Pyrolysis–capillary gas chromatography–mass spectrometry for the determination of polyvinyl chloride traces in solid environmental samples

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Abstract

A novel method based on pyrolysis–capillary gas chromatography–mass spectrometry (CGC–MS) was developed for the quantitative analysis of polyvinylchloride (PVC) in solid environmental samples like sludge and dust. The samples are extracted and the extract is fractionated by solid-phase extraction (SPE). Possibly interfering biological and frequently occuring synthetic polymers are removed by this clean-up. The final extract is analyzed by pyrolysis–CGC–MS. Selective detection of PVC is performed by using specific markers in the pyrogram. Quantitation is done on naphthalene. Good linearity was obtained in a range from 0.5 to 100 μg applied to the pyrolyser. The limit of quantitation (LOQ) in sludge and dust samples is 10 mg/kg dry mass. A correlation between PVC and phthalates was made for sewage sludge samples. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The worldwide use of phthalic acid esters (phthalates) has resulted in their widespread distribution in the environment and their presence in different matrices (air, water, soil, sediments, etc.) has been a topic of intensive research for several years [1–5]. Phthalates are in the first instance used as plasticizers in polymers (mainly polyvinylchloride, PVC), but they are also applied in cosmetics, paints, inks, etc. [6,7].

The toxicity of phthalates has been, and still is, the subject of controversial discussions [8–13]. As a contribution to phthalate risk assessment, it is interesting to evaluate possible pathways of how these compounds are transported in air, water and soil. This question can be partly answered by investigating the relationship between phthalate concentrations in environmental samples and the presence of PVC as main carrier. Phthalates are incorporated into the polymer in weight percentages of up to 60% and consequently when PVC products are dumped,

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phthalates can be released into the environment. To obtain information about the relationship between PVC and phthalates, analytical methods for the trace analysis of both PVC and phthalates are needed.

Several techniques have been described for the characterization of PVC. Gel permeation chromatography, for instance, can be used to determine the molecular mass distribution of the polymer [14–16]. Other techniques include infrared spectroscopy (IR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), etc. These techniques are, however, not suitable for trace analysis of PVC. The only method that has been applied to the trace analysis of PVC in sewage sludge, sewer film, compost and wastewater filtrates is based on ^{1}H-NMR spectroscopy [17,18]. Isolation of PVC from the matrix consists of extraction followed by fractionation of the polymer with tetrahydrofuran. The methylene signals of PVC in the NMR spectrum are used for quantification. The limit of detection is approximately 30 mg/kg dry mass.

Pyrolysis combined with mass spectrometry (MS) or coupled to capillary gas chromatography (CGC)–MS has shown to be a powerful tool for the characterization and identification of polymers [19,20]. In pyrolysis–CGC analysis, the sample is heated very fast to high temperatures (500–1400°C) and the resulting (semi-) volatile decomposition products are transferred on-line to the capillary column for GC-analysis. The nature and relative abundance of the pyrolysate compounds provide information on the structure of the polymer. By selecting marker compounds of a specific polymer quantitative pyrolysis–CGC can provide information on the concentration of a polymer in a defined matrix.

The degradation of PVC in combustion processes or at pyrolysis conditions (inert atmosphere) [21] is well understood. The reaction mechanism, called zipper elimination, is a complex chain dehydrochlorination. After HCl elimination, isolated double bonds are generated, followed by fast allylic activated dehydrochlorination to form conjugated bonds. These unsaturated chains are intermediates for cyclisation reactions resulting in aromatic compounds. As HCl is 'released' quantitatively at elevated temperatures, acidic titrations can be used either to measure degradation rates in stability tests or to estimate the amount of PVC that is present in the sample. Though, when PVC is to be determined in environmental matrices, the selectivity of this method is inadequate.

Pyrolysis–CGC–MS is more powerful in this respect and several systems have been developed [19,20]. Quantitative pyrolysis, however, requires high reproducibility of sample degradation at a preset temperature. Filament pulse pyrolysers provide very fast heating rates but the reproducibility of the time versus temperature profile leaves much to be desired. A system with temperature monitoring in the pyrolyser has been described [22,23]. The temperature is monitored by measuring the resistance over the filament. Additionally, applying pyrolysis temperatures above 600°C, a photodiode is measuring the light emitted by the filament during pyrolysis and a correlation with temperature is made. In this way, the temperature profile can be followed accurately and eventually be adjusted which results in excellent reproducibility.

In the present paper a pyrolysis–CGC–MS method for trace analysis of PVC in solid environmental samples is described. A correlation between PVC concentration and concentration of phthalates was made for sewage sludge samples.

2. Experimental

2.1. Solutes

Polyvinylchloride (PVC) powder 'EVIPOL' donated by the European Council for Plasticizers and Intermediates (ECPI, Brussels, Belgium) was used for calibration. This product does not contain additives. A stock solution of 10 mg/ml was prepared in pestiscan grade tetrahydrofuran (Labscan, Dublin, Ireland). Calibration standards were made by dilution of the stock solution with THF and were stored at room temperature. Several formulations of PVC were donated by Solvay Inc. (Antwerp, Belgium) and Exxon Chemical Europe Inc. (Machelen, Belgium) and contained different amounts of plasticizers (mainly DEHP), antioxidantia and stabilizers. Solutions were prepared in pestiscan grade THF in a concentration of 10 mg/ml. THF-d8 (99.5 at.%) and thymol (98%) used as solvent and internal standard

for ^{1}H-NMR analysis, respectively, were purchased from Sigma–Aldrich (Bornem, Belgium).

2.2. Instrumental set-up

2.2.1. Pyrolysis–CGC and pyrolysis–CGC–MS analysis of PVC

The pyrolysis unit is a filament pulse pyrolyser (Pyrola 2000, Pyrolab, Lund, Sweden). The system is mounted on an Agilent 6890 gas chromatograph (Agilent Technologies, Little Falls, DE, USA). The transfer line of the pyrolyser is inserted into a split-splitless injector. The split ratio is set at 1:50. Pyrolysis of the sample is done at 900°C (8 ms pulse, 2 s pyrolysis time) with a chamber temperature at 175°C. Helium is used as carrier gas. The injector temperature is set to 280°C. For CGC–flame ionization detector (FID) analysis a 10 m×0.1 mm I.D.× 0.4 μm d_f HP1–MS column was used. The oven temperature was ramped from 50°C to 325°C at a rate of 25°C/min. For CGC–MS analysis, a 30 m×0.25 mm I.D., 0.25 μm d_f HP5–MS column was used. In this case, the oven temperature was programmed from 40°C to 320°C at a rate of 20°C/min. Mass spectrometric detection was done with an Agilent 5972 mass selective detector (Agilent Technologies, Little Falls, DE, USA) in the scan mode (*m/z* 40–400).

2.2.2. ^{1}H-NMR analysis of PVC

^{1}H-NMR spectra were taken with a Bruker AM-500 NMR at 500 MHz.

2.2.3. CGC–MS analysis of phthalates

Gas chromatographic analysis of phthalates was performed on an Agilent 5890 GC coupled to an Agilent 5972 MSD. Injection was done using an Agilent 7673 autosampler. The samples were injected on-column in the oven track mode. Separation was performed on a 30 m×0.25 mm I.D.×0.25 μm d_f HP5–MS column. The oven was programmed from 50°C (1 min) to 320°C (3 min) at a rate of 15°C/min. The mass selective detector was operated in the selected ion mode at *m/z* 163 (dimethylphthalate (DMP)), *m/z* 149 (diethylphthalate (DEP), di-isobutylphthalate (DiBP), dibutylphthalate (DBP), butylbenzylphthalate (BBzP), bis(2-ethylhexyl)phthalate (DEHP)), *m/z* 293 (di-isononylphthalate

(DiNP)) and *m/z* 307 (di-isodecylphthalate (DiDP)). The transfer-line to the MS was set at 300°C.

2.3. Sample preparation

2.3.1. Pyrolysis–CGC analysis of PVC

Wet samples are dried overnight at 105°C. Five grams of dried solid sample is ultrasonically extracted with 25 ml tetrahydrofuran for 30 min. The sample is centrifuged and the supernatant is transferred to a test tube. The sample is washed with two additional portions of 10 ml of THF and the fractions are combined. The extract is concentrated to 0.5 ml under nitrogen. The concentrate is then applied onto a 500 mg silica SPE cartridge (Supelco, Bornem, Belgium). The solvent (THF) is removed by evaporation by applying a gentle stream of nitrogen in the upstream direction. The cartridge is then washed with 5 ml diethyl ether followed by 5 ml toluene applying a slight vacuum. Each time the solvent is left on the cartridge during 5 min before applying vacuum. Elution of PVC is done with 3×3 ml THF in the following way. The first 3 ml of solvent is applied to the cartridge to dissolve PVC traces. Only after 20 min, the THF is pushed through the cartridge using a slight vacuum. After elution, the cartridge is eluted with two additional portions of 3 ml THF. The extract is finally concentrated to 1 ml and 10 μl of the final solution is applied to the filament for pyrolysis.

2.3.2. ^{1}H-NMR analysis of PVC

Five grams of sample is extracted and purified following the method described above. The final extract is evaporated to dryness under a gentle stream of nitrogen. The residue is dissolved in 1 ml deuterated THF, containing 10 mg/ml thymol as internal standard. This extract is used to record the ^{1}H-NMR spectrum.

2.3.3. CGC-analysis of phthalates in sludge

Five grams of wet sludge is weighed and 5 ml methanol is added. The mixture is ultrasonically extracted for 15 min after which 20 ml saturated sodium chloride solution is added. The sample is extracted with 5 ml cyclohexane (15 min ultrasonic bath) and centrifuged. The supernatant is transferred to an autosampler vial for CGC–MS analysis. For

quantitation, the same sample amount is taken and dried at 105°C for dry mass determination. The method was validated for a concentration range between 10 and 10 000 ng/ml wet sludge. Recoveries were higher than 80%.

3. Results and discussion

3.1. The PVC pyrolysis profile

The pyrogram of PVC obtained by pyrolysis at 900°C is presented in Fig. 1. The CGC analysis of the pyrolysate was done on the HP1 column with FID detection. The main peaks were identified as benzene, toluene, styrene, indene and naphthalene. These compounds are the main markers for PVC. The triplet eluting before naphthalene (around 4.5–4.6 min) and the doublet eluting after naphthalene (around 5.4–5.6 min), were also found to be characteristic for PVC. These compounds were identified as

1-methylindene (**1**), 3-methylindene (**2**), 1,2-dihydronaphthalene (**3**), 2-methylnaphthalene (**4**) and 1-methylnaphthalene (**5**). In the analysis of PVC, these compounds can be used as markers to confirm the presence of the polymer (confirmation markers). The relative abundances of the markers in the PVC pyrogram are constant for pyrolysis temperatures between 700 and 900°C. By increasing the pyrolysis temperature from 700 to 900°C, however, the abundances of the marker peaks increased and therefore 900°C was used as pyrolysis temperature for trace quantification of PVC in environmental samples.

The consistency of the PVC profile was evaluated by the analysis of different formulations of PVC. A series of nine PVC batches containing different amounts of plasticizers (mainly DEHP), stabilizers and antioxidantia were analyzed. The ratios of the peak areas of the main markers (benzene, toluene, styrene and indene) were calculated relative to naphthalene. The relative standard deviations on the
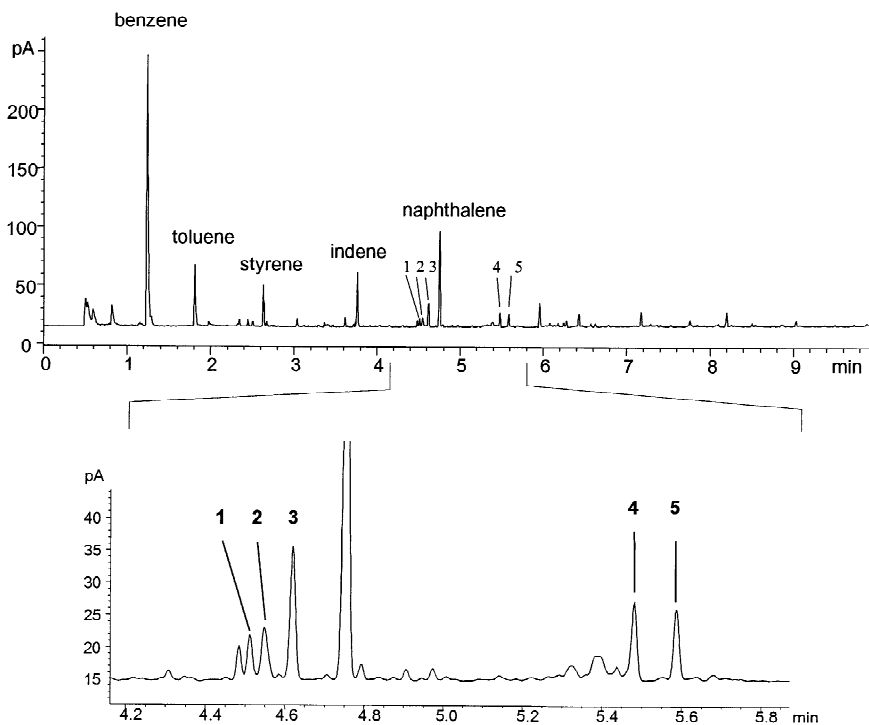

Fig. 1. Pyrolysis–CGC–FID of PVC at 900°C with detail of the fraction eluting between 4.2 and 5.8 min. Identified PVC markers: 1-methylindene (**1**), 3-methylindene (**2**), 1,2-dihydronaphthalene (**3**), 2-methylnaphthalene (**4**), 1-methylnaphthalene (**5**). Chromatographic conditions see text.

relative abundances did not exceeded 20% in the pyrograms of all PVC samples tested. This means that the above-mentioned markers can be used for the qualitative and quantitative determination of PVC and that the presence of additives does not significantly influence the program.

3.2. Trace analysis of PVC by pyrolysis–CGC–MS

Pyrolysis–CGC has been combined with mass spectrometric detection for the trace analysis of PVC in environmental samples. Although selected ion monitoring (SIM) provides higher sensitivity, all analyses were performed in the scan mode, allowing additional identification. Identification and quantification of PVC was done using extracted ion chromatograms at m/z 78 (benzene), 91 (toluene), 104 (styrene), 115 (indene), and 128 (naphthalene) (Fig. 2A). The confirmation markers were monitored at

m/z 130 (methylindenes and dihydronaphthalene) and 142 (methylnaphthalenes) (Fig. 2B).

In both CGC–FID and CGC–MS experiments, the injector was operated in the split mode using a 1:50 split ratio. Splitless injection or lower split flows could theoretically be used to increase the sensitivity, but peak broadening was observed. Because the solvent of the sample is evaporated on the filament before pyrolysis is started, relative large quantities could be dosed. Applying 10 µl samples, no change in peak shapes and areas was noticed compared to 1 µl samples of corresponding concentrations. In this way, the sensitivity could be increased by a factor of 10.

3.3. Linearity

Calibration standards of 0.5, 1, 10 and 100 µg PVC were pyrolysed by applying 10 µl of a 0.05,
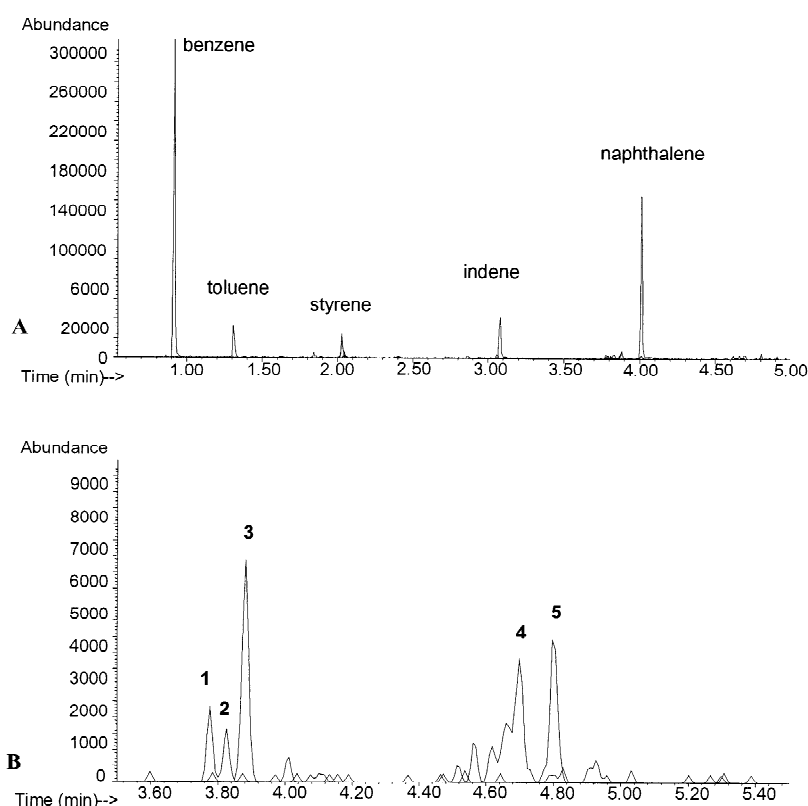

Fig. 2. Pyrolysis–CGC–MS of PVC at 900°C. Extracted ion chromatograms at m/z 78, 91, 104, 115 and 128 for main PVC markers (A) and at m/z 130 and 142 for PVC confirmation-markers. Chromatographic conditions see text, for peak numbering see Fig. 1.

Table 1
Correlation coefficients of calibration curves for PVC markers in the range from 0.5 to 100 µg PVC applied to the pyrolyser

Compound	Quantification of ion	Correlation coefficient
Benzene	78	1.000
Toluene	91	0.992
Styrene	104	0.997
Indene	115	0.994
Naphthalene	128	0.999
1-Methyl-1-H-indene	130	0.998
3-Methyl-1-H-indene	130	0.995
1,2-Dihydronaphthalene	130	0.998
2-Methylnaphthalene	142	0.999
3-Methylnaphthalene	142	1.000

0.1, 1 and 10 mg/ml PVC solution in THF. Peak areas were measured in the extracted ion mode (m/z 78, 91, 104, 115, 128, 130 and 142). The calibration curves showed correlation coefficients of 0.992 or higher. Table 1 illustrates the good linearity for all marker solutes. Naphthalene was used for quantification of PVC in environmental samples.

3.4. Detection limit

Applying a split ratio of 1:50, all marker peaks (benzene, toluene, styrene, indene and naphthalene) could be detected at an absolute amount of 150 ng PVC on the filament (LOD=150 ng, S/N=3). The quantification limit was set to 500 ng PVC absolute weight (LOQ=3.3×LOD). Consequently, when the PVC eluate is concentrated to 1 ml and 10 µl is injected on the pyrolyser filament, analysis of PVC in 5 g of an environmental sample corresponds to a quantification limit of 10 mg/kg dry mass.

3.5. Repeatability and reproducibility

Repeatability of the analysis of PVC by pyrolysis–CGC–MS was tested by performing a series of nine analyses of a PVC standard applying 10 µg PVC on the filament. The relative standard deviations on the absolute peak areas for the five main marker compounds using extracted ion chromatograms were around 10%. The reproducibility tested over a period of 4 days for 18 analyses in total and calculated on daily mean values is in the same order like the RSDs (Table 2).

3.6. Analysis of environmental samples

3.6.1. Selectivity of pyrolysis CGC–MS
Since PVC is well soluble in tetrahydrofuran, environmental samples can be extracted with this solvent. However, most uncrosslinked polymers with the exception of polyolefines, polyfluoro hydrocarbons, polyacrylamide, polyamides, polyurethanes,

Table 2
Repeatability and reproducibility expressed as RSD (%) on the marker peak abundances for the analysis of PVC by pyrolysis–CGC–MS[a]

Day Ion	n	Benzene (78)	Toluene (91)	Styrene (104)	Indene (115)	Naphthalene (128)
1	9	10	12	11	13	11
2	3	4	8	10	9	4
3	3	7	13	16	6	17
4	3	3	2	4	2	6
Reproducibility (%)		10	11	9	8	8

[a] Abundances were measured in the extracted ion mode.

urea and melamine resins, are also soluble in THF. Some frequently occurring THF soluble polymers are (expanded) polystyrene (PS), styrene-butadiene co-polymer (SB), polymethyl metacrylate (PMMA) and polycarbonate (PC). Consequently these polymers are co-extracted from environmental samples and interfere in the PVC pyrogram. For this reason, one sample of each of these polymers was pyrolysed at 900°C and the pyrograms were checked for the presence of benzene, toluene, styrene, indene and naphthalene. Absolute amounts (ng) of the main marker compounds that are produced during the pyrolysis of 1 μg of the individual polymer are given in Fig. 3. Most marker compounds were found in all pyrograms but their relative abundances are not equal to those of PVC. Naphthalene appeared to be the most interesting marker for PVC as only relatively small amounts of this aromatic hydrocarbon are produced during pyrolysis of the interfering polymers. Moreover, only polystyrene and styrene-butadiene co-polymer also show traces of the confirmation markers 1-methylindene, 2-methylindene, 1,2-dihydronaphthalene, 2-methylnaphthalene and 1-

methylnaphthalene. However, their relative abundances with styrene as reference are all below 0.003%. Nevertheless, PS, SB, PMMA and PC must be removed during clean-up of the sample to quantify PVC via the determination of naphthalene.

After application of the sample extract onto the silica cartridge, washing is performed with diethyl ether and toluene. These solvents do not solubilize PVC but diethyl ether is a good solvent for some styrene copolymers (e.g. styrene-butadiene co-polymer) and polycarbonate while toluene dissolves polystyrene and polymethyl metacrylate very well. These polymers are thus removed during the washing step. PVC is then finally eluted from the silica cartridge with THF. Natural organic polymers like cellulose or coal products also produce naphthalene when pyrolysed but these polymers are insoluble in THF and are therefore not extracted and retained on the silicagel. Consequently, they do not interfere in the analysis.

To demonstrate the selectivity of the enrichment procedure towards the isolation of PVC from a mixture of THF soluble polymers, 100 μl of a 10
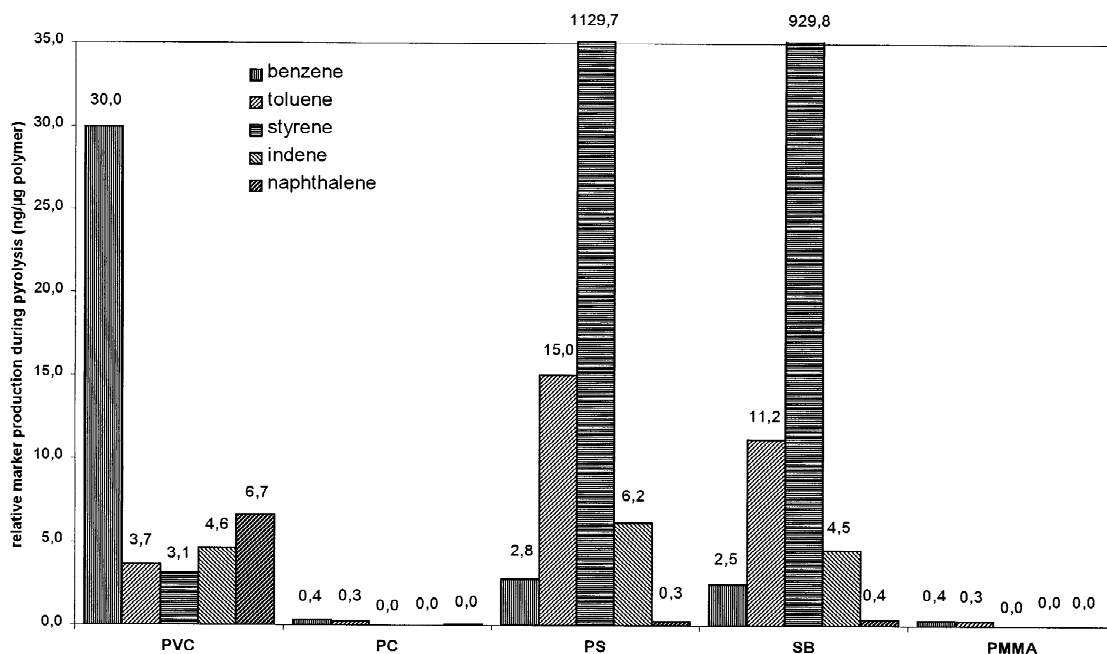

Fig. 3. Relative production (ng marker / μg polymer) of benzene, toluene, styrene, indene, naphthalene during pyrolysis of PVC, PS, SB, PMMA and PC.

mg/ml standard mixture of PVC, PS, SB, PMMA and PC was spiked on a 500 mg silica cartridge. After removal of the solvent (THF) the sample was submitted to the clean-up procedure described above. The final extract was concentrated to a volume of 1 ml and 10 μl of this solution was analysed by pyrolysis–CGC–MS. The pyrogram was compared with that of a 10 mg/ml PVC standard that was submitted to the same clean-up. Extracted ion chromatograms at m/z 78, 91, 104, 115 and 128 for the main marker compounds (Fig. 4) and at m/z 130 and
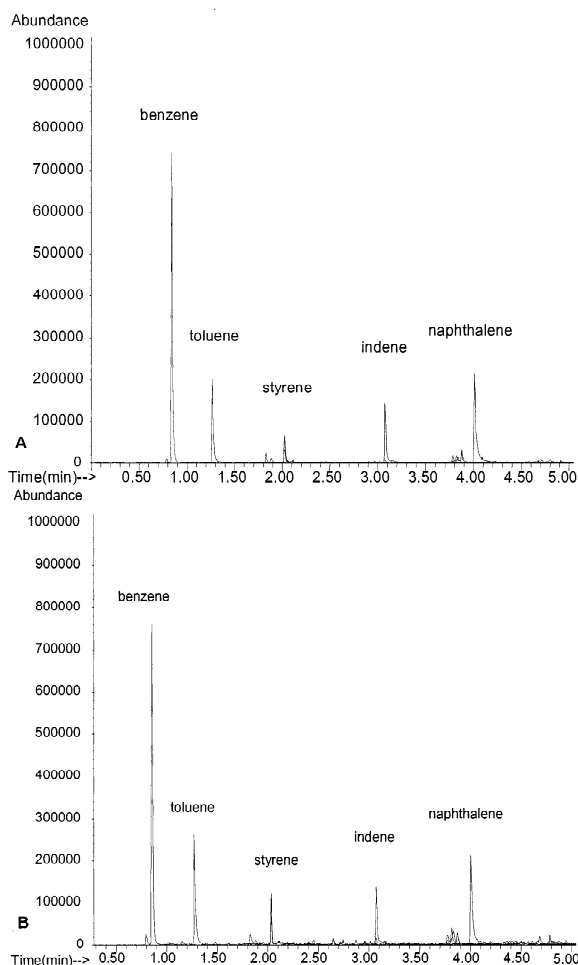

Fig. 4. Extracted ion chromatogram at m/z 78, 91, 104, 115, 128 for the main marker compounds of a 10 mg/ml standard of PVC (**A**) and a mixture of PS, SB, PMMA, PC and PVC (**B**) submitted to clean-up and pyrolysis–CGC–MS. Chromatographic conditions see text.

142 for the confirmation markers (Fig. 5) of both samples show that similar profiles are obtained. The recovery of the naphthalene peak in the sample of the polymer mixture was 96% relative to the naphthalene peak in the pure PVC standard.

3.6.2. Recovery and repeatability of the clean-up procedure

Dissolution of polymers is often a slow process. It is therefore important that the contact time of PVC with THF is sufficient long to dissolve all PVC. The first 3 ml of THF was kept in the cartridge for 20 min before it was eluted under slight vacuum. The cartridge was eluted with two additional portions of 3 ml THF. In these elutions, the solvent was left in the cartridge for 5 min before applying vacuum. If these precautions were taken, recoveries of higher than 80% could be obtained. This was tested in triplicate for a 100 μg PVC standard (86, 93 and 95% recovery relative to direct analysis of a standard) and for a 5 mg PVC standard (86, 85 and 83% recovery).

3.6.3. Linearity and repeatability after clean-up

The linearity of the total analysis (SPE–pyrolysis–CGC–MS) was verified by dosing respectively 0.1, 1 and 5 mg of a PVC standard on a silica SPE cartridge and performing the prescribed clean-up and elution procedure. The linearity curve of the naphthalene peak is graphically presented in Fig. 6 and shows a correlation coefficient of 0.9997.

The repeatability of the clean-up was tested with a dust extract. The sample was collected from a vacuum cleaner and thoroughly mixed. Three sub-samples of 5 g were submitted to extraction and clean-up. The RSD on the peak area of naphthalene in the extracted ion chromatogram (m/z 128) was 2%.

3.7. Accuracy of the PVC analysis

The analysis of PVC by pyrolysis–CGC–MS was validated by comparison with the ^{1}H-NMR method. Five grams of a dust sample was extracted and the

Fig. 5. Extracted ion chromatogram at m/z 130 and 142 for 1-methyl indene (**1**), 3-methyl indene (**2**), 1,2-dihydro naphthalene (**3**), 2-methyl naphthalene (**4**), 1-methyl naphthalene (**5**) of a 10 mg/ml standard mixture of PVC (**A**) and of a mixture of PS, SB, PMMA, PC and PVC (**B**) submitted to clean-up and pyrolysis–CGC–MS. Chromatographic conditions see text.
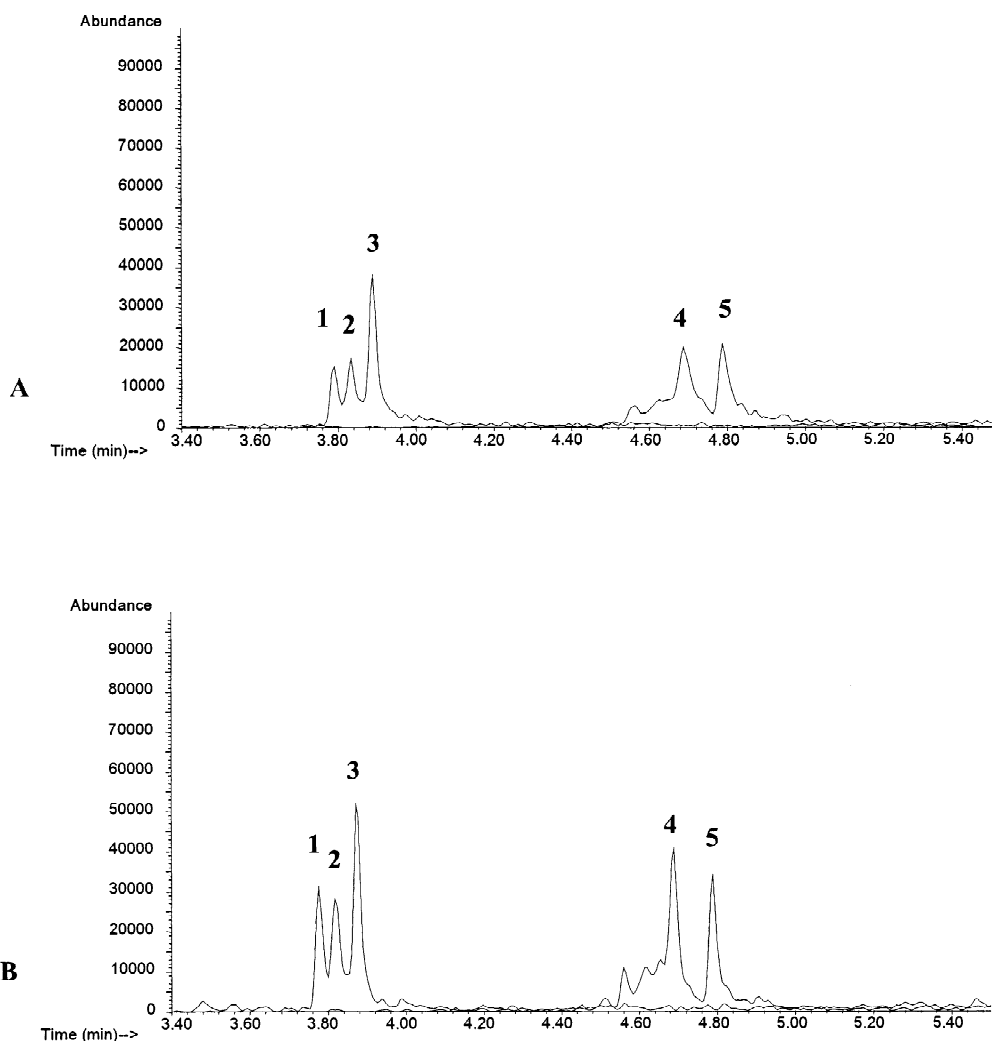
extract was concentrated to 1 ml. The dust extract and two standards of 1 and 5 mg PVC were submitted to the clean-up. Subsequently, 10 µl of the collected PVC fractions was pyrolysed. Quantitative analysis of the PVC concentration in the dust extract was done using a calibration line constructed from the areas of the naphthalene peaks (m/z 128) of the standards (Table 3). The resulting value was 3.86 mg/ml. The same extracts were analyzed by [1]H-

NMR. The samples were evaporated to dryness, and the residue was redissolved in 1 ml deuterated THF, containing 10 mg/ml of thymol (2-isopropyl-5-methylphenol) as internal standard. The ^{1}H-NMR spectrum of the dust extract is presented in Fig. 7. As described in the cited procedure [17,18], quantification of PVC was done by integration of the areas of the signals between 4.3 and 4.7 ppm and were compared with the internal standard signals between
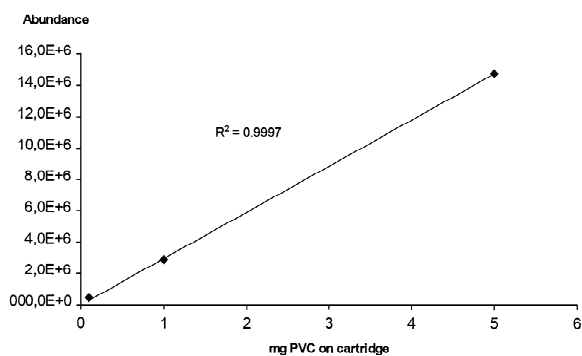
Fig. 6. Linearity of SPE–pyrolysis–CGC–MSD analysis of PVC using naphthalene as quantitative marker (extracted ion chromatogram at m/z 128).

6.4 and 6.6 ppm. The ratios of the integrated PVC and thymol signals were calculated and correlated to the PVC amount (Table 3). The PVC concentration was 3.50 mg/ml. The relative difference between the two values is ca. 10%, which proves that both techniques give comparable data. The accuracy was also verified in a standard addition experiment. PVC amounts of 10, 20, 50, 100 and 150 μg were added to 10 μl of the dust extract. Linear regression was performed on the resulting naphthalene peak abundances in the five analyses and the correlation factor was 0.9985 (Fig. 8). The Y-axis intercept of the curve ($16\,522 \times 10^3$) was compared to the peak area of the naphthalene peak of the original dust extract
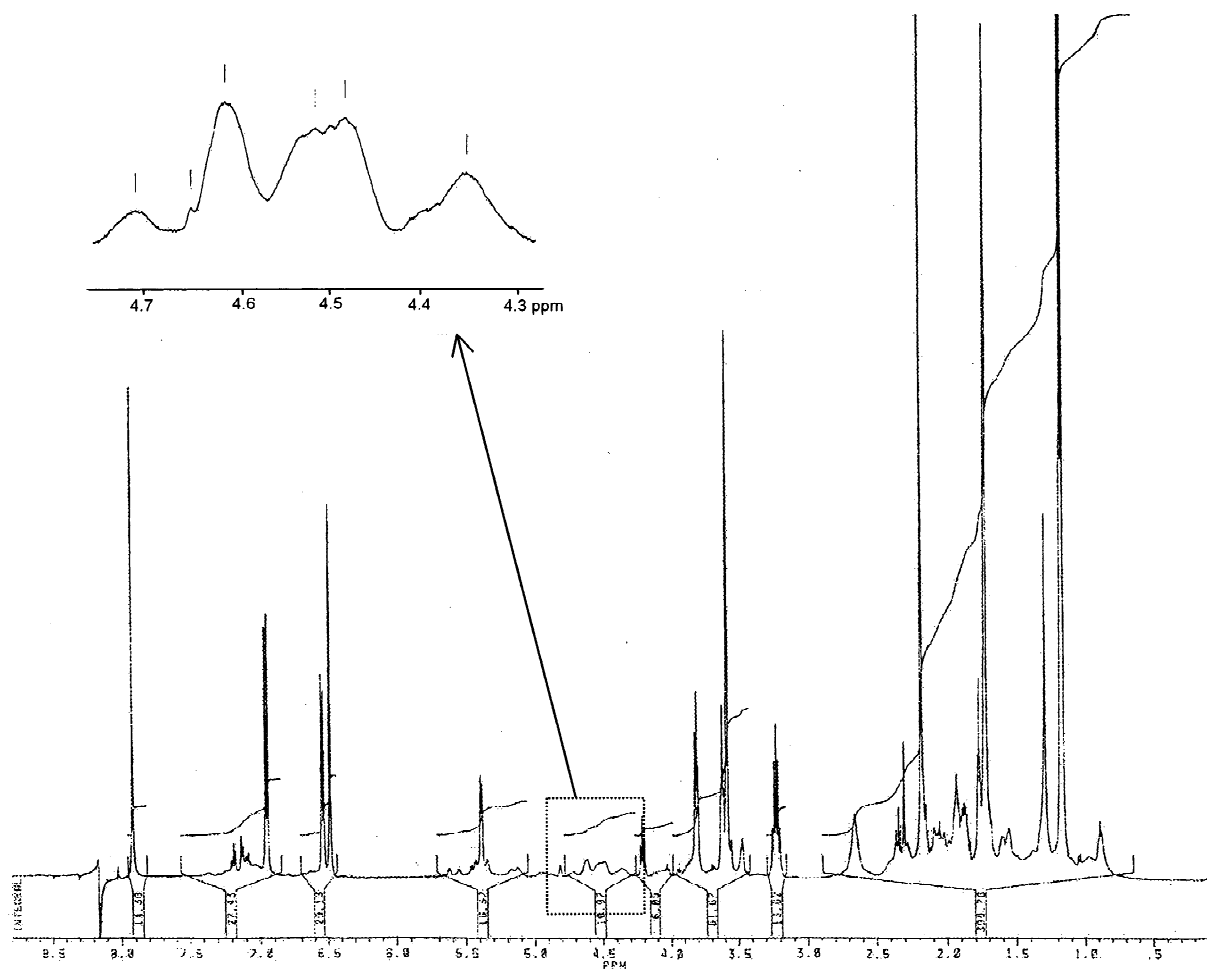

Fig. 7. ^{1}H-NMR spectrum of a dust extract with detail between 4.3 and 4.7 ppm.

Table 3
Concentration of PVC in a dust extract calculated from the pyrolysis–CGC–MS and ^{1}H-NMR method

	Pyrolysis–CGC–MSD Abundance naphthalene	^{1}H-NMR PVC/Thymol
Standard 1 mg/ml	5351×10^{3}	0.14
Standard 5 mg/ml	$21\,240\times10^{3}$	0.69
Sludge extract	$16\,721\times10^{3}$	0.49
Concentration PVC in sludge extract (mg/ml)	3.86	3.50

Table 4
PVC and phthalate concentrations in sludge (sl.) samples

Sample	Description	PVC (μg/g dry sludge)	Sum total phthalates (ppm)	Sum DEHP, DiNP, DiDP (ppm)
WWTP 1	Domestic sl.	174	175	33
WWTP 2	Industrial sl.	18	351	297
WWTP 3	Primary sl.	29	24	24
	Activated sl.	29	72	34
	Dewatered sl.	79	37	14
WWTP 4	Primary sl.	35	90	73
	Dewatered sl.	23	19	19
WWTP 5	Primary sl.	508	332	266
WWTP 6	Crude sl.	350	409	231
WWTP 7	Filter cake sl.	348	366	219
WWTP 8	Mixed crude sl.	227	289	137
WWTP 9	Primary sl.	52	88	69
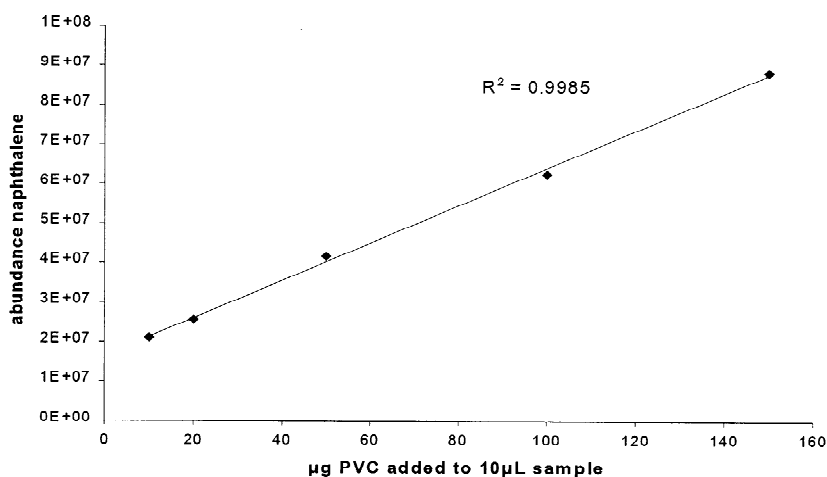
Fig. 8. Curve obtained for a standard addition of PVC to a dust extract. The peak area for naphthalene (extracted ion chromatogram on m/z 128) is plotted in function of added PVC amount.
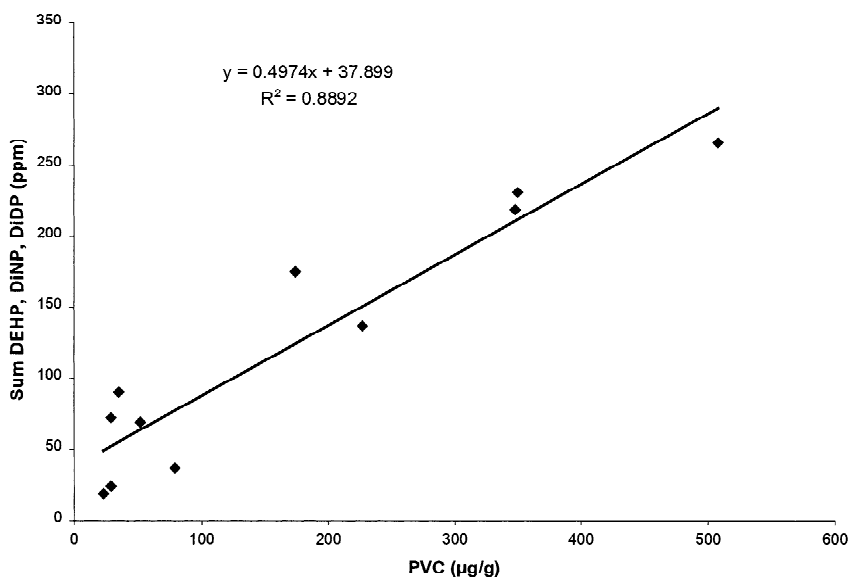
Fig. 9. Correlation between PVC and the sum concentration of DEHP, DiNP and DiDP in sewage sludge samples.

and differed only 1.2% with the measured value $(16\,721 \times 10^3$, Table 3).

3.8. Relationship between phthalate concentration and the presence of PVC in sewage sludge samples

Several sludge samples from different wastewater treatment plants (WWTP) were analyzed for PVC together with a low (0.1 mg) and high level (5 mg) PVC standard. In the same samples, the phthalates were also determined. The concentrations of PVC and phthalates in the sludges are listed in Table 4. Di-(2-ethylhexyl) phthalate (DEHP) was most abundant in the sludge samples. DEHP, DiNP and DiDP are the main plasticizers in the production of flexible PVC. If the sum concentration of these phthalates in sludge is plotted versus the PVC content, a correlation factor of 0.8892 was found (Fig. 9). Sludge WWTP 2 originated from an industrial wastewater treatment plant of a phthalate producer. The influent contained mainly DEHP and nearly no PVC. The sample was not taken into consideration for regression. This sample demonstrates the potential of the technique since it can filter out this special case.

4. Conclusions

Pyrolysis–CGC–MS offers a sensitive and robust tool for the qualitative and quantitative analysis of PVC in solid environmental samples. Isolation of PVC from other interfering polymers and compounds can be performed by a SPE clean-up on silicagel. Quantification is done using the naphthalene peak. Confirmation of the presence of PVC in sample extracts can be performed by measuring the relative abundances of other aromatic hydrocarbons as confirmation markers. For different sewage sludge samples, a good correlation between phthalates and PVC concentrations was found.

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