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Application of the new ion trap detector in doping control*

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Introduction

The ion trap detector (ITD) was introduced in 1983 as a simple commercial gas chromatographic detector [1] by Finnigan MAT. The ion trap is a three-dimensional quadrupole device and operates in the mass-selective instability mode using only radio frequency (RF) voltages to the ring electrode [2–4]. Compounds are introduced into the trap by a fused silica transfer line and are ionised by electron impact. Depending on the RF-voltage ions with a certain mass range can be trapped for a relatively long time. When the RF-voltage is raised, ions with increasing mass escape from their orbits and can be detected by an external device, such as an electronmultiplier. For best performance the motion of ions in the trap should be damped by introducing a high background of helium. However, at the time of introduction of the ITD700 as a detector, the ion trapping process was apparently not completely understood and therefore the ITD suffered from some serious disadvantages: (a) because of the relatively high background pressure of helium and the long lifetime of the ions generated, space charging effects occurred in the trap. This caused saturation of the trap resulting in ion/molecule reactions and self-ionisation, giving anomalously abundant $[M + 1]^+$-ions. Also resolution could be lost giving poor spectral quality; (b) because these saturation effects occurred at concentrations of 25–50 ng on-column, the dynamic range of the ITD was poor; (c) the ITD appeared to be very sensitive to water in the system or in the carrier gas, thus the presence of small quantities of water resulted in saturation of the trap and consequent loss of sensitivity.

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The new ITD 800 with variable ionisation current software

From the beginning of 1987 the authors evaluated the new Variable Ionisation Current (VIC) software as supplied by Finnigan MAT on their ITD 800 series. Instead of the fixed ionisation time of 1 ms used in the former versions, the ionisation time can now be varied between 78 and 25,000 μs. This time can be selected manually or automatically by the Automatic Gain Control (AGC) program. This AGC program measures the area of all ions entering the trap with a mass 45 or higher in 0.2 ms. From this area the program calculates the optimal ionisation time and sets this time. During a chromatogram this program will continuously adjust the ionisation time depending on the number of incoming ions and so prevent the trap from saturation.

The maximum ionisation time of 25,000 μs should provide higher sensitivities than with the previous software. The dynamic range of the trap can be shifted from high to low sensitivity depending on the application by changing a "B factor" in the tuning program. Furthermore the electron multiplier voltage has an effect on the AGC program.

Experimental

The Finnigan MAT ITD 700 coupled with a Carlo Erba 5160 High Resolution Gas Chromatograph (HRGC) was used. The ITD was upgraded with the revision 3.0 software. No Taylor disc to reduce the emission current was installed. The emission current was reduced to 5 μA. Mass range scanned: 40–450 in 1 s; the electron multiplier was set at 150 V above the voltage set by the ITD gain program; the transfer line temperature was 270°C.

GC conditions

On-column injection at 80°C and after 1 min, programmed at 10°C min^{-1} up to 250°C.

Results and Discussion

Sensitivity

The sensitivity of the new software was compared with the results obtained with the Hewlett–Packard M.S.D. 5970B. The results given are typical results run in between the day-to-day analysis of dope control samples. Sensitivity of mass spectrometers is normally specified as the amount of methylstearate giving a signal-to-noise ratio of 10 for mass 298 using the full scan mode. For the new ITD a sensitivity of 250 pg was measured (Figs 1 and 2), while the HP MSD gave 1 ng according to the specifications. As expected the full scan sensitivity of the ITD is very good. The sensitivity in the MID mode for both instruments was comparable: 100 pg.

Similar results were obtained when analysing a narcotics-mixture on both instruments. Full scan spectra of 1 ng could be obtained on the H.P. MSD, but with the Finnigan MAT ITD the spectra at 100 pg could still be identified by the file search program. Using the MID mode the detection limit was 5–10 pg for both instruments, depending on the compound.

Spectral quality

With the new software the spectral quality did improve considerably. The mass discrimination to higher masses as observed with the version 2.0 software has decreased

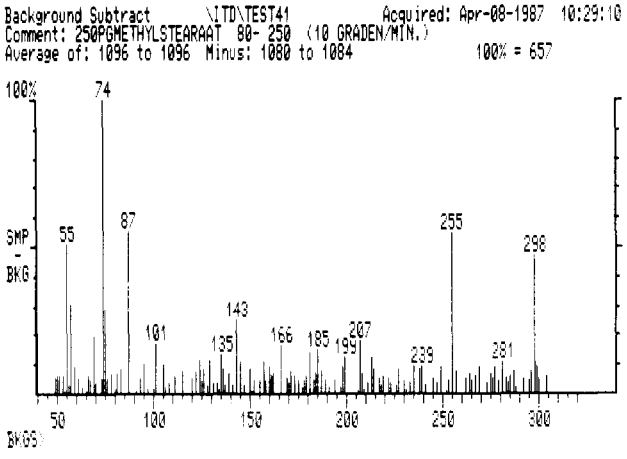

Figure 1
Background-subtracted EI-spectrum of 250 pg methyl stearate using the ion trap detector.

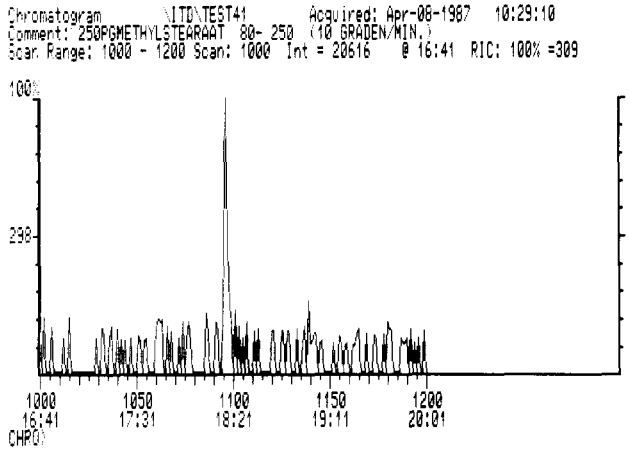

Figure 2
Mass spectral chromatogram of ion 298 when injecting 250 pg methyl stearate in the ion trap.

resulting in spectra with comparable abundances to those obtained with conventional quadrupole instruments (Figs 3 and 4). In Table 1 some examples are given of mass spectra obtained with the old and new ITD, compared to spectra from a conventional Finnigan 3200 quadrupole GC–MS.

Dynamic range

The occurrence of the $[M + 1]^+$ ions in the EI ITD spectra is less of a problem with the new VIC software because of the AGC program. The dynamic range was measured with methylstearate which will give an ion at mass 299 when saturation occurs. Concentrations from 250 pg to 325 ng methylstearate could be measured without spectral distortion, giving a dynamic range of 1300. Although this range is not wide, it is

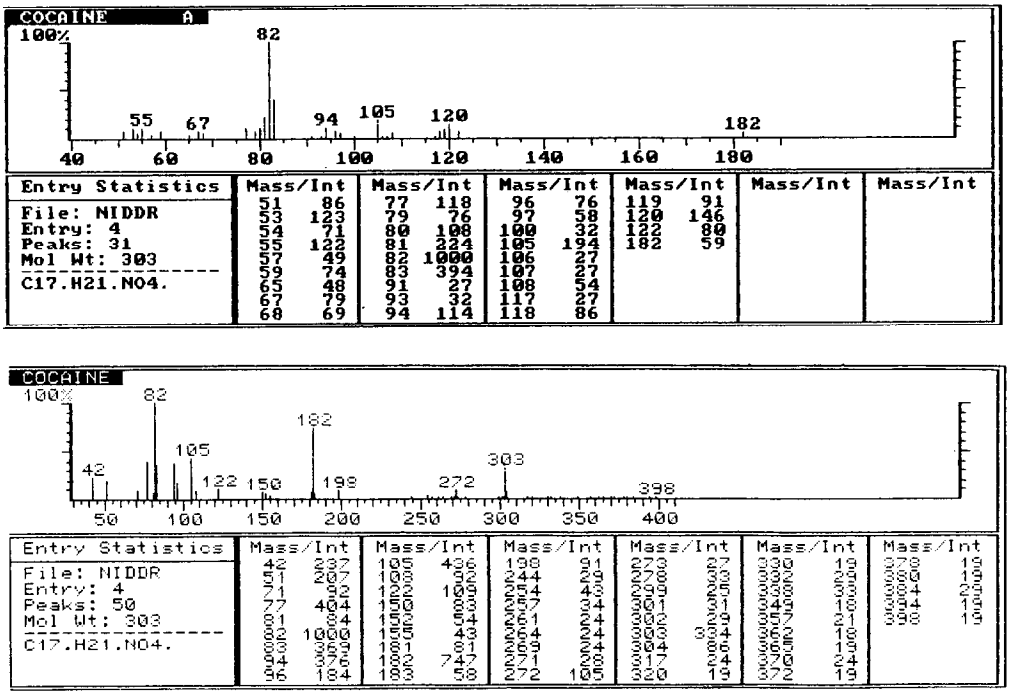

Figure 3
(a) Mass spectrum for cocaine in ITD with AGC "OFF" using Variable Ionisation Current (VIC) software. (b) Mass spectrum for cocaine in ITD with AGC "ON" using VIC software.

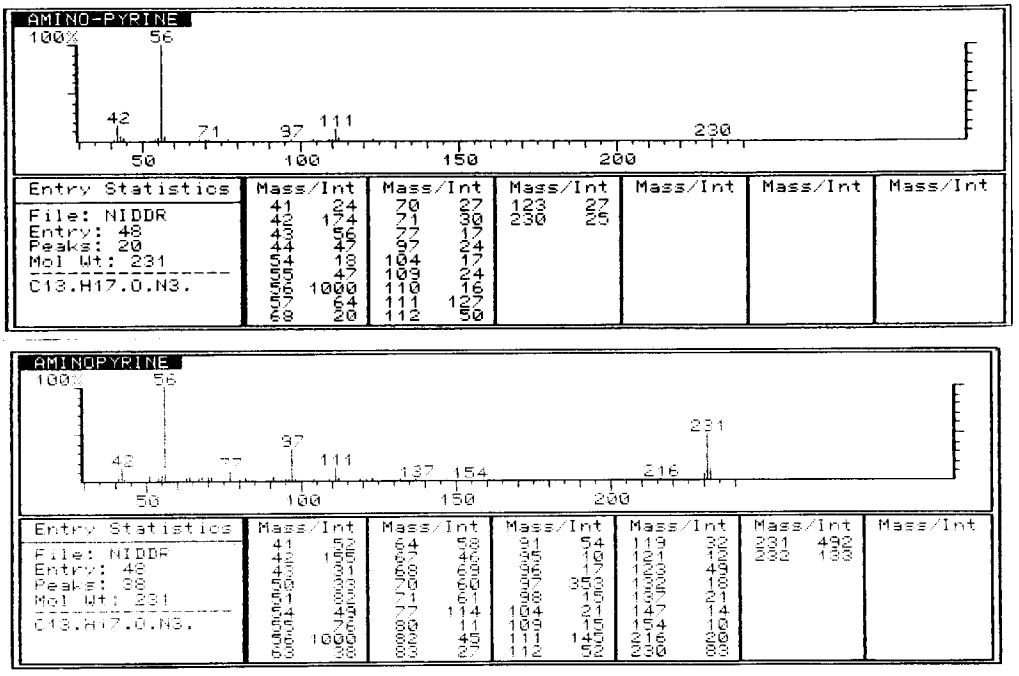

Figure 4
(a) Mass spectrum for aminopyrine in ITD with AGC "OFF" using VIC software. (b) Mass spectrum for aminopyrine in ITD with AGC "ON" using VIC software.

Table 1
Mass intensities in the spectra recorded on the earlier and new ITD compared with those recorded on a conventional quadrupole GC–MS (Finnigan 3200)

Compound	mass	ITD 700	ITD 800	Finnigan 3200
Caffeine	55	100%	51%	48%
	67	28%	50%	50%
	109	92%	41%	65%
	194	11%	100%	100%
Cocaine	82	100%	100%	100%
	182	6%	75%	70%
	198	—	9%	9%
	272	—	10%	5%
	303	—	33%	5%
Aminopyrine	56	100%	100%	100%
	97	2%	35%	38%
	111	13%	15%	5%
	230	2%	8%	—
	231	—	50%	20%
Methyl-Ibufenac	104	100%	67%	90%
	163	40%	100%	100%
	206	16%	41%	35%
Methylfenidate	91	100%	23%	28%
	84	27%	100%	100%
	56	16%	23%	22%
Pethidine	57	42%	24%	42%
	71	100%	100%	100%
	103	18%	28%	28%
	172	3%	41%	22%
	247	1%	32%	15%
Isopropyl-antipyrine	56	100%	37%	95%
	77	8%	23%	50%
	96	3%	12%	15%
	215	23%	100%	100%
	230	11%	39%	35%

acceptable for capillary chromatography. Higher concentrations can be measured without distortion by adjusting the tuning (set B to 1000).

Background

The problem with water does not apply to this system. However, another effect was observed in the authors' ITD with the new software, which has also been observed by some other users. When the AGC is "ON" there is a very high abundance of mass 44 in the background. This is not from the carrier gas (checked with H.P.MSD) or the column. If the AGC is switched "OFF" no mass 44 is present even when B is set high. (Figs 5 and 6).

Although the authors have seen traps without this background problem, this effect has not yet been explained or solved by Finnigan MAT. Because amphetamines have a base peak at mass 44 this background problem is particularly awkward in doping control.

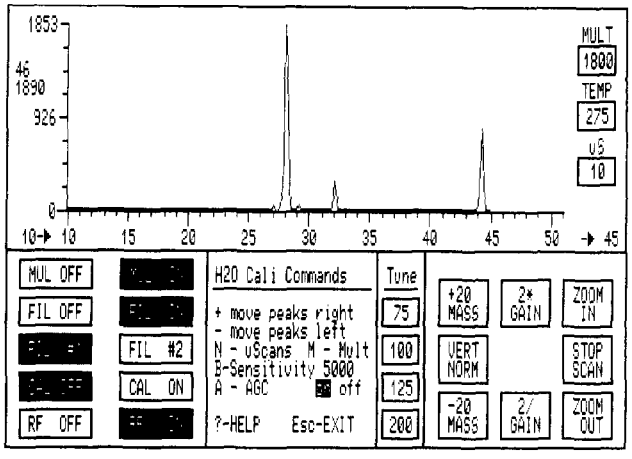

Figure 5
Background spectrum with AGC "ON", showing abundant m/e 44 peak.

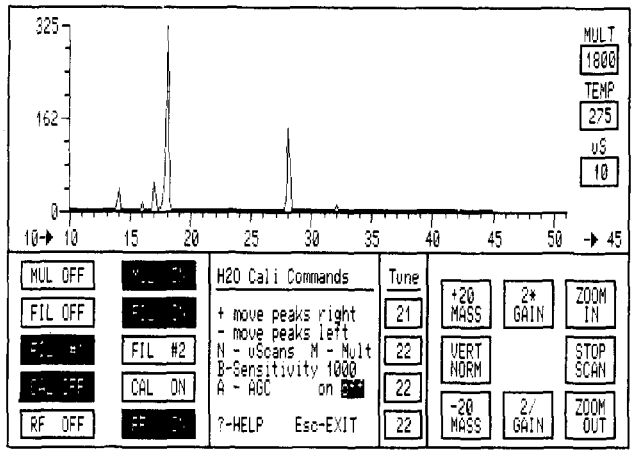

Figure 6
Background spectrum with AGC "OFF".

Conclusions

The new Finnigan MAT ITD 800 with VIC software is a very sensitive detector with excellent easy-to-use software. In particular, the file search programs are better and faster than those supplied with the MSD. The spectral quality and dynamic range have been improved to acceptable levels.

However, the VIC software involves more interactive parameters, such as multiplier voltage, emission current, factor B, resolution and background ions, all of which influence the performance of the ITD. The automatic tuning program will give good results, but better results are obtained by manual tuning. The new ITD software therefore requires the operator to acquire more experience and understanding of the process involved.

Disadvantages of the ITD include the interface coupling to the trap, which is prone to spontaneous leaking, and the longer down-time when opening the trap for service or repair compared to the MSD.

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