Preliminary Evaluation of ATEX-PTV-GC-QTOF-MS for the Determination of Pesticides in QuEChERS Extracts of Samples Containing High Concentrations of Chlorophyll

INTRODUCTION

- The GC-MS analysis of pesticides in green commodities is challenging because non-volatile components build up in the inlet liner causing gradual deterioration of chromatographic performance (tailing peak shapes and irreproducible response)
- Previously the use of difficult matrix introduction technique was reported to allow the injection of crude extracts (1)
- A similar, but more sophisticated ATEX-PTV-GC-(Q)TOFMS [Automated Tube (liner) Exchange–Programmable Thermal Vaporisation-Gas Chromatography-Time-of-Flight Mass Spectrometer] system has been evaluated for the direct analysis of crude extracts of fresh herbs with minimal or no clean-up

METHOD AND INSTRUMENTATION

- The (GC-QTOF-MS MultiFlex system (Anatune, UK) system utilises a Gerstel Multi-Purpose-Sampler (MPS), and a Gerstel Thermal Desorption Unit (TDU) connected to a Gerstel CIS 4 PTV inlet with liquid nitrogen cooling, coupled to an Agilent model 7200 GC-QTOF-MS

Figure 1. Gerstel ATEX system

Figure 2. Microvial after 1 injection

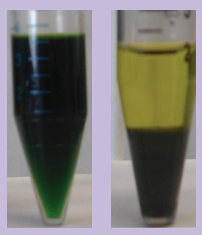

Figure 3a and 3b. (sample before and after clean-up with d-SPE (PSA, C18 and carbon)

- Direct analysis of sample extracts (QuEChERS citrate method with dSPE clean-up)
- Injection volume, 5 µL into microvial
- Column: (HP5 MS 30 m X 0.25 mm i.d 0.25 µm film thickness)
- 1 mL/min constant flow
- Agilent 7200 GC-QTOF
- EI at 70 eV, full scan acquisition
- low resolution mode (RP = 8000)
- Data processing: based on targeted extraction of most abundant accurate mass ion by Quant software

- The inlet system gives precise control of both, evaporation of solvent, and volatilisation and transfer of analytes. A PTV liner containing a microvial is transferred to the TDU and the sample is then injected into the microvial. After elimination of the solvent the TDU temperature is ramped to volatilise the pesticides which are then cold-trapped at -50˚C in the PTV. The temperature of the PTV is ramped to transfer the pesticides into the GC Column; the non-volatile components remain in the microvial avoiding contamination of the inlet
- The liner and micro-vial is exchanged automatically by the MPS, before injection of the next sample. The inexpensive microvial is disposed, whilst the liner can be re-used

RESULTS

- Fresh coriander herb was spiked with 132 GC-MS amenable analytes. A summary of the lowest calibrated levels (ng/g) detected with adequate S/N is presented in Figure 4

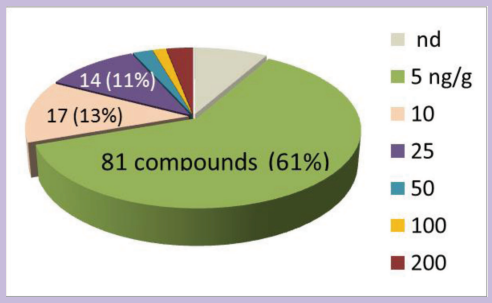

Figure 4: Summary of detection capability at the LCL

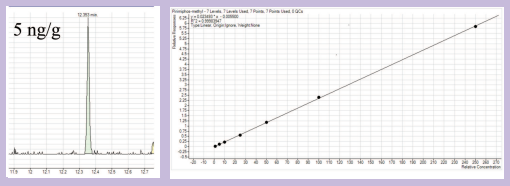

Figure 5: Extracted ion chromatogram (*m/z* 305.0963) and calibration curve for a well behaved compound (pirimiphos –methyl)

- The recovery and precision was assessed for samples spiked with pesticides at 10 ng/g and TPP internal standard
- 35 analytes : recoveries between 70-120 % and associated % CVs <20 %
- Results for ~40 analytes were just outside the 70-120 % recovery and 20 % CV limits
- Variable response observed for ~20 compounds including the early eluting compounds, dichlorvos, dichlobenil, biphenyl, propham, etridiazole and methacrifos
- Captan, and dicofol were thermally degraded under the conditions employed
- Circa 30 compounds did not give sufficient response at 10 ng/g including late eluting compounds such as cyfluthrin, permethrin, cypermethrin, pyridaben, coumaphos flucythrinate and deltamethrin

CONCLUSION

- These initial results are considered to be a preliminary assessment of the approach
- There are a large number of variables (injector and MS settings) that need to be further optimised, but results for a large number of the compounds are encouraging
- Further work on the optimisation of variables including selection of internal standards is ongoing

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References

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