Application Note

Materials Testing & Research

Agilent
Trusted Answers

High Temperature Dehydration Studies Using UV-Vis-NIR Diffuse Reflectance Spectroscopy

Studying chemical transformations up to 300 °C using the Agilent Cary 5000 UV-Vis-NIR with the Praying Mantis accessory

Authors

Geethika Weragoda,
Wesam Alwan, and Travis Burt
Agilent Technologies, Inc.

Abstract

High temperature dehydration of silicon dioxide (SiO_2) and hexahydrate nickel(II) sulfate ($NiSO_4{\cdot}6H_2O$) samples were studied using the Agilent Cary 5000 UV-Vis-NIR spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory. Measurements were taken between room temperature and 300 °C. The study shows that the Cary 5000 UV-Vis-NIR is ideally suited to the study of low reflectance samples and can be used under extreme sampling conditions.

Introduction

Diffuse reflectance spectroscopy (DRS) is used to measure the amount of light reflected or scattered from a material's surface. The technique is applicable to most solids and involves little or no-sample preparation. However, the best results are achieved with the sample in powdered form, as the large surface area of powders provides more opportunity for light to interact with the sample. DRS is the most versatile spectroscopic technique for studying powders involved in heterogeneous catalysis or reactions at the gas solid interface. The technique can be used under *in situ* conditions and is quantitative in nature.[1, 2]

The Agilent Cary 5000 UV-Vis-NIR spectrophotometer fitted with a Praying Mantis diffuse reflectance accessory (Harrick Scientific Products, Inc., Pleasantville, New York, USA) is suitable for studying chemical transformations over a wide temperature range in the UV-Vis NIR region. The Cary 5000 UV-Vis-NIR spectrophotometer is a high-performance UV-Vis and NIR spectrophotometer with excellent photometric performance in the 175 to 3,300 nm range. The broad wavelength range and wide dynamic range capabilities of the Cary 5000 provide the flexibility to study chemical transformations of a wide range of samples. Sample types include powders and crystals, solids with rough surfaces, minerals, plastics, and fibers. The range of sample forms makes DRS a valuable tool for the study of powders involved in heterogeneous catalysis or reactions at the gas solid interface.

Water crystallization refers to the incorporation of water molecules in the process of forming crystals from aqueous solutions or water containing solvents. Hydrous metal complexes and salts contain water molecules in their crystalline framework. The water molecules are not directly bonded to the metal cation, so they can be removed by heating, which often leads to the loss of a sample's crystalline properties. Dehydrating some hydrous metal complexes/salts is accompanied by a color change that is visible to the naked eye.

In this study, the Cary 5000 UV-Vis-NIR spectrophotometer fitted with a Praying Mantis diffuse reflectance accessory (DRA) was used to explore the dehydration of powdered silicon dioxide (SiO_2) and hexahydrate nickel sulfate ($NiSO_4{\cdot}6H_2O$) upon heating. The Praying Mantis DRA was fitted with the high temperature reaction chamber (HVC) sampling accessory. The HVC enables measurements of the sample to be taken inside an environmental cell where the temperature and gas atmosphere can be controlled. The HVC consists of a reaction chamber, heating cartridge, thermocouple, cooling ports, and an HVC dome (Figure 2). The HVC dome contains two KBr windows, which allow spectrophotometer radiation to enter and exit, and one quartz window for observation. The samples, which were placed in a small volume powder cup of the reaction chamber that was set inside the Praying Mantis, were measured by UV-Vis-NIR. Using this configuration, the Cary 5000 can deliver high quality data for small volumes of powder-samples.

Figure 1. The Agilent Cary 5000 UV-Vis-NIR spectrophotometer.

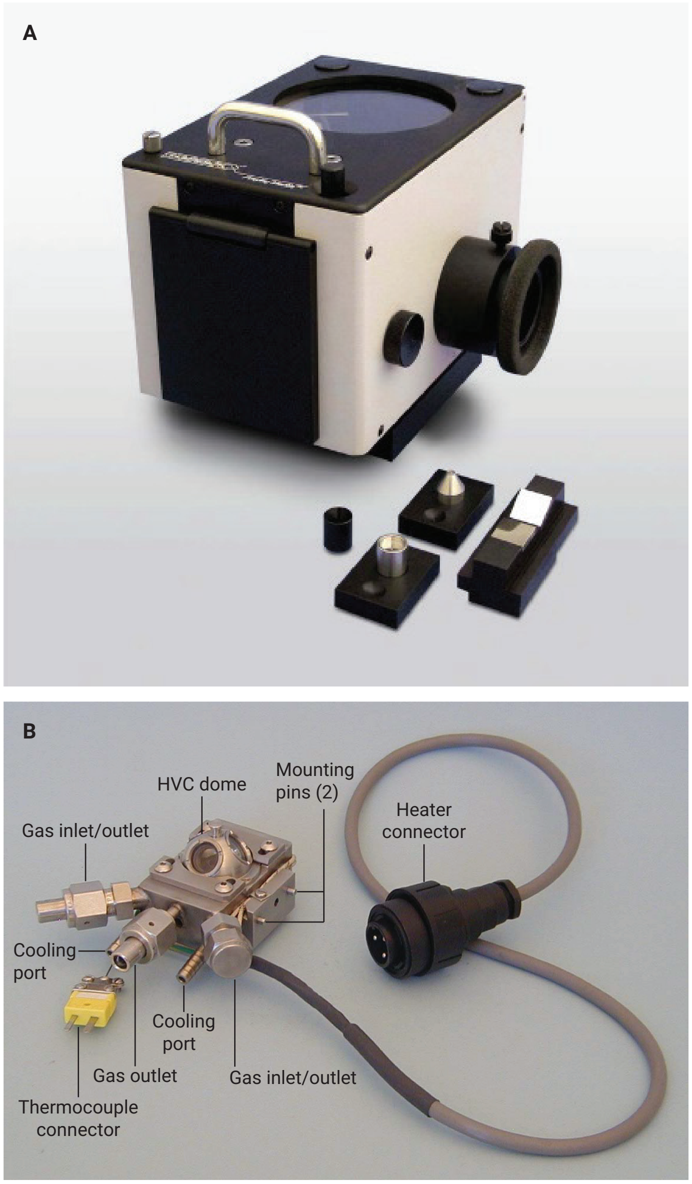


Figure 2. (A) Praying Mantis diffuse reflectance accessory. (B) High temperature reaction chamber for the Praying Mantis.

Experimental

Instrument setup and workflow

The Cary 5000 UV-Vis-NIR spectrophotometer with the Praying Mantis accessory fitted with the high reaction chamber was used to collect diffuse reflectance measurements. The reference spectra were collected using polytetrafluoroethylene (PTFE). The Agilent Cary WinUV software and the instrument operating parameters used in this study are shown in Table 1.

Table 1. Experimental parameters for the Agilent Cary 5000 UV-Vis-NIR spectrophotometer.

Parameter	Setting
Wavelength Range	250 to 2,500 nm
Reference (Baseline)	PTFE
Data Interval	2 nm
Signal Averaging Time	0.2 s

Instrument setup

To perform diffuse reflectance measurements of solids at various temperatures, the following steps were followed:

1. The Praying Mantis accessory was inserted into the Cary 5000 UV-Vis-NIR spectrophotometer, making sure that the two kinematic screws in the front of the Praying Mantis base plate engaged into the holes in the spectrometer floor. The accessory was locked using the lock-down mechanism handle.
2. The Praying Mantis is pre-aligned; however, minor adjustments are normally required to optimize its performance. The alignment procedure can be done using the alignment fixture and procedure supplied with the accessory.
3. A baseline PTFE spectrum was collected at room temperature (RT). The standard sampling cup (6.3 mm diameter) was overfilled with PTFE then the surface was leveled off using a flat blade. The height of the sample stage was adjusted to maximize the signal at the detector.
4. The high temperature reaction chamber sample cup was filled with the sample and secured with the dome provided.
5. The high temperature reaction chamber was installed in the Praying Mantis by removing the sample stage. This was done carefully to maintain alignment.
6. To perform temperature-controlled experiments, multiple connections were made to the high temperature reaction chamber (Figure 3), as follows:
   A. Since the reaction chamber was to be operated at temperatures above 100 °C, the cooling ports were connected to a water circulator. The Agilent PCB-1500 circulating water bath was used in this study. Flowing water or coolant through the cooling conduit improves the thermal isolation between the sample cup and the outer chamber, preventing damage to the O-rings and windows. Cooling also minimizes unwanted spectral artifacts, including extraneous noise.

B. The heater and the thermocouple were connected to the temperature controller (ATK-024-3) provided by Harrick Scientific Products, Inc. The gas inlet/outlet were not used in this study, however, if vacuum is desired, they can be used.

The temperature controller was programmed using the supplied software (Watlow EZ-Zone Configurator). Once the high temperature reaction chamber had reached the desired temperature, it was stabilized for four minutes, and then a spectrum was collected using the parameters listed in Table 1. To maintain best performance, it is recommended that the HVC is removed from the Praying Mantis before a sample is added.

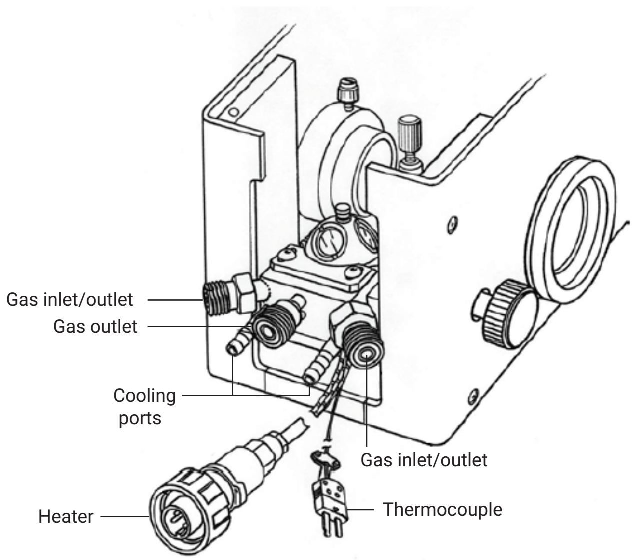


Figure 3. The high temperature reaction chamber installed in the Praying Mantis accessory.

Sample analysis

– Diffuse reflectance spectra of SiO_2 were collected at RT, 50, 100, 150, 200, 250, and 300 °C. The sample was then allowed to cool to RT and the corresponding spectrum was collected.

– Diffuse reflectance spectra of $NiSO_4 \cdot 6H_2O$ were collected at RT, 100, and 150 °C.

Note: Each sample was allowed to remain for a minimum of four minutes at the desired temperature to reach equilibrium before the spectrum was collected. Baseline correction was applied using the diffuse reflectance spectrum of PTFE collected at the same temperature as the samples.

Results and discussion

The Cary 5000 UV-Vis-NIR spectrophotometer is designed to work with very high absorbance or very low transmittance/reflectance signals. High-precision readings can be obtained for low reflectance samples or from a small volume of sample. As illustrated in Figure 4, the Cary 5000 produced highly repeatable scans for a small volume of finely powdered PTFE collected at RT.

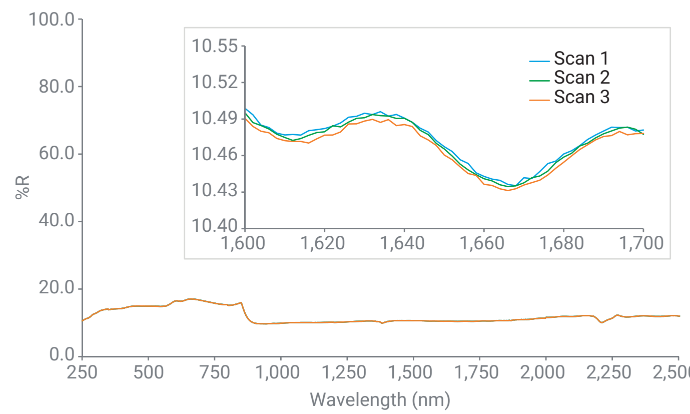


Figure 4. Three repeated wavelength scans of PTFE powder acquired at RT using the Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The inset shows the wavelength region between 1,600 and 1,700 nm, highlighting the repeatability of the measurements.

Diffuse reflectance spectra of SiO_2 at different temperatures

Diffuse reflectance spectra of powdered SiO_2 were recorded at seven different temperatures from RT to 300 °C. The melting point of SiO_2 is ~1,700 °C, so the spectra were expected to be stable within the temperature range of this experiment. While no significant changes were observed in the wavelength range from 250 to 2,500 nm upon heating as predicted, the intensity of the peak at 1,890 nm at RT gradually decreased with increasing temperature up to 200 °C. As can be seen in Figure 5, the peak disappeared completely when the sample temperature reached 250 °C, confirming the dehydration process of SiO_2.

Interestingly, the 1,890 nm peak returned when the sample cooled down to RT (the sample was left to cool inside the reaction chamber). The reversible dehydration and rehydration process is due to the water molecules that are bound to the surface of SiO_2. The dotted line in Figure 5 shows the spectrum obtained for the "rehydrated" SiO_2, collected when the sample had cooled to RT.

Note: Measurements at higher temperatures, over 400 °C, are feasible only in the UV-Vis region. The PbS detector of the Cary 5000 is sensitive to NIR emissions and will become saturated at temperatures over 400 °C, providing no useful information in the NIR region.

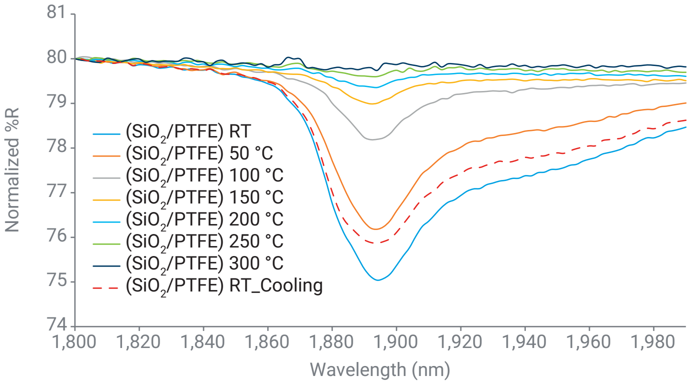
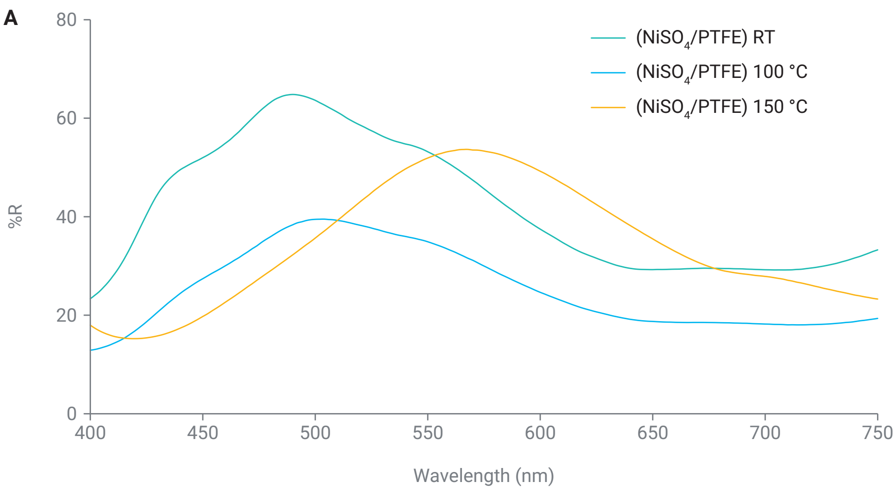


Figure 5. Diffuse reflectance spectra of SiO_2 measured at different temperature points from RT to 300 °C. The dotted line represents the trace collected when the sample was allowed to cool down to room temperature.

High temperature dehydration of $NiSO_4 \cdot 6H_2O$

$NiSO_4 \cdot 6H_2O$ is a blue-green colored salt that undergoes dehydration at high temperatures. The dehydration results in the formation of yellow-colored anhydrous $NiSO_4$. The color change is clearly visible to the naked eye. Figure 6A shows the spectra of $NiSO_4 \cdot 6H_2O$ recorded at different temperature points up to 150 °C. At RT, a peak can be seen in the spectrum at 490 nm, in the green region of the visible spectrum. As the sample was heated, the peak at 490 nm decreased in intensity and a new peak formed at 570 nm, in the yellow region, confirming the formation of anhydrous $NiSO_4$ (Figure 6).



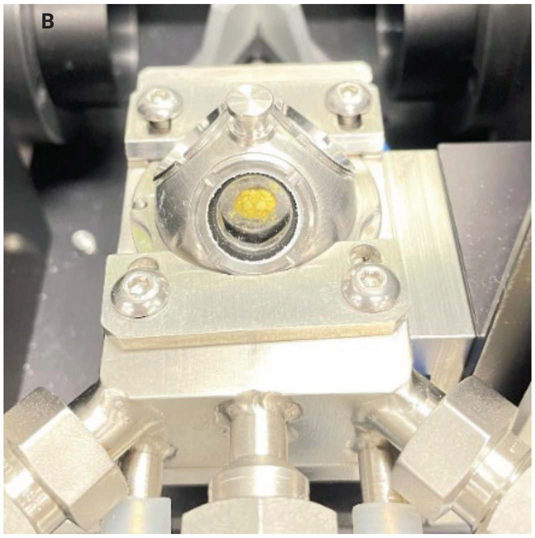


Figure 6. (A) Diffuse reflectance spectra of $NiSO_4 \cdot 6H_2O$ measured at 25, 100, and 150 °C. (B) $NiSO_4 \cdot 6H_2O$ converted into a yellow color anhydrous $NiSO_4$ upon heating.

Conclusion

The Agilent Cary 5000 UV-Vis-NIR spectrophotometer fitted with a Praying Mantis diffuse reflectance accessory was used to study temperature induced dehydration of SiO_2 and $NiSO_4{\cdot}6H_2O$.

The combination of the wide dynamic range and excellent signal-to-noise ratio of the Cary 5000 makes it suitable to study temperature induced changes of small volume powdered samples. Thermally stable SiO_2 undergoes dehydration of water molecules that are bound to its surface. The green-blue color of $NiSO_4{\cdot}6H_2O$ converts to a yellow-colored anhydrous powder at high temperatures, which corresponds to a wavelength shift from 490 to 570 nm.

These results demonstrate that diffuse reflectance spectroscopy (DRS) combined with a temperature-controlled chamber provides an effective way of studying temperature-induced changes in solid materials, such as powders and rough-surfaced solids. The instrumentation is also valuable for studying heterogeneous catalysts, as both d–d and charge transfer transitions of supported transition metal ions can be investigated.

References

1. Weckhuysen, B. M.; Schoonheydt, R. A., Recent Progress in Diffuse Reflectance Spectroscopy of Supported Metal Oxide Catalysts. *Catalysis Today* **2019**, *49(4)*, 441–451.
2. Weckhuysen, B. M., *et al.*, Synthesis, Spectroscopy, and Catalysis of [Cr(acac)3] Complexes Grafted onto MCM-41 materials: Formation of Polyethylene Nanofibers within Mesoporous Crystalline Aluminosilicates. *Chem. Eur. J.* **2020**, *6(16)*, 2960–2970.

Further information

- Agilent High-Performance UV-Vis, Cary 5000 UV-Vis-NIR spectrophotometer
- Agilent Cary WinUV Software for UV-Vis-NIR Applications
- Agilent Cary UV-Vis Spectrophotometer Accessories
- Agilent Praying Mantis DRA for Cary UV-Vis-NIR Instruments
- UV-Vis Spectroscopy & Spectrophotometer FAQs

www.agilent.com

DE04678824

Printed in the USA, May 4, 2023
5994-6104EN

Agilent
Trusted Answers