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OPTIMIZATION OF THE OPEN STRIPPING SYSTEM FOR THE ANALYSIS OF TRACE ORGANICS IN WATER

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SUMMARY

With the open modification of the system for closed-loop stripping analysis, the stripping conditions can be varied widely. By using stripping temperatures between 30 and 90°C, the technique can be optimized to meet specific analytical demands. In particular, the analysis of trace organics in water can be extended to less volatile and more polar compounds.

Desorption of the adsorbent is often the key step in the stripping procedure. Efficiency of extraction from the filter is generally low. This has been investigated, and a solvent mixture not used previously for stripping analysis (carbon disulphide–benzene–methanol, 65:30:5) is recommended.

INTRODUCTION

In 1973, Grob introduced the closed loop stripping analysis (CLSA) system for the analysis of trace organics in water[1]. Since then, numerous papers dealing with this system have been published[2–5]. Some studies have dealt specifically with the aspects of recovery efficiency[6], the extraction technique[7] and problems connected with contamination[8,9]. In a previous paper[10], we introduced the open stripping system, a modified system, which offers some important advantages, principally flexibility of the stripping conditions and a low contamination level.

The aim of the present study was to substantiate further the advantages of the open system and to investigate the limiting factors of the stripping technique. The complete stripping procedure can be divided into three steps: (1) purging, (2) adsorption and (3) desorption. We have studied these steps separately and in combination, with emphasis placed upon improving the purging and desorption steps.

By using the open system, purging may be undertaken at higher temperatures than when using the closed system and the use of elevated temperatures leads to a corresponding increase in purging efficiency. A series of purging experiments carried out at temperatures ranging between 30 and 90°C have given comprehensive results concerning the effects of temperature on several groups of organic compounds, including phenols.

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After improving the purging efficiency, desorption from the charcoal filter becomes the factor that limits the recovery of a great number of compounds. In the present study, the part that concerns the extraction efficiency of different solvents and solvent mixtures was inspired by similar investigations performed with large charcoal filters[11–13]. The results of our study enable us to recommend extraction solvents for different classes of compounds.

EXPERIMENTAL

The open stripping technique used was carried out according to methods previously described[10]. One litre of water was purged for 2 h at 30, 60 or 90°C, while the analytical filter was held at 50, 80 or 100°C, respectively.

For the stripping analysis of phenols, 1 μg of each compound was added to 1 l of laboratory tap water. All other compounds were analysed at a concentration of 50 ng/l. In all experiments, a mixture of carbon disulphide–benzene–methanol (65:30:5) was used for extraction from the charcoal filter. The desorption studies were performed by adding to the filter a mixture consisting of 50 ng of each compound in methylene dichloride. The solvent was evaporated at room temperature for 15 min and in an oven at 50°C for 30 min. The internal standard (1-chloroundecane, 100 ng in dichloromethane was added to all extracts.

Gas chromatography: Hewlett Packard 5880, flame ionization detector (FID) attenuation 2°; fused silica column (60 m × 0.32 mm I.D.) DB1 (J&W) 0.25 μm; helium carrier gas, 40 cm/s flow-rate; on-column injection technique is used throughout except for the desorption study which utilized the splitless injection technique while split valve closed for 60 s; 1.5 μl injected volume; program, 40°C for 5 min, raised at 5°/min to 220°C, finally kept at 220°C for 5 min.

RESULTS AND DISCUSSION

The open system versus the closed system

The introduction of the CLSA technique was a great accomplishment in the field of ultra trace analysis of organic compounds in water, the main advantage being the large factor of concentration that is attained without the need for an evaporation step[1]. However, the advantage of using a closed loop is doubtful. If breakthrough of volatile substances was a serious problem, the closed loop could certainly improve adsorption on the analytical filter, but experiments using two filters in series have shown that breakthrough is negligible. In Fig. 1, most peaks corresponding to the second filter have an area of *ca.* 5% of the corresponding peaks in the chromatogram from the first filter. For compounds with long hydrocarbon chains, the area quotients approach 10%. The highest area quotients, *ca.* 15%, were obtained for two very volatile compounds. This indicates that, with few exceptions, the theoretical gain of the closed loop should be in the range 5–10%. However, the gain is, in fact, much less. Thermally desorbed compounds do not only return to the filter after passing the closed loop, but can also be adsorbed to the pump and various other parts of the system. The latter phenomenon has been studied in experiments in which stripping time was prolonged (12 h or more), and this resulted in a gradual decrease in recovery from the filter[10].

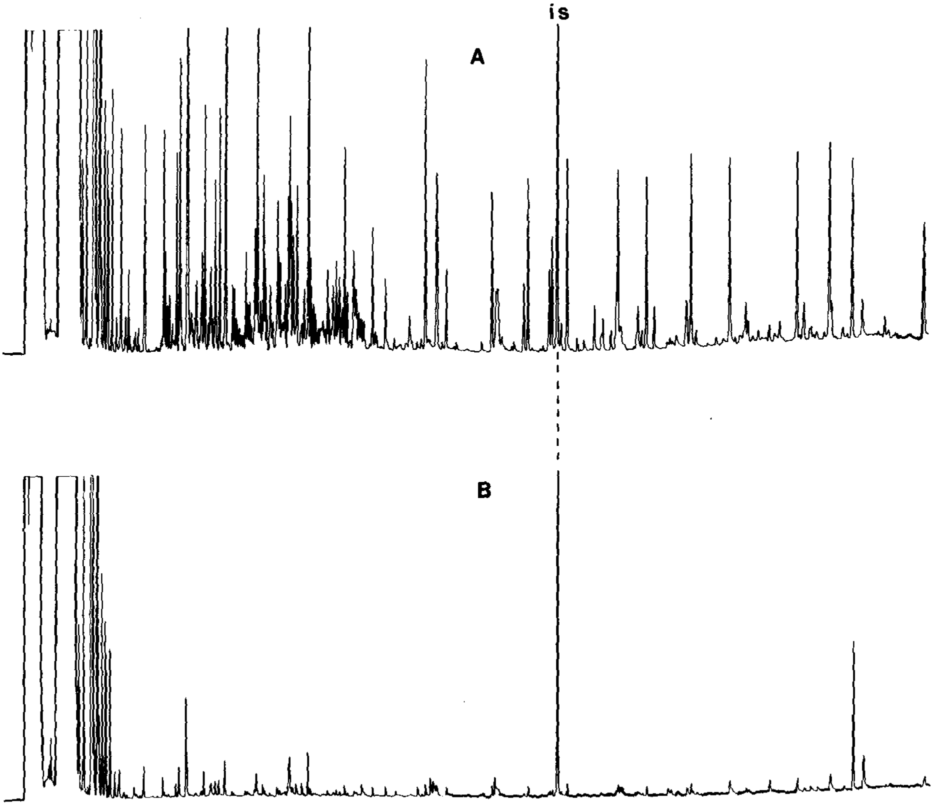

Fig. 1. Gas chromatograms from two consecutive analytical filters used in stripping analysis of 1 l of tap water spiked with 5 μl of a solution of 10 ng/μl of each of 35 compounds in acetone. The peak marked "is" is the internal standard 1-chloroundecane, added after extraction of the filter. Stripping conditions: 2 h at 60°C (open system). General gas chromatographic procedure but with an attenuation of 2^1.

One of the advantages of the open system is that contamination due to breakthrough is impossible. The PTFE tubing between the bottle and the analytical filter, however, may be contaminated after stripping heavily loaded waters, but it is easily cleaned before a new stripping run by purging tap water for a few hours. The greatest advantage of the open system is flexibility with regard to stripping temperature. There are no technical problems due to water vapour in the system or leakage, even at a stripping temperature as high as 90°C. The flow-rate of the purging gas can also be varied widely. In fact, when stripping at 60°C a flow-rate of 2 l/min for 1 h gives the same recoveries as a flow-rate of 1 l/min for 2 h; purging at this temperature for 2 h with a flow-rate of 2 l/min, however, reduces recovery of the most volatile compounds.

Stripping at elevated temperatures

In order to study the effect of stripping temperature on recovery, we performed a series of experiments with a standard mixture of model compounds added to laboratory tap water. According to chemical and physical characteristics, the model compounds of the standard mixture can be divided into the following groups:

(1) compounds with polar groups;
(2) compounds of low volatility;
(3) semivolatile compounds;
(4) volatile compounds;
(5) phenols.

A concentration of 50 ng/l was used for all the compounds except for phenols, which were analysed at a concentration of 1 μg/l. A solvent mixture of carbon disulphide–benzene–methanol (65:30:5) was used for extraction. Stripping was carried out for 2 h at temperatures of 30, 60 and 90°C.

When discussing the results shown in Tables I–V, it is important to note that they represent total recoveries after the complete stripping procedure, including the adsorption and desorption steps. Since the efficiency of extraction from the charcoal filter was generally low (60%), no recoveries approached 100% even when purging efficiency was close to 100%. Previous reports on recovery by the stripping procedure have often given relative yields, where the recovery of some easily purgable compound is arbitrarily set to 100%.

The recovery of polar compounds shows a significant dependence on stripping temperature (see Table I). Two of the five compounds, 1-octanol and 1-decanol, approach their extraction limits (see next section) at 90°C. Even at this temperature, the other three are not completely purged because of their polarity and their solubility in water.

Table II illustrates recoveries of compounds of low volatility. Most of these compounds can only be purged satisfactorily at 90°C, a temperature at which they approach their extraction limits. The most polar compounds of this group are not even purged acceptably at 90°C.

Table III presents the recoveries of the semivolatile, non-polar compounds. The results are only slightly affected by the stripping temperature. In all cases, however, the highest temperature gives the best yield.

In Table IV, the recoveries of the four most volatile compounds of the mixture are presented. The results show that recoveries are lower at higher temperatures; this is caused by thermal desorption from the analytical charcoal filter. Condensation of

TABLE I

EFFECT OF STRIPPING TEMPERATURE ON THE RECOVERY OF POLAR COMPOUNDS

Compound	*b.p. (°C)*	*Recovery (%)*				*Yield of extraction (%)*
		30°C	*60°C*	*90°C*	*R.S.D. (%)*	
1-Hexanol	158	tr*	17	44	1.8	59
Acetophenone	202	n.d.**	7	38	1.7	49
1-Octanol	194	11	36	58	5.2	61
3-Phenyl-1-propanol	236	n.d.	n.d.	7		51
1-Decanol	229	39	53	65	1.6	63

* tr = Traces.
** n.d. = Not detected.

TABLE II

EFFECT OF STRIPPING TEMPERATURE ON THE RECOVERY OF COMPOUNDS OF LOW VOLATILITY

Compound	*b.p. (°C)*	*Recovery (%)*				*Yield of extraction (%)*
		30°C	*60°C*	*90°C*	*R.S.D. (%)*	
Benzyl acetate	215	tr*	11	16	2.9	53
Naphthalene	218	36	40	52	1.6	50
Diphenyl ether	258	33	42	49	1.6	54
2-Methoxynaphthalene	274	3	10	33	0.2	38
Ethyl cinnamate	272	tr	9	28	1.2	38
1-Chlorododecane	260	65	52	81		61
Pentachlorobenzene	277	32	35	46	2.1	36
1-Chlorotetradecane	292	52	55	69	2.3	62
Anthracene	340	n.d.**	3	8	0.6	2
Octadecane	316	42	52	61	0.7	63
1-Chlorohexadecane	322	39	45	65		62
1-Chlorooctadecane	348	17	50	60		60

* tr = Traces.

** n.d. = Not detected.

water vapour onto the filter decreases its efficiency; in order to avoid this effect, the filter is held at 10 to 20°C above the stripping temperature.

The only phenol that could be stripped satisfactorily at 30°C was 2-*tert.*-butylphenol. In order to effect acceptable recovery of the other phenols in Table V, it was necessary to use a stripping temperature of 90°C. Many of the phenols were, however, still only recovered by less than 10%. The general trend in this group parallels the ability of the substituents in covering the hydroxy group. A *tertiary* alkyl group in the 2-position or small alkyl groups in the 2- and 6-positions contribute to a significant increase in recovery. Small substituents in one of the *ortho* positions

TABLE III

EFFECT OF STRIPPING TEMPERATURE ON RECOVERY OF SEMIVOLATILE COMPOUNDS

Compound	*b.p. (°C)*	*Recovery (%)*				*Yield of extraction (%)*
		30°C	*60°C*	*90°C*	*R.S.D. (%)*	
Anisole	155	41	49	53	2.7	63
Pentyl acetate	149	51	54	59	2.1	62
n-Propylbenzene	159	57	52	57	5.4	66
1,4-Dichlorobenzene	174	55	48	57	2.5	58
n-Decane	174	55	49	59	6.5	66
1-Chlorooctane	180	54	47	58	5.6	63
2,6-Dichloroanisole	220	41	45	53	0.8	58
1-Chlorodecane	223	52	46	55	5.4	64
1,2,3,5-Tetrachlorobenzene	246	42	37	51	2.3	47
Methyl decanoate	224	48	45	49	3.1	60
2,3,6-Trichloroanisole	240	34	39	45	1.2	51
Methyl dodecanoate	262	48	44	49	1.6	61

TABLE IV

EFFECT OF STRIPPING TEMPERATURE ON RECOVERY OF VOLATILE COMPOUNDS

Compound	*b.p. (°C)*	*Recovery (%)*				*Yield of extraction (%)*
		30°C	*60°C*	*90°C*	*R.S.D. (%)*	
3-Hexanone	145	31	46	6	3.6	61
Butyl acetate	125	47	59	25	5.0	62
Chlorobenzene	132	53	47	23	5.7	66
1-Chlorohexane	135	54	47	46	4.9	63

have an effect too, although this effect is smaller. Acidification of the water samples by a strong acid does not increase the yields.

Although the five different groups are not entirely distinct, the results show that a high stripping temperature is a very important factor for successful recovery, both for polar compounds and for compounds of low volatility. For other compounds, with the exception of those with the highest volatility (b.p. < 150°C), a high stripping temperature is no disadvantage.

The reproducibility of the stripping technique depends greatly on the precision of extraction. The standard deviations shown in Tables I–IV are calculated from the results of three repeated experiments performed at 60°C and using the same adsorption filter in order to avoid dissimilarities that may exist between different filters.

Fig. 2 demonstrates the effect of stripping temperature on an authentic raw water sample. The effect is even more dramatic than could be expected from the results for the standard compounds. The number of integrated peaks and the peak areas obtained further demonstrate the large difference in stripping efficiency at 60 and 90°C. There are 142 peaks integrated at 60°C, while the number of integrated peaks increased to 233 at 90°C. The increase in the total area of the integrated peaks was 60%. These results further support the fact that stripping is most successful when

TABLE V

EFFECT OF STRIPPING TEMPERATURE ON RECOVERY OF PHENOLS

Compound	*b.p. (°C)*	*Recovery (%)*		*Yield of extraction (%)*
		30°C	*90°C*	
Phenol	182	1	4	57
2-Methoxyphenol	205	1	12	63
2,6-Dimethylphenol	212	6	40	62
2-Ethylphenol	207	2	23	61
2-*tert.*-Butylphenol	221	19	65	66
3-Chloro-5-methoxyphenol	242	n.d.*	tr**	43
2,4,6-Trichlorophenol	246	tr	1	27
2-Hydroxybiphenyl	286	n.d.	7	53
Pentachlorophenol	310	n.d.	5	8

* n.d. = Not detected.

** tr = Traces.

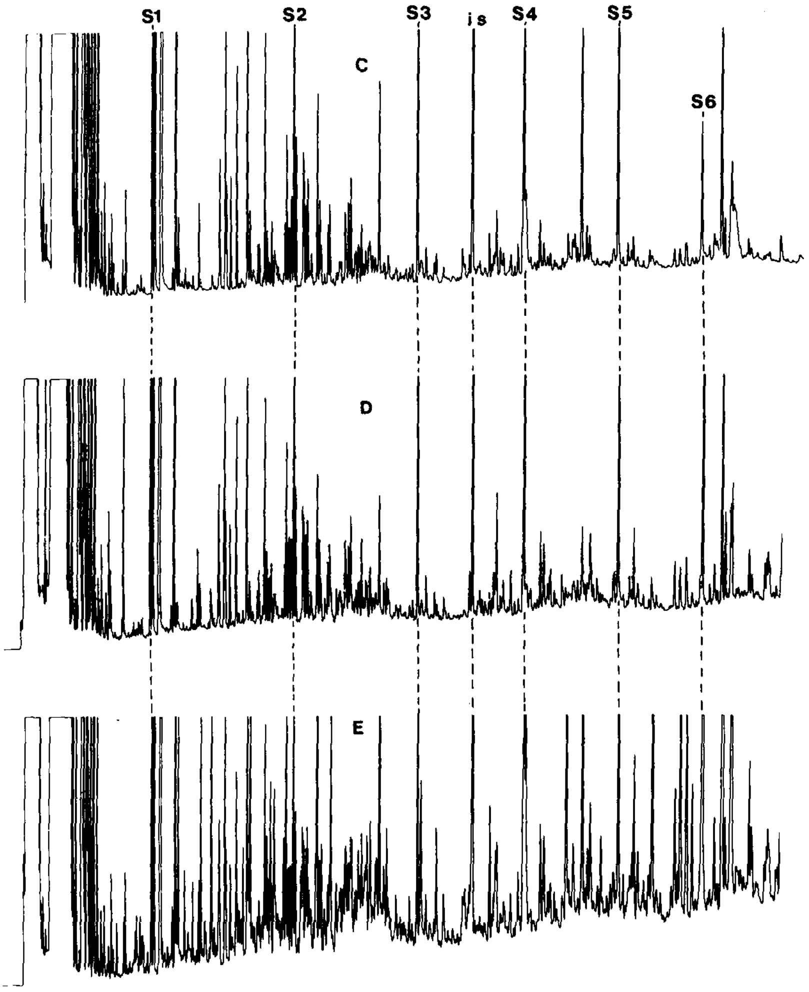

Fig. 2. Gas chromatograms of a raw water sample purged at 30°C (C), 60°C (D) and 90°C (E). General stripping and gas chromatographic procedures. Peaks S1–S6 are internal standards added to the water samples before stripping. The peak marked "is" is 1-chloroundecane, added after extraction of the filter.

performed at a temperature of 90°C, except when very volatile compounds are being analysed.

Extraction from the charcoal filter

The demands upon the charcoal filter of being an efficient adsorbent and being easily extractable are somewhat contradictory. For use in a stripping system, charcoal is an excellent adsorbent but is less satisfactory in terms of extractability. The use of the open system increases the purging efficiency of compounds of higher polarity and of lower volatility and this makes it essential to improve extraction of these compounds. From the use of larger charcoal filters for other analytical purposes, it is well known that the addition of small amounts of a polar solvent will increase the yield of polar compounds[11–13]. However, because of the differences in analytical conditions, these results may not be transferred directly to the use of filters for stripping analysis.

Table VI presents the results of the extraction of a mixture of a variety of compounds by seven different solvents and four solvent mixtures. The simple alkane, *n*-hexane, is an extremely poor extraction solvent for all kinds of aromatics. The only compound adequately extracted by *n*-hexane is *n*-decane. The other hydrocarbon, benzene, is very effective for aromatics but less so for polar substances. Diethyl ether, methyl acetate and acetone, all of comparable general efficiency, were all surprisingly poor as extraction solvents, despite their polarity. Diethyl ether was the least effective solvent for the aromatic compounds, probably due to the lack of π-electrons. Dichloromethane and carbon disulphide, which are often used as extraction solvents for charcoal filters, were both efficient, but carbon disulphide was more successful in extracting aromatic compounds.

TABLE VI

EFFECT OF EXTRACTION SOLVENT ON RECOVERY

Compound	*n-Hexane*	*Benzene*	*Carbon disulphide*	*Methylene dichloride*	*Diethyl ether*
Butyl acetate	43	64	55	63	62
Chlorobenzene	5	65	60	39	9
1-Chlorohexane	52	60	57	60	61
1-Hexanol	14	57	43	67	57
Anisole	3	72	62	48	7
Phenol	2	23	3	4	12
1,4-Dichlorobenzene	3	67	60	20	2
n-Decane	66	63	62	52	53
Acetophenone	1	56	44	38	2
1-Chlorooctane	49	63	63	63	52
Guaiacol	1	52	36	39	4
1-Octanol	8	54	45	62	47
2,6-Dimethylphenol	1	39	29	26	6
Naphthalene	tr*	49	27	3	n.d.
1-Chlorodecane	42	62	65	63	37
1-Decanol	5	42	49	68	28
Methyl decanoate	29	60	66	68	33
2-Methoxynaphthalene	n.d.	29	18	2	n.d.
1-Chlorododecane	34	57	67	62	45
Methyl dodecanoate	20	52	71	67	14
1-Chlorotetradecane	23	48	62	67	6
Anthracene	n.d.	4	n.d.**	n.d.	n.d.
1-Chlorohexadecane	23	48	47	49	n.d.
1-Chlorooctadecane	7	36	34	28	1
Mean	18	51	47	44	22

* tr = Traces.

** n.d. = Not detected.

The three most efficient simple solvents, benzene, carbon disulphide and methylene dichloride, exhibited differing degrees of success in extracting different kinds of compounds. For aromatic compounds, the order of efficiency was benzene > carbon disulphide > methylene dichloride, but for polar aliphatic compounds, methylene dichloride was by far the most effective solvent.

The different mixtures in which carbon disulphide was the main component were of similar strength. The addition of a polar compound had a positive effect, especially for the alcohols and phenols, as was expected. The addition of benzene further increased the recovery of aromatics such as the naphthalenes.

Recoveries in this report were obtained by using carbon disulphide–benzene–methanol (65:30:5), which we found to give the best yield. The somewhat complicated solvent peaks originating from this mixture when using the on-column technique or the splitless technique may conceal the peaks of some volatile compounds. If this is the case, carbon disulphide with 10% acetone is recommended as the extraction solvent.

Methyl acetate	*Acetone*	*Methyl acetate –carbon disulphide (10:90)*	*Acetone–carbon disulphide (10:90)*	*Methanol –carbon disulphide (5:95)*	*Methanol–benzene–carbon disulphide (5:30:65)*
62	62	61	61	58	65
24	19	59	56	57	62
51	49	60	61	59	60
53	61	60	62	58	66
24	21	59	62	62	62
27	22	46	52	41	52
5	1	65	60	62	60
37	31	63	63	63	59
11	8	51	55	55	60
46	43	63	63	63	63
19	17	48	52	50	58
50	51	62	63	61	57
11	9	49	54	49	53
1	1	24	27	29	46
31	26	63	64	64	65
33	37	55	59	62	67
37	29	65	65	65	65
1	n.d.	18	21	22	35
16	13	63	64	62	63
20	14	63	62	60	62
7	6	57	60	60	56
n.d.	n.d.	1	1	1	4
11	5	46	49	53	53
2	2	37	37	34	45
24	22	52	53	52	56

The efficiency of the extraction procedure is further demonstrated in Fig. 3. A standard solution of 50 ng of each of 35 neutral organic compounds was added directly to the filter. The solvent was evaporated at 50°C, and the filter was extracted in accordance with the standard procedure two times. The two extracts were analysed separately by gas chromatography after the addition of an internal standard (1-chloroundecane). For most compounds, the peak areas from the second extract were less than 10% of those of the first extract. For some compounds, however, the area quotients were quite large, which is the case for the less volatile aromatic compounds. As expected, the aromatic character of the charcoal created a strong affinity for these compounds, and this implies that the charcoal has sites which are extremely effective adsorbents for aromatics such as anthracene, 2-methoxynaphthalene and pentachlorobenzene.

Quantification

Quantification of recoveries has been accomplished by comparing peak areas obtained by direct injection of a standard solution of model compounds with peak areas obtained by first adding the same standard solution to water and then analysing the stripping extracts. To compensate for random variation in gas chromatographic

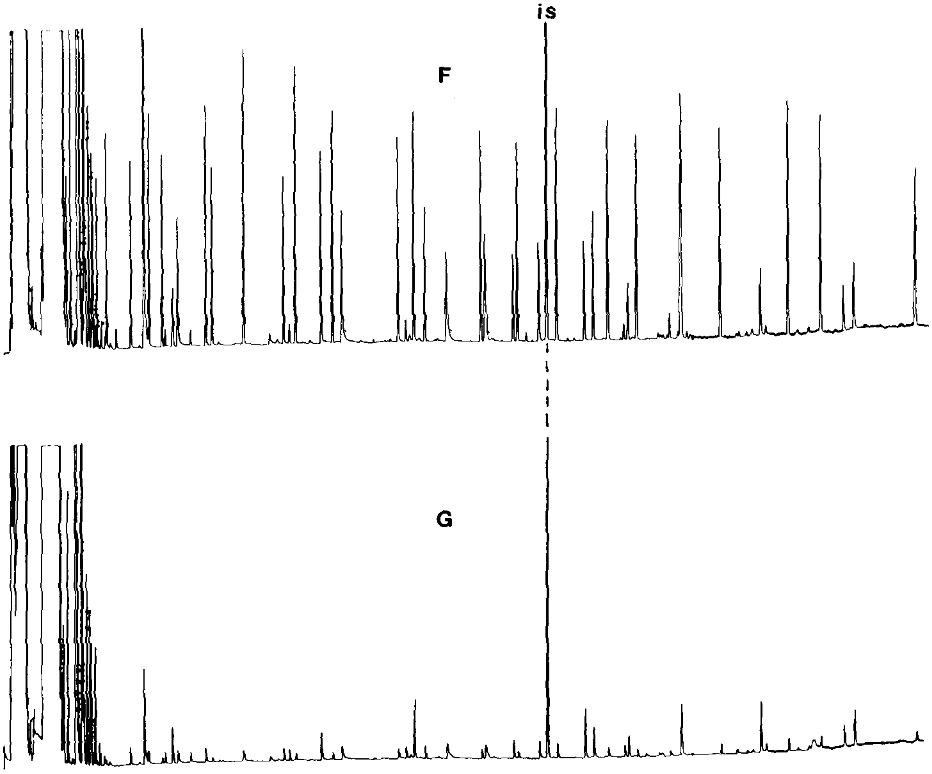

Fig. 3. Gas chromatograms of repeated extractions of a charcoal filter: first extraction (F) and second extraction (G). General gas chromatographic procedure but with an attenuation of 2^1. For further details see Experimental section. The peak marked "is" is 1-chloroundecane, added after extraction of the filter.

analysis and differences in volume between the extract of the standard solution and the stripping extract, an internal standard has been added to both extracts, and all peak areas have been given relative to the area of the internal standard. More precisely, the recovery of the *n*th model compound was calculated according to the following formula:

$$R_n = (A_n/A_{\text{is}})/(A_{n(\text{ref})}/A_{\text{is(ref)}}) \times 100$$

where R_n = recovery of *n*th compound; A_n = peak area of *n*th compound in the stripping extract; A_{is} = peak area of internal standard in the stripping extract; $A_{n(\text{ref})}$ = peak area of *n*th compound in the standard solution; $A_{\text{is(ref)}}$ = peak area of internal standard when added directly to the standard solution.

By using this formula an absolute recovery of the complete stripping procedure is obtained. For quantification of the extraction efficiency, the standard solution was added directly to the filter, and the internal standard was added to the extract.

CONCLUSIONS

This report greatly supports the use of stripping techniques for the analysis of trace organics in water. The open modification of the CLSA system is superior to the standard system in three respects: (1) it gives the best recoveries for compounds of low volatility and high polarity; (2) it is the method of choice when an extremely low blank level is of great importance; (3) it is the simplest system to operate.

When using the open system, stripping conditions can be varied widely. Our work has shown how the effect of stripping temperature on recovery is related to the chemical and physical character of the compounds that are analysed. Stripping analysis can be optimized to meet specific demands by using the results presented in Tables I–V.

When an improved purging technique is used, extraction from the charcoal filter becomes the step that limits the success of the complete stripping procedure for many compounds. Quantitative analysis has documented low-extraction efficiency and the advantages of using solvent mixtures.

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