Multi-residue Method Validation for Pesticide Residues in Soy Grain. Part 2: Determination of 169 Pesticides by LC-MS/MS (Positive and Negative ESI modes), without using any Clean up

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LC-MS/MS (positive and negative ESI) was used for the multi-residue pesticide analysis of soy grain samples, using two different extraction methods (based on acetone and acetonitrile). Clean up appeared not to be required for soy extracts.

Both extraction methods in combination with both LC-MS/MS modes were fully validated for 169 pesticides. From those 169 pesticides, 155 were analyzed in the ESI positive mode in a single chromatographic run time of 32 minutes, and 14 in the ESI negative mode with a run time of only 10 minutes. For recovery studies, milled and homogenized, blank soybean samples were spiked at 3 different spike levels (10, 50 and 100 µg kg^{-1}, n=6).

Even though no clean up was applied, no significant matrix effects were observed for most of the pesticides. LC-MS/MS thus showed a considerably lower matrix effect than that observed with the GC-MS methods. The linear dynamic range of the analytical curves was between 0.1 or 0.25 and 10 ng mL^{-1}. Circa 90% of the pesticides showed $r^2 \geq 0.999$, using standard solutions prepared either in matrix extract or in solvent. The ESI positive mode generated LOQs of 10 - 50 µg kg^{-1}, for 80% of the pesticides studied. In the ESI negative mode, it was not possible to detect flusulfamide at all spike levels, while 2,4–D, flucycloxuron and chlorfluazuron were not reliably quantified, due to low recoveries and/or high RSD values.

Comparing the two extraction methods tested, acetone and acetonitrile, it can be clearly observed that recoveries obtained from the last one are consistently (10 – 20%) higher than those from the first one. Especially at lower residues levels (10 – 50 µg kg^{-1}), precision is better (lower RSD%) for acetonitrile. The lower acetone extraction recoveries, with mostly still acceptable RSDs, though, could indicate to a less favorable partitioning of the pesticides between the organic phase and the aqueous phase.

Comparing GC- and LC-MS/MS, the latter technique was more efficient for pesticide analysis, taking into account sample throughput time, robustness and sensitivity. Also, the possibility to perform the determination of a large number of pesticides in just one single chromatographic run is another major advantage.

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