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Note

An Infrared Cell for Kinetic Studies of Liquid Samples

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The construction of a thermostated liquid infrared cell for the temperature range from —10°C to 90°C is described. The cell is designed specifically for the Perkin-Elmer 21 series of double beam infrared spectrophotometers (Perkin-Elmer 21, 221, 421 and 521), and can be conveniently used for kinetic studies.

Hitherto a number of infrared cells have been described[1-3] which are suitable for measurements of precisely thermostated liquid samples. The basic characteristics required for such a cell are summarized in a recent paper by Vinogradov and Crawford[1]. Beside construction requirements, such as simple handling, variable sample thickness and prevention of evaporation, the greatest difficulties in operating the cell lie in temperature control and fogging of the windows below 10°C.

In this paper we wish to describe a thermostated cell designed for use with the Perkin-Elmer 21 series of double beam spectrophotometers (Perkin--Elmer 21, 221, 421 and 521). The cell (Fig. 1) can be operated in the tempe-

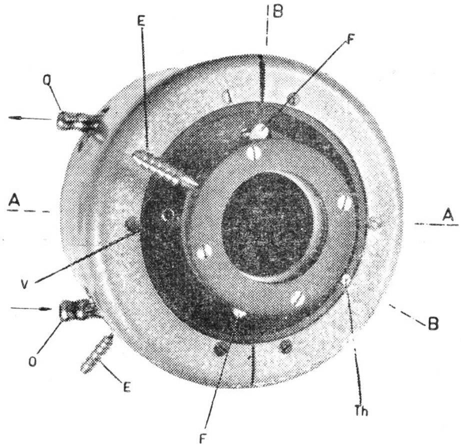

Fig. 1

rature range from —10°C to 90°C and is therefore particularly useful for studies of organic reaction mechanisms. Using this cell rate constants and activation energies can be determined. If the reaction mixture is circulated through the cell, the progress of chemical reaction can be followed.

In Fig. 2 two cross sections of the cell are presented. The body of the cell consists of two stainless steel parts (B_1 and B_2) connected with a rubber gasket seal. Through the so formed jacket J the thermostated liquid circulates, entering J through the opening O at the lower part of the cell. The outlet is placed diagonally from the inlet. In the central part of the cell there is a bore for the light beam. The conical shape of the bore corresponds to the geometry of the beam, simplifying also the construction of the essential parts of the cell by making them smaller and reducing the transmission of heat between the instrument and the cell.

The liquid sample is introduced into the space S by means of a hypodermic syringe through the opening F. The volume of the cell can be varied by using different spacers L, conveniently made of amalgamated lead foil. The spacer is tightly pressed to the cell body B_1 by a polished ring R with a plug which prevents the ring from rotating and crumpling the spacer. Ring R and windows W_1 and W_2 are fixed by nuts N_1 and N_2. Nut N_3 closes the back side of the cell.

The sliding adapter SA with fixed metal rails and mobile Textolite sledges permits attachment of the cell to the spectrophotometer. This adapter also makes

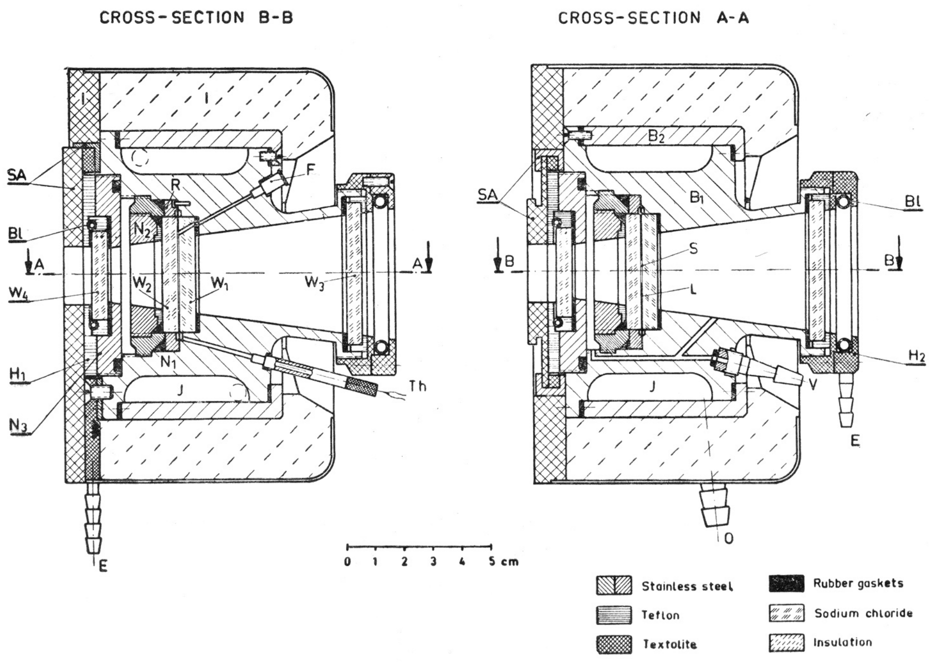

Fig. 2

possible easy exchange of the spacer and windows (W_1 and W_2). At the same time the Textolite sledges serve as an insulator. The whole cell is enclosed with the insulator I upholstered by sheet aluminum.

Fogging of windows W_1 and W_2 was observed below 15°C. This was avoided by installing windows W_3 and W_4, and by evacuating the internal part of the cell through V. External windows W_3 and W_4 are fixed by holders H_1 and H_2 (which at the same time serve as bearings for blowers Bl — see below). O-ring gaskets on nuts N_1, N_2 and N_3, and flat gaskets on windows W_1, W_3 and W_4 made it possible to evacuate the cell down to 10^{-4}mm. It should be noted that the gasket on window W_1 is made of chemically resistent rubber since it contacts the liquid sample. Fogging of external windows is successfully eliminated down to temperature —10°C by purging warm dry nitrogen through blowers Bl. Nitrogen is introduced through ducts E.

The temperature in the cell was measured by a copper-constantan thermocouple *Th* using the compensation method with the reference couple in ice water. The couple wires run through a thin metal duct and holder so that their joint touches the lead spacer. The relative positions of the described connections are presented on Fig. 1.

As a constant temperature reservoir for temperatures between 20°C and 90°C a Colora ultrathermostat was used. The temperature of the circulating medium was kept constant within ±0.01°C. For temperatures below room temperature a Lauda ultrakryostat MK-70D with ethanol was used. The maximum variation of the temperature was ±0.1°C. The actual temperature of the thermostated sample in the infrared beam was measured by a thermocouple made of thin copper and constantan wires introduced into *S* through the opening *F*. The sample temperature was always higher than the one measured by thermocouple *Th*. This difference decreased from 0.6°C at room temperature to 0.3°C at 90°C and 0.4°C at —10°C. The higher temperature of the sample is probably due to the infrared radiation.

The cell reaches the temperature equilibrium in about 30 minutes after connecting it to the thermostat, while the temperature of the sample is established in 2—3 minutes after injection. The maximum variation in the temperature of the cell observed during scanning (6 hous or more) was ±0.025°C when working above room temperature and ±0.075°C below room temperature.

The operating temperature range of the cell can be extended by using a higher boiling medium in the thermostat. On the other hand, lowering the temperature below —10°C is rather difficult because of more intense fogging of external windows. It might be possible to prevent this by better insulation of windows W_3 and W_4 and more efficient flushing with nitrogen so that temperatures down to about —20°C could be used.

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REFERENCES

1. S. N. Vinogradov and R. J. Crawford, *Spectrochim. Acta* **18** (1962) 429.
2. J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.* **73** (1951) 1815.
3. M. S. Smith and P. A. D. DeMaine, *Can. J. Chem.* **41** (1963) 812.

IZVOD

Ćelija za kinetičke studije tekućih uzoraka metodom infracrvene spektroskopije

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Opisana je konstrukcija termostatirane ćelije za kinetička ispitivanja tekućih uzoraka metodom infracrvene spektroskopije. Ćelija se može koristiti unutar temperaturnoga područja od —10°C do 90°C i konstruirana je specijalno za spektrofotometre Perkin-Elmerove serije 21 (21, 221, 421 i 521). Temperatura ćelije stabilizira se za najviše pola sata nakon početka termostatiranja i varira maksimalno za ±0.025°C iznad sobne temperature i ±0.075°C ispod sobne temperature.

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