LC/MS METHOD TO DETERMINE PLASTICIZERS IN INDOOR DUST

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ABSTRACT
The analysis of a broad range of plasticizers in indoor dust is necessary due to their widespread use, their ubiquitous occurrence in environmental media and their toxicological properties. Since commonly used GC methods are less suited to analyse compounds of low volatility a HPLC method has been developed. The method covers phthalates (up to C_{10}-alkylated), adipates, an azelate and a trimellitate and is suitable for compounds of even higher molecular weight. A mass spectrometer with atmospheric pressure chemical ionisation (APCI) was used as a detector, which yields mass spectra of low and specific fragmentation. Typical performance characteristics of this analytical method are: recovery of 105% to 130 %, limits of determination from 150 µg/g down to 1 µg/g (based on a 50 mg dust sample, depending on blank value), repetitive RSD from 3 % to 16 %.

INDEX TERMS
Plasticizer, LC/MS method, Indoor dust

INTRODUCTION
Plasticizers are being used on a large scale worldwide (Bizzari et al, 2000). Their occurrence in indoor dust has been demonstrated, with a content of up to 12 g/kg (Pöhner et al, 1998; Butte et al, 2001). The concern about elevated indoor concentrations and toxicological properties has induced a trend to substitute the more widespread plasticizers, especially diethylhexyl phthalate (DEHP). The substituting compounds exhibit increased aliphatic chain length to decrease volatility. Thus, the production of phthalate plasticizers with nonyl or decyl chains has increased, while that of DEHP has decreased constantly (Bizzari et al, 2000).

Commonly used GC methods are less suited to analyse compounds of low volatility. High-temperature GC is also not very appropriate for this case due to the risk of compound degradation and extended analysis time. To circumvent these difficulties a HPLC method has been developed to analyse the whole range of phthalates and other plasticizers. A mass spectrometer with atmospheric pressure chemical ionisation (APCI) or, alternatively, electrospray ionisation (ESI) was tested as a selective and sensitive detector. Both ionisation techniques produce distinct mass spectra different from typical electron impact (EI) mass spectra in general but similar to chemical ionisation mass spectra of GC/MS. The principles of APCI and ESI mass spectrometry have been described elsewhere (Linscheid, 1992; Finnigan, 1993).

The method described in this paper is suitable to determine phthalate plasticizers with a chain length of $\geq C_{10}$, alkylated adipates and high molecular compounds like trioctyl trimellitate. In order to demonstrate the usefulness of this method, a pilot study on the content of plasticizers in settled dust and house dust (content of vacuum cleaner bags) was carried out. The results are reported here.

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MATERIALS AND METHODS

Toluene of picograde quality (Promochem) and acetonitrile of hypergrade quality (Merck) were used as solvents. All standard compounds (from different suppliers) were of 98+**%** purity in general. Aqua bidest was obtained by a Millipore water purifier Milli-Q synthesis. Rectangular aluminium dishes of about 0.127 m^2 (0.27 cm x 0.47cm) were used to collect settled dust. Glass fibre filters, No. 10370302, diameter 5 cm, supplied by Schleicher and Schüll, were used to wipe the aluminium dishes. Solvents, although being of picograde quality, were found to contain noticeable amounts of dibutyl phthalate and diethylhexyl phthalate with the consequence of considerable blank values and high limits of determination. All other materials were tested for plasticizers and contained only negligible amounts of plasticizers.

Quantitative LC/MS analysis was performed using a HPLC Waters Alliance 2690 equipped with an autoinjector and an UV photodiode array detector PDA 996. The HPLC was connected to a mass spectrometer Finnigan SSQ 710 equipped with ESI and APCI ion sources.
The HPLC parameters were as follows:

Column:	RP 18 column, X Terra MS C_{18}, Waters, 2.1 x 100 mm, 5 μm.
HPLC pump:	Flow rate of 0.25 ml/min.
Gradient:	Acetonitrile (A) and aqua bidest (B); A = 60 %, B = 40 % at 0 min; A = 20 %, B = 80 % at 6 min; A = 0 %, B = 100 % at 28 min; holding for 2 min.
Injection:	5 μl by autoinjector.
PDA:	230 nm (quantification).
Software:	Millennium[32], vers. 3.2.

The optimisation of MS/APCI ion source parameters was performed using a DEHP solution in acetonitrile fed directly into the APCI source by a piston pump. Fine tuning of the parameters was performed with HPLC runs of standard solution of plasticizers. After evaluating and optimising the MS performance the pilot study on plasticizers in dust was carried out using the following MS and APCI parameters. All interesting compounds were determined using the individual molecular ion ($M+H^+$) as indicated in Table 1.

Sheath gas:	Nitrogen at a pressure of 60 psi (flow rate of about 5 l/min).
Interface conditions:	Vaporizer set to 400 ºC; corona needle potential: 5.2 μA; capillary temperature: 170 ºC; capillary voltage: 20 to 24 V, depending on mass fragment; tube lens potential: 50 to 80 V, depending on mass fragment; octapol voltage: –3.0 V; octapol offset voltage: 0 V.
Tuning:	MRFA-myoglobin and tetraalkyl ammonium hydroxide in a solution of acetonitrile (alkyl = methyl, ethyl and propyl).
SIM mode:	Centroid mode; 7 ions, 200 msec/ion (DMP – BBP, DcHP); 6 ions , 300 msec/ion (DiHP - DiDP); 1 ion 800 msec/ion (TOT); ions as given in Table 1.
Data software:	Finnigan ICIS 8.3.0 and Xcalibur vers. 1.2.

To control the performance and quality of the analytical method typical performance characteristics (limit of determination, recovery rate, standard deviation of replicate analysis)

were determined. In addition, the results obtained with APCI/MS and PDA were compared, and the standard deviation of duplicate field sampling was determined.

Table 1: Comparison of the base peaks in mass spectra of plasticizers used for APCI ($M+H^+$) and recorded for EI in a MS library

Plasticizer	**APCI**	**EI**
Dimethyl phthalate (DMP)	**m/z 195**	m/z 163
Diethyl phthalate (DEP)	**m/z 223**	m/z 149
Dibutyl phthalate (DBP)	**m/z 279**	m/z 149
Benzyl butyl phthalate (BBP)	**m/z 313**	m/z 149
Diisoheptyl phthalate (DiHP)	**m/z 363**	m/z 149
Diethyhexyl phthalate (DEHP)	**m/z 391**	m/z 149
Diisononyl phthalate (DiNP)	**m/z 419**	m/z 149
Diisodecyl phthalate (DiDP)	**m/z 447**	m/z 149
Dibutyl adipate (DBA)	**m/z 259**	m/z 185
Diethylhexyl adipate (DEHA)	**m/z 371**	m/z 129
Diethylhexyl azelate (DEHAz)	**m/z 413**	m/z 171
Trioctyl trimellitate (TOT)	**m/z 547**	m/z 305
Dicyclohexyl phthalate (DcHP = Internal Standard)	**m/z 331**	m/z 149

In the pilot study, plasticizers were mainly determined in settled dust collected in aluminium dishes over one year. In addition, house dust collected by vacuum cleaning was analysed. 34 duplicate samples of settled dust were obtained from two office rooms and six homes. Field blanks were obtained using aluminium dishes which had been placed indoors for the same sampling period, but closed with an aluminium lid.

The dust settled on the aluminium dish was wiped off six times using six different filters for each dish. The filters were weighed before and after wiping to determine the amount of dust settled. A second wiping procedure with six additional filters was used to control the completeness of dust removal. Actual blank values were obtained by using this second set of filters. The dishes for the field blanks were wiped with six filters only once to determine the field blank values. The sets of six filters, placed top on top, were spiked with an internal standard IS (100 µl of a solution of 50 µg DcHP in acetonitrile) and then extracted with 30 ml toluene in a jar using ultrasonication for 30 min followed by filtration by means of a G4-frit. The filtered extract was evaporated to dryness under vacuum by rotary evaporation and the residue was taken up in 1 ml acetonitrile. Aliquots of this solution were analysed.

House dust samples were collected by vacuum cleaning of the same office rooms where settled dust was sampled. All samples were sieved to three fractions (2000 – 63 µm, 63 – 30 µm and < 30 µm). Amounts of ≤ 100 mg were analysed as described for settled dust samples.

RESULTS AND DISCUSSION

HPLC/APCI-MS optimisation

In comparison to the ESI ionisation the APCI ionisation technique proved to be more sensitive, more specific and easier to interpret. ESI generated mass spectra often include various mass clusters depending on HPLC conditions. APCI can yield spectra at a superior S/N ratio with very low fragmentation similar to the spectra obtained by GC/MS with chemical ionisation. Additionally, structural information can be provided as well. Examples of

APCI mass spectra of DEHP are displayed in Figure 1a/b), the corresponding ESI mass spectrum is shown in Figure 1c). The EI mass spectrum in Figure 1d) was taken from a MS library.

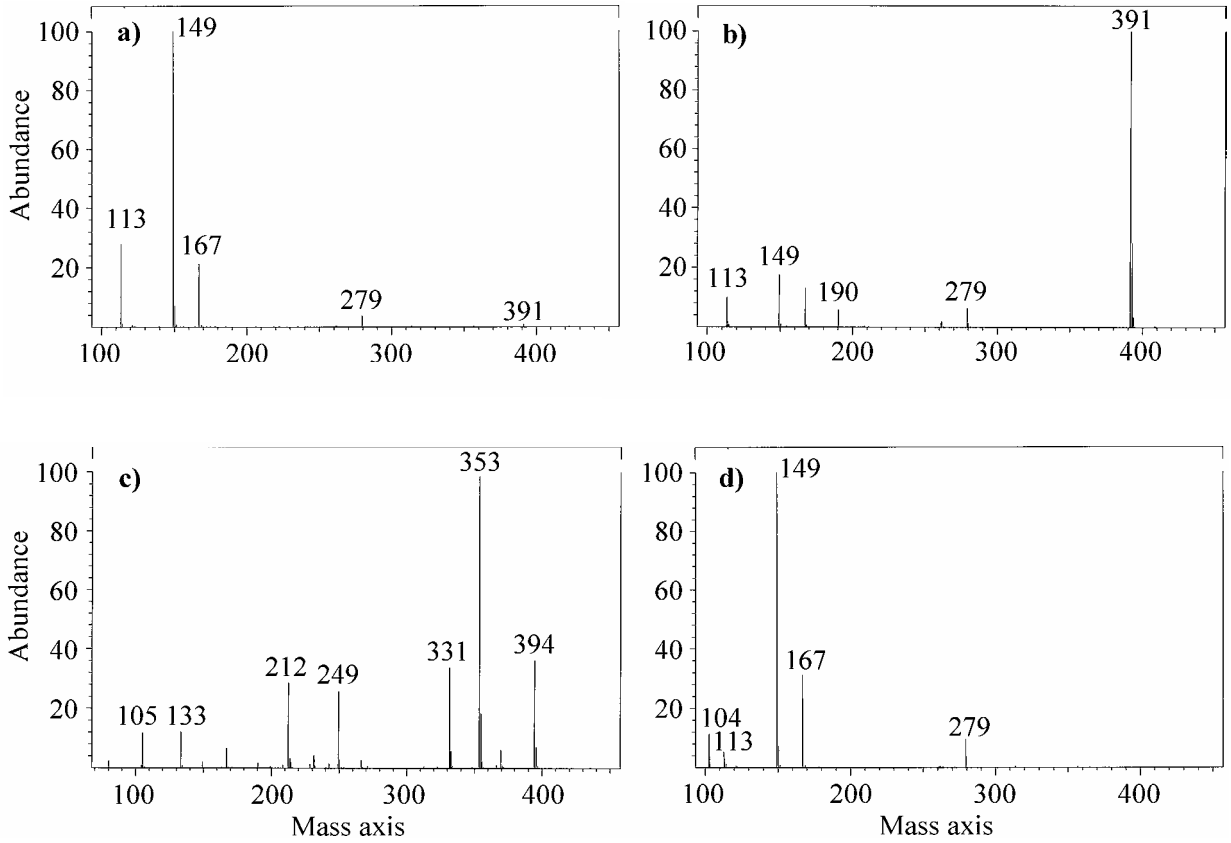


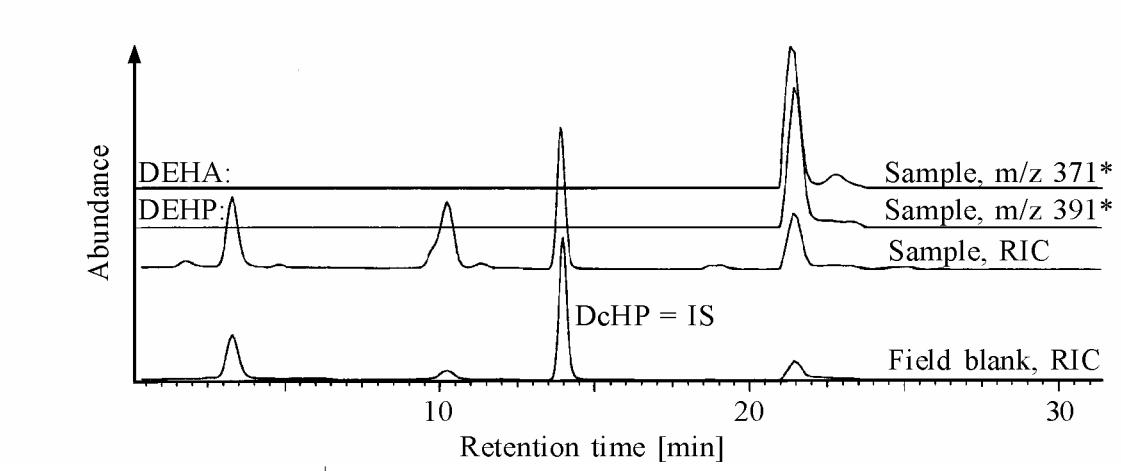
Figure 1. Mass spectrum of DEHP depending on various ionisation parameters:
a) APCI: tube lens voltage 75 V, octapol offset voltage 10 V;
b) APCI: tube lens voltage 50 V, octapol offset voltage 0 V;
c) ESI: tube lens voltage 75 V, octapol offset voltage 10 V;
d) EI: typical GC/MS spectrum from a MS library

The potential of the corona needle must be high enough to produce a current of 5.2 µA. However, at levels beyond this potential the peak shape becomes irregular and its area is difficult to determine. The sheath gas flow, temperature and voltage of the capillary which all have a significant influence on ion recovery were optimised and the respective values are given in the Methods section. The tube lens potential and the octapol offset voltage proved to be of essential influence on the mass fragmentation pattern, as shown in Figure 1a/b). The tube lens potential influenced the mass discrimination considerably and values of 50 to 80 V proved to be optimal for investigating compounds with mass ions up to m/z 550. The octapol offset voltage, especially at settings above 10 V, will increase the observed fragmentation. Typically, we obtained the best performance at 0 V when using the molecular ion as base mass peak.

Different settings of these parameters result in a widespread variation of mass spectra for each compound. If these are optimised, APCI is a very flexible and useful ionisation method. The individual molecular mass ($M+H^+$) is to be preferred generally in order to determine the plasticizers selectively and sensitively. The individual base mass peaks of plasticizers, after

optimisation of APCI parameters, are those reported in Table 1 which gives also the typical mass fragments of EI, e.g. m/z 149 for the group of phthalates.
The performance characteristics of the complete analytical method are as follows:
Limit of determination: From 150 µg/g for DEHP which shows high blank levels which, in addition, vary considerably down to 1 µg/g (for compounds with negligible blank values like e.g. TOT), referred to a sample of 50 mg dust.
Recovery rates: 105 % (DEP) to 130 % (DEHAz)
Relative SD of replicates: 3 % (DcHP) to 16 % (DEHAz), n = 12

HPLC/MS results of the plasticizer content in dust.
Field measurements of settled dust were carried out in several households and office rooms. Most of the investigated plasticizers have been found and a typical chromatogram is shown in Figure 2. Although DEHP and DEHA have the same retention time, the concentration of each compound can be determined without any interference using different molecular masses.



*Traces of $(M+H^+)$ of two selected compounds with the same retention time

Figure 2. LC/MS chromatograms of a settled dust sample (upper traces) and of a field blank (lower trace); the relative abundance of each trace was set to 100%

Information on the reliability of the analytical procedure used can be obtained by comparing the results of different detection methods. LC/MS and LC/PDA gave comparable results differing by only a few percent in general (1 % in the case of BBP and DEHP as best results). However, the PDA cannot detect all interesting compounds, some plasticizers will be overestimated due to the possible occurrence of unknown coeluents and the limits of determination are elevated in comparison to APCI/MS.

The standard deviation of duplicate sampling is given in Table 2 including both detection methods.

Table 2. Relative standard deviation of duplicate sampling of settled dust (all values, n = 34, at concentrations similar to those in column 2 of Table 3)

SD, %	DEP	DBA	DBP	BBP	DiHP	DEHA	DEHP	DiNP	DEHAz	DiDP	TOT
LC/APCI/MS	>50	44	**20**	**14**	>50	**18**	**16**	>100	>50	**26**	**22**
LC/PDA	>50	-	**17**	**26**	>50	-	**22**	-	-	>50	-

-: insufficient UV-response at 230 nm or very high limits of determination

As presented in Table 2 by bold figures the most important plasticizers can be analysed in dust samples satisfactorily when using APCI/MS. The results of DEP, DBA, DiHP, DiNP and DEHAz were considered as semi quantitative only due to the few values just above the limit of determination. However, even for those components the APCI/MS is a more sensitive detector than the PDA.

First results of a pilot study on settled dust are summarized in Table 3, which contains also the content of plasticizers in house dust collected by vacuum cleaning. Due to very small amounts of dust of the house dust fraction <30 µm (about 10 mg) high limits of determination were obtained in these cases. However, a dust sample of ≥50 mg (settled dust and house dust fractions >30 µm, this study) is quite sufficient to get a first information of the contents of the whole range of plasticizers in indoor dust.

Table 3. Occurrence of plasticizers in indoor dust of an office room, mean values in µg/g dust

	Settled dust	House dust, sieved, n=2		
	n=18	<30 µm	30-63 µm	63-2000µm
DEP	30	50	55	5.2
BBP	92	<30	38	25
DBP	86	1200*		78
DiHP	40	<100	2.0	1.8
DEHA	310	<100	53	23
DEHP	940	500	560	350
DiNP	80	<100	16	10
DiDP	110	<100	93	37
TOT	3.1	<5	1.6	2.6

* Two fractions combined

CONCLUSION

LC/APCI/MS has been shown to be a powerful system for the determination of different plasticizers in indoor dust including compounds of very low volatility. The method can be used to follow the observed trend to substitute the currently used plasticizers with other of higher molecular weight and, thus, lower volatility. The occurrence of such compounds in indoor dust needs to be followed more closely in the coming years.

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