

Pyrolysis of Cigarette Ingredients Labelled with Stable Isotopes*

by

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SUMMARY

It is important to know how tobacco additives behave when cigarettes are smoked, whether they transfer intact to the smoke or whether there is any decomposition during smoking. Pyrolysis-GC-MS is a technique that can be focussed upon the effects of combustion from a single material free from interference from the complex mixture of different components present in the smoke. However, because pyrolysis is a model technique, the results need to be validated by comparison with cigarette smoke chemistry.

In a previous paper we presented such a method for modelling the smoke chemistry from a burning cigarette using pyrolysis-GC-MS. The transfer and the extent of degradation of anisole, *p*-anisaldehyde, benzaldehyde, isoamyl isovalerate, methyl *trans*-cinnamate and vanillin within a burning cigarette were estimated using this pyrolysis method. When these data were compared with results from smoke studies from ¹⁴C-analogues of the materials, the high levels of transfer predicted by pyrolysis were found to be generally consistent with the smoke chemistry data. However, there were still two outstanding issues. Firstly, there was some ambiguity in the labelled study about whether vanillin actually transferred without degradation or not. Furthermore, the results from the ¹⁴C-labelled study showed a greater extent of degradation for *p*-anisaldehyde than that indicated from the pyrolysis experiments.

The purpose of the current study was to present some new information obtained to address these questions by

better understanding the effect upon the smoke chemistry from adding vanillin and *p*-anisaldehyde, and the relationship between the smoke chemistry and the pyrolysis results. Components were identified in the smoke from cigarettes loaded with *p*-anisaldehyde and vanillin labelled with ¹⁸O and ¹³C. The extent of degradation from each additive was estimated by identifying labelled degradation products in the smoke. Because there was a clear distinction between the mass spectra from the labelled compounds and their natural counterparts, the major degradation products from the labelled compounds could be readily identified in the chromatograms of the corresponding smoke extracts. Evidence of some degradation at above the transfer temperature was indicated for both additives.

The amount of degradation was found to be less than 1% for *p*-anisaldehyde and only 0.1% for vanillin. This low level of degradation was acceptably consistent with the intact transfer values of 97% and 100%, respectively, obtained by pyrolysis. [Beitr. Tabakforsch. Int. 19 (2000) 55–64]

ZUSAMMENFASSUNG

Es ist wichtig zu wissen, wie Tabakadditive sich verhalten, wenn Zigaretten geraucht werden, ob sie unverändert in den Hauptstromrauch übergehen oder ob während des Rauchens Zersetzungsprozesse stattfinden. Die Pyrolyse-GC-MS ist ein Verfahren, mit dem die Auswirkungen der Verbrennung von Einzelsubstanzen

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ohne Beeinflussung durch das komplexe Gemisch verschiedener Substanzen im Tabakrauch untersucht werden können. Da jedoch die Pyrolyse-GC-MS eine Modelltechnik ist, müssen die Ergebnisse durch den Vergleich mit der Zigarettenrauchchemie validiert werden.

In einer früheren Arbeit haben wir solch ein Verfahren vorgestellt, bei dem die Rauchchemie einer brennenden Zigarette mit Hilfe der Pyrolyse-GC-MS modelliert wurde. Der Transfer und das Ausmaß der Zersetzung von Anisol, *p*-Anisaldehyd, Benzaldehyd, Isoamylvalerat, Methyl-*trans*-zinnamat und Vanillin in einer brennenden Zigarette wurden mit dieser pyrolytischen Methode bestimmt. Der Vergleich dieser Ergebnisse mit den Werten aus Untersuchungen mit ¹⁴C-markierten analogen Substanzen zeigte, dass die durch die Pyrolyseexperimente vorhergesagten hohen Transferraten generell mit den Werten der Rauchchemie übereinstimmten. Zwei Fragen blieben jedoch weiterhin unklar. Erstens bestand in der ¹⁴C-Untersuchung eine gewisse Unsicherheit, ob Vanillin wirklich ohne Zersetzung in den Hauptstromrauch überging oder nicht. Darüber hinaus war in der Studie mit ¹⁴C-Markierung das Ausmaß der Zersetzung von *p*-Anisaldehyd größer als nach den Pyrolyseexperimenten zu erwarten gewesen wäre.

Zweck der vorliegenden Studie war es, neu gewonnene Informationen im Zusammenhang mit dieser Fragestellung zu präsentieren, um die Auswirkungen der Zugabe von Vanillin und *p*-Anisaldehyd auf die Rauchchemie sowie den Zusammenhang zwischen der Rauchchemie und den Pyrolyseergebnissen besser zu verstehen. Die Rauchinhaltsstoffe von Zigaretten, die mit ¹⁸O- und ¹³C-markiertem *p*-Anisaldehyd und Vanillin angereichert waren, wurden bestimmt. Das Ausmaß der Zersetzung jedes Additivs wurde abgeschätzt, indem die markierten Zersetzungsprodukte im Rauch identifiziert wurden. Weil es eine klare Trennung zwischen den Massenspektren der markierten und natürlichen Verbindungen gab, konnten die wichtigsten Zersetzungsprodukte der markierten Substanzen in den Chromatogrammen der entsprechenden Rauchextrakte direkt identifiziert werden. Bei beiden Additiven gab es Anzeichen für eine geringe Zersetzung oberhalb der Transfertemperatur.

Die Zersetzungsrate betrug weniger als 1% für *p*-Anisaldehyd und nur 0.1% für Vanillin. Diese geringe Zersetzungsrate befand sich in akzeptabler Übereinstimmung mit den durch Pyrolyseexperimente erhaltenen Werten des intakten Transfers von 97% bzw. 100%. [Beitr. Tabakforsch. Int. 19 (2000) 55–64]

RESUME

Il est important de savoir ce que deviennent les additifs du tabac dans une cigarette en cours de combustion, si ces additifs restent intacts lors du transfert dans la fumée du courant principal ou s'ils sont dégradés par la pyrolyse. La méthode pyrolyse-GC-MS permet d'étudier les effets de combustion d'un composant individuel sans

interférence avec les autres composants présents dans le mélange complexe de la fumée de cigarette. Cependant, la pyrolyse étant une approche analytique, les résultats doivent être validés par une comparaison avec la chimie de la fumée.

Dans une communication précédente une méthode de modélisation de la chimie de la fumée d'une cigarette en cours de combustion au moyen de la méthode pyrolyse-GC-MS a été décrite. Le transfert et le niveau de dégradation de l'anisol, *p*-anisaldehyde, benzaldehyde, isoamyl isovalérate, méthyl *trans*-cinnamate et de la vanilline dans une cigarette en cours de combustion ont été estimés par cette méthode analytique. La comparaison de ces données avec les résultats obtenus lors d'études dans lesquelles étaient utilisées les ¹⁴C-analogues de ces additifs a révélé que les taux de transfert élevés prédits par la méthode pyrolyse-GC-MS étaient généralement en accord avec les données sur la chimie de la fumée. Cependant, deux problèmes restaient à résoudre. D'abord, il restait une ambiguïté dans l'étude avec les composants marqués au ¹⁴C quant à la question de savoir si la vanilline est restée intacte ou non lors du transfert. Ensuite, les résultats obtenus par l'étude avec les composants marqués ont révélés pour le *p*-anisaldehyde une dégradation plus importante que prévue à partir des études de pyrolyse.

L'objectif de cette étude est de présenter des informations nouvelles relatives à ce sujet, pour mieux comprendre l'effet de la vanilline et du *p*-anisaldehyde sur la chimie de la fumée, de même que la relation entre la chimie de la fumée et les résultats de pyrolyse. Les composés de dégradation ont été identifiés dans la fumée de cigarettes chargées de *p*-anisaldehyde et de vanilline marqués au ¹⁸O et ¹³C. Le niveau de la dégradation de chacun des additifs a été estimé par l'identification des composés marqués dans la fumée. Parce que la distinction entre les spectres de masse des substances marquées et ceux des substances de référence naturelle était précise, les principaux produits de la dégradation ont pu être identifiés facilement à partir des chromatogrammes des extraits de fumée de tabac correspondants. Pour les deux additifs une légère dégradation en-dessous de la température de transfert était évidente.

Le niveau de dégradation est inférieure à 1% pour le *p*-anisaldehyde et à 0.1% seulement pour la vanilline. Le niveau de dégradation relativement bas est en accord satisfaisant avec les valeurs de transfert obtenues à partir de la pyrolyse, qui sont respectivement de 97% et de 100%. [Beitr. Tabakforsch. Int. 19 (2000) 55–64]

INTRODUCTION

It is important to know how tobacco additives behave when cigarettes are smoked, whether they transfer intact to the smoke or whether there is any decomposition during smoking. Being able to discern any but the most abundant two or three substances in the smoke arising from the use of a single additive is difficult. The number

Table 1.
Intact transfer indicated by pyrolysis and smoke chemistry from ^{14}C -labelled compounds (2, 3)

	Transfer predicted by pyrolysis	Transfer indicated by ^{14}C -labelling
Anisole (2)	100%	100%
<i>p</i>-Anisaldehyde (2)	97%	91.4%
Benzaldehyde (2)	74%	100%
Isoamyl isovalerate (2)	99.6%	100%
<i>t</i> -Methyl cinnamate (2)	98.8%	100%
Menthol (3)	99.5%	98.9%
Vanillin (2)	100%	(87% to 100%)*

* ^{14}C -labelling result inconclusive for vanillin

and diversity of chemical constituents within the smoke, coupled with the dynamic nature of reactions occurring within the burning cigarette makes this a challenging medium with which to work. Unfortunately, changes to the smoke chemistry that are insignificant in absolute terms, and thus likely to be missed from a general scan, can often include some very important classes of components.

Pyrolysis has several potential advantages for the assessment of additives and materials in cigarettes. These include rapid evaluation, relatively simple interpretation, minimal sample preparation, a scan that covers a large range of different components in a single run and producing data free of interference from the many other smoke components. However, the disadvantage of using an indirect analytical technique such as pyrolysis is in having to ascertain the extent to which the data are meaningful in terms of smoke chemistry.

It is necessary, therefore, to validate the results from pyrolysis experiments by comparing with smoke chemistry data obtained from cigarettes loaded with the substance under evaluation. Because it is often difficult to distinguish degradation products arising from thermal decomposition or combustion of the substance from the many other smoke components present, such studies are sometimes undertaken using cigarettes loaded with stable or radioactive isotopically labelled variants of the substance.

In a previous study (1) we established the need to consider a range of different burning zone conditions in our experimental approach to pyrolysis. We reasoned that we could understand something about the overall smoke chemistry by considering the combined impact from each set of individual combustion conditions. The transfer and the extent of degradation of anisole, *p*-anisaldehyde, benzaldehyde, isoamyl isovalerate, methyl *trans*-cinnamate and vanillin within a burning cigarette were estimated using this approach.

The results from the pyrolysis experiments indicated that:

- ▶ Anisole, isoamyl isovalerate and vanillin would probably transfer intact to the smoke at 200 °C.

- ▶ *p*-Anisaldehyde and methyl *trans*-cinnamate would be likely to transfer to the smoke at a higher temperature of around 400 °C leading to some decomposition/oxidation (3% and 1%, respectively).
- ▶ Benzaldehyde would probably transfer to the smoke at 200 °C, but at this temperature a significant amount (~26%) oxidised to benzoic acid. Both compounds appeared resilient to further degradation at higher temperatures.

These data were compared with results from smoke studies from ^{14}C -analogues of the materials, and the high levels of transfer predicted were found to be generally consistent with the smoke chemistry data (*see* Table 1). However, there were still two outstanding issues. Firstly, there was some ambiguity in the labelled study about whether vanillin actually transferred without degradation or not. Furthermore, the results from the ^{14}C -labelled study showed a greater extent of degradation for *p*-anisaldehyde than that indicated from the pyrolysis experiments.

It is these questions which have provided the impetus for the current study to follow-up the smoke chemistry for anisaldehyde and vanillin using stable isotopic variants of both substances.

NB: The discrepancy between the pyrolysis data and smoke chemistry for benzaldehyde has already been investigated and satisfactorily resolved (1).

Throughout this report the term 'transfer' will be used to describe how additives migrate from the tobacco to the smoke. Additive 'transfer to smoke' is a term usually applied to describe how much of the material from the original additive, including any degradation products, passes into the mainstream smoke. This is, therefore, the proportion of the additive that has the potential to be consumed. 'Intact transfer' is a term that is used to describe the proportion of the additive in the smoke that has not undergone any decomposition. Thus additive transfer to mainstream smoke is typically between 4 and 30% depending on the additive's volatility, its loading on the cigarette and the cigarette design, whereas values for intact transfer of over 95% are not uncommon for some volatile additives (2, 3).

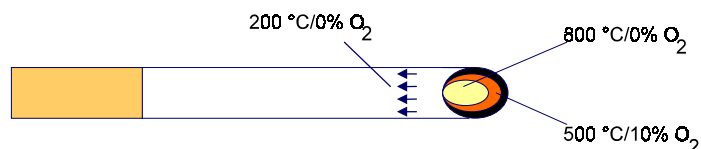


Figure 1.
Conditions within the burning cigarette.

PYROLYSIS METHODOLOGY

Figure 1 shows the major processes that occur in the cigarette, based on measurements of coal conditions by BAKER (4). These include a cool zone behind the burning zone where the transfer mechanism is predominantly distillation of volatiles. There is a hotter intermediate zone, with some available oxygen, where degradation products arise from combustion and are usually either structurally similar or else retain the functional group(s) present in the precursors. Finally there is a much hotter central zone with little available oxygen in which compounds quite unrelated to the precursors are formed.

In a previous report we presented an approach to pyrolysis of additives in which several different pyrolysis experiments were performed to capture a wider range of potential degradation compounds (1). Specifically we

considered temperature conditions at 200, 500 and $800\text{ }^{\circ}\text{C}$ with respective oxygen concentrations of 2, 10 and 2% in nitrogen.

Figure 2 shows the pyrolysis apparatus, an SGE Pyrojector II, with furnace temperature controllable from ambient to $900\text{ }^{\circ}\text{C}$, adapted to enable a combustion atmosphere of oxygen in nitrogen in all proportions.

In standby mode the furnace is constantly flushed with the helium carrier gas. Just prior to the point at which the sample is introduced, the supply to the furnace is switched by means of a six-way Valco valve from the carrier gas to the combustion gas. To initiate the pyrolysis, the sample was inserted into the centre of the furnace by means of a plunger. After allowing the sample to react in the presence of the combustion gas for 30 seconds, the Valco valve was switched back to flush the furnace with the carrier gas. By maintaining the carrier gas at a positive



Figure 2.
The pyrolysis apparatus.

Table 2.
Instrumental operating conditions.

Gas chromatograph	Analysis of volatile products from pyrolysis	Analysis of smoke extract
Instrument	HP 6890	HP 6890
Injection mode	Split	Split
Split flow	20 mL/min	20 mL/min
Split ratio	20:1	
Column	HP 5 MS	HP 5
Column dimensions		
Length	30 m	30 m
Inside diameter	250 μm	250 μm
Film thickness	0.25 μm	0.25 μm
Injector temperature	250 $^{\circ}\text{C}$	250 $^{\circ}\text{C}$
Carrier gas	Helium	Helium
Flow rate	1.0 mL/min	1.0 mL/min
Column mode	Constant flow	Constant flow
Initial temperature	-60 $^{\circ}\text{C}$	40 $^{\circ}\text{C}$
Initial time	3.00 min	3.00 min
Ramp rate	10 $^{\circ}\text{C}/\text{min}$	10 $^{\circ}\text{C}/\text{min}$
Final temperature	210 $^{\circ}\text{C}$	210 $^{\circ}\text{C}$
Total run time	45 min	35 min
Mass spectrometer		
Instrument	HP 5973 MSD	HP 5972 MSD
Mass range	33–400 amu	33–400 amu
Scan rate	3.92 sec^{-1}	
Solvent delay	none	3.00 min
Ionisation mode	EI	EI
Electron energy	-70 eV	-70 eV
Electron multiplier voltage	1600 V	1500 V
MS quadrupole temperature	106 $^{\circ}\text{C}$	Not measured
MS source temperature	230 $^{\circ}\text{C}$	280 $^{\circ}\text{C}$

pressure of at least 5 psi relative to the GC inlet, the gaseous products from the pyrolysis were pushed onto the top of the column, set at an initial temperature of -60 $^{\circ}\text{C}$.

Chromatography was achieved using a HP5 MS capillary column with dimensions 30 m \times 0.25 mm i.d. \times 0.25 μm film thickness, which enabled the separation of a large range of components with respect to both volatility (C_3 to C_{18}) and also polarity (acetic acid to alkanes). The oven was held at the initial temperature of -60 $^{\circ}\text{C}$ for three minutes and then progressively ramped to 210 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$, maintaining this temperature for a further 15 minutes. The instrument used was a HP 6890/5973 GC-MS adapted for cryogenic cooling of the oven by means of liquid nitrogen. A full list of chromatographic and mass spectrometric conditions is given in Table 2.

VALIDATION OF PYROLYSIS EXPERIMENTS

It is essential to understand how pyrolysis results relate to smoke chemistry by comparing the data directly with analysis of smoke from cigarettes loaded with a quantity of the additive.

Because the number and amount of different chemical components produced from cigarette smoke are so great it is often difficult to discern the small changes produced within the smoke chemistry from a single additive. The use of isotopically labelled additives makes the identification of degradation compounds specific to the additive much easier to detect.

Additives can be labelled with stable isotopes including ^2H , ^{13}C , ^{15}N and ^{18}O or with radio-isotopes such as ^3H or ^{14}C . Radiolabelled isotopes can be detected very easily and selectively at low concentrations. The application level of

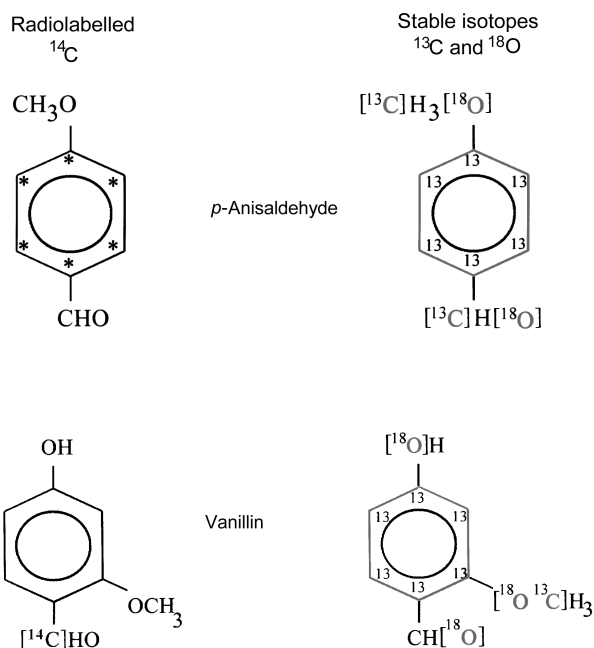


Figure 3.
Labelled additives (* = ^{14}C).

an additive labelled with stable isotopes may well need to be much higher than that normally applied to the cigarette. On the other hand, an MS detector, used in conjunction with stable isotopes, enables degradation products to be identified as detected. Materials incorporating stable isotopes are no more hazardous than their non-labelled counterparts and are therefore not subject to the safety constraints imposed when working with radiochemicals.

PYROLYSIS OF STABLE ISOTOPES: RESULTS AND DISCUSSION

One gram each of labelled anisaldehyde and vanillin (*see* Figure 3) were obtained from Europa Scientific Ltd. The next step was to perform pyrolysis experiments on the labelled and non-labelled additives under exactly the same conditions. The components separated in the chromatograms from each of the non-labelled additives were assigned directly from library searching and matching from a standard database of mass spectra. To obtain a corresponding list of peak assignments for the chromatograms produced from each of the labelled compounds, a comparison of the chromatograms at each set of pyrolysis conditions for the labelled *vs.* non-labelled additives was made and the assignments were matched on the basis of retention times. Figures 4 and 5 show the degree to which the retention times for the pyrolysis products of both anisaldehyde and vanillin were unaf-

fected by the labelled isotopes. Thus, assigning the peaks for the labelled pyrolysis products was a straightforward process.

Figure 6 shows how the mass spectrum for anisaldehyde is affected by the incorporation of labelled isotopes. In the labelled molecule every carbon was nominally ^{13}C and every oxygen was nominally ^{18}O . (The certificate of analysis indicated levels of enrichment of 99% for carbon and 93% for oxygen.) The parent ion is approximately 12 mass units higher (148) in the labelled compared with the unlabelled (136) anisaldehyde. The main features in the fragmentation patterns produced from both the labelled and unlabelled molecules were analogous. The fine structure around the parent ion was noticeably different and this reflected the different isotope ratios present. i.e.: In the natural molecule the abundance of $^{12}\text{C} : ^{13}\text{C}$ is 98.9% : 1.1% and $^{16}\text{O} : ^{18}\text{O}$ is 99.8% : 0.2%. In the labelled molecule $^{12}\text{C} : ^{13}\text{C}$ becomes 1% : 99% and $^{16}\text{O} : ^{18}\text{O}$ becomes 7% : 93%.

The mass spectra of labelled and non-labelled vanillin are compared in Figure 7. The vanillin was supplied with each of the oxygen and carbon atoms, except for the carbon atom in the aldehyde group, labelled. The parent ion of the labelled vanillin is a nominal 13 mass units higher (165) than natural vanillin (152). The carbon and oxygen isotopic ratios in the labelled molecule were 1% : 99% for $^{12}\text{C} : ^{13}\text{C}$ and 10% : 90% for $^{16}\text{O} : ^{18}\text{O}$. As with the *p*-anisaldehyde, the main fragmentation features were analogous. The fine structure, especially around the molecular ion was more noticeably different than in the *p*-anisaldehyde reflecting both the slightly poorer isotopic purity of the enriched oxygen, and the greater number of oxygen atoms in the vanillin molecule.

The spectra of two of the pyrolysis products are shown in Figures 8 and 9. The phenol spectra from both the labelled vanillin and anisaldehyde were in most respects identical. However, the benzaldehyde spectrum produced from the pyrolysis of vanillin was noticeably different from the spectrum produced from the pyrolysis of *p*-anisaldehyde. This is due to the presence of the non-labelled carbon in the aldehyde group of the vanillin – note that the fragmentation ions are not similarly affected.

Once the assignment process was complete, the mass spectra from all the different labelled degradation products were added to the on-line library of mass spectra to enable degradation products from the breakdown of the labelled compounds to be identified in the smoke.

CIGARETTE LOADING AND SMOKING

Essentially the method involved loading a number of cigarettes with labelled additives, collecting the smoke and then analysing the extracted smoke from the cigarettes loaded with the additives and comparing the results against those from smoke from a batch of control cigarettes.

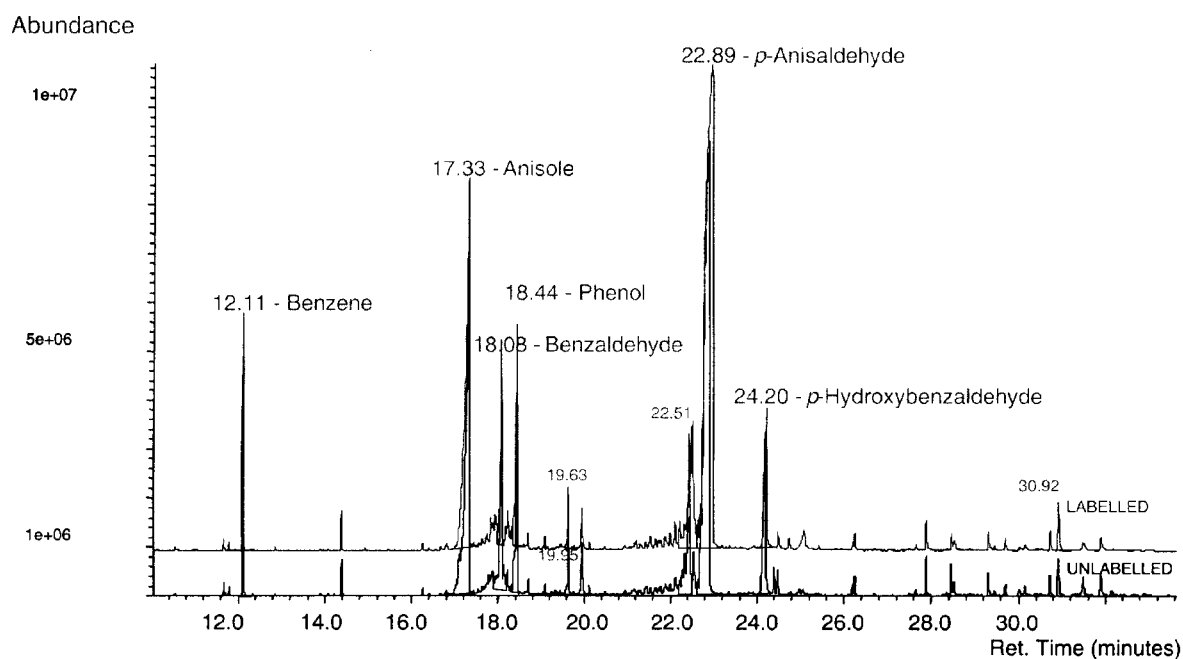


Figure 4.
Labelled and non-labelled *p*-anisaldehyde (800 °C/ 2% O₂).

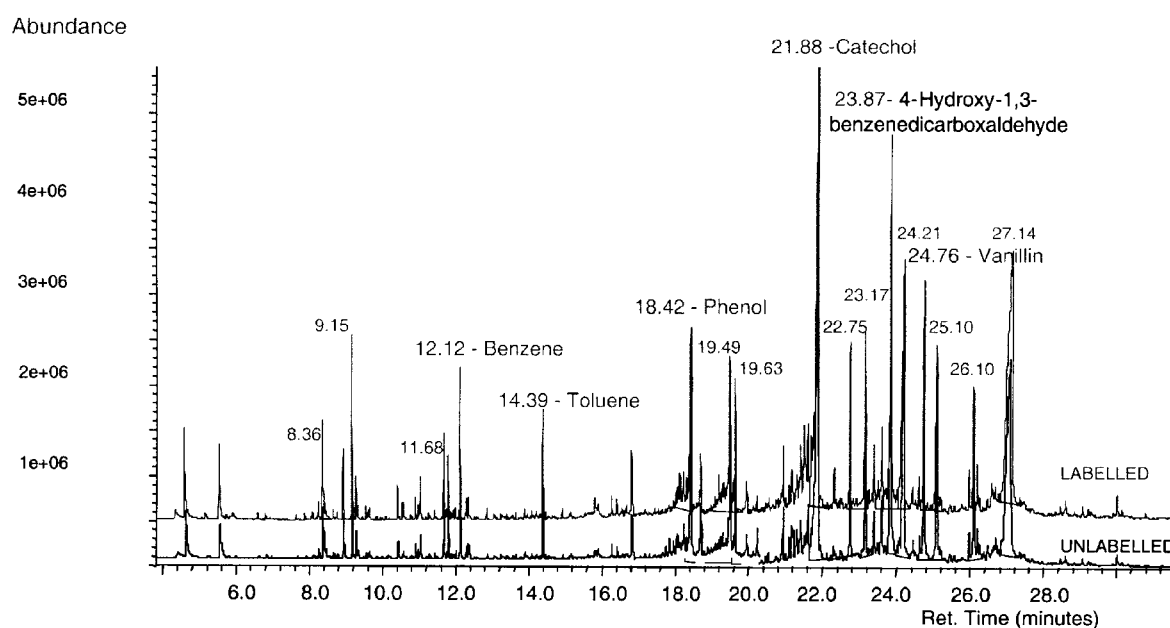


Figure 5.
Labelled and non-labelled vanillin (800 °C/2% O₂).

Stock solutions of 200 mg mL⁻¹ of each of the following additives in ethanol were prepared:

- ▶ unlabelled *p*-anisaldehyde
- ▶ labelled *p*-anisaldehyde
- ▶ unlabelled vanillin
- ▶ labelled vanillin

Separate batches of 20 cigarettes were each injected with 25 µL of each of the stock solutions to give an addition of 5000 µg of each additive per cigarette. 20 more cigarettes were each injected with 25 µL of ethanol to provide a control batch.

Each set of 20 cigarettes was smoked 48 hours after loading, using standard ISO (35 mL, 2 s puff, 60 s interval) smoking conditions and electrostatic precipitation for collection of the mainstream particulate matter. The voltage was set at 25 kV for the first puff, dropping to 15 kV for subsequent puffs.

The precipitated MS smoke was extracted with 5.0 mL methanol (Merck Pesticide Residue Grade). A 2 µL aliquot of this solution was injected manually onto a GC-MS (HP 6890/5972). A list of chromatographic and mass spectrometric conditions is given in Table 2.

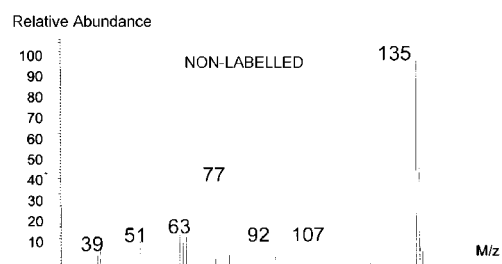
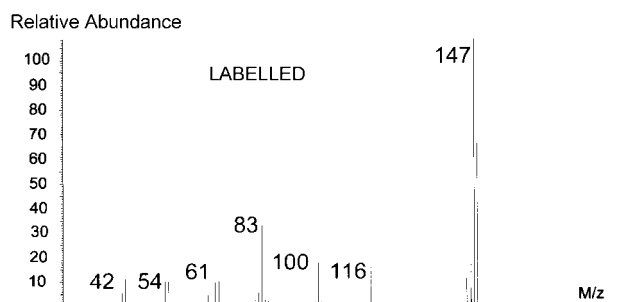
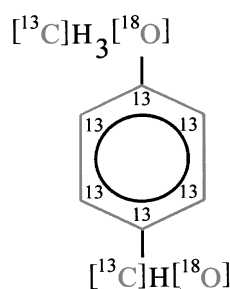


Figure 6.
Mass spectrum of labelled *p*-anisaldehyde.

Duplicate smoke runs and duplicate injections demonstrated that the reproducibility of the whole analysis was acceptably good. Comparison of the chromatographic scans from the control to both the labelled and unlabelled samples showed little degradation of the additives in any of the samples.

The results are summarised in Tables 3, 4 and 5. The additives were both found to transfer over 99% intact to the TPM (i.e. with less than 1% degradation). When the extent of intact transfer indicated in this study for both *p*-anisaldehyde and vanillin is compared with the pyrolysis prediction and the ^{14}C -study (shown in Table 3), the pyrolysis prediction agrees much more closely with the stable isotope smoke study.

Tables 4 and 5 show the degradation products unambiguously identified from *p*-anisaldehyde and vanillin in the cigarette smoke. Specifically, labelled anisole and phenol were produced from the anisaldehyde, and 2-methoxyphenol from the vanillin. Since none of these compounds are produced from the pyrolysis experiments conducted at lower relative temperatures, this is evidence of some

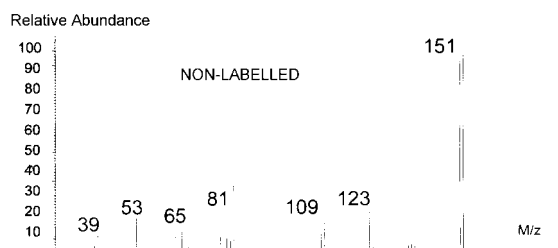
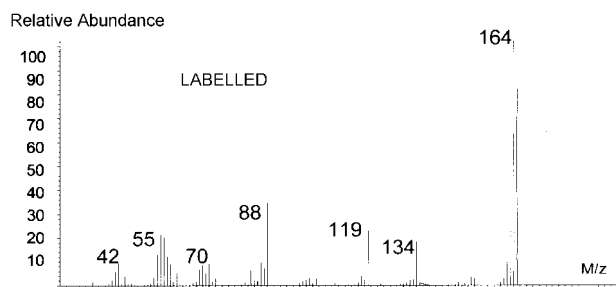
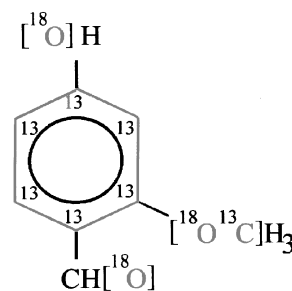


Figure 7.
Mass spectrum of labelled vanillin.

degradation occurring at above the transfer temperature of the additives.

An adjustment based on relative molecular weight was used to equate the extent of transfer to the smoke of the labelled additives compared with the natural additives. The density of labelled *p*-anisaldehyde was calculated from repeated weighing of 10 μL aliquots of the pure compound to be 1.219 g cm^{-3} (natural *p*-anisaldehyde is 1.119 g cm^{-3}). Since vanillin is a solid at room temperature it could be weighed directly.

The total extent of transfer to the smoke from each additive to the mainstream TPM (intact additive and degradation products) was thereby estimated to be 8.1% for *p*-anisaldehyde and 10.4% for vanillin.

CONCLUSIONS

Pyrolysis experiments on additives labelled with stable isotopes produced identical chromatograms to those from unlabelled compounds, with retention times apparently unaffected by isotopic effects. This enabled straightforward identification of the major potential degradation products from the labelled compounds, and their mass

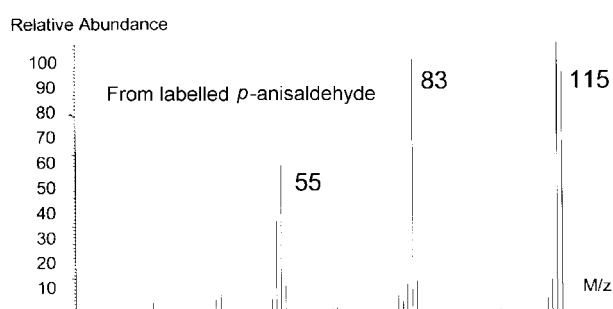
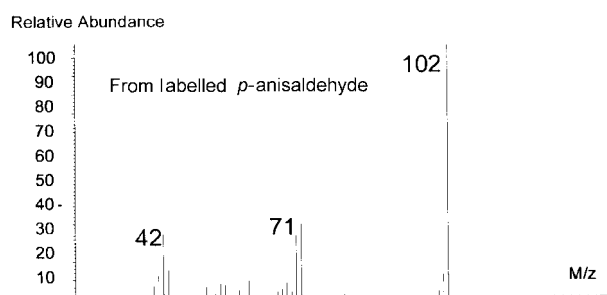
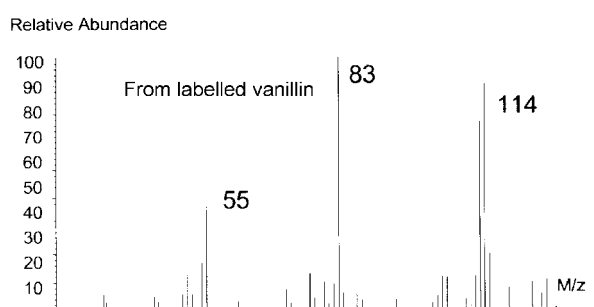
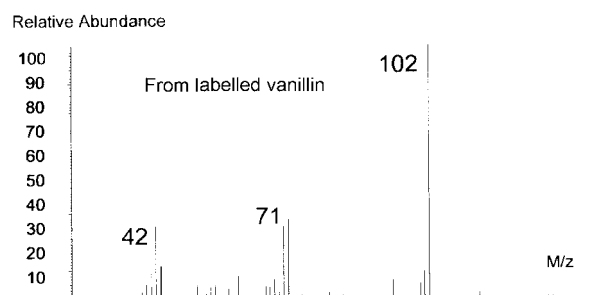
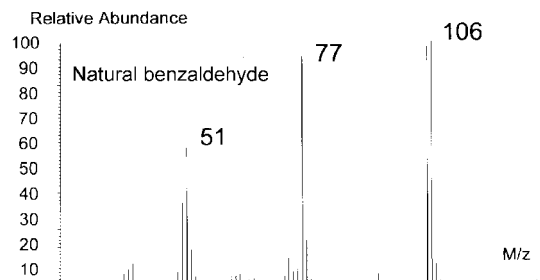
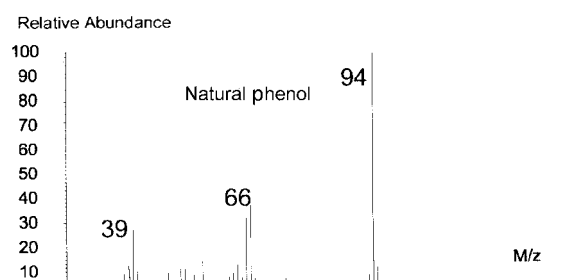


Figure 8.
Degradation to phenol.

spectra were added to an on-line library for subsequent identification in the particulate matter from the smoke. Because there was a clear differentiation between the mass spectra from the labelled compounds and their natural counterparts, the major degradation products from the

Figure 9.
Degradation to benzaldehyde.

labelled compounds were clearly identified in the chromatograms of the corresponding smoke extracts. The high levels of transfer as the intact additive, predicted

Table 3.
Intact transfer indicated by pyrolysis and smoke chemistry from ^{14}C - and ^{13}C -labelled compounds (2, 3).

Intact transfer	Predicted by pyrolysis	Indicated by ^{14}C -labelling	Indicated by ^{13}C -labelling
Anisole	100%	100% (2)	–
<i>p</i> -Anisaldehyde	97%	91.4% (2)	99.1%
Benzaldehyde	74%	100% (2)	–
Isoamyl isovalerate	97.5%	100% (2)	–
<i>t</i> -Methyl cinnamate	98.8%	100% (2)	–
Menthol	99.5%	98.9% (3)	–
Vanillin	100%	(87% to 100%)* (2)	99.9%

* ^{14}C -labelling result inconclusive for vanillin

Table 4.
Degradation of *p*-anisaldehyde.

Compound	Pyrolysis conditions			Smoke [¹³ C]
	200 °C	200 to 400 °C	200 to 800 °C	
<i>p</i> -Anisaldehyde	97.1%	97.0%	69.1%	99.1%
Anisole			7.6%	0.3%
Phenol			5.9%	0.6%
Benzaldehyde			3.7%	
Methyl-4-hydroxy benzoate	1.2%	1.0%	0.9%	
Methyl-4-methoxy benzoate	0.5%	0.9%	1.2%	
4-Hydroxy benzaldehyde			1.2%	

Table 5.
Degradation of vanillin.

Compound	Pyrolysis conditions		Smoke [¹³ C]
	200 °C	200 to 800 °C	
Vanillin	100.0%	50.2%	99.9%
Phenol		6.6%	
2-Methoxyphenol		6.2%	0.1%
<i>o</i> -Cresol		5.6%	
2-Hydroxy benzaldehyde		3.0%	
Toluene		2.7%	

from previous pyrolysis experiments, have been confirmed by these stable isotope studies. Evidence of some degradation at above the transfer temperature is indicated by the results.

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