



## Determination of the plasticizer content in poly(vinyl acetate) paint medium by pyrolysis–silylation–gas chromatography–mass spectrometry

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### ABSTRACT

The use of plasticizers in emulsion paints is intended to provide optimal mechanical properties to polyvinyl acetate polymers (PVA), making them suitable as binding media for paintings. The loss of these properties with ageing is often related to the slow migration and evaporation of such plasticizers, resulting in severe embrittlement and potential damage to the paint film.

A new method consisting of the quantification of the plasticizer content of PVAc samples with “on-line” silylation–pyrolysis with hexadimethyldisilazane (HMDS) as a derivatization agent in Py–GC–MS and using 1,4-dibromobenzene as an IS is proposed here. For this purpose, two series of specimens of Mowilith 50<sup>®</sup> (a pure PVAc resin) with the addition of two different plasticizers, diethylphthalate (DEP) and dibutylphthalate (DBP), were prepared as thin films and submitted to a multi-step UV-light artificial ageing program so that the plasticizer content was determined at each ageing stage.

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## 1. Introduction

Due to the importance achieved by the PVAc paints in the contemporary artistic production of artworks, the study and characterization of these resins and the identification of their deterioration mechanisms have become a challenge for the scientists in the field of conservation of cultural heritage. The effects of ageing are fairly known and have been extensively reported, including increased brittleness, loss of tensile strength, darkening, yellowing and loss of translucency among others [1–4].

Research on the ageing of these products, therefore, is of the most importance for both conservators and conservation scientists and, for this purpose, several instrumental techniques have been widely applied in the characterization of synthetic materials such as infrared spectroscopy [5–9], Raman spectroscopy [9,10] and direct temperature resolved mass spectrometry [11].

Pyrolysis–gas chromatography/mass spectrometry (Py–GC–MS) has been successfully used for identification of synthetic binders present in commercial paints [12–22]. More recently, thermally assisted hydrolysis and methylation with tetramethy-

lammonium hydroxide (TMAH) has been introduced for the analysis of synthetic resins [22–26]. This method has been reported to have better sensitivity and resolution in the analysis of synthetic resins.

Previous studies have shown that Py–GC–MS can be successfully used to identify monomers and plasticizers used in acrylic and vinyl resin based products [1,3]. Alternatively, Doménech et al. have recently optimized an “on-line” derivatization method using hexamethyldisilazane (HMDS) as a derivatization reagent for the study of acrylic and vinyl resins as well as some of the additives present in different commercial formulations. According to these studies, trimethylsilylation of the carboxylic acids present in both types of resins contributes to a better repeatability in results comparing to direct pyrolysis [1,23]. However, the application of this instrumental technique in the study of ageing of PVAc materials is scarce.

The change in the mechanical properties of PVAc products has been related to the loss of external plasticizers [2]. Thus, quantification of the changes in the content of plasticizer in PVAc films could be of great interest in order to better understand the behaviour of this binding medium when subjected to ageing.

This paper presents a new method devoted to the quantification of plasticizer content on PVAc specimens with Py–GC–MS based on the use of an internal standard (IS). For this purpose, a series of test

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specimens were prepared with Mowilith 50<sup>®</sup> (a pure PVAc resin), and one of the two commonly used plasticizers, diethylphthalate (DEP) and dibutylphthalate (DBP). The plasticizer was added to a PVAc resin solution in the range of concentrations typically used in commercial PVAc emulsions [3]. The use of a pure PVAc resin in a solution form instead of a waterborne PVAc dispersion allowed controlling the quantities of plasticizer and resins during the several stages of the experimental procedure.

These test specimens were analyzed with “on-line” silylation–pyrolysis using hexadimethyldisilazane (HMDS) as a derivatization agent in Py–GC–MS [1], and 1,4-dibromobenzene was applied as an IS for quantification purposes. This latter reagent has been proposed by Moldoveanu [24] as an IS for the quantification of the analysis of pyrolysates from tobacco samples by Py–GC–MS. This author discusses the possibility of the use of 1,4-dibromobenzene in an aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) matrix.

In order to establish an optimal methodology for the quantification of plasticizers in PVAc films, two different analytical methods including the addition of an IS have been compared. In the first one, the IS was introduced as a finely powdered solid mixed in Al<sub>2</sub>O<sub>3</sub>, as proposed by Moldoveanu [24]. This method has been compared with a second procedure in which the IS is solved in *o*-xylene. The efficiency of both methods was compared on the basis of the repeatability obtained on the series of specimens of Mowilith 50<sup>®</sup> + plasticizer.

As a second step of this work, other two series of test specimens were subjected to UV-light ageing and the changes in concentration of the plasticizer were followed by the proposed analytical method. This confirmed the suitability of Py–GC–MS as a complementary technique to other analytical methods, such as spectroscopic ones, for following the chemical changes in PVAc resins.

## 2. Experimental

### 2.1. Analytical reagents and reference materials

The reagents used to treat the samples and prepare specimens were hexamethyldisilazane (HMDS) (purity 99%), acetone and *o*-xylene (Sigma–Aldrich, Steinheim, Germany). The PVAc resin applied in this study was Mowilith 50<sup>®</sup> (solid) (Hoechst). Plasticizers studied were diethylphthalate (DEP) and dibutylphthalate (DBP), provided by Sigma–Aldrich. 1,4-dibromobenzene (Sigma–Aldrich) was used in this experiment as IS. Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) for the solid mixture and *o*-xylene was used as diluents of the internal standard (both from Sigma–Aldrich).

### 2.2. Instrumentation

Pyrolysis–gas chromatography–mass spectrometry was carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical Inc., New York, USA), and an Agilent Technologies (Palo Alto, Ca., USA) 6890N gas chromatograph coupled with an Agilent Technologies 5973N mass spectrometer and equipped with a pyrolysis injection system. An HP-5MS capillary column (5% phenyl methylpolysiloxane; 30 m, 0.25 mm i.d., 0.25 μm) was used.

On-line HMDS derivatization was performed with a temperature of pyrolysis of 700 °C, for 10 s using a precalibrated Pt coil-type pyrolyser (CDS Pyroprobe). The pyrolyser interface and the inlet were set at 250 °C. Samples were injected in split mode (split ratio 1:40). The GC temperature was initially 50 °C for 2 min, and then programmed at 5 °min<sup>-1</sup> to 100 °C, then at 15 °min<sup>-1</sup> to 295 °C, held for 10 min. The electronic pressure control was set to the constant flow mode with vacuum compensation. Helium gas flow was set at 1.2 mL min<sup>-1</sup>.

Ions were generated by electron-impact (EI) ionisation (electron energy 70 eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from *m/z* 20 to *m/z* 800, with a cycle time of 1 s. Agilent Chemstation software G1701CA MSD was used for GC–MS control, peak integration, and mass spectra evaluation. Tuning of the mass spectrometer was checked using perfluorotributylamine (PFTBA). EI mass spectra were acquired in the total-ion monitoring mode and peak area (TIC) data were used to obtain values of peak area percentage. The temperatures of the interface and the source were 280 and 150 °C, respectively. Compounds were identified by use of the NIST and Wiley Library of Mass Spectra and a library created by the authors for vinyl compounds.

### 2.3. Preparation of test specimens

#### 2.3.1. Test specimens

Two series of solutions were prepared where diethylphthalate (DEP) and dibutylphthalate (DBP) were added to a solution of Mowilith 50<sup>®</sup> in a proportion of 7:32 (w/v) using a solvent mixture of 82% acetone and 18% xylene. This low percentage of xylene was added in order to obtain homogeneous thin films delaying the evaporation rate of the solvent mixture and avoiding the formation of air bubbles. Plasticizers were added at three different concentrations, 1%, 2% and 5% (v/v). The preparation of the specimens was carried out in the Chemistry Laboratory of the Institut de Restauració del Patrimoni where the VOC (volatile organic compounds) values were lesser than a few μg m<sup>-3</sup>. This value is several orders of magnitude below the total amount of plasticizer present in the sample analysed so that contamination from the surrounding atmosphere can be neglected.

Test specimens were obtained by casting the prepared solutions on mylar<sup>®</sup> sheets, and left to dry horizontally over a plane surface for 1 month. Test specimens presented an average thickness of 0.015 mm.

#### 2.3.2. Internal standard

Two methods for adding the IS (1,4-dibromobenzene) to the samples for pyrolysis have been tested, in order to establish the analytical protocol which insures best repeatability.

- Powdered solid mixture with Al<sub>2</sub>O<sub>3</sub>

0.01 g of 1,4-dibromobenzene and 1 g of aluminium oxide were grinded and homogeneously mixed in an agate mortar. This mixture was stored in the refrigerator until the analysis.

- Solution in *o*-xylene

The IS prepared as a solution was obtained by dissolving 0.006 g of 1,4-dibromobenzene in 1 mL of *o*-xylene. This solvent was selected due to its slow evaporation rate as well as to its retention time, which does not overlap with any other compound in the pyrograms.

#### 2.3.3. Preparation of samples for analysis

The IS prepared (0.001 g) as a powdered solid mixture was placed together with 0.001 g of sample in a micro quartz pyrolysis tube. Small plugs of quartz wool were inserted in the ends of the tube to avoid undesirable displacement of the samples. One microliter of HMDS was afterwards added as derivatization reagent.

For the IS prepared as an *o*-xylene solution a small plug of quartz wool was inserted in a micro quartz pyrolysis tube and 1 μL of IS dissolution were afterwards added. This procedure ensures that the solution is retained inside the quartz tube by capillarity and no IS is lost. Afterward, in order to reduce the amount of solvent that might cause damage to the mass detector, the quartz

**Table 1**

Mean value of DEP/IS and DBP/IS peak area ratio and standard deviation obtained from six replicates of Mowilith 50<sup>®</sup> + plasticizer using the internal standard 1,4-dibromobenzene prepared as a powdered solid mixture in Al<sub>2</sub>O<sub>3</sub> and as *o*-xylene solution.

Content of plasticizer (%) (v/v)	DEP/IS <sup>a</sup>		DEP/IS <sup>b</sup>		DBP/IS <sup>b</sup>	
	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation
1	3.7	1.7	3.6	0.4	2.3	0.5
2	9	4.4	4.6	0.7	4.6	0.7
5	54	83	5.9	0.5	5.8	0.9

<sup>a</sup> Al<sub>2</sub>O<sub>3</sub> mixture.

<sup>b</sup> *o*-Xylene solution.

tube was inserted in the pyroprobe at 180 °C in order to evaporate the excess of solvent. After prior trials, 90 s was used as drying time. After this, 0.001 g of sample was placed in the quartz tube with the IS. A small plug of quartz wool was inserted in the end of the tube and 1 μL of HMDS was afterwards added.

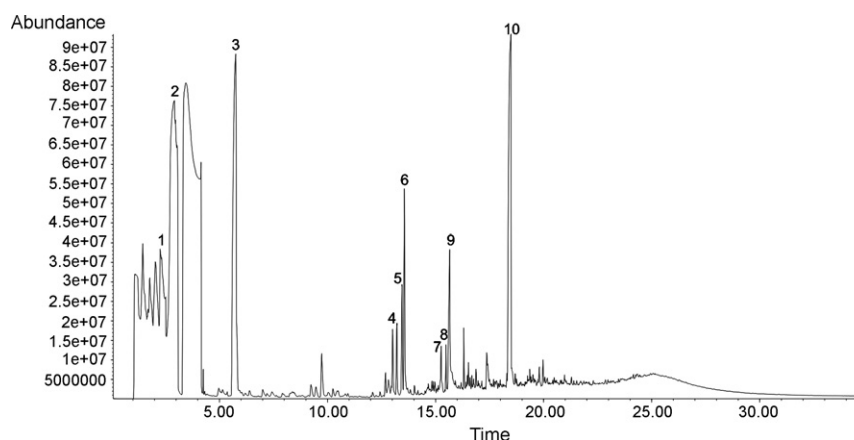
A first series of analysis were performed where the two preparation methods of the IS were applied on specimens containing DEP at different concentration. Table 1 summarizes the values of the DEP to IS peak area ratio obtained from six replicates for each specimen.

The results obtained evidence that the preparation of the IS in a solution form significantly improves the repeatability of the

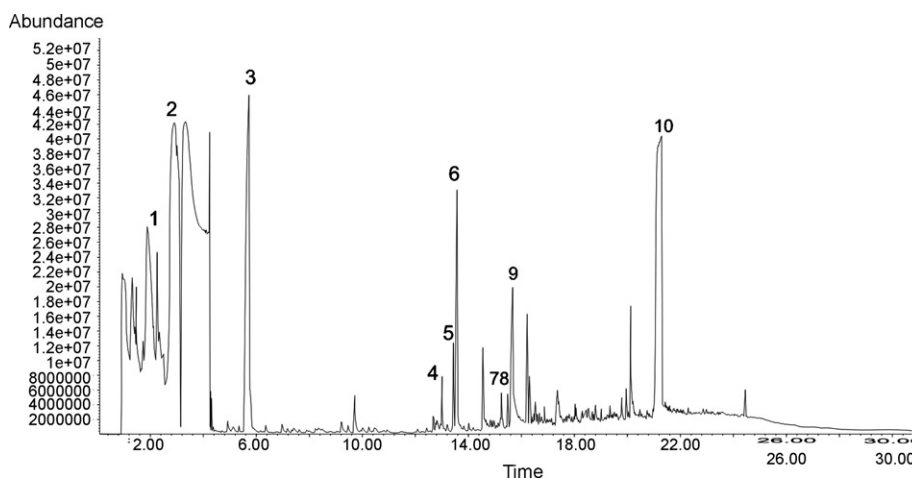
experimental data. In contrast, the preparation of IS as a powdered solid mixture introduces a significant scatter in the results which makes it unacceptable for quantification purposes. The dispersion of such values can be related to the difficulty of the homogenization of the mixture 1,4-dibromobenzene + alumina by grinding.

#### 2.4. Ageing treatments

A series of specimens was subjected to UV-light exposure by irradiating them in a climatic chamber provided with an UVB-313 EL UV lamp (Q-Panel Lab Products), which produces mostly short-wave UV with maximum intensity at ca. 313 nm and is equivalent



**Fig. 1.** Pyrogram of Mowilith 50<sup>®</sup> with 5% DEP obtained from on-line derivatization with 1 μL HMDS and 1 μL of 1,4-dibromobenzene in *o*-xylene. Compounds identified: (1) benzene; (2) ethanoic acid TMS ester; (3) *o*-xylene; (4) 1,2-dihydronaphthalene; (5) naphthalene; (6) 1,4-dibromobenzene; (7–8) 1-methylnaphthalene (isomers); (9) biphenyl; (10) diethylphthalate (DEP).



**Fig. 2.** Pyrogram of Mowilith 50<sup>®</sup> with 5% DBP obtained from on-line derivatization with 1 μL HMDS and 1 μL of 1,4-dibromobenzene in *o*-xylene. The same compounds shown in Fig. 1 are also identified: (1) benzene; (2) ethanoic acid TMS ester; (3) *o*-xylene; (4) 1,2-dihydronaphthalene; (5) naphthalene; (6) 1,4-dibromobenzene; (7–8) 1-methylnaphthalene (isomers); (9) biphenyl; (10) dibutylphthalate (DBP).

to a 40 W fluorescent lamp. Temperature was maintained below 45 °C. Specimens were exposed to UV-light for 48 and 96 h. Analyses by Py-GC-MS were performed in each ageing stage.

### 3. Results and discussion

Pyrograms corresponding to Mowilith 50<sup>®</sup> with 5% diethylphthalate (DEP) and 5% dibutylphthalate (DBP), respectively, are shown in Figs. 1 and 2. Characteristic peaks corresponding to benzene (1) and trimethylsilyl (TMS) derivative of ethanoic acid (2) are identified at low retention times. Peaks corresponding to the plasticizer DEP (peak 10 in Fig. 1) and DBP (peak 10 in Fig. 2), respectively, also appear in the pyrograms. 1,4-Dibromobenzene, the IS, appears to withstand the temperatures of the pyrolytic process since no isomers, secondary or recombination products, were identified and a single peak (peak 6) appears in the pyrogram which does not overlap with any other compound. Finally, a peak ascribed to *o*-xylene (3) was identified in the pyrograms, which did not overlap with other peaks. It is interesting to notice that the drying pre-treatment allows an adequate control of the intensity of the solvent peak, avoiding further damage to the mass detector.

According to Table 1, the increase of plasticizer content in the different test specimens is detected in the analysis by Py-GC-MS as the ratios of diethylphthalate to IS peak areas. The results presented show that the ratio increases accordingly to the percentage of DEP or DBP added to the test specimens thus evidencing that the proposed procedure using IS is suitable for quantification purposes in the range of concentrations normally found in paint media.

The results summarized in Table 1 were used as reference data for following changes in the plasticizer content of the test specimens after exposure to a multi-step artificial UV-light ageing

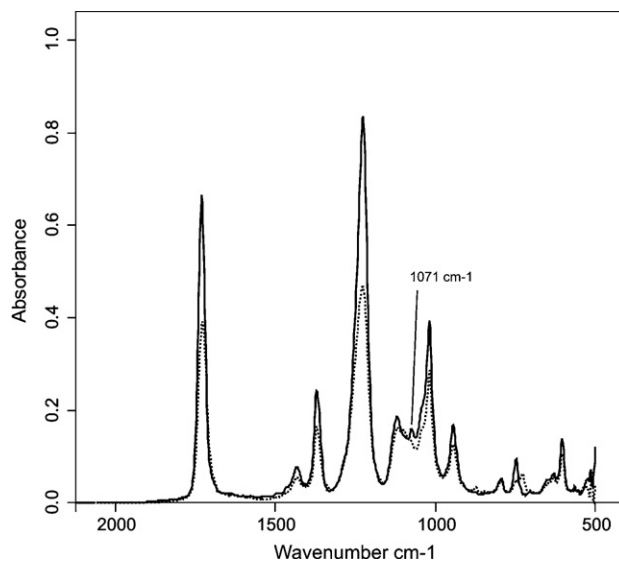


Fig. 5. IR absorption spectra of Mowilith 50<sup>®</sup> with 2% DBP before the ageing treatment (—) and after 96 h of UV-light ageing (···).

program. The effects of the ageing trials in the plasticizer content of the test specimens can be determined by calculating the plasticizer to IS ratio. The bar charts presented in Figs. 3 and 4 illustrate the results obtained after 48 and 96 h of exposition in the UV-light artificial ageing chamber, for DEP and DBP, respectively.

As it can be seen in Fig. 3, the more significant change in plasticizer content is observed in the first 48 h of artificial ageing for samples prepared with DEP at 1% and 2% concentration,

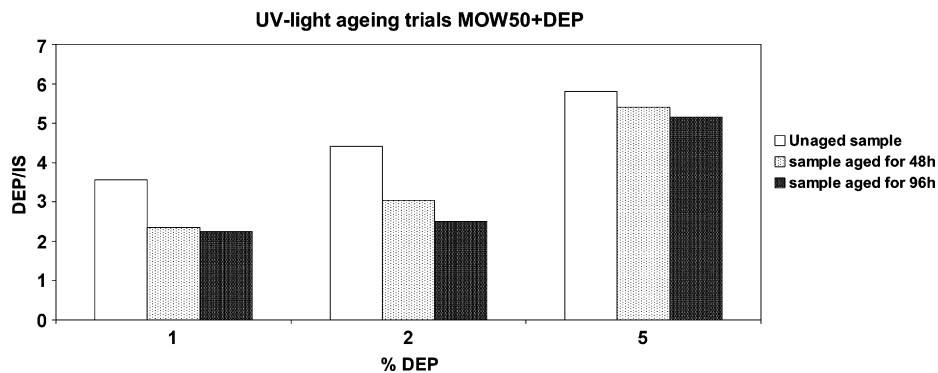


Fig. 3. Bar chart illustrating the changes in the DEP/IS ratio of the samples prepared with Mowilith 50<sup>®</sup> and DEP at 1%, 2% and 5% (v/v) concentrations, after 48 and 96 h of UV-light artificial ageing trials.

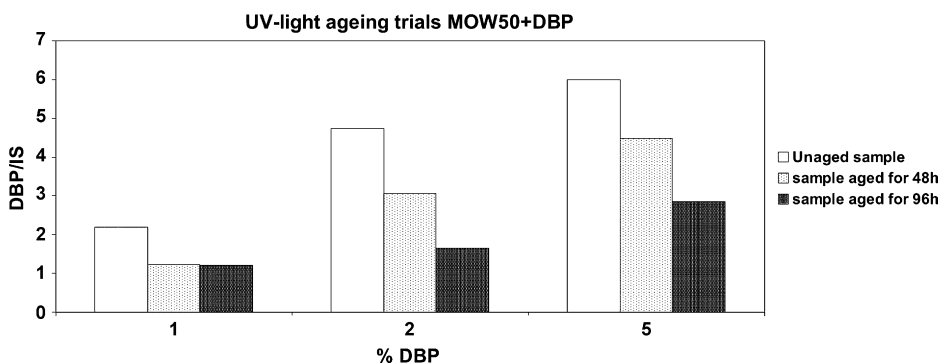


Fig. 4. Bar chart illustrating the changes in the DBP/IS ratio of the samples prepared with Mowilith 50<sup>®</sup> and DBP at 1%, 2% and 5% (v/v) concentrations, after 48 and 96 h of UV-light artificial ageing trials.

whereas the test specimen with 5% DEP exhibits small reduction in the content. Interestingly, no remarkable decrease in the plasticizer content for all test specimens prepared with DEP was observed in the following 48 h of ageing.

On the other hand, the set of specimens prepared with DBP exhibit a different behavior to those prepared with DEP, as illustrated in the bar chart shown in Fig. 4. A noticeable reduction in the DBP concentration is taking place during the first 48 h for all the specimens, irrespective of plasticizer content. Moreover, it is also observable a remarkable decrease in the DBP content for specimens at 2% and 5% DBP. This result suggests that despite the higher molecular weight of DBP regarding to DEP, this plasticizer has more tendency to migrate from the PVAc films during UV-light artificial ageing. These results obtained with Py-GC-MS are in agreement with the data obtained by means of FTIR spectroscopy. Thus, decrease in the intensity of the characteristic peak at  $1071\text{ cm}^{-1}$  ascribed to C–O stretching vibration of the phthalate group can be observed in the IR absorption spectra of the three specimens containing DBP as shown in Fig. 5.

#### 4. Conclusions

As a result of the present study a new method for determining the content of plasticizer in PVAc films using 1,4-dibromobenzene dissolved in *o*-xylene as IS has been proposed. This method is applicable not only for characterizing the content of plasticizer in pure PVAc films in the range of concentration usually found in paintings but also is applicable to the study of ageing of PVAc films containing DEP and DBP.

The proposed method has been successfully applied to monitor the plasticizer content of test specimens in a multi-step UV-light ageing trial. The results obtained evidenced that the two plasticizer tested exhibit a different behaviour facing the ageing conditions. Thus, whereas the DEP content has scarcely changed in the UV-light ageing conditions applied in the present study, the DBP specimens show a noticeable decrease in the plasticizer content, which is more evident at higher plasticizer concentrations.

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