# The Need for Speed Applying Triple Quadrupole MS in Pesticide Residue Analysis

Fast Pesticide Residue Analysis in a complex matrix using Triple Quadropole Mass Spectrometer

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Gas chromatography-mass spectrometry (GCMS) is a technique widely used in this sector, however with analysis runs that may take several hours to complete, and with repeat testing often needed, the market is inevitably calling for increased speed from both preparation methods and instrumentation. As regulations tighten, this speed must still be achieved without any loss of sensitivity and without compromising accuracy or reproducibility. Here we explore some of the latest technology enabling analysts to meet these heightened requirements.

### Pesticide residue analysis and GCMS

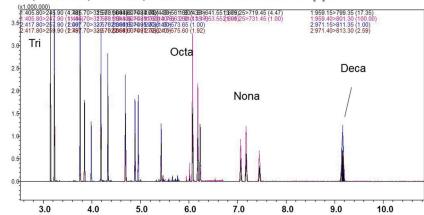
The analysis and detection of pesticide residues in foodstuffs is highly regulated, with the ongoing imposition of ever lower detection limits. The key challenge here lies in meeting these strict mandatory requirements, while maintaining the high sample throughput necessary for cost-efficient laboratory working and to ensure optimum turnaround times.

The high activity of modern pesticides at low concentrations means that even minimal amounts of residue can have an effect, and detecting these extremely low levels becomes an increasing challenge. Additionally, major pesticides may contain unexpected traces of contaminant pesticides, which require further analysis and identification. In 2005, the general EU limit for the maximum pesticide residue level in general foodstuffs was set at 0.01 mg/kg.1

Lowering detection levels means that analysts in this sector are increasingly coming up against issues with the sensitivity of instruments and inadequate separation of the individual components. Furthermore, the need for accuracy at these very low levels requires absolute rigour in eliminating any intrusive sample matrix effects. The sample matrix itself may cause interference that is detected alongside the analyte, a problem that has to be resolved if truly reliable measurement of the analytes of interest is to be achieved.

Turnaround times are always a challenge with laboratories being under pressure to quickly deliver definitive data. Using conventional chromatography it may take hours to separate components in a way that achieves sufficient resolution for acceptable quantification. Even then, these separations are frequently

## Fast GCMSMS of PBDEs in water and soil 10m, 0.1mm, 0.1 um, standard in nonane 50 ppB



 $Figure \ 1: Analysis \ of \ trace \ level \ polybrominated \ diphenyl \ ether \ (PBDE) \ using \ "Fast \ GC" \ columns.$ 

incomplete, especially for samples involving difficult mixtures and complex sample matrices. Several measurements and screenings are needed to ensure a complete separation, lengthening the process still further. Clearly this is not ideal in a high-throughput laboratory environment involved in pesticide residue analysis, especially where it may be necessary to analyse between 100 and 300 pesticides in a single run.

The need to accelerate sample preparation and analysis exacerbates further the challenges associated with achieving increased measurement sensitivity and solving the sample matrix problem. Methods such as the popular 'QuEChERs' ('Quick, Easy, Cheap, Effective, Rugged and Safe') procedure, whilst rapid, result in higher levels of background contamination in the final sample extract. The

real challenge comes when trying to combine the need for speed with the need for accuracy.

### Addressing the speed/sensitivity challenge

### Triple Quadrupole Mass Spectrometry and Multiple Reaction Monitoring

The increasingly important requirement for speed supported by sensitivity makes the power of tandem mass spectrometry (MS/MS) ideal when it comes to the spectroscopic separation of compounds. For ultra-trace level analysis (ppb – ppt) of organics, Triple Quadrupole MS is rapidly becoming the method of choice, and its use in determining pesticide residues in foodstuffs is a typical example.

Using Triple Quadrupole MS, a precursor ion is chosen from the mass spectrum of the compound. The first quadrupole filters this and allows it to pass the 'second quad', which in today's instruments is a hexapole or octapole. This serves as a collision cell where the single ion is further fragmented using a collision gas, usually Argon. The resulting product ions are then separated further in the 'third quad'. When using this technique, Multiple Reaction Monitoring (MRM) is applied whenever possible. In these cases, one or two ions are monitored - one is used for quantitation calculations and the other for compound confirmation.

When multiple target compounds are co-eluting, the quadrupoles and collision cell are rapidly switching electrical potentials, thereby removing the previously created ions to prevent 'cross talk'. This is crucial when it comes to the accurate identification and analysis of components to the critical levels required for pesticide residue applications. Modern equipment, such as the Shimadzu High Efficiency UF sweeper collision cell, can perform 600 MRM transitions per second with no cross talk. This allows collection of the maximum number of data points during the passage of a component 'peak' through the detector, giving the optimum quantitation precision.

It is now also possible to use 'Fast GC' columns to reduce conventional analysis times by a factor of three or four. These columns produce much smaller peak widths and require data sampling rates three to four times faster than conventional columns. An example of using such a column to analyse trace level PBDE is shown in Figure 1. This analysis was carried out using the Shimadzu Ultra Fast (UF) MS detector incorporating Advanced Scanning Protocol (ASSP).

Whilst the MRM technique for trace level determination of target compounds produces excellent results, it has the drawback of not providing any additional information about the presence of non-target compounds. For that, 'FullScan' data is required. In the past, this required a second analysis of the sample. Now, however, the ultra fast capabilities of modern instruments allow both MRM and FullScan data acquisition in a single run.

Both sets of data are available in a single data file, making possible trace level quantitation of target compounds and automatic qualitative analysis of every compound present in the sample. This halves the number of analyses required, minimises the analytical variables and dramatically reduces the time for a complete analysis.

Figure 2 shows an example of a combined MRM/FullScan analysis of metabolites in rat urine.

#### **QuEChERs Procedure**

The QuEChERS method is a streamlined approach that has been readily accepted by many pesticide residue analysts. This method makes it easier and less expensive for analytical chemists to examine pesticide residues in foodstuffs.

During the procedure, the analyst homogenises the sample in a blender. Sample is then placed in a centrifuge tube with reagent and agitated for one minute. The reagents used depend on the type of sample, with variables depending on the structure and type of matrix. Following this the sample is put through a cleanup column prior to chromatography analysis. With QuEChERS, eight samples can be prepared in 45 minutes.

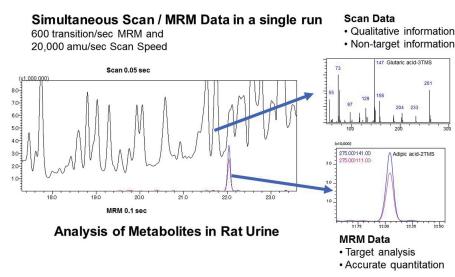


Figure 2: MRM/FullScan analysis of metabolites in rat urine using the Shimadzu Triple Quad GCMS

#### Conclusion

Triple Quadrupole MS is a powerful tool for fast and accurate analysis of a wide range of compounds in complex matrices. Modern high-performance instruments provide the correct data in one quick instrument run, rather than the several steps previously required. The added capability to run a full scan and MRM simultaneously, instead of these being two separate procedures, opens up multiple opportunities for an extensive range of analytical procedures within short timeframes.

The need for speed when running complex analyses will continue to become more crucial in the future, especially in dynamic

application areas such as pesticide residue testing. The techniques described above are used not only in food testing but also in determining pesticide degradation byproducts in water, sediment, and soils. These new technologies and practices are going a long way to meet the analytical speed and sensitivity demands across multiple testing applications and will continue to support analysts in

meeting the increasingly stringent regulatory requirements in pesticide residues and other controlled areas.

For more information on how Triple Quadrupole MS can improve your analysis, visit www.shimadzu.com

### References

1. Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC

