# ANALYSIS OF PLANT PROTECTION PRODUCTS FOR MONITORING PROGRAMME

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Angela Santilio
National Institute of Health
Department of Environmental and Primary Prevention
Pesticide Unit
Email: angela.santilio@iss.it

# INTRODUCTION

- PRESENTATION
- ACTIVITY OF PESTICIDE UNIT
- MONITORING PROGRAM PPPs
- EXPERIENCE ON COUNTERFEIT PRODUCTS

# INTRODUCTION

National Institute of Health (Istituto Superiore Sanità –ISS) is the technical body of the Italian Ministry of Health.

Its duty is:
Research
Scientific and technical advice at the Ministry of Health and at peripheral bodies of National Health Service.

# INTRODUCTION

# INTRODUCTION

Department of Environmental and Primary Prevention

Head of Department

(dr. Loredana Musmeci)

Secretary

16 Units

# INTRODUCTION

PESTICIDE UNIT

| | |
|---|---|
| Head of Unit | • Dr Danilo Attard Barbini |
| 4 Researchers | • Dr G. Amendola<br>• Dr T. Generali<br>• Dr. P. Pelosi<br>• Dr. A. Santilio |
| 2 Technician | • Mrs S. Girolimetti<br>• Dr. P. Stefanelli |

# ACTIVITY - PESTICIDE UNIT

Three National Reference Laboratories:

- pesticide residues in fruit and vegetables (multiresidue method- QuEChERS),
- animal origin products (multiresidue methods),
- single residue methods (phenoxyacid, BAC, DDAC, Chlormequat, Mepiquat, Fenbutatin oxide etc.)

Accredited by Italian accreditation body (UNI CEI EN ISO/IEC 17025)

# ACTIVITY - PESTICIDE UNIT

Technical support to the official laboratories and to the Health Ministry -Plant Protection Products Office

In the field of public health - research plans and projects on pesticide residues and on plant protection products.

# ACTIVITY - PESTICIDE UNIT

Evaluation of the technical dossiers for the authorisation of PPPs under EU Regulation 1107/2009 (chemical and physical properties, analytical methods, residues and their risk assessment for consumers)

For mammalian toxicology, environmental and eco-toxicology sections are involved other two units of the Department.

For efficacy section University of Napoli and Torino are involved.

# ACTIVITY - PESTICIDE UNIT

2° level analysis after enforcement activities of the official laboratories:

- residue of pesticides
- plant protection product active ingredient

# ACTIVITY - PESTICIDE UNIT

The Pesticide Unit is involved in the official control for plant protection product:

- Scientific and technical support to the official laboratory (monitoring programme)

- Information on the applicability of the analytical methods for determination of active substances in Plant Protection Products (CIPAC methods, methods developed by applicants)

- 2° level analysis after enforcement activities

# MONITORING PROGRAMME

In the monitoring programme the official laboratories check the composition of the PPP in terms of analysis of the products

- ✓identification of the active ingredient
- ✓content of active ingredient
- ✓physical and chemical properties

# MONITORING PROGRAMME

Results of the years 2011 and 2012 published by the Health Ministry
(http://www.salute.gov.it/imgs/C_17_pubblicazioni_1995_allegato.pdf)

During the years 2008 – 2011, the controls on PPPs are increased, even if only in the 2012 a decrease of 7% has been pointed out.

# MONITORING PROGRAMME

The control of PPPs is performed according to the State-Regions Permanent Conference adoption
*"Adoption of the control plan on the placing on the market and PPPs use for the years 2009-2013".*

This agreement contains uniform operational guidelines for the control plan implementation by Regions/Provinces on the placing on the market and PPPs use.

# MONITORING PROGRAMME

The controls are carried out by

❖the Regions through their services AASSLL for inspections and through ARPA for analytical controls

❖Carabinieri command for the protection of health through NAS

❖Central Inspectorate of fraud prevention and protecting the quality of agri-food through their office.

# MONITORING PROGRAMME

The controls are performed on:

- ✓Sale
- ✓Labelling- packaging and safety card
- ✓Composition on PPPs
- ✓User level

# MONITORING PROGRAMME

The analytical controls were performed on 36 active substances for a total of 226 samples of plant protection products.

Qualitative  and quantitative analysis

# MONITORING PROGRAMME

The 2° level after enforcement analysis is performed by the National Institute of Health (Pesticide Unit)

Content of the active ingredient

Confirmation or not of the results obtained from the official laboratory when the results is not according to the label content.

# MONITORING PROGRAMME

The analysis are performed by CIPAC Method or analytical methods submitted by applicant during the authorisation process.

GC/FID

HPLC/DAD

# MONITORING PROGRAMME

During the years 2000-2011

Chloridazon
Chlortalonil
α-naphthylacetic acid
Pendimethalin
2,4-D
Thiophanate methyl

# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits

During the years 2011-2013 samples of PPPs counterfeits were analysed.


- IR spectra
- Chromatographic analysis
  (active ingredient and impurities profile)

# PESTICIDE UNIT

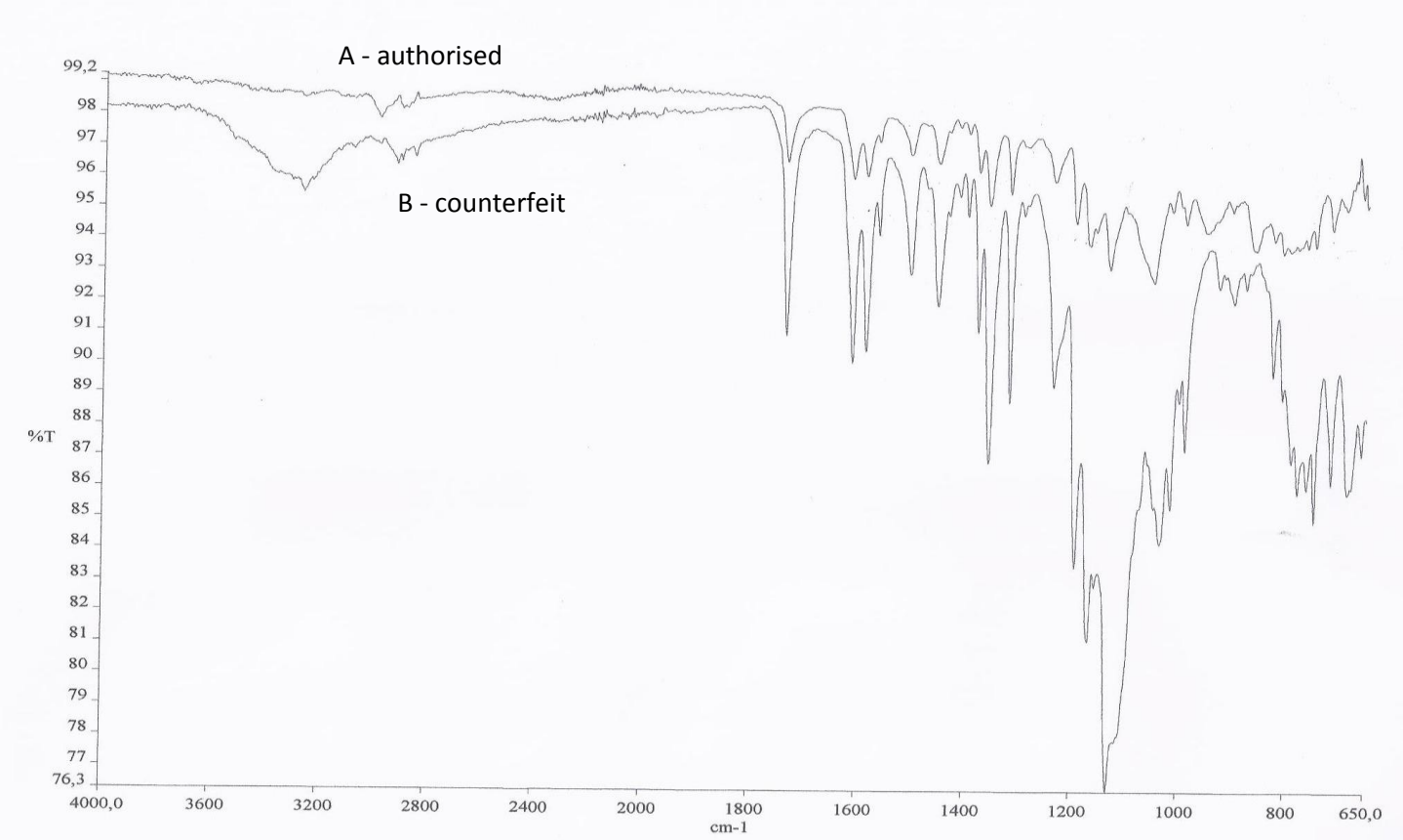
Experience on the analysis of PPPs counterfeits

The IR spectra were performed for the authorised products and for the counterfeit products.
(Perkin Elmer Spectrum one)

Examples of the comparison is given in the following figure 1 and 2

# PESTICIDE UNIT

## Experience on the analysis of PPPs counterfeits – Figure 1



# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits – Figure 2

# PESTICIDE UNIT

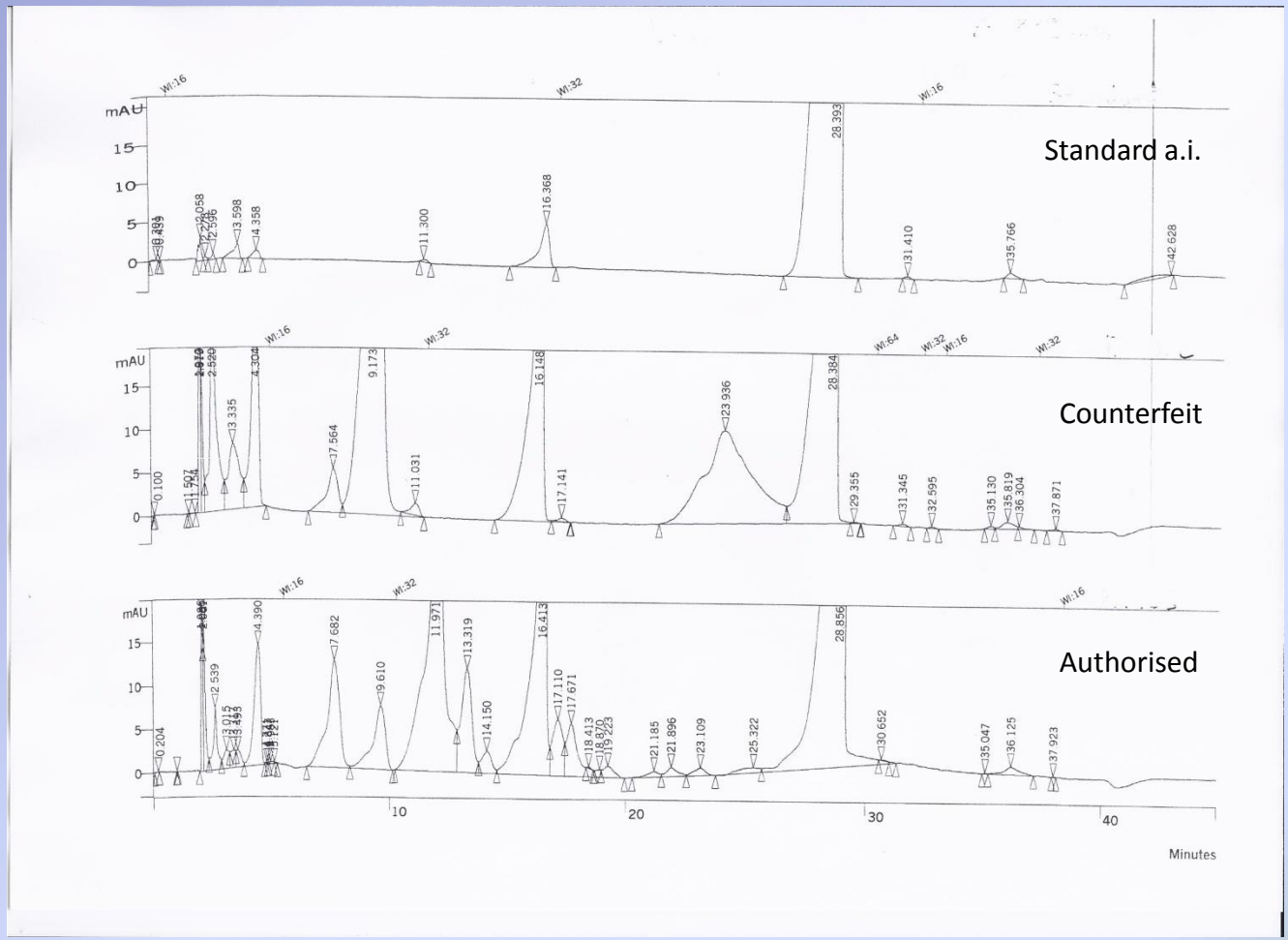
Experience on the analysis of PPPs counterfeits

The chromatographic profile is determined by HPLC/DAD and a comparison between the chromatographic profile is performed.

Examples of the chromatographic profile are given in the figure 2 and 3.

# PESTICIDE UNIT

## Experience on the analysis of PPPs counterfeits – Figure 3



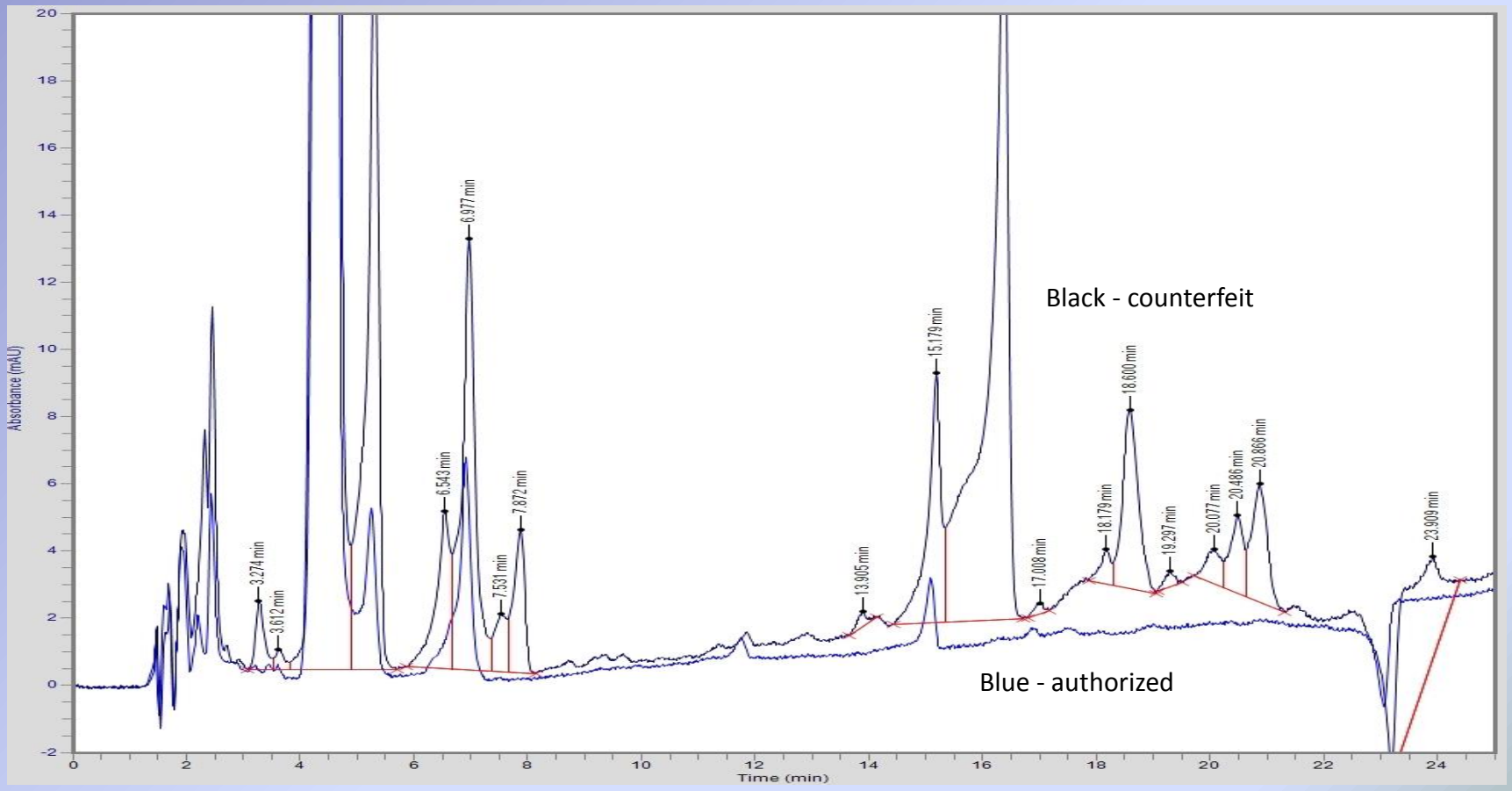
# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits

The chromatographic conditions:
HPLC Varian equipped with DAD
Column: Zorbax Rx C8, 250 x 4.6 mm; 5 μm
Gradient: 15%$CH_3CN$ (5 min), 40% $CH_3CN$ (35 min), 15% $CH_3CN$ (10min)
DAD: 229 nm

# PESTICIDE UNIT

## Experience on the analysis of PPPs counterfeits – Figure 4



# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits

The chromatographic conditions:
HPLC PERKIN ELMER equipped with DAD
Column: Zorbax SB C8, 150 x 4.6 mm; 5 μm
Gradient: 30% Eluent B (0 min), 100% Eluent B (23 min), 30% Eluent B (28 min)
Eluent B: mixture $CH_3CN/H_2O$/Acetic acid
DAD: 254 nm

# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits

Qualitative analysis

A comparison between the retention time of each compound referred to the active ingredient is performed.

Quantitative analysis

Referred to the active ingredient in the PPPs authorised and normalised to 100.

# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits

To confirm each components of the chromatographic profile we need of LC/MS/MS and GC/MS/MS.

# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits

To perform this analysis
we need to know

the spectra of each component
the most abundance ions
the parent and daughter ion

# PESTICIDE UNIT

Experience on the analysis of PPPs counterfeits - problem

No standards commercially available to check the components of the products.

# Thank you for attention