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HIGH-TEMPERATURE CELL FOR INFRARED SPECTROSCOPIC INVESTIGATIONS

UKD 536.45.002.54:542.422.4:[549.623:552.52 montmorillonit

**A b s t r a c t.** The paper deals with the construction and application of high-temperature vacuum cell for infrared absorption study produced in the Department of Mineralogy and Geochemistry of the Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy in Cracow. The use of this equipment enables examination of preparations in the range 20-700°C in vacuum and subject to the action of gaseous sorbates. A method of preparation of samples as self-supporting films is described. Research possibilities of this method are exemplified by the results of infrared absorption investigations of surface properties of two kinds of silica gel and on the nature of acidic properties of the surface of acid-activated montmorillonite.

INTRODUCTION

Infrared absorption spectroscopy is actually one of the main methods of investigation of surfaces of solids, its chemical nature and absorption phenomena on these surfaces. The possibilities of this method can be considerably increased by applying high-temperature vacuum cell enabling "observations" of the surface examined in the course of reactions taking place on it, as well as investigations of temperature effect on its structure. First cells of this type and their applications have been described by Karge and Close /1973/, Cant and Hall/1972/, Parry /1963/, Hughes and White /1967/, Tarasevich and Ovcharenko /1974/, Little /1966/, Kiselev and Lyghin /1972/. Recently these cells are produced by some firms as additional equipment for their infrared absorption spectrometers.

This paper deals with the construction and research possibilities of high-temperature cell produced in the Department of Mineralogy and

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Geochemistry of the Academy of Mining and Metallurgy in Cracow. It differs from other equipments of this type by enabling the increase of temperature up to  $700^{\circ}\text{C}$ , whilst in the majority of them the maximum temperature is approx.  $500^{\circ}\text{C}$ . Besides, because of original design it is reliable and easy to operate.

## EXPERIMENTAL

### Apparatus

The construction of the cell is presented in Fig. 1. It can be used with the infrared spectrometer UR-10 /Zeiss/ for recording absorption spectra of minerals and chemical compounds in temperature range

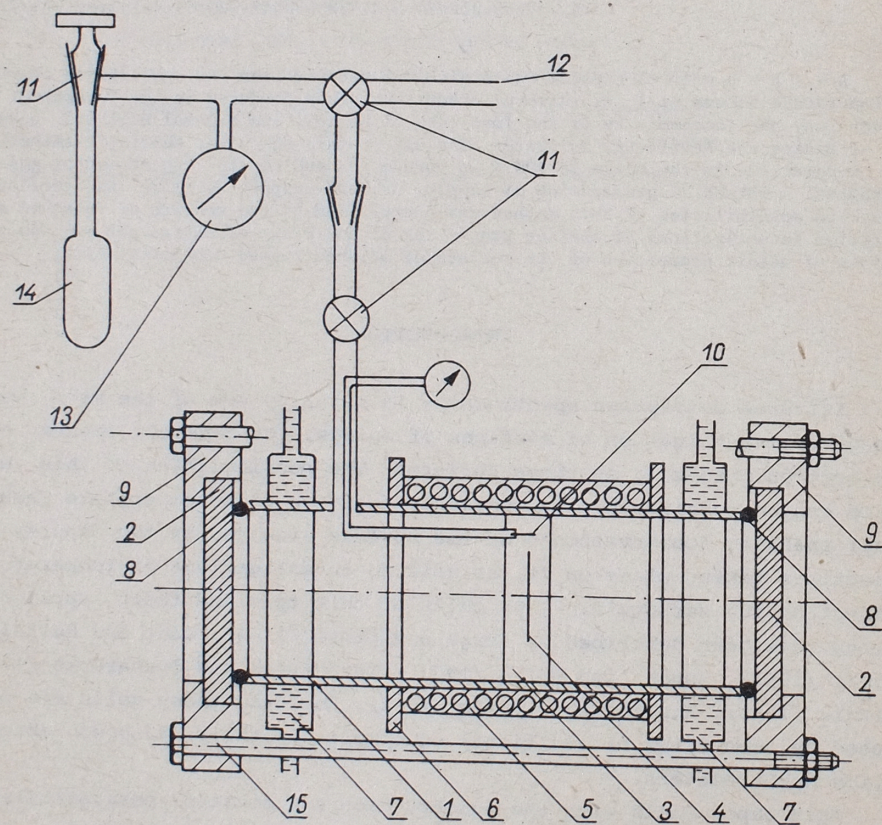


Fig. 1. The construction of the high-temperature vacuum-cell:

1 - quartz tube, 2 - KBr-windows, 3 - sample holder, 4 - sample, 5 - heater, 6 - guards of asbestos, 7 - water-cooling rings, 8 - tightening rings, 9 - gasket, 10 - thermocouple, 11 - vacuum taps, 12 - outlet to a vacuum pump, 13 - pressure gauge, 14 - ampoule for liquid sorbates, 15 - tightening screws

$20-700^{\circ}\text{C}$  in vacuum and subject to the action of gaseous sorbates under definite pressures. It is necessary to apply specific preparation of samples for such high-temperature equipment - the self-supporting film technique. Only this method can allow for spectroscopic surface "observations" of groups not disturbed by interaction with dispersing medium as it is the case with KBr disks or suspensions obtained in liquid organic substances. Moreover, evacuation of the sample placed in a cell allows to get the spectroscopic characteristic of the surface free from physically adsorbed molecules  $/\text{H}_2\text{O}, \text{CO}_2 \text{ etc.}/$ . Besides, this technique enables thermal treatment of the sample in cell and operating the sorption of gaseous sorbates on its surface. Preparations in the form of self-supporting films are obtained by means of two methods, depending on the character of the substance studied. Fine-dispersed materials, composed of grains less than  $0.2 \mu\text{m}$  in diameter /eg. montmorillonite/ are prepared by evaporation of their suspension in water on thin polyethylene foil and subsequent separation of the film thus obtained. More coarse-grained samples /eg. from silica/ are obtained by pressing at  $40 \cdot 10^4 - 80 \cdot 10^4 \text{ Nm}^{-2}$  on a matrix of silicon carbide or polyester foil. The preparations applied are  $5-10 \text{ mg/cm}^2$  in mass, transparent and stable. Both these methods have been described by Serratosa /1958/.

### Applications

The possibilities of the method in question will be now exemplified by selected results of studies on adsorption properties of surfaces of silica gels and on the nature of acidic properties of activated montmorillonite /Fijał, Olkiewicz, 1978/.

Spectroscopic characteristics of surface groups were obtained for two synthetic silica gels of Polish and French production /the latter is denoted as Ze-O-Sil/. The results are presented in Fig. 2. Preparations were placed in the cell and vacuum obtained by means of rotation pump for ca. 6 hrs. I. R. absorption spectra were recorded in the ranges  $700-1800 \text{ cm}^{-1}$  and  $2500-3800 \text{ cm}^{-1}$  /Fig. 2a, b/. The preparations were subsequently heated in the cell with simultaneous vacuum pumping at ca.  $500^{\circ}\text{C}$  to get equilibrium state, manifested by stabilization of the position and intensities of absorption bands on continuously recorded spectrum within the above ranges. Finally, the cell was cooled under vacuum conditions down to room temperature and the spectra recorded as for initial samples /Fig. 2c, d/. The spectrum of the Ze-O-Sil sample differs from that of the other one by the presence of fairly intense  $3740 \text{ cm}^{-1}$  band, due to free OH groups, superposing on the slope of bands resulting from valence vibrations of water molecules and

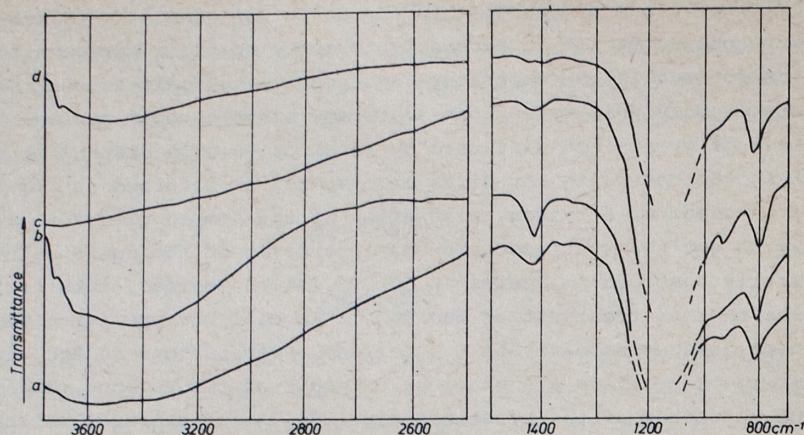


Fig. 2. IR-spectra of two kinds of silicagel recorded in vacuum cell / $10^{-3}$  mm Hg/  $a$  - sample 1 /Polish production gel/,  $b$  - sample 2 -/gel Ze-O-Sil/, evacuated at room temperature,  $c$  - sample 1,  $d$  - sample 2 calcinated at  $500^{\circ}\text{C}$ . Samples prepared in the form of thin self-supporting film

H-bounded.OH groups. This band is practically lacking in the spectrum of gel of Polish origin /Fig. 2a/. The presence of a weak band at ca.  $3670\text{ cm}^{-1}$  indicates that its OH groups are involved into hydrogen bonds. As follows from a comparison of spectra of these silica gels heated at  $500^{\circ}\text{C}$ , the Polish one shows much more pronounced tendency to dehydroxylation with temperature increase /Fig. 2c, d/. In the spectrum of this preparation we observe practical disappearance of the  $3670\text{ cm}^{-1}$  band /Fig. 2c/ whilst in that of the Ze-O-Sil sample /Fig. 2d/ the presence of an intense band ca.  $3750\text{ cm}^{-1}$  indicates the existence of free OH groups, displaying thermal stability. These data evidence that Ze-O-Sil gel is characterized by more developed surface of different structure when compared with the other one. Distinct stability of free OH groups can be explained by their single coordination by Si atoms. Most probably, the Polish gel examined is composed of silica granules of larger size and surface hydroxyl groups in it occur mostly in a system of pairs bound with the same silica atom, considerably influencing dehydroxylation ability.

Spectrograms showing dehydration of H-form of montmorillonite from Chmielnik with increasing temperature are presented in Fig. 3. The spectra were obtained after evacuating the sample at room temperature /Fig. 3a/ and after heating at  $300^{\circ}$  and  $600^{\circ}\text{C}$  respectively /Fig. 3b and c/. In the spectrum 3a the  $1630\text{ cm}^{-1}$  band corresponds to deformation vibrations of  $\text{H}_2\text{O}$  molecules and the broad band  $3000\text{--}3500\text{ cm}^{-1}$  with maximum at ca.  $3400\text{ cm}^{-1}$  - to stretching vibrations of these mo-

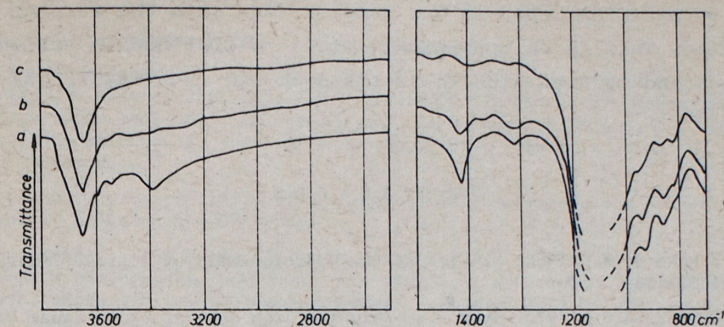


Fig. 3. IR-spectra of H-montmorillonite from Chmielnik, recorded in vacuum cell under pressure  $10^{-3}$  mm Hg, after calcination

$a$  - at room temperature,  $b$  - at  $300^{\circ}\text{C}$ ,  $c$  - at  $600^{\circ}\text{C}$ . Sample prepared in the form of thin self-supporting film

lecules. Heating accompanied by evacuation results in dehydration, manifested by a decrease of intensity of bands connected with vibrations of water molecules /spectra 3b and c/. This causes an exposition of the band  $1570\text{ cm}^{-1}$  and of a broad plateau in the wave number range  $2400\text{--}3500\text{ cm}^{-1}$  which are, probably, due to vibrations of  $\text{H}_3\text{O}^+$  ion present in crystal lattice of the sample. In order to determine the acidity of heated and unheated samples at temp.  $600^{\circ}\text{C}$ , experiments with sorption of gaseous pyridine on the surface of preparations placed in the cell in question have been carried out. Spectrograms of H-montmorillonite sample studied after treatment with gaseous pyridine at the pressure 22 mm Hg for 12 hrs. and subsequent removal of excess of pyridine by evacuation at  $100^{\circ}\text{C}$  are presented in Fig. 4, whereby the curve 4a corresponds to unheated sample whilst 4b - to heated in cell at  $600^{\circ}\text{C}$ . In the former spectrum we observe 1445, 1470, 1550 and  $1635\text{ cm}^{-1}$  bands characteristic for pyridinium ions. This indicates binding of sorbate at the surface Brönsted centres. On the other hand, distinct bands 1445, 1470, 1495 and  $1598\text{ cm}^{-1}$  in the spectrum of heated sample

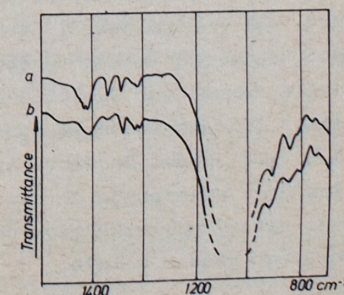


Fig. 4. IR-spectra of H-montmorillonite after pyridine vapour sorption:

$a$  - on the sample heated with evacuation at  $150^{\circ}\text{C}$ ,  $b$  - on the sample calcinated at  $600^{\circ}\text{C}$ . An excess of pyridine vapour evacuated at  $100^{\circ}\text{C}$  during 1 hour. Samples prepared in the form of thin self-supporting film

are due to pyridine bound in the complex form with the surface at Lewis centres. This is a convenient method to distinguish acidic surface centres and to determine their strength and quantity /Fijał, Olkiewicz, 1978/.

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#### WYSOKOTEMPERATUROWA KUWETA DO BADAŃ SPEKTROSKOPOWYCH W PODCZERWIENI

#### Streszczenie

Przedstawiono budowę i zastosowanie wysokotemperaturowej kuwety próżniowej do badań spektroskopowych w podczerwieni skonstruowanej w Zakładzie Mineralogii i Geochemii Akademii Górniczo-Hutniczej w Krakowie. Zastosowanie kuwety stwarza możliwości badania preparatów w zakresie temperatur 20-700°C w próżni oraz poddanych działaniu par sorbatów. Opisano metodykę sporządzania preparatów w postaci samoniesących błon. Możliwości badawcze zilustrowano wynikami badań w podczerwieni własności adsorpcyjnych dwu rodzajów syntetycznych żeli krzemionkowych oraz natury powierzchniowych własności kwasowych montmorillonitu aktywowanego kwasem solnym.

#### OBJAŚNIENIA DO FIGUR

- Fig. 1. Budowa wysokotemperaturowej kuwety próżniowej  
1 - rura kwarcowa, 2 - płytki z KBr, 3 - uchwyt preparatu, 4 - preparat, 5 - piec, 6 - osłony azbestowe, 7 - pierścienie chłodzące, 8 - uszczelka, 9 - pierścienie dociskowe, 10 - termopara, 11 - krany próżniowe, 12 - wyjście do pompy próżniowej, 13 - manometr rtęciowy, 14 - ampulka z sorbatem, 15 - śruby dociskowe
- Fig. 2. Spektrogramy dwu rodzajów syntetycznych żeli krzemionkowych rejestrowane w kuwecie próżniowej /10<sup>-3</sup> mmHg/  
a - próbka 1 /żel produkcji krajowej, b - próbka 2 /żel Ze-O-Sil/ - odpróżniane w temperaturze pokojowej, c - próbka 1, d - próbka 2-kalcynowane w temp. około 500°C. Stosowano preparaty w formie cienkich błon
- Fig. 3. Spektrogramy montmorillonitu z Chmielnika, rejestrowane w kuwecie pod ciśnieniem 10<sup>-3</sup> mmHg, po kalcynacji  
a - temperatura pokojowa, b - temp. 300°C, c - temp. 600°C. Preparat w formie cienkiej błony
- Fig. 4. Spektrogramy H-montmorillonitu po sorpcji par pirydyny  
a - na preparacie wygrzewanym z odpróżnianiem w temp. 150°C, b - na preparacie kalcynowanym w temp. 600°C. Nadmiar pirydyny ewakuowano w temp. 100°C przez 1 h. Preparat w formie cienkiej błony

Станислав ОЛКЕВИЧ

#### ВЫСОКОТЕМПЕРАТУРНАЯ КУВЕТА ДЛЯ ИК-СПЕКТРОСКОПИЧЕСКИХ ИССЛЕДОВАНИЙ

#### Резюме

В статье представлены конструкция и применение высокотемпературной вакуумной куветы для ик-спектроскопических исследований, изготовленной в Отделе Минералогии и Геохимии Горно-Металлургической Академии в Кракове. Применение куветы создаёт возможность исследования препаратов в диапазоне температур 20 - 700°C в вакууме, а также подвергнутых действию паров сорбента. Описана методика изготовления препаратов в форме самонесущих плёнок. Исследовательские возможности иллюстрируются результатами ик-спектроскопических исследований адсорбционных свойств двух видов синтетических силикагелей, а также существом кислотных поверхностных свойств монтмориллонита активированного соляной кислотой.

#### ОБЪЯСНЕНИЕ ФИГУР

- Фиг. 1. Конструкция высокотемпературной вакуумной куветы  
1 - кварцевая труба, 2 - плитки из KBr, 3 - держатель препарата; 4 - препарат, 5 - печь, 6 - асбестовые экраны, 7 - охлаждающие кольца, 8 - прокладка, 9 -

нажимные кольца, 10 - термopapa, 11 - вакуумные краны, 12 - выход к вакуумному насосу, 13 - ртутный манометр, 14 - ампула с сорбентом, 15 - нажимные болты

Фиг. 2. Ик-спектры двух видов синтетических силикагелей, полученные в вакуумной кювете / $10^{-3}$  мм Hg/

*a* - проба 1 /гель отечественного производства/, *b* - проба 2 /гель Ze-O-Sil/ - отсасывание при комнатной температуре, *c* - проба 1, *d* - проба 2 - кальцинированная при температуре около 500°C. Применялись препараты в виде тонких плёнок

Фиг. 3 . Ик-спектры R-монтмориллонита из Хмельника, полученные в кювете под давлением  $10^{-3}$  мм Hg, после кальцинирования

*a* - комнатная температура, *b* - температура 300°C, *c* - температура 600°C. Препарат в виде тонкой плёнки

Фиг. 4. Ик-спектры H-монтмориллонита после сорбции паров пиридина

*a* - на препарате выгреваемом с отсасыванием при температуре 150°C, *b* - на препарате кальцинированном при температуре 600°C. Избыток пиридина удалялся при температуре 100°C в течение 1 часа. Препарат в виде тонкой плёнки