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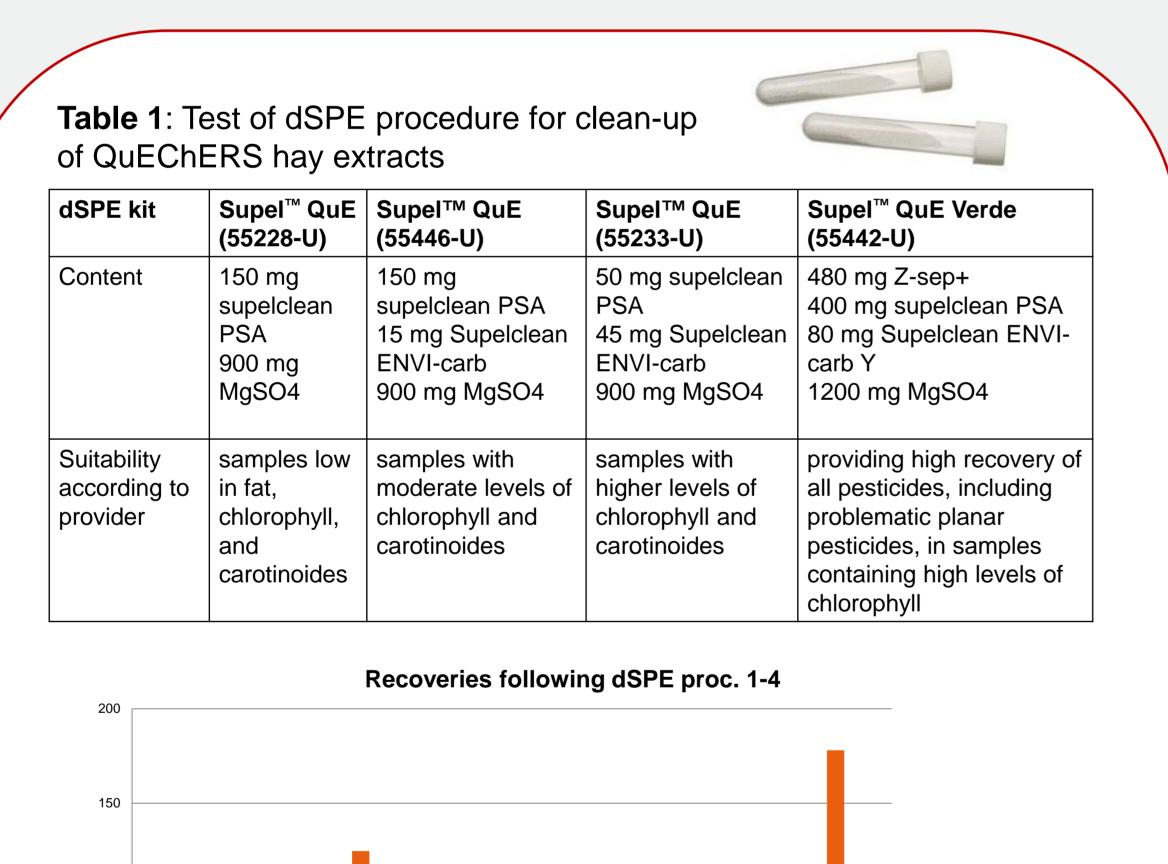


Hay for livestock feeding – Method validation

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Background:

Hay and grass may account for up to 100% of the feed for dairy and beef cattle. Thus hay may be of high importance for the pesticide residue exposure of livestock. Hay was therefore chosen as test material for EUPT-CF12 carried in January/February 2018. Method performance using QuEChERS according to EN 15662 and dSPE employing three different kits (Tabel 1) were studied for a selection of analytes (Figure 1). Using 1 gram of sample QuEChERS (EN 15662) performed equally well or better than when modifying the method by using one of the three other dSPE kits. 402 pesticides and metabolites of pesticides were therefore validated on hay using QuEChERS extraction according to EN 15662 and analysis by LC-MSMS and GC-MSMS. The pesticides and metabolites validated are listed in Table 3. The validation was performed in accordance with the requirements outlined in SANTE/11813/20173¹.



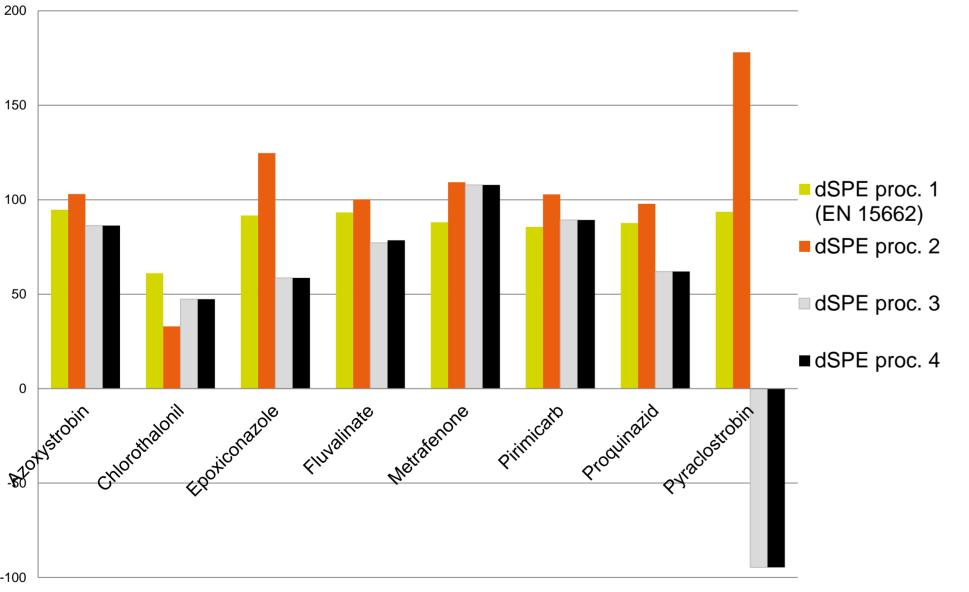
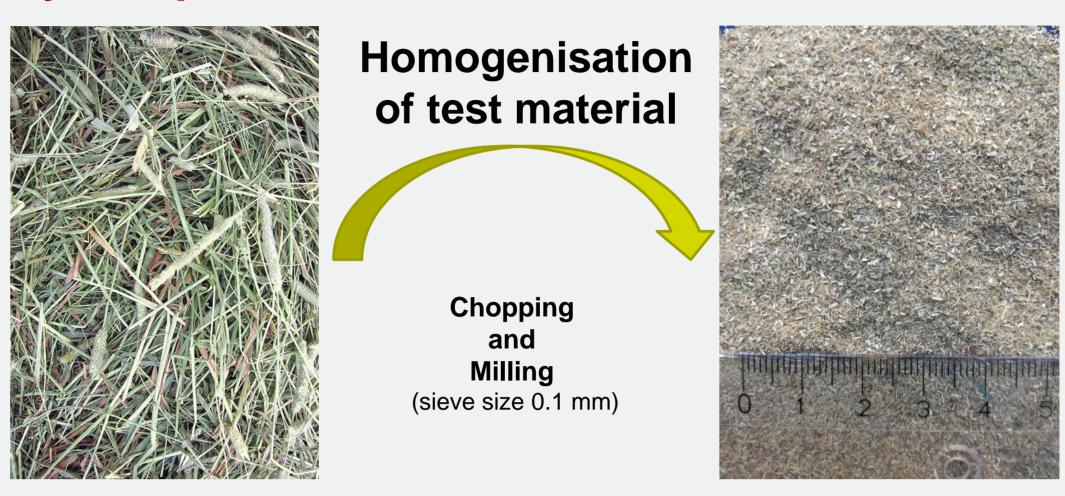


Figure 1: Recoveries of selection of pesticides spiked into blank hay samples (0.05 mg/kg) using QuEChERS extraction with dSPE according to proc. 1-4.

Conclusion: QuEChERS (EN 15662) gave satisfactory extraction of analytes from hay (Figure 1, Table 2). In total 402 pesticides and metabolites of pesticides were validated. 296 were GC-MSMS amenable compounds and 297 were LC-MSMS amenable. An LOQ of 0.025 mg/kg were obtained for majority of the pesticides and metabolites (see Table 2).

From inspection of GC-MS full scan chromatogram the hay extract obtained with QuEChERS (EN 15662) was found to be relatively low compared to the amount of coextract observed for oat (Figure 2).

Analytical procedure:



Extraction procedure employed for the validation

Weigh **1 g** hay (milled to flour)

Add a ceramic homogenizer and 10 g water and shake briefly

Add 10 ml acetonitrile and shake vigorously by hand for 1 min.

Add 4 g MgSO4, 1 g NaCl, 1 g Na₃ citrate dihydrate and 0.5 g Na₂H cirate sesquihydrate. Shake vigorously for 1 min.

Centrifuge for 10 min at 4500 rpm

Transfer the supernatant to a 15 ml tube and store in the freezer (-80°C) for 1 hour or over night. Thaw until slush ice consistency and then centrifuge for 5 min. at 4500 g

Transfer 6 ml of the supernatant to a 15 ml tube containing 150 mg PSA and 900 mg MgSO₄ and shake for 30 seconds.

Centrifuge for 5 min. at 4500 rpm

To an aliquot add 10 µl/ml of 5% formic acid solution in acetonitrile. Dilute the extract 1:1 with acetonitrile and analyse by LC- and GC-MSMS

Analytical setup

GC(EI)-MSMS: 5 µl injection on a TG-5SILMS (30mx0.25 mm ID, 0.5 µm film thickness) column, detection in MRM mode with 70 eV ionisation, source temp at 180°C and transfer line at 250°C.

LC(ESI)-MSMS: 1 µl injection separated on a Acquity UPLC, BEH C18 (1,7 µm, 2,1x100 mm) column. Gradient elution going from 98% water w. 0.1% formic acid and 0.02% ammonium hydroxide solution to 98% methanol in 10 min. Ionisation in both positive and negative mode and detection in MRM mode.

Results:

Table 2: Overall results for validation performed on hay using QuEChERS (EN 15662) with sample size reduced to 1 gram. (* recoveries for chlorothalonil was 47%)

	LOQ (mg/kg)			Recoveries		RSDr		
	0.025	0.05	0.5	Range	Mean	Range	Mean	Total no. validated
GC-MSMS	219	39	38	59(47)*-128	93	2-28	10	296
LC-MSMS	214	58	25	69-120	87	1-20	7	297
Total no. of validated compounds excluding duplicates								402

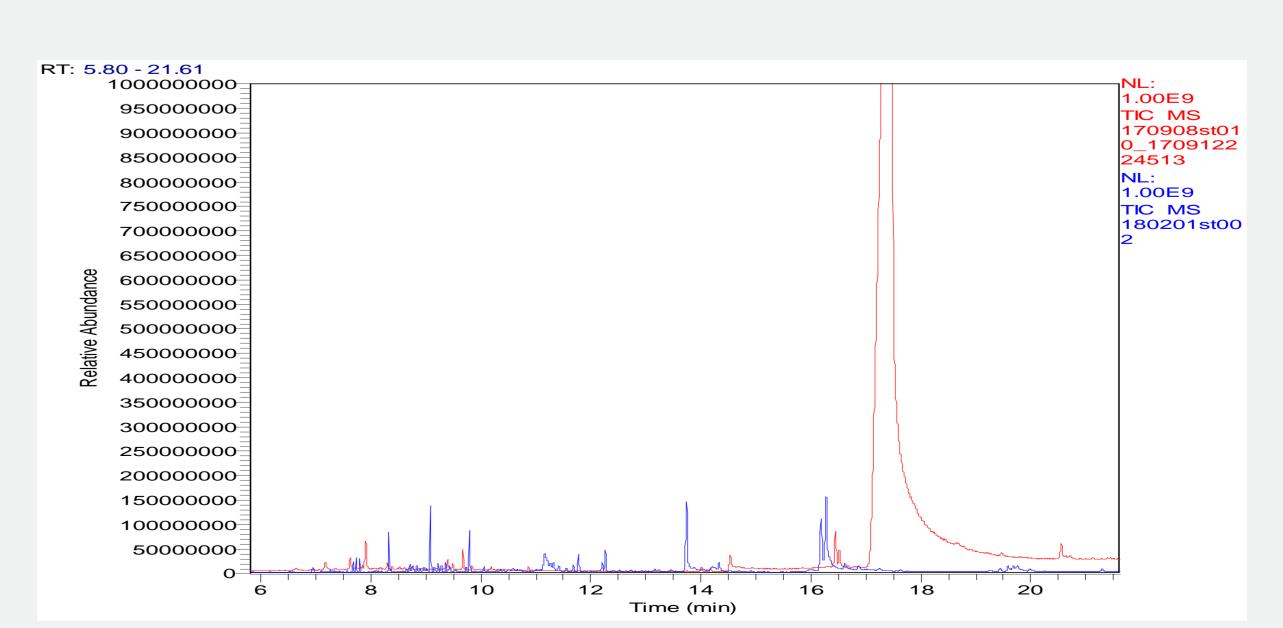


Figure 2: GC-MS full scan chromatogram of QuEChERS hay extract (1 g sample)(blue line) illustrate that the level of co-extracts are relatively low compared to the levels found for and QuEChERS oat extract (5 g sample)(red line).

Table 3: Pesticides and metabolites validated on hay using QuEChERS method

Pencycuron Pentachloraniline Demeton-S-methy Phenmediphan Phosmet oxor Phosphamidor Picolinafen Piperonyl Butoxide Pirimicarb-desmetl ropamocarl Propiconazole Propyzamide **Pyraclofos**

Dicofol, p,p

Pyraclostrobir

Pyridaben

Rotenone

Silafluofen

Spinetoram

Spirodiclofer

Teflubenzuron

Tepraloxydim

Tetradifon

Tetramethrir

Thiacloprid

Thiobencarb

Thiodicarb

Thiometon

Tolylfluanid

Tralkoxydim Tralomethrii

Triadimefon

Triadimenol

Triasulfuron Triazophos

Trichlorfon

Trichloronate Tricyclazole Trifloxystrobir

Triflumizole Triflumuron

Trifluralin

Tritosulfuron Valifenalate

Vamidothion

Vinclozolin

Triflusulfuron-methyl Triticonazole

Thiophanate-methy Tolclofos-methyl

Thiabendazole

Thiamethoxam

Thiencarbazone-methy Thifensulfuron-methy

Tetrasul

enthion oxon sulfone

enthion oxon sulfoxide

enthion sulfone

enthion sulfoxide

Fipronil-sulfid

Fluazifop-P-buty

Flubendiamid

Flutriafol

Fluvalinate I +I

Forchlorfenuron

Terbuthylazine

Tetrachlorvinpho

Pyraflufen-ethyl

Pyridaphenthior

EURL-CF: EU Reference Laboratory for pesticide Residues in Cereals and Feeding stuff, DTU National Food Institute, e-mail: eurl-cf@foood.dtu.dk, www.eurl-pesticides.eu 1: SANTE/11813/20173. Method Validation & Quality Control Procedures for Pesticide Residues Analysis in Food & Feed