Current Developments of Pesticide SRMs

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Introduction and Objectives

During the last years a tremendous methodological progress was achieved by the invention of MRMs like QuEChERS, QuePPe, and SweEt for sample preparation prior to instrumental analysis by means of QQQ or Q-TOF instruments. The commonly accepted feeling about the capability of these widely used MRMs and many customized variants regarding sensitivity, trueness and robustness in pesticide analysis is: most of pesticide parameter scopes of interest can be analyzed in most of the basic commodities.

Several relevant and widely-spread pesticides are not covered by these sample preparation strategies especially in complex commodities like tea, tea-like products or spices. Just a few references referring to these pesticides occur in the common residue databases like pesticides-online. Trace levels of these "difficult" pesticides are not detectable by conventional MRMs in these commodities.

We note that a sensitive determination of pesticide parameters is impossible either due to poor recovery rates or negative matrix effects and chromatographic interferences by coextractives in the sample extract. The fungicide biphenyl is a parameter affected by these latter effects in complex commodities. Furthermore for polar herbicides like glyphosate, glufosinate, the glyphosate metabolite AMPA and several phenoxy carboxylic acids there is a need for a respective pre-column derivatization step to overcome the poor detector sensitivity and chromatographic performance of non-derivatized pesticide compounds in LC-MS-MS and GC-MS.

Methodologies

SRM for Glyphosate, Glufosinate, AMPA Analysis

The methodological steps of the determination of glyphosate, glufosinate and AMPA are as follows: after addition of $C^{13}N^{15}$-labelled internal standards the compounds of interest were extracted with an aqueous solvent. The resulting extract was submitted to a Dispersive Solid Phase Extraction (DSPE) cleanup step with cation exchange sorbents and subsequently derivatized with FMOC chloride. The FMOC derivatives were extracted into acetonitrile and analyzed by UPLC-MS-MS.
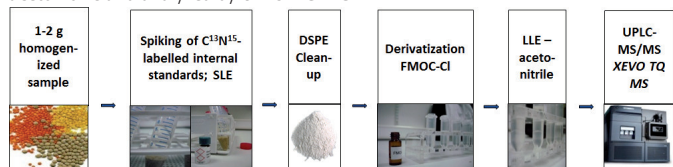

Figure 1: Workflow of the analysis of glyphosate, glufosinate and AMPA.

SRM for Phenoxy Carboxylic Acids Analysis

After addition of deuterated internal standards the phenoxy carboxylic acids were extracted with an aqueous solvent. The resulting extract was submitted to a Dispersive Solid Phase Extraction (DSPE) cleanup step extracted by LLE with dichlormethane and afterwards derivatized with pentafluorobenzyl bromide. The resulting PFB derivatives were analyzed by GC-NCI-MSD.
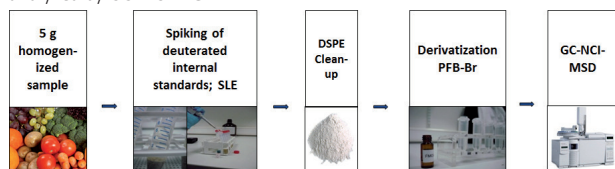

Figure 2: Workflow of the analysis of phenoxy carboxylic acids.

SRM for Biphenyl Analysis

After addition of the deuterated internal standard the compound of interest was extracted with acetone/hexane. After a solvent change the organic phase was epoxidized by m-chloroperbenzoic acid and cleaned by silica gel SPE. The resulting extract was submitted to GC-MS-MS.
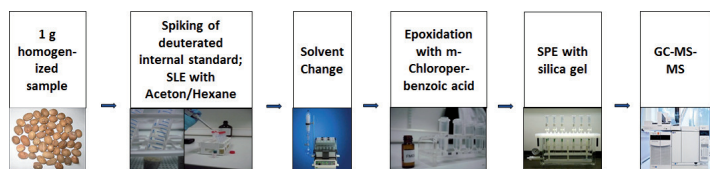

Figure 3: Workflow of biphenyl analysis.

Results and Discussion

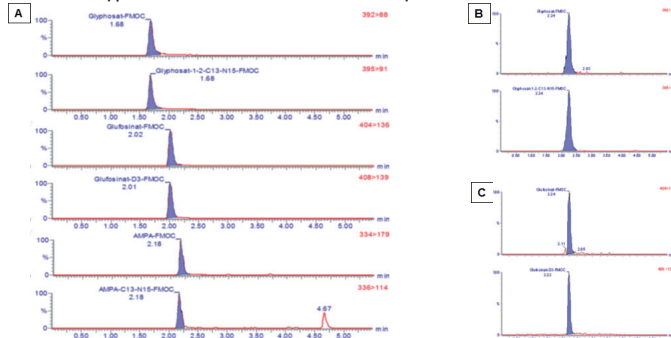### SRM for Glyphosate, Glufosinate, AMPA Analysis

Figure 4: UPLC-MS/MS chromatograms of glyphosate, glufosinate, and AMPA. **A)** 100 ng/mL solvent standard; **B)** 0,043 ppm glyphosate in rape seed; **C)** 0,166 ppm glufosinate in grape sample.
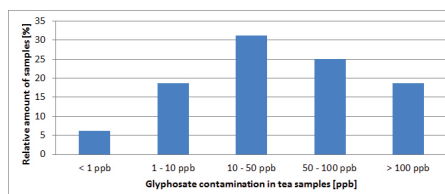

Figure 5: Relative distribution of glyphosate levels determined in green and black tea samples.
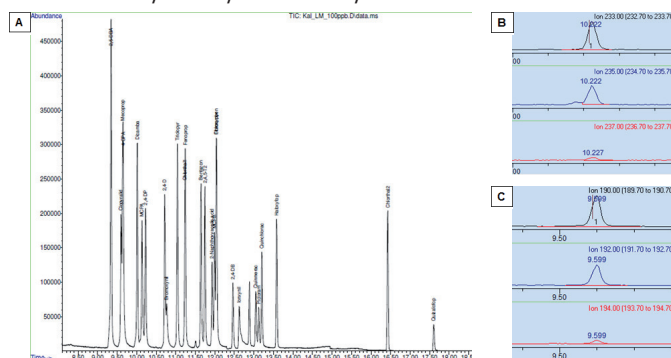
SRM for Phenoxy Carboxylic Acids Analysis

Figure 6: GC-NCI-MSD chomatograms of phenox carboxylic acids. **A)** 100 ng/mL solvent standard with 23 compounds; **B)** 0,011 ppm 2,4-D in lemon sample; **C)** 0,134 ppm Clopyralide in a green tea sample.
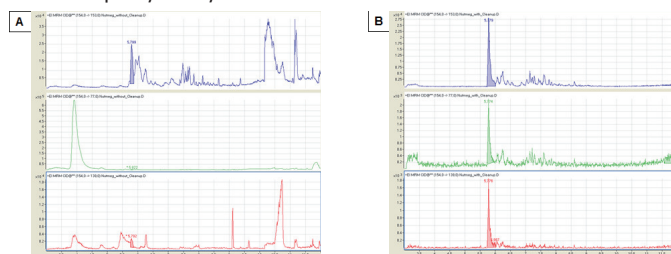
SRM for Biphenyl Analysis

Figure 7: GC/MS/MS chromatograms of 0,013 ppm biphenyl in a nutmeg sample. **A)** before **B)** after cleanup.

Take Home Messages:

- New SRMs display high sensitivity/selectivity, accuracy and robustness.
- LODs for all parameters analyzed were determined at 1 ppb.
- Validation acc. to SANCO/12495/2011 in all plant-derived commodity groups.
- Reporting limits of 10 ppb with recovery rates within a range of 90 –110 %.
- The method performance is superior to traditional MRMs and SRMs.
- Black/green tea seems to be predominantly contaminated with glyphosate.