# Determination of O-Dichlorobenzene in Soil by Ionic Liquid-Based Single Drop Micro-Extraction

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**Abstract:** A new method for determination of o-dichlorobenzene in the soil samples has been developed using the ionic liquid 1–butyl-3–methyl-imidazole hexafluorophosphate for the headspace single-drop liquid-phase micro extraction with gas chromatography analysis. Experimental parameters affecting the performance of extraction are studied including media types inspected the solution, pH, extraction time, temperature and salt effect. The results show that extraction time and temperature are the main influencing factors. Under the optimum extraction conditions, limit of detection is 0.028 μg $g^{-1}$, and the measured value of o-dichlorobenzene in the soil samples is 0.316 μg $g^{-1}$. It can also be extended to be applied in extraction evaporative organics matter.

**Keywords**: ionic liquid; gas chromatography; o-dichlorobenzene; soil sample

# 离子液体单液滴顶空微萃取土壤中的邻二氯苯

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**摘要**：本文建立了以 1-丁基-3-甲基咪唑六氟磷酸盐离子液体为萃取剂的单液滴顶空液相微萃取-气相色谱分析土壤样品中邻二氯苯的新方法。研究了溶液介质种类、pH 值、萃取时间、温度、盐效应等对顶空微萃取的影响。结果表明，萃取时间和萃取温度为主要影响因素。在较佳条件下，测得最低检测限为 0.028 μg $g^{-1}$ 及土壤样品中邻二氯苯的含量为 0.316 μg $g^{-1}$，此法可进一步运用于易挥发性有机物的萃取。

**关键词**：离子液体；气相色谱；邻二氯苯；土壤样品

O-dichlorobenzene as the pesticides and synthesis intermediates has been widely used in chemical industry. Due to the fact that it has stable chemical properties and biological toxicity of the environment, o-dichlorobenzene can not be decomposed by micro-organisms. Thus, it may be accumulated by multiple residues in the soil. Therefore, it is very important to investigate the concentration levels of o-dichlorobenzene in soil.

It is well known that ionic liquid (IL) is emerging as an alternative to these conventional solvents as they present unique and valuable properties such as low vapor pressure, high viscosity and good thermal stability. These properties make them perfectly suitable for headspace single drop micro extraction (HS-SDME) since larger and more reproducible extracting volumes can be used [1]. Meanwhile, the use of ionic liquid in HS-SDME can simplify numerous extraction procedures and avoid the pollution of organic solvents. Recently, the ionic liquid-based single drop micro extraction has been previously used for the determination of pollutants in water [2-4]. However, there appears to be no report on the detection of o-dichlorobenzene in soil in this way. This work focuses on the GC analysis of o-dichlorobenzene in soil by HS-SDME of the ionic liquid 1-butyl-3-methyl-imidazolium hexaflourophosphate (Bmim-$PF_6$). In addition, experimental parameters affecting the performance of extraction are also discussed including media types inspected the solution, pH, extraction time,

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temperature and salt effect. The results will be great importance to guide the determination of p-dichlorobenzene and m-dichlorobenzene in soil. Moreover, it is possible to simultaneously determinate dichlorobenzene in soil in this way.

## 1. Experiment

All reagents were of analytical grade or better. Bmim-$PF_6$ was synthesized according to the literature [5], IR (KBr) ν: 3170.97, 2966.52, 1573.91, 1465.90, 1168.86, 837.11, 748.38/cm. O-dichlorobenzene (GCS, Tianjin Chemical Plant, Tianjin, China). Working solutions were prepared on a daily basis by rigorous dilution of the stocks in the appropriate solvent. Experiments were carried out by using a Shimadzu GC-14C as chromatograph with the technique of flame ionization detection (FID) and the injection volume of 0.2 μL. A capillary-fused silica column (30 m×0.25 mm i.d×0.25 μm film thickness) was used for GC separation. The injection port and ion source temperatures were maintained throughout the experiments at 220℃. The temperature program of the chromatographic oven was 100℃ (2 min), ramped to 220℃ at 10℃ min−1and held for 8 min.

15 g sample was placed in 30 mL vial and added 4.2 g sodium chloride and 14 mL of KCl-HCl buffer, which was tightly sealed with a silicone septum. The GC bevel tip syringe was filled with 4 μL of Bmim-PF6 and was inserted in the vial through the septum. The syringe was clamped to locate the needle tip in a constant position in the headspace of the vial. The plunger was depressed and a micro-drop of the acceptor phase was exposed on the headspace above the aqueous solution at 40℃ for 30 min. Then, the IL was retracted and stored in 2 mL vial. Repeat four times and then analyze in GC.

## 2. Results and Discussion

### 2.1 Optimization of Ionic Liquid-Based Single Drop Micro-Extraction

### 2.1.1 The Effect of Medium Solution and PH

O-dichlorobenzene was adsorbed easily by organic carbon in soil, and there was a hysteresis between adsorption and desorption [6]. Thus, the effect of different medium on reaching larger o-dichlorobenzene extraction efficiency was discussed. Fig. 1 showed the influence of the medium solution on the extraction efficiency of the o-dichlorobenzene, which was measured from the peak area of the o-dichlorobenzene. The results revealed that the peak area of o-dichlorobenzene was the largest one under the KCl-HCl buffer. This is related to a large number of Cl- in KCl-HCl buffer which increases the activity coefficient of o-dichlorobenzene. Furthermore, the influence of pH on extraction was also studied from 1.0 to 2.2 (inset). A high of the peak signal was observed closed to pH=1.8. Further increase of pH may cause the enhancing of the polarity of humus substances in the soil and the reducing of affinity for hydrophobic organic compounds. Consequently, KCl-HCl buffer at pH=1.8 was selected for further experiments.

### 2.1.2 The Effect of Enrichment Time

To obtain extraction equilibrium in a reasonable analysis time, the extraction time was optimized in the range of 10–60 min. The enrichment yield of o-dichlorobenzene gradually increased with the increasing of the enrichment time. Due to the uncertainty hanging droplets, extraction has less effective when the extraction time continues to increase. On the other hand, o-dichlorobenzene will be volatilized with the time extension. Thus, 30 min was chosen as the optimum condition.

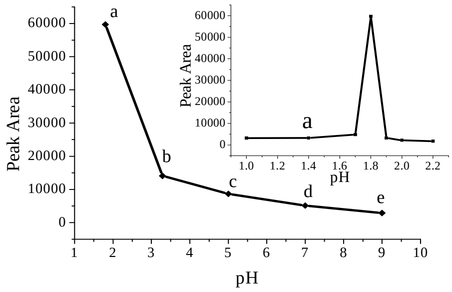

**Figure. 1 The influence of the medium solution on the extraction of the o-dichlorobenzene a- KCl-HCl buffer; b- Britton-Robinson buffer; c- $KH_2PO_3$-NaOH buffer; d-water; e- $Na_2HPO_3$-NaOH buffer**

### 2.1.3 The Effect of Enrichment Temperature

The effect of temperature on the extraction efficiency was investigated from 30 to 70℃. The increase in temperature leads to a significant decrease in sensitivity for the o-dichlorobenzene. It has been reported that high temperatures can decrease the partition coefficients of analytes in IL drop, which results in a decrease of the rate of analyte adsorption on the outer surface of the micro-drop [7]. In addition, working at high temperatures increases the concentration of water molecules in the headspace, which can disturb the adsorption of the analytes in the micro-drop. Thus, extraction temperature of 40℃ was adopted for the following studies.

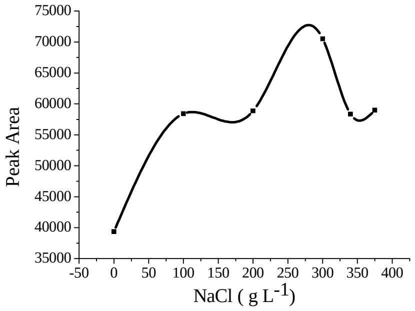

**Figure 3. Influence of NaCl concentration on the extraction of the o-dichlorobenzene**

### 2.1.4 Addition of Salt

The addition of salt and the consequent increase of the ionic strength decrease the solubility of analytes in the aqueous sample enhancing their extraction. The salting-out effect was examined by monitoring the variation of peak areas with a salt concentration ranging from 0 g $L^{-1}$ to 375 g $L^{-1}$. It is clear from Fig. 3 that the peak area of the analytes increases with NaCl concentration achieving the best results at 300 g $L^{-1}$. This value was considered as optimum for further experiments.

## 2.2 Analytical Performance of the Proposed Method

Under the above menthened optimal experimental conditions, a series of experiments were designed for obtaining linear ranges, precision, detection limits and other characteristics of the method. The calibration curve of the solution was linear in the range of 26 mg $L^{-1}$ to 520 mg $L^{-1}$. The linear equation was $y = 42.914x + 903.51$, and linear correlation coefficient R was 0.999. The limit of detection was 26 mg L-1 and the RSD (n=3) of the system was 3.8%.These excellent results indicated that the present approach was a simple and sensitive procedure to o-dichlorobenzene determine at trace level. It can also be extended to be applied in isomers of dichlorobenzene (show Fig. 4).

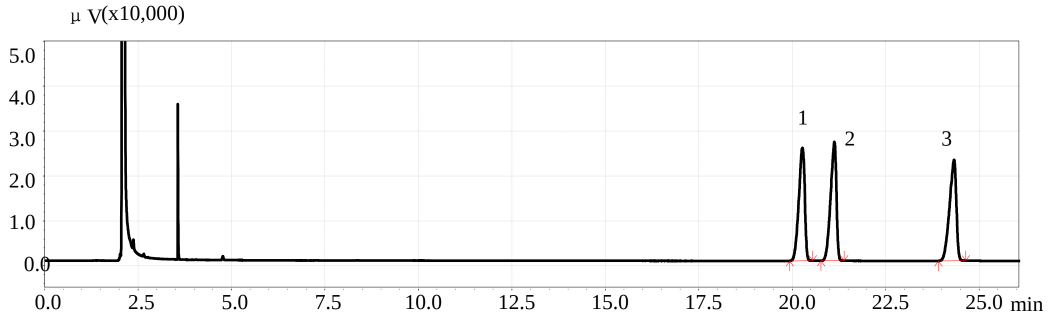

**Figure 4. GC chromatograph: with the flame ionization detection (FID); injection volume 0.2μL; the injection port and ion source temperatures were maintained throughout the experiments at 200℃ and 220℃; the temperature program was 50℃, ramped to 80℃ at 0.1℃ $min^{-1}$; 1- m-dichlorobenzene; 2 – Para dichlorobenzene; 3- o-dichlorobenzene**

## 2.3 Real Soil Sample Analysis

The proposed method was applied to the determination of the o-dichlorobenzene in agriculture soil in the suburbs of Xi'an by GC. The limit of detection of the o-dichlorobenzene in the soil was 0.028 μg $g^{-1}$. Under the optimum condition, the result for the positive sample was 0.316 μg $g^{-1}$.

## References

[1] J.F. Liu, J.A. Jönsson, G.B. Jiang, Trends Anal. Chem. 24 (2005) 20.
[2] E. Aguilera-Herrador, R. Lucena, S. Cardenas, M. Valcarcel, J. Chromatogr. A1201 (2008) 106-111.
[3] E. Aguilera-Herrador, R. Lucena, S. Cardenas, M. Valcarcel, J. Chromatogr. A1209 (2008) 76-82.
[4] Lorena Vidal, Elefteria Psillakis, Claudia E. Domini, Nuria Grane, Anal Chem Acta. 584 (2007) 189–195.
[5] Yucai H, Huidi Y, Qingyi X, and Tao L, Applied Chemical Industry. 35 (2006) 267-272.
[6] Xing B, Environmental Pollution. 111 (2001) 303- 309.
[7] Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143.