Targeted versus non targeted screening in pesticide analysis

Jim Garvey

The Pesticide Control Laboratory

Department of Agriculture, Food and the Marine
An Roinn Talmhaíochta, Bia agus Mara

Summary

1. Introduction
2. Starting point
3. The need for something different
4. Screening protocol
5. Some results
6. A pleasant surprise
7. Conclusions and general thoughts

Introduction

- There are approximately 800 pesticide active substances registered for use around the world
- When isomers, metabolites and pesticide active substances no longer used are included then the number goes well over 1000 analytes
- This poses an analytical problem for pesticide residue analysts who are expected to screen for as many of these analytes as possible
- In European terms the major countries would have scopes which range from 400 to 600 analytes

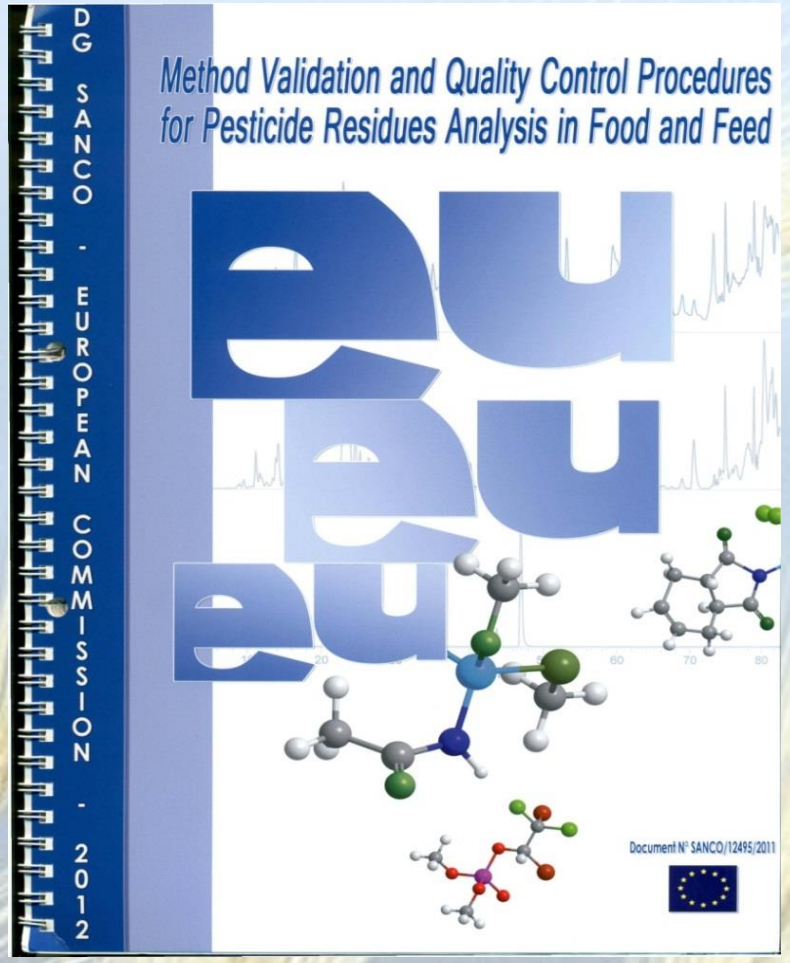
Introduction

- There are reasons why these numbers fall well short of the 1000+ total
  - Standards are not available for these analytes
  - The analytes degrade readily and therefore cannot be analysed reliably
  - The analytes are difficult or impossible to extract from food matrices
  - The identity of the analytes, particularly metabolites, are only known to the manufacturing companies and are not released as part of the patent process
- In spite of this laboratories are under increasing pressure from legislators to increase their scope

Introduction

- **ToF and QToF Systems**
- **Look for a large number of pesticides in one run**
- **Don’t necessarily have to have the standards to identify the pesticides and/or metabolites**
- **Systems give accurate mass measurements giving greater certainty of identification**
- **Allow for retrospective analysis of historical data**

Validation of Non-Targeted methods



- Spiking of blank samples at the screening detection limit (SDL)
- At least 20 samples at the SDL with a mixture of commodities with at least 2 samples per commodity
- Identification is considered tentative and must be confirmed by a validated, quantitative multi-residue method
- A false negative rate of 5% is considered acceptable

Introduction

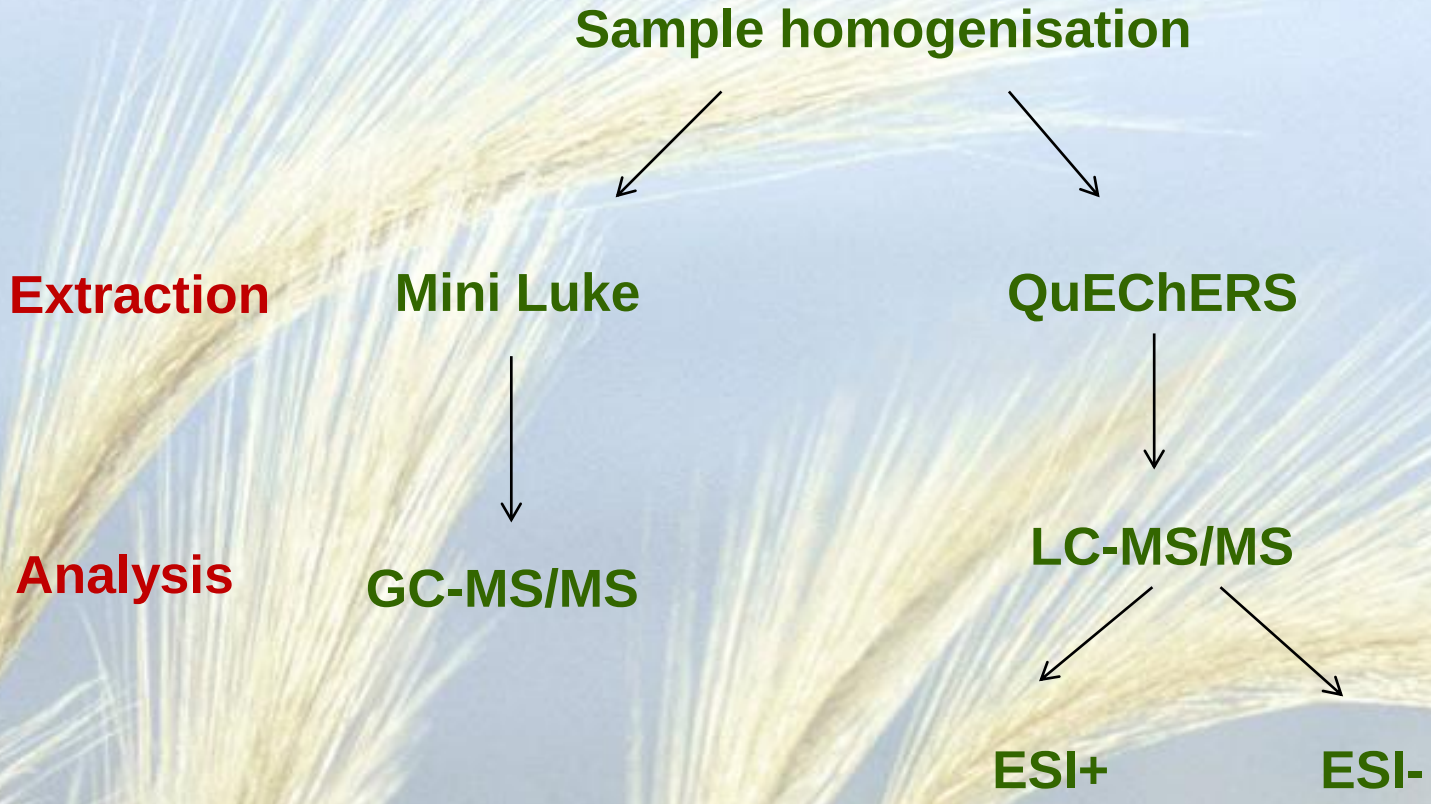
- There is no such thing as non-targeted screening !!

Targeted or non targeted

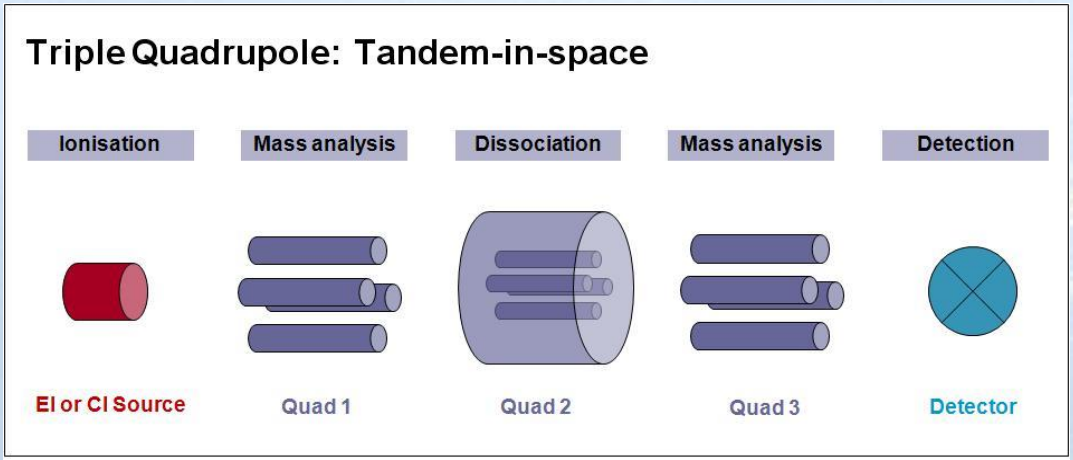
- Why ?
- There's always a list
- Commercial libraries do not take into account the extraction
- There is no quantitave element
- The danger is you think you are doing something you’re not !!

The starting point – F&V

- **The analytical protocol in the PCL in 2010 was:**



Analysis



- Ionisation takes place in the ion source
- The precursor ion is isolated in Q1
- Secondary fragmentation takes place in the collision cell - Q2
- The product ion is isolated in Q3
- The signal from the product ion is monitored in the detector

Carbendazim

192 [M + H] +

160

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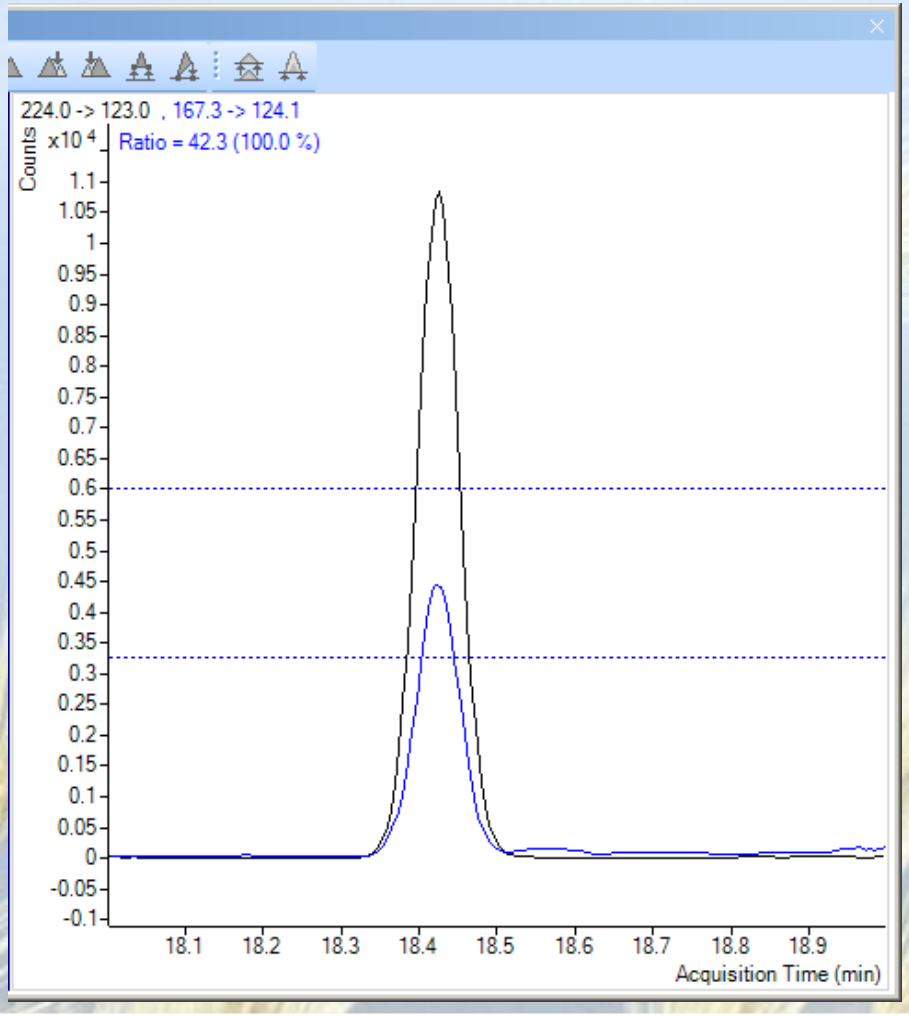
Analysis



Dichlofluainid

T1 = 224 → 123

T2 = 167 → 124.1

Ratio = 42.3%

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The good and bad

- **This system had certain advantages**
  - Because there were two extraction streams difficult pesticides could be analysed by both methods giving an easy cross check
  - Potential sample mix-ups could easily be checked for by analysing the GC fraction on LC or the LC fraction on GC
- **And some disadvantages**
  - The increasing number of standards required made their handling extremely complicated
  - Recovery points are being collected for each pesticide and someone has to evaluate this data
  - It is labour intensive

Expanding this system

- **As the system grows a number of factors need to be taken into account:**
  - **Standard handling becomes even more complex**
  - **Data processing becomes even more time consuming**
  - **Are we approaching the capacity of the triple quads to deal with this situation**
- **And most importantly !!!!!**
  - **We only find a fraction of these compounds !!!!**
  - **Are we doing a whole lot of work here simply to accumulate recovery data and is this an efficient way to carry out screening ?**
  - **The answers are YES and NO in that order.**

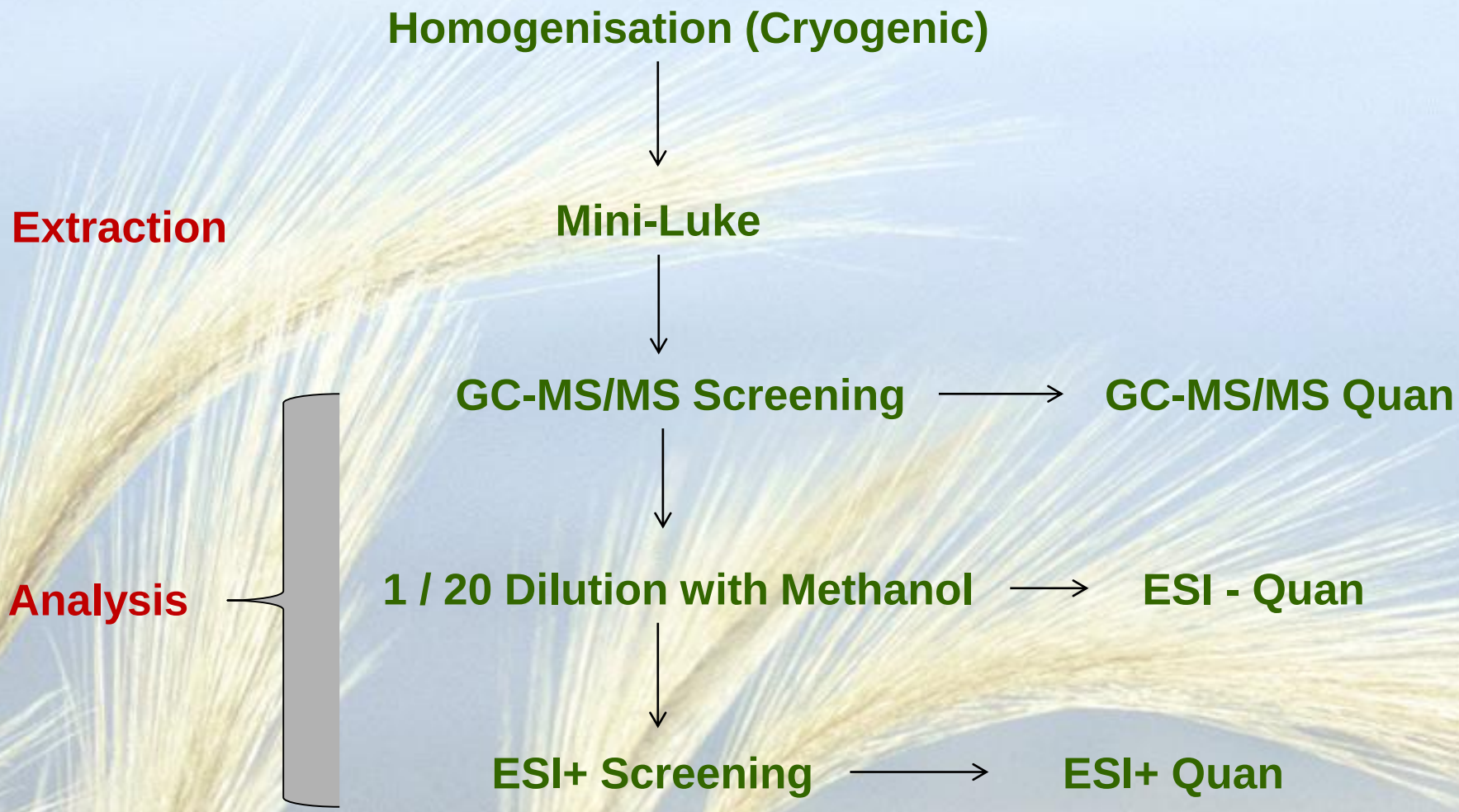
Something has to change

- The first step in changing this system was to evaluate which pesticides and metabolites had actually been found in Europe over the previous three years
- This review showed that 129 LC compounds and 105 GC compounds had been found in this time period.
- This included pesticides and metabolites which had only been found once or twice during this time
- From a standards management point of view these then became the GC calibration standard and the LC calibration standard
- A second mix was then made up which contained all the compounds which had not been found and the two mixes were combined to give a screening mix

Advantages of this system

- The screening acquisition method is used to collect all data in one sweep
- Calibration standards and recovery are only being run for what we expect to find but a screening standard containing all the pesticides and metabolites in the method is run at reporting limit level.
- If we have chosen correctly all positives should be in the quantitation mixes
- We are still screening for the pesticides and metabolites we don't expect to find and if we get a positive we have to go back and re-analyse
- Only one extraction – MRL breaches have to be re-extracted and re-analysed
- The increased sensitivity of the 6490 LC-MS/MS means that samples can be diluted 1/20 and retain sensitivity. This minimises matrix effects and eliminates the need for matrix matched standards

New protocol



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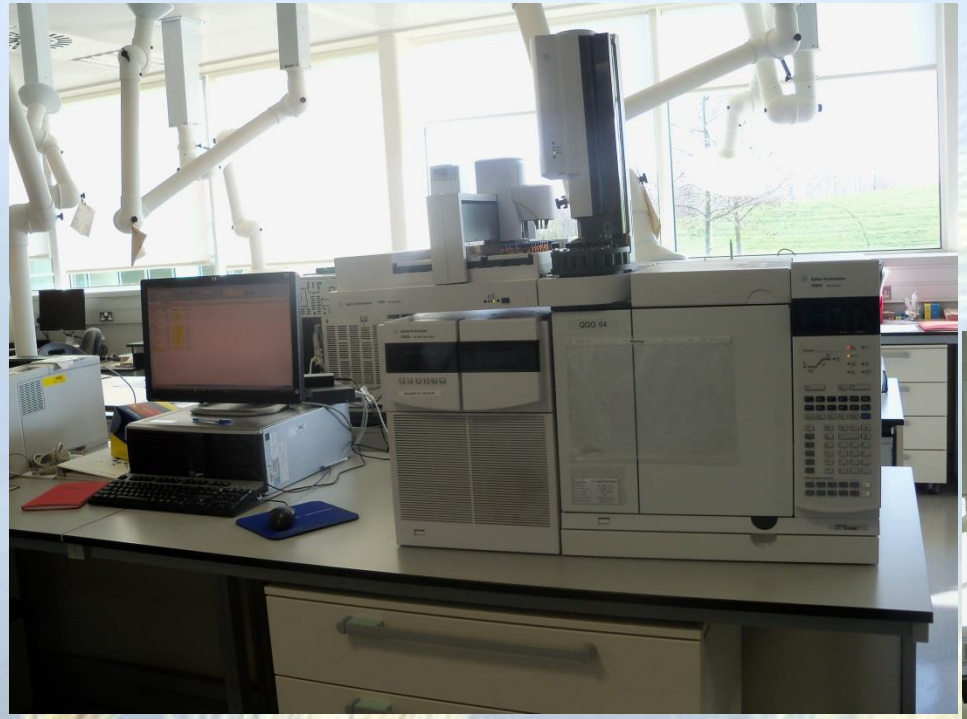
Workhorses



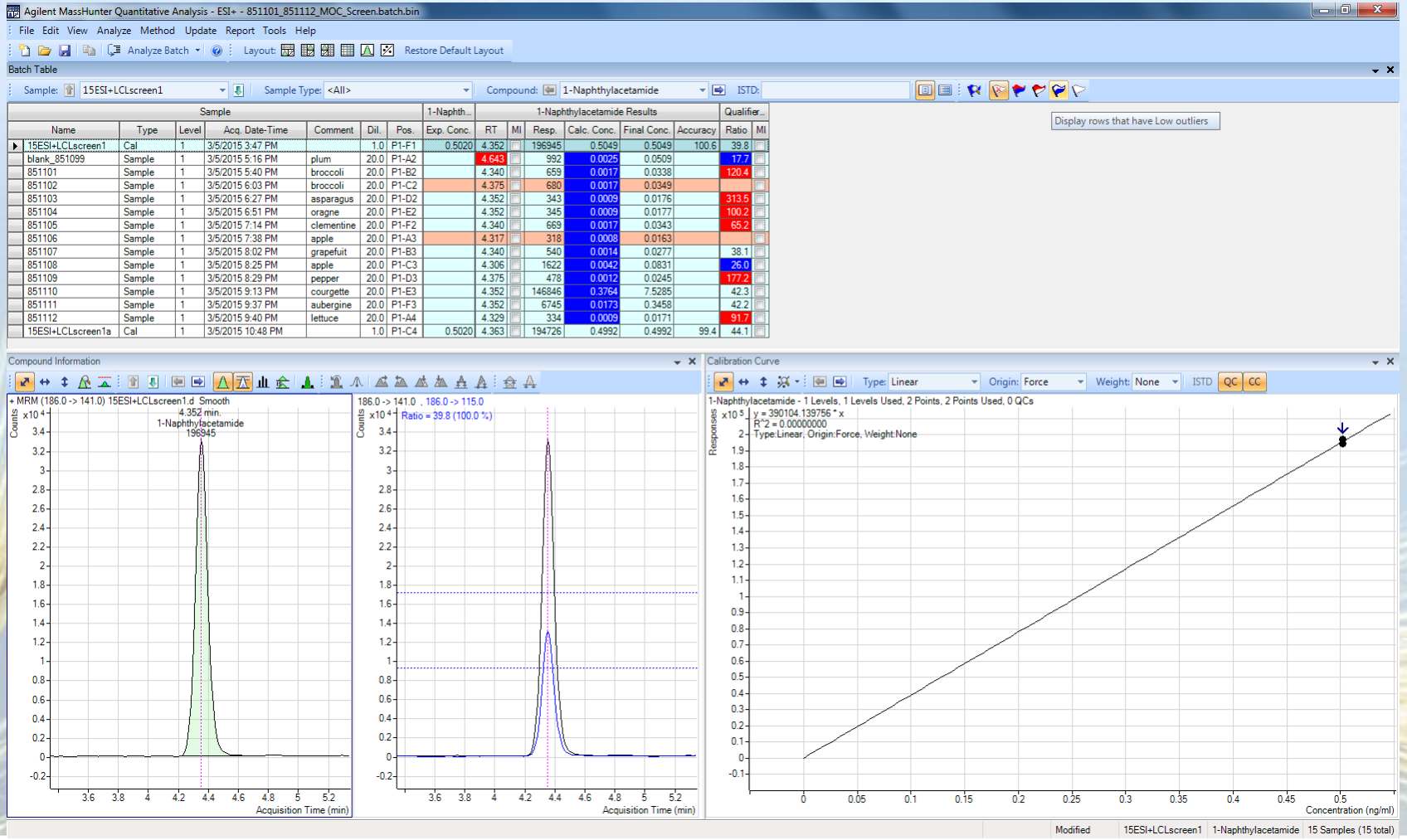
Typical sequence

- Conditioning injections x 2
- Calibration standards x 5
- Screening standard at reporting limit level
- Samples
- Recovery spike
- Screening standard at reporting limit level
- Calibration standards x 5

Screening

- The analytical system is the same as before:
- Two transitions are collected one for quantitation and one as a qualifier.
- If this is not enough more transitions can be added to the method easily
- The retention time of the peak and the ratio of the transitions are used to determine presence or absence of the pesticide or metabolite.
- The single point calibration is forced through zero to give an estimate of the concentration in the screening run although this is not really used for anything except giving the analyst a rough idea of the concentration

Screening



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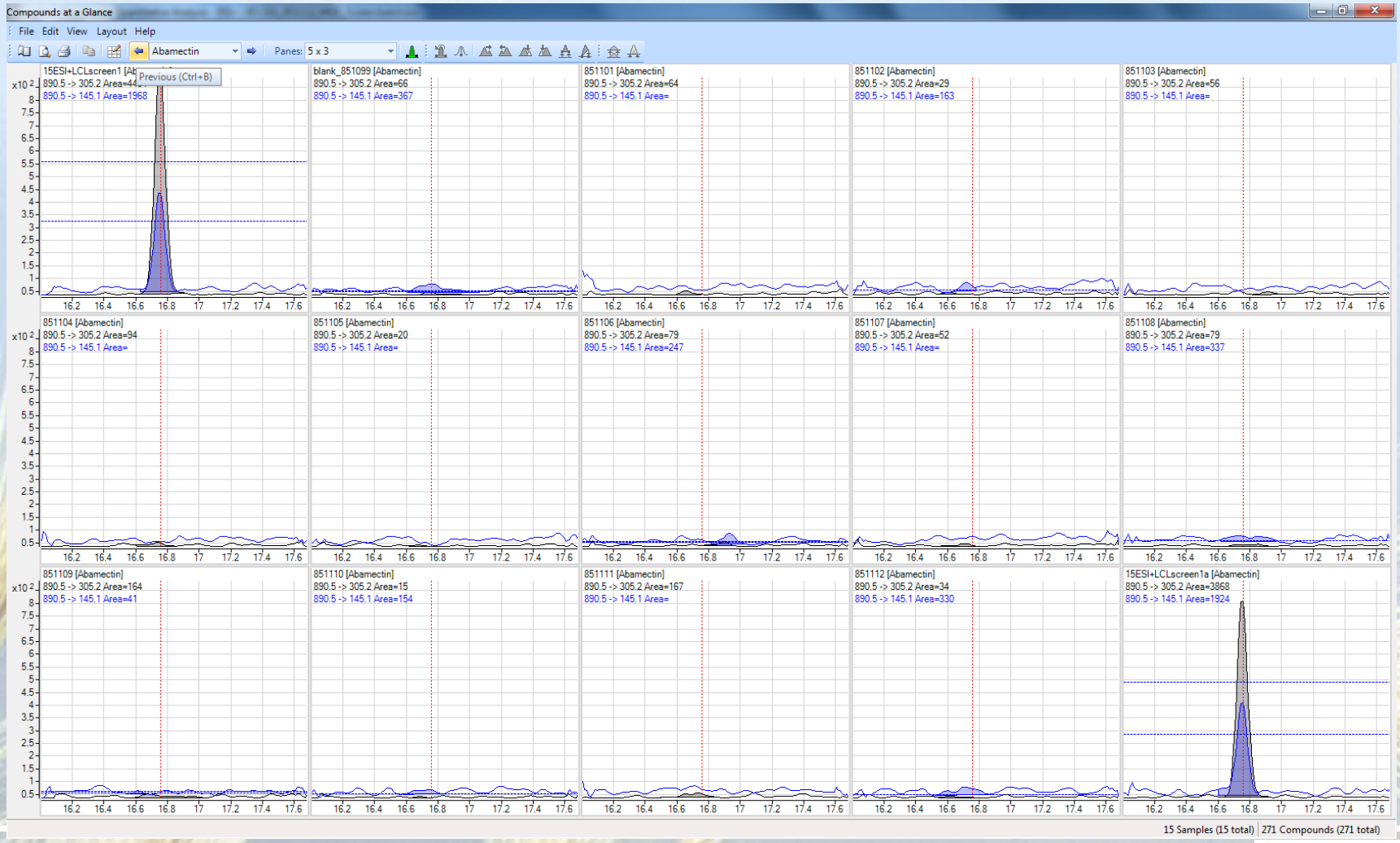
Screening

- Compounds at a glance function of the software is used for screening
- Set up properly screening can be done quickly and efficiently
- The screening standard is at reporting limit level which is usually equivalent to the default MRL value of 10ppb from EU396/2005
- A screening batch is set up from the acquisition data
- A peak with a response greater than 90% of the response of the peak in the screening standard is regarded as a positive and is noted for quantitation
- At the end of the screening process the analyst has a list of compounds which need to be quantified

Screening



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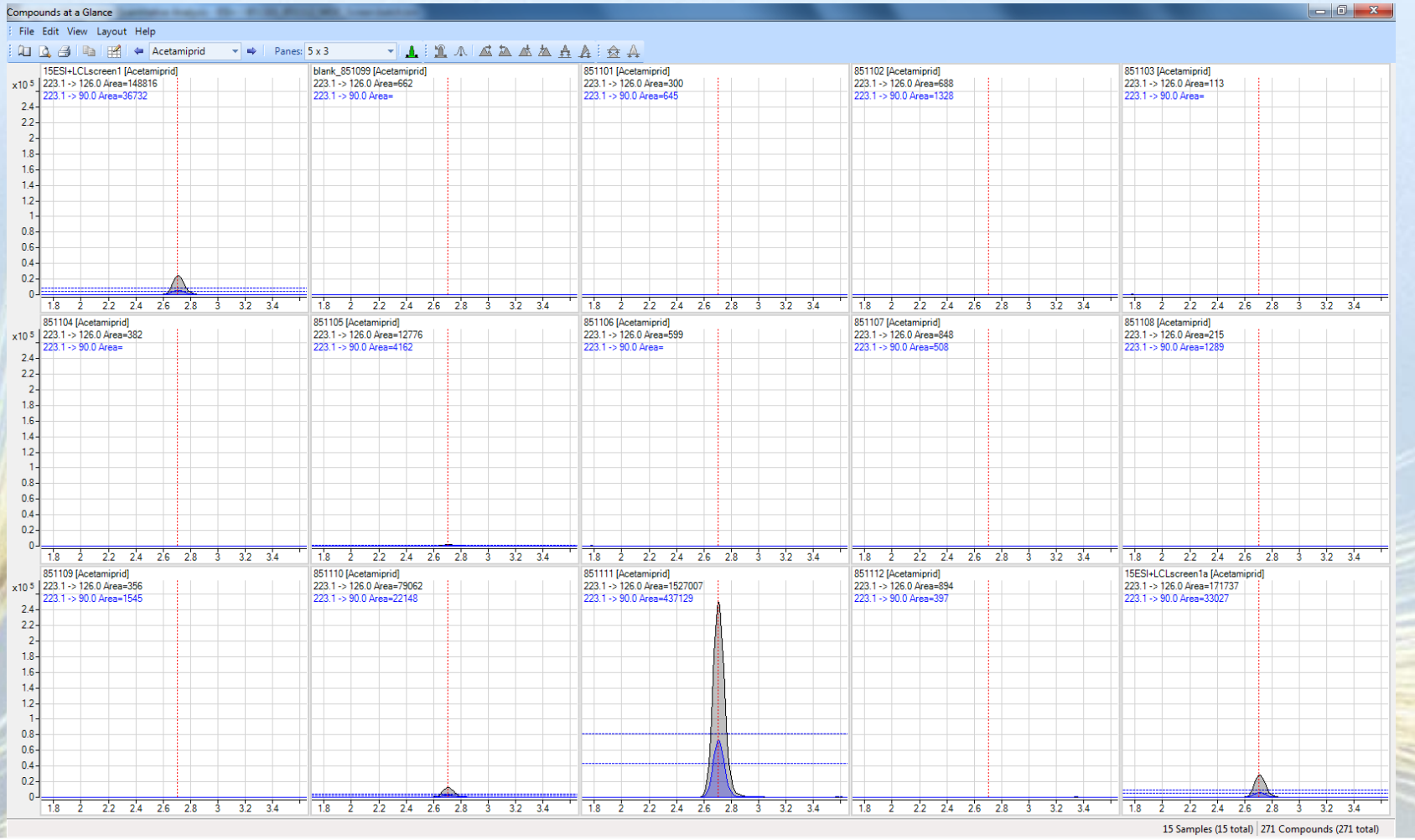
Screening



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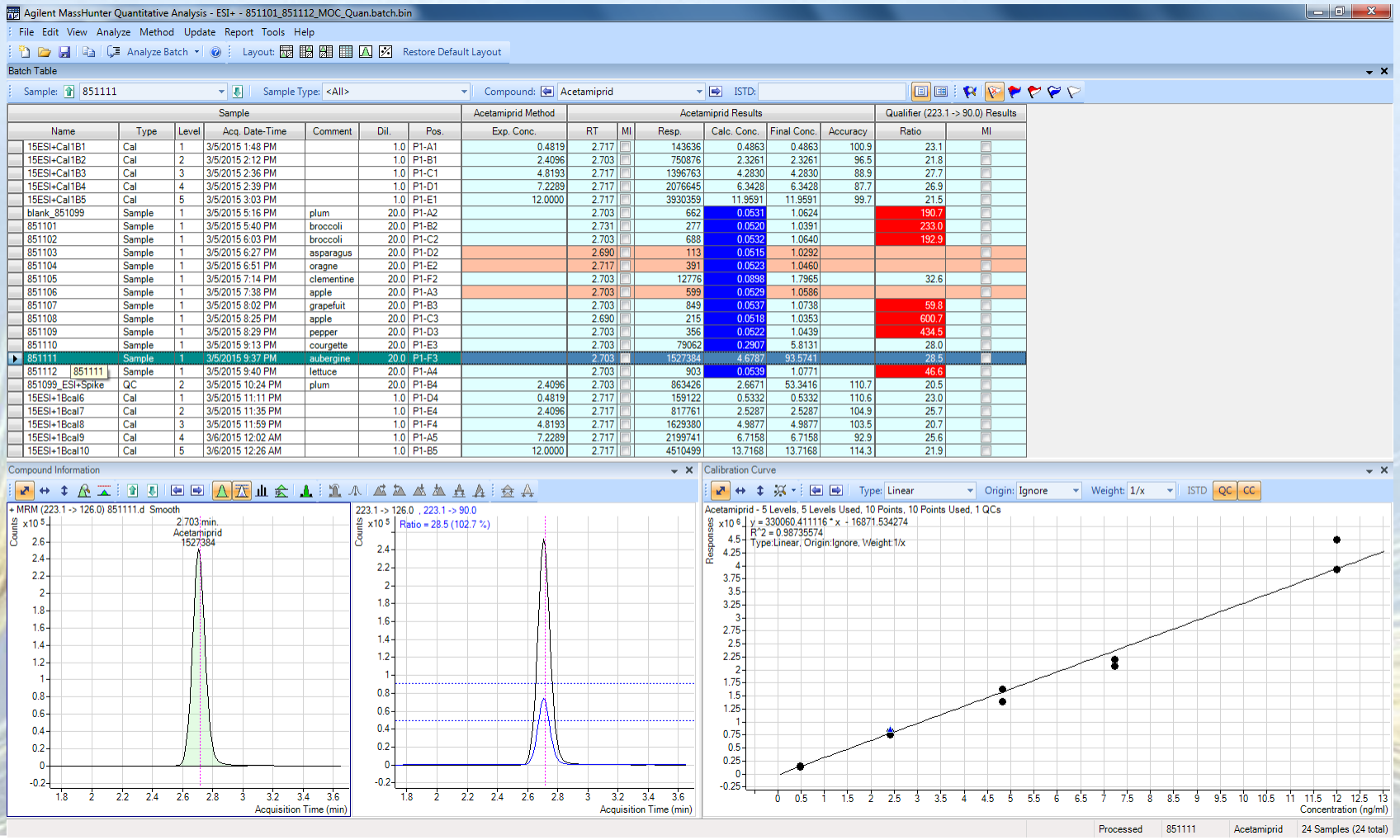
Quantitation

- All the data required for quantitation has already been collected with the initial acquisition run
- Assuming that everything we need to quantitate is in our calibration standard all we need to do is now set up a second quan batch in the software.
- This time we add the calibration standards and the samples to be quantified as well as the recovery spike to the Quan batch
- A five point calibration curve is used for the calibration

Quantitation



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Quantitation

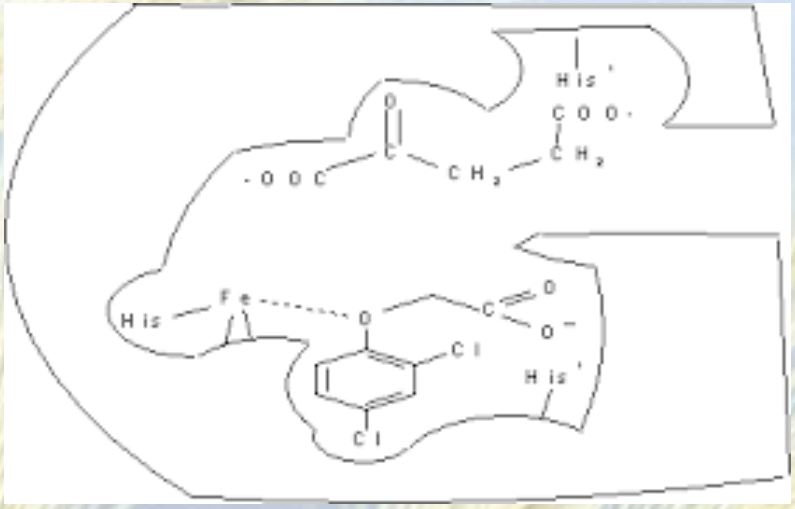
- All the data required for the quantitation of Acetamiprid is contained in this window including the QC data
- Two transition are present in the correct ratio
- The pesticide quantifies as 93.6 μg/kg
- The linearity is very good with a correlation co-efficient of 0.987
- And the recovery is very good
  - $Recovery = \left(\frac{53}{50}\right) x100 = 106\%$
- A screen shot of this window contains all the data required to report this result

ESI -

- The exception to this protocol is the ESI- part of this screen
- This part of the method contains all the phenoxyacetic acids herbicides
- Because there is such a small number of these (~30) screening in this way is not required
- In this case the samples and recovery work are run bracketed by two sets of calibration standards as normal
- One possibility for improving the workflow even more in the future is to incorporate the ESI- compounds into the ESI+ method and use pos/neg switching
- This would mean only one LC-MS/MS method was required further enhancing the efficiency of the screening

ESI -

- One unexpected surprise with this protocol was the effect the extraction had on the acid herbicides.
- Using the QuEChERS method these have a tendency to bind to matrix or PSA and this results in very low recoveries



- The use of the mini-Luke extraction in this case resulted in a significant improvement in the recoveries for these compounds

ESI- Recovery results

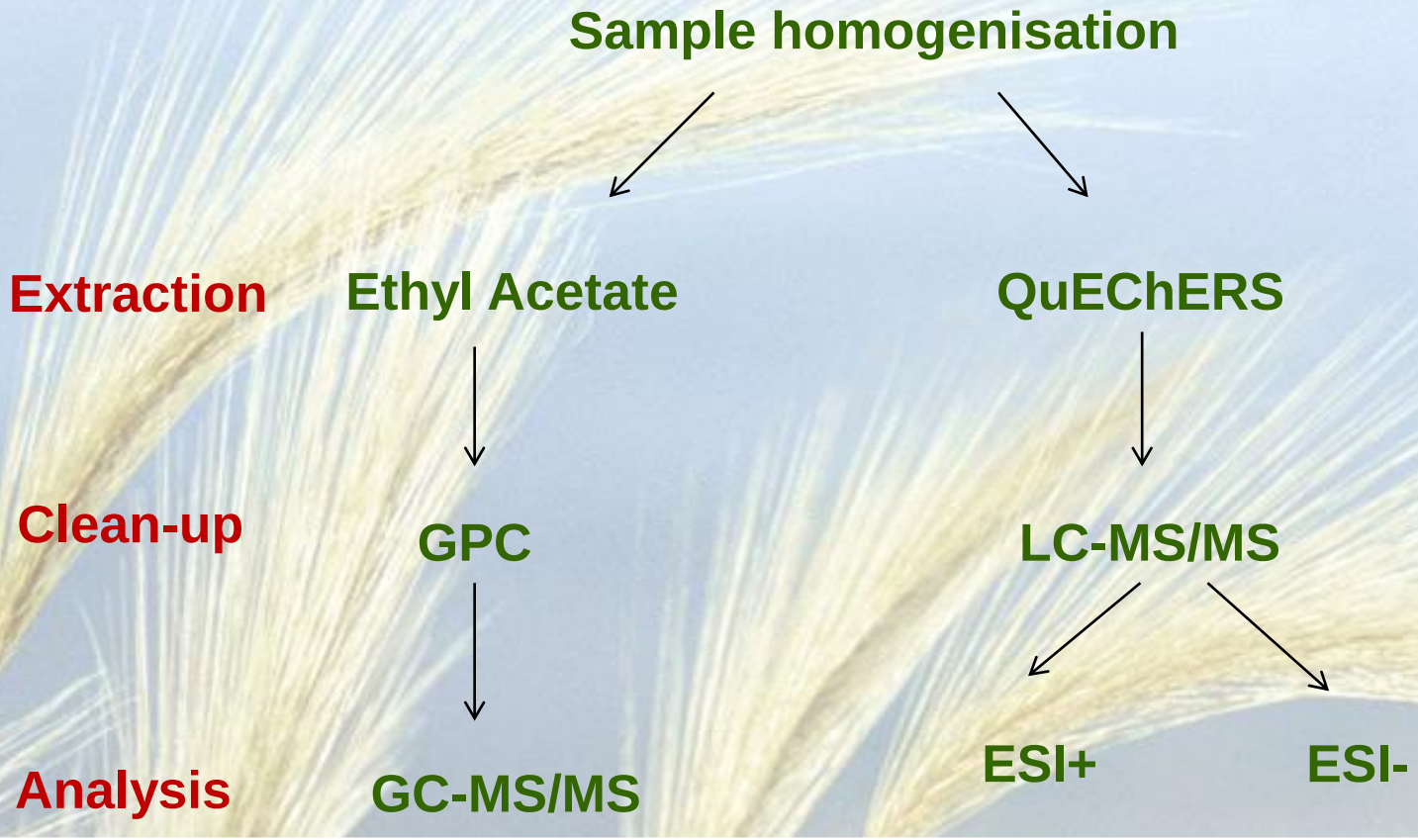
	Mean	s	% RSD		Mean	s	% RSD
2,4,5-T	90.2	17.5	19.4	Fipronil desulfynil	88.7	12.3	13.8
2,4-D	90.9	19.7	21.7	Fipronil sulfide	89.0	12.1	13.6
2,4-DB	106.0	13.9	13.1	Fipronil sulfone	90.1	12.6	14.0
Bentazone	100.8	19.5	19.3	Fluazifop	96.0	13.3	13.8
Bixafen	89.5	12.4	13.8	Fluazinam	89.7	12.8	14.2
Bromoxynil	94.8	10.5	11.0	Flubendiamide	85.9	12.0	13.9
Chlorfluazuron	94.1	10.9	11.6	Fludioxonil	93.4	10.5	11.3
Clethodim	32.8	23.9	72.6	Haloxyfop	101.1	15.5	15.3
Clothianidin	99.3	11.5	11.5	Hexaflumuron	95.5	12.3	12.9
Cyclanilide	94.5	14.8	15.6	Ioxynil	96.4	12.1	12.6
Cycloxydim	24.6	18.0	73.1	MCPA	93.0	15.8	17.0
Dichlorprop	97.0	14.2	14.6	MCPB	110.6	17.6	15.9
Diflubenzuron	91.6	12.2	13.3	Mecoprop	97.9	11.3	11.6
Dinoseb	93.1	10.8	11.6	Methoxyfenozide	92.1	11.6	12.6
Dinoterb	95.3	10.5	11.0	Quizalofop	98.8	15.7	15.8
DNOC	93.9	10.5	11.1	Sulfentrazone	97.9	12.0	12.2
Endosulfan sulfate	90.2	12.3	13.6	Teflubenzuron	91.5	12.2	13.4
Fenoprop (2,4,5 TP)	104.7	17.5	16.7	Triclopyr	97.7	28.7	29.4
Fipronil	89.1	11.9	13.4	Triflumuron	90.9	12.2	13.5

Cereals

- After the success with the fruit and veg method the attention was turned to cereals
- This method has always been problematic
- The method is prone to poor recoveries especially in matrices such as oats and wheat where the high fat content and the high starch content respectively have always caused issues with the extraction
- This means that an extra clean-up step (GPC) has always been required for GC work with cereals
- This adds an extra day to the analysis

Cereals

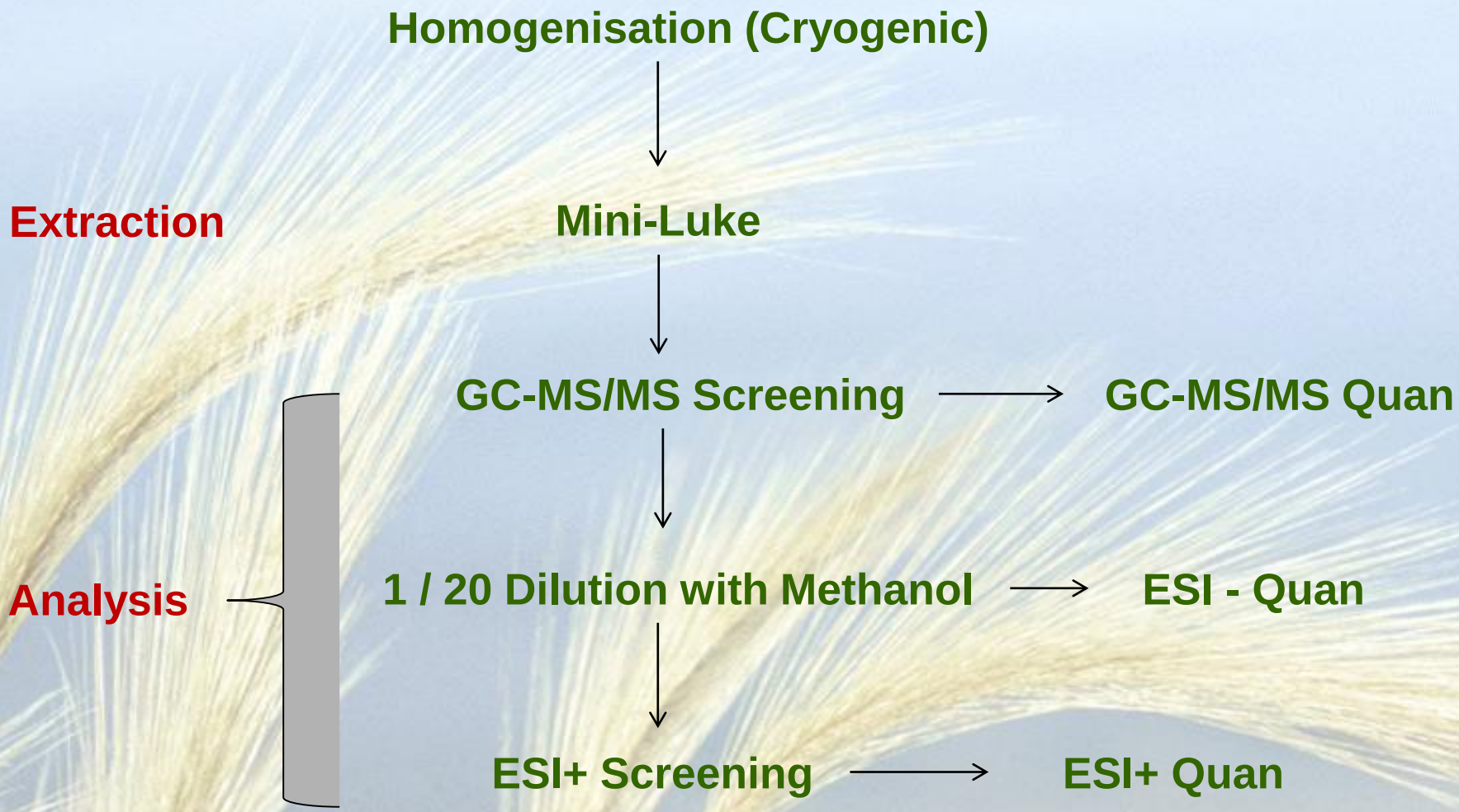
- **The analytical protocol in the PCL in 2010 was:**



Cereals

- The protocol is identical to that used for fruit and vegetables
- The screening acquisition method is used to collect all data in one sweep
- Calibration standards and recovery are only being run for what we expect to find
- If we have chosen correctly all positives should be in this mix
- We are still screening for the pesticides and metabolites we don't expect to find and if we get a positive we have to go back and re-analyse
- Only one extraction – MRL breaches have to be re-extracted and re-analysed
- The increased sensitivity of the LC-MS/MS is utilised to minimise matrix effects

New protocol



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Recovery work

ESI+ Mix 2 Reproducibility

Table 13 - LC Reproducibility

	Abamectin	Acetochlor	Acibenzolar-S-methyl	Aldicarb	Aldicarb-sulfone	Aldicarb-sulfoxide	Ametryn	Amidosulfuron	Aminocarb	Asulam	Atrazine	Atrazine-desethyl
10ppb RG	83.5	95.0	153.1	93.6	104.8	104.7	88.9	96.4	100.5	120.3	98.5	99.6
10ppb Cat	105.5	89.6	159.7	89.7	101.0	110.7	88.3	75.2	94.1	89.4	85.7	96.2
20ppb RG	74.5	83.2	134.5	86.5	93.0	89.9	82.6	80.8	88.1	74.6	83.2	86.3
20ppb Cat	111.7	88.8	152.6	85.9	95.0	107.5	91.0	89.2	91.4	74.8	92.3	94.2
50ppb RG	63.6	79.0	125.8	79.5	86.7	89.9	77.4	76.0	80.9	76.6	78.2	83.9
50ppb Cat	99.7	84.8	138.4	82.8	90.8	92.4	84.7	76.1	85.2	79.1	86.2	89.3
average	95.0	86.7	144.0	86.3	95.2	99.2	85.5	82.3	90.0	85.8	87.3	91.6
sd	15.5	5.6	13.1	5.0	6.7	9.5	5.0	8.7	6.9	17.7	7.2	6.1
%rsd	16.4	6.4	9.1	5.8	7.0	9.6	5.8	10.5	7.7	20.7	8.2	6.6

	Chlorotoluron	Chloroxuron	Chlorsulfuron	Clethodim	Clodinafop-propargyl	Clomazone	Clopyralid	Cyanazine	Cycloate	Cymiazol	DEET	Demeton-S-methyl-sulfoxide
10ppb RG	90.6	99.3	90.3	33.4	128.7	89.8	20959.7	103.8	89.8	80.5	77.7	113.6
10ppb Cat	89.7	84.4	75.3	40.2	129.6	93.1	269.2	90.4	98.3	66.7	59.3	103.4
20ppb RG	82.4	84.0	75.7	27.5	112.1	80.1	11996.6	87.6	85.4	59.9	80.5	95.7
20ppb Cat	88.7	81.2	85.0	22.2	123.6	86.7	4328.7	91.5	99.6	60.5	88.1	96.8
50ppb RG	77.2	73.7	76.1	20.6	100.5	77.6	5153.1	81.7	78.7	47.3	90.5	88.6
50ppb Cat	79.3	74.2	78.7	25.7	119.7	82.1	332.2	84.0	84.5	53.1	89.3	92.0
average	84.6	82.8	80.2	28.3	110.1	84.9	7173.2	89.8	89.4	61.3	85.2	98.3
sd	5.8	9.3	6.1	7.4	13.6	6.0	7999.6	7.8	8.2	11.5	5.7	9.0
%rsd	6.8	11.3	7.7	26.1	12.3	7.0	111.5	8.7	9.2	18.8	6.7	9.1

	DMST	EPTC	Ethiofencarb	Ethiofencarb-sulfone	Ethiofencarb-sulfoxide	Ethofumesate	Etrimfos	Fenamiphos	Fenamiphos-sulfone	Fenamiphos-sulfoxide	Fenothiocarb	Fenoxaprop-ethyl
10ppb RG												
10ppb Cat	98.3	77.0	50.4	101.6	172.4	96.6	92.4	91.4	111.1	105.4	85.3	108.9
20ppb RG	86.3	71.0	41.9	94.2	161.9	99.5	98.6	83.7	89.6	101.7	79.4	98.2
20ppb Cat	84.4	63.9	38.9	93.0	157.2	78.2	81.4	77.4	87.6	94.3	73.0	89.9
50ppb RG	85.2	81.6	40.8	97.8	179.0	86.3	93.7	81.7	97.5	110.9	80.3	92.6
50ppb Cat	78.7	53.9	29.2	96.6	171.1	73.5	77.1	69.5	84.0	95.5	67.3	87.6
average	83.4	70.8	32.1	101.2	175.9	81.2	88.0	76.5	88.9	102.4	76.6	89.9
sd	86.1	69.7	38.9	97.4	169.6	85.9	88.5	80.1	93.1	101.7	78.9	94.5
%rsd	6.6	9.8	7.5	3.6	8.4	10.4	8.1	7.4	9.9	6.2	4.6	7.9
	7.6	14.1	19.4	3.7	5.0	12.1	9.1	9.2	10.6	6.1	5.8	8.4

	Haloxyfop-methyl	Heptenophos	Imazamox	Imazaquin	Imazethapyr	Iodosulfuron-methyl	Isofenphos	Isoprocarb	Isoproturon	Lufenuron	Mefenpyr-Diethyl	Mephosfolan
10ppb RG	99.7	105.9	85.4	87.8	104.1	92.8	89.4	102.9	95.5	111.1	107.1	108.6
10ppb Cat	98.4	99.5	85.1	80.0	92.3	88.8	94.2	84.0	86.3	107.8	106.5	99.4
20ppb RG	87.8	93.1	70.1	78.0	86.2	82.5	75.9	86.4	81.5	98.8	94.1	92.4
20ppb Cat	95.1	94.6	77.6	83.8	104.6	89.1	95.2	87.8	85.0	99.7	101.0	100.6
50ppb RG	78.5	86.1	66.0	69.6	76.8	79.3	72.2	83.3	77.6	95.7	88.4	88.7
50ppb Cat	88.4	90.1	69.9	82.1	82.7	82.9	86.6	82.2	81.7	98.9	96.7	92.5
average	91.3	94.9	77.6	80.2	91.1	85.9	85.6	87.8	84.6	102.0	99.0	97.0
sd	8.0	7.0	7.6	6.2	11.4	5.1	9.5	7.7	6.1	6.0	7.3	7.2
%rsd	8.7	7.4	9.8	7.7	12.5	5.9	11.1	8.8	7.2	5.9	7.4	7.5

	Naptalam	Neburon	Nicosulfuron	Nitenpyram	Oxadiazon	Oxyfluorfen	Paraoxon-ethyl	Pethoxamid	Phorate	Phorate Sulfoxide	Phoxim	Picloram
10ppb RG	93.6	101.0	101.1	106.7	112.4	110.1	90.6	100.4	108.5	364.4	127.9	33.1
10ppb Cat	72.3	96.7	77.6	108.9	102.0	118.5	87.2	90.0	85.0	235.3	141.2	229.2
20ppb RG	74.2	88.1	76.2	96.8	95.9	97.0	77.7	83.4	93.6	329.0	111.9	4.8
20ppb Cat	76.4	92.2	80.9	109.8	99.7	94.8	81.7	91.4	116.5	345.9	130.4	40.1
50ppb RG	64.3	81.3	73.6	94.6	89.4	99.6	72.7	79.2	78.9	330.1	105.2	9.8
50ppb Cat	64.7	87.4	74.0	103.4	97.4	94.9	76.1	85.5	93.7	317.6	120.9	12.1
average	74.3	91.1	80.6	103.4	99.5	102.5	81.0	88.3	96.0	320.4	122.9	54.9
sd	10.7	7.1	10.4	6.4	7.6	9.7	6.9	7.4	14.1	44.7	13.1	86.5
%rsd	14.4	7.7	12.9	6.2	7.7	9.5	8.5	8.4	14.7	14.0	10.6	157.8

	Quinclorac	Quizalofop-ethyl	Rimsulfuron	Rotenone	Simazine	Simetryn	Sulfotep	Sulprofos	Terbufos	Terbumeton	Terbuthylazine-2-hydroxy	Terbuthylazine-desethyl
10ppb RG	38.8	108.3	202.7	117.7	100.2	92.6	104.0	71.5	82.1	102.2	79.1	97.9
10ppb Cat	66.7	100.4	222.9	103.8	87.6	89.2	108.2	96.9	92.6	98.3	75.2	92.1
20ppb RG	23.3	92.5	163.0	102.1	86.7	82.1	94.2	65.8	79.5	88.0	61.3	81.3
20ppb Cat	35.3	94.9	177.5	105.5	90.3	89.9	99.4	78.0	86.9	89.4	74.9	84.5
50ppb RG	22.4	86.8	136.8	98.6	82.5	79.4	86.2	57.4	76.1	78.5	56.4	77.7
50ppb Cat	26.0	91.3	154.9	103.3	85.1	87.6	94.4	74.1	81.8	85.0	66.1	81.5
average	35.4	95.7	176.3	105.1	88.7	86.8	97.7	73.9	83.2	90.2	68.8	85.8
sd	16.7	7.6	31.8	6.6	6.2	5.0	7.8	13.4	5.8	8.7	9.0	7.6
%rsd	47.2	7.9	18.0	6.2	7.0	5.8	8.0	18.1	7.0	9.6	13.0	8.9

Recovery work

ESI+ Mix 2 Reproducibility

Atrazine-desisopropyl	Benthiavalicarb-isopropyl	Benzoximate	Bioresmethrin	Bromuconazole I	Bromuconazole II	Butocarboxim Sulfoxide	Butoxycarboxim	Cadusafos	Carboxin	Carfentrazone-ethyl	Chlorbromuron	Chloridazon
97.0	100.6	99.9	77.2	93.6	108.2	92.1	105.4	100.7	64.4	110.4	105.8	98.2
93.0	94.9	94.1	87.4	98.3	90.9	99.3	98.2	90.9	62.7	106.9	100.8	86.5
77.5	86.6	91.0	76.4	78.9	83.4	78.2	87.7	86.7	55.2	98.3	89.9	81.9
86.1	90.6	99.4	79.8	81.7	85.5	88.8	97.5	88.7	47.0	105.6	88.7	85.6
78.5	79.0	84.3	70.1	74.1	76.3	77.7	92.1	77.3	42.5	89.8	81.2	79.6
83.5	84.9	90.8	74.9	75.5	82.0	86.6	83.4	86.9	45.7	96.4	83.2	81.9
86.0	89.4	93.3	77.6	83.7	87.7	87.1	94.1	88.5	52.9	101.2	91.6	85.6
7.8	7.6	5.9	5.8	10.0	11.1	8.3	7.9	7.5	9.3	7.7	9.8	6.7
9.1	8.5	6.3	7.4	11.9	12.7	9.5	8.4	8.5	17.5	7.6	10.7	7.8

Desmedipham	Dichlofenthion	Diclobutrazol	Dicrotophos	Diflufenican	Dimethenamid	Diniconazole	Dinitramine	Dioxacarb	Diphenamid	Ditalimfos	Diuron	DMSA
97.1	103.4	93.4	105.1	106.4	102.6	99.1	178.5	98.3	93.7	101.0	85.4	102.5
94.6	101.7	88.7	94.7	106.2	88.6	95.8	195.0	95.7	78.6	109.7	76.5	92.6
83.8	96.2	72.2	90.2	86.7	83.3	82.2	161.7	87.0	81.4	90.1	75.1	89.4
86.4	96.5	80.0	97.6	93.9	86.8	92.1	180.4	95.9	85.6	98.8	83.0	93.2
79.8	89.9	82.7	87.4	78.6	77.4	76.4	164.9	86.4	77.3	79.8	69.5	84.6
83.5	100.9	78.0	94.6	97.0	84.3	86.0	172.7	88.0	79.8	88.8	75.6	87.0
87.5	98.1	82.5	94.9	94.8	87.2	88.6	175.5	91.9	82.7	94.7	77.5	91.5
6.8	5.0	8.5	6.2	10.9	8.5	8.6	12.0	5.3	6.1	10.6	5.8	6.3
7.8	5.1	10.3	6.5	11.5	9.7	9.7	6.8	5.8	7.4	11.2	7.4	6.8

Fenpiclonil	Fenuron	Flamprop-isopropyl	Flazasulfuron	Florasulam	Fluazifop-P-butyl	Flucycloxuron	Flufenacet	Flurochloridone	Forchlorfenuron	Fuberidazole	Furathiocarb	Furmecyclox
97.7	101.3	103.8	139.3	94.6	101.1	77.5	96.7	95.9	84.7	90.5	99.1	58.4
88.7	95.6	94.9	124.7	80.8	101.0	97.3	88.8	95.9	67.2	91.3	95.8	64.8
83.1	91.8	90.1	110.4	90.4	85.8	63.7	81.2	87.5	64.6	79.7	86.1	54.9
85.3	101.6	94.7	120.7	96.1	94.3	95.2	87.5	91.5	72.2	83.9	87.9	70.3
80.5	96.6	83.7	99.6	84.8	84.9	59.3	76.6	81.0	57.7	76.7	86.7	52.6
84.6	99.8	90.0	102.3	90.1	88.5	91.3	85.3	90.2	63.5	74.8	87.6	73.1
86.6	97.8	92.9	100.9	89.5	92.6	80.7	86.0	90.3	68.3	82.8	90.5	62.3
6.1	3.8	6.7	1.9	5.8	7.3	16.5	6.9	5.6	9.3	7.0	5.5	8.4
7.0	3.9	7.2	1.9	6.5	7.9	20.4	8.0	6.3	13.7	8.4	6.1	13.4

Mepronil	Mesosulfuron methyl	Metazachlor	Metconazole	Methamidophos	Methoprene	Metobromuron	Metolachlor	Metosulam	Metoxuron	Metsulfuron-methyl	Monolinuron	Napropamide
98.0	116.0	99.8	103.6	84.4	56.1	90.0	100.1	93.2	98.7	107.1	101.8	103.0
97.9	110.6	82.0	93.2	83.6	62.5	81.2	94.1	87.8	91.9	96.0	88.7	92.5
85.8	99.9	85.5	82.7	73.7	44.2	79.6	86.3	85.0	89.1	90.5	89.6	89.7
87.6	110.8	87.9	89.5	77.5	67.4	88.6	87.9	89.1	93.1	98.1	89.3	92.1
79.5	93.8	77.9	77.5	67.8	35.8	76.1	74.8	81.3	82.5	87.5	84.1	80.8
83.3	98.2	85.1	84.4	72.0	62.4	81.7	83.3	82.9	84.3	87.5	86.9	89.0
88.7	104.9	86.4	88.5	76.5	54.7	82.9	87.8	86.5	89.9	94.5	90.1	91.2
7.7	8.8	7.4	9.2	6.6	12.3	5.4	8.7	4.4	6.0	7.6	6.1	7.2
8.6	8.3	8.6	10.4	8.6	22.4	6.5	9.9	5.0	6.7	8.0	6.7	7.9

Picoxystrobin	Promecarb	Promethryn	Prometon	Propaquizafop	Propazine	Propoxur	Propoxycarbazone	Prosulfuron	Pyrazophos	Pyridaben	Pyridaphenthion	Quinalphos
98.0	91.8	105.9	104.4	111.5	101.7	104.8	116.4	89.7	108.8	100.7	104.1	103.9
90.4	82.3	95.9	95.1	104.8	91.3	94.7	104.4	77.2	100.9	108.1	100.9	106.1
87.2	79.3	93.0	89.6	99.2	88.2	89.5	97.1	72.0	91.9	97.3	87.3	92.8
94.4	86.2	94.9	92.8	99.3	90.5	95.8	105.9	76.1	97.9	107.4	92.2	98.8
82.8	74.9	84.4	78.5	92.0	78.6	83.6	92.4	73.8	86.4	87.8	82.6	85.3
91.6	85.5	90.9	86.0	96.9	86.9	90.4	84.8	74.2	94.1	99.5	86.3	91.3
90.7	83.3	94.2	91.1	100.6	89.5	93.1	100.2	77.2	96.7	100.1	91.0	96.4
5.3	5.9	7.1	8.8	6.7	7.5	7.2	11.1	6.4	7.8	7.4	7.6	8.0
5.9	7.1	7.5	9.6	6.7	8.4	7.7	11.1	8.3	8.1	7.4	8.3	8.3

Terbutryn	Thifensulfuron-methyl	Thiobencarb	Thionazin	Topramezone	Tri-Allat	Triasulfuron	Trichlorfon	Triflumizole	Triflusulfuron-methyl	Triticonazole	Vamidothion
100.9	103.8	98.9	94.0	59.2	101.6	110.3	166.8	132.2	2913.4	87.9	95.8
97.6	94.6	95.4	94.2	55.5	106.3	94.2	159.5	109.3	2973.1	90.5	100.3
87.7	93.5	87.4	80.4	31.1	89.6	96.1	164.0	113.2	3170.5	70.8	88.0
94.7	105.1	95.1	92.6	62.8	100.6	106.9	166.4	107.8	3506.2	87.2	87.4
81.8	93.8	82.7	80.0	29.2	84.1	91.2	160.0	100.1	2911.5	65.1	79.8
87.9	90.3	89.7	82.2	32.5	92.6	97.4	161.9	106.0	3158.3	80.8	82.3
91.8	96.9	91.5	87.2	41.7	95.8	99.3	163.1	107.3	3105.5	80.4	88.9
7.2	6.1	6.0	7.1	13.0	8.4	7.5	3.2	4.8	227.9	10.3	7.8
7.8	6.3	6.6	8.1	31.3	8.8	7.6	1.9	4.5	7.3	12.8	8.8

The Pesticide Control Laboratory

Department of Agriculture, Food and the Marine
An Roinn Talmhaíochta, Bia agus Mara

Proficiency work

- In the case of cereals very few positives are found in routine work.
- To get data for incurred residues we went back and re-analysed proficiency studies from previous years
- The results and z-scores are given on the next slide
- In general these results are very good

Proficiency work

Table 16 - Extracted EUPT results

EUPT C4 (rye flour)

	Result	Assigned value	s	z
2,4 D	0.11	0.355	0.09	-2.76
Azoxystrobin	0.17	0.316	0.08	-1.85
Carbaryl	0.14	0.16	0.04	-0.50
Carbendazim	1.28	1.28	0.32	0.00
Chlorpyrifos methyl	0.1	0.125	0.03	-0.80
Deltamethrin	0.052	0.061	0.02	-0.59
Fenitrothion	0.16	0.188	0.05	-0.60
Fenpropimorph	1.64	2.1	0.53	-0.88
Fluquinconazole	1.07	0.74	0.19	1.78
Flutriafol	1.1	2.18	0.55	-1.98
Isoproturon	0.13	0.164	0.04	-0.83
Kresoxim methyl	0.25	0.396	0.10	-1.47
lambda Cyhalothin	0.047	0.065	0.02	-1.11
Malathion	0.067	0.109	0.03	-1.54
Pirimiphos methyl	0.055	0.078	0.02	-1.18
Spiroxamine	0.54	1.1	0.28	-2.04
Triademenol	1.29	1.62	0.41	-0.81

where 2,4 D is giving a recovery of 60% - if corrected for recovery - 0.18ppm z score: -1.56

EUPT C6 (barley)

	Result	Assigned value	s	z
Azoxystrobin	0.10	0.19	0.05	-1.98
Boscalid	0.56	0.89	0.22	-1.47
Carbendazim	0.22	0.22	0.06	-0.02
Carboxim	0.08	0.14	0.04	-1.75
Chlorpropham	0.16	0.23	0.06	-1.26
Chlorpyrifos	0.15	0.17	0.04	-0.47
Cypermethrim	0.19	0.28	0.07	-1.32
Cyprodinil	0.14	0.15	0.04	-0.24
Diflubenzuron	0.10	0.13	0.03	-0.97
Epoxiconazole	0.35	0.58	0.14	-1.57
Fenpropidin	0.61	0.93	0.23	-1.37
Isoprothiolane	0.06	0.08	0.02	-1.02
Pendimethilin	0.07	0.11	0.03	-1.37
Pirimicarb	0.30	0.25	0.06	0.78
Propiconazole	0.10	0.20	0.05	-2.02
Prothioconazole-desthio	0.06	0.09	0.02	-1.47
Pyraclostrobin	0.29	0.47	0.12	-1.51
Tebuconazole	0.28	0.42	0.11	-1.35

EUPT C8 (wheat flour)

	Result	Assigned value	s	z
Azoxystrobin	0.20	0.23	0.06	-0.49
Bixafen	0.06	0.08	0.02	-1.01
Boscalid	0.29	0.33	0.08	-0.46
Carbendazim	0.08	0.07	0.02	0.11
Chlorothalonil	0.02	0.04	0.01	-1.81
Cypermethrin	0.65	0.77	0.19	-0.61
Deltamethrin	0.04	0.04	0.01	-0.20
Endosulfan-sulfate	0.04	0.04	0.01	0.10
Epoxyconizole	0.09	0.12	0.03	-1.03
Flonicamid	0.09	0.10	0.03	-0.65
Fluxapyroxad	0.13	0.17	0.04	-0.85
Lindane	0.02	0.04	0.01	-2.21
Linuron	0.06	0.07	0.02	-0.70
Metconazole	0.07	0.10	0.03	-1.11
Metrafenone	0.35	0.38	0.09	-0.28
Prothioconazole-desthio	0.16	0.20	0.05	-0.82
Pyraclostrobin	0.05	0.07	0.02	-1.19
Spiroxamine	0.04	0.06	0.02	-1.07
Trifluralin	0.04	0.04	0.01	-0.10

where b-HCH and lindane are co-eluting

EUPT C8 (wheat flour)

	Result	Assigned value	s	z
Azoxystrobin	0.20	0.23	0.06	-0.49
Bixafen	0.06	0.08	0.02	-1.01
Boscalid	0.29	0.33	0.08	-0.46
Carbendazim	0.08	0.07	0.02	0.11
Chlorothalonil	0.02	0.04	0.01	-1.81
Cypermethrin	0.65	0.77	0.19	-0.61
Deltamethrin	0.04	0.04	0.01	-0.20
Endosulfan-sulfate	0.04	0.04	0.01	0.10
Epoxyconizole	0.09	0.12	0.03	-1.03
Flonicamid	0.09	0.10	0.03	-0.65
Fluxapyroxad	0.13	0.17	0.04	-0.85
Lindane	0.02	0.04	0.01	-2.21
Linuron	0.06	0.07	0.02	-0.70
Metconazole	0.07	0.10	0.03	-1.11
Metrafenone	0.35	0.38	0.09	-0.28
Prothioconazole-desthio	0.16	0.20	0.05	-0.82
Pyraclostrobin	0.05	0.07	0.02	-1.19
Spiroxamine	0.04	0.06	0.02	-1.07
Trifluralin	0.04	0.04	0.01	-0.10

where b-HCH and lindane are co-eluting

Conclusion

- This protocol provides a mechanism for expanding the pesticide scope in a logical and systematic way
- Provided that new pesticides don't all fall in the crowded area of the chromatogram the capacity of the GC and LC triple quads have not yet been reached
- There is a quantitative element to the screening which is essential for pesticide residue analysis
- The protocol takes into account the extraction efficiency of the pesticides
- The only downside is that because there is only one extraction route MRL breaches and invalid uses must be re-extracted and re-analysed


THANK YOU!