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Sample Handling for Qualitative Infrared Microspectroscopy

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TO IDENTIFY minute amounts of materials, a need arose for simple techniques for handling liquids and solutions in infrared microspectroscopy. While several ingenious methods have been described (1), they usually require special equipment. For example, in one very elegant technique the samples are contained in capillary tubes made from silver chloride (2). These specially prepared capillaries were about 0.075 mm. in diameter and held only about 0.005 μ l., although a somewhat larger volume was needed for manipulation of the sample. Another type of microcell in which the sample fills an etched-out space between polished-salt flats has been described (4, 5). These latter cells used minimum sample volumes ranging between about 6 μ l. for a cell of 0.1-mm. thickness and about 0.2 μ l. for a 0.01-mm. cell.

APPARATUS AND PROCEDURE

All measurements were made using a Perkin-Elmer Model 112 Spectrometer, equipped with the Model 85 microscope attachment (3). The entire optical path of the instrument was continuously flushed with a stream of air dried over activated alumina.

A. Measurements on Self-Supporting Films, Suitable for Nonvolatile Liquids. A relatively nonvolatile liquid is measured as a thin film contained in a small hole drilled or cut in a thin sheet of suitable material. For example, a hole approximately 0.5 mm. in diameter was carefully drilled with a diamond-tipped pencil in a glass coverslip of 0.09-mm. thickness. After thorough cleaning of the glass surface, 4 μ l. of a 0.4% solution of *n*-decyl alcohol in carbon tetrachloride was delivered over this hole from a micropipet. The amount of solute actually delivered was 13 γ (0.016 μ l.). As the solvent evaporated, a thin film of the pure alcohol collected in the hole and was used to obtain a satisfactory spectrum. In like manner, a satisfactory spectrum was obtained from 20 γ (0.018 μ l.) of benzyl

benzoate. Support for this film was provided by a Teflon sheet of 0.03-mm. thickness with a hole 0.5 mm. in diameter. The end of a thin glass capillary was a convenient tool for cutting symmetrical holes in the thin plastic sheet.

The effective film thickness of both samples was estimated to be 0.04 mm. by comparing their spectra with those obtained by conventional means in a 0.03-mm. cell. The films remained intact for at least 1 hour. Some liquids form satisfactory films more readily on one supporting material than on another. It is evident that such factors as the surface tension of the liquid and the wettability of the solid influence the formation of these films. Delivery of a liquid to the hole via a volatile solvent was preferred over direct delivery of the liquid from a micropipet or rod, for in the latter case the film thickness was apt to be too great.

B. Measurements on Liquids Contained in Potassium Bromide "Sandwich" Cells, Suitable for Volatile Liquids and for Solutions. The sample cell consisted of a loop of thin platinum wire sandwiched between potassium bromide disks, and was very easily constructed with the aid of a press and a die used for making potassium bromide pellets (6). The cells were made in the following manner: Sufficient potassium bromide powder for a thin disk was packed firmly with hand pressure into the pellet die. Two loops of wire, approximately 1 and 4 mm. in diameter, were formed from platinum wire 0.010 inch in diameter, placed on top of the packed powder and covered with a thin potassium bromide pellet. All this was pressed together (25,000-pound total load) to form a unit, which was then separated at the interface with a razor blade and used as a demountable cell, as indicated in Figure 1. The wire was thus partially embedded in the bottom disk, A, and caused indentations in the top disk, B. The larger wire loop was used around the inner sample loop as a guide for refitting the cell together and to keep the stopcock grease, which was used to seal the cell, away from the sample loop. It was necessary to use insoluble stopcock greases whenever volatile solvents or solutes were placed in the cell. An esterification resin (7) and a glycerol-bentonite clay mixture were both satisfactory greases for this purpose. The cells were filled by touching the sample loop with the tip of a

glass capillary containing the sample, and then covering it immediately with the top pellet.

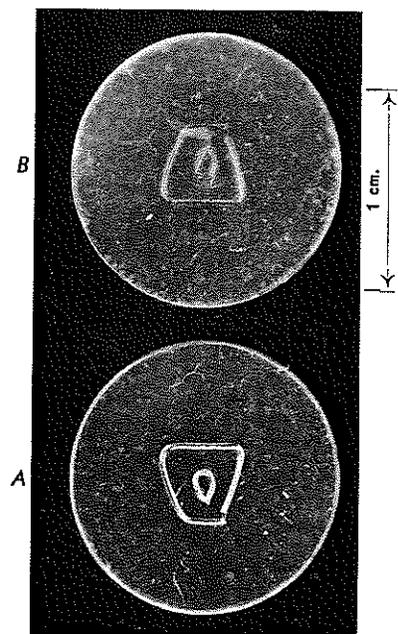


Figure 1. Potassium bromide infrared microcell

Because of its relatively high boiling point and good transparency in the 2- to 13-micron region, bromoform (Eastman Kodak, spectrograde) was found to be the most convenient solvent for use in these cells. (On exposure to room light this diphenylamine-stabilized bromoform turned yellow. However, this color change did not cause a detectable change in its infrared spectrum.) A typical cell used only 0.075 μ l. of bromoform to fill it, and gave a solvent thickness of approximately 0.08 ± 0.01 mm. To check this method, satisfactory spectra were obtained for solutions of ethyl propionate, isobutyraldehyde, and azobenzene in bromoform. Each filling of the cell required about 5 to 20 γ of solute, depending upon the concentration of the solution. Carbon tetrachloride can also be used as a solvent (demonstrated by obtaining a satisfactory spectrum of benzoic acid in this medium), but, because of its greater volatility, carbon

tetrachloride is more difficult to handle in such minute volumes. Best results were obtained by placing an excess of a precooled carbon tetrachloride solution in the area of the sample loop, thus using 0.1 to 0.2 μ l. of solution.

The main advantage of the above techniques is their relative simplicity. An additional advantage lies in the ease of locating and focusing on the samples, which had a larger cross section than that of the infrared beam at its focus point. However, because the thickness of the samples is not accurately reproducible, these methods are suitable

only for qualitative measurements. The sample volumes required are small; approximately 0.02 μ l. of liquid by Method A and about 0.08 μ l. of solution by Method B. The relative ease of handling tends to compensate for the larger volumes that are required here as compared to the silver chloride capillary method.

ACKNOWLEDGMENT

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