RAPPORTI ISTISAN 25|30

ISSN: 1123-3117 (cartaceo) • 2384-8936 (online)

Results of the proficiency test on pesticide residues in olive oil in 2023

T. Generali, P. Stefanelli, S. Girolimetti

AMBIENTE E SALUTE

ISTITUTO SUPERIORE DI SANITÀ

Results of the proficiency test on pesticide residues in olive oil in 2023

Tiziana Generali, Patrizia Stefanelli, Silvana Girolimetti
Dipartimento Ambiente e Salute

ISSN: 1123-3117 (cartaceo) • 2384-8936 (online)

**Rapporti ISTISAN
25/30**

Istituto Superiore di Sanità
Results of the proficiency test on pesticide residues in olive oil in 2023.
Tiziana Generali, Patrizia Stefanelli, Silvana Girolimetti
2025, v, 39 p. Rapporti ISTISAN 25/30

In December 2023, as every year, the Italian National Reference Laboratory for pesticide residues in products of Animal Origin and commodities with high fat content (NRL-AO), organized in cooperation with the IOC (International Olive Council) a new Proficiency Test (PT) for the determination of pesticide residues in olive oil named COIPT-23. Laboratories invited to participate in these PTs are Mediterranean laboratories of IOC and European laboratories (NRLs, official control laboratories and private laboratories), involved in the National and European monitoring programs for pesticide residues in food. The exercise consisted in the determination of unknown six different pesticides in a spiked extra virgin olive oil sample, chosen from a target list of thirty-seven compounds. Thirty-nine laboratories participated and provided results with thirty participants analysing all spiked compounds. The majority of participants obtained a satisfactory performance (z-score) for all tested pesticides.

Key words: National Reference Laboratory; International Olive Council; Pesticide residues; Proficiency Test; Olive oil

Istituto Superiore di Sanità
Risultati del circuito interlaboratorio su residui di antiparassitari in olio di oliva nel 2023.
Tiziana Generali, Patrizia Stefanelli, Silvana Girolimetti
2025, v, 39 p. Rapporti ISTISAN 25/30 (in inglese)

Nel dicembre 2023, come ogni anno, il Laboratorio Nazionale di Riferimento italiano per i residui di pesticidi nei prodotti di origine animale e materie prime ad alto contenuto di grasso (*National Reference Laboratory for pesticide residues in products of Animal Origin and commodities with high fat content*, NRL-AO), ha organizzato in collaborazione con il Consiglio Oleicolo Internazionale (COI) un nuovo circuito interlaboratorio (*Proficiency Test*, PT) per la determinazione di residui di pesticidi in olio d'oliva chiamato COIPT-23. I laboratori invitati a partecipare in questi circuiti interlaboratorio sono laboratori mediterranei del COI e laboratori europei (NRL, laboratori di controllo ufficiali e laboratori privati), coinvolti nei programmi di monitoraggio nazionali ed europei per i residui di pesticidi negli alimenti. L'esercizio consisteva nella determinazione di sei diversi pesticidi sconosciuti in un campione di olio extravergine di oliva, scelti da una lista prestabilita di trentasette composti. Trentanove laboratori hanno partecipato e fornito risultati con trenta partecipanti che hanno analizzato tutti i composti addizionati. La maggior parte dei partecipanti ha ottenuto una soddisfacente prestazione (z-score) per tutti gli antiparassitari oggetto del test.

Parole chiave: Laboratorio Nazionale di Riferimento; Consiglio Oleicolo Internazionale; Residui di antiparassitari; Circuito interlaboratorio; Olio di oliva

Per informazioni su questo documento scrivere a: tiziana.generali@iss.it

Il rapporto è accessibile online dal sito di questo Istituto: www.iss.it.

Citare questo documento come segue:

Generali T, Stefanelli P, Girolimetti S. *Results of the proficiency test on pesticide residues in olive oil in 2023.* Roma: Istituto Superiore di Sanità; 2025. (Rapporti ISTISAN 25/30).

Legale rappresentante dell'Istituto Superiore di Sanità: *Rocco Bellantone*
Registro della Stampa - Tribunale di Roma n. 114 (cartaceo) e n. 115 (online) del 16 maggio 2014

Direttore responsabile della serie: *Antonio Mistretta*
Redazione*: Sandra Salinetti*
La responsabilità dei dati scientifici e tecnici è dei singoli autori, che dichiarano di non avere conflitti di interesse.

TABLE OF CONTENTS

ABBREVIATIONS

ADI	Acceptable Daily Intake
ARfD	Acute Reference Dose
AZ²	Average of the Squared z-scores
CAS	Chemical Abstract Service
EC	European Commission
EU	European Union
EUPT	European Union Proficiency Test
EURL	European Reference Laboratory
FFP	Fitness for Purpose
GAP	Good Agricultural Practice
GC	Gas Chromatography
ILAC	International Laboratory Accreditation Cooperation
ISO	International Organization for Standardization
LC	Liquid Chromatography
LOQ	Limit of Quantification
MRL	Maximum Residue Limit
MS	Mass Spectrometry
MU	Measurement Uncertainty
NRL-AO	National Reference Laboratory - Animal Origin
NRL	National Reference Laboratory
PPP	Plant Protection Product
PT	Proficiency Test
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RL	Reporting Limit
RSD	Relative Standard Deviation
SD	Standard Deviation

Symbols

s*	*robust standard deviation*
u	*uncertainty measurement*
σ	*target standard deviation*
X	*consensus value*

PREFACE

Food safety is a priority in Europe: governments and regulators have been increasing the controls and surveillances on food and they have been established a network of National Reference Laboratories (NRLs) and official control laboratories. The overall objective is to improve the quality, accuracy and comparability of the analytical results regarding the determination of pesticide residues in food.

Current European legislation on pesticides in and on food requires the official laboratory participation in specific proficiency tests, particularly those organized by the NRLs. Regular participation in Proficiency Test (PT) programs is considered a suitable external quality control system for assessing reliability of their results (1).

Furthermore, in accordance with article 37 of Regulation (EU) 2017/625, the laboratories designated for official control have to adopt the general quality criteria for testing laboratories laid down in ISO/IEC 17025 (2). In particular, all the official laboratories, involved in the European Union (EU) coordinated control pesticide residue monitoring programs, follow the same European analytical quality control technical guidance document SANTE/11312/2021v2 (3)

The Italian NRL for pesticide residues in products of Animal Origin and commodities with high fat content (NRL-AO) yearly organizes PTs on olive oil in cooperation with the International Olive Council (IOC), which is the only intergovernmental organization involved in the field of olive oil and table olives and has its headquarters in Madrid.

GENERAL CONSIDERATION ON MAXIMUM RESIDUE LEVEL IN OLIVE OIL

The olive tree is one of the most important and ancient crops of the Mediterranean:

According to official data of the IOC (year 2024-2025) relating to the production of olive oil area the 96% of the olive oil in the world is produced by Mediterranean countries with 60% of the olive oil provided by Spain, Greece, Italy and Portugal (4).

Olive oil is one of the great components of the Mediterranean diet and as consequence of the high content of monounsaturated fats, the consumption of virgin olive oil prevents the onset of the coronary heart diseases, tumours, diabetes, neurodegenerative diseases and autoimmune and immuno-inflammatory diseases (5).

The olive tree is vulnerable to several pest attacks, flattening the production curve even in term of quality of the crop and the processed product thereof. Most Plant Protection Products (PPP) used on the olive trees are insecticides, acaricides and fungicides. Herbicides are used to remove weeds from olive tree fields and considering that the olives are also harvested with the beating technique from tents placed on the ground, a contamination of the olives and therefore of the olive oil is possible.

The pesticides arising as a result of use in plant protection products, in veterinary medicine and as a biocide are defined "residues".

A Maximum Residue Level (MRL) is the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly (Good Agricultural Practice, GAP). Other considerations on the definition of MRL are linked with possible amounts of residues in food that must be evaluate as safe for consumers and must be as low as possible.

The European Commission (EC) has established MRLs in or on food and feed of plant and animal origin, and these MRLs for all crops and all pesticides can be found in the MRL database on the Commission website.

The EC fixes MRLs for all food and animal feed and these MRLs for all crops and all pesticides can be found in the MRL database on the EC website.

To set any MRL different subjects, applicants (e.g., producers of plant protection products), farmers, importers, EU or non-EU countries must submit the following key points:

- directions of use of a PPP in/on the crop (GAP) – e.g., number of treatments, quantity of the active ingredient, frequency of the treatments, growth stage of the plant, Pre Harvest Interval (PHI, days from the last treatment and the harvest);
- experimental data on the expected residues when the pesticide is applied according to the GAP;
- toxicological reference values for the pesticide – chronic toxicity is measured with the Acceptable Daily Intake (ADI) and acute toxicity with the Acute Reference Dose (ARfD).

Based on the available information, the intake of residues through all food that may be treated with that pesticide is compared with the:

- ADI;
- ARfD for long and short-term intake and for all European consumer groups.

If daily intake does not exceed the toxicological values, then the GAP can be considered "safe" for the proposed use; the MRLs is then established in olives (as for all crops) by the Regulation (EC) 396/2005 (6) and amendments. For those pesticides not allowed in/on olive and for pesticides that do not cause any quantifiable residue in olive fruit, the MRL can be set by default at the lowest quantification value (LOQ).

The Regulation (EC) 396/2005 set at 0.01 mg/kg this value. To calculate MRL values in processed products such as olive oil, it is necessary to use processing factors. Pending the publication of annex VI of the Regulation (EC) 396/2005 containing the list of processing factors of processed products, in coordinated multiannual control programmes of the EU (7), is declared that each Member States are requested to report the processing factors used to analyse virgin olive oil samples (8). Currently in Italy this processing factor is equal to 5.

PROFICIENCY TEST ON OLIVE OIL: THE COIPT-23

Rationale

In the last decade, many laboratories have been invited by the Italian NRL-AO to participate in PTs on olive oil: Mediterranean laboratories of the IOC, European laboratories (NRLs, official control laboratories and private laboratories), involved in the national and European monitoring programs. The main aim of these PTs was 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.

The last PT organized in 2023 on olive oil was named COIPT-23.

The exercise consisted in the determination of six different pesticides in an extra virgin olive oil sample spiked with a definite range of concentration (0.050-0.350 mg/kg). These pesticides were chosen from a list of thirty-seven compounds presented in COIPT-23 Announcement that was sent to participant on 20 December 2023. The possible list of compounds includes mainly those considered in the official control plans, with spiked concentration levels around their reference values set in the European Regulations.

Thirty-nine laboratories agreed to participate in this PT: three NRLs, sixteen official control laboratories and twenty private laboratories. To assess the performance of the participating laboratories, z-scores are used following the norms of the International Organization for Standardization (ISO) (9, 10).

To investigate the impact on the analytical results of different testing procedures, detailed information of the methodologies was requested to the whole participants as well. The results and information received from the participants have provided indications with respect to satisfactory and unsatisfactory performance and potential analytical problems.

The analytical information highlighted that in some cases unsatisfactory performance could be connected with the use of selective detectors without mass spectrometry (MS) confirmation or by methods excluding matrix-matched calibration and clean up step, very crucial for a matrix such as olive oil.

The instrumental measurement was not the only factor affecting the final results. Due to the complexity of analysis, problems can occur at every step in the analytical procedure.

Test materials

The test materials consisted of 2.7 kg of olive oil from an olive oil company. All the olive oil was homogenized for 3 hours under magnetic stirrer. A portion of the test material was analysed in twice to verify the absence of all listed pesticides. No levels of these compounds were found.

In this PT it was decided to ship to participants only the *spiked sampl*e and not the corresponding *blank sample.* The blank oil, was spiked with the following pesticides: Chlorpyrifos-methyl, Diazinon, Tau-fluvalinate, Kresoxim-methyl, Phosmet and Procymidone

Aliquots of 50 g of this spiked oil named COIPT-23 SPIKED OIL were transferred into dark glass bottles sealed and stored at ambient temperature before the shipment to participants. The current MRLs for these six pesticides are showed in Table 1 (11-16).

Table 1. COIPT-23: current MRLs for the six pesticides spiked in the blank oil

Compounds	Current EU Regulation	MRL on olive for oil production (mg/kg)
Chlorpyrifos-methyl	Regulation (EC) 2020/1085 applicable from: 13/11/2020	**0.01***
Diazinon	Regulation (EU) 834/2013 Applicable from: 27/04/203	**0.02***
Tau-fluvalinate	Regulation (EU) 2022/93 aplicable from: 14/02/2022	**0.01*** Fluvalinate (sum of isomers) resulting from the use of tau-fluvalinate
Kresoxim-methyl	Regulation (EU) 2020/856 applicable from: 09/07/2020	**0.2**
Phosmet	Regulation (EU) 2023/1029 applicable from: 15/09/2023	**0.01***
Procymidone	Regulation (EU) 1096/2014 applicable from: 07/5/2015	**0.02***

* Limit of analytical determination

Homogeneity and stability tests

Homogeneity and stability were tested according to ISO 13528:2015 (10).

Regarding the homogeneity test ten bottles of the spiked oil samples were randomly chosen and analysed in duplicate. A pesticide was considered to be adequately homogeneus if $SD/\sigma \leq 0.3$ where SD is the Standard Deviation and σ is the target standard deviation used for proficiency assessment. All results are presented in Table 2.

Table 2. COIPT-23: homogeneity results (mg/kg)

Sample number	Chlorpyrifos methyl	Diazinon	Tau-fluvalinate	Kresoxim methyl	Phosmet	Procymidone
61	0.085	0.200	0.152	0.325	0.227	0.136
64	0.086	0.230	0.150	0.327	0.230	0.135
76	0.077	0.186	0.129	0.289	0.218	0.126
80	0.083	0.220	0.147	0.328	0.230	0.140
87	0.084	0.221	0.146	0.330	0.211	0.128
92	0.082	0.228	0.160	0.320	0.227	0.142
97	0.093	0.199	0.142	0.325	0.223	0.134
100	0.080	0.191	0.141	0.313	0.219	0.132
103	0.088	0.205	0.154	0.320	0.200	0.140
110	0.098	0.189	0.170	0.380	0.203	0.143
Mean	0.086	0.207	0.149	0.326	0.219	0.136
SD	0.006	0.017	0.011	0.022	0.011	0.006
σ	0.022	0.056	0.037	0.076	0.051	0.032
SD/σ	0.280	0.296	0.302	0.296	0.214	0.181
Critical value	0.3	0.3	0.3	0.3	0.3	
SD/σ≤0.3	yes	yes	yes	yes	yes	

SD Standard Deviation; σ = Standard Deviation *target*
Critical value = critical value according to ISO 13528:2015
SD/σ ≤0.3 = If SD/σ≤0.3 the material has sufficient homogeneity

The stability test was performed using three bottles (chosen randomly) which were analysed in duplicate in two occasions:

- Day 1: after the shipment of the samples on 12 February 2024;
- Day 2: after two months by the deadline for reporting results on 11 April 2024.

A pesticide was considered to be adequately stable if $|x_i - y_i| \leq 0.3\times\sigma$, where x_i is the mean value of the first stability test, y_i the mean value of the last stability test and σ the target standard deviation used for proficiency assessment. The individual results are indicated in Table 3. All the six spiked compounds passed the homogeneity and stability tests.

Table 3. COIPT-23: data (mg/kg) of the stability test

Pesticide	Concentration mg/kg				
	Mean 1 (M1) n=6	Mean 2 (M2) n=6	(M1-M2)	σ	0.3xσ
Chlorpyrifos-methyl	0.077	0.083	-0.006	0.022	0.007
Diazinon	0.207	0.192	0.016	0.056	0.017
Fluvalinate-tau	0.146	0.137	0.009	0.037	0.011
Kresoxim-methyl	0.328	0.309	0.019	0.076	0.023
Phosmet	0.220	0.220	0.000	0.051	0.015
Procymidone	0.126	0.131	-0.005	0.032	0.010

M1 = mean of duplicates of three bottles analysed in the first day
M2 = mean of duplicates of three bottles analysed in the second day
σ = target standard deviation
The acceptance criterion of the stability test is = |M1-M2| < 0.3xσ

Distribution of samples and instructions to participants

One dark glass bottle containing 50 g of spiked oil was sent to the participating laboratories. Because olive oil usually is disposable at ambient temperature samples were shipped without refrigeration.

An information message was sent out by e-mail before shipment so that laboratories could make their own arrangements for the reception of the package.

The participants (see Appendix A) were asked:

- to treat the test material as if it were a sample for their routine analysis;
- to report results in the appropriate form and sent to the organizer by e-mail along with the details of methodology used.

The samples were sent out on 7 February 2024. The deadline for results was 18 March 2024.

The final report was dispatched to all participant at the end of June 2024.

Statistical evaluation of results

The organiser of this PT decided to use the z-score parameter to evaluate the laboratory performance for each compound using the same model of the PTs carried out by the European Reference Laboratories (EURLs) (17, 18) for the statistical treatment of the initial results.

The median value and the robust mean (according to algorithm A) were calculated. The median is a simple and highly outlier resistant estimator of the population means for symmetric distributions. The algorithm A minimises the influence of outlying results and provides good estimations of the standard deviation. In comparison with the median, the robust mean is less influenced by deviating results and for this reason at the end the *robust mean* was used as consensus value calculated in accordance with the algorithm A as explained in the Annex C.3.1 of ISO 13528:2015 document (Appendix B).

The z-score has been calculated:

$$\text{z-score} = \frac{(x-X)}{\sigma}$$

where x is the laboratory mean, X is the *consensus* value (the robust mean), σ a relative target standard deviation (FFP RSD) corresponding at the 25% of the robust mean value.

The usual interpretation of the z-score parameter is that values between +2 and –2 indicate an acceptable performance, |z-score| between 2 and 3 indicate that results are questionable and some attention should be paid to the methods and/or operations in the laboratory, while |z-score| greater than 3 are unacceptable.

Results for pesticides analysed by laboratories but reported as < RL (RL=Reporting Limit of the laboratory) have been considered as not detected and has been judged as false negative. For false negative results, a z score of -4.0 will be assigned. These z scores have also been included in the graphical representation. Any z-score > 5 will be typically reported as 5*.

No z-score has been calculated for false positive result.

The spread of the results for each compound was evaluated performing some statistical tests (asymmetry test, normality tests by using the SPSS software).

When the assigned value is derived as a robust mean, the standard uncertainty (*u*, mg/kg) of the consensus value X may be estimated using the following formula, where s* is the robust standard deviation and n is the total number of results:

$$u = 1.25 \text{ x } \frac{s*}{\sqrt{\text{n}}}$$

If the following criterion is met: $u \leq 0.3\ \sigma$, then the uncertainty of the assigned value may be considered to be negligible and need not be included in the interpretation of the results of the proficiency testing.

Furthermore, the global performance (19) of each participating laboratory was assessed by calculating the Average of the Squared z-scores (AZ^2).

The global performance of each participating laboratory has been assessed only for laboratories which have achieved the *sufficient scope.* The $|AZ^2|$ is estimated using the following formula:

$$AZ^2 = \frac{\sum_{i=1}^{n} |Z_i| \omega(Z_i)}{\text{n}}$$

The formula is the sum of the z-score value, multiplied by itself [$\omega(Z_i) = Z_i$] and divided by the number of z-scores (n) including those from false negatives.

The AZ^2 was used to evaluate the global performance of each laboratory with three sub-classifications:

- *Good* $|AZ^2| \leq 2.0$
- *Satisfactory* $2.0 < |AZ^2| < 3.0$
- *Unsatisfactory* $|AZ^2| \geq 3.0$

Combined z-scores are considered to be of lesser importance than individual z scores and should be used with caution according to ISO 13528:2015 (10). However, the AZ^2 parameter is normally used in the evaluation of a multiresidue method for the analysis of pesticides residues in food.

COIPT-23: RESULTS

Description and statistical evaluation of the results are presented for each compound separately and as final comments.

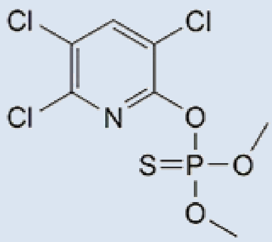
All data for each compound were analysed for normal distribution by applying the Shapiro-Wilk test (α=0.05).

The distribution of the concentrations of the pesticides reported by the laboratories has been plotted as histograms with a bandwidth of 0.75 σ where σ represents the target standard deviation.

In addition, Kernel density plots were used to identify multi-modality in the data distributions All the compound data sets were normally distributed except for Chlorpyrifos-methyl, Tau-fluvalinate and Procymidone. In any case, the Kernel density plots displayed one main mode indicating homogeneous data populations for all compounds.

The frequency histograms report also the Gaussian curve.

Chlorpyrifos-methyl



Common name
Chlorpyrifos-methyl, chlorpyriphos-methyl

Structure formula $C_7H_7Cl_3NO_3PS$

CAS number 5598-13-0

Its physical form consists of white crystals with a slight mercapatane odour with weight molecular of 322.5. This compound is soluble in organic solvents.
It is an organophosphate non-systemic insecticide and acaricide with contact, stomach and respiratory action.
Not authorized on olive tree with a MRL value of 0.01 mg/kg on olive as established by the Regulation (EC) 396/2005 that corresponds at limit of analytical determination.
It could be present in olive oil as contaminant.

Figure 1 shows the results of Chlorpyrifos-methyl (mg/kg) submitted by all laboratories with the Kernel density plot. The distribution of the results is not symmetric.

Statistical evaluation of the Chlorpyrifos-methyl results is presented in Table 4.

In the case of Chlorpyrifos-methyl, submitted results can be considered good, with Robust RSD% and uncertainty of the assigned values *u* acceptable.

All z-score values with recoveries estimated as numerical values are presented in Table 5. Furthermore, in Figure 2 the z-score values are presented in graphical form.

Chlorpyrifos-methyl was analysed by thirty-seven out of thirty-nine laboratories with good z-score except a false negative value of -4.0 for Lab 06.

It was noted that the majority of recoveries were in the range 70-120%.

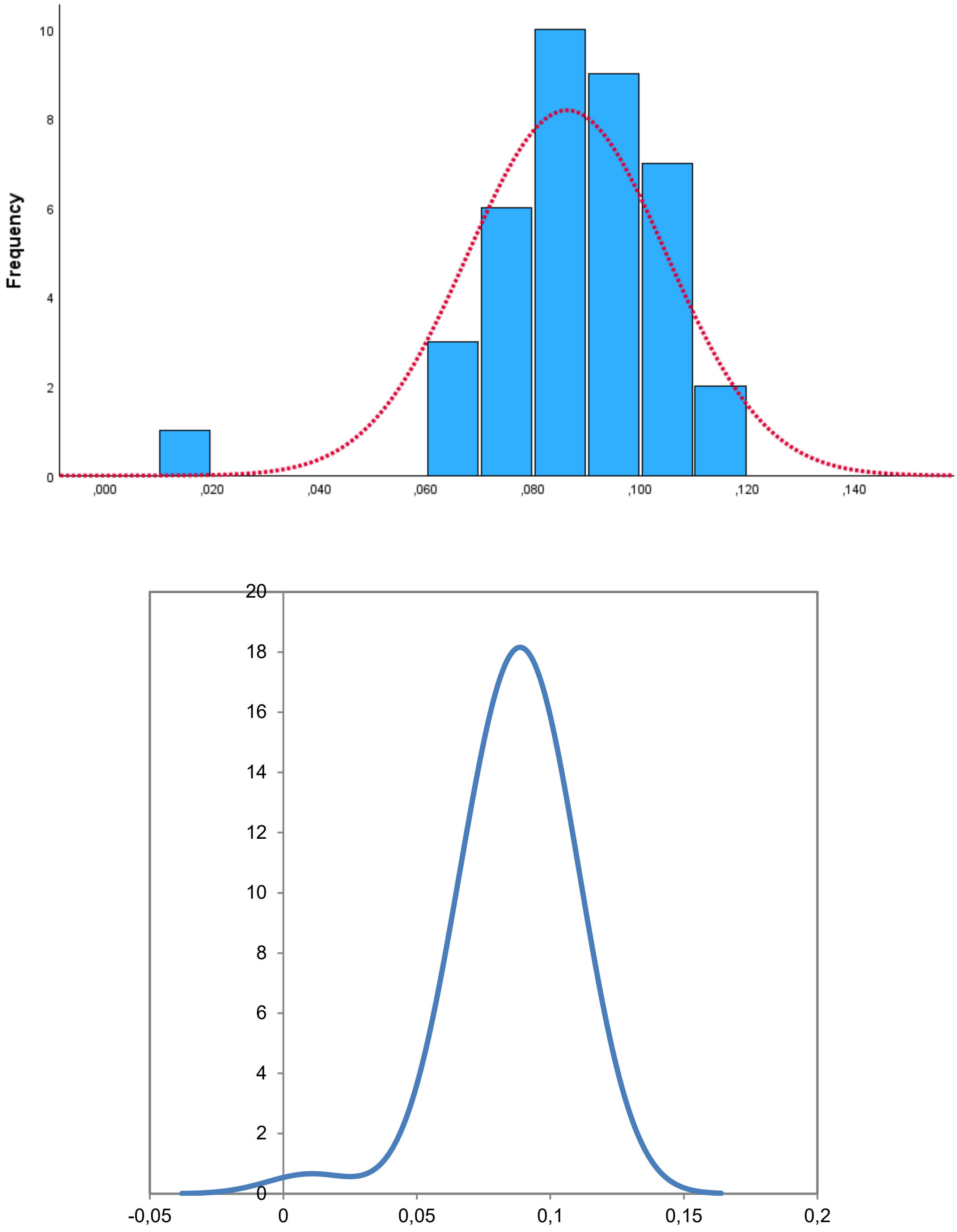


Figure 1. CHLORPYRIFOS-METHYL: frequency histogram of the results (mg/kg) and Kernel density plot. COIPT-23

Table 4. CHLORPYRIFOS-METHYL: statistical parameters (mg/kg). COIPT-23

Parameter	Value
Spiked value	0.087
Mean	0.086
Median	0.088
Robust mean or Assigned value (mg/kg)	0.088
s*	0.016
σ	0.022
Uncertainty (u) (mg/kg)	0.003
u/σ *	0.136
FFP RSD (%)	25
Robust RSD (%)	18

s*= robust standard deviation
* u/σ ≤ 0.3; RSD: Relative Standard Deviation

Table 5. CHLORPYRIFOS-METHYL: z-score and recovery (%) values. COIPT-23

Lab Code	z-score	Recovery %
1	-0.77	69
2	-0.73	100
3	0.36	98
4	-0.73	70
5	0.23	-
7	-0.59	72
9	-0.36	89
10	-0.36	100
11	0.23	65*
12	0.18	87
13	0.55	74
14	0.36	112
15	-0.14	98
16	-0.05	105
17	0.14	84
18	-0.27	70*
19	0.00	90
20	0.27	92
21	-0.32	100
22	0.91	108
23	-0.27	82
24	1.27	99
25	1.00	91
26	-0.05	75
27	-1.14	75
28	-1.00	60
29	0.00	86
30	0.59	92
31	0.27	115
32	0.55	105
33	0.91	87
34	0.82	98
35	0.32	119
36	-1.05	112
37	0.77	114
38	-0.73	87
39	-0.55	95

*Adjusted for recovery

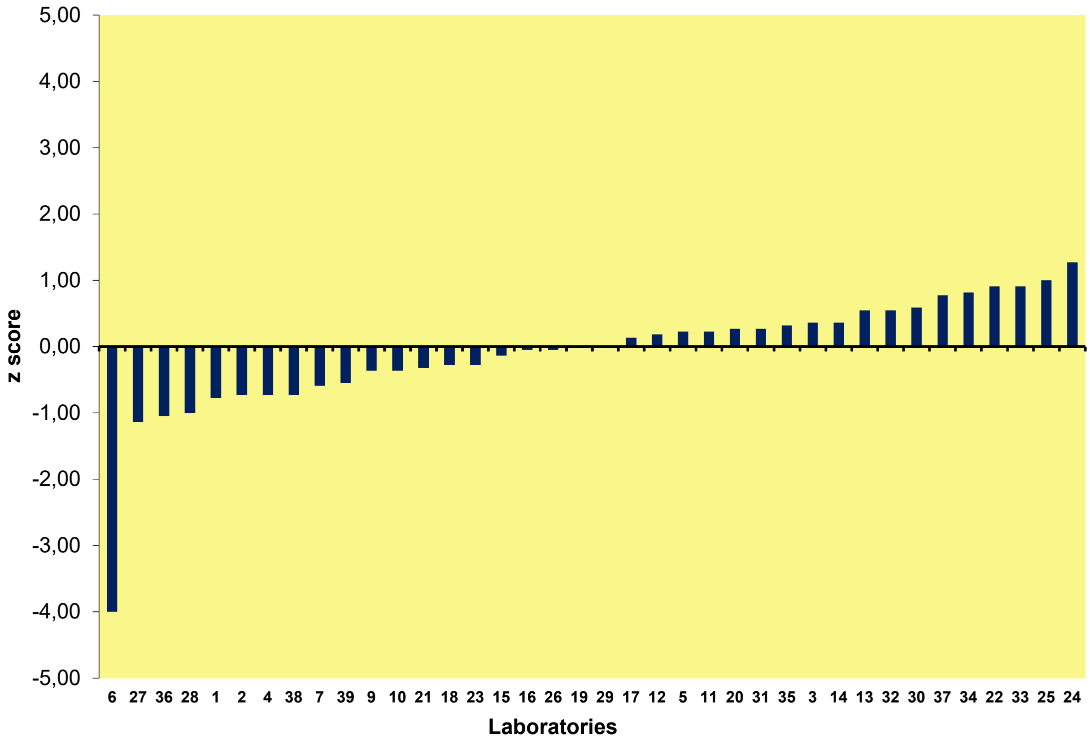
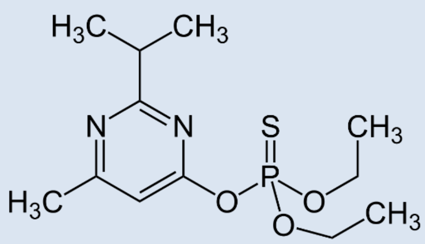


Figure 2. CHLORPYRIFOS-METHYL: z-score values (spiked value = 0.087 mg/kg). COIPT-23

Diazinon

	**Common name** diazinon or dimpylate **Structure formula** $C_{12}H_{21}N_2O_3PS$ **CAS number** 333-41-5 **EC no.** 206-373-8 It is a thiophosphoric acid ester, faint and colourless to yellow-dark brown liquid with weight molecular of 304.34 g/mol. It is a non-systemic organophosphate insecticide and acaricide with contact, stomach and respiratory action. This compound is highly soluble in organic solvents and stable only in neutral media, but it is susceptible to oxidation above 100°C and decomposes above 120°C. Not authorized on olive tree with a MRL value of 0.02 mg/kg on olive as established by the Regulation (EC) 396/2005 that corresponds at limit of analytical determination. It could be present in olive oil as contaminant as consequence of his liphofilic properties.

In the case of Diazinon the distribution of submitted data resulted symmetric as indicated in Figure 3.

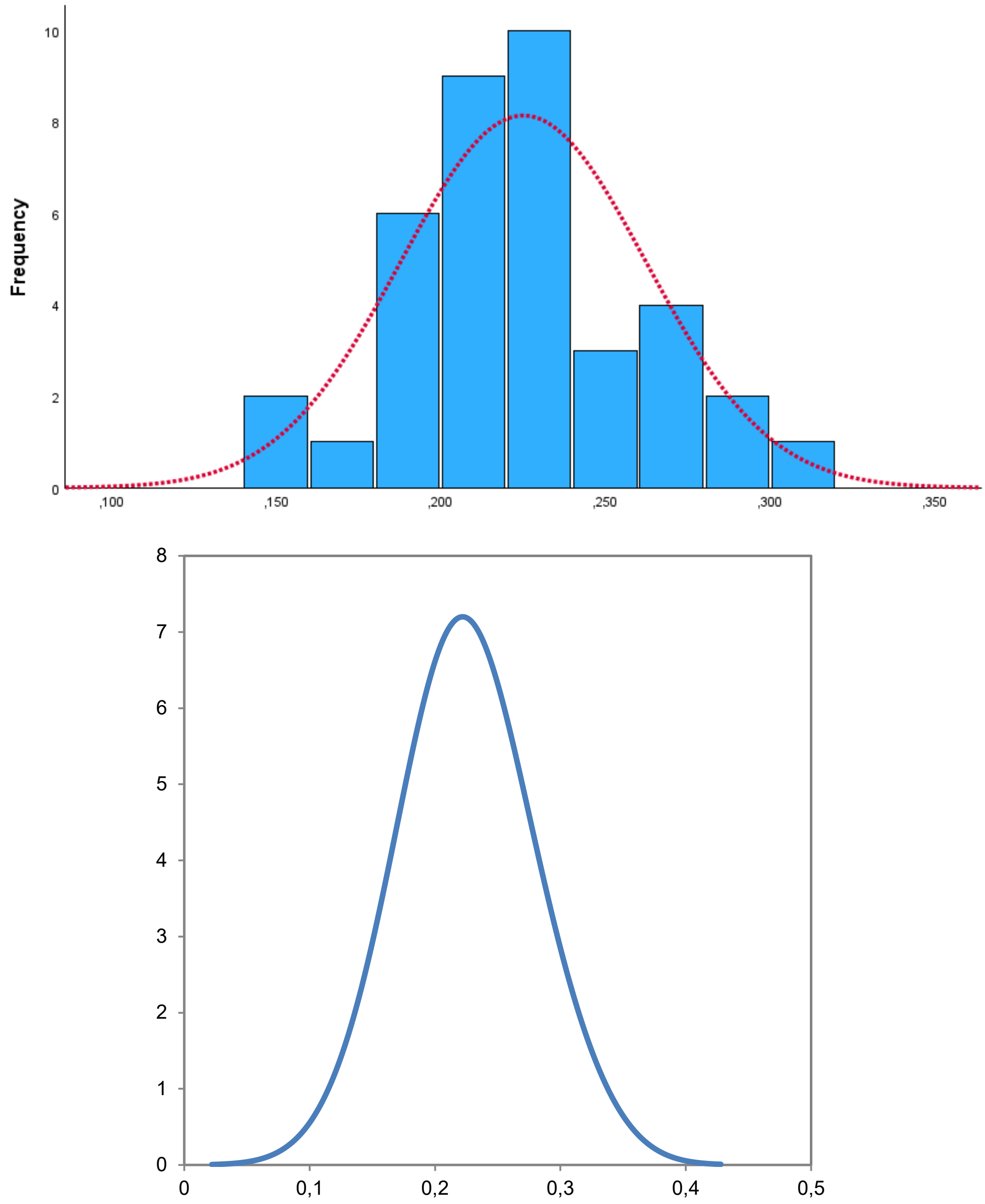


Figure 3. DIAZINON: frequency histogram of the results (mg/kg) and Kernel density plot. COIPT-23

Statistical evaluation of the Diazinon results is presented in Table 6. The supplied results for Diazinon can be considered good, with Robust RSD% of 16 and uncertainty value of 0.01 mg/kg.

All z-score values with recoveries estimated as numerical values are presented in Table 7 with z-score showed as graphical representation in Figure 4. In the case of Diazinon thirty-eight laboratories supplied results with good calculated z-score values in the range 0.1-2.0 as absolute values.

Table 6. DIAZINON: statistical parameters (mg/kg). COIPT-23

Parameter	Value
Spiked value	0.244
Mean	0.225
Median	0.223
Robust mean or Assigned value (mg/kg)	0.225
s*	0.037
σ	0.056
Uncertainty (u) (mg/kg)	0.01
u/σ *	0.179
FFP RSD (%)	25
Robust RSD (%)	16

s*= robust standard deviation; * u/σ ≤ 0.3; RSD: Relative Standard Deviation

Table 7. DIAZINON: z-score and recovery (%) values. COIPT-23

Lab Code	z-score	Recovery %
1	0.02	66
2	-0.25	100
3	-0.46	90
4	-0.63	73
5	0.88	-
6	-1.38	85
7	-0.21	83
9	0.21	81
10	0.79	100
11	0.13	70*
12	0.04	87
13	0.09	83
14	-0.64	72
15	0.20	101
16	0.09	105
17	-0.77	79
18	0.02	75*
19	0.27	90
20	0.27	-
21	-0.13	100
22	1.29	107
23	-0.14	86
24	1.38	92
25	0.54	89
26	-0.09	90
27	-1.09	72
28	-0.64	77
29	0.89	88
30	-0.39	88
31	-0.73	89
32	-0.13	84
33	1.30	102
34	0.93	98
35	-0.11	108
36	-0.25	113
37	0.20	99
38	-1.20	86
39	-0.21	101

*Adjusted for recovery

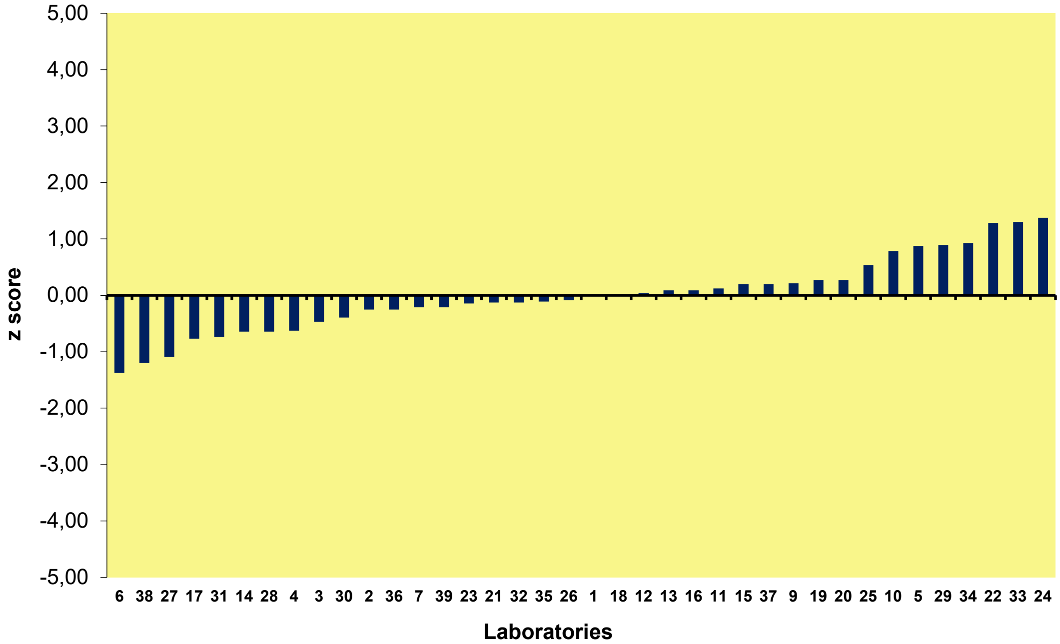
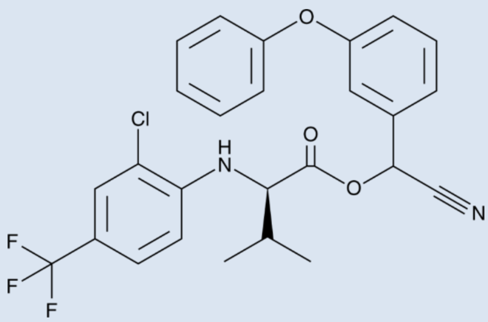


Figure 4. DIAZINON: z-score values (spiked value = 0.244 mg/kg). COIPT-23

Tau-fluvalinate

<table>
<tr>
<td></td>
<td>Common name
tau-Fluvalinate
CAS number 102851-06-9
Structure formula $C_{26}H_{22}ClF_3N_2O_3$

This compound belongs to the pyrethroid family. Material is a 1:1 mixture of 2 diasteroisomers. Its phisycal form consiste of viscous amber oil with a moderate sweetish odour with a molecular weight of 502.9.
Insecticide and acaricide with contact and stomach action. This pesticide has a good solubility in organic solvents and it is stable for two years at room temperature.
Not authorized on olive tree with a MRL value of 0.01 mg/kg on olive as established by the Regulation (EC) 396/2005 that corresponds at limit of analytical determination.
It could be present in olive oil as contaminant.</td>
</tr>
</table>

Figure 5 shows the results of Tau-fluvalinate (mg/kg) submitted by all laboratories in the COIPT-23. The distribution of the results is not symmetric.

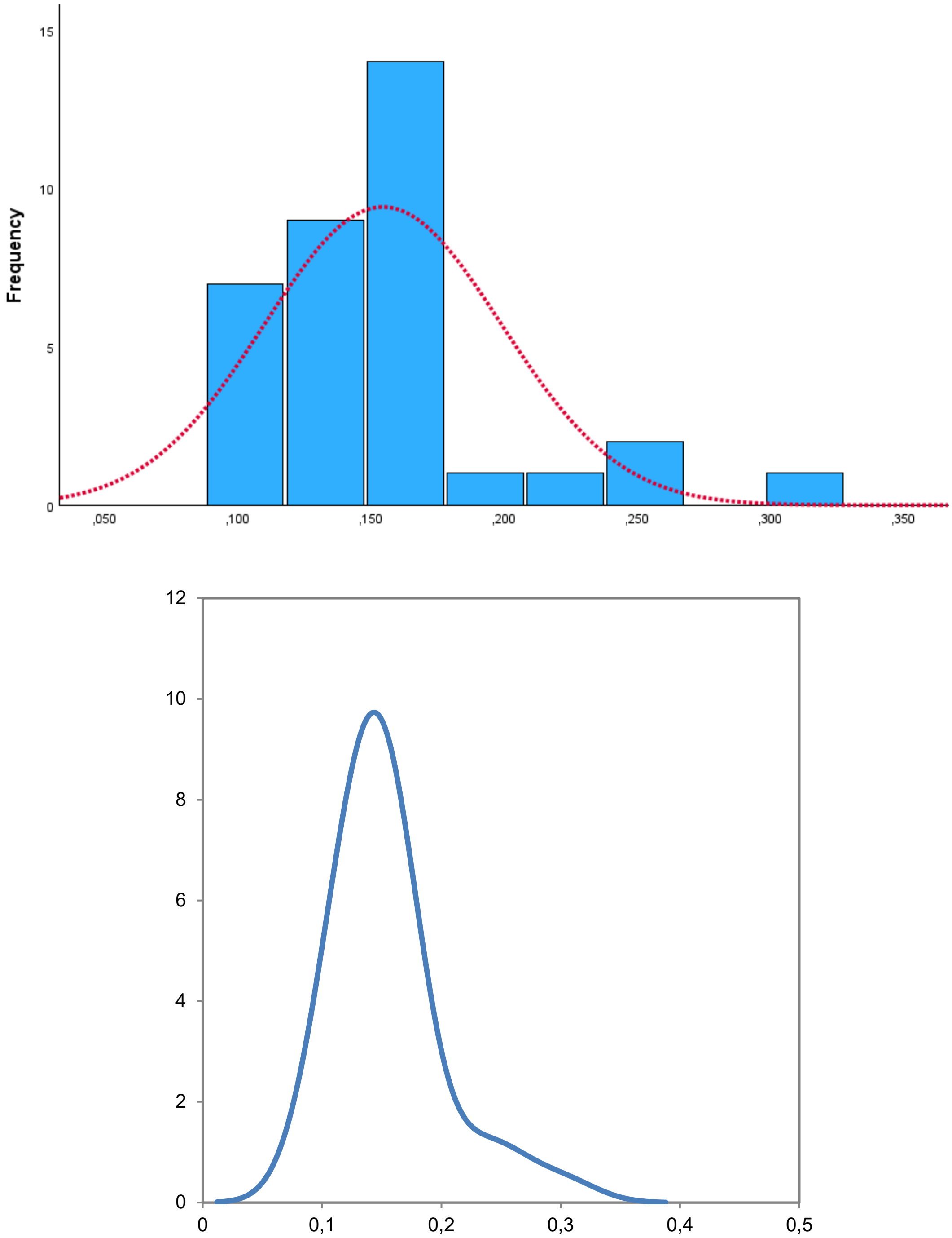


Figure 5. TAU-FLUVALINATE: frequency histogram of the results (mg/kg) and Kernel density plot. COIPT-23

Statistical evaluation of the Tau-fluvalinate results is presented in Table 8. Regarding Tau-fluvalinate data the obtained performance can be considered good with a Robust RSD% value of 20 and an uncertainty value of 0.006 mg/kg.

Table 8. TAU-FLUVALINATE: statistical parameters (mg/kg). COIPT-23

Parameter	Value
Spiked value	0.153
Mean	0.155
Median	0.150
Robust mean or Assigned value (mg/kg)	0.147
s*	0.030
σ	0.037
Uncertainty (u) (mg/kg)	0.006
u/σ *	0.162
FFP RSD (%)	25
Robust RSD (%)	20

s*= robust standard deviation; * u/σ ≤ 0.3; RSD: Relative Standard Deviation

All z-score values with recoveries estimated as numerical values are presented in Table 9.

Table 9. TAU-FLUVALINATE: z-score and recovery (%) values. COIPT-23

Lab Code	z-score	Recovery %
1	-0.86	86
2	0.41	100
4	-0.86	92
5	-0.43	-
6	-0.97	83
7	3.05	102
8	-1.00	96
9	-0.05	84
10	0.49	100
11	1.03	60*
12	-0.24	107
13	0.08	84
14	-0.65	94
15	-0.11	95
16	0.08	101
17	2.51	86
19	-0.32	90
21	2.24	100
22	4.24	69*
23	0.05	83
24	0.46	99
25	0.08	85
26	0.22	78
27	-1.19	85
29	0.14	99
30	-0.16	107
31	0.24	80
32	0.54	82
33	-1.38	105
34	0.73	103
35	-0.41	100
36	-1.00	123
37	0.59	114
38	0.11	120
39	-0.43	97

*Adjusted for recovery

Furthermore, in Figure 6 the z-score values are presented in graphical form.

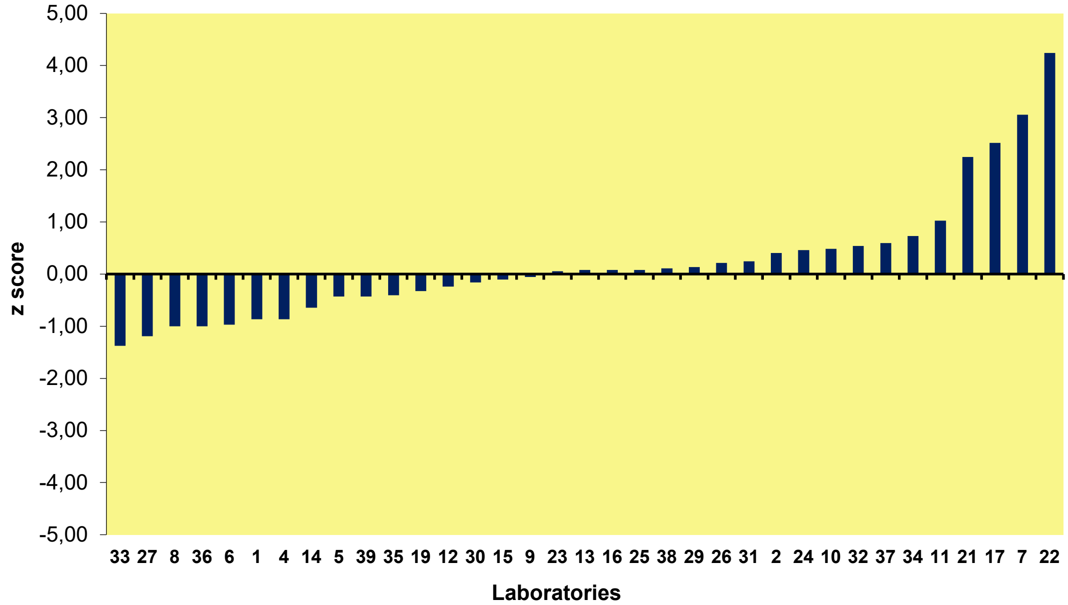
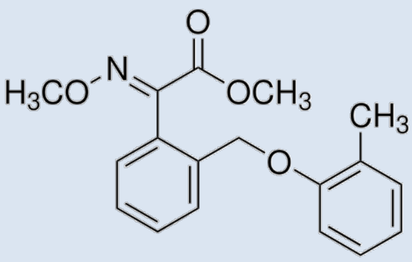


Figure 6. TAU-FLUVALINATE: z-score values (spiked value = 0.153 mg/kg). COIPT-23

In the case of Tau-fluvalinate thirty-five laboratories supplied results with thirty-one good calculated z-score values in the range 0.1-2.0 as absolute values, three questionable z-scores for Lab 7, Lab 17 and Lab 21 with values of 3.05, 2.52 and 2.24 respectively, and one unacceptable z-score value of 4.24 in the case of Lab 22.

Kresoxim-methyl



Common name
kresoxim-methyl or krésoxim-méthyle

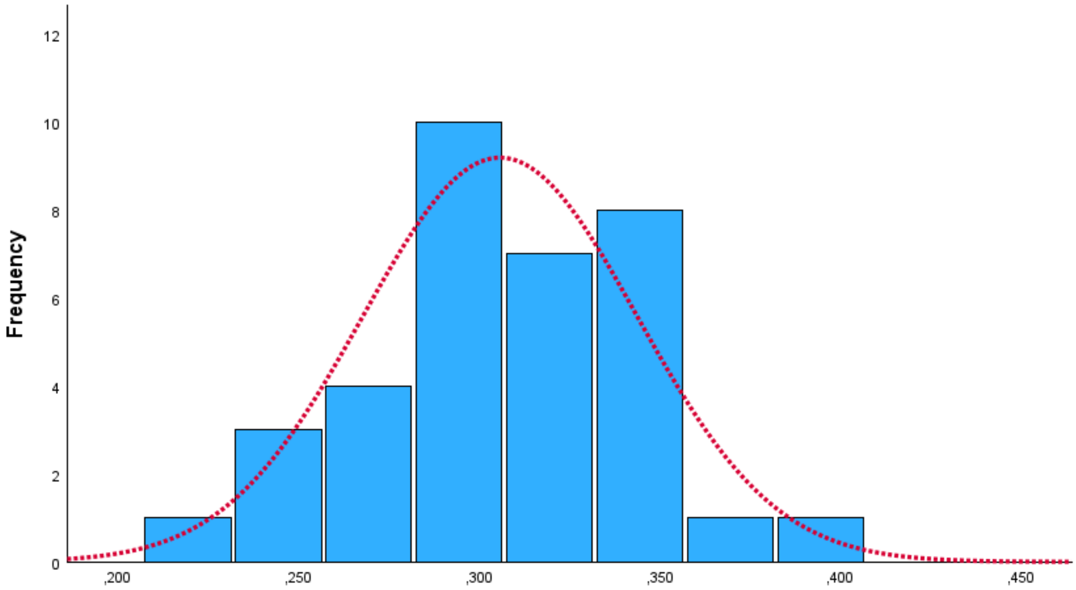
Structure formula $C_{18}H_{19}NO_4$

CAS number 143390-89-0

EC no. 417-880-0

Its physical form consists of odorless or mildly aromatic, white or colourless solid crystals with weight molecular of 313.4 g/mol. It is a carboxylic ester with the function of long lasting, protective, curative fungicide through the inhibition of mithocondrial respiration. It has good solubulity in organic solvent and it is relatively stable at pH 5, but it hydrolyses in alkaline media.
Authorized on olive tree with a MRL value of 0.2 mg/kg on olive as established by the Regulation (EC) 396/2005.
Nine formulations of PPP type WG (Water dispersible Granules) and two SC (soluble concentrate) formulations containing Kresoxim-methyl are authorized in Italy.

Also in the case of Kresoxim-methyl the distribution of submitted data resulted symmetric as indicated in Figure 7.



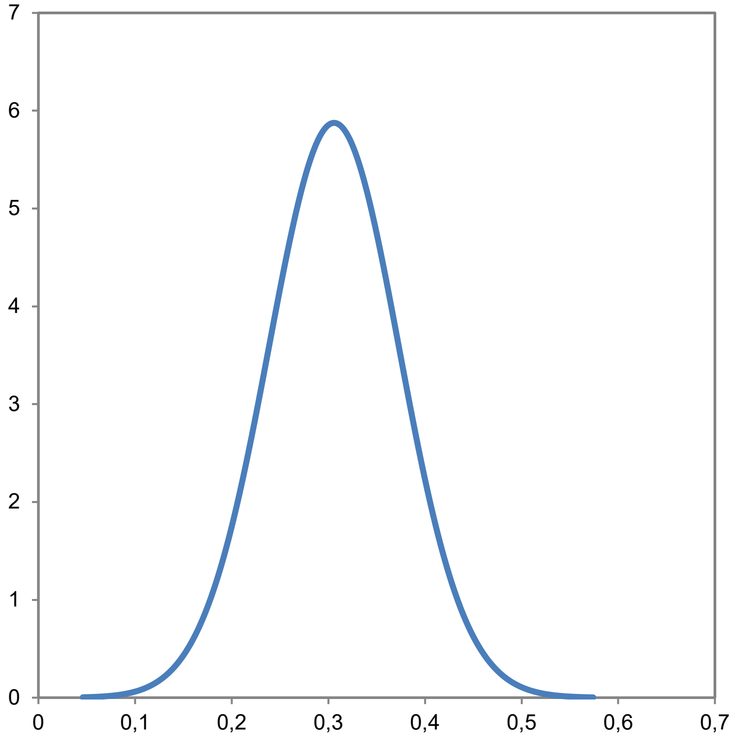


Figure 7. KRESOXIM-METHYL: frequency histogram of the results (mg/kg) and Kernel density plot. COIPT-23

Statistical evaluation of the Kresoxim-methyl results is presented in Table 10.

Table 10. KRESOXIM-METHYL: statistical parameters (mg/kg). COIPT-23

Parameter	Value
Spiked value	0.312
Mean	0.306
Median	0.306
Robust mean or Assigned value (mg/kg)	0.306
s*	0.037
σ	0.076
Uncertainty (u) (mg/kg)	0.008
u/σ *	0.105
FFP RSD (%)	25
Robust RSD (%)	15

s*= robust standard deviation; * u/σ ≤ 0.3; RSD: Relative Standard Deviation

Regarding Kresoxim-methyl data the obtained performance can be considered acceptable. All z-score values with recoveries estimated as numerical values are presented in Table 11.

Table 11. KRESOXIM-METHYL: z-score and recovery (%) values. COIPT-23

Lab Code	z-score	Recovery %
1	-0.16	78
2	-0.29	100
3	-1.17	95
4	0.82	88
5	0.08	-
6	-0.38	83
7	0.38	91
9	0.34	88
10	-0.79	101
11	0.36	75*
12	0.28	96
13	0.25	91
14	-0.09	76
17	-0.51	75
18	-0.76	87*
19	0.64	90
20	-0.21	98
21	-0.21	100
22	0.38	97
23	-0.20	86
24	0.05	96
25	0.51	96
26	0.05	95
27	-0.76	90
28	-0.18	103
29	0.14	93
30	-0.01	114
31	0.00	80
33	1.28	103
34	0.47	101
35	0.57	133
36	-0.46	118
37	-0.14	100
38	-0.43	111
39	0.09	100

*Adjusted for recovery

Graphical representation of z-score is showed in Figure 8.

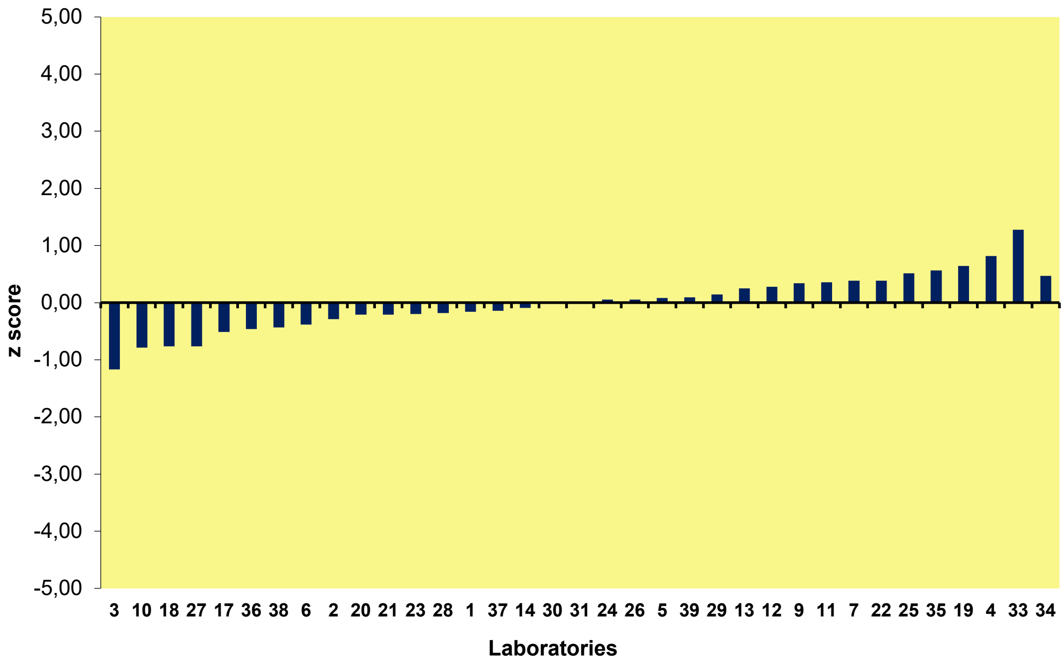


Figure 8. KRESOXIM-METHYL: z-score values (spiked value = 0.312 mg/kg). COIPT-23

Also the Kresoxim-methyl was analysed by thirty-five laboratories supplied results with good calculated z-score in the range 0.1-2.0 as absolute values.

Phosmet

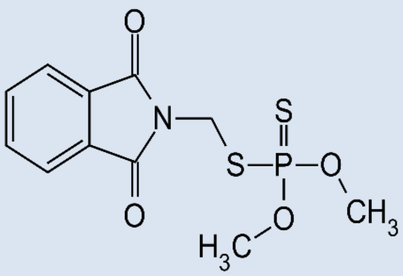
 	**Common name** phosmet or phtalofos/phthalophos **Structure formula** $C_{11}H_{12}NO_4PS_2$ **CAS number** 732-11-6 **EC no.** 211-987-4 This compound belongs to the organophosphate family. Its physical form consists of colourless crystals with weight molecular of 317.3 This pesticide has a good solubility in organic solvents and it is rapidly hydrolysed in alkaline media. Non-systemic insecticide and acaricide with predominantly contact action. Not authorized on olive tree with a MRL value of 0.01 mg/kg on olive as established by the Regulation (EC) 396/2005 that corresponds at limit of analytical determination. It could be present in olive oil as contaminant.

Figure 9 shows the results of Phosmet (mg/kg) submitted by all laboratories in the COIPT-23. The distribution of the results was symmetric.

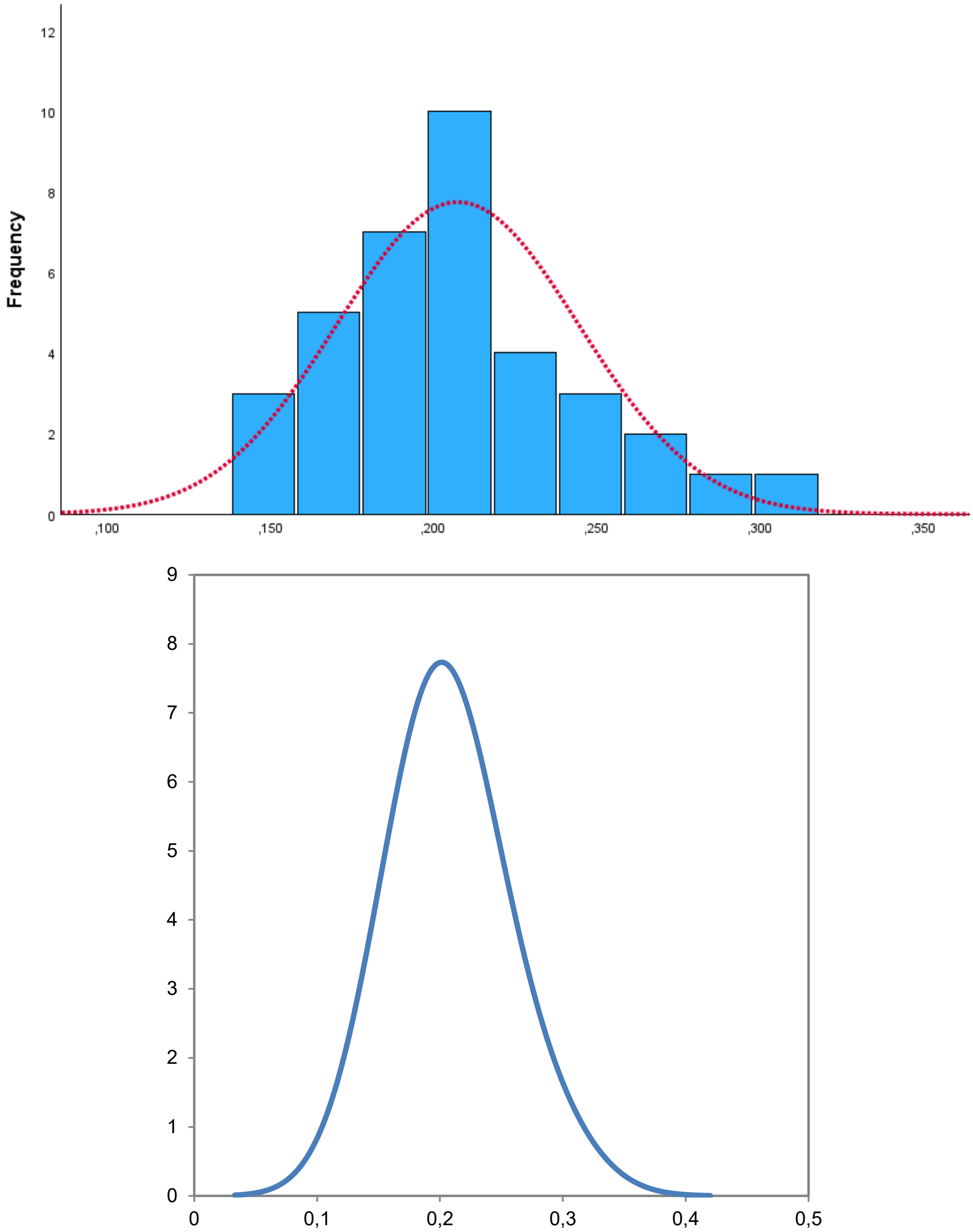


Figure 9. PHOSMET: frequency histogram of the results (mg/kg) and Kernel density plot. COIPT-23

Statistical evaluation of Phosmet results is presented in Table 12 while in Table 13 are listed all z-score values with corresponding recoveries estimated.

Table 12. PHOSMET: statistical parameters (mg/kg). COIPT-23

Parameter	Value
Spiked value	0.215
Mean	0.207
Median	0.207
Robust mean or Assigned value (mg/kg)	0.205
s*	0.036
σ	0.051
Uncertainty (u) (mg/kg)	0.007
u/σ *	0.137
FFP RSD (%)	25
Robust RSD (%)	17

s*= robust standard deviation
* u/σ ≤ 0.3; RSD: Relative Standard Deviation

Table 13. PHOSMET: z-score and recovery (%) values. COIPT-23

Lab Code	z-score	Recovery %
1	0.76	76
2	-0.20	100
3	-0.41	75
4	-0.22	105
5	-0.10	-
6	-1.14	101
7	0.22	90
9	0.33	90
10	0.35	114
11	-0.65	72*
12	-0.98	106
13	0.20	93
14	0.16	112
15	0.10	100
16	0.02	98
17	-0.71	81
18	-0.61	89*
19	-0.49	90
21	-0.16	100
22	1.22	110
23	0.18	98
24	-0.33	78
25	0.88	92
26	-0.12	82
27	-1.14	94
29	0.39	98
30	0.69	103
31	1.45	99
32	-0.43	134
33	1.98	109
34	1.37	102
35	0.08	86
36	-0.67	122
37	0.06	118
38	-0.75	87
39	0.35	100

*Adjusted for recovery

Statistically results for Phosmet can be considered satisfactory. The median and the robust mean are similar with a good value for Robust RSD% of 17 as the uncertainty equal to 0.007 mg/kg.

The z-score values presented in Table 13 are represented as graphical form in Figure 10. In the case of Phosmet thirty-six laboratories supplied results with good calculated z-score values in the range 0.1-2.0 as absolute values.

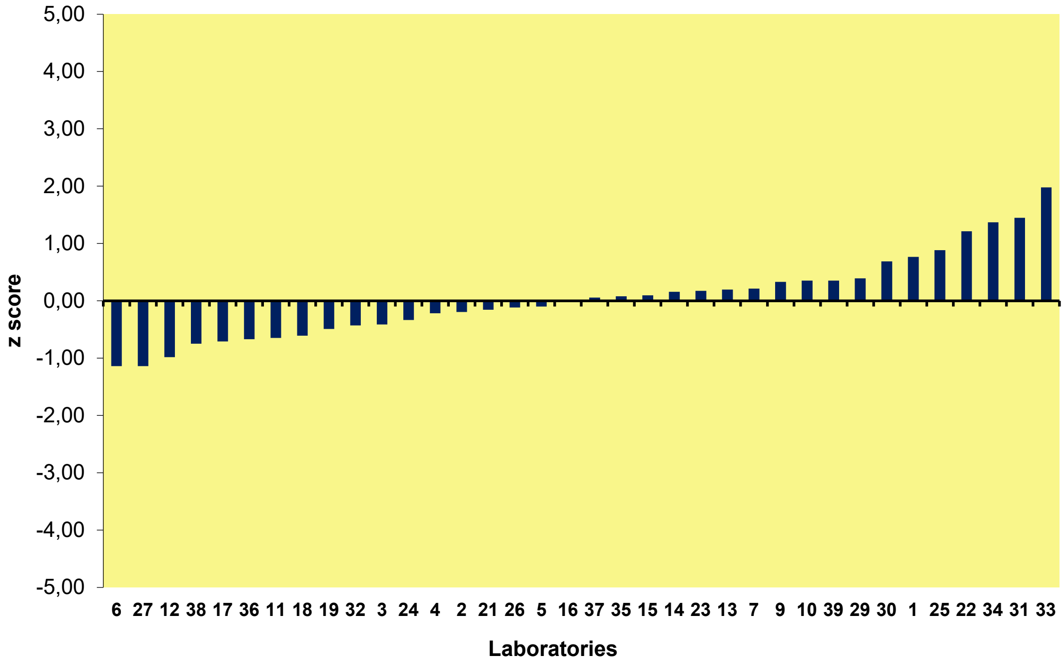
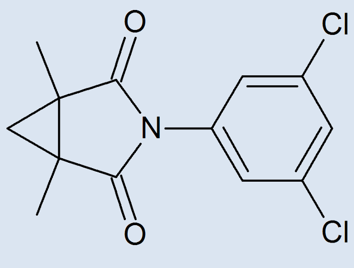


Figure 10. PHOSMET: z-score values (spiked value = 0.215 mg/kg). COIPT-23

Procymidone



Common name
procymidone

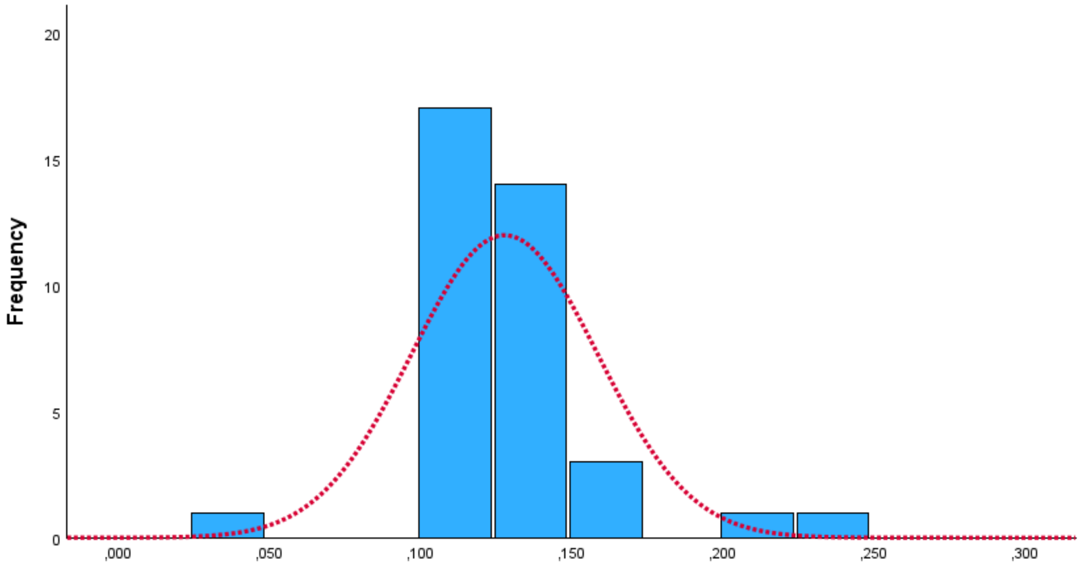
Structure formula $C_{13}H_{11}Cl_2NO_2$

CAS number 32809-16-8

EC no. 251-233-1

This compound presents colourless crystals or a light brown solid with weight molecular of 284.14 g/mol.
It is a moderate systemic fungicide and an endocrine distruptor, soluble in organic solvents and stable both under normal storage conditions and to light, heat and moisture.
Not authorized in Italy on olive tree with a MRL value of 0.02 mg/kg on olive as established by the Regulation (EC) 396/2005 that correspond at limit of analytical determination.
It could be present in olive oil as contaminant as consequence of his liphofilic properties.

Figure 11 shows the results of Procymidone (mg/kg) submitted by all laboratories in the COIPT-23. The distribution of data resulted not symmetric.



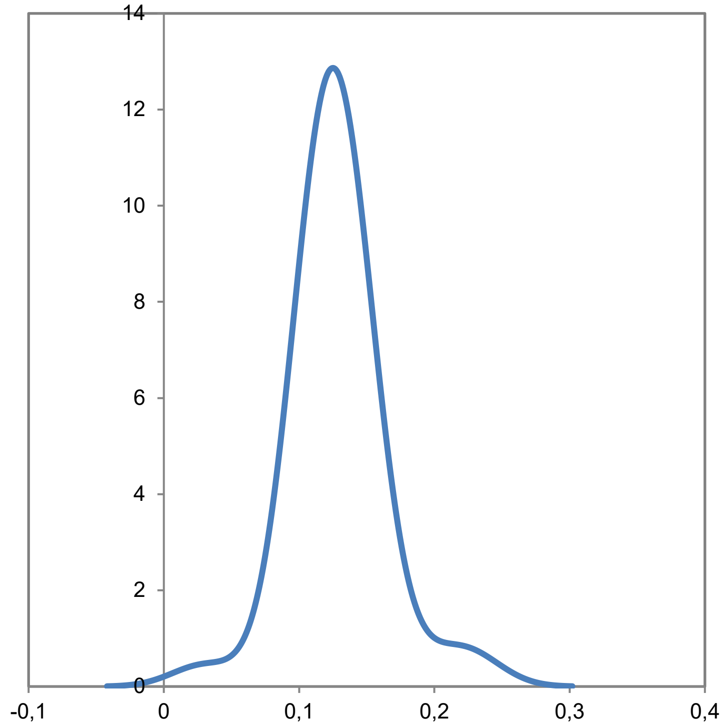


Figure 11. Procymidone: frequency histogram of the results (mg/kg) and Kernel density plot. COIPT-23

Statistical evaluation of Procymidone results is presented in Table 14 while in Table 15 are listed all z-score values with corresponding recoveries estimated. Statistically results for

Procymidone can be considered satisfactory. The median and the robust mean are similar with a good value for Robust RSD% of 15 as the uncertainty equal to 0.004 mg/kg.

Table 14. PROCYMIDONE: statistical parameters (mg/kg). COIPT-23

Parameter	Value
Spiked value	0.130
Mean	0.128
Median	0.125
Robust mean or Assigned value (mg/kg)	0.126
s*	0.019
σ	0.032
Uncertainty (u) (mg/kg)	0.004
u/σ *	0.125
FFP RSD (%)	25
Robust RSD (%)	15

s*= robust standard deviation; * u/σ ≤ 0.3; RSD: Relative Standard Deviation

Table 15. PROCYMIDONE: z-score and recovery (%) values. COIPT-23

Lab Code	z-score	Recovery %
1	-0.22	76
2	-0.66	100
3	-0.72	87
4	-0.78	85
5	-0.03	-
6	3.25	89
7	0.09	86
9	0.41	94
10	-0.22	100
11	-0.34	64*
12	-0.28	94
13	0.28	84
14	-0.28	85
15	0.31	89
16	0.22	102
17	-0.09	90
18	-0.44	105*
19	0.75	90
21	-0.19	98
22	0.44	97
23	-0.03	89
24	0.31	96
25	0.44	99
26	-0.19	78
27	-0.69	82
29	0.28	73
30	0.63	98
31	-0.59	87
33	0.84	109
34	0.66	103
35	-0.09	130
36	-0.03	111
37	-0.56	100
38	-0.53	112
39	-0.19	100

*Adjusted for recovery

The z-score values presented in Table 15 are represented as graphical form in Figure 12.

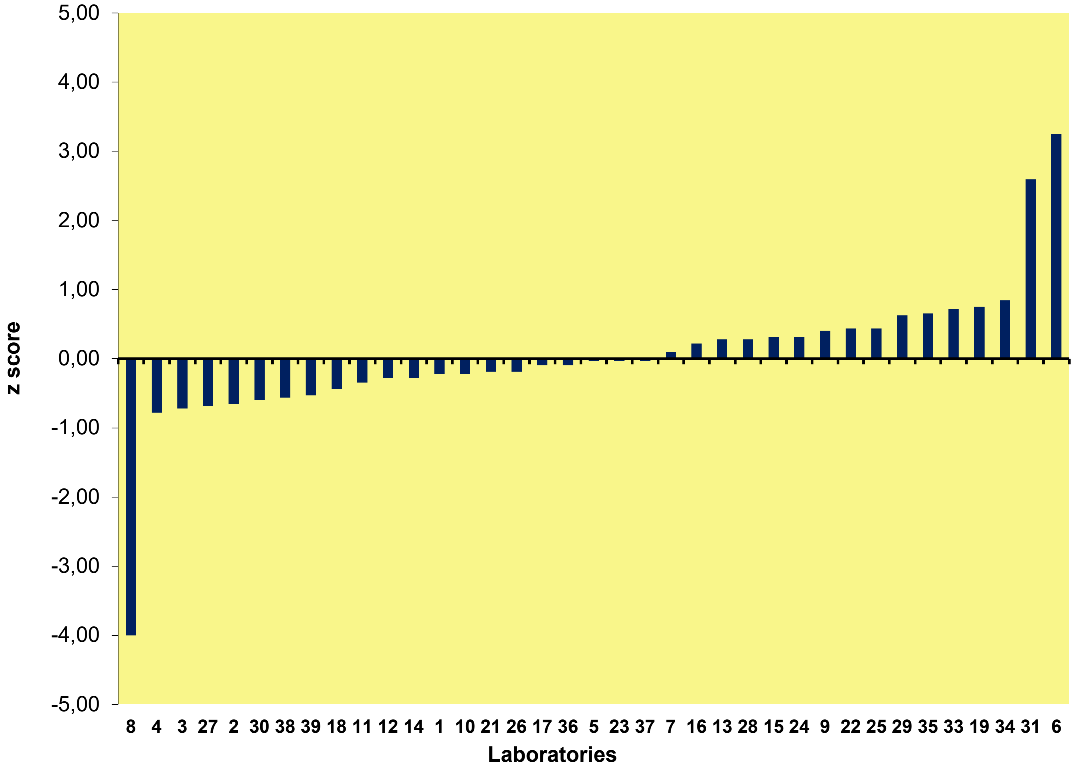


Figure 12. PROCYMIDONE: z-score values (spiked value = 0.130 mg/kg). COIPT-23

In the case of Procymidone thirty-six laboratories supplied results with good calculated z-score values except for a questionable z-score of 2.59 for Lab 31 and two unacceptable values for Lab 6 and Lab 8 of 3.25 and -4.00 respectively. In the case of Lab 8 the z-score value represents a false Negative z-score.

COIPT-23: FINAL CONSIDERATION

From a statistical point of view the results for the six compounds object of the COIPT-23 can be considered satisfactory.

The *Robust Standard Deviation (Robust RSD)* and the uncertainty of the assigned values u (x_{pt}) were presented for all pesticides. The range of Robust RSD% values was good from 12 to 20 while the range of u was from 0.003 to 0.1 mg/kg.

All thirty-nine participants laboratories submitted results and thirty (equal to 77%) analysed all compounds with Chlorpyrifos-methyl and Diazinon that resulted the most analysed compounds.

For three compounds Diazinon, Kresoxim-methyl and Phosmet has been obtained good z-score values in the range 0.1-2.0.

Two false negative values*, Chlorpyrifos-methyl* to Lab 06 as well as *Procymidone* to Lab 08.

No false positive *z scores* have been observed.

The global performance of each participating laboratory has been assessed only for laboratories which have achieved the sufficient scope, by calculating the Average of the Squared z-scores (AZ^2). Figure 13 was an accurate representation of the results of the AZ^2.

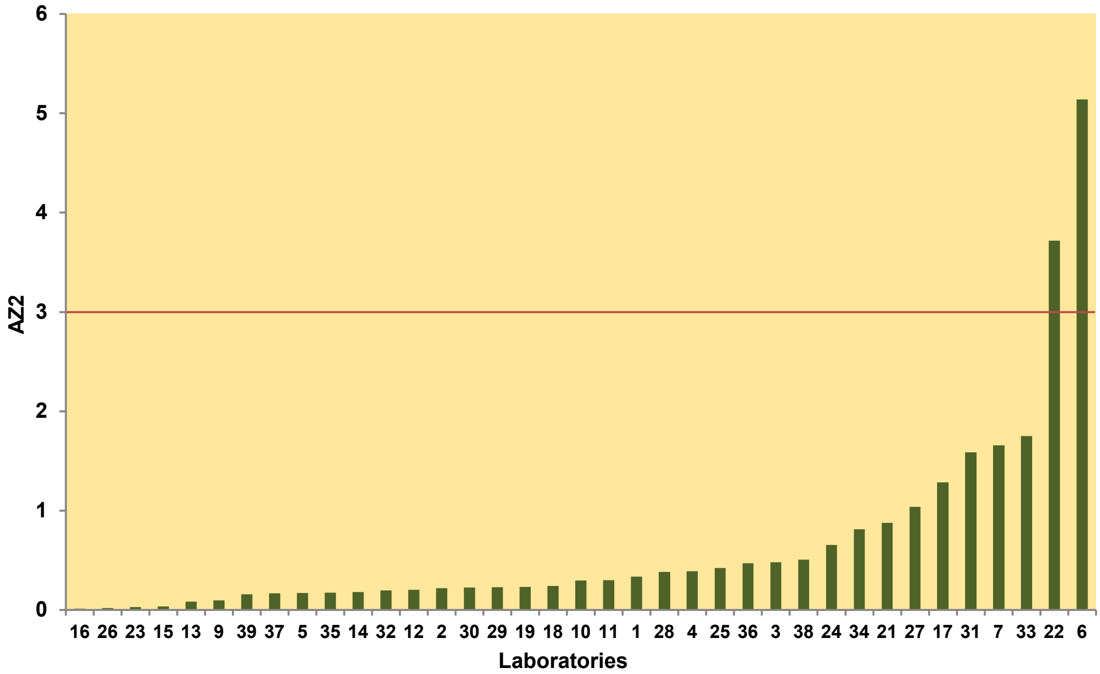


Figure 13. Global performance of laboratories: AZ^2 values. COIPT-23

Respect to the analytical methods applied by participants, the majority of laboratories corresponding to twenty-nine participants out of thirty-nine used the QuEChERS methodology or methods based on QuEChERS (19).

The QuEChERS method is a streamlined approach that makes it easier and less expensive for analytical chemists to examine pesticide residues in food. The name is a portmanteau word formed from "Quick, Easy, Cheap, Effective, Rugged, and Safe". Since 2008 the QuEChERS method has been a standard procedure published by the European Committee for Standardization and transposed in Italy in 2009 (20).

Seven laboratories used in house methods with an extraction step followed by a clean-up phase; only one of them without any purification.

Two laboratories followed the method QuOil (21) and the EURL FV (2012-M6) method (22) respectively.

In the above-mentioned methods, the purification was carried out using the GPC (Gel Permeation Chromatography) technique, C_{18} or OASIS cartridges or using combination of different materials as PSA+C_{18} as SPE or PSA+GCB or freezing technique. The amount of the sample test was in the range 1-15 g while the final analysis volume was between 0.15 and 10 ml.

In the analysis of pesticide residues, the laboratories use Multi-Residue Methods (MRM) because of the large number of analytes enclosed in official control plans (23-25).

The majority of the laboratories as instrumental detection techniques have used GC (Gas Chromatography) or LC (Liquid Chromatography) coupled with MS/MS detector using two or three transitions.

In the large part of the cases the quantification has been carried out with matrix calibration at single or multiple levels. Five laboratories used instead the solvent calibration with two laboratories that performed the standard addition procedure. Most laboratories used internal or process standards for quantification.

CONCLUSIONS

The outcome of the COIPT-23 can be considered satisfactory from several point of view.

One is the good participation of laboratories. Thirty-nine laboratories: three NRLs, sixteen official control laboratories and twenty private laboratories. The other regards the performance expressed in terms of z-score. The laboratory performance obtained for each tested pesticide was satisfactory by almost all participants with three compounds Diazinon, Kresoxim-methyl and Phosmet that obtained good z-score values in the range 0.1-2.0.

Moreover, the global performance (AZ^2 scores) assessed only for laboratories which achieved the *sufficient scope* was proper. By supplied data, thirty-five laboratories obtained a satisfactory performance for all tested compounds.

Regarding the methodologies used in this PT, the analysis for the majority of laboratories were performed according QuEChERS method or QuEChERS based analytical methods with limited modifications.

It is important to consider that participation in these PTs on a routine basis is the only disposable tool for laboratories to monitor their competence in the pesticide residues analysis in olive oil.

REFERENCES

1. Europe. Regulation (EU) 2017/625 of the European Parliament and the Council of 15 march 2017 on official controls and other official activities performed to ensure the application of food and feed law, rules on animal health and welfare, plant health and plant protection products. *Official Journal of the European Union* L95/1, 7 April 2017.
2. ISO/IEC 17025:2017. *General requirements for the competence of testing and calibration laboratories.* Geneva: International Organization for Standardization; 2017.
3. European Commission - Directorate-General for Health and Food Safety. *Guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed*. Brussels: European Commission; 2024. (SANTE/11312/2021v2).
4. IOC. *Huiles d'olive – Olive oils*. *Mondial production.* Madrid: International Olive Council; 2024.
5. Fabiani R, Rosignoli P. Olio d'oliva e salute. In: Conte L, Servili M (Ed.). *Oleum. Qualità, tecnologia e sostenibilità degli oli da olive*. Milano: Edagricole 2022. p. 295-306.
6. Europe. Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC. *Official Journal of the European Union* L70/1, 16 March 2005.
7. Europe. Commission Implementing Regulation (EU) 2021/601 of 13 April 2021 concerning a coordinated multiannual control program of the Union for 2022, 2023 and 2024 to ensure compliance with maximum residue levels of pesticides and to assess the consumer exposure to pesticide residues in and on food of plant and animal origin. *Official Journal of the European Union* L 127/29, 14 April 2021.
8. European Commission - Directorate-General for Health and Food Safety. Information note on Article 20 of Regulation (EC) No 396/2005 as regards processing factors, processed and composite food and feed. Brussels: European Commission; 2021. (SANTE/ 10704/2021).
9. ISO 17043:2010. *Conformity Assessment – General requirements for proficiency testing* Geneva: International Organization for Standardization; 2010.
10. ISO 13528:2015. *Statistical methods for use in proficiency testing by interlaboratory comparison.* Geneva: International Organization for Standardization; 2015.
11. Europe. Regulation (EC) No 2020/1085 of 23 July 2020 amending Annexes II and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for chlorpyrifos and chlorpyrifos-methyl in or on certain products. *Official Journal of the European Union* L 239/7, 24 July 2020.
12. Europe. Regulation (EU) No 834/2013 of 30 August 2013 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for acequinocyl, bixafen, diazinon, difenoconazole, etoxazole, fenhexamid, fludioxonil, isopyrazam, lambda-cyhalothrin, profenofos and prothioconazole in or on certain products. *Official Journal of the European Union* L 233/11, 31 August 2013.
13. Europe. Regulation (EU) No 2022/93 of 20 January 2022 amending Annexes II, III and IV to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for acrinathrin, fluvalinate, folpet, fosetyl, isofetamid, 'Pepino Mosaic Virus, EU strain, mild isolate Abp1', 'Pepino Mosaic Virus, CH2 strain, mild isolate Abp2', spinetoram and spirotetramat in or on certain products. *Official Journal of the European Union* L 15/1, 25 January 2022.

14. Europe. Regulation (EU) No 2020/856 of 9 June 2020 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for cyantraniliprole, cyazofamid, cyprodinil, fenpyroximate, fludioxonil, fluxapyroxad, imazalil, isofetamid, kresoxim-methyl, lufenuron, mandipropamid, propamocarb, pyraclostrobin, pyriofenone, pyriproxyfen and spinetoram in or on certain products. *Official Journal of the European Union* L 195/9, 19 June 2020.

15. Europe. Regulation (EU) No 2023/1029 of 25 May 2023 amending Annexes III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for phosmet in or on certain products. *Official Journal of the European Union* L 139/15, 26 May 2023.

16. Europe. Regulation (EU) No 1096/2014 of 15 October 2014 amending Annexes II, III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for carbaryl, procymidone and profenofos in or on certain products. *Official Journal of the European Union* L 300/5, 18 October 2014.

17. European Reference Laboratories for Residues of Pesticides. *General protocol for EU Proficiency Tests on pesticide residues in food and feed*. Edition 9. Brussels: European Commission; 2021.

18. Medina-Pastor P, Rodriguez-Torreblanca C, Andersson A, Fernandez-Alba AR. European Commission proficiency tests for pesticide residues in fruits and vegetables. *Trends Anal Chem* 2010;29(1):70-83.

19. Medina-Pastor P, Mezcua M, Rodriguez-Torreblanca C, Fernandez-Alba AR. Laboratory assessment by combined z-score values in proficiency tests: experience gained through the European Union proficiency tests for pesticide residues in fruits and vegetables. *Anal Bioanal Chem* 2010; 397:3061-70.

20. UNI EN 15662:2018. *Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE -Modular QuEChERS-method.* Milano: Ente Nazionale Italiano di Unificazione; 2018.

21. UNI CEN/TS 17062. *Foods of plant origin – Multimethod for the determination of pesticide residues in vegetable oils by LC-MS/MS (QuOIL).* Milano: Ente Nazionale Italiano di Unificazione; 2019.

22. European Reference Laboratory - Pesticides in Fruits and Vegetables. *Validation data of 127 pesticides using a multiresidue method by LC-MS/MS and GC-MS/MS in olive oil*. European Commission; 2012. EURL-FV (2012-M6). Available from: https://www.eurl-pesticides.eu/library/docs/fv/Validation-OliveOil.pdf; last visited 12/12/2025.

23. Motohashi N, Nagashima H, Párkányi C, Subrahmanyam B, Zhang GW. Official multiresidue methods of pesticide analysis in vegetables, fruits and soil. *J Chromatogr A.* 1996;754(1-2):333-46.

24. Stefanelli P, Santilio A, Cataldi L, Dommarco R. Multiresidue analysis of organochlorine and pyrethroid pesticides in ground beef meat by gas chromatography-mass spectrometry. *J Environ Sci Health, Part B.* 2009;44:350-6.

25. Rajski Ł, Lozano A, Belmonte-Valles N, Uclés A, Uclés S, Mezcua M, Fernandez-Alba AR. Comparison of three multiresidue methods to analyse pesticides in green tea with liquid and gas chromatography/tandem mass spectrometry. *Analyst.* 2013;138(3):921-31.

APPENDIX A
List of participants

The participants in COIPT-23 are listed below.

BELGIUM
Primoris Belgium (Zwijnaarde)
GERMANY
Institut Kirchoff Berlin GmbH (Berlin)
Niedersaechsisches Landesamt Fuer Verbraucherschutz Und Lebensmittelsicherheit Lebensmittel Und Veterinaerinstitut Oldenburg (Oldenburg)
FRANCE
ITERG (Canejan)
GREECE
CADMION (Kiato)
Benaki Phytopathological Institute – Pesticide Residues Laboratory (Athens)
Lagouvardou-Spantidaki O.E. (Rethymno, Crete)
General Chemical State Laboratory, Pesticide Residues Laboratory, D Chemical Division (Athens)
Multichrom Lab Crete (Heraklion, Crete)
Multichrom Lab Main (Athens)
TUV Austria Food Allergens Labs (Attica)
TUV Austria Food Allergens Labs (Crete)
SKYLAB – Med S.A. (Athens)
ITALY
Agenzia delle Dogane e dei Monopoli DT VII Sicilia- Ufficio Laboratorio chimico di Palermo (Palermo)
Agro.biolab Laboratory srl (Rutigliano, BA)
Analytical srl (Firenze)
ARPA Emilia Romagna Area Fitofarmaci (Ferrara)
ARPA Friuli Venezia Giulia (Udine)
ARPA Lazio (Latina)
ARPA Puglia, Polo di Specializzazione “Alimenti” (Bari)
ARPAL (La Spezia)
ATS Bergamo (Bergamo)
ATS Milano (Milano)
Cadir Lab (Alessandria)
CHEMISERVICE srl (Monopoli, BA)
INNOVHUB-SSI Srl, (Milano)
Istituto Superiore di Sanità, Dipartimento Ambiente e Salute (Roma)
IZS Abruzzo e Molise (Teramo)
IZSLER (Brescia)
IZSLT (Roma)
IZS Piemonte, Liguria e Valle d’Aosta (Cuneo)
IZS della Sicilia (Palermo)

LABCAM srl (Albenga, SV)
PH TUV SUD (Firenze)
USL Toscana Centro (Firenze)
Water e Life Lab srl (Bergamo)
POLAND
Voievodship Sanitary-Epidemiological Station in Rzeszow (Rezeszow)
SPAIN
Borges Agricultural & Industrial Edible Oils (Tàrrega, Lléida)
(CNTA) National Center for technology and food Safety (San Adrian, Navarra)
Laboratorio Agroalimentario (Granada)

APPENDIX B
Robust analysis: algorithm A

This algorithm yields robust estimates of the mean and standard deviation of the data to which it is applied. We have followed the indication and equations descripted in Appendix C of the ISO 13528: 2015.

This appendix reports in detail the calculation performed in order to obtain the robust mean (x^*) and the robust standard deviation (s^*). The algorithm A given in this appendix is reproduced from ISO 5725-5, with a slight addition to specify a stopping criterion: no change in the 3rd significant figures of the robust mean and standard deviation.

Calculate initial values for x^* and s^* as:

$$x^* = \text{median of } x_i \quad (i = 1, 2, \ldots, p) \tag{1}$$

$$s^* = 1.483 \text{ median of } |x_i - x^*| \quad \text{with } (i = 1, 2, \ldots, p) \tag{2}$$

Denote the p items of data, sorted into increasing order, by:

$$x_{(1)}, x_{(2)}, x_{(3)}, x_{(4)}, \ldots\ldots x_{(p)}$$

Update the values of $x^*$and s^* as follows. Calculate:

$$\delta = 1.5\, s^* \tag{3}$$

For each x_i ($i = 1, 2, \ldots p$), calculate:

$$x_i^* = \begin{cases} x* - \text{d}, \text{when } x_i < x* - \text{d} \\ x* + \text{d}, \text{when } x_i > x* + \text{d} \\ x_i \text{ otherwise} \end{cases} \tag{4}$$

Calculate the new values of x^* and s^* from:

$$x^* = \sum_{i=1}^{p} \frac{x_i^*}{p} \tag{5}$$

$$s^* = 1.134 \sqrt{\sum_{i=1}^{p} \frac{(x_i^* - x^*)^2}{p-1}} \tag{6}$$

where the summation is over *i.*

The robust estimates x^* and s^* may be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times using the modified data in equations 3 to 6, until the process converges. Convergence may be assumed when there is no change from one iteration to the next in the third significant figures of the robust mean and robust standard deviation (x^* and s^*).

Serie Rapporti ISTISAN
numero di dicembre 2025, 11° Suppl.

Stampato in proprio
Servizio Comunicazione Scientifica – Istituto Superiore di Sanità

Roma, febbraio 2026