

A Novel Approach to Overcoming Sample Complexity in Food Contaminant Testing

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INTRODUCTION

The complexity and variety of sample matrices encountered is one of the biggest challenges in the analysis of food contaminants. Samples can range from relatively simple (e.g. most fruit and vegetables), to very complex (e.g. eggs, edible oils, spices). Methods for extraction of potential contaminants and clean up of samples to make them suitable for detection are numerous.

TYPICAL METHODS EMPLOYED

In the majority of cases the analysis of food contaminants is carried out using gas or liquid chromatography (GC or LC) coupled with tandem quadrupole mass spectrometry utilizing multiple reaction monitoring (MRM) for sensitive and accurate quantitation. MRM involves the selection and acquisition of a number of 'transitions' per analyte (targeted analysis) and offers enhanced sensitivity over 'full scan' ('non-targeted') MS methods where a selected mass range is acquired.

POTENTIAL ANALYTICAL ISSUES

Due to the complexity of matrices encountered (see Figure 1) and sample preparation methods employed, it is often desirable to monitor the efficiency of the sample preparation process to ensure there are no issues that could affect the quality of results.

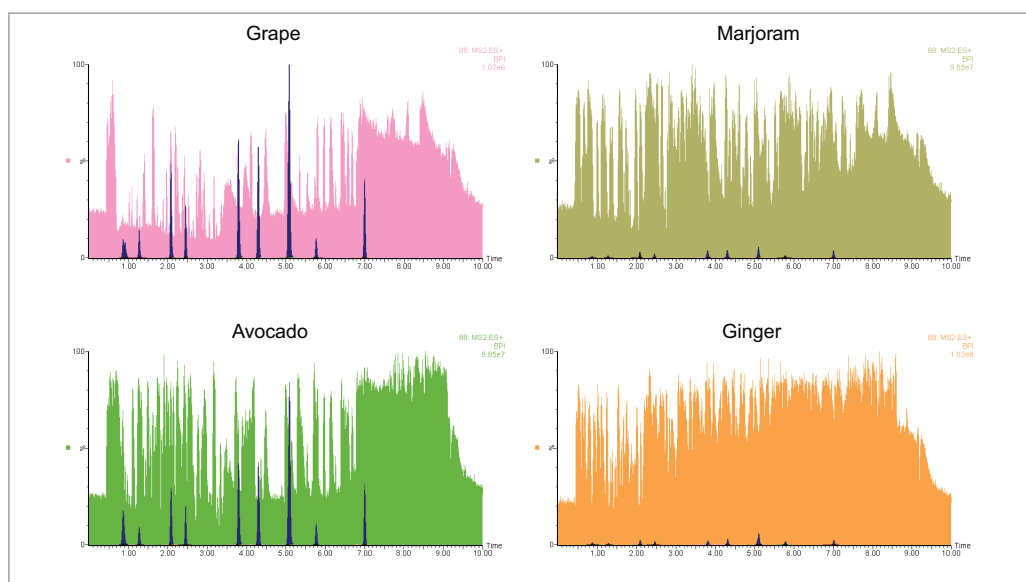


Figure 1. Matrix complexity – RADAR acquisitions of grape and avocado (1 g/mL matrix), marjoram, and ginger (0.1 g/mL matrix) spiked with pesticides at 0.01 mg/kg (overlaid MRMs).

An example of this is 'breakthrough,' when the capacity of the sample preparation device is exceeded for the analyte(s) of interest and all of the analyte(s) cannot be retained on that device.

This leads to under-reporting of target analyte concentration in the final results of the analysis, i.e., potentially a false negative. In addition, the presence of co-eluting compounds in complex matrices can lead to chromatographic interference as well as suppression or enhancement of the MS response leading to incorrect results. Care needs to be taken when undertaking both sample preparation and chromatographic method development to minimize the effects of interferences wherever possible.

MONITORING THE MATRIX BACKGROUND

As described previously, 'targeted' MRM methods, meaning that data is only acquired for the analytes of interest, are the most typically used by food testing laboratories. The ideal scenario would be to acquire the desired MRM transitions and monitor the matrix background using a 'full scan' acquisition in the same analytical run. This requires the MS system to switch rapidly between the two types of acquisition, even when the number of MRMs is high (can often be >100) without a compromise in performance.

Waters' tandem quadrupole MS systems use innovative T-Wave™ Collision Cell technology to switch between MRM (MS/MS) and full scan (MS); this acquisition mode is called RADAR.™ Setting up RADAR experiments is a simple process, where the analyst can add an MS scan function to any MRM method and use the Automatic Dwell Time function to optimize the MRM acquisition parameters, as shown in Figure 2.

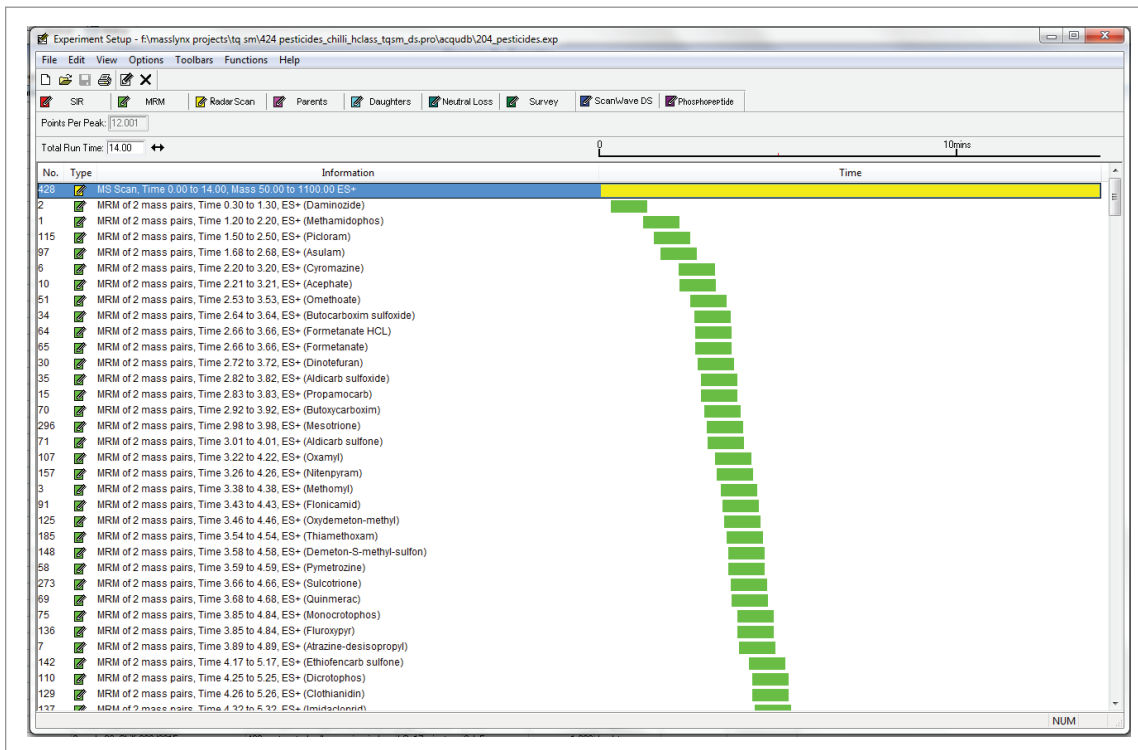


Figure 2. RADAR-enabled method showing multiple target MRMs for pesticides with a continuous background monitoring full scan function.

It is clear that monitoring the background produced from sample matrices is advantageous to check the development, efficiency, and consistency of sample preparation procedures for chromatographic method development, and to obtain a more complete picture of what is in the sample. Figure 3 illustrates the use of RADAR for sample preparation method development, where adding the Oasis® HLB SPE step removes a potential interference for chloramphenicol in chicken.

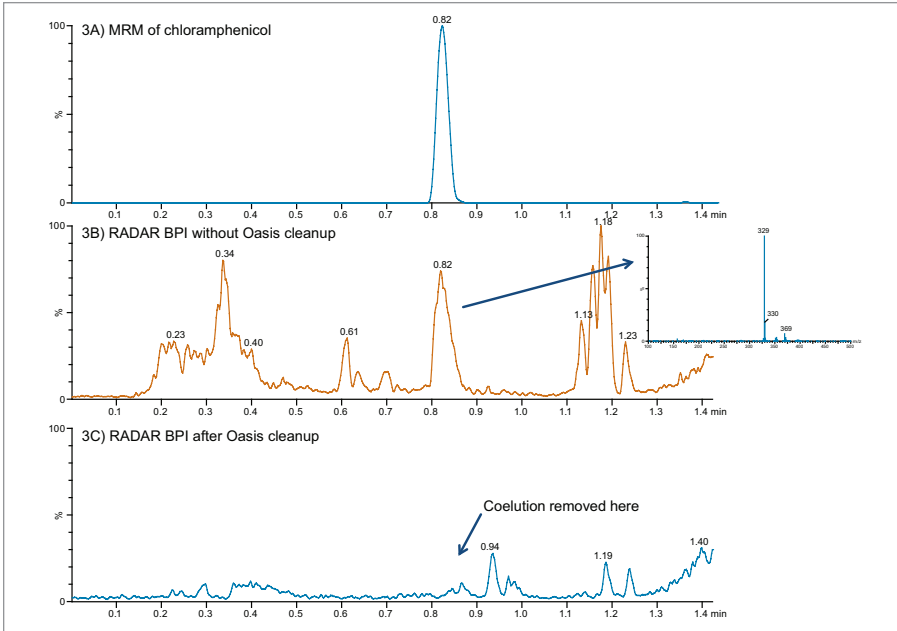


Figure 3. Sample preparation method development. 3A. Chloramphenicol standard, 3B. RADAR without Oasis HLB step, 3C. RADAR with Oasis HLB cleanup step.

The use of RADAR for chromatographic method development is shown in Figures 4A and 4B for the analysis of coccidiostats in animal feed. By elongating the chromatographic gradient used in (4A), the interference can be separated from the analyte of interest (4B).

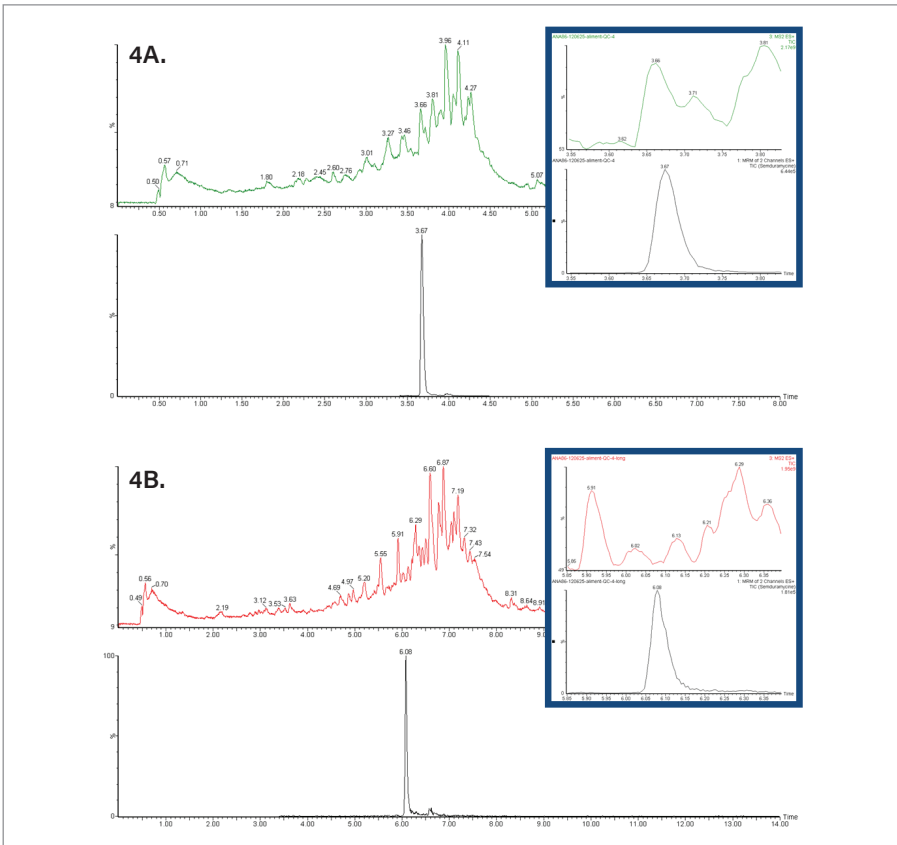


Figure 4A. MRM (lower) and RADAR (upper) of semduramicin in animal feed showing chromatographic interference from matrix.

Figure 4B. MRM (lower) and RADAR (upper) of semduramicin in animal feed showing chromatographic separation of interference and analyte.

UNEXPECTED CONTAMINANTS

The acquisition of the matrix background as the analysis proceeds can potentially enable the analyst to spot unexpected contaminants, either at the time of analysis, or retrospectively if a food safety issue is reported with that food commodity. A full scan MS spectrum can be obtained for any peak in the chromatogram to aid identification of an unexpected interference or contaminant of concern. The use of RADAR showing the possible presence of melamine is shown in Figure 5.

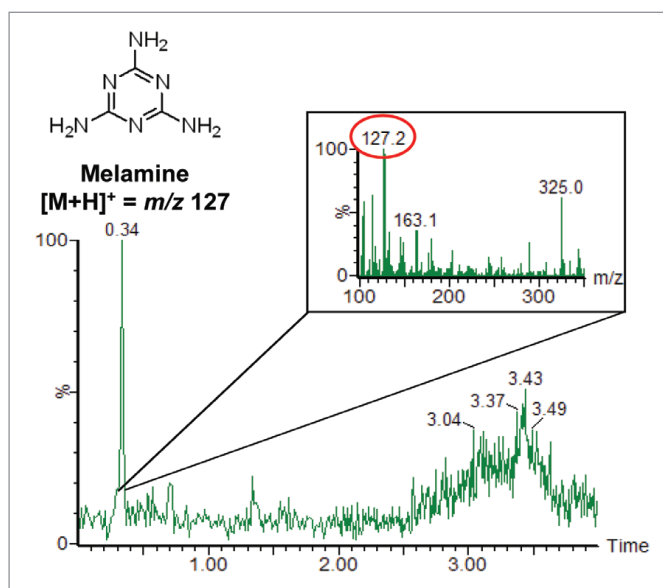


Figure 5. A chromatographic peak in a full scan RADAR trace showing the possible presence of melamine from the full scan spectrum.

Many countries around the world have food safety legislation that dictates contaminants to be monitored in specific food commodities; these typically form the lists of target analytes in methods performed by food safety testing laboratories. In some cases, however, the discovery of unexpected contaminants in food commodities does not occur until after some negative impact on consumers. An example of this is the China melamine scandal in 2008, when milk, infant formula, and other food ingredients were adulterated with very high levels of melamine. China reported an estimated 300,000 victims in total with six infants dying, and an estimated 54,000 babies being hospitalized. Melamine is normally used in the manufacture of plastics (not in food), but is cheap and gives the appearance of higher protein content when added to milk, leading to protein deficiency in the formula.

CONCLUSIONS

RADAR is an extremely useful tool in the food testing laboratory for the development of sample preparation and chromatographic methods, as well as for monitoring final methods when in use. It provides a fuller picture of the sample including the identification of interferences, sample preparation and chromatographic issues, and unexpected contaminants. RADAR is available on all Waters tandem quadrupole MS systems, it is easy to set up, and will not compromise quantitative performance.

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