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TECHNICAL REPORT 9114

MASS SPECTROMETRIC CHARACTERIZATION OF
N,N'-BIS(2,4,6-TRICHLOROPHENYL)UREA

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<p>The title compound, an environmentally persistent contaminant of estuarine sediments, has been characterized by direct exposure desorption mass spectrometry. Under electron impact and positive chemical ionization conditions fragmentation to trichloroanilinium species was the predominant process, and the respective molecular ion species were less abundant. In methane enhanced negative chemical ionization mass spectrometry the predominant process was loss of hydrogen and chlorine from the molecular anion. Relative abundances of the molecular ion species in the two chemical ionization modes were similar.</p>			
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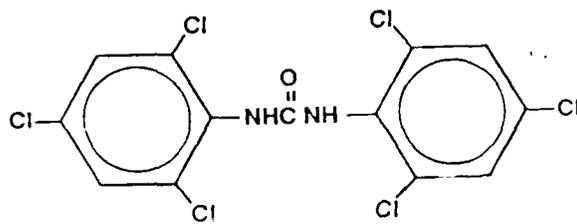
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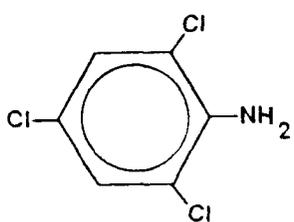
INTRODUCTION

In the early 1980s there was widespread concern over environmental and health hazards due to contamination of aquatic sediments in certain areas of the Gunpowder River adjacent to Aberdeen Proving Ground, MD, with a chlorinated compound initially believed to be 2,4,6-trichloroaniline. In 1982 this compound was positively identified as *N,N'*-bis(2,4,6-trichlorophenyl)urea (1), and was shown to decompose cleanly on introduction to the mass spectrometer by both gas chromatography (GC) and by solid probe to a mixture of 2,4,6-trichloroaniline (2) and 2,4,6-trichlorophenylisocyanate (3), which was readily separable by GC[1]. The urea itself, however, has not been previously characterized by mass spectrometry.

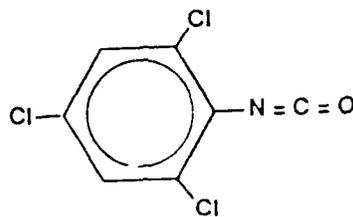
Recently we observed that the thermally labile acetylnitramines 1-acetylhexahydro-3,5-dinitro-1,3,5-triazine (TAX) and 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX), environmentally important byproducts of the manufacture of the nitramine munitions compounds RDX and HMX, were readily introduced into the mass spectrometer without decomposition by means of a direct exposure probe (DEP)[2]. Samples were introduced by desorption from a rapidly heated rhenium filament inserted directly into the electron beam or reagent gas plasma. This method proved to be equally applicable for characterization of the urea 1.



1



2



3

INSTRUMENTATION AND METHODS

The instrument used was a Finnigan MAT TSQ-70B with a 20 kV dynode detector. Operating parameters in electron impact (EI) mode and in both chemical ionization (CI) modes were electron energy 70 eV, emission current 200 μ A, dynode 6-8 kV, electrometer amplifier gain 10^{-4} mA V⁻¹ and scan time 0.5 s. Source temperature for the EI spectra was 150 °C. CI spectra were determined at 80 °C with methane as the reagent gas at 0.6 Torr. The rhenium filament was heated at 16-17 °C s⁻¹ to desorb the samples. Introduction by GC was made at 50 °C with a Varian on-column capillary injector, and the 15 m x 0.25 mm DB5 column was heated to 250 °C at 20 °C min⁻¹. The GC/MS transfer line was maintained at 250 °C.

Urea 1 was synthesized by the following modification of the patent literature [3]. A mixture of urea (9.0 g), 2,4,6-trichloroaniline (2, 9.2 g), glacial HOAc (80 mL), and H₂O (0.8 mL) was allowed to reflux while conc H₂SO₄ (8 mL) was added slowly during a 2 hr period. Reflux was continued 3 hr longer, then the mixture was cooled and the white crystalline precipitate was collected by suction filtration and washed with water. The resulting urea 1 (0.8 g) had mp 330-340 °C (d) (lit. mp 326-327 °C) [4] and was pure by HPLC.

RESULTS AND DISCUSSION

Electron Impact

All chlorine-containing compounds display ion clusters due to the stable isotopes ³⁵C and ³⁷C, which have natural abundances of approximately 3 to 1, respectively. The relative abundances of the cluster ions are thus characteristic of the number of chlorine atoms in the molecule or the fragment. Electron impact data for urea 1, displayed in Figure 1 and summarized in Table 1, showed a weak but distinct isotope cluster for the 4 most abundant molecular ion species (a, a+2, a+4, a+6) at m/z 416, 418, 420, and 422. The cluster due to loss of chlorine from the molecular ion was of greater relative abundance, and 7 species were clearly observable. The facile loss of chlorine observed for aromatic ureas with an ortho chlorine substituent on electron impact has been attributed to stabilization of a resulting 5-membered oxonium ion [5]. Of the fragment ion clusters, [Cl₃ArNH₂]⁺ predominated and [Cl₃ArNCO]⁺ was seen to a much lesser extent.

Sample introduction by direct exposure desorption has been less frequently used in EI than in CI mode, and the molecular ion species observed in EI mode have been variable. Cases of only molecular ions [6,7], only proton adducts [2,8,9], both species [10], and no molecular ion species [11] have been documented. It is noteworthy that in the case of 1 the relative intensities of the cluster are in accord with the molecular ion species of a hexachloro compound [12].

These characteristics of the intact urea 1 are in marked contrast to its pyrolysis products 2 and 3, which in the earlier work [1] appeared as two distinct peaks on GC after pyrolysis in the injector at 250 °C and as a mixture of products on introduction by heated solid probe. A similar mixture was obtained in this work when urea 1 was decomposed by pyrolysis in the heated GC/MS transfer line (Figure 2 and Table 2).

Chemical Ionization

The PCI spectrum is displayed in Figure 3. While the cluster for the protonated trichloroaniline fragment was still the most abundant, the protonated molecular ion cluster was second in relative abundance, and 9 species were observed with the anticipated relative ratios (Table 3). The cluster due to the protonated isocyanate fragments was third in relative abundance. Loss of chlorine or hydrogen and chlorine was not observed in PCI mode.

In contrast, by far the most abundant species in NCI mode was the anion corresponding to loss of hydrogen and chlorine from the molecular anion (Figure 4). A similar prominent anion corresponding to loss of hydrogen and chlorine was observed in the methane and methane-oxygen enhanced NCI spectra of a number of polychloroanisoles. It was shown that chlorine was lost exclusively from the ortho positions and hydrogen from the methyl group [13]. Also, in cases where ortho hydrogen was present the molecular ion species observed was $[M-1]^-$ rather than M^- . Thus the most abundant anion cluster for 1 most probably arose from loss of ortho chlorine and urea hydrogen. The relative abundances of the cluster for the molecular anion of 1 (Table 4) also support the fact that there is no ortho hydrogen to be lost.

CONCLUSION

The observed mass spectra are fully in accord with the assigned structure of the symmetrical hexachlorophenylurea, and further demonstrate the general utility of the desorption introduction method for characterization of involatile, thermally labile molecules. In contrast to its thermal decomposition products 2 and 3, which are chemically and photolytically reactive, urea 1 is chemically very stable and unlikely to biodegrade appreciably, and consequently would be expected to persist for prolonged periods in aquatic sediments. If a need for environmental monitoring should surface, this study has shown that DEP mass spectrometry in both PCI and NCI modes would constitute a unique and specific procedure for the detection of trace amounts of 1 without decomposition.

Table 1. Electron Impact Mass Spectrum of 1

Identity of Cluster	m/z	Observed Relative Abundance	Adjusted Relative Abundance	Natural Abundance ^a
[ArNH ₂] ⁺	195	100		100
	196	14		
	197	90		97.5
	198	9		
	199	27		32
	200	2		
	201	3		3.4
[ArNCO] ⁺	221	3.6	90	100
	222	0.9		
	223	4.0	100	97.5
	224	0.8		
	225	1.3	32	32
	226	0.2		
[M-C1] ⁺	381	2.2	81	61.5
	382	0.2		
	383	2.7	100	100
	384	0.7		
	385	2.0	74	65
	386	0.2		
	387	0.9	33	21
[M] ⁺	416	0.2	29	51
	418	0.7	100	100
	420	0.4	57	81
	422	0.2	29	35

^aData from reference 12, pp 275-277.

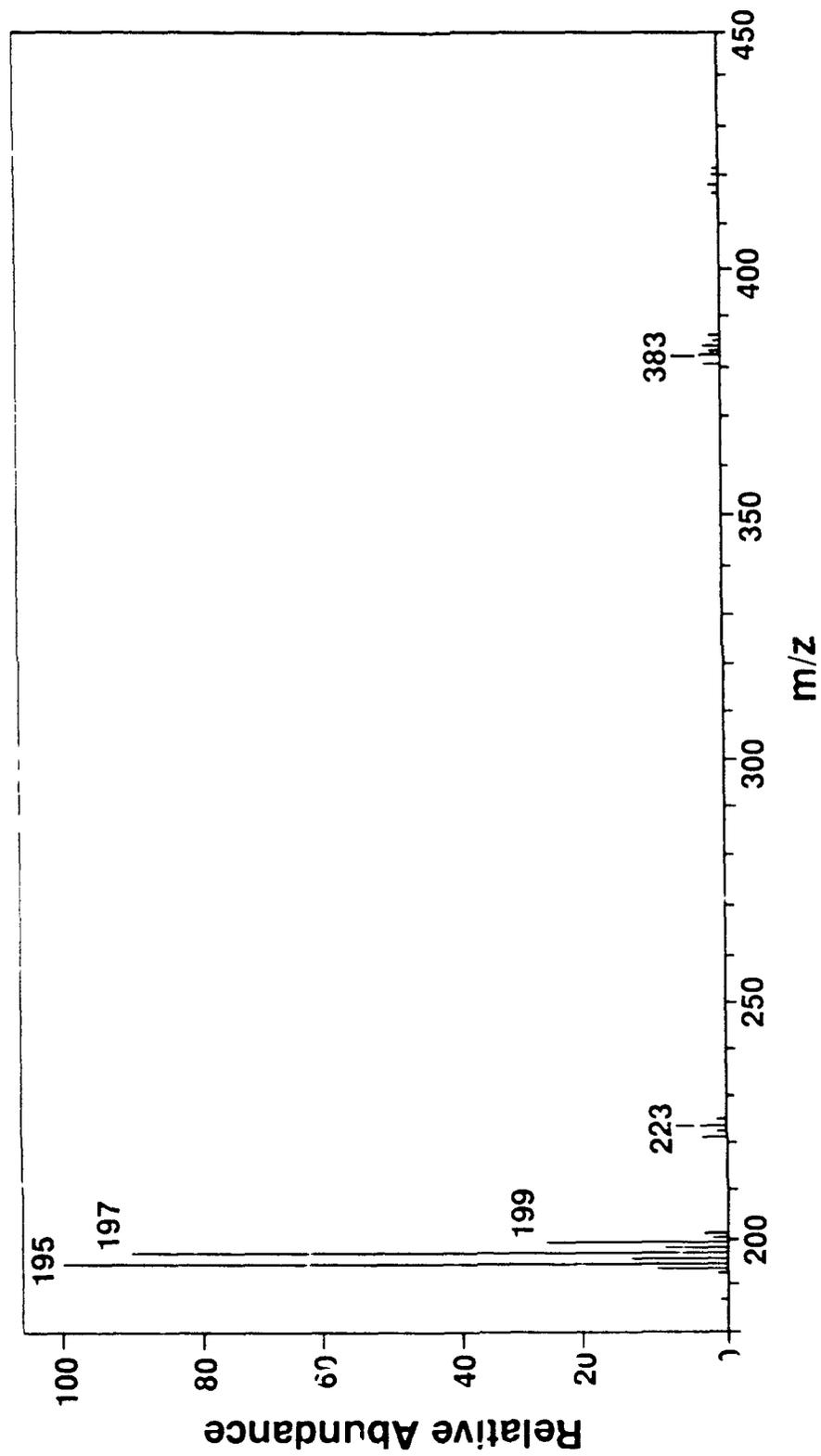


Figure 1. Electron Impact Mass Spectrum of 1

Table 2. Electron Impact Mass Spectra of Mixture from Pyrolysis of 1

Cluster Identity	m/z	Observed Relative Abundance ^a	Observed Relative Abundance ^b	Natural Abundance ^c
[ArNH ₂] ⁺	195	100	100	100
	196	8		
	197	86	90	97.5
	198	6		
	199	25	30	32
	200	2		
	201	3		3.4
[ArNCO] ⁺	221	56	45	100
	222	4		
	223	55	44	97.5
	224	4		
	225	18	15	32
	226	1		

^aThis work.

^bEstimated from reference 1.

^cData from reference 12, p 275.

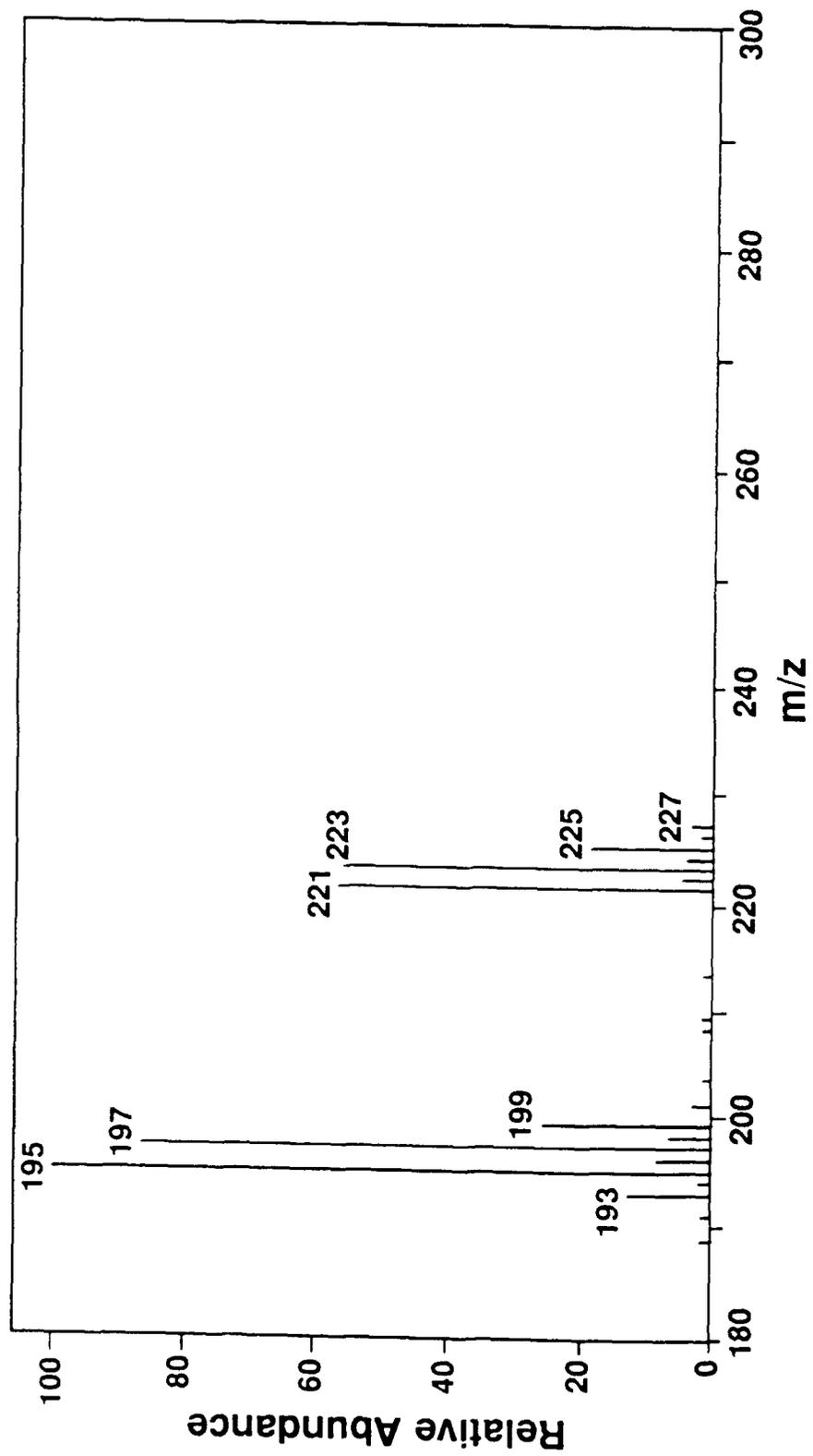


Figure 2. Electron Impact Mass Spectrum of Mixture from Pyrolysis of **1**

Table 3. Positive Chemical Ionization Mass Spectrum of 1

Identity of Cluster	m/z	Observed Relative Abundance	Adjusted Relative Abundance	Natural Abundance ^a
[ArNH ₃] ⁺	195	66		
	196	100		100
	197	65		
	198	85		97.5
	199	24		
	200	23		32
	201	3.5		
	202	1.5		3.4
[ArNHCO] ⁺	222	15	68	100
	223	4		
	224	22	100	97.5
	225	3		
	226	13	59	32
	227	1.5		
[MH] ⁺	417	17	45	51
	418	4		
	419	38	100	100
	420	4		
	421	31	81	81
	422	4		
	423	13	34	35
	424	1.5		
425	3	8	8.5	

^aData from reference 12, pp 276-277.

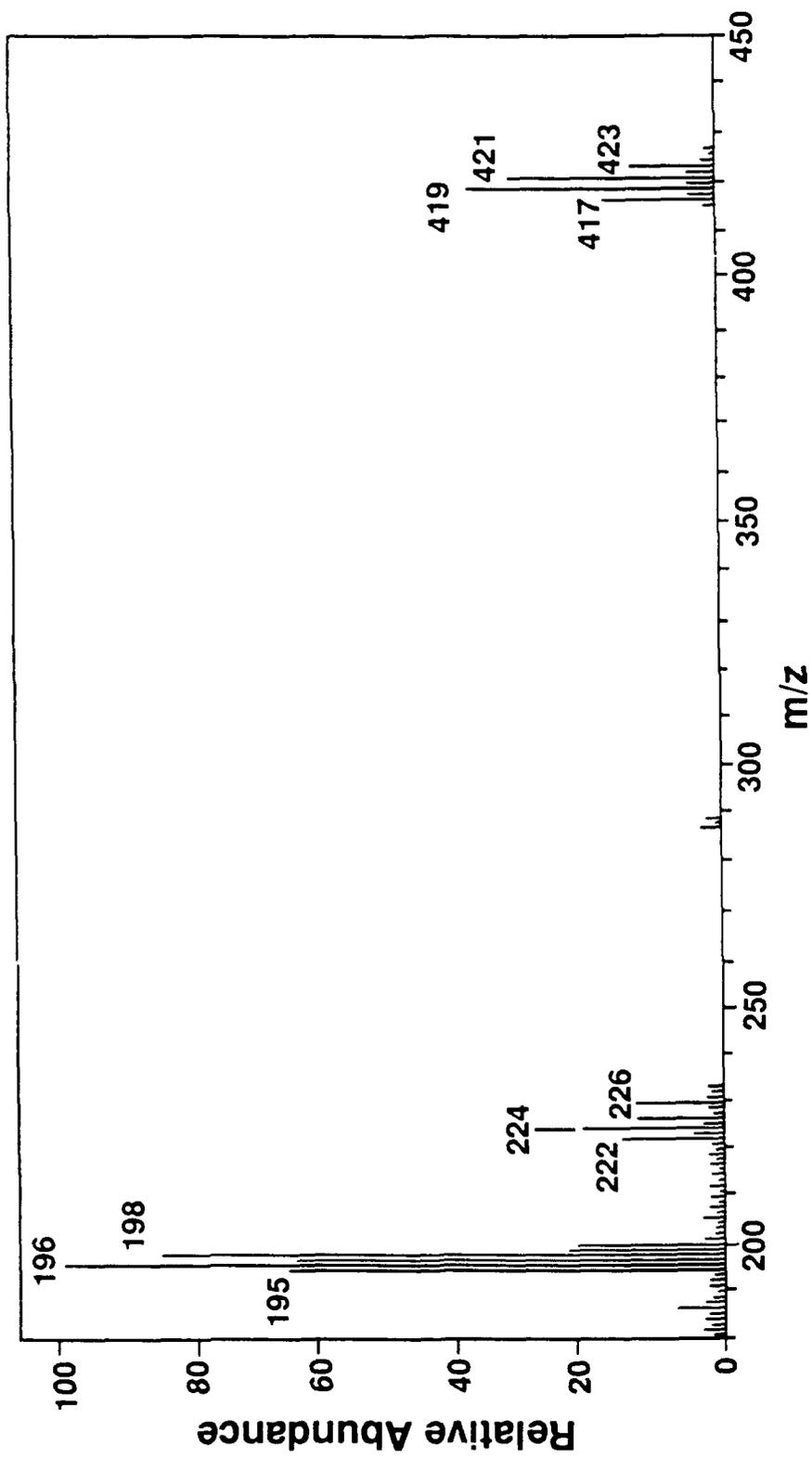


Figure 3. Positive Chemical Ionization Mass Spectrum of **1**

Table 4. Methane Enhanced Negative Chemical Ionization Mass Spectra of 1

Identity of Cluster	m/z	Observed Relative Abundance ^a		Adjusted Relative Abundance		Natural Abundance ^b
[ArNCO] ⁻	221	16	12	100	100	100
	223	15	11	94	92	97.5
	225	5	3	31	25	32
[M-2HCl] ⁻	344	28	20	78	74	77
	345	10	6			
	346	36	27	100	100	100
	347	9	6			
	348	16	13	44	48	49
	349	4	2			
[M-HCl] ⁻	350	4	2	11	7	10.5
	380	75	68			61.5
	381	11	10			
	382	100	100			100
	383	13	16			
	384	52	64			65
	385	8	11			
[M] ⁻	386	16	21			21
	387	2	3			
	388	2	3			3.4
	416	14	15	56	50	51
	417	2	3			
	418	25	30	100	100	100
[M] ⁻	419	4	4			
	420	19	24	76	80	81
	421	3	3			
	422	7	10	28	33	35
	423	1	1			
	424	2	2	8	7	8.5

^aRelative abundances differed significantly on successive samplings.

^bData from reference 12, pp 276-277.

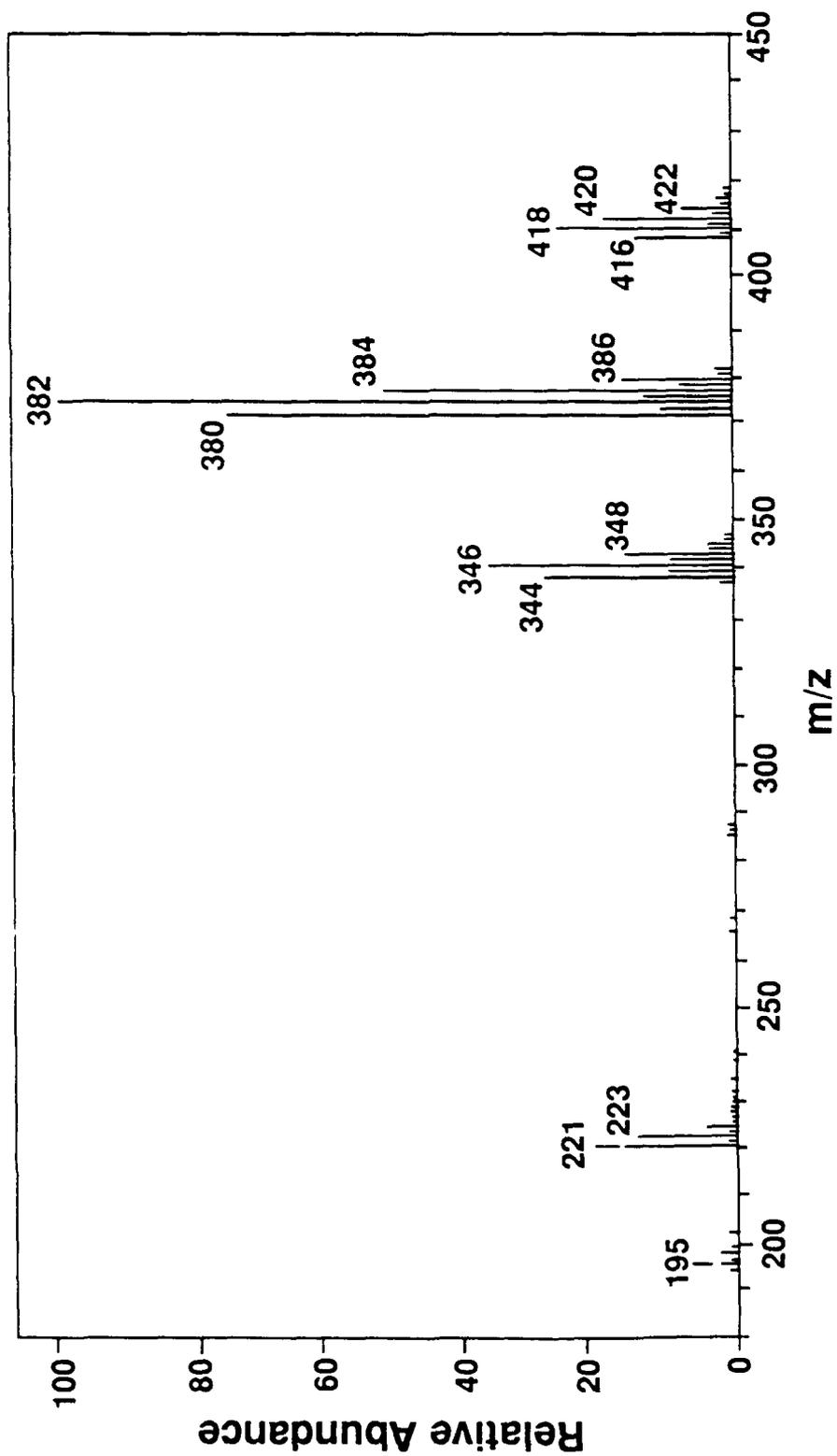


Figure 4. Methane Enhanced Negative Chemical Ionization Mass Spectrum of **1**

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