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Bisegmented flow system for determination of low concentrations of gaseous constituents in gaseous samples

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Abstract

The monosegmented flow approach has been modified to produce a bisegmented flow system aimed at the determination of gaseous analytes present in low concentrations in gaseous samples. The concentration ranges can vary from < 1% (v/v) to nl l^{-1}. A flow pattern constituted of b#1-ls#1-b#2-ls#2-b#3, where b indicate a gas bubble and ls a liquid segment, is produced by a single movement of the injection device. The system is computer controlled and two procedures can be used for the determination of the gaseous analytes. In the first the b#2 segment constitutes the sample and a suitable reagent is added in ls#1 after the whole pattern is present inside the glass flow manifold. The gas sample is forced to flow over the liquid reagent layer left behind by ls#1 and a detectable specimen is formed. The ls#2 collects the product and carries it to the detection point. In the second procedure ls#1 contains a suitable absorbing reagent and forms an absorbing layer on the tube wall. The carrier flow is stopped when b#2 reaches an entrance arranged perpendicular to the glass reactor tube. Through this entrance a large volume of a gaseous sample is impelled. The gaseous analyte is absorbed and concentrated in the liquid layer. About 85% of the analyte can be retained by the absorbing layer. When this operation is finished the carrier flow is re-established and ls#2 removes the absorbed analyte from the liquid layer. This segment may or may not contain a suitable reagent. The system has been applied for the determination of O_2 (0–1% v/v) in the atmosphere of food packages by reacting the analyte with pyrogallate and of NO_2 in synthetic air by absorbing the analyte in triethanolamine and reacting it with Saltzman reagent in ls#2. The system is capable of determining NO_2 in air samples in the range 25–250 nl l^{-1}.

Keywords: Bisegmented flow system; Oxygen; Nitrogen dioxide; Food packages; Gaseous samples

1. Introduction

The use of flow systems for determination of gaseous analytes in gaseous samples is very seldom described in the literature, despite the necessity for procedures that are rapid, robust, less reagent demanding, less prone to interference and with lower cost per analysis. Gaseous constituents can range, on a volume basis, from 50% or more to a few nl l^{-1} for those analytes of interest for pollution studies, such as nitrogen dioxide and ozone.

The flow injection (FI) approach [1] has been employed in the past aiming for the determination of SO_2, Cl_2, Br_2 and CO_2 [2–5]. In some cases the flow system was employed only for sample transportation [2] while in others an in line reaction was promoted

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between the gaseous analyte and a reagent stream [3]. Low sensitivity and lack of versatility were, perhaps, the most unfavourable characteristics of such proposals. Recently an interesting flow cell has been developed for the spectrophotometric determination of low contents of NO_2 in gaseous samples employing permeation through a PTFE membrane and a static reagent acceptor containing Saltzman reagent [6]. The sensitivity attained was very good and demonstrates that the chemical approach to gas determination still has many aspects to be exploited. However, the analyte transportation to the reagent solution is restricted by the membrane and, at suitable flow rates, only about 2% of the analyte reaches the reagent solution.

Even more recently the monosegmented approach to flow analysis [7] has been used for gas analysis. The monosegmented system has intrinsically the characteristic that gas and liquid segments are simultaneously generated in the system by a single movement of an injection device [8]. Aiming at the determination of gaseous analytes, one of the gaseous segments is constituted by the sample and various strategies can be carried out in order to provide an analytical response dependent on the analyte concentration. The first approach employs the volume contraction of the gas segment, occurring after selective absorption of a given analyte, as the analytical parameter. O_2 and CO_2 have been determined using this approach in samples containing 2–80% (v/v) and 2–50% (v/v) of the gaseous analytes, respectively [9]. Further development of the monosegmented system allowed the determination of CO_2 in atmospheric samples containing a low concentration of this substance (100–800 $\mu l\,l^{-1}$) using conductimetric detection of the ions formed after CO_2 dissolution in the deionized water layer of the reactor tube[10]. These ions were collected in a liquid monosegment, also constituted of deionized water. Therefore, no reagent is necessary to perform CO_2 determination.

On the other hand, many chemical procedures for spectrophotometric determination of gaseous analytes are based on the absorption of the analyte in a suitable reagent that can produce a detectable product or simply retain the analyte in a solid or liquid substrate. Liquid absorbing reagents have the advantage of being renewed from one determination to other and are attractive for use within flow systems. Unfortunately, the monosegmented system, as originally conceived, is not capable of realising the two basic operations necessary for gas determination, namely, the gas absorption/reaction and product transportation to the detector. Furthermore, the determination of low concentration samples (for instance, in the range of nl l^{-1}) would require a pre-concentration of the analyte/product which can not be supplied by the simpler monosegmented systems described so far.

In view of the drawbacks indicated above, this paper proposes, a new flow system that produces a bisegmented flow pattern which can ensure in full the requirements for determination of low content gaseous samples. As the system produces a pattern containing two sequentially arranged liquid segments bordered by three gas bubbles it was named as 'bisegmented flow system'. The use and performance of this system for determination of O_2 in the atmosphere of food packages and of NO_2 in synthetic atmospheric air are described below.

2. Experimental

2.1. The bisegmented system

Fig. 1 depicts the arrangement of the injection device in the injection (A) and sampling (B) positions used to produce the bisegmented pattern employed in this work (C). The injection device is made of acrylic and the manifold tubing was made of 1.0 mm id PTFE.

The overall idea is that of producing a liquid segment (ls#1) which already contains a reagent or to which a reagent will be added on the path to the detector. This segment is employed to produce an absorbing or reactant layer in the glass tube of the flow manifold. Gaseous samples will, in some way, flow over this layer, promoting the absorption and/or reaction of the gaseous analyte. Bubble #2 (b#2) would contain the sample or an inert gas to be used only to separate the first liquid segment from the second one (ls#2). This segment, in turn, is employed for collection of the absorbed substances from the layer left behind by ls#1 or that resulting from a reaction of the gaseous analyte and a reagent left in the layer by ls#1. Bubble #1 and b#3 have similar functions of avoiding, respectively, the dispersion of the reagents and of the product collected by ls#2 [10].

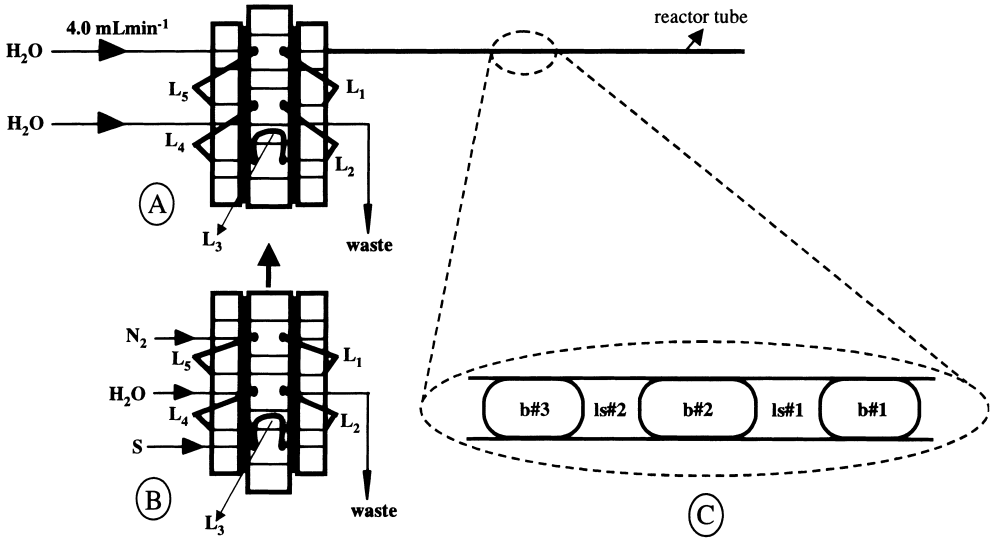

Fig. 1. (A) Injection device arrangement for sample introduction and (B) sampling operation. (C) This depicts the flow pattern produce inside the reactor tube. L_{1-5}, are loops for gas or liquid sampling.

2.2. Flow manifold and analytical procedures

Fig. 2 shows the manifold for gas determination. The injection device is shown only in the injection position. The reactor/absorber tube is made of 2 mm i.d. borosilicate glass. The final length was selected to be 50 cm and it has been constructed as a series of interconnected loops.

The spectrophotometric detector and flow cell were home made. A light emitting diode (LED) with peak intensity at 560 nm (for determination of NO_2) or 480 nm (for determination of O_2) and a photodiode (RS-9901) with an operational amplifier integrated on a chip, were employed. The light of the LED was allow to pass through a 1.5 cm optical path formed by the flat base of an 'U' modelled glass tube of the same i.d. as used in the manifold. The analogue signal generated by the detection system was presented to a home made analogue-to-digital interface [11] that is also employed for optical switch logical level access and for valve actuation.

2.3. Procedure I

When the concentration of the analyte in the gaseous sample and/or the sensitivity of the spectrophotometric reaction allow, the sample can be injected as a b#2 (typical volumes 100–1000 μl). The ls#1 initially contains water and when it reaches the point in between optical switches 2 and 3 (in Fig. 2), the controlling program turn the valves 1 and 2 on and perform the addition of the reagents only in the liquid segment. The segment continues to flow through the manifold and produces a layer of reagent. The sample flows over this layer and the analyte is absorbed and reacts. Late addition of the reagents helps to prevent the formation of product in the initial stages of the manifold which is made of non-polar materials and its adsorption on this material occurs in an irreversible way. Also, the formation of droplets of reagent on non-polar parts of the manifold is irreproducible while the liquid film formed on the glass tube is not. Liquid segment #2 collects the reagent from the layer and transports it, under restricted dispersion conditions ensured by segmentation, to the spectrophotometric detector. This procedure was employed for determination of O_2 present in the range of 0.5–2.0% (v/v).

2.4. Procedure II

This procedure was developed to include a pre-concentration step permitting the determination of low contents (nl l^{-1}) of analytes present in gaseous samples. The same bisegmented pattern is generated but

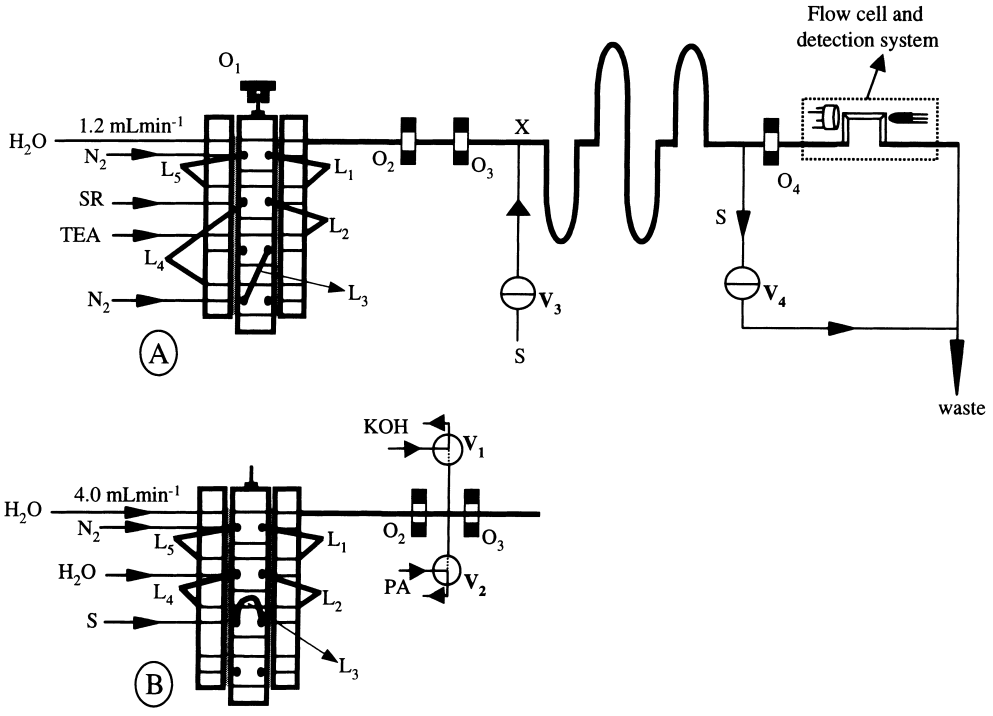

Fig. 2. Bisegmented flow manifolds for determination of NO_2 (A). SR, Saltzman reagent; TEA, triethanolamine solution; O_{1-4}, optical switches; V_{1-4}, electromechanical valves; S, sample path. (B) arrangement for the injection device for O_2 determination. The rest of the system is the same as showed for NO_2 determination. PA, pyrogallic acid solution. L_{1-5} are loops for gas or liquid sampling.

b#2 contains an inert gas such as argon or nitrogen. When the middle of this bubble reaches the point *X* in the manifold depicted in Fig. 2 (detected by the optical switch 3) the carrier flow is stopped and Valve 3 is opened allowing a large volume of the gas sample (typically in the range 1–10 l) to flow through the manifold in contact with the liquid absorbing layer created by ls#1, as in Section 2.3. The analyte is retained and concentrated in the absorbing layer. After the sample has been pumped, the peristaltic pump is restarted and liquid segment #2 (typical volume 75 μl) collects the absorbed analyte and promotes a reaction for its spectrophotometric determination. This procedure was employed for the determination of NO_2 in concentrations down to 25 nl l^{-1}.

2.5. Reagents and solutions

Analytical grade reagents were employed throughout. Pyrogallic acid and potassium hydroxide solution were prepared daily as previously described [9]. After optimisation, the final composition of the Saltzman reagent was obtained by mixing 1.0 g analytical grade suphanilamide and 0.02 g of *N*-(1-naphthyl)ethylenediamine hydrochloride in 100 ml of 1.5 mol L^{-1} HCl. The final absorbing solution for NO_2 determination was 10% (v/v) triethanolamine solution prepared by dilution of the analytical-grade reagent in deionised water. Deionised water was employed throughout.

2.6. Gas chromatographic determination of O_2

For comparison purposes the O_2 present in the atmosphere of cheese and powdered milk packages was analysed by gas chromatography. 300 μl of the sample were injected (injector temperature = 70°C), using a gas tight syringe, into a Shimadzu CGA 14A equipped with a thermal conductivity detector at 140°C. Separations were carried out on a Porapak Q column and 13X molecular sieve column connected in series inside the oven, kept at 50°C.

2.7. Gas standards

Certified standards of O_2 containing 0.25, 0.50, 1.10 and 2.00% (v/v) of this compound, in nitrogen and of NO_2 (1.0 μl l^{-1}) in synthetic air, all supplied by Air Liquide, SP, Brazil, were used for calibration of the flow systems. Low content standards for NO_2 were obtained by dilution of the 1.0 μl l^{-1} solution in synthetic air. The dilution was produced inside a Tedlar (bag of 3.8 or 8.1 l using a gas-tight microsyringe or by proportional pumping using a peristaltic pump furnished with eight Tygon® tubes of equal inner diameter (2.6 mm) joined at a common outlet. This system is called the 'gas dilutor system' and besides the preparation of the different standards, the system was employed for studies related to the effect of the sample flow rate in Section 2.4. The total maximum flow rate for the set of eight tubes was 270 ml min^{-1}. Different concentrations (in the range 20–250 nl l^{-1}) were obtained by pumping the 1.0 μl l^{-1} NO_2, in one or more tubes, while the others were kept pumping synthetic air. For standards containing the analyte in concentrations below 125 nl l^{-1} a stock standard containing 1000 nl l^{-1}, prepared by dilution in a Tedlar® bag, was employed. The outlet of the system was directly connected to point *X* in the flow manifold depicted in Fig. 2.

3. Results and discussion

3.1. Determination of oxygen

The flow method for determination of O_2 was developed for the determination of this analyte in the atmosphere of food packages where typical values are in the range 0.25–2.0% (v/v). Frequently, the limiting factor for such determinations is the size of the sample, as some food packages have a very small 'free' inner space. The determination is based on the reaction between oxygen and potassium pyrogallate (KP) in a strongly alkaline medium. The product formed can vary from purple to yellow in colour. In the final conditions employed in this work, the reaction generates the yellow compound that is monitored at 480 nm. A reproducible blank signal is always present due the oxygen dissolved in the solutions and the deionised water employed.

The initial studies for optimisation of the flow system aimed at investigating the effect of the reagent concentration and sample volume on the precision and sensitivity. A 50 cm long reactor tube, a sample volume of 100 μl, a 100 μl water collector segment and a flow rate of the reagents of 2.9 and 3.8 mL min^{-1}, respectively, for KOH and KP, were employed during this stage. The results point to the use of 1.5 mol l^{-1} KP and 1.0 mol l^{-1} KOH. These concentrations were selected as a compromise between sensitivity, reproducibility and linearity in the 0.25–2.0% (v/v) concentration range. The use of 1.0 mol l^{-1} KOH has the merit of permitting the system to also work in the volumetric determination of CO_2, as previously described [9].

A typical calibration graph obtained under these conditions obeys the relationship $[O_2] = -0.321 + 2.730\,A$, where $[O_2]$ is the oxygen concentration (%, v/v) present in the gaseous sample and A is the measured absorbance. A typical correlation coefficient is 0.9995 ($n = 5$) and the signals have a mean relative standard deviation of 2.3% ($n = 4$) in the concentration range 0.5–2.0%.

The effect of the sample and collector segment volume can be observed in Fig. 3. The sensitivity increases with the volume of the sample and is inversely proportional to the volume of the collecting segment. These results demonstrate the characteristics of signal enhancement that can be obtained by increasing the production of the monitored substance in the liquid absorbing layer and collecting it in a segment of low volume. Here, reproducibility, reagent exhaustion and flow cell volume are the limiting factors. The flow cell volume, at the moment, limits the volume of the collector segment to 75 μl.

The optimised system has been applied to the determination of O_2 present in the atmosphere of food packages. Modern food packing technology employs a controlled atmosphere in order to extend the shelf-life of some products. Usually the minimum oxygen content of the free space of food packages is desired. In real samples, the O_2 content can oscillate from 0.1–2.0% (v/v). Table 1 shows the results obtained for determinations of O_2 in the atmospheres of grated cheese, fresh pasta and powdered milk packages employing the proposed spectrophotometric bisegmented system or gas chromatography. The results

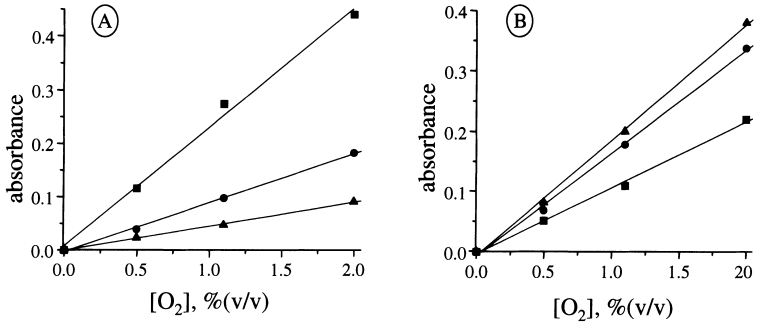

Fig. 3. Effect of the sample volume (A) and of the volume of the collector segment (B) on the calibration graph for O_2 using the bisegmented system. A; ■,●,▲, 500, 200 and 100 μL, respectively. B; ▲,●,■, 50, 100, 200 μl, respectively.

obtained for the flow system are in general slightly lower than those obtained by gas chromatography. This can be explained by considering that the same group of samples were analysed by both the methods in different laboratories. The temperature control of the samples was not rigorous and it is well known that this factor can affect the quantity of gas adsorbed by the product inside the package. However, the results are consistent and allow the bisegmented system to be used for O_2 determinations in food package atmospheres.

Some results obtained by the bisegmented system showed higher concentrations of O_2. These results probably reflect a leakage of the seal applied to the food package to allow syringe sampling of the inner atmosphere. The typical average estimate of the absolute standard deviation for the determinations made by the bisegmented flow system was 0.08% (v/v). The sample size was 100 μl against 300 μl for the chromatographic method and the results for the flow system were obtained in about 60 s while a chromatographic determination takes 20 min. Is true that gas chromatography can give a measurement of the content of other gaseous analytes in the same chromatogram. However, evaluation of the quality of the food packaging can be accessed only by the determination of the O_2 content. Besides this advantage, the proposed bisegmented system has the advantage of low reagent consumption and of being a low cost system, both in terms of initial implementation and of maintenance.

3.2. Determination of NO_2

The determination of this compound in gaseous samples was selected to illustrate the pre-concentra-

Table 1
Comparison of results for determinations of O_2 in the atmosphere of food packages made by the bisegmented flow system (BFS) and gas chromatography

Grated cheese		Fresh pasta		Powdered milk	
$[O_2]$ %(v/v)		$[O_2]$ %(v/v)		$[O_2]$ %(v/v)	
GC ($s = \pm 0.04$)	BFS ($s = \pm 0.03$)	GC ($s = \pm 0.08$)	BFS ($s = \pm 0.05$)	GC ($s = \pm 0.12$)	BFS ($s = \pm 0.17$)
0.06	0.05	1.40	0.88	1.69	2.48
0.46	1.10	1.79	3.30	2.74	2.15
0.04	0.06	1.63	1.14	4.11	3.45
0.08	0.01	1.50	1.03	3.87	3.41
0.11	0.09	1.46	1.03	2.97	2.90
0.11	0.07	1.55	1.09	2.38	1.96
0.08	0.03	1.50	1.13	2.27	2.16

s refers to the estimate of absolute standard deviation for five measurements on the last sample for GC and BFS.

tion capability of the bisegmented system. The occurrence of this substance in atmospheric air requires the sensitivity of the system to reach few nl l^{-1}.

To reach such low detection limits a large volume of sample must be employed and the analyte must be concentrated in a low volume of absorbing solution. Previous work has shown that triethanolamine (TEA) is effective as absorbing reagent for NO_2 [12–14]. Therefore, the first liquid segment (100 μl) of the bisegmented system contained a solution of this reagent. Its passage through the glass tube generates a film of absorbing solution with a large contact area with the gaseous sample. After analyte absorption the second segment containing the Saltzman reagent is passed through the glass tube and the absorbed NO_2 is removed and transported to the detector while the spectrophotometric reaction is occurring and the pink product is monitored at 560 nm.

The optimisation studies sought to find the best reagent composition for the absorbing and spectrophotometric reaction when a 50 cm long reactor tube was employed. It is important to observe that the determination reaction occurs in an acidic medium while the absorber is an alkaline reagent. The best balance must be found between the TEA concentration and the acid content of the Saltzman reagent. The studies revealed that the best composition for the absorbing solution was 10% (v/v) of TEA. A Saltzman reagent with the following composition was found to maximise the analytical signal: 0.02 g of *N*-(1-naphthyl)ethylenediamine hydrochloride, 1 g of sulphanilamide and 12.4 ml of concentrated HCl in a 100 ml total volume. The volume of liquid segment containing the Saltzman reagent, 75 μl, was the smallest possible. The composition of the reagent follows the proportions described previously [9]. However, the final concentrations have been doubled in relation to the sulphanilamide and *N*-(1-naphthyl)ethylenediamine hydrochloride while the acid concentration is about five times greater because the reagent solution needed to neutralise the alkaline absorbing solution.

Under these conditions the effects of sample volume and sample flow rate were investigated. For investigation of the sample volume, a peristaltic pump was employed to impel the sample through the reactor tube. The maximum flow rate was employed (270 ml min^{-1}). Obviously the sensitivity can be increased by increasing the sample volume. However, there is a practical limit related to the time necessary for the sampling operation. In order to obtain a good signal for a sample containing 25 nl l^{-1} NO_2 it was found that about 6.0 l of sample need to be pumped at the maximum flow rate. This operation takes about 20 min to be completed, using the maximum speed of the peristaltic pump. The gas dilutor system was kept connected in the system in order to investigate the flow rate in the range of 100–270 ml min^{-1} and to easily prepare the NO_2 standards necessary for calibration of the system.

In the range possible to be investigated with the use of the peristaltic pump, the effect of the sample flow rate was negligible. Some slight decrease of the analytical signal was observed at higher flow rates.

The analytical curve obtained in the range from 25 to 160 nl l^{-1} NO_2 is linear and showed a typical correlation coefficient of 0.9965 ($n = 5$) for the equation $[NO_2] = -0.766 + 1020.5$ A; where $[NO_2]$ is the concentration of NO_2 in nl l^{-1} and A is the measured absorbance of the collector segment.

Some compounds which could possibly cause interference in the determination of NO_2 employing the Saltzman reagent were investigated; these were NO, H_2S and SO_2.

The difficulty associated with the investigation of the effect of NO has been previously described [15]. This compound can, in the presence of the O_2, be converted to NO_2. In fact, a positive interference of NO was observed with its analytical response in synthetic air being equivalent to that of the NO_2. The presence of H_2S was found not to cause any interference up to the concentration of 10 μl l^{-1} when present concomitantly with 125 nl l^{-1} of NO_2. The SO_2 only interferes negatively at concentrations higher than 18 μl l^{-1}. The results obtained for the effects of concomitants showed good agreement with those previously reported for a discrete system employing the same Saltzman reaction. Considering the high concentration levels at which SO_2 and H_2S were found to interfere it is possible to affirm that the proposed system is free of interference from these substances when they are present in the concentrations normally found in atmospheric air.

Some experiments were carried out to find the efficiency of the system for collecting the NO_2 present in the sample. About 6.0 l of a sample containing NO_2

at 125 or 250 nl l^{-1} were pumped through the system at 270 ml min^{-1} and the gas was collected at the outlet of the system in another Tedlar® bag. The collected gas was then used as a sample and re-pumped through the system. The signals obtained revealed that about 85% of the NO_2 was retained for both the initial concentrations of NO_2. The quantity of NO_2 absorbed is greater than in the previously described system that employs a PTFE membrane to isolate the gas phase from the absorbing Saltzman reagent [6]. These authors determined that about 2% of the analyte could be transferred to the absorbing reagent under an acceptable flow rate of sample. However the calculated increase of the sensitivity (considering the difference in the optical path and the quantity of NO_2 present in the sample volumes employed in both procedures) was not about 40 times, as predicted by the increase in the analyte absorption obtained by the bisegmented system. In fact the increase is only about four times, evaluated in terms of the absorbance obtained. This reflects, probably, the use of a non optimised, although simple, detection system that is based on a LED light source and a glass tube cell (subjected to stray light) and to the dilution of the absorbed specimen by partition between the collecting segment and the liquid film on the glass tube. However, the overall comparison revealed a net increase in the sensitivity.

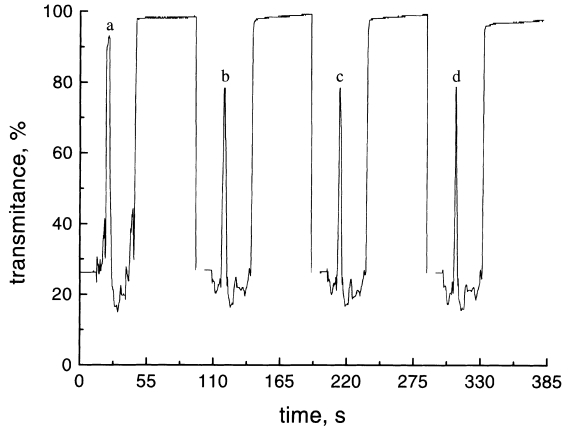

Fig. 4. Signals obtained for determination of NO_2 by the bisegmented flow system measuring the absorbance of the collecting segment. a, blank; b–d, three signals obtained in different days for 125 nl l^{-1} NO_2. Sample volume = 5.5 l. Sampling time 6 min.

Fig. 4 shows some typical signals obtained for the determination of NO_2 by the bisegmented system. A blank signal (a) and three signals (b,c,d) obtained for 125 nl l^{-1} NO_2 sample in three successive days. The estimate of the relative standard deviation for signals 125 nl l^{-1} obtained in five different days was 6.8%.

An evaluation of the effect of increasing the sample flow rate beyond the limit achieved by the peristaltic pump was carried out in order to decrease the sampling time operation. Preliminary results showed that there was little effect in increasing the flow rate up to the limit of 270 ml min^{-1}, achieved by the peristaltic pump. However, with this flow rate the time required for a determination capable of reaching the necessary detection limit is about 20 min. Therefore, investigation of the effect of higher sampling flow rate is important and was carried out by aspirating, with a vacuum pump, a sample contained in a Tedlar® bag. The results showed that, at a flow rate of 1.4 l min^{-1}, the analytical signal is not decreased. These results shown that the bisegmented system is capable of determining about 10 samples an hour. Obviously this sampling rate can be increased if higher concentrations samples are to be analysed.

4. Conclusions

The bisegmented flow system described in this work showed very good performance for the determination of gaseous constituents in gaseous samples. The ability of simultaneous management of the necessary reagent solutions for analyte absorption and collection/reaction is a unique characteristic that increases the versatility of the system allowing it to be used for the determination of many kinds of analytes over a wide concentration range. The spectrophotometric reaction can supply the selectivity to the method and the pre-concentration featured by the system can be used to reach the necessary sensitivity for determination of the samples of environmental interest. When sensitivity is not mandatory, the system can successfully be applied to determination of samples for which a very small volume is available.

The suggested approach can be extended to include other detection forms such as those based on electrochemical detectors using, for example, voltammetry and/or potentiometry.

5. Acknowledgement

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