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CHEMICAL IONIZATION STUDIES WITH A DuPONT 21-490 ANALYTICAL MASS SPECTROMETER

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TECHNICAL REPORT AFML-TR-72-35

MARCH 1972

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FOREWORD

This work was conducted by Dr. Arun K. Bhattacharya, Dr. Kenneth A. G. MacNeil and Dr. Jean H. Futrell of the University of Utah, Salt Lake City, Utah 84112 under Contract No. F33615-71-C-1172. (Dr. A. K. Bhattacharya was under a contract with Miami University, Oxford, Ohio, while a portion of the work was performed.) This work was initiated under Project 7367, "Research on Characterization and Properties of Materials for Air Force Systems," Task 736702, "Physical-Chemical Methods for Materials Analysis." The Project Engineer was Mr. Wilbert R. Powell of the Air Force Materials Laboratory (LPA).

The report covers work conducted from February 1971 to January 1972 and was submitted by the authors in February 1972.

This technical report has been reviewed and approved.

Freeman F Bentley

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ABSTRACT

A DuPont 21-490 analytical mass spectrometer has been modified to operate as a chemical ionization instrument. The basic requirements of a CIMS system and details of the actual mechanical, electrical and other changes have been described. Propane and a mixture of propane/benzene has been used to demonstrate the performance of the system. A method has been designed to estimate the ion-source pressure. A series of selected ketones have been used to obtain their chemical ionization mass spectra with propane reagent gas.

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SECTION I

INTRODUCTION

Chemical ionization mass spectrometry (CIMS) is a form of mass spectrometry wherein the ionization of the substance under investigation is affected by reactions between the molecules of the substance and a set of ions which serve as ionizing reagents. In other words, from the standpoint of its utilization by the Analytical Branch (LPA), CIMS may be understood as that branch of gaseous ion-molecule chemistry in which emphasis is placed upon the generation and determination under identical conditions of the spectra of various substances with particular attention being paid to the possibility that a method of practical application in qualitative and quantitative analysis might result. These have been discussed in earlier reports[1,2] and in the references cited therein.

One of the primary requirements of a chemical ionization mass spectrometer is its capability of operating and maintaining the ion-source at elevated gas pressures. In the case of electron impact mass spectrometry, an ionization pressure of $\sim 1 \times 10^{-5}$ torr is normal; whereas for a chemical ionization source, this must be raised to the region of 1 torr. The actual physical modifications which this requires can be classified as follows:

1) Improvement of gas-tightness of the source block to allow a greater pressure differential between this region and the remainder of the analyzer assembly;

2) Increased pumping capacity to handle the larger gas flow used;

3) Alteration of electrical insulation within and around the instrument to protect against possible high voltage discharge or hazard to users, and;

4) Modification of the instrument electronic system to handle the new conditions within the ion source.

SECTION II

INSTRUMENT MODIFICATIONS

The standard ion-source of a DuPont 21-490 analytical mass spectrometer contains several orifices which allow gas leakage; these are the inlet slit for the ionizing electron beam, the ion exit slit and the loosely fitting entries for both the sample gas inlet line and the sample probe. To reduce gas loss at the electron entrance slit, this has been covered over and replaced with an aperture consisting of three small tunnels which simultaneously allow electrons to enter the ionization region and presents a high impedance to gas flow out of the source block.[3] Since the standard source provides no means of measuring the actual ionizing electron current, (but rather regulates the total ion current impinging on the block whether or not it has entered the ionization region), it is not possible to measure directly any loss of ion-forming electrons resulting from this change. However, measurements of the total ion current produced from a sample gas, under similar conditions, both before and after the modification, indicate that this loss is not serious and signal is reduced only by approximately a factor of 2.

Because the ion beam is clipped by a beam-limiting stop ahead of the magnet, the ion-exit slit of the source can also be somewhat reduced with no detrimental effect on the instrument sensitivity. This has been achieved by spot-welding a tab to the analyzer side of the ion-exit slit plate. In our modification the tab was a disc of stainless steel, 0.010 in. thick with a circular hole of 0.080 in. diameter drilled through the center. The loose-fitting vapor entrance lines have been modified by tapping both parts with screw threads and threading the end of the gas inlet line and the tip of the sample probe. This has necessitated the replacing of the standard ceramic probe tip with one of stainless steel.

At the same time that the ion-source has been made more gas-tight, the pumping system has been improved to cope with the increased overall gas flow. The existing source pumps have been replaced by an N.R.C. 4" VHS diffusion pump and a Welch Model 1376 mechanical pump; no changes have been made in the systems for evacuation of the ion-detector region or of the inlet oven assembly.

These modifications thus allow the ion-source to be operated at a pressure of several hundred microns while the analyzer region is maintained at about 7 - 8 x 10^{-4} torr. The standard instrument gauge is replaced by an N.R.C. ion-gauge to measure the pressure which is external to the block. The method used to estimate the ion-source pressure will be explained later.

It should be noted that the high pressures generated in this way lead to the possibility of electrical discharge along the gas inlet lines and also cause the probe to operate at accelerator voltage. In order to overcome these problems and to protect the operator from high-voltage hazards, the following changes have been made:

1) The gas-inlet line has been redesigned to allow part of it to float at accelerator potential;

2) Various sections have been insulated to prevent conduction to ground;

3) A glass insulator section has been included on the high pressure side of the inlet leak;

4) All external electrically conducting parts on the low pressure side of the gas inlet line have been insulated, and;

5) The sample probe handle has been sheathed in insulating material.

Finally, the increase in ion-source pressure requires some changes in the electronics of the instrument. Because electrons of energy higher than the usual 70 eV are needed to penetrate the source region, the electron accelerating voltage power supply has been replaced with an external supply capable of providing up to 500 volts. Experiments have shown, however, that an energy of about 200 eV is optimal in causing ionization under the present conditions. For flexibility of operation, the original 70 volts supply can be restored by means of a switch built on the electronics chassis. An important feature of the modification is that it allows the normal mode of operation (electron impact) by merely the quick throwing of this switch. Since the sample probe now works at accelerator voltage, the circuitry involved in heating and measuring the temperature of the tip has been floated at probe voltage.

SECTION III

EVALUATION OF SYSTEM PERFORMANCE

The mass spectrum of propane has been examined over the range of source housing pressures 1 - 10 x 10^{-4} torr as indicated by the ionization gauge installed in the pumping line of the mass spectrometer. Figure 1 represents the high pressure data for the two most prominent ions, m/e 43 and m/e 44. Munson, et al.[4], have reported similar results earlier. An attempt has been made to compare these results. It should be pointed out that a pressure calibration will only be valid if the source residence times were identical in both sets of experiments. We have estimated our field strengths and they are very close to the value of 12.5 v/cm used in Munson's data. This has been accomplished by measuring the repeller voltage employed and the ion paths. The following Table I shows both these results by considering the ion $C_3H_7^+$ (m/e 43) as a fraction of all ions formed.

TABLE I

HIGH PRESSURE DATA FOR PROPANE

Pressure as Read on N.R.C. Ion Gauge x 10^{-4} torr	$C_3H_7^+$ as % of All Ions In Propane (Our Data)	Pressure in μ Data of Munson, et al.	$C_3H_7^+$ as % of All Ions in Propane
1.2	46.5	20	25
2.1	58.5	40	38
3.2	63.3	60	48
4.2	71.4	80	54
5.3	69.0	100	60
6.0	73.0	120	65
7.1	71.0	140	68
8.4	73.0		
8.9	73.0		
10.0	76.0		

As is clear from Figure 1, beyond about 6 x 10^{-4} torr the $C_3H_7^+$ ionic abundance does not change with pressure. If the present data are plotted to serve as a base curve, the results of Munson, et al., can be used to relate the two pressure scales. For example, taking the point where $C_3H_7^+$ is 38% of all ions, the pressure according to Munson, et al., is 40 μ. In the present case this corresponds to 0.8 x 10^{-4} torr external to the source. Proceeding in this way the following Table II can be generated.

TABLE II

DATA GENERATED FROM THE EXPERIMENTAL CURVES

$C_3H_7^+$ as % of All Ions in Propane	Pressure Munson, et al., μ	Housing Pressure x 10^{-4} torr	Pressure Ratio (Munson, et al.)/(Housing Pressure)
38	40	0.8	500
48	60	1.3	462
54	80	1.7	471
60	100	2.3	435
65	120	3.0	400
68	140	3.6	389

Ignoring the <u>ca.</u> 16% change in the ratio of pressures with increasing pressure and assuming fairly similar source conditions in the two experiments (as indicated earlier), we can average these values to give a rough idea of the present source pressure. The average value of the pressure ratios is ~ 450; i.e., at an indicated ion-gauge pressure of 8 x 10^{-4} torr, the source pressure is roughly 360 μ.

A similar set of experiments were conducted with the propane/benzene system (benzene being the additive at ~ 0.2% concentration). The results have been plotted in Figure 2, where only the prominent ions have been shown. As expected, the intensity of $C_3H_7^+$ and $C_3H_8^+$ ions decrease at increasing pressure, whereas the intensities of $C_6H_6^+$, $C_6H_7^+$ and $C_{12}H_{13}^+$ ions increase. If only the chemical ionization products are considered, then their normalized intensities, after truncating the peaks due to propane alone, are plotted in Figure 3. This can be called the chemical ionization spectra of benzene at increasing pressure with propane as a reagent gas. Now if the ions formed by chemical ionization, computed as a fraction of all ions formed, are considered, it will be noticed as shown in the following Table III that this ratio of % C. I./Σ I increases monotonically with total pressure but at a decreasing rate.

TABLE III

PRESSURE DATA OF PROPANE/BENZENE SYSTEM

Pressure as Read on N.R.C. Ion Gauge x 10^{-4} Torr	% [(C.I.)/Σ I]
1.2	15.4
2.3	38.6
3.1	49.0
4.4	64.2
6.0	72.0
6.8	73.3
7.4	75.2
8.6	76.8
9.6	79.6

These data are plotted in Figure 4. The above results indicate that a reasonable pressure for operation is about 8 x 10^{-4} torr, as read on the instrument ion-gauge, and this was the pressure used in acquiring the C.I. mass spectra of the several ketones described in the next section. The source temperature was 250°C and the repellers were set approximately to zero.

SECTION IV

CHEMICAL IONIZATION STUDIES OF SELECTED KETONES

The first phase of the actual experimental work designed to use the CIMS technique for the purpose of structural characterization was a series of selected ketones. In this report we will briefly describe the results obtained for the following ketones with propane serving as a reagent gas:

3-butene-2-one	(I)
4-methyl-3-pentene-2-one	(II)
2,4-pentanedione	(III)
3-methyl-2-pentanone	(IV)
cycloheptanone	(V)
methylcyclopropylketone	(VI)
dicyclopropylketone	(VII)
2-methylcyclohexanone	(VIII)
3-methylcyclohexanone	(IX)
2,6-dimethylcyclohexanone	(X)
2-isopropylcyclohexanone	(XI)

The normalized chemical ionization mass spectra of all the above eleven compounds are shown in Figures 5-15. Salient features of these spectra are summarized in Table IV.

It can be observed that the (M + 1) peak is the most abundant peak in all the spectra. We are, therefore, in good agreement with the previous results.[2] We have already shown a substantial presence of $C_3H_8^+$ ions in addition to the $C_3H_7^+$ which are responsible for the CIMS peaks. Simple thermal computations show that $C_3H_8^+$ ions will undergo charge transfer process to yield M^+ ions in these cases. The disolvated proton is also a common product and its mechanism has already been established. (M - 17) peak corresponds to $[(M + 1) - H_2O]$, which has been established earlier[2] with methane as a reagent gas. We have noticed the cleavage of the molecule as seen in VII and XI. These correspond to (M - 35) and (M - 37), respectively, and tend to suggest that the (M + 1) substance initially

TABLE IV

TRENDS OF CIMS OF SOME KETONES

Compound	No.	Mol. Wt.	M - 43	M - 42	M - 41	M - 28	M - 17	M - 15	M - 1	M	M + 1	M + 17	M + 43	2M + 1
3-butene-2-one	I	70						0.92		1.34	100			1.34
4-methyl-3-pentene-2-one	II	98					4.05			9.80	100			0.40
2,4-pentanedione	III	100		0.19	0.97	0.97		1.03	0.84	7.09	100		0.39	0.32
3-methyl-2-pentanone	IV	100			2.42		0.38	3.02	0.66	7.19	100			1.34
cycloheptanone	V	112					1.61		0.61	10.58	100			1.11
methylcyclopropylketone	VI	84						4.02		2.15	100			1.57
dicyclopropylketone	VII	110			13.97			0.96	1.47	4.70	100	1.10		0.44
2-methylcyclohexanone	VIII	112				0.46	1.87	1.65	1.25	14.85	100			1.25
3-methylcyclohexanone	IX	112	1.43				1.71	0.55	1.43	14.29	100			4.62
2,6-dimethylcyclohexanone	X	126	0.94			1.37	11.63	0.69	2.37	25.00	100			1.12
2-isopropylcyclohexanone	XI	140	1.45	11.57	1.33	0.36	15.80	2.66	5.92	12.54	100	2.05		0.72

formed eliminates the small molecules C_3H_6 and C_3H_8. Small peaks due to (M - 1) ion are also seen in most of the cases, which may be ascribed to the loss of a hydrogen molecule from the (M + 1) ion. Similarly, the (M - 15) peak is obtained as a result of the loss of methane molecule from the (M + 1) ion. Further details will be communicated later.[5]

SECTION V

CONCLUSIONS

We have reported the first measurements carried out using a modified DuPont 21-490 analytical mass spectrometer to produce chemical ionization mass spectra. Propane has been used to test the capability of the system and to optimize the experimental parameters. The results obtained agree with previously published work. A series of selected ketones have been subjected to chemical ionization with propane as a reagent gas. Future work will be directed to the use of different reagent gases and to establishing the relationship between structural features of compounds and their chemical ionization spectra.

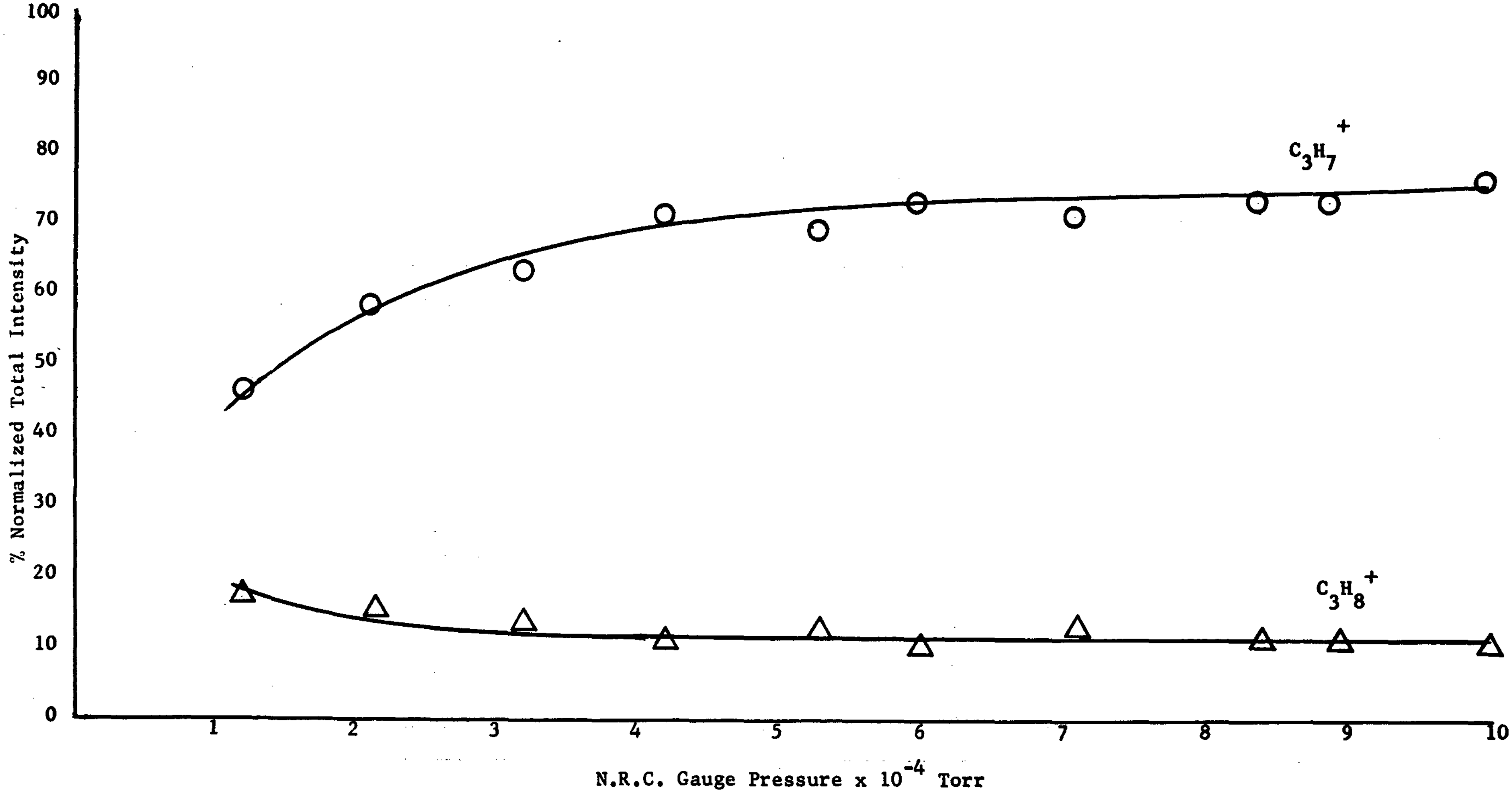

Figure 1 High pressure data for propane

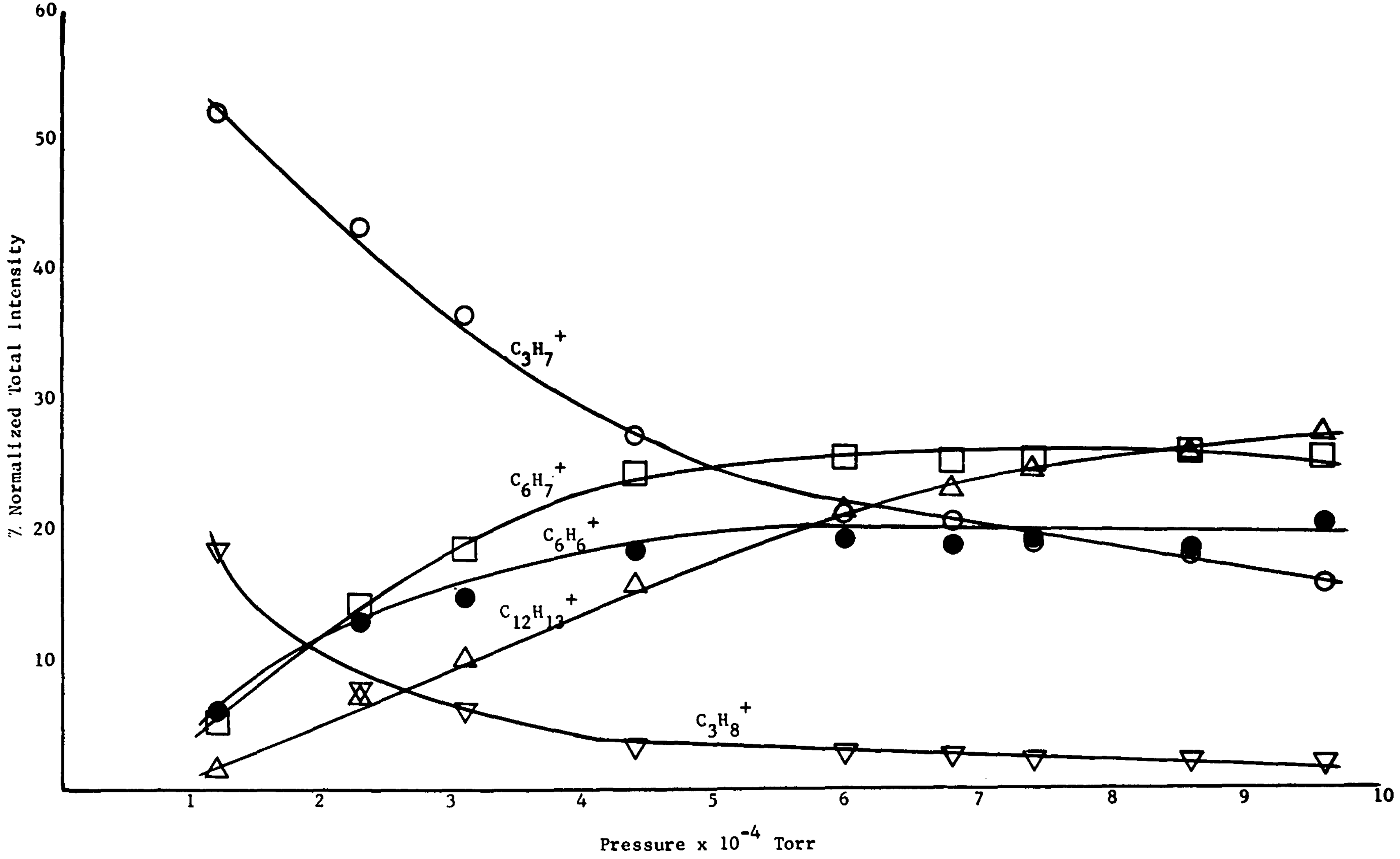

Figure 2 High pressure data for propane/benzene system

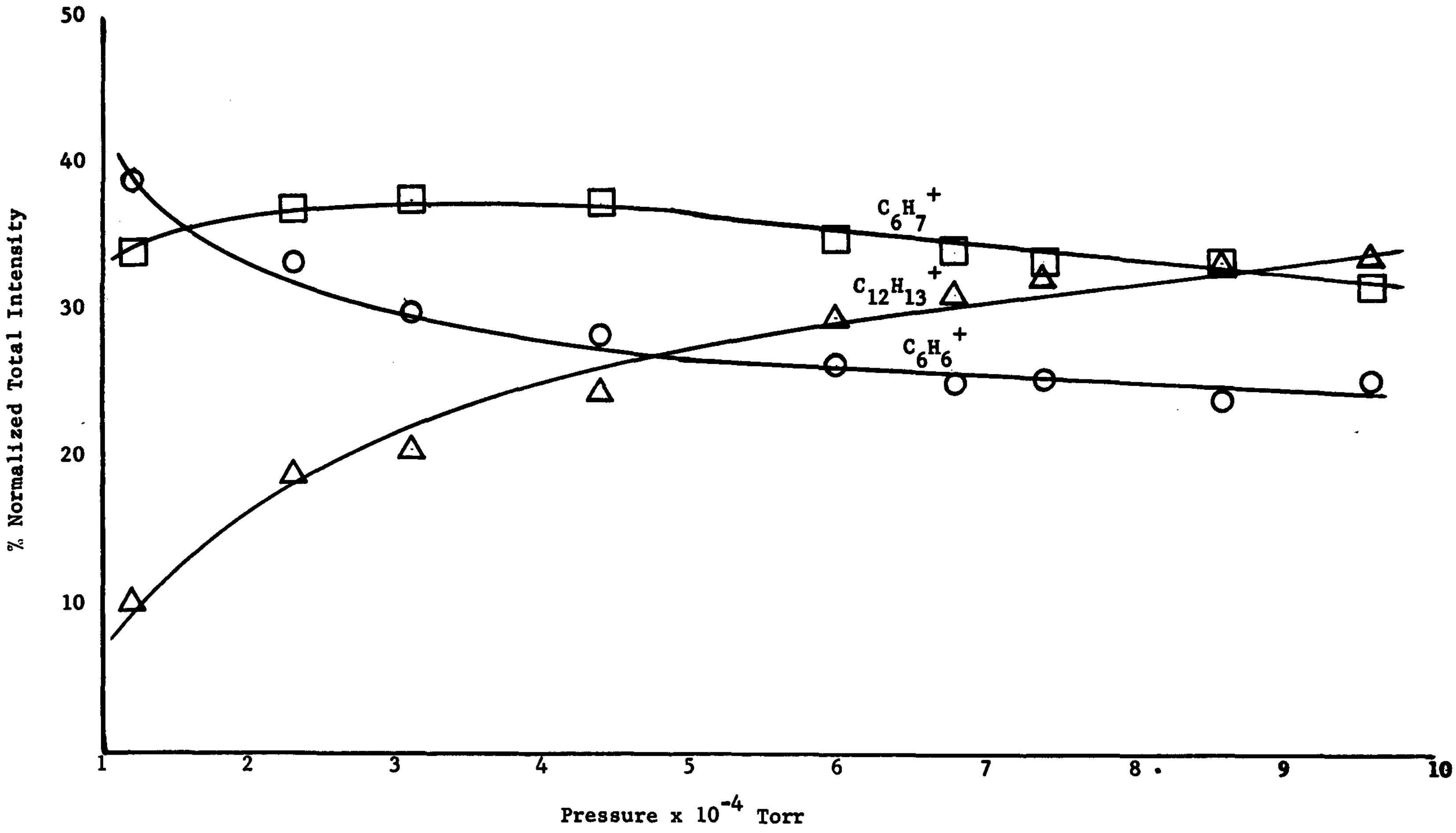

Figure 3 Chemical ionization products in the propane/benzene system

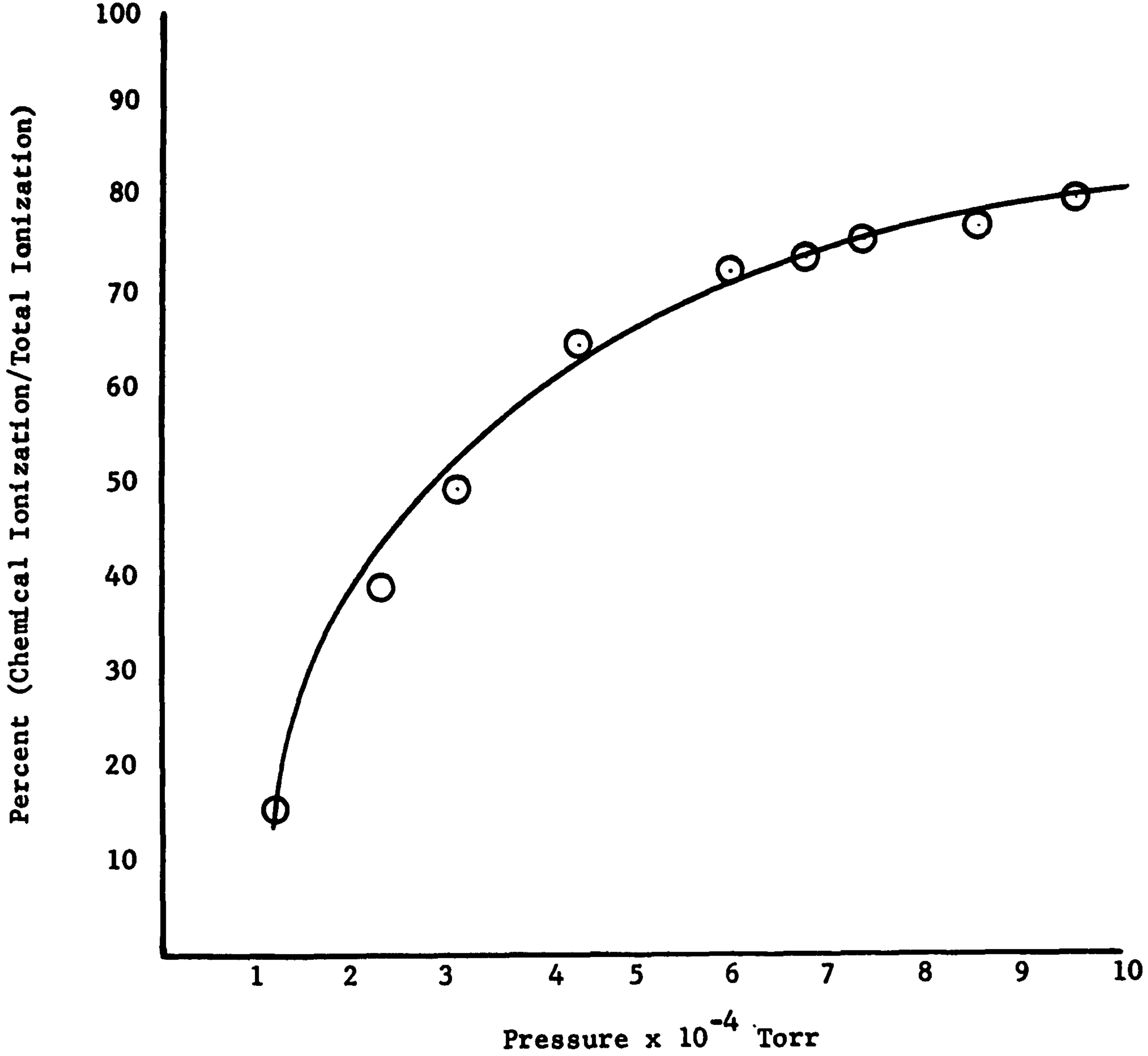

Figure 4 The ions formed by chemical ionization computed as a fraction of total ions in the propane/benzene system

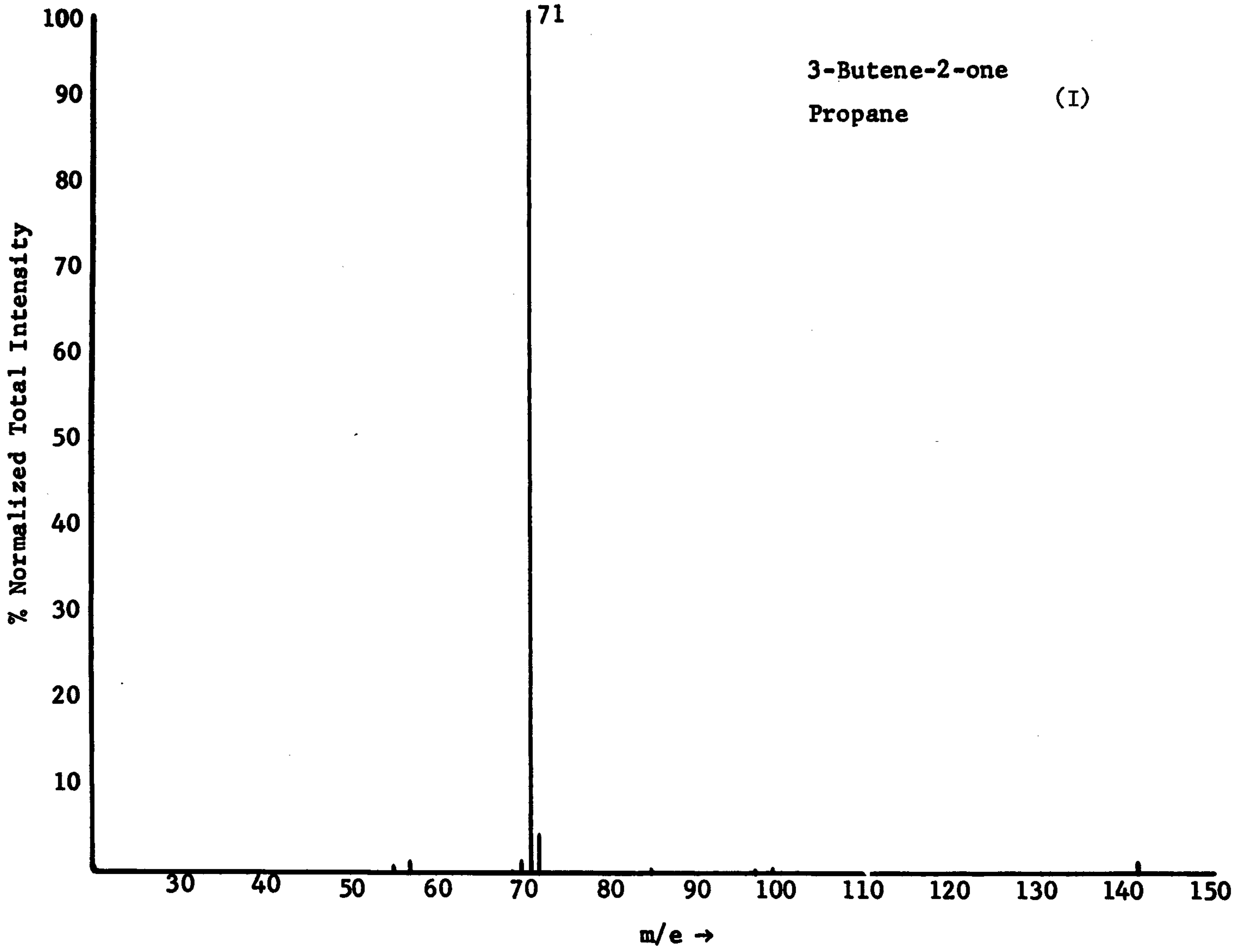

Figure 5 Chemical ionization spectrum of 3-butene-2-one using propane reagent

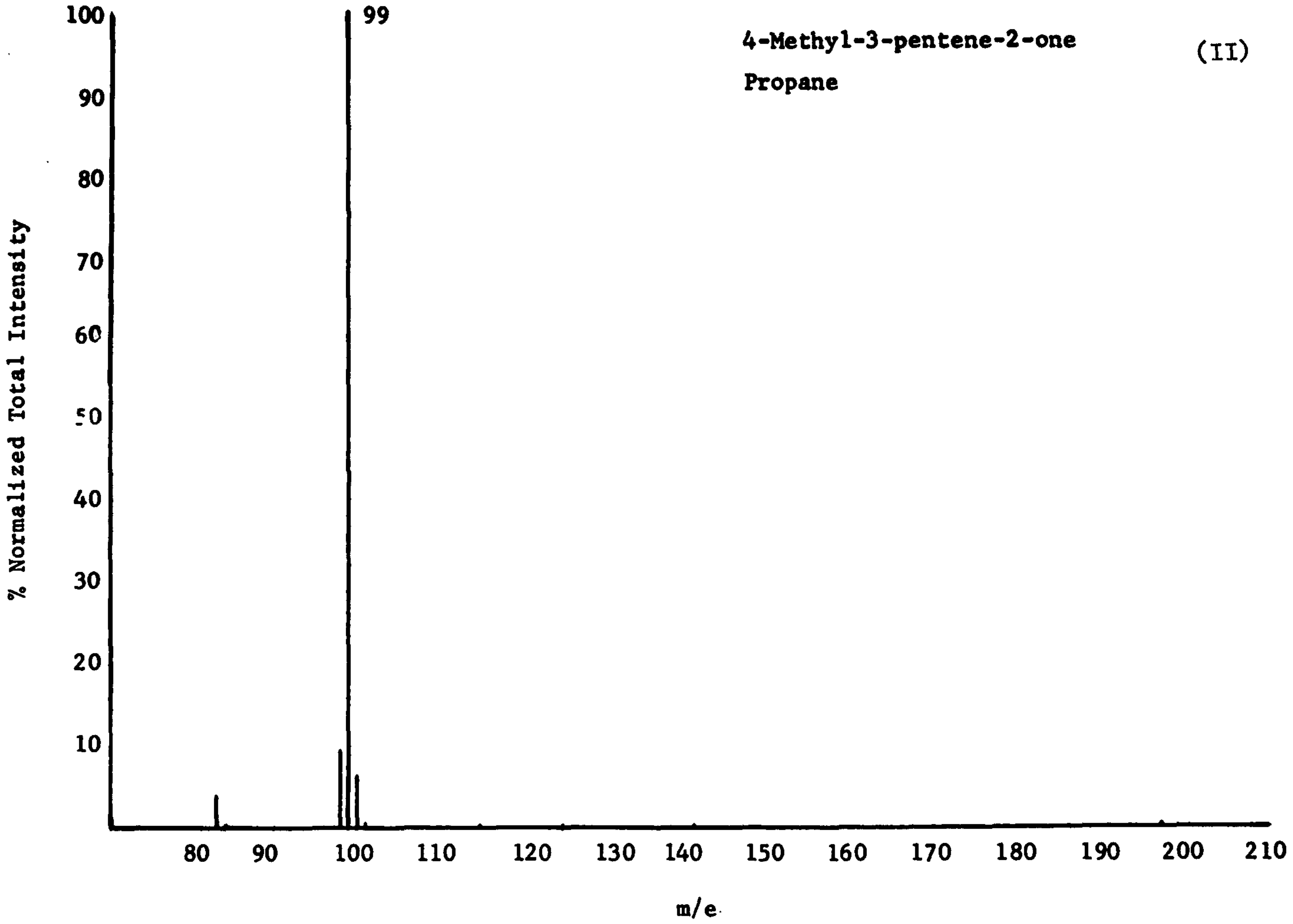

Figure 6 Chemical ionization spectrum of 4-methyl-3-pentene-2-one using propane reagent

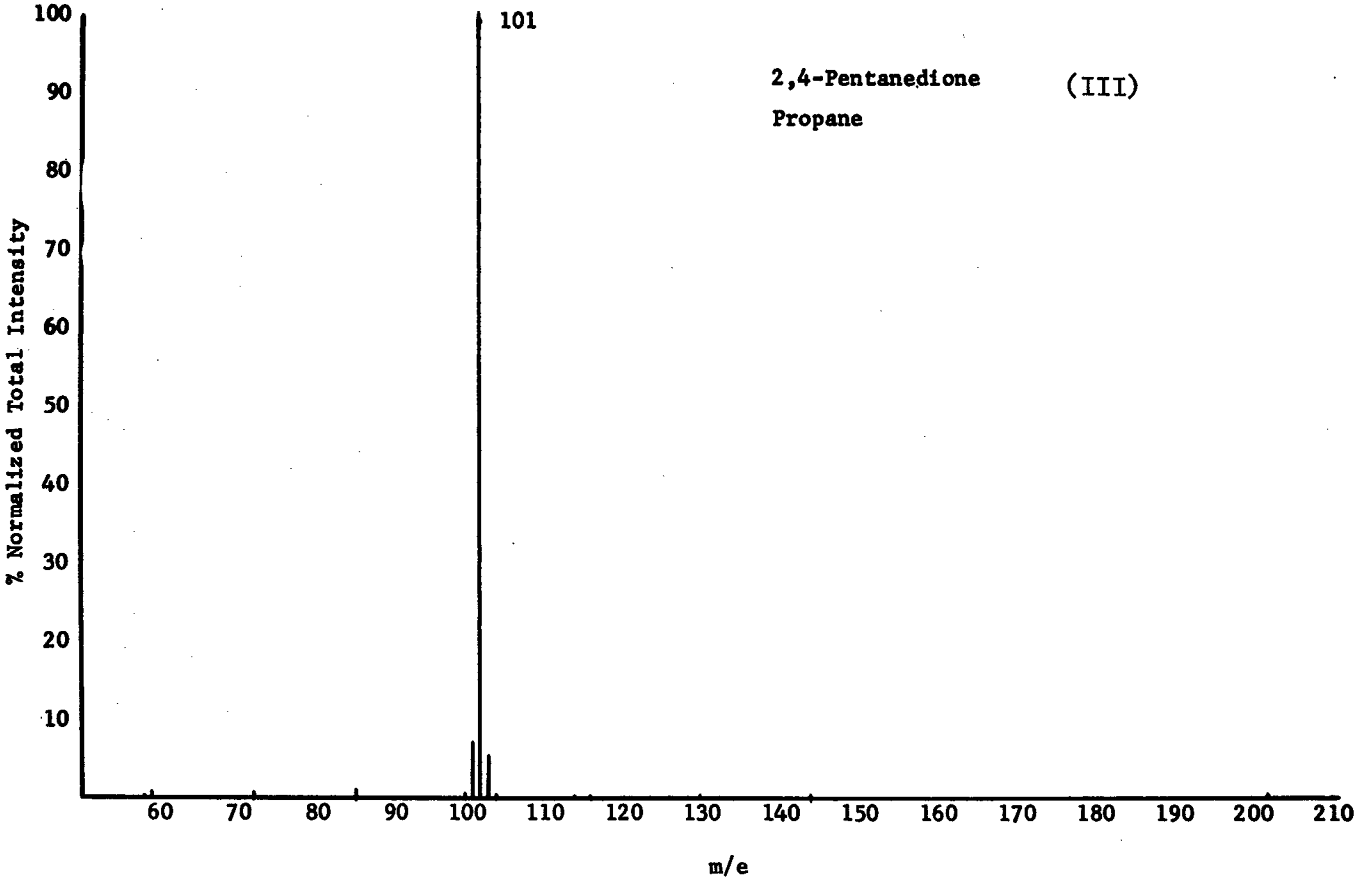

Figure 7 Chemical ionization spectrum of 2,4-pentanedione using propane reagent

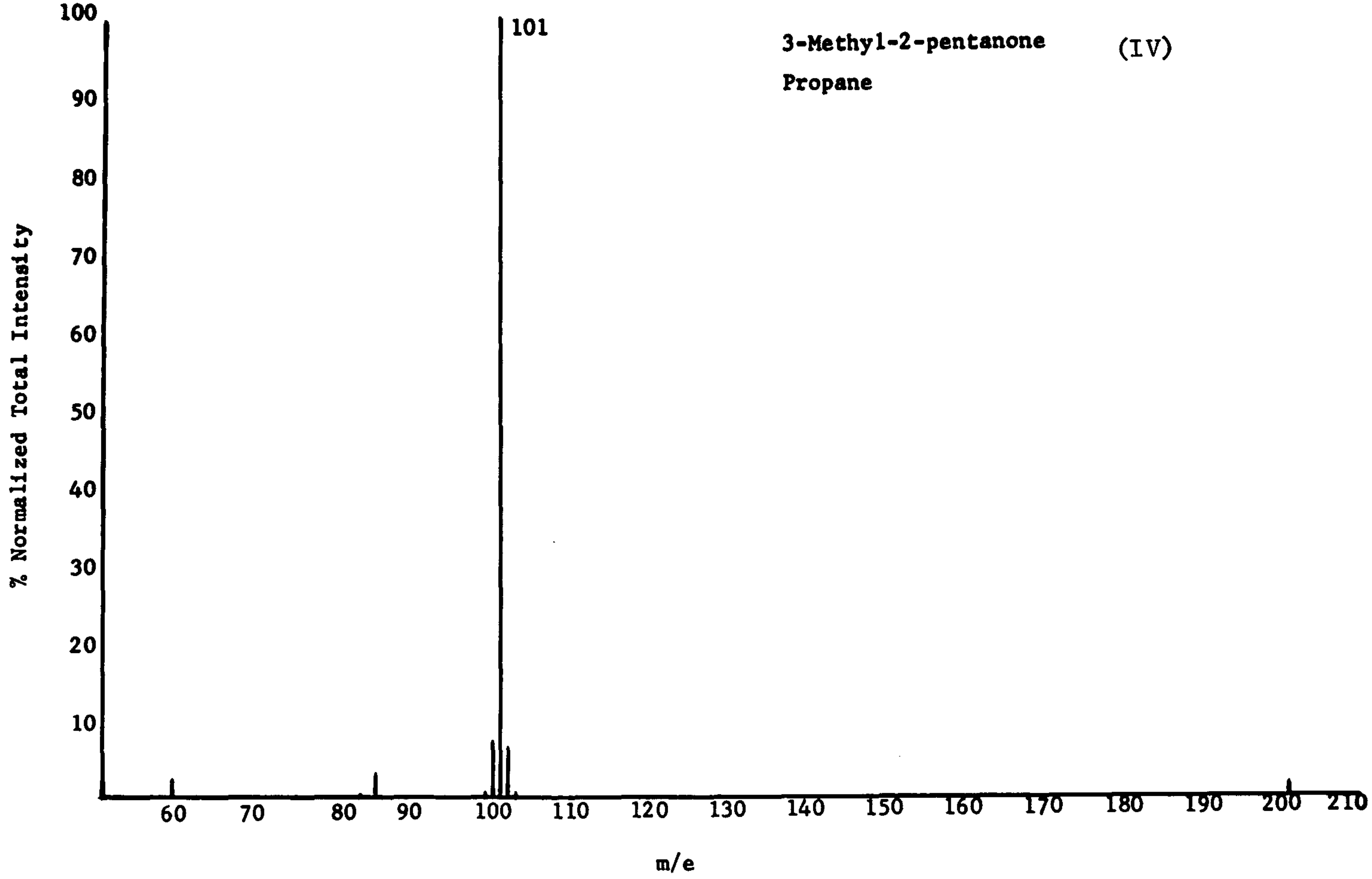

Figure 8 Chemical ionization spectrum of 3-methyl-2-pentanone using propane reagent

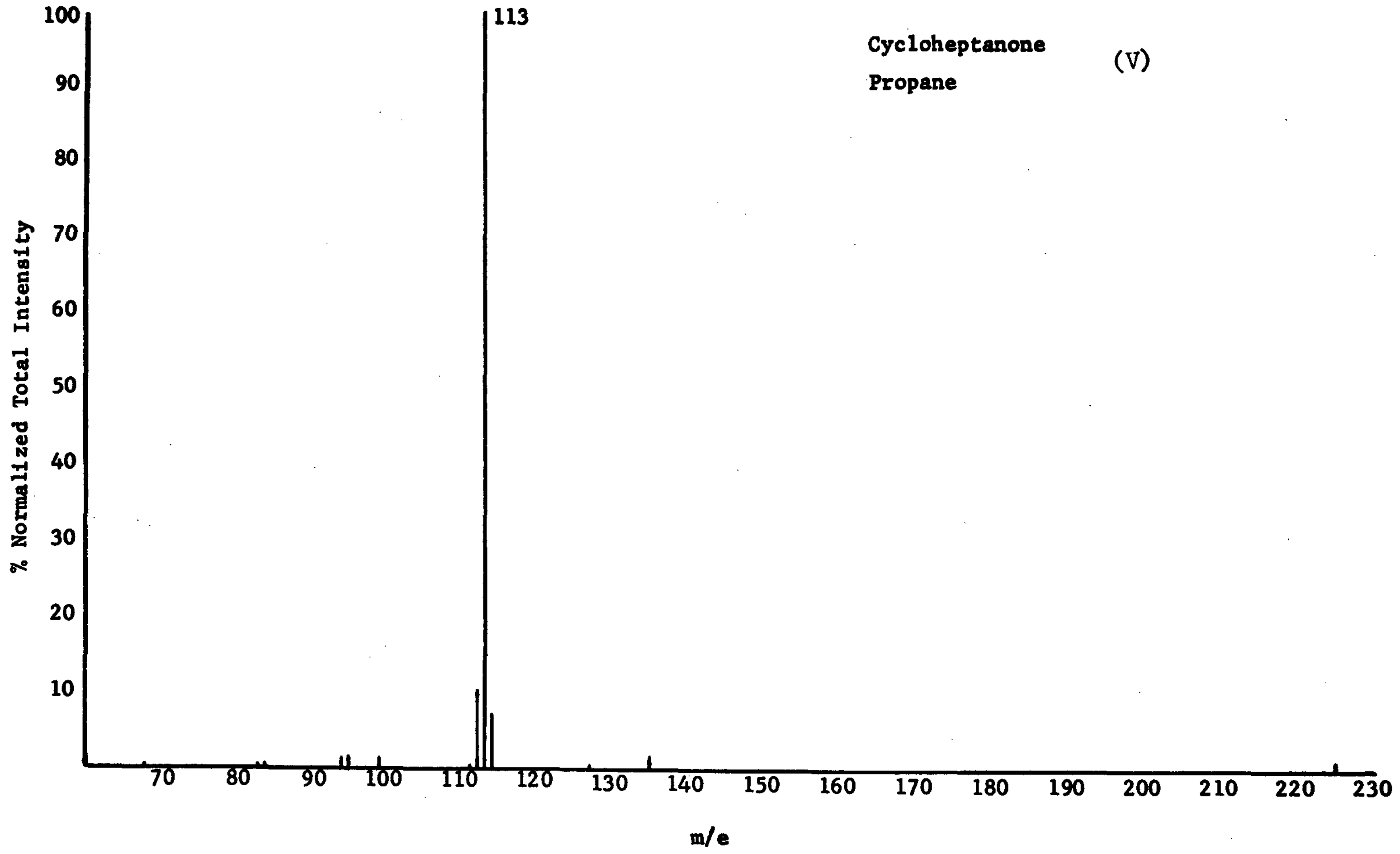

Figure 9 Chemical ionization spectrum of cycloheptanone using propane reagent

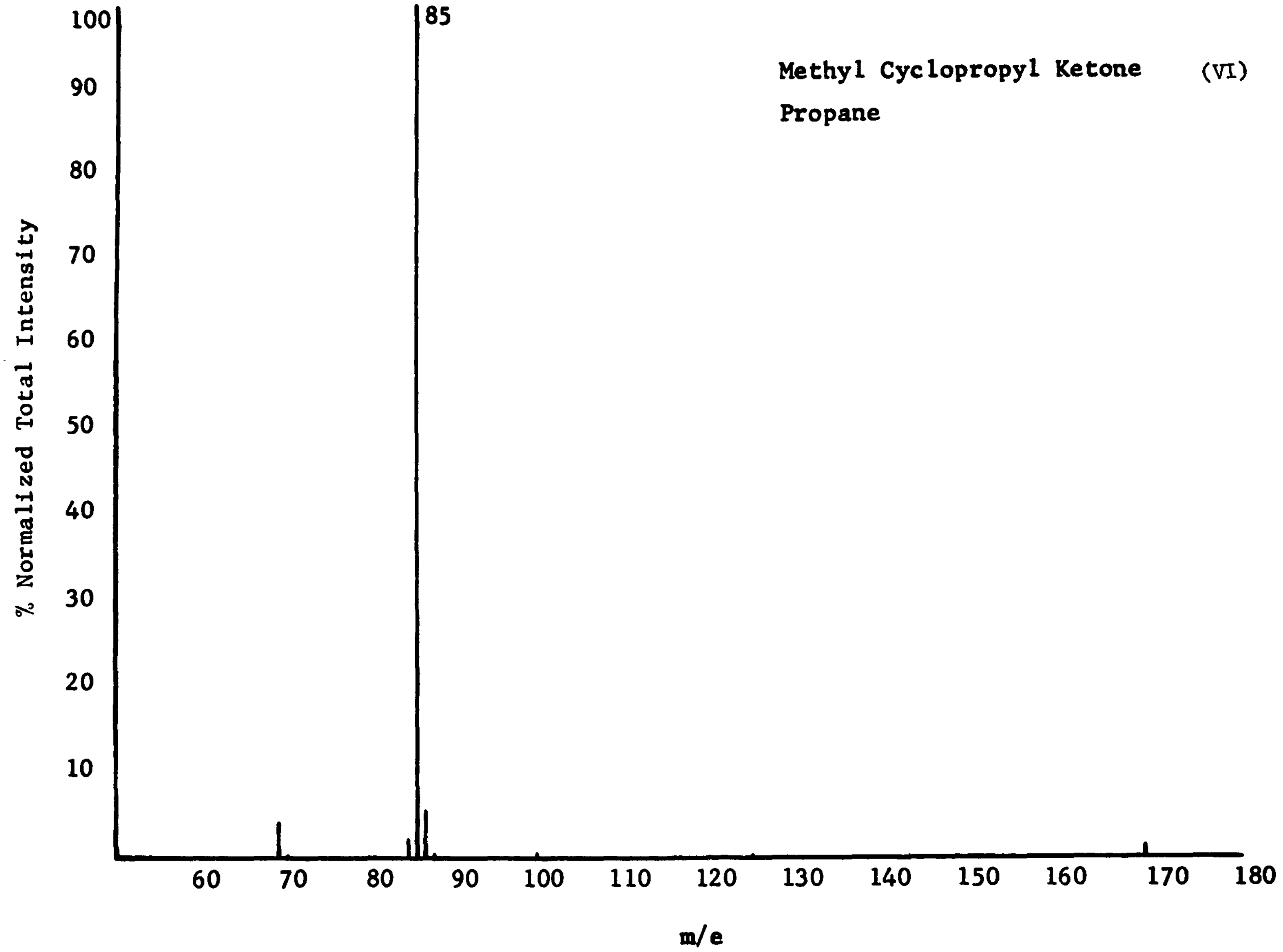

Figure 10 Chemical ionization spectrum of methylcyclopropylketone using propane reagent

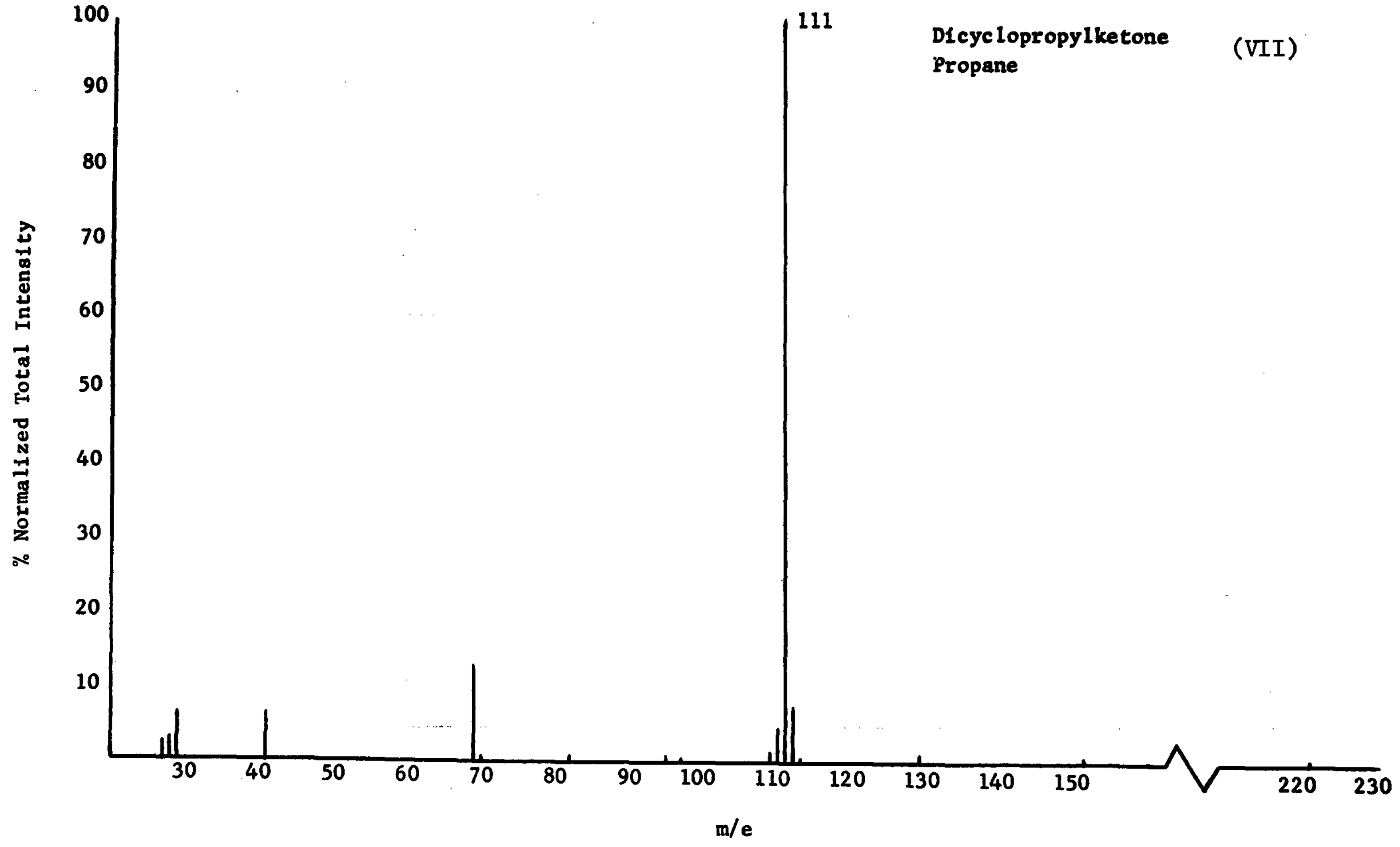

Figure 11 Chemical ionization spectrum of dicyclopropylketone using propane reagent

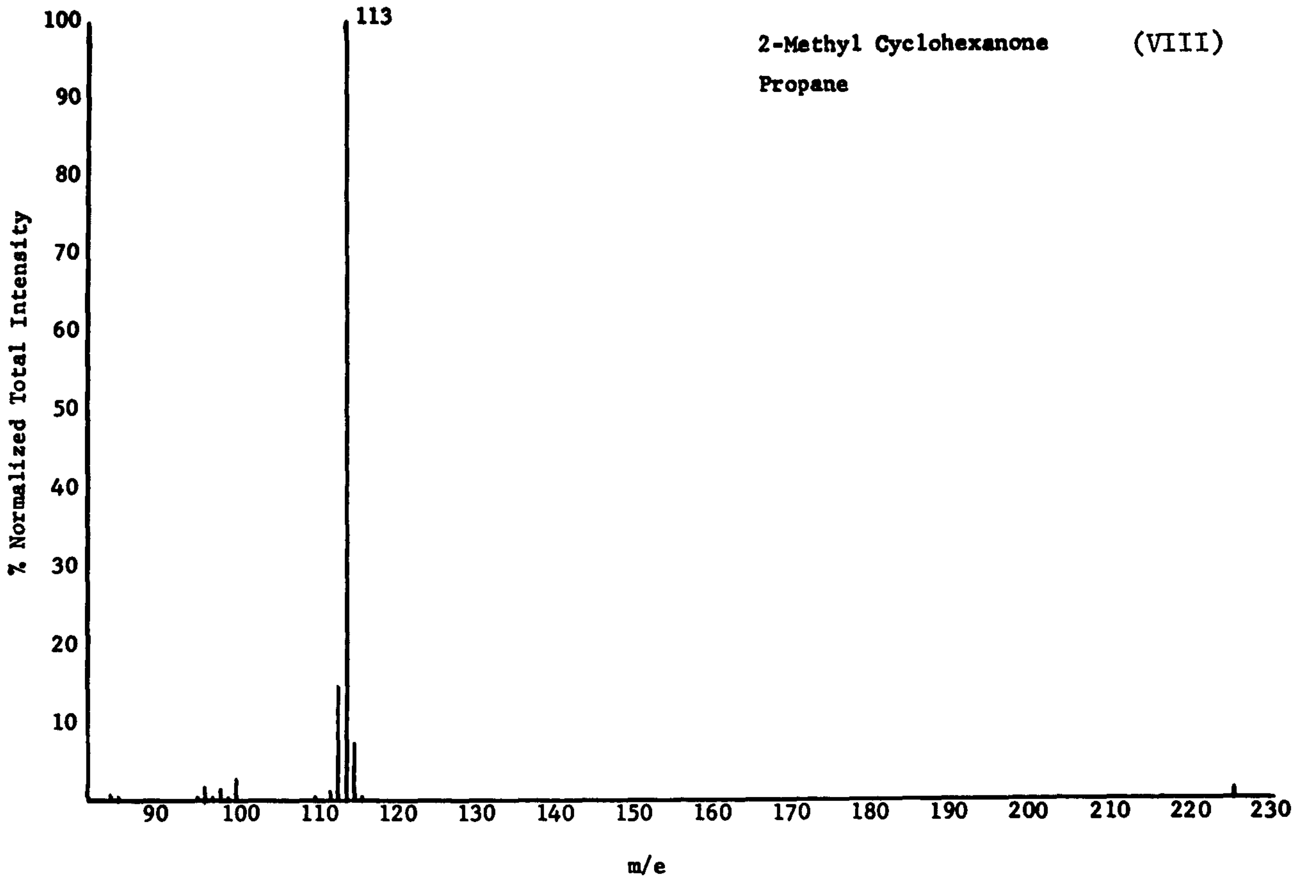

Figure 12 Chemical ionization spectrum of 2-methylcyclohexanone using propane reagent

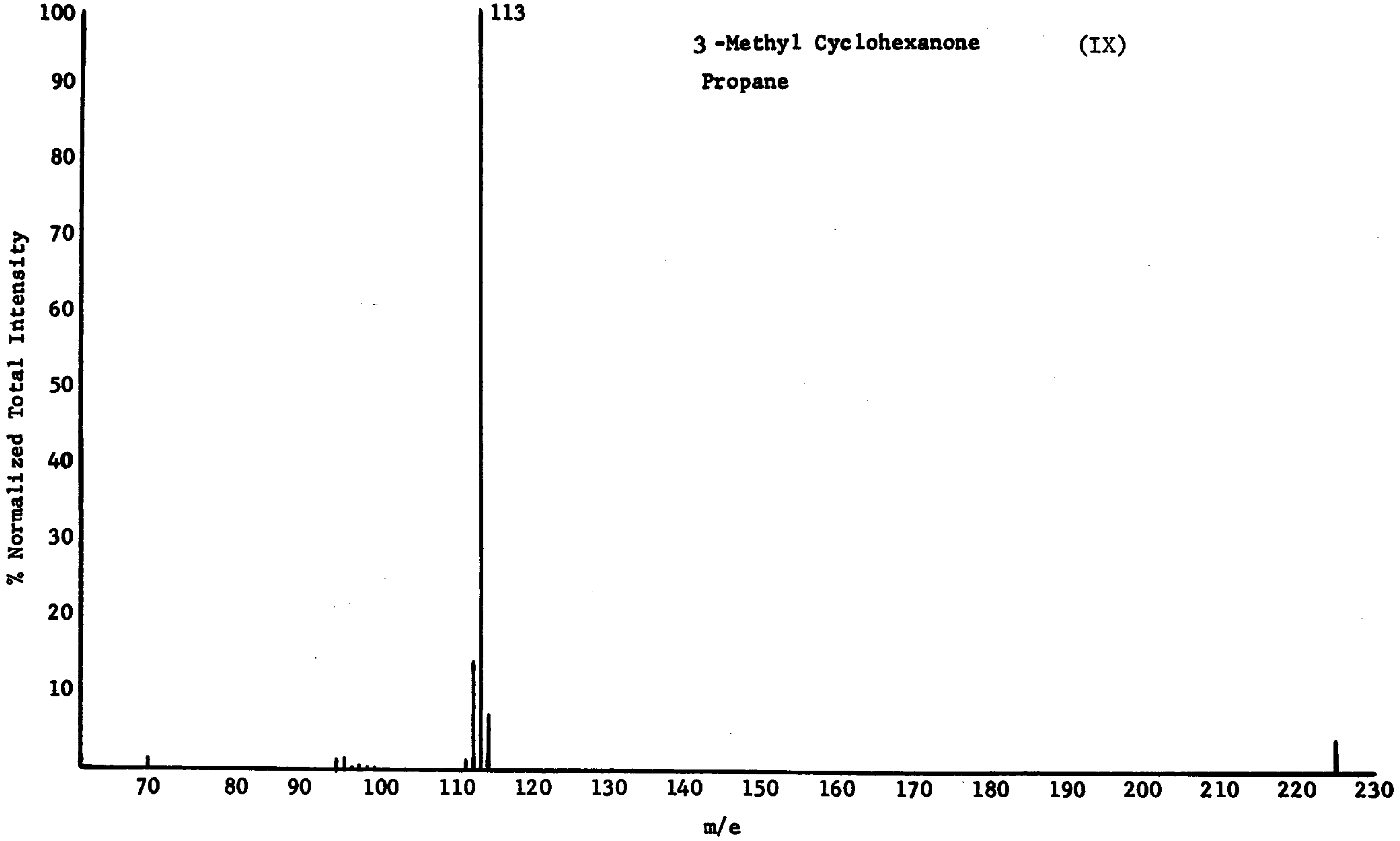

Figure 13 Chemical ionization spectrum of 3-methylcyclohexanone using propane reagent

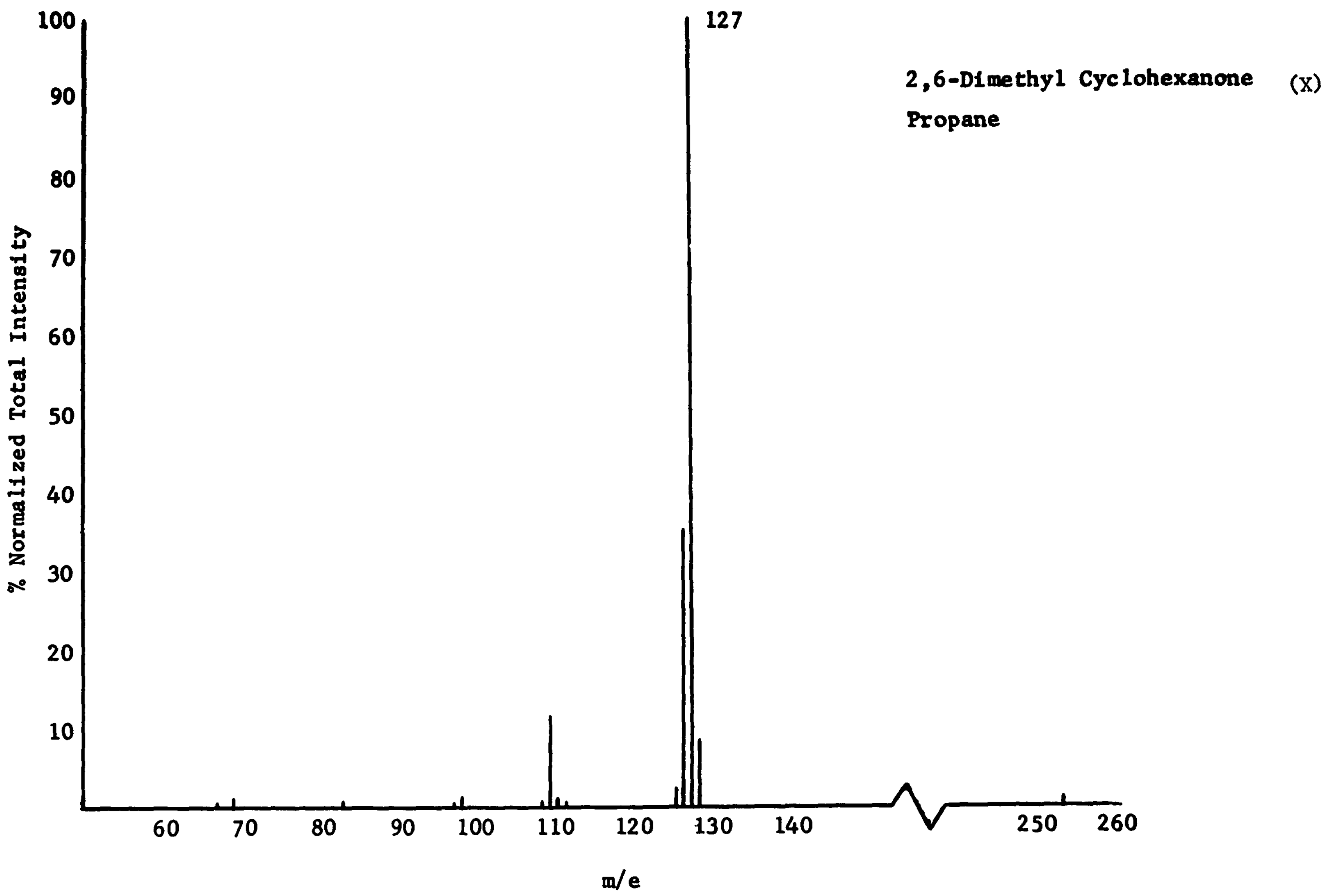

Figure 14 Chemical ionization spectrum of 2,6-dimethylcyclohexanone using propane reagent

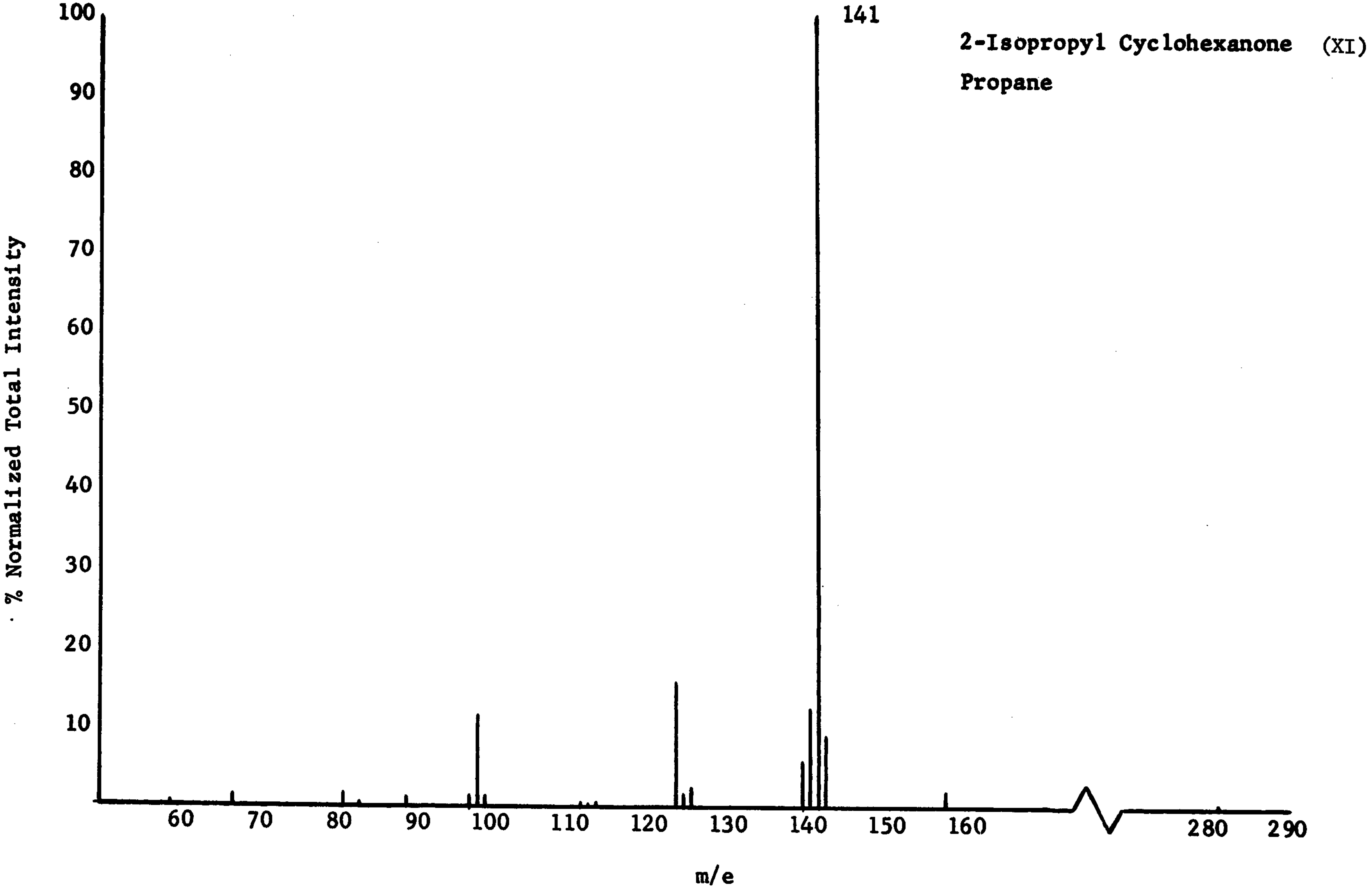

Figure 15 Chemical ionization spectrum of 2-isopropylcyclohexanone using propane reagent

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* University of Utah Salt Lake City, Utah 84112	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

CHEMICAL IONIZATION STUDIES WITH A DuPONT 21-490 ANALYTICAL MASS SPECTROMETER

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Technical Report - February 1971 to January 1972

5. AUTHOR(S) *(First name, middle initial, last name)*

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JEAN H. FUTRELL

6. REPORT DATE February 1972	7a. TOTAL NO. OF PAGES 40	7b. NO. OF REFS 5

8a. CONTRACT OR GRANT NO. F33615-71-C-1172 b. PROJECT NO. 7367 c. Task No. 736702 d.	9a. ORIGINATOR'S REPORT NUMBER(S) 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* AFML-TR-72-35

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433

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DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Analytical mass spectrometer						
Chemical ionization						
Propane						
Ketones						

☆U.S.Government Printing Office: 1972 — 759-084/506

UNCLASSIFIED
Security Classification