# QuEChERS Validation Method for acidic pesticides


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# Outline

- Overview: acidic pesticides
- Interlaboratory method validation experiment 2006
- alkaline hydrolysis
- Conclusion

# Acidic pesticides

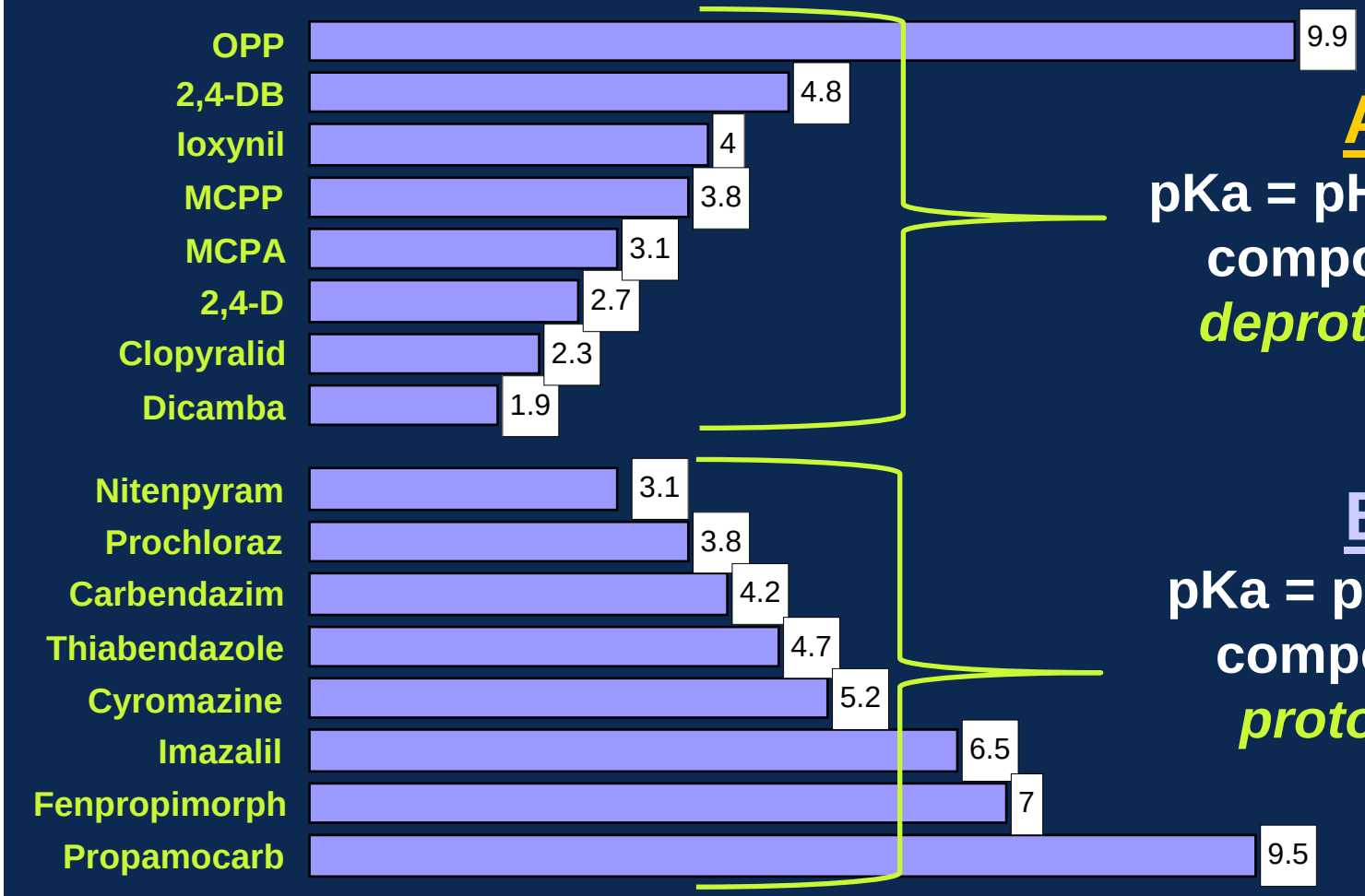
pH-issue: Ionization of pesticides at low or high pH-values

- **Acids:** $HX \leftrightarrows H^+ + X^-$
- **Bases:** $B + H^+ \leftrightarrows BH^+$

⇨ **Ionic form prefers to stay in the water phase**

**pH-range of agricultural samples: ~2.5 – 7**

# Acidic pesticides – pKa-values




## Acids

pKa = pH *above* which compounds lay in *deprotonized* form

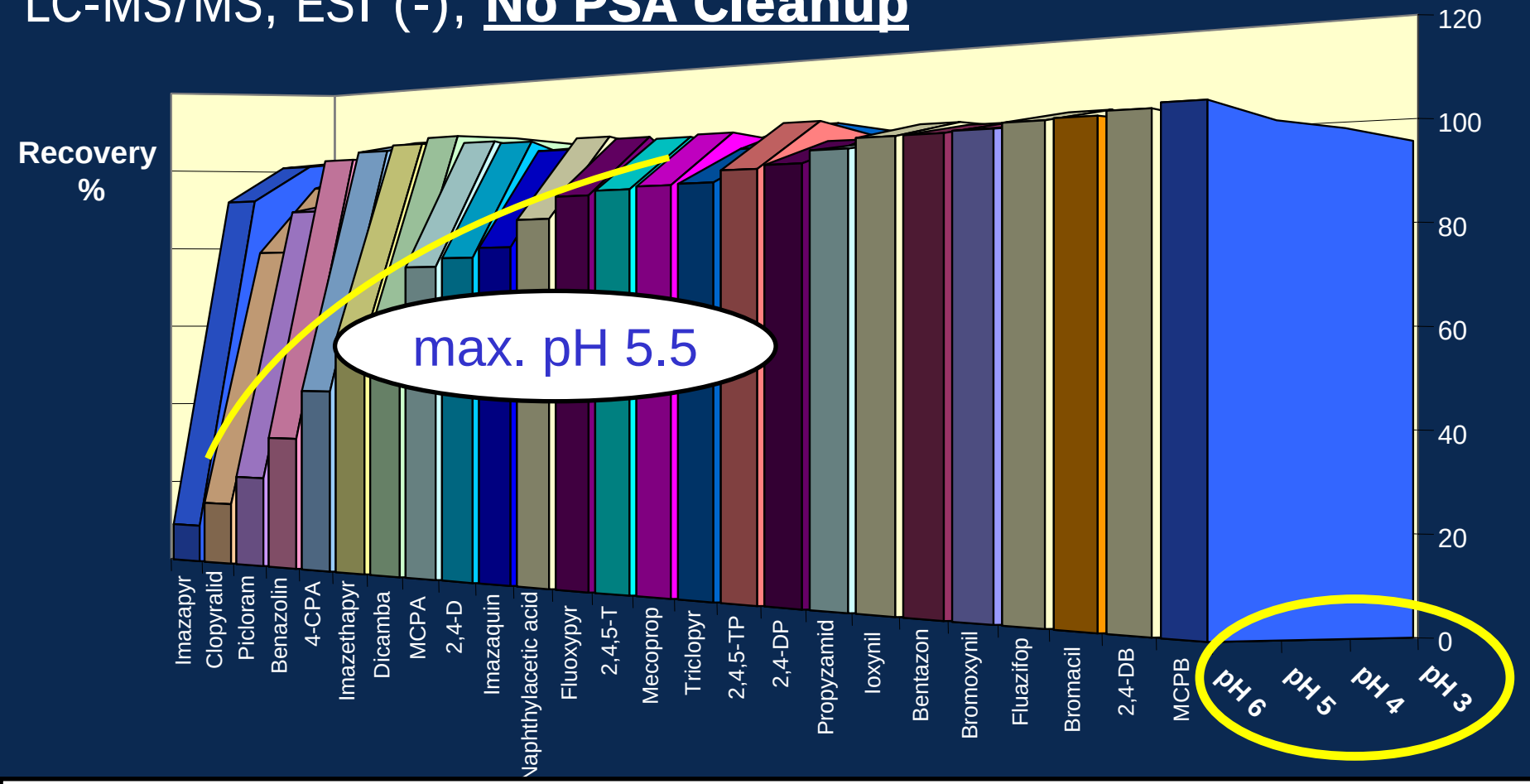
## Bases

pKa = pH *below* which compounds lay in *protonized* form

**pH-adjustment 1-2 units > or < pKa is recommended for quantitative recoveries**

# Acidic pesticides – influence of pH on recovery

## LC-MS/MS, ESI (-), **No PSA Cleanup**

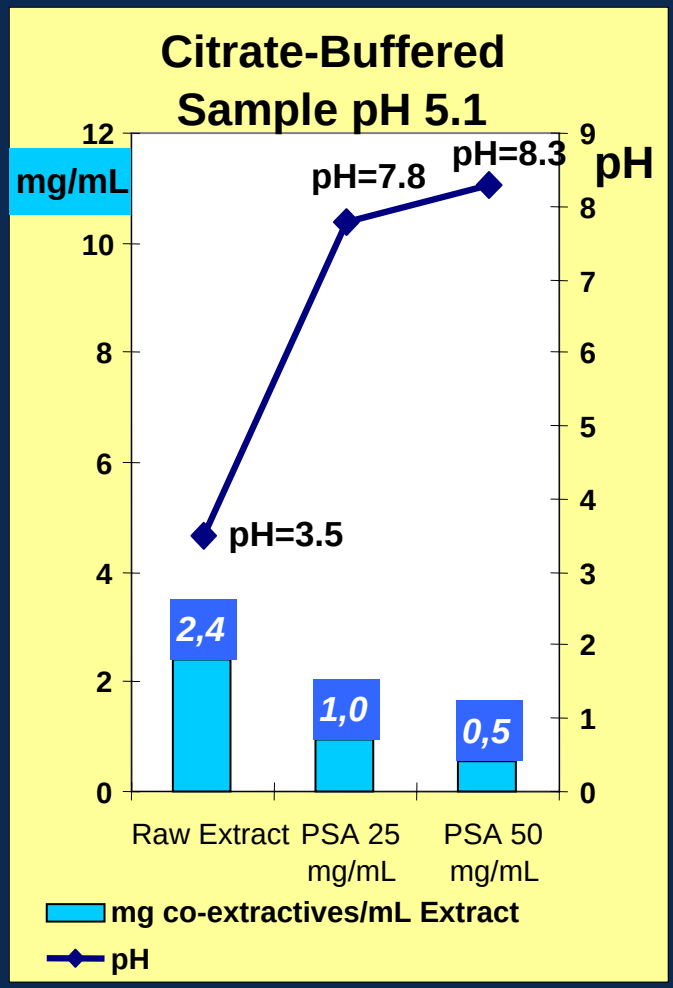



**lower pKa ← general trend → higher pKa**

# Acidic pesticides – cleanup issue

Example: Extract of red currant

- Losses of acidic components after cleanup
- Acidic compounds interact with PSA

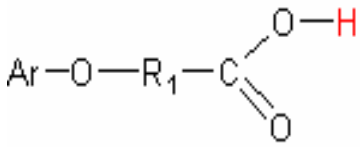
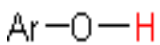
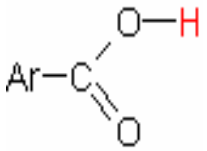
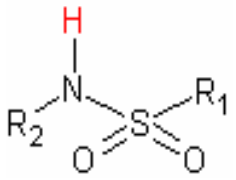


# Acidic pesticides – including into QuEChERS

QuEChERS has to be modified,
to include acidic pesticides

- Avoid special cleanup procedures
- Special conditions during extraction and chromatography

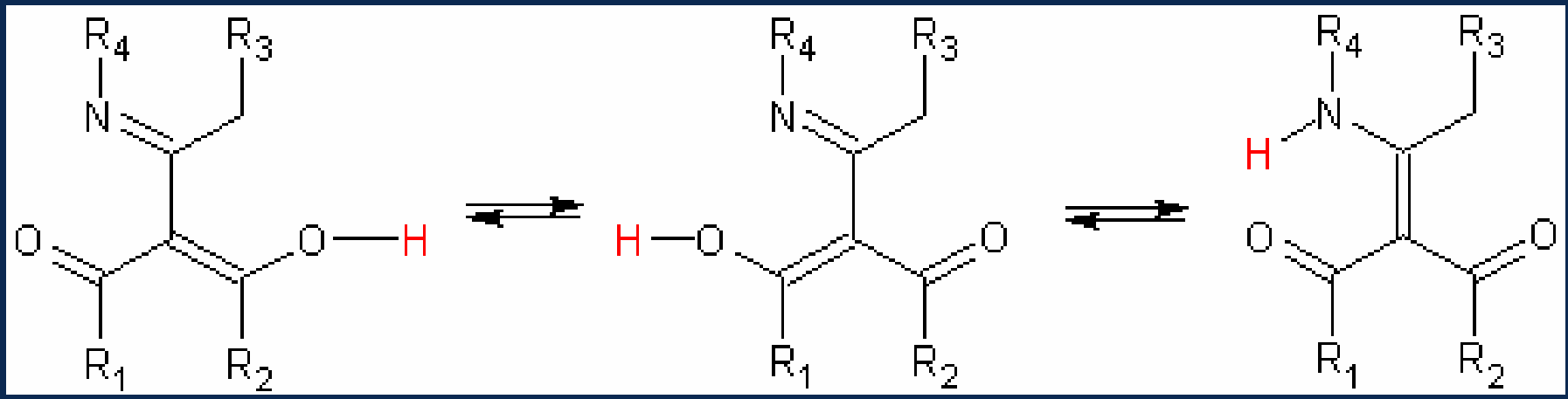
# Acidic pesticides – pesticide list

| Compound | pKa-value | Chemical Class | acidic structure |
|---|---|---|---|
| 2,4,5-T | 2,85 | phenoxyalcanoic acid |  |
| 2,4,5-TP | 2,84 | | |
| 2,4-D | 2,73 | | |
| 2,4-DB | 4,8 | | |
| 2,4-DP | 3,67 | | |
| 4-CPA | 3,56 | | |
| Fenoxaprop-P | 3,2 | | |
| Fluazifop | 3,2 | | |
| Fluazifop-P-Butyl | 3,1 | | |
| Haloxyfop | 2,9 | | |
| MCPA | 3,07 | | |
| MCPB | 4,84 | | |
| MCPP | 3,78 | | |
| Fluroxypyr | 2,94 | pyridine herbicide | |
| Triclopyr | 3,97 | | |
| Naphthoxyacetic acid, 2- | | naphthoxyacetic herbicide | |
| Bromoxynil | 3,86 | phenolic herbicide |  |
| Ioxynil | 3,96 | | |
| Clopyralid | 2 | pyridine herbicide |  |
| Dicamba | 1,97 | benzoic acid | |
| Imazapyr | 1,9 | imidazolinone herbicide | |
| Imazaquin | 3,8 | | |
| Imazethapyr | 2,1 | | |
| Quinmerac | 4,32 | quinolinecarboxylic acid | |
| Picloram | 2,3 | pyridine herbicide | |
| Bentazone | 3,3 | unclassified |  |
| Fomesafen | 2,83 | amide herbicide | |
| Imazosulfuron | 4 | pyrimidinylsulfonylurea herbicides | |
| Thifensulfuron-Methyl | 4 | triazinylsulfonylurea herbicides | |
| Metsulfuron-Methyl | 3,3 | | |
| Metosulam | 4,8 | sulfonanilide herbicide | |
| Cycloxydim | 4,17 | cyclohexene oxime herbicide | special case |
| Fludioxonil | | | no acid |

# Acidic pesticides – pesticide list

## Cycloxidim

- Three mesomeric structures
- Difficult chromatogramic behaviour



# Acidic pesticides - findings

Relatively often found:

- Fluazifop
- 2,4-D

| | N° of samples with positive findings 2004 - 2007 | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Pesticide | CITRUS & POME FRUIT | LEAFY VEGET. | FRUITING VEGET. | CEREALS | LEGUMES | ROOT & TUBER | ALL COMMOD. | Annex I 91/414 |
| Fludioxonil | 45 | 297 | 651 | | 7 | 10 | 3283 | Pending |
| Fluazifop | 1 | 125 | 47 | | 9 | 85 | 421 | Out |
| 2,4-D | 98 | 17 | 7 | 1 | | 1 | 314 | In |
| Haloxyfop | 1 | 44 | 5 | | 2 | 6 | 146 | Out |
| Bentazone | | 72 | | | 1 | | 94 | In |
| MCPA | | 6 | 1 | | | | 81 | In |
| Clopyralid | | 30 | | 1 | | | 49 | In |
| Dicamba | | 8 | | 4 | | | 31 | Pending |
| 2,4-DP | 14 | 2 | | | | | 25 | In |
| MCPP | 2 | 2 | | | | | 24 | Pending |
| 4-CPA | | | 18 | | | | 18 | Pending |
| Naphthoxyacetic acid, 2- | 1 | | 16 | | | | 18 | pending |
| Bromoxynil | | 10 | | | | | 16 | In |
| Triclopyr | | 2 | | | | | 9 | |
| Imazaquin | | | | | | | 7 | Pending |
| 2,4,5-T | 1 | | | | | | 6 | In |
| Quinmerac | 1 | | | | | | 3 | |
| Fluroxypyr | | | | | | 1 | 2 | In |
| Ioxynil | | 2 | | | | | 2 | In |
| 2,4-DB | | | | | | | 1 | In |
| Cycloxydim | | | | | | | 1 | Pending |
| Metosulam | | | 1 | | | | 1 | Pending |
| 2,4,5-TP | | | | | | | | In |
| Fenoxaprop-P | | | | | | | | Pending |
| Formesafen | | | | | | | | |
| Imazapyr | | | | | | | | Out |
| Imazethapyr | | | | | | | | Out |
| Imazosulfuron | | | | | | | | In |
| MCPB | | | | | | | | Out |
| Metsulfuron-Methyl | | | | | | | | |
| Picloram | | | | | | | | Out |
| Thifensulfuron-Methyl | | | | | | | | In |

# Method Validation Experiment 2006 - facts

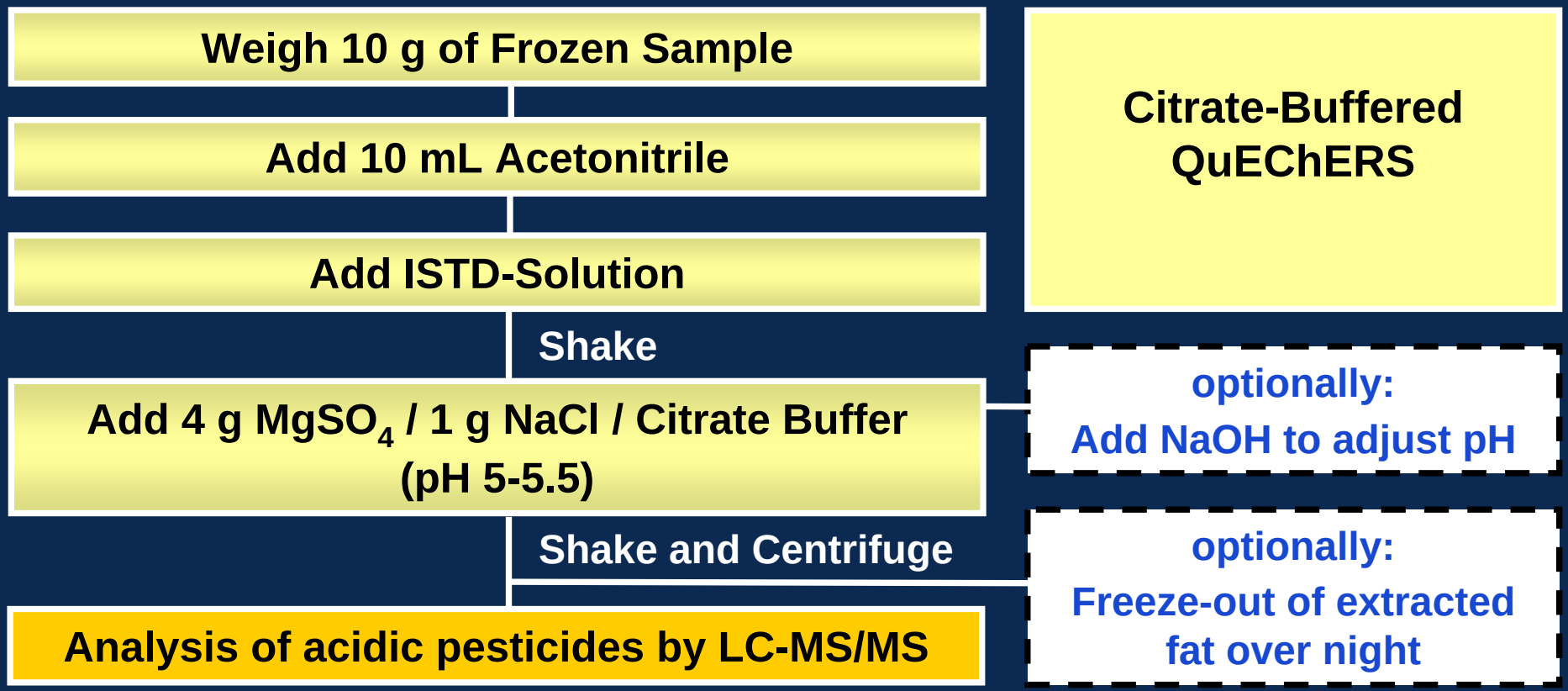
Method validation experiment

Modified QuEChERS without PSA-cleanup

August 2006:

- 19 Labs expressed interest from 9 Countries (Germany, Latvia, Spain, Czech Republic, Switzerland, Finland, Austria, The Netherlands and Great Britain)
- 4 Matrices (Raisins, Cucumber, Lemon, Wheat Flour)
- 32 Pesticides (LC-MS/MS, ESI pos and neg) with 2 Levels (0.1 and 0.01 mg/kg)

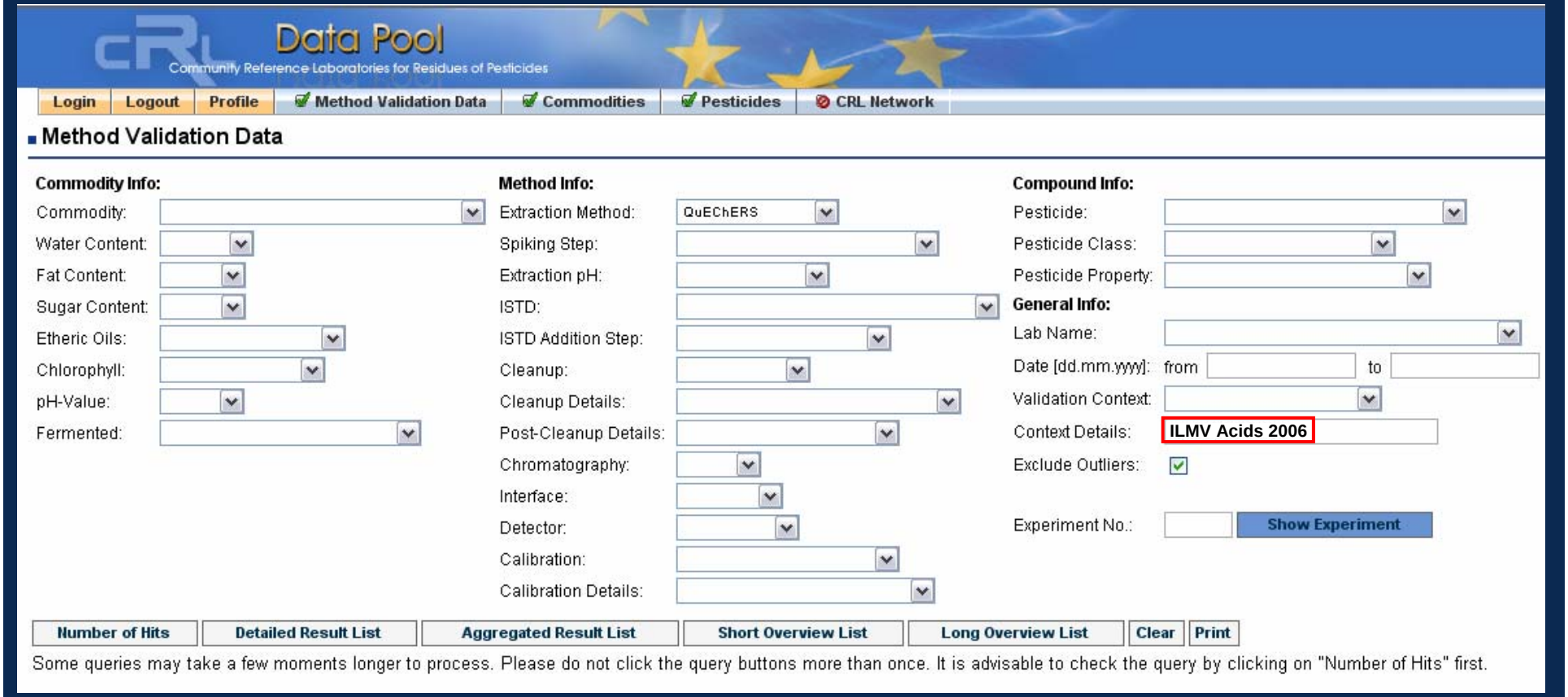
# QuEChERS – schematic method description



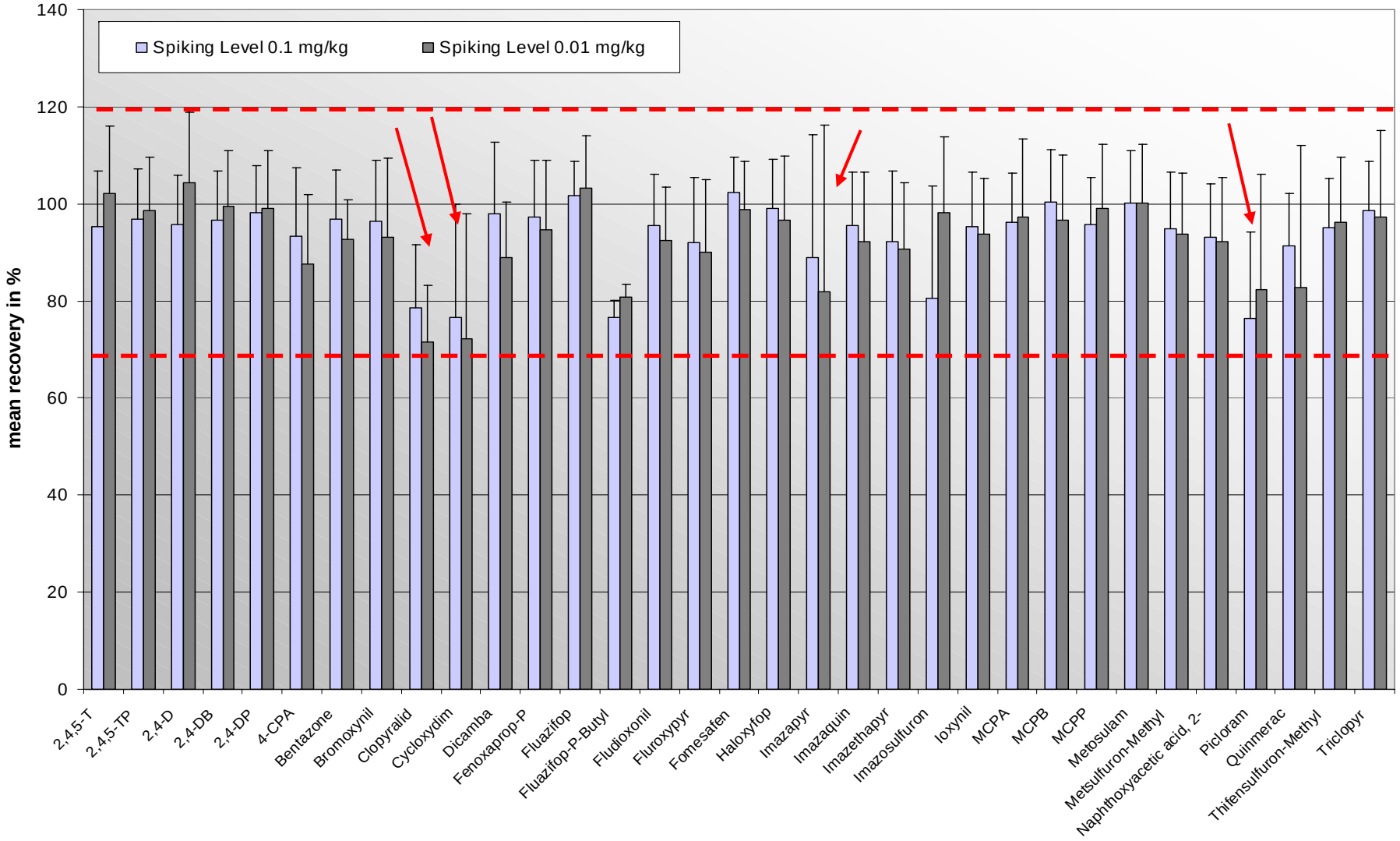
# Interlab. Method Validation Experiment - evaluation

Collection of data and evaluation

- www.crl-pesticides-datapool.eu



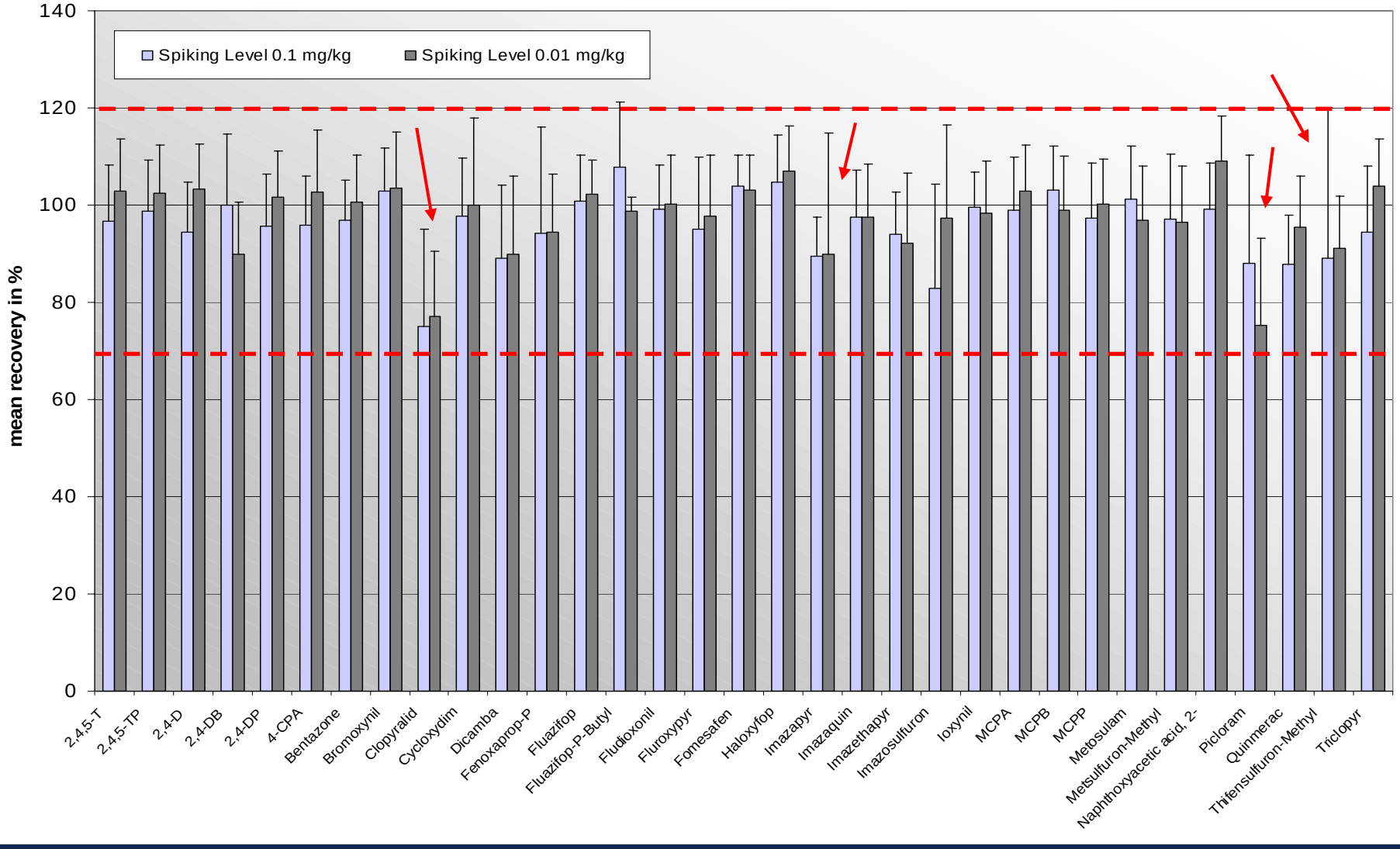
# ILMV 2006 Acids – Results Cucumber



## Cucumber

- High water content
- Satisfying results for all pesticides
- Slightly problematic (mean recovery) for:
  - Clopyralid
  - Cycloxydim
  - Picloram
- RSD > 20% for:
  - Imazapyr
  - Cycloxydim
  - Picloram

# ILMV 2006 Acids – Results Lemon

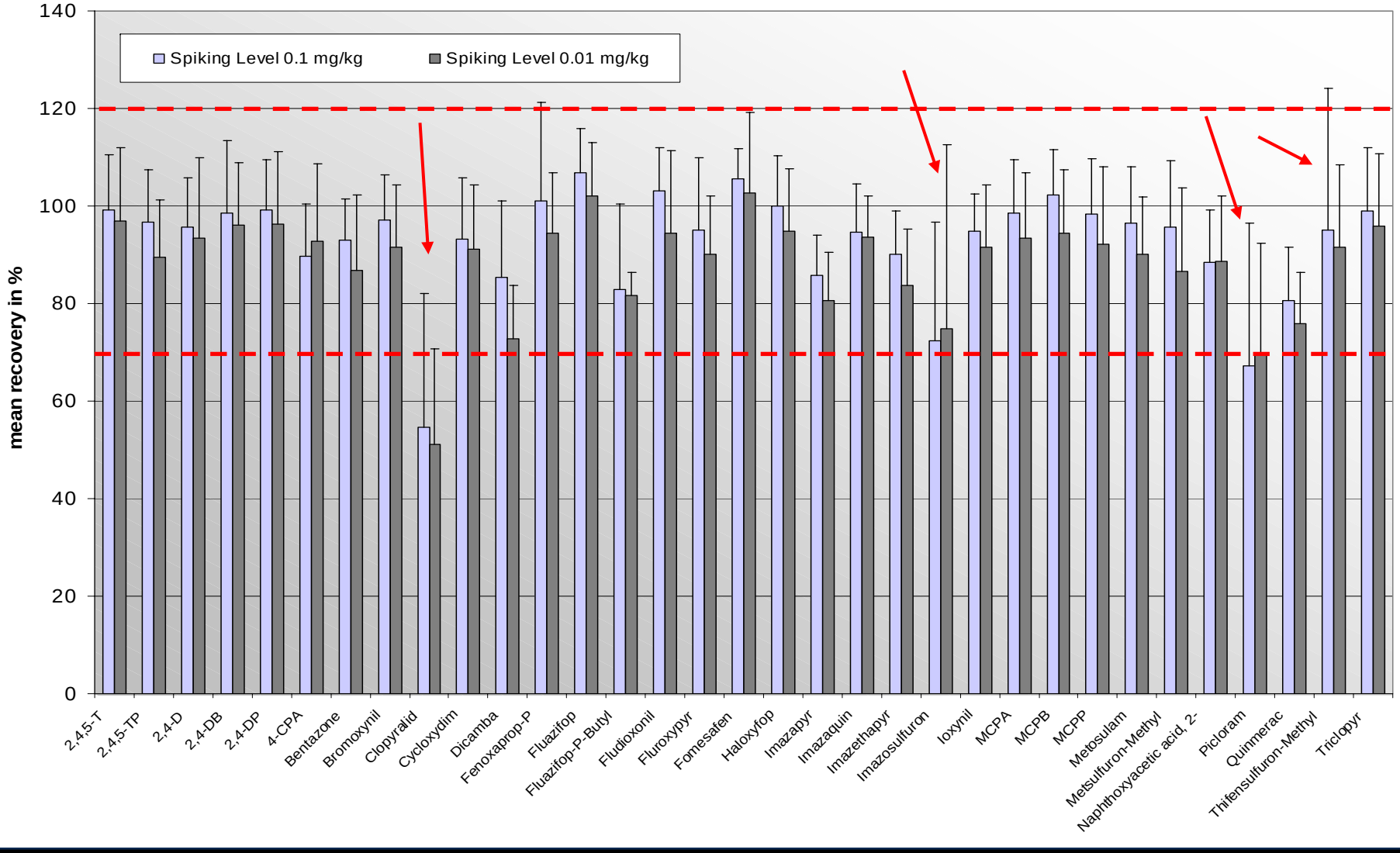


## ILMV 2006 Acids – Results Lemon

### Lemon

- Acidic matrix
- Satisfying results for most pesticides
- Slightly problematic (mean recovery) for:
  - Clopyralid
  - Picloram
- RSD > 20% for:
  - Imazapyr (only 0.01 mg/kg)
  - Picloram
  - Thifensulfuron-Methyl (only 0.1 mg/kg)

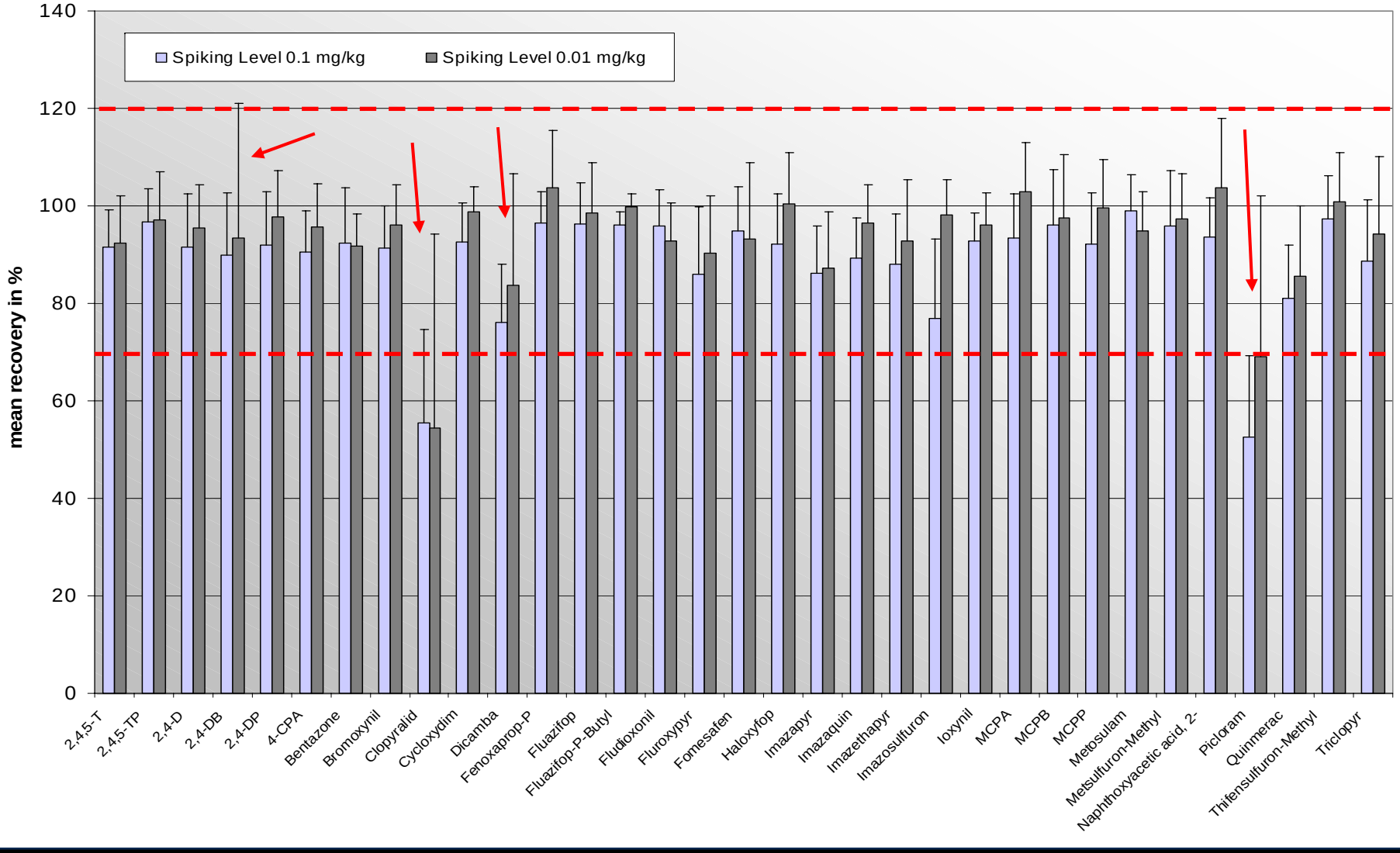
# ILMV 2006 Acids – Results Raisins



## Raisins

- Dry and sugar containing matrix
- Satisfying results for most pesticides
- Problematic (mean recovery) for:
  - Clopyralid
  - Picloram
- RSD > 20% for:
  - Imazosulfuron
  - Clopyralid
  - Picloram
  - Thifensulfuron-Methyl (only 0.1 mg/kg)

# ILMV 2006 Acids – Results Wheat Flour

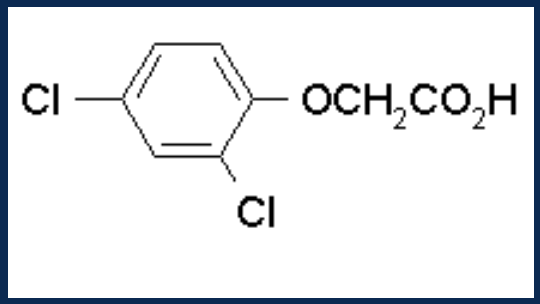


## Wheat Flour

- Fat containing matrix
- Satisfying results for most pesticides
- problematic (mean recovery) for:
  - Clopyralid
  - Picloram
- RSD > 20% for:
  - 2,4-DB (only 0.01 mg/kg)
  - Clopyralid
  - Dicamba
  - Picloram

# QuEChERS – alkaline hydrolysis

Example 2,4-D




- Selective systemic herbicide
- Control of broad leaved weed
- Plant growth regulator used to prevent premature fruit drop
- Formulations include free acid, salts, esters
- May form conjugates
- Method designed to convert all possible residues to free acid

- Acids are often covalently bound to matrix components and thus their concentration underestimated!

# QuEChERS – schematic description with AH

**Citrate-Buffered QuEChERS**

**Weigh 10 g of Frozen Sample**

**Shake**

**Add 10 mL Acetonitrile**

**Add ISTD-Solution**

**Shake**

**Add 4 g $MgSO_4$ / 1 g NaCl / Citrate Buffer (pH 5-5.5)**

**Shake and Centrifuge**

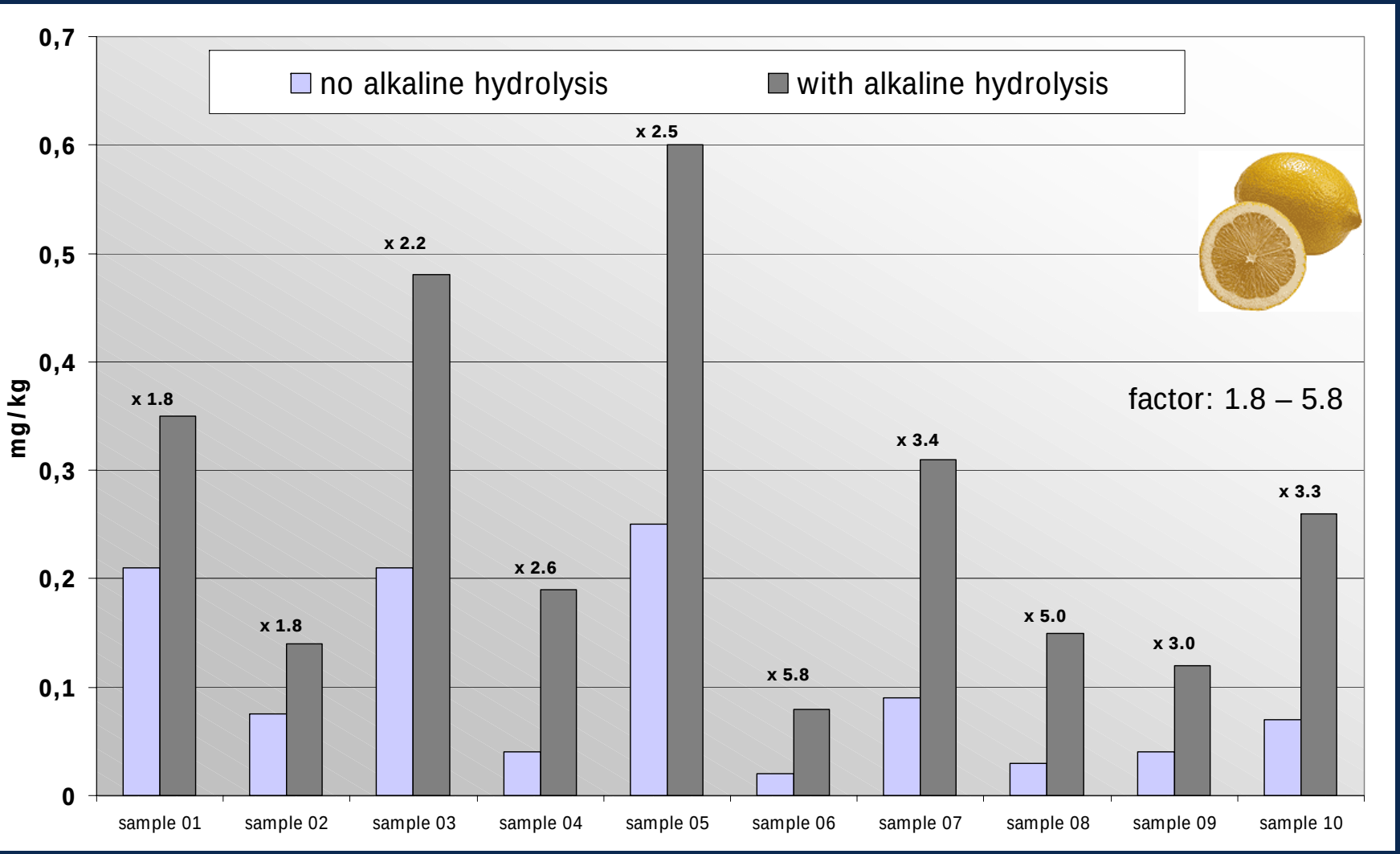
**Analysis of acidic pesticides by LC-MS/MS**

**alkaline hydrolysis:**
**Add NaOH and store for 30 min at RT, then neutralize**

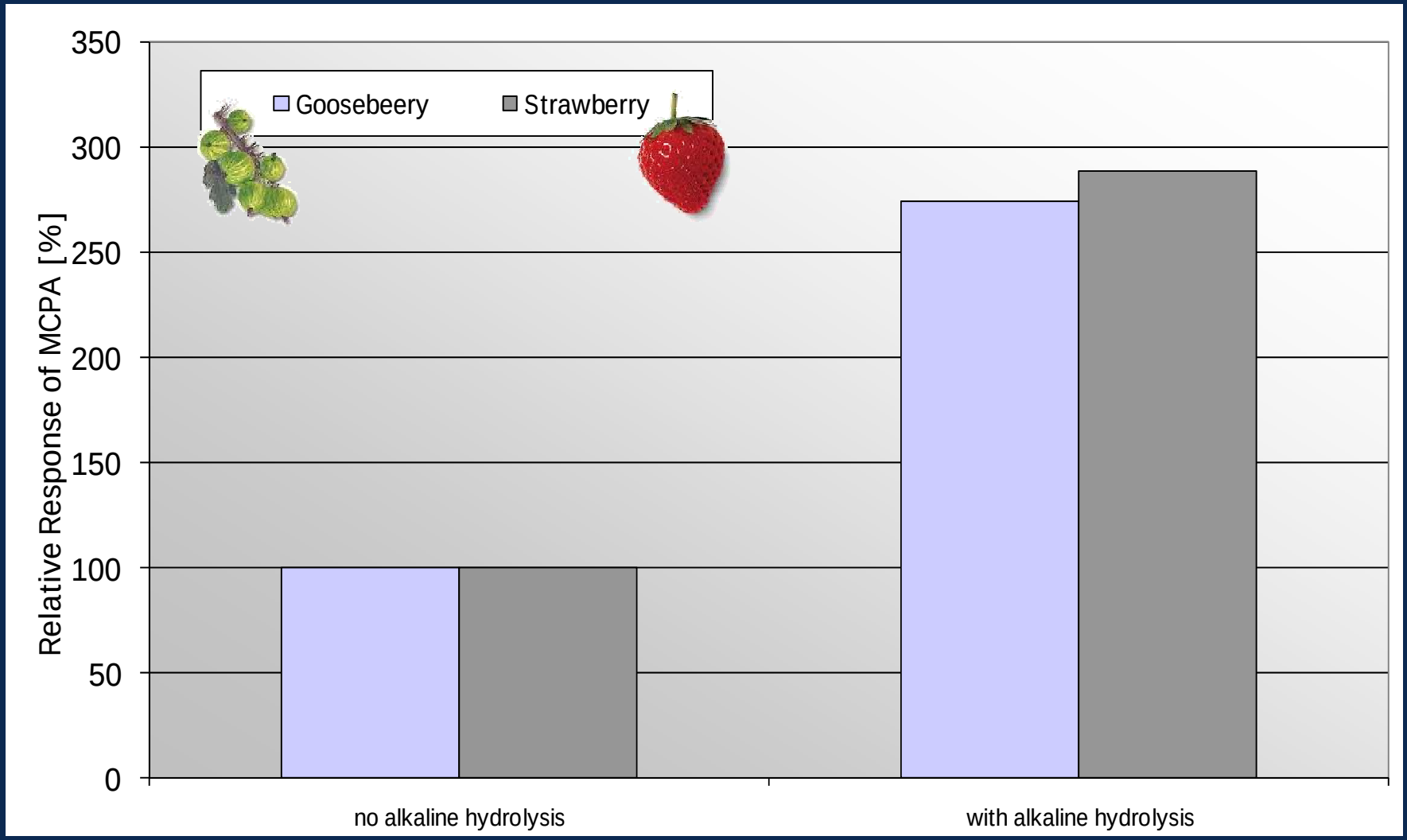
**optionally:**
**Add NaOH to adjust pH**

**optionally:**
**Freeze-out of extracted fat over night**

# Alkaline Hydrolysis – Level of 2,4-D in different citrus samples



# Alkaline Hydrolysis – Level of MCPA in berries



# Acidic pesticides – alk. hydrolysis legally required

## Current residue definitions

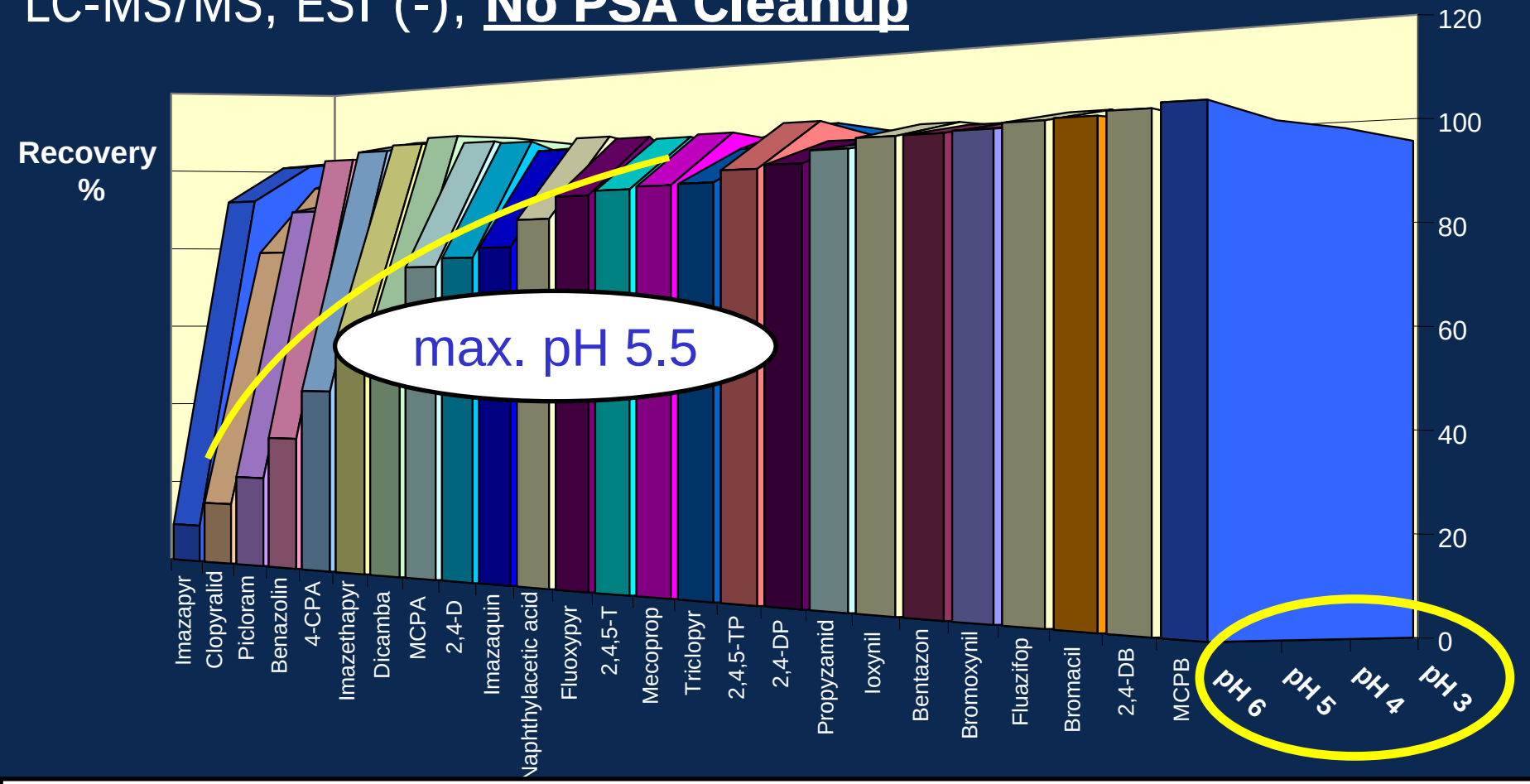
| Name | Annex I 91/414 | Chem. group | EU-Harmonized MRL? | Free Acid | ESTERS | SALTS | CONJUGATES | NOTES |
|---|---|---|---|---|---|---|---|---|
| Dichlorprop (2,4-DP) | In | **COOH** | since 31.12.1993 | YES | | | | incl. Dichlorprop-P |
| Mecoprop (MCPP) | In | **COOH** | since 04.12.2006 | YES | | | | incl. Mecoprop-P |
| 2,4-DB | In | **COOH** | since 04.06.2005 | YES | | | | |
| 2,4-D | In | **COOH** | since 01.07.2003 | YES | YES | YES | | |
| Fluroxypyr | In | **COOH** | since 01.03.2002 | YES | YES | | | |
| Clopyralid | In | **COOH** | Pending | | | | | |
| MCPA | In | **COOH** | Pending | ***(YES)*** | ***(YES)*** | ***(YES)*** | ***(YES)*** | |
| MCPB | In | **COOH** | Pending | | | | | |
| Mesosulfuron | In | **COOH** | Pending | | | | | |
| Triclopyr | In | **COOH** | Pending | | | | | |
| Quinmerac | Pending | **COOH** | No | | | | | |
| Picloram | Pending | **COOH** | No | | | | | |
| Imazaquin | Pending | **COOH** | No | | | | | |
| Haloxyfop-R | Pending | **COOH** | No | | | | | |
| Fenoxaprop-P | Pending | **COOH** | No | | | | | |
| Dicamba | Pending | **COOH** | No | | | | | |
| 2-Naphthyloxyacetic acid | Notified | **COOH** | No | | | | | |
| Bromoxynil | In | **OH** | **after 21.04.2007** | YES | YES | YES | | |
| Ioxynil | In | **OH** | **after 21.04.2007** | YES | YES | YES | | |

## Conclusion

- Modified QuEChERS method without PSA cleanup is suitable for analysis of most acidic pesticides
- Problematic in all matrices are:
  - Clopyralid
  - Picloram
- Some other pesticides have RSD (> 20%)
- Alkaline hydrolysis is strongly recommended, in order not to underestimate the level of acidic pesticides
- EU should reconsider the existing residue definitions of harmonized MRLs to include conjugates where appropriate

# Acidic pesticides – influence of pH on recovery

## LC-MS/MS, ESI (-), **No PSA Cleanup**




**lower pKa ← general trend → higher pKa**

# www.QuEChERS.com

QuEChERS.com

Home Contact

## QuEChERS

Since its introduction, the QuEChERS method [1] has been readily accepted by many pesticide residue analysts. Some modifications to the original QuEChERS method had to be introduced to ensure efficient extraction of pH dependent compounds (e.g. phenoxyalkanoic acids), to minimize degradation of susceptible

....the modified QuEChERS method including all presented modifications and a lot of background information is available via the internet.

Two inter-laboratory ring tests were performed in 2005 using the modified method, leading to very good recoveries and repeatabilities for numerous pesticide/commodity combinations at different spiking levels using GC-MS or LC-MS/MS.

▷ QuEChERS validation data (PDF 76 KB; opens in a new window)

QuEChERS has been used in several EU Proficiency Tests by the CVUA Stuttgart.

▷ Participation in Proficiency Tests using the QuEChERS-Method (PDF 129 KB; opens in a new window)

For more than 300 different pesticides recovery studies have been made by the CVUA Stuttgart.

www.quechers.com

# Thank you very much for your Attention!

# Acids validation - Matrices

## Cucumber

- High water content

**Short Overview List**

| Pesticide | Level min | Level max | Rec Median | Rec Mean | CV [%] | # of rec | # of outl | % Rec (70-120%) | # of Labs |
|---|---|---|---|---|---|---|---|---|---|
| 2,4,5-T | 0,01 | 0,1 | **93** | 99 | 13,2 | 60 | 0 | **92** | 6 |
| 2,4,5-TP | 0,01 | 0,1 | **91** | 98 | 10,6 | 63 | 0 | **98** | 7 |
| 2,4-D | 0,01 | 0,1 | **86** | 100 | 13,2 | 68 | 0 | **94** | 7 |
| 2,4-DB | 0,01 | 0,1 | **104** | 98 | 10,7 | 59 | 0 | **97** | 6 |
| 2,4-DP | 0,01 | 0,1 | **104** | 99 | 10,7 | 73 | 0 | **97** | 8 |
| 4-CPA | 0,01 | 0,1 | **101** | 91 | 14,4 | 54 | 0 | **100** | 6 |
| Bentazone | 0,01 | 0,1 | **96** | 95 | 9,6 | 68 | 0 | **100** | 8 |
| Bromoxynil | 0,01 | 0,1 | **84** | 95 | 14,3 | 58 | 0 | **95** | 6 |
| Clopyralid | 0,01 | 0,1 | **75** | 76 | 13,2 | 32 | 0 | **62** | 4 |
| Cycloxydim | 0,01 | 0,1 | **73** | 74 | 24,6 | 51 | 0 | **69** | 7 |
| Dicamba | 0,01 | 0,1 | **67** | 94 | 14,3 | 59 | 0 | **90** | 7 |
| Fenoxaprop-P | 0,01 | 0,1 | **102** | 96 | 12,8 | 59 | 0 | **95** | 6 |
| Fluazifop | 0,01 | 0,1 | **102** | 102 | 9 | 65 | 0 | **95** | 6 |
| Fluazifop-P-Butyl | 0,01 | 0,1 | **80** | 79 | 4 | 10 | 0 | **100** | 1 |
| Fludioxonil | 0,01 | 0,1 | **92** | 94 | 10,8 | 65 | 0 | **98** | 7 |
| Fluroxypyr | 0,01 | 0,1 | **99** | 91 | 14 | 45 | 0 | **93** | 5 |
| Fomesafen | 0,01 | 0,1 | **100** | 101 | 8,4 | 50 | 0 | **98** | 6 |
| Formesafen | 0,01 | 0,1 | **75** | 76 | 5,5 | 10 | 0 | **100** | 1 |
| Haloxyfop | 0,01 | 0,1 | **92** | 98 | 11,6 | 64 | 0 | **98** | 7 |
| Imazapyr | 0,01 | 0,1 | **100** | 86 | 29,4 | 54 | 0 | **80** | 6 |
| Imazaquin | 0,01 | 0,1 | **89** | 94 | 12,7 | 73 | 0 | **100** | 7 |
| Imazethapyr | 0,01 | 0,1 | **102** | 92 | 14 | 83 | 0 | **99** | 7 |
| Imazosulfuron | 0,01 | 0,1 | **97** | 89 | 21,7 | 64 | 0 | **77** | 7 |
| Ioxynil | 0,01 | 0,1 | **99** | 95 | 11,3 | 65 | 0 | **100** | 7 |
| MCPA | 0,01 | 0,1 | **104** | 97 | 13,1 | 74 | 0 | **97** | 8 |
| MCPB | 0,01 | 0,1 | **106** | 99 | 12,1 | 65 | 0 | **95** | 7 |
| MCPP | 0,01 | 0,1 | **105** | 97 | 11,6 | 74 | 0 | **96** | 8 |
| Metosulam | 0,01 | 0,1 | **82** | 100 | 11,3 | 65 | 0 | **97** | 7 |
| Metsulfuron-Methyl | 0,01 | 0,1 | **100** | 94 | 11,9 | 63 | 0 | **98** | 7 |
| Naphthoxyacetic acid, 2- | 0,01 | 0,1 | **90** | 93 | 11,7 | 57 | 0 | **100** | 7 |
| Picloram | 0,01 | 0,1 | **84** | 79 | 20,8 | 35 | 0 | **60** | 4 |
| Quinmerac | 0,01 | 0,1 | **75** | 87 | 21,6 | 59 | 0 | **92** | 7 |
| Thifensulfuron | 0,01 | 0,1 | **96** | 100 | 7,8 | 45 | 0 | **100** | 5 |
| Thifensulfuron-Methyl | 0,01 | 0,1 | **75** | 82 | 12,7 | 14 | 0 | **100** | 2 |
| Triclopyr | 0,01 | 0,1 | **119** | 98 | 14,3 | 69 | 0 | **93** | 7 |

# Acids validation - Matrices

## Lemon

- Acidic matrix

**Short Overview List**

| Pesticide | Level min | Level max | Rec Median | Rec Mean | CV [%] | # of rec | # of outl | % Rec (70-120%) | # of Labs |
|---|---|---|---|---|---|---|---|---|---|
| 2,4,5-T | 0,01 | 0,1 | 104 | 100 | 11,6 | 70 | 0 | 97 | 7 |
| 2,4,5-TP | 0,01 | 0,1 | 100 | 101 | 9,5 | 70 | 0 | 99 | 7 |
| 2,4-D | 0,01 | 0,1 | 92 | 99 | 10,7 | 70 | 0 | 96 | 7 |
| 2,4-DB | 0,01 | 0,1 | 86 | 95 | 20,2 | 49 | 0 | 80 | 5 |
| 2,4-DP | 0,01 | 0,1 | 100 | 99 | 11,1 | 70 | 0 | 94 | 7 |
| 4-CPA | 0,01 | 0,1 | 101 | 99 | 11,9 | 70 | 0 | 93 | 7 |
| Bentazone | 0,01 | 0,1 | 90 | 98 | 9,1 | 70 | 0 | 97 | 7 |
| Bromoxynil | 0,01 | 0,1 | 113 | 103 | 14,2 | 69 | 0 | 93 | 7 |
| Clopyralid | 0,01 | 0,1 | 55 | 76 | 16,7 | 35 | 0 | 74 | 4 |
| Cycloxydim | 0,01 | 0,1 | 93 | 99 | 12,6 | 55 | 0 | 95 | 7 |
| Dicamba | 0,01 | 0,1 | 82 | 89 | 15,1 | 53 | 0 | 98 | 6 |
| Fenoxaprop-P | 0,01 | 0,1 | 102 | 94 | 22,9 | 59 | 0 | 83 | 6 |
| Fluazifop | 0,01 | 0,1 | 106 | 102 | 8,9 | 64 | 0 | 98 | 6 |
| Fluazifop-P-Butyl | 0,01 | 0,1 | 96 | 103 | 10,9 | 10 | 0 | 90 | 1 |
| Fludioxonil | 0,01 | 0,1 | 97 | 100 | 8,9 | 64 | 0 | 98 | 7 |
| Fluroxypyr | 0,01 | 0,1 | 92 | 96 | 13,4 | 50 | 0 | 96 | 6 |
| Fomesafen | 0,01 | 0,1 | 99 | 104 | 8,2 | 48 | 0 | 98 | 6 |
| Formesafen | 0,01 | 0,1 | 80 | 71 | 17,3 | 10 | 0 | 50 | 1 |
| Haloxyfop | 0,01 | 0,1 | 84 | 106 | 11,6 | 65 | 0 | 88 | 7 |
| Imazapyr | 0,01 | 0,1 | 93 | 90 | 15,5 | 55 | 0 | 93 | 6 |
| Imazaquin | 0,01 | 0,1 | 92 | 98 | 9,7 | 80 | 0 | 99 | 7 |
| Imazethapyr | 0,01 | 0,1 | 88 | 93 | 11,8 | 89 | 0 | 98 | 7 |
| Imazosulfuron | 0,01 | 0,1 | 86 | 90 | 18,2 | 67 | 0 | 88 | 7 |
| Ioxynil | 0,01 | 0,1 | 97 | 99 | 7,5 | 70 | 0 | 97 | 7 |
| MCPA | 0,01 | 0,1 | 94 | 101 | 9,9 | 69 | 0 | 97 | 7 |
| MCPB | 0,01 | 0,1 | 97 | 101 | 12 | 64 | 0 | 92 | 7 |
| MCPP | 0,01 | 0,1 | 94 | 99 | 9,8 | 70 | 0 | 99 | 7 |
| Metosulam | 0,01 | 0,1 | 92 | 99 | 11,8 | 69 | 0 | 97 | 7 |
| Metsulfuron-Methyl | 0,01 | 0,1 | 97 | 97 | 12,5 | 70 | 0 | 94 | 7 |
| Naphthoxyacetic acid, 2- | 0,01 | 0,1 | 99 | 104 | 13,2 | 70 | 0 | 87 | 7 |
| Picloram | 0,01 | 0,1 | 81 | 82 | 23,3 | 40 | 0 | 65 | 4 |
| Quinmerac | 0,01 | 0,1 | 93 | 91 | 17,4 | 65 | 0 | 86 | 7 |
| Thifensulfuron | 0,01 | 0,1 | 105 | 101 | 12 | 50 | 0 | 98 | 5 |
| Thifensulfuron-Methyl | 0,01 | 0,1 | 43 | 34 | 31,5 | 10 | 0 | 0 | 1 |
| Triclopyr | 0,01 | 0,1 | 95 | 98 | 15,7 | 60 | 0 | 93 | 7 |

# Acids validation - Matrices

## Raisins

- Sugar containing matrix

**Short Overview List**

| Pesticide | Level min | Level max | Rec Median | Rec Mean | CV [%] | # of rec | # of outl | % Rec (70-120%) | # of Labs |
|---|---|---|---|---|---|---|---|---|---|
| 2,4,5-T | 0,01 | 0,1 | 92 | 98 | 11,7 | 45 | 0 | 98 | 5 |
| 2,4,5-TP | 0,01 | 0,1 | 88 | 93 | 10 | 45 | 0 | 100 | 5 |
| 2,4-D | 0,01 | 0,1 | 90 | 95 | 13,7 | 45 | 0 | 93 | 5 |
| 2,4-DB | 0,01 | 0,1 | 83 | 97 | 11,7 | 40 | 0 | 100 | 4 |
| 2,4-DP | 0,01 | 0,1 | 78 | 98 | 13,3 | 44 | 0 | 98 | 5 |
| 4-CPA | 0,01 | 0,1 | 101 | 91 | 13,8 | 45 | 0 | 93 | 5 |
| Bentazone | 0,01 | 0,1 | 82 | 90 | 14 | 45 | 0 | 96 | 5 |
| Bromoxynil | 0,01 | 0,1 | 98 | 95 | 11,4 | 45 | 0 | 98 | 5 |
| Clopyralid | 0,01 | 0,1 | 46 | 53 | 16,7 | 40 | 0 | 0 | 4 |
| Cycloxydim | 0,01 | 0,1 | 90 | 92 | 13,6 | 45 | 0 | 100 | 5 |
| Dicamba | 0,01 | 0,1 | 85 | 80 | 14 | 35 | 0 | 83 | 4 |
| Fenoxaprop-P | 0,01 | 0,1 | 103 | 98 | 11,7 | 40 | 0 | 98 | 4 |
| Fluazifop | 0,01 | 0,1 | 106 | 105 | 10,2 | 45 | 0 | 91 | 4 |
| Fluazifop-P-Butyl | 0,01 | 0,1 | 78 | 82 | 4,6 | 10 | 0 | 100 | 1 |
| Fludioxonil | 0,01 | 0,1 | 115 | 99 | 14,2 | 45 | 0 | 93 | 5 |
| Fluroxypyr | 0,01 | 0,1 | 89 | 93 | 13 | 45 | 0 | 91 | 5 |
| Fomesafen | 0,01 | 0,1 | 95 | 104 | 11,4 | 35 | 0 | 89 | 4 |
| Formesafen | 0,01 | 0,1 | 75 | 79 | 7,7 | 10 | 0 | 100 | 1 |
| Haloxyfop | 0,01 | 0,1 | 94 | 98 | 10,3 | 45 | 0 | 98 | 5 |
| Imazapyr | 0,01 | 0,1 | 79 | 84 | 10,8 | 35 | 0 | 94 | 4 |
| Imazaquin | 0,01 | 0,1 | 81 | 94 | 8,9 | 55 | 0 | 100 | 5 |
| Imazethapyr | 0,01 | 0,1 | 66 | 87 | 11,4 | 65 | 0 | 95 | 5 |
| Imazosulfuron | 0,01 | 0,1 | 76 | 74 | 28,6 | 45 | 0 | 58 | 5 |
| Ioxynil | 0,01 | 0,1 | 87 | 93 | 11,1 | 45 | 0 | 100 | 5 |
| MCPA | 0,01 | 0,1 | 96 | 96 | 10,7 | 45 | 0 | 98 | 5 |
| MCPB | 0,01 | 0,1 | 91 | 99 | 12,2 | 45 | 0 | 100 | 5 |
| MCPP | 0,01 | 0,1 | 89 | 96 | 12,6 | 44 | 0 | 95 | 5 |
| Metosulam | 0,01 | 0,1 | 82 | 94 | 10,9 | 45 | 0 | 100 | 5 |
| Metsulfuron-Methyl | 0,01 | 0,1 | 102 | 92 | 13,7 | 45 | 0 | 93 | 5 |
| Naphthoxyacetic acid, 2- | 0,01 | 0,1 | 90 | 89 | 13,2 | 45 | 0 | 91 | 5 |
| Picloram | 0,01 | 0,1 | 59 | 68 | 18,8 | 35 | 0 | 43 | 4 |
| Quinmerac | 0,01 | 0,1 | 73 | 78 | 15,2 | 45 | 0 | 91 | 5 |
| Thifensulfuron | 0,01 | 0,1 | 97 | 97 | 11 | 35 | 0 | 100 | 4 |
| Thifensulfuron-Methyl | 0,01 | 0,1 | 78 | 80 | 8,7 | 10 | 0 | 100 | 1 |
| Triclopyr | 0,01 | 0,1 | 92 | 98 | 12,8 | 45 | 0 | 96 | 5 |

# Acids validation - Matrices

## Wheat Flour

- Fat containing matrix

**Short Overview List**

| Pesticide | Level min | Level max | Rec Median | Rec Mean | CV [%] | # of rec | # of outl | % Rec (70-120%) | # of Labs |
|---|---|---|---|---|---|---|---|---|---|
| 2,4,5-T | 0,01 | 0,1 | **102** | 92 | 9,1 | 44 | 0 | **100** | 5 |
| 2,4,5-TP | 0,01 | 0,1 | **89** | 98 | 8,3 | 43 | 0 | **98** | 5 |
| 2,4-D | 0,01 | 0,1 | **92** | 93 | 10,8 | 54 | 0 | **98** | 6 |
| 2,4-DB | 0,01 | 0,1 | **103** | 89 | 23,5 | 39 | 0 | **79** | 4 |
| 2,4-DP | 0,01 | 0,1 | **112** | 94 | 11,3 | 54 | 0 | **94** | 6 |
| 4-CPA | 0,01 | 0,1 | **79** | 93 | 9,3 | 44 | 0 | **100** | 5 |
| Bentazone | 0,01 | 0,1 | **109** | 92 | 10,1 | 49 | 0 | **100** | 6 |
| Bromoxynil | 0,01 | 0,1 | **76** | 93 | 9,6 | 45 | 0 | **100** | 5 |
| Clopyralid | 0,01 | 0,1 | **74** | 57 | 33,1 | 30 | 0 | **23** | 3 |
| Cycloxydim | 0,01 | 0,1 | **90** | 95 | 8 | 39 | 0 | **100** | 4 |
| Dicamba | 0,01 | 0,1 | **89** | 81 | 20,5 | 33 | 0 | **64** | 4 |
| Fenoxaprop-P | 0,01 | 0,1 | **101** | 103 | 9,5 | 40 | 0 | **88** | 4 |
| Fluazifop | 0,01 | 0,1 | **92** | 97 | 9,3 | 55 | 0 | **100** | 5 |
| Fludioxonil | 0,01 | 0,1 | **96** | 95 | 8,1 | 43 | 0 | **100** | 5 |
| Fluroxypyr | 0,01 | 0,1 | **92** | 92 | 9,3 | 40 | 0 | **98** | 5 |
| Fomesafen | 0,01 | 0,1 | **90** | 93 | 12,4 | 47 | 0 | **96** | 5 |
| Haloxyfop | 0,01 | 0,1 | **97** | 98 | 9,3 | 49 | 0 | **98** | 5 |
| Imazapyr | 0,01 | 0,1 | **99** | 87 | 10,4 | 48 | 0 | **100** | 5 |
| Imazaquin | 0,01 | 0,1 | **89** | 92 | 9,5 | 59 | 0 | **100** | 5 |
| Imazethapyr | 0,01 | 0,1 | **98** | 94 | 10,8 | 49 | 0 | **98** | 5 |
| Imazosulfuron | 0,01 | 0,1 | **88** | 83 | 18,8 | 44 | 0 | **75** | 5 |
| Ioxynil | 0,01 | 0,1 | **83** | 95 | 6,7 | 43 | 0 | **100** | 5 |
| MCPA | 0,01 | 0,1 | **107** | 97 | 11,2 | 55 | 0 | **95** | 6 |
| MCPB | 0,01 | 0,1 | **97** | 96 | 12,8 | 44 | 0 | **100** | 5 |
| MCPP | 0,01 | 0,1 | **115** | 95 | 11,6 | 54 | 0 | **98** | 6 |
| Metosulam | 0,01 | 0,1 | **110** | 97 | 8,2 | 49 | 0 | **100** | 5 |
| Metsulfuron-Methyl | 0,01 | 0,1 | **106** | 97 | 11,3 | 47 | 0 | **100** | 5 |
| Naphthoxyacetic acid, 2- | 0,01 | 0,1 | **110** | 99 | 13,5 | 44 | 0 | **91** | 5 |
| Picloram | 0,01 | 0,1 | **46** | 51 | 13,2 | 20 | 0 | **0** | 3 |
| Quinmerac | 0,01 | 0,1 | **77** | 84 | 13,1 | 48 | 0 | **96** | 5 |
| Thifensulfuron | 0,01 | 0,1 | **95** | 102 | 9 | 35 | 0 | **94** | 4 |
| Thifensulfuron-Methyl | 0,01 | 0,1 | **86** | 92 | 9,1 | 13 | 0 | **100** | 1 |
| Triclopyr | 0,01 | 0,1 | **86** | 89 | 14,6 | 45 | 0 | **91** | 5 |