



Rapid mapping of various chemicals in personal care and healthcare products by direct analysis in real time mass spectrometry



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ABSTRACT

Residual chemicals on personal care and healthcare products, such as sanitary articles, sterile gauze bandages, nappies, plasters, were studied by direct analysis in real time mass spectrometry (DART-MS). We have identified around 40 compounds in seventeen different commercially available items. The tentative identification was further supported for about half of the chemicals by tandem mass spectrometric experiments (DART MS/MS). The most notable hazardous substances were tributyl phosphate, tris(2,4-di-*tert*-butylphenyl) phosphite, phthalic acid esters, erucamide, and nonylphenol ethoxylates (NPEs). In addition, we developed an efficient DART-MS analysis to determine the concentration of NPE in a swab sample. The quantitative result obtained by DART-MS was confirmed by liquid chromatography with mass spectrometric detection (LC-MS).

1. Introduction

The manufacture of personal care and healthcare products, such as sanitary articles, sterile gauze bandages, nappies, plasters employs a diverse range of processes using a large number of chemicals. Residues of some of these chemical substances may remain in the finished products. The investigation of chemicals, harmless or dangerous, in these hygiene articles is very important since they represent products that can get into direct contact with skin and the mucous membrane. However, only few reports were published about the survey of chemical substances in personal care and healthcare products [1,2], and most of them are specialized for the analysis and risk assessment of dioxins in sanitary products of women [3–6]. These studies conventionally use gas chromatography-mass spectrometry (GC-MS) for the detection and quantification of the residual substances in the feminine hygiene products. However, the ambient mass spectrometric methods, e.g. direct analysis in real time mass spectrometry (DART-MS), allows the analysis of ordinary objects without complicated sample preparation and time-consuming chromatographic separation [7]. Moreover, DART-MS could be an effective technique for screening the residual chemicals near the surface of the personal care and healthcare products, because it can desorb and ionize molecules directly from the surface of the objects. However, to the best of our knowledge, there have been no reports about the detection of chemicals from this class of product by a DART-MS method. Accordingly, the main aim of our work was the DART mass spectrometric and tandem mass spectrometric (MS/MS) analysis of

various residual chemicals, a few of them potentially allergen or toxic, on the personal care and healthcare articles.

2. Material and methods

2.1. Samples, chemicals

17 personal care and healthcare products with a variety of types and countries of origin were analyzed. The articles were bought between January 2017 and May 2017 in different supermarkets and drugstores, the cleanroom swab (Sample 17) was purchased from VWR International (Leuven, Belgium). The types and origins of the samples are listed in Table S1 in the Supporting Information. HPLC grade methanol was obtained from VWR International, nonylphenol ethoxylate with average molecular weight of 680 was purchased from Sigma-Aldrich (Taufkirchen, Germany). Water was purified by Direct-Q (Millipore, Molsheim, France).

2.2. Quadrupole–time-of-flight mass spectrometry

A MicroTOF-Q type Qq-TOF MS instrument was used (Bruker Daltoniks, Bremen, Germany). Nitrogen was used as the collision gas in the MS/MS experiments, and the collision energies were varied in the range from 5 to 50 eV (in the lab frame). The collision cell pressure was estimated to be $\sim 1.2 \times 10^{-2}$ mbar. For MS/MS, the precursor ions were selected with an isolation window of 2 m/z unit. The spectra were

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recorded by a sampling rate of 2 GHz. The mass spectra were processed by the DataAnalysis 3.4 software from Bruker.

2.3. Direct analysis in real time (DART) ion-source

A DART SVP source (IonSense, Saugus, MA, USA) was used in the positive-ion mode with helium 5.0 (purity > 99.999%). The gas heater temperature was 350 °C. The samples were manually placed into the DART gas stream. The gap between the spectrometer inlet and the ion source was 2.5 cm. Samples were introduced into the middle of the gap. For semi-quantitative analysis an autosampler was used for the introduction of the samples.

2.4. Semi-quantitative analysis of nonylphenol ethoxylate (NPE)

A standard solution of NPE was prepared by dissolving 0.92 mg of NPE in 1 mL of methanol. Dilutions of this solution were prepared in order to obtain four concentration levels (27.6, 64.4, 92 and 138 µg/mL). NPE free swabs with the same size and material as Sample 17 were dipped into each NPE solution and one of them into pure methanol, thus standard samples with 0.000%, 0.007%, 0.015%, 0.022% and 0.032% (w/w) of NPE were prepared. The standard swabs and Sample 17 were introduced into the DART ion source by an autosampler with a constant resident time of 5 s in the source gas stream.

For the determination of the limit of detection (LOD) standard samples were prepared in the concentration range from 0.0001 to 0.01 mg/kg. The limit of detection by DART-MS was determined as the concentration that represents 3-fold the signal-to noise ratio.

2.5. High-Performance Liquid Chromatography – Mass Spectrometry (HPLC-MS) analysis

The heads of 3 swabs (Sample 17) were cut off with a total mass of 0.9985 g and were extracted for 2 h in 10 mL methanol with an ultrasonic device (continuing the extraction for additional 2 h, the same result was obtained). 6 standard samples in the concentration range 0.0092 – 0.131 mg/mL were prepared by dissolving NPE in methanol.

For chromatography, 10 µL of the sample solutions were injected into the chromatograph system consisting of a Waters 2695 Separations Module equipped with a thermostable autosampler (5 °C) and a column module (45 °C) (each from Waters, Milford, MA, USA), and an Agilent Extend C18 column (4.6 × 100 mm, 3.5 µm) (Agilent technologies, Palo Alto, CA, USA). Isocratic method was used with the mobile phase methanol: water 3:1 and flow rate of 1.5 mL/min. The sample runtime was 25 min.

A MicroTOF-Q type Qq-TOF MS instrument (Bruker Daltonics, Bremen, Germany) was used equipped with Atmospheric Pressure Chemical Ionization (APCI) ion source. The drying gas (N₂) temperature was 390 °C and the flow rate was 7.5 L/min. The pressure of the nebulizer gas (N₂) was 1.8 bar. The spectra were recorded at a sampling rate of 2 GHz. For the quantization extracted ion chromatograms were utilized selecting the members of the NPE series. The mass spectra were calibrated externally using APCI/APPI calibrant solution from Bruker.

3. Results and discussion

The DART-MS spectra of the various personal care and healthcare articles are shown in Fig. 1a–d and in Fig. S1a–s in the Supporting Information. As can be seen in Fig. 1 and Fig. S1, many peaks appeared in the spectra, indicating that various residual chemicals can be found on the surface of the hygiene and healthcare products, and they can be analyzed effectively by DART-MS. All the peaks labeled with m/z values in Figs. 1 and S1 were assigned to chemicals that are probably used in the manufacture of the products, or to possible contaminants originating, for example, from the packaging of the articles. Although DART is a soft ionization method, the relatively high DART source

temperature induces in-source fragmentation of the less stable compounds. The gray color m/z labels in Figs. 1 and S1 belong to fragments, as it was confirmed by tandem mass spectrometric experiments, as detailed later. The assignment of the mass peaks was based on mass accuracy, the *MolWeightToFormula* tool of the *DataAnalysis* software (Bruker) was used to derive the molecular formulas. The identified compounds are listed in Table 1 and compiled by samples in Table S2 in the Supporting Information.

If the intensity of the assigned m/z peaks was high enough, DART-MS/MS experiments were also performed. The proposed chemical assignments of more than 20 compounds were confirmed by comparing the MS/MS spectra to those obtained from the literature and/or mass spectral databases, as it will be detailed later. The MS/MS spectra are presented in Fig. 2a–d and in Fig. S2a–q, and the compounds verified by tandem mass spectrometric experiments are listed in Table 2.

As Tables 1 and 2 show, a wide variety of compounds were detected, and about half of the tentative chemical identifications was supported by MS/MS experiments. In the following, the analysis of the most remarkable, possibly harmful chemicals will be detailed. These compounds could be hazardous or irritating being in direct contact with skin and the mucous membrane for over a period of time.

Tributyl phosphate (TBP) was one of the most frequently detected compounds, it was found in 9 samples. TBP is extensively used, among others, as a solvent or as a plasticizer in the manufacture of plastics. DART-MS was able to detect it in various articles, such as sanitary napkin, pantyliner, tampon, cotton pad and cotton bud, sterile gauze rolls and sticking plasters (see Table S2). TBP has neurotoxicity and other toxic effects, and besides, it causes irritation of skin [8], thus its quick detection in hygiene articles and bandages by DART-MS can have a great importance. As can be seen in Fig. 1c, the measured m/z 267.172 value agrees with the theoretical m/z of 267.172, corresponding to the elemental composition $[C_{12}H_{27}O_4P + H]^+$ of the protonated TBP. To confirm the identification of $C_{12}H_{27}O_4P$ as TBP, DART-MS/MS measurement was also performed by selecting of the ion at m/z 267 as the precursor ion (see Fig. 2a and Table 2). The product ions at m/z 211, 155 and 98 are in agreement with the characteristic ions of the ESI FTMS (electrospray Fourier transform mass spectrometry) [9] and IT (iontrap) [10] MS/MS spectra of TBP found in mass spectral databases. The most abundant product ion at m/z 98.984 corresponds to the central $[PO_4H_3 + H]^+$ moiety of TBP with the theoretical m/z of 98.984.

Another organophosphorus compound, tris(2,4-di-*tert*-butylphenyl) phosphite (TBPP) and its oxidized form tris(2,4-di-*tert*-butylphenyl) phosphate, was also detected in many articles (9 and 5 samples, respectively). TBPP, commercial name Irgafos 186, is a common antioxidant additive to plastics. Recent papers have reported the detrimental effect of bis(2,4-di-*tert*-butylphenyl)phosphate (bDtBPP) to cell growth [11–13]. It was also shown, that bDtBPP is derived from the breakdown of TBPP [11–13]. The protonated TBPP, protonated oxidized TBPP, and the ammoniated oxidized TBPP were detected with remarkable intensity from the two nappies (Sample 9 and 10) at m/z 647, 663 and 680, respectively, as can be seen in Figs. S1i and S1j. The identification of TBPP was verified by MS/MS experiments. The product ions at m/z 591, 441, 403, 385, 347, and 291 (see Fig. 2d, and Table 2) are the same as found in the literature for TBPP [14].

A major class of hazardous chemicals found in hygiene and healthcare items is phthalic acid esters (PAEs), which are widely used in the chemical industry, mainly as polymer plasticizers. PAEs are not bound covalently to their parent materials, therefore, they can significantly migrate into the environment. PAEs reveal a variety of health risk and biological toxicity, for example gestational complication and neurodevelopmental damage [15,16]. Regulations of PAEs were issued by the Council of the European Union [17] and by the US Congress [18]. Accordingly, it is especially harmful, that bis(2-ethylhexyl) phthalate (DEHP) was detected with remarkable high intensity from the sterile gauze pad (Sample 5, see Fig. 1a, at m/z 391.283 in line with the

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