Contributions to the ethyl acetate application in residue analysis
I. Micro method for extracting atrazine residues from soil samples

H. Steinwandter
Hessische Landwirtschaftliche Versuchsanstalt, Rheinstrasse 91, W-6100 Darmstadt, Federal Republic of Germany

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Summary. Atrazine was extracted from two weathered soil samples with the proposed micro extraction method using ethyl acetate as the extracting agent. The results were compared with other extraction methods tested. The proposed micro method was equally effective as the micro on-line method using acetone for the extraction and more effective than the Soxhlet extraction using acetone and methanol. Therefore, the proposed micro ethyl acetate method can be used for routine analysis.

1 Introduction

The amount of chemicals and solvents that are used in residue analysis and thereby released into the environment is usually by a factor of $10^9 - 10^{10}$ greater than that of the polluting analytes to be determined. The analysis of human foods in order to protect health is therefore closely linked with the contamination of the environment that arises from these very analyses. The discharge of solvents and chemicals must be minimized if a further aim of the analytical work is to protect and conserve our environment. Micro methods are therefore necessary and are indeed the right concept.

This increased awareness of the chemist of the need for protection of both public health and environment is in accordance with “Extended Categorical Imperative” [1–3], postulated in 1989.

This involves not only the moral aspect but also the general conservation of both life and the environment and unites the person with the environment.

Applied to residue analysis, this imperative means for example that any analysis should be conducted in such a way that the advantages (e.g. information) and the disadvantages (e.g. emission of solvents into the environment) of such an analysis are balanced and therefore in harmony with the paradigm of the “Extended Categorical Imperative”. Without anticipating the matter, the right answer to our chemicals’ problem is the consistent use of micro methods in which the amount of solvents and chemicals for the extraction and clean-up steps is reduced to $1/10 - 1/100$ of that used in the conventional macro methods.

Whereas any conventional clean-up method could be miniaturized very easily [4–10], this miniaturization procedure of any conventional extraction method [11–16] was not possible without greater inconvenience, because in these methods the extraction, the filtration and partitioning steps are conducted off-line, that is, these steps are separated from each other by space and time.

This situation changed in 1985, when a new extraction technique using a ternary solvent system was developed [17] in which the filtration, the partition and shake-out steps were eliminated.

Because all individual steps of this so-called on-line method are conducted in the same vessel either simultaneously or sequentially, it is inherent to the on-line method, that this technique was for the first time perfectly suitable for miniaturization.

A further reduction of the solvent emission of the micro on-line technique is possible, if the non-polar solvents of the above ternary solvent system are eliminated.

In this connection it was found [18] that anhydrous MgSO$_4$ is a suitable substitute for the non-polar solvents petroleum ether, dichloromethane and ethyl acetate used in the on-line method for the removal of water from the binary acetone-water phase, so that finally a pure acetone phase remains for the determination of the analytes.

For several years we have been searching for another solvent, which can be introduced in addition to acetone as a universal extraction solvent. Finally we decided, after some screening experiments with different matrix samples and analytes, to use ethyl acetate as the second universal extraction solvent in our laboratory.

However, if ethyl acetate is used as a universal extraction solvent, the same principles must be considered as discussed in the two preceding papers [3, 10] when acetone was used for the development of the earlier described universal on-line extraction system, which should not be repeated here.

In this connection it is of interest to note, that if the polar organic solvent acetone in the above mentioned ternary solvent system water-acetone-ethyl acetate of the on-line extraction method [17, 18] is eliminated, we directly obtain the binary solvent system water-ethyl acetate for the extraction described earlier [19–22].

From that follows that both extraction methods are related systems.
Up to now however, these ethyl acetate procedures were not presented in the miniaturized extraction technique.

Therefore, the major objective of this research is focused on finding the optimal conditions for the proposed micro extraction method for analysing atrazine residues in weathered soil samples.

In order to obtain results as fast as possible and to take full advantage of the speed of the extraction stage of the proposed micro extraction method, it was considered to employ this micro extraction technique in combination with GC-NP-D determination without the need of a prior clean-up.

Because the true atrazine values of the analysed two weathered soils are not known, the results of the proposed micro ethyl acetate method were compared with already tested extraction procedures [23 – 27]. From these results we can define the best method as that procedure, which removes the highest atrazine concentrations.

First results of the micro ethyl acetate extraction of atrazine from two weathered soil samples are showing that the extraction power of the micro ethyl acetate method is comparable to those of the acetone extraction of the micro on-line method [23, 24], while the Soxhlet extraction [25 – 27] yields significantly lower recoveries.

Similar micro extraction studies with ethyl acetate described in this paper have not yet been employed in residue analysis.

2 Experimental

2.1 Apparatus and reagents

Apparatus. 100 ml flask with ISO thread GL 45; screw cap (red) with gum septum covered with a teflon layer; rotary evaporator with vacuum controller; 50 ml pear-shaped flasks; 50 ml Erlenmeyer flasks; 1, 2 and 5 ml graduated test tubes; pasteur pipettes (l = 210 mm); magnetic stirrer; stirrer bar; mechanical shaker with time clock; Soxhlet extractor.

Reagents. Ethyl acetate for residue analysis (r.a.); petroleum ether for r.a.; dichloromethane for r.a.; acetone for r.a.; hexane for r.a.; methanol for r.a.; Na2SO4, p.a.; solvent mixture: ethyl acetate + petroleum ether = 3 + 7 (v/v).

Stock standard solution: Dissolve 100 mg of atrazine in 100 ml of ethyl acetate + petroleum ether (3 + 7).

Gas chromatography standard solution: Dilute the stock solution with the same solvent mixture to obtain concentrations, for example, of 10, 20, 30, 40 and 50 ng/ml.

2.2 Soil sample

10 kg of each of the two soil samples contaminated with atrazine were passed through a 2 mm sieve and well mixed at field moisture to obtain representative samples. The samples were stored in well closed vessels at 7°C.

Soil 1 is a loamy sand with pH of 5.1, organic matter 0.9% and moisture content 5.3%.

Soil 2 is also a loamy sand with pH of 5.0, organic matter 1.3% and moisture content 4.1%.

2.3 Extraction of soil

Weigh 5 g of soil into a 100 ml flask and add 10 ml of water and 20 ml of ethyl acetate, close the flask and extract atrazine by shaking on a mechanical shaker (ca. 120 cycles/min) for 16 h at 20°C.

2.4 Preparation for the sample extract

Pour the organic extract obtained in 2.3 into a 50 ml Erlenmeyer-flask containing some Na2SO4. Stopper the flask and dry the extract on a magnetic stirrer using a stirrer bar. Transfer 10 ml (= 2.5 g of soil) of the organic phase into a 50 ml pear-shaped flask and evaporate under reduced pressure. Fill up with the above mentioned solvent mixture to a volume of 1 ml. If necessary, reduce volume to 200 – 500 µl.

2.5 GC-determination

Atrazine is determined without further clean-up by GC-NPD in combination with fused silica capillary columns (0.25 mm i.d. × 30 m) coated with the non-extractable bonded DB-1 or DB-5 phases.

Detector temperature: 250°C; injector temperature: 250°C; flow rate of carrier gas (He): 2 ml/min; temperature program: 70°C (2 min) – (6°C/min) – 190°C (0 min) – (10°C/min) – 230°C; injection volume: 1 µl.

3 Results and discussion

The atrazine concentrations of the two weathered soil samples (soil 1 and soil 2) analysed by the proposed micro method using ethyl acetate for the extraction are listed in the first column of Table 1.

Because the true atrazine values of these two weathered soil samples are not known, these results were also compared with the following two extraction methods tested [23 – 27]. The best method is defined as that procedure, which removes the highest atrazine concentrations from the two soil samples:

Method 1: Micro on-line extraction method in the sequential extraction mode [23, 24] with acetone as the polar organic solvent and with petroleum ether, dichloromethane and ethyl acetate as the non-polar organic solvents [17, 18].

Method 2: Soxhlet extraction with acetone [25] and methanol [26, 27] as the extracting solvents.

The corresponding atrazine values of the above described tested methods are also listed in Table 1.

From these results the following two points can be stated:

1. The atrazine values of the proposed micro method using ethyl acetate are similar to those of the micro on-line method tested [23, 24] with the non-polar solvents ethyl acetate, petroleum ether and dichloromethane, so that the following statistical procedure can be carried out: if the four atrazine values of soil 1 and soil 2 analysed by the above mentioned micro methods are averaged, the mean atrazine value of soil 1 is x1 = 26 µg/kg and that of soil 2 is x2 = 36.7 µg/kg, while the corresponding total errors, expressed as the coefficient of variances, are CV1 = 7.0% and CV2 = 4.1%. The latter values are in accordance with other CV data [18, 29], when intra-laboratory comparison is conducted.

2. The atrazine recovery of 27 µg/kg of soil 1 analysed by the proposed micro extraction method is about 40% and 30% higher than the atrazine values obtained by the Soxhlet extraction using acetone (19 µg/kg) and methanol (21 µg/kg), while the atrazine value of 36 µg/kg in soil 2 is increased...