



Versatile microanalytical system with porous polypropylene capillary membrane for calibration gas generation and trace gaseous pollutants sampling applied to the analysis of formaldehyde, formic acid, acetic acid and ammonia in outdoor air

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ABSTRACT

The analytical determination of atmospheric pollutants still presents challenges due to the low-level concentrations (frequently in the $\mu\text{g m}^{-3}$ range) and their variations with sampling site and time. In this work, a capillary membrane diffusion scrubber (CMDS) was scaled down to match with capillary electrophoresis (CE), a quick separation technique that requires nothing more than some nanoliters of sample and, when combined with capacitively coupled contactless conductometric detection (C^4D), is particularly favorable for ionic species that do not absorb in the UV–vis region, like the target analytes formaldehyde, formic acid, acetic acid and ammonium. The CMDS was coaxially assembled inside a PTFE tube and fed with acceptor phase (deionized water for species with a high Henry's constant such as formaldehyde and carboxylic acids, or acidic solution for ammonia sampling with equilibrium displacement to the non-volatile ammonium ion) at a low flow rate (8.3 nL s^{-1}), while the sample was aspirated through the annular gap of the concentric tubes at 2.5 mL s^{-1} . A second unit, in all similar to the CMDS, was operated as a capillary membrane diffusion emitter (CMDE), generating a gas flow with known concentrations of ammonia for the evaluation of the CMDS. The fluids of the system were driven with inexpensive aquarium air pumps, and the collected samples were stored in vials cooled by a Peltier element. Complete protocols were developed for the analysis, in air, of NH_3 , CH_3COOH , HCOOH and, with a derivatization setup, CH_2O , by associating the CMDS collection with the determination by $\text{CE-C}^4\text{D}$. The ammonia concentrations obtained by electrophoresis were checked against the reference spectrophotometric method based on Berthelot's reaction. Sensitivity enhancements of this reference method were achieved by using a modified Berthelot reaction, solenoid micro-pumps for liquid propulsion and a long optical path cell based on a liquid core waveguide (LCW). All techniques and methods of this work are in line with the green analytical chemistry trends.

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1. Introduction

Ideally, analytical techniques for the measurement of tropospheric species should exempt the use of sampling devices or preconcentrators, allowing the continuous monitoring of trace levels of gaseous pollutants with selectivity and sensitivity [1]. However, most current analytical techniques cannot fulfill these requirements for a huge number of species or demand too expensive and complex instrumentation, sometimes inappropriate for field use. Therefore, the most convenient alternative is to promote off-line sampling with preconcentration and to do the separation and determination of the analytes afterwards.

For sampling purposes, the use of membranes (porous, permeable or semi-permeable) at the interface between the flow donor (in this case, a gas) and the acceptor (a liquid phase) has advantages compared to the impingers, such as exclusion (filtration) of particulate matter, improved contact area/volume ratio and no aerosol formation due to bubble bursting. On the other hand, the membrane constitutes an additional barrier to overcome by diffusion or permeation, affecting the response time [2].

The membrane-based diffusion scrubber (DS) was first developed over two decades ago by Dasgupta, who used a Nafion tube as diffusion membrane [3]. The gaseous analyte, NH_3 , is collected as NH_4^+ at the outer hydrated surface of the polymer and this ion diffuses through the cation exchange lattice of the polymer, reaching the collector solution inside the tube.

Preconcentration becomes an additional requirement for the collection system as the concentration of the target species approaches the detection limit of the analytical technique. Favor-

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able Henry constants (e.g., formaldehyde sampling in deionized water) and displacement of chemical equilibrium of the species (e.g., the collection of the gaseous NH_3 as the soluble species NH_4^+ in acidic media) help to increase the collection efficiency and enrichment factors.

Diffusion scrubbers were employed for the sampling of carbonyl compounds followed by spectrophotometry or chemiluminescence determination [4,5]. In view of the low analyte concentrations in the atmosphere, chromatographic methods available for carbonyls are always preceded by a sampling step with preconcentration. The most widely used sampling procedure consists in aspirating air through silica gel or C18 cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) [6,7]. The carbonyl-hydrazones formed are then extracted in acetonitrile, and the analysis is usually performed by high performance liquid chromatography (HPLC).

Ammonia is the main atmospheric pollutant responsible for the neutralization of atmospheric acidity [8]. Ammonium salts are present in the inhalable fraction of the atmospheric particulate matter [9]. Sensitive and affordable methods for determining NH_3 are essential to improve the real-time resolution of atmospheric measurements. Traditionally, indophenol blue reaction [10] and Nessler's reaction [11] are employed in the photometric determination of NH_4^+ . In 1971, Roth [12] explored the ternary reaction of *o*-phthalaldehyde with ammonia and primary amines to produce intensely fluorescent products [13]. Ion chromatography (IC) is also favorable for ammonium determination, as well as the anions of acidic pollutants such as formic acid and acetic acid after an accumulation step [14].

Recently, membrane samplers have been directly coupled with miniature detectors for continuous gas measurement, a particularly attractive approach for field monitoring. Typically, they make use of chemical reactions that lead to the formation of absorbing or fluorescent species. These devices are comprised by a solid-state light source, e.g. light-emitting diode (LED) or laser, and a detector, such as a photodiode or miniature photomultiplier [15]. Higher sensitivity is obtainable by using a liquid core waveguide (LCW) long path cell made of Teflon AF tubing [16]. For chemiluminescence and photoluminescence detection, the Teflon AF tube is illuminated transversely instead of longitudinally. The simple design of the sampling device made it possible to manufacture flow through detectors where the light from the cell is coupled to a photodetector through an optical fiber [16].

Capillary electrophoresis (CE) is an alternative technique for the chromatographic analysis of air pollutants and environmental species [17]. In general, CE has lower sensitivity than HPLC or IC so that sampling with preconcentration is required for trace gas analysis. Although the most common detection mode for CE is based on UV–vis spectrophotometry, in the present study, conductivity detection (CD) was chosen, as it is a particularly attractive alternative for ionic compounds, specially the non-colored ones, otherwise demanding indirect UV detection. In this context, low-molecular-weight carboxylic acids (mainly formic and acetic acids) in rainwater and formaldehyde in air were successfully quantified before by CE with capacitively coupled conductivity detection (CE-C⁴D) [18–20].

At least one membrane sampling device for gases is commercially available (Global FIA, WA, USA) [21]. Although compact and robust, this relatively expensive unit was designed for sequential injection analysis or stopped flow injection analysis, with an internal volume of 100 μL for each 10 cm of membrane tubing, still oversized and non-optimized for association with techniques with very low sample volume needs like capillary electrophoresis (CE). A diffusion sampler based on a bundle of microporous capillaries, formerly proposed by the authors, is also oversized for CE [18] since few microliters of sample are sufficient for repeated CE

analysis (only a few nanoliters are introduced in the capillary by hydrodynamic or electrokinetic injection).

Development of sampling and determination methods for gaseous pollutants in air demands reliable gas standards for calibration, preferably in concentrations and conditions that satisfactorily emulate the environment under study. Compressed gas cylinders with a known concentration of the pollutant in a ballast gas such as nitrogen can be ordered for a number of species, while permeation tubes with constant-emission rates constitute an alternative for a limited range of volatile liquid or solid pollutants (eventually with expensive shipping costs). These devices require operation in rigorously thermostated cells, with accurate control of dilution gas flow and periodic check of the emission rate with a microbalance. Simple methods for gas generation exploiting evaporation or sublimation of known quantities of the compounds into a defined air volume (with sampling of the standard gas by headspace or continuous gas flow through systems) are also available as well as chemical reactions that conduct to stoichiometric amounts of the generated gas. In this paper, known concentrations of formaldehyde, acetic acid and formic acid were generated by emission from permeation tubes, as previously described [18]. For the production of a test gas with known trace concentrations of NH_3 a new generator is proposed: a capillary membrane diffusion emitter device (CMDE), in which the gaseous NH_3 , produced by deprotonation of NH_4^+ in a solution flowing along the porous tube, diffuses through the pores and is diluted in a gas flow (inert gas or purified air).

Based on the favorable experience with capillaries that have a high density of sub-micrometric pores, which favors collection efficiency and rejection of solid particulate matter from the air, a new complete and inexpensive microvolume gas sampling system was developed, comprising flow propulsion and a sample cooling unit, particularly suited for association with CE analysis. Once the operational parameters were defined, the applicability of the capillary membrane diffusion scrubber (CMDS) was demonstrated for the sampling of NH_3 , formaldehyde, acetic acid and formic acid, followed by separation and determination of anionic compounds in liquid phase (formate, acetate and hydroxymethanesulfonate—an adduct produced by derivatization of formaldehyde with bisulfite) or cationic species, mainly ammonium, by CE-C⁴D.

Generally, conventional spectrophotometric determinations, coupled or not with flow methodologies, present lower detection limits (LDs) than CE-C⁴D [22]. Most commercial UV–vis spectrophotometers are designed for cells with optical paths no longer than 10 cm, although instruments coupled with optical fibers do not have this restriction, being particularly suitable for operation with long optical paths obtainable with liquid core waveguides (LCW) [23]. In the present study, a 100-cm long LCW was used for NH_3 determination based on a modification of Berthelot reaction, with liquid propulsion automated by solenoid micro-pumps. The analytical features of this methodology were compared with the CE-C⁴D for the determination of ammonia in air sampled with the CMDS.

2. Experimental

2.1. Chemicals and solutions

All reagents used were of analytical grade. Acetic acid, formic acid, formaldehyde, N-cetyl-N,N,N-trimethylammonium bromide (CTAB), 18-crown-6 and 2-[N-morpholino]ethanesulfonic acid (MES), sodium sulfite, sodium hydroxide and ammonium chloride were supplied by Merck (Darmstadt, Germany). L-Histidine (His) was from Sigma Chemical Co. (St. Luis, MO, USA).

Running buffers and standards were prepared daily by dilution of 0.1 mol L⁻¹ stock solutions with deionized water (NANOpure UV, Barnstead/Thermolyne Co., IA, USA). The buffer optimized

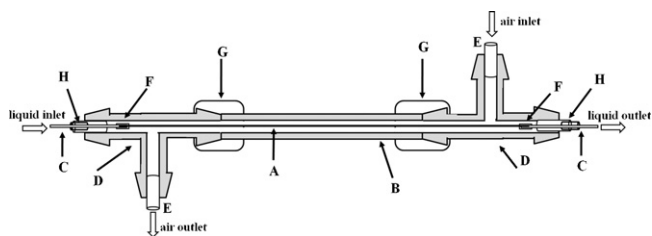


Fig. 1. Capillary membrane diffusion scrubber (schematic cross section): (A) monofilament of Oxyphan® polypropylene porous capillary tube (387 μm O.D., 50 cm long and 0.2 μm pores); (B) Teflon® tube (40 cm, 5 mm I.D.); (C) microbore Tygon® tube (0.79 mm O.D., 0.4 mm I.D., 4 cm long); (D) polyethylene T-connector; (E) silicone bushing (4 mm I.D. tube, 1 cm long) for pressure-fitting of the PTFE tubing of sample air inlet or outlet to membrane pump; (F) silicone tube connector (0.8 mm I.D., 1 cm long); (G) silicone tube connector (5 mm I.D., 1 cm long); (H) silicone bushing (5 mm O.D. tube on a 2 mm O.D., 0.2 mm I.D. tube, 1 cm long).

for the analysis of anionic compounds by CE- C^{4}D was MES/His 20 and 0.2 mmol L^{-1} CTAB for electroosmotic flow inversion (pH = 6.0). Ammonium determination by CE- C^{4}D was performed in 20 mmol L^{-1} MES/His electrolyte (pH = 6.2) [19].

The experiments were conducted at room temperature or under controlled temperature when required.

2.2. CMDS and CMDE construction

The capillary of polypropylene microporous membrane Oxyphan® type PP50/280 (MEMBRANA, Wuppertal, Germany) has external, internal and mean pore diameters of 387 μm , 280 μm and 200 nm, respectively. This hydrophobic hollow fiber membrane is particularly favorable to the efficient absorption of gases due to a high density of $\sim 200\text{ nm}$ pores and a high ratio between the diffusive collection area and the volume of acceptor liquid contained in the capillary.

A capillary tube of 50 cm length, presenting an internal volume of about 30 μL , was mounted coaxially in a PTFE tube (I.D. = 5 mm), as shown in Fig. 1. Two polyethylene T-connectors were firmly attached to the PTFE tube using pressure fitted silicone rubber pieces (5 mm I.D., 1 cm long). The inlet and outlet ends of the porous capillary were connected to Tygon® microbore tubes (4 cm, 400 μm I.D.) by using silicone tubing (800 μm I.D., 1 cm long) as hose. These Tygon® tubes were sustained near the ends of the T-connectors by annular bushings made from silicone tube pieces.

2.3. Low flow rate pneumatic impeller

Borosilicate glass bottles, reference 21806-245 (Schott Duran, Stafford, UK), with 100 mL volume and a large and tight cap, were used as liquid's reservoirs. The cap of the bottles was perforated for the introduction of two polypropylene tubes (2 mm I.D.); one for the liquid outlet and the other for pressurization with a low cost aquarium air pump (Betta®, Brazil). This device was capable of maintaining a constant pressure close to 4 psi (0.28 bar) for long periods, generating maximum outcoming flow rates of 12.5 mL min^{-1} through 100-cm long 0.8 mm I.D. tubing [24]. A polyimide coated silica capillary like the one used in CE (50 μm I.D. and 20 cm long) was connected in series with the supplying polyethylene tube as a hydrodynamic resistor to drastically restrain the flow rate; a needle valve was added for fine adjustment of the liquid flow rate to 1.0 $\mu\text{L min}^{-1}$.

During sampling, air was aspirated through the collector with another aquarium membrane pump. The flow rate was read on a rotameter model N112-02 (Cole-Palmer, IL, USA) and adjusted with a pinch valve. The flow rate readings of the factory calibrated rotameter were periodically checked against a digital flowmeter

model ADM2000 (Agilent, CA, USA) and, once a year, confirmed against a displacement device in which the volume of water drawn-out by the gas was accurately collected and weighted.

2.4. CH_3COOH standard test gas generator

The efficiency of the sampling system was evaluated using a standard atmosphere generator based on volatilization of CH_3COOH through a permeation membrane. A volume of 500 μL of glacial acetic acid was introduced in a 1.5 mL glass vial, covered by a silicone septum held in place by a perforated plastic screw cap. This vial was introduced in a 100 mL Schott Duran flask with a perforated cap to provide inlet and outlet gas lines made from thick walled polytetrafluoroethylene (PTFE) tubing. The flask was thermostated at $30.0 \pm 0.5^\circ\text{C}$ in a water bath. Nitrogen was fed to the flask with the permeation tube at flow rate of 350 mL min^{-1} . The flask was weighed every 24 h and an emission rate of 6.0 $\mu\text{g min}^{-1}$ of acetic acid into the gas stream was determined using the measurement of mass loss. A concentration near $3 \times 10^{-7} \text{ mol L}^{-1}$ of gaseous CH_3COOH was delivered by the system. The CMDS was connected to the generator output, directly or after extra dilution with N_2 . Dilution ratios and air sampling flow rates were controlled with needle valves and flowmeters. All flowrates were periodically checked as described in Section 2.3.

2.5. CMDE for NH_3 gas standard generation

The construction of the new system for in situ standard NH_3 gas generation is similar to the CMDS, with the difference that it is continuously fed with merging flows of NH_4Cl and NaOH solutions that react producing the volatile ammonia, emitted into the gas flow through the membrane pores, thus acting as a generator or capillary membrane diffusion emitter, CMDE.

The emission rate was calculated from the known flow rates of incoming NH_4Cl and NaOH solutions and the concentration of NH_4Cl , since NaOH is in great excess (0.1 mol L^{-1} NaOH), thus assuring quantitative displacement of the equilibrium to the formation of NH_3 , released through the membrane pores. The final concentration of ammonia in the gas flow is defined by the carrier gas flow and the emission rate. The effects of the variation of gas and liquid flow rates were evaluated in order to find the best conditions for ammonia collection.

A Schott Duran flask was used as reservoir for the ammonia solution and a polypropylene flask for the alkali. The cap of each flask was perforated to allow the introduction of two polyethylene tubes (2 mm I.D.). An aquarium air pump was used for simultaneous propulsion of the liquids. A polyethylene T-connector was attached to the air pump outlet with the help of a pressure fitted silicone rubber (5 mm I.D., 1 cm long). Each T-connector outlet was joined to the flasks by a 10 cm polyethylene tube (3 mm I.D.) bushed with silicone rubber pieces (3 mm I.D., 1 cm long). The solutions were propelled to a T-confluence followed by a reaction coil (0.8 mm I.D., 50 cm long). The mixture was directed to a 50 cm length CMDE. The generated NH_3 passed through Oxyphan® pores and was dragged out by an air flow, maintained by a membrane aquarium pump or by a nitrogen flow, both at 150 mL min^{-1} . The NH_3 concentration in the gas phase can be adjusted either by changing the concentration of the stock solutions or by varying the outflow of the carrier gas (air pump or purge gas from a cylinder). The output flow of the CMDE with known NH_3 concentration was connected to the CMDS directly or after extra dilution with N_2 . Dilution ratio was controlled with two needle valves and two flowmeters. The CMDS was fluxed with diluted HNO_3 solution (pH = 4) for fixation of ammonia as the non-volatile species NH_4^+ .

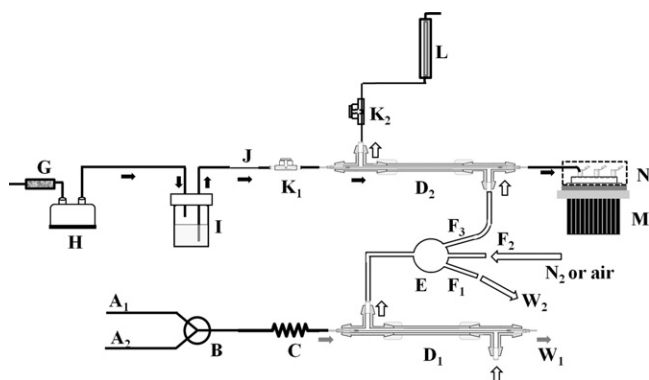


Fig. 2. System for standard NH_3 generation/ NH_4^+ sampling: A_1 and A_2 – flasks with NH_4Cl and NaOH solutions, each connected to a low volume pneumatic impeller; B – acrylic T-confluence; C – 50 cm long polyethylene coil; D_1 – CMDE and D_2) CMDS; E – mix chamber; F_1 , F_2 and F_3 – outlet tubes; G – activated charcoal cartridge; H – aquarium pump; I – Schott bottle containing the acceptor solution ($0.1 \text{ mmol L}^{-1} \text{ HNO}_3$); J – silica capillary covered by polyimide ($50 \mu\text{m}$ I.D., 20 cm long); K_1 and K_2 – flow control pinch valves; L – calibrated rotameter; M – 96-well block Peltier cooler for $200 \mu\text{L}$ PCR vials, fed with 12 V DC; N – styrofoam box; W – drainage waste.

2.6. Refrigerated multi-sample collection and storage device

A Peltier cooler coupled to a 96-well polymerase chain reaction (PCR) plate model CP 1435 (TE Technology Inc., MI, USA) was adapted for refrigeration and insulation of the tubes during and after sampling. The cold plate of the Peltier element, with the sample vials, was enclosed in a styrofoam box. Temperatures were measured with an integrated circuit LM35 (sensitivity of $10 \text{ mV}/^\circ\text{C}$) connected to a digital voltmeter. When the Peltier element is supplied with 12 V, a temperature 14°C below the room temperature is maintained inside the sample vials. A sketch of the complete air collection system is shown in Fig. 2. The volumes of the collected acceptor phase were determined by weighing the polypropylene tubes before and after sampling with the CMDS. If not promptly evaluated, samples were stored in a freezer (-15°C) and thawed immediately before injection in the CE- C^4D equipment.

2.7. CE- C^4D equipment and description of the analysis method

The complete CE equipment interfaced to a microcomputer, including a capacitively coupled contactless conductivity detector (C^4D) was built in the laboratory by do Lago and coworkers, and full details of the construction and performance are presented elsewhere [25–27]. The fused silica capillary ($75 \mu\text{m}$ I.D., $375 \mu\text{m}$ O.D.) was from Agilent Technologies (São Paulo, Brazil). The total length of the capillary was 65 cm and the effective path from the inlet to the C^4D was 55 cm long. The capillary was conditioned by the following sequence of 20 min flushes: (i) $0.1 \text{ mol L}^{-1} \text{ NaOH}$; (ii) water; and (iii) running electrolyte. Before the first injection, high voltage (-25 kV) was applied for approximately 20 min. The capillary was flushed between runs with electrolyte solution for 2 min. The introduction of samples in the capillary was done by hydrodynamic injection (9.8 mbar for 30 s) by pressure reduction at the detection end of the capillary with a membrane pump. The detector was operated at 550 kHz. All data were processed with the commercial program Origin[®] 8.0 Pro (Microcal, Northampton, MA, USA).

2.8. Determination of NH_3 by the indophenol blue method

The results for ammonia concentration in the air obtained by CMDS sampling and CE- C^4D determination were compared with those obtained with the reference method for NH_3 consisting in bubbling the air in an impinger containing nitric acid solution ($\text{pH}=4$) followed by the spectrophotometric determination

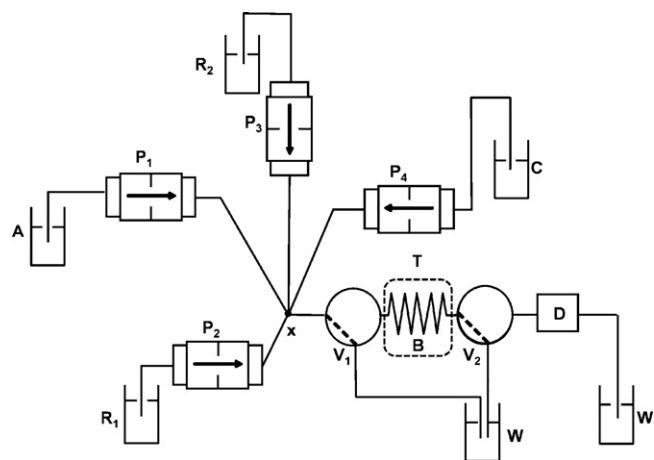


Fig. 3. Flow diagram of the system for spectrophotometric ammonium determination. P_1 – P_4 – solenoid micro-pumps; V_1 , V_2 – three-way solenoid valves; S – sample; C – carrier stream; R_1 – sodium nitroprusside and sodium salicylate; R_2 – sodium hypochlorite in NaOH ; B – 25 cm long polyethylene coil; T – thermostated water bath; D – spectrophotometer (624 nm); X – Perspex joint point; and W – waste vessel.

using Berthelot reaction, which comprises ammonium, phenol and hypochlorite in alkaline media, in the presence of sodium nitroprusside as catalyst [28].

The ammonia sampling for spectrophotometry was made bubbling air in an impinger containing 5 mL of HNO_3 (0.1 mmol L^{-1}) at an outflow of 1 L min^{-1} for 1 h. The samples were frozen at -15°C and thawed at the moment of the determination.

The chromogenic reagent was prepared with 10 mmol L^{-1} of phenol, solubilized in 50% (v/v) of analytical grade ethanol and in 50% alkaline oxidant solution. The oxidant contained sodium citrate, NaOH and sodium hypochlorite and was prepared on a daily basis adding 20 mL 0.5 mol L^{-1} sodium citrate (adjusted with NaOH to $\text{pH} \sim 12$) to previously standardized 5 mL of NaOCl ($\sim 5 \text{ mmol L}^{-1}$). After the addition of the reagents, the samples were protected against ambient light for at least 30 min. The spectrophotometric determinations were performed in a diode array equipment model 8452A from Hewlett Packard (now Agilent), measuring the absorbance at 624 nm.

2.9. Improved spectrophotometric determination of NH_3 based on solenoid micro-pumps and liquid core waveguide

The modified Berthelot reaction with salicylate was exploited for the ammonia determination (in the NH_4^+ form). Reagent R_1 was prepared with 3 mmol L^{-1} sodium salicylate and 0.8 mmol L^{-1} sodium nitroprusside. Reagent R_2 was a solution containing 0.5 mmol L^{-1} sodium hypochlorite and $25 \text{ mmol L}^{-1} \text{ NaOH}$ [29]. A thermostated water bath was assembled with a mercury contact thermometer coupled to a relay that delivers power to a heating element (60 W, 110 V). The reaction coil, the heater and temperature controller were immersed in water contained in a 450 mL capacity aluminum can, thermally shielded with bubble plastic and Styrofoam. Once the bath reached the setting temperature, the voltage was reduced from 110 to 30 V with a variable transformer model 171 (Variat, ISE Incorporation, OH, USA), to reduce power dissipation and minimize on/off temperature fluctuations. Water bath temperatures varying from 25 to 70°C were evaluated for flow injection measurements.

The spectrophotometric determination of NH_3 was performed according to the flow system depicted in Fig. 3. The system was composed by four solenoid micro-pumps, 090SP model (Biochem Valve Inc., Boonton, NJ, USA), with $12 \mu\text{L}$ (P_1 , P_2 and P_3) and $7 \mu\text{L}$ (P_4)

nominal volume per pulse, two solenoid valves (V_1 and V_2) (NResearch, West Caldwell, NJ, USA), 0.7 mm I.D. polyethylene tubes and Perspex joint points. The control software was developed in Visual Basic® 6.0 (Microsoft, Redmond, WA, USA) and the software supplied by the manufacturer of the multi-channel spectrophotometer was used for data acquisition. The solenoid micro-pumps and valves were controlled through a parallel port of the micro-computer by using a power drive based on a ULN2803 integrated circuit. A Pentium I microcomputer was used for system control and data acquisition. Spectrophotometric measurements were carried out with a multi-channel charge-coupled device (CCD) spectrophotometer model USB2000 (Ocean Optics, Dunedin, FL, USA) with a tungsten-halogen light source model LS-1. Optical fibers (100 or 600 μm) were used to transmit the radiation and 100 cm optical path LCW flow cell model LPC-1 (250 μL internal volume, 0.55 mm I.D.) was employed to increase sensitivity.

The binary sampling approach [30] was adopted for solution handling. Small aliquots of the solutions were inserted in tandem into the analytical path, generating a sampling profile that was repeated until completing the programmed number of sampling cycles. The volume of each solution was defined by the programmed number of pulses of the corresponding micro-pump.

The analytical cycle was started by pumping sample and reagents through P_1 , P_2 and P_3 pumps (3, 3 and 1 pulses, respectively) in a sequence that was repeated eight times to form the sample zone. After stopping the flow in the heated reaction coil (20 s at 60 °C), the sample zone was displaced into the LCW by actuation of P_4 with continuous absorbance monitoring at 624 nm. The analytical signal was based on peak height and measurements were taken in triplicate.

Valves V_1 and V_2 are shortcuts to the waste used to speed-up sample change. To fill the system with a new sample, valve V_1 was switched on while pump P_1 was actuated (100 pulses). Pump P_4 was then actuated (50 pulses) to clean the entire circuit with carrier from the merging point, including the LCW, with valves V_1 and V_2 on.

2.10. Sampling site

The site of Cidade Universitária, located in the southwestern area of São Paulo (latitude = -23.564° ; longitude = -46.726°), is potentially impacted by primary and secondary pollution sources. The campus is a green area located in the very center of the metropolitan area, comprising 6 million vehicles as main emitters, besides industrial ones. At this site, sampling took place at the Instituto de Química building, about 6 m above ground level and ~ 2 km apart from a major 15-lane highway with heavy vehicle traffic fueled by gasohol (gasoline with 25% of ethanol), diesel and ethanol.

3. Results and discussion

3.1. Evaluation of the CMDS system

Scaling-down of the previously described diffusive sampling device comprising a bundle of hollow microporous capillaries of Oxyphan® with ~ 900 μL of acceptor phase capacity [18] was conducted carefully and creatively, in order to preserve and improve attractive features, while closer matching the sample volume with the low demands of CE- C^4D (< 100 nL/injection).

Although the combination of the bundle CMDS with CE- C^4D has been successfully applied to the analysis of formaldehyde in the urban atmosphere [18] and not before to acetic acid, this molecule was chosen for most evaluations that will be discussed later. Acetic and formic acids have been sensibly and selectively analysed by CE-

C^4D directly in rainwater [19], a matrix that contains many other species.

The mass transfer rate Q (mol min^{-1}) of the analyte through the membrane surface S (m^2), under gas flow rate F_g ($\text{m}^3 \text{min}^{-1}$), can be expressed by the mass transfer efficiency, f (from 0 to 1), and the equation of state with the gas temperature T (K), atmospheric pressure P (Pa), concentration of the analyte in the gas phase (C_g) and the gas constant R ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) [2]:

$$Q = \frac{SPF_g f C_g}{RT} \quad (1)$$

Therefore, at low F_g , Q is almost proportional to F_g as long as the supply of gas molecules to the membrane surface is the rate-determining step (constant f). Above a given F_g , f starts to decay until a limiting value is reached, dictated by the gas permeation rate through the membrane [2].

Generally, the concentration of the analyte in the acceptor solution, C_s , is determined after collection, as it is the case here. C_s can be expressed as the ratio between the mass transfer rate Q and the flow rate of acceptor solution, F_s or the volume of the solution V_s inside the capillary at stopped flow. Therefore, a lower F_s renders a higher preconcentration factor; since the volume required for CE is very low, this can be attained with a short monofilament capillary.

In order to decrease the temperature dependence of the sampling procedure, operation under high collection efficiency conditions ($f \geq 0.8$) is recommended to deplete the analyte from the incoming flow during the residence time in the sampler. For a given geometry of the device, specially the diameters of the concentric tubes and their lengths, there is a minimum residence time of the gaseous stream in the sampler (or maximum flow rate of the gas) to attain the quantitative depletion of the analyte. This species reaches the capillary surface by diffusion and convection, and then travels diffusively through the nanochannels of the membrane wall to reach the gas/liquid interface where it is dissolved (considering a sticking coefficient close to one and a high Henry's coefficient, or displacement of a chemical equilibrium).

To find out the required area of the gas/liquid interface, with the purpose of assuring high collection efficiency at certain flow rates, various lengths of polypropylene capillary and coaxial PTFE pipe were evaluated as a function of the internal surface area of the membrane filament, given by $2\pi rL$ (L = length of the capillary; r = inner radius of the Oxyphan® capillary, ca. 140 μm). The large exposed interfacial area/internal volume ratio favors the preconcentration of the gaseous species in the liquid phase, so that a 50-cm long capillary (about 6 cm^2 of surface area and 30 μL internal volume) presents a collection efficiency greater than 95% ($f \geq 0.95$) for CH_3COOH from a gas stream of 150 mL min^{-1} .

The gas flow rate effect on f has been evaluated in the range of 45–400 mL min^{-1} , at constant acceptor flow of 1.0 $\mu\text{L min}^{-1}$ and a fixed CH_3COOH inflow of $3.0 \times 10^{-11} \text{ mol min}^{-1}$, obtained by suitable dilution of the gas stream from the constant-emission permeation source. This results in an acetic acid concentration of nearly 30 $\mu\text{mol L}^{-1}$ in the liquid acceptor phase for an unitary f , convenient for precise CE- C^4D determination. In the region from 150 to 200 mL min^{-1} , the determined collection efficiency f was of 1.0 ± 0.05 , declining steadily by increasing the flow rate. Due to the simultaneous variation of the CH_3COOH concentration in an inversely proportional fashion, there could be some combined effect of the two parameters on the f decay above 200 mL min^{-1} . Therefore, at a fixed flow rate of 150 mL min^{-1} , the effect of the analyte concentration in the gas phase was evaluated and a linear relation with the CE- C^4D peak area was observed, with nearly null intercept. At the chosen optimum flow rate of 150 mL min^{-1} for a 50 cm long capillary membrane, the average residence time of the air in the sampler is quite short, 5.2 s, but still sufficient to collect

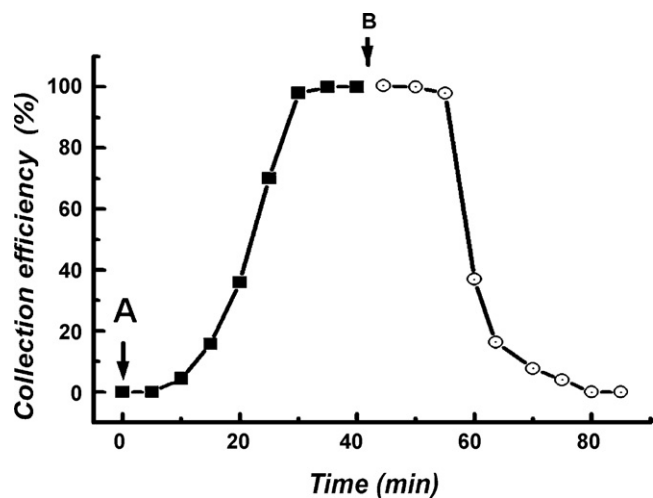


Fig. 4. Evaluation of the response time of the capillary microporous polypropylene sampling system with a $20 \mu\text{L}$ transfer line to the sample vial. A – $6.0 \mu\text{g min}^{-1}$ of CH_3COOH in air at 150 mL min^{-1} ; B – N_2 flux, 150 mL min^{-1} . Collection in deionized water at flow rate of $1.0 \mu\text{L min}^{-1}$.

the analytes quantitatively. The high overall efficiency of the system ($>95\%$) is an ideal condition for the sampling process, because there is no need to determine a temperature and flow rate dependent f by calibration and use it afterward.

The response time of the CMDS device to a sudden change in the analyte concentration in the gas phase was also evaluated. A diluted CH_3COOH /air solution flow was established with the standard atmosphere generator at a flow rate of 150 mL min^{-1} ; the blank consisted of nitrogen at the same flow rate. The microporous capillary was filled with deionized water and, after switching from N_2 to the standard atmosphere of CH_3COOH , aliquots of acceptor were collected every 5 min. After a 40 min sampling period, the flow was switched back to N_2 while the fraction collection at 5 min intervals was maintained. Fig. 4 illustrates the efficiency of CH_3COOH collection during the exposure and the signal decay with N_2 purge. The samples of about $5 \mu\text{L}$ each were collected in $200 \mu\text{L}$ PCR vials on the Peltier refrigerated plate and stored afterwards in a freezer until analysis by CE- C^4D .

At the given operational conditions, the electropherogram of the second collected fraction after exposure to gaseous CH_3COOH (average period of 7.5 min) presented a 10% signal raise and the fraction corresponding to 27.5 min, reached 95% of the maximum signal. A similar profile was observed for the decay under N_2 flow, with 5% of the full signal remaining after 22.5 min.

For the very low flow rate of the acceptor phase used ($1.0 \mu\text{L min}^{-1}$), taking into account the internal volume of the filament ($\sim 30 \mu\text{L}$), the expected residence time of the liquid is 30 min. The outlet tubing (from the end of the porous capillary to the vial) presents a dead volume of about $20 \mu\text{L}$, indicating that it is the determining factor of the time lag of the sampler. Subtraction of this 20 min transit time from the results of Fig. 4 reveals that the gas/liquid equilibrium is established quite rapidly inside the sampler.

As soon as the analyst acquires the necessary skills to handle the microporous capillary, it will take half an hour to put up a sampler in the laboratory. The sampler is well suited for long-lasting use. However, after one month of use in air with an average ozone concentration of $0.1 \mu\text{g m}^{-3}$, as it is the case in São Paulo metropolis, the microporous membrane may loose mechanical strength and need replacement.

Regarding the sample preservation by refrigeration of the vials during the collection followed by freezing until the moment of use, no loss in the electrophoretic signal was noticed in the comparison

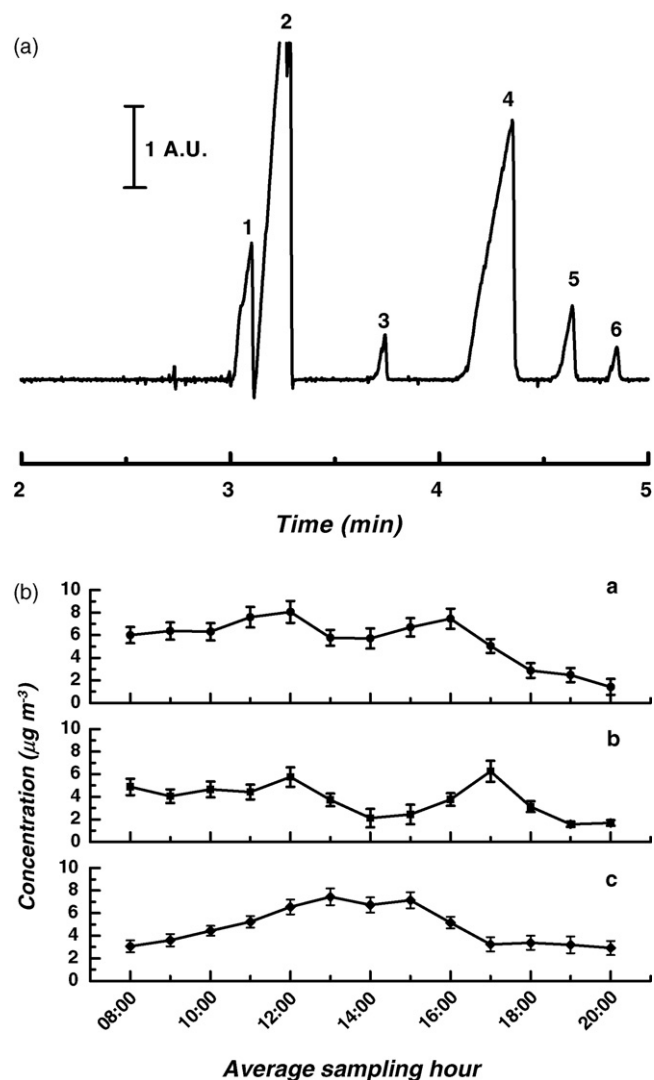


Fig. 5. (a) Electropherogram of air sample collected at October 28th 2006, in CMDS followed by CE- C^4D determination. Operational conditions: air collection in deionized water (flow rate of $1.0 \mu\text{L min}^{-1}$) for 1 h with air outflow of 150 mL min^{-1} . Electrolyte 20 mmol L^{-1} MES/His, 0.2 mmol L^{-1} CTAB. Silica capillary ($75 \mu\text{m I.D.} \times 65 \text{ cm}$), potential -25 kV , hydrodynamic injection (9.8 mbar , 30 s), C^4D frequency 550 kHz . Samples injected in triplicate in the CE- C^4D : (1) Cl^- ; (2) SO_4^{2-} ; (3) HCOO^- $34.4 \pm 2.7 \mu\text{mol L}^{-1}$; (4) HSO_3^- ; (5) HMS^- $26.5 \pm 3.0 \mu\text{mol L}^{-1}$; (6) CH_3COO^- $28.7 \pm 1.9 \mu\text{mol L}^{-1}$; (b) concentrations of the target compounds in the gaseous phase of the atmosphere during a 12-h sampling period; error bars indicate SD of triplicate determinations: a – CH_2O (as HMS^-); b – HCOOH ; c – CH_3COOH .

of the results of samples analysed immediately or some weeks after storage in the freezer.

3.2. Determination of HCOOH , CH_2O and CH_3COOH in atmospheric air

Air samples were collected with the CMDS device on October 28, 2006 from 8:00 to 20:00 h, outdoors, near the Instituto de Química building. The Peltier cooled sampling vials were changed every sampling hour, capped and, after a working period (6 h or so), stored in a freezer for preservation. Immediately before determination by CE- C^4D , the samples were defrosted, each one in its turn, and treated with $100 \mu\text{L HSO}_3^-$ (5 mmol L^{-1}) to allow the detection of formaldehyde by CE- C^4D in the form of the stable adduct hydroxymethanesulfonate (HMS^-). Fig. 5a illustrates an electropherogram of an air sample collected at 17:00 h.

The concentrations of the three analytes in the collected samples were determined by using calibration curves covering the range of 3–50 $\mu\text{mol L}^{-1}$ of each (responses are linear up to at least 1 mmol L^{-1}). From the known volume of collected sample, the number of moles of the analytes absorbed in the CMDS was calculated and converted in atmospheric concentrations by taking in account the volume of air aspirated during the sampling time (measured with the calibrated flowmeter). Regarding the detection and quantitation limits of the analytical methods, for formic acid, acetic acid and derivatized formaldehyde in the liquid phase, the estimated LDs were 0.8, 1.5 and 1.0 $\mu\text{mol L}^{-1}$, with a confidence level of 99%. These values correspond, respectively, to 1.0, 3.0 and 0.9 $\mu\text{g m}^{-3}$ of the species in air. The quantitation limits (LQs) for HCOOH, CH₃COOH and CH₂O were calculated as 3.3, 10.0 and 3.0 $\mu\text{g m}^{-3}$, respectively (considering ten times the standard deviation of the blank measurements).

During the 12 h of air sampling, HCOOH, CH₃COOH and CH₂O (in the form of HMS) showed variations in the interval from 1.9 to 6.3, 3.1 to 7.1 and 1.4 to 8.0 $\mu\text{g m}^{-3}$, respectively, as it can be seen in Fig. 5b. For this clear spring day, the concentrations oscillated around the lower ends of the reported concentration ranges of these analytes in an urban atmosphere, e.g., in Brazil [31,32], respectively, 6–190, 5–80 and 4–90 $\mu\text{g m}^{-3}$. While the LQs for formaldehyde and formic acid are adequate for these ranges, at sites with acetic acid concentrations always near the lower end of the range (as observed on the single sampling day of Fig. 5b), the LQ can be improved by lowering the acceptor flow rate of the sampler and/or by injecting larger volumes of sample in the CE, what is feasible because the peaks 3, 5 and 6 of Fig. 5a are very well resolved.

Even in lower concentrations, the formaldehyde profile along the day was very similar to those shown in the literature [31,33–37]. Correlation between formaldehyde and formic acid concentrations is apparent during sampling in a sunny day, with the second species concentration rise being delayed about 1 h, suggesting the photochemical production of the carboxylic acid from the aldehyde. Certainly, more data is necessary to give support to such assumption, which is outside the scope of this work, but can now be conveniently investigated with the new microsystem in combination with CE-C⁴D.

3.3. Determination of NH₃ by CE-C⁴D and evaluation of the CMDE

As NH₃, collected in the protonated form in the aqueous acidic media, is the major species present in tropospheric air, to use a long CE separation path is a waste of time. Thus, the C⁴D detector can be placed 10 cm after the injection tip, so that the NH₄⁺ peak is recorded in less than 1 min of run, a strategy adopted in this work. Just in case other amines are present at detectable concentrations, the C⁴D detector must be repositioned as far as possible from the injection point to increase the resolution.

The injection of NH₄⁺ standards in the CE-C⁴D showed a wide linear response range from 5 to 1.5 mmol L^{-1} . The LD was calculated as 1.2 $\mu\text{mol L}^{-1}$, with a confidence level of 99%, corresponding to about 0.7 $\mu\text{g m}^{-3}$ of this species in air at the operational condition described in the experimental part. The repeatability of peak areas was very good, with 10 consecutive injections of NH₄Cl standard solution (20 $\mu\text{mol L}^{-1}$) with a relative standard deviation (RSD) of 3.0%.

The generated concentration of NH₃ was calculated as a function of the liquid outflows and the concentration of ammonium chloride (the NaOH solution was in excess to guarantee the quantitative formation of the volatile species). The collection efficiency was calculated through the comparison of the number of moles of NH₃ emitted with the one determined after the analysis by CE-C⁴D.

Variable concentrations of NH₃ from the generation system were collected in the CMDS device and the acceptor liquid was anal-

ysed by CE-C⁴D. The collection of the generated gas, made in HNO₃ solution (pH = 4.0), showed an efficiency greater than 95% for NH₃ with outflows of 1.0 $\mu\text{L min}^{-1}$ and 150 mL min^{-1} for acceptor solution and sampled air, respectively. The gas phase calibration curve showed a linear response from 5 to 100 $\mu\text{mol L}^{-1}$. The narrower concentration range is attributable to the decrease of the acidity of the acceptor solution with the continuous absorption of higher concentrations of gaseous NH₃, compromising the collection efficiency along the sampling period (e.g., 100 $\mu\text{mol L}^{-1}$ of NH₃ raises the pH of the acceptor solution to 6.9). A more acidic acceptor solution would assure highest sampling efficiencies at upper NH₃ levels, but is not advisable at the lowest analyte levels due to an increased background signal in the CE-C⁴D determination.

No detectable signal of NH₄⁺ was observed by CE-C⁴D in samples taken from the alkaline solution outflow of the CMDE, indicating almost quantitative emission of ammonia in the generation system, even though the Henry's constant is relatively high ($\sim 60 \text{ mol L}^{-1} \text{ atm}^{-1}$).

3.4. Determination of NH₃ in atmospheric air

The collection of NH₃ with the CMDS device does not require the use of particulate matter filters for the removal of salts containing NH₄⁺ once the nanometric pores of the polypropylene membrane act as a barrier. This is a clear advantage in comparison with impingers or reactant impregnated filters, where the use of pre-filters is required and might cause the formation of artifacts during the sampling step [38,39]. The improvement of the interfacial contact area/volume of acceptor ratio solution also represents an advantage of the CMDS device in comparison to impingers with regard to the preconcentration ability.

Denuder collection significantly reduces the problem of artifacts formation because the partition equilibrium between NH₃/NH₄⁺ is not disturbed. However, the residence time of species within the diffusion device should be as short as possible (in the order of a few tenths of second) [40]. The requirement of solvent elution of the analytes after collection, followed by the disposal or laborious regeneration of the sampling device and the need of large number of denuders for time resolved measurements are drawbacks in comparison with the CMDS.

Air samples were collected with the CMDS on July 3rd 2007 over the period from 8:00 to 20:00 h outdoor near the Instituto de Química building with 1-h sampling times. Fig. 6a shows the electropherogram of the 14:00–15:00 h sample. Collections with the impinger containing acidic solution were simultaneously performed. The samples were quantified at the same day by both CE-C⁴D and spectrophotometry. The methodologies yielded consistent values for the concentration of NH₃ in the air within the experimental error, considering a confidence interval of 95%, as it can be seen in Fig. 6b.

As mentioned, with NH₃ as the most abundant gaseous alkalinizing species in the outdoor air, along with alkyl-amines at much lower levels, the selectivity of spectrophotometric methodology is acceptable for the determination of gaseous ammonia after preconcentration in acidic media.

Table 1 shows the comparison of the analytical features between the reference method, the spectrophotometric determination with LCW and solenoid micro-pumps and the CE-C⁴D. An improvement of almost one order of magnitude in the detection limit of NH₄⁺ over usual crossbeam detection arrangement was achieved with the long optical path cell in the spectrophotometric determination.

The conventional spectrophotometric method for NH₃ determination based on the Berthelot reaction demands higher volumes of hazardous reagents such as phenol and nitroprusside. The modified Berthelot reaction generates smaller amounts of less toxic residues due to the low volumes required (around 300 μL per determina-

Table 1
Comparison of the figures of merit of sampling and determination methods for NH_3 .

Parameter	CMDS-CE-C ⁴ D ^a	Impinger-Spec ^b	CMDS-LCW-Spec ^c
Linear range ($\mu\text{mol L}^{-1}$)	5–1500	10–100	1–15
RSD (% , $n = 10$)	3.0	5.0	2.4
L.D. liquid phase ($\mu\text{mol L}^{-1}$)	1.2	2.0	0.3
L.D. gas phase ($\mu\text{g m}^{-3}$)	0.7	3.0	0.2
Sampling time (min)	30	60	30
Determination time (min)	3	30 ^d	2
Sample volume (μL) ^e	~ 0.01	100	80
Residue generation ^e	<50 μL , non-toxic	5 mL containing phenol and nitroprusside	<1 mL containing nitroprusside

^a CMDS sampling followed by CE-C⁴D determination.

^b Impinger sampling with spectrophotometric determination based on Berthelot reaction.

^c CMDS sampling and improved determination with modified Berthelot reaction, flow system with heated reaction coil, solenoid micro-pumps and LCW cell spectrophotometry.

^d Berthelot's reaction kinetics is the determining factor.

^e Volume of liquid residue per determination.

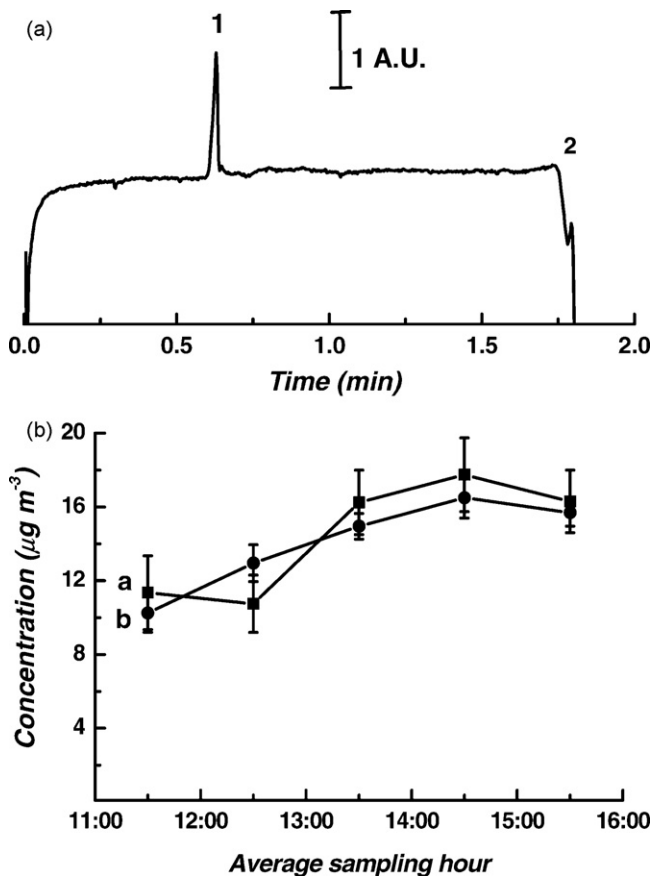


Fig. 6. (a) Electropherogram of air sample collected at July 3rd 2007 with the CMDS. Operational conditions: 1 h air sampling at 150 mL min^{-1} ; acceptor flow, HNO_3 pH=4 ($1.0 \mu\text{L min}^{-1}$); samples injected in triplicate in the CE-C⁴D; electrolyte, 20 mmol L^{-1} MES/His; silica capillary ($75 \mu\text{m I.D.} \times 65 \text{ cm}$ with 10 cm until the C⁴D detector); hydrodynamic injection (9.8 mbar , 30 s); applied voltage, -25 kV ; C⁴D frequency, 550 kHz ; 1 – NH_4^+ $31.5 \pm 3.7 \mu\text{mol L}^{-1}$; 2 – electroosmotic flow. (b) Concentrations of ammonia in the gaseous phase of the atmosphere during a 5-h sampling period at July 3rd 2007: a – CMDS sampling followed by CE-C⁴D determination; b – impinger sampling followed by spectrophotometric determination; error bars indicate SD of triplicate determinations.

tion) and the replacement of phenol by salicylate (despite the fact that nitroprusside is still used as a catalyst of the reaction, but in small quantities.

4. Conclusions

The CMDS is a versatile, highly efficient, inexpensive system, compatible with fieldwork and simple to operate, once no manual extraction steps (mechanical stirring or ultrasound) are involved.

It operates under low gas flow rates in comparison with typical impingers, denuders or sampling cartridges, a relevant aspect for sampling from small environmental chambers, indoor or from sample bags. Despite the low flow rate, the mean residence time of the gas passing through the sampler is only 5 s, which is still sufficient for quantitative collection efficiency (better than 95%). Such excellent performance of the CMDS prevents the otherwise mandatory calibration of the sampling device with expensive gaseous standards, cumbersome to handle in the field. Reduced size and low energy demands of the inexpensive flow propulsion devices are also interesting for field operation.

The successful application example of the CMDS collection followed by the determination by CE-C⁴D demonstrated that formic acid, acetic acid and formaldehyde (derivatized) in air can be sampled and quantified at once and, due to the high preconcentration, with detection limits comparable to the ones achieved by collection in cartridges and determination by HPLC or IC. Advantages include rapidity, simplicity and versatility, as well as lower consumption of sample and reagents and practically no generation of residues, besides of lower operational cost in comparison with HPLC, once high pressure pumps or costly separation columns are not required.

For gaseous analytes that are unstable, toxic or malodorous and can be generated by a chemical reaction in the liquid phase, the described CDME is an attractive alternative to generate calibration gas standards, as demonstrated for ammonia (unpleasant, irritating smell), by mixing non-toxic and non-volatile solutions. The system is flexible and can be used for gas calibration in flow systems or even to validate solid phase microextraction (SPME) sampling methodologies. Moreover, the CMDE device avoids the use of expensive or risky compressed gas cylinders or permeation tubes.

The simple photometric determination of ammonia with a LCW cell coupled to a flow-based system is an interesting alternative to increase sensitivity. It is compatible with the spectrophotometric determination of NH_3 based on the modified Berthelot reaction. In the near future, the CMDS could be directly interfaced with the LCW cell for online monitoring of NH_3 at near real-time resolution.

Pollutant analysis with the CMDS in combination with CE-C⁴D or the improved spectrophotometric implementation of the Berthelot method is in line with green analytical chemistry goals by minimizing reagent and energy consumption and residue generation.

Due to the excellent matching of CMDS with CE, the authors are now undertaking a direct hyphenation aiming to obtain a total analytical system for multi-species monitoring, suitable for laboratory and field use as well as remote operation.

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