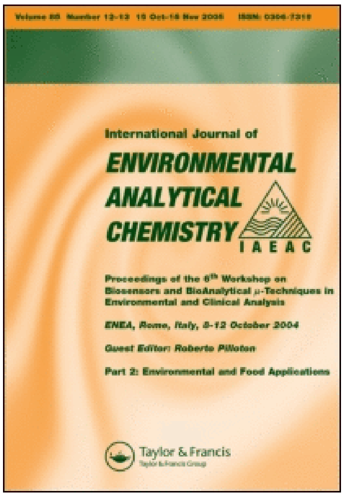

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Solvent Extraction of Organic Water Pollutants

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Solvent Extraction of Organic Water Pollutants

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Based on experiments with model systems of known organic water pollutants and environmental samples, conclusions are reached concerning the best general solvent for extraction and the most appropriate methods for related manipulations. Chloroform, methylene chloride–ether mixtures, and methylene chloride are the best solvents for general extraction purposes. Methylene chloride is recommended. Most samples should be extracted first at basic and then acidic pH. The analyst has very little control over emulsion formation through choice of solvent or by pH adjustment, but continuous liquid–liquid extractors overcome most emulsion problems. For highest recovery of extracted pollutants, extracts should not be treated with drying agents before concentration. Final evaporation of extracts using a micro-Snyder column is recommended over evaporation with a steam of inert gas.

KEY WORDS: Methylene chloride, emulsions, pH adjustment, glass wool, sodium sulfate, Kuderna-Danish evaporation, inhalation toxicity, sewage, paper mill, and petrochemical wastewaters.

Selection of the extraction solvent is an important initial consideration when a general organic survey of a water sample is required. In addition to the choice of solvent decisions have to be made about pH adjustment, how to treat emulsions, whether to dry the extract, and how to concentrate to a small volume with minimal losses. Experiments with model systems of known water pollutants and with true environmental samples have provided some valuable guidelines.

EXPERIMENTAL

Solvent extraction of model systems

A stock solution of 19 selected water pollutants (Table I) was prepared in acetone. Model solutions were prepared by adding 1 ml of the stock

TABLE I

Solvent extraction efficiencies for model compounds

	Percent recovery[a]										
	$CHCl_3$		CH_2Cl_2		$CH_2Cl_2:Et_2O$		Et_2O		EtOAc	CCl_4	15% CH_2Cl_2 in Hexane
Compound[b]	Neutral	Acid	Neutral	Acid	Neutral	Acid	Neutral	Acid	Neutral	Neutral	Neutral
ıne	U[c]	U[c]	U[c]	U[c]	U[c]	U[c]	55	16	64	40	42
ɔl	73	8	64	8	66	T[d]	75	—	72	36	18
roethane	49	—	45	—	49	T[d]	U[c]	—	69	82	49
obenzene	70	—	62	—	60	—	U[c]	—	94	78	46
oroisopropyl) ether	90	—	84	—	89	—	83	—	96	83	60
	87	—	89	—	86	—	111	—	93	87	68
oroethyl) ether	89	—	88	—	82	—	93	T[d]	91	77	39
ic acid	—	—	—	5	5	T[d]	15	32	35	—	—
cane	30	17	29	19	45	T[d]	49	29	U[c]	40	50
ic acid	T[d]	17	—	17	17	20	30	38	51	—	—
pineol	89	—	82	—	86	—	87	—	56	86	U[c]
luene	92	—	88	—	84	—	96	—	94	90	60
hiazole	93	—	95	—	87	—	85	8	102	94	54
	25	20	35	24	71	—	77	7	81	T[d]	—
ic acid	90	8	86	15	90	8	90	T[d]	100	36	T[d]
hene	92	—	92	—	86	—	89	—	86	92	66
l phosphate	126	—	105	—	98	—	98	—	104	92	70
hylene	96	—	92	—	82	—	77	—	58	74	62
almitate	83	21	72	31	84	—	77	15	92	49	56
% recovery[e]	71	—	67	—	75	—	77	—	77	61	38
duplicate difference	3	—	6	—	5	—	7	—	8	5	3

aces indicate compound was not detected.

order of elution from a packed Carbowax 20M-TPA column. The initial standard of *n*-octadecane elutes after *o*-nitrotoluene.

uitable for quantification because of solvent tailing or impurities.

ss than 5%.

ounds included except tridecane and those obscured by solvent impurities; compounds not detected or detected only as trace acoumts were counted as zero recovery.

solution to 1-l of distilled water, forming a solution containing 10–50 μg of each compound. Only hexachloroethane (50 ppb) and octanoic acid (30 ppb) concentrations were greater than 25 ppb. The pH of the stock solution was about 5.

Each 1-l model solution was extracted with three 50 ml portions of commercial, distilled-in-glass solvent. Each portion was agitated in a 2-l separatory funnel for precisely 1 min. For the acid extracts at pH 2–3, 1 ml of concentrated hydrochloric acid was added after the neutral extractions, and the water was re-extracted with three additional portions of solvent.

In the methylene chloride–ether experiment, 40 ml of ether was added to the water solution and dissolved by shaking for 1 min, and the sample was extracted with three 50-ml portions of methylene chloride. In the ethyl acetate and diethyl ether extractions, 100 ml of each solvent was added and three 50-ml extractions were made. No additional ether was added before starting the acid extractions.

No extract was dried before concentration. Each was evaporated in a 500-ml Kuderna–Danish (K–D) apparatus to 5–10 ml. The ether extract was exchanged into methylene chloride at this point by adding 50 ml of methylene chloride and re-evaporating the mixture to 5–10 ml. After cooling, each K–D bottom was fitted with a two-chamber micro-Snyder column, and the extract was evaporated to about 1 ml and cooled before spiking with *n*-octadecane for the internal standard. Analysis was by FID–GC using a 2.1 m × 2 mm I.D. glass column packed with 5% Carbowax 20M-TPA on 80/100 Gas Chrom Q. The carrier gas was helium at 20–30 ml/min. After isothermal operation at 80°C for 3 min, the column temperature was programmed at 8°/min from 80° to 170°C for 12 min. An autosampler was used for sample injections and GC program initiation. Data were recorded using an electronic integrator and a strip chart recorder.

The model solution was chromatographed between every two samples. Results were calculated by the internal standard method using integrator programs for some samples and manual peak–height measurements for others.

Solvent extraction of environmental samples

Sodium hydroxide solution was added to adjust the pH of 500 ml of each effluent sample in a 1-l separatory funnel to 11 (pH paper). Each sample was extracted with four 50-ml portions of distilled-in-glass solvent. Before extraction with ethyl acetate, 50 ml of this solvent was added to saturate the sample. After adjustment to pH 2 with concentrated HCl, each sample was re-extracted with four 50 ml portions of solvent. Emulsions were broken by passing the solvent–emulsion layer through a 2.5-cm-I.D. column containing approximately 5 cm of glass wool prewet with clean solvent. Extracts were concentrated to about 1 ml by methods described earlier. Acid extracts were evaporated to near dryness under a stream of nitrogen, methylated with diazomethane in ether and methanol,[1] and adjusted to a volume of 1.0 ml with the original solvent. Each extract was chromatographed on a non-polar (SP–2100) and a polar (Carbowax 20M-TPA) column. The SP-2100 was 3% on 80/100 Supelcoport in a 3 m × 2 mm I.D. glass column with helium flowing at 30 ml/min. Column temperature was programmed from 80° to 210°C at 6°/min. The Carbowax conditions were similar to those given earlier.

Sewage emulsion study

The pH of 500 ml of fresh treated sewage was adjusted in a 1-l separatory funnel to the desired neutral, basic or acidic value, and 50 ml of solvent was added. After shaking for exactly 1 min, the funnel was allowed to stand undisturbed for exactly 5 min. The solvent layer was drained into a graduated cylinder, and the volumes of clear solvent and emulsion were recorded immediately and again after 10 min. After this procedure had been repeated with two additional 50-ml portions of solvent, the pH was changed and three more extractions made. Neutral pH was 6–8, basic was 11, and acidic was 2.

RESULTS AND DISCUSSION

Extraction of model compounds

Among EPA analysts, the most popular extraction solvents are chloroform or methylene chloride followed by diethyl ether, hexane, 15% methylene chloride in hexane, and ether–hexane mixtures.[2]

These solvents were tested for extraction efficiency using model compounds in distilled water. All compounds in the model solution have been found in drinking waters or industrial effluents[3] and represent most common organic classes and functional groups except bases. This experiment was meant to provide some guidance to the best solvent to use for a sample that might contain any or all of these types of materials. Probably the best criterion for overall efficiency in such a situation is the average recovery of all compounds in the solution as shown at the bottom of Table I.

Using the average recovery criterion, chloroform was a slightly better solvent than methylene chloride. The difference was slight, however, and in an experiment using a distilled water solution of compounds found in paper mill wastes and petrochemical refineries, no significant differences were found.[4]

Eichelberger and co-workers[5] suggested that the addition of a small amount of ether to a sample before methylene chloride extraction would improve recovery of acids and phenols. The data of Table I show this to be true and suggest that recovery of alkanes and fatty acid esters was also improved. Additional experiments, not given in Table I, showed that solvent mixtures containing 20–40% ether in chloroform gave recoveries of 70% for phenol and a range of 20 to 80% for butyric to octanoic acids. Apparently, ether improves the ability of both chloroform and methylene chloride to extract acids and phenols. Further, it does not seem to matter whether the 20% ether is added separately to the sample solution (the methylene chloride experiment) or is mixed with solvent (chloroform).

Ethyl acetate has been used to isolate drugs from human body fluids[6] but has not been commonly applied to water pollutant analysis. It was as efficient as any solvent tested, and is similar to ether in density and water solubility but does not form peroxides and is not as flammable.

Diethyl ether and ethyl acetate are both so soluble in water that about 100 ml/l had to be added before a separate layer began to develop. For this reason it could be argued that 250 ml of these solvents were used for extraction and that the results cannot be considered as equal to the other solvents in the table. More relevant perhaps is the fact that the solvent that did separate contained more of the test compounds than did equal volumes of the insoluble solvents.

Carbon tetrachloride or hexane would seem to be most useful for isolating hydrocarbons. Carbon tetrachloride was very effective for aromatic hydrocarbons (acenaphthene and acenaphthylene) but less so for *n*-alkanes. Hexane had the reverse characteristics.

Although all solvents used were distilled-in-glass, ether, ethyl acetate, and hexane all contained materials that interfered with test mixture components (marked "U" in Table I). Tridecane sometimes eluted too high on the solvent tail for accurate quantitation.

Extraction of environmental samples

As many chemists have learned, analysis methods that work well on model systems sometimes behave differently when applied to "real" situations. Final effluents from a petrochemical plant, a paper mill, and a sewage treatment plant were extracted under basic conditions followed by an acidic extraction. Four solvents were evaluated: chloroform, methylene chloride, 20% diethyl ether in methylene chloride, and ethyl acetate. Each extract was chromatographed on a polar and a nonpolar column. Evaluation of the resulting 48 chromatograms by counting the number of

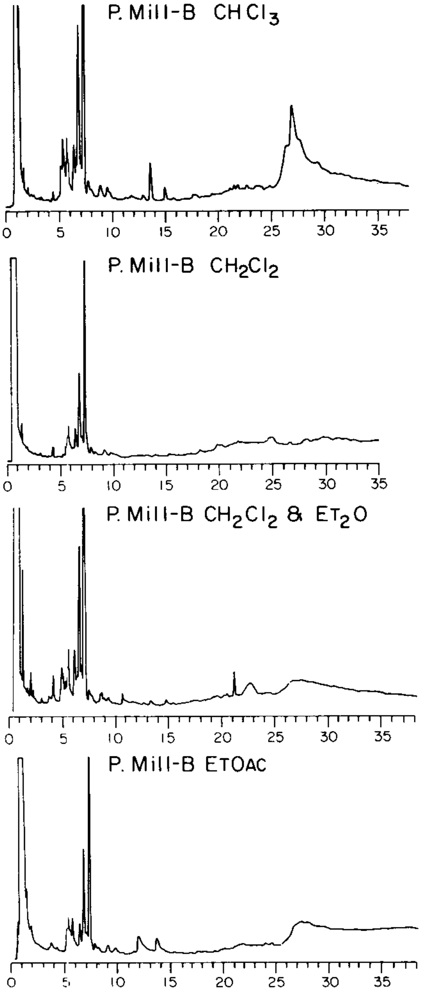

FIGURE 1 Solvent dependent differences among materials eluting after 10 min in base-neutral paper mill wastewater extracts

individual discernible peaks led to ranking the solvents in decreasing order of extraction efficiency as chloroform > methylene chloride–ether 20% > methylene chloride > ethyl acetate. Rating the solvents on the number of extract peaks ≧20% of full recorder scale gave chloroform (79 peaks), methylene chloride–ether (78), methylene chloride (70), ethyl acetate (56). As a general example of the differences among the four solvents, Figure 1 shows the paper mill effluent base-neutral fraction chromatographed on the nonpolar SP–2100 phase. Differences among peaks eluting before the 10 min retention time are probably intensity differences rather than identity differences. However, though the peaks are small in the four solvent extracts, there is a great contrast in peaks eluting after 10 min.

Figures 2 and 3 show the effect of extraction efficiency and the effect that the choice of GC column has on the information obtained. In Figure 2, each solvent extract appears qualitatively equivalent when chromato-

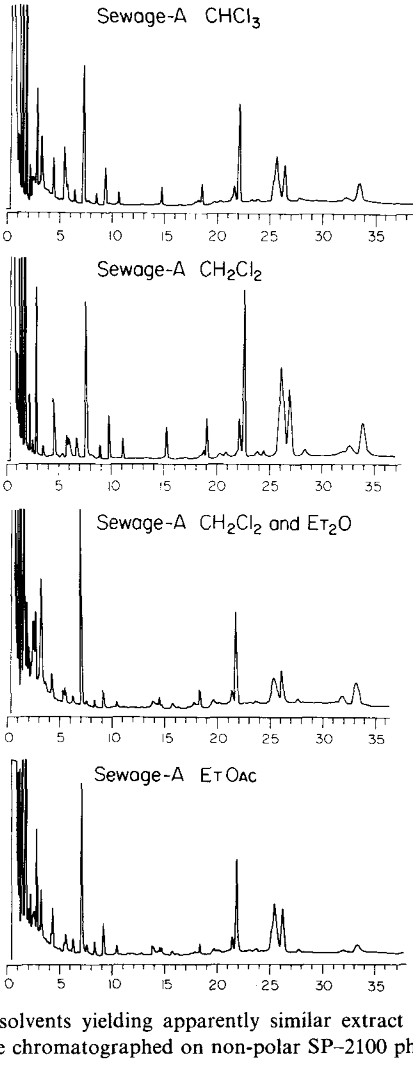

FIGURE 2 Different solvents yielding apparently similar extract profiles when acids and phenols from sewage are chromatographed on non-polar SP–2100 phase.

graphed on a nonpolar column. The same extracts chromatographed on a polar column (Figure 3), however, show marked differences among the solvents. For example, the chloroform sewage extract chromatogram contains at least eight significant peaks eluting between 5 and 10.5 min; the methylene chloride extract chromatogram contains only four. The chloroform extract component producing the most intense peak is barely discernible in the methylene chloride extract chromatogram. Therefore,

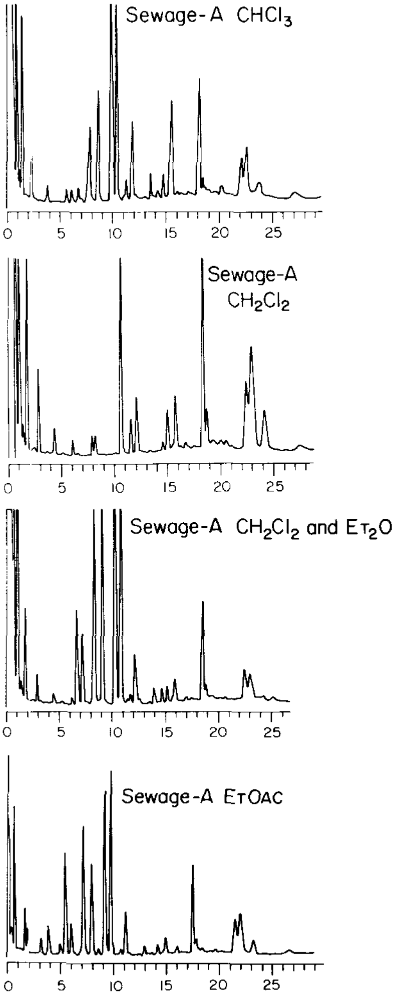

FIGURE 3 Different solvents yielding differing GC profiles when the extracts from Figure 2 are chromatographed on polar Carbowax 20M-TPA.

what will be found by extraction depends both on the solvent and the chromatographic conditions.

Recommended solvent

Based solely on these data, the top three solvent choices are chloroform, methylene chloride–ether, and methylene chloride. The solvent recommended for general use is methylene chloride. In overall efficiency, there is probably only a range of about 10% between the three solvents and that difference depends mainly on the individual characteristics of the sample being extracted. For example, comparison of polar column chromatograms showed that methylene chloride and chloroform were equal in extracting the neutrals of the petrochemical plant effluent; chloroform was better than methylene chloride for the paper mill effluent neutrals and poorer for sewage effluent neutrals.

Separatory funnel extractions invariably expose the chemist to solvent vapors. On this basis, chloroform is not recommended. A recent toxicity compilation[7] lists inhalation studies that show adverse effects on humans exposed to chloroform at a concentration of 10 ppm over a year's time. A much higher level (500 ppm) of methylene chloride was required to produce similar effects. A time-weighted average of 400 ppm of diethyl ether is allowed as the U.S. Occupational Standard.

The use of pure ether is not recommended because of its volatility and flammability and because it forms peroxides and impurities. Before using it as a 20% solution in methylene chloride, the ether must be evaporated 100:1 and checked on the GC column to be used for the analysis. Impurities can usually be removed by passing 250 ml of ether through a column of 30 g of basic alumina. This cleaned ether must be checked by GC. The importance of this verification step was illustrated by a recent shipment received by this laboratory. Of two different bottles from the same box, one was found to be pure-as-is and the other was grossly contaminated. Unless phenols are the main compounds of interest, the use of methylene chloride–ether is probably not worth the extra effort involved.

Adjustment of pH

Neutral and acidic compounds are found in water far more often than bases.[3] Because phenols and acids usually require special GC columns or derivatization procedures, they should be isolated as a separate fraction. Initial extraction at a nominal neutral pH contaminates the neutral fraction with some acids and phenols (Table I). Experience has shown that, contrary to earlier practice[4], it is best to extract the sample first at a pH of about 11 to isolate the bases and neutrals and then to make the sample strongly acidic to isolate the acids and phenols.

Emulsions

Formation of emulsions is one of the most frustrating problems encountered in solvent extraction of various water samples. Although emulsions can usually be broken by forcing the material through solvent-wetted glass wool, the time involved and the unknown analytical losses that occur make emulsions undesirable.

In a study of different sample types, different original pH's, and different solvents, only the nature (source) of the sample made a consistent difference in emulsion formation. For the effluents tested, the order according to degree of emulsion formation, measured by volume under a standard set of conditions, was paper mill effluent > raw sewage > petroleum refinery effluent. This order held whether the original pH was adjusted to either alkaline or acidic. This order also held for the four solvents tested (chloroform, methylene chloride, and 25% ether in methylene chloride) except ethyl acetate. Ethyl acetate extraction of sewage and paper mill effluents produced heavy emulsions.

In a separate experiment, treated sewage samples were initially extracted at neutral, basic, or acidic pH. The pH was then changed (neutral to acidic, basic to acidic, and acidic to basic) and the samples re-extracted. The results are given in Table II. The neutral sample gave very light emulsions with all solvents except ethyl acetate, which was completely emulsified. The basic and acidic samples gave medium emulsions. After the pH change, the neutral-to-acidic sample gave a medium emulsion, but the other two samples gave practically no emulsion with any solvent tested.

These experiments indicate that the analyst has little control over emulsion formation, that emulsions ordinarily become less of a problem as a multistep extraction scheme progresses, and that ethyl acetate should not be used as a general solvent because it often gives no definite boundary between the emulsion and the aqueous layer. It was, in fact, this last problem and the attendant losses on breaking the emulsions that probably caused poor results with ethyl acetate in the effluent extraction study.

Separatory funnel extractions sometimes produced emulsions that could not be broken by usual techniques (glass wool, centrifugation, addition of a trace of methanol, or addition of sodium sulfate). Tannery wastes and a soap and detergent company effluent fit this category. They were successfully extracted without emulsion formation using methylene chloride in a continuous liquid–liquid extractor.

TABLE II
Emulsion formation in sewage with pH adjustment

	CH_2Cl_2			$CHCl_3$			25% Et_2O in CH_2Cl_2			EtOAc			25% Et_2O in $CHCl_3$		
	1[a]	2[a]	3[a]	1	2	3	1	2	3	1	2	3	1	2	3
Neutral	A[b]	A	A	B	B	A	A	B	A	E	F	F	A	A	A
Neutral acidic	F	A	A	D	B	A	F	C	A	B	A	A	F	B	A
Neutral basic acidic	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Acidic	E	E	A	E	D	A	E	F	C	F	A	A	C	D	A
Acidic basic	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Basic	E	B	A	D	A	A	E	C	B	D	A	A	B	A	A
Basic acidic	D	A	A	C	A	A	D	A	A	A	A	A	C	A	A

[a] First, second and third successive extractions.

[b] The ratings are A, 0–10 ml of emulsion; B, 11–20; C, 21–30; D, 31–40; E, 41–50; F, >50 ml.

Comparison of extraction efficiency with samples from four industries (petroleum, tannery, pesticide, and soap and detergent) by both separatory funnel and continuous extraction indicated that the two techniques are comparable. For some individual cases one technique was better than the other but no clear pattern emerged.

Drying solvent extracts

After a water sample is extracted with an organic solvent, the solvent is usually dried to remove dissolved water and then evaporated to a smaller volume before analysis. As shown below, for quantitative recovery of many common industrial pollutants, there is no advantage in drying a chloroform extract. Concern for losses during evaporation due to a steam distillation effect in undried extracts is unfounded.

Identical 1-l samples of water containing 33 μg of each of 13 industrial pollutants were extracted with two 50-ml portions of chloroform by the usual separatory funnel technique. The extracts were dried by passing them through a short column of anhydrous sodium sulfate or a short column of glass wool pre-wet with solvent. The extracts were evaporated to about 6 ml in a Kuderna–Danish apparatus and then to 1 ml by

TABLE III
Percent recovery of drying methods

Compound[a]	Na_2SO_4	Glass wool	Undried	Evap. ref.
Bis(2-chloroisopropyl) ether	87	82	92	91
sym-Tetrachloroethane	76	70	83	89
n-Hexadecane	29	23	36	93
alpha-Terpineol	86	81	92	91
Naphthalene,	82	76	87	91
o-Nitrotoluene	84	81	91	93
2-Methyl naphthalene	80	75	86	93
1-Methyl naphthalene	81	77	86	93
Benzothiazole	85	83	96	94
Phenol	19	17	19	91
p-Cresol	46	44	50	83
Acenaphthene	85	82	91	93
Dibenzofuran	84	83	92	92
Average	71	67	78	91

[a]Listed in elution order from a Carbowax 20M-TPA column.

blowing a stream of nitrogen over the sample. An undried extract and a reference sample of 100 ml of chloroform spiked with 33 μg of each compound were concentrated similarly. The experiments were done in duplicate, and each sample was analyzed by GC and quantitated by a computer-assisted data system.

The results are tabulated in Table III as percentage recovery of the amount added to the water. The last column in Table III shows the maximum amount of each evaporation reference component that could be recovered if extraction were 100% efficient and indicates the magnitude of losses on evaporation of the 100 ml reference solution to 1 ml. Low recoveries of hexadecane, phenol, and *p*-cresol in the extracts are due to extraction inefficiency rather than to a drying procedure.

Undried samples gave the best overall results. Recoveries from duplicate experiments with undried samples differed by an average of only two percentage points. With sodium-sulfate-dried samples, the average recovery difference was 6%; for the glass wool samples, it was 16%. The evaporation reference was very reproducible with an average difference in results of 2%.

For several years, undried chloroform and chloroform–acetone[8] extracts of water have been analyzed by GC and GC–MS without any problem. Methylene chloride extracts also behave similarly. In all three cases, the solvent distills as an azeotrope with water[9] and thus the water is removed early in the evaporation. This method is strongly recommended.

Concentration of extracts

Three groups of investigators[8,10,11] have recently reported that the majority of losses that occur during evaporation take place when the volume is being reduced from about 10 ml to 1 ml or less. All three groups caution against the use of an air or nitrogen stream to "blow-down" the extract. They all give illustrations of the recommended micro-Snyder column and some form of a semi-cone shaped receiver. When a chloroform extract was reduced to 1 ml with a micro-Snyder column, recoveries of model compounds were 95–100%.[8] The airstream method gave an average of 91% (see Table III).

Sometimes an extract must be evaporated to less than 1-ml to attain adequate concentrations for analysis. Recovery experiments were done with the reference mixture of Table III; 1-ml aliquots were evaporated to 0.7, 0.5, 0.3, 0.2, and 0.1 ml by the micro-Snyder column and the airstream–waterbath methods. Tests were also made by both methods using spiked water extracts that were evaporated to these levels.

The micro-Snyder column method was the best way to evaporate a sample to 0.3 ml; recovery at this volume was 90–95%, compared to an airstream recovery of 81–87%. Below 0.3 ml, however, the analyst has more control over the final volume under the mild conditions of the airstream–waterbath method. Results became highly variable from sample to sample at <0.5 ml volumes. The airstream method at 0.2 ml gave recoveries of 55–80% for the same compounds in duplicate tests, and 60–80% at 0.1 ml. The micro-Snyder column gave 60–80% recovery at 0.2 ml and 50–60% recovery at 0.1 ml. Therefore, for quantitation, samples should not be evaporated below 1 ml.

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Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

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