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NitroMAC: An instrument for the measurement of HONO and intercomparison with a long-path absorption photometer

Charbel Afif[1,2,*], *Corinne Jambert*[2,**], *Vincent Michoud*[2], *Aurélie Colomb*[2,***], *Gregory Eyglunent*[3], *Agnès Borbon*[2], *Véronique Daële*[3], *Jean-François Doussin*[2], *Pascal Perros*[2]

1. *Emissions, Measurements and Modeling of the Atmosphere Laboratory, EGFEM Unit, Center for Analysis and Research, Faculty of Sciences, Saint Joseph University, Beirut, Lebanon*
2. *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR7583, CNRS, Université Paris-Est-Créteil (UPEC) et Université Paris Diderot (UPD), Institut Pierre Simon Laplace (IPSL), Créteil, France*
3. *Institut de Combustion, Aérothermique, Réactivité et Environnement, CNRS, Orléans, France*

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ABSTRACT

NitroMAC (French acronym for continuous atmospheric measurements of nitrogenous compounds) is an instrument which has been developed for the semi-continuous measurement of atmospheric nitrous acid (HONO). This instrument relies on wet chemical sampling and detection using high performance liquid chromatography (HPLC)-visible absorption at 540 nm. Sampling proceeds by dissolution of gaseous HONO in a phosphate buffer solution followed by derivatization with sulfanilamide/N-(1-naphthyl)-ethylenediamine. The performance of this instrument was found to be as follows: a detection limit of around 3 ppt with measurement uncertainty of 10% over an analysis time of 10 min. Intercomparison was made between the instrument and a long-path absorption photometer (LOPAP) during two experiments in different environments. First, air was sampled in a smog chamber with concentrations up to 18 ppb of nitrous acid. NitroMAC and LOPAP measurements showed very good agreement. Then, in a second experiment, ambient air with HONO concentrations below 250 ppt was sampled. While NitroMAC showed its capability of measuring HONO in moderate and highly polluted environments, the intercomparison results in ambient air highlighted that corrections must be made for minor interferences when low concentrations are measured.
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Introduction

At present, it is well recognized that the photolysis of nitrous acid (HONO) plays an important role in the production of hydroxyl radicals (OH) in urban atmospheres (Winer and Biermann, 1994; Kleffmann, 2007; Michoud et al., 2012). Indeed, HONO is known to be photolyzed into NO and OH (reaction R1) by radiation with wavelengths shorter than 400 nm.

$$HONO + h\nu \rightarrow OH + NO \quad (R1)$$

It has been suggested that HONO accumulates during the night and is photolyzed in the morning by sunlight (Alicke et

* *Corresponding author*. E–mail: afif@lisa.u-pec.fr, charbel.afif@usj.edu.lb (Charbel Afif).
** *Present address: Laboratoire d'Aérologie (LA) UMR 5560, Université de Toulouse and CNRS, France.*
*** *Present address: Laboratoire de Métrologie Physique (LaMP), CNRS, Université Blaise Pascal, Aubière, France.*

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al., 2003; Amoroso et al., 2008; Sjödin and Ferm, 1985), starting the radical cycles leading to photo-oxidant formation. This photolytic reaction has been long considered to play an important role in the production of OH only in the early hours when other sources of the hydroxyl radical are still of minor importance (Harris et al., 1982). HONO can account for up to 33% of the total net OH production (Kleffmann et al., 2005) and it has been proposed, thanks to low level measurement, to be a major HO_x source during the day (Ren et al., 2006; Acker et al., 2006; Michoud et al., 2012).

HONO urban mixing ratios vary widely from a few tens of ppt up to several ppb (Dibb et al., 2002; Calvert et al., 1994; Acker et al., 2004). Typically, HONO accumulates slowly during the night. A peak of nitrous acid concentration marks the early morning and the concentration decreases rapidly, reaching a photo-stationary state under sunlight, before it increases again after the sunset (Kleffmann, 2007).

Nitrous acid is produced by different sources, *e.g.* direct emissions from combustion sources, gas-phase reaction of NO and OH radical, and heterogeneous phase reactions where NO_2 plays a key role (Kleffmann, 2007). Since these sources could not explain observed HONO concentrations, new sources have been proposed, such as the photolysis of adsorbed HNO_3 on surfaces (Zhou et al., 2001, 2002a, 2002b, 2003), the photo-induced conversion of NO_2 into HONO on various surfaces (George et al., 2005; Ndour et al., 2008) and the photolysis of o-nitrophenols in the gas phase (Bejan et al., 2006). Nevertheless, the observed HONO concentrations often remain unexplained even if these newly proposed sources are taken into account.

Due to its atmospheric concentrations from ppt to ppb levels, short term variability and chemical properties, the measurement of nitrous acid is complex and challenging, which is a source of some of the uncertainties faced in our understanding of the HONO processes. During past field campaigns, nitrous acid has been monitored using various methods and instruments. These techniques include gas phase measurements by optical techniques and dry or wet chemical methods. On one hand, HONO can be detected directly using differential optical absorption spectrometry (DOAS) with a detection limit of *ca.* 100 ppt (Alicke et al., 2003). This method requires a very long optical path length (several hundred meters or kilometers). Another optical method is based on laser-induced detection of the OH radical following the photo-fragmentation of HONO, with a typical detection limit of 2–3 pptV and a sample integration time of 10 min. The relative uncertainty is estimated to be about 35%, due largely to the calibration uncertainty and laser power fluctuations (Liao et al., 2006). Fourier transform infrared spectroscopy (Hanst et al., 1982) and cavity ring-down spectroscopy (Wang and Zhang, 2000) have also been proposed, with a detection limit of ~5 ppb and a sampling time of 20 min and 15 sec respectively, whereas incoherent broadband cavity-enhanced absorption spectroscopy in the near-ultraviolet requires a path-length of kilometers and hence has a detection limit of few hundred of ppt–ppb within a few minute integration time (Gherman et al., 2008; Wu et al., 2012). Pérez et al. (2007) proposed a new thermal dissociation chemiluminescence method for *in situ* detection of nitrous acid. They proposed several improvements to be made to their instrument in order to be suitable for real atmosphere measurements but, to our knowledge, it has not been used in the field so far.

On the other hand, wet chemical methods have been proposed as a successful alternative for the measurement of HONO. These methods include base-coated dry annular denuder, elution and wet chemical analysis (Sjödin and Ferm, 1985; Febo et al., 1989), wet denuder coupled with ion chromatography (Acker et al., 2001; Oms et al., 1996; Simon and Dasgupta, 1993), scrubbing in mixing coils, followed by derivatization and determination of the complex by high performance liquid chromatography (HPLC) (Zhou et al., 1999) or long-path absorption spectroscopy (LOPAP) in a liquid core wave guide (Heland et al., 2001; Kleffmann et al., 2002). These methods are highly sensitive, with ppt level detection limits. They have a sampling time from a few minutes to a few hours. However, they may suffer from interference from different species under different pH values.

In order to identify new sources of HONO in either field campaigns or simulation chambers and determine its role in atmospheric chemistry, it is important to have an instrument that measures HONO with a high time resolution and a low detection limit in order to determine its concentration accurately, thus improving the wet chemical methods.

In this paper we describe the development of an instrument for measuring HONO at low mixing ratios and high time frequency. Based on a wet chemical method, the NitroMAC (French acronym for continuous atmospheric measurements of nitrogenous compounds) was developed at Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) relying on the work of Huang et al. (2002). The description of NitroMAC and the results of its intercomparison with the long path absorption photometer (LOPAP) are presented and discussed. In addition, a field testing campaign conducted in the surrounding of Paris (France) presents HONO concentrations measured with NitroMAC.

1. Materials and methods

1.1. NitroMAC instrument

NitroMAC is based on aqueous scrubbing using a coil sampler, derivatization of nitrite to a highly light-absorbing azo-dye with sulfanilamide (SA) and N-(1-naphthyl)-ethylenediamine (NED), and analysis using HPLC and visible absorption. The HONO concentration is determined from integration of the peak and a calibration calculation. It has two operation modes, both comprising two coils connected in parallel or in series.

For the first configuration comprising parallel coils (Fig. 1), one coil is dedicated to HONO derivatization while the other coil can be used for the measurement of another pollutant such as HNO_3 with the proper derivatization chemistry. It can also be employed to double the frequency of HONO measurement.

As illustrated in Fig. 1, air is driven into the sampling coils by a 2-m Teflon tube (o.d. 1/4 in.). The tube is maintained at 60°C in order to prevent adsorption of HONO or any other pollutant on the surface of the tube, which could cause artifacts (Keene et al., 2006).

Air is pumped into a 24-turn coil at 2 L/min by a vacuum pump (0–2000 mL/min) (Model 1079, MKS, USA) controlled by a mass flow controller (0–2000 mL/min, MKS, USA). The sampling

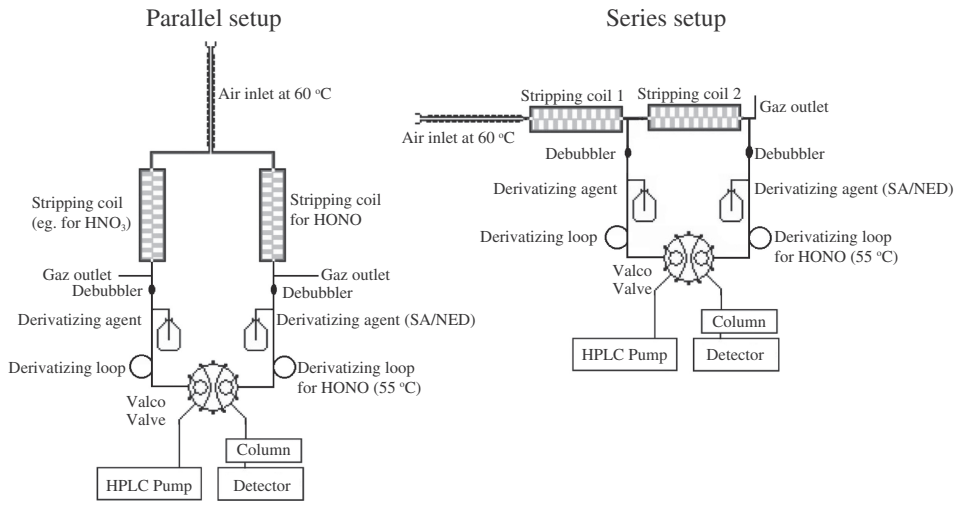


Fig. 1 – Schematic diagrams of NitroMAC in parallel and series set-ups. HPLC: high performance liquid chromatography; NitroMAC: French acronym for continuous atmospheric measurements of nitrogenous compounds; SA/NED: sulfanilamide/ N-(1-naphthyl)-ethylenediamine.

solution is a 1 mmol/L phosphate buffer (pH = 7) pumped at a flow rate of 0.18 mL/min using a peristaltic pump (MS/CA, Ismatec, Germany). The solution passes through a debubbler in which the air is separated from the liquid. The air-free solution is derivatized using SA/NED solution to form the azo-dye. The derivatization solution is formed by sulfanilamide at 4×10^{-3} mol/L and N-(1-naphthyl)-ethylenediamine at 4×10^{-4} mol/L in hydrochloric acid at 48×10^{-3} mol/L. A thermostatted loop (55°C) is added to accelerate the derivatization kinetics. Residence time in the loop is optimized to obtain quantitative derivatization (the optimum time was found to be 7 min). Samples are then analyzed by HPLC and visible absorption.

The derivatization process involves a two-step azo-dye production (Strickland and Parsons, 1968). In the first step, nitrite ions are reacted with sulfanilamide in acidic media to form a diazonium salt (Fig. 2). In the second step, the diazonium ion is allowed to react with NED to form an azo-dye that exhibits maximum absorption at 540 nm.

The HPLC system consists of a pump (PU2089, JASCO, USA), a 10-port electrically activated auto-injection valve (Valco, USA) with two 300 μL sample loops, a C18 reverse phase column (3 μm, 5 cm, 4.6 mm, Alltech, USA), and a UV–visible absorption detector (UV2070, JASCO, USA). Isocratic elution was accomplished with 18% acetonitrile in 15 mmol/L HCl solution at a flow rate of 0.7 mL/min. The detection wavelength is fixed at 540 nm in a 1-cm optical cell. The samples are alternatively loaded into the sample loop and injected into the HPLC system. The analysis time is 5 min for each channel, resulting in a 10-min sampling frequency for both channels. In the current configuration, a 1-min air sample is analyzed for nitrite determination. The system is automated by using a computer-based HPLC data system. HONO collection efficiency was evaluated to be higher than 99.9%. The detection limit is approximately 3 ppt with a relative standard deviation of 2%, and the relative expanded measurement uncertainty is 10% with a coverage factor equal to 2 (2σ).

The arrangement of the two identical coils in series allows the determination of sampling efficiency or the evaluation of possible interferences in HONO measurements (Fig. 1). In this configuration, air is pulled through the first coil, where almost all of the initial HONO is collected (>99.9%) along with a fraction of the interferences. The same air continues to arrive to the second coil, which collects the remainder (<0.0999%) of the initial HONO and about the same quantity of interferences. Both collected solutions are derivatized with SA/NED and analyzed alternatively by the HPLC/Visible system. The HONO concentration is calculated by subtracting the signal of the second coil

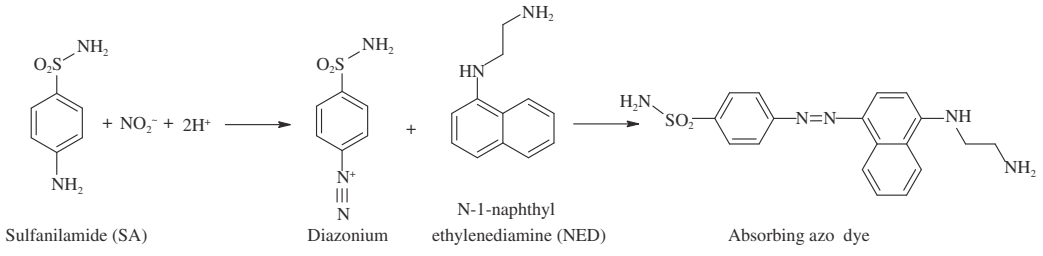


Fig. 2 – Nitrite ion SA/NED derivatization mechanism.

from the signal of the first coil. This configuration will minimize the unknown interferences collected.

Two types of calibration were compared during this study, *i.e.*, HONO generation system based on the work of Febo et al. (1995) and $NaNO_2$ standard solutions.

The HONO generation system used is based on the system developed by Febo et al. (1995):

$$HCl(g) + NaNO_2(s) \rightarrow NaCl(s) + HONO(g). \quad (R2)$$

HONO is produced by passing a flow of humidified HCl(g) over a bed of $NaNO_2$(s), resulting in the near 100% production of HONO from the HCl *via* reaction (R2). The production of HONO proceeds only in the presence of water vapor. The average RH of the HONO generation system was 40% ± 2% over the measurement period. In this range of RH, deliquescence was not observed, ensuring a fairly stable HONO output source. The HONO generation system was temperature-controlled using a thermostatted bath at approximately 35°C.

The nitrite powder was continuously mixed in order to ensure a highly pure output source.

The generated nitrous acid was quantified by collecting it into a pH 10 $NaHCO_3/Na_2CO_3$ solution, followed by subsequent analysis of the nitrite and chloride contents by ion chromatography (IC) (Dionex, DX-100 Ion Chromatograph, Thermo Scientific, USA, 4 mm × 250 mm analytical ion-exchange column).

During the measurement period, the HONO generation system produced on average a HONO mixing ratio of 100 ± 0.9 ppbV, equivalent to a generation rate of 1.35 ± 0.01 nmol/min. The stability of the HONO generation system was excellent, with a deviation of ~2% over several months.

The HONO produced over the measurement period was found to be highly pure with an average conversion efficiency of 98.5% ± 1.1%.

The second method used to calibrate NitroMAC was the use of $NaNO_2$ solutions. The $NaNO_2$ standard solutions were added to the SA/NED solution, placed at 55°C for 7 min and then injected directly into HPLC by means of the 10-port valve.

The difference between the 2 methods was within 3%, allowing the adoption of the latter method, which is easier to deploy for *in-situ* calibration.

On the other hand, previous studies reported that wet chemical methods suffer from interferences caused by various compounds in ambient air (Kleffmann et al., 2002; Huang et al., 2002; Kleffmann and Wiesen, 2008). The interferences caused by NO_2, NO, peroxyacetyl nitrate (PAN) and O_3 were investigated by Huang et al. (2002) in an urban environment. They stated that NO_2, PAN, and NO interferences were detectable but not significant, compared to the ambient HONO concentration. In remote clean environments, interferences from NO_x, PAN and O_3 are either negligible or too low to be detected (Huang et al., 2002; Amoroso et al., 2006). Heland et al. (2001) found that other pollutants generally account for less than the interference of NO_2. As for NitroMAC, the interferences of pure NO_2, NO, PAN, O_3 and HNO_3 were investigated in the laboratory over a large concentration range. Using the set-up in series, the interference of pure NO_2 was found to be the highest among the other tested compounds: it accounted for 0.018%, which is comparable to that found by Heland et al. (2001). Interference from HNO_3 cannot be expected, because the SA/NED solution does not react with nitrate. However, the main known interferences may come from reactions involving NO_2, *e.g.* NO_2 and aromatics (Ammann et al., 2005) and NO_2 and diesel exhaust (Gutzwiller et al., 2002), *etc.* When operating using the set-up in series, NitroMAC can correct for most of the known interferences, as they are subtracted from the original signal (Fig. 3).

1.2. Long path absorption photometer instrument

The long path absorption photometer (LOPAP) is an instrument developed by the Bergische Universität Wuppertal in order to measure gaseous HONO, and commercialized by QUMA Elektronik & Analytik GmbH (Germany). It has been validated by intercomparison with a differential optical absorption spectroscopy (DOAS) instrument for moderate and high concentrations due to the DOAS high detection limit (Kleffmann et al., 2006). The instrument is described in detail elsewhere (Kleffmann et al., 2002). Briefly, HONO is sampled in a stripping coil by a fast chemical reaction and converted into an azo-dye, which is photometrically detected in a special Teflon tube acting as a long-path absorption cell in a liquid core waveguide. Because of the two-channel concept of the instrument, all tested interferences are corrected (Kleffmann et al., 2002). The LOPAP instrument performance depends on the set-up adopted (in particular the length of the waveguide). Detection limits usually fall in the range of 1–2 ppt over a 1–5 min sampling time (for example in Kleffmann and Wiesen, 2008, it is indicated that with an optical path length of 6 m, the LOPAP has a detection limit of 0.2 pptV for a response time of 7 min). In the present study, the LOPAP detection limit was 2–20 pptV, depending on the chosen measurement range. The time resolution was 5 min with an uncertainty of 12%.

An intercomparison has been made between the LOPAP and the DOAS technique (Kleffmann et al., 2006): First, a comparison took place in the European Photoreactor (EUPHORE) in Valencia (Spain) consisting of a 200 m^3 chamber made of FEP (fluorinated ethylene propylene). As the DOAS system used exhibited a detection limit of ~200 pptV, the concentrations involved were quite high: the HONO concentration reached ~30 ppbV. The correlation showed an excellent agreement between the two instruments (Kleffmann et al., 2006). Another intercomparison was conducted in ambient air and showed also very good agreement between the respective values.

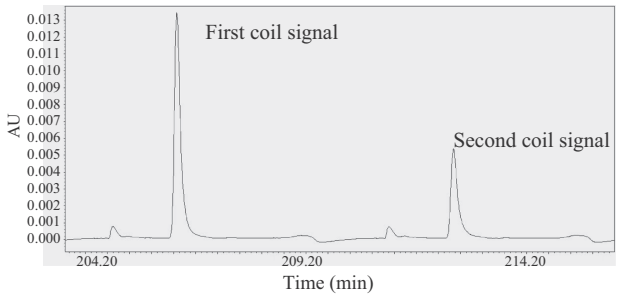


Fig. 3 – Example of a chromatogram showing the first coil and the second coil signals. Correction for interferences is made by subtracting the azo dye signal of the second coil from that of the first coil. AU: absorption unit.

In the present study, the LOPAP measurements were acquired every 15 sec and were carefully averaged over the time steps of the NitroMAC instruments (10 min) for the purpose of the intercomparison.

1.3. Intercomparison study

An intercomparison was made between NitroMAC and LOPAP during two experiments: the first one with high HONO concentrations in a smog chamber, and the second one in ambient air with lower HONO concentrations during ~24 hr.

1.3.1. Intercomparison in simulated atmosphere — high HONO range

The experimental protocol used for the first experiment relies on the well documented HONO production from NO_x in Teflon™ chambers when irradiated (Bloss et al., 2005; Carter et al., 2005; Hynes et al., 2005; Rohrer et al., 2005; Carter, 2006). Here, an outdoor atmospheric simulation chamber was used at the "Institut de Combustion Aérothermique Réactivité et Environnement" (ICARE). This chamber is a cube of 1.5 m on edge with a volume of 3.4 m^3 made of 200 μm ethylene tetrafluoroethylene (ETFE) film. To enhance the HONO production, a glass surface of 120 cm × 40 cm coated with TiO_2 and exposed to ambient air for several days was introduced in the chamber. The detailed procedure can be found in Monge et al. (2010).

The chamber was equipped with ozone, NO_x and NitroMAC and LOPAP for HONO monitoring, a temperature and hygrometer sensor, and a radiometer calibrated to measure the NO_2 photolysis frequency (J_{NO2}). A fan allowed the homogenization of the gaseous and particulate phases in the chamber in less than 2 min. Reactant introduction, sampling and extraction valves are located at the bottom of the chamber. It is provided with a black and opaque cloth in order to protect the reactants from light radiation. This protection can be easily removed, in less than 10 sec, to allow immediate irradiation by sunlight.

The chamber was first flushed with a 25 L/min flow of purified air for several hours, typically during the night. During the whole experiment, a flow of 5 L/min was maintained in the chamber in order to compensate sampling flows (monitors) and to have a small overpressure in the chamber to avoid contamination by outdoor air. The chamber background was monitored for 30 min by all analytical instruments. Then, several ppb of NO and NO_2 were introduced with a gas-tight glass syringe, and all parameters were again monitored for 30 min in the dark. The chamber black cover was then removed to irradiate the chamber and the chemical system was analyzed for 4 hr.

1.3.2. Intercomparison in real atmosphere — low HONO range

Most of the available comparison studies support the supposition that interferences are a problem for HONO wet chemical instruments (Liao et al., 2006; Kleffmann and Wiesen, 2008) and especially when low concentrations of HONO are measured. Therefore, a second experiment was conducted in ambient air during 19 h on the roof of ICARE (Orléans, France; latitude: 47°50′21.50″N; longitude: 1°56′40.44″E) in order to assess the agreement between the two instruments in low-polluted conditions and the contribution of interferences to measured HONO concentrations. The experiment took place between the 30th of September 5:00 pm UTC and the 1st of October 2008 noon UTC. During the sampling period, the temperature ranged from 13 to 16°C and no precipitation was recorded, while the weather was quite cloudy. NitroMAC and LOPAP instruments were installed side by side. Special care was taken with the sampling inlets as the distance between them was less than 5 cm. In this experiment, the mass flow controller of NitroMAC was substituted by a volumetric flow controller due to a technical problem. Hence the uncertainty of the measurement was determined to be 20% since the uncertainty on the air flow became much higher. Throughout the experiment, NitroMAC settings adopted two stripping coils in series in order to evaluate interferences, and the second coil signal was also compared to the corrected HONO value (First coil signal–second coil signal).

2. Results and discussion

As expected, the two experiments led to very different ranges of HONO concentrations. The first intercomparison experiment, which took place in the ICARE chamber, led to HONO concentrations ranging from few hundreds of ppt to 17 ppb. The NO_x mixture introduced in the chamber before the irradiation consisted of 155 ppb NO and 43 ppb NO_2. In the dark, a slow increase of the HONO concentration from 200 to 700 ppt was recorded. Once exposed to light, a fast HONO build-up was observed, as concentrations reached up to 17 ppb within less than 1 hr. Then, HONO underwent a slow decay down to 8 ppb within 5 hrs. The temporal variation of the different parameters monitored during this experience is presented in Fig. 4.

As can be seen on the correlation plot displayed on Fig. 5, excellent agreement between the 2 instruments was observed in this concentration range. A slope value near unity (0.996 ±0.013 at 2σ), a negligible intercept of (−34.4 ± 74.9 at 2σ) ppt, and R^2 of 0.9984 were determined, as illustrated by the trend line in Fig. 5.

As it cannot be excluded that during such a photo-oxidation experiment, other possibly interfering species might be formed from the chamber background or from pollutants that remained adsorbed on the glass surface, the "2 stripping coils" arrangement was adopted. This setup allowed us to quantify these hypothetical interferences during the experiment. It was found that they ranged from 2% to 4% of the total HONO concentration.

Finally, this first experiment shows that both instruments agree well in moderate and highly polluted environments.

For the second intercomparison experiment, the HONO concentration observed in the real atmosphere ranged from 60 to 250 ppt. Fig. 6 shows the variation of HONO concentrations for both instruments. Both instruments captured 3 peaks of HONO between 8 pm and 11 pm and one large peak in the morning (between 8 am and 10 am), with concentrations higher than 140 ppt. During this night the base concentration were between 60 and 100 ppt. While a general agreement can be found on the diel variation of the concentrations, the two instruments differed significantly in the upper value recorded during the highest peaks. To investigate possible interferences, results considering the one coil and 2-coil settings are presented.

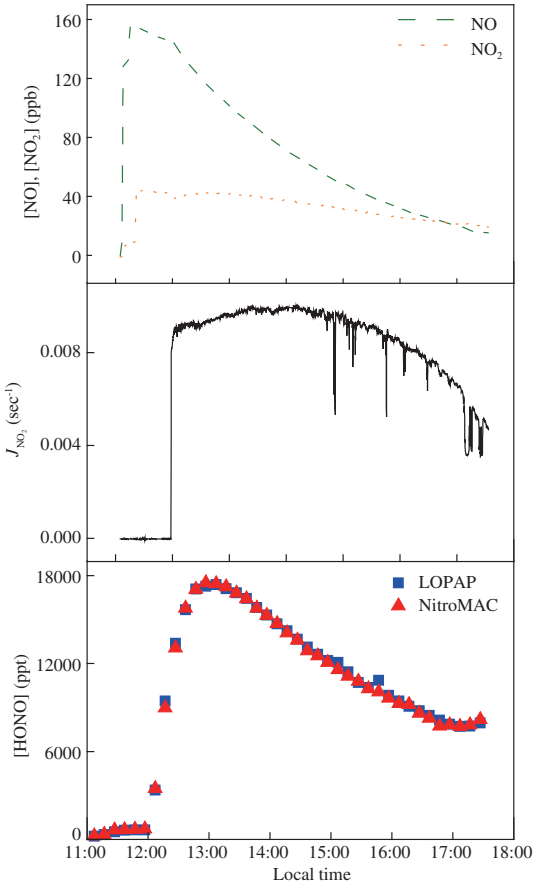


Fig. 4 – Temporal variations of different parameters during the simulation chamber experiment. LOPAP: long-path absorption photometer; J_{NO2}: NO_2 photolysis frequency.

The concentrations of HONO measured by a NitroMAC for 1 and 2 coils were plotted against those observed by a LOPAP. This correlation analysis led to the identification of a 20% overestimation by a NitroMAC. The linear regression of these data led to a slope of (1.17 ± 0.2 at 2σ), a bias of (−0.39 ± 22 at 2σ) ppt and a Pearson's correlation coefficient of 0.76 for the one-coil setting and a slope of (1.2 ± 0.2 at 2σ), a bias of (−21 ± 20 at 2σ) ppt and a Pearson's correlation coefficient of 0.8 when considering the two-coil setting.

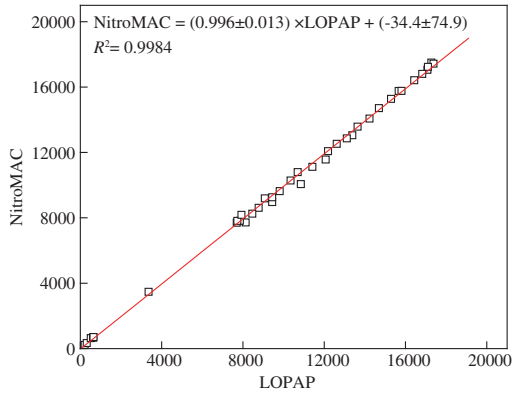


Fig. 5 – Plot of NitroMAC against the LOPAP data for the smog chamber experiment.

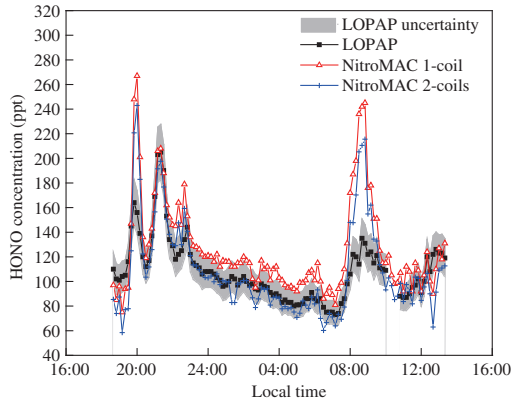


Fig. 6 – HONO concentrations measured by NitroMAC and LOPAP instruments during the intercomparison in ambient air. HONO: nitrous acid.

Aside from the 20% general overestimation, it must be said that NitroMAC values were higher by 60% and 80% respectively than the ones observed by a LOPAP during the peak hours (at 8 pm and 8 am).

The interferences measured using the 2-coil setup varied between 10% and 30% (Fig. 7). Higher values of interferences occur when HONO concentrations are low. This observation is in accordance with Kleffmann and Wiesen (2008) and Kleffmann et al. (2006).

The largest overestimations by NitroMAC during the peaks remained unexplained. Nevertheless, the 1-coil *vs.* 2-coil analysis suggests that any interfering compound resulting in nitrite ion formation in the system was mainly trapped in the first coil, since the interferences in the second coil measured as HONO equivalent in ppt did not vary considerably over a large concentration range. Considering that a similar trapping efficiency of 66.7% can be found for the two peaks for this unknown species, it is reasonable to assume that this interference arises from a single compound.

In the NitroMAC instrument, sampled air passes through a heated Teflon sampling inlet before arriving to the stripping coil. Even though the LOPAP was not intercompared with DOAS in the low range of HONO concentrations (<250 ppt) (Kleffmann et al., 2006), this instrument has no sampling line and thus does not suffer from the presence of HONO sources during the transit of sampled air to the coil. It has been shown that small interferences during sampling result in forming HONO from the combination of several pollutants and parameters (Amoroso et al., 2008). One of the potential reactions involves NO_2 and H_2O under humid conditions to form HONO and HNO_3 on the tubing walls (Amoroso et al., 2008; Syomin and Finlayson-Pitts, 2003). However, the uptake coefficient of NO_2 on pure water is on the order of 10^{-7} or below (Ammann et al., 2005 and references therein). It consists of a slow hydrolysis of NO_2 proceeding through a complex mechanism (Ammann et al., 2005; Cheung et al., 2000). In parallel, NO_2 uptake coefficients on solutions containing aromatics increase with pH up to values of 10^{-5} at pH values above 10 (Ammann et al., 2005). Another reasonable source of overestimation is the one proposed by Gutzwiller et al. (2002) consisting of the reaction

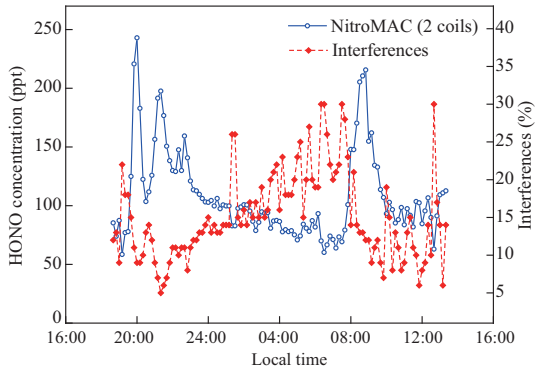


Fig. 7 – Temporal variation of HONO concentration (circles) with the 2-coil setup and the percentage of interferences detected.

of NO_2 with organic exhausts, forming HONO under humid conditions. In their experiment, 2.3% of NO_x emitted was converted to HONO. The reactions suggested by Ammann et al. (2005) and Gutzwiller et al. (2002) might be better candidates than NO_2 hydrolysis on pure water in forming HONO on the inner surface of the sampling line. If HONO is produced in the sampling inlet, it will be totally collected by the first coil, thus does not cause an increase in the signal of the second coil.

Moreover, the long stripping coil in NitroMAC offers high contact time between the sampled air and the stripping solution. Consequently, interfering compounds with relatively high Henry's constants (K_H) may be trapped efficiently in the first coil. In this case, even with a 2-coil setup, the trapped quantity in the first coil is larger than the one in the second, resulting in a partial correction of interferences. Reaction of NO_2 with dissolved phenols is a good example of potential interference in this case, with K_H of *o*-cresol and phenol of 8.2×10^{-3} and 2.9×10^{-2} mol/(L·Pa) respectively (Ervens, 2001). In addition, pH of the stripping solution plays an important role in the trapping efficiency of the compounds; NO_2 coefficient uptake into solutions containing aromatics was observed to be pH dependent (Ammann et al., 2005; Gutzwiller et al., 2002), with values increasing from below 10^{-7} under acidic conditions to ~10^{-5} under pH values higher than 10. Moreover, the $NO_2 + SO_2$ reaction is also pH dependent, forming higher quantities of nitrite at higher pH, resulting in an interfering signal accounted for as HONO (Littlejohn et al., 1993), *etc.* All these considerations indicate that the correction for interferences is of major importance when low concentrations are measured as in the case for rural, remote or polar conditions. However, in any 2-coil setup like the NitroMAC instrument, the interferences determined by this setup are only the lower limit of the real interferences.

3. Conclusions

NitroMAC, an instrument for the measurement of HONO, was built based on the work of Huang et al. (2002).

The intercomparison of NitroMAC with the LOPAP showed very good agreement in a simulation chamber, with a range of concentrations between 0.2 and 17 ppb. However, in ambient air, the comparison showed the presence of significant interferences. A 2-coil setup allowed us to partially correct for the interferences detected. Heterogeneous reactions on the surface of the sampling tubes are highly suspected to be the cause of these interferences. In consequence, a newer version of NitroMAC with no sampling line was developed, in which shorter stripping coils were integrated while maintaining the same trapping efficiency. The correction of these interferences is of significant importance in low concentration environments such as rural, remote or polar conditions. This instrument has a low detection limit and can correct for most of the interferences with a variable sampling frequency.

Indeed, it has been deployed successfully in various field campaigns for the measurement of HONO in urban sites (Paris, France and Beirut, Lebanon) and suburban sites as well (Michoud et al., 2012, 2014). Moreover, in the FIONA (Formal Intercomparisons of Observations of Nitrous Acid) intercomparison Campaign at Euphore (Ródenas et al., 2012), NitroMAC showed good agreement with the DOAS. This technique allowed continuous measurements with high sampling frequency and low detection limits.

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