

SERVICE COMMUN DES LABORATOIRES  
LABORATOIRE de STRASBOURG

**INTRALABORATORY VALIDATION:**

**Multiresidue Method**

Due to the harmonization of the pesticides residue research in the SCL labs our analytical method based on full scan identification and SIM quantification were upgraded to be conducted in full scan for both identification and quantification.

The determination of the requested parameters has to be done within the routine analysis and we ensured the different steps:

Part I : characterisation and validation of the sequence

Part II : Validation of the identification and detection limits

Part III : Validation of the quantification : limits of quantification, recovery, repeatability, intermediate fidelity, matrix effect.

**Part I : Characterization and  
validation of the sequence**

2007/04/28 to 2007/10/25

According the SOP IN167/80/ANA/24 the repeatability, the intermediate fidelity and the limit of acceptability of the injection point 1000ppb at the end of the usual sequence were determined.

This injection is repeated 3 times on 3 different days according the following plan where “RE” is the recalculated quantity using the calibration curve built on 6 different standards.

The sequence is as follow:

6 standards, 24 vials (12 samples 2 dilutions) and 3 times standard 1000 ppb

D1		D2		D3	
1000-11	RE_1000-11	1000-21	RE_1000-21	1000-31	RE_1000-31
1000-12	RE_1000-12	1000-22	RE_1000-22	1000-32	RE_1000-32
1000-13	RE_1000-13	1000-23	RE_1000-23	1000-33	RE_1000-33

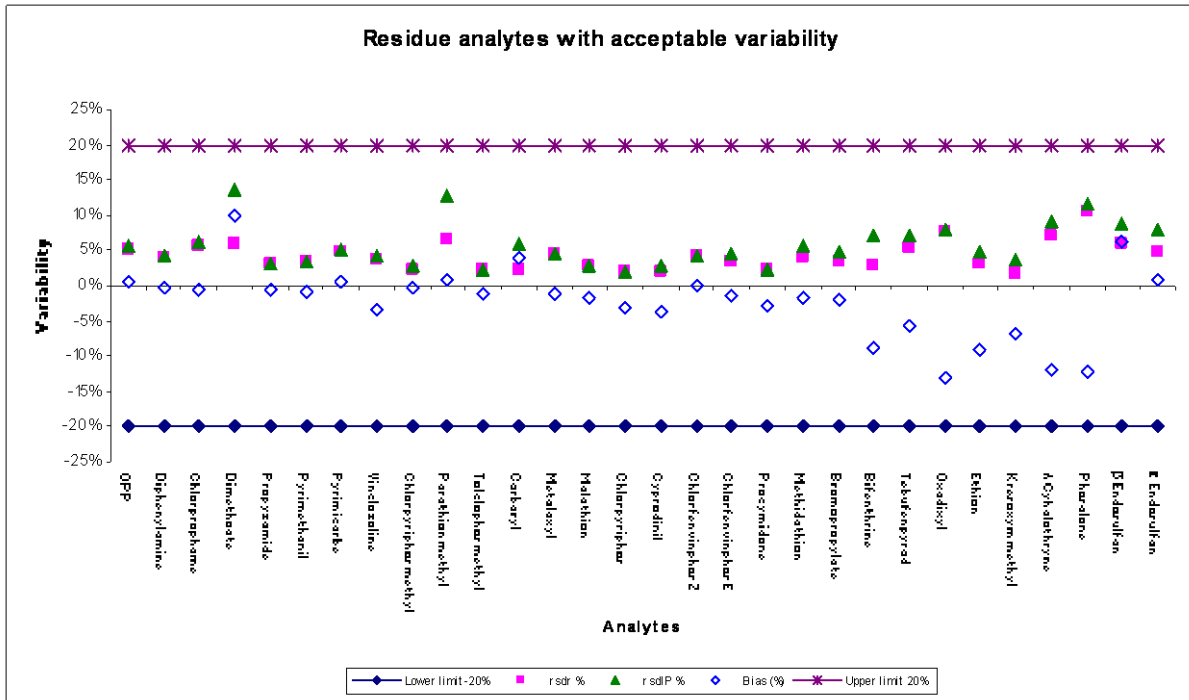
The characterization parameters shown in the template 1 were obtained according the calculation for 1 level

Precision : Repeatability and Intermediate Precision

Trueness : Bias

Template 1 : Residue analytes with acceptable variability

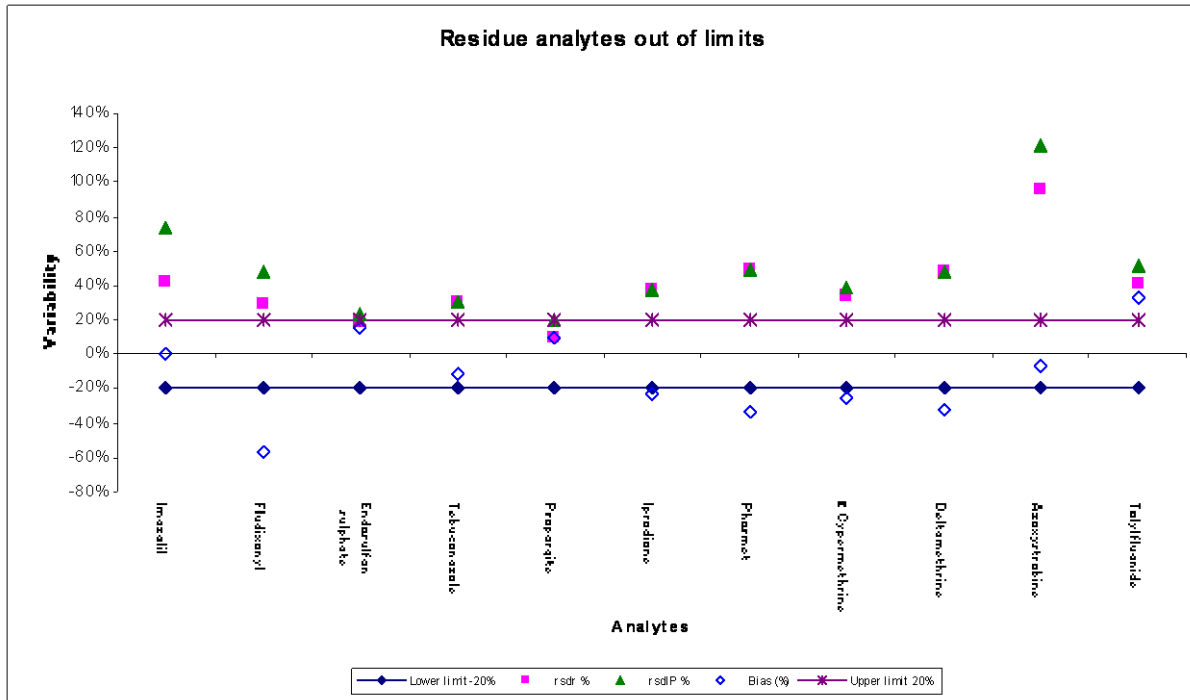
MA Acceptables	Lower limit - 20%	rsdr %	rsdIP %	Bias (%)	Upper limit 20%
OPP	-20%	5,0%	5,7%	0,7%	20%
Diphenylamine	-20%	4,0%	4,3%	-0,2%	20%
Chlorprophame	-20%	5,6%	6,4%	-0,5%	20%
Dimethoate	-20%	5,9%	13,6%	10,0%	20%
Propyzamide	-20%	3,0%	3,3%	-0,7%	20%
Pyrimethanil	-20%	3,5%	3,5%	-0,9%	20%
Pyrimicarbe	-20%	4,7%	5,1%	0,5%	20%
Vinclozoline	-20%	3,7%	4,3%	-3,3%	20%
Chlorpyriphos methyl	-20%	2,2%	2,8%	-0,4%	20%
Parathion methyl	-20%	6,5%	12,7%	0,9%	20%
Tolclophos methyl	-20%	2,3%	2,3%	-1,2%	20%
Carbaryl	-20%	2,2%	5,9%	3,9%	20%
Metalaxyl	-20%	4,5%	4,5%	-1,1%	20%
Malathion	-20%	2,8%	2,8%	-1,7%	20%
Chlorpyriphos	-20%	1,9%	1,9%	-3,1%	20%
Cyprodinil	-20%	2,1%	2,8%	-3,7%	20%
Chlorfenvinphos Z	-20%	4,2%	4,2%	-0,1%	20%
Chlorfenvinphos E	-20%	3,3%	4,6%	-1,3%	20%
Procymidone	-20%	2,2%	2,2%	-2,8%	20%
Methidathion	-20%	3,9%	5,6%	-1,8%	20%
Bromopropylate	-20%	3,4%	4,8%	-2,1%	20%
Bifenthrine	-20%	2,9%	7,1%	-8,9%	20%
Tebufenpyrad	-20%	5,5%	7,2%	-5,8%	20%
Oxadixyl	-20%	7,7%	8,0%	-13,0%	20%
Ethion	-20%	3,1%	4,7%	-9,2%	20%
Kresoxym methyl	-20%	1,6%	3,6%	-6,7%	20%
λ Cyhalothryn	-20%	7,2%	9,0%	-11,8%	20%
Phosalone	-20%	10,5%	11,6%	-12,3%	20%
β Endosulfan	-20%	6,0%	8,8%	6,3%	20%
α Endosulfan	-20%	4,8%	7,8%	0,9%	20%



Graph 1 : Residue analytes with acceptable variability

Residues out of limit	Lower limit - 20%	rsdr %	rsdIP %	Bias (%)	Upper limit 20%
Imazalil	-20%	42,6%	74,0%	0,9%	20%
Fludixonyl	-20%	28,8%	47,9%	-56,3%	20%
Endosulfan sulphate	-20%	18,9%	23,6%	15,2%	20%
Tebuconazole	-20%	30,0%	30,0%	-11,8%	20%
Propargite	-20%	10,2%	19,9%	9,3%	20%
Iprodione	-20%	37,1%	37,1%	-23,4%	20%
Phosmet	-20%	48,8%	48,8%	-33,3%	20%
α Cypermethrin	-20%	34,2%	39,1%	-25,9%	20%
Deltamethrin	-20%	47,9%	48,5%	-31,8%	20%
Azoxystrobin	-20%	95,8%	121,4%	-6,8%	20%
Tolyfluanide	-20%	40,7%	51,8%	32,4%	20%

Template 2 : Residue analytes out of limits



Graph 2 : Residue analytes out of limits

**Discussion :**

The characterization is conducted on 3 different days with 3 repetition. All the analytes with a repeatability and Intermediate precision within -20% and 20% are shown in the template 1, the analytes with a larger variability are summarised in template 2. The mathematic function of the 6 level of standards is a straight of first degree and the results are treated as such by the software. Depending of the detection limits 4 levels of calibration are practicable, specially for residues “out of limit.”

**Decision :**

None of the Analytes can be discarded at this step of the characterization. The observed variability is a reference for coming results : any values within the observed interval will be retained.

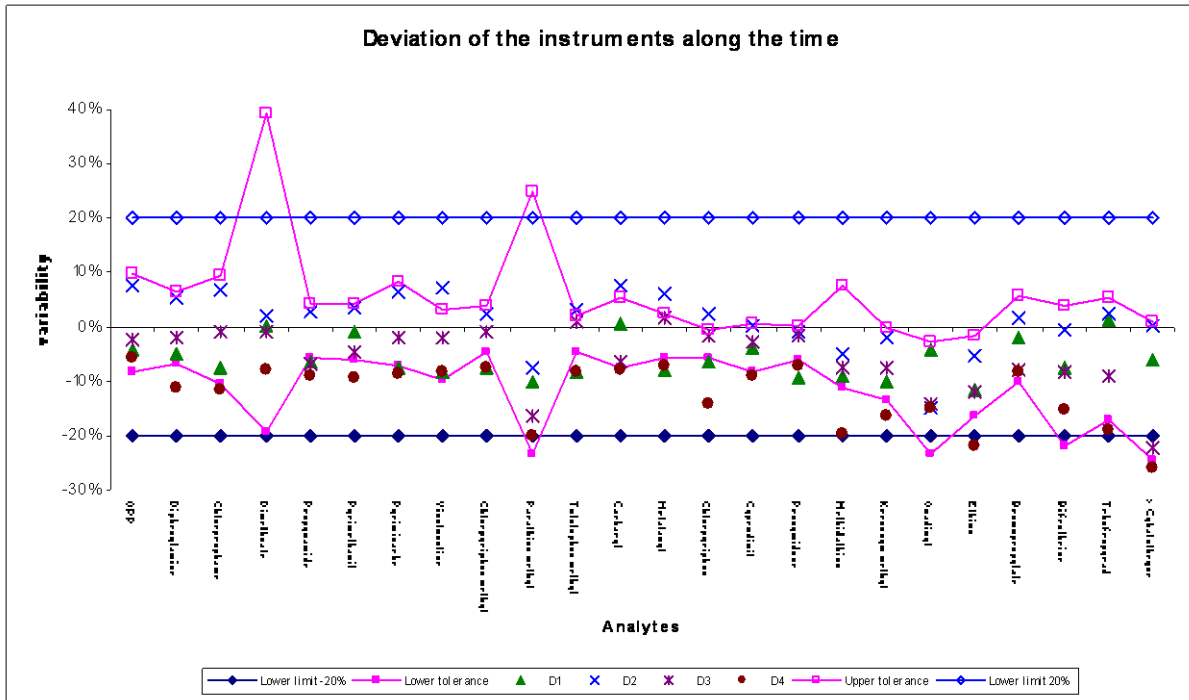
The quantification should be conducted according a linear model

The sequence should manage 6 standards, 26 vials (12 samples corresponding to 10g of matrix per mL and 12 samples corresponding to 1g of matrix per mL) and in addition 3 samples for on going control (recovery or any other use).

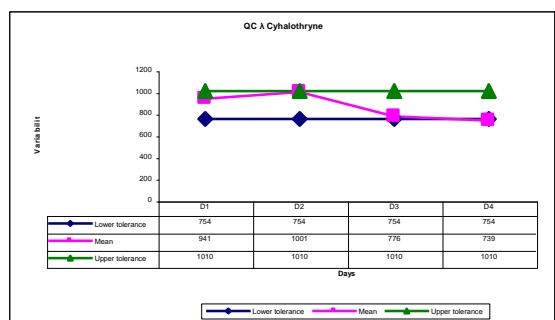
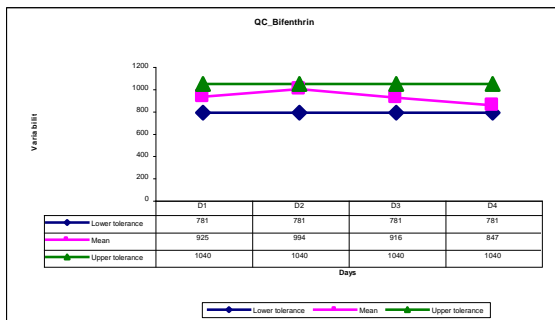
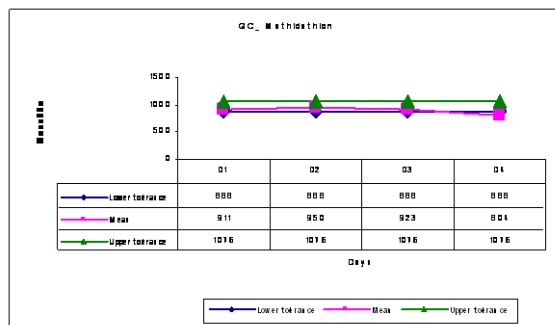
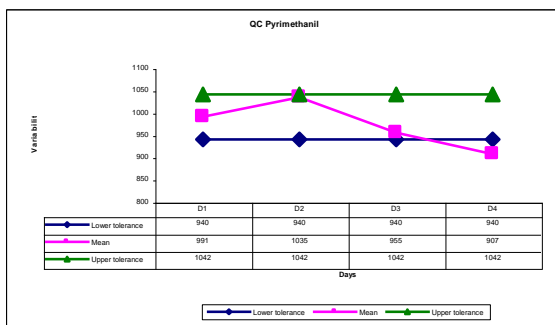
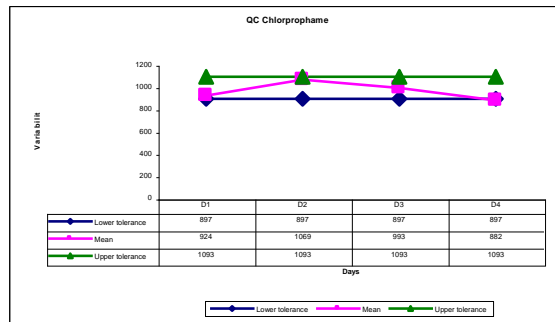
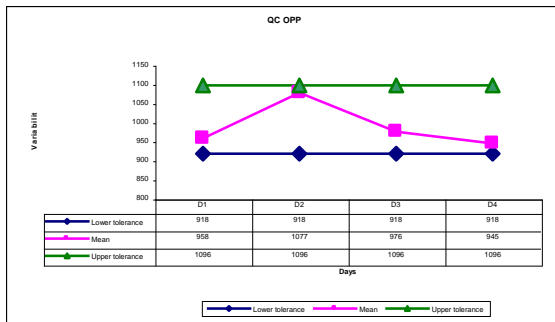
**Quality Control :**

The re injection of the standard 1000 ppb at the end of the sequence validates the daily sequence and manages the deviation along the time.

If the full recovery is lower as the lowest tolerance the values are accepted BUT the maintenance of the instrument (GC, column, MS) must be done



The QC will be followed up recording the OPP, Chlorprophame, Pyriméthanil, Méthidathion, Bifenthrin et  $\lambda$  Cyhalothryne values on a control chart



When 3 analytes are exceeding the lower tolerance, the system must be cleaned and the column shortened (10 cm)

## Part II : Characterization and validation of identification

2007/0428 / to 2008/01/10

### Validation

The validation was conducted on salads

The MRL or LOQ of Regulation 396/2005 must be imperatively reached

The calibration at 100, 200, 500ppb corresponds to 0.01, 0.02, 0.05 mg/kg representing the MRL

All the residues have to be recovered at their official limits.

This characterization was developed for the first accreditation after a study of recovery and matrix effect for the leafy vegetables group.

After each sequence the verification of amenable spectra of each residue is registered in the IM167/80/ANA21



IM16780 ANA21\_orig  
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### Revalidation

The mixture of analytes is spiked at 0.01 ; 0.02 ; 0.05 mg/kg to 50g of communitated salads extracted and injected in scan mode against calibration standards.

Except Tolyfluanid, Fludioxonil, Oxadixyl, Deltamethrin, Azoxystrobin all the analytes are recovered at their MRL or LOQ respectively as shown in template below

Analytes mg/kg	LOD/LOQ mg/kg			Analytes	LOD/LOQ mg/kg		
	0,01	0,02	0,05		0,01	0,02	0,05
OPP (2-Phénylphénol)	84%	84%	77%	α ENDOSULFAN	244%	696%	475%
DIPHENYLAMINE	14%	41%	42%	IMAZALIL	130%	7%	23%
CHLORPROPHAM	99%	234%	78%	FLUDIOXONIL	69%	744%	142%
DIMETHOATE	1400%	1400%	1400%	KRESOXIM METHYL	116%	22%	75%
PROPYZAMIDE	96%	0%	67%	β ENDOSULFAN	41%	121%	72%
PYRIMETHANIL	61%	86%	65%	OXADIXYL	3000%	1000%	2000%
PYRIMICARB	84%	107%	68%	ETHION	132%	1%	71%
VINCHLOZOLINE	76%	107%	80%	ENDOSULFAN SULPHATE	217%	152%	78%
CHLORPYRIPHOS METHYL	81%	95%	65%	TEBUCONAZOLE	48%	1%	40%
PARATHION METHYL	153%	166%	97%	PROPARGITE	483%	1900%	84%
TOLCLOPHOS METHYL	65%	1%	61%	IPRODIONE	131%	48%	55%
CARBARYL	71%	600%	60%	PHOSMET	141%	97%	58%
METALAXYL	58%	108%	68%	BROMOPROPYLATE	125%	99%	59%
MALATHION	257%	235%	96%	BIFENTHRIN	102%	90%	59%
CHLORPYRIPHOS	61%	37%	58%	TEBUFENPYRAD	88000%	13000%	5000%
CYPRODINIL	2000%	3000%	2100%	PHOSALONE	127%	1%	53%
TOLYLFLUANID	306%	381%	137%	λ CYHALOTHRIN	131%	104%	55%

<b>CHLORFENVINPHOS</b>	<b>129%</b>	<b>14%</b>	<b>76%</b>	<b>α CYPERMETHRIN</b>	<b>89%</b>	<b>108%</b>	<b>65%</b>
<b>PROCYMIDONE</b>	<b>468%</b>	<b>1020%</b>	<b>76%</b>	<b>DELTA METHRIN</b>	<b>111%</b>	<b>53%</b>	<b>22%</b>
<b>METHIDATHION</b>	<b>84%</b>	<b>33%</b>	<b>83%</b>	<b>AZOXYSTROBIN</b>	<b>187%</b>	<b>171%</b>	<b>38%</b>

The integration of the high values should be checked manually.

The matrix effect seems to enhance the identification but provides some erroneous results.

This effect can be checked by spiking matrix extracts or by surrogating the sample.