

THE STUDY OF INORGANIC MATERIALS USING DIFFUSE REFLECTANCE

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(Received 07 October 2002)

ABSTRACT: In recent years, Fourier transform spectrometers are being used for studying in all of the IR spectrum regions. However, choosing the correct sampling technique can still have a problem which sometimes obstructs the spectroscopists' measurements. The diffuse reflectance (DR) spectrometry with another sampling technique has become handy for the IR spectrometry of solids, especially inorganic materials. Nevertheless, it could be seen that DR spectra aren't entirely free of problems. The aim of the work is to point out some difficulties that might appear when measuring DR spectra of inorganic materials and to suggest methods of removing them.

I. INTRODUCTION

The technique of diffuse reflection spectroscopy has been used successfully in many fields as an adjunct to more well known spectroscopic methods, and is often useful where traditional technique fail. Coal, for instance, proves extremely difficult to analyze by classical techniques, but excellent spectra can be obtained by diffuse reflectance. Many substances in their natural states (e.g., powders and rough surface solids) exhibit diffuse reflection, i.e. incident light is scattered in all directions as opposed to specular (mirror-like) reflection where the angle of incidence equals the angle of reflection. In practice, DR spectra are complex and are strongly dependent upon the conditions under which they are obtained.

These spectra can exhibit both absorbance and reflectance features due to contributions from transmission, internal and specular reflectance components as well as scattering phenomena in the collected radiation. DR spectra are further complicated by sample preparation, particle size, sample concentration and optical geometry effects,...

In fact, so far this method has not been widely used in Vietnam yet. In this work, two powdered inorganic materials to be analyzed in some detail are copper sulfate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and potassium iodate KIO_3 .

II. CALCULATION

The *ab initio* calculation using software Gaussian 98 with *theory level* HF (Hartree-Fock) and appropriate *basic set* can predict reliably fundamental vibration frequencies, intensities as well as kind of symmetry of ion or molecule. The calculation results of free ion SO_4^{2-} and IO_3^- are listed respectively in table 1 and table 2. In the free state, the symmetry of ions are T_d and C_{3v} respectively [1,3]. Basing on the results and combining with group theory, the assignment and interpretation of their spectra are able to carry out readily [2,3,4].

Table 1. Calculation results for free sulfate ion SO_4^{2-} (with basic set 6-31G(d))

Designation	Ab initio Calculation			Experimental Freq. [1,7]	Symmetry Class	Description
	Freq.	I_{IR}	I_{R}			
ν_1	1008	-	29.4	983	A_1	ν_s S-O
ν_2	460	-	1.8	450	E	δ_d O-S-O
ν_3	1157	570.8	7.8	1104	F_2	ν_d S-O
ν_4	651	49.5	2.2	613	F_2	δ_d O-S-O

Table 2. Calculation results for free iodate ion IO_3^- (with basic set LANL2DZ)

Designation	Ab initio Calculation			Experimental Freq. [7]	Symmetry Class	Description
	Freq.	I_{IR}	I_{R}			
ν_1	802	0.6	50.4	796	A_1	ν_s I-O
ν_2	360	94.9	13.4	348	A_1	δ_s O-I-O
ν_3	755	0.5	28.4	745	E	ν_d I-O
ν_4	315	24.6	18.0	306	E	δ_d O-I-O

I_{R} : Infrared Intensity; I_{R} : Raman Intensity

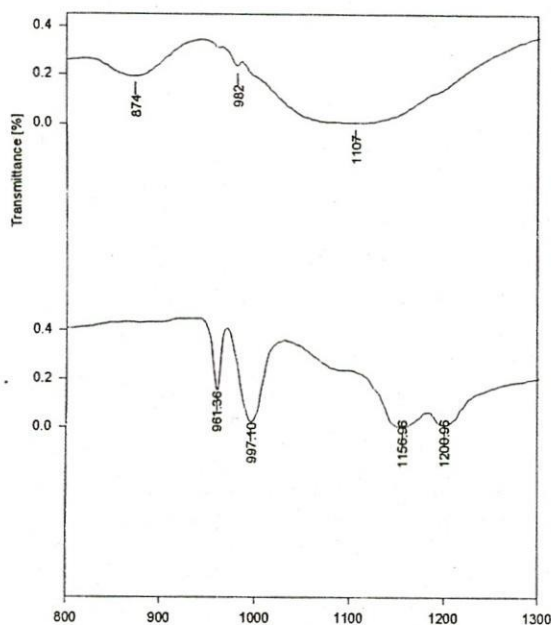


Fig. 1. Transmittance spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

III. EXPERIMENTAL

In order to produce a DR spectrum, a background must first be collected. Here, the samples used for this background spectrum are the pure matrix materials KBr, KCl. The background sample is placed in position on the same holder. The prepared sample to be analyzed is placed the other same position. The resulting spectrum is produced by ratioing the sample spectrum to the background spectrum.

The DR spectra of the materials are measured by spectrometer EQINOX 55 combined with a cell EASIDIFF and detector DTGS (deuterated triglycine sulfate).

IV. RESULTS AND DISCUSSION

Fig. 1 gives the transmittance spectra of copper sulfate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ prepared as KBr discs in two cases: the sample mixed with KBr and then the mixture ground for 10 min (below trace); the sample ground separately and then mixed with KBr with the same time (above trace).

From Fig. 1, more new-come bands appear in the second case than in the first one because the sample and the matrix KBr were compressed during the preparation of the disc, thus ion exchange reaction probably occurred [8].

These results prove that IR spectra of inorganic materials can vary strongly when powdered alkali halides are used as matrices.

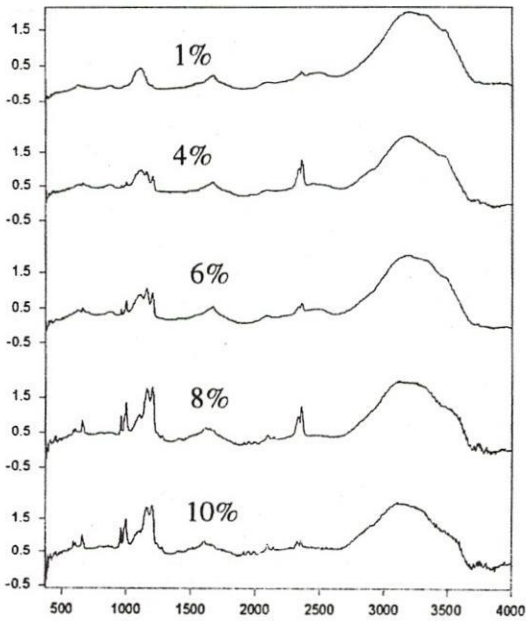


Fig. 2. DR spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ mixed and ground with KBr with different ratios (1, 4, 6, 8, 10%)

DR spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ground with the diluent KBr with different ratios (1, 4, 6, 8, 10%) are shown in Fig. 2.

The bands at 3200 cm^{-1} and 1600 cm^{-1} are due to the stretching and bending vibrations of H_2O respectively [5].

It can be seen that a lot of bands appearing in spectral region of $500 - 1250 \text{ cm}^{-1}$ in case of the 5 to 10 percent (5-10%) mixtures, meanwhile the 1 percent (1%) mixture gives only one band in spectral region of $1000 - 1250 \text{ cm}^{-1}$.

On the contrary, when $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KBr are ground separately and then mixed together, the spectrum keeps unchanged and there is not any strange band appearing at all (Fig. 3).

Therefore, it can be affirmed that the effect of ion exchange is readily apparent when DR spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is measured after mixing and grinding with KBr during the preparation of the disc.

Similarly, it is seen that the DR spectra of the mixtures prepared by grinding $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with either KBr and KCl are identical.

Beside the problems discussed above, one additional effect can also be observed occasionally when inorganic samples with layer structures are investigated. For example, if $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is ground then either mixed or ground with nonabsorbing matrix, such as KBr, the spectrum can vary with grinding time of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fig. 4, 5, 6).

After $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is ground with, for example KBr, the DR spectrum varies with grinding time.

Indeed, comparing the DR spectra in Fig.4, it can be seen that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KBr are mixed and then ground in the various length of time to produce 10% dispersions (for 1, 5, 10, 15 min), some new bands appear in $750 - 1250 \text{ cm}^{-1}$ region such as $962, 1000, 1185, 1201 \text{ cm}^{-1}$ in spectrum of grinding time of 5 min (below trace). The spectra of the grinding time of 10 and 15 min are in similar shape with that of 5 min, however their bands are separated much more (Fig. 5).

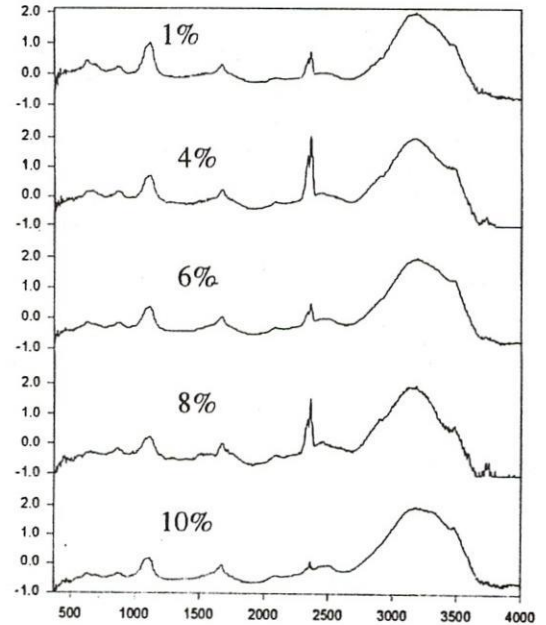


Fig. 3. DR spectra $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KBr are ground separately and then mixed with ratios 1, 5, 10, 15 %.

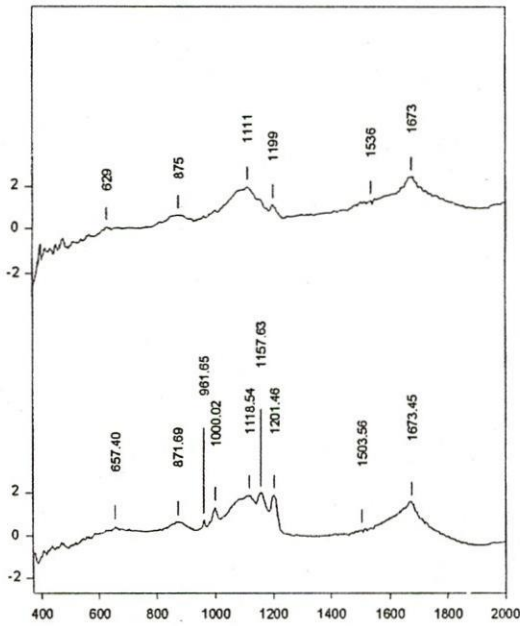


Fig. 4. DR spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ground with KBr for 1 min (above), 5 min (below).

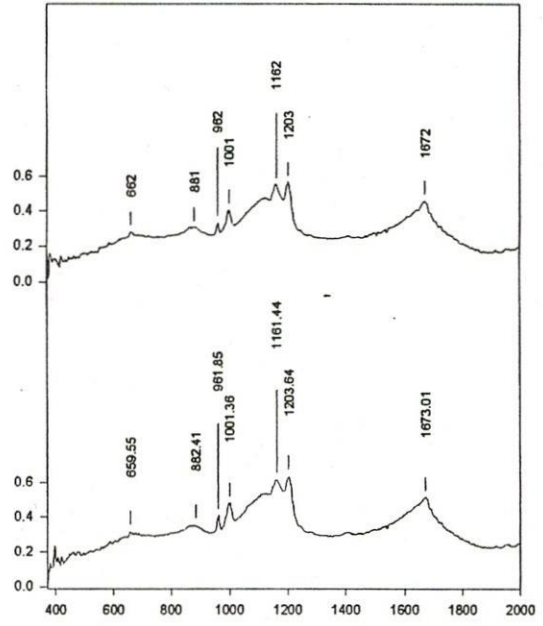


Fig. 5. DR spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ground with KBr for 10 min (above), 15 min (below).

In the manner, thus, the longer the grinding time the more bands appear because increase in contact time between $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KBr raises the ion exchange reaction.

In case $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is ground separately from the KBr diluent and then mixed, the spectrum has a small change (Fig. 6). If the grinding time is longer the bands will be separated much more and their intensities are somewhat changed. No new band comes. According to Teiki Iwaoka [8], the layer structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ becomes less ordered during the grinding process. This leads to the distortion of the spectra.

When the spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is measured with the different grinding time, sample should be ground by itself from KBr diluent and then mixed, the grinding time is about 5 min to avoid effect of ion exchange causing some difficulties in process.

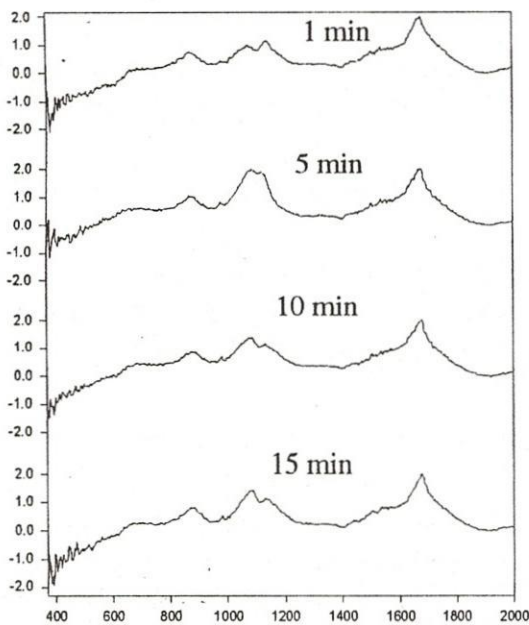


Fig. 6 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is ground separately from the KBr diluent (for 1, 5, 10, 15 min) and then mixed

It is interesting to note that when either a large amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is ground by itself, or a small amount is ground with an transparent diluent, only relatively small changes in the spectrum are noted even after extensive grinding. Apparently, when a large quantity of material is present, it can act as a cushion and prevent disordering of the layer structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

What would be now happened to the DR spectrum of potassium iodate KIO_3 as if the sample preparing procedures like above still are used.

Fig. 8 shows the transmittance IR and DR spectra of KIO_3 . Both of them have two bands with a strong intensity at 798 m^{-1} and 755 cm^{-1} in transmittance IR spectrum at 798 m^{-1} and 762 cm^{-1} in DR spectrum, respectively, they are ν_1 and ν_3 . A few very weak bands at $400\text{-}650 \text{ cm}^{-1}$ in both transmittance IR and DR spectra may be due to the metal - oxygen vibrations [7].

The two remaining vibrations, respectively ν_2 at 348 cm^{-1} and ν_4 at 306 cm^{-1} (table 2) couldn't be observed because of wavenumber limitation of the spectrometer.

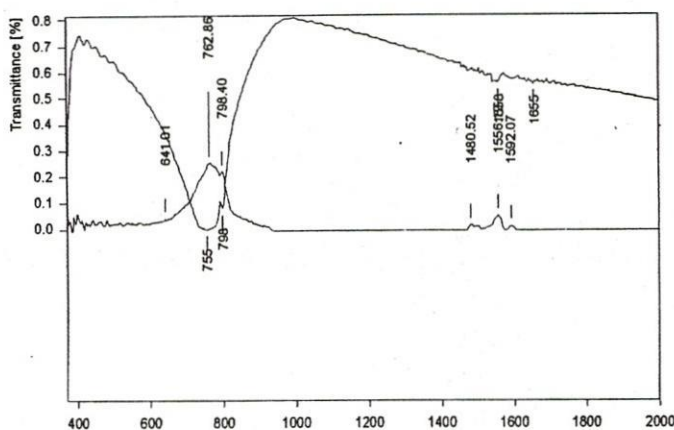


Fig. 7. Transmittance IR and DR spectra of KIO_3

Fig. 8 gives the DR spectra of KIO_3 diluted with KBr by grinding separately for 1, 5, 10 and 15 min and then mixing to form 10% dispersions.

Fig. 9 shows DR spectra of KIO_3 diluted also with KBr according to the inverse order, namely mixing and then grinding with the time likes above.

Observing the spectra, it could be seen that both of two cases, the spectra are almost unchanged. This means that there may be not the ion exchange reaction between KIO_3 and the diluent [8].

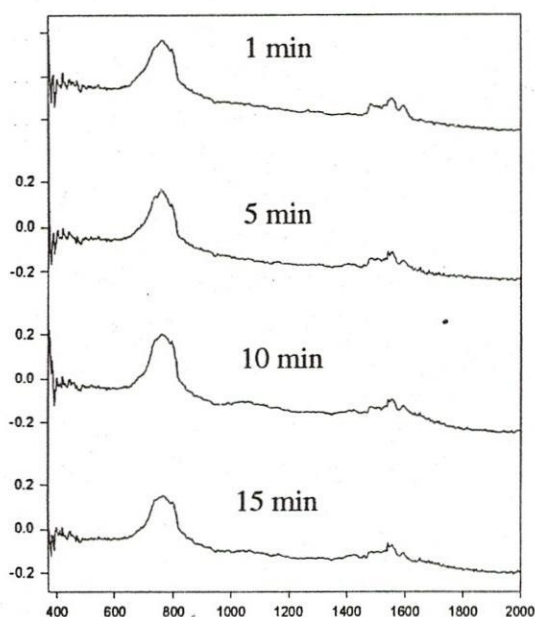


Fig. 8. DR spectra of KIO_3 ground separately (for 1, 5, 10, 15 min) and then mixed with KBr

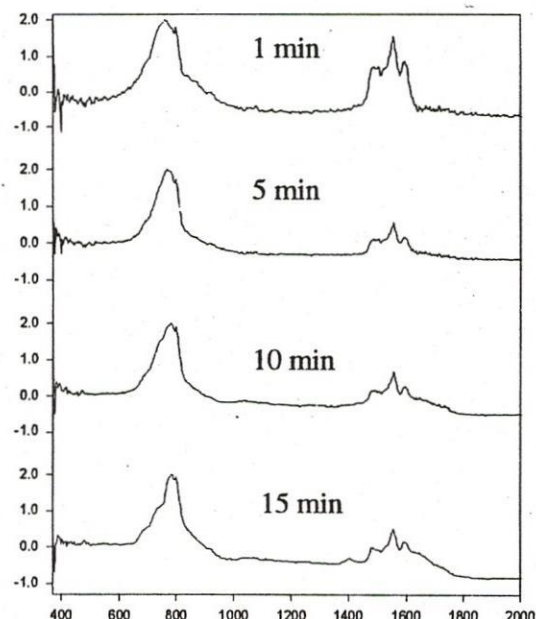


Fig. 9. DR spectra of KIO_3 mixed with KBr and then ground (for 1, 5, 10, 15 min)

V. CONCLUSIONS

The results above indicate that the use of powdered alkali halide matrices for diffuse reflectance IR spectrometry of inorganic materials can lead to problems. If the analyte is ground on its own prior to mixing with the alkali halide, there is a change that the crystalline structure can be distorted.

Conversely, if it is ground with the alkali halide, ion - exchange can occur. Beside the spectra are also affected by grinding time and amount of dispersion. So that excellent spectra of inorganic samples can be measured with very short grinding times. The grinding time required was only 5 min with a small dilution. It should be noted that the sample is ground separately and then mixed with matrix. The experience of working suggests that all

that condition should be associated to avoid ion-exchange and effect of restraints bands, to have a reliable spectra of inorganic materials to be measured by using diffuse reflectance spectrometry.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Council of Vietnam.

NGHIÊN CỨU CÁC VẬT LIỆU VÔ CƠ BẰNG PHƯƠNG PHÁP QUANG PHỔ PHẢN XẠ KHUẾCH TÁN

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(Bài nhận ngày 07 tháng 10 năm 2002)

TÓM TẮT: Trong những năm gần đây, phương pháp ghi phổ dựa vào phép biến đổi Fourier đã và đang được sử dụng ở tất cả các vùng phổ hồng ngoại. Tuy nhiên, việc chọn lựa phương pháp chuẩn bị mẫu cũng còn không ít vấn đề mà nhiều khi làm trở ngại rất nhiều cho các nhà nghiên cứu trong khi ghi phổ. Sự phát triển phương pháp phản xạ khuếch tán với kỹ thuật chuẩn bị mẫu đơn giản hơn đã hỗ trợ cho việc nghiên cứu các mẫu rắn, đặc biệt là đối với các vật liệu vô cơ. Tuy nhiên, có thể thấy rằng không phải hoàn toàn không còn vấn đề khó khăn đối với phương pháp này. Mục đích của bài báo này chỉ ra những khó khăn trong quá trình ghi phổ và cách khắc phục chúng.

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