Determination of pesticides in drinking, surface and ground water

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Pesticides having different structures and biological activities are widely used for agricultural and non purposes throughout the world. Due to their widespread use, pesticides need to be determined in various environmental matrices, such as soil, water and air. A wide range of analytical techniques, mostly gas or liquid chromatography with a variety of detection systems, have been developed for their determination and identification. Pesticides most commonly used in Cyprus, divided into three different groups according to their stability, are determined and identified both qualitative and quantitatively. For this purpose, in our laboratory three different techniques have been developed and fully validated including the calculation of % recovery, repeatability, reproducibility and uncertainty. Pesticides of Group A are extracted from water using Liquid – Liquid or SPE extraction and determined with GC/MS, pesticides of Group B are extracted using Liquid-Liquid extraction and determined using GC/ECD and also GC/MS for qualitative analysis and pesticides of Group C are extracted from water using Solid Phase Extraction (C18 cartridge) and determined with UPLC/MS/MS.

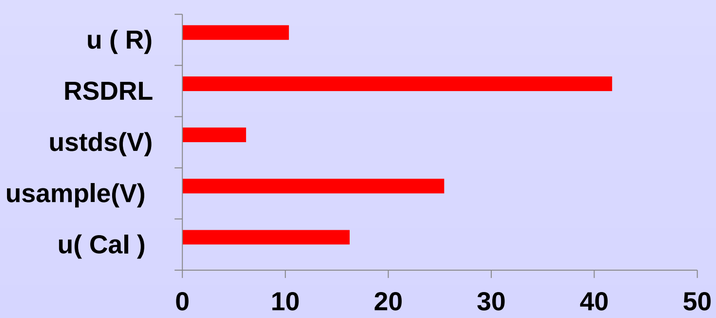
Important part of the validation was the estimation of uncertainty according to the requirements of ISO 17025. Both combined and expanded uncertainty, were calculated using Eurachem/CITAC Guide, for pesticides considered as priority substances, according to WFD 2000/60/EC and the amending Directives 2008/105/EC and 2013/39/EC. During the validation, uncertainty was estimated in both surface and MilliQ water. Values showed no significant difference among the two matrices, while the calculated uncertainty was in compliance with the Directive 2009/90/EC, which states that % Uncertainty has to be lower than 50% at parametric value (Legal Limit). The component with the most significant contribution to the estimation of uncertainty was the laboratory reproducibility. However in routine analysis, if the concentration of any of the pesticides is found to be near or above the legal limit (considering the calculated method uncertainty), then uncertainty value is recalculated for the specific compound using daily data. Also it is included in the final result, when requested by customer or for any other reason according to ISO 17025.

A. COMPOUNDS

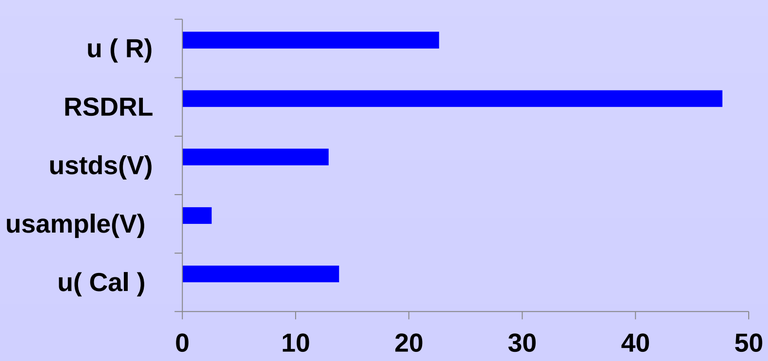
Group A (GC/MS)	Group B (GC/ECD)	Group C (UPLC/MS/MS)
Trifluralin	Hexachlorobenzene	Cymoxanil
Diazinon	a-Hexachlorocyclohexane	Dimethoate
Chlorothalonil	b-Hexachlorocyclohexane	Carbofuran
Formothion	Lindane	Diuron
Alachlor	Heptachlor	Linuron
Fenitrothion	Heptachlor- epoxide	Thiophanate methyl
Chlorpyrifos	Aldrin	Isoproturon
Dicofol	Endrin	Chlorfenvinphos
Captan	Dieldrin	Metribuzin
Folpet	**Isondrin	Tribenuron methyl
Iprodione	ppDDD	Simazine
	opDDT	Atrazine
	ppDDT	Kresoxim methyl
	ppDDE	Propyzamide
	a-endosulfan	Flusilazole
	b-endosulfan	Penconazole
	*Pentachlorobenzene	Prosulfocarb

% Contribution of Uncertainty components

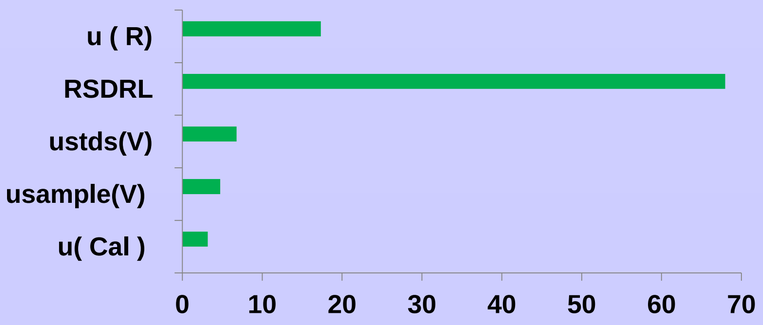
Alachlor (Group A)



b-Hexachlorocyclohexane (Group B)



Isoproturon (Group C)



B. EVALUATION : Uncertainty

"A parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand"

Uncertainty Components

Usample(v)/v: Uncertainty from glassware used for the sample preparation
Ustds(v)/v: Uncertainty from glassware used for standards preparation
Ucal/C: Uncertainty from the use of calibration curve
URSD: Uncertainty from reproducibility RSDRL
U(Rec): Uncertainty from %recovery

$$\frac{uc}{c} = \sqrt{\left(\frac{U(Cal)}{C}\right)^2 + \left(\frac{Usample(V)}{V}\right)^2 + \left(\frac{Ustd(V)}{V}\right)^2 + (U(Rec))^2 + (URSD_{RL})^2}$$

Expanded Uncertainty: $U = 2 \times u_c$

C. RESULTS: % Recoveries, % RSD and %Uexp

Pesticides of Group A

Matrix \ Spiking level	0.03 µg/L		
	% Rec	%RSDRL	% Uexp
Surface Water	63-118	8-23	26-36
MilliQ Water	68-115	9-15	17-29

Pesticides of Group B

Matrix \ Spiking level	0.05, 0.007*, 0.0098** µg/L		
	% Rec	%RSDRL	% Uexp
Surface Water	60-139	6-11	14-24
MilliQ Water	59-133	5-23	12-49

Pesticides of Group C

Matrix \ Spiking level	0.1 µg/L		
	% Rec	%RSDRL	% Uexp
Surface Water	85-98	8-13	11-24
MilliQ Water	71-88	3-12	22-35

D. CONCLUSSIONS

- The use of Gas and Liquid Chromatography in combination with different detection systems gives the advantage of determine a variety of different properties compounds in a single sample saving also the laboratory time, money and consumables.
- The range of recoveries indicates the suitability of all three methods for routine analysis (Fitness for purpose)
- The % U of all compounds is lower than 50% for all matrices, in agreement with the Directive 2009/90/EC
- The component with the most significant contribution in the estimation of expanded uncertainty is the laboratory reproducibility

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