Improving the Efficiency of Pesticide Multiresidue Analysis in Laboratories

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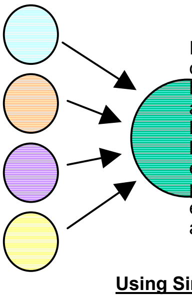
INTRODUCTION

Due to the high costs of pesticide residue analysis, laboratories are often not able to fulfil their tasks to the degree expected. Many agree that the benefits from pesticide residue analysis (e.g. monitoring programs) are often in no relation to the immense costs and efforts invested. There has therefore always been a great necessity to increase the efficiency of pesticide residue analysis (i.e. to find ways to achieve the highest possible impact and benefit for the consumer using the limited resources available).

The advancing liberalisation of the global market has initiated significant advancements in the harmonisation of pesticide regulations and analysis. All these developments, however, have hardly improved the efficiency in the laboratories. In this poster, we will discuss existing trends and further possibilities to improve the overall efficiency of pesticide residue analysis ranging from the organisational structure of laboratories to the analytical approach.

Organisational structure



In the last few years there has been a trend in many countries for a more centralised organisation and a better co-ordination in the field of pesticide residue analysis. Following this trend smaller laboratories have been merging into bigger more capable ones. Bigger laboratories can afford to buy and efficiently use expensive instruments, have a greater potential to perform praxis-oriented research activities and are more efficient in performing administrative and quality assurance tasks.

Using Simpler and Faster Analytical Methodologies

Many currently used pesticide multiresidue methods (MRMs) are complicated, laborious, time consuming, require high amounts of solvents and are therefore inatractive. Considering that the time spent for instrumental analysis is also continuously growing due to the introduction of new analytes and instrument techniques, laboratories are not able to analyse the number of samples they would like to. In addition, some important analytes are not be adequately recovered by many common MRMs (e.g. basic, acidic and very polar compounds). In order to cover such analytes, laboratories have, therefore, to additionally perform laborious single analyte methods, which is often not possible. This results in a large grey area of pesticides which are not routinely monitored by most laboratories.

In the last decade there has been a general trend to develop faster analytical methods. The automated instrument based extraction procedures SFE and ASE, which were introduced in the mid 1990s to speed up extraction, did, however, not succeed to replace traditional multiresidue approaches.

Ideally, a multiresidue method should be fast and easy to perform, require a minimum amount of chemicals, provide a certain degree of selectivity to avoid complicated cleanup procedures and at the same time cover a sufficiently broad spectrum of analytes.

Example of a fast and simple MRM

- Weigh 10 g sample
- Add 10 ml acetonitrile, shake
- Add 5 g $MgSO_4$ and 1 g NaCl, shake
- Add internal standard, shake
- Zentrifugation
- Clean-up with 25 mg PSA and 150 mg $MgSO_4$, shake
- Zentrifugation
- Chromatography

Analysts accustomed to performing complex traditional analytical procedures often hesitate to switch to simpler ones assuming that a simpler and faster analytical procedure can not be at the same time accurate enough and should, if at all, only be used for screening procedures. In reality, however, the more analytical steps a procedure entails and the more complicated it is the more likely is it to introduce systematic and random errors.

Targeted analysis

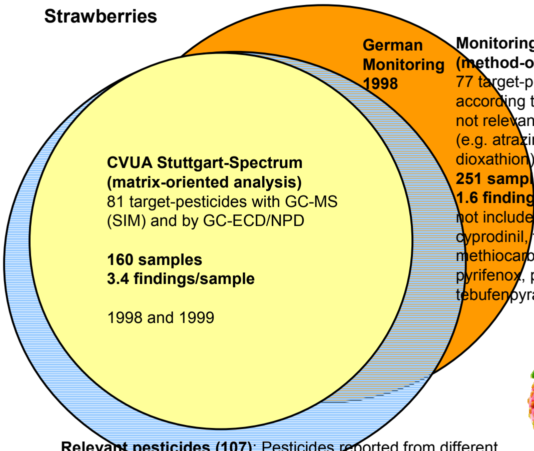
Analytical and financial limitations make it is practically impossible for laboratories to routinely monitor the entire pesticide spectrum. In general, the analytical cost increases with the number of targeted pesticides. In order to improve efficiency a more targeted analytical approach is necessary. Generally, the potential analyte spectrum is limited by the extraction method(s) and the analytical instrumentation used in every laboratory. The criteria applied to further restrict this spectrum of targeted analytes vary from laboratory to laboratory. Unfortunately, the inherent differences between the different matrices in terms of the pesticide use pattern are often not taken into consideration. It is not uncommon, that laboratories analyse all kinds of samples for one and the same pesticide spectrum, which often includes many matrix-irrelevant and at the same time ignores many relevant pesticides. This "method-oriented" approach, can be very inefficient. More efficient is the **"matrix-oriented" analysis**, where each sample is analysed more targeted for pesticides, which are relevant to the specific sample. In order to determine which analytes are relevant for which matrix, the collection of a large amount of data about pesticide use and residues is necessary. This kind of data is, however, often not easy to access for residue analysts.

At the CVUA Stuttgart we have been collecting pesticide residue related data and successfully performing "matrix-oriented" analyses for the last 6 years. The following two examples from the praxis clearly demonstrate the superiority of this approach in terms of efficiency and impact.

Sweet pepper	CVUA Stuttgart 2000	German Monitoring 1999
No. of samples analyzed	39	246
No. of findings	264	294
Residues per sample	**6.7**	**1.2**

The following pesticides, relevant to sweet pepper, were not included in the German Monitoring program in 1999 but were frequently detected at the CVUA Stuttgart in 2000: Lufenuron (detected in 19 out of 39 sample), tebufenozide (17), pyridaben (15), carbendazim (15), acrinathrin (11) buprofezin (10), pyrimethanil (9) teflubenzuron (8), bifenthrin (8) cyprodinil (6) diethofencarb (2), hexaflumuron (1).

Strawberries



Relevant pesticides (107): Pesticides reported from different laboratories in 1997 and 1998 or recommended for use during strawberry production in various countries

Another aspect related to the matrix oriented analysis concept is analysing samples of the same type in larger groups (e.g. 30 in a week) instead of randomly analysing samples of many different types. An important advantage of this approach is, that the analysts can familiarise with the particularities of the specific sample type during extraction, cleanup and measurement. Calibration standards and necessary recovery experiments for the most relevant pesticides can be performed using the same matrix type, while only a single extraction is necessary to isolate the blank matrix extract necessary to prepare matrix-matched standard solutions.

Database: we have developed a database with information about pesticides in food including: 1) Residue findings in laboratories, 2) usage data (mostly crop-specific recommendations of various agricultural authorities to farmers for the use of pesticides), 3) some relevant physicochemical properties and information about analytical behaviour.

We are planning to make our database accessible via Internet giving the possibility to other laboratories to extract existing or submit own data.

Who can profit from these data?

<u>Pesticide residue chemists, analytical method developers, planers of monitoring programs</u>:

- find out about the most relevant spectrum of pesticides for each matrix and get animated to focus analysis and selectively expand the pesticide spectrum covered

<u>Importers, exporters, food industry,</u>

- getting informed about the analytes which are relevant for each crop to minimize risks of violations and properly exercise their duty of care

<u>Farmers, agronomist</u>

- feedback

Conclusion

Improving the overall efficiency of pesticide analysis is a complex task, involving many aspects such as laboratory organization, accessibility of information and analytical approach.

Matrix oriented, targeted pesticide analysis has been shown to be more successful and efficient than the method oriented approach followed by many laboratories.