Phthalate and organophosphate plasticizers in nail polish: evaluation of labels and ingredients

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Methods for plasticizer laboratory analysis

We analyzed each nail polish sample for 22 compounds: dimethyl phthalate [DMP], diethyl phthalate [DEP], butyl benzyl phthalate [BBP], di-n-butyl phthalate [DnBP], diisobutyl phthalate [DiBP], bis(2-ethylhexyl) phthalate [DEHP], di-n-hexyl phthalate [DnHP], dicyclohexyl phthalate [DCHP], di-n-octyl phthalate [DnOP], di-isononyl phthalate [DiNP], bis(2-ethylhexyl) adipate [DEHA], bis(2-ethylhexyl) terephthalate [DEHtP], triphenyl phosphate [TPHP], tris(methylphenyl) phosphate [TMPP], triethyl phosphate [TEP], tripropyl phosphate [TPP], tris(2-chloroethyl)phosphate [TCEP], tris(1-chloro-2-propyl)phosphate [TCIPP], tris(1,3-dichloro-2-propyl)phosphate [TDCIPP], p,p′-1,3-phenylene p,p,p′,p′-tetraphenyl ester phosphate [PBDPP], 2-ethylhexyl diphenyl phosphate [EHDPP], and tris(4-butylphenyl)phosphate [TBPhP]. We used abbreviations following guidelines by Bergman et al. (2012).[1]

To avoid background contamination, all glassware (e.g. test tube, Pasteur pipette, GC vial and glass inserts) was baked at 450 °C overnight prior to use and polypropylene (PP) tubes were pre-cleaned with organic solvents. Each sample (100 mg) was transferred into two separate PP tubes and dissolved in 1 mL of dichloromethane for the analysis of phthalate diesters and 1 mL of methanol for the analysis of organophosphate compounds. After equilibration (30 min, room temperature), each tube was spiked with 250 ng of isotope-labeled internal standards and vortexed for 30 sec. For phthalates, 11 deuterated compounds comprising DMP-d4, DEP-d4, BBP-d4, DnHP-d4, DCHP-d4, DnBP-d4, DiBP-d4, DEHP-d4, DnOP-d4, DiNP-d4, DEHA-d4 were spiked. For organophosphates, eight deuterated compounds comprising TnBP-d27, TPP-d21, TCEP-d12, TCIPP-d18, TDCIPP-d15, TPHP-d15 and TEP-d15 were spiked. For the extraction of phthalates, 3 mL of dichloromethane:hexane (DCM:Hx, 3:1 v/v) were added, vortexed for 1 min, followed by mechanical shaking for 20 min and ultrasonication (Branson, Danbury, CT) at 100 W for 20 min. The procedure was repeated with 3 mL of DCM:Hx (3:1 v/v) and 3 mL of hexane in that order. The

samples for organophosphate analysis were extracted twice with 4 mL of methanol and 5 mL of acetone:ethyl acetate (1:1 v/v) in sequence for 30 min by mechanical shaking followed by 30 min ultrasonication. Extracts were combined (10 mL) and 1 mL was transferred into gas chromatographic (GC) vial for instrumental analysis.

Twelve phthalate diesters and 11 deuterated internal standards were measured using a GC (Agilent Technologies 6890N; Agilent Technologies, Santa Clara, CA) coupled with a mass spectrometer (Agilent Technologies 5973 MSD) in the selected ion monitoring mode. A fused-silica capillary column (DB-5; 30 m × 0.25 mm i.d.; 0.25 mm film thickness) was used for separation. Samples (1 μL) were injected in the splitless mode. The temperatures of the injector and ion source were 280 °C and 230 °C, respectively. The oven temperature was programmed from 80 °C (held for 1 min), raised to 180 °C at 12 °C/min (held for 1 min), increased to 230 °C at 6 °C/min, then to 270 °C at 8 °C/min (held for 2 min), and finally to 300 °C at 30 °C/min (held for 12 min). Ion fragments m/z 129, 163, m/z 261, and m/z 293 were monitored for DEHA, DMP, DEHtP, and DiNP, respectively. The other eight phthalates were monitored at m/z 149 for quantification. The responses of deuterated internal standards (m/z 167 for DMP-d4 and m/z 153 for all others) for each phthalate were used in quantification. BBP, DEHA and DEHP were present in procedural blanks (0.16–2.47 ng/mL) and the average values found in blanks were subtracted from sample values. The limits of detection (LODs) were 0.5–2.0 ng/mL. Two matrix spikes (50 ng) were analyzed, which showed recoveries of target chemicals ranging from 85 to 121%. A detailed description of the method and quality assurance and quality control (QA/QC) protocols have been reported previously.[2,3]

The nail polish extracts were analyzed for 10 organophosphates and eight corresponding deuterated compounds using high-performance liquid chromatography (Agilent 1100 series HPLC; Agilent Technologies, Santa Clara, CA) coupled with electrospray triple quadrupole mass spectrometry (API 2000, Applied Biosystems, Foster City, CA). The chromatographic separation of

target analytes was accomplished by a Luna C18 column (150 mm × 4.6 mm, 3 μm; Phenomenex, Torrance, CA) serially connected to a Betasil C18 guard column (20 mm × 2.1 mm, 5 μm; Thermo, Waltham, MA). The mobile phase consisted of methanol and Milli-Q water (1:9) with 0.15% formic acid (A) and methanol with 0.2% formic acid (B) at a flow rate of 300 μL/min. The gradient flow started at 55% B and increased linearly to 70% in 1 min and then to 100% in 7 min, held for 8 min before reverting to the original conditions in 4 min. Electrospray positive ionization and multiple reaction monitoring (MRM) modes were used for the identification and quantification of target analytes. The LOD was 10 ng/mL for EHDPP and ranged between 0.2 and 5 ng/mL for the other nine organophosphates. Matrix spikes (n=2, 100 ng) were analyzed which showed that recoveries of target chemicals ranged between 85 and 116%. None of the analytes were found in procedural blanks. Detailed information with regard to MRM transitions and QA/QC protocols were reported elsewhere.[4]

References

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