Practical experience gained with testing the effect of sample processing on the stability of residues and uncertainty of the results

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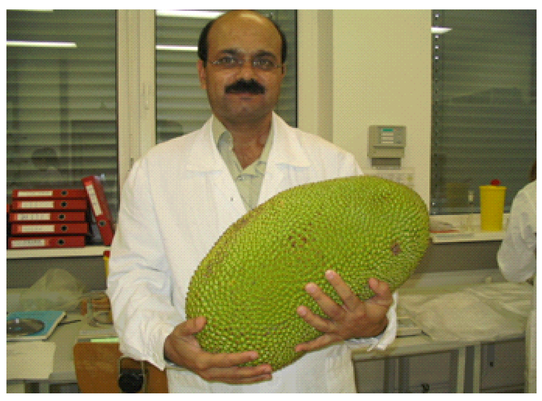
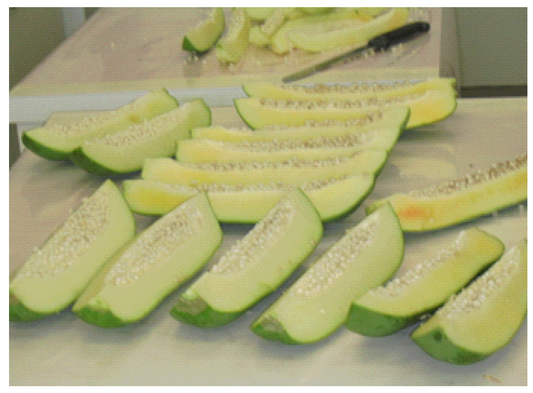
BACKGROUND

Mass reduction and comminution of laboratory samples may significantly increase the uncertainty and decrease the accuracy of detected residue concentrations. These are not revealed by recovery and proficiency tests.

The residues are unevenly distributed in/on and among treated crops. To obtain representative test portions of 1-15 g from five large crops (e.g. jackfruit, watermelon, pumpkin) is a real challenge.



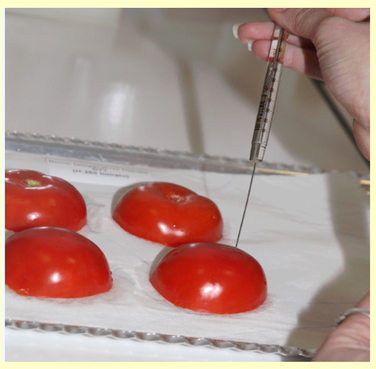


Picture 1. Jackfruit and sliced papaya sample

OBJECTIVES

To show the practical application of a simple method for testing the uncertainty and bias caused by sample processing.

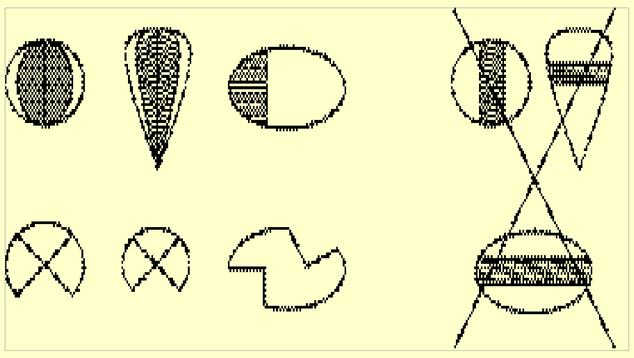
METHOD



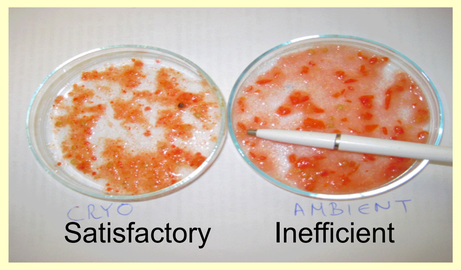
Crops: To represent the worst case scenario, treat a small portion of the *surface of crop units* with pesticide mixture containing analytes of stable, labile and unknown properties.

Grains: A portion of small grains is treated with the standard solution and then mixed with untreated ones in about 1:9 ratio.

Take one segment from each large fruits (top surface of a large one is treated)



Chop or grind the treated material *to the smallest particle size* possible preferably under cryogenic conditions, test the efficiency of comminution by spreading the material on Petri-dish.



Satisfactory Inefficient

If particle size is satisfactory, withdraw test portions [(m_e [g]) and ≥10×m_e =m_{lg}]. Calculate CV_L from the measured concentrations of stable compounds.

Spike test portions of untreated sample material for determining the recovery (Q) and its uncertainty (CV_A) for all components of test mixture.

Perform all tests with minimum **5** replicates.

Complement initial validation results, as part of quality control, with *reanalysis of retained test portions* containing well detectable residues.

EVALUATION OF THE RESULTS

The combined uncertainty of measured residue, CV_L, resulted from sample mass reduction (CV_{SS}), sample comminution (CV_{SP}) and analysis (CV_A):

$$CV_L = \sqrt{CV_{SS}^2 + CV_{Sp}^2 + CV_A^2}$$

For large fruits:

$$CV_{Sp'} = \sqrt{CV_{SS}^2 + CV_{Sp}^2}$$

$$CV_{Sp'} = \sqrt{CV_L^2 - CV_A^2}$$

The comminuted sample is well mixed if:

$$\left[\frac{m_e CV_{me}^2}{m_{lg} CV_{mlg}^2}\right] \leq 4.11 = F_{(0,1;v_1;v_{2;})}$$

If the analytical recovery of stable reference compound is Q_r and the measured concentrations are C_r and C_i (for the i^{th} component) in the surface treated test portions, then the relative concentration of the tested analytes ($C_{i,r}$) during sample processing and analysis is calculated as:

$$C_{i,r} = \frac{\bar{Q}_r \times C_i}{C_r}$$

The measurements should be made with ≥5 replicates. The loss during sample processing can be calculated from the relative average recoveries of tested compounds and their average relative concentration obtained from surface treated samples.

CONCLUSIONS

- Buprofezin and chlorpyrifos proved to be suitable reference compounds for LC-MS/MS and GC-MS/MS detections.
- Chlorothalonil, chlozolinate, dichlorvos, etridiazole were significantly lost when tomato and lettuce were processed.
- Efficiency of sample processing depends on the equipment, temperature and sample material, but independent from the analytes.
- The CV_{Sp} is inversely proportional to the square root of test portion mass (m_e) and rapidly increases if particle size (d) increases.

$$CV_{Sp} = \sqrt[2]{\frac{Cd^3}{m_e}}$$

- Cryogenic processing reduces CV_{Sp} and improves the stability of analytes.
- Under unfavourable conditions the CV_{Sp} can be as large as 20-30%, therefore it should be tested regularly with reanalysis of retained test portions containing detectable residues.
- To meet the EU decision criterion [$CV_L \leq 25\%$] for acceptance of residue levels in tested sample, the difference between the results (C_1, C_2) of two replicate analyses of test portions obtained from the laboratory sample shall be:

$$|C_1 - C_2| \leq 2.8 \times 0.25 \times \bar{C}$$

- Reduction of test portion size should only be done after verification of the efficiency of sample processing. Ideally, CV_{SP} should be ≤ $0.3CV_A$, as in this case it practically does not increase the combined uncertainty (CV_L) of the measured residue concentrations.

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