

Determination of Ethylene and Isoprene in the Gas Phase of Cigarette Smoke by Infrared Spectroscopy*

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INTRODUCTION

Ethylene and isoprene in cigarette smoke have been determined quantitatively by means of infrared and mass spectrometric (1, 2) and gas chromatographic (3, 4, 5) methods. Because of the specificity of the infrared analysis, a study was made to investigate the possibility of applying the infrared instrumentation to a gas phase cigarette smoke analysis which would be sufficiently rapid to permit the determination of isoprene and ethylene on a puff-by-puff basis. This paper describes such an infrared method for gas phase smoke analysis. The method can be applied to determine isoprene and ethylene deliveries per cigarette and per a specific puff. It also can be used to test filter efficiency for isoprene and ethylene removal.

EXPERIMENTAL

A. Materials and Equipment

The infrared spectra were recorded with a Perkin-Elmer Model 221 double-beam infrared spectrophotometer equipped with a sodium chloride prism and ordinate scale expansion. The cigarettes were smoked on a five-port syringe type smoking machine built to have a minimum dead volume. The gas phase smoke was collected and analyzed in a Perkin-Elmer one-meter gas cell. A solenoid unit between the smoking machine and the gas cell regulated the collection of smoke samples. A plastic housing unit was placed around the smoking machine to eliminate draft.

Ethylene gas, 99.5% minimum purity, obtained from Matheson Gas Products and isoprene purchased from Eastman Organic Chemicals were used to standardize the procedure.

B. Preparation of Working Curves

The working curves for isoprene and ethylene were prepared by placing known amounts of these compounds in gaseous state in the one-meter gas cell and recording their infrared spectra between 10.3 and

11.8 μm employing the 5X ordinate scale expansion. The cell was brought to atmospheric pressure with air prior to the analysis. The instrument was adjusted to the manufacturer's recommended settings. Known gaseous isoprene was obtained by placing freshly distilled liquid isoprene into an evacuated glass flask equipped with a pressure gauge and a septum through which a predetermined amount of sample was withdrawn.

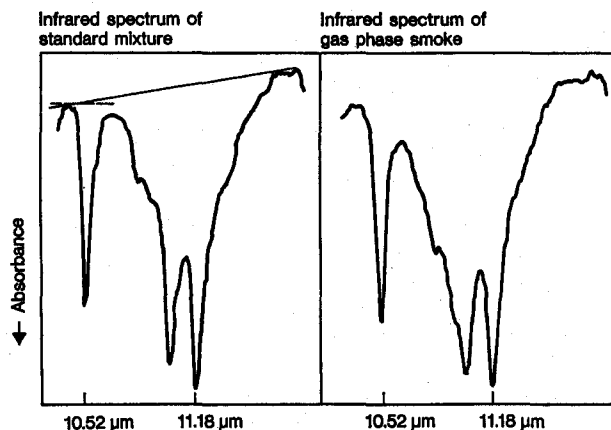
The isoprene working curve and absorptivity was determined from the corrected absorbance of the 11.18 μm band. The background correction was taken from the tangent drawn between 10.37 and 11.80 μm (Figure 1). A linear relationship between 11.18 μm band intensity and concentration existed in the normal working range from 180 to 450 micrograms.

The ethylene working curve was made by plotting the corrected absorbance of the 10.52 μm band versus concentration taking as the background correction the line parallel to 100% T from 10.37 μm (Figure 1). A linear relationship between the absorbance band intensity and concentration existed in the range from 50 to 200 micrograms.

C. Cigarette Smoke Collection and Analysis

The cigarettes were smoked to the desired butt length on a five-port syringe type smoking machine set to take a 35 cm^3 puff per cigarette of 2 seconds duration at 60-second intervals. The number of cigarettes smoked

Figure 1. Infrared spectra of ethylene and isoprene.



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Figure 2. Diagram of the smoking system.

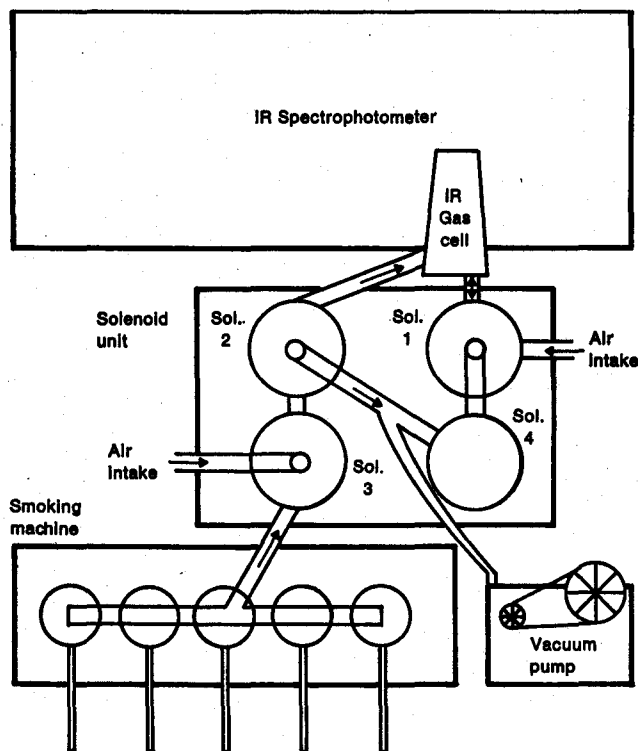
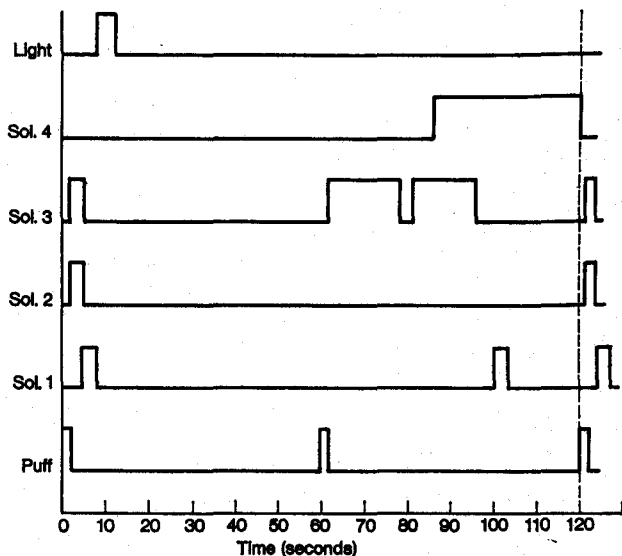


Figure 3. Timing diagram.



at one time could be varied from 1 to 5 depending on the isoprene and ethylene deliveries. The cigarettes were conditioned for moisture content prior to analysis. The smoke was drawn through a conditioned Cambridge filter pad and delivered through a solenoid valve system into an evacuated one-meter gas cell positioned in the spectrophotometer for the complete analysis. The cell was brought to atmospheric pressure with air, and the infrared spectrum was recorded from 10.30 to 11.80 μm . It required 75 seconds to cover this region. Therefore, this method was capable of analyzing either odd or even numbered puffs. An automatic solenoid system was designed to regulate the following steps:

[1] to evacuate the gas cell to be ready to receive the odd (even) puff, [2] to bring the cell to atmospheric pressure, [3] to remove the smoke sample from the cell without a residual sample left in the cell, [4] to discard the even (odd) puff without leaving residual smoke in the connecting lines (Figure 2). The timing diagram of the solenoid system shows the step-by-step action of the sampling procedure (Figure 3). The timing sequence was as follows:

- 0 – 2 seconds: The first puff, 35 cm^3 volume of 2 seconds duration, was taken;
- 2 – 5 seconds: Solenoids # 2 and # 3 opened to transfer the sample to the gas cell;
- 5 – 8 seconds: Solenoid # 1 opened to bring the cell to atmospheric pressure;
- 8 – 12 seconds: Ready light signaled the operator to start the scan;

- 60 – 62 seconds: Second puff was taken;
- 62 – 78 seconds: Solenoid # 3 opened to the vacuum pump to discard the second puff and clear the lines of any smoke;
- 78 – 81 seconds: Solenoid # 3 opened to air to flush the lines;
- 81 – 96 seconds: Solenoid # 3 opened to pump to reevacuate the lines;
- 86 – 120 seconds: Solenoid # 4 opened to pump to remove puff # 1 and evacuate the gas cell;
- 100 – 102 seconds: Solenoid # 1 opened to air to flush the gas cell;
- 120 – 122 seconds: Puff # 3 was collected, and the cycle was repeated.

For the "even" number puff analysis, the same sequence was followed except that this time the solenoid unit was set to discard the "odd" number puffs and collect the "even" number puffs in the gas cell. In this manner, either the "odd" or "even" number puffs were analyzed from one set of cigarettes. A second set was smoked to get the other set of puffs. The deliveries of ethylene and isoprene for each puff were calculated using the corrected absorbances of the 10.52 and 11.18 μm bands, respectively, and the absorptivities or working curves obtained from gas mixtures containing known amounts of isoprene and ethylene. The deliveries per cigarette of these two components were obtained by adding the individual puffs.

D. Aging Effects

Gas phase cigarette smoke was introduced in the one-meter gas cell, and the contents were analyzed repetitively for ten minutes. No changes were observed in the concentration of ethylene in this period. The

isoprene concentration showed no significant decrease for about three to four minutes. After about eight minutes, however, the isoprene concentration had decreased by about 20 percent. No reduction in isoprene or ethylene was noted when only the pure gases of these two compounds were subjected to the same type procedure, thereby showing that the isoprene decrease in smoke was caused by reaction of isoprene with another smoke component. No adverse effects due to the isoprene reaction in gas phase smoke were present in this method because the analysis was completed in 75 seconds.

RESULTS AND DISCUSSION

The infrared spectrum of the gas phase smoke showed a ratio difference of the 11.03 and 11.18 μm isoprene bands and a change in the shape of the 11.03 μm band when compared with the mixture of the known compounds (Figure 1). This interference by an unknown compound with the 11.03 μm isoprene band eliminated use of this band for quantitative measurements. The 11.18 μm band was selected for quantitative determination of isoprene in cigarette smoke. To verify the results obtained by the infrared technique, two different types of cigarettes were smoked, and the isoprene delivery in the gas phase was determined by a gas chromatographic technique as well as by the infrared method. No significant differences in the results from the two different methods were observed (6). Therefore, it was concluded that the 11.18 μm isoprene band was suitable for the quantitative determination.

A minor modification in the solenoid unit coupled with installation of a plastic shield to prevent draft improved the precision of this method over values previously reported (7). The precision of this method based on ten replicate determinations of gas phase smoke from a

Table 1. Isoprene and ethylene deliveries from commercial cellulose acetate filter cigarettes.

Set	Isoprene ($\mu\text{g}/\text{cigt.}$)	Ethylene ($\mu\text{g}/\text{cigt.}$)
1	583	196
2	599	200
3	592	197
4	594	195
5	603	199
6	606	203
7	597	197
8	606	204
9	588	194
10	593	199
Average	596	198
Standard deviation (S. D.)	7.6	3.3
% of $2 \times \text{S. D.}$	2.6	3.3

Figure 4. Isoprene concentration in cigarette smoke ($\mu\text{g}/\text{puff} \pm$ standard deviation).

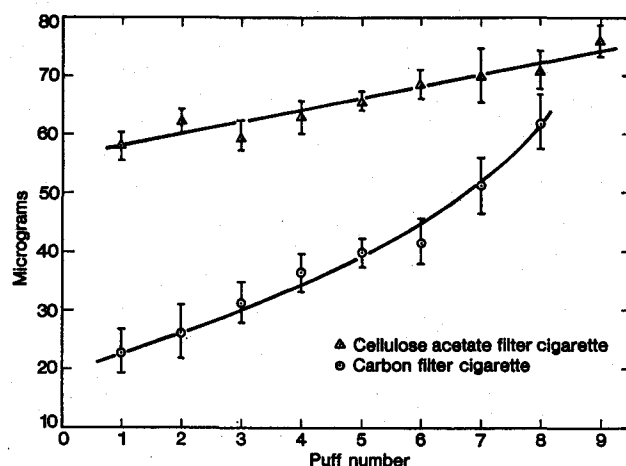
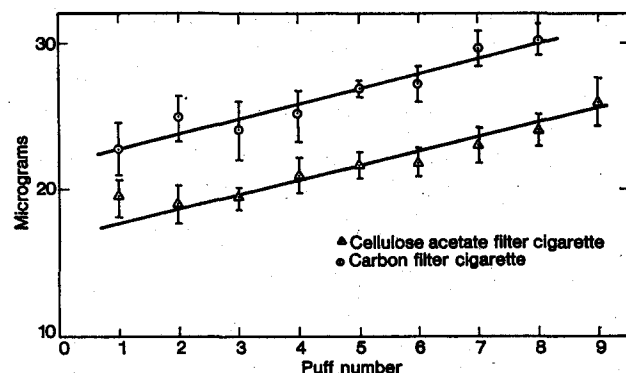


Figure 5. Ethylene concentration in cigarette smoke ($\mu\text{g}/\text{puff} \pm$ standard deviation).



commercial cellulose acetate filter cigarette was 3% at the 2-sigma level for both isoprene and ethylene (Table 1). The results of typical analyses of isoprene and ethylene in gas phase smoke from different types of cigarettes are shown in Table 2.

The puff-by-puff deliveries of isoprene (Figure 4) and ethylene (Figure 5) for a commercial carbon filter cigarette and a cellulose acetate filter cigarette showed a gradual linear increase in ethylene delivery for both types of cigarettes. The isoprene delivery for the cellulose acetate filter cigarettes also showed a gradual increase similar to that of ethylene. Isoprene, however, was removed substantially by the carbon filter on the early puffs. As the filter became poisoned by the smoke, the carbon filter efficiency decreased and the isoprene

Table 2. Isoprene and ethylene concentrations in gas phase of cigarette smoke.

Cigarette	Isoprene in $\mu\text{g}/\text{cigt.}$	Ethylene in $\mu\text{g}/\text{cigt.}$
Kentucky Reference	600	242
Cellulose acetate filter	596	198
Carbon filter	314	206
All bright	1040	333

Table 3. Deliveries in $\mu\text{g}/\text{cigarette}$ and precision ($\% \times 2 \times \text{standard deviation}$).

Type of cigarette	Determined from					
	A. All puffs		B. Even no. puffs		C. 5th puff	
	Delivery	Precision	Delivery	Precision	Delivery	Precision
1) Isoprene						
Cellulose acetate filter	596	2.6	597	5.7	594	5.4
Carbon filter	314	6.2	341	11.2	320	21.6
2) Ethylene						
Cellulose acetate filter	198	3.3	197	6.8	194	8.0
Carbon filter	211	2.9	215	4.7	214	4.3

delivery increased rapidly on the later puffs. The eighth puff had an isoprene delivery comparable to that of the cellulose acetate filter cigarette. The precision for the isoprene delivery of the carbon filter cigarette was not as good as for the cellulose acetate filter cigarettes. This was believed to be caused by the variation of the individual carbon filters. The fifth puff was found to be the most reproducible puff for both types of cigarettes. Ethylene deliveries for the lighting puff are significantly influenced by the manner of lighting the cigarette. This factor sometimes caused the values to be higher or lower than expected for the lighting puff.

In situations where the results were needed quickly, the total deliveries of isoprene and ethylene were calculated from only the even number puffs. This was accomplished by multiplying the determined average delivery per puff from the analyzed even number puffs by the total number of puffs obtained from the cigarette. Evaluation of the data showed that in most cases this type of calculation of the total delivery of isoprene and ethylene in micrograms per cigarette was sufficient to obtain accurate results with a small loss in precision (Table 3). The total delivery values obtained from the fifth puff only showed that the fifth puff was the most representative puff of the carbon and cellulose acetate filter cigarettes analyzed. The odd number puffs only were not considered for total delivery calculations because of the large influence of the variable lighting puff on the final values.

Gas phase compounds absorbing in the 10.3 to 11.8 μm region would interfere with the ethylene and isoprene determination in the gas phase cigarette smoke. However, from the large number of different cigarettes smoked for this analysis, only one experimental type cigarette produced a component which prevented the ethylene and isoprene determination in its gas phase of smoke.

SUMMARY

An infrared method was developed for the quantitative determination of ethylene and isoprene in the gas phase of cigarette smoke. The smoke was collected by smoking the cigarettes on a five-port syringe type smoking

machine and transferring it to a gas cell positioned in a double-beam infrared spectrophotometer for the duration of the analysis. The smoke transfer to the gas cell and its subsequent removal from the cell were accomplished by connecting the smoking machine to a vacuum pump through the automated solenoid valve unit which controlled the analysis system. In this manner any specific puff of interest could be analyzed for the ethylene and isoprene concentrations by measuring the corrected absorbance of the 10.52 μm and 11.18 μm absorbance bands, respectively. Total deliveries of ethylene and isoprene per cigarette were obtained by adding the deliveries from the individual puffs. The puff-by-puff delivery profile also was obtainable at the same time. In addition filter efficiency for ethylene and isoprene removal may be determined by this method. The relative standard deviation at the two-sigma level was 3% for ethylene and isoprene in the gas phase smoke from commercial cellulose acetate filter cigarettes. The analysis of a particular puff of smoke required only 75 seconds insuring the analysis of a relatively fresh smoke with good reproducibility and accuracy.

ZUSAMMENFASSUNG

Für die quantitative Bestimmung von Äthylen und Isopren in der Gasphase von Zigarettenrauch wurde eine Infrarot-Methode entwickelt. Der Rauch wird durch Verrauchen der Zigaretten auf einer Kolben-Rauchmaschine mit einem Rauchkopf für fünf Zigaretten gewonnen und in eine Gaszelle geleitet, die sich während des Analysenvorganges in einem doppelstrahligen Infrarot-Spektrophotometer befindet. Die Überleitung des Rauches zur Gaszelle und die nachfolgende Rückgewinnung desselben erfolgt durch Anschließen der Rauchmaschine an eine Vakuumpumpe mittels einer automatischen Magnetventileinheit, die das Analysensystem steuert. Auf diese Weise kann jeder gewünschte Zug auf die Konzentration von Äthylen und Isopren dadurch untersucht werden, daß die korrigierte Absorption der 10,52- μm - bzw. 11,18- μm -Absorptions-Banden gemessen wird. Der Gesamtgehalt an Äthylen und Isopren je Zigarette ergibt sich durch Addierung der Ausbeuten der einzel-

nen Züge. Gleichzeitig können für die einzelnen Züge nacheinander die Ausbeuteprofile erstellt werden. Darüber hinaus ist es möglich, die Filterwirksamkeit für Äthylen und Isopren zu bestimmen. Für den Gehalt an Äthylen und Isopren der Gasphase des Rauches von handelsüblichen Cigaretten mit Celluloseacetatfilter ergab sich bei einer Standardabweichung von $\sigma \approx 2$ ein Variationskoeffizient von 3%. Die Untersuchung eines einzelnen Rauchzuges erfordert einen Zeitraum von nur 75 Sekunden und sichert die Analyse von verhältnismäßig frischem Rauch bei guter Reproduzierbarkeit und guter Genauigkeit.

RESUME

On a développé une méthode de spectroscopie infrarouge pour déterminer quantitativement l'éthylène et l'isoprène dans la phase gazeuse de la fumée de cigarette. La fumée a été recueillie en fumant les cigarettes dans une machine à cinq orifices du type à seringue, puis en la transférant dans une cellule à gaz, logée dans un spectrophotomètre à double faisceau pour la durée de l'analyse. Le transfert de la fumée dans la cellule à gaz, et sa récupération ultérieure ont été obtenus en connectant la machine à fumer à une pompe à vide, au moyen du dispositif automatique à valve solénoïde qui contrôle le système analytique. De cette manière, chaque bouffée intéressante pouvait être analysée quant à sa teneur en éthylène et isoprène, en mesurant l'absorption corrigée dans les bandes de 10,52 μm et 11,18 μm respectivement. Les productions totales d'éthylène et d'isoprène par cigarette sont obtenues par intégration des résultats des bouffées individuelles, ainsi que la courbe bouffée par bouffée. De plus, l'efficacité des filtres pour l'élimination de l'éthylène et de l'isoprène peut être étudiée par cette méthode. La déviation standard relative au niveau de 2σ est de 3% pour l'isoprène et l'éthylène dans la phase gazeuse de la fumée de cigarettes commerciales à filtre d'acétate de cellulose. L'analyse d'une

bouffée particulière de fumée ne prend que 75 secondes, ce qui permet l'analyse avec une bonne reproductibilité et une bonne précision de la fumée relativement fraîche.

REFERENCES

1. Osborne, J. S., S. Adamek and M. E. Hobbs: *Anal. Chem.* 28 (1956) 211.
2. Philippe, R. J., and M. E. Hobbs: *Anal. Chem.* 28 (1956) 2002.
3. Patton, H. W., and G. P. Touey: *Anal. Chem.* 28 (1956) 1685.
4. Philippe, R. J., H. Moore, R. G. Honeycutt and J. M. Ruth: *Anal. Chem.* 36 (1964) 859.
5. Newsome, J. R., V. Norman and C. H. Keith: *Tobacco Science* 9 (1965) 102.
6. Parrish, M. E.: Personal communication of gas chromatographic work done at Philip Morris Research Center, 1973.
7. Vilcins, G.: Infrared analysis of ethylene and isoprene in the gas phase of cigarette smoke; Paper presented at the 27th Tobacco Chemists' Research Conference, Winston-Salem, N. C., 1973.

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