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## Overview

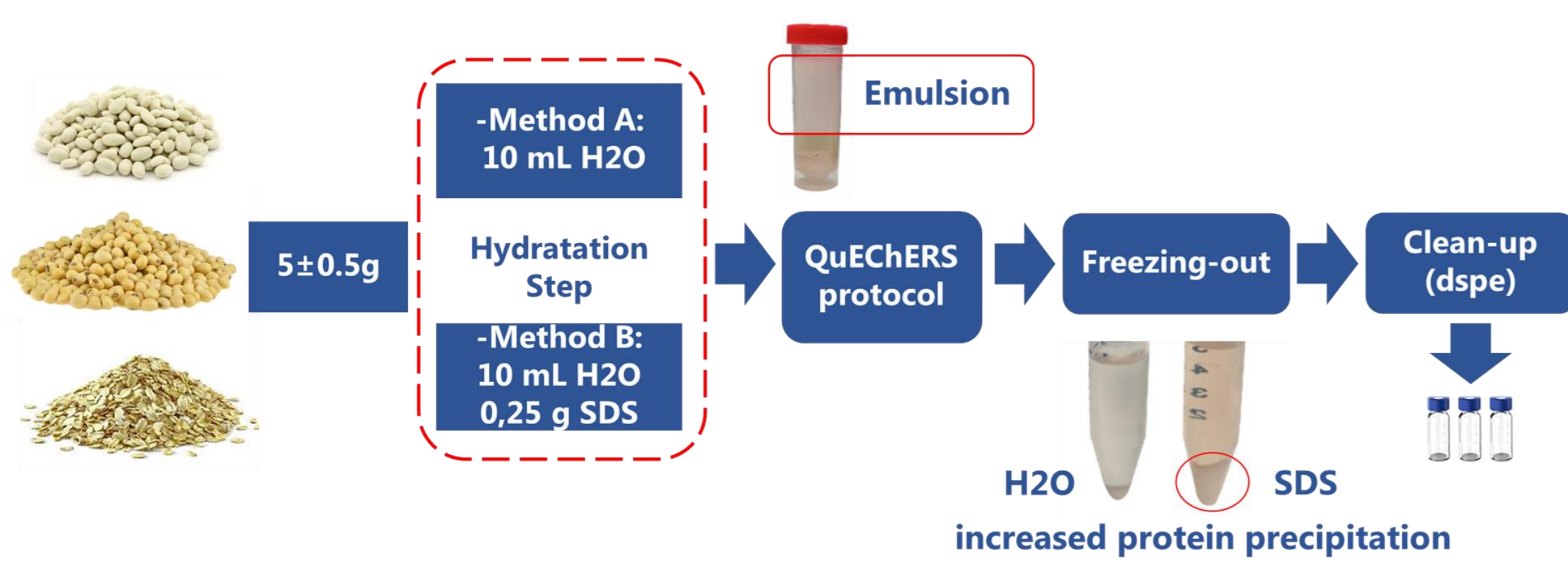
Pesticides have played a key role in the development of agricultural and animal production. This has also posed a risk to food safety and human health, which has increasingly become a focus of global attention. It is therefore essential to develop analytical methods that cover as many pesticides in food as possible. The difficulty in developing multi-residual methods resides mainly in two points. The first is the different nature and composition of the matrices to be analysed, the second is the different physicochemical properties of the analytes of interest. Liquid chromatography (LC) has advantages such as good sensitivity and the capacity to adequately separate many pesticides. Liquid chromatography coupled with tandem mass spectrometry is the most powerful qualitative and quantitative analytical technique and the most widely used tool for pesticide analysis due to its high capabilities.

It has been observed that in matrices with high protein content and low aqueous content, an emulsion is formed during the hydration of the samples. The analysis of such matrices is an analytical challenge, as during the extraction these dry samples need a hydration step. This step causes the co-extraction of matrix compounds that form flocs in the extract, in the case of samples with high starch or fat content, something similar happens and fatty acids are co-extracted. For this reason, the extraction of such matrices involves many steps to obtain a cleaner extract for analysis.

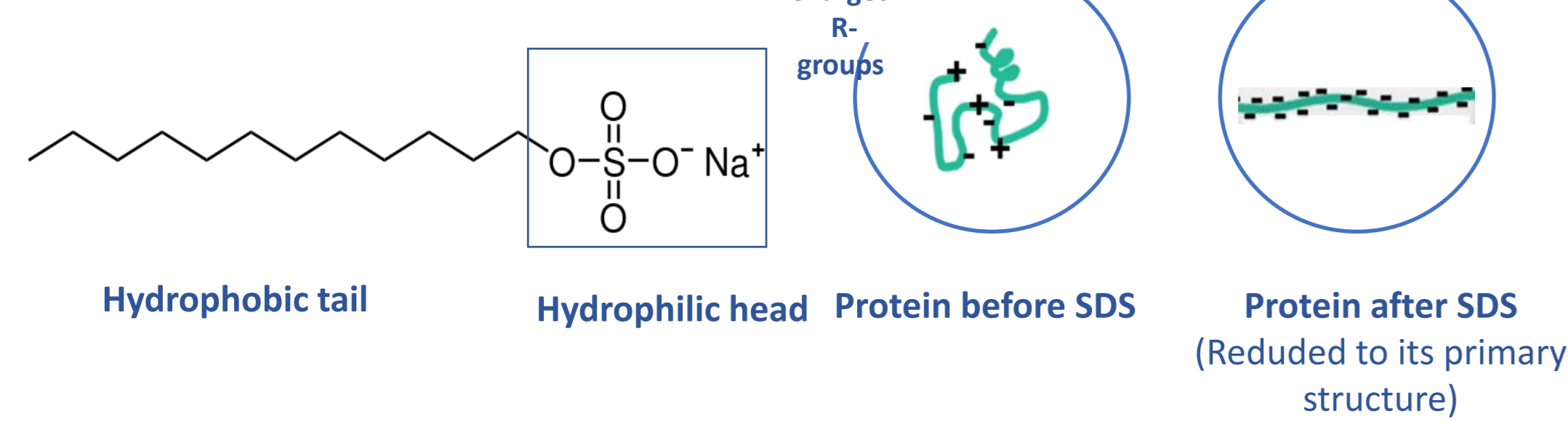
In this study, new approaches for the extraction of pesticide residues from difficult vegetable commodities with high protein content such as white beans, oats and soybeans have been developed and validated. For this purpose, samples were fortified to a level of 0.010 mg/kg of a list of 250 pesticides and the "regular" QuEChERS citrate method and a modified were evaluated. This modification consisted of the addition of sodium dodecyl sulphate (SDS) during the hydration step. In both methods a freezing out step before the clean-up was performed. The extracts obtained were analysed by LC-MS/MS using dual-channel technology to shorten the analysis time. The validation of the extraction methods has been carried out in terms of precision (recovery at 0.010 mg/kg), repeatability (5 replicates) and matrix effect.

In the case of white beans and oats, an improvement in terms of recovery has been observed with a greater (25% of the scope) number of compounds recovered between 70-120% with the method adding SDS compared to QuEChERS citrate. In the case of soybean, the results referring to recovery values obtained are quite similar in the two methods. Some compounds significantly improve their recovery values in the three matrices evaluated, such as chlorpyrifos, dichlorvos, trinexpac-ethyl and trinexpac-methyl, among others.

## Methods



### Sodium Dodecyl Sulfate (SDS)



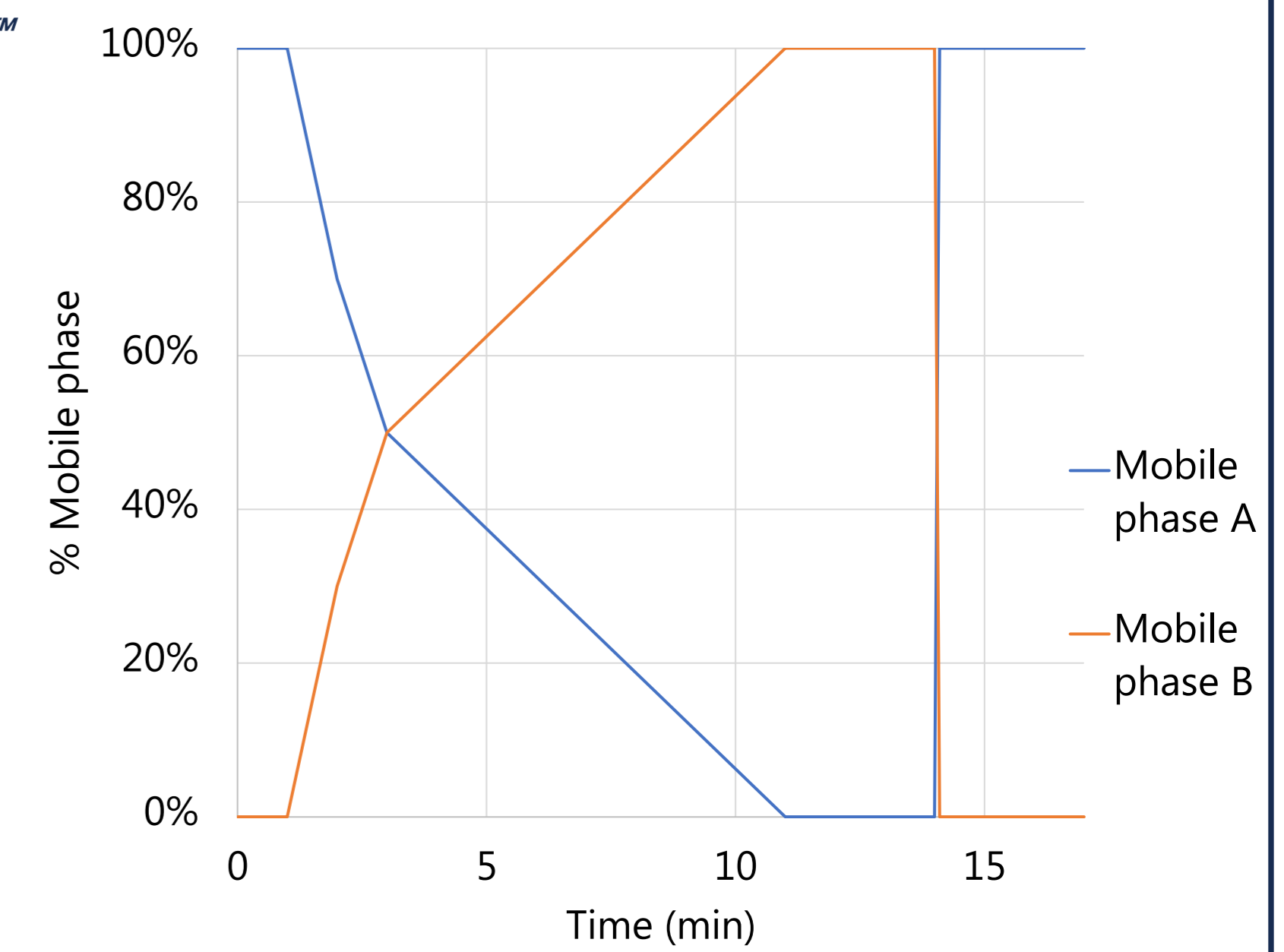
### UHPLC (Thermo Scientific™ Transcend™ DUO LX-2-LC)

Column: Accucore C<sub>18</sub>  
2.1 x 100 mm, particle size 2.6 μm  
Column temperature: 30°C  
Flow rate: 0.35 ml/min  
Injection volume: 2.5 μL  
Autosampler temperature: 10°C



### Triple Quadrupole TSQ Altis™

Ion spray voltage (+): 3500 V  
Ion spray voltage (-): 2500 V  
Sheath gas: 50  
Sweep gas: 1 (arbitrary units)  
Ion transfer tube: 325 °C  
Vaporiser temp.: 350 °C  
Working mode: SRM



- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)
- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)

### Dual channel technology:

The dual-channel mode produces very stable retention times and results, which are equivalent to the single-channel mode, with the advantage of reducing the analysis time considerably.

## Results

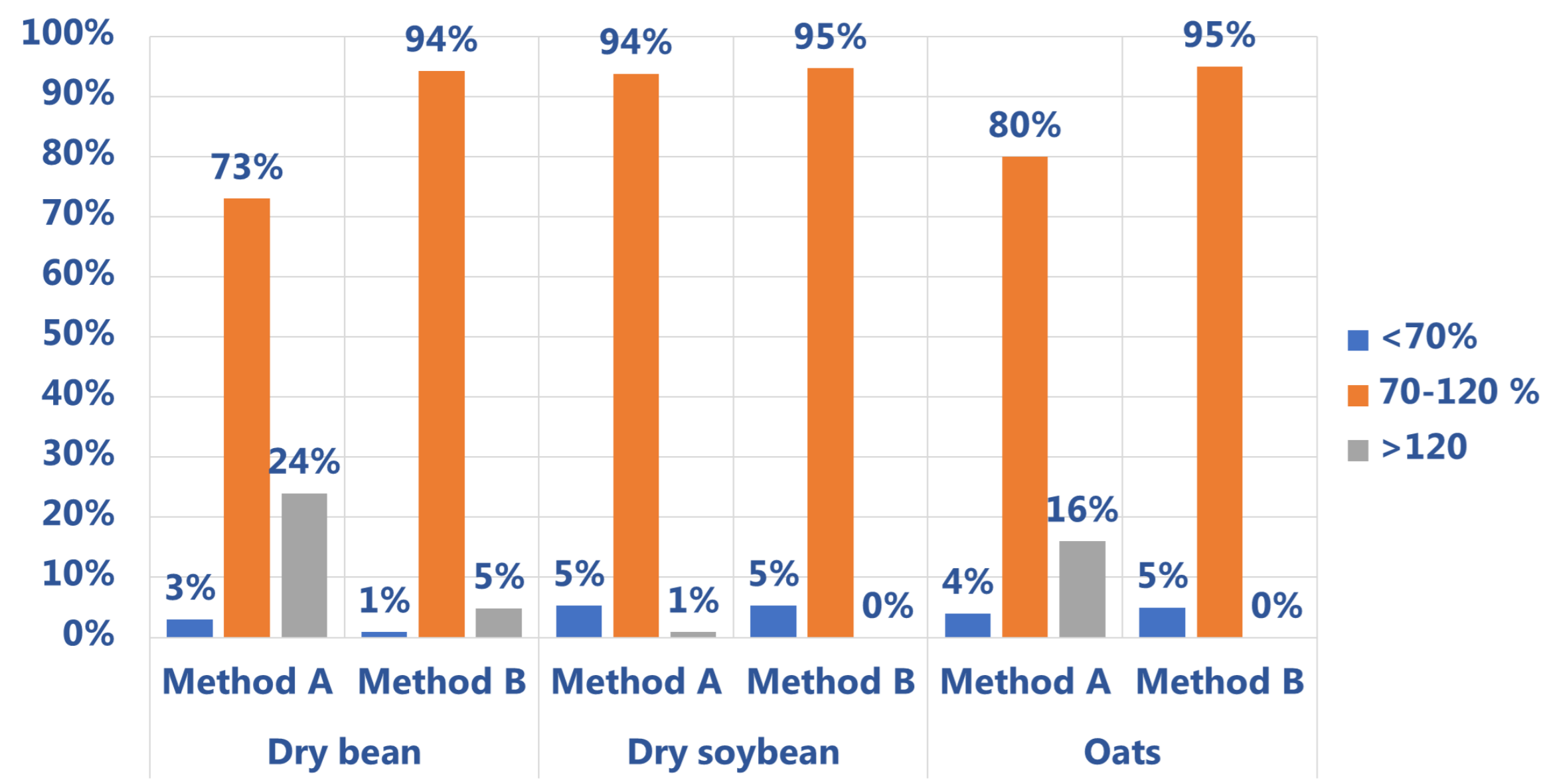
### Method validation:

#### Recoveries and RSDs:

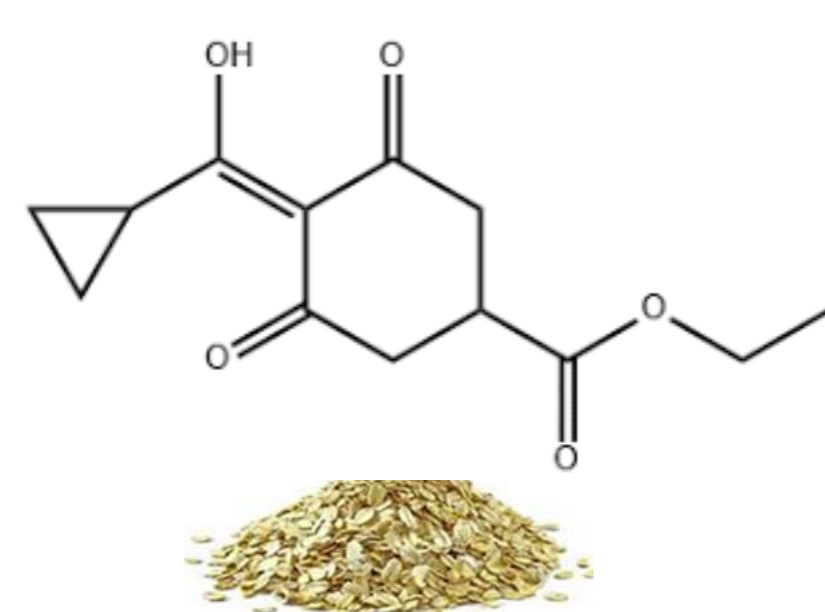
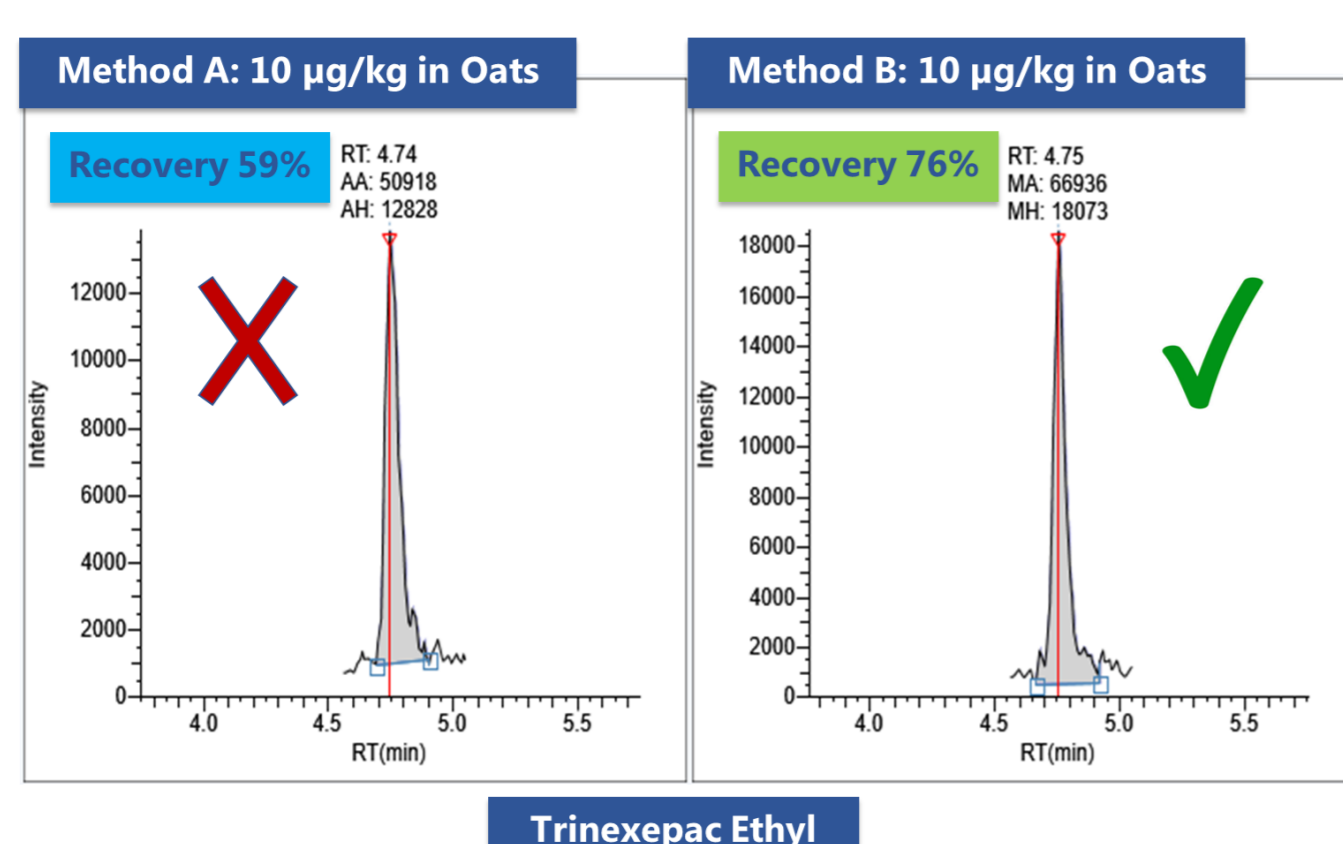
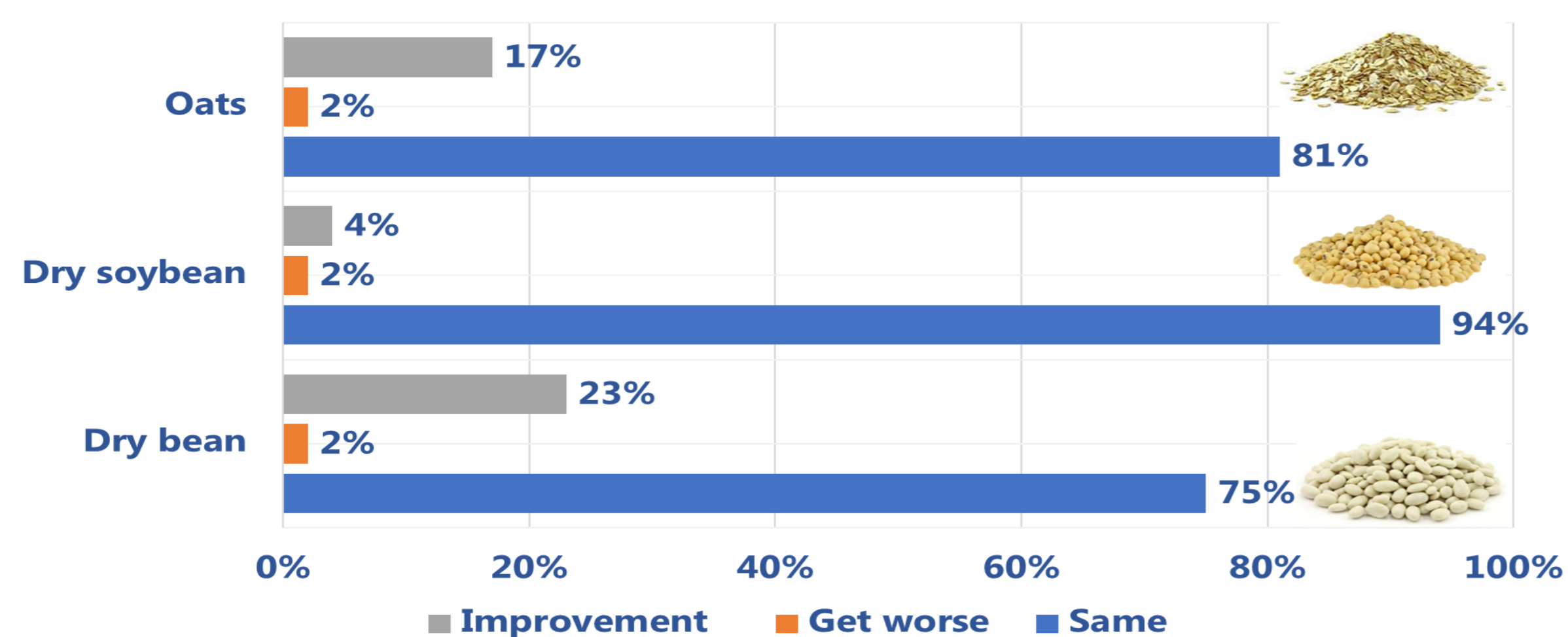
To assess precision, recoveries were performed at 0.010 mg/Kg, while to assess repeatability (5 replicates)

The relative standard deviation between the five replicates was found to be less than 20% for most of the compounds.

### Comparison recoveries values between methods



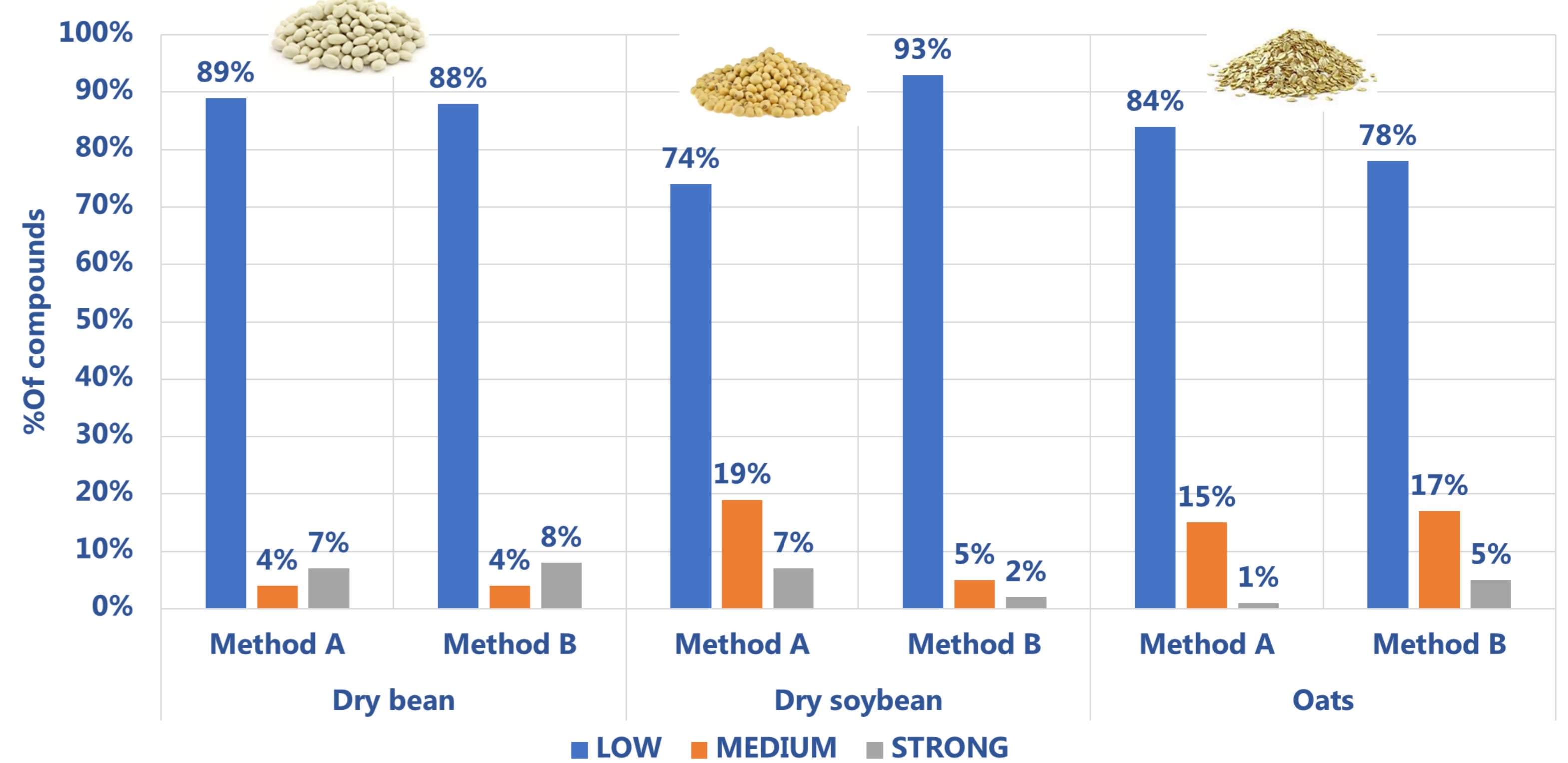
### comparison of the method B with the method A



### Matrix effects:

Matrix effects were assessed by comparison of the slopes of four-point matrix-matched calibration curves with the slopes of the calibration curves in solvent. For values (in absolute terms) between 0 and 20 %, the matrix effect is considered low; between 20 % and 50 % there is a moderate matrix effect, and for compounds with a value over 50 % matrix effect is classified as strong.

### Matrix effects



## Conclusions

- Sodium dodecyl sulphate is an anionic surfactant that denatures proteins. The use of SDS causes an increase in protein precipitation after the freezing-out phase.
- For most compounds, the matrix effect is low in both methods. For the soy matrix, with SDS (method B) a slight improvement in the decrease of the matrix effect is observed.
- In terms of precision, most of the compounds are in the 70-120% recovery range. Method B shows better recovery results compared to method A, this improvement can be observed mainly in the case of white beans and oats, where an improvement of 23% and 17% in recoveries respectively is observed.
- In all three matrices compounds such as chlorpyrifos, dichlorvos, trinexpac-ethyl and trinexpac-methyl significantly improve their recovery values with SDS (method B).