

Determination of Water- and Methanol-Extractable Pentachlorophenol in Soils Using Vortex-assisted Liquid-Liquid Extraction and Gas Chromatography



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Abstract: An analytical procedure for determination of water- and methanol-extractable pentachlorophenol (PCP) in soils was developed using vortex-assisted liquid-liquid extraction (VALLE) and gas chromatography (GC). Significant extraction parameters such as vortex speed and liquid-liquid volume ratio were optimized for extracting PCP from solution. The recovery of PCP was the highest (97.4%) with good reproducibility and a small relative standard deviation (RSD, 0.5%) when the vortex speed was at 2000 rpm. Meanwhile, when the volume ratio of derivatization solution to *n*-hexane was at 10:4, the recovery of PCP was 103% with a RSD of 0.7%. The linearity of the calibration curve for PCP determination ranged from 1.25 $\mu\text{g L}^{-1}$ to 4000 $\mu\text{g L}^{-1}$, with a correlation coefficient (R^2) of 0.9999. The detection limit of PCP in water samples was below 0.2 $\mu\text{g L}^{-1}$ and the measuring range was relatively wide, and suitable for trace- and micro-analysis of PCP. Compared with traditional extraction methods (liquid-liquid and solid-phase), VALLE consumes less extractant, requires fewer steps, and achieves higher recovery (96.8%) and smaller RSD (3.7%). The reliability of VALLE was verified in four distinct types (paddy, red, black and alluvial) of soil samples spiked with 1 and 10 mg kg^{-1} PCP. The total recoveries of PCP in the soil samples were in the range of 89.5%–98.9% by water extraction and 88.7%–98.4% by 3 consecutive extractions with methanol in a sequential procedure. The results indicated that VALLE-GC satisfied the requirements for extracting and determining water- and methanol-extractable PCP in soils polluted by PCP at varying levels.

Key Words: Pentachlorophenol; Vortex-assistance; Liquid-liquid extraction; Water-extractable fraction; Methanol-extractable fraction; Soil contamination

1 Introduction

Pentachlorophenol (PCP) and its sodium salts are widely used in the world as fungicides, bactericides, insecticides, herbicides, pesticides and wood-preserving agents. In China, PCP are used to kill *Oncomelania* snails, the intermediate host of schistosomiasis (commonly known as bilharzia, bilharziosis or snail fever), in traditional epidemic areas for a long time^[1].

Due to its chemical stability, broad-spectrum toxicity and mutagenicity to living organism, PCP was included in the list

of priority monitoring of persistent organic pollutants in the environment^[2]. Although several countries including China banned or restricted the use of PCP, we still applied it to kill *Oncomelania* snail associated with the risk of schistosomiasis. Nowadays, micro or trace amount of PCP can be detected in water and soil environments, threatening agricultural and natural ecosystems as well as human health^[3].

Sample pretreatment (extraction and concentration) is important for the determination of PCP^[4]. The traditional procedures for PCP extraction from solution include

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liquid-liquid extraction (LLE)^[5] and solid-phase extraction (SPE)^[6,7]. However, both LLE and SPE consume large volumes of organic solvents and samples, and the operation procedures are sophisticated due to the need for sample concentration before determination. In particular, SPE is expensive to analyze, and the target compound may be adsorbed onto the column, causing clogging in complex systems.

In recent years, the development of PCP extraction methods has tended to decrease the sample volume, reduce solvent consumption, mitigate environmental contamination, improve the detection sensitivity, and consume less labor, thus solid-phase micro-extraction^[8], liquid-phase micro-extraction^[9] and their improving methods have been applied to the PCP extraction. Nevertheless, these micro-extraction methods have some disadvantages, for instance, they require special devices, and the water from a small amount of reagent can easily corrode the instruments used in the methods. Thus, it is necessary to optimize the existing procedures for LLE towards less organic solvent consumption and adequate sample volume for dehydration, making them have a wide range of application.

Common methods of PCP determination include gas chromatography-electron capture detector (GC-ECD)^[10,11], high performance liquid chromatography-ultraviolet detection (HPLC-UV)^[12], gas chromatography-tandem mass spectrometry^[7] and high performance liquid chromatography-tandem mass spectrometry^[6]. Once derivatized, GC-ECD shows higher sensitivity in the detection of PCP than HPLC-UV. Additionally, GC-ECD is universally used for the determination of trace PCP.

Water-extractable PCP is the most bioavailable and toxic fraction in polluted soils, and it could further contaminate water resources when leached into groundwater and rivers^[13,14]. Methanol-extractable PCP can be easily adsorbed and fixed by soil components such as organic matter^[15]. Thus, it is of great significance in environmental monitoring to measure the two PCP fractions simultaneously.

In this study, we optimized the parameters for PCP extraction from solution, and determined the water- and methanol-extractable PCP in soils using vortex-assisted liquid-liquid extraction (VALLE) and gas chromatography (GC). The optimized method was a success in decreasing organic solvent consumption, with a low limit of detection (LOD). The study will provide the basis for selecting methods to accurately determine water- and methanol-extractable PCP

in different types of soils.

2 Experimental

2.1 Instruments and reagents

GC system (6890N, Agilent Technologies, Wilmington, USA) equipped with a 63Ni micro ECD, an Agilent 7683B series automatic injector and a HP-5 capillary column (30.0 m × 320 μm, 0.25 μm). Vortex (MixMate, Eppendorf, Westbury, USA), ultrasonic bath (SK8210HP, Kudos, Shanghai, China), ultra-pure water purifier (Milli-Q, Millipore, Saint-Quentin en Yvelines, France), rotary shaker (HZ-9210K, Hualida, Taicang, China) and centrifuge (Multifuge 3S, Heraeus, Hanau, Germany) were used in the experiment.

The reagents used in the experiment included PCP (98%, Sigma, USA), *n*-hexane and methanol (Chromatographic grade, Scharlab, Spain), acetone (Chromatographic grade, Tida, USA), acetic anhydride, K₂CO₃, sulfuric acid and anhydrous Na₂SO₄ (Analytical grade, Sinopharm, China).

2.2 Collection and pretreatment of soil samples

Four distinct types (paddy, red, black and alluvial) of uncontaminated soils were chosen and the soil samples were collected from the surface soil layer at 0–20 cm depth in fields in Zhejiang, Jiangxi, Heilongjiang and Henan provinces of China, respectively. The soil samples were air-dried and passed through a 2-mm sieve. The physicochemical properties of the experimental soils are given in Table 1.

The four soil samples were spiked with two levels of PCP (1 and 10 mg kg⁻¹). Briefly, 20 g of each soil was weighed into two 60-mL glass tubes separately, followed by addition of 1 mL of PCP solutions (20 and 200 mg L⁻¹) in acetone. The PCP solution was carefully added into five aliquots and mixed thoroughly with the soil. The polluted soils were placed in a fume hood until the acetone had evaporated. The same procedure was followed to prepare the different types of soils.

2.3 PCP extraction

2.3.1 Calibration curve

Firstly, 100 and 2000 μg L⁻¹ PCP-K₂CO₃ stock solutions were prepared. Then, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0 and 8.0

Table 1 Major physicochemical properties of four types of soils used in this study

Soil type	Sampling site	pH (H ₂ O)	Total N (g kg ⁻¹)	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)
Paddy soil	Zhejiang	4.40	1.10	1.41	32.6	30.2	37.2
Red soil	Jiangxi	4.71	0.34	0.50	75.1	12.4	12.6
Black soil	Heilongjiang	7.23	3.75	4.27	73.3	24.5	2.20
Alluvial soil	Henan	8.28	1.74	0.83	21.4	63.2	15.4

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