HOW TO SAMPLE PPB LEVELS OF VOCS IN THE PRESENCE OF OZONE: AN EVALUATION OF A POTASSIUM IODINE SCRUBBER

J Fick[1,2 *], L Pommer[1,2], B Andersson[1,2] and C Nilsson[3]

[1] Department of Chemistry, Environmental Chemistry, Umeå University, SE-901 87 Umeå, Sweden.
[2] Centre for Musculoskeletal Research, National Institute for Working Life, Umeå, Sweden.
[3] Unit for Biomass Technology and Chemistry, Swedish University of Agricultural Sciences, Umeå, Sweden.

ABSTRACT

Some reactive volatile organic compounds (VOCs) are prone to degradation during sampling in an ozone rich environment, which interferes with the results. A wide variety of different chemicals have been used to remove the ozone prior to sampling but the possibility of interference by such chemicals with the sampled VOCs has not been thoroughly examined. In the present investigation the retention/degradation at different settings of four terpenes (α-pinene, β-pinene, 3-carene and limonene) and isoprene has been studied when using potassium iodine, KI, as an ozone scrubber. The ozone removing capacity of the chemical was also examined at different relative humidities.

INDEX TERMS

Ozone scrubber, Tenax, terpenes, Isoprene, Ozone removal

INTRODUCTION

Vegetation emits a large amount of diverse volatile organic compounds (VOCs), and these play an important role in the overall chemistry of the atmosphere (Atkinson and Arey, 1998; Fuentes et al, 2000). They are considered potential sources of aerosols and are important precursors in the formation of tropospheric ozone and OH radicals (Yu et al, 1999). A group of these VOCs, the terpenes, are also considered as possible precursors to indoor contaminants (Weschler and Shields, 1997) and were reported to be the main indoor pollutants due to emissions from wood materials (Brown et al, 1994).

Many of these VOC's are reactive compounds that react or degrade during sampling. During sampling VOCs are concentrated on the adsorbent and exposed to a high amount of oxidizing agents such as ozone, NO_3 radicals and OH radicals. The oxidants have been shown to react not only with the sampled VOCs but also with the trap material (Cao and Hewitt, 1994, Calogirou et al, 1996). In order to avoid this problem various materials have been used to remove the ozone prior to sampling (Helmig, 1997, Fick et al, 2001).

In the present study the terpenes, α-pinene, β-pinene, 3-carene, and limonene and also isoprene were studied. They are present in outdoor and indoor air and they are all unsaturated, which makes them especially susceptible to ozonolysis (Brown et al, 1994; Fuentes et al, 2000).

---

[*] Contact author email jerker.fick@chem.umu.se

METHODS

Generation of terpene and isoprene samples

The experimental set-up has been presented elsewhere (Andersson et al, 1996). The pure terpenes and isoprene were injected with a micro-syringe injector (CMA/100, CMA/Microdialysis) in a purified air stream at 20-24 ºC with a flow rate of 37-38 L min^{-1} and a relative humidity (RH) of 20 or 50%, to generate a gas-phase concentration of the terpenes of 28 ppb (157 µg m^{-3}) and 28 ppb (78 µg m^{-3}) for isoprene. The total amount collected and analyzed were 1.1-1.3 nmole (150-180 ng) for the terpenes and 1.1-1.3 nmole (75-90 ng) for isoprene. Four parallel samples were collected, two without scrubbers and two with one scrubber each. This sampling sequence was repeated three times giving a total of 12 samples, 6 without and 6 with scrubbers.

Ozone capacity experiments

The scrubbers were connected to the sample inlet of a photometric ozone analyzer (ML®9811 O3, Monitor Labs, Inc.) and were tested with a sampling rate of 500 mL min^{-1} until a 10% breakthrough could be detected. This was done in the presence of 73-78 ppb (150-160 µg m^{-3}) ozone in purified air at 20-22 ºC with a relative humidity, RH of 10-70%. These experiments were done twice with freshly made scrubbers. All the ozone was generated with an ozone generator (500MM, Fischer) connected to pure oxygen.

Sampling and analysis

Sampling was made using stainless steel adsorbent tubes (Perkin-Elmer) filled with 200 mg Tenax TA (60-80 mesh, Perkin Elmer). Prior to each sampling the adsorbent tubes were conditioned for 1 h at 300 ºC with a flow of 100 mL min^{-1} nitrogen, in a sample-tube conditioning rig (TC-20, Markes). The conditioned tubes were sealed with Swagelok caps with Teflon ferrules. The sampling time was 10 min and the flow rate was between 90-120 mL min^{-1} yielding a sampling volume of approximately 1 L. The Tenax TA tubes were analyzed using thermal desorption (ATD 400, Perkin-Elmer) gas chromatography (GC) (HP6890, Hewlett-Packard) with a flame-ionization detector (FID).

RESULTS AND DISCUSSION

The potassium iodine (KI) scrubber proved to be the most suitable for these applications in an earlier investigation (Fick et al, 2001), and was studied further.

In order to elucidate the impact of RH on the sampling, the KI scrubber's ozone removing capacity was tested at different RH's. The levels of 0, 10, 15, 20, 40, 60, and 70% RH were chosen to accommodate most possible indoor settings, Table 3.

Table 3. Ozone removing capacity of KI at different RH's [a].

RH (%) (at 22 °C)						
0	10	15	20	40	60	70
0 h [b]	0 h [c]	0 h [d]	>24 h	>24 h	>24 h	nd [e]

nd = No Data. [a] The ozone removing capacity was measured by the time the scrubber could remove 10% of 75 ppb ozone at a flow rate of 500 mL min^{-1}. [b] The scrubber removed 21% of the ozone. [c] The scrubber removed 78% of the ozone. [d] The scrubber removed 83% of the ozone. [e] The KI started to dissolve.

The upper limit proved to be 70% RH at 22 °C, which correlates to an actual humidity of 13.59 g m^{-3}, where the crystalline KI started to dissolve. These results show a strong dependence on the presence of water, which correlates with the proposed reaction 1:

$$O_3 + 2KI(s) + H_2O \rightarrow O_2 + I_2 + 2\,KOH \tag{1}$$

The lower limit proved to be 20% RH which restricts the use indoors. If the flow rate was lowered to 100 mL min^{-1} the ozone removing capacity was increased to >24 h even at < 1% RH. This is most likely due to the five-fold increase in residence time, which gives the ozone ample time to interact with the scrubber.

The effects of an increased RH on the sampling were investigated by testing the recoveries for the terpenes and isoprene at an RH of 50%, as shown in Table 4.

Table 4. Recoveries of terpenes at 50% RH[a]

	Recoveries of terpenes (%)				
Scrubber	3-Carene	α-Pinene	β-Pinene	Limonene	Isoprene
KI	99 (1)	100 (1)	100 (1)	99 (1)	94 (5)

Relative standard deviations in brackets.

The RH did not affect the sampling of the terpenes, but the recovery of isoprene showed a statistically significant decrease of 6%. This could perhaps be explained by the fact that isoprene was the most water-soluble of the tested chemicals.

The possibility of a carry-over effect was investigated by reusing the same scrubbers in the sampling of α-pinene. The recoveries were tested after the scrubbers had been used 3, 5, 10 and 20 times, as summarized in Table 5.

Table 5. The recovery after reuse.

	Minutes of usage [a]				
	30 [b]	50 [c]	100 [c]	200 [c]	500 [b]
Recovery of α-pinene (%)	100	100	100	100	100

[a] 28 ppb a-pinene, 50% RH and 22 °C. [b] n=2. [c] n=4.

The KI scrubbers were shown to have no memory effects even after 500 minutes, which further enhances the usefulness of the scrubber.

CONCLUSIONS

The implications of our study are that it is possible to remove the ozone without affecting the recovery of the sampled VOCs and thereby make it possible to sample reactive VOCs that would otherwise be degraded by the ozone. The KI scrubber was the most suitable scrubber for these applications and further studies showed that this scrubber has the high ozone removing capacity, the selectivity and the reusability that distinguish the ideal scrubber.

ACKNOWLEDGEMENT

This study was funded in part by the Swedish Council for Building research grant 19970219, the Swedish Council for Work Life Research grant 96-0825 and the National Institute for Working Life (97/0557).

REFERENCES

Andersson B, Andersson K, Nilsson C-A, *et al*. 1996. Chemical reactions in ventilation ducts. *Proceedings of the 7th International Conference on Indoor Air Quality and Climate - In Indoor Air* '96, pp 947-952. Nagoya: Indoor Air '96

Atkinson R, and Arey J. 1998. Atmospheric Chemistry of Biogenic Organic Compounds. *Accounts of Chemical Research*, Vol. 31, pp 574-583.

Brown SK, Sim MR., Abramson MJ, *et al*. 1994. Concentrations of Volatile Organic Compounds in indoor Air- A Review. *Indoor Air*, Vol. 4, pp 123-134.

Calogirou A, Larsen BR, Brussol C, *et al*. 1996. Decomposition of terpenes by ozone during sampling on tenax. *Analytical Chemistry*, Vol. 68, pp 1499-1506.

Cao XL, and Hewitt CN. 1994. Study of the degradation by ozone of adsorbents and of hydrocarbons adsorbed during the passive sampling of air. *Environmental Science and Technology*, Vol. 28, pp 757-762.

Fick J, Pommer L, Andersson B, *et al*. 2001. Ozone Removal in the Sampling of Parts per Billion Levels of Terpenoid Compounds: An Evaluation of Different Scrubber Materials. *Environmental Science and Technology*, Vol. 35, pp 1458-1462.

Fuentes JD, Lerdau M, Atkinson R, *et al*. 2000. Biogenic hydrocarbons in the atmospheric boundary layer: A review. *Bulletin of the American Meteorological Society*, Vol. 81, pp 1537-1575.

Helmig D. 1997. Ozone removal techniques in the sampling of atmospheric volatile organic trace gases. *Atmospheric Environment*, Vol. 31, pp 3635-3651.

Weschler CJ, and Shields HC. 1997. Potential reactions among indoor pollutants. *Atmospheric Environment*, Vol. 31, pp 3487-3495.

Yu J, Cocker DR, Griffin III RJ, *et al*. 1999. Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products. *Journal of Atmospheric Chemistry*, Vol. 34, pp 207-258.