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Short communication

Attenuated total reflectance powder cell for infrared analysis of hygroscopic samples

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1. Introduction

In recent years, attenuated total reflection (ATR) has grown steadily as the preferred sampling method for solid, liquid and even thin film samples [1]. The reasons for this are that the technique addresses the most challenging aspects of infrared analyses, namely sample preparation and reproducibility of spectra. Generally, sample preparation is easier for liquid transmission studies than for solid transmission studies. The latter requires that the sample be dispersed in a matrix, whether this is nujol mineral oil or alternatively potassium bromide (KBr) powder. Our experience in the laboratory is that the sample preparation process where a solid is ground to a fine powder and subsequently mixed to a uniform dispersion is time consuming and in the case of the use of nuiol, an operation that is usually difficult to deal with. Special care is also required when handling and storing KBr as a matrix material since it is hygroscopic and the presence of moisture in the matrix adversely affects the quality of the spectra. Due to the complexity of the sample preparation process associated with the respective matrix compounds, systematic error is difficult to avoid and resultantly, spectral reproducibility is not easily achieved.

The advent of ATR as an internal reflection sampling technique in infrared spectroscopy has witnessed the alleviation of the sampling challenges associated with transmission studies as outlined above. In most instances, samples can be analyzed using ATR in a non-destructive manner without any sample preparation. The reproducibility of the shallow penetration depth of the internally

ABSTRACT

An attenuated total reflectance (ATR) sample cell has been designed, manufactured and subsequently used for the mid-infrared analysis of hygroscopic samples. This sample cell was installed as a simple drop-in replacement for the cell supplied with our commercially available Harrick Mvp-Pro FTIR–ATR accessory. Calcium chloride, a well-known desiccant that has a propensity to absorb water into its crystal lattice, was selected as non-infrared active substrate to accentuate the efficacy of the cell in preserving the anhydrous state of the sample by straightforward monitoring of the water bands. In contrast, mid-infrared spectra are presented that qualitatively demonstrate the rapid rate at which atmospheric moisture is incorporated into the anhydrous sample when analyzed using the conventional ATR cell assembly.

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reflected beam's evanescent wave serves to facilitate the collection of reproducible spectra without signal saturation [2–5]. Furthermore, the introduction of ATR accessories having very small crystals that rely only on a single reflection has further enhanced this technique's versatility to accommodate non-deformable solid samples that require high ATR crystal contact pressures for deriving quality spectra [3]. In spite of all these improvements in the ATR technique, it has been our experience that often, current commercially available fleet of ATR accessories do not allow for the convenient handling of hygroscopic samples. Current ATR sampling crystal plates do not prevent atmospheric moisture ingress into the sample. This shortcoming makes it difficult to attain ATR spectra of anhydrous hygroscopic material. This paper reports on the design and commissioning of a sample cell that can be used to analyze hygroscopic samples. This cell was designed as a drop-in replacement for the commercially available Harrick Mvp-Pro FTIR-ATR accessory. Mention is also made of an extension of the design philosophy that the cell can be used for in situ gas-solid interaction studies.

2. The design

With reference to Fig. 1, the cell components are labelled with the prefix C and the number associated with the prefix refers to the specific component. A stainless steel body (C1) is flattened at the bottom and fitted with a dowel pin (C2) to align it properly during attachment onto a Harrick Mvp-Pro type ATR crystal plate, which is a removable item from the Mvp-Pro ATR cell itself. The sample compartment is fitted with a plunger (C4) used to drive the applied force onto the sample and hence ensure better contact with the crystal used. This sample pressurizing technique is similar

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Fig. 1. An exploded view drawing for the dry sample holder used for ATR-infrared analysis of moisture sensitive samples. The number next to the prefix C refers to the particular component.

to the one used by Balik and Simendinger [6], where pressurized gas was used to maintain contact between the polymer sample and the ATR crystal. A screw cap (C3) secures the fitted plunger into place. The vent valve (C7) is used to relieve the gas pressure when the plunger is pushed into place after loading the sample within an inert gas atmosphere. An inlet with a valve (C9) may be used as an alternative to the side screw to draw vacuum or allow flow of various gases into the analyte, hence allowing the device to be used as a reaction cell during an infrared measurement. The O-rings (C5, C6, and C8) ensure that the cell assembly is leak tight.

To attach the new sample cell to the existing ATR crystal plate, the existing powder cell is first detached from the crystal plate and then replaced with a new sample cell shown in Fig. 1. This is conveniently executed by simply undoing and subsequently retightening the single screw that normally fixes the sample cell onto the crystal plate. For the purpose of deriving FTIR–ATR spectra of a hygroscopic sample, the complete sample cell and crystal plate assembly is firstly detached from the ATR accessory. The assembly is thereafter transferred into a dry nitrogen filled glove box and then charged with the sample. The sample is finally sealed in the cell assembly by inserting the plunger (C4), then securing this in place by means of its screw cap (C3) and then finally tightening the vent valve (C7).

3. Experimental

3.1. Materials

Calcium chloride dihydrate from Merck (99.5% purity) was dehydrated in an oven at $150 \,^{\circ}$ C and then handled inside a glove box with a circulating dry nitrogen atmosphere. All sampling was done inside a dry nitrogen glove box.

3.2. Apparatus and procedure

The anhydrous ATR cell which was designed, manufactured and described in this work (Fig. 1) was used inside a dry nitrogen glove box to ensure that the influence of atmospheric water vapour on the sample was eliminated. This sample holder was attached to a Harrick MvPro ATR plate fitted with a diamond crystal. The top of this plate attaches the sample cell and the bottom can be attached to or detached from the main Mvp-Pro ATR accessory. This accessory



Fig. 2. FTIR–ATR spectra of anhydrous calcium chloride collected 0.5 min (top) and 10 min (bottom) using a dry sample cell. A straight line is observed because the sample is infrared inactive in the mid infrared region.

has a built-in pressure reader. The powder sample was loaded into the cell then the plunger and a screw cap were fitted into place (see Section 2). The vent valve (C7) was tightened before the whole cell assembly was transferred to a Bruker T27 FTIR spectrometer fitted with a Harrick MvPro ATR accessory. An appropriate force of 70 N was applied onto the plunger of the sample cell to ensure better contact between the sample and the diamond crystal. The pressure was applied by means of a pressure applicator which is an intricate part of the ATR accessory and is outfitted with a built-in sensor and pressure readout. A spectrum of an anhydrous sample was collected using this new cell. In a separate experiment, another sample of calcium chloride was exposed to air atmosphere from several seconds to minutes, and the infrared spectra were collected using a commercially available sample cell.

4. Results and discussion

Calcium chloride does not absorb mid-infrared radiation, and therefore unity infrared beam reflectance is expected. Indeed anhydrous samples of calcium chloride analyzed using the designed sample cell have demonstrated unity reflectance even after leaving them in the sample cell for a period of 10 min (Fig. 2).

When calcium chloride samples are exposed to air atmosphere during ATR infrared analysis using a conventional ATR sample cell, moisture bands are observed. The 1630 and 3400 cm⁻¹ bands are associated with crystalline water's bending and stretching modes respectively (Fig. 3).

The water content of hydrated calcium chloride was monitored over a period of time from 0.5 to 10 min and there was an indication of increasing moisture band intensity (Fig. 3), suggesting that the sample was still adsorbing water.

The rapid rate at which calcium chloride hydrolyzes was studied using FTIR–ATR as shown in Fig. 3. The two prominent bands are the 1629 cm^{-1} due to the bending mode of water, normally, in crystalline form, and the 3451 cm^{-1} due to the –O–H stretch. The noise in the $2000-2200 \text{ cm}^{-1}$ spectral region is due to interference by the diamond crystal used for the ATR-infrared measurements.

Other hydrolyzing samples such as fluorinated inorganic compounds are known to produce toxic gases when exposed to moisture, for example, lithium hexafluorophosphate decomposes rapidly in the presence of moisture (300 ppm) to give off HF gas [7], a poisonous and corrosive substance. As a result, the use of a closed system such as the sample cell described here is important to maintain sample integrity and eliminate health hazards.



Fig. 3. FTIR-ATR spectra of hydrolyzed calcium chloride samples. The spectra from top to bottom indicate samples exposed to air for 0.5, 3, 5, 7 and 10 min respectively. The amount of moisture in each sample depends on the time the sample was exposed to air atmosphere.

5. Conclusion

The analysis of calcium chloride as a representative sample of a hygroscopic species has shown that the designed sample cell does avoid atmospheric moisture from interfering with the analyte. Anhydrous CaCl₂ quickly hydrates when a conventional ATR sample cell is used during ATR measurements, and the extend of hydration on the sample is time dependant. The sample cell designed and explained in this work clearly has advantages over the conventional ATR sample cell designs because a spectrum of the hygroscopic sample can now be obtained in an inert environment. This is particularly important for the infrared analysis fluorides and chlorides which are known to be very reactive to atmospheric moisture and rapidly decompose to release toxic gases.

An inlet with a valve may be used to replace the side screw on the new cell and in this configuration, the cell provides special infrared analysis conditions such as vacuum or specific gas environment to study solid–gas interactions.

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