Electronic Supplementary Material (ESI) for Analytical Methods.

Simultaneous quantification of bisphenol A, alkylphenols and alkylphenol ethoxylates in indoor dust by gas chromatography-tandem mass spectrometry and a comparison between two sampling techniques

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LC-MS/MS Method

Solvent extraction and sample cleanup

The procedures of solvent extraction and SPE sample cleanup for LC-MS/MS analysis were the same as those for GC-MS/MS except that the final dried residue of the sample extract was reconstituted in 250 μL of acetonitrile prior to analysis.

LC-MS/MS Analysis

Sample extracts were analyzed using a Finnigan Surveyor Plus HPLC System coupled with Thermo Finnigan TSQ Quantum Ultra EMR triple quadrupole mass spectrometer (Thermo Electron Corporation, San Jose, USA). Separation was achieved using a Supelco Discovery HS C18 column (7.5 cm x 2.1 mm; 3 μm). Dust extracts were each injected and analyzed twice on LC-MS/MS using two separate LC-MS/MS methods. The MS was operated in negative ion mode electrospray ionization (ES-) for BPA, NP and OP, and in positive mode (ES+) for NP_1EO, NP_2EO, using selected reaction monitoring (SRM) mode. The mobile phase for ES- mode consisted of 10% acetonitrile (A) and 90% acetonitrile (B) in water. Solvents were degassed online, and the column temperature was maintained at 25 °C. The gradient elution started with 90% A for 1 min, followed by linear gradient to 100% B in 4 min, held at 100% B for 10 min, and returned back to 90% A in 1 min,. The system was equilibrated for 3 min at the initial conditions before the next injection. Sample injection volume was 5 μL, and the flow rate was set at 0.25 mL min^{-1}. Post column adjustment of pH was achieved with 10% ammonium hydroxide (NH_4OH) in isopropanol infused at 0.15 μL min^{-1}. The mobile phase for ES+ mode consisted of 10% methanol in water (C) and methanol (D). Solvents were also degassed online; however the column temperature was maintained at 30 °C. The gradient elution started with 100% C for 1 min, followed by a linear gradient to 100% D in 9 min, held at 100% D for 5 min,

and returned back to 100% C in 1 min. The system was equilibrated for 2 min at the initial conditions before the next injection. Sample injection volume was 10 μL, and the flow rate was set at 0.25 mL min^{-1}. Xcalibur version 2 was used for data acquisition and processing. The following SRM transitions (*m/z*) monitored and other parameters are listed in Table SI1.

Comparison of LC-MS/MS and GC/MS/MS

In the course of the method development, methods based on LC and GC coupled with tandem mass spectrometry were evaluated. Isomers of branched NP, NP_1EO, and NP_2EO were separated by GC (Fig. SI1) but not by LC (Fig. SI2); in addition, electrospray ionization (ESI) is much more sensitive to matrix effects than electron impact (EI) ionization. Furthermore, in order to increase the sensitivity for the target analytes, ES- was used for the ionization of BPA, NP and OP, while ES+ was for NP_1EO, NP_2EO.

Moreover, to effectively ionize the BPA, NP and OP using ESI, and thereby increase the method sensitivity, a post column pH adjustment with NH_4OH was required. Therefore, use of LC-MS/MS for the measurement of BPA, alkylphenols and alkylphenol ethoxylates would require instrumental analysis to be split in two separate runs hence doubling the analysis time. Although derivatization is required for the analysis of target analytes by GC-MS/MS, this technique was found to be more sensitive than LC-MS/MS, and it should be considered as the analytical method of choice for the simultaneously determination of BPA, alkylphenols and alkylphenol ethoxylates.

Table SI1. LC-MS/MS parameters for target analytes

Compound	SRM transition (*m/z*)	Cone voltage (V)	Collision energy (eV)
BPA	227 → 212	45	19
NP	219 → 133	45	22
OP	205 → 133	45	22
NP_1EO	282 → 127	45	11
NP_2EO	326 → 121	45	17
$^{13}C_{12}$-BPA	239 → 224	45	20
$^{13}C_6$-NP	225 → 139	45	22

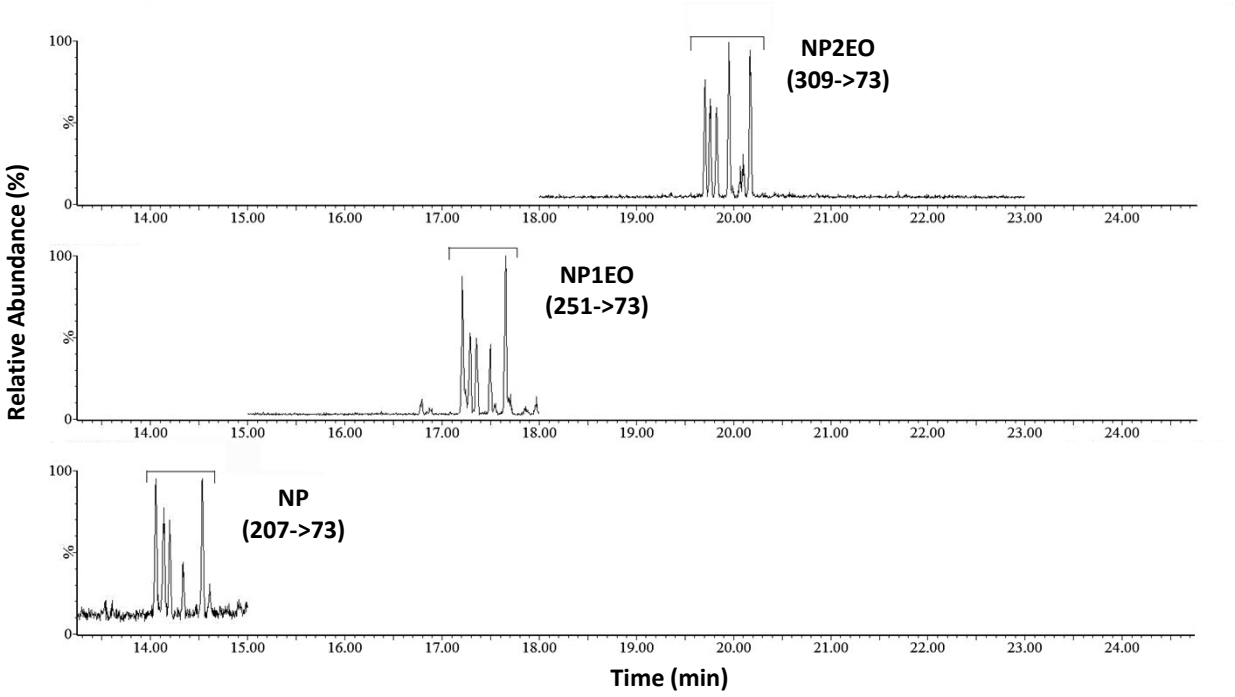

Fig. SI1 GC chromatograms of NP (125 ng mL^{-1}), NP_1EO (250 ng mL^{-1}), and NP_2EO in a standard mixture (500 ng mL^{-1})

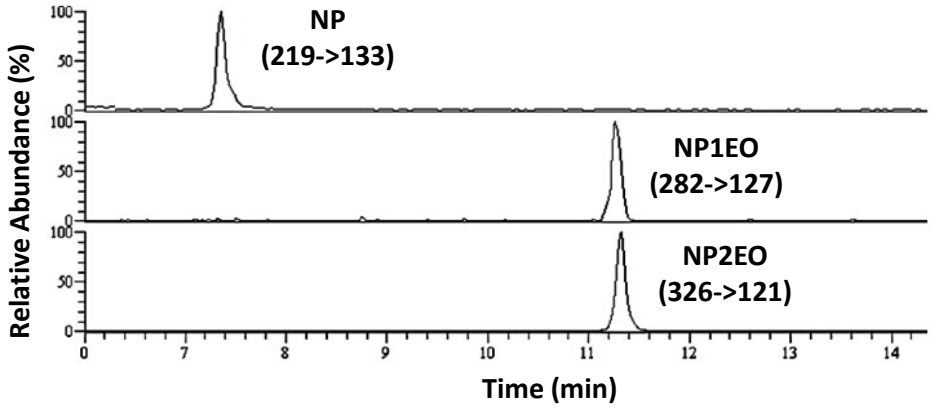

Fig. SI2 LC chromatograms of NP (320 ng mL^{-1}), NP_1EO (640 ng mL^{-1}), and NP_2EO in a standard mixture (1280 ng mL^{-1})