An Automated Procedure for CO in Cigarette Smoke, Using a 20-Port Syringe Smoking Machine*

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INTRODUCTION

The use of nondispersive infrared analysis for the determination of carbon monoxide (CO) in the gas phase of cigarette smoke has been reported by Williams and Belk (3). They found this method of analysis particularly advantageous in that the gas phase does not contain any constituents at a sufficient concentration to cause interference, thus allowing the gas phase to be passed directly into the infrared analyzer for immediate measurement of CO concentration. The smoking system utilized by these authors was of the multiport, critical flow orifice type with provision for manually transferring a portion of each puff into the analyzer, thereby obtaining a puff by puff measurement of CO.

The present work was directed toward developing a routine method which would give an average value representative of the CO delivery of a cigarette brand. A rather large sample should be analyzed for adequate characterization of a brand and this made it desirable to develop a procedure which would utilize the gas phase produced in our routine analysis for tar and nicotine levels where large samples of cigarettes were being smoked.

In our laboratory the determination of smoke solids and nicotine is carried out using a 20-port syringe-type smoking machine. An investigation into the possibility of using the gas phase exhaust from this machine as the sample for infrared analysis resulted in the procedure described in the following sections. A specially designed gas phase sampling unit is employed to receive the gas phase from the smoker and, after mixing, to present it to the analyzer with these operations being carried out automatically. This procedure yields reliable and precise results for CO in gas phase with a minimum of operator intervention and without affecting appreciably the results for smoke solids and nicotine.

EXPERIMENTAL

Apparatus

Gas Phase Sampling Unit: The function of the sampling unit is to receive the 700 ml of gas discharged by the 20-port syringe smoker during each cycle, allow time for this volume of gas to become mixed and then to pass it into the infrared analyzer for measurement of CO concentration. The unit includes a gas reservoir and

several solenoid-activated valves interconnected as shown in Figure 1, with an associated electrical circuit shown in Figure 2. The parts are listed in Table 1. The system is somewhat more complex than required for routine use, but a number of switching options were included for testing purposes.

The gas reservoir consists of a gas-tight, 1-quart capacity polyethylene bag (4" × 2" × 12", Bes-Pac, Montgomery, Alabama) enclosed in a 2-liter aspirator bottle, with the open end of the bag extending through the neck of the bottle so that it is sealed with the rubber stopper. Connecting lines between the gas phase exit manifold of the smoking machine and the gas reservoir and from the bottle to solenoid valve S-2 are 1/4 in. i.d. rubber tubing. The lines from the reservoir to solenoid valve S-3 and to the infrared analyzer are 1/8 in. i.d. Tygon tubing while the other lines are 1/8 in. o.d. copper or Tygon tubing. The sampling unit is electrically connected by means of a 2-conductor cable to the coil of relay 21 of the smoking machine. This connection provides a 110 volt AC signal to the sampling unit for the 2-second duration of each puff which serves to initiate the sampling cycle.

Solenoid valves S-1, S-2, and S-3 are controlled by the cycle timer and the timing cams must be properly adjusted. The signal from the smoking machine starts the timer motor and the cam which operates microswitch 1 is adjusted so that the motor continues running for 55 seconds, but then stops until the beginning of the next puff. The cam which operates microswitch 2 is adjusted so that the discharge of the bag (S-2 and S-3

Table 1. Parts list for sampling unit.

S-1	Valcor No. 55P7605E solenoid valve, 3-way, N.O., 3/16 in. orifices, 115 VAC.
S-2	Valcor No. 55P76C5E solenoid valve, 3-way, N. C., 3/16 in. orifices, 115 VAC.
S-3, 4, 5	Skinner V 5 solenoid valve, 3-way multi-purpose, 3/32 in. orifices, 115 VAC.
FR 1	Flow regulator, No. 69 critical flow orifice.
FR 2	Flow regulator, 2 in. of 0.015 in. i. d. Tygon tubing.
SW-1, 3, 4, 5	Switch, SPST.
SW-2	Switch, DPDT, momentary contact in test position.
R-1	Relay, PB No. KRP11A, 115 VAC, shown not energized.
Timer	Cramer Model 540, 2 poles, 55-second cycle.
L-1 to L-6	Leecraft Snaplite, Neon, 115 VAC.

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Figure 1. Flow diagram of sampling unit.

actuated) begins 20 seconds after the start of the cycle and continues for 33 seconds.

The operation of the sampling unit is as follows. With the unit powered and connected to the smoker, a "wait" state is entered until the beginning of the puff at which time the cycle timer starts. At the moment the puff is completed, S-1 is actuated and the gas discharged by the smoker passes into the plastic bag. After allowing 16 seconds for mixing, solenoids S-2 and S-3 are actuated and S-1 is released. This allows air to flow into the bottle forcing the gas phase to flow from the plastic bag through S-3 to the infrared analyzer. Usually the bag is deflated after 20 to 25 seconds although the discharge cycle continues for a total of 33 seconds. Then solenoid S-1 is momentarily activated for about 2 seconds until the unit returns to the "wait" state.

Solenoid valves S-4 and S-5 are manually switched and control the flow of gas through the infrared analyzer except during discharge of the bag. With neither solenoid actuated, air passes through the analyzer. Actuation of S-5 stops the air flow and actuation of S-4 allows the flow of the standard gas.

The switch, Sw-2, is provided for manual initiation of the sampling unit cycle and Sw-3 allows valve S-1 to be deactivated at any time. These switches are not used in routine operation but left in position as shown in Figure 2. The pilot lights indicate various events: L-1, power on; L-2, the puff signal from the smoker; L-3, cycle in progress; L-4, actuation of valve S-1; L-5, bag discharge with valves S-2 and S-3 actuated; and L-6, actuation of valve S-4 to allow the standard gas to flow into the analyzer.

Figure 2. Electrical circuit of sampling unit.

Smoking Machine: The 20-port syringe type smoking machine described by Wiley and Ferri (2) and marketed by Phipps and Bird, Inc. is used. The only modification of the machine involves the electrical and exhaust manifold connections to the sampling unit. The machine is operated normally except puffs must not be taken more often than once each 60 seconds and clearing puffs are necessary, as discussed later.

Infrared Analyzer: A Beckman Model 215B analyzer with a range of 0 to 10% CO and equipped with a 0 to 10 millivolt recorder is used. A standard gas mixture containing about 9% by volume CO in air is employed for calibration of the analyzer and room air is used to adjust the zero.

Procedure

Calibration of Analyzer: Determine the reading which should be obtained for the standard gas from the calibration data supplied with the instrument; in this investigation, the standard contained 8.87% CO and the gain was adjusted to obtain a reading of 92 or 9.2 mv. The gain and the zero adjustment are made each time the instrument is used. To prepare the calibration curve, dilute 20, 40, 60, and 80 ml volumes of the standard gas each to 100 ml with air using a 100 ml Luer-type syringe which has been lightly lubricated with mineral oil. Several mixtures of each concentration are prepared and measured with the analyzer. Calculate the concentration of the gas mixtures in ml of CO per 35 ml and plot recorder reading vs. concentration; a typical calibration curve is shown in Figure 3.

Figure 3. Typical calibration curve for Infrared analyzer.

If the computational equipment is available, it is convenient to obtain the equation for the calibration curve and use this equation to calculate concentrations from the readings, thereby eliminating the need to read values from the calibration graph. In this work, a Hewlett-Packard Model 9100B computing calculator was used. It was found that if the readings, R (on a scale of 0 to 100), are transformed to R_t values where $R_t = \log(100-R)$, then the calibration data closely fit a least squares parabolic curve of the form

$$\text{ml CO per 35 ml} = a_2 R_t^2 + a_1 R_t + a_0.$$

The constants in this equation are determined from the calibration data and subsequently used to calculate sample concentrations.

Analysis of Cigarettes: The smoking machine with the sampling unit has a considerable hold-up volume and to adequately remove CO from the system, it is necessary to take 6 clearing puffs prior to smoking the sample. The infrared analyzer should be allowed to warm up for several hours before use. Connect the sampling unit to the smoking machine and standardize the analyzer, properly adjusting both the zero with air and the gain with the standard gas. Smoke the 100-cigarette sample in sets of 20 with the sampling unit set so that air flows through the analyzer between bag discharges. The smoking procedure is as described by Bates et al. (1) except cigarettes from the same sample must be smoked at all ports. Also, in this work, the butt length used for non-filter cigarettes was 23 mm and for filter cigarettes, tipping paper + 3 mm. After smoking the 100 cigarettes, take 6 clearing puffs through the entire system, also recording these peaks.

Read the peaks that were recorded during the smoking of each set of 20 cigarettes and convert these readings to ml of CO per 35 ml. Sum these values for each set, including the values for the clearing puffs with the first set of 20 cigarettes. Each of the five totals represents the average ml of CO per cigarette for a set of 20 cigarettes and these are then averaged to obtain the overall average for the sample. This is then divided by the average number of puffs per cigarette to obtain an average ml of CO per puff.

RESULTS AND DISCUSSION

The necessity of using a sampling unit to interface the infrared analyzer to the smoking machine arises primarily from the requirement to have a representative sample of the gas phase for analysis. With the 20-port smoker, 700 ml of gas is discharged in 2 seconds, and since the volume of the sample cell is only a few ml or less, the gas phase must be well mixed if a single reading is to be indicative of the whole volume. Initial tests with a single port syringe-type smoker indicated that the discharged gas phase was not homogeneous with regard to CO concentration and there would seem to be much less opportunity for the gas phase to become mixed in the case of the 20-port smoker. The possibility of passing the gas directly into the analyzer and averaging the response throughout the 2-second interval does not appear feasible due to the relative slowness of response of the analyzer which is rated at 90% in 0.5 second. Further, the rapid flow rate would result in a pressure increase in the sample cell which would alter the response of the analyzer and also slow the speed of discharge by the smoking machine. With the gas phase sampling unit, the 700 ml of gas is discharged into the gas reservoir without an appreciable slowing of the smoking machine, and the gas is allowed to mix by standing in the reservoir for 16 seconds before measurement is begun. The flow rate of the gas when it is then

Figure 4. Chart recording of analyzer output.

passed through the sample cell of the analyzer is low enough to cause only a minor variation in response.

A typical recording of the output of the analyzer obtained during the analysis of a cigarette sample is reproduced in part in Figure 4. Shown are the peaks obtained during the smoking of the first and fifth sets of 20 cigarettes each and the final clearing puffs; the peaks recorded during the smoking of sets 2, 3, and 4 are omitted for clarity but are similar to those in set 5. The sampling unit was adjusted so that air flowed through the analyzer except during discharge of the gas reservoir, thereby causing a return to the baseline between peaks. The adequacy of mixing is indicated by the relatively flat peaks. The slight elevation seen for about the first two thirds of most peaks is due to the pressure increase within the sample cell during actual discharge of the bag so, for calculation, the response measured during the last part of the puff after flow has essentially stopped is used. Peaks which follow a higher peak generally show a momentary excursion approaching the height of the preceding peak due to hold-up in the lines between the analyzer and gas reservoir and this is ignored. Before smoking set 1, the apparatus had been cleared of CO and the low response found for the first few puffs in set 1 reflects the considerable hold-up volume of the smoking machine and sampling unit. No clearing puffs were then taken until the completion of set 5, and this means that part of the CO indicated for puffs one through six in set 5 was actually produced by the previous set. The last few peaks during the smoking of any set show a decreasing concentration of CO. At this time, many of the cigarettes have been smoked to the designated butt length and on these puffs air is taken into the syringe during the puff, subsequently diluting the gas phase produced by the cigarettes still being smoked.

In developing this procedure it was considered important not to modify the standard procedure for particulate

phase analysis (1) any more than necessary and this is the reason clearing puffs are taken only at the completion of the entire 100-cigarette sample. Without clearing puffs between sets, many of the peaks obtained include CO produced in part by the present set of cigarettes and partly by the preceding set which makes it impossible to calculate the exact amount of CO produced specifically by any one of the 5 sets. However, if the final clearing puffs are included with the first set, then the peaks recorded during the smoking of any set essentially represent the CO produced by 20 cigarettes. Five separate values can thus be calculated which serve to give an estimate of the variability of the analysis.

A further indication of the adequacy of mixing of the gas discharged from the smoker was obtained in an experiment in which pure CO was added to one port for 10 puffs while puffing air at the other 19 ports. Five tests were carried out, adding the CO at a different port each time. The recovery of the CO ranged from 97 to 100% with an average of 99% which demonstrates adequate mixing as well as the absence of losses in the system.

The design of the sampling unit is such that it should have no effect on the puffing action of the smoking machine. During the duration of the puff, the exhaust manifold of the smoker, though connected to solenoid valve S-1, is open to the air just as it is in normal operation without the sampling unit. The possible effect of the sampling unit on results for smoke solids and nicotine in the particulate phase was investigated by analyzing 100-cigarette samples with and without attachment of the unit. The results are summarized in Table 2, and it is considered that the variation in the values is no greater than is normally encountered, indicating that the unit does not appreciably affect the level of these particulate phase components.

The present procedure differs from that described by

Table 2. Nicotine and smoke solids found with and without attachment of sampling unit.

Sample*	Nicotine**		Smoke solids**	
	With unit	W/O unit	With unit	W/O unit
1	1.43	1.42, 1.44	20.2	20.0, 19.4
2	1.23	1.28, 1.23	17.6	17.8, 17.2
3	1.93	1.90	30.4	29.5

* All cigarettes were 85 mm. Samples 1 and 2 had non-perforated filters and sample 3 was a non-filter type.

** Results in mg per cigarette with each value representing 100 cigarettes. Smoke solids are on a dry, nicotine-free basis.

Table 3. Results for gas phase CO by two procedures.

Cigarette description	ml of CO per puff	
	Present procedure	Williams and Belk procedure
Brand A, non-perforated filter	1.9	1.9
Brand B, perforated filter	1.5	1.7
Brand C, perforated filter	1.3	1.2
Brand D, perforated filter	1.3	1.3

Table 4. Gas phase delivery of CO found for various domestic cigarettes.

Cigarette type	Brands	ml of CO*	
		Per puff	Per cigarette
Perforated filter	4	1.19–1.47	9.9–12.1
Non-perforated filter	20	1.64–1.96	13.1–18.4
Non-filter	4	1.31–1.89	13.8–16.2
1-R-1**	1	1.58	18.0

* The values represent the range of the averages found for the various brands in each category. A 100-cigarette sample of each brand was analyzed.

** University of Kentucky Research Cigarette. An average of 11.4 puffs per cigarette was obtained.

Table 5. CO delivery found throughout a 4-month period for a standard cigarette.

Day	ml of CO found*	
	Per cigarette	Per puff
1	15.32	1.78
32	14.42	1.74
111	15.16	1.74
117	14.85	1.73
120	14.65	1.72
123	14.54	1.75
124	14.79	1.76
Average	14.82	1.75
S. D.	0.33	0.02
Relative S. D.	2.2 %	1.1 %

* Each value represents 100 cigarettes.

Williams and Belk (3) primarily in the type of smoking machine used and the manner of collecting the gas phase for analysis. The two methods yield values in good agreement as can be seen from the results obtained for four commercial cigarette brands as shown in Table 3.

Application of the present procedure to a variety of domestic cigarettes has given values for CO delivery ranging from 1.19 to 1.96 ml per puff. These results are summarized in Table 4.

To estimate the precision of the procedure, a carefully prepared 85 mm standard cigarette with cellulose acetate filter was analyzed seven times over a four-month period. A 100-cigarette sample was smoked for each analysis with results as shown in Table 5. The relative standard deviation of a result for ml of CO per cigarette representing 100 cigarettes is 2.2 % and for ml of CO per puff, 1.1 %.

An estimate of the precision within a single 100-cigarette analysis can be calculated from the five values for ml of CO per cigarette which are obtained. This has been done for 62 samples representing a variety of cigarette types and the relative standard deviation for a single set of 20 cigarettes was found to range from 0.8 to 7.1 % with an average of 3.4 %. The value of 3.4 % for a set of 20 cigarettes indicates a relative standard deviation of $3.4\% / \sqrt{5} = 1.5\%$ for the average value representing 100 cigarettes. This estimate of the precision is in good agreement with that found from replicate analyses of the standard cigarette.

It is concluded that the present procedure can be advantageously substituted for the Williams and Belk procedure whenever individual puff-by-puff analyses are not needed. In so doing, a considerable saving of time should be realized since the separate smoking of cigarettes for CO analysis is eliminated and less operator attention is required due to the automation of the gas phase sampling system.

SUMMARY

A procedure for the determination of CO in the gas phase of cigarette smoke has been developed. Cigarettes are smoked on a 20-port syringe-type smoking machine and the gas phase is sampled by a specially designed sampling unit without appreciably affecting the level of particulate phase components or the operation of the smoker. After mixing, the concentration of CO in the gas phase is measured by nondispersive infrared analysis. All operations are carried out automatically except the initial start-up, calibration of the analyzer, and calculation of results. The procedure has been applied to a variety of cigarette brands with results ranging from 1.2 to 2.0 ml of CO per puff. The precision of the procedure was determined by repeated analysis of a standard cigarette over a four-month period. For a single value representing 100 cigarettes, the relative standard deviation was found to be 2.2 % for ml of CO per cigarette and 1.1 % for ml of CO per puff.

ZUSAMMENFASSUNG

Die Autoren entwickelten ein Verfahren zur Bestimmung von CO in der Gasphase von Zigarettenrauch. Die Zigaretten werden auf einer Kolben-Rauchmaschine mit einem Rauchkopf für 20 Zigaretten abgeraucht; die Gasphase wird durch eine besonders konstruierte Probenahme-Vorrichtung gesammelt, ohne daß der Anteil an Komponenten der Partikelphase oder der Abrauchvorgang wesentlich beeinträchtigt werden. Nach der Durchmischung wird die CO-Konzentration in der Gasphase durch Infrarotanalyse gemessen. Mit Ausnahme des Starts, der Eichung der Analyseninstrumente und der Berechnung der Ergebnisse laufen alle Arbeitsgänge des Verfahrens automatisch ab. Die Methode wurde bei verschiedenen Zigarettenmarken angewendet und ergab CO-Werte zwischen 1,2 und 2,0 ml je Zug. Die Genauigkeit des Verfahrens wurde durch mehrmalige Analyse einer Standardzigarette über einen Zeitraum von vier Monaten bestimmt. Für einen 100 Zigaretten umfassenden Einzelwert ergab sich ein Variationskoeffizient von 2,2 % für 1 ml CO je Zigarette und von 1,1 % für 1 ml CO je Zug.

RESUME

On a mis au point un procédé capable de déterminer le CO dans la phase gazeuse de la fumée de cigarette. Les cigarettes sont fumées dans une machine à fumer du type seringue munie d'une tête de fumage à 20 canaux. La phase gazeuse est échantillonnée grâce à un appareil conçu spécialement pour échantillonner, n'affectant d'une façon appréciable ni la teneur en composants de la phase particulaire, ni la marche de la machine à fumer. Après mélange, on mesure la con-

centration de CO dans la phase gazeuse par analyse infra-rouge non dispersante. Toutes les opérations s'effectuent automatiquement excepté la mise en route, le calibrage de l'analyseur et le calcul des résultats. On a appliqué ce procédé à différentes marques de cigarettes et les résultats varient de 1,2 à 2,0 ml de CO par bouffée. On a déterminé la précision de la méthode par des analyses répétées d'une cigarette standard durant une période de quatre mois. Pour une valeur unique représentant 100 cigarettes, la déviation standard relative s'élevait à 2,2 % pour 1 ml de CO par cigarette et à 1,1 % pour 1 ml de CO par bouffée.

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