Determination of Carbon Monoxide in Cigarette Smoke Using an Electrochemical transducer*

by

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INTRODUCTION

There has recently been much medical and public concern about the health hazards associated with the inhalation of carbon monoxide from cigarette smoke (1 to 14). In addition, the first report of the Independent Scientific Committee on Smoking and Health (Hunter Committee) (15) recommends that carbon monoxide yield figures should accompany submissions to the Committee for approval to market tobacco substitute materials. As one of its regular routine functions, the Laboratory of the Government Chemist already provides the Health Departments of the United Kingdom with tar and nicotine yields for over 100 cigarette brands available on the domestic market. The Health Departments issue these results in tabular form at regular intervals. As a logical extension to this work, it was decided to evaluate possible methods for the production of the corresponding carbon monoxide yields.

System Criteria and Constraints

Routine smokings for tar and nicotine yields are carried out on a 20-channel piston smoking machine, and it was considered desirable to conserve manpower by avoiding duplication both of smoking and smoking equipment. Additionally, statistical confidence in any comparisons between carbon monoxide yields and tar and nicotine yields would be enhanced by the knowledge that all values referred to the same actual cigarettes selected and tested according to the well proven, statistically-based sampling and smoking procedures.

For these reasons, it was decided to investigate a system for in-line carbon monoxide analysis which could run simultaneously with the tar and nicotine collection, leaving the smoking regime undisturbed. Ideally, the detector would be placed in the gas stream directly behind the Cambridge filter and would require only intermittent calibration. The system described here is

based upon a suitably modified electrochemical carbon monoxide transducer, developed originally at the Safety in Mines Research Establishment for monitoring low carbon monoxide levels in mine atmospheres (16).

Carbon monoxide levels are obtained puff-by-puff, which allows direct comparison of carbon monoxide generation patterns between different cigarette types (e.g. plain, filter, ventilated filter). Carbon monoxide yields in milligrams per cigarette are also obtained for inter-brand comparison, by calculation from a summation of individual puff contents.

EXPERIMENTAL

Apparatus

Carbon Monoxide Electrochemical Transducer: Detailed descriptions of the carbon monoxide transducer cell have been published previously (16, 17). In essence, the cell (Figure 1) comprises a 25 μ m PTFE membrane coated on its inner face with a sputtered layer of platinum which is in contact with cell electrolyte (0.1 M sulphuric acid). The membrane is supported on its outer face by a porous polythene disc and a brass sinter. Carbon monoxide passing through the PTFE by a process of "activated diffusion" is oxidised catalytically at the platinum surface at a controlled potential with reference to a mercury/mercurous sulphate electrode. Cell current is carried through a third platinum auxiliary electrode.

The current flowing in the cell, which is proportional to the partial pressure of carbon monoxide in contact with the membrane, is amplified as a voltage and displayed on a potentiometric recorder. There is provision for variable gain and zero offset, and an output typically in the range 100 mV-1V is obtained from cigarettes smoked with the system. The current-to-voltage converter also incorporates a thermistor in a negative feedback mode which compensates for the otherwise exponential temperature dependence of the cell sensitivity.

Gas/Cell Interface: This consists of a drilled PTFE block, sealed gas-tight to the carbon monoxide cell face with silicone rubber cement.

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Figure 1. Metallised-membrane electrode cell, schematic.

- a: Gasket clamping plate and sintered disc.
b: Gasket with porous disc.
c: Metallised membrane (working electrode).
d: Dialysis membrane.
e: Dialysis membrane recess with electrolyte-feed holes.
f: Contact spot.
g: Auxiliary electrode.
h: Reference electrode.
i: Cell body with reservoir containing electrolyte (0.1 M H₂SO₄).
j: Thermistor.

Modifications to Smoking Machine: The following modifications were made to one channel of a Filtrona Model 300 20-channel smoking machine (Cigarette Components Ltd.):

1. The carbon monoxide transducer was installed behind the Cambridge filter holder as close to the holder as possible (Figures 2 and 3). It was not convenient to fit the transducer within the transparent hood of the smoking machine and a hole was drilled to allow the tubing to pass through the back of the hood directly behind the Cambridge filter holder.

2. The three-way solenoid valves (V_1 and V_2) were installed on either side of the carbon monoxide cell to

Figure 2. Carbon monoxide transducer, as installed on single channel of Filtrona 300 smoking machine.

- a: Carbon monoxide electrochemical transducer.
b: Cambridge filter holder.
c: Three-way valves, V_1 and V_2 .
d: Air flush inlet.
e: Air flush outlet.
f: Flow to piston of smoking machine.

Figure 3. Switching arrangement for gas flow on smoking machine.

V_1 and V_2 : Additional solenoid valves.
 V_3 : Basic solenoid valve above piston.
a: Cambridge filter holder.
b: Piston.
Machine shown in smoking condition.

allow the cell to be flushed with air between puffs. Dead space was minimised by keeping inter-connections as short as possible. A controlled supply of filtered air was fed to the valve nearest to the Cambridge filter holder at 50 ml min⁻¹.

3. The cam shaft was fitted with an additional inductive timing switch which allowed the additional valves (V_1 and V_2) to be actuated reproducibly 0.5 s before and

Figure 4. Puff profile measured with carbon monoxide transducer in-line showing actuation of various valves.

- a: Actuation of valve V_3 .
b: Actuation of valves V_1 and V_2 outside smoking puff.

0.5 s after the smoking puff. This was necessary to ensure that the puff profile before and after installation of the cell was unchanged. A typical puff profile obtained with the carbon monoxide cell installed, is shown in Figure 4.

Gas Chromatographic Apparatus: Vapour phase from each puff was exhausted through valve V_3 (Figure 3) and collected in bags made in the Laboratory from polyethylene/polypropylene laminate (Metathene; Metal Box Co. Ltd.). The collected gas samples were mixed by manipulating the bag and the carbon monoxide was determined chromatographically. A dual column chromatograph (Pye-Unicam Ltd. Model 104), fitted with a katharometer detector and gas sampling valve (2 ml gas loop) was used for the analysis. Columns were 2 m long, 2 mm internal diameter glass, packed with Molecular Sieve 5X (80–100 mesh) and conditioned at 240 °C overnight. Oven temperature for analysis was 85 °C and the flow rate 75 ml min⁻¹. The sensitivity of the system decreased slowly with time and regular calibration with standard mixtures was necessary. No attempt was made to remove water or carbon dioxide from the sample with a pre-column. When sensitivity or resolution became unacceptable, the column was re-conditioned by heating overnight at 240 °C with helium as the carrier gas.

System Operation of the Smoking Machine with Carbon Monoxide Cell In-line: The smoking machine was set to operate at the standard tar and nicotine smoking parameters of a 35 ml puff of 2 s duration at 1 min intervals. During the cigarette's 58 s smoulder period, air (50 ml min⁻¹) was passed continuously across the carbon monoxide cell via the deactivated valves V_1 and V_2 *. As the crankshaft rotated at the commencement of the puff cycle, valves V_1 and V_2 were activated 0.5 s in advance of valve V_3 by the additional inductive cam switch. This stopped the air flow to the carbon monoxide cell and opened the pathway from the cigarette to valve V_3 . After the normal puff had been taken, valves V_1 and V_2 were deactivated 0.5 s after valve V_3 and the air flow thus restored to the carbon monoxide cell. All three valves were deactivated at the cigarette butt mark by the normal operation of the cotton gate smoking terminator, and one clearing puff was taken.

Under normal operating conditions the 20 channels of the smoking machine are occupied by 20 different cigarette brands, and 5 cigarettes from each brand are smoked through a single Cambridge filter for tar and nicotine analysis. Measurements were also taken from each cigarette smoked on the channel containing the carbon monoxide transducer to produce the related carbon monoxide yield.

Calibration of Carbon Monoxide Transducer: The transducer was calibrated before and after each smoking by drawing 8% v/v carbon monoxide standard gas mixture (92% nitrogen; British Oxygen Co. Analysed Gas Standard Mixture) over the carbon monoxide transducer.

The gas mixture was contained in a polyethylene/polypropylene bag, which was connected to the front of the Cambridge filter holder, in place of the cigarette and was cycled using the normal smoking machine operating procedure. Five measured puffs (6 were taken and the first disregarded to avoid the need for dead space correction) provided adequate precision for calibration. A clearing puff was taken after each calibration.

RESULTS AND DISCUSSION

Performance of Transducer In-line to Smoking Machine

Selectivity: The most critical aspect of the performance of the electrochemical carbon monoxide transducer is its specificity to carbon monoxide. The cell has an inherent sensitivity towards hydrogen, which has been reported to be present at quite high levels behind the burning coals of cigarettes (18) and in smoke emerging from the butt end of the cigarette (19). However, by careful adjustment of cell potential, a discrimination of 8:1 for carbon monoxide:hydrogen was obtained corresponding to a maximum positive error in the carbon monoxide measurement of 6%, at reported hydrogen levels in cigarettes (19). The carbon monoxide transducer has been found not to be sensitive to any of the other major components of cigarette smoke vapour phase e.g. nitrogen, oxygen, carbon dioxide, and methane).

Operation of Transducer at High Carbon Monoxide Concentrations: The original electrochemical carbon monoxide transducer was designed specifically for operation at low (ppm) levels in mine atmospheres. At the carbon monoxide concentrations found in cigarette smoke (typically 1–10% v/v carbon monoxide), the cell membrane can become saturated if left in continuous contact with the gas. This results in decreased sensitivity to subsequent gas mixtures and is clearly undesirable. This problem was overcome in the present system by flushing the cell with air so that carbon monoxide is in contact with the membrane for a maximum of 3 s, insufficient time to saturate the cell.

Readout and Response Time: Figure 5 shows a typical output obtained on a recorder for a series of repetitive cycles of a standard carbon monoxide gas mixture. There is a marked time lag between the start of the smoking puff and the response of the carbon monoxide transducer. One second after completion of the puff, the voltage output rises rapidly and reaches its maximum value in about 18 s. Thereafter, there is an exponential decay towards baseline, which is reached just prior to the start of the next smoking puff. The response function is determined largely by the system design, particularly by the carbon monoxide cell geometry. The peak maximum is an average of the carbon monoxide concentration gradient within a puff, therefore complicated calibration routines are unnecessary.

* This procedure avoided cell saturation by carbon monoxide and also ensured return of the signal to baseline.

Figure 5. Repetitive cycling of standard carbon monoxide mixture.

Gas mixture: 8% v/v CO, 92% N₂.
Cycle rate: 1 min⁻¹.

Air Flush Rate: The peak height varies in relation to the rate air flows through the cell (Figure 6). A relatively high air-flow (50 ml min⁻¹) was selected as optimum, in order to avoid any possible saturation problems. The

Figure 6. Influence of air purge flow rate on transducer response.

1% v/v carbon monoxide gas mixture cycled.

Figure 7. Calibration of carbon monoxide transducer with standard gas mixtures.

signal to noise ratio was quite acceptable under these conditions.

Reproducibility and Calibration Linearity: The standard deviation for 20 repeated cycles of 1% v/v carbon monoxide standard gas mixture was 0.01%. Calibration linearity in the range 0.5–8% v/v carbon monoxide was excellent (Figure 7), requiring the use of only one standard gas mixture periodically to check for sensitivity drift.

Partial Puffs: The peak readout of the carbon monoxide transducer, under controlled standard conditions of air flushing, is an accurate measure of carbon monoxide partial pressure only with complete puffs. Incomplete puffs (partial puffs) generated as the cigarette burns to the butt mark (smoking termination point) do not result in a drop in signal proportional to the puff fraction (Figure 8). However, it is possible from a plot of this form to deduce a corrected value for peaks arising from partial puffs, using a least square fit to a parabolic

Figure 8. Variation of peak height with puff fraction.
Standard 8% v/v carbon monoxide gas mixture.

curve. If the measured peak height is $H(\text{actual})$ and the puff fraction p , then:

$$H(\text{actual}) = k(a_0 + a_1 p + a_2 p^2), \quad [1]$$

where:

k = normalization factor (= peak height for standard carbon monoxide mixture, with 1 complete puff),
 a_0 = the axis intercept of the extrapolated peak height,
 a_1 = 1st order constant,
 a_2 = 2nd order constant.

Constants for the present system are: $ka_0 = 11.24$, $ka_1 = 26.96$ and $ka_2 = -10.20$ (RMS* residual = 0.189), where $k = 28$.

The value $H(\text{corrected})$, which is used in carbon monoxide yield calculations, can now be derived:

$$H(\text{corrected}) = kp, \quad [2]$$

therefore, from [1] and [2]

$$H(\text{corrected}) = \frac{p \cdot H(\text{actual})}{a_0 + a_1 p + a_2 p^2}. \quad [3]$$

If this correction were ignored, the partial puff at the butt mark could have a maximum positive bias of 300% (for 0.2 puffs on final puff), giving a result 5% high on the total carbon monoxide yield for that sample.

The first and clearing puffs are also treated for carbon monoxide yield calculations as partial puffs, in the same manner as true partial puffs, but here the puff fraction will be constant and set by the dead volume of the system between the Cambridge filter holder and the carbon monoxide cell.

Calculation of Carbon Monoxide Yield: Carbon monoxide yield per puff is given by:

$$\begin{aligned} \text{CO (per puff)} &= \\ &= \frac{\text{CO } (\%) }{100} \cdot \frac{273.2}{760} \cdot \frac{P}{T} \cdot V \cdot \frac{28}{22.4} \text{ mg}, \end{aligned} \quad [4]$$

where:

V = puff volume (ml),

P = measurement pressure (Torr),

T = measurement temperature (K).

This may be simplified to:

$$\text{CO (per puff)} = \text{CO } (\%) \cdot \frac{P}{T} \cdot V \cdot 0.00449 \text{ mg}. \quad [5]$$

For puff counting purposes, the first puff should be registered as a full puff and the clearing puff not counted.

If

$H(1)_c$ = corrected value for 1st smoking puff,

$H(T)$ = total peak height for smoking puffs 2 to n where n is the last complete puff,

$H(\text{part})_c$ = corrected value for partial smoking puff, if any,

$H(\text{clear})_c$ = corrected value for clearing puff,

Figure 9. Typical smoking traces with carbon monoxide transducer.

a: Ventilated filter cigarette.
b: Non-ventilated filter cigarette.

$H(\text{std})$ = peak height of standard,

S = concentration of standard gas mixture used for calibration,

then:

$$\begin{aligned} \text{CO yield} &= \left(\frac{0.00449 \text{ PVS}}{T} \right) \times \\ &\times \left(\frac{H(1)_c + H(T) + H(\text{part})_c + H(\text{clear})_c}{H(\text{std})} \right) \text{ mg}. \end{aligned} \quad [6]$$

This carbon monoxide value will be averaged for 5 cigarettes.

Preliminary Smoking Trials

The electrochemical carbon monoxide transducer was installed on one channel of the smoking machine and several brands of cigarettes, representing a variety of types and carbon monoxide yields, were smoked. The exhaust gas, collected simultaneously, was used for gas chromatography correlation. The carbon monoxide yields obtained from the carbon monoxide transducer are shown in Table 1. Typical smoking traces from ventilated and non-ventilated type filter cigarettes are shown in Figure 9.

Table 1. Carbon monoxide yields with electrochemical transducer.

Cigarette type	Mean no. of puffs per cigarette	Mean carbon monoxide yield (mg per cigarette)
Regular ventilated filter/1	8.2	5.0
Regular ventilated filter/2	9.1	5.3
Small filter	8.9	15.2
King size filter	8.0	17.3
Regular filter/1	7.9	17.7
Regular filter/2	6.6	18.3
Regular plain	10.5	22.4

* RMS = Root mean square.

Table 2. Comparative electrochemical and gas chromatographic carbon monoxide results.

Cigarette	Average carbon monoxide per puff (v/v %)	
	Electrochemical detector	Gas chromatograph
Ventilated filter	1.3	1.2
Non-ventilated filter/1	4.2	4.1
Non-ventilated filter/2	4.2	4.0
Non-ventilated filter/3	4.8	4.8

The smoking machine used was not ideal for the collection of the exhaust gas, due to the large dead volume between cigarette and bag (approx. 35 ml) and also because of the introduction of air by the gas purge mechanism. Consequently, correlation with gas chromatography was only possible on a per cigarette basis if the first and last puffs were disregarded, or on a per puff basis if the puff collected for gas chromatographic analysis was compared with the previous puff on the carbon monoxide transducer. Some comparative results for the two systems are shown in Table 2. Correlation appears to be satisfactory, but more extensive trials are continuing.

The carbon monoxide transducer was also left in-line during routine smoking for tar and nicotine determinations. No significant variations in the tar and nicotine yields were observed.

CONCLUSIONS AND FUTURE WORK

The initial objective of the work, which was to devise a reliable method for the determination of carbon monoxide yields simultaneously with tar and nicotine determinations, has largely been achieved. Areas still remain in which further developments can be made, such as in improving carbon monoxide:hydrogen discrimination of the electrochemical transducer even further by modifications of cell design and possibly by using different membrane thicknesses, electrodes and electrolytes; work on these is proceeding.

However, the next major step is the scaling-up of the present single-channel system to a fully automated 20-channel system, in which data retrieval and processing will be carried out partly by local electronic hardware and partly by transmission to an in-house computer. Work on this aspect is well under way. The possibility of using similar electrochemical detectors to monitor other components of cigarette smoke (e.g. sulphur dioxide and oxides of nitrogen) is also under investigation.

SUMMARY

A system for the in-line measurement of puff-by-puff levels of carbon monoxide on a Filtrona 300 smoking machine during routine smoking of cigarette for tar and

nicotine yields has been developed. The technique involves the introduction of a transducer into the suction line behind the Cambridge filter. This transducer comprises an electrochemical cell bridged by a pair of solenoid valves which are under the control of the cotton gate smoking terminator. These valves are actuated, other than at the butt mark, by an additional inductive timing switch on the crankshaft. Results using this technique compare well with results from existing off-line techniques such as gas-solid chromatography.

ZUSAMMENFASSUNG

Es wurde ein Verfahren entwickelt für die direkte zugweise Messung des Kohlenmonoxidgehaltes von Zigarettenrauch während der routinemäßigen Bestimmung des Kondensat- und Nikotingehaltes beim Abrauchen auf einer Rauchmaschine des Typs Filtrona 300. Die Methode beruht auf der Einführung eines Umwandlers in die Saugleitung hinter dem Cambridge-Filter. Dieser Umwandler umfaßt eine elektrochemische Zelle, welche von einem Paar elektromagnetischer Ventile überbrückt ist, die von dem Endabschalter (Auslösung durch Baumwollfaden) gesteuert, aber — anders als bei der Stummelmarkierung — durch einen zusätzlichen induktiven Zeitschalter an der Kurbelwelle betätigt werden. Die mit dieser Methode erzielten Ergebnisse stehen im Einklang mit den Befunden, die mittels bisher bekannter indirekter Verfahren wie z. B. der Gaschromatographie erhalten wurden.

RÉSUMÉ

On a développé une méthode permettant la mesure des niveaux de monoxyde de carbone de la fumée de cigarettes, en ligne et bouffée par bouffée, sur une machine à fumer Filtrona 300, durant l'analyse de routine déterminant le rendement en nicotine et en condensat. La technique comprend l'introduction d'un transmetteur dans la ligne de succion derrière le filtre Cambridge. Ce transmetteur est composé d'une cellule électrochimique pontée par deux valves solénoïdes. Ces valves sont commandées par le limiteur terminal de fumage (fil de coton), mais sont actionnées — en opposition au repérage de la limite du mégot — par un interrupteur à temps inductif supplémentaire relié au vilebrequin. Les résultats obtenus par cette technique sont comparables à ceux obtenus par des techniques hors-ligne connues, telles que la chromatographie en phase gazeuse.

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