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Analysis of Cigarette Smoke by Fourier Transform Infrared Spectrometry

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The application of Fourier transform infrared spectrometry (FT-IR) to the quantitative determination of several components in the gas phase of whole, dilute tobacco smoke was demonstrated. The 18-cm absorption cell 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 of a measurement in 22% smoke ranged from 3% for carbon dioxide to 34% for ethylene. Absorbances measured for isoprene and hydrogen cyanide followed expected concentrations in different cigarette smokes. It was shown that the concentrations of these components remain constant during a 30-s hold-up following each puff on the cigarettes.

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

Tobacco smoke is a complex mixture which consists of a particulate phase that has 10^8 to 10^{10} particles/cm^3 (diameters of most of the particles fall in the range of 0.1 to 1.0 μm) surrounded by a gas phase (GP) containing air and the volatile products of tobacco combustion (1). The particulate matter is conveniently removed from the gas phase by filtration with a glass-fiber Cambridge filter (2) which removes 99.9% of particles greater than 0.3 μm in diameter; this is the customary basis for an arbitrary definition of the two phases.

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. At present, chemical analysis of smoke in exposure chambers is accomplished by withdrawing a portion of the smoke from the chamber and determining selected com-

ponents in that sample by gas chromatography (GC) (3). Up to now, dosimetry data have been available after the fact, e.g., by addition of radioactive tracers to the tobacco and sacrifice of the animals immediately after a short exposure to the smoke (4). An instrument that could frequently observe in situ some of the smoke constituents would enable the acquisition of data on chemical composition and hence dosimetry immediately. Rapid-scan Fourier transform infrared (FT-IR) spectrometry is characterized by speed and sensitivity which may make it an attractive approach for such on-line analysis of smoke in exposure chambers.

Lephardt and Vilcins (5, 6) described the application of FT-IR to the study of kinetics in undiluted *gas-phase* smoke. A review of the work by Vilcins and Lephardt (7) has appeared since the submission of this paper. We are grateful to one of our reviewers for calling our attention to this reference. We have applied FT-IR to the determination of certain gas-phase components in *whole* smoke under conditions (path length, cell volume, dilution, exposure time) which might be encountered in an animal exposure experiment. Strong absorption bands due to carbon dioxide, carbon monoxide, methane, water, and hydrogen cyanide are readily observed in the mid-IR spectrum of dilute whole smoke. Other components such as isoprene, methanol, and ethylene, yield weaker yet analytically useful bands.

EXPERIMENTAL

Materials. *Cigarettes.* The University of Kentucky Standard Reference Cigarette—1R1, and other special cigarettes, manufactured to National Cancer Institute (NCI) specifications (8), are supplied by the NCI to the Oak Ridge National Laboratory and other NCI contractors for research in smoking and health. Codes 1, 6, 13, and 16 from the first experimental series were used. Code 1 is the Kentucky Reference cigarette and the 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.

Apparatus. *Spectrometer.* The spectrometer used was the Digilab Model FTS-20 (Digilab, Inc., Cambridge, Mass.), a high-resolution, rapid-scanning, computer-controlled instrument with a range capability of 10 to 10 000 cm^{-1} and having nominal resolutions of 16, 8, 4, 2, 1, 0.5, 0.25, and 0.125 cm^{-1}. 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 a TGS (triglycine sulfate) pyroelectric bolometer. The beamsplitter is a film of germanium deposited on a potassium bromide substrate. Data acquisition times during each scan with this instrument are 0.4 s at 8 cm^{-1} resolution, 1.6 s at 2 cm^{-1} resolution, and 3.2 s at 1 cm^{-1} resolution. Running times are longer; with the software employed,
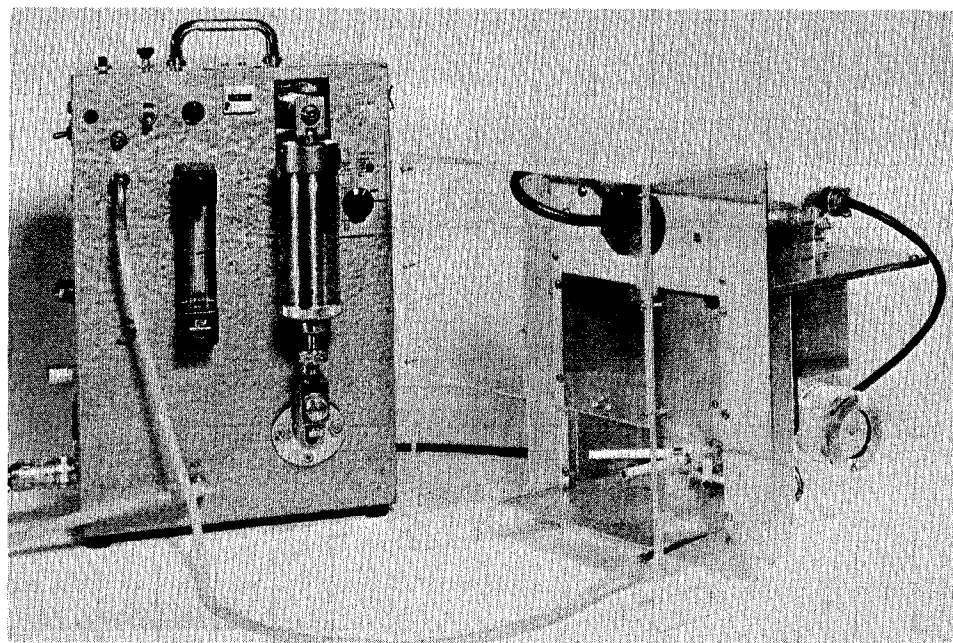
Figure 1. Photograph of the smoking apparatus

using no programmed delay between scans, the first scan at RES = 2 (resolution setting of 2 cm^{-1}) commences about 2 s after the execute command and succeeding scans start at approximately 3.7-s intervals.

Smoking Machine. The cigarettes were smoked with the apparatus shown in Figure 1. This is basically an inhalation smoker (9) in which the exposure chamber has been modified to fit into the cell compartment of the FTS-20 spectrometer. The smoke chamber, indicated in cross section in Figure 2, is a rectangular Plexiglas box with cylindrical extensions which allow an 18-cm optical path. Its volume is 475 cm^3. The device shown on the left in Figure 1 is a "Filamatic Vial Filler" (National Instrument Company, Inc., Baltimore, Md.) which serves as an intermittent pump. A puff begins when the Filamatic pump is actuated and the cigarette holder/valve (b, Figure 2) 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 a 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, ensures rapid and continued mixing of the smoke. The solenoid valve, i, admits compressed air to purge smoke from the chamber between puffs. A throttled rotameter, j, controls and measures the flow rate of the purge air. The cigarette holder (Figure 1) allows parallel smoking of 3 cigarettes; glass capillaries with 72-mm RTD (*resistance-to-draw*, mm H$_2$O, at an air flow rate of 17.5 cm^3/sec) were inserted in the vacant holes when fewer cigarettes were smoked. The cigarette fittings were designed so that Cambridge filter holders could be attached when GP smoke was desired.

Standard puff parameters (interval, 60 s; duration, 2 ± 0.1 s; volume, 35 ± 0.5 cm^3) were achieved by mechanical and electrical adjustments of the apparatus: A repeat cycle timer initiates puffs at 1-min intervals, the speed of the pump is adjusted to obtain the desired downstroke (puff) duration, and the volume of air drawn during the puff through a 72-mm RTD is adjusted by setting the arm length of the Filamatic crank.

Pressure Drop Tester. A "Filtrona" Mark 4 Pressure Drop Tester (Cigarette Components, Ltd., Wembley, Middlesex, England) was used to measure RTD.

Procedures. *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 (8) for cigarette conditioning and analytical smoking were followed closely during this investigation. The cigarettes of Codes 1,
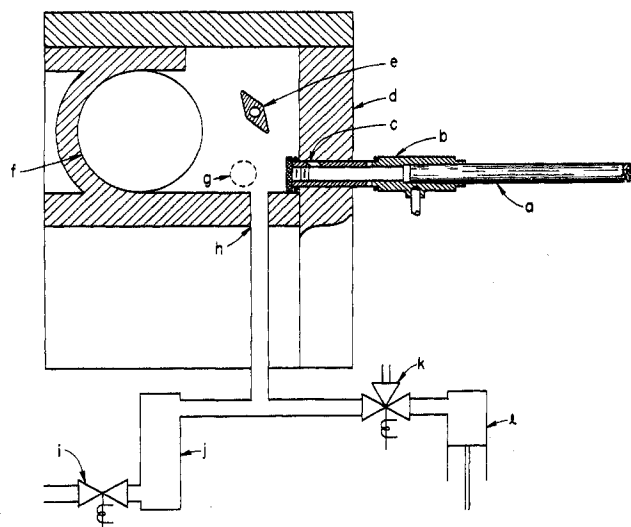

Figure 2. Schematic diagram of the smoking apparatus

6, and 16 were selected for weights within ±20 mg of the batch mean, and for RTD within ±10 mm H$_2$O of the mean from large batches of cigarettes which had been conditioned in an atmosphere of 24 °C and 60% relative humidity for at least 48 h. It was impossible to select the highly variable Code 13 cigarettes to these specifications; they were chosen by visual inspection. Selected cigarettes were kept in a desiccator vessel in which the relative humidity was maintained at 60% by a mixture of 74% glycerol and 26% water (1) until just before they were smoked, usually within a few days and never after more than 2 weeks. All cigarettes were lit with matches (utilizing a holder for two matches so that three cigarettes could be lit simultaneously by one person). Data were obtained from puffs 2–11 of the Code 1 cigarettes, 2–10 of Code 6, 2–8 of Codes 13 and 16. These puff numbers left butts of approximately 23-mm length.

In a typical inhalation experiment, the "stand time" during which smoke is allowed to remain in the chamber after each puff, including the 2-s required to admit the puff, is about 30 s. Following this time, compressed air is admitted to the chamber to purge the spent smoke and provide fresh air for the experimental subjects. A 30-s stand time was adopted for the chemical experiments described herein. The purge air was passed through Drierite.

RESULTS AND DISCUSSION

Smoke Spectra. Typical smoke spectra taken with RES = 2 are shown in Figure 3. The possibilities of using lower
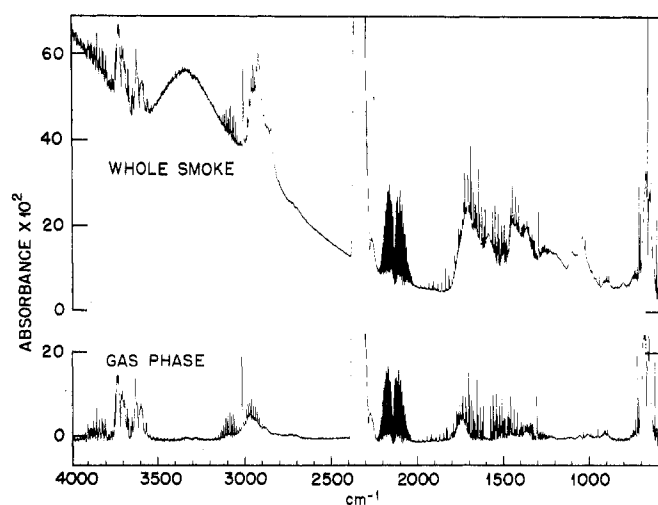
Figure 3. Infrared absorption spectra of smoke with RES = 2

Figure 4. Superimposed spectra of whole smoke and CO_2, 750–700 cm^{-1}

resolution in order to obtain more scans to improve the S/N ratio, or of higher resolution to secure more spectral information were considered. The weaker lines were not found in the spectrum of dilute smoke at a resolution of 8 cm^{-1}; therefore, the possibility of using low resolution was dismissed. Apparently, no additional usable spectral information was gained at the higher resolution (setting RES = 1) while the noise and the time to acquire and compute the spectra were significantly increased. For smoke chamber analysis, RES = 2 was used to get the maximum resolution consistent with obtaining data for two distinctly separated periods during the 30-s puff stand time. The spectra were computed without apodization or zero-filling (10), and were plotted without smoothing.

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

A systematic search of the smoke spectrum was made by scale-expanding sections of the spectrum in the vicinity of every band of these component spectra. Bands that had intensities distinctly above the noise level in 22% smoke (3 cigarettes) were chosen for further study. The spectral features of NO and CHONO (7) were not observed at our usual dilution level. A summary of the lines chosen for analysis is given in Table II. Assignment of these lines, except that of HCN, was confirmed by superimposition of the spectral plots of pure constituents on that of smoke, as illustrated in Figure 4. This Figure shows that the 720 cm^{-1} line in smoke is due to CO_2 (12). 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 (7).

Measurement. Smoke spectra were plotted for quantitative measurement by scale-expanding sections surrounding the lines of interest. The sections expanded are shown in Figure 5. Baselines were drawn under the peaks as indicated. Usually, only the R branch of the CO band 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}. The C_2H_4 band, which was measured at 949 cm^{-1}, has several rotational lines in the 906–893 cm^{-1} vicinity where the lines of isoprene are seen. These diminish rapidly in intensity toward the lower frequency. This prompted a decision to draw the baseline for isoprene under the line at 893 cm^{-1} only. Figure 6 presents the contrast between the smoke spectra of the Code 1 cigarette,
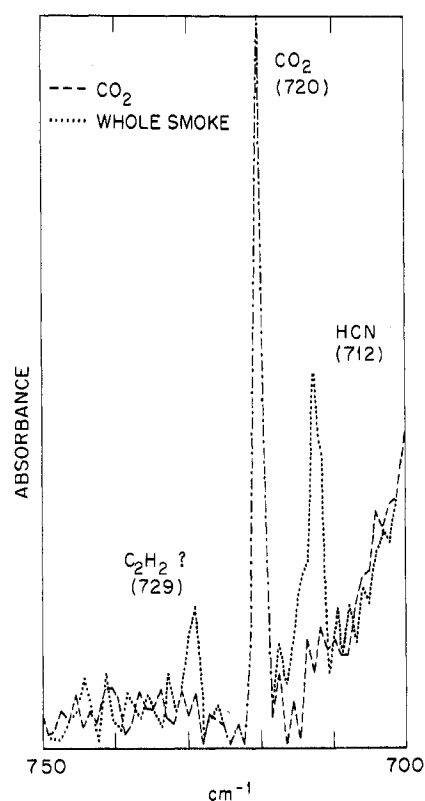
Table I. Major Gas Phase Components

Component	Yield, μg per cigarette	Ref
Acetaldehyde	700–1300[a]	8
Acetone	400–500	11, 12
Acrolein	50–140[a]	8
Carbon dioxide	68×10^3	3
Carbon monoxide	16×10^3	3
Ethylene	200	11
Hydrogen cyanide	60–240[a]	8
Isoprene	15–740[a]	8
Methane	770	11
Methanol	100–200	11
Water	5.8×10^3	3

[a] Range covered by NCI variants.

Table II. Frequencies Selected for Analysis

Component	Frequency, (cm^{-1}) Obsd	Lit	Ref.
CO	2169	2169.2	14
CO_2	720	720.5	13
CH_4	1306	1306.2	13, 15
C_2H_4	949	949.2	13, 15
CH_3OH	1033	1033.9	13
HCN	712	712.1	13, 16
C_5H_8	893	893	17

which delivers an appreciable quantity of isoprene and of Code 13, which delivers essentially none. In the Code 1 spectrum the isoprene lines at 906 and 893 cm^{-1} are admittedly not well defined, but measurement of the absorbance at 893 cm^{-1} is feasible. In the Code 13 spectrum on the other hand, only noise is apparent at these frequencies. A common baseline was drawn for the CO_2 (720 cm^{-1}) and HCN (712 cm^{-1}) lines.
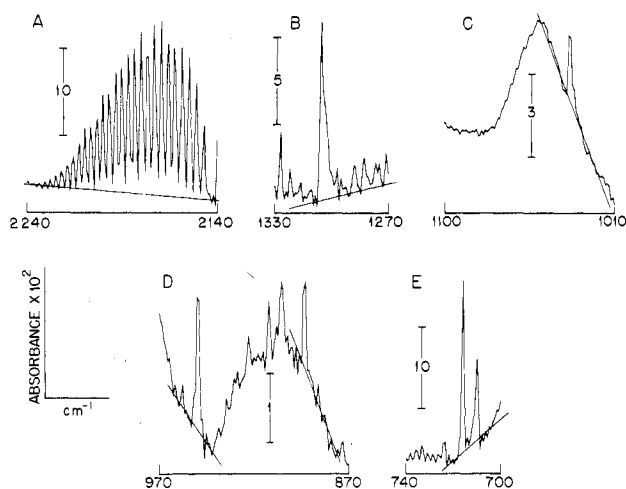
Figure 5. Sectioned whole-smoke spectrum. (A) CO; (B) CH₄; (C) methanol; (D) C₂H₄, isoprene; (E) CO₂, HCN

Figure 7. Variation of concentration with puff number

Table III. Linear Regression Constants for Standards

Component	A[a] (intercept)	B (slope)	S[b]
CO	5.18	11.8	0.45
CO₂	1.08	8.36	0.69
CH₄	1.01[c]	76.8	0.95
C₂H₄	0.480	120	0.18
CH₃OH	0.069[c]	119	0.09

[a] Y = absorbance $\times 10^2$ = A + B (concn). [b] Standard deviation of Y. [c] 95% confidence limits include the origin.
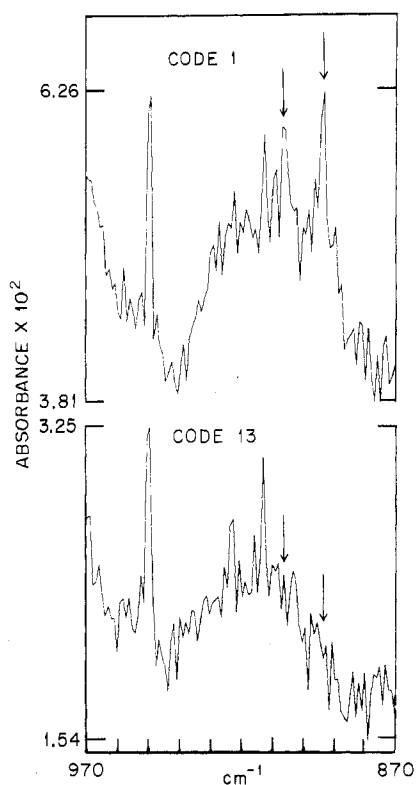

Figure 6. Whole-smoke spectra in the 970–870 cm⁻¹ region

Calibration. Five components were studied quantitatively by calibration curves plotted for standard mixtures of CH₄, CO, and CO₂, and for dilute C₂H₄ and CH₃OH vapor mixed with dry air in Saran gas-sampling bags. Samples were taken from the bags and introduced into the partially evacuated smoke chamber with a large hypodermic syringe, or the chamber was flushed with an excess of the mixed gas standard from a cylinder. At least 3 samples were taken at each of 3 concentrations of each substance. Absorbance measurements were made, as in smoke, on scale-expanded portions of the spectra, and straight lines relating absorbance to concentration were fitted to the data by least-squares formulas (*18*). The constants computed for these lines are given in Table III. The intercepts were statistically significant at the 95% confidence level for CO, CO₂, C₂H₄, and not significant for CH₄ and CH₃OH.
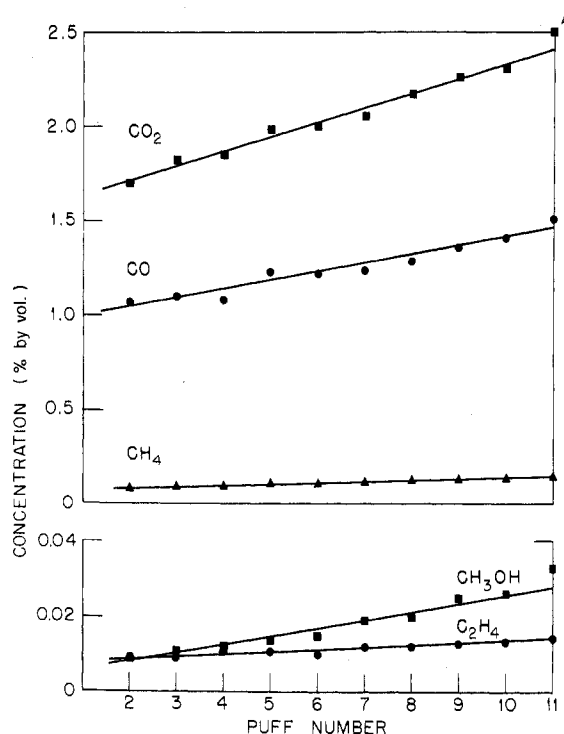
Variability. *Puff-to-Puff and Sample-to-Sample.* Figure 7 summarizes the results obtained by smoking Code 1 cigarettes in samples of 3 simultaneously and collecting 4 spectral scans during every puff after the first. These data, therefore, represent measurements averaged over a period from approximately 7 to 22 s after the puff started. An upward trend in the concentration is to be expected (*1*) as a cigarette is smoked. This trend is clearly seen in the plots which show the puff-by-puff average chamber concentrations for 8 samples of 3 cigarettes each. These observations show that in dilute whole smoke, with an 18-cm optical path, real concentration changes in the GP components can be measured. Illustrative data, obtained from the determination of methane are presented in Table IV. Similar data obtained for the other components showed column (between-sample) standard deviations of 4–14% for CO, 3–9% for CO₂, 9–34% for C₂H₄, and 8–20% for CH₃OH.

Between Codes. Puff-by-puff data were also taken for cigarettes of Codes 6, 13, and 16. Five samples, 3 cigarettes each, were smoked of Codes 6 and 13, and 4 samples, 2 cigarettes each, of 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—primarily of HCN and isoprene—between codes. The results of this experiment are shown in Table V. Comparison was made between average concentrations (absorbances for HCN and isoprene) for all measured puffs and cor-

Table IV. Chamber Concentrations of CH_4 [a,b]

Sample	Puff No.										
	2	3	4	5	6	7	8	9	10	11	Av.
1	0.079	0.093	0.097	0.099	0.104	0.096	0.125	0.122	0.137	0.135	0.109
2	0.085	0.095	0.085	0.098	0.107	0.116	0.134	0.126	0.128	0.143	0.112
3	0.077	0.102	0.104	0.117	0.115	0.118	0.113	0.134	0.134	0.154	0.117
4	0.078	0.076	0.099	0.107	0.108	0.114	0.129	0.129	0.131	0.146	0.112
5	0.085	0.098	0.094	0.112	0.122	0.110	0.139	0.134	0.135	0.147	0.118
6	0.083	0.087	0.098	0.113	0.103	0.115	0.105	0.130	0.135	0.145	0.111
7	0.077	0.096	0.094	0.096	0.109	0.120	0.128	0.137	0.146	0.146	0.115
8	0.102	0.098	0.105	0.125	0.105	0.127	0.131	0.134	0.137	0.156	0.122
Av.	0.083	0.093	0.097	0.108	0.109	0.115	0.125	0.131	0.135	0.146	0.114
% RSD	10	9	7	10	6	8	9	4	4	4	4

[a] 3 cigarettes/sample, Code 1 cigarette. [b] Vol % in chamber.

Table V. 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
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 Ref. 7. [d] Relative to Code 1. [e] Not measurable.

Table VI. Comparison of FT-IR and GC Analysis [a]

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	0.90	0.47
CH_4	0.11	0.10	0.056	0.066	0.032	0.031
C_2H_4	0.011	0.013	0.005	0.008	0.004	0.004

[a] Vol % in the chamber.

responding data for Code 1 cigarettes. The FT-IR observations paralleled the expected yields.

Comparison with GC Analysis. Table VI shows the results of experiments in which samples of 1, 2, and 3 Code 1 cigarettes were smoked for analysis by FT-IR, compared with a similar set in which concentrations were measured by GC. 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 s; the volume drawn in 25 s 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 fair agreement between the measurements made by GC and those made by FT-IR. At these low concentrations, taking into account the different batches of cigarettes in different laboratories, the factor of 2 shown here is not too surprising.

Effect of Smoke Aging. An obvious application of a technique proposed for studying inhalation chamber experiments is in observation of changes in the chamber environment occurring during each puff. Whole-smoke spectra recorded early and late in the stand time were compared by collecting 2 scans between 4–9 s and 2 scans between 24–29 s after the puff start. Aside from the generally lower scattering at wavenumbers

above 2500 cm^{-1} and the fact that the water line at 1700 cm^{-1} is more intense late in the puff, little other change was 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 7 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 between measurements taken early and late in the puff stand time.

Time of Analysis. While no attempt was made, as such, to minimize time spent in analysis, notes were kept on the approximate time expenditures involved in the FT-IR experiments. To obtain data on the 7 components studied for all puffs, 2 through 11, required 65 min to compute and plot with automatic scale (ordinate) 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 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 by, e.g., plotting and measuring spectra only for every other puff.

An important point that follows from the results obtained is that the FT-IR technique allows measurement of several smoke components during a single puff. Since the FTS-20 spectrometer is capable of collecting 7 scans at RES = 2 during the 30-s stand time, and could compute and plot data for one or two components during the succeeding puff, an essentially "real-time" monitoring procedure should be possible. This is not possible with the present GC procedures, which depend on accumulation of a sample over the whole delivery of a cigarette.

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CORRESPONDENCE

Determination of Mercury by Atomic Absorption Spectrometry with Graphite Tube Atomization

Sir: The high volatility of mercury—even at room temperature—results in mercury being a very difficult element to determine by electrothermal atomization atomic absorption: even the drying of a mercury solution will produce a significant loss of mercury. It is this high volatility of mercury, and its ability to produce a monatomic vapor, which made possible Woodson's (*1*) flameless atomic absorption determination of mercury in 1939, a determination which predated the classical work by Walsh (*2*) on atomic absorption with flame atomization. The determination of mercury by atomic absorption with an air–acetylene flame is not very sensitive [sensitivity for 1% absorption = 7.5 μg/ml (*3*)], and although the toxicity of mercury has been recognized for many years, it is only within the past seven that methods have become available which are capable of determining mercury reliably at the low levels encountered in biological and environmental samples. These methods can be traced to the work of Brandenberger and Bader (*4, 5*) and Hatch and Ott (*6*); variations of the reduction–aeration continuous recirculation technique for the cold vapor determination of mercury, introduced by Hatch and Ott, are now employed in many laboratories. These highly sensitive techniques have led to a large volume of data on mercury levels.

While offering considerable sensitivity, the cold vapor method for mercury is essentially unique for this element, and consequently would not be easily applicable to a multielement atomic absorption determination utilizing a heated graphite tube as atom cell (*7*). Additionally, for the determination of trace metals in urine by ashing and atomizing directly in the graphite tube, the high volatility of mercury will preclude any ashing of the urine matrix.

The chemical stabilization of mercury in a graphite tube has been described by Ediger (*8*). He reported that the addition of ammonium sulfide to mercury in nitric acid solution allowed ashing temperatures of up to 300 °C to be employed; a detection limit of 0.2 ng was achieved. Issaq and Zielinski (*9*) studied the determination of mercury in a graphite tube atomizer, and reported a 50X signal enhancement by the addition of hydrogen peroxide to aqueous mercury solutions. They found that ashing temperatures up to at least 200 °C could be used, and postulated the formation of a stable peroxy–mercury complex. A correspondence by Owens and Gladney (*10*) concluded that the presence of hydrochloric acid is desirable as an additional stabilizer when hydrogen peroxide is used to stabilize mercury in a graphite furnace.

This correspondence reports our study on the chemical stabilization of mercury in the heated graphite tube by the use of hydrochloric acid and hydrogen peroxide.

EXPERIMENTAL

Apparatus. The atomic absorption spectrophotometer used was a Perkin-Elmer Model 300S equipped with background correction; absorbance values were recorded with an Oxford Instruments series 3000 potentiometric recorder (response time for full scale deflection 0.25 s). For flame atomization an air–acetylene flame was supported on a 10-cm single slot titanium burner, but for the principal part of this work the Perkin-Elmer HGA 74 electrothermal furnace was