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Application Note

Quantitative Analysis of Pesticides in QuEChERs Extracts Using APGC-MS/MS

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This is an Application Brief and does not contain a detailed Experimental section.

Abstract

In this application brief 25 pesticides were successfully analyzed using multi-residue GC–MS/MS method. Xevo TQ-S in combination with the ACQUITY UPLC and APGC makes it an ideal MS for routine food testing laboratories.

Benefits

APGC-MS/MS allows sensitive and accurate determination of multiple pesticide residues in fruit and vegetable QuEChERs extracts.

Introduction

Pesticides are widely used in agriculture across the globe. Regulatory authorities and food producers are under

ever-increasing pressure to ensure the safety of the food supply. Pesticide residues are high on the list of consumer concerns and consequently laboratories are tasked to screen samples for as many pesticides as possible in a single analysis within an appropriate timescale. Most countries have clearly defined regulations governing pesticide residues. Legislation imposes Maximum Residue Limits (MRLs) for pesticide residues in food commodities requiring analytical techniques that are sensitive, accurate, and robust.

Multi-residue analysis is challenging due to the low limits of detection required to achieve MRL compliance for a diverse range of pesticides in a wide range of food commodities. There are currently in excess of 1000 pesticides known to be in use, and laboratories are under increasing pressure to increase the scope of the analytical methods for routine monitoring purposes. Typically, this analysis is performed using a combination of GC-MS/MS (with an EI source) and LC-MS/MS. EI is a "hard" ionization technique which results in high degree of in source analyte fragmentation.

Atmospheric Pressure Gas Chromatography (APGC) is a "soft" ionization technique resulting in a lower degree of fragmentation, thus enhancing both the sensitivity and selectivity of the molecular ion species. The APGC source is readily interchangeable with the ESI source enabling a single MS platform to be used for the analysis of both LC and GC amenable pesticides that provides a complete analytical solution for pesticide residue analysis.

In this application brief we report a novel analytical strategy for the targeted analysis of trace-level pesticide residues in strawberry, pear, spinach, and tomato.

Results and Discussion

Strawberry, pear, tomato, and spinach samples were extracted using the DisQuE QuEChERS (CEN) protocol to generate blank matrix extract in acetonitrile. A ninepoint calibration range from 0 to 50 ng/mL (µg/Kg) was prepared by addition of a mixed pesticide standard to each matrix. A deuterated internal standard, chrysene -d12, was added at a fixed concentration of 2 ng/mL to each vial prior to analysis and used as an injection standard. All standards were analysed in triplicate using the Waters Xevo TQ-S with an APGC source and a 7890A GC. Two MRM transitions were monitored for each pesticide, the most abundant species for quantification and the less abundant species for confirmation. A selection of 20 pesticides known to be problematic to analyze under EI conditions due to excessive fragmentation were included. Depending on the source operating conditions, the analyst can choose to promote either proton transfer or charge transfer as the major ionization process. In the

presence of a proton donor, (wet source conditions), APGC typically produces spectra with a major $[M+H]^+$ ion. The high intensity of the parent ion makes it possible to generate specific and sensitive MRM transitions for the target analytes. In contrast, many pesticide MRM's using an EI source rely on using a lower molecular weight, less specific fragment ion as the parent. These features of APGC ensure that the analyst has confidence in identifying and quantifying pesticides in a variety of fruit and vegetable matrices.

APGC with Xevo TQ-S

Figure 1 shows a typical calibration curve and residuals plot for azinphos methyl generated from the triplicate injection of each matrix matched calibration standard in strawberry extract. The response is linear from 0.05 to 50 ng/mL with a correlation coefficient R^2 of 0.997. All of the residuals are less than 20% demonstrating excellent linearity and repeatability of the APGC System. The limits of detection and linearity achieved for all 20 pesticides using the APGC-Xevo TQ-S are summarized in Table 1. The limits of detection range from 0.01 to 0.5 ng/mL with excellent linearity R^2 >0.99 for all 20 pesticides. Figure 2 illustrates representative examples of APGC-MS/MS chromatograms obtained for heptachlor epox B at 1 ng/mL in solvent and spiked into the four different sample matrices. No significant matrix effects are observed and the retention time, the peak shape and the response are shown to be repeatable. Only a slight enhancement of the response in some of the sample extracts (tomato and pear) was observed for this compound. These data show that the enhanced parent ion intensity observed using APGC on the Xevo TQ-S permits sensitive and routine analysis of GC amenable pesticides in fruit and vegetable matrices.

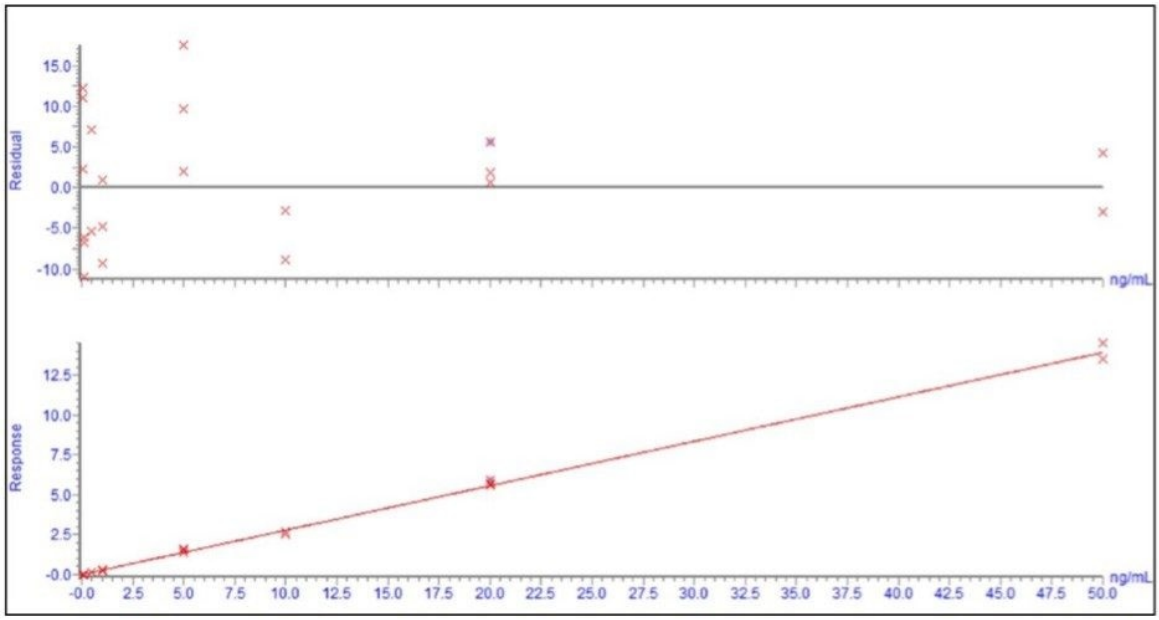

Figure 1. Calibration and residuals plot of azinphos-methyl in strawberry matrix constructed using triplicate injections of each calibration point.

Compound	MRM quantification	Retention time (min)	Limit of detection (ng/mL)	Correlation coefficient (R^2)
Aldrin	363>159	13.4	0.5	0.992
Azinphos-Ethyl	289>261	14.2	0.05	0.99
Azinphos-Methyl	261>125	20.0	0.50	0.99
Buprofezin	306>106	15.9	0.05	0.99
Chlorfenvinphos	359>170	14.3	0.05	0.994
Chlorpyriphos	350>198	13.2	0.10	0.995
Chlorpyriphos-Methyl	322>125	12.1	0.05	0.99
Dichlorvos	221>145	6.3	0.01	0.99
Dicrotophos	238>112	9.6	0.05	0.99
Dieldrin	379>325	16.0	0.10	0.995
Endosulfan I	405>323	15.3	0.10	0.99
Endosulfan-Ether	341>205	18.7	0.01	0.995
Endosulfan-Sulphate	323>217	17.7	0.05	0.99
Endrin	379>243	16.5	0.05	0.997
Ethion	385>143	16.8	0.05	0.99
Fenarimol	331>139	20.7	0.10	0.997
Heptachlor Epox B	387>217	17.7	0.10	0.99
Mevinphos	225>127	7.5	0.05	0.99
Phenthoate	321>135	14.4	0.05	0.99
Phosphamidon	300>127	12.0	0.10	0.993

Table 1. Summary of the pesticides analyzed, MRM's monitored and quantitative performance results.

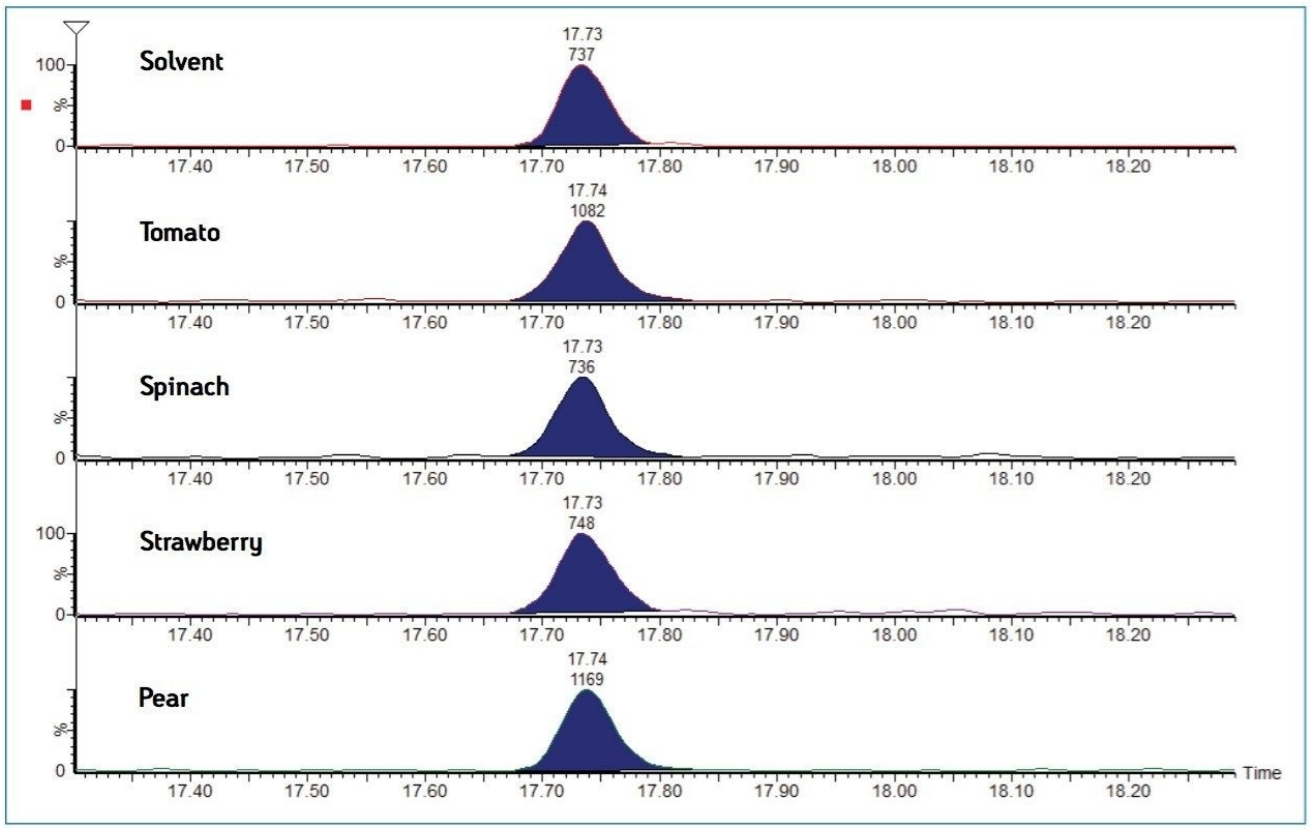

Figure 2. Example APGC-MS/MS chromatogram for heptachlor Epox B in solvent and four sample matrices at 1 ng/mL.

Conclusion

APGC is a soft ionization technique that produces abundant $[M+H]^+$ ions making it possible to generate selective and sensitive MRM transitions for pesticides. The universal ionization source offered by Waters instrumentation facilitates the quick and simple coupling of APGC, UPLC or ACQUITY UPC^2 on a single MS platform and therefore maximizing the utilization of the MS system within the laboratory. Coupled with Xevo TQ-S, APGC enables low level, accurate quantification of pesticides in a variety of sample matrices.

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720004776, August 2013