Comparison and Analysis of Organochlorine Pesticides and Hexabromobiphenyls in Environmental Samples by Gas Chromatography–Electron Capture Detector and Gas Chromatography–Mass Spectrometry

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Two analytical methods, gas chromatography–electron capture detector (GC–ECD) and gas chromatography–negative chemical ionization–mass spectrometry (GC–NCI-MS), were evaluated and compared for the measurement of persistent organic pollutants, specifically for 26 organochlorine pesticides and two hexabromobiphenyls, in atmospheric particulate matter and soil samples. The hypothesis tested was that the coelution of non-target compounds may lead to false positives when analyzed by GC–ECD, and that the overestimation associated with these false positives can be eliminated using GC–NCI-MS. The study showed that both methods had satisfactory linearity and reproducibility for the target compounds. Although the sensitivities of GC–ECD for most of the compounds investigated were higher than those observed with the GC–NCI-MS method, the matrices interference was obvious with GC–ECD. There was indeed an apparently high false-positive rate or overestimate when GC–ECD was used for environmental samples, implying that the GC–ECD method has been used with care and that GC–NCI-MS is generally superior for the analysis of trace amounts of these compounds in environmental samples. Based on these results, the sample extraction and cleanup procedures of the GC–NCI-MS method were optimized for achieving acceptable recoveries and less matrices interference.

Introduction

Persistent organic pollutants (POPs) are those compounds that are long-lasting and mobile in the environment and can be biomagnified in food chains (1). Because of the global concern, 21 POPs have been listed in the Stockholm convention on POPs (2, 3). Among those listed in the convention, organochlorine pesticides (OCPs) and hexabromobiphenyls (HBBs) are of particular concern, as OCPs had been widely applied in agricultural settings around the globe for decades, and HBBs had been widely used as flame retardants until they were banned in 2010 (4, 5). Despite the banning of most of these chemicals, both OCPs and HBBs are often detected in various environmental media in many places in China owing to their high persistence (6, 7).

As volatile or semivolatile compounds, OCPs and HBBs in various environmental samples are most often measured using gas chromatography (GC), coupled with electron capture detector (ECD), which has a relatively higher sensitivity for many compounds compared with other detection devices (8–12). However, because of the complex matrices and trace amounts of analytes involved in environmental samples, matrices interference and false positives are always challenges in a GC–ECD-based procedure (13). In contrast, mass spectrometry (MS) has certain advantages over ECD for identifying specific compounds and reducing matrix interferences. In practice, GC–MS with electron ionization (GC–EI-MS) or negative chemical ionization (GC–NCI-MS) has been used for the determination of OCPs and HBBs in water and biological samples (14–16). GC, coupled with tandem mass chromatography (MS–MS), has also been applied to the analysis of HBBs in sediment, using programmable temperature vaporization and large volume injection (17). GC–NCI-MS–MS and GC with high-resolution mass spectrometry (GC–HR-MS) have also been successfully used in the analysis of polybromobiphenyl (PBB) in biota (7).

Unfortunately, in spite of the concern associated with possible false positives (13), GC–ECD is still widely used to analyze OCPs in food and environment (8, 18), largely due to its high sensitive and low cost. Because of these potential false-positives, it is possible that there has been an overestimation of OCP and HBB concentrations in the environment. Although there are many advanced methods such as GC–NCI-MS–MS or GC–HR-MS besides GC–NCI-MS, GC–NCI-MS has comparable lower cost and also could avoid many false-positive results to some extent. Therefore, in this work, we selected the GC–NCI-MS to determine the real sample and compare with that by GC–ECD.

The primary objective of this study was to test and verify that non-target compounds can be coeluted in GC–ECD systems that could lead to a significant number of false positives when measuring OCPs and HBBs in air particulate matter (PM) samples and soil samples. Because any compounds with electron withdrawing groups have response on ECD detector. If the retention time of these non-target compounds is also same to that of target compounds, they will be identified the target OCPs or HBBs. These false-positive data will lead to the overestimation of these OCPs and HBBs. Although there are many methods to analyze OCPs and HBBs by GC–MS or GC–ECD, they did not compare the result between the two methods. Therefore, there is literature to mention the false-positive data with GC–ECD (13), but no specific data to certify the result. In this paper, the GC–NCI-MS method, together with a microwave-assisted extraction and cleanup procedure, was optimized with a two-layer column to develop an improved analytical method for the determination of OCPs and HBBs in the environment. Above all, direct comparison of the results by both GC–ECD and GC–NCI-MS analyses was investigated, and the specific data were presented to remind some environmental workers that there might be serious overestimate phenomena when the GC–ECD was used to determine the POPs in their research work, especially in trace analysis.
Materials and methods

Materials and chemicals

2,2',4,4',6,6'-hexabromobiphenyl (PBB155), 3,3',4,4',5,5'-hexabromobiphenyl (PBB169), a mixed OCP standard containing aldrin, hexachlorocyclohexane isomers (HCHs, including α-, β-, γ- and δ-HCH), α-chlordane, γ-chlordane, dichlorodiphenyldichloroethane and metabolites (o, p'-DDD, p, p'-DDD, o, p'-DDE, p, p'-DDE, o, p'-DDT and p, p'-DDT), dieldrin, endosulfan I, endosulfan II, endrin, heptachlor, heptachlor exide (isomers A and B) (hep-ox(A) and hep-ox(B)), hexachlorobenzene (HCB), isodrin, methoxychlor, mirex, oxychlordane (all at a concentration of 10 μg mL⁻¹ in toluene), pentachlorobenzene (pentachlor), pentachloronitrobenzene (PCNB) as an internal standard and 1-bromo-2-nitrobenzene (1-Br-2NP) as a surrogate for the target compounds were from AccuStandard (USA). Analytical grade acetone, n-hexane and dichloromethane (DCM) were obtained from Beijing Reagent Company, China, and redistilled before use. Silica gel and aluminum oxide with 100–200 mesh (Sinopharm, China) were heated at 450°C for 6 h and then activated at 140°C for 16 h before use.

Sample collection

The ambient air PM (aerodynamic size of 2.5 μm, PM2.5) was collected using a medium-volume sampler (Guangzhou Mingye, China) with a glass fiber filter (20 cm × 15 cm) that was heated at 450°C for 6 h and allowed to cool in a dessicator for 24 h on the roof of a seven-floor building in Peking University campus in Beijing and Enshi in Hu Bei province, respectively. Soil samples were also collected from Taiyuan in Shan xi province. Twenty samples, including 10 soil samples and 10 air particulate samples, were examined by GC–ECD and GC–MS to compare the difference between the two methods.

Sample extraction and cleanup

The soil and air particle samples were all extracted with 20 mL of hexane/acetone (1 : 1, v/v) solution using microwave extraction (Mars Express, CEM, USA, 1200 W, and held for 10 min) respectively. The extracts were filtered through glass fiber filter and the vessel was rinsed twice with 3 mL of hexane/acetone (1 : 1, v/v). The filtrate was concentrated to ~1 mL using a rotary evaporator. The concentrated extracts were transferred to solid-phase extraction columns (10 mm i.d. × 350 mm length) packed sequentially with 10 g alumina, 10 g silica gel and 1 cm anhydrous sodium sulfate. The alumina and silica gel were deactivated by 3% (w/w) distilled water before use. The column was first washed with 10 mL of n-hexane, and the eluate was discarded. Then, the extract was eluted with a 50 mL mixture of hexane/DCM (1 : 1, v/v). This eluate was concentrated to 1 ml by rotary evaporation. After 10 mL of hexane was added, the solution was concentrated to ~1 ml again, and then internal standard solution was added. The concentrated sample with internal standard solution was removed to vial and analyzed by GC–MS.

Equipment and conditions

GC–ECD analysis was performed using an Agilent GC 6890, equipped with a Nickel 63 ECD, and an autosampler. An HP-5 column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used for the separation. The column was maintained at 80°C for 2 min, ramped at 10°C min⁻¹ to 100°C, increased at 5°C min⁻¹ to 180°C and held for 2 min, increased at 3°C min⁻¹ to 200°C and held for 5 min, and finally increased at 8°C min⁻¹ to 300°C and held for another 5 min. Splitless injection was used at an inlet temperature of 220°C.

GC–MS analysis was performed using another Agilent GC 6890, coupled with 5975 MSD mass spectrometer, and equipped with EI and CI sources and an autosampler. The analyses were carried out using an HP-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium was used as the carrier gas with a constant flow rate of 1.0 mL min⁻¹. The oven temperature was 50°C (held for 2 min) ramped to 150°C at 10°C min⁻¹, then to 240°C at 3°C min⁻¹ and held for 5 min, and finally ramped to 300°C at 10°C min⁻¹ and held for another 5 min. Splitless injection was used at an inlet temperature of 220°C. The mass spectrometer was operated in the NCI mode and with scan range of m/z 30–700. The transfer line temperature was kept at 250°C. The ion source temperature was at 200°C, and MS quadrupole temperature was at 150°C. The selected ion monitoring (SIM) mode was used for quantitative analysis. The monitored ions are listed in Table I.

Results

Optimization of chromatographic conditions

Before comparing their performance, the chromatographic conditions of both GC–ECD and GC–NCI-MS were optimized for a full separation of the 28 target compounds and the surrogate and internal standard. After a series of trials, a preferred set of conditions was determined as described in section Equipment and conditions. Under these conditions, all the compounds could be well separated by GC–ECD. It was found that the same conditions could not be satisfactorily used in the GC–NCI-MS in the scan mode, since the resolution decreased significantly to the extent that most of the target compounds could not be separated. Therefore, the oven temperature program, the ion source temperature and the transfer temperature were further adjusted in achieve a satisfactory separation (Figure 1). After the optimization, SIM ions of these compounds were selected for further quantitative analysis because of its higher sensitivity, and those selected ions are listed in Table I.

Method evaluation

Both the GC–ECD and GC–NCI-MS methods were calibrated using a set of standard solutions of varying concentrations (0, 1, 10, 25, 50, 150, 300 and 450 ng mL⁻¹). Plots of the ratio of the area under the peak for a target compound to the area under the peak for the internal standard [(Area)target/(Area)Int. Std] against the ratio of the target compound concentration to the internal standard concentration [(Concn target)/(Concn Int. Std)] showed satisfactory linearity over this concentration range with coefficients of determination (r²) >0.99 for each of the target compounds investigated. As for reproducibility, five injections were performed consecutively, and the coefficients of deviation were all below 10%. Based on these measurements, the limits of detection (defined here as a signal-to-noise ratio of 3) for individual compounds are listed in Table I.
Optimization of the sample preparation procedure

It is well known that the cleanup is essential part of the analysis of environmental samples owing to the complex matrix of these samples. Therefore, it is important to optimize the cleanup procedure to obtain satisfactory recovery, better purification and accurate results in an efficient manner. In this study, the solvent selected for the extraction of the air particulate samples was hexane/acetone (1:1, v/v), because this mixture has been shown to be effective for the extraction of pesticides (19, 20).

The loaded column with silica and alumina was eluted using the following two similar procedures. Procedure 1: the column was eluted four times with 5 mL of hexane, followed by four times with 20 mL of DCM. Procedure 2: the column was eluted four times with 5 mL of hexane, followed by two times with 20 mL of hexane/DCM (1:1, v/v), and two times with 20 mL of DCM. The elution curves resulting from the two procedures were similar to each other, with an exception that the eluting capacity of hexane/DCM (1:1, v/v) was lower than that of DCM. The results of the procedures applied to several typical compounds are shown in Figure 2.

Recovery

With the optimized cleanup procedure adopted, the recoveries and reproducibilities of the methods were tested for all compounds by GC–MS. The recovery was calculated by the concentration of the determined to that of standard samples. Because the real blank without target compounds could not be acquired, the 100-ng standard mixtures were added to each of five blank filters, and the filter was extracted and cleaned up with the optimized procedure.

Furthermore, three blank filters without standard samples and three solvent blank without the filter were also carried out with above procedure. The recoveries of the individual compounds varied from 93.0 to 128.3%. In testing the reproducibility of the procedure for various compounds, coefficients of variation from 3.0 to 10.8% were observed. To identify the effect of real matrix, the standard mixture with 100 ng was also added to real air particle samples to be analyzed by the above-mentioned procedure, and the recoveries of most these compounds were ranged from 82.4 to 113.0%.

Comparison between GC–ECD and GC–NCI-MS methods

For complex matrices such as ambient air PM, soil, sediment or biological samples, false-positive results of OCPs emerge frequently in GC–ECD owing to its lack of specificity. This is particularly true for the samples with trace amount of the target compounds (13). Most OCPs listed in the Stockholm convention have been banned in China for years, and today only trace amounts of these residues are found in various environmental media (18, 21). However, the possibility of false positives associated with GC–ECD methods may result in an overestimation of

**Figure 1.** A typical chromatogram of the target compounds (Table I) by GC–NCI-MS.
the concentrations of these compounds in the environment. To test this hypothesis, 10 PM2.5 samples and 10 soil samples were collected, extracted and analyzed for OCPs and HBBs using both the optimized GC–ECD and GC–NCI-MS methods. Every extracts of the actual samples were determined two times and compared by the two methods. Figure 3 shows the typical chromatograms from the GC–ECD and GC–NCI-MS procedures applied to actual soil samples.

Figure 2. Elution curves of OCPs and HBBs in two preparation procedures: (a) Procedure 1 and (b) Procedure 2, where mix = hex/DCM (1 : 1, v/v). The compounds are numbered in Table I.

Discussion

Method evaluation

After the optimization of chromatographic conditions, the 28 target compounds and the surrogate and internal standard could be separated with baseline by GC–ECD and GC–NCI-MS. The two methods showed satisfactory linearity and reproducibility. From Table I, we can see that the detection limits of the GC–ECD analyses were significantly lower than those of the GC–NCI-MS
analyses for the compounds tested, with only three exceptions: 1-Br-2NP, HCB and pentachlorobenzene. In most cases, the differences were between one and two orders of magnitude. Therefore, if there were no matrix interference or false positives, GC–ECD would clearly be preferable over GC–NCI-MS.

Optimization of the sample preparation procedure
To analyze real environmental samples, the extraction and cleanup procedures were also optimized for obtaining better accuracy. Figure 2 shows that nothing was eluted by the first 10 mL of hexane. A number of OCP compounds, including HCB, pentachlor, mirex, heptachlor, aldrin, isodrin, p,p’-DDE, methoxychlor and 2,4,6-HBB, were detected in the second 10 mL of hexane. The peaks of most compounds appeared in the first 20 mL of DCM and nothing appearing after 40 mL of DCM or hexane/DCM (1:1, v/v) had passed through the column. Taking into consideration that more interferences could be retained in silica and alumina by the hexane/DCM (1:1, v/v) because of its lower eluting capacity, the final cleanup procedure selected for this study was...
10 mL of hexane (discarded) followed by 50 mL of hexane/DCM (1:1, v/v).

**Recovery**

Accuracy was expressed as the percent recovery and relative error (RSD %). As can be seen from above results, the accuracy of the method for all mixtures with satisfactory recoveries and small relative errors, the matrix has little effect on the determination by GC–MS.

### Comparison Between the GC–ECD and GC–NCI-MS Methods

In Figure 3, there are many more peaks in the GC–ECD chromatogram than in GC–NCI-MS in the SIM mode, because any volatile or semivolatile compounds with electron withdraw group could have response in this chromatogram. Some peaks in real sample have same retention times with target compounds in standard solutions, and the observed peaks often does not constitute a definitive identification of the compound associated with a particular peak. For example, the heptachlor epoxide (isomer A) and oxychlordane were always coeluted in GC and cannot be distinguished by ECD, but they can be determined exactly by GC–NCI-MS with their own characteristic fragmentation ions. Further questions about any such assignments are raised by the fact that most of these additional peaks were not detected by GC–NCI-MS in the SIM mode. Therefore, it appears that there are significant possibilities of false positives and overestimation in the GC–ECD chromatogram. Besides these, the integration was very difficult, and too much interference peak was in increase the difficulty of data processing, and decreasing the accuracy of the data.

To compare the results between the two methods, the measured concentrations of various OCPs and HBBs were calculated (after blank subtraction), and the typical actual samples are presented in Table II. Note that the recovery of the surrogate (1-bromo-2-nitrobenzene) was ~75%. Because the purpose of the study was to evaluate the two methods, the results were not converted into concentrations (mass of target compounds per mass of PM2.5 or soil samples) of pollutants in the sample. Instead, the concentrations in the extracts are presented and compared directly.

As can be seen in Table II, the concentrations of a number of compounds, including pentachlorobenzene, heptachlor, aldrin, and mirex, were quite high based on GC–ECD measurement, and the concentrations of these compounds reported by GC–ECD were all significantly higher than the detection limits of GC–NCI-MS. Among these OCPs detected by the two methods, the concentration detected by GC–ECD was almost more than those detected by GC–NCI-MS, except α-HCH and p,p’-DDE, in which they can observe the approximate results. Since the GC–ECD-reported concentrations of these compounds were all higher than the detection limits of GC–NCI-MS, and the individual compounds were identified merely on the basis of retention times, the peaks detected by the GC–ECD method may be incorrectly assigned. For GC–NCI-MS, besides the retention time, the molecule fragmentation can provide a further structure identification and avoid more false-positive results. Other soil and air particle samples also acquired the comparable results, and some false positives and overestimations were also observed by GC–ECD.

Based on these results, GC–NCI-MS analysis, rather than GC–ECD analysis, is recommended for the determination of trace amounts of OCPs and HBBs in complex environmental samples.

### Conclusions

An analytical method for the determination of 26 OCP and 2 HBB compounds in air particle and soil samples had been developed using GC–NCI-MS. The cleanup program using silica and alumina combination column was optimized to prepare the actual samples. Satisfactory results can be achieved using the optimized extraction and cleanup procedure. Although it is well known that the selectivity of GC–ECD was less than that of GC–MS, false-positive and overestimation of GC–ECD in complex environmental samples still did not arise enough attention to environmental worker. In this paper, the GC–ECD and GC–NCI-MS methods were established, and some real environmental samples were all determined by the two methods and compared to verify the accuracy. The result indicated that these compounds can be

<table>
<thead>
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<th>No.</th>
<th>Compound</th>
<th>Conc. (ng mL⁻¹)</th>
<th>GC–ECD</th>
<th>GC–NCI-MS</th>
<th>GC–ECD</th>
<th>GC–NCI-MS</th>
</tr>
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<tr>
<td>1</td>
<td>1-Br-NO₂-Ph (SS)</td>
<td>74.9</td>
<td>74.0</td>
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<tr>
<td>2</td>
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<td>α-HCH</td>
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<td>25.4</td>
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<td>Dieldrin</td>
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<td>β-HCH</td>
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<td></td>
<td>p,p’-DDE</td>
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<td>γ-HCH</td>
<td>3.28</td>
<td>2.74</td>
<td></td>
<td>p,p’-DDT</td>
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<td>7</td>
<td>PCNB (IS)</td>
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<td>–</td>
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<td>Endrin</td>
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<td>8</td>
<td>δ-HCH</td>
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<td>0.67</td>
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<td>Endosulfan II</td>
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<td>–</td>
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</tr>
<tr>
<td>22</td>
<td>Mirex</td>
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<td>–</td>
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<tr>
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<tr>
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<td>Endosulfan I</td>
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</table>

*p, not detected; †, could be detected but lower than limit of quantification (LOQ = 10 S/N); SS, surrogate; IS, internal standard.

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Table II: Comparison Between the GC–MS-NCI and GC–ECD Methods for Measuring Concentrations of OCPs and HBBs in Extracts of Soil Samples
analyzed by GC–ECD and GC–NCI-MS methods, but apparent false positives and overestimation were found by the GC–ECD method for the determination of OCPs and HBBs in air particle or soil samples. Therefore, GC–NCI-MS method is recommended for the analysis of trace amounts of OCPs and HBBs in environmental samples with complex matrices compared with GC–ECD, and the GC–ECD should be used with caution in real environmental sample analysis.

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