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RESEARCH PAPER

Detection of Plasticizers in Soil Using Surface Desorption Atmospheric Pressure Chemical Ionization Imaging Mass Spectrometry

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Abstract: To address the widespread contamination of surface soil by phthalate esters (PAEs), a method based on the surface desorption atmospheric pressure chemical ionization tandem mass spectrometry (SDAPCI-MS^n) imaging technology was successfully applied for the direct determination of diethyl phthalate (DEP) in soil without any pretreatment. The precursor ion, protonated diethyl phthalate (*m/z* 223), was confirmed by collision-induced dissociation (CID) experiments to exclude false-positive results. The protonated DEP (*m/z* 223) and the characteristic fragment (*m/z* 177) were used to obtain the distribution of DEP molecules in the soil using imaging mass spectrometry. The two ion images without any pretreatment showed that the distribution of DEP was inhomogeneous in the shape of clusters, but these two distributions were changed after adding deionized water evenly into the surface of soil. The spatial resolution and the analysis speed per pixel were 0.25 mm^2 and 4.5 s. This new method may be applicable for the study of content and distribution of PAEs in other complex solid samples.

Key Words: Surface desorption atmospheric pressure chemical ionization tandem mass spectrometry; Diethyl phthalate; Soil; Mass spectrometry imaging

1 Introduction

Phthalate esters (PAEs) are plasticizers and are “the second biggest global polychlorinated biphenyls (PCBs) contamination”[1]. PAE-pollution of land occurs by industrial soot, sewage, soot from burning garbage, agricultural plastic films and pesticides. The esters bioaccumulate in the human body via migration and transformation, and eventually cause illness such as cardiovascular disease, cancer and deformities[2–6]. Currently, the PAEs in an environmental sample are mainly monitored by high performance liquid chromatography (HPLC)[7], liquid chromatography-mass spectrometry (LC-MS)[8], and gas chromatography-mass spectrometry (GC-MS)[9,10]. But these three methods are tedious, time-consuming[11], and cannot give either the content or the distribution of DEP in soil. A simple and effective method is urgently needed to characterize PAEs in polluted land.

The surface desorption atmospheric pressure chemical ionization (SDAPCI)[12] combines the advantages of atmospheric pressure chemical ionization (APCI)[13,14] and desorption electrospray ionization (DESI)[15] and has features such as minimal sample pretreatment, trace analysis for solid surfaces at atmospheric pressure, high sensitivity, and high specificity. The SDAPCI was successfully used in the fields of food safety[16], pharmaceutical analysis[17], pesticide testing[18], and textile studies[19], etc. In this study, the surface desorption atmospheric pressure chemical ionization tandem mass

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spectrometry ($SDAPCI-MS^n$) imaging technique and a *XYZ*-stage were used to measure the content and to show the distribution of (DEP) on soil.

2 Experimental

2.1 Instruments and reagents

Experiments were carried out on a Thermo Finnigan LTQ-XL ion trap mass spectrometer with Xcalibur data processing system (San Jose, CA, USA) and coupled with a homemade SDAPCI source[12]. A stepper motor controller a *XYZ*-stage, and an insulated sample stage was made by Beijing Optical Century Instrument Co., Ltd (China). The digital photomicrographs of the soil samples were recorded by an AM413T Dino-Lite USB digital microscope (Huatang Optical Industries Co., Ltd, Taiwan). Glassware was cleaned with 60 ºC deionized water in an ultrasonic apparatus (KQ3200B, Kunshan Ultrasonic Instruments Co., Ltd, Jiangsu, China) and was used for 0.1 ppm DEP standard solution.

Diethyl phthalate (AR grade) was purchased from the Shanghai Qingxi Chemical Technology Co., Ltd (China). A cotton cloth was purchased in local eyewear shop. Two soil samples were collected from the top soil (thickness: 0–5 cm) in a campus in Nanchang, Jiangxi. The first one was directly tested without any treatment, but the other one was tested after a certain amount of deionized water dropped evenly over it.

2.2 Experimental method

The SDAPCI-LTQ-MS was set to the positive ion detection mode and the mass spectra were recorded in the range of *m/z* 50–500 Da. The corona discharge voltage was +3.5 kV and the temperature of the inlet capillary was 200 ºC. The voltage of capillary and tube lens were 10 and 90 V, respectively. In the collision-induced dissociation (CID) experiments, the *m/z* 223 ion was isolated with a window width of 1.6 Da and with the collision energy set at 30%. The other parameters were the default values of the LTQ instrument. The schematic diagram of the SDAPCI device was shown in Fig.1.

After the optimization of instrument parameters, the angle (α) formed between the discharge needle and sample was set as 45°, the distance (a) between the discharge tip and the surface of sample was set to 3–5 mm, and the distance (b) between the discharge tip and the inlet of the LTQ instrument was set as 10 mm. The scan origin and direction (*XYZ*, as shown in Fig.1) were defined before scanning, and the digital photomicrographs of samples were matched with mass spectrometry images. The related parameters of the stepper-motor controller were set according to the size of sample. The scanning length in *X*-direction was 10 mm every time and the speed was at 3.3 mm min^{-1}. Each moving step (ΔY) in the *Y*-direction was 0.5 mm, and the total width was 3.5 mm.

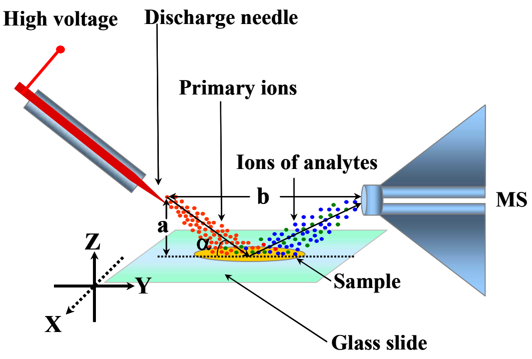

Fig.1 Schematic of SDAPCI device

In this experiment, the relative location of discharge needle to the mass spectrometer was kept still and the sample stage was moved along the *X*-direction from the origin to record the mass spectra continuously for about 3 min. The intensity values (*Z*) of the characteristic peaks of *m/z* 223 and 177 were exported to the Excel spreadsheets from the Xcalibur data processing system. Then the value of abscissa were calculated according to the time and scan speed. Finally the mass spectrometric images were obtained based on all the values of *X*, *Y* and *Z* using the Surfer software.

3 Results and discussion

3.1 Analysis of standard DEP sample with $SDAPCI-MS^n$

Firstly, the standard DEP solution sample was analyzed to verify the validity of $SDAPCI-MS^n$ method for detection of DEP. One μL was directly detected by the SDAPCI tandem mass spectrometry on the surface of a clean glass slide. Under the positive ion detection mode, the precursor ion, protonated diethyl phthalate ($[M + H]^+$, *m/z* 223), was confirmed by collision-induced dissociation (CID) experiments to exclude false-positive results. The results were shown in Fig.2. The major fragments are *m/z* 177 ($C_{10}H_9O_3^+$) and *m/z* 149 ($C_8H_5O_3^+$) and were produced by the loss of CH_3CH_2OH and CH_3CH_2OH+CH_2=CH_2, respectively. The results are consistent with consistent with that of the literature[20,21].

3.2 Detection of actual soil sample

The cotton cloth was used as the substrate to fix the soil samples. The single-scan mass spectra of blank cotton cloth (Fig.3a) and the actual soil sample (Fig.3b) were obtained. As can be seen from Fig.3, the intensity of the peak at *m/z* 223 in the actual soil sample was significantly higher than in the blank. This comparison shows that the actual soil contained DEP.

To exclude false-positive results, the precursor ions (*m/z* 223) in the actual soil sample were further fragmented in the CID experiment (as shown in Fig.4), and the characteristic