The Determination of Formaldehyde in Cigarette Smoke

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INTRODUCTION

The aldehyde content of cigarette smoke is such that spectrophotometric procedures for the determination of aliphatic aldehydes with chromotropic, phenyl J Acid, J Acid, 3-methyl benzothiazolone hydrazone and acetyl acetone (1-6) can only be applied to the determination of formaldehyde in smoke after the removal of acetaldehyde and acrolein. Similarly, fluorimetric procedures involving the use of J Acid (7) and acetyl acetone (8, 9) suffer from similar limitations and can only be applied to the detection of formaldehyde in cigarette smoke after the application of separational techniques. Most workers have overcome these difficulties by the application of gas chromatographic procedures to the determination of formaldehyde in the presence of other aldehydes (10).

In order to avoid the use of chromatographic techniques, which are rarely satisfactory for application to routine procedures, we considered the novel, specific spectrophotometric method for the determination of formaldehyde suggested by Dokládalová et al. (11). The method outlined by Dokládalová involved the reaction of formaldehyde with p-rosaniline in the presence of sulphur dioxide to form p-rosaniline methyl sulphonic acid, the sulphur dioxide being present in the form of the stable disulphite mercurate (II) complex. The final solution is acidic and the product has the p-quinoid structure and is red violet having an absorption maximum at 571 nm, while the excess p-rosaniline reagent is in the anilinium cationic form which is colourless.

EXPERIMENTAL

Level of Sulphur Dioxide

The work of Dokládalová (11) showed that the concentration of sulphur dioxide in the reaction mixture had a marked effect on the sensitivity of formaldehyde detection.

Addition of sulphur dioxide to the reaction mixture was conveniently achieved by the use of standard sodium hydrogen sulphite solution. Our investigations have shown that maximum colour development was produced when the level of sulphur dioxide, in a reaction mixture of 25 ml volume, was between 700 and 1120 µg. The addition of some 1600 µg of sulphur dioxide was found to destroy the colour. The level of added sulphur dioxide was standardised at 800 µg.

Time of Colour Development

At laboratory temperatures (18°-25° C) maximum colour was produced in 100 minutes and remained stable for at least a further three hours. At a temperature of 39° C the colour was fully developed in less than one hour whereas at 0° C some eighteen hours were required for the attainment of maximum colour. The sensitivity of detection, after full colour development, was identical for each of the temperatures at which colour development was investigated.

These investigations showed that temperature control during colour development was unnecessary unless extremely low laboratory temperatures prevail.

Sensitivity of Detection

The molar extinction coefficient for formaldehyde by this method was found to be $1.54 \times 10^4 \text{ g mole}^{-1} \text{ cm}^{-1}$. Beer's law was obeyed up to formaldehyde concentrations in the final solution of at least 3.5 µg/ml formaldehyde.

Interference from Smoke Components

The most likely interference in smoke was expected to be due to the oxides of nitrogen which would be trapped as nitrite in a liquid absorption trap containing sodium tetrachloro mercurate (II). The addition of sodium nitrite to standard formaldehyde solutions revealed that as little as 67 µg of nitrite reduced the colour by some 14.5%. The addition of 1 ml of 1% w/v aqueous sulphamic acid completely overcame the interference from oxides of nitrogen up to a level of 16 µg/ml as nitrite.

In the presence of sulphamic acid no interference in the formaldehyde determination was observed for cigarettes delivering less than 1250 µg per cigarette of formamide, phenylamine, acetone, acetaldehyde, acrolein or glycerol, 690 µg per cigarette of hydrogen cyanide, 770 µg per cigarette of hydrogen sulphide and 500 µg of nitric oxide.

No spectral interferences were observed from individual smoke components but smoke samples had a considerable absorption in the detection region. This background absorption from smoke samples was minimised by chloroform extraction of the samples prior to submission to the colour reaction. No formaldehyde was removed from the aqueous sample by the chloroform extraction. Some background absorption was observed for smoke samples after chloroform extraction and it was necessary to read the absorption of smoke samples against a

* Received for publication: 19th November, 1970.

smoke blank. This blank was prepared treating a second aliquot of smoke sample in exactly the same way as the test sample but without the addition of sodium hydrogen sulphite.

Smokings Parameters

Conditioned and sorted cigarettes were smoked by taking a 25 ml puff of 2 seconds duration once every minute. Cigarettes were conditioned for at least 48 hours prior to smoking in air 60% relative humidity at a temperature of 21°C.

Cigarettes were sorted by weight to within 20 mg of the mean weight of the whole of the conditioned batch of cigarettes and by pressure drop to within 4% of the mean pressure drop of the whole of the batch of conditioned cigarettes.

Trapping of Smoke Samples

Initial work was carried out by smoking cigarettes directly into two liquid absorption traps placed in series, each containing 10 ml of sodium tetrachloro mercurate (II) and 1 ml of sulphamic acid. Determination of the amount of formaldehyde collected in each trap revealed the trapping efficiency of a single trap was 94%.

Determinations carried out using cold trapping techniques revealed that deliveries from a flue-cured filter cigarette by this procedure were significantly higher than those previously obtained by the use of liquid absorption traps (Table 1). It was found that although smokings were carried out taking a puff nominally of 2 seconds duration the puff duration for the liquid absorption traps was in fact three seconds. Deliveries of formaldehyde determined by the cold trapping technique with a puff duration of three seconds were found to be identical to those obtained using the liquid absorption trapping procedure (Table 1).

Table 1. Formaldehyde deliveries determined by liquid absorption and cold trap procedures.

Liquid absorption trap		Cold trap 2 sec. puff duration		Cold trap 3 sec. puff duration	
Delivery (µg/cig.)	s.d.	Delivery (µg/cig.)	s.d.	Delivery (µg/cig.)	s.d.
25.4	2.7	36.4	2.3	25.4	2.0

Deliveries are the mean of twelve determinations.
s.d. is the standard deviation of results.

Table 3. Addition of standards to smoke samples.

Added formaldehyde (µg)	Volume of smoke solution (ml)	Optical density Mixture	Net optical density Smoke	Net optical density Standard	Recovery standard (%)	Formaldehyde delivery (µg/cig.)
20	0	0.460	—	0.460	—	—
40	0	0.920	—	0.920	—	—
0	5	0.435	0.435	—	—	63.0
0	10	0.880	0.880	—	—	63.9
20	5	0.900	0.440	0.465	101.0	63.7
40	5	1.350	0.430	0.915	99.4	62.4
20	10	1.340	0.880	0.460	100.0	63.7
40	10	1.820	0.900	0.940	102.5	65.1

The cold trap technique was adopted due to its ease of operation and that it resulted in constant and reproducible puff profile characteristics during smoking. Using a freezing mixture with a temperature of -80°C for the trapping procedure removed any possibility of interference from nitric oxide, the major oxide of nitrogen present in smoke.

Effect of Puff Volume on Delivery

Having found that the duration of the puff used to smoke cigarettes affected the delivery of formaldehyde, the effect of puff volume on the formaldehyde yield was examined. The delivery from a flue-cured plain cigarette was determined taking 20 ml, 25 ml and 30 ml puffs of 2 seconds duration once every minute. The formaldehyde delivery was found to increase with puff volume (Table 2).

Table 2. The effect of puff volume on formaldehyde delivery.

Puff volume (ml)	Delivery (µg/cig.)
25.0	60.9
25.0	68.1
30.0	76.8

The results are the mean of four determinations.

Addition of Standards to Smoke Samples

A smoke sample was prepared in which the smoke from six flue-cured plain cigarettes was contained in 100 ml of sodium tetrachloro mercurate (II). Aliquots of standard formaldehyde solutions were added to aliquots of this smoke sample and the formaldehyde content of the mixtures determined. The recovery of added standards and the calculated cigarette delivery from smoke samples in the presence of added standards both agreed closely with results obtained for the formaldehyde content of the unmixed solutions. (Table 3.)

Effect of Cambridge Filters on Formaldehyde Delivery

The formaldehyde delivery from four flue-cured plain cigarettes was determined after passing the smoke through a Cambridge filter and compared with that from two similar cigarettes determined without the use

Table 4. The effect of Cambridge filters on formaldehyde delivery.

Cigarette	Butt length (mm)	Delivery ($\mu\text{g}/\text{cig.}$)		TPM deposited on Cambridge filter (mg)	Retention of formaldehyde by Cambridge filter (%)
		No Cambridge filter	Cambridge filter		
Flue-cured plain	20	65.5	16.8	116.0	74.4
Flue-cured filter tipped	23*	41.6	29.8	42.3	28.6
Flue-cured filter detipped	7	103.6	35.6	88.6	65.6

* This butt length includes 16 mm filter.

Table 5. The effect of particulate matter deposited on a Cambridge filter on formaldehyde delivery.

No. of cigarettes	TPM deposited on Cambridge filter	Delivery ($\mu\text{g}/\text{cig.}$)		Retention of formaldehyde by Cambridge filter	
		With Cambridge filter	Without Cambridge filter	μg	%
1/2 (5 puffs)	6.6	26.3	43.8	8.8	40.2
1	21.2	19.5	44.2	24.6	55.5
2	40.4	12.7	41.3	57.3	69.3
3	59.1	10.5	41.5	93.0	74.3
4	73.2	9.3	41.6	129.2	77.8

TPM is total particulate matter.

These results are the mean of four determinations.

of a Cambridge filter. A similar comparison was made between the deliveries from two tipped and detipped flue-cured filter cigarettes determined both with and without the use of Cambridge filters. The results (Table 4) suggested that the percentage of formaldehyde retained by the Cambridge filter depends upon the amount of total particulate matter (TPM) deposited on the filter during smoking.

In order to confirm that these observations were due to absorption of formaldehyde by the total particulate matter deposited on the Cambridge filter and not to differences in the composition of the smoke from the three cigarette types a further investigation was carried out using a single cigarette type. Deliveries from different numbers of cigarettes were determined both with and without the use of a Cambridge filter. The results (Table 5) clearly show that the retention of formaldehyde on a Cambridge filter depends upon the amount of particulate matter deposited on the Cambridge filter and that it is necessary to determine formaldehyde delivery from cigarettes on whole smoke samples.

The results of these investigations suggest that a large portion of formaldehyde in cigarette smoke (approximately 40%) is associated with the particulate phase and that formaldehyde is readily absorbed by particulate matter during filtration due to its hydrophilic nature.

PROCEDURE

Reagents

Sodium Tetrachloro Mercurate (II): Dissolve 27.2 g analytical reagent grade mercuric chloride and 11.6 g laboratory reagent grade sodium chloride in distilled water and dilute to one litre.

Sulphamic Acid: 1% w/v solution of analytical reagent grade sulphamic in distilled water.

p-Rosaniline: 0.04% w/v solution of laboratory reagent grade p-rosaniline hydrochloride in 0.72 N hydrochloric acid. This solution is allowed to stand prior to use, until it has attained an orange colour.

Sodium Hydrogen Sulphite: Dilute a 5 ml ampoule of 35% w/v analytical reagent grade sodium hydrogen sulphite to two litres with distilled water. This solution is stable for 1–2 weeks.

Calibration

Dilute a 36% w/v aqueous solution of analytical reagent grade formaldehyde one thousand times to yield a solution containing approximately 400 $\mu\text{g}/\text{ml}$ of formaldehyde. Standardise this solution, which is stable for several weeks, by iodimetry to determine the actual formaldehyde concentration. Dilute this standardised solution forty times with distilled water and use this solution (approximately 10 $\mu\text{g}/\text{ml}$) for calibrations. This dilution should be carried out daily as the final solution is only stable for 24–48 hours.

Place aliquots of the dilute standard solution (0–5 ml) into volumetric flasks (25 ml) containing 8 ml sodium tetrachloro mercurate (II) and 0.4 ml sulphamic acid and dilute to approximately 20 ml with distilled water. Add 1.5 ml sodium hydrogen sulphite 2.5 ml p-rosaniline and mix thoroughly. Dilute the solution to volume with distilled water, mix thoroughly and allow to stand for 100 minutes. Prepare a blank solution in a similar manner but without the addition of formaldehyde and sodium hydrogen sulphite. Read with optical densities of the standard solutions at 571 nm in 1 cm cells against the blank. Construct a calibration curve.

Treatment of Smoke Samples

Smoke two cigarettes directly into a cold trap packed with glass helices, cooled in a freezing mixture of acetone and solid carbon dioxide (-80°C), using standard smoking parameters. Take two clearing puffs at the end of each cigarette. Add sodium tetrachloro mercurate (II) (20 ml) and sulphamic acid (1 ml) to the trap and remove it from the coolant. Allow the trap to attain ambient temperature with occasional agitation and pour the contents of the trap into a separating funnel (100 ml). Wash the trap with two aliquots (5 ml) chloroform and a further aliquot (10 ml) of chloroform and add these washings to the funnel. Stopper the funnel and shake vigorously for one minute, allow the two phases to separate and discard the chloroform. Re-extract the aqueous phase with a further portion (15 ml) of chloroform. Transfer the aqueous phase to a volumetric flask (50 ml) and make up to volume with distilled water. Place an aliquot (20 ml) of this solution in a volumetric flask (25 ml) add 1.5 ml sodium hydrogen sulphite and 2.5 ml p-rosaniline reagent, mix thoroughly and allow to stand for 100 minutes.

Prepare a smoke blank by placing a further aliquot of the sample in a volumetric flask (25 ml), add 2.5 ml p-rosaniline reagent, mix thoroughly and make up to volume with distilled water. Mix thoroughly and stand for 100 minutes.

Read the optical density of the smoke sample at 571 nm in 1 cm cells against the sample blank. Compare the optical density obtained with the standard calibration curve and calculate the formaldehyde delivery of the cigarette.

At least one standard must be coloured with each set of samples to check that the sodium hydrogen sulphite solution has not deteriorated sufficiently to lower the sensitivity of detection.

Calculation

Formaldehyde delivery = Optical Density Sample $\times$ $31.25 \times Y$ $\mu\text{g/cigarette}$, where Y is the concentration of formaldehyde in the final solution that produces an optical density of 1.0. We have found that $Y = 1.95$.

RESULTS

The procedure has been applied to the determination of formaldehyde deliveries from a variety of cigarettes, types and results are given in Table 6. No interferences or difficulties have been encountered in the analysis of smoke from cigarettes manufactured from any tobacco types yet examined.

Discussion of Results

The standard deviations of results for the formaldehyde deliveries of cigarettes determined by this procedure were less than 5 μg . The coefficient of variation of results was less than 7% except for those cigarettes delivering less than 25 μg formaldehyde and also for the U.S. Blend cigarette.

The formaldehyde deliveries from cigarettes manufactured from flue-cured tobaccos were found to be greater than those from cigarettes manufactured from burley and fermented tobaccos.

The formaldehyde retention by conventional crimped paper and cellulose acetate is some 80% of the nominal total particulate matter retention of these filters. The presence of carbon in the filter increases formaldehyde retention.

The formaldehyde retention of conventional crimped paper and cellulose acetate filters and of Cambridge filters suggests that much of the formaldehyde in cigarette smoke is associated with TPM, probably due to its hydrophilic nature.

Table 6. Formaldehyde deliveries from various cigarettes.

Tobacco types	Cigarette filter	No. of determinations	Delivery ($\mu\text{g/cig.}$)			Retention %
			Mean	s.d.	C.V.	
Flue-cured (I)	None	6	65.5	4.4	6.6	—
Flue-cured (II)	Crimped paper / C/A	12	36.4	2.3	6.3	41.9
	None	12	62.6	2.3	3.7	—
	Dual C/A	4	34.3	1.9	5.5	22.0
Flue-cured (III)	C/A / carbon / C/A	4	22.2	2.3	10.4	49.7
	None	4	44.0	2.3	5.2	—
		4	53.8	2.5	4.6	—
Flue-cured (IV)	Crimped paper / C/A	4	43.5	1.6	3.7	—
25% Burley + 75% (IV)		4	34.2	1.1	3.1	—
50% Burley + 50% (IV)		4				
Fermented	C/A	8	16.9	1.0	5.9	23.5
	None	8	22.1	1.7	7.6	—
Burley	None	8	28.5	2.7	9.5	—
U.S. Blend	C/A	4	46.4	4.7	10.1	—

s.d. is standard deviation of results.

C.V. is the percentage coefficient of variation of the results.

C/A filters are cellulose acetate.

SUMMARY

A specific, sensitive method for the determination of formaldehyde in cigarette smoke is described employing the spectrophotometric detection of the product formed by reaction of formaldehyde with p-rosaniline and sulphur dioxide. The procedure is applicable to the analysis of smoke from cigarettes manufactured from flue-cured, burley and fermented tobaccos. Smoking parameters and the use of Cambridge filters have been found to affect delivery markedly. The effect of several commercial filters on formaldehyde delivery has been examined.

ZUSAMMENFASSUNG

Für die Bestimmung des Formaldehyds in Cigarettenrauch wird eine spezifische und empfindliche Methode beschrieben, die auf dem spektrophotometrischen Nachweis des Reaktionsproduktes von Formaldehyd mit p-Rosanilin und Schwefeldioxid beruht. Das Verfahren ist für die Untersuchung des Rauches von Cigaretten aus Burley-Tabak, aus fermentiertem und aus röhrengetrocknetem Tabak geeignet. Es zeigte sich, daß die Abrauchparameter und die Benutzung von Cambridge-Filtern die Ausbeute merklich beeinflussen. Die Wirkung mehrerer handelsüblicher Filter auf die Ausbeute an Formaldehyd wurde untersucht.

RESUME

On décrit une méthode spécifique et sensible pour déterminer la formation de formaldéhyde dans la fumée de cigarettes par la détection spectrophotométrique du produit de réaction de la formaldéhyde avec la p-rosaniline et le dioxyde de soufre. Ce procédé peut être appliqué pour l'analyse de la fumée de ciga-

rettes contenant du tabac flue-cured, burley et fermenté. La manière de fumer et l'emploi de filtres Cambridge influencent sensiblement la formation du produit. On a aussi examiné l'influence de différents filtres commerciaux sur la formation de formaldéhyde.

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Acknowledgement

The authors are grateful to the Directors of Imperial Tobacco Group for permission to publish this work.

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