INVESTIGATION OF INTERFEROMETRY FOR THE ANALYSIS OF ENCLOSED HABITABLE ATMOSPHERES

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and

J. MORRIS WEINBERG, Ph.D.

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FOREWORD

This study was initiated by the Biomedical Laboratory of the Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The research was conducted by Block Engineering Incorporated, Cambridge, Massachusetts, under contract AF 33(615)-3374. Mr. Richard N. Briskman was the principal investigator, J. Morris Weinberg, Ph.D. was the program manager and Miss Marjorie Korman assisted in the data reduction for Block Engineering Incorporated. Mr. William H. Toliver, Sr., of the Biotechnology Branch, Life Support Division, was the contract monitor for the Aerospace Medical Research Laboratories. The work was performed in support of project 6373, "Equipment for Life Support in Aerospace", and task 637302, "Respiratory Support Equipment". The research was performed between December, 1965 and December, 1966.

This technical report has been reviewed and is approved.

WAYNE H. McCANDLESS
Technical Director
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ABSTRACT

To develop a small and highly sensitive optical spectrometer for providing repeatable qualitative and quantitative analysis of contaminant gases in enclosed habitable atmospheres, a feasibility study and measurements program was conducted. An infrared interferometer spectrometer was employed in conjunction with a gas absorption cell for trace gas analysis. During the program, spectra were taken of 43 compounds, 10 binary, 10 trinary, 5 five-order, and 1 fifteen-order mixture. Typical minimum detectable concentrations range from 1 to 40 mg/l. The results of this program have defined a system that will satisfy the criteria for a prototype flight instrument.

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SECTION I

INTRODUCTION

This report describes the results of a research and empirical investigation program to determine the applicability of interference spectroscopy to qualitative and quantitative analysis of trace contaminants in enclosed, habitable atmospheres. An examination of the spectral data strongly suggests several instrument refinements and modifications which would ultimately define a flight instrument having the following highly desirable charactersitics: (1) simple and direct, (2) relatively small in mass, volume and power requirements, (3) sensitive to 1-10 ppm or ppb concentrations, (4) operate in continuous automatic manner, and (5) relatively insensitive to vibration.

QUALITATIVE AND QUANTITATIVE ANALYSIS BY ABSORPTION OF INFRARED RADIATION

If infrared radiation having a continuous frequency distribution is passed through a gas, some radiation frequencies are absorbed in various amounts and some are transmitted unattenuated. All of the compounds analyzed herein have one or more distinct absorption bands in the 3 to 16μ spectral region. A gas mixture containing two or more compounds will have an absorption spectrum having all of the absorption bands of its constituents. In a many mixture spectra, each compound will have at least one band that does not overlap any others. In these cases, a unique qualitative analysis of the mixture by infrared absorption spectroscopy is possible.

If an absorption band is due to the presence of one compound, often:

$$\log_e \frac{P_o}{P} = k\ell C$$

where P_o is the amount of radiation of one wavelength incident on the sample, P is the amount of radiation of the same wavelength transmitted by the sample, k is a constant for a given absorbant and wavelength, ℓ is the path length in the sample, and C is the concentration of the sample. This relationship is known as Beer's Law. Hence, quantitative analysis is possible since K and ℓ are known beforehand and $\ell n \frac{P_o}{P}$ is a measureable quantity. Quantitative analysis is also possible in certain cases when a band is due to two or more compounds. This point will be discussed in a later section of this report.

The chemical nature and concentration of spacecraft atmospheres have been studied by Toliver and Morris (1966) and by Saunders (1963). The sources of these contaminants are human metabolic processes, outgassing of wire insulation, outgassing of refrigeration pumps, and association and disassociation products of the above.

Spacecraft contaminants of interest are organics with vapor pressures greater than .01 mm Hg. at 25°C and with molecular weights less than 200, and also some inorganics such as NH_3, H_2S, and oxides of N,S and C. The most useful region for these compounds is in the 3 to 16μ region.

During this research, absorption spectra were taken for 43 compounds, 10 binary, 10 trinary, five 5-order and one 15-order mixture.* These spectra were taken with a single-pass gas cell, 1 meter in length by use of an interferometer spectrometer. Minimum detectable concentrations for the single compounds range from 1 to 60 milligrams per litre. The spectra of mixtures were taken to investigate the problems of qualitative analysis of mixtures by infrared absorption spectroscopy. These problems are: (1) band overlapping, (2) band center shifts of one compound due to the presence of another, and (3) band broadening of one compound due to the presence of another. A discussion of band shifts and broadening and the spectral results will be presented in detail in a later section of this report.

THE INSTRUMENT

The interferometer spectrometer differs from the more well-known, dispersive-type, prism-and-grating spectrometers in the manner the incident radiation is separated into component wavelengths.

Dispersive spectrometers contain three basic elements: a slit, a dispersing device (prism or diffraction grating) which separates radiation according to wavelength, and a detector (either photographic, electronic or physiological). In a dispersive spectrometer designed to draw a spectral graph, radiation from only a very narrow frequency interval reaches the detector at any one time. The spectral interval

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*See Appendixes I and II.

reaching the detector is slowly changed by varying a geometrical factor in the system, e.g., a mirror angle.

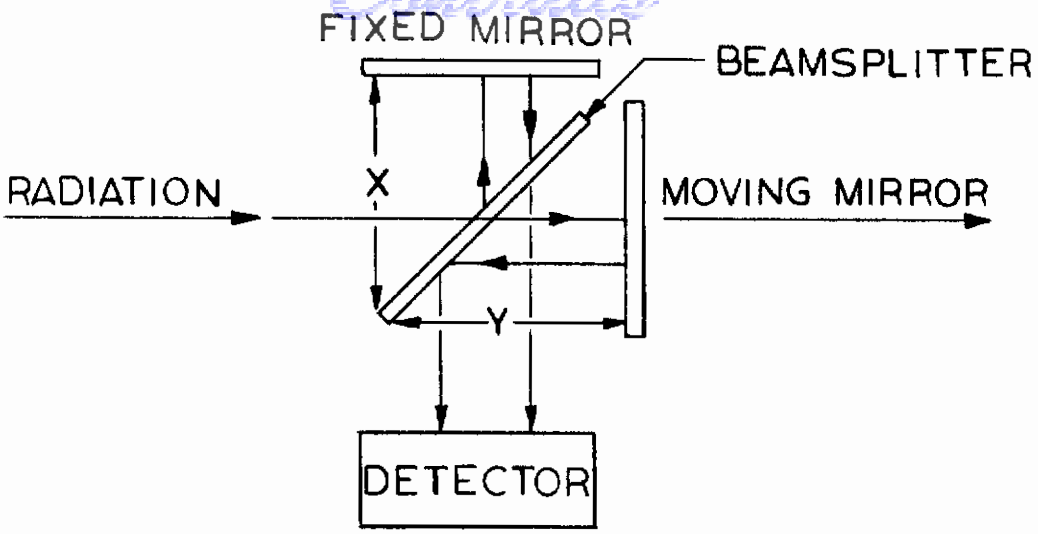
An interferometer spectrometer, however, uses the principle of constructive and destructive interference of light waves. The interferometer used in this study utilizes the Michelson geometry of which a schematic drawing is shown in figure 1. Radiation of all frequencies enters the interferometer and is broken up into two beams by a semi-reflective mirror or beam splitter. One beam is reflected from a fixed mirror, and the other beam is reflected from a moving mirror which is driven at constant velocity. The two beams then interfere and produce a net intensity at the detector. The intensity reaching the detector at a particular frequency is a function of the difference of the two path lengths, x-y. The net intensity at all frequencies reaching the detector vs. x-y or interferogram, is essentially a Fourier Transform of the desired spectrum, i.e., intensity vs. frequency. The infrared spectrum is converted to an analogous audio spectrum by this process, i.e., all of the infrared frequencies are divided by a constant factor. The interferogram may be processed by analog or digital methods, or a combination of the two methods, to yield a spectrum.

There are many advantages of the interferometer spectrometer over the dispersive type spectrometer.

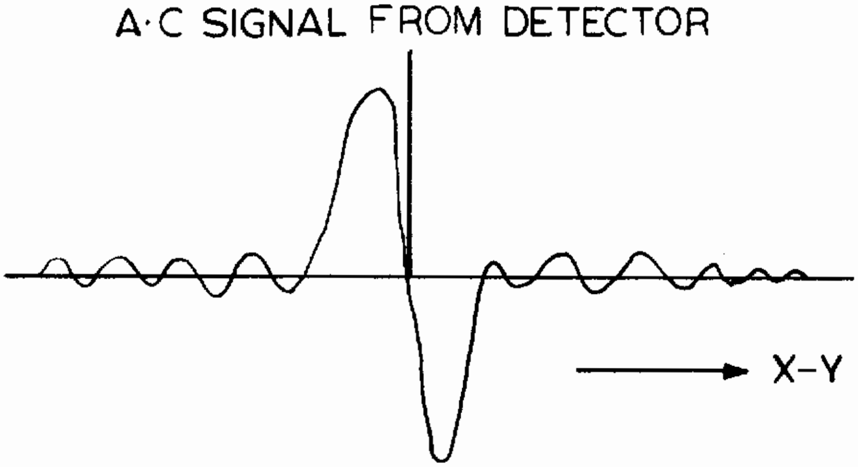
1. The interferometer spectrometer measures intensity vs. frequency at all frequencies simultaneously. This multiplexing process yields an increase of $\sqrt{N}$, (N being the number of resolution elements), of S/N, over comparable dispersion instruments. This can be shown from strictly information theoretical considerations and is discussed in Appendix III.

2. The elimination of entrance slits and the instrument's ability to accept large cones of radiation without resolution degradation makes the interferometer inherently superior when viewing weak sources. This high sensitivity allows analysis to be conducted very rapidly.

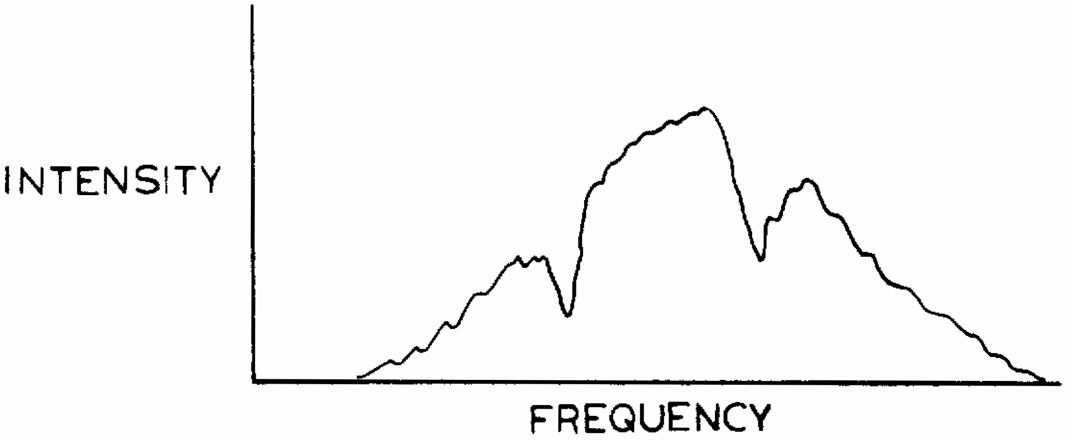
3. As will be shown later, the infrared spectrum is converted to an analogous spectrum by the interferometer, i.e., all of the infrared light frequencies are divided by a constant factor. Hence, any spectral band can be isolated



MICHELSON INTERFEROMETER SPECTROMETER



INTERFEROGRAM



SPECTRUM

Figure 1 Geometry of the Michelson Interferometer Spectrometer with Typical Interferogram and Spectrum by electrical filters and processed in a variety of ways using efficient, direct and precise electronic means. Spectral band isolation with a dispersive instrument would be inherently more fragile and expensive, since precise mechanical alignment of the optical components would have to be used.

4. Dispersive instruments are inherently larger and heavier than interferometers because large optical lengths are required for adequate spatial separation of wavelengths and extreme mechanical stability of the entire system is required.

CONTRACTUAL RESULTS

The results of this program have defined a system with the following characteristics, (as described in Air Force Contract AF 33(615)-3374, Item 5):

(a) Is easily sensitive in the ppm and ppb range of concentrations.

The system used in the present ivestigation is easily sensitive in the ppm range. Typical minimum detectable concentrations for the compounds investigated range from 1 to 40 ppm. A table of minimum detectable concentrations is found on page 27. A system capable of operation in the ppb range is described in Section IV of this report.

(b) Is simple and direct.

(c) Is continuous and automatic.

An interferometer spectrometer trace gas analyzer transmits infrared radiation through the test atmosphere. The resultant absorption spectrum is converted to an analogous audio spectrum by the interferometer and is then processed by digital and analog techniques. The resultant data have sufficient information for a qualitative and quantitative analysis of the atmosphere. A typical instrument records approximately one spectrum per second. In a final system, successive scans would have to be coherently added for signal-to-noise ratio enhancement. A complete analysis with data reduction can be done in 2 to 5 minutes.

(d) Is relatively small in mass, volume and power requirements

Interferometer spectrometers are inherently smaller in mass and volume than dispersive spectrometers as mentioned on page 5. A prototype for a flight instrument has been proposed which has the following characteristics: power consumption of 100 watts, weight of 84 lbs., dimensions of 32" x 32" x 11".

Reduction in weight and volume is feasible for a flight instrument.

(e) Does not compound the trace contaminant problem by its own operation.

A spectrometer performs only a passive measurement on the atmosphere. Since only electronic and optical components are used, no gas efflux is produced.

SECTION II

THE EXPERIMENT

THE EXPERIMENT

A complete schematic drawing of the experimental setup is shown in figure 2.

GAS HANDLING SYSTEM AND PROCEDURE

The gas cell used in the present experimental setup is 1 meter in length, and 1½ inches in diameter. It is copper with aluminum end fittings and has KRS-5 windows on each end.

The cell is first evacuated by the vacuum pump and then filled with nitrogen to approximately atmospheric pressure. The process is then repeated three of four times to initially purge the cell. After the final evacuation of the purging process, the sample gas or gases are added to the cell. The concentration is measured by the Hg filled manometer. The perfect gas law states that:

$$PV = NRT,$$

where P is the partial pressure of the gas contaminant, V is the volume, N is the number of moles of the contaminant, and T is the temperature. Therefore,

$$P = \frac{WRT}{MV},$$

where W is the weight of the contaminant, and M is the molecular weight of the contaminant. Assuming T = 298°K and using:

$R = 62.37 \frac{(\text{mm.Hg.})(\text{L})}{(^\circ\text{K})\ (\text{g mol})}$, we find that:

$$P = \frac{18.6\ C}{M},$$

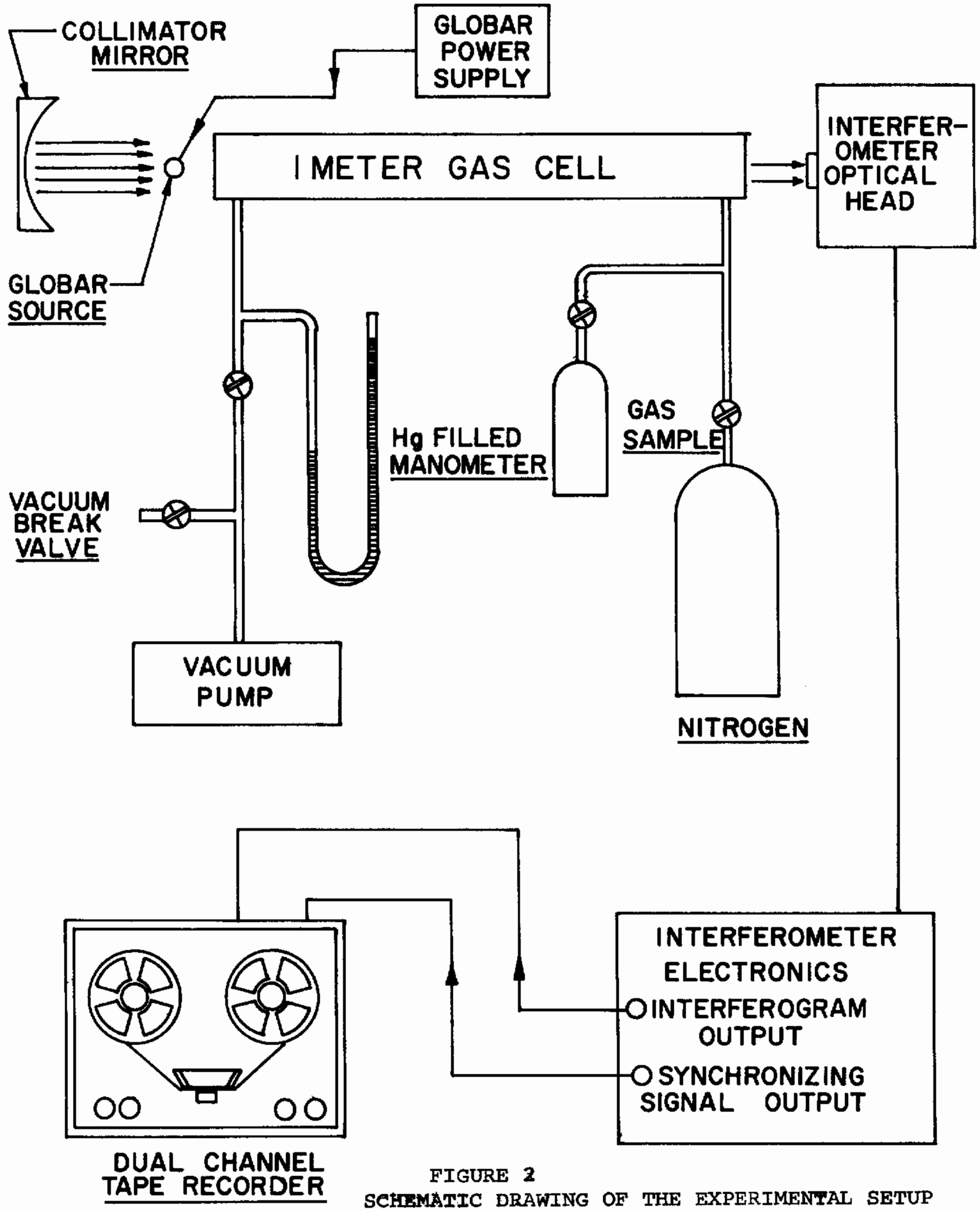


FIGURE 2
SCHEMATIC DRAWING OF THE EXPERIMENTAL SETUP

where $C = \frac{W}{V}$ is the concentration in mg/l., M is the molecular weight in gm./gm. mole., and P is the pressure in mm. Hg. The gas cell is then backfilled with nitrogen to atmospheric pressure and then a spectrum is recorded. The gas cell is then partially evacuated by the vacuum pump, backfilled with nitrogen, and another spectrum is taken. Typically, for a single compound, spectra are taken for concentration of 100, 60, 40, 20, 10, 5 and 2½ mg/l, and lower if necessary. These levels were chosen after some initial experimentation which indicated that typical minimum detectabilities were in this concentration range, and adjacent numbers, e.g., 40 and 20 mg/l formed convenient upper and lower bounds for the minimum detectable concentrations. That is, a band was visible at 40 mg/l and absent at 20 mg/l. Also, for each contaminant spectrum, a spectrum with just nitrogen in the gas cell was taken for comparison purposes. The function of the nitrogen in this application is twofold: (1) Backfilling with nitrogen to atmospheric pressure minimized inward diffusion of atmospheric gases into the cell, and (2) since all dilutions are relative to a 76 cm. pressure differential in the manometer, the error in reading the manometer, typically ± 1 mm, represents a smaller percentage error than if just the contaminant gas alone were present. Nitrogen was chosen for this application, because it is spectroscopically inert in the infrared and readily available.

The compounds used were either in the gas phase, contained in gas cylinders supplied by Matheson Co., or in the liquid phase. For the liquids, in most cases their vapor pressures were sufficiently high to provide a high enough initial concentration. The dissolved air in the liquids was first allowed to boil off into the gas cell. The cell was then purged and evacuated and filled with the pure vapor from the contaminant liquids.

THE COMPOUNDS STUDIED

The compounds studied were determined by discussion and written correspondence with the Aerospace Medical Branch of Wright-Patterson Air Force Base. They are:

A. Saturated Hydrocarbons ($C_N H_{2N+2}$)

   1. Methane - CH_4

2. Ethane - C_2H_6
3. Propane - C_3H_8
4. Butane - C_4H_{10}
5. n-Hexane - C_6H_{14}
6. Octane - C_8H_{18}

B. Unsaturated Hydrocarbons, Ethylene Series (C_NH_{2N})

1. Ethylene - C_2H_4
2. Propylene - C_3H_6
3. 1-Butene - C_4H_8

C. Unsaturated Hydrocarbons, Acetylene Series (C_NH_{2N-2})

1. Acetylene - C_2H_2

D. Alcohols ($C_N H_{2N+1} OH$)

1. Methanol - CH_3OH
2. Ethanol - C_2H_5OH
3. Propanol - C_3H_5OH
4. Butanol - C_4H_9OH

E. Aldehydes

1. Butyraldehyde - $CH_3(CH_2)_2CHO$

F. Ketones

1. Acetone - $CH_3CO\ CH_3$
2. 2-Pentanone - $CH_3CO(CH_2)_2CH_3$

G. Acids

1. Acetic - CH_3COOH
2. Formic - $H\ COOH$

H. Esters

1. Methyl Acetate - $CH_3CO_2CH_3$
2. Ethyl Formate - $HCO_2CH_2CH_3$
3. Butyl Acetate - $CH_3CO_2(CH_2)_3CH_3$

I. Inorganics

1. Carbon Monoxide - CO
2. Ammonia - NH_3
3. Nitrous Oxide - N_2O
4. Nitric Oxide - NO
5. Nitrogen Dioxide, Dinitrogen Tetroxide - NO_2, N_2O_4
6. Hydrogen Sulfide - H_2S
7. Sulfur Dioxide - SO_2

J. Ethers

1. Diethyl Ether - $C_2H_5O\ C_2H_5$
2. Dimethyl Ether - $CH_3\ O\ CH_3$

K. Methyl Halides - CH_3 + Halogen

1. Methyl Chloride - CH_3Cl
2. Methyl Bromide - CH_3Br
3. Methyl Fluoride - CH_3F
4. Methyl Iodide - CH_3I

L. Freons

1. Freon-12[1] - CCl_2F_2

M. Miscellaneous Organics

1. Allene - C_3H_4
2. Benzene - C_6H_6
3. Toluene - $C_6H_5CH_3$
4. Methyl Mercaptan - CH_3SH
5. Xylene (m,o,p) - $C_6H_4(CH_3)_2$

OPERATION OF THE INSTRUMENT

The source of infrared radiation is a water-cooled Globar. The Globar is a ceramic element made from silicon carbide or carborundum. The Globar operates at a temperature of approximately 1400°K. The ability of the Globar to operate at relatively high temperatures in air combined with its relatively high emissivity make it one of the most widely used sources for the 3 to 16μ range.

The radiation from the Globar is collimated by a spherical mirror and passed through the gas cell into the interferomter optical head. Collimation is required because large light cones entering the interferometer would degrade resolution. The interferometer optical head converts the infrared electromagnetic spectrum into an analogous audio spectrum, i.e., all of the infrared frequencies are divided by a constant factor. The audio frequencies corresponding to the infrared frequencies of interest lie between 50 and 500 Hz. The audio signal is recorded on one channel of a dual-channel tape recorder. The other channel records a synchronizing signal which indicates the beginning of the mirror sweep cycle in the interferometer.

DATA PROCESSING

The signal from the tape recorder is fed into an audio prefilter that removes audio frequencies not in the spectral

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[1] Registered DuPont trade mark.

range of interest. The signals from the audio prefilter are then fed into a coadder. The function of the coadder is to increase the signal-to-noise ratio of the interferogram by coherently adding successive scans. The increase in signal-to-noise ratio is proportional to the square root of the number of scans coherently added. In our data processing, we coadded 100 scans yielding a signal-to-noise ratio enhancement of 10. A detailed discussion of the interferometer and coadder is contained in Appendix III.

Most of the spectra in this program were reduced by analog methods. In this approach, the signal from the coadder is fed to an audio wave analyzer and chart recorder which draws a graph of the spectrum.

In analog processing, the wave analyzer puts out a large voltage spike corresponding to the zero of frequency. Also, in all of our spectra a dip was found corresponding to the 2375 cm^{-1} band of CO_2. This was due to the air path of approximately 10 cm. in the optical system. Since the spectrum is linear in wave number, these two points on the spectral graph contain enough information for calibration. Through use of a thin film of polystyrene which contains many known bands in our spectral range, this calibration scheme was found to be consistent.

SPECIFICATIONS OF EXPERIMENTAL INTERFEROMETER

Resolution - 30 cm^{-1}

Range - 3 to 16μ

Sensitivity (NESI) - $5 \times 10^{-9} \dfrac{\text{watts}}{\text{cm}^2 \text{ ster cm}^{-1}}$

Sweep Time - 1 sec.

SECTION III

SPECTRAL THEORY AND RESULTS

SPECTRAL THEORY

The simplest molecule with an infrared absorption spectrum is the diatomic molecule. A valid model of the diatomic molecule is one in which the individual atoms, held together by chemical bands, are in vibratory motion along these bands, while the molecule as a whole is rotating. When infrared radiation of the proper frequency impinges on the molecule and is absorbed, the vibrational and/or rotational energies are excited to higher levels. From quantum mechanics, we know that the vibrational and rotational energies are quantized. Since energy is conserved in the absorption process and no other particles are produced, it follows that the allowable absorption frequencies are also quantized.

A quantum mechanical treatment, which assumes that diatomic molecule vibrates like a harmonic oscillator and rotates like a rigid rotor, gives the following expression for the total quantized vibrational, plus rotational energy:

$$E = \underbrace{H\nu_{osc}\,(v + \tfrac{1}{2})}_{\text{VIBRATION}} + \underbrace{\frac{h^2 J(J+1)}{8\pi^2 I}}_{\text{ROTATION}}$$

where h is Planck's constant, ν_{osc} is the classical harmonic oscillator vibration frequency, I is the moment of inertia of the molecule about the rotation axis and v and J are the vibrational and rotational quantum numbers respectively. If a molecule absorbs infrared radiation, it is increased in energy by $\Delta E = hc_{\nu}$, where ν is the wavenumber of the absorbed radiation. If, upon absorbing the infrared radiation, a molecule undergoes a transition from an energy level represented by quantum numbers v" and J" to a new level v' and J' then:

$$\nu = \frac{\nu_{osc}}{c} [v' - v"] + \frac{h}{8\pi^2 cI} [J'(J' + 1) - J"(J" + 1)].$$

At room temperatures it is highly probable that J' and J" are less than 20. When v' - v" is greater than or equal to 1 the vibrational energy term is much larger than the rotational energy term. In these cases, the gross band position is determined by the vibrational energy term, and the fine structure by the rotational energy term.

The fundamental band position occurs when v' - v" = 1. The allowable changes in J for a molecule like HCl are J' - J" = ± 1, denoted as R-Branch transitions and the J' - J" = -1 transitions, denoted as P-Branch transitions. The J' - J" = 0 transitions, which do not usually occur in diatomic molecules, are denoted as Q-branch transitions.

A general picture of a polyatmoic molecule involves complex motion of all the atoms in the molecule. This motion can be resolved into a combination of a small number of fundamental or normal vibration modes of the molecule. It may be shown that a nonlinear molecule with N atoms has 3N-6 fundamental vibration modes. The observed infrared absorption frequencies can be correlated with these fundamental vibration modes. Absorption frequencies corresponding to energy changes in one fundamental vibration mode are denoted by ν_1, ν_2, ... It is also possible to absorb radiation which produces an energy change in more than one mode. For example, we may observe absorption at $\nu_n + \nu_m$ (a sum band), $\nu_n - \nu_m$ (a difference band), or more complicated linear combination such as $\nu_n + \nu_m - \nu_1$. Also overtone bands such as $2\nu_n$ are observable. These absorptions correspond to a change of 2 in the quantum number of one of the fundamental vibration modes.

It may be shown from a quantum mechanical theoretical treatment that a molecule will only absorb radiation strongly if an oscillating dipole moment accompanies the vibration. However, this point may be seen from classical considerations. Assume that infrared radiation is impinging on a linear diatomic molecule, NO, with the electric vector along the interatomic axis. Due to the asymmetry of the molecule, the oxygen atom is more negative than the nitrogen atom. Hence, the oscillating electric vector of the impinging radiation can cause an oscillation in the interatomic distance. However, for a symmetric molecule, such as N_2, each nitrogen atom is electrically neutral; hence, an oscillating electric field along the interatomic axis cannot produce an oscillation in the interatomic distance. The absorption coefficient for a particular allowed dipole transition for a particular molecule is proportional to:

$$[\int \psi_i^* M \psi_j \, dV]^2 \quad ,$$

where ψ_i and ψ_j are the initial and final state wave functions of the molecule, M is the electric dipole operator, and dV is a volume element in configuration space. Generally, a molecule will have widely varying absorption coefficients for different allowed transitions.

In certain cases, isolated parts of a molecule can vibrate relatively independent of the rest of the molecule. For example, an OH group contained in a larger group of atoms acts like a diatomic molecule and has a characteristic stretching frequency. This stretching frequency is an observed infrared absorption frequency in all molecules containing this group.

An attractive force exists between different molecules of a gas, liquid or solid. This is known as the Van der Waal's attraction. The mechanism for this force is electric dipole-dipole interaction. The magnitude varies as r^{-7} where r is the intermolecular spacing and is also a function of the angle between the two dipole vectors, θ. Each value of r and θ will produce a corresponding distortion in each of the molecules and, hence, a corresponding perturbation in the spectra. Since r and θ can take on a continuous range of values, the Van der Waal's interaction produces a broadening of the spectral lines. In some cases, the average over all the r's and θ's of the force is not zero and hence, leads to a shift of the band center relative to its position in the infinite dilution limit. Both of these effects are increasing functions of pressure, since the average value of r^{-7} is an increasing function of pressure.

SPECTRAL RESULTS

These concepts are illustrated in Figures 3 and 4.

Figure 3 is an absorption spectrum of ammonia at a concentration of 10 mg/l. Note that there are two clearly resolved bands at approximately 931 and 968 cm^{-1}. Figure 4 is an absorption spectrum of a binary mixture of 60 mg/l of ammonia and 60 mg/l of ethanol. Due to the presence of the additional ammonia and ethanol, the two bands at 931 and 968 cm^{-1} have been broadened into a single wide band centered at approximately 950 cm^{-1}.

Assume that each molecule in a single compound gas has, at a particular allowed absorption frequency, associated with it a cross sectional area for absorption. Therefore, the total absorption cross section in a thin layer of gas normal to the radiation propagation direction is proportional to the number of molecules in the layer and, hence, to the concentration. Thus, $dI = -kCdl$, where dI is the incremental change in the intensity of the radiation in going through a layer of gas of thickness dl, C is the concentration and k is a constant. The negative sign indicates the beam has decreased in intensity.

The solution to this differential equation is: $I = I_o e^{-kC\ell}$

where I is the intensity of the radiation beam and I_o the initial intensity. This is the Beer-Lambert absorption law as discussed earlier, which may be equivalent written as

$$\log_e \frac{I_o}{I} = k\ell C.$$

We will now illustrate how spectra for a typical gas, Freon-12, were analyzed. Initially, the expected spectral bands were determined in a standard reference work, such as "Spectra of Diatomic Molecules", G. Herzberg (1950). Figure 5 is a reference spectrum taken with the gas cell filled with nitrogen, an infrared spectroscopically inert gas. The structure in this spectrum is due to one of three causes: (1) structure in the infrared source, (2) atmospheric absorption due to H_2O and CO_2, (3) instrument response characteristics. This structure impedes interpreting spectra of contaminants, and a system which does not have this undesirable characteristic is discussed in the following sections of this report. Figure 6 is a spectrum of Freon-12 at a concentration of 100 mg/l. Note the two strong absorption bands at 900 and 1150 cm^{-1}, and the two weak bands at 670 and 2270 cm^{-1}. Figure 7 is a spectrum of Freon-12 at a concentration of 60 mg/l. Note that the bands at the 900 and 1150 cm^{-1} are only slightly diminished, the 2270 cm^{-1} band is strongly diminished and split

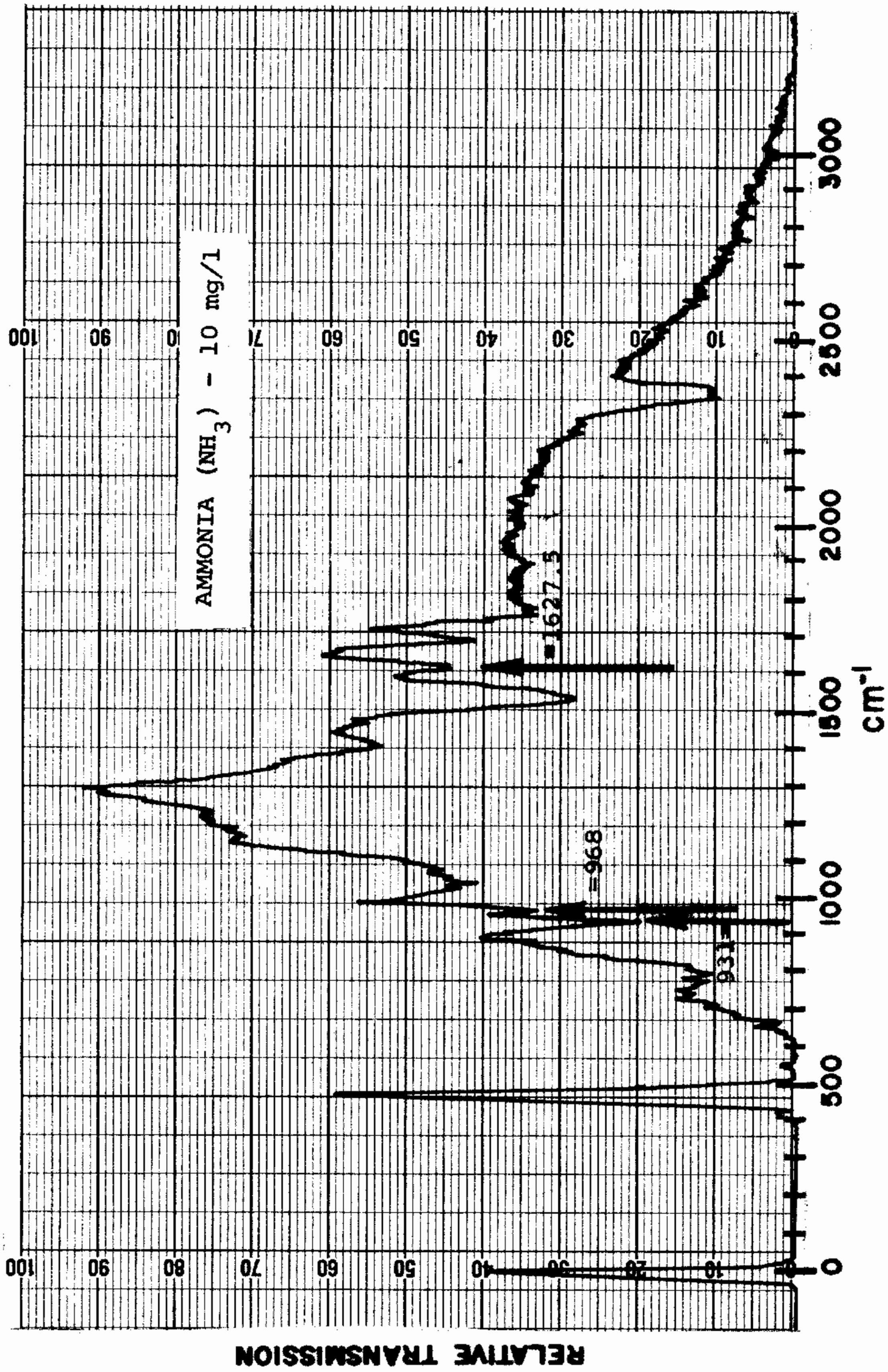

AMMONIA (NH_3) - 10 mg/1
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}
1627.5
968
931
RELATIVE TRANSMISSION

Figure 3

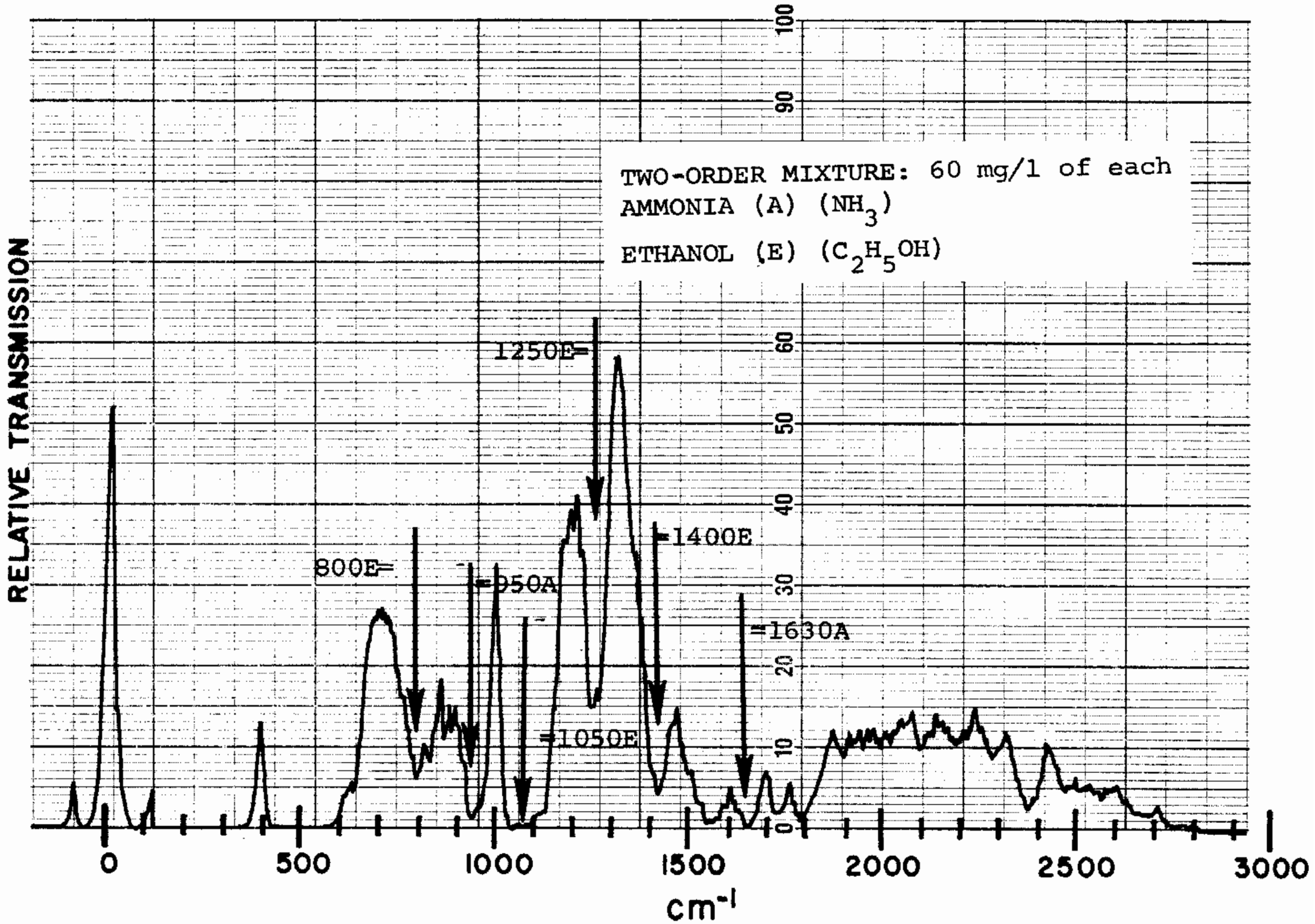

TWO-ORDER MIXTURE: 60 mg/l of each
AMMONIA (A) (NH_3)
ETHANOL (E) (C_2H_5OH)
RELATIVE TRANSMISSION
100
90
60
50
40
30
20
10
0
1250E
800E
950A
1400E
1630A
1050E
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 4

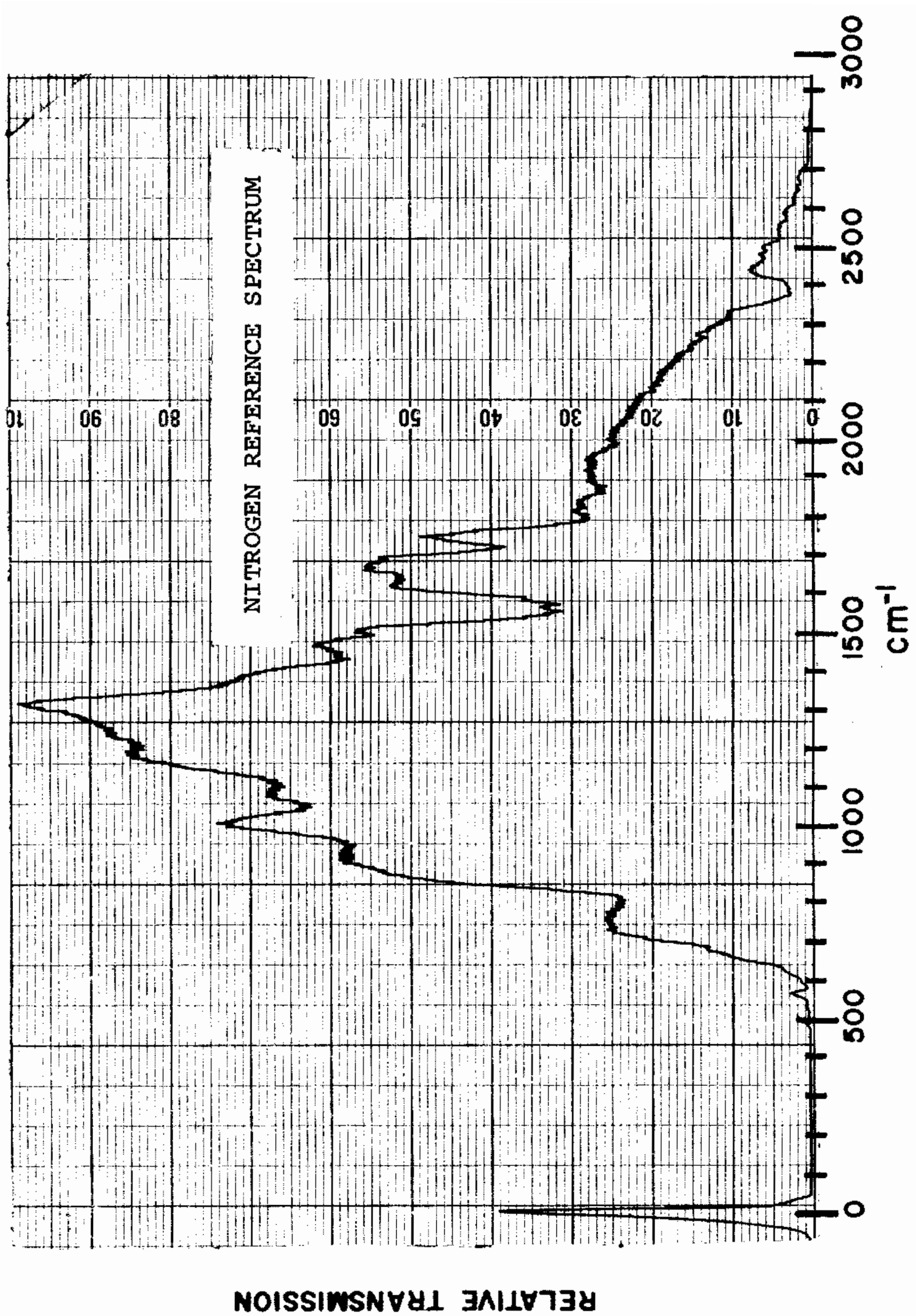

NITROGEN REFERENCE SPECTRUM
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 5

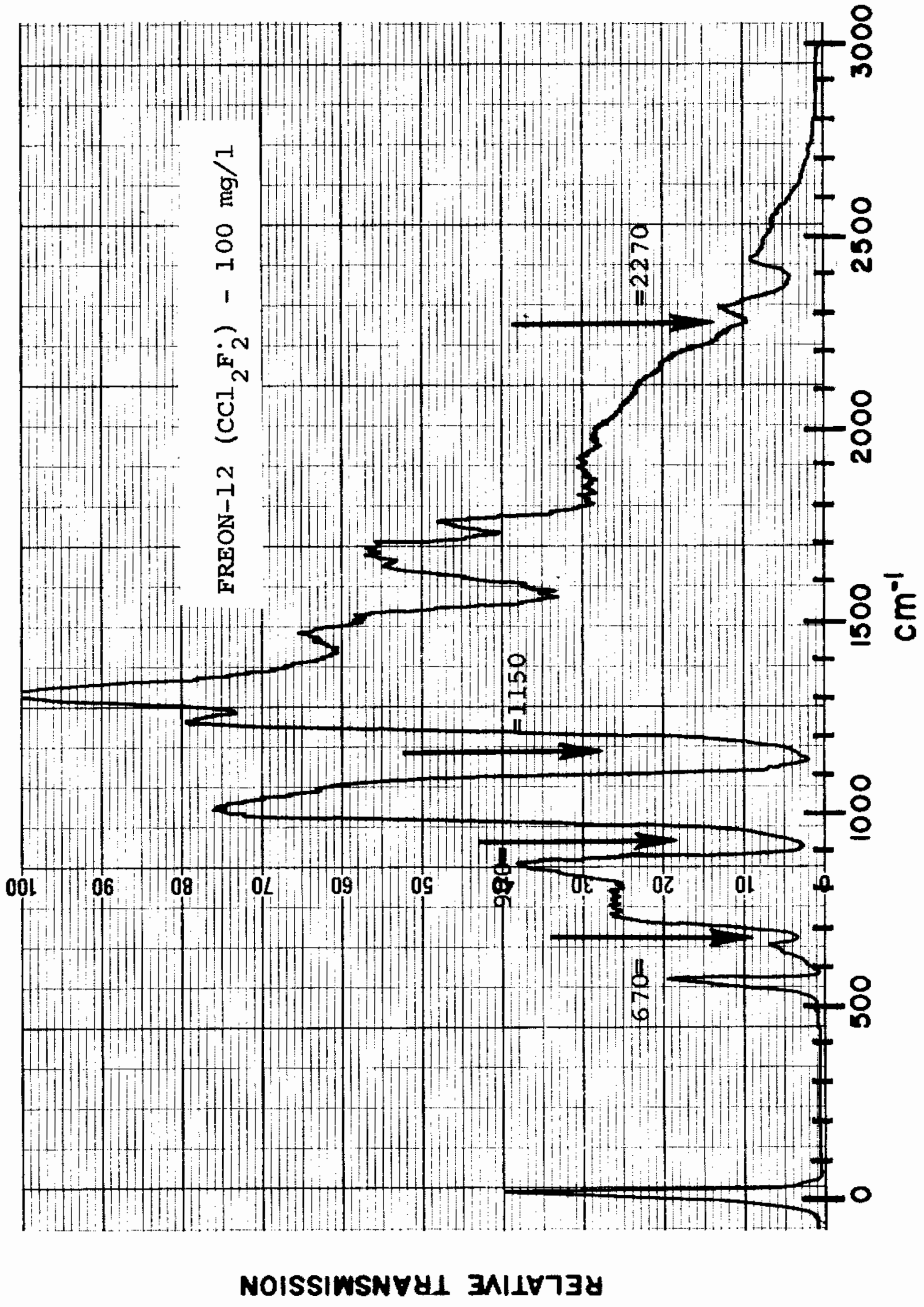

FREON-12 $(CCl_2F'_2)$ - 100 mg/1
=2270
=1150
980=
670=
0
500
1000
1500
2000
2500
3000
cm⁻¹
100
90
80
70
60
50
40
30
20
10
0
RELATIVE TRANSMISSION

Figure 6

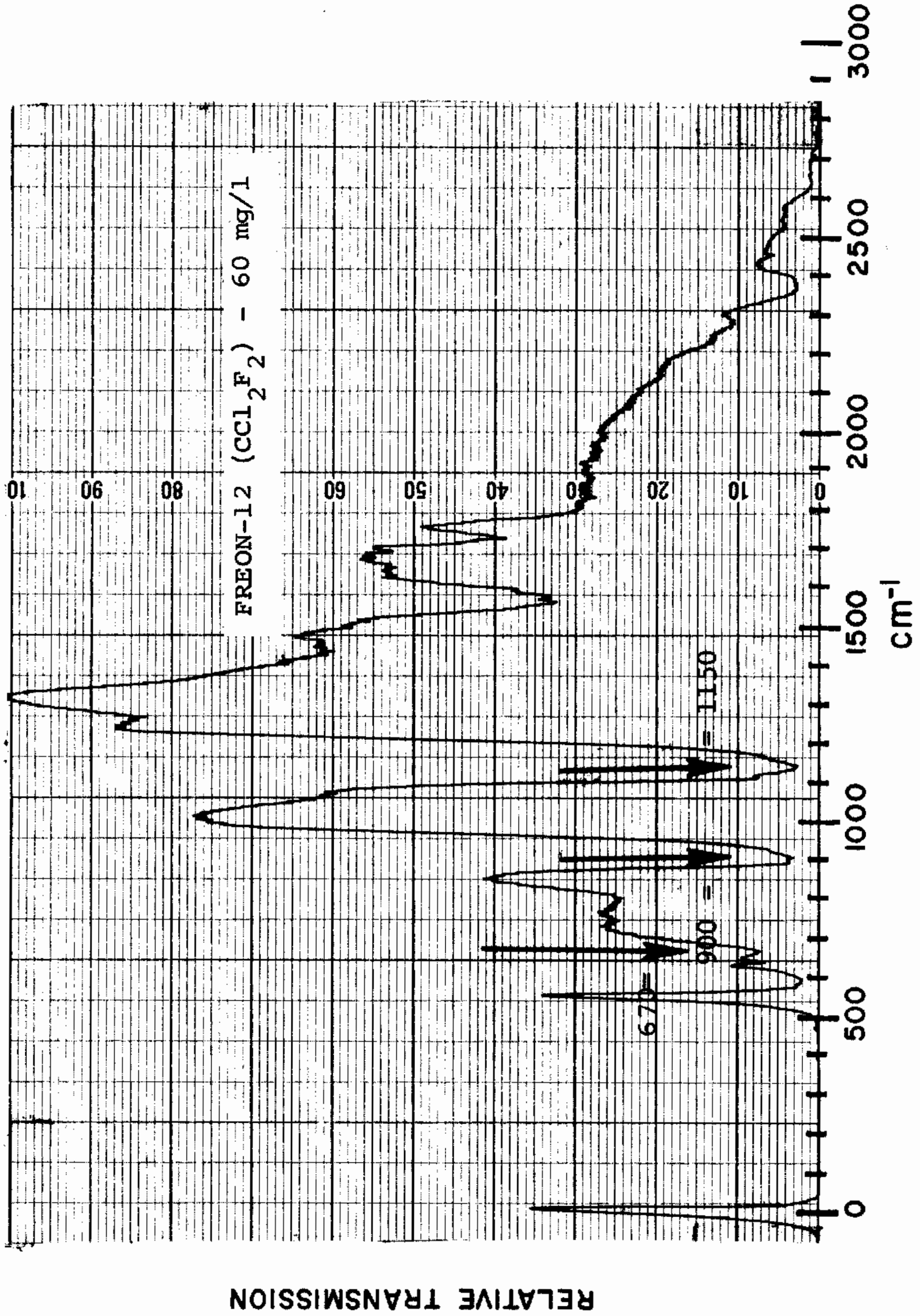

FREON-12 (CCl_2F_2) - 60 mg/l
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
670 =
900 =
= 1150
RELATIVE TRANSMISSION

Figure 7

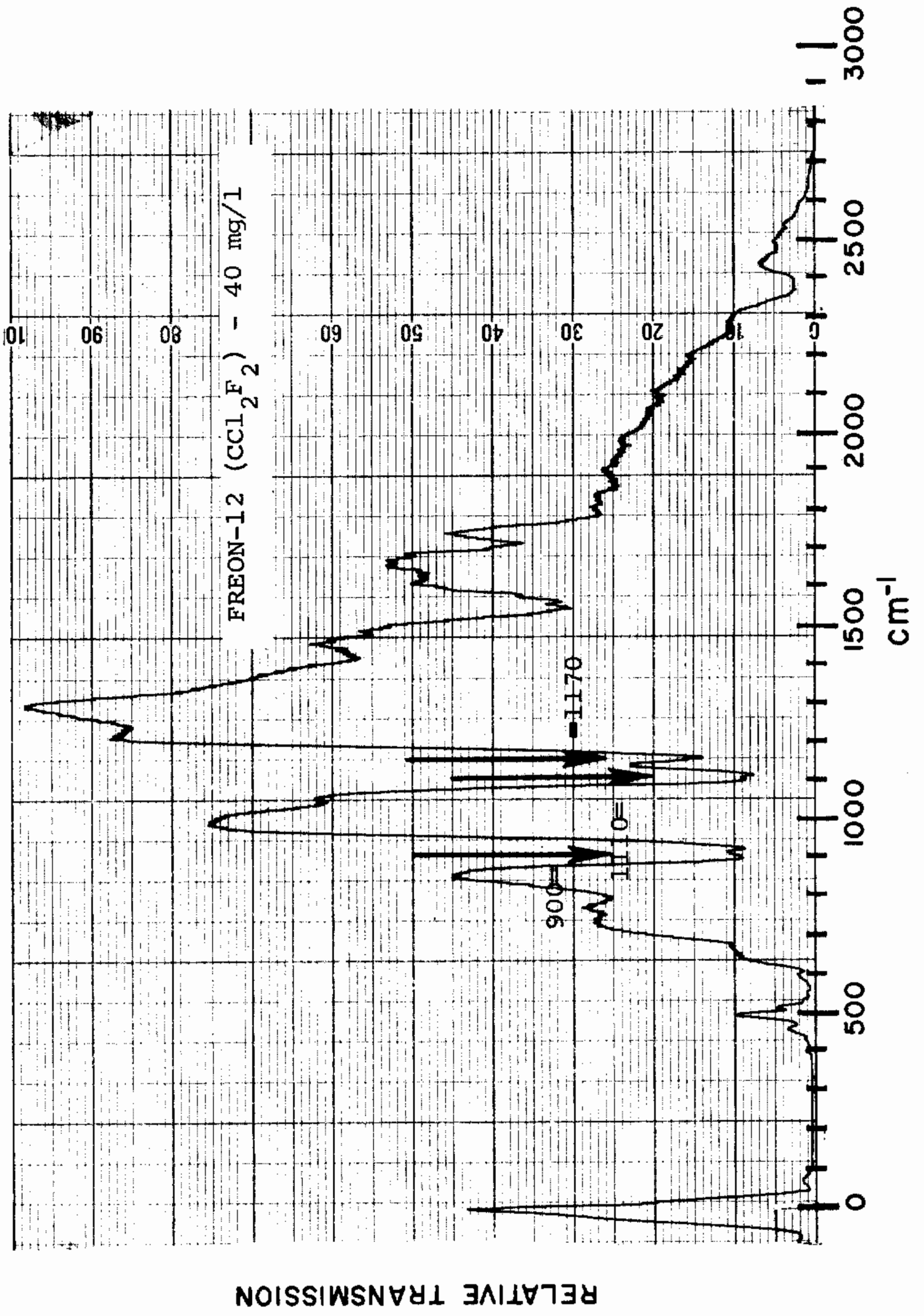

FREON-12 (CCl_2F_2) - 40 mg/1
100
90
80
60
50
40
30
20
10
0
1170
1110
900
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 8

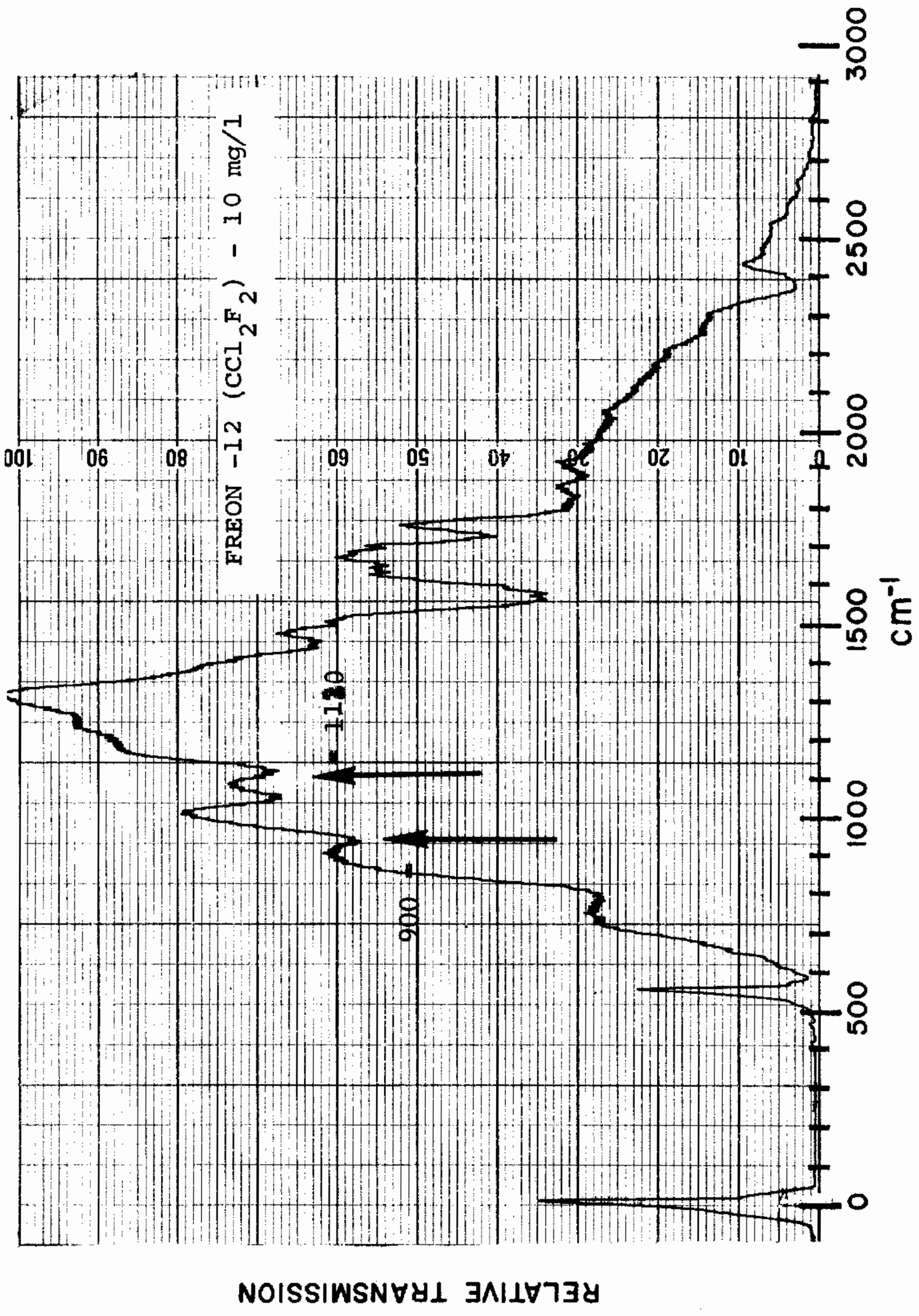

FREON -12 (CCl_2F_2) - 10 mg/1
100
90
80
60
50
40
30
20
10
0
RELATIVE TRANSMISSION
1120
900
3000
2500
2000
1500
1000
500
0
cm^{-1}

Figure 9

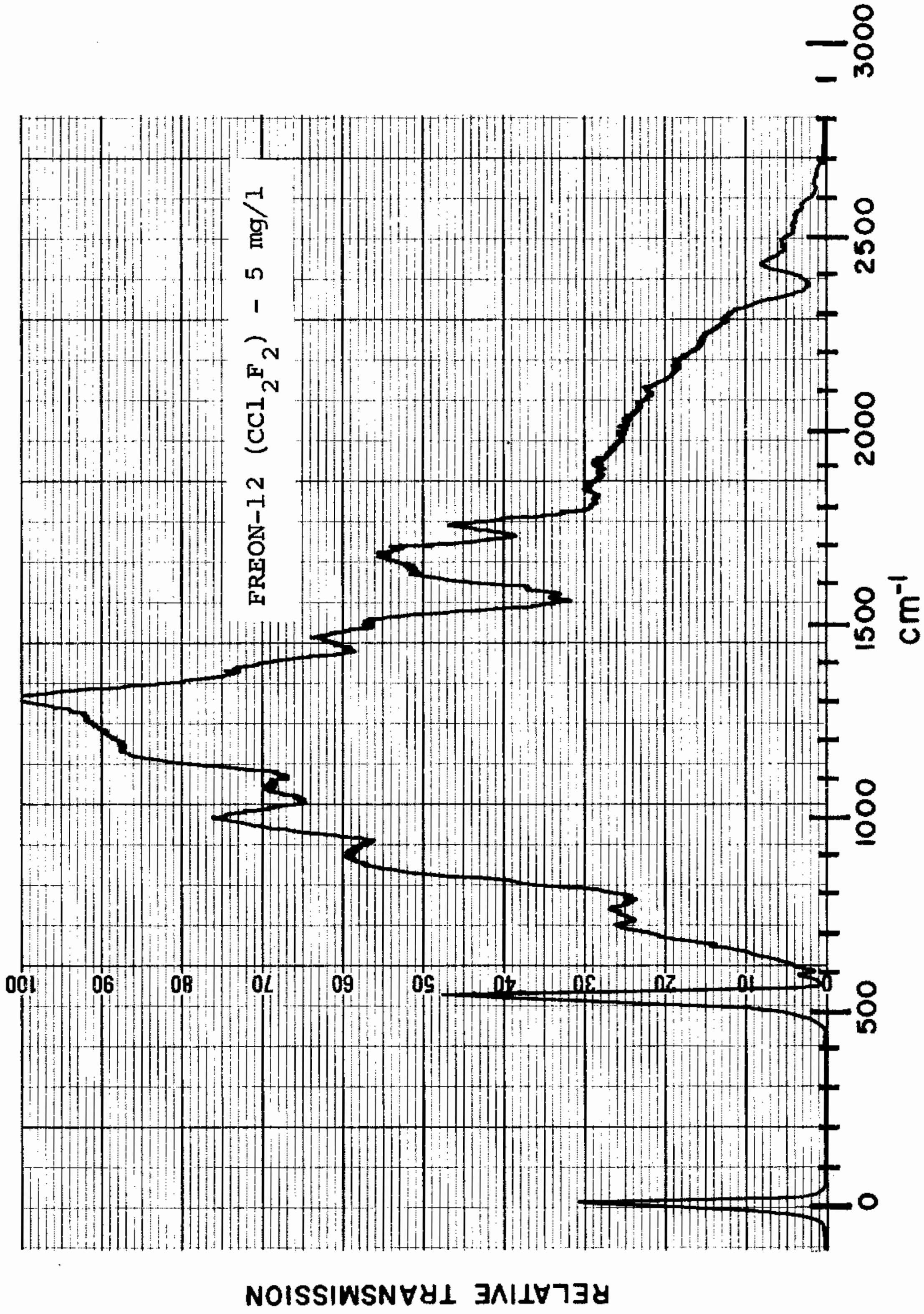

FREON-12 (CCl_2F_2) - 5 mg/1
100
90
80
70
60
50
40
30
20
10
0
RELATIVE TRANSMISSION
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 10

into a doublet with band centers at 1110 cm^{-1} and 1170 cm^{-1} and diminished, and the 900 cm^{-1} band is also diminished and shows a doublet structure. Figure 9 is a spectrum of Freon-12 at a concentration of 10 mg/l. Note that the 1170 cm^{-1} band is absent, but that the 1110 cm^{-1} and 900 cm^{-1} bands are still observable in comparison with the nitrogen reference spectrum. Figure 10 is a spectrum of Freon-12 at a concentration of 5 mg/l. Note that all bands are effectively absent. From this analysis, we may conservatively state that the minimum detectable concentration for Freon-12 is 10 mg/l. Here our criterion for our not being able to see a band is that the corresponding dip in the graph is of such a low amplitude as to be indistinguishable from the noise, and the dips in the spectrum are due to the three causes mentioned previously. A table of minimum detectable concentrations obtained by this method and the spectral bands used for identification are shown in Tables I and II, respectively. Spectra of each compound at the minimum detectable concentration are found in Appendix I.

After completion of the analysis of the simple compound spectra and compilation of observed spectral bands, spectra for binary and higher order mixtures were taken. Generally, the spectral band positions compiled for the single compound spectra could be used for a definitive qualitative analysis of the mixture spectra. Band broadening and band center shifts of one compound due to the presence of others were generally negligible. In an actual flight instrument used in an enclosed habitable atmosphere, the concentrations of the contaminants will generally be smaller than the concentrations studied in this program; hence, band shifts and broadening will even be more insignificant. In certain cases, bands for two or more compounds overlapped. However, even in these cases a qualitative and quantitative analysis is possible as will be shown in Section IV. Figure 12 is a typical mixture spectrum. The mixture contained ethane, ammonia, methane, Freon-12, and benzene, each at a concentration of 4 mg/l. Note that there are fourteen well-defined bands. Three of these bands are due to the presence of two different compounds, i.e., compounds with overlapping bands. The 930 cm^{-1} band is due to ammonia and Freon-12, and the 1430 and 1500 cm^{-1} bands are due to benzene and ethane. Spectra for 10 binary mixtures, 5 trinary mixtures, two 5-order mixtures, and one 15-order mixture are shown in Appendix II.

TABLE I

MINIMUM DETECTABLE CONCENTRATIONS

	Compound	Min. Det. Conc. In mg/l
1.	Acetic Acid - CH_3COOH	20
2.	Acetone - $CH_3CO\ CH_3$	10
3.	Acetylene - C_2H_2	20
4.	Allene - C_3H_4	40
5.	Ammonia - $N\ H_3$	1
6.	Benzene - C_6H_6	60
7.	Butane - C_4H_{10}	20
8.	Butanol - C_4H_9OH	60
9.	1-Butene - C_4H_8	40
10.	Butyl Acetate - $CH_3CO_2(CH_2)_3CH_3$	10
11.	Butyraldehyde - $CH_3(CH_2)_2CHO$	10
12.	Carbon Monoxide - CO	60
13.	Diethyl Ether - $C_2H_5OC_2H_5$	5
14.	Dimethyl Ether - CH_3OCH_3	20
15.	Ethane - C_2H_6	80
16.	Ethanol - C_2H_5OH	30
17.	Ethylene - C_2H_4	40
18.	Ethyl Formate - $HCO_2CH_2CH_3$	5
19.	Formic Acid - HCOOH	10

Table I continued

	Compound	Min. Det. Conc. In mg/l
20.	Freon-12 - CCl_2F_2	10
21.	n-Hexane - C_6H_{14}	40
22.	Hydrogen Sulfide - H_2S	200
23.	Methane - CH_4	10
24.	Methanol - CH_3OH	20
25.	Methyl Acetate - $CH_3CO_2CH_3$	5
26.	Methyl Bromide - CH_3Br	40
27.	Methyl Chloride - CH_3Cl	40
28.	Methyl Fluoride - CH_3F	20
29.	Methyl Iodide - CH_3I	40
30.	Methyl Mercaptan - CH_3SH	20
31.	Nitric Oxide - NO	20
32.	Nitrogen Dioxide (Dinitrogen Tetroxide) - NO_2, N_2O_4	9
33.	Nitrous Oxide - N_2O	20
34.	Octane - C_8H_{18}	40
35.	2-Pentanone - $CH_3CO\ (CH_2)_2CH_3$	10
36.	Propane - C_3H_8	20
37.	Propanol - C_3H_7OH	30
38.	Propylene - C_3H_6	40

Table I continued

Compound	Min. Det. Conc. In mg/l
39. Sulfur Dioxide - SO_2	20
40. Toluene - $C_6H_5CH_3$	8
41. m-Xylene - $C_6H_4(CH_3)_2$	5
42. o-Xylene - $C_6H_4(CH_3)_2$	5
43. p-Xylene - $C_6H_4(CH_3)_2$	2

TABLE II

OBSERVED SPECTRAL BANDS IN ORDER OF DECREASING STRENGTH, IN cm^{-1}

	Compound	cm^{-1}					
1.	Acetic Acid	1440					
2.	Acetone	1220	1380	1420	1750		
3.	Acetylene	740	1380	1330			
4.	Allene	840	1700	1400	1040	1550	
5.	Ammonia	1630	930	960			
6.	Benzene	1050	1500				
7.	Butane	1470	1390	1300	1150	970	740
8.	Butanol	1050					
9.	1-Butene	920	1670	1470	1000	790	1840
10.	Butyl Acetate	1780	1250	1050			
11.	Butyraldehyde	800	1770	950	1120	1430	1500
12.	Carbon Monoxide	2150					
13.	Diethyl Ether	1100	930	850	1360		
14.	Dimethyl Ether	1110	1180	1470	930		
15.	Ethane	1500	850				
16.	Ethanol	1080	1420	1270	900		
17.	Ethylene	950	1420	1480	1930		
18.	Ethyl Formate	1170	1760	1020			
19.	Formic Acid	1100	1770	1220	920	700	1380
20.	Freon-12	1110	900	1170	670	2270	
21.	n-Hexane	1470	1390				

Table II Continued

	Compound	cm^{-1}					
22.	Hydrogen Sulfide	1330					
23.	Methane	1370	1320				
24.	Methanol	1050	1390				
25.	Methyl Acetate	1260	1450	1375	1050	850	
26.	Methyl Bromide	1330	950				
27.	Methyl Chloride	730	1350	1390	1040		
28.	Methyl Flouride	1060					
29.	Methyl Iodide	1280					
30.	Methyl Mercaptan	1070	1370	1450			
31.	Nitric Oxide	1880					
32.	Nitrogen Dioxide	1320	1620				
	Dinitiogen Tetroxide	1750	750	1360			
33.	Nitrous Oxide	1310	1190				
34.	Octane	1470	1390	730			
35.	2-Pentanone	1180	1380	1760	1145		
36.	Propane	1500					
37.	Propanol	1050					
38.	Propylene	900	1460	1650	1820		
39.	Sulfur Dioxide	1360	1150	2500			
40.	Toluene	1790	1250	1380	1450	1050	720
41.	m-Xylene	780					
42.	o-Xylene	760					
43.	p-Xylene	790	1520				

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The results of this program have defined a system that will satisfy the following criteria for a flight model interferometer spectrometer for qualitative and quantitative infrared absorption analysis of contaminant gases in enclosed habitable atmospheres: (1) simple and direct, (2) highly sensitive, (3) relatively small in mass, volume, and power requirements, and (4) operates in a continuous automatic manner. The proposed new instrument has the following new features: (1) improved resolution, (2) multiple path cell, (3) optical subtraction, and (4) fringe reference cube, to lower the minimum detectable concentrations and make possible new data processing methods.

RESULTS OF IMPROVED RESOLUTION

Figure 11 depicts two acetylene spectra. Note the band centered at approximately 740 cm^{-1}. The interferometer spectrometer used in this program did not clearly resolve the sharp dip located at the band center. The proposed new instrument has a resolution of 10 cm^{-1} which is a factor of three better than the present instrument. Consequently, in cases like this one, the improved resolution will result in lower minimum detectable concentrations.

RESULTS OF USING A MULTIPLE-PATH GAS CELL

As mentioned previously, fractional absorption in a gas cell is equal to: $1 - e^{-kC\ell}$, where k is the absorption coefficient, C is the concentration, and ℓ is the path length. Since fractional absorption is a function of the product of C and ℓ, if ℓ is increased by a given factor, the minimum detectable concentration will be reduced by that same factor. The multiple-path cell used in the proposed instrument achieves an effective ℓ of 10 meters, a factor of 10 more than the path length used on the present system. The multiple-path cell achieves a large effective path length, while keeping the physical dimensions of the system small, by reflecting the source beam back and forth through the absorbing gas many times by a system of mirrors. The proposed instrument uses 20 reflections over a 0.5 meter path.

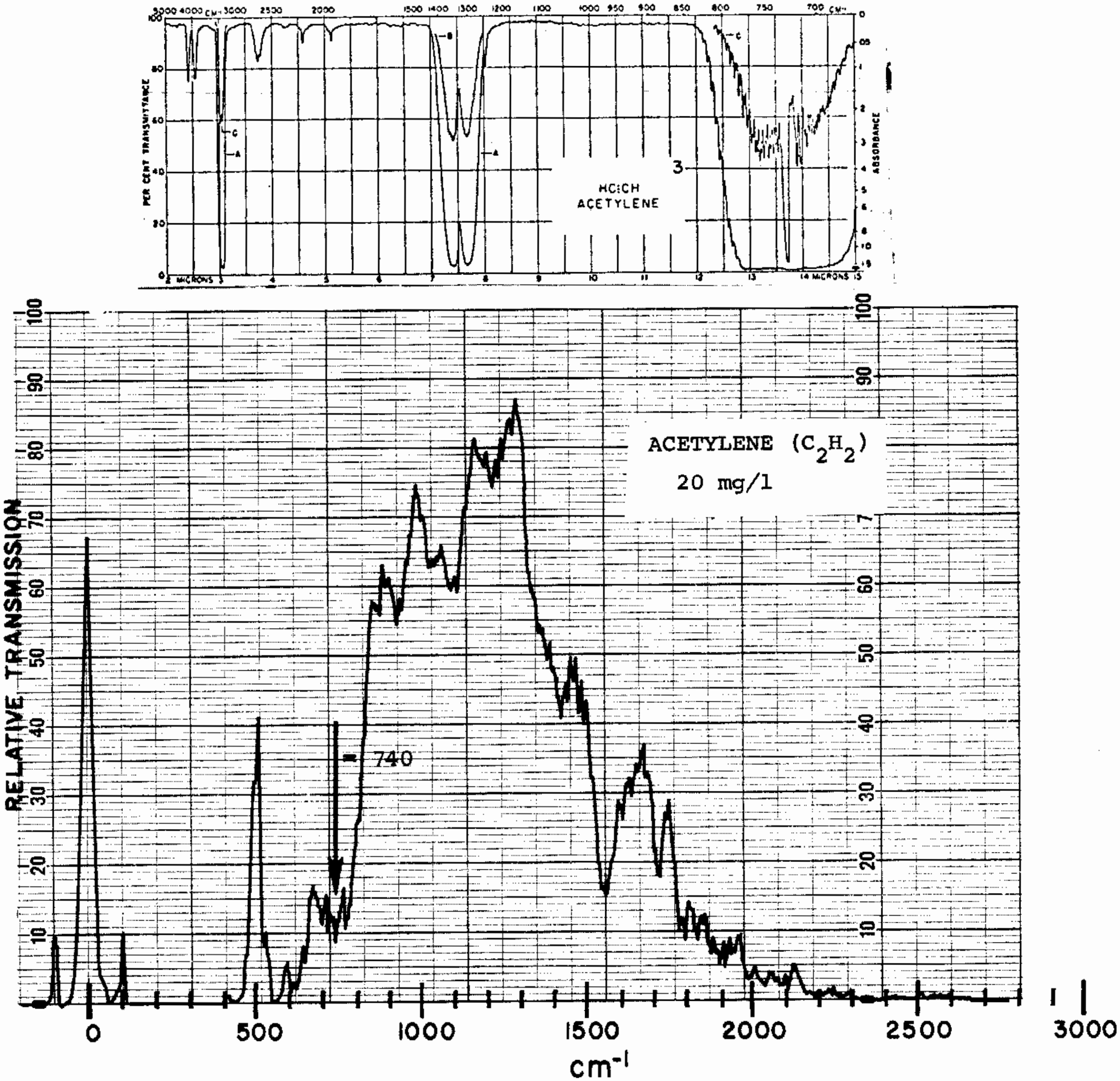


Figure 11 Two Acetylene Spectra

THE NEED FOR AN OPTICAL SUBTRACTION OR DUAL-BEAM SYSTEM

The proposed instrument uses the technique of optical subtraction or dual-beam spectroscopy. The optical subtraction system yields a true spectrum of absorption, whereas the single beam instrument yields a transmission spectrum. Figure 12 illustrates this point. The advantages of the dual-beam configuration are manifold. Figures 13 and 14 are a nitrogen reference spectrum, and a spectrum of ammonia at a concentration of 10 mg/l, respectively. Note the confusing anomalous dips in the nitrogen spectrum occuring at the same spectral positions as the ammonia absorption bands, 931-968 cm^{-1} and 1627.5 cm^{-1}. These anomalous dips make it difficult to detect small absorptions. The dips are caused by one of three factors: (1) atmospheric absorption by H_2O and CO_2, (It was difficult to eliminate atmospheric absorption in this single beam instrument because radiation traverses an air path between source and instrument.), (2) frequency dependent instrument characteristics such as beamsplitter transmission and detector sensitivity, and (3) source spectrum characteristics. The dual-beam instrument takes the difference of an absorption spectrum and a reference spectrum; hence, these anomalous dips are cancelled. Hence, differential spectroscopy should yield a lower minimum detectability than a single-beam instrument with the same resolution. That there is an output at a particular audio frequency proportional to the absorption at the corresponding infrared frequency, makes feasible some new data processing techniques which will be discussed later.

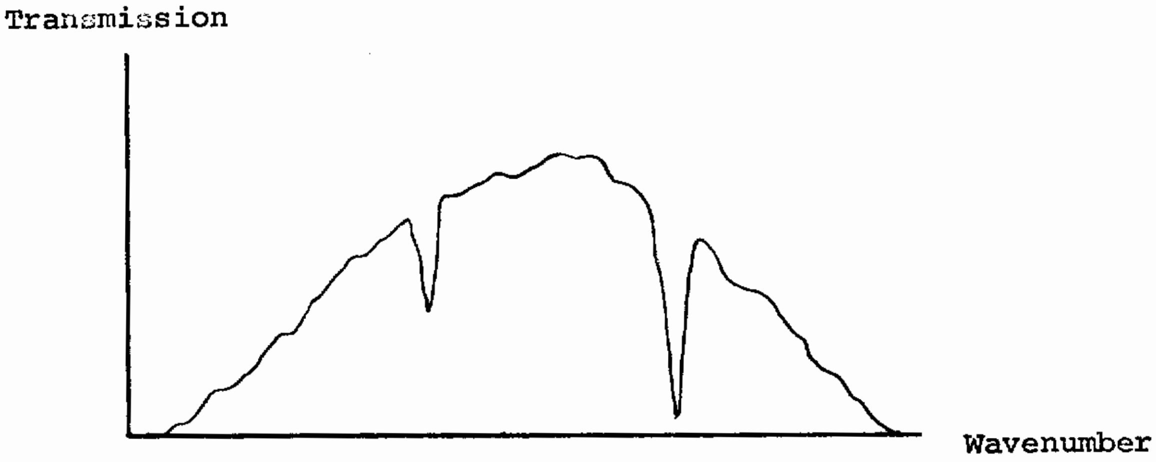
The dynamic range of the signal would be reduced, since in the single-beam instrument we frequently have a small absorption dip superimposed on a large black-body curve. The use of differential spectroscopy would elminate many data processing and telemetry problems.

Since what is obtained is the difference of two spectra, and two gas cells are utilized, one of them could be filled with a reference atmosphere rather than a vacuum or inert gas. Then the output of the instrument would be a direct measure of the deviation of the actual cabin atmosphere from the reference atmosphere.

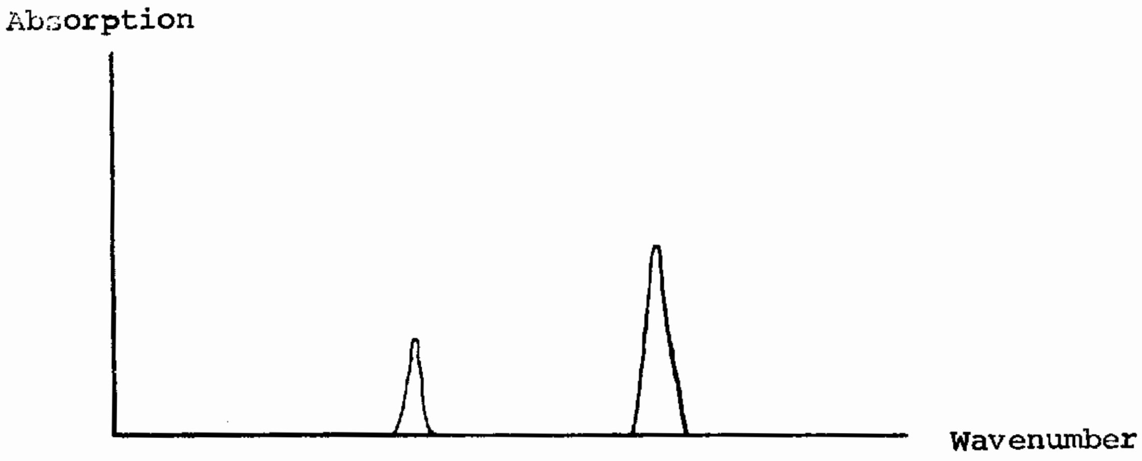
The theory of the single and dual-beam interferometers are discussed in detail in Appendices III and IV.

THE FRINGE REFERENCE CUBE

The output of the dual-beam interferometer is a plot of



SINGLE-BEAM SPECTRUM



DUAL-BEAM SPECTRUM

Figure 12 Single and Dual-Beam Spectra

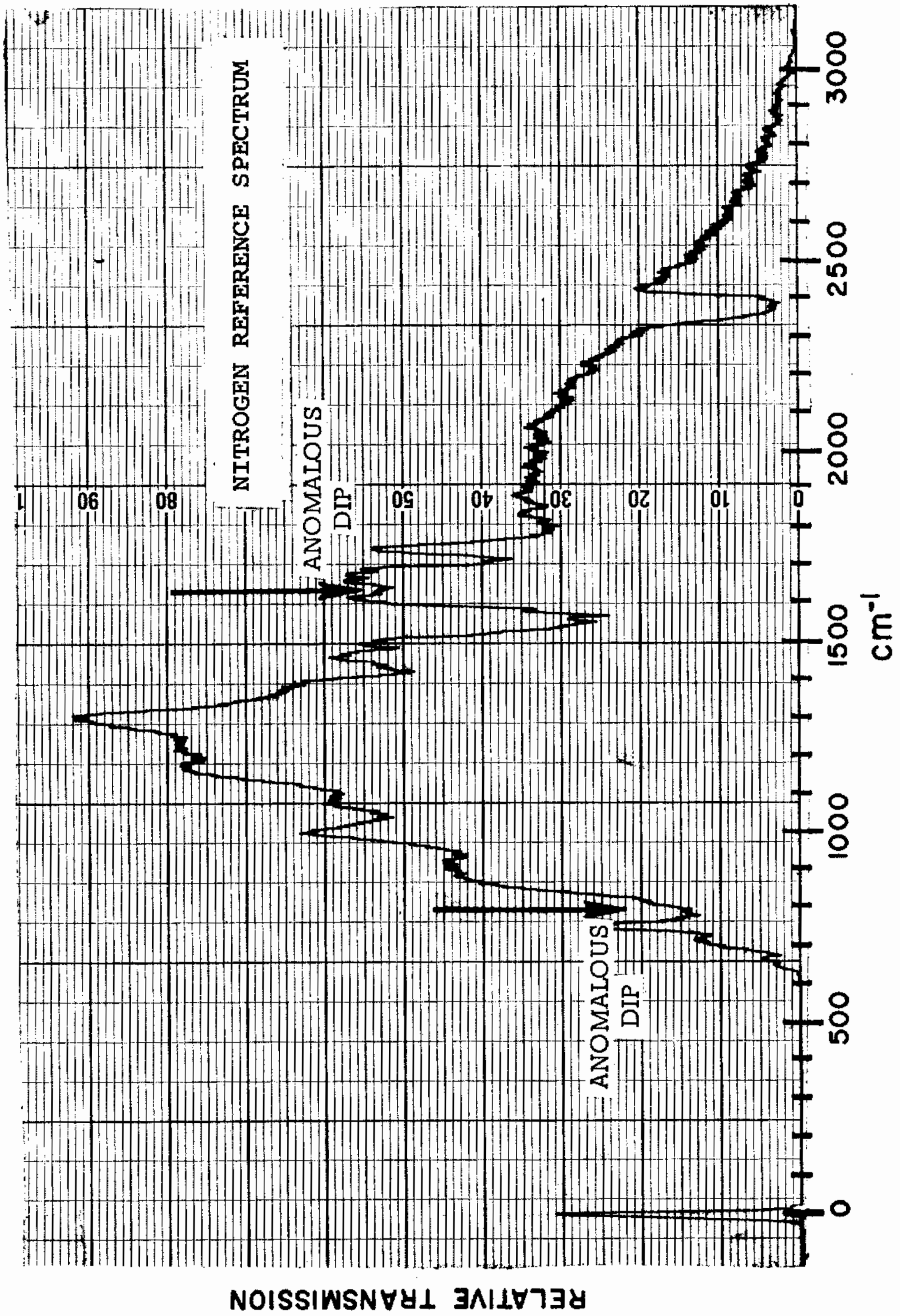

NITROGEN REFERENCE SPECTRUM
ANOMALOUS DIP
ANOMALOUS DIP
0
10
20
30
40
50
60
70
80
90
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 13

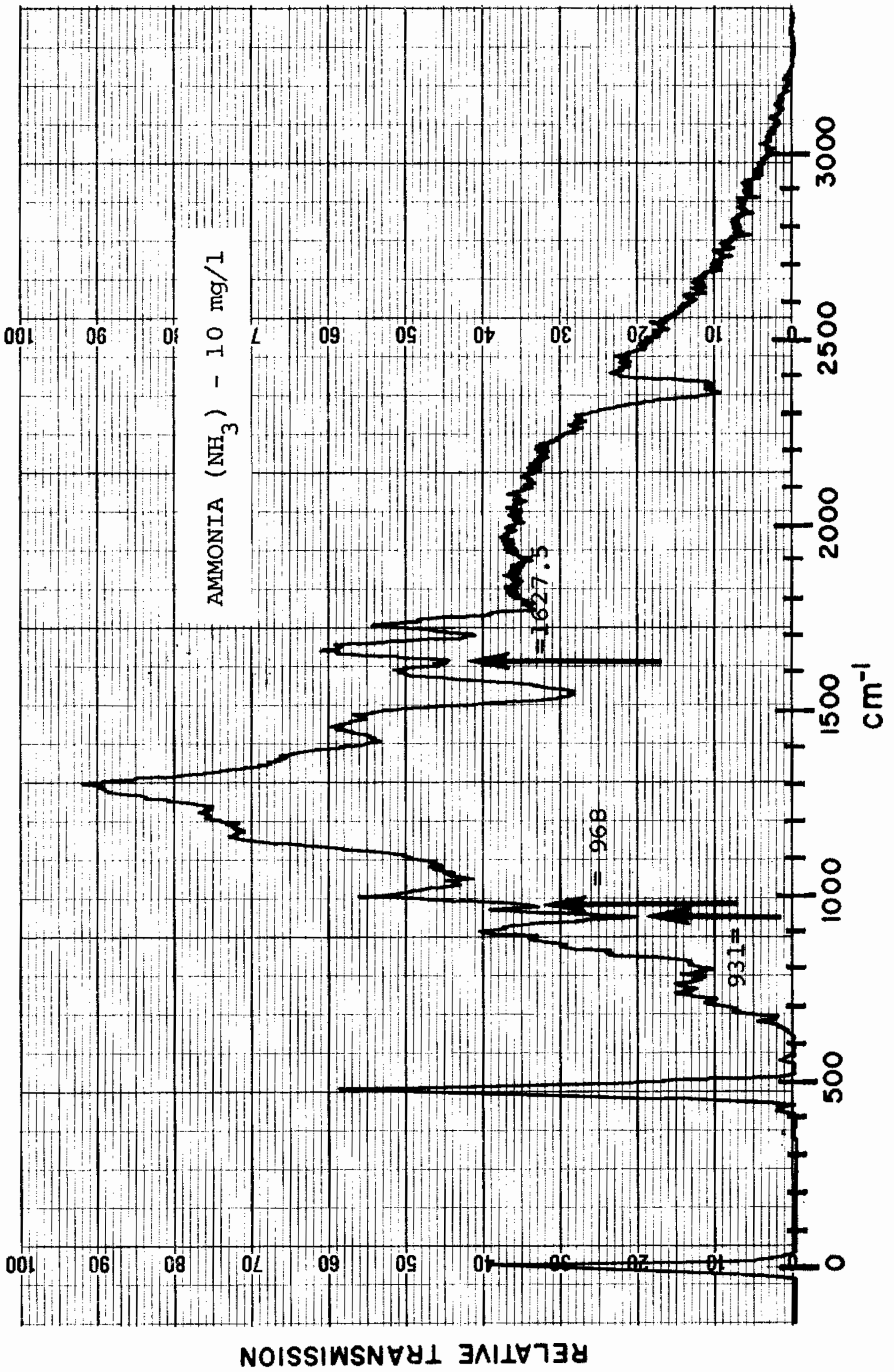

AMMONIA (NH3) - 10 mg/l
1627.5
968
931
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm-1
RELATIVE TRANSMISSION

Figure 14

intensity vs. mirror position. To process this data to yield a spectrum, i.e., intensity vs. frequency, when analyzing a particular point on the interferogram, it is necessary to know precisely the corresponding mirror position. If the transducer is driven with a perfect sawtooth wave and the spring suspension is perfectly linear and the system is not subjected to any vibration, the mirror moves at constant velocity; hence, the mirror position is proportional to the time from the beginning of the sweep. When any of the above conditions are not met, we need an auxiliary signal to determine the mirror position corresponding to a particular interferogram point. The fringe reference cube provides this auxiliary signal. A second cube, illuminated with monochromatic light, has its moving mirror actuated by the same transducer that actuates the moving mirror in the signal cube. The zero crossover points in the signal from the fringe reference cube correspond to definite mirror positions. Hence, we can add the interferograms coherently in the coadder, even if the mirror velocity is not constant, by using the zero crossover points as the interferogram sampling times.

QUALITATIVE AND QUANTITATIVE ANALYSIS USING THE DUAL-BEAM

INTERFEROMETER SPECTROMETER

In many cases Beer's Law is obeyed in a mixture of compounds. That is:

$$A = 1 - e^{-(k_1C_1\ell + k_2C_2\ell + \dots + k_NC_N\ell)}$$

where A is the absorption at a particular frequency and k_i and C_i are the absorption coefficients and concentrations, respectively, of the i^{th} compound in the mixture and ℓ is the path length. In the small concentration limit, we obtain (using a Taylor expansion for the exponential and retaining only the first two terms):

$$A = k_1C_1\ell + k_2C_2\ell + \dots + k_NC_N\ell$$

As an illustration, assume we have two compounds in the mixture and two absorption bands. We obtain two simultaneous linear equations for the two concentrations:

$$A_1 = k_{11} \ell C_1 + k_{12} \ell C_2$$

$$A_2 = k_{21} \ell C_2 + k_{22} \ell C_2$$

where A_i is the absorption at the i^{th} frequency and k_{ij} is the absorption at the i^{th} frequency due to the j^{th} compound. Hence, under very general conditions, a unique solution exists for the C's. Generally, an N component mixture requires N bands for a unique qualitative and quantitative analysis. The dual-beam interferometer is well-suited for this application, since its output at a particular audio frequency is proportional to the absorption at the corresponding infrared frequency by digital and possibly analog methods.

APPENDIX I

SPECTRA OF SINGLE COMPOUNDS

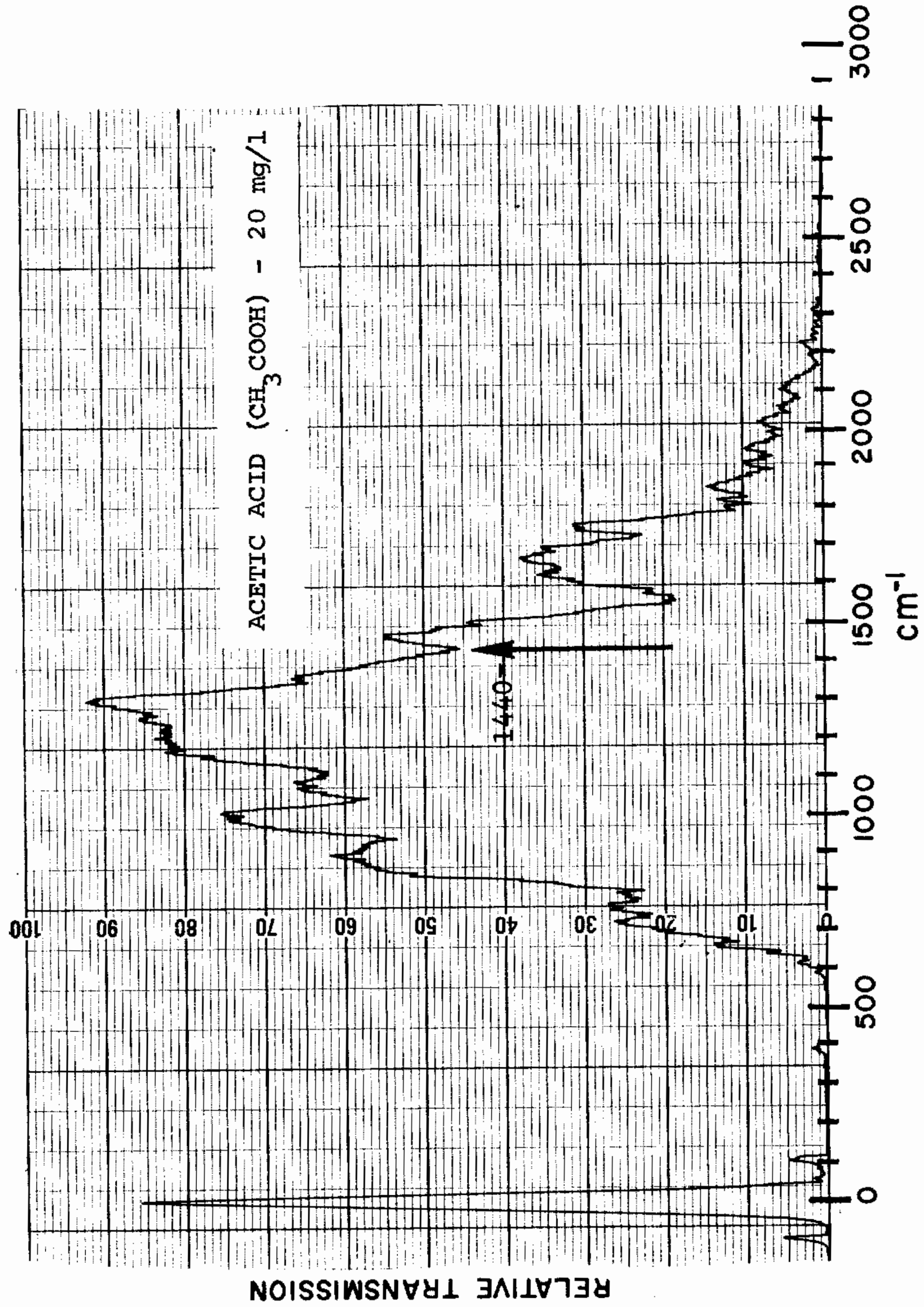

ACETIC ACID (CH_3COOH) - 20 mg/l
1440
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 15

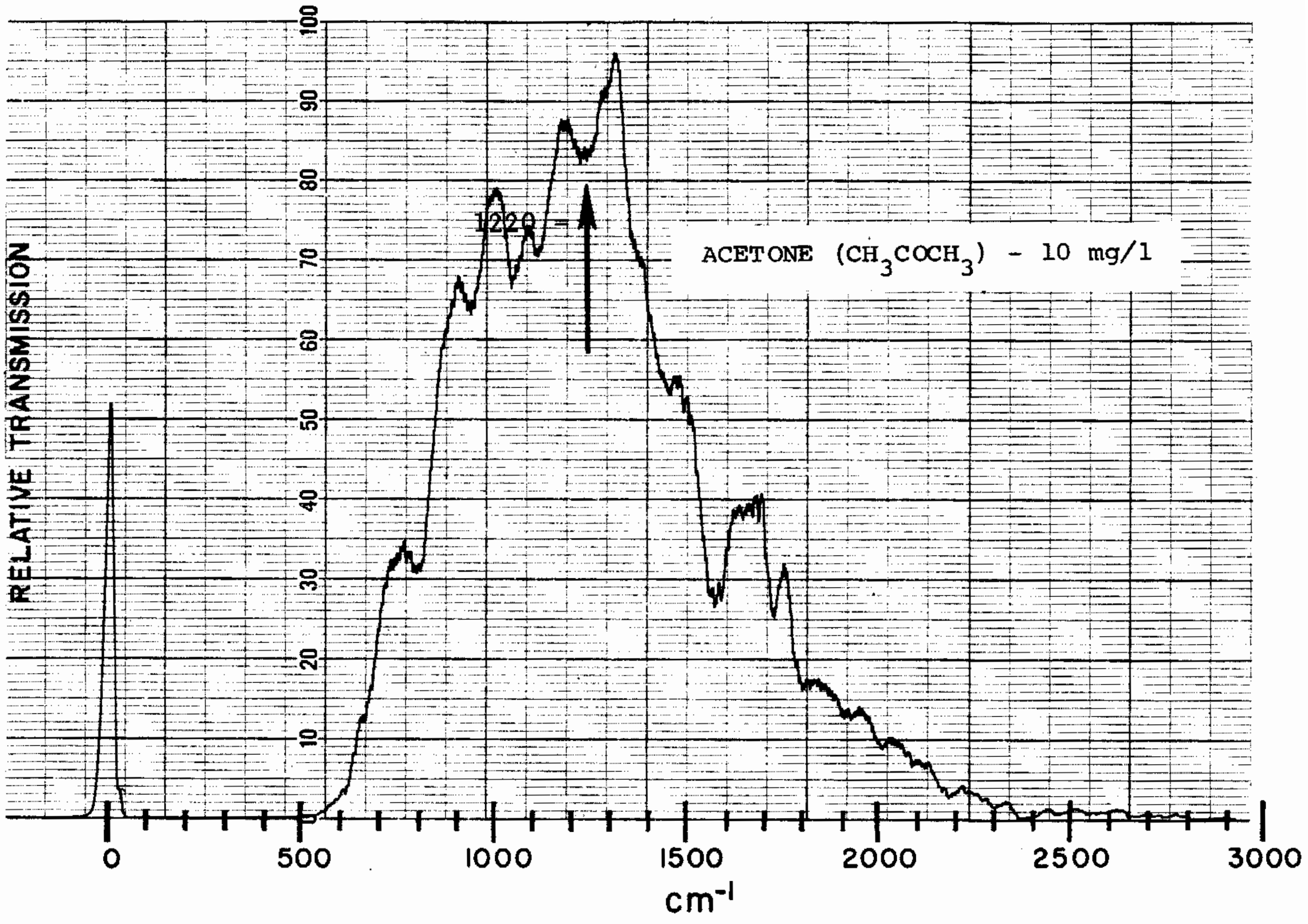
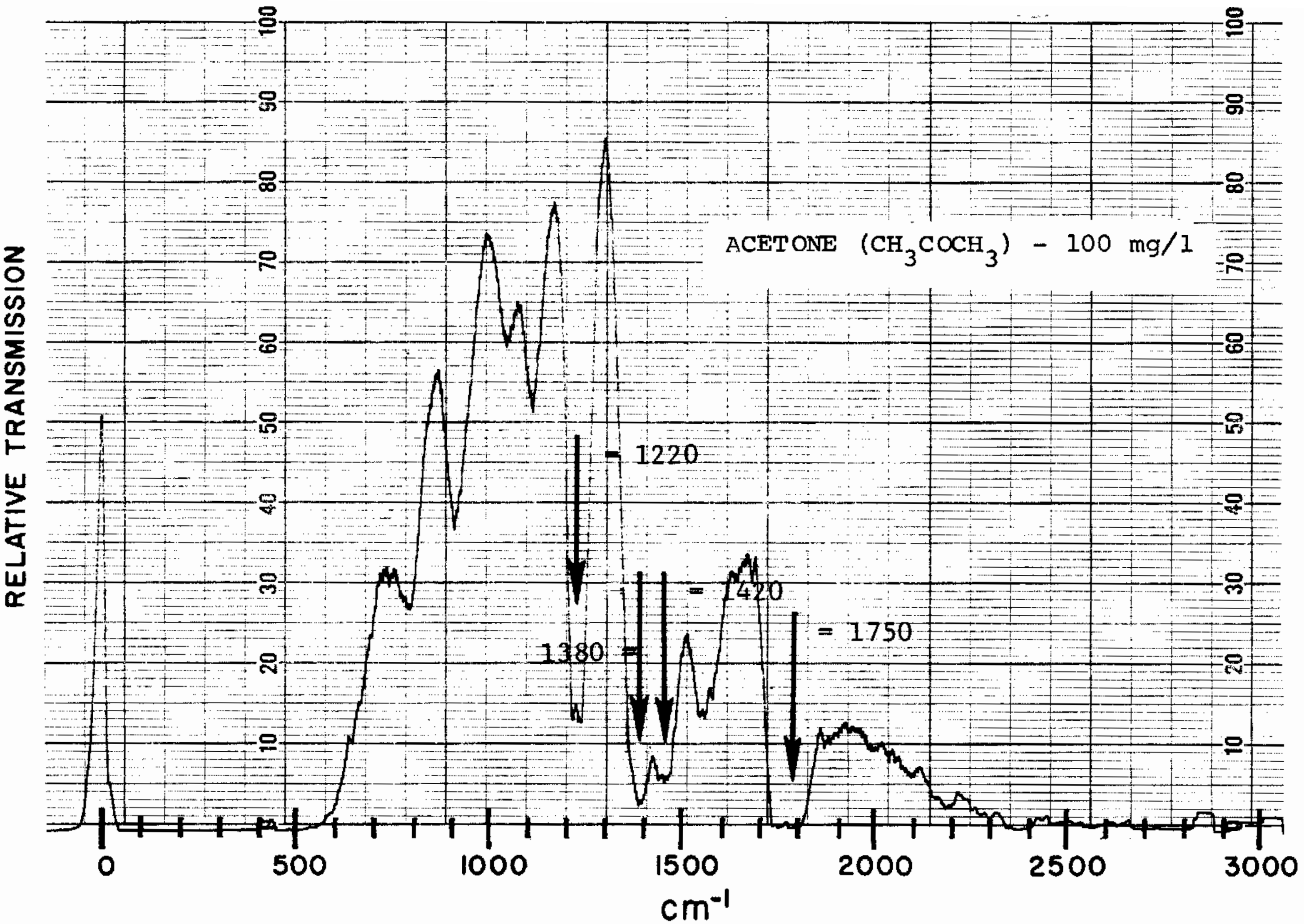

RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
1220
ACETONE (CH_3COCH_3) - 10 mg/1
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 16



ACETONE (CH_3COCH_3) - 100 mg/1

Figure 17

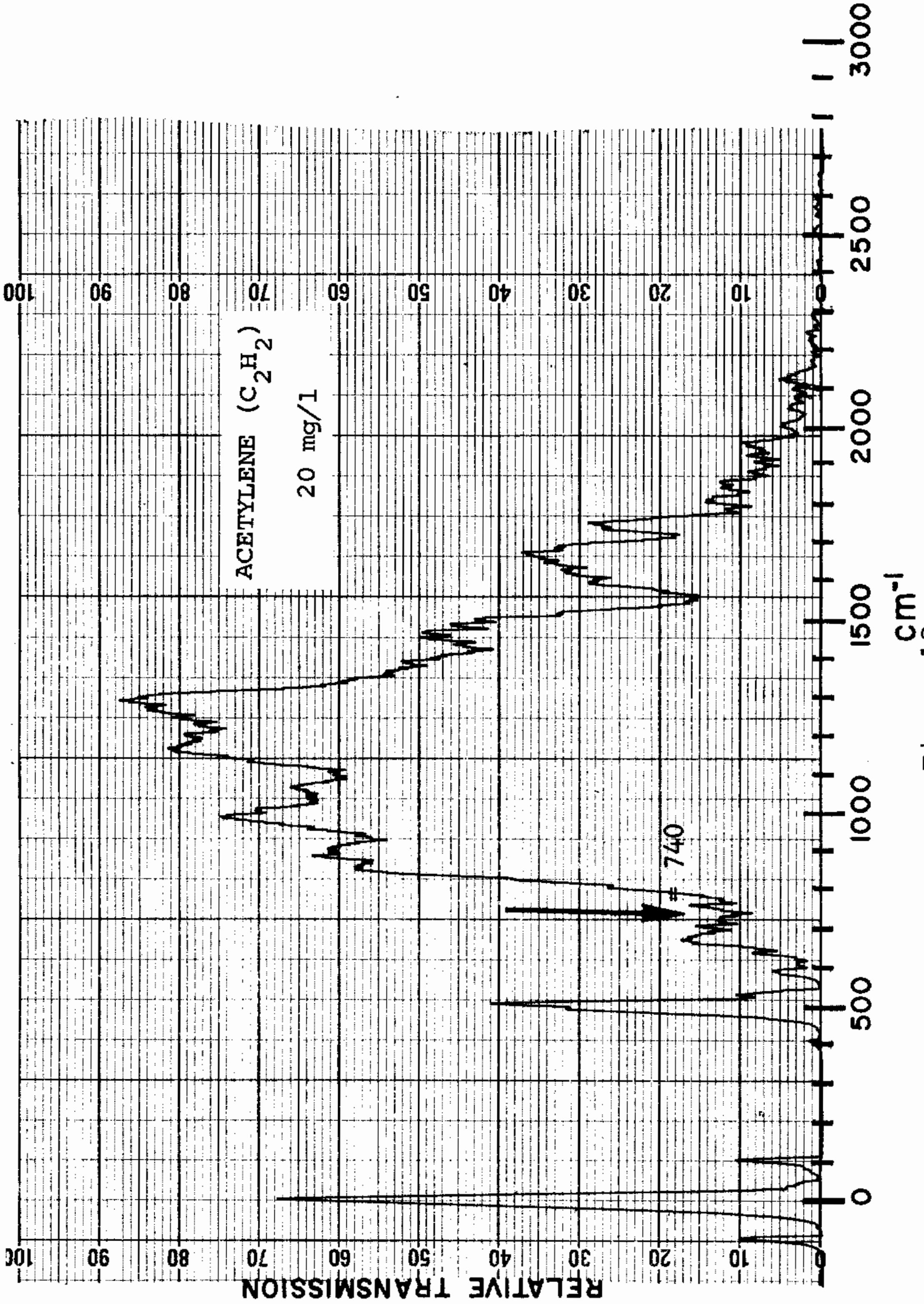
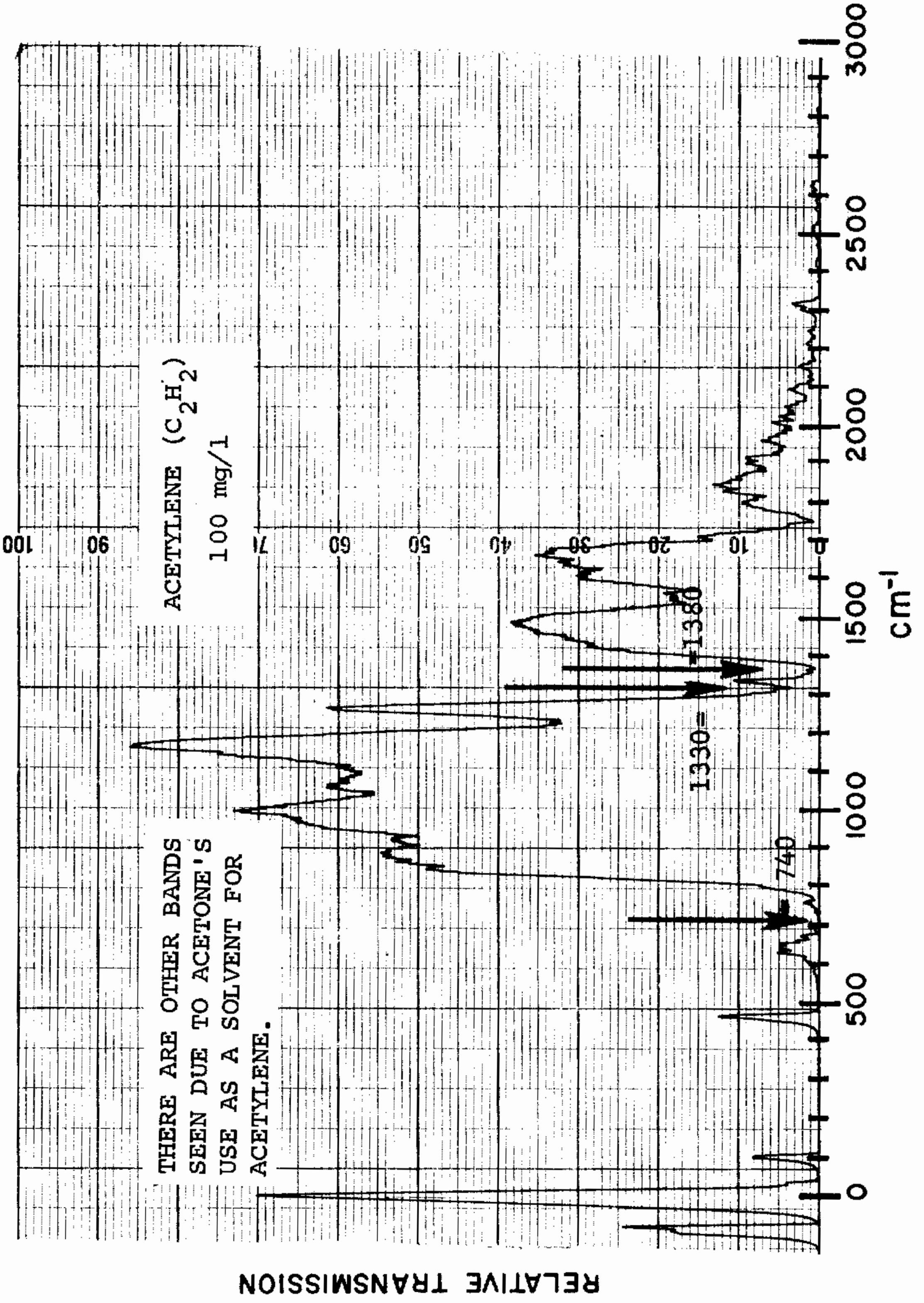

ACETYLENE (C_2H_2)
20 mg/l
740
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 18



THERE ARE OTHER BANDS SEEN DUE TO ACETONE'S USE AS A SOLVENT FOR ACETYLENE.

Figure 19

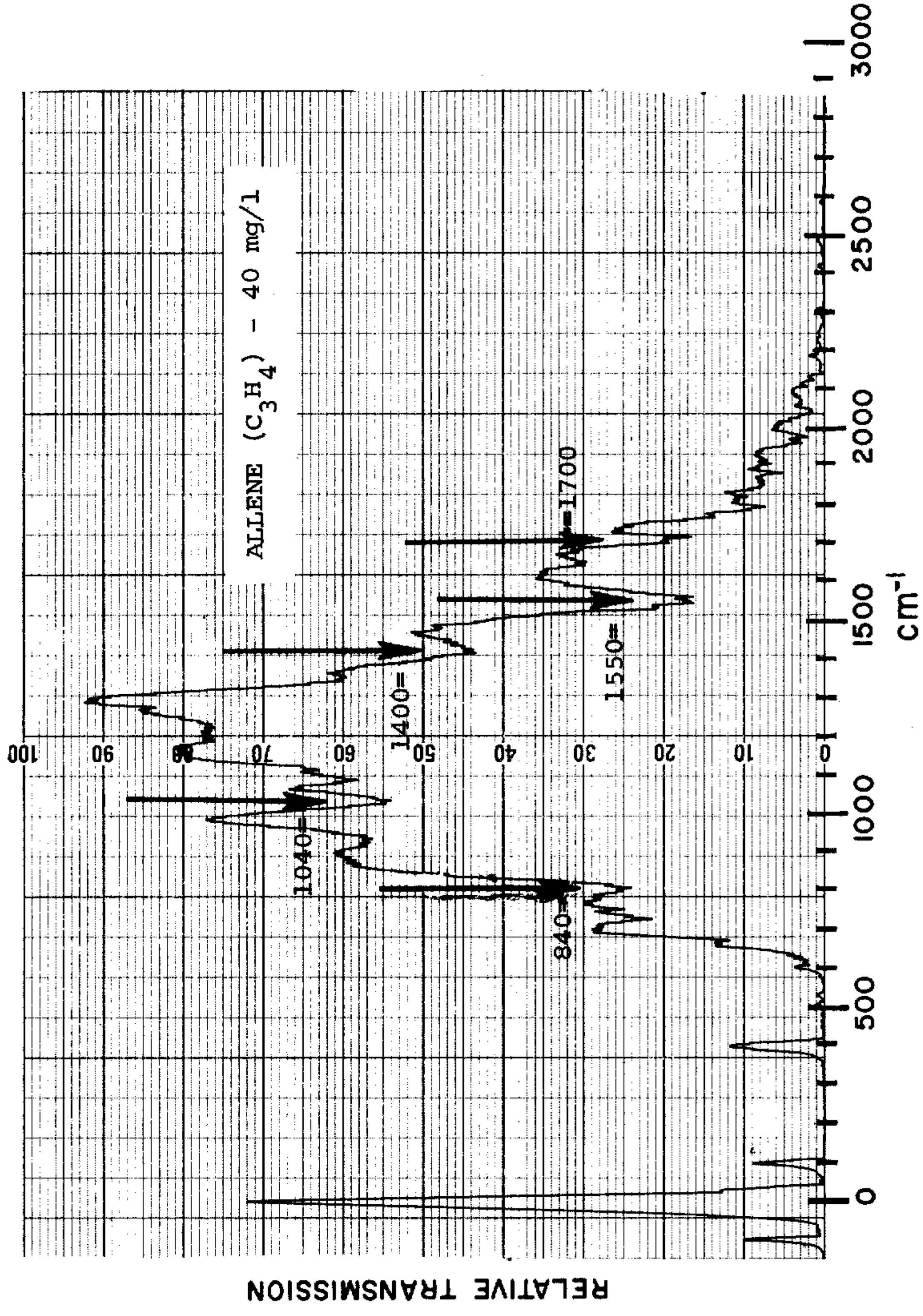

ALLENE (C_3H_4) - 40 mg/1
1700
1550
1400
1040
840
0
500
1000
1500
2000
2500
3000
cm^{-1}
100
90
80
70
60
50
40
30
20
10
0
RELATIVE TRANSMISSION

Figure 20

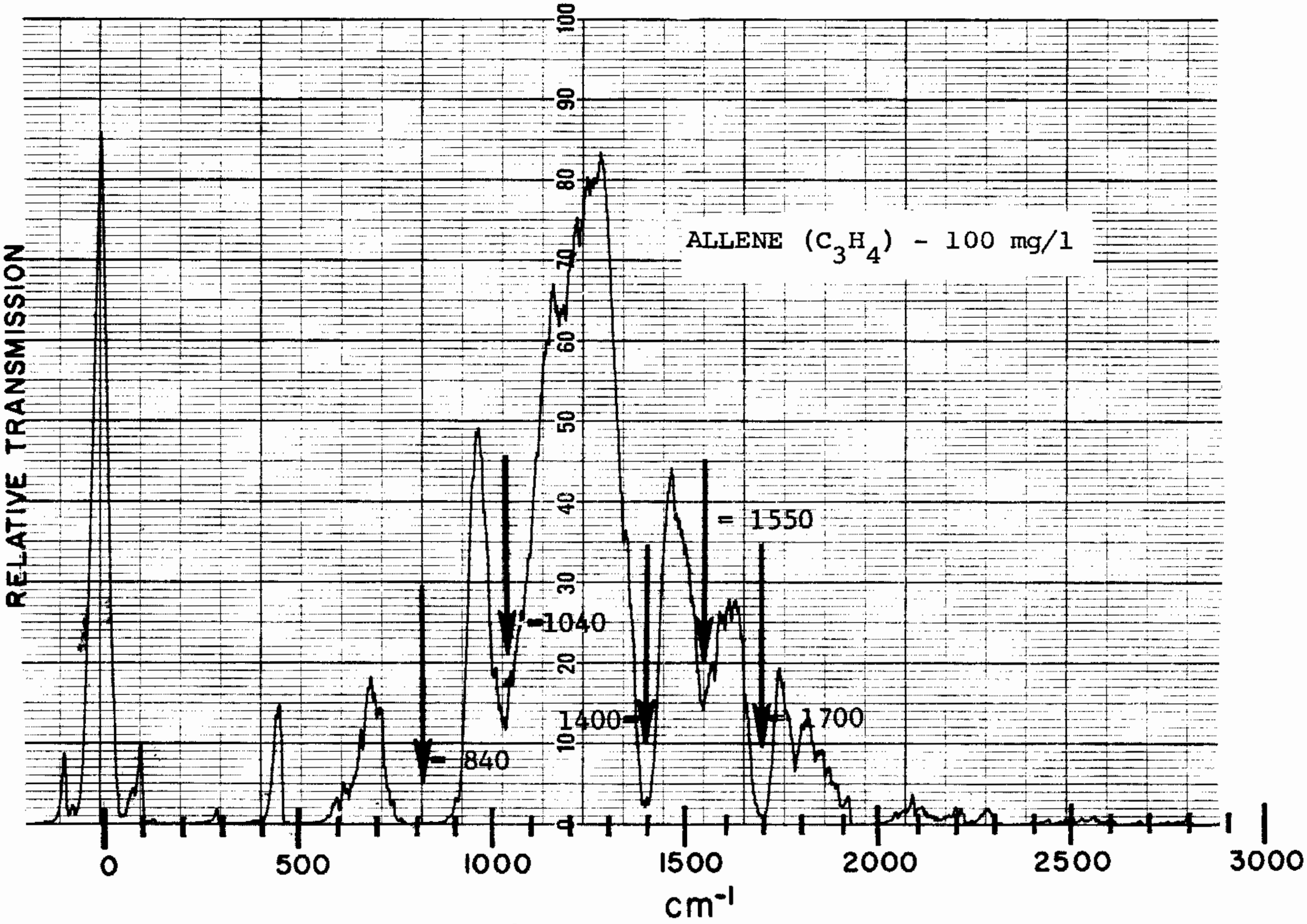

ALLENE (C_3H_4) - 100 mg/1
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
= 1550
1040
1400
1700
840
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 21

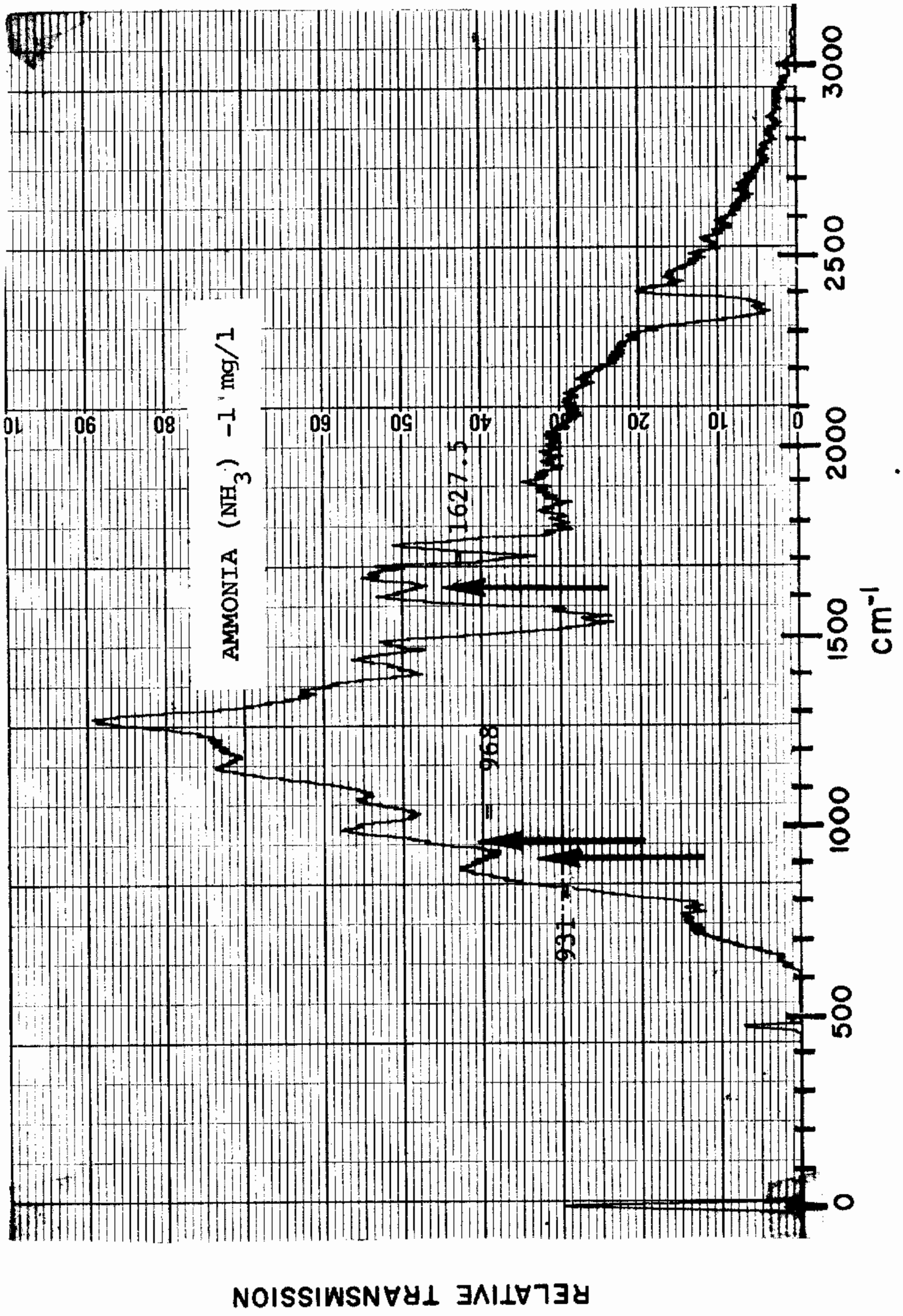

AMMONIA (NH_3) -1 mg/1
1627.5
968
931
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 22

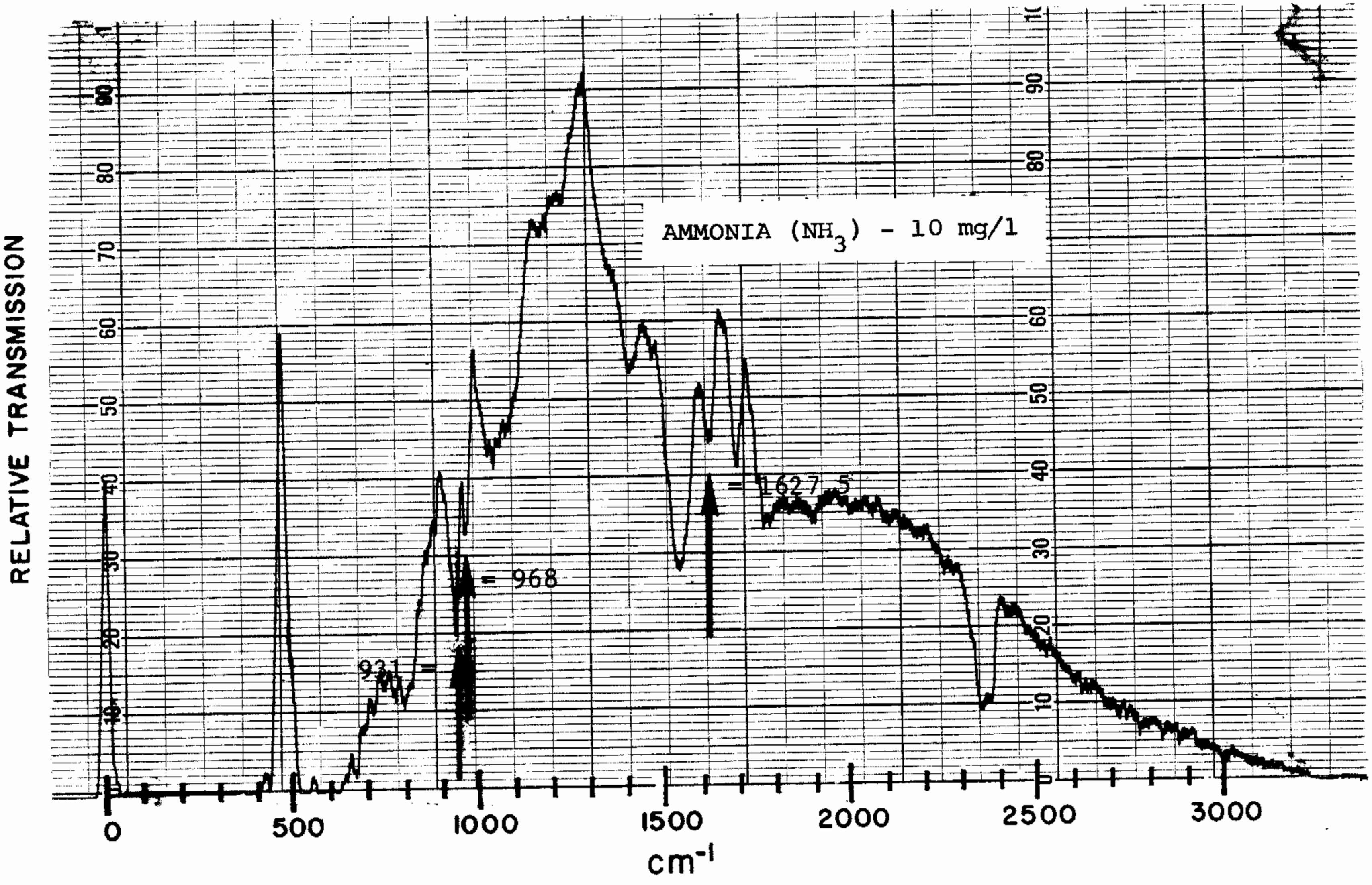

AMMONIA (NH_3) - 10 mg/1
RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
0
500
1000
1500
2000
2500
3000
cm^{-1}
931 =
= 968
= 1627.5

Figure 23

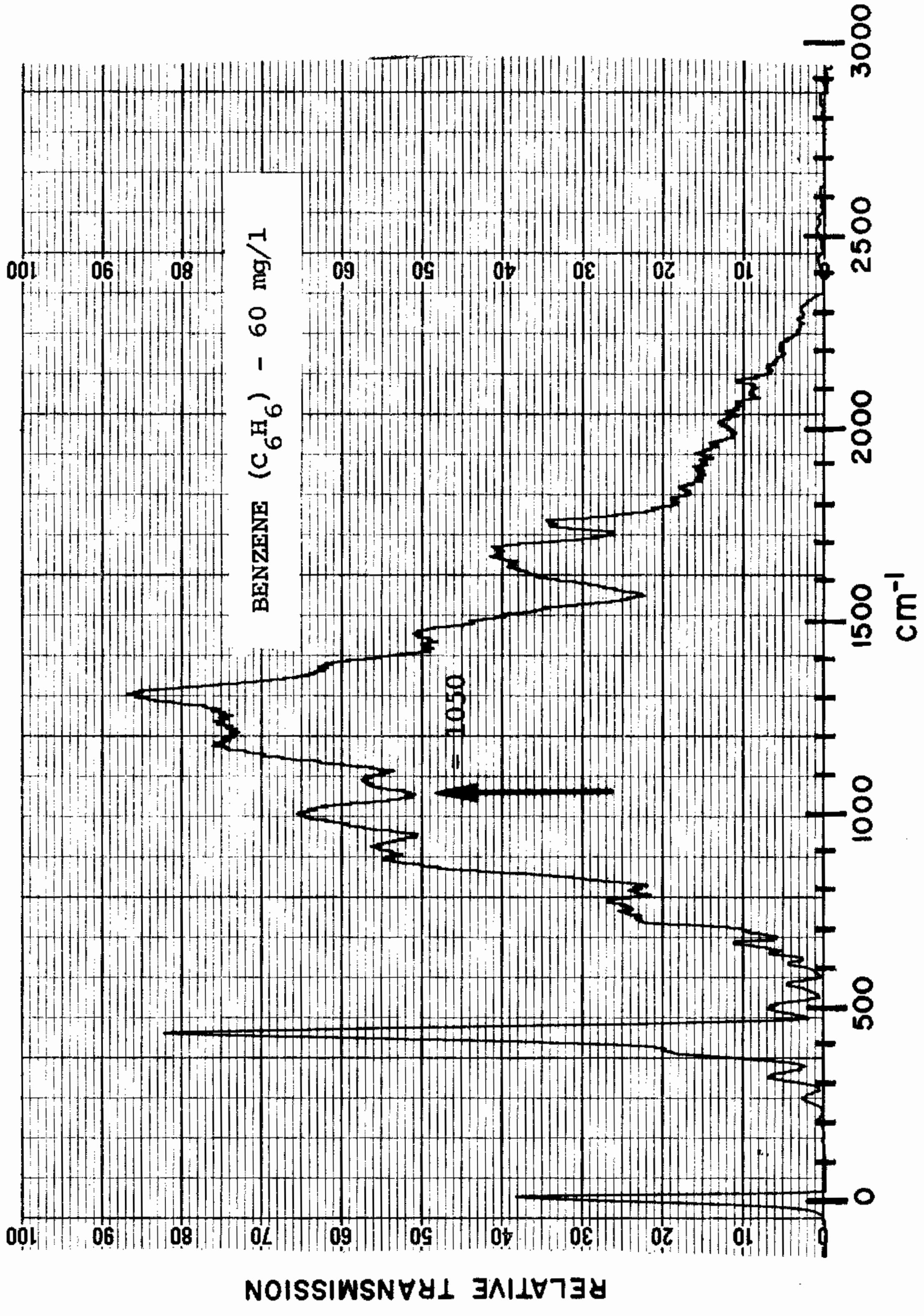

BENZENE (C_6H_6) - 60 mg/1
1050
100
90
80
70
60
50
40
30
20
10
0
RELATIVE TRANSMISSION
0
500
1000
1500
2000
2500
3000
cm-1

Figure 24

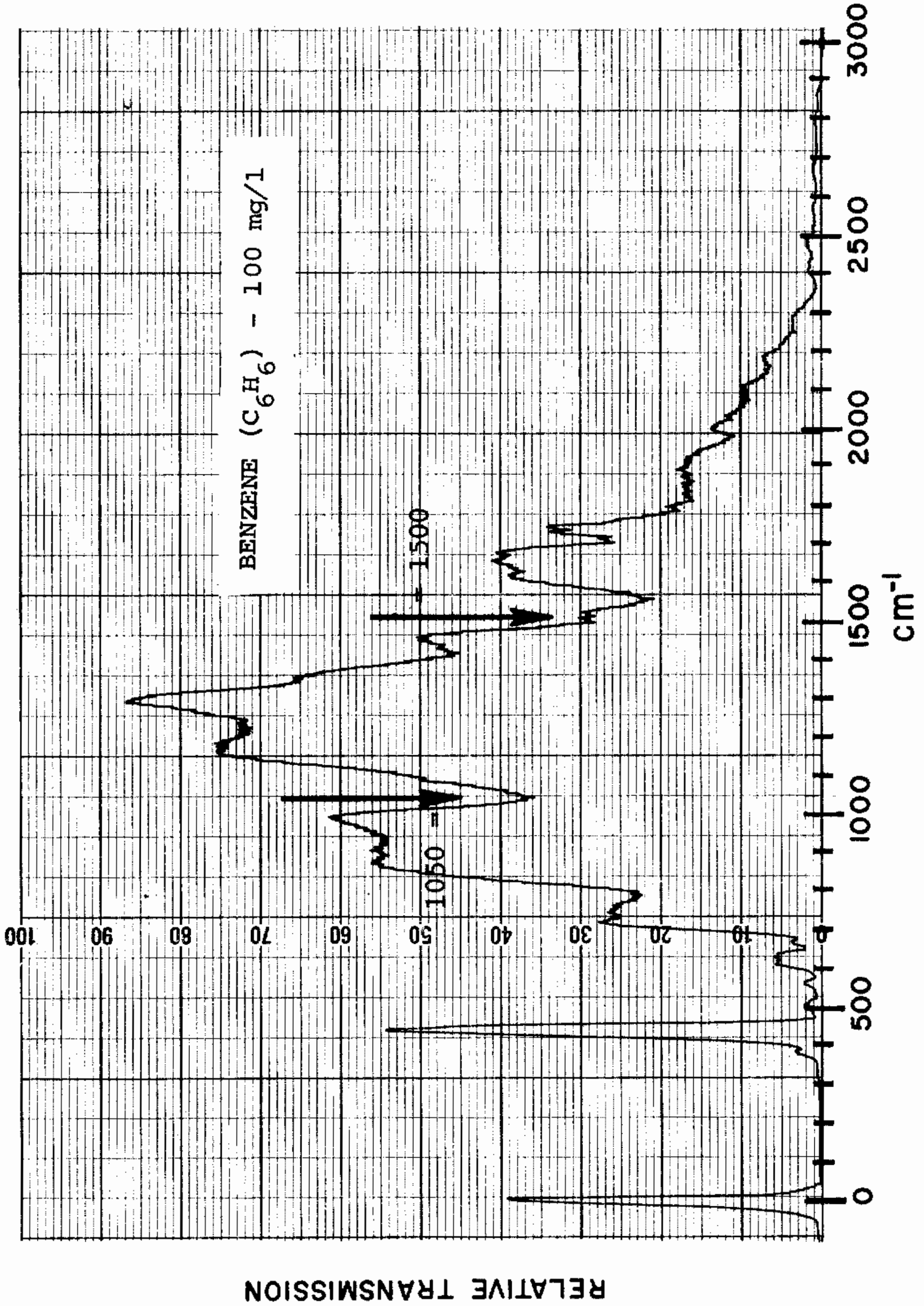

BENZENE (C_6H_6) - 100 mg/1
1500
1050
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 25

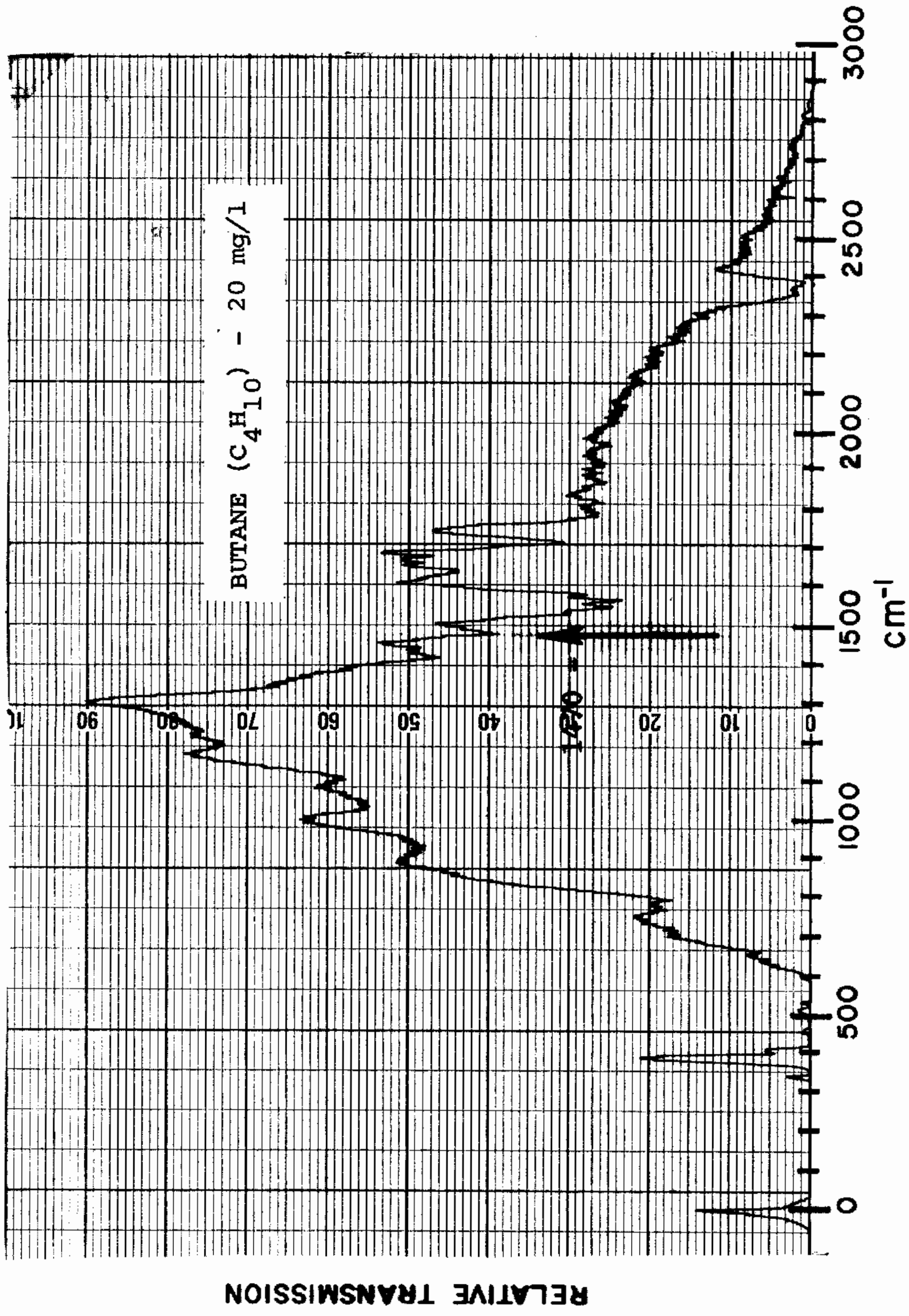

BUTANE (C_4H_{10}) - 20 mg/1
0
500
1000
1500
2000
2500
3000
cm^{-1}
0
10
20
1470
40
50
60
70
80
90
RELATIVE TRANSMISSION

Figure 26

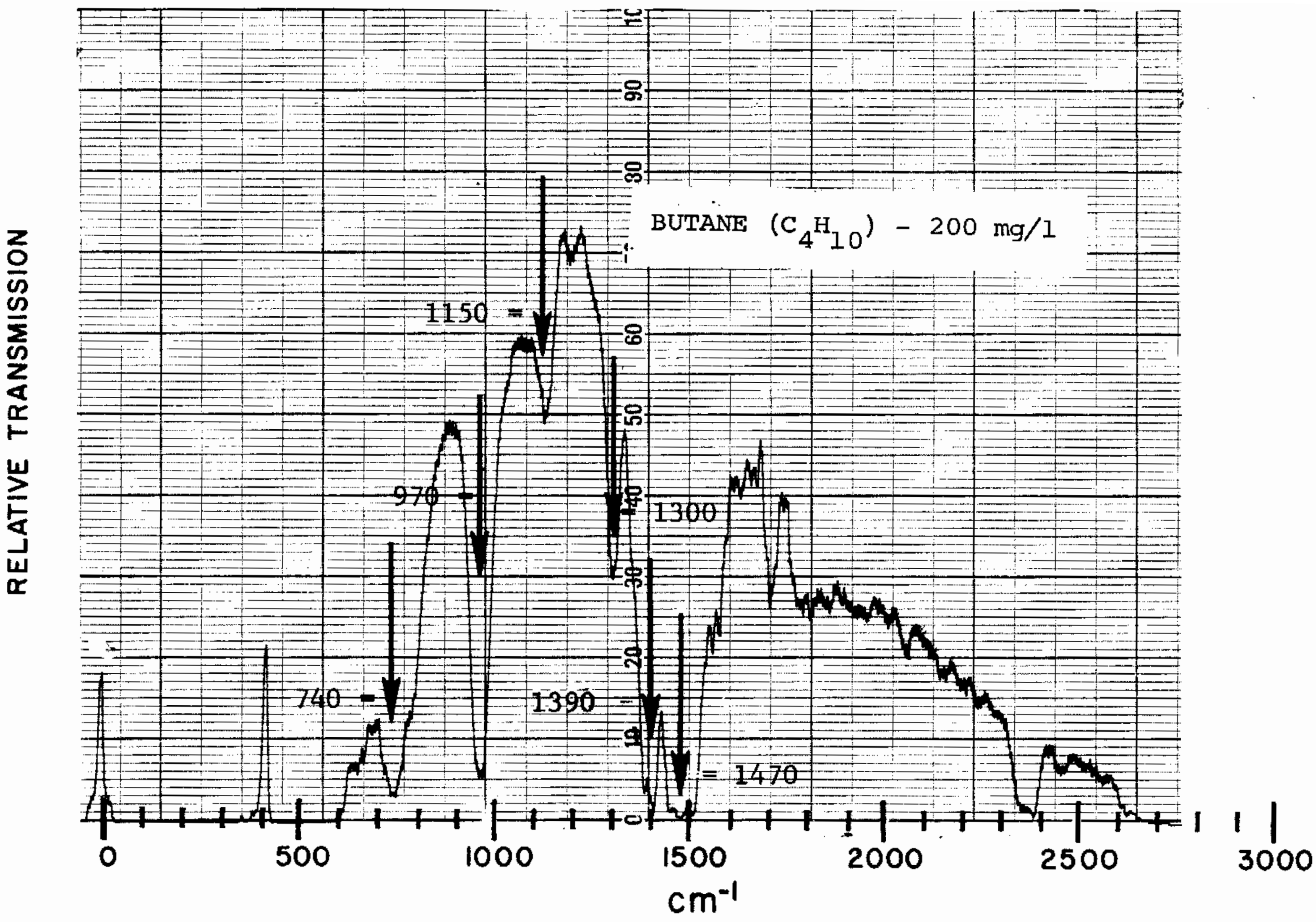
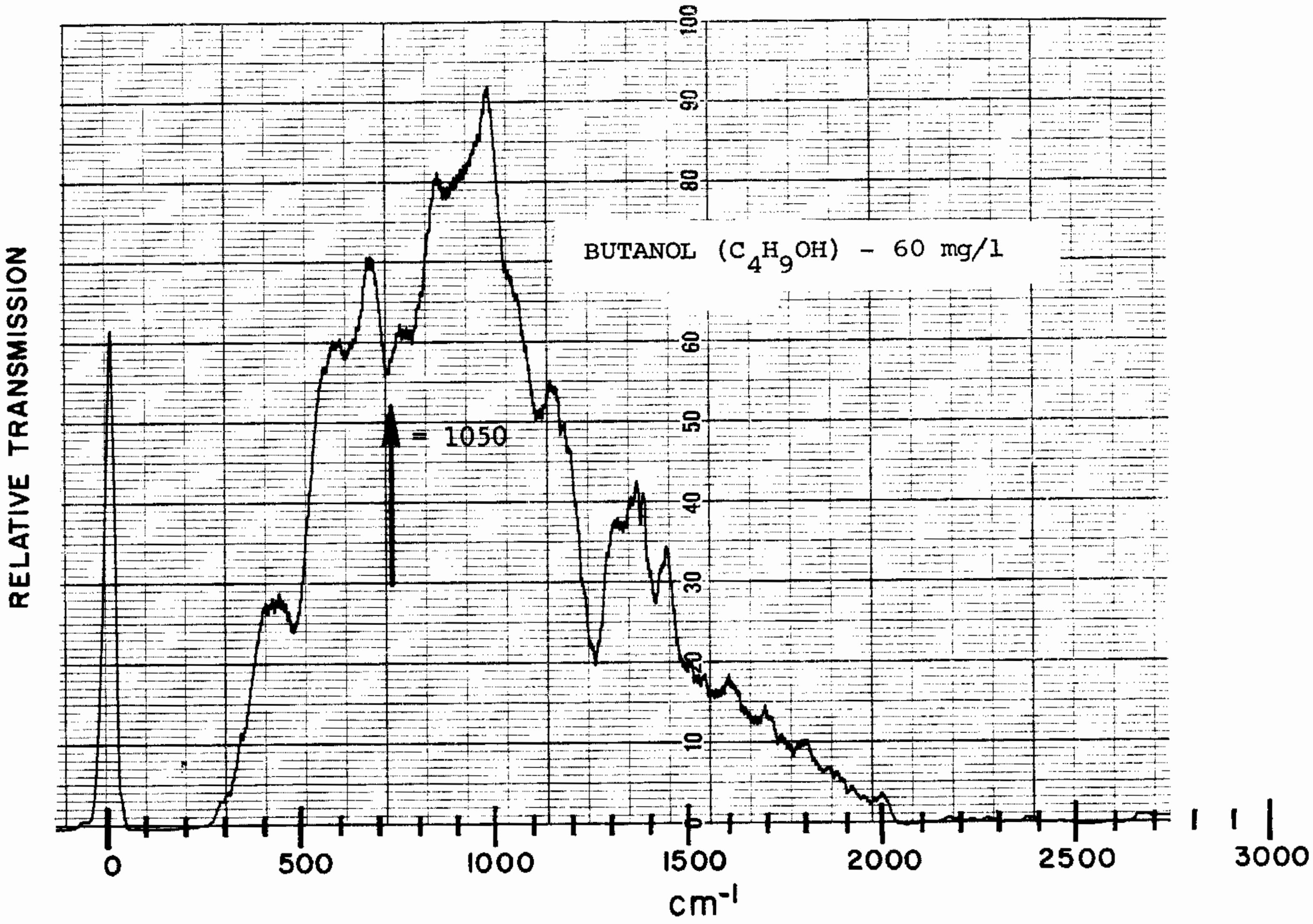

BUTANE (C_4H_{10}) - 200 mg/1
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
1150
970
740
1300
1390
1470
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 27



BUTANOL (C_4H_9OH) - 60 mg/1

Figure 28

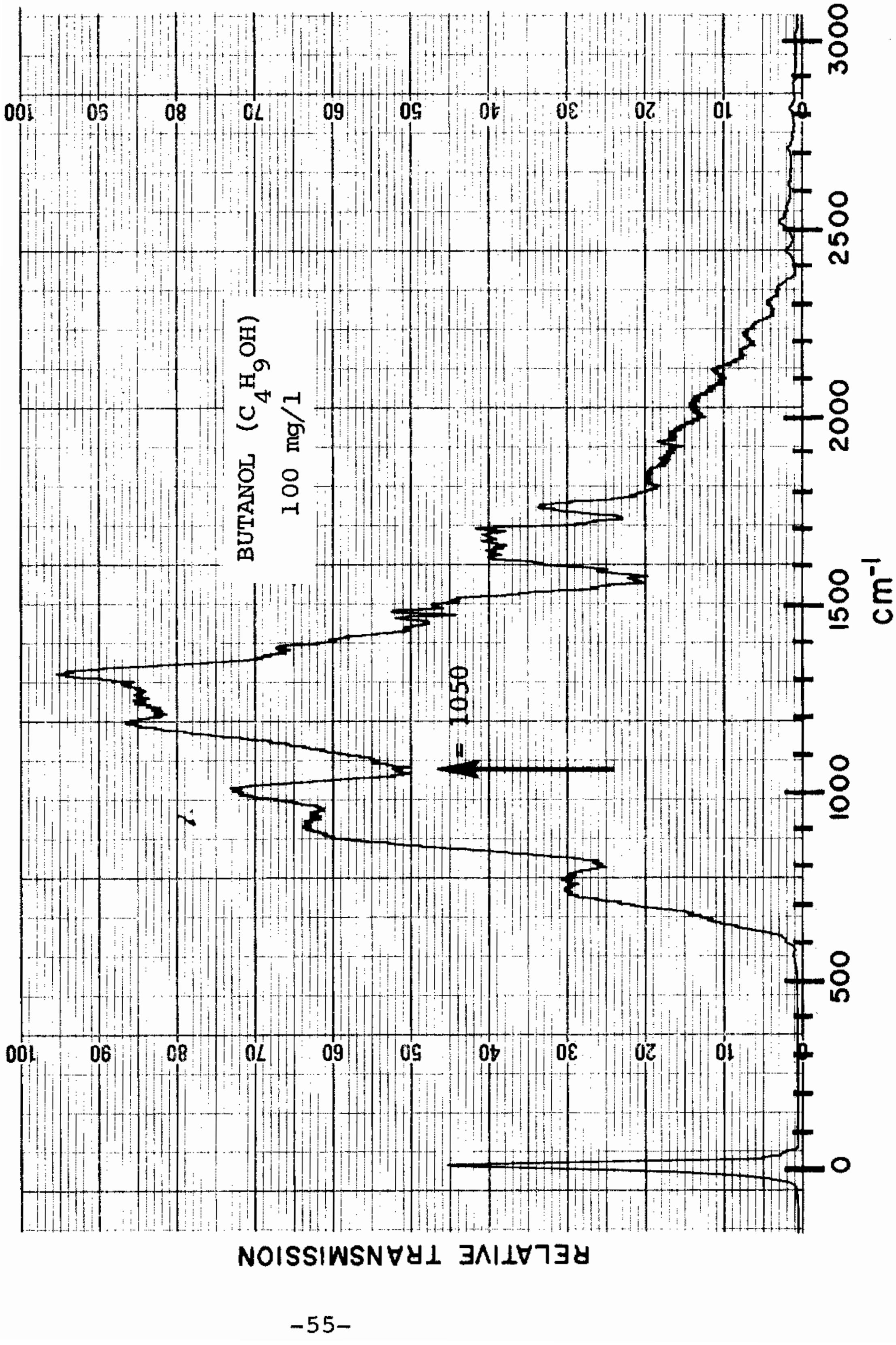

BUTANOL (C_4H_9OH)
100 mg/l
1050
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 29

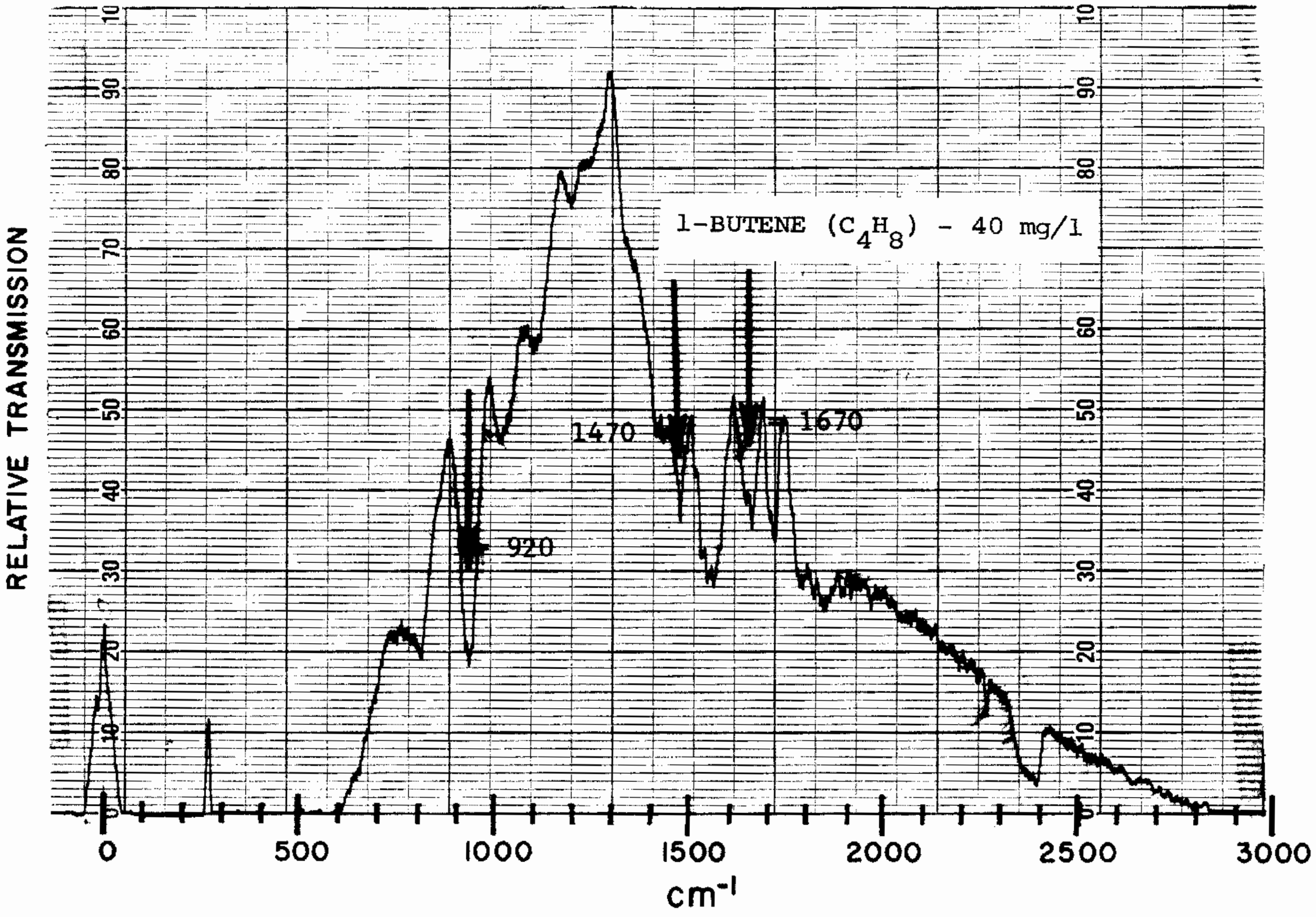

1-BUTENE (C_4H_8) - 40 mg/l
RELATIVE TRANSMISSION
10
90
80
70
60
50
40
30
20
10
0
920
1470
1670
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 30

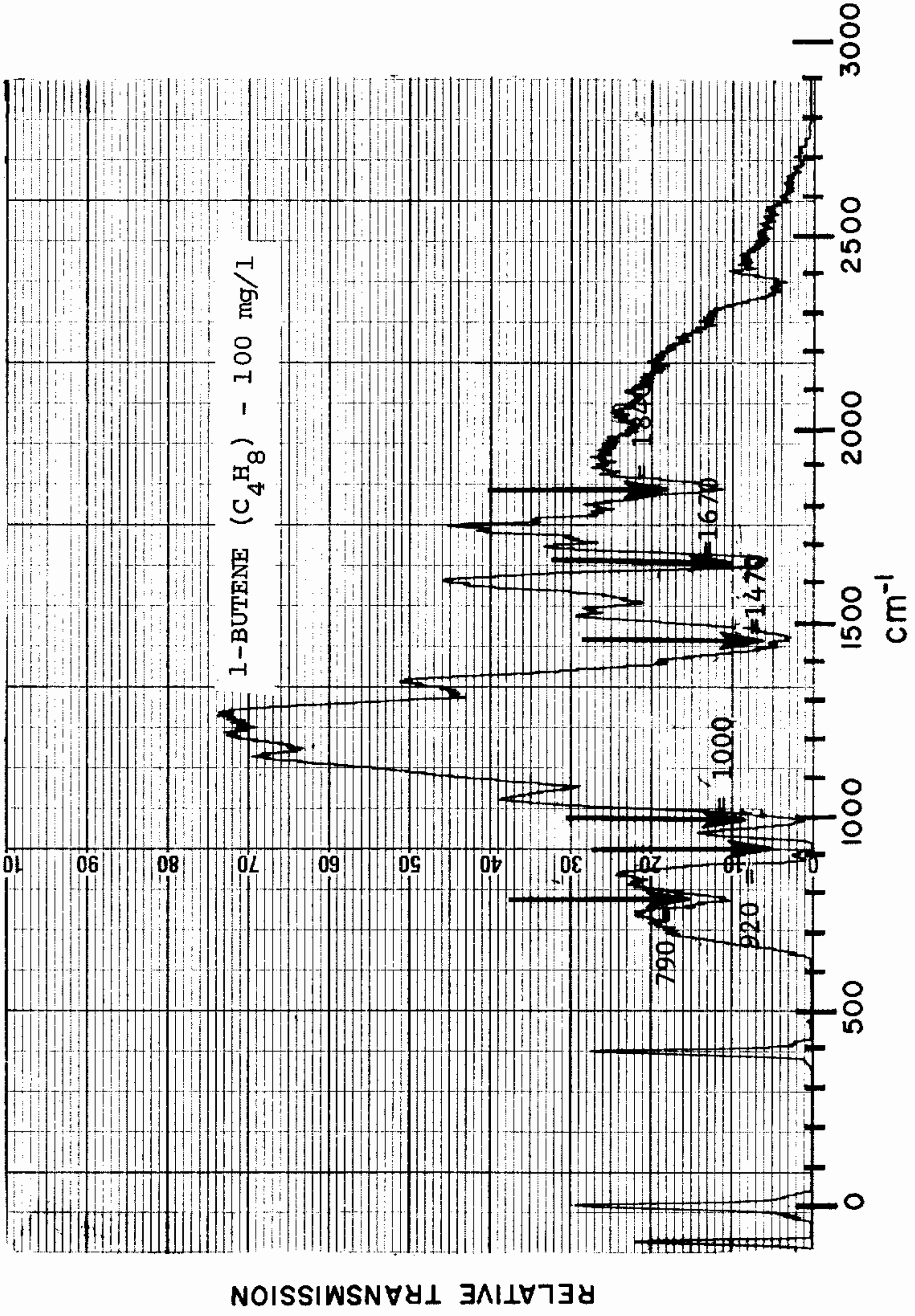
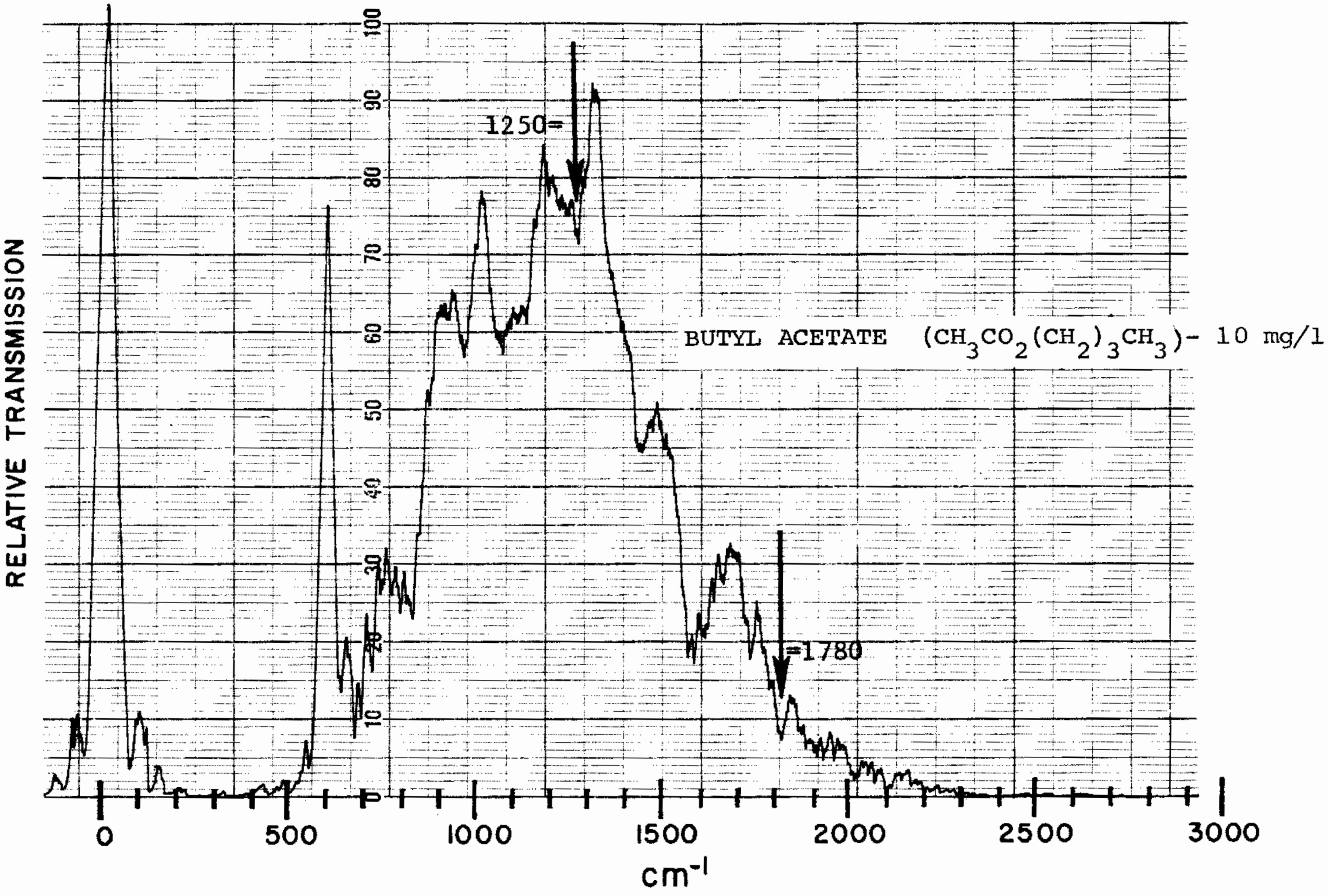
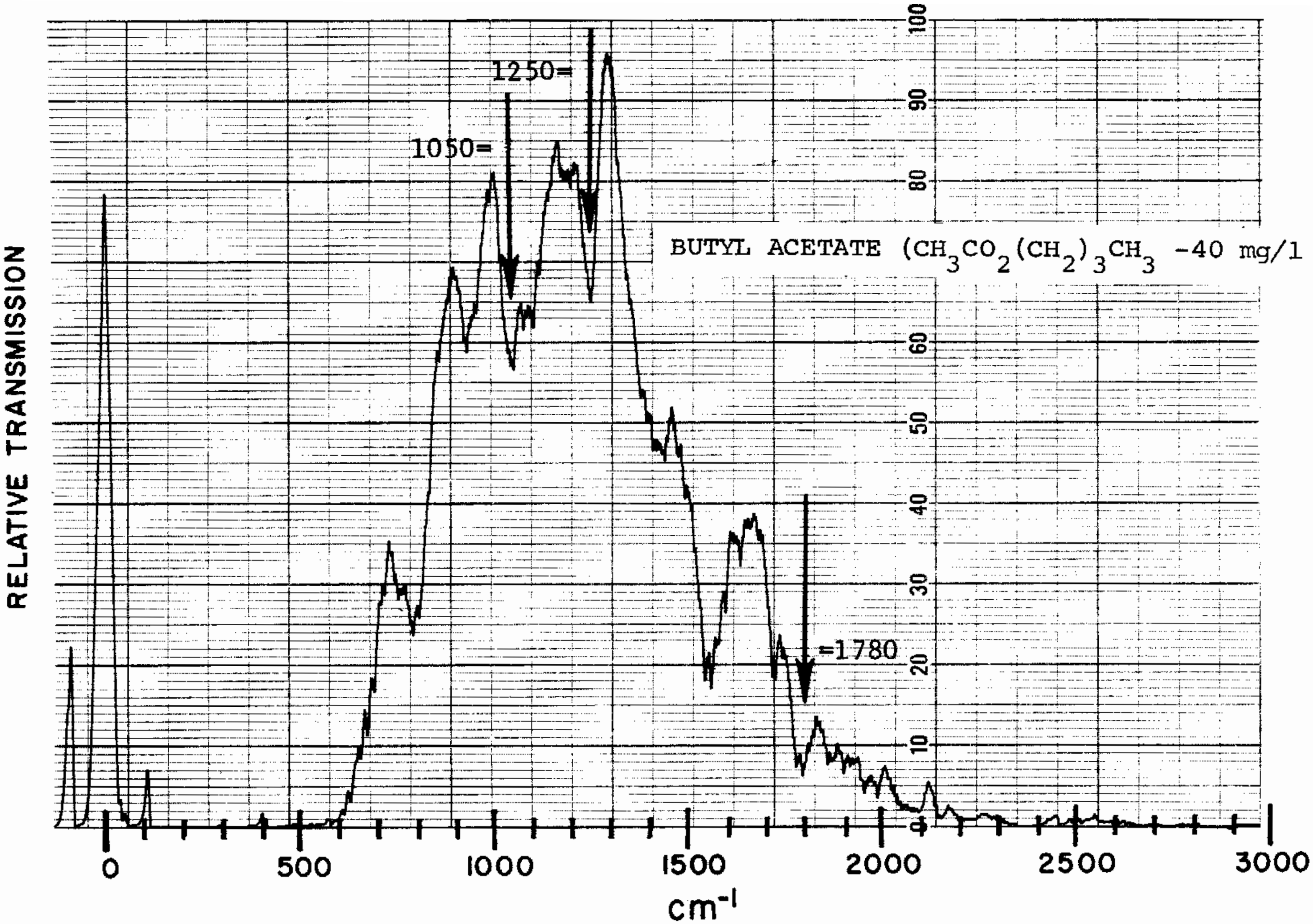

1-BUTENE (C_4H_8) - 100 mg/1
RELATIVE TRANSMISSION
10
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹
790
920
1000
1470
1670
1840

Figure 31



BUTYL ACETATE $(CH_3CO_2(CH_2)_3CH_3)$- 10 mg/l

Figure 32



BUTYL ACETATE $(CH_3CO_2(CH_2)_3CH_3$ -40 mg/1

Figure 33

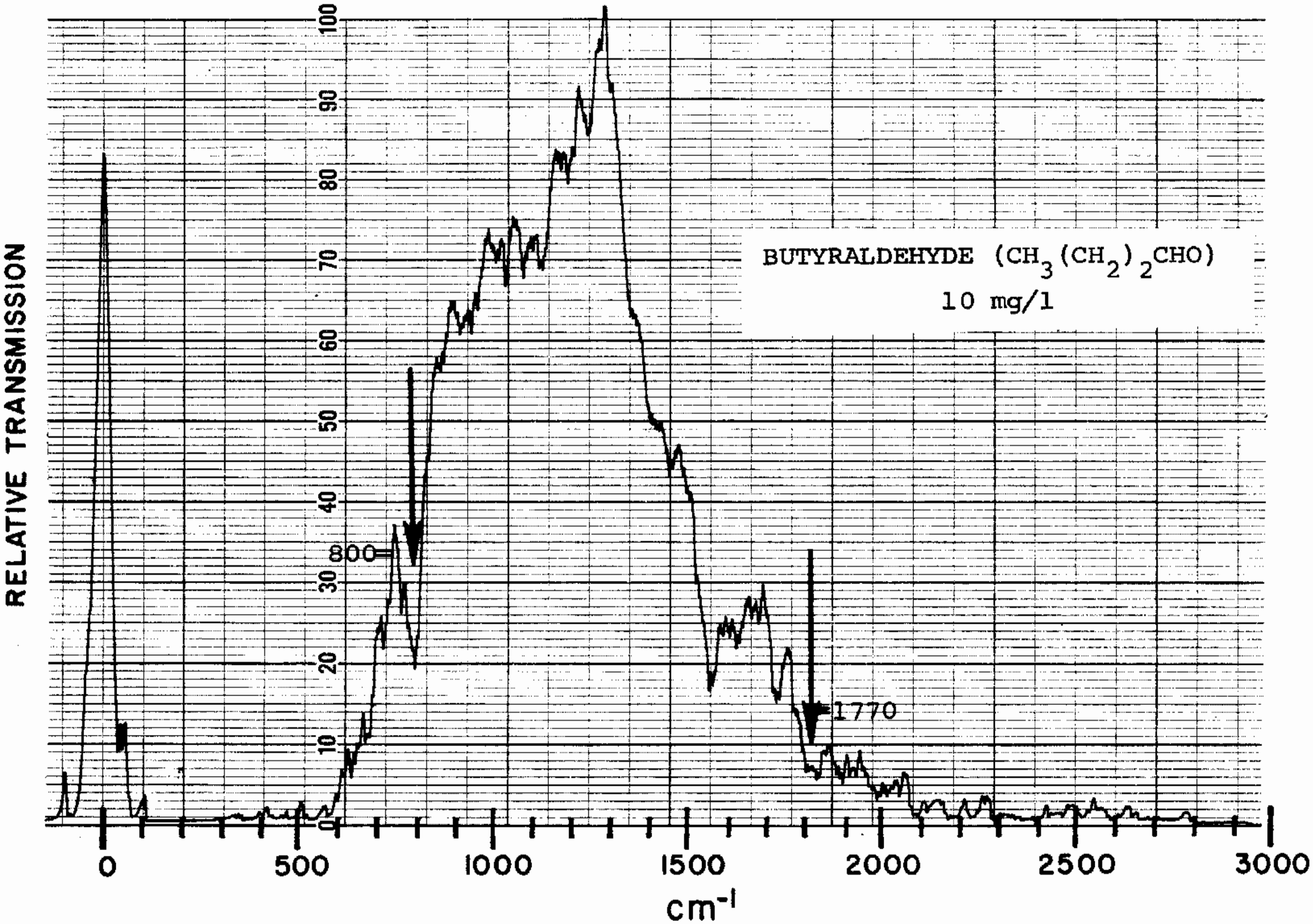

BUTYRALDEHYDE $(CH_3(CH_2)_2CHO)$
10 mg/l
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
800
1770
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 34

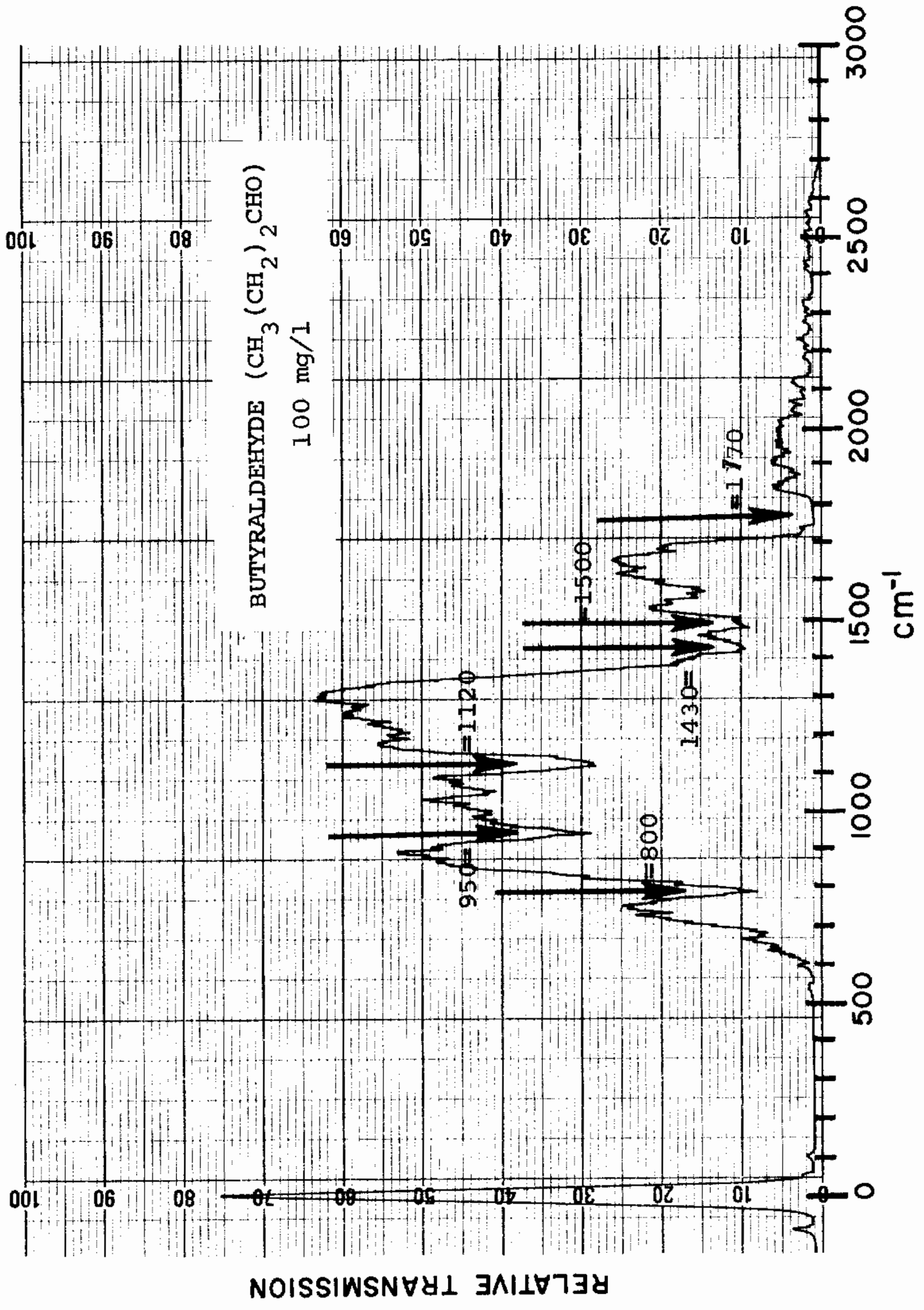

BUTYRALDEHYDE $(CH_3(CH_2)_2CHO)$
100 mg/1
1770
1500
1430
1120
950
800
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100

Figure 35

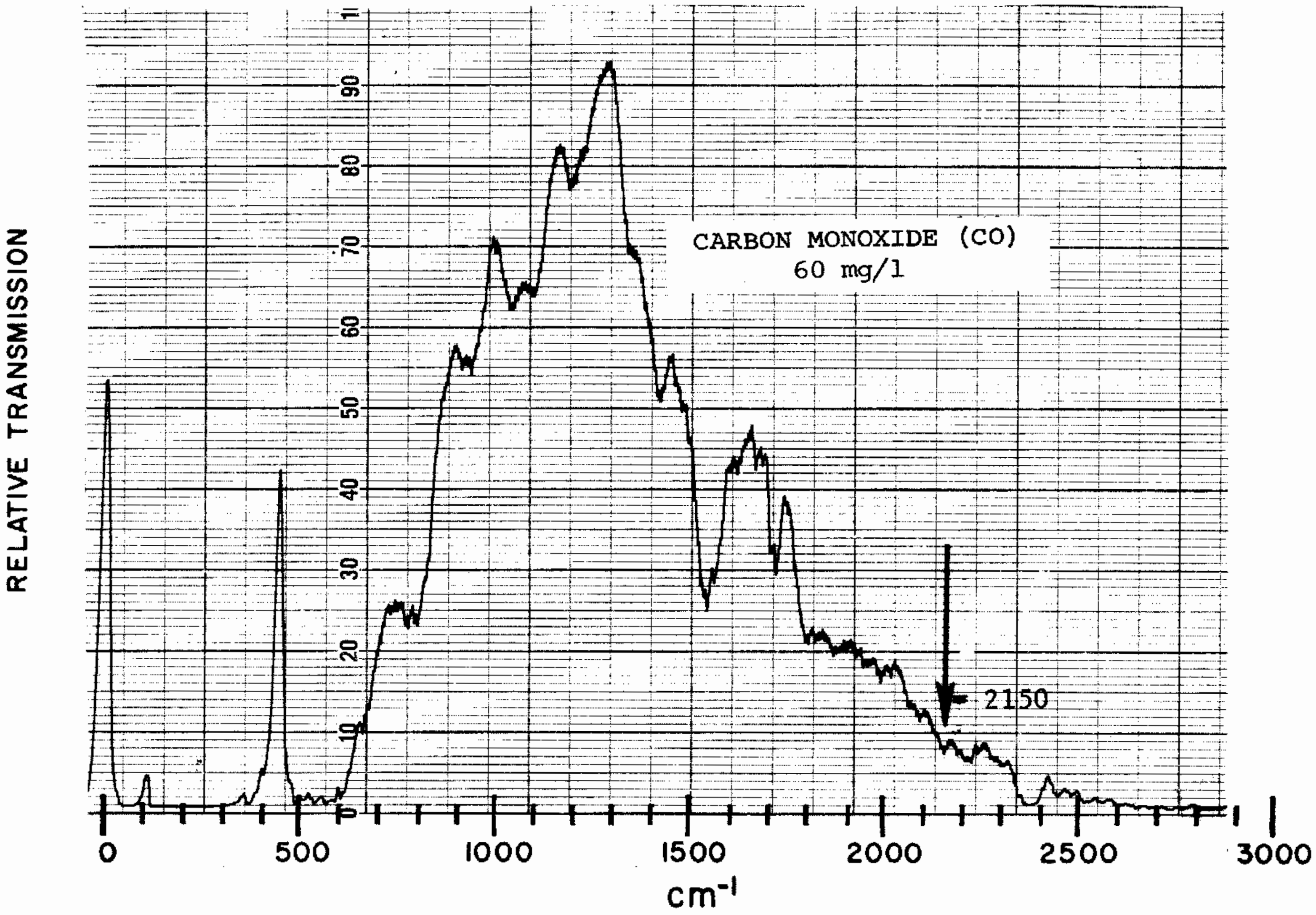

RELATIVE TRANSMISSION
CARBON MONOXIDE (CO)
60 mg/1
2150
0
10
20
30
40
50
60
70
80
90
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 36

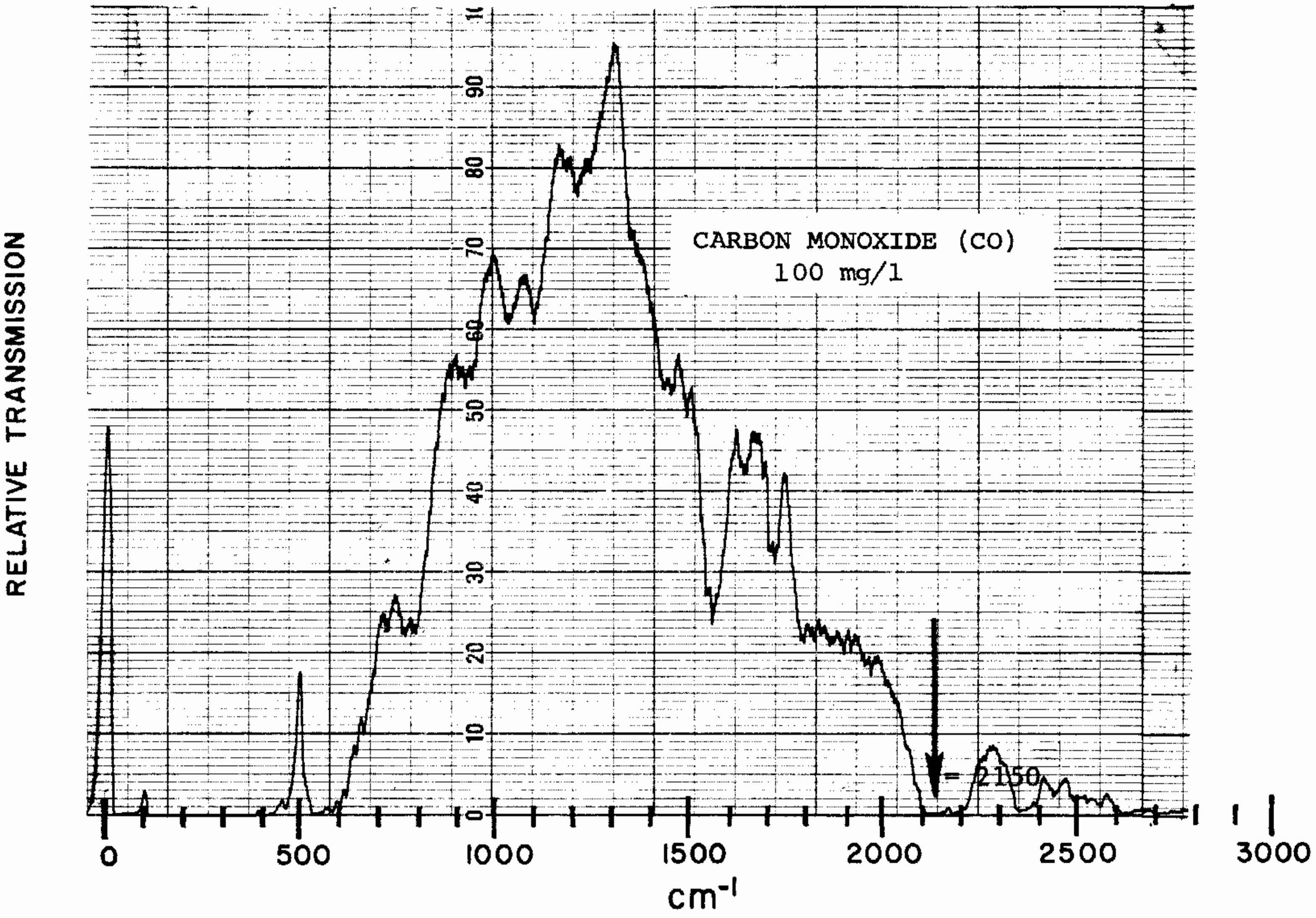

RELATIVE TRANSMISSION
10
90
80
70
60
50
40
30
20
10
0
CARBON MONOXIDE (CO)
100 mg/l
2150
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 37

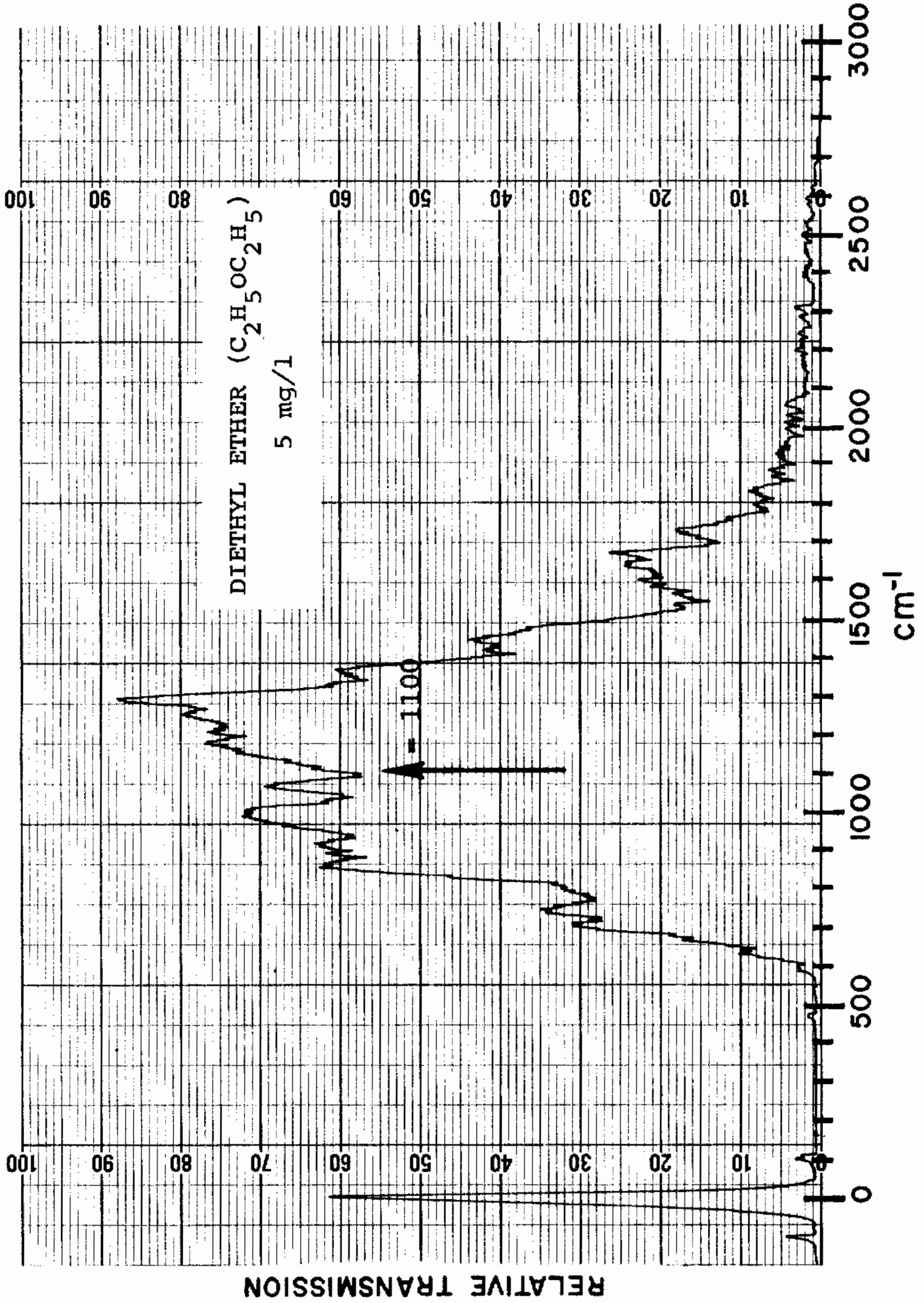

DIETHYL ETHER ($C_2H_5OC_2H_5$)
5 mg/1
1100
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 38

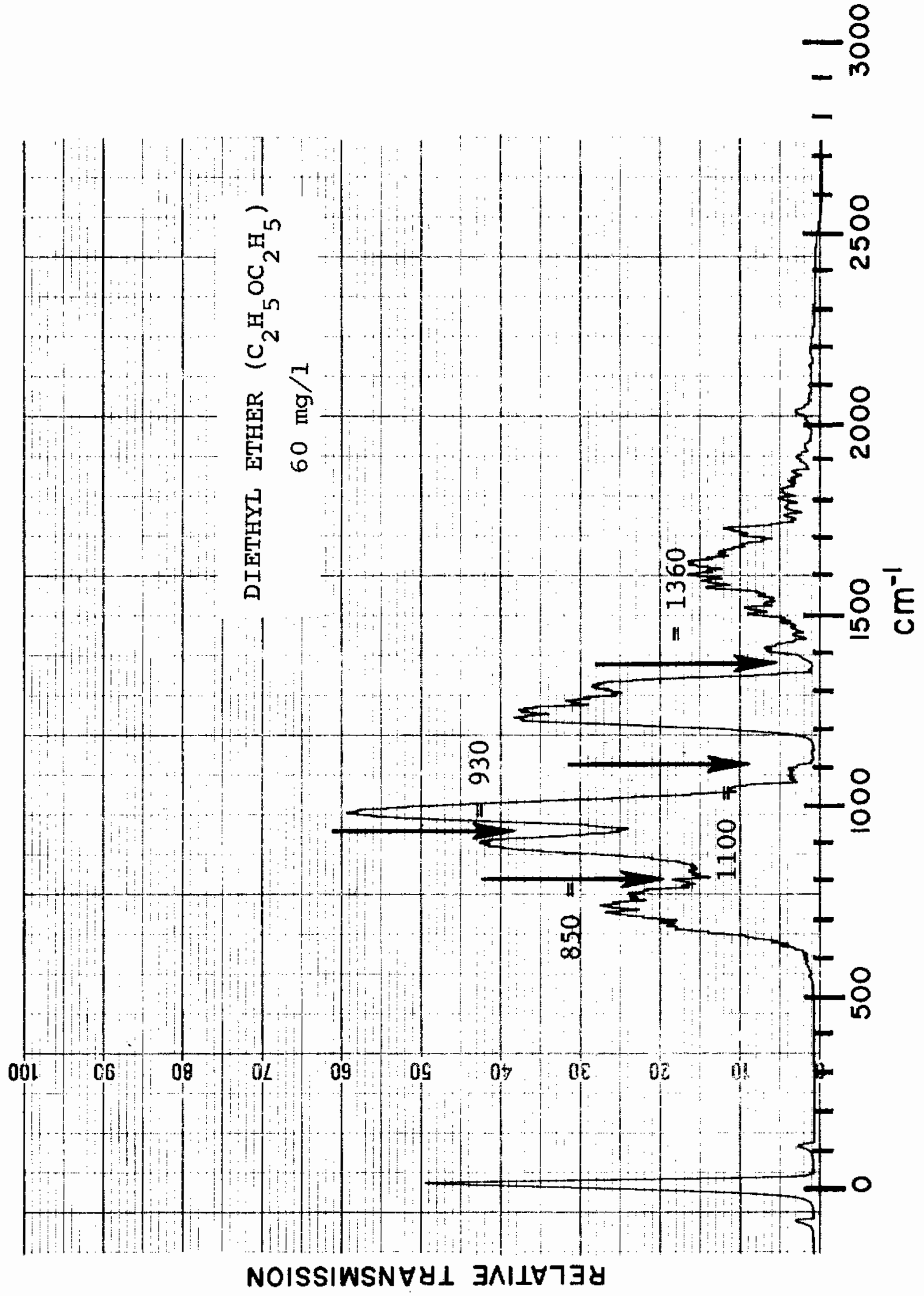

DIETHYL ETHER ($C_2H_5OC_2H_5$)
60 mg/l
930
850
1100
1360
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 39

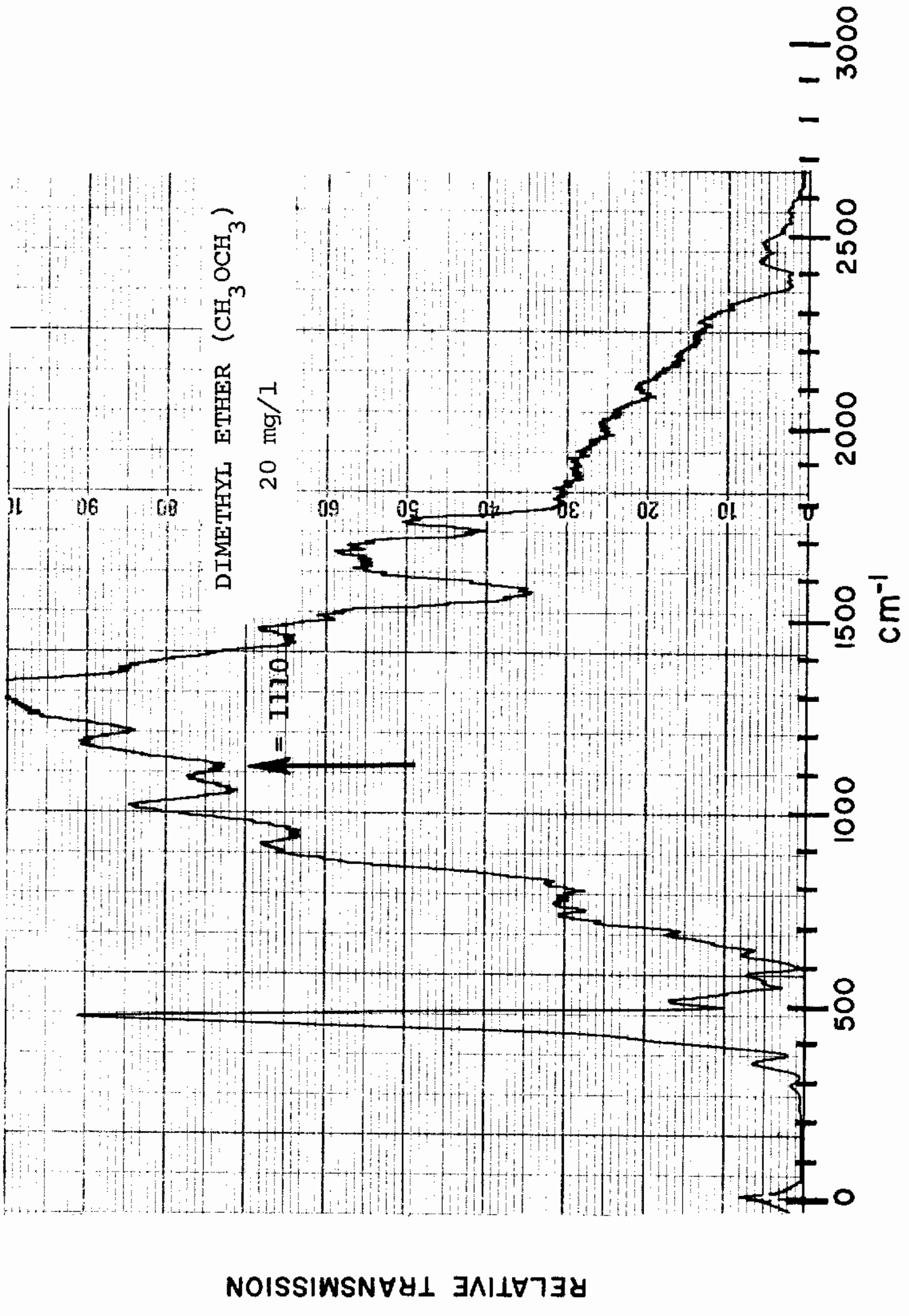

DIMETHYL ETHER (CH_3OCH_3)
20 mg/l
= 1110
10
20
30
40
50
60
80
90
10
0
500
1000
1500
2000
2500
3000
cm⁻¹
RELATIVE TRANSMISSION

Figure 40

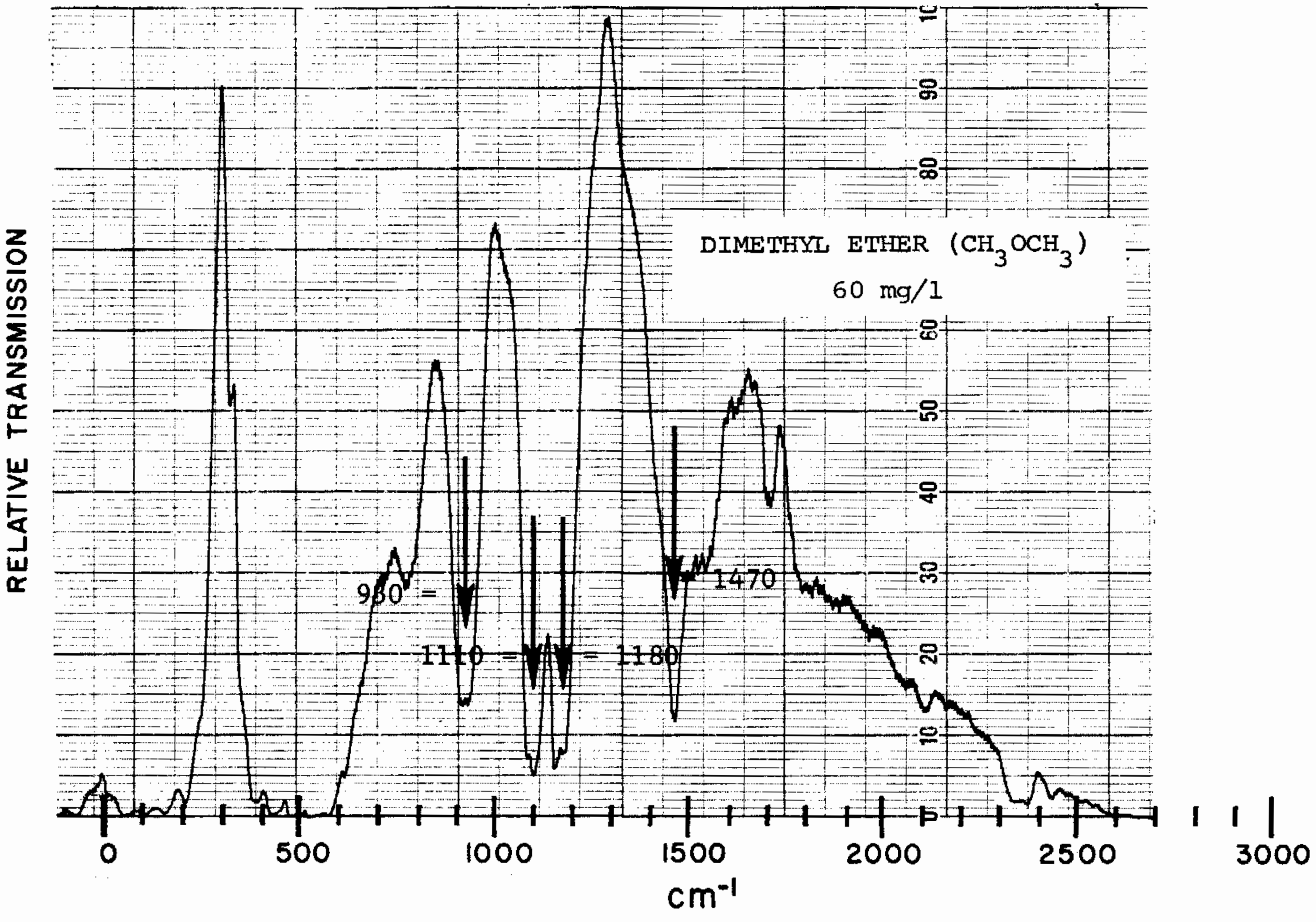
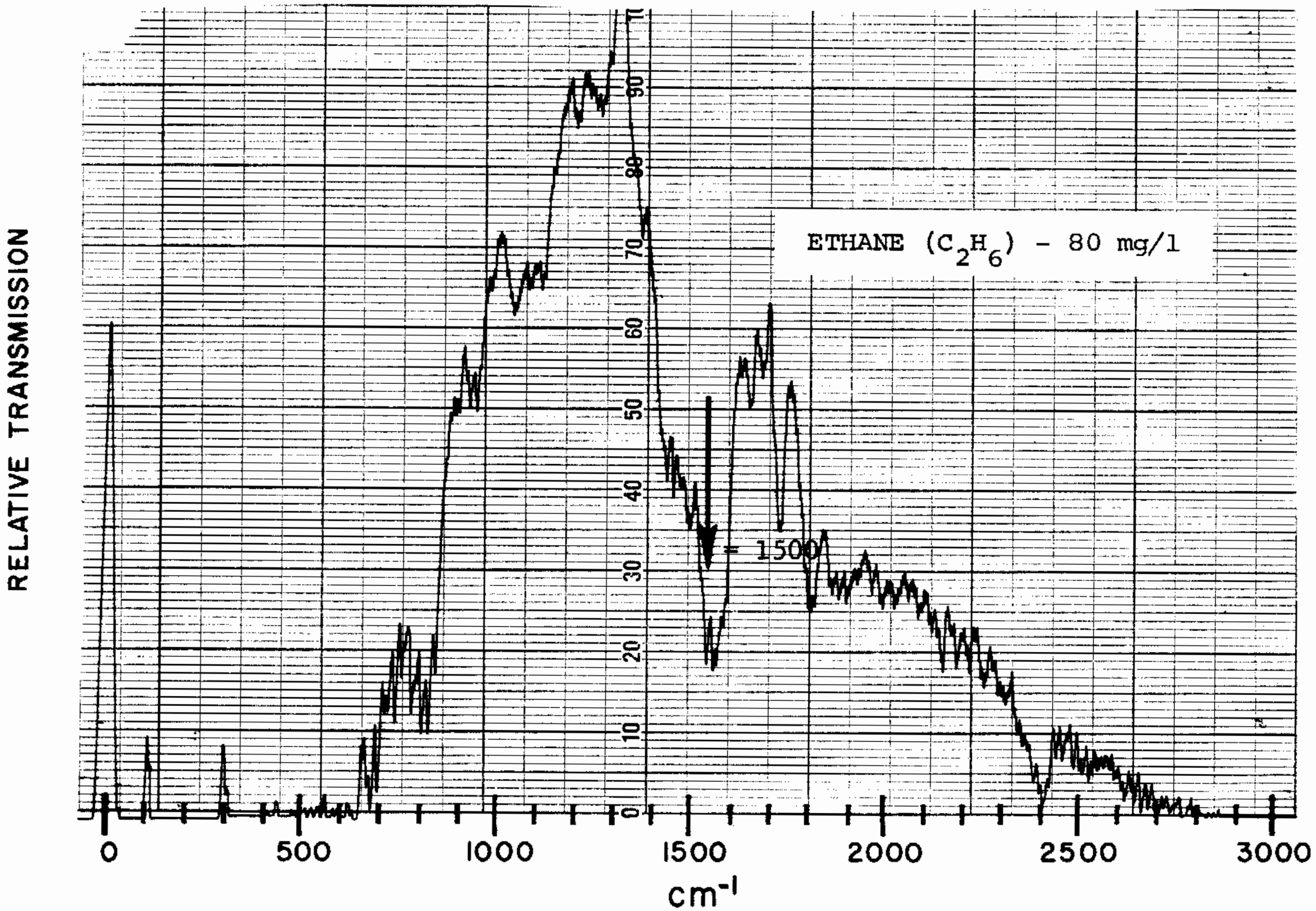

DIMETHYL ETHER (CH_3OCH_3)
60 mg/1
RELATIVE TRANSMISSION
10
90
80
60
50
40
30
20
10
0
930 =
1110 =
= 1180
1470
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 41



ETHANE (C_2H_6) - 80 mg/l

Figure 42

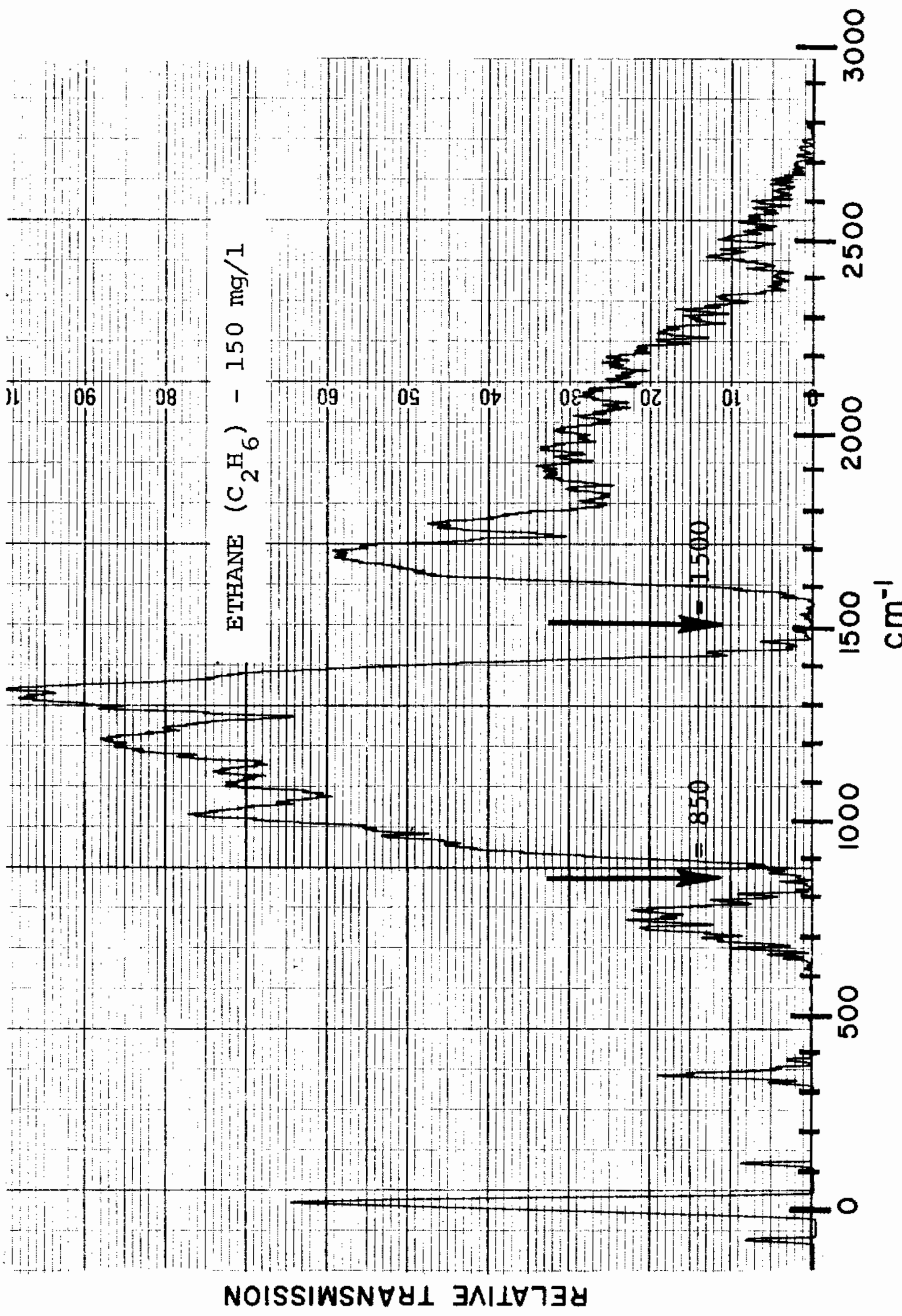

ETHANE (C_2H_6) - 150 mg/1
1500
850
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 43

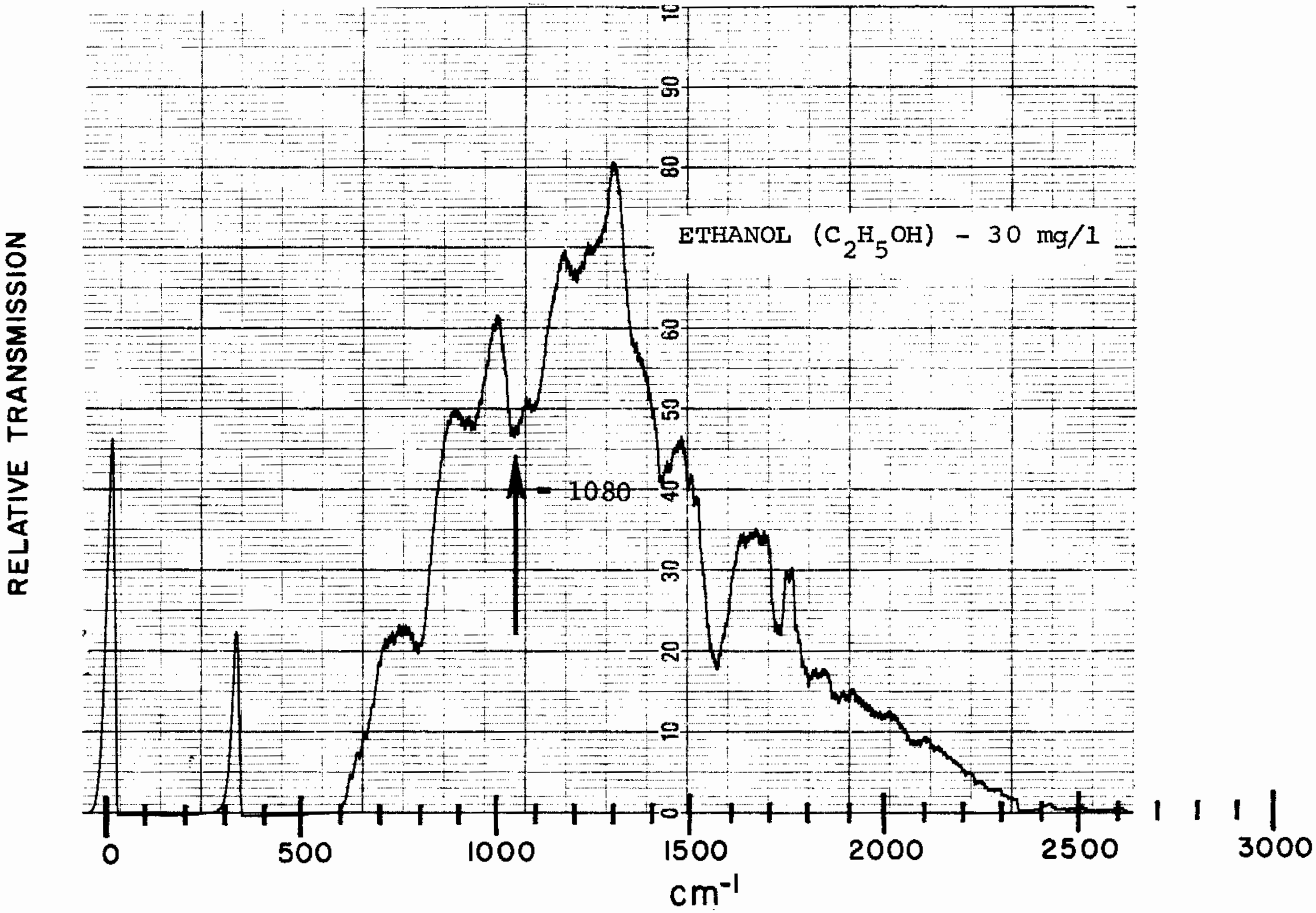

RELATIVE TRANSMISSION
ETHANOL (C_2H_5OH) - 30 mg/1
1080
10
90
80
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 44

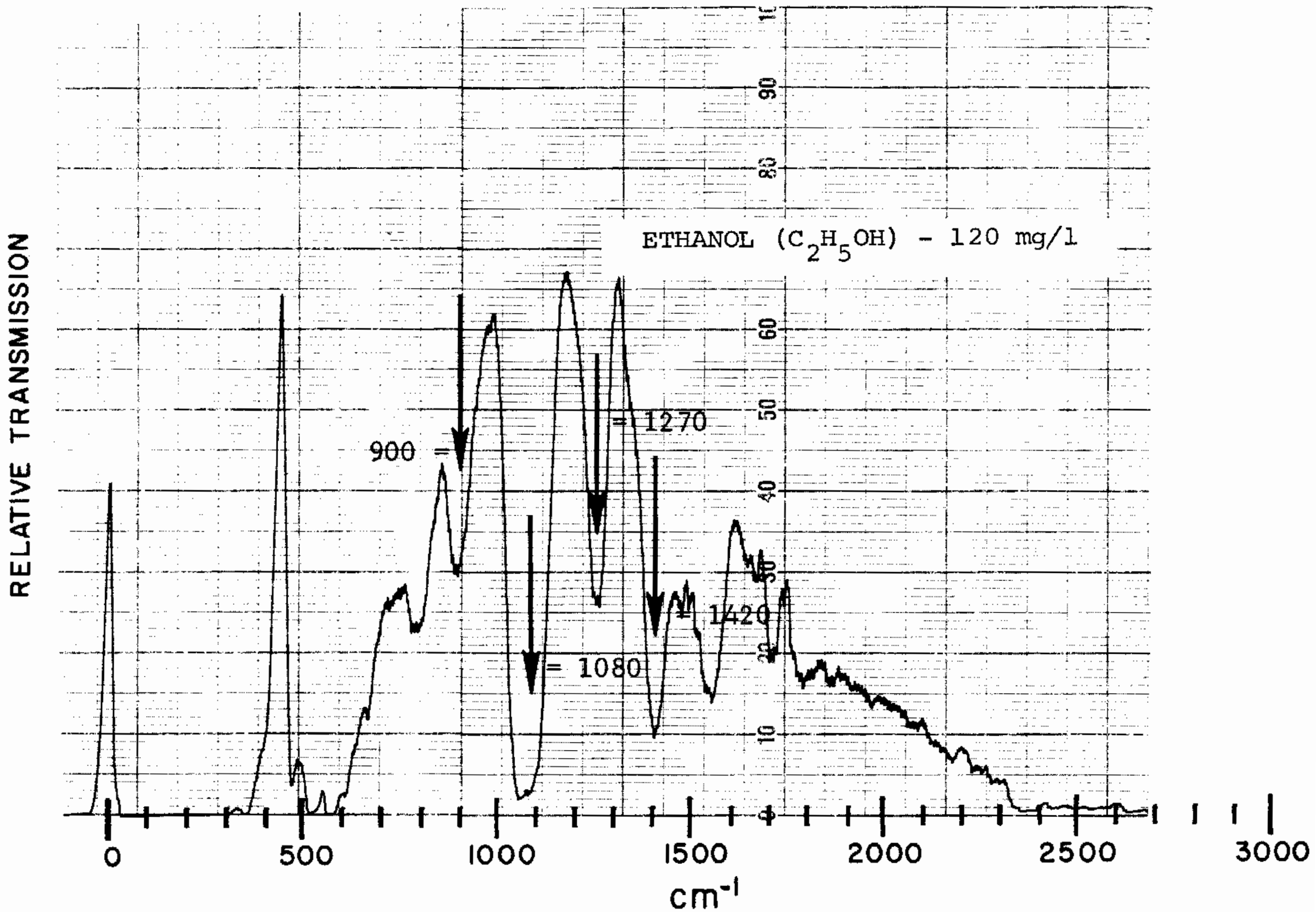

ETHANOL (C_2H_5OH) - 120 mg/l

Figure 45

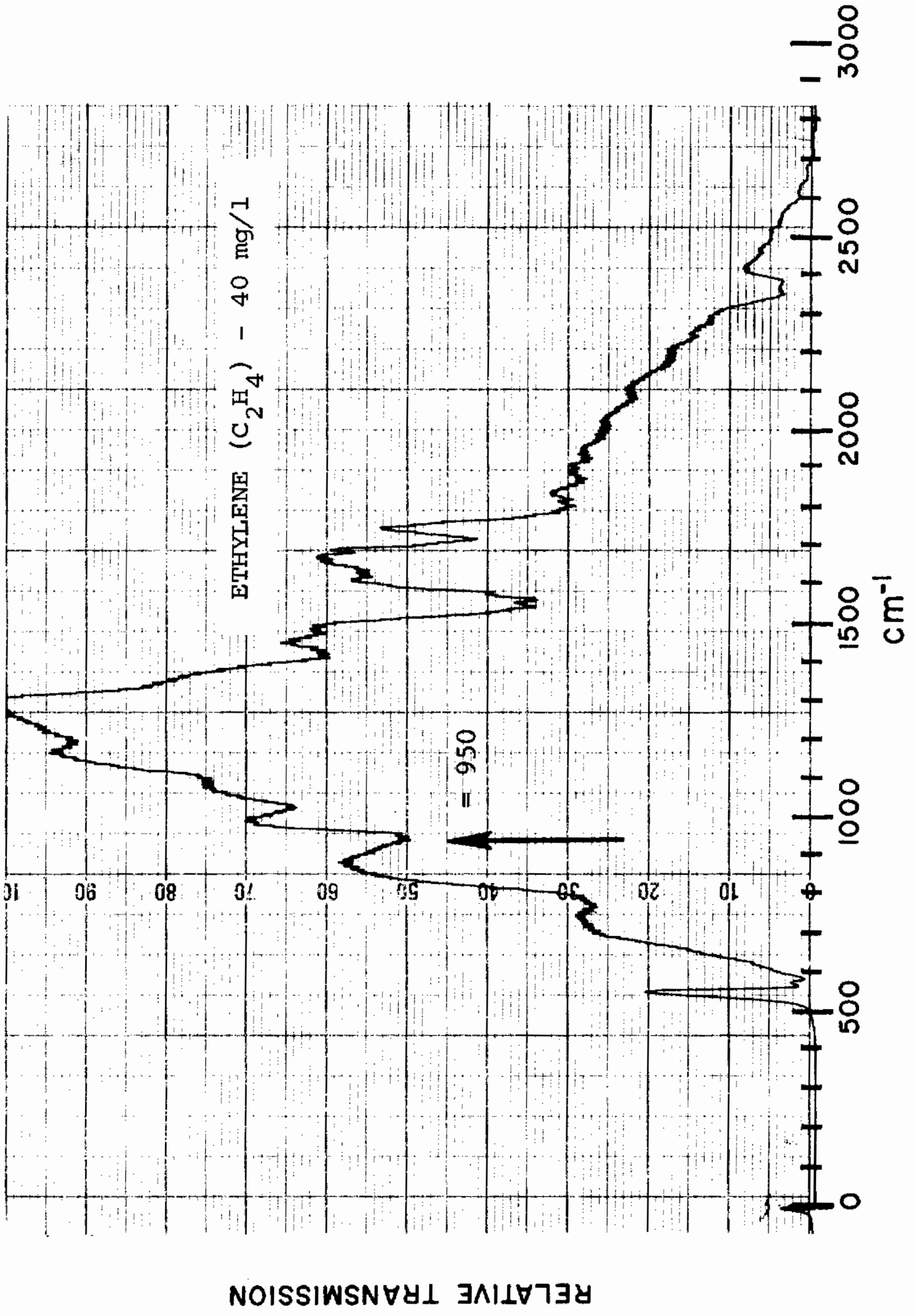

ETHYLENE (C_2H_4) - 40 mg/l
= 950
RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
10
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 46

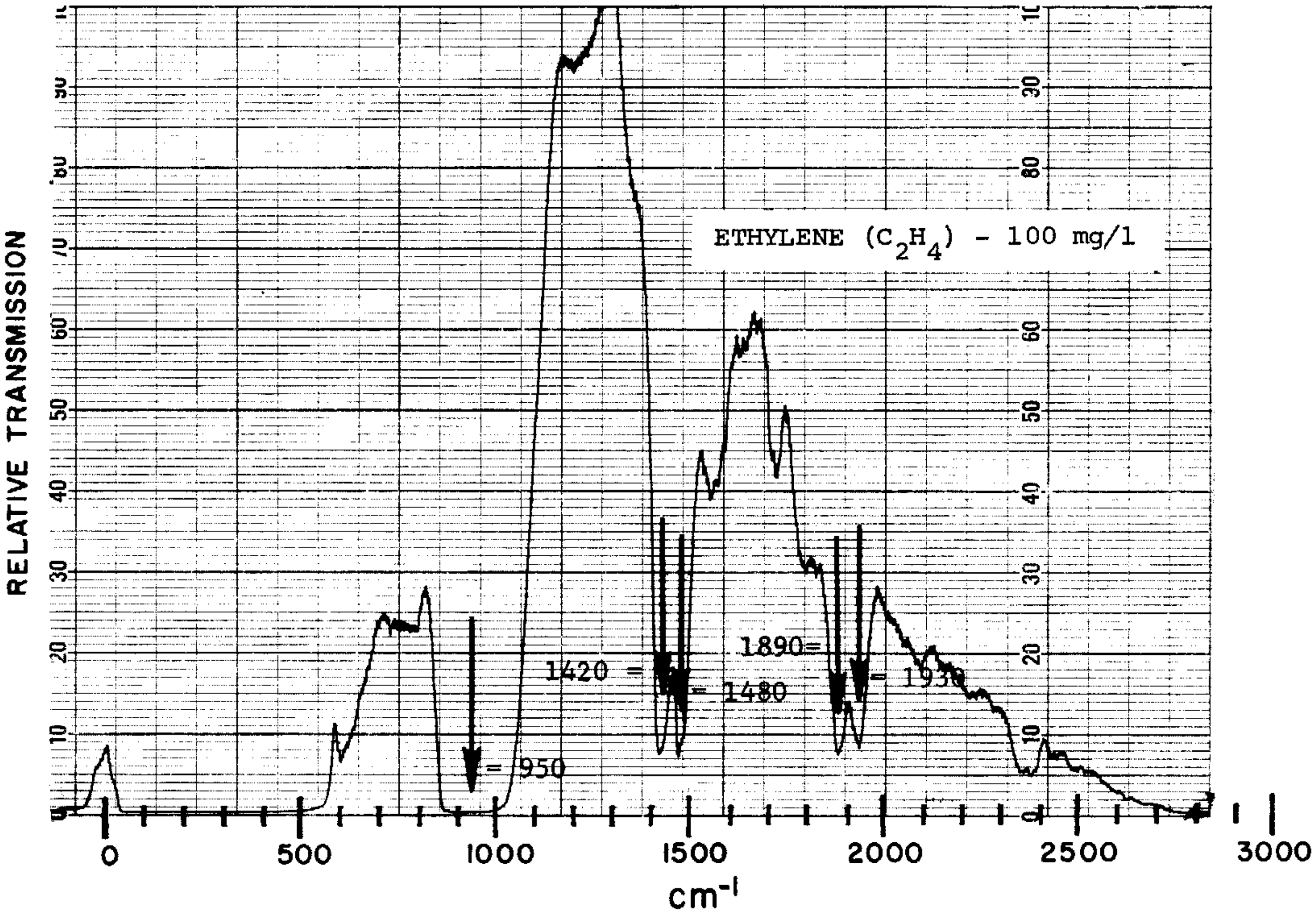

RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
ETHYLENE (C_2H_4) - 100 mg/1
950
1420
1480
1890
1930
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 47

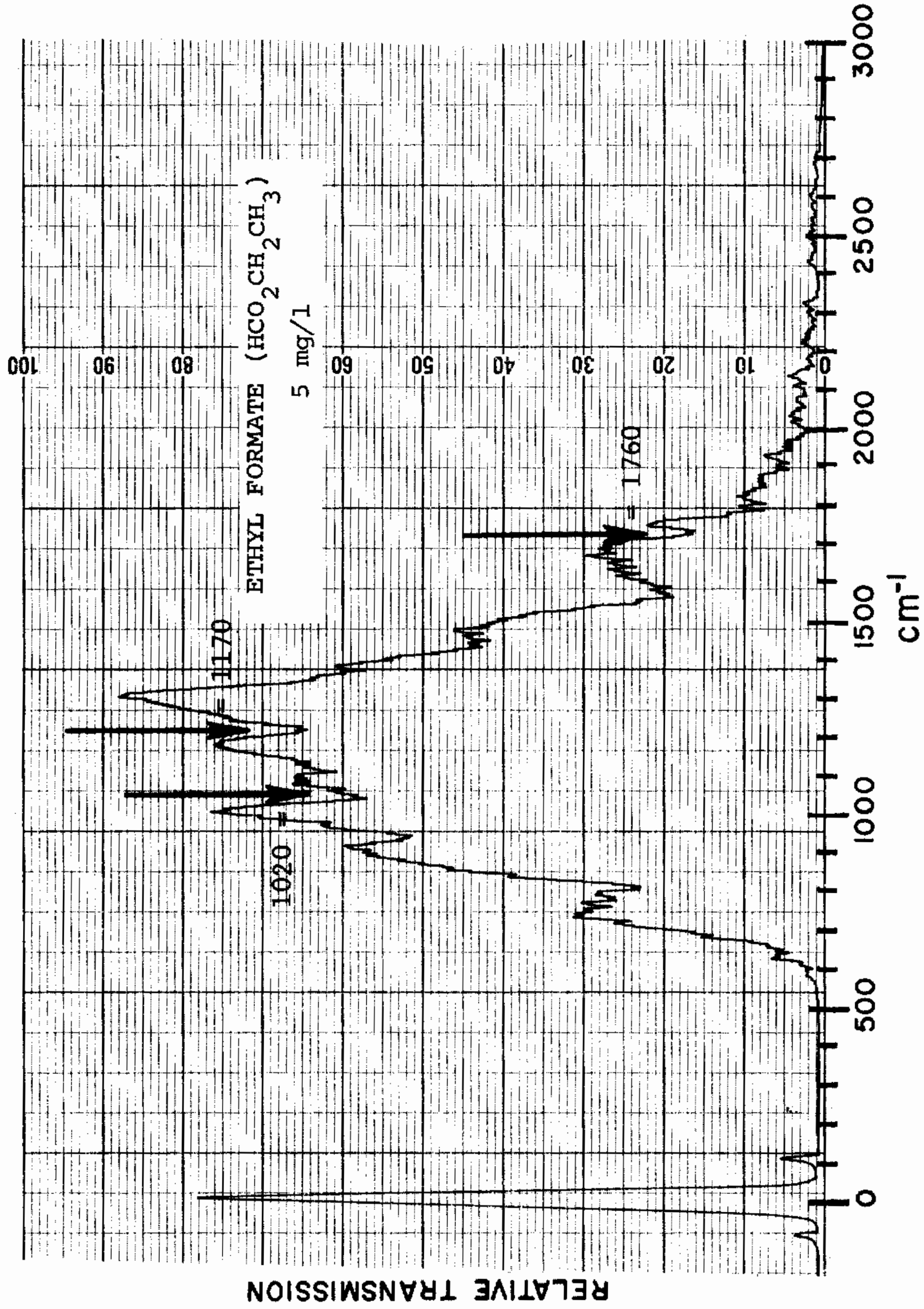

ETHYL FORMATE (HCO$_2$CH$_2$CH$_3$)
5 mg/1
= 1170
1020 =
= 1760
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 48

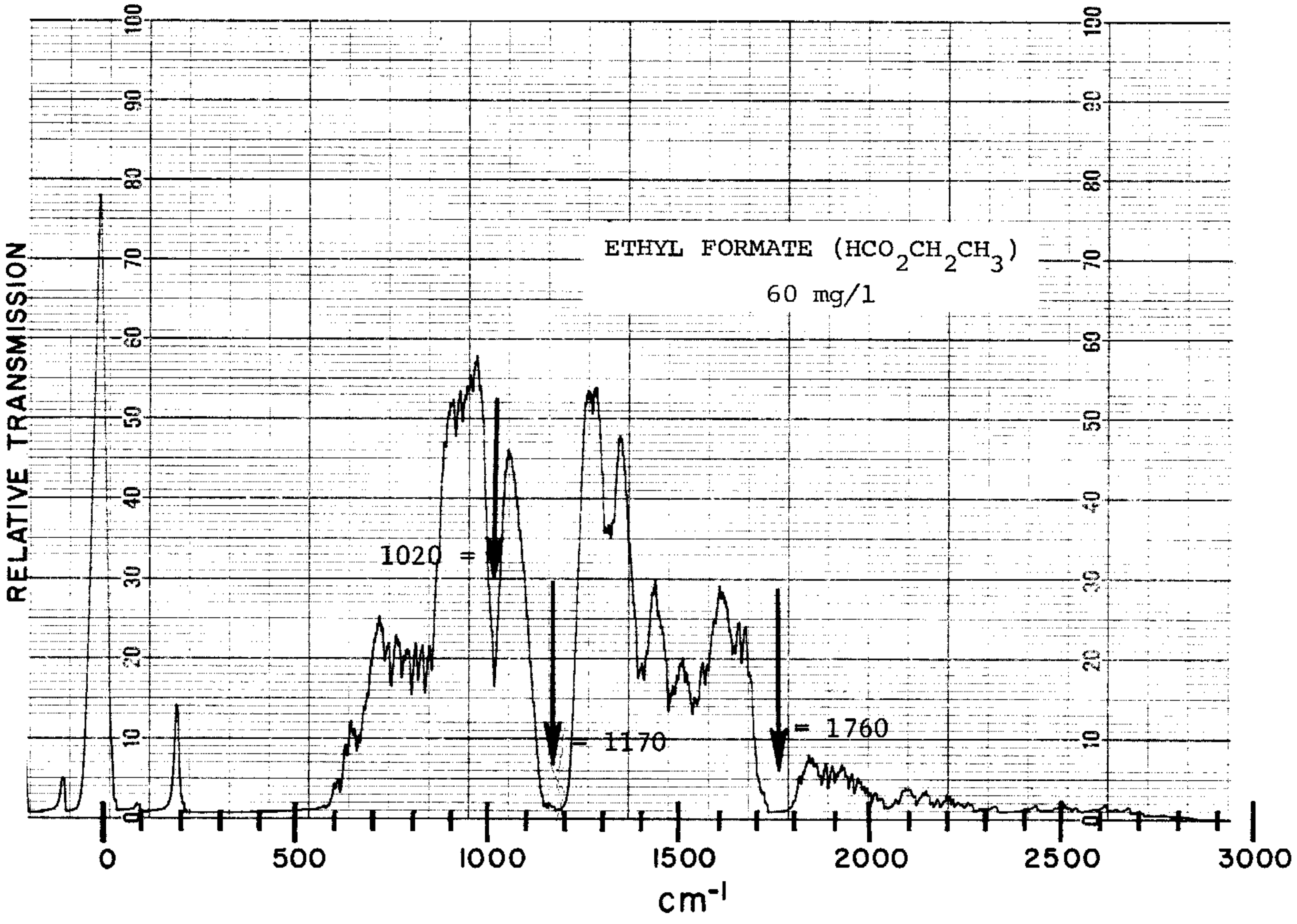

ETHYL FORMATE ($HCO_2CH_2CH_3$)
60 mg/1
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
1020 =
= 1170
= 1760
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 49

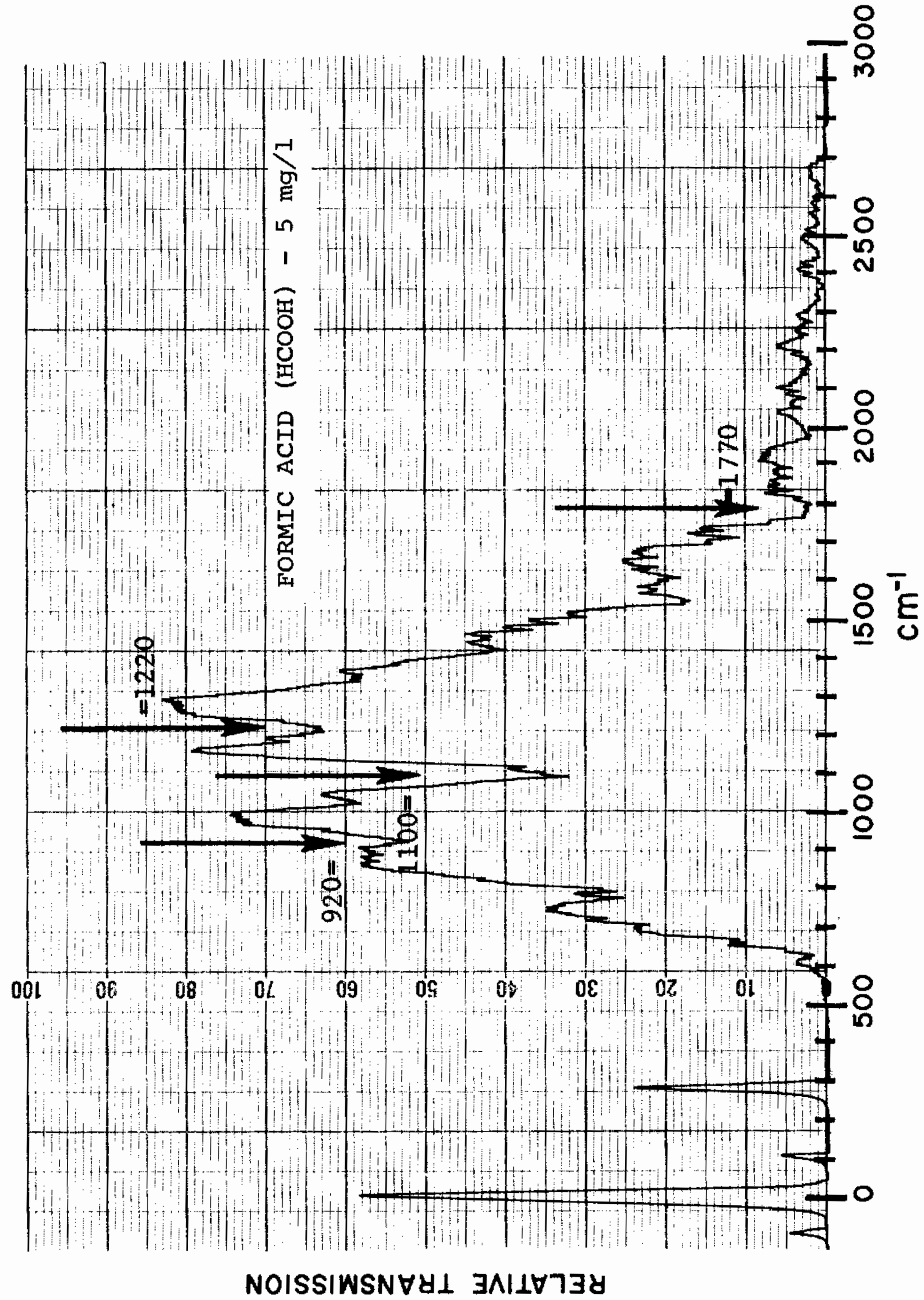

FORMIC ACID (HCOOH) - 5 mg/1
1220
1100
920
1770
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 50

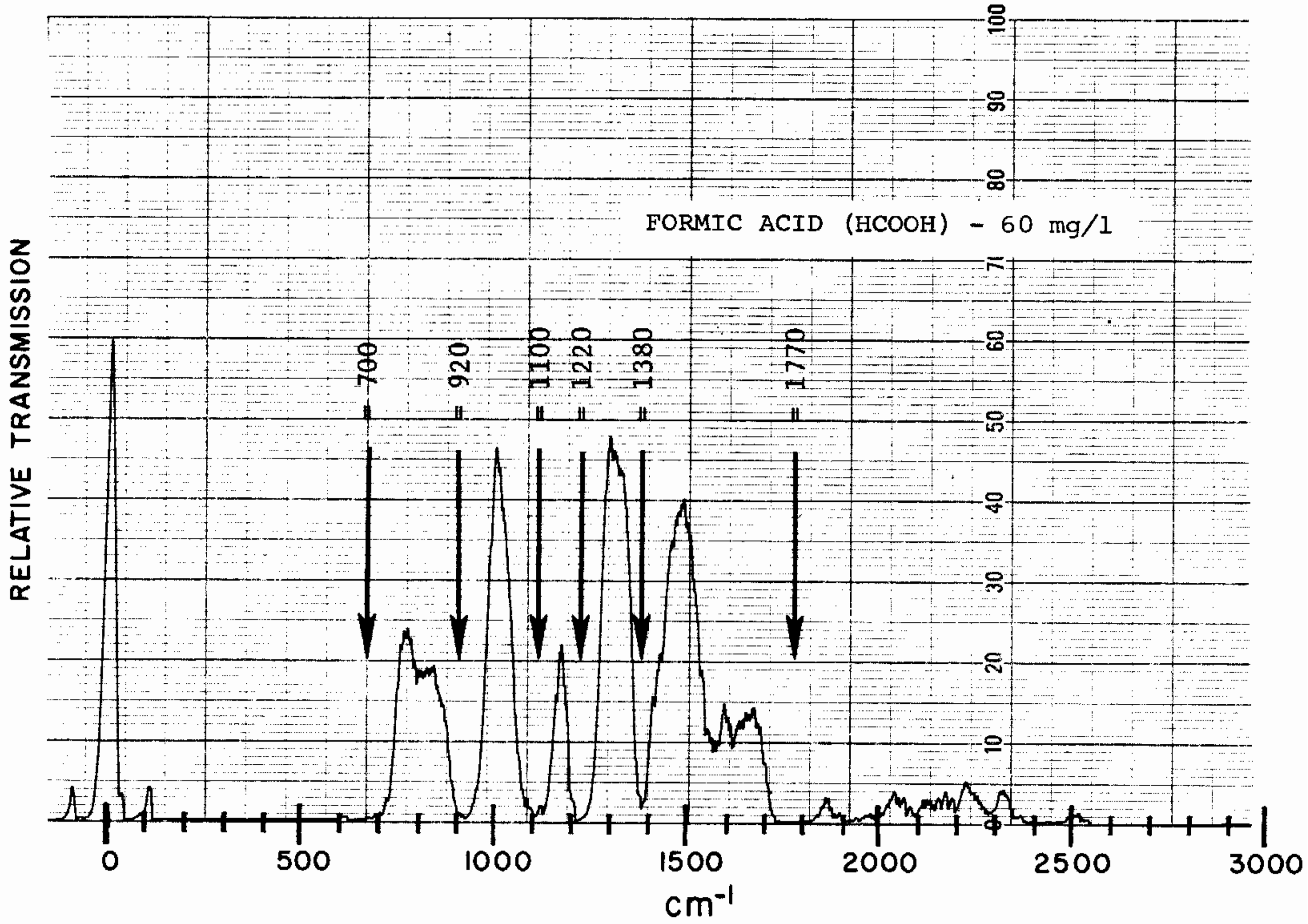

FORMIC ACID (HCOOH) - 60 mg/l
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
700
920
1100
1220
1380
1770
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 51

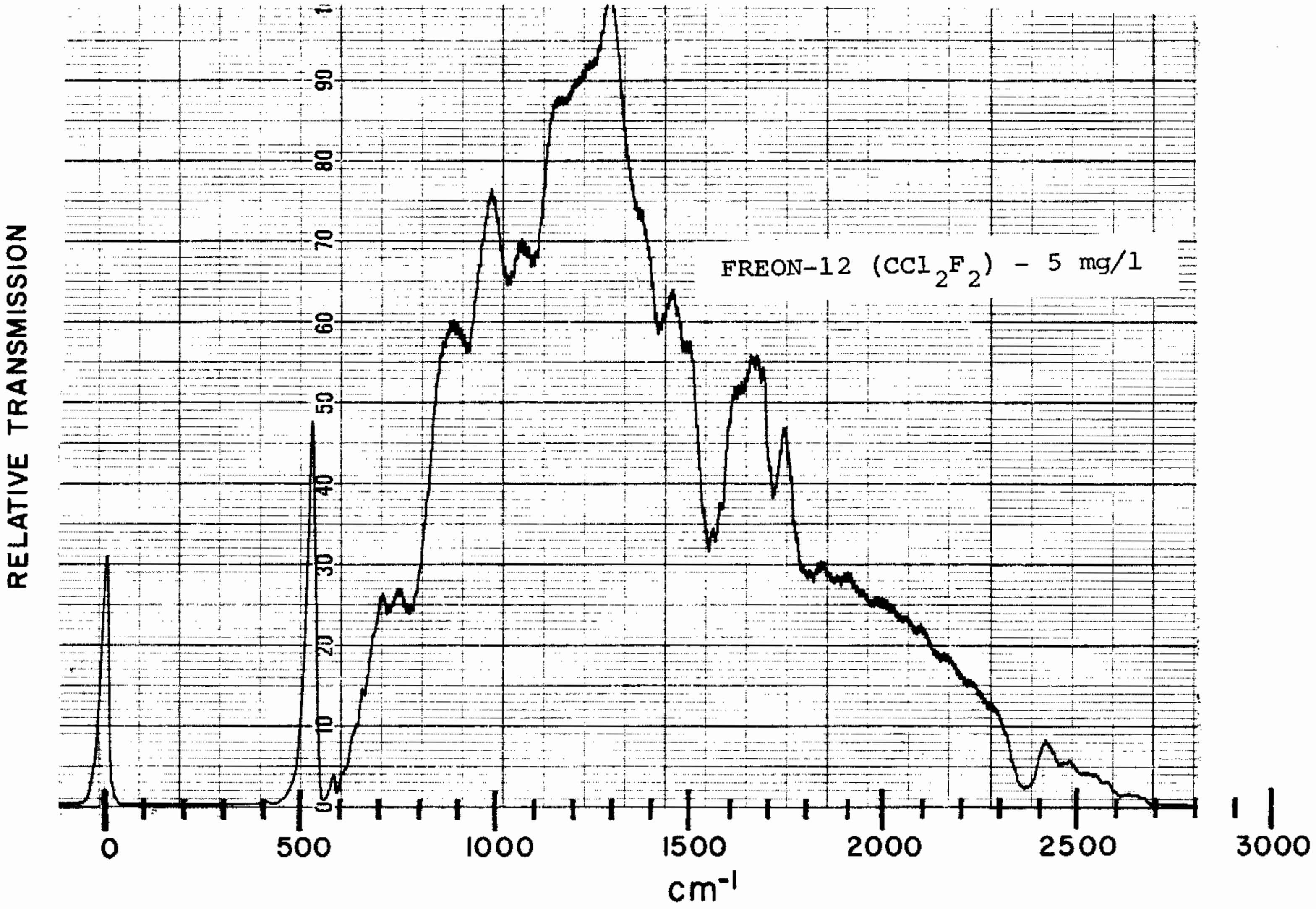
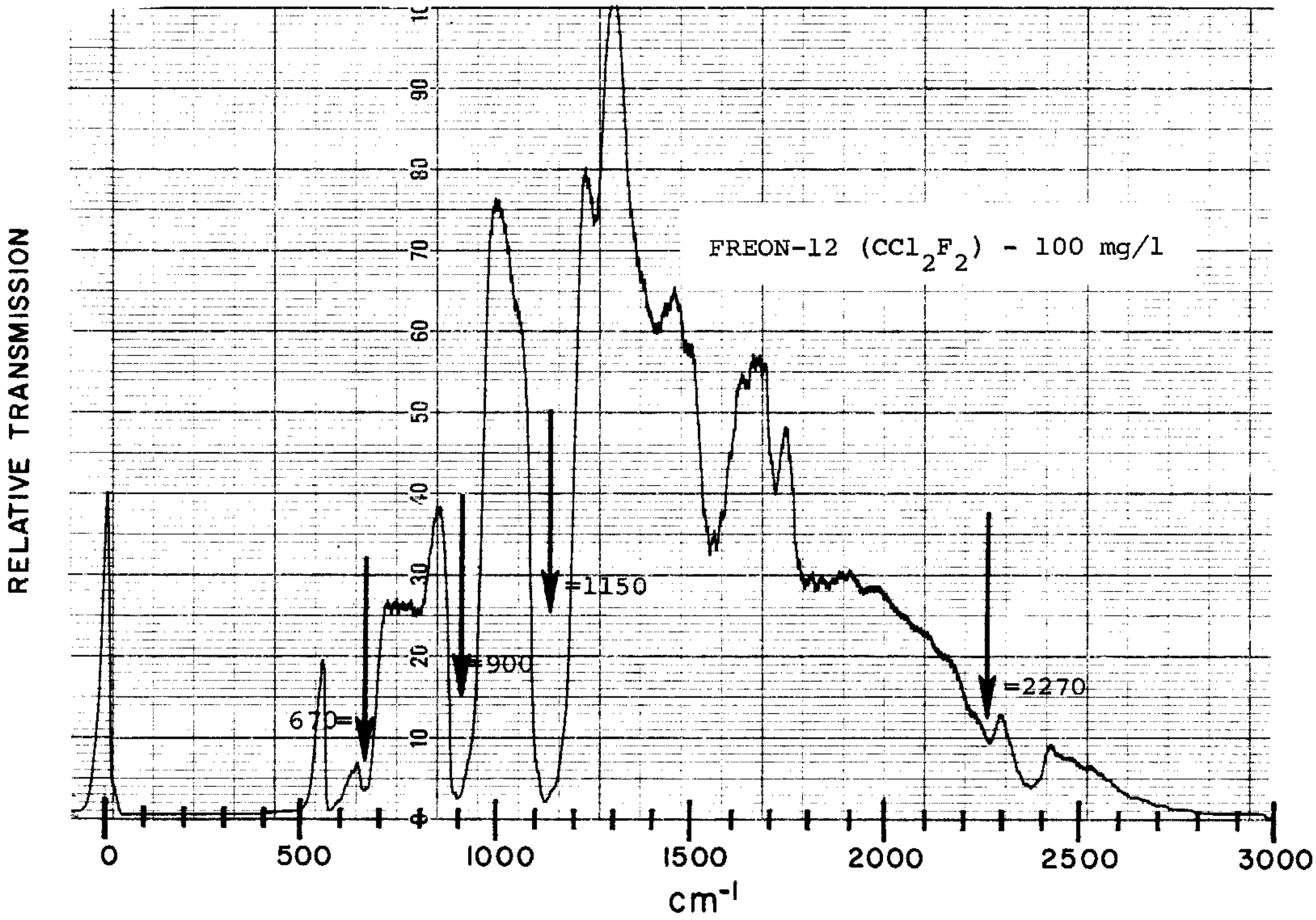

FREON-12 (CCl_2F_2) - 5 mg/1
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
1
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 52



FREON-12 (CCl_2F_2) - 100 mg/l

Figure 53

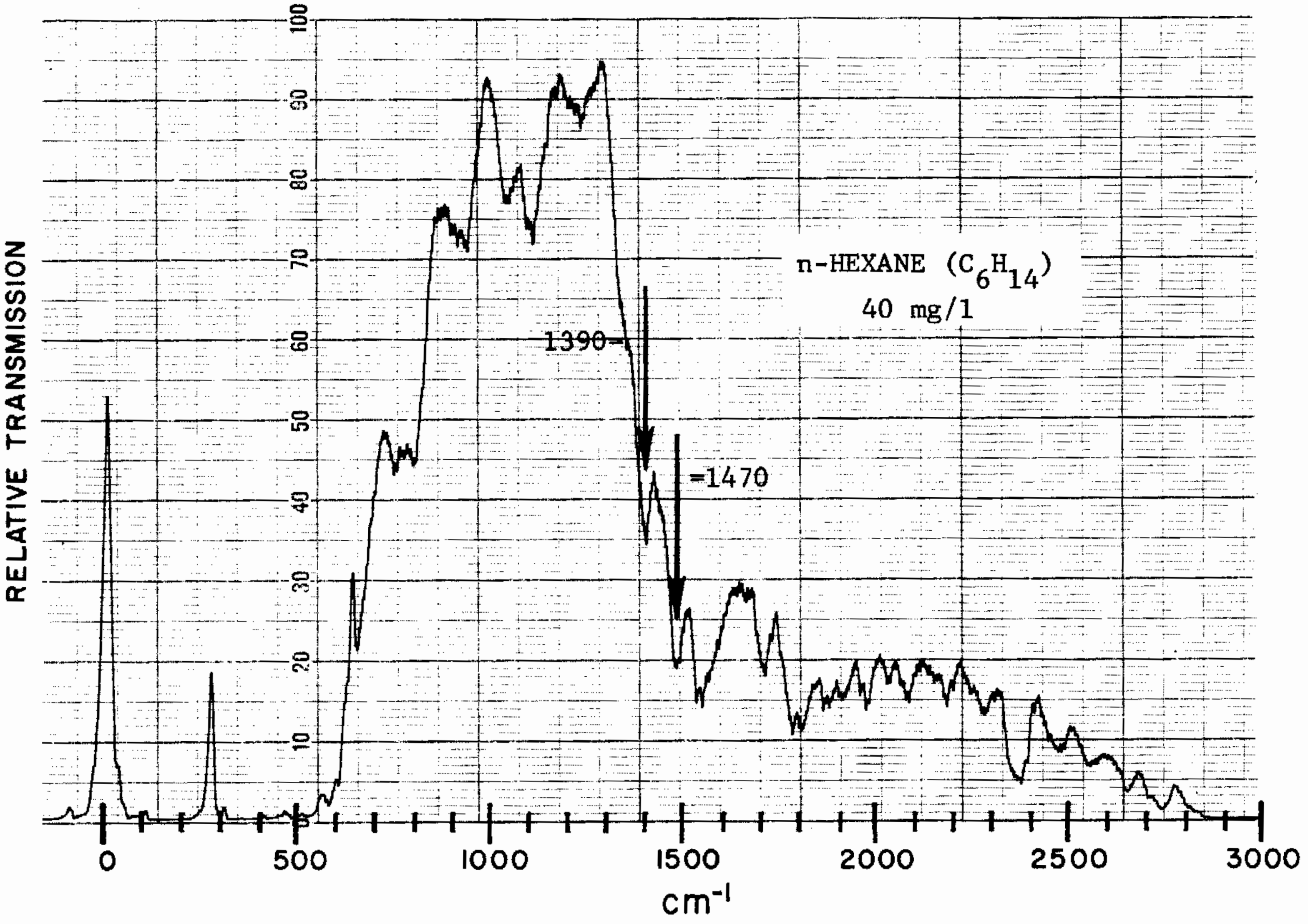
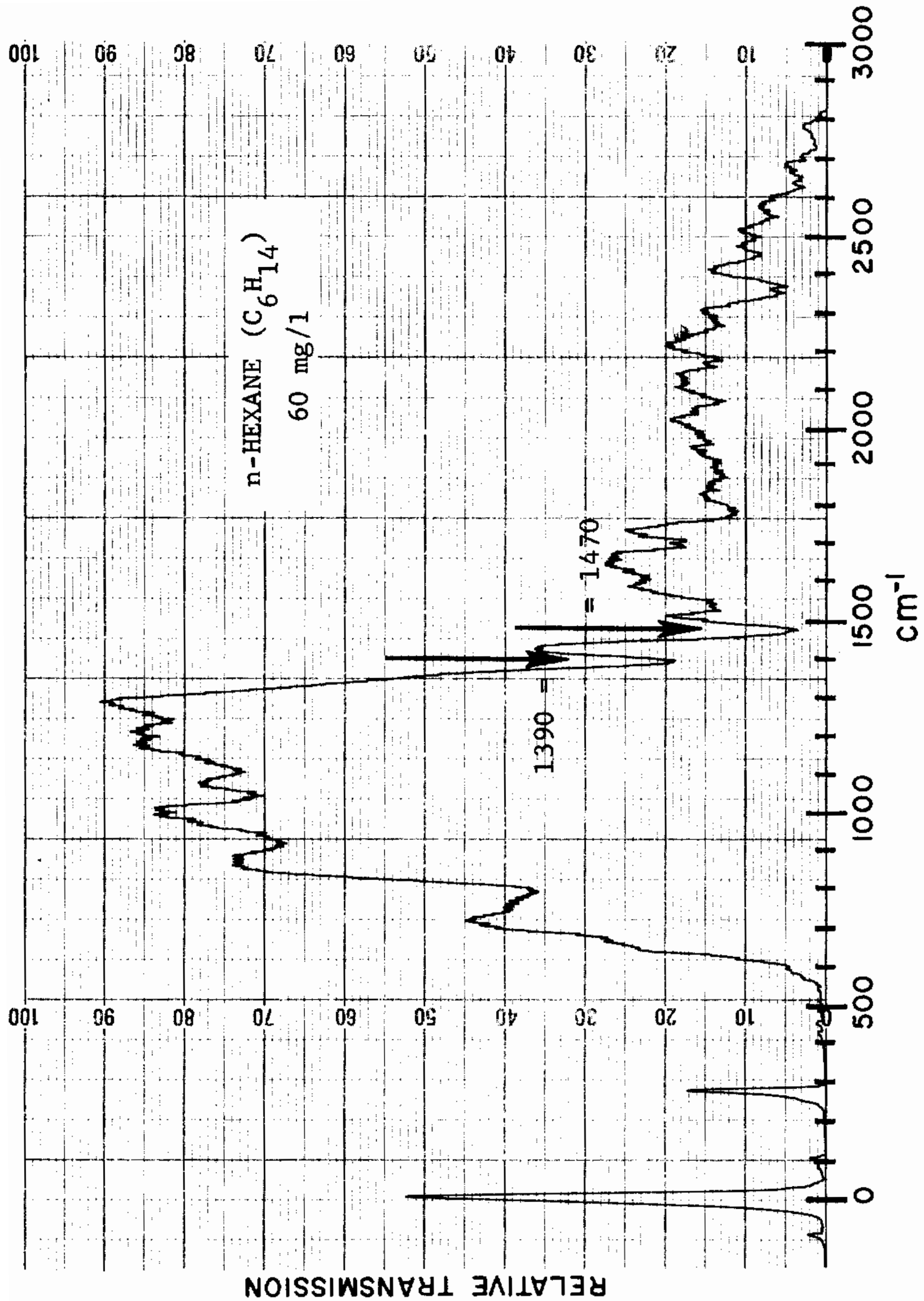

RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
n-HEXANE (C_6H_{14})
40 mg/1
1390
=1470
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 54



n-HEXANE (C_6H_{14})
60 mg/l
1390 =
= 1470
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 55

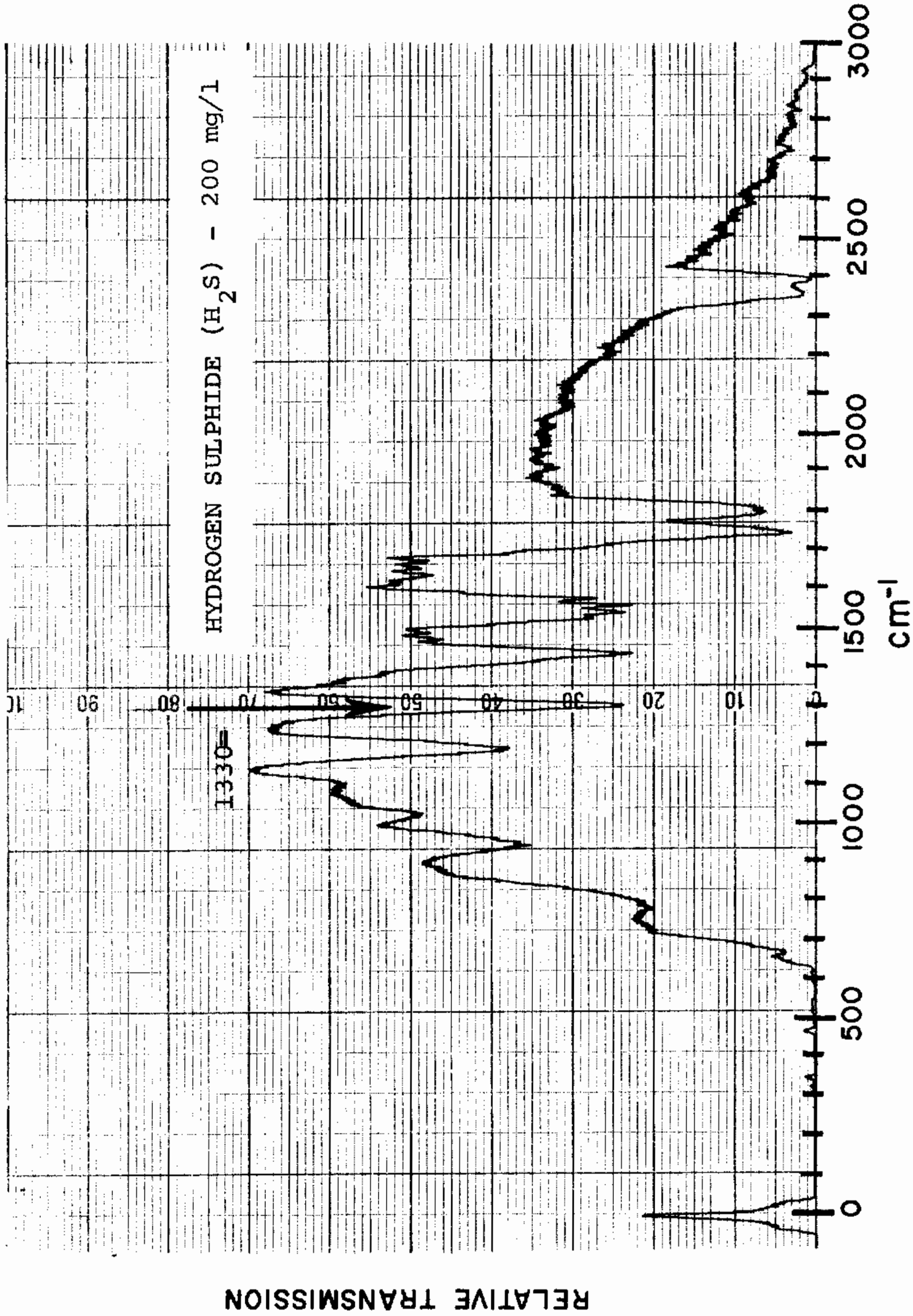

HYDROGEN SULPHIDE (H_2S) - 200 mg/1
1330
0
500
1000
1500
2000
2500
3000
cm^{-1}
10
20
30
40
50
60
70
80
90
100
RELATIVE TRANSMISSION

Figure 56

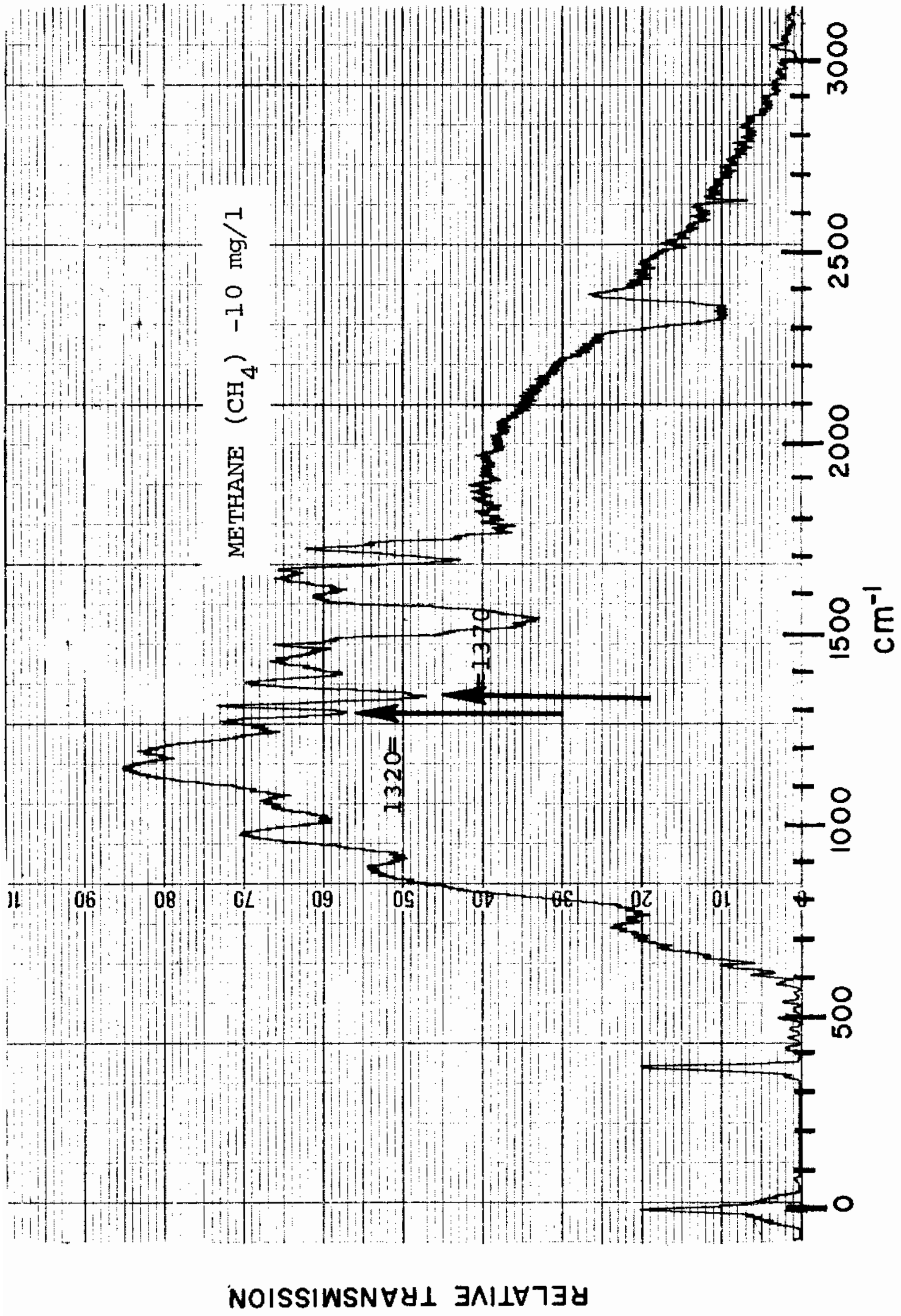

METHANE (CH_4) -10 mg/1
1320
1370
0
500
1000
1500
2000
2500
3000
cm^{-1}
10
20
30
40
50
60
70
80
90
RELATIVE TRANSMISSION

Figure 57

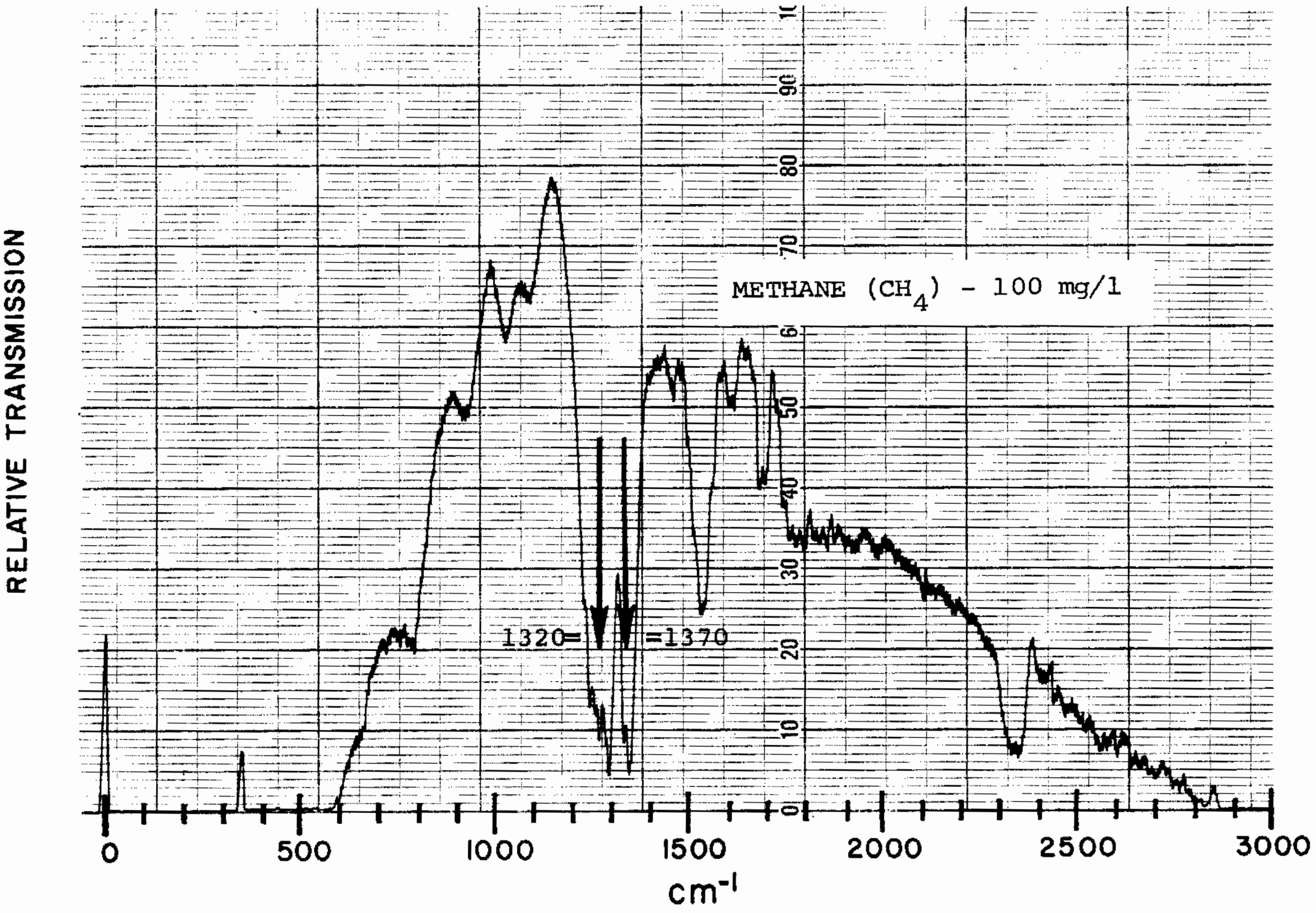

RELATIVE TRANSMISSION
METHANE (CH_4) - 100 mg/1
1320=
=1370
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 58

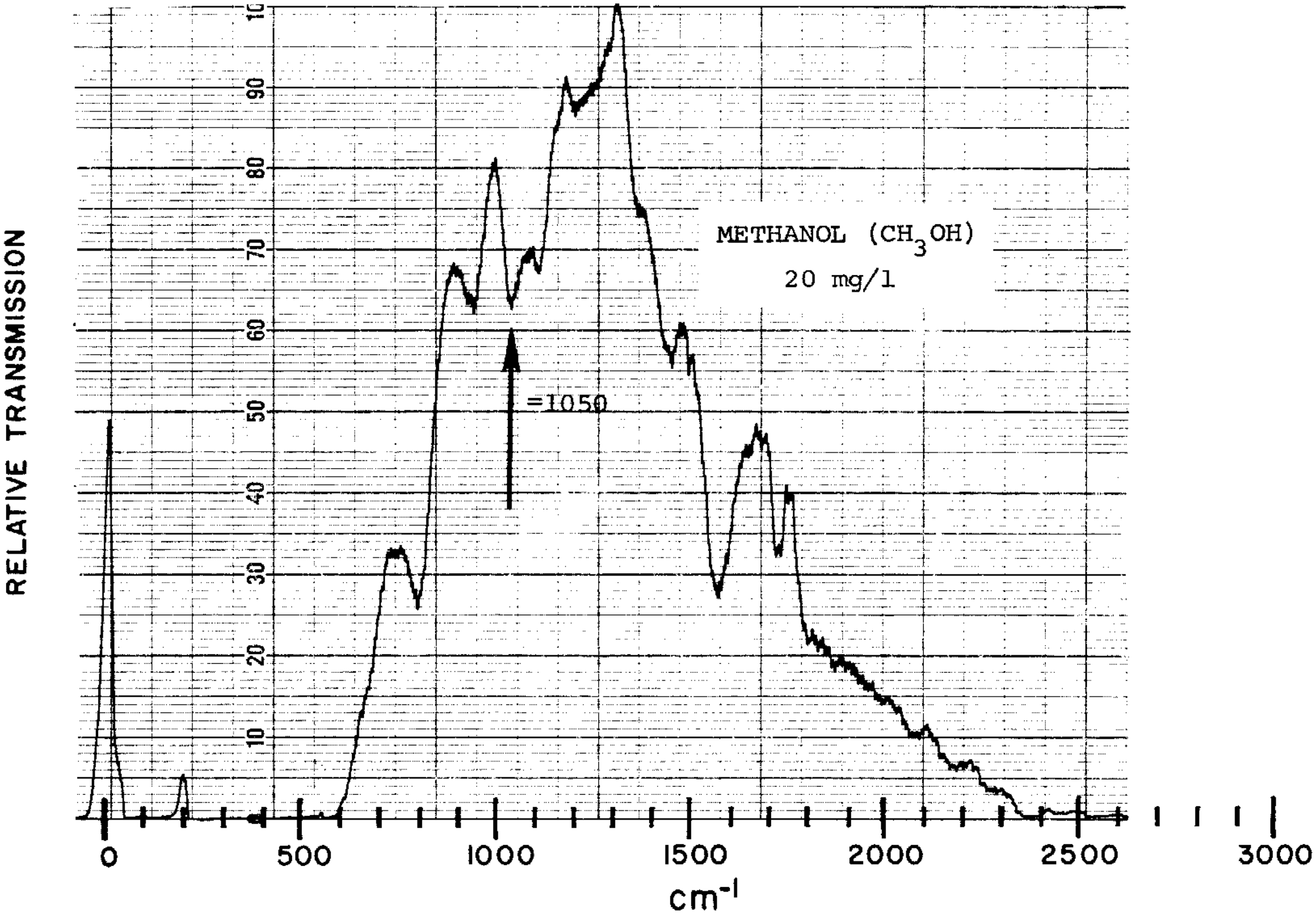

METHANOL (CH_3OH)
20 mg/l
=1050
RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 59

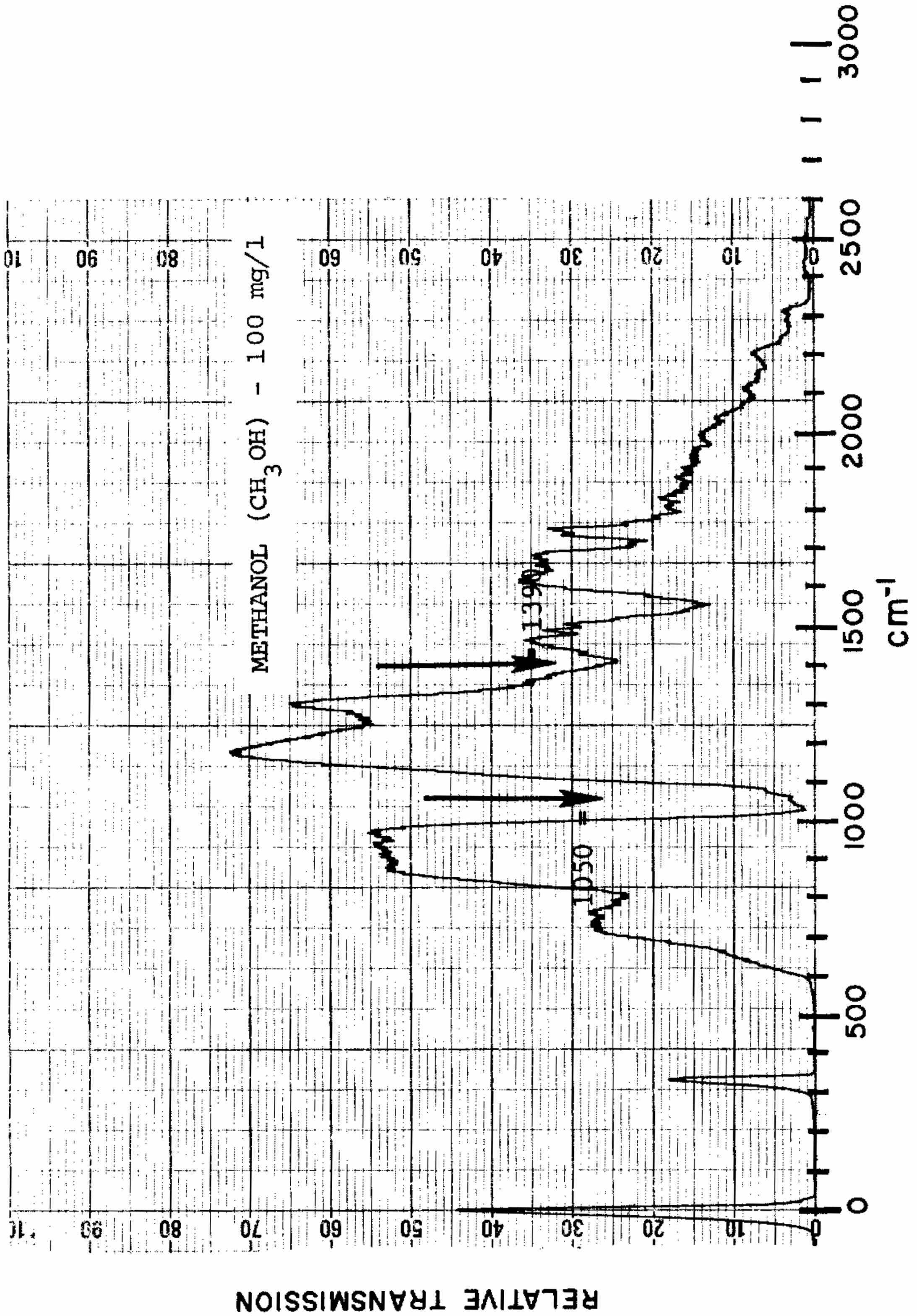

METHANOL (CH$_3$OH) - 100 mg/l
1139
1050
0
500
1000
1500
2000
2500
3000
cm^{-1}
0
10
20
30
40
50
60
70
80
90
10
RELATIVE TRANSMISSION

Figure 60

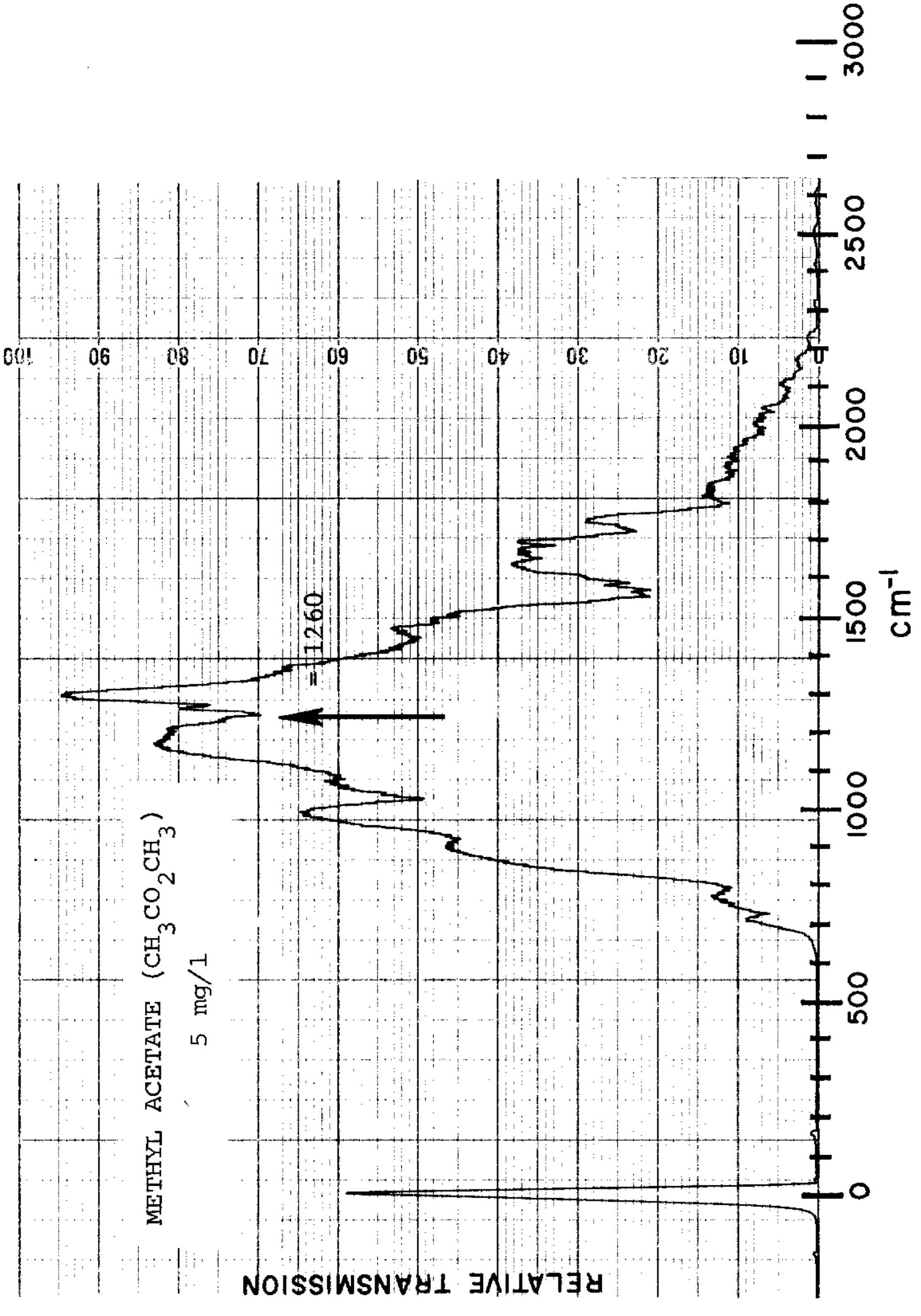

METHYL ACETATE $(CH_3CO_2CH_3)$
5 mg/1
= 1260
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 61

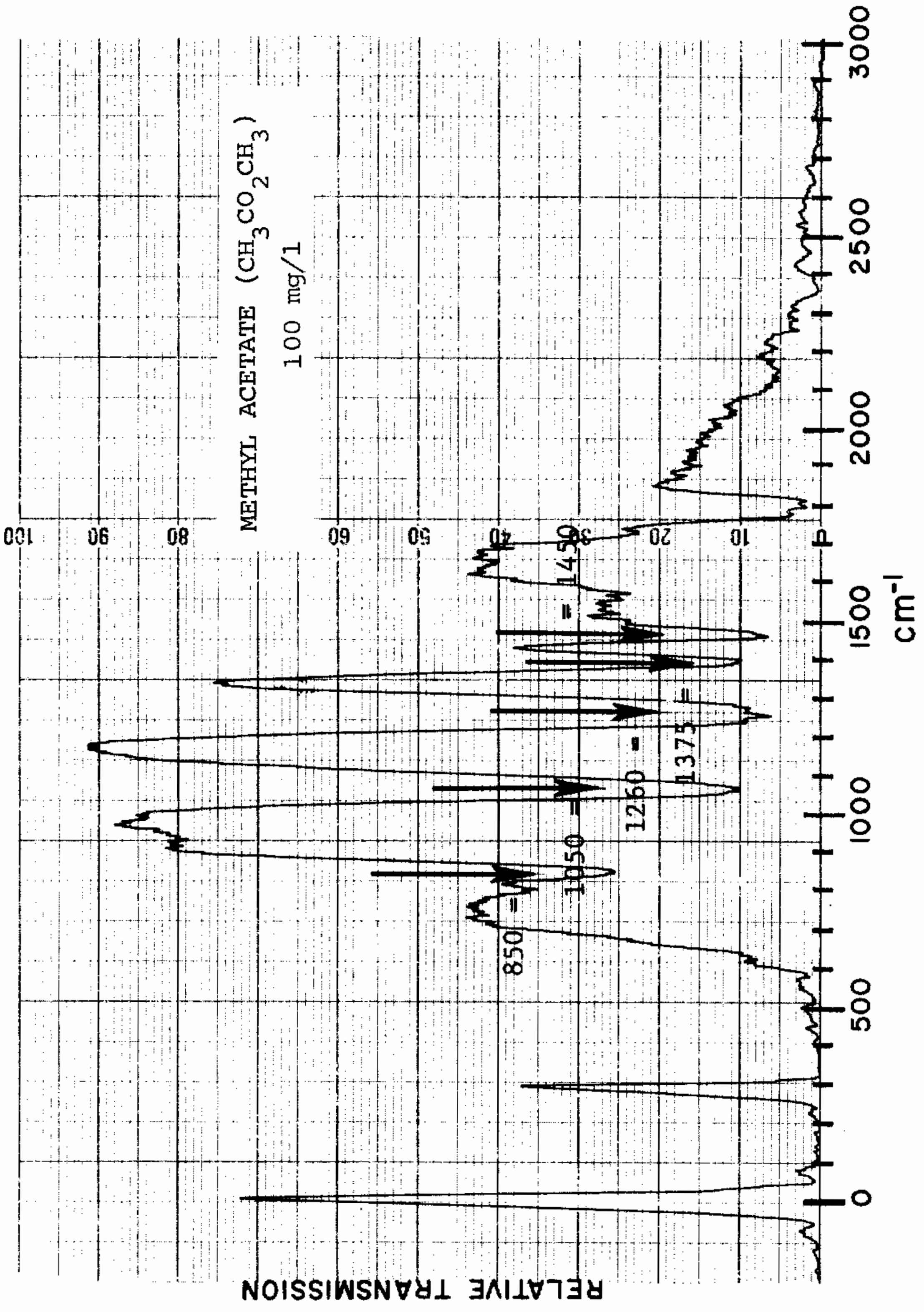

METHYL ACETATE ($CH_3CO_2CH_3$)
100 mg/l
850 =
1050 =
1260 =
1375 =
1450 =
0
500
1000
1500
2000
2500
3000
cm^{-1}
0
10
20
30
40
50
60
80
90
100
RELATIVE TRANSMISSION

Figure 62

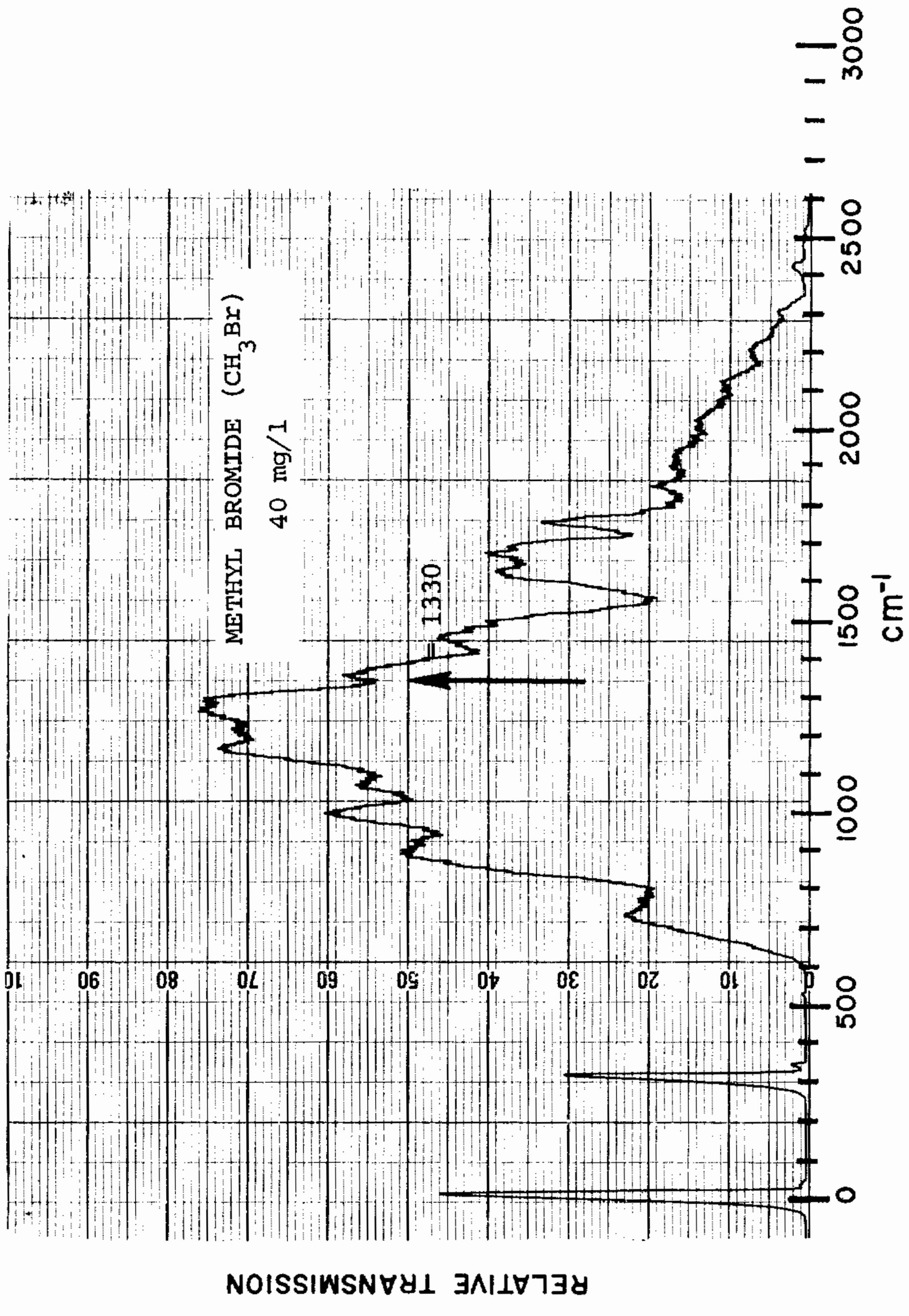

METHYL BROMIDE (CH_3Br)
40 mg/1
1330
cm^{-1}
0
500
1000
1500
2000
2500
3000
0
10
20
30
40
50
60
70
80
90
10
RELATIVE TRANSMISSION

Figure 63

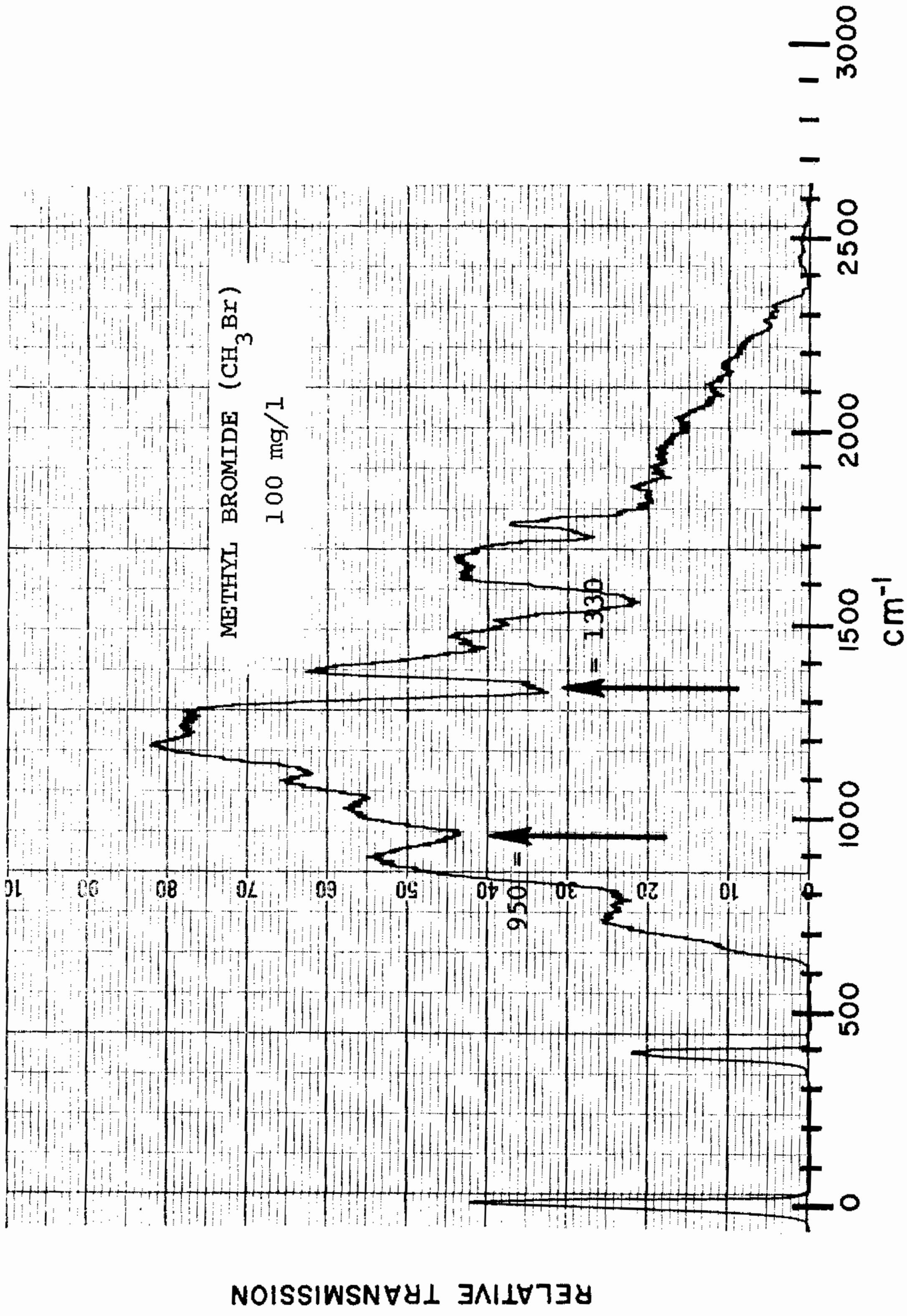

METHYL BROMIDE (CH_3Br)
100 mg/1
950 =
= 1330
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
10
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 64

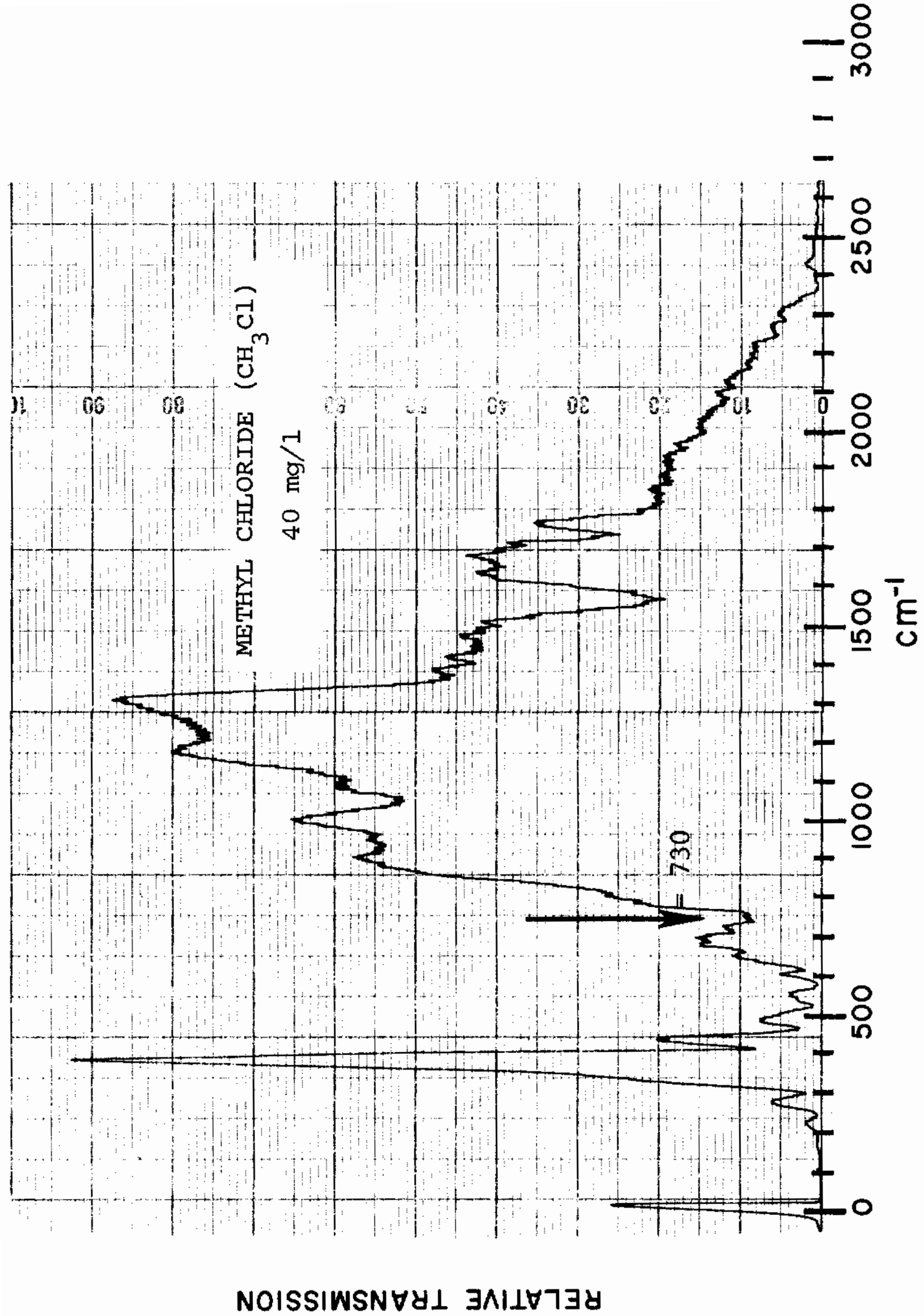

METHYL CHLORIDE (CH$_3$Cl)
40 mg/1
730
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 65

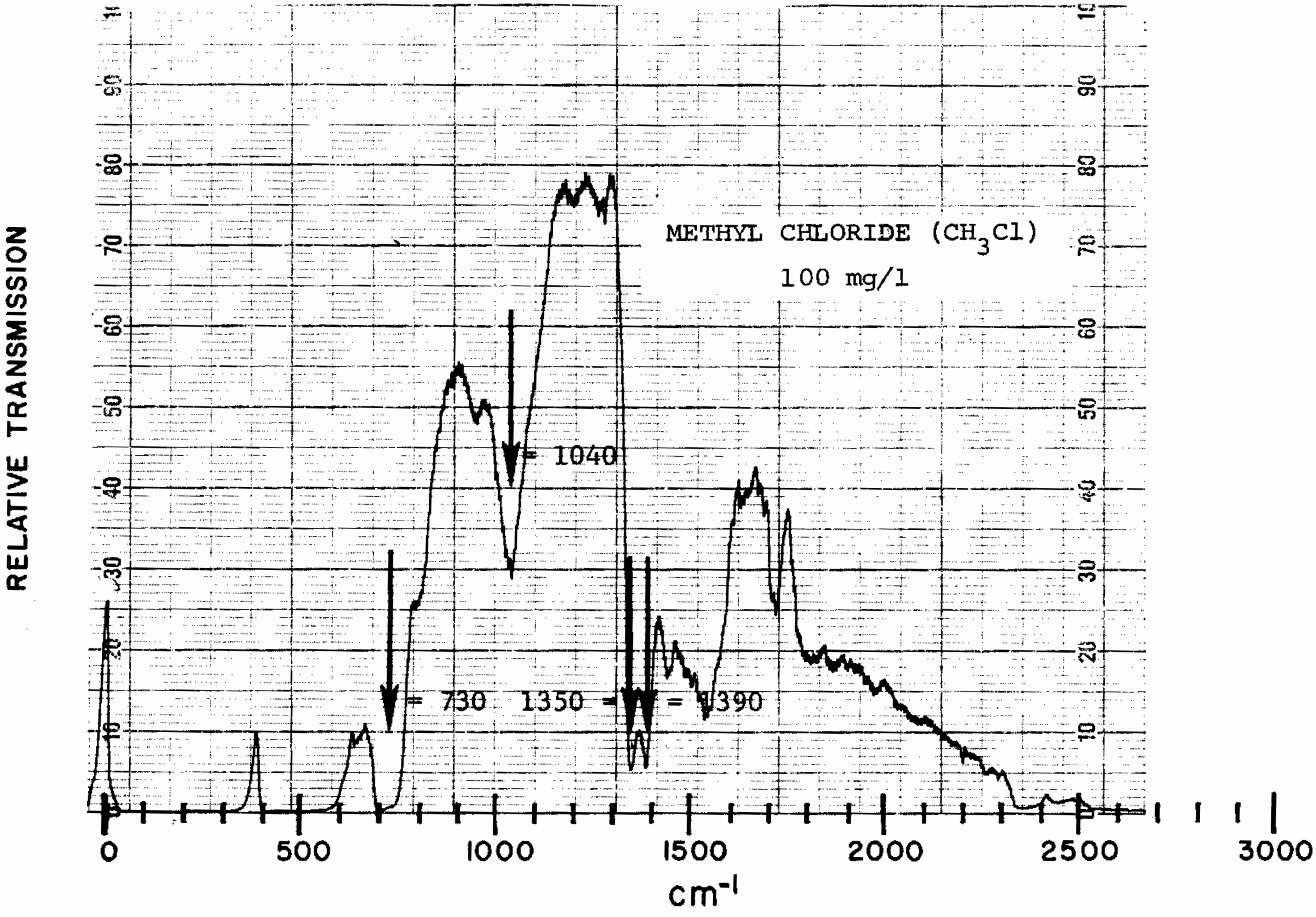

RELATIVE TRANSMISSION
METHYL CHLORIDE (CH_3Cl)
100 mg/l
= 1040
= 730
1350 =
= 1390
10
20
30
40
50
60
70
80
90
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 66

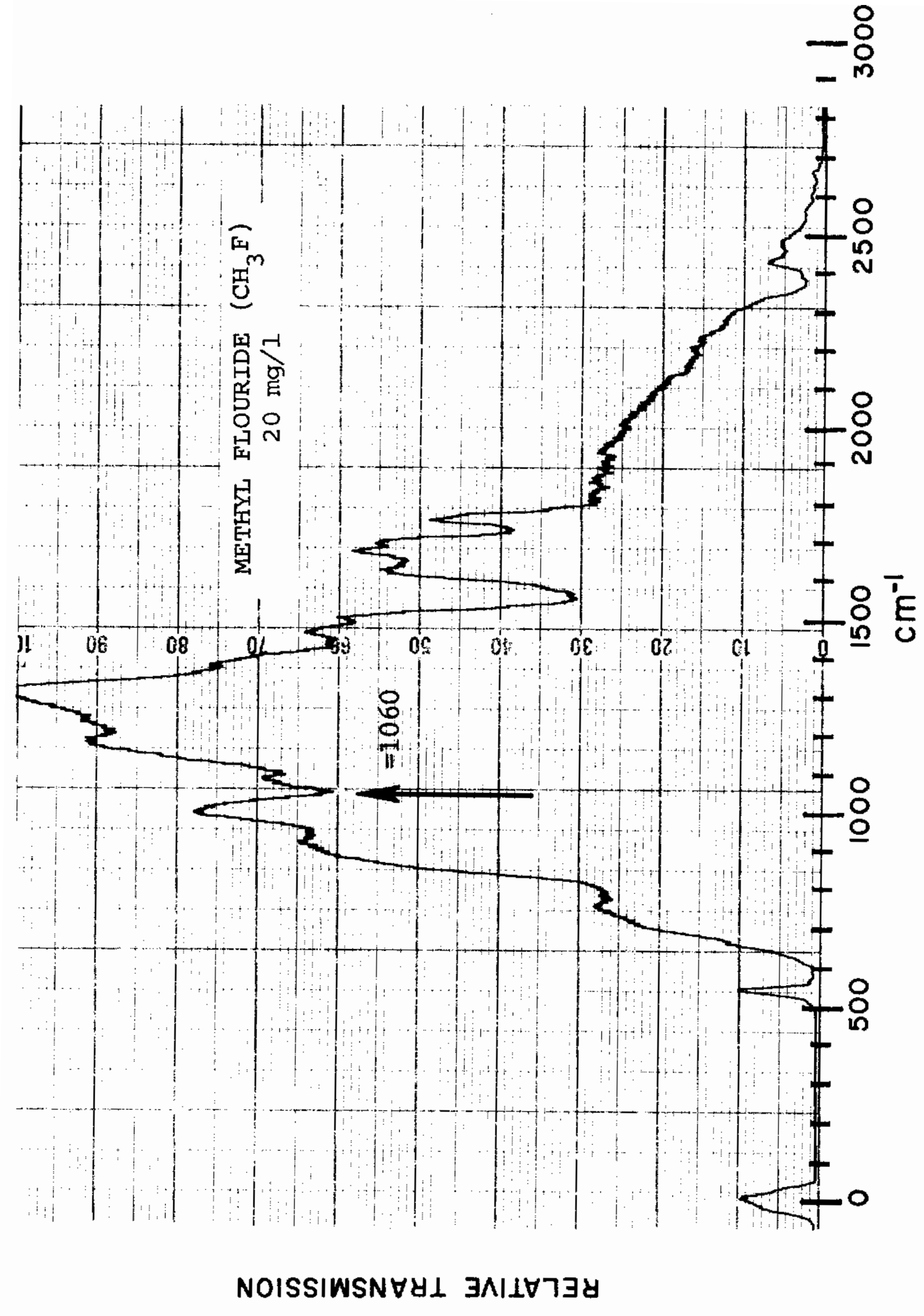

METHYL FLOURIDE (CH_3F)
20 mg/1
≈1060
RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 67

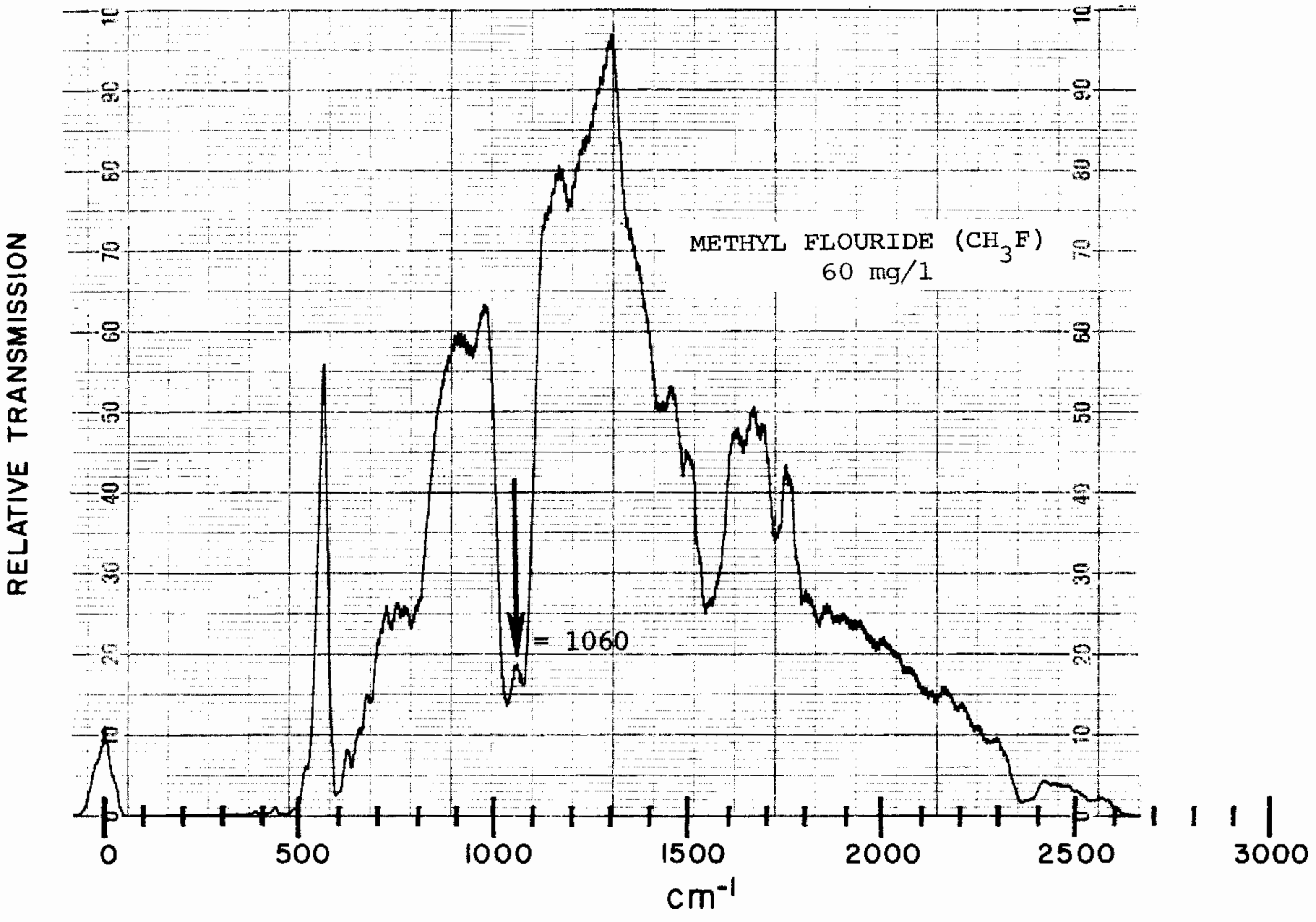

METHYL FLOURIDE (CH_3F)
60 mg/1
= 1060
RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 68

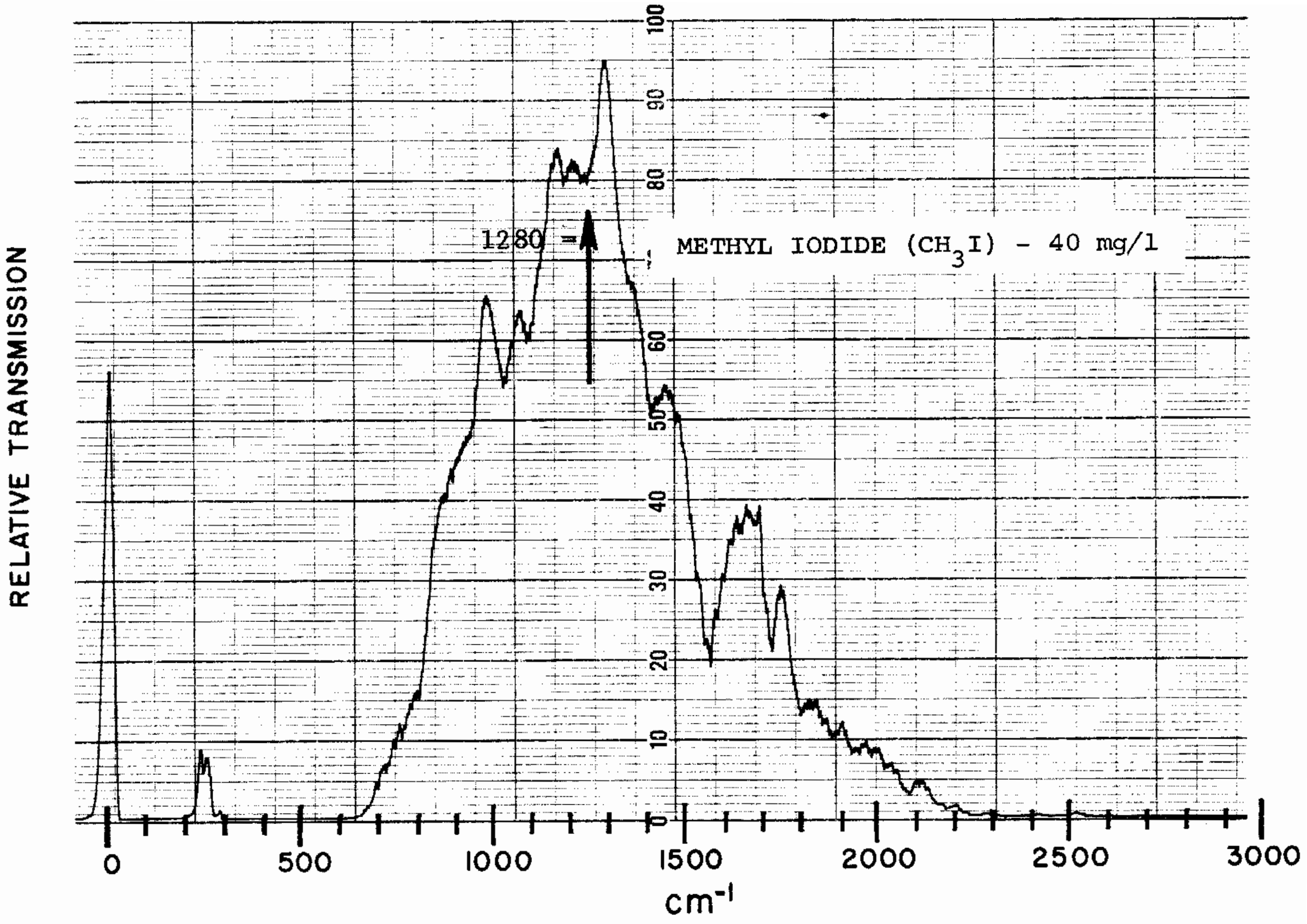

RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
1280 =
METHYL IODIDE (CH_3I) - 40 mg/l
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 69

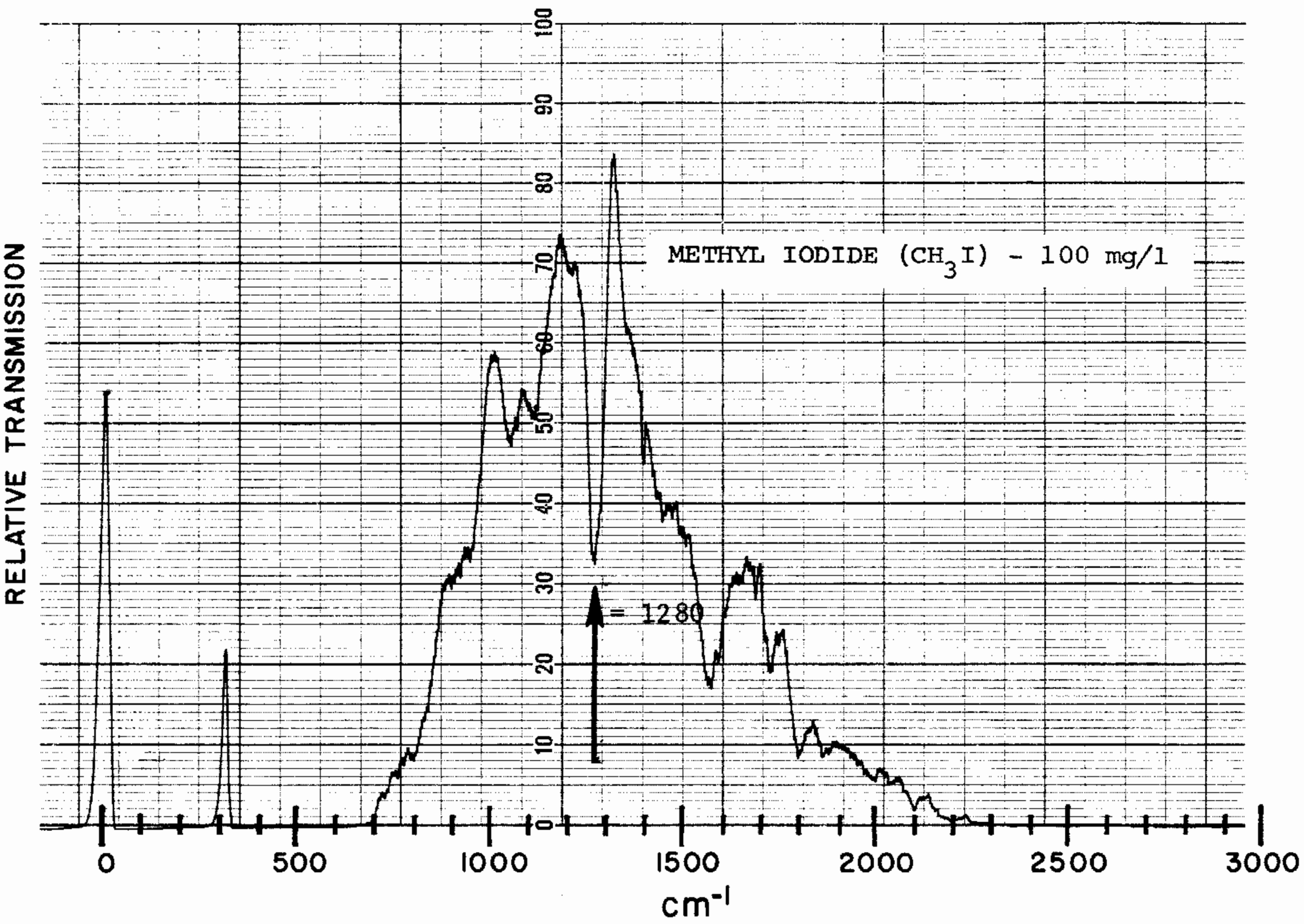

METHYL IODIDE (CH_3I) - 100 mg/l
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
= 1280
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 70

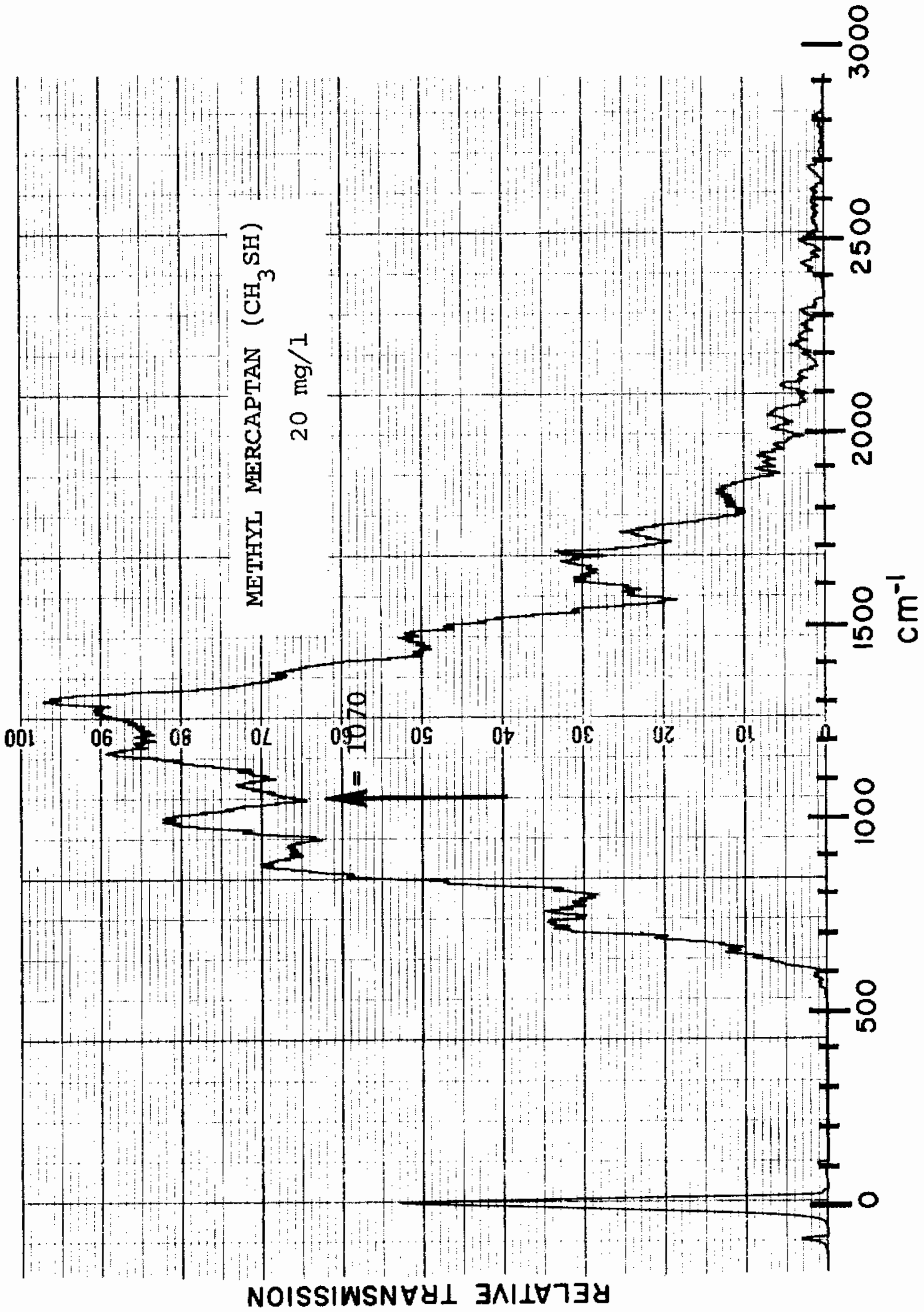

METHYL MERCAPTAN (CH_3SH)
20 mg/l
= 1070
100
90
80
70
60
50
40
30
20
10
P
RELATIVE TRANSMISSION
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 71

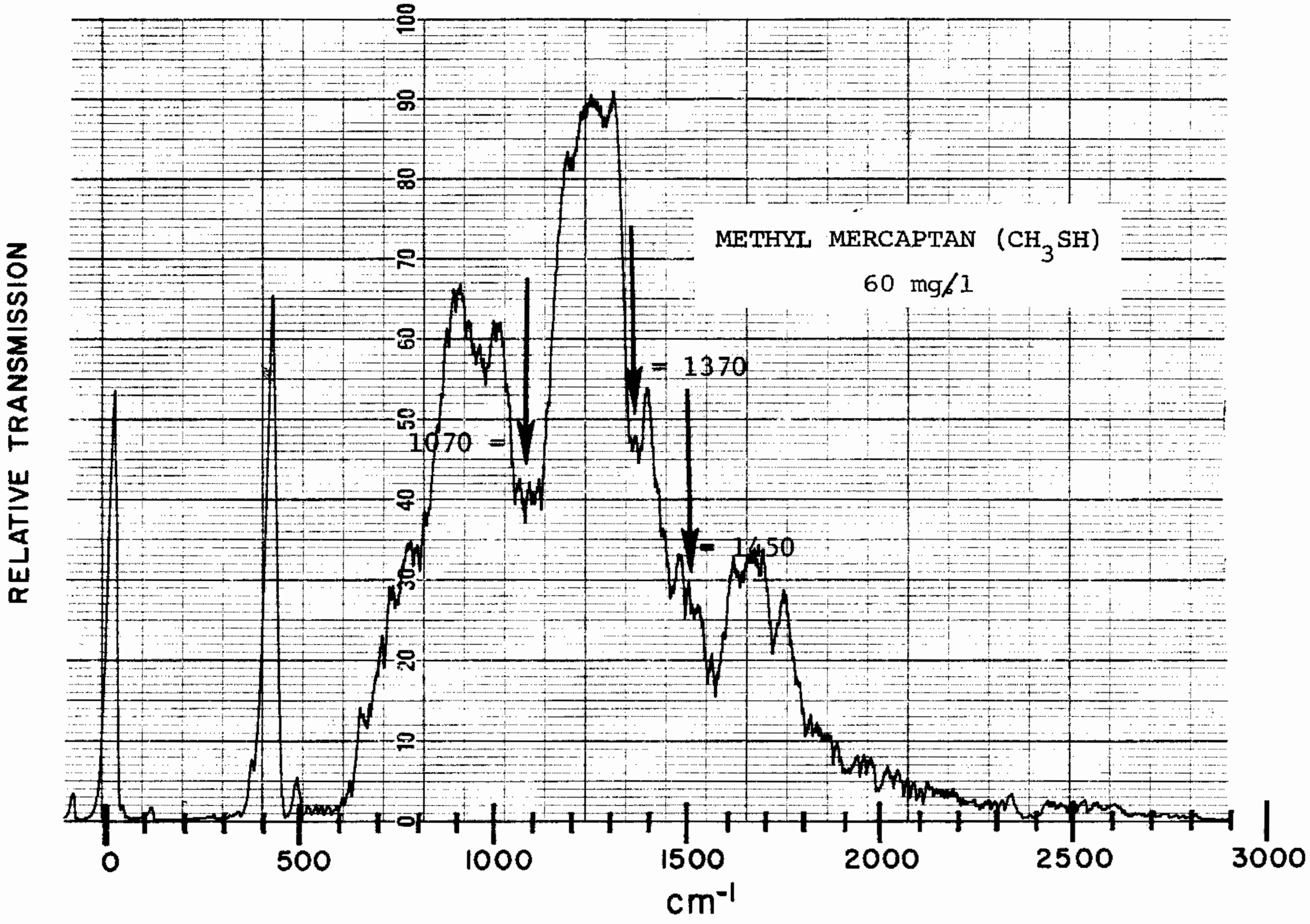
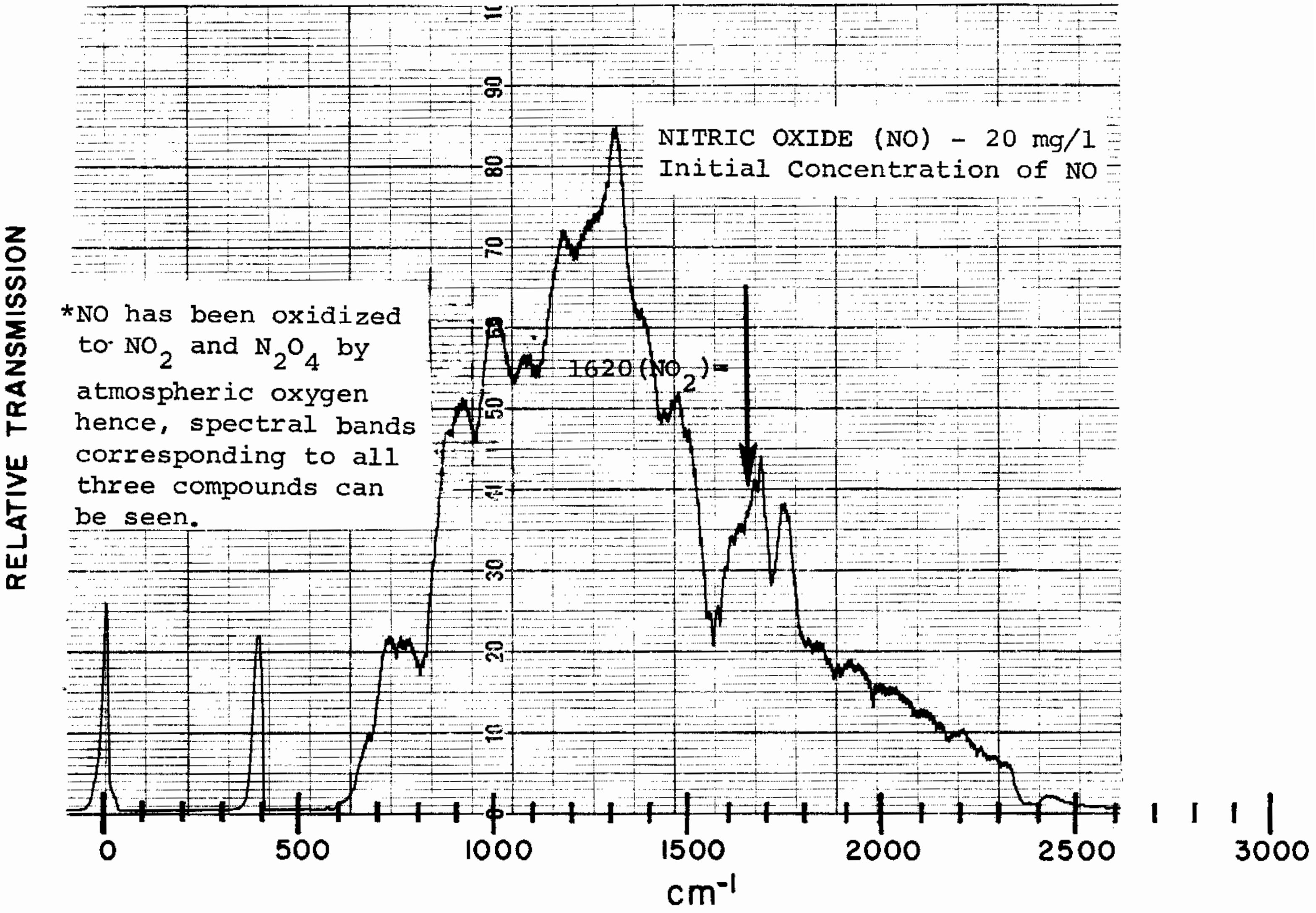

RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
METHYL MERCAPTAN (CH_3SH)
60 mg/l
1070 =
= 1370
= 1450
0
500
1000
1500
2000
2500
3000
cm⁻¹

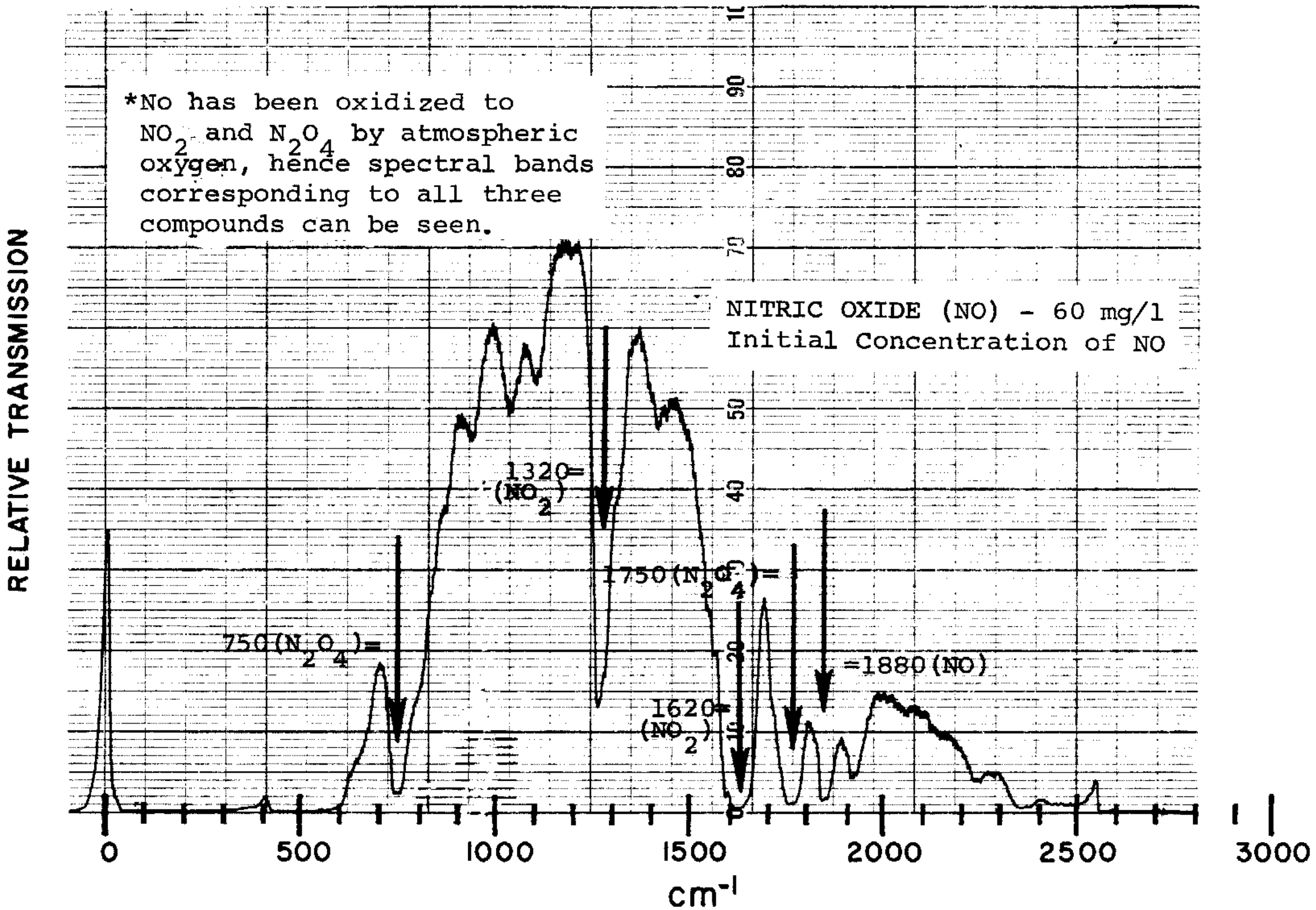
Figure 72



NITRIC OXIDE (NO) - 20 mg/1
Initial Concentration of NO

*NO has been oxidized to NO_2 and N_2O_4 by atmospheric oxygen hence, spectral bands corresponding to all three compounds can be seen.

Figure 73



NITRIC OXIDE (NO) - 60 mg/l
Initial Concentration of NO

*No has been oxidized to NO_2 and N_2O_4 by atmospheric oxygen, hence spectral bands corresponding to all three compounds can be seen.

Figure 74

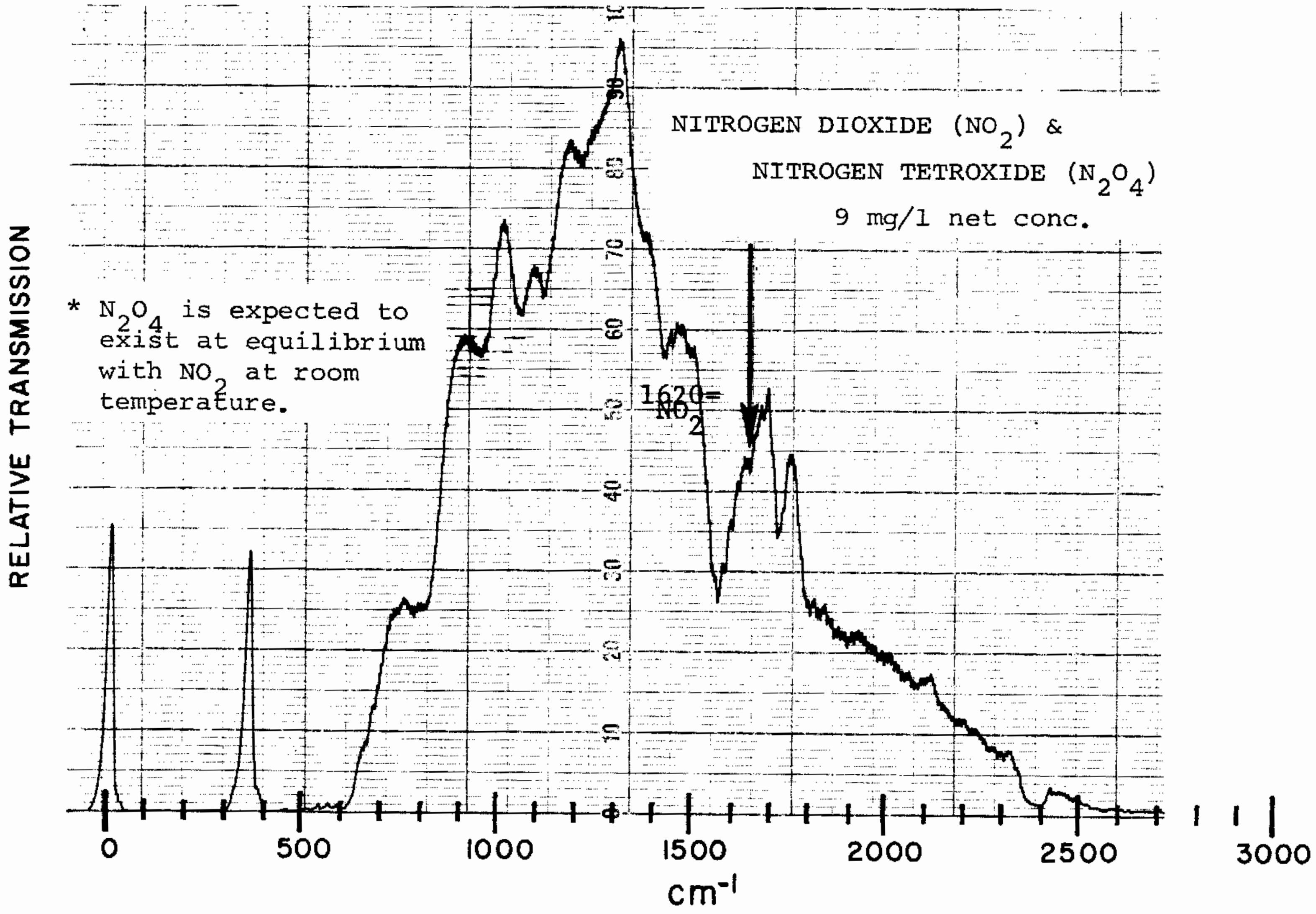

RELATIVE TRANSMISSION
NITROGEN DIOXIDE (NO_2) &
NITROGEN TETROXIDE (N_2O_4)
9 mg/l net conc.
* N_2O_4 is expected to exist at equilibrium with NO_2 at room temperature.
1620= NO_2
10
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 75

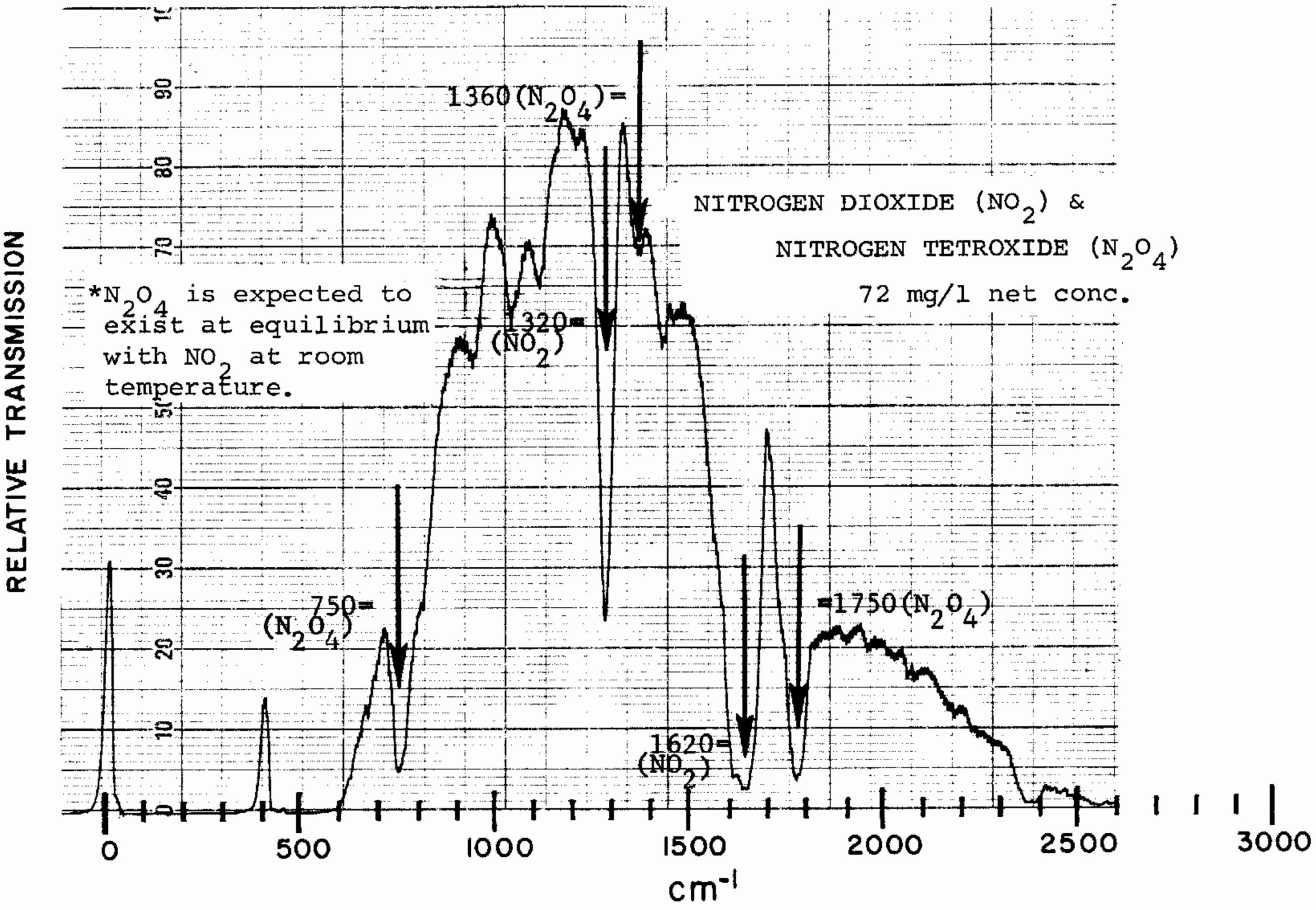

NITROGEN DIOXIDE (NO_2) &
NITROGEN TETROXIDE (N_2O_4)
72 mg/l net conc.
*N_2O_4 is expected to exist at equilibrium with NO_2 at room temperature.
1360(N_2O_4)=
1320=(NO_2)
750=(N_2O_4)
1620=(NO_2)
=1750(N_2O_4)
RELATIVE TRANSMISSION
10
20
30
40
50
70
80
90
10
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 76

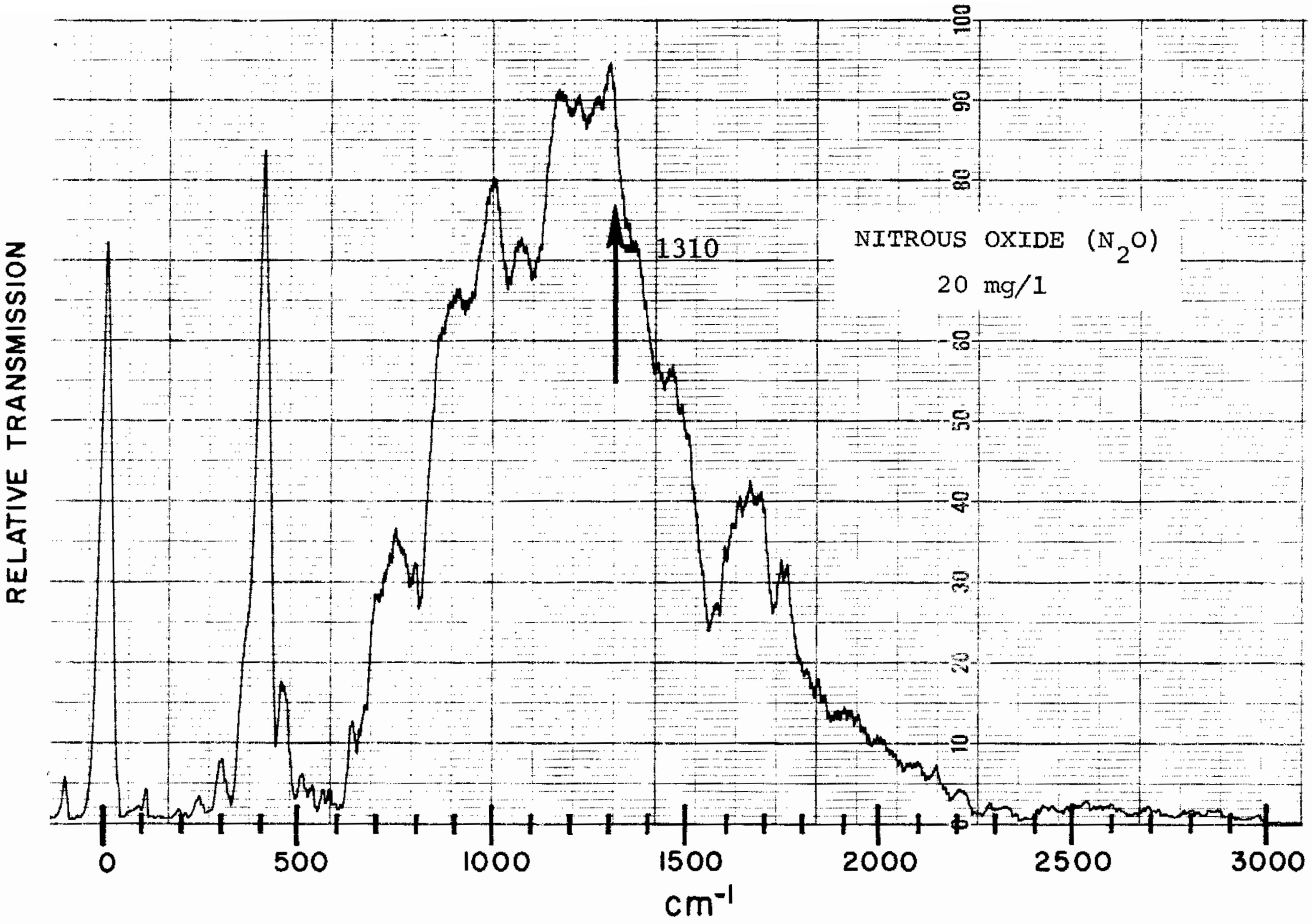

NITROUS OXIDE (N_2O)
20 mg/1
1310
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 77

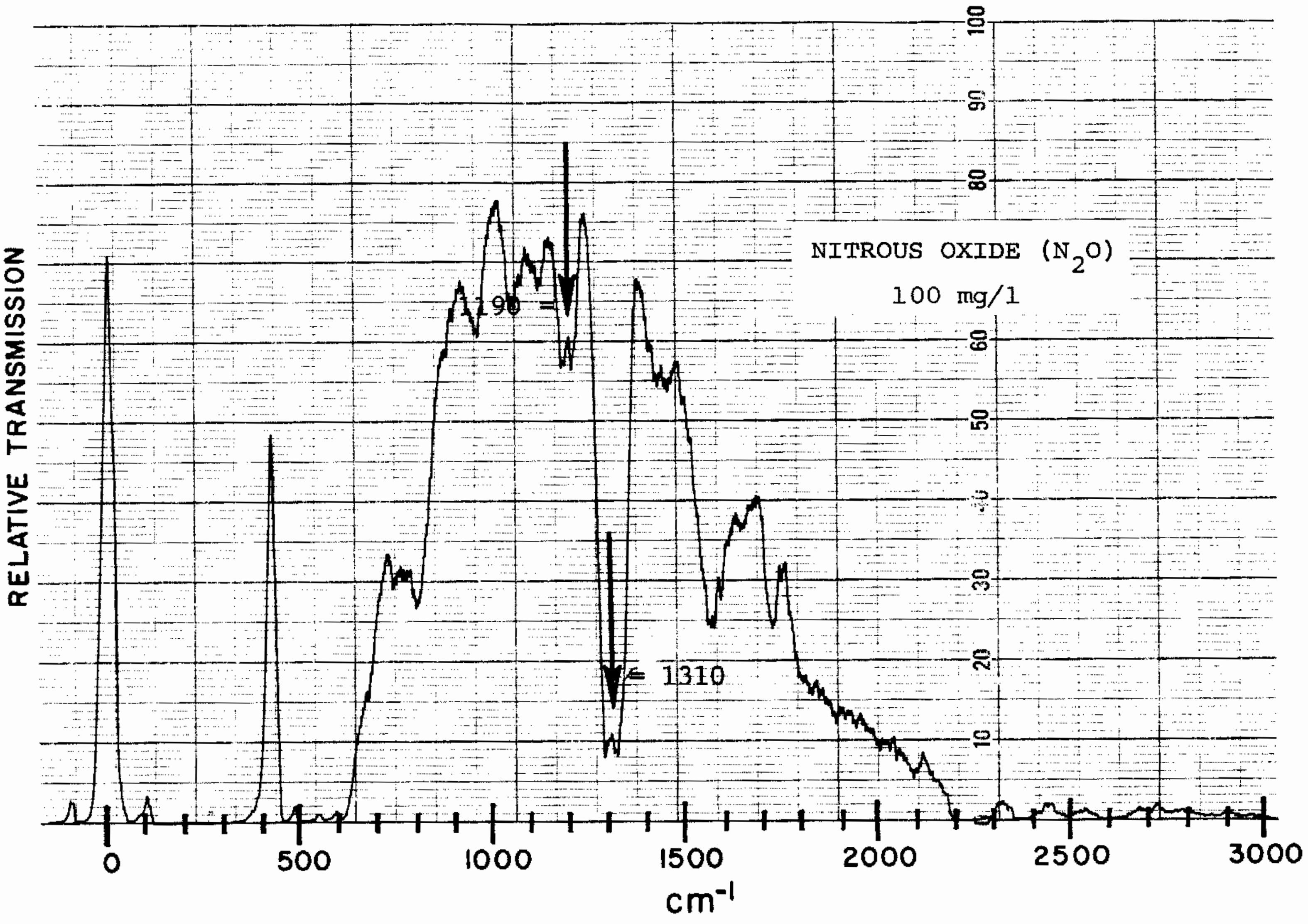

NITROUS OXIDE (N_2O)
100 mg/1
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
190 =
= 1310
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 78

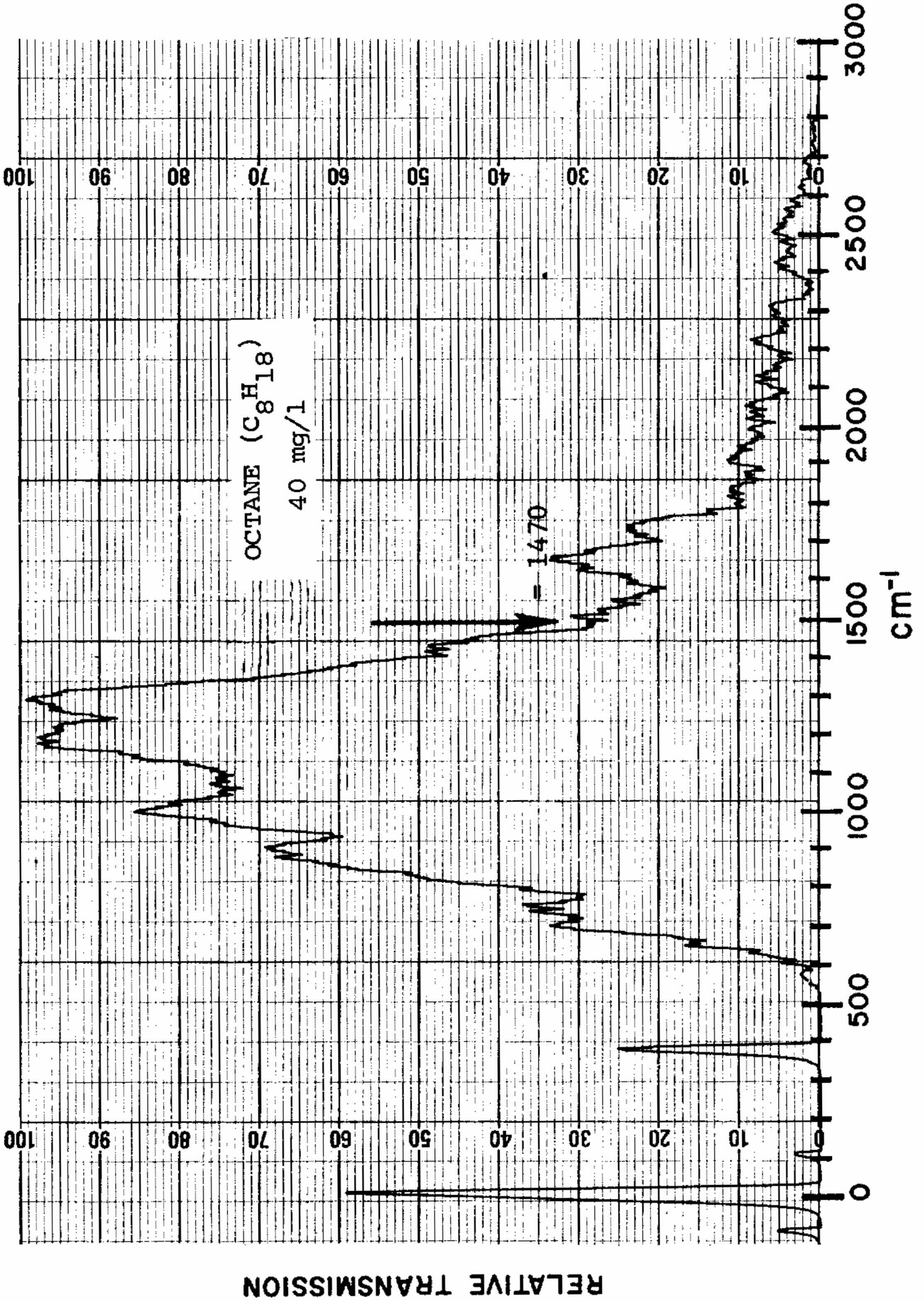
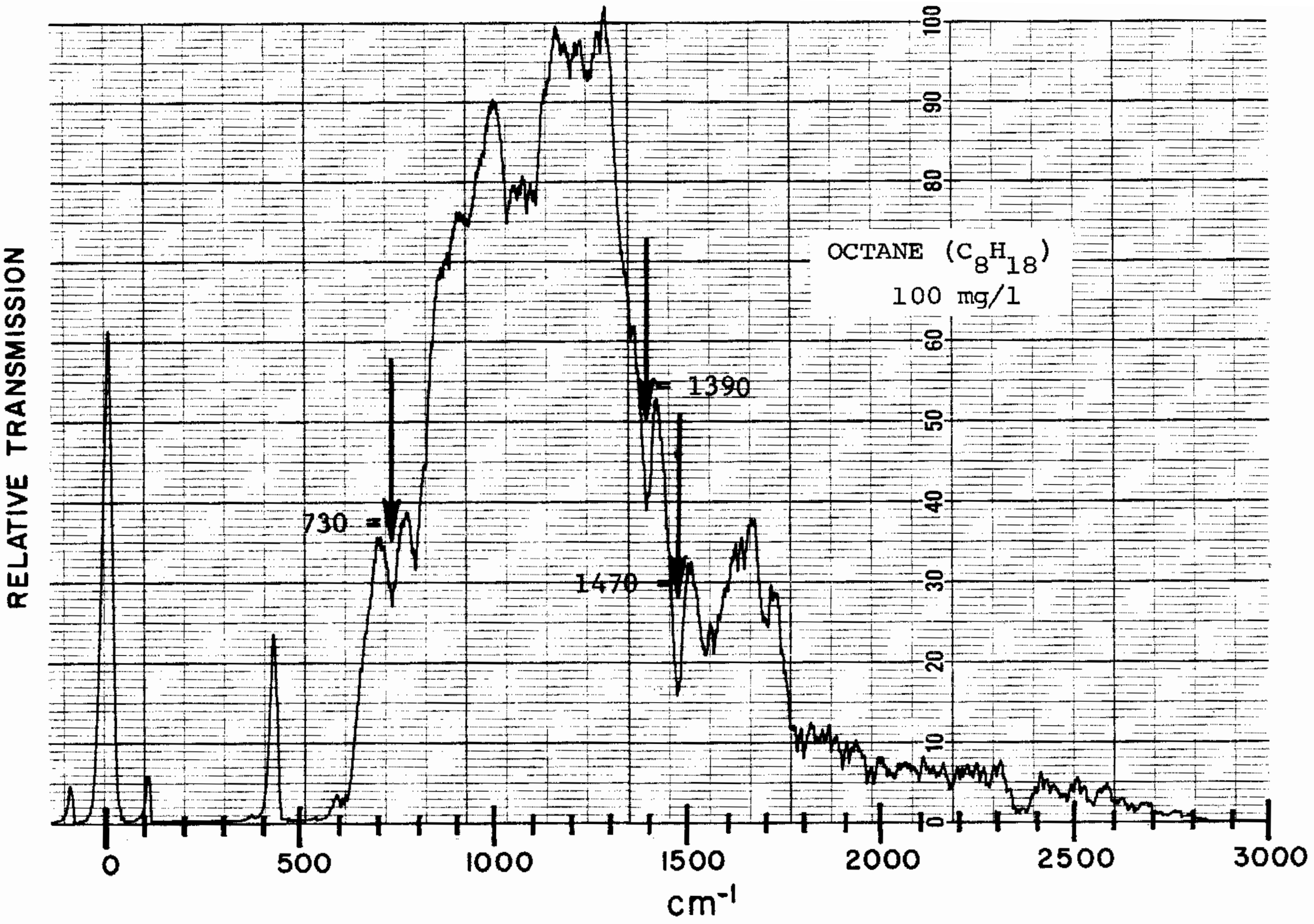

OCTANE (C_8H_{18})
40 mg/1
1470
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 79



OCTANE (C_8H_{18})
100 mg/l
1390
1470
730
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 80

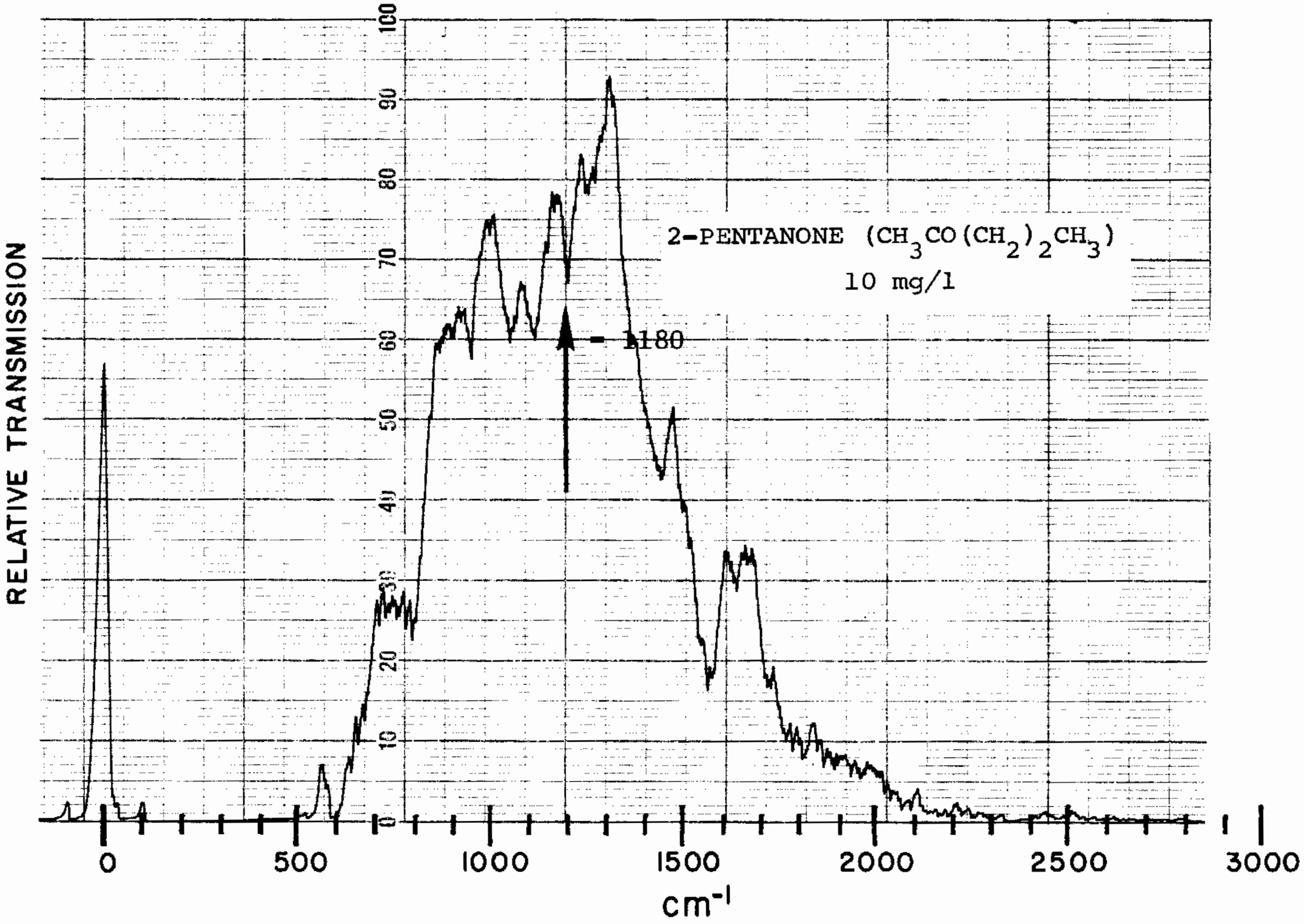

2-PENTANONE (CH$_3$CO(CH$_2$)$_2$CH$_3$)
10 mg/l
1180
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 81

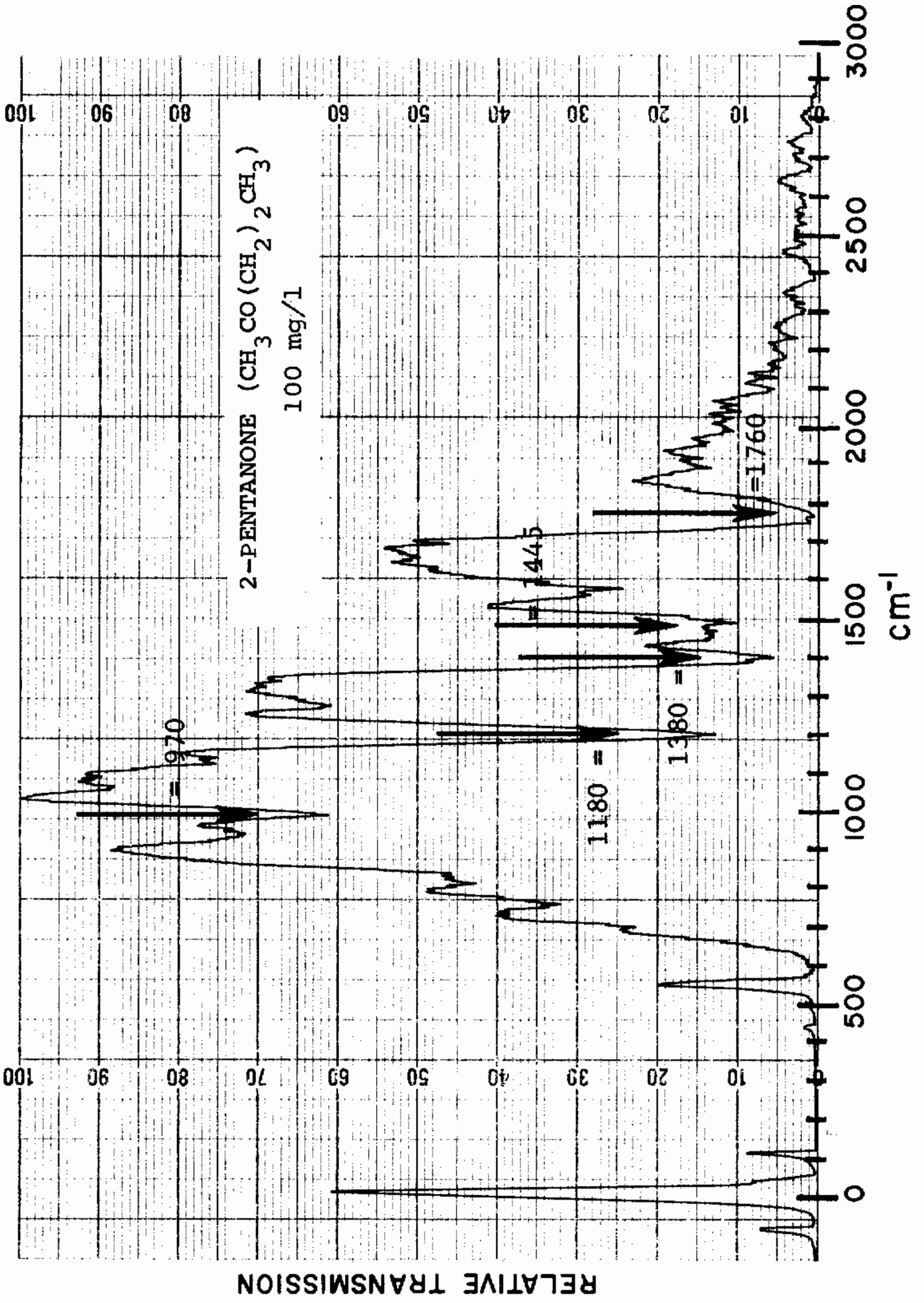

2-PENTANONE $(CH_3CO(CH_2)_2CH_3)$
100 mg/l
= 970
1180 =
1380 =
= 1445
=1760
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 82

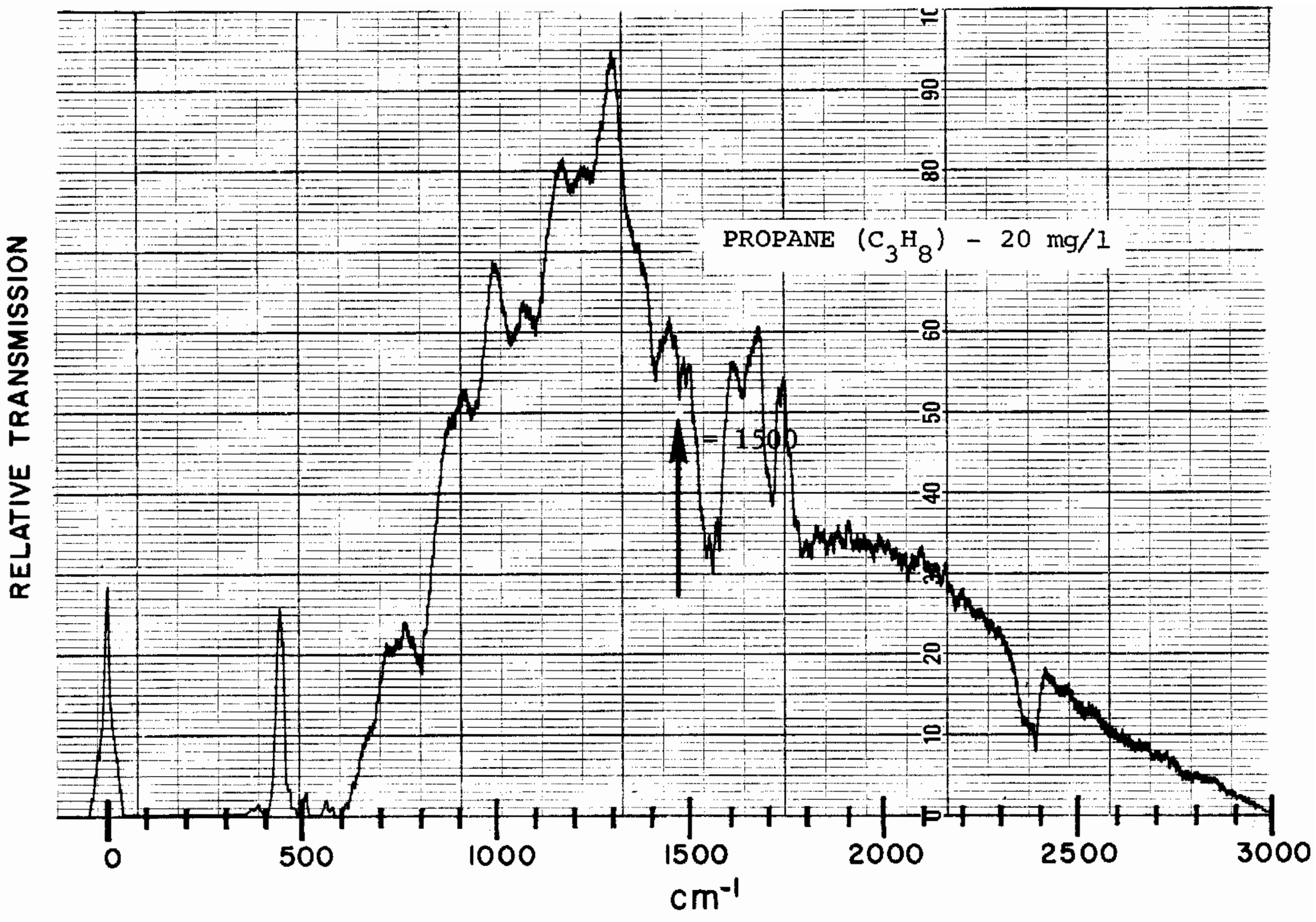

PROPANE (C_3H_8) - 20 mg/1
RELATIVE TRANSMISSION
10
90
80
60
50
40
30
20
10
0
= 1500
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 83

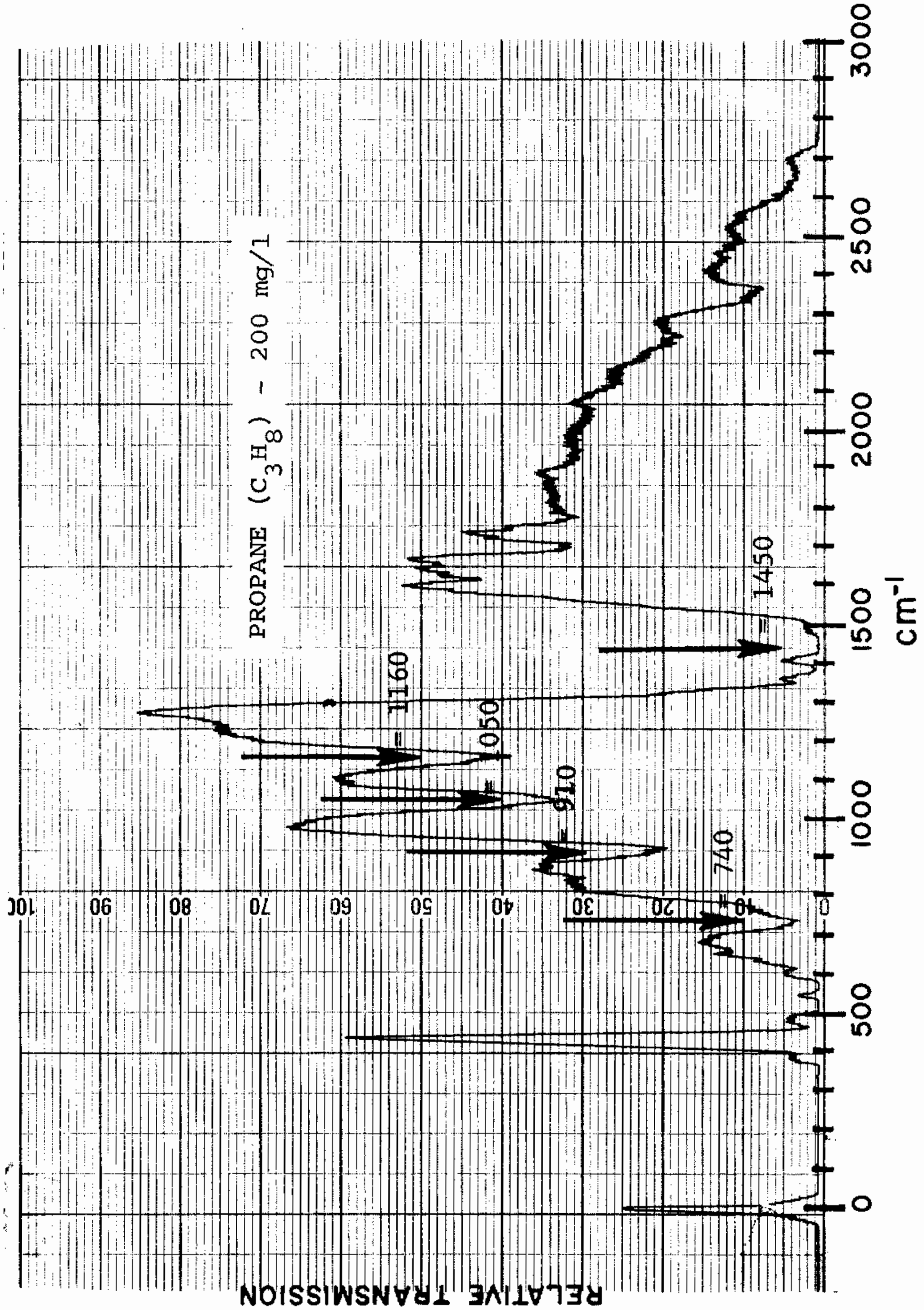

PROPANE (C_3H_8) - 200 mg/1
1160
1050
910
740
1450
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm^{-1}

Figure 84

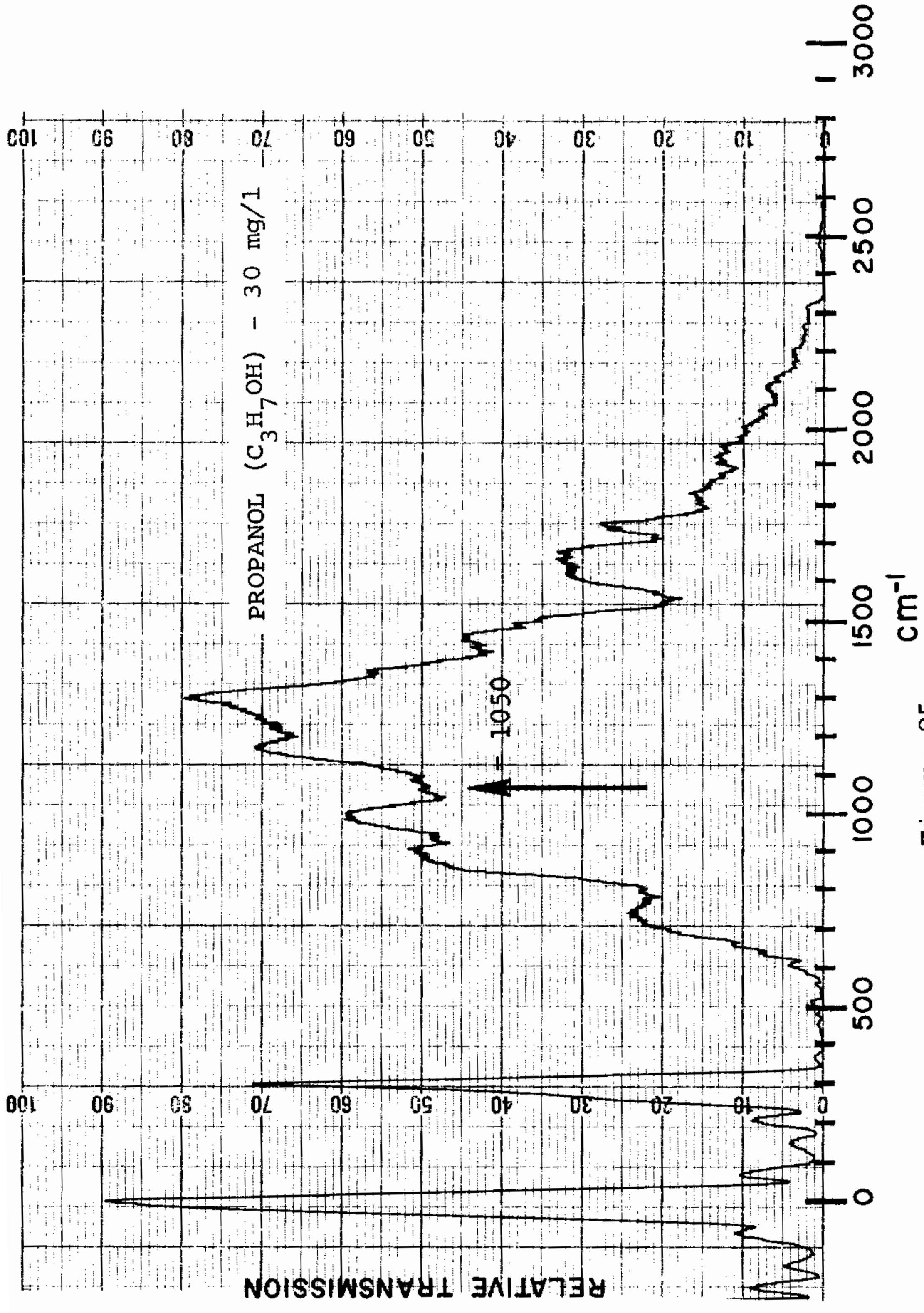

PROPANOL (C_3H_7OH) - 30 mg/1
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
← 1050
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 85

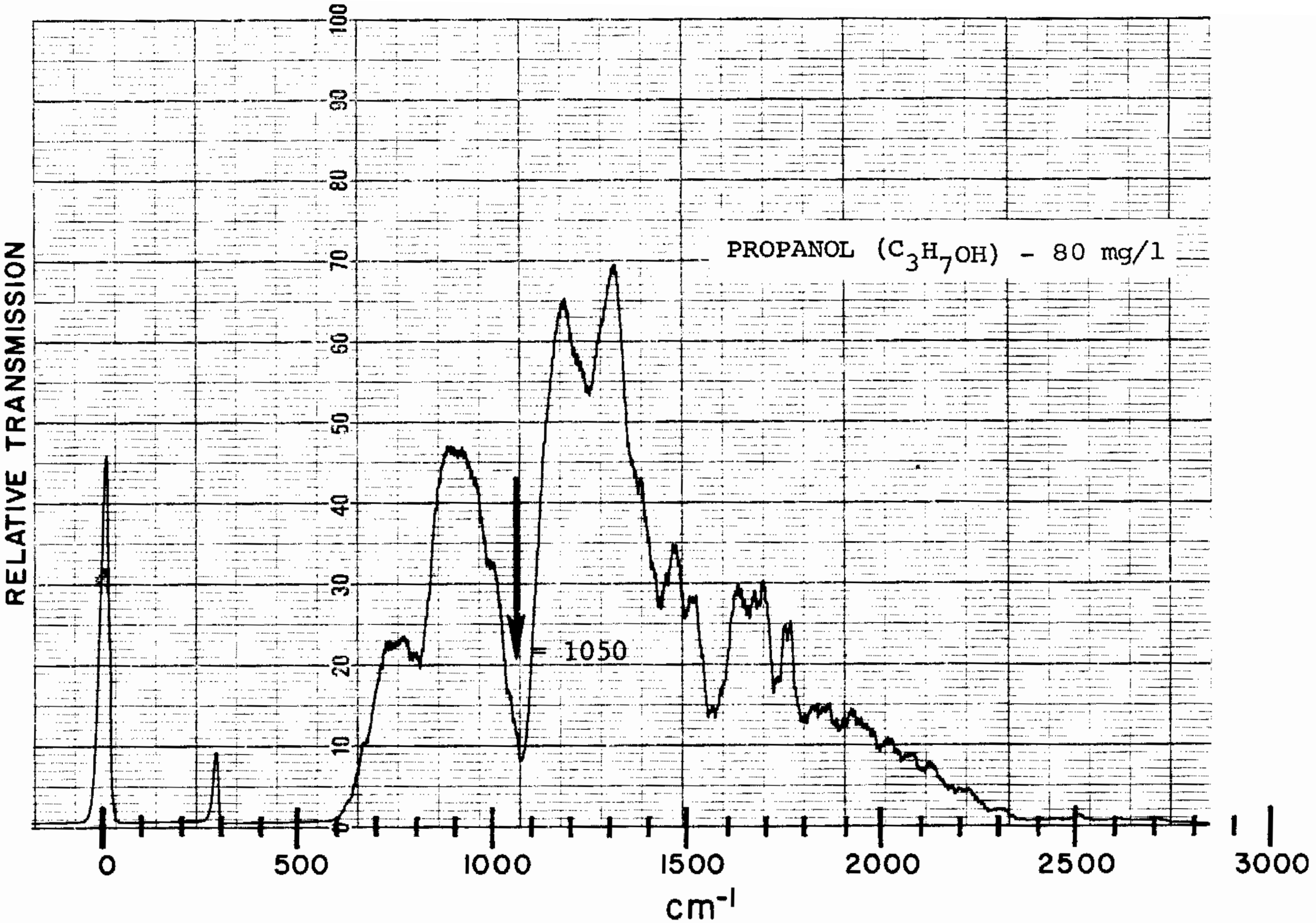

PROPANOL (C_3H_7OH) - 80 mg/1
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
1050
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 86

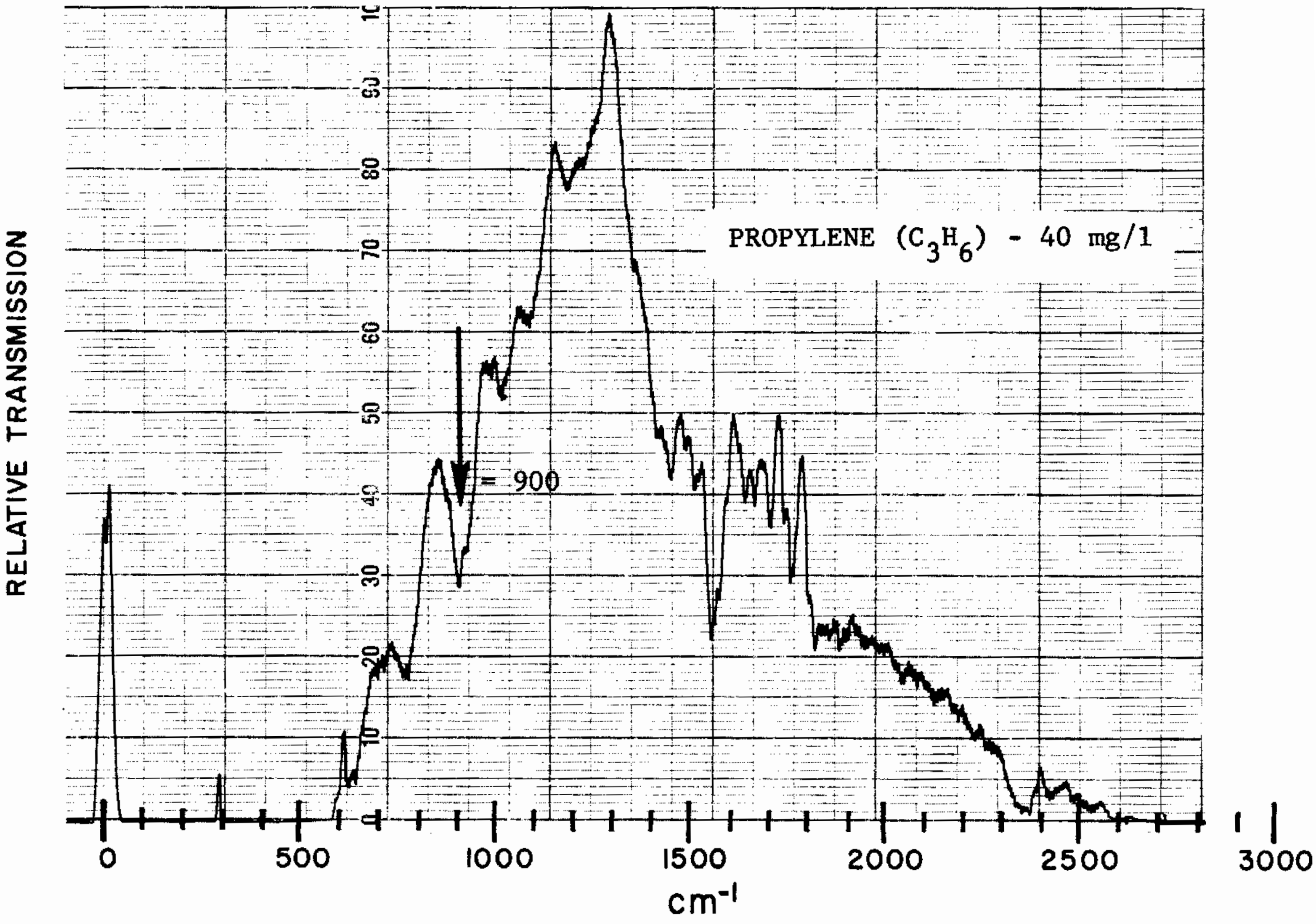

PROPYLENE (C_3H_6) - 40 mg/1
RELATIVE TRANSMISSION
10
90
80
70
60
50
40
30
20
10
0
= 900
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 87

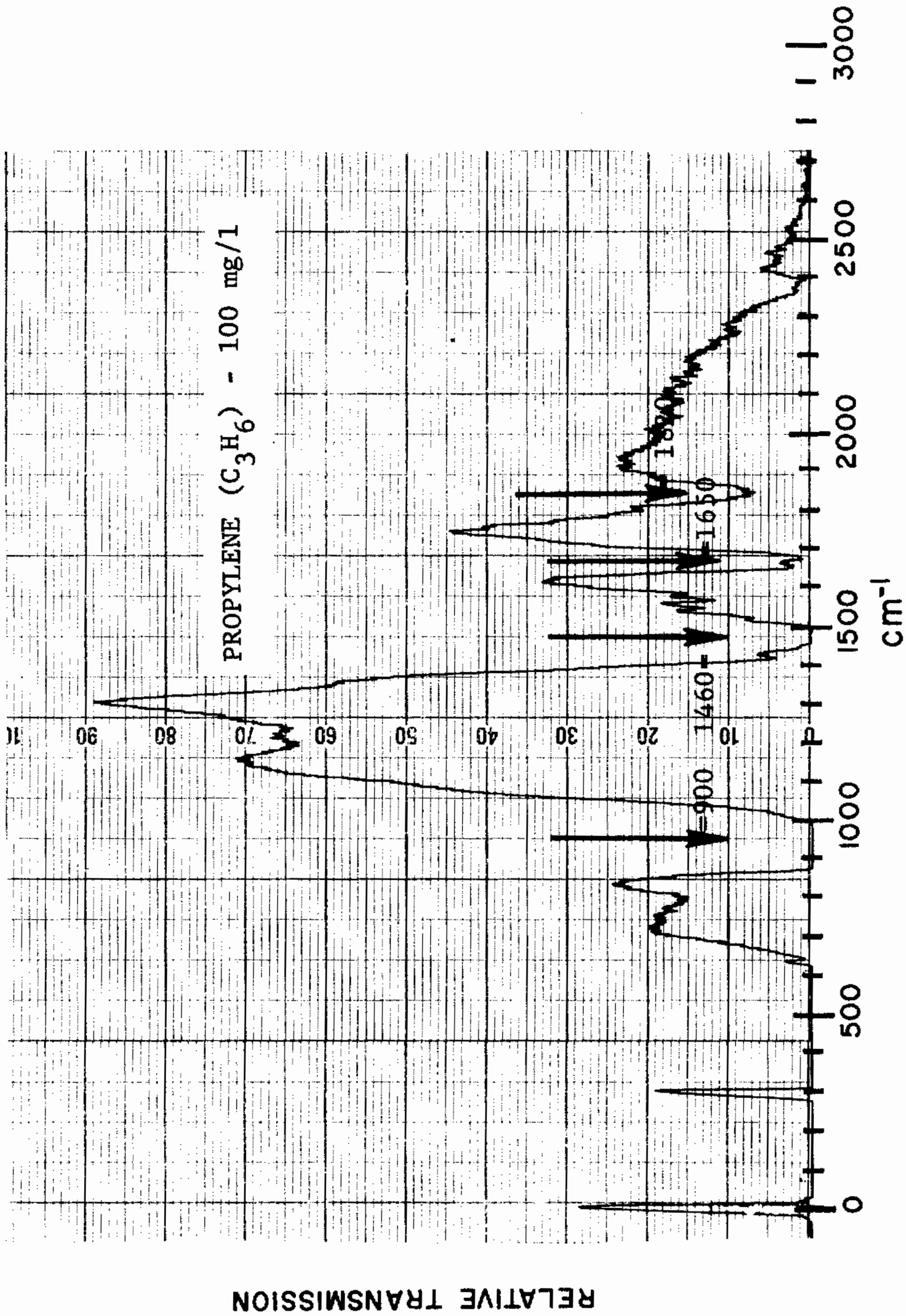

PROPYLENE (C_3H_6) - 100 mg/1
0
500
1000
1500
2000
2500
3000
cm^{-1}
10
20
30
40
50
60
70
80
90
900
1460
1650
1890
P
RELATIVE TRANSMISSION

Figure 88

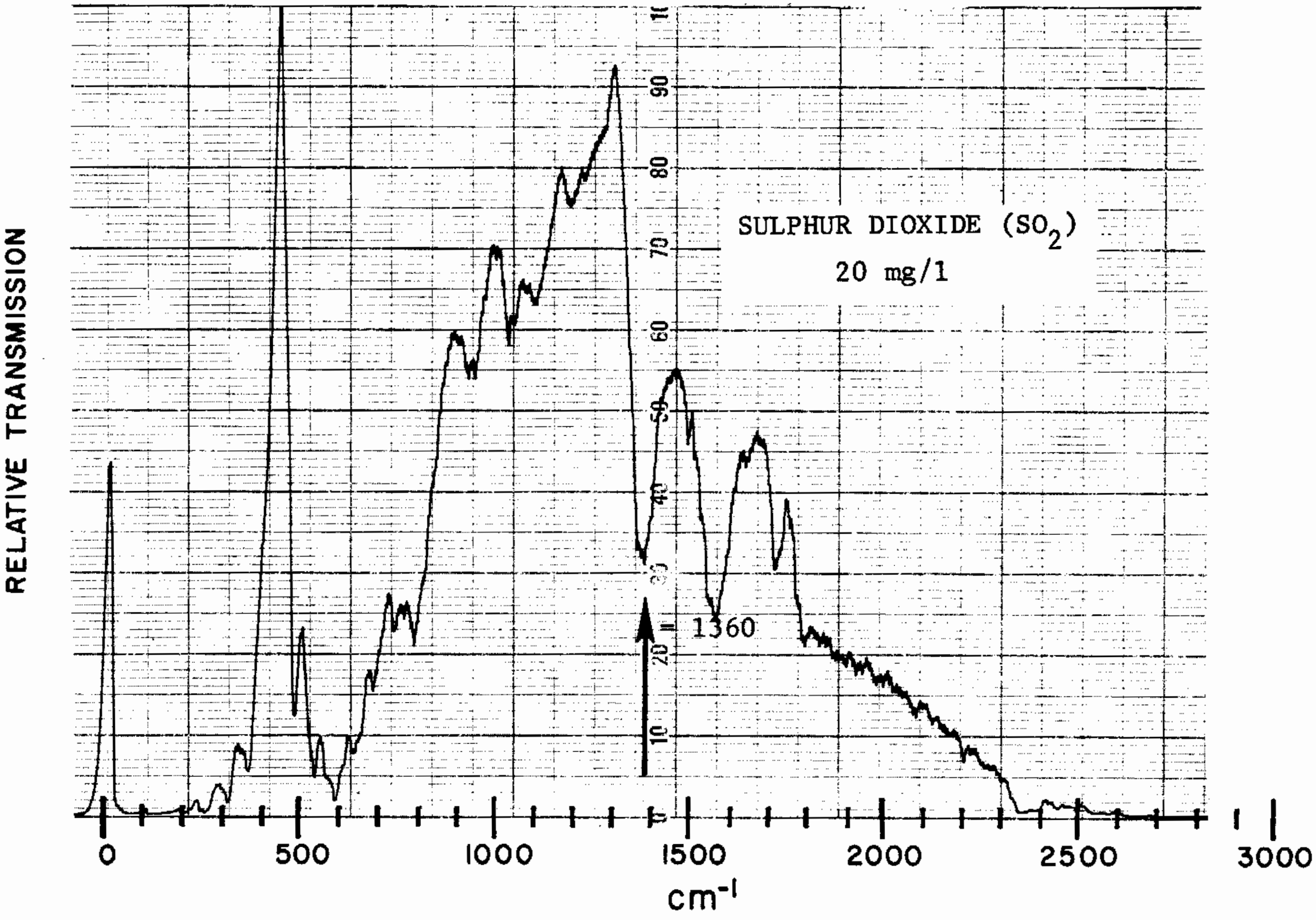

SULPHUR DIOXIDE (SO_2)
20 mg/1
RELATIVE TRANSMISSION
10
20
30
40
50
60
70
80
90
1360
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 89

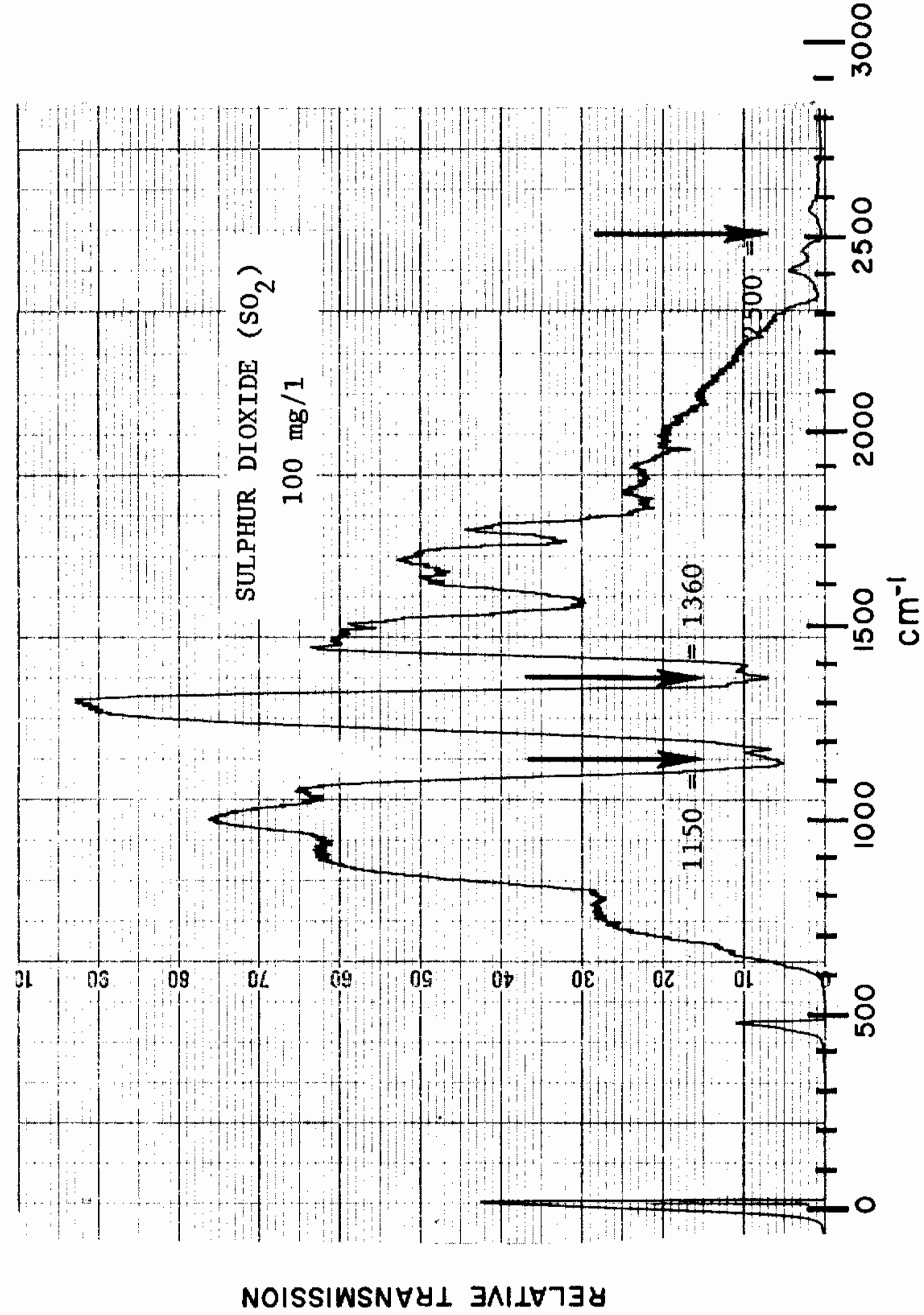

SULPHUR DIOXIDE (SO_2)
100 mg/1
1150 =
= 1360
2500 =
0
500
1000
1500
2000
2500
3000
cm^{-1}
10
20
30
40
50
60
70
80
90
10
RELATIVE TRANSMISSION

Figure 90

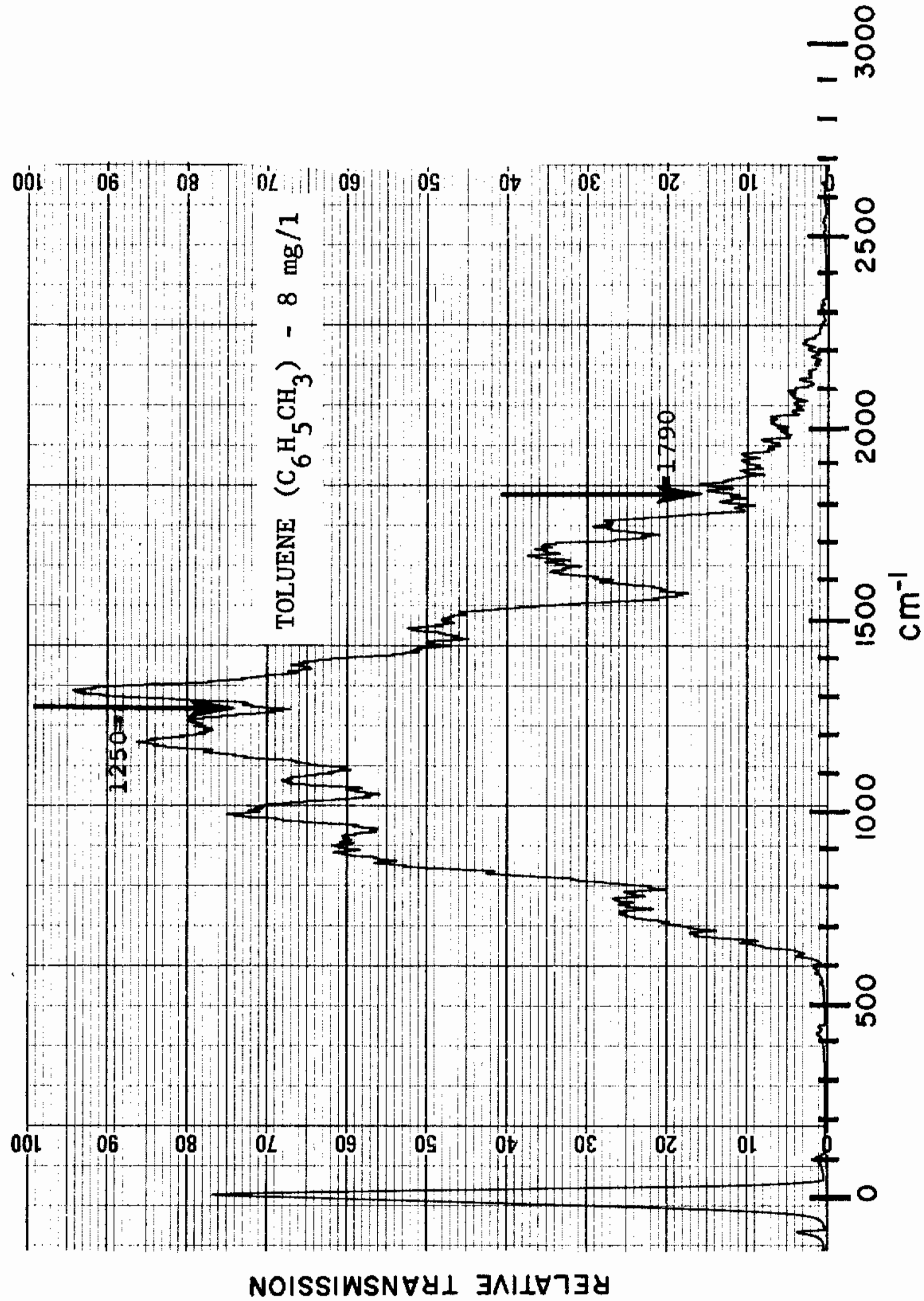

TOLUENE ($C_6H_5CH_3$) - 8 mg/1
1250
1790
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 91

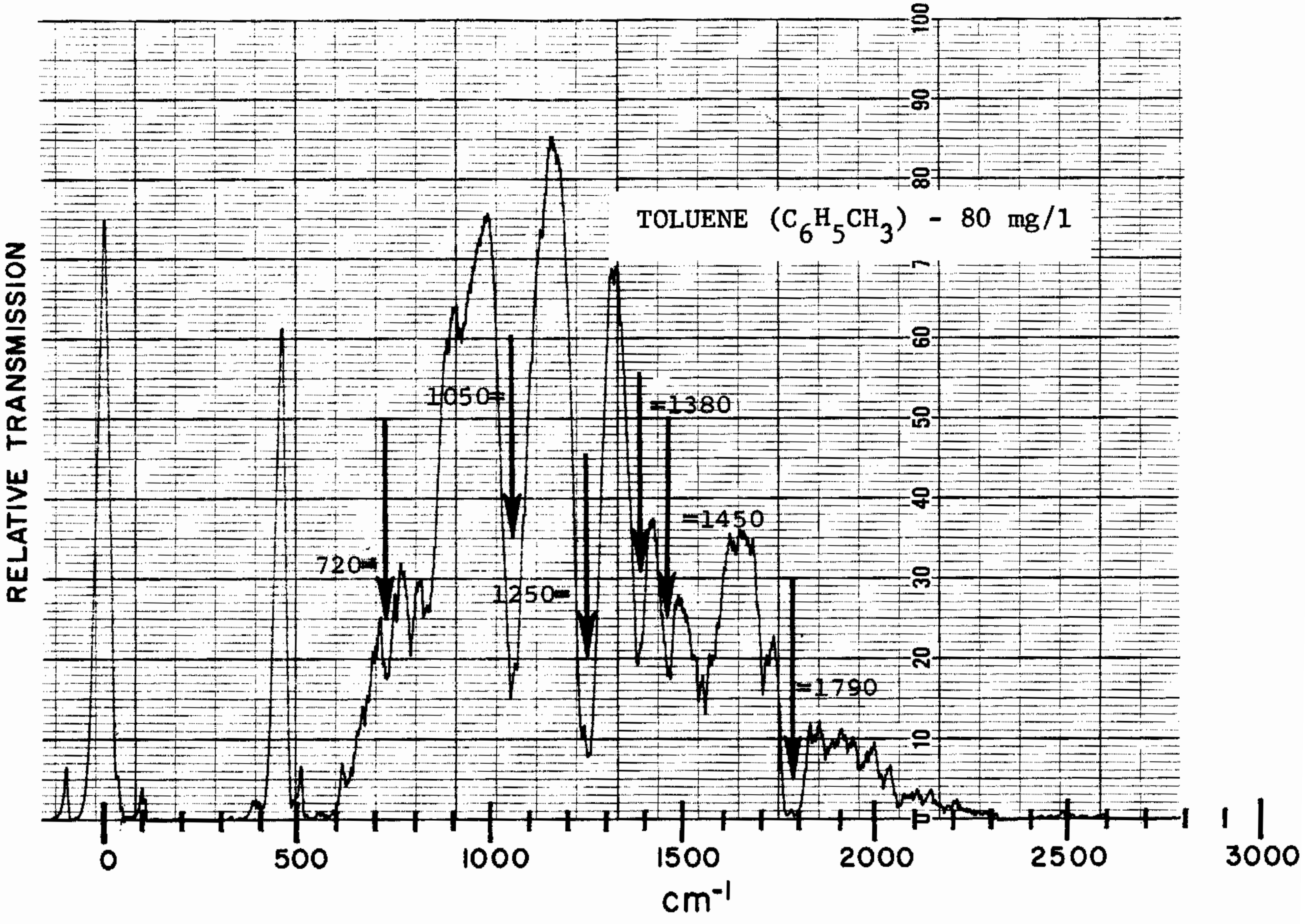

TOLUENE $(C_6H_5CH_3)$ - 80 mg/1
RELATIVE TRANSMISSION
100
90
80
7
60
50
40
30
20
10
720
1050
1250
1380
1450
1790
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 92

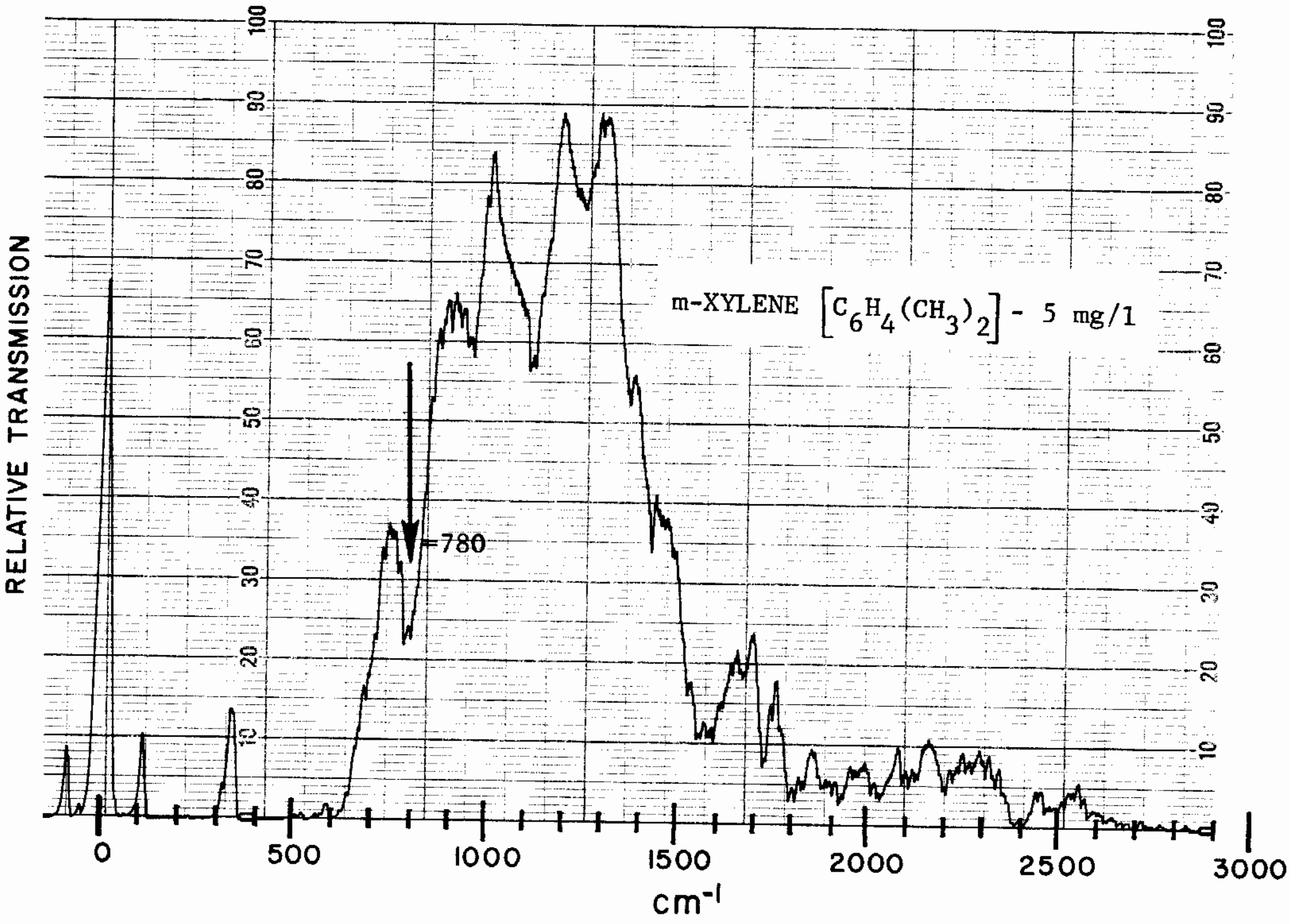

m-XYLENE $[C_6H_4(CH_3)_2]$ - 5 mg/1
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
780
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 93

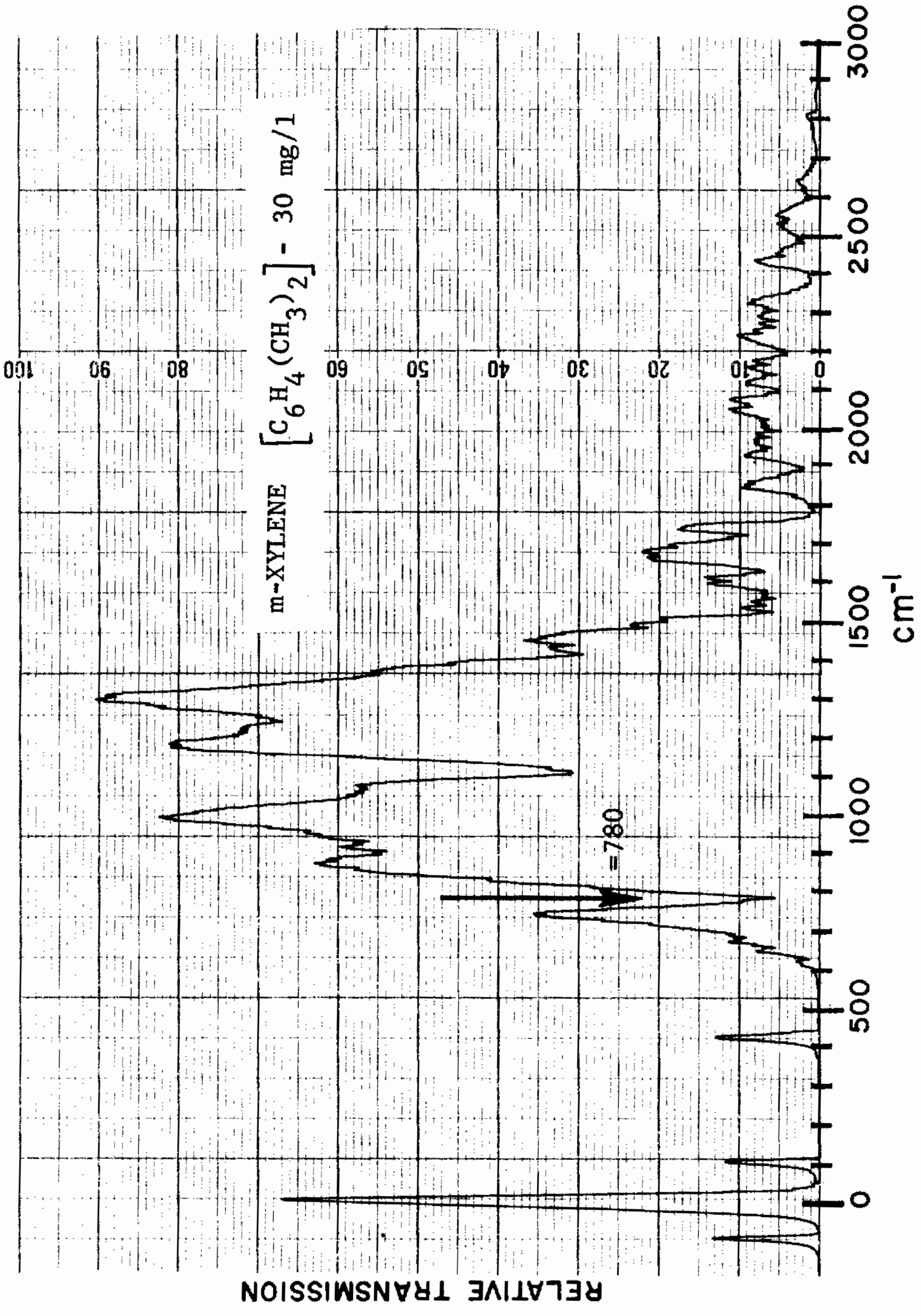

m-XYLENE $[C_6H_4(CH_3)_2]$ - 30 mg/1
≈780
RELATIVE TRANSMISSION
100
90
80
60
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm^{-1}

Figure 94

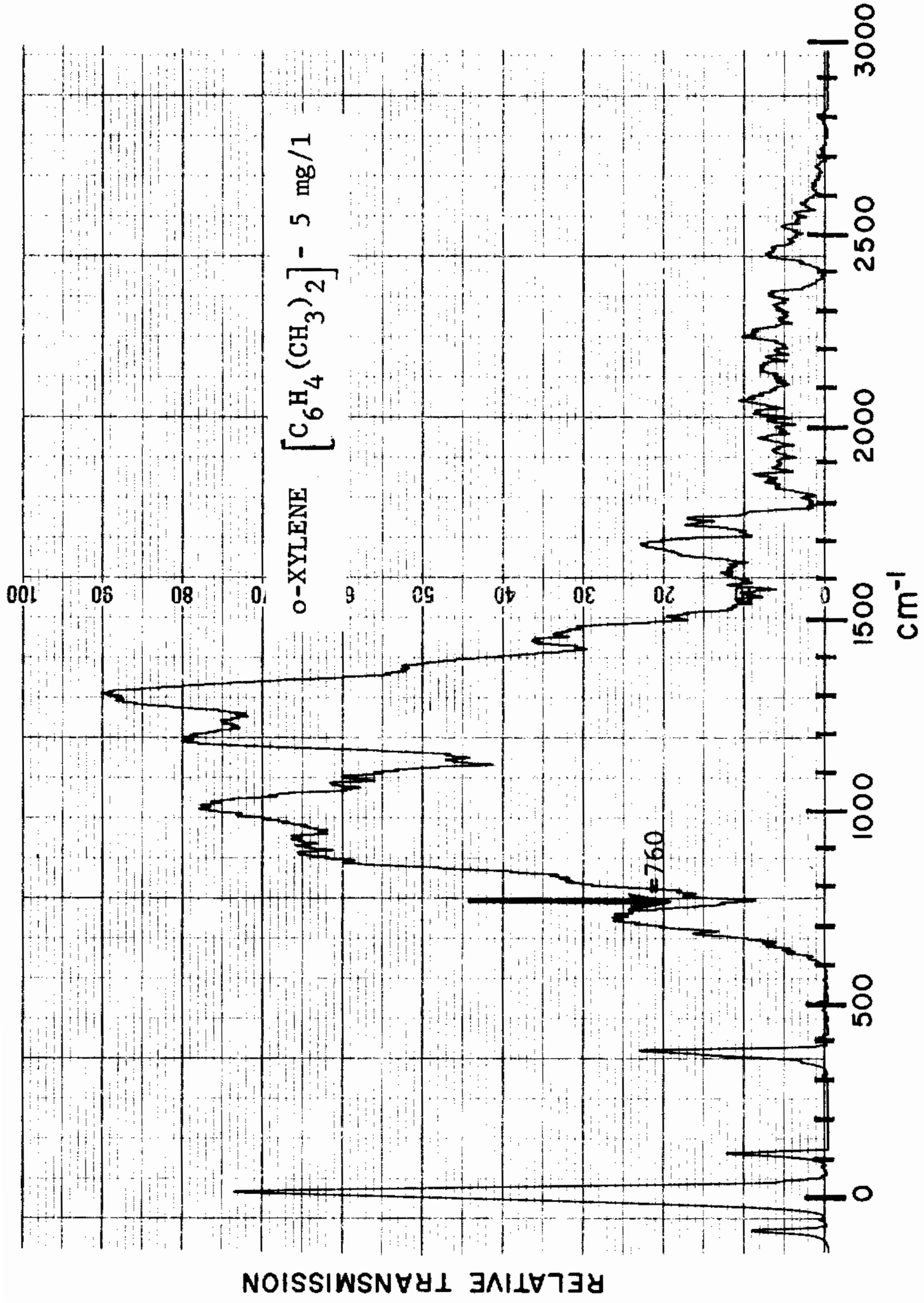
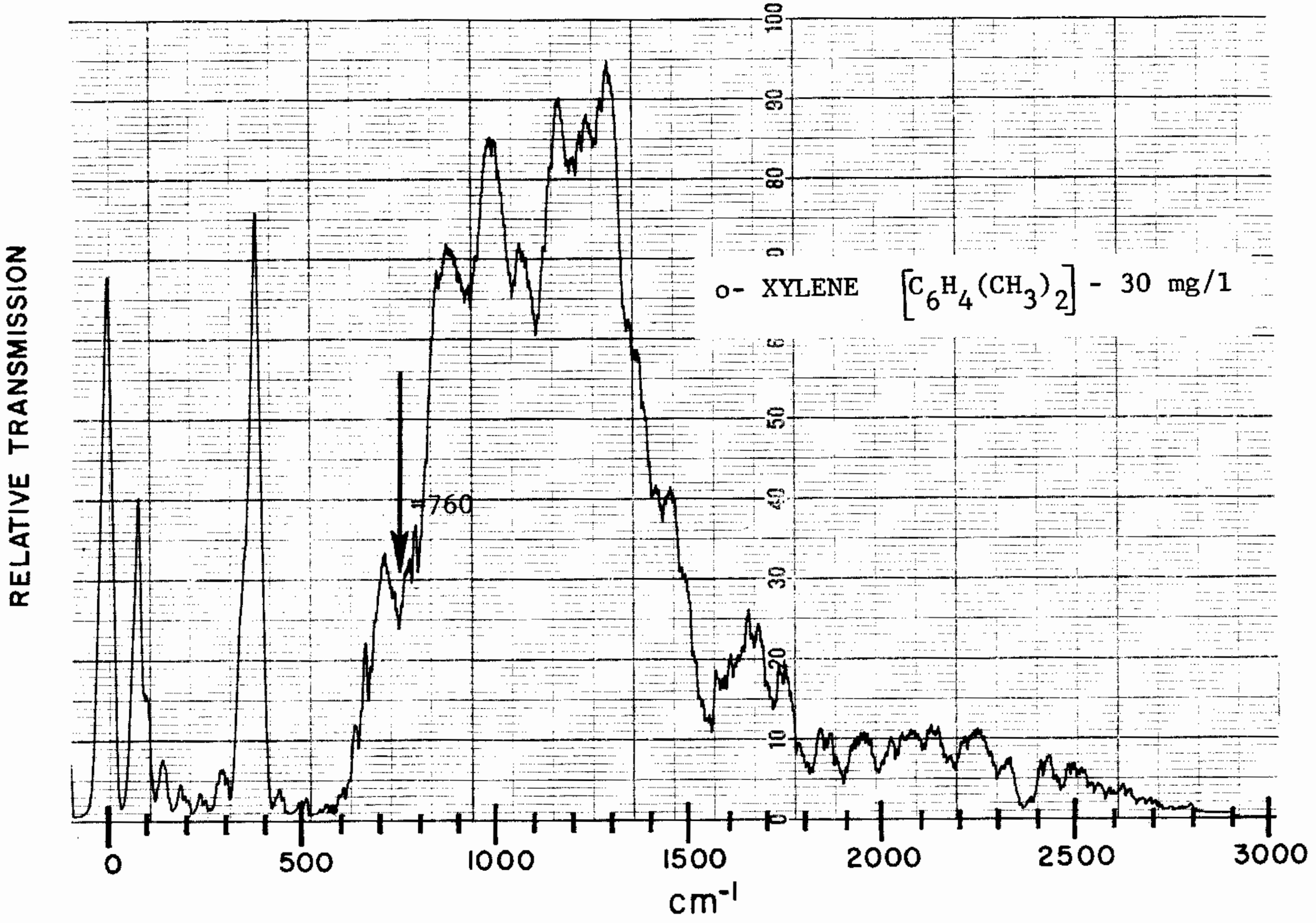

o-XYLENE
[$C_6H_4(CH_3)_2$] - 5 mg/l
760
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 95



o- XYLENE $[C_6H_4(CH_3)_2]$ - 30 mg/1

Figure 96

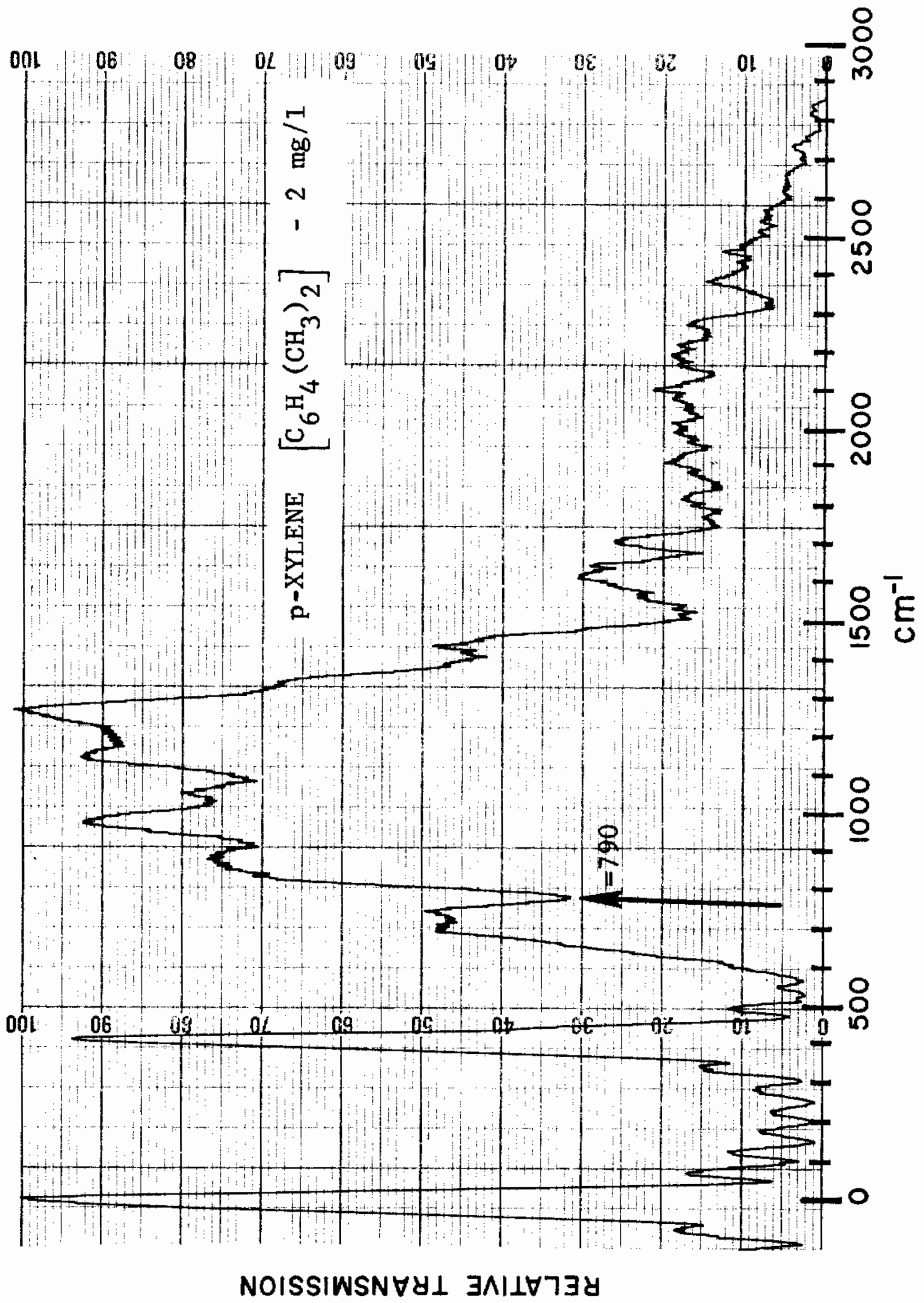

p-XYLENE $[C_6H_4(CH_3)_2]$ - 2 mg/1
=790
cm^{-1}
0
500
1000
1500
2000
2500
3000
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100

Figure 97

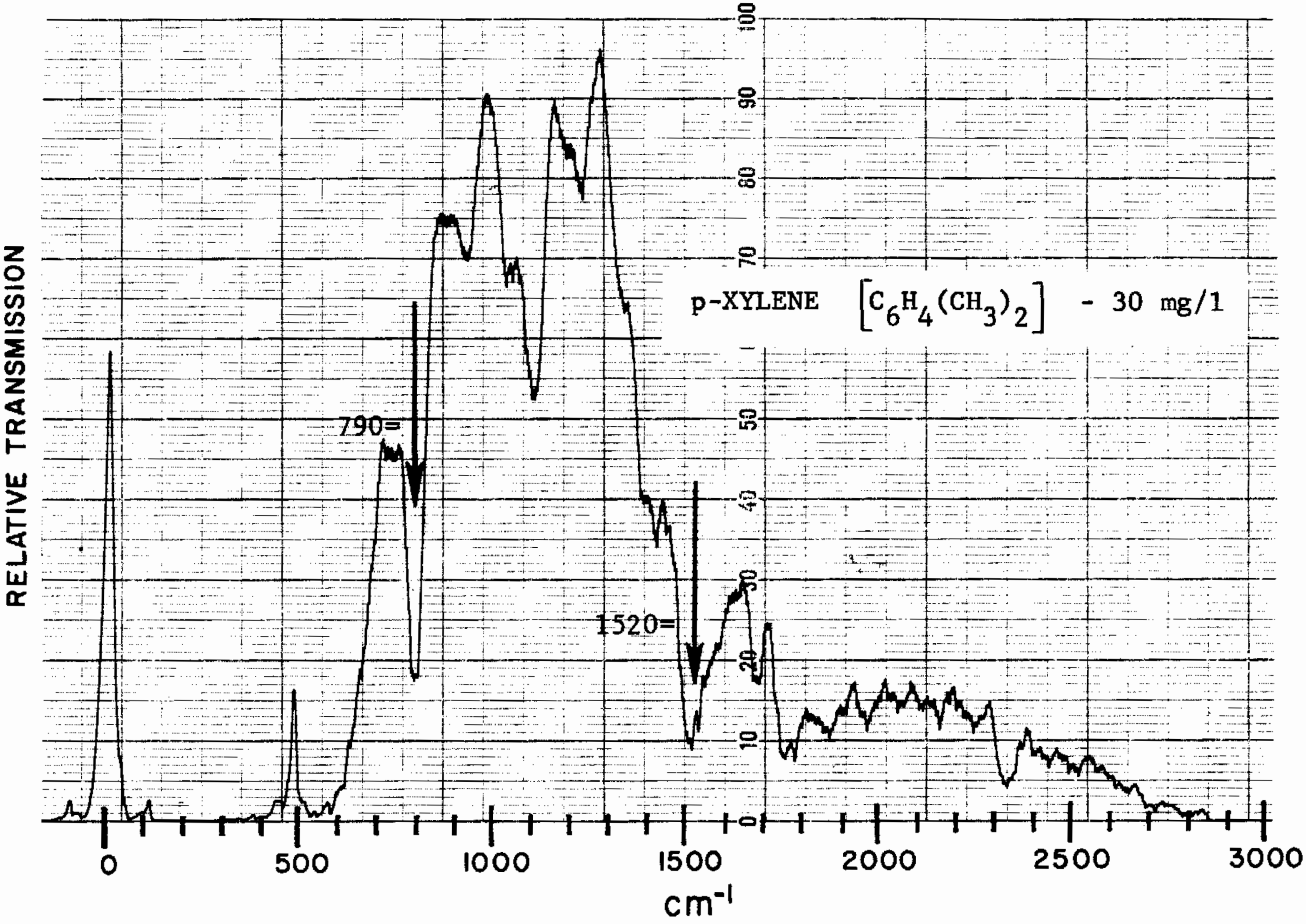

p-XYLENE $\left[C_6H_4(CH_3)_2\right]$ - 30 mg/1
RELATIVE TRANSMISSION
cm^{-1}
790=
1520=
0
10
20
30
40
50
70
80
90
100
0
500
1000
1500
2000
2500
3000

Figure 98

APPENDIX II

SPECTRA OF MIXTURES

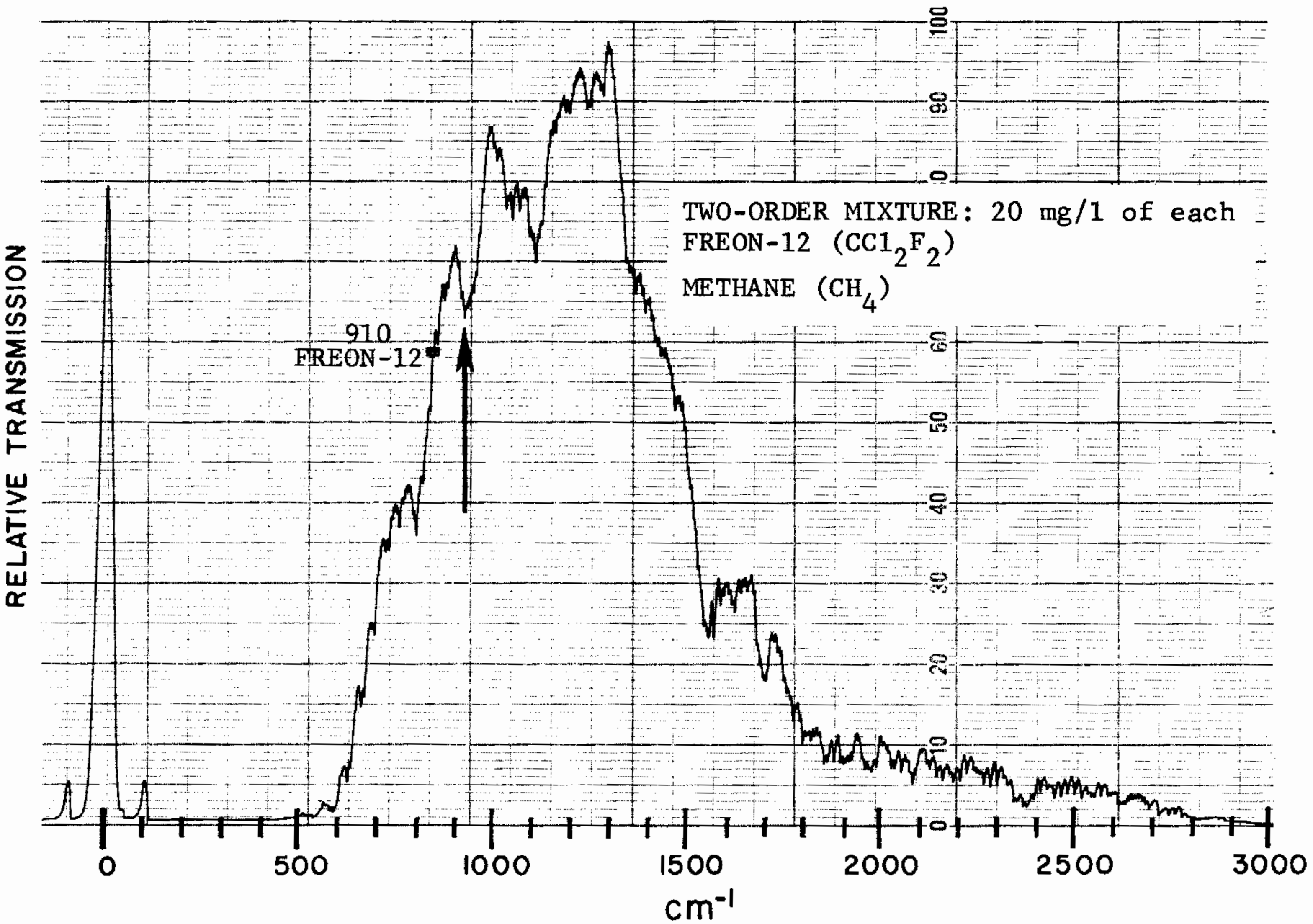

TWO-ORDER MIXTURE: 20 mg/1 of each
FREON-12 (CCl_2F_2)
METHANE (CH_4)
910
FREON-12
RELATIVE TRANSMISSION
100
90
0
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 99

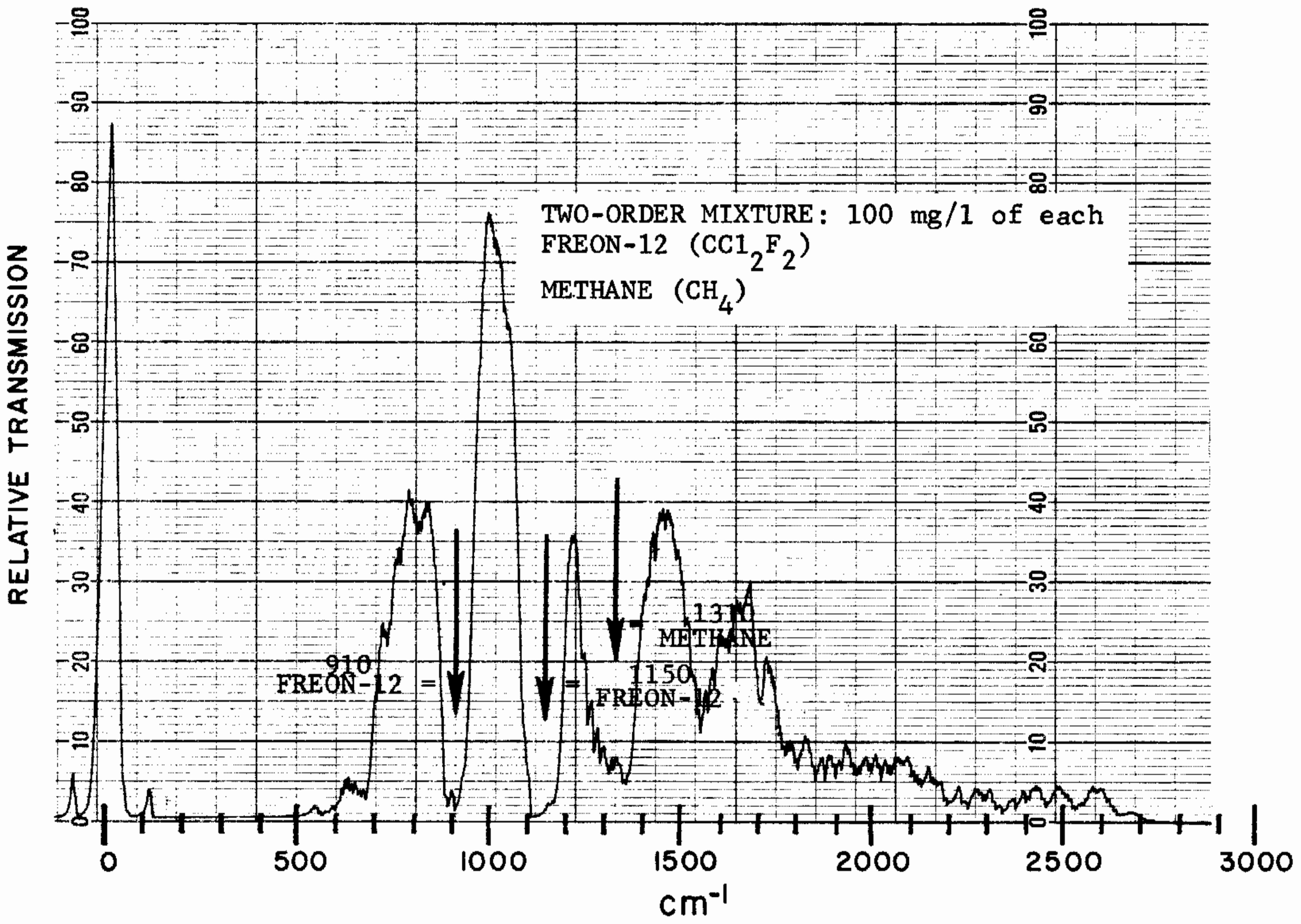

TWO-ORDER MIXTURE: 100 mg/1 of each
FREON-12 (CCl_2F_2)
METHANE (CH_4)
910
FREON-12 =
1150
= FREON-12
1310
= METHANE
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 100

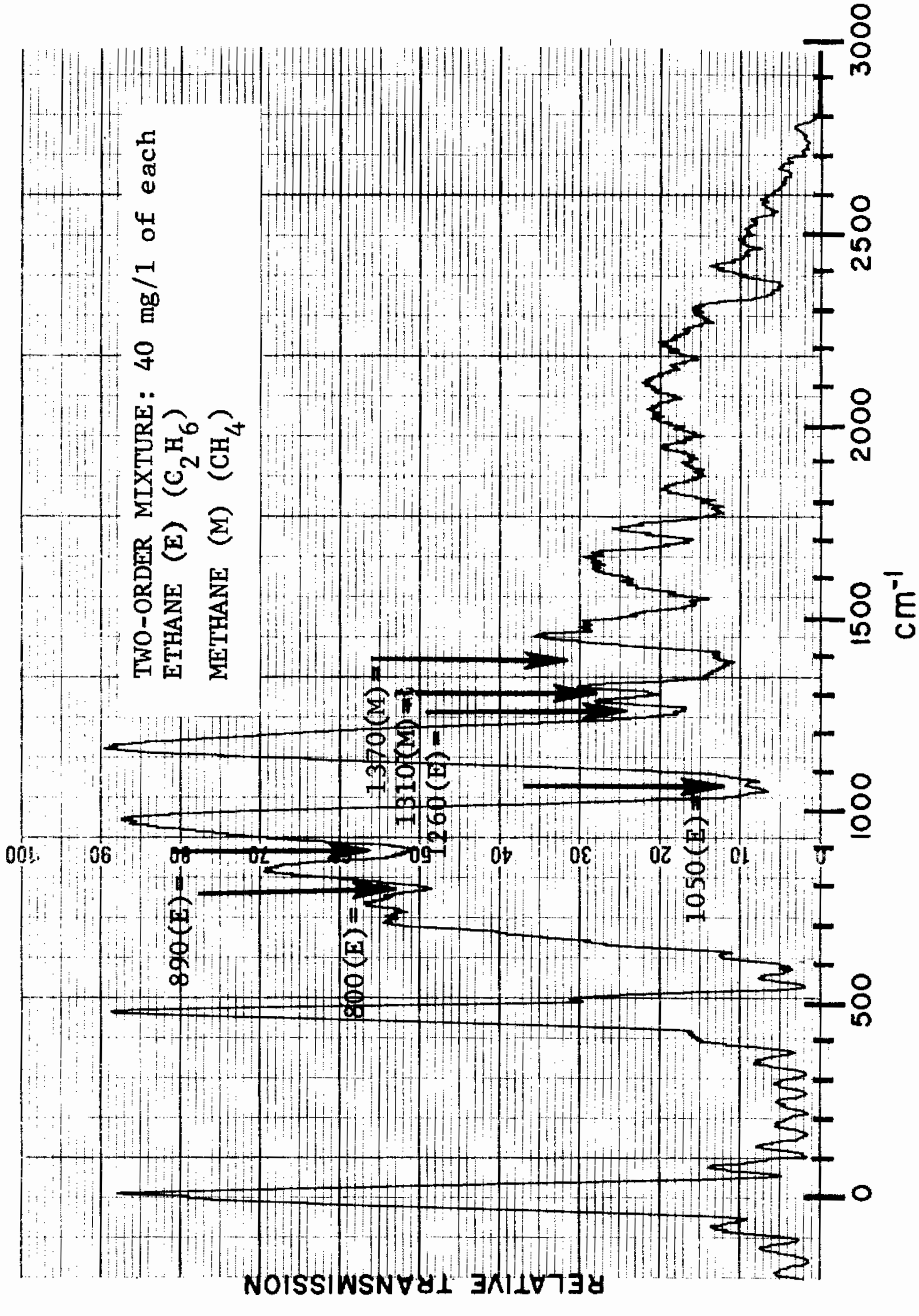

TWO-ORDER MIXTURE: 40 mg/1 of each
ETHANE (E) (C_2H_6)
METHANE (M) (CH_4)
1370(M)
1310(M)
1260(E)
1050(E)
890(E)
800(E)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm^{-1}

Figure 101

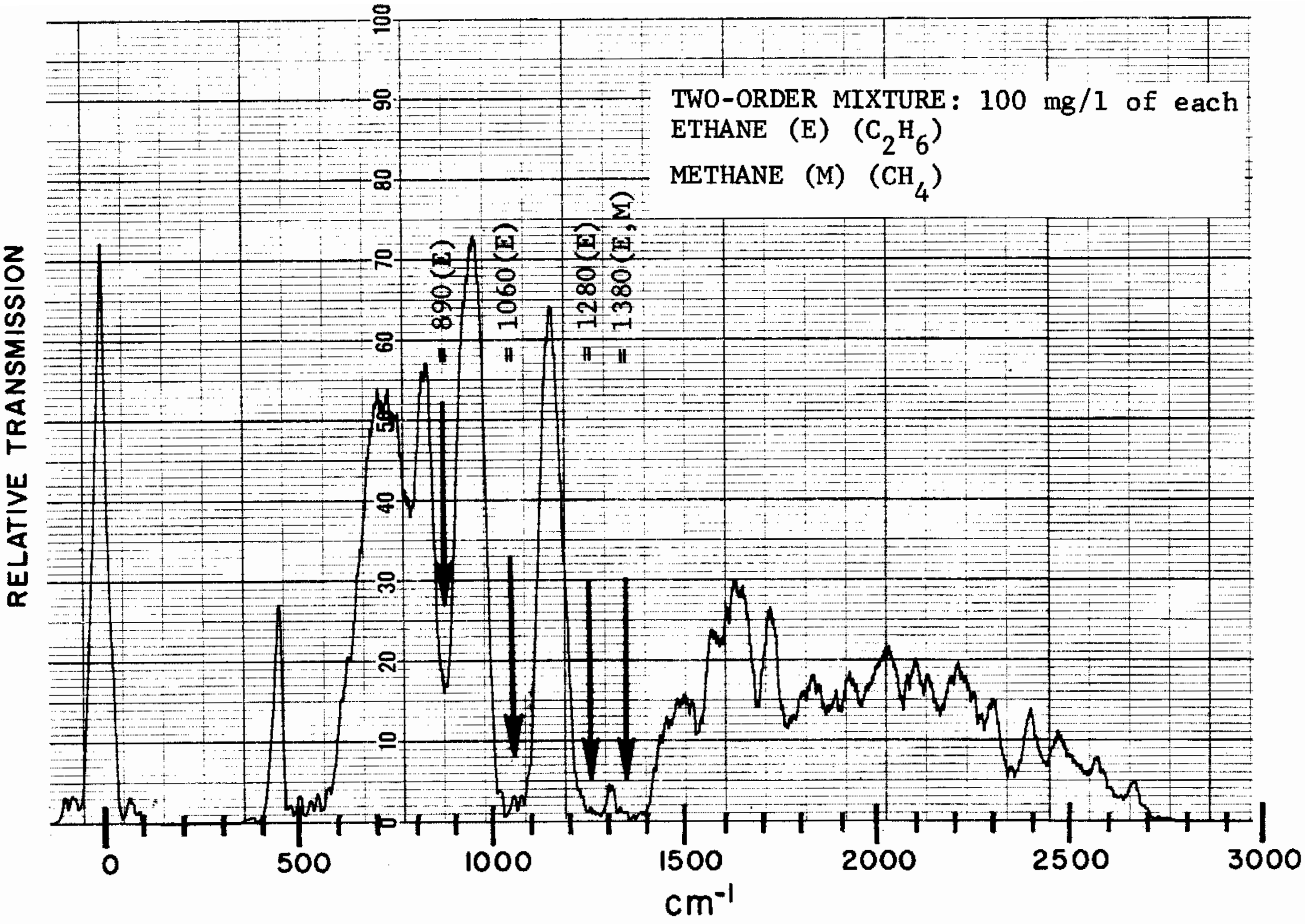

TWO-ORDER MIXTURE: 100 mg/1 of each
ETHANE (E) (C_2H_6)
METHANE (M) (CH_4)
= 890(E)
= 1060(E)
= 1280(E)
= 1380(E,M)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 102

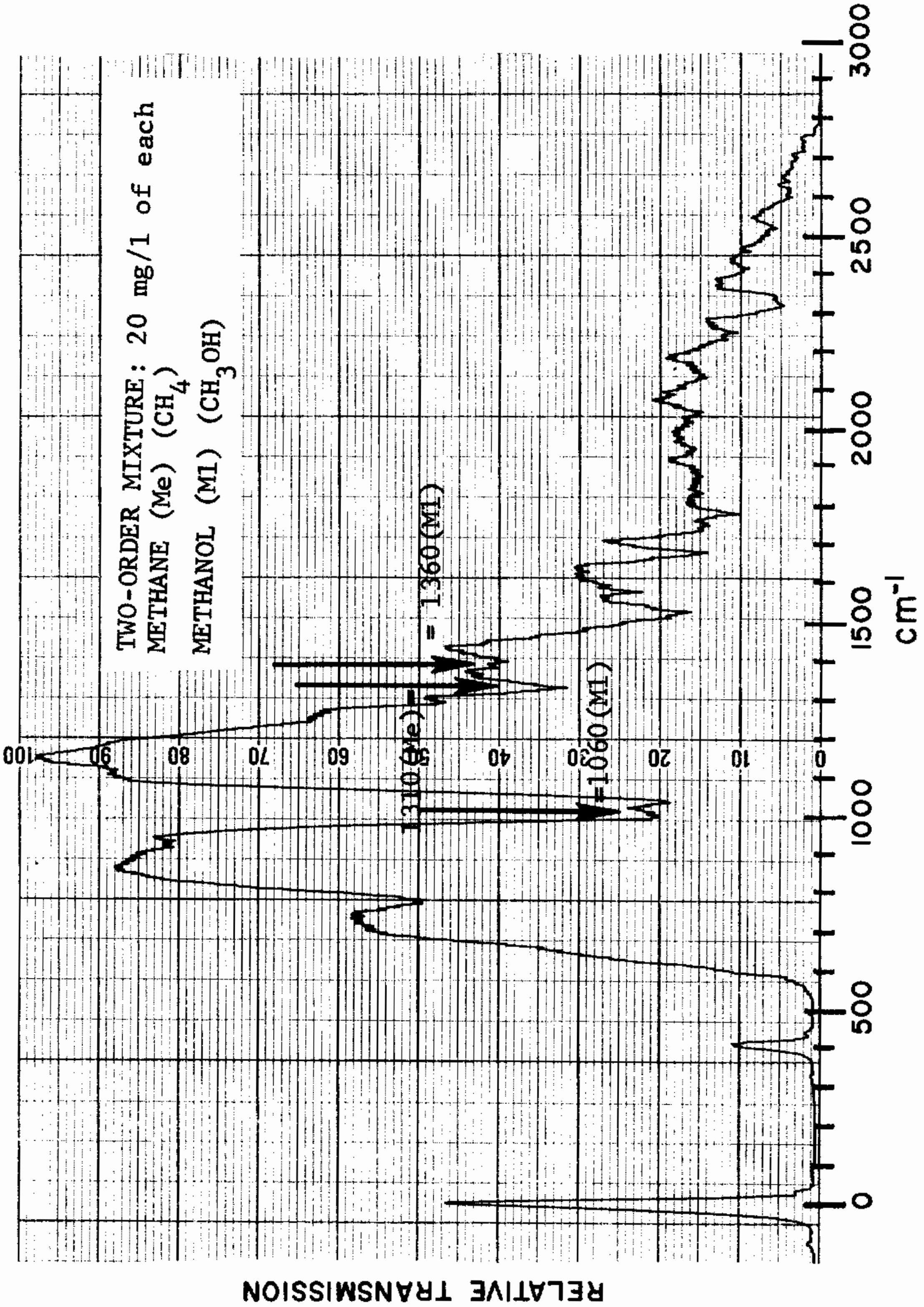

TWO-ORDER MIXTURE: 20 mg/1 of each
METHANE (Me) (CH_4)
METHANOL (Ml) (CH_3OH)
= 1360 (Ml)
1310 (Me) =
=1060 (Ml)
100
90
80
70
60
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm^{-1}
RELATIVE TRANSMISSION

Figure 103

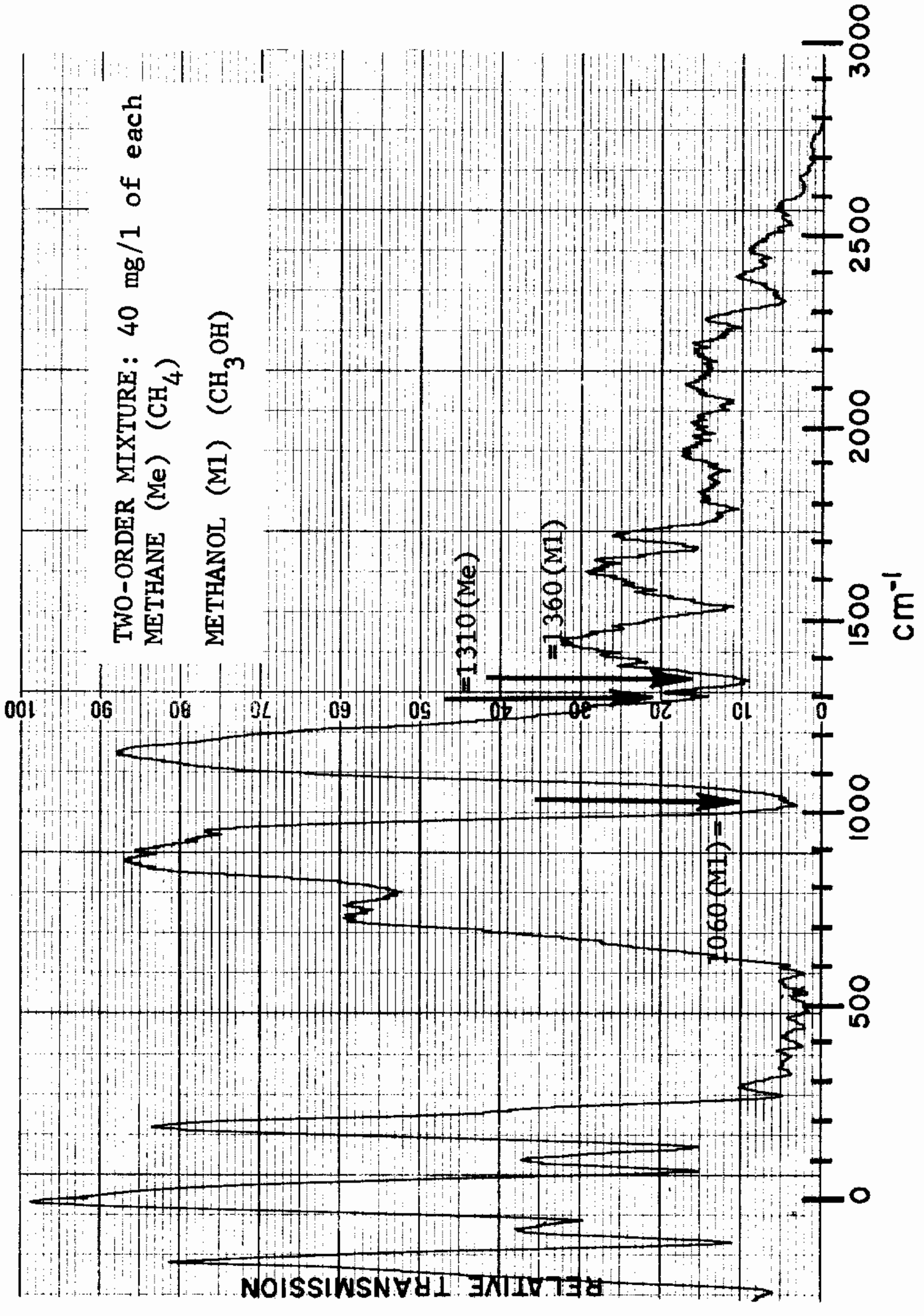

TWO-ORDER MIXTURE: 40 mg/1 of each
METHANE (Me) (CH4)
METHANOL (M1) (CH3OH)
1310 (Me)
1360 (M1)
1060 (M1)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm-1

Figure 104

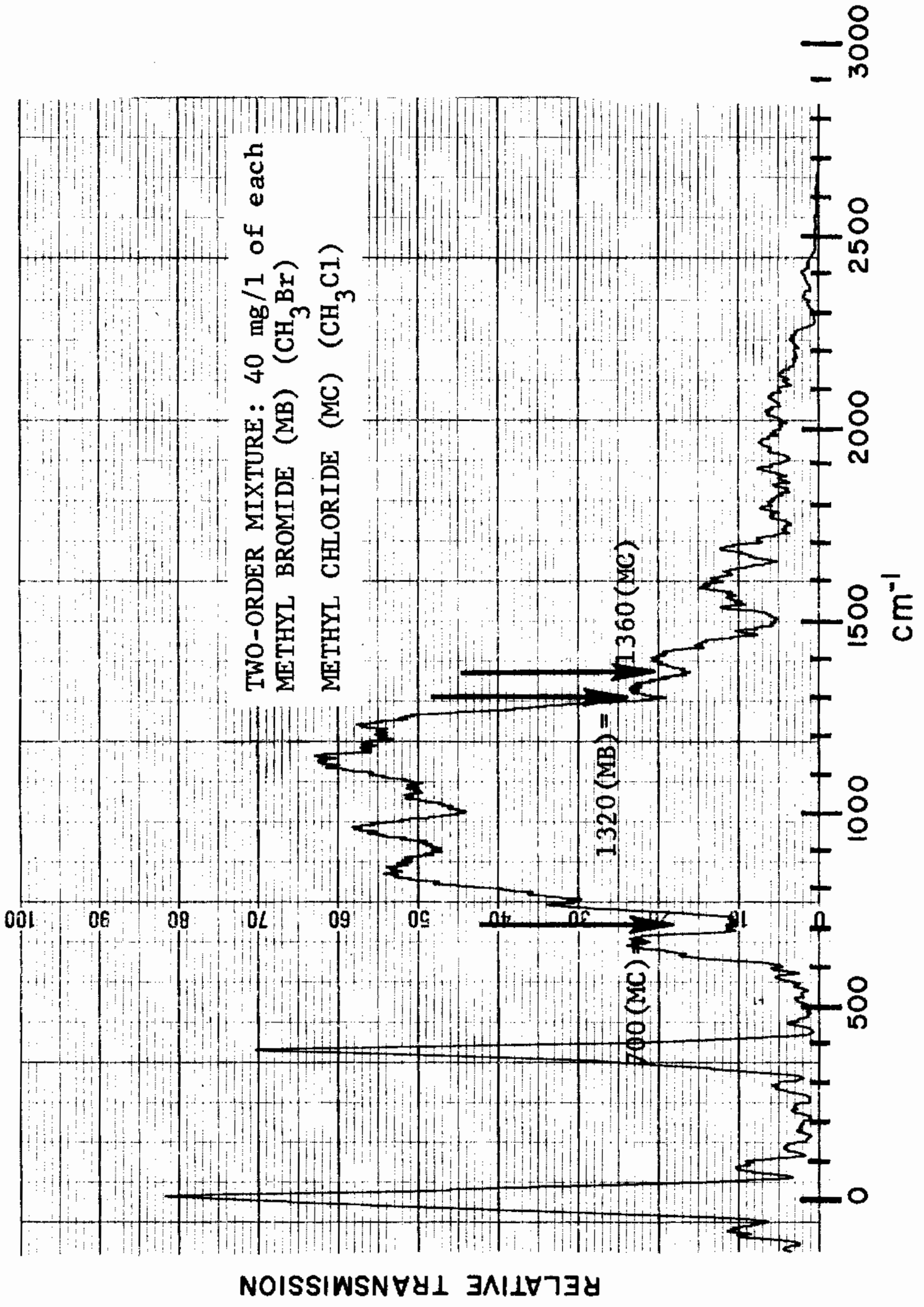

TWO-ORDER MIXTURE: 40 mg/1 of each
METHYL BROMIDE (MB) (CH_3Br)
METHYL CHLORIDE (MC) (CH_3Cl)
1320 (MB) = 1360 (MC)
700 (MC)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 105

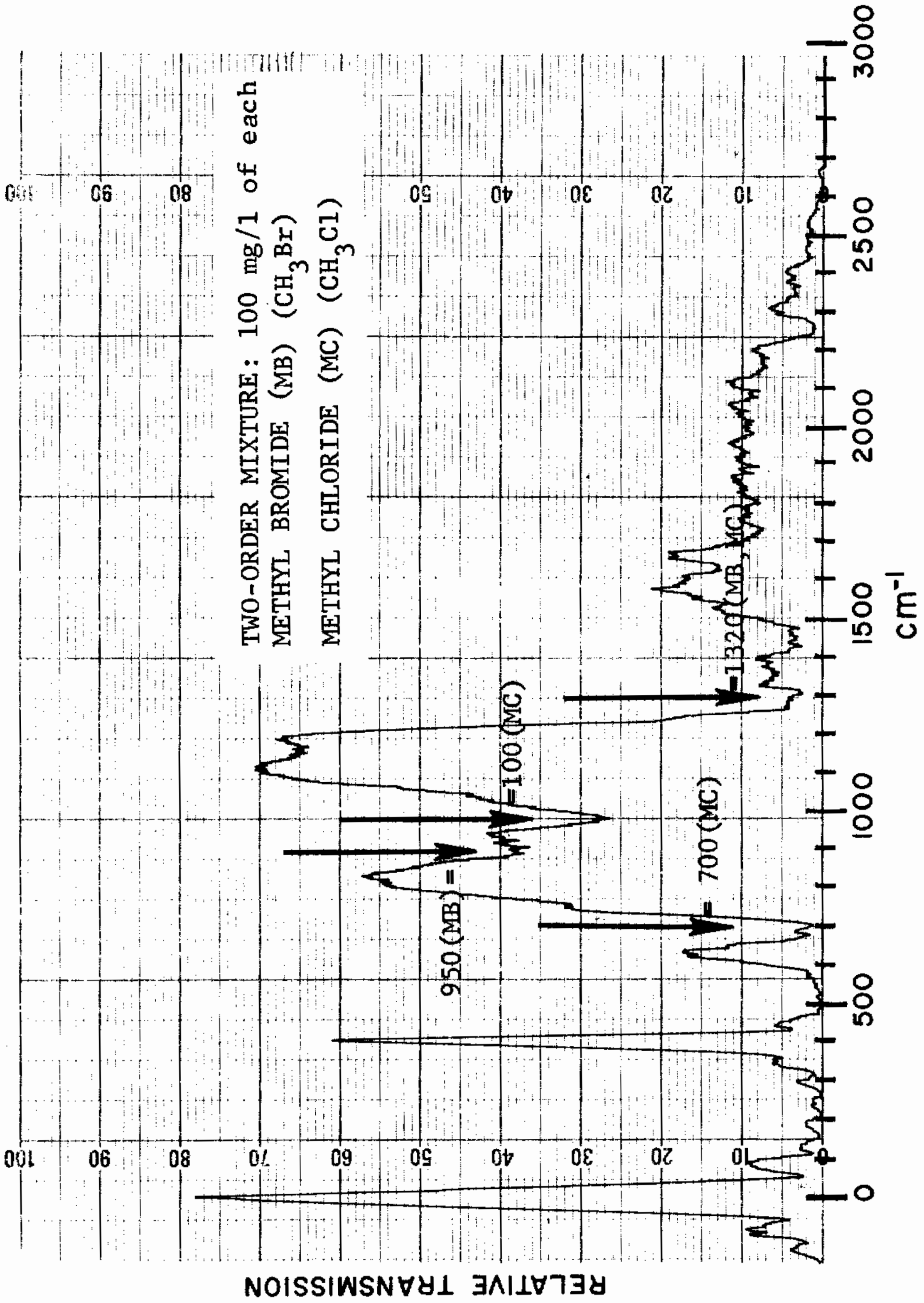

TWO-ORDER MIXTURE: 100 mg/1 of each
METHYL BROMIDE (MB) (CH_3Br)
METHYL CHLORIDE (MC) (CH_3Cl)
1320 (MB, MC)
1100 (MC)
950 (MB)
700 (MC)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 106

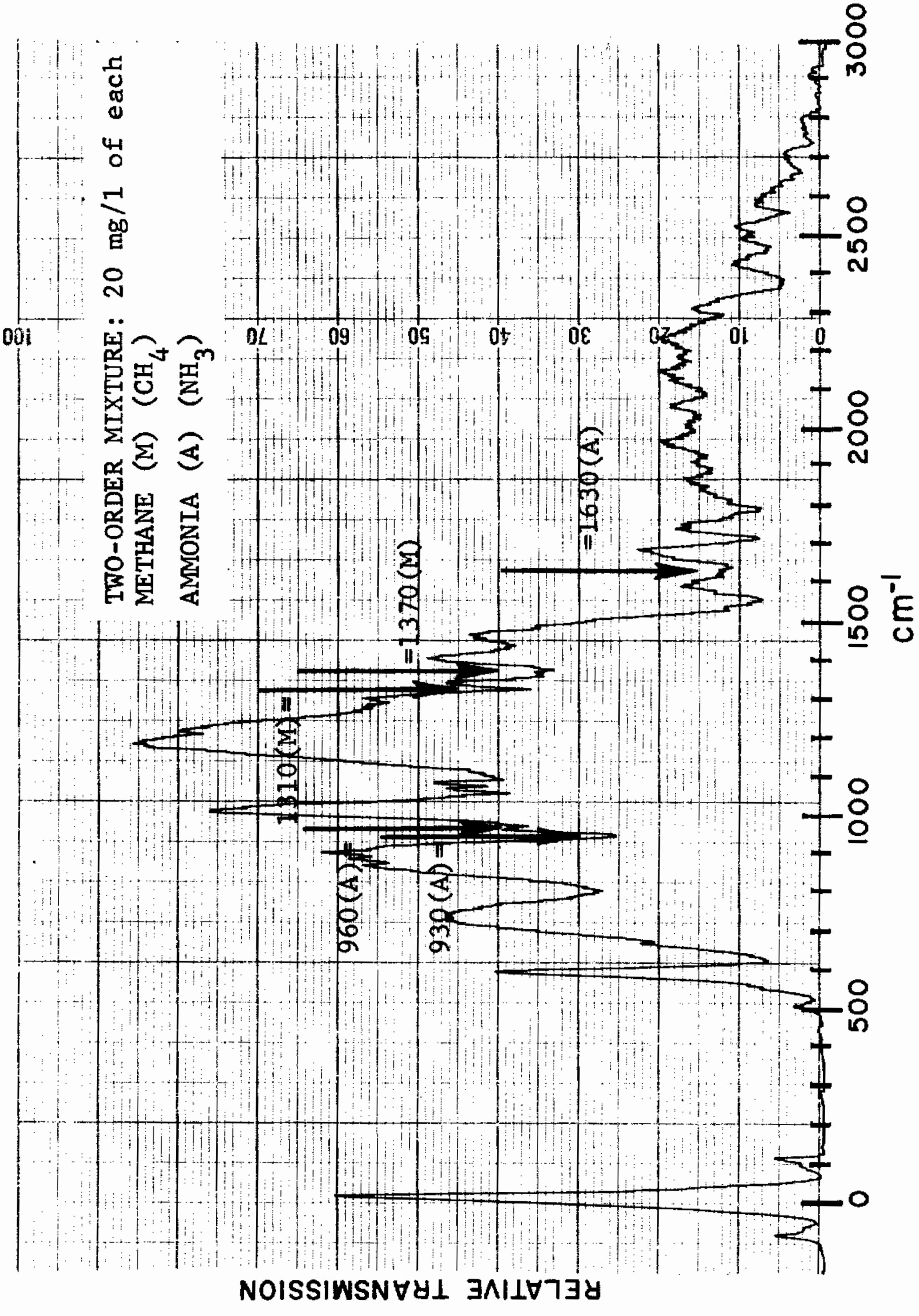

TWO-ORDER MIXTURE: 20 mg/1 of each
METHANE (M) (CH4)
AMMONIA (A) (NH3)
1310(M)
1370(M)
1630(A)
960(A)
930(A)
100
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm-1
RELATIVE TRANSMISSION

Figure 107

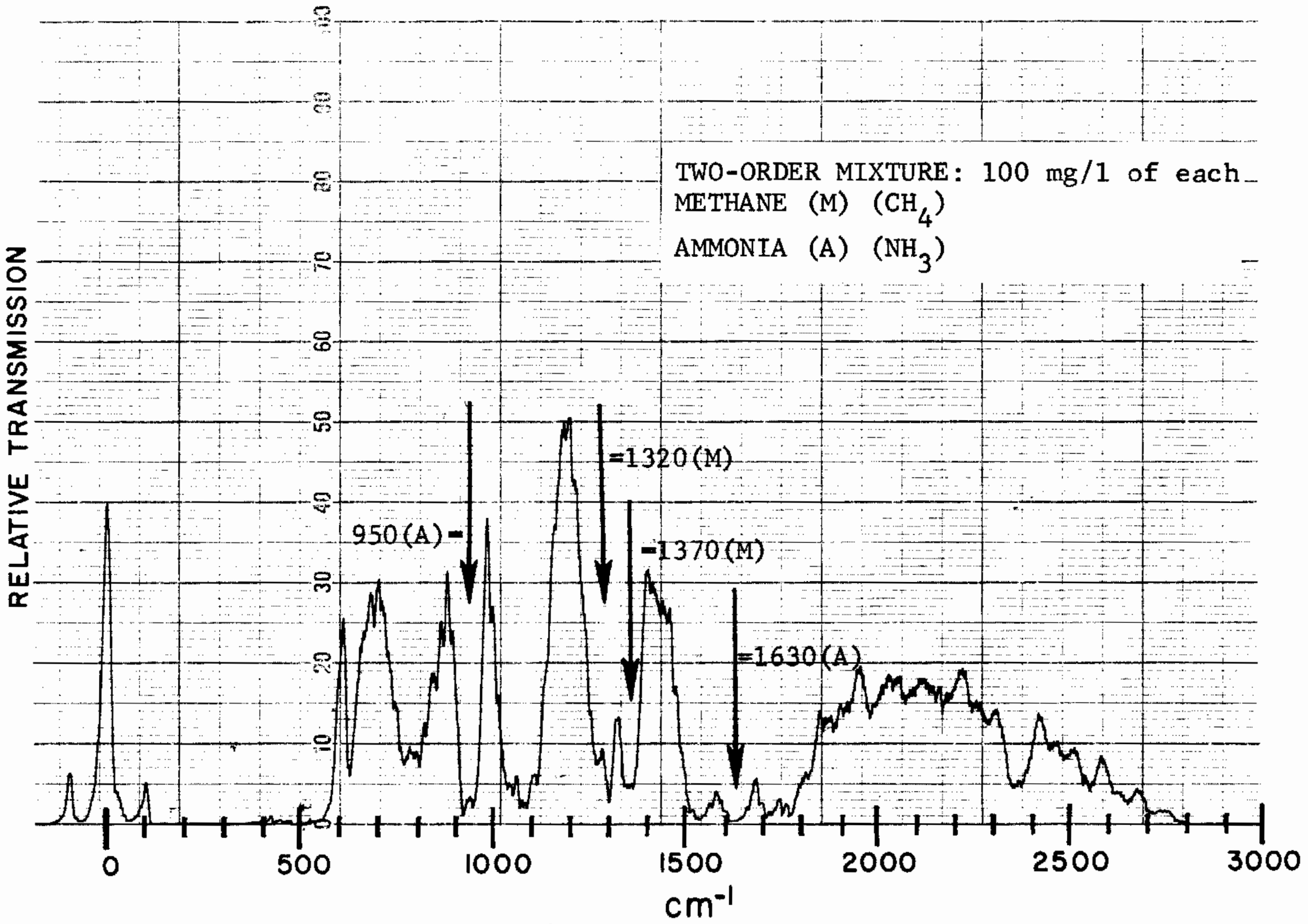

TWO-ORDER MIXTURE: 100 mg/1 of each
METHANE (M) (CH_4)
AMMONIA (A) (NH_3)
950(A)
1320(M)
1370(M)
1630(A)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 108

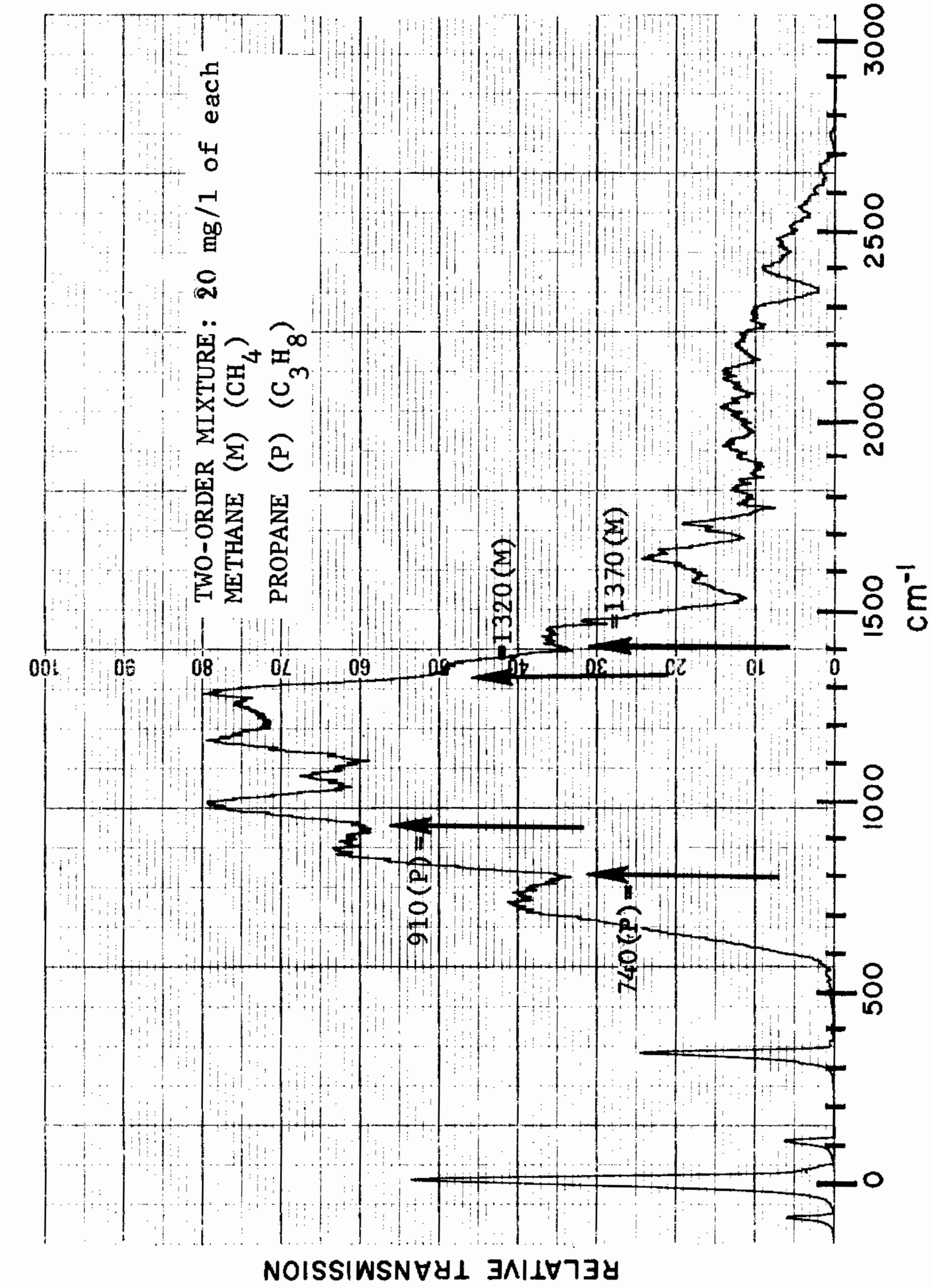

TWO-ORDER MIXTURE: 20 mg/1 of each
METHANE (M) (CH4)
PROPANE (P) (C3H8)
1320(M)
1370(M)
910(P)
740(P)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
cm-1
0
500
1000
1500
2000
2500
3000

Figure 109

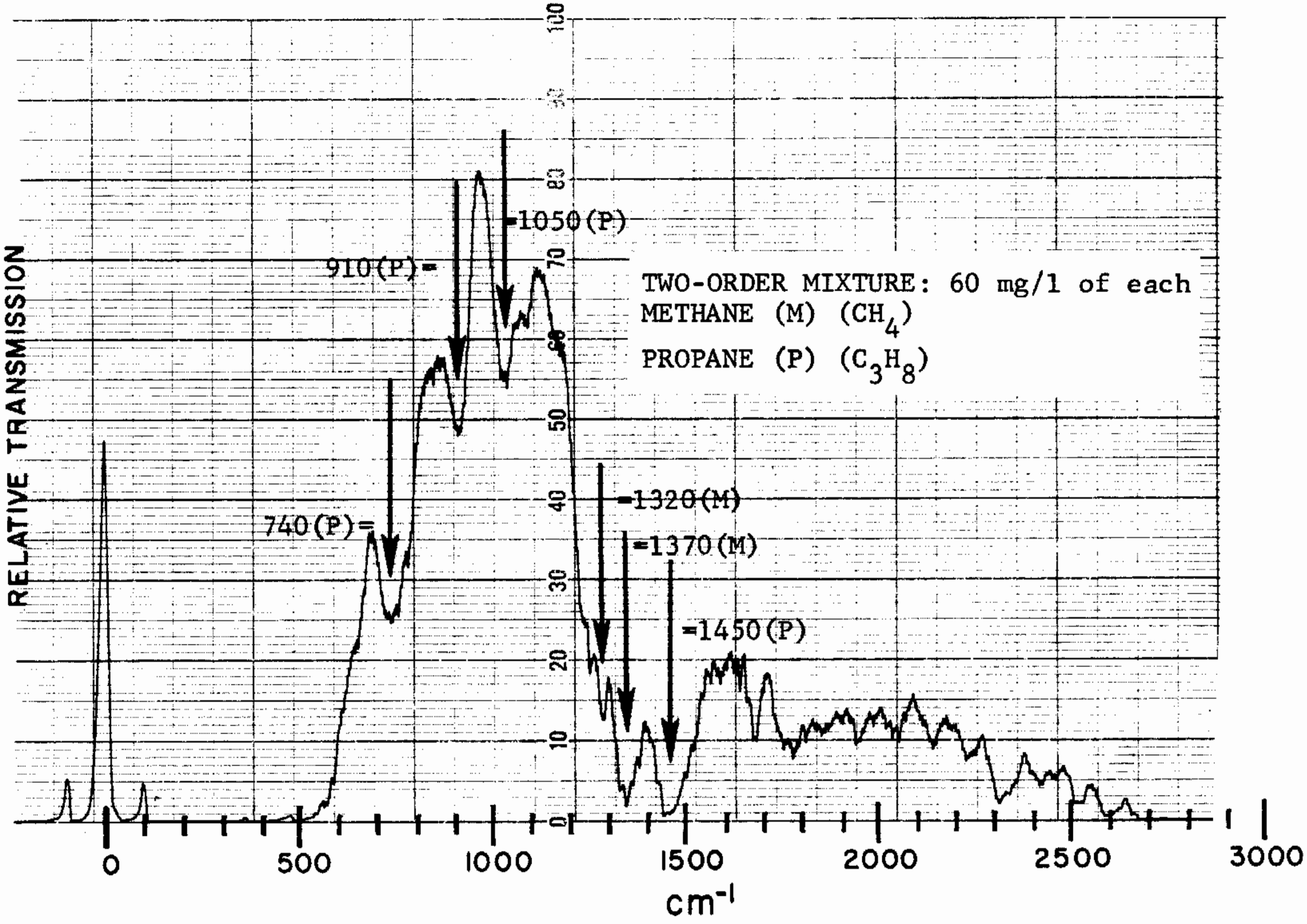

RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
1050(P)
910(P)
740(P)
1320(M)
1370(M)
1450(P)
TWO-ORDER MIXTURE: 60 mg/1 of each
METHANE (M) (CH_4)
PROPANE (P) (C_3H_8)

Figure 110

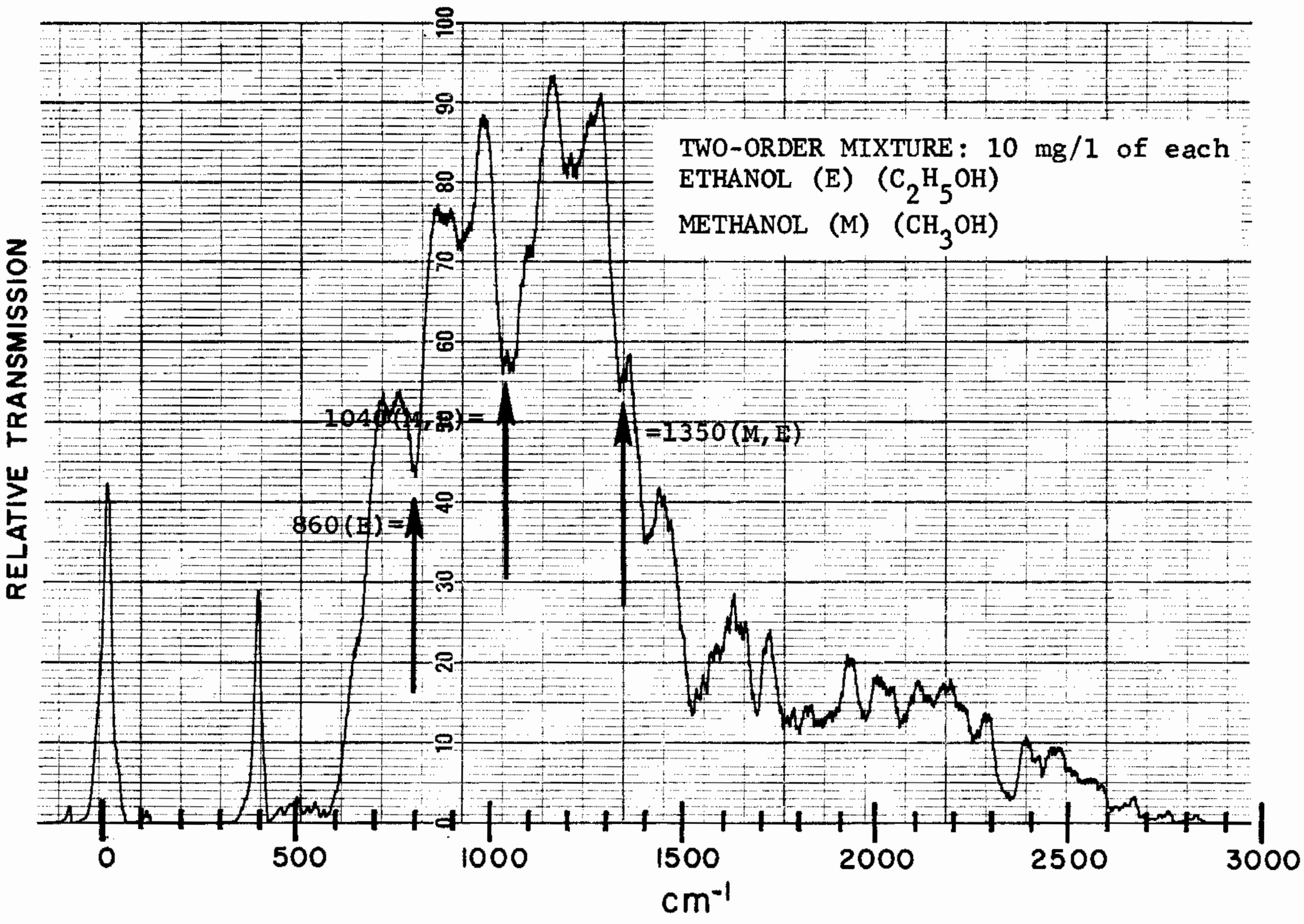

TWO-ORDER MIXTURE: 10 mg/1 of each
ETHANOL (E) (C_2H_5OH)
METHANOL (M) (CH_3OH)
1040(M,E)=
860(E)=
=1350(M,E)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 111

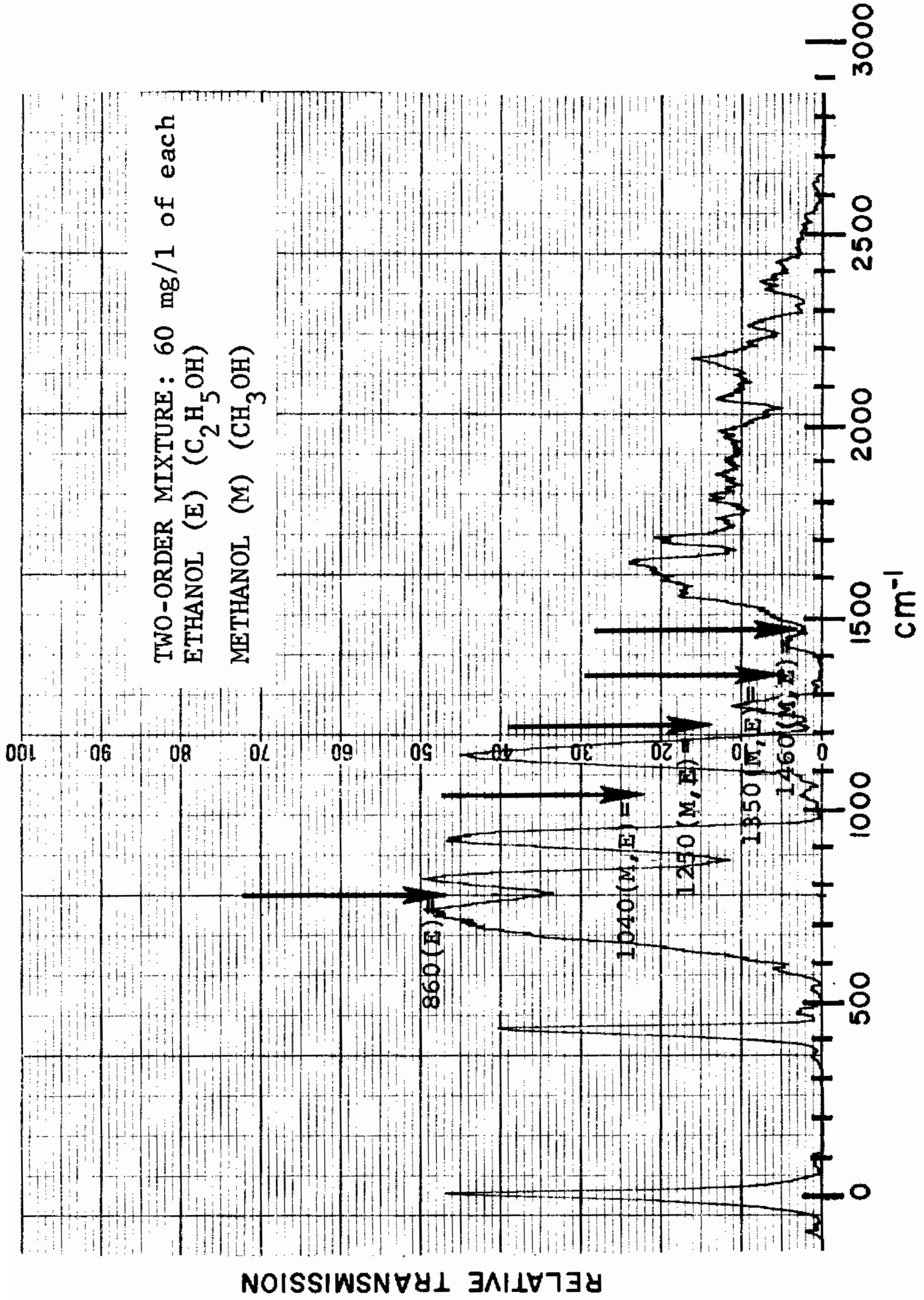

TWO-ORDER MIXTURE: 60 mg/1 of each
ETHANOL (E) (C_2H_5OH)
METHANOL (M) (CH_3OH)
860(E)
1040(M,E)=
1250(M,E)=
1350(M,E)=
1460(M,E)
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹
RELATIVE TRANSMISSION

Figure 112

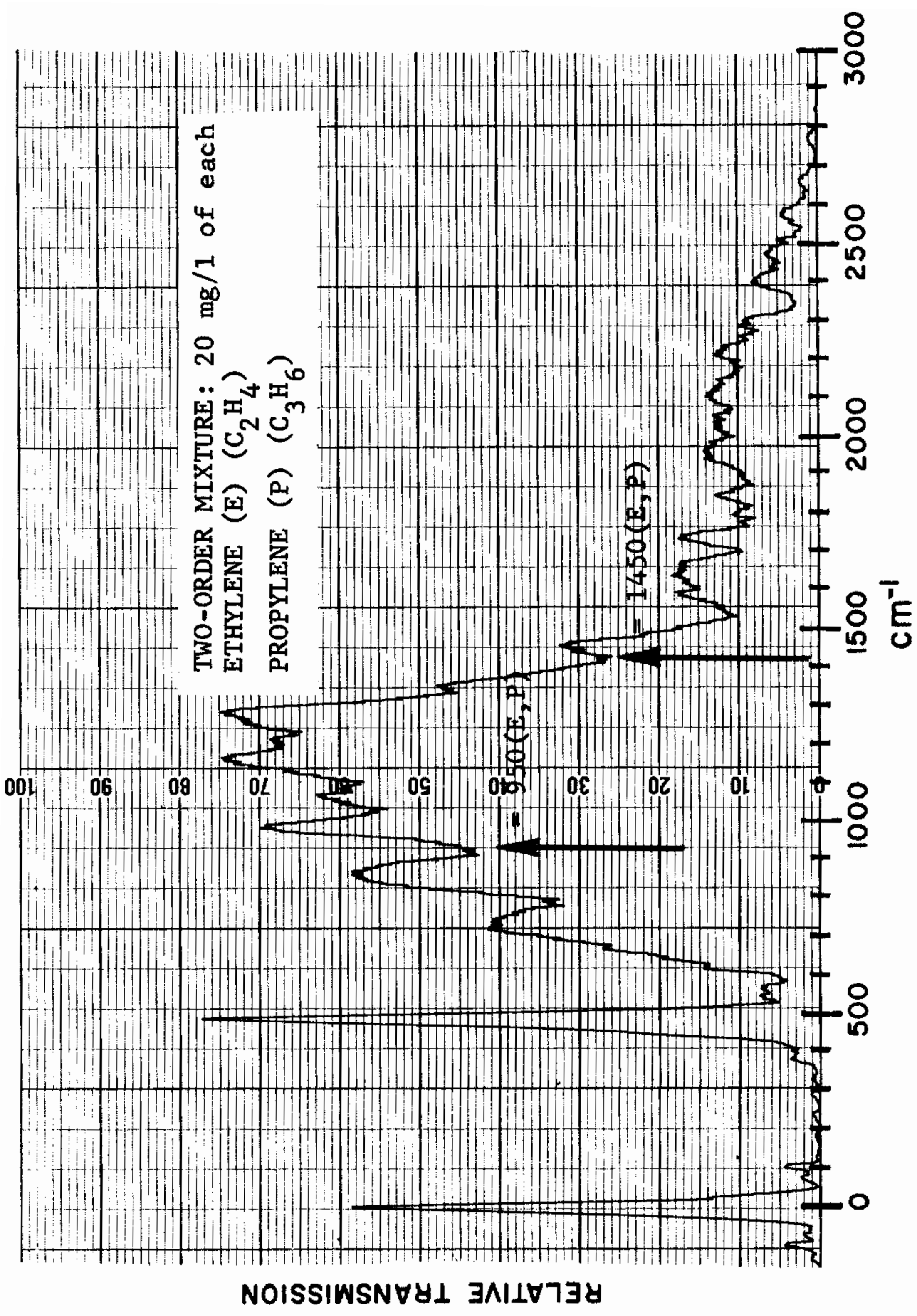

TWO-ORDER MIXTURE: 20 mg/1 of each
ETHYLENE (E) (C_2H_4)
PROPYLENE (P) (C_3H_6)
950(E,P)
1450(E,P)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
cm^{-1}
3000
2500
2000
1500
1000
500
0

Figure 113

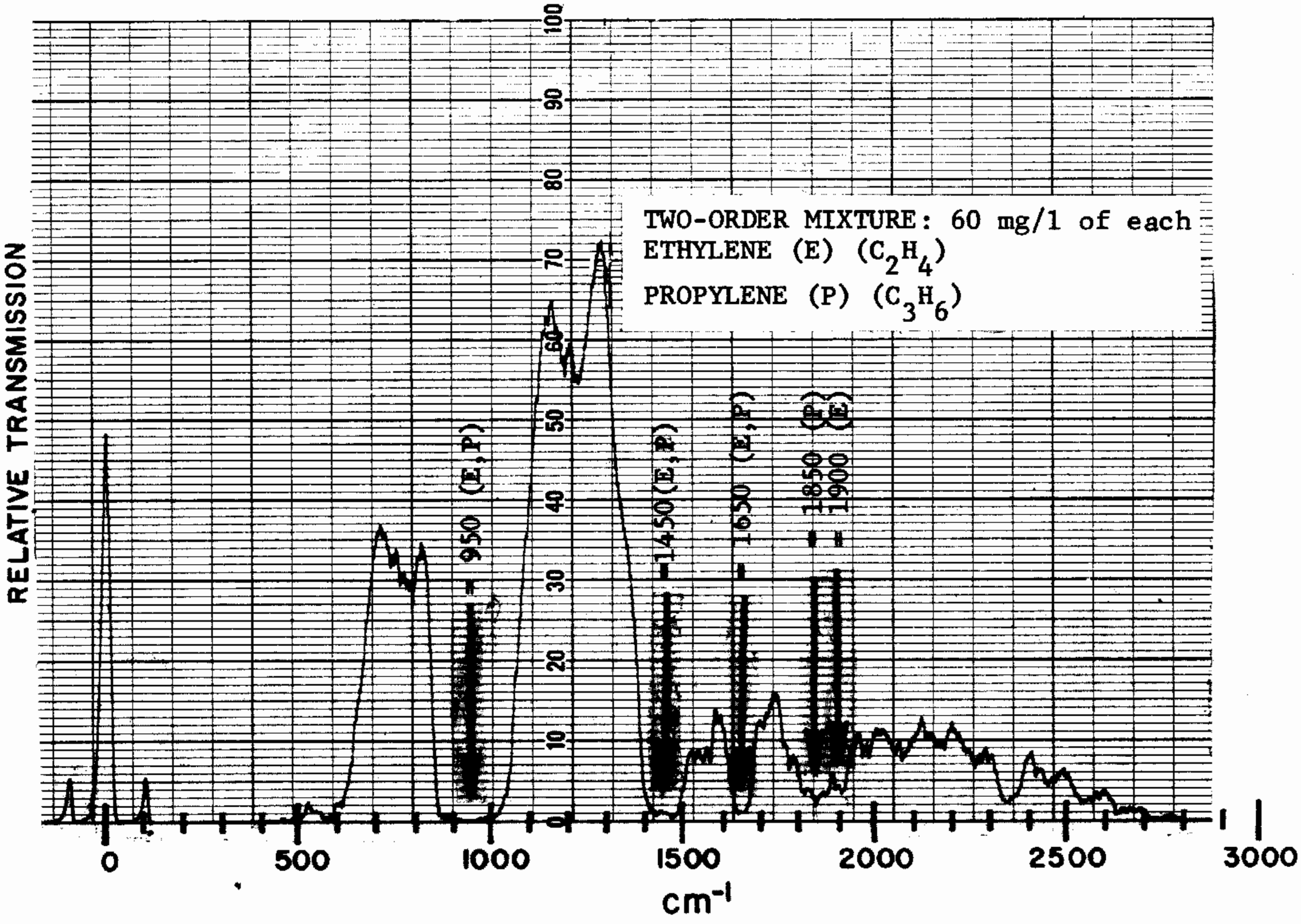

TWO-ORDER MIXTURE: 60 mg/1 of each
ETHYLENE (E) (C_2H_4)
PROPYLENE (P) (C_3H_6)
950 (E,P)
1450(E,P)
1650 (E,P)
1850 (P)
1900 (E)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 114

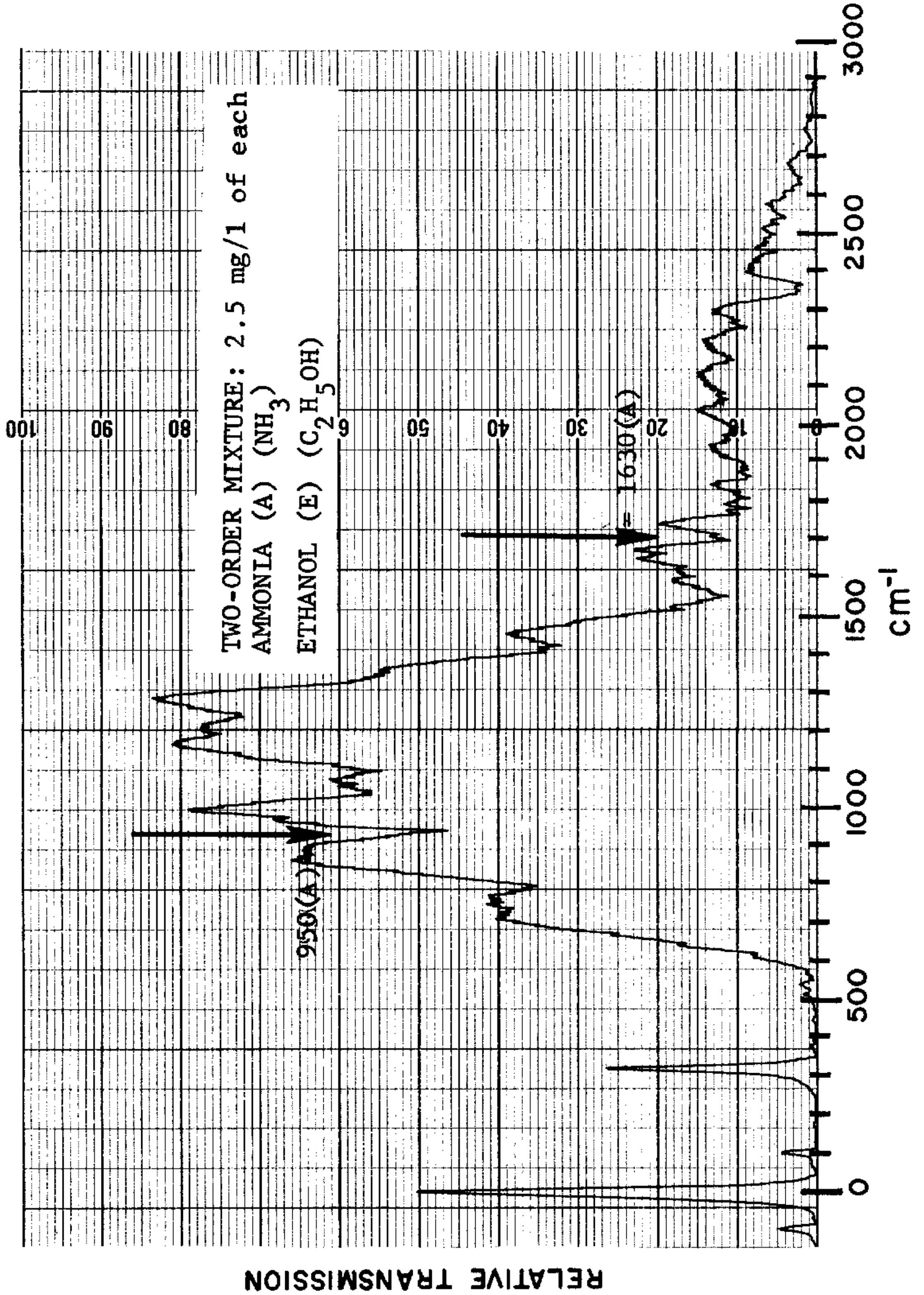

TWO-ORDER MIXTURE: 2.5 mg/1 of each
AMMONIA (A) (NH_3)
ETHANOL (E) (C_2H_5OH)
1630(A)
950(A)
100
90
80
60
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm^{-1}
RELATIVE TRANSMISSION

Figure 115

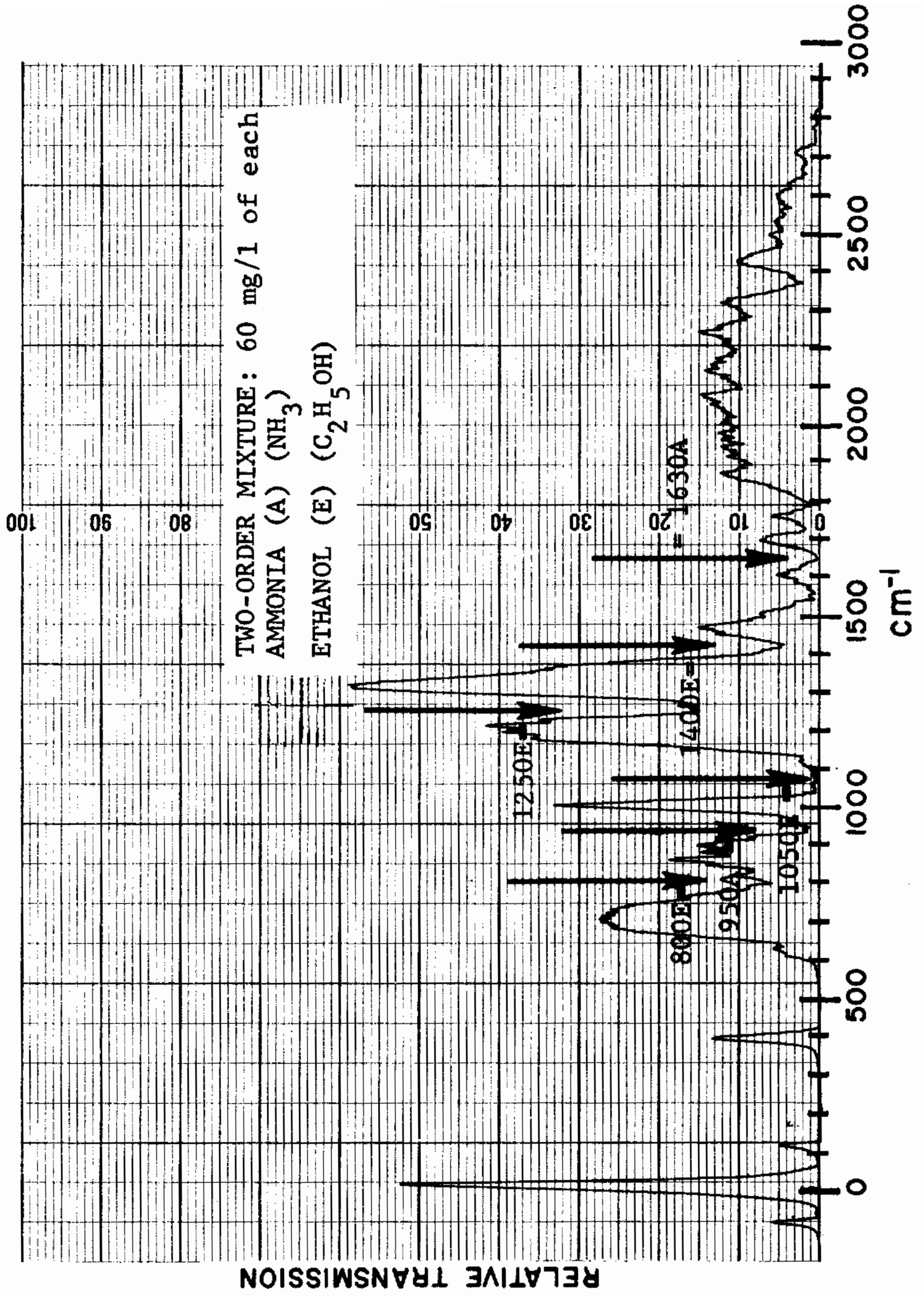

TWO-ORDER MIXTURE: 60 mg/1 of each
AMMONIA (A) (NH3)
ETHANOL (E) (C2H5OH)
1630A
1400E
1250E
1050A
950A
800E
100
90
80
50
40
30
20
10
0
RELATIVE TRANSMISSION
cm-1
0
500
1000
1500
2000
2500
3000

Figure 116

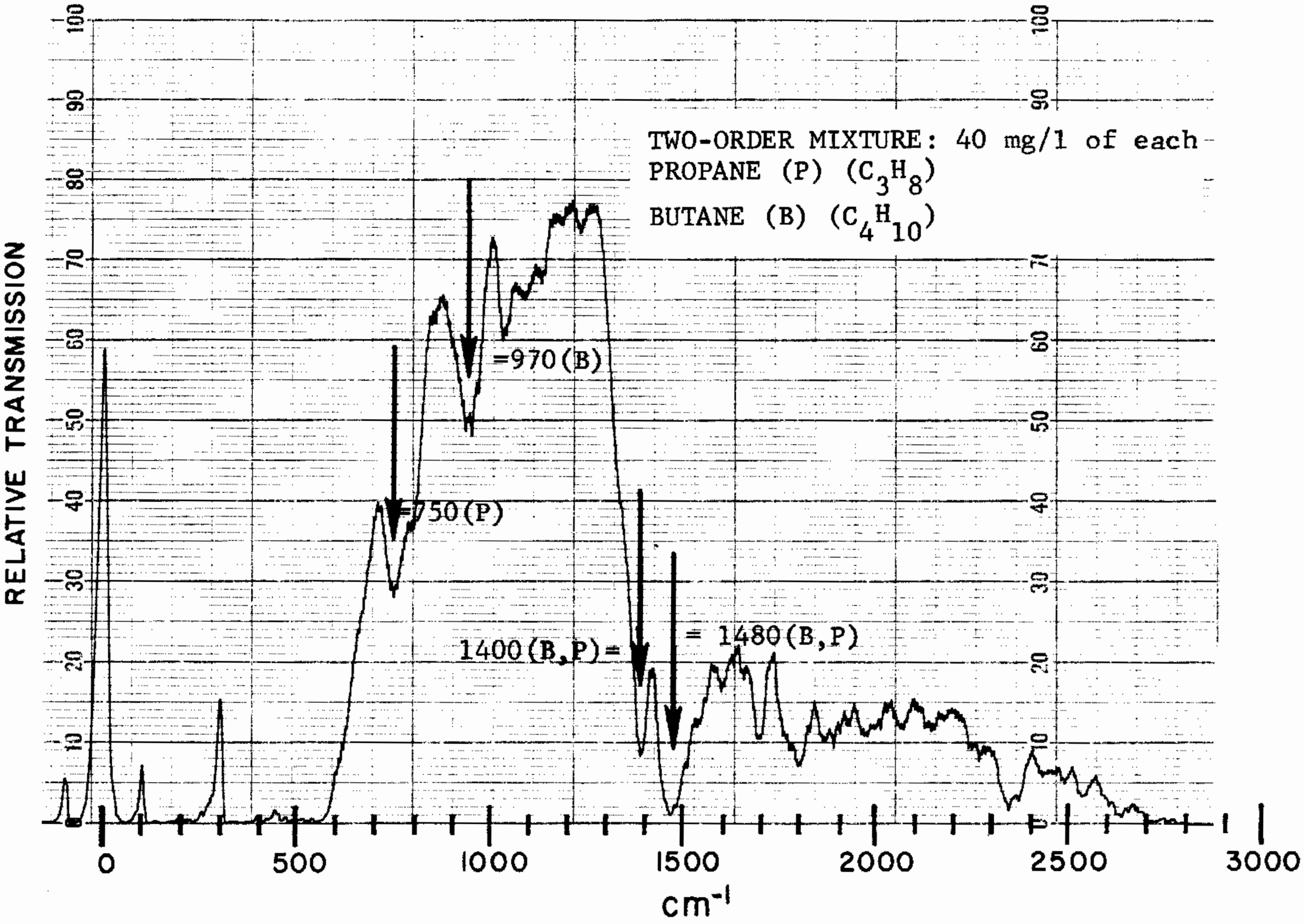

TWO-ORDER MIXTURE: 40 mg/1 of each
PROPANE (P) (C_3H_8)
BUTANE (B) (C_4H_{10})
=970(B)
=750(P)
1400(B,P)=
= 1480(B,P)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 117

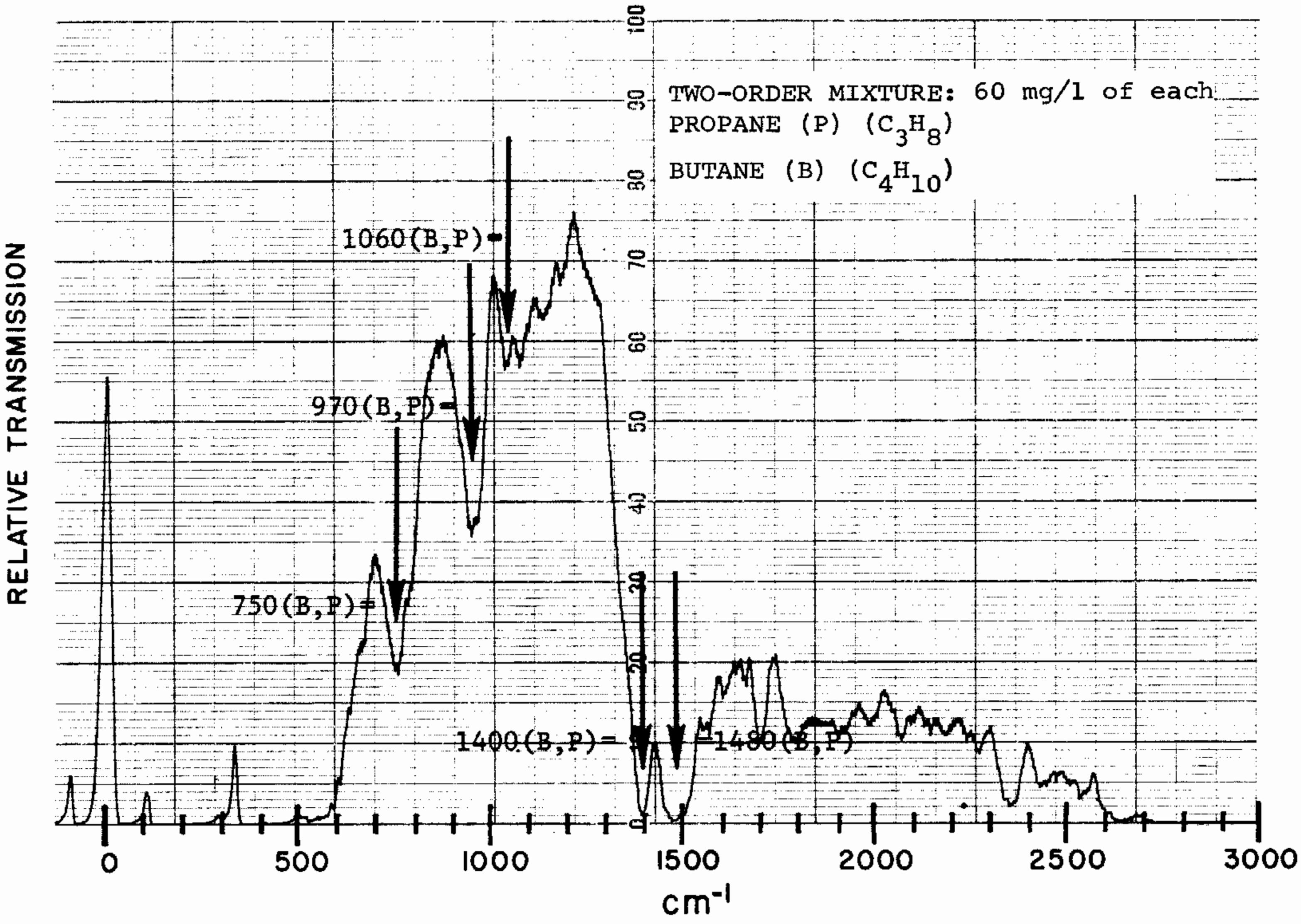

TWO-ORDER MIXTURE: 60 mg/l of each
PROPANE (P) (C_3H_8)
BUTANE (B) (C_4H_{10})
1060(B,P)
970(B,P)
750(B,P)
1400(B,P)
1480(B,P)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 118

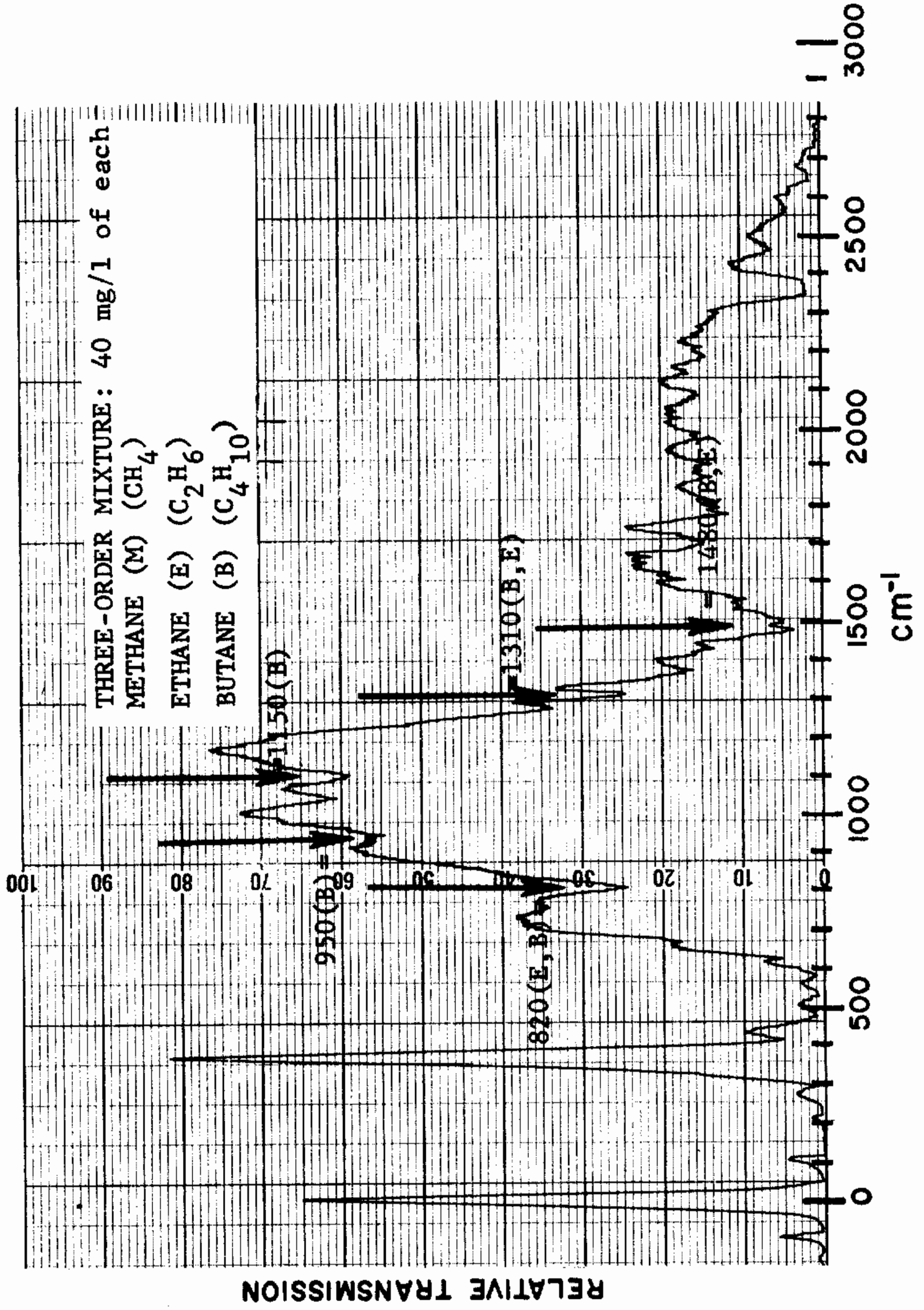

THREE-ORDER MIXTURE: 40 mg/l of each
METHANE (M) (CH_4)
ETHANE (E) (C_2H_6)
BUTANE (B) (C_4H_{10})
1150(B)
1310(B,E)
1450(B,E)
950(B)
820(E,B)
0
500
1000
1500
2000
2500
3000
cm^{-1}
0
10
20
30
40
50
60
70
80
90
100
RELATIVE TRANSMISSION

Figure 119

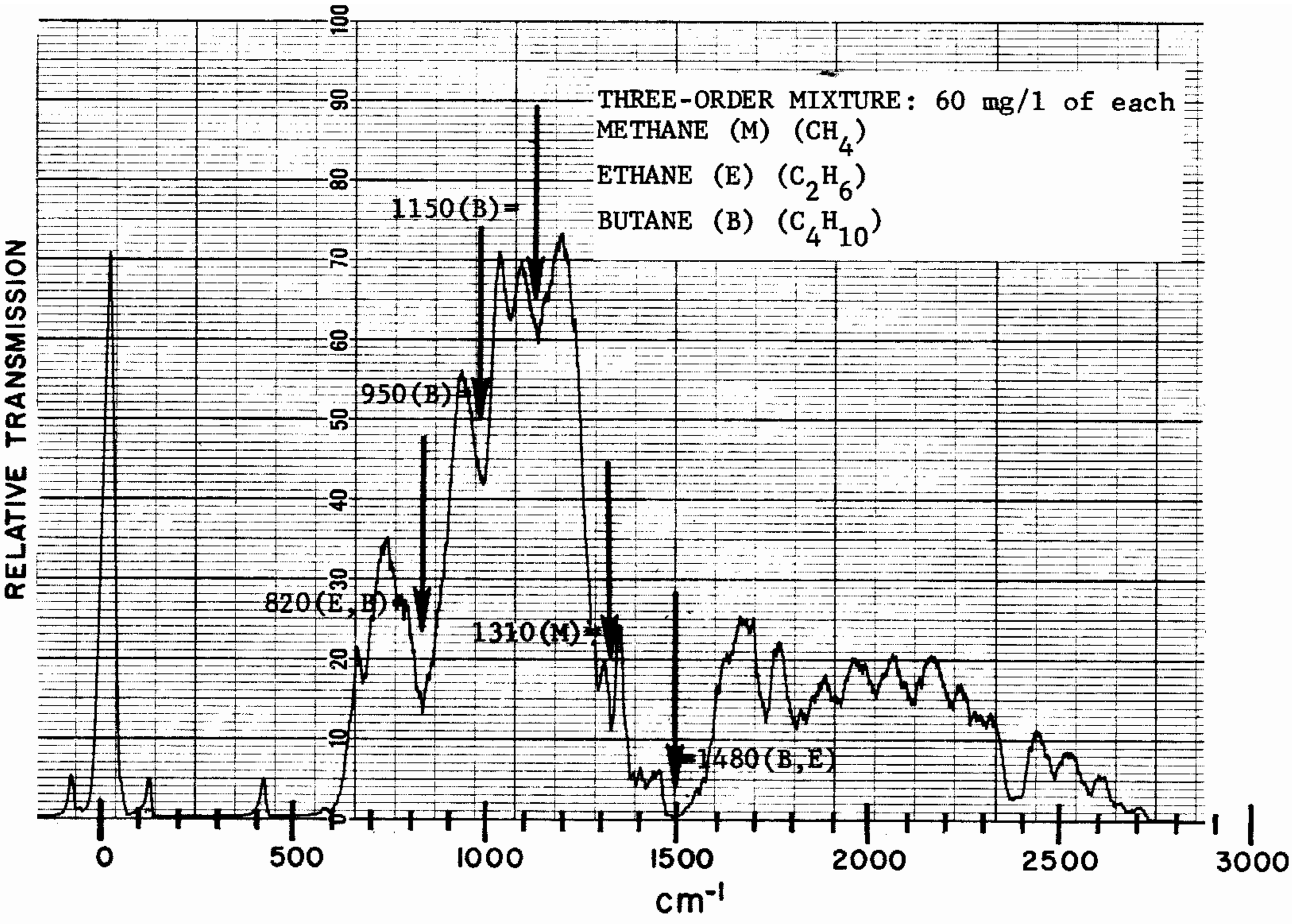

THREE-ORDER MIXTURE: 60 mg/1 of each
METHANE (M) (CH_4)
ETHANE (E) (C_2H_6)
BUTANE (B) (C_4H_{10})
1150(B)
950(B)
820(E,B)
1310(M)
1480(B,E)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 120

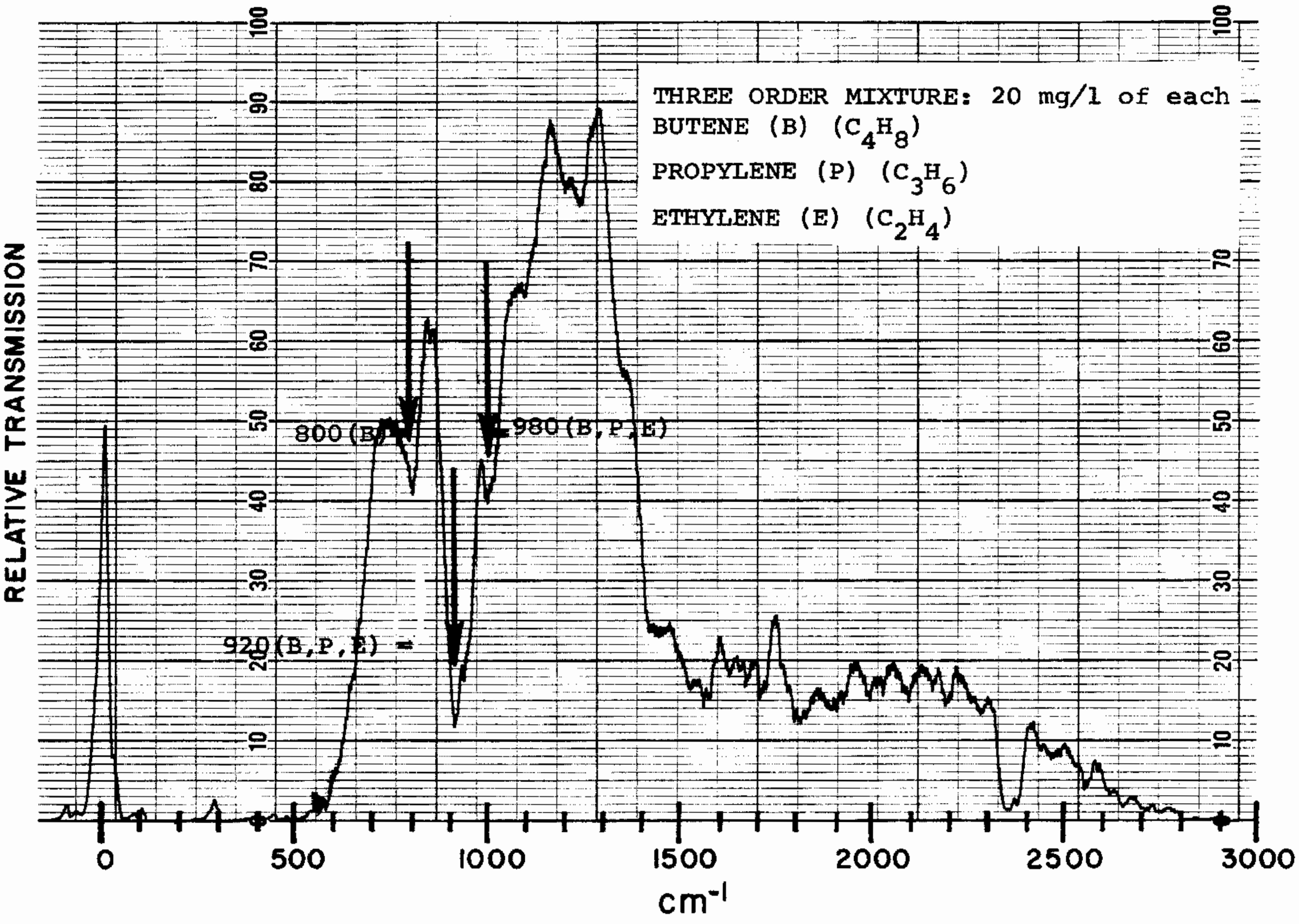

THREE ORDER MIXTURE: 20 mg/l of each
BUTENE (B) (C_4H_8)
PROPYLENE (P) (C_3H_6)
ETHYLENE (E) (C_2H_4)
800(B)
980(B,P,E)
920(B,P,E)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 120

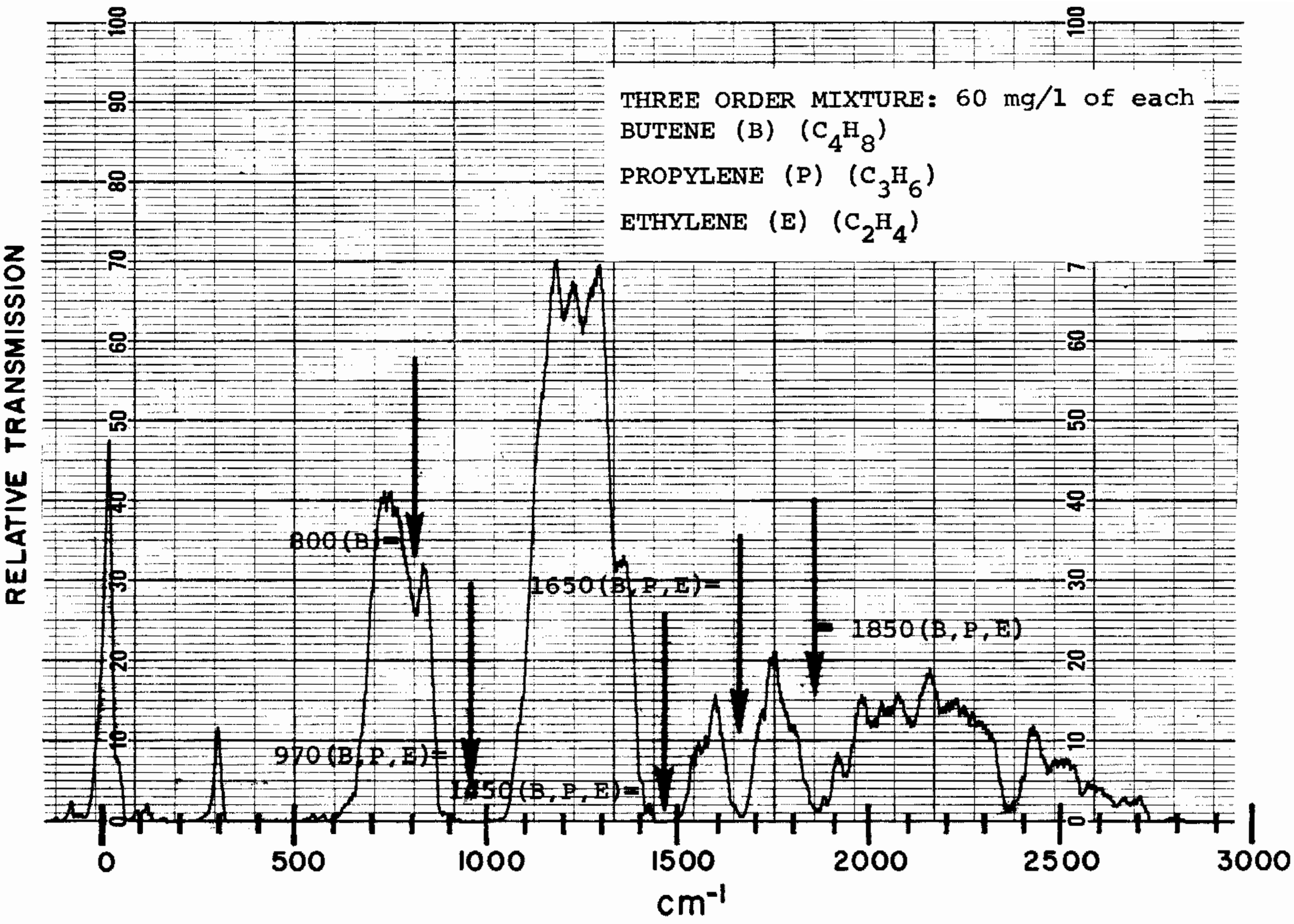

THREE ORDER MIXTURE: 60 mg/l of each
BUTENE (B) (C_4H_8)
PROPYLENE (P) (C_3H_6)
ETHYLENE (E) (C_2H_4)
800(B)
970(B,P,E)
1450(B,P,E)
1650(B,P,E)
1850(B,P,E)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 122

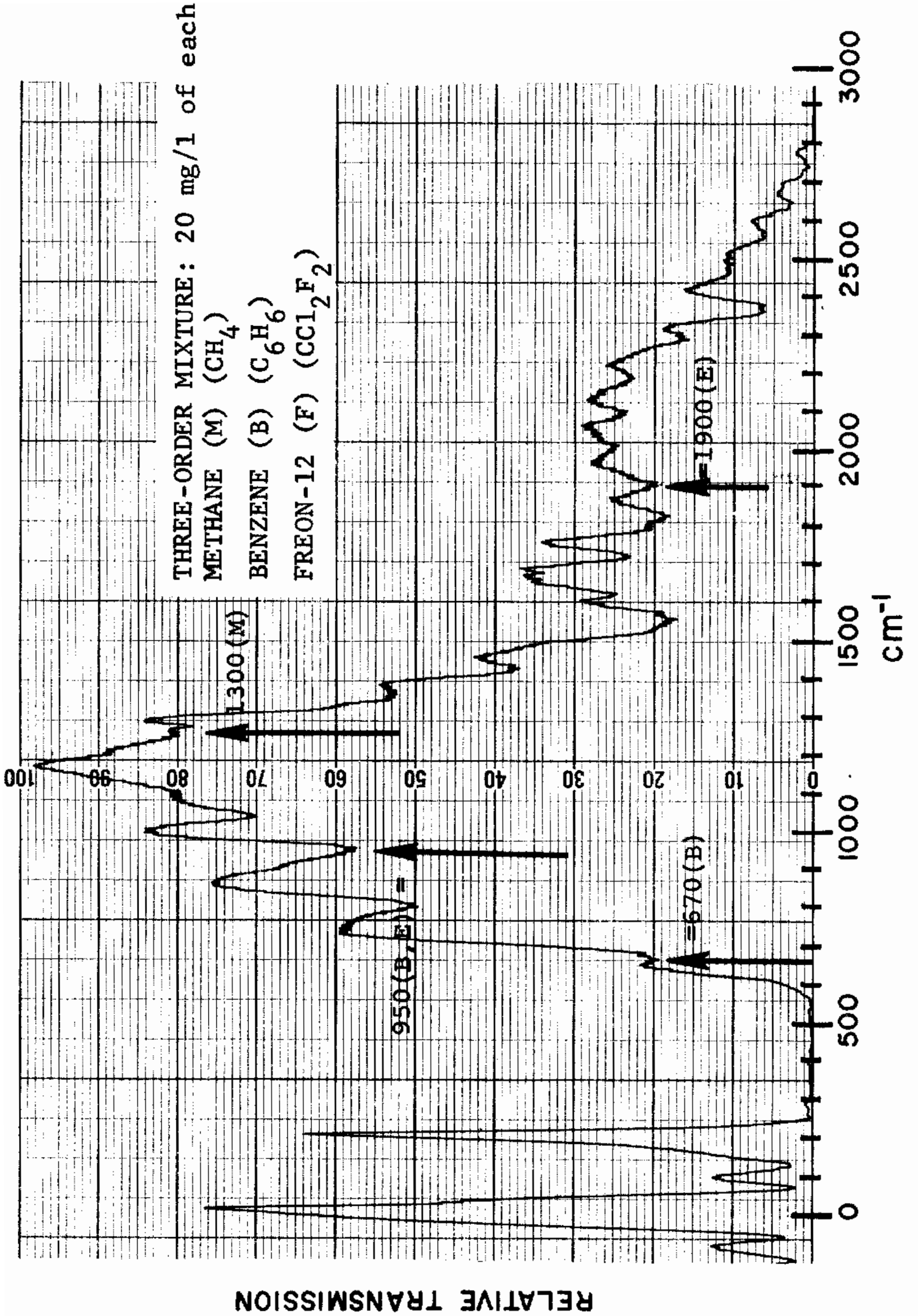

THREE-ORDER MIXTURE: 20 mg/1 of each
METHANE (M) (CH4)
BENZENE (B) (C6H6)
FREON-12 (F) (CC12F2)
1300(M)
1900(E)
950(B,E) =
=670(B)
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm-1
RELATIVE TRANSMISSION

Figure 123

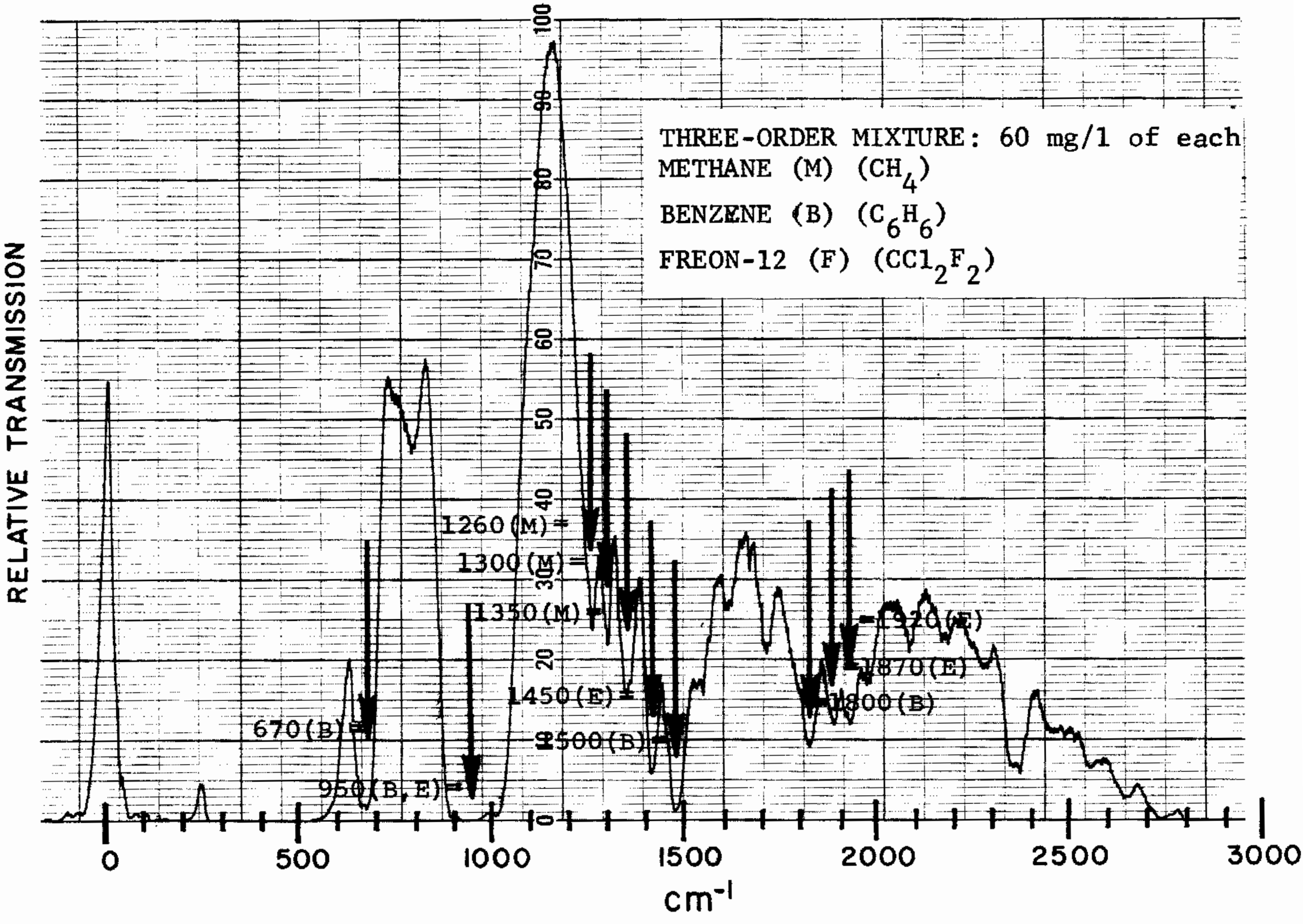

THREE-ORDER MIXTURE: 60 mg/1 of each
METHANE (M) (CH4)
BENZENE (B) (C6H6)
FREON-12 (F) (CCl2F2)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
1260(M)
1300(M)
1350(M)
1450(E)
1500(B)
670(B)
950(B,E)
1920(E)
1870(E)
1800(B)
0
500
1000
1500
2000
2500
3000
cm-1

Figure 124

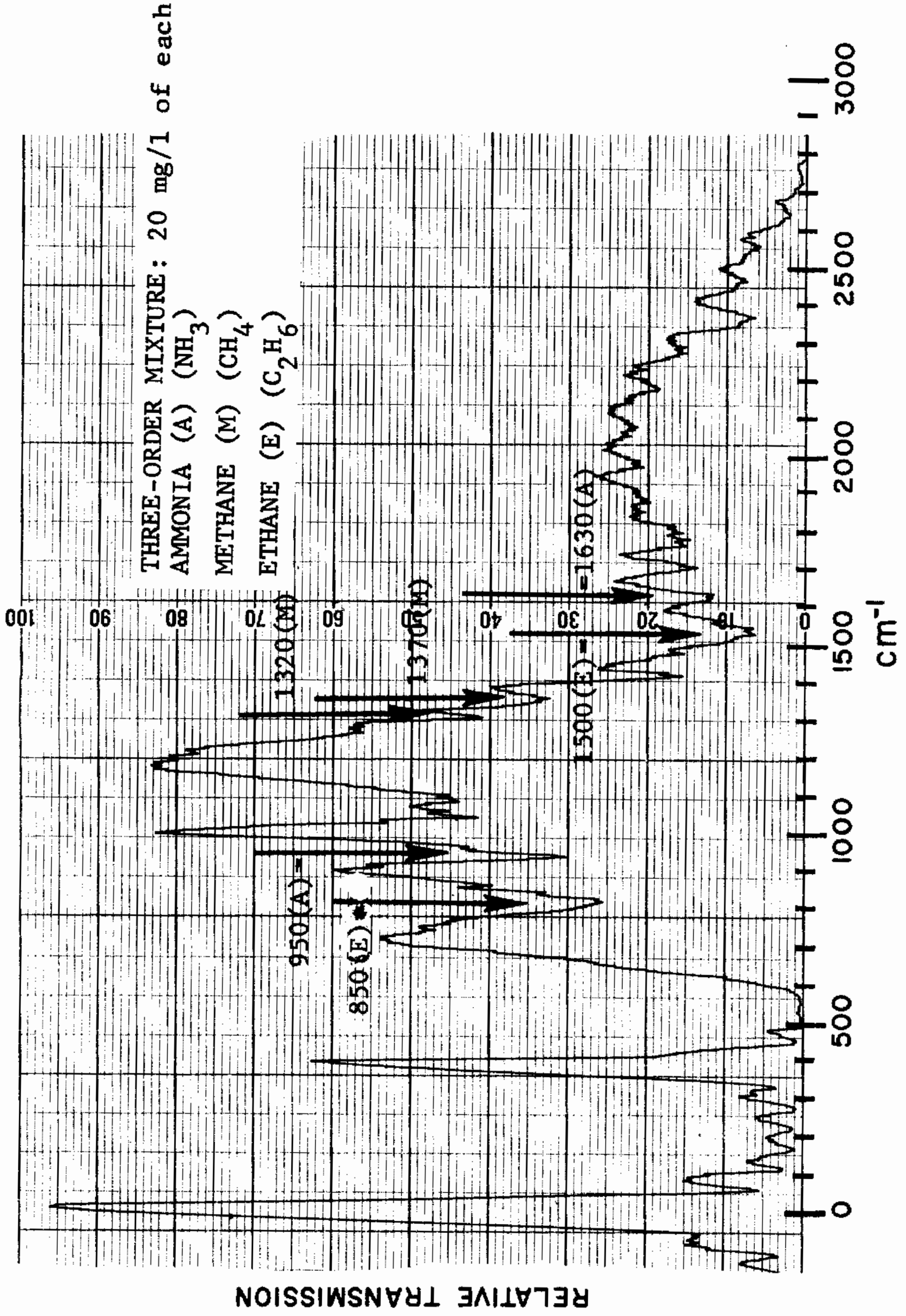

THREE-ORDER MIXTURE: 20 mg/1 of each
AMMONIA (A) (NH$_3$)
METHANE (M) (CH$_4$)
ETHANE (E) (C$_2$H$_6$)
1320(M)
1370(M)
1630(A)
1500(E)
950(A)
850(E)
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 125

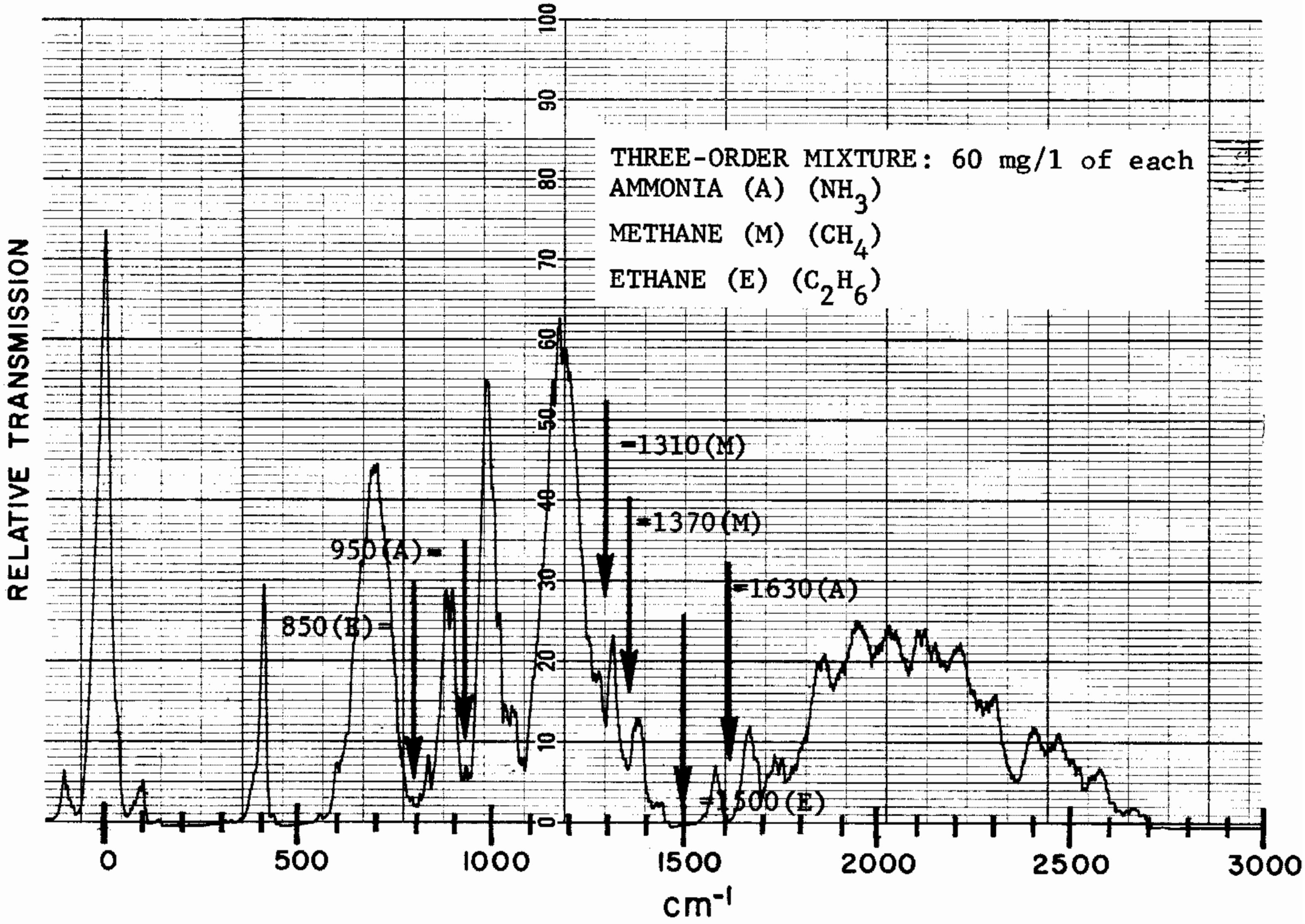

THREE-ORDER MIXTURE: 60 mg/1 of each
AMMONIA (A) (NH_3)
METHANE (M) (CH_4)
ETHANE (E) (C_2H_6)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
950(A)
850(E)
1310(M)
1370(M)
1630(A)
1500(E)

Figure 126

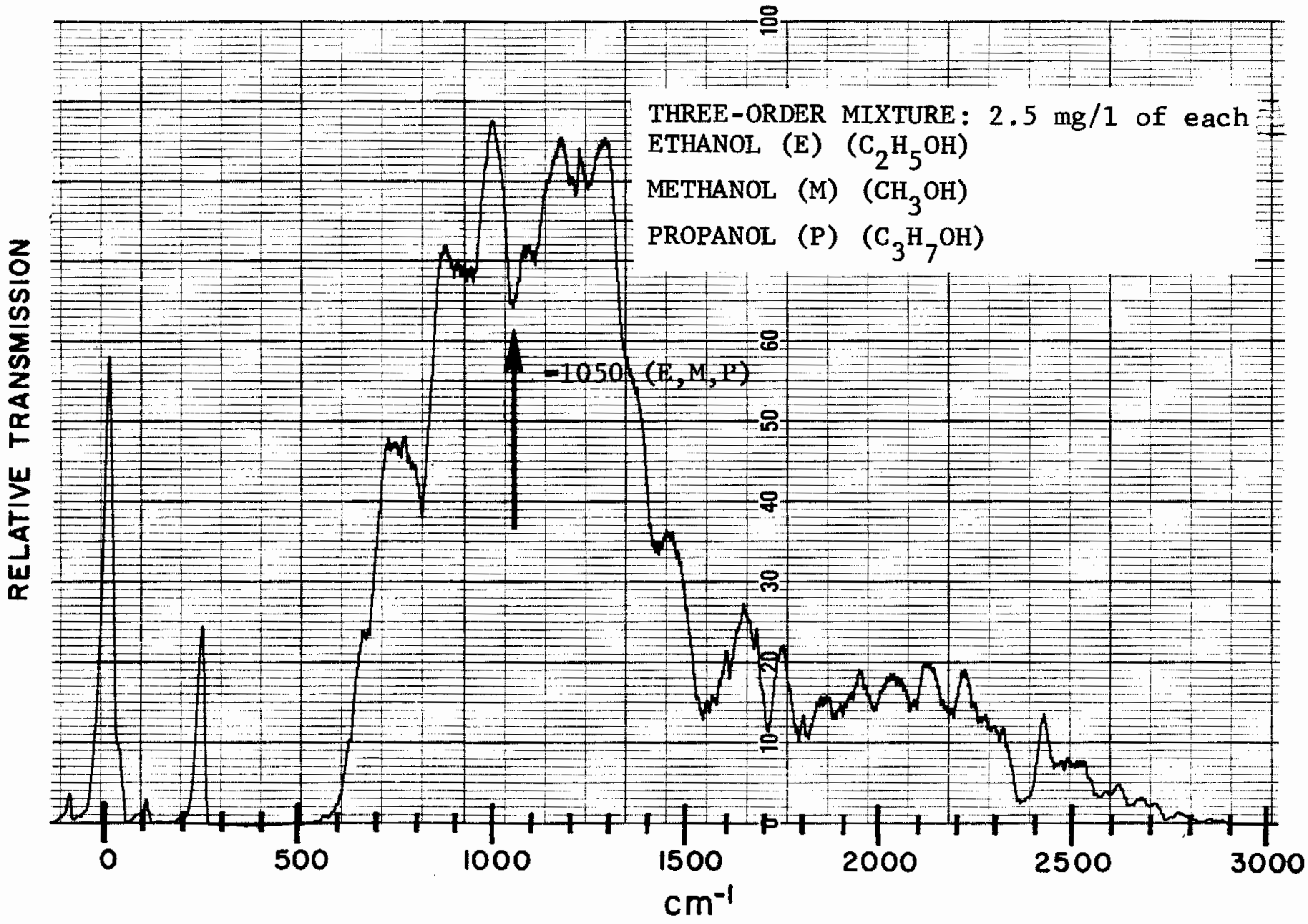

THREE-ORDER MIXTURE: 2.5 mg/1 of each
ETHANOL (E) (C_2H_5OH)
METHANOL (M) (CH_3OH)
PROPANOL (P) (C_3H_7OH)
1050 (E,M,P)
RELATIVE TRANSMISSION
100
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 127

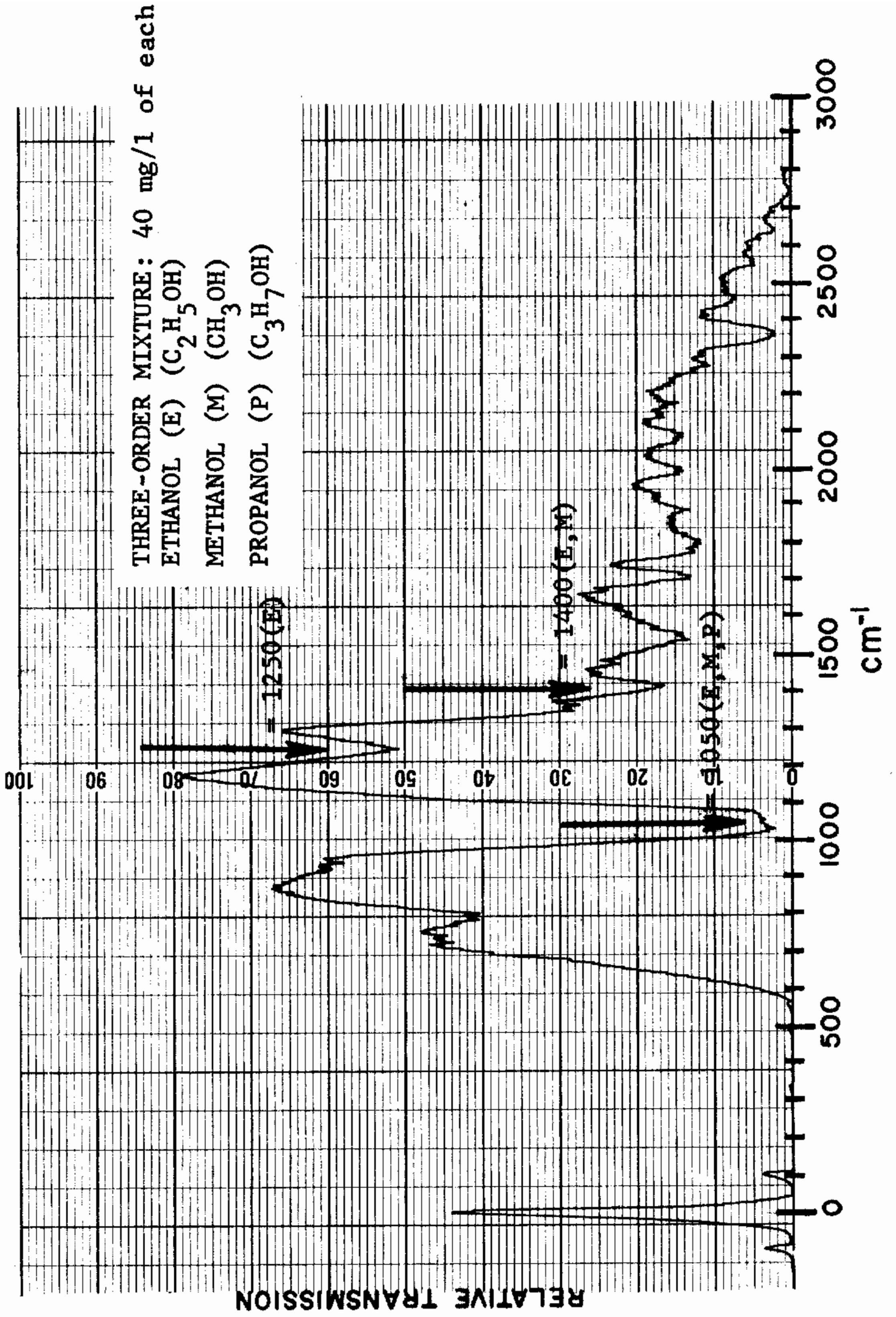

THREE-ORDER MIXTURE: 40 mg/1 of each
ETHANOL (E) (C_2H_5OH)
METHANOL (M) (CH_3OH)
PROPANOL (P) (C_3H_7OH)
= 1250 (E)
= 1400 (E,M)
1050 (E,M,P)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 128

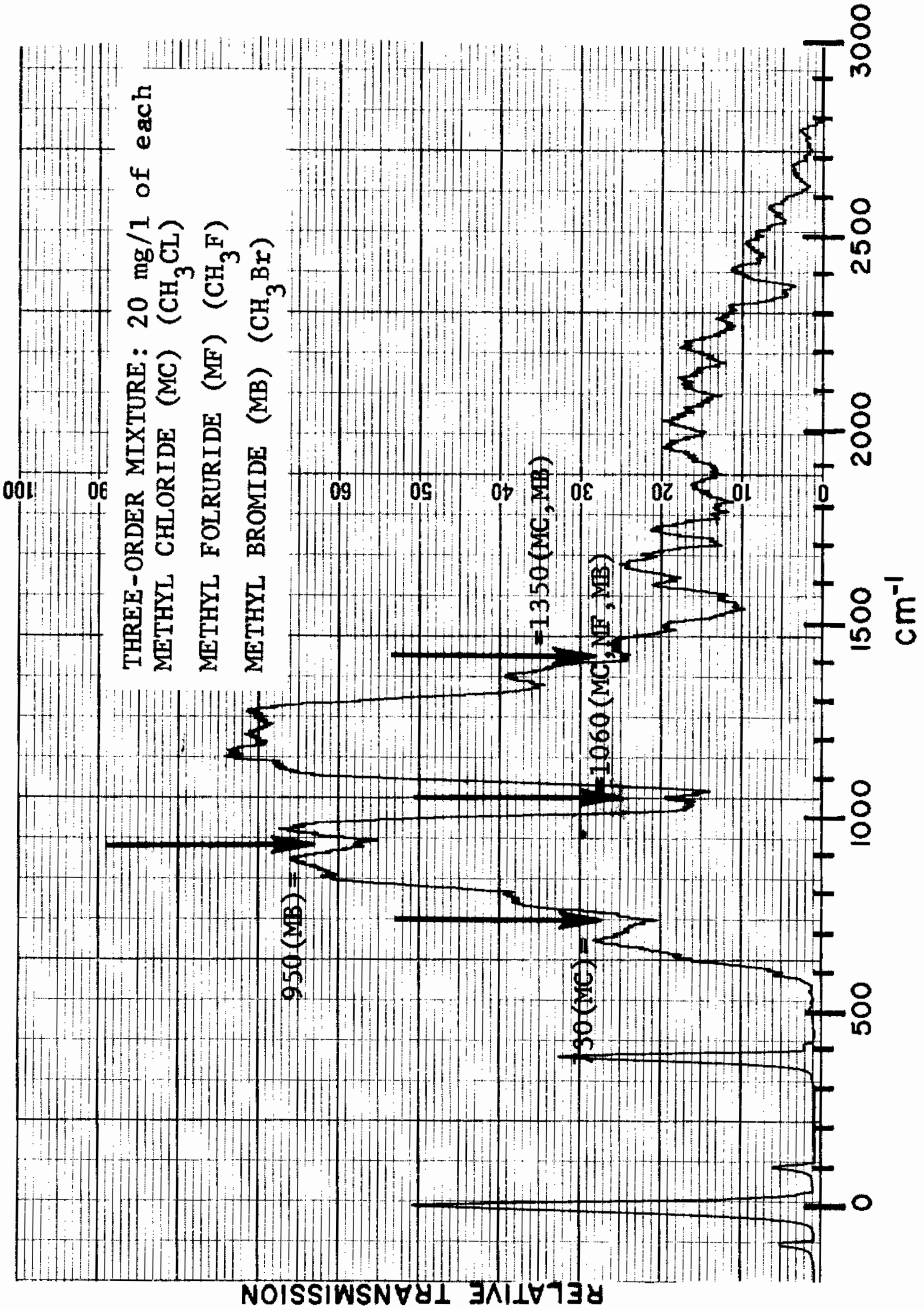

THREE-ORDER MIXTURE: 20 mg/1 of each
METHYL CHLORIDE (MC) (CH_3CL)
METHYL FOLRURIDE (MF) (CH_3F)
METHYL BROMIDE (MB) (CH_3Br)
1350(MC,MB)
1060(MC,MF,MB)
950(MB)
730(MC)
RELATIVE TRANSMISSION
100
90
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 129

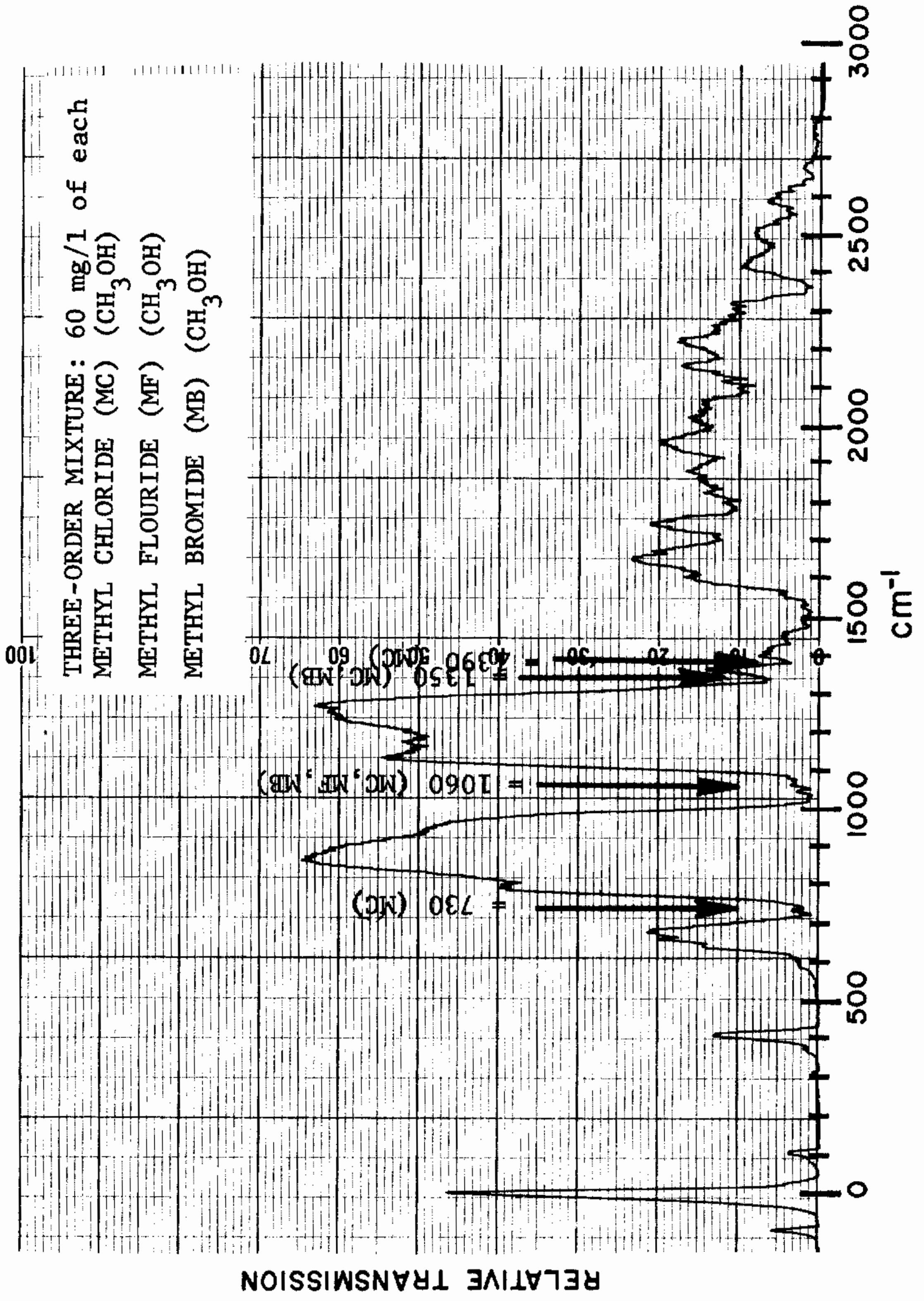

THREE-ORDER MIXTURE: 60 mg/l of each
METHYL CHLORIDE (MC) (CH_3OH)
METHYL FLOURIDE (MF) (CH_3OH)
METHYL BROMIDE (MB) (CH_3OH)
= 1390 (MC)
= 1350 (MC,MB)
= 1060 (MC,MF,MB)
= 730 (MC)
100
70
60
40
30
20
10
0
RELATIVE TRANSMISSION
3000
2500
2000
1500
1000
500
0
cm^{-1}

Figure 130

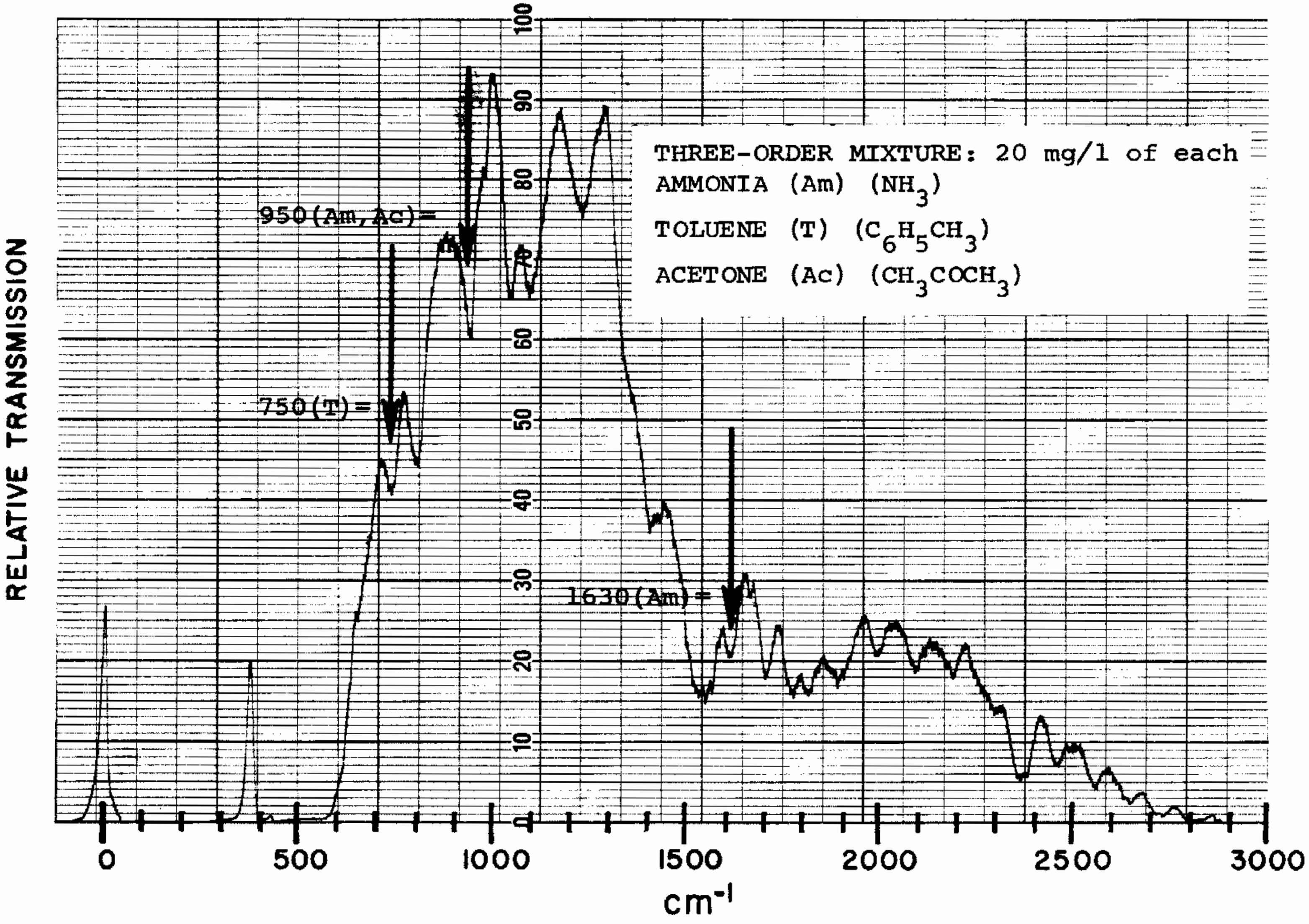

THREE-ORDER MIXTURE: 20 mg/l of each
AMMONIA (Am) (NH3)
TOLUENE (T) (C6H5CH3)
ACETONE (Ac) (CH3COCH3)
950(Am,Ac)=
750(T)=
1630(Am)=
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm-1

Figure 131

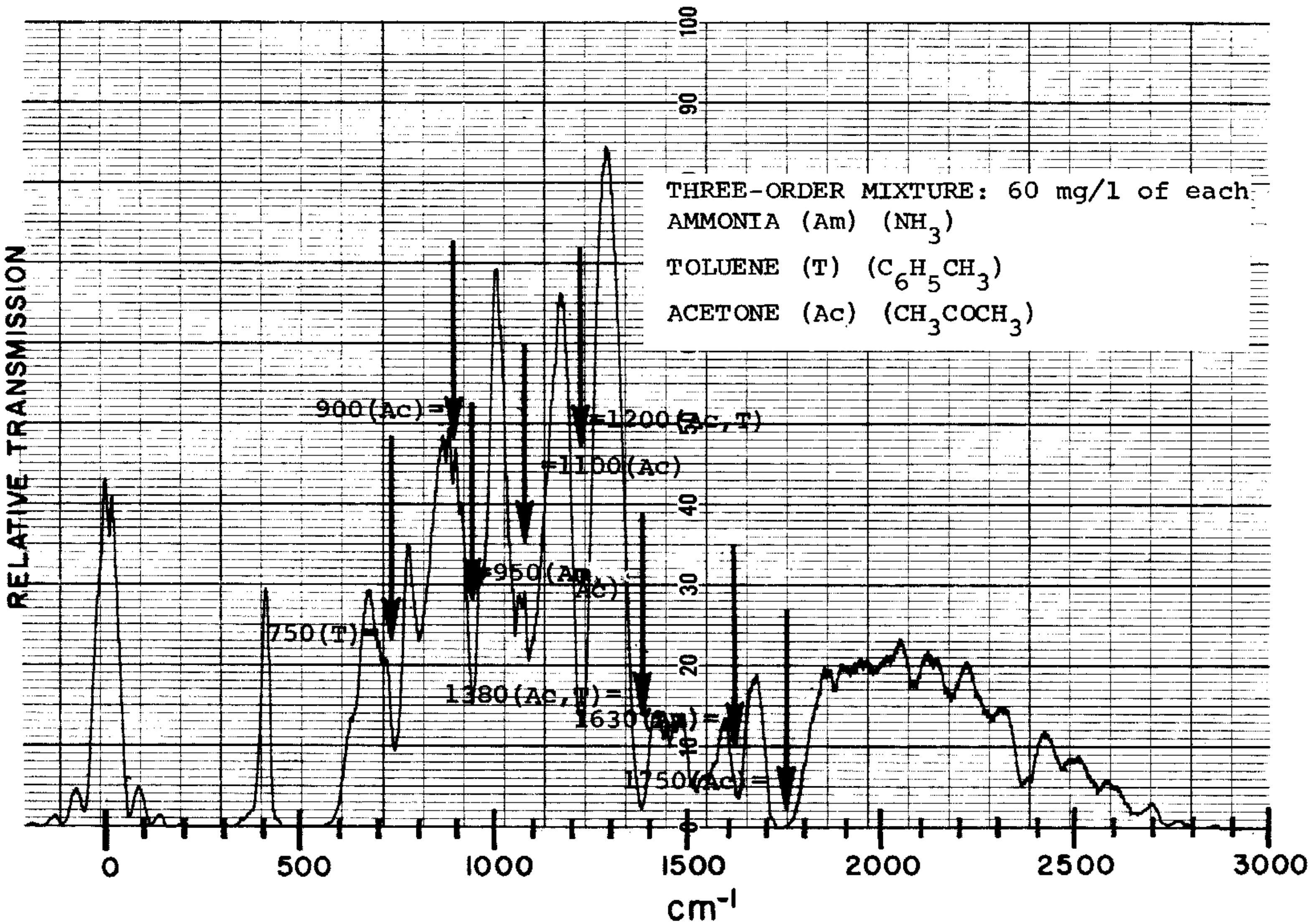

THREE-ORDER MIXTURE: 60 mg/1 of each
AMMONIA (Am) (NH_3)
TOLUENE (T) ($C_6H_5CH_3$)
ACETONE (Ac) (CH_3COCH_3)
RELATIVE TRANSMISSION
100
90
40
30
20
10
0
750(T)=
900(Ac)=
=950(Am, Ac)
=1100(Ac)
=1200(Ac,T)
1380(Ac,T)=
1630(Am)=
1750(Ac)=
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 132

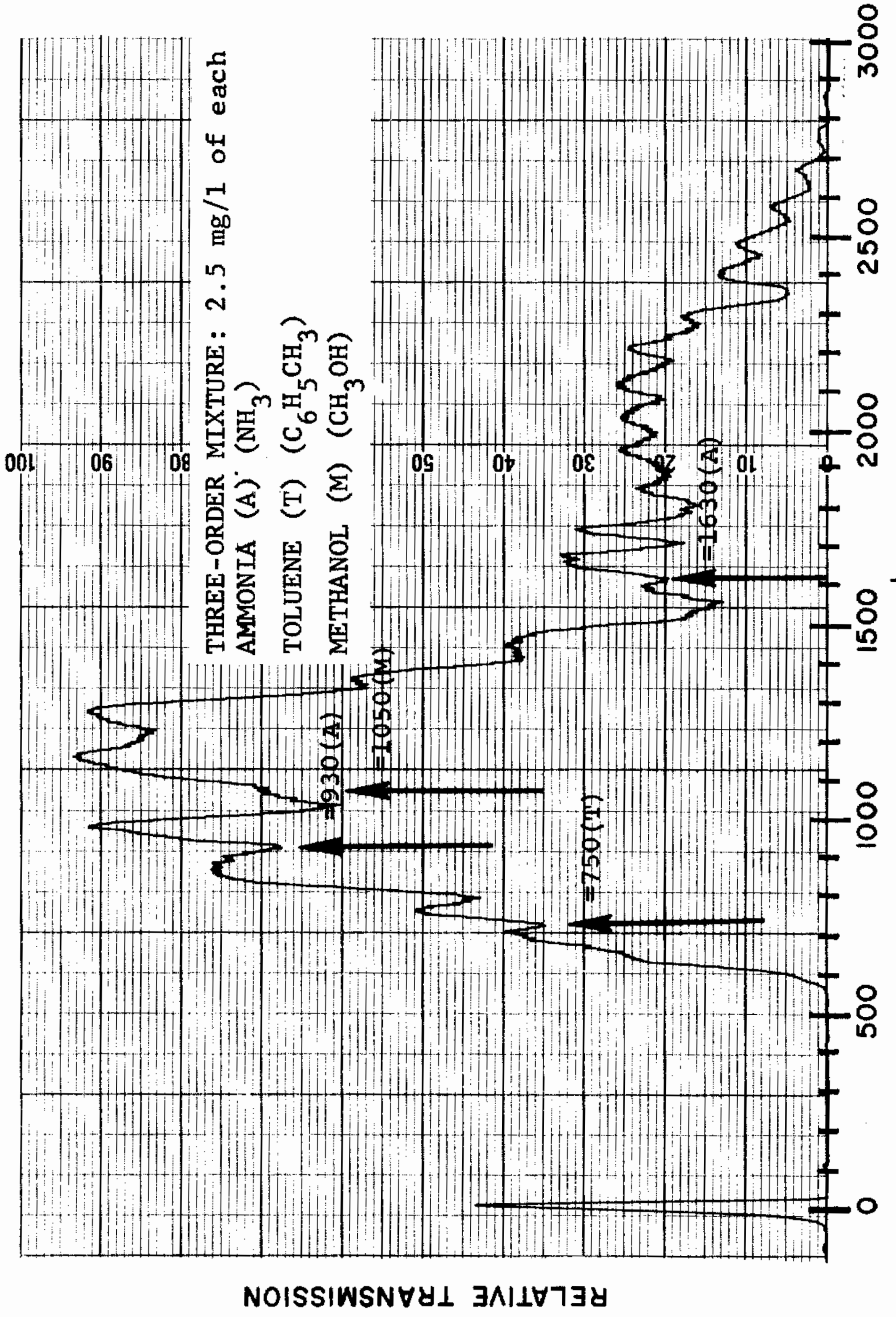

THREE-ORDER MIXTURE: 2.5 mg/1 of each
AMMONIA (A) (NH_3)
TOLUENE (T) $(C_6H_5CH_3)$
METHANOL (M) (CH_3OH)
≈930(A)
≈1050(M)
≈750(T)
≈1630(A)
100
90
80
50
40
30
20
10
0
RELATIVE TRANSMISSION
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 133

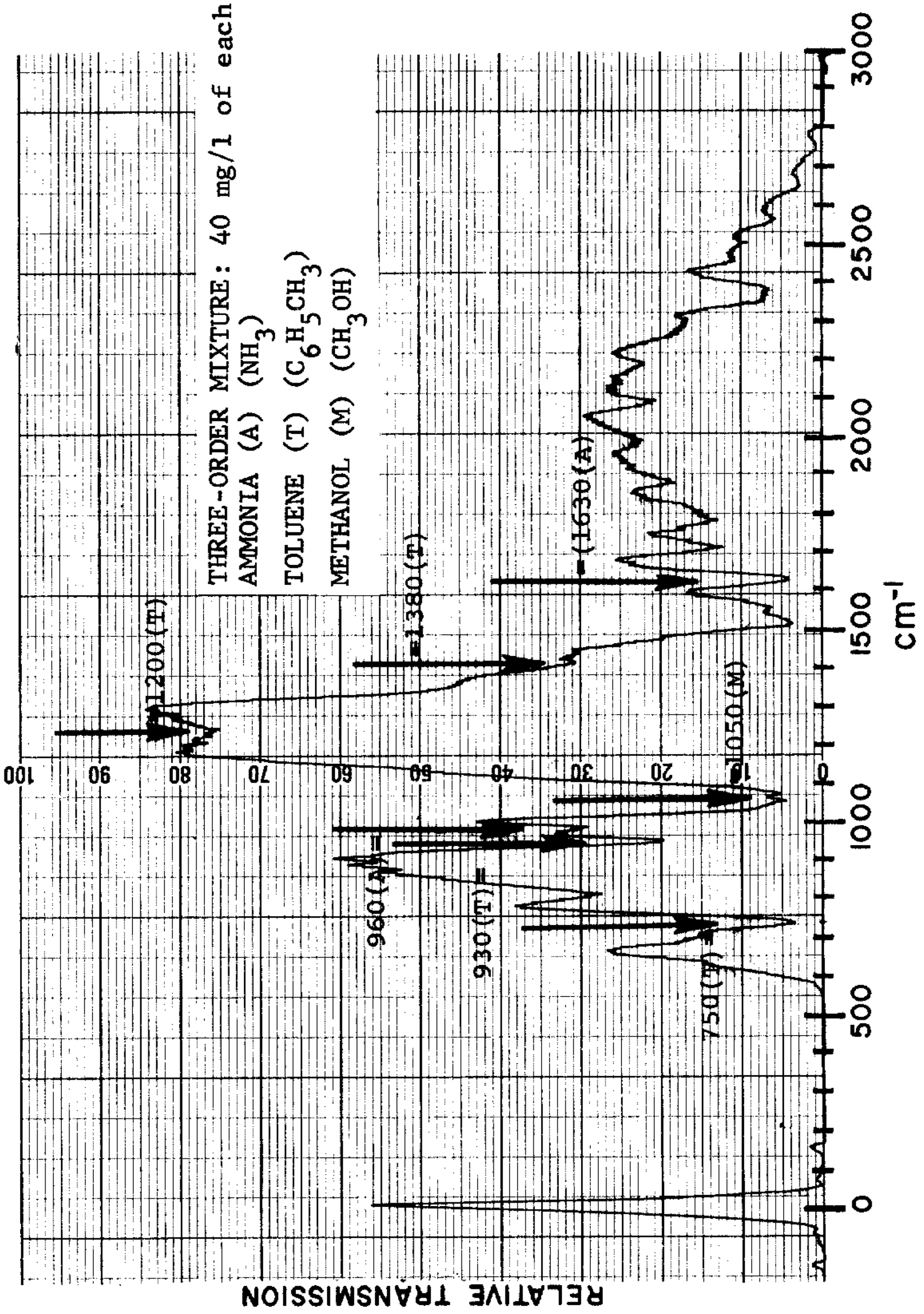

THREE-ORDER MIXTURE: 40 mg/1 of each
AMMONIA (A) (NH_3)
TOLUENE (T) ($C_6H_5CH_3$)
METHANOL (M) (CH_3OH)
1200(T)
1380(T)
1630(A)
1050(M)
960(A)
930(T)
750(T)
RELATIVE TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
cm^{-1}
0
500
1000
1500
2000
2500
3000

Figure 134

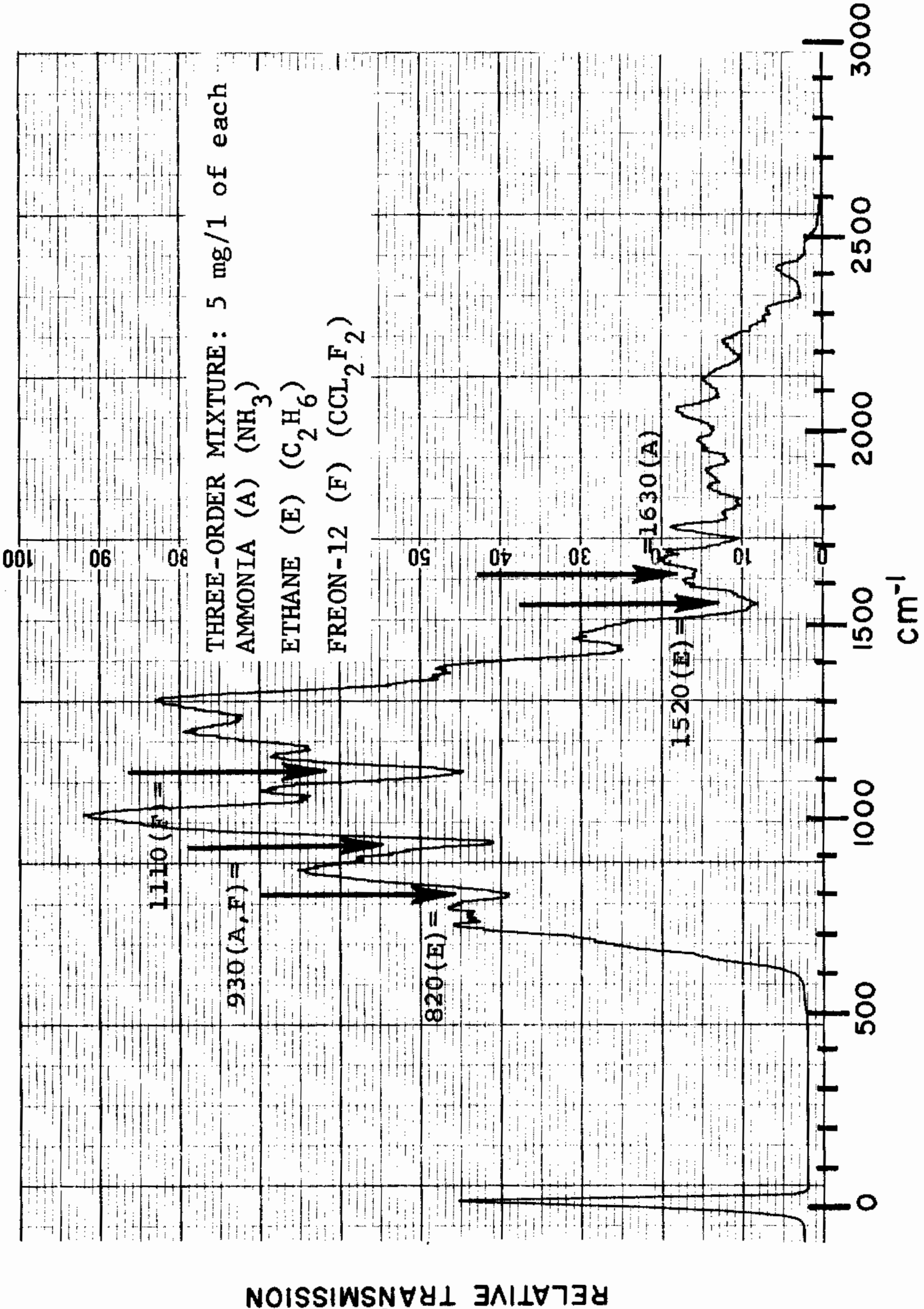

THREE-ORDER MIXTURE: 5 mg/1 of each
AMMONIA (A) (NH_3)
ETHANE (E) (C_2H_6)
FREON-12 (F) (CCL_2F_2)
1110(F) =
930(A,F) =
820(E) =
1520(E) =
=1630(A)
100
90
80
50
40
30
20
10
0
3000
2500
2000
1500
1000
500
0
cm^{-1}
RELATIVE TRANSMISSION

Figure 135

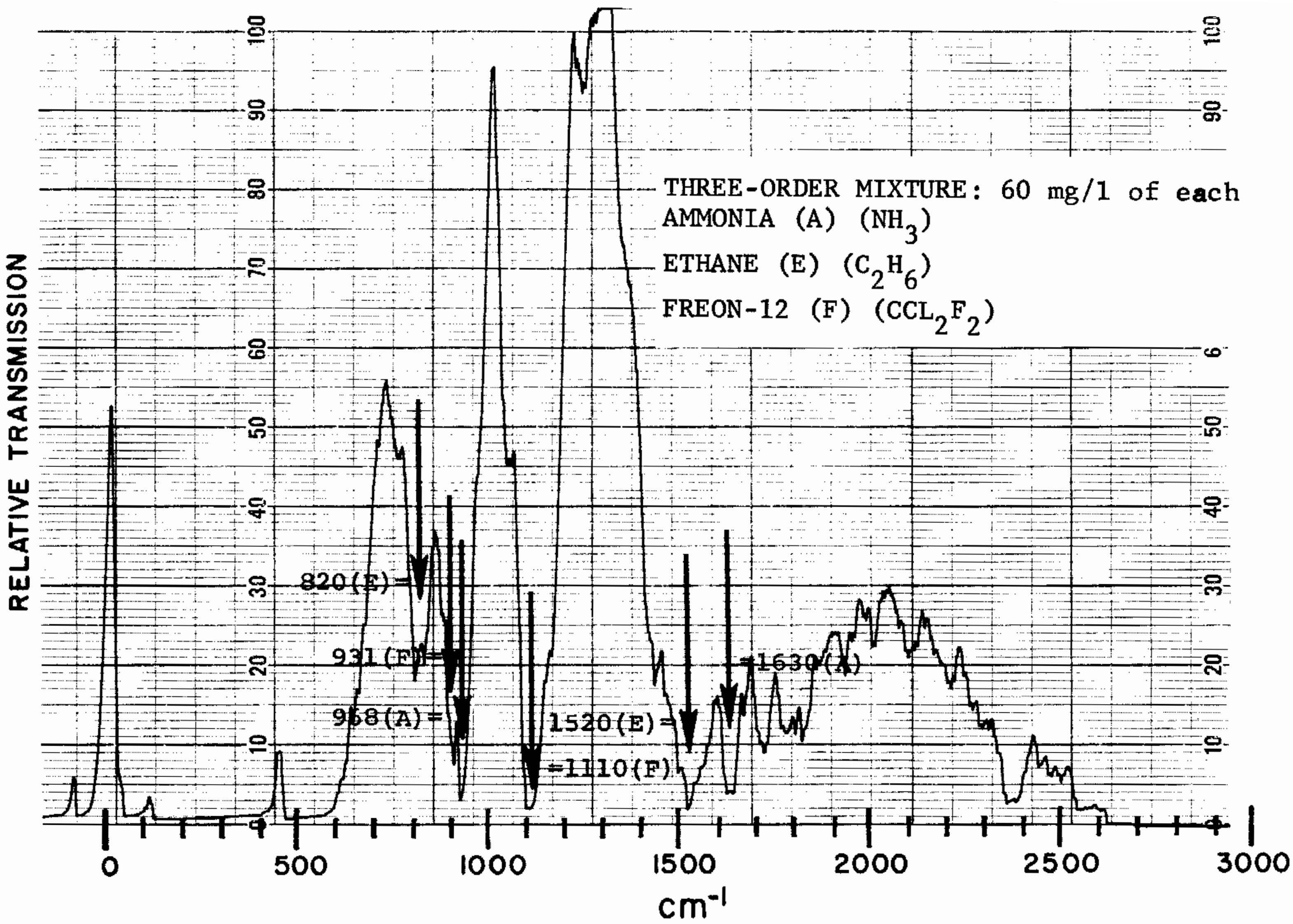

THREE-ORDER MIXTURE: 60 mg/1 of each
AMMONIA (A) (NH3)
ETHANE (E) (C2H6)
FREON-12 (F) (CCL2F2)
820(E)
931(F)
968(A)
1110(F)
1520(E)
1630(A)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm-1

Figure 136

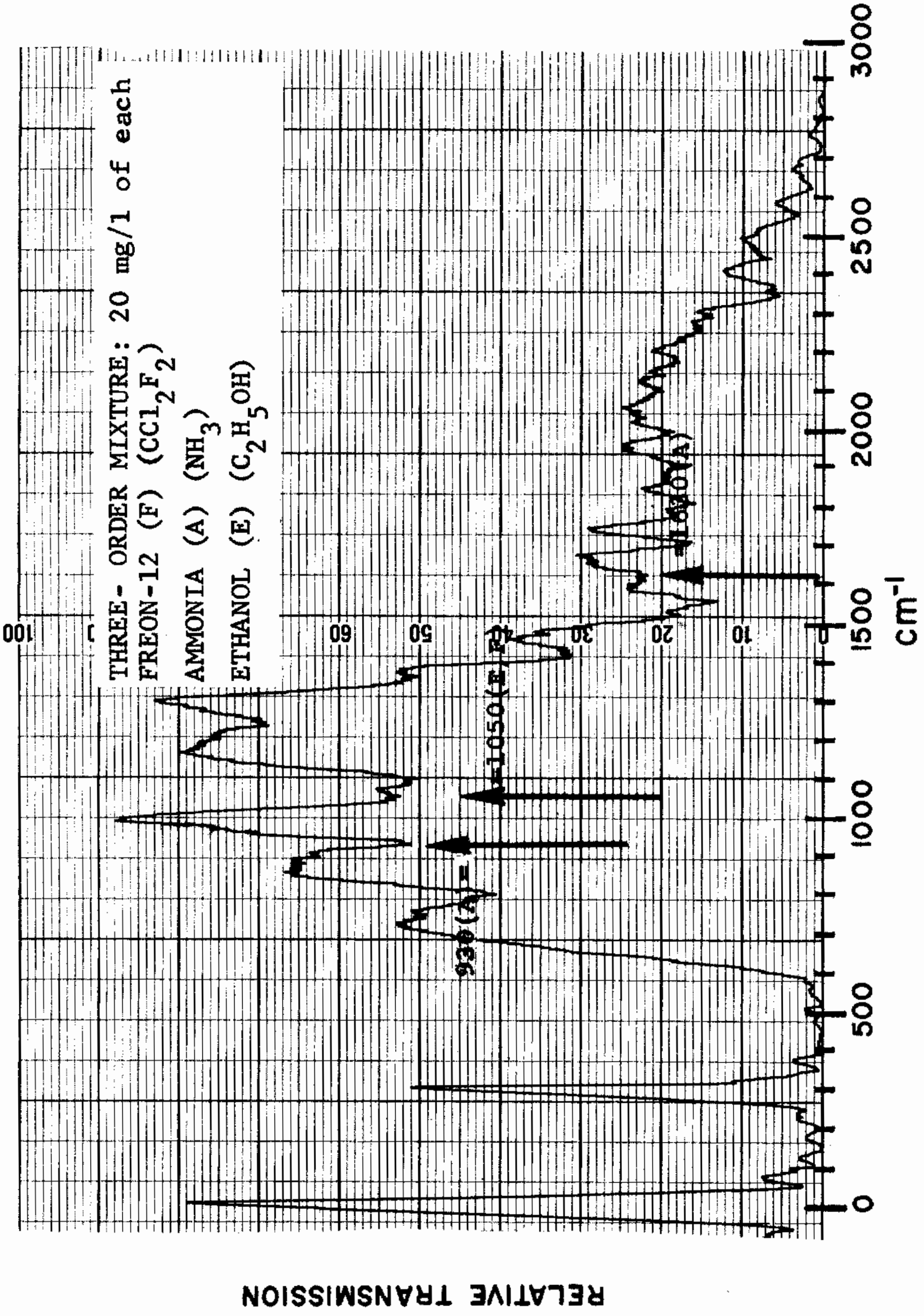

THREE- ORDER MIXTURE: 20 mg/1 of each
FREON-12 (F) (CCl_2F_2)
AMMONIA (A) (NH_3)
ETHANOL (E) (C_2H_5OH)
930(A)
1050(E,F)
1630(A)
100
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}
RELATIVE TRANSMISSION

Figure 137

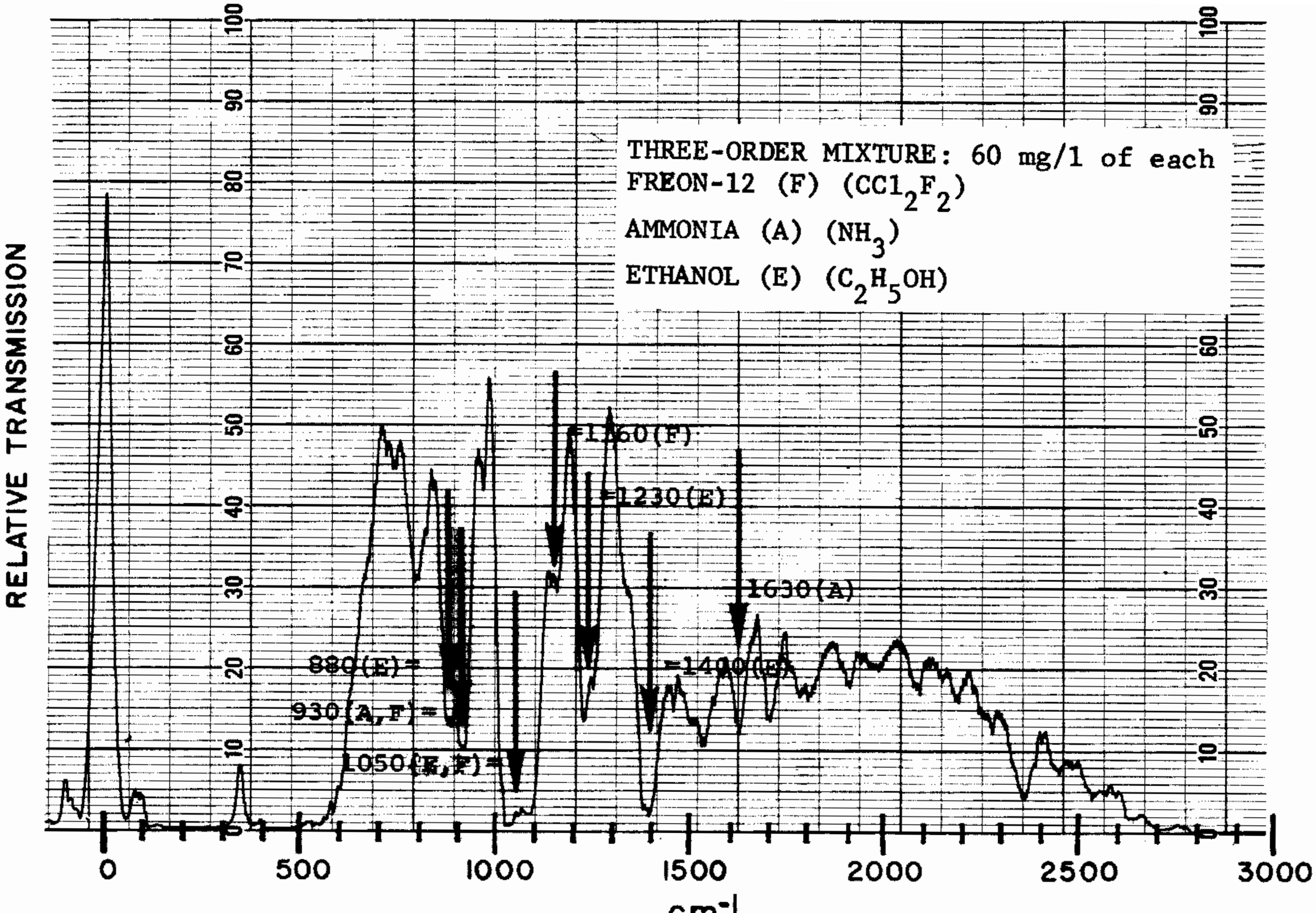

THREE-ORDER MIXTURE: 60 mg/1 of each
FREON-12 (F) (CCl_2F_2)
AMMONIA (A) (NH_3)
ETHANOL (E) (C_2H_5OH)
880(E)
930(A,F)
1050(E,F)
1160(F)
1230(E)
1400(E)
1630(A)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 138

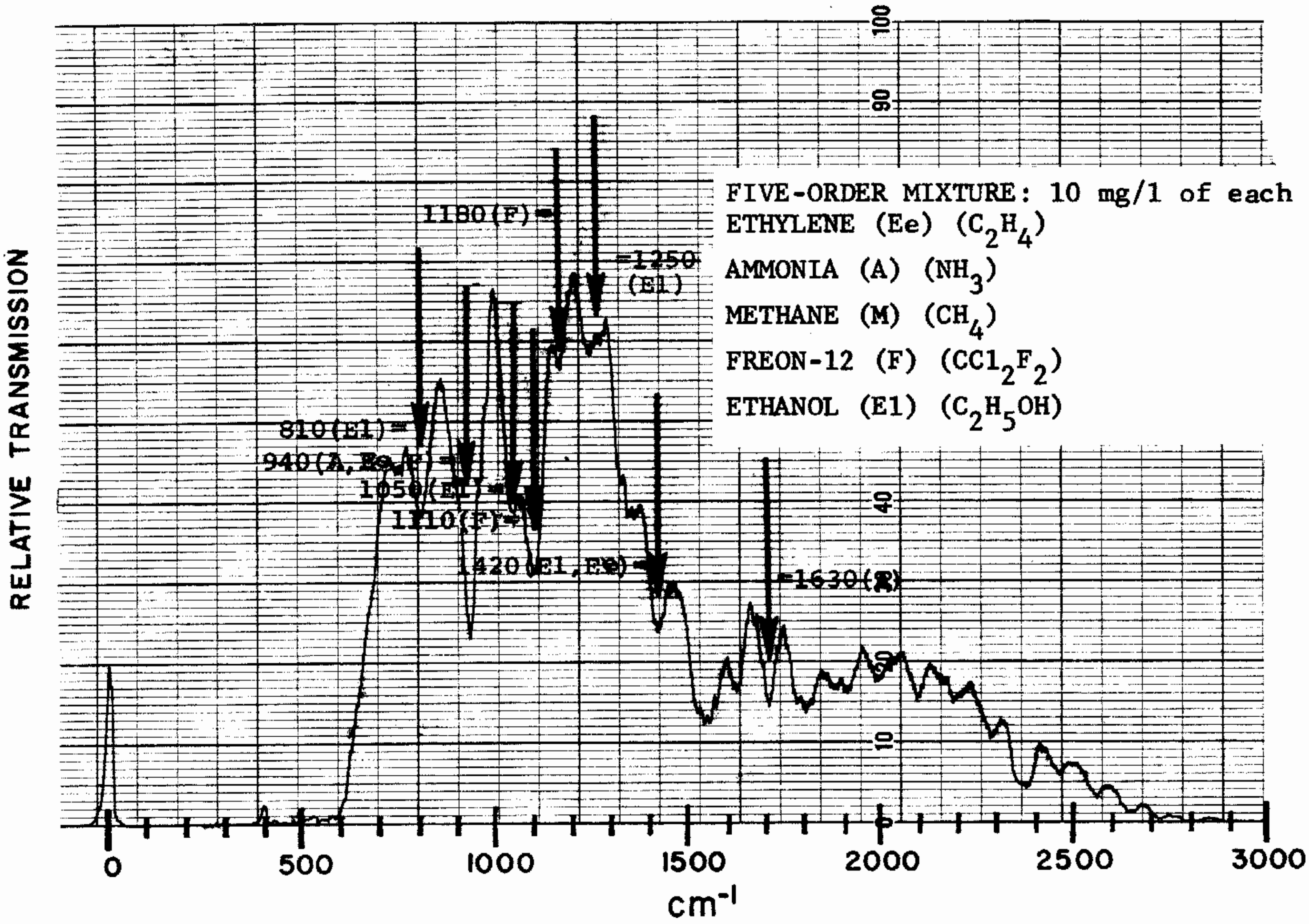

FIVE-ORDER MIXTURE: 10 mg/1 of each
ETHYLENE (Ee) (C_2H_4)
AMMONIA (A) (NH_3)
METHANE (M) (CH_4)
FREON-12 (F) (CCl_2F_2)
ETHANOL (E1) (C_2H_5OH)
810(E1)
940(A,Ee,F)
1050(E1)
1110(F)
1180(F)
1250 (E1)
1420(E1,Ee)
1630(A)
RELATIVE TRANSMISSION
100
90
40
20
10
0
0
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 139

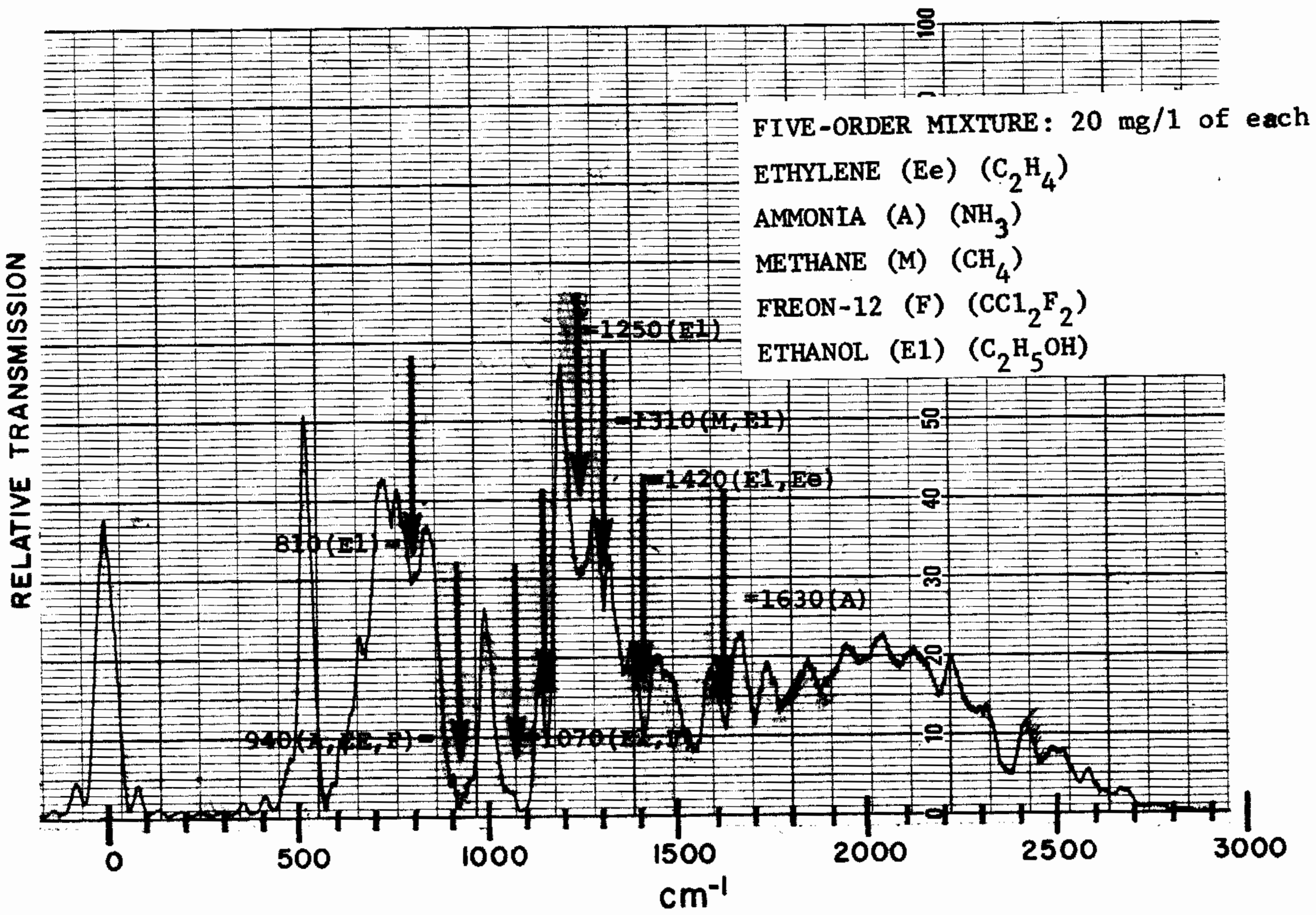

FIVE-ORDER MIXTURE: 20 mg/1 of each
ETHYLENE (Ee) (C_2H_4)
AMMONIA (A) (NH_3)
METHANE (M) (CH_4)
FREON-12 (F) (CCl_2F_2)
ETHANOL (El) (C_2H_5OH)
1250(El)
1310(M,El)
1420(El,Ee)
1630(A)
810(El)
940(A,EE,F)
1070(El,F)
RELATIVE TRANSMISSION
100
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 140

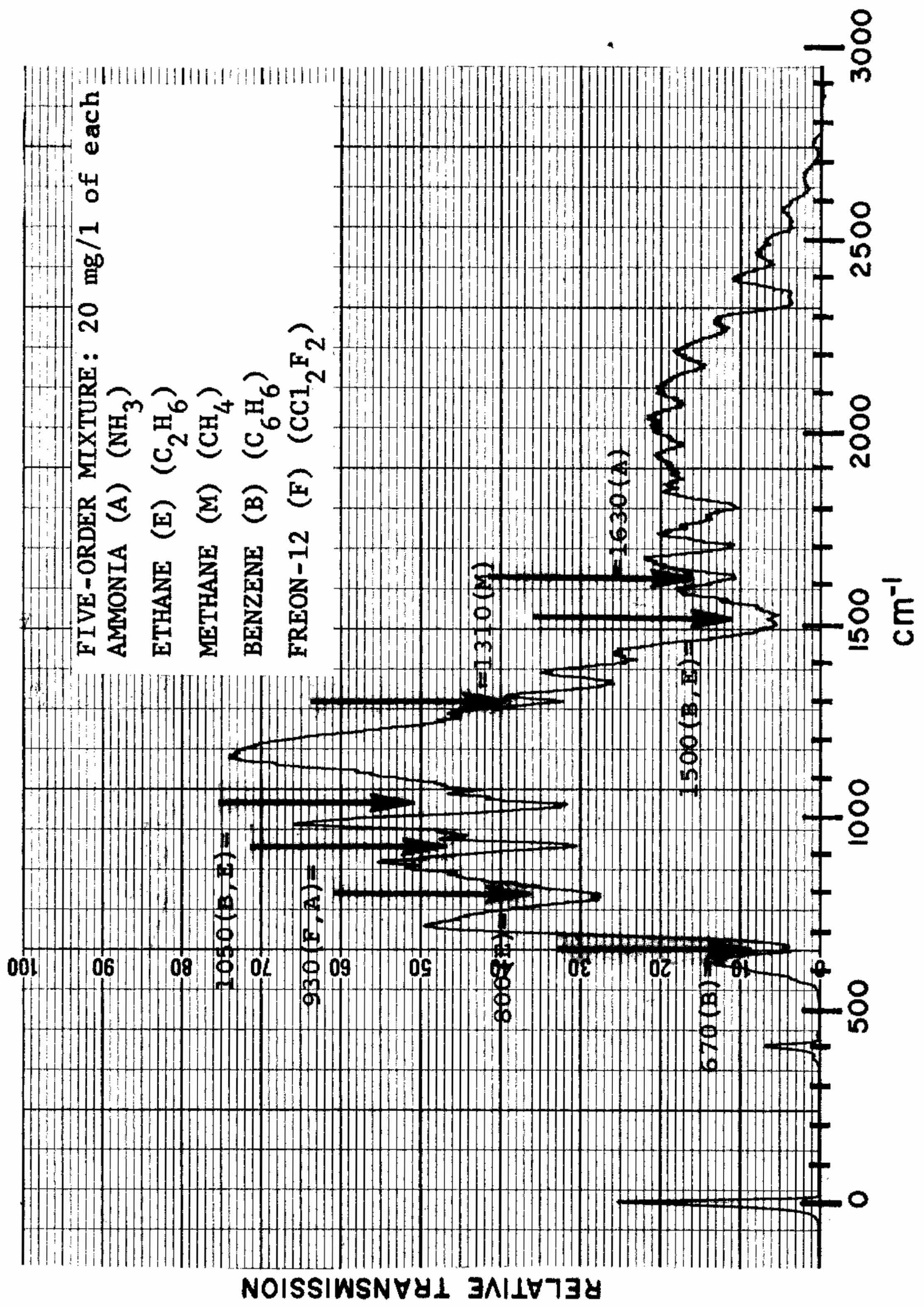

FIVE-ORDER MIXTURE: 20 mg/1 of each
AMMONIA (A) (NH_3)
ETHANE (E) (C_2H_6)
METHANE (M) (CH_4)
BENZENE (B) (C_6H_6)
FREON-12 (F) (CCl_2F_2)
1630(A)
1310(M)
1500(B,E)
1050(B,E)
930(F,A)
800(E)
670(B)
100
90
80
70
60
50
40
30
20
10
0
500
1000
1500
2000
2500
3000
cm⁻¹
RELATIVE TRANSMISSION

Figure 141

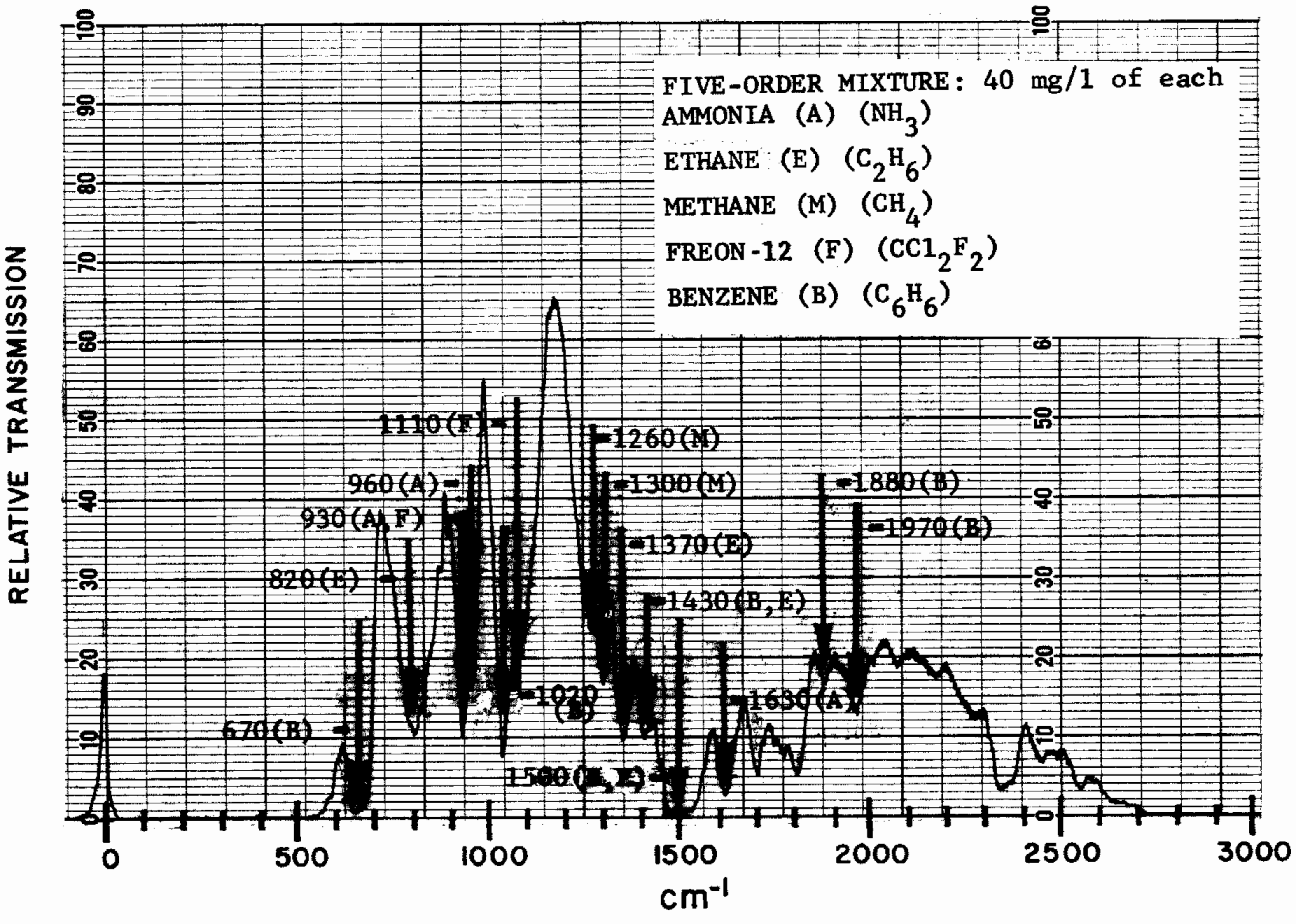

FIVE-ORDER MIXTURE: 40 mg/1 of each
AMMONIA (A) (NH_3)
ETHANE (E) (C_2H_6)
METHANE (M) (CH_4)
FREON-12 (F) (CCl_2F_2)
BENZENE (B) (C_6H_6)
1110(F)
960(A)
930(A,F)
820(E)
670(B)
1020 (B)
1260(M)
1300(M)
1370(E)
1430(B,E)
1500(B,E)
1630(A)
1880(B)
1970(B)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
500
1000
1500
2000
2500
3000
cm⁻¹

Figure 142

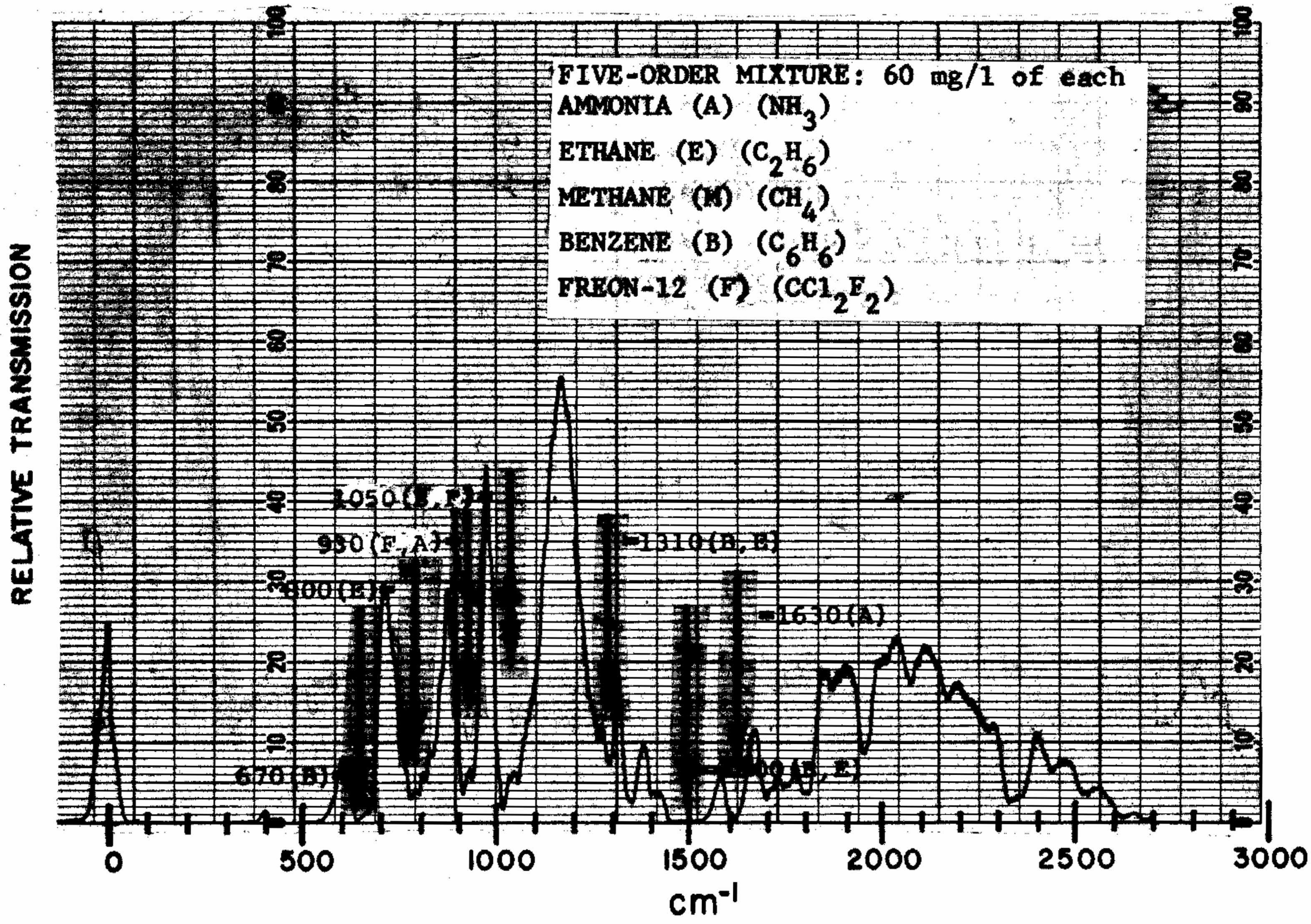

FIVE-ORDER MIXTURE: 60 mg/1 of each
AMMONIA (A) (NH_3)
ETHANE (E) (C_2H_6)
METHANE (M) (CH_4)
BENZENE (B) (C_6H_6)
FREON-12 (F) (CCl_2F_2)
RELATIVE TRANSMISSION
0
10
20
30
40
50
60
70
80
90
100
1050(E,F)
930(F,A)
800(E)
670(B)
1310(B,E)
1630(A)
(A,E)
0
500
1000
1500
2000
2500
3000
cm^{-1}

Figure 143

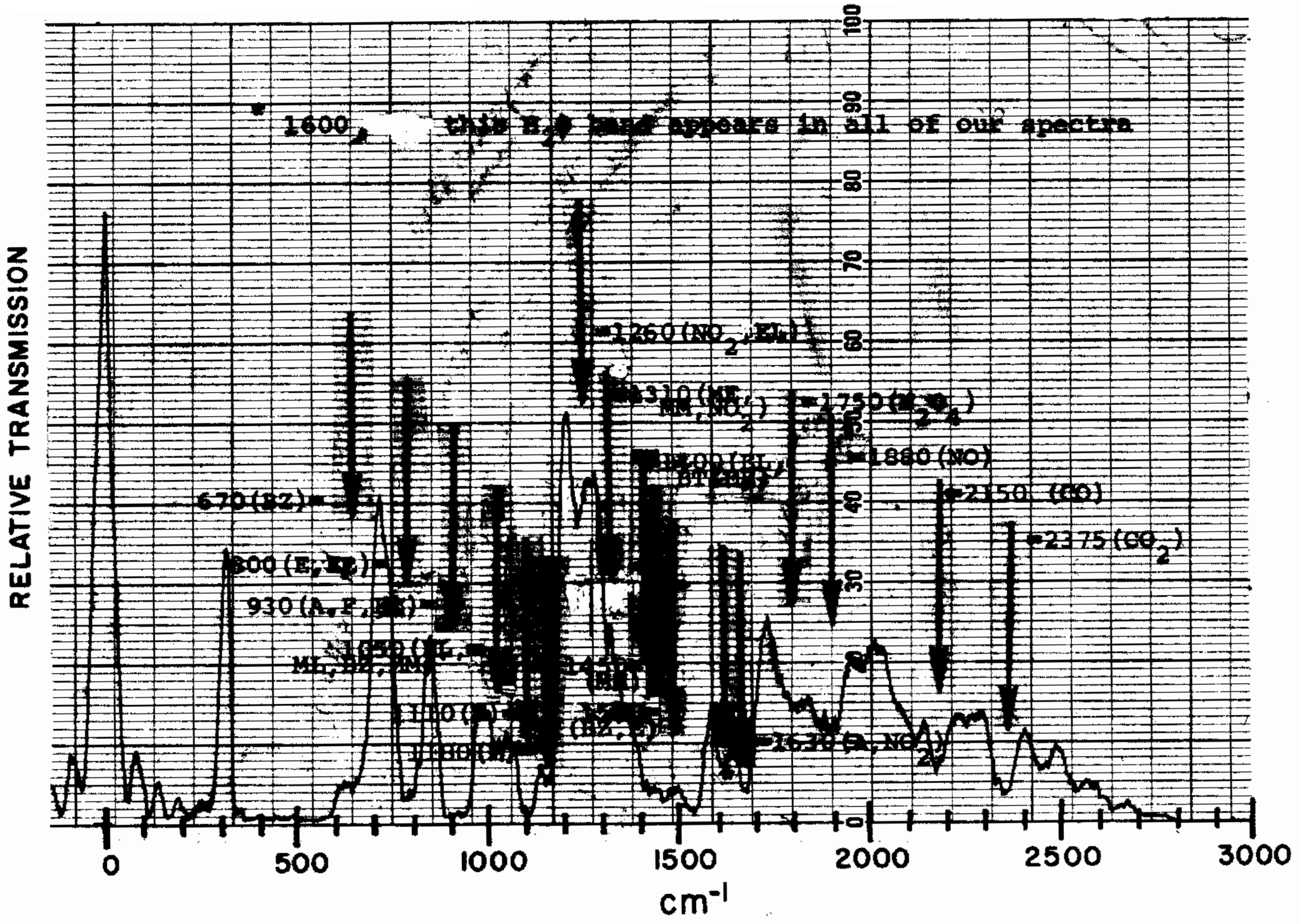


FIGURE 144 <u>FIFTEEN-ORDER MIXTURE</u>

WATER (H_2O), partially from atmospheric radiation path of 10 cm. plus additional 0.6 cm Hg added gas cell

ETHANOL (EL) 25 mg/1	ETHYLENE (EE) 45 mg/1
METHANOL (ML) 20 mg/1	METHYL MERCAPTAN (MM) 25 mg/1
BENZENE (BZ) 25 mg/1	BUTANE (BT) 50 mg/1
ETHANE (E) 45 mg/1	NITRIC OXIDE (NO) (this will combine with residual oxygen in gas cell forming NO_2 and N_2O_4 20 mg/1
AMMONIA (A) 5 mg/1	CARBON MONOXIDE (CO) 50 mg/1
METHANE (ME) 25 mg/1	CARBON DIOXIDE (CO_2) from atmospheric radiation path of 10 cm.
FREON-12 (F) 25 mg/1	

APPENDIX III

THEORY OF THE SINGLE-BEAM INTERFEROMETER SPECTROMETER

The interferometer spectrometer differs from conventional prism and grating spectrometers in the manner in which the incident radiation is separated into component wavelengths.

Both prism and grating spectrometers contain three basic elements: a slit, a dispersing device (prism or diffraction grating) which separates radiation according to wavelenth, and a suitable optical system to produce the spectrum lines which are monochromatic images of the slit.

Interference spectroscopy, however, uses the principle of constructive and destructive interference of light waves.

GENERAL DESCRIPTION OF SYSTEM

Figure 145 is a block diagram of the electronics chassis and optical head of the Model 195T Interferometer Spectrometer. The electronics can be divided into three subgroups: the input regulator and plus and minus 12-volt regulator, the transducer sweep generator and drive amplifier, and the post amplifier. The optical head consists of the optical cube with its associated lenses, mirrors, beamsplitter, and detector, together with the preamplifier and detector bias supply.

The function of the optical cube is to heterodyne the extremely high electromagnetic frequencies of the infrared radiation down to audio frequencies which available infrared detectors can follow. The audio frequencies generated at the detector are an exact analog of the original light frequencies, since the frequency transformation which takes place in the interferometer is linear. The interferogram or audio frequency spectrum may be tape recorded for later playback into a narrow-band, variable-frequency bandpass filter which is slowly tuned over the appropriate audio frequency range. The result is a record of the amount of energy at each frequency. The optical cube accomplishes the Fourier transform of the original light spectrum, and the variable band-pass filter electronically takes the inverse Fourier transform yielding the original spectrum. The inverse Fourier transform may also be computed in a digital computer, which allows a great deal of versatility in processing the spectra (e.g. the spectra can be corrected for the instrument's response, ratios can be taken, scales can be linearized or made logarithmic, etc.).

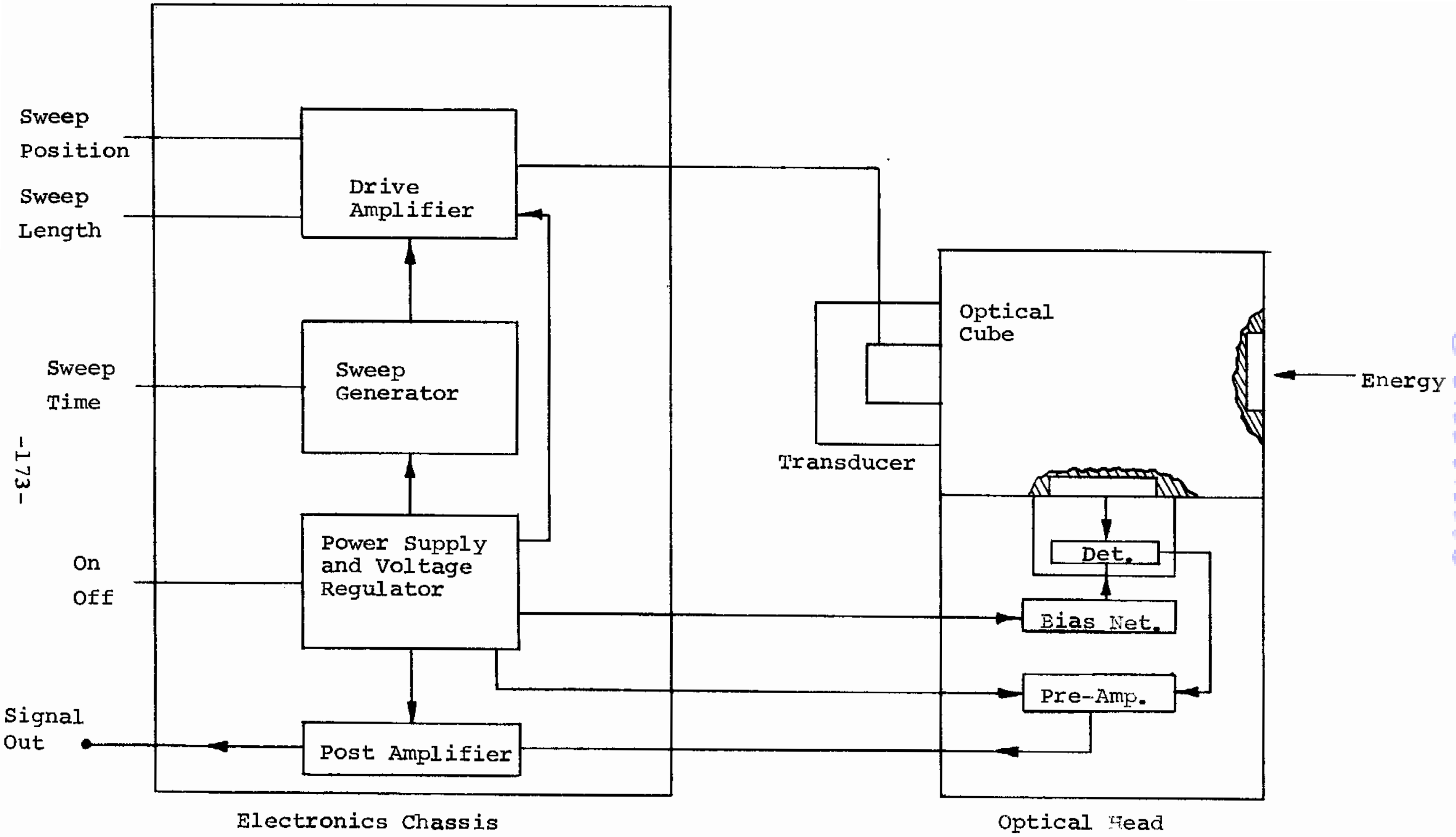


Figure 145 Block Diagram

DETAILED THEORY

The Model 195T interferometer spectrometer utilizes the Michelson optical system. (Optical ray traces are shown in figure 146). S is a semireflective mirror (called a beamsplitter) which reflects 50% of the light which strikes it but permits the other 50% to pass. M_1 and M_2 are mirrors which reflect all the light reaching them; they are identical, except M_1 can be displaced a distance Δx. C is a compensator plate to equalize optical paths.

The beamsplitter's semireflective coating (a thin germanium film) is deposited on a sodium chloride plate. A ray travelling the M_1 leg passes through the beamsplitter plate 3 times while the one traversing leg M_2 passes through it only once. Because of the dispersion of the sodium chloride, a compensator plate, C, of the same material and thickness as the beamsplitter, S, is included to insure symmetry (equal optical path length) of the M_2 and M_1 legs.

If a light beam enters as shown, 50% of it will pass through the beamsplitter and continue toward M_1 while the other 50% will be reflected toward M_2. Upon reaching mirrors M_1 and M_2, each fractional half of the original energy will be completely reflected back toward the beamsplitter. Upon striking the beamsplitter, the portion of the light transmitted to the detector and the portion of the light lost from the interferometer depend on the relative phases of the recombined rays in the exit and detector legs of the interferometer.

The phases are equal for the case where the optical distances in legs M_1 and M_2 are equal and the splitter is a thin dielectric film. Thus when the legs are of equal length, of the light entering the spectrometer, less absorptions, is transmitted to the detector. The result of this constructive interference of the two beams is a bright central fringe.

When the optical path lengths of the M_1 leg and the M_2 leg are equal, all of the original light energy which reaches the detector via route M_1 is in phase with that arriving via route M_2. If, however, we cause the M_1 mirror to be displaced an amount Δx, we find that the phase of the light arriving at the detector via route M_1 is retarded by an amount $2\Delta x$ from that arriving via route M_2. For monochromatic light of wavelength λ, a displacement $\Delta x = \lambda/4$ will cause a retardation of $2\Delta x = 2\lambda/4 = \lambda/2$. The two equal amplitude light fractions

M_1 = Transducer Mirror

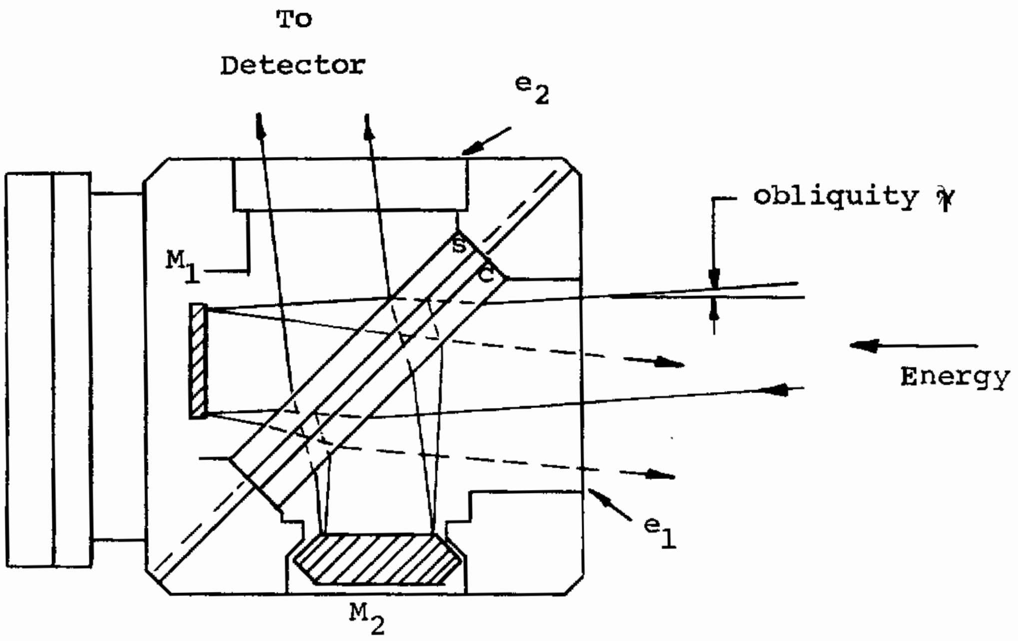
M_2 = Fixed Mirror

s = Beamsplitter

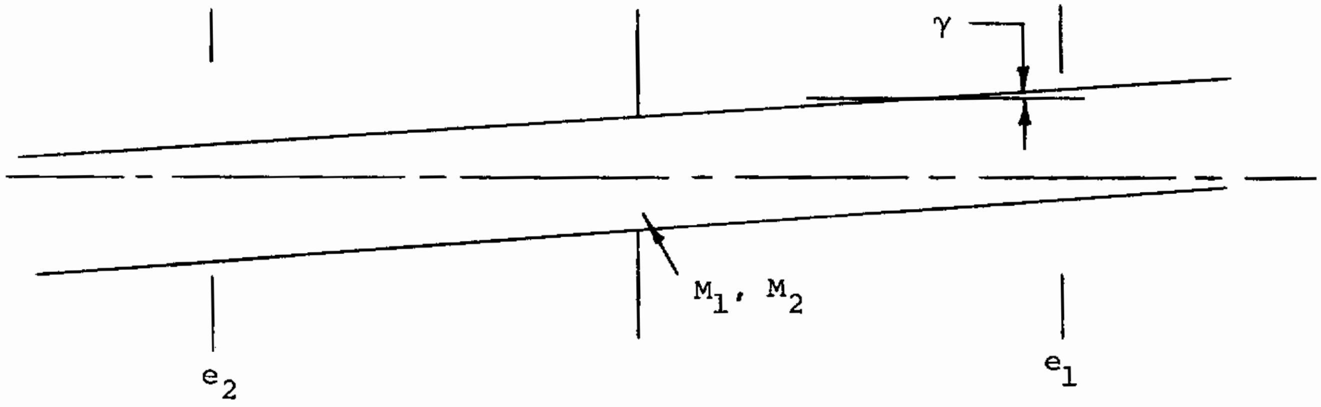
c = Compensator

e_1 = Location of Window

e_2 = Location of Cube Lens



Path of an Oblique Parallel Bundle



Optical Equivalent to Show Ray Paths

Figure 146

will therefore reach the detector an increment of π out of phase, cancellation will result and the net signal of wavelength λ to the detector will be zero. The detector signal will, in fact, be zero for all displacements Δx which are odd multiples of $\lambda/4$ ($\pm \lambda/4$, $\pm 3\lambda/4$, $\pm 5\lambda/4$, etc.) and will be equal to the total input energy (minus absorptions) for all even multiples of $\lambda/4$ beginning with zero (0, $\pm \lambda/2$, $\pm \lambda$, $\pm 3/2\lambda$, $\pm 2\lambda$. etc.), where the plus and minus signs denote displacements on both sides of zero retardation corresponding to increased or decreased optical path lengths (retardations) respectively.

If the displacement of mirror M_1 is slowly changed, the energy at the detector goes through a series of maxima and minima (light and dark "fringes") as the retardation of the optical path lengths of the two legs differs by integral numbers of wavelengths, according to the expression

$$I = 0.5\, I_o(1 + \cos 2\pi\nu Bt/T) \qquad (1)$$

where ν is the wavenumber of the incident radiation in cm^{-1}, and $Bt/2T$ is the instantaneous displacement, x, of the mirror moving a distance $B/2$ in time T. That is, the frequency of the energy transmitted to the detector is a joint function of the wavenumber of the input radiation and the mirror velocity $B/2T$.

Since the optical retardation, B, is twice the mirror displacement,

$$f_\nu = 2 \cdot \nu \cdot \frac{B}{2T} = \nu \cdot \frac{B}{T} \qquad (2)$$

The detector signal for incident radiation of only one wavelength is a simple sine wave. For incident radiation composed of many wavelengths the signal is a complex one called an interferogram. Since all of the wavelengths are processed simultaneously, an interferogram is the superposition of all of the sine waves that would have been generated had each of the incident wavelengths been processed separately.

In the actual Model 195T, the movable mirror is mounted on the armature of an electromagnet and is displaced by changing the d-c current through the armature. Figure 147 is a plot of the mirror position in time showing the linear mirror

T = Sweep Time

F = Flyback Time

R = Recovery Time

B = Excursion

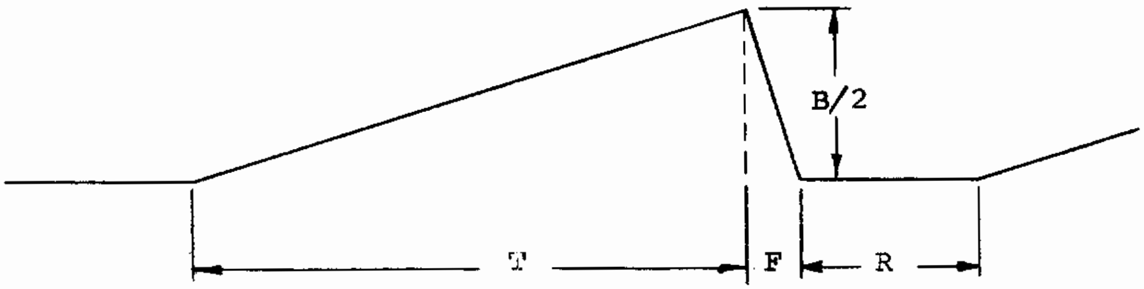


Figure 147 Mirror Motion

displacement.

Clearly, the audio frequency range to which the incident radiation is heterodyned can be changed by varying the sweep velocity. For example, if T is halved while B is kept the same, the resulting audio frequency (for a given monochromatic input) will double. Also, if two or more light frequencies are present in the input radiation, there will be two or more uniquely corresponding audio frequencies present in the audio output spectrum.

The capability of a practical instrument to resolve two neighboring frequencies is specified in terms of the smallest increment of wavelength, $\Delta\lambda$, which can be distinguished at the output (or, alternatively, in terms of wave number, $\Delta\nu$). The limit of spectral resolution can be shown to be a constant, dependent only on the maximum internal retardation, B, according to $\Delta\nu = K/B$ where K is determined by the amount of refraction at the entrance aperture. For our instrument, K = 1, approximately, so that $\Delta\nu = \frac{1}{B}$.

The interferometer spectrometer is run as a d-c system: that is, the input is not chopped and rectified but rather the scanning of the interferometer modulates the frequency of the signal which is picked up by the detector. The response time constant of the detector sets an upper bound to the rate T^{-1} at which the instrument may be scanned for any given ν maximum according to $f_\nu = \nu B/T$. Problems of detector drift and of time variation of the target radiation set a lower bound. In general, it is found that optimum scan rates fall within the range of 0.5 to 8 $\sec^{-1}$.

Block Engineering's time averaging computer (Coadder) is used with the interferometer spectrometer to improve the signal-to-noise ratio of spectra. Input interferograms are repeatedly sampled at a rate which is more than twice the maximum frequency present in the signal. The samples are sequentially digitized and stored in the core memory. Each series of samples is initiated by a triggering pulse supplied by the interferometer at the beginning of each interferometer scan. Therefore, the samples from successive interferograms correspond precisely in time and their levels are digitally added in the memory, so that the coherent signal increases linearly in amplitude with the number of interferograms accumulated. The noise present at the input accumulates, due to its random character, in such a way that the RMS noise power increases with the square root of the number of scans. The resultant gain in signal-to-noise is thus $\sqrt{n}$, where n is the number of times the same signal is sampled. For example, if the Coadder accumulates as few as 16 interferograms, the S/N will be increased by a factor of four.

The Coadder memory contains 1024 words; so that a maximum of 1024 sample points may be taken. Each sample is digitized by an 8-bit A to D converter that is set to accept a maximum signal of 9 volts peak to peak. Since the capacity of each word in the memory is 16 bits, it is possible to co-add up to 256 interferograms with a 9-volt peak to peak component. Smaller amplitude interferograms, of course, may be co-added many more times.

In addition to improving the signal quality of interferograms, the Coadder lends a greater dimension of versatility to the basic interferometer spectrometer system. For example, the SUBTRACT function makes it possible to effectively eliminate unwanted bakground information whenever circumstances allow the background to be sampled in the absence of the desired source.

The interferometer has a size advantage as well over comparably sensitive dispersive instruments; due to the use of a large aperture hole rather than flux-limiting slits, it intercepts more spectral power from the target. In particular, if the target fills the field-of-view, the collected spectral power, P, is independent of the distance from the source and is a function only of the aperture stop and focal ratio of the optical system. This function is called throughput (θ) and is equal to the product of acceptance solid angle(Ω) and the aperture stop area (A)

$$\theta = A\Omega$$

In the interferometer spectrometer, the aperture stop is typically about 200 mm^2 whereas the aperture stop (slit area) of a comparable dispersive instrument would be on the order of 2 mm^2. Moreover, the interferometer's focal ratio is f/3.8, rather fast for a dispersive instrument, which would be typically f/6, a factor in solid angle of about 3. Together, these give the interferometer an advantage in throughput (and, hence, in signal-to-noise ratio) of from 100 to 1000. This, added to the above discussed advantage (in the instrument noise limited case) of $\sqrt{M}$ where M is the number of resolution elements, usually on the order of 100, will yield an overall advantage of 10^3 to 10^4 in signal-to-noise in one scan over a comparable dispersive instrument. When the Coadder is used, further increase in signal-to-noise ratio of $\sqrt{n}$ where n is the number of scans co-added, and may be greater than 10^3 itself in some instances, will yield total advantage of 10^4 to 10^6.

APPENDIX IV

THE DUAL-BEAM INTERFEROMETER

The ideal interferometer may be abstractly visualized as a black box with two optical windows as depicted schematically in figure 148. The transmission between windows is a function of the position of the moving mirror for a particular optical frequency. Light from the absorbant gas reaches the detector in the same manner as in the single-beam instrument discussed previously. Light from the reference cell is reflected from a mirror, enters the bottom window of the interferometer where part of it is reflected back to the detector. For a particular optical frequency, when the moving mirror is in such a position so as to produce maximum transmission through the interferometer there will be a maximum amount of light from the absorbant gas cell reaching the detector. However, this will correspond to a minimum of light from the reference cell reaching the detector since most of the light will be transmitted out the side window.

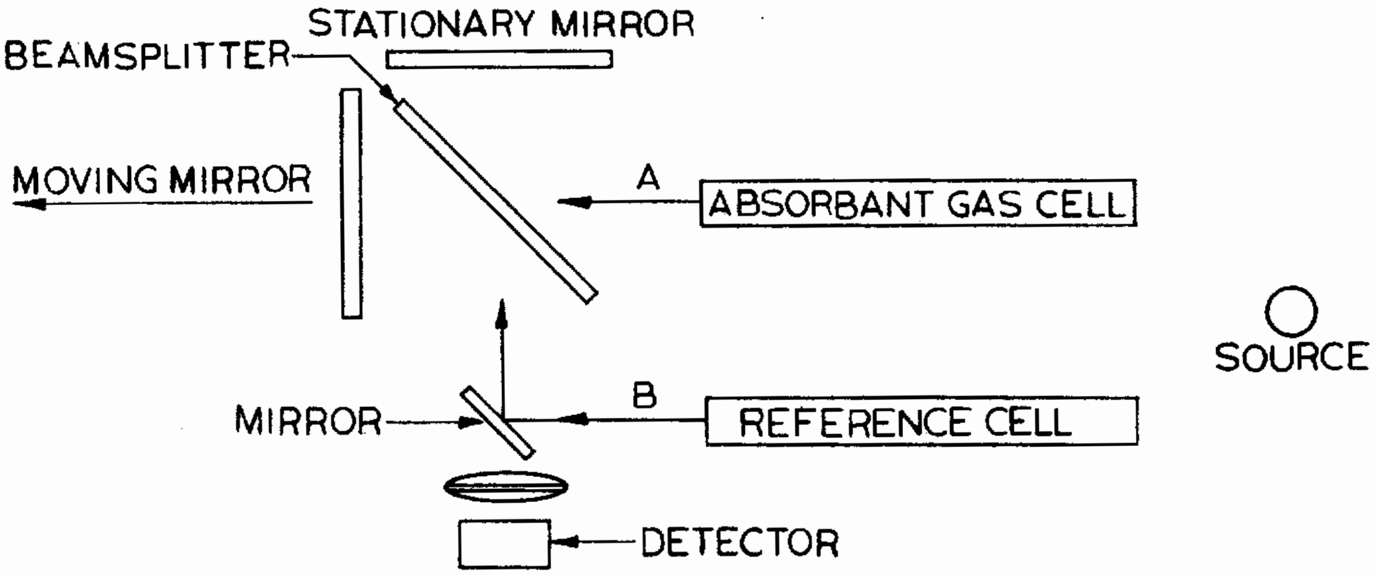
The spectrum from the absorbant gas cell is a spectrum of $B(\nu)\ T(\nu)$, where $B(\nu)$ is the output of the source at frequency ν and $T(\nu)$ is the transmission of the absorbant gas cell at frequency ν. The spectrum from the reference cell is just $B(\nu)$ assuming it is filled with an inert gas. Therefore, the resultant spectrum at the detector is

$$B(\nu) - B(\nu)T(\nu) = B(\nu)[1 - T(\nu)] = B(\nu)\ A(\nu),$$

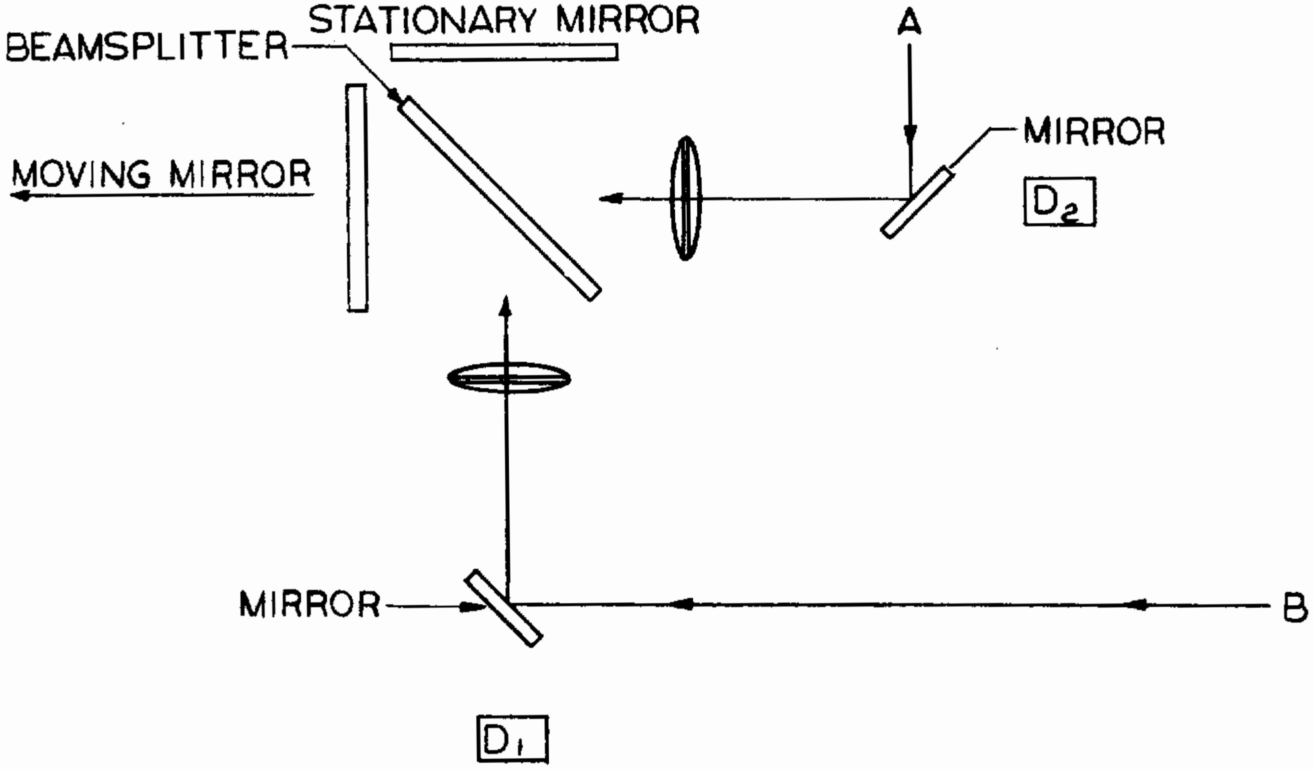
where $A(\nu)$ is the absorption of the absorbant gas cell at frequencies ν. Hence, as stated previously, an output at a particular audio frequency is proportional to the absorption at the corresponding infrared frequency.

The actual proposed dual-beam instrument is represented schematically in figure 148. Note that two additional mirrors and two detectors are utilized. The two input beams are labeled A and B. This more complicated geometry is necessary because the transmission, T, and the reflectance, R, of the beamsplitter are strongly wavelength dependent. Let us consider the spectrum of A and B as seen by the detector D_1. Each of the two interfering beams from A are transmitted once and reflected once by the beamsplitter before reaching D_1. One of the two interfering beams from B is transmitted twice by the

Figure 148



IDEAL INTERFEROMETER USED IN DUAL-BEAM MODE



THE PROPOSED DUAL-BEAM INSTRUMENT

beamsplitter, and the other is reflected twice by the beamsplitter before reaching D_1. Hence, the spectrum seen by D_1 is of the form:

$$S_1 = 2\,ART - B(T^2 + R^2)$$

Note that if T = R = ½ for all wavelengths and if A = B the resultant signal would be zero. However, in practice, R and T are wavelength dependent and hence, optical nulling at all wavelengths is impossible. From the symmetry of the geometry, the spectrum seen by D_2 is of the form:

$$S_2 = 2BRT - A(T^2 + R^2).$$

In the proposed instrument, the two detector signals are subtracted electrically and, therefore, the resultant spectrum S is given by:

$$S = S_1 - S_2 = (A-B)(2RT + R^2 + T^2) = (A-B)(T + R)^2$$

$$= A-B,$$

since $T + R = 1$.

Therefore, the wavelength characteristics of the beamsplitter are cancelled out and optical nulling at all wavelengths is possible.

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To develop a small and highly sensitive optical spectrometer for providing repeatable qualitative and quantitative analysis of contaminant gases in enclosed habitable atmospheres, a feasibility study and measurements program was conducted. An infrared interferometer spectrometer was employed in conjunction with a gas absorption cell for trace gas analysis. During the program, spectra were taken of 43 compounds, 10 binary, 10 trinary, 5 five-order, and 1 fifteen-order mixture. Typical minimum detectable concentrations range from 1 to 40 mg/l. The results of this program have defined a system that will satisfy the criteria for a prototype flight instrument.

DD FORM 1 JAN 64 1473

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Trace gas analysis						
Optical subtraction						

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