Determination of Pentachlorophenol in Drinking Water


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Este trabalho relata um método envolvendo derivação in situ e extração para determinação de resíduos de PCP em amostras de água. O derivado acetilado de PCP é analisado por cromatografia a gás com detector por captura de elétrons. O limite de detecção do método é de 1 µg/L e sua eficiência é demonstrada pelos valores médios de recuperação (78-108%) estudados em três níveis de fortificação (2; 10 e 20 µg/L).

In this study, an in situ derivatization and extraction method for the determination of pentachlorophenol (PCP) has been applied successfully in the analysis of water samples. The PCP derivative analysis was performed by gas-liquid chromatography with electron capture detection. The limit of detection of the method is 1 µg/L and recoveries averaged 78-108% for PCP acetate at levels of 2, 10 and 20 µg/L.

Keywords: pentachlorophenol, water, gas chromatography, in-situ derivatization

Introduction

Pentachlorophenol (PCP), a fungicide and insecticide used in wood treatment, agriculture, paper production, and the leather industry, has become a serious environmental concern because of its toxicity to fish and mammals. Several methods have been described to determine PCP by using various analytical techniques1-4. Among these techniques, gas liquid chromatography with higher sensitivity of the electron capture detector (ECD) allows the PCP determination at very low concentration levels4,5, but requires a derivatization step before GC analysis.

Many studies have been reported for derivatization of PCP in water, including acetylation with acetic anhydride leading to pentachlorophenyl acetate6 or preparation of the pentachlorophenylmethyl ether derivative with diazomethane7. Although the derivatization methods require special pre-chromatographic treatment, the analysis of undervatized phenols by high resolution gas chromatography (HRGC) also has disadvantages. Thus, the derivatization of phenols prior to chromatography is often recommended8. The analyses of PCP in water are done using two approaches. One involves the extraction of PCP from samples by solvents before the derivatization, while the other involves the direct derivatization of PCP in aqueous solution (in situ derivatization). The advantages of the in situ derivatization eliminate the deficiencies of incomplete recovery of free PCP from water samples by solvent extraction6, and permit derivatization and extraction in a single step. This paper describes a modification of the method proposed by Lee et al.9, and involves: in situ acetylation of PCP with acetic anhydride in the presence of potassium carbonate, plus extraction by hexane, and analysis of the extract using gas-liquid chromatography with electron capture detection. The method was used to determine PCP in drinking water samples from different cities of the State of São Paulo, Brazil.

Experimental

Apparatus and reagents

A Varian 3300 gas chromatograph equipped with a glass column (2 m x 2 mm id.) packed with 3% OV 210 on 80-100 mesh Chromosorb WHP, and a constant current 63Ni electron capture detector (ECD) was used for qualitative and quantitative analyses. The signal from the ECD was monitored with a Varian 4290 Integrator. Operating conditions were as follows: injector temperature, 210 °C; column oven temperature, 180 °C; detector temperature, 300 °C; and carrier gas (N2) at 30 mL/min.
All solvents used were of pesticide grade quality (Carlo Erba): n-hexane, and acetone. Acetic anhydride, anhydrous sodium sulfate and potassium carbonate were of analytical reagent grade (Merck). The PCP standard (99.73%) was obtained from the Environmental Protection Agency (Triangle Park, NC). Water, deionized and purified with a Milli-Q® apparatus (Millipore), was used in the recovery study.

Method

The analyses were performed as shown in Fig. 1. In recovery experiments, water samples were fortified with 5.0 mL of PCP solutions in acetone at appropriate concentrations (2, 10 and 20 µg/L) and were allowed to equilibrate for 30 min in an ultrasonic bath before analysis. The percentage recoveries were calculated by comparing the average chromatographic peak areas of the fortified sample, unfortified sample and derivatized standard solution. The scheme of the standard solution derivatization is presented in Fig. 2.

Water samples (two liters) were collected in glass bottles, from five cities in the State of São Paulo, and were analyzed in duplicate.

Results and Discussion

The establishment of the experimental conditions was based on a method described by Lee et al.6 for the analyses of chlorophenols in natural water by in situ acetylation. In this method, phenols were acetylated in the presence of KHCO₃ and the resulting acetates were extracted by petroleum ether followed by silica gel column chromatography cleanup. In the present study preliminary investigations were performed by using Na₂CO₃, KHCO₃, K₂CO₃ and n-hexane in the acetylation and extraction of PCP acetate. The highest efficiency was achieved by using K₂CO₃, thus, starting from optimized conditions, a recovery study with fortified samples at three concentration levels was carried out. Recovery data (Table 1) ranged from 78 to 108% and the detection limit, calculated as described by Thier and Zeumer9, was 1 µg/L. Although these values are in good agreement with the results obtained by Lee et al.6, the described procedure presents certain advantages. It permits a reduction in both time and the amount of solvent required for extraction. Furthermore, gas chromatograms (Fig. 3) indicate the absence of interferents.

Table 1. Recovery of pentachlorophenol (PCP) as acetate from water.

<table>
<thead>
<tr>
<th>Analyses</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 µg/L</td>
</tr>
<tr>
<td>1</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>108</td>
</tr>
<tr>
<td>Mean</td>
<td>89</td>
</tr>
</tbody>
</table>

Standard deviation

11.8  9.2  6.3

Figure 1. Scheme of experimental procedure.

Figure 2. Scheme of standard solution derivatization.
show that no additional cleanup step was needed after the extraction procedure. For determining the recovery values, standard solutions of PCP were derivatized parallel to the samples. This procedure has been discussed by several authors\textsuperscript{6,10-11}.

Governmental norms were established for controlling pollution of water by chemicals in Brazil\textsuperscript{12} and the maximum residue limit recommended for PCP in drinking water is 10 µg/L. This value is the same as that recommended by the World Health Organization\textsuperscript{13}. In order to assess PCP municipal drinking water contamination, nine samples were collected from cities of the most developed industrial state of Brazil. Some geographical data of the cities selected are presented in Table 2. The cities were selected depending on their proximity to leather, chemical, or paper industries.

All samples contained residues of PCP, but at lower levels than the detection limit of the method. On the basis of the results obtained in this study, it was concluded that PCP does not represent an expressive environmental contaminant to these cities. However, further monitoring studies are necessary to evaluate PCP pollution in the Brazilian environment.

References


Table 2. Geographical data of the selected cities and collected samples.

<table>
<thead>
<tr>
<th>City</th>
<th>Localization</th>
<th>Population</th>
<th>Economic activities</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Araraquara</td>
<td>S21°47', W48°10'</td>
<td>172,786</td>
<td>agriculture and industry</td>
<td>tap water, ground water</td>
</tr>
<tr>
<td>Batatais</td>
<td>S20°54', W47°35'</td>
<td>46,313</td>
<td>agriculture and cattle breeding</td>
<td>tap water, _</td>
</tr>
<tr>
<td>Franca</td>
<td>S20°32', W47°24'</td>
<td>253,876</td>
<td>agriculture and leather industry</td>
<td>tap water, ground water</td>
</tr>
<tr>
<td>Rio Claro</td>
<td>S22°25', W47°33'</td>
<td>145,168</td>
<td>agriculture and industry</td>
<td>tap water, well water, ground water</td>
</tr>
<tr>
<td>Sorocaba</td>
<td>S23°30', W47°28'</td>
<td>405,979</td>
<td>industry</td>
<td>tap water, ground water</td>
</tr>
</tbody>
</table>

Figure 3. Gas chromatograms of A derivatized standard solution; B fortified water sample (10 µg/L); C unfortified water sample; D well water sample.

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