NON-TARGET SCREENING AND SEMI-QUANTITATIVE ANALYSIS OF ORGANIC POLLUTANTS IN DUST FROM INTERNET CAFE BASED ON GC-QTOF/MS

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1 Introduction

Indoors are an important place for human life and work. According to estimates, humans spend about 70% to 90% of their time indoor, and indoor environmental pollution has been attracted much attention. The analysis of indoor dust is considered to be an effective method to study the chemical substances in the indoor environment. As a heterogeneous particle mixture, it contains a wide range of chemical pollutants (insecticides, plasticizers, flame retardants, personal care products, polyfluorinated compounds, etc.). Once entering the human body, or through skin contact, it may cause harm to human health. Relevant studies have now revealed the distribution characteristics and health risk assessment of dust pollutants in different typical indoor microenvironments[1-3].

As a special micro-environment, Internet cafes are densely populated, and various human activities, such as smoking, drinking and spraying perfume, will affect the quality of the indoor environment. Moreover, the environment of Internet cafes is relatively closed, and pollutants are easy to accumulate indoors and are not easy to be discharged. Therefore, people staying in Internet cafes for a long time pose a threat to their health. At present, the research on indoor dust in Internet cafes is limited to the quantitative analysis of designated target compounds[4], and the potential toxic and harmful pollutants cannot be identified. Therefore, how to quickly and accurately screen out toxic and harmful pollutants is a problem that needs to be solved urgently.

Recently, with the development of organic high-resolution mass spectrometry instruments, especially the widespread application of time-of-flight mass spectrometry (TOF) and orbitrap, technical support has been provided for the identification of potential pollutants in environmental samples. Moschet et al.[5] used suspect screening and non-target screening based on LC-QTOF/MS and GC-QTOF/MS to comprehensively characterize the chemical substances in the dust. Castro et al.[6] used GC-QTOF/MS to screen semi-volatile compounds in indoor dust, and confirmed the presence of some potentially harmful compounds in the indoor environment, such as 2,4-toluene di-isocyanate and octyl isothiazolinone, etc., which have not been quantified in previous indoor dust research, and further research is needed.

In this study, indoor dust samples were collected from an Internet cafe in Shanghai, and analyzed by gas chromatography-quadrupole time-of-flight mass spectrometry (GC-QTOF/MS). Non-target screening of organic pollutants in the dust, and semi-quantitative analysis were conducted. The purpose of this research is to identify some new or potentially toxic and harmful pollutants, and provide technical support for the later accurate quantitative analysis and environmental risk assessment.

2 Materials and methods

2.1 Sample collection

The dust samples were collected at computer chassis (W-1), exhaust fan (W-2) and air conditioner (W-3) with a disposable nylon brush, from an Internet cafe in Shanghai City. After wrapped in aluminum foil, they were transferred to laboratory. Residue and debris were removed through a 0.2 mm screen, then the prepared samples were kept in the brown glass bottle at 4°C for the next analysis.

2.2 Chemicals and solvents

Acetone, dichloromethane and n-hexane used in the study were all pesticide residues, which were purchased from Honeywell (Morristown, NJ) Company. Three isotopic standard solvents (Phenanthrene-D_{10}, Pyrene-D_{10}, and Phenacene-D_{12}) were purchased from Accustandard Inc. (New Haven, CT, USA).

2.3 Sample preparation

0.1 g of dust sample was extracted using an accelerated solvent extractor (ASE 300, Dionex Corp.) with extraction solvent acetone/n-hexane (*v*/*v*, 1:1). Instrument parameters were as follows: temperature of 100°C, pressure of 1500 psi, preheating balance time of 5 min, static extraction time of 8 min, solvent leaching volume of

60% extraction tank volume, purification time of 60 second, static extraction cycle for 2 times. The collected extract was concentrated and transferred to 1 mL of n-hexane, then filtered by 0.22 μm filter membrane. After adding 1000 ng isotopic standard solvent, they were injected into the GC-TOF-MS system for analysis.

2.4 Instrumental analysis

The dust samples were analyzed by gas chromatography-quadrupole time-of-flight high resolution mass spectrometer (GC-QTOF/MS, 7250, Agilent, Wilmington, DE, USA), configured with 2× HP-5 MS UI column (15×0.25 mm, 0.25 μm film). The chromatographic conditions were set as follows: the flow rate of two column was 1.0 mL·min^{-1} and 1.2 mL·min^{-1}, the injection volume was 1 μL. The temperature was maintained in 6°C for 1 min, then increased to 120°C with the rate of 40°C·min^{-1}, and at last increased to 310°C with the rate of 5°C·min^{-1}. Helium was chosen as carrier gas. The mass spectrum conditions were set as follows: data was collected in EI mode, ion source temperature was 280°C, quadrupole temperature was 150°C, scanning speed was 5 Spectra·s^{-1}, solvent delay was 3 min, and mass scanning range was 45-550 amu.

2.5 Suspect screening and non-target screening workflow

The data were analyzed in two methods: one was based on the high resolution mass spectrometry database for suspect screening; the other was based on the NIST library for non-target screening. The high resolution mass spectrometry personal compound database and library contains more than 1200 compounds, mainly including polycyclic aromatic hydrocarbons (PAHs) and their derivatives, polychlorinated biphenyls, pesticides and other pollutants. According to the "Guidance Document on Quality Control and Method Validation for Analysis of Pesticide Residues in Food and Feed (SANTE/12682/2019)"[7] issued by the EU Directorate General for Health and Food Safety, the screening parameters were set as follows: there are at least 2 matching with exact mass ions with mass accuracy deviation less than 5×10^{-6}, retention time deviation was within 0.15 min, and matching score was greater than 75%. The screening results of NIST database were confirmed by matching score, retention index, exact mass number deviation, isotopic abundance ratio, mass spectrum and the ratio of base peak to secondary base peak. Furthermore, the identified compounds in this paper have been deducted of blank interference. The semi-quantitative concentration of a single compound was calculated by the compare with added three isotope standard solvents.

3 Results and discussion

3.1 Results of suspect screening

A total of 61 compounds in dust samples were identified through the suspect screening based on the high-resolution mass spectrometry database, mainly including PAHs, PAH derivatives, phthalic acid esters (PAEs), organic phosphate esters (OPEs) and organic synthesis intermediates, as shown in the Figure.1. In addition to the PAHs that are prioritized by EPA, biphenyl and benzo[e]pyrene was also identified. More PAH derivatives are identified, mainly substituted by different amount of methyl groups, such as 2-methylnaphthalene, 1-methylpyrene, 1,3-dimethylnaphthalene, 5-methylchrysene and 2-methylbenz[a]anthracene, etc. Furthermore, typical heterocyclic compounds identified are dibenzofuran, triadimenol, nicotine and carbazole, etc.

Seven PAEs were also found in the samples, such dimethyl phthalate (DBP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), bis(2-ethylhexyl) phthalate (DEHP), and dioctyl phthalate. As a common plasticizer, high levels of plasticizers in the environment may have adverse effects on human health, such as reproductive and developmental toxicity, neurotoxicity, and kidney and liver abnormalities[8]. 8 kinds of OPEs, including triethyl phosphate (TEP), triphenyl phosphate (TPPA), and tris(2-chloroethyl) phosphate (TCEP) were also identified. Other characteristic compounds detected in dust samples was 2-phenylphenol, (1R)-trans-permethrin, 2-undecanone, 1-naphthol, anthraquinone, and 2-methylphenol.

Figure 1. Screening compounds for suspect screening in dust samples

3.2 Results of nontarget Screening

The disadvantage of suspect screening lied in the limited compounds in the library, they were helpless for the organic pollutants outside the database. In this time, NIST database provided a non-targeted screening through matching with hundreds of thousands of mass spectrometry. The sample data was firstly deconvoluted to generate a list of hits, and then searched against a library. Several principles such as retention index, isotopic abundance ratio, match score and so on were also used to identify the suspect results. 131 typical contaminants were identified, in which 70 were not found by suspect screening. More unregulated heterocyclic compounds and intermediates were found in dust samples.

The PAHs identified in the three dust samples were triphenylene and naphthalene. PAHs derivatives included 8-isopropyl-1,3-dimethylphenanthrene, 2,5-dimethyl-phenanthrene, 2-ethyl-anthracene and so on. Substances of the plasticizer class included tris(2,4-di-tert-butylphenyl) phosphate, 1,2-benzenedicarboxylic acid, dinonyl ester, diisononyl phthalate and so on. In addition to the above substances, heterocyclic compounds containing nitrogen, oxygen and sulfur were also identified, such as 2-methyl-9,10-anthradione, 6-hydroxy-2(1H)-pyridinone, 9H-fluoren-9-one, 2,3'-bipyridinyl, 2,5-furandialdehyde etc. The other typical pollutants were shown in Table 1.

3.3 Semi-quantitative analysis

The environmental risks of pollutants are directly related to their concentrations. In this paper, the organic pollutants in dust samples were semi-quantitatively analyzed by adding three isotope standard solvents and based on the ratio of peak area. The total semi-quantitative concentrations of organic pollutants in three dust samples were 6430, 5619 and 9092 ng·g^{-1}, respectively, with average concentration 7047 ng·g^{-1}. The semi-quantitative concentration of PAEs was the highest, which was 4164, 2906 and 3760 ng·g^{-1}, respectively, accounting for 64.8%, 51.7% and 41.4% of the total concentration.

In addition, Table 1 listed the semi-quantitative concentrations of some typical pollutants, in which the semi-quantitative concentrations of nicotine had the highest level (750.2, 1245 and 2853 ng·g^{-1}), accounting for 11.7%, 22.2% and 40.5% of the total concentration, respectively. The semi-quantitative concentrations of stigmasterol, triphenylene, cotinine and carbazole, were 75.4, 40.5, 38.8 and 36.2 ng·g^{-1} respectively.

There were still a large number of un-identified contaminants in the samples, which suggested that an analysis of only a limited number of designated targets will underestimate the harm caused by toxic pollutants in indoor dust. In the later study, substances in samples can be confirmed by low energy EI and liquid chromatography-high resolution mass spectrometry, to obtain more comprehensive information of potential pollutants in dust.

Table 1. Semi-quantitative concentration of typical contaminants in the samples

Compounds name	CAS number	Formula	Concentration/(ng·g^{-1})			
			W-1	W-2	W-3	Mean
Naphthacene	92-24-0	$C_{18}H_{12}$	8.95	10.8	24.1	14.6
Benzothiazole	95-16-9	C_7H_5NS	7.75	2.86	0.77	3.79
1,2-Dihydro-3H-1,2,4-Triazol-3-one	930-33-6	$C_2H_3N_3O$	3.44	2.19	2.78	2.80
Anthrone	90-44-8	$C_{14}H_{10}O$	0.74	2.42	3.96	2.37
Chloroxylenol	88-04-0	C_8H_9ClO	1.24	2.02	3.01	2.09
2-Methyl-9,10-Anthracenedione	84-54-8	$C_{15}H_{10}O_2$	2.90	5.32	12.8	7.01
Stigmasterol	83-48-7	$C_{29}H_{48}O$	54.8	72.5	98.9	75.4
2-Pyrrolidinone	616-45-5	C_4H_7NO	1.47	4.24	7.03	4.25
2,3'-Dipyridyl	581-50-0	$C_{10}H_8N_2$	10.7	30.7	58.1	33.2
3-Quinolinamine	580-17-6	$C_9H_8N_2$	2.21	4.60	9.09	5.3
Nicotine	54-11-5	$C_{10}H_{14}N_2$	750	1245	2853	1616
3-(3,4-dihydro-2H-pyrrol-5-yl)-Pyridine	532-12-7	$C_9H_{10}N_2$	13.7	25.4	50.0	29.7
Cotinine	486-56-6	$C_{10}H_{12}N_2O$	26.7	32.6	57.2	38.8
9H-Fluoren-9-one	486-25-9	$C_{13}H_8O$	2.24	6.65	6.51	5.13
Cyclo(L-prolyl-L-valine)	2854-40-2	$C_{10}H_{16}N_2O_2$	3.41	5.52	10.8	6.58
Triphenylene	217-59-4	$C_{18}H_{12}$	24.1	29.2	68.3	40.5
Tripyridyl	1148-79-4	$C_{15}H_{11}N_3$	32.8	30.0	39.7	34.2
3-Pyridinol	109-00-2	C_5H_5NO	1.57	5.41	12.5	6.49
Carbazole	86-74-8	$C_{12}H_9N$	14.7	30.0	63.8	36.2

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