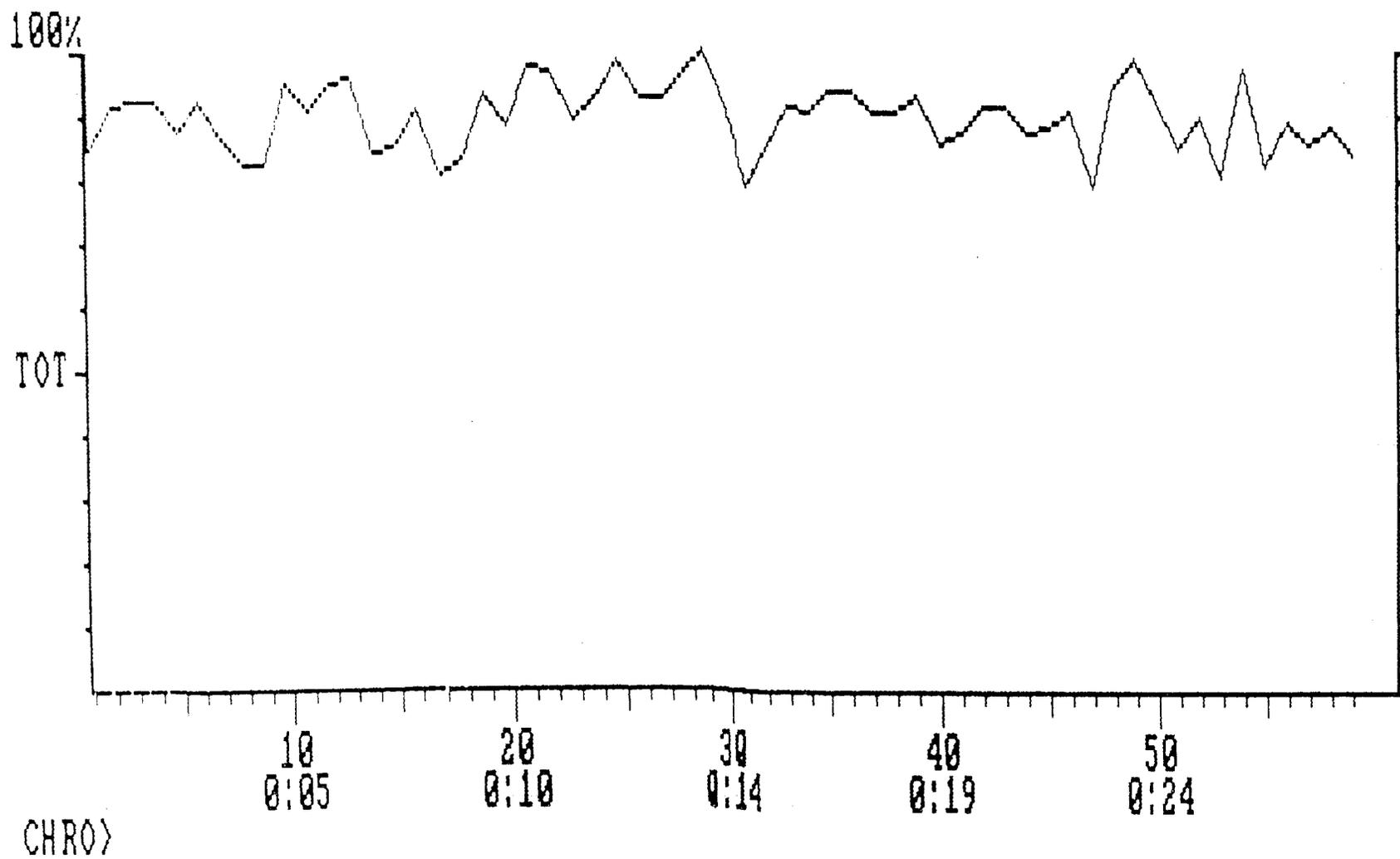
COMPOUND: INDOLE

CAD EFFICIENCY FOR EI MS/MS OF M/Z 117



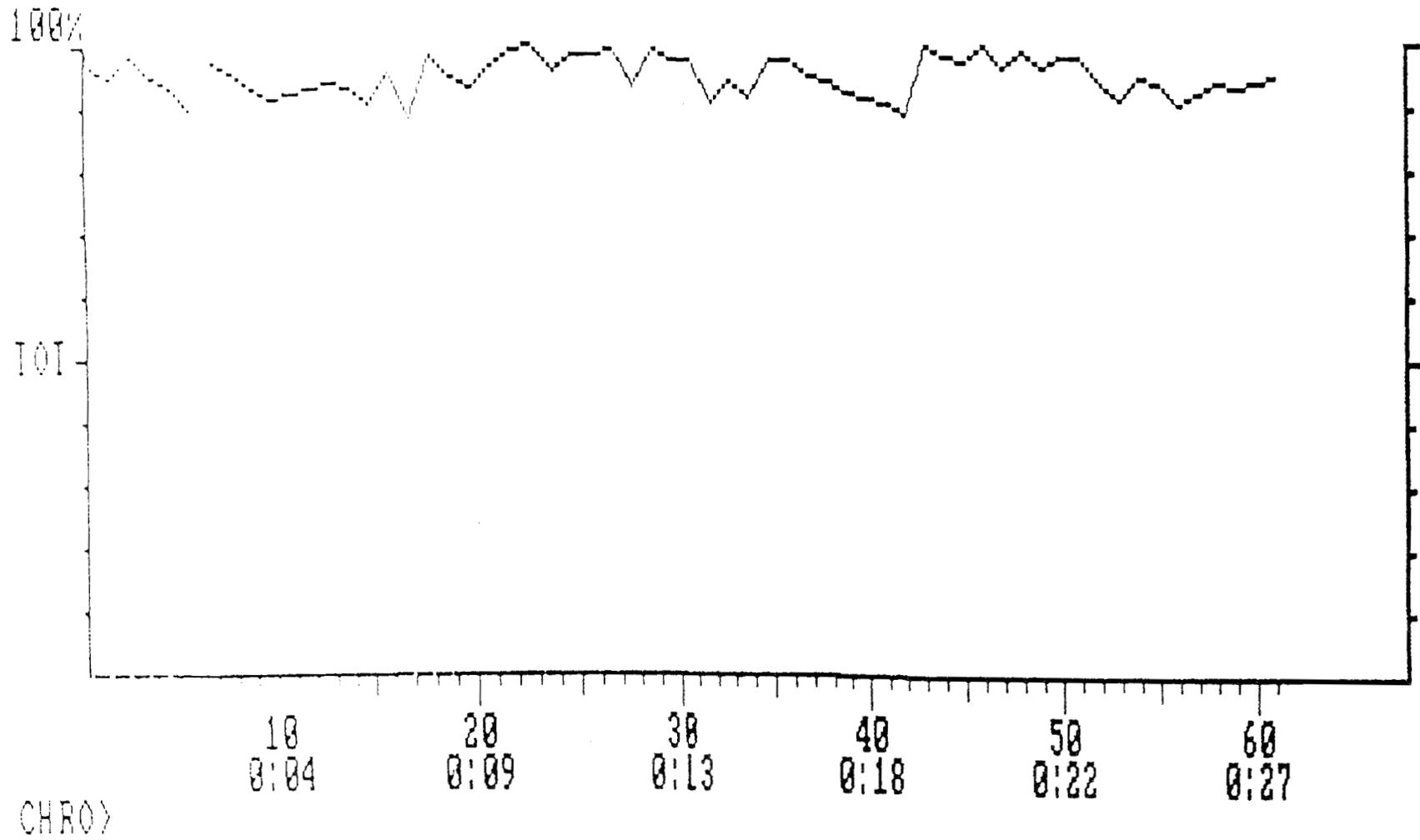
COMPOUND: CUMENE

CAD EFFICIENCY FOR EI MS/MS OF M/Z 120

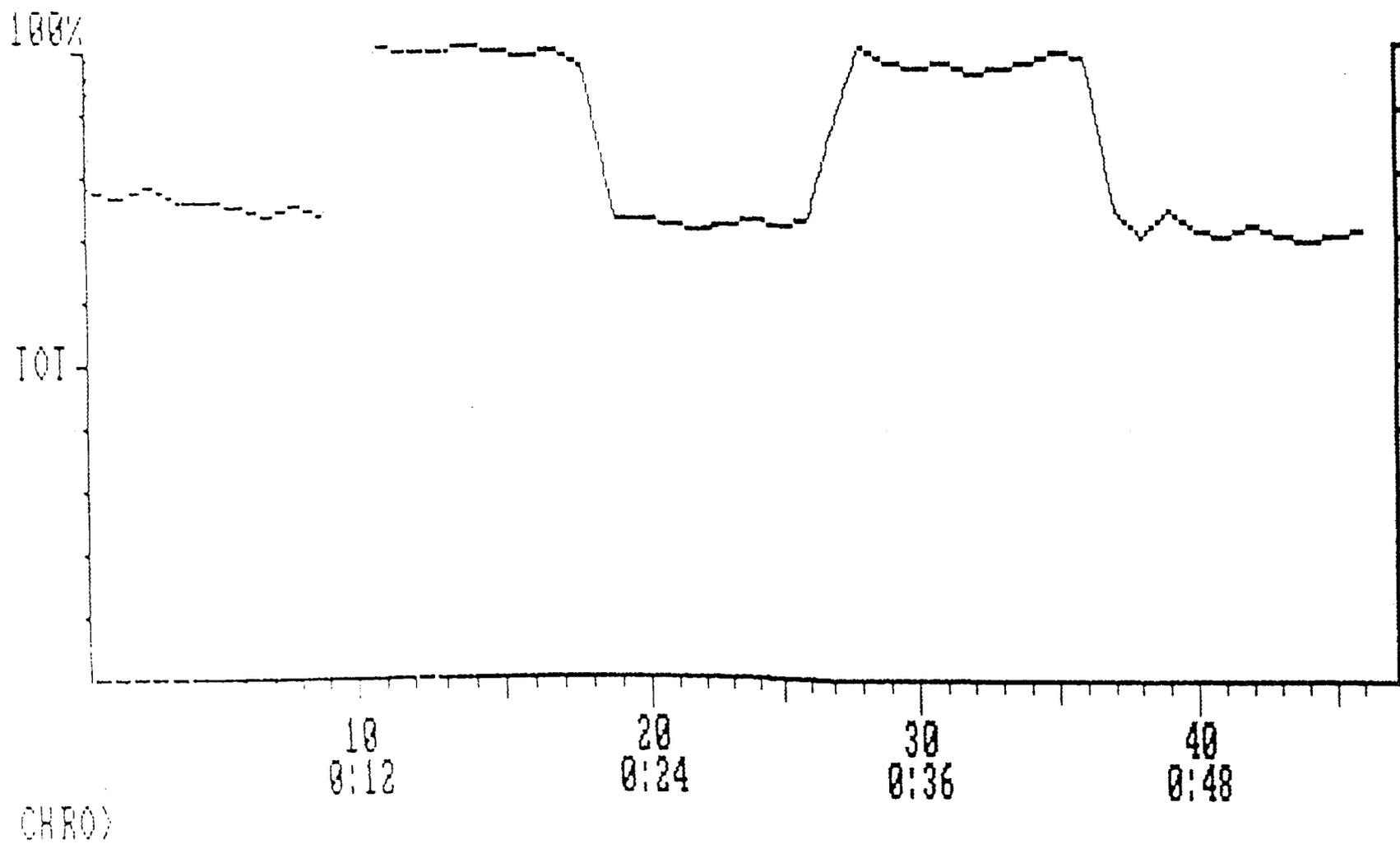


COMPOUND: N-PROPYLBENZENE

CAD EFFICIENCY FOR EI MS/MS OF m/z 120

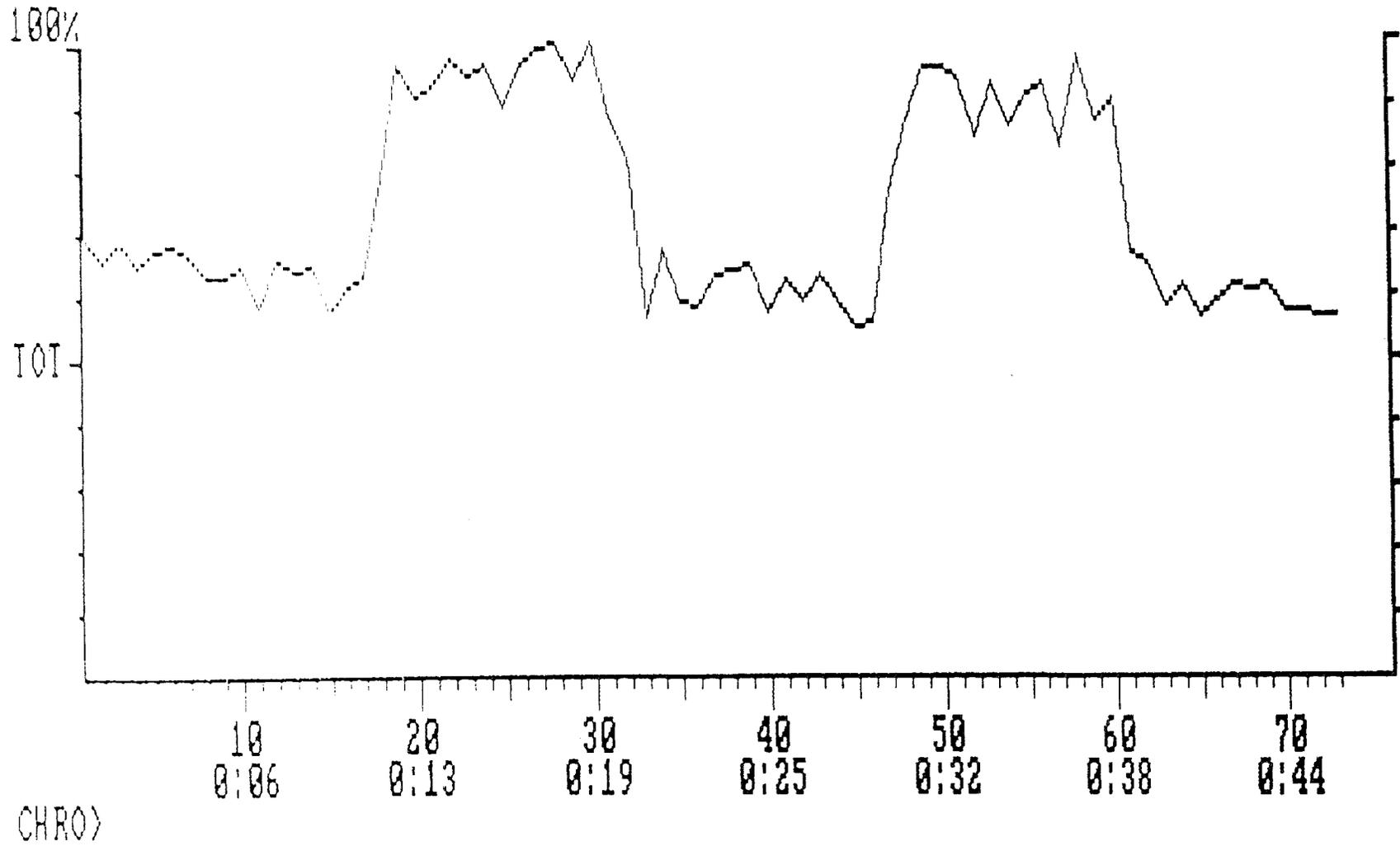


COMPOUND: TRICHLOROETHYLENE
CAD EFFICIENCY FOR EI MS/MS OF m/z 130



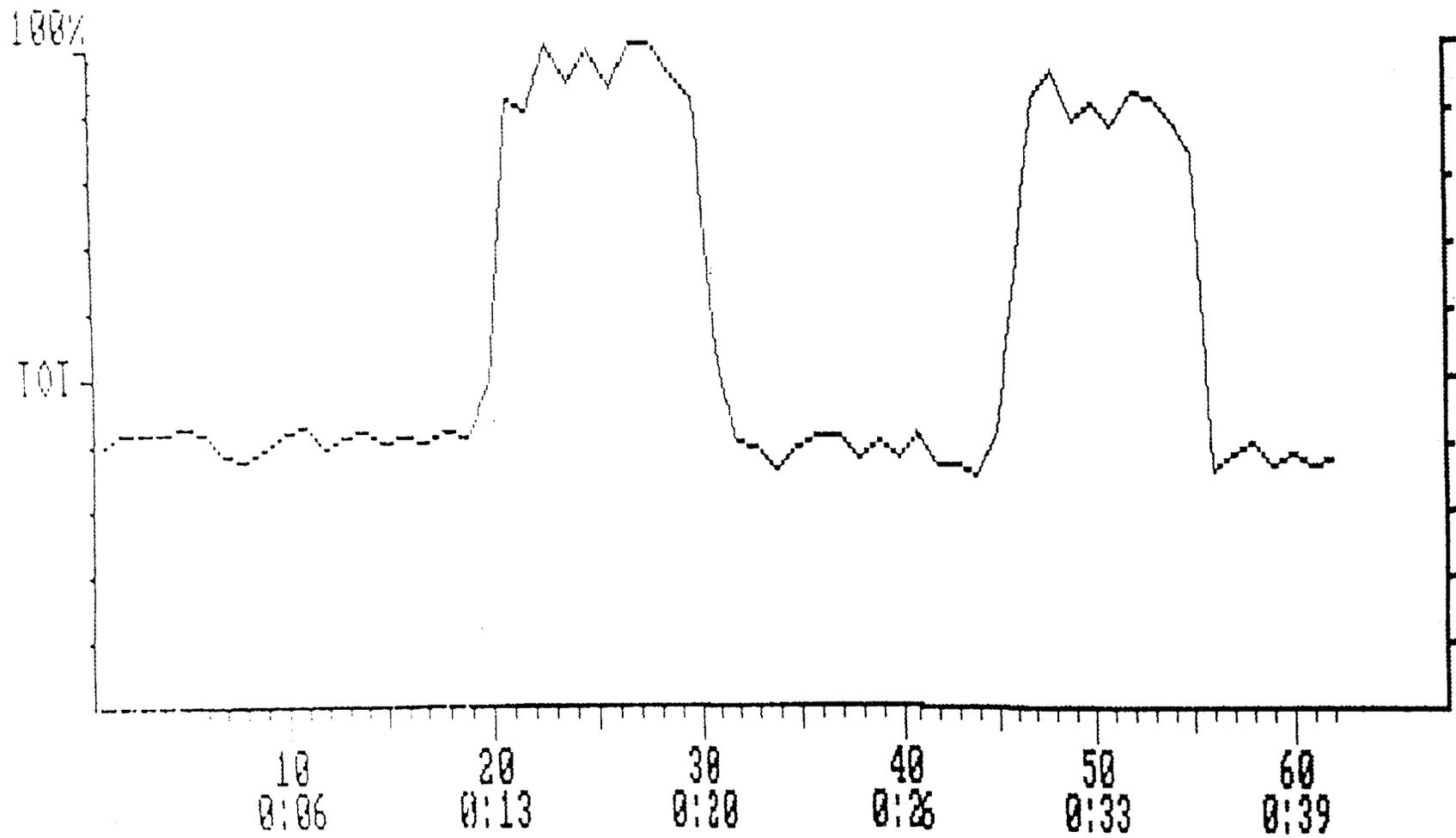
COMPOUND: FREON 113

CAD EFFICIENCY FOR EI MS/MS OF M/Z 151



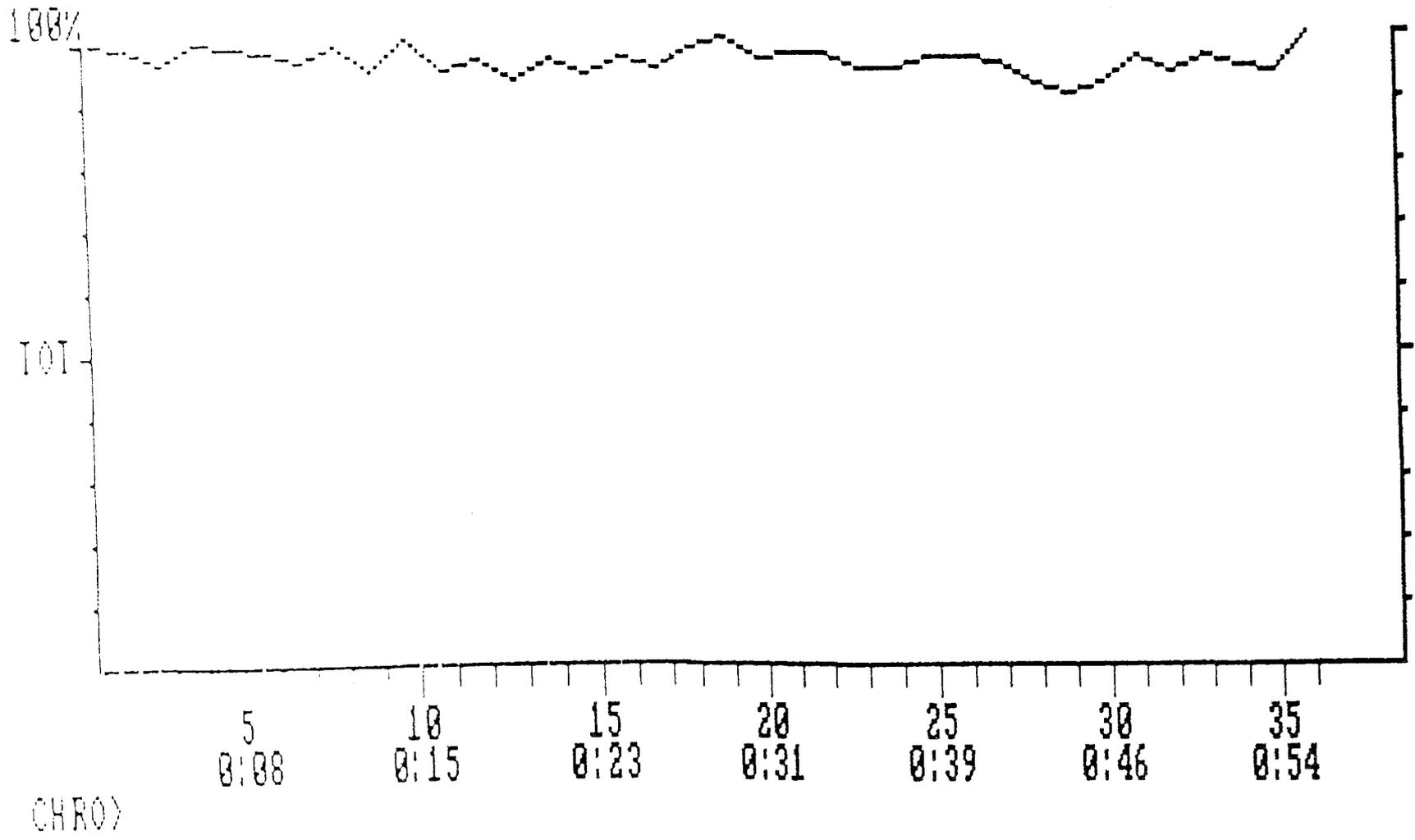
COMPOUND: FREON 113

CAD EFFICIENCY FOR EI MS/MS OF M/Z 153



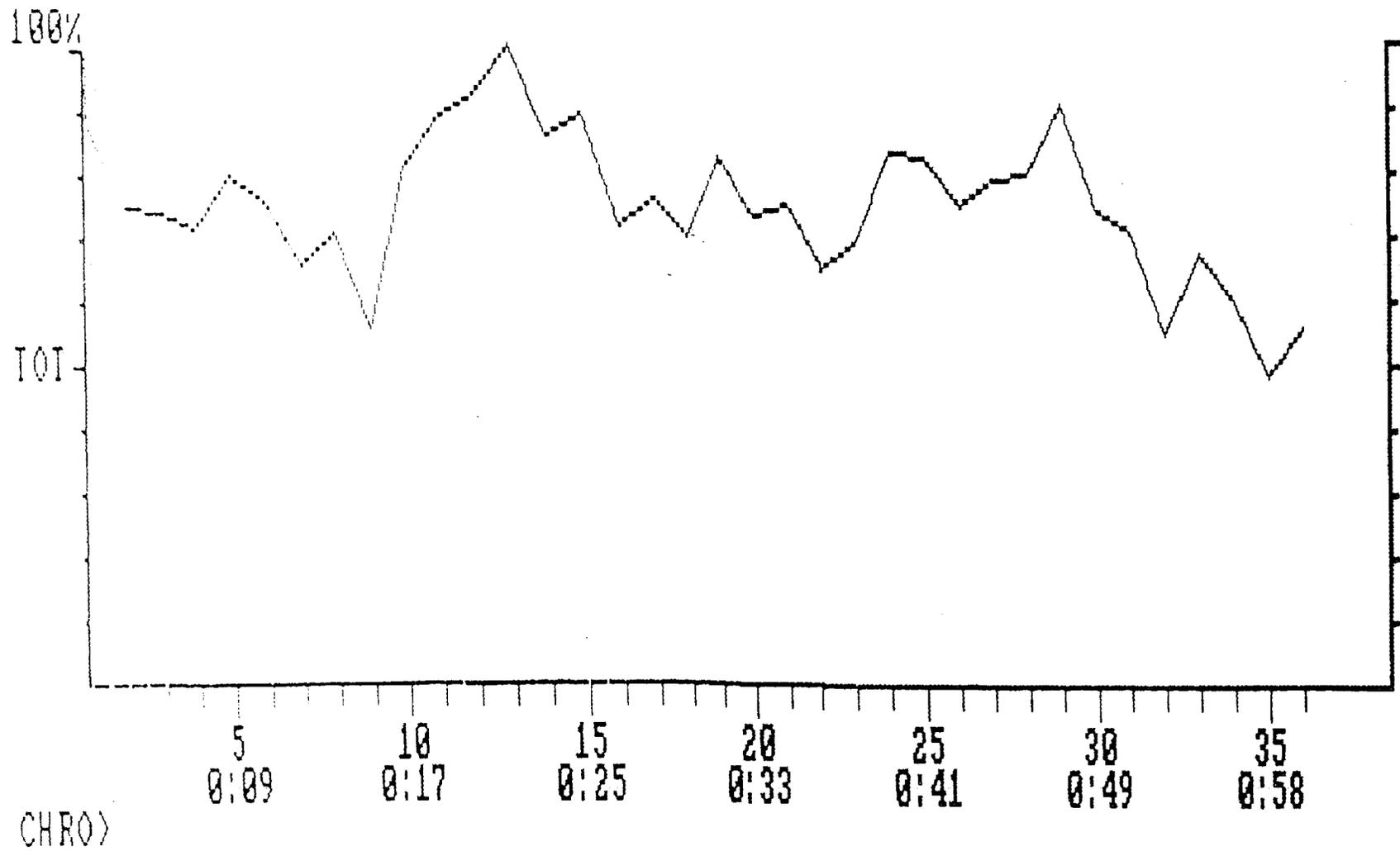
COMPOUND: TETRADECANE

CAD EFFICIENCY FOR EI MS/MS OF M/Z 198

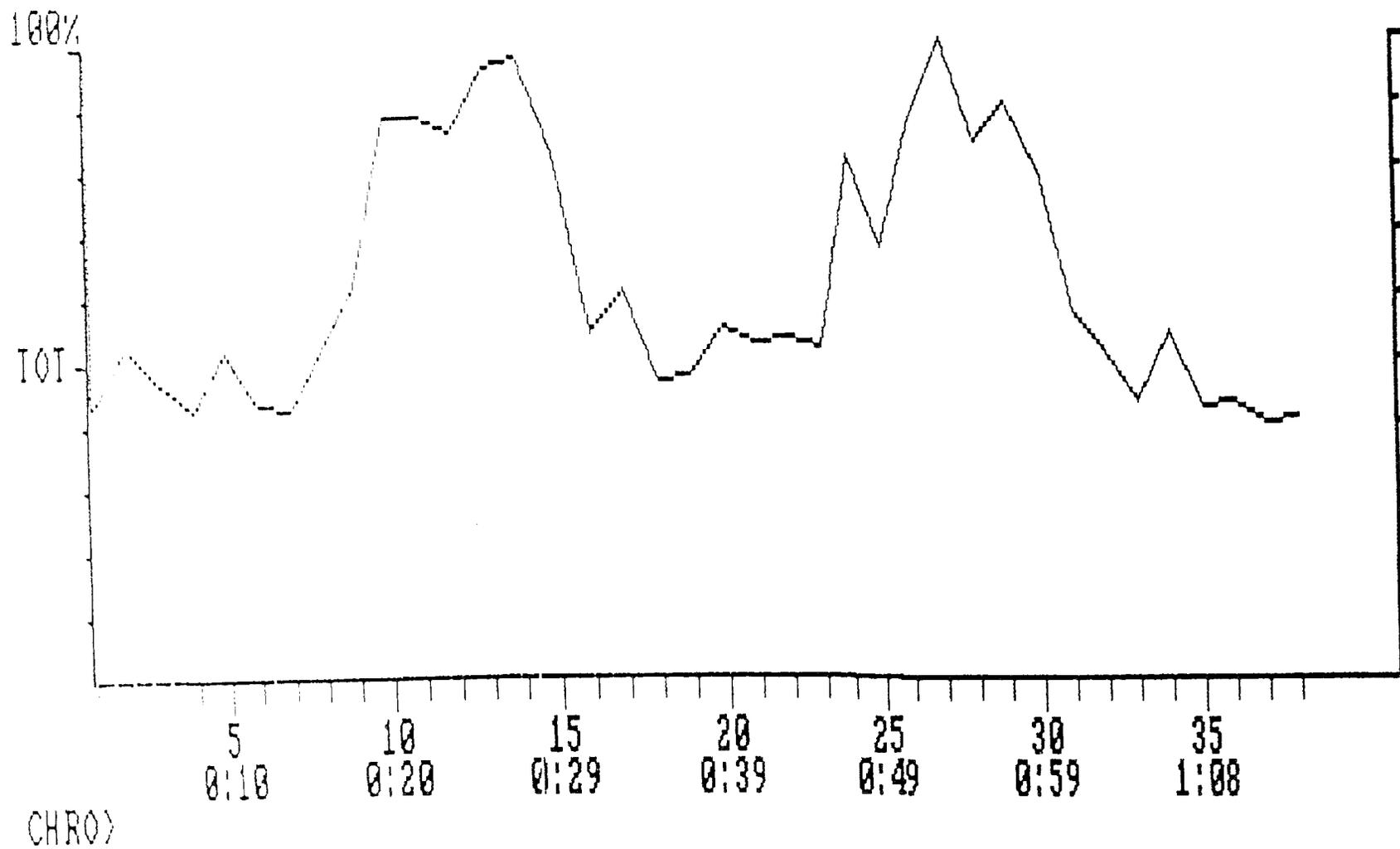


COMPOUND: STEARIC ANHYDRIDE

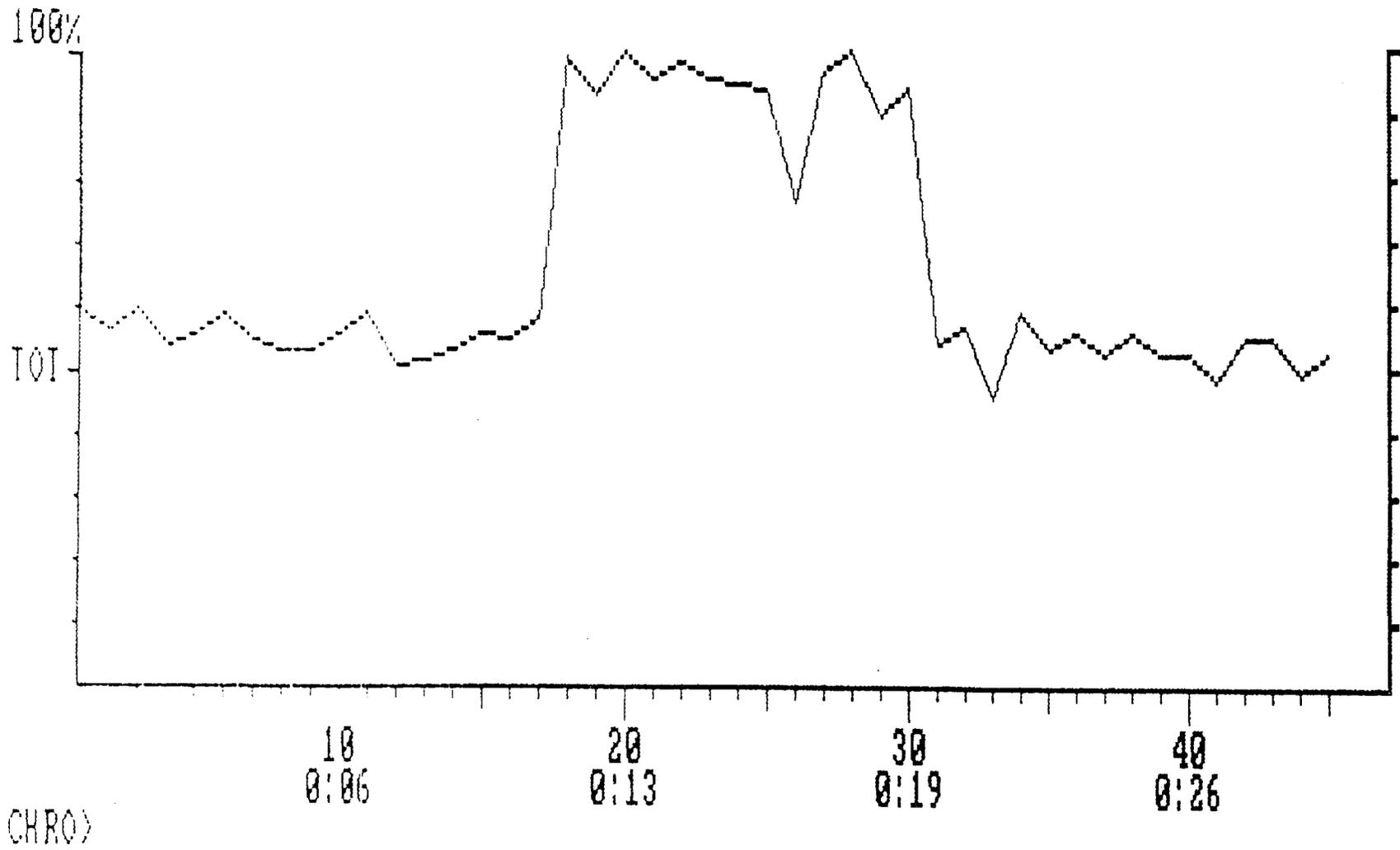
CAD EFFICIENCY FOR EI MS/MS OF M/Z 267



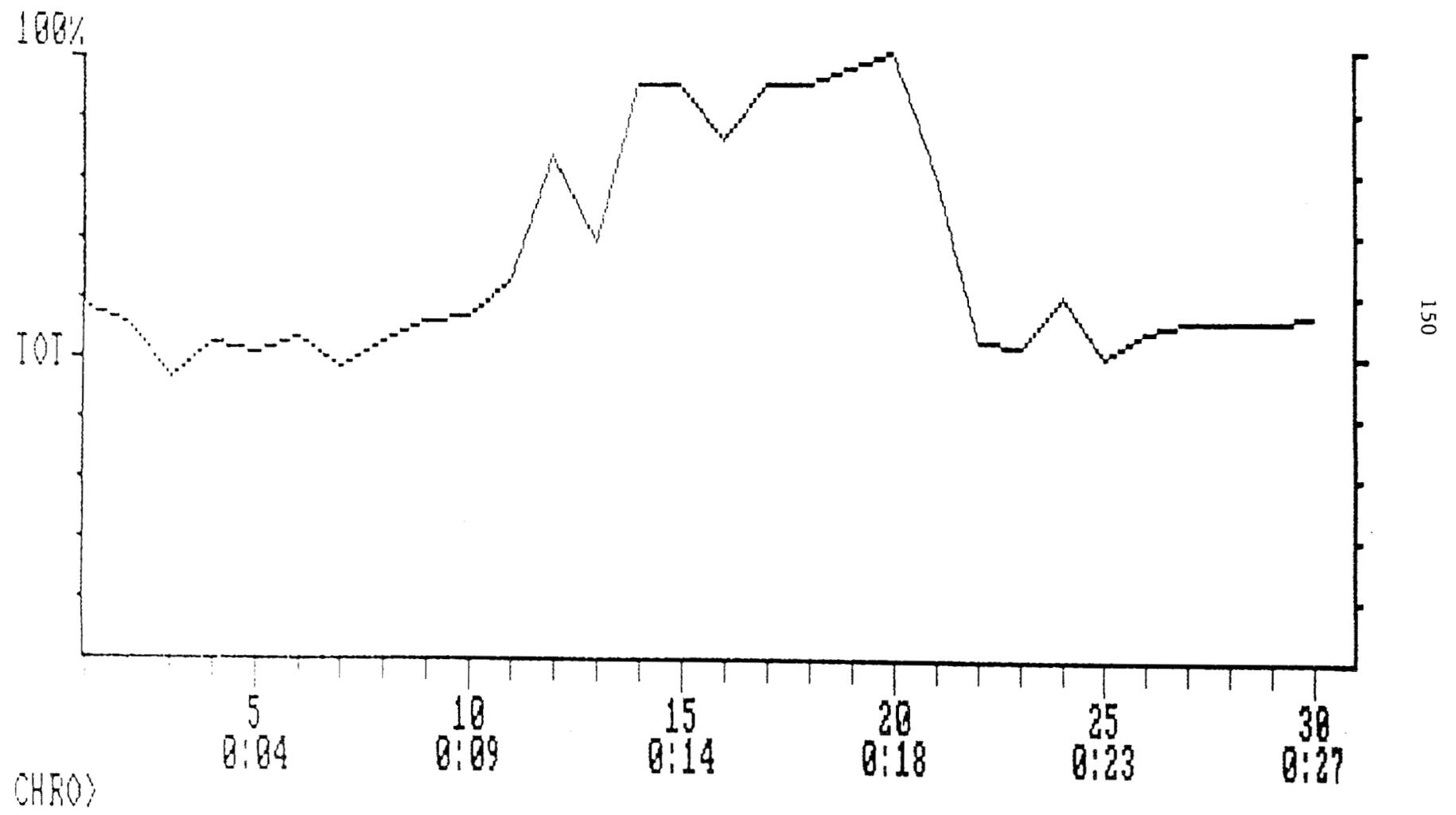
COMPOUND: STEARIC ANHYDRIDE
CAD EFFICIENCY FOR EI MS/MS OF M/Z 284



COMPOUND: PERFLUOROKEROSENE
CAD EFFICIENCY FOR EI MS/MS OF M/Z 264

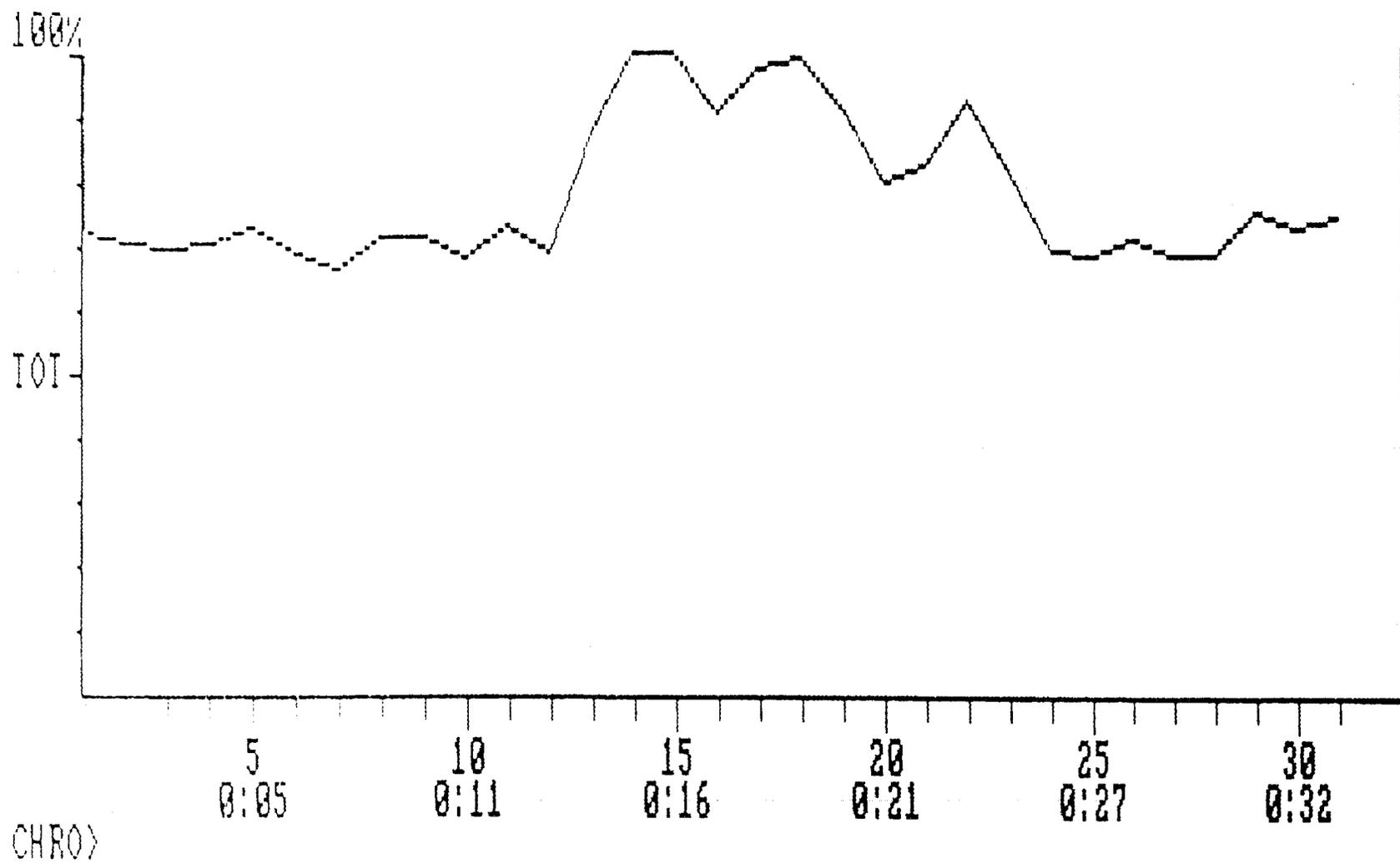


COMPOUND: PERFLUOROKEROSENE
CAD EFFICIENCY FOR EI MS/MS OF M/Z 414



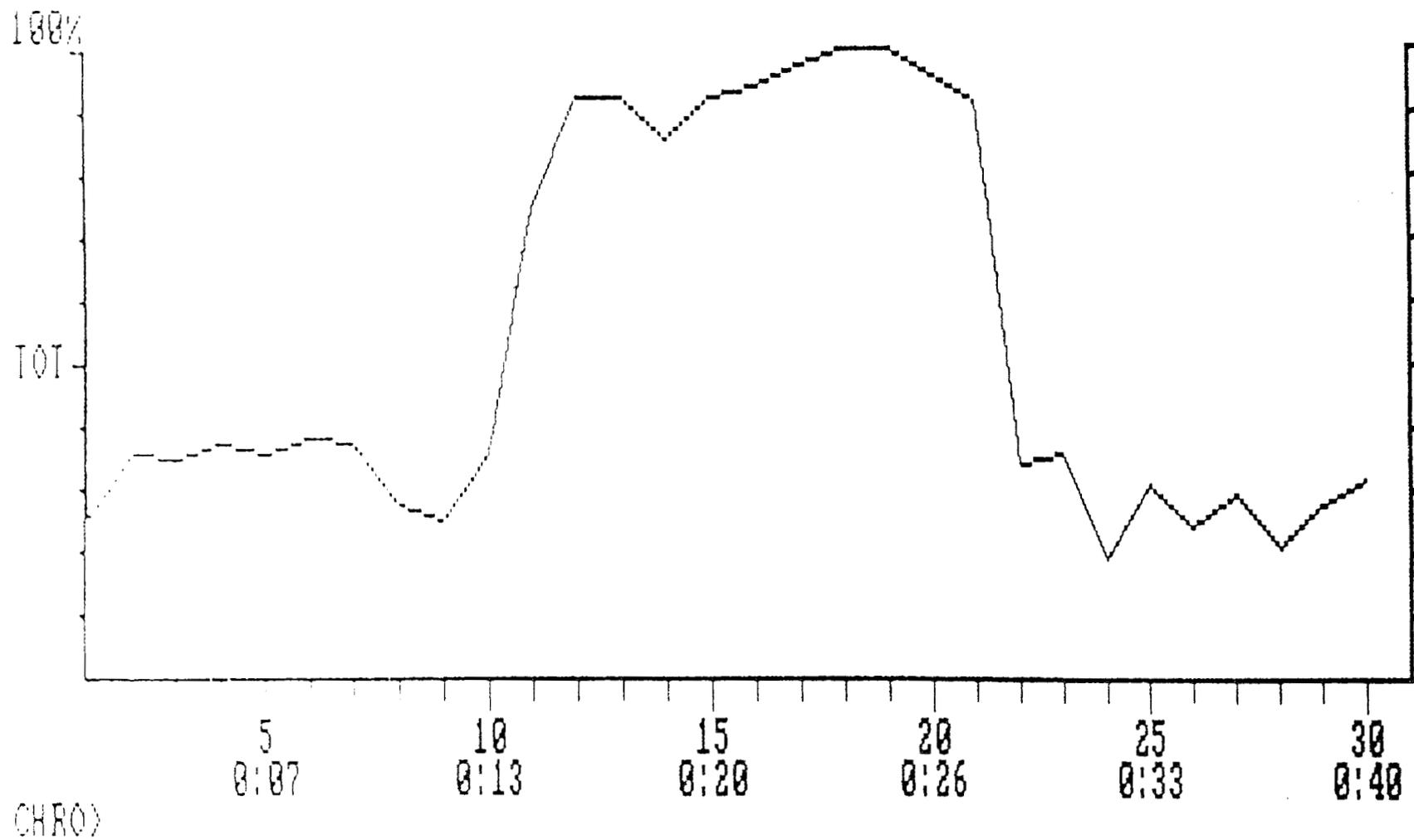
COMPOUND: PERFLUOROKEROSENE

CAD EFFICIENCY FOR EI MS/MS OF M/Z 502



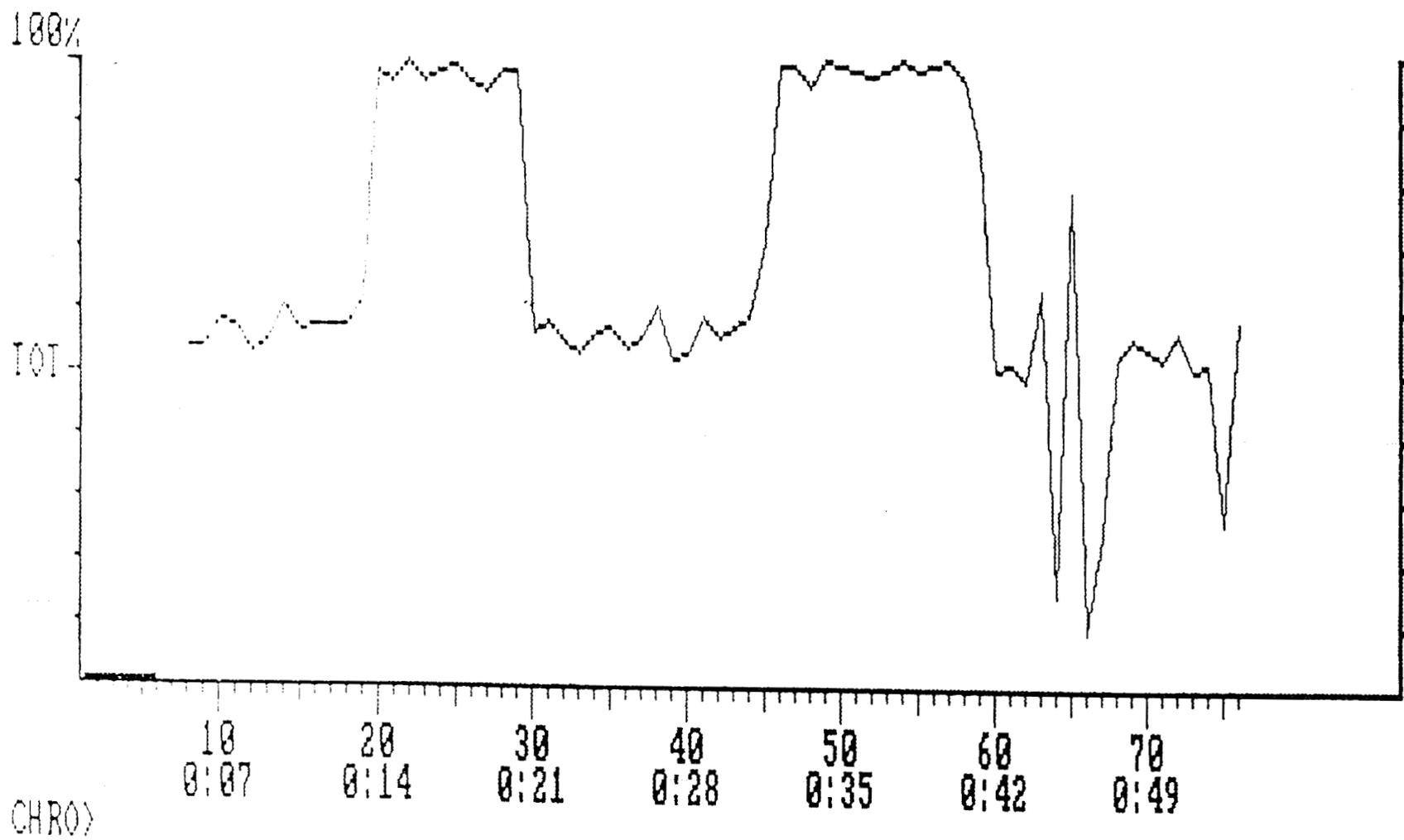
151

COMPOUND: PERFLUOROKEROSENE
CAD EFFICIENCY FOR EI MS/MS OF M/Z 614

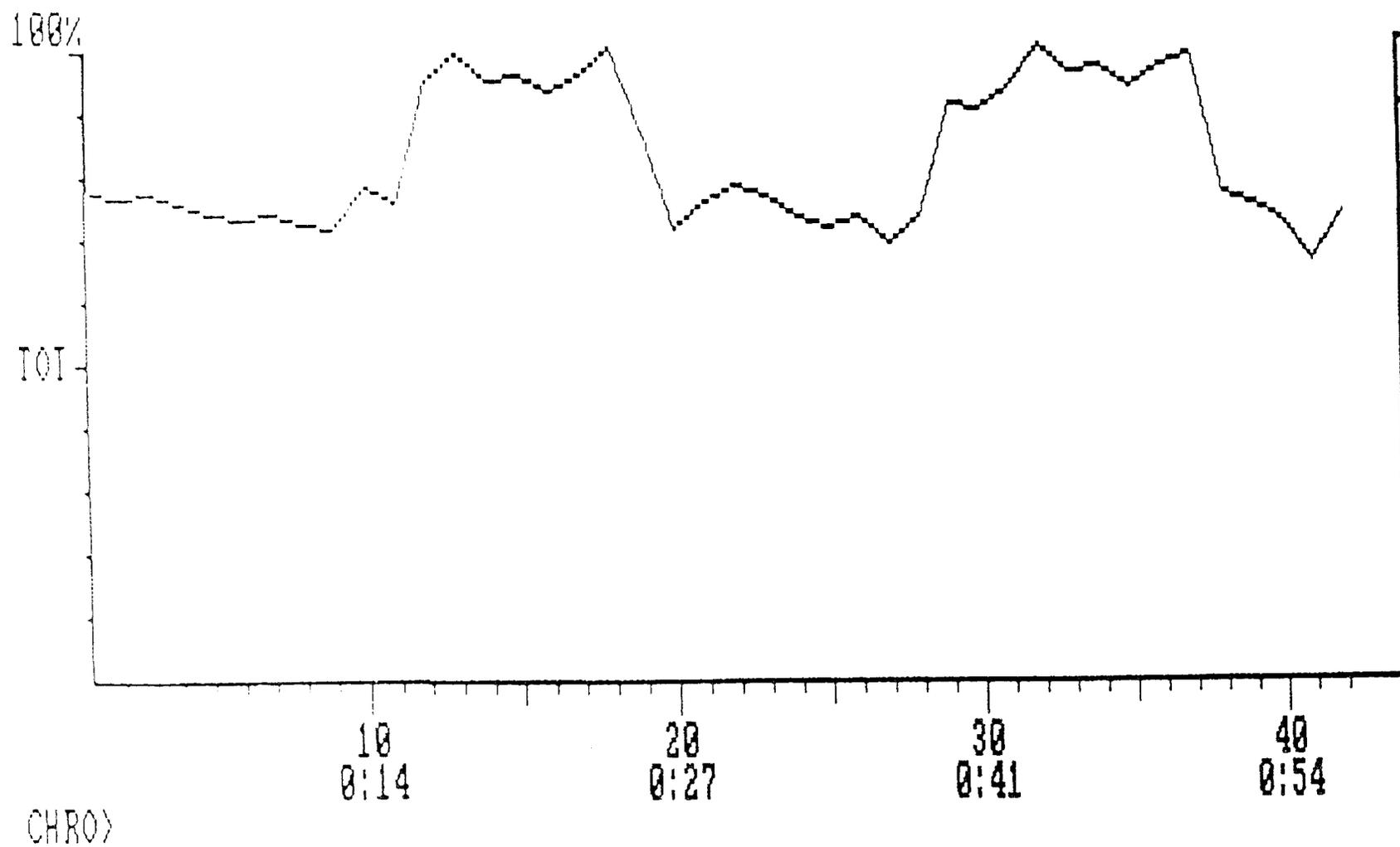


COMPOUND: ETHANOL

CAD EFFICIENCY FOR CI MS/MS OF M/Z 47

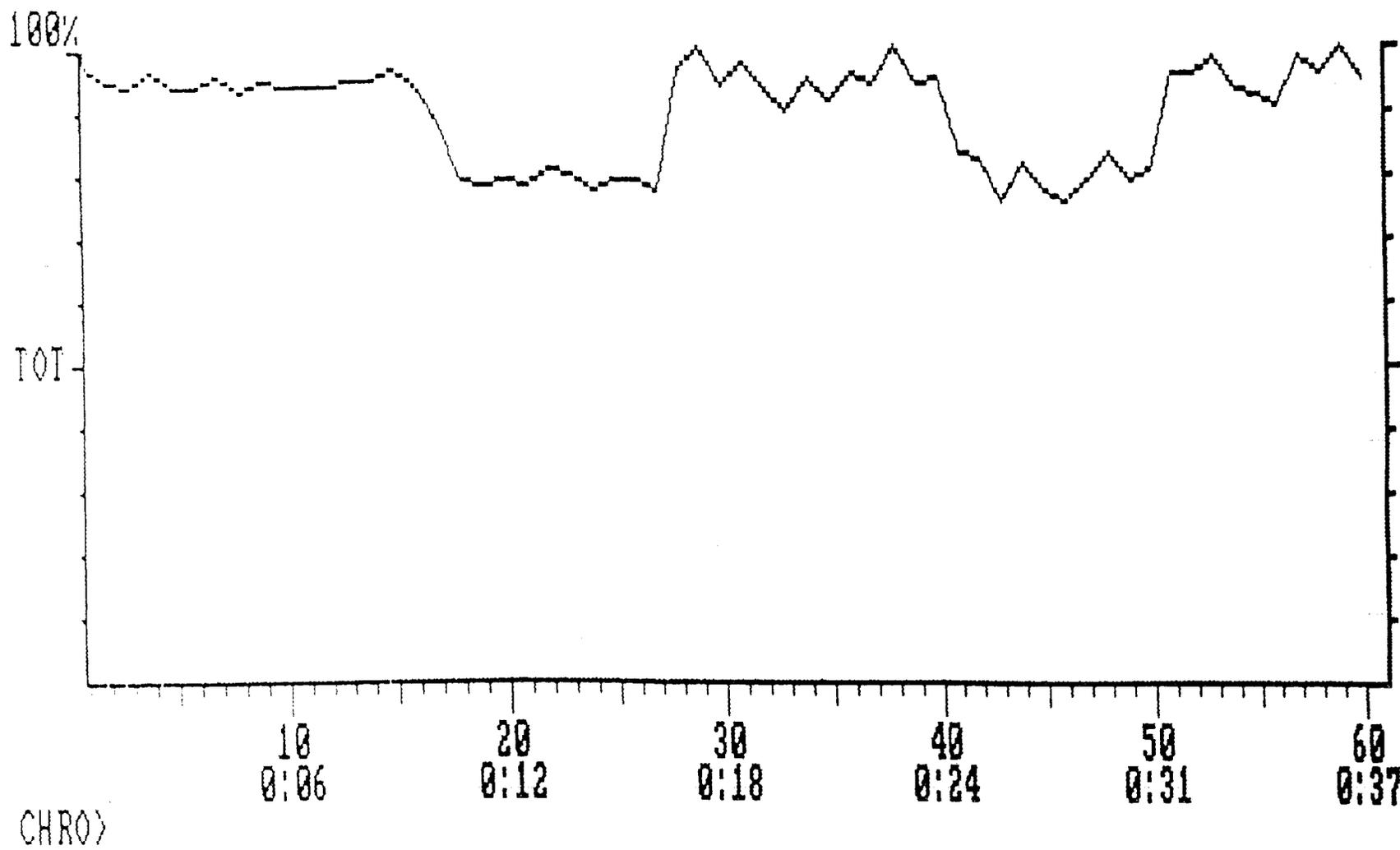


COMPOUND: METHYLETHYLKETONE
CAD EFFICIENCY FOR CI MS/MS OF M/Z 73



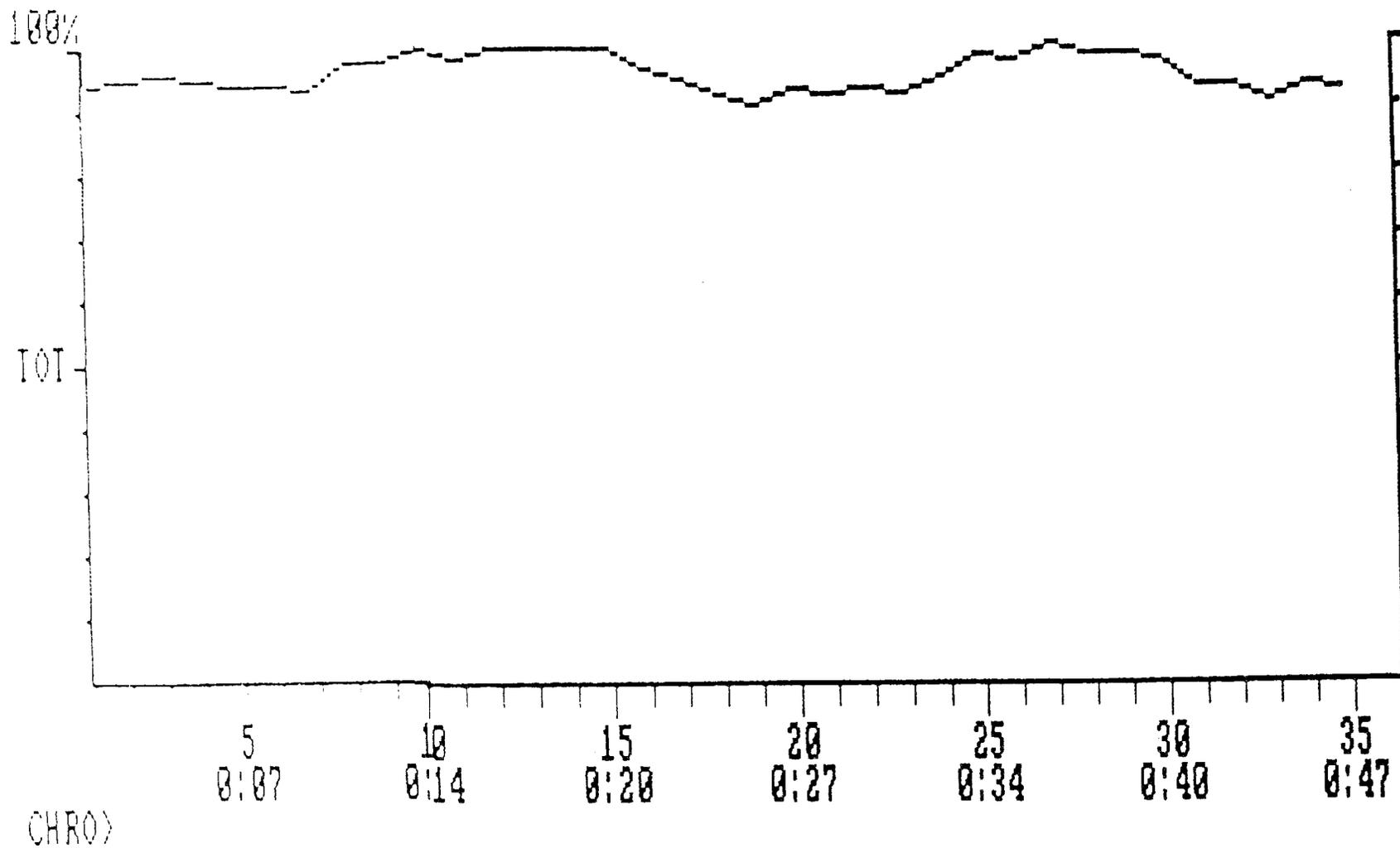
COMPOUND: BUTANOL

CAD EFFICIENCY FOR CI MS/MS OF M/Z 75



COMPOUND: DIETHYLETHER

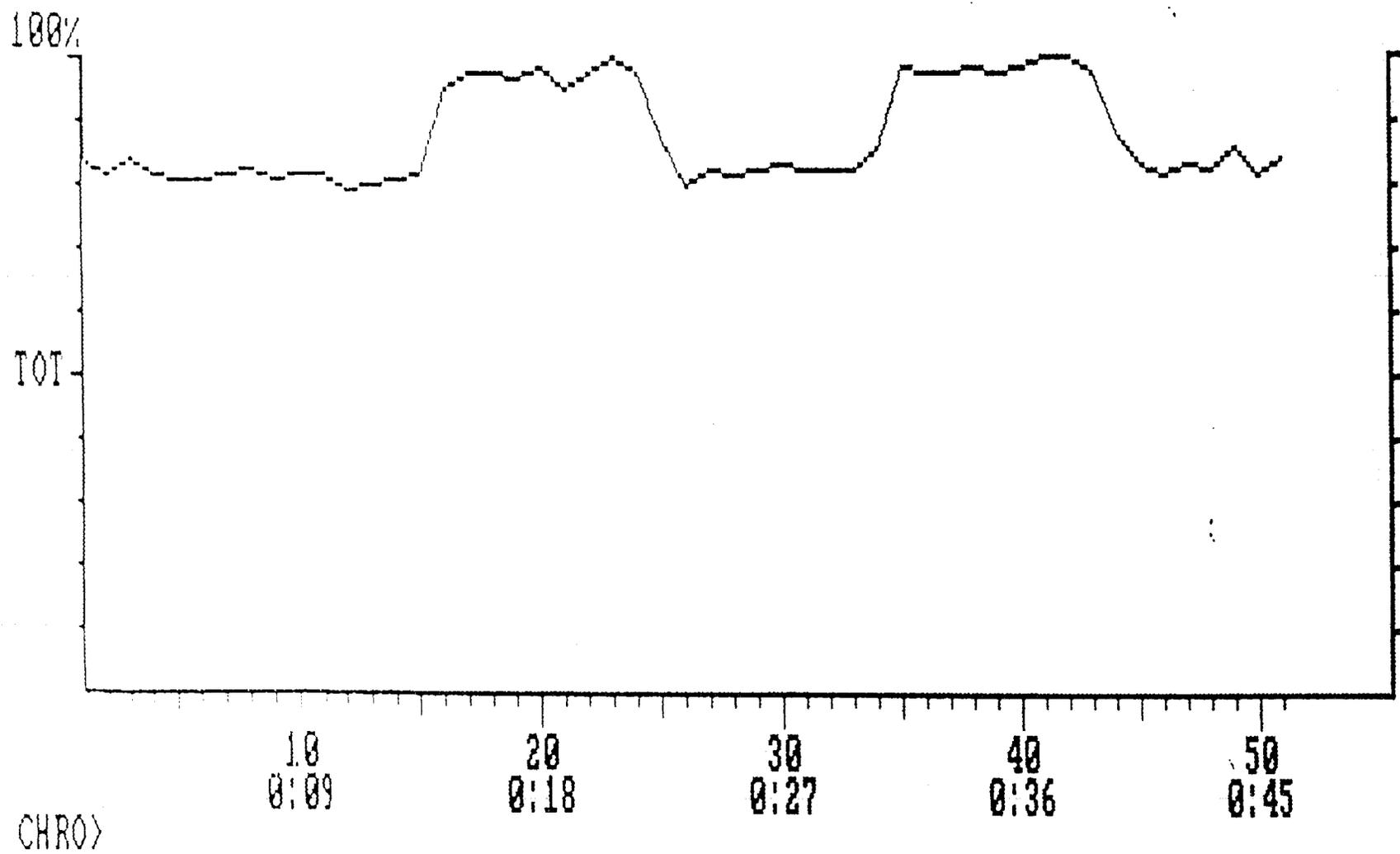
CAD EFFICIENCY FOR CI MS/MS OF M/Z 75



COMPOUND: ETHYLFORMATE

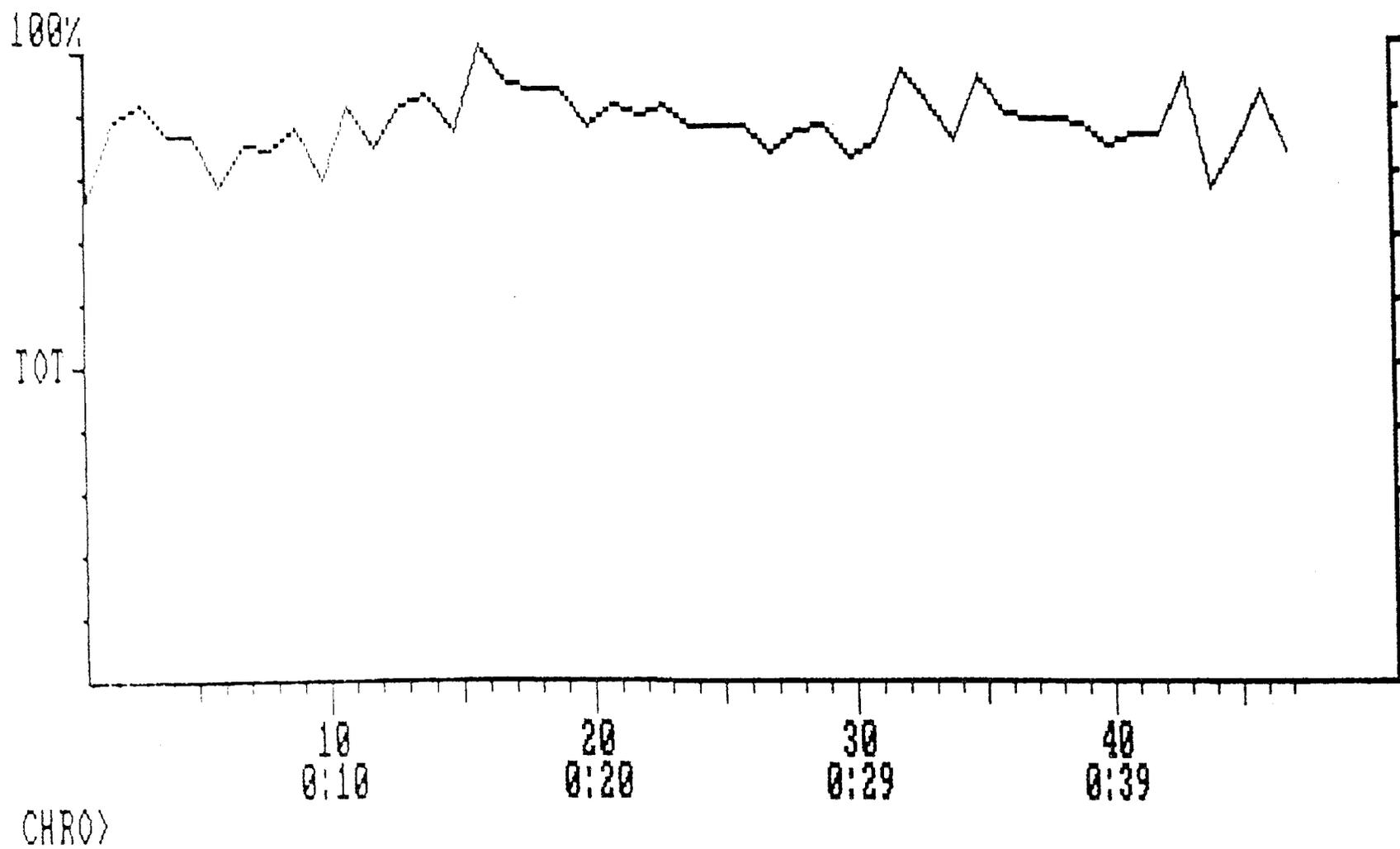
CAD EFFICIENCY FOR CI MS/MS OF M/Z 75

(50 MSEC REACTION TIME)



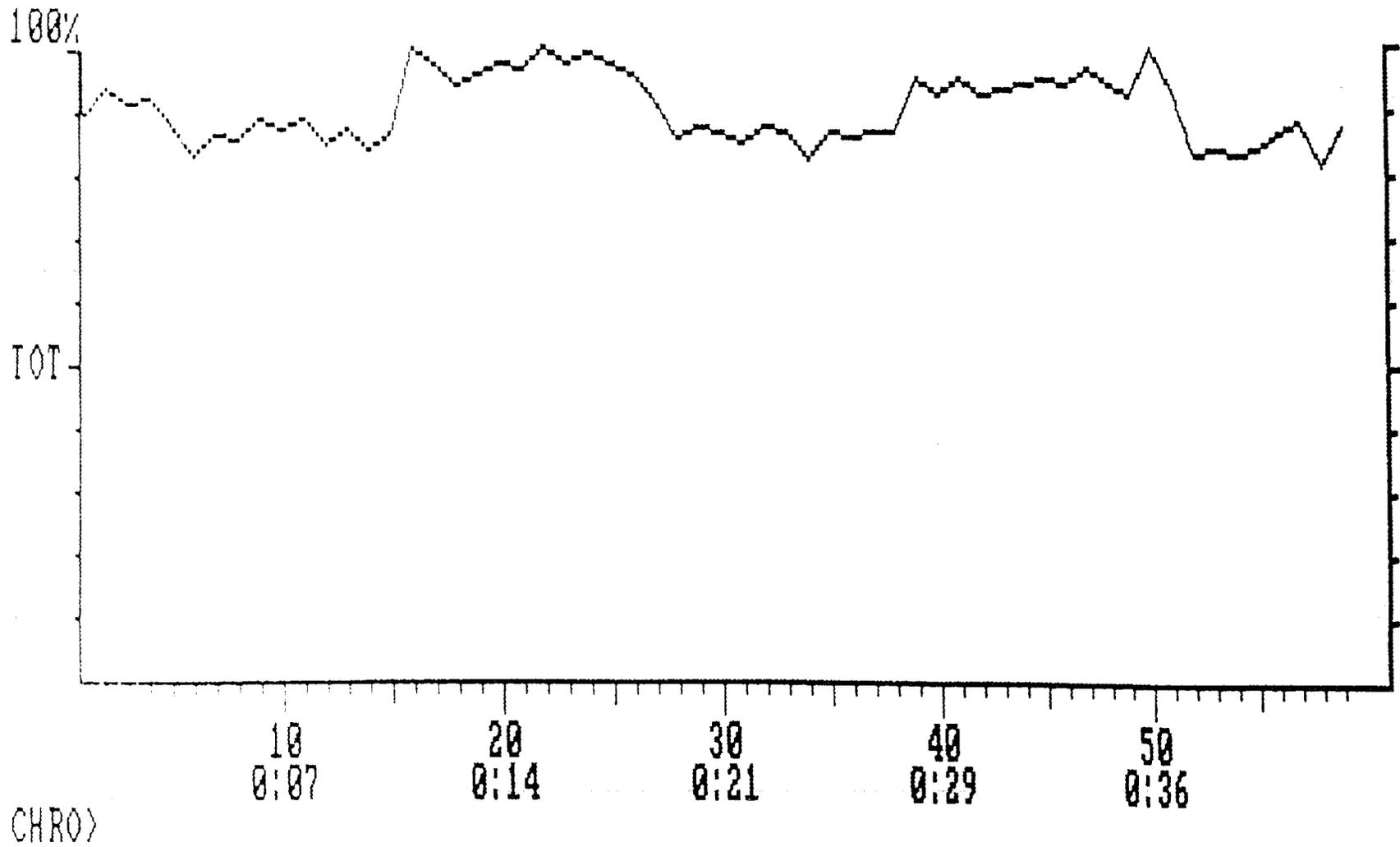
COMPOUND: ETHYLFORMATE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 149

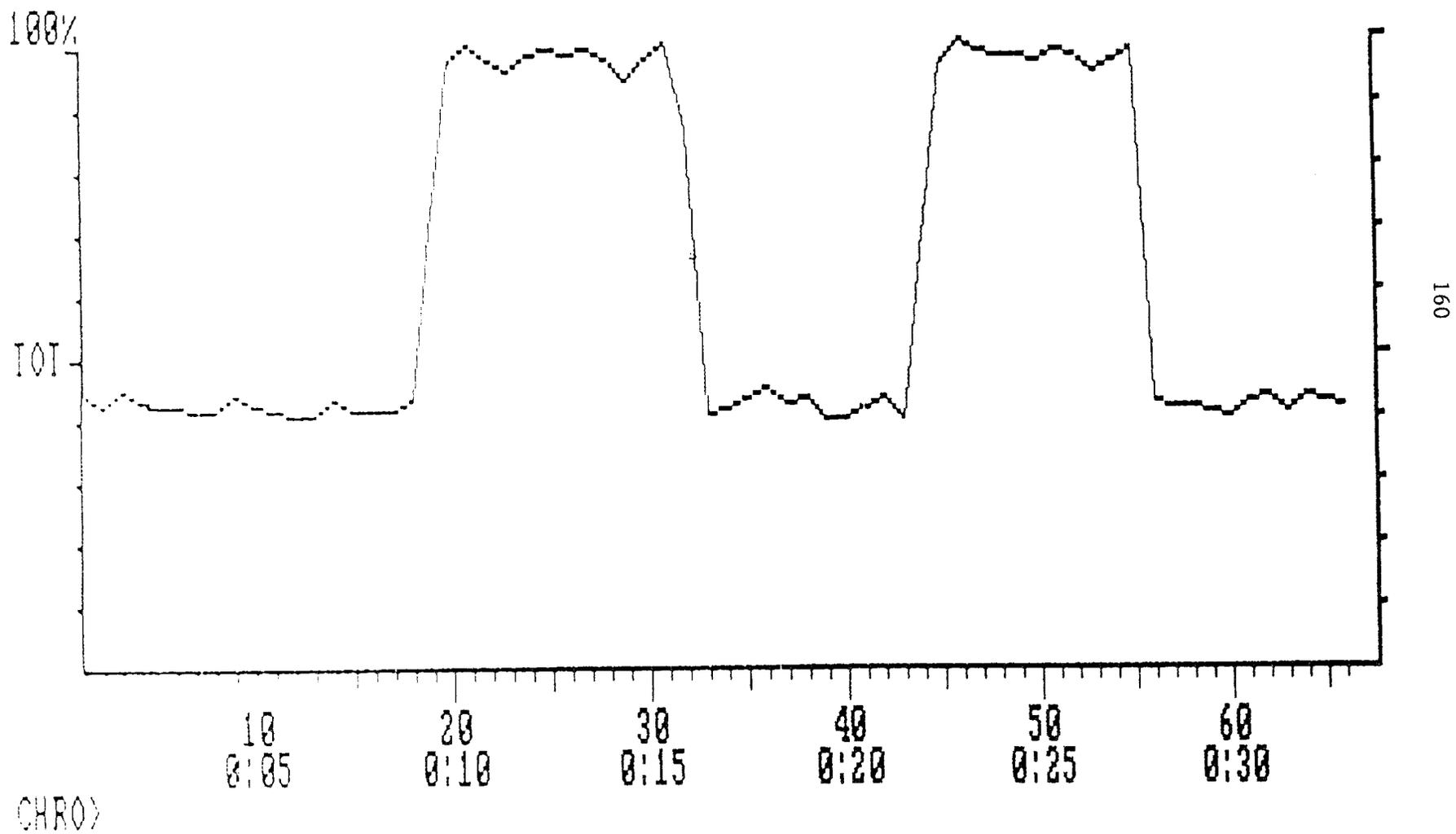


COMPOUND: PROPIONIC ACID

CAD EFFICIENCY FOR CI MS/MS OF M/Z 75

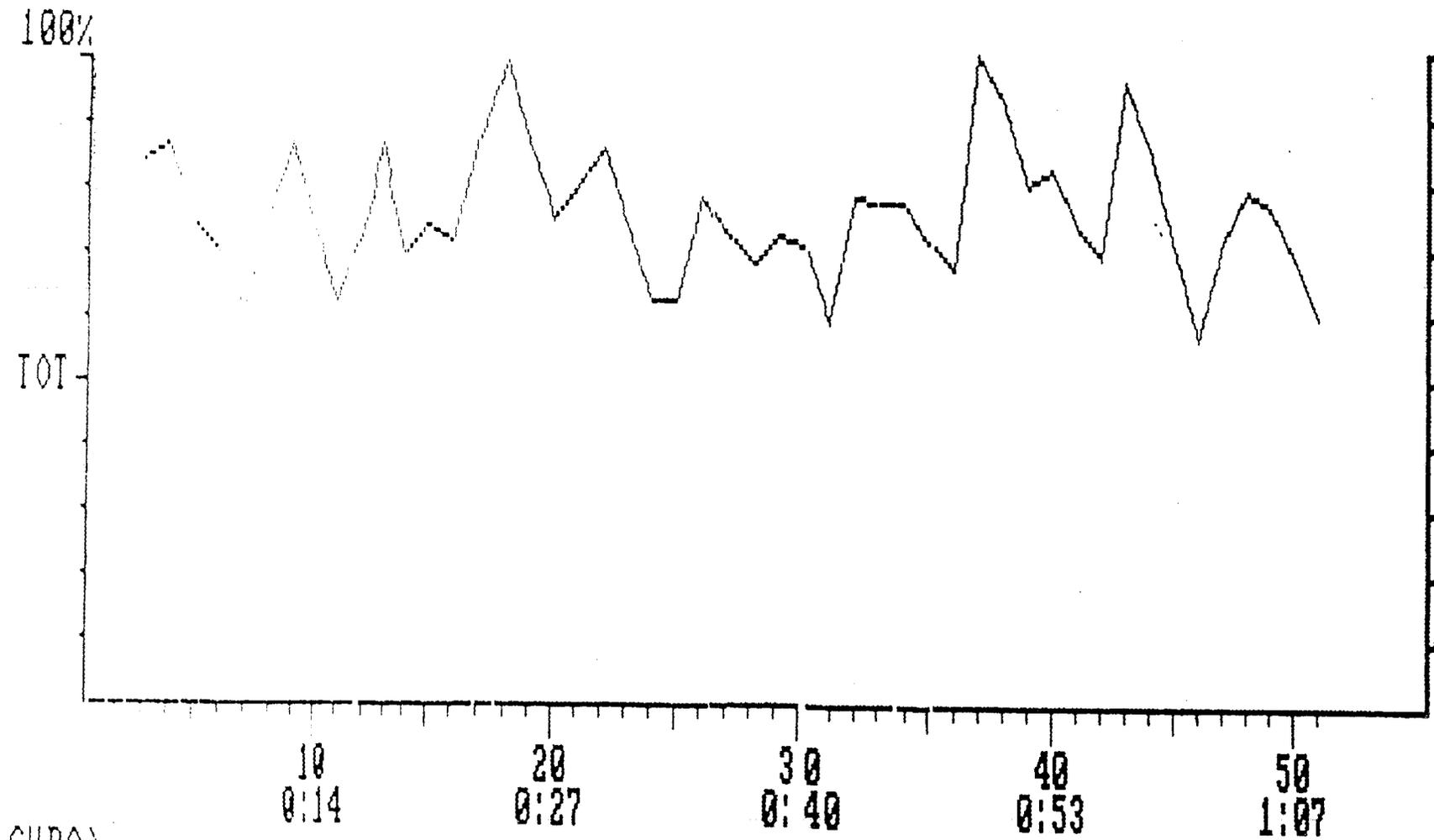


COMPOUND: CARBON DISULFIDE
CAD EFFICIENCY FOR CI MS/MS OF M/Z 77



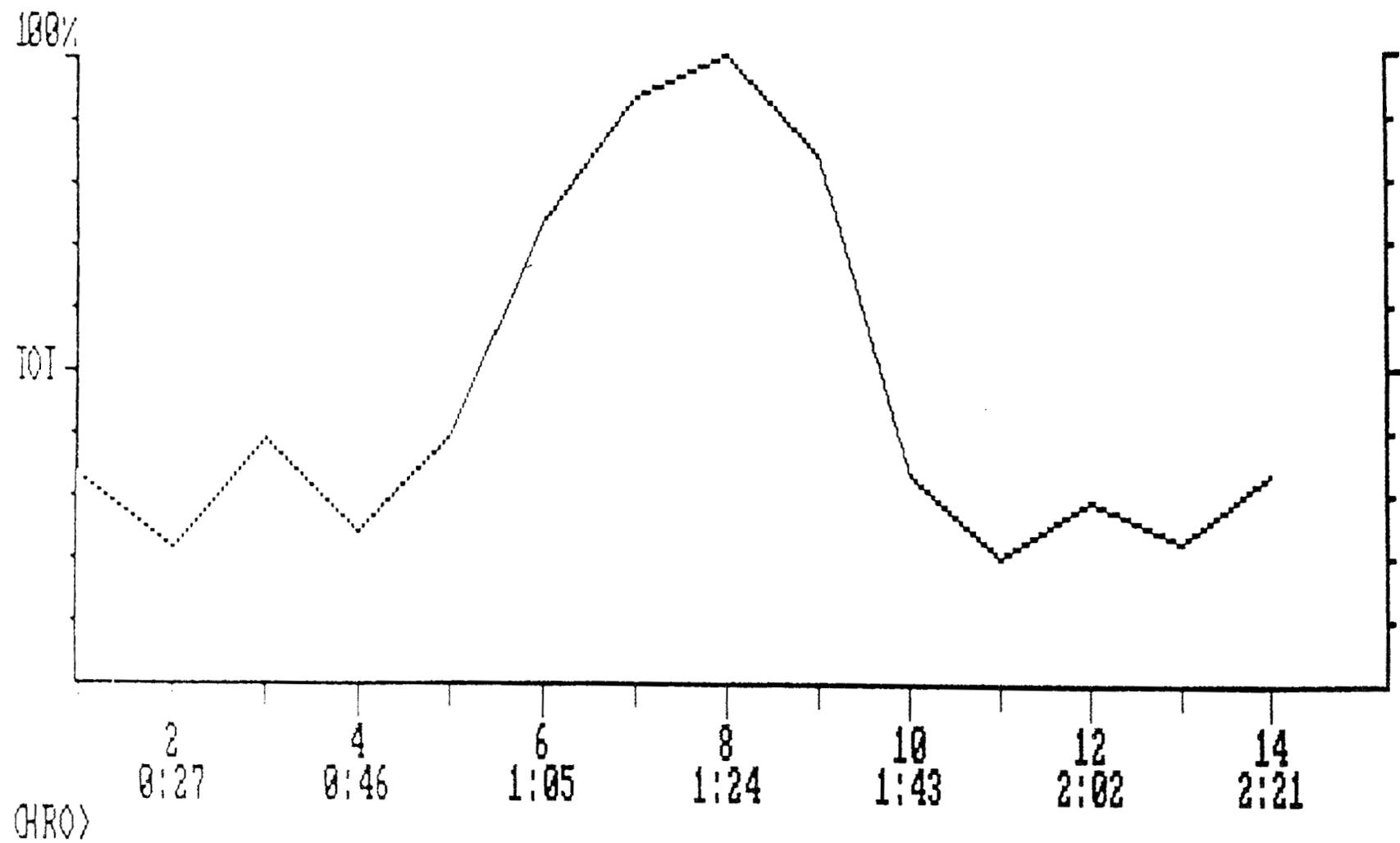
COMPOUND: NITROGEN TETRAOXIDE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 48



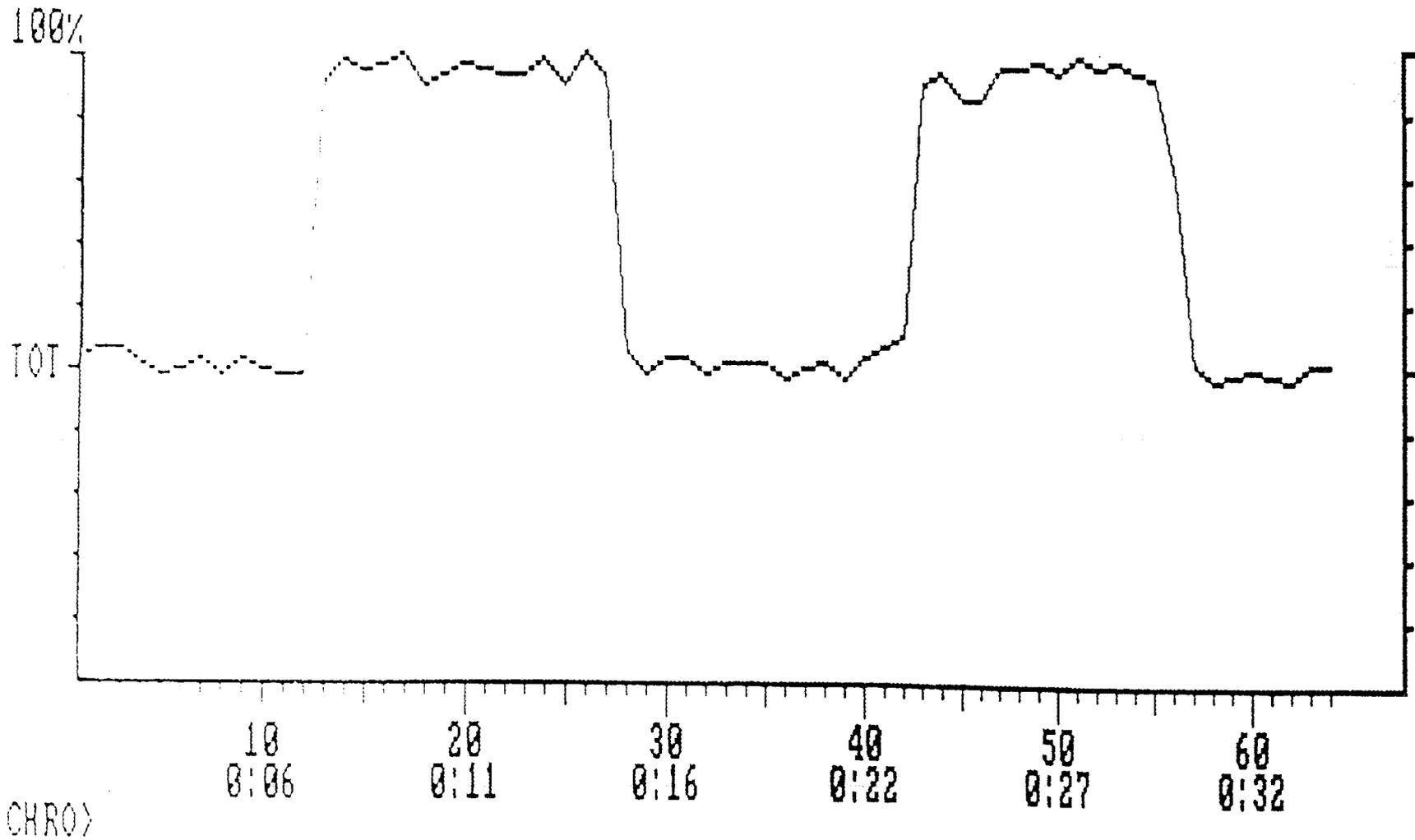
COMPOUND: NITROGEN TETRAOXIDE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 95



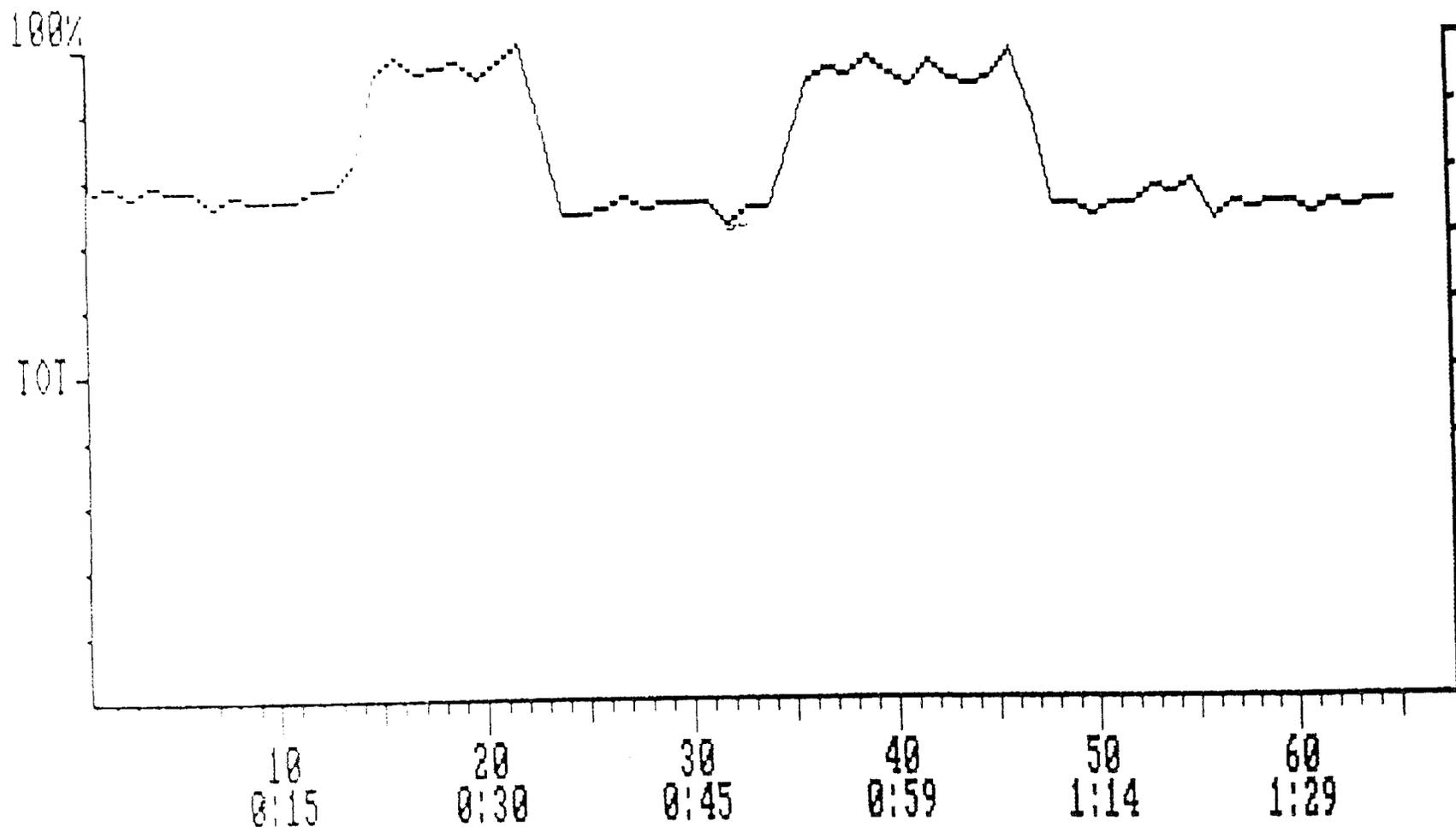
COMPOUND: INDOLE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 118

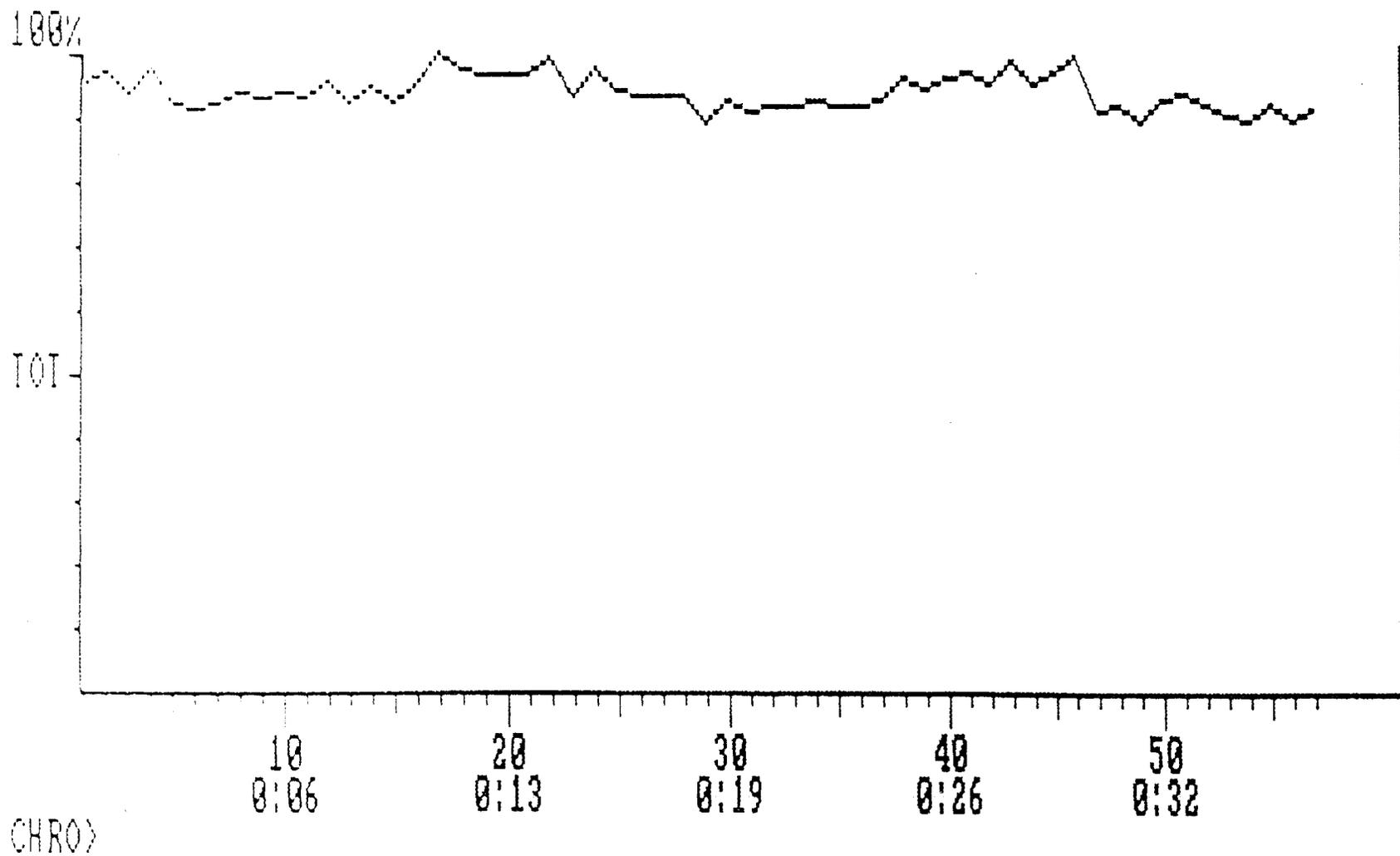


COMPOUND: CUMENE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 121

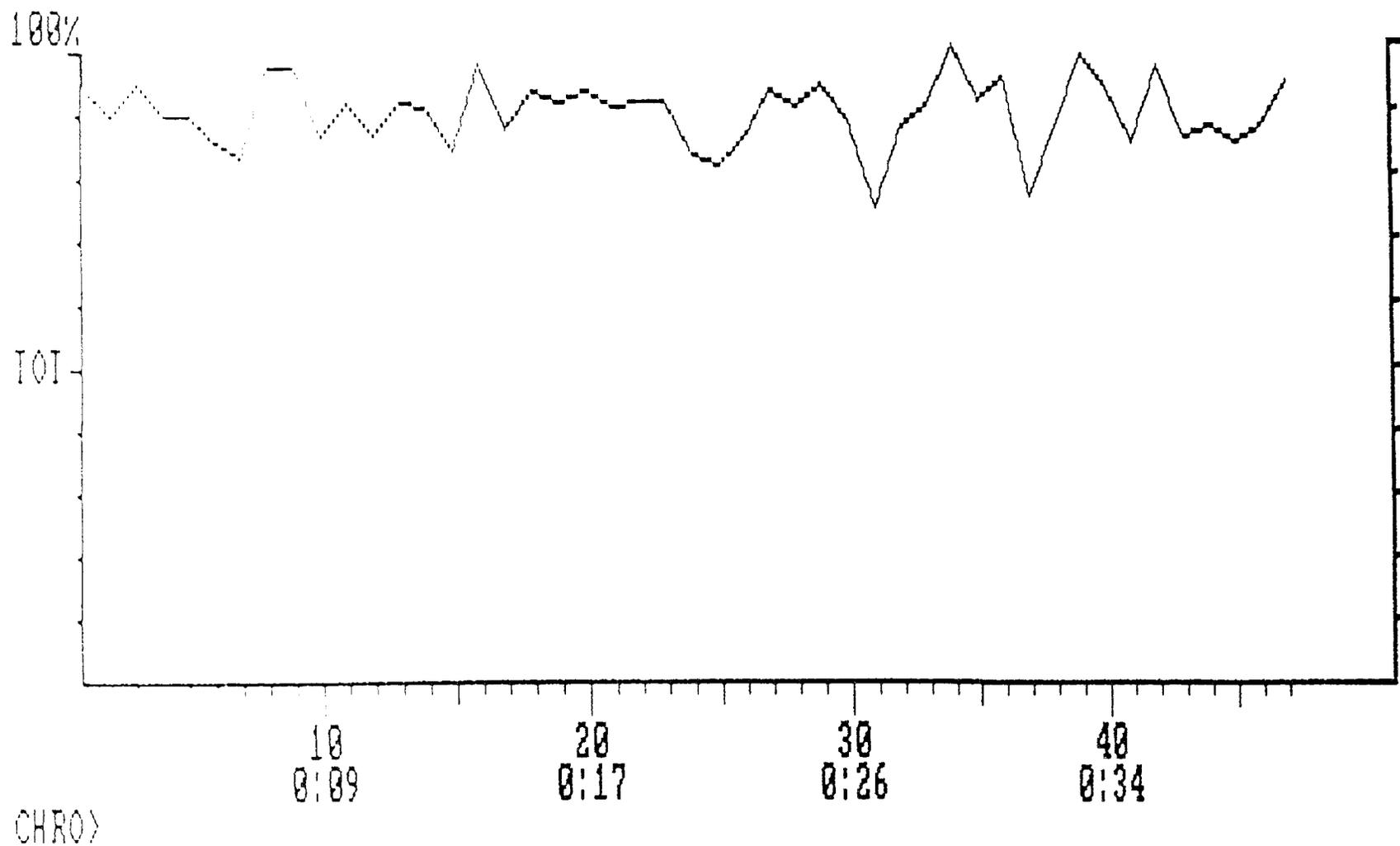


COMPOUND: N-PROPYLBENZENE
CAD EFFICIENCY FOR CI MS/MS OF M/Z 121



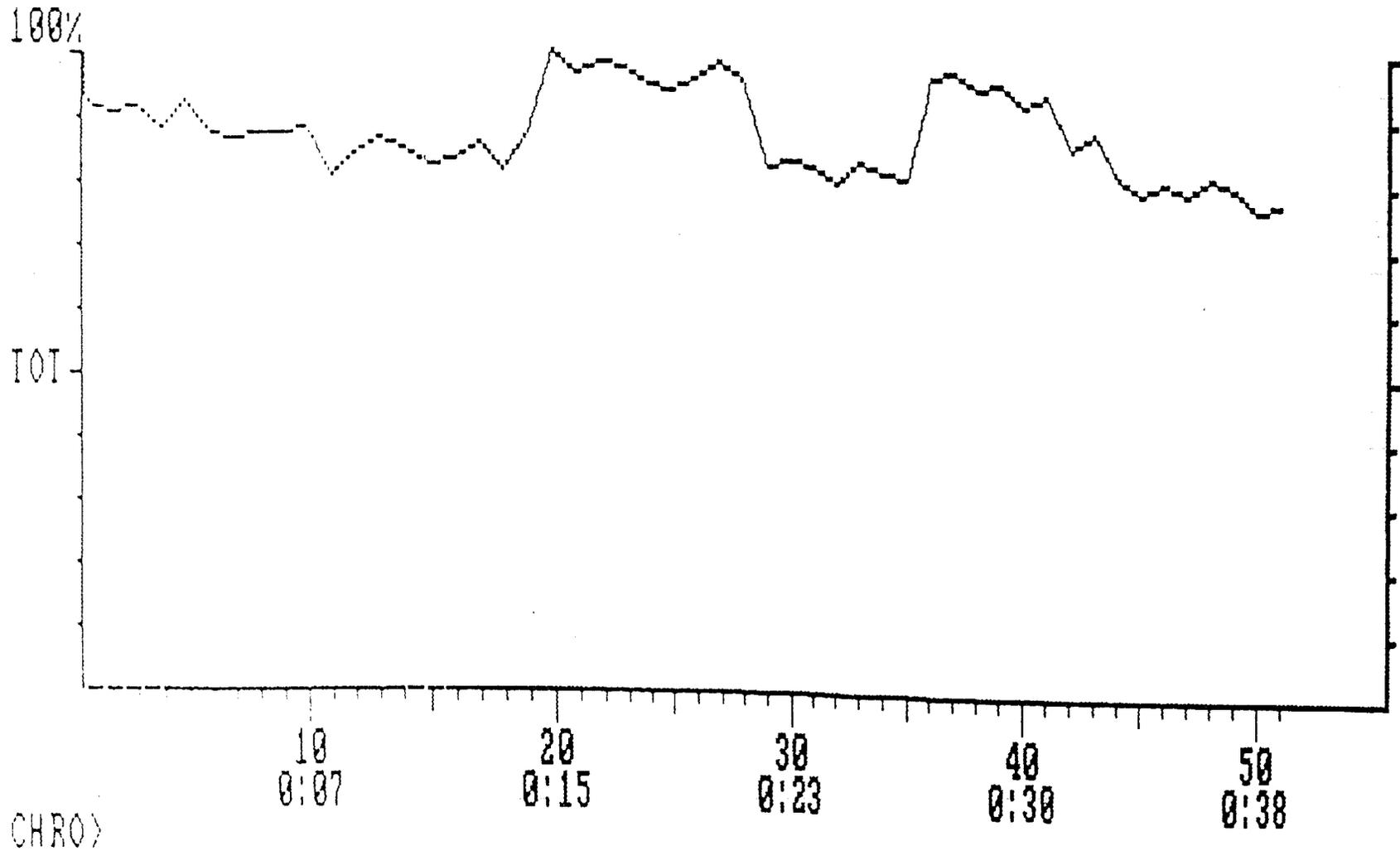
COMPOUND: N-PROPYLBENZENE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 133



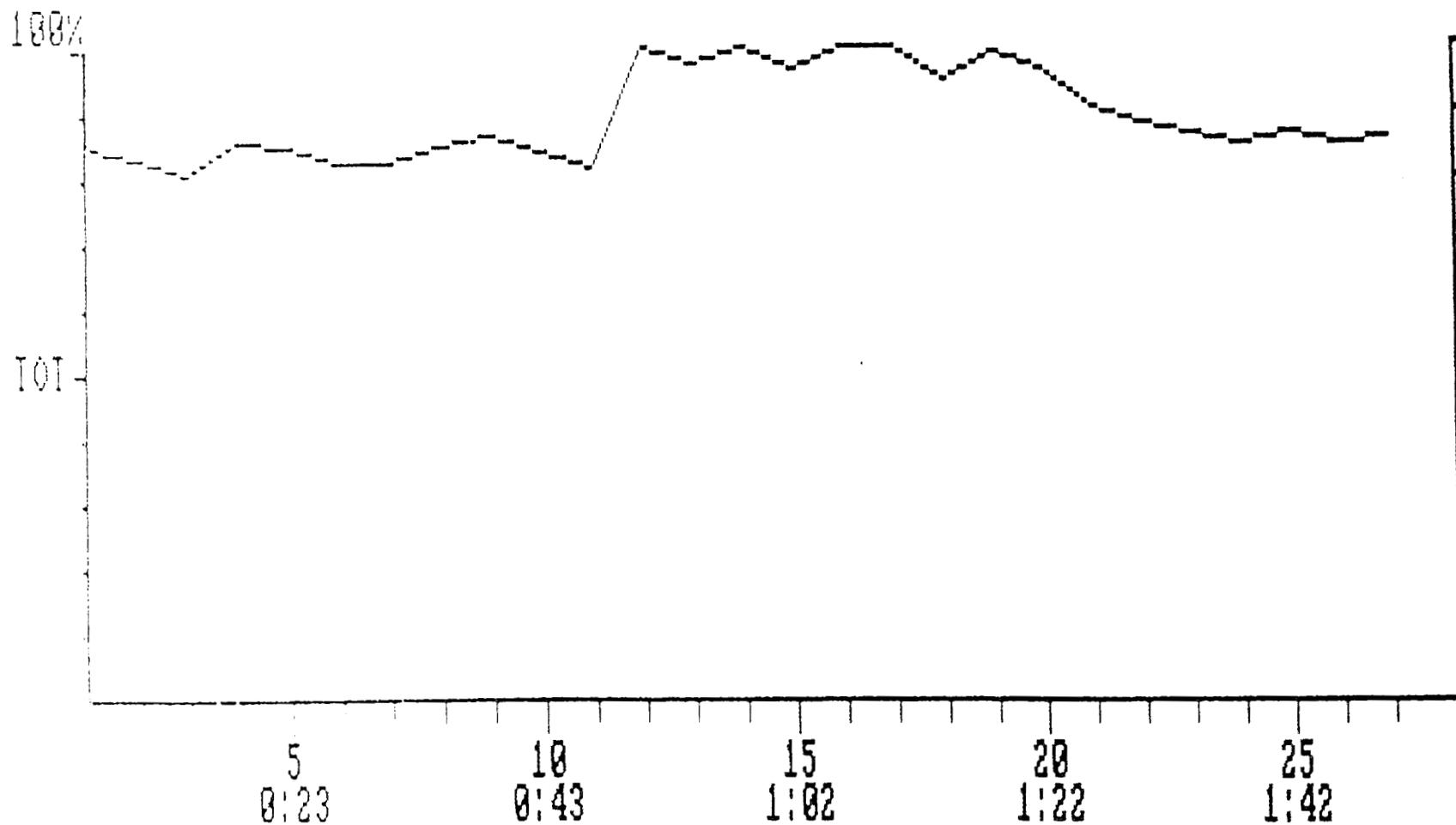
COMPOUND: TRICHLOROETHYLENE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 131



COMPOUND: FREON 113

CAD EFFICIENCY FOR CI MS/MS OF M/Z 167



CHRO>

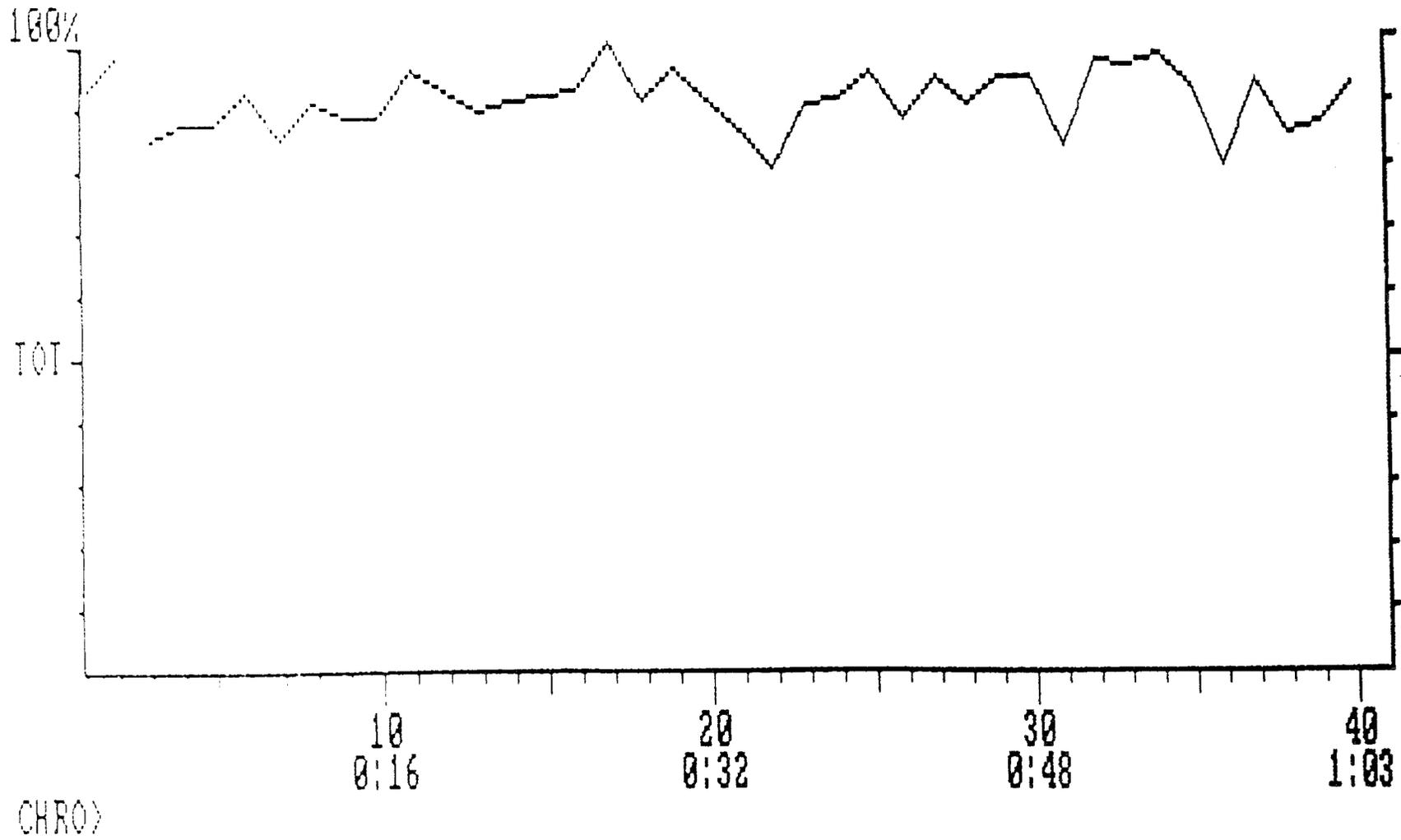
COMPOUND: FREON 113

CAD EFFICIENCY FOR CI MS/MS OF M/Z 169



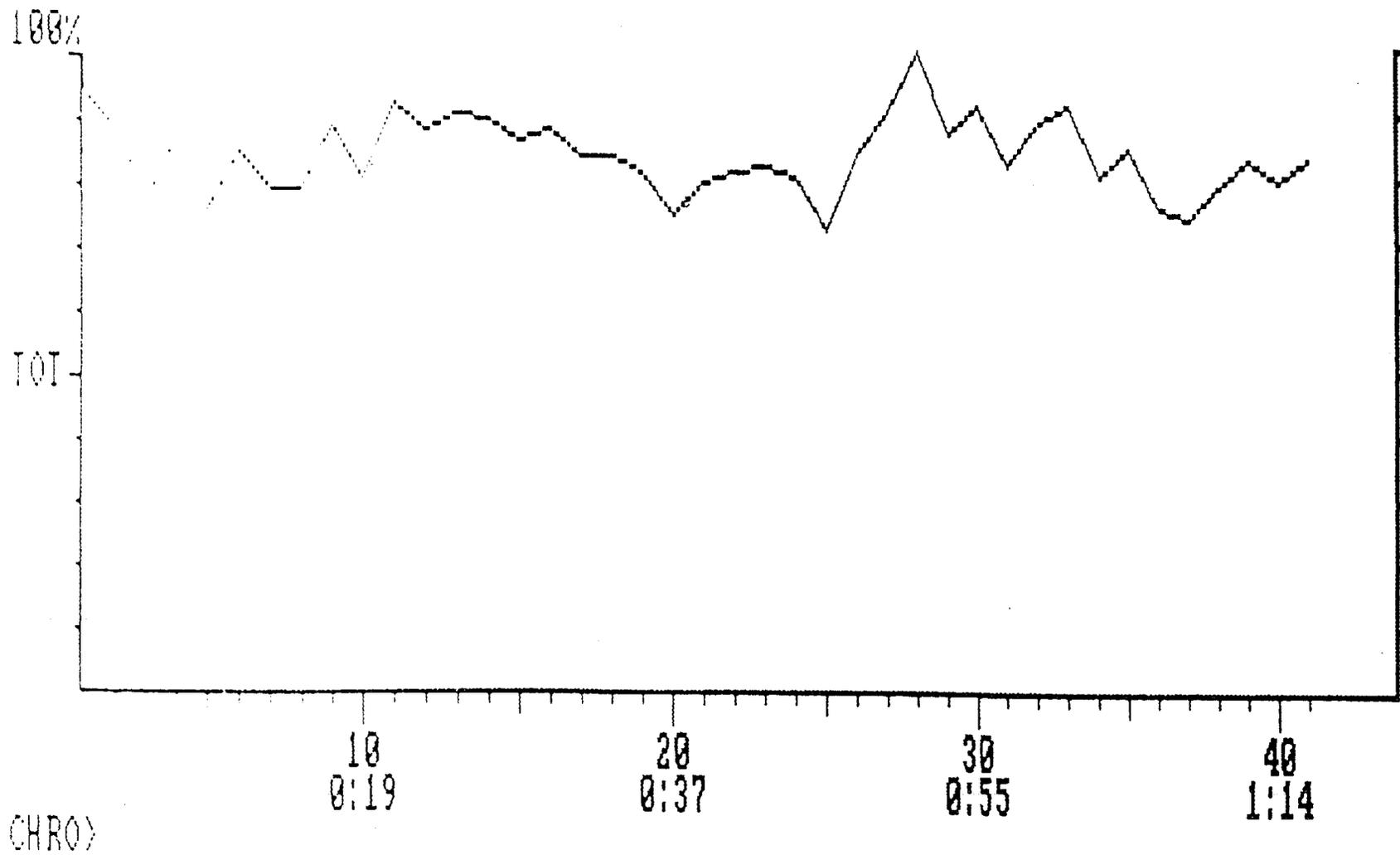
COMPOUND: TETRADECANE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 197



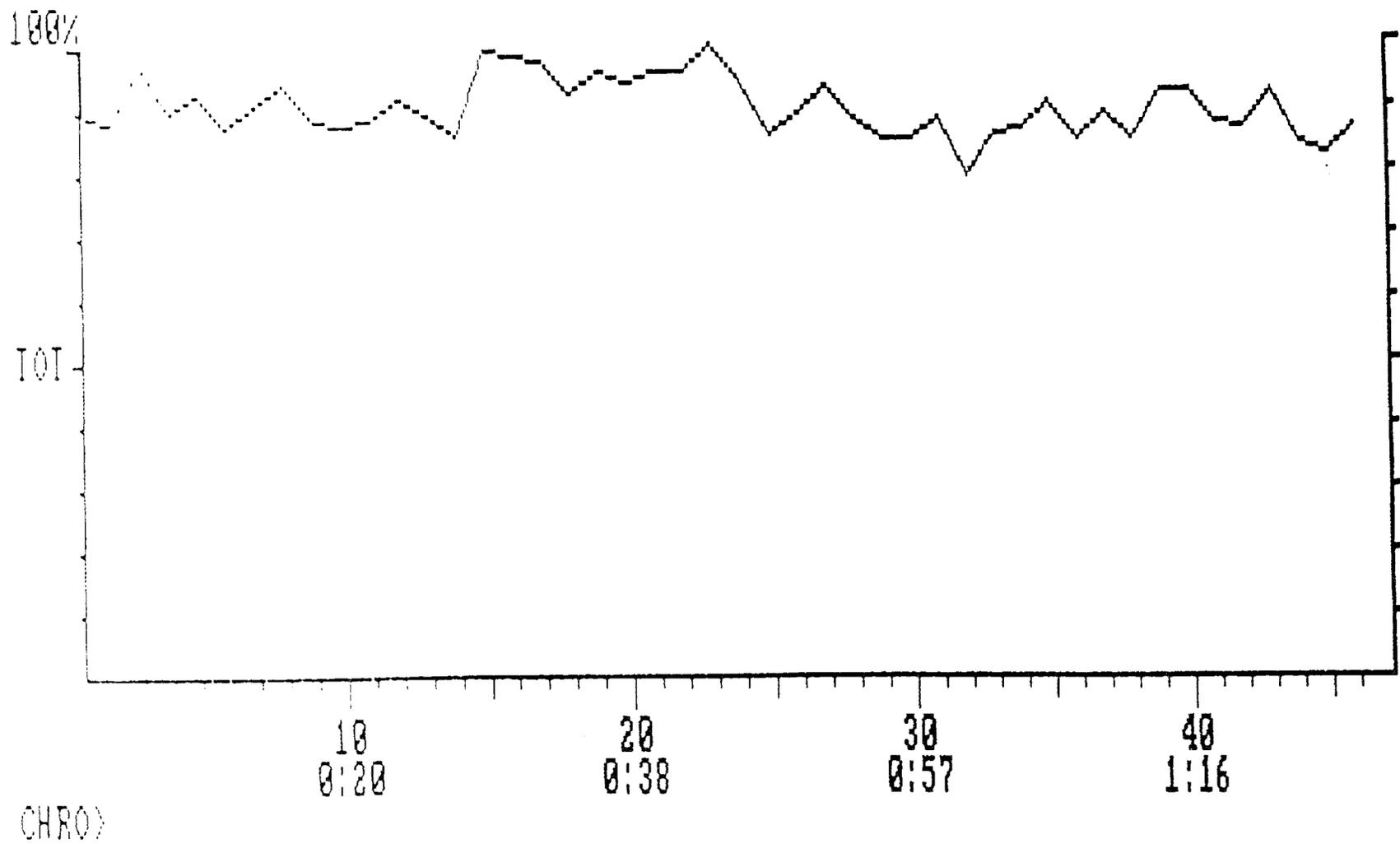
COMPOUND: STEARIC ANHYDRIDE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 267



COMPOUND: STEARIC ANHYDRIDE

CAD EFFICIENCY FOR CI MS/MS OF M/Z 285



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