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Internal Quality Control as tool for planning a ruggedness study regarding a pesticide multi residue method in olive oil

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INTRODUCTION

Internal quality control tools, such as the recovery control chart, was employed in this study to enhance the stability of the recovery rates and to investigate (in connection with a ruggedness study) the factors that have major influence on the quantification of the recovery rates. The method investigated in this study permits the determination of 18 pesticides in olive oil with a concentration range of 0,010-0,054 mg/kg, using Gas Chromatography – Mass Spectrometry (GC-MS) technique. This method was accredited to the ISO 17025 standards and was applied for one year in routine conditions, at the Italian National Reference Laboratory (NRL) for pesticide residues. To calculate the ruggedness of the investigated method, was used the Youden, and Steiner (1975) approach as described in the design of the Table 1.

METHOD ON PESTICIDE RESIDUES IN OLIVE OIL

Dissolve 5 g of virgin olive oil in 16 mL *n*-hexane in a Erlenmeyer flask.

↓

Transfer the solution into an Extrelut® NT20 cartridge (wash the flask with 2x2 mL *n*-hexane) and wait 10 min.
Remove the solvent with a Nitrogen flow at 1 mL/min for 60 min.

↓

Connect a Sep-pak silicagel cartridge to the Extrelut® NT20 and put a C18 cartridge (2 g) in series.
Elute the system of cartridges with 100 mL of acetonitrile.

↓

Concentrate the solution, dissolve with 1 mL of *n*-hexane and add internal standard (Triphenyl-phosphate)

↓

GC-MS (matrix-matched calibration)

The ruggedeness test has involved the following three factors
A = change of the solvent used to dissolve final sample: iso-octane instead of hexane
B = change of internal standard: PCB 209 instead of TPP
C = change of matrix: virgin olive oil not filtered instead of olive oil
y_1 = mean recovery % (n=5) of the studied method
y_2 = mean recovery % (n=5) of the studied method with the following variations: iso-octane instead of hexane and virgin olive oil not filtered instead of olive oil
y_3 = mean recovery % (n=5) of the studied method with the following variations: PCB 209 instead of TPP and virgin olive oil not filtered instead of olive oil
y_4 = mean recovery % (n=5) of the studied method with the following variations: iso-octane instead of hexane and PCB 209 instead of TPP

Table 1 – Design to calculate the ruggedness of the method

	Factors			
Experiment	A	B	C	Result
1	+	+	+	y_1
2	-	+	-	y_2
3	+	-	-	y_3
4	-	-	+	y_4

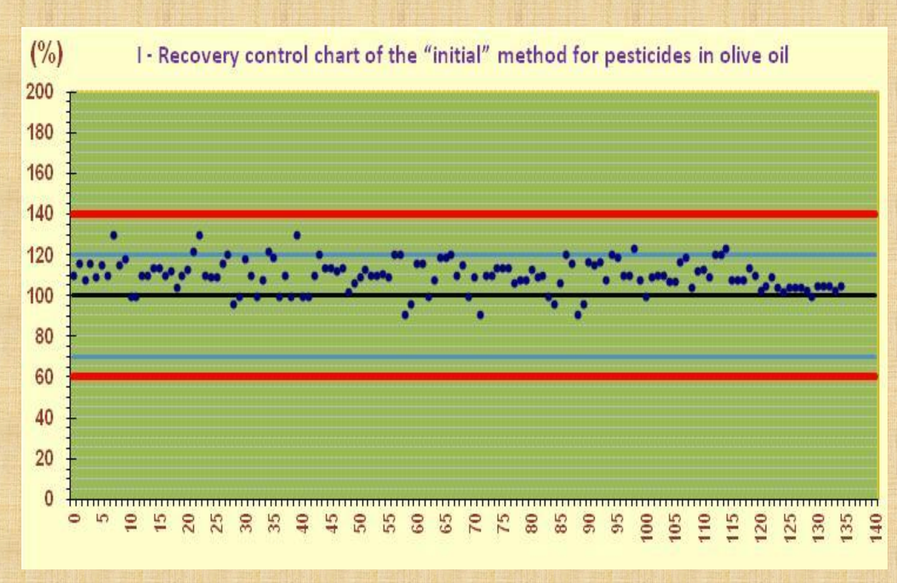
The parameter effects are estimated as follows (it is shown the example of the factor A)

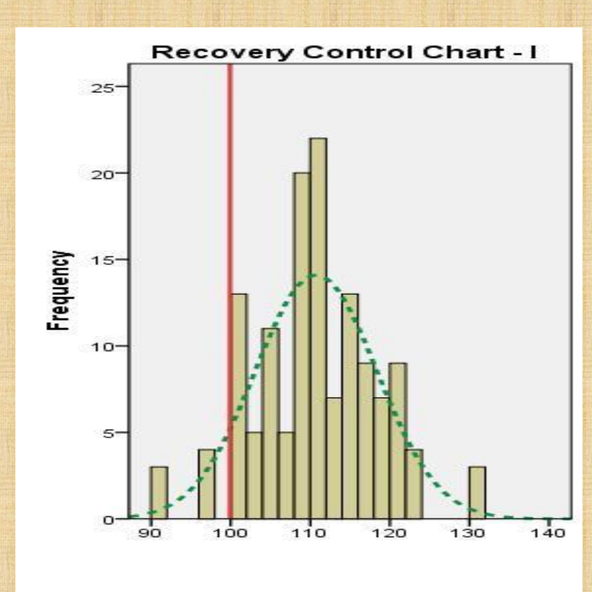
$$Effect\ A = \left[\left(\frac{y_1 + y_3}{2}\right) - \left(\frac{y_2 + y_4}{2}\right)\right] = E_A$$

To evaluate if the E_A is statistically significant was used the t-test approach as described by Dejaegher and Heyden (2007). The parameter *t-experimental* was calculated by the formula (considering as example the factor A):

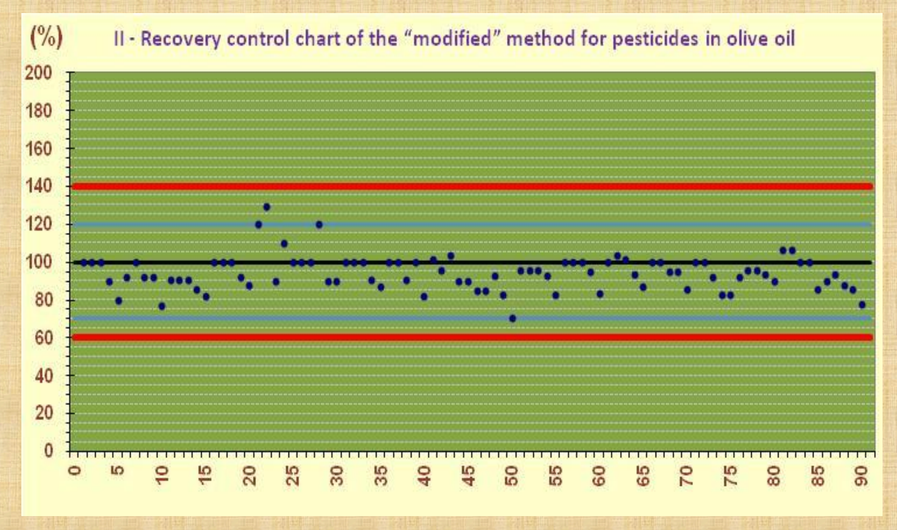
$$t = \frac{|E_A|}{(SE)_e}$$ Where E_A = Effect A (SE)e = standard error of effect A $$(SE)_e = \sqrt{\frac{2s^2}{n}}$$

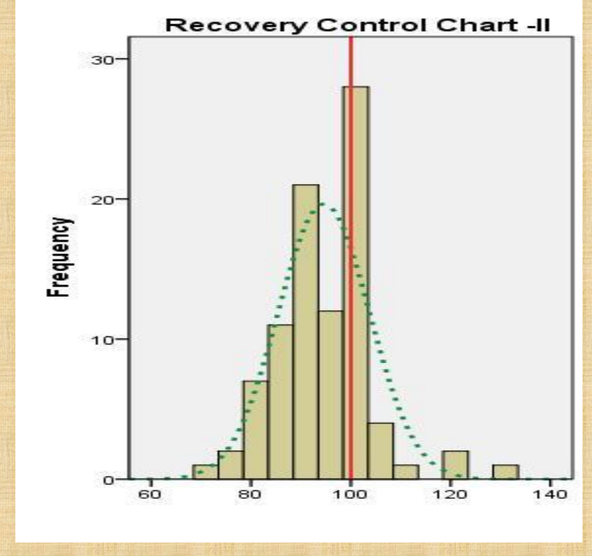
Where s^2 is the variance of replicate experiments and n= the number of experiments carried out for each factor (n=5 in our experimental plan).
The *t-experimental* was compared with a tabulated t-value depending on the number of degrees of freedom (in this case 8) associated with (SE)e and at a significance level α =0,05. The considering tabulated t-value is 1,86.
If *t-experimental* is greater than *t-tabulated* (1,86) the investigated factor shows a significant influence and the method is not sufficiently robust against the chosen modification.





Considering the 18 tested pesticides with the investigated method and the three studied factories it was possible summarized the following results:
Regarding E_A,13 pesticides out of 18 showed a *t-experimental* > *t-tabulated* while 5 out of 18 a *t-experimental* < *t-tabulated.*
Concerning E_B 12 pesticides out of 18 obtained *t-experimental* < *t-tabulated* and 6 pesticides *t-experimental* > *t-tabulated*
Finally for E_C, 11 pesticides out of 18 showed *t-experimental* > *t-tabulated* and on the contrary 7 compounds *t-experimental* < *t-tabulated.*





RESULTS AND DISCUSSION

As consequence of these results it was decide to modify the method, in order to improve the recovery chart control (see Recovery chart control I). In this chart all recovery rates were next to the maximum limit of 120% of recovery performance criteria showed consequently a persistent bias.
Changing in the investigated method two parameters: 1) solvent used to dissolve final sample: iso-octane instead of hexane and 2) internal standard: PCB 209 instead of TPP it was obtained a recovery chart control (Recovery chart control II) with a better values dispersion.
The improvement of the recoveries trend is clearly showed by the frequency histograms.