A Q&A

The Role of Ion Chromatography in Food Safety Laboratories

Stuart Adams
Senior Analytical Chemist
Fera Science Ltd., UK

Stuart Adams, Senior Analytical Chemist, Fera Science Ltd., UK

Polar ionic pesticides, such as glyphosate and chlorate, are often extracted using the *Quick Polar Pesticides Extraction* (QuPPe) method. This method, which uses acidified methanol, does not incorporate solvent partitioning or cleanup steps. The extracts can contain high amounts of co-extracted matrix compounds and thus difficult to analyze. Individual extracts must be analyzed multiple times using different chromatographic columns and conditions to be able to obtain sufficient chromatographic retention and acceptable peak shapes. Suppressed ion chromatography (IC) coupled with mass spectrometry (MS) has a number of advantages in the analysis of ionic pesticides. To find out more about the use of ion chromatography in food safety laboratories, *LCGC* talked with Dr Stuart Adams.

LCGC: Why is the analysis of ionic pesticides important in food safety?

ADAMS: Ionic pesticides are used frequently in agriculture, and we often detect residues in our food. Glyphosate for example, is one of the most widely used pesticides in the world. Within the European Union (EU) there's growing concern about how glyphosate is used and about people's exposure to this pesticide in food. The International Agency for Research and Cancer, which informs the World Health Organization classified glyphosate as a probable carcinogen in March 2015.

Chlorate has also been identified as a problem substance. Current investigations are examining chlorate residues in fruits, vegetables, and processed foods. Ironically, the presence of chlorate in food is not from its use as a pesticide but from biocidal solutions used in food preparation facilities.

LCGC: Can you summarize the advantages and limitations of ion chromatography compared to other chromatographic separation techniques, especially when coupled to mass spectrometry?

ADAMS: In my opinion, there are more advantages than disadvantages in using ion chromatography coupled with mass spectrometry for the analysis of polar pesticides. One minor disadvantage of using IC-MS is that analytical run times are longer than those for conventional LC-MS, and especially UHPLC-MS.

The smaller particle sizes now being used in some IC columns are improving run times, and newer IC systems are designed to handle the higher backpressure from these columns. One of the problems we've faced at Fera is that the demand for IC-MS analysis is exceeding available capacity.

One major advantage, is the fact we can now carry out multiresidue analysis from one simple extraction. In the past we spent a lot of time using single residue methods that involved specific extraction, and often derivatization procedures, for one or just a few related analytes.

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So, instead of two or three chromatographic runs, we may only need one. Using IC-MS we easily achieve the regulatory limits of quantification, which typically are about 10 µg/kg for nearly all the compounds of interest. We obtain better precision and have less need to re-analyze as compared to the derivatization methods.

I've read a number of publications on ionic pesticides that describe working methods with little or no retention of the analyte on the column. I've experienced problems with a lack of stability of retention times on the LC columns recommended for the Quick Polar Pesticides Extraction (QuPPe) method. With IC we've always experienced good retention of ionic pesticides. When we use the electrolytic eluent generator in combination with IC we achieve more reproducible retention times and better results.

The advantages of using a mass spectrometer include; the selectivity it provides in discriminating the analyte from the background signal, especially when looking at low *m/z* (<200 values), and the ion ratio information it provides to identify the analyte definitively in accordance with the current SANTE analytical quality control guidelines.

LCGC: The use of potassium hydroxide as a mobile phase must have some system complexity especially when coupled to MS. Does this cause any particular problems in routine analysis?

ADAMS: The potassium hydroxide eluent isn't compatible with the mass spectrometer. However, we use a postcolumn eluent suppressor device that electrolytically converts the hydroxide to water and removes the potassium counterions from the system.

We use an organic modifier, acetonitrile in our case, to assist the desolvation of water in the mass spectrometer. This process requires an auxiliary pump, but the benefits make it worth doing. The process is somewhat more complicated than using a conventional LC system, but it's automated, and an inline conductivity detector is used. We have a feedback loop, so if a sudden spike in conductivity occurs that correlates with the breakthrough of hydroxide the system shuts down, preventing damage to the mass spectrometer.

LCGC: How robust is the system, and can you give some tips and tricks that underpin your success?

ADAMS: We routinely use IC-MS at Fera for the analysis of ionic pesticides, which is a strong indicator of the robustness of the system. Our IC-MS system undergoes weekly preventative maintenance. Each week, columns are switched out for cleaning, deionized water needed for generation of the eluent is replaced, and the mass spectrometer source is cleaned to remove any matrix contamination.

When we use the Thermo Scientific™ TSQ™ Quantiva™ mass spectrometer, the ability to exchange the ion transfer tube while it is under vacuum allows us to return the system to operation quickly. We don't spend any more time maintaining the IC-MS system than we do our conventional LC-MS systems.

LCGC: You have reported a lot of results for anions. Have you tried the cations like glyphosate counter ion, trimesium, diquat, and paraquat?

ADAMS: We've looked at cation analysis in the past, but we have not devoted significant time to it. Our initial results weren't as promising as the results we've had with the anions, so we've focused primarily on anions. Recently, Thermo Fisher Scientific shared information on new IC separations of a large number of cationic pesticides. The results are quite interesting and we'd like to evaluate how these separations compare to other methods we run in this area.

LCGC: Apart from pesticides, have you analyzed other types of analytes using IC-MS?

ADAMS: We run our IC-MS systems almost continuously for polar pesticide analysis, so we don't often have the opportunity to explore other areas of work. However, we have conducted projects monitoring oxalic acid in honey, perchlorate and chlorate in vegetables, fluoroacetate in baby foods, nitrates and nitrites in meat and other food products, and food packaging contaminants in vegetables.

LCGC: You said that you consider IC-MS to be an essential technique for a food and environmental analytical laboratory. What other applications could be developed for this technique?

ADAMS: IC-MS could be used for a broad range of applications such as bromides, haloacetic acids, speciation of metals, organic acids, carbohydrates, and amines. I take a simple approach to method development. If the compound is ionic, then there's a very good chance that we can analyze it using IC-MS.

I've invested a lot of time at Fera demonstrating that IC-MS is a robust technique that can be used for routine analysis. I've witnessed substantial improvements in IC-MS technology, and the results I've seen from the Thermo Scientific™ ICS-5000 HPIC™ coupled with the TSQ™ Quantiva™ reinforce my belief that IC will continue to play an important role in food safety analysis in the future.