

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/8921527>

# Combination of Sorption Tube Sampling and Thermal Desorption with Hollow Waveguide FT-IR Spectroscopy for Atmospheric Trace Gas Analysis: Determination of Atmospheric Ethene at the...

ARTICLE in ANALYTICAL CHEMISTRY · FEBRUARY 2004

Impact Factor: 5.64 · DOI: 10.1021/ac034396j · Source: PubMed

---

CITATIONS

19

---

READS

97

9 AUTHORS, INCLUDING:



**Erwin Rosenberg**

TU Wien

99 PUBLICATIONS 1,581 CITATIONS

SEE PROFILE



**Hans Puxbaum**

TU Wien

271 PUBLICATIONS 8,211 CITATIONS

SEE PROFILE



**Alexandra Inberg**

Tel Aviv University

27 PUBLICATIONS 166 CITATIONS

SEE PROFILE



**Boris Mizaikoff**

Universität Ulm

310 PUBLICATIONS 4,799 CITATIONS

SEE PROFILE

# Combination of Sorption Tube Sampling and Thermal Desorption with Hollow Waveguide FT-IR Spectroscopy for Atmospheric Trace Gas Analysis: Determination of Atmospheric Ethene at the Lower ppb Level

Olga A. Pogodina,<sup>†</sup> Victor V. Pustogov,<sup>†</sup> Fabiano de Melas,<sup>†</sup> Christina Haberhauer-Troyer,<sup>†</sup> Erwin Rosenberg,<sup>†</sup> Hans Puxbaum,<sup>\*,†</sup> Alexandra Inberg,<sup>‡</sup> Nathan Croitoru,<sup>‡</sup> and Boris Mizaikoff<sup>\*,§</sup>

*Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, A-1060 Vienna, Austria, Department of Electrical Engineering and Physical Electronics, Tel Aviv University, Tel Aviv 69978, Israel, and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400*

**The determination of organic trace gases in the ambient environment at the lower ppb level is demonstrated based on a novel technique combining sorption tube sampling on Molsieve and Carbosieve S-III, thermal desorption, and detection of the trace analyte by hollow waveguide Fourier transform infrared (HWG-FT-IR) spectroscopy. While ethene concentrations of ~5 ppm can be directly observed using HWG-FT-IR, enrichment factors of up to 5000 were achieved by sorption tube sampling and thermal desorption. Detection limits of ~1 ppb are reported. Efficient enrichment by the sampling tube is achieved due to the favorable internal volume (~0.4 cm<sup>3</sup> at a length of 470 mm) of the hollow waveguide serving as a miniaturized gas cell. This new method was validated for ethene by thermodesorption-cryofocusing-GC-FID as the reference method. Analytical performance has been compared for standard gas mixtures and for ethene measurements in urban air. Finally, ethene data from a sampling campaign at two alpine sites in Tyrol/Austria are presented.**

Monitoring of trace gas concentrations in the atmosphere is an important task for the evaluation of air quality. Particular attention is required during the analysis of volatile organic compounds (VOCs), since they have both biogenic and anthropogenic origin and are widely distributed in the atmospheric environment.<sup>1</sup> The current status of analytical methods used for the determination of organic compounds in ambient air has been reviewed by Aragon et al.<sup>2</sup> Requirements for the novel monitoring

technique are high sensitivity at the lower ppb concentration level, absence of artifacts during analysis, and continuous operation for long-term environmental observations.

Gas analyzers operating in the mid-infrared (MIR) spectral region have been designed using several different principles. Generally, IR spectroscopic devices take advantage of the high molecular specificity in the wavelength range from 3 to 20  $\mu\text{m}$  due to excitation of fundamental vibrational and rotational transitions. The unique IR absorption pattern of most organic and inorganic gaseous compounds provides inherent discrimination against many atmospheric constituents. However, limits of detection of conventional instrumentation for ground-based/container-type measurements do not allow routine analysis of common ambient organic species in the low- or sub-ppb ( $\mu\text{g}/\text{m}^3$ ) concentration range. Relatively low detection limits for organic constituents have been achieved by using nondispersive IR analyzers,<sup>3</sup> photoacoustic analyzers,<sup>4–6</sup> tunable diode laser spectroscopy,<sup>7–8</sup> quantum cascade lasers,<sup>9–10</sup> and long-path gas cells or open path measurement techniques<sup>11</sup> in combination with FT-IR detection schemes.<sup>12</sup> However, routine applications for background air measurements are not reported with any of these systems.

\* Corresponding authors: (e-mail) boris.mizaikoff@chemistry.gatech.edu; (phone) +1-404-894-4030; (fax) +1-404-894-7452. (e-mail) hpuxbaum@mail.zserv.tuwien.ac.at; (phone) ++43-1-58801-15170; (fax) ++43-1-58801-15199.

<sup>†</sup> Vienna University of Technology.

<sup>‡</sup> Tel Aviv University.

<sup>§</sup> Georgia Institute of Technology.

(1) Bloemen, H. J. Th.; Burn, J., Eds. *Chemistry and Analysis of Volatile Organic Compounds in the Environment*, 1st ed.; Chapman & Hall: New York, 1993; Chapter 1.

(2) Aragon, P.; Atienza, J.; Climent, M. D. *Crit. Rev. Anal. Chem.* **2000**, *30*, 121–151.

(3) Lee, D.-D.; Lee, D.-S. *IEEE Sens. J.* **2001**, *1*, 214–224.

(4) Sigrist, M. W.; Naegele, M.; Romann, A. *Proc. SPIE—Int. Soc. Opt. Eng.* **2001**, *4419*, 14–17.

(5) Moeckli, M. A.; Fierz, M.; Sigrist, M. W. *Environ. Sci. Technol.* **1996**, *30*, 2864–2867.

(6) Kühnemann, F.; Wolfertz, M.; Arnold, S.; Lagemann, M.; Popp, A.; Schüler, G.; Jux, A.; Boland, W. *Appl. Phys. B* **2002**, *75*, 397–403.

(7) Werle, P.; Kormann, R. *Proc. SPIE—Int. Soc. Opt. Eng.* **1999**, *3821*, 124–135.

(8) Richter, D.; Fried, A.; Wert, B. P.; Walega, J. G.; Tittel, F. K. *Appl. Phys. B* **2002**, *75*, 281–288.

(9) Nelson, D. D.; Shorter, J. H.; Mcmanus, J. B.; Zahniser, M. S. *Appl. Phys. B* **2002**, *75*, 343–350.

(10) Hvozďara, L.; Gianordoli, S.; Strasser, G.; Schrenk, W.; Unterrainer, K.; Gornik, E.; Murthy, Ch.; Kraft, M.; Pustogov, V.; Mizaikoff, B.; Inberg, A.; Croitoru, N. *Appl. Opt.* **2000**, *39*, 6926–6930.

(11) David, P. A.; Pauls, R. E.; Baughman, E. H. *Proc. SPIE—Int. Soc. Opt. Eng.* **1995**, *2365*, 25–36.

An innovative approach for monitoring individual hydrocarbon species at low concentrations is proton-transfer-reaction mass spectroscopy. Detection limits of a few pptv are reported.<sup>13–14</sup> A combination of cryosampling and FT-IR detection for a gas cell with an optical path length of 1.1 m folded inside a volume of 200 cm<sup>3</sup> providing a path-to-volume ratio of 5.5 has recently been applied for FT-IR gas analysis at low concentration levels. While the advantage of the cryosampling with high enrichment factors up to  $1 \times 10^6$  is reported,<sup>15</sup> the requirement of water and carbon dioxide removal and difficult transport of representative samples from measurement campaigns to the laboratory are among the disadvantages of this method.

At present, the only method widely used for individual “non-methane hydrocarbon” (C<sub>2</sub>–C<sub>10</sub> hydrocarbons) determination in urban, rural, and background air is a combined method based on sampling using chromatographic sorbent materials and determination with a gas chromatographic (GC) system combined with thermodesorption, cryofocusing, and capillary-GC with FID and MS detection.<sup>16–18</sup>

The concept we pursue in the current study is a new generation of instruments based on a combination of sampling comprising an enrichment step utilizing chromatographic sorbents followed by thermodesorption, in combination with newly developed hollow waveguide (HWG) gas sensing modules<sup>19</sup> coupled to a FT-IR detection system. The analyzer we describe here is based on HWGs simultaneously serving as low-volume miniaturized gas cells and IR waveguide. HWGs have recently been introduced for gas analytical applications, combining a HWG gas-sensing module with conventional FT-IR and different forms of IR laser spectroscopy.<sup>10,20–23</sup> HWG gas cells are optical fibers with a hollow core guiding IR radiation due to reflection at the inside walls, resulting in an increase of the effective optical path length. The inside walls are coated with a layer of silver and protected by a thin layer of AgI. Among the main advantages of HWGs compared to conventional multipass gas cells are the considerably decreased sample volume probed inside the HWG and the relatively long optical path length in a yet compact system. The gaseous sample is pumped into or through the hollow core of the waveguide. IR radiation is coupled into the waveguide by a focusing mirror and is transported through the HWG by reflection at the waveguide walls. The large number of reflections results in an enhanced

optical path length and, consequently, increased sensitivity compared to a single-pass transmission gas cell for IR absorption measurements. Concentrations of organic gases detected with direct HWG-MIR applications are typically at lower ppm (v/v) levels (ref 20 and our own preliminary data). This concentration range is still  $\sim 4$  orders of magnitude above concentrations of organic compounds to be detected in ambient air. Low-volume HWG gas cells with a path length of 50–100 cm exhibit volumes of around 0.1–3 cm<sup>3</sup>. Hence, they provide remarkably large optical path length-to-volume ratios of more than 100 (in comparison with typically less than 10 for multireflection cells<sup>15</sup>).

Yang and co-workers demonstrated the suitability of HWG gas sensing in combination with preconcentration membranes by coating various polymers onto the interior surface of the HWG.<sup>24,25</sup> Conventional enrichment systems in ambient air gas chromatography sample typically 1–5 dm<sup>3</sup> of air and desorb analytes into small volumes below 1 cm<sup>3</sup>, which are ideally compatible with the sample volume of the developed HWG gas-sensing modules. Therefore, we propose here to use enrichment systems commonly applied in ambient air gas chromatography (e.g., cryosampling or sampling on absorption tubes), where volume-based enrichment of 10<sup>4</sup> and more can be achieved, lowering the limit of detection to the required ppb (v/v) concentration level. The present work demonstrates the feasibility of continuous, accurate, and reproducible measurements of atmospheric trace gases by the combination of enrichment tubes with a HWG-FT-IR spectrometer. The system is validated and used for determination of ambient ethene in a field measurement campaign. Ethene is a confirmed plant toxic compound with a threshold level of 9 ppbv set by the Austrian Academy of Science.<sup>26</sup>

## EXPERIMENTAL SECTION

Since the goal of this work was to develop a method that is usable in both environments, in the laboratory and in the field, particular consideration was given to the development of the FT-IR sensing module, which should be robust and compact and provide uncompromised performance. The Midac Illuminator FT-IR spectrometer (Midac Corp.) provides a compact platform to efficiently integrate a variety of sampling interfaces. IR signals were detected with a broadband LN<sub>2</sub>-cooled mercury–cadmium–telluride detector (Belov Inc.) equipped with a 2 × 2 mm detector element.

In this work, a small-bore silica hollow waveguide developed by our collaborators at Tel-Aviv University with a length of 0.47 m, a reflective silver layer with a thickness of 0.3 μm, and a dielectric protective coating (AgI) with a thickness of 0.9 μm was used.<sup>27,28</sup> Attenuation losses of these HWGs are near 1 dB/m (at 10.6 μm) due to the inner surface roughness of  $\sim 10$  nm. Since silica glass is fragile, the HWG was protected with a flexible polyimide coating on the outside for facile handling. The ends of the HWG were cut using chromatographic column cutters and inserted into especially designed gastight HWG cell interface

- (12) Griffith, D. W. T.; Jamie, I. M. Fourier transform infrared spectroscopy in atmospheric and trace gas analysis. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; Wiley: Chichester, 2000; pp 1979–2007.
- (13) Hayward, S.; Hewitt, C. N.; Sartin, J. H.; Owen, S. M. *Environ. Sci. Technol.* **2002**, *36*, 1554–1560.
- (14) Hansel, A.; Jordan, A.; Warneke, C.; Holzinger, R.; Wisthaler, A.; Lindinger, W. *Plasma Sources Sci. Technol.* **1999**, *8*, 332–336.
- (15) Hanst, P. L. *Appl. Opt.* **1978**, *17*, 1360–1366.
- (16) Haunold, A. Doctoral Thesis, Vienna University of Technology, 1997.
- (17) Hallama, R. A.; Rosenberg, E.; Grasserbauer, M. *J. Chromatogr., A* **1998**, *809*, 47–63.
- (18) Fung, Y. S.; Wu, Z. *Analyst* **1996**, *121*, 1955–1961.
- (19) De Melas, F.; Pustogov, V. V.; Croitoru, N.; Mizaikoff, B. *Appl. Spectrosc.* **2003**, *57*, 600–606.
- (20) Worrell, C. A.; Giles, I. P.; Adatia, N. A. *Electron. Lett.* **1992**, *28*, 615–617.
- (21) Haan, D. J.; Harrington, J. A. *Proc. SPIE—Int. Soc. Opt. Eng.* **1999**, *3596*, 43–49.
- (22) De Melas, F.; Pustogov, V. V.; Wolcott, D. K.; Olson, D. C.; Inberg, A.; Croitoru, N.; Mizaikoff, B. *Int. J. Environ. Anal. Chem.* **2003**, *83*, 573–583.
- (23) Worrell, C. A.; Gallen, N. A.; Niall, A. *J. Phys. D: Appl. Phys.* **1997**, *30*, 1984–1995.

- (24) Yang, J.; Her, J.-W.; Chen, S.-H. *Anal. Chem.* **1999**, *71*, 3740–3746.

- (25) Yang, J.; Her, J.-W. *Anal. Chem.* **2000**, *72*, 878–884.

- (26) Oesterreichische Akademie der Wissenschaften, Kommission zur Reinhaltung der Luft. Fluechtige Kohlenwasserstoffe in Atmosphaere – Entstehung, Verhalten und Wirkung; Luftqualitaetskriterien VOC. Wien, December 1996.

- (27) Croitoru, N. *Trends Lightwave Technol.* **1994**, *1*, 73–86.

- (28) Croitoru, N.; Dror, J.; Goldenberg, E.; Mendlovic, D.; Gannot, I. U.S. Patent 4,930,863, 1990.

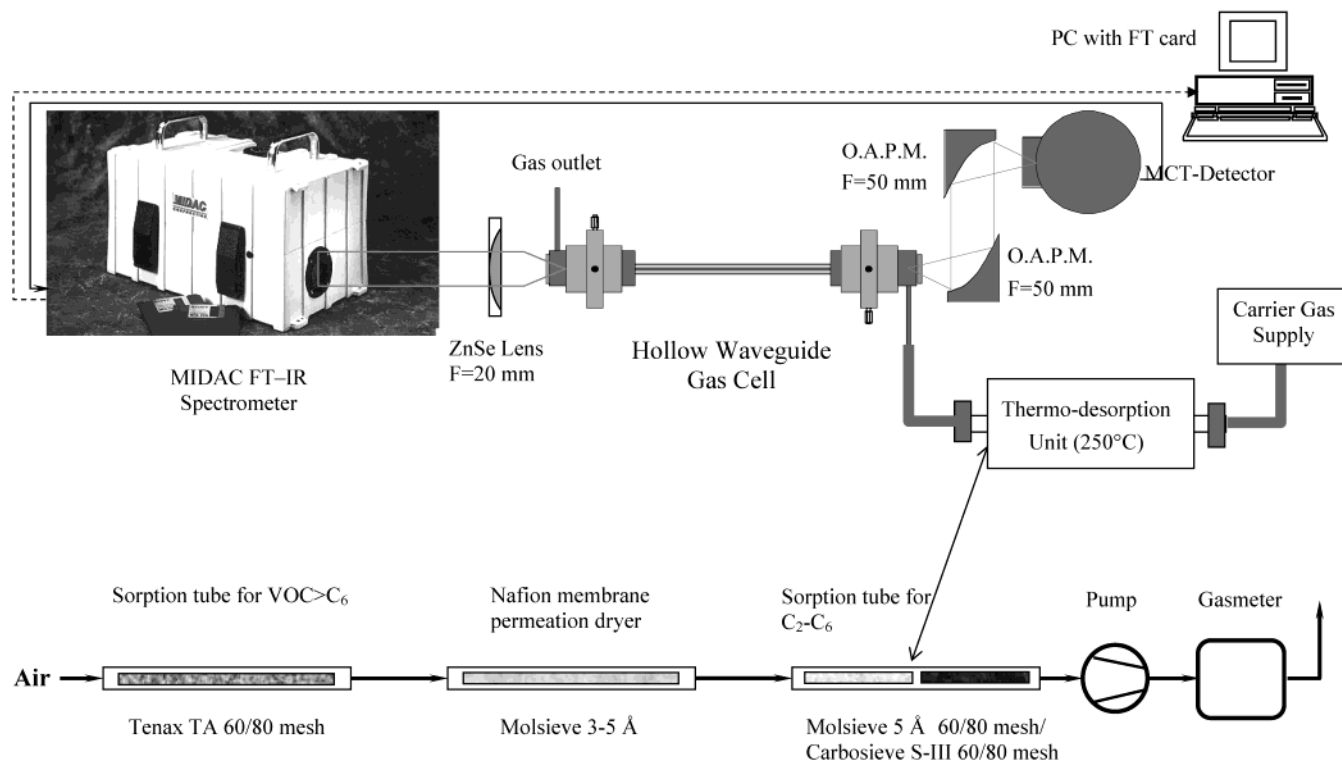


Figure 1. Schematic of the instrumental setup of the thermal desorption-HWG-FT-IR system.

modules<sup>19</sup> with antireflection (AR) coated ZnSe windows (MacroOptica, Moscow, Russia). The developed HWG sensing module provides high optical throughput and adjustment precision for facile integration with FT-IR spectroscopy or laser sensing techniques.

The optical setup of the HWG gas-sensing module was optimized for the Midac FT-IR spectrometer. The extended light source (hot SiC filament with typical minimum dimensions of 5 mm) of the FT-IR spectrometer delivers a parallel IR beam at the external beam port with a typical diameter of 40 mm after collimation by an off-axis parabolic mirror (oapm). Hence, precise imaging of the light source onto the HWG tip with an inner diameter of  $\sim 700 \mu\text{m}$  is an important prerequisite ensuring efficient energy throughput. Optimum light coupling efficiency was achieved using a lens (AR-coated ZnSe, diameter 38.1 mm, focal length 20 mm, MacroOptica Ltd.) for coupling radiation into the HWG and a set of two oapm's with a diameter of 50 mm and relatively short focal length of 50 mm at the distal end of the HWG.

This optical setup enabled direct measurements of ethene concentrations down to a concentration level of  $\sim 5$  ppm with a response time of 30–60 s. Direct calibration of the HWG-FT-IR system with ethene gas mixtures<sup>29</sup> produced by diluting a gas flow of 100 ppmv  $\text{C}_2\text{H}_4$  test gas (Linde Austria GmbH) by a high-purity nitrogen flow was performed in the range of 2–100 ppmv with limits of detection ( $\text{LOD} = 3 \times \text{root-mean-square, rms}$ ) at 2 ppm and limits of quantification ( $\text{LOQ} = 6 \times \text{rms}$ ) at 5 ppm ethene, yielding a linear response in the examined concentration range. The dimensions of the optical setup including the FT-IR spectrometer and HWG gas-sensing module were 600 mm  $\times$  400 mm with a total weight below 15 kg.

(29) Barratt, R. S. *Analyst* **1981**, *106*, 817–849.

Since atmospheric trace gas concentrations are significantly lower than the instrumental detection limits achieved during direct measurements with the HWG-FT-IR setup, a sample preconcentration step has been introduced. For preconcentration of atmospheric samples, a dual-tube approach<sup>30</sup> for sampling VOCs in the range of  $\text{C}_2$ – $\text{C}_{10}$  was applied. The sorption tubes (18 cm  $\times$  6 mm o.d.  $\times$  4 mm i.d.) made from Duran glass were filled with either  $\sim 375$  mg of Tenax TA 60/80 mesh or  $\sim 425$  mg of Molsieve 5-Å 60/80 mesh and  $\sim 500$  mg of Carbosieve S-III 60/80 mesh; sorbent positions were fixed by plugs of silanized glass wool (all adsorbent materials were obtained from Sigma-Aldrich Handels GmbH). A scheme of the resulting combination of enrichment tube sampling and thermal desorption HWG-FT-IR system is given in Figure 1.

The following measurement procedure has been established: sampling was carried out on two separate sorption tubes in series, first a Tenax-tube, then a Nafion dryer between the two tubes, and then the second tube filled with Molsieve and Carbosieve.<sup>31–32</sup> In this setup compounds of  $> \text{C}_6$  were trapped on the first sorption tube, which served as a filter. Then water vapor was removed, and finally,  $\text{C}_2$ – $\text{C}_5$  compounds were trapped. The sampling system also included a Peltier cooling device ensuring complete trapping of VOCs, water and gas pumps, flowmeter, and control electronics.<sup>30</sup> The dimensions of the sampling system were 400 mm  $\times$  400 mm  $\times$  150 mm with a weight of  $\sim 8$  kg, which is convenient for field applications. Analytes were preconcentrated from volumes of 1–10 L of air on the sorption tubes. Desorption was

(30) Haunold, A.; Rosenberg, E.; Grasserbauer, M. *Int. J. Environ. Anal. Chem.* **1997**, *67*, 157–172.

(31) Harper, M. J. *Chromatogr., A* **2000**, *885*, 129–151.

(32) Pawliszyn, J. Solid-phase microextraction in environmental analysis. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; Wiley: Chichester, 2000; pp 3363–3397.



achieved in the smallest possible volume to maintain the advantage of high enrichment factors. For this purpose, the Molsieve/Carbosieve sorption tube (the Tenax sorption tube was not analyzed) was desorbed at a temperature of 250 °C in a manually operated thermodesorption unit. A manually controlled gas stream (volume of 5 mL) passed through the sorption tube at a carrier gas speed of 1 mL/min and transported the analyte into the HWG cell. Total analysis time was ~15 min (corresponding to the achievable sampling period for on-site analysis). The short measurement time enables spectroscopic analysis of two samples in the time required to preconcentrate a new one; i.e., the samples from two measuring stations could be analyzed by one HWG-FT-IR system.

**Parameters for Laboratory Experiments with HWG-FT-IR System.** The investigated spectral range was between 4000 and 400 cm<sup>-1</sup> averaging 25 scans, which corresponds to a recording time of 30 s. Interferograms were collected at a spectral resolution of 0.5 cm<sup>-1</sup>, correlating with the width of the main adsorption feature of ethene (Q-branch at 949.3 cm<sup>-1</sup>).

**Parameters for Validation Experiments with GC System.** A GC/MS (Hewlett-Packard model 5890 Series II) system with an automatic thermodesorption unit with two-stage cryofocusing at the temperature of LN<sub>2</sub> (Tekmar AEROTrap 6000 with external cryofocusing module) was used. The analysis of C<sub>2</sub>–C<sub>5</sub> hydrocarbons was performed using a 50 m × 0.32 mm Chrompack fused-silica column. The parameters for analysis, cryofocusing steps, and the applied temperature programming are described in the literature.<sup>30</sup>

## RESULTS AND DISCUSSION

**Determination of HWG-FT-IR System Parameters.** The signal-to-noise ratio (SNR) of the analyzer system was determined by recording pure nitrogen reference spectra. A range of 200 spectral data points around the wavenumber region of interest (950 cm<sup>-1</sup>) was used to calculate the rms noise of the 100% line. Root-mean-square noise values were calculated by the standard deviation method<sup>33</sup> and correspond to 0.20 milliabsorbance units (mau) used for further calculations and resulted in LOD of 0.60 mau and LOQ of 1.8 mau for the described HWG-FT-IR setup (corresponding to LOD = 2 ppmv and LOQ = 5 ppmv of direct ethene measurements).

**System Calibration.** Calibration of the combined system (HWG-FT-IR system with sorption/desorption procedure) was performed by sampling of calibration gas on a sorption tube followed by desorption into the HWG-FT-IR unit. For this purpose, 0.06, 0.5, 1.0, 1.5, 2.0, and 2.5 L of ethene with a concentration of 605 ppbv (certified calibration gas, Linde Austria GmbH) were applied onto sorption tubes using the gas-sampling unit for ambient air collection. Subsequently, the sorption tubes were analyzed by two methods: thermodesorption-HWG-FT-IR spectroscopy and gas chromatography as reference method. The chromatographic analysis was performed after thermal desorption in an automatic thermodesorption unit. Desorption for analysis with the HWG-FT-IR unit was achieved by passing 5 mL of nitrogen stepwise in 1-mL batches through the desorption tube using a gastight syringe over a period 1 min for each step. The

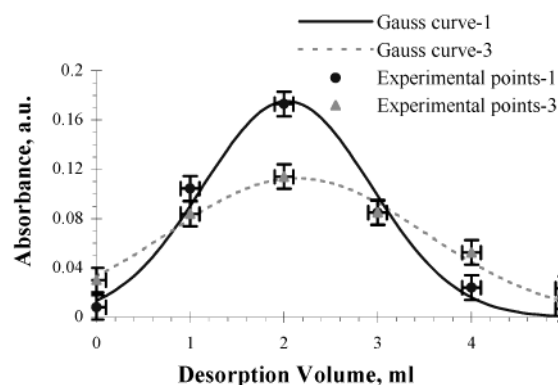


Figure 2. Examples of ethene desorption profiles with different amplitude but the same peak area (variation <4%). The desorption volume is manually controlled and synchronized with the data acquisition of the FT-IR spectrometer.

following evaluation procedure was established: (i) continuous acquisition of IR spectra during the whole desorption process, the number of scans accumulated during the desorption procedure being synchronized with the desorption step duration (1 min); (ii) evaluation of the corresponding analyte signal; and (iii) fit of a Gaussian function to the accumulated data points (see Figure 2) resulting in the analyte desorption profile following

$$\text{signal}(x) = H \exp(-(x - x_0)^2 / 2s^2) \quad (1)$$

where  $H$  is the absorbance height obtained from the Q-branch maximum of the ethene absorption within the individual gas spectra recorded by the HWG-FT-IR system,  $x_0$  is the position of the maximum, and  $s$  denotes the standard deviation. The area of the Gauss profile can be calculated as  $2H(\pi)^{1/2}s$ .

The precision of this evaluation procedure revealed significant improvement (standard deviations 3–4 times lower) compared to evaluating the maximum absorbance signal only during the desorption process, which approximately equals  $H$  in eq 1.

To validate the newly developed method, the obtained results have been compared with calibration data from the automated thermodesorption GC-FID analysis. Both methods confirmed linear behavior of the sorption tube sampling for the HWG-FT-IR approach and absence of bias or other systematic errors. Furthermore, this novel method demonstrates sufficient correlation with GC techniques: standard deviation and variance of both methods were comparable within 3%.

The detection limit of the HWG-FT-IR system following thermal desorption was 6.9 ng of ethene per tube (see Table 1). The working range was selected between the limit of quantification –0.014 µg of ethene per tube—and ~2 µg of ethene per tube and proven to be linear. The variance of the method was calculated for the lowest and highest concentration levels. Method validation has demonstrated that the application of the proposed method for rural air sampling is feasible.

**Rural Air Sampling.** Continuous sampling of ethene was performed for two mountain stations in Achenkirch, Tirol, Austria (Muehlegerkoepfl, 920 m and Christlunkopf, 1758 m asl) during a measurement campaign in August 2001. The air samples were collected on sorption tubes mounted onto platforms 3 m above

(33) Mark, H.; Workman, J. *Statistics in Spectroscopy*; Academic Press: New York, 1991.

Table 1. Analytical Figures of Merit for the Developed Thermal Desorption HWG-FT-IR System and Comparison with GC Validation

analytical figures of merit	GC system		HWG-FT-IR desorption system	
	ng of ethene/tube	ppb ethene <sup>a</sup>	ng of ethene/tube	ppb ethene <sup>a</sup>
LOD	1.32	0.29	6.9	1.1 <sup>b</sup>
LOQ	6.6	1.05	13.75	2.2 <sup>c</sup>
working range	6.6–1730	1.05–277	13.8–1730	2.2–277
calibration equation	$y = 2.001x + 6.901$ , $R^2 = 0.998$ $x$ , ethene amt (ng of C <sub>2</sub> H <sub>4</sub> /tube) $y$ , peak area		$y = 0.363x + 0.008$ , $R^2 = 0.994$ $x$ , ethene amt (ng of C <sub>2</sub> H <sub>4</sub> /tube) $y$ , peak area	
variance	3.51% ( $n = 3$ )		3.18% ( $n = 5$ )	
standard deviation of the method	0.04	6.37	0.03	4.48

<sup>a</sup> Obtained validation data correspond to the units “ng of C<sub>2</sub>H<sub>4</sub>” per sorption tube and were converted into ppb ethene taking into account an optimum sampling volume of 5 L per tube:  $C_2H_4$  (ppbv) =  $(C_2H_4(\text{ng}/\text{tube}) \times 24.5) / (0.005 \text{ m}^3/\text{tube} \times M_{C_2H_4} \times 1000)$ . <sup>b</sup> LOD =  $1.2\Phi_{n,\alpha}(S_L/b)$ , where  $\Phi_{n,\alpha}$  is a factor for rapid estimation of LOD and LOQ derived as a function of Student criterion and degrees of freedom,  $S_L$  standard deviation of blanks, and  $b$  slope of the calibration curve.<sup>35</sup> <sup>c</sup> LOQ =  $6S_L/b$ .

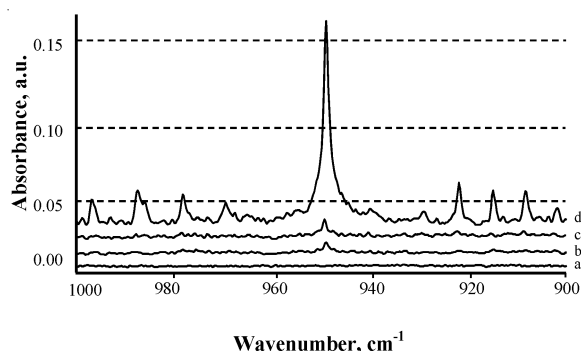


Figure 3. Ethene spectra obtained with the thermal desorption-HWG-FT-IR system: (a) background signal used for SNR measurements; (b) spectrum of a calibration sample containing 0.04 µg of ethene per tube (0.06 L of 605 ppbv ethene sampled in a sorption tube); (c) characteristic signal of ethene obtained during field campaign in August 2001; (d) spectrum of a calibration sample containing 1.04 µg of ethene per tube (1.5 L of 605 ppbv ethene sampled in a sorption tube). Synthetic offset between the curves, 0.01 au.

the ground and afterward analyzed by HWG-FT-IR. Maximum ethene concentrations at Muehleggerkoepfl reached 38 ppbv with an average concentration at the level of 10 ppbv. On Christlumpf, the peak concentration of ethene was 10 ppbv and an average concentration of 2 ppbv ethene was observed. In Figure 3, a typical ethene spectrum of rural air together with two calibration spectra is presented.

During the sampling campaign, the average concentrations as well as maximum values at the upper and lower station differed significantly by a factor of 5. The elevated ethene concentrations at Muehleggerkoepfl are explained by the presence of a municipal road close to that sampling station. The obtained data are in a

good agreement with previous measurements using conventional discontinuous measurement techniques<sup>34</sup> and corroborate the feasibility of the developed HWG-FT-IR analyzer system for rural ethene analysis.

## CONCLUSIONS

Based on results of laboratory experiments, which have demonstrated the feasibility of the proposed sensor system, the developed HWG-FT-IR analyzer was optimized for field measurements of ethene at lower ppb concentration levels.

The sensitivity of this novel approach was enhanced significantly by combination with a preconcentration procedure based on selective sorption tubes. The overall sensitivity was lowered to ~1.1 ppb, which is suitable for trace ethene analysis at field conditions. It is expected to further extend the sensitivity to the sub-ppb level with technical improvements of the desorption system and optimized sample transfer to the HWG-FT-IR analyzer.

## ACKNOWLEDGMENT

We gratefully acknowledge financial support of our research by the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management (FBVA), Project GZ. 56.810/09-VA 2b/2000 and the Austrian Science Foundation (FWF), Project P14121-CHE.

Received for review April 16, 2003. Accepted October 22, 2003.

AC034396J

- (34) Rosenberg, E.; Haunold, A.; Schubert, P.; Grasserbauer, M. *Environ. Sci. Pollut. Res.* **1998**, (1), 32–37 (Special Issue).
- (35) DIN 32 645: Deutsches Institut fuer Normung. Chemische Analytik; Nachweis-, Erfassungs- und Bestimmungsgrenze; Ermittlung unter Wiederholbedingungen; Begriffe, Verfahren, Auswertung. May 1994; pp 5–6.