Flow system to gas capture from a nebulized solution

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Received 20 June 2002; received in revised form 26 November 2002; accepted 4 December 2002

Abstract

The use of aerosol produced in a nebulization chamber is proposed as an alternative to gas sample capture in flow systems. This paper describes the coupling of a sampling interface with a flow system, for in situ gas monitoring. Aspects related with the behavior of aerosol formation and gas solubilization in liquid drops are discussed. The method is applied to the determination of residual lime in acidic soils. Aliquots of 5.0 ml of 1.0 mol l\textsuperscript{-1} HCl were mixed with soil samples (1 g). The CO\textsubscript{2} released from these samples was captured by a nebulized aerosol and determined conductivity. The analytical curve from 1.0 \times 10^{-2} to 5.0 \times 10^{-2} mol kg\textsuperscript{-1} CaCO\textsubscript{3} was ploted applying the matrix matching approach. This proposition, allowed an increase in the sensibility with detection limit of 6.0 \times 10^{-3} mol kg\textsuperscript{-1}. The precision was good (R.S.D. < 3\%) for an analytical frequency of 22 determinations per hour. A fair agreement, at 95\% confidence level, was found between the results from the proposed method and certified values of the investigated samples.

Keywords: Aerosol; CO\textsubscript{2}; Flow system; Nebulization; Residual lime; Soil

1. Introduction

In pluvial water it is possible to determine a lot of different species of the atmosphere. Gaseous compounds can be dissolved inside the raindrop, and some factors, such as the gas solubility in the water should be taken into account [1].

In the literature, several methods using gaseous capture in solution, have been proposed to reduce time, reagents, and samples consumption to achieve the results and to overcome the residues generation [2]. Liu and Dasgupta [3] proposed a capture system in drops to determine the analyte directly inside the drop, while Pasquini and Hespanhol-Silva [4] and Oms et al. [5] used hydrophobic membrane for gas diffusion and analyte matrix separation. A pervaporation approach, composed by a vaporization cell and a hydrophobic membrane [6,7], and soluble gas absorption by a polydispersive aerosol of a liquid [8] have also been suitable for gaseous capture. In latter case, when a gas containing the analyte is in contact with an aerosol able to sorb the analyte, the sorption reaches equilibrium at a certain definite rate.

Aerosols are nebulized solutions transformed to reduced size drops (<12 \mu m) by a concentric nebulizer, typically used in flame photometers and flame atomic absorption spectrometers [9]. The nebulizer capillary gas outlet is smaller than the solution outlet, generating a gas flow faster than the liquid flow, providing the aerosol formation. The nebulizer efficiency depends on the gas and liquid flow rates, the nebulizer configuration, the solution viscosity and the
liquid superficial tension. The small diameter of the formed drops increases the gas absorption due to the high superficial area produced. According to Liu and Dasgupta [3], smaller drops sizes provide faster reaction speed, reaching an elevated concentration of the gaseous components.

The Southern Brazilian soils are acidic and normally need pH correction through lime addition. Due to lime main components Ca and Mg carbonates, the soil pH increases and favorable effects in the chemical and physical properties of soil are achieved [10,11]. Carbonate determination gives information on the lime remaining in the soil, and indicates the lack or the need of a new lime application. This evaluation plays an important role in agriculture.

The residual lime present in the soil can be quantified with the dissolution of carbonate in acid medium and subsequent determination of evolved CO₂ gas [10].

This work proposes the coupled between a nebulized solution, used to gas sampling, with a flow system. With this approach, the CO₂ released from soil samples after acid attack is dissolved in the liquid drops. The solubilized CO₂ can be then quantified. The method was applied for residual lime determination without sample pretreatment.

2. Experimental
2.1. Reagents and samples

All solutions were prepared with the use of analytical grade reagents (Merck, USA) and high-purity water (Milli-Q Water System, Millipore, EUA) was used throughout. A 1.0 mol l⁻¹ HCl solution was prepared from appropriate dilution of concentrated acid. Gaseous CO₂ (99% pure White Martins, Brazil) was used for comparative results.

Soil samples were oven-dried at 50 °C for 48 h in a forced air oven and graded in a hammer mill (Marconi, Brazil) fitted with a 2-mm screen sieve at the bottom of the cutting chamber. After drying and sieving, these samples were homogenized and stored at drying conditions.

Solid standard 1 mol kg⁻¹ CaCO₃ was prepared according to a previously work [7], in which 10.0 g of CaCO₃ was mixed with 100.0 g of carbonate-free soil. Working matrix matching samples containing 1.0 × 10⁻² to 5.0 × 10⁻² mol kg⁻¹ CaCO₃ were prepared from the above standard by dilution with carbonate-free soil.

2.2. Apparatus

The flow system worked with two three-way electrically actuated solenoid valves (NResearch, USA), two peristaltic pumps (ISM 761 Ismatec, Switzerland) with Tygon pumping tubes, non-collapsible PTFE transmission tubing with 0.8 mm i.d., and a laboratory-made conductivity flow cell [12]. Conductivity meter equipped with a RS232 interface (Fisher Scientific, USA), and a PC with PCL 711-5 interface board (American Advantech, USA), allowed the valves and pumps control, and the data acquisition. The selection of the different way of the valves in accurate times provided the flow control. A heat plate at 40 °C with a magnetic stirrer (Penem, Brazil) was used for the reaction process, providing better and faster homogenization of HCl solution and samples. For nebulization performance, an air compressor (Marconi, Brazil) was used.

2.3. Nebulization chamber

The nebulization module consisted of a cyclone chamber made of borosilicate glass, and a concentric nebulizer (Glass Expansion, Victory, Australia). The nebulization was conducted at 0.5 bar, forming a water aerosol that captures the gaseous CO₂ released from the samples. The drops in contact with the wall were collected and aspirated into the flow system. The chamber, containing three inlets, was used to insert and aspirate samples and reagents. A purification system composed by a saturated NaOH solution was designed to filter the air used for nebulization and sample transportation (Fig. 1), by trapping the contaminants.

2.4. Procedure

The proposed flow-setup is depicted in Fig. 2. Water and air were separately carried to the nebulizer, through a peristaltic pump, for the aerosol formation. After switching solenoid valve SV₁, 5.0 ml of 1 mol l⁻¹ HCl were added to the sample vial (S), to
react with the carbonate from the sample to promote the evolution of CO₂. As the reaction was completed, the solenoid valve SV₂ was switched carrying air to the sample vial. This air transports CO₂ from the soil to the nebulization chamber. Carbon dioxide diffused around the aerosol surface and was captured by the droplets that were subsequently condensed in the lower part of the chamber. The solution was aspirated and driven directly to the conductivity cell for CO₂ determination. The solenoid valve provided the flow shift and then a new sample was processed. In order to increase the analysis speed, each sample was weighed in its own container. The method was optimized by applying an univariate analysis. The main analytical features of the procedure, such as sample size, carrier and airflow speed, and reaction speed were evaluated.

The proposed nebulization system was compared with a previously designed gas diffusion process [7], in order to evaluate the system performance. Firstly, a 5.01 min⁻¹ CO₂ flow was directly connected to the systems without a sample injection device. As the diffusion process provides the possibility of performing a pre-concentration step, a selected sample volume of 250 µl was also evaluated using of both systems. The nebulization system was optimized for residual lime determination. In this context, parameters such as the sample vial geometry, the amount of sample, the air transport flow rate, and the carrier transport rate, were evaluated to increase sensitivity and reproducibility. The method validation was also assessed by using samples from an international collaborative program of soil samples, the International Soil-Analytical Exchange, WEPAL—Wageningen Evaluating Programmes for Analytical Laboratories (ISE) [13].

3. Results and discussion

3.1. Nebulization module characterization

The compromise between the nebulized and acceptor solutions is an important parameter to be evaluated. Nebulization and aspiration flow rates should be the same, to avoid bubbles formation or accumulation of the acceptor solution inside the system. Bubbles harm the analytical signal, and the solution accumulation provides larger dispersion and/or broadening of the analytical signal in addition to memory effects. The proposed flow setup required the use of two peristaltic pumps, because the aspiration flow rate was around 5% lower than the nebulization flow rate. The use of the pumps with different flow rates provided a better flow control and consequently higher accuracy within the results, by decreasing the flow variation.

To look for better linearity, owing to the narrow linear range of the CO₂ conductivity, a NaOH 0.01 mol l⁻¹ solution was evaluated as nebulizer solution. The measured would be done by the decrease in conductance of the analytical signal. Otherwise, a slightly conductance variation was observed with

Fig. 1. Schematic diagram of the CO₂ capture in the aerosol with the solubilization products, bicarbonate, carbonates, and dissolved CO₂. PC, role for pressure compensation.

Fig. 2. Proposed flow-setup. S, sample vial; PP1 and PP2, peristaltic pumps; AC, air compressor; SV1 and SV2, solenoid valves; NC, nebulization chamber; D, detector.
Analytical signals obtained in a 5.0 l min$^{-1}$ continuous CO$_2$ flow with the proposed system shown in Fig. 2 (nebulization) and with the gas diffusion system [7].

Fig. 3. Analytical signals obtained in a fixed 250-μl volume of CO$_2$ with the proposed system shown in Fig. 2 (nebulization) and with the gas diffusion system [7].

this alternative way. It would be occurred due to the higher conductivity of the NaOH solution compared with the CO$_2$ conductivity, decreasing sensitivity.

Analytical signal from a continuous CO$_2$ gas capture (5.01 min$^{-1}$) in the proposed nebulization approach compared with the gas diffusion process [7], is presented in Fig. 3. As can be observed, the efficiency of CO$_2$ capture using the nebulization chamber was almost two times better than that obtained with the diffusion approach. However, for a sample insertion of a defined volume (250/36 ml) of CO$_2$, the analytical signal was three times lower (Fig. 4). As the carrier volume was constant, the continuous CO$_2$ injection increased the amount of gas inside the aerosol, enhancing the analytical signal. However, the diffusion system was limited by the efficiency of the hydrophobic membrane. In the second approach, while 250μl of CO$_2$ were injected, the sample dispersion inside the nebulization chamber increased and, consequently, the analytical signal and the sensitivity decreased. However, the dispersion is smaller with the use of the diffusion system. Under the described pervaporation conditions [7], the signals remain almost the same and higher than the nebulization approach. Thus, it is possible to conclude that the nebulization procedure is suitable for gas monitoring, in which the amount of gas is continuous. Although the poor results with the studied conditions using a defined volume of gas, the nebulization capture system could also be applied to the residual lime determination, with some system improvements. The following sections describe these studies.

3.2. Flow system for residual lime

Once the volume of the sample vial affects the CO$_2$ transport through the nebulization chamber, 10, 15, 20, and 36 ml vials were evaluated. The 20-ml size allowed lower relative standard deviation (R.S.D. <3%) and higher analytical signals. Vials of lower volumes provided a previous mass transfer through the nebulization chamber, generating a double signal. Higher vial volumes produced low reproducibility signals, increasing the R.S.D.

A small aliquot of airflow, provided by the trap system, was split for the gas transportation inside the vial containing the sample. Added acid high flow rate harm the conductivity measurements due to its transport from the vial to the nebulization chamber. The CO$_2$ transportation time was set as 20 s, which allowed good analytical frequency, increasing sensitivity.

Calcium carbonate (3.0×10$^{-2}$ mol kg$^{-1}$) at different mass range was investigated in order to evaluate the sample mass required. The results showed that 1.0 g provided a stable analytical signal. Amounts of this CaCO$_3$ standard higher than 1.0 g presented homogenization problems by acid addition, increasing the R.S.D. To improve homogenization, a magnetic stirrer was used to mix the sample.
3.3. Analytical reference curves

The use of a matrix matching approach with carbonate at $1 \times 10^{-2}$ to $5 \times 10^{-2}$ mol kg$^{-1}$ concentration range allowed the application of the method to different kinds of soil. The use of a loamy carbonate-free soil to build the analytical curve simplified the preparation of the reference samples, improving the system accuracy. The analytical curve of the reference soil samples results, shown in peaks area, presented good linearity ($y = 356.73 + 2047.00x$, $R = 0.9970$).

3.4. Interference evaluation

The analytical signals obtained with the high CaCO$_3$ concentration provided by the lime soil used were slightly affected by the other gaseous species. Ammonia, the most abundant soil gaseous compound, is not available when in acid medium, as the used in the present approach. Other gaseous forms possible present in soil samples, such as SO$_2$, H$_2$S, and CO, were present in smaller amounts and were eliminated during the soil drying step. Upon these results, the proposed system is suitable to CO$_2$ determination in corrected lime soil.

3.5. Analytical applications

After the experimental conditions were set (sample mass, aerosol and aspirated flow rates, and capture efficiency), the system was tested for soil samples. The R.S.D. for these samples were around 3.0% for 10 replicates, the detection limit was $6.0 \times 10^{-3}$ mol kg$^{-1}$ and the sampling rate was 22 samples h$^{-1}$. The method accuracy was confirmed by comparing the results of the soil analysis samples with the ISE collaborative program (Table 1) samples contents. After paired $t$-test application, a fair agreement, at 95% confidence level, was found between the results from the proposed method and certified values of the investigated samples. Slight variations in the coefficients of the calibration equations (usually <3%) were observed during 4-h working periods.

4. Conclusions

It was demonstrated the feasibility of a new flow injection type of gaseous analyte collection system, which uses a nebulization chamber to provide an aerosol to gaseous adsorption. Coupled to electrochemical or spectrophotometric detector, can be use to enhance sensitivity. Its efficiency is due to the large contact area obtained with the approach. The nebulization system can be applied for the capture and determination of different gaseous samples to in situ gas monitoring and proved to be suitable for the applied analytical process, allowing rapid in situ pretreatment and analysis of soil samples for CO$_3^{2-}$ determination.

Acknowledgements

The authors express their gratitude to Fundação de Amparo à Pesquisa do Estado de São Paulo for it financial support (98/10814-3) and fellowship provide to M.Y.K.

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