



Technical Note

A Micro-impinger Sampling Device for Determination of Atmospheric Nitrogen Dioxide

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ABSTRACT

There is an increasing demand for the determination of gaseous pollutants present in both outdoor and indoor environments. It is the result of a growing awareness that good air quality is fundamental to the health of the population. Gas monitors capable of reliable measurements are a global necessity. In this work, we developed a low cost and portable micro-sampler for gaseous pollutants, using a μ -impinger bubbler containing 500 μ L of absorbing reagent. The micro-sampler was evaluated in the detection of NO_2 using the Griess-Saltzman reagent (GS). The μ -impinger enabled the determination of NO_2 concentrations lower than 15 $\mu\text{g m}^{-3}$ (~ 8 ppb) using a 50 mL min^{-1} sample flow rate during 30 min. This NO_2 concentration is 10 times lower than the EPA air quality standard. In the calibration procedure, standard atmospheres with NO_2 concentrations from 15 to 165 $\mu\text{g m}^{-3}$ were used. The limit of detection was 14 $\mu\text{g m}^{-3}$ considering 3.3 times the standard deviation of the blank signal. The relative error was 12.0%, and the coefficient of variation was 6.9%. The portable sampling procedure can be used in remote areas where there is no public electricity supply. The detection limit could be improved further by using longer sampling times and/or higher sampling flow rates. The method is selective and highly sensitive.

Keywords: μ -Impinger bubbler; NO_2 determination; Air analysis; Gas samplers.

INTRODUCTION

The levels of pollutants in urban and semirural atmospheres are increasing in many developing regions, accompanied by more frequent extreme pollution episodes. Atmospheric pollution can affect human health, natural vegetation, and agricultural productivity (Daisey *et al.*, 2003; Richter *et al.*, 2005; Allen *et al.*, 2011; Achakulwisut *et al.*, 2019).

NO_2 gas is ubiquitous in the outdoor and indoor atmospheres as a consequence of emissions (of NO_2 or precursors) from all types of combustion, as well as from biogenic sources. The National Institute for Occupational Safety and Health (NIOSH) has established a limit of 1 ppm (1.8 mg m^{-3}) as a 15-minute short-term limit for the concentration of NO_2 (NIOSH, 2011). The United States Environmental Protection Agency (U.S. EPA) has established NO_2 concentrations of 100 ppb (one hour average) as a primary air quality standard and 53 ppb as a secondary standard in the outdoor atmosphere (U.S. EPA, 2018). The establishment of air quality control measures requires the existence of reliable analytical techniques for measuring pollutant gases. Direct methods based on physical measurements are usually costly and/or are

insufficiently sensitive for the measurement of gases at the concentrations stated in the air quality standards. Alternatives are chemical methods that require previous sampling and preconcentration steps for the determination of gaseous pollutants at low concentrations (Lodge, 1989; Stern, 1989; Handbook of air pollution analysis, 2012). Various sampling techniques have been used for the extraction and preconcentration of gases from air, such as adsorbent tubes, impregnated filters, bubblers and impingers (Kim and Allen, 1997; Kleindienst, *et al.*, 1998; Fuertes, *et al.*, 2003; Das, *et al.*, 2004; Gallego, *et al.*, 2010; Verrielle, *et al.*, 2012). Our experience using impregnated filters (Felix *et al.*, 2011; da Silveira Petrucci *et al.*, 2015; Garcia *et al.*, 2010) has shown that they can sample large quantities of air; they are easy to prepare and are easily transported between field sites and the laboratory, but may require procedures for extraction of the analyte and are incompatible with volatile impregnating solutions. The advantage of impingers is the wide variety of reagent solutions that can be used to collect different gases (Lodge, 1989; Destailats *et al.*, 2002; Harrison, 2012; Verrielle, *et al.*, 2012). Different designs of impingers have been constructed from glass or Teflon, with the dispersion tube below the surface of the liquid being either open-ended or provided with small holes (frit). The sample gas aspirated through the dispersion tube forms bubbles that are dispersed into the liquid. The reaction of NO_2 with the Griess-Saltzman (GS) absorbing reagent produces a red-violet color

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(Saltzman, 1954). The reagent has been used since the 1960s in different analytical methods. Only over the last 30 years, several examples can be cited (Nagashima and Nakano, 1999; Ohyama *et al.*, 2000; Milani *et al.*, 2001; Izumi *et al.*, 2015; Fàbrega *et al.*, 2017). The Griess-Saltzman (GS) solution has been included as a recommended NO₂ chemical method in *Methods of Air Sampling and Analysis* (Method 406, James P. Lodge, Jr., 1989) a handbook for air pollution control and industrial hygiene and also as a standard test method for nitrogen dioxide content of the atmosphere, method ASTM D1607-91(2011) in American Society for Testing and Materials (ASTM D1607-91(2018)e1). The main drawback of impinge is evaporation of the solvent during long sampling times. Another serious limitation that has discouraged the use of impingers in the field is the typical requirement for a complete sampling train including a vacuum pump, an air metering device, and a source of electrical power, which can be inconvenient to handle in the field. The smallest volumes of absorbent solutions used in impingers are typically restricted to around 5–10 mL (Stern, 1976; Lodge, 1989; Harrison, 2012). In this work, we propose the use of a μ -impinger containing 500 μ L of absorbent solution, connected to a flow controller and a vacuum pump powered by a 1.5 V battery. All these approaches have shown new devices that allow analysis in situ or with less sampling time and with low cost.

METHODS

The μ -impinger Bubbler

The μ -impinger bubbler arrangement is shown in Fig. 1. The μ -impinger was constructed of glass, with dimensions of 13.1 mm (o.d.) and 106.30 mm (height) (Fig. 1(a)). A PEEK tube (0.76 mm id., 1.6 mm o.d.) was inserted through a lateral hole and was used to bubble the gas through the absorbent solution (Fig. 1(b)). On the inner wall of the μ -impinger, at 68.80 mm from the base of the tube, glass fingers (similar to those of a Vigreux-type condenser) projected into the central space in order to collect small droplets flowing upwards, helping to prevent exit of droplets of the absorbent solution

during the gas bubbling phase (Fig. 1(c)). A 45 μ m Teflon membrane filter (SLHV033RS, Merck) was connected at the air inlet of the PEEK tube sampler in order to prevent the entry of aerosol (Fig. 1(d)). An aquarium non-return check valve was placed between the μ -impinger and the vacuum pump to prevent transfer of any absorbent solution to the air pump (Fig. 1(e)).

The sampling flow rate (Fig. 2(a)) was controlled using an acrylic flowmeter for air fitted with a valve (0–100 mL min⁻¹, Cole Palmer, USA) (Fig. 2(b)). Air was aspirated using a 0.5 W diaphragm pump (BOYU, China) (Fig. 2(c)). Power for the diaphragm pump (Fig. 2(d)) was provided by a 1.5 V battery.

The complete sampling train weighed about 600 g, making it easy to transport to field locations. After sampling, the absorbent solutions were transferred to Eppendorf tubes prior to the absorbance measurements. The removal of the solution from the interior of the impinger was done with the aid of a 5.0 mL syringe that was connected to the top of the μ -impinger. Compressing the syringe, the air intake into the μ -impinger propelled the solution through the PEEK tube and this was collected by the Eppendorf tube.

Reagents and Solutions

All solutions were prepared using deionized water (Milli-Q system, Millipore, USA) with conductivity of 18.1 μ S cm⁻¹. The Griess-Saltzman reagent was prepared by dissolving 5.0 g of sulfanilic acid (Carlo Erba, Italy) in a solution containing 600 mL of water, 140 mL of glacial acetic acid (Maia, Brazil), and 20 mg of N-(1-naphthyl)-ethylenediamine (Merck, USA). The final volume was made up to 1 L with deionized water (Milli-Q system, Millipore, USA). The reagent was stored in an amber flask in a refrigerator. An aliquot of 500 μ L of this solution was used as the absorbent in the μ -impinger.

Spectrophotometric Determination

The reaction of NO₂ with the absorbing reagent produces a red-violet color. The dye development was complete within 15 min at room temperature. For the analysis, the

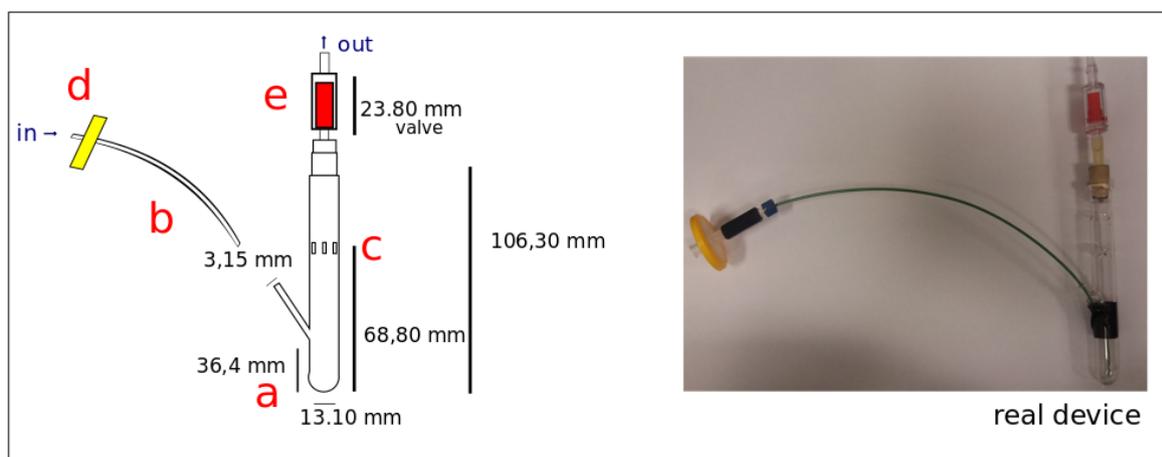


Fig. 1. Diagram and photograph of the μ -impinger bubbler: (a) μ -impinger bubbler tube, (b) PEEK tube, (c) glass fingers, (d) 45 μ m Teflon filter, and (e) check valve.

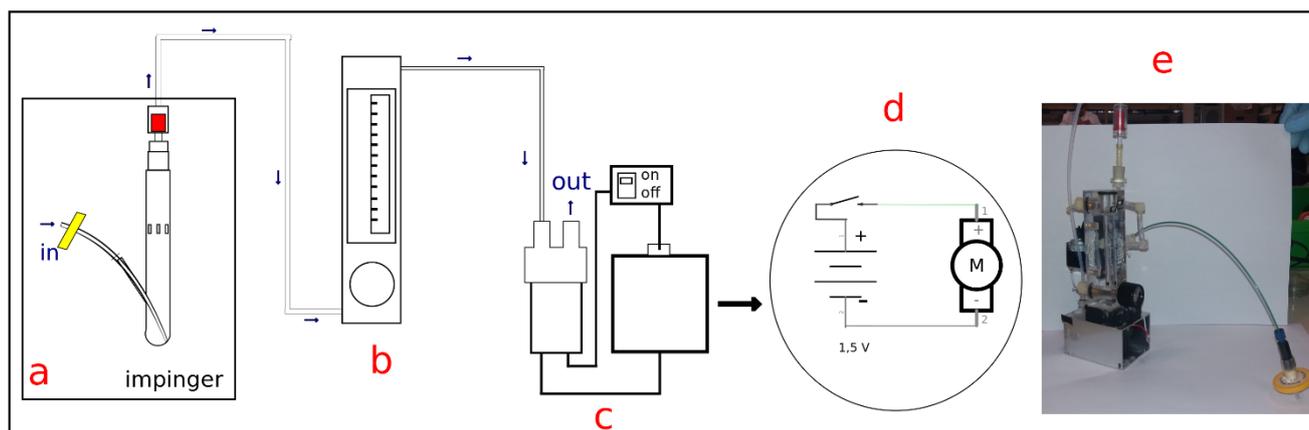


Fig. 2. Diagram of the μ -impinger sampling train arrangement: (a) diagram of the μ -impinger sampler, (b) 100 mL min^{-1} rotameter, (c) diaphragm pump, and (d) schematic diagram of the system used to power the pump motor.

solution was transferred to a micro-cuvette with a 5 mm light path and the absorbance was measured at 540 nm with a spectrophotometer (UV-1800, Shimadzu, Japan), using the unexposed reagent as a reference.

Generation of the Standard Gas Mixture

All experiments were performed with atmospheric air contaminated with NO_2 . The system used to generate the NO_2 standard gas was similar to others described previously (Passaretti Filho et al., 2015). All the gas flows were regulated using flowmeters with valves (Cole Palmer, USA). Compressed air was purified by passage through columns of activated carbon and silica gel. The clean air was split into two lines. The first stream of clean air passed through a permeation chamber containing a nitrogen dioxide permeation tube (VICI Metronics, Santa Clara, USA) that emitted NO_2 at a rate of $81.25 \text{ ng min}^{-1}$. The resulting gas stream containing NO_2 was diluted to different concentrations using pure air metered by a second flowmeter. As regulatory NO_2 concentrations are usually expressed in ppb units, the concentrations can be converted considering that at 25.0°C , 10.0 ppb of NO_2 is equivalent to $18.8 \mu\text{g m}^{-3}$.

RESULTS AND DISCUSSION

Firstly, the effects of sampling time and flow rate were evaluated. Suitable values of these parameters are important for obtaining reliable results. When the gas to be determined is very dilute in the atmosphere, a higher sampling rate increases the amount of gas in contact with the absorbent solution, but the higher flow rate decreases the contact time of the gas with the solution and the evaporation of the solution increases. On the other hand, when the environment is heavily polluted, lower flow rates combined with shorter sampling times may be necessary to avoid saturating the collection capacity of the liquid.

In the experimental protocol adopted, the μ -impinger was filled with $500 \mu\text{L}$ of the absorbent solution and sampling was initiated. At the end of the sampling period, the solution was transferred directly to a cuvette and the absorbance was determined at $\lambda = 540 \text{ nm}$. In the case of the field samples,

the solution was transferred to an Eppendorf tube wrapped in aluminum foil for storage. Tests showed that the dye formed was stable for up to 4 h.

Evaporation of the Absorbent Solution

The standard mixture of NO_2 was generated by passing a stream of clean dry air into the permeation chamber. This gas was subsequently diluted with clean air. The relative humidity of the gas, measured using a digital thermohygrometer AM2302/DHT22 (AOSONG-Canada) before sampling, was always below 10%. Aliquots of $500 \mu\text{L}$ of the absorbent solution were added to the μ -impinger and mass measurements were made using a balance with sensitivity of 0.1 mg . The standard gas mixture was passed through the μ -impinger for 60 min at different flow rates (between 25 and 100 mL min^{-1}).

The results (Fig. 3), obtained as the difference between the masses measured at the beginning and end of sampling, showed that the mass loss of the solution increased exponentially as the flow rate was increased. Sampling maintained at a flow rate of about 50 mL min^{-1} resulted in a

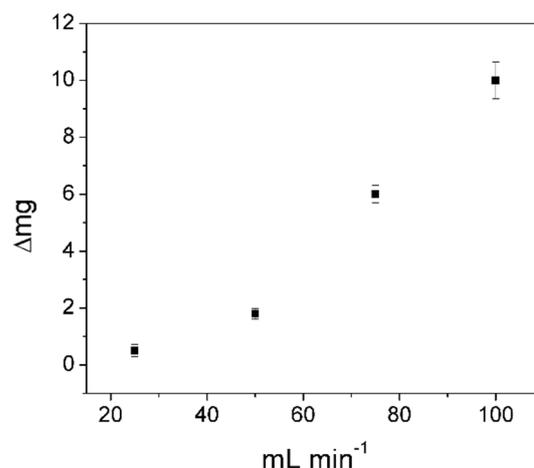


Fig. 3. Effect of evaporation of absorbent solution during sampling for 60 min at flow rates of 25 , 50 , 75 , and 100 mL min^{-1} ; Δmg is the mass difference of the solution before and after the end of sampling.

mass loss by evaporation of less than 2% and that may not be significant considering other sources of error. However, it is possible to adjust the volume with the addition of GS solution using a pipette. A two-fold increase in the sampling flow rate resulted in a mass loss by evaporation of around 10%. Initial experiments with μ -impinger showed loss of collecting solution that condenses into droplets at the top of the sampler. With the μ -impinger reconstructed with the glass fingers on the inner wall no further droplet formation was observed.

Response as a Function of the Sampled NO_2 Concentration and Flow Rate

The response of the μ -impinger to NO_2 concentrations in the ambient range was determined as a function of sampling flow rate. Fig. 4 shows the absorbance profiles resulting from the sampling of NO_2 in the concentration range from 15 to $70 \mu\text{g m}^{-3}$ for 30 min at different flow rates (from 25 to 100 mL min^{-1}). The results showed that a flow rate of 25 mL min^{-1} could only be used for concentrations exceeding $60 \mu\text{g m}^{-3}$.

When the sampling flow rate was doubled, the analytical signal increased by approximately 2.5-fold and 1.6-fold for NO_2 concentrations of 15 and $45 \mu\text{g m}^{-3}$, respectively. In complementary experiments, it was found that even at a concentration of $118 \mu\text{g m}^{-3}$ and a sampling flow rate of 50 mL min^{-1} , it was possible to sample the atmosphere for about 60 minutes, without loss of collection efficiency by the solution (Fig. 5).

Calibration Behavior

The μ -impinger operated most reliably at atmospheric NO_2 levels ranging from 15 to $200 \mu\text{g m}^{-3}$, using sampling for 30 min at a flow rate of 50 mL min^{-1} . Annual mean concentrations of NO_2 in urban areas worldwide are generally in up to 45 ppb ($90 \mu\text{g m}^{-3}$) (U.S. EPA, 2013).

Calibration was performed by a dynamic method, sampling

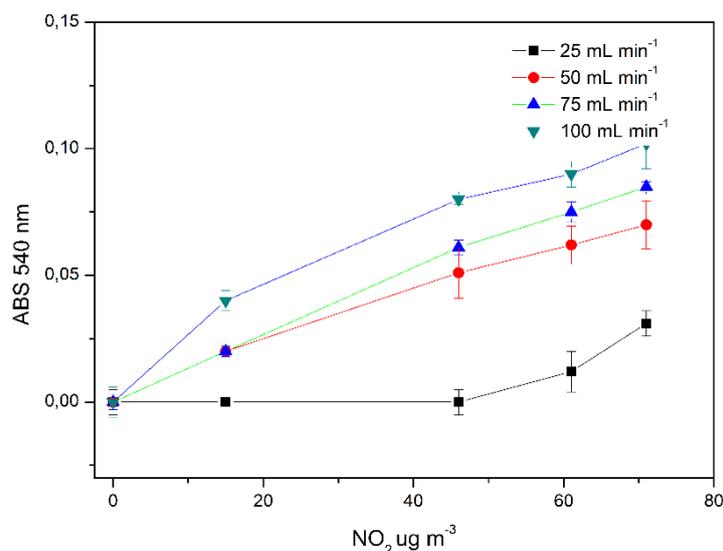


Fig. 4. Effect of sampling flow rate on the analytical signals for sampling during 30 min at flow rates of 25, 50, 75, and 100 mL min^{-1} , using NO_2 concentrations of 15, 46, 61, and $71 \mu\text{g m}^{-3}$.

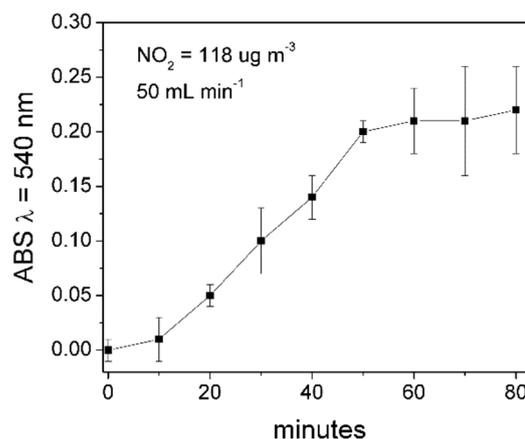


Fig. 5. Absorbance response as a function of sampling time, flow rate of 50 mL min^{-1} and NO_2 at $118 \mu\text{g m}^{-3}$.

a gas of known concentration in order to simulate the flow and reagent conditions encountered during normal operation. A calibration curve was plotted of the sampler response against the NO_2 concentration. Evaluation was made of the response of the sampler to NO_2 concentrations from 15 to $165 \mu\text{g m}^{-3}$. The sampling flow rate was 50 mL min^{-1} and the sampling time was 30 min. A linear relationship was obtained within the NO_2 concentration range evaluated, using seven samples with different concentrations, described by Eq. (1):

$$A_{(540 \text{ nm})} = 917 (\pm 25) \times 10^{-6} [\text{NO}_2, \mu\text{g m}^{-3}] + 0.006 (\pm 0.002) \quad (1)$$

where $A_{(540 \text{ nm})}$ is the absorbance at 540 nm and $[\text{NO}_2, \mu\text{g m}^{-3}]$ is the nitrogen dioxide concentration in $\mu\text{g m}^{-3}$. The detection limit, considering 3.3 times the standard deviation of the blank signal, was $14 \mu\text{g m}^{-3}$. For comparison purposes, with 100% gas collection efficiency (NO_2 concentration of

14 $\mu\text{g m}^{-3}$ is equivalent to 0.29 $\mu\text{mol m}^{-3}$) for 30 min of sampling by the 500 μL solution, it results in an equivalent concentration in NO_2 of about 1 $\mu\text{mol L}^{-1}$. This concentration is close to the recommended concentration limit for the spectrophotometric methods (Passaretti Filho *et al.*, 2015). To obtain a solution of the same concentration using the recommended method (Lodge, 1989), (0.4 L min^{-1} sampling flow and 10 mL of absorbent solution) the sampling time used would be 2.8 times greater. Therefore, μ -impinger not only reduces reagent use but also enables measurements with shorter sampling times. In this way, it can accompany changes of gas concentration in the atmosphere that is associated with human activities that change throughout the day. The analytical and performance parameters of the sampler are summarized in Table 1. Previous experiments suggested that other detection limit and the measurable NO_2 concentration range achieved using the method could be improved by using longer or shorter sampling times. The applicability of the method using other sampling times or flow rates would require calibration in the desired NO_2 concentration range.

The GS reagent has been widely used for the determination of NO_2 in air, and the interference of other compounds in this reaction has been investigated in detail (Harrison, 2012; Method 406 in Lodge, 1989). Interferences from most other gases usually present in polluted atmospheres are negligible, with the exception of sulfur dioxide. A 30:1 ratio of sulfur dioxide to nitrogen dioxide causes slow bleaching of the color of the dye formed and the color should be determined within 1 h. The addition of 1% acetone to the reagent before use retards the fading. Peroxyacetyl nitrate (PAN) gives 15–

30% an equivalent molar concentration of NO_2 , but the PAN concentration is too low to cause a significant error. The sampler was evaluated in outdoor samplings in the urban center of the city of Araraquara (São Paulo State, Brazil). The samplings were performed in parallel with a NO_x analyzer (Model 42iTL, Thermo Environmental Instruments, USA), which was installed at the same location and operated by the São Paulo State environmental control agency (CETESB). The inlet of the commercial NO_x analyzer was positioned adjacent to the sampler. Measurements were made on June 14, 2016. The values obtained with the two techniques (Table 2) showed good agreement, applying the paired test t was no statistically distinguishable the difference at the 95% confidence level.

CONCLUSIONS

A novel sampling system was developed and tested for the determination of NO_2 in air. The μ -impinger with chicanes (similar to those of a Vigreux-type condenser) into the central space of sampler, prevents the exit of droplets of the absorbent solution during the gas sampling and apparently improves the mixing between gas/solution by increases the interfacial area and therefore there is a gain in gas collecting. The results showed that the μ -impinger provided an efficient and repeatable collection of the gas and that the NO_2 concentrations obtained were in agreement with an official method. The μ -impinger sampler is inexpensive, straightforward, compact, and easily deployed for indoor or outdoor measurements.

An additional advantage of the method, compared to other

Table 1. Analytical parameters and performance of the proposed method.

Parameters	Values
Linear range	15–165 $\mu\text{g m}^{-3}$
Calibration equation	$A_{(540\text{ nm})} = 917 (\pm 25) \times 10^{-6} [\text{NO}_2, \mu\text{g m}^{-3}] + 0.006 (\pm 0.002) \text{ (SD} = 0.004)$
R^2	0.992
n	36
Limit of detection (3 \times SD of blank)	14 $\mu\text{g m}^{-3}$
Sampling time	30 min
Relative error (n = 10)	12.0%
Relative standard deviation (n = 10)	6.9%
Sampling solution volume	500 μL
Sampling flow rate	50 mL min^{-1}

Table 2. Comparative measurements using the proposed method and the NO_2 monitor (paired t-test).

Experiments	$\text{NO}_2 \mu\text{g m}^{-3}$		difference
	NO_2 (Proposed Method)	NO_2 (NO_x Analyser)	
1	31,0	30,0	1,023
2	16,0	16,5	–0,003
3	15,0	14,9	–0,079
4	14,0	12,5	1,500
		Average	0,610
		Standard Deviation	0,673
		t	0,453
		t_{labeled} (df = 3, Confidence level 95%)	3,182
			0,453 < 3,182

current sampling techniques, is the drastically reduced volume of solution used per measurement and limits of detection suitable to applications ranging from environmental to occupational health monitoring purposes. As a consequence, the sampling time can be shortened even at a concentration of about $15 \mu\text{g m}^{-3}$, which makes it possible to monitor changes in NO_2 concentration in time not longer than 30 min. The NO_2 concentration can be easily determined by measuring the absorbance of the solution at the end of the sampling period. The dye concentration in the solution can be obtained using a standard photometer or even by a simple visual image-based technique, similar to the one described previously (Passaretti Filho et al., 2015). While this method obviously cannot form the basis for continuous measurements of NO_2 in real time, it is nonetheless faster than many another chemical sampling/analysis procedures. It would also be possible to construct a simple LED-based photometer in order to perform in situ determinations (Dasgupta, et al., 1993). Therefore, the analyst can, according to his/her needs, select the most convenient way to determine the concentration of atmospheric NO_2 . The collection of gas by the solution in the μ -impinger depends on the dilution of the gas in the collection solution and subsequent gas fixation as a stable species via a chemical reaction. We believe that gases such as SO_2 and formaldehyde can be collected by the μ -impinger. Other gases are testing in this laboratory, and we hope to report on that in the near future.

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