To the Graduate Council:

I am submitting herewith a dissertation written by Wayne Leon Maddox entitled "Analysis of Cigarette Smoke by Fourier Transform Infrared Spectroscopy." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Gleb Mamantov

Gleb Mamantov, Major Professor

We have read this dissertation
and recommend its acceptance:

E Bruchey

Clifton Woods, III

Lucille H. Turner

Myron T. Kelley

Michael P. Maguire

Accepted for the Council:

Hilton A. Smith

Vice Chancellor
Graduate Studies and Research

Science-Engr.
Thesis
76b
.M233
Cop.2

ANALYSIS OF CIGARETTE SMOKE BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee

Wayne Leon Maddox

March 1976

1270500

ACKNOWLEDGMENTS

The author expresses his appreciation to his supervision in the ORNL Analytical Chemistry Division for permission to perform this research, and to his colleagues for their helpful suggestions and support, especially to J. H. Moneyhun for his analyses of the smoke chamber by gas chromatography.

Thanks are due to Professor Gleb Mamantov, without whose encouragement and guidance the work would not have been possible.

Special gratitude is expressed to his wife who endured much and provided help and encouragement at critical times, and to Lucille Broyles for her competent and gracious help in preparing the manuscript.

ABSTRACT

The application of Fourier transform infrared spectroscopy to the quantitative analysis of several components in whole dilute tobacco smoke was demonstrated. The absorption cell which had a path length of 18 cm was part of a cigarette smoking system similar to the intermittent inhalation exposure devices used in smoking and health research with rodents.

Concentrations were measured for carbon monoxide, carbon dioxide, methane, ethylene, and methanol in 7 to 22% smoke. The precision (relative standard deviation) of a single observation in 22% smoke ranged from 3-4% for carbon monoxide, carbon dioxide, and methane (best cases) to 34% (worst case) for ethylene.

Absorbances measured for isoprene and hydrogen cyanide followed known concentrations in different cigarette smokes.

It was shown that the concentrations of each of these constituents are approximately constant during the 30-sec puff stand time. The results obtained show clearly the possibility of determining several smoke components in a single puff by means of FT-IR spectroscopy.

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
	A. Statement of Purpose	1
	B. Tobacco Smoke	2
	C. Related Literature	3
	D. FT-IR Spectroscopy	5
	1. The Michelson interferometer	6
	2. Non-ideal interferometers	8
	3. Polychromatic sources	9
	4. Instrumental line shapes	11
	5. Resolution	13
II.	EXPERIMENTAL	14
	A. Materials	14
	1. Cigarettes	14
	2. Pure reference materials	14
	B. Apparatus	15
	1. FTS-20 spectrometer	15
	2. Smoking apparatus	20
	3. Ancillary apparatus	23
	C. Procedures	24
	1. Cigarette selection and smoking	24
	2. Standard sample preparation	26
	3. Introduction of samples	27
III.	RESULTS AND DISCUSSION	30
	A. Smoke Spectra	30
	B. Component Spectra	34
	C. Quantitative Analysis	48
	1. Measurement of smoke spectra	48
	2. Calibration	52
	3. Variability Studies	61
	4. Comparison with GC analysis	79
	5. Early vs. late in the stand time	79
	6. Time of analysis	81
IV.	SUMMARY	84
REFERENCES		86
APPENDIX		90
VITA		94

LIST OF TABLES

TABLE		PAGE
I.	Material Balance of Mainstream Cigarette Smoke	4
II.	Major Gas Phase Components	35
III.	CO Frequency Comparison	46
IV.	Lines Selected for Analysis	54
V.	Calibration Data for CO (2169 cm^{-1})	56
VI.	Calibration Data for CO_2 (720 cm^{-1})	57
VII.	Calibration Data for CH_4 (1306 cm^{-1})	58
VIII.	Calibration Data for C_2H_4 (949 cm^{-1})	59
IX.	Calibration Data for CH_3OH (1033 cm^{-1})	60
X.	Constants of Linear Regression Lines for Standards	67
XI.	Code 1, Concentrations of CO	68
XII.	Code 1, Concentrations of CO_2	69
XIII.	Code 1, Concentrations of CH_4	70
XIV.	Code 1, Concentrations of C_2H_4	71
XV.	Code 1, Concentrations of CH_3OH	72
XVI.	Absorbances, Fourth Puffs, 4-Fold Zero-Filled, Apodized	75
XVII.	Absorbances, Fourth Puffs, Unfilled, Unapodized	76
XVIII.	Cigarette Yields	77
XIX.	Between-Code Comparison	78
XX.	Comparison of FT-IR and GC Analysis	80

LIST OF FIGURES

FIGURE		PAGE
1.	Schematic Diagram of the Michelson Interferometer	7
2.	Typical Interferograms	10
3.	Instrumental Line Shapes	12
4.	Optical Layout of the FTS-20 Spectrometer	17
5.	Photograph of the Smoking Apparatus	21
6.	Schematic Diagram of the Smoking Apparatus	22
7.	Schematic Diagram of Sample Introduction	28
8.	Absorption Spectra of Smoke with RES=2	31
9.	Whole-Smoke Absorption Spectrum with RES=8	32
10.	Whole-Smoke Absorption Spectrum with RES=1	33
11.	Transmission Spectrum of CH_3COCH_3 Vapor	36
12.	Transmission Spectrum of CH_2CHCHO Vapor	37
13.	Transmission Spectrum of C_5H_8 Vapor	38
14.	Transmission Spectrum of CH_3OH Vapor	39
15.	Absorption Spectrum of H_2O Vapor	41
16.	Transmission Spectrum of CO_2	42
17.	Transmission Spectrum of CH_4	43
18.	Transmission Spectrum of C_2H_4	44
19.	Absorption Spectrum of CO in GP Smoke	45
20.	Sectioned Whole-Smoke Spectrum	50
21.	The ν_7 Band of C_2H_4 in Air	51
22.	Whole-Smoke Spectra in the 970-870 cm^{-1} Region	53

FIGURE PAGE

23. Superimposed Spectra of Whole Smoke and CO_2, 750-700 cm^{-1} . 55

24. Calibration Curve for CO(2169 cm^{-1}) 62

25. Calibration Curve for CO_2(720 cm^{-1}) 63

26. Calibration Curve for CH_4(1306 cm^{-1}) 64

27. Calibration Curve for C_2H_4(949 cm^{-1}) 65

28. Calibration Curve for CH_3OH(1033 cm^{-1}) 66

29. Variation of Concentration with Puff Number 73

30. Whole-Smoke Spectra, Recorded (A) Late and (B) Early in Stand Time 82

CHAPTER I

INTRODUCTION

A. Statement of Purpose

Investigation of the relationship between smoking and health has resulted in an increasing interest in inhalation studies wherein animals are confined in an exposure device and exposed to mechanically generated smoke. The need for placing these experiments on an improved quantitative basis requires means of chemically and physically characterizing the environment within the exposure chamber during exposure of the animals.

Chemical characterization of tobacco smoke in an exposure machine containing animals is a challenging analytical problem, since the smoke is neither a simple nor a stable mixture, and is furthermore being disturbed by the animals' respiration. The analytical task involves determining rapidly as many smoke components as possible, preferably without affecting either the animal subjects or the atmosphere to which they are exposed.

An instrument that could continuously or frequently observe in situ some of the smoke constituents would be most desirable. This would enable the acquisition of data on chemical composition and hence dosimetry data immediately. Up to now dosimetry data have been available after the fact, by, e.g., addition of radioactive tracers to the smoke and sacrifice of the animals immediately after a short exposure.[1]

At present, chemical analysis of exposure chamber smoke is accomplished by withdrawing a portion of the smoke from the chamber and determining the composition of that sample by gas chromatography (GC).[2]

Fourier transform infrared (FT-IR) spectroscopy has as some of its characteristic features speed and sensitivity which may make it an attractive approach for on-line monitoring of smoke in exposure chambers. As will be shown in this dissertation, strong bands due to several components—carbon dioxide, carbon monoxide, methane, water, and hydrogen cyanide—are readily observed in the mid-IR spectrum of dilute whole smoke, while others, such as isoprene (C_5H_8), methanol (CH_3OH), and ethylene (C_2H_4), yield weaker, yet analytically useful bands.

The purpose of this research was to investigate the quantitative application of FT-IR spectroscopy to dilute whole smoke by determining several gas phase (GP) smoke components under conditions similar to those which might be employed in an inhalation exposure study.

B. Tobacco Smoke

Tobacco smoke consists of a particulate phase having particle densities on the order of 10^8 to 10^{10} particles/cm^3. These particles are surrounded by a gas phase (GP) containing air and the volatile products of tobacco combustion. Diameters of most of the particles fall in the range of 0.1 to 1.0 μm.[3] The particulate matter is conveniently removed from the GP by filtration with a glass-fiber Cambridge filter,[4] which removes 99.9% of particles greater than 0.3 μm in diameter, and this is the customary basis for an arbitrary definition of the two phases.

Tobacco smoke is a extraordinarily complex mixture. In 1968, Stedman's[5] review indicated the presence of more than 1200 known compounds in tobacco and tobacco smoke. Another review[6] listed 250 GP compounds. Wynder and Hoffmann,[7] in presenting a general summary of the GP composition, made it clear that most of the constituents are present in trace quantities.

Mainstream smoke (that which passes through the mouthpiece) has been the subject of most studies. One study[8] showed a material balance for mainstream smoke which is presented in Table I.

Much of the analytical work on tobacco smoke has been done by GC, and as mentioned above, GC is the basis for present smoke exposure chamber analyses.

C. Related Literature

The group of GP components considered in this dissertation overlaps the group of air pollutants studied by Hanst and coworkers,[9] who presented IR grating spectra for CH_3CHO (acetaldehyde), CH_4, CO, C_2H_4, CH_3OH, and other atmospheric contaminants. In more recent work, Hanst et al.[10] utilized very long path lengths (multiple-pass cells) in order to extend the range of detection and high resolution to circumvent interferences. An FT-IR spectrometer was used in the latter work.

Recently, Lephardt and Vilcins applied FT-IR spectroscopy to the study of undiluted GP smoke.[11] These authors utilized the Digilab FTS-14 spectrometer to study the kinetics of formation of methyl nitrite in cigarette smoke.[12] The latest work by Vilcins and Lephardt[13,14] has

TABLE I

MATERIAL BALANCE OF MAINSTREAM CIGARETTE SMOKE[a,b]

Material	Weight (mg/cig)	Percent (by weight) of total
Particulate matter[c]	40.6	8.2
Nitrogen	295.4	59.0
Oxygen	66.8	13.4
Carbon dioxide	68.1	13.6
Carbon monoxide	16.2	3.2
Hydrogen	0.7	0.1
Argon	5.0	1.0
Methane	1.3	0.3
Water vapor[d]	5.8	1.2
C_2-C_6 hydrocarbons	2.5	0.5
Carbonyls	1.9	0.4
Hydrogen cyanide	0.3	0.1
Other known gaseous materials	1.0	0.2
Total	505.6	101.2

[a]E. L. Wynder and D. Hoffmann, "Tobacco and Tobacco Smoke," Academic Press, New York, NY, 1967, pp 317-318.

[b]85-mm nonfilter cigarettes, 10 puffs of 38.9 ml, 30 mm butt length.

[c]including condensed water.

[d]60% relative humidity.

involved further kinetic studies on the absorption of smoke constituents by carbon filtering materials and chromatography-IR applications.

D. FT-IR Spectroscopy

The name, Fourier transform spectroscopy, is derived from the fact that the output signal (interferogram) of an interferometer and the input signal (spectrum) are related by the Fourier transform.[15] The spectrum of the source is obtained by taking the Fourier transform of the interferogram. The major advantage[15] of the Fourier transform spectrometer over an instrument that uses a monochromator is a reduction in measurement time. The monochromator permits measurement of the intensity of one spectral element at a time; the interferometer permits measurement of all frequencies simultaneously. Spectra can be measured in seconds with the interferometer that would require hours to measure with a monochromator. This is usually called Fellgett's, or the multiplex advantage.

Recognition of the Fourier transform relation between the input and output signals of the interferometer came as early as 1892,[15] but practical application of the interferometric method to spectroscopy had to await the advent of high-speed digital computers. Even then, the numerical solution of the Fourier transform was a formidable task. The Cooley-Tukey algorithm, or fast Fourier transform, was described[16] in 1965 and was first applied[15] to interferometry in 1966. Since then, fast, powerful minicomputers have become available and instruments incorporating these computers to accomplish the necessary mathematics in a

short time, as well as to control the interferometer and accessories have been developed.

1. The Michelson Interferometer

Consider the interferometer as shown schematically in Figure 1. A collimated, monochromatic beam of radiation having a frequency, $\bar{\nu}(cm^{-1})$, emanates from a source, S, and impinges at 45° on a perfect beamsplitter, B, which divides the radiation into two beams of equal intensity—one reflected, the other transmitted.

The beamsplitter is formed by depositing a thin film on a transparent substrate, and a second identical plate of the substrate material (the compensator, C) is placed in one interferometer arm to equalize the optical paths.[17] The transmitted and reflected beams are reflected back to the beamsplitter by two mutually perpendicular plane mirrors, M1 and M2, and emerge to strike a detector, D, placed at 90° with respect to the beam from the source. When the optical paths of the two beams are identical, the intensity at the detector is equal to the sum of the two,[15] since they are in phase when recombined at the beamsplitter and, therefore, interfere constructively.

If M2 is displaced along a line perpendicular to its front surface by a distance equal to one-fourth of the source wavelength, λ, the difference in optical paths (retardation, δ) becomes $\lambda/2$, the beams are 180° out of phase and the interference is destructive. At any position of M2, the signal intensity, $I'(\delta)$, is related to the source intensity, $I(\bar{\nu})$ by[15]

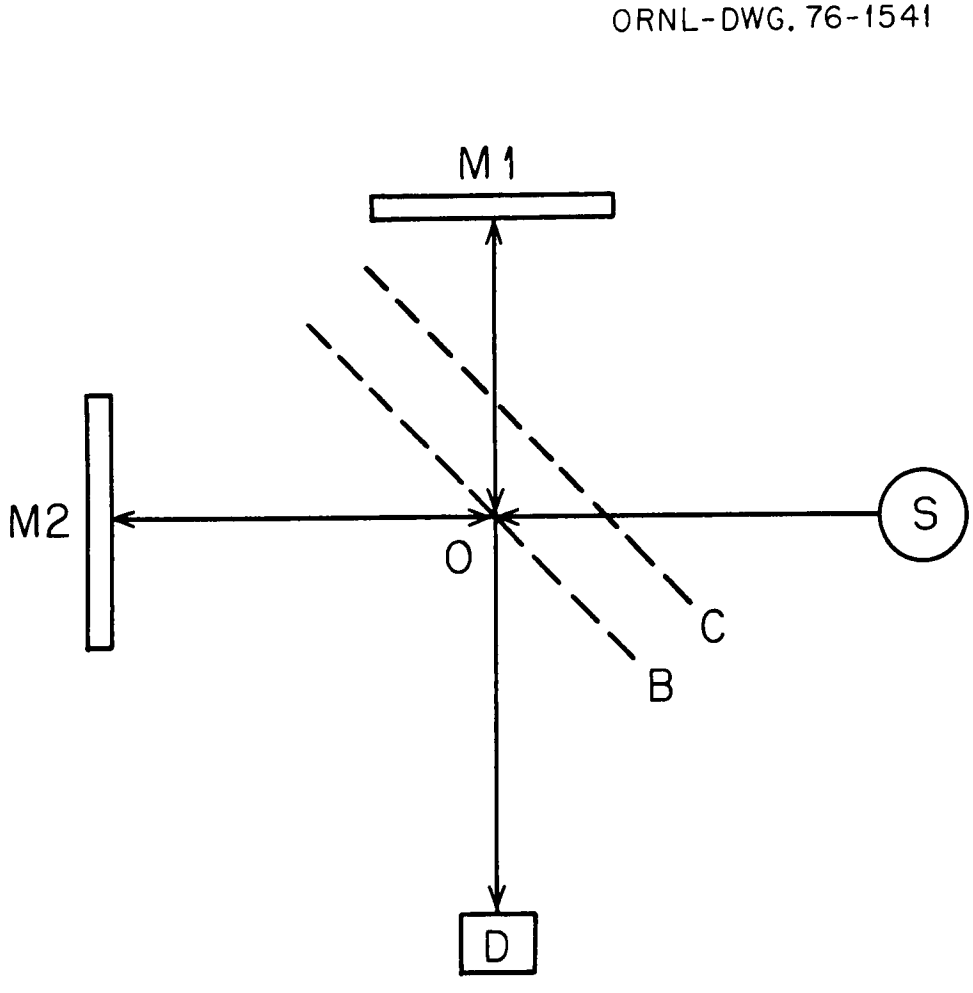


Figure 1. Schematic diagram of the Michelson interferometer.

$$I'(\delta) = 0.5\ I(\bar{\nu})[1 + \cos 2\pi\delta/\bar{\lambda}] \ , \tag{1}$$

or, since

$$\bar{\nu} = 1/\lambda \ , \tag{2}$$

$$I'(\delta) = 0.5\ I(\bar{\nu})[1 + \cos 2\pi\bar{\nu}\delta] \ . \tag{3}$$

The modulated portion, $0.5\ I(\bar{\nu})\cos 2\pi\bar{\nu}\delta$, is commonly termed the interferogram, and the expression for an interferogram obtained with an ideal interferometer from a monochromatic source is

$$I(\delta) = 0.5\ I(\bar{\nu})\ \cos 2\pi\bar{\nu}\delta \ . \tag{4}$$

Equation 4 describes a pure cosine wave.

2. Non-Ideal Interferometers

Departures from ideality arise partly because real beamsplitters do not divide the beam from the source into two exactly equal beams and because detectors and the associated amplifiers have frequency dependent responses. These factors can be combined into a correction factor, $H(\bar{\nu})$, which modifies equation 4:

$$I(\delta) = 0.5\ H(\bar{\nu})I(\bar{\nu})\ \cos 2\pi\bar{\nu}\delta \tag{5}$$

or

$$I(\delta) = B(\bar{\nu})\ \cos 2\pi\bar{\nu}\delta \ . \tag{6}$$

When M2 moves at a constant velocity, V (cm/sec), the signal intensity varies sinusoidally with time. The resulting wave has an audio frequency, $f_{\bar{\nu}}$, given by

$$f_{\bar{\nu}} = 2V\bar{\nu} \quad (\text{Hz}) \; . \tag{7}$$

3. Polychromatic Sources

For polychromatic radiation, the interferogram becomes the sum of the cosine waves generated by all frequencies of the source. The integrals[15]

$$I(\delta) = \int_0^\infty B(\bar{\nu}) \cos 2\pi\bar{\nu}\delta \cdot d\bar{\nu} \tag{8}$$

and

$$B(\bar{\nu}) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi\bar{\nu}\delta \cdot d\delta \tag{9}$$

express the ideal interferogram and spectrum, respectively. In practice,[18] more complex expressions are required to account for instrumental effects (phase shifts) which contribute sine components to the interferograms. Phase correction is required in the Fourier transform to remove these sine components.

Only at zero retardation will all of the oscillations be in phase, and the resulting interferogram will show a large central fringe. As M2 is displaced from zero, the sum of these oscillations is rapidly damped to a small value as depicted in Figure 2A. The interferograms shown in Figure 2 were recorded with the FTS-20 spectrometer: (A) with an empty chamber, and (B) with a smoke sample in the beam. The presence of narrow absorption bands in the beam from the source gives rise to an interferogram, as in Figure 2B, in which the smaller oscillations

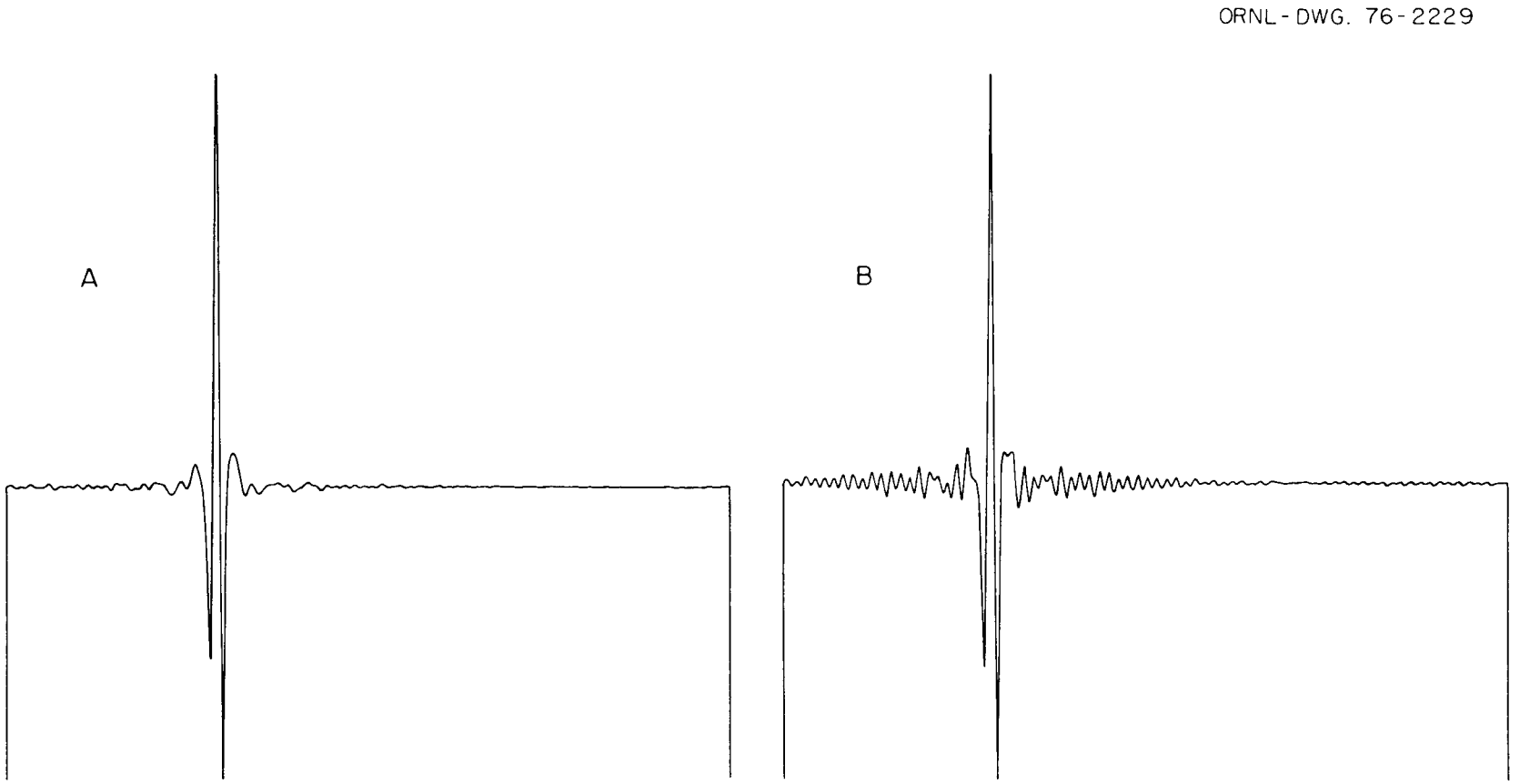


Figure 2. Typical interferograms. Generated by A, a broadband IR spectrum, and B, a spectrum with narrow absorption bands.

diminish more gradually with increasing retardation. This suggests that extending the retardation increases the amount of narrow band information available from the interferogram.

The interferogram can only be scanned through a finite mirror displacement and it may only be sampled (digitized) at a finite number of points. This leads to replacement of an integral having infinite limits by a summation over a limited number of points. The digitization is best done at equal increments of mirror travel,[19] rather than at equal intervals of time, since no mirror transport mechanism yields a perfectly uniform velocity. Laser-fringe referencing of the mirror position may be obtained by utilizing a second (reference) interferometer coupled to the main mirror drive. A He-Ne laser beam passes through the reference interferometer to produce a sinusoidal interferogram which is utilized by the system electronics to actuate the digitizer. Light from a white light source is also passed through the reference interferometer to produce a sharp signal similar to that shown in Figure 2A by which sampling is initiated at the same point each time the mirror is scanned.

4. Instrumental Line Shapes

Terminating the mirror travel at a finite distance has the effect of multiplying the interferogram by a boxcar function[17] which has the value of unity between the limits of mirror travel, and zero elsewhere. The Fourier transform of the truncated cosine wave has the form sin x/x, which has a finite width and distinct negative minima, or "side lobes," as shown in Figure 3A.

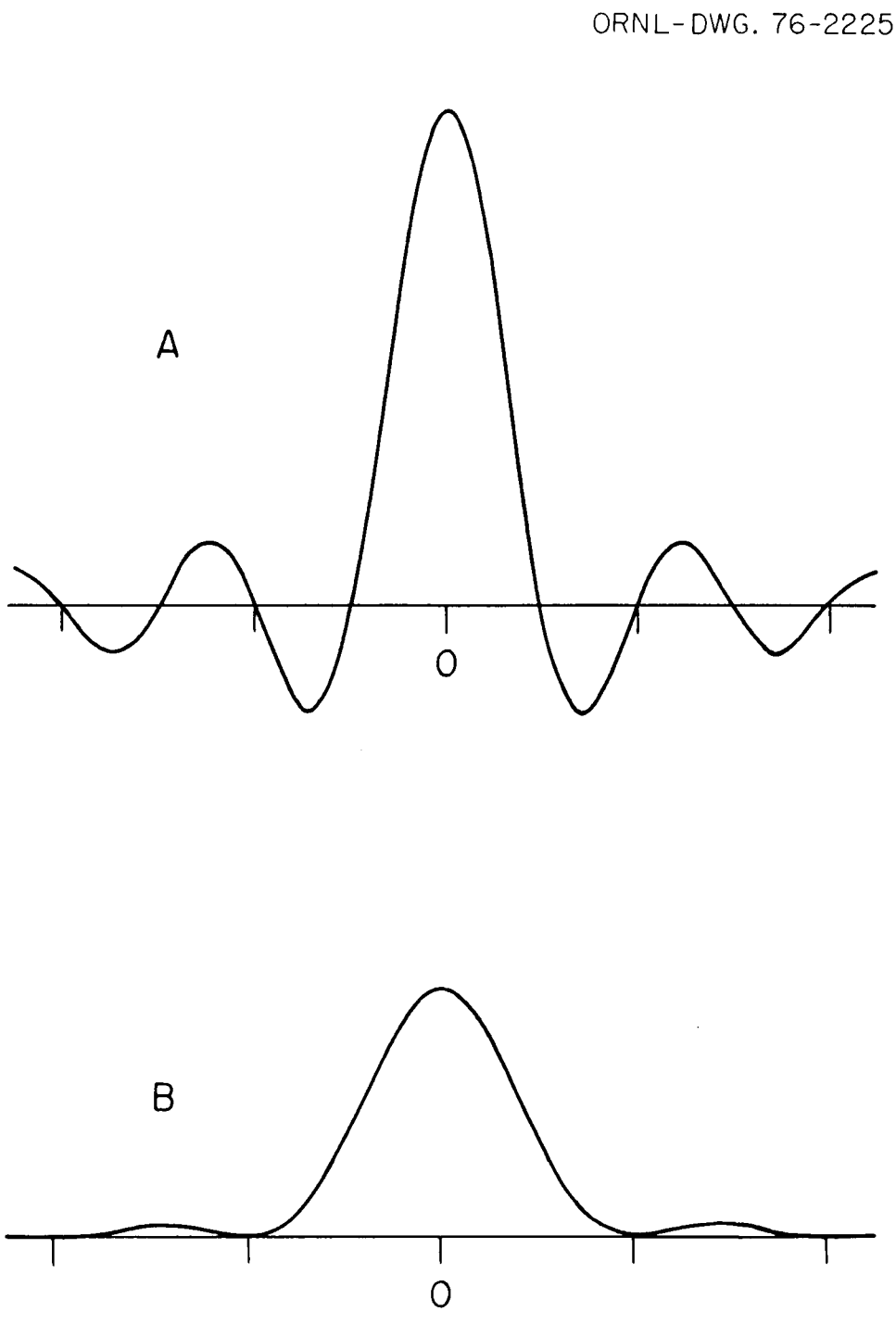


Figure 3. Instrumental line shapes. A: sin x/x; B: $\sin^2 x/x^2$.

The interferogram may instead be multiplied by a triangular "apodizing" function to yield the $\sin^2 x/x^2$ line shape shown in Figure 3B. The apodization process removes the negative side lobes, and broadens the instrumental line. Other apodizing functions which may be used were discussed by Codding and Horlick.[20]

5. Resolution

Higher resolution is achieved by increasing the retardation. As more of the interferogram is taken inside the apodizing function, the transformed lines become narrower. Horlick[17] showed interferograms and the resulting spectra which illustrate the effects of increasing the mirror travel.

CHAPTER II

EXPERIMENTAL

A. Materials

1. Cigarettes

The University of Kentucky Standard Reference Cigarette--IRI, and a special series of cigarettes,[21] manufactured to National Cancer Institute (NCI) specifications, were supplied by the NCI to the Oak Ridge National Laboratory (and other NCI contractors) for research in smoking and health. These research cigarettes are designated only by "codes." Code 1 is the IRI standard cigarette and higher-numbered codes are variants produced by various manufacturing techniques from a "Standard Experimental Blend" of tobaccos and other ingredients. When smoked, these variants produce smokes which differ in chemical composition, and consequently in biological effects. For this investigation, Codes 1, 6, 13, and 16 were used.

2. Pure Reference Materials

a. Ethylene. The C_2H_4 used was 99.8 mol % minimum, obtained from Phillips Petroleum Company, Bartlesville, OK.

b. Mixed gases. CO, CO_2 and CH_4, mixed with N_2, air, or He were obtained from the Product Certification Division of the Y-12 Plant, Oak Ridge, TN. These mixtures were prepared to order from the pure gases and analyzed by mass spectrometry and GC. The mixtures utilized were:

0.6% CH_4 in He, 0.064% CH_4 in He, 1% CH_4 in N_2, 1.07% CO_2 in N_2, 5.5% CO in N_2, 0.58% CO+1.05% CO_2 in air, 2.68% CO+3.92% CO_2 in air, 5.06% CO+8.15% CO_2 in He.

c. Acetaldehyde and acrolein. These 99% purity chemicals were obtained from Aldrich Chemical Company, Milwaukee, WI.

d. Acetone and methanol. These were Baker analyzed reagents, from the J. T. Baker Chemical Co., Phillipsburg, NJ.

e. Isoprene. The C_5H_8 was 99.5 mol % minimum, from Phillips Petroleum Company, Bartlesville, OK.

B. Apparatus

1. FTS-20 Spectrometer

The spectrometer used in this research was the Digilab Model FTS-20 (Digilab, Inc., a Subsidiary of Block Engineering, Cambridge, MA). The operation of this instrument is described in detail in the Digilab Software Manual.[22] The Digilab spectrometers are described more generally in books by Bell[23] and Griffiths.[24] A brief description of the FTS-20 spectrometer is presented here.

This spectrometer is a high-resolution, rapid-scanning, computer-controlled instrument with a range capability of 10 to 10000 cm^{-1} and having nominal resolutions of 16, 8, 4, 2, 1, 0.5, 0.25, and 0.125 cm^{-1}.

The interferometer, Digilab Model 496, is housed in a heavy-walled, vibration-isolated box, which may be evacuated to remove interferences

from atmospheric CO_2 and H_2O. The mid-IR range, 4000-400 cm^{-1}, is covered by a beamsplitter of germanium deposited on a potassium bromide substrate. Figure 4 is a diagram of the optical layout of this instrument, showing placement of the sample compartment in the beam. Absorption cells or accessories up to 20 cm in overall length may be utilized in the sample compartment. The mid-IR source is a heated nichrome filament and the detector is a TGS (triglycine sulfate) pyroelectric bolometer.

The built-in minicomputer is the Data General Nova 1200, which has a 4096-word (16 bit) core; its basic cycle time is 2.6 μsec. The system includes a 15-bit ADC (analog to digital converter), a 256 K (K=1024 words) disk (Alpha Data, Inc., Canoga Park, CA), a Houston Model DP-1 Complot Digital Plotter (Houston Instruments, Inc., Division of Bausch and Lomb, Austin, TX), and a Model 9700 Synchronous Digital Magnetic Tape Recorder (Kennedy Company, Altadena, CA). A Tektronix Type 561 oscilloscope (Tektronix, Inc., Beaverton, OR) is used as an accessory with the spectrometer system.

Operationally, the instrument is automatic. A program and the necessary parameters are entered into the computer by means of the Teletype (Model ASR 33, Teletype Corp., Skokie, IL). All commands and parameters are typed in the form of 2- or 3-letter mnemonics; a partial list of these is given in Appendix I. As many as 31 commands may be entered as a single program, although the programs are usually much shorter. Punched paper tape may be used to input program and/or parameter changes during operation. The paper tape also allows storage of frequently used or complicated programs (a real convenience).

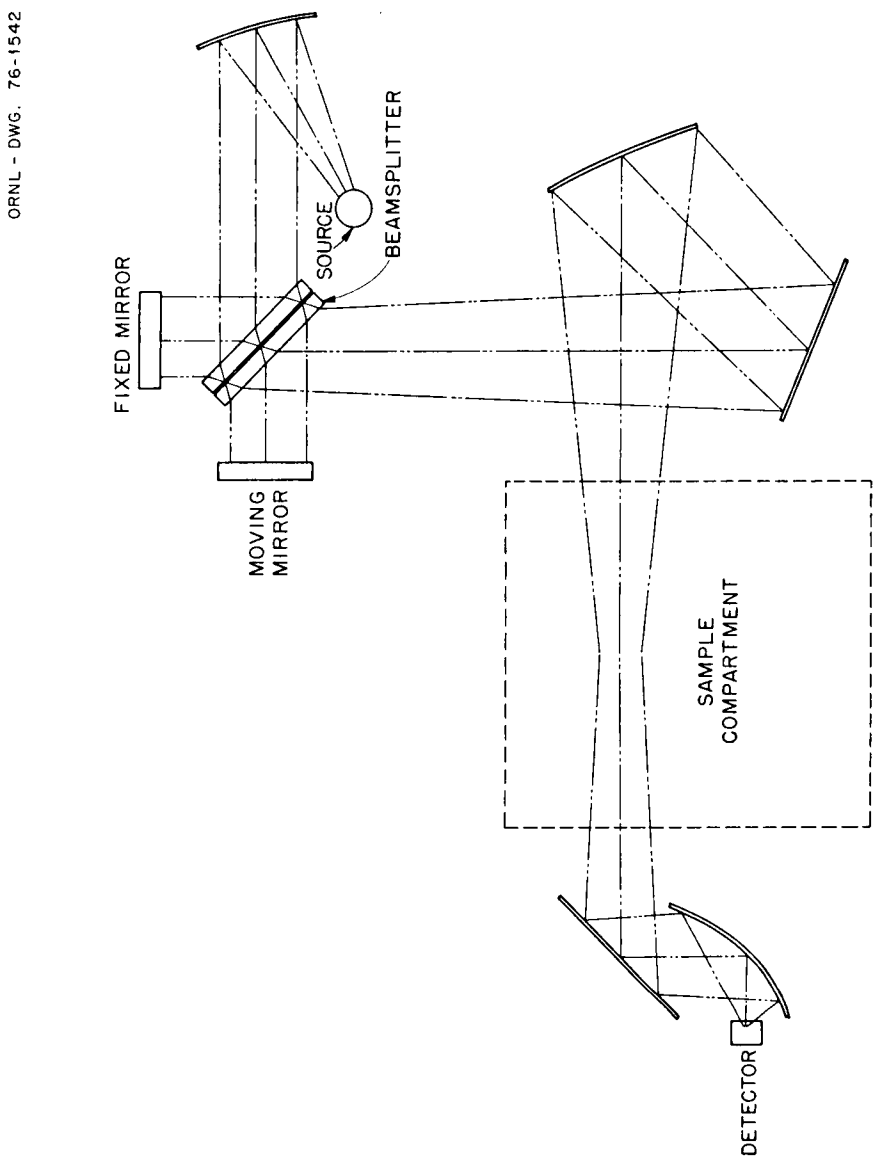


Figure 4. Optical layout of the FTS-20 spectrometer.

When the execute command (!) is given, the computer initiates scans, collects interferograms, performs necessary computations, including phase correction, and plots or stores the data without further attention.

Data are acquired by the spectrometer in the form of a "file," which includes a header that contains pertinent descriptive information, and the digitized values of the interferogram. Successive interferograms are coadded (coherently added) to the data file for signal averaging in accordance with the NSS (number of scans, sample) parameter, and the collection file may be preserved for the addition of more scans after computation and presentation of the current data.

Measurements are made only in single beam mode. A reference interferogram is collected with the empty absorption cell in the beam. This file may be stored in the reference file (File 2) by the STO (store) command for later computation or the spectrum may be computed and stored. Other locations are also available for storage. In any event, the interferogram due to the sample is then collected by substituting the sample for the empty cell. Ratio spectra are computed by point-by-point division of the sample and reference spectra.

The disk allows prompt storage and recall of as many as 27 files—interferograms or spectra—of 8K (8192) words each. Simple program instructions permit interchange of files singly or in groups between the tape and disk units in a few minutes. Each reel of magnetic tape can store over 150 8K files.

Any file may be moved to File 1 for presentation on an oscilloscope by means of the PLS (plot on scope) command, to allow a quick look at

the entire file or any portion thereof. Keyboard control of the display permits expansion of the display for closer inspection. The portion displayed may also be plotted on the digital plotter.

The plotter provides a facile but rather slow means of producing a permanent output. The choice of plotting parameters is considerable; spectra may be plotted in single beam, transmittance, or absorbance modes. In the latter two modes, ratios are computed between the reference and sample files. Other possibilities are available,[22] but were not used in this research. The chart width is 10 in and any portion of this may be utilized for the ordinate scale (YSL). Any number of units may be specified to fill the scale by the choice of the parameters, MXY (maximum Y) and MNY (minimum Y). The limits of the abscissa are specified by STP (start plot) and ENP (end plot). Any integral number may be specified as the value of the basic abscissa unit (XSL); for example, one inch may represent 1, 100, or 1000 cm^{-1}. Automatic scale expansion (ASE) may be applied to the ordinate, in which case the computer will find maximum and minimum values within the specified abscissa limits and adjust the ordinate limits to these values. Each graphical presentation is accompanied by a typeout of the maximum and minimum values plotted.

The actual data acquisition times during each scan with this instrument are 0.4 sec at 8 cm^{-1} resolution, 1.6 sec at 2 cm^{-1} resolution, and 3.2 sec at 1 cm^{-1} resolution.[22] Running times are longer; with the present software, using no programmed delay between scans, the first scan at RES=2 (resolution of 2 cm^{-1}) commences about 2 sec after the ! command and succeeding scans start at approximately 3.7 sec intervals.

2. Smoking Apparatus

The cigarettes were smoked with an apparatus which is basically a modified Maddox/ORNL inhalation smoker.[25] In this apparatus, which is shown in Figure 5, a "Filamatic Vial Filler" (National Instrument Company, Inc., Baltimore, MD) serves as an intermittent pump. This is the device shown on the left in Figure 5. Standard smoking parameters were achieved by mechanical and electrical adjustments of the apparatus as indicated below. The standard parameters are: puff interval = 60 sec; puff duration = 2 ± 0.1 sec; puff volume = 35 ± 0.5 cm^3.

The other part of the apparatus is an exposure chamber, whose configuration has been modified to fit the FTS-20 spectrometer. Figure 5 shows the aluminum and stainless steel cigarette holder, with 3 cigarettes in place, the Plexiglas (methyl methacrylate) hood provided to remove smoke from the vicinity of the spectrometer, and one of the NaCl windows of the optical section. The smoke chamber, not shown in Figure 5, but indicated in cross section in Figure 6, is a rectangular Plexiglas box of 350 cm^3 volume and has a 10 cm dimension along the optical path. The NaCl windows can be mounted directly on this box, or on cylindrical extensions which allow an 18-cm optical path and enlarge the chamber volume to 475 cm^3. All quantitative data presented in Chapter III were taken with the latter configuration.

The schematic diagram of the smoking apparatus is given in Figure 6. A repeat cycle timer (not shown) initiates the smoking cycle at 1-min intervals. The solenoid valve, i, admits compressed air to purge smoke from the chamber between puffs. A throttled rotameter, j,

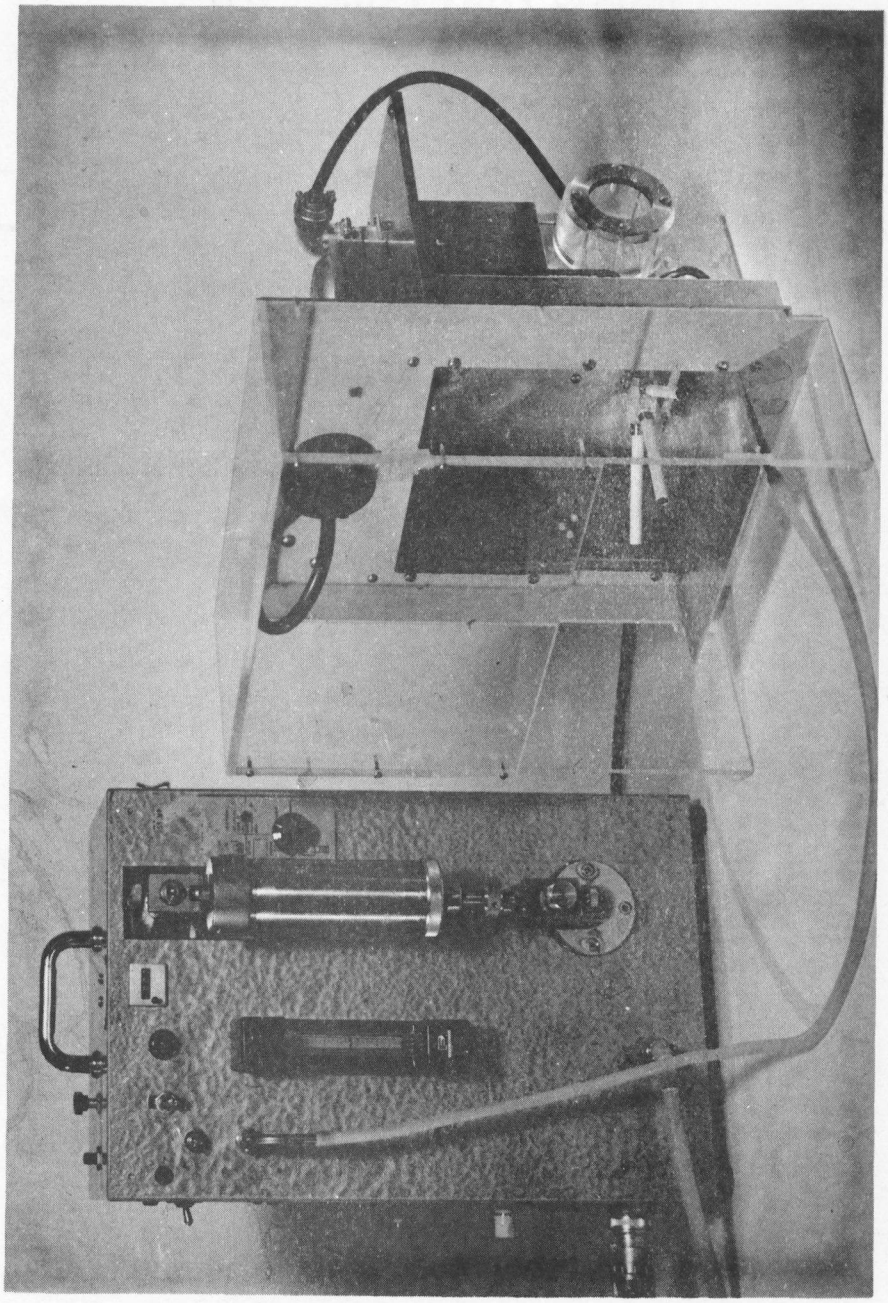


Figure 5. Photograph of the smoking apparatus.

ORNL-DWG. 76-2226

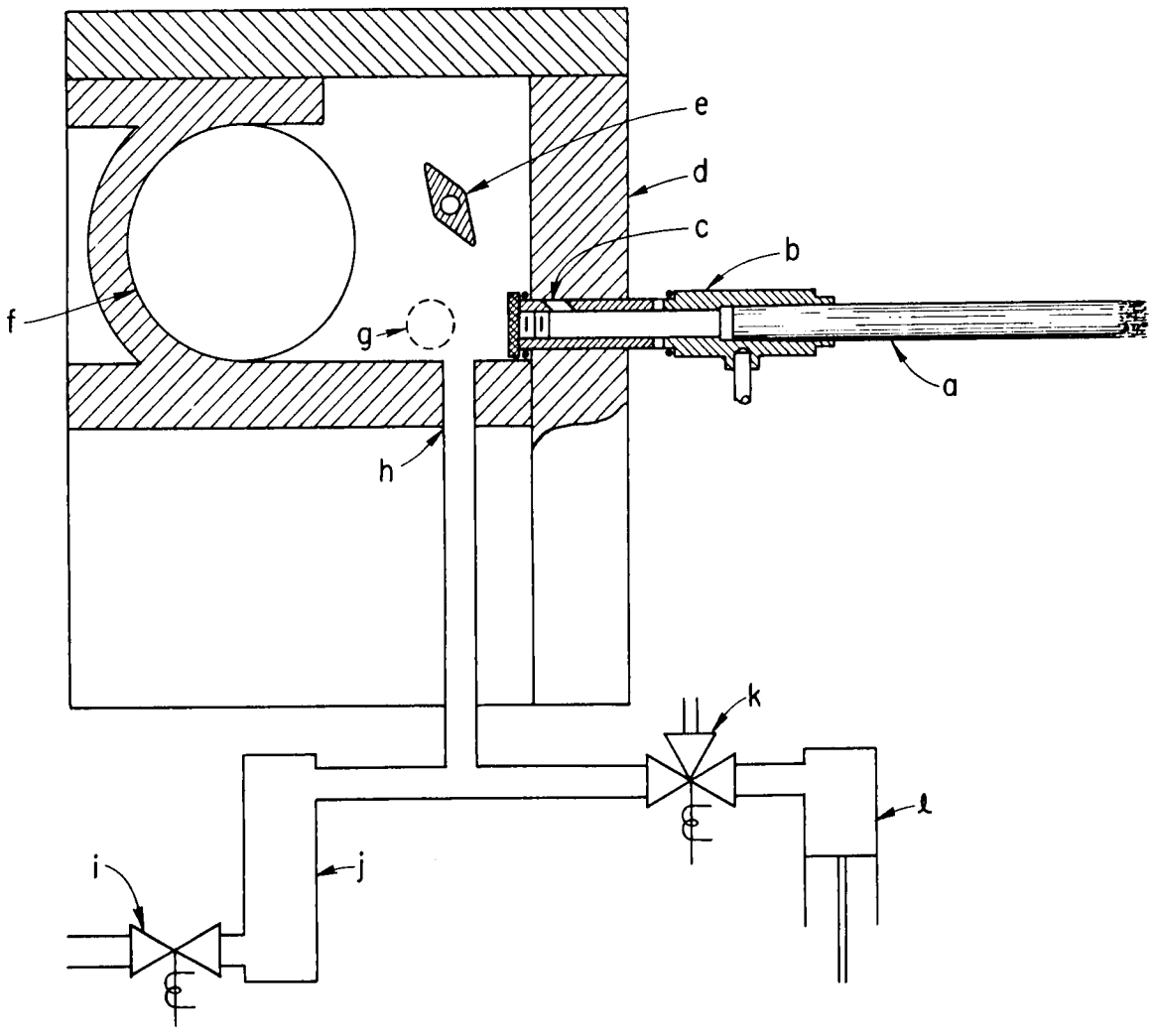


Figure 6. Schematic diagram of the smoking apparatus.
a. cigarette, b. holder, c. smoke inlet, d. smoke chamber, e. stirrer, f. NaCl window, g. chamber vent port, h. puff-out/air-in orifice, i. solenoid valve, j. rotameter, k. solenoid valve, l. pump.

controls and measures the flow rate of the purge air. The smoking cycle begins when the Filamatic pump is actuated and the cigarette holder/valve, b, is pushed into puffing position, which opens the smoke inlet, c, into the smoke chamber, d. Simultaneously, a solenoid valve closes the chamber vent port, g. Air is withdrawn from the chamber and smoke is drawn in through the cigarettes, a, as the piston descends. At the bottom of its stroke, a switch is engaged to reverse the valves (g, k) and cigarette holder drive, abruptly terminating the puff. The pump completes one revolution and is stopped precisely at top center by a switch. A stirrer, e, consisting of a plastic vane approximately 8 cm long and 2 cm wide, rotating at 1200 rpm, insures rapid and continued mixing of the smoke.

The speed of the pump is adjusted to obtain a downstroke (puff) duration of 2 ± 0.1 sec and the volume of air drawn during the puff through an unlit cigarette or a glass capillary having a resistance to draw (RTD) of 72 mm H_2O at a flow rate of 17.5 cm^3/sec is adjusted to 35 ± 0.5 cm^3 by setting the arm length of the Filament crank.

The cigarette holder was designed for parallel smoking of three cigarettes; glass capillaries with 72 mm RTD were inserted in the vacant holes when fewer cigarettes were smoked. The cigarette fittings were designed so that standard Cambridge filter holders[4] could be attached when GP smoke was desired.

3. Ancillary Apparatus

a. Soap-film buret. A 100-ml buret modified by replacement of the stopcock and tip with a glass tee was used to measure puff volumes

by displacement of a soap film meniscus drawn into the (inverted) buret.

b. Saran sample bags. Flat, flexible, bags of approximately 2-l capacity, having short fused-in entry tubes of rigid Saran (The Anspec Company, Inc., Ann Arbor, MI) were used.

c. Pressure drop tester. "Filtrona" Mark 4 Pressure Drop Tester, Cigarette Components, Ltd., Wembley, Middlesex, Eng. was used.

d. Hypodermic syringes. 100-ml (glass) and 50- and 10-ml (plastic), Becton, Dickinson, and Co., Rutherford, NJ, were used.

C. Procedures

1. Cigarette Selection and Smoking

Despite precautions taken to render cigarettes uniform in manufacture and to standardize their condition at the time of smoking, the samples remain notoriously variable. Real effects on the overall mass of the smoke and the chemical makeup of both particulate and gas phases arise from the irregularities in composition and packing of the tobacco within a single cigarette and from the dynamics of its combustion at varying rates, in a varying atmosphere during smoking. Accepted procedures[21] for cigarette conditioning and analytical smoking were followed closely during this investigation.

The Codes 1, 6, and 16 cigarettes used in these experiments were selected for weights within ± 20 mg of the batch mean, and for RTD

within ± 10 mm H_2O, from large batches of cigarettes which had been stored at -20°. Prior to selection, they were thawed and conditioned in an atmosphere of 24° and 60% relative humidity for at least 48 hours. It was impossible to select the Code 13 cigarettes to these specifications because of their poor and variable quality at the outset. They were chosen by visual inspection (the wrapper was nearly full of tobacco).

After selection at ORNL, the cigarettes were sealed in polyethylene bags and transported to the UT laboratory, where the bags were opened and the cigarettes were transferred to a glass (desiccator) vessel in which the relative humidity was maintained by a mixture of 74% glycerol and 26% water. The relative humidity produced by this mixture is 60% at 22°.[26] The cigarettes were kept in this container until just before they were smoked, usually within a few days, and never after more than 2 weeks. The standard smoking parameters mentioned above (p 20) were uniformly followed.

The puff volume was determined with the soap-film buret prior to smoking the first group of cigarettes and frequently thereafter. At the conclusion of each smoke, butt lengths were estimated as a check on the integrity of the smoking process. The butts were seldom less than 23 mm and never more than 30 mm in length.

All cigarettes were lit with matches, utilizing a holder for two matches so that three cigarettes could be lit simultaneously by one person. No data were taken during the lighting puffs. Data were obtained from puffs 2 through 11 of the Code 1 cigarettes, 2 through 10 of Code 6, 2 through 8 of Code 13, and 2 through 8 of Code 16.

In a typical inhalation experiment, the time during which smoke is allowed to remain in the chamber (stand time), including the 2 sec required to admit the puff, is on the order of 30 sec. Following this time, compressed air is admitted to the chamber to purge the spent smoke and provide a respite in fresh air for the experimental subjects. A 30-sec stand time was adopted for the chemical experiments described herein.

Beginning with the second puff, the data-collection program was started just as the Filamatic pump crank came to rest at the completion of a revolution. This was an easily detected starting point which allowed sufficient time for mixing the smoke before the first scan.

2. Standard Sample Preparation

Samples were taken from small steel cylinders of the compressed gases ($\sim$ 150 psi) by the following procedure. A short rubber tube was attached to the cylinder valve which was then opened for a few seconds to displace the air from the tube. While a slight flow of the gas was maintained, the tube was closed with a pinchclamp. The cylinder valve was then quickly closed. Samples were taken from the rubber tube by piercing it with a hypodermic needle. Opening the cylinder valve slightly permitted the gas to push back the plunger of the hypodermic syringe. The valve was closed and the needle withdrawn after the plunger had passed the mark for the desired volume. The plunger was pushed back to the mark just before the sample was injected into the smoke chamber. The syringes used in this way were calibrated against the soap-film buret which was used to measure puff volumes.

Dilutions were prepared from the pure C_2H_4 by taking samples as above and diluting in a Saran gas-sampling bag in the following way. The sample-bag inlet tube was fitted with a rubber septum and the bag was evacuated. One hundred ml of dry air were then injected through the septum with a hypodermic syringe. This was followed by injection of the gas sample and by further injections of air until the desired dilution was obtained. The bag was kneaded to insure mixing. Dilute CH_3OH vapor was prepared by withdrawing 10 ml of the saturated vapor close to the surface of the pure liquid with a hypodermic syringe. The temperature was noted and the vapor concentration was calculated from handbook data.[27] The vapor was diluted with 500 ml of dry air in a Saran bag as described above.

3. Introduction of Samples

Samples of gases were introduced into the smoke chamber in two ways. The first way was by flushing the chamber from a cylinder of the compressed gas. A sufficient quantity (about 4 l) was swept through the chamber each time to purge it. This procedure was used because the chamber could not be evacuated to less than 10 in Hg without causing blow-in of the rotating seals on the stirrer shaft. The second way, shown schematically in Figure 7, was by syringe injection. A rubber septum was substituted for the cigarette valve, and a tubing cross with two attached valves and a vacuum gauge was substituted for the exhaust valve. A 10-in Hg vacuum was drawn on the chamber by closing the vent and Filamatic valves and opening the vacuum valve. Then the vacuum

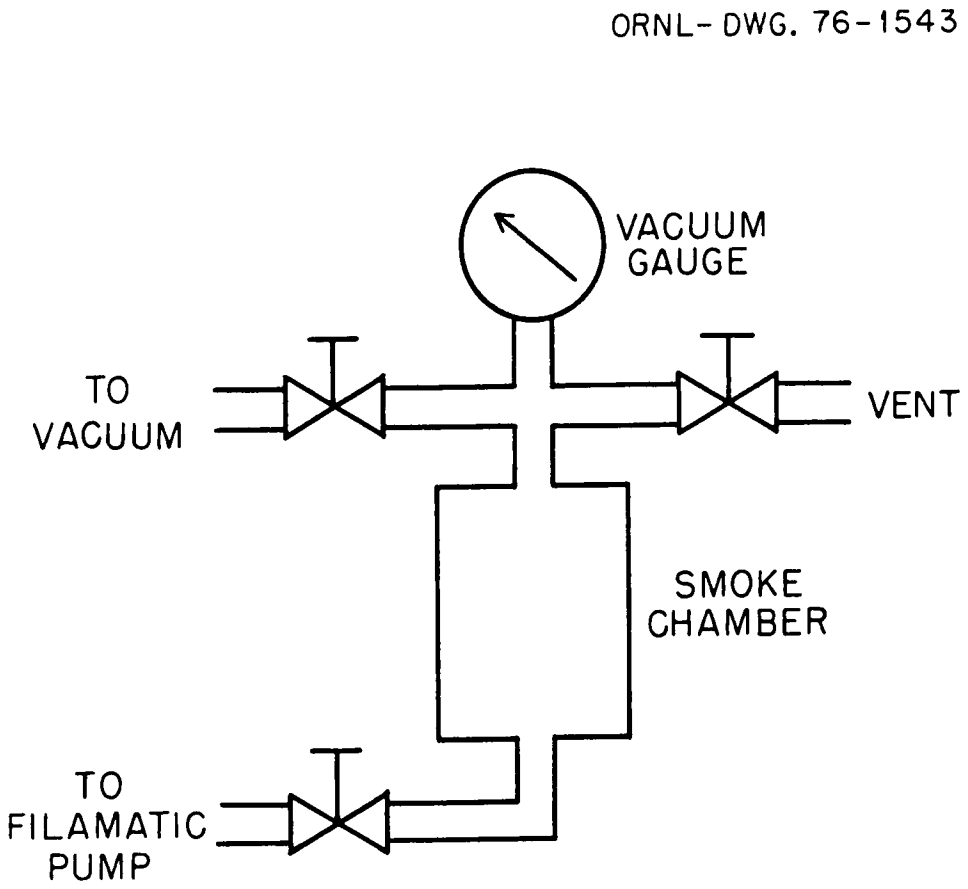


Figure 7. Schematic diagram of sample introduction.

valve was closed and the needle of the syringe that contained the sample was inserted through the septum whereupon the sample was promptly drawn into the chamber. Sufficient dry air was then admitted through the Filamatic valve to virtually restore atmospheric pressure. Then the Filamatic valve was closed and the vent valve was opened momentarily to insure atmospheric pressure. The latter procedure was employed for the introduction of samples of the diluted CH_3OH vapor.

CHAPTER III

RESULTS AND DISCUSSION

A. Smoke Spectra

It was anticipated that only the strongest bands of most components would be of any utility in the FT-IR analysis of smoke because of the dilution and relatively short pathlength proposed for investigation. Typical smoke spectra taken with RES=2, as shown in Figure 8, are rich in resolved lines and can be obtained in an acceptable length of time. The possibility of using low resolution in order to obtain more scans and thus reduce noise, was considered. The spectrum shown in Figure 9 is typical of the results at low (8 cm^{-1}) resolution. The weaker lines were not found in a spectrum of dilute smoke at this resolution (although the peaks of CO and CH_4 should be measurable); therefore, the possibility of using low resolution was dismissed. A few spectra were taken also with RES=1, for comparison with the RES=2 results. Figure 10 shows a typical RES=1 spectrum. No additional usable spectral information was apparently produced at the higher resolution, while the noise and the time to acquire and compute the data were significantly increased. In this, as in many experiments, a trade-off was demanded by the end purpose: scanning time should be as short as possible while preserving the desired information. For the purpose of smoke chamber monitoring, a number of observations is desired during a 30-sec period. The decision was made to use RES=2, which appeared to be the maximum

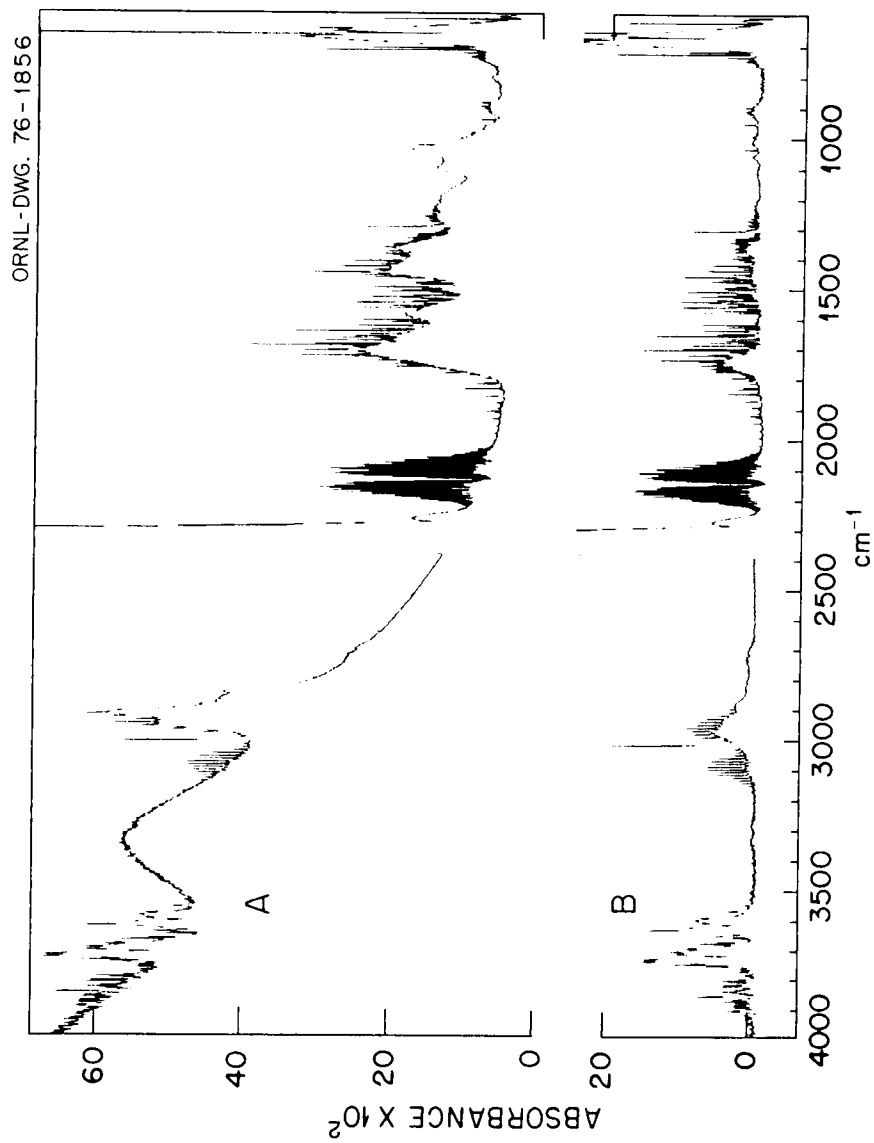


Figure 8. Absorption spectra of smoke with RES=2. A. whole smoke; B. gas phase.

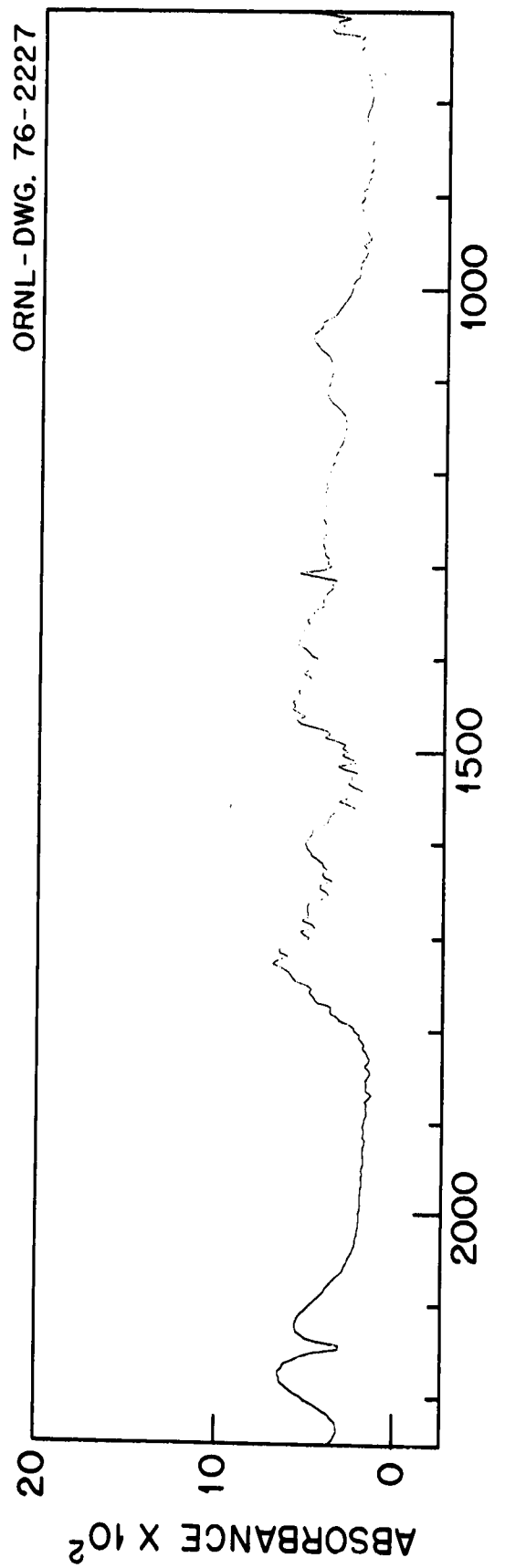


Figure 9. Whole-smoke absorption spectrum with RES=8.

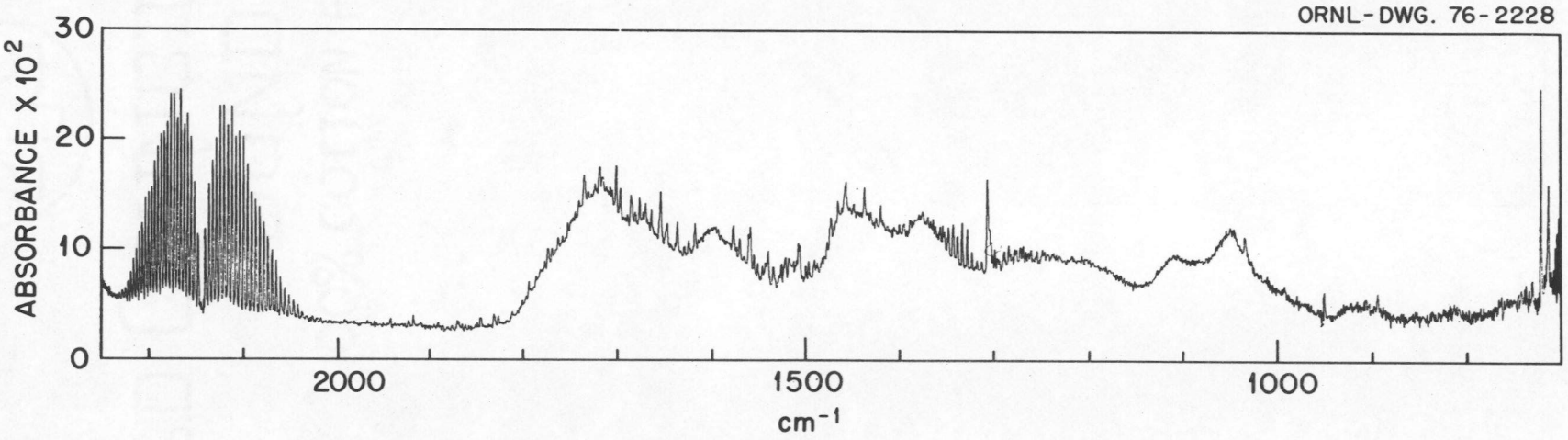


Figure 10. Whole-smoke absorption spectrum with RES=1.

resolution consistent with obtaining data for two distinctly separated periods during the 30-sec puff stand time. All data taken subsequent to these initial observations were recorded with RES=2.

From the smoke spectra presented in Figure 8, it appeared that most spectral information at frequencies greater than 2400 cm^{-1} would not be usable, partly because of severe scattering in the whole smoke spectrum and partly because little evidence of absorption bands appeared above the noise, other than the water band at 3756 cm^{-1}, the CO_2 combination bands at 3716 and 3609 cm^{-1}, and the CH_4 band at 3108 cm^{-1}.[28]

The CO_2 fundamental bands[28] at 2349 cm^{-1} and 667 cm^{-1} were too intense at the concentration chosen (22% smoke), and the water band centered at 1595 cm^{-1} would probably obscure most lines between 1800 cm^{-1} and 1300 cm^{-1}. Several lines appeared above the background between 1350 and 700 cm^{-1}.

B. Component Spectra

A list of GP components whose yields in smoke seemed high enough to offer a reasonable possibility of detection by FT-IR is given in Table II. The yields shown in this Table should only be considered indicative of the general range of smoke component yields.

Spectra were obtained early in this investigation for the vapors of acetone (CH_3COCH_3), acrolein (CH_2CHCHO), C_5H_8, and CH_3OH. These spectra are shown in Figures 11-14. The vapor samples were taken by injecting air through gas-scrubbing bottles containing the liquids into the smoke chamber. At the time, no provision had been made to evacuate or purge

TABLE II

MAJOR GAS PHASE COMPONENTS

Component	Yield, µg per cigarette	Reference
Acetaldehyde	700-1300[a]	21
Acetone	400-500	29, 30
Acrolein	50-140[a]	21
Carbon dioxide	$68X10^3$	3
Carbon monoxide	$16X10^3$	3
Ethylene	200	29
Hydrogen cyanide	60-240[a]	21
Isoprene	15-740[a]	21
Methane	770	29
Methanol	100-200	29
Water	$5.8X10^3$	3

[a]Range covered by NCI variants.

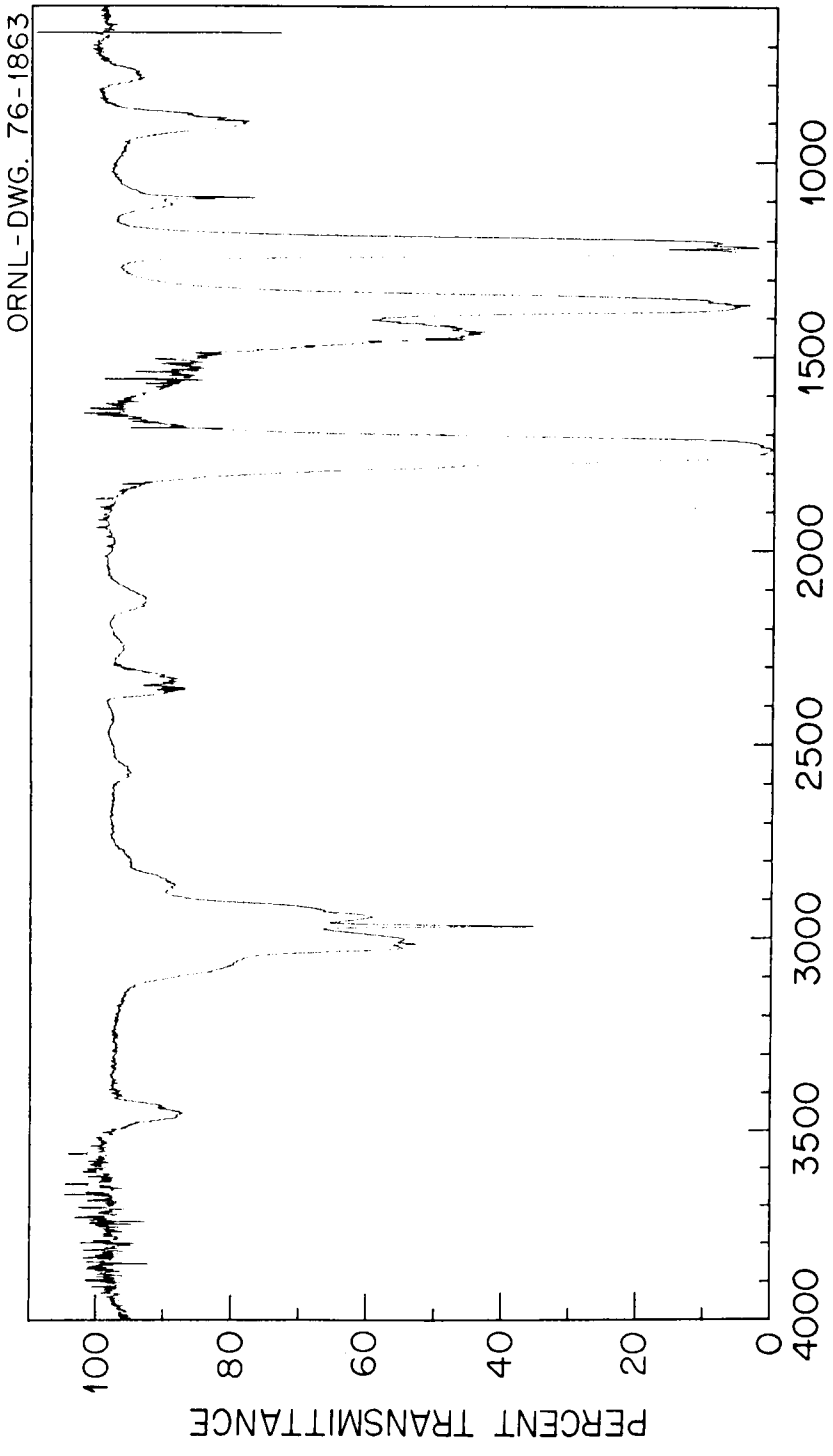


Figure 11. Transmission spectrum of CH_3COCH_3 vapor.

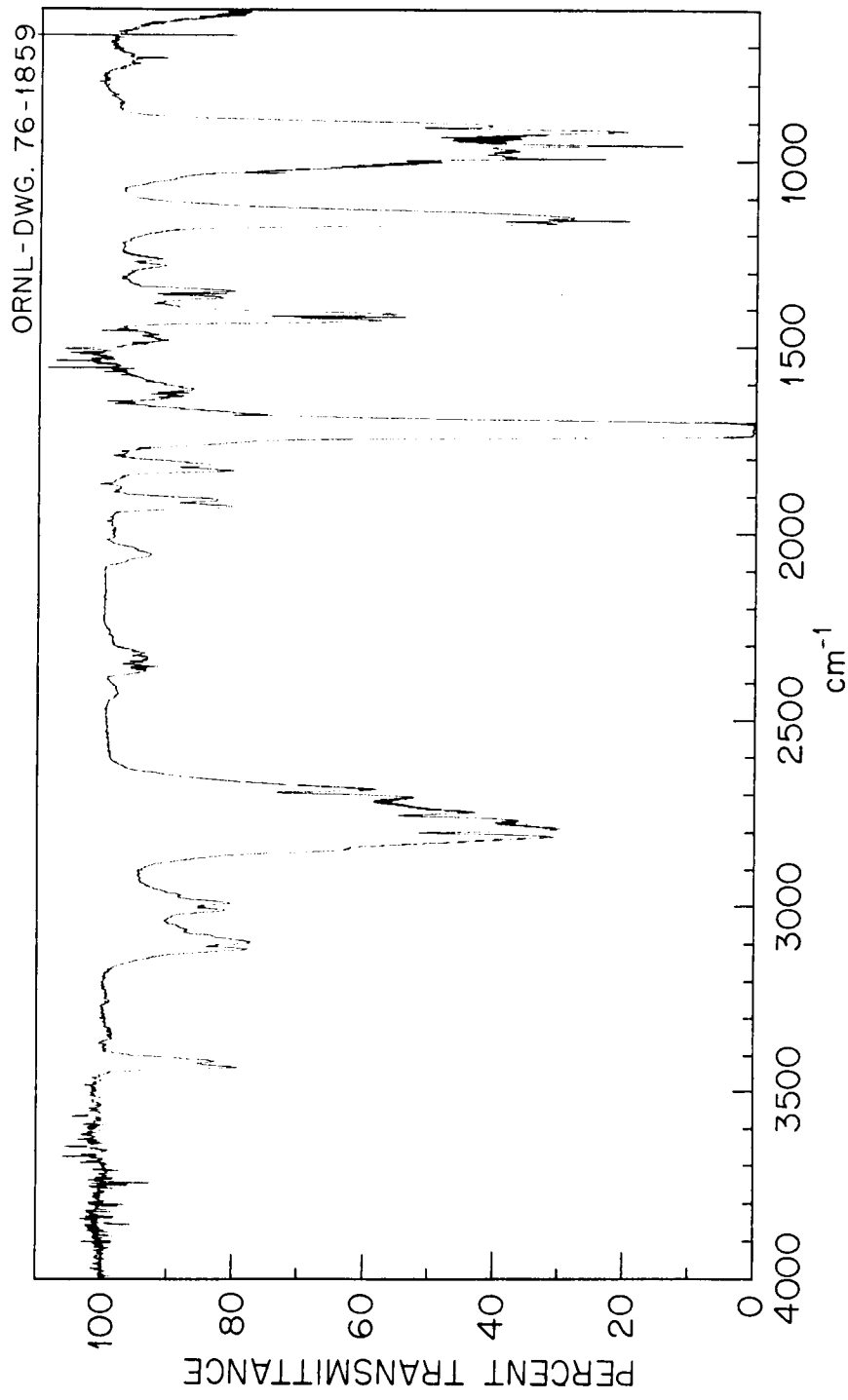


Figure 12. Transmission spectrum of CH_2CHCHO vapor.

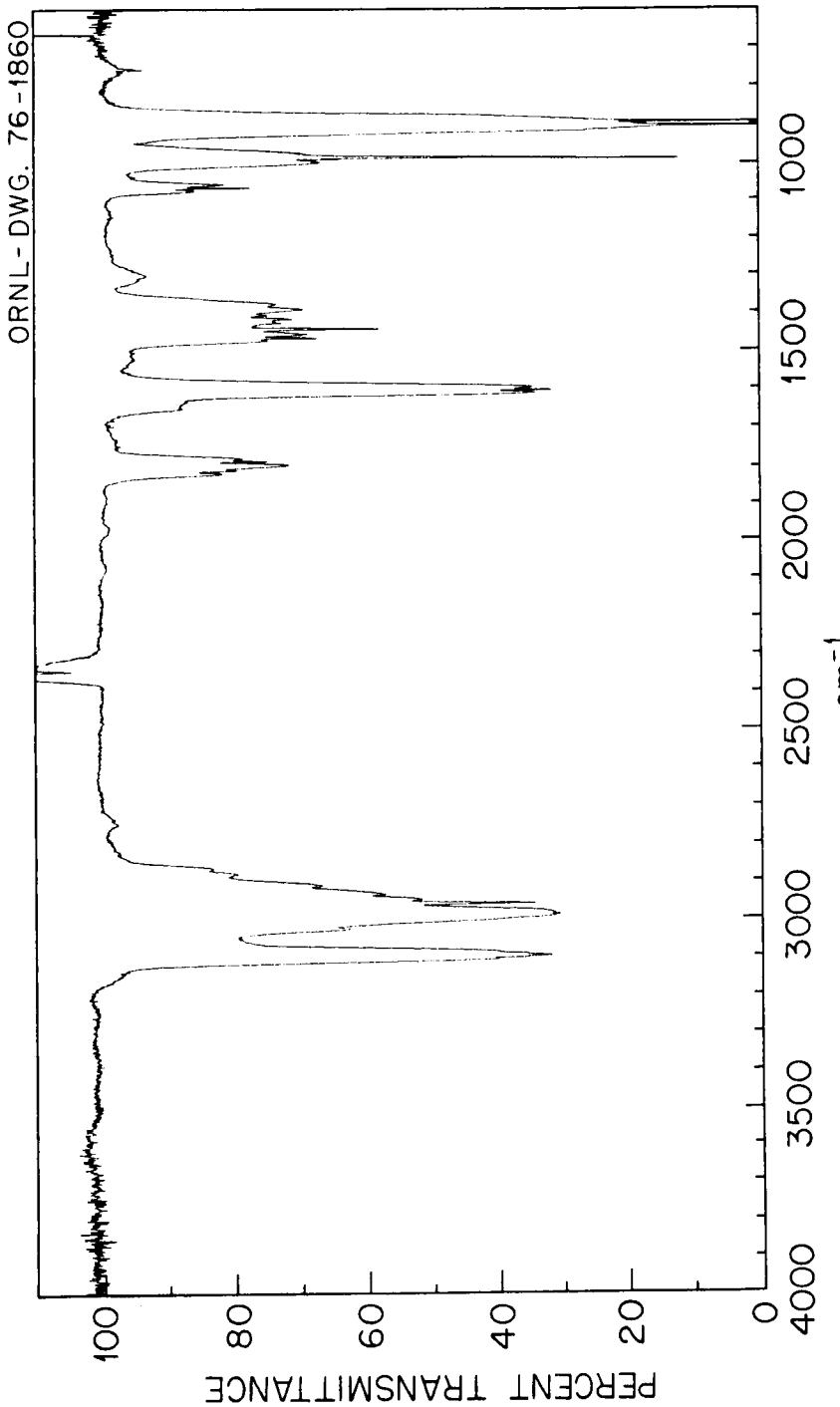


Figure 13. Transmission spectrum of C_5H_8 vapor.

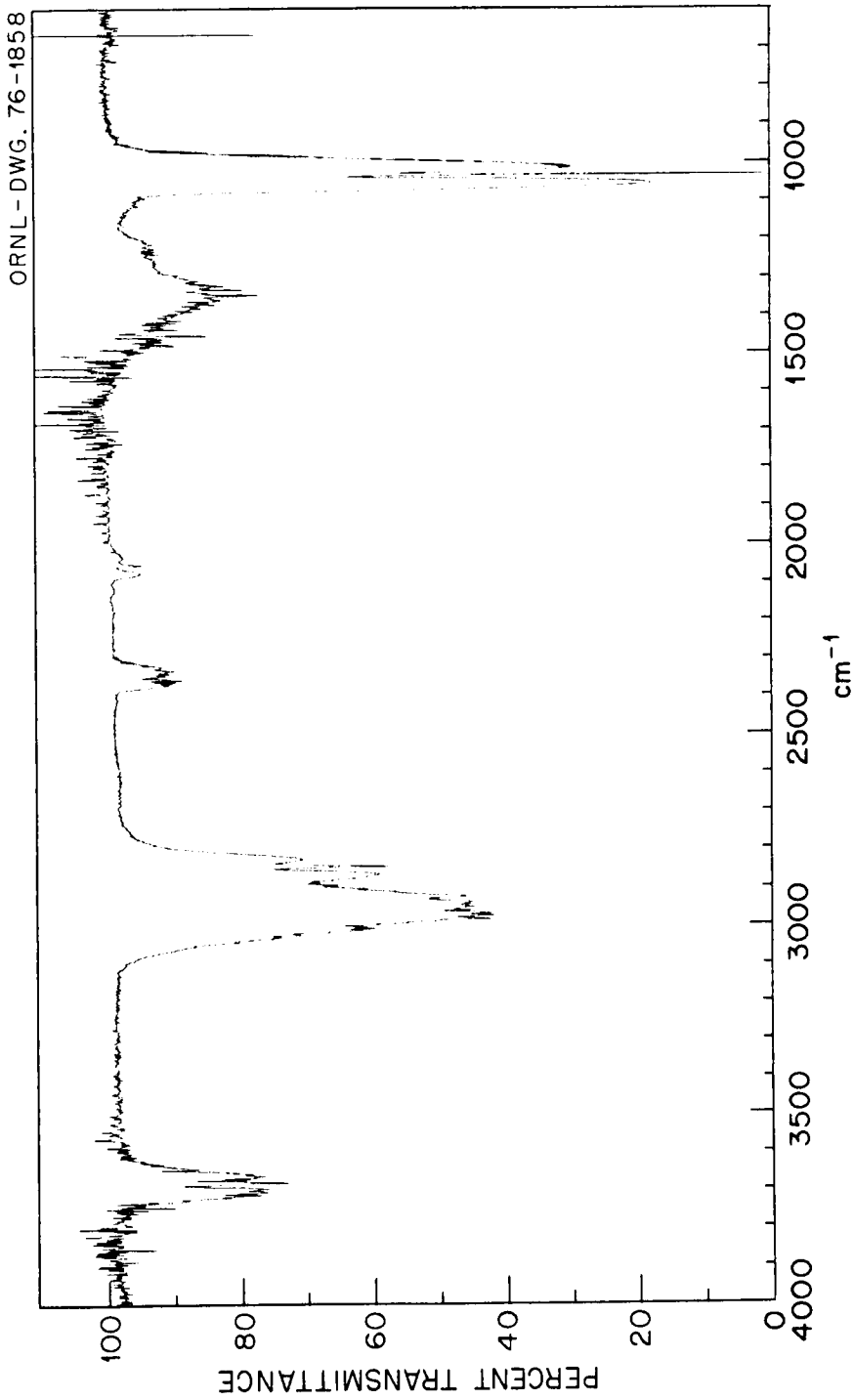


Figure 14. Transmission spectrum of CH_3OH vapor.

the optical path while the smoke chamber was in place, so the spectra showed significant contamination from atmospheric H_2O and CO_2. The water lines were partially removed by spectral subtraction, utilizing the arithmetic functions of the FTS-20.[22] Although the water subtraction was not particularly effective, the intensities and frequencies of the bands could readily be determined and matched with those of published spectra.[31] The water spectrum shown in Figure 15 was obtained by subtracting the normal atmospheric spectrum from one obtained at high humidity.

The CO_2 spectrum shown in Figure 16 and the CH_4 spectrum shown in Figure 17 were obtained later, in the evacuated spectrometer, from mixtures of CO_2 and CH_4 with dry N_2. The C_2H_4 spectrum shown in Figure 18 was obtained from C_2H_4 mixed with air that had been passed through a "Drierite" (anhydrous $CaSO_4$) dryer.

The spectrum of CO shown in Figure 19 was measured in GP smoke. The reference was dry air and the optical path, except that in the cell compartment, was evacuated. This Figure shows the CO stretch band centered at 2143 cm^{-1} as taken (A) and after 4-fold zero-filling (B). Zero-filling, a mathematical procedure for improving the overall photometric precision of the spectrum, was discussed by Griffiths.[32] This procedure was done in order to witness the possible improvement and to compare the performance of this particular spectrometer with other published results. A comparison of the frequencies measured here with wavelength standards[33] is shown in Table III. Only for the R30 line is the discrepancy between the frequency of the standard and of

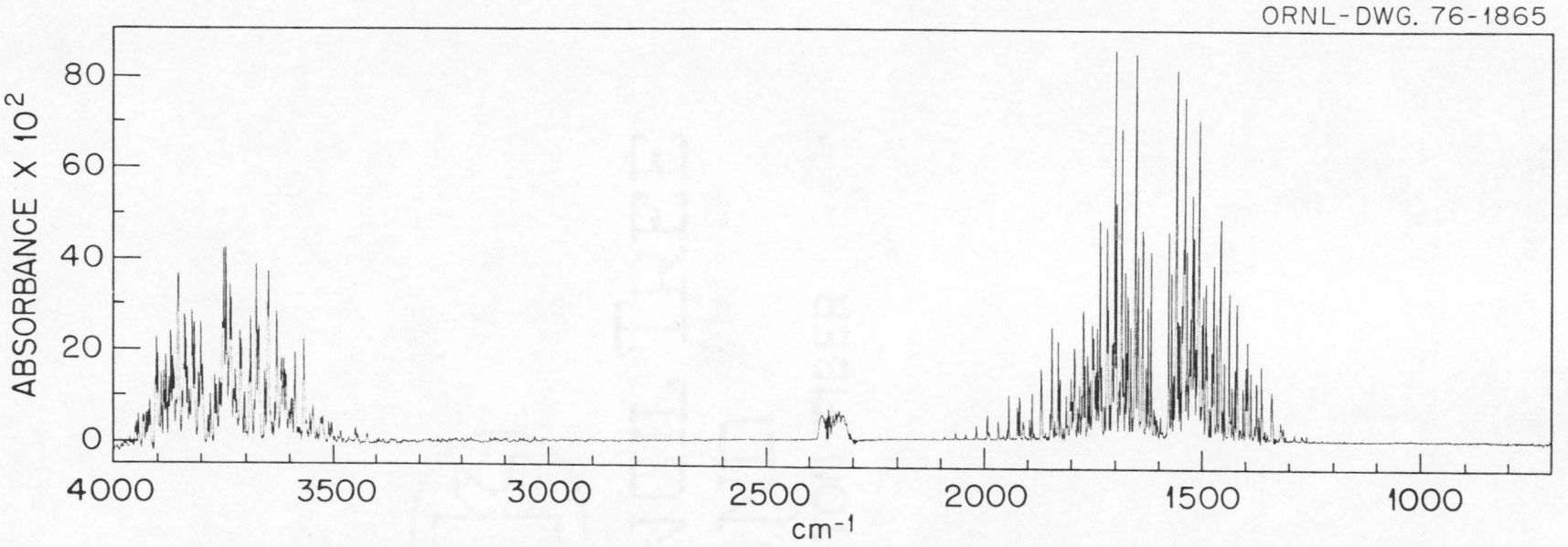


Figure 15. Absorption spectrum of H_2O vapor.

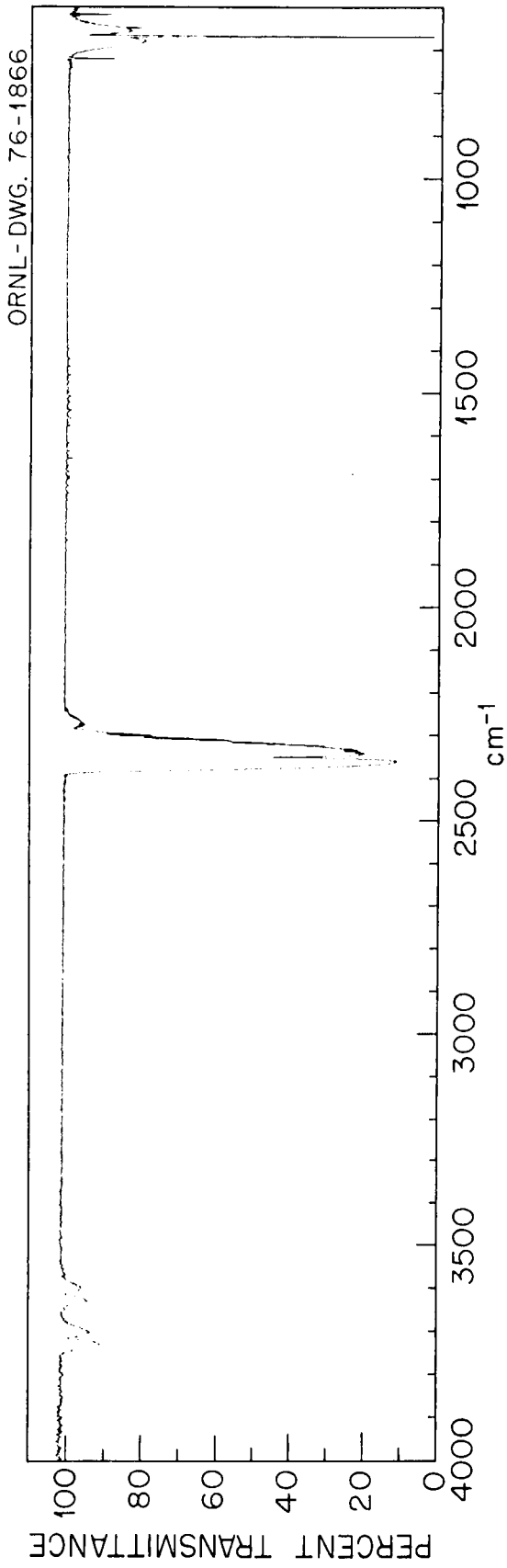


Figure 16. Transmission spectrum of CO_2.

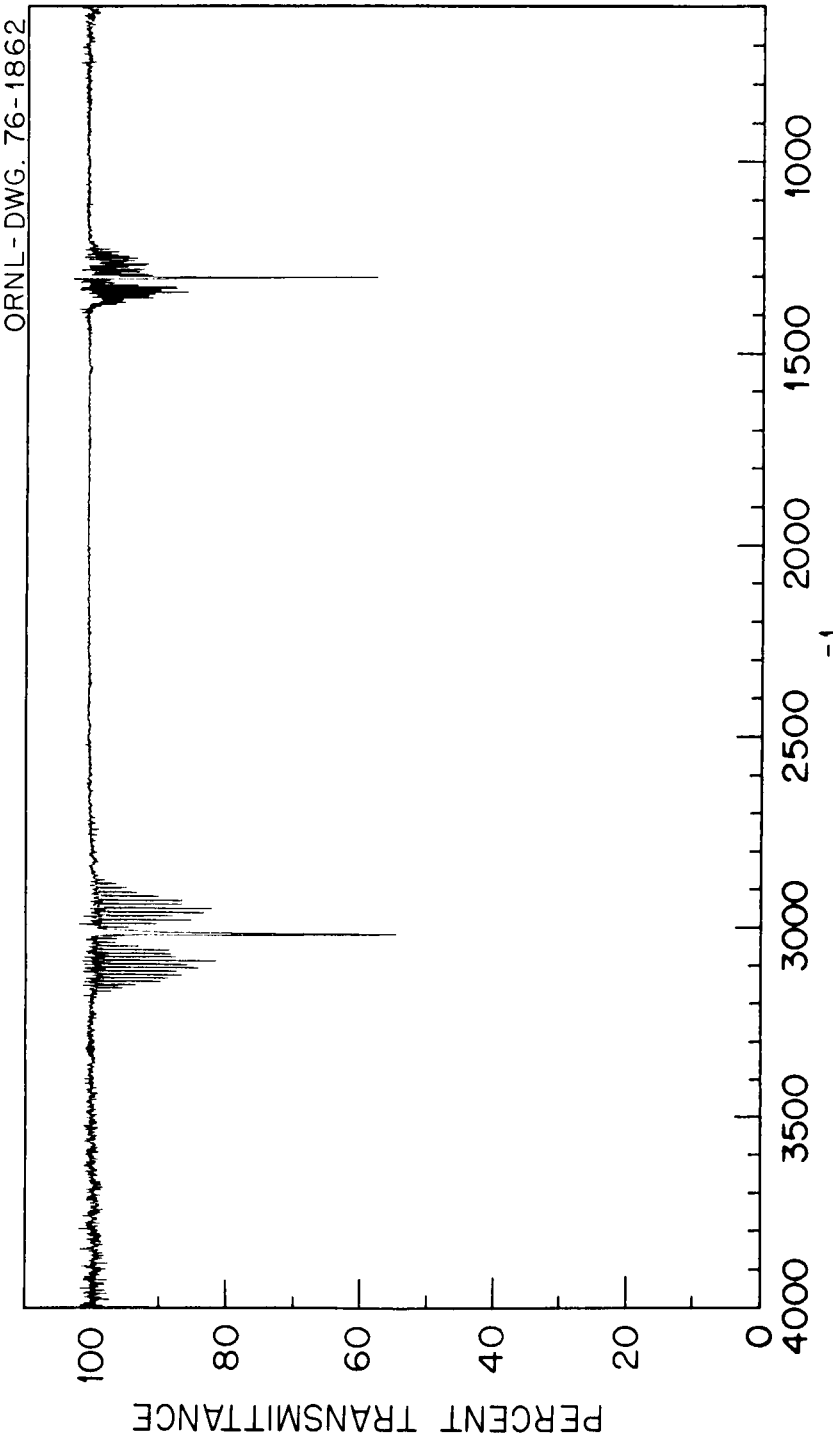


Figure 17. Transmission spectrum of CH_4.

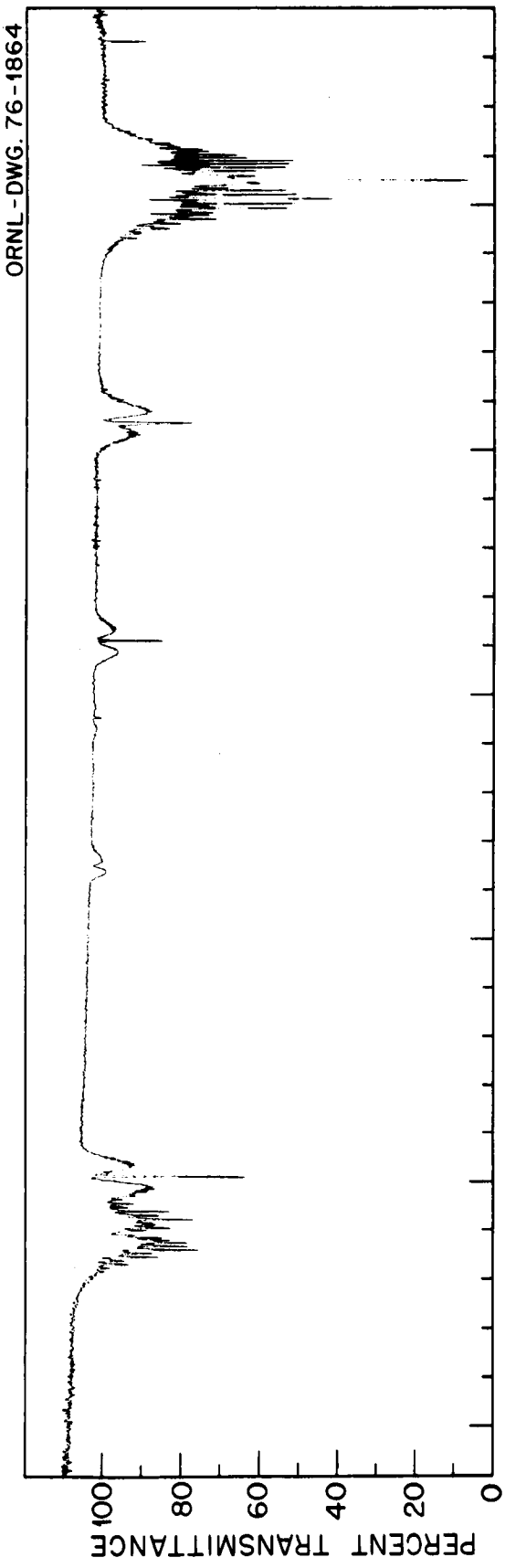


Figure 18. Transmission spectrum of C_2H_4.

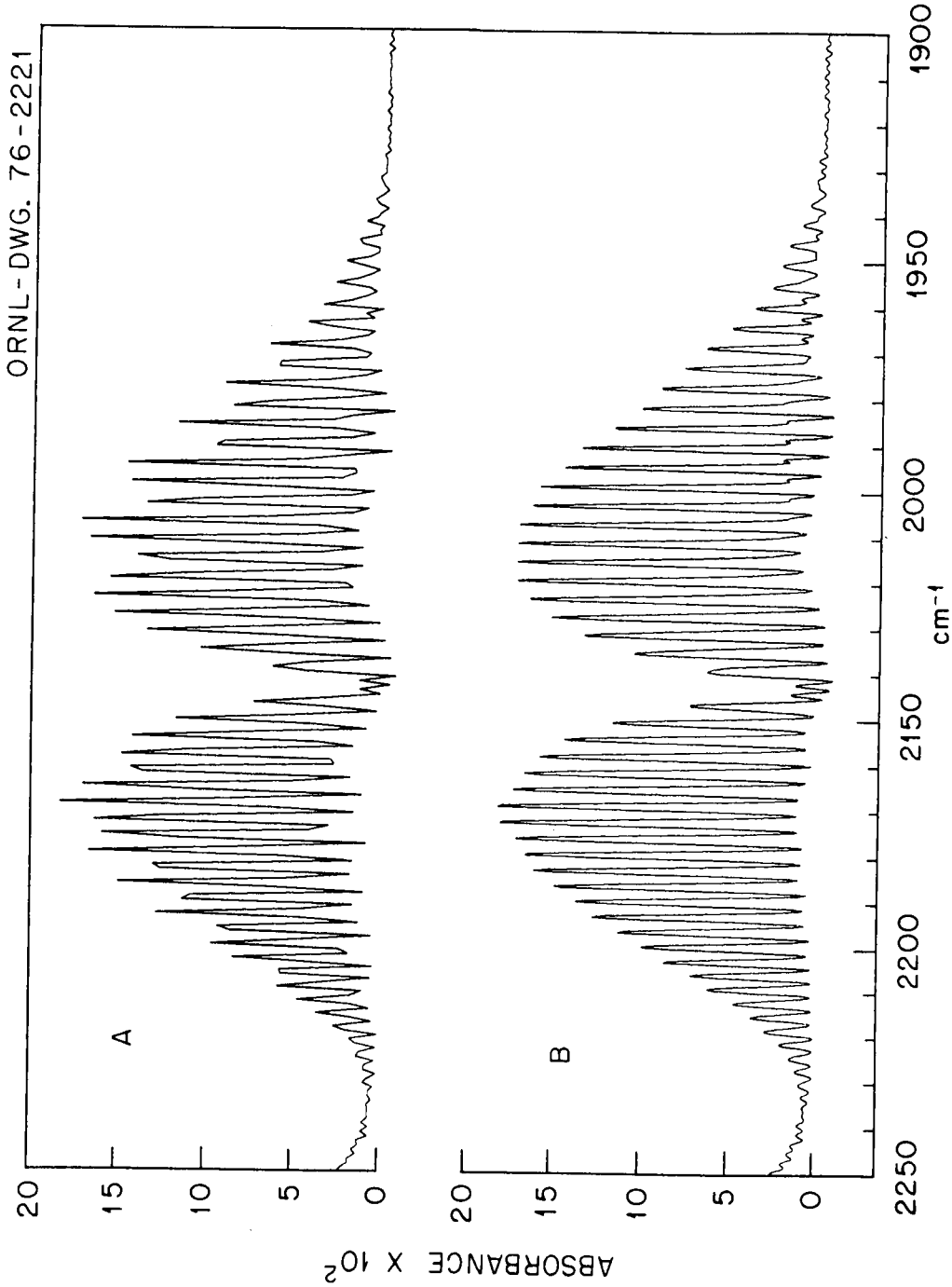


Figure 19. Absorption spectrum of CO in GP smoke. A. as taken; B. 4-fold zero-filled.

TABLE III

CO FREQUENCY COMPARISON

Line	Accepted[a] (cm^{-1})	Measured		Line	Accepted[a] (cm^{-1})	Measured	
		Z´ Filled (cm^{-1})	Unfilled (cm^{-1})			Z´ Filled (cm^{-1})	Unfilled (cm^{-1})
R30	2244.4	2243.4	2243.3	R7	2172.8	2172.5	2173.0
R29	2241.7	2241.3	2241.5	R6	2169.2	2168.9	2169.2
R28	2239.0	2239.1	2239.6	R5	2165.6	2165.4	2165.3
R27	2236.2	2235.8	2236.6	R4	2162.0	2161.6	2161.5
R26	2233.4	2233.1	-	R3	2158.3	2158.2	2158.5
R25	2230.5	2230.3	2231	R2	2154.6	2154.5	2154.7
R24	2227.6	2227.4	2228	R1	2150.9	2150.5	2151.0
R23	2224.7	2224.5	2225	R0	2147.1	2146.8	2147.0
R22	2221.7	2221.4	2216	P1	2139.4	2139.4	2139.2
R21	2218.7	2218.5	2218.4	P2	2135.5	2135.5	2135.3
R20	2215.7	2215.4	2215.5	P3	2131.6	2131.5	2131.4
R19	2212.6	2212.5	2212.5	P4	2127.7	2127.5	2127.6
R18	2209.6	2209.4	2209.7	P5	2123.7	2123.5	2123.6
R17	2206.4	2206.3	2206	P6	2119.7	2119.6	2120.0
R16	2203.2	2203.2	2202.8	P7	2115.6	2115.5	2115.0
R15	2199.9	2199.7	2200.0	P8	2111.5	2111.5	2111.2
R14	2196.7	2196.7	2196	P9	2107.4	2107.4	2107.4
R13	2193.4	2193.1	2193.0	P10	2103.3	2103.1	2103.5
R12	2190.0	2189.8	2190.2	P11	2099.1	2098.9	2098.6
R11	2186.6	2186.5	2186.3	P12	2094.9	2094.7	2094.7
R10	2183.2	2183.0	2183	P13	2090.6	2090.5	2091
R9	2179.8	2179.4	2179.7	P14	2086.3	2086.3	2086.3
R8	2176.3	2176.3	2175.8	P15	2082.0	2081.8	2082.4

TABLE III (continued)

Line	Accepted[a] (cm^{-1})	Measured		Line	Accepted[a] (cm^{-1})	Measured	
		Z´ Filled (cm^{-1})	Unfilled (cm^{-1})			Z´ Filled (cm^{-1})	Unfilled (cm^{-1})
P16	2077.7	2077.5	2077.5	P22	2050.9	2050.5	2050.6
P17	2073.3	2073.2	2073.6	P23	2046.3	2046.2	2045.6
P18	2068.8	2068.6	2069.0	P24	2041.7	2041.5	2041.7
P19	2064.4	2064.4	2064.0	P25	2037.0	2037.5	2037.0
P20	2059.9	2059.9	2060.2	P26	2032.4	2032.4	2032.3
P21	2055.4	2055.4	2055.4	P27	2027.6	2027.5	2027.4

[a]K. N. Rao, C. J. Humphreys, and D. H. Rank, "Wavelength Standards in the Infrared," Academic Press, New York, NY, 1966.

the observed zero-filled spectrum greater than 0.5 cm^{-1}. The envelope of intensities shown by the zero-filled spectrum compares favorably with that of a spectrum of pure CO obtained by Chan and coworkers[34] with an FTS-14 spectrometer at 0.5 cm^{-1} resolution. While the "unfilled" spectrum is not as appealing in overall appearance, it shows reasonable wavelength accuracy and can be obtained much more quickly. Zero-filling requires a few minutes to add zeros to the interferograms and an increased computational time because of the larger file size.

The spectrum of HCN was not run during this investigation. The positions and shapes of the bands were obtained from the literature.[28,36] A spectrum of acetaldehyde vapor diluted with dry N_2 was obtained. In this spectrum the minimum transmittance was 90% at 1760 cm^{-1}. Four other strong bands shown in the Sadtler spectrum[31] could be discerned, all at transmittances greater than 97%.

C. Quantitative Analysis

A systematic search of the smoke spectrum was made by scale expanding sections of the spectrum in the vicinity of every band of the component spectra, and the lines that had intensities distinctly above the noise level in 22% smoke (from 3 cigarettes) were chosen for further study.

1. Measurement of Smoke Spectra

Smoke spectra were plotted for quantitative measurement by scale-expanding sections surrounding the lines of interest. The sections

expanded are shown in Figure 20, which was drawn by tracing a typical expanded chart. "Unfilled" spectra were used for all quantitative work.

Baselines under each peak were drawn as indicated on the Figure. A baseline was constructed for each line by visually estimating the average of the noise. A transparent scale was used for drawing the baseline and for measuring the perpendicular from that baseline to the peak. Absorbances were then calculated by using the expression

$$A = (\text{max-min})(L/YSL) \quad , \tag{10}$$

where A is the absorbance ($X10^2$), max and min are maximum and minimum values printed on the Teletype, and L is the length of the perpendicular, in the same units as the ordinate scale, YSL (in or cm).

Usually, only the R branch of the CO band, shown in Figure 20A, was plotted, after a number of trials had shown that the same baseline would be drawn under this portion as under the whole band, and the time saved by not plotting the entire band was appreciable. The measurement was made at 2169 cm^{-1} (R6), because this line was symmetrical in the unfilled spectrum, and was consistently the most intense. For CH_3OH, the Q branch shown in Figure 20C, at 1033 cm^{-1} was measured. The C_2H_4 (ν_7) line measured at 949 cm^{-1} was often accompanied by a negative excursion near 938 cm^{-1} as shown in Figure 21. This was ignored when constructing the baseline for this region (shown in Figure 20D).

The C_2H_4 band has several rotational lines in the 906-893 cm^{-1} vicinity where the lines of C_5H_8 are seen (compare Figures 18 and 20D, pp 44 and 50). These diminish rapidly in intensity toward the lower frequency. This prompted a decision to draw the baseline for C_5H_8 under

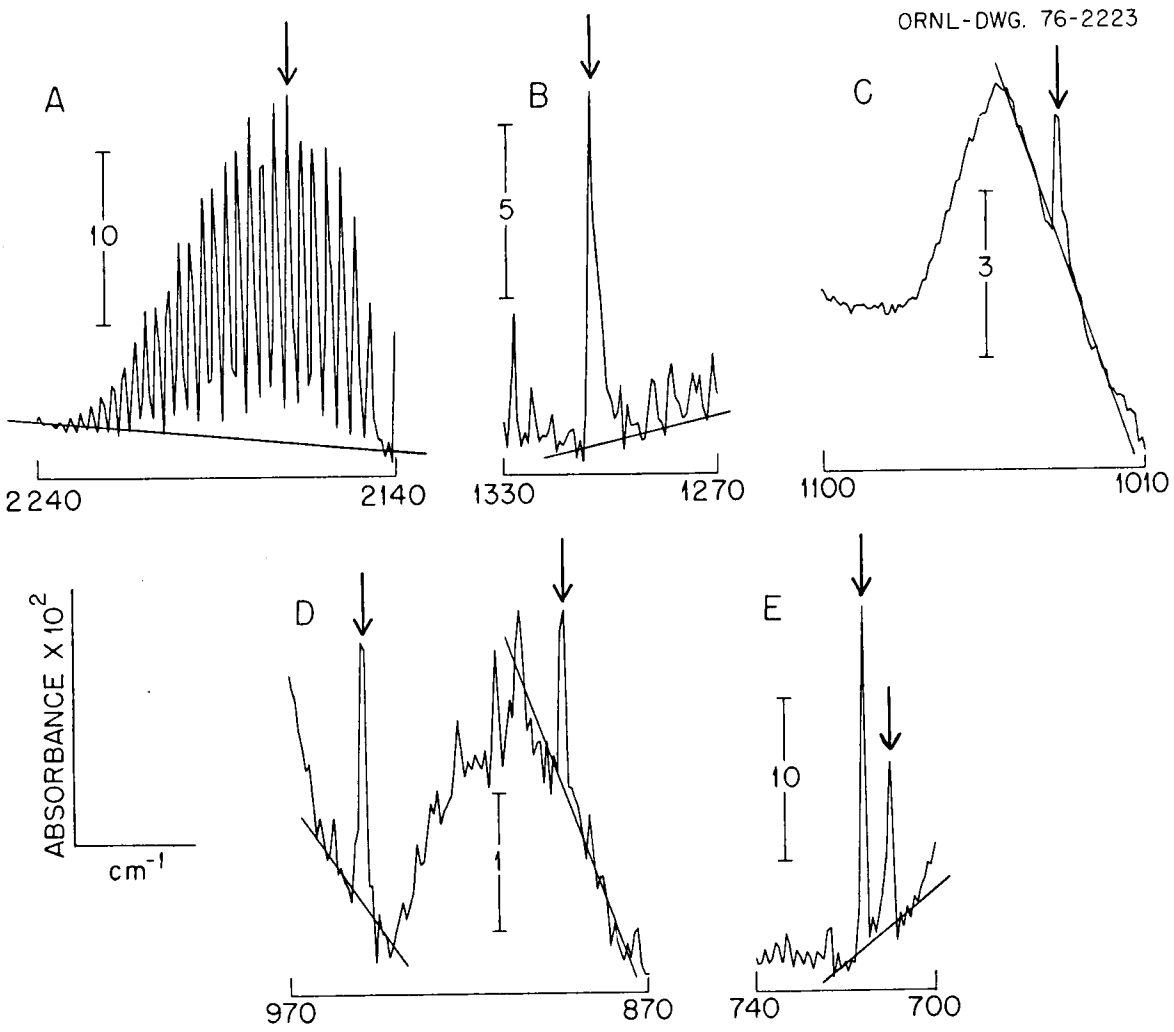


Figure 20. Sectioned whole-smoke spectrum. A. CO; B. CH_4; C. CH_3OH; D. C_2H_4, C_5H_8; E. CO_2, HCN.

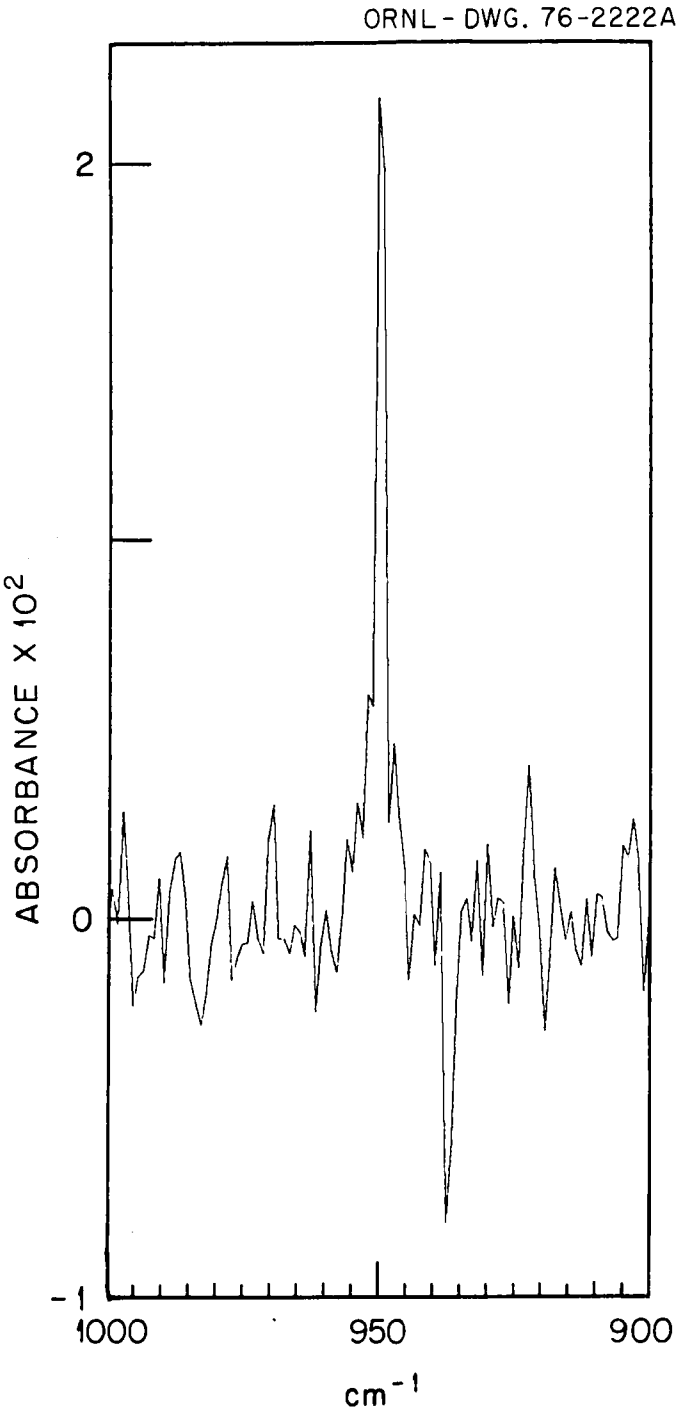


Figure 21. The ν_7 band of C_2H_4 in air.

the line at 893 cm^{-1} only. A single baseline was drawn for the CO_2 (720 cm^{-1}) and HCN (712 cm^{-1}) lines, as shown in Figure 20E.

Figure 22 presents the contrast between the smoke spectra of Code 1 cigarette (A), which delivers an appreciable quantity of C_5H_8, and of Code 13 (B), which delivers essentially none. In A, the C_5H_8 lines at 906 and 893 cm^{-1} are admittedly not well defined, but measurement of the 893 cm^{-1} line is possible. In the Code 13 spectrum (B) on the other hand, only noise is apparent at these frequencies.

A summary of the lines chosen for analysis is given in Table IV. Locations for each of these lines, except that of HCN, were confirmed by superimposition of their spectral plots on that of smoke. An illustration of the superimposition is shown in Figure 23. This figure shows clearly that the identity of the 720 cm^{-1} line in smoke is due to CO_2. The line at 712 cm^{-1}, attributed to HCN, is clearly not in the CO_2 spectrum. The third line appearing in this region (729 cm^{-1}) may be due to C_2H_2.[28]

2. Calibration

Calibration curves were plotted for standard mixtures of CH_4, CO, and CO_2, and for C_2H_4 and CH_3OH mixed in a Saran bag as described earlier (p 27). At least 3 samples were taken at each of 3 concentrations of each substance. The data are shown in Tables V-IX.

Absorbance measurements were made, as in smoke, on scale-expanded portions of the spectra.

Straight lines relating absorbance to concentration were fitted to the data by least squares formulae.[38] The plots are shown in

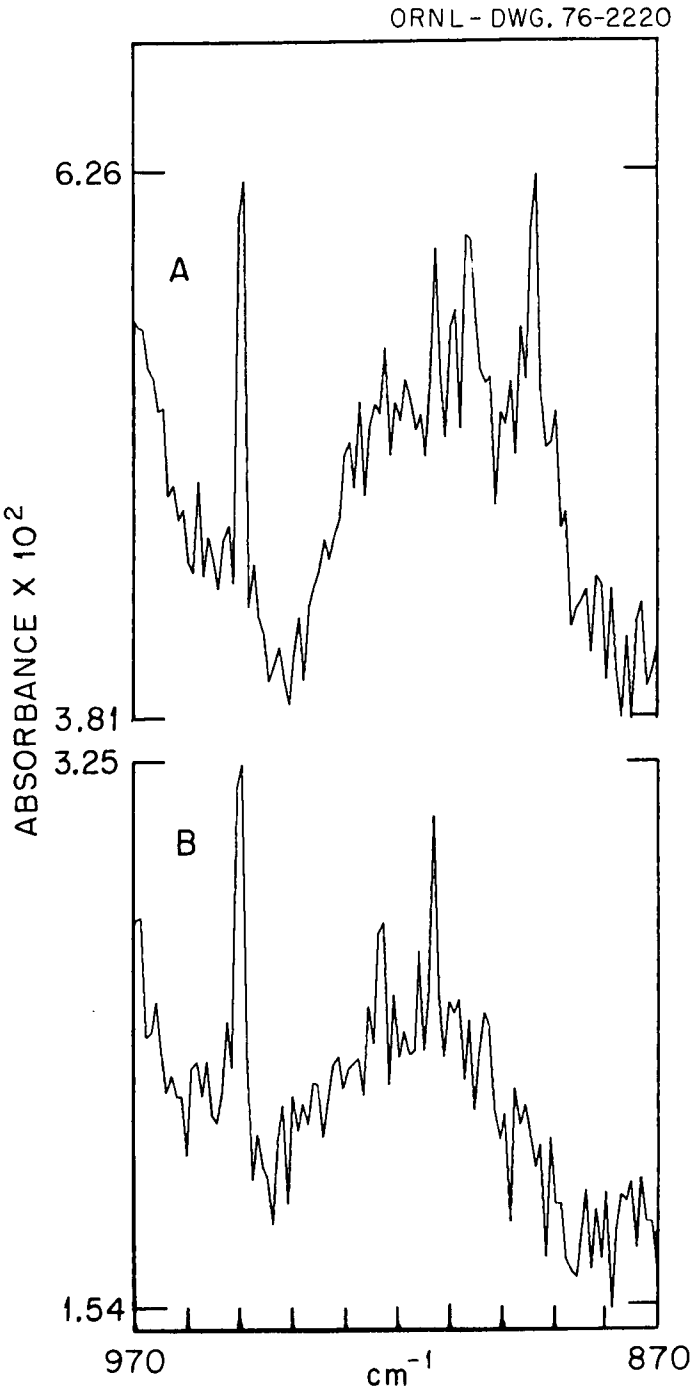


Figure 22. Whole-smoke spectra in the 970-870 cm^{-1} region. A. Code 1; B. Code 13.

TABLE IV

LINES SELECTED FOR ANALYSIS

Component	Frequency		Reference
	Observed (cm^{-1})	Literature (cm^{-1})	
CO	2169	2169.2	33
CO_2	720	720.5	28
CH_4	1306	1306.2	28, 35
C_2H_4	949	949.2	28, 35
CH_3OH	1033	1033.9	28
HCN	712	712.1	28, 36
C_5H_8	893	893	37

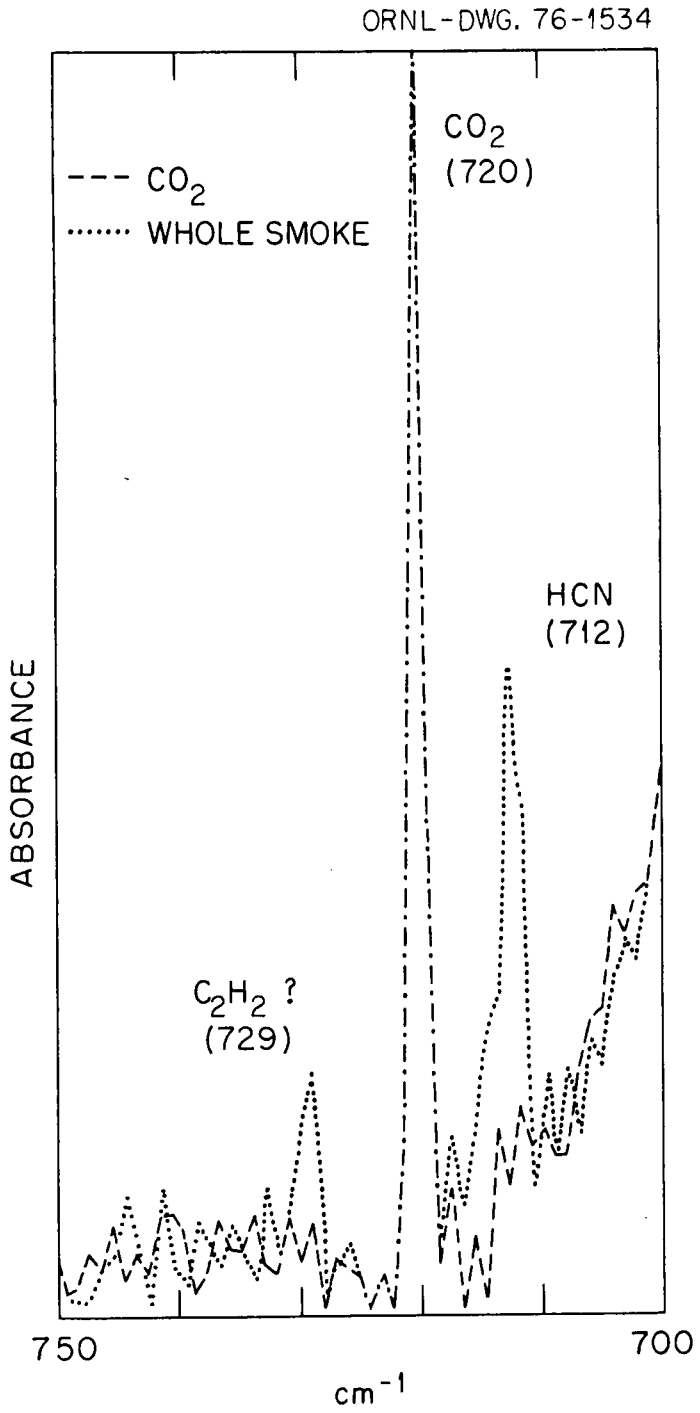


Figure 23. Superimposed spectra of whole smoke and CO_2, 750-700 cm^{-1}.

TABLE V

CALIBRATION DATA FOR CO (2169 cm^{-1})

Concentration (% by vol.)	Absorbance ($X10^2$)
0.27	7.80
.27	7.84
.27	7.64
.53	12.20
.53	11.80
.53	11.90
.58	12.35
.58	12.35
.58	12.30
1.07	18.10
1.07	17.60
1.07	17.40
2.68	36.50
2.68	37.00
2.68	36.60
2.68	37.10
2.68	37.20

TABLE VI

CALIBRATION DATA FOR CO_2 (720 cm^{-1})

Concentration (% by vol.)	Absorbance ($X10^2$)
0.429	3.96
.429	3.86
.429	3.88
.858	8.38
.858	7.69
.858	8.30
1.05	10.66
1.05	10.70
1.05	10.72
1.05	10.36
1.72	15.94
1.72	15.40
1.72	15.32
3.92	33.25
3.92	33.80
3.92	32.50
3.92	33.60
3.92	33.90
3.92	34.30
3.92	35.00

TABLE VII

CALIBRATION DATA FOR CH_4 (1306 cm^{-1})

Concentration (% by vol.)	Absorbance ($X10^2$)
0.064	5.54
.064	5.30
.064	5.38
.60	47.20
.60	48.30
.60	46.70
.60	48.60
.60	48.40
1.00	76.80
1.00	77.00
1.00	77.60

TABLE VIII

CALIBRATION DATA FOR C_2H_4 (949 cm^{-1})

Concentration (% by vol.)	Absorbance ($X10^2$)
0.0158	2.26
.0158	2.14
.0158	2.27
.0210	3.13
.0210	3.31
.0210	3.23
.0316	4.17
.0316	4.30
.0316	4.20
.0316	4.19

TABLE IX

CALIBRATION DATA FOR CH_3OH (1033 cm^{-1})

Concentration (% by vol.)	Absorbance ($X10^2$)
0.0066	0.78
.0066	.86
.0066	.95
.0165	1.89
.0165	2.07
.0165	2.07
.033	4.10
.033	3.98
.033	3.90

Figures 24-28. Each point plotted is the average of the individual measurements at that concentration. The constants computed for these curves are given in Table X. The height of the error bar shown at each concentration in Figures 24-28 is twice the standard deviation of "Y" computed from all points of the curve. The intercept was significant at the 95% confidence level for CO, CO_2, and C_2H_4, and not significant for CH_4 and CH_3OH.

3. Variability Studies

a. Puff-to-puff and sample-to-sample. Tables XI-XV summarize the results obtained by smoking Code 1 cigarettes in groups of 3 simultaneously and collecting spectra during every puff after the first with the program, COL, MID, !, and the parameters NSS=4, RES=2. A reference spectrum (empty chamber) was collected just prior to smoking each group. The execute command was given at the completion of each pump cycle (5 sec). These data, therefore, represent measurements averaged over a period from approximately 7 to 22 sec after the puff started. The tabular entries are concentrations calculated from the calibration factors given in Table X.

An upward trend in the concentrations is to be expected[7] as a cigarette is smoked. This trend is clearly seen in the plots of Figure 29, which shows the puff-by-puff average concentrations for 8 samples. The data from Tables XI-XV were used in constructing this Figure. This Figure demonstrates that in dilute whole smoke, and with an 18-cm optical path, real concentration changes in the GP constituents can be measured.

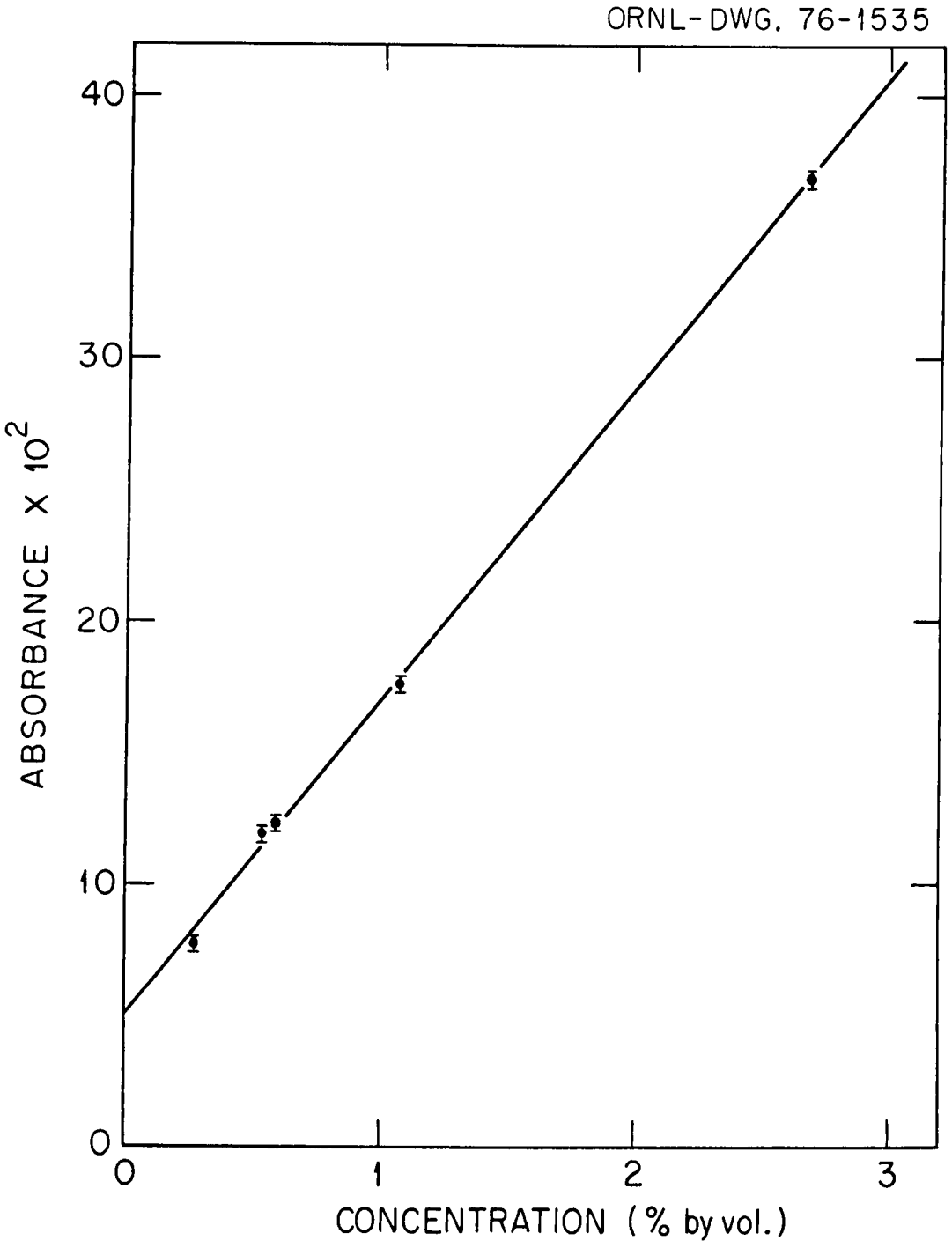


Figure 24. Calibration curve for CO(2169 cm^{-1}).

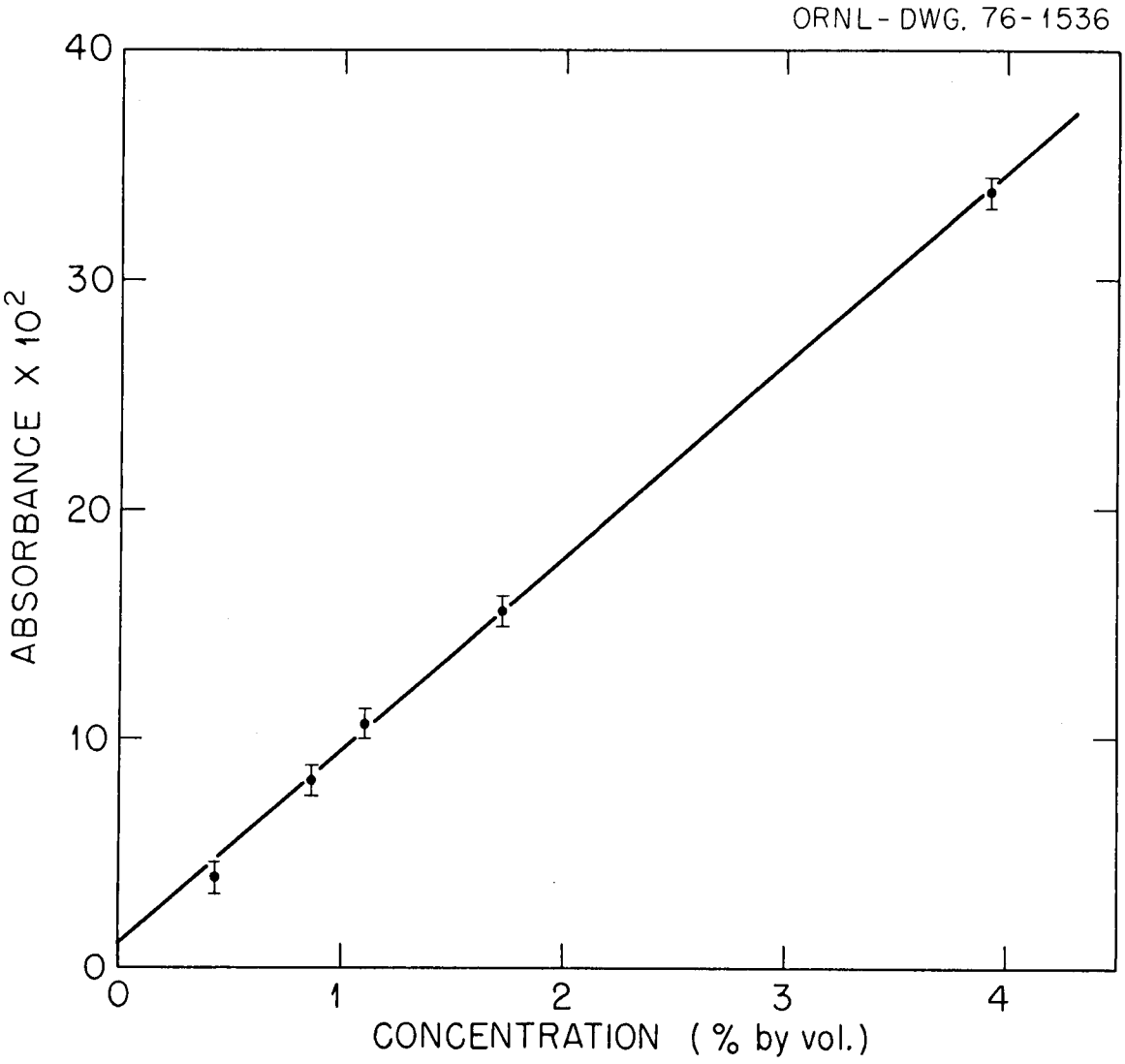


Figure 25. Calibration curve for CO_2(720 cm^{-1}).

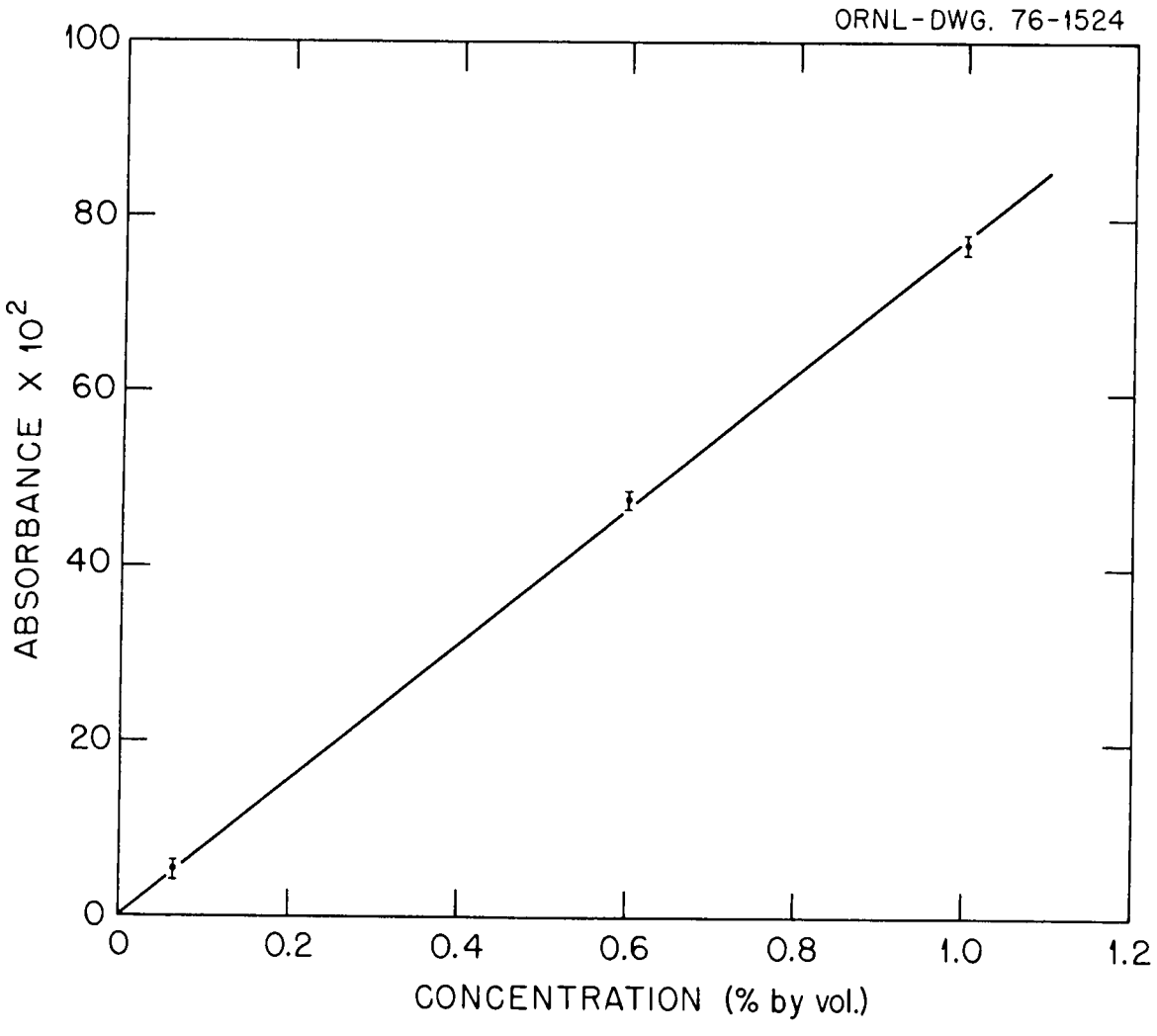


Figure 26. Calibration curve for CH_4 (1306 cm^{-1}).

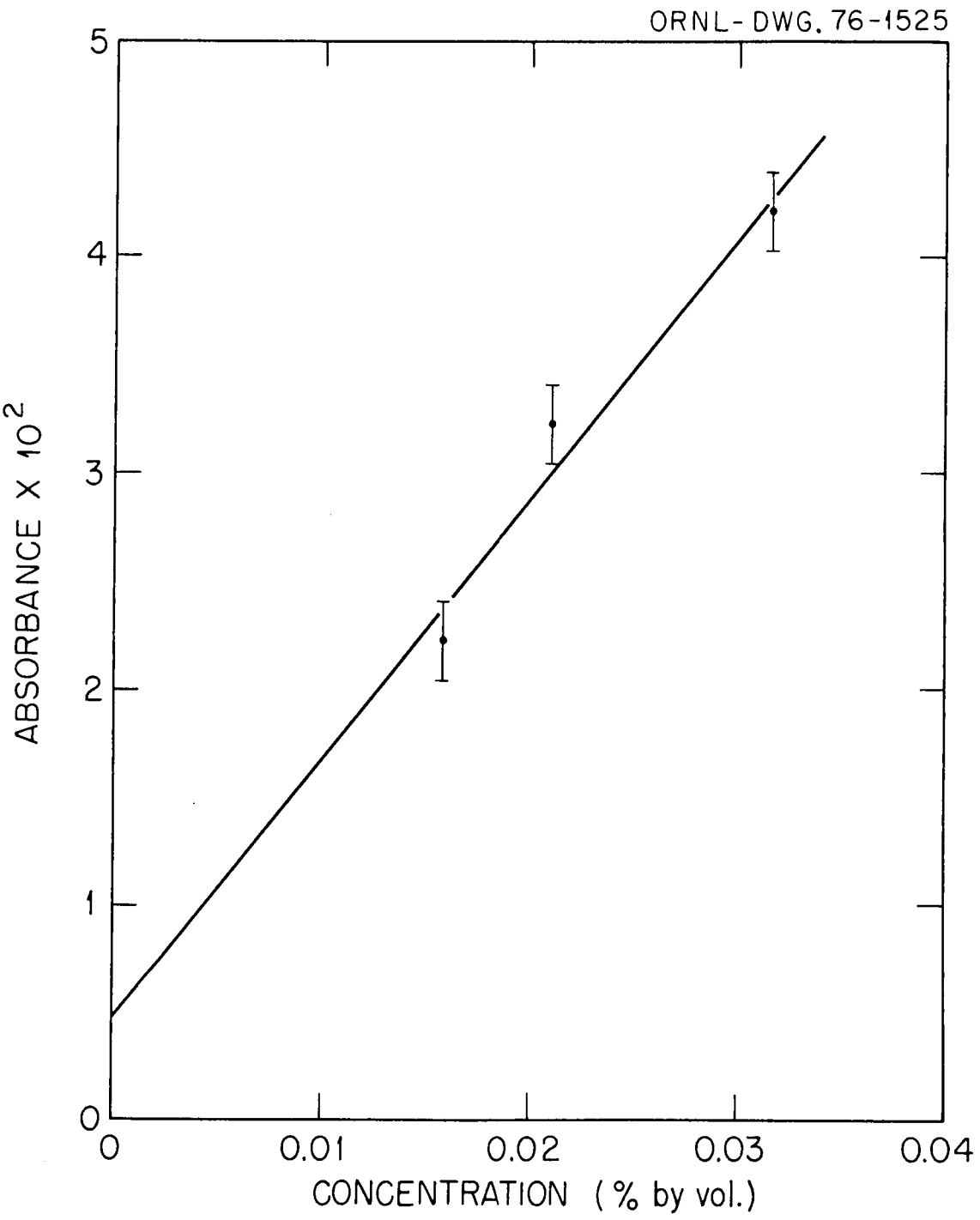


Figure 27. Calibration curve for C_2H_4(949 cm^{-1}).

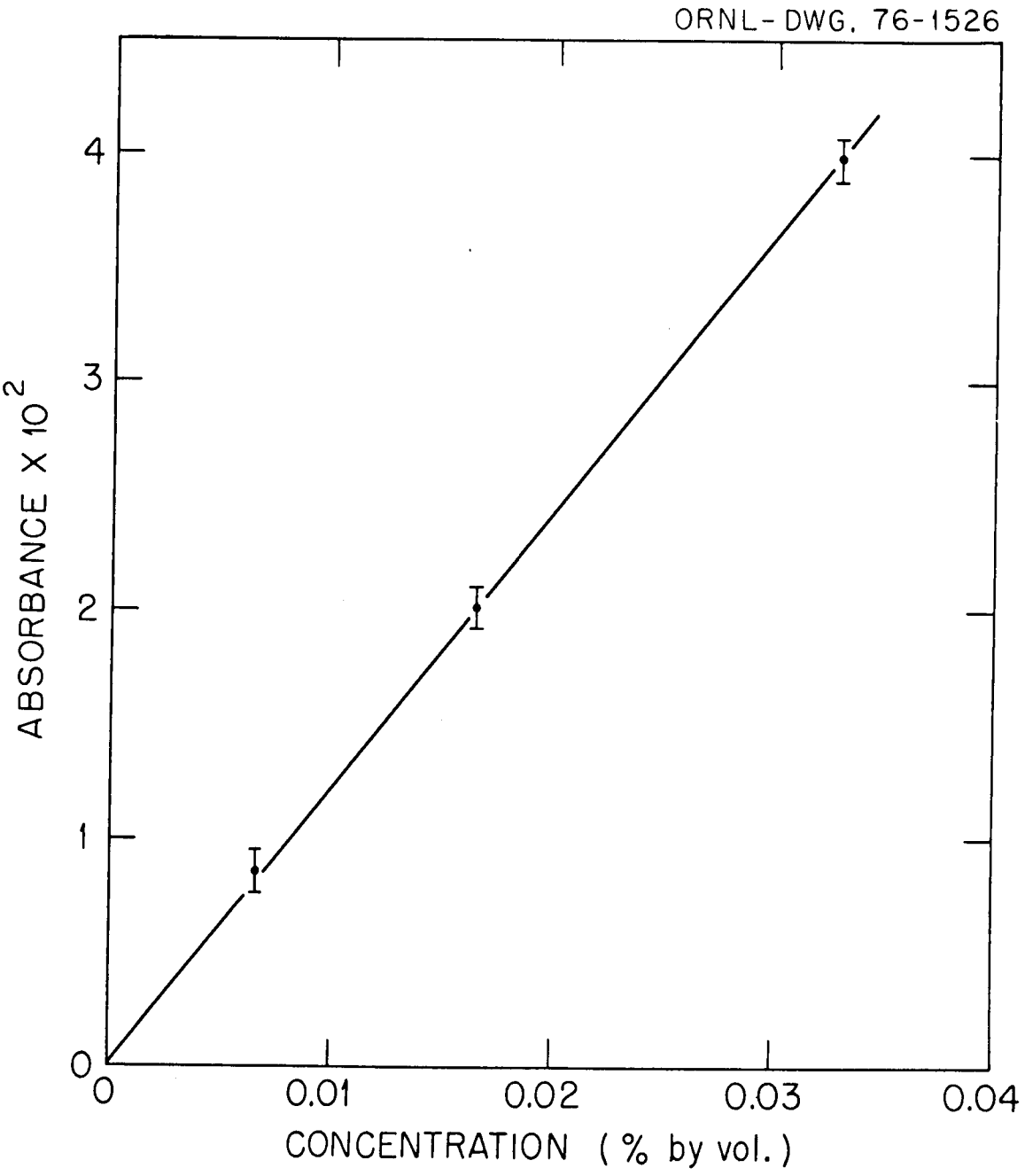


Figure 28. Calibration curve for CH_3OH(1033 cm^{-1}).

TABLE X

CONSTANTS OF LINEAR REGRESSION LINES FOR STANDARDS[a]

Component	A (intercept)	B (slope)	Sy^b
CO	5.177	11.84	0.45
CO_2	1.082	8.359	.69
CH_4	1.013[c]	76.82	.95
C_2H_4	0.4802	119.9	.18
CH_3OH	.0687[c]	118.7	.091

[a] Y = absorbance x 10^2 = A + B (concentration).

[b] Standard deviation of Y.

[c] 95% confidence limits include the origin.

TABLE XI

CODE 1,[a] CONCENTRATIONS OF CO[b]

Puff No. Sample	2	3	4	5	6	7	8	9	10	11	Ave.
1	1.02	1.09	1.08	1.15	1.15	1.08	1.32	1.26	1.36	1.37	1.19
2	0.97	1.09	0.87	1.16	1.22	1.17	1.36	1.23	1.36	1.43	1.18
3	1.03	1.20	1.09	1.32	1.27	1.33	1.13	1.47	1.41	1.73	1.30
4	1.01	0.89	1.08	1.22	1.19	1.27	1.28	1.34	1.47	1.47	1.22
5	1.24	1.25	1.13	1.33	1.41	1.13	1.51	1.46	1.48	1.54	1.35
6	1.07	0.87	1.11	1.30	1.12	1.27	1.12	1.42	1.41	1.49	1.22
7	0.96	1.13	1.05	0.98	1.22	1.33	1.39	1.45	1.44	1.57	1.25
8	1.28	1.25	1.21	1.35	1.17	1.35	1.23	1.29	1.36	1.49	1.30
Ave.	1.07	1.10	1.08	1.23	1.22	1.24	1.29	1.36	1.41	1.51	1.25
S	0.12	0.15	0.10	0.13	0.09	0.10	0.13	0.10	0.05	0.11	
%RSD	11	14	9	10	7	8	10	7	4	7	

[a] 3 cigarettes/sample.

[b] % by vol. in chamber.

TABLE XII

CODE 1,[a] CONCENTRATIONS OF CO_2[b]

Puff No. Sample	2	3	4	5	6	7	8	9	10	11	Ave.
1	1.73	1.85	1.77	1.90	1.95	1.85	2.20	2.18	2.18	2.43	2.00
2	1.60	1.76	1.60	1.88	1.91	1.96	2.19	2.27	2.17	2.29	1.96
3	1.59	2.00	1.90	2.06	1.96	2.18	1.96	2.23	2.35	2.81	2.11
4	1.64	1.56	1.89	2.10	2.02	2.05	2.22	2.30	2.30	2.50	2.06
5	1.85	1.88	1.94	2.00	2.26	2.17	2.55	2.34	2.25	2.48	2.17
6	1.77	1.75	1.90	2.12	1.94	2.04	1.96	2.35	2.49	2.36	2.07
7	1.59	1.88	1.85	1.77	2.04	2.11	2.25	2.28	2.49	2.67	2.09
8	1.88	1.94	1.94	2.09	1.94	2.16	2.09	2.22	2.84	2.55	2.11
Ave.	1.71	1.83	1.85	1.99	2.00	2.06	2.18	2.27	2.31	2.51	2.07
S	0.12	0.14	0.12	0.12	0.11	0.12	0.19	0.06	0.12	0.17	
%RSD	7	8	6	6	6	6	9	3	5	7	

[a] 3 cigarettes/sample.

[b] % by vol. in chamber.

TABLE XIII

CODE 1,[a] CONCENTRATIONS OF CH_4[b]

Puff No. / Sample	2	3	4	5	6	7	8	9	10	11	Ave.
1	0.079	0.093	0.097	0.099	0.104	0.096	0.125	0.122	0.137	0.135	0.109
2	.085	.095	.085	.098	.107	.116	.134	.126	.128	.143	.112
3	.077	.102	.104	.117	.115	.118	.113	.134	.134	.154	.117
4	.078	.076	.099	.107	.108	.114	.129	.129	.131	.146	.112
5	.085	.098	.094	.112	.122	.110	.139	.134	.135	.147	.118
6	.083	.087	.098	.113	.103	.115	.105	.130	.135	.145	.111
7	.077	.096	.094	.096	.109	.120	.128	.137	.146	.146	.115
8	.102	.098	.105	.125	.105	.127	.131	.134	.137	.156	.122
Ave.	.083	.093	.097	.108	.109	.115	.125	.131	.135	.146	.114
S	.008	.008	.006	.010	.007	.009	.011	.005	.005	.006	
%RSD	10	9	7	10	6	8	9	4	4	4	

[a] 3 cigarettes/sample.

[b] % by vol. in chamber.

TABLE XIV

CODE 1,[a] CONCENTRATIONS OF C_2H_4[b]

Puff No. / Sample	2	3	4	5	6	7	8	9	10	11	Ave.
1	0.011	0.008	0.009	0.009	0.011	0.009	0.012	0.010	0.013	0.014	0.011
2	.007	.008	.010	.011	.012	.012	.013	.012	.012	.013	.011
3	.010	.011	.014	.009	.012	.013	.011	.013	.013	.017	.012
4	.008	.006	.011	.010	.009	.010	.011	.011	.012	.014	.010
5	.008	.014	.009	.013	.008	.012	.017	.015	.015	.008	.012
6	.007	.005	.012	.011	.008	.012	.008	.014	.012	.018	.011
7	.007	.009	.012	.008	.007	.008	.011	.011	.013	.011	.010
8	.016	.008	.012	.020	.012	.016	.011	.016	.011	.018	.014
Ave.	.009	.009	.011	.011	.010	.012	.012	.013	.013	.014	.011
S	.003	.003	.002	.004	.002	.003	.002	.002	.001	.003	
%RSD	32	32	17	34	21	23	20	16	9	24	

[a] 3 cigarettes/sample.

[b] % by vol. in chamber.

TABLE XV

CODE 1,[a] CONCENTRATIONS OF CH_3OH[b]

Puff No. Sample	2	3	4	5	6	7	8	9	10	11	Ave.
1	0.008	0.012	0.013	0.013	0.016	0.015	0.020	0.024	0.025	0.036	0.018
2	.007	.012	.011	.014	.012	.019	.021	.024	.023	.028	.017
3	.009	.012	.013	.016	.015	.018	.019	.022	.027	.033	.018
4	.008	.006	.011	.015	.016	.017	.020	.023	.024	.040	.018
5	.010	.012	.011	.012	.018	.027	.023	.027	.026	.032	.020
6	.008	.009	.009	.012	.013	.017	.014	.022	.026	.030	.016
7	.009	.011	.014	.014	.015	.019	.022	.025	.030	.032	.019
8	.011	.013	.015	.015	.016	.019	.024	.032	.027	.031	.020
Ave.	.009	.011	.012	.014	.015	.019	.020	.025	.026	.033	.018
S	.001	.002	.002	.001	.002	.004	.003	.003	.002	.004	
%RSD	13	20	15	10	12	19	15	14	8	11	

[a] 3 cigarettes/sample.

[b] % by vol. in chamber.

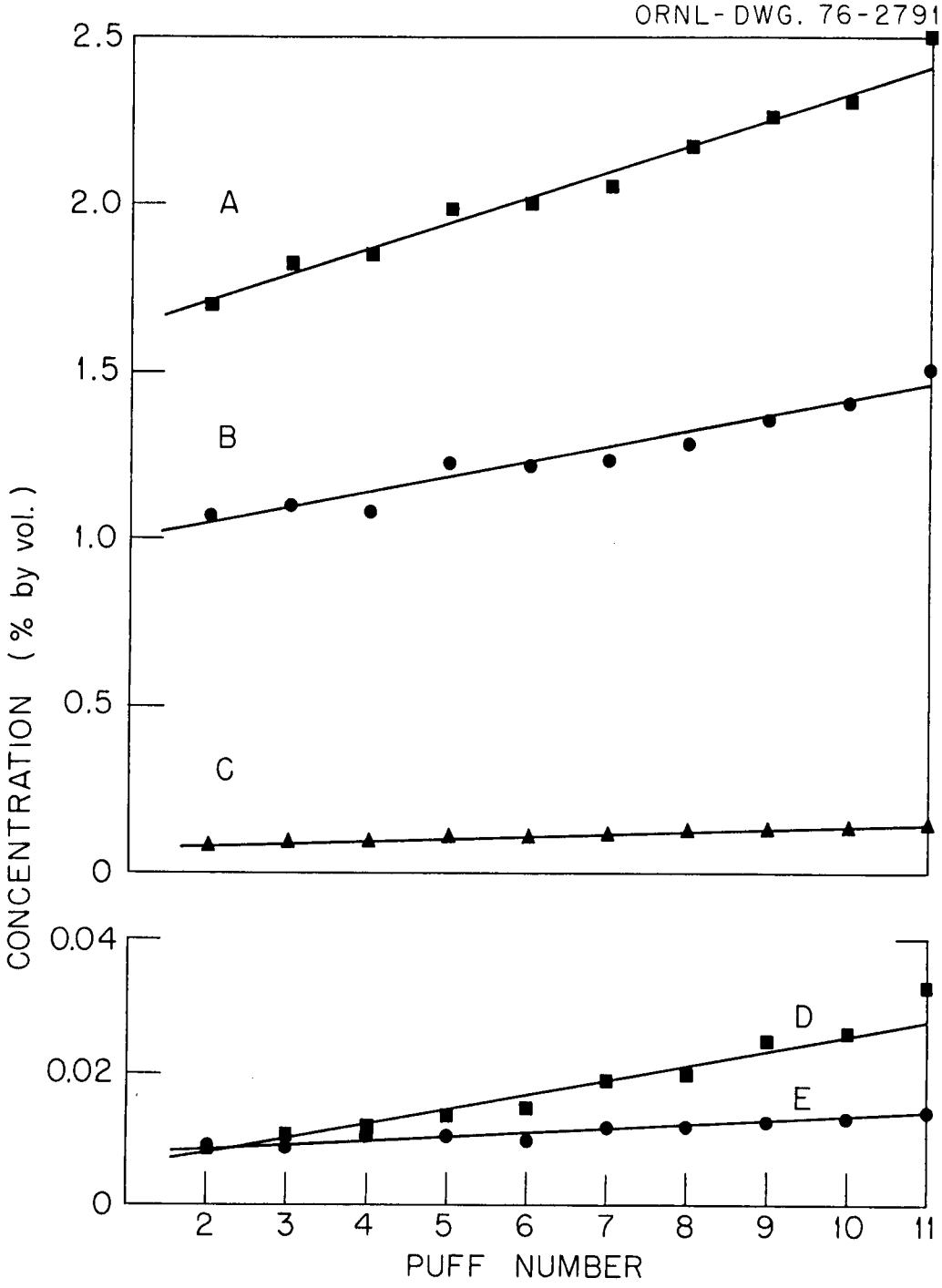


Figure 29. Variation of concentration with puff number. A. CO_2; B. CO; C. CH_4; D. CH_3OH; E. C_2H_4.

b. Zero-filling. The potential gain in precision by zero-filling procedure mentioned earlier (p 40) was assessed by 4-fold zero-filling of the fourth puff interferograms from the above experiment and recomputation of the spectra. Triangular apodization was applied during the computation of the zero-filled spectra. The results of these manipulations are shown in Table XVI. For comparison, data for the unapodized and unfilled spectra corresponding to the fourth puff are shown in Table XVII. A gain in precision of analysis was not apparent since the relative standard deviations are essentially the same. Again, time invested in zero-filling was considerable.

c. Between codes. Puff-by-puff and sample-by-sample data were also taken for cigarettes of Codes 6, 13 and 16. Five samples of 3 cigarettes each were smoked for Codes 6 and 13, and 4 samples of 2 cigarettes each for Code 16. Alternate puffs, beginning with the second, were analyzed. These data were taken to correlate the FT-IR observations with anticipated differences in component deliveries—particularly of HCN and C_5H_8—between the codes. Table XVIII shows the known yields of the components from the 4 Codes. The results of this experiment are shown in Table XIX. Comparison was made between the average concentrations for all measured puffs with corresponding data for the Code 1 cigarettes taken from Tables XI-XV (pp 68-72). A similar comparison was made between average absorbances for HCN and C_5H_8. In all cases, the FT-IR observations paralleled the expected yields.

TABLE XVI

ABSORBANCES,[a] FOURTH PUFFS, 4-FOLD ZERO-FILLED, APODIZED

Component Sample	CO	CO_2	CH_4	C_2H_4	CH_3OH	C_5H_8	HCN
1	11.8	8.66	5.53	1.54	1.13	1.14	5.90
2	10.0	7.95	4.90	1.09	1.26	0.91	3.85
3	11.7	10.05	6.12	1.81	1.47	1.09	4.93
4	12.2	9.61	6.15	1.56	1.11	1.02	5.14
5	12.2	9.69	5.79	1.12	1.33	1.08	5.73
6	11.8	9.43	5.84	1.41	1.11	1.24	5.02
7	11.3	9.39	5.41	1.33	1.21	1.01	4.54
8	12.4	9.69	6.24	1.49	1.43	1.38	6.48
Ave.	11.68	9.31	5.75	1.42	1.26	1.11	5.20
S	0.76	0.68	0.45	0.24	0.14	0.15	0.83
%RSD	6.5	7.3	7.9	17	11	13	16

[a]Absorbance $X10^2$.

TABLE XVII

ABSORBANCES,[a] FOURTH PUFFS, UNFILLED, UNAPODIZED

Component Sample	CO	CO_2	CH_4	C_2H_4	CH_3OH	C_5H_8	HCN
1	18.00	15.90	8.45	1.53	1.65	1.26	7.89
2	15.45	14.44	7.52	1.61	1.37	1.16	6.10
3	18.10	17.00	8.98	2.11	1.58	1.25	7.11
4	17.90	16.90	8.58	1.76	1.35	1.10	7.80
5	18.60	17.30	8.25	1.51	1.40	0.98	7.12
6	18.32	16.96	8.50	1.96	1.13	1.26	7.12
7	17.56	16.57	8.22	1.85	1.70	0.87	6.76
8	19.44	17.32	9.10	1.88	1.78	1.44	9.48
Ave.	17.92	16.55	8.45	1.78	1.50	1.17	7.67
S	1.15	0.97	0.49	0.21	0.22	0.18	1.15
%RSD	6.4	5.8	5.8	12	15	15	15

[a]Absorbance $X10^2$.

TABLE XVIII

CIGARETTE YIELDS[a]

Code	Gas-Phase Yields, Per Puff			
	CO (ml)	CO_2 (ml)	C_5H_8 (ratio)[b]	HCN (μg)
1	1.58	2.94	1.17	21.5
6	1.50	3.05	1.25	15.0
13	1.48	3.12	0.03	7.7
16	1.83	3.15	.23	12.4

[a]"Towards Less-Hazardous Cigarettes. Report No. 1—The First Set of Experimental Cigarettes," National Cancer Institute, Bethesda, MD, in press.

[b]Relative to a monitor cigarette.

TABLE XIX

BETWEEN-CODE COMPARISON

Component	Code 6[a]			Code 13[a]			Code 16[b]		
	Yield[c,d]	Absorbance[d]	Concentration[d]	Yield[c,d]	Absorbance[d]	Concentration[d]	Yield[c,d]	Absorbance[d]	Concentration[d]
CO	0.95		0.85	0.94		1.17	1.15		1.59
CO_2	1.04		1.06	1.06		1.14	1.07		1.27
CH_4			0.96			0.91			1.25
C_2H_4			1.04			0.68			0.99
CH_3OH			0.86			0.98			1.48
C_5H_8	1.10	1.06		0.03	——[e]		0.23	——[e]	
HCN	0.70	0.89		0.36	0.47		0.58	0.84	

[a] 3 cigarettes/sample.

[b] 2 cigarettes/sample.

[c] Calculated from "Towards Less-Hazardous Cigarettes. Report No. 1—The First Set of Experimental Cigarettes," National Cancer Institute, Bethesda, MD, in press.

[d] Relative to Code 1.

[e] Not measurable.

4. Comparison with GC Analysis

Table XX shows the results of experiments in which samples of 1, 2, and 3 Code 1 cigarettes were smoked, compared with a similar set in which concentrations were measured by GC. The GC analyses were performed by J. H. Moneyhun of the ORNL Analytical Chemistry Division.

Samples for GC were withdrawn from the smoke chamber through a small Cambridge filter by a motor driven syringe. During the stand time of each puff, the syringe drive was actuated for 25 sec; the volume drawn in 25 sec was 3 ml. By sampling puffs 2-11 in this way, a total volume of 30 ml of GP smoke was accumulated. This accumulated sample was divided between 2 gas chromatographs—one for the determination of CO and CO_2, and the other for the determination of CH_4 and C_2H_4. The tabulated data show reasonable agreement between the measurements made by GC and those made by FT-IR except for the CO and CO_2 measurements with 1 cigarette. At these low concentrations and taking into account the factor of comparing different batches of cigarettes in different laboratories, the factor of 2 shown here is not too extraordinary. Still, the GC data tend to follow a straight line relationship between concentration and number of cigarettes per sample while the FT-IR data do not, which makes it appear that the 1-cigarette measurement by FT-IR is in error.

5. Early vs. Late in the Stand Time

The obvious application of a technique proposed for monitoring inhalation chamber experiments is in observation of changes in the chamber environment occurring during each puff. The appearance of

TABLE XX

COMPARISON OF FT-IR AND GC[a] ANALYSIS[b]

Component	3 Cigarettes		2 Cigarettes		1 Cigarette	
	FT-IR	GC	FT-IR	GC	FT-IR	GC
CO	1.25	1.04	0.60	0.61	0.42	0.23
CO_2	2.07	1.72	1.13	1.09	.90	.47
CH_4	0.11	0.10	0.056	0.066	.032	.031
C_2H_4	.011	.013	.005	.008	.004	.004

[a]Data of J. H. Moneyhun, January, 1976.

[b]% by volume.

typical whole smoke spectra recorded early and late in the stand time is shown in Figure 30. These spectra were obtained with the parameters, RES=2 and NSS=2, and the program COL, MID, COL, MID, !. It was necessary to initiate the program 2 sec after the start of the puff in order to insure completion of the scans during a stand time. This gave an early observation at 4-9 sec after the puff start and a late observation at 24-29 sec after the puff start. Aside from the generally lower scattering at wavenumbers above 2500 cm^{-1} as the smoke ages and the fact that the water line at 1700 cm^{-1} is much more intense late in the puff rather than early, little other change is apparent.

The absorbances measured for each component early and late in the stand time were compared by taking the ratio: A(late)/A(early). For 77 observations distributed over all puffs and over all the measured components, the average ratio was 1.03 and the relative standard deviation was 13%. This indicates that no instrumental artifact is imposing a bias on measurements taken early and late in the puff stand time.

6. Time of Analysis

While no attempt was made, as such, during this research to minimize time spent in analysis, notes were kept on the approximate time expenditures involved in the FT-IR experiments.

To obtain complete data on the 7 components studied for all puffs, 2 through 11, required 65 min to compute and plot with automatic scale expansion to 20 cm. About 10 min per file was required to measure the chart and calculate absorbances. This can be done while plotting proceeds, so by assuming that measurements are begun immediately after the

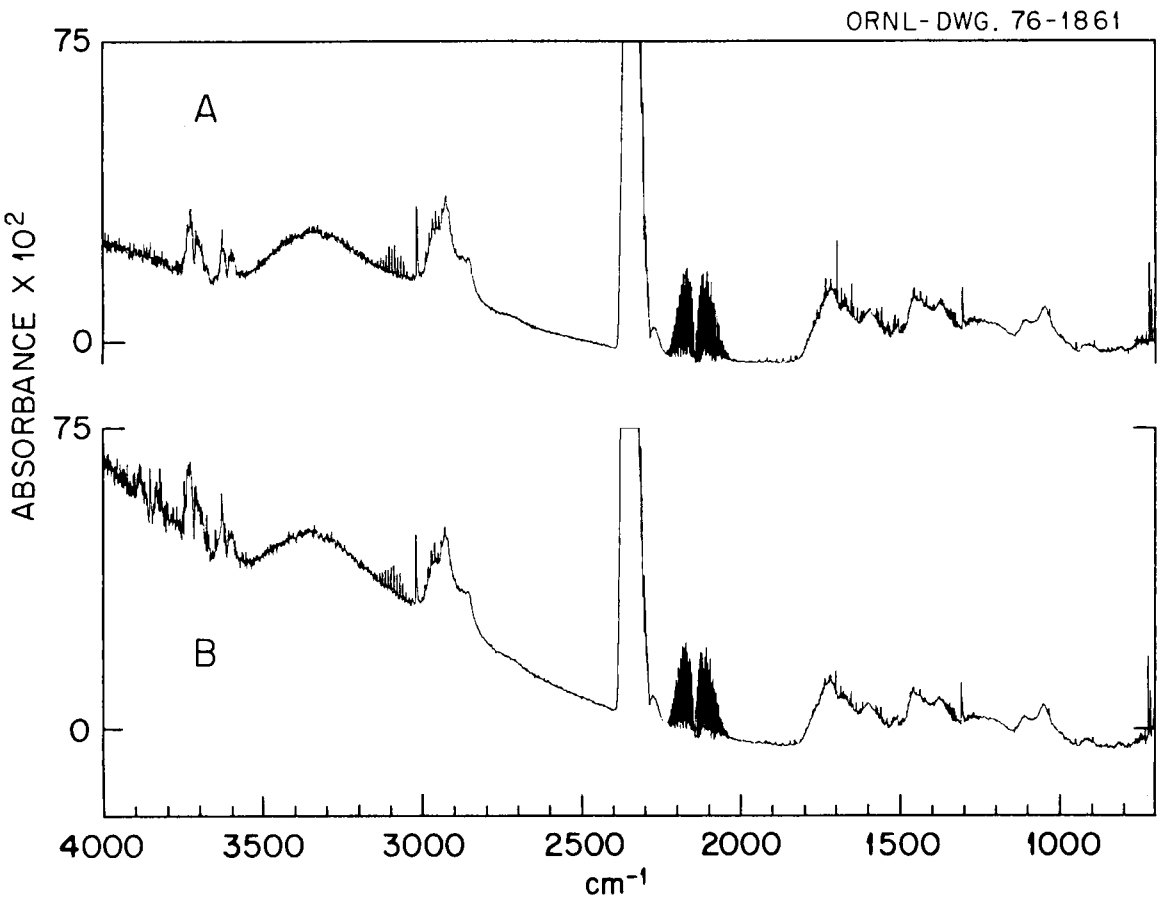


Figure 30. Whole-smoke spectra, recorded (A) late and (B) early in stand time.

6.5 min required to compute and plot the first file, one arrives at an estimate of 106 min to reduce the results of a 10-puff smoking experiment to notebook entries. Time economies can be achieved, e.g., by plotting spectra only for every other puff, in which case the measurement time would be halved.

An important point that follows from the results obtained is that the FT-IR technique allows measurement of smoke components during a single puff. This is not possible with the present GC procedures, which depend on accumulation of a sample over the whole delivery of a cigarette. Since the FTS-20 spectrometer is capable of collecting 7 scans during each puff, which would average the composition over the 30-sec puff stand time, and could compute and plot data for one or two components on every other puff, an essentially "real time" monitoring procedure should be possible.

An application of this instrument which was not attempted in this study is the acquisition and storage of data for scans (with RES=2) at roughly 4-sec intervals. Our software did not permit achievement of this possibility.

CHAPTER IV

SUMMARY

The application of the FT-IR spectrometer for rapid in situ multicomponent analysis (monitoring) of whole dilute tobacco smoke under conditions of smoke concentration and absorption path length that might be utilized in an animal inhalation exposure study was demonstrated.

The smoke was generated by puffing 1, 2 or 3 cigarettes simultaneously (with resulting smoke concentrations of approximately 7, 15, or 22%) in a mechanical smoking apparatus, following accepted smoking procedures—puffs of 2 sec duration and 35 cm^3 volume, at intervals of 1 min. The smoke of each puff was immediately diluted and allowed to stand in the chamber (absorption cell) 30 sec including the time to introduce each puff. Most data were obtained in 22% smoke and with 4 scans by the instrument, which gave data for the period 7 to 22 sec following each puff.

After searching the smoke spectra for bands due to a number of significant GP smoke components, 7 components were selected which had strong lines in portions of the smoke spectrum which were relatively free of interfering lines, principally those of water, and where scattering due to particulate matter was not too severe.

Concentrations of CO, CO_2, CH_4, C_2H_4, and CH_3OH were obtained by reference to calibration curves prepared by introducing the pure materials into the smoke chamber. The precision of analyses varied, as

one might expect, essentially in proportion to the measured line intensity relative to the noise. The precision of analysis for CO, CO_2, CH_4 was on the order of 15% or better where band intensities were 0.07 to 0.23 absorbance units. For CH_3OH, where band intensities were 0.01 to 0.023 absorbance units, the precision was about 8-20%. For C_2H_4 the intensities were in the range 0.015 to 0.025 absorbance units, and the precision ranged from 34% (5th puff) to 9% (10th puff). For C_5H_8 and HCN, the concentrations of which were not measured by calibration, the band intensities were 0.01-0.013 and 0.06-0.14 absorbance units, respectively. Studies were made comparing these peak intensities with known cigarette yields, of C_5H_8 and HCN and correspondence between absorbance and yield was demonstrated. A comparison indicated reasonable agreement between FT-IR and GC procedures for analyzing the chamber concentrations of CO, CO_2, CH_4, and C_2H_4.

The same concentrations were obtained from observations made early and late in the 30-sec exposure period, which established the possibility of using FT-IR spectrometry for obtaining GP dosimetry data in a straightforward manner.

REFERENCES

REFERENCES

1. P. Nettesheim, M. R. Guerin, J. Kendrick, I. B. Rubin, J. R. Stokely, D. A. Creasia, W. L. Maddox, and J. E. Caton in "Proceedings of the Tobacco Smoke Inhalation Workshop on Experimental Methods in Smoking and Health Research," National Cancer Institute, Bethesda, MD, June 1974, DHEW Pub. No. (NIH) 75-906, p 17.

2. J. R. Stokely and M. R. Guerin, presented at the 27th Tobacco Chemists' Research Conference, Winston Salem, NC, Oct. 1973, No. 31.

3. E. L. Wynder and D. Hoffmann, "Tobacco and Tobacco Smoke," Academic Press, New York, NY, 1967, pp 317-318.

4. W. B. Wartman, Jr., E. C. Cogbill, and E. S. Harlow, Anal. Chem., 31, 1705 (1959).

5. R. L. Stedman, Chem. Rev., 68, 153 (1968).

6. H. Elmenhorst and C. Schultz, Beitr. zur Tabakforsch., 4, 90 (1968).

7. E. L. Wynder and D. Hoffmann, "Tobacco and Tobacco Smoke," Academic Press, New York, NY, 1967, pp 438-453.

8. C. H. Keith and P. G. Tesh, Tobacco Sci., 9, 61 (1965); E. L. Wynder and D. Hoffmann, "Tobacco and Tobacco Smoke," Academic Press, New York, NY, 1967, p 318.

9. P. L. Hanst in "Advances in Environmental Science and Technology," J. N. Pitts, Jr. and R. L. Metcalf, Eds., Wiley-Interscience, New York, NY, 1971, pp 91-213.

10. P. L. Hanst, A. S. Lefohn, and B. W. Gay, Jr., Appl. Spectrosc., 27, 188 (1973).

11. J. O. Lephardt and G. Vilcins, presented at the 28th Tobacco Chemists' Research Conference, Raleigh, NC, Oct. 1974, No. 51.

12. G. Vilcins and J. O. Lephardt, presented at the 28th Tobacco Chemists' Research Conference, Raleigh, NC, Oct. 1974, No. 52.

13. J. O. Lephardt and G. Vilcins, Appl. Spectrosc., 29, 221 (1975).

14. G. Vilcins and J. O. Lephardt, presented at the 29th Tobacco Chemists' Research Conference, College Park, MD, Oct. 1975, No. S-6.

15. P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy," John Wiley and Sons, New York, NY, 1975, pp 2-15.

16. J. W. Cooley and J. W. Tukey, Math. Comput., 19, 297 (1965).

17. G. Horlick, Appl. Spectrosc., 22, 617 (1968).

18. P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy," John Wiley and Sons, New York, NY, 1975, pp 23-31.

19. P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy," John Wiley and Sons, New York, NY, 1975, pp 60-64.

20. E. G. Codding and G. Horlick, Appl. Spectrosc., 27, 85 (1973).

21. "Towards Less-Hazardous Cigarettes. Report No. 1—The First Set of Experimental Cigarettes," National Cancer Institute, Bethesda, MD, in press.

22. Digilab, Inc., "Software Reference Manual FTS Disk Systems," MO 18-0001, Ed. 1, Nov. 1973.

23. R. J. Bell, "Introductory Fourier Transform Spectroscopy," Academic Press, New York, NY, 1972, pp 273-278.

24. P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy," John Wiley and Sons, New York, NY, 1975, pp 98-103, 158-165.

25. M. R. Guerin, W. L. Maddox, and J. R. Stokely in "Proceedings of the Tobacco Smoke Inhalation Workshop on Experimental Methods in Smoking and Health Research," National Cancer Institute, Bethesda, MD, June 1974, DHEW Pub. No. (NIH) 75-906, p 31.

26. E. L. Wynder and D. Hoffman, "Tobacco and Tobacco Smoke," Academic Press, New York, NY, 1967, p 157.

27. "Handbook of Chemistry and Physics," The Chemical Rubber Company, Cleveland, OH, 1966, p D-117.

28. G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, NY, 1945.

29. J. R. Newsome and C. H. Keith, Tobacco Sci., 9, 65 (1965).

30. A. H. Laurene, L. A. Lyerly, and G. W. Young, Tobacco Sci., 8, 150 (1964).

31. "Standard Grating Spectra," Numbers 1131, 1142, 1919, 1924, 4063, 5824, 6309, 6645, 7454, Sadtler Research Laboratories, Philadelphia, PA, 1966.

32. P. R. Griffiths, Appl. Spectrosc., 29, 11 (1975).

33. K. N. Rao, C. J. Humphreys, and D. H. Rank, "Wavelength Standards in the Infrared," Academic Press, New York, NY, 1966.

34. S. H. Chan, D. Nelson, M. J. D. Low, and H. Mark, J. Quant. Spectrosc. Radiat. Transfer, 14, 287 (1974).

35. W. J. Jones in "Infrared Spectroscopy and Molecular Structure," M. Davies, Ed., Elsevier Publishing Company, New York, NY, 1963, pp 111-165.

36. "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," International Union of Pure and Applied Chemistry, Butterworth and Co., London, 1961.

37. R. S. Rasmussen and R. R. Brittain, J. Chem. Phys., 15, 131 (1947).

38. N. R. Draper and H. Smith, "Applied Regression Analysis," John Wiley and Sons, New York, NY, 1966.

APPENDIX

APPENDIX

PARTIAL LIST OF FTS COMMANDS AND PARAMETERS

Each command or parameter entered via the Teletype occupies a line in the printout. The programs listed in the text are separated by commas for convenience in presentation where in actual use, a carriage return and line feed would be used, placing each entry on a separate line. A typical list of parameters would have the following appearance:

```
NSS=4
RES=2
APD=1P
BRK=0,0,1,1
STP=4000
ENP=700
PLM=A
MXY=100
MNY=0
FLS=1
FLD=3.
```

The program would follow:

```
COL
MID
CMP
MID
PLT
!
```

This program would collect and signal-average 4 interferograms, store the resulting file in disk file 3, compute the spectrum, store it in file 4, and do an absorbance plot from 4000 to 700 cm^{-1} of the ratio of this spectrum and a (previously collected, computed and stored) reference spectrum located in file 2.

A. Parameters

1. NSS: Number of scans (sample). An integer between 1 and 32,767.
2. RES: Desired resolution of the output (cm^{-1}). Values may be 16, 8, 4, 2, 1, 0.5, 0.25, or 0.125.
3. APD: Apodization specified. Values may be 1P or 4P. The value IP allows the operator to specify one breakpoint of the apodization function; 4P allows explicit specification of all 4 breakpoints.
4. BRK: Breakpoints for apodization. Four entries, having values between 0 and 1.0.

   BRK and APD together specify the apodizing function which may be varied from triangular to rectangular. The program treats all apodizing functions as trapezoids.
5. PLM: Plot mode. Values may be E (single beam), T (% transmittance), A (absorbance $X10^2$), and others.[22]
6. BSU: Base units. Usually in or cm.
7. XSL: Abscissa scale. Normally cm^{-1} per BSU.
8. YSL: Ordinate scale. The total number of BSU's to be used for the ordinate.
9. MXY, MNY: Maximum and minimum values that will be displayed.
10. STP, ENP: Starting and ending points of the plot; must be integers.
11. ASE: Automatic scale expansion. Values may be Y or N (yes or no). ASE=Y will cause the computer to expand the spectral data between STP and ENP to fill the ordinate.
12. FLS, FLD: Source file, destination file. Used when moving files or using the arithmetic functions.[22]

B. Commands

1. COL: Collect data, under control of NSS and other parameters.
2. MOR: Co-add NSS more scans.
3. CMP: Compute the spectrum from the input data.
4. PLT: Plot the spectrum.
5. PLS: Plot file 1 data on the oscilloscope.
6. MOV: Move data from FLS to FLD.
7. MID: Move and increment destination. Does a move and then sets FLD=FLD+1.
8. STO: Move the contents of file 1 to file 2, regardless of FLS, FLD values.

VITA

Wayne Leon Maddox was born in Memphis, Tennessee, on December 11, 1929. He was graduated from Corbin High School in Corbin, Kentucky, in 1947, and received the BS degree in chemistry from the University of Kentucky, Lexington, Kentucky, in 1951. Since September, 1951, he has been employed as a chemist at the Oak Ridge National Laboratory, Oak Ridge, Tennessee. He entered the Graduate School of The University of Tennessee (Oak Ridge Resident Graduate Program) in the Fall of 1955 and received the MS degree in chemistry in 1960. He reentered the Graduate School in the Fall of 1969.

He is the author or co-author of 18 publications and the holder of 1 patent in the fields of electroanalytical chemistry, instrumental methods of analysis, computer applications in chemistry, instrumentation and apparatus for remote chemical analysis, fast photometric analysis, and tobacco smoke inhalation apparatus and methodology.