

METHOD OF INFRARED SPECTRA REGISTRATION OF ACTIVATED CARBONS IN POTASSIUM BROMIDE PELLETS

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Abstract. This communication is devoted to the elaboration of a new optimal technique of infrared spectra registration of activated carbons in potassium bromide pellets. Authors investigated the dependence of the intensity of the least overlapping infrared bands of activated carbons on the conditions of preparation, recording of the spectrum, and the degree of homogenization with KBr.

Keywords: infrared spectroscopy, activated carbons, potassium bromide KBr pellets.

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Introduction

Infrared (IR) spectroscopy has an important role in the study of the active carbon structure. In the study of carbons, research of pressed pellets with alkali metal halides is used for this purpose, as well as IR spectroscopy of attenuated total reflectance (ATR). Tableting method has become the most popular method of obtaining IR spectra of active carbons [1-3]. However, errors may occur in the measurement of the intensity of the bands due to the inhomogeneous distribution of the sample in the pellet. When the sample is distributed unevenly in the pellet, the beam of the Fourier Transform Infrared (FTIR) spectrometer can fall on pure KBr regions with no test substance and this may lead to distortion of the measured intensities of the bands. The increase of voids caused by the inhomogeneous distribution of the test substance in the pellet leads to the decrease of recorded bands intensities and stronger bands decrease more significantly than weaker ones. Thus the so-called smoothing of the spectrum occurs.

The aim of this work was to study the dependence of the intensity of the least overlapping infrared bands of activated carbons on the conditions of preparation, recording of the spectrum, the degree of homogenization with KBr, as well as the elaboration of an optimal method of sample preparation as a pellet of active carbon homogenate with KBr for IR spectrum registration.

Experimental

The method of IR spectra registration of activated carbons in KBr pellets.

Amount of 0.40-0.50 mg of activated carbon was homogenized in an agate mortar with 300 mg of optically pure KBr, vacuumized for 5 min and pressed under 10 ton/cm² for 15 min. The area (S, cm²) of the KBr pellet was 1.13 cm² (Zeiss standard). A light grey transparent pellet without visually noticeable grains was obtained. IR spectra were recorded on a PerkinElmer FTIR Spectrometer Spectrum 100, (2007) in the wave number range of 4000-400 cm⁻¹. Prior to the preparation of pellets and spectral analysis, the samples of carbons and KBr were dried and stored above anhydrous silica gel in an exicator. The optimal conditions of spectra recording were as follows: spectral resolution - 2 cm⁻¹, the scan number - 10, the number of automatic spectrum smooth - 2. Spectral data handling and baseline correction was carried out by the Spectrum software Version 6.2.0.0055 (2007). After the first registration of the spectrum the pellet was transferred quantitatively into a mortar and triturated (homogenized). The powder was repressed and IR spectrum was rerecorded. The operations of homogenization and IR spectrum registration were repeated until maximal stable values of absorption (A) were obtained. The IR spectrum was recorded using as control the same pellet made from pure ground potassium bromide.

Effects of various factors during the IR spectra registration in the KBr pellets have been examined on the example of a modified activated carbon AG-5ox (Table 1) obtained from a commercial sample of carbon AG-5. Activated carbon AG-5 was produced in granulated form from coal dust (coals mixture) and an adhesion agent by steam treatment at 850 - 950 °C [4]. Sample of AG-5ox has been prepared by oxidation of AG-5 with concentrated nitric acid as described in [5]. 0.480 mg of the active carbon sample AG-5ox was taken to prepare the KBr pellet according to the above-mentioned method. The concentration of AG-5ox was C = 0.425 mg/cm² and was held constant during the experiment.

Results and discussion

This communication described the method of sample preparation in the form of homogenate pellets of active carbon with KBr for recording the IR spectrum. The dependence of the intensity of the least overlapping infrared bands of activated carbons on the conditions of preparation, recording of the spectrum, and the degree of homogenization with potassium bromide has been investigated.

The recorded intensities of the IR bands depend on several factors:

1. Dependence on particle sizes. With all other conditions maintained equal, light scattering increases with the particle size in comparison with the wavelength. The particle size is comparable to the wavelength of the absorbed light in the ideal case. In the spectral region 4000 - 400 cm^{-1} , particle size 2.5 - 25 microns and particle size greater than 2.5 microns, the scattering of light decreases with increasing wavelength. The baseline correction method was used to compensate for the scattered light effect, consisting in the measurement of light absorption relative to a line drawn through the minima of the absorption (A) spectrum, respectively, through the transmittance (T,%) maxima.

2. Dependence on the uniformity of particle distribution in the KBr pellets. The recorded intensity of bands (A) depends not only on particle size but also on the equal distribution in the pellet. In the case of an uneven distribution of particles in the pellet, voids consisting of the pure KBr are formed between particles of analyzed sample, i.e. defects observed in the continuous distribution of particles. The increase in defects leads to the decrease of measured bands intensities, and this decrease is proportional to band intensity. The result is a so-called smoothing of the spectrum [6,7]. We have used techniques of consecutive sample homogenization with KBr to eliminate this defect. The pressed pellet has been reground and repressed consecutively several times to achieve constancy of the measured value A of the bands of varying intensity.

3. Homogenization of the mixture of investigated sample and KBr in an open atmosphere leads to moisture sorption. The bands of water absorbed by KBr appear in the spectrum $\nu(\text{OH})$ at 3450 cm^{-1} and $\delta(\text{HOH})$ at 1630 cm^{-1} [1, 8]. This absorption is compensated by the introduction of the control pellet of pure KBr in the reference beam of the spectrometer.

4. The measured value of absorption A depends on the weight of analyzed substance (g, mg) that is uniformly distributed over the area of the pellet (S, cm^2).

At a constant area of the pellet, any variation in the amount of KBr in the homogenate only leads to a change in the thickness of the pellet, but the quantity of the analyte projected in the beam onto the slit of the instrument is not changed. Thus the classic formula of the Lambert-Beer law for solid substance homogenized in the pellet with KBr has the form $K = \frac{A}{C}$. The K values (Eqs.(1) and (2)) of the intensities of the bands in the spectrum were compared.

$$C = \frac{g}{S}, \quad (1)$$

$$K = \frac{A \cdot S}{g}, \text{ cm}^2 \times \text{mg}^{-1}, \quad (2)$$

where A - measured absorbance (optical density); S - area of the pellet, cm^2 ; g - weight of the sample in the pellet, mg.

In order to compensate water absorption by the pellet during homogenization, the control pellet made from pure KB was placed in the beam of the FTIR spectrometer. The Carl Zeiss Company recommended a weight 300 mg of KBr on a standard area 1.13 cm^2 of a branded pellet to obtain sufficient firmness.

The results of investigations of the influence of various factors on the registration of the IR spectra of the modified activated carbon AG-5ox in KBr pellets are shown in Table 1.

Table 1

The dependence of optical density (A) of the least overlapping bands on the conditions of preparation and registration of the IR spectrum of the sample AG-5ox.

Conditions of spectrum registration	Band ₁		Band ₂		Band ₃	
	ν_1, cm^{-1}	$A_1 \cdot 10^3$	ν_2, cm^{-1}	$A_2 \cdot 10^3$	ν_3, cm^{-1}	$A_3 \cdot 10^3$
Immediately after pressing	1711	415	1561	433	1101	457
In 20 hours	1717	428	1559	451	1096	474
Rotation of the pellet by 90°	1717	430	1560	454	1096	477

It was found that rotation of the pellet in the beam of the instrument didn't produce any changes. Consequently, the sample was uniformly distributed in the pellet. The spectrum of the sample in the pellet did not change after 20 hours, showing there was no interaction of the pressed AG-5ox with KBr during that time. No changes in the spectrum were observed after reapplying pressure on the uncrushed pellet during 3 hours.

The sample of AG-5ox was also used to investigate the dependence of the evenness of its distribution on the degree of homogenization in the KBr pellet (Table 2, Figure 1). After the first registration of the IR spectrum the pellet was subjected to repeated homogenization in a mortar, and another repressing. Pellet trituration in a mortar and pressing were repeated until stable values of absorption (A) were obtained.

Figure 1 shows the spectra of the AG-5ox sample as function of the degree of homogenization. Three least overlapping bands 1713 (C=O), 1560 (C=C), 1098 (C-C) cm^{-1} were chosen for quantitative characterization of the changes in the spectrum of AG-5ox during sample homogenization (Table 2). The first and second homogenizations

were insufficient to obtain a deeply embossed spectrum. The maximum and constant values of the IR bands intensities were achieved only after the third and fourth homogenizations. The increase in the homogenization degree made the spectra more relief and the latter reached a limit, which corresponded to previously reported data [1, 2, 6-8].

Table 2

The dependence of the IR bands intensities of modified activated carbon AG-5ox on the degree of homogenization.

Degree of homogenization	Band ₁		Band ₂		Band ₃	
	ν_1, cm^{-1}	$A_1 \cdot 10^3$	ν_2, cm^{-1}	$A_2 \cdot 10^3$	ν_3, cm^{-1}	$A_3 \cdot 10^3$
1	1719	424	1567	449	1098	474
2	1714	464	1548	485	1097	519
3	1713	482	1548	514	1098	560
4	1713	489	1560	526	1099	574

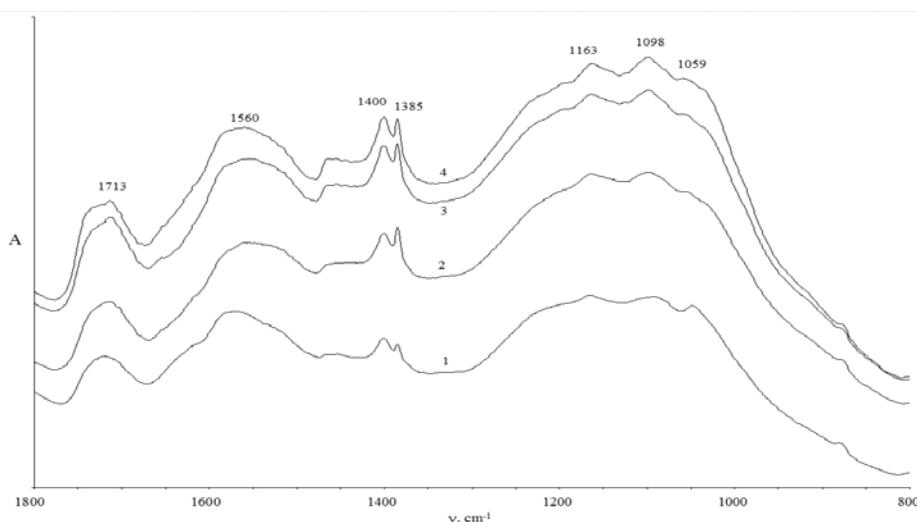


Figure 1. IR spectra of the sample AG-5ox as function of the degree of homogenization with KBr. The spectrum number corresponds to the degree of homogenization.

Conclusions

The investigation of the dependence of the optical density of the least overlapping bands in the IR spectrum of the activated carbon on the conditions of preparation and registration of the spectrum showed that the pressed sample of activated carbon was distributed evenly in the pellet and didn't suffer any changes after homogenization with KBr. An optimum technique for IR spectra registration of activated carbons in the KBr pellets has been proposed. The maximum and constant values of the intensities of the IR bands were achieved after the third and fourth homogenization of the KBr pellets.

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