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Some observations on clean-up procedures using sulphuric acid and Florisil

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ABSTRACT

The stability and recovery of 84 pesticides and 12 polychlorinated biphenyls after treatment with sulphuric acid have been studied. The results of these studies have been applied to the analysis of samples with different fat contents and compared with the results obtained using Florisil. The treatment with acid has a narrower field of application than treatment on a Florisil column.

INTRODUCTION

The determination of pesticides by high-resolution gas chromatography (HRGC) usually requires preliminary purification of the extracts before injection to simplify the process and to protect the instrumentation used. Extracts can be purified by various procedures such as liquid–liquid partitioning [1], treatment with acids [2] and bases [3], adsorption chromatography over Florisil [4], silica gel [5] or alumina [6], or gel permeation chromatography (GPC) [7]. These procedures are used alone or in combination depending on the complexity of the sample matrix. For example, a combination of GPC plus adsorption chromatography over silica gel, has been applied to clean-up more than 400 pesticides and metabolites in foods of animal and vegetable origin [8].

In this work we studied in detail the treatment with sulphuric acid, which is recommended by some workers [9–11] for the purification of organochlorine compounds and, in particular, for the rapid determination of polychlorinated biphenyls (PCBs) because of its economy and effectiveness. The main difficulty in the study was to determine the stability of various compounds to the treatment. In fact, although there are much data available for organochlorine substances, there is little information available on pesticides except for that published by the Royal Society of Chemistry [12] and the British Crop Protection Council [13], which give no precise numerical data but state whether the pesticides are stable or are partly or completely destroyed by sulphuric acid treatment. In this context, there seems to be universal agreement about the stability of products such as chlorinated hexanes (HCHs), chlordane, DDT, hexachlorobenzene (HCB) and PCBs. Also, although dieldrin, tetradifon and heptachlor epoxide are generally accepted to be destroyed, other pesticides, including aldrin, are believed by some workers to remain unaltered and to be partly or fully destroyed on treatment by others [14–22].

It is therefore important to obtain a fairly good idea of the effect that a given acid treatment has on pesticides before it is applied to them. We carried out a comprehensive study of the behaviour of different pesticides and PCBs towards sulphuric acid and determined the amounts remaining after treatment wherever possible. The conclusions drawn from this study were subsequently applied to real samples of different fat contents and the results obtained were compared with those achieved by the most commonly used procedure for this purpose: subfractionation on a Florisil column.

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EXPERIMENTAL

Chromatographic system

The chromatographic system consisted of a Hewlett-Packard 5890 gas chromatograph equipped with a ^{63}Ni electron-capture detector, using argon–methane as the auxiliary gas, and a nitrogen–phosphorus thermionic detector. An HP 7673A automatic injector and DB-5 and DB-17 capillary columns (30 m × 0.25 mm I.D., 0.25 μm film thickness) from J&W Scientific were used with 0.6 ml/min of helium as the carrier gas. The equipment was controlled via an HP 3363 ChemStation. The temperature of the injection port was 200°C, whereas that of the detector was 300°C. The temperature programme used was as follows: initial temperature, 57°C for 1 min; 15°C/min ramp up to 130°C, hold for 1 min; 2.3°C/min ramp; final temperature, 270°C for 20 min.

Standards

Chromatographically pure (97% minimum) pesticide and PCB standards were purchased from Chemservice (West Chester, PA, USA), Riedel de Haën (Seelze, Hannover, Germany), Scharlau (Barcelona, Spain) and Promochem (Wesel, Germany). Certified reference materials of different products were supplied by Promochem: potato (R900070), carrot (R900062), olive oil (R900080), butter (R900010) and lyophilized fish tissue (MAB-30C).

Reagents

Trace-analysis-grade methanol, diethyl ether, *n*-hexane and dichloromethane were purchased from Scharlau and SDS (Pepyn, France). Florisil of 60–100 mesh was supplied by Baker (Deventer, Netherlands). Pro-analysis anhydrous sodium sulphate (99% minimum purity) and concentrated 95–97% sulphuric acid were purchased from Scharlau. Ultrapure water obtained with a Nanopure II apparatus from Barnstead (Newton, MA, USA) was used throughout.

Extraction of certified samples

Organochlorine compounds were extracted from the reference materials using a Soxhlet battery and *n*-hexane as the solvent. A 1.5-g amount of each sample was mixed homogeneously with anhydrous sodium sulphate in a 1:3 (w/w) ratio and was subjected to extraction for 3.5 h. The resulting extract was concentrated at 40°C in a rotary evaporator Büchi (Plawil, Switzerland) evacuated to a final volume of 1 ml.

Acid clean-up

Certified reference materials. A 1-ml volume of each *n*-hexane extract was treated with 1 ml of concentrated sulphuric acid in screw-cap septum vials and immersed in an ultrasonic bath (Selecta, Barcelona, Spain) for 10 min. After separation, the organic phase was collected and the acid phase was washed with 2 ml of *n*-hexane. Each organic portion was added to the previous organic portion and then washed with 5 ml of ultrapure water. The organic portion was dried with anhydrous sodium sulphate that had previously been washed with *n*-hexane, and was concentrated at low temperature in the rotary evaporator under vacuum (1 ml); the sample was then ready for analysis by HRGC.

Individual pesticides. Pesticides and PCBs were dissolved in *n*-hexane with the exception of the more polar substances, which were dissolved in *n*-hexane–dichloromethane (1:1, v/v). The working concentration used was 0.1 mg/l. A 1-ml volume of the organic phase was treated with 1 ml of concentrated sulphuric acid in screw-cap septum vials and immersed in an ultrasonic bath for 10 min. After the phases were separated, the acid was washed with 2 ml of *n*-hexane, and the organic phases were combined and concentrated to 1 ml in the rotary evaporator.

Clean-up with Florisil

The organochlorine compounds in the certified reference materials were cleaned up using a glass column packed with 5 g of Florisil that was previously activated by heating. Subfractionation was started by elution first with 11.5 ml of *n*-hexane and then with 15 ml of *n*-hexane–dichloromethane (1:1, v/v). All PCBs were determined in the first fraction and most pesticides were determined in the second. The recovery from individual standards (at a concentration of 0.1 mg/l) was studied and then the same procedure was applied to extracts from the certified samples.

In every instance, the volume eluted in each fraction was evaporated to dryness under vacuum in the rotary evaporator and then dissolved in 1 ml of *n*-hexane.

Quantitation of the compounds

The compounds assayed were quantified by HRGC with an electron-capture detector or a nitrogen–phosphorus thermionic detector. Chlorpyrifos, a chlorinated organophosphorus pesticide, was used as a reference standard to correct instrumental fluctuations. An injected volume of 1 μl was used in all assays, which were performed in quintuplicate.

RESULTS AND DISCUSSION

Treatment of individual compounds with sulphuric acid

Tables I and II list the results obtained in the stability assays performed on the organochlorine compounds and other pesticides, respectively.

A recovery of 95% is considered to be acceptable for the organochlorine compounds (Table I). As expected, compounds such as HCB, HCHs, DDT, dichlorodiphenyldichloroethylene (DDE), tetrachlorodiphenylethane (TDE), dicofol, pentachloronitrobenzene (PCNB) and heptachlor are not affected by the acid. However, compounds such as chlorbenside, chlortal dimethil, endrin aldehyde, endosulfan A and B, endrin and dieldrin are vulnerable to the acid treatment, the last two as reported elsewhere [15,16,19,22]. Aldrin seems to withstand the acid treatment to some extent as only 34% of the initial content is lost, although other workers [19] have found that it is recovered almost completely. Heptachlor epoxide (recovery 52.5%) is not destroyed fully, contrary to previous reports [14]. Tetradifon (recovery 9.9%) and chlorfenson (recovery 22.5%) are only poorly recovered, consistent with earlier findings [15], as are silvex (13.2%) and methoxychlor (15.0%).

With respect to the PCBs, the less chlorinated compounds (*i.e.* those containing one to five chlorine atoms) are recovered in lower proportions (less than 98%) than the others.

It is worth noting the diverse recoveries of the phenols, which in theory should not have been destroyed. Although the recovery of pentachlorophenol can be regarded as normal, those of dichlorophenol and trichlorophenol are not. These anomalies can be attributed to the higher volatility of these two compounds, which implies a greater loss in the clean-up process. In addition, they can be dehydrated by sulphuric acid.

TABLE I

RECOVERY (MEAN AND STANDARD DEVIATION) OF ORGANOCHLORINE COMPOUNDS AFTER PURIFICATION WITH SULPHURIC ACID

Samples were analysed in quintuplicate.

Compound	Recovery (%)	
	Mean	σ_{n-1}
2,4-Dichlorophenol	38.3	7.2
2,4,5-Trichlorophenol	15.7	3.6
Pentachlorophenol	92.0	4.8
α-HCH	91.4	3.8
β-HCH	96.6	4.1
Lindane	97.8	4.6
δ-HCH	97.0	3.5
Aldrin	66.0	4.3
Endrin	N.D.[a]	–
Endrin aldehyde	N.D.	–
Dieldrin	N.D.	–
4,4'-DDT	98.4	3.2
4,4'-DDE	96.3	3.5
4,4'-TDE	97.2	4.3
Methoxychlor	15.0	4.6
Dicofol	95.1	2.6
Heptachlor epoxide	52.5	8.6
Heptachlor	99.4	4.1
PCNB	97.5	8.0
HCB	97.4	4.4
Chlorthal dimethil	N.D.	–
Chlorfenson	22.5	4.6
Chlorbenside	N.D.	–
Tetradifon	9.9	1.7
Endosulfan A	N.D.	–
Endosulfan B	N.D.	–
Fenoprop	13.2	2.1
PCB 2	95.4	4.7
PCB 7	96.8	5.0
PCB 28	97.3	3.7
PCB 47	97.8	4.6
PCB 52	97.6	4.6
PCB 101	97.9	3.5
PCB 138	98.9	3.7
PCB 153	99.5	3.2
PCB 180	98.9	4.0
PCB 194	99.8	2.6
PCB 206	99.4	4.7
PCB 209	99.3	5.0

[a] Not detected.

Most of the members of the other pesticide families (Table II) react to a greater or lesser extent with the acid. This clean-up procedure cannot be applied to compounds such as organophosphates, pyreth-

TABLE II

RECOVERY OF OTHER PESTICIDES AFTER TREATMENT WITH SULPHURIC ACID

Pesticide	Recovery (%)	Pesticide	Recovery (%)
Organophosphates		*Oxazolidine*	
TEPP	N.D.[a]	Vinclozolin	N.D.
Chlorpyrifos	N.D.	*Triazapentadiene*	
Tetrachlorvinphos	1	Amitraz	N.D.
Ethion	N.D.	*Phthalimides*	
Malathion	N.D.	Captan	N.D.
Phorat	N.D.	Captafol	N.D.
Phosalone	1	Dialifos	N.D.
Demeton-s-methyl	N.D.	*Pyrethroids*	
Triazophos	N.D.	Permethrin	32
Phosdrin mevinphos	N.D.	Cypermethrin	10
Azinphos methyl	N.D.	*Acetamides*	
Acephat	N.D.	Alachlor	N.D.
Fenitrothion	18	Propachlor	N.D.
Parathion ethyl	23	Propanil	N.D.
Dichlorvos	3	*Nitro compounds*	
Naled	7	Dinoseb	76
Pirimiphos ethyl	N.D.	Dinobuton	N.D.
Pirimiphos methyl	N.D.	*Ureas*	
Pyrazophos	N.D.	Chlorsulfuron	N.D.
Diazinon	N.D.	Chlortoluron	N.D
Carbamates		Chlorbromuron	N.D.
Triallate	N.D.	Diuron	N.D.
Aldicarb sulphoxide	N.D.	*Amides*	
Pirimicarb	N.D.	Napropamide	N.D.
Sulfallate	N.D.	Dichlofluanid	N.D.
Propham	29	*Imidazols*	
Carbaryl	25	Imazalil	N.D.
Triazines		Prochloraz	N.D.
Atrazine	N.D.	*Nitroanilines*	
Simazine	N.D.	Trifluralin	78
Terbutryn	N.D.	Dicloran	70
Metamitron	16		
Prometryne	10		
Uracil			
Bromacil	N.D.		
Nitriles			
Bromoxynil octano	N.D.		
Chlorothalonil	66		
Dichlobenil	68		

[a] Not detected.

roids, triazines, carbamates, phthalimides and amides. Only a few of the pesticides assayed, such as dinoseb (76%), dicloram (70%), trifluralin (78%), dichlobenil (68%) and chlorothalonil (66%) appear to withstand the acid treatment to some extent. It should be noted that our experimental results diverge from previous reports. Thus acephate and fenitrothion, which are stable against the acid according to some workers [17], were destroyed in this study, [the former completely and the latter almost fully (recovery 18%)]. Also, trifluralin and dicloran, which have been reported as unstable [15], were recovered at rates of 78 and 79%, respectively; in addition our results show that pirimiphos methyl is

completely destroyed on acid treatment and malathion is not recovered. This contrasts with previous reports [20].

The full destruction of compounds such as fenoprop, tetradifon, chlorfenson, methoxychlor and heptachlor epoxide, and the low recoveries obtained for others such as dinoseb, dicloran, trifluralin, dichlobenil and chlorothalonil, make it advisable to conduct preliminary assays to determine their recoveries before any real analyses are undertaken.

Fractionation of organochlorine compounds on a Florisil column

Table III lists the results obtained for the organochlorine compounds and the PCBs. The first fraction contained the PCBs, which were recovered quantitatively, plus some compounds that could not be fully resolved, *e.g.* 2,4-dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol, aldrin, *p,p'*-DDE, heptachlor and HCB. All these, with the exception of the three chlorophenols, were eluted by 60–70% in the first fraction.

The reproducibility achieved in these assays was fairly good for those compounds that were fully eluted in the first or second fraction (small standard deviations, σ_{n-1}), and poorer for those compounds that divided between two fractions.

Comparison of the treatments with sulphuric acid or Florisil as applied to certified reference materials

To check the results obtained in the individual assays the organochlorine compounds were also extracted from samples of certified composition, aliquots of which were subjected to acid treatment or subfractionation on a Florisil column. The results obtained are summarized in Tables IV–VII for olive oil, butter, lyophilized fish tissue and potato and carrot, respectively. Some interesting conclusions were drawn.

As can be seen in the tables, the clean-up on a Florisil column is as efficient as that obtained with sulphuric acid for a given sample matrix; therefore the recovery is higher than 95% except for the pesticides altered by the acid. The reproducibility (expressed as the relative standard deviation) of the Florisil clean-up procedure (3–4.5%) is higher than that of the sulphuric acid treatment (4.5–5.5%). The chromatograms obtained differed markedly from matrix to matrix. The extracts treated with Florisil (Fig. 1) were noiseless, with a well defined baseline reaching as far as 45 min, after which a large number of tall and well defined peaks appear. The baseline is restored after 65 min.

TABLE III

RECOVERIES (MEAN AND STANDARD DEVIATION) OF ORGANOCHLORINE COMPOUNDS IN THE FIRST AND SECOND FRACTION OBTAINED AFTER TREATMENT WITH A FLORISIL COLUMN

See Experimental for the details of fractionation. Samples were analysed in quintuplicate.

Compound	Recovery (%)		
	First fraction	Second fraction	
		Mean	σ_{n-1}
2,4-Dichlorophenol	5.3	94.7	2.5
2,4,5-Trichlorophenol	6.7	93.3	2.6
Pentachlorofenol	7.6	92.4	3.8
Endosulfan A	–	98.0	0.6
Endosulfan B	–	96.9	0.5
α-HCH	–	97.4	0.4
β-HCH	–	98.6	0.5
Lindane	–	99.5	0.3
δ-HCH	–	98.4	0.4
Endrin	–	98.2	0.4
Dieldrin	–	98.2	0.2
Aldrin	89.4	10.6	7.1
4,4'-DDT	–	99.0	0.5
4,4'-DDE	61.6	38.4	3.2
4,4'-TDE	–	94.3	0.6
Methoxychlor	–	98.0	0.4
Heptachlor epoxide	–	98.4	0.5
Heptachlor	69.6	30.4	7.8
PCNB	–	97.4	0.3
HCB	67.2	32.8	3.3
Chlorthal dimethyl	–	97.8	0.4
Tetradifon	–	96.0	0.6
Chlorfenson	–	98.4	0.2
Fenoprop	–	97.2	1.6
Chlorbenside	–	98.3	1.6
PCB 2	97.8	–	0.2
PCB 7	98.7	–	0.2
PCB 28	99.0	–	0.3
PCB 47	99.4	–	0.2
PCB 52	99.1	–	0.2
PCB 101	99.3	–	0.2
PCB 138	99.5	–	0.2
PCB 153	99.5	–	0.1
PCB 180	99.4	–	0.1
PCB 194	99.8	–	0.2
PCB 206	99.5	–	0.3
PCB 209	99.6	–	0.2

TABLE IV

RECOVERIES (MEAN AND STANDARD DEVIATION) OBTAINED AFTER ACID OR FLORISIL TREATMENT OF CERTIFIED REFERENCE MATERIAL OLIVE OIL

Samples were analysed in quintuplicate.

Compound	Certified amount (μg/g)	Recovery (%)			
		Florisil		H_2SO_4	
		Mean	σ_{n-1}	Mean	σ_{n-1}
Lindane	0.20	95.0	4.6	95.0	5.8
HCB	0.15	96.7	4.2	95.8	4.4
α-HCH	0.20	96.0	4.4	95.4	6.5
β-HCH	0.10	95.4	4.5	96.3	4.7
4,4'-TDE	0.10	94.9	3.6	95.5	5.0
4,4'-DDT	0.30	97.8	3.0	96.4	4.6
Dieldrin	0.25	95.6	3.9	N.D.[a]	N.D.
PCB 52	0.10	98.6	4.1	98.5	5.3
PCB 101	0.20	98.5	4.0	98.9	4.0
PCB 153	0.15	98.5	3.8	98.4	4.7

[a] Not detected.

TABLE V

RECOVERIES (MEAN AND STANDARD DEVIATION) OBTAINED AFTER ACID OR FLORISIL TREATMENT OF CERTIFIED REFERENCE MATERIAL BUTTERFAT

Samples were analysed in quintuplicate.

Compound	Certified amount (μg/g)	Recovery (%)			
		Florisil		H_2SO_4	
		Mean	σ_{n-1}	Mean	σ_{n-1}
Endosulfan A	0.35	98.6	3.1	N.D.[a]	N.D.
Endosulfan B	0.25	97.5	4.7	N.D.	N.D.
α-HCH	0.25	96.9	2.7	97.4	5.3
Lindane	0.30	98.6	3.6	98.0	6.0
Methoxychlor	0.15	96.3	3.8	N.D.	N.D.
HCB	0.20	98.4	3.8	99.0	5.3
PCB 28	0.20	98.4	2.9	98.7	5.0
PCB 52	0.25	98.6	3.1	98.6	4.8
PCB 101	0.30	98.4	3.4	98.7	5.2
PCB 138	0.30	98.5	3.7	98.3	4.7
PCB 153	0.25	98.0	2.8	98.5	5.5
PCB 180	0.20	98.7	3.6	98.4	4.3

[a] Not detected.

TABLE VI

RECOVERIES (MEAN AND STANDARD DEVIATION) OBTAINED AFTER ACID OR FLORISIL TREATMENT OF CERTIFIED REFERENCE MATERIAL LYOPHILIZED FISH

Samples were analysed in quintuplicate.

Compound	Certified amount (ng/g)	Recovery (%)			
		Florisil		H_2SO_4	
		Mean	σ_{n-1}	Mean	σ_{n-1}
Lindane	3.4	99.9	8.7	99.8	9.1
HCB	1.5	99.8	6.8	100.7	10.0
α-HCH	10	100.0	6.9	99.4	8.0
4,4'-DDE	160	98.3	5.3	98.0	6.0
4,4'-DDT	65	99.5	5.0	99.4	7.6
4,4'-TDE	46	99.8	5.5	99.7	7.4
Aldrin	1.8	99.7	7.4	N.D.[a]	N.D.
Dieldrin	5.3	101.0	6.6	N.D.	N.D.
PCB 101	61	99.8	5.2	99.9	8.1
PCB 138	170	98.5	4.2	98.4	5.5
PCB 153	120	98.3	4.3	98.9	5.3
PCB 180	35	99.9	5.1	99.7	6.5

[a] Not detected.

TABLE VII

RECOVERIES (MEAN AND STANDARD DEVIATION) OBTAINED AFTER ACID OR FLORISIL TREATMENT OF CERTIFIED REFERENCE MATERIALS POTATO AND CARROT (NO FATTY SAMPLES)

Samples were analysed in quintuplicate.

Compound	Certified amount (μg/g)	Recovery (%)			
		Florisil		H_2SO_4	
		Mean	σ_{n-1}	Mean	σ_{n-1}
Potato					
Endosulfan A	0.70	97.5	2.8	N.D.[a]	N.D.
Endosulfan B	0.30	97.9	4.1	N.D.	N.D.
Lindane	0.20	99.0	3.4	98.4	5.1
Methoxychlor	0.90	98.4	3.0	N.D.	N.D.
HCB	0.20	99.1	4.0	97.9	4.3
4,4'-DDT	0.50	98.2	3.6	98.5	6.5
PCB 52	0.25	98.5	4.2	97.9	4.5
PCB 101	0.30	98.6	3.6	99.0	5.1
PCB 180	0.50	98.3	3.5	98.5	4.2
PCB 209	0.50	98.5	3.5	98.1	4.4
Carrot					
Pentachlorophenol	1.00	98.5	4.2	95.0	5.2

[a] Not detected.

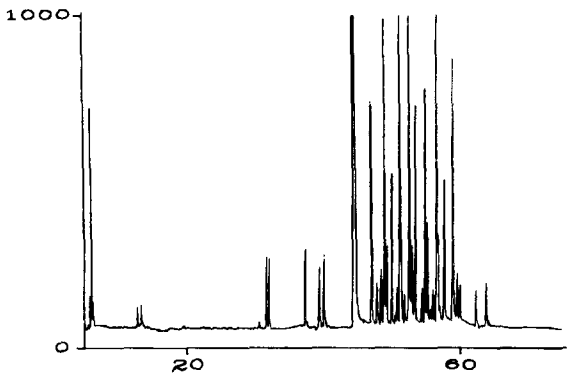

Fig. 1. Chromatogram of a butterfat extract obtained after treatment on a Florisil column. x-Axis in min; y-axis in counts.

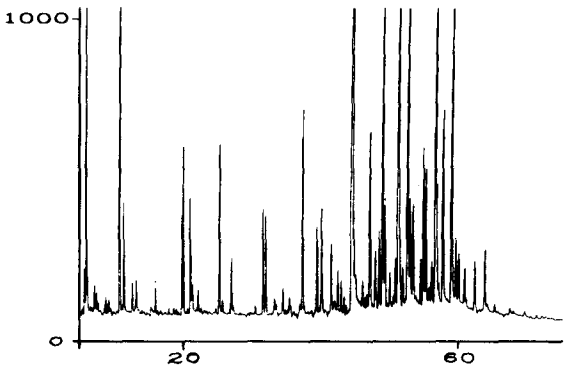

Fig. 2. Chromatogram of a butterfat extract obtained after treatment with sulphuric acid. x- and y-axes as in Fig. 1.

The chromatograms obtained with the acid-treated extracts (Fig. 2) have a noisy baseline, generally after 25 min but occasionally from the beginning. There are low-intensity peaks that can be assigned to the decomposition products.

CONCLUSIONS

Although the acid treatment offers major advantages in terms of simplicity, economy, rapidity and efficiency, it should be applied cautiously as it completely or partly destroys many compounds, which may in turn give rise to spurious results. Thus, although it does not affect the determination of PCBs, HCHs, DDT, DDE, TDE, dicofol, HCB, PCNB or heptachlor, it does decompose organochlorine compounds such as endosulfan A and B, chlorbenside, chlortal dimethil, endrin, endrin aldehyde and dieldrin, and most organophosphorus compounds, pyrethroids, triazines, carbamates, phthalimides and amides. This requires the extent of decomposition to be determined before any analyses are performed or an alternative treatment applied. If the behaviour of the compounds towards the acid is known, then complex samples can be analysed with similar results in terms of recoveries to those provided by Florisil subfractionation, even though the scope of application is more limited.

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