INFRARED SPECTROMETER ACCESSORIES

Aggressive Aqueous Solution Study Using the Specac Quest ATR Accessory

Introduction

Aggressive liquid samples (solutions or solvents) which are acidic by nature can be analysed by IR liquid transmission cells. To comply with certain Pharmacopeia regulations, chemicals and samples are required to have infrared spectral data collected for them between the frequency range of 4000cm^{-1} to 400cm^{-1} (2.5microns to 25 microns wavelength). This stipulation may limit the type of liquid transmission cell that can be used as the optical materials (windows of the cell) for chemical compatibility of the liquid sample itself may not provide the required transmission frequency range for study. Traditionally, common and relatively cost effective window materials such as CaF_2 and BaF_2 are used as they will allow for the handling and containment (at low risk of damage) of acid based aqueous solutions, but their spectral range is limited between 4000cm^{-1} and 900cm^{-1} and 4000cm^{-1} and 800cm^{-1} respectively in the mid infra red. Additionally, as water based samples are inherently highly absorbing of infra red radiation if the water solvent is in excess of a solution, for transmission liquid cell measurements short pathlengths cells of the order of 6 or 12 microns may need to be constructed for use to obtain sufficient spectral information.

An alternative method for spectral collection of liquid samples is to use the Attenuated Total Reflectance (ATR) technique, whereby a liquid (or solid) sample is bought 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. Study of liquid samples by ATR can also 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

Specac's Quest ATR Accessory

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 a crystal material 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.

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 pucks 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. Specifically if choosing the diamond ATR crystal puck option for sampling, many different types of liquid samples, be they organic or aqueous

based in nature, can be analysed with minimal risk of chemical damage to the ATR crystal material.

Application

ATR measurement study of an aggressive aqueous solution or solvent (acidic in nature) in order to try and obtain as wide a spectral transmission range of light frequency collection for the sample as possible.

Equipment and Method

For the ATR measurement of an "aggressive" liquid to obtain a full spectral range for the sample between 4000cm^{-1} and 400cm^{-1}, 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.

The spectra were collected on a Thermo Nicolet iS5 instrument using the standard room temperature detector system set at a resolution of 4cm^{-1} for 16 scans.

Three "aggressive" liquid samples were chosen to be studied. They were:-

Acetic Acid (CH3COOH) 100% strength.
Nitric Acid (HNO3) 60% strength.
Orthophosphoric Acid (H3PO4) 85% strength.

For preparation of the sample for the ATR spectral measurement a small amount of each acid sample was taken "as is" and spotted (transferred by a glass rod bulb) over the diamond ATR crystal of the Quest ATR puck option. The sample was allowed to sit uncovered over the diamond crystal and the acquisition of an IR spectrum was taken as quickly as possible after initial spotting into place. Each of the three acid samples were repeated three times for the collection of a consistent set of results.

Once the spectral data had been collected and stored the sample was washed away from the puck as quickly as possible thereafter to reduce the amount of sample contact time to a minimum with the diamond ATR puck. Cleaning between these sample types was achieved specifically by removal of the diamond crystal puck from the Quest ATR optical unit and carefully carrying the puck with sample to a cold running water supply and rinsing away the acid sample. (Be safety conscious – wear gloves and safety spectacles when cleaning this way). After initial washing with excess water, the puck was cleaned with a tissue moistened with methanol and finally dried clean using a dry tissue, before readiness for the next sample.

Spectral Data

The Infra red spectra collected for three aggressive liquid samples are presented as Figures 1, 2 and 3.

Discussion

The objective was to demonstrate that an aggressive aqueous based liquid sample exhibits an ATR spectrum from 4000cm^{-1} to 400cm^{-1} - and would hence be compliant with any Pharmacopeia stipulations for ATR technique use in the mid IR range - with use of the diamond crystal top plate. This might be a preferred alternative method of quick and easy liquid analysis by FTIR replacing a liquid cell transmission measurement.

The diamond crystal itself is not going to be affected by contact with the sample, but this application of use of the Quest ATR accessory is a test of the Indium sealing integrity between the diamond crystal and the stainless steel puck mounting surround with such aggressive sample types and a test of the chemical robustness of the stainless steel puck too.

Between each sample measurement event, which took about 2 minutes in total from spotting of the sample and spectral acquisition of the data and after adopting the specified cleaning regime, subsequent investigation of the top plate by use of a 10X magnification microscope did not show any visible signs of damage to the diamond crystal, indium sealing or surrounding stainless steel surface area.

The examples of the ATR spectra produced shown from Figures 1, 2 and 3 for each sample are all entirely consistent, when the sample type had been repeated under the same conditions for acquisition.

Fig. 1. Acetic Acid 100% on diamond crystal puck of Quest ATR Accessory

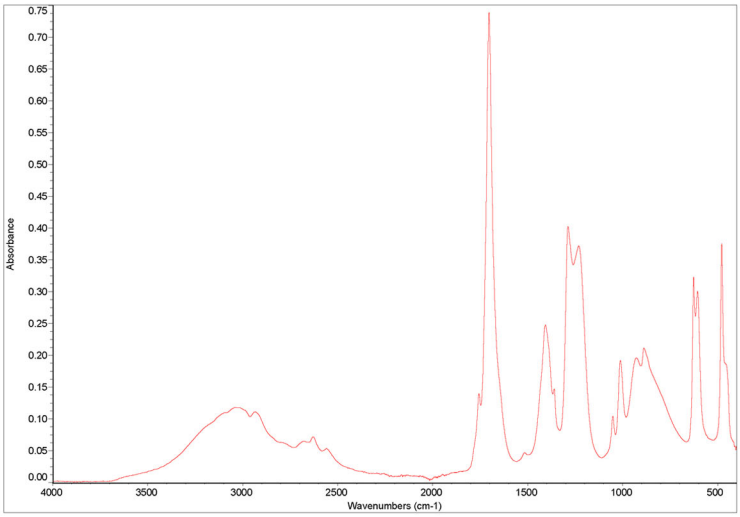


Fig. 2. Nitric Acid 60% on diamond crystal puck of Quest ATR Accessory

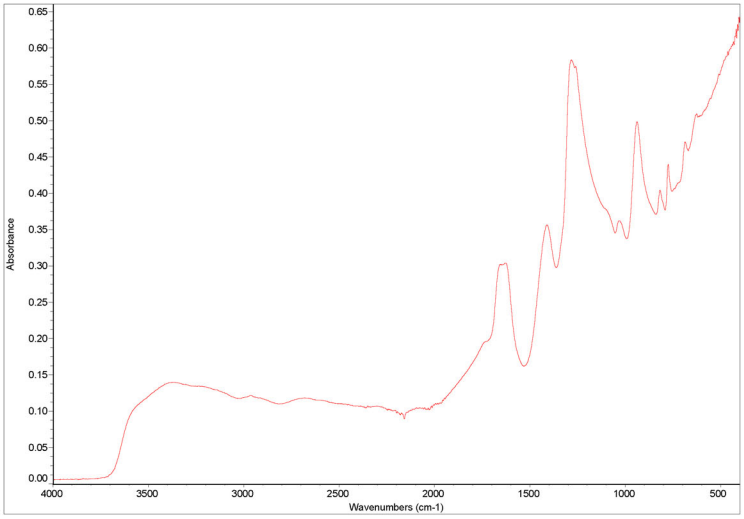
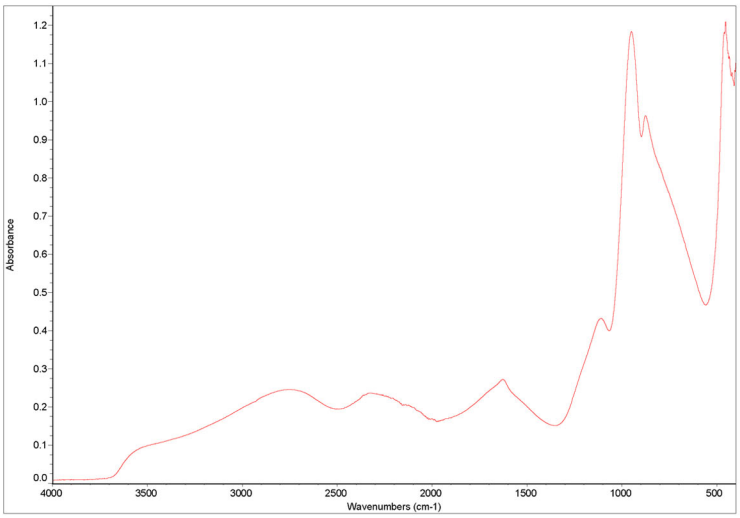


Fig. 3. Orthophosphoric Acid 85% on diamond puck of Quest ATR Accessory



Conclusion

In testing of the three aggressive liquid samples chosen - Acetic Acid 100%, Nitric Acid 60% and Orthophosphoric Acid 85% - the Quest diamond ATR accessory is capable of handling and measuring such sample types for their IR ATR spectra provided the sample testing is kept to a minimum time for sample contact to the diamond crystal and puck area.

It should be borne in mind that it is difficult to determine how many aggressive sample types such as the examples tested could be tested before there were signs of degradation and breakdown in the puck integrity for its sealing and structure. However, the design offering of a puck for Quest ATR does not include provision for long term containment of samples at elevated temperatures and pressure conditions (which generally exacerbates any aggressive tendencies in the nature of a sample type), or to be analysed in a flowing environment for liquid sample types.

Therefore, if the measurement of a chemically aggressive, liquid sample type cannot be made using a conventional liquid sampling transmission cell, because of chemical degradation to the cell window materials, or the window material cannot offer the wavenumber frequency region to be studied, then the Quest ATR Accessory with the diamond puck option can be used for the short term analysis of aggressive liquid sample types at static, room temperature and pressure conditions. The diamond crystal will not be affected and the optical design of the Quest ATR Accessory with the diamond crystal puck combination allows for the spectral region of 4000cm^{-1} to 400cm^{-1} to be studied.

Acknowlegement

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
Specac is part of Smiths Group plc