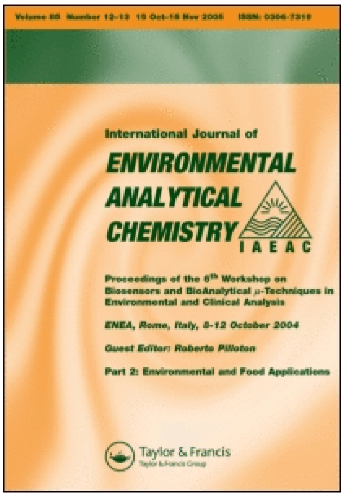

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Organic Pollutants in Water. I. Optimization of Operational Parameters of the CLSA Technique*

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The closed-loop stripping analysis (CLSA) is a well established method for quantitative determination of volatile organic pollutants in water. However, little attention has been paid to the reduction of the analysis time for a better application in monitoring studies. To this end extraction efficiencies with respect to compound volatility, water temperature (30, 35, 45 and 55°C) and time (0.5 and 2 hrs) have been calculated for a series of 21 *n*-alkanes, alkylaromatics and chlorinated hydrocarbons. The stripping at 45°C during 0.5 hrs gave better performances than the conventional 35°C/2 hrs, thus representing suitable conditions for large survey studies. Some applications as well as the overcoming of background contamination are discussed in the paper.

KEY WORDS: Volatile organic pollutants, water analysis, linear alkylbenzenes, closed-loop stripping analysis (CLSA).

INTRODUCTION

The closed-loop stripping (CLS) procedure, as developed by Grob,[1] is a very convenient method for the preconcentration of volatile organic compounds in water at trace levels (ng/l) before GC or GC-MS analysis. Applications of the method have been described for a

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variety of waters (e.g. drinking, surface, ground and marine)[2–5] and with the later technical modifications introduced[6] has been made amenable to routine work.

To this end, the different procedural steps have been accurately standardised for optimal compound recoveries, extraction efficiencies and quantitative determinations. However, little attention has been paid to the reduction of the operational time which is advisable when the system has to be used in monitoring studies requiring the handling of a great number of samples.

We assess in the present paper the influence of the parameters enabling the optimization of the analysis time, on the recovery of a broad mixture of non polar compounds (aliphatic and aromatic hydrocarbons and their chlorinated derivatives), in order to determine acceptable conditions for routine work. Attention is also given to the possible sources of contamination of the system producing unacceptable blanks.

EXPERIMENTAL

Materials

The compounds used for the optimization of the CLS analysis (CLSA) are those shown in Figure 1 and were obtained from Fluka and Aldrich. A reference methanol solution containing individual compound concentrations of 20–30 ng/μl was used for spiking 2 l of water to be analysed. The water was MilliQ quality and stripped. 1-chloroalkanes were selected as internal standards for calculating both stripping efficiencies and filter extraction recoveries as previously suggested by Grob.[6] In this respect, the primary solution containing C_4, C_6, C_{12} and C_{18} 1-chloroalkanes (underlined in Figure 1) was used for calculating stripping efficiencies, whereas secondary CS_2 solutions containing 31–37 ng/μl of C_8, C_{10} and C_{16} 1-chloroalkanes (encircled in Figure 1) were used for spiking the filter after stripping.

Field samples were collected in 2 l ambar bottles, thoroughly rinsed with the water being sampled, filled completely, closed with glass stoppers and stored at 4°C until analysis, which was performed within 24 hrs.

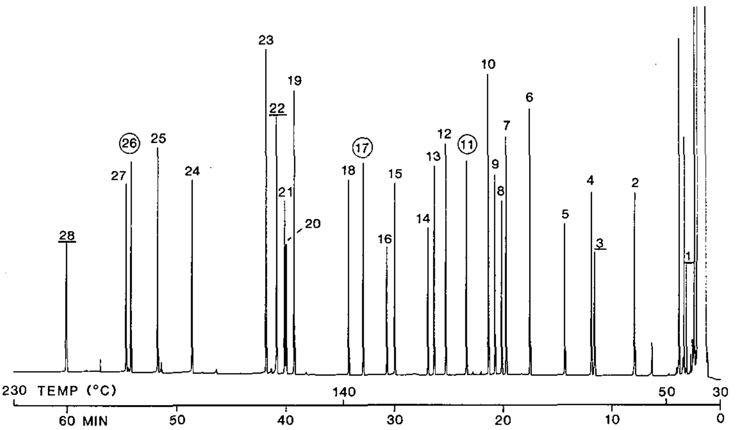


Figure 1 Standard mixture for the evaluation of operational conditions of CLSA. (1) Chlorobutane. (2) *n*-Octane. (3) 1-Chlorohexane. (4) Ethylbenzene. (5) *n*-Nonane. (6) *n*-Propylbenzene. (7) tert-Butylbenzene. (8) *n*-Decane. (9) *p*-dichlorobenzene. (10) Trimethyl-1,2,3-benzene. (11) 1-Chlorooctane. (12) *n*-Undecane. (13) Tetramethyl-1,2,3,5-benzene. (14) Trichloro-1,3,5-benzene. (15) *n*-Dodecane. (16) Trichloro-1,2,3-benzene. (17) 1-Chlorodecane. (18) *n*-Tridecane. (19) Dimethyl-1,3-naphthalene. (20) Dimethyl-2,3-naphthalene. (21) Dimethyl-1,5-naphthalene. (22) 1-Chlorododecane. (23) *n*-Pentadecane. (24) *n*-Heptadecane. (25) *n*-Octadecane. (26) 1-Chlorohexadecane. (27) *n*-Nonadedecane. (28) 1-Chlorooctadecane. Underlined compounds correspond to internal standards used for calculating stripping efficiencies. Encircled compounds correspond to standards used for calculating filter extraction recoveries.

Closed-loop stripping

The CLSA was performed in a commercially available apparatus (Brechbühler, A.G.) designed according to the Grob's idea.[6] The filter contained 1.5 mg of charcoal.

The water (2 l), spiked with 5 μl of the standard solution, was stripped for different periods of time and water temperatures. The gas stream leaving the water was always heated about 10°C above the bath temperature in order to prevent water condensation and optimize the adsorption of organics onto charcoal.[6] The filters were worked up according to the procedure described by Grob and Zürcher[6] using 5 μl of the chloroalkanes secondary solution and 10 μl of redistilled CS_2 (Merck).

Gas chromatography

Aliquots of the charcoal extracts were analyzed in a Carlo Erba 4160 GC instrument equipped with splitless injector and a 45 m × 0.25 mm i.d. SE-52 fused silica capillary column, prepared in the laboratory according to described deactivation and st. phase immobilization methods,[7,8] in order to ensure a film thickness bigger than 0.40 μm. Injections were made with the column held at 30°C for 1 min, then heated quickly (40°C/min) to 50°C and temperature programmed at 3°C/min to 230°C. The carrier gas was hydrogen (0.5 m/sec linear velocity). Under these conditions, the last standard (1-chlorooctadecane) eluted at the final oven temperature (Figure 1). The injector and the detector were maintained at 225°C and 250°C, respectively.

Compound identifications in field samples were carried out by interfacing the GC column directly into the ion source of an HP 5995 mass spectrometer, coupled to a data system HP 9825A.

Quantitative determination

The quantitation of the extracted compounds was accomplished by the use of 1-chloroalkanes as internal standards, added both to the water (primary st. solution) and to the charcoal filters (secondary st. solution) for the determination of water stripping and filter extraction efficiencies, respectively. Then, the quantitative analysis encompasses the comparison of the peak areas of the sample constituents, corrected for relative responses, with those of the internal standards in the chromatograms. Therefore, the accuracy of the quantitation will be influenced by the reproducibility of these determinations.

FID relative response factors (in arbitrary units) for the four families of compounds analysed are indicated in Table I. The accuracy in the chromatographic analysis of each group of components is also indicated in Table I. The reproducibility of the determination of the reference compounds (chloroalkanes) is fairly good and obviously decreases for the other compounds, which are measured with respect to the closest chloroalkane. The aromatic hydrocarbons exhibit a slightly lower reproducibility than the alkanes. In conclusion, a 3–5% of error in the whole analysis will be simply attributable to inaccuracies in the chromatographic analysis.

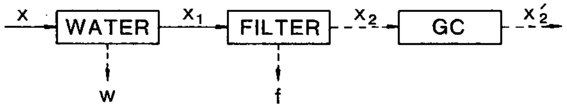
Table I FID response factors (R.F.) and accuracy of the quantitation (E) of compounds analysed by GC with respect to 1-chloroalkanes. Mean of ten determinations

	R.F.	C.V.(%)	E(%)
Chloroalkanes	100	–	0.5
Alkanes	134±4	3	3.0
Alkylbenzenes	165±4	3	5.4
Alkylnaphthalenes	126±5	4	5.7
Chlorobenzenes	68±2	3	–

RESULTS AND DISCUSSION

Evaluation of operational conditions

The recovery rates of volatile organic compounds in water by the CLSA technique are influenced by the efficiency of stripping from the water, the efficiency of adsorption on the filter and the efficiency of extraction from the filter and subsequent transfer to the GC. Then, as indicated in Figure 2, the global recovery is a combination of the stripping and filter extraction recoveries. These have been calculated in the present work for series of compounds exhibiting a broad volatility range, namely *n*-alkanes, alkylaromatics and chlorinated hydrocarbons, under a variety of operational conditions with particular reference to the analysis time.



$$\%\ \text{stripping recovery} = \frac{x_1}{x} \cdot 100 \qquad (x = x_1 + w)$$

$$\%\ \text{filter extraction} = \frac{x_2}{x_1} \cdot 100 \qquad (x_1 = x_2 + f)$$

$$\%\ \text{total recovery} = \frac{x_2}{x} \cdot 100 \qquad (x_2 \approx x_2')$$

Figure 2 Calculation of partial and total recoveries of component X in CLSA. w and f represent the unextracted fraction from the water and the filter, respectively.

Among the parameters that govern the efficiency of stripping both the water temperature and the stripping time are the most important. Several authors have investigated their influence on the recovery of the heavier substances[6,9,10] and a general consensus exists in performing the stripping at 30–35°C for 2 hrs, although times up to 24 hrs have also been proposed.[2] However, prolonged stripping has several drawbacks. On one hand substances of interest may be affected by biological degradation and, on the other, long times are impractical because this reduces the number of samples that can be analysed daily.

Despite the fact that the operational standard conditions have been precisely established, the variability of stripping recovery data in the literature, which is summarized in Figure 3, indicates the difficulty in extrapolating conclusions from one laboratory to another and the need for a quality assessment of data generated by this procedure in each case.

The influence of water temperature and stripping time on the recovery of the homologous series of 1-chloroalkanes is indicated in Table II. The data shows that a significant increase in the recovery

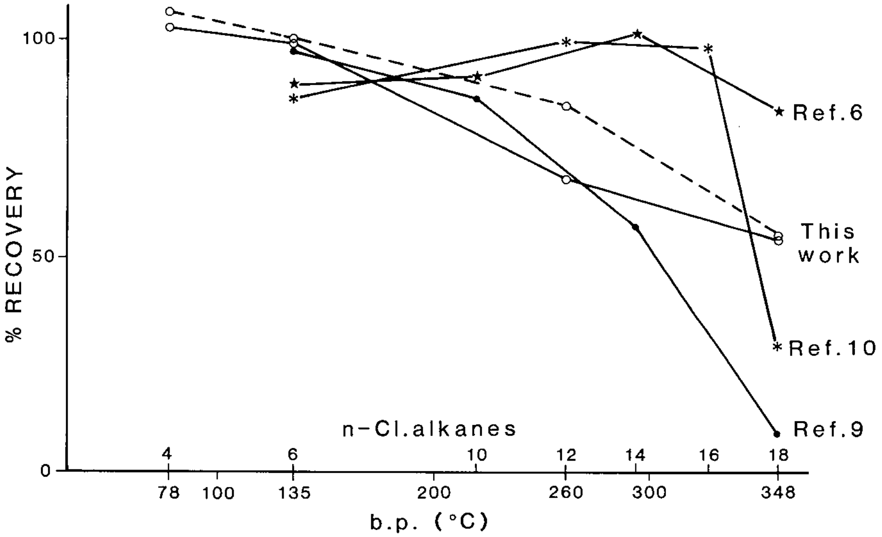


Figure 3 Recovery rates for 1-chloroalkanes after closed-loop stripping. Solid lines: 35°C/2 hrs. Dotted line: 45°C/0.5 hrs.

Table II Recovery of 1-chloroalkanes after CLS at different water temperatures and stripping times. Mean of ten determinations

Compound (b.p.°C)	2 hrs			0.5 hrs
	35°C	40°C (ref. 10)	45°C	45°C
1-chlorobutane (78)	102 ± 5	—	106 ± 10	105 ± 5
1-chlorohexane (135)	99 ± 8	98	99 ± 5	100 ± 3
1-chlorododecane (260)	67 ± 11	99	89 ± 9	84 ± 5
1-chlorooctadecane (348)	54 ± 6	63	88 ± 6	55 ± 4

of substances exhibiting boiling points higher than 250°C is obtained by increasing the water temperature from 35° to 45°C. At this temperature and after 2 hrs of stripping almost quantitative recoveries, with accuracies (C.V.) better than 10%, were obtained for dissolved compounds with boiling points as high as 350°C. We usually have encountered better accuracies in the analysis at higher water temperatures.

However, as indicated in Table II, the substances boiling up to 260°C are already recovered after 0.5 hrs of stripping at 45°C and even more than 50% of those heavier. It is apparent that compared to the conventional standard conditions these provide a better performance with the great advantage of the reduction of the analysis time. Therefore, they were considered to be optimal for studies involving the analysis of large numbers of samples.

In an attempt to improve the recovery of the heavier compounds, a test was performed at 55°C but problems derived from water condensation were observed as well as a certain shortening of the life of the charcoal filters (see next section).

These variety of conditions were also used for determining the stripping recovery factors (Figure 2) of the 21 compounds in the reference solution (Figure 1), using the chloroalkanes as internal standards. The data are summarized in Table III. In general, there is not much difference in performance with respect to the compound volatility and to the operational conditions, being the stripping recovery factors in the order of 95–100% with coefficients of variation lower than 10%. As it has been mentioned in the experimental

Table III Stripping recovery factors of reference compounds. Water skiped with about 50 ng/l of each

Compound	2 hrs			0.5 hrs
	30°C	35°C	45°C	45°C
n-C$_8$	113±14	106±15	113±10	105±11
n-C$_9$	102±14	98±12	110±4	101±3
n-C$_{10}$	102±7	103±5	105±4	104±6
n-C$_{11}$	86±3	97±4	105±4	103±5
n-C$_{12}$	86±11	102±6	102±3	107±8
n-C$_{13}$	86±11	98±4	97±7	106±4
n-C$_{15}$	96±7	98±5	98±6	99±4
n-C$_{17}$	88±7	95±6	100±8	100±2
n-C$_{18}$	91±8	93±7	108±8	99±6
n-C$_{19}$	76±15	79±7	96±6	91±5
mean of				
n-alkanes	93±10	97±7	103±6	101±5
alkylbenzenes	102±8	98±4	108±9	105±8
chlorobenzenes	92±9	92±8	95±6	98±8
alkylnaphthalenes	62±30	68±14	61±29	44±19

section 3–5% of this variation may be due to the chromatographic analysis itself.

However, the accuracy decreases significantly for the dimethylnaphthalenes, suggesting that not only the volatility but the nature of the substances influences the recovery in CLSA. Recovery efficiencies in the range of 40–50% (12–19% RSD) have also been reported previously for 1,6-dimethylnaphthalene.[10]

The extraction step of the compounds from the charcoal filter is governed by the amount of moisture on the charcoal and the solvent used. As far as the solvent is concerned it is well established that carbon disulphide gives the higher extraction efficiencies.[6,9] The moisture of the filter can be reduced to the level that no wettability problems occur with the solvent when the filter temperature is kept at least 10°C above the water temperature.[6] Using these conditions and the secondary standard solution of chloroalkanes for quantitation we were able to calculate the mean recoveries in the extraction step of the 21 reference compounds (Figure 1). The results are shown in Table IV and here again is observed the poor recovery of the

Table IV Mean recoveries of reference compounds adsorbed on charcoal by elution with CS_2 (15 μl) spiked with about 50 ng/l of each

Compounds	%
n-alkanes (C_8–C_{19})	94±2
alkylbenzenes	95±1
chlorobenzenes	89±4
naphthalenes	69±5

more polar components, the alkylnaphthalenes, although in this case it is much higher than that reported by Marchand and Caprais (28±5%),[10] probably because of the careful consideration of the moisture effect.

In conclusion we summarize in Table V the total recoveries for the compounds studied under different conditions. Average recoveries increase slightly with temperature and no significant differences were observed when at 45°C the stripping time was reduced to 0.5 hrs, thus providing convenient operational conditions for large survey studies.

To illustrate the performance of this procedure a typical gas chromatogram of an extract from river water being monitored since 1984 is shown in Figure 4. The major identified compounds consist of hydrocarbons extending up to 20 carbon atoms even though only 0.5 hrs of stripping were used. The *n*-alkane distribution centered at

Table V Total recoveries of reference compounds in CLSA at different operational conditions

	2 hrs			0.5 hrs
	30°C	35°C	45°C	45°C
Alkanes	90±14	93±11	101±11	100±10
Alkylaromatics	97± 7	94± 4	105± 8	101± 7
Chlorobenzenes	84±11	84±12	86± 7	92±12
Naphthalenes	45±19	49±11	46±20	31±17

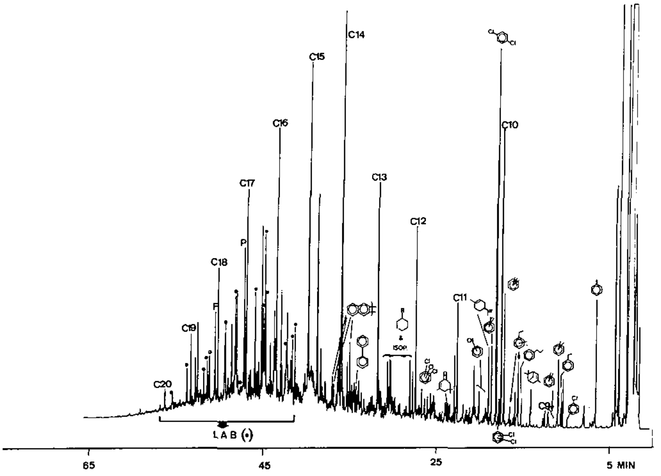


Figure 4 Gas chromatogram of the volatile organic fraction isolated by CLSA (45°C/0.5 hrs) from a water sample taken in April 1985 from the Llobregat river (Barcelona, Spain). Chromatographic conditions as in Figure 1.

n-C_{14} and with no carbon number predominance clearly suggests a middle petroleum distillate, e.g., diesel oil. The occurrence of the isoprenoid hydrocarbons pristane (P) and phytane (F) in similar concentrations is consistent with such interpretation. Grob[2] obtained a similar profile by adding 1 ppb of diesel oil to pure water and much longer stripping times. Toluene, C_2- and C_3-alkylbenzenes may also reflect petrogenic inputs either by direct spillage or water surface runoff.

A suite of chlorobenzenes, from mono to trichlorobenzenes, were recovered being the 1,4-dichloro isomer particularly abundant, agreeing with industrial uses of these substances. A final group of anthropogenic pollutants, identified for the first time by CLSA, is the series of long chain alkylbenzenes (LABs) eluting as a complex mixture in the range of C_{15}–C_{20} n-alkanes and exhibiting a unique m/z 91 profile in mass fragmentography. These compounds are considered as indicators of domestic wastewaters because they derive from detergent-bearing residues.[11]

Besides the variety of anthropogenic substances present in the waters of the Llobregat river, which result from the densely populated and industrialised area of Barcelona, causing problems to the drinking water supply of the City as well as to the quality of the coastal waters, some substances of natural origin appear. Among them, terpenes such as limonene and pinene have been currently found. Terpenes of any functionality (hydrocarbons, ketones, alcohols,...) usually occur in surface waters, though not in important concentrations because of their biological breakdown.[2]

This example confirms the utility of the CLSA technique for the assessment of surface waters pollution (sources and levels) and the validity of the optimization of operational parameters proposed for monitoring studies.

Background contamination

Clean blanks are a prerequisite for the above studies. Two main sources of contamination have been reported in CLSA, namely contamination of the system and that of the charcoal filter.[11,12]

After the intensive use of the CLSA technique in monitoring studies of volatile organics in surface waters we also observed memory effects in the system which produced unacceptable blanks and a great waste of time in trying to identify the source. Therefore, it is worth to report here our experience in dealing with this problem.

In Figure 5 is exemplified the sequence of results obtained. The first chromatogram (A) shows a typical profile of volatile organic pollutants in a surface water (Llobregat river). However, when the water sample was stripped again still some components were apparently extracted (chromatogram B), although surprisingly at the high volatility range. After repeating the process several times no significant improvement was observed, so that the problem was attributed to some sort of contamination. The test was then carried out with the system open, enabling the laboratory air to be sucked through the filter, but a similar profile was obtained (chromatogram C), thus suggesting the possibility of external contamination. The careful examination and testing of the system did not permit to confirm this hypothesis, so we suspected that memory effects were due to some active points within the system.

Grob[12] has recently indicated that the major source of contamination in CLSA is a damaged adsorbent filter. A mechanical stress

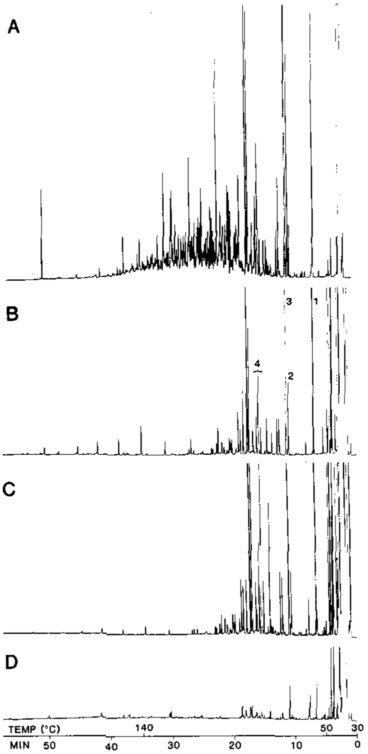


Figure 5 Gas chromatograms obtained during elimination of background contamination.

A—profile of the first stripping of a surface water sample (Llobregat river).
B—second stripping of the same water sample.
C—profile obtained with the system open and without water.
D—profile obtained after cleaning the system.

may break some carbon particles producing carbon dust which may be blown into the system and be deposited on the internal surfaces of the pump and the lines, creating severe ghosting. In order to overcome this problem the pump was opened and carefully wiped with a tissue and the lines were sonicated with water. After running the empty system overnight with a high capacity filter (5.0 mg) we finally obtained acceptable blanks as shown in chromatogram D.

We attribute the damage of the filter to the fact that during the optimization of operational parameters a broad range of temperatures were used from 30 to 70°C. The stress produced by the continued operation at relatively high temperatures may cause the dislodging of some carbon particles, thus producing the aforementioned contamination. Apart from this no other problems were found with the operation of the CLSA technique.

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