

INFRARED SPECTROMETER ACCESSORIES

Measurement of Volatile Solutions and Solvents Using the Specac Quest ATR Accessory

Introduction

For collection of Infra Red spectral data of liquid or solid samples it is desirable to achieve a spectral range extending from 4000cm^{-1} to 400cm^{-1} . Traditionally, the use of liquid transmission cells with KBr windows allows for this transmission range of light to be collected, but there may be compromise of the liquid cells structural integrity if the liquid sample itself contains any aqueous component which will attack the KBr windows.

An alternative method for spectral collection is to use the Attenuated Total Reflectance (ATR) technique, whereby any liquid sample type is brought into direct contact with an ATR crystal material and internally reflected and measurable light from the sample crystal interface results in a spectrum being collected for the sample from a specific penetration depth into the sample material itself.

To achieve a similar spectral range of collection for the transmission range of 4000cm^{-1} to 400cm^{-1} from the ATR technique a monocrystalline type IIIa diamond ATR crystal element can be used. The Specac Quest ATR accessory offers the choice of a diamond, ZnSe or germanium ATR crystal puck to be used on a dedicated optical unit with mirrored reflectance optical components only. This optical combination allows for the full transmission spectral range capability of the ATR crystal chosen to be achieved.

Application

ATR measurement study of a volatile solution or solvent.

Equipment and Method

The spectra were collected on a Thermo Nicolet iS5 instrument using the standard room temperature



Specac's Quest ATR Accessory

detector system set at a resolution of 4cm^{-1} for 16 scans with a gain setting of 1.

Three different volatile solvents were used for the study.

- 1) Methanol.
- 2) Acetone.
- 3) Cuvertin X8536 (from LORD) - (This is a proprietary solvent mixture of Xylene (60-100%) and Ethylbenzene (< 25%) in content, used for polymer surface stripping and preparation).

For the ATR measurement of a volatile liquid sample, the Quest ATR Accessory P/N GS10801-B was used with the single reflection diamond extended range ATR crystal puck option on the black surface coloured optical unit.

A volatiles cover P/N GS10825 was used to cover over the volatile solvent or solution when this had been spotted into position over the diamond ATR

crystal. To obtain a good sealing from the O-ring at the base of the volatiles cover and to enable long term containment and contact of the volatile liquid sample over the ATR crystal, the flat anvil P/N GS10820 was fitted to the anvil arm assembly of the Quest ATR accessory and this was employed to force down onto the top of the volatiles cover.

When the volatile liquid sample had been prepared in this way it was then ready for spectral data collection. Each sample was repeated twice for consistency of measurement.

Spectral Data

The Infra Red spectra collected for these volatile liquid samples are shown as Figures 1, 2 and 3.

Discussion

It is dependent upon the actual mobility and volatility of a liquid sample type, after it has been spotted into position over the ATR crystal, as to how long the sample will cover the crystal to a sufficient depth of penetration (at least 2 microns) for collection of a representative IR spectrum before the sample contact is lost. For the three volatile liquid sample types chosen for this study, from prior testing there was just enough time within a 60 second period to acquire a consistent representative ATR spectrum for

Fig. 1. Methanol solvent with volatiles cover on diamond crystal puck of Quest ATR Accessory

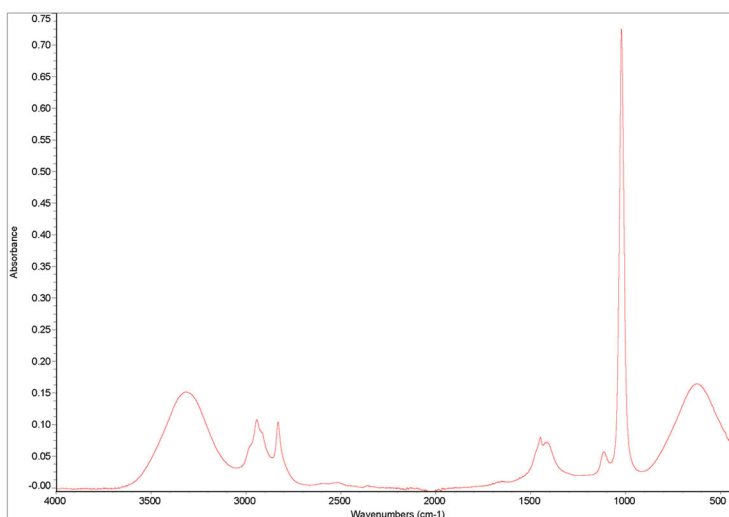
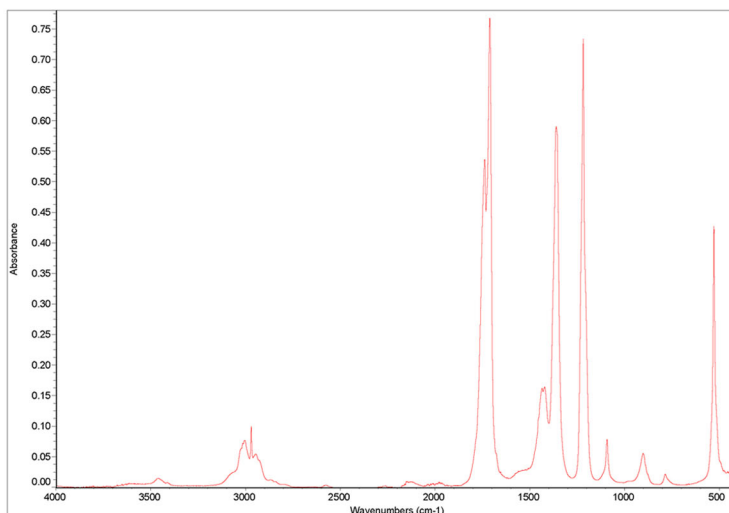


Fig. 2. Acetone solvent with volatiles cover on diamond crystal puck of Quest ATR Accessory



each sample before sufficient contact was lost, after spotting the sample into position over the diamond crystal and leaving exposed to the atmosphere.

However, by placing the volatiles cover into position over the spotted sample to cover the diamond and then by clamping the volatiles cover down into position to seal the liquid sample into place, each solvent sample was measured for a minimum of 10 minutes hold time with no loss of signal absorbance intensity in the spectrum obtained from the start of the hold time and after a 10 minute hold period. The spectra shown as Figures 1, 2 and 3 are all representative of the volatile liquid sample type taken after a 10 minute hold time against the diamond

crystal puck with the volatiles cover clamped into place.

Before the volatiles cover was employed for containment and consistent measurement of all three volatile liquid sample types over a prolonged period, when the original prior testing of the spotted Cuvertin solvent/solution sample had evaporated from the diamond after exposure to the environment, a thin film residue was left in place covering the diamond crystal and surrounding area. The resulting spectrum for the residue left is seen as Figure 4. and although relatively weak in spectroscopic band intensity, is a good match for syndiotactic polypropylene material, indicating that this polymeric type

Fig. 3. Cuvertin X8536 solvent/solution with volatiles cover on diamond crystal puck of Quest ATR Accessory

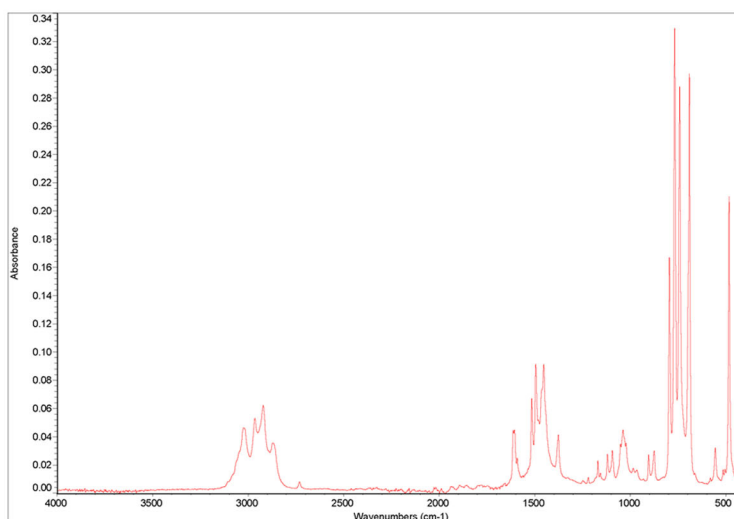
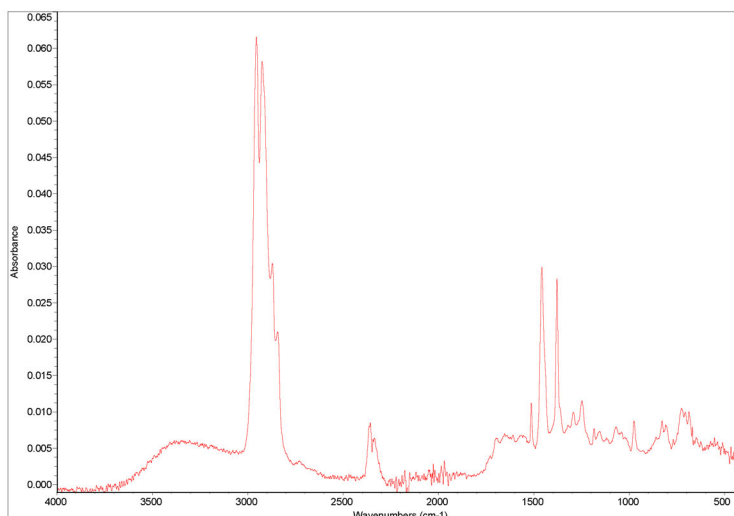


Fig. 4. Cuvertin X8536 solvent/solution residue after evaporation from the diamond crystal puck of Quest ATR Accessory



material has been deposited as a thin film from evaporation of the volatile solvent components of the solution.

Conclusion

Although, volatile liquid samples (solutions or solvents) can be analysed by IR liquid transmission cells, study of liquid samples by ATR can be an inherently easier way of handling the sample than using a traditional liquid transmission cell assembly. However, as ATR is a reflection technique, measurement of the liquid sample takes place at the surface only to a depth of a few microns rather than as a "bulk" measurement through 10's to 100's microns of pathlength in a transmission cell. Also, the same consideration of an ATR crystal being chemically compatible with the sample will determine the choice of ATR crystal that can be used to obtain the optimum infra red spectral data needed.

The objective of this application was to demonstrate that a volatile liquid sample could be analysed for obtainment of an infrared spectrum over the spectral range of 4000cm^{-1} to 400cm^{-1} by use of the ATR technique in preference to a liquid transmission cell. This has been achievable by use of the diamond ATR crystal top plate on the Quest ATR accessory with the purpose designed volatiles cover for these types of sample to be fully contained for increased duration of analysis, should this be necessary.

With regards to the Cuvertin solvent/solution sample, it had been assumed that the sample taken was "pure", but the result of the testing by non-use of the volatiles cover has demonstrated that this particular sample has an unexpected component - polypropylene is dissolved within. It has been possible in this instance, from the way the sample was analysed by the ATR technique, to see the difference between a start mixture of components in a solution spectrum (Figure 3.) and a resultant spectrum for the "impurity" (Figure 4.) when the most volatile components have been lost. Therefore, if a sample dissolved in solution of a volatile solvent is at a level of concentration measurable by the ATR technique, then by allowing

for evaporation of the volatile solvent any dissolved components may be deposited upon the ATR crystal surface for measurement and identification.

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The study was carried out by: C. Moss, Specac Limited, Orpington, Kent, UK.

Specac Ltd
River House, 97 Cray Avenue, Orpington
Kent BR5 4HE UK
T: +44 (0) 1689 873134 F: +44 (0) 1689 878527
E: sales@specac.co.uk W: www.specac.com

Specac Inc
301 Berkeley Drive, Swedesboro, NJ 08085 USA
T: Toll Free +1 800 447 2558
E: sales@specac.com W: www.specac.com
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