

The Transfer of Tobacco Additives to Cigarette Smoke

Examination of the Possible Contribution of Pyrolysis Products to Mainstream Smoke Composition *

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SUMMARY

The distribution of six radiolabelled model flavourants in cigarette smoke has been described. The possibility of pyrolytic products occurring in the mainstream smoke has been thoroughly examined. Of the six flavourants used four showed no detectable decomposition. Anisaldehyde underwent some decomposition that was detectable in the mainstream smoke. Even so the major radiolabelled smoke product was unchanged anisaldehyde (91.4%). Vanillin decomposition, although suspected, was only detected in the sidestream gases in these experiments.

ZUSAMMENFASSUNG

Die Verteilung von sechs radioaktiv markierten und als Modellsubstanz dienenden Aromaverbindungen im Zigarettenrauch wurde untersucht. Es wurde geprüft, inwieweit Pyrolyseprodukte dieser Aromastoffe im Hauptstromrauch auffindbar sind. Vier der sechs untersuchten Substanzen veränderten sich durch Pyrolyse nicht. Für Anisaldehyd ließ sich zwar im Hauptstromrauch in geringem Ausmaß ein pyrolytischer Abbau nachweisen, zum überwiegenden Teil (91,4 %) war es aber unverändert als radioaktiv markiertes Anisaldehyd im Rauch enthalten. Obwohl auch bei Vanillin ein Abbau angenommen wurde, konnte ein solcher im Rahmen dieser Untersuchung nur im Nebenstromrauch nachgewiesen werden.

RESUME

Ce travail a porté sur l'étude de la répartition dans la fumée de cigarette de six composés aromatisants marqués au carbone radioactif et tenant lieu de modèles. Il a été examiné dans quelle mesure on pouvait détecter des produits de pyrolyse de ces composés dans la fumée du courant principal. Quatre des six substances étudiées ne sont pas modifiées par la pyrolyse. Dans le cas de l'anisaldéhyde, l'analyse de la fumée du courant principal a montré qu'il y avait eu une faible décomposition pyrolytique, mais la majeure partie (91,4 %) de l'anisaldéhyde radioactive a été retrouvée non dégradée dans la fumée. Alors que l'on avait supposé que la vanilline se dégradait aussi, les produits de sa décomposition n'ont pu être mis en évidence que dans la fumée secondaire dans le cadre de ces expériences.

INTRODUCTION

Flavours constitute one of the major cigarette additives. Whilst menthol is by far the most well known a wide variety of materials are included in compounded flavours and added in small quantities as top dressings. Apart from menthol, which has been studied in detail by JENKINS et al. (1), and vanillin, recently examined by GREEN et al. (2), little is published regarding the extent of pyrolytic decomposition of the chemicals involved.

As in previous studies radiochemical tracer methods have been used in order to facilitate the analysis of minor components in the inherently complex cigarette-smoke condensate.

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Table 1.
Radiochemicals used.

Radiochemical	Specific activity (mCi/mmol)	Radiochemical purity	Chemical purity
<i>p</i> -[ring- ¹⁴ C]Anisaldehyde	186	97% (radio GLC)	97% (GLC)
[ring- ¹⁴ C]Anisole	112	>95% (radio GLC)	95% (GLC)
[carbonyl- ¹⁴ C]Benzaldehyde	54	96% (radio GLC)	n.a.*
Isoamyl [carbonyl- ¹⁴ C]isovalerate	54	95–97% (TLC systems)	98% (GLC)
Methyl [side chain-3- ¹⁴ C]Cinnamate	50	97–98% (TLC systems)	Satisfactory by IR spectroscopy
[carbonyl- ¹⁴ C]Vanillin	53	97% (TLC)	IR spectroscopy

* Not available although purity was judged to be high using gas-liquid chromatography (GLC) during transfer experiments.

Table 2.
Cigarette samples examined.

<i>Description</i>	
U.S.-style blended cigarettes with cellulose acetate filter	
<i>Origin</i>	
University of Kentucky (Tobacco and Health Research Institute)	
<i>Code</i>	
IR4F	
<i>Dimensions</i>	
total length	83 mm
tobacco rod	57 mm
filter	26 mm
<i>Physical measurements</i>	
tip ventilation	29.4%
cigarette-paper permeability	28 C.U.*
total pressure drop	129 mm w.g.**
tobacco-rod pressure drop	54 mm w.g.
<i>Chemical analyses</i>	
tobacco:	
nicotine	2.11%
total sugar	12 %
reducing sugar	10.7 %
moisture	12.5 %
smoke:	
tar	9.3 mg / cigarette
total particulate matter	10.8 mg / cigarette
nicotine	0.9 mg / cigarette
carbon monoxide	12.9 mg / cigarette

* CORESTA unit of paper permeability: cm min⁻¹ cbar⁻¹.

** mm water gauge at an air flow of 17.5 cm³ s⁻¹.

Table 3.
Quantities of additive applied to experimental cigarettes.

Additive	Radioactivity/cigarette (μCi)	Mass/cigarette (μg)
Anisaldehyde	85	65
Anisole	8.7	8.7
Benzaldehyde	52	104
Isoamyl isovalerate	44	142
Methyl Cinnamate	69	227
Vanillin	77	223

Table 4.
Chromatographic details.

Instrument:	Carlo Erba 4200G.
Column:	2 m × 3 mm inside diameter (glass).
Column packing:	5% Carbowax 20M on Supelcoport (100–120 mesh).
Oven temperature:	Isothermal set at between 80 °C and 210 °C depending on particular compound being examined.
Carrier gas:	Argon; 64 cm ³ min ⁻¹ through GC column, 24 cm ³ min ⁻¹ to FID, 40 cm ³ min ⁻¹ to radioactivity detector.
Detectors:	a. FID (Carlo Erba), b. Radio gas detector (ESI Nuclear).

This work describes the distribution of several ^{14}C -radiolabelled model-flavourant compounds in cigarette-smoke fractions and also their combustion-pyrolysis contributions to mainstream smoke.

EXPERIMENTAL

The radiochemicals used, which were supplied by Amersham International p.l.c., are listed in Table 1 together with the criteria of purity. Whilst it would have been preferable to use all uniformly labelled materials, these were not readily available at the time of this study.

Cigarettes, as detailed in Table 2, were spiked with radiolabelled flavours using a manual syringe-injection technique. The quantities of flavour added in each case are given in Table 3, they were kept within limits commonly encountered in top dressing flavours whilst maintaining an adequate addition of radioactivity to facilitate subsequent smoke analysis.

The sample cigarettes were equilibrated in batches for up to eight weeks. Throughout the equilibration period cigarettes were examined to determine the distribution of additive (in terms of radioactivity) in the samples. This was done by sectioning the tobacco rod into four equal lengths and measuring the radioactivity extracted from each section. After eight weeks the equilibration, for the purposes of the current experiments, was complete.

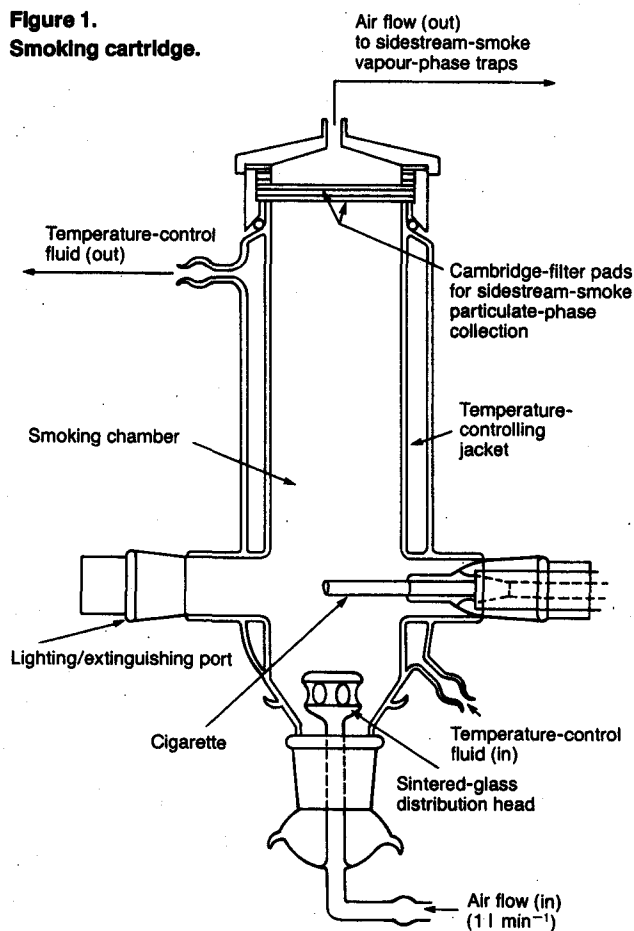
Control cigarettes were extracted in order to determine the radioactivity present and its distribution in the equilibrated cigarettes at the time of smoking. A considerable loss of added flavour and therefore radioactivity occurred during the equilibration period. Consequently, high levels of activity were added originally so that sufficient remained on the cigarette at the time of smoking to allow the analysis to be effective.

Liquid-scintillation counting was used to determine the distribution of the radiolabelled additives in the various smoke fractions and cigarette-butt residues. The procedure involved smoking, collection, solvent extraction and finally scintillation counting.

The smoking procedure involved the use of the cartridge shown in Figure 1 and was similar in principle to methods reported previously (3) using alternative designs of cartridge. In the collection of mainstream-smoke fractions for examination by radio gas chromatography a second additional, non-cartridge, standard CORESTA procedure was also used to ensure that the slightly modified smoking conditions prevalent in cartridge smoking were not affecting the results.

The mainstream smoke fractions were extracted with ethanol and the resultant solution was examined by radio gas chromatography in order to establish the extent of any pyrolytic decomposition that had occurred to the additive on smoking. Complete chromatographic details are given in Table 4, the method included a post-column splitter allowing both flame ionization and

Figure 1.
Smoking cartridge.



radioactivity detectors to be employed simultaneously. The radio gas detector (model 504) and the data-collection and handling system (Videochrom 3 computing integrator) were supplied by ESI Nuclear*.

The radio gas chromatography used in this way produced both a radioactivity and mass trace relating to the effluent from the separating column. No pyrolytic decomposition was therefore indicated by a single chromatographic peak at a retention time corresponding to that of the original additive. The existence of more than a single radioactive peak indicated some decomposition, the extent of which could be assessed by integration of the peaks concerned.

Calibration graphs for all the additives used relating the radioactivity detected by scintillation counting to that from radio gas chromatography were used to determine the detection limits prior to sample preparation and smoking. In addition these calibration graphs were used during the assessment of the mainstream smoking results to establish that all the radioactivity injected into the gas chromatograph had been detected by the radio gas detector. This confirmed that pyrolysis and the analytical procedures had not resulted in products which failed to pass through the gas-chromatographic system.

* ESI Panax, Rotheroe and Mitchell Ltd.,
Victoria Road, Ruislip, Middlesex, England.

Table 5.
Total smoke distribution.

Additive	Smoke fraction and cigarette residue (percentage of radioactivity on cigarette at time of smoking)					Total recovery
	Mainstream-smoke total particulate matter	Mainstream-smoke vapour phase	Sidestream-smoke total particulate matter + vapour phase	Tobacco residue	Filter butts	
Anisaldehyde	11.6	0.1	34.0	6.9	48.8	101.4
Anisole	3.9	9.3	38.9	1.5	44.4	98.0
Benzaldehyde	8.6	1.1	36.9	3.5	47.5	97.6
Isoamyl isovalerate	11.7	6.7	30.5	4.0	48.6	101.5
Methyl cinnamate	7.4	0.2	30.2	5.0	51.5	94.3
Vanillin	15.9	0.2	22.7	8.7	15.7	63.2

RESULTS AND DISCUSSION

The distribution of radioactivity in the collected smoke fractions and cigarette residues is given in Table 5 for each of the model flavourants examined. No regular determination of the activity in the ash was made as this was found in preliminary examinations to be minimal (<1%).

In order that discussions relating to the distribution of radiolabelled additives be valid the total recoveries must be close to 100%. In all except the vanillin case this is approximately so.

The explanation of the low recovery in the case of the vanillin may be taken from the recent work of GREEN *et al.* who suggest that vanillin is decomposed and ends up in the sidestream gases.

Some direct experimental evidence has been obtained to support this explanation in the current work by using both a carbon-monoxide specific vapour-phase trap (ammoniacal cuprous chloride) and an oxidizing furnace followed by an ethanolamine-containing trap. A significant increase in the radioactivity detected in the sidestream gases was obtained for both cases. For example the recovery of 22.7% added radioactivity quoted in Table 5 for the combined sidestream total-particulate-matter and vapour-phase fractions become 46.9% when a furnace and ethanolamine trap were used. These supporting experiments show that in the case of vanillin there is vapour-phase activity, some of which appears to be in the form of carbon monoxide, which escapes the simple trapping system normally employed in such experiments.

The other five model flavourants examined — anisaldehyde, anisole, benzaldehyde, isoamyl isovalerate, and methyl cinnamate — give high recoveries without using special trapping techniques to detect radioactivity in vapour-phase gases. For these compounds therefore no decomposition occurs to volatile gases. However the possibility of other less-volatile pyrolytic products is considered below.

Whilst the activity in the sidestream smoke was collected and counted as particulate and vapour phases the quoted figure (Table 5) is a combined value. This single figure is more realistic because the collection method used results in volatile components being swept continuously from the Cambridge-filter pads to the vapour-phase traps throughout the experimental period. The distinction between particulate and vapour phases for sidestream smoke under these conditions is therefore rather ill-defined.

Most radioactivity is found in the filter butts where much of the mainstream particulate phase is deposited. However a significant proportion of the filter-butt radioactivity arises as a result of additive migration from the tobacco as the cigarette equilibrates.

For the cigarette samples used in this study the majority of additive, measured in terms of radioactivity, is transferred towards the mainstream smoke although the filter is responsible for removing a significant quantity of the particulate phase and therefore the associated radioactivity. With the exception of vanillin, for which the figures, as explained above, are unreliable, between 30% and 40% of the radioactivity is transferred to the sidestream smoke. The ratio of activity found in the sidestream smoke to that found in the mainstream smoke varies for all the model flavourants added between 1 and 4.

In the mainstream smoke the ratio of activities found in the particulate and vapour phases is dependent upon the particular compound examined. Generally the greater the volatility of the additive the more it is found in the vapour-phase fraction as might be predicted. However there may be some minor chemical influences upon this partition between smoke fractions. Tobacco residues from the experimental cigarettes were found to contain up to 9% of the radioactivity depending on the particular additive. These figures can only be approximations as the value is strongly influenced by the precision with which the cigarettes can be extinguished and the phase of the puffing regime at the time.

Table 6.
Radio gas-chromatographic analysis of mainstream-smoke fraction.

Additive	Number of peaks detected containing radioactivity	Radioactivity detected (nCi)**		Extent of decomposition (%)*
		as additive	as decomposition products	
Anisaldehyde	2	1.71	0.16	8.6
Anisole	1	0.23	n.d.†	0
Benzaldehyde	1	0.15	n.d.	0
Isoamyl isovalerate	1	0.17	n.d.	0
Methyl cinnamate	1	1.45	n.d.	0
Vanillin	1	1.44	n.d.	0

* extent of decomposition (%) = $\frac{\text{radioactivity detected in decomposition products}}{\text{total radioactivity detected}} \times 100.$

** Only low levels of radioactivity were detected because injection volumes of 1 μ l were made from a sample solution of 25 cm³.

† not detected.

Radio gas chromatography has been used to examine the collected smoke fractions for decomposition products. Attention is confined in this work to the mainstream smoke and only to the particulate fraction in which most of the radioactivity is found.

The summarized analysis is detailed in Table 6. Of the six compounds examined only one gave any detectable decomposition in the mainstream particulate fraction. The major contribution to the mainstream activity for all the additives used was due to the additive itself. To underline the importance of this result it is desirable to discuss the detection levels and the supporting evidence for these results.

The minimum detectable activity quoted by the manufacturer of the apparatus, ESI Panax, is 0.02 nCi. In order to obtain this for a given chromatographic peak it was necessary in our experience to modify the furnace tube and subsequent drying tube so as to reduce the dead volume to a minimum whilst still maintaining the effectiveness of these components. It was however necessary to change the furnace packing more often with this modification. The reduced dead volume reduced the peak broadening and consequently improved the sensitivity. Nevertheless to obtain the quoted detection limit it was still essential to purge the equipment of residual activity to minimize the background counts.

The use of the Videochrom 3 computing integrator system facilitated the analysis of the radiochromatogram using background subtraction routines.

No significant differences would be expected in detection limits for chemically different compounds because all are detected as radiolabelled carbon dioxide. Consequently even unknown compounds, if present, would have similar limits of detection. The chromatographic retention time could influence the detection limit to a minor extent mainly as a result of peak-broadening effects.

The most volatile compounds examined such as benzaldehyde and isoamyl isovalerate are lost very rapidly

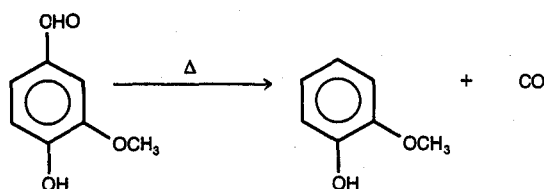
from the cigarettes during the course of the eight-week equilibration time. This results in detectable degrees of decomposition being rather higher than for the less volatile additives. After allowing for the migration that occurs during the eight-week aging 13.3% and 11.7% decomposition could have been detected for benzaldehyde and isoamyl isovalerate respectively. In fact no decomposition was detected for either of these additives in these eight-week old samples. However both these compounds, and all the others used in this study were examined shortly after preparation and then again after a two-week aging period. For these samples, in which migration of the additive had only occurred to a lesser degree, more radioactivity was transferred to the mainstream particulate phase for subsequent examination by radio gas chromatography. Consequently it would have been possible to detect a lower level of decomposition in a single chromatographic peak, the values being 11% for benzaldehyde and 5% for isoamyl isovalerate. No decomposition products were however detected.

A further consideration should be given to the possibility of pyrolysis either giving rise to many different decomposition products each of which could be below the detection limit of the radio gas-chromatographic technique or pyrolysis producing compounds such as polymers not amenable to gas-chromatographic analysis. This possibility may be excluded however for all the additives detailed in Table 6 except benzaldehyde. Each sample prior to analysis by radio gas chromatography was examined by liquid-scintillation counting. For each of the model flavourants used a correlation graph was drawn relating the liquid-scintillation values obtained to the radio gas-chromatography values over a range of activity expected from the extracted smoke and cigarette-residue samples. This allowed a correction of the radio gas-chromatography values to be made and then the figures obtained by both techniques could be compared. Similar values confirmed that all the injected

radioactivity had been detected by the radio gas-chromatographic detection system. Table 7 shows the values obtained and in all cases except benzaldehyde the figures correspond within the limits of experimental error. For benzaldehyde the correspondence is not so convincing. However this may be a result of the low levels of radioactivity transferred or the inherent unreliability at such levels of the calibration curve used to correct the experimental value from the radio gas chromatography.

Most additives transfer to mainstream smoke without detectable decomposition. For anisaldehyde decomposition was detected; however it occurs to less than 10%. For vanillin, supporting sidestream-smoke studies suggest that decomposition does occur although, using a non-uniformly labelled compound, this was not detectable in the collected mainstream-smoke fractions. No carbon-monoxide specific vapour-phase traps had been used in collecting the mainstream-smoke fractions.

When the vapour-phase experiments, involving the use of a carbon-monoxide specific trap, are taken into account together with the results quoted in Table 5 the total recovery becomes 87.4% of the added radioactivity present at the time of smoking ($15.9 + 0.2 + 46.9 + 8.7 + 15.7 = 87.4\%$). It may therefore be inferred that the maximum decomposition of the vanillin that could be detected in the mainstream vapour-phase components of the samples in question would be approximately 13% of the activity on the cigarette at the time of smoking. A possible decomposition to account for this has been suggested by other workers:



With the aldehydic carbon carrying the label the activity would be released from the vanillin as carbon monoxide and consequently only be detected in the vapour-phase components.

Decomposition is more likely to occur when the additive experiences the higher temperatures of the burning zone. Thus additives that distil readily are vaporized and advance along the tobacco rod away from the hot zone. Both the rising temperature at a given point in the tobacco rod and the draw of gases along the rod assist this process. Anisaldehyde and vanillin, the additives showing some decomposition, are amongst the least volatile compounds used and, as a result, may not escape the hot zone of the burning tobacco. Volatility alone however cannot totally account for the observations and the specific chemical interactions between additive and tobacco could prevent distillation and thereby cause some decomposition.

No attempt has been made to identify the minor deg-

Table 7.

Corresponding values of radioactivity determined from liquid-scintillation counting and radio gas chromatography.

Additive	Radioactivity* by liquid-scintillation counting (LSC) (counts registered per unit sample volume)	Radioactivity by radio gas chromatography (corrected counts following GC analysis)	Radio GC (corrected counts) to LSC (counts) ratio
Anisaldehyde	3289	3100	0.94
Anisole	495	497	1.00
Benzaldehyde	576	325	0.56
Isoamyl isovalerate	425	400	0.94
Methyl cinnamate	2373	2612	1.10
Vanillin	2951	2725	0.92

* Expressed as counts registered.

These values may be converted to absolute units of radioactivity by using the conversion: 2.22×10^6 counts = $1 \mu\text{Ci}$.

radation product detectable in the mainstream smoke of the anisaldehyde-impregnated cigarette. Retention data however excludes the *o*- and *m*-anisaldehyde and benzaldehyde as possibilities.

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