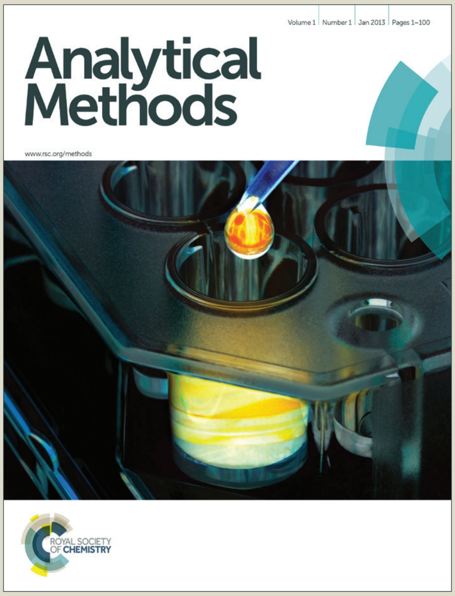
Analytical Methods

Accepted Manuscript



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In situ thermal degradation of isopropanol under typical thermal desorption conditions for GC/MS analysis of VOCs

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Abstract

Thermal desorption (TD) coupled with gas chromatograph (GC) has been widely used for the analysis of airborne volatile organic compounds (VOCs) due to its effectiveness in detecting a wide range of compounds. While residual and artifacts of thermal adsorbents are studied for common adsorbents, thermal decomposition of VOCs in relation to VOC analysis has not been well studied. We are reporting our observations on the possible thermal decomposition of isopropanol and its degradation products under typical TD conditions for GC/MS analysis of VOCs. Acetone and propene are two products of such thermal decomposition in Carbopack B, while only a small amount (0.05%) of products was observed in Tenax TA absorbent. Our results showed that there is a possibility that reported indoor air levels of isopropanol and acetone may be affected by the possible thermal degradation of isopropanol if they are collected on adsorbents that are made of graphitized carbon black and analysed using thermal desorption GC/MS. Cautions therefore have also to be exercised when selecting thermal desorption adsorbents to minimize possible thermal conversions of VOCs.

Keywords: Adsorbent, thermal decomposition, alcohols, Carbopack B

Introduction

Volatile organic compounds (VOCs) are primarily present in gas phase in the environment due to their relatively high volatility.[1] Many VOCs have known toxicities.[2] For example, trichloroethylene and perchloroethylene have been associated with adverse birth outcomes.[3] It is known that exposure to indoor air VOCs may increase risks of having respiratory symptoms[4] and asthma in young children in particular.[5] Therefore, understanding VOC levels, in both indoor and outdoor environments, is important to assess health risks of human exposure.

Different measurement methods have been used to collect and analyse airborne VOCs. US EPA adopted a gas chromatographic (GC) method for airborne VOCs using canisters to collect air samples (Standard Method TO-14)[6] in the 1990s, and subsequently adopted a thermal desorption (TD) based GC method using adsorbent-based tubes to collect air samples (Standard Method TO-17).[7] At the same time, many methods using thermal desorption techniques have been published by different jurisdictions due to their effectiveness in the determination of VOCs.[8-12] Stainless steel or glass tubes are pre-packed with a single adsorbent or multi-bed adsorbents used to firstly collect VOCs which are then thermally desorbed to a GC instrument for analysis.[7] Because of its effectiveness in trapping a wide variety of organic compounds, easy sample handling and its ultra low detection limits, thermal desorption technique has become an attractive means to measure airborne VOCs and has been used in several large scale surveys to understand human exposure to indoor air VOCs including a national survey of selected VOCs in Canadian residential indoor air between 2009 and 2011.[13]

Polymers and graphitized carbon black (GCB) are the two most common adsorbent types used in TD tubes. Tenax (e.g., Tenax TA, Tenax GC, or Tenax GR) is porous polymer resin based on 2,6-diphenyl-p-phenylene oxide. Generally considered to be a relatively weak adsorbent, Tenax has low affinity to water and is thermally stable up to 350°C. GCBs (e.g., Carbopack or Carbotrap) consist of graphitized carbon, which are non-porous and are stable over 400°C, having medium to strong collection capacity for VOCs.[7]

Potential artifacts from various adsorbents including Tenax and GCBs, have been described in the TO-17 method.[7] Potential artifacts included benzaldehyde, phenol and acetophenone from the oxidation of Tenax.[7] Benzaldehyde, along with several n-aldehydes in the C_5 - C_{10} range have been reported as artifacts from Carbopack as well.[14] However, potential thermal degradation of VOCs during thermal desorption in GC/MS analysis has not been well documented yet, despite the report on possible thermal decomposition of α- and β-pinenes on carbotrap adsorbent in the early 1990s.[15] In this study, we investigated possible thermal degradation of isopropanol, and the degradation products including acetone under typical TD conditions for GC/MS analysis. The study was carried out on Tenax TA and Carbopack B, both widely used adsorbents in TD tubes.

Materials and Methods

Chemicals. Isopropanol (99.7% purity, Caledon Labs, Georgetown, Ontario, Canada) and acetone (99.5% purity, EMD Millipore, Canada) standard solutions were prepared in methanol (99.9% purity, Caledon Labs) at concentrations between 450 µg/ml and 5000 µg/ml. One microlitre (1 µl) of standard solution was spiked onto TD tubes and followed by a purge with 200 ml of pure nitrogen for 1 min to diffuse the chemicals into the adsorbent.

TD Tubes. Stainless steel TD tubes (1/4" O.D. x 3.5" long) were purchased from Perkin-Elmer (Waltham, MA, USA), pre-packed with approximately 200-400 mg 60/80 mesh size of either Tenax TA or Carbopack B adsorbent. All tubes were thermally conditioned for 20 minutes at 350°C at a flow of 60 $ml\cdot min^{-1}$ of pure nitrogen and then sealed with PTFE analytical end caps prior to use.

Instruments. A 650ATD thermal desorber (Perkin-Elmer) was used to thermally desorb the TD tubes and transfer analytes into a 7890A GC (Agilent, Santa Clara, CA, USA) for separation with a J&W DB-624 column (60 m x 0.25 mm ID, 1.4 µm film thickness). The GC was coupled with a 5975C MSD (Agilent) for positive identification of analytes. GC oven temperature was set at 45°C for 2 min, increased afterwards at $5°C\cdot min^{-1}$ to 75 °C, then $20°C\cdot min^{-1}$ to 200°C and held at this temperature for 2 min. MS was operated in electron impact (EI, 70eV) mode at a source and quadrupole temperature of 230°C and 150°C, respectively. MS detector was operated in full scan mode with mass recording range of m/z 33 to m/z 400. Results were calculated based on peak areas in total ion chromatogram, assuming equal response for all analytes.

To assess the effects of desorption temperature and time on thermal conversion of analytes, the TD tubes were desorbed at either 200°C or 330°C for either a 6 or 12 min duration while the internal trap temperature was kept at -30°C. A 60 $ml\cdot min^{-1}$ desorption flow was used at a 10:1 split ratio. Internal trap afterwards was rapidly heated to 300°C for desorbing VOCs from internal trap to GC column at a desorption flow of 1.1 $ml\cdot min^{-1}$ for 3 min.

Results and Discussion

Thermal decomposition of isopropanol and the conversion rates were first investigated in the 1970s. Trenwith studied the pyrolysis of isopropanol in a temperature range of 382°C – 427°C and a pressure range of 10 and 100 Torr, using a KCl-coated silica reaction vessel.[16] Up to 30 % conversion was observed. Major products were hydrogen and acetone, together with smaller amounts of water and propene and a few other molecules. A free radical chain mechanism was proposed. Furthermore, McClenny et al. showed that approximately 27% of isopropyl alcohol adsorbed on graphitized carbon underwent decomposition when ozone was present at a concentration as low as 50 ppb.[17] However, the breakdown products of isopropanol were not reported in the McClenny study.

We first tested the effects of adsorbent type (Tenax TA and Carbopack B) on the possible conversion of isopropanol. For comparison purposes, we also tested acetone under the same condition (Table 1). The results were expressed as the percentage of thermal decomposition products to the amount of spiked chemical. Under the thermal desorption condition of 330°C and 12 min, isopropanol formed only a negligible to small amount of propene and acetone in Tenax TA tubes, while a noticeable amount of propene (1.4%) and acetone (14%) was formed in Carbopack tubes. However, when acetone was spiked, no isopropanol was formed in either Tenax TA or Carbopack B tubes and only a tiny amount of propene (0.05%) was observed in Carbopack B tubes (Table 1).

To better understand the extent of thermal degradation of isopropanol in Carbopack B, we tested the effects of thermal desorption temperature (200°C vs. 330°C), thermal desorption duration (6 min vs. 12 min) and spiking amount of isopropanol (450 ng, 1000 ng, 3000 ng and 5000 ng). There was an increase in the formation of both propene and acetone when the thermal desorption temperature increased, as well as when desorption times increased (Figure 1). However, there was no relationship between the percentage of products formed and the spiked amount of isopropanol (Figure 2).

This is the first report on the possible thermal degradation of isopropanol under the typical thermal desorption conditions for the GC/MS analysis of airborne VOCs. Large standard deviation (s.d.) in the results (Figure 1) showed tube to tube variation and indicated that characteristics of Carbopack B adsorbent in each tube may play an important role in the decomposition of isopropanol under the thermal desorption. Although all tubes contain the same Carbopack B adsorbent and conditioned equally prior to use, the surface characteristics of the adsorbent among tubes might be different due to difference in packing of the tubes, such as changes of the compactness of the material in the tube as result of repeated use.

Under the thermal desorption conditions, the degradation of isopropanol to form acetone as well as propene was only observed in Carbopack B tubes and not in Tenax TA tubes. Graphitized carbon black may have a much more effective catalytic effect than organic polymer based adsorbent such as Tenax TA leading to the breakdown of isopropanol during thermal desorption.[18] It is possible that metal impurities in the graphite might act as the catalysts of such reactions;[7] it is known that isopropanol may undergo dehydrogenation over heat and a copper catalyst.[17]

Both isopropanol and acetone are widely used as general solvents for a variety of commercial products and both are commonly found in indoor air environments[14] and included in a number of indoor air studies involving thermal desorption analysis using graphite based adsorbents like Carbopack B.[13, 19] The extend of the degradation of isopropanol on Carbopack B was not correlated to the amount of spiked isopropanol as there was no observed correlation of acetone and propene formed in relationship to isopropanol amount (Figure 2). In light of this, any correction is difficult and unreliable. The uncertainty of the reported value may be further aggravated by the fact that such the thermal degradation of isopropanol could happen in the calibration tubes as well.

Conclusion

The thermal degradation of isopropanol observed in this study may have a greater implication than for the interpretation of isopropanol data itself. Although only isopropanol was investigated in this study, other thermally labile VOCs, especially the secondary and tertiary alcohols, which have similar structure as isopropanol, may undergo similar thermal degradation during analysis. Therefore, possible thermal instability of VOCs under thermal desorption conditions must be considered when selecting thermal desorption based analytical methods for airborne VOCs.

Acknowledgement

Yingjie Li is a postdoc supported by the Canadian Government Laboratory Visiting Fellow program. We thank Dr. Xinghua Fan and Dr. Xu-liang Cao of Health Canada for their review of the manuscript.

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Table 1. Formation of thermal degradation products on two adsorbents (Tenax TA and Carbopack B) under thermal desorption temperature of 330°C and duration of 12 minutes. The spiked amount was 5000 ng. (IPA = isopropanol)

Tenax TA spiked with Acetone	%Propene/Acetone	%IPA/Acetone
Average	0	0
Standard deviation	NA	NA
Tenax TA spiked with IPA	%Propene/IPA	%Acetone/IPA
Average	0.11	0.43
Standard deviation	0.05	0.12
Carbopack B spiked with Acetone	%Propene/Acetone	%IPA/Acetone
Average	0.05	0
Standard deviation	0.05	NA
Carbopack B spiked with IPA	%Propene/IPA	%Acetone/IPA
Average	1.4	14
Standard deviation	0.5	9

Figure 1: Percentage of products formed from isopropanol (IPA) under various thermal desorption conditions.

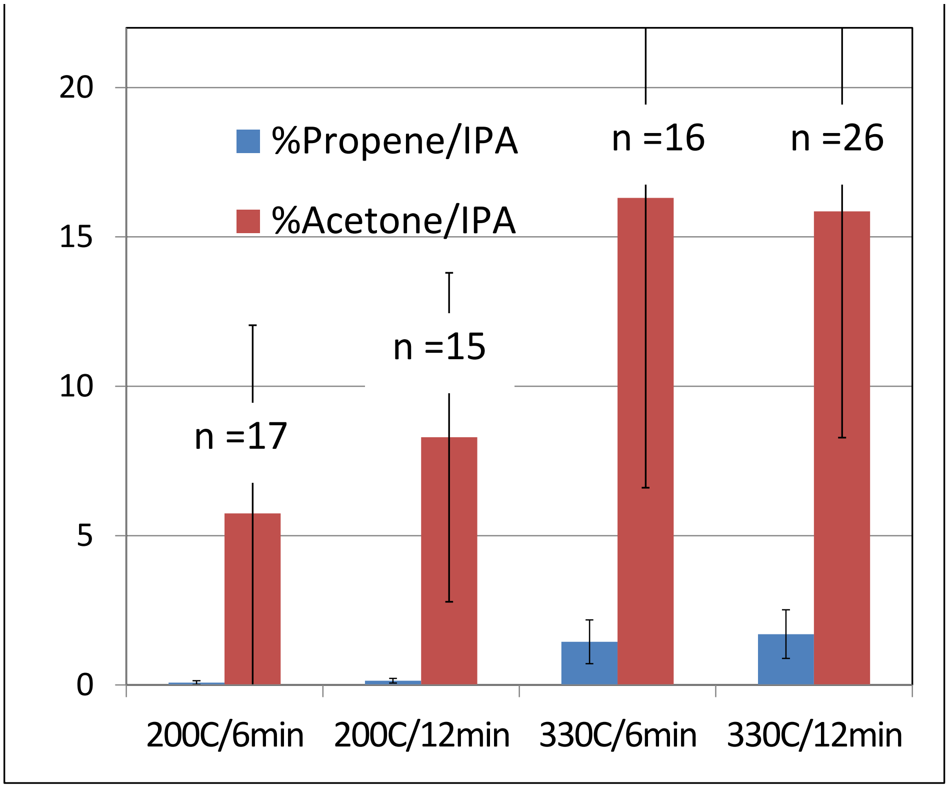
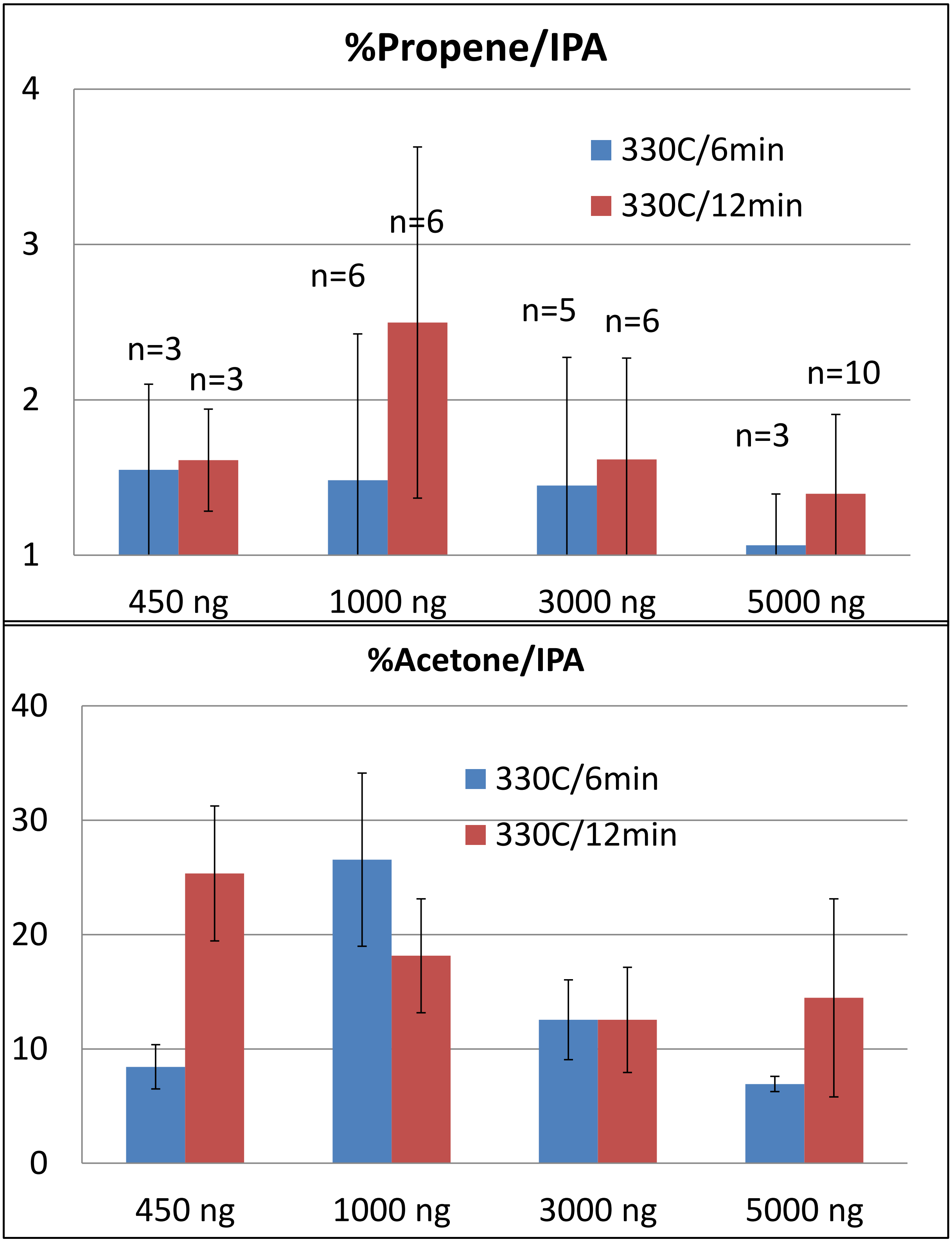


Figure 2: Percentage of degradation products of isopropanol (IPA) at various initial spiking amounts.



Graphic Abstract (TOC)