Determination of Carbon Monoxide in Cigarette Smoke by Gas Chromatography[1]

By R. C. Mumpower, J. S. Lewis and G. P. Touey

Research Laboratories, Tennessee Eastman Company,
Division of Eastman Kodak Company, Kingsport, Tennessee, U.S.A.

Introduction

A number of investigators have reported the presence of carbon monoxide in cigarette smoke (Armstrong and Evans, 1922; Baumberger, 1923; Bogen, 1929; Osborne *et al.*, 1956). In general, the methods employed for detecting this compound were based on chemical reactions, infrared spectroscopy, or mass spectrometry. Such procedures are time consuming, involve elaborate or expensive equipment, and normally require the smoking of several cigarettes. In addition, the reported values for the amount of carbon monoxide in cigarette smoke have varied from 0.6% to 5.8%.

This paper concerns a reliable and rapid method for determining the carbon monoxide content of the smoke from a puff of a single cigarette. One object of the work was to determine the amount of carbon monoxide produced by a cigarette when it is smoked under a standard set of conditions. The other object was to ascertain if certain changes in the cigarette or in the smoking procedure had an effect on the carbon monoxide content of the smoke.

The method to be described for this determination is similar to the gas chromatographic method reported by Patton and Touey (1956) for measuring certain hydrocarbons in cigarette smoke; however, a molecular sieve was used as the active solid for the column packing instead of silica gel.

Materials and Methods

Types of Cigarettes. Three groups of cigarettes were used in the experiments. The first group represented a commercial brand of nonfilter, king-size cigarettes. These were used in all of those determinations in which certain physical properties of the cigarette or certain conditions of smoking were altered. For convenience, the cigarettes from this group are designated as "Brand *A*" cigarettes through this report. The second group consisted of experimental cigarettes wrapped in cigarette paper which had been vapor-coated with aluminum. The tobacco in these cigarettes was the same as that in the cigarettes in the first group. The final group represented samples from fifteen brands of commercial, king-size and regular-size cigarettes with and without filters. For most of the experiments, the cigarettes were conditioned to 12% moisture content. They were then so selected that their weights and pressure drops were within 1% of the average weight and pressure drop of the brand under consideration.

Apparatus. A diagram of the smoking assembly and gas chromatographic apparatus is shown in **Figure 1.** The smoking assembly consisted of a cigarette holder with its accompanying thin rubber diaphragm seal, a glass-asbestos filter disc (30 mm in diameter) sealed between two glass funnels, and an automatic smoking machine. The total volume of this filter arrangement was 25 ml. A similar filter for removing over 99% of the particulate phase of cigarette smoke was described by Touey in 1955. The smoking machine has also been described (Mumpower *et al.*, 1960). Except when specified it produced a 35-ml puff at the rate of 1 puff/min. The machine was so designed that the duration of the puff

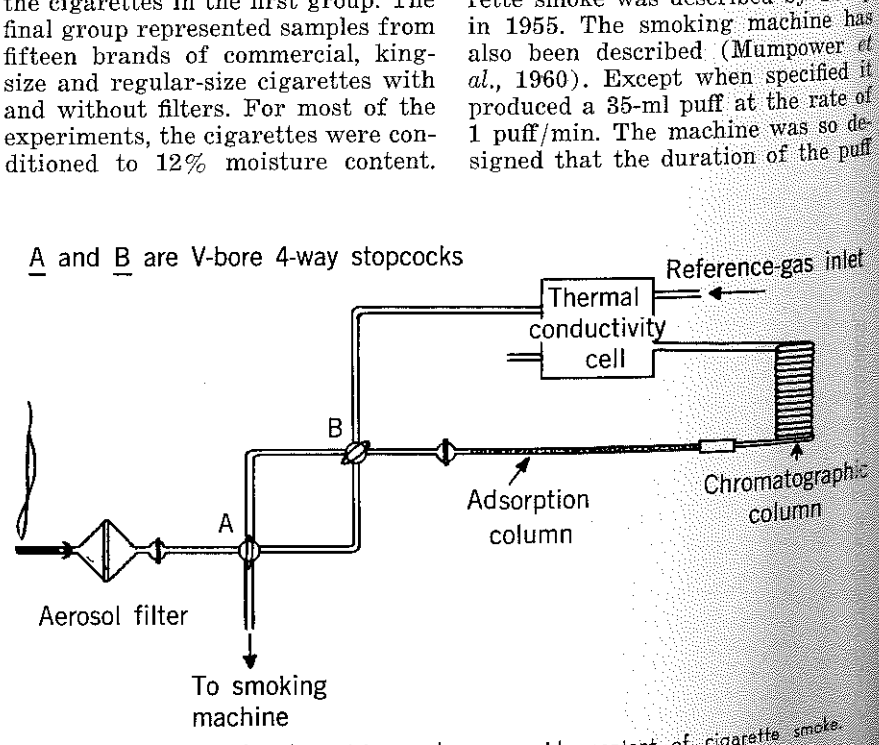

Figure 1. Apparatus for determining carbon monoxide content of cigarette smoke.

[1] *Presented at the Fifteenth Tobacco Chemist's Research Conference, Philadelphia, Pennsylvania, October 4-6, 1961.*

was 2 sec regardless of the pressure drop of the cigarette.

The gas chromatographic apparatus consisted of a bypass injector, an adsorption tube, a gas-solid column, a detector, and a recording potentiometer. The sample loop of the bypass injector had a volume of 3.94 ml and was temporarily isolated from the system by 4-way stopcocks. Stopcock *A* was turned so that the smoke gases being drawn through the system by the smoking machine either flowed through the sample loop or bypassed it. Stopcock *B* was turned so that the smoke gases in the sample loop were swept onto the chromatographic column by the carrier gas. Hydrogen was used as the carrier gas at a flow rate of 94 ml/min. The adsorption tube, ¼ in. by 6 in., was packed with 20 to 30 mesh Ascarite from a freshly opened container. The function of this column was to remove the moisture and carbon dioxide from the sample of smoke gases. The gas-solid column consisted of ¼-in. aluminum tubing 8 ft. long packed with $\frac{1}{16}$-in. pellets of Linde molecular sieve, Type 13X. This column was maintained at a temperture of 25° C. The thermal conductivity cell used as the detector was operated at a current of 150 ma. The electrical output of the cell was measured by a recording potentiometer.

Procedure. With this equipment, it was possible to analyze gas samples from several puffs of a single cigarette. Usually, the samples were taken during the third, eighth, and thirteenth puffs, with the thirteenth puff being the last puff. This corresponded to a final butt length of about 20 mm. The cycle of operation was a follows: Stopcock *B* was adjusted to prevent the carrier gas from entering the sample loop. Then Stopcock *A* was turned to allow the smoking machine to draw a puff from the burning cigarette through the aerosol filter and sample loop. On completion of the puff, Stopcock *A* was readjusted so that the next puff would bypass the sample loop. Finally, Stopcock *B* was turned so that the carrier gas swept the smoke gases from the sample loop through the adsorption tube and onto the chromatographic column.

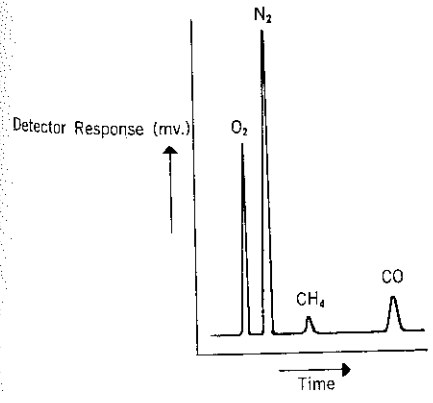

Figure 2. Typical gas chromatogram of gaseous portion of smoke.

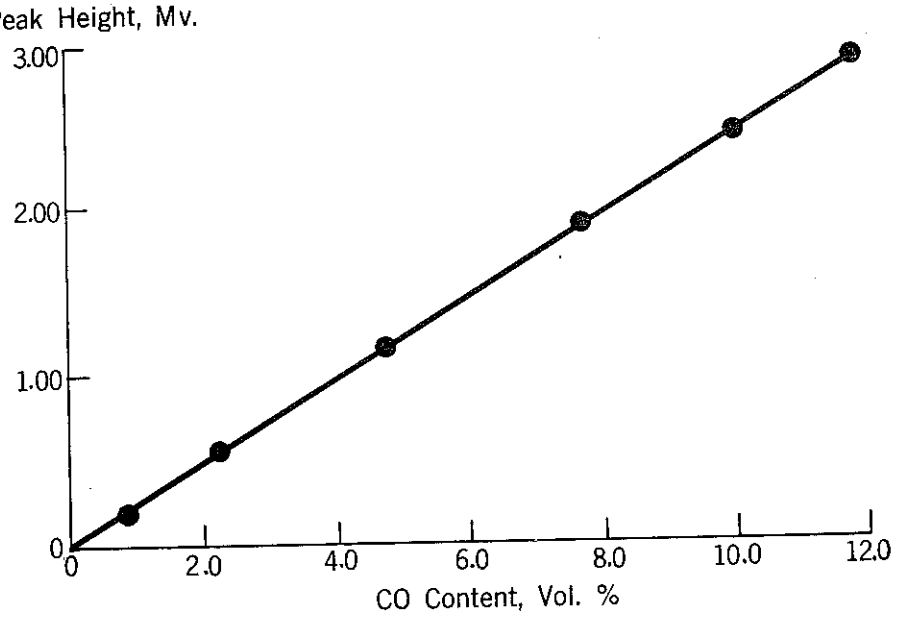

Figure 3. Calibration curve.

A typical chromatogram for one of the routine determinations obtained under a standard set of smoking conditions (one 35-ml puff of 2-sec duration per minute) is shown in **Figure 2.** Note that there are four peaks. The work reported in this paper is concerned only with the peak representing the carbon monoxide content of the smoke; however, it is obvious that quantitative values may also be obtained for the oxygen, nitrogen, and methane contents of cigarette smoke by this method. The carbon monoxide peak was amplified for the quantitative measurements. Preliminary experiments had shown that the adsorption of carbon dioxide and water from the smoke gases by the Ascarite had no effect on the subsequent quantitative determinations.

The calibration curve that was used is shown in **Figure 3.** This curve was obtained by allowing known mixtures of carbon monoxide and air to pass into the sample loop. The peak heights of carbon monoxide obtained from the chromatogram were then plotted against the known concentration of carbon monoxide in the sample. Those samples which contained more than 4.76% carbon monoxide were prepared by diluting pure carbon monoxide with dry air in a specially designed apparatus previously reported by Patton and Touey (1956). Samples from a cylinder containing 4.76% carbon monoxide and 95.24% dry air were further diluted with dry air in a similar manner to obtain the samples containing less than 4.76% carbon monoxide. Samples from this cylinder, which was obtained from The Matheson Company, were also used for periodically checking the calibration curve. Each point shown on this curve represents the average of five determinations. The standard deviation for each point was ±0.05 absolute % carbon monoxide.

Results and Discussion

The first experiment consisted of measuring the amount of carbon monoxide in the smoke of a nonfilter, king-size cigarette. Ten Brand *A* cigarettes conditioned to 12% moisture content were smoked. Samples of the gaseous phase of the smoke were taken during the third, eighth, and thirteenth puffs. The results are listed in **Table 1.** In all of the runs, the minimum carbon monoxide content was obtained from the first puff taken; the maximum value was observed for the last puff taken. The average carbon monoxide content for the third puff was 3.1%; the values for the eighth and thirteenth puffs were 4.4% and 5.0%, respectively. The over-all average per cigarette was 4.2% carbon monoxide. Statistical analysis of the values indicated that the increase in carbon monoxide content with the corresponding decrease in butt length was significant at the 95% confidence level.

Table 1.—Carbon monoxide content of smoke from Brand *A* cigarettes

Puff	CO in Smoke, % Av*	Range
3rd	3.1	2.7 - 3.5
8th	4.4	4.0 - 4.7
13th	5.0	4.7 - 6.0

* *Ten determinations.*

Table 2.—Effect of moisture content and weight of the cigarette on carbon monoxide content of smoke

Wt of Cigarette, G.	Moisture Content of Cigarette, %	CO in Smoke, %*
1.200	7.0	4.1
1.200	12.0	4.2
1.200	17.0	3.6
1.107	12.0	3.7
1.280	12.0	3.6

* *Average for five cigarettes.*

Table 3.—Effect of puff volume on carbon monoxide content of smoke

Puff Vol, Ml	CO in Smoke, %* 3rd Puff	8th Puff	13th Puff
20	0.9	1.3	2.1
35	3.1	4.4	5.0
60	4.8	5.3	7.7

* *Average for five cigarettes.*

The data in **Table 2** show the effect of the moisture content and weight of Brand *A* cigarettes on the carbon monoxide content of the smoke. The results in the upper section of the table were obtained from three sets of five cigarettes. Each of these cigarettes weighed 1.200 g at 12% moisture content before being conditioned to the moisture content shown. These cigarettes had a weight at 12% moisture content equal to the average weight of the brand. The results in the lower section of the table were obtained from cigarettes having weights higher and lower than the average weight of the brand. They were conditioned to the standard 12% moisture content. Each result shown represents an average value. It was obtained by analyzing the third, eighth, and thirteenth puffs from five cigarettes and obtaining an average of these measurements. As the results indicate, these factors have little effect on the carbon monoxide concentration.

Another variable studied was the effect of altering the volume of the 2-sec puff on the amount of carbon monoxide in the smoke. The results obtained when the Brand *A* cigarettes were smoked with a 20-, 35-, and 60-ml puff, respectively, are shown in **Table 3.** Since this variable had a more pronounced effect on the carbon monoxide content of the smoke than the weight or moisture content of the cigarette, the average results for the three puffs analyzed are reported separately. From these results, it is obvious that a marked increase in the volume of the 2-sec puff produces a substantial increase in the concentration of carbon monoxide in the smoke.

In the next experiment the carbon monoxide content of the smoke from cigarettes wrapped with aluminum-coated paper was determined. The aluminum was applied to cigarette paper by a vapor-coating technique. Tobacco from Brand *A* cigarettes was wrapped in this paper by a hand-operated cigarette-"rolling" device. The cigarettes were then selected for smoking on the basis of their average weight and pressure drop. The carbon monoxide content of the smoke from these experimental cigarettes is shown in **Table 4.** Also shown in the table are the results obtained with the same tobacco wrapped, by hand, in conventional cigarette paper. The carbon monoxide content of the smoke from these cigarettes ranged from 4.0% for the third puff to 5.7% for the ninth puff; the average for the cigarettes was 5.1%. In contrast, the carbon monoxide content of the smoke from the cigarettes with the aluminum-coated paper ranged from 8.8% to 14.4%; the average for the cigarettes was 11.5%. This represents an increase of 130% carbon monoxide. The cause for the increased carbon monoxide concentration for these cigarettes has not been determined.

The final experiment consisted of smoking 15 brands of commercial cigarettes and determining the amount of carbon monoxide produced in the smoke. The results shown in **Table 5** represent the average of five cigarettes for each brand. In all of these tests the smoke sample was taken as the burning zone reached the center section of the cigarette. The minimum carbon monoxide concentration found was 3.0%; the maximum was 5.0%. These results indicate that such factors as tobacco blend, cigarette size, pressure drop, or type of filter have little, if any, effect on the amount of carbon monoxide produced by domestic cigarettes.

In summary, with the gas chromatographic method described for determining the carbon monoxide content of cigarette smoke, it is possible to analyze several puffs from a single cigarette smoked under various conditions. The concentration of carbon monoxide in the smoke of a king-size, nonfilter cigarette increased as the cigarette was smoked. The third puff had 3.1% carbon monoxide while the last puff had 5.0% carbon monoxide. The weight and moisture content of the tobacco in the cigarette had little or no effect on the amount of carbon monoxide produced in the smoke; however, an increase in puff volume, at a constant duration, caused an increase in the carbon monoxide content. Also, it was shown that tobacco wrapped in an aluminum-coated cigarette paper produced 130% more carbon monoxide in the smoke than cigarettes with uncoated paper. The average carbon monoxide contents of the smoke from the 15 brands of cigarettes tested

ranged from 3.0 to 5.0%. These results indicate that the cigarette size, tobacco blend, type of cigarette, or pressure drop of the cigarette have little effect on the carbon monoxide content of the smoke.

Literature Cited

Armstrong, H. E. and E. V. Evans, *Brit. Med. J.*, **1**: 992-993 (1922).

Baumberger, J. P., *Pharmacol. Exptl. Therap.* 21: 23-57 (1923).

Bogen, Emil, *J. Am. Med. Assoc.* 93: 1110-1114 (1929).

Mumpower, R. C., J. E. Kiefer, and G. P. Touey, *Tobacco Science* 5: 31-35 (1961).

Osborne, J. S., S. Adamek, and M. E. Hobbs, *Anal. Chem.* 28: 211-215 (1956).

Patton, H. W. and G. P. Touey, *Anal. Chem.* 28: 1685 (1956).

Touey, G. P., *Anal. Chem.* 27: 1788-1790 (1955).

Table 4.—Carbon monoxide content of smoke from experimental cigarettes

Paper	CO in Smoke, %* 3rd Puff	6th Puff	9th Puff	Av.
Conventional	4.0	5.5	5.7	5.1
Al-coated	8.8	11.2	14.7	11.5

* *Average for five cigarettes.*

Table 5.—Carbon monoxide content of smoke from various cigarettes

Type of Cigarette	No. of Brands	CO Content of Smoke, %* Low	High
Nonfilter, regular size	3	4.2	5.0
Nonfilter, king-size	2	3.0	4.4
Filter, regular size	2	3.5	4.5
Filter, king-size	8	3.3	4.6

* *Average for five cigarettes.*