Purification of Hydrocarbons for Use as Solvents in Far Ultraviolet Spectroscopy

by W. J. Potts Jr.[1]

For the farther ultraviolet region of solution spectroscopy (below 2200A.), there are at present three classes of practical solvents: water, with transmission to about 1800A. in thin cells[2], is not generally applicable for organic molecules because of insolubility; certain fluorocarbons, in which most organic molecules have very low solubility, have shown transmission to as far as 1565A. in a thin cell, after careful and repeated purification[3]; and certain paraffin hydrocarbons, which can be purified without great difficulty, and which dissolve most organic compounds to a sufficient extent for use in this spectral region, where molar extinction coefficients are generally high. Other solvents all show high extinction coefficients in this region[2,4,5]. The purpose of this paper is to point out the remarkable transmission in thick cells of isopentane, one such hydrocarbon studied, and also to mention its value as one of the components of a rigid glass at $77^{\circ}K$.

Four hydrocarbons, n-heptane, isopentane, 3-methylpentane and methylcyclohexane, were examined for their transmission at various stages of purification. The n-heptane was obtained from Westvaco Chemical Co., the other three are Phillips Petroleum Co. "pure" grade hydrocarbons. On the curves shown, the data above 2100A. was obtained with a Beckman model DU quartz spectrophotometer, using 1 cm. silica cells, with water, redistilled from $KMnO_4$ as a blank[6]. Below 2100A., the data was obtained with a Cario-Schmitt-Ott Vacuum fluorite spectrograph[7], using a liquid path length of 1 cm., with a path of 0.13 mm. as a blank; the resulting plates were traced on a Leeds and Northrup recording densitometer, and readings converted to percent transmission[8]. The error is within 5 transmission percent throughout the curves. The purification procedure for each hydrocarbon was the same.

Curve #1 in each figure shows the transmission of the untreated hydrocarbon.

Curve #2 gives the transmission after vigorously stirring with C.P. H_2SO_4 for four hours, then washing twice with distilled water, and drying over anhydrous $CaSO_4$. Longer or repeated treatment with H_2SO_4 was found to have no further effect.

Curve #3 gives the transmission after passing the hydrocarbon through a silica gel column 18" long, 1" in diameter, employing Davidson #200 mesh silica gel. The column is water-jacketed to absorb the heat of surface adsorption and prevent boiling of the more volatile hydrocarbons. Treatment with silica gel was found to have lessened effect unless the gel and the hydrocarbon were absolutely dry. Hence it is necessary to activate the silica gel in its own glass column by heating at 350° C. for 12 hours in a furnace, and to cool it in a moisture-free atmosphere. The hydrocarbon is then refluxed with sodium wire for one hour, to remove the last traces of water, and then distilled from fresh sodium wire, through a Podbielniak Column of 40 theoretical plates, directly into the silica gel column; that is, the silica gel column is attached to the head of the fractionating column with ground glass joints, the only vent to the air being a $CaCl_2$ tube. If these precautions are not taken, the effectiveness of the silica gel treatment, particularly in the case of isopentane, is greatly reduced.

Curve #4 shows transmission after a repetition of the silica gel treatment, omitting the one hour reflux with sodium prior to distillation. In the case of isopentane, only the first fraction coming through the silica gel the second time is used, for best results.

Conclusions.

n-heptane transmits almost 100% to 2100A. in a 1 cm cell; the useful transmission limit in a 0.13 mm. cell is 1720A. These results can be obtained simply by H_2SO_4 treatment alone, and the purity is maintained with storage. Thus, n-heptane is recommended for all studies at room temperature above 2100A., and in short path lengths below 2100A.

Isopentane shows useful transmission to 1790A. in a 1 cm. cell, to 1720A. in a 0.13 mm. cell. It keeps its purity for a few months if kept in a tightly stoppered bottle; upon longer standing, it again begins to show the same absorption region at 2050A. (see curve #3, isopentane). Hence for longer path length studies below 2100A., isopentane is recommended.

<u>3-methylpentane</u> has slightly better transmission properties than n-heptane, with nearly 100% transmission to about 2050A. It has the additional advantage that it forms a rigid glass by itself on cooling to 77°K. Its keeping properties are poor, however[9].

Methylcyclohexane used alone does not have such good transmission properties; however, it retains its purity with storage. A mixture of 1 part methylcyclohexane and 6 parts isopentane has useful transmission to 1850A. in a 1 cm. cell; at 77°K., the mixture forms a good rigid glass[10], and the "thermal tail" toward the red disappears, giving useful transmission to 1700A. in a cell 1.2 cm. long (to be discussed in a forthcoming paper).

<u>Fluorocarbons.</u> An attempt by the author to find a mixture of fluorocarbons which would form a good rigid glass at low temperatures met with failure, even though a variety of fluorocarbons and perfluoroethers was used.

References

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6. Technique described by Maclean, Jencks and Acree, J. Research Natl. Bur. Stds., 34, 271, (1945). The data in their paper on n-heptane and methylcyclohexane above 2100A. is in substantial agreement with the present paper.
7. Kindly loaned to us by the Physics Department of The University of Michigan.
8. Technique described by Jacobs and Platt, J. Chem. Phys., 16, 1137, (1948).
9. W. R. Brattain, Shell Development Co., private communication.
10. In an unpublished work M. Kasha, Florida State University, noted that various mixtures of isopentane and methylcyclohexane form stable glasses at 77°K.

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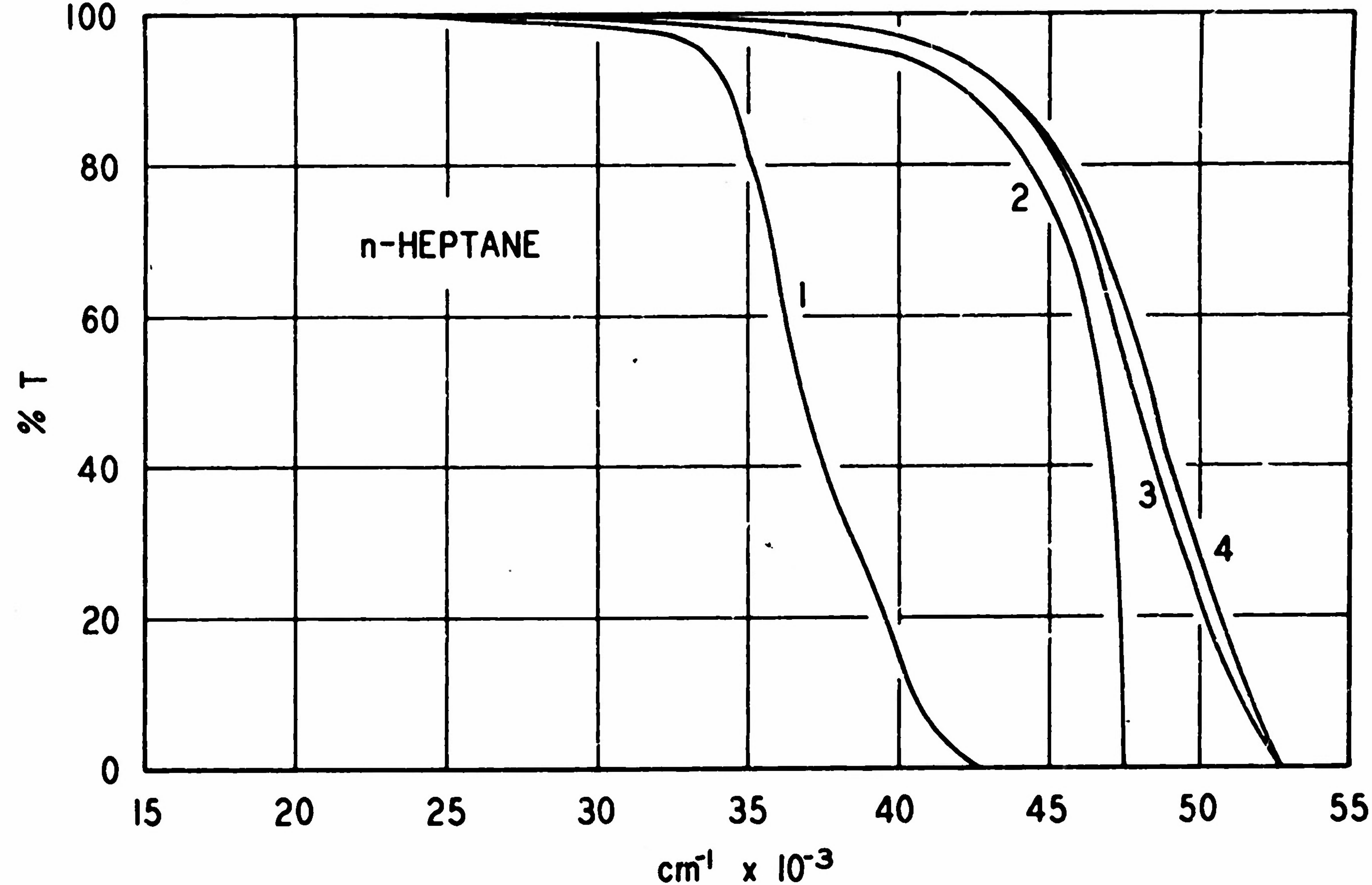

100
80
60
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20
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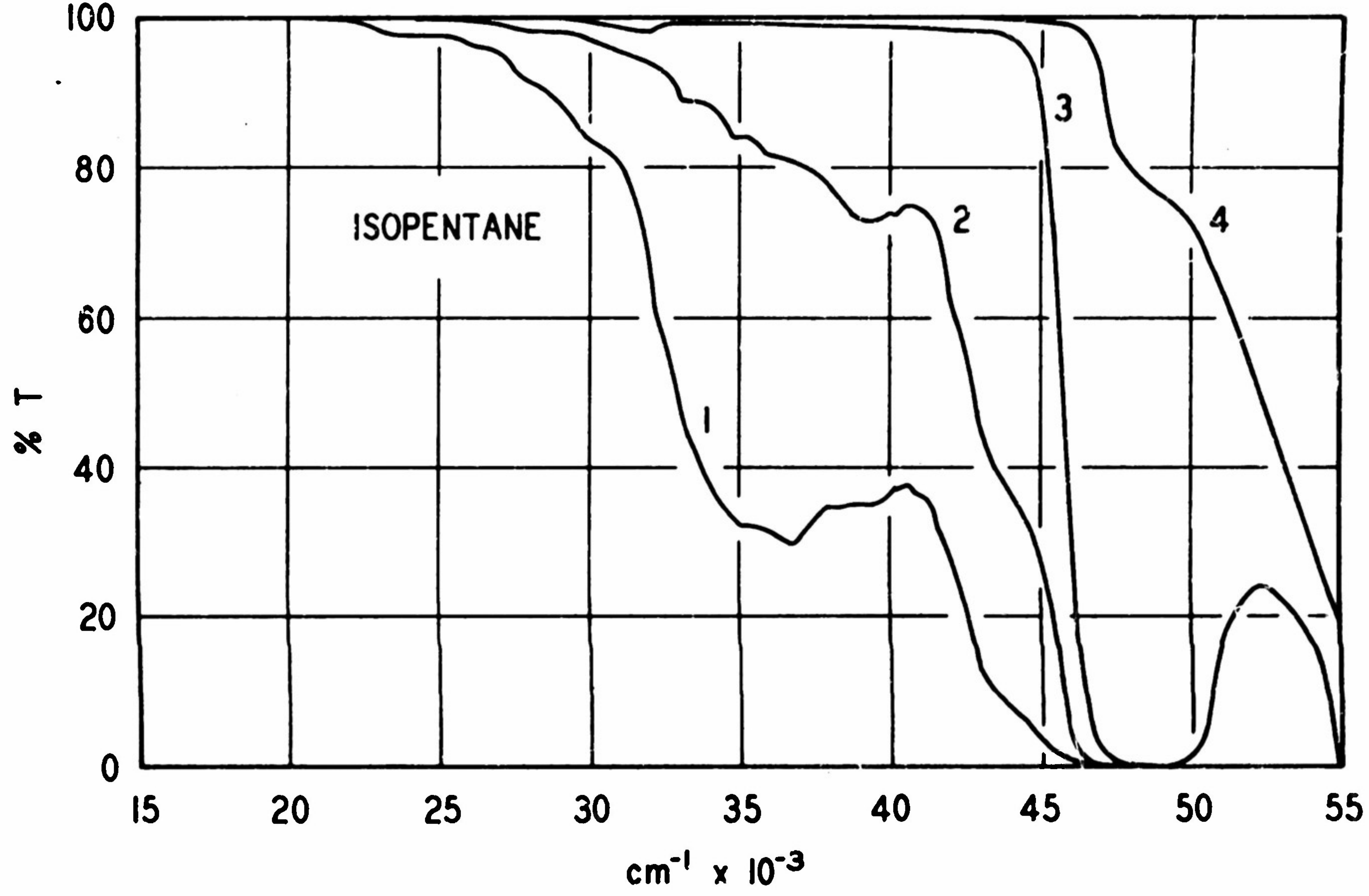
% T
n-HEPTANE
1
2
3
4
15
20
25
30
35
40
45
50
55
cm-1 x 10-3

AP-129-2


100
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ISOPENTANE
1
2
3
4
15
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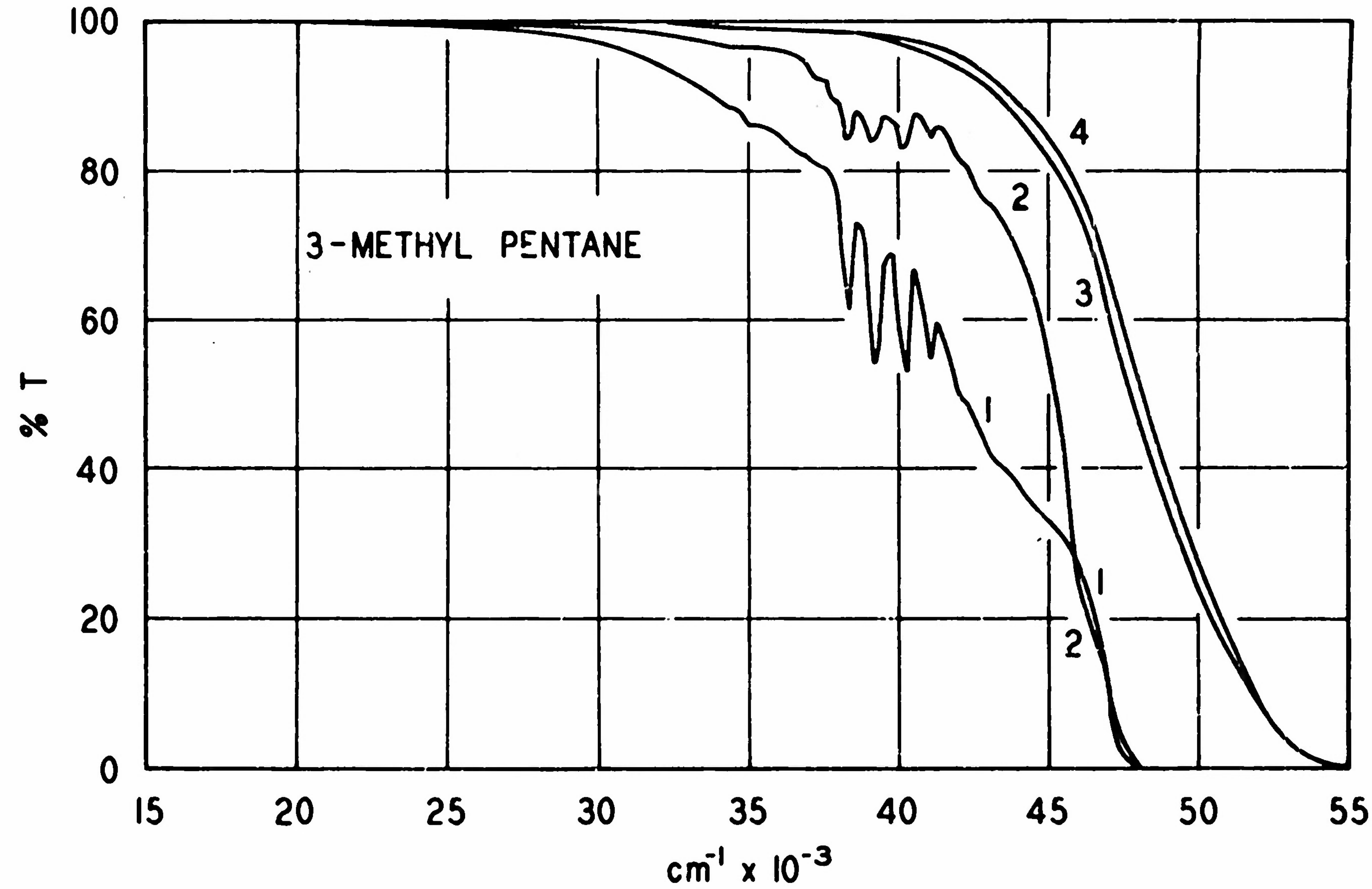
25
30
35
40
45
50
55
cm^{-1} x 10^{-3}

AP-129-1


100
80
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20
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% T
3-METHYL PENTANE
1
2
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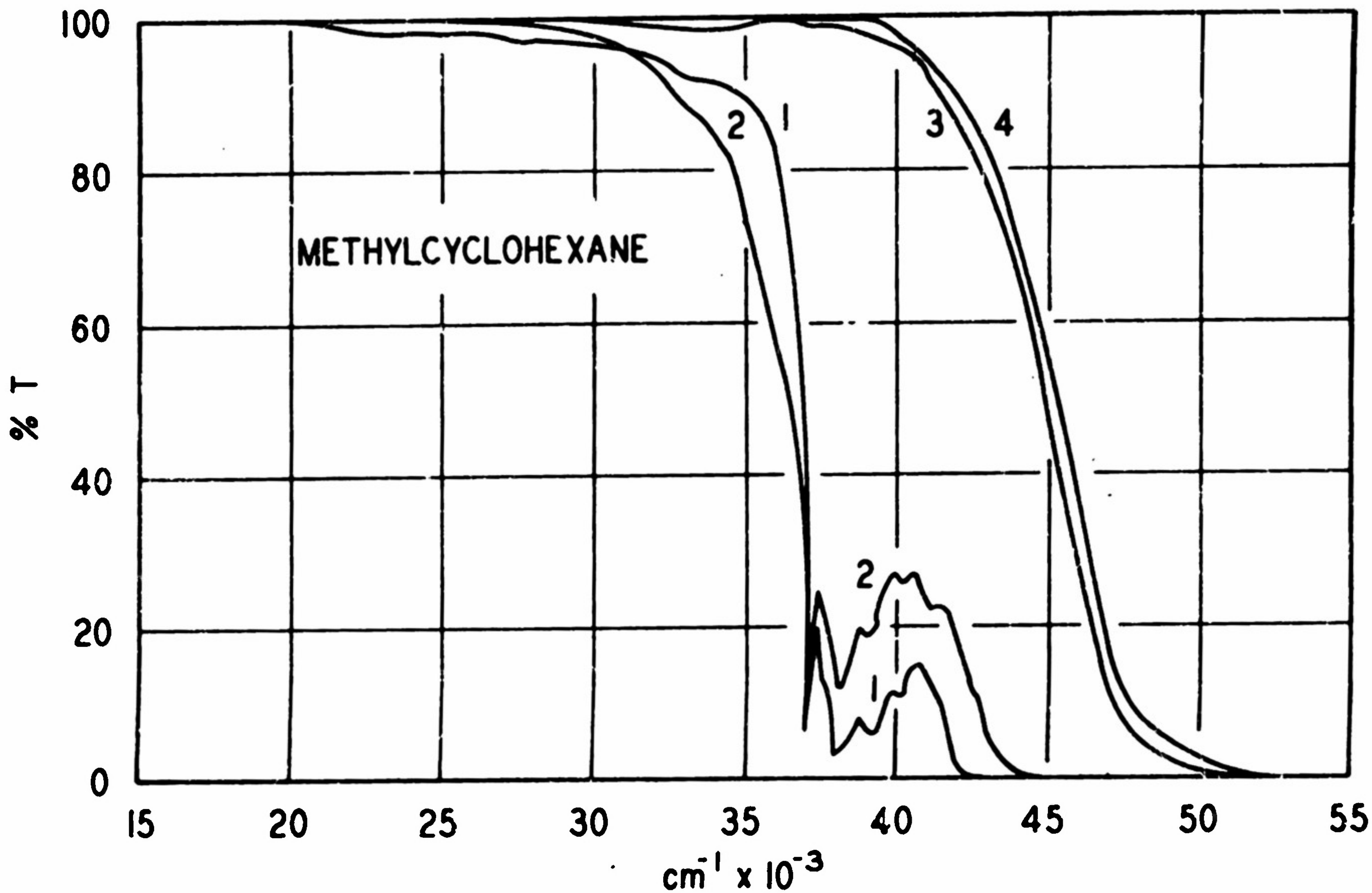
4
15
20
25
30
35
40
45
50
55
cm⁻¹ x 10⁻³

AP-129-3


METHYLCYCLOHEXANE
% T
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0
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40
45
50
55
$cm^{-1} \times 10^{-3}$
1
2
3
4

AP - 129 - 4