Table 3.1 A comparison of various adsorbents [19,71-75,79,82]

	ADSORBENT	COMPOSITION	SURFACE AREA (m^2/g)	PORE DIAMETER (nm)	APPLICATIONS	ADVANTAGES	DISDAVANTAGES
CARBON – BASED	Activated carbon Anasorb 747	Coconut/petroleum based charcoal	800-1000	2.0 / 1.8-2.2	Non-specific i.e. Most organic and inorganic compounds. Non-polar, polar, reactive and/or volatile. Mercury-vapour.	Cheap, efficient, permanent gases not adsorbed – H_2, N_2, O_2, CO, CH_4. Anasorb absorbs less H_2O and desorption efficiencies for polar compounds are improved.	Polar compounds irreversibly adsorbed. Incomplete desorption. H_2O reduces sorption of other compounds. Catalytic activity. Reacts with oxygen or sulphur derivatives.
	Graphitised carbon black Carbotraps	Pre-treated carbon black under vacuum and inert gas/ reductive atmosphere at 3000°C			Non-specific, as above.	No irreversible adsorption sites. No retention of H_2O and low molecular mass compounds (CO_x, CH_4)	High desorption temperatures (400°C) required. Tiny particles of carbon can enter desorption unit.
	Carbon molecular sieves Carbosieves	Thermally decomposed polymer eg. polyvinyl chloride			Adsorption of hydrocarbons and low-boiling C1-C4 hydrocarbons, methyl formate and alkyl mercury compounds.	High capacity for small volatile molecules. Suitable for themal desorption.	Inefficient retention of polar compounds. Solvent with high heat of adsorption required for displacement of adsorbates. H_2O can block cryotrap.

INORGANIC	Silica gel	Si-OH groups on surface	100-800	2-4	Polar compounds from air. Amines, halogens, oxygen derivatives, organo-metallics, MeOH, HCHO and DMF. Silica gel is often used as a substrate for coating with derivatising reagents.	Cooling the sorbent allows trapping of C1-C4 hydrocarbons	Hydrophilicity decreases sorption capacity. Thermal desorption difficult. Silica gel retains H_2O and CO_2
	Aluminium oxide	Al_2O_3					
	Molecular sieves	Zeolites	Varied	Varied	Toxic inorganic compounds. Small conc. of H_2S	Thermally desorbed at 240°C/extract with ice H_2O	Organic compounds are irreversibly adsorbed excl. HCHO, acrolein and certain S-compounds. H_2O block cryotrap
POROUS POLYMERS	Tenax	2,6-diphenyl-p-phenylene oxide	19	140	Organic bases, neutral and high boiling compounds. Chlorohydrocarbons. Support for derivatising reagents. Broad trapping range of compounds of varied molecular mass and polarity.	Tenax has a high thermal limit 350-400°C. Ideal for thermal desorption.	Not suited to solvent extraction due to low capacity for volatiles and is incompatible with many solvent systems.
	XAD-2 (Amberlite, Chromosorb 102)	Copolymer of 2,6-diphenyl-p-phenylene oxide in which one moiety is styrene or ethylvinylbenzene and the other monomer a polar vinyl compound.	300-400	8.5	Nitroso-compounds and polychlorinatedbiphenyls, aromatic, aliphatic nitro-compounds.	XAD's, Porapaks and Chromosorbs come in wide ranges of polarity. Chromosorb 106 greater capacity than tenax, suited to thermal desorption.	
	Porapak		600-650	7.5	Depending on polarity. Non-polar to polar compounds can be adsorbed. Chromosorbs adsorb inorganic compounds		Polar Porapaks retain H_2O and require great amount of energy to remove sorbates. Can't withstand high temp.
	Chromosorb101, 103, 104, 106, 108.		50 varied	300-400 varied			

APPENDIX 2

CALCULATION OF GAS CONCENTRATIONS

The gas standard in a dilution system provides a certain concentration of gas. The concentration, C, with units part-per-million volume/volume (ppm v/v) can be calculated from the following equation:

$$C = [f / (f + F)] \times 10^6 \qquad (1)$$

Where f is the permeation/diffusion rate with units ml/min. F is the flow rate of the diluting gas in ml/min. Equation 1 can be simplified, since F >> f, to:

$$C = (f / F) \times 10^6 \qquad (2)$$

The permeation/diffusion rate, however, is usually determined gravimetrically in ng/min. It is important then to convert mass of gas to volume of gas, using the following equation:

$$f = (22.4 / M) \times (T / 273) \times (760 / P) \times r \times 10^{-6} \qquad (3)$$

The molar gas volume is given as 22.4 L/mol. M, is the molecular mass of the compound in g/mol. T, is the absolute temperature in Kelvin (K) at which permeation/diffusion is occuring. P, is the pressure in mm/Hg, at which permeation/diffusion rate is measured and r, is the permeation/diffusion rate in ng/min.

Equation 3 is substituted into equation 2 resulting in:

$$C = (22.4 / M) \times (T / 273) \times (760 / P) \times (r / F) \qquad (4)$$

At 25°C and atmospheric pressure (760mmHg), equation 4 reduces to:

$$C = (24.45 / M) \times (r / F) \qquad (5)$$

From equation 4 and 5 it can be seen that the concentration of the standard is dependant on the diluting gas flow rate. The formaldehyde gas concentration, in an 80°C oven, will be worked out below using equation 4.

M (g/mol)	T (K)	P (mmHg)	r (ng/min)	F (ml/min)	C (ppm v/v)
30	353	760	1.333	10	0.1287

The acetaldehyde concentration at 25°C, is worked out similarly using equation 5.

M (g/mol)	r (ng/min)	F (ml/min)	C (ppm v/v)
44	40	10	2.218

To convert the units ppm (v/v) for a gas **z**, to $\mu g/m^3$ ie. ng/L, the following method can be used:

$$1 \text{ ppm (v/v) } \mathbf{z} = \frac{1 \text{ L } \mathbf{z}}{10^6 \text{ L air}} \qquad (6)$$

assuming the ideal gas law is valid under ambient conditions, 25°C and 760mmHg, then:

$$1 \text{ ppm (v/v) } z = \frac{(1\text{ L } \mathbf{z} / 22.4) \times \text{M } (\mathbf{z}) \times 10^{6}\ \mu\text{g/g}}{(10^{6}\text{ L}) \times (298\text{K}/273\text{K}) \times 10^{-3}\ \text{m}^{3}/\text{L}} \qquad (7)$$

$$= 40.9 \times \text{M } (\mathbf{z})\ \mu\text{g/m}^{3} \text{ or ng/L}$$

[1 m^3 = 1000 L]

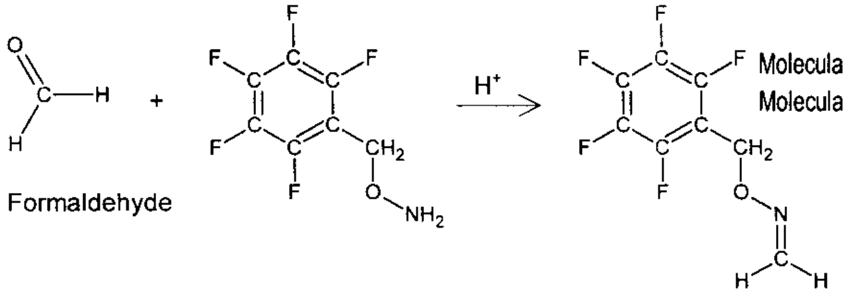
For example, a 1 ppm (v/v) HCHO atmosphere is equivalent to 123 ng/L or 1.23 ng/ml.

With these units of measurement one can easily determine the concentration of the gas in an atmosphere, and if the collection volume is known, the mass of compound collected can also be determined.

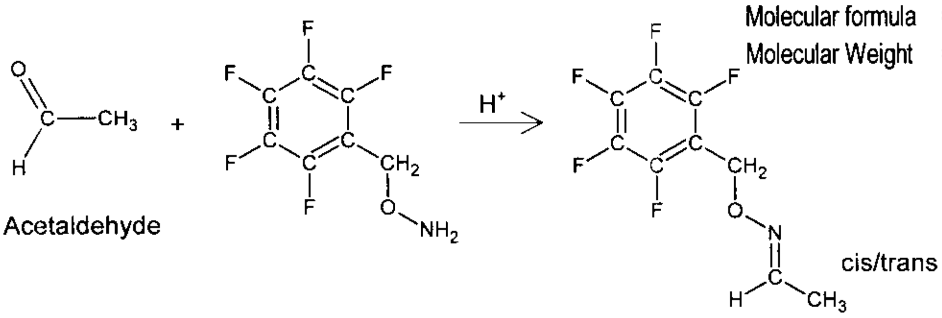
APPENDIX 3

PFBHA - ALDEHYDE REACTION SCHEMES

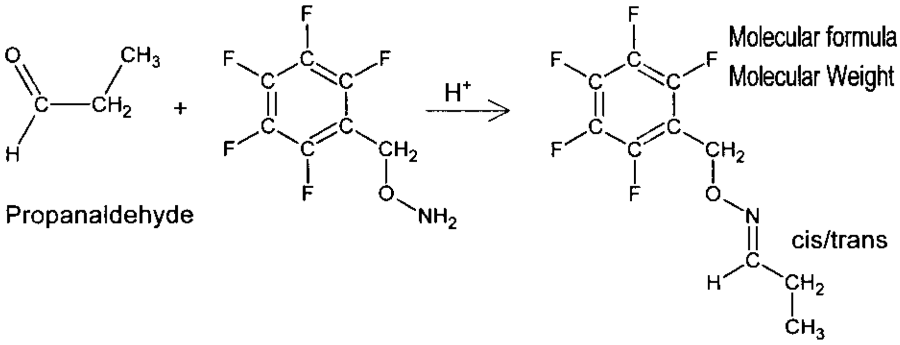
ALDEHYDE + **PFBHA** ⟶ **OXIME**



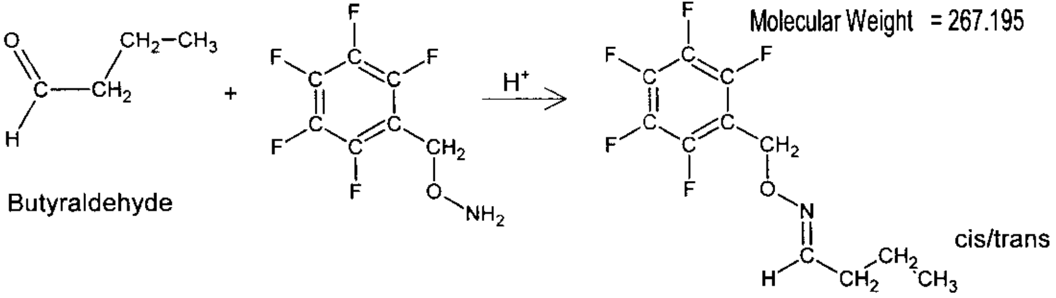
Molecular formula = $C_8H_4F_5NO$
Molecular Mass = 225.116



Molecular formula = $C_9H_6F_5NO$
Molecular Weight = 239.142



Molecular formula = $C_{10}H_8F_5NO$
Molecular Weight = 253.169

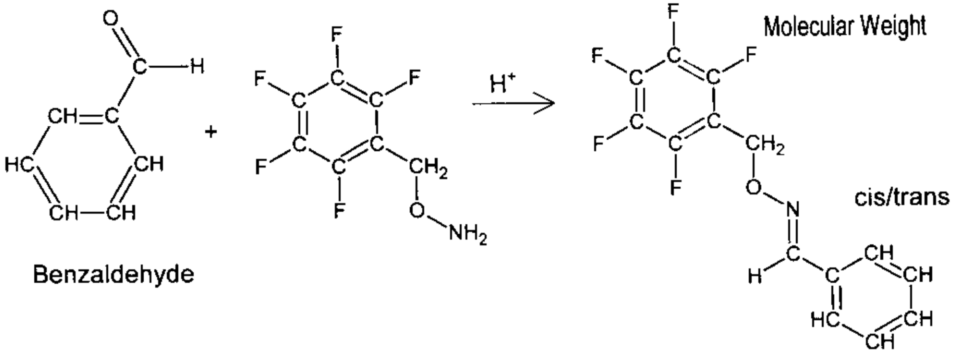


Molecular formula = $C_{11}H_{10}F_5NO$
Molecular Weight = 267.195

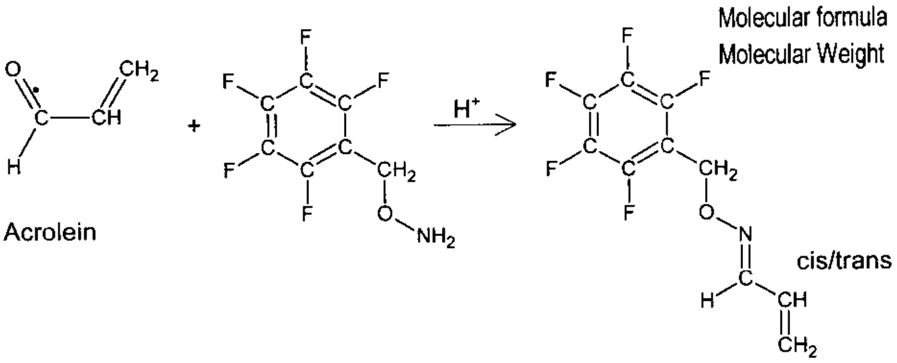
APPENDIX 3

(continued)

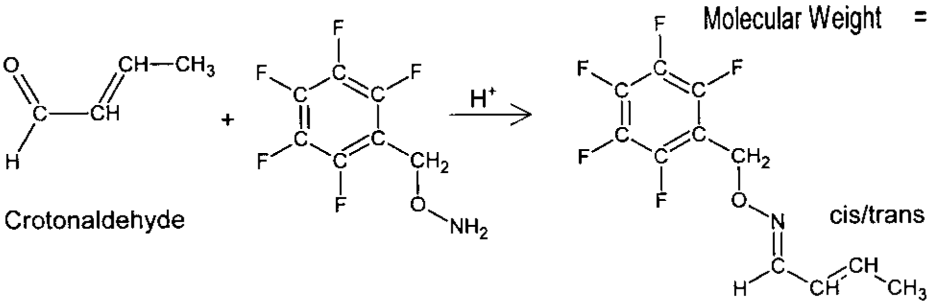
Molecular formula = $C_{14}H_8F_5NO$
Molecular Weight = 301.211



Molecular formula = $C_{10}H_6F_5NO$
Molecular Weight = 251.153

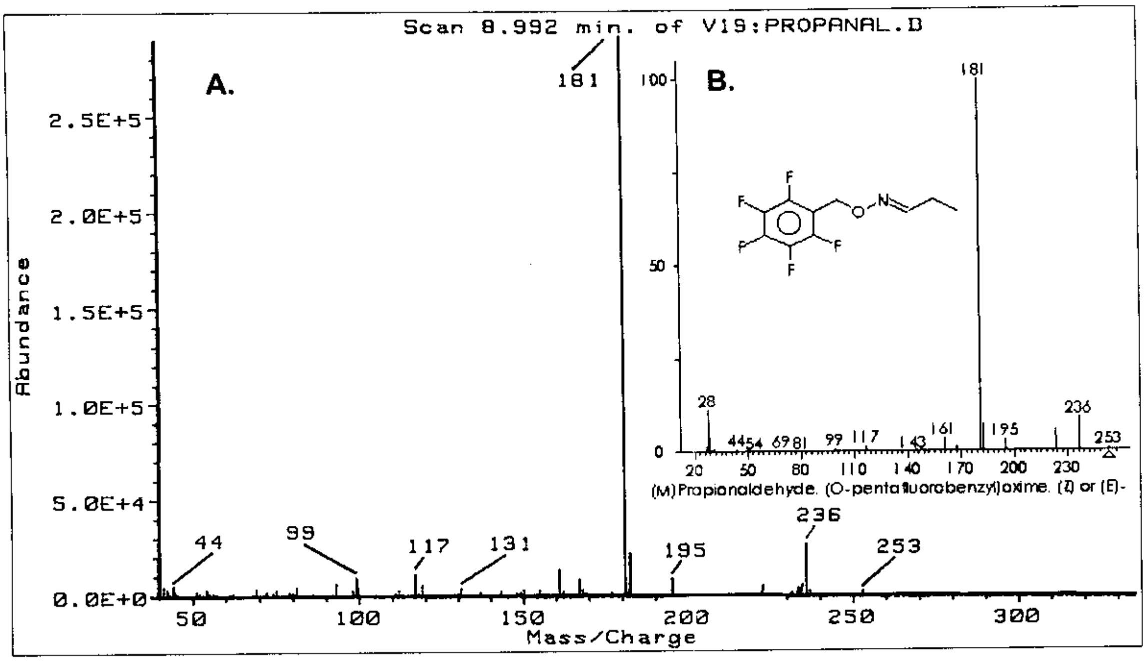


Molecular formula = $C_{11}H_8F_5NO$
Molecular Weight = 265.179

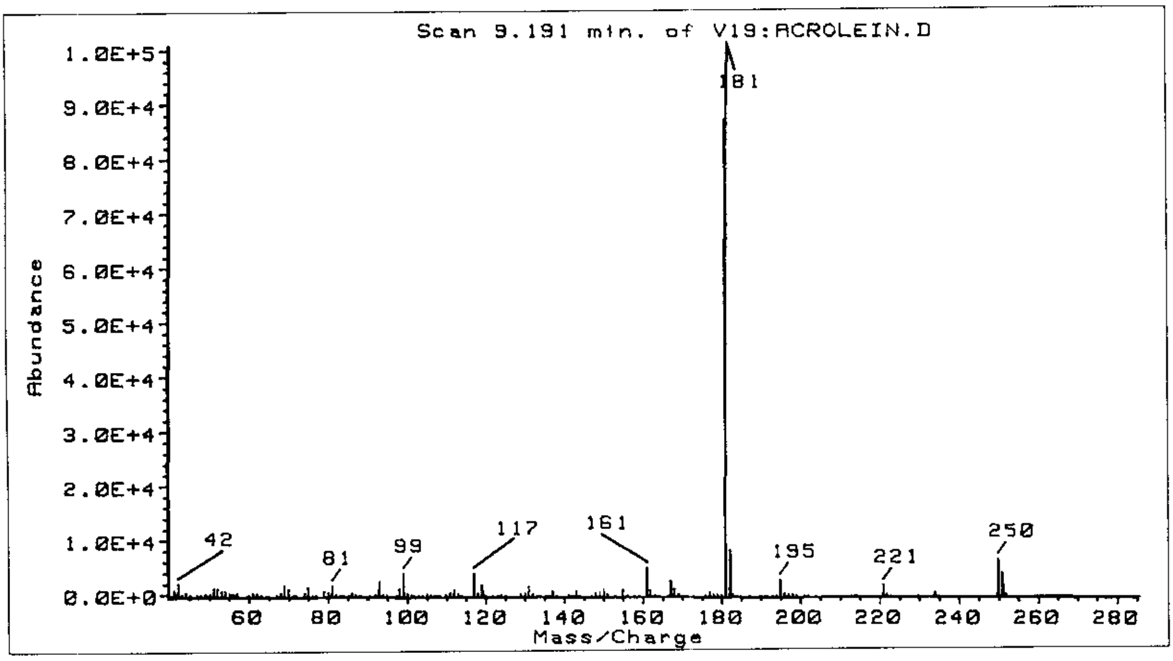


APPENDIX 4

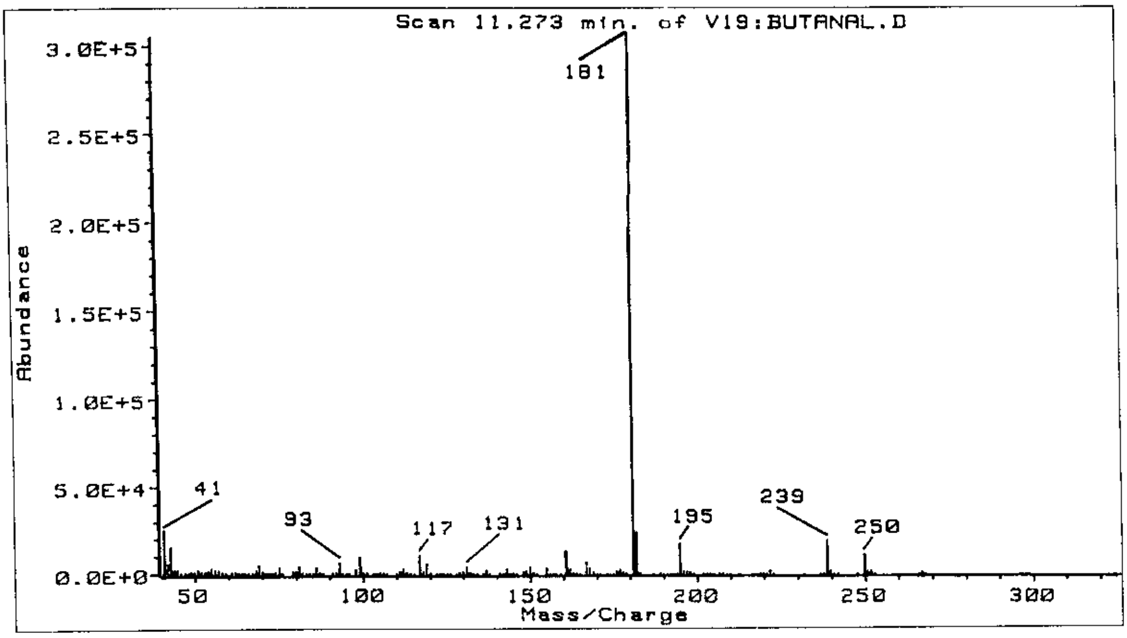
EI-MASS SPECTRA OF PFBHA ALDEHYDE-OXIMES



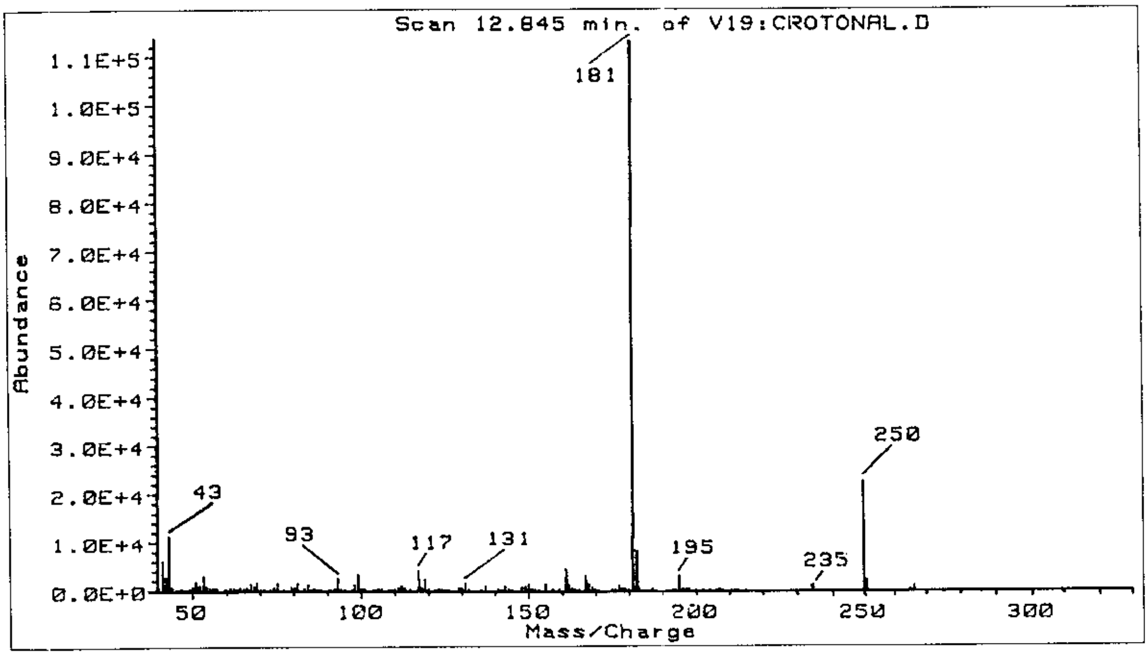
Appendix 4.1. **A.** Obtained EI-Mass spectrum of the propanal-oxime.
B. NIST library EI-Mass spectrum of the propanal-oxime.



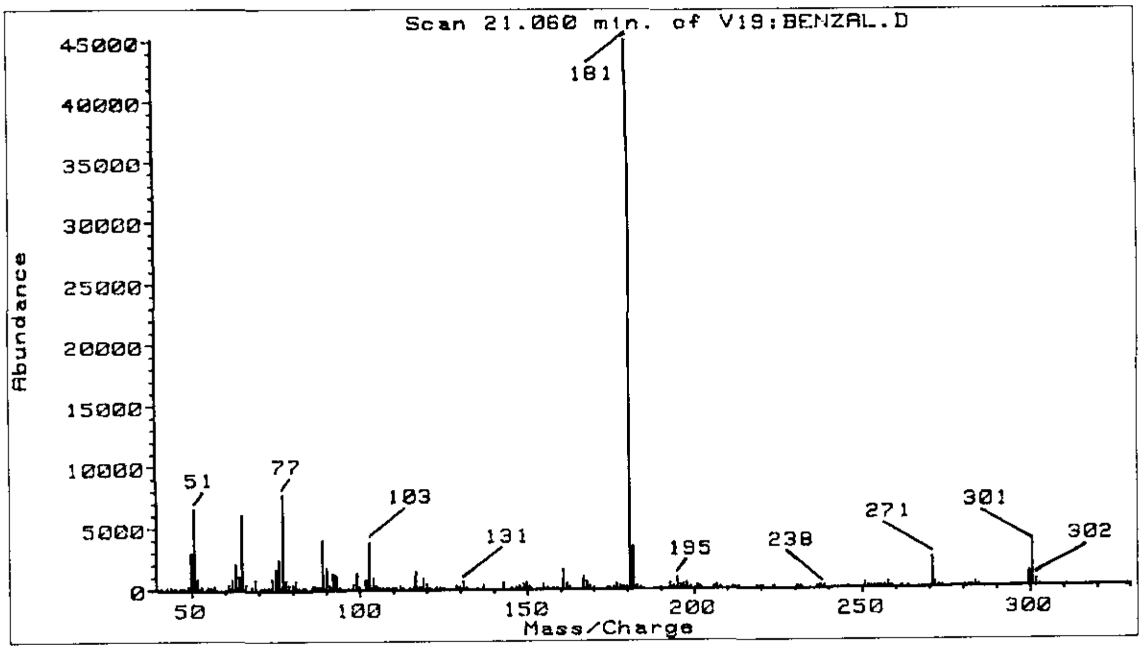
Appendix 4.2. Obtained EI-Mass spectrum of acrolein-oxime.



Appendix 4.3. Obtained EI-Mass spectrum of butanal-oxime.



Appendix 4.4. Obtained EI-Mass spectrum of crotonal-oxime.



Appendix 4.5. Obtained EI-Mass spectrum of the benzaldehyde-oxime.