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Pesticide Residue Analysis with Automated EDGE Extraction System and Multi-Layer GC/MS Sandwich Injection

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Increased demand for automation of sample preparation

The QuEChERS method is the industry standard for pesticide clean-up and extraction of a wide variety of food samples. QuEChERS kits are easy to use and enable fast sample preparation resulting in excellent pesticide recoveries.

However, QuEChERS is still a manual multi-step process. Automated sample prep reduces time, costs, and human error associated with manual multi-step processes.

In this work, EDGE automated solvent extraction system was evaluated for extraction of 235 pesticides from tomatoes.

We also demonstrated the use of a multi-layer sandwich injection for automated matrix-matched calibration on GC/MS.

Baseline - QuEChERS extraction

The QuEChERS AOAC 2007.01 method used in this work, combines a salting out liquid-liquid extraction, and dispersive solid phase extraction (dSPE). The steps are shown in Fig.1.
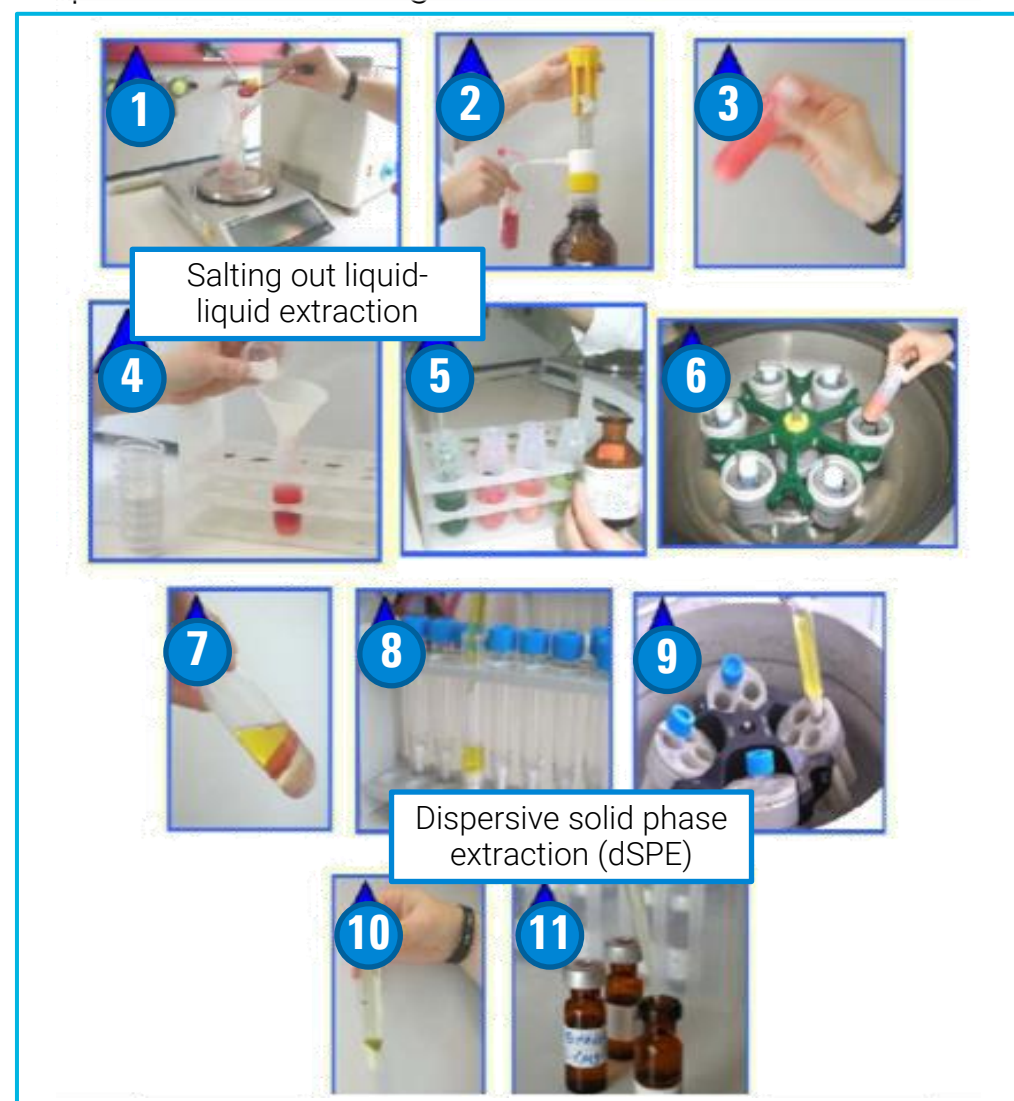

Figure 1. QuEChERS manual extraction steps.

EDGE automated solvent extraction

The EDGE (Fig. 2a) allowed for automating pesticide extraction with running up to 12 samples in one batch. The sample preparation and extraction steps are shown in Fig. 2b.
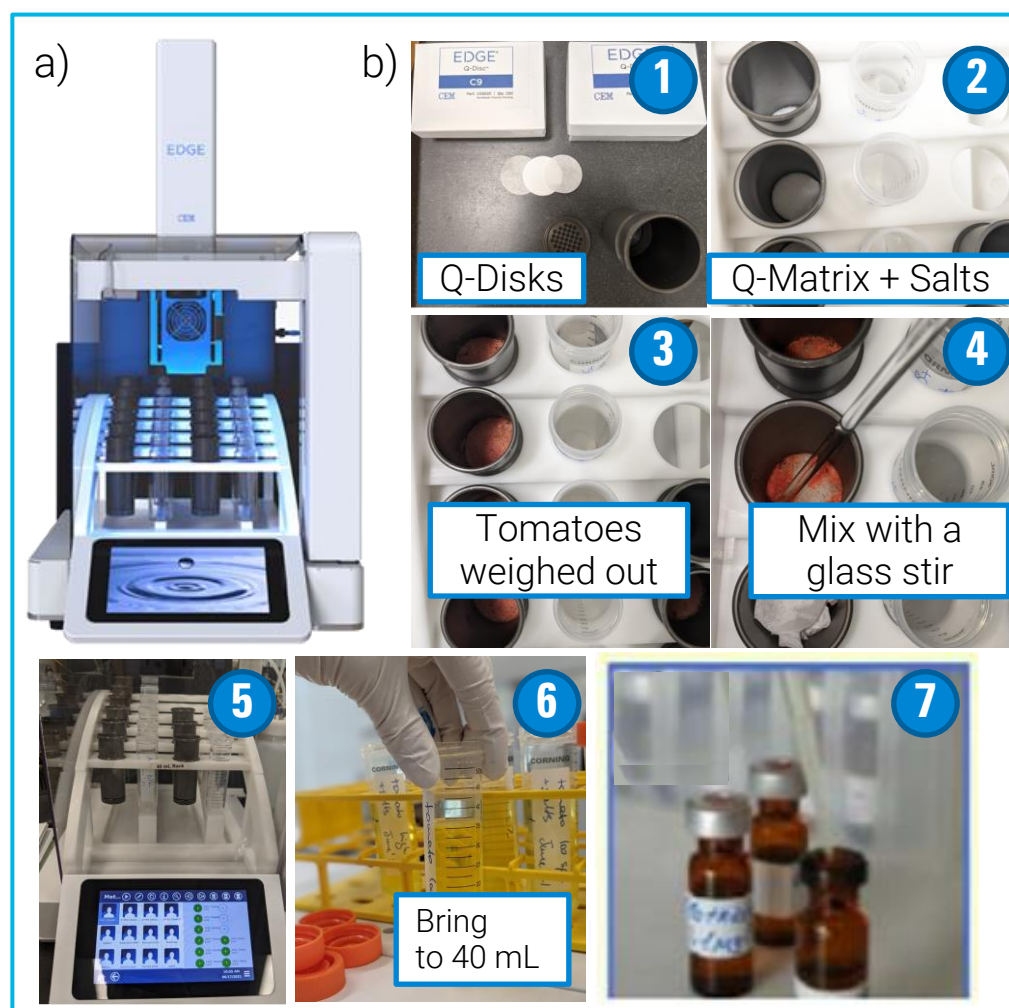

Figure 2. Automated solvent extraction with EDGE.

Pesticide Analysis with the Triple Quadrupole GC/MS

TQ GC/MS operated in dynamic MRM mode, monitoring 729 MRM transitions. The acquisition method was retention time-locked. The Agilent P&EP 4.0 Database allowed for seamless and automated development of the acquisition method.[1]
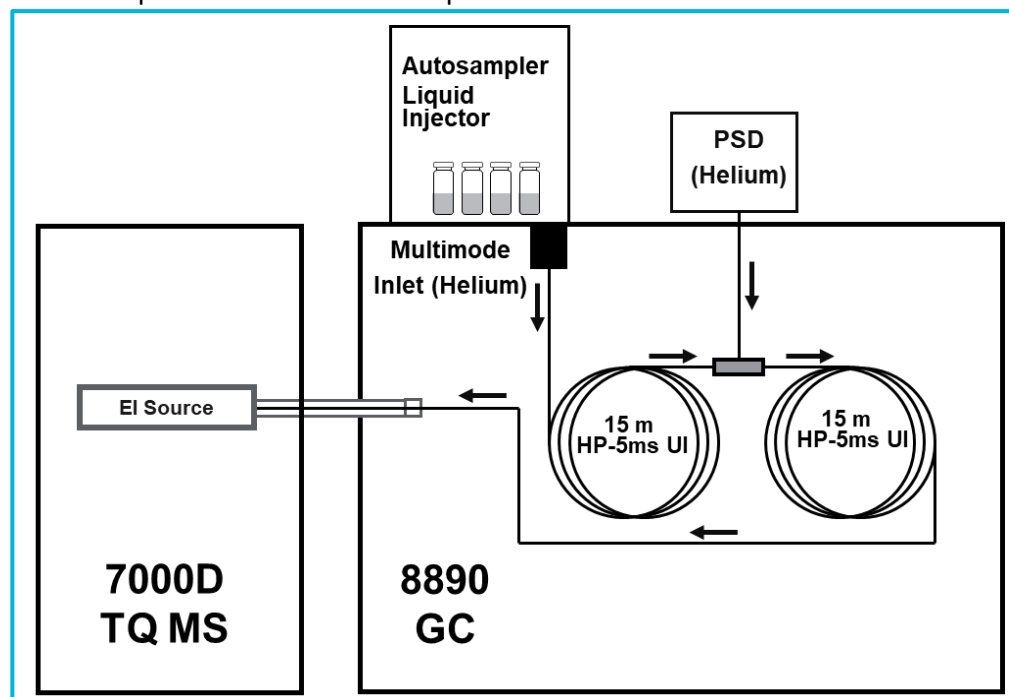

Figure 3. Triple Quadrupole GC/MS Configuration.

Extraction efficiency with high recoveries was achieved with both QuEChERS and EDGE

The EDGE offered the benefit of a simplified automated extraction in a single step with acceptable recoveries for a broad range of over 200 tested pesticides. The extraction time per sample was 10 minutes and 120 minutes for a batch of 12 samples, with no user intervention needed.

As shown in Figures 4 and 5:

- With **EDGE**, acceptable recoveries between 70 and 130% were seen in 96% of the pre-spiked 235 pesticides at 100 ppb (w/w in tomato), and 90% of those at 10 ppb (w/w in tomato)

- With **traditional QuEChERS** 99% and 97% of pesticides had recoveries between 70 and 130% at 100 and 10 ppb, respectively.
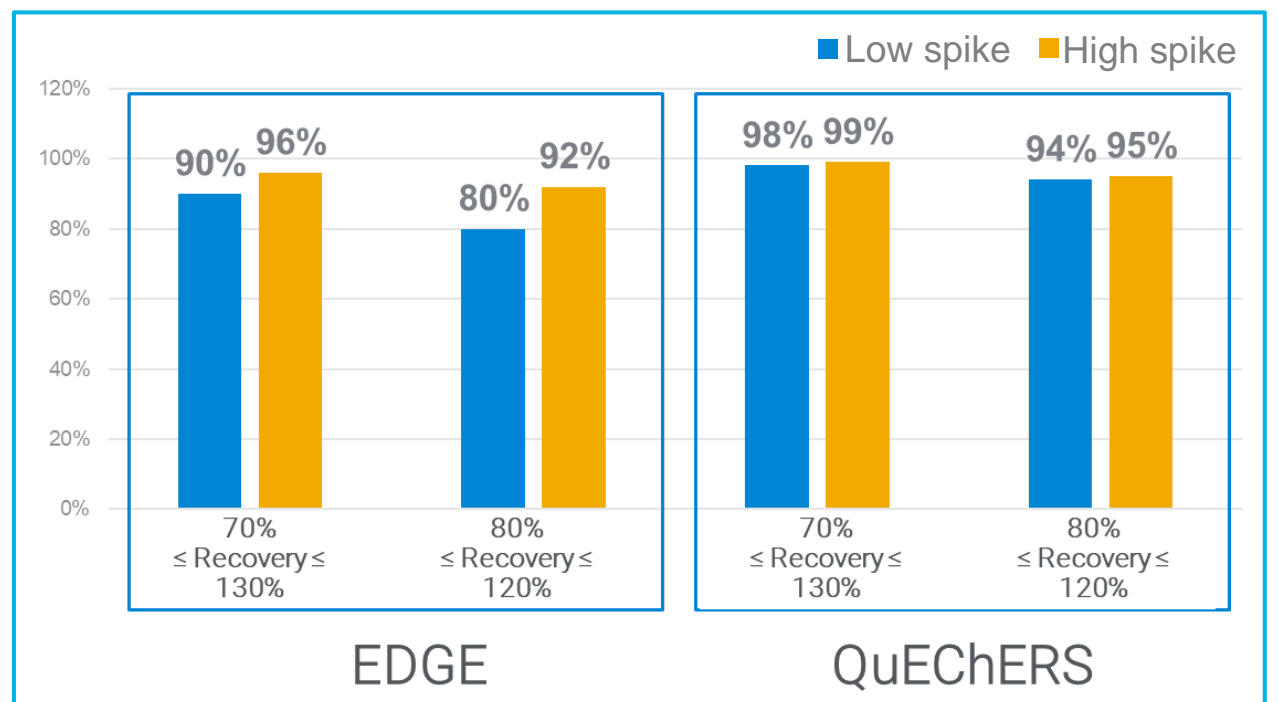

Figure 4. Pesticides (out of 235) with recoveries between 70 and 130% (on the left) and 80 and 120% (on the right) with EDGE and QuEChERS
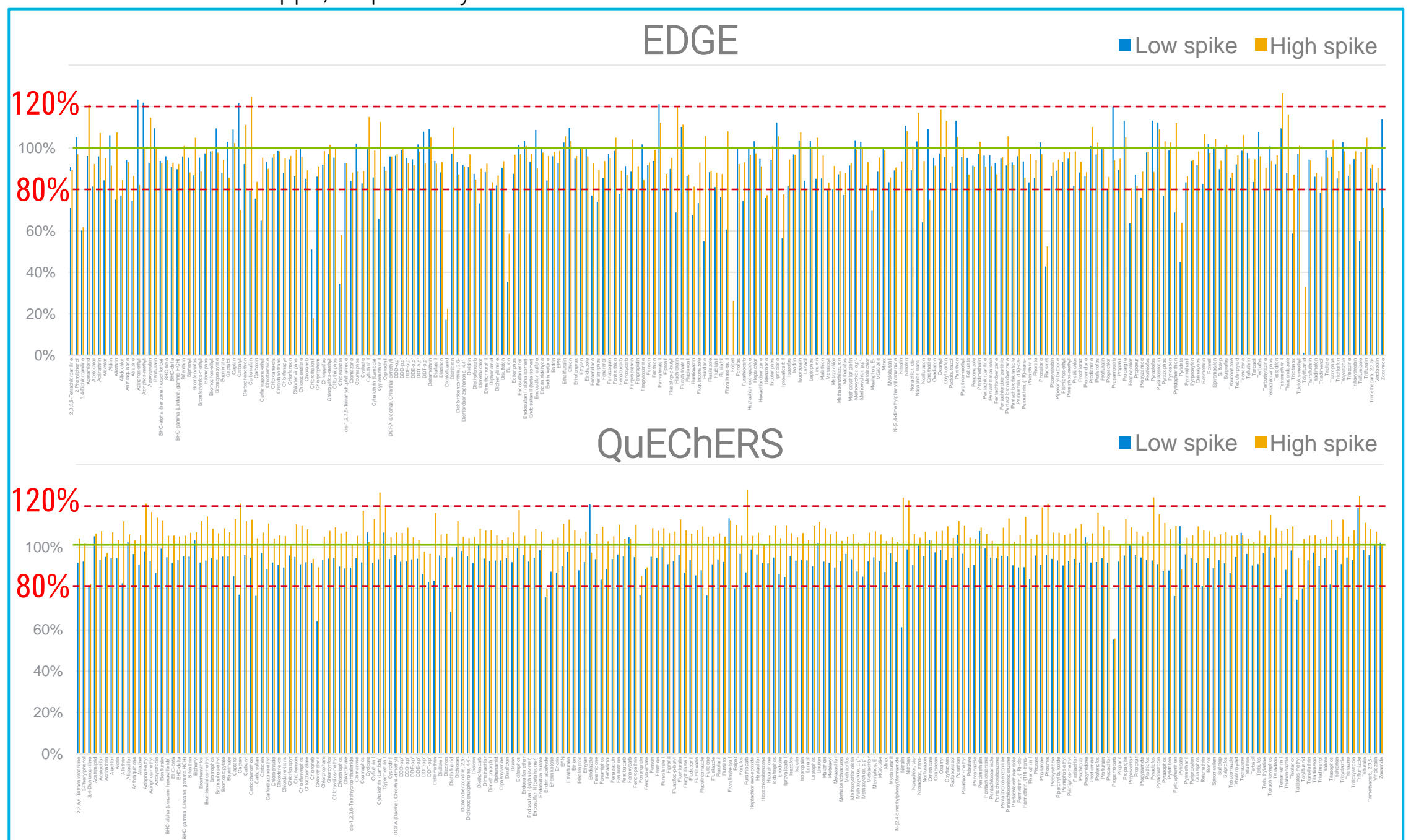

Figure 5. Recovery for 235 pesticides with EDGE (top) and QuEChERS (bottom) at 10 ppb (low) and 100 ppb (high) spikes.

Dilution factor and solvent consumption with EDGE solvent extraction and QuEChERS

It is of note that QuEChERS extraction yields the same concentration of pesticides in the extract (w/v) as the pesticide concentration in the commodity (w/w). Also, with the QuEChERS AOAC 2007.01 method, 15 mL of acetonitrile (ACN) were used for extracting 15 g of sample.

With EDGE, 40 mL of ACN were used per extracting 10 g of sample, yielding a 4-fold dilution of matrix and pesticides.

Sample Cleanup with EDGE and QuEChERS

EDGE and QuEChERS yielded comparable sample cleanup as indicated by the similar abundance of total ion chromatogram (TIC) acquired in full scan data acquisition mode of tomato sample (Fig. 6).

The EDGE extract had lower TIC abundance, especially at later retention times corresponding to high-boiling compounds. This may be attributed to a 4-fold dilution that occurs with EDGE extraction, unlike no dilution with QuEChERS.
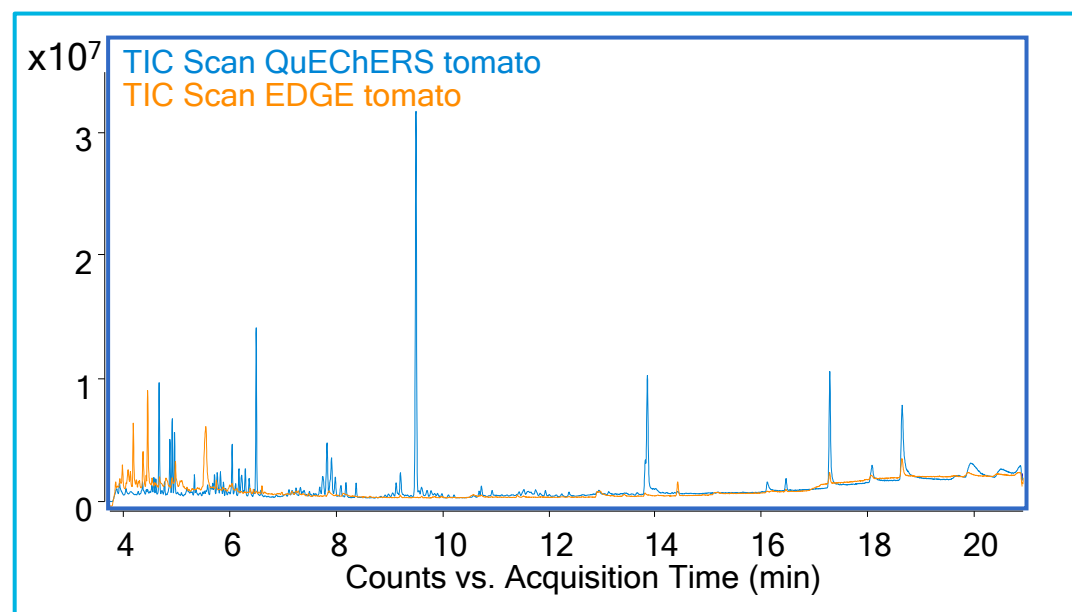

Figure 6. TIC of tomato extract with QuEChERS (blue) and EDGE (orange) acquired in full scan.

Sandwich injection for internal standard (ISTD) addition and matrix-matched calibration

For the analysis of samples and calibration, the autosampler was used for sandwich injections in two modes:

- 2-Layer reversed sandwich mode was used for the addition of ISTD and analyte protectants (AP) to the samples

- 3-Layer sandwich mode was used for creating matrix-matched calibration standards and for the ISTD and AP addition.

To create the matrix-matched calibration standards (0.5-500 ppb), first the calibration standards were prepared in solvent with the concentration 10-times higher than the target concentration of the matrix-matched calibration standards (5-5,000 ppb).

Then, the solvent standards (5-5,000 ppb) were used to make the matrix-matched calibration standards in an automated manner by the GC autosampler via a 3-layer sandwich injection technique.[2] The order of the different aliquots in the syringe was optimized to match the response of the matrix-matched calibration standards preprepared conventionally.

Linearity with an R^2 over 0.99 was observed over a wide calibration range of 0.5-500 ppb (w/v).

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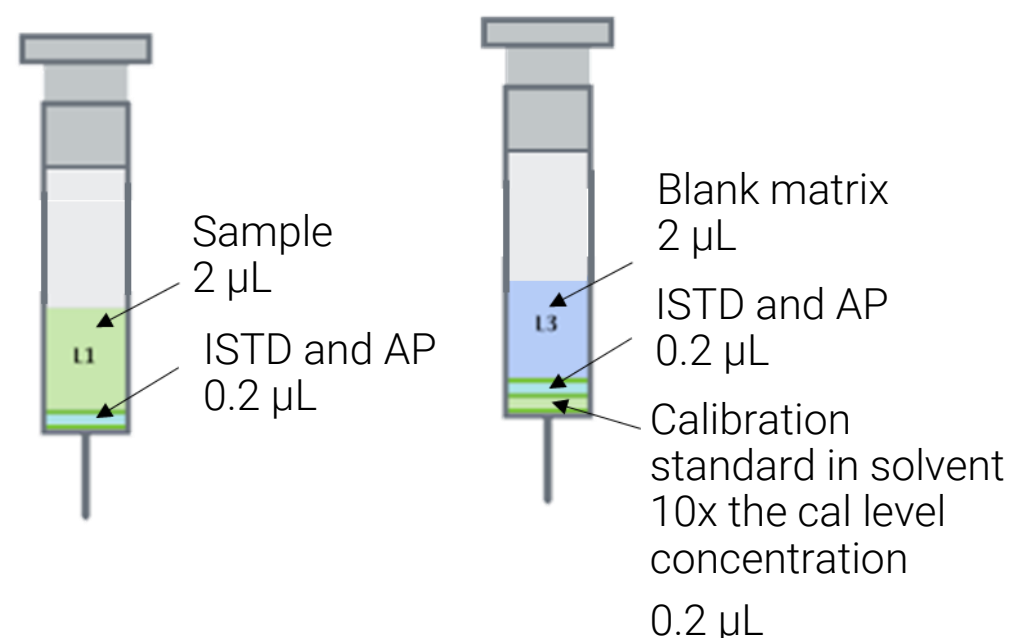
Figure 7. Reversed 2-layer sandwich and 3-layer sandwich injection method.

EDGE automated solvent extraction simplified pesticide extraction from tomatoes

Automated solvent extraction with EDGE offers the following advantages to pesticide extraction:

- decreased time and manual error

- acceptable recoveries comparable to the manual QuEChERS technique.

Automation in preparing calibration standard

The use of the 2-layer and 3-layer sandwich injection technique enabled:

- automated addition of ISTD and AP

- creating matrix-matched calibration standards automatically with various matrices using one set of solvent standards.

[1] Agilent Pesticides and Environmental Pollutants Analyzer 4.0.
https://www.agilent.com/cs/library/flyers/public/5991-7418EN_Enviro_Food_Analyzer_flyer_LR.pdf

[2] J. Westland. Advantages of Reversed Sandwich Injection for Pesticide Residue Analysis. *Agilent Technologies application note*, publication number 5991-7973EN, 2017.