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The Determination of Chlorinated Pesticide Residues by Entrainment Distillation with Water

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1. Introduction

Pesticide residue analysis is usually performed by an extraction procedure with a suitable solvent, followed by a number of clean-up steps involving solvent partition and column chromatography. Although this procedure is generally considered reliable and fairly accurate, there is still a need for a reference method which should preferably be entirely different.

During a study on several methods for the determination of hexachlorobenzene residues, we obtained excellent results by simple entrainment distillation with water with continuous extraction of the distillate (1). This method has now been investigated as a possible alternative procedure for the determination of all chlorinated and possibly phosphated pesticides which are commonly encountered in foodstuffs.

2. Description of the apparatus

The distillation apparatus that we used in our experiments is shown in figure I. It is basically the classic apparatus as designed for the isolation of essential oils which are lighter than water from herbs and spices, but the condensor was elongated to avoid over-heating of the receiver.

A certain quantity of the sample was weighed in the round bottom flask, water was added and the flask was connected to the apparatus. As extracting solvent 5 ml of toluene was pipetted into the receiver. When heating the flask in a 150 W heating mantle, the water started to boil, the vapour entraining possible present pesticides. On condensation the distillate flowed into the receiver and the toluene separated from the water as a 5 cm upper layer. Via the system of communicating vessels, the water returned to the flask at the same speed at which the distillate condensed into the receiver. In this way a prolonged distillation with continuous extraction of the distillate was achieved, because all droplets of condensed water passed through the toluene layer before flowing back into the boiling flask.

After distilling for a certain time, the apparatus was allowed to cool, the lower layer of water was drained via the stopcock and the toluene extract was gathered in a 10 ml volumetric flask. The receiver was rinsed with small portions of toluene and these washings were added to the extract, which was brought to volume and used for gaschromatographic analysis.

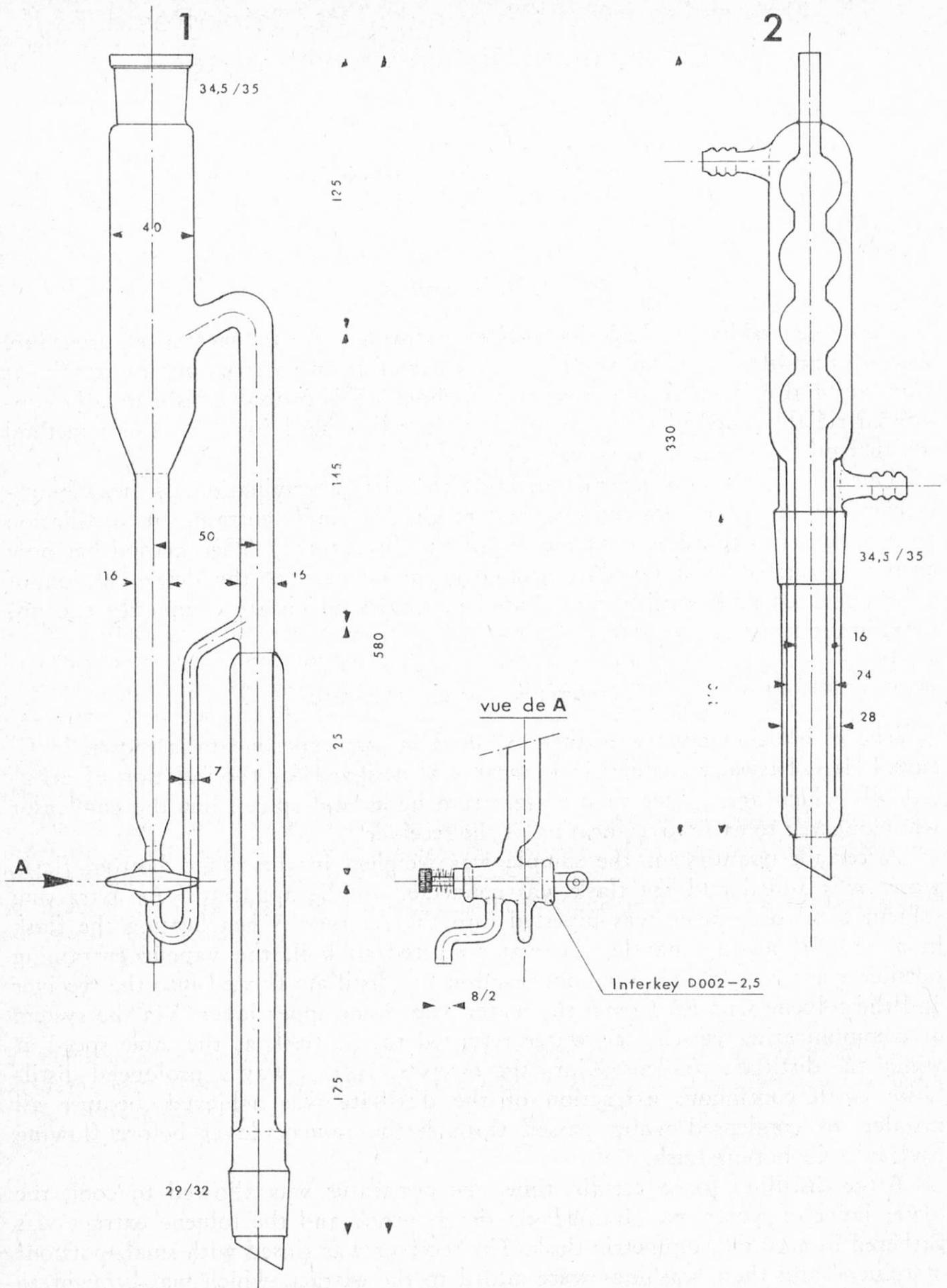


Fig. 1

3. Entrainment distillation of pesticides from non fatty foods

Apple purée was fortified with known amounts of five pesticides. Four recovery experiments were performed on this spiked sample, each time distilling during 1 hour, but with different volumes of water.

The results which are given in table I indicate that the volume of water used had no significant influence on the recovery of lindane, dieldrin, tetrasul and phenkapton. Furthermore, the results show that the recoveries were equal to or even better than those obtained by other methods of residue analysis. However, the thio-phosphate ester parathion was apparently partly hydrolysed during distillations with more than 50 ml of water.

Table I

Influence of the volume of water in the distillation flask on the recovery of 5 pesticides from apple purée. Time of distillation 1 hour. Sample size 10 g

Pesticide	Quantity added in ppm	Recovery in ppm with different volumes of water			
		50 ml	200 ml	800 ml	1600 ml
Lindane	0,07	0,061	0,060	0,062	0,059
Dieldrin	0,10	0,070	0,064	0,076	0,072
Parathion	0,45	0,50	0,29	0,26	0,21
Tetrasul	0,50	0,42	0,43	0,46	0,46
Phenkapton	0,25	0,24	0,22	0,25	0,26

It is worth noting that no interference was observed from codistilled aroma compounds, but impurities from the distilled water contributed some peaks to the chromatograms. Consequently, in all further experiments the water was purified by washing it with toluene prior to use.

One hour of distillation seemed to be sufficient for obtaining a satisfactory recovery of the pesticides listed in table I. There are, however, a number of pesticides such as beta-BHC, p,p'TDE and p,p'DDT, which are far less volatile with steam. It is possible that the nature of the substrate subjected to the distillation procedure has a considerable influence on the rate of volatilisation of the individual pesticides.

For example, in plant material containing waxy or fatty substances, the lipophilic organochlorine compounds are probably with difficulty entrained by the water vapour. In that case, the time of distillation should be prolonged.

On the other hand, prolonged contact with reducing of acidic sample constituents at a high temperature could result in a breakdown of certain pesticides. In order to study the possible decomposition of the earlier mentioned pesticides during a longer distillation time, we performed three recovery experiments by steam distilling 10 g of spiked apple purées with 750 ml of water during 4 hours.

The samples were also analysed by the A.O.A.C. method (2) and the recoveries obtained by both procedures are listed in table II.

Table II

Recoveries of pesticides obtained from apple purée by the distillation procedure and by the A.O.A.C. method

Time of distillation 4 hours, sample size 10 g, volume of water 750 ml

Sample no	Pesticides added	Quantity in ppm	Recovery by the distillation method		Recovery by the A.O.A.C. method	
			in ppm	in percent.	in ppm	in percent.
1	Lindane	0,04	0,033	82,5	0,031	77,5
2	Lindane	0,10	0,080	80	0,084	84
	Tetrasul	0,05	0,041	82	0,042	84
	Phenkapton	0,50	0,33	66	0,29	58
	Parathion	0,20	0,054	27	0,19	95
3	Lindane	0,02	0,023	115	0,023	115
	Tetrasul	0,20	0,15	75	0,18	90
	Phenkapton	0,50	0,31	62	0,31	62
	Parathion	0,40	0,14	35	0,28	70

The yield obtained with both methods for lindane, tetrasul and phenkapton was of the same order of magnitude. The low recoveries for parathion obtained by the distillation method indicate that this procedure is not suitable for the determination of this pesticide. The yields for phenkapton were found to be definitely lower than those obtained during the first experiments. It is not excluded that this thiophosphate ester also was hydrolysed to some extent during the prolonged distillation.

Although these first results were certainly encouraging, it was decided that the method could not be considered reliable merely on the basis of high recoveries. Good yields from a fortified sample may be obtained when the yield of entrainment distillation of an actually «field-incurred» residue is poor.

For this reason, fourteen actually contaminated samples of different raw materials of which the pesticide content had been carefully determined by the A.O.A.C. procedure were re-analysed by the distillation method. The results of these comparative analyses are given in table III. With very few exceptions, the agreement between the results of both methods was satisfying.

When analysing chicory and one sample of tobacco containing appreciable amounts of DDT residues, we observed an interesting phenomenon: although the results for total DDT obtained by both methods were quite similar, the amounts of the individual analogues differed considerably. The distillation method yielded less DDT and more TDE than the A.O.A.C. technique. This can only be

Table III
Comparative analyses of chlorinated pesticide residues in various non fatty substrates

Conditions of the distillation procedure: 10 g of sample was distilled with 750 ml of distilled water during 4 hours

Sample	Pesticides found	Quantity in ppm found by the distillation procedure	Quantity in ppm found by the A.O.A.C. method
Tomato flakes	gamma-BHC	2,14	1,80
	Endrin	1,33	1,60
Tomato flakes	gamma-BHC	2,05	2,30
	Endrin	1,20	1,13
Tomato flakes	gamma-BHC	0,19	0,19
Tomato flakes	alpha-BHC	0,007	0,005
	gamma-BHC	0,005	0,006
Asparagus powder	Aldrin	0,045	0,044
	Dieldrin	0,57	0,43
Rice straw feedstuff	alpha-BHC	0,62	0,48
	gamma-BHC	0,14	0,14
	beta-BHC	0,68	0,79
	delta-BHC	0,22	0,20
	alpha-PCCH	0,046	0,078
	gamma-PCCH	0,011	0,017
	delta-PCCH	0,069	0,068
	Heptachlor	0,21	0,20
	gamma-chlordane	0,017	0,019
	p,p'DDE	0,007	0,014
p,p'DDT	0,074	0,10	
Vermicelli	gamma-BHC	1,00	1,02
Wheat flour	gamma-BHC	0,014	0,010
Wheat flour	gamma-BHC	0,063	0,075
	Dieldrin	0,004	0,006
Wheat flour	gamma-BHC	0,14	0,15
	Dieldrin	0,003	0,003
Dehydrated carrots	alpha-BHC	0,16	0,11
	gamma-BHC	0,47	0,32
	beta-BHC	0,46	0,45
	delta-BHC	0,24	0,23
	epsilon-BHC	0,078	0,089

Sample	Pesticides found	Quantity in ppm found by the distillation procedure	Quantity in ppm found by the A.O.A.C. method
Chicory raw	gamma-BHC	0,18	0,14
	p,p'DDE	0,099	0,11
	p,p'TDE	0,14	0,037
	o,p'TDE	0,069	0,017
	p,p'DDT	0,094	0,23
	o,p'DDT	0,063	0,11
	Total DDT	0,47	0,50
Tobacco	p,p'DDE	0,45	0,75
	o,p'TDE	1,51	1,10
	p,p'TDE	8,73	12,0
	o,p'DDT	0,54	0,42
	p,p'DDT	3,50	3,42
	Total DDT	14,73	17,69
Tobacco	p,p'DDE	11,5	13,0
	o,p'TDE	0,61	trace
	p,p'TDE	8,3	2,5
	o,p'DDT	4,25	5,84
	p,p'DDT	26,5	33,0
	Total DDT	51,2	54,3

explained by assuming that during distillation the DDT isomers were reductively dehydrochlorinated to their TDE analogues.

Somewhat surprisingly, no evidence was obtained concerning a possible decomposition of other chlorinated pesticides. Even endrin proved to be stable.

The toluene extracts had mostly a noticeable odour of the commodity analysed, indicating the presence of aroma compounds. Not seldom the presence of co-distilled electron capturing material could be concluded from several peaks with very short retention times which were superimposed on a tailing solvent peak. In most cases, however, it was necessary to dilute the toluene extract, especially when more than 0,05 ppm of a pesticide was present, in order to measure the peaks within the linear range of the electron capture detector. Upon dilution, the interferences were minimized and clean-cut chromatograms were obtained.

It should be remarked that certain electron capture detectors are far more sensitive to co-distilled organic matter than others: with the ^{63}Ni device of Perkin Elmer the interference was limited to a broad and tailing solvent peak which took generally 5 minutes to return to the baseline, i. e. the sensitivity was quickly restored. On the other hand, heavy fading was often observed when working with the Techmation electron capture detector. In some cases the analysis of concentrated extracts was found impossible, because it took several hours to regain the original sensitivity.

Fortunately, interferences could be removed by shaking the toluene extract during 1 minute with half a teaspoon quantity of Nuchar attaclay adsorbent. After filtration over a prewashed filter paper, the extract was suitable for gas chromatography.

Concerning confirmatory analysis by thin-layer chromatography (3) it can be said that this was always possible when more than 0,02 ppm of a pesticide was present. No interferences were observed, but the concentration of the toluene extract had to be performed carefully in order to avoid losses of the more volatile pesticides such as lindane.

An additional field of application of the distillation method may ly in the determination of PCBs in non fatty substrates. The data listed in table IV indicate that lower chlorinated isomers are quantitatively entrained with water vapour. However, for Aroclor 1260 which contains several relatively non volatile hexa- and heptachlorobiphenyls, the yield was not better than 50 percent.

Table IV
Comparative analyses of PCBs in four samples

Substrate	Type of PCB found	Quantity in ppm found by the distillation method	Quantity in ppm found by exhaustive extraction with light petroleum
Sugar	Aroclor 1242	0,42	0,42
Wheat flour	Aroclor 1242	4,5	6,0
Wheat flour	Aroclor 1248	1,5	1,5
Carton	Aroclor 1260	310	610

4. Entrainment distillation of pesticides from fats and oils

Entrainment distillation of the strongly lipophilic organochlorine pesticides from fats and oils was found to be considerably more difficult than from flours, fruits and vegetables. Recovery experiments performed on 10 g of sample were disappointing. Almost no volatilisation of the pesticides was observed, except for HCB and heptachlor, and even for these compounds the recovery was not better than 10 percent.

Only by drastically lowering the sample size and by prolonging the time of distillation could the yield be improved as was shown by the following experiment: 1 g quantities of almond oil, spiked with 6 pesticides, were distilled from 750 ml of distilled water during 1—10 hours.

The yields for the individual pesticides, as listed in table V, were found to depend strongly on their volatility. HCB, aldrin and gamma-BHC were virtually quantitatively recovered after 4 hours, but the complete entrainment of gamma-chlordane, dieldrin and p,p' DDT required an unpractically long time of distillation.

Table V

Influence of distillation time on the recoveries of 6 pesticides from fat

Experimental conditions: 1 g of oil distilled with 750 ml of distilled water.
Pesticides were recovered in 5 ml of toluene

Pesticides added	Quantity in ppm	Recovery in ppm after				
		1	2	4	8 and 10 hours of distillation	
Hexachlorobenzene	0,10	0,059	0,087	0,097	0,12	0,11
Aldrin	0,02	0,009	0,013	0,018	0,021	0,019
gamma-BHC	0,20	0,11	0,13	0,18	0,20	0,19
gamma-chlordane	0,40	0,078	0,12	0,21	0,26	0,31
Dieldrin	0,20	0,043	0,064	0,13	0,16	0,19
p'p'DDT	2,0	0,087	0,26	0,64	0,86	1,21

Table VI

Comparative analyses of chlorinated pesticides in fats and oils

Experimental conditions: 1 g of sample in 750 ml of water,
distilled during 8 hours

Sample	Pesticides found	Quantity in ppm found by the distillation method	Quantity in ppm found by the Langlois method
Chicken fat	HCB	0,80	0,94
Chicken fat	HCB	0,33	0,28
	p,p'DDE	0,69	0,80
	p,p'DDT	0,099	0,17
Beef fat	HCB	0,26	0,26
Maize oil	Heptachlor	0,11	0,10
	gamma-chlordane	0,022	0,035
	alpha-chlordane	0,010	0,015
Cocoa butter	alpha-BHC	0,010	0,006
	gamma-BHC	0,024	0,025
Cocoa butter	alpha-BHC	0,037	0,040
	gamma-BHC	0,77	1,10
Codliver oil	HCB	0,12	0,14
	alpha-BHC	0,11	0,11
	Dieldrin	0,18	0,19
	p,p'DDE	0,55	0,53
	p,p'DDT	0,57	0,82

Sample	Pesticides found	Quantity in ppm found by the distillation method	Quantity in ppm found by the Langlois method
Butter oil	alpha-BHC	0,17	0,18
	gamma-BHC	0,048	0,035
	beta-BHC	0,046	0,067
	p,p'DDE	0,070	0,073
	p,p'TDE	0,052	0,086
	p,p'DDT	0,17	0,20
Butter oil	HCB	0,078	0,068
	gamma-BHC	0,064	0,059
	p,p'DDT	0,082	0,13
Milk fat	alpha-BHC	2,08	2,20
	gamma-BHC	0,12	0,11
	beta-BHC	6,66	10,6
	delta-BHC	0,19	0,25
	p,p'DDE	0,10	0,12
	p,p'DDT	0,092	0,11
	Dieldrin	0,13	0,18
Milk fat	Toxaphene	10	14
Milk fat	alpha-BHC	0,16	0,15
	gamma-BHC	0,030	0,046
Human milk fat, probably from a woman occupationally exposed to pesticides	HCB	0,40	0,43
	beta-BHC	0,85	1,53
	Aldrin	0,15	0,13
	Dieldrin	1,54	1,60
	Heptachlor	4,05	3,50
	Heptachlor epoxide	0,064	0,050
	gamma-chlordane	0,46	0,50
	alpha-chlordane	0,040	0,060
	p,p'DDE	2,50	2,66
	Milk fat	HCB	3,10
alpha-BHC		0,066	0,090
gamma-BHC		0,29	0,31
beta-BHC		0,052	0,10
Pentachloronitrobenzene		0,12	0,14
Pentachloroaniline		0,73	0,72
Methylpentachloro-phenylsulfide		0,015	0,035
Heptachlor epoxide		0,78	0,77
p,p'DDE		0,074	0,11
p,p'DDT		0,058	0,084

Similarly to the experiments with the non fatty foods, we continued our study on fourteen actually contaminated samples and compared the results to those obtained by the Langlois method (4) which is currently used in our laboratory for the analysis of all fatty foods.

In the majority of cases the agreement between the results obtained by the two methods was satisfying (see table VI). As expected, unacceptable discrepancies were sometimes observed for p,p'DDT and beta-BHC which are both not very volatile with steam.

No interferences from co-distilled organic matter were observed. In fact, the chromatograms obtained by the two methods were of the same quality.

5. Conclusion

The distillation procedure as described in this paper has some definite advantages over the usual methods of pesticide residue analysis:

1. Low cost: no expensive solvents or adsorbents are needed. Costly precautions against fire hazards are not necessary.
2. It is not time consuming, because the distillation requires only a minimum of attention.
3. Its results are mostly reliable, because the possibility of human error and the risk of cross contamination during manipulation is greatly reduced.

However, there are also some disadvantages: The method cannot be used for the determination of organophosphorus pesticides, because these compounds are hydrolysed under the conditions of distillation. Furthermore, it has only a somewhat limited value for the analyses of chlorinated pesticides in fats and oils, because of the insufficient volatility of beta-BHC and p,p'DDT.

The possibility of interference from co-distilled naturally occurring compounds should also be considered, but this pitfall is easily avoided if the analyst uses thin-layer chromatography or derivatization procedures as confirmatory techniques.

Summarizing, we can conclude that entrainment distillation could be used as a supplementary tool for the analysis of chlorinated pesticide residues. In our laboratory it has already proven its utility as a reference method in cases where we had to confirm the results obtained by the A.O.A.C. or the Langlois procedures.

Acknowledgement: We thank Mr. *J. M. Diserens* for his valuable assistance in carrying out the analyses.

Summary

A method is described for the determination of chlorinated pesticide residues by entrainment distillation with water under continuous extraction of the distillate with toluene. The apparatus used is basically the classic instruments as designed for the isolation of essential oils which are lighter than water from herbs and spices. Interference from co-distilled naturally occurring compounds was found to be rare and could be eliminated by a rapid clean-up with Nuchar attaclay adsorbent.

Organochlorine pesticide residues in flours, fruits, vegetables and tobacco could be quantitatively distilled in four hours from 10 g of sample and the results obtained were similar to those found by the A.O.A.C. procedure. In tobacco and chicory the DDT isomers were partly broken down to their TDE analogues during distillation, but this conversion did not affect the results for «total DDT».

Quantitative entrainment of most organochlorine pesticides from fats and oils required a sample size of not more than 1 g and 8 hours of distillation, although the more volatile compounds such as HCB, gamma-BHC and aldrin were already completely recovered after 4 hours.

A comparison with the Langlois method for residue analysis in fatty foods revealed that the distillation procedure gave significantly lower results for beta-BHC and p,p'DDT.

Because of its low cost and simplicity, entrainment distillation is recommended as an alternative method for the analysis of chlorinated pesticide residues, especially in non fatty substrates.

Résumé

Les auteurs décrivent une méthode pour la détermination des résidus de pesticides organo-chlorés utilisant une technique d'entraînement par distillation à la vapeur d'eau combinés à une extraction continue du distillat par le toluène. L'appareil est celui qui est utilisé de façon classique pour l'isolation des huiles essentielles plus légères que l'eau à partir des herbes aromatiques et des épices. Les interférences, dues à des substances naturelles co-distillées, ont été rares et ont pu être éliminées par une purification rapide sur un adsorbant, le Nuchar attaclay.

Dans les farines, les fruits, les légumes et le tabac, les résidus de pesticides organochlorés ont été obtenus quantitativement par une distillation de 4 heures sur un échantillon de 10 g. Les résultats sont semblables à ceux qui ont été obtenus selon le mode opératoire AOAC. Dans les échantillons de tabac et de chicorée brute, les isomères du DDT ont été partiellement dégradés au cours de la distillation en leurs homologues DDD, sans que cette conversion n'influence les résultats du «DDT total».

Dans les graisses et les huiles, l'entraînement quantitatif de la plupart des pesticides organochlorés exige une distillation de 8 heures sur un échantillon ne dépassant pas 1 g, bien que les composés plus volatils comme le HCB, le gamma-HCH et l'aldrine soient déjà complètement récupérés après 4 heures de distillation.

Comparée à la méthode de Langlois qui permet l'analyse des résidus dans les aliments gras, la méthode par distillation a donné de façon significative des résultats plus faibles pour le beta-HCH et le p,p'DDT.

En raison de son économie et de sa simplicité, l'entraînement par distillation est recommandé comme méthode d'appoint pour l'analyse des résidus de pesticides chlorés, en particulier dans les échantillons non gras.

Zusammenfassung

Die Autoren beschreiben eine Methode zur Bestimmung chlorhaltiger Pestizid-Rückstände mittels eines Verfahrens, das eine Wasserdampfdestillation mit einer kontinuierlichen Toluolextraktion des Distillats verbindet. Die Apparatur ist die, welche auf klassische Weise für die Gewinnung auf Wasser schwimmender ätherischer Öle aus aromatischen Kräutern und Wurzeln verwendet wird. Von mitdestillierenden Naturstoffen ver-

ursachte Störeffekte waren selten und ließen sich mittels einer schnellen Reinigung auf einem Adsorbens beseitigen.

Aus Mehlen, Obst, Gemüse und Tabak wurden chlorhaltige Pestizid-Rückstände mit einer Distillationszeit von 4 Stunden aus 10 g Probe quantitativ erhalten. Die Resultate sind den nach dem AOAC-Verfahren erhaltenen Werten ähnlich. Bei Tabakproben und roher Chicorée wurden die DDT-Isomeren während der Distillation teilweise in ihre DDD-Homologe degradiert, ohne daß diese Umwandlung die Werte für «Gesamt-DDT» beeinflusste.

Die quantitative Extraktion der meisten chlorhaltigen Pestizide aus Fetten und Oelen erfordert eine Probenmenge von maximal 1 g und eine Distillationszeit von 8 Stunden, obwohl die flüchtigeren Verbindungen wie HCB, gamma-HCH und Aldrin schon nach 4stündiger Distillation völlig extrahiert werden.

Im Vergleich mit der Langlois'schen Methode, die die Rückstandsbestimmung in fettreichen Lebensmitteln ermöglicht, ergab die Distillationsmethode für beta-HCH und p,p'-DDT signifikant niedriger Werte.

Mit Rücksicht auf ihre Wirtschaftlichkeit und Einfachheit wird die Distillationsmethode als Hilfsmethode für die Bestimmung chlorhaltiger Pestizid-Rückstände besonders bei fettarmen Proben empfohlen.

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