

Analysis of Phthalate Ester Content in Poly(vinyl chloride) Plastics by Means of Fourier Transform Raman Spectroscopy

T. NØRBYGAARD and R. W. BERG*

Department of Chemistry, The Technical University of Denmark, Kemitorvet, B. 207, DK.2800 Lyngby, Denmark

Fourier transform (FT) Raman spectroscopy is applied to a range of phthalate ester plasticizers in pure form as well as in poly(vinyl chloride) (PVC) samples. It is found that phthalate esters as a group can be identified by a set of six characteristic Raman bands. FT-Raman spectra of 22 phthalate esters are given. It is demonstrated that the presence of phthalate esters in PVC products is readily detectable by FT-Raman spectroscopy. By use of proper reference samples quantitative determination of the phthalate ester content becomes possible as well.

Index headings: Fourier transform Raman; Quantitative Raman spectroscopy; Phthalate; Poly(vinyl chloride); PVC.

INTRODUCTION

Poly(vinyl chloride), PVC or $[\text{CH}_2\text{-CHCl}]_n$, is a common polymer used extensively for a wide range of industrial and household products. To achieve the proper material characteristics (e.g., softness, ductility), plasticizers such as phthalates are usually added to the otherwise hard and brittle PVC, sometimes in very large (10–60 wt %) concentrations. Phthalates are not chemically bonded to the PVC and will with time escape by evaporation or by extraction when in contact with liquids. There is serious concern that fat-soluble phthalates such as di(2-ethylhexyl) phthalate, or DEHP, in e.g., vinyl food film, medical devices, and toys, may harm, e.g., the reproductive organs of infants exposed to them.^{1,2}

Poly(vinyl chloride) is readily distinguished from other common polymers (e.g., polyethylene, polypropylene, polystyrene) by the use of Raman spectroscopy. For comprehensive overviews of the general application of Raman spectroscopy on polymers the literature, e.g., Everall³ and Hendra,⁴ should be consulted. A recent book by Hummel⁵ gives an overview of plastic additive analysis by spectroscopic methods, mainly infrared (IR) spectroscopy.

In this project we tried to use Raman spectroscopy to detect traces of phthalate esters (see Fig. 1) in PVC products. As the Raman literature is quite sparse on these compounds, we measured a range of commonly used as well as more rare phthalate esters for reference purposes. In a previous comprehensive study, Nyquist⁶ reported only parts of the spectra of 21 phthalate esters, and the Bio-Rad Sadtler 4701 Raman database of Basic Monomers & Polymers⁷ contains only 11 spectra of phthalate esters.

The measurements that we have performed include

spectra of the following 22 esters: dimethyl, diethyl, di-n-propyl, diallyl, dibutyl, diisobutyl, bis-(2-methoxyethyl), dipentyl, butyl benzyl, diphenyl, dicyclohexyl, butyl octyl, diheptyl, diisooheptyl, di-n-octyl, di(2-ethylhexyl), dinonyl, diisononyl, diisodecyl, diundecyl, undecyl dodecyl, and ditridecyl phthalate.

By far the most commonly used phthalate plasticizer in PVC is di(2-ethylhexyl) phthalate, DEHP (also referred to as dioctyl phthalate, DOP), and many products containing this phthalate are in common use.

EXPERIMENTAL

Spectra were obtained using a Bruker IFS 66 Fourier-Transform spectrometer with an FRA-106 Raman attachment. The exciting source was a 1064 nm near-infrared Nd-YAG laser with a nominal power of 100 mW. The scattered light was filtered and collected on a liquid N₂ cooled Ge diode detector giving a resolution of approximately 2 cm⁻¹ between individual pixels.⁸

All Raman spectra were collected over the range 3500 (Stokes) to 1000 cm⁻¹ (anti-Stokes) at approximately 23 °C with no particular specimen preparation for the solids.

All mentioned phthalates, with a single exception (diphenyl phthalate), are liquids at room temperature and were measured in small glass test tubes. The FT-Raman spectra of the pure phthalates were corrected for instrument response by multiplication point-by-point according to Eq. 1:

$$\frac{(\text{Black Body Spectrum})}{(\text{Reference Spectrum})}(\text{Raman spectrum}) \quad (1)$$

where *Reference Spectrum* refers to a recently measured spectrum of a tungsten lamp and *Black Body Spectrum* refers to a theoretically calculated spectrum of such a light source at the given temperature. This correction was done using the OPUS software.⁸ The iso-phthalate esters are mixtures of the possible isomers unless otherwise stated. Minor background subtraction was performed on five of the pure phthalate spectra. Phthalate ester spectra are obtainable from the authors.⁹

Poly(vinyl chloride) reference samples containing DEHP in known amounts were prepared. For each sample powdered PVC (molar weight of approximately 175 000) was thoroughly mixed with liquid DEHP and placed in a sealed glass container followed by heat treatment for 6 min in an oven at 140 °C. FT-Raman spectra were subsequently measured directly on the samples in the containers. Samples with good homogeneity were achieved in the range of 20–55 wt % DEHP.

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* Author to whom correspondence should be sent. E-mail: rwb@kemi.dtu.dk.

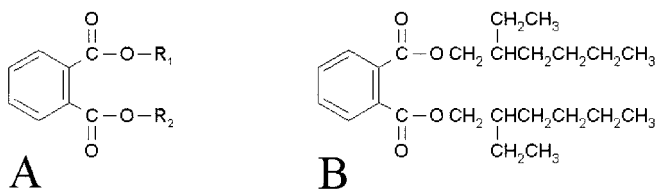


FIG. 1. (A) General structure of a phthalate ester. The diesters of the phthalic acid are often symmetric ($R_1 = R_2$) like, e.g., DEHP; (B) structure of di(2-ethylhexyl) phthalate, commonly known as DEHP.

RESULTS AND DISCUSSION

In Fig. 2 the Raman spectra of fifteen dialkyl phthalate esters are shown. The spectra have been normalized according to the 1726 cm^{-1} peak, making the relationship among the spectra readily apparent. It is seen that as the size of the alkyl group increases, so naturally does the intensity of the multiple bands in the $2800\text{--}3000\text{ cm}^{-1}$ range. Likewise, we see a rise of the 1450 cm^{-1} peak with increasing alkyl group size, while the rest of the major bands in the $500\text{--}1800\text{ cm}^{-1}$ range are largely undisturbed by these differences.

At the bottom of Fig. 2 six spikes are seen that represent the characteristic bands of the phthalate group. Pre-

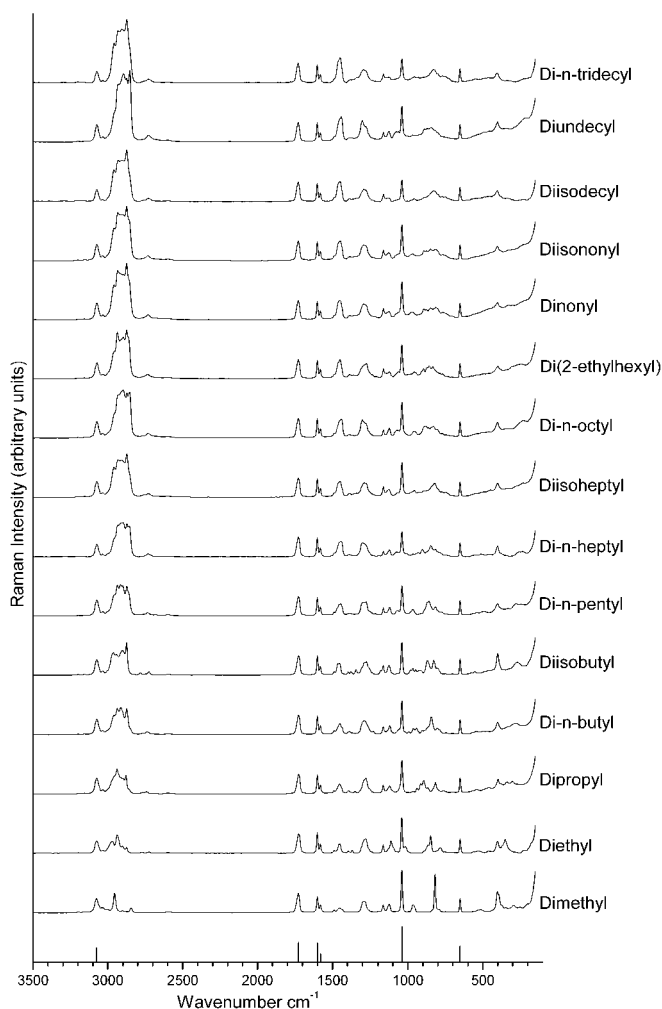


FIG. 2. Raman spectra of 15 dialkyl phthalate esters, arranged in order of increasing molecular weight. Bottom: line spectrum of characteristic phthalate ester bands.

TABLE I. Listing of the six characteristic Raman bands found for all measured phthalate esters.

Wavenumber (cm^{-1})	3074	1726	1600	1580	1040	652
Relative intensity ^a	s	s	s	m	vs	m
Polarization ^b	pol	pol	depol	pol	pol	pol

^a Code: vs = very strong, s = strong, m = medium.

^b As determined by Nyquist.⁶

viously⁶ the band at approximately 1726 cm^{-1} has been assigned to the carbonyl ($\text{C}=\text{O}$) stretching vibration of the ester group, while the peaks at approximately 3074 , 1600 , 1580 , 1040 , and 652 cm^{-1} were assigned to various vibrations of the ortho-phenyl group. Apart from these six bands, most of the phthalate ester bands are either very weak, poorly resolved, or partly due to vibrations of the R_1 and R_2 groups. The six bands, which are summarized in Table I, are accordingly assigned to the dicarbonyl ortho-phenyl group. It is seen that the relative intensities of the six bands vary only slightly from one phthalate ester to the next, and thus we have obtained an identifiable, characteristic fingerprint of the phthalate ester group as a whole. The 3074 cm^{-1} band is common to all phenyl-containing compounds and is thus the least characteristic of the total ensemble of bands in Table I.

In Fig. 3 is shown the spectra of seven phthalates with types of ester groups other than the symmetric alkyls. As seen, these compounds display additional peaks in the Raman spectra, due to, e.g., $\text{C}=\text{C}$ double bonds or cyclic structures. It is seen that the set of six characteristic bands of Table I are readily found in these spectra as well. The relative intensities of the six bands vary somewhat in some of these cases, depending on the exact structure of the R_1 and R_2 groups, but basically the main characteristics of the 'fingerprint' are preserved.

By use of the set of six bands, which are common to all the measured Raman spectra, we thus foresee an easy way to identify the presence of phthalates in a range of different products.

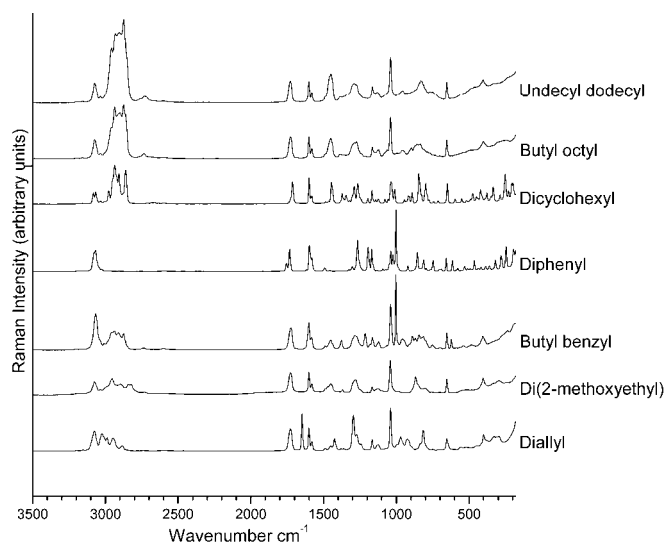


FIG. 3. Raman spectra of seven phthalates. Diphenyl phthalate is crystalline at room temperature. Bottom: line spectrum of characteristic phthalate ester bands.

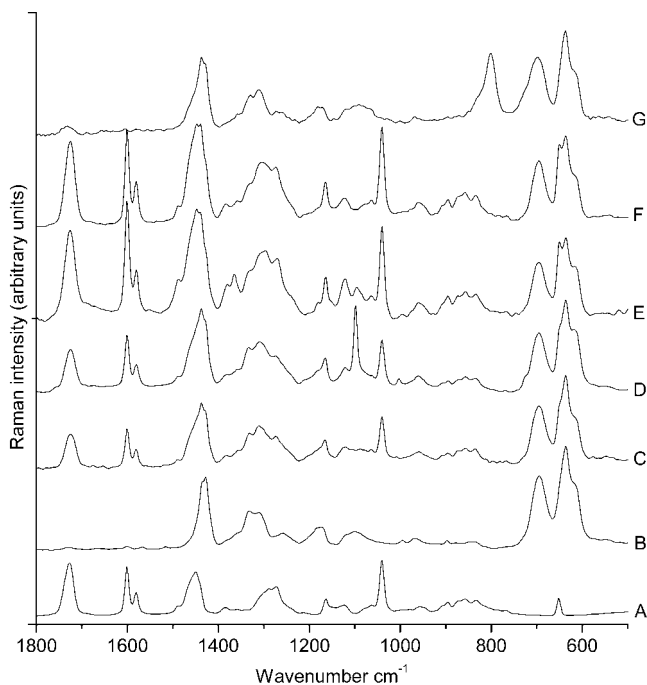


FIG. 4. Examples of FT-Raman spectra of PVC products. (A) DEHP; (B) hard PVC from our workshop; (C) shower curtain, uncolored and opaque; (D) floor tile, white; (E) rubber glove, red; (F) pencil erasing rubber, uncolored and opaque; and (G) food foil, declared free of phthalates.

Phthalate Esters in Poly(vinyl chloride). To test the suggestion mentioned above, we have measured the Raman spectra for a range of different PVC consumer products. In Fig. 4 the Raman spectra of four PVC products and two reference spectra are shown. The presence of DEHP in the PVC products C, D, and E has been established by chemical analysis, and the Raman spectra of these three samples clearly display peaks that can be recognized as due to PVC and DEHP, respectively. The Raman spectrum of the product C consists almost exclusively of peaks that can be found in spectra A (pure PVC) and B (DEHP), whereas products D and E display some peaks that must be ascribed to the other substances present in the samples (for D probably a carbonate filler).

The product F is an example of a sample of unknown chemical composition. The resemblance of the Raman spectrum to the products C, D, and E led us to suspect that it was PVC containing quite large amounts of DEHP, and this composition was verified by the manufacturer of the product.

Sample G shows an example of a PVC product softened with a non-phthalate plasticizer, a fact that clearly shows up in the Raman spectrum.

As the examples show, the detection of a phthalate ester content in an unknown sample is quick and easy by means of FT-Raman spectroscopy. Due to similarities in the spectra of the common di-alkyl phthalates it is, however, doubtful whether it will always be possible to qualitatively determine the exact kind of phthalate ester (or esters) present in a mixed sample.

Quantitative Raman. Additionally, we have found that the intensity of the FT-Raman signal for phthalate is clearly correlated to the amount present in a sample. To establish this connection we measured the FT-Raman

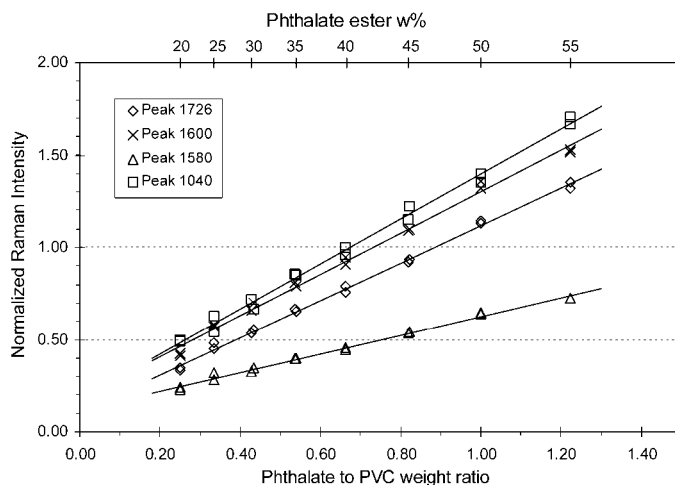


FIG. 5. Normalized Raman intensity of individual phthalate peaks given as a function of relative phthalate content ($m_{\text{phthalate}}/m_{\text{PVC}}$). Raman spectra were normalized according to the PVC peak at 696 cm^{-1} . R^2 for calculated trend lines ranges from 0.994 to 0.997.

spectra of a range of homemade PVC reference samples containing different amounts of DEHP. Considering PVC to be the solvent as well as an internal standard¹⁰ for the reference samples, we thus normalized the measured FT-Raman spectra according to the strong PVC peak at 696 cm^{-1} , where the Raman signal from DEHP is negligible. As the PVC signal then became constant from one Raman spectrum to the next, the differing phthalate contents were directly reflected in the differing intensity of the phthalate signal (i.e., the six characteristic phthalate bands). The intensities of the phthalate signals, as given by individual peak heights for the characteristic phthalate bands, are then plotted as a function of the relative phthalate content, as seen in Fig. 5. In each case a nice linear relationship is demonstrated. Use of the phthalate peak at 3074 cm^{-1} yields equally nice results, while the 652 cm^{-1} peak is camouflaged under the massive PVC bands and is thus not suitable.

By use of Fig. 5 it is therefore possible to estimate quantitatively from a single Raman measurement the amount of phthalate ester in PVC samples of unknown composition. First, the normalized Raman intensity (e.g., $I_{\text{peak } 1726}/I_{\text{peak } 696}$) must be determined from the Raman spectrum. Then, by use of the appropriate graph in Fig. 5 the phthalate-to-PVC ratio or the absolute phthalate content (wt %) of the sample can be obtained. Of course, one needs to take into account possible tertiary contents as well (e.g., filler materials). Such information can to some extent also be detected or determined from the Raman spectrum.

From the present work we estimate the detection limit for phthalate ester detection by means of the FT-Raman technique to be on the order of 0.5 wt % in PVC products.

CONCLUSION

Fourier transform Raman spectroscopy seems to be a suitable and easy technique for fast analysis of PVC samples, with respect to identifying the base polymer (PVC) as well as for identifying certain commonly used phthalate ester plasticizers. We estimate this method to be very

viable for the screening of large amounts of consumer products, e.g., children's toys, for possible phthalate ester contents.

Quantitative determination of the phthalate ester content can be accomplished from a single Raman measurement using appropriate reference sample data, such as ours.

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