An Exhaustive Steam-Distillation and Solvent-Extraction Unit for Pesticides and Industrial Chemicals

G. D. Veith and L. M. Kiwus
U.S. Environmental Protection Agency
Environmental Research Laboratory-Duluth
Duluth, Minn. 55804

Steam distillation is one of the oldest methods of separating chemicals on the basis of differences in vapor pressures over water. Conventional steam-distillation techniques use an external steam generator that jets steam into the sample and collects the chemicals by condensing the steam and volatile chemicals in a cooled flask. Although steam distillation is commonly used in flavor and drug analysis (NIELSON and KRYGER 1969; SIEK and LINDSAY 1968; TAMSMA et al. 1969), the large surface areas of the glassware and the low collection efficiency of conventional apparatus have prevented the use of steam distillation as a quantitative technique in the analysis of trace amounts of less volatile organic chemicals.

Despite the apparent shortcomings of steam distillation, this technique offers unique possibilities in trace analysis. The vapor pressures of many pesticides and industrial chemicals are appreciably greater than those of water-soluble chemicals in wastewaters and sediments (MACKAY and WOLKOFF 1973; STORHERR et al. 1971). Moreover, the vapor pressures of many trace chemicals are greater than those of the high molecular weight triglyceride lipids in fish and warm-blooded animals. Because exhaustive solvent-extraction techniques remove lipids, waxes, and related natural products, as well as the trace contaminants, extensive chromatographic separations are necessary before the extracts can be analyzed for the trace chemicals.

We have developed a modified Nielsen-Kryger steam-distillation apparatus that provides exhaustive distillation of pesticides and industrial chemicals from water, sediments, and tissue and the simultaneous extraction of the distillate by a small volume of organic solvent. The extract is generally suitable for direct gas-liquid chromatography (GLC) analysis without the time-consuming concentration and cleanup procedures.

Materials and Methods

Figure 1 illustrates the exhaustive steam-distillation unit for the simultaneous distillation and extraction of organic chemicals. The water sample, or sample blended with water, is placed in a distilling flask fitted with a

Bulletin of Environmental Contamination & Toxicology,
Vol. 17, No. 6 © 1977 by Springer-Verlag New York Inc.

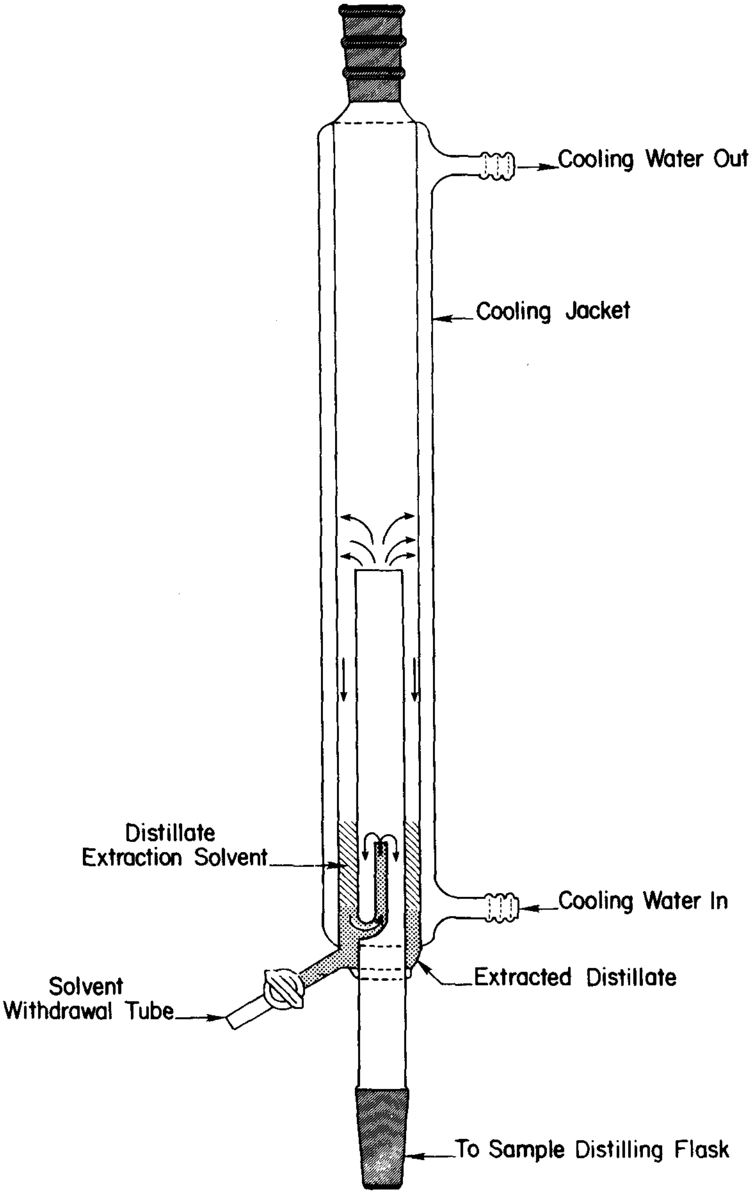

Fig. 1. Exhaustive steam-distillation and solvent-extraction apparatus.

24/40 glass joint. The solution is boiled and the steam distillate passes through the inner tube and condenses on the inside walls of the cooling jacket. The condensate passes through a layer of a lower density solvent such as isooctane or toluene into which the trace chemicals are partitioned. The water passes into the overflow tube, which serves as a solvent trap and permits only the water to drip back into the sample-distilling flask. The extract is removed through a stopcock, and the inner walls of the unit are rinsed with solvent to assure a quantitative transfer of the extract.

This steam-distillation unit has overall dimensions of 55 mm x 500 mm with 24/40 joints and a solvent capacity of approximately 15 ml (Fig 1.). The unit is available commercially from Ace Glass Company[1] (Vineland, New Jersey) for $98.00.

Water samples may be distilled directly by using a 2- to 3-liter round-bottom flask and a suitable heating mantle. Sediments and fish tissue (10-300 g) are blended with distilled water in a Waring blender and added to the distilling flask. The sample is boiled rigorously for 1-7 hr depending on the type of sample. For the analyses of PCB and chlorinated pesticides presented in this paper, the extract may be injected directly into the gas chromatograph without further cleanup.

Results and Discussion

The results of a series of experiments to assess the potential of our steam-distillation unit to provide quantitative estimates of trace chemicals are shown in Table 1. Boiling 2.5-liter water samples for 60 min resulted in greater than 85% recovery for all PCB's, pp'DDE, mirex, and heptachlor epoxide. Previous studies (MINSLEY 1973) suggested that this technique is also quantitative for the analysis of gasoline, fuel oils, kerosine, and some heavier motor oils found in natural waters. For volatile chemicals that may be obscured by the solvent peak, hexadecane or other less volatile solvents can be used so that the solvent peak elutes after the major part of the chromatogram. Moreover, the problems of emulsions and interferences commonly observed in solvent extraction of wastewaters are eliminated with this steam-distillation technique.

The analysis of Hudson River sediments taken from an area contaminated with PCB's showed that 78% of the PCB's could be steam distilled within 60 min. Conventional Soxhlet extraction of sediments typically produces a dark green-yellow or black extract because of the pigments and waxes that are also extracted from the sediments. The

---

[1] The U.S. Environmental Protection Agency neither recommends nor endorses any commercial product; trade names are used only for identification purposes.

steam-distillate extract is colorless and can be analyzed directly unless the sediments contain large quantities of elemental sulfur. The interference by sulfur is eliminated by refluxing the extract with rainy-copper before GLC analyses.

The results of exhaustive steam distillation of fish tissue indicate that the recovery of PCB's was greater than 80% at the 1.7 μg/g concentration in wet tissue. Although this recovery is somewhat less than expected from a conventional solvent extraction and cleanup and may never replace established analytical procedures, steam distillation has several important advantages. First, many monitoring and surveillance programs require a large number of analyses. With this steam-distillation unit samples can be blended with water without special preparation and when boiled overnight, they will produce an extract for GLC analysis that does not require concentration and lipid cleanup steps. Thus more samples may be screened with ample reliability, and more extensive studies may be conducted on specific samples with higher concentrations.

TABLE 1.

Recovery of PCB's and Related Chemicals from Water, Sediments, and Fish by Steam Distillation

Sample description	Quantity of chemical present (μg)	Steam-distillation recovery (%)
2.5-liter water sample		
Aroclor 1016 for 45 min	0.04[a]	97.9
Aroclor 1242 for 45 min	0.04	99.4
Aroclor 1248 for 60 min	0.04	100.0
Aroclor 1254 for 60 min	0.04	99.1
pp'DDE for 60 min	0.02	104.0
Heptachlor epoxide for 60 min	0.01	89.9
Mirex for 60 min	0.04	89.5
Sediments -- 2.5 liters distilled water		
Aroclor 1016 in 50 g of Hudson River mud, 60 min	2,500[b]	78.0
Fish tissue -- 2.5 liters distilled water		
PCB's in 10 g Ohio River catfish for 7 hr	17[b]	82.0
PCB's in 10 g Ohio River catfish for 14 hr	17[b]	84.7

[a] Quantity added to water, individual analyses.

[b] Quantity determined by solvent extraction.

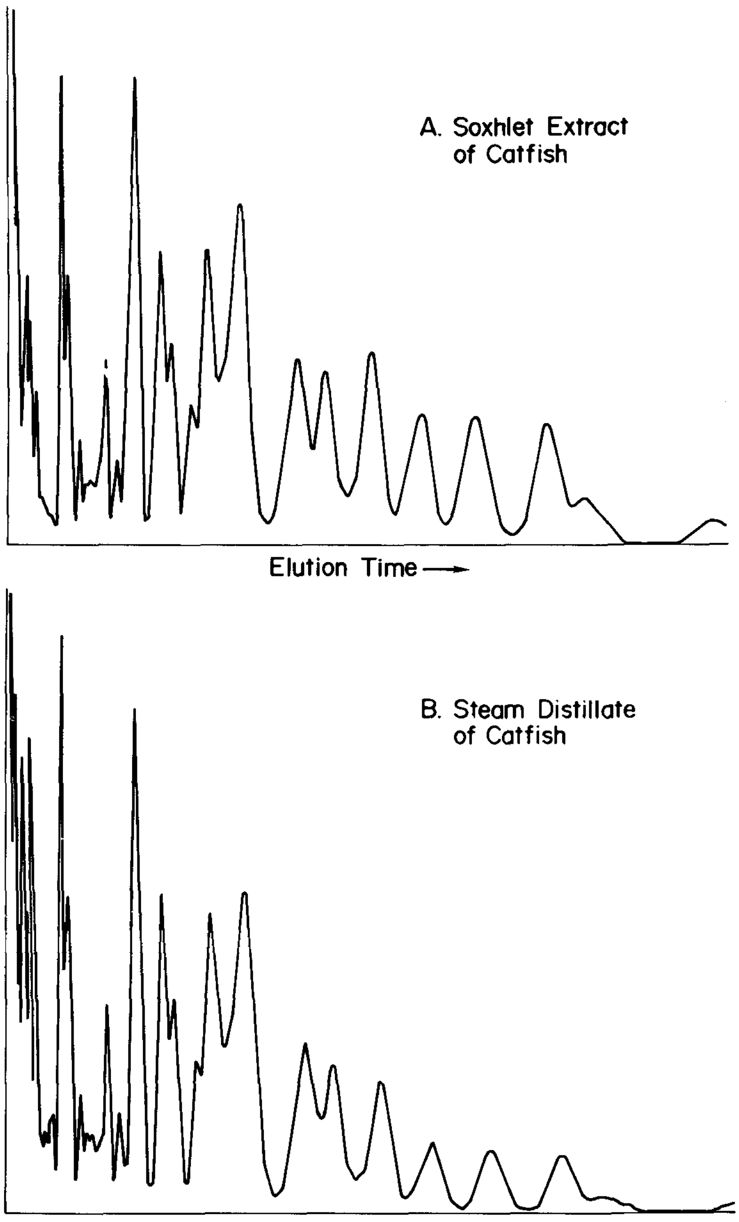

Fig. 2. Chromatograms of (A) a Soxhlet extract of catfish after Florisil cleanup and (B) a steam-distillate extract without cleanup.

Second, considerable effort has been expended on methodology for gas chromatographic/mass spectral (GC/MS) analysis of chemicals less than 0.1 µg/g in fish tissue. Despite recent advances (STALLING et al. 1972; VEITH et al. 1975) the procedure for adequately removing the lipids from a 100- to 400-g fish extract is tedious and limited by reagent blanks from the large quantities of Na_2SO_4 and solvents used in the extraction and cleanup. We have used this exhaustive steam-distillation unit for 100- to 200-g fish samples with an average of 75% recovery of most of the major contaminants such as PCB's, chlordane, and DDT. Comparison of chromatograms of a Soxhlet extract of a catfish after Florisil cleanup and a steam-distillate extract without cleanup shows that recovery of the early-eluting (more volatile) components is greater by steam distillation than by Soxhlet extraction (Fig. 2).

The quantity of lipid in the extract increases with increasing distillation time. Consequently, a volatile fraction can be removed after 1 hr, and a second fraction can be collected after 20 ml of isooctane is poured in the top of the unit and the distillation continued.

Acknowledgment

We wish to thank Mr. Frank Puglisi for his helpful suggestions and assistance.

References

MACKAY, D., and A. W. WOLKOFF: Environ. Sci. Technol. 7, 611 (1973).

MINSLEY, B.: Detection and identification of trace levels of petroleum products in aquatic environments. M.S. Thesis, Univ. of Wisconsin (Water Chemistry), Madison, Wis. 91 p. (1973).

NIELSON, T. K., and S. KRYGER: Dansk Tidsskr. Farm. 43, 39 (1969).

SIEK, T. J. and R. C. LINDSAY: J. Dairy Sci. 58, 1887 (1968).

STALLING, D. L., R. C. TINDLE, and J. L. JOHNSON: J. Assoc. Off. Anal. Chem. 55, 32 (1972).

STORHERR, R. W., R. R. WATTS, A. M. GARDNER, and T. OSGOOD: J. Assoc. Off. Anal. Chem. 54, 218 (1971).

TAMSMA, A., F. E. KURTZ, A. KONTSON, and M. J. PALLANSCH: J. Dairy Sci. 52, 152 (1969).

VEITH, G. D., D. W. KUEHL, and J. ROSENTHAL: J. Assoc. Off. Anal. Chem. 58, 1 (1975).