Application Brief
Environmental

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Combination of Chemical Ionization (CI) and Low Energy Ionization (EI) Capabilities with High-Resolution Q-TOF GC/MS

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Introduction

Important applications for high-resolution gas chromatography mass spectrometer (GC/MS) systems include untargeted screening approaches as well as unknown compound identification. For many classes of compounds, low energy electron ionization (EI) provides significant improvements in the relative abundance of molecular ions compared to standard (70 eV) EI, and enables enhancement in selectivity and compound identification capability without any down time due to changing the ion source or additional tuning. However, there is still an opportunity for alternative ionization sources as a complimentary technique (that is, chemical ionization), combined with high-resolution GC/MS, predominantly for selected compounds of environmental significance. In this work, a comparison of low energy EI and chemical ionization (CI) data acquired on the Agilent 7250 GC/Q-TOF will be reviewed.

Experimental

All experiments were performed using an Agilent 7890B GC system coupled to a high-resolution Agilent 7250 GC/Q-TOF equipped with a low-energy-capable EI source and an interchangeable CI source. The data were collected in both EI modes, as well as positive and negative CI modes (PCI and NCI), with methane as a reagent gas. Selected groups of compounds included chlorinated phenols, nitroaromatics, and pesticides, among others. Table 1 lists typical MS parameters.

The GC separation was done on a 30 m × 0.25 mm id, 0.25 µm HP-5MS capillary column using He as the carrier gas at 1.2 mL/min. The injector temperature and the MS interface were set at 280 °C. Methane (99.995 %) was used as the reagent gas. The methane flow was set to 20 % for PCI, and 40 % for NCI. For NCI, the source and quadrupole temperatures were set to 150 °C. For PCI, the source temperature was set to 280 °C and the quadrupole temperature to 150 °C. The spectral data were acquired at 5 Hz, and the mass range was 50–1,200 *m/z*. 2H-Perfluoro-5,8-dimethyl-3,6,9-trioxa-dodecane (PFDTD) was used to tune the mass spectrometer in the CI mode.

Data analysis was performed using Agilent MassHunter Qualitative Analysis software version B.08 as well as MassHunter Quantitative Analysis software version B.09.

The limit of detection (LOD) for both negative and positive CI were statistically derived based on repetitive injections of benzophenone and octofluoronaphthalene (OFN), respectively. In PCI mode, the LOD was calculated based on 10 pg/µL benzophenone injections, and was estimated to be 3.4 pg on-column. For NCI, the LOD was calculated based on the injections of 10 and 1 fg/µL OFN, and was estimated to be 2.3 and 0.5 fg on-column, respectively. Figure 1 shows examples of EICs for OFN.

Table 1. GC/Q-TOF MS acquisition parameters. The source temperature was chosen separately for each experiment based on the compound group and ionization mode. Emission current was optimized for each electron energy.

Ionization mode	Standard EI	Low energy EI	Positive CI	Negative CI
Electron energy	70 eV	9–17 eV	110 eV	70–200 eV
Emission current	5 µA	0.3–1 µA	150 µA	50–130 µA
Source temperature	200–280 °C	200 °C	280 °C	150 °C
Mass range	50–1,200 *m/z*			
Spectral acquisition rate	5 Hz			

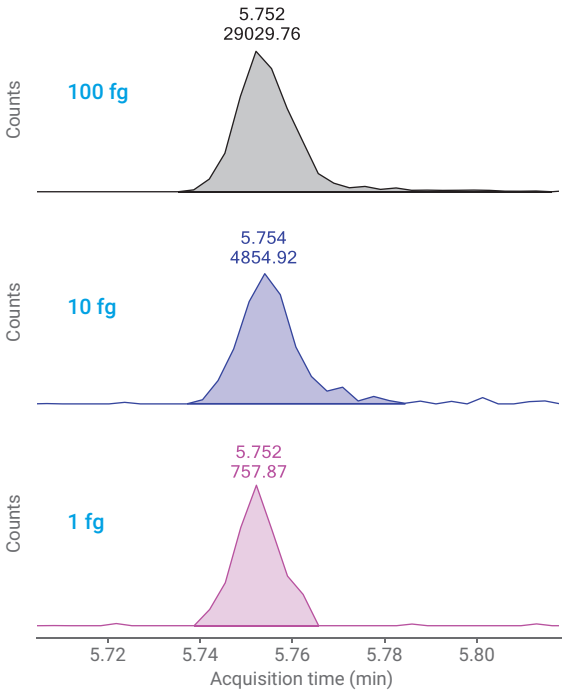

Figure 1. EICs for the molecular ion of OFN (1–100 fg on-column) in NCI, 271.9878 ±20 ppm.

Results and discussion

Low-electron-energy-capable EI versus positive CI

To confirm fundamental CI performance, the functionality of the interchangeable CI source was evaluated with traditional positive and negative CI checkout compounds. Then, fragmentation patterns of different compound classes of interest were compared between EI (standard, 70 eV, and low energy) and CI modes (Figure 2).

While some compounds form a significant $(M+H)^+$ ion as well as methane adducts in PCI, others showed higher degrees of fragmentation in PCI compared to low energy EI (Figure 2).

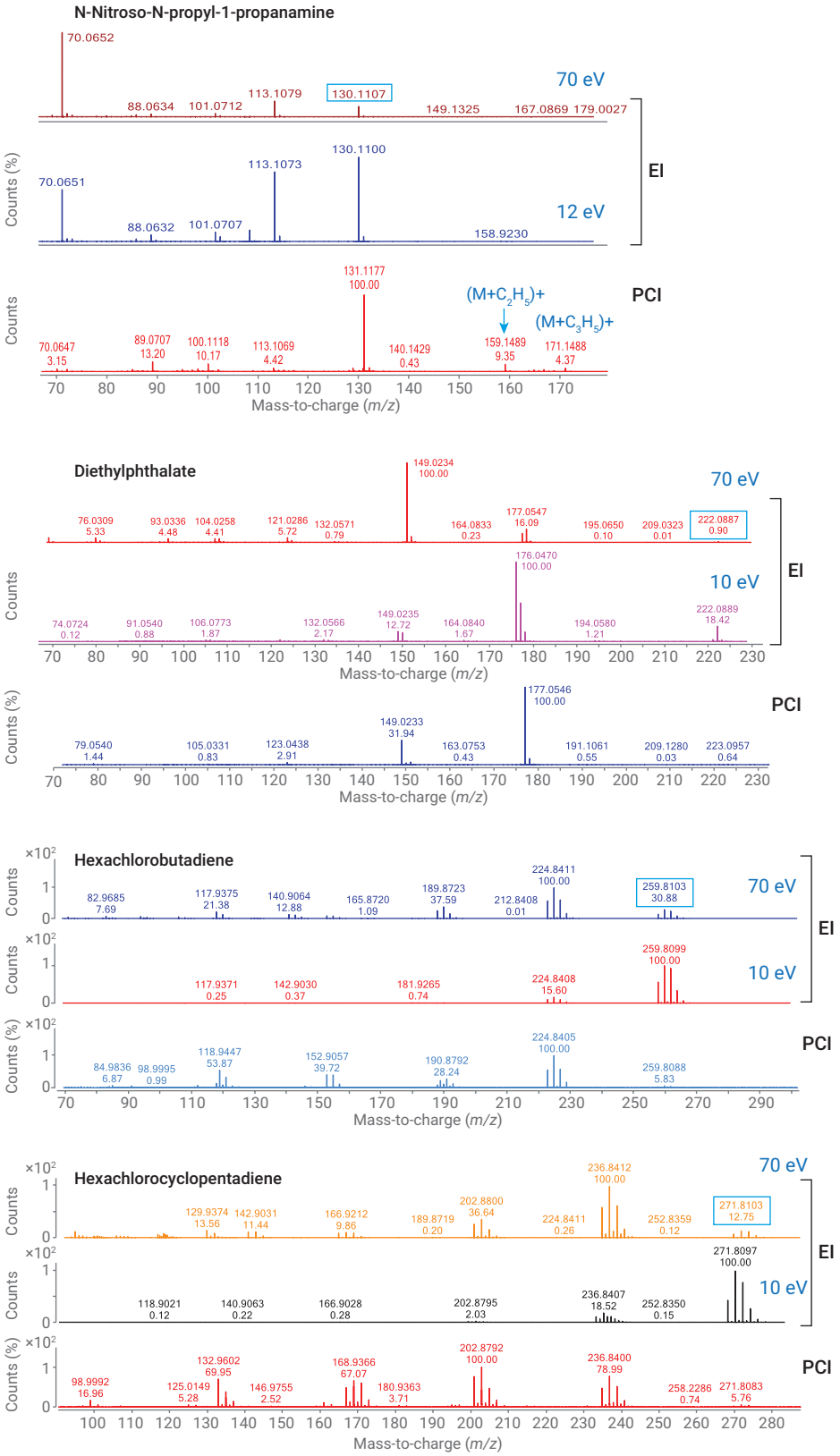

Figure 2. Fragmentation examples of spectra obtained in standard and low energy EI, compared to PCI. The molecular ion is indicated by a blue square.

Negative CI

Negative CI was found to be particularly sensitive and selective for organophosphate, organochlorine, and pyrethroid pesticides.

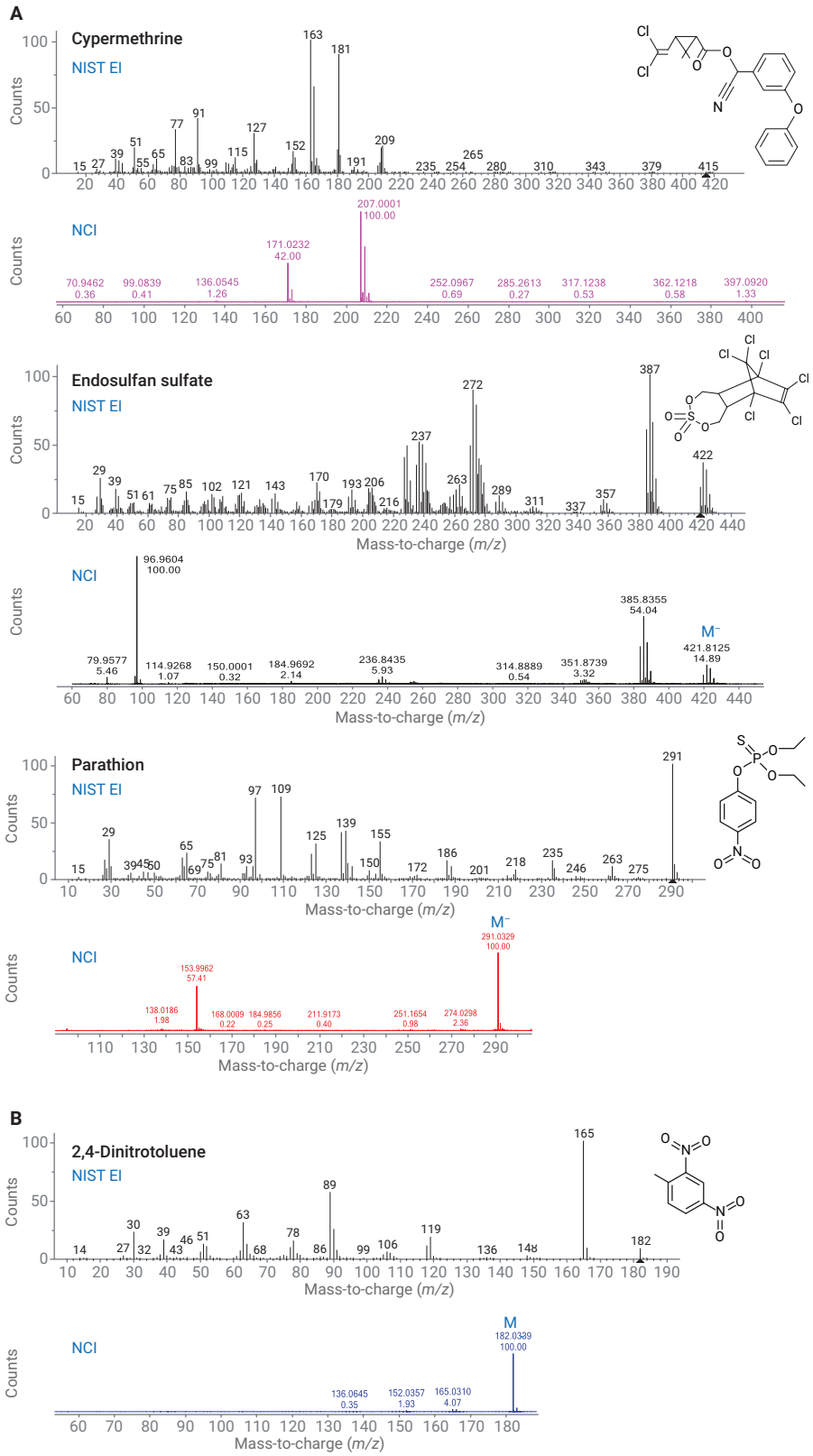

Figure 3. A) A significant decrease in fragmentation with a concentration of the relative abundance in the molecular ion or characteristic fragment ions is typically observed for pyrethroid, organochlorine, and organophosphate pesticides. B) This trend is also typical for nitroaromatic compounds.

Identification of *cis* versus *trans* stereoisomers of various conazoles

Stereoisomers of etaconazole, propiconazole, and difeno-conazole were investigated using negative CI. These compounds have two chiral centers at the 2- and 4-positions on the dioxolane ring, existing as two pairs of diastereoisomers (*cis* and *trans*), and two pairs of enantiomers that require chiral columns for separation.

As shown in Figure 4, NCI has a different fragmentation mechanism than EI. The EI mechanism is through elimination of the triazole ring ($C_3H_4N_3$) to form a stable tertiary ion at *m/z* 259.0289 ($C_{12}H_{13}O_2Cl_2$), followed by the opening of the 1,3-dioxolane ring and elimination of the side chain to form an abundant ion at *m/z* 172.9555 ($C_7H_3OCl_2$). In contrast, the NCI spectra of the *cis* and *trans* isomers are quite different, making it possible to uniquely identify them. For the *cis* isomers, the most abundant peak in the spectra of eta- and propiconazole is the ion at *m/z* 126.0309 ($C_4H_4N_3O_2$), corresponding to the elimination of the dichlorophenyl group as well as the side chain including carbons 4 and 5 on the 1,3-dioxolane ring.

Table 2. LOD for pesticides analyzed in NCI spiked to the broccoli extract. Injection volume 1 µL.

Compound	LOD (pg)
Trifluralin	1.6
Dicloran	1.1
BHC-*gamma* (Lindane)	1.6
Fonofos	0.9
Tefluthrin	1.1
Parathion-methyl	1.7
Chlorpyrifos-methyl	1.7
Heptachlor	1.4
Fenitrothion	1.5
Malathion	1.3
Aldrin	1.4
Chlorpyrifos	1.2
Parathion	1.2
Pendimethalin	1.4
Heptachlor exo-epoxide isomer B	1.3

Compound	LOD (pg)
Chlorfenvinphos	1.6
Methidathion	2.9
Tetrachlorvinphos	1.9
Endosulfan	1.1
Prothiofos	1.4
Dieldrin	1.4
Ethion	1.2
Endosulfansulfate	1.4
Bifenthrin	1.4
Tetradifon	1.0
Phosalone	1.5
Cyhalothrin (*lambda*)	1.3
Pyrazophos	2.4
Cypermethrin I	2.8
Flucythrinatel	1.0

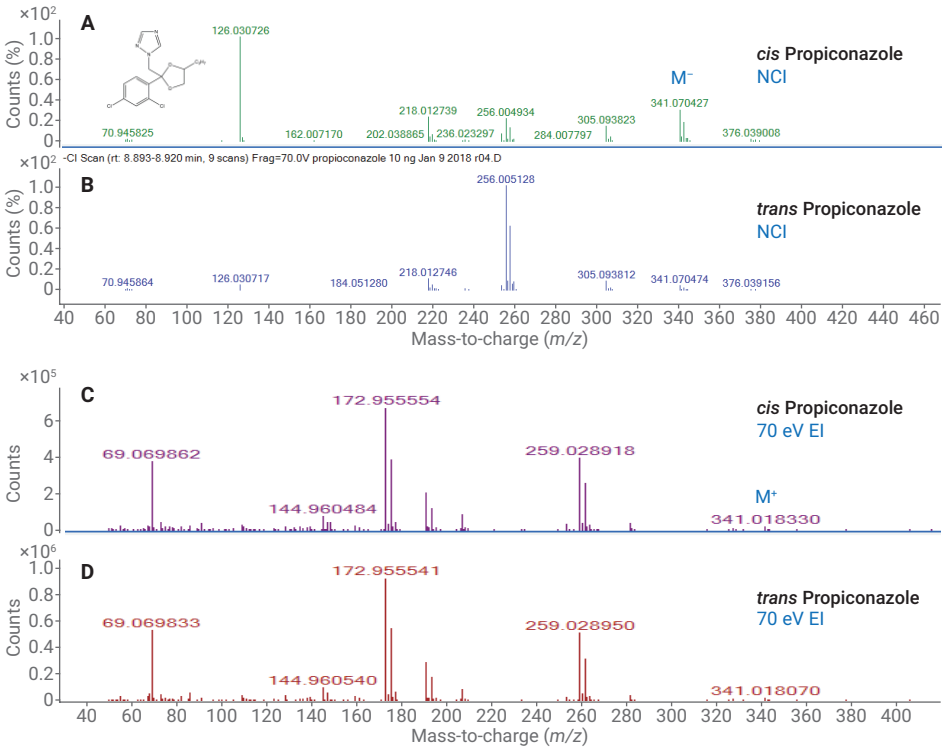

Figure 4. NCI spectra of *cis* and *trans* propiconazole (A and B) and the EI spectra of the same *cis* and *trans* stereoisomers (C and D).

The presence of the phenoxy group in *cis* difenoconazole stabilizes the molecular ion somewhat, thus leading to the formation of the fragment ion at *m/z* 310.038943 ($C_{16}H_9N_3O_2Cl$). For the *trans* conazoles, the most abundant ions were at *m/z* 256.004991 ($C_{10}H_8N_3OCl_2$) for eta- and propiconazole, and *m/z* 348.031206 ($C_{16}H_{12}N_3O_2Cl_2$) for difenoconazole due to the additional phenoxy ring; these ions correspond to the elimination of the side chain attached to the 1,3-dioxolane ring. Table 3 gives the mass accuracy and % abundance of the molecular ions for the *cis* stereoisomers. The relative abundances of the negative molecular ions (M^-) for the *trans* stereoisomers are below 4 %.

Conclusions

The benefits of the 7250 GC/Q-TOF system equipped with a low energy-capable EI source as well as an interchangeable CI source provide a unique combination of performance factors for targeted and untargeted analysis applications.

Chemical ionization alone or in combination with low energy EI and a high-resolution GC/Q-TOF provides new opportunities in compound identification. The ability of low energy EI to provide accessible molecular ion information on the 7250 GC/Q-TOF is complimented by an interchangeable CI source for an additional degree of confidence in molecular ion determination for compound identification workflows.

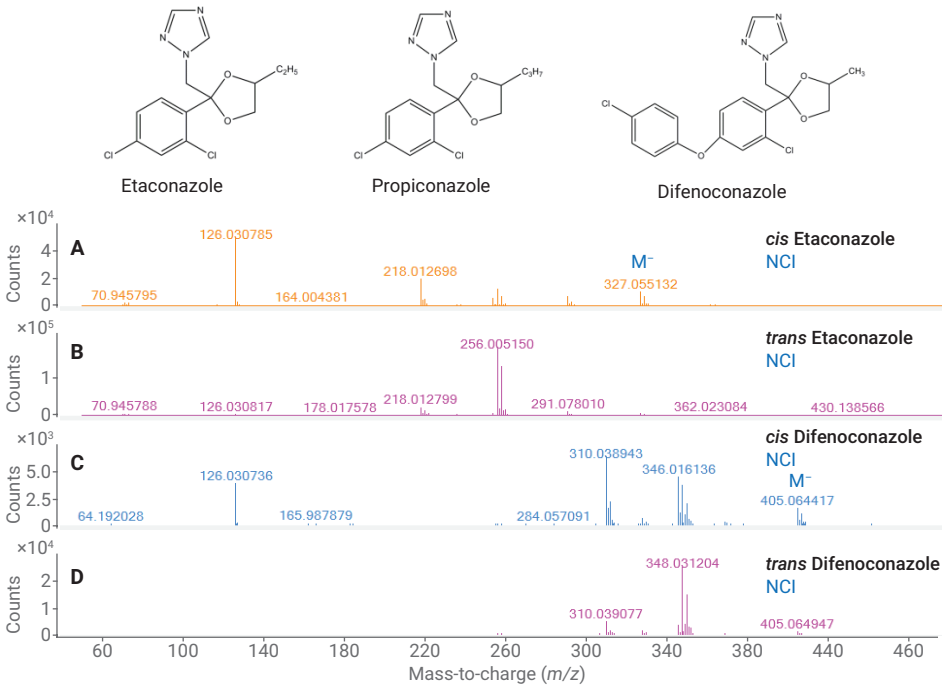

Figure 5. NCI spectra of *cis* and *trans* etaconazole (A and B) and difenoconazole (C and D).

Table 3. Mass accuracy data for the *cis/trans* conazole stereoisomers and the % abundances of the molecular ions of the *cis* stereoisomers.

	cis		*trans*		M^-	
	exp. *m/z*	Mass error (ppm)	exp. *m/z*	Mass error (ppm)	*cis*	% Abundance
Etaconazole	126.030785	-0.9	256.00515	0.6	327.0551	20
Propiconazole	126.030726	-1.4	256.00513	0.5	341.0704	29
Difenoconazole	126.030736	-1.3	310.03894	0.2	405.0644	24

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