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Counterfeit and illegal pesticides: Strategies for addressing the issue in the analytical laboratory

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Counterfeit-illegal pesticides

The production and sale of counterfeit Plant Protection Products (PPPs) is increasing worldwide, representing a serious risk for public health and the environment.

Counterfeiting has been reported in the form of:

- **absence of the active ingredient,**
- **wrong active ingredient (in many cases not authorized in EU),**
- **insufficient active ingredient,**
- **fake packaging and**
- **contamination with unexpected substances that might lead to intoxication incidents.**

Counterfeit-illegal pesticides

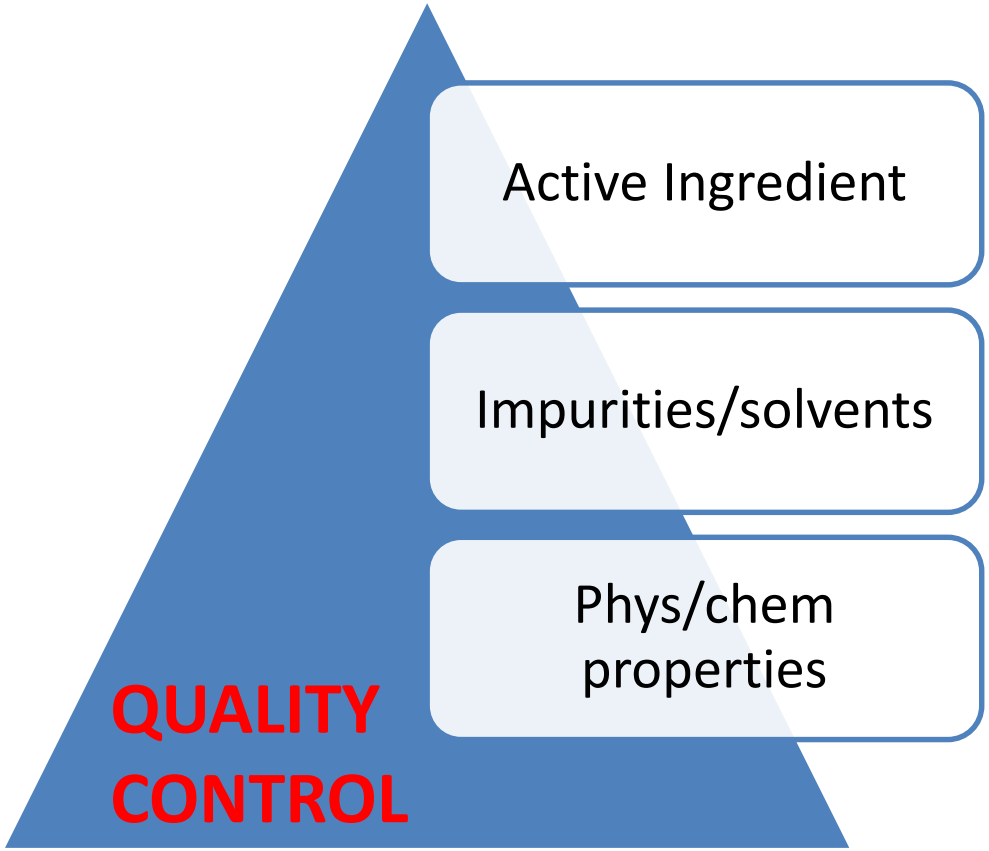
AVAILABLE from many sources:

- The worldwide web
- Illegal dealers etc.

IMPACTS

- Ineffective PPPs
- Phytotoxic PPPs
- Persistent field contamination
- Hazard to the environment
- Risk for the operators, bystanders and consumers (residues in the treated commodities)

Quality Control



Plant protection policy: aims to the safeguarding of the harmless use of pesticides.

The analysis of illegal and counterfeit PPPs presents new challenges for the analytical laboratories

Laboratory of Chemical Control of Pesticides

of Benaki Phytopathological Institute

(Central Official Laboratory in Greece)

Monitoring program

Through the Monitoring Program official laboratories oversee that commercially available PPPs fulfill FAO/WHO and authorization specifications in terms of:

- **identification and quantification of the active ingredient**
- **physical and chemical properties**

Monitoring program (2)

- **The chemical analysis is performed by CIPAC official methods or methods submitted by the applicant during the authorization process or in-house methods.**

- **Official methods employ GC-FID or HPLC-UV**

Potential Targets for PPP Authenticity Control

- Co-formulants/solvents
- Impurities
- Isomers (in the case of single isomer a.i.)
- Physical and Chemical Properties (e.g. pH, specific gravity, etc)
- Formulation characteristics (microscopic and macroscopic)

Strategy
Inspection of container/label

In order to deal with the continuously increasing number of samples that require authenticity control, each of them represents a unique and special case, thus we developed and applied general procedures that include the following steps:

CASE BY CASE APPROACH

- **Inspection of the container and the label**

  (poor quality containers/not properly sealed/plain printout label)

Strategy
Active Ingredient

Analysis of the parallel import in comparison with two different batches of the original reference formulation

A.I. content is determined and significant differences in the chromatographic profile are detected

- **Official CIPAC method (if available),**
- **The method submitted by the applicant, or**
- **In-house method**

Strategy

Solvents, Co-formulants, Impurities, Cross-contaminants

- **Analysis *with full scan GC-MS*: Initial determination and identification using MS-libraries of volatile components of the formulation is performed using a column oven temperature ramp with low initial temperature (below boiling point of organic solvents of formulations).**

Cross contamination from the production line may also be detected during this analysis

- **Analysis with GC-MS/MS or LC-MS/MS is performed in order to *confirm* the *presence of cross contaminants*, *co-formulants* or *known relevant impurities***

Strategy
Other parameters

- **Physical-chemical properties (pH, specific gravity, etc) as well as appearance (color, opacity etc) and odor are examined in comparison to reference original products**

- **Optical observation (microscopic and macroscopic**

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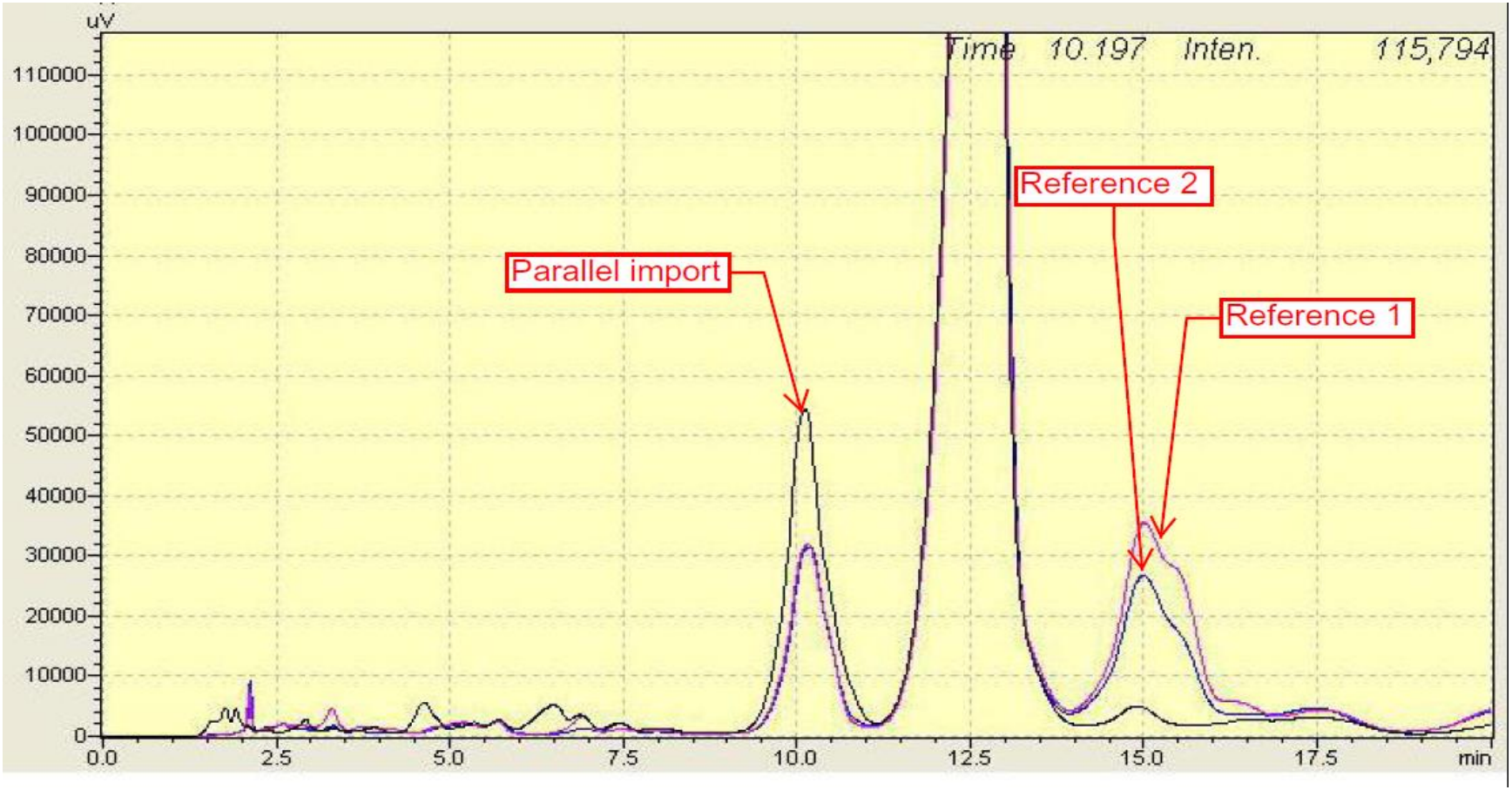
Abamectin-First Step: HPLC –UV at 254 nm

Pesticide product chromatographic profiling as a method of evaluating parallel imports and counterfeit products



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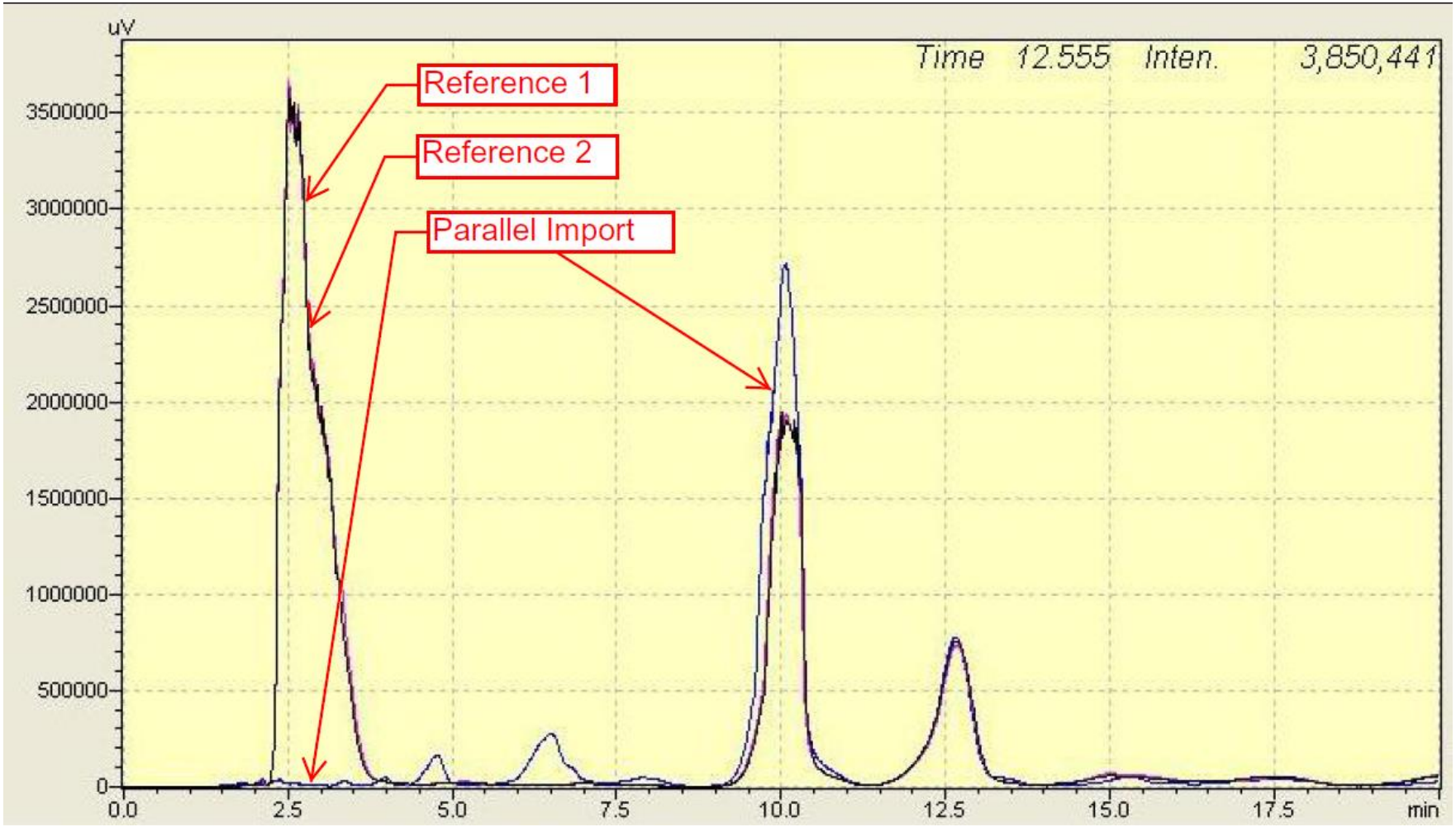
Abamectin-Second Step HPLC-DAD Scan (190-500nm)



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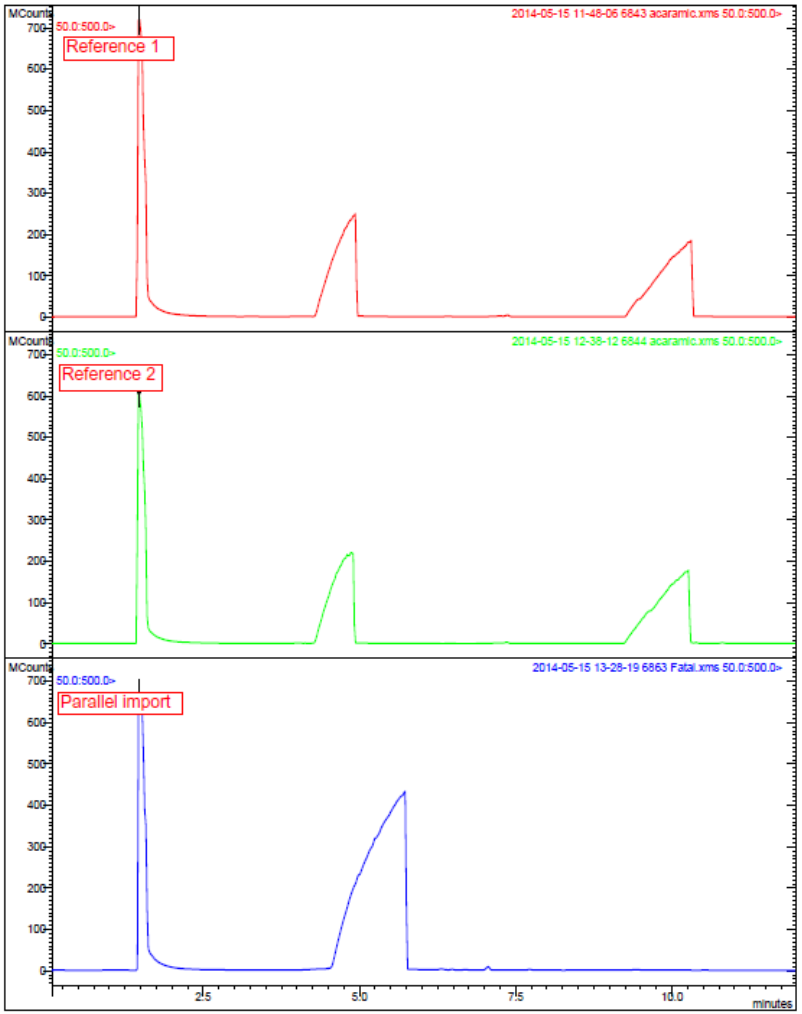
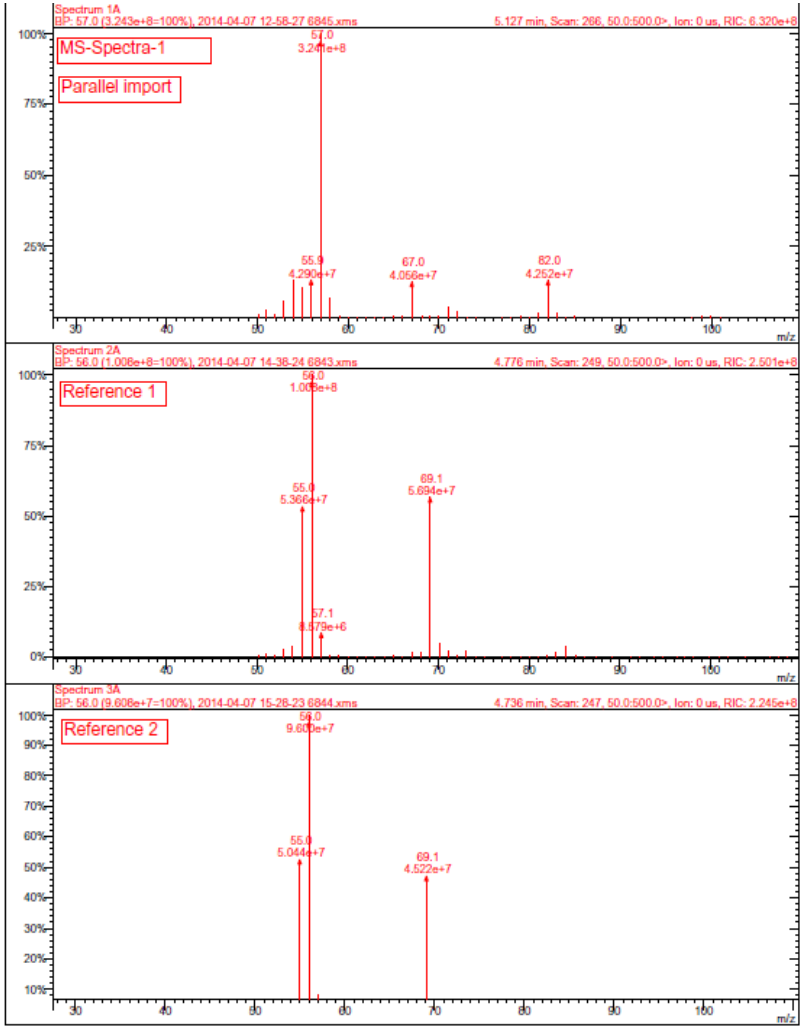
Abamectin-Third Step: GC-MS (full Scan) chromatogram and spectra of the early eluting peaks

Example of Reference PPP versus parallel





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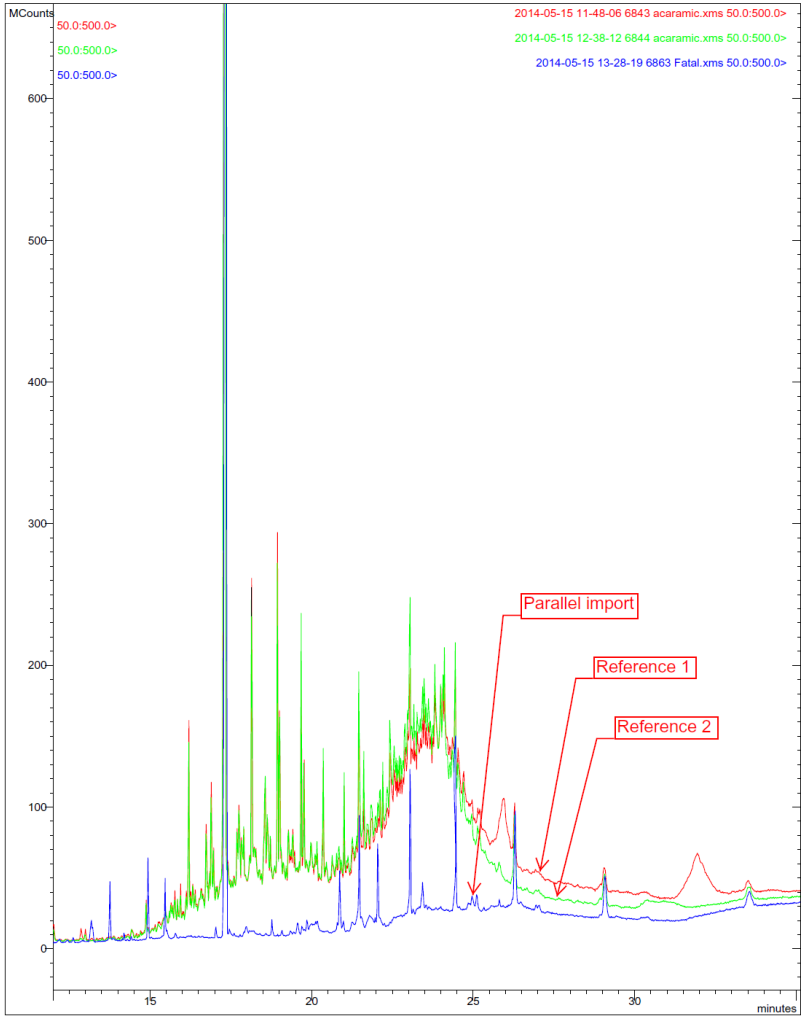
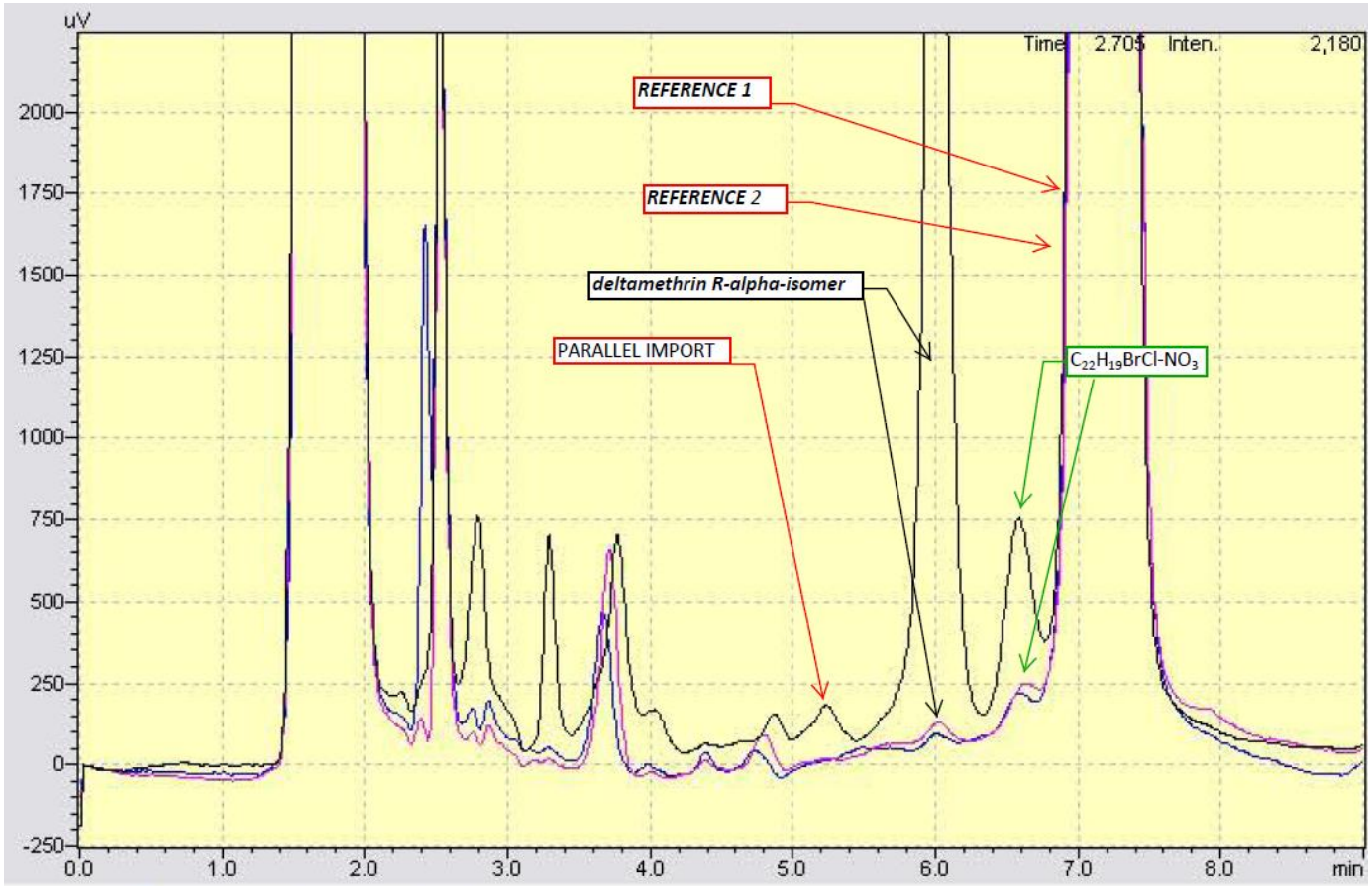
Abamectin-Fourth Step: GC-MS (full Scan) chromatogram of the later eluting peaks



HPLC-UV at 230 nm
Deltamethrin isomers

Example of Authentic versus parallel



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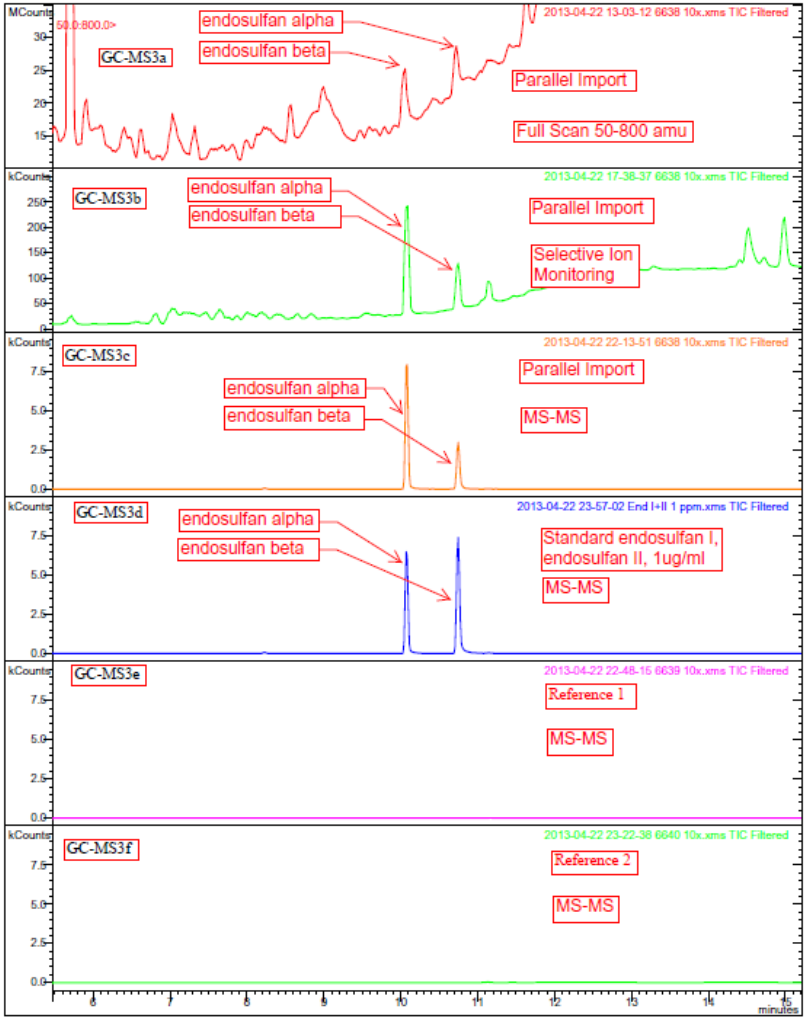
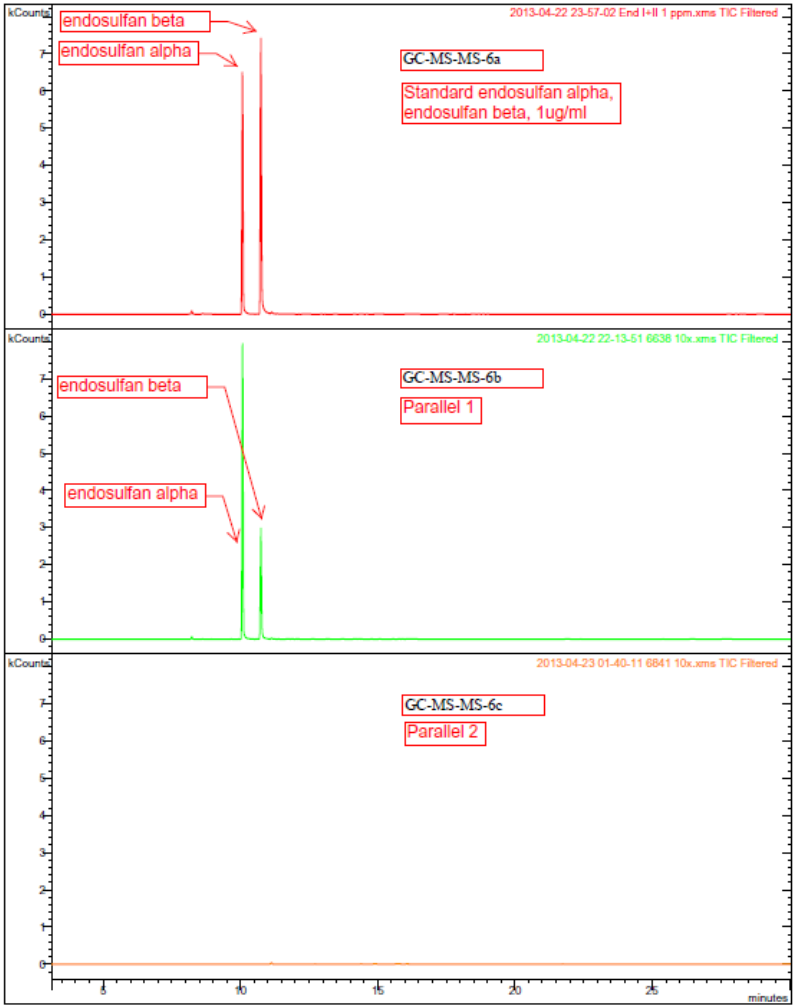
Deltamethrin formulation containing endosulfan as impurity

Example of Authentic versus parallel product



Comparison of declared "identical" batches



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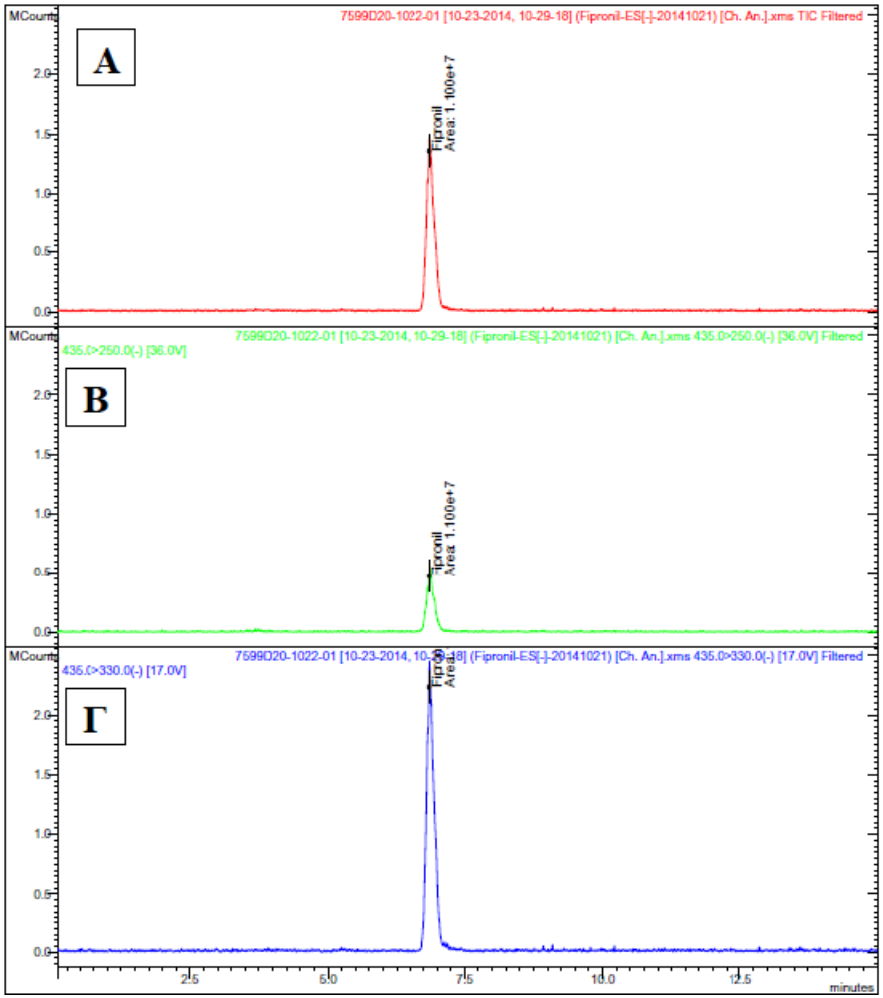
Cross Contamination (insecticide inside a fungicide)



POTENTIAL TARGETS FOR PPP IDENTITY CONTROL

Assessing *impurities* (especially in the case of cross-contamination) of a pesticide *might be a difficult task*.

Analytical techniques used for the detection of impurities or unexpected compounds can include *gas or liquid chromatography* coupled with mass spectrometry to achieve the *selectivity* and *sensitivity* required

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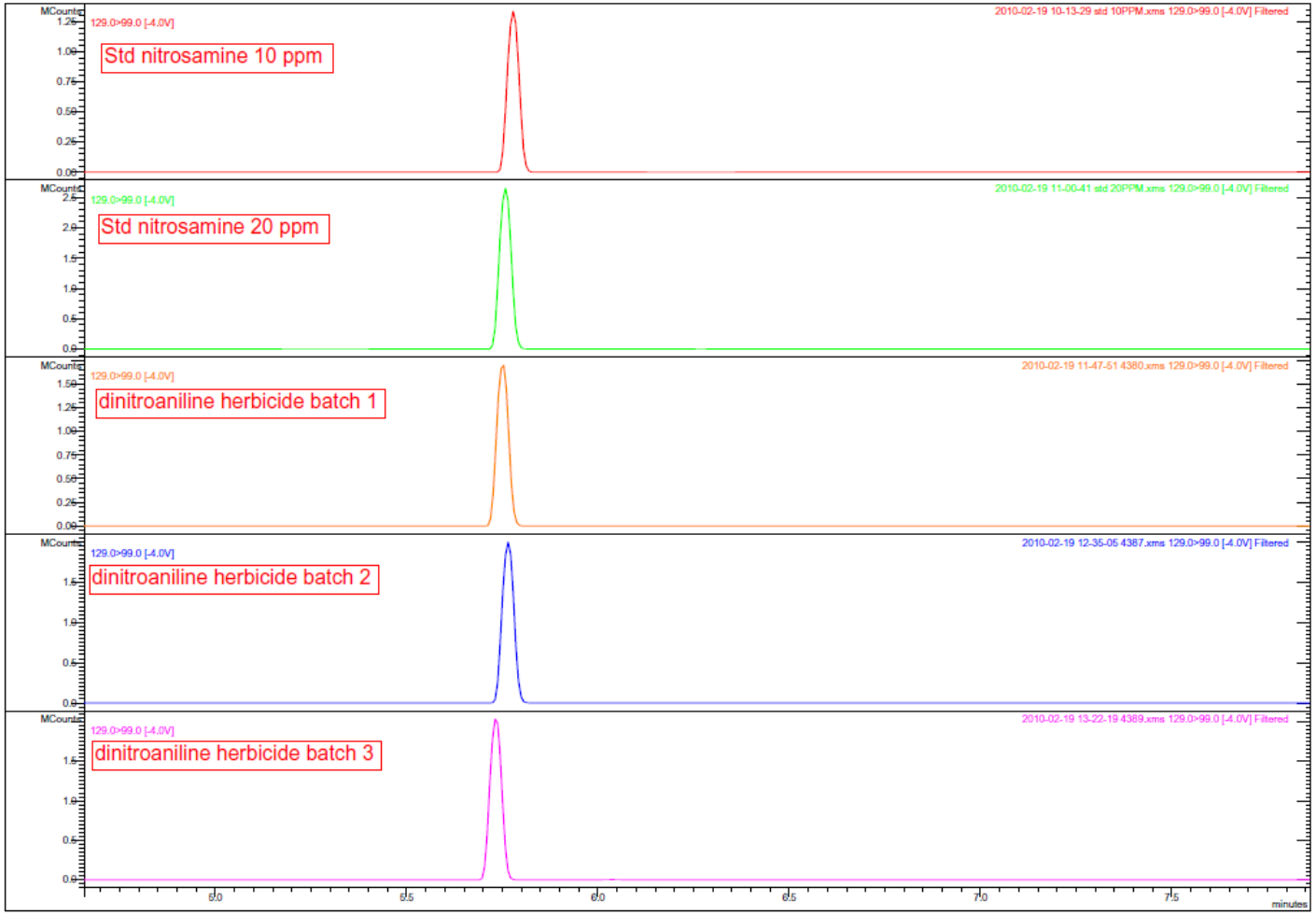
GC-CI(+)-MS/MS nitrosamines in dinitroaniline herbicide formulation (FAO: <1μg/g in TC)



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Macroscopic Evaluation: the case of a-cypermethrin

Original product

Fake product

Original product

Fake product

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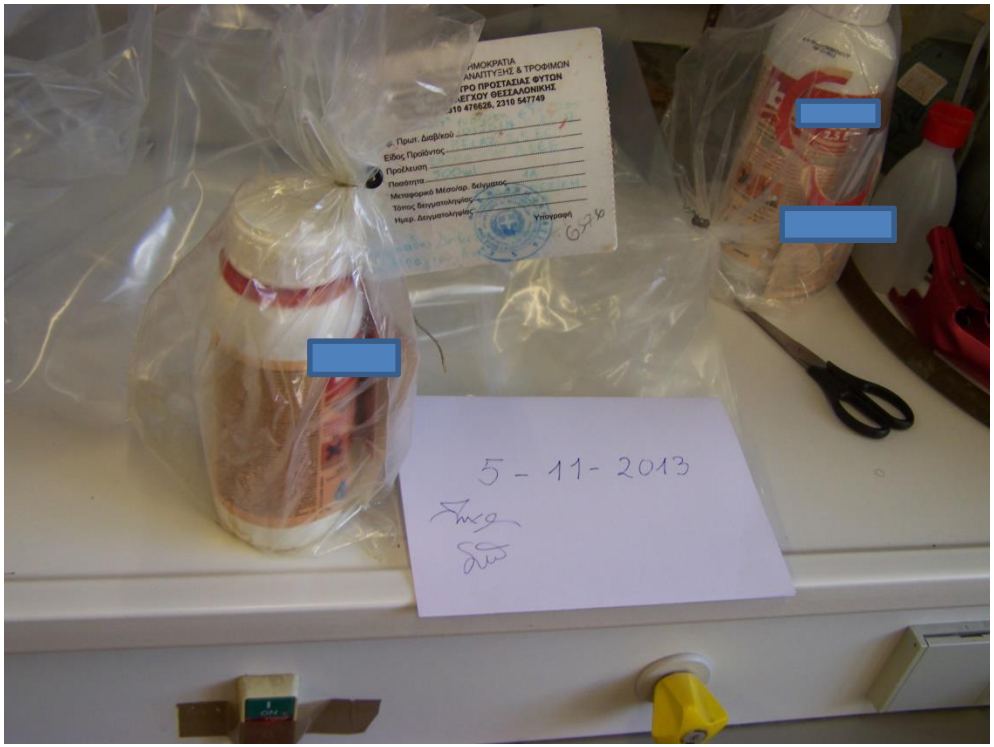
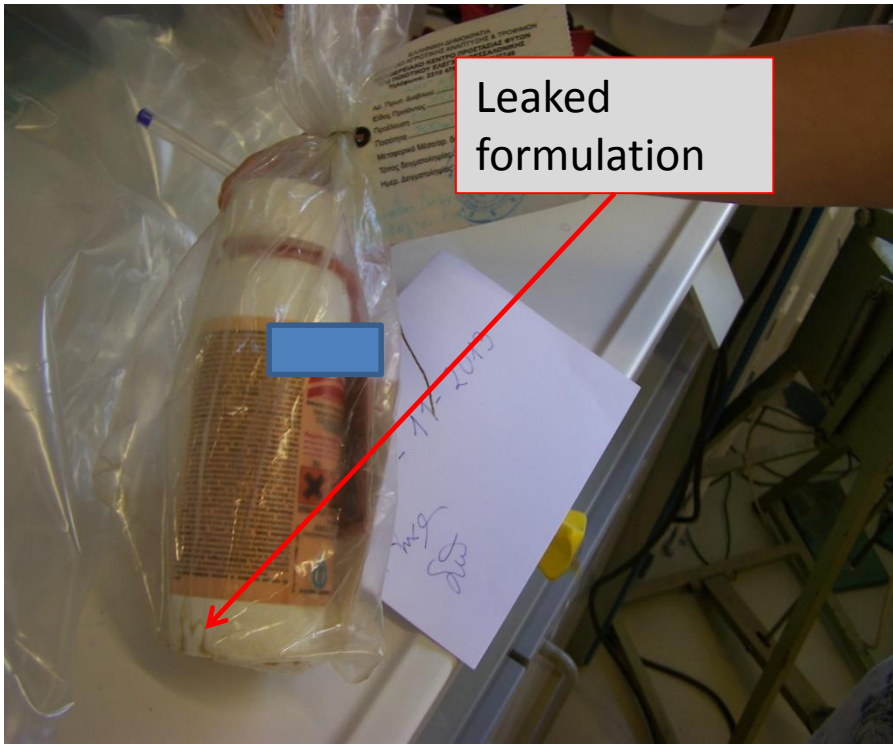
Macroscopic Evaluation: the case of deltamethrin





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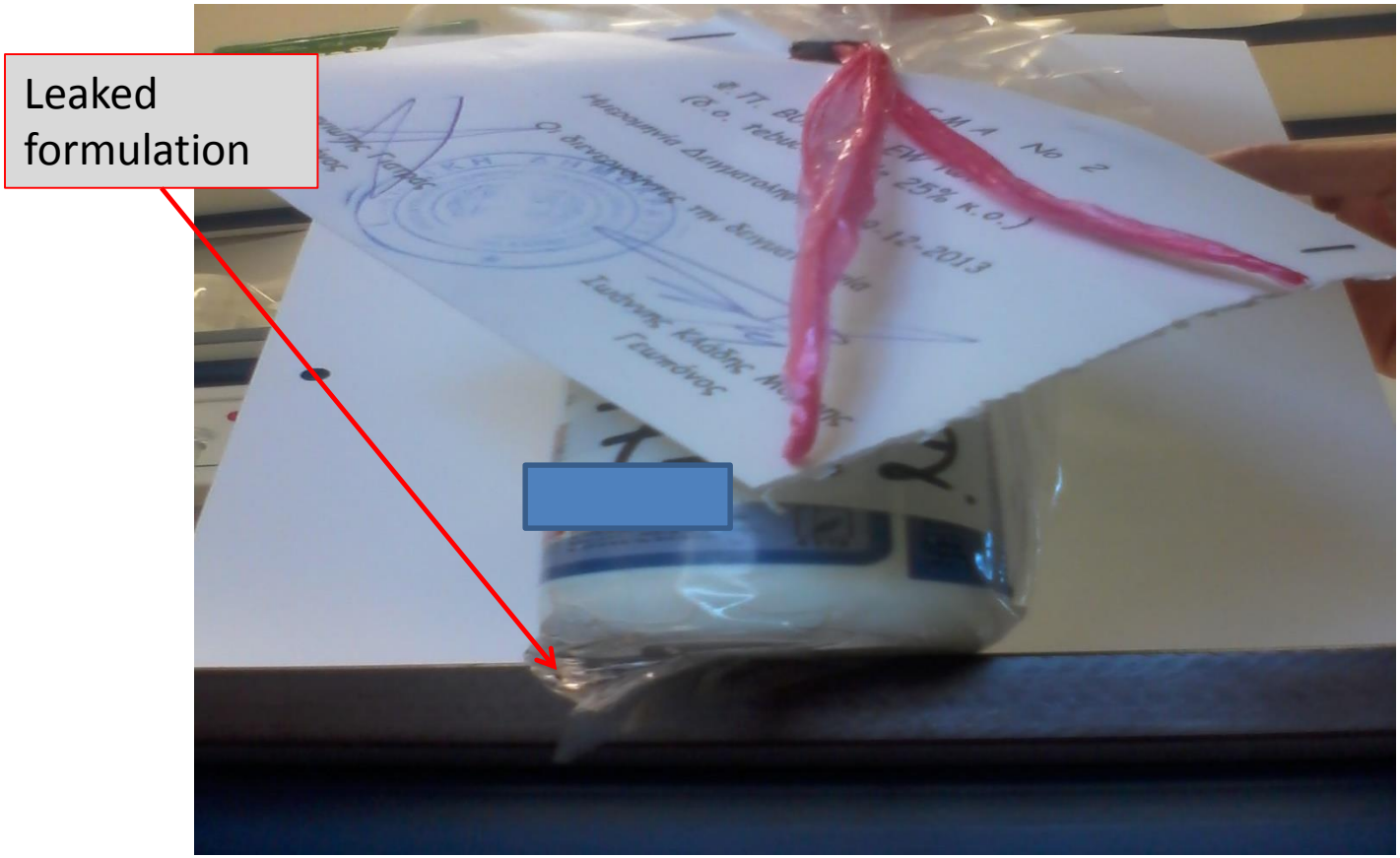
Macroscopic Evaluation: the case of tebuconazole



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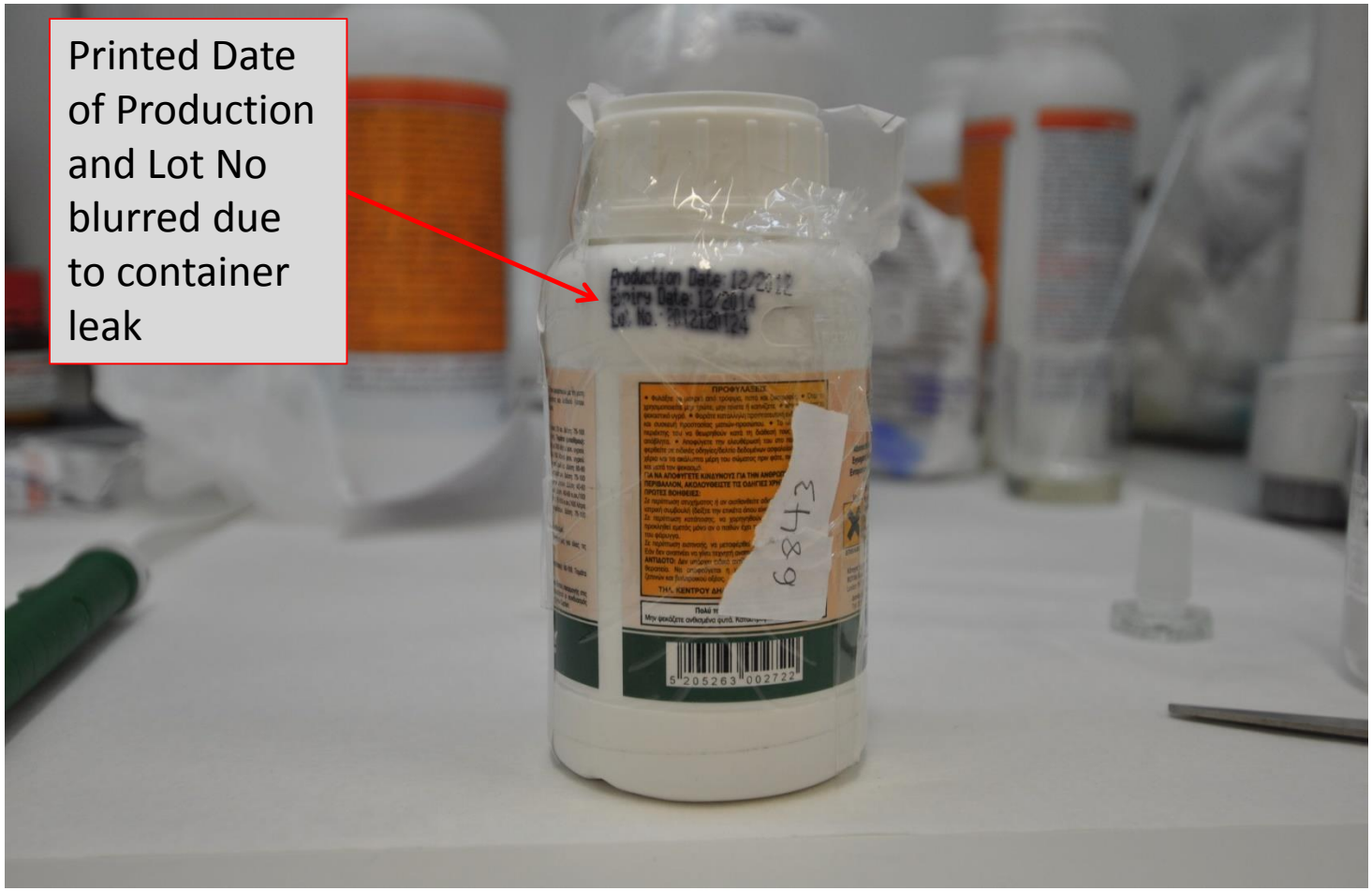
Macroscopic Evaluation: the case of abamectin



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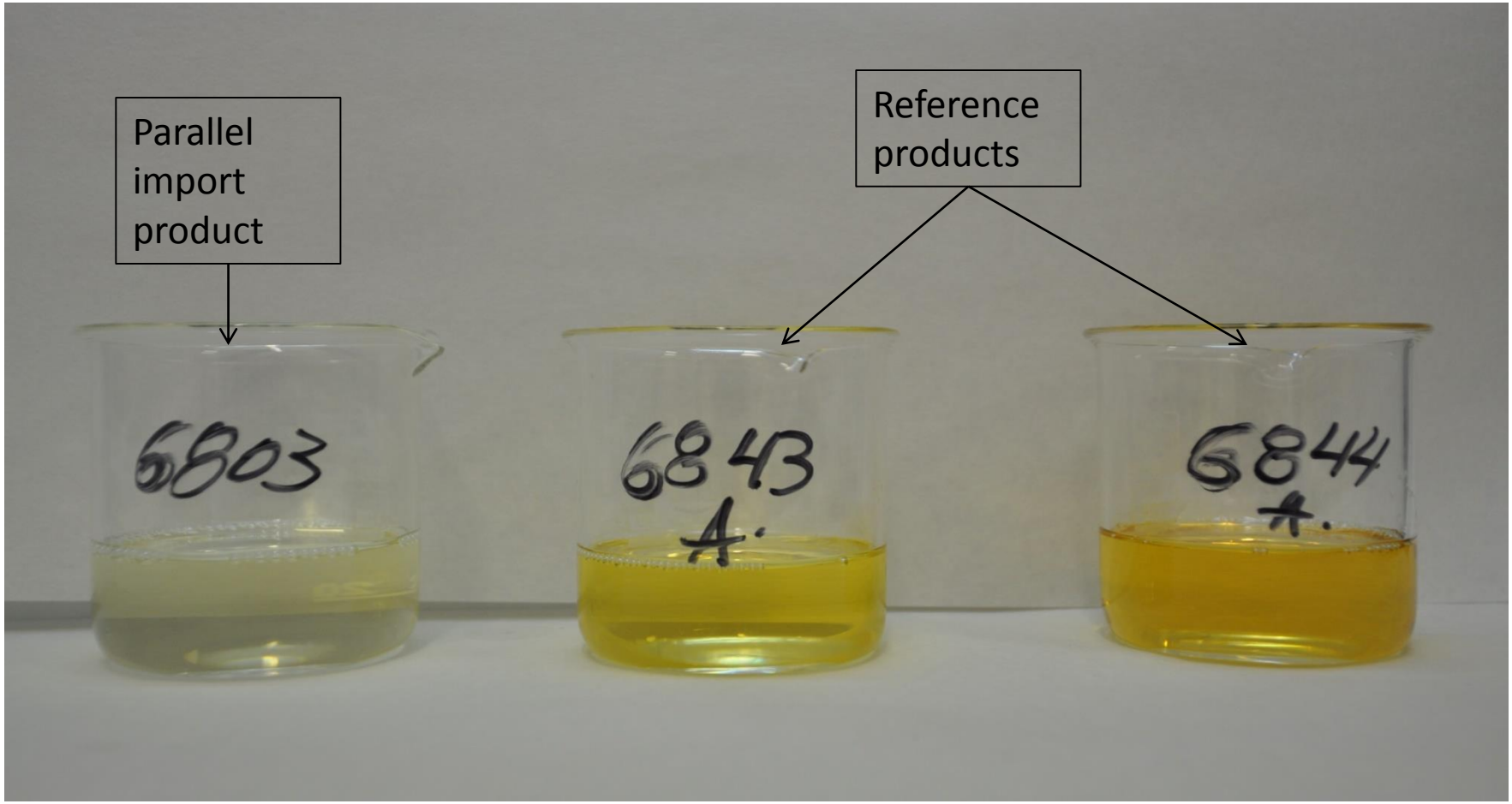
Macroscopic Evaluation: the case of abamectin



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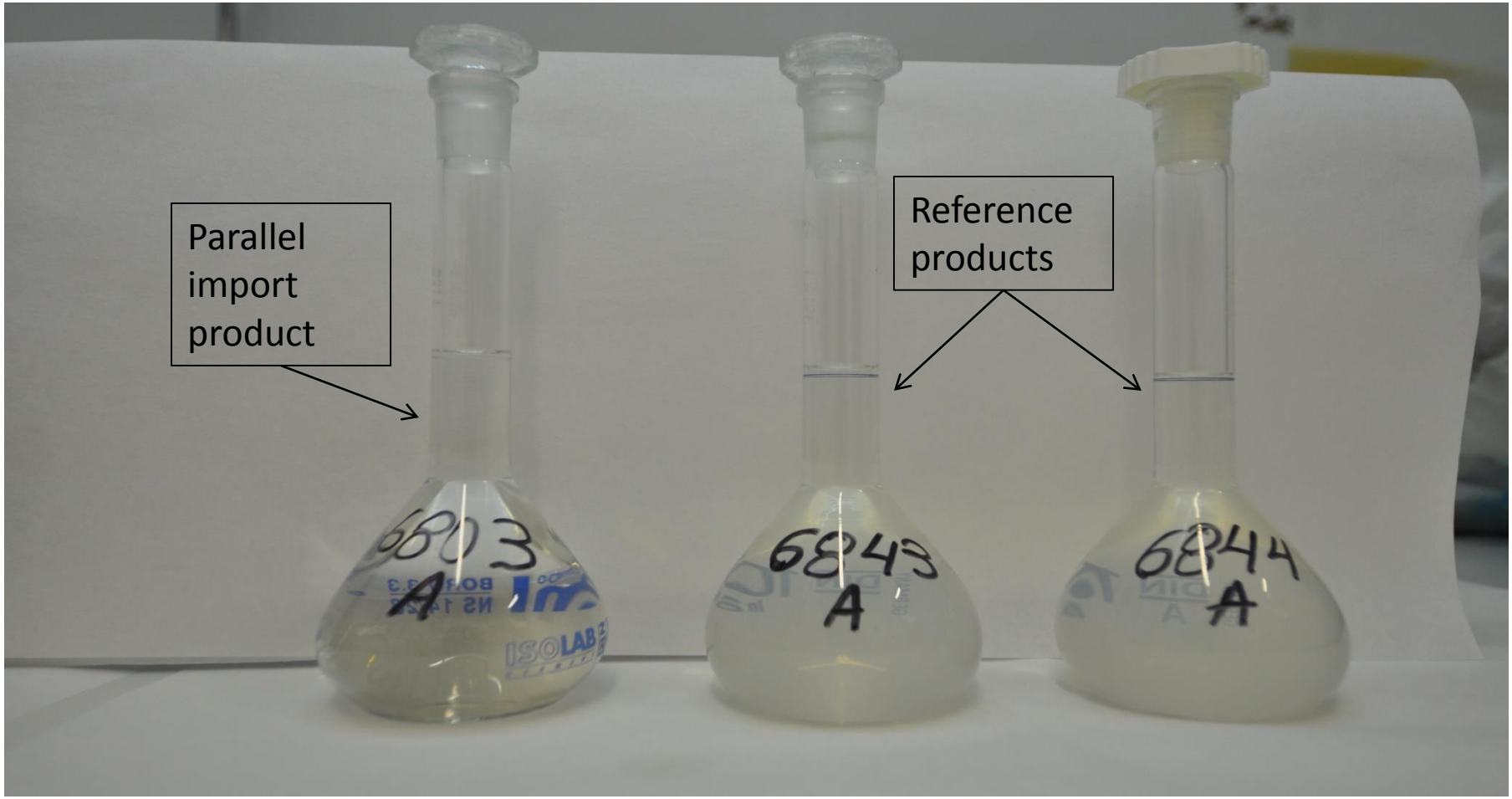
Macroscopic Evaluation: the case of abamectin



Parallel Imports: The Case of lambda cyhalothrin CS Formulation

'CS is the designation for a stable suspension of micro-encapsulated active ingredient in an aqueous continuous phase, intended for dilution with water before use' **(Manual on development and use of FAO and WHO specifications for pesticides)**

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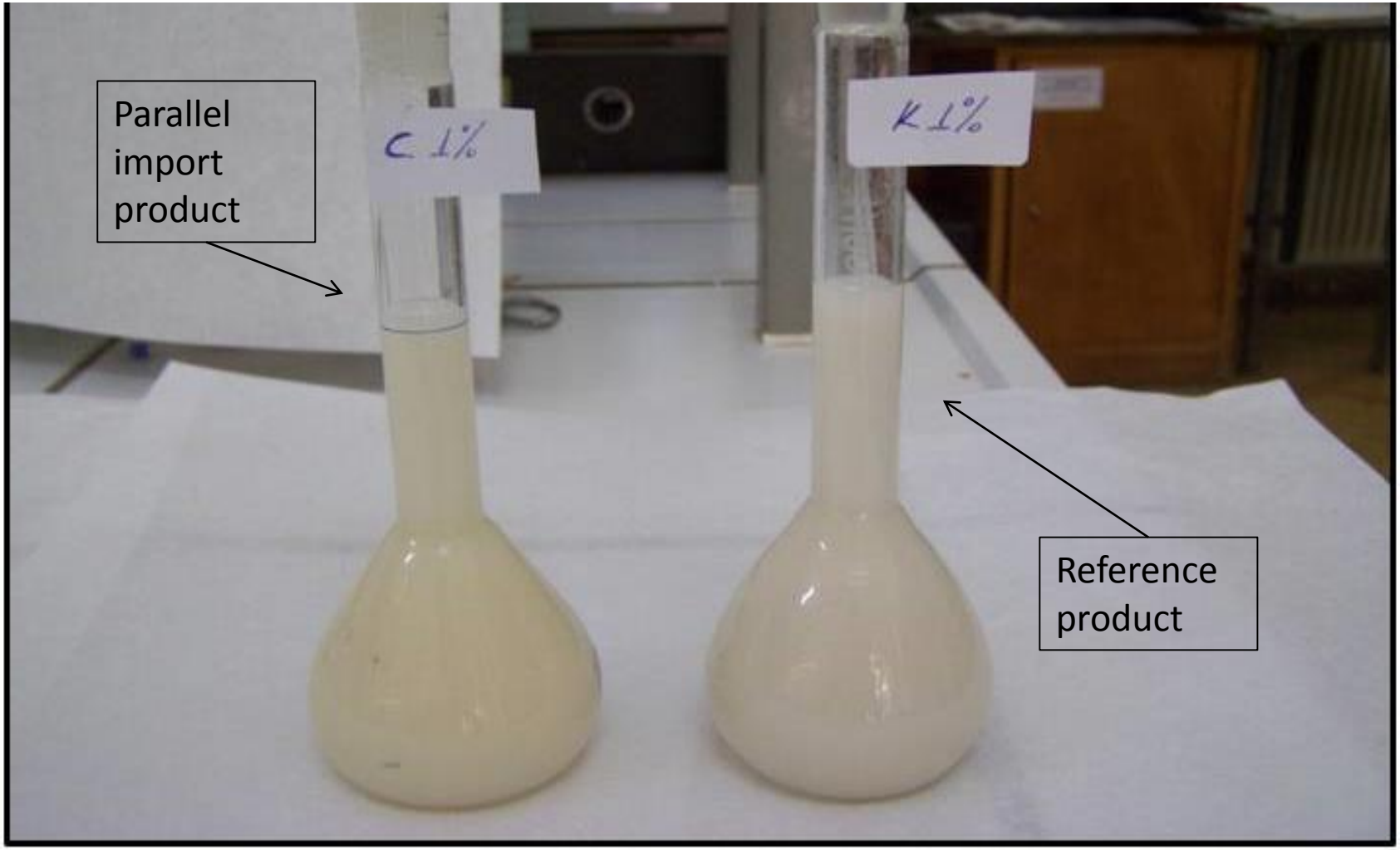
Macroscopic Evaluation: the case of l-cyhalothrin



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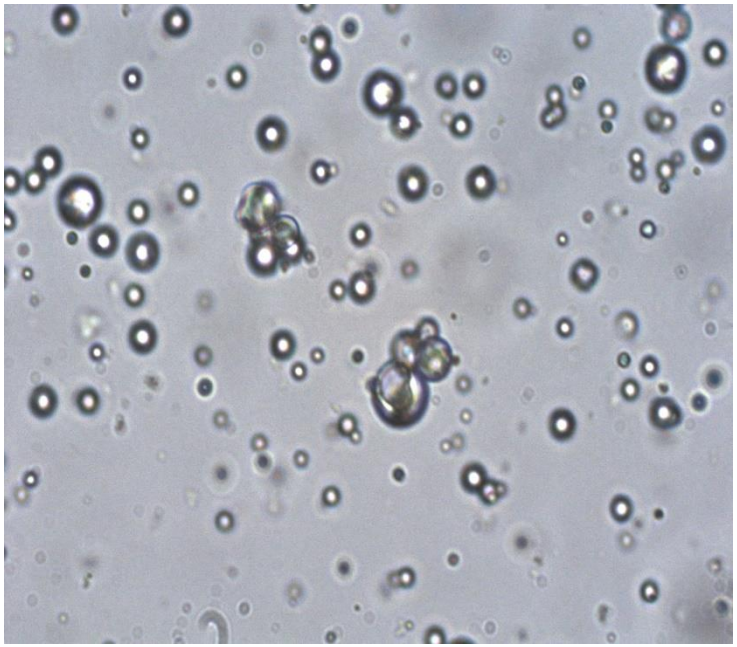
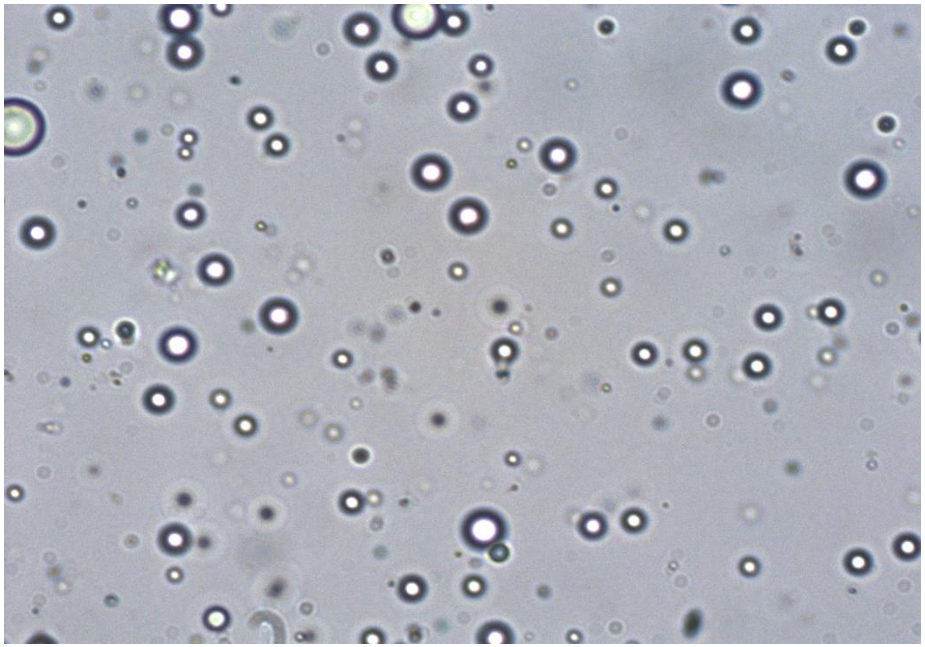
Microscopic Evaluation: the case of l-cyhalothrin

(Optical microscope: LEICA DM2500)

REFERENCE-20min



PARALLEL-20min



Initial formation of aggregates

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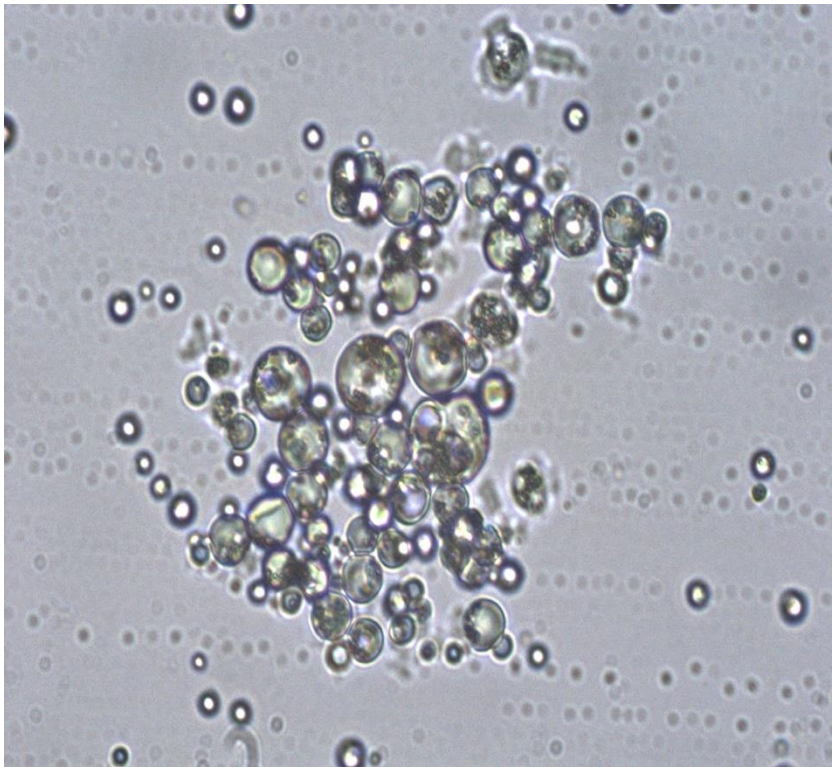
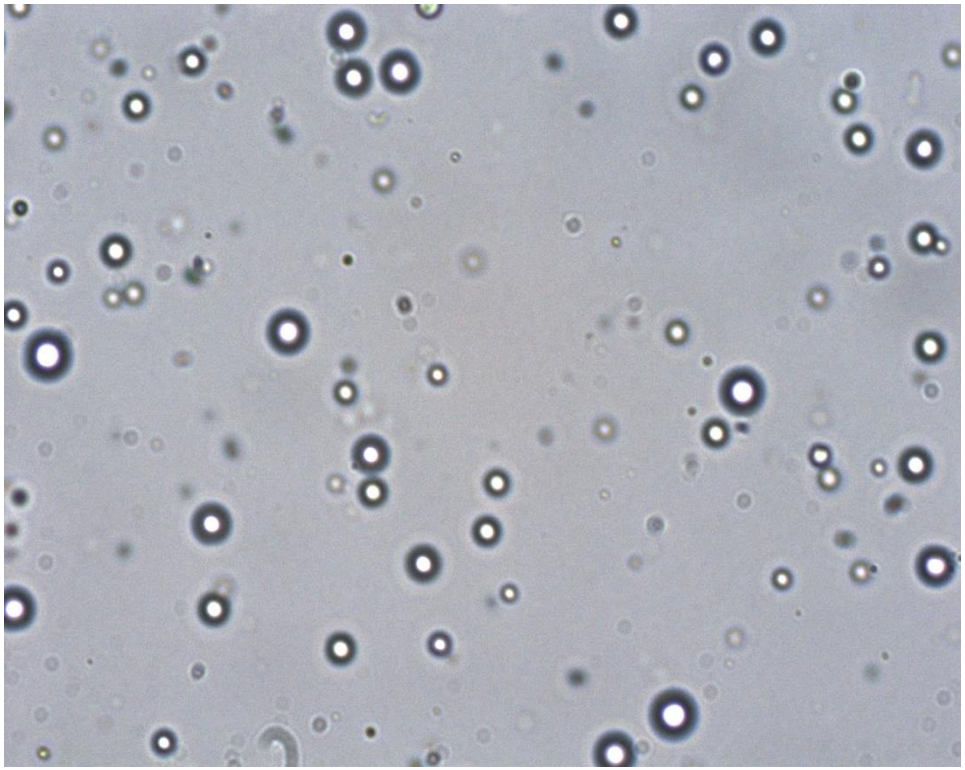
Microscopic Evaluation: the case of l-cyhalothrin

(Optical microscope: LEICA DM2500)

REFERENCE-40min



PARALLEL-40min



Aggregates formation

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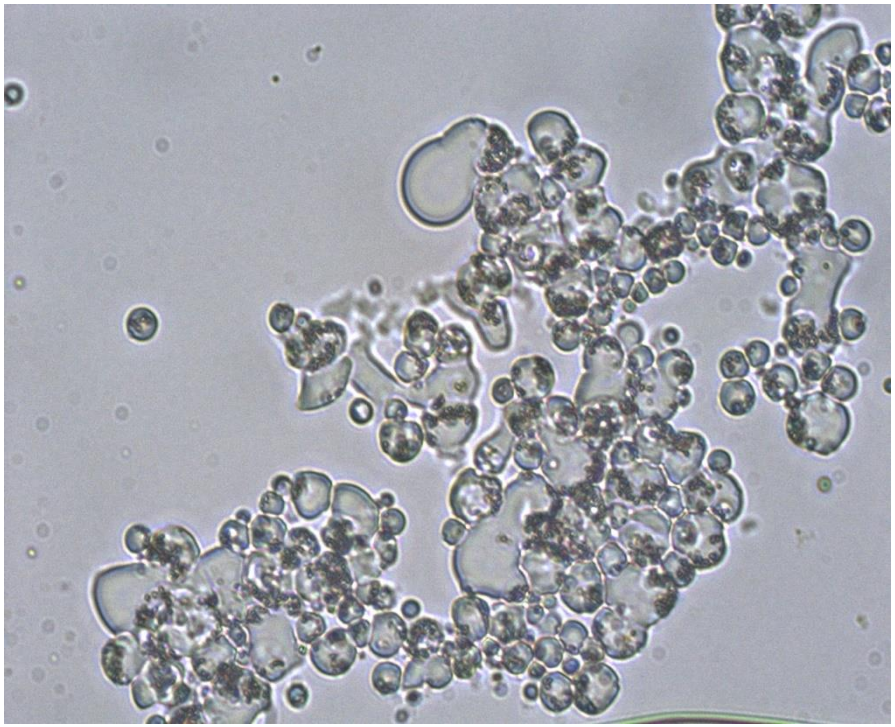
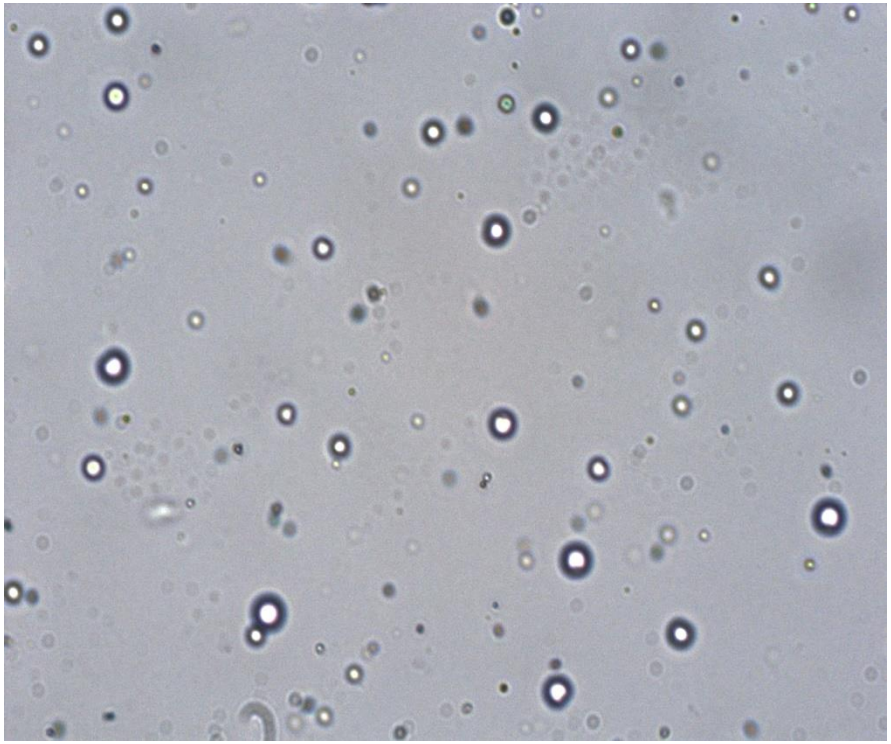
Microscopic Evaluation: the case of l-cyhalothrin

(Optical microscope: LEICA DM2500)

REFERENCE-60min



PARALLEL-60min



Capsules burst and release of content

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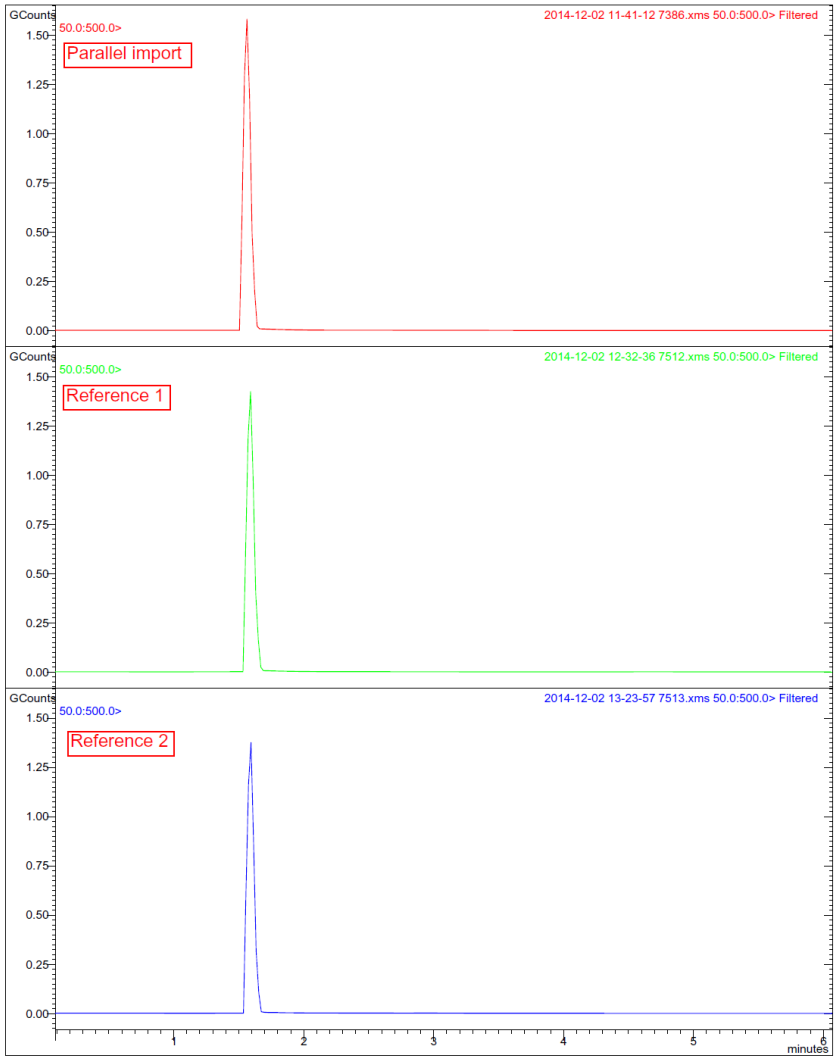
Parallel Imports: the Case of azoxystrobin



Parallel Product equivalent to the reference product

Instrumentation

- **Gas chromatographs (4) with FID, ECD, NPD, PFPD and MS/MS detectors**
- **HPLC (3) with DAD, UV and MS/MS detectors**
- **Flame Atomic Absorption Spectroscopy.**
- **Heubach-Dustmeter**

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Laboratory of Chemical Control of Pesticides

- **The Team of the lab of chemical analysis:**
  - ✓ **6 chemists (PhD and MSc)**
  - ✓ **2 environmental scientists**
  - ✓ **1 agronomist and**
  - ✓ **1 lab technician**

The Laboratory is implementing a *Quality System* in chemical tests (since 2004) and is currently certified by the National Accreditation System (ESYD) in compliance to *ISO 17025:2005* (Accred. No. 606-2)

Laboratory Evaluation- FVO Inspection (2011)

http://ec.europa.eu/food/fvo/rep_details_en.cfm?rep_id=2927

'The laboratory has extended the methods to the determination of targeted impurities by GC-MS/MS and LC-MS/MS. In 2011, the laboratory started to apply a GC-MS and LC-MS screening method to detect ***unexpected active substances and co-formulants***. These analyses are performed for parallel trade products and suspected illegal pesticides. A non-compliant parallel trade product was identified and enforcement measures taken.

The targeted checks to **control illegal or counterfeit pesticides** are effective, because they are carried out in co-operation with institutions in Greece and other Member States, and supported by ***innovative formulation analysis of PPPs*** in the well equipped laboratory for Chemical Control of Pesticides of BPI'

Main fields of Scientific Activities and Research

Development and validation:

a. **of single and multi pesticide methods for the quality control of PPPs**
b. **of methods for the determination of relevant impurities**
c. **of multi-residue methods for the determination of pesticide residues in soil samples using the techniques of liquid and gas chromatography with mass-spectrometry (LC-MS/MS, GC-MS/MS)**

Main fields of Scientific Activities and Research (2)

Development and validation (2nd):

d. **of methods for determining pesticide residues in empty PPP containers after the triple-rinsing process**

e. **of methods for determining heavy metals and trace elements in apiculture products (honey, pollen, bees, propolis) and herbal extracts by flame-atomic absorption spectrometry**

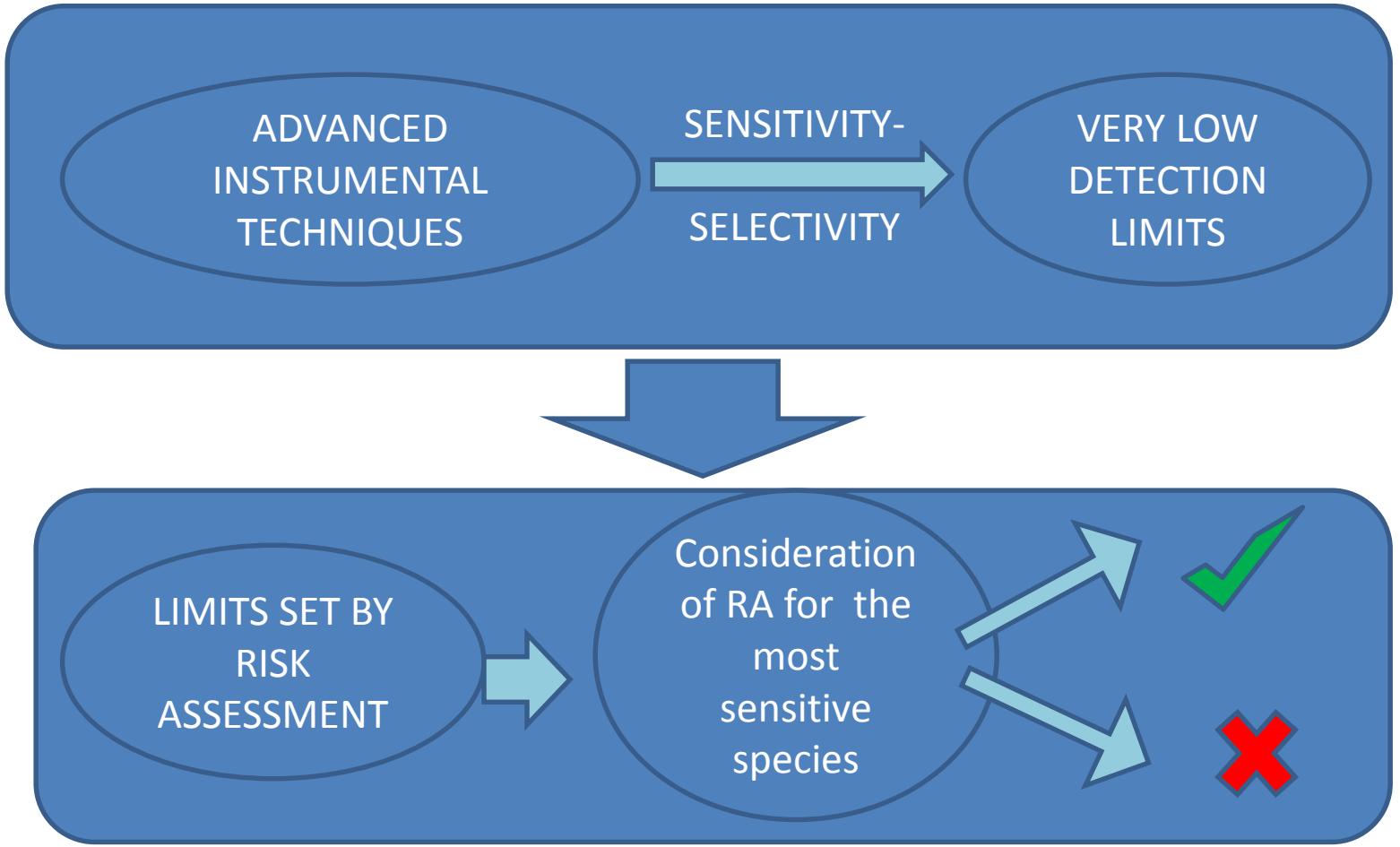
Main fields of Scientific Activities and Research (3)

- Laboratory Control of illegal and counterfeit PPPs
- Equivalence evaluation of parallel import PPPs
- Storage Stability Studies

Main fields of Scientific Activities and Research (4)

- Determination of floating dust amount of treated seeds as a parameter of Seed-Treatment Quality (Heubach-Test)
- Determination of PPP loading on treated seeds
- EU & National Evaluation of Pesticides and Biocides on E-Fate, Chemical Composition and Analytical Methods (Authorization & DARs)

Further Regulatory needs



Thank you for your attention!