DETERMINATION OF TRIPROPYL Tin CHLORIDE IN ENVIRONMENTAL WATER AND SEDIMENT

YUKIKAZU HATTORI, YOSHIO KUGE, and MASAO NAKAMOTO

Environmental Pollution Control Center of Osaka Prefecture, 1-3-62, Nakamichi, Higashinari-ku, Osaka-shi, Osaka, 537

An analytical procedure was described for the determination of tripropyltin chloride (TPTC) in the environmental water and sediment. TPTC was extracted into hexane with hydrochloric acid from water sample, and into methanolic hydrochloric acid from sediment sample and converted into hexane. After cleaning up of the extract by the aluminum oxide column with phosphoric acid, TPTC was measured by gas chromatograph with an electron-capture detector. Recoveries of TPTC were 90 to 97% from water samples and 89% from sediment samples. The detection limits were 0.30 μg/l in water and 0.015 μg/g in sediment samples.

Organotin compounds have been produced for use in industrial and agricultural fields. In particular, trialkyltin compounds, which exhibit fungicidal activity, are widely used as sterilizers, wood preservatives, anti-fouling paints for ships' bottoms. The environmental contamination by these compounds may cause serious problems. Tripropyltin chloride (TPTC) possesses the stronger toxicity than the other trialkyltin compounds and is used as an agricultural fungicide.

Many analytical procedures have been reported with respect to trialkyltin compounds in biological samples, textiles and paints1)-4). However, only few reports have been published concerning the analyses of environmental samples5)-7). Furthermore, no report has been published concerning the analysis of tripropyltin compounds in the environmental water and sediment. In this paper, the determination method of TPTC in the environmental water and sediment by gas chromatograph with an electron-capture detector (GC-ECD) was reported.

EXPERIMENTAL

Apparatus and reagents

A Varian aerograph 2100 type gas chromatograph with an ECD(63Ni, 8.5 mCi) was used for analyses. The glass column(2 mm φ x 1 m) was packed with Chromosorb W(AW-DMCS) (80-100 mesh) coated with 20% DEGS-HG. The flow rate of nitrogen carrier gas was 30 cm³/min. The column temperature was set at 100°C. The injector and detector temperature were 200°C and 250°C respectively. A Shimadzu LKB-9000B type gas chromatograph-mass spectrometer was used.

TPTC was obtained from Alfa Division. Hexane, methanol, benzene, and acetone (pesticide analytical grade) were obtained from Wako Pure Chemical Industries, Ltd.
Sodium sulfate was washed with hexane and dried before use. Aluminium oxide was obtained from Merck Co., Ltd. (Aluminium oxid 90 activ(saur)). Three milliliters of concd. phosphoric acid and a proper amount of water were added to a hundred grams of aluminium oxide. They were mixed homogeneously and heated on a hot plate with stirring up to dry. They were activated for 4 hours by heating at 150°C and hydrated 10%. The glass column (1 cm x 30 cm) for cleanup was packed with 12 g of aluminium oxide and sodium sulfate ca. 1 cm long. Other reagents were commercially available (special grade).

Procedure

A 500 ml of water sample in a 1 l separatory funnel was mixed with 2.5 ml of hydrochloric acid and 10 g of sodium chloride. The mixture was extracted with 50 ml of hexane two times, and the pooled extract was dehydrated, concentrated to about 10 ml by a Kuderna-Danish concentrator (KD concentrator).

Ten grams of sediment sample in a flat-bottom flask was mixed with 50 ml of 5% of methanolic hydrochloric acid. The mixture was refluxed in a water bath (about 80°C), with a reflux condenser for 30 minutes, cooled, and then filtrated. The extract in a 300 ml separatory funnel was mixed with 10 g of sodium chloride and the mixed solution was extracted with 50 ml of hexane two times. The pooled extract was dehydrated, concentrated in the same way as the water sample.

A 5 ml of the extract was applied on to an aluminium oxide column coated with phosphoric acid and eluted with hexane. The first 30 ml of the eluate was discarded, and the second 100 ml of the eluate was collected and concentrated to about 5 ml by KD concentrator and then to 2 ml by heating gently with a dryer under nitrogen stream.

RESULTS AND DISCUSSION

A typical gas chromatogram of standard solution of TPTC was shown in Fig. 1. The detection limit of the standard solution was 0.19 ng (based on 2 x noise signal). Meinema et al.⁶ and Maguire et al.⁷ reported the analytical methods of methyltin compounds and butyltin compounds in sea and lake water. These compounds were alkylated with Grignard reagent and measured with gas chromatograph-mass spectrometer (GC-MS) and gas chromatograph-modified flame photometric detector. The minimum detectable amounts injected were about 100 pg. In our method, TPTC is measured with GC-ECD as sensitively as their methods without derivatization. Various trialkyltin chlorides can be determined separately with the gas chromatographic column of 20% DEGS-HG. Braman et al.⁵ analyzed methyltin compounds with an atomic absorption spectrometer. It may be difficult to separate an organotin compound from many other organotin compounds in their method compared with GC method.

As analytical reports about organotin compounds
in sediment sample have not been published, the cleaning up for the analyses of
TPTC in the environmental water and
sediment samples was studied. Okumoto
et al.3) reported that trace amount
of tributyltin(TBT) did not elute
from silica gel and the cleanup
resulted in loss of TBT. Kojima
et al.4) reported that aluminium
oxide column was used for cleanup
for the analyses of TBT and triphenyltin
in paints. In our study, TPTC did not elute
from 5 g of aluminium oxide(ICN Phar mauceu-
tical Co.Ltd.,Aluminium oxide W 200,
neutral, activity I) with 100 ml of
33 % acetone in benzene. While, TPTC
eluted from 5 g of aluminium oxide
column containing 10 % of water with
17 % acetone in benzene. The first
20 ml of eluate contained 100 % of
added TPTC. But, as the same fraction
contains most of nonpolar and intermediate polar
compounds in sediment sample, it is not
suitable for cleanup of TPTC. When the polarity
of eluting solvent is weak, for example 0.03 %
acetone in benzene, TPTC do not elute in the
first 70 ml of eluate. When standard solution
of TPTC was mixed with 5 ml of ethanol solution
of 1 N-potassium hydroxide and shaken, the peak
height of TPTC in gas chromatogram was reduced
to 80 to 90 % in initial peak height. TPTC may
be changed during passing through the aluminium
oxide column, because the column is nearly basic.
Then aluminium oxide(Merck Co., Ltd., activ(saur)) was
coated with phosphoric acid and contained 10 %
of water. TPTC eluted from 12 g of this aluminium
oxide column with 100 ml of hexane. The recovery
resulted in about 100 %. The elution pattern was
shown in Fig. 2. In this case, as the first 40 ml
of eluate was discarded, nonpolar hydrocarbons and
halogeno compounds were removed and no
interference peaks appeared in the gas chromatogram
of sediment samples. Figure 3 shows the gas
chromatogram of the extract from Yodo-River
sediment, which is added 10 μg of TPTC.

To test recoveries of TPTC from pure water,
river water, sea water, and bottom sediment, 5 - 10 μg
of TPTC was added to a 500 ml of water or 10 g of sediment sample. The results are shown in Table 1. The recoveries from water and sediment samples were 88 to 97%. Detection limits of TPTC throughout this analytical procedure were 0.30 µg/l in water and 0.015 µg/g in sediment samples.

Table 1 Recoveries of tripropyltin chloride from water and sediment samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added(µg)</th>
<th>Recovery(%)</th>
<th>CV(%)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>5</td>
<td>97.4</td>
<td>5.2</td>
<td>4</td>
</tr>
<tr>
<td>River water</td>
<td>5</td>
<td>96.6</td>
<td>4.3</td>
<td>4</td>
</tr>
<tr>
<td>Sea water</td>
<td>5</td>
<td>90.9</td>
<td>3.7</td>
<td>3</td>
</tr>
<tr>
<td>Bottom sediment</td>
<td>10</td>
<td>88.6</td>
<td>3.6</td>
<td>4</td>
</tr>
</tbody>
</table>

(Presented in part at the Annual Meeting on Analysis of Chemicals in Environment under the auspices of Office of Health Studies, Department of Environmental Health, Environment Agency in Tokorozawa, March, 1982.)

REFERENCES


Keyword phrases
determination of organotin compounds in the environmental water and sediment; tripropyltin chloride; gas chromatograph with an electron-capture detector; aluminium oxide column coated with phosphoric acid.

(Received September 14, 1983)