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## Review

# Minimization of solvent consumption in pesticide residue analysis

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### Abstract

The present paper reviews various pathways that will lead to reduction of organic solvent usage in pesticide residue analysis. Considerable reduction of solvent consumption can be achieved by miniaturizing the scale of sample extraction and cleanup and by simplifying the analytical procedures. Adoption of new analytical techniques, such as solid-phase microextraction and supercritical fluid extraction can also help to reduce the solvent consumption considerably. With the development of various new techniques in analytical chemistry, reduction of solvent consumption in pesticide residue analysis should not be a big technical problem anymore. The important point is to treat the issue as equally important as sensitivity and accuracy when developing a method.

*Keywords:* Reviews; Solvent consumption; Environmental analysis; Pesticides

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### 1. Introduction

Large amounts of organic solvents are consumed in pesticide residue analysis. Nowadays, it is still common to use several hundred millilitres of solvent for the treatment of one sample. These solvents normally require special purification and are thus costly. The recovery and disposal of these solvents are sometimes difficult and incomplete. They can enter the atmos-

phere easily and some of them can be hazardous to the environment and the laboratory analysts.

Although the usage of hazardous solvents in pesticide residue analysis has been highlighted in some publications [1,2], in the development of a pesticide residue method, the major efforts are still spent on the sensitivity, accuracy and ease of operation. With the rapid development of new techniques in analytical chemistry, the potential for reducing the solvent consumption in pesticide residue analysis is tremendous. This article will review various pathways and techniques that will lead to considerable

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reduction of organic solvent usage in pesticide residue analysis.

The methods for pesticide residue analysis generally consist of the following steps:

1. Extraction of the analytes from the sample matrix.
2. Cleanup to remove interfering coextractives and conversion of the analytes to a readily analyzed derivative if needed.
3. Instrumental analysis.

Among the three steps, extraction and cleanup consume the most solvent. The following discussion will be centred on these two steps.

## 2. Miniaturization of scale

Among the published methods for pesticide residue analysis, the size of samples varies from a few grams to over 100 grams and the volume of solvent for extraction ranges from 40 ml to several hundred millilitres. Solvent consumption can be considerably reduced by miniaturization of the extraction scale. For example, Bushway et al. [3] developed a method for analysis of thiobendazole in plant samples in which 5 g plant sample (potatoes, fruits or juice) was extracted in a 50-ml centrifugal tube [3]. The volume of solvent for extracting one sample was as little as 40 ml. Ammonium chloride was used to precipitate out the interfering coextractives. After separation by centrifugation, the sample was ready for analysis by HPLC. A detection limit as low as 2.5 ppb was achieved by using fluorescence detection. It is understandable that certain scale of extraction must be maintained in order to obtain satisfactory and reproducible results. The minimum scale used depends on many factors such as the property of the sample matrix, the sensitivity of instrumental detection and the skills of the analysts. However, in most of the methods being adopted, this has been decided by the rule of thumb. Although there have been many optimization studies on instrumental determination, miniaturization of scale has seldom been addressed.

Miniaturization of cleanup scale is also very helpful in reducing the solvent consumption. A clear trend in pesticide residue analysis is the increased use of minicolumns and disposable cartridges for

column cleanup [4–11]. In these miniaturized methods, only a small aliquot of the extracts is cleaned up and used for analysis, instead of taking the whole portion of the extracts for further treatment which is a common practice in traditional pesticide residue methods. The miniaturization of the cleanup step not only reduces the solvent consumption but also cuts the analysis time greatly.

## 3. Simplification

Simplification of analysis procedure can cut the analysis time and reduce the solvent consumption at the same time. There are two kinds of practice in handling the sample extracts. One practice is trying to remove the analytes from the sample matrix as thorough as possible by extracting the samples more than one time and washing the remainder with large amount of solvents (over 100 ml). All these extracts and the wash are combined prior to subsequent treatment. The other practice is extracting the sample only once and taking an aliquot of the extracts for subsequent cleanup. In the latter practice the extracts is separated from the sample matrix by filtration (without washing the extracted remainder), centrifugation or simply by allowing the blended slurry to stand for ca 10 min. This is based on the assumption that the analytes will distribute evenly in the extracts and the adsorption of the sample matrix to the analytes is negligible when soaked in solvents. The validity of this practice can be verified by recovery tests with fortified samples. The former practice requires solvents three times as much as the latter practice. However, in cases where there are low extraction efficiencies, the former practice is necessary. Recent examples which adopted the latter practice are the work by Bushway et al. [3], Wan et al. [2] and Holstege et al. [11].

To simplify the procedure for reducing the analysis time and the solvent consumption, the cleanup step is sometimes omitted [12,13]. For samples with complex matrix, this can have negative effects on the quality of analysis [14]. Even if the selective detectors can minimize the interferences, repeated injections of samples with large amount of coextractives are detrimental to GC columns, especially to

capillary columns. Therefore, this kind of simplification is generally not recommended.

Simplification of procedure can be achieved by combining several operations into one step. Thus Kadenczki et al. [14] reported a faster and less laborious multi-residue method, in which extraction and column cleanup were simultaneously conducted by mixing the sample pulp with florisil to obtain free-flowing powder and packing the powder into a chromatographic column [14]. A similar technique called matrix solid-phase dispersion was developed for analysis of animal tissue samples [15,16]. In this method, a small amount of tissue is homogenized and dispersed in a solid support in one step. The solid is then packed into a chromatographic column and eluted with organic solvent. The tissue actually becomes part of the column packing.

#### 4. New extraction techniques

Many new extraction techniques appeared in the past few years which can help to reduce the solvent consumption considerably or even can achieve solvent free extraction. Among these techniques, solid-phase extraction, supercritical fluid extraction, and solid-phase microextraction are the most attractive.

Solid-phase extraction has been used mainly for the trace enrichment of water samples prior to the instrumental determination. Two comprehensive reviews on the application of solid-phase extraction are available [17,18]. It has the following advantages over conventional liquid–liquid extraction:

1. Decreased use of hazardous solvents;
2. Extractions that are not hindered by the formation of emulsions;
3. High extraction efficiency;
4. Convenience in automation.

Octadecyl bonded silica is the most commonly used sorbent for solid-phase extraction. Graphitized carbon black was reported to be more suitable for polar compounds such as phenols [19]. This technique is normally suitable for clean waters. When solid-phase extraction is applied to 'dirty' samples, care should be taken to prevent clogging of the extraction cartridge and the adverse effects of humic

substances on the extraction efficiency [20,21]. Solid-phase extraction has also been applied to the analysis of pesticide residues in vegetable and animal food samples [8–10]. In the treatment of vegetable samples and animal food samples, the organic extracts are diluted with water before passing through a solid-phase extraction cartridge, so that the pesticides can be retained by the sorbent. The pesticides retained are then selectively eluted from the cartridge with different solvents. In this case the solid-phase extraction is equivalent to liquid–liquid extraction plus column cleanup in the conventional pesticide residue methods.

Solid-phase microextraction is a very new technique. This solvent-free extraction technique is fast, simple and sensitive. In solid-phase microextraction, sorbent coated silica fibres are used to extract analytes from aqueous or gaseous samples. After extraction, the fibres are directly transferred into the injection port of a GC by the use of a modified syringe, where the analytes are thermally desorbed and subsequently analyzed by the instrument. This technique was first described by Belardi and Pawliszyn in 1989 [22]. Since then it has been applied to the analysis of various organic pollutants in water [23–30]. Some very polar compounds such as phenols and metal ions were successfully extracted by fibres coated with polar or ion selective sorbents [25,31,32]. Extensive studies on dynamics of extraction and optimization of extraction have also been conducted by Pawliszyn and other coworkers [33–35]. Now commercialized products for solid-phase microextraction have been available.

Supercritical fluid extraction (SFE) is another extraction technique that has received wide attention in the past several years. In comparison with the liquid solvent, supercritical fluid has high diffusivity and low density and viscosity, thus allowing rapid extraction. Carbon dioxide is most frequently used as a supercritical fluid because of its suitable critical temperature (31.2 °C) and pressure (72.8 atm; 1 atm = 101 325 Pa). SFE using carbon dioxide is essentially a solvent-free extraction where the carbon dioxide can easily be removed by reducing the pressure. In addition to this advantage, SFE also improves extraction selectivity, saves time and laboratory space and lends itself to automation.

SFE has been applied to extracting pesticides from

soil and plant samples [36–40]. Soil samples can be directly packed into an extraction cartridge and extracted, while plant samples are normally blended with diatomaceous earth to form free-flowing powder before being packed into an extraction cartridge for the extraction. Satisfactory extraction efficiency can be readily achieved with pesticides of low polarity. For pesticides of high polarity, such as methamidophos and omethoate, addition of modifiers is necessary. The modifier can be mixed with the supercritical fluid or added directly to the sample matrix. The most commonly used modifier is methanol. For some basic analytes, a basic modifier (e.g. pyridine or triethyl amine) is more suitable [37]. A model describing quantitative structure of analytes–extraction relationship has been proposed by Kane et al. [41]. However, in cases of some polar pesticides, SFE may not be the technique of choice.

## 5. Conclusions

As discussed above, the potential for solvent reduction in pesticide residue analysis is tremendous. This issue should not be a big technical problem any more with the development of various new techniques in analytical chemistry. The important point is to treat the issue as equally important as sensitivity and accuracy when developing a method. It would be a mockery for an environmental chemist if his work generates more environmental pollutants.

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