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Assessment of gas chromatography time-of-flight mass spectrometry for the screening of semi-volatile compounds in indoor dust

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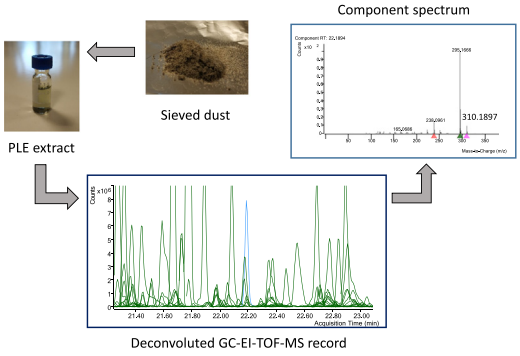
HIGHLIGHTS

- Comprehensive screening of semi-volatile compounds in indoor dust extracts
- Deconvolution of accurate electron ionization scan mass spectra
- Compounds identification guided by comparison with low resolution library spectra
- Novel compounds detected in dust from indoor environments
- Concentration ranges estimated for a selection of 44 pollutants in dust samples

GRAPHICAL ABSTRACT



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ABSTRACT

Indoor dust contains a complex mixture of anthropogenic and synthetic compounds closely related to dermal and respiratory diseases. Target methods have been developed for the quantification of distinct groups of substances in dust samples; however, the comprehensive characterization of the different species existing in this matrix remains a challenging issue. Herein, we assess the performance of gas chromatography (GC) time-of-flight mass spectrometry (TOF-MS), using electron ionization (EI), for the screening of compounds present in indoor dust. Samples are processed by pressurized-liquid extraction (PLE) before GC-EI-TOF-MS analysis. The study proposes a data mining workflow for the non-target identification of species contained in dust extracts, aided by preliminary comparison with nominal resolution EI-MS spectra in the NIST17 library. The possibilities, and the limitations, of the above approach are discussed and the identities of >75 compounds are confirmed by comparison with authentic standards in dust from indoor environments. Some species, such as indigo, phthalic anhydride, 2,4-toluene di-isocyanate, phthalimide, certain UV absorbers and octyl isothiazolinone, identified in this research, have not been previously considered in target methods dealing with dust analysis. The study also evaluates two different algorithms for the suspected-target screening of dust extracts using a customized library of accurate EI-MS spectra. Finally, a semi-quantitative estimation of the range of concentrations for a group of 44 pollutants in a set of 27 dust samples is provided.

1. Introduction

Citizens living in urban locations spend a relevant fraction of their lives in confined areas, such as homes, vehicles, shopping centres,

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work places and administrative buildings. These indoor environments contain different chemicals related to building materials, furniture and upholstery, to the developed activities and to certain human habits (i.e. smoking, consumption of illicit substances). Previous studies have established correlations between human exposure to this pool of chemicals and certain dermal and/or respiratory diseases, usually grouped under the so-called sick building syndrome (Ait Bamai et al., 2016; Kanchongkittiphon et al., 2015; Xiang et al., 2016).

Chemicals are released interiors through volatilization, mechanical abrasion of host materials and non-intended spills (Sukiene et al., 2016). Depending on their vapour pressure, polarity and molecular weight, released species are distributed between the gas phase and dust particles (Lucattini et al., 2018). Moreover, direct transfer of semi-volatile compounds from host materials to dust particles settled on their surface has been also demonstrated (Tokumura et al., 2019). Therefore, the analysis of dust samples is considered a valuable approach to investigate the chemicals affecting indoor environments, and the human exposure to these species, through dermal contact and ingestion (W. Wang et al., 2013). So far, the compounds most often determined in dust are halogenated and non-halogenated flame retardants (Velázquez-Gómez et al., 2018), plasticizers (particularly phthalates) (Christia et al., 2019), PAHs (Cao et al., 2019), pesticides, benzothiazoles (L. Wang et al., 2013), and several classes of personal care products, such as UV-filters, fragrances and phenolic preservatives (Ao et al., 2017; Chen et al., 2018).

Target procedures, facing the quantification of pre-defined species, combine well-tuned sample preparation approaches with selective analytical techniques. Very often, tandem mass spectrometry (MS/MS), after a chromatographic separation step, is the preferred option (Velázquez-Gómez et al., 2018). These procedures permit the sensitive determination of pre-selected compounds in the complex dust matrix; however, they are blind to any compound not included in the list of MS/MS transitions.

Accurate and/or high-resolution (HR) MS analyzers, such as time-of-flight (TOF) and Orbitrap instruments, provide spectral information of any compound recovered in the sample preparation process, and amenable to chromatographic separation and ionization steps. Thus, LC- and GC–MS accurate platforms, integrating soft ionization interfaces (i.e. electrospray, ESI; or vacuum chemical ionization, CI), permit to identify the molecular formulae of compounds present in chromatographic records (Chiaia-Hernández et al., 2014). Then, accurate product ion scan (MS/MS) spectra serve to discriminate among species with the same formula. These spectra are being progressively included in open libraries; so, compounds mined from HR MS and HR MS/MS records can be identified with a confidence level 2, accordingly to the categorization scale proposed by Schymanski and co-workers (Schymanski et al., 2015). Software developments allow to record accurate MS/MS, or pseudo-MS/MS (usually referred as all-ions, or MS^n modes), spectra for hundreds of compounds in the same chromatographic injection, either with, or without, a pre-selection of precursor ions (Moschet et al., 2017). So, above techniques become of paramount usefulness in non-target comprehensive screening studies. Unfortunately, the efficiency of ESI ionization is unsuitable for the determination of many semi-volatile compounds, as those expected in indoor dust, and vacuum CI is not considered a universal ionization source in GC–MS.

GC-electron ionization (EI) accurate MS platforms, such as GC-EI-TOF and GC-EI-Orbitrap (Peterson et al., 2014), provide characteristic fingerprints of thermally stable compounds suitable for GC analysis. In many cases, the accurate *m/z* values for fragment ions, combined with that for the molecular ion (when observed), are specific enough for the unambiguous identification of a given compound without the need of extra spectral information (MS/MS data) (Fontana et al., 2018; Uclés et al., 2017). Despite this advantage, other factors have slowed down the applicability of GC-EI-accurate MS in screening studies. The most relevant ones are: (1) the lack of accurate EI-MS spectral libraries (Kwiecien et al., 2015) (apart from that developed for pesticides), and (2) software limitations to mine comprehensively the information contained in GC-EI-accurate MS files. These records usually contain dozens of fragment ions from non-chromatographically resolved compounds. Thus, data mining algorithms designed to handle MS data obtained using soft-ionization sources (such as ESI, which contains limited groups of ionic clusters directly linked to molecular ions of co-eluting species) are not suitable for processing the GC-EI-MS scan data files.

Herein, we evaluate the possibilities of a non-targeted approach for the comprehensive identification of semi-volatile compounds existing in dust from indoor environments. The main purpose of the study is to develop a systematic data mining workflow, suitable to process accurate spectral information contained in raw GC-EI-MS files, assuming that every ionized compound provides a rich and complex fingerprint of fragment ions, often overlapped with those from co-eluting species. A second aim was to expand the knowledge on the chemical composition of indoor dust. To this end, samples are processed by pressurized liquid extraction (PLE) and extracts are analysed using a GC-EI-TOF-MS system. After chromatographic deconvolution, accurate EI-MS spectra are firstly compared with those existing in the low (nominal) resolution NIST17 library. In addition to experimental *m/z* values compiled in this library, the calculated accurate ratios for fragment ions with known structures are also considered. Tentative identifications are verified by injection of authentic standards of candidate compounds. The study also investigates the performance of two different algorithms for the suspected-target screening of compounds in dust extracts using a customized library containing the accurate EI-MS spectra for a selection of semi-volatile compounds. Finally, a semi-quantitative estimation of the concentration ranges for >40 compounds in different dust samples is given.

2. Material and methods

2.1. Solvents, sorbents and standards

Ethyl acetate (AcOEt) (trace analysis grade), methanol (MeOH) and acetonitrile (ACN) (LC gradient quality) were obtained from Merck (Darmstadt, Germany). Acid washed, calcined sand and silica sorbent (0.04–0.063 mm particle size) were purchased from Sigma-Aldrich (St. Louis, MO, USA), and Merck, respectively. Standards of compounds employed through this study were provided by Sigma Aldrich, Riedel de Häen (Seelze, Germany) and Restek (Bellefonte, PA, USA), either as individual species, or as technical mixtures (case of polybrominated diphenyl ethers, PBDEs, fragrances and other ingredients of personal care products). A mixture of n-alkanes (C_8-C_{40}) in dichloromethane, provided by Supelco (Bellefonte, PA, USA), was employed to calculate the linear retention index (LRI) of compounds identified in dust samples. Anthracene d_{10} was used as internal surrogate (IS) added to samples (1 μg g^{-1}) before PLE extraction. This compound turns unsuitable to mimic the behaviour of the set of compounds identified in dust samples during extraction and determination steps; however, it serves to compensate variations in the volume of the final extract, and to detect changes in the sensitivity of the GC-TOF-MS instrument. Table 1 summarizes the selection of compounds considered to evaluate the performance of the GC-TOF-MS system, and the efficiency of the PLE extraction.

Stock solutions of each compound were prepared in MeOH (unless otherwise stated). Further dilutions and mixtures of analytes were made in AcOEt. The concentration of standards employed to build a customized library of accurate EI-MS spectra were in the range from 0.5 to 2 μg mL^{-1}.

2.2. Samples and sample preparation

Samples of dust were obtained from domestic vacuum cleaners equipped with cellulose bags. After reception, bags were opened and

Table 1
Analytical features of the determination method for a selection of compounds.

Compound	CAS number	Quantification ion	Qualification ion (relative abundance)	Retention time (min)	Linear range (ng mL^{-1})	Determination Coefficient (R^2)	Intra-day repeatability (%RSD) (100 ng mL^{-1}, $n = 12$)	Mass error (mDa)	LOQs (ng mL^{-1})	Recovery (%) ± SD[a]
Benzothiazole	95-16-9	135.0143	108.0034 (29)	7.93	2–1000	0.9997	11	0.4	2	110 ± 8
Dibutyl phthalate	84-74-2	149.0239	223.0971 (2)	16.64	8–1000	0.9995	9	- 0.1	8	105 ± 5
Anthracene	120-12-7	178.0783	152.0619 (11)	15.06	2–1000	0.9992	8	0.3	2	107 ± 10
1,2,4-Trichlorobenzene	120-82-1	179.9297	181.9268 (98)	7.21	2–1000	0.9988	12	1.8	2	113 ± 8
Chlorpyrifos	2921-88-2	196.9204	313.9577 (87)	17.01	2–1000	0.9986	9	−0.3	2	106 ± 10
BHT	128-37-0	205.1600	220.1832 (24)	11.75	2–1000	0.9992	11	−0.4	2	114 ± 10
Benzophenone 3	131-57-7	227.0696	151.0383 (69)	17.40	2–1000	0.9987	11	0.3	2	117 ± 7
Tonalide	21145-77-7	243.1753	187.1127 (33)	15.76	2–1000	0.9985	10	−0.2	2	106 ± 2
Tris (2-chloroethyl) phosphate	115-96-8	248.9853	204.9587 (70)	14.61	8–1000	0.9926	9	0.2	8	112 ± 10
Triclosan	3380-34-5	287.9506 (72)	218.0129 (100)	18.10	8–1000	0.9985	6	- 2.0	8	120 ± 9
Tinuvin 320	3846-71-7	308.1792	323.2026 (23)	21.15	2–1000	0.9992	6	−0.8	2	110 ± 4
Octocrylene	6197-30-4	360.1972 (59)	248.0713 (100)	22.73	4–1000	0.9995	5	−1.2	4	108 ± 1
Anthracene d_{10} (IS)	1719-06-8	188.1409	160.1122 (11)	15.04	–	–	–	0.2	–	–

[a] Recovery values for samples spiked at 1 μg g^{-1}.

their content sieved in order to remove course materials and debris. The fraction below 0.2 mm was selected for extraction. Sieved samples were stored at room temperature in closed, amber glass vessels. A total of 27 samples were processed. Most of them corresponded to homes (coded as H1 to H20) and cars (codes C1 to C5); moreover, a sample from a recreational yacht (Y), and another from an administrative building (AB) were also processed.

PLE extractions were carried out using 0.5 g of dust thoroughly mixed with 1 g of sand and transferred to PLE cells (11 mL volume) containing 1 g of silica at the bottom. The free volume above the dispersed sample was packed with sand. PLE conditions were adapted from a previous study dealing with the determination of UV absorbers in dust (Carpinteiro et al., 2010). In brief, extractions were carried out with AcOEt, at 90 °C and 1500 PSI. Two static extraction cycles (5 min each) were applied. Flush volume and purge time were set to 100% of the cell volume and 60 s, respectively. Primary extracts were concentrated to 5 mL, using a gentle stream of nitrogen, and filtered (0.20 μm pore size) before injection in the GC-TOF-MS system.

Spiked dust, employed to investigate the efficiency of the PLE extraction, was prepared by addition of a standard mixture of 12 selected compounds to a pool of sieved samples (added concentration 1 μg g^{-1}). Before extraction, the slurry was equilibrated overnight.

Procedural extraction blanks were prepared with each series of processed samples (typically a blank was extracted every 5–6 samples). Blank extracts, obtained from sorbent packed cells without the dust matrix, were adjusted to 5 mL and injected in the GC-TOF-MS system under same conditions as dust extracts. When noticeable, responses of compounds identified in blank extracts were subtracted from those obtained for dust samples.

2.3. Equipment

PLE extractions were carried out in an ASE 200 system, acquired from Dionex (Sunnyvale, CA, USA). Extracts were analysed using a GC-QTOF-MS instrument, obtained from Agilent (Wilmington, DE, USA), comprised of a 7890A gas chromatograph and a 7200 QTOF MS spectrometer, furnished with an EI source. The TOF mass analyzer was operated in the 2 GHz mode, offering typical mass resolution values (FWHM) of 6500 at m/z 131 Da. MS spectra were recorded in the profile mode (required for spectral deconvolution) at 2.5 Hz (5430 transients per spectrum) in the range of m/z values from 45 to 700 Da. The m/z axis was automatically recalibrated, every 3 injections, by infusion of perfluoro-tributyl amine (PFTBA) in the EI source.

Compounds were separated with a BP-5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) acquired from Agilent. The carrier gas (Helium) flow rate was 1 mL min^{-1}. The temperature of the GC oven was programmed as follows: 80 °C (2 min), rated at 10 °C min^{-1} to 280 °C (5 min). Standards and sample extracts (1 μL) were injected in the pulsed splitless mode (25 PSI, 1 min), with the injector temperature set at 280 °C. The splitless time and the split flow were 1 min and 50 mL min^{-1}, respectively. The transfer line and the EI source temperatures were 280 °C and 230 °C.

2.4. Software

The *MassHunter* software package was used to control all acquisition parameters in the GC-QTOF-MS system (including automated recalibration of the mass axis in the sequence of injections), and to process the obtained data. *MassHunter Qualitative* software (version B.08.00) was employed during inspection of raw GC-TOF-MS chromatograms, to extract the accurate EI-MS spectra of pure compounds, and to transfer these spectra to a customized library (PCDL). Deconvolution was carried out using the *Unknowns Analysis* (UA) function (based on the *SureMass* algorithm), integrated in the *MassHunter Quantitative* software (version B.08.00). The PCDL library was also managed using dedicated functions in the *MassHunter* software.

The *MS Search (v. 2.3)* software was employed to manage spectra compiled in the NIST17 low resolution EI-MS library, and to calculate the theoretical m/z ratios of fragment ions with known structures using the NIST-MS interpreter tool.

2.5. Method characterization and data analysis

The performance of the analytical procedure (compounds extraction and determination steps) was investigated for a selection of 12 compounds belonging to different chemical families, recognized as common pollutants in indoor dust, and covering different retention time regions. The recoveries of PLE extraction were estimated as the differences between concentrations obtained in spiked and non-spiked fractions of a pooled dust sample, divided by the added amount and multiplied by 100. Concentrations in dust extracts were calculated against calibration curves obtained for solvent-based standards, with anthracene-d_{10} added to calibration standards and samples (1 μg g^{-1} in the dust sample, equivalent to 0.1 μg mL^{-1} in extracts and standards) before PLE extraction.

Non-target screening of pollutants in dust extracts was based on deconvolution of raw GC-TOF-MS chromatograms, preliminary spectral comparison with the NIST17 library, and further confirmation against authentic standards. A PCDL library with accurate scan EI-MS spectra

of all the injected standard solutions (independently of whether compounds were finally confirmed in dust samples, or not) was created.

The concentration values corresponding to a group of 44 compounds in dust samples were estimated spiking the obtained extracts with increased concentrations (5 different addition levels) of these species. After subtraction of signals observed in procedural blanks (case of some organophosphorus compounds, diethyl phthalate and certain fragrances), the responses for each compound were corrected with the signal of anthracene-d_{10} and plotted versus added concentrations. Data were fitted to a linear model and values (semi-quantitative estimation of concentrations) in the dust samples were obtained considering the final extract volume (5 mL) and the extracted sample amount (0.5 g).

3. Results and discussion

3.1. Characterization of the determination procedure

This section shows an evaluation of several features of the analytical procedure in relation to accuracy of *m/z* values, the limits of quantification (LOQs) of the determination technique, and the efficiency of the extraction step for a selection of 12 model compounds. The GC-EI-TOF-MS system provided linear responses in the range of concentrations up to 1000 ng mL^{-1}. The instrumental LOQs (without considering sample preparation), defined as the lowest concentration providing a signal to noise ratio of 10 for the quantification ions, ranged between 2 and 8 ng mL^{-1}. The highest values corresponded to tris (2-chloroethyl) phosphate and triclosan, which are the species showing the poorest chromatographic performance within the group of model compounds. The intra-day repeatability in the responses (peak areas) for a standard mixture (100 ng mL^{-1} concentration) injected in three consecutive days ($n = 12$ injections) varied between 5 and 12%. Mass errors, calculated for the quantification ion at the above concentration level, stayed below 2 mDa, Table 1.

Sample preparation has a major effect in screening studies. Obviously, any compound not recovered from the dust matrix will remain undetected. On the other side, hard extraction conditions might result in too rich extracts, increasing the complexity of the obtained chromatograms. PLE extractions were carried out with AcOEt, under conditions reported in Section 2.2. The recoveries obtained for model compounds varied from 105% to 120%, with relative standard deviations below 10%.

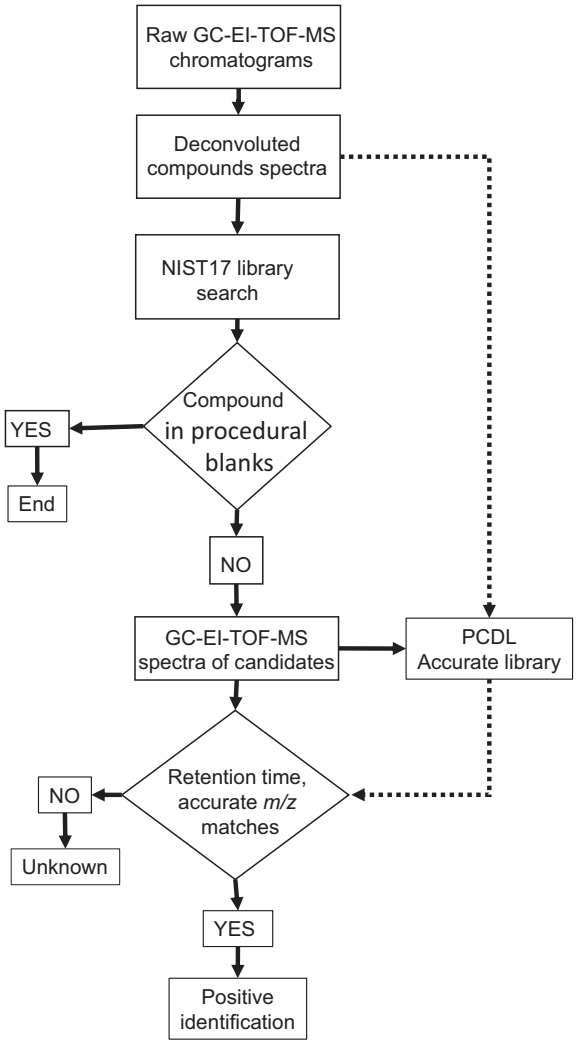

Fig. 1. Workflow followed during the non-target screening of semi-volatile compounds in dust samples.

3.2. Non-target screening of semi-volatile compounds

Fig. 1 shows the workflow followed to mine compounds from GC-EI-TOF-MS records of dust extracts. Deconvolution was limited to entities with a peak height above 5000 units, admitting a maximum variation of 5 mDa in the *m/z* ratios of ions through the series of spectra assigned to each compound (Zhang et al., 2014). Chromatograms were deconvoluted using four different time windows, ranging from 25 to 200% of the average peak width in each record.

Spectra of deconvoluted species were compared to those existing in the NIST17 library. In a first step, only nominal *m/z* values were considered. The comparison algorithm was a mix between forward and reverse modes (Blum et al., 2019) (weight factor 0.7, with 0 and 1 corresponding to pure reverse and forward modes, respectively). Candidates displaying normalized scores (0−100) above 70 and tentatively identified (at the same retention time) in at least 3 out of 27 processed samples (10% of samples) were pre-selected. Thereafter, the accurate *m/z* values for ions in the deconvoluted spectrum were compared with those provided by MS Interpreter (calculated *m/z* data) for fragment ions in the spectra of candidate compounds in the NIST17 library. Tentative identifications required differences lower than 5 mDa for two intense ions (including the molecular ion), or three fragment ions, when the molecular ion was absent in the EI-MS spectrum. Species showing similar intensities in procedural extraction blanks and dust extracts (average response for processed samples), such as benzophenone and iso-vanillin, were excluded from this list of tentatively identified semi-volatiles in dust. Other compounds detected in blanks, but present at relatively low levels in comparison with chromatographic peaks obtained for dust extracts (below 10%), were maintained in the list of tentative identifications. Some examples are certain phthalates (such as diethyl, dibutyl and bis (2-ethylhexyl) phthalate), organophosphorus species (tributyl, triphenyl and tris (1-chloroisopropyl) phosphate, fragrances (tonalide and galaxolide) and even some high production volume UV filters (octocrylene). Finally, commercial standards of each candidate were injected in the GC-EI-TOF-MS system for retention times and spectral match (maximum allowable differences equal to 0.1 min and 5 mDa, respectively) with those corresponding to deconvoluted species, Fig. 1. The experimental EI-TOF-MS spectra of all the injected standards (c.a. 170 compounds) were incorporated in a customized library, containing also their CAS numbers, retention times and LRI values.

Fig. 2 illustrates the workflow shown in Fig. 1 leading to identification of cannabinol in the extract from a dust sample. The raw chromatogram and that for deconvoluted components in the region from 21.4 to 23 min are shown in Fig. 2A and B, respectively. The spectra of component at retention time 22.19 min (peak highlighted in blue), and the low resolution spectrum (NIST17 library) of the candidate with the highest score are given in Fig. 2C and D, respectively. Differences between

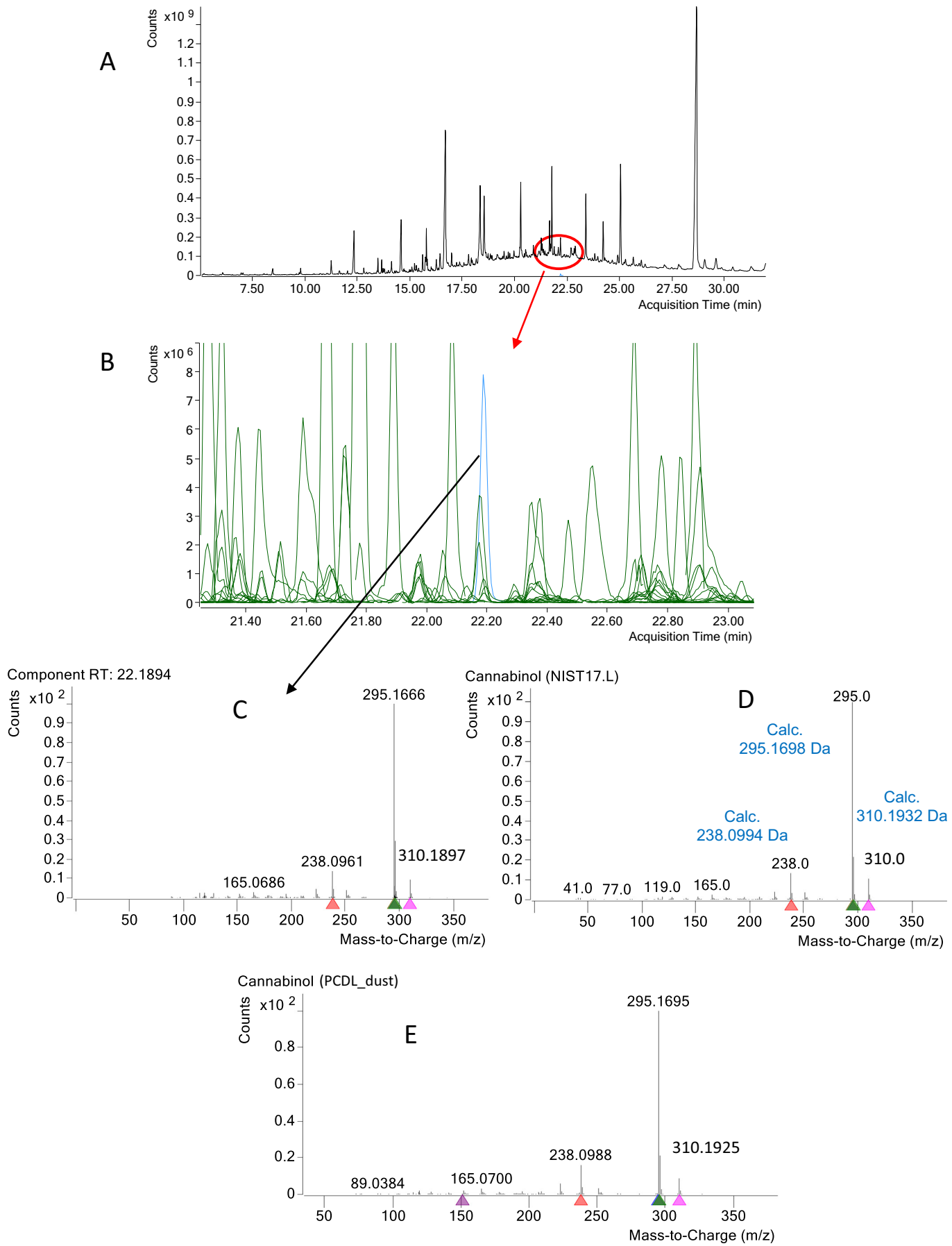

Fig. 2. Raw chromatogram (A) and deconvoluted components (B) for a non-spiked dust sample. Spectrum of a deconvoluted component(C), NIST17 spectrum of the candidate compound (D), and experimental accurate spectrum of cannabinol (E).

Table 2
Summary of compounds identified in the extracts from dust samples using a non-target screening approach.

Compound	CAS number	Known use	Retention time (min)	LRI	Molecular weight (Da)	Most intense ion (*m*/*z*)	Second ion (*m*/*z*) (relative intensity)	Other ions (*m*/*z*) (relative intensity)
Octanoic acid	124-07-2	Biogenic origin	7.10	1173	144.1150	73.0292	101.0577 (45)	115.0761 (17)
Nonanoic acid	112-05-0	Biogenic origin	8.48	1274	158.1307	73.0293	115.0762 (46)	129.0921 (36)
Dodecanoic acid	143-07-7	Biogenic origin	12.26	1561	200.1776	73.0291	129.0920 (50)	157.1232 (37)
Cholesterol	57-88-5	Biogenic origin	28.39	3140	386.3549	386.3546	301.2893 (94)	213.1642 (74)
Nicotine	54-11-5	Drug	9.64	1357	162.1157	84.0808	133.0761 (36)	161.1073 (21)
Ibuprofen	15687-27-1	Drug	13.03	1629	206.1307	161.1339	107.0500 (54)	163.0769 (77)
Cotinine	486-56-6	Drug	14.07	1722	176.0950	98.0559	176.0941 (25)	147.0687 (15)
Caffeine	58-08-2	Drug	15.56	1862	194.0804	194.0809	109.0625 (20)	137.0592 (5)
Cocaine	50-36-2	Drug	19.31	2263	303.1471	82.0651	182.1177 (84)	303.1467 (15)
Dronabinol	1972 08 3	Drug	21.58	2543	314.2246	299.2015	231.1387 (90)	314.2249 (70)
Cannabinol	521-35-7	Drug	22.10	2611	310.1933	295.1695	238.0988 (16)	310.1925 (9)
p-Toluidine	106-49-0	Dye	5.58	<1100	107.0735	106.0654	107.0727 (67)	77.0385 (14)
Benzenamine, 2,4,5-trichloro-	636-30-6	Dye	12.15	1554	194.9409	194.9411	123.9953 (18)	196.9383 (96)
Indigo	482-89-3	Dye	25.21	2926	262.0742	262.0753	205.0772 (24)	234.0799 (22)
Tributyl phosphate	126-73-8	Flame retardant	13.30	1652	266.1647	98.9843	155.0469 (11)	211.1095 (4)
Tris (2-chloroethyl) phosphate	115-96-8	Flame retardant	14.61	1771	283.9539	248.9853	204.9587 (70)	142.9661 (66)
Tris (1-chloroisopropyl) phosphate[a]	13674-84-5	Flame retardant	15.03	1811	326.0008	125.0010	98.9843 (90)	277.0165 (15)
Tris (1,3-dichloroisopropyl) phosphate	13674-87-8	Flame retardant	20.07	2353	427.8839	98.9844	190.9438 (70)	380.8985 (38)
Tris (2-butoxyethyl) phosphate	78-51-3	Flame retardant	20.59	2417	398.2433	125.9998	85.0647 (99)	299.1618 (19)
Triphenyl phosphate	115-86-6	Flame retardant	20.62	2421	326.0708	326.0672	215.0275 (30)	169.0658 (28)
Tris (2-ethylhexyl) phosphate	78-42-2	Flame retardant	21.06	2477	434.3525	98.9844	71.0854 (12)	211.1096 (1)
Cresyl diphenylphosphate	26444-49-5	Flame retardant	21.30	2507	340.0865	340.0871	165.0709 (25)	229.0428 (20)
BDE-47	5436-43-1	Flame retardant	21.65	2553	485.7106	325.8772	485.7124 (91)	487.7104 (59)
Tricresyl phosphate[a]	563-04-2	Flame retardant	22.83	2702	368.1167	368.1180	165.0706 (33)	243.0578 (21)
BDE-100	189084-64-8	Flame retardant	23.34	2758	564.6245	403.7863	563.6223 (95)	296.8737 (22)
BDE-99	60348-60-9	Flame retardant	23.84	2811	564.6245	403.7863	563.6223 (95)	296.8737 (22)
Methyl anthranilate	134-20-3	Fragrance	9.59	1354	151.0633	119.0377	151.0642 (56)	92.0258 (36)
Coumarin	91-64-5	Fragrance	10.90	1453	146.0368	118.0412	146.0362 (87)	89.0384 (40)
Ethyl vanillin	121-32-4	Fragrance	11.36	1489	166.0630	137.0251	166.0646 (35)	109.0299 (13)
alpha-Isomethylionone	127-51-5	Fragrance	11.37	1490	206.1671	135.0806	107.0856 (57)	150.1039 (40)
Lilial	80-54-6	Fragrance	11.94	1537	204.1514	189.1277	131.0854 (50)	147.1165 (36)
2-Naphthyl methyl ketone	93-08-3	Fragrance	13.05	1630	170.0732	155.0496	127.0545 (94)	170.0729 (49)
Alpha-Hexylcinnamaldehyde	101-86-0	Fragrance	14.47	1758	216.1514	129.0699	115.0542 (70)	145.0662 (37)
Benzyl Benzoate	120-51-4	Fragrance	14.70	1780	212.0837	105.0335	194.0728 (21)	91.0541 (38)
Isopropyl myristate	110-27-0	Fragrance	15.23	1830	270.2559	60.0215	229.2705 (55)	211.2076 (39)
Galaxolide	1222-05-5	Fragrance	15.66	1872	258.1984	243.1747	213.1633 (40)	258.1973 (16)
Tonalide	21145-77-7	Fragrance	15.77	1882	258.1984	243.1753	187.1127 (32)	258.1980 (18)
Benzyl salicylate	118-58-1	Fragrance	15.81	1887	228.0786	91.0542	228.0780 (5)	65.0385 (9)
2,4-Toluene diisocyanate (2,4-TDI)	584-84-9	Isocyanate	9.69	1367	174.0429	174.0422	145.0396 (78)	146.0468 (55)
Fluorene	86-73-7	Pah	12.72	1601	166.0783	166.0776	82.5345 (11)	165.0702 (99)
Phenanthrene	85-01-8	Pah	14.95	1803	178.0783	178.0781	152.0619 (13)	176.0624 (20)
Anthracene	120-12-7	Pah	15.06	1814	178.0783	178.0780	152.0619 (11)	176.0622 (20)
9,10-Anthracenedione	84-65-1	Pah	16.90	2005	208.0524	208.0518	180.0570 (78)	152.0617 (74)
Pyrene	129-00-0	Pah	17.79	2091	202.0783	202.0781	101.0387 (14)	200.0622 (22)
Fluoranthene	206-44-0	Pah	18.30	2148	202.0783	202.0782	101.0388 (16)	200.0624 (23)
Chrysene	218-01-9	Pah	21.28	2504	228.0939	228.0950	113.0384 (12)	226.0787 (31)
Phthalimide	85-41-6	Pesticide	11.11	1469	147.0320	147.0278	104.0235 (63)	103.0386 (55)
Piperonyl butoxide	51-03-6	Pesticide	20.70	2431	338.2053	176.0839	149.0603 (15)	119.0855 (9)
Tetramethrin[a]	7696-12-0	Pesticide	21.08	2479	331.1784	164.0711	123.1170 (21)	107.0494 (7)
Phthalic anhydride	85-44-9	Plasticizer intermediate	9.21	1326	148.0160	104.0227	76.0282 (56)	50.0134 (7)
Dimethyl phthalate	131-11-3	Plasticizer	11.02	1463	194.0579	163.0422	77.0406 (18)	133.0306 (14)
Diethyl Phthalate	84-66-2	Plasticizer	12.72	1602	222.0089	149.0234	177.0544 (15)	121.0283 (7)
4-Methyl benzene sulfonamide	70-55-3	Plasticizer	13.58	1677	171.0354	91.0544	171.0352 (44)	155.0164 (24)
N-butyl benzene sulfonamide	3622-84-2	Plasticizer	14.87	1795	213.0823	141.0010	170.0276 (62)	158.0274 (14)
Dibutyl phthalate	84-74-2	Plasticizer	16.64	1970	278.1518	149.0234	121.0309 (4)	104.0257 (2)
Tributylacetyl citrate	77-90-7	Plasticizer	19.34	2267	402.2254	185.0769	129.0149 (73)	329.1533 (3)
Benzyl butyl phthalate	85-68-7	Plasticizer	20.18	2637	312.1362	149.0232	91.0537 (35)	206.0930 (12)
Bis (2-ethylhexyl) phthalate	117-81-7	Plasticizer	21.69	2557	390.2770	149.0240	167.0338 (19)	279.1589 (4)
Bisphenol A	80-05-7	Polymer additive	18.69	2191	228.1150	213.0909	119.0487 (24)	228.1143 (16)
Ethanol, 2-phenoxy-	122-99-6	Preservative	7.99	1240	138.0681	94.0423	138.0688 (36)	77.0394 (24)
Methylparaben	99-76-3	Preservative	10.96	1458	152.0473	121.0299	152.0467 (26)	93.0333 (11)
Benzoic acid, p-tert-butyl-	98-73-7	Preservative	11.40	1491	178.0994	163.0757	135.0442 (31)	178.0988 (7)
BHT	128-37-0	Preservative	11.75	1521	220.1827	205.1600	220.1832 (25)	177.1285 (19)
Ethyl paraben	120-47-8	Preservative	11.82	1527	166.0630	121.0301	138.0309 (31)	166.0623 (12)
2-Hydroxy-biphenyl	90-43-7	Preservative	11.93	1536	170.0732	170.0721	141.0696 (42)	115.0540 (28)
Propyl paraben	94-13-3	Preservative	13.00	1626	180.0786	121.0294	138.0312 (62)	93.0335 (8)
Butyl paraben	94-26-8	Preservative	13.66	1685	194.0943	121.0294	138.0311 (82)	93.0329 (8)
Octyl isothiazolinone	26530-20-1	Preservative	15.46	1853	213.1187	100.9927	114.0008 (87)	180.1378 (32)
Triclosan	3380-34-5	Preservative	18.12	2127	287.9512	218.0129	287.9506 (72)	145.9685 (54)
Benzophenone 3	131-57-7	UV filter	17.41	2051	228.0786	227.0696	151.0383 (69)	228.0761 (53)
Tinuvin P	2440-22-4	UV filter	17.77	2089	225.0902	225.0868	168.0816 (14)	196.0788 (9)
Ethylhexyl-metoxycinnamate	5466-77-3	UV filter	19.88	2330	290.1882	178.0639	161.0690 (43)	133.0654 (15)
Tinuvin 326	3896-11-5	UV filter	21.83	2577	315.1138	300.0925	315.119 (40)	272.0609 (23)

(continued on next page)

Table 2 (*continued*)

Compound	CAS number	Known use	Retention time (min)	LRI	Molecular weight (Da)	Most intense ion (*m/z*)	Second ion (*m/z*) (relative intensity)	Other ions (*m/z*) (relative intensity)
Octocrylene	6197-30-4	UV filter	22.74	2690	361.2042	248.0713	232.0766 (89)	360.1972 (59)
Octabenzone	1843-05-6	UV filter	23.59	2785	326.1883	213.0555	326.1880 (31)	137.0236 (26)
Avobenzone	70356-09-1	UV filter	23.80	2807	310.1569	135.0444	310.1564 (78)	161.0963 (38)
Benzothiazole	95-16-9	Vulcanization accelerator	7.93	1236	135.0143	135.0145	108.0034 (29)	68.9796 (10)
2-Hydroxy-benzothiazole	934-34-9	Vulcanization accelerator	13.59	1683	151.0092	151.0090	96.0027 (58)	123.0138 (55)

[a] Compounds showing several isomers. The reported retention times and LRI values correspond to the 1st isomer.

calculated and *m/z* ratios for three intense fragments in these two spectra remain around 3 mDa. The accurate experimental spectrum for a standard of the candidate (CAS number 521-35-7, Fig. 2E) confirmed that it corresponded to cannabinol.

The information provided by accurate EI-MS spectra was not always as selective as that depicted in Fig. 2 for cannabinol. Sometimes, several candidates show very similar scores when performing the NIST17 library search. Typical examples are certain series of homologue compounds, whose spectra do not contain the molecular ion (i.e. most congeners in the series of parabens and phthalates); and isomeric species displaying identical (such as anthracene and phenanthrene), or very similar EI-MS spectra (case of galaxolide and tonalide). In these cases, final compound identification requires combining spectral information and retention time, or LRI, values.

Table 2 summarizes a list of 78 compounds identified (confirmed against authentic standards) following the non-target screening workflow described in Fig. 1. The table includes their CAS numbers, LRI data, monoisotopic molecular mass, and the experimental *m/z* values for three representative ions in their spectra. The list of compounds is not comprehensive (attending to the tentative identification criteria showed in Fig. 1), but limited to species available in the laboratory for identity confirmation. Compounds are classified attending to known applications (in some cases the same species could be included in different groups), and sorted by increasing retention times within each family. Most of them belong to the groups of plasticizers, including phthalates and alternative species already reported in indoor dust (i.e. tributylacetyl citrate) (Christia et al., 2019); flame retardants, particularly organophosphorus compounds; substances used as preservatives, fragrances and UV filters in personal care products and textiles; biogenic species (such as fatty acids and cholesterol from epithelial cells); and anthropogenic origin compounds, as PAHs. Other compounds mined from raw chromatograms are benzothiazole and its hydroxylated derivative, and residues of several drugs (pharmaceuticals, caffeine, nicotine and the illicit substances: cocaine and cannabinoids). In the latter case, our findings agree with previous studies by Cecinato and co-workers (Cecinato et al., 2017a, b) describing the presence of residues of illicit drugs and anti-inflammatory pharmaceuticals in interior environments.

Several compounds included in Table 2 have been hardly reported in dust. Some examples to highlight are: 2,4-toluene di-isocyanate (2,4-TDI), which is employed in polyurethane foams (Bekki et al., 2018) and it is considered as a dermal irritant and responsible of occupational asthma (Agarwal et al., 2012); high production volume dyes, such as indigo; and benzene sulphonamides (i.e. N-butylbenzene sulphonamide) employed as plasticizers (Marrocco et al., 2015). Phthalic anhydride, used as curing agent in the preparation of epoxy resins (Su et al., 2002), was also noticed in most samples. Octyl isothiazolinone, added to detergents, cosmetics and paints as preservative, and considered as a contact allergen (Garcia-Hidalgo et al., 2018), is reported in dust for the first time. Phthalimide, which has been previously found in atmospheric aerosols and urban dust (Falkovich and Rudich, 2001), was often detected in the processed samples. An additional example of species scarcely investigated in indoor dust is the highly toxic 2,4,5-trichlorobenzenamine (2,4,5-trichloroaniline), which likely results from degradation of dyes. To the best of our knowledge, above compounds were not previously determined in dust from indoor environments, neither using target methods, nor in the screening study of Moschet and co-workers (Moschet et al., 2018) based on combining data obtained by GC-TOF-MS and LC-QTOF-MS for extracts from indoor dust. However, a very recent report by the NORMAN network of laboratories has confirmed the presence of phthalic anhydride in dust. In the same work, phthalimide, indigo and 2,4-TDI are tentatively identified (confidence level 2 in the Schymanski scale), as well as some UV filters, i.e. avobenzone (confidence level 3), in a pooled sample of dust from indoor areas (Rostkowski et al., 2019). It is worth noting that, the NORMAN collaborative research involved the participation of >20 laboratories, sometimes using multidimensional GC with accurate MS detection. This approach offers higher chromatographic and spectral resolution than single GC combined with a first generation TOF-MS instrument employed in the current study. This fact reinforces the suitability of the workflow depicted in Fig. 1 for the non-target screening of unknown semi-volatiles in dust.

In most cases, the tentative identification of above compounds was just possible when combining accurate *m/z* values with sensitive EI-MS scan records and deconvolution tools. As example, under conditions reported in Section 2.3, the chromatographic peak of 2,4-TDI was partially overlapped with those of nicotine and a fatty acid (decanoic acid). Nicotine was present in few samples, and it does not share common fragment ions with 2,4-TDI. On the contrary, decanoic acid was ubiquitous in dust; moreover, the cluster of signals for the molecular ion of this fatty acid (172, 173 and 174 Da) overlapped that of 2,4-TDI (174 Da) when using a nominal resolution MS analyzer. The TIC and EIC chromatograms of both species (extraction window 5 mDa) are shown in Fig. 3A. Accurate spectra associated to the front and the tail regions of their partially overlapped peaks display fragmentation patterns compatible with the chemical structures of 2,4-TDI (Fig. 3B) and the fatty acid (Fig. 3C). In both spectra, the mass errors for fragment ions remained below 1 mDa.

3.3. Approaches for suspected-targets screening

Once an accurate EI-MS library is available, different strategies can be considered to evaluate the occurrence of compiled species (suspected-targets) in raw GC-EI-TOF-MS records. The first one is indicated with the dotted path shown in Fig. 1. It consists on deconvolution, using the *UA* algorithm, followed by comparison of obtained spectra with those included in the library. This option presents a relevant limitation: *UA* produces a shift in the *m/z* values of fragment ions in deconvoluted spectra. The bias, which showed always a negative sign (through our study), was in the range of 2–3 mDa. For instance, Fig. 4 illustrates the above statement with data obtained for diethyl phthalate. Plots included in this figure are: the EIC chromatogram for the most intense ion of the compound (*m/z* 149.0234 ± 0.005 Da) in a non-spiked sample (Fig. 4A); the average spectrum for the chromatographic peak (Fig. 4B); the PCDL spectrum for a standard of diethyl phthalate (Fig. 4C); and the deconvoluted spectrum (Fig. 4D) of the peak shown in Fig. 4A. Differences between *m/z* values of ions 149, 177 and 121 Da (nominal mass values) in the average peak spectrum and the library spectrum (Fig. 4B and C, respectively) stayed below 0.5 mDa. Same ions appeared at 2–3 mDa lower *m/z* values in the de-convoluted spectrum (Fig. 4D). So, the *UA* algorithm worsened the accuracy of the

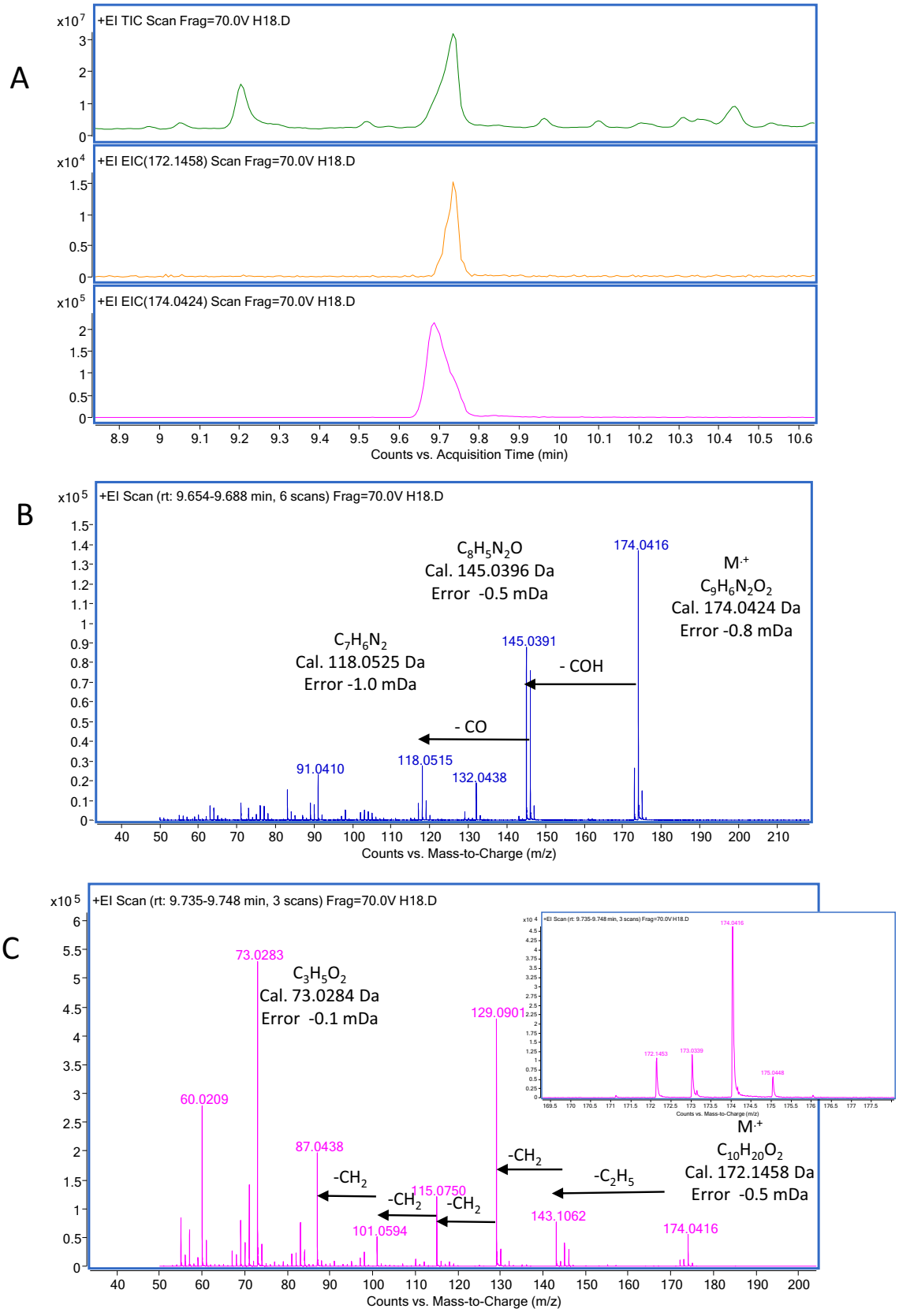

Fig. 3. Chromatograms (A) and spectra corresponding to partially overlapped species identified as 2,4-TDI (B) and decanoic acid (C).

experimental *m/z* values. This trend was also observed for cannabinol (see Fig. 2C).

As alternative to *UA*, the *Find by Fragments* (*FBF*) function can be used for the screening of suspected-targets. *FBF* searches for a reference fragment of every compound included in the accurate library (selected as that showing the highest value for the product between abundance and square *m/z* ratio) in raw GC-EI-TOF-MS records. When noticed, the presence of coeluting qualification ions (again selected from library

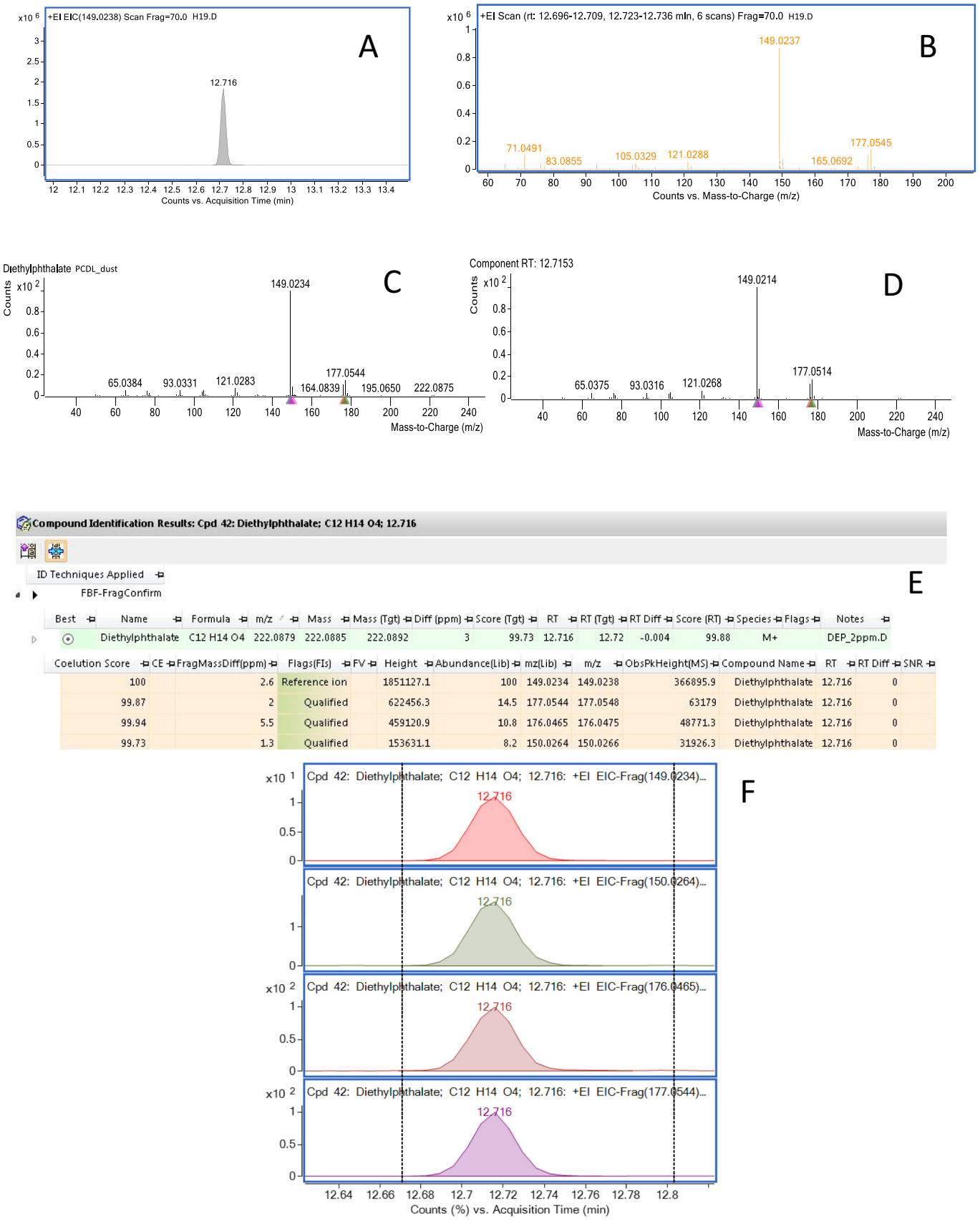

Fig. 4. Suspected-target identification of diethyl phthalate in a non-spiked dust extract. A, EIC chromatogram for *m/z* 149.0234 ± 0.005 Da. B, C and D, experimental, accurate library and deconvoluted spectra provided by the *Unknowns Analysis* algorithm. E and F, results obtained using the *Find by Fragments* function during identification diethyl phthalate in the same GC-EI-TOF-MS chromatogram.

spectra) is investigated. Threshold values regarding the minimum number of qualifying ions, the normalized coelution scores (0–100) with the reference ion, mass errors and retention time differences with the library are set by the user (values considered in the current research were 2 ions, 90 for coelution score, 5 mDa and 15 s). Fig. 4E and F show the results provided by this search function for the compound depicted in Fig. 4A. *FBF* identified the peak at 12.716 min (Fig. 4A) as diethyl phthalate, considering a reference ion at *m/z* 149.0234 Da and 3 qualifying ions. The match between experimental and library *m/z* values for the four ions ranged between 1 and 6 ppm (equivalent to <1 mDa for *m/z* 149), Fig. 4E. The coelution between reference and confirmation ions is shown in the EIC chromatograms depicted in Fig. 4F. In summary, on the contrary to *UA* deconvolution, *FBF* did not disturb experimental *m/z* values provided by the GC-TOF-MS instrument. Moreover, *FBF* dealt with centroid and profile spectra, whereas *UA* required storing the acquired data in the profile mode, which led to much heavier files for each raw chromatogram.

Fig. S1 compares the number of compounds identified by *UA* and *FBF* applied to process the same GC-EI-TOF-MS records, corresponding to 8 different dust samples. In both search approaches, the maximum allowed difference with library retention times was set at 15 s, and the minimum peak intensity set at 5000 units. *UA* positive identifications required differences below 5 mDa for at least three intense ions between deconvoluted and the PCDL spectra. Using *FBF*, same mass error was permitted for the reference and two qualifying ions. For six out of eight samples, FBF reported a slightly higher number of positive identifications than UA. The percentage of common species identified using both algorithms stayed around 80%. So, despite the above reported advantages of *FBF*, the use of both algorithms provides complementary information (increasing the number of identified species) during screening of suspected targets.

3.4. Semi-quantitative determination of semi-volatile compounds

Table 3 summarizes the percentage of positive samples, the median, the 1st and the 3rd quartiles of the semi-quantitative concentrations (μg g^{-1}) estimated for a selection of 44 compounds in 27 samples of dust. Reported values were obtained by addition of known amounts of these compounds to a dust extract (matrix-matched calibration), after blank subtraction, following the methodology reported in Section 2.5. The estimated concentrations for each sample, the determination coefficients (R^2) of the addition graphs, and the quantification ion selected for each compound are given as Supplementary material, Table S1. The qualifying ions were selected from Table 2. Data in Table 3 and Table S2 are semi-quantitative estimations. For most compounds (except those compiled in Table 1), the reported data are uncorrected neither for uncomplete PLE extraction yields, nor for potential changes in the response of the GC-TOF-MS system among different dust sample extracts.

Fig. S2 shows the EIC chromatograms (extracted mass window 5 mDa) for the quantification and a qualifying ion of four compounds (tributylacetyl citrate, octyl isothiazolinone, benzothiazole and ibuprofen), in non-spiked (dotted line) and spiked (continuous line) fractions of the same dust extract. The spiked concentration is given in the heading of each EIC chromatogram. Chromatograms corresponding to selected compounds in a procedural blank and in the extract from a non-spiked sample (code H16, Table S1) are shown in Fig. S3. In all cases, blank responses remained below 10% of those obtained for the non-spiked dust sample. In general, bis (2-ethylhexyl) phthalate was the compound displaying the highest response in blanks. However, when compared with that in dust extracts (semi-quantitative estimation of its concentration required to change from splitless to split injection mode), the blank contribution was negligible.

Apart from the drugs of abuse (cocaine, dronabinol, nicotine and the related species cotinine) the rest of compounds in Table 3 were found in >60% of the processed samples. The median concentrations for 20 out of 44 compounds stayed above 1 μg g^{-1}. This group included not only well-known indoor pollutants (phthalates, phosphates, vulcanization agents and certain UV filters), but also four compounds (phthalimide, avobenzone, 2,4-TDI and indigo) whose concentrations are estimated for the first time in indoor dust, Table 3. The interval of concentrations comprised between the 1st and the 3rd quartile for these compounds varied from 0.89 μg g^{-1} (phthalimide) to >30 μg g^{-1} (indigo). Despite data summarized in Table 3 and Table S1 are semi-quantitative estimations, they are in consonance with concentrations reported in previous works dealing with quantification of preselected target compounds using validated analytical procedures, see Table S2.

Table 3
Percentage of positive samples, median, 1st and 3rd quartile of concentrations estimated in 27 samples of indoor dust. Values in μg g^{-1}.

Compound	Positives (%)	Median	1st quartile	3rd quartile
Fluorene	81%	0.09	0.03	0.20
Benzenamine, 2,4,5-trichloro-	85%	0.11	0.06	0.24
Anthracene	70%	0.14	0.03	0.21
2-Hydroxy biphenyl	93%	0.15	0.05	0.33
Tributyl phosphate	93%	0.16	0.09	0.22
Tricresyl phosphate	100%	0.19	0.14	0.96
Tinuvin 326	100%	0.20	0.12	0.62
Pyrene	100%	0.23	0.15	1.00
Tetramethrin	89%	0.25	0.12	0.80
Tris (2-chloroethyl) phosphate	96%	0.26	0.07	0.89
Triclosan	93%	0.28	0.13	0.84
Fluoranthene	100%	0.33	0.18	1.79
Tinuvin P	93%	0.34	0.13	0.81
Phthalic anhydride	96%	0.37	0.18	5.01
Propylparaben	70%	0.42	0.24	0.74
Cotinine	44%	0.44	0.13	1.16
Octabenzone	89%	0.50	0.24	1.66
Tonalide	100%	0.52	0.25	2.22
Tris (1,3-dichloroisopropyl) phosphate	100%	0.66	0.09	4.51
Phenanthrene	100%	0.67	0.34	1.53
Ibuprofen	70%	0.69	0.42	2.60
Galaxolide	100%	0.75	0.54	12.53
Octyl isothiazolinone	63%	0.82	0.31	3.88
Dronabinol	30%	0.82	0.36	18.20
Nicotine	48%	1.15	0.50	7.47
Methylparaben	67%	1.45	0.52	3.69
E-ethylhexylmetoxycinnamate	100%	1.54	0.75	6.53
Phtalimide	93%	1.77	0.89	4.81
Tributyl acetylcitrate	100%	1.94	1.17	5.55
Diethyl Phthalate	100%	1.94	1.19	3.89
Benzophenone 3	100%	1.96	0.88	7.06
Caffeine	96%	2.12	0.86	10.49
Triphenyl phosphate	100%	2.27	0.50	4.66
Avobenzone	100%	2.58	0.91	6.41
2,4-TDI	100%	2.87	1.40	5.87
Benzothiazole	100%	2.96	1.27	7.83
Bisphenol A	96%	3.36	1.61	6.97
Tris (1-chloroisoproyl) phosphate	100%	3.38	1.78	11.85
2-Hydroxybenzothiazole	100%	3.61	1.56	9.81
Benzoic acid, p-tertbutyl	74%	3.98	1.80	6.84
Cocaine	30%	4.25	0.39	10.55
Indigo	89%	10.30	1.26	34.75
Bis(2-ethylhexyl)phthalate	100%	14.06	8.26	27.00
Octocrylene	100%	17.70	4.62	33.57

4. Conclusions

Accurate EI-MS spectra contain valuable information for the comprehensive screening of semi-volatile compounds existing in dust samples extracts. Comparison with low-resolution MS libraries serves as a first sieve for tentative identification after chromatographic deconvolution. The algorithm employed by the *Unknowns Analysis* software still requires some refining to correct the bias in the *m/z* values

assigned to ions in deconvoluted spectra. Such requirement is mandatory to fully exploit the benefits of state-of-art TOF mass analyzers, rendering experimental errors below 1 mDa. Given that EI is regarded a universal ionization technique in GC analysis, the spread of GC-EI-HRMS systems for screening purposes will be controlled by the compilation rate of accurate in EI-MS libraries. Combination of the data mining strategy described in this study, with molecular information provided by the same instrument, under positive chemical ionization (PCI), would increase the number of semi-volatile compounds identified in indoor dust. The complementary character of both ionization modes is particularly relevant to discern among compounds whose EI spectra contain just common fragment ions, despite they show different molecular weights.

Results obtained in the current study have confirmed the presence of some potentially hazardous compounds in indoor environments, such as 2,4-TDI, N-butylbenzene sulphonamide, indigo, phthalic anhydride and octyl isothiazolinone, which have not been previously quantified in dust. Further research should address the optimization and validation of extraction and determination approaches for the quantitative determination of these compounds. Obtained data will serve to obtain a more reliable assessment of potential risks associated to dermal exposure and ingestion of dust in indoor environments.

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Conflict of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.192.

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