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Note

Gas chromatographic-mass spectrometric identification of *o*-chloroacetophenone, *o*-chlorobenzylidenemalononitrile and dibenz[*b,f*]-1:4-oxazepine

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The two most commonly used irritants namely CN (*o*-chloroacetophenone) and CS (*o*-chlorobenzylidenemalononitrile) had been analyzed by gas-liquid chromatography (GLC) as early as in 1971¹. CS in the form of an unknown sample was characterized by IR, NMR and mass spectral (MS) data². More recently³, reversed-phase high-performance liquid chromatography (HPLC) has been successfully employed in our laboratory for determination of these two irritants together with CR (dibenz[*b,f*]-1:4-oxazepine). However, both GLC and HPLC have limitations when the question of identification arises and more so when confronted with an unknown sample. Since MS identification is more dependable in terms of specificity and precision even in the nanogram range, the GC-MS procedure now described further increases the analytical potential for these compounds.

EXPERIMENTAL

Apparatus

A JEOL gas chromatograph-mass spectrometer Model JMS-DX 300 combined with a JMA 2000 data-analysis system was used. The separation of a mixture of the three compounds (each 10 $\mu\text{g}/\text{ml}$ in acetone) was achieved on a 1-m 5% OV-17 column.

Chemicals

The acetone used was of analytical grade. The compounds were synthesized by the procedure reported previously³. Their purity before analysis was checked by spectroscopic methods, thin-layer chromatography and elemental analysis.

Procedure

The mass spectrometer was calibrated with perfluorokerosene (PFK) and the data system was set for recording reconstructed ion chromatograms. The column was programmed from 25 to 250°C at a rate of 8°C/min. The injector and separator temperatures were 150 and 200°C respectively. Samples of 1 μl were injected. The mass spectra were obtained by electron impact ionization at 70 eV.

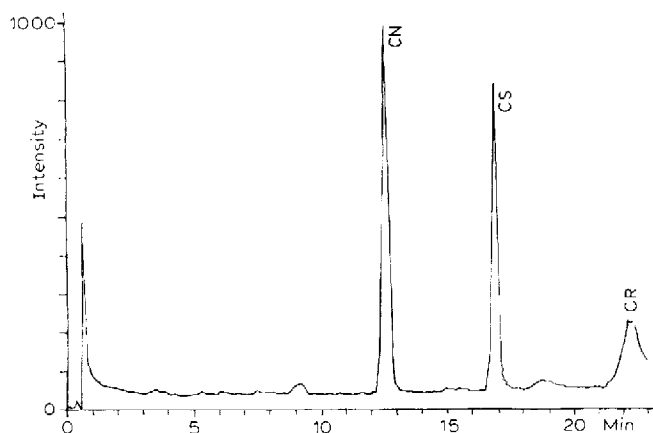


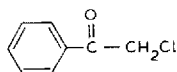
Fig. 1. Reconstructed ion chromatogram of CN, CS and CR.

RESULTS AND DISCUSSION

The reconstructed ion chromatogram (Fig. 1) shows good separation of the three compounds within 22 min. However, with a heating rate of 16°C/min, the separation time can be decreased to approximately 10 min. Mass spectral peaks are given in Tables I, II and III for CN, CS and CR respectively together with their structural formulae and molecular weights. The data in Table II are in agreement with those in ref. 2. However, our experiment gave the molecular ion peak as the base peak, in contrast to m/e 153 as the base peak observed previously. The spectrum of CN contains a prominent molecular ion peak at m/e 154 with isotope peaks. The base peak at m/e 105 is due to benzoyl ion caused by loss of CH_2Cl from the molecule.

TABLE I

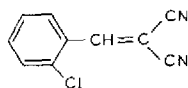
MASS SPECTRAL CHARACTERISTICS OF CN ($M = 154$)



m/e	Rel. intensity
57.0	3.0
65.0	2.2
77.0	154.8
78.0	13.5
91.0	20.7
102.0	3.3
104.0	3.3
105.0	1000.0
106.0	76.4
107.0	3.3
154.0	28.1
155.0	1.9
156.0	8.0

TABLE II

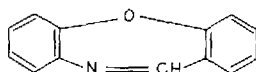
MASS SPECTRAL CHARACTERISTICS OF CS (M = 188)



<i>m/e</i>	<i>Rel. intensity</i>
126.0	56.8
137.0	65.8
153.0	724.5
154.0	77.3
161.0	99.4
188.0	1000.0
189.0	114.6
190.0	319.2

TABLE III

MASS SPECTRAL CHARACTERISTICS OF CR (M = 195)



<i>m/e</i>	<i>Rel. intensity</i>
51.0	68.9
65.0	247.7
77.0	52.2
93.0	108.1
119.0	64.6
120.0	1000.0
121.0	162.3
165.0	53.7
167.0	105.8
195.0	61.5
196.0	453.1

Loss of the carbonyl group from this moiety gives rise to a peak at *m/e* 77 due to $(C_6H_5)^+$. For CR, the molecular ion peak at *m/e* 195 and its protonated species at *m/e* 196 are quite prominent. The base peak at *m/e* 120 is due to loss of a phenyl moiety and the peak at *m/e* 167 is formed by loss of $(HCN + H)^+$ from the CR molecule. The phenyl ion is also present at 77. Cleavage of the phenyl ring yields $(C_5H_5)^+$ and a peak at *m/e* 65.

ACKNOWLEDGEMENTS

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REFERENCES

- 1 S. Sass, T. L. Fisher, M. J. Jascot and J. Herban, *Anal. Chem.*, 43 (1971) 111.
- 2 H. W. Avdovich, A. By. J. C. Ethier and G. A. Neville, *Can. Soc. Forens. Sci. J.*, 14 (1981) 172.
- 3 C. D. Raghuvveeran and R. C. Malhotra, *J. Chromatogr.*, 240 (1982) 243.