

APPLICATION OF UNKNOWN AND SUSPECT SCREENING ANALYSIS FOR THE IDENTIFICATION OF VOLATILE CO-FORMULANTS IN DIFFERENT PLANT PROTECTION PRODUCTS BY GAS CHROMATOGRAPHY-HIGH RESOLUTION MASS ACCURACY SPECTROMETRY

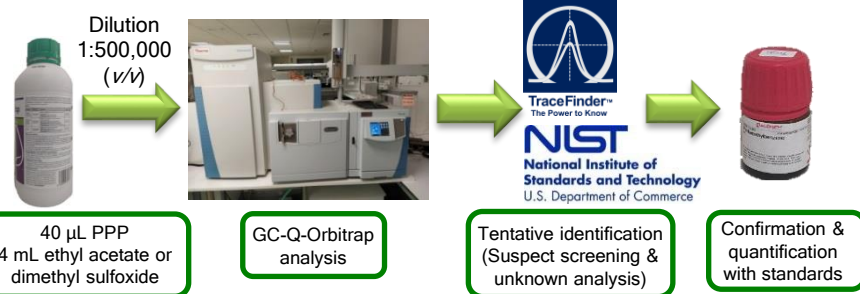
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INTRODUCTION

Plant protection products (PPPs) are agrochemicals containing at least one pesticide and several co-formulants, such as solvents, surfactants, wetting agents, emulsifiers or preservatives. However, these co-formulants usually remain undisclosed by manufacturers, and they are not reported in labels to protect their business interests. Several authors have suggested a likely synergistic effect of co-formulants and pesticides resulting in enhanced toxicity. Thus, a characterisation of these compounds should be done. In this study, several volatile organic compounds were confirmed and quantified in 14 different PPPs (EC, DC, SC & ZC) by suspect screening and unknown analysis, using gas chromatography coupled to high resolution mass accuracy spectrometry (Q-Orbitrap-Exactive).



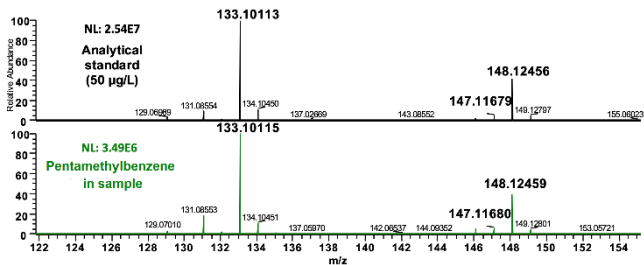
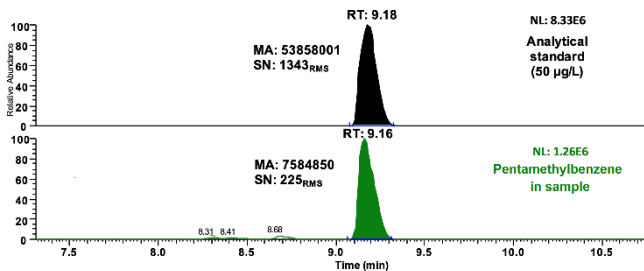
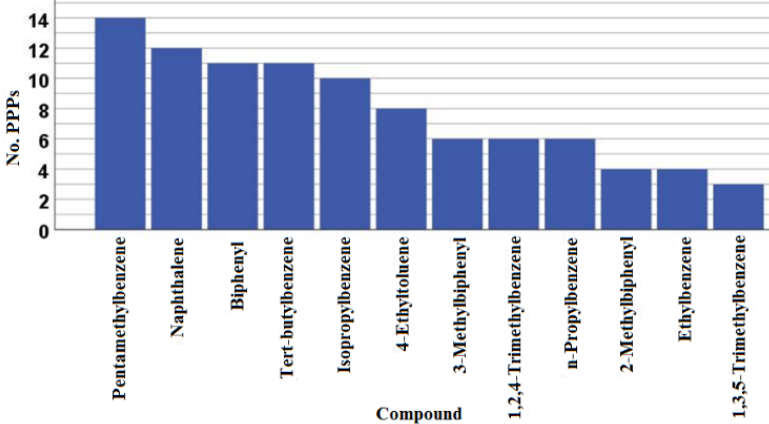
METHODOLOGY

| | |
|------------------|---|
| Column | Varian VF-5ms (30 x 0.25 mm, 0.25 µm) |
| Injection | 2 µL, 280 °C, gradient |
| Flow | 1 ml/min; He |
| Detector | Q-Orbitrap-Exactive |
| Ionisation mode | El: 70 eV |
| Acquisition mode | Full Scan MS (60,000 FWHM at m/z 200), m/z 50-500 |
| AGC target | 1e6 |

RESULTS

42 tentatively identified compounds
12 confirmed compounds

Number of PPPs containing each confirmed co-formulant



Confirmed co-formulants, identification method & concentration range

Chromatograms and mass spectra of pentamethylbenzene in sample and a standard solution

Pentamethylbenzene: Unknown analysis (0.10-9.63 g/L)
Naphthalene: Unknown analysis (0.34-4.32 g/L)
Biphenyl: Unknown analysis (0.11-2.20 g/L)
Tert-butylbenzene: Unknown analysis (0.04-0.36 g/L)
Isopropylbenzene: Unknown analysis (0.09-0.41 g/L)
4-Ethyltoluene: Unknown analysis (0.12-0.55 g/L)
3-Methylbiphenyl: Unknown analysis (0.25-4.34 g/L)
1,2,4-Trimethylbenzene: Suspect screening (0.28-1.01 g/L)
n-Propylbenzene: Unknown analysis (0.36-0.47 g/L)
2-Methylbiphenyl: Unknown analysis (0.07-0.81 g/L)
Ethylbenzene: Unknown analysis (2.19-4.81 g/L)
1,3,5-Trimethylbenzene: Suspect screening (0.69-9.61 g/L)

CONCLUSIONS

- ❖ Tentative identification of 42 naphthalene and benzene-based co-formulants and confirmation of 12 compounds was performed in 14 different PPPs by GC-HRMAS.
- ❖ Several co-formulants were found at high concentrations, which may pose a threat to human health.
- ❖ Further toxicological studies concerning these compounds should be carried out.