

# Ammonia release from heated 'street' cannabis leaf and its potential toxic effects on cannabis users

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## ABSTRACT

**Aims** To use selected ion flow tube mass spectrometry (SIFT-MS) to analyse the molecular species emitted by heated 'street' cannabis plant material, especially targeting ammonia. **Materials and methods** Samples of 'street' cannabis leaf, held under a UK Home Office licence, were prepared by finely chopping and mixing the material. The samples were then heated in commercially available devices. The air containing the released gaseous compounds was sampled into the SIFT-MS instrument for analysis. Smoke from standard 3% National Institute on Drug Abuse (NIDA) cannabis cigarettes was also analysed. **Findings** For 'street' cannabis, ammonia was present in the air samples from the devices at levels approaching 200 parts per million (p.p.m.). This is compared with peak levels of 10 p.p.m. using NIDA samples of known provenance and tetrahydrocannabinol content (3%). Several other compounds were present at lower levels, including acetaldehyde, methanol, acetone, acetic acid and uncharacterized terpenes. **Conclusions** Awareness of the risks of inhaling the smoke directly from burning cannabis has led to the development of a number of alternative methods of delivery, which are claimed to be safer than direct smoking. Ammonia at toxic levels is produced from heating 'street' cannabis in these commercially available devices. Thus, the use of these devices to deliver 'street' cannabis is now open to question and further research is needed to investigate their safety.

**Keywords** Ammonia, cannabis, respiratory, SIFT-MS, smoking, toxicity.

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## INTRODUCTION

Studies of the effect of cannabis smoking on respiratory and general health indicate that the use of cannabis alone has an adverse effect on respiratory health and that when used with tobacco the negative effects are additive [1], although the separate effects are then often difficult to identify. A review of the respiratory risks of cannabis smoking [2] concludes that those who smoke cannabis but not tobacco are more likely to have symptoms of chronic bronchitis than non-smokers and that those who smoke cannabis on a daily basis over many years face a risk of developing respiratory complications. Awareness of the risks of inhaling the smoke directly from the burning cannabis has led to the development of a number of alternative methods of delivery, which are claimed to be safer than direct smoking.

The use of smoking devices with water filters (water bong) has been advocated, but there is evidence that that this does not reduce the risks of inhalation of toxic products and that the amount of tar inhaled is not reduced significantly [3]. The use of devices that exploit electrical heating of cannabis has also been suggested as a means of reducing respiratory hazards [4]. Some such devices utilize an electrically heated plate on which the cannabis is pyrolysed and partially combusted; an alternative vaporizer uses a hot airstream that heats the cannabis to a temperature below which combustion occurs. In these devices the gaseous products are collected into a sealed container from which they are inhaled, usually through an attached tube. The data obtained in the present study utilizes these devices.

Studies of these devices and methods have concentrated on assessing their efficiency in delivering

tetrahydrocannabinol (THC), which is the psychoactive product of cannabis, while reducing the delivery of toxic pyrolytic compounds. A recent study has concluded that vaporization can deliver therapeutic levels of active cannabis products with a drastic reduction in delivery of toxic products, suggesting this as a vehicle for delivering medicinal cannabis [5]. These studies have, in the main, focused on higher molecular weight (MW) pyrolysis products that are preferentially measured using gas chromatography-mass spectrometry (GC-MS) techniques. The lower MW toxic substances have not been analysed [5], although these are known to be produced in the pyrolysis and combustion of cannabis [6].

A major advantage of selected ion flow tube mass spectrometry (SIFT-MS) [7,8] is that it allows the quantification in real time of the gaseous products of cannabis pyrolysis, ranging from compounds with very low MW, such as ammonia and hydrogen cyanide, to species with MW up to about 200 Daltons, such as lower-order aldehydes, ketones, alcohols and hydrocarbons, at concentrations in air down to parts-per-billion (p.p.b) levels [9]. Estimates of the concentrations of the higher MW compounds, such as THC, are also possible [9]. In order to evaluate the claims of increased safety of vaporizers for cannabis use, as referred to above, we have utilized our SIFT-MS techniques for the real-time analysis of the lower MW, potentially toxic volatile compounds produced by the heating of samples of 'street' cannabis leaf.

## MATERIAL AND METHODS

### Cannabis samples

Samples of cannabis leaf available to users, 'street cannabis', were held under a UK Home Office licence and supplied from material seized by the local police force. Five samples were selected randomly from recent seizures from cannabis users and were stored in sealed plastic enclosures to minimize the loss of moisture. Five samples of standard 3% cultivated cannabis supplied under an import licence from the National Institute on Drug Abuse (NIDA, USA) were also used.

Samples for use in apparatus 1 and apparatus 2 (see below) were prepared by finely chopping and mixing the plant material, each sample weighed 200 mg.

### Cannabis heating systems

Two systems of apparatus were selected from those commercially available and advertised widely within the United Kingdom; the Volcano system was selected to allow comparison with previous research [5].

#### Apparatus 1

A commercial electrically heated drug 'vaporizer' was used (the 'Blue Meanie'). This consists of an electrically

heated metal cup which is enclosed in a glass container. The cup is temperature-controlled but not adjustable and reached a temperature of about 250°C, which is below the temperature which can initiate significant spontaneous combustion of cannabis leaf. An air entry port is located at the base of the heater and an exhaust port is provided with an outlet to a plastic tube via which the volatile pyrolysis products can be inhaled. In the present experiments, analysis of the gases and vapours was achieved by connecting the plastic tube directly to the sampling inlet port of the SIFT-MS instrument.

#### Apparatus 2

A commercial hot-air 'drug vaporizer' was used (the 'Volcano'). This consists of a ceramic heater with a heat vent; a removable chamber is positioned above the heat vent into which the cannabis sample is placed. Hot air is blown through the chamber to release vapours from the sample without initiating combustion. The vapour inflates a disposable plastic balloon, which can be detached once it is filled. The vapour can then be inhaled from the balloon. For the purpose of the present experiment, the bag was sealed once it had been inflated and the gases and vapours contained within it were sampled for analysis by perforating the plastic wall using a sampling needle attached directly to the SIFT-MS sampling port. The temperature of the heater is adjustable and was set to its highest setting of 9, which equates to 218°C at the heater screen and 155°C at the sample surface [5].

### Brief description of the SIFT-MS analytical technique

SIFT-MS allows the detection and quantification of trace gases in air, exhaled breath and liquid headspace, currently down to a level of 2 parts per billion (p.p.b.) per second of analysis time. The trace gases are analysed in real time, obviating the need to concentrate the trace gases in the sample or remove water vapour, as is required for most other analytical methods. This technique relies on the chemical ionization of the trace gases in an air sample to the exclusion of the major composite gases (especially nitrogen and oxygen). The precursor ions  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$  are generated in a gas discharge ion source and then species of a given mass-to-charge ratio ( $m/z$ ), e.g.  $\text{H}_3\text{O}^+$  at an  $m/z$  of 19, are selected by a quadrupole mass filter and injected into fast-flowing helium gas carrier. The air sample to be analysed is introduced through a heated, calibrated capillary inlet port into the carrier gas, where the trace gases in the sample react with the chosen precursor ion species. The count rates of both the precursor ions and the characteristic product ions of the reactions are then determined by a downstream quadrupole mass spectrometer. It is the ratio of the product ion to the precursor ion count rates that provides

the quantification of the trace gases in the sample. SIFT-MS can be operated in the full scan mode (FS), where the downstream mass spectrometer scans and detects the precursor and product ions to form a mass spectrum, which is used to identify the particular trace gases that are present, Figure 1 is a mass spectrum obtained in this mode [7,8,10,11] and the multi-ion monitoring mode (MIM) in which the analytical mass spectrometer is switched rapidly between chosen  $m/z$  values to target particular trace gases for more accurate quantification. Full details of the SIFT-MS techniques have been described in earlier publications [10]. A thorough validation of the SIFT-MS method has been carried out using standard techniques [11], and it is shown that the simultaneous quantification of several organic vapours in air samples can be achieved to an accuracy of 10% at the 100 p.p.b. level.

## EXPERIMENTAL PROCEDURE

### Experimental protocol: apparatus 1 (the 'Blue Meanie')

#### *Sampling procedure*

The cannabis leaf (200 mg) was placed on the metal cup within the glass container and the heater was switched on. The temperature of the surface of the metal cup reached about 250°C. The set-up described above ensures that the air containing the volatile compounds is sampled directly into the SIFT-MS instrument at a known flow rate via the heated calibrated capillary, where they are analysed in the usual way using the appropriate precursor ions. Specifically, all three available precursor ions, namely  $H_3O^+$ ,  $NO^+$  and  $O_2^+$ , were used with the SIFT-MS instrument usually operated in the FS mode within the  $m/z$  range from 10 to 180, but some measurements were taken up to the higher  $m/z$  value of 250. Because of the unusually high levels of ammonia detected in some samples, the sample gas flow rate into the instrument had to be reduced below the value used normally for trace gas analysis. This was achieved using an in-line metering valve with a flow meter as the simplest practical option. We anticipate that for more detailed studies of such high levels of ammonia and other gases a smaller conductance capillary will be used. FS spectra were taken 2 and 4 minutes after the heating was initiated. The levels of water, ammonia, methanol, acetaldehyde and total terpenes were obtained using  $H_3O^+$  precursor ions, and acetone, acetic acid and isoprene were obtained using  $NO^+$  precursor ions [7].

### Experimental protocol: apparatus 2 (the 'Volcano')

#### *Sampling procedure*

The vaporizer heater was set to maximum for 3–5 minutes, after which it reached its highest temperature of about 200°C. Then 200 mg of the cannabis leaf was

introduced and the air flow initiated. The collection balloon was inflated totally in about 45 seconds. Again, the trace gases in the samples were analysed using all three available precursor ions as described in the previous section using the FS mode. Additionally, some MIM data were taken using  $O_2^+$  precursor ions targeting product ions with  $m/z$  values of 104, 204, 205, 231, 244 and 246, as these had been seen in earlier SIFT-MS experiments [8].

### Experimental protocol: smoked cannabis

#### *Sampling procedure*

The main stream smoke from standard 3% NIDA cannabis cigarettes was collected via a vacuum system into a 5 L Nalophan bag. Sidestream smoke was collected into a Pyrex collecting hood and extracted into a 5 L Nalophan bag. Sidestream and mainstream smoke were collected at the same time and the collection continued until one-third of the cigarette was consumed.

Mainstream smoke was diluted 5 : 1 and sidestream smoke 10 : 1 before trace gases were analysed using all three available precursor ions, as described previously. The results were corrected by the dilution factors indicated.

## FINDINGS

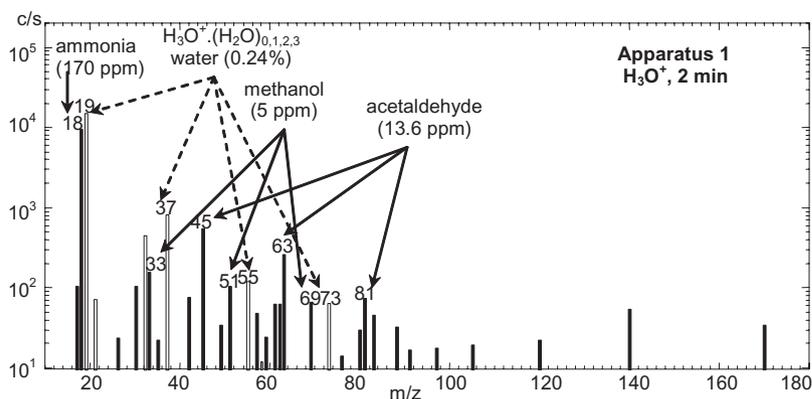
The FS spectra obtained for samples from both apparatus 1 and apparatus 2 revealed the presence of several compounds, those most readily identifiable being ammonia, methanol, acetaldehyde and terpenes (which are  $C_{10}H_{16}$  hydrocarbons, of which there are many isomers [12]; the particular isomers present were not identified in these initial experiments). A sample FS spectrum is shown in Fig. 1, where the very high ammonia content of the sample is revealed.

### Apparatus 1

A partial list of the compounds detected in the sampled air 2 minutes and 4 minutes after the heater was switched on is given in Table 1. The most abundant species detected was ammonia, which reached a partial pressure of about 170 parts per million (p.p.m.) from 'street' cannabis samples compared with peak levels of 10 p.p.m. using NIDA samples of known provenance and THC content (3%). The variety of compounds produced increased with time as the pyrolytic process proceeded. Note that the water vapour pressure (absolute humidity of the sample) is also determined by SIFT-MS and that for these samples it was very low in the sampled gas.

### Apparatus 2

Those compounds that have been identified and quantified definitively shown in Table 2 and are in common with



**Figure 1** Sample selected ion flow tube mass spectrometry full scan mode mass spectra (ion counts per second against mass-to-charge ratio) obtained using  $\text{H}_3\text{O}^+$  precursor ions for the analysis of volatile compounds produced from heating 'street' cannabis leaf in apparatus 1, 2 minutes after heating was initiated. The precursor ions are indicated by open bars and the product ions by filled bars [7,8,10,11]. The major constituents are indicated with their levels in parts per million (p.p.m.) and water vapour in %, both given in brackets

**Table 1** A partial list of the compounds, and their concentrations in parts per million generated by heating cannabis leaf for 5 minutes using apparatus 1. Also given is the measured humidity of the sample in %.

Compound	Street cannabis		NIDA 3% cannabis	
	Mean	Range (%)	Mean	Range (%)
Water vapour	1.2%	0.6–1.8	1.3%	0.5–1.7
Ammonia	205	170–240	4	1–10
Methanol	212	24–400	73.8	33–91
Acetaldehyde	24.5	24–25	36.8	22–50
Acetone	15	10–20	16.5	
Acetic acid/methyl formate	4.5	4–5	10	<1–29
Isoprene	3	1–5	2.8	<1–6
Terpenes, total	20.5	1–40	2.4	<1–7.5

NIDA: National Institute on Drug Abuse.

**Table 2** A partial list of the compounds, and their concentrations in parts per million, collected into bag samples, generated by heating cannabis leaf using apparatus 2. Also given is the measured humidity of the sample in %.

Compound	Street cannabis		NIDA 3% cannabis	
	Mean (%)	Range (%)	Mean (%)	Range (%)
Water vapour	2.2	1.5–3	1.4	1.1–2
Ammonia	60	50–70	4.3	3–6
Methanol	4.6	2–10	13.8	7–20
Acetic acid	3.6	1–5	2.1	0.9–3.5
Terpenes	4.3	3–7	1	0.2–2

NIDA: National Institute on Drug Abuse.

those shown in Table 1. The most abundant species detected was again ammonia, which reached a partial pressure of about 70 p.p.m. for 'street' samples compared with a maximum of 6 p.p.m. for NIDA samples of known provenance and THC content (3%). The humidity of the 'street' samples in this case is greater than those from apparatus 1 at about 2–3%.

### Smoked cannabis

A partial list of compounds identified in mainstream and sidestream smoke is seen in Table 3. The samples were collected into a similar volume in the same time. The most abundant species in mainstream smoke was acetaldehyde, that reached a partial pressure of around 45 p.p.m., and ammonia, that reached a partial pressure of 20 p.p.m. Ammonia was the most abundant species in sidestream smoke reaching a partial pressure of 250 p.p.m.

### DISCUSSION

Attempts to maximize delivery of the psychoactive components of cannabis, while reducing the toxic components of the vapour, have been attempted by a variety of methods. The use of the closed systems described above, i.e. lower temperature vaporizers and pyrolysis devices, have been suggested as safer methods of delivery of medicinal cannabis [3,4]. These assertions have been made based on the observed reduction in the high MW components of the inhaled vapour.

The current study indicates that 'street' cannabis plant material produces high levels of ammonia when heated and that the use of closed systems, such as the

**Table 3** Some compounds present in the mainstream and sidestream smoke of one-third National Institute on Drug Abuse standard cannabis (3%, 6 cm in total length) cigarette. Concentrations are given in parts per million, except for water (in %). See the text for further explanation.

		Mainstream (%)	Sidestream (%)
H <sub>3</sub> O <sup>+</sup> analysis	H <sub>2</sub> O	1.7	1.2
	Ammonia	10	250
	HCN	11	6
	Methanol	26	5
	Acetonitrile	15	12
	Ethanol	–	6
	Total terpene	2	11
	Acetaldehyde	45	16
	Acetone	24	10
NO <sup>+</sup> analysis	Acetaldehyde	40	21
	Acetic acid/methyl formate	3	0
	Propenal	25	5
	Acetone	19	10
	Isoprene	39	38
	Butadiene	14	12
	Ethanol	6	9

HCN: hydrogen cyananide.

'Blue Meanie' and the 'Volcano' devices used for the present study, rather than cannabis cigarettes, result in more ammonia being available for inhalation. The ammonia levels in the air in these enclosed volumes, which are within the range 50–170 p.p.m., greatly exceeding the short term (15-minute) upper limit occupational exposure limit, which is given as 35 p.p.m. [13].

The levels of ammonia produced by hot air vaporization are lower than those produced by direct heating, but are higher than levels measured in cigarette smoke, which have been reported to be at a maximum of 10–12 p.p.m. [14,15]. The levels of ammonia and other low MW weight toxic products of tobacco smoking are lower in mainstream smoke than in sidestream smoke from cigarettes [15]. Our results indicate that a similar pattern exists in the mainstream and sidestream smoke from standardized NIDA cannabis cigarettes, with ammonia levels of 10 p.p.m. in collected mainstream smoke and 250 p.p.m. in sidestream smoke collected into a similar volume in the same time. During regular smoking, sidestream smoke is produced from the burning edge of a cigarette and is dispersed mainly into the atmosphere; mainstream smoke is inhaled by the smoker. The use of closed systems to produce cannabis vapour results in the inhalation of most of the products of pyrolysis and thus exposure to higher levels of toxic products, such as ammonia, which may otherwise have been mainly lost to sidestream smoke.

Experimental exposure of healthy individuals to ammonia levels of 25 p.p.m. for a period of 3 hours results in symptoms related to irritation and central

nervous system effects with no evidence of adaptation over the exposure period. At these levels no detectable effects on respiratory function were found [16]. Exposure to higher levels of ammonia for shorter periods has been studied following an accidental release of ammonia into the atmosphere. Exposure to levels of 24–200 p.p.m. for periods ranging from a few minutes to several hours resulted in neurobehavioural impairment lasting for up to 22 months [17]. There is little in the literature concerning the effects of long-term intermittent exposure to high levels of inhaled ammonia. However, the effects of increased levels of ammonia resulting from hepatic disease are well recognized and include hepatic coma and encephalopathy, the severity of which correlate with venous ammonia levels [18].

Exposure of animals to cannabis smoke on alternate days has been shown to result in markedly increased levels of blood ammonia [19], which was not related to any induction of liver damage from the inhalation of cannabis because the liver enzymes remained normal. No such studies have been undertaken in man; however, a study of oral ingestion of cannabis by baboons showed no effect on serum ammonia levels [20].

Effects of acute exposure to ammonia on the respiratory tract are well documented and include asthma provocation at levels of 12 p.p.m. [21]. There are also reports of cases of bronchial hyperreactivity associated with exposure to ammonia [22,23]. An association between smoking heroin and cocaine from aluminium foil and bronchial hyperreactivity has also been reported [24], the study concluding that vapours from the

ammonia used to prepare freebase cocaine may also affect the airway in these users. The respiratory effects of smoking cannabis have been reviewed, and in addition to significant functional respiratory impairment greater than that found in comparable tobacco smokers [25,26], there is clear evidence of an increased rate of inflammatory and pre-cancerous changes in long-term cannabis users [27].

Through SIFT-MS analysis of the vapour from both vaporization and combustion of 'street' cannabis plant material we have shown that ammonia is generated at levels up to 170 p.p.m. in the air that would be inhaled. The current study was not designed to define the exact mechanism of production of the low MW products of vaporization, including ammonia, and cannabis obtained from illegal sources may contain additives which could possibly change the composition of the smoke produced during heating. Should ammonia be present at these high levels it would raise concern with regard to toxicity, and the use of systems such as those utilized for this study could not be viewed as a safe method of delivery of cannabis.

Further detailed investigations of the products of combustion of larger numbers of samples of standardized cannabis, 'street cannabis' and cannabis resin samples of known THC content are planned.

## CONCLUSIONS

We have demonstrated that the use of heating devices for cannabis use in order to decrease the inhalation of toxic high MW compounds (including tar) may increase the exposure to low MW toxic compounds such as ammonia. Recommendations for the use of these devices in the delivery of 'street' cannabis have not acknowledged this risk and further research is needed to ascertain their relative safety. The risks involved in smoking cannabis have been assumed to be equivalent to those involved in smoking tobacco. Our finding that ammonia levels generated by heated 'street' cannabis are much higher than those from smoking tobacco may require a revision of the relative risks.

## Declarations of interest

Professors Smith and Spanel are directors of Trans Spectra Ltd UK, that develops the SIFT-MS instruments. These instruments are now manufactured and marketed by Instrument Science Ltd UK.

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