# PESTICIDE RESIDUE RESEARCH GROUP

European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables
UNIVERSITY OF ALMERÍA, ALMERÍA, SPAIN

EURL EUROPEAN UNION REFERENCE LABORATORY — FRUITS AND VEGETABLES

UNIVERSITY OF ALMERIA

# Main analytical methodologies used by EU official laboratories for pesticide residues analyses in fruits and vegetables

## Carmen Ferrer, Milagros Mezcua, Octavio Malato, Ana Lozano, Amadeo R. Fernández-Alba

*University of Almeria, Agrifood Campus of International Excellence (ceiA3). European Union Reference Laboratory for Pesticide Residues in Fruit & Vegetables, Ctra. Sacramento s/n, 04120 Almería, Spain; email - cferrer@ual.es*
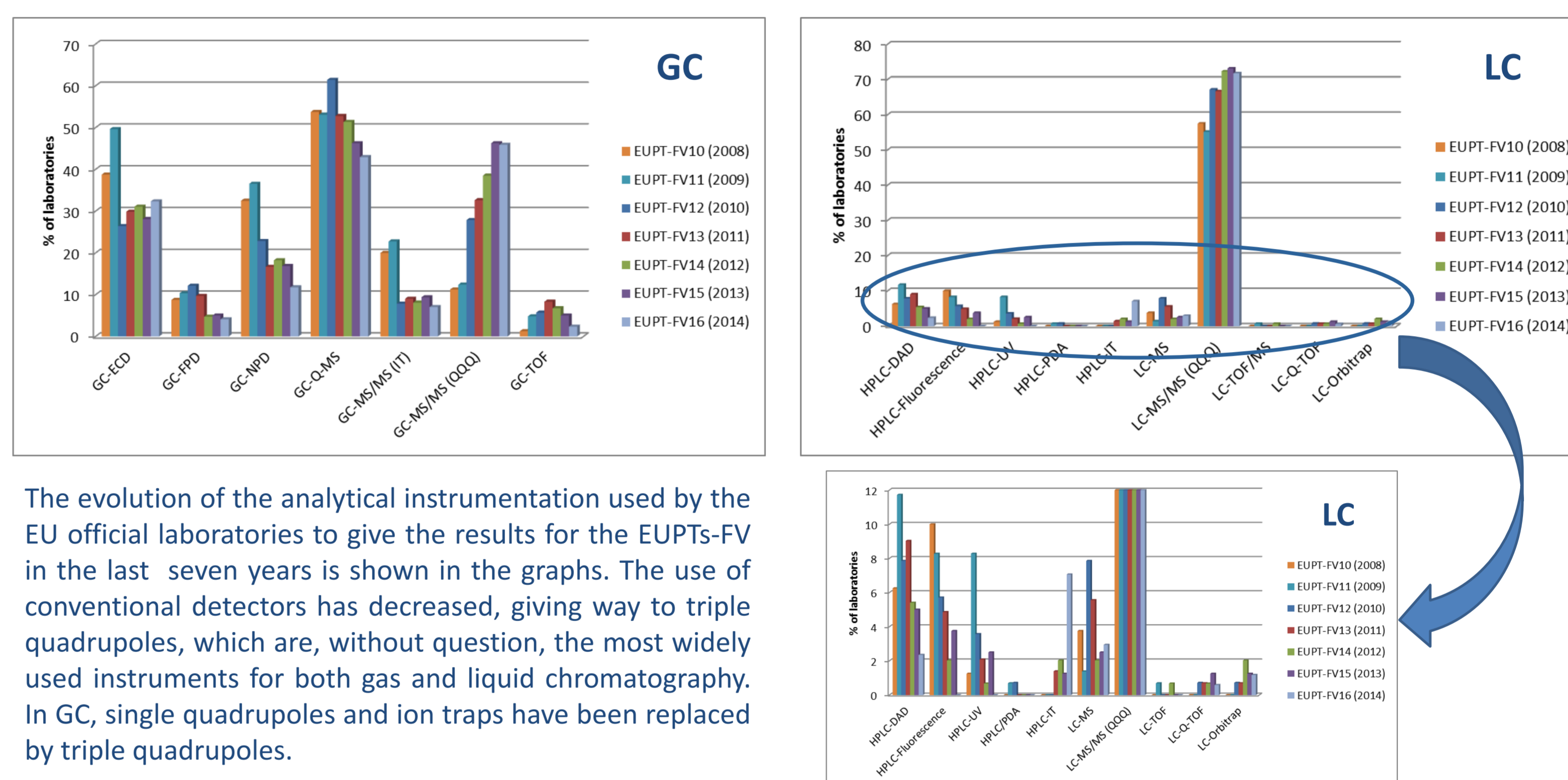
## ABSTRACT

Since 2006 the European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables (EURL-FV) in Almería, Spain, has organised European Proficiency Test in Fruits and Vegetables (EUPT-FV) on behalf of the European Commission, Health & Consumer Protection Directorate-General (DG-SANCO). The collection of information during the past nine years as regards the analytical methodologies has allowed us to learn how the official laboratories perform along the different steps of the analysis of pesticide residues in fruits and vegetables: sample treatment, analytical instruments, quantification procedure, quality control, etc… This knowledge has been reflected into different graphs and tables comparing the effect of the extraction method or the analytical instrumentation on the results of the EUPTs-FV for selected pesticides.

Additionally, an overview of the main analytical methods used by the EU official laboratories will be presented, for both target analysis and screening analysis, using the data obtained from the proficiency test based on the analyses of pesticide residues by making use of screening methodologies (EUPT-SM).
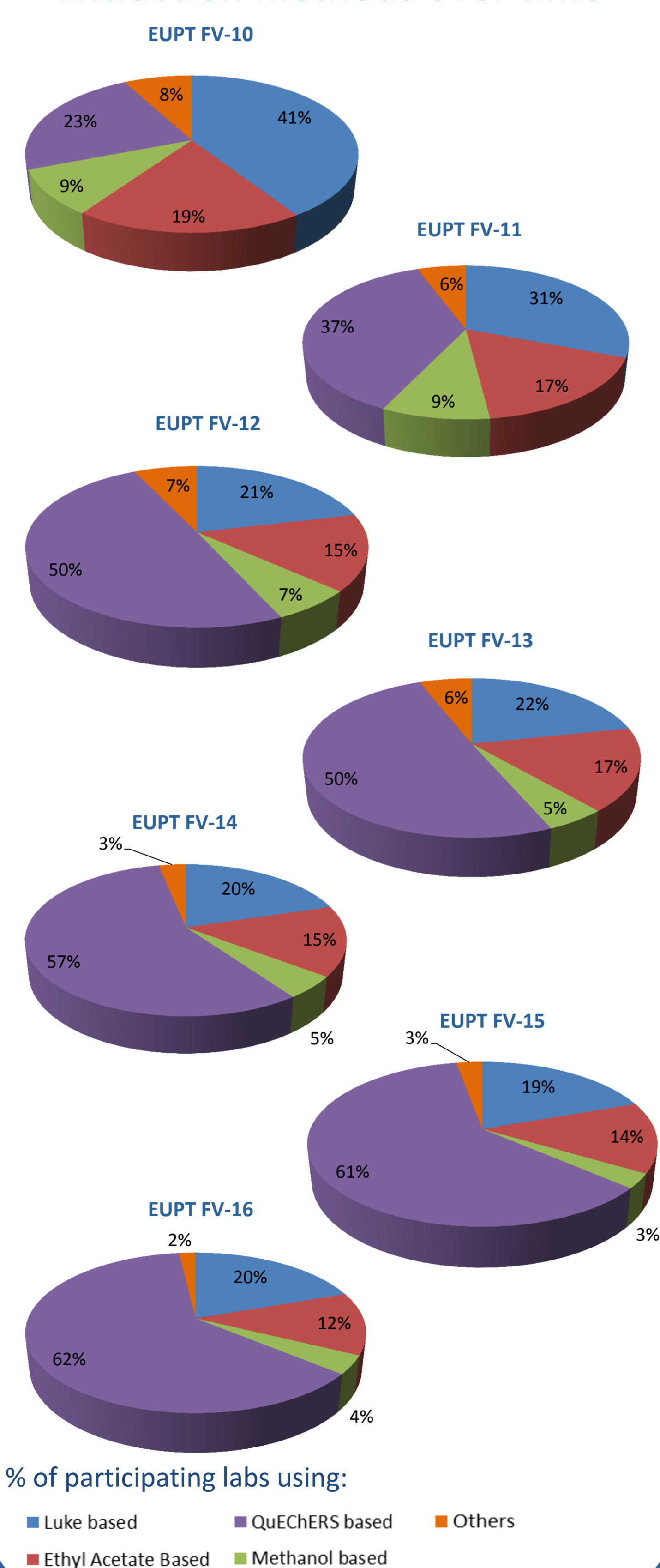
## EUPT-FV1 to EUPT-FV16 in numbers

| EUPT Nº | Matrices | Nº of Participants | Nº of Possible Pesticides | Nº of pesticides present in test item |
|---|---|---|---|---|
| 1 | Pepper | 88 | 33 | 6 |
| 2 | Apple | 85 | 41 | 6 |
| 3 | Cucumber | 116 | 48 | 14 |
| 4 | Orange | 117 | 57 | 14 |
| 5 | Lettuce | 127 | 57 | 15 |
| 6 | Tomato | 130 | 57 | 13 |
| 7 | Grape | 128 | 65 | 16 |
| 8 | Aubergine | 129 | 68 | 16 |
| 9 | Strawberry | 137 | 82 | 19 |
| 10 | Carrot | 132 | 113 | 18 |
| 11 | Cauliflower | 151 | 128 | 21 |
| 12 | Leek | 153 | 144 | 17 |
| 13 | Mandarin | 154 | 144 | 19 |
| 14 | Pear | 167 | 175 | 18 |
| 15 | Potato | 175 | 175 | 18 |
| 16 | Pepper | 183 | 175 | 22 |

## Analytical techniques used for the EUPTs



The evolution of the analytical instrumentation used by the EU official laboratories to give the results for the EUPTs-FV in the last seven years is shown in the graphs. The use of conventional detectors has decreased, giving way to triple quadrupoles, which are, without question, the most widely used instruments for both gas and liquid chromatography. In GC, single quadrupoles and ion traps have been replaced by triple quadrupoles.

## Extraction methods over time



% of participating labs using:
- Luke based
- QuEChERS based
- Others
- Ethyl Acetate Based
- Methanol based

## Evolution of data dispersion along the EUPT-FV history (Qn RSD, %)

The dispersion of the results submitted by the laboratories is evaluated with the robust dispersion (Qn RSD). The graph shows the different Qn RSD values for all the pesticides present in the test items from EUPT-FV1 to EUPT-FV16. Along the years, the dispersion of the results has decreased, highlighting the improvement of the participant laboratories.
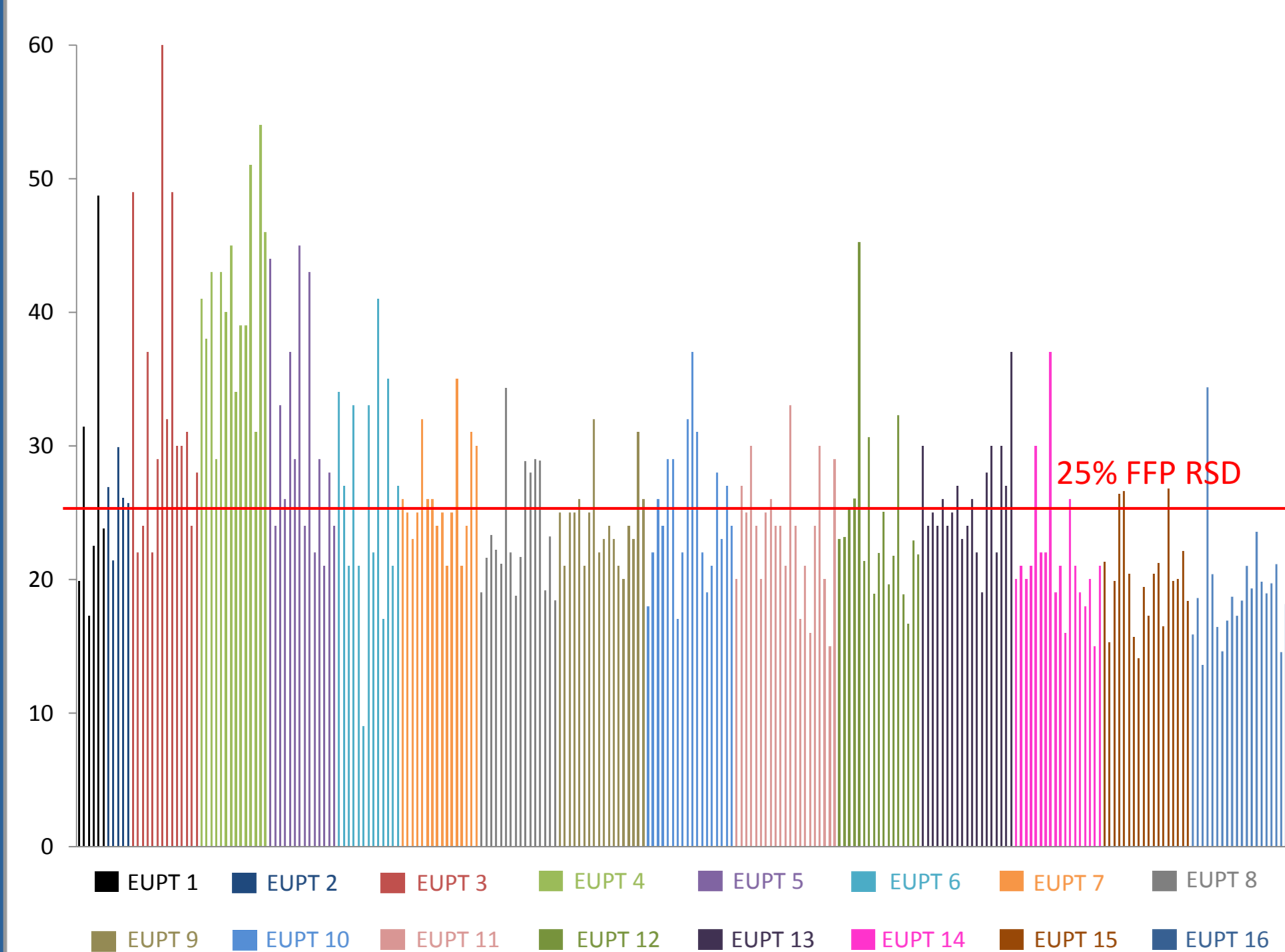


### 15 EUPTs z-Score results: 23764
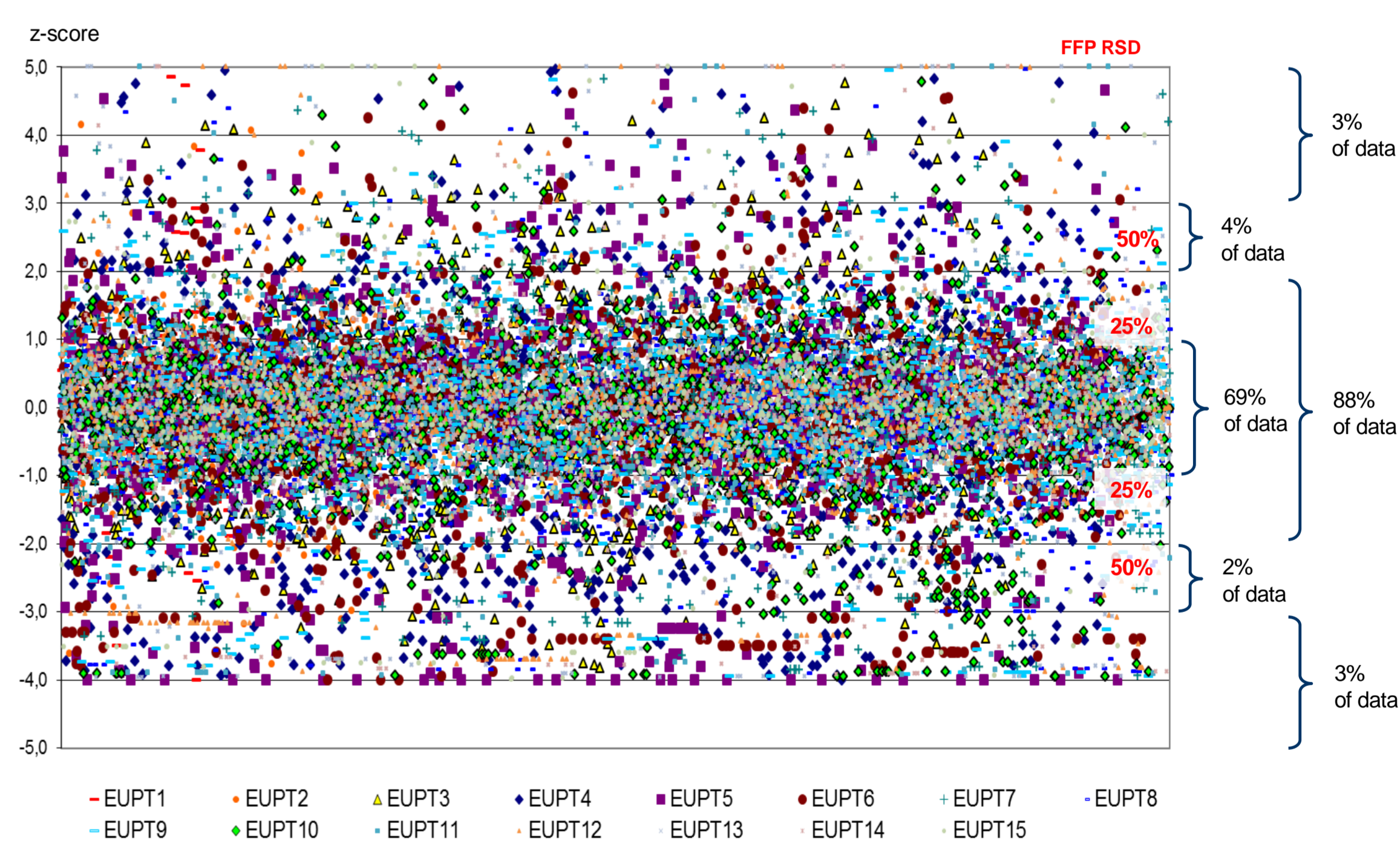


The EUPTs have generated more than 23000 data results that have led to a strengthening in the use of the 25% FFP-RSD as well as the use of an internationally accepted 50% target measurement expanded uncertainty for multiresidue analysis of pesticides for laboratories participating over the years in these PTs and achieving acceptable results, which implies a great achievement in data dispersion and statistical evaluation.

## Influence of the Extraction method on the results

Although in general for experienced laboratories there is not a strong dependency on the results of the EUPTs-FV as a consequence of the extraction method used, in some specific combinations commodity/residue the dispersion of the results (Qn RSD) depends on the extraction method.

### Dispersion of results (Qn RSD, %) using different extraction methods

| Method | Metamidophos FV10 - Carrot | Chlorothalonil FV12 - Leek | Tolyfluanid FV13 - Mandarin | Folpet FV14 - Pear |
|---|---|---|---|---|
| Mini-Luke | 63 | 50 | 24 | 25 |
| Quechers | 26 | All false negatives | 43 | 42 |
| Ethyl Acetate | 42 | 43 | 43 | 73 |

### EUPT-FV12 – z-scores Leek- Chlorothalonil



|z| ≤ 2 Acceptable — 35% of Reported Results
2 < |z| ≤ 3 Questionable — 40% of False Negative Results
3 < |z| Unacceptable — 25% of Not Analysed Results

Acetone — Acetonitrile — Dichloromethane — Ethyl Acetate — Methanol