

AN APPROACH TO THE DETERMINATION OF AVERAGE AIRBORNE CONCENTRATION OF CO₂, BY MEANS OF A LONG-TERM DIFFUSIVE SAMPLING DEVICE

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ABSTRACT

A diffusive sampling device, exploiting a tube-type geometry of the diffusion path, is proposed for long-term determination of average airborne concentration of CO₂ in urban and industrial areas, so as in indoor sites. A hydro-alcoholic barium hydroxide solution is employed as a CO₂ reagent sink. The analytical connected method is based on the determination of the solute barium hydroxide remaining after the acid-base reaction, in which its insoluble carbonate salt precipitate. Some indoor laboratory experiments show that, this technique exhibits a good precision and reproducibility. A six-week internal consistency test demonstrate that this device has a constant uptake rate, allowing proposing it as a suitable and inexpensive tool in performing the monitoring of urban and industrial sites over long periods and in indoor-outdoor studies, like those involved in the sick-building syndrome problem. Preliminary results of a monitoring campaign performed in the city of Rome (Italy) are also shown.

INTRODUCTION

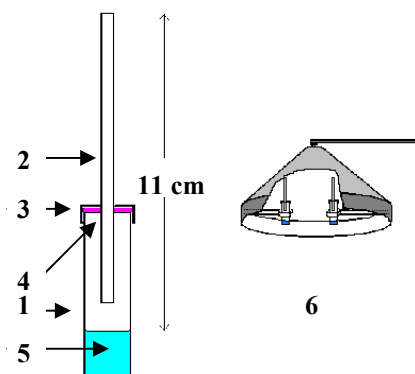
A large number of works, performed in the field of indoor air quality characterisation, show that CO₂ concentration values around and over 1,000 ppm in houses, schools, restaurants, and so on are often measured, depending on both internal sources (human breathing, cigarette smoking, cooking) and external air pollution, coupled with low air change levels [1-7]. In last years some governments of important cities promoted regional and local studies in this field and results showed that CO₂ values of twice the background value (about 370 ppm) are not unusual at the urban centres of the main cities, where a "dome effect" has been highlighted.. The common denominator of the above-mentioned investigations is that in this kind of determinations great differences point by point are measured, in the order of tenth and up to hundred of ppm, and differential values are more relevant than the absolute determined value which, in the contrast, is the basic parameter when background values of remote sites are required. The instruments usually employed in these determinations consist basically of infrared detectors allowing a continuous or semi-continuous ambient plotting. Such devices need an electric source, have a not negligible cost and must be manipulated from specialised people. The obtained data are characterised by a good degree of accuracy and precision. Nevertheless the use of electronic devices is limiting to perform an extensive mapping work, both in spatial and temporal terms, because of the large number of devices and specialised people, which should be involved. For this purpose, passive sampling technique is recognised to be the cheapest and easiest way to perform extensive monitoring campaigns. In fact, diffusive samplers do not need any energy source, are little, silent and quite inexpensive and only a little training is required for people charged to the positioning and retiring devices work. Moreover if a long-term sampling strategy [8-10] is adopted costs are further lowered. In this work we studied a simple passive device, conceived for the above mentioned long-term sampling strategy, employing a hydro-alcoholic Ba(OH)₂ solution as a CO₂ absorbent

and a titration instrumental method for its quantitative determination. A laboratory test has been carried out in order to evaluate the performance of the proposed method and its internal consistency, in a six-week sampling trial. A preliminary sampling campaign, performed at a few sites in Rome and surrounds, has been carried out, in order to verify the correlation between CO₂ levels and benzene, a classic air pollution index.

EXPERIMENTAL

Diffusive sampling device. A schematic diagram of the diffusive sampling device we used and of the shelter used to expose it is presented in **Figure 1**. Device consists of glass vials (20 mm I.D. x 50 mm height.), filled with 5 mL of a hydro alcoholic solution (35 parts, in volume, of water + 65 parts of methanol), at a concentration of about 5g/L of Ba(OH)₂. A plastic screwed cap retains a through passing, calibrated glass tube (6 mm O.D. x 4mm I.D.), which provide a suitable diffusive path length and surface. A silicone/Teflon septum, inserted between the screwed cap and the top of the vial, ensure the airtight of both the cap and the inserted glass tube. In the following illustrated experiments a device having a 11 cm diffusive path length has been tested. The path length is the distance between the inner point of the tube and the adsorbing surface, which, in our case, is maintained 1cm away from the end of the internal tube. Although in this experimental phase we performed an indoor study, we positioned the samplers in a shelter (see Figure 1) conceived to protect the device, when it is used in ambient environments.

Fig. 1 - Structure of the diffusive devices: 1.glass vials (20 mm I.D.x 50 mm height); 2.diffusive path length determining glass tubes (4 mm I.D.); 3.plastic screwed caps; 4.rubber-teflon septum; 5.adsorbing solution; 6.exposure shelter.



Reagents and materials. Pure water, purchased from Fluka-Sigma-Aldrich (Fluka, ACS, for inorganic trace analysis), certified for a barium content $\leq 5\mu\text{g/Kg}$ and purified from CO₂ traces by boiling it over an heating-stirrer apparatus was used in all preparation and dilution phases of the experiments; analytical grade Ba (OH)₂ · 8 H₂O and analytical grade methyl alcohol (both ACS, ISO, RP – Carlo Erba, Milan, I), with a barium content $\leq 1\text{mg/Kg}$ were used to prepare the absorbing solution; pure nitrogen cylinders were used to prepare a CO₂ free atmosphere inside a laboratory glove box; a (37%) HCl solution (RS – Carlo Erba, Milan, I) with a barium content $\leq 1\mu\text{g/Kg}$ was used to prepare a 0.1N solution, employed for the analysis of samples; an ICP Standard (Reference Materials – Inorganic Ventures Inc., Lakewood, N.J., USA) nitric solution of barium (Ba = 1.000 g/L) was used for the calibration of the atomic-absorption spectrometer used for quantitative Ba determinations; a “personal-type”, low flow pump (mod SP 15, by Casella London Ltd, G.B.) was used to perform a comparison with an active sampling method; a centrifuge was used to separate barium carbonate from the basic solution in sampled vials and an ICP-AES atomic mass spectrometric apparatus was used for the determinations of Ba solute concentrations. The

calibration curve, performed in the range 0.01-10.0 $\mu\text{g/mL}$, at the wavelength of 405.403 nm for BaII, exhibited a $R^2 = 0.9999$ correlation factor. The net analyte to background intensity ratio (I_n/I_b) had a 230.0 value and the detection limit was 0.0013 $\mu\text{g/mL}$.

Diffusive and active samplers preparation. A bottle with a saturated aqueous barium hydroxide solution, a flask of the above mentioned pure water, methanol and other suitable laboratory equipment, useful for the following described manipulations, were stored inside a glove box. 35 open vials, their “storage” caps and a 5 mL Hirschmann dispenser (Sigma-Aldrich, Milano, I) were stored together. Storage caps differ from those used for the sampling assembly only for the septum, which, in this case, is not perforated. The plastic cap is perforated in the centre, in order to allow manipulations described in the following, prior of the analytical step. The glove box was filled with pure nitrogen with a CO_2 level lower than 0.1 ppm. A 200 mL aliquot of the saturated $\text{Ba}(\text{OH})_2$ solution, having a concentration of about 30 g/L at ambient temperature, was mixed with 150 mL of pure water and 650 mL of methanol. The obtained reagent solution was used to fill, by means of the precision dispenser, the vials with 5 mL each. The starting concentration of the reagent solution was determined by analysing it with the method illustrated in the following “analytical procedure” section. We avoided determining “a priori” this value, because the employed barium hydroxide is not a gravimetric standard. Vials were then stopped with their storage caps and a 500 mL solution was used to fill the bubbler that we used as an “active sampler”, in order to determine the experimental uptake rate of diffusive samplers. A suitable set of “sampling caps”, with the glass tubes determining the diffusive path length yet inserted, was prepared. In order to start diffusive sampling, the storage caps of the positioned vials must be quickly removed and substituted with those equipped with glass tubes. Substituting sampling caps with the storage ones stops sampling.

Internal consistency and uptake rate testing procedure. A necessary condition to correlate the collected amount of a sampler with the environmental concentrations is that, at each sampling time, sampling rate must remain invariant. In order to verify this condition, a simple way is that to perform a series of exposures in multiple lapses of time and in defined units of time. If the sum of the amounts collected in the time units agrees with the amounts determined in the correspondent multiple periods, so linearity is demonstrated [11]. The exposure period where a loss of linearity is found represent the “sampling time limit”, at the experimental conditions.

To evaluate the internal consistency of the proposed diffusive device and to determine its uptake rate, a six-week field test was planned. The employed (indoor) ambient was our laboratory, a large room with a natural air-change. A two-week “sampling time units” was chosen for this trial and a series of samplers were positioned. The chosen multiple sampling periods were 2 three-week, 1 four-week and 1 six-week period (the three-week periods cannot be correlated with the two-week units but they allowed a further comparison of their sum with the six-week determinations).

For each sampling period, three devices were exposed. Two and three-week samplers were substituted at the end of each sampling period. Six blank (closed) vials were also used. Finally we used 21 diffusive samplers and 6 blanks for this experiment.

A bubbler, containing a 500 mL of absorbing solution, was positioned at the same ambient and time. An air flux of 16.7 mL/min was aspirated through the solution by means of a “personal-type” pump for a three-week period. The bubbler acts as a “reference” active sampler.

The uptake rate determination was further repeated for a next three-week period, against a set of 6 diffusive devices, in order to confirm obtained data and to evaluate the repeatability.

The procedure to calculate the uptake rate of diffusive samplers is rather simple. By calculating from the procedure described in the following, the quantity Q_r of CO_2 sampled in the active sampler, where sampling volume V_r is known being sampled by pump, a simple expression is employed: $Q_r V_r = Q_c V_v$ Where Q_c is the analytically determined quantity of CO_2 sampled by the passive sampler. The virtually sampled volume V_v is therefore determined from the product of the V_r , actively sampled volume, to the ratio of the calculated sampled quantities. Dividing V_v by the exposure time of the sampler, the following expression is obtained: $\Phi_v = V_v \cdot t^{-1}$, corresponding to the diffusion uptake rate.

Field campaign. A little field campaign has been performed by positioning three CO_2 and one Analyst BTX [12] passive samplers at six ambient positions in different points of Rome and surrounds, corresponding to different air pollution and traffic conditions.

Analytical procedure. After sampling vials were plugged with their storage caps and centrifuged, in order to obtain a limpid solution, over standing the barium carbonate solid phase. By means of a syringe, little quantities of CO_2 -free water were added, in order to restore the initial meniscus level into the vial (This operation is necessary because of the evaporative phenomenon, due to the back-diffusion of the solvent, occurring during the exposure time). A 50 μL aliquot of the limpid solution was taken out of the vial and fast injected into a 50 mL 0.1 N hydrochloric acid solution vial. This operation is performed for both blank and sampled disposals and also for the solution coming from the active sampling process. The obtained hydrochloric barium solutions were used for the quantitative determinations. It must be pointed out that the above-mentioned procedure does not need to operate in a controlled atmosphere. In fact every manipulation is conducted without opening vials, but just piercing the septa with the syringe needles. The Ba content of the prepared acid solutions was determined with the above described ICP-AES apparatus. A three replicates of each determination was carried out and the 0.1N HCl solvent solution was employed to subtract the “matrix” blank value. Quantitative data were obtained by comparison with the multipoint calibration curve, obtained by serial dilution of a standard (1.000 g L^{-1}) Ba nitrate solution.

The differences between the starting Ba amounts in the blank samplers and those found in sampled vials and in the bubbler, relate to the precipitate $\text{Ba}(\text{CO}_3)$ and, consequently, to the sampled airborne CO_2 .

RESULTS AND DISCUSSION

Table I summarize results obtained in the “internal consistency” test. It lists the quantities of consumed reagent (expressed as Ba), averaged over the three devices employed in each sampling period. The sums of shorter, consecutive, sampling periods, compared with the correspondent multi-week samplings, are also shown.

Figure 2 shows the correlation lines, between the sums of sampling time units and multiple sampling periods. Closeness to the 1 value of both the R^2 correlation factor and the slope coefficient value, relates to the “internal consistency” of the method.

Table II shows experimental data from the second three-week experimental trial, having the purpose of confirming the previous determined diffusion uptake rate of devices, in which a series of 6 diffusive devices and an actively sampling bubbler were involved. From the results obtained in the homogeneous series of devices we can also deduce, with a significant

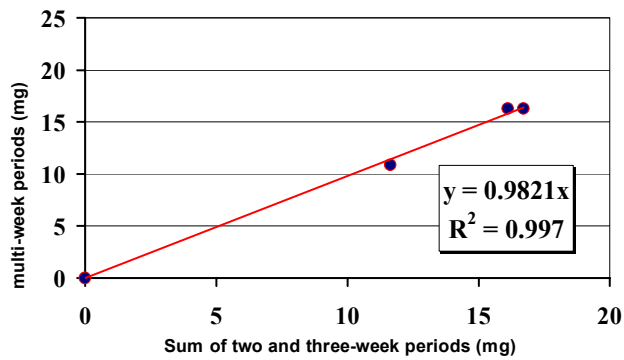


Fig. 2. Correlation between the amounts of CO₂ (expressed as “consumed” Ba) collected during exposure for two weeks in multiple weeks. A point related to the correlation between the sum of three-week periods and the six-week exposure is also inserted.

Table I. Comparison between the quantities (mg) of barium consumed during multi-week exposure of diffusive devices and the sum of those consumed in shorter, consecutive, exposures. Values reported in each cell relate to a three sampler averaged measure.

SAMPLING PERIODS	1st-2nd week	3rd-4th week	5th-6th week
sampling time units (two-week)	5.82 ± 1.02	5.82 ± 0.77	5.02 ± 0.59
three-week samplings	7.94 ± 0.44		8.20 ± 0.67
four-week sampling	10.89 ± 0.74		
time units sum	11.64 ± 0.77		
six-week sampling	16.33 ± 0.52		
time units sum	16.66 ± 0.59		
three-week sum	16.14 ± 0.67		

Table II. Parameters related to the second three-week sampling trial (see text). A is the reference active sampler (bubbler) used to calculate the experimental uptake rate (sampling flow) of diffusive devices, according to the procedure described in the text.

Sampler n°	Ba (mg)	CO ₂ concentrations (ppmv)	Sampling flow (ml·min ⁻¹)
L1	8.70	402	0.134
L2	8.25	381	0.127
L3	7.75	358	0.119
L4	8.55	395	0.132
L5	7.15	331	0.110
L6	8.25	381	0.127
Mean	8.11	375	0.125
Standard Deviation	0.57	26	0.009
A	1083.72	375	16.70

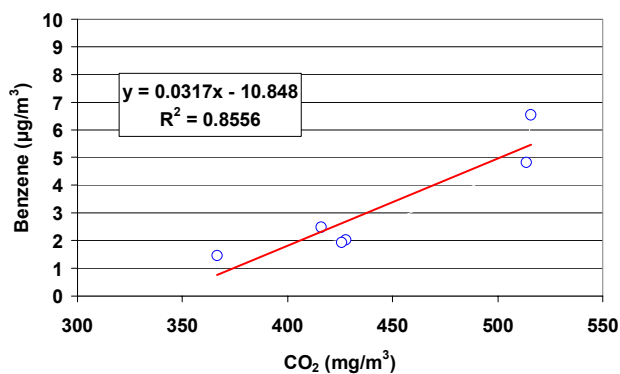


Fig. 3. Correlation between benzene and CO₂ ambient concentrations at 6 different sites of Rome and surrounds, measured in a monthly campaign.

statistics, precision and repeatability of the proposed method, for the three-week sampling period, by means of the determined standard deviation factor.

Figure 3 shows the correlation between the CO₂ and benzene measurements performed in a monthly campaign at different outdoor sites in Rome and surrounds. The graph shows a quite parallel trend highlighting a common, anthropogenic, source of benzene and spare CO₂.

From the standard deviation data of Table I we can deduce that the precision of the method increase as longer is the time exposure. That means that the main source of error is the analytical error, due to the fact that the percentage of “consumed” reagent (which is determined as a difference) is as lower as lower is time exposure, increasing the expanded error. Best results, in this sense, are obtained when the remaining reagent is lower then the consumed one. Nevertheless correlation between the sums of shorter periods and long-term exposures (figure 2) is very good, showing a R² factor and a slope coefficient quite close to 1. That gives evidence of a constant sampling rate during the whole sampling period. Standard deviation, related to the second, three-week trial, confirm the fact that a better reproducibility is obtained when the majority of the reactant species is consumed. However the standard deviation values are excellent, as long as it concern the passive sampling technique.

The determined diffusive sampling rate is 0.125±0.005 mL min⁻¹. This value agrees, under the experimental error limits, with that theoretically calculated from the D value found in the literature (1.39·10⁻⁵ m² sec⁻¹) and the device geometry (according with the first Fick’s law).

CONCLUSIONS

Both “internal consistency” results and precision parameters demonstrate that the proposed device and method is useful for the determination of CO₂ airborne concentration when a long-term sampling strategy is required. Data obtained in the urban and suburban ambients confirm that CO₂ measurements are consistent with the traffic related sources intensity.

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