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ORGANIC SUBSTANCES IN POTABLE WATER AND IN ITS PRECURSOR

III*. THE CLOSED-LOOP STRIPPING PROCEDURE COMPARED WITH RAPID LIQUID EXTRACTION

K. GROB, K. GROB, Jr. and G. GROB
GC Laboratory, ETH Zürich, EAWAG, 8600 Dübendorf (Switzerland)
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SUMMARY

An attempt is made to define the role of gas chromatography in the investigation of organic substances in water, which is important because the handling of water samples before gas chromatographic (GC) analysis depends entirely on the information expected from the subsequent separation, identification and quantification.

Practical long-term experience with the previously published closed-loop stripping procedure (with intermediate adsorption on activated carbon) is described and further refinements are reported. A rapid and simple liquid extraction method is described, based on shaking 1 l of water with a small volume (0.5–1 ml) of solvent and subsequent high-resolution GC analysis of the extract. Qualitative and semi-quantitative information at the parts per 10^{12} level is easily obtained. Further studies of recovery rates under conditions where the volatility and polarity of extracted organic substances are varied are described for both methods. The suitability of both methods for the analysis of different types of water samples is discussed.

THE ROLE OF GAS CHROMATOGRAPHY IN WATER ANALYSIS

Most analyses of organic compounds in water are carried out in two steps, the first involving extraction and concentration of organic pollutants and the second qualitative and quantitative analysis of the organic mixture.

While many principles and techniques have been developed for the first step, the method used almost exclusively for the second step is gas chromatography (GC), despite the fact that most organic substances in water (at least in terms of amounts), as a consequence of their volatility and polarity, are unsuitable for GC analysis.

The main reason for the wide application of GC, apart from sample size and ease of operation, is its high separating power. Most other separation methods are completely inadequate for separating such complex mixtures as are extracted from

* For Parts I and II, see refs. 1 and 2.

water. It is hoped that liquid chromatography will become suitable for water analysis in the future, but at present its separating efficiency is not sufficient. Consequently, present knowledge about organic substances in water is biased, as analytical research is not directed by what is in the water or by what we want to find out, but entirely by what we are able to find out by using the available methods.

The fact that GC will probably remain the analytical method of choice for some time raises the question of the limits within which GC should be applied to water analysis. The answer is important, as it results in guidelines for the preparation of water samples for GC analysis.

It seems obvious that these limits should include the widest volatility range that can be covered by GC. It is less obvious whether or not this range has to be extended by forming derivatives of non-volatile polar substances, but this is outside the authors' remit. We feel, nonetheless, that except for a few low-molecular-weight substances, derivative formation should be avoided in water analysis, as it further complicates the already extremely complex material involved. We consider that non-volatile polar substances should be studied by liquid chromatography, and we hope that work in this direction will be intensified in the near future, possibly including suitable pre-separations if the separating power of GC does not permit the analysis of original water samples.

As its separating power is a major argument for the application of GC, full use of its potential should be made. It is difficult to imagine what information would remain in the separations presented in Fig. 1, as well as in many previously published examples, if they were carried out on packed columns. This is particularly so when the identification of individual substances is required. It is well known that substances of specific interest (*e.g.*, those causing toxicity or bad odours) may be minor components of a complex mixture and will, therefore, be lost in low-resolution separations. The principles and techniques of routine high-resolution separations are available and the careful acquisition of some additional knowhow as an essential prerequisite should not be a serious problem.

The application of high-resolution GC to the separation of organic compounds extracted from water includes certain requirements for the technique of sample preparation. This aspect of the analytical procedure is considered below.

DETECTION LIMITS

Routine analysis of many types of water samples over more than 1 year showed the sensitivities with which the different types had to be treated in order to obtain the information required. This allowed us to set certain rules for detection limits based not on theoretical considerations but entirely on practical experience (Table I).

Practical detection limits are indicated in order to provide a basis for the discussion of procedures that have to fulfil the sensitivity requirements set by these limits.

A concentration of, *e.g.*, 5 ppt of a single internal standard substance is produced by adding to 1 l of water 5 μl of a $1:10^6$ solution of the standard substance in acetone (we never add more than 20 μl of acetone to a 1-l sample in order to avoid modified solubility conditions). The use of internal standards is described in more detail under *Practical procedure* below.

TABLE I

DETECTION LIMITS

Type of sample	*Detection limit (amount of single substance producing a peak ten times higher than noise level)*	*Internal standard (concn. of single standard substance added to sample of given type)*
Purest samples: spring water, very pure ground or tap water	0.1 ppt*	5 ppt
Lightly contaminated samples: average tap water, clean surface water from river	2.0 ppt	50 ppt
Heavily contaminated samples: sewage water, accidentally polluted surface water	100 ppt	10 ppb**

* 1 ppt = 1 nanogram per litre of water (1 part in 10^{12}).
** 1 ppb = 1 part in 10^9.

EXPERIENCE WITH THE STRIPPING METHOD

The principles and some applications of the stripping procedure for the analysis of organic compounds in water have been described previously[1,2]. Routine application for almost 1 year has led to some additional observations and minor modifications that are reported here.

Trapping of stripped substances

We discussed this aspect extensively in Part I[1]. However, in the light of new developments, a brief reconsideration is required.

We are dealing with a special application of headspace analysis. Some well known techniques are clearly unsuitable for our particular purpose. Cold trapping fails because of excessive trapping of water. This method is useful only when used as an intermediate concentration step to produce a more concentrated water sample that can be extracted by a solvent. Direct transfer of stripping gas on to a column is possible only with heavily polluted samples and with high-capacity columns (packed columns).

A special device, called a gradient tube, has been designed[3–5] for water and other headspace analyses. Not having had personal experience with it, we are unable to comment on this.

There is considerable emphasis on the use of packed pre-columns[6,7] or trapping columns filled with uncoated polymers[8,9]. These materials have the following disadvantages compared with activated carbon: a much larger bed volume, owing to a lower specific surface area, resulting in relatively high water retention, even when filled with hydrophobic material; desorption by extraction with solvent (the only method that eliminates artefacts) in most applications is not feasible; difficult transfer (by evaporation) from the large volume on to a capillary column to form a narrow band; constant release of (at best, very small amounts) bleed; and no possibility of manufacturing a rugged, chemically and thermally inert filter (no use of glass blow-

ing). While these drawbacks may still allow reasonable use in subsequent low-resolution GC analysis, they preclude analysis on high-efficiency capillary columns, especially when relatively pure water is to be analyzed.

In conclusion, we still see no reason why an adsorbent material other than activated carbon, which is the only adsorbent that does not show the above drawbacks, should be used.

In the special case of the most volatile hydrocarbons (methane–butane), a combination of stripping with cold trapping has been used successfully[10].

Optimization of equipment

The parameter that has the most influence on the stripping and the subsequent desorption process is the size and geometry of the adsorbent filter. The filter disc should be as small as possible, to contain the smallest possible carbon particles while still retaining a low flow resistance to the stripping gas; it should be mechanically stable so as to allow a virtually unlimited number of runs with unchanged characteristics, and should not be too difficult to prepare.

These partly contradictory requirements can at best lead to a compromise. Our best figures, the difference between which and the optimum values we ignore, are as follows. A 1–1.5-mg amount of activated carbon of specially pure and active quality* and of particle size 0.05–0.1 mm (unchanged) is assembled in a cylindrical disc 2.5 mm in diameter and 0.8–1.2 mm thick. The filter is made basically as described in Part I[1], with a modified size and shape. As it is not easy to make, we have helped to initiate regular production and distribution. The same applies to the complete set of precision-manufactured materials (plastic-free filter holder, sample tube for liquid desorption, etc.).

Optimization of stripping procedure

Our previous work was carried out using 5-l water samples. We have now reduced the standard sample size to 1 l because, except for the purest waters, this volume proved to be sufficient for all types of samples. This reduction in volume brings two advantages. Firstly, we can immerse the whole of a 1-l flask, including the ground-glass joint, in a water-bath containing fresh tap water. This completely eliminates difficulties caused by leakage of the joint and the consequent influence of ambient air. Secondly, the reduced sample size, together with optimized adsorption and flow conditions (*i.e.*, filter geometry), leads to a reduction in the stripping time from 12–24 h to 2 h. In addition to the simplification of routine work, it also results in almost complete elimination of sample alteration, probably caused by biological processes during stripping. This is best shown by a test carried out with the easily extractable *n*-alkanes, from octane to dodecane, added in concentrations of 100 ppt to fresh tap water. After 10 h of stripping, more than half of the added material had disappeared. Stripping for 5 h caused a reduction of about one third, whereas after 1, 2 and 3 h good and virtually identical recoveries were obtained. This influence will, of course, be even more important when more biologically active samples are analyzed.

The reduced stripping time causes some losses in the recovery of heavier substances, *e.g.*, for the alkanes beyond eicosane. However, except for samples containing

* Dr. Bender and Dr. Hobein A.G., Rietlistrasse 15, Zürich, Switzerland.

heavy pollutants of special interest, this does not justify prolongation of the standard stripping time.

For extraction of the carbon filter, we still have no solvent as effective as carbon disulphide. Extraction is carried out according to the earlier descriptions, using 10–30 μl of solvent, depending on the sensitivity required. Subsequent concentration of the extract is normally avoided but may be necessary with extremely pure samples.

Long-term experience

When bubbling through the water sample, the stripping gas produces, as a by-product, an aerosol-like water mist which penetrates into the metal tubing between sample flask and filter holder, and some even on to the carbon filter. During prolonged use, this causes deposits of non-volatile, mostly inorganic material. We therefore rinse the metal coil with 1 *M* hydrochloric acid once a week. About twice a month, we rinse the filter with a few millilitres of 1 *M* hydrochloric acid, then with large amounts of water, with dry acetone, and finally with carbon disulphide. In any event, we clean the filter as soon as we observe indications of increased flow resistance. The activity of the filter is not affected by this treatment; no activation is required during continuous use.

We observed that stainless steel as a material for the connection between sample flask and filter does not stand the prolonged and combined influence of moist air, salts and elevated temperature (40–50°, obtained by means of a simple lamp to evaporate water droplets and reduce the relative humidity below the dew-point). We have now replaced stainless steel with gold or glass-lined steel.

RAPID LIQUID EXTRACTION

The most common and simple extraction of organic compounds from water is carried out by shaking with a water-immiscible solvent. The procedure has been applied successfully in water analysis, even for extreme trace concentrations[11,12], when specific detection, *e.g.*, for halogenated hydrocarbons, was possible. The sensitivity becomes much poorer, however, if organic substances in general have to be analyzed with non-specific detection. The reasons are shown by the following simple example.

We assume that a 1-l sample containing individual pollutants at concentrations of 10 ppt (10 ng) can be extracted with 100% recovery by shaking with 100 ml of solvent. The small amounts of dissolved substances will allow a reasonable GC separation, provided that the total extract is concentrated to a single injection (*e.g.*, to 2 μl for splitless injection on a capillary column). Thus, the extract has to be concentrated by a factor of 50,000, yielding a "concentrated" extract containing the individual substances still at a concentration of only 1:200,000. This strong dilution means that the subsequent GC run represents a trace analysis. The analyzed trace amounts, however, consist not only of the substances extracted from water, but also of the perhaps even more abundant and inevitable impurities contained in the 50,000-fold concentrated solvent. Thus, the accumulation of solvent impurities as well as severe losses of extracted substances during concentration render the procedure impracticable.

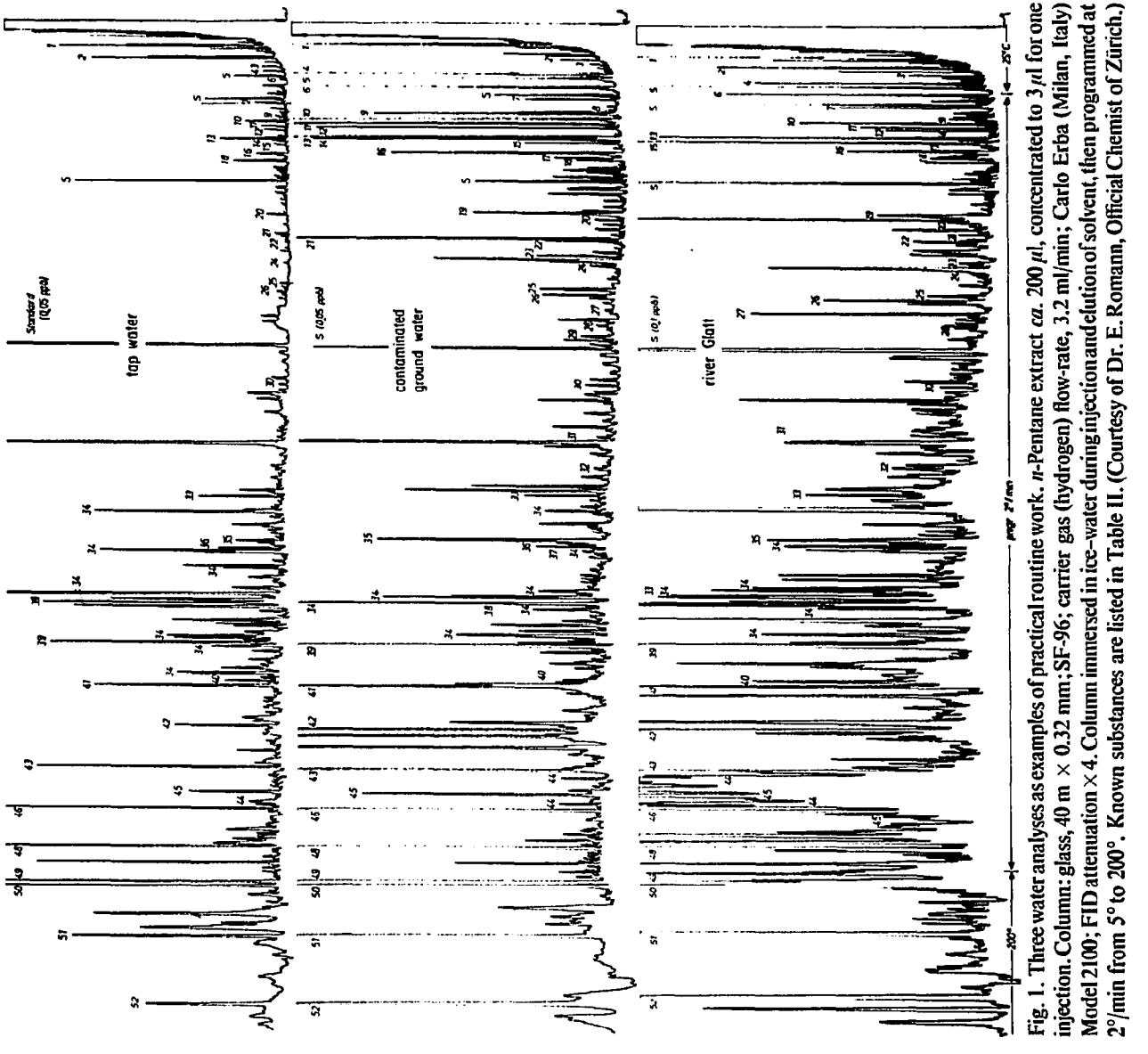

Fig. 1. Three water analyses as examples of practical routine work. *n*-Pentane extract *ca.* 200 µl, concentrated to 3 µl for one injection. Column: glass, 40 m × 0.32 mm; SF-96; carrier gas (hydrogen) flow-rate, 3.2 ml/min; Carlo Erba (Milan, Italy) Model 2100; FID attenuation × 4. Column immersed in ice–water during injection and elution of solvent, then programmed at 2°/min from 5° to 200°. Known substances are listed in Table II. (Courtesy of Dr. E. Romann, Official Chemist of Zürich.)

In agreement with these findings, liquid extraction has been used regularly for water analysis at concentration levels above 1 ppb (refs. 13 and 14).

In our rapid extraction procedure, we separate from 1 l of water a solvent volume of 200 μl instead of 100 ml. Thus, solvent by-products are decreased 500-fold. Simultaneously, much less further concentration, if any, is required. This makes the procedure a practical routine analysis, as shown in Fig. 1, which gives results obtained by this method at an official water control laboratory. A list of the substances identified is given in Table II.

TABLE II

SUBSTANCES IDENTIFIED IN WATER SAMPLES

Numbers correspond to Fig. 1.

No.	*Substance*	*No.*	*Substance*
1	Toluene	27	1,2,3,4-Tetrachlorobenzene
2	Tetrachloroethylene	28	C_{13} Alkane
3	Chlorobenzene	29	1,2,3,4-Tetrachlorobenzene
4	Ethylbenzene	30	C_{14} Alkane
5	1,3- + 1,4-Dimethylbenzene	31	C_{15} Alkane
6	1,2 Dimethylbenzene	32	Diethyl phthalate
7	C_9 Alkane	33	C_{16} Alkane
8	Chlorotoluenes	34	Polychlorobiphenyl (PCB)
9	Isopropylbenzene	35	Phenanthrene + 1-heptadecene
10	1,2,3-Trimethylbenzene	36	C_{17} Alkane
11	3- + 4-Ethyltoluene	37	Anthracene
12	2-Ethyltoluene	38	C_{18} Alkane
13	1,2,4-Trimethylbenzene	39	Dibutyl phthalate + C_{19} alkane
14	1,3-Dichlorobenzene	40	Pyrene
15	1,4-Dichlorobenzene	41	C_{20} Alkane
16	1,3,5-Trimethylbenzene	42	C_{21} Alkane
17	1,2-Dichlorobenzene	43	C_{22} Alkane
18	C_{10} Alkane	44	Dihexyl phthalate
19	1,3,5-Trichlorobenzene	45	Benzyl butyl phthalate
20	C_{11} Alkane	46	C_{23} Alkane
21	1,3,4-Trichlorobenzene	47	Fluoranthene
22	Naphthalene	48	Unknown
23	1,2,3-Trichlorobenzene	49	Dioctyl phthalate
24	C_{12} Alkane	50	C_{25} Alkane
25	2-Methylnaphthalene	51	C_{26} Alkane
26	1-Methylnaphthalene	52	C_{27} Alkane

Selection of solvent

Initial experiments showed that only a few solvents were suitable for our procedure. The essential parameter proved to be solubility in water. Figures for some common solvents are given in Table III[15].

The conclusion drawn from experiments with many different solvents was that, under our unusual quantitative conditions, only the least water-soluble solvents gave reasonable extraction. More indicative of this effect than solubility itself is the relationship between the (very small) amount of solvent collected as a separate phase and the amount of the same solvent dissolved in water. It seems that this latter fraction solubilizes trace organic material in water. It seems, furthermore, that at extreme

TABLE III

SOLUBILITIES OF SOLVENTS IN WATER

Solvent	*Solubility in water (g/l)*	*Ratio of separated to dissolved solvent**
n-Hexane	0.01	20
n-pentane	0.04	5
Carbon tetrachloride	0.8	0.25
Carbon disulphide	2.9	0.06
Methylene chloride	13.0	0.015
Diethyl ether	60	0.003

* Ratio valid under the assumption that under equilibrium conditions 200 µl of pure solvent are in contact with 1 l of water saturated with the same solvent (figures not corrected for specific gravities).

trace levels, this solubilizing effect becomes the main influence on the distribution of trace organic substances between water and the organic phase, producing extraction effects that would not have been expected from known partition coefficients.

Thus, in agreement with our experiments, the most efficient solvents for our procedure are the higher alkanes. The increase in efficiency with increasing chain length, however, is not important. On the other hand, the period of shaking, producing partition equilibrium, becomes much longer, probably as a consequence of decreased diffusion rates. In addition, the higher alkanes increasingly obscure the most volatile extraction components. It is, furthermore, more difficult to obtain them in sufficient purity. The surprising result of these effects is that *n*-pentane was found to be the most suitable solvent for our purpose.

Under regular conditions of liquid extraction (*e.g.*, 100 ml of solvent per litre of water) there is, of course, a much wider choice of solvents, based on dipole moment considerations[12,13], and information on the solubility of organic compounds in water or sea water[16,17].

Practical procedure

Sample preparation. Suspended material in the water sample is the most important source of difficulties in our procedure, yielding, after shaking, a supernatant layer of sludge instead of a clear layer of solvent. Turbid samples therefore have to be filtered before extraction.

The internal standards added to samples that contain unknown pollutants are a series of 1-chloroalkanes; we use the even-numbered members from C_6 to C_{18} (Fluka, Buchs, Switzerland). These substances are normally not present in polluted waters, and they are available as a homologous series. The internal standard in the form of a homologous series facilitates the interpretation of varying recovery rates with varying volatility of extracted substances. A purely practical advantage is that members of a series are easily identified in a complex mixture. It often occurs that one standard peak cannot be used because of coincidence with a sample component. This again calls for a wider choice of standard substances.

Rules for the concentration of standard substances added to water samples of different types are given above under Detection limits.

Extraction procedure. Very thorough mixing of solvent and water is of primary importance. With the aim of improving the reproducibility of this step, we have tried various mixing techniques, including mechanical shaking and stirring and ultrasonic and low-frequency vibration. Unfortunately, in our hands, none of these techniques was able to replace very vigorous shaking by hand. We use 1-l volumetric flasks with narrow necks, offering a relatively small water surface on which the solvent layer is formed. At first we pour in only 900 ml of water, thus leaving about 150 ml of space so as to allow efficient shaking.

The amount of pentane added depends on several factors. More pentane is required the higher the water temperature, the larger the empty space in the closed flask and the greater the pollution. For rough information we can give the following example. Approximately 200 μl of extract are collected after shaking for 2 min, when 900 ml of tap water at 12° have been placed in a flask with 150 ml of empty space, and 0.6 ml of pentane are added to the sample. Immediately after the 2-min shaking, we add cold tap water to raise the level of the water surface into the lower part of the narrow neck. After standing for about 1 min, we apply a moderate vacuum (0.4 atm below ambient pressure) so as to drive out the bubbles and to recover the remaining traces of liquid solvent, as well as to overcome possible foaming. By simple pipetting (we use a 1-ml gas-tight syringe with a 12-cm needle), a mixture of water and solvent is collected and transferred into an approximately 15 cm long and 4 mm wide glass tube. When no further pentane can be collected, the tube is shaken like a clinical thermometer in order to separate the phases. The organic phase is transferred with a smaller syringe (allowing determination of solvent volume) into a 4 cm long and 2.5 mm wide glass tube with a conical bottom. In the case of heavy pollution, the extract may be suitable for GC analysis. Any desired degree of concentration can be carried out in the case of less contaminated samples. For the purest waters, the extract is evaporated down to about 3 μl. With some experience, it is easy to judge when this remaining volume in the conical part of the tube is attained. The entire remainder is then injected for GC analysis.

For semi-quantitative determinations, known contaminants together with suitable concentrations of internal standard are prepared and analyzed.

It must be emphasized that concentration of the extract causes important osses of substances over a wide volatility range. Fortunately, we found that these losses are not significantly different for different types of substances. Thus, it is not unreasonable to assume that the internal standard and the extracted substances are similarly affected.

Gas chromatography. Splitless injection of 2–3 μl of extract on to a capillary column is carried out. As the solvent is pentane, the desired solvent effect[18], producing sharp single bands, may not be sufficient on the column at room temperature. We routinely immerse the column in cold water (4–6°) and start the temperature programme only when the solvent peak has been eluted.

Selection of GC column. In the analysis of water extracts obtained by the stripping method selection of the column is not restricted by special requirements, but the columns have to fulfil two basic demands when liquid extraction is used. On the one hand, injection at cold-water temperature requires a liquid phase with low or moderate viscosity at 0°. All phases that are solids at this temperature are therefore excluded. On the other hand, liquid extracts often contain relatively large amounts

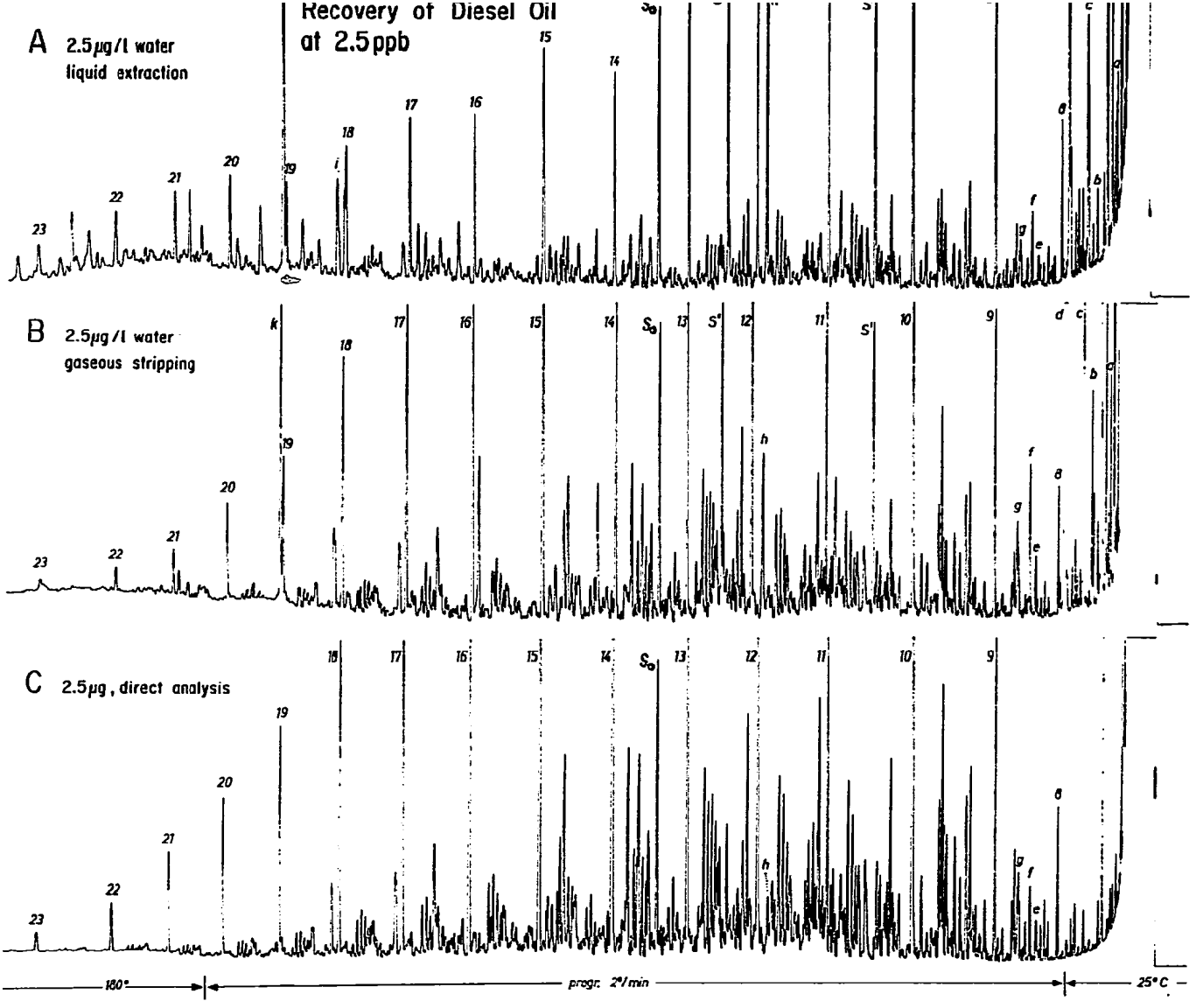

Fig. 2. Analysis of tap water spiked with 2.5 ppb of Diesel oil. (A) Liquid extraction with *n*-pentane. (B) Stripping. Both extracts concentrated to one splitless injection. (C) Analysis of original Diesel solution, containing same amount of Diesel oil as added to 1 l of water for A and B. Column and chromatographic conditions as in Fig. 1. Examples of quantitative interpretation of single peaks: concentration in spiked water, octane 4 ppt, tetradecane 60 ppt, eicosane 6 ppt.

of heavy substances that cannot be reasonably eluted from columns with a low temperature limit. Therefore, phases with high temperature limits should be selected. In conclusion, this means that columns with a specially wide temperature range, *e.g.*, OV-101 and OV-61, are recommended.

COMPARISON OF STRIPPING WITH LIQUID EXTRACTION

Quantitative recovery of alkanes

In order to obtain information on recoveries over a wide volatility range for alkanes, we conducted a test series on Diesel oil. Typical chromatograms are shown in Fig. 2.

The two upper chromatograms represent extracts from identical water samples. One litre of tap water was spiked with 2.5 ppb of Diesel oil (1:1000 solution in acetone). Chromatogram A was obtained after shaking with *n*-pentane and concentrating the pentane extract (250 μl) to 3 μl for a single injection. Chromatogram B is the result from the stripping method, in which the total carbon disulphide extract (10 μl) from the carbon filter was concentrated to 3 μl. Chromatogram C was produced by injecting 2.5 μl of an *n*-pentane solution containing the same amount of Diesel oil that had been added to water for A and B. C, therefore, simulates an analysis with 100% recovery. Typically, in this chromatogram several peaks are missing, namely the peaks in A and B stemming from impurities in tap water.

From the integrated peak areas for the *n*-alkanes, Fig. 3 was prepared. An identical procedure was also carried out using ten times more Diesel oil. A striking result is that recovery rates depend less on concentration than was generally expected. The high yield from liquid extraction in the C_{20}–C_{23} range at the 2.5 ppb level must, to a large extent, be considered as an artefact produced by the occurrence of the alkanes in tap water.

In the low and medium molecular weight regions, stripping is 3–4 times more efficient than liquid extraction. For eicosane both methods are equivalent, while for heavier substances stripping rapidly loses efficiency. It is interesting to note that markedly lower recoveries are observed when similar amounts of single alkanes instead of the whole, complex oil mixture are added to water. It seems that the extraction is enhanced by additional substances of the same type.

Recovery of organic compounds from different types of substances

For a broader investigation of recovery, we selected from seven types of substance groups of compounds with decreasing volatility. A solution in acetone of all of the substances indicated in Table IV was prepared containing the individual substances at concentrations of 1:10,000. For recovery tests, 1-l water samples (tap water) were spiked with 5 μl of the acetone solution, giving concentrations of single substances of 0.5 ppb. This relatively high concentration was chosen for two reasons. On one hand, we wished to eliminate the effects of concentrating the organic extract. Thus, a 250-μl pentane extract from liquid extraction had to contain the substances in amounts that would allow immediate GC analysis of the untreated extract. On the other hand, the relatively high concentrations allowed us to use tap water to prepare the samples because, except for tetrachloroethylene, the pollutant levels in tap water were negligible in comparison with the amounts added.

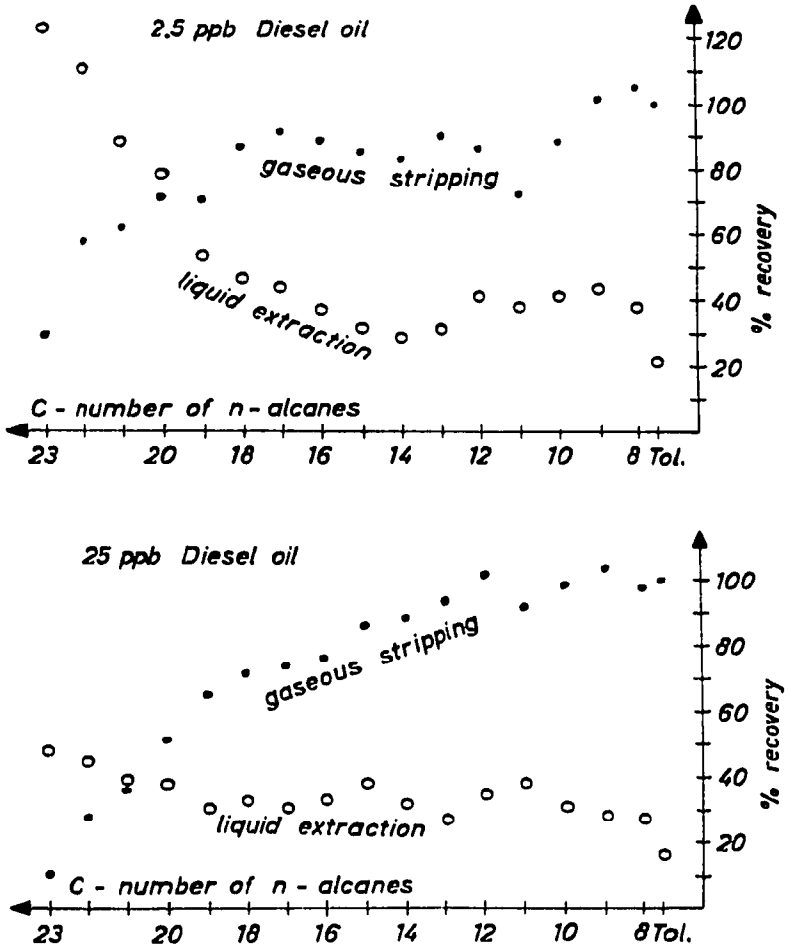

Fig. 3. Recovery rates for single *n*-alkanes obtained either by liquid extraction with *n*-pentane or by stripping from water spiked with 2.5 and 25 ppb of Diesel oil.

GC analysis was carried out on three kinds of sample solutions.

(1) *Original mixture.* A 5-μl volume of the acetone solution was added to 245 μl of pentane, thus yielding a sample solution simulating an extract from water with 100% recovery. Fig. 4 is a chromatogram obtained from such an original mixture. It was run on a slightly acidic column, with the effect that the phenols were eluted reasonably while the pyridine derivatives completely disappeared. (On a polar column, it is possible, of course, to elute both groups of substances perfectly.)

(2) *Stripping.* A 1-l spiked water sample was analyzed by the stripping method. The 20-μl carbon disulphide extract from the carbon filter was diluted with pentane to 250 μl so as to become comparable with the original mixture.

(3) *Liquid extraction.* A 1-l spiked water sample was shaken with pentane to yield a pentane extract of approximately 200 μl, which was then made up to 250 μl.

From all three sample solutions, 3.0 μl were injected on to columns at 5° without splitting.

TABLE IV

CONSTITUENTS OF RECOVERY TEST MIXTURE AS SHOWN IN FIG. 4–6

No.	*Type of substance*	*Member*	*No.*	*Type of substance*	*Member*
1	*n*-Alkanes		4	Ketones	
1a		*n*-C_8	4a		3-Pentanone
1b		*n*-C_9	4b		4-Heptanone
1c		*n*-C_{10}	4c		5-Nonanone
1d		*n*-C_{11}	4d		2-Dodecanone
1e		*n*-C_{12}			
1f		*n*-C_{13}	5	Alcohols	
1g		*n*-C_{14}	5a		1-Octanol
			5b		1-Decanol
2	Aromatics		5c		1-Dodecanol
2a		Benzene			
2b		Toluene	6	Pyridines	
2d		Ethylbenzene	6a		Pyridine
2e		*m*-Xylene	6b		2-Picoline
2f		1,2,3-Trimethylbenzene	6c		4-Picoline
2g		Naphthalene	6d		2,3-Lutidine
2h		1-Methylnaphthalene	6e		3,4-Lutidine
3	Chlorinated hydrocarbons		7	Phenols	
			7a		Phenol
3a		Tetrachloroethylene	7b		*p*-Cresol
3b		Chlorobenzene			
3c		1,2-Dichlorobenzene	8	Miscellaneous	
3d		1,2,3-Trichlorobenzene	8a		4-Methoxytoluene

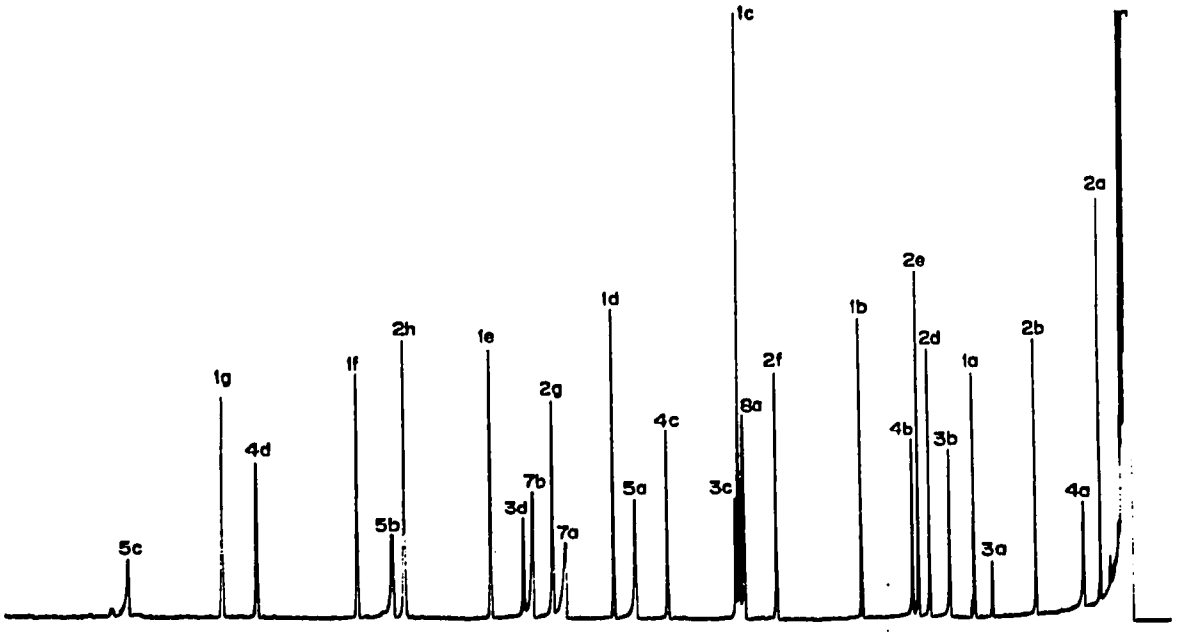

Fig. 4. Original recovery test mixture (for substances, see Table IV), analyzed on a 50 m × 0.30 mm, SF-96, slightly acidic column. Carrier gas (hydrogen) flow-rate 3.0 ml/min. Column programmed at 2°/min from 5° to 140°. Amount of each substance, 5 ng (decane, 10 ng).

Fig. 5 shows an arbitrarily selected set of chromatograms obtained from the different sample solutions on one column. We selected a slightly basic column in order to show the elution of the pyridine group with the corresponding disappearance of phenols. In addition, the effect of concentration is shown in the following way. The extract from liquid extraction was concentrated to 3 μl. While normally this concentrated solution is then immediately injected, we made it up again to 250 μl;

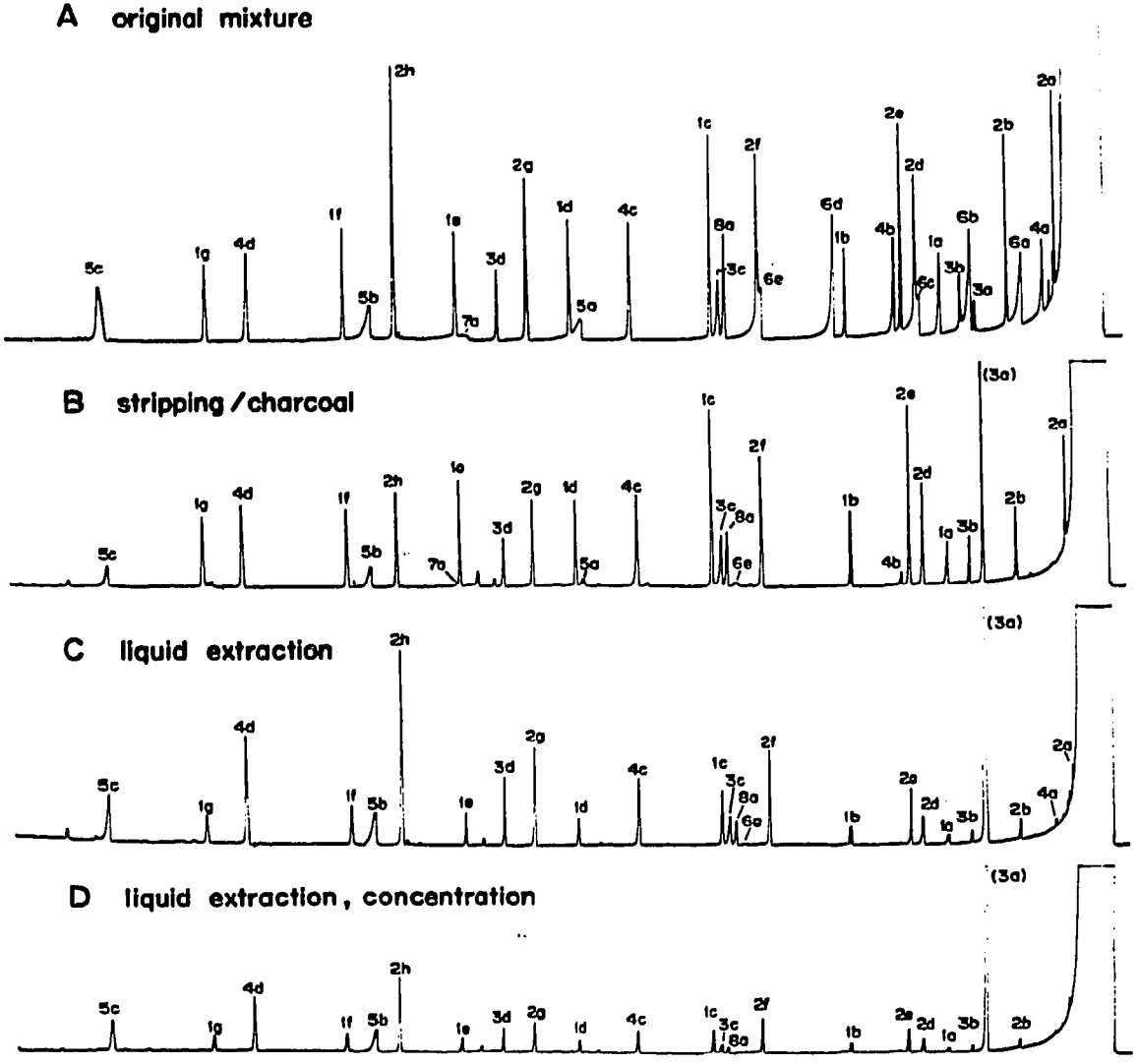

Fig. 5. Same test mixture as in Fig. 4 and specified in Table IV, using a 50 m × 0.29 mm, SF-96, slightly basic column. (A) Original mixture, representing 100% recovery. (B) Same amount of mixture added to tap water and extracted by stripping. (C) Identical sample as used for B, extracted with *n*-pentane. Splitless injection of 3 μl of extracts made up to 250 μl (no concentration step). (D) *n*-Pentane extract as obtained in C, concentrated to 3 μl and diluted to original volume of 250 μl to show losses from concentration.

3 μl of this diluted solution produced the bottom chromatogram in Fig. 5, which, compared with the chromatogram from liquid injection, reveals severe losses caused by the evaporation step. A rough comparison shows that the different types of substances are affected in a similar manner.

Fig. 6 gives average recoveries obtained from four stripping and six liquid extraction analyses on the same type of sample. The sample solutions were analyzed on neutral, acidic and basic columns. The most important results of this test are as follows.

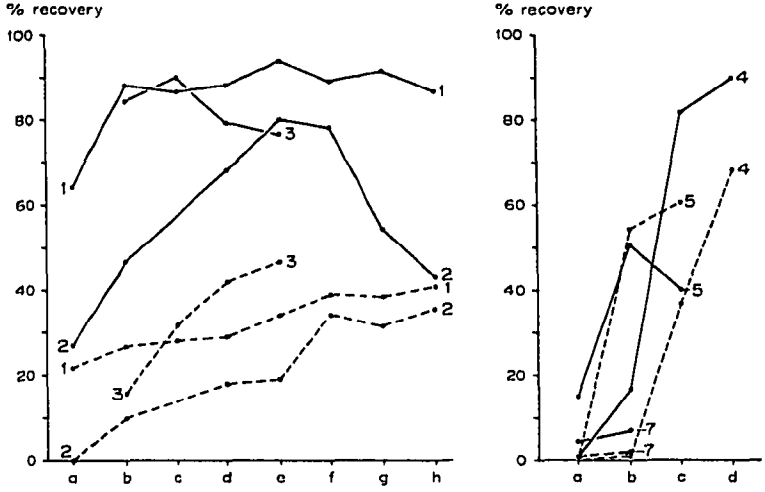

Fig. 6. Recovery rates for different types of substances (concentration of each substance in water, 0.5 ppb), obtained by stripping (solid line) and by rapid liquid extraction (broken line). No concentration step. Numbers and letters as in Table IV.

While the stripping procedure shows the expected high efficiency for alkanes, this is not so for liquid extraction, although it was carried out with pentane as a solvent; we have no explanation for this effect. The same applies to the surprisingly high recoveries for polar substances such as ketones and primary alcohols compared with hydrocarbons. (In order to avoid possible errors, we should point out that, while a single curve gives the true dependence of recovery on volatility, no direct comparison between two curves at a given point on the horizontal axis is permitted, as there is no defined volatility comparison for substances of different types.)

In addition, the results are in agreement with those obtained with Diesel oil. While stripping is superior in the more volatile range, the efficiency of liquid extraction increases with decreasing volatility.

While it is not possible positively to detect pyridine and its derivatives at the 0.5 ppb level by both methods, the simple phenols are detected with poor efficiency by stripping. It is important to know that this applies to neutral water. An artificial shift to the basic or acidic side greatly enhances recoveries of both types of substances.

Summary of comparison of stripping and liquid extraction

Overall sensitivity. There is no sound basis for direct comparison. The detection limit with stripping is about ten times lower for more volatile substances, while liquid extraction is far more sensitive for heavy materials. The methods are equivalent, *e.g.*, for eicosane, dimethylnaphthalene, pentadecanone and decanol.

Sensitivity depending on type of substance. There is no essential difference between the methods. Substances of all types are efficiently detected, provided that the hydrophilic effect of certain functional groups is sufficiently balanced by apolar groups. Critical substances in this respect are, *e.g.*, hexanone and heptanol.

Quantitative reproducibility. This is better with stripping, as this procedure can be standardized to a higher degree than liquid extraction.

Suitability for routine work. Provided that the equipment is available, stripping is more suitable for routine replicate analyses by laboratory technicians.

Time requirements. The preparation of a sample solution ready for GC analysis, with 2 h for stripping, requires 3 h. The corresponding time for liquid extraction is 30 min. The opposite relationship applies to the GC analysis because of the heavy substances present in liquid extracts.

Turbid water samples. These can be analyzed immediately by stripping without difficulty, whereas even trace amounts of suspended material may seriously interfere in liquid extraction.

GC columns. GC columns are heavily stressed by liquid extracts because of prolonged use at high temperatures for the elution of heavy components. Material that is essentially non-volatile may seriously shorten their life-time. In contrast, extracts from stripping contain only substances with sufficient volatility for simple GC analysis without harmful effects to the columns.

Equipment. The equipment for liquid extraction is extremely simple and inexpensive, while for stripping the suitability and quality of the equipment are of primary importance.

The final decision in favour of one or other method will probably depend in most instances on two fundamental conditions: (1) availability of the equipment for stripping; (2) the relative importance of the volatility range for light and medium *versus* heavy pollutants.

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