

PAMSGRAM

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THE USE OF KI-COATED COPPER OZONE DENUDEERS FOR CARBONYL MEASUREMENTS AT PAMS

The use of ozone denuders is required at PAMS to remove the interference caused by ozone when using the 2,4-dinitrophenylhydrazine (DNPH) coated sorbent cartridge methodology described in Compendium Method TO-11A¹. During the recent Measurement of Toxic and Related Air Pollutants conference in Cary, North Carolina, a paper was presented concerning potassium iodide (KI) coated ozone scrubbers for carbonyl measurements. The paper entitled "A Study of the Suitability of KI Denuders for O₃ Removal During Carbonyl Measurements"², presented results from zero air and carbonyl sampling using glass and copper denuders coated with KI. The paper observed that copper surfaces coated with KI + water + methanol + glycerol produce high concentrations of aldehydes, especially unusually high concentrations of formaldehyde. The information presented at the conference warrants clarification for the use of O₃ scrubbers at PAMS and the need for a reminder of previous guidance as given below.

KI coated copper denuders are recommended and acceptable for use at PAMS if prepared according to the PAMS Technical Assistance Document (TAD)³ and Method TO-11A by using a KI saturated water coating solution. **The use of methanol, glycerol or other organic wetting agents is not recommended.** The use of these agents is typical in the preparation of annular glass denuders. The presence of formaldehyde and other carbonyls may be significantly affected when using these wetting agents and is the subject of the paper referenced above. **If you do not prepare your own KI scrubbers, it is important to check with the manufacture of the device to ensure that the scrubber does not contain materials which may cause interferences.**

Ozone Scrubbers

The EPA has determined that ozone causes sampling interferences that must be removed during carbonyl sampling using Method TO-11A. Ozone can interfere with carbonyl measurements in the following ways:

¹Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by HPLC, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, EPA/625/R-96/010b, January 1997.

²Parmar, S.S., de Vera, V., Parmar, P., Hossain, M. and J. Cawyer, "A Study of the Suitability of KI Denuders for O₃ Removal During Carbonyl Measurements", presented at the Air and Waste Management Association sponsored Measurement of Toxic and Related Air Pollutants conference, Cary, NC, September 1-3, 1998.

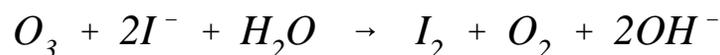
³Note that the **Technical Assistance Document for the Monitoring of Ozone Precursors**, EPA/600-8-91/215, has been undergoing revision; draft chapters have been published in the **PAMS Implementation Manual**, Appendix N, U.S. Environmental Protection Agency, EPA-454/B-93-051, March 1994.

- Ozone degrades the carbonyl derivatives formed on the cartridge during sampling resulting in low or inaccurate concentrations for the carbonyl compounds;
- Ozone reacts with the DNPH on the cartridge, making the DNPH unavailable for derivatizing carbonyl compounds and;
- If the analytical separation is inefficient, the DNPH degradation products can coelute with the target carbonyl derivatives, likewise producing inaccurate carbonyl results.

The extent of the ozone interference depends on the temporal variations of both the ozone and the carbonyl compounds and duration of sampling. Eliminating this measurement interference problem by removing or scrubbing ozone from the sampling stream prior to the collection of the carbonyl compounds is a mandatory facet of PAMS. Two types of scrubbers, the denuder ozone scrubber and the cartridge ozone scrubber have been tested and therefore may be used in the PAMS program for ozone removal. Both scrubber types use KI as the scrubbing agent. Both scrubber designs remove ozone at a collection flow rate up to 1 liter/minute and have sufficient scrubbing capacity to meet the needs of PAMS.

The denuder ozone scrubber (Figure 1) is a copper tube coated internally with a saturated solution of KI and water. The tube is coiled and housed in a temperature controlled chamber that is heated to, and maintained at, 66°C during sample collection. Heating prevents condensation from occurring in the tube during sampling. The scrubber is connected to the inlet of the sample collection system. The denuder O₃ Scrubber is reusable. The copper tube should be recoated with a saturated solution of KI after every six months of use. The denuder O₃ Scrubber prepared as described in TO-11A has been found to effectively remove ozone from the air stream for up to 100,000 ppb-hours. Thus, the scrubber is expected to last for six months of 24-hour sampling on every sixth day when sampling air with an average ozone concentration of 120 ppbv; however, a more frequent replacement program is recommended.

The cartridge O₃ Scrubber is a standard Sep-Pak® Plus cartridge (Figure 2) and is filled with 1.4 grams of granular KI. The particle size of the KI granules is optimized for mass transfer and flow. The scrubber is positioned at the inlet of the sample collection system. When sample air is pulled through the packed bed, iodide is oxidized to iodine, consuming the ozone, according to the following reaction:



The cartridge O₃ Scrubber is commercially available (Waters Corporation) and is disposable. The theoretical removal capacity of the scrubber, based on 100% consumption of KI, is 200 mg of O₃⁴. Based on field experience, the cartridge O₃ scrubber should be replaced every three weeks. Heating the cartridge to 35°C may be advisable under certain circumstances to prevent the water condensation. The user should evaluate the length of time for use of the denuder or scrubber under their specific field conditions. Caution should be taken when using these devices for extensive periods of time at high humidity (>65%). Regarding 24-hour samples, precaution should be taken while sampling nighttime periods when relative humidities approaching 100% are frequently encountered. It is recommended that a routine schedule of replacement be implemented as part of the sampling program. Additional detail on these issues may be obtained from the TAD and TO-11A.

For further information or questions please contact Joann Rice at rice.joann@epa.gov, (919) 541-3372.

Disclaimer: Mention of trade names or commercial products in this EPA *PAMSGRAM* are not intended to constitute endorsement or recommendation for use.

⁴Sample Prep Note (SPN) 2, "New Device Removes Ozone from Air Samples", Waters Corporation, www.waters.com/dwwwrootwaterswebsite/sprep.htm, July 19, 1995.

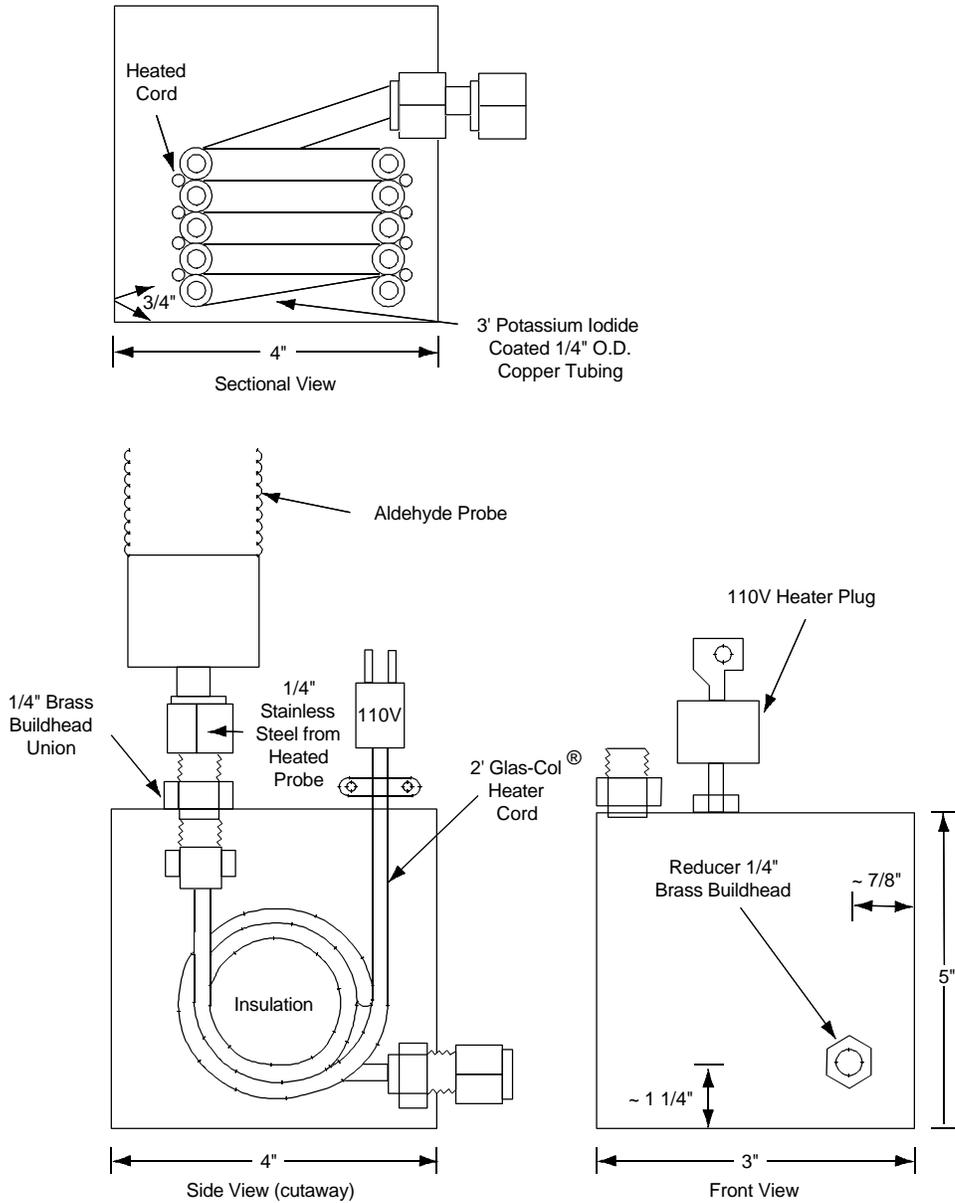


Figure 1. Cross-Sectional View of the KI-Copper Denuder O₃ Scrubber

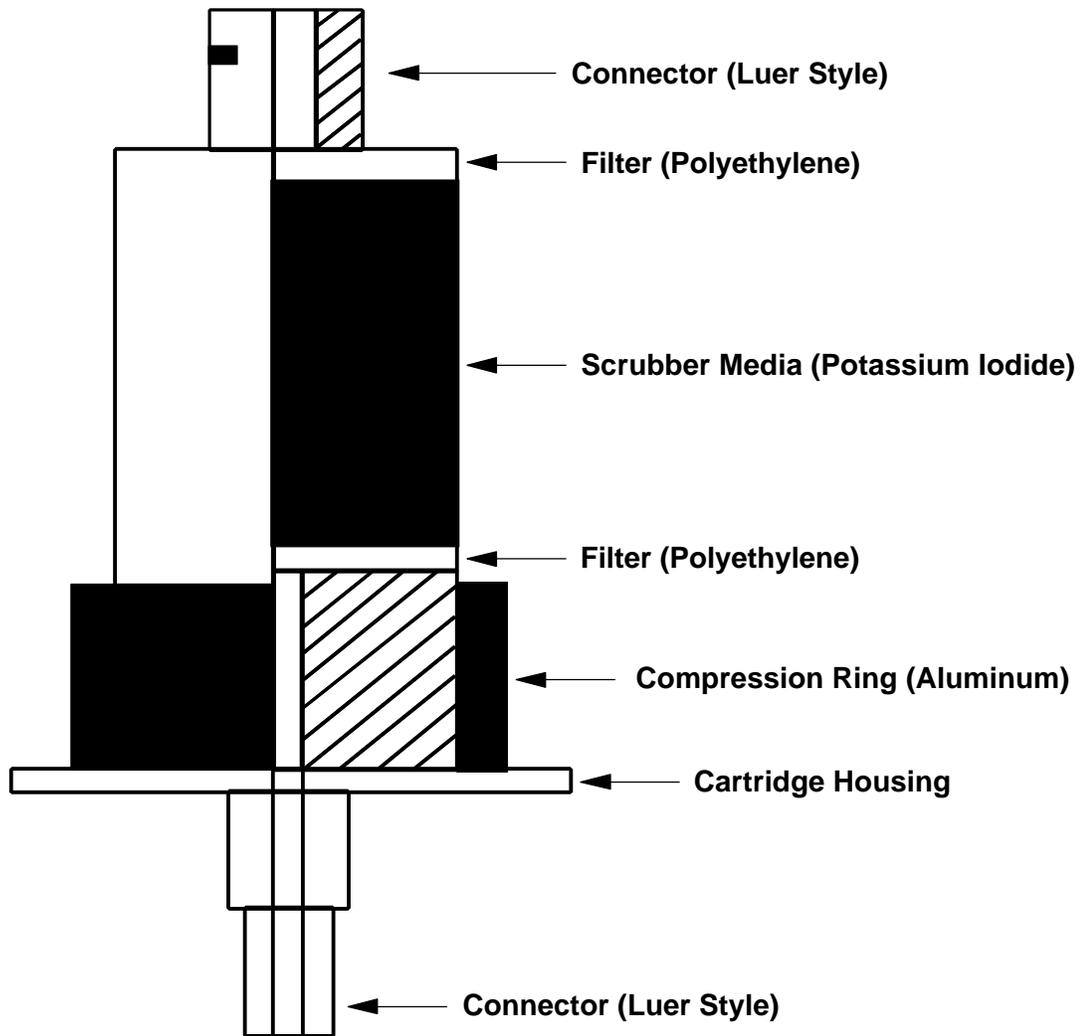


Figure 2. Cross-Section View of the Cartridge O₃ Scrubber