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ISOTACHOPHORETIC DETERMINATION OF SHORT-CHAIN FATTY ACIDS IN DRINKING WATER AFTER SOLID-PHASE EXTRACTION WITH A CARBONACEOUS SORBENT

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SUMMARY

A macroporous carbon sorbent, packed into disposable columns (Separcol-Carb), was investigated for the off-line preconcentration of short-chain fatty acids from drinking water in conjunction with their determination by capillary isotachophoresis (ITP). Of the acids investigated (C_1–C_9), butyric acid and higher homologues could be enriched into a high degree from samples of drinking water. Their detection limits from the ITP conductivity detector were in the low parts per 10^9 range when an amount equivalent to 8 ml of the sample was taken for analysis. The lowest homologues (C_1–C_3) were not adsorbed sufficiently to achieve their reasonable enrichment by the sorbent under the working conditions employed (acidification of the sample to pH 2.0). Acetone and diethyl ether were employed for the elution of the adsorbed analytes. The latter was more convenient in the analysis of practical samples as it co-eluted a considerably smaller number of the adsorbed anionic constituents. Octadecyl-bonded silica, evaluated in parallel, was found to be of only very limited utility for the same purpose.

INTRODUCTION

The presence of fatty acids (FAs) in sources of drinking water can be associated with human activities (*e.g.*, leaks from industrial and agricultural wastes) and also with biological processes and/or degradation of organic material naturally occurring in water (see, *e.g.*, ref. 1). As this group of ionogenic compounds need to be determined in water in general (waste, surface, precipitation, drinking water), considerable efforts have been devoted to the development of suitable analytical methods.

Gas–liquid chromatography (GLC), after conversion of FAs into suitable

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derivatives or without a derivatization step, plays a dominant rôle in this area[2–8]. In reversed-phase high-performance liquid chromatography (RP-HPLC), FAs are only seldom determined as the free acids[9] and their derivatization to improve both the separability and detection limits is commonly used[2,4,10–13]. When either GLC or RP-HPLC is used for the determination of FAs in water, a sample preparation step (trace enrichment, sample clean-up) is usually included in the analytical procedure. The same often applies also in ion chromatography, in spite of the fact that this method was shown to be very useful in the direct determination of short-chain (C_1–C_3) FAs in relatively clean samples (rain water)[14].

Capillary isotachophoresis (ITP), having an inherent analytical specificity for ionogenic compounds, is an alternative separation method suitable for the determination of FAs[15–22]. Its use is very convenient when the acids need to be determined in complex non-ionic matrices[20] or when their concentrations in the sample are comparable to those of other anionic macro constituents[17–19]. A column-coupling configuration of the separation unit[23] was advantageous in the ITP determination of some short-chain FAs present in high salinity waters associated with oil-bearing formations[21,22]. In the ITP work quoted no sample praparation steps were necessary (excluding filtration, sample dilution, etc.).

We have studied the use of ITP in the determination of C_1–C_9 FAs in water samples taken from (potential) sources of drinking water[24]. When the separation was carried out in a water–methanol operational system[20] (see also Table I) and the ITP analyser was assembled in the column-coupling mode, we could detect *ca.* 10^{-6} mol/l concentrations of FAs (*i.e.*, 50–160 ppb for the C_1–C_9 homologues) present in a 150-μl volume of directly injected sample. A further increase in the injection volume to achieve detection limits of low ppb concentrations was not convenient as a considerable higher load capacity of the separation compartment[25] became essential. In addition, long analysis times and/or problems associated with impurities present in the electrolyte system are obvious disadvantages of such an approach[26,27]. To solve this problem, the use of one of the sample preparation procedures elaborated for GLC and RP-HPLC (see, *e.g.*, refs. 3–9) appeared to be an alternative solution for our purposes. When these procedures were evaluated and/or preliminarily tested for use in combination with ITP, we found them to be less suitable (low recoveries of some acids, long sample preparation time, low clean-up efficiency).

Solid-phase extraction (SPE) is one of the preferred sample preparation techniques, especially in HPLC (for reviews see, *e.g.*, refs. 28–33). Carbon, porous polymers, ion exchangers and metal-loaded chelating resins are suitable alternatives for medium- and high-polarity compounds[28,29]. Of these, carbon sorbents were found to be advantageous in the trace analysis of various groups of ionogenic compounds[34–37]. Although data from a detailed investigation of the adsorption properties of graphitized carbon black by Laganà *et al.*[38] suggested a good potential of carbon sorbents for the trace enrichment of organic acids, no attention was paid to their use for sample preparation in FA analysis.

In this work we evaluated a macroporous carbonaceous sorbent[39,40] for the trace enrichment of C_1–C_9 FAs from aqueous solutions and its capabilities for sample preparation in the determination of these compounds in drinking water by ITP. Measurements of the retention characteristics of FAs on octadecyl-bonded silica (Si-C_{18}) showed[24] that this sorbent could be useful for the clean-up of samples

containing butyric acid and higher FA homologous. Therefore, we also evaluated this possibility, which could be useful in combining clean-up of the sample on a disposable Si-C_{18} column with the inherent concentrating power of ITP (a high injection volume of the sample free from inorganic macro constituents).

EXPERIMENTAL

Instrumentation

A CS Isotachophoretic Analyser (VVZ PJT, Spišská Nová Ves, Czechoslovakia) was assembled with the column-coupling configuration of the separation unit[23,41] using module provided by the manufacturer. The samples were injected with the aid of a 30-μl sampling valve. The lengths of the zones from the conductivity detector were measured electronically[42].

A laboratory-made vacuum manifold capable of simultaneously handling ten disposable columns (see below) was used in SPE experiments.

A Model 915 B total organic carbon analyser (Beckman, Irvine, CA, U.S.A.) was used for the measurements of total organic carbon present in water samples taken for the determination of FAs.

Chemicals and purification

Histidine was obtained from Reanal (Budapest, Hungary) and morpholinoethanesulphonic acid (MES) and hydroxyethylcellulose 4000 (HEC) from Serva (Heidelberg, F.R.G.). Histidine and MES were purified by repeated precipitation (dissolution in water, purified as described below, and precipitation with doubly distilled ethanol and acetone). A 1% (w/v) aqueous stock solution of HEC was purified on a mixed-bed ion exchanger (Amberlite MB-1; BDH, Poole, U.K.).

Water delivered by a RODEM-1 two-stage demineralization unit (OPP, Tišnov, Czechoslovakia) was further purified by circulation through laboratory-made polytetrafluoroethylene (PTFE) cartridges packed with Amberlite MB-1 mixed-bed ion exchanger and only freshly recirculated water was employed for the preparation of the solutions and for the SPE experiments.

Doubly glass-distilled methanol and acetone of analytical-reagent grade were employed throughout. Diethyl ether was purified from ionogenic impurities on an activated alumina column[43] and its ionic purity was checked by ITP analysis of its aqueous extract.

FAs obtained from Lachema (Brno, Czechoslovakia), Loba-Chemie (Vienna, Austria), Reachim (Moscow, U.S.S.R.) and Fluka (Buchs, Switzerland) were used without further purification. The other chemicals were purchased from the above manufacturers in analytical-reagent grade purity and were used as received.

Disposable SPE minicolumns packed with octadecyl-bonded silica (Si-C_{18}L, 250 mg sorbent bed) and macroporous carbon (Carb, 250 mg sorbent bed) were obtained from the Centre of Chemical Research (Slovak Academy of Sciences, Bratislava, Czechoslovakia). The Si-C_{18}L columns were washed with 5-ml volumes of acetone, methanol and water before use. The Carb columns were cleaned successively with 5 ml of dimethylformamide, 5 ml of acetone, 5 ml of diethyl ether, 5 ml of methanol and 10 ml of water. The columns were used repeatedly and before their re-use the sorbent beds were washed (activated) in the same way. The activation solvent was removed by percolating 5 ml of water through the sorbent bed.

Sample preparation

Procedure A. The sample volume (100, 250 or 500 ml) was acidified to pH 2.0 with sulphuric acid then percolated through the column at 10 ml/min. The sorbent bed was washed with 5 ml of water and the adsorbed compounds were eluted with 4 ml of acetone. The eluate was mixed with 700 μl of aqueous histidine ($5 \cdot 10^{-3}$ mol/l). Acetone was evaporated by a flow of nitrogen at ambient temperature to a final sample volume of 1 ml. A 30-μl volume of this sample solution was analysed by ITP.

Procedure B. The sorption and washing steps were the same as in *Procedure A.* Water present in the voids of the column bed was sucked out and the elution was carried out with two 2-ml volumes of diethyl ether. The eluate was mixed with 500 μl of aqueous sodium hydroxide (10^{-2} mol/l). The organic phase was evaporated under a stream of nitrogen and the aqueous phase was diluted with water and methanol to 1 ml so that the final concentration of the latter solvent in the sample was 25% (v/v).

RESULTS AND DISCUSSION

ITP analysis of fatty acids

The composition of the operational system used in the ITP analyses throughout this work is given in Table I. In this instance, the concentration of the leading ion was lower than that suggested previously[20] in order to decrease the detection limits of the analytes.

Relative differences in the effective mobilities of FAs in the steady state are clear from the isotachopherogram in Fig. 1. Here, a model mixture with a composition similar to that of drinking water was spiked with C_1–C_9 normal saturated FAs. With the exception of the C_1 and C_4 compounds the concentration of the acids present in the mixture were identical with the maximum values in the measurements of the calibration lines (Table II).

From the numerical values of the parameters of the regression equation characterizing the slopes of the calibration lines, it can be seen that these experimentally based values did not follow exactly the tendency that could be expected from the simulated data[44]. We found that these deviations could be ascribed to lower

TABLE I

OPERATIONAL SYSTEM EMPLOYED IN THE ITP ANALYSIS OF FATTY ACIDS

Parameter	*Electrolyte*	
	Leading	*Terminating*
Solvent	H_2O–CH_3OH	H_2O–CH_3OH
Proportions (v/v)	80:20	70:30
Anion	Cl^-	MES
Concentration (m*M*)	5	2.5
pH[a]	6.0	6.0
Additive	HEC	–
Concentration (%, w/v)	0.1	–

[a] Methanol was added to the aqueous solutions containing the required constituents at appropriate concentrations and pH values as measured for aqueous solutions are given.

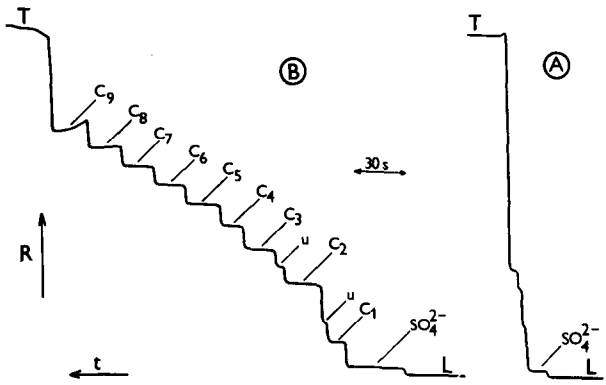

Fig. 1. Isotachopherograms from the analysis of short-chain fatty acids (C_1–C_9) present in a model mixture with a composition of inorganic constituents similar to that of drinking water. The records from the conductivity detector in the analytical column are only given. A = Blank run (no sample injection); B = model mixture spiked with fatty acids (C_1 at $4 \cdot 10^{-5}$ mol/l, C_4 at $6 \cdot 10^{-5}$ mol/l and the other acids at $8 \cdot 10^{-5}$ mol/l). The driving currents were 100 and 15 μA in the preseparation and analytical columns, respectively. L = Leading anion; T = terminating anion; u = unidentified impurities present in the operational system. R, t = increasing resistance and time, respectively.

actual contents of the acids in the preparations used (titrimetric analysis of some of the preparations). However, as the same preparations were used throughout and our measurements were relative rather than absolute (breakthrough curves, recovery data), no systematic errors were involved in this way.

The reproducibilities of the ITP analyses of the acids present in the samples at $3 \cdot 10^{-5}$–$8 \cdot 10^{-5}$ mol/l concentrations were typically in the range 1.5–3%.

Measurements of breakthrough curves

The breakthrough characteristics of the analytes on the sorbents used gave data relevant to their applicabilities for sample preparation. These characteristics were

TABLE II

REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS FOR C_1–C_9 FATTY ACIDS IN THE $8 \cdot 10^{-6}$–$80 \cdot 10^{-6}$ mol/l CONCENTRATION RANGE

No. of data points = 10.

Acid	*Regression equation*[a]	*Correlation coefficient*
C_1	$y = 2.36 + 0.1868x$	0.9993
C_2	$y = 1.82 + 0.2458x$	0.9996
C_3	$y = 0.61 + 0.2152x$	0.9999
C_4	$y = 0.57 + 0.2172x$	0.9998
C_5	$y = 0.67 + 0.2179x$	0.9998
C_6	$y = 0.96 + 0.2194x$	0.9999
C_7	$y = 0.52 + 0.2393x$	0.9997
C_8	$y = 0.41 + 0.2314x$	0.9997
C_9	$y = 0.09 + 0.2446x$	0.9996

[a] x = concentration (10^{-6} mol/l); y = zone length (s).

measured for the sorbents packed in disposable columns and treated before the use as described under Experimental.

The Si-C_{18}L sorbent was studied for two modes of the sorption process, *viz.*, ion suppresion (by decreasing the pH of the sample solution to *ca.* 3.0) and ion exchange [by modifying the surface of the sorbent by strongly retained cetyltrimethylammonium cation ($CTMA^+$) before the sample application]. In both modes the sample solutions percolating through the beds were collected into 1–2-ml fractions. The fractions were analysed by ITP and the breakthrough curves given in Fig. 2 were reconstructed from the results of the analyses. These curves clearly show that in both instances the sorbent provides only a very limited utility from the point of view of sample preparation.

Analogous data for the Carb sorbent (Fig. 3) indicate considerable higher breakthrough volumes, especially for the C_4–C_9 homologues. For obvious reasons only this sorbent, having a surface area of 1600 m^2/g (refs. 39 and 40), was studied in detail for sample preparation in the ITP determination of FAs in drinking water.

Recoveries of fatty acids on the Carb sorbent

In experiments with model samples spiked with FAs at concentrations of 10^{-6} mol/l or less, we found that the adsorption by the Carb columns was quantitative for the C_4–C_9 homologues and a very high enrichment factor (>250) was easily achieved for these constituents. On the other hand, propionic acid could be quantitatively adsorbed only from *ca.* 10-ml sample volumes and acetic and formic acids were not adsorbed with reasonable recoveries even from smaller sample volumes. From the practical point of view it is important that inorganic macro and micro constituents which are present in drinking water (Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, F^- and PO_4^{3-}) are not retained by this sorbent. Hence it provides a very effective clean-up of the adsorbed

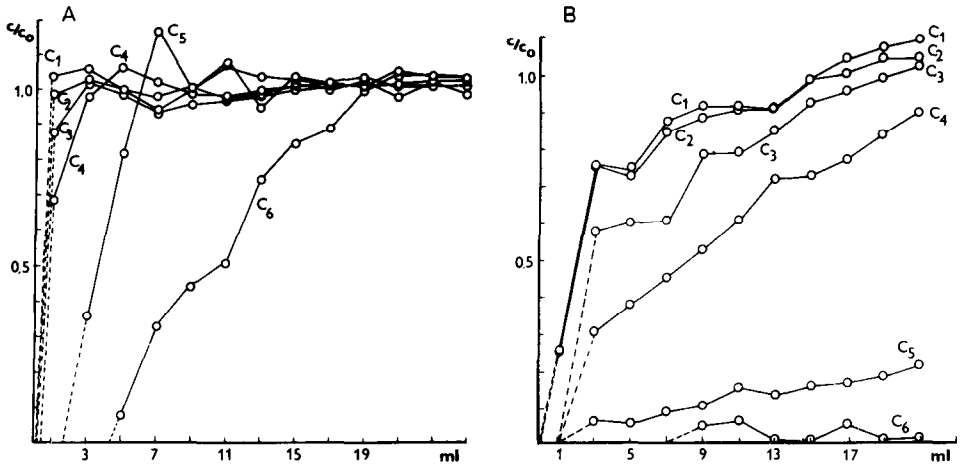

Fig. 2. Breakthrough curves of C_1–C_6 fatty acids on octadecyl-bonded silica. (A) Sample acidified to pH 3.0 with H_2SO_4 percolated through the column; (B) sample applied to the column with surface modified by $CTMA^+$ (35 ml of 10^{-3} mol/l aqueous $CTMA^+$ Br^- was percolated through the column before the application of the sample). In both instances tap water spiked with fatty acids at $5 \cdot 10^{-5}$ mol/l were percolated through the columns at 1 ml/min. c_0, c = Initial and post-column concentrations of the acids, respectively.

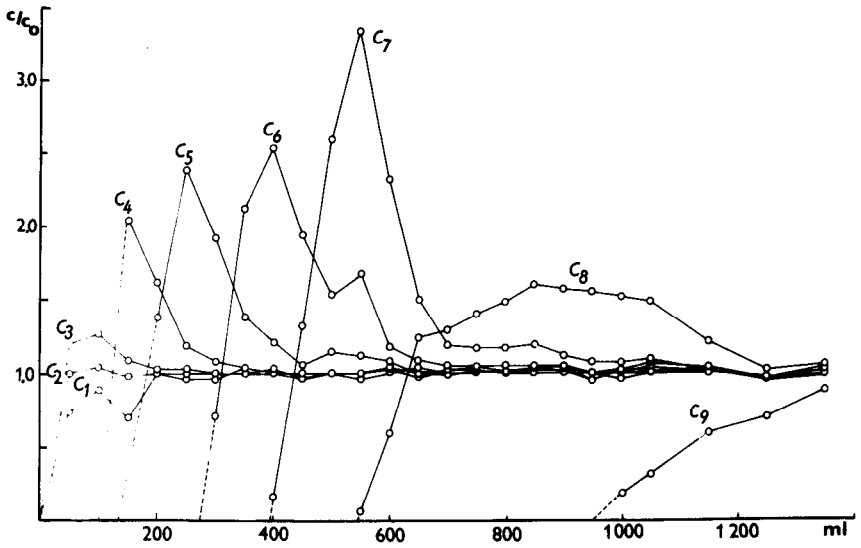

Fig. 3. Breakthrough curves of C_1–C_9 fatty acids on a macroporous carbon sorbent (Separcol-Carb). The same sample as in Fig. 2 was percolated through the sorbent bed at 10 ml/min. Fractions of 50 ml collected from the column were evaluated by ITP (the first 50-ml portion was collected in 10-ml fractions).

FAs. In the model experiments acetone was used as a suitable eluting solvent for FAs (see *Procedure A* in Experimental).

Drinking water contains organic compounds of various polarities in trace concentrations[45] and these compounds can be evaluated as total organic carbon (TOC). When we consider that carbonaceous sorbents are not very selective in the adsorption step (see, *e.g.*, refs. 38 and 45), many of these compounds can be expected to be trapped by the Carb column. From the point of view of the ITP determination of FAs various groups of organic acids (*e.g.*, subgroups of humic and fulvic acids[1,45]) need to be considered as potential interferents introduced in this way. As it is almost impossible to prepare model samples of the corresponding compositions, we employed samples of drinking water with relatively high TOC values (17–19 mg/l) to investigate problems of this kind and to optimize the elution conditions for the FAs. The isotachopherograms in Fig. 4 were taken from the analysis of such a sample of drinking water. Volumes of 500 ml of the same sample treated by the sample preparation procedures as described under Experimental were used. It is apparent that *Procedure B* (Fig. 4B) provided a less complex anionic profile. Consequently, in the analysis of samples spiked with FAs (see Fig. 5) it gave a lower bias of the quantitations due to the enriched matrix constituents.

The recovery experiments summarized in Table III were carried out within a period of 2 months with nine samples of drinking water taken from the same sampling site (TOC = 19 mg/l). For obvious reasons, in these experiments we employed sample preparation *Procedure B*. The samples and those spiked at various concentrations with FAs (see Table III) were processed identically. The spiking concentrations were chosen so that the total amounts of the individual FAs were constant.

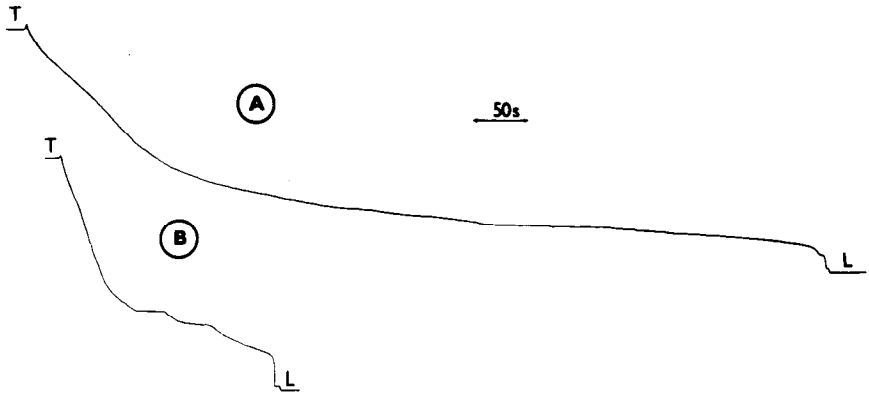

Fig. 4. Comparison of (A) acetone and (B) diethyl ether in the desorption of organic anionic constituents from the Carb sorbent. In both instances 500-ml volumes of the same sample taken from a potential source of drinking water (TOC = 19 mg/l) were adsorbed in an identical manner (for further details see the text). For the impurities introduced from the operational system, see Fig. 1A. ITP working conditions as in Fig. 1.

With the exception of 500-ml sample volumes, the reproducibilities of the recoveries for the same sample repeatedly processed on the same column were 2–3 times higher than the long-term reproducibility data. However, the evaluation of a set of data obtained over a long period of time gives a better measure of the overall reproducibility of the proposed sample preparation procedure because it includes random errors in the sample manipulation steps, dispersion in the sorption properties of the columns and errors due to variability of the matrix. In these long-term recovery data systematic errors due to changes in the compositions of the calibration mixtures (gradual decreases in the concentrations of some FAs) were avoided by relating the concentrations of the recovered acids to those in the reference sample from which the samples of drinking water were spiked.

In general, the lower mean values and higher relative standard deviations of the recoveries for 500-ml sample volumes can be ascribed to the displacement effects of preferentially adsorbed organic constituents from drinking water. This problem can be

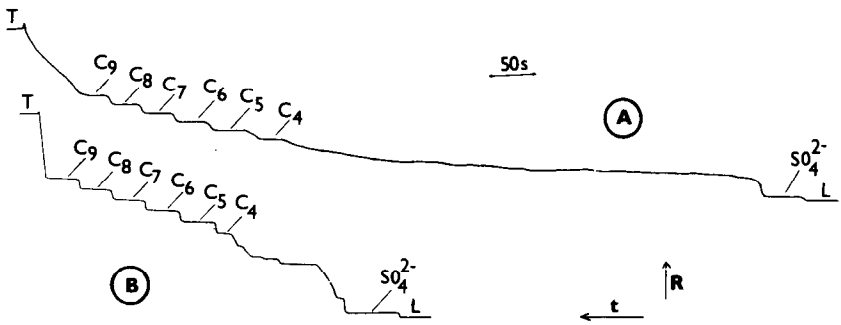

Fig. 5. Isotachopherograms from the analysis of drinking water spiked with fatty acids at $1.6 \cdot 10^{-7}$ mol/l with different sample preparation procedures. (A) Elution with acetone; (B) elution with diethyl ether. The same samples and procedures as in Fig. 4 were used. ITP working conditions as in Fig. 1.

TABLE III

RECOVERIES OF C_4–C_9 FATTY ACIDS FROM DRINKING WATER ON THE SEPARCOL-CARB COLUMN

Relative standard deviations of the recoveries for 100-, 250- and 500-ml sample volumes were calculated from the analyses of 14, 9 and 13 samples, respectively. The analyses were carried out within a period of 2 months. The concentrations of FA in the samples were $8 \cdot 10^{-7}$, $3.2 \cdot 10^{-7}$ and $1.6 \cdot 10^{-7}$ mol/l for sample volumes of 100, 250 and 500 ml, respectively.

Acid	*Sample volume*[a]					
	100 ml		*250 ml*		*500 ml*	
	$\bar{x}$ (%)	s_r (%)	$\bar{x}$ (%)	s_r (%)	$\bar{x}$ (%)	s_r (%)
C_4	96.6	16.7	100.7	7.8	100.2	21.5
C_5	92.0	10.5	95.8	5.5	97.3	16.1
C_6	93.4	10.8	94.0	7.2	90.3	22.5
C_7	95.7	11.3	100.3	8.4	87.6	20.9
C_8	88.7	13.7	93.8	5.3	76.6	26.7
C_9	86.9	12.3	101.3	10.8	79.5	28.0

[a] $\bar{x}$ = mean recovery; s_r = relative standard deviation.

solved by packing a larger amount of the sorbent in the column when a further decrease in the detection limits is to be achieved via the use of higher sample volumes. Such a solution, however, is not necessary in our particular case when it is realized that only 3% of the final sample volume was taken for one ITP run. Therefore, when desirable a larger injection volume can provide a more convenient means of decreasing the detection limits. Here, it is important that the Carb sorbent is very effective in removing inorganic anionic macro constituents (Cl^-, SO_4^{2-} and NO_3^-) from the sample, thus minimizing the requirements concerning the load capacity of the separation compartment. In this work 250-ml volumes of the samples of drinking water were taken for analysis. After the sample preparation step the enriched acids were present in a 1-ml volume, 30 μl of which were analysed by ITP. Under these conditions we could detect with confidence *ca.* $5 \cdot 10^{-8}$ mol/l concentrations of the analytes (*i.e.*, 4.5–8.0 parts per 10^9, ppb, for the C_4–C_9 homologues). A 10-fold decrease in this value appears feasible by simply increasing the injection volume to 300 μl.

Typical isotachopherograms for the determination of FAs in a practical sample of drinking water are shown in Fig. 6. In this instance, the sample and that spiked with FA at $3.2 \cdot 10^{-7}$ mol/l were preconcentrated 250-fold before the ITP analyses. The recoveries of the acids in this particular instance were in the range 90–100% and the reproducibilities of the recoveries were in the range 6–9% (three parallel analyses).

CONCLUSIONS

Solid-phase extraction on a macroporous carbon sorbent (Separcol-Carb) has been shown to be effective in decreasing the detection limit in the ITP determination of some short-chain FAs in drinking water to the low ppb level even when the acids are

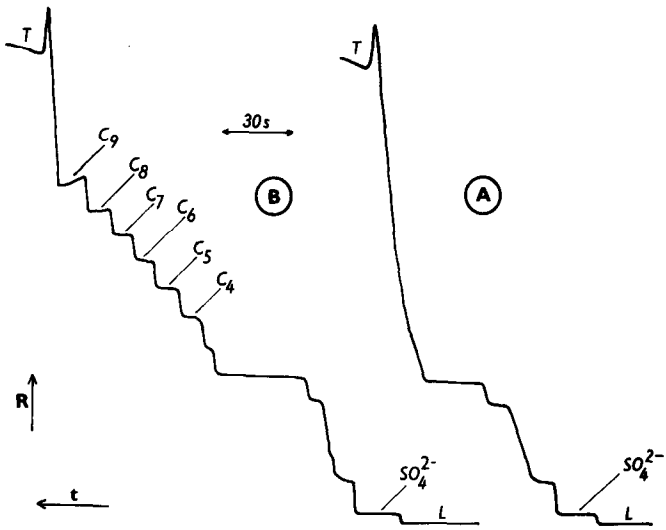

Fig. 6. Determination of C_4–C_9 fatty acids in drinking water of TOC 19 mg/l. The sample was taken from the same site as shown in Figs. 4 and 5 with a 2-month delay. Volumes of 250 ml of (A) the sample and (B) the sample spiked with fatty acids at $3.2 \cdot 10^{-7}$ mol/l were pretreated by the sample preparation *Procedure B* (see Experimental). The zones of the acids were six times longer than the values calculated as the detection limits. ITP working conditions as in Fig. 1.

present in complex organic matrices. This sorbent was found to be of only limited utility in adsorbing the C_1–C_3 homologues and thus it did not provide a sample preparation procedure applicable to the complete group of investigated acids. However, analogous disadvantages are common also to other sample preparation procedures currently in use in the determination of FAs with prior separation methods.

In spite of the fact that the Carb sorbent (like other types of carbonaceous sorbents) is inherently less selective and it adsorbs both apolar and polar organic compounds, its use for sample preparation in the ITP determination of FAs is convenient when a high analytical specificity of ITP to the ionogenic compounds is considered. From the practical point of view, by using this sorbent we could achieve simple and rapid sample preparation (*ca.* 30 min by simultaneously handling ten samples) with good recoveries of the adsorbed acids. It is also important that this procedure can be easily adapted for field work and can be used for simple sample storage (we found that the acids adsorbed on the column bed and stored for 1 week at 4°C in a capped tube gave recoveries that agreed well with a control experiment).

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