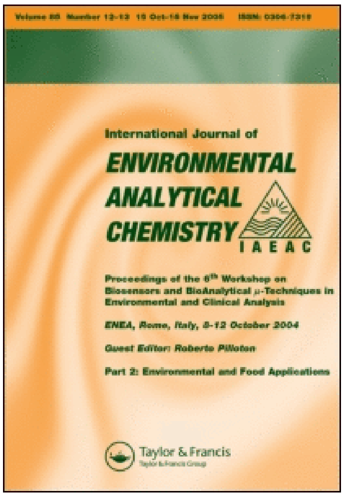

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Monitoring So_2 With Passive Samplers: A Laboratory Evaluation of Na_2Co_3 and Triethanolamine as Absorbing Media

B. A. Scheeren[a]; F. De Santis[b]; I. Allegrini[b]; P. Heeres[a]
[a] Dept. of Air Pollution, Agricultural University of Wageningen, The Netherlands [b] CNR, Istituto Inquinamento Atmosferico, Area della Ricerca di Roma, Monterotondo Staz. Roma, Italy

To cite this Article Scheeren, B. A. , De Santis, F. , Allegrini, I. and Heeres, P.(1994) 'Monitoring So_2 With Passive Samplers: A Laboratory Evaluation of Na_2Co_3 and Triethanolamine as Absorbing Media', International Journal of Environmental Analytical Chemistry, 56: 1, 73 — 85

To link to this Article: DOI: 10.1080/03067319408044419
URL: http://dx.doi.org/10.1080/03067319408044419

Intern. J. Environ. Anal. Chem., Vol. 56, pp. 73-85
Reprints available directly from the publisher
Photocopying permitted by license only

MONITORING SO_2 WITH PASSIVE SAMPLERS: A LABORATORY EVALUATION OF Na_2CO_3 AND TRIETHANOLAMINE AS ABSORBING MEDIA

B. A. SCHEEREN[1], F. DE SANTIS[2]†, I. ALLEGRINI[2] and P. HEERES[1]

[1]*Dept. of Air Pollution, Agricultural University of Wageningen, The Netherlands;* [2]*CNR, Istituto Inquinamento Atmosferico, Area della Ricerca di Roma, Via Salaria Km 29,3, C. P. 10, Monterotondo Staz. Roma, Italy*

(Received, 27 April 1993, in final form, 29 November 1993)

Two different types of passive samplers (a badge and a tube-type) for the determination of SO_2 have been developed. Both samplers make use of a Na_2CO_3 coated quartz fiber filter as sampling layer. SO_2 is collected as sulfite which, after extraction and oxidation, is determined as sulfate using ion-chromatography. In laboratory calibration tests good linearity of the average uptake has been found over a SO_2 concentration range from 20 to 400 ppb. The sensitivity and capacity of the method is sufficient to cover a wide range of ambient concentrations, while the badge and the tube have detection limits for a one week exposure of about 4 and 34 µg/m3 respectively. Precision, calculated on replicates, for both samplers was found to be between 5 and 10%. The influence of humidity was studied in comparison to triethanolamine (TEA) coated substrates. It was seen that for the collection efficiency TEA coated filters show a 2 to 3 times stronger dependency on relative humidity in comparison to Na_2CO_3. It was also found that the badge type sampler showed good performance with an average windspeed higher than 1 m/s. The tube sampler was found to give reliable and accurate results at windspeeds lower than 1 m/s. Accuracy was investigated in the field in comparison with a diffusion denuder technique. Regression analysis of the data indicated good agreement between the two methods.

KEY WORDS: Sulfur dioxide, passive sampling, triethanolamine.

INTRODUCTION

Passive methods for SO_2, a major air pollutant which plays a key role in acid deposition, have only sporadically been reported over the past years. The oldest passive device, the sulfation plate, was first applied over 50 years ago by Wilsdon and McConnell[1] and later modified by Huey[2]. It consisted basically of a glass or plastic plate coated with a slurry of PbO_2 exposed to the atmosphere for a specified period. Lynch *et al.*[3] and recently Sickles *et al.*[4]

---

†To whom correspondence should be addressed.

showed that the usefulness of this and similar commercially available devices (also for passive determination of NO_2) is very limited due to the lack of specificity (e.g. interference of particulate matter) and poor linear response with exposure. Furthermore they are severely affected by relative humidity and wind velocity. Reiszner and West[5] studied a passive sampler which consisted of a gas permeable dimethylsilicone polymer membrane fitted to the end of a glass tube filled with a dichlorosulfitomercurate (II) solution. In a successive modification McDermott *et al.*[6] used a manganese (II) chloride-glycerol solution. Orr *et al.*[7], however, found that the Reiszner-West sampler had a very low sensitivity and, also, that it was unreliable because of the possibility of the solution freezing at low temperatures during cold weather.

Orr *et al.*[7] developed as an alternative to the Reiszner-West device, a passive sampler using a polycarbonate filter as a permeable membrane and a potassium carbonate/glycerol impregnated cellulose filter as trapping agent. However, this sampler was tested only for air velocities higher than 2.5 m s^{-1} and for a concentration range much higher than normally encountered in the atmosphere. Hangartner *et al.*[8] used a passive method based on the concept of the Palmes-tube (Palmes *et al.*[9]). Their sampler was a polypropylene tube containing 3 stainless steel screens as support for the adsorbing material which consisted of a triethanolamine (TEA)/glycol (3:1) mixture. They found a strong decrease in the recovery after exposure when stored at room temperature (22°C) and also a back diffusion of about 6% per day of storage. They also found a strong negative effect of the relative humidity on the recovery of SO_2. Consideration of the existing methods reported above, leads to the conclusion that at present a sensitive and reliable passive sampling method, with a detection limit low enough to be able to measure shorter than 24 hours, has not yet been developed. Our aim was to study a passive measurement method for SO_2 with the possibility to sample for less than 1 day (at common ppb levels of a moderately polluted site), and to focus on precision and low dependency on relative humidity, windspeed and particulate sulfate. To obtain high sensitivity a sampler was required with a large cross-sectional area (compared to commonly used samplers like the Palmes-tube) and a short diffusion path length. For this reason a short circular badge was chosen after the design of the Willems-badge (W-badge) which was previously adopted in a short term passive sampling method for NH_3 by Willems and Hofschreuder[10]. Because of the behavior of TEA as reagent for collecting ambient SO_2, (dependency on relative humidity, bad storability of the samplers after exposure and low stability of the TEA/SO_2 complex) it was necessary to search for an alternative collecting species. A better reagent was found in an absorbent based on Na_2CO_3. With the same trapping reagent a long term sampling method based on a longer tube with a smaller cross sectional area was also developed.

EXPERIMENTAL

Sampler preparation

For the experiments two types of samplers were used: a badge-type based on the concept of the Willems-badge (Willems and Hofschreuder[10]) for short term and a tube-type for long-term sampling. The W-badge is a circular polystyrene vessel 28 mm in diameter and 9 mm deep. In this study we have used a shorter version of the original W-badge design only 6 mm deep. The W-badge contains on the bottom a coated quartz filter, then a polystyrene spacer ring followed by a second uncoated Teflon filter also fixed with a polystyrene ring. The Teflon filter has a double purpose: it prevents turbulence from interfering with the diffusion process and avoids the interference of sulfate particles. The second type of sampler used in this study was meant for long-term exposure purposes. For this reason a design similar to the Palmes-tube (Palmes *et al.*[9]) was chosen. The polystyrene tube (from here on referred to as DS-tube), which contains a coated quartz fiber filter fixed at its bottom with a polystyrene ring, is 6.0 cm long and has a diameter of 2.0 cm. A preliminary investigation of several commercially available glass filters (Whatman A, Whatman GFA and Whatman QM) has shown that Whatman QM filters contain a significantly lower amount of sulfate after extraction in comparison to the others. They are also thicker and therefore able to be exposed for a longer period before saturation. For the preparation of the samplers a laminar flow bench with a built-in charcoal filter was used. Before assembling the badges and spacer rings they were first cleaned with water and then with ethanol. The DS-tubes and fixation rings were treated in the same way. The QM filters were cleaned with a hot 30% v/v ethanol/water solution and then washed twice with acetone, while the Teflon filters were washed with ethanol. For the impregnation the cleaned filters were put into a beaker with the coating solution for about 5 minutes. The filters were dried horizontally supported at the edges on parallel glass rods glued to a glass plate.

Coating reagents and analysis

In this study Na_2CO_3 and K_2CO_3 have been tested in comparison to TEA as absorbents for SO_2. These alkaline compounds have proven to be good collectors for SO_2 in other methods (Allegrini *et al.*[11] and references in this paper; Orr *et al.*[7]). It was seen that both Na_2CO_3 and K_2CO_3 coated glass fiber filters had a good collection efficiency in comparison to TEA when relatively low concentration coating solutions were used. No significant difference in uptake efficiency was found between Na_2CO_3 and K_2CO_3, consequently Na_2CO_3 was arbitrarily chosen to be investigated more intensively.

The following solutions were tested:

With Na_2CO_3:

A. 0.05 g Na_2CO_3 in 25 ml of H_2O/ethanediol/methanol 2.5:2.5:20.

With TEA:

B. 6 ml TEA and 2 ml ethanediol to 50 ml with acetone.

C. 6 ml TEA, 2 ml ethanediol and 2 ml H_2O to 50 ml with acetone.

The drying time for solution A was 30 minutes and 5 minutes for solutions B and C. After exposing the samples to the atmosphere, (normally in triplicate), the absorbent filters were put into polyethylene vials. 5 ml of Dionex eluent containing 0.3% H_2O_2 were added and the solutions extracted for 5 min in an ultrasonic bath. The vials were centrifugated at 4500 rpm for 10 min and then analyzed by ion-chromatography (Dionex QIC Analyzer, column: Dionex HPIC-AS3).

Laboratory validation

A laminar flow vessel and a wind tunnel to carry out turbulent flow experiments were built for the simultaneous exposure in the laboratory of up to ten badges. The laminar flow exposure vessel consisted of a large glass vessel (length = 37.0 cm, internal diameter = 14.6 cm), closed with a removable leak proof cap, in which air flow, humidity, temperature and gas concentration could be controlled. A pump was used to create a steady laminar flow through the vessel of 10.0 l min^{-1}. The corresponding Reynolds number, under standard atmospheric conditions and with an average flow velocity in the vessel of about 1 cm/s, was 96. Permeation tubes were used to generate SO_2 which was diluted at the inlet with purified ambient air. The humidity of the air in the vessel was controlled by drying the stream of dilution air with silica gel for low relative humidities or by passing the dilution air through a bubbler with water to obtain a high relative humidity. In this way a range of 0 to 70% relative humidity was available. Higher relative humidities were obtained by mixing the stream of dilution air with water vapor from boiling water. The wind tunnel consisted of a P.V.C tube with a length of 46 cm and an internal diameter of 15.2 cm placed in front of a fan. A honey-comb structure at the entrance of the windtunnel was used to create a homogeneous concentration field. SO_2 atmospheres were generated in the tunnel using SO_2 from a cylinder diluted with purified ambient air. The maximum average wind speed in the wind tunnel measured with a propeller anemometer (Wessels Messtechnik model DA 4000) was 2.0 m/s. The Reynolds number for the wind tunnel, with an average wind speed of 1.25 m/s, was 12700. High relative humidities up to 100% were obtained by sucking in water vapor from boiling water at the wind tunnel inlet. The samplers were exposed in the middle of the wind tunnel in a horizontal position.

In both set-ups temperature and relative humidity were measured with an electronic thermo/hygrometer (Hanna Instruments, HI 8564 thermo/hygrometer) and SO_2 concentrations continuously monitored with a Monitor Labs Fluorescence Analyzer Mod. 8850.

THEORY AND CALCULATION

The average concentration during the exposure of a passive sampler can be estimated according to Fick's First Law;

$$J = D * A * (C - Co)/L \tag{1}$$

Where: J = mass flux of gas (µg/s)
D = diffusion coefficient of the gas in air (m^2/s)
A = cross sectional area of the diffusion path of the monitor (m^2)
C = external concentration of the gas in air ($\mu g/m^3$)
Co = concentration of the gas at the interface of the sorbent ($\mu g/m^3$)
L = diffusion length (m)

The flux may be interpreted by analogy with an electric circuit, therefore the ratio L/D can be regarded as a the resistance against transport of the gas in air over the diffusion length L. In the case of the W-badge the total transport resistance (R_t) is made up of the following three components: resistance of the air layer within the badge ridge above the Teflon filter (R_1); the filter resistance (R_2); the resistance of the air layer between sorbent and Teflon filter (R_3). The importance of R_1 is determined by the height of the ridge above the Teflon filter and the average air velocity at the sampling site. It can be expected that R_1 is significant under less turbulent conditions as a consequence of the formation of a stagnant air layer above the Teflon filter (Willems and Hofschreuder[10]). In a turbulent atmosphere, however, R_1 is negligible. The filter resistance R_2 will depend on a host of different factors among which the diffusion coefficient D of the gas, the filter thickness, the filter porosity and pore size. Finally, the resistance of the air layer between the Teflon filter and the sorbent (R_3) can be described by L/D. Now, according to equation (1), the mass flux of a gas in a W-badge can be defined as;

$$J = A * (C - Co)/(R_1 + R_2 + R_3) \tag{2}$$

Where:

R_1 = stagnant layer resistance (s/m)
R_2 = filter resistance (s/m)
R_3 = L/D (s/m)

A temperature correction for D of about 5%/10° K should be taken into account (Fish and Durham[12]). The influence of pressure is proportionally inverse to the diffusion coefficient. Within a pressure range of 0.95 to 1.05 Bar and at the same temperature, the diffusion coefficient for SO_2 will vary from 0.127 to 0.115. The deviation over this pressure range is less than 10% and thus considered negligible compared to the temperature dependence.

For a certain exposure time the total amount of absorbed gas can be defined as:

$$Q = J * t \tag{3}$$

Where: Q = total amount of absorbed gas (μg).
J = average mass flux during exposure time t (μg/s).
t = exposure time (s)

When the absorption surface can be considered as a perfect sink for the diffusing gas, the concentration Co at the absorption surface can be assumed to be zero. According to Posner and Moore[13] the absorption process is reversible so the perfect sink assumption is not entirely correct. However, when the absorption capacity of the treated filter is large compared to the sampled mass of the gas, this assumption is considered to be close to the actual situation. Assuming that the concentration Co above the absorbing surface is zero equation (3) becomes;

$$C_{av} = \frac{Q \times R_t}{A \times t} \tag{4}$$

Where: C_{av} = average concentration during exposure ($\mu g/m^3$)

In equation (4) A * t/R_t is equivalent to the volume of air from which the SO_2 was sampled. For the W-badge with entrance filter, R_t was determined empirically by calibrating the sampler under turbulent conditions in the wind tunnel.

The W-badge without the entrance filter and the DS-tube were calibrated in the laminar flow exposure vessel. Under these non-turbulent conditions the total transport resistance R_t was considered to correspond to L/D, where L (diffusion path) was the total depth of the sampler.

RESULTS AND DISCUSSION

Calibration of the samplers

The samplers have been tested and calibrated in the laminar flow vessel and in the turbulent wind tunnel according to their potential application. The samplers were calibrated by exposing them to a wide range of SO_2-concentrations under different relative humidities, ranging from 35 to 90% in the case of the W-badge and from 35 to 70% in the case of the DS-tube. Regression analysis was performed on the experimental data using the SO_2-uptake per hour as a function of average SO_2-concentration during exposure. In all calculations the line was forced through the origin. Figures 1 and 2 illustrate the relationship between the hourly mean SO_2-uptake and the SO_2-concentration.

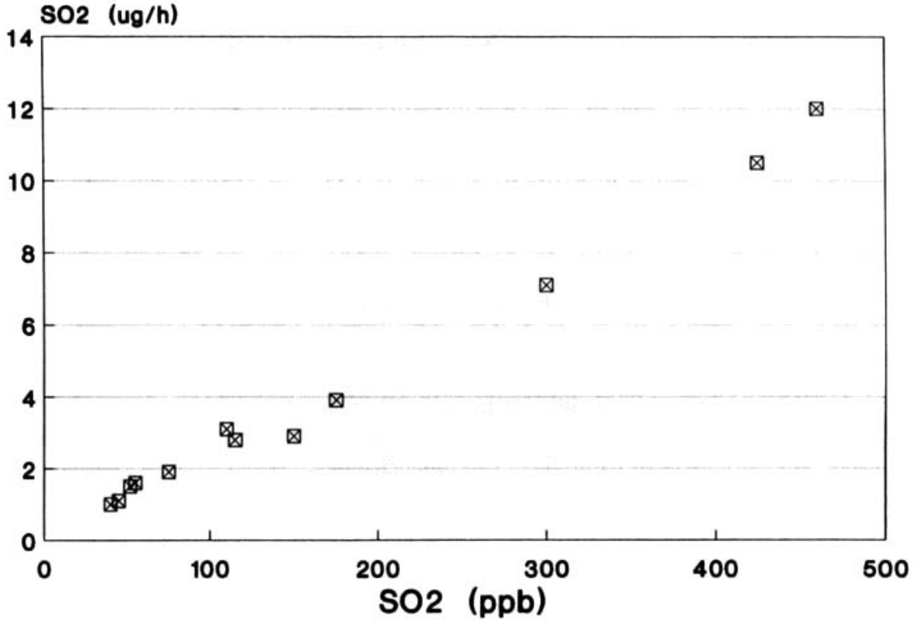

Figure 1. Hourly average SO_2 collected as a function of SO_2 concentration for the W-badge. R. H. from 35 to 90%, exposure time from 4 to 8 hrs, temperature 20°C.

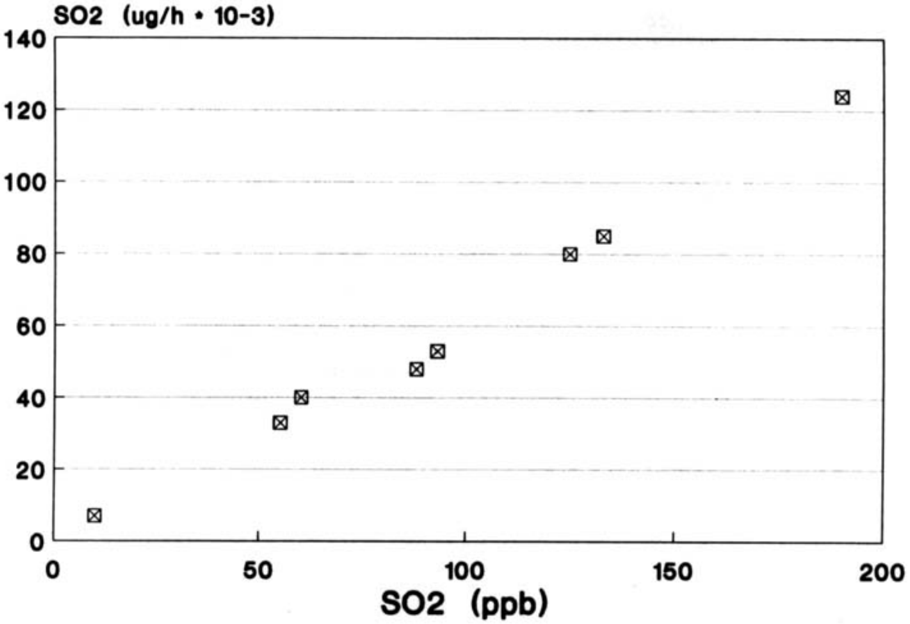

Figure 2. Hourly average SO_2 collected as a function of SO_2 concentration for the DS-tube. R. H. from 35 to 70%, exposure time from 4 to 8 hrs, temperature 20°.

The values obtained in the calibration tests (conducted on quadruplicate samples) lie on a straight line with a correlation coefficient of 0.996 and 0.991 at 97% and 94% confidence level for the W-badge and the DS-tube respectively.

A good way of checking the validity of a passive sampler is to compare the experimentally determined R_t-values with their corresponding values calculated on the basis of theory. For this comparison it is assumed for the W-badge that under turbulent atmospheric conditions the stagnant layer resistance R_1 is negligible. Consequently R_t is equal to $R_2 + R_3$. With R_3 equal to L/D the filter resistance R_2 can be calculated from the empirically determined R_t. In this way R_2 was found to be 58 s/m out of 11 experiments with a relative standard deviation of 8%. The same comparison was carried out on the DS-tube and on the W-badge without Teflon filter in a non-turbulent atmosphere where by assumption the resistance to mass transfer is equal to L/D. Table 1 reports the results obtained in the experiments. The diffusion

Table 1 Comparison between experimental and calculated R_t.

Sampler	*D_{SO_2}-theory*	*R_t-theory*	*R_t-exp.*	*D_{SO_2}-exp.*	*R_t-theory/R_t-exp.*
W-badge (no T-filter)	0.134	671	770	0.117	0.87
W-badge	0.136	$R_2 + R_3$	205	$L/(205 - R_2)$	$(R_2 + R_3)/205$
DS-tube	0.134	4478	4635	0.129	0.97

Table 2 Detection limits for the samplers.

Sampler	*Aver. blank* *(ug SO_4^{2-})*	R_{sd} *(%)*	*n*	*Minimum conc. (ug/m^3)* *1 h*	*12 h*	*24 h*	*3 days*	*1 week*
W-badge	0.54	52	14	300	25	13	5	4
DS-tube	0.17	84	7	5740	478	239	80	34

R_{sd} = Relative standard deviation, n = number of replicate samples

coefficients for SO_2 have been corrected according to the temperature relationship postulated by Fish and Durham (1971) and the average temperature during the experiments.

The ratio between R_t-theory and R_t-experiment presented in the table, shows that the agreement between the calculated and the measured R_t values is good.

Precision and detection limits

In order to evaluate the precision that can be attained both in high and low levels of SO_2, wind tunnel experiments on 2 to 4 simultaneously exposed W-badges were carried out for a sampling time ranging from 1.7 to 16.5 hours. The precision, expressed as relative standard deviation, was 7.1% on average for the lower concentrations (from 35 to 78 ppb). For higher concentrations (from 120 to 455 ppb) the precision was found to be 9.2% on average.

For the DS-tube the precision at low levels of SO_2 (from 10 to 58 ppb) was 7% whereas at higher SO_2 levels (between 80 and 135 ppb) it was 5.5%.

The detection limits for the samplers (reported in Table 2) were calculated as the tenfold standard deviation of the mean blank. In this way the minimum uptake amount of sulfate for the W-badge and DS-tube was 2.8 and 1.4 ug respectively.

According to laboratory experiments the maximum uptake is estimated to be between 60 and 65 µg of sulfate for the SO2-badge; this corresponds to a maximum average concentration of 140 ppb SO_2 and 20 ppb SO_2 for 24 hour and week sampling respectively.

Storage of exposed samplers

Exposed SO_2 badges were capped and stored at room temperature (22°) and at 5° in a refrigerator to study the effect of storage time on the recovery of sulfate.

The samplers, coated with solutions A and C, had previously been exposed at 24°C and 35% r. h. in the wind tunnel to a concentration of 375 ug/m^3 for one hour and forty minutes.

It was found, (Table 3), that for short term storage TEA is slightly more stable than Na_2CO_3. When the passive samplers are stored for a longer period (more than a week), Na_2CO_3 samplers are more stable than TEA samplers. For longer term storage the results show for both TEA and Na_2CO_3 that storage in the refrigerator limits the loss of sulfate due to back diffusion. Thus storage in a freezer should be recommended as the best method for long term storage.

Table 3 Storage stability for W-badges.

Coating	*Storage Temp.* (°C)	*Recovery (%)* Day 0	Day 7	Day 32
Sol. A	5	100	97	95
	22	100	93	90
Sol. C	5	100	100	87
	22	100	101	85

Results are average of three replicates.

Influence of humidity

To study the influence of relative humidity on the collection efficiency of Na_2CO_3 coated filters, the total transport resistance R_t has been determined over a range of 5 to 85% relative humidity. Normally coated filters have been compared with coated filters that were dried in a hot dry air stream for 5 minutes, after the normal drying procedure, to minimize the amount of water in the absorbent medium ("dry" Na_2CO_3). Additionally two types of TEA coating solutions were compared under the same circumstances: "dry" TEA without water (sol. B.) and "wet" TEA containing water (sol. C). In Figure 3 the relation between R_t and the relative humidity for dry Na_2CO_3 and normal (wet) Na_2CO_3 is illustrated. Analogously, figure 4 shows the relation between R_t and the relative humidity for wet and dry TEA.

When looking at the results for Na_2CO_3 as presented in Figure 3, it can be seen that wet and dry Na_2CO_3 behave in opposite ways with increasing humidity. The same pattern was found for TEA as illustrated in Figure 4.

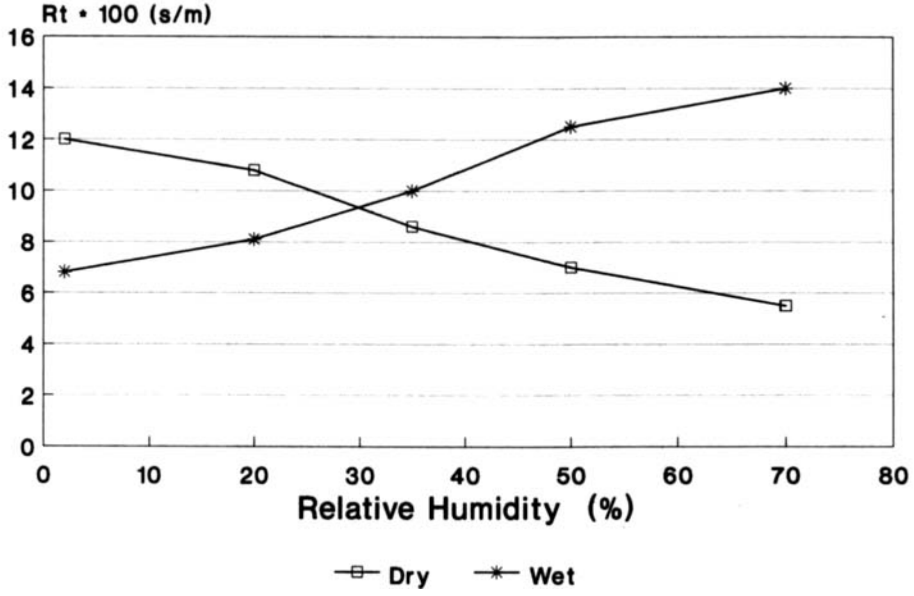

Figure 3. Influence of humidity on R_t W-badges prepared by using the carbonate solution.

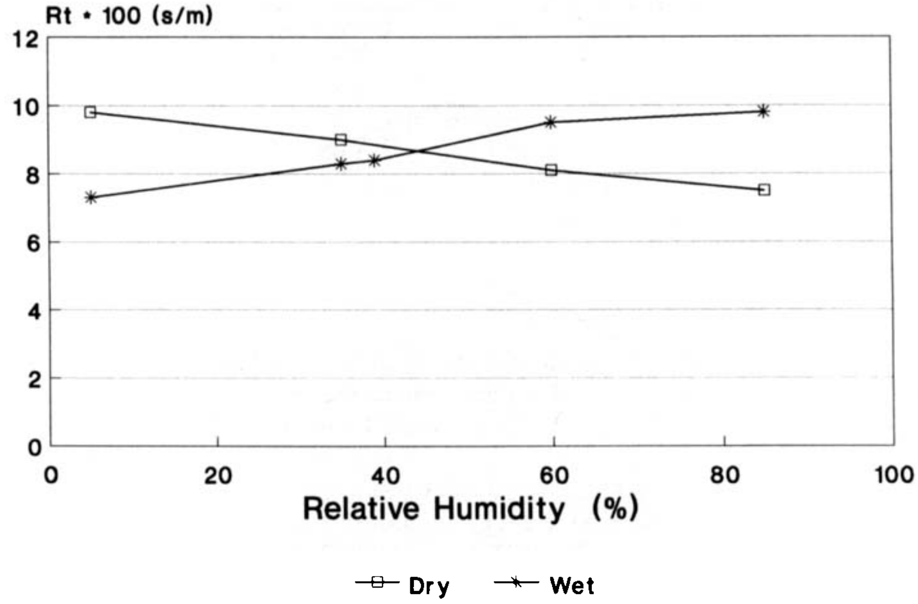

Figure 4. Influence of humidity on R_t W-badges prepared by using the TEA solution.

The results obtained show that at low relative humidity a "dry" absorbent medium is clearly less efficient in the conversion of SO_2 to sulfite in comparison to a "wet" absorbent, most likely because of the lack of water necessary for a rapid conversion. The results imply that in a dry atmosphere the presence of water in the absorbent medium itself is able to promote a rapid conversion of SO_2 to sulfite which minimizes back diffusion and results in a relatively high uptake rate. Obviously, during sampling a final equilibrium will be established between the absorbent surface and the gas phase above it. The water uptake of the "dry" medium at high r. h. is able to promote conversion in essentially "dry" filters. The higher the average r. h. the higher will be the efficiency of the "dry" absorbent. However, when the medium contains water from the beginning, an effective absorption under dry atmospheric conditions occurs. When sampling in a dry atmosphere the effect of water in the medium will, of course, only be temporary. Both TEA and Na_2CO_3, as hydrofilic compounds can incorporate water molecules and, consequently, this lead to a decrease of the reaction possibilities for SO_2.

Our results show that the absorption capacity of the "wet" Na_2CO_3 medium is less sensitive to r. h. (over the range 5%–70%) by a factor of 2 than "wet" TEA. For the "dry" media the difference is as great as a factor of 3 in favor of Na_2CO_3. The reason is probably that TEA, which has a stronger hydrofilic character in comparison to Na_2CO_3, can cause a certain degree of saturation at higher r.h., most likely because water which is present in a much higher concentration, tends to compete with SO_2.

Effect of wind velocity

The Teflon filter used for excluding the interference of turbulence on the W-badge can cause the build-up of a stagnant air layer, the influence of which is related to the windspeed and to the ridge height above the entrance.

The state of turbulence of the atmosphere at the sampling site, which can be seen as a function of the wind speed, will determine the presence and significance of this stagnant layer. In scanning an increasing range of wind velocities the corresponding overall transport resistance shows an exponential pattern, with R_t leveling asymptotically at higher wind speeds. The asymptotic value corresponds to a situation where the presence of a stagnant layer above the entrance filter is of no significant importance, or does not exist anymore.

According to the findings of Willems and Hofschreuder[10] this asymptotic value can be observed above a wind speed of 1 m/s (border-windspeed-value) in the wind tunnel. Our results confirm this threshold value. At lower windspeeds the total transport resistance increases. In practice, since in the range 0–1 m/s the total transport resistance is dependent on the extent of the stagnant layer, the W-badge can only be used in a windspeed over 1 m/s or when an artificial turbulence is created near the sampler.

The long term sampler presented in this paper (DS-tube) was found to be accurate only under conditions of low atmospheric turbulence or low wind speed and is therefore only appropriate to measure indoor air.

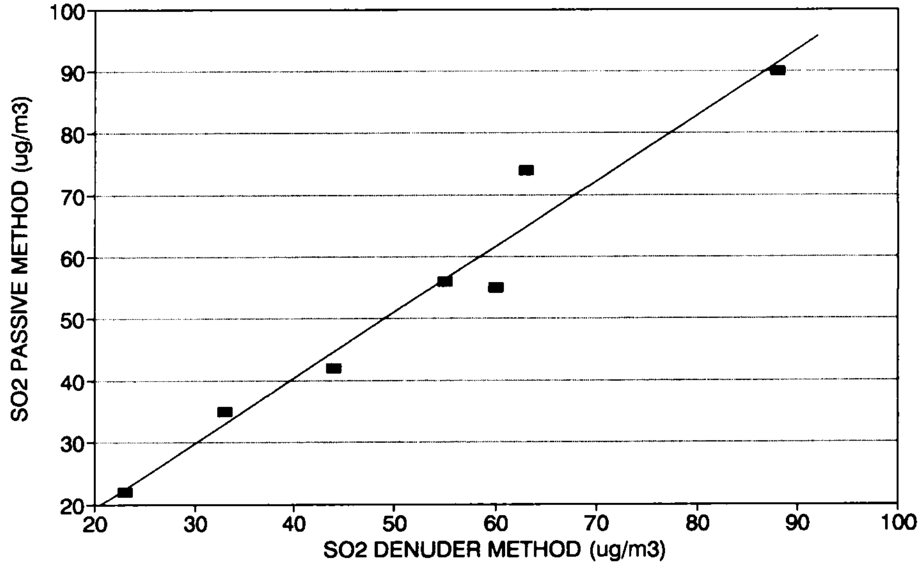

Figure 5. SO_2 concentration measured by W-badge vs diffusion denuder under field conditions.

Field validation

A field validation exercise was undertaken in which the W-badge was exposed side-by-side with a conventional sampling system based on carbonate denuders[11]. The experiments were performed during some selected days of March–April 1993 at the CNR Research Area, Rome, located 30 km north-east of the urban centre. Figure 5 shows the relationship between the concentration of SO_2 determined by the method proposed and those obtained by the reference method, respectively. All results are for average 24 h concentrations and were obtained by using triplicate sets of W-badges. The R. H. and temperature during sampling ranged from 60% to 90% and from 10°C to 17°C respectively.

Regression analysis (where the active system was the X variable) gives a correlation coefficient of 0.956 and a slope of 1.06 for data over the range of 23 to 90 ug/m^3 as sampled by the active method.

Application of the different samplers

Taking into consideration the design and dimensions of the sampler as well as the desired accuracy and measurement strategy the following scheme is suggested:

sampler	indoor (still air)	indoor (artificial turbulence)	outdoor V > 1 m/s	outdoor V < 1 m/s
W-badge (no T-filter)	++	—	—	—
W-badge	+	+++	+++	+
DS-tube	+++	++	—	+

performance: + = reasonable, ++ = good, +++ = very good, — = bad

CONCLUSIONS

A badge and a tube type passive sampler have been described to measure ambient levels of SO_2. The badge type sampler can be used for short term purposes while the tube is suitable for long-term sampling. The method makes use of Na_2CO_3 as collection agent. This species was found to be relatively independent of relative humidity compared to TEA. The influence of windspeed on the collection efficiency of the samplers determines their applicability. The results of the calibrations obtained from laboratory experiments showed good agreement with theory. When using such a method in the field the calibration factors should be checked by calibration experiments at the sampling site and furthermore meteorological data (temperature, relative humidity and windspeed) should be collected during sampling.

The validation of the method under field conditions, although on a limited set of data, shows a very good agreement with a conventional method based on active sampling.

Acknowledgment

The financial support of the "Progetto Finalizzato Chimica Fine II" and of the CEC under a STEP contract (CT90-0108) is gratefully acknowledged.

References

1. B. H. Wilsdon and F. J. McConnell. *J. Soc. Chem. Ind.* **12,** 385T-388T (1934).
2. N. A. Huey. *J. Air Pollut. Control Assoc.*, **18,** 610–611 (1968).
3. A. J. Lynch, N. R. McQuaker and M. Gurrey. *Envir. Sci. Technol.* **12,** 167–173 (1978).
4. J. E. Sickles and R. M. Michie. *Atmos. Environ.* **21,** 1385–1391. (1987).
5. K. W. Reiszner and P. W. West. *Envir. Sci. Technol.* **7,** 526–532 (1973).
6. D. L. McDermott, K. D. Reiszner and P. W. West. *Environ. Sci. Technol.* **13,** 1087–1090 (1979).
7. D. B. Orr, J. C. Hipfner, W. H. Chan, M. A. Lusis and J. E. Hunt. *Atmos. Environ.* **21,** 1473–1475 (1987).
8. M. Hangartner, P. Burri and C. Monn: in *Man and his Ecosystem.* Proceedings of the 8th World Clean Air Congress 1989, The Hague, The Netherlands, 11-15 September 1989. (L. J. Brasser and W. C. Mulder Editors. Elsevier Science Publishers B. V., Amsterdam, 1989) Volume 3. pp 681–686.
9. E. D. Palmes, A. F. Gunnison, J. Di Mattio and C. Tomczyk. *J. Am. Ind. Hyg. Ass.* **37,** 570–577 (1976).
10. J. J. H. Willems and P. Hofschreuder: *Field Intercomparison Exercise on Ammonia and Ammonium Measurement,* Proceedings of a field study organized by CEE and CNR- Istitute for Atmospheric Pollution, Rome, April 29-May 4, 1990. (I. Allegrini, A Febo, C. Perrino Editors. Air Pollution Research Report 37. Guyot, Brussels, 1990) pp. 113–121
11. I. Allegrini, F. De Santis, V. Di Palo, A. Febo, C. Perrino, and M. Possanzini. *Sci. Total Environ.* **67,** 1-16 (1987).
12. B. R. Fish and J. L. Durham. *Environ. Lett.* **2,** 13–21 (1971).
13. J. D. Posner and G. Moore. *J. Am. Ind. Hyg. Ass.* **46,** 277–285 (1985).