Fresenius J Anal Chem (1992) 342:150–153

Fresenius' Journal of Analytical Chemistry

Contributions to the on-line method for the extraction and isolation of pesticide residues and environmental chemicals

III. A new extraction principle of the micro on-line method using the binary solvent system water + acetone

H. Steinwandter

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

Received March 23, 1991

Summary. A new extraction principle of the on-line method using the binary solvent system water + acetone is presented. The water amount of the organic phase containing the pesticides is removed by anhydrous $MgSO_4$, instead of previously used non-polar solvents. Therefore, a further reduction of the solvent emission into the environment is reached. In addition, the working sequences of the two simultaneous and sequential extraction steps of this new technique are discussed and illustrated.

1 Introduction

It was pointed out earlier [1–6] that by the introduction of the new extraction technique of the on-line method all extraction steps are conducted in the same extraction vessel, so that no filtration step and no separatory funnel is necessary. Therefore, the following three steps are characteristic for the one-line method using the ternary solvent system:

1. The *e*xtraction step E of the sample with acetone to reach an acetone to water ratio of ~ 2:1.
2. The *p*artition step P of pesticides by the addition of solid sodium chloride.
3. The *r*emoval of water step R by the addition of a non-polar solvent.

As reported earlier [2–5], it was also possible to reduce all extraction methods using acetone [8–11] or acetonitrile [12, 13] to one single on-line method, provided that the aqueous sample extract has an acetone or acetonitrile to water ratio of about 2:1 and is saturated with NaCl. Under these conditions the on-line method is always a ternary solvent system, which can be illustrated graphically – as already discussed [2–5] – by the so-called Gibbs triangle, as shown in Fig. 1. Unfortunately, the principle of the on-line method cannot be explained in detail by this illustration.

The reason for this is, that the Gibbs triangle only represents the composition of binary and ternary mixtures by a point in the system and does not describe individual steps by which the composition of that point in the system is reached: from that is follows, that the composition of one point in the Gibbs triangle is independent wether it was reached in one or several steps.

This problem is overcome, if the sequence of the working steps is completely described, which leads to one of the two organic phases b and d, where phase b is a binary and phase d is a ternary solvent system. The resulting sequence of the working steps E, P and R are then indicated in brackets behind the points b and d, as discussed earlier [5, 7] and shown in Fig. 2. One can see that it is inherent to the on-line method that all working steps can be conducted simultaneously and sequentially in all variations, leading to a total of six sequences: that is, two sequences to reach phase b, which is a binary solvent system and four sequences to reach phase d, which is a ternary solvent system.

Although significant progress was made for routine analysis by the introduction of this on-line extraction method, another important consequence of this technique is that the on-line method – in contrast to any conventional extraction method [8–13] – is perfectly suitable for miniaturization, so that the solvent consumption of the corresponding micro method [6, 7] can be reduced down to 1/10–1/100 of the original amount. Therefore, also the emission of solvents and chemicals into the environment is reduced to a large extent, which is in addition another demand for the "extended categorical imperative" [14, 15].

A further reduction of the solvent emission of the micro on-line technique into the environment is possible, if the non-polar solvent of the above ternary solvent system is eliminated. In this case however, a new technique for the removal of water from phase b must be found. Therefore, the major objective of this study is focused on finding another technique to remove the water from the pesticide containing phase b.

In this connection we found that anhydrous $MgSO_4$ is a suitable substitute for the non-polar solvents used for the quantitative removal of water from phase b, so that finally a pure acetone phase remains for the determination of pesticides. A further advantage of $MgSO_4$ is that the used salt can be heated to 450° C for reuse.

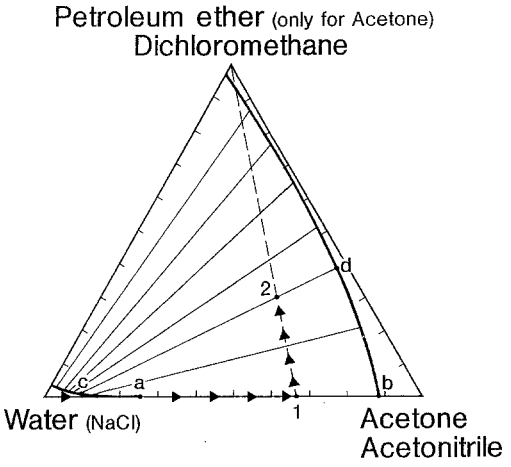

Fig. 1. The common principle of all extraction methods represented by the Gibbs triangle

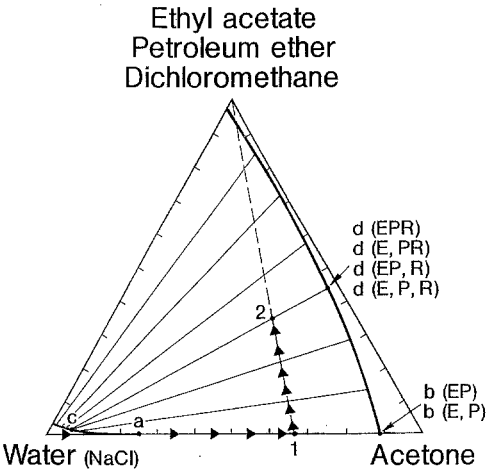

Fig. 2. The six extraction sequences for the characterization of the on-line method to reach the organic phases b and d using the ternary solvent system

Because it was analysed [4] that pesticides are distributed quantitatively into the organic phase b, some theoretical and practical aspects are discussed regarding the use of anhydrous $MgSO_4$ and the above mentioned binary solvent system in residue analysis.

Fig. 3. The two extraction sequences of the on-line method to reach the organic phase b using the binary solvent system acetone + water (NaCl)

2 Theoretical aspects

As described elsewhere [1 – 6], the original described on-line method is a ternary solvent system, which can be represented by the so-called Gibbs triangle with the convention that water is in the left corner of the triangle, the polar solvent acetone in the right and the non-polar solvent in the top corner, as shown in Fig. 2.

If the non-polar solvent in such a ternary system is eliminated, the partially miscible solvent system water (NaCl) + acetone remains as shown in Fig. 3.

2.1 The binary solvent system water-acetone

Let us consider the extraction of a 5 g sample containing 4.75 g of water. After blending the sample with 10 ml of acetone a completely miscible binary solvent system is obtained. Such a binary solvent system can be represented by a straight line (see Fig. 3) where the two endpoints are the pure solvents water and acetone, while points in between give the composition of any mixtures. Point 1 in Fig. 3 shows the binary system obtained above. If this sample extract of composition 1 is mixed with ~ 2 g of NaCl a partially miscible binary solvent system with the two conjugate solutions a and b are obtained. The relative amounts V of layers a and b jointed by the tieline are given by

$$\frac{\text{V of a}}{\text{V of b}} = \text{distance}\ \frac{1\,b}{1\,a}.$$

The closer the point 1 is to a, the larger will be the proportion of that layer.

However, the following problem arises using this binary solvent system for the pesticide extraction: because the relative amount of the two layers a and b are proportional to the segments of the tieline (see Fig. 3), the volume of phase b (containing the pesticides) depends on the solvent composition of point 1. Therefore, if the water content of the sample is not known, also the volume of phase b cannot be calculated, so that, if an aliquot of the organic phase b is dried with anhydrous $MgSO_4$ also the volume of the remaining acetone phase is not known, which is necessary for the determination of the analysed sample weight.

Therefore, the sample extraction must be standardized: in order to reach always the same water amount of phase b, the water-acetone composition of point 1 in Figs. 1, 2 and 3 must be kept constant. This is realized by adjusting a constant acetone: water ratio, for example, of 2:1 for each extraction. That is, if any sample is extracted with 10 ml of acetone the total water amount of the sample plus added water must be adjusted to 5 ml. This procedure is described in the following section.

2.2 Standardization of the sample extraction

To bring all samples to the same starting condition each sample is adjusted to a total of 5 g water prior to the 10 ml of acetone extraction. This is done by the use of the corresponding tables in which the average water contents of the original samples are listed [16, 17]. Suppose, for example, a potato and a cereal sample with an average water content of 80% and 10% should be extracted: then add to a representative 5 g potato subsample 1 ml of water and to a 1 g cereal subsample 4.90 ml of water. Both samples have now exactly 5 g of water. These so prepared samples can now be extracted with 10 ml of acetone and ~ 2 g NaCl to obtain the two conjugate layers a and b (see Fig. 3). Phase b is separated and dried with ~ 2 g anhydrous $MgSO_4$, so that a pure acetone phase is reached containing the pesticides. However,

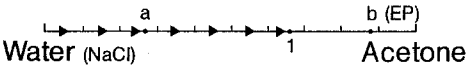

Fig. 4. The extraction sequence b (EP) of the on-line method for the determination of pesticides in samples with water contents > 70%

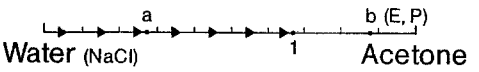

Fig. 5. The extraction sequence b (E, P) of the on-line method for the determination of pesticides in samples with water contents < 15%

to determine the sample weight in the above aliquot acetone volume of phase b it is prior necessary to analyse the solvent composition of phase b.

2.3 The solvent composition of phase b

The total volume and the water content of phase b is determined, for example, by mixing 5 g of water, 10 ml of acetone and ~ 2 g NaCl. On this condition the total volume of phase b is 9.1 ml. The water amount of this phase (measured by Karl-Fischer titration) is 1.1 ml, so that the total acetone volume of phase b is 8.0 ml.

2.4 Determination of the sample weight in the aliquot acetone volume

After standardization, the acetone rich phase b consists of 8.0 ml acetone and 1.1 ml of water. If this 1.1 ml water is removed by ~ 2 g anhydrous $MgSO_4$, a pure acetone phase with a total volume of 8.0 ml remains. Finally an aliquot of the latter phase is used for the determination of pesticides by GC or HPLC.

With $g_0 = 5$ g and $V_0 = 8.0$ ml, the sample weight g in the aliquot volume V of the organic extract is therefore

$$g = g_0 \frac{V}{V_0}$$

where

g_0 = total weight of sample taken
V = aliquot volume of acetone phase
V_0 = total volume of acetone phase.

2.5 How does the micro on-line method using the binary solvent system work?

Let us assume a 5 g representative fruit or vegetable subsample adjusted to 5 g of water. Then, add to this sample 10 ml of acetone, ~ 2 g of NaCl and extract for ~ 15–30 s with Ultra-Turrax [6]. Because the extraction is conducted in the same vessel the extraction step E and the partition step P take place simultaneously in one step. Therefore, the on-line extraction of this procedure can be described as follows: the original composition of the sample represented by the left water point of the straight line (see Fig. 3) moves after the addition of 10 ml acetone and ~ 2 g NaCl to point 1 yielding simultaneously the two conjugate layers a and b produced by the salting-out effect of the electrolyte.

The following two steps are therefore characteristic for this on-line extraction technique:

1. the *e*xtraction step E of the sample with acetone,
2. the *p*artition step P of pesticides by the addition of solid sodium chloride.

Therefore, if we ask [5], what are the working sequences to reach the organic phase b, we can write the two sequences b (EP) and b (E, P), as shown in Fig. 3. That means, that the samples can be extracted (E) and partitioned (P) either simultaneously or sequentially depending on the water content of the original sample.

3 Conclusions

The use of these two different extraction modes b (EP) and b (E, P) is depending (as mentioned above) on the original water content of the samples to be extracted. Therefore, various strategies are offered by this technique to decide, what extraction sequence for what kind of sample is the most suitable.

3.1 Products with water contents > 70%

Weigh 5 g of a homogeneous and representative fruit or vegetable subsample into the extraction vessel [6], add the corresponding water amount [16, 17] to reach exactly a total of 5 g of water, 10 ml of acetone and ~ 2 g of NaCl. Extract with Ultra-Turrax for 15–30 s. Let stand for ~ 5 min, or centrifuge directly after extraction. Pour the upper organic phase into a 25 ml Erlenmeyer flask containing ~ 2 g anhydrous $MgSO_4$. Stopper the flask and dry for ~ 15 min on a magnetic stirrer using a stirrer bar. Take an aliquot, for example, of 4.0 ml of the acetone phase (= 2.5 g of sample) and reduce the volume to ~ 0.5 ml. Transfer the solution quantitatively into a 1 ml graduated flask and fill up with acetone. If another solvent is necessary, remove the acetone and fill up with the appropriate solvent.

Because the extraction (E) and the partition (P) steps are conducted simultaneously, the corresponding working sequence [5] of this extraction procedure to reach the organic phase b is b (EP), as shown in Fig. 4.

3.2 Products with water contents < 15%

Weigh 0.5–1 g of dried products, e.g. feedstuffs or cereals, into a suitable extraction vessel [6], add the corresponding amount of water [16, 17] to reach exactly a total of 5 g of water, 10 ml of acetone and ~ 2 g of NaCl. Mix with Ultra-Turrax for ~ 10 s. Let stand for ~ 10 min. Add ~ 2 g NaCl and mix again for 15–30 s. Continue as described in 3.1.

If we now ask how phase b is reached, we have to write (E, P) (as shown in Fig. 5), because at first the extraction step E is carried out followed by the separate partition step P [5]. Important consequences and results of the described extraction technique using the binary solvent system will be discussed in a forthcoming paper.

Acknowledgement. The author thanks the companies E. Merck and Riedel-de-Haen for the determination of water in phase b by Karl-Fischer titration.

References

1. Steinwandter H (1985) Fresenius Z Anal Chem 322:752
2. Steinwandter H (1988) Universelle Extractionsmethoden zur Bestimmung organischer Rückstände – Beginn und Evolution.

Lecture presented on the 100. VDLUFA-congress in Bonn, 20.9.1988
3. Steinwandter H (1989) VDLUFA-Schriftenreihe 28:1069
4. Steinwandter H (1989) Universal extraction and cleanup methods. In: Sherma J (ed) Analytical methods for pesticides and plant growth regulators, vol XVII. Academic Press, Orlando, Florida, p 35
5. Steinwandter H (1989) Fresenius Z Anal Chem 335:475
6. Steinwandter H (1990) Fresenius J Anal Chem 336:8
7. Steinwandter H (1991) Fresenius J Anal Chem 339:30
8. Goodwin ES, Goulden R, Reynolds JG (1961) Analyst 86:697
9. Becker G (1971) Dtsch Lebensm Rundsch 67:125
10. Luke MA, Froberg JE, Masumoto HT (1975) J Assoc Off Anal Chem 58:1020
11. Specht W, Tillkes M (1979) Beitr Tabakforsch Int 10:73
12. Mills PA, Onley JH, Gaither RA (1963) J Assoc Off Anal Chem 46:186
13. Storherr RW, Ott P, Watts RR (1971) J Assoc Off Anal Chem 51:513
14. Steinwandter H (1989) Umweltanalytik – Nutzen oder Schaden. Lecture presented at the 101. VDLUFA-congress in Bayreuth, 21.9.1989
15. Steinwandter H (1990) VDLUFA-Schriftenreihe 30:543
16. Thier HP, Zeumer H (eds) (1987) In: Manual of pesticide residue analysis, vol 1. Dtsch Forschungsgem, Pesticide Comm. Verlag Chemie, Weinheim New York, p 386
17. Luke MA, Masumoto HT (1986) In: Zweig G, Sherma J (eds) Analytical methods for pesticides and plant growth regulators, vol XV. Academic Press, Orlando, Florida, p 170