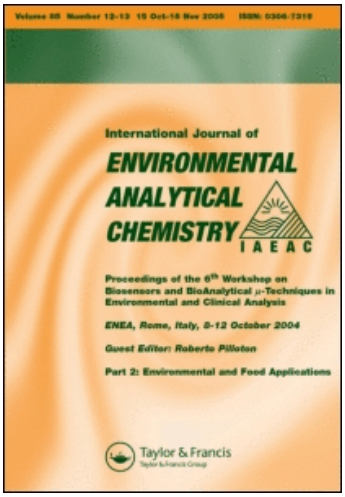

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S. E. Maljaars[a]; M. W. F. Nielen[a]
[a] Department of Analytical Chemistry, MT-TNO, AE DELFT, The Netherlands

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Evaluation of Adsorption Tubes for Air Sampling of C_2—C_4 Unsaturated Hydrocarbons

S. E. MALJAARS AND M. W. F. NIELEN*

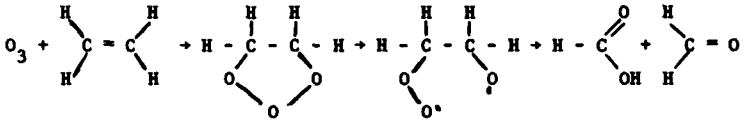
MT-TNO, Department of Analytical Chemistry, P.O. Box 217, 2600 AE DELFT, The Netherlands

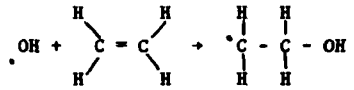
Three different types of adsorption tubes have been tested for suitability in sampling C_2—C_4 unsaturated hydrocarbons. Tubes packed with both a section of Molecular sieve 5A and Tenax GC showed the best retention towards these compounds, and were evaluated with the aid of humidified test atmospheres. Glass tubes packed with anhydrous potassium carbonate and a permeation drier were used in order to reduce the relative humidity of the sample prior to collection onto the adsorption tube. Breakthrough volumes and recoveries were studied in relation to relative humidity and sampling rate. The method has been applied to real air samples. The results indicate that the Molecular sieve 5A/Tenax GC adsorption tube can be successfully used for sampling of C_2—C_4 unsaturated hydrocarbons provided that a drying device is used to reduce the humidity of the sample.

KEY WORDS: Adsorption tubes, air sampling, C_2—C_4 unsaturated hydrocarbons, humidity, capillary gas chromatography.

1. INTRODUCTION

Unsaturated hydrocarbons play an important role in photochemical air pollution. Ethylene for example is highly reactive: with ozone peroxides and with hydroxyl radicals ethanol radicals are formed:[1–3]





Reactions of this type may give rise to malodorous compounds, such as aldehydes, ketones and organic acids. Propylene reacts indirectly with nitrogen dioxide and, in the presence of oxygen, forms 1,2-propanediol dinitrate (PGDN).

Research into photochemical air pollution and the chemical processes involved in it requires sensitive and versatile methods of sampling and determining C_2—C_4 unsaturated hydrocarbons in air. Several sampling methods are available:[4] Collection in evacuated glass or stainless steel cylinders, in plastic bags, absorption by some reagent (impinger methods) and adsorption in small glass tubes packed with suitable adsorbents. Methods using cylinders or bags limit the sample volume by their contents and suffer from losses or reaction with their inner wall. Cryogenic sampling, impingers or cylinders of large volume are very impractical for field sampling, especially when this is carried out from an aircraft. Therefore we focussed our attention on adsorption tubes only.

Leuenberger *et al.*[1] used an adsorption tube packed with sections of Tenax TA, Carbosieve S-11, silica and Molecular sieve 5A. Adsorption was done in this sequence but desorption was carried out in the backflush mode. Their results were quite promising, but unfortunately the study was rather brief.

Holzer, *et al.*[5] used the carbonaceous polymer Ambersorb XE-340, and found retention volumes of 0.8 and 8.5 l/g for ethane and propane, respectively. On basis of the literature data, we evaluated three adsorbents, *viz.* Tenax GC/Molecular sieve 5A, Tenax GC/Ambersorb XE-340 and Amberlite XAD-4, all with a known retentive power for C_5—C_{12} hydrocarbons, but an unknown retentive power for C_2—C_4 unsaturated hydrocarbons.

Throughout this paper the retention in the adsorption tubes is

expressed in terms of the breakthrough volume (V_b), which is defined as the sample volume of a particular compound which might be introduced into a single adsorption tube before 5% of the sampled amount is found after the adsorbent on a second "breakthrough" adsorption tube:

$$V_b = V_t - V_t\left(\frac{A_2}{A_1 + A_2} - 0.05\right)$$

where:

V_b = breakthrough volume (l) for a particular compound,
V_t = total sample volume (l) which has passed the adsorbent,
A_1 = peak area of the particular component obtained by analysis of the adsorption tube,
A_2 = peak area obtained via a second "breakthrough" adsorption tube placed in series with the first.

This formula is valid and useful if $V_t > V_b$ and $A_1 > A_2$, i.e. some breakthrough should have occurred in the first tube, but none in the second.

If a sampling method is to be validated, the effects of sampling rate and water content of the sample on breakthrough volume and recovery have to be studied.[6–8] Water can also interfere, as it may ice up the cold trap of thermal desorption cold-trap (TCT) injectors.[9] It is clearly preferable to remove as much water as possible before sampling and analysis. For this reason we also tested two types of drying devices, *viz.* drying tubes and permeation driers.[10]

2. EXPERIMENTAL

2.1 Apparatus

The adsorption tubes were analysed using a Varian (Sunnyvale, CA, U.S.A.) model 3700 gas chromatograph equipped with a flame ionization detector and a home-made TCT injector (cf. Figure. 1) coupled on-line with an A1203/KC1 PLOT fused silica column (50 m × 0.32 mm I.D.) supplied by Chrompack (Middelburg, The Netherlands). The carrier gas was helium. In preliminary experiments

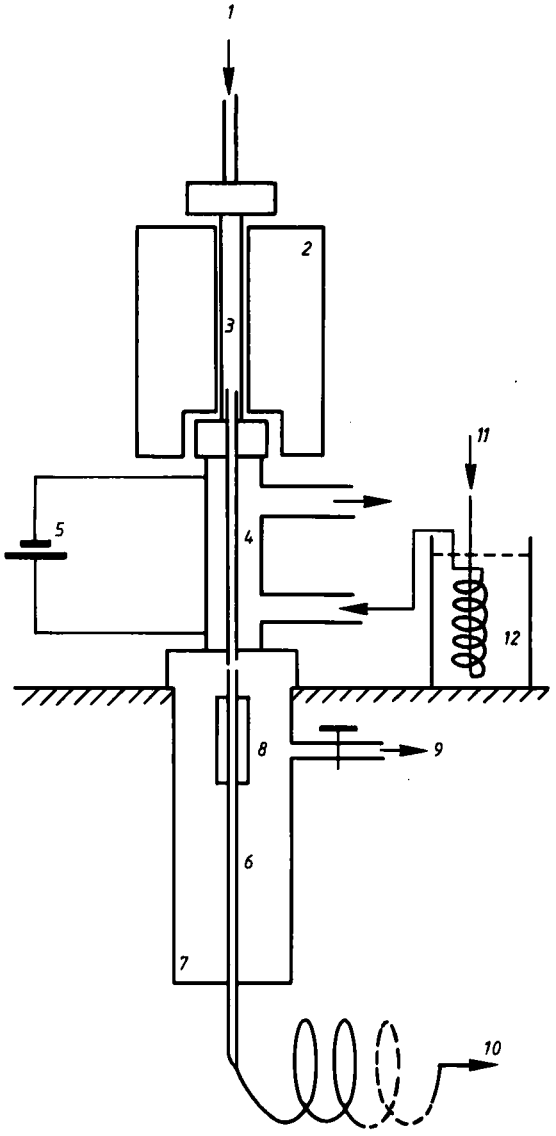


Figure 1 Home-made TCT injector. 1—carrier gas; 2—desorption oven; 3—adsorption tube; 4—cold trap (20 cm × 0.32 mm I.D. A1203/KCl PLOT column); 5—flash-heater; 6—GC column; 7—injector block; 8—liner; 9—vent; 10—to FID; 11—nitrogen (g); 12—nitrogen (liquid).

we also used a J&W (Folsom, CA, U.S.A.) column (30 m × 0.32 mm I.D.) coated with a 5 μm film of DB-1.

We used two permeation driers (in series) supplied by Perma Pure Products (Farmingdale, U.S.A.), model MD-250-72-pf. The relative humidity meter was a Vaisala (Finland), model HMI33. The mass-flow controller was a Hi-Tec (Pennsylvania, PA, U.S.A.), model F-100/200.

2.2 Materials

Home-made glass tubes (18 cm × 3 mm I.D./6.2 mm O.D.) equipped with 1/4 inch Swagelok caps and teflon ferrules were used. A plug of quartz wool (Chrompack) was inserted in each tube and they were dry-filled with the aid of a funnel.

Another plug of quartz wool was inserted on the top of the packed bed. Sections of different adsorbents in one tube were separated from each other by another plug of quartz wool. The adsorbents are listed in Table 1. The three different types of adsorption tubes studied were composed as follows: a tube with 260 mg of XAD-4; a tube with a combination of 50 mg of Tenax GC and 350 mg of Ambersorb XE-340; a tube with a combination of 50 mg of Tenax GC and 300 mg of Molecular sieve 5A.

A glass filter holder (3 cm I.D.) was filled with 20 g of anhydrous potassium carbonate (Baker Chemicals, Deventer, The Netherlands) resulting in a bed length of 3 cm. The K_2CO_3 was kept in place by plugs of quartz wool (Chrompack). The calibration gases were made by Aga Gas (Amsterdam, The Netherlands): a cylinder with 100 ppmv ethylene in synthetic air and a cylinder containing ethylene, propylene, 1-butene, i-butene (all 20 ppbv), cis-2-butene and

Table 1 Characteristics of the adsorbents under investigation

Adsorbent	*Structure*	*Pore size (A)*	*Specific area (m^2/g)*	*Supplier*
Tenax GC	Diphenyl-p-phenylene oxide	720	18.6	Chrompack
Amberlite XAD-4	styrene-divinylbenze	75	750	Rohm & Haas
Ambersorb XE-340	Carbonaceous polymer	300	400	Rohm & Haas
Molecular sieve 5A	Inorganic	5	725	Applied Science Lab. Inc.

trans-2-butene (10 ppbv) and 1,3-butadiene (12 ppbv) in nitrogen. The actual concentrations were stated to be within 10% of these nominal values.

2.3 Procedures

The different types of adsorption tubes were all re-used after purging with a 20 ml/min flow of purified helium in an oven for 16 hours. The regeneration temperature was 150 °C (for XAD-4) or 250 °C (other adsorbents), depending on the thermostability of the adsorbent in question.

The test atmosphere was generated with the aid of the equipment shown in Figure 2. The atmosphere can be humidified by insertion of a round-bottomed flask with water. The humidity was varied by diluting the humidified test atmosphere with an appropriate flow of dry test gas (not shown in Figure 2). In case of humidifed samples a

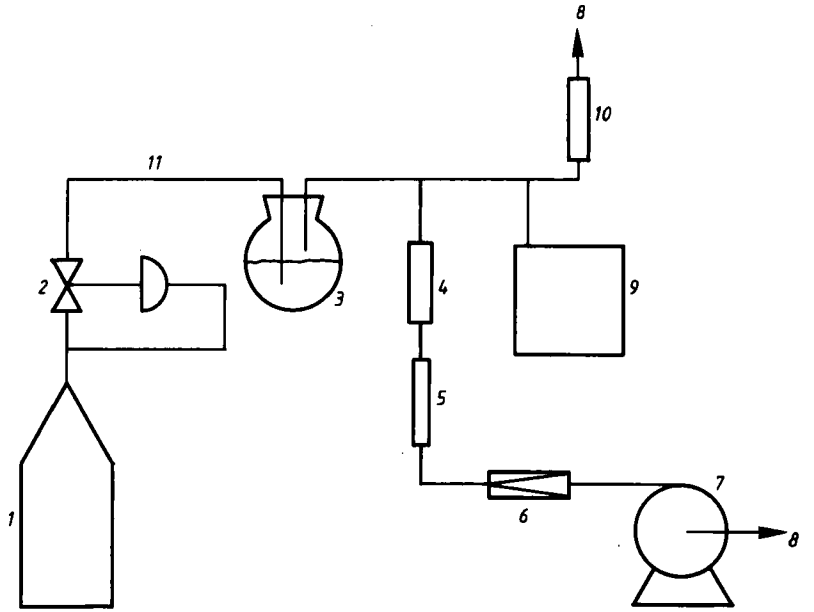


Figure 2 Set-up for the generation of test atmospheres. 1—cylinder with calibration gas; 2—mass-flow controller; 3—round bottomed flask with water; 4—drying device; 5—adsorption tubes (in series); 6—critical orifice; 7—vacuum pump; 8—vent; 9—RH meter; 10—flow meter; 11—silanized glass tubes.

drying device was incorporated ahead of the actual adsorption tube in the sampling line. The real relative humidity was checked by insertion of the RH-meter in the sampling line between the drying device and the adsorption tube. The flow passing the adsorption tubes was checked with a Rotameter (Brooks, Inc.).

Through the tubes containing two adsorbents, the sample is passed in such a manner that it first passes Tenac GC, and then the other adsorbent. Desorption is conducted in the opposite direction, i.e. in the backflush mode. As a rule, adsorbent tubes were equipped in series with a second so-called breakthrough tube, enabling the breakthrough volume to be calculated (cf. Introduction). All adsorption tubes were sampled at 21 ± 1 °C.

The TCT injector is operated as follows: after cooling the cold-trap to -100 °C, the adsorption tube is thermally desorbed at 150 °C or 250 °C (cf. above) in a helium flow of 20 ml/min. The cold trap is flash-heated after 500 s to 200 °C, and the desorbed compounds are injected onto the column.

3. RESULTS AND DISCUSSION

3.1 Comparison of adsorption tubes

Before evaluating the sampling, we analysed all types of adsorption tubes in order to obtain some blank values. In spite of some impurities showing up in the chromatograms, we decided to continue the experiments, because we did not expect the impurities to interfere with the analysis of the calibration gases. The temperature program of the gas chromatograph was adjusted both for optimum resolution of the components of the calibration gas (especially the butene cluster) and acceptable peak shapes. A chromatogram, including the conditions used, is shown in Figure 3. The calculated response factors (area/nMol) were not consistent with the stated concentrations of all of the components in the calibration mixture. Especially for propylene which was too low and for trans-2-butene, which was found to be too high. A possible explanation might be an error in the stated concentrations or some loss or rearrangements in the cylinder. In addition, the identification of the peaks in the chromatogram was based on retention times only.

The efficiency and peak shape obtained with the thick-film DB-1

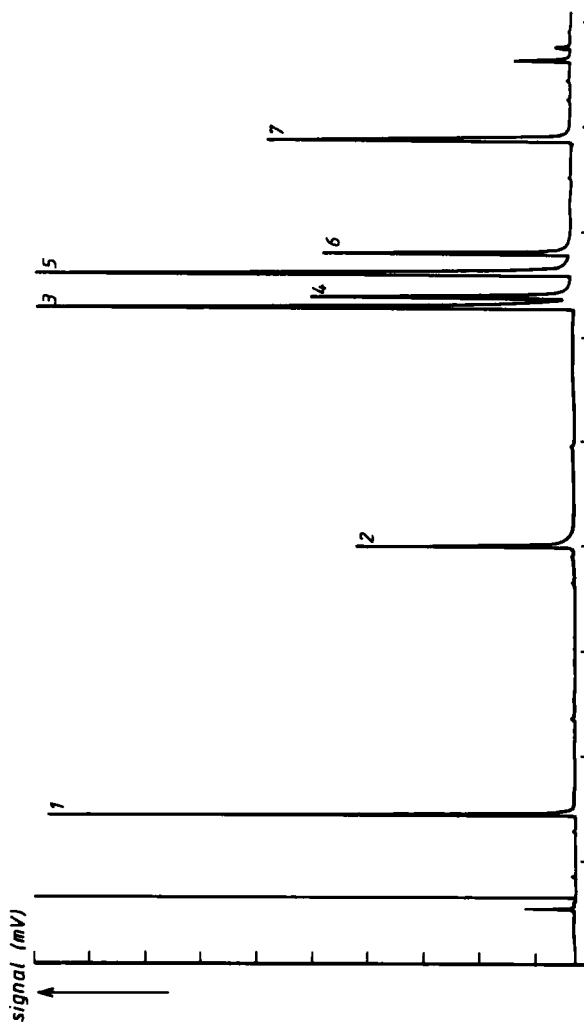


Figure 3 Chromatogram of C_2—C_4 compounds of the calibration gas. Conditions: A1203/KCl PLOT column. Initial temperature 0°C; to 200°C at 3°C/min. 1—ethylene; 2—propylene; 3—trans-2-butene; 4—1-butene; 5—*i*-butene; 6—cis-2-butene; 7—1,3-butadiene. Peak identification based on retention times.

Table 2 Mean breakthrough volume (V_b) of ethylene on different adsorption tubes.
Conditions: Sampling rate 100 ml/min, temperature 21 ± 1 °C, relative humidity 0%; results are the averages of four experiments

Adsorption tube	V_b (*l*)
Amberlite XAD-4	0.32 ± 0.09
Tenax GC/Ambersorb XE-340	0.31 ± 0.02
Tenax GC/Molecular sieve 5A	4.26 ± 0.62

column was rather poor, so we continued our experiments with the A1203/KCl PLOT column only.

Breakthrough volumes were determined with a dry test atmosphere of 20 ppbv ethylene at a sampling rate of 100 ml/min. The results are summarized in Table 2, which clearly shows that, even under favourable conditions, only one type of adsorption tube is suitable for ethylene (the C_3—C_4 hydrocarbons will have higher V_b values). Therefore the influence of humidity and sampling rate was studied with the Tenax GC/Molecular sieve 5A tube only. Repeatability was checked by sampling 2.85 l of a dry test atmosphere containing the calibration mix, and found to be better than 6% rel. S.D. ($n=6$) for all but one (cis-2-butene: 9%) of the components. These results are quite satisfactory because they include the repeatability of the gas generation system, the sampling system, the TCT injector and the gas chromatographic analysis.

3.2 K_2CO_3 drying tube

Several types of drying tubes were tested. The type described in the experimental section was able to reduce an initial relative humidity of 90% down to 10% relative humidity at a sampling rate of 100 ml/min. After the passage of more than 75 l of air with a relative humidity of 90%, the humidity at the outlet of the K_2 CO_3 tube still was only 25%. However, the sampling rate decreased from 100 to 50 ml/min, owing to the higher resistance of the wet K_2CO_3.

A dry test atmosphere of C_2—C_4 unsaturated hydrocarbons (10–20 ppbv) was sampled (in triplicate) via the K_2CO_3 tube. Recoveries were found to be 100%, so the drying tube causes no losses. Next we tested atmospheres (in duplicate) with 45%, 70% and 90% relative

humidity, and found a decreasing breakthrough volume down to 2.1. The total recovery, i.e. the sum of the peak areas of the first adsorption tube and its second "breakthrough" tube, was also reduced and typically 40–80% for the compounds under investigation. Obviously compounds are partly lost in the wet drying tube (breakthrough in the second adsorption tube is rather unlikely, because of the relatively small peak areas as compared to the first adsorption tube). Losses in the round bottomed flask did not occur, as was shown in the experiments with the permeation drier (cf. below).

The influence of sampling rate was studied with a test atmosphere of 90% relative humidity and varied between 75 and 175 ml/min. A linear decrease in breakthrough volume (down to 1 l) was observed for all C_4 unsaturated hydrocarbons (no conclusions could be drawn for ethylene and propylene) owing to the reduced contact between solutes and adsorbent. The total recovery did not decrease significantly with increasing sampling rate, although more experiments are required to support this statement statistically.

3.3 Permeation drier

The permeation drier was operated with dry air flowing at 2 l/min in the opposite direction to the sample flow (130 ml/min). It reduced an initial humidity of 90% to 1%. A dry test atmosphere of C_2—C_4 unsaturated hydrocarbons (10–20 ppbv) was sampled (in triplicate) via the permeation drier. Recoveries were found to be 90–100%, except for ethylene (65%) and cis-2-butene (70%). Some ethylene may have passed the permeable wall. The loss of cis-2-butene could not be explained by adsorption in the gas generation system (no losses occurred in the tests of the K_2CO_3 tube with a dry atmosphere). Next we tested an atmosphere with a relative humidity of 90%. The breakthrough volume was found to be still in excess of 2.7 l, the maximum volume tested. The total recovery was 85–118%, except for ethylene and cis-2-butene (55%).

3.4 Air samples

A volume of 2.3 l of outdoor air with a relative humidity of 70% was sampled via a K_2CO_3 drying tube at 76 ml/min. No breakthrough was found to occur. The resulting chromatogram is given in Figure 4. The concentrations found and the detection limits are given in

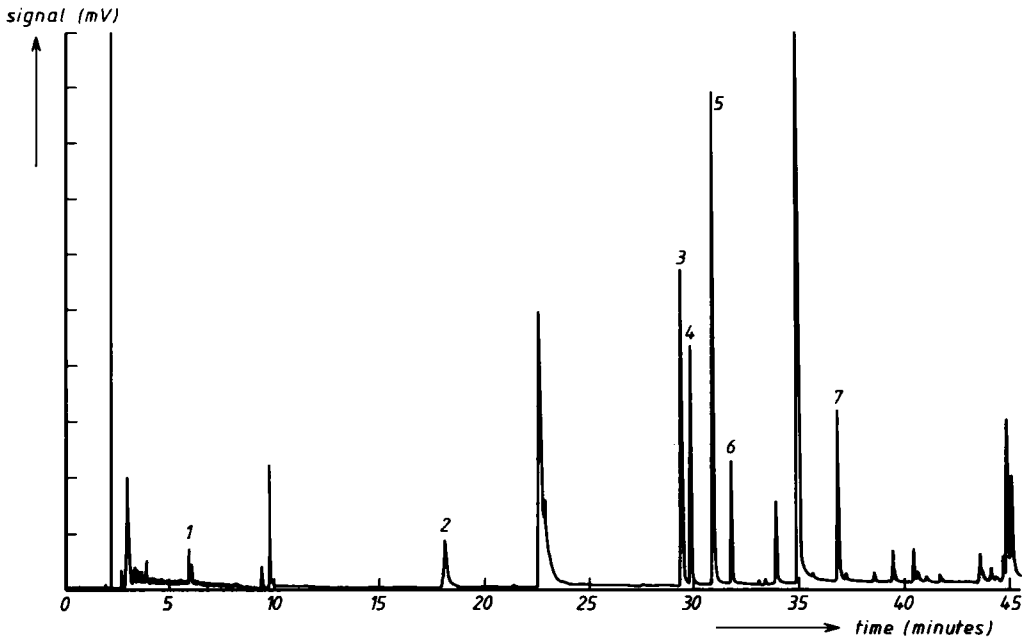


Figure 4 Chromatogram of an air sample. Conditions: Sampling on Tenax GC/Molecular sieve 5A at 76 ml/min. Drying device: K_2CO_3 tube. On-line TCT injection onto the GC column. Sample volume 2.31. Other conditions as in Figure 3.

Table 3. The results have not been corrected for the incomplete recovery. The relatively high values of the detection limit for ethylene and propylene can be explained by the noise-level in the beginning of the chromatogram and the (too) low response factor, respectively. The low value for trans-2-butene can be explained by its (too) high response factor (cf. paragraph 3.1).

Table 3 Concentrations and detection limits of C_2—C_4 unsaturated hydrocarbons in outdoor air

Component	*Concentration (ppbv)*	*M.D.L. (ppbv)**
Ethylene	0.6	0.21
Propylene	1.5	0.10
Trans-2-butene	0.94	0.02
1-butene	1.7	0.03
i-butene	1.8	0.04
cis-2-butene	0.64	0.04
1,3-butadiene	0.85	0.04

*M.D.L. = method detection limit, s/n = 3, sample 2.3 l.

4. CONCLUSIONS

Adsorption tubes packed with Tenax GC/Molecular sieve 5A can be used for the sampling of C_2—C_4 unsaturated hydrocarbons in air. The sample should be dried with either a K_2CO_3 tube or a permeation drier. Breakthrough volumes were found to decrease linearly with increased sampling rate. Total recovery was reduced by an increase of the relative humidity of the sample, especially when the K_2CO_3 drying option was used. The permeation drier causes some loss of ethylene and cis-2-butene, but generally performs satisfactorily for all other components. In particular, it does not decrease the sampling flow rate, as does the wet K_2CO_3 tube.

Method detection limits are typically in the part-per-trillion (v/v) range, and the method described has potential for photochemical air pollution studies in which samples are collected on board aircraft.

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