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A method for rapid, non-targeted screening for environmental contaminants in household dust

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ABSTRACT

Household dust can be a major source of human exposure to environmental contaminants such as polybrominated diphenyl ethers, pesticides, and other compounds. This work shows a screening technique that may be used to identify components in an environmental sample as xenobiotics based on mass spectral characteristics of classes of compounds that may be expected to be present in the environment. Household dust (SRM-2585) from the National Institute of Standards and Technology (NIST) was extracted with hexane using accelerated solvent extraction. Large molecules, such as triglycerides and fatty acids were removed with gel permeation chromatography. The extract was then concentrated and analyzed by comprehensive two dimensional gas chromatography coupled to a time of flight mass spectrometer. The resulting peak table was automatically filtered to identify compound classes such as phthalates, polycyclic aromatic hydrocarbons and their heterocyclic analogs, chlorinated compounds, brominated compounds, and nitro compounds. While phthalates can be identified by abundances at specific masses, the identification of the remaining classes is based on the identification of the molecular ion and identification of isotope clusters or other spectral characteristics. The technique detected compounds identified and quantified by NIST as well as compounds not identified by NIST in the sample. By comparison with concentrations determined by NIST for the analytes found, the technique is able to identify analytes in these compound classes at concentrations as low as 10–20 ng/g dust.

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1. Introduction

Human exposure to environmental contaminants occurs through routes such as food ingestion, inhalation and/or dermal contact. Humans are primarily exposed to traditional environmental pollutants, such as polychlorinated biphenyls and persistent pesticides, through ingestion of food such as fatty fish. However, household dust has also become recognized as a significant exposure source for an increasing number of compounds. Recently it has been shown that the main route of exposure of Americans to polybrominated diphenyl ethers (PBDEs) may be through exposure to indoor dust [1]. However, even when it is not the principal source of exposure in children, household dust has been identified as a major source of environmental contaminants including pesticides, polycyclic aromatic hydrocarbons (PAHs), phthalates, several metals, and other chemicals of human health concern [2]. One review of pollutants in house dusts lists over 50 pesticides, 14 endocrine-disrupting compounds, and various flame retardants, plasticizers, and other xenobiotics [3]. It would then follow that household dust should be further examined for the presence of other chemicals of human health concern to give us a more complete understanding of exposure risks in the home.

Searching for such unknown and even unanticipated chemicals requires a non-targeted, analytical approach. The quantity of data becomes an issue, however, as was noted in the non-target analysis of ground and surface water with GC-TOFMS and LC-TOFMS [4,5]. The authors of these works recommend use of mass spectral libraries, including theoretically derived libraries for anticipated compounds, and they recommend manual review and interpretation for spectra not identified by searches of these libraries.

But the more complex matrix of household dust requires a more powerful separation technique, such as GCxGC. Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC-TOFMS) allows for separation and collection of full scan spectral data for thousands of compounds to low pg/μL concentrations. With this increased analytical capability, the task of identifying which compounds might be of interest for further study increases significantly. Without advance knowledge of which compounds might be of interest, manual evaluation of each compound found in the sample would be time-prohibitive.

The scripting feature in the LECO ChromaTOF® software allows for the classification of chromatographic peaks based on recognizable features in fragmentation patterns. The user creates scripts, written in Microsoft® VBScripts language, to evaluate the mass

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spectral data for these features. This approach has been used to identify chlorine, bromine, and sulfur containing compounds in a GCxGC-TOFMS chromatogram of citrus oil [6] using isotopic ratios obtained from acquired spectra. Because of the effort involved in obtaining spectra and creating scripts, however, this effort was limited to compounds containing fewer than 8 chlorine or 4 bromine atoms. Other techniques previously applied to GCxGC-TOFMS data have made use of rules determined by multivariate or neural network analysis of spectra, resulting in mathematically determined sets of ratios of signals at specific mass values [7–9].

The mass spectra for polycyclic aromatic hydrocarbons (PAHs) have a less distinct signature than compounds containing bromine or chlorine. While these compounds have little to distinguish them as PAHs beyond a significant molecular ion and a lack of fragmentation, separation into two chromatographic dimensions allows the location on the two-dimensional plane to aid in classification. In previous work, PAHs have been identified in GCxGC chromatograms of airborne particulate matter [9,7] and of tobacco smoke [8]. In the cited works, the identification of PAHs and other compounds was determined by examination for specific, characteristic masses. For example, PAHs were sought by looking for compounds with a base peak of m/z 128, 178, 202, or 228. Alkyl substituted PAHs were sought by examining for compounds with other base peaks. While effective in the examples shown, this strategy lacks specificity for use with samples containing greater chemical diversity. This leads to the need for a more general filter that may be expected to provide detection of a wider number of structurally related compounds, but a filter sufficiently specific to provide a manageable number of false positive results. Such structurally related compounds could include benzothiophenes and aza-PAHs, which could pose a human health risk in occupational settings, such as for asphalt workers [10].

This paper presents a method for screening complex environmental samples and for classifying detected analytes belonging to the compound classes: PAHs, phthalates, halogen containing compounds and nitro compounds. Automated identification of signature mass spectral patterns combined with location in the GCxGC chromatographic plane is used to identify compounds that may be members of these classes. This technique is applied to a dust sample – certified reference material (SRM-2585) from the National Institute of Standards and Technology (NIST). The reference material is certified to contain specified amounts of compounds belonging to the classes sought.

2. Experimental

2.1. Chemicals and materials

Dichloromethane and n-hexane were of pesticide grade and obtained from Tedia Co. Inc. (Fairfield, OH). Research grade nitrogen and helium were obtained from Airgas South Co. (Chamblee, GA) and Hydromatrix used in the accelerated solvent extractor (ASE) as a filler was from Varian, Inc. (Palo Alto, CA).

Household dust used in this study was NIST Standard Reference Material SRM-2585 and was obtained from National Institute of Standards and Technology (Gaithersburg, MD). This dust is provided at approximately 2.1% moisture and of a particle size sufficient to pass through a 90 μm sieve.

2.2. Sample preparation

One gram of dust was extracted with hexane in a Dionex ASE 200. The extraction was performed in an 11 mL cell with three extraction cycles at 110° C and a static time of 10 min. The flush volume was 60% of the cell volume, and the purge time was 60 sec with no preheating. This method has previously been shown yield a complete extraction of PBDEs [11].

The extract was evaporated to 1 mL in a TurboVap LV (Caliper Life Sciences, Hopkinton, MA). Removal of triglycerides, fatty acids and long-chain aliphatic compounds was performed on a high resolution gel permeation (GPC) column, PLgel 7.5 mm x 300 mm, with 50 Å pore size and 5 μ particle size (Varian, Inc., Palo Alto, CA, USA). Using a Gilson (Middleton, WI) high pressure liquid chromatography (HPLC) system, the injections and fraction collection were performed with a Gilson 215 liquid handler interfaced with a 306 pump and a UV/VIS-153 detector. The sample (100 μL of the 1 mL extract) was injected onto the GPC column using dichloromethane as the mobile phase at a flow rate of 1 mL/minute. The lipid fraction, defined as complete elution of all components of olive oil (0.5% by volume solution in dichloromethane), was discarded. The remaining sample components were collected until 12 minutes. The collected fraction was evaporated to 100 μL under a gentle stream of nitrogen using the TurboVap evaporator.

2.3. GCxGC-TOFMS

A LECO Pegasus® 4D system (LECO Corp., St. Joseph, MI, USA) with a 18 m x 0.18 mm x 0.18 μ Rxi5-MS (Restek, Bellefonte, PA, USA) column as the first dimension and a 1.2 m x 0.10 m x 0.10 μ BPx-50 (SGE Inc., Austin, TX, USA) column as the second dimension was used. The carrier gas was helium at a constant flow of 0.6 mL/min. One microliter of sample was injected in the splitless mode. The primary GC oven was programmed from 85° C, held for 2 minutes, and then ramped at 10° C/min to 325 degrees with a final hold time of 5 min. The secondary oven was programmed starting at 105° C, held for two minutes, and ramped at 11° C/min to 365° C with a final hold time of 5.39 min. The modulator was maintained at a temperature 30° C higher than the secondary GC oven using a modulation period of 4 sec and a hot pulse of 0.8 sec. The Pegasus 4D model used in this work uses liquid nitrogen cooling of the cold jets. Data were acquired over the mass range of 50 – 1000 amu at a scan rate of 150 spectra/sec.

The data were processed with a peak finding threshold of S/N 50:1. Deconvolution of mass spectra was performed automatically as a normal function of the instrument's software (ChromaTOF®). All chromatographic peaks were searched against the NIST (2008), Wiley (2008), and MPW (2007) mass spectral libraries (John Wiley & Sons Inc, Somerset, NJ). The scripting option was enabled in the ChromaTOF® software, allowing user-written scripts to be added as constraints to classification regions. These scripts filter chromatographic peaks to be included in classes according to criteria given for masses, abundances of masses, and ratios of abundances between masses, cf. Section 2.4. Scripts are constructed with Microsoft® VBScript language, a Visual Basic dialect.

2.4. Automated classification

Classification filters were created using the ChromaTOF classification feature to select compounds with spectral characteristics for the class, as established in scripts for the various classes. For PAHs, a specific region of the chromatographic plane was selected to restrict classification further and to thereby reduce the false hit rate. The classification region was drawn widely to include all of the PAHs seen in a standard mixture, but not so widely as to include compounds giving rise to false hits in the dust sample. In all other cases, the entire chromatographic plane was searched for compounds of each class. The critical features in the scripts are outlined below, and the scripts used in this paper are given in Supplemental Information 1 (SI 1). Names of functions are noted in this paper to assist in locating pertinent portions of the scripts listed in SI 1.

2.4.1. Identification of compounds containing chlorine or bromine

Compounds containing Chlorine or bromine were identified by matches to empirically derived ranges of isotope ratios used in the analysis of orange oil [6] or by a match to a theoretically predicted isotope cluster with computed match score. The theoretical isotopic ratios in the cluster are calculated based on a binomial expansion (function ionclusterA2()).

With both techniques, the probable molecular ion is identified in the spectrum by examining ions from high mass to low mass and seeking the first instance of an ion with an intensity at least six standard deviations greater than the mean of previously examined signals. When the abundance of a mass (m) is identified as significantly greater than the masses already examined, the next lower masses (m-1 and m-2) are examined to determine whether they are sufficiently more intense to indicate that the mass found would be the isotope peak of an A + 1 or an A + 2 element. If the mass examined does not meet these qualifications and does not show the presence of an m + 1 peak (expected for the molecular ion of a carbon containing compound), the signal for the ion being examined is deemed to be noise. If the intensity of this noise is greater than 10% relative abundance, the spectrum is assumed to be of poor quality and the search for a molecular ion is abandoned in that spectrum. If the noise is less that 10% relative abundance, the noise intensity is included in the computation of the cumulative mean and standard deviation of the noise encountered this far in the examination of the spectrum and the examination of ions continues to the next lower mass. This continues until a probable molecular ion is identified or the search is abandoned in the particular spectrum (function First_Parent()).

With the empirically determined ranges expected for isotope ratios, the masses in the spectrum are aligned with the expected ratios based on the most abundant mass in the cluster. If the ratios are within tolerance, the spectrum is accepted as a match.

When matching to the isotope pattern generated by binomial expansion, the entire spectrum is examined from the highest mass acquired to the apparent molecular ion for a match to an isotope cluster function (BrClMultipleByScore()). A match score between the computed ratios for the isotope cluster and for ions in the region of the spectrum under evaluation is computed as the cosine of the angle between two vectors. Each vector is constructed by using the abundance of the ions at M, M + 2, M + 4, etc. as the magnitude in a dimension of the vector, with as many dimensions as expected ions at M, M + 2, M + 4, etc. This method of detection is similar to that described by Anderegg [12]. The matching strategy is further constrained to avoid confusing weak, noisy halogen isotope clusters with noise. Masses farther from the most abundant mass in the cluster must have lower abundances than those closer to the most abundant mass when those masses are expected to have a significant difference in relative abundance from one to the next. Additionally, masses between the M, M + 2, M + 4, etc. must be less abundant than are the neighboring masses. Both techniques allows for the identification of chlorinated or brominated compounds that are minor components in spectra that are principally of other compounds. With polyhalogenated compounds, a sufficient number of masses is used to obtain a match, that attempts to match along the spectrum at masses above the apparent molecular ion do not result in excessive numbers of false negative hits and permit detection of isotope clusters that may be missed with the technique of matching molecular ions to sets of empirically derived ion ratios.

2.4.2. Identification of phthalates

The filter for dialkyl phthalates identifies spectra with a base peak of m/z 149 and the presence of m/z 150. The number of false hits was reduced by the additional constraint of the requiring the detection of masses 76 and 104 in the spectrum. These ions are expected as fragments resulting from the decomposition of the m/z 149 ion in phthalates [13] and thus would be expected to be highly likely to be found in the spectrum of any phthalate, reducing the number of false positives (function phthalate()).

2.4.3. Identification of PAHs

The script for identification of PAHs uses two strategies. In the first strategy, the filter selects spectra with a strong abundance of the molecular ion and possibly a strong abundance for M-1. The molecular ion was identified by the same procedure used to identify the molecular ion in of a halogen containing compound, cf. Section 2.4.1. The classification was further restricted by selecting only spectra in which all other ions have abundances below an empirically determined relative abundance of 50% of the molecular ion. In the second strategy, the filter classifies spectra with a strong molecular ion and may also have strong abundances for losses of 1 ($H^{\bullet}$), 15 ($CH3^{\bullet}$), and/or 29 ($C2H5^{\bullet}$). The search was further restricted by requiring all other ions to have an abundance of less than 25% relative to the molecular ion (functions onebigMolIon_thresh() and pahhuntert()). The PAH classification was further restricted by defining a region of the two-dimensional chromatogram where PAHs are expected, given that other molecules will have similar spectral properties.

2.4.4. Identification of aromatic nitro compounds

The filter for aromatic compounds containing a nitro-group presumes a detectable molecular ion and detectable ions for the neutral loss of $NO^{\bullet}$ and $NO_2^{\bullet}$ from the molecule. The probable molecular ion is identified by the same procedures as was used to identify the molecular ion in a halogen containing compound, cf Section 2.4.1. The probable molecular ion is examined to determine whether it would be a member of a pattern showing the molecular ion at M and fragments at M-30 and M-46. If the spectrum meets this criterion, the regions between M-46, M-30 and M are tested to ensure no signal in these regions is more abundant than the weakest of the M, M-30 or M-46 ions (function nitro()).

2.4.5. Evaluation of scripting-based classifications

Scripts were evaluated by analysis of a combined standard containing a mixture of two semi-volatiles standard mixtures (SVM-8270 and SVM-8271, Ultra Scientific, Kingston, RI) and 13 PBDE congeners (tri- to nonaBDE). The degree of accuracy was determined by counting the number of correct and incorrect assignments.

3. Results and discussion

3.1. Chromatographic considerations

The GCxGC-TOF chromatogram of the dust extract has over 10,000 peaks, as shown in Fig. 1. PAHs were observed in the chromatogram up to the limit imposed by the upper temperature limit of the column set (to PAHs of about C_{24}). While fatty acids were sufficiently reduced by GCP separation, some residue remains indicated by the large, tailing blobs seen between 1.5 and 2.0 seconds in the second dimension. This reduction in fatty acid content was sufficient to avoid excessive overloading of the second dimension column. No further reduction of the fatty acid content was attempted.

3.2. Filtering of the peak table by scripts

3.2.1. Effectiveness of filters

The filters correctly identified 78% of the target compounds in the GCxGC chromatogram of a standard mixture of semivolatiles and PBDEs, as demonstrated in Table 1. Additionally, the filters

Table 1
Frequency of correct classification by scripts of compounds in a standard mixture.

Compound class	Peaks present (N)	Peaks correctly identified [N (%)]
Chlorine and/or bromine compounds	37	29 (78%)
Phthalates	5	5 (100%)
PAHs	21	19 (90%)
Nitro compounds	11	5 (45%)

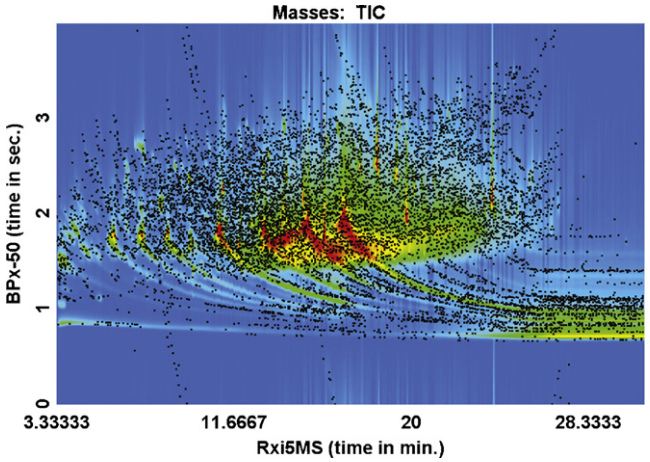

Fig. 1. GCxGC Chromatogram of the hexane extract of household dust with over 10,000 chromatographic peaks marked. The chromatogram is displayed showing retention times for two modes of sepration along two axes and signal intensity by color. The signal rises out of a plane (blue) and increasing signal is shown by a change of color from light blue to green, through yellow, and to red.

classified a number of compounds that were impurities in the standard mixture. The mass spectra and locations in the chromatogram were consistent with the class assignments made by the filters. The filter for PAHs was designed to include analogs containing heteroatoms—hence carbazoles and thiophenes were detected.

3.3. Identification of compounds in household dust

3.3.1. Compounds containing chlorine and bromine

When the scripts were applied to the chromatogram of the dust extract, the filters selected 240 peaks as compounds potentially containing chlorine, bromine, or both, shown in Fig. 2. The halogen cluster could be verified by visual inspection in 117 spectra.

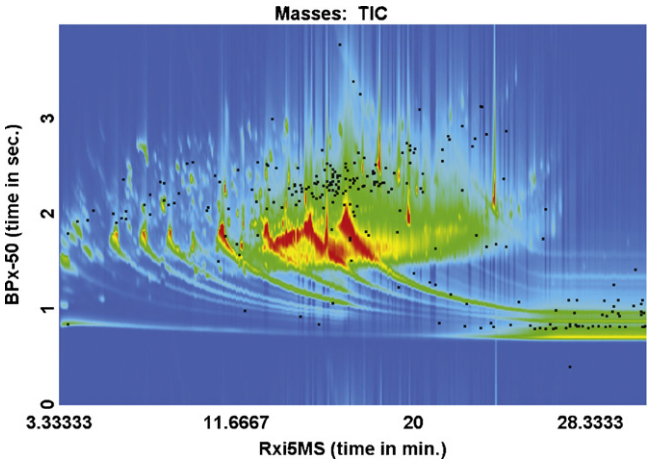

Fig. 2. Identification of chlorine and bromine-containing compounds in dust. 240 Chromatographic peaks were identified by the filters as containing chlorine or bromine. After manual review, 117 of these were confirmed to contain chlorine or bromine.

The application of scripts reduced the number of compounds for manual review from 10,000 to 240, thus making manual review a realistic possibility. The sensitivity of the scripts in classifying a compound as containing chlorine or bromine is further illustrated in Fig. 3. The major component of the mass spectrum is not a halogenated compound. A minor component, with its strongest signal at less than 3.5% relative abundance is identified only by the presence of the isotope cluster. According to a library search **constrained** to a mass range around the isotope cluster, the portion of spectrum corresponds to a hexachlorobiphenyl. The peak also falls on the trend line of other PCBs in the GCxGC chromatogram, supporting the identification of this minor component as a hexachlorobiphenyl. The coeluting, chlorinated compound in this case would not have been identified by a general library search — only the script indicated its presence. While not all spectra identified as representing chlorinated or brominated compounds can be tentatively identified to the level of a specific compound, as was the compound shown in Fig. 3, the presence of such a compound is shown, and the compound can be more specifically identified by other techniques, if needed.

The compounds identified in SRM-2585 included PCBs, PBDEs, chloroalkyl phosphate, pesticides, and pesticide degradation products, cf. Supplementary Information (SI 2). In the dust sample, NIST quantified 42 PCBs with concentrations ranging from 2 to 40 ng/g dust, while the screening technique identified 25 PCBs. Assuming that the screening technique has identified the more concentrated PCBs reported by NIST, the filtering technique can be estimated to identify PCBs at concentrations as low as about 10 ng/g dust. Similarly, NIST found 19 PBDEs at quantifiable levels, while the screening technique identified 11. NIST reported 14 pesticides, while the filtering technique detected 8. The filter identified dieldrin, *cis*- and *trans*-chlordane, heptachlor, and *trans*-nonachlor and 4,4'-DDE. According to NIST, their concentrations ranged from 88 to 261 ng/g dust. 4,4'-DDT, with a concentration of 111 ng/g dust as determined by NIST, was not detected. The filter identified heptachlor epoxide and pentachlorobenzene (11 and 21 ng/g dust), while 4,4'-DDD and 2,4'-DDT (27 and 45 ppb in dust) were not identified.

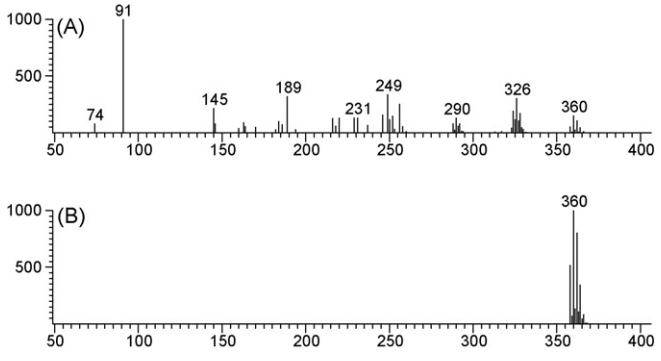

Fig. 3. Coeluting peak classified as containing chlorine by scripts (Spectrum A). The isotope cluster at m/z 358–368 has a maximum relative abundance of less than 3.5% in this spectrum. With a constrained search, the isotope cluster was identified as belonging to a hexachlorobiphenyl (Spectrum B).

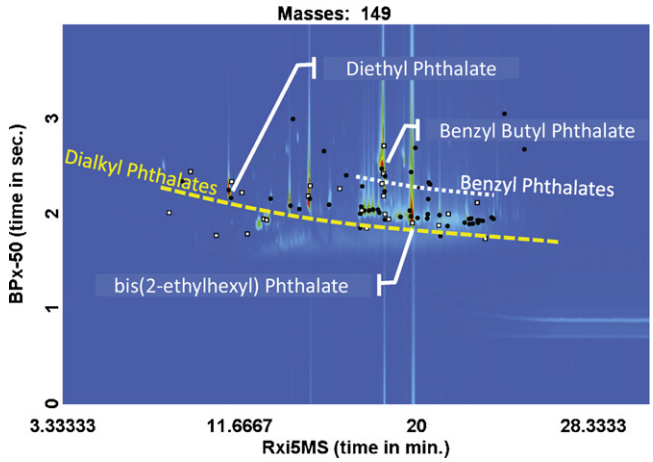

Fig. 4. Identification of dialkyl and alkyl benzyl phthalates by scripts. Of the 76 chromatographic peaks identified as having a base peak of m/z 149 (all marked peaks), 52 peaks were identified as potentially being phthalates (Solid black peak markers), based on the presence of m/z 104 and m/z 76. Of these, 33 spectra were consistent with phthalates. Trend lines for the two groups of phthalates are indicated.

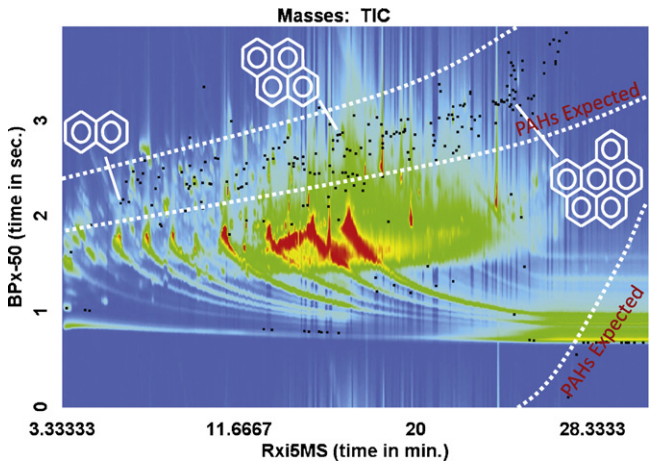

Fig. 5. Location of peaks matching the PAH spectral pattern with those identified by library searching. PAHs can be expected to fall into a band, shown starting at about 2 seconds in the second dimension and, as the chromatogram proceeds, falling later in the second dimension.

Other compounds tentatively identified in the dust sample included tris(2-chloroethyl)phosphate, tris(1,3-dichloroisopropyl) phosphate, and isomers of bromophenol, chloroaniline, dichloroaniline, trichloroanilne, trichlorobenzene, trichlorophenol, and tribromophenol. Compounds selected by the filters as containing chlorine are further detailed in Supplemental Information (SI 3).

3.4. Phthalates

Seventy six chromatographic peaks show m/z 149 as the base peak. The addition of a requirement that signals be detected for m/z 56 and 104, left only 52 peaks selected. The peaks dropped by the addition of this constraint were either clearly not phthalates or showed little, if any, additional information to help identify the compounds.

Compounds matching the criteria given for phthalates show the bulk falling close to two trend lines, cf. Fig. 4. The lower trend line represents peaks consistent with dialkyl phthalates. The most intense peaks on this trend line correspond to diethyl phthalate, dioctyl phthalate, and bis(2-ethylhexyl)phthalate, which were confirmed by comparison to a reference standard. A parallel trend line is drawn just below the peak for butylbenzylphthalate. Benzylalkylphthalates would be expected to fall along this parallel line. Peaks falling between these two trend lines are consistent with cyclohexyl alkyl esters. Thirty-three of the 52 peaks identified by the scripts can be confirmed as phthalates.

3.5. PAHs and PAH analogs

PAHs and analogs were identified by searching the spectral data for a molecular ion or molecular ion minus one as the base peak and allowing for fragment ions below an empirically determined threshold of 50% relative abundance (function onebigMollon_thresh()). A cutoff of 50% relative abundance was selected because above that level, the number of molecules incorrectly classified increases rapidly. In a second strategy, allowance was made for abundances above 50% for loss of methyl or ethyl from the molecular ion (function pahhuntert()). With this second approach, a cutoff of 25% relative abundance for all was selected, to avoid increasing numbers of incorrectly classified peaks. If a compound was identified by either strategy, it was added to the list of identified compounds. NIST reported concentrations for 70 PAHs, including biphenyls and one sulfur-containing analog. With the screening technique, we were able to classify 106 compounds as PAHs or analogs. We were able to detect all of the PAHs reported by NIST at a concentration over 300 ng/g dust. The additional compounds found by the filtering technique included biphenyls and sulfur, nitrogen, and oxygen analogs of PAHs (listed in supplementary Table 3). Additionally, the technique selected some PAH oxides, such as fluorenone, and other compounds identified as probable PAH ketones of higher carbon numbers (Fig. 5).

3.6. Nitro compounds

Application of the nitro compounds filter to the dust sample resulted in eight compounds flagged as potential nitro compounds. Of these, one was identified as dichloran (2,6-dichloro-4-nitroaniline) and was confirmed by injection of authentic material.

3.7. Effectiveness of this approach

The peak table is reduced from over 10,000 peaks to 370, with the majority of the peaks (273) identified by the scripts being plausible by either identification of the desired spectral features (such as isotope cluster) in manual review or by match to a library spectrum (Table 2). The number of peaks that cannot be deemed to be plausible is only about 1% of the 10,000 peaks found, which should not be an undue burden on a person reviewing data in search of possible environmental contaminants.

While the filters provided a short list of compounds rich in compounds of interest, some compounds known to be present were not identified in this sample. With the techniques based around a search for a molecular ion, spectral noise or coelution of other

Table 2
Summary of compound identification in household dust extract by filters and in expected region for compounds.

Compound class	Number found by filter	Plausible on review
Chlorine/bromine-containing	165	145 (93%)
Phthalates	52	33 (57%)
PAHs	145	94 (65%)
Nitro compounds	8	1 (13%)

compounds may mask a molecular ion with the characteristic sought. The scripts use a few ions to identify a compound as belonging to a class, so noise affecting a single ion may result in a false negative, even though the entire spectrum would provide a good match to a reference spectrum. Thus, in screening applications the use of a target analyte list along with the screening technique described here will help to ensure that compounds known to be in the environment are not overlooked.

4. Conclusion

The automated classification of potential environmental contaminants in a GCxGC-TOFMS chromatogram locates PAHs, phthalates, and compounds containing chlorine, bromine, or nitro groups. The ability to specifically detect chlorinated and brominated compounds—even when they are coeluting contaminants with other compounds—is particularly important, given that many of these compounds and their degradation products are found in the environment, and are found at concentrations low enough to make them otherwise difficult to detect in a complex matrix by a non-targeted method.

It can be estimated that compounds at concentrations as low as 10-20 ng/g dust were classified by the scripts. The loading of compounds of interest was limited by the presence of a few compounds at high concentration in the extract. This made injection of a more concentrated extract unfeasible. But, further fractionation of the sample can be expected to allow not only for the injection of higher levels of the compounds of interest on column; it can also provide for further separation of compounds of interest, similar to that shown in a previous GCxGC-TOFMS analysis of river sediment [14].

In this sample, a peak table of over 10,000 entries was reduced to a list of about 370 peaks of interest. Of the 370 peaks, 273 show spectra indicating that they are of the classes of compounds sought, and that they merit further work for identification or confirmation.

Comparison of the results obtained by NIST with that obtained by the filters shows that target analysis is required to ensure the detection of specific analytes in a sample. The important point is, however, that use of filters in the GCxGC analysis allows for the rapid identification of compounds of interest beyond a target analyte list.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2010.08.039.

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