Food (Analysis) for Thought

Driving the quality and scope of pesticide residue analysis forward is a constant and global endeavor. Is it time to embrace full scan, high resolution and accurate mass?

By Amadeo Rodríguez Fernández-Alba, Professor of Analytical Chemistry and Director of the Department of Chemistry and Physics, University of Almeria, Spain.

To watch the online presentation, visit: http://tas.txp.to/0815/pesticide

Originally from Madrid, my deep interest in food analysis and control actually began when I came to Almeria 20 years ago. Almeria is the main producer and exporter of fruit and vegetables during Europe's winter; focusing on pesticides control made a great deal of sense to me as an analytical chemist. And over the years I've been fortunate enough to collaborate with a number of regional institutions and producers to ensure that Almeria is at the leading edge of pesticide analysis and control. We recognized that one of the most serious issues in pesticide control was unacceptable discrepancies in the results obtained by different laboratories – and that can have a big impact on trade. We began to focus on analytical quality control and method validation procedures for routine pesticide control laboratories.

Harmonizing quality

It was also clear back then that a forum for knowledge exchange would help address those same challenges, and in 1996 the first European Pesticide Residue Workshop (EPRW) was held in Alkmaar, the Netherlands. I presented results from the procedures we had developed, which in some ways was the starting point for cooperation between the whole network of routine laboratories.

Another important step to get us where we are today came in 2006, when the European Commission's Directorate-General for Health and Consumer Affairs made an open call for four European Reference Laboratories (EURLs) for residues of pesticides. We became the EURL for fruits and vegetables (EURL-FV), and I've been its head ever since. We work together with the three other pesticide EURLs (cereals and feeding stuffs; foods of animal origin; and single residue methods).

In a nutshell, our main duties are to harmonize results and improve the quality of the whole network. Today, I am proud to say that the European Union has the world's best network of routine laboratories for pesticide residue analysis, at least in my opinion.

The role of technology

Much of my research is dedicated to the development and validation of new and improved analytical methods. Part of that responsibility means ensuring that National Reference Laboratories are kept up to speed on the latest advances in instrumentation, including mass spectrometry. New technology can have an impact on development of more appropriate or comprehensive methods, and ultimately improve the quality and equivalence of results between laboratories.

There have always been two main issues in our field: sensitivity and scope, both of which have grown in importance as international trade has increased. Go back 20 years, when I first joined this field, and the limit of quantitation (LOQ) was typically close to 1 mg/kg and the typical scope was 20-50 compounds in each run. Instrumentation in an average lab was a GC-single quad MS and LC with UV and florescence detection – and laboratories would spend half a day on very few samples. Today, laboratories must now routinely monitor hundreds of pesticides at very low detection limits – very rapidly. In terms of technology, it's a totally different world; today's instrumentation has risen to help analysts meet the challenges.

The most notable recent advancement in technology comes in the form of high resolution, accurate mass (HRAM) mass spectrometry, which I believe will play a big role in increasing scope and capacity. Introducing such technology for GC and LC into routine laboratories for pesticide residues is the next step, but obviously represents a significant change throughout our network and will take time to implement. We are very much involved in this process, and the instrument companies also have a role to play – and that includes making such technology affordable; after all, pesticide

control laboratories, by their very nature, need high-throughput, broad scope, and cost-effective analytical methodologies.

A new way to fish

My university is close to the sea, so you can see fisherman at work – sometimes fishing with a rod and line, sometimes with a net. I can draw an analogy to mass spectrometry. Line fishing is targeted – you select your line weight and appropriate bait to catch the right size and kind of fish, tossing away rogue catches. In triple-quad MS, we target selected ions using the quadrupole filter. Fishing with a net is a completely different approach – as is full-scan MS – as it captures all fish (or ions). With full-scan MS, the software determines detectability, as the hardware collects all information, and that means that we have the opportunity to not only investigate thouasands of compounds of interest, but also to revisit data for retrospective analysis – something that is very useful in unusual cases or amidst food scandals. It's essentially a much more flexible analysis concept – and it really opens the door in terms of identification. When it comes to pesticide control, there are two important aspects: i) enforcement of regulations and ii) assessment of risk. And an increase in scope allows us to gain a better understanding of current and future risks.

When they were first introduced, full-scan HRAM instruments were considered complementary to triple-quad instrumentation in routine analysis – sensitivity was an issue, as was cost, so they were reserved for challenging samples. But over the last few years, the sensitivity of Orbitrap-based instruments has increased, software has become much more powerful, and cost is coming down. Such instrumentation is no longer simply complementary – rather they are viable contenders to be the workhorses of routine analysis.

New, more affordable technology, such as the Thermo Scientific Q Exactive Focus mass spectrometer, allows us to conduct routine analysis as we would with a triple quad instrument; there are no major differences in analytical performance in terms of sensitivity, reproducibility, and linearity. And though the analytical performance is similar, the advantages in selectivity are significant.

One main advantage is that the identification capability is higher than triple-quad instruments, which is especially notable in dirty matrices with many endogenous compounds, such as tea or orange. In such complex samples, retention time and transition ratio overlaps can lead to false negative or false positive results. The production of false positives and negatives using accurate mass is much lower, because you're not working with nominal mass transitions; you have two or three ions at accurate mass. In a recent presentation (see sidebar), I offered a particularly good example, involving a false negative of linuron in coriander. A second major point is the overarching fact that information is not missed with full-scan MS – everything is collected by the instrument. Of course, advanced software is required to extract that information – but nothing is lost.

Embracing change

The switch to full-scan HRAM instruments is not going to happen overnight – but I do believe that we've reached a tipping point in pesticide analysis. Comparable performance – and price – coupled with the advantages of full scan mode and accurate mass for identification make more widespread adoption almost inevitable.

I'd like to conclude by quickly thanking all of the National Reference and official laboratories in Europe for their past and continued cooperation. Four years ago, we conducted a proficiency test on screening methods and many laboratories have participated voluntarily. I am very proud of our network, which is very motivated to introduce new methods and technologies to increase analytical performance. And that makes my job a lot easier.

Evaluating Q Exactive LC-MS

Amadeo Fernández-Alba presented at the 1st International Symposium on Recent Developments in Pesticide Analysis in Prague. You can view the full presentation online: http://tas.txp.to/0815/pesticide. Here, we present a brief summary.

Four main evaluation areas:
- Sensitivity
- Reproducibility
- Resolution
- Linearity

"In food analysis, quantification is a very critical issue. The results of our analysis can mean the exclusion of a consignment."

Evaluated four different commodities, representing a range of challenges:
- Tomato
- Pepper
- Green tea
- Orange

Considered a number of factors:
- Influence of resolution on detection
- Influence of resolution on peak shape
- Number of points per peak at different resolution

Pilot Study (full scan + MS/MS)
- 100 samples
- Over 180 pesticides
- Mass accuracy (full scan) <5 ppm
- Mass accuracy (MS/MS) <10 ppm
- Sensitivity = 0.01 mg/kg
- Linearity = no saturation
- Reproducibility + linearity < 20% + 10-500 ppb

Conclusions:
- Similar level of quantification to triple quad MS
- More robust identification; no false positives or negatives

Introducing the Pesticide Explorer Collection

Simplified workflows to support pesticide analysis from start to finish.

Conscious of the increasing demands placed on routine pesticide control laboratories, Thermo Fisher Scientific has developed the Pesticide Explorer Collection, comprising four complete solutions that cover all levels of pesticide analysis. Here, we share details of the first: the Triple Quadrupole "Standard Quan" solution.

The standard quantitation configuration – just like its stablemates – includes all the workflow components needed, from consumables and hardware through to software and built-in instrument and data processing methods. Dipankar Ghosh (Director, Enviro & Food Safety, LSMS, at Thermo Fisher Scientific) says, "The Pesticides Explorer Standard Quantitation configuration is designed to meet the complete needs of high throughput laboratories running routine targeted quantitation of pesticides. It provides the analyst the complete tools from sample preparation and analytical methodologies to reporting templates to achieve the desired results fast."

Pre-configured and pre-tested to get you up-and-running as soon as possible, the standard quantitation solution features a TSQ Endura triple quadrupole mass spectrometer to ensure compliance against regulated levels of detection in a routine environment.

Standardized sample prep and separations

Irrespective of the depth of analysis, accurate results are essential. To that end, all configurations of the Pesticide Explorer Collection include the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) sample preparation reagent kit and HPLC columns, both of which facilitate more accurate pesticide determinations in high moisture samples. QuEChERS is rapidly becoming the method of choice in food sample preparation and clean-up because of its high recoveries, time-savings, and simplicity. Moreover, QuEChERS generates minimal solvent waste but retains the power to cover a wide pesticide range, including polar and pH-sensitive compounds.

Regarding column choice, Mike Oliver (Product Manager, Sample Preparation and Accucore LC Products) says, "Pesticide analysis requires the separation of highly complex samples. In order to quantify and qualify accurately and provide confidence in analysis, highly reproducible and robust separations are required. To meet this challenge, the Pesticide Explorer Collection contains Thermo Scientific Accucore solid core HPLC columns, which deliver greater separation efficiencies in combination with robust formats."

Software that works with you

Pre-configured methods are simple to access on the included USB drive and can be easily set up and adapted in just a few steps.

Compounds can be selected from the database to automatically create the instrument and processing method. But flexibility allows you to upload, create or modify pre-configured methods with SRM transitions and retention times with ease.

Once the optimized data acquisition has been completed, the color flagging features in the bundled TraceFinder software enable you to quickly review data. The final step? The generation of high-quality standard or custom reports that turn your data into results.

Ed George, Senior Application Scientist in Environmental and Food Safety at Thermo Fisher Scientific, was heavily involved in the development of the Pesticide Explorer Collection, and believes the solutions reflect the constant drive for reproducible and robust results in pesticide control. George highlights the key goal of the Standard Quan solution: "The package for the TSQ Endura includes proven multi-class pesticide methods with compound databases and consumables to help you save time."