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Determination of chlorophenols in drinking water samples at the subnanogram per millilitre level by gas chromatography with atomic emission detection

M.I. Turnes, I. Rodriguez, M.C. Mejuto, R. Cela*

Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Abstract

The use of an atomic emission detector following a process of preconcentration of drinking water samples by a factor of 1500:1 allows the highly selective determination of chlorophenols present in samples below the maximum limit of 0.5 ng/ml set by international regulations. The preconcentration of the samples is carried out using 0.25-g commercial graphitized carbon cartridges without the need for sample derivatization prior to solid-phase extraction.

1. Introduction

Scientific interest in recent years has focused on the determination of trace levels of organic pollutants in natural waters and industrial effluents. The US Environmental Protection Agency [1] has drawn up a list of eleven phenolic compounds considered major pollutants. Chlorophenols are among the most toxic and carcinogenic of these.

In 1982 the European Community adopted the EC Priority Pollutants List that has been subsequently expanded and updated. Among the eleven phenols considered by EPA, only chlorophenols are in the EC list, although the maximum admissible concentration of phenols in water used for consumption has been set at 0.5 ng/ml [2].

For the individual compounds, EC regulations do not specify mandatory analytical methods. However, with the current analytical methods it is not possible to measure directly the phenols in drinking waters at the stipulated levels. This had led to the development of several analytical procedures making use of preconcentration and derivatization processes. Prior derivatization (esterification with acetic anhydride and treatments with alkylating reagents such as diazomethane or methyl iodide and with halogen-containing reagents such as pentafluorobenzyl bromide, pentafluorobenzoyl chloride and heptafluorobutyric anhydride of phenols prevents adsorption problems and improves peak shape and detectability, in most cases enhancing liquid- or solid-phase extraction recoveries [3–5]. For sample concentration, several workers have used liquid–liquid extraction with organic solvents [6–8]. As an alternative, solid-phase extraction processes have been examined, using different adsorbent materials, such as resins [9,10], a variety of bonded reversed phases [11–13] and graphitized carbon materials [14–16].

* Corresponding author.

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When dealing with waste-water samples, HPLC gives excellent results, but for drinking water gas chromatography (GC) is preferred [17,18]. However, when large volumes of water have to be processed to obtain high concentration factors, the final extracts tend to be rich in multiple organic compounds, producing chromatograms that are difficult to assess, when a non-specific detection method flame ionization detection (FID) is used and even with much more selective detectors such as the electron-capture detector. For this kind of sample GC–MS is often recommended [19], using targeted ^{13}C-labelled chlorophenols as internal standards. Up to 5 l of water sample can be concentrated by solid-phase extraction (SPE) after conversion of phenols into their acetates to avoid the low breakthrough volumes often exhibited by polar compounds in C_{18} cartridges.

In 1989 the first commercial instrument for atomic emission detection (AED) [20] was put on the market. GC–AED is a powerful tool when the species of interest contain some element that is not common to the other compounds of the matrix [21–24], as it allows for the specific determination of that particular element.

In this work, we studied the capability of CG–AED to detect and determine chlorophenols in drinking waters by carrying out a preconcentration process on SPE graphitized carbon cartridges. The proposed procedure has the inherent advantages of selectivity of detection for chlorinated compounds coupled with high sensitivity. This, together with the high degree of preconcentration obtained by graphitized carbon SPE cartridges, allows the necessary sensitivity levels to be reached to carry out the determination of these compounds within the legal limits that have been established without the need for sample derivatization and a specialized internal standard.

2. Experimental

2.1. Reagents

The reagents used (methanol, dichloromethane, formic acid) (Merck, Darmstadt, Germany) were of the maximum purity available. In the preconcentration process, commercial cartridges of graphitized carbon black, Supelclean, ENVI-Carb SPE of 0.25 g (Supelco, Bellafonte, PA, USA) and octadecyl (C_{18})-bonded silica Mega Bond Elut (Varian, Sunnyvale, CA, USA) and Environmental Sep-Pak Plus (Millipore–Waters, Milford, MA, USA) cartridges were used.

Standards of the different chlorophenols to be determined, 2-chlorophenol (2CP), 2,4-dichlorophenol (24DCP), 4-chloro-3-methylphenol (4C3MP), 2,4,6-trichlorophenol (246TCP) and pentachlorophenol (PCP), were supplied by Merck and Aldrich (Milwaukee, WI, USA). Stock standard solutions (4.0 mg/ml) were prepared of each separately in methanol. From these solutions, kept in a dark, refrigerated environment, the corresponding working standard solutions to be used in spiking samples were obtained by dilution with methanol. Those to be used as calibrants were dissolved in dichlorometane –methanol (90:10, v/v), 0.25 *M* in formic acid.

2.2. Apparatus

The analyses were carried out using a Hewlett-Packard (Avondale, PA, USA) Model 5890 Series II gas chromatograph, equipped with a split–splitless injection port and a microwave-induced plasma atomic emission detector (Hewlett-Packard Model 5921A). All the system was controlled by a CG–ECD Chemstation (HP 35920A). A Scientific Glass Engineering (Ringwood, Victoria, Australia) BP-5 (50 m × 0.32 mm I.D.) methylphenylsilicone capillary column, 1 μm film thickness, was used in all experiments. Helium (99.9999%) was used as the carrier gas. The quantification of peaks was carried out by bracketing standards. The optimum parameters for the determination of the compounds under study are shown in Table 1.

2.3. Sample preparation

Before processing the water samples, the cartridge must be conditioned. First, it is washed with 5 ml of dichloromethane–methanol (80:20, v/v), 2 ml of methanol and 15 ml of a 10 g/l

Table 1
CG–AED conditions for the separation of chlorophenols.

GC parameters	
Injection port	Split–splitless
Purge time on	200 s
Injection port temperature	250°C
Injection volume	2 μl
Column head pressure	135 kPa
Split flow	6.4 ml/min
Over temperature programme	
Initial temperature	80°C
Rate	15°C/min
Final temperature	250°C
Final time	10 min
AED parameters	
Transfer line temperature	260°C
Cavity block temperature	260°C
Wavelengths	Chlorine 480.192 nm Carbon 495.724 nm
Helium make-up flow	44.4 ml/min
Ferrule purge	28 ml/min
Spectrometer purge flow	2 l/min (N_2)
Solvent vent beginning	2.5 min
Solvent vent end	7.2 min
Reagent gas	Oxygen

solution of ascorbic acid in HCl-acidified ultrapure water at pH 2. This acidic treatment, described by Di Corcia and Marchetti [25], is necessary to reduce the quinone groups to hydroquinone, which are less reactive. The presence of these quinone groups as impurities in the carbon surface may cause irreversible adsorption of certain compounds, including some of the phenols studied in this work.

The drinking water samples or the spiked samples are forced through the cartridge at a flow-rate of 10–15 ml/min with the help of vacuum membrane pumps. The cartridge is then washed with 7 ml of HCl-acidified ultrapure water (pH3), rinsing slowly. After large volumes of water have been flushed through, shrinking of the sorbent bed may occur. When this happens, before the washing stage, the upper polypropylene frit is pressed against the bed. This helps by the elimination of the water and makes the eluent system more effective, as it flushes through the carbon bed more homogeneously [26]. Finally, 1 ml of methanol is flushed through very slowly in order to eliminate the residual water. Dry air is blown through the cartridge for 5 min with the same pumps as used for the suction of the samples.

The cartridge is eluted with 8 ml of a 0.25 *M* formic acid solution in dichloromethane–methanol (90:10, v/v). This final extract is concentrated on a Turbo Vap II concentration workstation (Zymark) by means of a 55 kPa nitrogen current and a 30°C water-bath until it reaches a final volume of ca. 0.5 ml. To ensure repeatable results, it is diluted to exactly 1 ml. The extract is then ready to be injected into the GC–AED system.

3. Results and discussion

Under the working conditions described in Table 1, the separation of the five chlorophenols under study is very good. Fig. 1 show the chlorine (479.53-nm line) and carbon (495.71-nm line) traces of a sample of 500 ml of ultrapure water (Milli-Q water), spiked with the five compounds under study at a level of ca. 2 ng/ml each, when submitted to the whole experimental procedure described. In the chromatogram monitored at the chlorine line (Fig. 1a) there were only five peaks corresponding to the five phenols added. The signal corresponding to the carbon emission line (Fig. 1b) produces a chromatogram relatively more complicated with a large number of peaks. In this case, accurate quantification of the species under study is possible except for 2-chlorophenol and 4-chloro-3-methylphenol, which overlap other small peaks. In Fig. 1 it is also evident that the chromatographic conditions used can be modified to speed up the analysis, provided that AED is used and that no other di-, tri- or tetrachlorophenols could be expected to be present in the samples. However, the conditions in Table 1 were finally adopted to ensure that the 2CP peak did not fall into the solvent vent time-window.

Obviously, the situation with a surface or drinking water sample is much more difficult. The chromotograms in Fig. 2 correspond to the analysis of 1-l tap water samples. In Fig. 2a the chlorine traces for the unspiked sample and a sample spiked with the five species (1–2 ng/ml

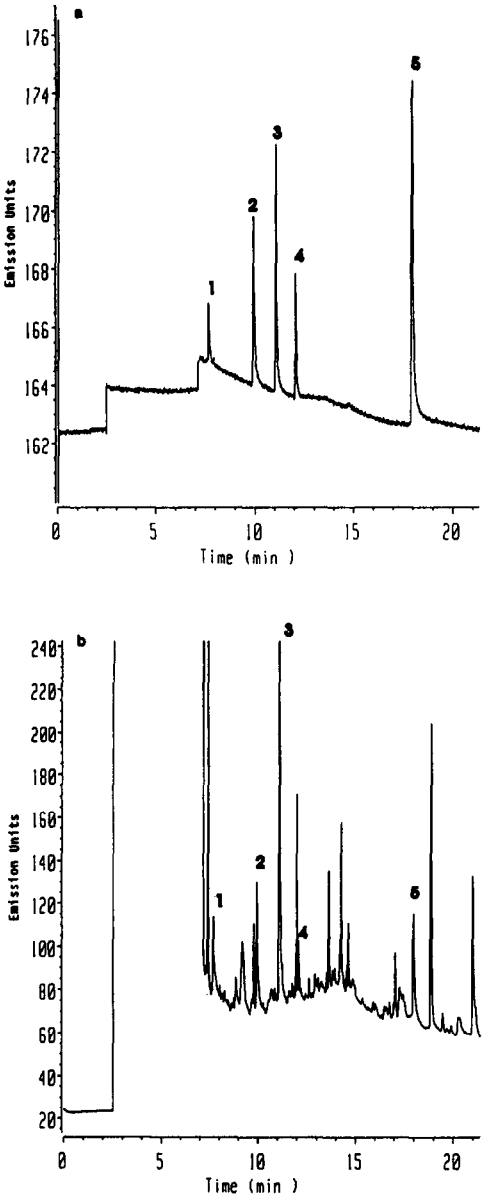

Fig. 1. Chromatograms for the Cl479-nm and C496-nm emission lines of a chlorophenol standard solution analysed by the proposed procedure. (a) Trace of chlorine line; (b) trace of carbon line. Peaks: 1 = 2CP (3.2 ng/ml); 2 = 24DCP (3.2 ng/ml); 3 = 4C3MCP (6.4 ng/ml); 4 = 246 TCP (1.6 ng/ml); 5 = PCP (9.9 ng/ml). For operating conditions, see Table 1.

each) have been superimposed to show the differences more clearly. Fig. 2b depicts the carbon trace for the unspiked sample and Fig. 2c the chromatogram obtained when analysing the spiked sample but using FID. The advantages of using AED become clear from the comparison of these chromatograms.

Under the conditions described under Experimental, the quantification limits (signal-to-noise ratio = 10) in water samples were 2CP 0.12, 24DCP 0.08, 4C3MP 0.15, 246TCP 0.07 and PCP 0.48 ng/ml. Therefore, the proposed procedure allows for the accurate quantification of the five species on an individual basis below the limits stipulated by the international regulations. On the other hand, calibration graphs for all five species show good linearity in the range 0.1–10 μg/ml, provided that consistent inertness of the chromatographic system is ensured. However, we found that the column degraded rapidly when routine injections of extracts were carried out. As it is very difficult to find appropriate internal standards that match adequately the inertness differences in the system for all the species considered, it is advisable to use the bracketing standard technique for quantitative measurements.

3.1. Sample preparation and extract concentration

There have been many studies of the use of the solid–liquid extraction technique (SPE) for the concentration of aqueous phenol samples. In fact, chlorophenols have been used as model compounds in many SPE studies [27–29]. Most of these studies were focused on the use of two types of adsorbents: C_{18}-bonded silica and graphitized carbon black materials.

Although the aim of this work was to develop a procedure capable of quantifying chlorophenols at concentrations under 0.5 ng/ml without the need for any derivatization step, some data were obtained comparing the efficiency and some practical aspects of the two adsorbents in concentrating aqueous samples of chlorophenols. Table 2 shows the recoveries of the five chlorophenols with both types of sorbents. The data in Table 2 are the averages of four independent experiments measured in duplicate. With GCB cartridges, experiments with sample volumes of 2 l were also carried out. Although the recoveries

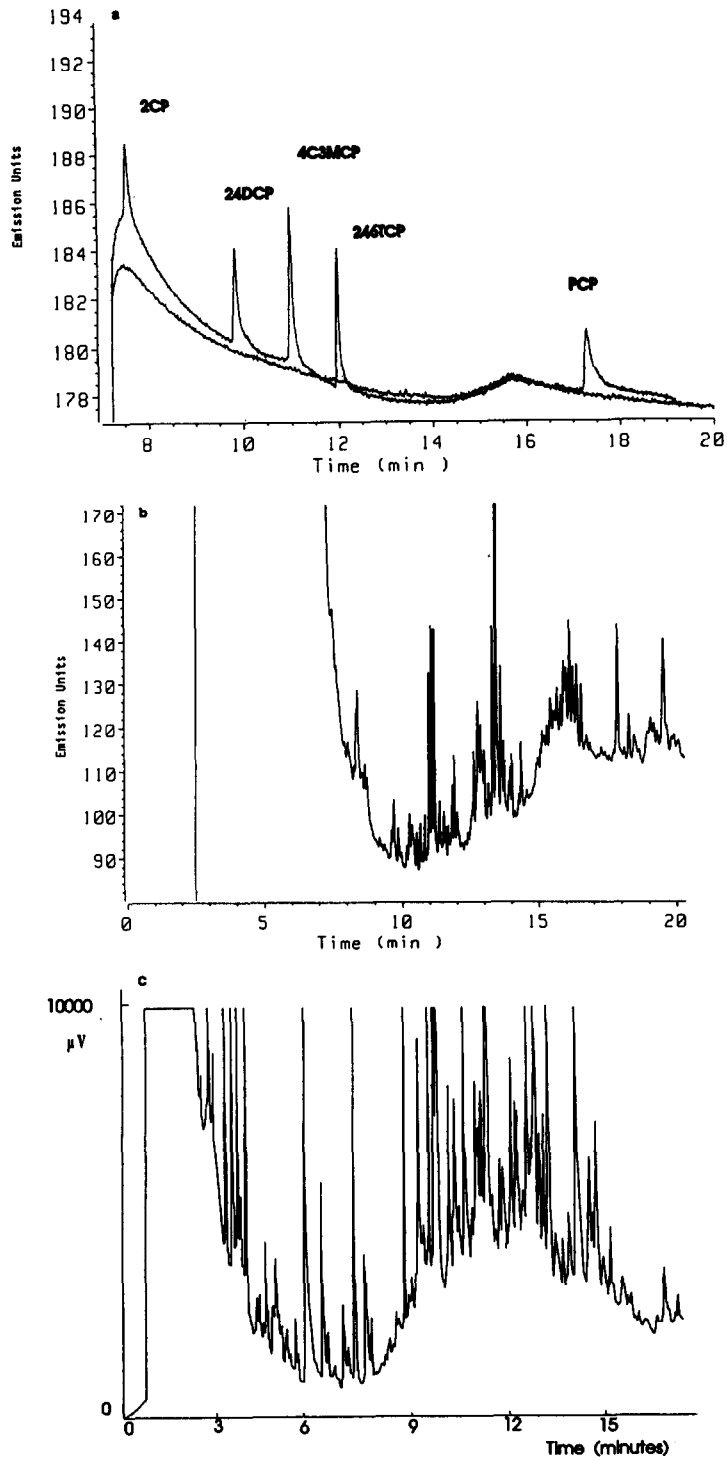

Fig. 2. Chromatograms of a tap water sample. (a) Superimposed traces of chlorine line for an unspiked sample (lower trace) and a spiked sample (upper trace). (b) Carbon trace for the unspiked sample. (c) FID trace for the spiked sample. Peaks as in Fig. 1; operating conditions as in Table 1.

Table 2
Recoveries of the chlorophenols using graphitized carbon black and C_{18} cartridges.

Compound	Concentration range in samples (ng/ml)	Recovery (%)[a]				
		GCB cartridges			C_{18} cartridges	
		Sample volume (ml)			Sample volume (ml)	
		500	1000	1500	250	500
2CP	1–3	70 ± 7	87 ± 14	73 ± 9	40 ± 5	37 ± 8
24DCPO	0.5–3	100 ± 4	107 ± 17	97 ± 10	107 ± 14	96 ± 4
4C-3MCP	0.5–6	88 ± 1	87 ± 12	92 ± 9	80 ± 12	114 ± 13
246TCP	0.2–1.5	83 ± 3	97 ± 12	97 ± 10	86 ± 6	89 ± 15
PCP	0.5–20	76 ± 9	95 ± 18	100 ± 14	48[b]	nd[c]

[a] Values corrected for evaporation losses.
[b] Only two measurements were carried out.
[c] Not detected.

obtained were not significantly lower than those shown in Table 2, greater variability in the results was found. Hence 1.5 l of sample were considered a practical limit for the proposed procedure. We also examined the recovery for various chlorophenol concentrations in sample volumes of 1.5 l, and found no noticeable differences in the recoveries and repeatability. However, the data in Table 2 show poor precision of the measurements. This can be attributed mainly to the evaporative concentration stage.

As cartridge eluates have to be concentrated under a nitrogen flow at a temperature similar to that found in the laboratory, we proceeded to evaluate the possible losses that this process might entail. These losses were measured by preparing a standard solution of the five phenols studied in the same solvent as used to extract the carbon cartridges. Aliquots of 8 ml of this solution were concentrated until a final volume of ca. 0.5 ml was reached, then diluted to 1 ml and injected into the chromatograph. The results suggested that substantial evaporation losses (30–40 ± 10%) occur for all the species considered. Other similar evaporation control experiments (with the same evaporation device) carried in our laboratory [30], which among others included the same species here considered but dissolved in hexame, did not show noticeable losses except for 2-chlorophenol. Therefore, evaporation losses cannot be attributed to defective running of the evaporation device and the solvent used must have a critical role in the observed losses. Although the losses, being almost constant for all the species, can be compensated for at the time of calculating chlorophenol concentrations in the samples, it is evident from Table 2 that the variability of evaporation losses determines the variance of the final results. Evaporation losses are clearly the weakest aspect of the proposed procedure and will need to be improved.

Another point in Table 2 is to appreciate that once corrected for evaporative losses, all the species studied except 2-chlorophenol shows recoveries higher than 90% with GCB cartridges. For 2-chlorophenol we checked that no breakthrough took place under the described conditions, by using two cartridges in series. Although we have no clear explanation for the observed virtually constant losses of 2-chlorophenol, this can be attributed also to evaporation losses. According to Borra et al. [15], drastic losses of 2-chlorophenol occur when evaporating solutions that had been made alkaline.

Regarding the C_{18} data in Table 2, another practical aspect has to be considered. Here the aqueous samples containing chlorophenols were

acidified with 0.1 *M* HCl until they reached a pH of ca. 2.5–3, before passing through the C_{18} cartridges. Cartridge elution was carried out using a hexane–ethanol (79:21) azeotrope. Under these conditions, complete recoveries for 24DCP, 4C3MP and 246TCP were obtained, provided that the sample volume did not exceed 500 ml, in which case breakthrough occurred, making the recoveries much poorer. The low recovery of 2CP has to be attributed to the low breakthrough volumes that have been shown [10] for monochlorophenols. On the other hand, the low recovery of PCP can be justified by the relatively high pH of samples. Complete recovery of PCP can be obtained by acidifying the samples to below pH ≈ 2. However, when highly

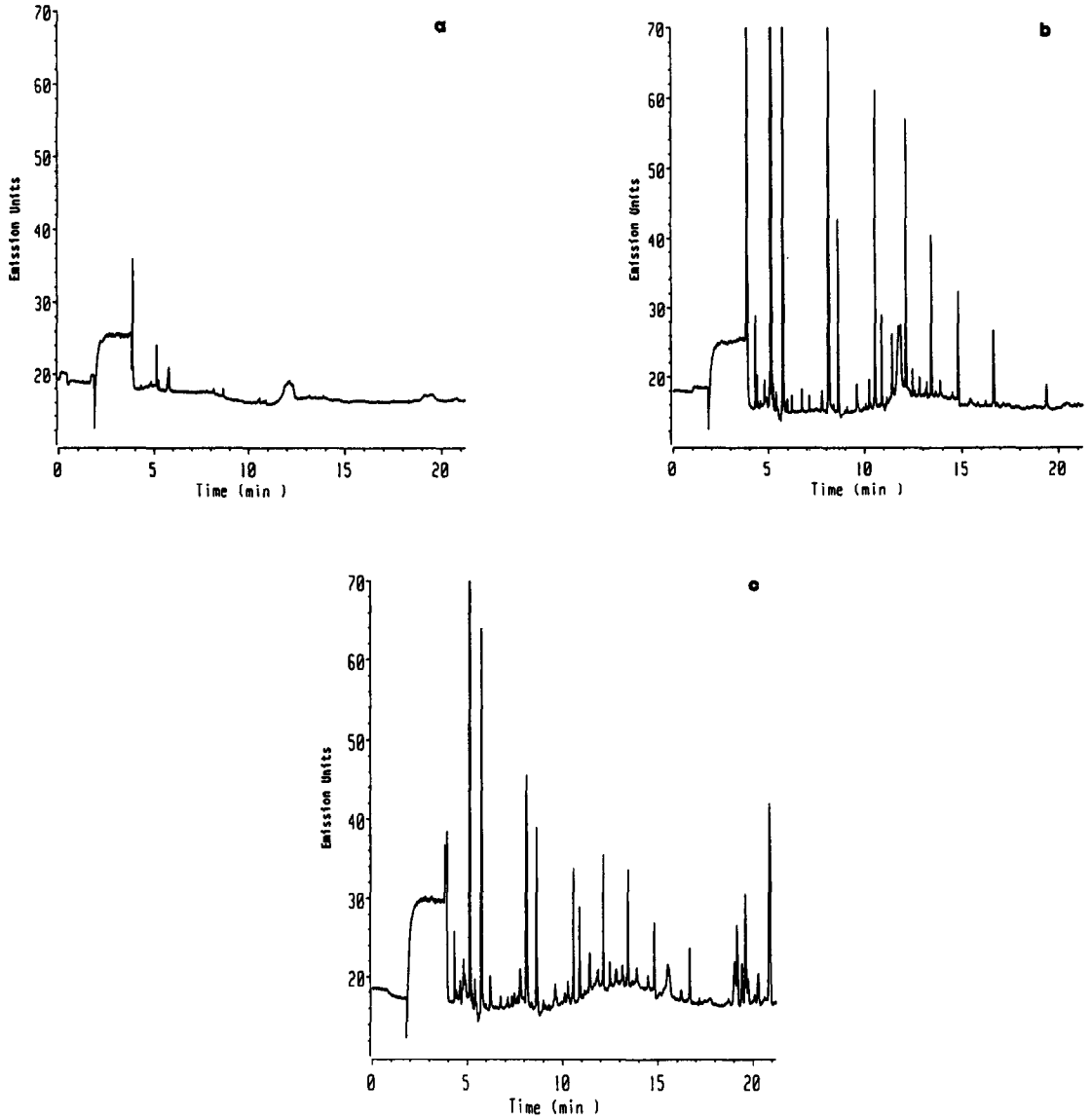

Fig. 3. Chromatograms for the Si252-nm emission line of (a) a solvent injection, (b) an acidified sample of Milli-Q water flushed through a Mega Bond Elut C_{18} cartridge and (c) the same type of sample flushed through a Sep-Pak Plus C_{18} cartridge. All the chromatograms were obtained using the same operating conditions (see Table 1).

acidic samples are concentrated in C_{18} cartridges appreciable amounts of silica can be dissolved. In fact, we have sometimes observed that concentrated extracts of samples acidified to pH 1.5–2 and stored in a refrigerator for several weeks develop a fine, white, cloudy precipitate. Also, we have observed previously that the inertness of the column and injection port quickly degrades when repeated injections of these types of extracts were carried out. In Fig. 3 AED traces corresponding to the silicon emission line for a blank (solvent) (Fig. 3a) and an acidic sample concentrated by means of C_{18} Mega Bond Elut (Fig. 3b) and Sep-Pak Plus (Fig. 3c) cartridges can be compared. It is evident that the silicon signals in the sample chromatograms cannot be attributed to column bleeding. The conclusion was that the proper pH control necessary to ensure good recoveries of PCP with C_{18} cartridges would have adverse effects on the inertness of the chromatographic system and column lifetime. When using GCB cartridges it is obvious that this effect cannot arise and pH control of the samples is not a critical factor regarding the retention of chlorophenols, making its use advantageous instead of C_{18} cartridges.

4. Conclusions

With the quantification limits obtained, the reported method allows the determination of chlorophenols in drinking water samples at levels below 0.5 ng/ml without derivatization. It is of little use to monitor the chromatograms obtained using the carbon emission line in AED or to use FID. However, the chromatogram obtained from the chlorine emission line clearly reveals the presence of the peaks corresponding to chlorophenols. The concentration of the extracts results in losses that are higher than those in the solid-phase extraction process with GCB cartridges and leads to most of the variability found in the results. Hence, improvements to this stage of the analytical process are necessary in order to obtain full benefits of the proposed procedure.

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