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A gas chromatographic instrument for measurement of hydrogen cyanide in the lower atmosphere

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Abstract

A gas-chromatographic (GC) instrument was developed for measuring hydrogen cyanide (HCN) in the lower atmosphere. The main features of the instrument are (1) a cryogen-free cooler for sample dehumidification and enrichment, (2) a porous polymer PLOT column for analyte separation, (3) a flame thermionic detector (FTD) for sensitive and selective detection and (4) a dynamic dilution system for calibration. We deployed the instrument for a ~4 month period from January–June 2010 at the AIRMAP atmospheric monitoring station Thompson Farm 2 (THF2) in rural Durham, NH. A subset of measurements made during 3–31 March is presented here with a detailed description of the instrument features and performance characteristics. The temporal resolution of the measurements was ~20 min, with a 75 s sample capture time. The 1σ measurement precision was <10% and the instrument response linearity was excellent on a calibration scale of 0.10–0.75 ppbv ($\pm 5\%$). The estimated method detection limit (MDL) and accuracy were 0.021 ppbv and 15%, respectively. From 3–31 March 2010, ambient HCN mixing ratios ranged from 0.15–1.0 ppbv ($\pm 15\%$), with a mean value of 0.36 ± 0.16 ppbv (1σ). The approximate mean background HCN mixing ratio of 0.20 ± 0.04 ppbv appeared to agree well with tropospheric column measurements reported previously. The GC-FTD HCN measurements were strongly correlated with acetonitrile (CH_3CN) measured concurrently with a proton transfer-reaction mass spectrometer (PTR-MS), as anticipated given our understanding that the nitriles share a common primary biomass burning source to the global atmosphere. The nitriles were overall only weakly correlated with CO, which is reasonable considering the greater diversity of sources for CO. However, strong correlations with CO were observed on several nights under stable atmospheric conditions and suggest regional combustion-based sources for the nitriles. These results demonstrate that the GC-FTD instrument is capable of making long term, in-situ measurements of HCN in the lower atmosphere. To date, similar measurements have not been performed, yet they are critically needed to (1) better evaluate the regional scale distribution of HCN in the atmosphere and (2) discern the influence of biomass burning on surface air composition in remote regions.

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1 Introduction

Biomass burning (BB) is generally thought to be the major source of HCN in the atmosphere (Li et al., 2000, 2003, 2009; Shim et al., 2007). Pyrolysis of N-containing functionalities in the fuel is the primary mechanism proposed for HCN release from biomass combustion (Johnson and Kang, 1971; Glarborg et al., 2003). Hydrogen cyanide has been measured from field biomass fires (Hurst et al., 1994a, b; Goode et al., 2000; Yokelson et al., 2007; Crouse et al., 2009), and from laboratory biomass combustion systems (Lobert et al., 1991; Holzinger et al., 1999; Christian et al., 2004; Becidan et al., 2007). Elevated free tropospheric HCN columns were measured from the International Scientific Station of the Jungfraujoch (ISSJ) in the Swiss Alps by solar infrared (IR) spectroscopy during 1998, coinciding with a period of intense BB in the tropics (Rinsland et al., 2000).

Low HCN mixing ratios were observed by aircraft in urban plumes off the Pacific coast of the United States, suggesting that automobile emissions make a small contribution to the total global HCN budget (Singh et al., 2003). However, it is well known that HCN is an important intermediate in combustion-based nitric oxide (NO) formation, even for non-N containing fuels (Dagaut et al., 2008). Variability in the correlation between column abundances of HCN and carbon monoxide (CO), a general combustion tracer, measured at ISSJ suggested that fossil fuel combustion sources of HCN could be significant (Rinsland et al., 2000). Two recent studies reported the direct measurement of HCN in automobile exhaust samples (Karlsson, 2004; Baum et al., 2007). While the correlations between HCN and CO in vehicle exhaust plumes at a suburban site in Boston, MA were positive, they were highly variable (Knighton et al., 2009). Additionally, domestic coal burning could potentially be an important fossil fuel source of HCN in certain regions (Li et al., 2003).

Moreover, non-combustion-based anthropogenic HCN sources cited previously include fugitive emissions from industry and episodic release associated with the use of HCN as a fumigant (Singh et al., 2003). Such sources are expected to be minor.

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The significance of biogenic emissions to the global HCN budget has long been questioned (Cicerone and Zellner, 1983; Mahieu et al., 1997; Rinsland et al., 2000; Fall et al., 2001; Li et al., 2003; Singh et al., 2003; Shim et al., 2007). Many plant species are known to produce cyanogenic glycosides, which may produce HCN through enzymatic mechanisms (Vetter, 2000). A large number of plant species have been shown to be potential HCN emitters (Aikman et al., 1996). It was determined for several plant species that cyanogenic glycosides and the enzymes responsible for HCN production are separately compartmentalized within the plant tissue, which presumably prevents large scale HCN release (Poulton and Li, 1994). Physical damage to the plant tissue, e.g., by herbivory, is therefore likely necessary to induce plant-based, biogenic HCN release to the atmosphere (Fall et al., 2001). Emissions of HCN from wounded plant tissue samples were directly observed using negative ion-chemical ionization mass spectrometry (NI-CIMS) with HO^- as the reagent ion, and by selected ion flow tube-mass spectrometry (SIFT-MS) with HO^- and H_3O^+ as reagent ions (Custer et al., 2000, 2003). Additionally, bacterial HCN emissions from laboratory cultures were measured by SIFT-MS with H_3O^+ as reagent ion (Španl et al., 2004). A positive matrix factorization analysis of airborne trace-gas measurements over the western Pacific suggested that biogenic emissions were potentially of comparable importance to biomass burning emissions in that region during the spring of 2001 (Shim et al., 2007).

The atmospheric chemistry of HCN has been described in detail previously (Cicerone and Zellner, 1983), with some modifications discussed recently by Kleinböhl et al. (2006). Reaction with hydroxyl radical (OH) in the troposphere is the primary gas-phase loss mechanism for HCN in the atmosphere, imposing a lifetime of a few years. Reaction with singlet oxygen (O^1D) is estimated to become important in the lower stratosphere. Uptake to the ocean has been shown to be the dominant atmospheric sink for HCN (Li et al., 2000). Estimates of the HCN lifetime with respect to ocean uptake range from 2 to 5.3 months (Li et al., 2001, 2003; Singh et al., 2003). However, details of the ocean sink mechanism are lacking at this time.

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Although HCN does not appear to play a significant role in atmospheric chemistry, it may represent an important N source in remote oceanic environments (Li et al., 2000). Additionally, it is expected to be a useful tracer for BB emissions (Yokelson et al., 2007; Crouse et al., 2009). Finally, biogenic production of HCN and carbonyl compounds are known to be associated (Vetter, 2000); strong, positive correlations were observed between biogenic emissions of HCN and carbonyl compounds from wounded tissue of several cyanogenic plants (Custer et al., 2003).

Most previous atmospheric HCN measurements have been made using solar infrared (IR) spectroscopy (c.f., Coffey et al., 1981; Zhao et al., 2002; Kleinböhl et al., 2006 and references therein; Rinsland et al., 2007). In-situ HCN measurements were first made in the stratosphere by NI-CIMS (e.g., Schneider et al., 1997). Later, in-situ measurements in the troposphere were made by (1) long-path Fourier transform IR (FTIR) spectroscopy within BB plumes (Goode et al., 2000; Yokelson et al., 2007), (2) a GC system, using a reduction gas detector (RGD) (Singh et al., 2003), (3) NI-CIMS using CF_3O^- as reagent ion (Crouse et al., 2006, 2009; Yokelson et al., 2007), and (4) PTR-MS (Knighton et al., 2009). Additionally, matrix-isolation FTIR spectroscopy was performed offline for measurement of HCN in grab samples of BB plumes (Hurst et al., 1994a, b). In-situ measurements of background HCN levels by IR spectroscopy have not been reported. Instruments based on NI-CIMS typically exhibit reduced sensitivity at elevated H_2O vapor pressures (Crouse et al., 2006); therefore their use has been inhibited in much of the lower atmosphere. The low proton affinity of HCN (Holzinger et al., 1999; Španl et al., 2004) and potential interference from ethene (Knighton et al., 2009) have complicated measurement of HCN in the atmosphere by PTR-MS, though Knighton et al. (2009) demonstrated that these issues may be overcome through calibration. In addition to the challenges of measuring HCN in the atmosphere by NI-CIMS and PTR-MS, sample dilution in the flow tube buffer gas reduces detectability via SIFT-MS (Blake et al., 2009).

Considerable uncertainties remain regarding contributions of different combustion and non-combustion sources to the budget and ambient levels of HCN on regional

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scales. Measurements in the lower atmosphere may provide the best means for reducing such uncertainties, but are lacking at this time. Only one report of in-situ surface measurements of HCN has appeared in the literature (Knighton et al., 2009). In order to improve our understanding of the distribution of HCN in the lower atmosphere a GC instrument, incorporating a flame thermionic detector (FTD), was developed and deployed for atmospheric measurement of HCN at the AIRMAP atmospheric monitoring station THF2 during January–June 2010. A description of the measurement site and supporting measurements used in this work, together with a detailed description of the GC-FTD instrument, including operating parameters, the calibration scheme, and data analysis methods are presented. Instrument performance is discussed and ambient measurements presented to demonstrate the utility of this system. For this analysis, we focus on a subset of measurements made during 3–31 March, when (1) there were relatively few interruptions in sample collection, (2) acetonitrile (CH_3CN) was concurrently measured by PTR-MS, and (3) ambient levels of the nitriles exhibited relatively large ranges. Further analyses of the ambient measurements are presented separately (e.g., Talbot et al., 2011).

2 Experimental

2.1 Measurement site location

The GC-FTD instrument was deployed for ambient measurements between 24 January and 11 June 2010 at the University of New Hampshire's AIRMAP atmospheric monitoring station at Thompson Farm (THF2; 43.1078°N , 70.9517°W , 40 m elevation above sea level), located within a stand of mixed hardwood/pine forest ~ 320 m from the original Thompson Farm monitoring station (THF) in rural Durham, NH (Talbot et al., 2005). Construction of THF2 began during winter 2007–2008 and the station was brought on-line for atmospheric monitoring during the following summer. At THF2 a 24 m observation tower extends above the surrounding forest canopy. Ambient air was drawn

at $\sim 1500 \text{ l min}^{-1}$ (STP) through a PFA Teflon-lined aluminum manifold from the top of the tower using a Gast R7-Series regenerative blower (Gast Manufacturing, Inc., Benton Harbor, MI). Sub-samples were directed to a suite of trace gas analyzers, including the GC-FTD instrument, housed at the base of the tower. The temperature in the instrument room was maintained at $21.8 \pm 0.4^\circ\text{C}$ during 3–10 March and $19.6 \pm 0.4^\circ\text{C}$ during 10–31 March.

2.2 The GC-FTD instrument

2.2.1 Configuration

Figure 1 shows a schematic of the GC-FTD instrument. The HCN calibration standard was a permeation tube source (VICI Metronics, Inc., Poughkeepsie, NY) contained in a glass chamber, imbedded in an aluminum block which was temperature-regulated at $30.0 \pm 1.5^\circ\text{C}$ using an OMEGA CN76000 Series temperature controller (OMEGA Engineering, Inc., Stamford, CT). The NIST traceable gravimetric emission rate of the permeation tube was $122 \pm 5 \text{ ng min}^{-1}$ at $30.0 \pm 0.5^\circ\text{C}$. Standard samples of HCN were prepared in ultra-high purity (UHP) N_2 (Maine Oxy, Auburn, Maine) using an MKS type 1479A mass flow controller (MFC) (MKS Instruments, Inc., Andover, MA) coupled with an MKS type 247D digital readout. The standard samples were further diluted in zero air to ambient levels (0.1–1 ppbv) using a zero air generator (Apel Riemer Environmental, Inc., Broomfield, CO). The zero air generator's catalytic converter (0.5% Pd on Al_2O_3) was operated at 425°C .

Samples were dried at -15°C in a $20 \text{ cm} \times 0.3175 \text{ cm}$ i.d. Silonite-coated loop (Entech Instruments, Inc., Simi Valley, CA) contained in an MMR model CC2202 Cryofocus System (MMR Technologies, Mountain View, CA; see Sive et al. (2005) for further details). Sample volumes of 250 STP cm^3 were enriched at -130°C in a second $20 \text{ cm} \times 0.3175 \text{ cm}$ i.d. Silonite-coated loop (Entech Instruments, Inc., Simi Valley, CA), packed with 1 mm diameter glass beads (Ohio Valley Specialty Co., Marietta, OH), and contained in the Cryofocus System. Negligible HCN loss in the dehumidification loop

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was confirmed at temperatures as low as -30°C , which was the threshold temperature that could be achieved with the Cryofocus System. Trapping of HCN in the sample enrichment loop was confirmed to be quantitative for temperatures $\leq -110^{\circ}\text{C}$. The sample flow rate during trapping was controlled at $200\text{ STP cm}^3\text{ min}^{-1}$ by a downstream MFC (Aalborg Instruments and Controls, Inc., Orangeburg, NY), yielding a sample integration time of 75 s. Ambient air was sub-sampled from the main sample inlet manifold and supplied to the instrument using a single-head metal bellows pump (Senior Flexonics, Sharon, MA).

The Cryofocus System was incorporated in a custom built, fully automated sample acquisition system, designed after the prototype acquisition system that was described in detail by Sive et al. (2005). For measurement of HCN, an additional Valco 4-port SV (Valco Instruments Company, Inc., Houston, TX) was incorporated into the acquisition system to permit isolation of the sample enrichment loop between sample trapping and injection (Fig. 1). A Valco 8-port stream select valve (SSV) and downstream solenoid valves (ASCO, Novato, CA) directed the sample stream to the Cryofocus System for enrichment and to the GC for analysis, and they allowed the system to step between ambient air, the permeation source, and UHP He during analysis, calibration, and purging, respectively, or to be isolated from the input gas streams while the sample and dehumidification loops cooled. Sample injections were performed in UHP He onto a $25\text{ m} \times 0.32\text{ mm i.d.}$, $5\text{ }\mu\text{m}$ film thickness CP PoraBOND Q column (Varian, Inc., Palo Alto, CA) using a Valco 8-port switching valve (SV). According to the manufacturer's specifications the CP PoraBOND Q column is a bonded porous polymer PLOT column exhibiting low bleed and high stability under exposure to water. A similar type of stationary phase, in combination with an FTD, was previously employed for separation and detection of cyanides from the headspace of blood samples (Seto et al., 1993).

The column and a Shimadzu FTD (Shimadzu Corporation, Columbia, MD) were housed in a Shimadzu model 2014c GC. The GC oven temperature program was 40°C for 7.5 min, $15^{\circ}\text{C min}^{-1}$ to 150°C , 150°C for 4 min. The FTD was operated at 200°C and a voltage of 80–90% relative to maximum. The carrier flow rate at the

initial column temperature was 21.6 ± 0.2 (1σ) STP $\text{cm}^3 \text{min}^{-1}$. The makeup gas was UHP He at a flow rate of 8 ± 1 $\text{cm}^3 \text{min}^{-1}$, while UHP H_2 and purified ambient air from an Aadco 737-series Pure Air Generator (Aadco, Cleves, OH) were also supplied to the FTD at flow rates of 0.9 ± 0.1 $\text{cm}^3 \text{min}^{-1}$ and 123 ± 6 $\text{cm}^3 \text{min}^{-1}$, respectively. Activated charcoal/molecular sieve (13X) traps, prepared in-house and purchased from Ohio Valley, were used with all cylinders for further purification. Additionally, a Valco HP2 helium purifier was used for the He carrier gas. Gas transfer lines were constructed of Silcosteel (Restek, Bellefonte, PA) and PFA 450 Teflon (E & S Technologies, Inc., Chelmsford, MA).

2.2.2 Overview of the FTD

Thermionic detectors have not been commonly used for ambient air analysis. Previous applications of an FTD in the atmospheric sciences appear to be limited to measurement of ammonia by Yamamoto et al. (1991, 1994). Therefore, a brief description of the Shimadzu FTD (hereinafter abbreviated as FTD-2014c) and the FTD response mechanism is presented.

The FTD-2014c consists of a Rb_2SO_4 -coated Pt filament, enveloped by a cylindrical collector electrode mounted on the jet of a flame ionization detector (FID) (Arimoto et al., 1992; Shimadzu Corporation, 2004). An electrical current supplied to the filament by a power controller resistively heats the filament, thereby controlling the surface reactivity. The filament current can be adjusted by the operator, either directly or indirectly via the applied voltage.

The analytical signal in the FTD arises from the negative ion current generated by ionization of analytes at the surface of the heated filament. Application of a positive voltage bias to the collector facilitates transfer of ion current from the filament to the collector. Previous studies with thermionic detectors suggested that the heated filament induces a combination of gas-phase and surface ionization processes, the relative importance of which depends on the composition of the filament coating (Patterson, 1982;

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van de Weijer et al., 1988; Bombick and Allison, 1989). Incorporating alkali metal in the surface coating reduces the work function of the surface, and was empirically determined to yield sensitive, selective detection for N and P containing analytes (Bombick and Allison, 1989). The H₂ and air supplied to the detector participate in the ionization chemistry and partially control selectivity and sensitivity (c.f., Bombick and Allison, 1989; Shimadzu Corporation, 2004). Impurities in the carrier and makeup gases further contribute to the detector background level.

In the present work the FTD-2014c was operated using detector gas flows which conformed to the manufacturer's recommendations for selective detection of N-containing analytes (Shimadzu Corporation, 2004). The FTD power controller voltage was set to a value that yielded maximum sensitivity to HCN.

2.2.3 Operational protocol

Here we briefly describe the operational protocol of the instrument (please refer to Fig. 1 and Table 1). An analysis cycle was initiated when the sample dehumidification (T1) and enrichment (T2) loops cooled to -30°C and $\leq -110^{\circ}\text{C}$, respectively. Once the loops reached their initial cold trapping temperatures, the inlet lines were flushed with ambient air or calibration gas to condition them prior to trapping. Following conditioning, the gas stream was directed to the Cryofocus System where it was dehumidified in T1 and low-boiling constituents, including HCN and CH₃CN, were trapped in T2. The inlet lines were then flushed with UHP He, after which the Cryofocus System was flushed with UHP He at a flow rate of $200\text{ STP cm}^3\text{ min}^{-1}$ for 1 min to displace low boiling compounds (e.g., N₂, O₂ and O₃) from T2. Subsequently, T2 was isolated at the 4-port SV and heated in ~ 1 min to 75°C to re-volatilize the trapped HCN. When T2 reached 75°C the sample was injected in UHP He by sequentially switching the 8-port SV and the 4-port SV. After a 2 min injection, T1 and T2 were heated to 80°C and flushed with UHP He, at a flow rate of $\sim 300\text{ STP cm}^3\text{ min}^{-1}$ for 5 min in preparation for the next sample. Table 1 indicates the positions of the valves in Fig. 1 during each sample cycle stage. The measurement time resolution, which was largely governed by the

cycle time of the Cryofocus System, was on average 21.4 ± 0.5 min during March 2010. Valve actuation, the Cryofocus System temperature set points, and triggering of the GC were controlled by a program written in LabVIEW software (National Instruments Corporation, Austin, TX) and run from a personal computer (PC). Chromatograms were recorded on a second PC using Shimadzu Class-VP (7.4) data acquisition/analysis software.

2.2.4 Calibration

Instrument calibration was performed daily by sampling the standard dilution system output for 5 cycles. The standard HCN mixing ratio was usually set to 0.25 ± 0.01 ppbv. Additionally, it was periodically varied over four levels within the range 0.101 ± 0.005 to 0.75 ± 0.04 ppbv to quantify the system linearity. The instrument continuously stepped between sampling ambient air and the standard dilution system output. Between each daily set of standard samples, the zero air generator was isolated to quantify the non-zero HCN background in the zero air diluent. Additionally, a qualitative CH_3CN standard was analyzed to confirm the identification of the corresponding chromatographic peak.

2.2.5 Data analysis

Chromatograms were integrated manually using Shimadzu Class-VP software. For each ambient sample, the recorded raw chromatographic peak area, A_r , was converted to a corresponding HCN volume mixing ratio (hereinafter abbreviated simply as mixing ratio), $\text{VMR}(\text{HCN})_a$, using the calibration standard chromatographic peak area, A_s , the zero air background chromatographic peak area, A_b , and the calibration standard HCN mixing ratio, $\text{VMR}(\text{HCN})_s$:

$$\text{VMR}(\text{HCN})_a = A_r \cdot \left(\frac{\text{VMR}(\text{HCN})_s}{A_s - A_b} \right). \quad (1)$$

The bracketed term in Eq. (1), which represents the instrument sensitivity to HCN, was calculated by interpolation between each daily set of calibration measurements

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at $\text{VMR}(\text{HCN})_s = 0.25 \pm 0.01$ ppbv. The value of $\text{VMR}(\text{HCN})_s$ was determined by the calibration standard emission rate, e_0 (ng min^{-1}), the N_2 diluent flow rate through the permeation chamber, $f(\text{N}_2)$, the zero air generator standard inlet flow rate, f_i , and the zero air diluent flow rate, $f(\text{ZA})$:

$$\text{VMR}(\text{HCN})_s = e_0 \cdot \left(\frac{22.40}{f(\text{N}_2) \cdot \text{FW}} \right) \cdot \left(\frac{f_i}{f_i + f(\text{ZA})} \right), \quad (2)$$

In Eq. (2), flow rate units are l min^{-1} (STP), 22.40 (STP l mol^{-1}) is the standard molar volume of N_2 and FW is the molecular weight of HCN (27.03 g mol^{-1}).

2.3 Supporting measurements

To assist with the interpretation of the ambient HCN measurements (Sect. 3.2), we present concurrent measurements of several additional atmospheric parameters as discussed below.

Acetonitrile was measured with a high-sensitivity PTR-MS instrument (Ionicon Analytik, Innsbruck Austria) at mass to charge ratio, $m/z = 42$ (Jordan et al., 2009). The PTR-MS drift tube temperature, pressure and voltage were 45°C , 2.00 mbar and 600 V, respectively. Acetonitrile was monitored together with 46 additional m/z , with dwell times of 1–20 s, yielding a sample cycle time of ~ 6.5 min. Under the sampling scheme employed, ambient air was monitored for ~ 24 h (220 cycles), followed by ~ 72 min (10 cycles) during which zero air was analyzed to quantify the instrument background. Zero air was generated by passing ambient air through a stainless steel tube packed with $\text{Pt}/\text{Al}_2\text{O}_3$ beads (0.5 % Pt), heated to 600°C . The PTR-MS sensitivity to CH_3CN was $15.9 \text{ ncps ppbv}^{-1}$ (ncps, normalized counts per second), based on calibrations with a high pressure cylinder (Apel-Riemer Environmental, Inc., Denver, CO) containing CH_3CN at the ppbv level with an accuracy of better than 5%. The calibration gas was dynamically diluted to pptv–ppbv levels in zero air. The method detection limit (MDL), estimated as 2σ of the instrument background response at $m/z = 42$ was 0.031 ppbv.

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Ozone was measured by UV photometry at 254 nm using a Thermo Environmental Instruments model 49C-PS analyzer (Mao and Talbot, 2004). The MDL and accuracy were ~ 1 ppbv.

Carbon monoxide was measured by IR absorbance at $4.6\ \mu\text{m}$ using a modified Thermo Environmental Instruments model 48CTL analyzer (Mao and Talbot, 2004). The MDL was 40 ppbv and the accuracy was $\sim 2\%$.

Nitrogen dioxide photolysis frequency ($J(\text{NO}_2)$) was measured by filter radiometer (Griffin et al., 2007). The measurement uncertainty is $< 5\%$ based on factory calibration, though it is likely larger at high solar zenith angle.

The O_3 , CO and $J(\text{NO}_2)$ measurements were made at 1 min time resolution and reduced to 10-min averages for presentation here.

3 Results and discussion

3.1 Instrument performance characteristics

3.1.1 Selectivity

A chromatogram recorded with the GC-FTD instrument on 20 March, under conditions when the HCN mixing ratio was relatively enhanced, is shown in Fig. 2. Only two chromatographic peaks (HCN and CH_3CN) were observed in ambient chromatograms recorded at THF2. The second peak, with a retention time of ~ 7.5 min was attributed to CH_3CN based on analysis of a CH_3CN qualitative standard. Thus, the GC-FTD instrument appeared to be highly selective for nitriles under the ambient conditions probed. Although quantitative analysis of CH_3CN was not the goal of the present work, and was not thoroughly tested, it is anticipated that further development of the instrument will yield simultaneous quantitative measurements for both HCN and CH_3CN .

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3.1.2 Sensitivity

It is known that FTD detectors exhibit loss of sensitivity with operation time (e.g., Colón and Baird, 2004). The rate of sensitivity decrease for the FTD-2014c used in the present work is proportional to the detector bead voltage (Shimadzu Corporation, 2004). Carrier and detector gas purity also partially govern the rate of sensitivity decrease (M. Smith, Shimadzu Corporation, personal communication, 2009).

A time series of the daily average HCN chromatographic peak area measured for each set of standard samples prepared at the 0.25 ppbv level during March 2010 is shown in Fig. 3. The values have been corrected for the non-zero HCN background from the zero air generator (Sect. 3.1.5). The time for each data point corresponds with the time difference between the daily median run time for the standards and the instrument start time, $t = 0$, on 3 March. As illustrated in Fig. 3, the sensitivity of the FTD-2014c to HCN as measured with our system was well described by a 3-parameter exponential function of the form:

$$y = ae^{-bt} + c, \quad (3)$$

The fit parameters for the data in Fig. 3 were: $a = (10.4 \pm 0.2) \times 10^3$ AU, $b = (5.8 \pm 0.3) \times 10^3 \text{ h}^{-1}$ and $c = (3.2 \pm 0.1) \times 10^3$ AU. The corresponding coefficient of determination, r^2 , was 0.997. The absolute value of the fit residuals was $<10\%$. The fit in Fig. 3 excludes the first two sets of standard measurements made during the initial ~ 24 h warm-up period, which followed an extended power outage at THF2. On intermediate timescales (~ 1 – 2 weeks) the sensitivity trend was nearly linear. Although the loss of sensitivity demonstrated in Fig. 3 is undesirable, it could be accurately accounted for by calibration.

It is important to note that the day-to-day variability in response to HCN appeared to be greater for more aged surface coatings than shown in Fig. 3. It was therefore concluded that linear interpolation between daily standard measurements would yield more accurate calibration than the application of a fitting function during such time

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periods. In order to process the data in the most systematic and consistent manner, all calibration was performed via the interpolation method as described in Sect. 2.2.5.

The loss of sensitivity of the FTD with time requires that the filament be periodically recoated. It is also feasible to replace the filament assembly entirely. A new coating of Rb_2SO_4 is applied to the heated filament by contact melting using a kit supplied by the manufacturer. Under the operating conditions employed, we observed a maximum bead lifetime of ~ 2 months. From our experience, detector sensitivity was recovered through 3 recoating cycles. Although we have not fully characterized the filament lifetime, our experience suggest that >6 months of semi-continuous HCN measurement should be achievable under our operating conditions.

3.1.3 Precision

The error bars in Fig. 3 represent 1σ of the mean daily peak area values ($n = 5$) and range from 3–13 %, with a mean value of 7 %. The measurement precision did not depend significantly on the standard mixing ratio or detector sensitivity over the range of conditions tested. For example, in the course of multi-point calibration measurements performed during 18–26 March (Sect. 3.1.4), the precision ranged from 4–6 %. The precision of the zero air generator background was somewhat poorer. For the blank measurements corresponding with the calibration data shown in Fig. 3, the mean precision was 12 %.

3.1.4 Linearity

A multipoint calibration curve constructed from measurements made during 18–26 March is shown in Fig. 4. The non-zero measurements of the zero air generator are included in the calibration plot. The instrument showed good linearity on the calibration scale employed. A least squares regression analysis yielded a slope and intercept of $(21.3 \pm 0.3) \times 10^3 \text{ AU ppbv}^{-1}$ and $(1.1 \pm 0.1) \times 10^3 \text{ AU}$, respectively, with $r^2 = 0.994$. The LOD was estimated as $3\sigma_b/b = 0.021 \text{ ppbv}$, where σ_b is the standard deviation of

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the intercept b of the calibration plot, derived from least squares analysis (Lavagnini and Magno, 2007).

3.1.5 Zero air background

As indicated above, the HCN level in the zero air diluent was non-zero. However, the relative background level was remarkably stable. During 3–31 March, the ratio A_b/A_s for the 0.25 ppbv standards ranged from 0.20–0.29 with a mean value of 0.24 ± 0.03 .

We note that the variability in the ambient HCN mixing ratios was significantly greater than that in the zero air background. For instance, the range of the ratio A_b/A_a was 0.18–0.55 with a mean value of 0.3 ± 0.1 . This suggests that incomplete chemical conversion of HCN within the catalytic converter may only partly have governed the background HCN level in the zero air diluent.

The dependence of the background signal on the zero air generator operating parameters was not investigated, though it is a goal for future work with this system to do so. We sought to calibrate the instrument at a level which most closely matched the typical ambient HCN mixing ratio. Having demonstrated the instrument linearity (Sect. 3.1.4), we could minimize the relative significance of the background level in the future by using a slightly higher standard mixing ratio for daily single-point calibrations.

3.1.6 Accuracy

The accuracy of the HCN measurements is governed by the individual accuracies of the permeation chamber temperature ($\pm 1.5^\circ\text{C}$) and the standard dilution system flow rates ($\leq \pm 5\%$). The accuracy of the permeation chamber temperature was slightly poorer than that of the chamber in which the HCN emission rate was calibrated ($\pm 0.5^\circ\text{C}$); therefore, it is likely that the accuracy of the HCN emission rate was also slightly poorer than the value of $\pm 5 \text{ ng min}^{-1}$ ($\pm 4\%$) specified by the manufacturer. For instance, at 30°C the HCN vapor pressure varies by $\pm 2\%$ and $\pm 6\%$ for temperature differences of $\pm 0.5^\circ\text{C}$ and $\pm 1.5^\circ\text{C}$, respectively, based on published vapor pressure

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data (Lide, 2008). The accuracy of the HCN emission rate in our permeation chamber was estimated using the emission rate temperature dependence specified by the manufacturer (VICI Metronics, Inc., 2004):

$$\log(e_{\Delta T}) = \log(e_0) + \alpha \cdot (\Delta T) \quad (4)$$

where ΔT is the permeation chamber temperature accuracy, $e_{\Delta T}$ is the emission rate at the calibration temperature $\pm \Delta T$ (e.g., $30.0 \pm 1.5^\circ\text{C}$), and α is the permeation source temperature coefficient (0.034 for our permeation tube). Based on the value of $e_{\Delta T}$ calculated using Eq. (4) (e.g., 137 ng min^{-1} at 31.5°C) we estimated the accuracy of the HCN emission rate to be $\pm 12\%$.

Propagating the estimated accuracy of the HCN emission rate and the individual flow rate accuracies through the HCN VMR calculation (Eq. 2) yields an estimated overall accuracy in the reported mixing ratios of $\pm 15\%$. We do not have an independent measure of the overall accuracy of the instrument at this time. However, cross-calibration of the HCN standard emission rate in-situ using a multi-pass IR instrument has been demonstrated elsewhere (Crouse et al., 2009).

3.2 Ambient Air Analysis

We present here a subset of ambient HCN measurements made with the GC-FTD instrument during 3–31 March 2010. Figure 5a shows a time series of the ambient HCN mixing ratio, derived from the calibration data in Fig. 3. Also included in Fig. 5a are the PTR-MS CH_3CN mixing ratios. Figure 5b presents the 10 min averaged mixing ratios of CO and O_3 . In both panes of Fig. 5, a time series of 10 min averaged $J(\text{NO}_2)$, normalized to the maximum value of $5.6 \times 10^{-3} \text{ s}^{-1}$ recorded during March, delineates daytime and nighttime periods and provides a relative measure of solar actinic flux.

The range of the ambient HCN mixing ratios was 0.15–1.0 ($\pm 15\%$) ppbv, with a mean and median of 0.36 ± 0.16 and 0.34 ppbv, respectively. Our measurements are not directly comparable to most measurements reported previously in the middle and

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upper troposphere. It appears that the mean HCN mixing ratio measured in the planetary boundary layer (PBL) in the 0–2 km altitude bin during early spring in the western Pacific region was lower at 0.23 ± 0.16 ppbv (Singh et al., 2003). Taking the period of 14–15 March to be representative of the background troposphere, corresponding with minima in the levels of the nitriles and CO, yielded an average HCN mixing ratio of 0.20 ± 0.04 ppbv; by comparison an average level of 0.21 ± 0.05 ppbv was measured between 0–12 km in the western Pacific region under relatively clean conditions (Singh et al., 2003). Measurements of HCN at a suburban site in Boston, MA during October 2007 ranged from <0.1 to ~ 0.6 ppbv and yielded a background HCN mixing ratio of ~ 0.2 ppbv (Knighton et al., 2009). A significant trend in tropospheric HCN levels is not anticipated over the past decade, based on available long-term records (Rinsland et al., 2007).

Figure 5a demonstrates that HCN and CH_3CN were highly correlated at THF2 during the measurement period. Similar concurrent measurements of these two gases have not previously been reported from a surface atmospheric observing station. Since HCN and CH_3CN are thought to share common primary BB sources, a significant correlation between their levels in ambient air is to be expected. Singh et al. (2003) observed a slightly non-linear correlation between HCN and CH_3CN measurements in the western Pacific free troposphere, which included influences from SE Asian BB plumes. A strong linear $\text{CH}_3\text{CN}/\text{HCN}$ correlation was recently reported from airborne measurements made over the Mexico City area, which included fresh BB plumes (Crouse et al., 2009).

A clear, consistent relationship between the abundances of the nitriles and that of CO, a general combustion tracer, was not evident at THF2 during the measurement period. For instance, the nitriles appeared to be correlated with CO on several nights (e.g., 10–11 and 25–26 March) and all three compounds attained minimum levels during 14–15 March; however, the persistent buildup of the nitriles between 16–20 March and their subsequent rapid decline during 20 March appeared to be largely independent of CO during the same time period.

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Several previous studies have highlighted the role of the nocturnal boundary layer in regulating trace gas abundances in the region encompassing the Thompson Farm observing stations (Mao and Talbot, 2004; Talbot et al., 2005; Mao et al., 2006; White et al., 2008; Ambrose et al., 2010). Levels of trace gases with local emission sources (e.g., CO) are enhanced during nighttime beneath the inversion layer; conversely, depletion is observed for trace gases with chemical sinks at the surface (e.g., O₃). During daytime, when surface warming induces turbulent decay of the nocturnal inversion, trace gases in the overlying residual layer are mixed down to the surface, leading to dilution of trace gases with surface sources and replenishment of trace gases with surface sinks. The influence of the nocturnal inversion layer on O₃ and CO levels at THF2 was evident during several days in March, including 7–13 and 17–20 (Fig. 5b). The correlated enhancements in nitriles and CO on the nights of 10–11 and 25–26 March suggest a common emission source for these compounds in the region surrounding THF2 during those nights. However, it appears that HCN levels were only weakly influenced by the PBL dynamics during most of March. Thus, the increasing HCN levels observed during 16–20 March appeared not to have been isolated to the surface layer but rather to have been consistent throughout the tropospheric mixed layer, consistent with a large-scale, BB influence. In order to fully explain the observed variations in the nitriles, further analysis of the data is necessary, though it is beyond the scope of this work.

4 Summary

A GC-FTD instrument was developed for measurement of HCN in the lower atmosphere and was deployed for ambient air analysis at the AIRMAP atmospheric monitoring station THF2 for a ~4 month period during January–June 2010. The FTD was chosen for its superior sensitivity and selectivity for N-containing organic compounds. A low bleed, robust porous polymer PLOT column was chosen for analyte separation. Ambient samples were pre-concentrated on a glass bead-packed Silonite-coated

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stainless steel loop in a cryogen-free cooler. Quantitative calibration of the HCN measurements was performed by dynamic dilution of a permeation tube standard in a near-ambient matrix. The measurement time resolution was ~ 20 min, with a sample integration period of ~ 75 s for a 250 STP cm^3 sample volume. Measurements made during 3–31 March were used to illustrate the performance characteristics of the instrument. The following conclusions were drawn:

The instrument's selectivity for HCN was excellent. Only one additional compound was observed in the chromatograms of the ambient air samples analyzed at THF2. This compound was identified as CH_3CN based on the retention time of a qualitative standard. With further characterization and proper calibrations, the instrument will yield concurrent CH_3CN measurements.

Although the FTD was sufficiently sensitive to HCN for quantitative analysis, the sensitivity decreased with time as is characteristic of this type of detector. Although undesirable from a long-term monitoring perspective, the sensitivity trend was accurately quantified by the daily calibration scheme employed. For long-term operation in the field, periodic recoating of the FTD filament is required. Under our operating conditions a maximum measurement interval of ~ 2 months was achieved between successive recoatings, which should at least yield maintenance-free operation on typical field campaign timescales.

The instrument linearity was excellent over a standard mixing ratio range of 0.10–0.75 ppbv ($\pm 5\%$), which mostly bracketed ambient levels. The measurement precision was $< 10\%$, the overall accuracy $\pm 15\%$ and the instrument MDL 0.021 ppbv. With independent methods under development for ground-based HCN measurement (e.g., PTR-MS) side-by-side intercomparison exercises should be feasible in the future.

The range of the ambient HCN mixing ratios was 0.15–1.0 ppbv ($\pm 15\%$), with a mean value of 0.36 ± 0.16 ppbv. The average mixing ratio appeared to be higher than observed previously during early spring via aircraft GC-RGD measurements in the PBL over the western Pacific (Singh et al., 2003). However, the estimated background level at THF2 appeared to agree better with the western Pacific tropospheric background

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levels and with background levels derived from ground-based PTR-MS measurements made at a suburban site in the northeastern US during fall (Knighton et al., 2009). Strong correlation was observed between the GC-FTD HCN measurements and simultaneous CH₃CN measurements made by PTR-MS, in agreement with our understanding that both nitriles share a common primary biomass burning source to the atmosphere. A preliminary analysis of the nitrile measurements, together with measurements of O₃ and CO suggests that local combustion was a minor, episodic source of HCN at THF2 during March. Additionally, a significant buildup of the nitriles from 16–20 March is consistent with a large-scale, BB influence on atmospheric composition at THF2, which was not clearly evident from the CO measurements.

Results from the first field deployment of the GC-FTD instrument suggest that the instrument has the capability to measure HCN in the PBL with high sensitivity, selectivity and precision. Future deployment of this type of instrument should yield valuable information regarding (1) the temporal variability and budget of HCN in the lower atmosphere and (2) the influence of biomass combustion on atmospheric composition at Earth's surface.

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Table 1. Operational protocol of the GC-FTD instrument.

Valve ^a	Sample cycle stage, valve position								
	1. Cool ^b	2. Preflush ^c	3. Trap ^c	4. Preflush ^d	5. Trap ^d	6. Desorb ^b	7. Inject ^d	8. Bake	
SSV	6, 7, 8	1, 3, 4, 5	1, 3, 4, 5		2	2	6, 7, 8	2	2
SV ^e	A	A	A		A	A	A	B	A
SV ^f	A	A	A		A	A	B	A	A
V1	closed	open	closed		open	closed	closed	closed	closed
V2	closed	closed	open		closed	open	closed	closed	closed
V3	closed	open	closed		open	closed	closed	closed	closed

^aAs labeled in Fig. 1.

^bSSV is in a dead end position.

^cAmbient or standard sample.

^dUHP He.

^eEight-port SV.

^fFour-port SV.

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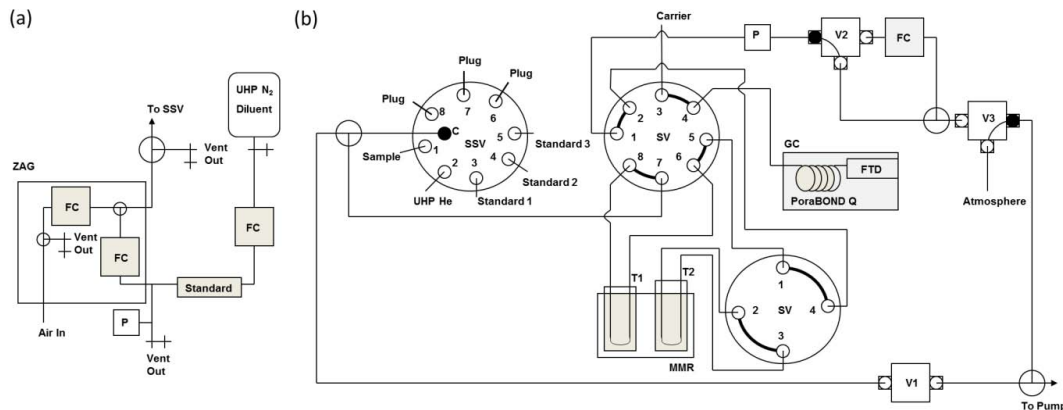


Fig. 1. Schematic of the GC-FTD instrument. System segregated into (a) standard dilution, (b) sample capture and analysis components. Configuration in (b) shows 8-port SV in position A and 4-port SV in position B (for sample desorption). Components: SV, switching valve; SSV, stream select valve; V, solenoid valve; P, pressure gauge; FC, flow controller; MMR, Cryofocus System; T1, sample dehumidification chamber; T2, sample enrichment chamber; ZAG, Apel-Reimer zero air generator (with only the dilution components shown for clarity).

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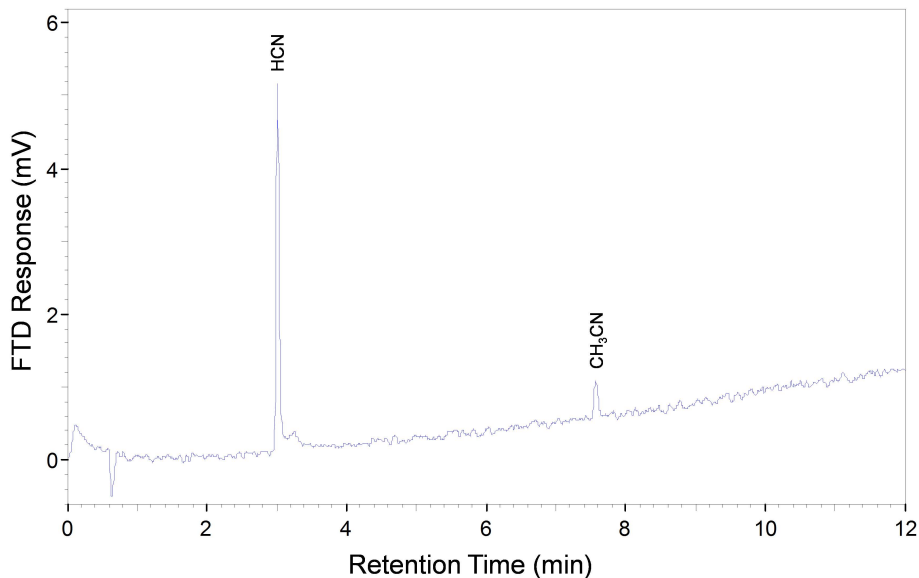


Fig. 2. An ambient chromatogram recorded with the GC-FTD instrument on 20 March, 16:35 LT during a period of relatively enhanced HCN mixing ratios. The small feature on the HCN peak tail represents a minor, reproducible peak splitting which depended on the desorption parameters of the Cryofocus System.

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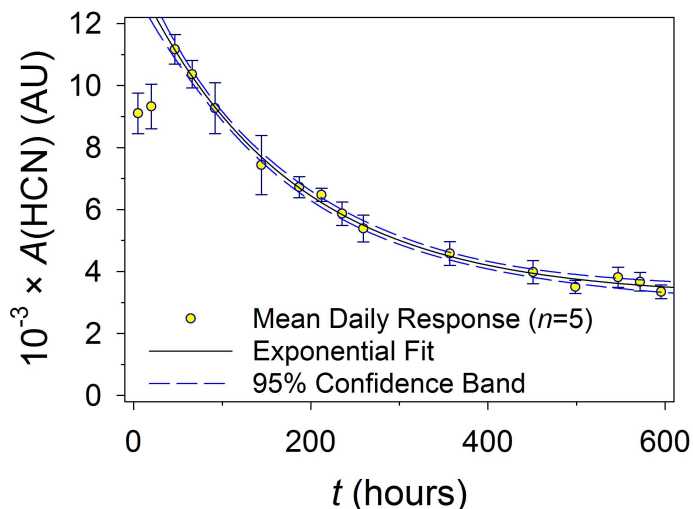


Fig. 3. Mean daily chromatographic peak areas ($n = 5$) measured for standard HCN samples (VMR = 0.25 ± 0.01 ppbv) analyzed during a period of continuous operation of the GC-FTD instrument from 3–31 March 2010. Error bars represent 1σ of the mean peak area values and range from 3–13%. Measurement times correspond with the elapsed time following instrument startup on 3 March ($t = 0$). Measurements were corrected for the non-zero background from the zero air generator. The fit represents a 3-parameter exponential function, which excluded measurements made during the initial ~ 24 h warm-up period.

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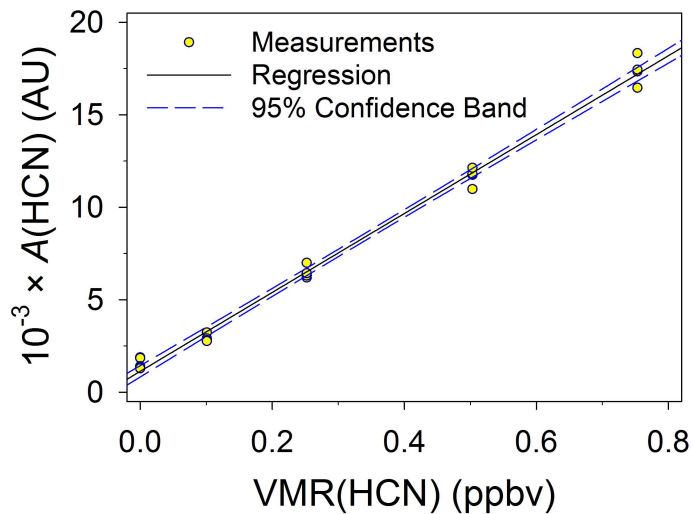


Fig. 4. A calibration curve constructed from de-trended standard and blank measurements made during 18–26 March 2010.

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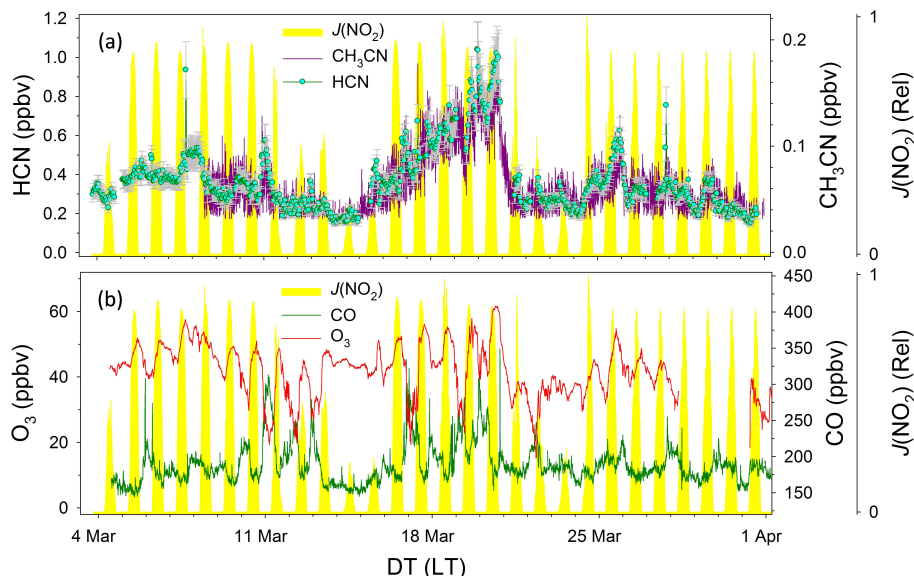


Fig. 5. (a) Time series of ambient HCN VMR measured at THF2 during 3–31 March 2010 with the GC-FTD instrument together with CH_3CN VMR measured by PTR-MS. (b) Time series of O_3 and CO VMR (10-min averages). Error bars on the HCN measurements represent the estimated overall measurement accuracy of $\pm 15\%$. A time series of $J(\text{NO}_2)$ (10-min averages) is shown to delineate daytime and nighttime periods. Note that the filter radiometer was removed from THF2 for calibration on 25 March; therefore, the $J(\text{NO}_2)$ values for the period 25 March 09:05 LT to 1 April 06:00 LT represent the median profile for the period 17–24 March.

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