Title
Methyl chloride and the U.S. cigarette.

Permalink
https://escholarship.org/uc/item/1k47d1hv

Journal
Nicotine & Tobacco Research, 10(11)

ISSN
1462-2203

Authors
Novak, Brian J
Meinardi, Simone
Blake, Donald R

Publication Date
2008-11-01

DOI
10.1080/14622200802410014

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, available at https://creativecommons.org/licenses/by/4.0/

Peer reviewed
Methyl chloride and the U.S. cigarette

Brian J. Novak, Simone Meinardi, Donald R. Blake

Received 10 October 2006; accepted 10 January 2008

Various brands and types of cigarettes were purchased at retail locations in southern California. Volatile gas samples were analyzed using multicolumn/multidetector gas chromatography. Results showed methyl chloride (CH₃Cl) levels as much as four orders of magnitude higher than typical urban levels, about 30–500 ppbv (1.5–5.3 mg/cigarette), compared with about 500 pptv in urban air. The concentration of CH₃Cl correlated well with the levels of both CO ($r^2 = 0.63$) and CO₂ ($r^2 = 0.77$), showing the link between CH₃Cl and combustion. In some brands, CH₃Cl levels were well above the U.S. Environmental Protection Agency’s maximum exposure limit of 200 ppbv. Light branded cigarettes tended to have higher CH₃Cl levels than the heavier and filtered brands, possibly showing the dependence of cigarette packing on CH₃Cl production. In addition, CH₃Cl emitted from cigarette smoke may prove to be an important anthropogenic source of CH₃Cl in the United States, at about 5%.

Introduction

In the 1950s, it was postulated that cigarette smoking might be linked to cancer. Since then, smoking has been shown to lead to pulmonary and cardiovascular disorders such as emphysema (Baglole et al., 2006; Evans & Pryor, 1994), atherosclerosis (Cerami et al., 1997), and cancer (Ames, Gold, & Willet, 1995; Hecht, 1999, 2006; Morton et al., 2006). Cigarette smoke contains over 4,000 different compounds (Caroff, Veron, Badre, & Guillerm, 1964; Dong, Glass, & Moldoveanu, 2000), several of which are harmful to humans. The volatile phase of mainstream cigarette smoke contains primarily nitrogen, oxygen, carbon dioxide, carbon monoxide, and water. However, many other trace gases are present in the volatile phase, typically at concentrations much higher than those found in urban air, and many are carcinogenic.

One such gas in the volatile phase of cigarette smoke is chloromethane (methyl chloride, CH₃Cl). Methyl chloride in a typical urban sample ranges from about 500 to 700 parts per trillion by volume (pptv; Blake et al., 1991). At enhanced concentrations, CH₃Cl has many adverse effects on human health, causes cancer in rats, and is a class D carcinogen (U.S. Environmental Protection Agency [USEPA], 2005).

Methyl chloride was first reported in cigarette smoke in 1956 (Philippe & Hobbs, 1956). Since then, several studies have reported on its levels in cigarette smoke (Chopra & Sherman, 1972; Hasanen, Manninen, Himberg, & Vaatainen, 1990). In most experiments, cigarette smoking machines are used to sample the cigarette in a manner that is consistent with actual human smoking. This method of collection is followed by quantification by any number of methods including but not limited to gas chromatography–mass spectrometry (Moldoveanu & Kiser, 2007; Polzin, Kosa-Maines, Ashley, & Watson, 2007) and infrared spectroscopy (Bacsik, McGregor, & Mink, 2007; Shorter et al., 2006). In the present study, we introduce a new method for collecting vapor-phase gas samples from cigarette smoke.

Method

Cigarette packs were purchased from retail locations in southern California. Different varieties were purchased consisting of lights, regular, and full-flavored cigarettes. Each cigarette that was used for the experiment was marked with a pencil 2 cm from the end opposite the filter.

Typical experiments focusing on cigarette smoke use smoking machines, which attempt to simulate real-life human smoking conditions (Ritter, Knebel,
We have developed a new, rapid, cost-effective method to reproducibly quantify the vapor phase of cigarette smoke. A schematic of the device used to collect the samples is shown in Figure 1. For this method, samples were collected in evacuated 2-L stainless-steel electropolished canisters. Canisters were prepared by evacuating them to $10^{-6}$ atm, flushed with ultra-pure helium, and evacuated again to $10^{-6}$ atm. An Ultra-Torr union was used to connect the cigarette adapter to the canisters. Each cigarette was secured in the cigarette adapter, which was machined from stainless steel and fit the cigarette filters snugly so that no outside air could enter the sampling apparatus without passing through the cigarette first.

Before entering the sample canister, the mainstream smoke was passed through a 5-µm particle filter to remove the majority of the particulate phase of the cigarette smoke. In addition, the particle filter dictated maximum flow rate into the canister by restricting the total flow. Therefore, different maximum flow rates could be achieved by changing the particle filter to different pore sizes. As the sample can was opened, the cigarette was lit and the first 2 cm of the cigarette was gradually “smoked.” When the 2-cm mark was reached, usually within 30 s of lighting, the canister was closed and the air sample was analyzed within 2 hr. Samples also were collected with no cigarette present to assess the ambient air.

We used the same method to analyze commercially available cigarette paper, as well as cigarette paper from cigarettes with the tobacco removed, yielding negligible levels of CH$_3$Cl in comparison with cigarette smoke. Unlit cigarettes also were analyzed to make sure that what we observed with the lit cigarette was not related to the cigarette itself. No enhanced CH$_3$Cl was observed when air was drawn through the unlit cigarettes.

A 12.0-cm$^3$ portion of cigarette smoke sample was passed through a stainless steel loop containing glass beads submerged in liquid nitrogen ($-196^\circ$C) to a pump that vented to the room. This procedure allows the more volatile compounds (oxygen, nitrogen, methane, argon) to be removed from the sample, effectively concentrating the remaining less volatile gases on the glass beads. Once completed, the loop was isolated and submerged in hot water ($\sim 90^\circ$C) to make the concentrated sample volatile again.

The loop was then flushed with a helium carrier and the contents carried to a splitter that divided the flow into five streams. Each flow was directed to different column detector combinations. The five-column, five-detector combinations allowed us to separate and detect a variety of compounds. The analytical system used three ovens, each with independent temperature programs. Oven 1 had a single DB-1 column connected to a flame ionization detector (FID). This column-detector combination allowed for separation and quantification of C$_3$-C$_{10}$ hydrocarbons, various oxygenated hydrocarbons,
and some aldehydes. Oven 2 housed a DB-5MS column output to a quadrupole mass spectrometer. This column-detector combination allowed for identification of various compounds using selected ion monitoring. Oven 2 also contained a DB-5 column connected in series to a Restek-1701 column, outputted to an electron capture detector (ECD). These columns and detector provided separation and detection of halocarbons and alkyl nitrates. Oven 3 contained a Restek-1701 column connected to an ECD. This column-detector combination allowed for quantification of various halocarbons and alkyl nitrates. Oven 3 also housed a GS-Alumina PLOT column connected in series to a DB-1 column, outputted to an FID. This column-detector combination allowed for resolution and detection of C$_2$–C$_6$ hydrocarbons. For a more detailed description of this system, see Colman et al. (2001).

Both carbon monoxide (CO) and carbon dioxide (CO$_2$) were analyzed on separate independent systems. Carbon monoxide was separated from other gases using a 3-m molecular sieve 5A packed column, converted to methane via reaction with hydrogen gas on a nickel catalyst, and detected (as methane) via an FID. Carbon dioxide is separated from other components on a Carbosphere 80/100 packed column and detected by a thermal conductivity detector.

**Results**

Methyl chloride was quantified on both the FID and the mass spectrometer. Concentrations in outside air during the sampling period were consistently 550 ± 40 pptv. The levels seen in the cigarette smoke were between 30 and 520 ppmv (Table 1). Concentrations (in mg/cigarette) were calculated based on our reported concentrations in ppmv, knowing the volume of the sample canister, the molecular weight of CH$_3$Cl, and the fact that one-third of each cigarette was smoked. The Occupational Safety and Health Administration’s (OSHA) permissible exposure limit is 200 ppmv, the concentration of the gas that should not be exceeded at any time (USEPA, 2005). This OSHA value was exceeded for 50% of the cigarettes.

The cigarettes with the highest CH$_3$Cl concentrations in the smoke tended to be the faster burning, “light” brand cigarettes. Both Marlboro Lights and Camel Lights had CH$_3$Cl levels that exceeded the OSHA level. Therefore, our results suggest that smoking light brand cigarettes will increase one’s exposure to CH$_3$Cl.

Concentrations for both CO (14–23 mg/cigarette) and CO$_2$ (45–65 mg/cigarette) have been reported previously (Hoffmann, Djordjevic, & Hoffmann, 1997). Our concentrations were about 10 times higher for CO (44–220 mg/cigarette) and 15 times higher for CO$_2$ (324–522 mg/cigarette; Table 1). This difference is reasonable because our estimates are based on continuous smoking whereas the smoking machine assumes a much reduced smoking rate. The ratios of CH$_3$Cl to CO and CO$_2$ that we found were significantly higher than those reported for biomass burning experiments, indicating that something in addition to cellulose is being combusted. (Andreae, 1991; Colman et al., 2001; Crutzen, Heidt, Krasnec, Pollock, & Seiler, 1979).

**Discussion**

The use of a standardized smoking machine is a good analytical tool for the majority of cigarette smoke experiments. However, the technique does not allow for accurate representation of smoking habits of all smokers. We have developed a method that studies one of the two extremes of smoking. With our procedure, the cigarette is smoked at a high to moderate drag the entire time. This procedure yields data that are representative of tobacco combusted more completely. For example, comparing the CO/CO$_2$ ratio of 0.33 for the previous work from smoking machines (Hoffmann et al., 1997) with our results of 0.17 indicates a higher combustion efficiency.

Typical urban CO levels range from 0.5 to 5 ppmv. In the cigarette smoke, CO concentrations ranged from 0.1% to 4.6%, or about four orders of magnitude higher. Similarly, typical urban CO$_2$ concentrations range from 400 to 500 ppmv, whereas

<table>
<thead>
<tr>
<th>Cigarette</th>
<th>CH$_3$Cl (ppmv)</th>
<th>CH$_3$Cl (mg/cig)</th>
<th>CO (ppthv)</th>
<th>CO (mg/cig)</th>
<th>CO$_2$ (ppthv)</th>
<th>CO$_2$ (mg/cig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic full flavor</td>
<td>209</td>
<td>2.6</td>
<td>20</td>
<td>137</td>
<td>73</td>
<td>788</td>
</tr>
<tr>
<td>Camel Filter</td>
<td>159</td>
<td>2.0</td>
<td>19</td>
<td>131</td>
<td>71</td>
<td>767</td>
</tr>
<tr>
<td>Camel Lights</td>
<td>274</td>
<td>3.5</td>
<td>23</td>
<td>158</td>
<td>76</td>
<td>821</td>
</tr>
<tr>
<td>Marlboro Light</td>
<td>418</td>
<td>5.3</td>
<td>32</td>
<td>220</td>
<td>141</td>
<td>1522</td>
</tr>
<tr>
<td>Marlboro Red</td>
<td>140</td>
<td>1.8</td>
<td>6</td>
<td>44</td>
<td>30</td>
<td>324</td>
</tr>
<tr>
<td>Newport</td>
<td>224</td>
<td>2.8</td>
<td>16</td>
<td>110</td>
<td>76</td>
<td>821</td>
</tr>
<tr>
<td>Pall Mall</td>
<td>122</td>
<td>1.5</td>
<td>10</td>
<td>69</td>
<td>45</td>
<td>486</td>
</tr>
<tr>
<td>Salem</td>
<td>219</td>
<td>2.8</td>
<td>18</td>
<td>124</td>
<td>57</td>
<td>615</td>
</tr>
<tr>
<td>Winston Filters</td>
<td>174</td>
<td>2.2</td>
<td>19</td>
<td>131</td>
<td>54</td>
<td>583</td>
</tr>
</tbody>
</table>

**Note.** ppmv, parts-per-million by volume; ppthv, parts-per-thousand by volume.
the cigarette smoke concentrations ranged from 0.8% to 17%.

It is no surprise that CH$_3$Cl levels in cigarette smoke are high. This fact has been known for 50 years. In addition to cigarette smoke, methyl halides (which include CH$_3$Cl) are emitted with CO and CO$_2$ during combustion and biomass burning (Andreae, 1991; Crutzen et al., 1979). However, no published papers have documented the correlation of CH$_3$Cl with CO or CO$_2$ in cigarette smoke. When plotted versus CO and CO$_2$, CH$_3$Cl is correlated well, $r^2 = .63$ and $r^2 = .77$ (Figure 2). These data can be valuable in allowing CO$_2$ to be measured and the slope used to determine the smoker’s level of CH$_3$Cl inhalation.

In our study, the average CH$_3$Cl/CO ratio was $15 \times 10^{-3}$ and the average CH$_3$Cl/CO$_2$ ratio was $3.2 \times 10^{-3}$. These values are higher than those seen in airborne and land-based biomass burning experiments (Table 2). This finding suggests that cigarettes may contain an additional source of CH$_3$Cl or it may be created during the burning process from something added to the cigarette. Possible sources of chlorine in tobacco are pesticides, herbicides, additives, fillers, blending, or remnants of the washing and curing process, all of which could have contributed to observed high CH$_3$Cl concentrations remnants of the curing process.

Previous studies have looked at the possible origin of CH$_3$Cl from pesticide-treated tobacco (Chopra & Sherman, 1972). However, the use of chlorinated pesticides on U.S. tobacco was prohibited in 1969. Therefore, the main source of chlorinated pesticides in U.S. cigarettes today is the blending process, in which foreign-grown and U.S.-grown tobacco is mixed. If a cigarette (untreated and unblended) were smoked using our method, we could determine the CH$_3$Cl/CO or CH$_3$Cl/CO$_2$ ratios. If that sample contained ratios that were not consistent with biomass burning data, we would know that the treated and blended cigarettes had undergone some process that resulted in enhanced CH$_3$Cl emissions during combustion.

In addition to looking at CH$_3$Cl on a per-smoker basis, we can look at the effect of CH$_3$Cl emitted from cigarette smokers in the United States. When considering total CH$_3$Cl emissions from the United States, it is estimated that 99% of the emissions are nonanthropogenic (Agency for Toxic Substances and Disease Registry, 1998). The small percentage of emissions that are anthropogenic come mainly from processing facilities spread across the country. Annual U.S. emission estimates for CH$_3$Cl in 1996 were 2.4 billion grams, mainly from processing plants (Agency for Toxic Substances and Disease Registry, 1998; Lof, Wallen, & Bard, 2000). In comparison,

![Figure 2.](image)

**Figure 2.** CO and CO$_2$ plotted versus CH$_3$Cl. Each data point in each of the two series represents a single cigarette.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>ER relative to CO $\times 10^{-3}$</th>
<th>$r^2$</th>
<th>ER relative to CO$_2$ $\times 10^{-6}$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>—</td>
<td>15</td>
<td>.63</td>
<td>3200</td>
</tr>
<tr>
<td>Trace A (flight 6, South America) (Blake et al., 1991)</td>
<td>Airborne</td>
<td>0.85</td>
<td>.88</td>
<td>—</td>
</tr>
<tr>
<td>Trace A (flight 10, Africa) (Blake et al., 1991)</td>
<td>Airborne</td>
<td>0.57</td>
<td>.92</td>
<td>—</td>
</tr>
<tr>
<td>Brazil Fire Assessment Project 1994 (Blake et al., 1991)</td>
<td>Ground</td>
<td>0.31</td>
<td>.90</td>
<td>—</td>
</tr>
<tr>
<td>Ivory Coast (Rudolph et al., 1995)</td>
<td>Ground</td>
<td>0.49</td>
<td>.96</td>
<td>43</td>
</tr>
<tr>
<td>Wild Basin fire (Colorado) (Crutzen et al., 1979)</td>
<td>Ground</td>
<td>—</td>
<td>—</td>
<td>23</td>
</tr>
</tbody>
</table>

**Note.** ER, emission ratio of CH$_3$Cl.
based on values of 18.5 ± 5.5 mg of CO or 55 ± 10 mg of CO₂ per cigarette (Hoffmann et al., 1997), data acquired in the present experiment, and the estimated 425 billion cigarettes smoked per year in the United States, we estimate that an additional 104 million grams of CH₃Cl are emitted as a result of cigarette smoking. This number represents 5.4% ± 1% of the total anthropogenic emissions from the United States.

Acknowledgments

The authors thank the University of California, Irvine, Transdisciplinary Tobacco Use Research Center (TTURC) for funding for this study (Trainee Fellowship 2003–2005), as well as Brent Love for data production.

References


