

Rapid and nondestructive analysis of phthalic acid esters in toys made of poly(vinyl chloride) by direct analysis in real time single-quadrupole mass spectrometry

Thorsten Rothenbacher and Wolfgang Schwack*

Institut für Lebensmittelchemie, Universität Hohenheim, Garbenstr. 28, 70599 Stuttgart, Germany

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In the European Community, selected phthalic acid esters (PAE) are restricted in their use for the manufacture of toys and childcare articles to a content of 0.1% by weight. As PAE are mainly used as plasticisers for poly(vinyl chloride) (PVC), a rapid screening method for PVC samples with direct analysis in real time ionisation and single-quadrupole mass spectrometry (DART-MS) was developed. Using the ions for the protonated molecules, a limit of detection (LOD) of 0.05% was obtained for benzyl butyl phthalate, bis(2-ethylhexyl) phthalate and diisononyl phthalate, while for dibutyl phthalate, di-*n*-octyl phthalate and diisodecyl phthalate the LOD was 0.1%. Validation of identification by the presence of ammonium adducts and characteristic fragment ions was possible to a content of $\geq 1\%$ for all PAE, except for benzyl butyl phthalate ($\geq 5\%$). Based on the fragment ions, bis(2-ethylhexyl) phthalate could clearly be distinguished from di-*n*-octyl phthalate, if the concentrations were $\geq 5\%$ and $\geq 1\%$ at measured DART helium temperatures of 130 and 310°C, respectively. The complete analysis of one sample only took about 8 min. At the generally used gas temperature of 130°C, most toy and childcare samples did not sustain damage if their shape fitted into the DART source. Copyright © 2009 John Wiley & Sons, Ltd.

Phthalic acid esters (PAE) represent an important group of plasticisers for poly(vinyl chloride) (PVC), and they have been used for many years in the fabrication of PVC toys and childcare articles. In 1999 several European Member States expressed concerns about the adverse effects of phthalates on the health of children,¹ and six PAE in toys and childcare articles were temporarily banned from the European market. Because (i) the toxicology of all phthalates in humans was not totally clarified, (ii) bis(2-ethylhexyl) phthalate (DEHP), in particular, clearly showed adverse effects on the development and reproduction of laboratory animals,^{2,3} and (iii) a high level of health protection, especially for children, was demanded, the permanent regulation of PAE was introduced.⁴ It has been shown that different PAE act on the same target organ, but that they individually possess complex modes of action.⁵ Therefore, the Council Directive 76/769/EEC of the European Commission prohibits the placing of toys and childcare articles on the market which contain bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP) or benzyl butyl phthalate (BBP) at concentrations of greater than 0.1% by mass of the material. There is an equivalent level for diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) or di-*n*-octyl phthalate (DNOP), if the articles can be taken into the mouth by children.⁶

A survey of 72 toys made from PVC and purchased in 17 different countries showed that nearly all toys or at least their PVC subsections contained PAE, mainly in the range 10–40% by weight.⁷ More actual data were obtained from the European Union rapid alert system for all dangerous consumer products (RAPEX),⁸ in which toys or childcare products are named together with the reason for them being hazardous. A search for the phrase ‘phthalate’ in the notifications of 2008 resulted in 143 hits, but cosmetics, clothing and stationery products were also included herein, and the search result only represented those entries in which a nomenclature was used that contained the term ‘phthalate’. Entries that used nomenclature such as, for example, ‘* phthalic acid ester’ did not result in a hit. A closer look at each alert of 2008 identified that 140 toys or childcare products had been withdrawn from the market due to PAE violations. In seven samples, the PAE content was below 3%, and in nine samples only an analysis result of $>0.1\%$ was given. However, 95% of the notified samples revealed PAE at 3% or more.

For the determination of PAE in plastic toys using published methods, about 1 g of the sample is directly Soxhlet-extracted with dichloromethane for 16 h⁹ or is finely ground and extracted twice by sonication in hexane for 30 min.⁷ The extracted phthalates are determined by gas chromatography with flame ionisation or mass spectrometric detection. Extraction of PVC by accelerated solvent extraction also led to good results.¹⁰ Another approach for the analysis of PAE in PVC consists of completely dissolving the plastic in tetrahydrofuran and precipitating PVC by the

*Correspondence to: W. Schwack, Institut für Lebensmittelchemie, Universität Hohenheim, Garbenstr. 28, 70599 Stuttgart, Germany.
E-mail: wschwack@uni-hohenheim.de

addition of methanol. Determination was performed by high-performance liquid chromatography (HPLC) or high-performance thin-layer chromatography (HPTLC).¹¹ HPTLC was used, in particular, to facilitate quantification of the isoalkyl PAE DINP and DIDP, which are both mixtures of several compounds, as this technique results in a sharply separated HPTLC zone for both DINP and DIDP instead of the hump produced by HPLC.

As toys or childcare products normally contain alternative plasticisers in place of PAE, the analysis of such items for the presence of PAE is possibly pointless. To avoid waste of solvents, instrumental time and staff working time, the availability of rapid identification methods to check for the presence of phthalates in the specimens prior to exact determination is useful. As PAE are regulated differentially by the authorities, the method should be at least able to distinguish DEHP, DBP and BBP from DIDP, DINP and DNOP. Following this objective, different pure phthalates were measured by Fourier transform Raman spectroscopy (FTRS), but an identification in PVC was successfully demonstrated only for DEHP.¹² However, due to similarities in the spectra of the common dialkyl phthalates, it is doubtful whether it would be possible to qualitatively determine the exact type of phthalate ester present in a sample containing a mixture of phthalates.

The aim of the present study was to evaluate if a rapid screening test for PAE in PVC materials can be developed by using direct analysis in real time mass spectrometry (DART-MS), with an open interface allowing us to directly insert solid specimens.^{13,14} DART-MS has been successfully employed for the analysis of different compounds in almost solid samples, like strobilurin fungicides in wheat,¹⁵ flavors in perfumery raw materials,¹⁶ and isopropylthioxanthone¹⁷ or lubricant additives¹⁸ from HPTLC plates.

As DART is a relatively new ionisation technique, characteristic ions of phthalates as standards and in PVC plastics containing additives (also called plastisols) had to be identified, the sensitivity of identification evaluated, and the applicability to toy samples of known PAE concentrations shown.

EXPERIMENTAL

Chemicals and reagents

The following chemicals were of analytical grade unless otherwise specified. Toluene was from Roth (Karlsruhe, Germany), benzyl butyl phthalate (BBP) from Merck (Darmstadt, Germany), and dibutyl phthalate (DBP) and dioctyl phthalate (DNOP) from Sigma-Aldrich (Taufkirchen, Germany). Bis(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), and 1,2-cyclohexanedicarboxylic acid 1,2-diisononyl ester (DINCH) were of technical grade and were provided by a plastisol producing company. Vinnolit P 70 was used as the PVC material and was provided by Vinnolit GmbH & Co. KG, Wacker Chemie AG (Burghausen, Germany).

Plastisol samples

Twenty-five different plastisols of three different types containing (a) DBP and DINP, (b) DEHP and DIDP and (c)

BBP and DNOP at mass percentages of 0%, 0.05%, 0.01%, 0.5%, 1%, 5%, 10%, 15% and 25% were prepared. Generally, the plastisols contained 60% PVC and the respective PAE, which were filled up to 40% with DINCH. In case of the plastisols with 25% PAE, PVC was only present at 50%, and DINCH was not used. To prepare the plastisols, about 0.5–1 g of the PVC and the plasticisers were mixed with a metal spatula in a 10 mL glass beaker until the mixture was a homogenous and colourless paste. It was then coated with about 1 mm thickness on a heating plate covered by aluminum foil at 200°C. After 1 min, the aluminum foil was removed from the plate to cool off the plastisol.

Toy samples

Five toys made from PVC and containing PAE or DINCH were provided by Chemisches und Veterinäruntersuchungsamt, Stuttgart, Germany, and had already been analysed for plasticisers: a horror mask (42.6% DEHP), childrens' swimming aids (16.2% DEHP and 23.0% DINP), two puppet heads (containing 22.0% DINP or 35.4% DINCH), and a fish (30.8% DINCH). In addition, three toys that were about 25 year old with an unknown PAE content were used for analysis: one lizard, one bicycle driver and one squeaky toy.

DART-MS

An Ion Sense DART 100 with Vapur API-Interface, DART control software version 2.19 (KR Analytical, Sandbach, UK) and a G1956B MSD single-quadrupole mass spectrometer with ChemStation B.02.01 SR2 software (Agilent Technologies, Waldbronn, Germany) were used. The DART needle voltage was 4000 V, and the discharge and grid electrode were each at 280 V. The DART system was operated at 200°C with helium 5.0 (purity > 99.999%) at a flow rate of 5–6 L min⁻¹, controlled by a GFM 17 flow meter (Analyt-MTC, Müllheim, Germany). The MSD was operated in positive ion fast-scan mode m/z 140–920 with a step size of 0.1 m/z units, a cycle time of 0.79 s cycle⁻¹, a capillary voltage of 6000 V, a fragmentor voltage of 200 V, a gain of 1.00 and a threshold of 0. The data were recorded in profile mode.

Mass spectra of the target PAE were obtained by dissolving the substances in toluene (0.1–1 g L⁻¹) and introducing the samples by means of DIP-it liquid samplers (KR Analytical) under the same MS conditions as described above. Plastisol specimens of about 2 × 0.2 cm were manually introduced into the DART gas stream by the use of tweezers. Replicate measurements of plastisols were performed from the same spot, and no depletion of the signals was observed. The gap between the DART gas outlet and the Vapur API interface inlet was 1.1 cm, the length of the ceramic tube was 3.9 cm and the sampling point was in the middle of the gap (Fig. 1). Each sample was measured six times, consecutively, while keeping it in the same position in the helium stream for about 30 s. When the sample was inserted, the signal immediately increased, remained at a constant level and, after sample removal, generally decreased within several seconds, depending on the PAE content. In replicate measurements, the signal heights showed deviations of the signal intensity.

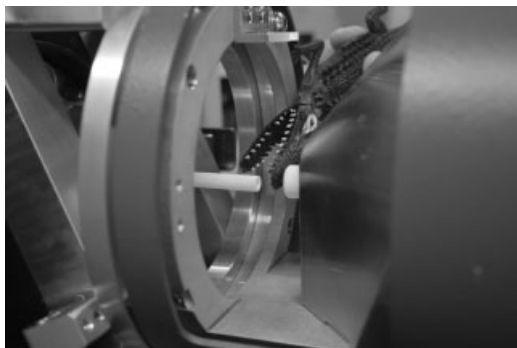


Figure 1. Positioning of a sample in the DART source.

For data evaluation, the set of mass spectra recorded during the measuring time (30 s) and resulting in a total ion current 'peak' was averaged. Background correction was performed manually by subtracting scans both ahead of and behind the peak.

To determine the limits of detection for a specific ion of the known plastisol samples, a signal-to-noise (s/n) ratio of 3, referring to the height of the mass signal, was taken as a basis, having been fulfilled for at least four of the six measurements, and an averaged noise value of two different regions in the background-corrected mass spectrum was used.

Gas chromatography/mass spectrometry (GC/MS)

A Fisons (Manchester, UK) GC-8000 gas chromatograph with a split/splitless injector coupled to a Fisons MD800 quadrupole mass spectrometer was used with electron ionisation (EI) at 70 eV in the positive ion mode. Data acquisition and analysis were performed using standard software supplied by the manufacturer (Mass Lab software version 1.3). The injection volume was 1 μL splitless. The GC oven started at a temperature of 80°C, increased by 12 $^{\circ}\text{C s}^{-1}$ to 300°C and this temperature was held for 10 min. The ion source and transfer line temperatures were 200 and 300°C, respectively. Helium was used as the carrier gas with a column head pressure of 70 kPa with a ZB50 column (30 m length, 0.25 mm id., 0.25 μm film; Phenomenex, Aschaffenburg, Germany) and a 0.7 m uncoated and deactivated retention gap. The mass spectrometer was operated over a scan range from m/z 50 to 420 with a scan time of 0.6 scans s^{-1} .

RESULTS AND DISCUSSION

DART spectra of phthalic acid esters

The phthalic acid esters generally provided the protonated molecule as the base peak and an $[\text{M}+18]^+$ peak in different intensities of about 10–40%, which was assigned to the respective ammonium adduct (Figs. 2 and 3). In addition, proton and ammonium adducts of PAE dimers could be detected, especially if solutions of a concentration $>100 \text{ mg L}^{-1}$ were measured. Low intensity fragment ions of m/z 149 and 167 were obtained for all PAE, formed by consecutive neutral losses of alcohol and alkene moieties (Fig. 4).

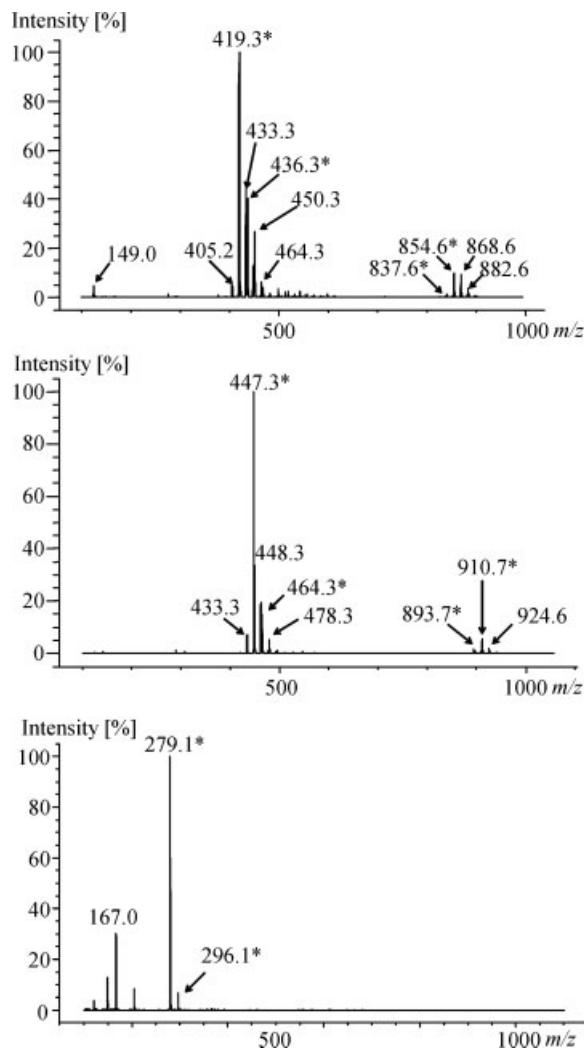


Figure 2. Typical DART-MS spectra obtained from PAE dissolved in toluene, for DINP (top), DIDP (middle) and DBP (bottom). The proton and ammonium adducts are marked with an asterisk.

Since technical grade PAE are used in fabrication processes, impurities have also to be considered, and these can be readily detected by DART-MS, as shown for DINP and DIDP (Fig. 2). Additional $[\text{M}+\text{H}]^+$ ions with signal intensities of 5–20% surround the main protonated molecules at distances of 14 and 28 m/z units accompanied by the respective ammonium adducts. Obviously, the technical alcohols used for the preparation of PAE contained significant levels of homologues as impurities.

From the characteristic PAE ions obtained by DART-MS (Table 1), the protonated molecules of highest intensities were selected for the identification of the respective PAE in PVC samples, and the ammonium adducts were used as additional qualifiers.

Differentiation of DEHP and DNOP

Interestingly, there is a great chance to differentiate between the isomers DEHP and DNOP, which may be important due to their different treatment by the European legislation. Both DEHP and DNOP produce fragment ions at m/z 261 and 279, but in clearly reversed ratios of signal intensity (Fig. 3). Loss of octanol from the protonated molecule is favoured by

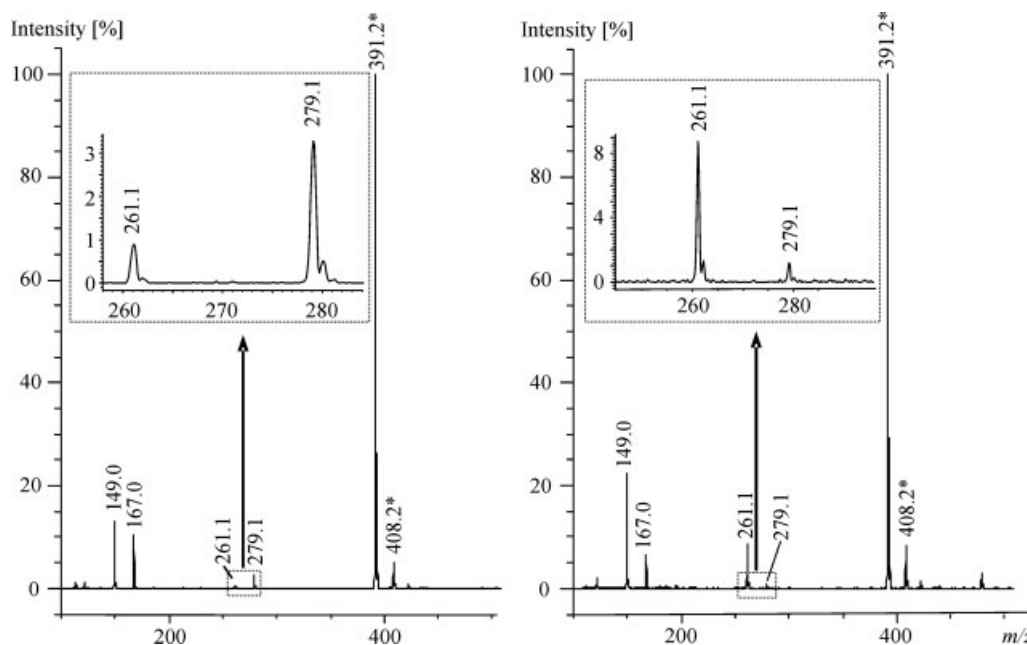


Figure 3. DART-MS spectra of DEHP (left) and DNOP (right), both at a concentration of 1 g L^{-1} in toluene. The proton and ammonium adducts are marked with an asterisk.

DNOP, whereas DEHP preferably eliminates 2-ethyl-1-hexene (Fig. 4). By ESI-MS/MS experiments, it could be shown that loss of water from m/z 279, also resulting in the formation of m/z 261, does not occur (data not shown). Similar results were obtained during GC/(E)MS analyses, when the fragment ion at m/z 261 from DNOP was found to be more abundant than that from DEHP (Fig. 5). Thus, the results strongly support the proposed fragmentation processes (Fig. 4) and the possibility of being able to certainly differentiate DEHP from DNOP.

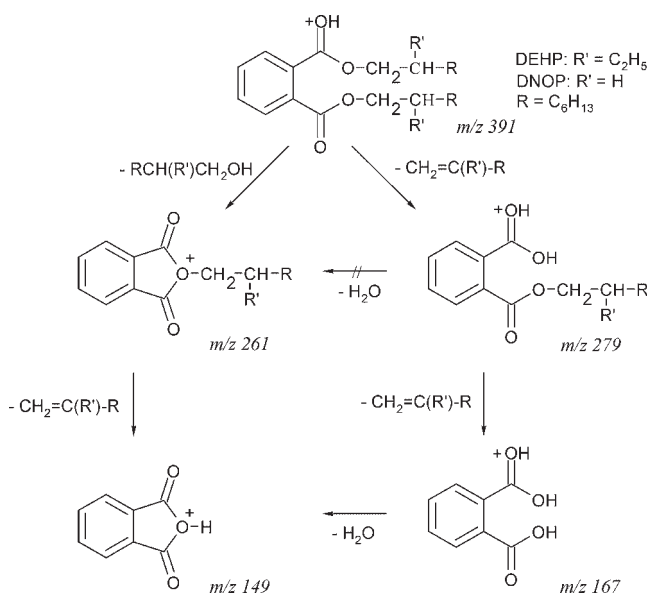


Figure 4. Proposed fragmentation processes of phthalic acid esters, especially shown for the differentiation of DEHP and DNOP.

In DNOP-containing plastisols, the ion at m/z 261 could be detected in a concentration range of 5–25%, but m/z 279 only at 25%. In the case of DEHP, both fragment ions were detectable at concentrations $\geq 5\%$ in plastisol samples. It was possible to increase the sensitivity by increasing the DART helium temperature setting to 450°C , which resulted in the detection of the characteristic fragment ions at concentrations of 1% in plastisols for both DEHP and DNOP.

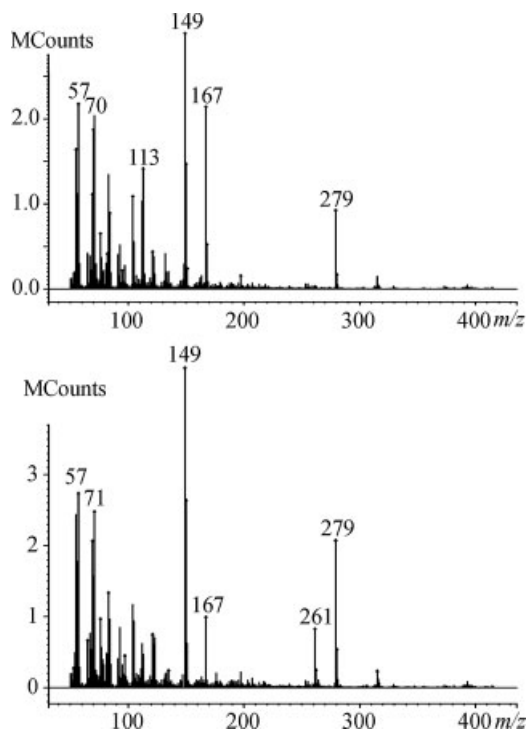
Since there also is the possibility of a DBP impurity in DNOP and DEHP with a protonated molecule at m/z 279, we had to confirm that m/z 279 is only a fragment ion of DNOP and DEHP, and not due to the presence of DBP. GC/MS analysis proved that the DBP content for both DNOP and DEHP was below 0.5% (data not shown).

Limits of detection and blank values

Since toy samples have to be manually introduced into the DART interface, we expect that this procedure will be associated with low repeatability, and since there is no chance to employ internal standards, calibration and quantification are complicated. Therefore, PVC plastisols with different concentrations of PAE (0–25%) were prepared to derive limits of detection (LODs) from the obtained DART-MS signals. Diisononyl 1,2-cyclohexanedicarboxylate (DINCH) was additionally used to provide a plasticiser level of at least 40% in all samples. To largely overcome the variations by manual operation, samples were generally measured six times, consecutively. The LOD was defined, if the s/n ratio for a specific ion of the background corrected mass spectrum (Fig. 6) was ≥ 3 for at least four of the six recordings. As six measurements were obtained in 3 min, and the analysis time was about 5 min, screening a sample takes about 8 min.

Table 1. Characteristic DART-MS ions (calculated) of phthalic acid esters with corresponding LODs given in mass percentages

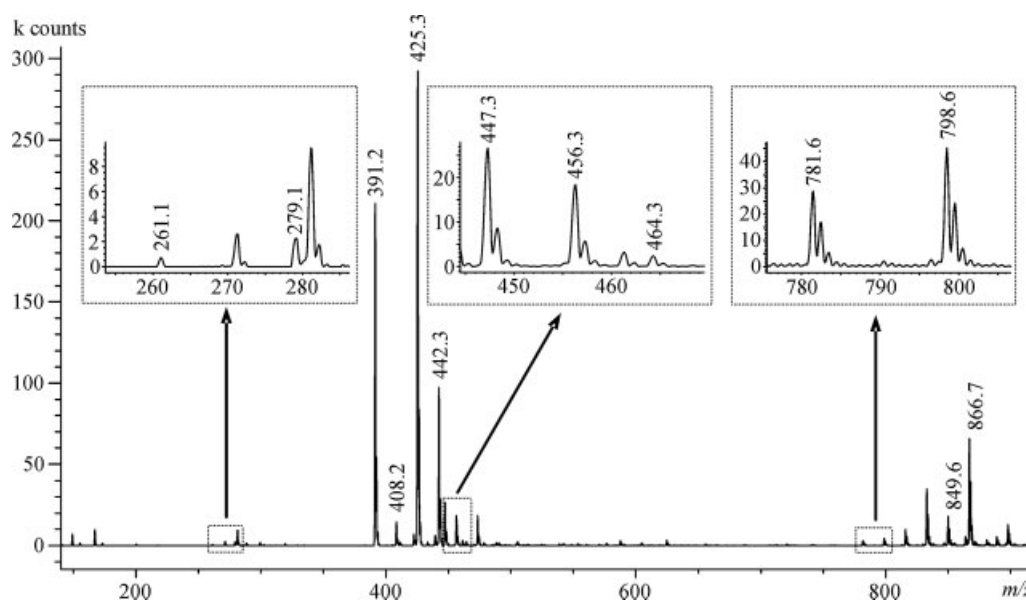
	DBP	BBP	DEHP	DNOP	DINP	DIDP
Molecular formula	C ₁₆ H ₂₂ O ₄	C ₁₉ H ₂₀ O ₄	C ₂₄ H ₃₈ O ₄	C ₂₄ H ₃₈ O ₄	C ₂₆ H ₄₂ O ₄	C ₂₈ H ₄₆ O ₄
<i>m/z</i> [M+H] ⁺	279.2	313.1	391.3	391.3	419.3	447.3
LOD of [M+H] ⁺	0.1%	0.05%	0.05%	0.1%	0.05%	0.1%
<i>m/z</i> [M+NH ₄] ⁺	296.2	330.2	408.3	408.3	436.3	464.4
LOD of [M+NH ₄] ⁺	1%	5%	5%	1%	1%	1%
<i>m/z</i> [2M+H] ⁺	557.3	625.3	781.6	781.6	837.6	893.7
LOD of [2M+H] ⁺	5%	10%	1%	5%	10%	10%

**Figure 5.** GC/70eV EI-MS spectra of DEHP (top) and DNOP (bottom), both at a concentration of 0.01 g L⁻¹ in toluene.

The LODs determined by this procedure were $\leq 0.1\%$, if the ions from the protonated molecules were used (Table 1). Therefore, the DART-MS method is able to identify PAE in PVC down to the actual limit of the council directive 76/769/EEC.⁶ A validation of identification by using the ammonium adducts was possible for four of the tested PAE, if the concentration was $\geq 1\%$ (Table 1). In the case of BBP and DEHP, validation was only possible with the next higher concentration tested. The protonated dimers were almost only detectable at higher concentrations of 5–10%.

Despite the complications to be expected in such a method, a linear correlation was obtained in the low concentration range of most interest, if the mean of six replicates was plotted versus the noise-corrected height of the ion signal (Fig. 7).

For the PAE blank values, the direct sample measurement method excludes contaminants from solvents or vessels. In spite of this, there are sources of PAE in the atmosphere that could be detectable by DART-MS: if, for example, the flooring consists of PVC (Fig. 8). Working with an open interface such as DART, such background signals have generally to be kept in mind, demanding careful background correction to avoid false positive identifications. To check this possibility, a sample only containing DINCH as the plasticiser was analysed, and no PAE signals arising from atmospheric sources were detectable.

**Figure 6.** DART-MS spectrum of a PVC sample containing 5% DEHP, 5% DIDP and 30% DINCH. DEHP: *m/z* 261.1, 279.1, 391.2 [M+H]⁺, 408.2 [M+NH₄]⁺, 781.6 [2M+H]⁺, 798.6 [2M+NH₄]⁺; DIDP: *m/z* 447.3 [M+H]⁺, 464.3 [M+NH₄]⁺; DINCH: 425.3 [M+H]⁺, 442.3 [M+NH₄]⁺, 849.6 [2M+H]⁺, 866.7 [2M+NH₄]⁺.

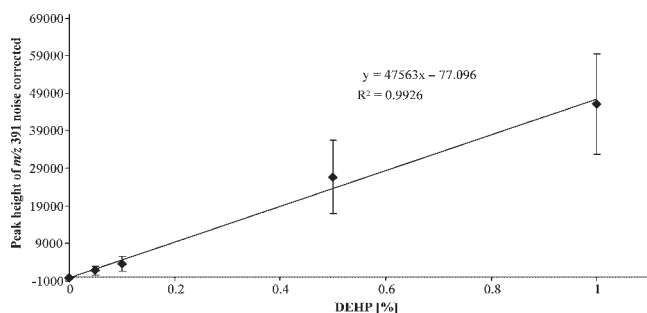


Figure 7. Calibration curve exemplarily obtained from plastic samples containing DEHP in the range 0–1%.

Analysis of real samples and destructiveness of the method

Five toy samples pre-analysed by GC/MS were studied by the DART-MS method. The mass spectra of a horror mask provided m/z 391 as base peak, the corresponding ammonium adduct and the dimeric ions, including the typical PAE fragment ions at m/z 149 and 167 (Fig. 9). The signal ratio of m/z 261 and 279 proved the presence of DEHP instead of DNOP. The childrens' swimming aids provided the same ions characteristic of DEHP, but also showed the protonated molecule (m/z 419) and the ammonium adduct (m/z 436) of DINP (Fig. 9). The mass spectra of a puppet head containing DINP only exhibited the corresponding signals of the protonated molecule and the ammonium adduct. In addition, the $[2M+NH_4]^+$ ion was present at 10% intensity, but the $[2M+H]^+$ ion was missing. Similar results were obtained for another puppet head (Fig. 9) and a fish; both only containing DINCH. In addition to the protonated molecule and the ammonium adduct, the $[2M+NH_4]^+$ at m/z 867 was considerably more abundant than the protonated dimer at m/z 849. Three further 25-year-old toy samples (lizard, bike driver, squeaky toy) not analysed by GC/MS all provided ions clearly proving just the presence of DEHP.

Generally, the DART helium temperature was set to 200°C, but the temperature at the point of sampling was measured as 130°C. Under these conditions, none of the studied

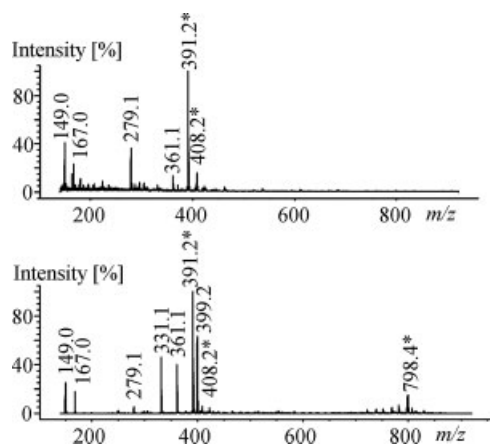


Figure 8. DART-MS spectra of the laboratory atmosphere (top) and a piece of flooring (bottom), both showing DEHP ions. The proton and ammonium adducts are marked with an asterisk.

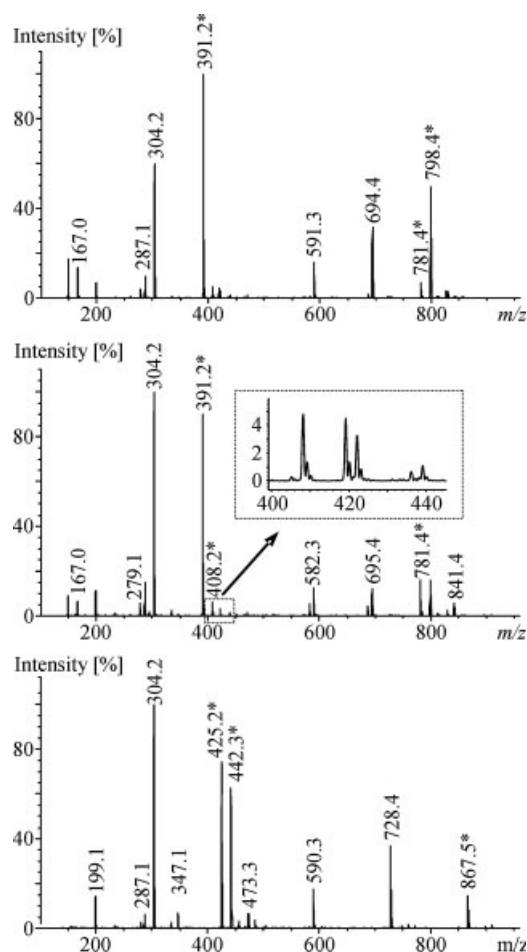


Figure 9. DART-MS spectra of a horror mask containing 42.6% DEHP (top), childrens' swimming aids with 16.2% DEHP and 23.0% DINP (middle) and a puppet head containing 35.4% DINCH (bottom). The proton and ammonium adducts are marked with an asterisk.

samples sustained visible damage, except for the 25-year-old squeaky toy which started to melt. To increase the sensitivity for PAE, the temperature was set to 450°C (measured 310°C), but most samples decomposed at this temperature. Consequently, the range of operating conditions is limited if DART-MS screening is to be used for nondestructive controls. As to be expected, however, there is another limit for a nondestructive analysis. To obtain a suitable sample size, the shape of a toy had to be at least a cone of 5 cm in height and below 3 cm in diameter to easily be introduced into the DART source. If these shape requirements are not fulfilled, cutting into proper subsamples is essential. However, new designs of the DART ion source such as the DART-ET (KR Analytical) may allow wider sample shapes.

CONCLUSIONS

The presented DART-MS method enables rapid identification of PAE in PVC samples as toys and childcare articles at the limits actually fixed by European regulations. Validation of a positive finding based on the protonated molecule does work for a concentration of 1% for all PAE, except for BBP. As

95% of the toys and childcare articles submitted in 2008 to RAPEX had more than 3% PAE, the obtained sensitivity for validation is sufficient for most samples. Since for the present study only a single-quadrupole mass spectrometer was available, it should be possible to expectedly increase the sensitivity with a triple-quadrupole system. Thus, DART-MS provides a powerful up-to-date screening tool, well suited for surveillance purposes to screen with a high sample throughput.

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