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Note

Response of nitramines in the thermal analyzer

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There is no reason to doubt the high selectivity for N-nitroso compounds of detection systems such as the thermal energy anlyzer (TEA), which are based on the determination by chemiluminescence of nitric oxide produced under mild conditions of pyrolysis. This has been demonstrated in practice by Gough *et al.*[1], who compared the results obtained by both high-resolution mass spectrometry (MS) of the molecular ions and with use of the TEA for a wide range of foodstuffs, and by collaborative studies on spiked processed meat[2]. On the other hand, while rare in practice, the possibility of a response to compounds other than nitrosamines must always be considered[3,4]. Hotchkiss *et al.*[5] recently found that N-nitrodipropylamine (dipropylnitramine) was responsible for a false TEA peak occurring during the analysis of a herbicide formulation, and they suggested that nitramines could be responsible for false evidence of nitrosamines in other types of herbicide formulation.

We have studied the response of seven nitramines (purity exceeding 99%) that had been synthesised by oxidation of the corresponding nitrosamine for MS studies[6]; all elicited a response from the TEA detector.

The chromatogram shown in Fig. 1 displays the results obtained from separation of a mixture of the seven nitramines and their parent nitrosamines under typical analytical conditions. The compounds were chromatographed on a glass column (2 m × 0.25 in. O.D.) packed with 15% of FFAP on Chromosorb W at 170° and an indicated temperature of 500° in the pyrolysis unit. Under these conditions, two peaks are found for which a nitrosamine and a nitramine have coincident retention times. Thus, N-nitrodimethylamine could be mistaken for N-nitrosodipropylamine, and N-nitrodipropylamine for N-nitrosodibutylamine. Table I shows the retention times of the nitramines relative to the parent nitrosamine and also the relative molar response in the detector. It will be observed that values for the relative retention times (R_T) do not differ widely (*ca.* 1.6–1.9), and that the responses of the nitramines relative to the nitrosamines are all similar. The difference between the values for the relative molar response (0.73–0.87) reported here and the value of 0.5 of Hotchkiss *et al.*[5] can probably be accounted for by differences in conditions in the catalytic pyrolyser, such as temperature or state of the catalyst. Doerr and Fiddler[7], who used UV irradiation to destroy nitrosamines, found that the TEA gave negligible response to the reaction products, although Althorpe *et al.*[8] showed that, under certain conditions, nitramines could be formed. While this lack of

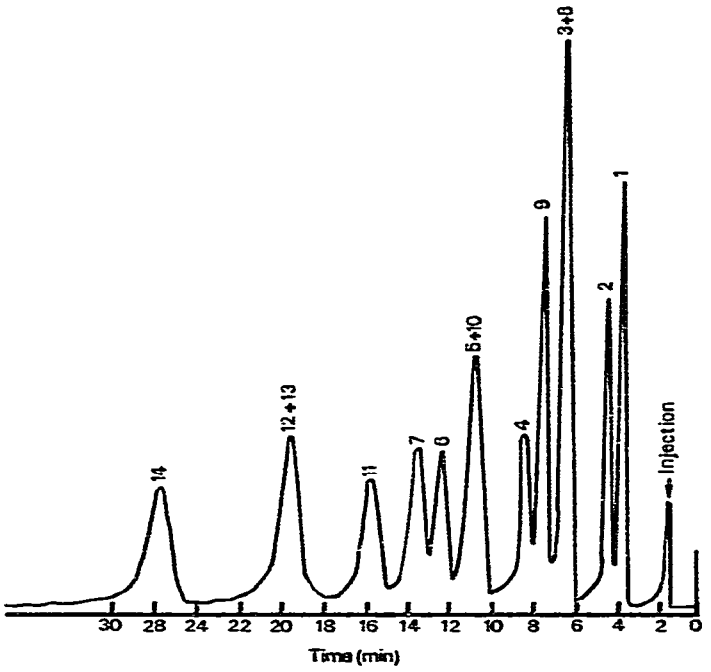

Fig. 1. Chromatogram of a mixture of seven nitrosamines and the corresponding nitramines. Nitrosamine peaks: 1, N-nitrosodimethylamine; 2, N-nitrosodiethylamine; 3, N-nitrosodipropylamine; 4, N-nitrosomethylpentylamine; 5, N-nitrosodibutylamine; 6, N-nitrosopiperidine; 7, N-nitrosopyrrolidine. Nitramine peaks: 8, N-nitrodimethylamine; 9, N-nitrodiethylamine; 10, N-nitrodipropylamine; 11, N-nitromethylpentylamine; 12, N-nitrodibutylamine; 13, N-nitropiperidine; 14, N-nitropyrrolidine.

response might be due to differences in pyrolysis conditions, in our experience, the initial formation of nitramines on irradiation is followed by further degradation. It seems more likely that, under the conditions employed by Doerr and Fiddler[7], nitramines are possibly degraded to amines[9–11], which do not respond in the TEA.

The results from the present study serve to emphasise the importance of

TABLE I

GAS CHROMATOGRAPHIC RETENTION TIMES AND MOLAR RESPONSES OF NITRAMINES RELATIVE TO THE CORRESPONDING NITROSAMINES

Nitramine	R_T*	*Molar response relative to nitrosamine*
N-Nitrodimethylamine	1.77	0.87
N-Nitrodiethylamine	1.72	0.82
N-Nitrodipropylamine	1.69	0.78
N-Nitromethylpentylamine	1.91	0.81
N-Nitrodibutylamine	1.83	0.75
N-Nitropiperidine	1.59	0.80
N-Nitropyrrolidine	1.93	0.73

* $R_T = \frac{\text{retention time for nitramine}}{\text{retention time for corresponding nitrosamine}}$

checking nitrosamines by a second technique. Normally, monitoring of a specific ion by high-resolution MS is the method of choice[12]. However, care must be taken in interpreting the results if the NO^+ ion is employed for monitoring, as nitramines also give this ion[6].

The fact that nitramines respond in the TEA is not without merit. As the R_T values and relative responses are similar, and as nitrosamines are readily converted to nitramines[6,7], this offers a potential preliminary check on the validity of a peak. A test such as this could be useful in checking unknown peaks, particularly those at low concentrations, which are difficult to confirm by MS.

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