

Short Communication

Comparison of mass spectrometric techniques for the analysis of trace amounts of 1-methylaminoanthraquinone, used as smoke dye in exploding money suitcases

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ABSTRACT

Results are presented for different chromatographic and mass spectrometric methods of analysis of the smoke dye MAAQ. When applying gas chromatography various mass spectrometric (ionization) methods can be employed to reach the low picogram range, but for difficult samples full of other dirt preference has to be given to an MS–MS method in the daughter (negative) ion mode. The results of LC–thermospray-MS and LC–thermospray-MS–MS are somewhat less sensitive.

INTRODUCTION

The dye 1-methylaminoanthraquinone (MAAQ), C.I. 60505, is used as a smoke dye in explosive devices installed in suitcases used to transport banknotes. During a robbery, activation of the explosive device causes a cloud of dye particles to be deposited on clothes, banknotes and other objects. Laboratory tests can determine the presence of the dye on articles such as banknotes and clothes and thus can link a suspect to the robbery.

For the analysis of MAAQ gas chromatography–mass spectrometry is the method of choice [1]. Electron impact (EI) and positive- or negative-ion chemical ionization (CI) are used as

ionization methods. In this paper attention is given to the use of tandem mass spectrometric methods using gas chromatography with the common ionization methods and thermospray (TSP) liquid chromatography, thus giving excellent selectivity and/or good sensitivity compared with the more conventional GC–MS methods for the analysis of small amounts of the smoke dye.

EXPERIMENTAL

Materials/extraction

Pellets containing 1-methylaminoanthraquinone together with potassium chlorate and cane sugar were a gift from ICI. MAAQ was obtained in pure state by a dichloromethane extraction of the crushed pellets. All other reagents used were of analytical grade.

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Solutions of MAAQ in methanol (100 ng/ μ l) were spotted five times in 10- μ l quantities at several points on the banknote. After drying the spots, the banknote was extracted three times with methanol. The methanol was evaporated by a gentle stream of nitrogen and the residue dissolved in 100 μ l of methanol. Recovery of MAAQ appeared to be of the order of 25%.

Apparatus

GC. A Varian 3400 gas chromatograph was used, with a J&W DB-5 fused-silica column (30

m \times 0.25 mm I.D., film thickness 0.25 μ m). The oven was programmed from 100°C to 250°C at 10°C/min. The carrier gas was helium. The flow-rate was ca. 1 ml/min and the split ratio was ca. 10:1.

HPLC. A Waters 600-MS programmable pump equipped with a U6K injector was used to pump 0.4 ml/min (methanol-50 mM ammonium acetate in water of pH 4.0; 85:15) through a Waters 4- μ m Nova-Pack C₁₈ 150 mm \times 3.9 mm HPLC cartridge column. Post column, an extra 0.8 ml/min ammonium acetate in water was

TABLE I

RESULTS (STANDARD SOLUTIONS) FOR THE VARIOUS CHROMATOGRAPHIC/MASS SPECTROMETRIC METHODS IN THE ANALYSIS OF MAAQ

Abbreviations: EI = Electron impact ionization; CI = Chemical ionization; MID = Multiple ion detection; SIM = Single-ion monitoring; SRM = Selected reaction monitoring; TSP = Thermospray interface.

Chromatography	Ionization technique	Scan type	Detection limit (pg) (S/N \approx 3)
1 Gas	EI	Full scan	100
2 Gas	CI, positive ion ^a	Full scan	50
3 Gas	CI, negative ion ^a	Full scan	5
4 Gas	EI	MID 237, 220	20
5 Gas	CI, positive ion ^a	SIM 238	10
6 Gas	CI, negative ion ^a	SIM 237	2
7 Gas	EI	SRM 237 > 164	100
8 Gas	MS-MS daughter ion ^b		
	CI, positive ion ^a	SRM 238 > 165	10
9 Gas	MS-MS Daughter ion ^c		
	CI, negative ion ^a	SRM 237 > 195	10
10 Liquid	MS-MS daughter ion ^d		
	TSP (positive) ^e	Full scan	100
11 Liquid	TSP (positive) ^e	SIM 238	10
12 Liquid	TSP (positive) ^e	SRM 238 > 139	100
	MS-MS daughter ion ^f		

^a Reaction gas, isobutane; pressure, 8150 mT.

MS-MS parameters:

	Collision offset voltage	MSMSC	Argon pressure (mT)
^b	-27.5	0	3.5 mT
^c	-30.0	10	3.5 mT
^d	+35.0	0	3.5 mT
^f	-30.0	10	3.0 mT

^e TSP-MS parameters: vaporizer temperature, 145°C; source temperature, 200°C; repeller, 30 V; multiplier voltage, 1500 V; dynode power, 15 kV; scan time, 1.20 s. GC-MS parameters: Source temperature, 150°C; scan time 0.5 s; multiplier voltage, 1500 V; dynode power 15 kV.

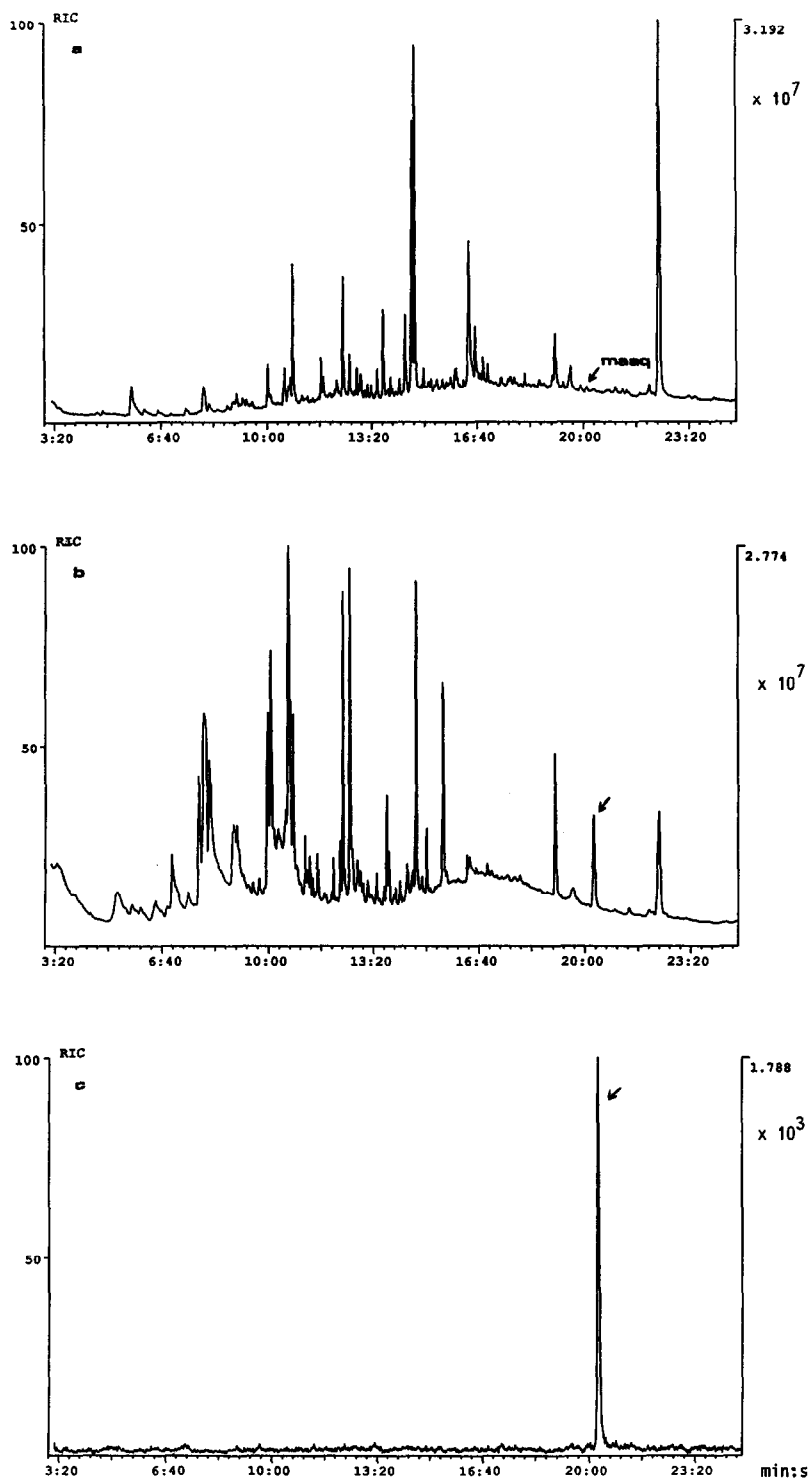


Fig. 1. RIC traces of an extracted banknote supplied with MAAQ. (a) EI full scan, (b) negative-ion CI full scan, (c) MS-MS negative-ion CI (237 > 195).

added by a Waters 590-MS isocratic pump for ionizing enhancement in thermospray applications.

MS. A Finnigan MAT TSO 700 tandem quadrupole mass spectrometer coupled to a DECstation 2100 was used. In gas chromatography the column was directly coupled to the mass spectrometer, while the liquid chromatograph was connected to the mass spectrometer by the Finnigan MAT TSP-2 interface. The operating conditions of the TSP interface, such as the repeller voltage, vaporizer temperature, source temperature and ionic strength of the eluent, were all optimized. These parameters are given in the footnotes to Table I.

MS–MS experiments in the daughter-ion mode [2–4] were done using argon (99.999%) as collision gas for the M^- ion generated by negative-ion isobutane CI (in gas chromatography) and the $[M + H]^+$ ions generated by the thermospray interface (in liquid chromatography). In order to obtain optimum selectivity not the full scan but selected reaction monitoring (SRM) technique [2,3] was applied. Collision offset voltage, argon pressure and MSMSC factor (a correction factor for increasing the transmission of ions in the MS–MS mode) were optimized for several ions in the MS–MS spectrum and the most intense ion in the MS–MS spectrum was chosen for MS–MS experiments. For these parameters see the footnotes to Table I.

RESULTS AND DISCUSSION

In Table I the results of the various chromatographic and mass spectrometric methods that can be used in the analysis of MAAQ are tabulated. Some attention was paid to the LC–TSP method, which gave no results with negative ions. With the TSP interface only $[M + H]^+$ ions of MAAQ were created, even when the pH of the eluent was varied between 3.5 and 10.0. In LC–TSP the detection limits for the full scan and MS–MS daughter methods were in the high picogram range, whereas the SIM method had a

detection limit in the low picogram range. In GC sensitivities in the low picogram range can be found for negative-ion CI in full scan mode, both negative- and positive-ion CI in SIM mode and both negative- and positive-ion CI in MS–MS in the daughter-ion mode.

However, the best method of analysing trace amounts of MAAQ in embarrassing samples full of all kind of dirt is without doubt the GC–CI–MS–MS method in the daughter negative-ion mode for reasons of both selectivity and sensitivity.

In the MS–MS method in the daughter-ion mode the chemical noise (caused by all kind of compounds in the extract) is efficiently suppressed and the selectivity for MAAQ raised, by choosing to pass the molecular ion of MAAQ (237) through the first quadrupole, an ion that dissociates by collision with argon in the second quadrupole to the ion 195, the ion which is chosen only to pass the third quadrupole. (This is also called selected reaction monitoring.) See Table I for the appropriate parameters.

Furthermore, negative-ion CI is better suited to compounds with electronegative group(s), thus giving better selectivity.

It can be seen from Fig. 1, in which an MS–MS reconstructed ion chromatogram (RIC) is compared with the RICs for EI and negative-ion CI for an extract of an MAAQ-spiked banknote, that the chemical noise level in the EI and CI chromatograms is quite high compared with the MS–MS chromatogram.

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