FTIR analysis of gaseous compounds in the mainstream smoke of regular and light cigarettes

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Abstract

Fourier-transform infrared (FTIR) spectroscopy has been applied to the study of mainstream cigarette smoke from cigarettes of different stated strengths (regular and various light cigarettes with different reported nicotine, tar and CO contents). This technique has allowed for the measurement of a variety of gaseous components including hydrocarbons and both nitrogen and carbon oxides. The results demonstrate that the strength of the cigarette does not have a significant bearing on the quantity of the observed components produced.

Additionally, open-path FTIR studies of diluted sidestream and exhaled smoke have been conducted. These measurements revealed that the majority of gaseous pollutants originated from the sidestream smoke, while the primary smoke was 'purified' or diluted upon exhalation by the smoker.

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1. Introduction

1.1. Methods of analysis of cigarette smoke

Cigarette smoke is a very complex mixture and over the years numerous attempts have been made to identify and quantify its constituents, of which there are tens of thousands. The most common technique used for analysis is gas chromatography (GC). This may utilise, e.g., a nitrogen phosphorous detector (Miyake and Shibamoto, 1995) or be integrated with mass spectrometry (GC–MS) (e.g., Dong et al., 2000; Ding et al., 2005). Proton-transfer-reaction mass spectrometry (Prazeller et al., 1998), time-of-flight mass spectrometry (Dallüge et al., 2002) and capillary electro chromatography (Saeed et al., 1999) have also been applied to study different target analytes in both mainstream and sidestream cigarette smoke. In some cases the whole smoke (i.e. both the solid and the gaseous components) is investigated while in other cases the solid (Ding et al., 2005) and gas phases (e.g., Dong et al., 2000; Cole and Martin, 1996) of the smoke are separated on a Cambridge filter pad. This allows for either or both of the phases to be studied (Parrish et al., 2001). Elsewhere, simultaneous analysis of mainstream and sidestream cigarette smoke has been carried out using quantum cascade laser spectroscopy (Baren et al., 2004; Shi et al., 2003) and also with a tuneable diode laser system, providing millisecond time-resolved measurements (Plunkett et al., 2001).

Fourier transform infrared spectroscopy (FTIR) has, in previous studies, been used to measure gaseous air

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pollutants in the atmosphere (Bacsik et al., 2004, 2005). This method offers the potential for the non-destructive, simultaneous, real-time measurement of multiple gas phase compounds in complex mixtures such as cigarette smoke. Maddox and Mamontov (Maddox and Mamantov, 1977) measured 12 components (in the whole smoke) by means of FTIR using an 18-cm absorption cell. The results were compared puff by puff and from sample to sample. The oxidation of NO to NO_2 and the reaction of these oxides with other smoke components, and the quantitative analysis of these components was studied and the results were compared to model smoke mixtures by Cueto et al. (Cueto et al., 1989; Cueto and Pryor, 1994). Furthermore, on line, real time analysis of mainstream cigarette smoke, with a high precision sampling technique has previously been achieved (Parrish et al., 2001; Li et al., 2002). A special sidestream smoke analysis system has also been built and the results of the measurements compared to the results originating from using standard analytical techniques. Good agreement was found for ammonia and CO_2, but results for CO, HCN and NO differed significantly (Cole and Martin, 1996).

1.2. "Strength of cigarettes"

The strength of a specific cigarette type, e.g., King Size or Ultra Light, is determined by its tar, nicotine and carbon monoxide content. Tar and nicotine yield numbers reported for cigarette brands are not meant to communicate the precise amount of tar or nicotine inhaled by any individual smoker from any particular cigarette. These numbers originate from standardised testing methods, which compare different brands when "smoked" by a machine under identical laboratory conditions. To compare different samples a standard smoking engine is used which allows quantification of the investigated constituents in μg per cigarette (Philip Morris International Management, 2004).

A variety of studies (e.g., Kelbsch et al., 2005; Cummings et al., 2004; Etter et al., 2003) have asked smokers about their reasons for choosing to smoke Light or Ultra Light cigarettes or their reasons for switching to such cigarettes. The results show that the desire to reduce the risk of disease is one of the main factors guiding these choices (National Cancer Institute, 2001). The World Health Organisation however, reports that switching to lower tar products offers no significant health benefits (WHO, 2001). Furthermore, a recent study of six varieties of cigarette (Gendreau and Vitaro, 2005) found that "light" cigarettes do not differ substantially from "regular" cigarettes in terms of smoke yields as determined by a modified ISO method. As a result, smokers of cigarette brands with lower "tar" and nicotine ratings may get as much "tar" and nicotine as smokers of much higher rated brands (Federal Trade Commission, 2000). A recent study (Hecht et al., 2005) showed that there were no statistically significant differences in urinary levels of different lung carcinogens in smokers of regular, light, and ultralight cigarettes.

1.3. Conditions of data acquisition

Most studies comparing the effects of smoking cigarettes of different strengths, e.g., regular and light, focus on measurements of tar and nicotine or some other biomarker (e.g. Benowitz et al., 2005). In this study, it has been investigated as to whether there is a statistical difference in the uptake of gaseous compounds from cigarettes of different advertised "strengths". The method of analysis was FTIR spectrometry employing a simple sampling methodology. This methodology is closer to genuine conditions than that of obtaining results with smoking machines, however while such machines determine yields per cigarette we have evaluated the concentrations of the compounds in a single puff. It has been demonstrated by Maddox et al. (Maddox and Mamantov, 1977), through an investigation of the whole cigarette smoke, that the concentration of the compounds does not change randomly, but instead rises linearly from puff to puff. This means that differences and trends observed in the first puff can be extrapolated to provide information about the entire cigarette. The FTIR technique employed herein is capable only of detecting gas-phase components. As such, any constituents of the smoke present as condensates will not be recorded, however some compounds may be present both as condensates and vapours.

2. Experimental

2.1. Laboratory measurements

Both laboratory (extractive) and field (open-path) spectroscopic measurements have been performed. Laboratory infrared spectra were obtained on a Bio-Rad FTS-185 Series dynamically aligned Fourier transform spectrometer, equipped with a simple 10-cm gas cell of volume 125 ml equipped with an MCT detector.

Measurements were performed by co-adding 64 interferograms. The spectral range was 4000–650 cm^{-1} and the spectral resolution was 0.5 cm^{-1} for all laboratory spectra. "Clean air" spectra were used as the background. These were created by taking a relatively clean air sample to the gas cell from the laboratory.

For quantitative analysis, the region integration and subtraction routine of QASoft software package (Infrared Analysis, 1994) was used and the major absorption band(s) of the selected compounds (Table 1) were accounted for. To aid spectral analysis a library of compound spectra was created. Such a library exists within QASoft for Grams32, however these required to be corrected for slight frequency shifts relative to the samples. The accuracy of the measurements is highly dependent upon the accuracy of the absorption coefficients of the reference spectra. This is estimated to be within ±5% in the QASoft library.

Table 1
Compounds studied, and their frequencies

Compounds	Frequency (cm^{-1})
Methane	3000–2500
Ethane	3050–2900
Acetaldehyde	2900–2600
Carbon monoxide	2250–2050
Nitrogen monoxide	1876 (Q-branch)
Ammonia	970–920
Methanol	1033 (Q-branch)
Ethylene	950 (Q-branch)
Isoprene	900 (Q-branch)
Propylene	913 (Q-branch)
Hydrogen cyanide	712 (Q-branch)

To determine the unknown concentrations only one reference spectrum has been employed for each compound. It is therefore necessary that the typical absorbances fall within the linear range of the Beer–Lambert law. When the intensity of the bands (using triangular apodisation) has a true absorbance below 0.7, the measured absorbance is linearly proportional to the true absorbance and hence to the sample concentration (Griffiths and Haseth, 1986). The typical apparent absorbances in our measurements were, for all compounds bar CO, in the region 10^{-4}–10^{-1} absorbance units (A.U.). In case of CO the value was 0.3 A.U. This method ensures that the overall accuracy of the measurement is limited only by the accuracy of the reference spectra ($\pm 5\%$).

Sampling for the extractive method: for primary (mainstream) smoke sampling the cigarette was lit orally and placed in a glass cigarette holder such that the ventilation holes on the filter were not blocked. The cigarette holder was attached to the evacuated spectrometer cell and air was drawn in through the cigarette by means of opening the tap of the cell by a controlled and pre-determined amount. All of the air drawn through the cigarette was collected in the spectrometer cell. The first part of the cigarette to enkindle, i.e. that at the opposite end from the filter, was used. The smoke was not diluted.

2.2. Field measurements

Field spectroscopic measurements were performed with an open path MIDAC FTIR air-monitoring system (Midac Co., Irvine CA, USA) equipped with a liquid nitrogen cooled MCT detector, a Newtonian telescope (aperture 25.4 cm) and a Michelson interferometer. The system was set up in bistatic monitoring mode with a distance of 4 m between the source and the interferometer. SpectraCalc software (Gallactic Corp.) was used to collect the spectra. The quantitative evaluation of the spectra was carried out in an identical manner to that for data acquired from laboratory measurements, vide supra.

Sampling for the open path method: during sampling it was necessary to ensure that the cigarette smoke between the source and detector was sufficiently concentrated to allow the compounds under study to be detected. To this end, the region between the source and detector was enclosed within a plastic cylinder with an approximate volume of 785 l. The gaseous products of burning the cigarettes were transferred to this region via diffusion through three apertures in the cylinder wall. Two cigarettes were smoked entirely, immediately prior to the measurement of the diluted smoke in the cylinder.

3. Results and discussion

3.1. Laboratory measurements

The cigarettes selected for the cell-based mainstream smoke study were commercial cigarettes of the same brand but of varying strength. These were King Size, Extra Light, Super Light and Ultra Light with 12, 8, 5, 3 mg tar and 0.8, 0.6, 0.4, 0.3 mg nicotine content per cigarette, respectively. An assortment of at least six individual cigarettes of each type was analysed. In general, the relative standard deviations within a group were under 20% (see, e.g., results for Super Light cigarettes in Table 2). This fact demonstrates the reproducibility of the sampling and measurement technique for the study of systems such as this.

Table 2
Concentrations (in percentage of the entire investigated compounds) of compounds measured in primary smoke of the Super Light cigarette samples of the same brand (Marking: P-primary, S1-S6-Super Light samples)

	Concentration (%)								
	PS1	PS2	PS3	PS4	PS5	PS6	Mean	SD	Rel. SD (%)
Methane	13.2	12.1	14.5	13.9	15.2	13.2	13.7	1.1	8.1
Ethane	3.0	2.9	3.5	3.2	3.6	3.2	3.2	0.3	7.9
Acetaldehyde	2.9	3.1	3.1	3.3	3.3	3.3	3.2	0.2	5.3
CO	74.2	74.2	71.9	72.5	69.9	73.2	72.6	1.6	2.3
Methanol	2.2	2.7	2.5	2.8	3.1	2.6	2.7	0.3	10.6
Ethylene	1.2	1.2	1.2	1.2	1.4	1.2	1.2	0.1	6.3
Isoprene	0.9	0.8	0.6	0.6	0.7	0.6	0.7	0.1	16.8
Propene	0.6	0.8	0.8	0.7	0.8	0.7	0.7	0.1	10.9
HCN	1.0	1.2	1.2	1.0	1.0	1.1	1.1	0.1	7.3
NO	0.8	1.0	0.8	0.8	1.0	0.8	0.9	0.1	13.9

Table 3
Mean concentration and standard deviation for each compound in primary smoke

Compound	Concentration/ppm			
	King size	Extra light	Super light	Ultra light
Methane	1210 ± 134	1100 ± 116	896 ± 85	1060 ± 219
Ethane	273 ± 24	294 ± 53	212 ± 22	225 ± 33
Acetaldehyde	272 ± 48	330 ± 97	210 ± 31	245 ± 75
CO	6230 ± 659	6920 ± 948	4810 ± 781	5840 ± 963
Methanol	213 ± 25	247 ± 41	175 ± 26	168 ± 50
Ethene	104 ± 14	123 ± 38	82 ± 9	108 ± 37
Isoprene	47 ± 12	55 ± 14	46 ± 11	66 ± 28
Propene	62 ± 6	71 ± 19	48 ± 7	57 ± 16
HCN	95 ± 13	123 ± 43	71 ± 12	92 ± 43
NO	96 ± 15	83 ± 23	57 ± 10	76 ± 25

The mean concentrations for the investigated compounds are included in Table 3. A number of trends are apparent in the results despite the fact that there appears to be little consistency in the overall order of the cigarettes with respect to the quantity of each gaseous compound produced. Firstly, for most of the components, the King Size cigarette (that with the most nicotine and tar) produces either the greatest, or second greatest, quantity. In all cases the Extra Light cigarette (that with the second most nicotine and tar) produces greater amounts of the detected compounds than those cigarettes with lower nicotine and tar levels.

The difference in the quantity of a single component produced by the cigarettes in the top and bottom positions varies from a maximum of 42% (for NO) to a minimum of 20% (for CO). The average difference between the top and bottom cigarette is 28%. This number is close to the standard deviation of the analysis results. Not surprisingly, no specific statistical (cluster analysis, T-probe) relationship has been found to relate differences in cigarette strength to differences in their gas evolution. It is therefore possible to conclude that, in the case of primary smoke, the strength of cigarette does not have a bearing on the quantity of these gaseous compounds produced upon smoking.

Considering CO concentrations in the cell after puffs of different cigarette types however, does show that extra light cigarettes (PX) are always in the upper region in terms of CO evolution, while super light cigarettes (PS) are always in the bottom region (Fig. 1). Specific trends however cannot be established. These results are inconsistent with the carbon monoxide yields for cigarette brands stated by the manufacturer which suggest a much greater difference in the quantity of CO. Recently very similar results were published for CO yields measured by a modified ISO laboratory protocol (Gendreau and Vitaro, 2005). In their study only one out of six light cigarette brands showed more than a 25% reduction in the yield of carbon monoxide (CO) compared with regular cigarettes. Conversely, the yield of CO was 24% higher for another type of light cigarette compared with the analogous regular cigarette. (The CO yield data are not included in this work, as they were not indicated on the cigarette packets at the time of this study.)

3.2. Field measurements

Additionally, studies have also been carried out using Open-Path FTIR (OP/FTIR) spectroscopy. Only one type of cigarette was used in these studies. One of the benefits of OP/FTIR is that it eliminates both wall and mirror loss, thus allowing the concentrations of reactive compounds to be measured more accurately. However, it is impossible to use this method to examine the contents of primary smoke, hence only results for diluted secondary and exhaled smoke are reported. For the purposes of analysing
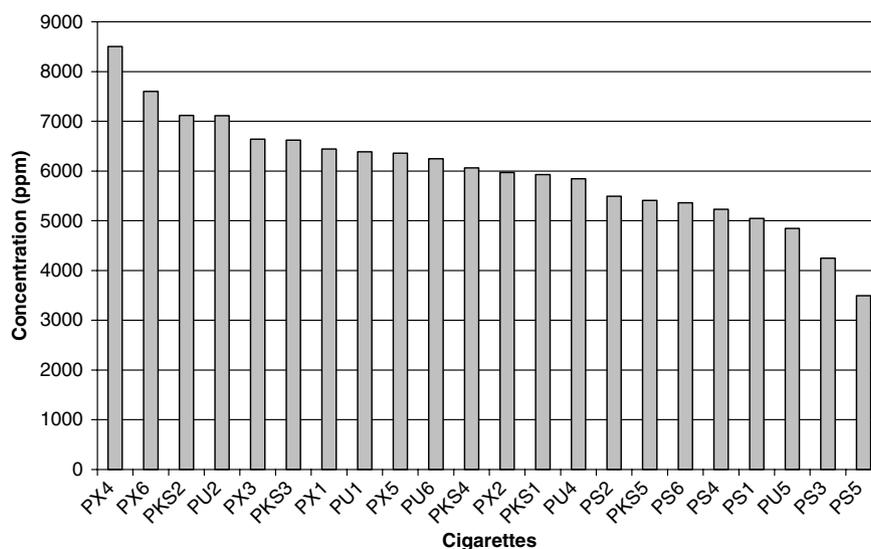

Fig. 1. Carbon monoxide concentration in the cell after a puff of different cigarettes (Marking: P-primary, KS-king size, X-extra light, S-super light, U-ultra light and the number of the sample).
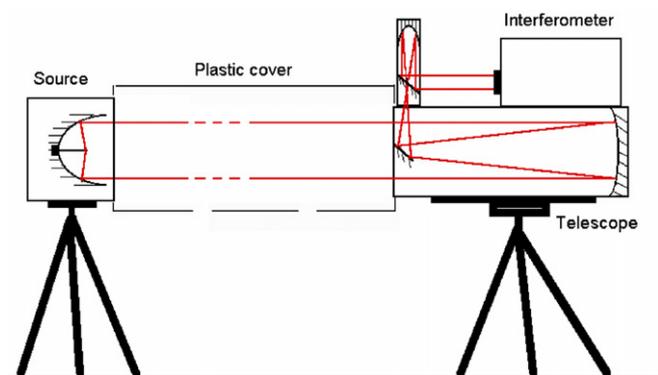
Fig. 2. Experimental set-up for open-path measurements.

the sample spectra, a background spectrum was generated by the zero target method. This entailed collecting a spectrum of smoke free air prior to sampling (Fig. 2).

Different components of the environmental tobacco smoke (ETS) were investigated by means of the OP/FTIR method. Firstly, a sampling region containing both 100% of the secondary smoke which evolved from the lit end of 2 smoked cigarettes and the exhaled smoke from the same cigarettes, was investigated. Additional measurements were carried out by excluding the secondary smoke and measuring only smoke exhaled directly into the sampling volume. In the latter case the majority of compounds were undetectable (Table 4). This is most likely because they interact with the lungs and react to form other compounds (Cueto et al., 1989) or are captured in the lungs and released only slowly. The latter phenomenon has previously been measured by several groups (e.g. Laakso et al., 2004).

The measured data need to be carefully evaluated as there are numerous conditions (e.g., smoking behaviour), which may not be constant. The results however do indicate that exhaled smoke contains far fewer pollutants than that which has not been processed by the smoker.

Table 4
Analysis results of exhaled and secondary smoke in the air, and exhaled smoke

Compound	Concentration/ppm		Detection limits
	Exhaled and secondary smoke	Exhaled smoke	
Methane	5.01	1.97	0.50
Ethane	0.50	n.d.	0.34
Acetaldehyde	n.d.[*]	n.d.	1.5
CO	29.30	7.02	0.4
Ammonia	6.04	n.d.	0.13
Methanol	1.48	n.d.	0.19
Ethylene	1.29	0.25	0.13
Isoprene	0.85	n.d.	0.19
Propene	0.67	n.d.	0.25
HCN	n.d.	n.d.	0.1
NO	n.d.	n.d.	1.00

[*] Not detected.

3.3. Summary

The results of primary smoke analysis, by means of an extractive FTIR method, provide evidence that gaseous compound uptake during the first puff of different "strength" (reported tar, nicotine and carbon monoxide contents) cigarettes of the same brand is similar. Since the concentrations in the first puff are related directly to the total quantity of material produced over the entire cigarette (Maddox and Mamantov, 1977), it can be concluded that the uptake of the investigated compounds is approximately the same whether regular or light cigarettes are smoked.

With the help of open-path FTIR spectroscopy it was established that the major source of environmental tobacco smoke is sidestream (secondary) smoke. The human lung cleans and retains the constituents of the primary smoke with exhaled smoke containing only very low concentrations of the analysed compounds.

Acknowledgements

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