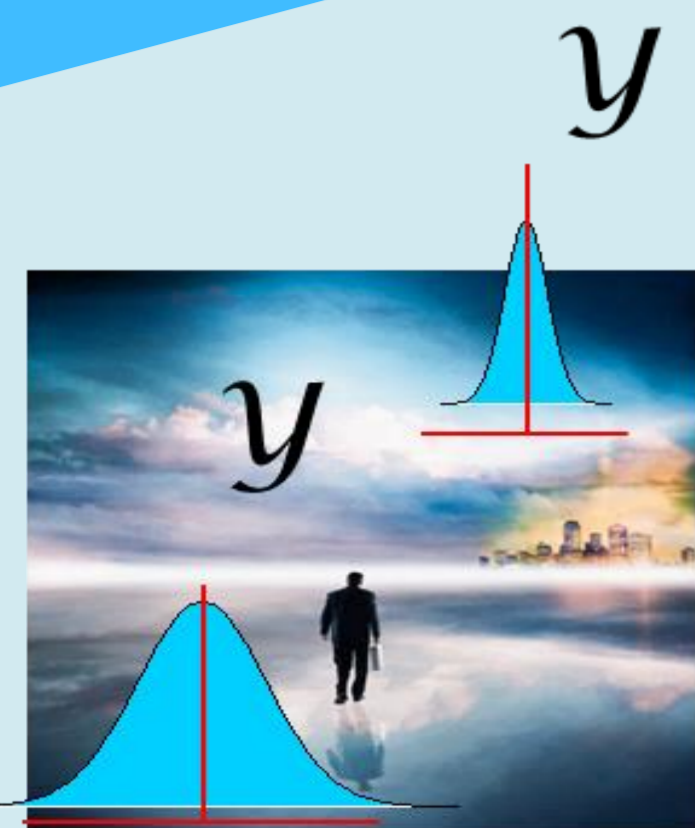# Evaluation of the Reproducibility Standard Deviation in the Pesticide Multiresidue Methods on Olive Oil from Past Proficiency Tests

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INTRODUCTION

The data reported in the frame of proficiency testing (PT) exercises organized from 2007 to 2016 have been statistically re-evaluated using Algorithm A of the ISO 13528:2015. Trends in relative reproducibility standard deviation of multi-residue methods for the determination of pesticides in olive oil could then evaluated. Usually, the between-laboratories variability in PTs on pesticide residues is fixed/set to 25 %. This value was then compared to the calculated robust relative reproducibility standard deviation (RRSD). A total of 1527 analytical results were collected in the ten PTs olive oil. An overall mean value and a median value of 21 % were obtained for the robust RSD, well below the set maximum value of 25%. If all participants use the same instrumental techniques and the same analytical approaches a lower value of the reproducibility standard deviation would be expecting.
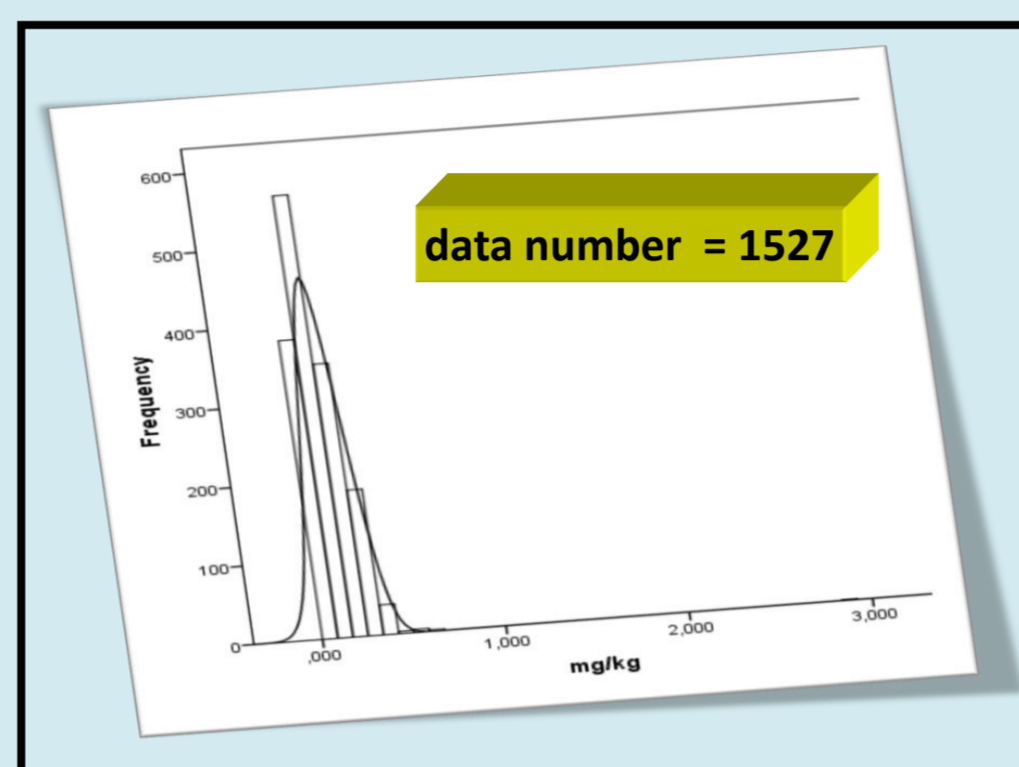
Summary Analytical Methods used for Olive Oil

Extraction solvents: Acetonitrile
Hexane / Acetonitrile
cyclo – Hexane / Ethyl acetate

Clean-up technique: dispersive SPE with PSA
Freezing (overnight)
GPC
without clean up
cartridge SPE C18, cartridge SPE silica
cartridge Extrelut NT20 / C18

Sample weight: usually 1.5 g – 2g – 5g – 10 g of olive oil

Detection: Chromatography (GC /LC) - Mass Spectrometry (MS – MS/MS – TOF – HRMS Orbitrap).
In some cases selective detectors with limited specificity, such as ECD, FPD and NPD, without mass spectrometry (MS) confirmation.

Selective Methods for Compound Groups

HPLC-DAD GC-ECD GC-FPD GC-NPD
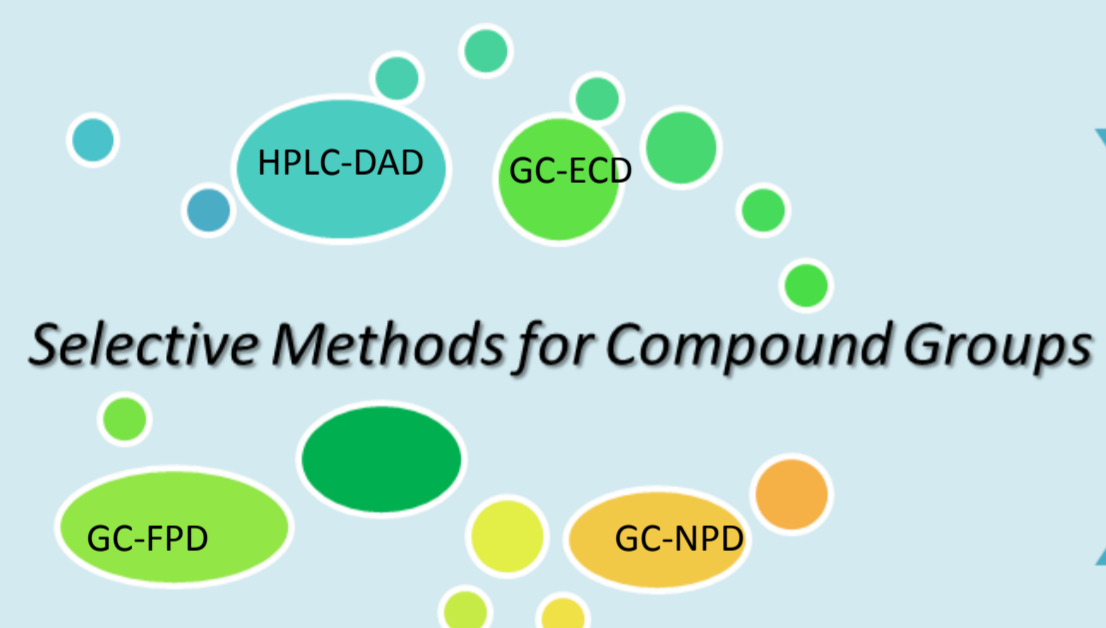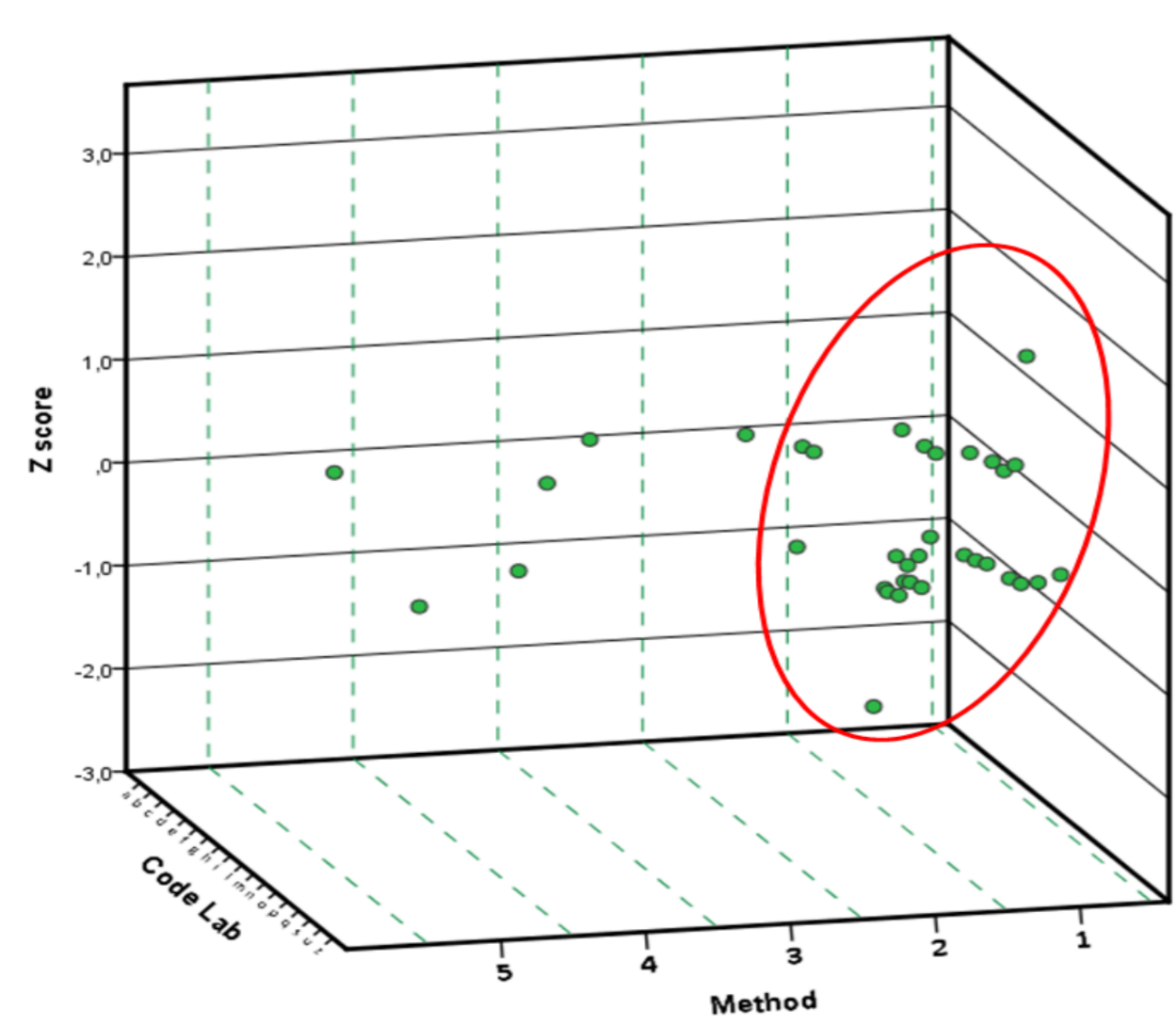
Multiresidue Methods
QuEChERS
GC/MS-MS
HPLC/MS-MS
LOQ ≤ 0.01 mg/kg

The QuEChERS method, introduced by Anastassiades et al [1], coupled with LC-MS/MS and GC MS/MS has become an important methodology for the analysis of pesticide residues. This is due to its simplicity, the use of low quantities of acetonitrile, the possibility to analyse a large number of pesticides with fewer steps and high efficiency. This method may harmonize the future analyses of pesticide residues. Recently, it has been successfully applied to the analysis of olive oil [2]. Furthermore, about 70 % of the laboratories participating to our last PT exercises applied QuEChERS as their routine method with few minor modifications.

Case Study

1) **QuEChERS or based on QuEChERS**
2) **In house method**
3) **Method EURL – FV**
4) **Based on Manual of Pesticide Analysis Vol. 1 DFG**
5) **Lentza Rizos, J of Chromatography A921, 2001 (297 – 304)**

PT 2014

data number = 1527

Evaluation Reproducibility (RRSD)

Year 2007 · Year 2008 · Year 2009 · Year 2010 · Year 2011 · Year 2012 · Year 2013 · Year 2014 · Year 2015 · Year 2016
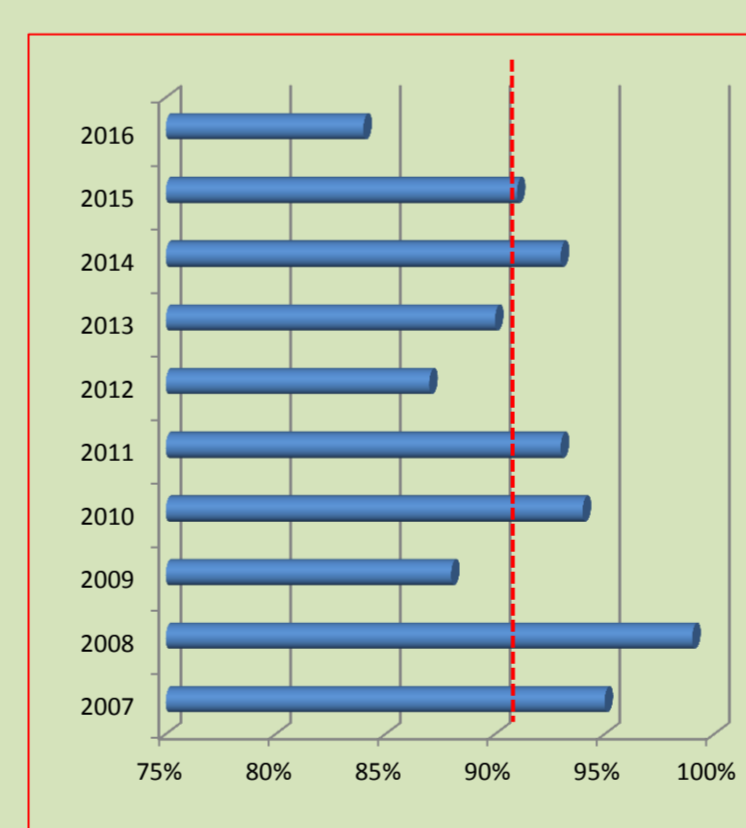
Reproducibility — An overall mean value and median value of 21 % were obtained for the Robust Relative Standard Deviation (RRSD)

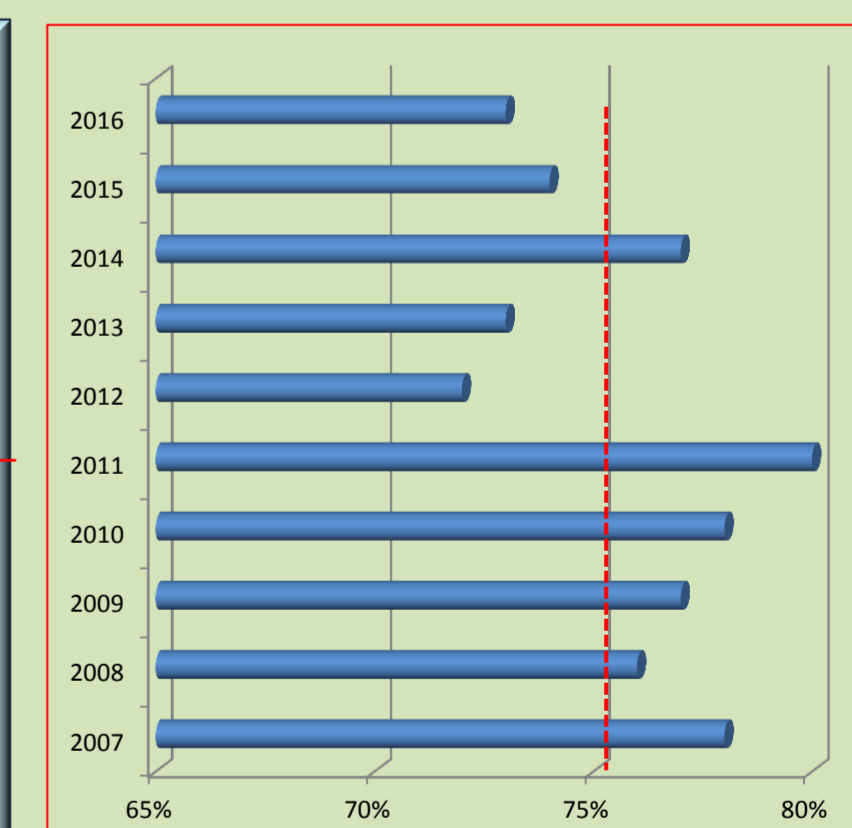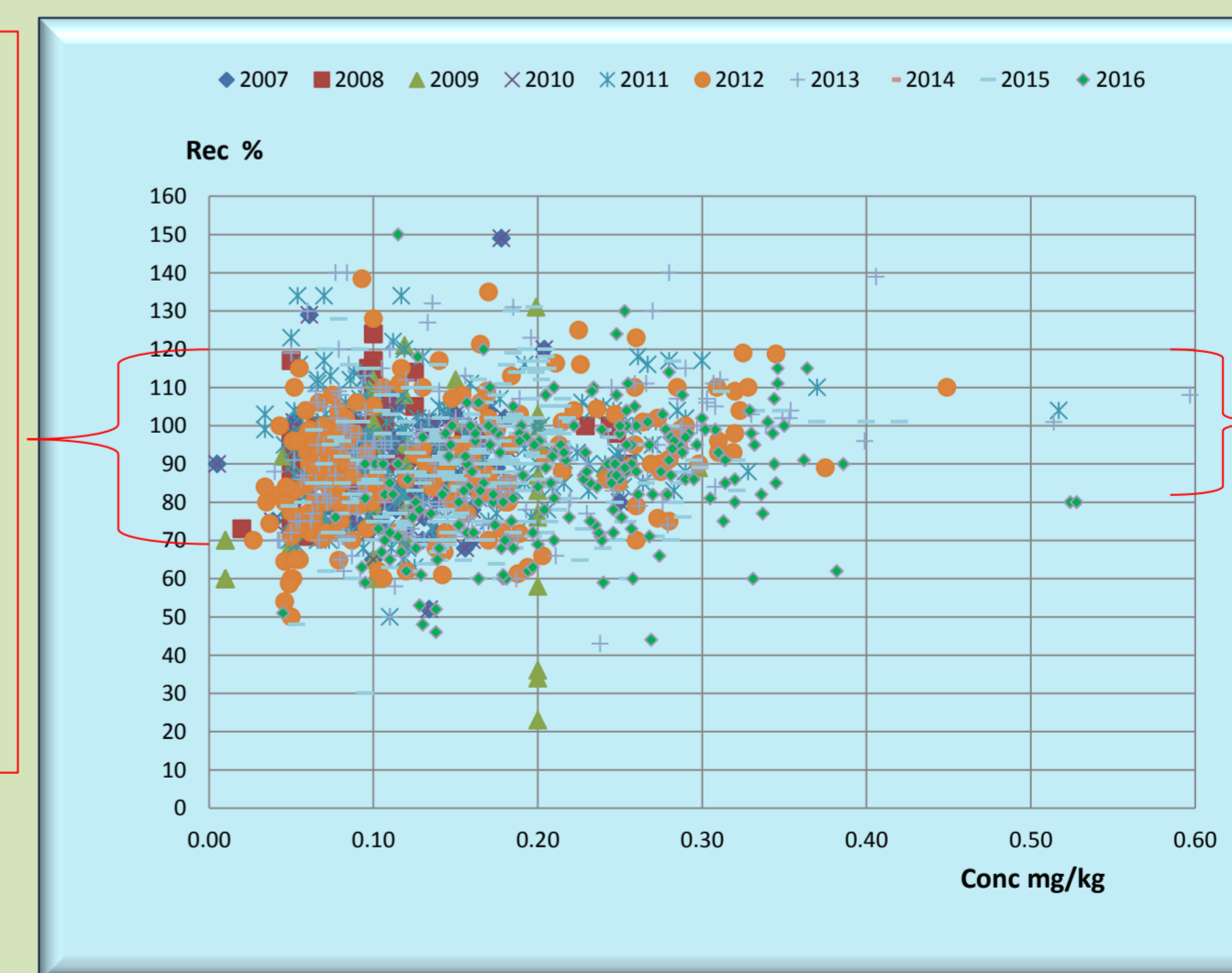Different Concentration Levels – Same Matrix (olive oil)

Trueness — The 91% of the mean recoveries submitted by the participants fall within the range 70% – 120% whereas only the 75% in the range 80%-120%

Evaluation Trueness (mean recoveries)

Rec %

Recoveries Percentage falling within the range 70 %– 120%

Recoveries Percentage falling within the range 80 %– 120%

$$U(y) = 2sR$$

An expanded uncertainty of 50 % has been systematically applied in Europe since 2006 for the analyses of pesticides, due to the fixed maximum between-laboratory variability of 25 %. The systematic use of the QuEChERS methodology may then reduce the expanded uncertainties about to 40
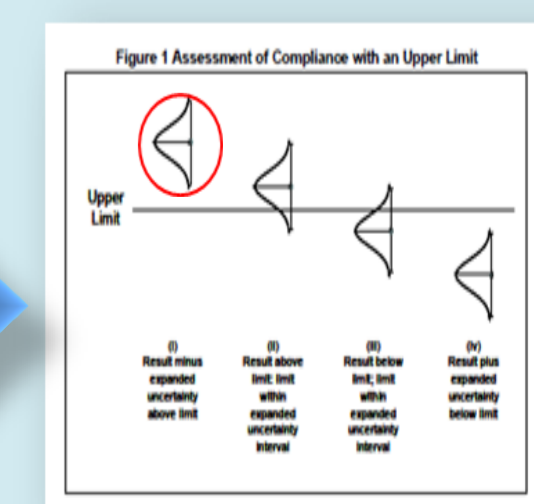
REFERENCES

1) M. Anastassiades, S. J. Lehotay, D. Stajnbaher, F. J. Schenck, Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid- phase extraction for the determination of pesticide residues in produce, J. AOAC Int. 86 (2003) 412-431
2) N. Chamkasem, T. Harmon, Analysis of pesticides in olive oil using a modified QuEChERS method with LC-MS/MS and GC-MS/MS, Journal of Regulatory Science 3 (1) (2015) 16 – 35.
3) ISO 13528: 2015 Statistical methods for use in proficiency testing by interlaboratory comparison. International Standard . Second Edition 2015 08 01