Proficiency Tests on olive oil organized by the Italian National Reference Laboratory for pesticides residues: laboratories long-term performance

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INTRODUCTION

The Italian National Reference Laboratory (NRL) for pesticide residues yearly organizes Proficiency Tests (PTs) on olive oil. The main aim of these PTs is to compare the performances of the laboratories in Mediterranean and European countries in order to promote mutual acceptance of pesticide residue data regarding the analytical controls of olive oil.

In this paper were compared the laboratories performance during the last 3 PTs (COIPT-11, COIPT-12, COIPT-13) using the SWZ or SZ^2 parameters.

TEST MATERIAL

The PTs test material consisted of commercial olive oil spiked with *six* different pesticides in a definite range of 0.050-0.350 mg/kg, chosen in each exercise from a possible list of 23-26 pesticides (with 21 compounds always considered see Table I). An homogeneity test was performed according to the ISO 13528:2005 as plotted in Figure 1.

RESULTS AND DISCUSSION

The dispersion of the Z-scores results for the three PTs is reported in Figure 2. According to the Z-scores value, the 90% of the data were considered acceptable, the 6% were questionable, and only the 4% were unacceptable. The performance classified as unsatisfactory were observed with showing a positive bias.

The laboratories global performance was assessed by SWZ and SZ^2 parameters. The comparison of these parameters obtained in the last 3 PTs is shown in Figure 3 where Italian laboratories are highlighted in red. The best performance was obtained in the COIPT-12 especially for the Italian laboratories. In the COIPT-13 the unsatisfactory performance of two Italian laboratories could be explained with a transcription error.

In Figure 4 we have compared the effect of the analytical methodologies on the SWZ and SZ^2 data. In some cases unsatisfactory performance could be connected with the use of selective detectors without MS confirmation or by methods excluding matrix calibration and cleanup step, particularly important with a matrix as olive oil. Another case of poor performance could be the quantification with uncertified standard. Especially in the COIPT-13 the majority of laboratories have started to use the QuEChERS methodology.

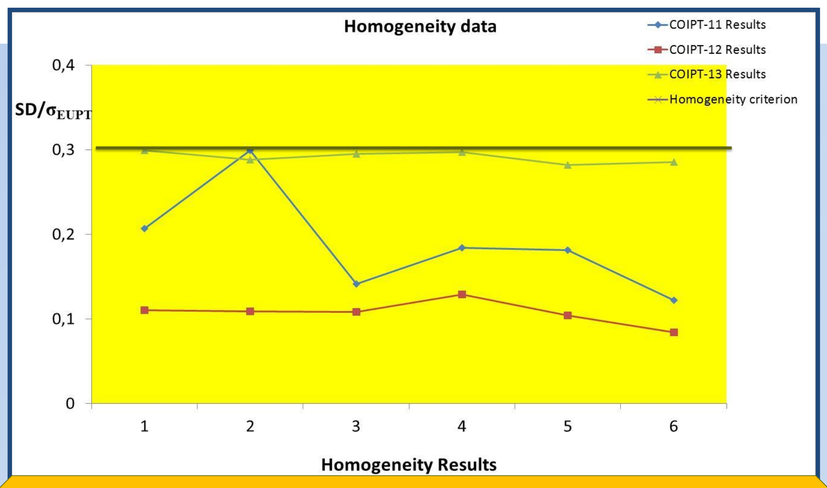

Figure 1 – Homogeneity plots of 3 PTs

SD = Standard Deviation
σ_{EUPT} = fit-for-purpose relative target standard deviation (FFP RSD%) = 25% median value
Homogeneity criterion = $SD/\sigma_{EUPT} \leq 0.3$

TABLE I - OVERALL LIST OF CONSIDERED PESTICIDES

Buprofezin	Methidathion
Chlorpyrifos	Omethoate
Chlorpyrifos-methyl	Oxyfluorfen
lambda-Cyhalothrin	Phosalone
Deltamethrin	Phosmet
Diazinon	Procymidone
Diflufenican	Quinalfos
Dimethoate	Kresoxim methyl
alfa-Endosulfan	Simazine
beta-Endosulfan	Terbuthylazine
Endosulfan sulphate	Tolclofos methyl
Fenitrothion	Trifloxystrobin
Fenoxycarb	Trifluralin
Fenthion	
Fenthion sulfone	
Fenthion sulfoxide	

COIPT-11 spiked pesticides
COIPT-12 spiked pesticides
COIPT-13 spiked pesticides

$$Z-score = \frac{x - X}{\sigma EUPT}$$

$$|SZ2| = \frac{\sum_{i=1}^{n} |Zi|\,|Zi|}{n}$$

$$|SWZ2| = \frac{\sum_{i=1}^{n} |Zi|\omega\,|Zi|}{n}$$

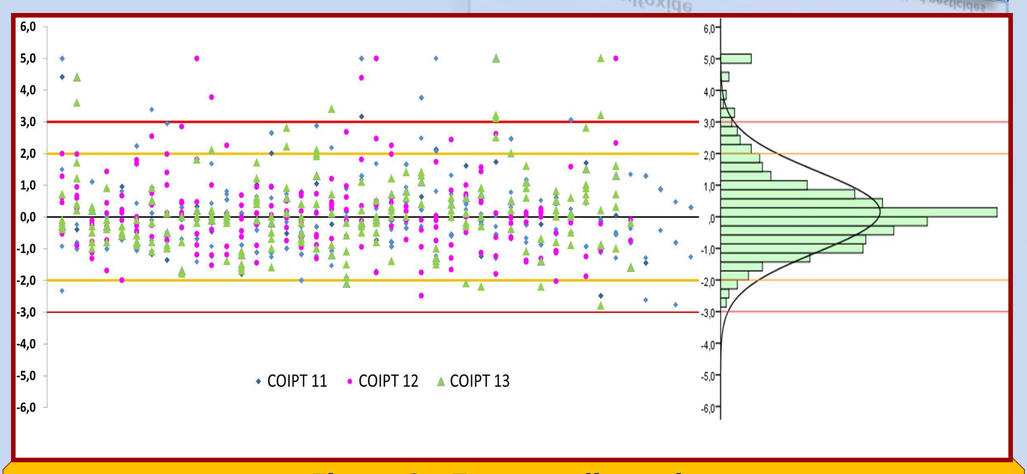

Figure 2 - Z-scores dispersion

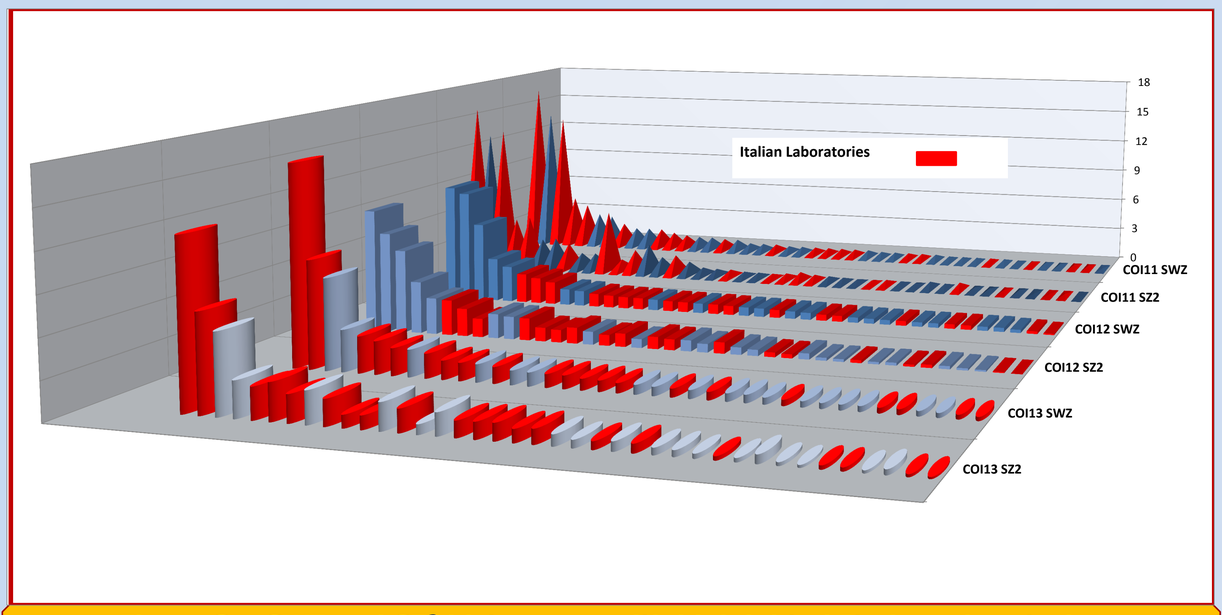

Figure 3 – SWZ and SZ^2 histograms with highlighted Italian laboratories

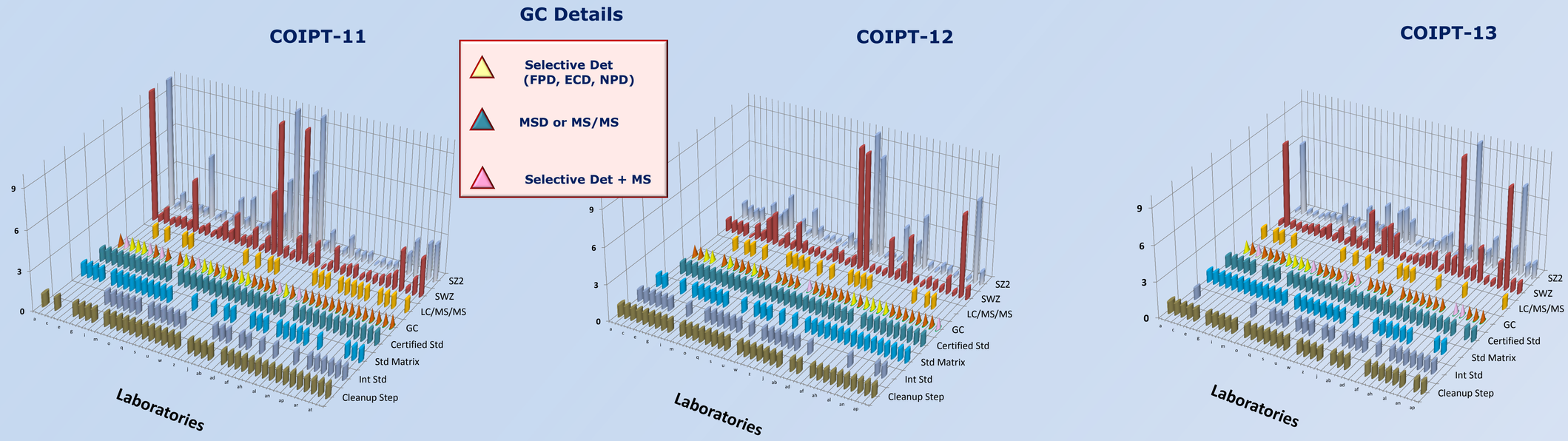

Figure 4 – Analytical methods used for the PTs

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