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Short communication

Determination of tris(2-chloroethyl) phosphate in leachates from landfills by capillary gas chromatography using flame photometric detection

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Abstract

Tris(2-chloroethyl) phosphate (TCEP) in leachates from landfills for hazardous wastes was determined by wide-bore capillary gas chromatography using flame photometric detection. Its concentration levels ranged from 0.137 to 5.43 mg/l. The origin of TCEP seems to be waste plastics. No TCEP was detected in underground water and tap water.

1. Introduction

Tris(2-chloroethyl) phosphate (TCEP) is widely used as a plasticizer and a fire retardant in various kinds of synthetic resins. As the LD_{50} value of TCEP aqueous solution in acute toxicity using carp has been estimated to be 5 mg/l [1], environmental contamination with TCEP has attracted strong interest. Careless disposal of waste plastics might cause important problems. Several studies on environmental contamination with TCEP have been reported. The concentration of TCEP in water samples in Japan [2-4] has been found to be higher than that in the USA [5] or Spain [6]. It is of serious concern to people who live near waste disposal sites and use underground water or river water as drinking water how high the concentration of TCEP in leachates from landfill sites is. This paper describes the determination of the concentration of TCEP in leachates in Japan.

2. Experimental

2.1. Materials and samples

TCEP (analytical-reagent grade) was purchased from Wako (Osaka, Japan). Dichloromethane, anhydrous sodium sulfate, hexane, benzene and acetonitrile were of pesticide grade (Wako). Hydrochloric acid and sodium hydroxide were of extra-pure grade (Wako). Silica gel (particle size 75-150 μm) (Wako) was used without any activation procedure. Pure water was prepared by passing distilled water through a Milli-Q system (Millipore).

Leachates from landfill sites located in the central area and in the north-eastern part of Japan, underground water from the north-eastern part of Japan, and tap water from the National Institute for Environmental Studies were used as samples.

2.2. Sample preparation

The pH of a water sample was adjusted at 7.5–4.0 with 1 M hydrochloric acid or 1 M sodium hydroxide solution. TCEP in each water sample (1 l) was extracted three times with dichloromethane (100, 50 and 50 ml) using a separating funnel for 5 min and the extracts were combined. The combined extract was passed through a short column packed with anhydrous sodium sulfate and concentrated by distillation of the solvent under atmospheric pressure. The concentrated extract solution (1 ml) was subjected to silica gel column chromatography on a glass column (150 × 12 mm I.D.) containing 5 g of silica gel packed with hexane. The following solvents were used for chromatography; fraction A, dichloromethane–hexane (1:9), 40 ml; fraction C, dichloromethane, 40 ml; and fraction D, acetonitrile–dichloromethane (1:9), 50 ml. TCEP eluted in fraction D. Fraction D was concentrated by distillation under atmospheric pressure and an aliquot of the concentrated solution was injected into a gas chromatograph (see below).

2.3. Chromatographic analysis

The gas chromatographic conditions were as follows: gas chromatograph, Hewlett-Packard Model 5890A equipped with a Hewlett-Packard Model 3396A integrator; column, J&W DB-1 (1.5 μm) (30 m × 0.53 mm I.D.); column temperature, 180°C for 5 min, increased to 240°C at 8°C/min; carrier gas (helium) flow velocity, 43.1 cm/s at 25°C; injector temperature, 250°C; injection mode, whole injection; detector, flame photometric; detector temperature, 230°C; and make-up gas (nitrogen) flow-rate, 33.5 ml/min.

3. Results and discussion

The distribution coefficients of TCEP between organic solvents and water were measured in order to select the best solvent for the extraction of TCEP. The distribution coefficients were 0.320 for hexane, 16.3 for benzene and 115 for

dichloromethane. Therefore, dichloromethane was chosen as the extraction solvent.

The relationship between pH and recovery was studied. The recoveries were 94, 89 and 78% at pH 4, 7 and 10, respectively. Hence alkaline conditions are not to be preferred, and also strongly basic or acidic conditions should be avoided because of hydrolysis of TCEP. Therefore, neutral or weakly acidic conditions are suitable for the extraction of TCEP.

Recovery experiments were performed using aqueous solutions of TCEP at the concentrations of 300, 900 and 3000 ng/l. The recoveries were 98.1, 102.0 and 97.4%, respectively. As mean recovery was 99.2%, it is concluded that all the TCEP was recovered.

Instrumental stability in the measurement of TCEP was studied by replicated measurements of standard TCEP solution at a concentration of 139 ng/ml. The relative standard deviation was around 9%. This fairly high relative standard deviation might be due to the flame photometric detector.

Linearity of the detector response with respect to TCEP concentration was investigated. The calibration graph is shown in Fig. 1. The linearity range was fairly narrow. The reason seems to be the strong absorbability of TCEP on the inner surface of the capillary column. The ratio of the inner surface area to the inner volume of the

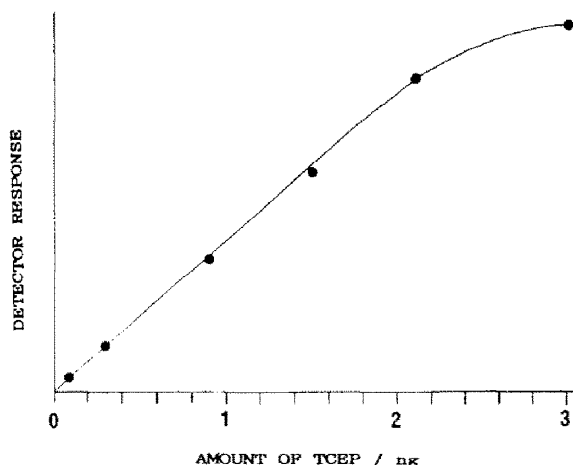


Fig. 1. Calibration graph for TCEP using flame photometric detection.

capillary column affects the range of linearity. The larger the inner diameter of a capillary column is, the wider the linearity range becomes. This phenomenon has been observed in the determination of TCEP by other workers [7]. Therefore, a wide-bore capillary column was used in this study.

The blank in the analytical procedure was examined using pure water. No contamination with TCEP was observed.

The detection limit (DL) and quantification limit (QL) were calculated according to the following equation [8] defined by the Japan Environmental Agency on instrumental analysis for chemical components in replicated recovery experiments using water samples:

$$DL = 3D$$

$$QL = 10D$$

$$D = t(n - 1, 0.05) \cdot (S.D./n) \cdot (C/R)$$

where $t(n - 1, 0.05)$, S.D., n , C and R are a value in a Student's t examination for 95% reliability, standard deviation in the response of the detector, total run number, concentration in water sample and the mean of the detector responses, respectively. D is called the detection power. In this recovery experiment, it is most important that the concentration in the water sample should be near the estimated value, which is calculated to be around ten times the instrumental detection limit. Generally D is the mean obtained in experiments using several different concentrations. In this study, aqueous solutions of TCEP of concentrations 200 and 400 ng/l were prepared and recovery experiments were performed. The mean D value was 22.5 ng/l. Therefore, DL and QL were 67.5 and 225 ng/l, respectively. When the concentration of TCEP in actual samples is below 67.5 ng/l, the concentration is considered as "not detected". When the concentration of TCEP in actual samples ranges between 67.5 and 225 ng/l, the concentration is considered as "detected, but not determined".

The effect of clean-up by silica gel column chromatography is shown in Fig. 2. Large amounts of organic components give false signals

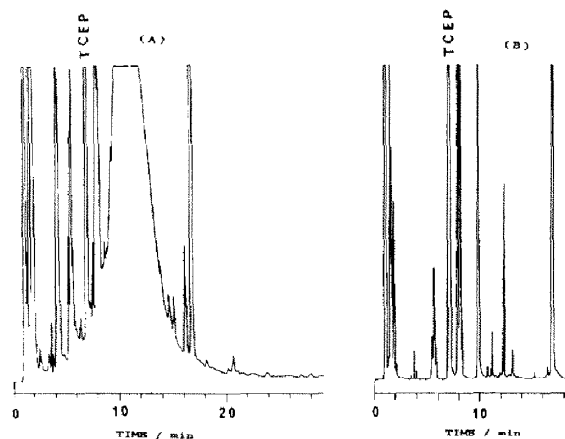


Fig. 2. Gas chromatograms of extracts of the leachate from landfill site D. (A) Before clean-up; (B) after clean-up with silica gel column chromatography.

with flame photometric detection. As especially leachates from landfill sites contain large amounts of chemical components, this clean-up procedure is essential. On the other hand, this clean-up procedure may be omitted for underground water and tap water, which contain only trace amounts of organic components.

Analytical results for actual samples are given in Table 1. No TCEP was detected in underground water and tap water. High concentrations of TCEP were detected in all leachate samples. These high concentrations were much higher than those in river waters in Japan [2-4]. These high concentrations of TCEP can reasonably be expected because large amounts of municipal, industrial and sewage wastes are disposed of every day. Kawagoshi et al. [9] reported that concentrations of TCEP in leachates from landfills in Japan reach extremely high levels. Also,

Table 1
Concentrations of TCEP in water samples

Samples	TCEP concentration (mg/l)
Tap water	Not detected
Underground water	Not detected
Leachate from landfill site A	0.137
Leachate from landfill site B	0.336
Leachate from landfill site C	0.534
Leachate from landfill site D	5.43

high concentrations of TCEP in leachates were confirmed by gas chromatography–mass spectrometry. It is serious that the concentration of TCEP in the leachate from the landfill site D exceeded the LD₅₀ value. Experiments on leaching TCEP from plastics are in progress. Most waste plastics are buried rather than burned in the Japanese administration system. Detailed investigations on TCEP in leachates from landfills will be performed in near future.

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