DETERMINATION OF PESTICIDES IN EDIBLE OILS BY GC-MS/MS

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INTRODUCTION

The determination of pesticides in food oils, such as olive oil, has many challenges. Due to the complexity of the matrix, which is high in lipids, sample clean-up is crucial to ensure a robust methodology, which does not lead to significant contamination of GC liners and columns, resulting in poor chromatography. Traditional approaches to the clean-up of high fat content samples such as olive oil have used a liquid-liquid extraction followed by GPC clean-up. This technique, although still in use today, is no longer attractive due to high solvent consumption and lengthy sample preparation times.

An alternative approach using acetonitrile as an extraction solvent, either through use of QuEChERS or a solvent extraction, followed by SPE clean-up to remove lipids is becoming increasingly popular in many residue laboratories.

In this poster, such an approach is discussed for 150 pesticides in olive oil, with a further evaluation given to the procedural standards approach appearing in the SANTE guidelines for overcoming some challenges of low analyte recovery in such complex commodities. [1]

METHODS

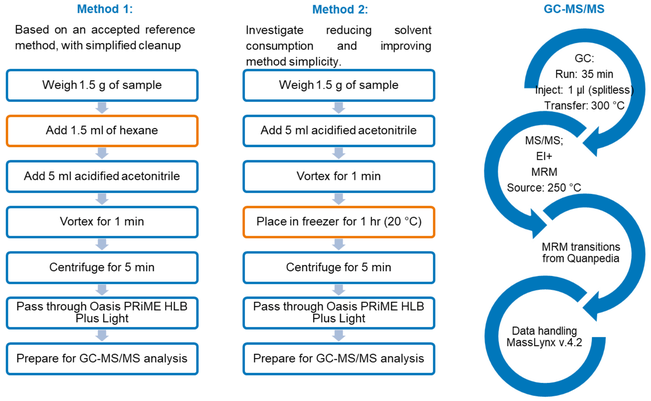
Sample preparation, extraction and analysis:

Samples were purchased from retail outlets, bottles inverted and sampled. Spiking all samples with over 150 pesticides, extraction efficiency and simplified sample cleanup was investigated. These methods are summarised in **Figure 1** below and results are then discussed.

Taking a previously published and accepted reference method for the extraction and cleanup of edible oils, the extraction procedure was replicated and GPC cleanup was replaced by simple SPE pass through, as summarized in Method 1 below. Method 2 attempted further to reduce the consumption of nonpolar solvents, replaced instead by a freeze out step (as highlighted by orange below). All extracts were acquired on the Xevo TQ-GC (GC-EI-MS/MS) system, with triphenylphosphate added used as internal standard prior to injection. The GC-MS/MS method is briefly summarized.

Full method details are available. For more information, scan the QR code below.

Figure 1. Summarized sample preparation approaches, including extraction and cleanup, and GC-MS/MS methods applied in this study.



RESULTS AND DISCUSSION

Evaluating analyte extraction and simplifying sample cleanup :

While hexane is a useful solvent for the extraction of nonpolar contaminants (such as fat), one observation when using the approach is poor recoveries of some pesticides, specifically organochlorines, due to their solubility. This is shown in **Table 1**, where the recoveries for Method 1 are significantly less than the 70% limit indicated in the SANTE guidelines.

By avoiding the use of hexane, and instead applying a freeze out defatting step, significant improvements were observed for the recoveries of many of the representative organochlorine compounds. Some low recoveries (< 60 %) were still observed for some analytes, suggesting limited extraction using this generic acetonitrile procedure for these complex food types.

Table 1. Recoveries are shown for a selection of more challenging analytes, where the hexane based defatting step shows low recoveries while replacing this solvent based extraction of nonpolars with a freezing step, analyte recovery is improved. Method recoveries for cleanup by Oasis PRiME HLB passthrough was evaluated (by spiking samples post extraction), yielding recoveries > 70%, showing that the spiked analytes are not retained on the SPE cartridge during either Method 1 or 2.

Compound	Method 1 % recovery	Method 2 % recovery	Oasis PRiME HLB Step % recovery
Aldrin	29.6	58.7	93.5
Alpha-BHC	53.0	98.7	96.5
Gamma-BHC	71.2	101.0	98.0
Chlordane, cis-	63.5	67.7	97.0
DDT, o,p'-	45.3	52.7	93.0
Dieldrin	53.0	46.7	74.5
Endrin aldehyde	71.5	100.7	91.0
Heptachlor	41.3	79.0	94.5
Hexachlorobenzene	15.2	38.0	77.5
Nonachlor, trans	37.6	60.7	84.5
Mirex	24.8	27.7	86.0
Pentachloroanisol	26.4	57.7	86.0

Applying an alternative calibration approach for improved quantitation:

The use of procedural standards is an alternative type of calibration which compensates for matrix effects and low extraction recoveries, which can occur with certain pesticide/commodity combinations. Procedural standards are prepared by spiking a series of blanks from the target commodity with different concentrations of analyte before extraction to create a calibration curve. Procedural standards are then analysed in exactly the same way as the samples for improved accuracy.

An example of procedural calibration curves for hexachlorobenzene and aldrin are shown in **Figure 2**. The improvements in method performance for low analyte recoveries are shown in **Table 2**, where spiked samples which have gone through the same extraction and clean-up (the procedural standards) are compared to the traditional calibration curve type for complex matrices (matrix matched curve).

It should be noted that the use of the procedural calibration results in higher measured recoveries (trueness of the method), however, actual extraction recovery is not improved.

Scan QR Bar Code for More Information

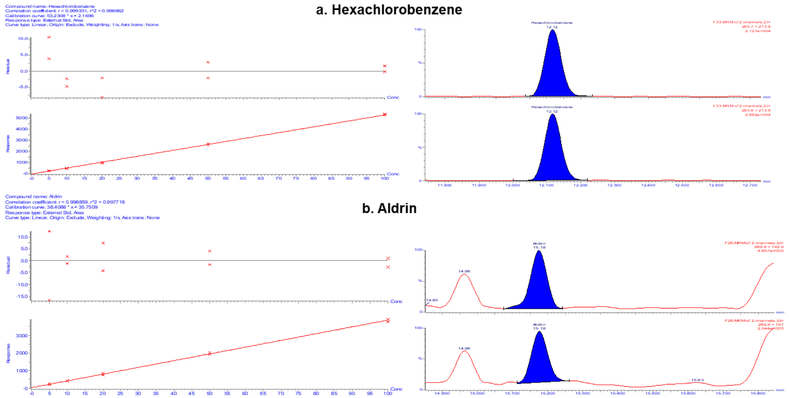


Figure 2. Example of procedural calibration curves (0.005 mg/kg to 0.1 mg/kg) and chromatogram for the lowest calibration point (0.005 mg/kg) for a. HCB and b. aldrin.

Table 2. While this alternative calibration type, procedural standards does not improve overall method recovery, significant improvement in terms of trueness are evident below for HCB and aldrin, where the measured concentration are corrected for low recoveries by the procedural standards.

Compound	Matrix matched curve % measured recovery	Procedural standard approach % measured recovery	Procedural standard calibration R^2
Hexachlorobenzene	39	100	0.999
Aldrin	57	102	0.998

CONCLUSIONS

- Replacing traditional methodology of hexane defatting and GPC cleanup with a simple defatting step by freezing out and passthrough SPE cleanup, respectively, a greener, less solvent intensive method is achieved for these highly complex edible oil samples.
- All 150 pesticide analytes yielded satisfactory recoveries when applying a passthrough SPE cleanup using Oasis PRiME HLB, while some analytes still showed low recoveries from the samples.
- Use of procedural standards offered an alternative approach to compensate for low recoveries in challenging food commodities.
- Applying Method 2, excellent method performance is delivered by the Xevo TQ-GC, where sensitivity of at least 0.005 mg/kg was achieved for the most challenging compounds.

References

1. European Union (2017), Document No. SANTE 11813/2017. Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed

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