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A New Device for Automatic Exposition of Passive Samplers in Air Pollution Monitoring

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Abstract: This paper describes a new sampler intended for automatic exposition of passive samplers in indoor and outdoor air pollution monitoring. The sampler overcome most of the limitations in the use of passive samplers since it allows time and event programming, thus extending the flexibility in practical applications. The implemented software allows a full control of environmental parameters which can be input by analog or digital data. Preliminary tests have been carried out by indoor monitoring of Hydrogen Sulphide and monitoring of ambient Ozone. Data show that Hydrogen Sulphide accumulates in indoor atmosphere while Ozone can be monitored in specific time intervals in which it is expected to show the highest concentration, thus the highest exposition risk to population. Additional applications are discussed with the aim to reconsider the use of passive samplers in the solution of several environmental problems related to human exposure to atmospheric pollutants.

Key words: air pollution, passive sampler, ozone, hydrogen sulphide, indoor pollution

1. Introduction

Most measurements of atmospheric pollutants are carried out by using automatic instruments which are able to provide concentration data in almost real time. Unfortunately, automatic techniques are limited to just a few pollutants since sensors are available for a limited number of species. In addition, they are very expensive either in terms of investment and maintenance. For those pollutants that cannot be evaluated by automatic instruments, accumulation methods are used. They are based on sampling a volume of air over a suitable substrate (Filters, traps, etc.) in which the relevant chemical species are irreversibly collected. After sampling, the substrates are analyzed by using a variety of method and the pollutant concentrations can be derived. This type of sampling can be defined as "active" in that air is forced through the absorbing substrates.

Alternative popular methods to measure pollutant concentration are based on "passive" sampling. In this case, pollutants are forced by molecular diffusion on suitable adsorbing surfaces where they are irreversibly adsorbed. On this surface, a concentration gradient is developed and, according to the physical nature of molecular diffusion, such a concentration gradient induces additional transport of pollutants from the air to the surface. This, in turn, causes an apparent flow rate of air which is equivalent to that defined in active samplers. Therefore, after a suitable time, the substrate accumulates an amount of pollutants which can be analysed by proper analytical methods. The apparent airflow is defined by the Fick law according to which the actual flow rate depends upon the diffusion coefficient of the molecules and upon the geometry of the sampler.

Several types of passive samplers are now available for most pollutants of environmental interest. They offer a variety of design and practical applications [1]. Such applications exclude particulate matter since the diffusion coefficient is very low. In addition to ambient

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air monitoring, passive samplers found application in conservation science and technology [2]. Interesting applications were also developed for water pollution [3].

Among the variety of passive samplers now available, Analyst® (Trademark by Envint srl) passive sampler was developed with the main objective to collects pollutants over a very long time span, allowing unsurpassed sensitivity, repeatability and reliability [4, 5].

This type of sampler is small in size and suitable for most applications in ambient air as well as in indoor pollution. The design is very flexible allowing applications for most pollutants including those requiring a chemical reaction to take place inside the sampler (for instance NOx) [6]. According to the experience gained upon several years of applications, it can be concluded that passive samplers provide a useful tool for air pollution assessment in ambient atmospheres and in indoor pollution.

In fact, they do not require electric supply, then they can be used in remote locations or where power is not available. Accuracy and precision of the analytical methods are fully acceptable, especially for the so-called "preliminary assessment" or "indicative measurements". They can be also be used for the control of working sites and for indoor environments.

Despite these obvious advantages, passive sampling technique shows several limitations. These are mainly related to the limited operating flexibility. For instance, they do not allow sampling for a fixed periods of time since, and, unless an operator remove them, they continue to sample pollutants from the air. Also, they cannot be controlled on changing conditions related, for instance, to meteorological situations. Finally, they are always active. This limitation is very important since it does not allow to measure concentrations and expositions of important group of people according to their exposition to pollutants which is changing on time. For instance, monitoring in schools after lessons is not useful since it dilutes and confuses the data gathered during the students' permanence.

In order to overcome those limitations, a sampler designated as PAS06/15 has been developed by Envint srl. It is specifically designed for Analyst passive samplers and is able to start simultaneously the sampling on one or more passive samplers through date and time programming, also in a sequential application. It can start or interrupt sampling according to pre-defined conditions and restart sampling when those conditions are over. In addition, it is able to sample one or more passive samplers according to meteorological variables such as wind speed or wind direction. Also, the sampler record ambient temperature and relative humidity and it is able to read several analog inputs from other sensors and analysers.

This paper describes the basic design and operation of the sampler with a detailed description of the operational features toward a number of practical applications in air pollution monitoring. Moreover, some practical applications related to time discrimination of outdoor Ozone pollution and indoor Hydrogen Sulphide content will be described.

2. Material and Methods

2.1 Basic Design and Operation of the Sampler

The basic design of PAS 06/15 is shown in Fig. 1.

A fixed plate A contains the passive samplers (in this case up to six) while a rotating plate B includes or does not include plugs. If plugs are not present then the hole allows pollutant molecules to diffuse into the passive sampler (sampler 2). Plate C is just an inert felt spacer for mechanical coupling between the plates. If plugs are present (Sampler 1), then diffusion is just stopped and the relevant passive sampler is not active. Upon software command, an electric stepping small motor separates the two plates and a second motor allows the rotating plate to move CW or CCW by a programmed number of steps. In the case of Fig. 1, the rotation of one step CCW will set sampler 1 under sampling, while sampler 2 will be closed. Sampler 1 and 2 are, for the sake of simplicity, are supposed to be made by the

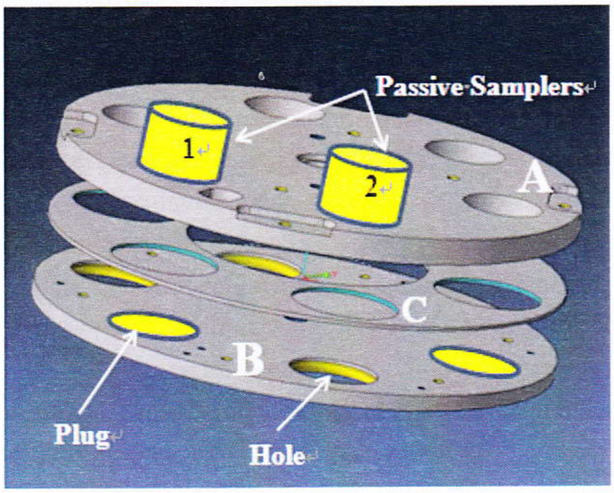

Fig. 1 Basic of automatic sampler PAS 06/15.

same type of passive samplers. However, different types of samplers for monitoring different species may be accommodated on the plate A.

By properly combining the number, type and timing of the sampler, it will be possible to program a large number of different combinations covering most of the needs for an effective and efficient monitoring. For example, Fig. 2 shows how a simultaneous measurement of Nitrogen Oxides and Ozone during selected intervals of the day (for instance between 10:00 and 17:00 (When Ozone reaches the maximum levels); and the same measurement between 17:00 and 10:00 (When Ozone reach the minimum values) can be easily carried out.

In this configuration, passive samplers in position 1 and 3 are for one species (suppose Ozone) and positions 2 and 4 for the other species (Suppose NOx). The mobile plate has plugs in positions 1, 2, 3, 4. In such configuration, Table 1 would explain what happens when the mobile plate will rotate CW by one step.

Initially (step 1), no sampler is active. One step CW will cause the sampling on O3/1 only. An additional step (3) will cause sampling on O3/1 and NOx/1 but not on the other two samplers. On step 5, the sampling configuration is reversed. According to this scheme, every day the sampler can move to position 3 from 10:00 to 17:00 to accumulate pollutants on passive

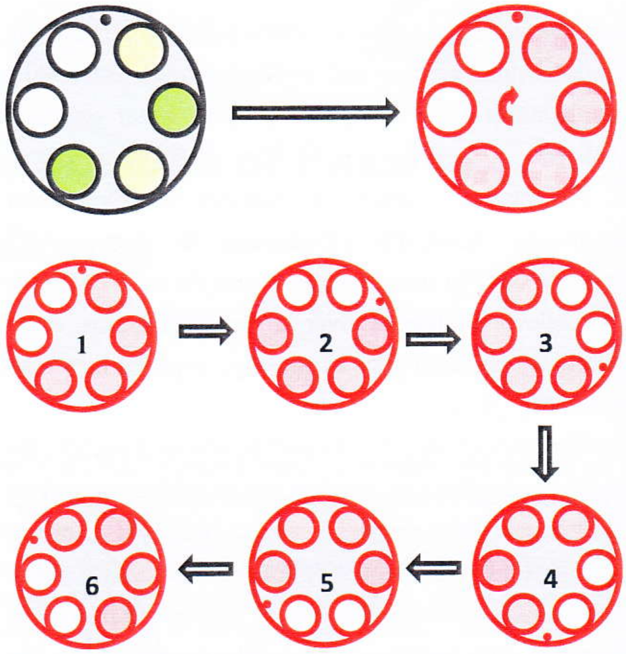

Fig. 2 Sampling sequence for two pairs of passive samplers in two different time intervals.

Table 1 Logic sequence of sampling (Y = Yes; N = Not) relevant to Fig. 2.

Step	O3/1	O3/2	NOx/1	NOx/2
1	N	N	N	N
2	Y	N	N	N
3	Y	N	Y	N
4	N	Y	Y	N
5	N	Y	N	Y
6	N	N	N	Y

samplers O3/1 and NOx/1. Moving the sampler to position 5 from 17:00 to 10:00, accumulation on O3/2 and NOx/2 occurs. After, for instance, one or two weeks of alternate sampling, the sampler is moved again into position 1 where sampling is stopped on all four passive samplers. At this point, the two pairs of passive samplers can be collected and analysed to provide the average ozone and nitrogen oxide concentrations between 10:00 and 17:00 and the same values between 17:00 and 10:00.

2.2 Electronics and Software

The example synthetically described in Table 1 shows the flexibility of the sampler in terms of different passive samplers configuration. However, such flexibility is very much increased by taking profit of features of PAS 06/15 in terms of electronic interface. This is depicted in Fig. 3.

The core of PAS 0/15 is a microprocessor programmed by a tablet with Android® operating system. The microprocessor is programmed by using a Wi-Fi connection which is externally activated by a small magnet. The tablet is serving as output for the programming procedures and as input for data provided by the instrument according to programming. By default, the instrument outputs in programmed time intervals (from 1 minute up);

- Programmed sequence
- Status of instrument (sampling positions)
- Ambient temperature and relative humidity
- Status of digital inputs
- Status of power supply battery

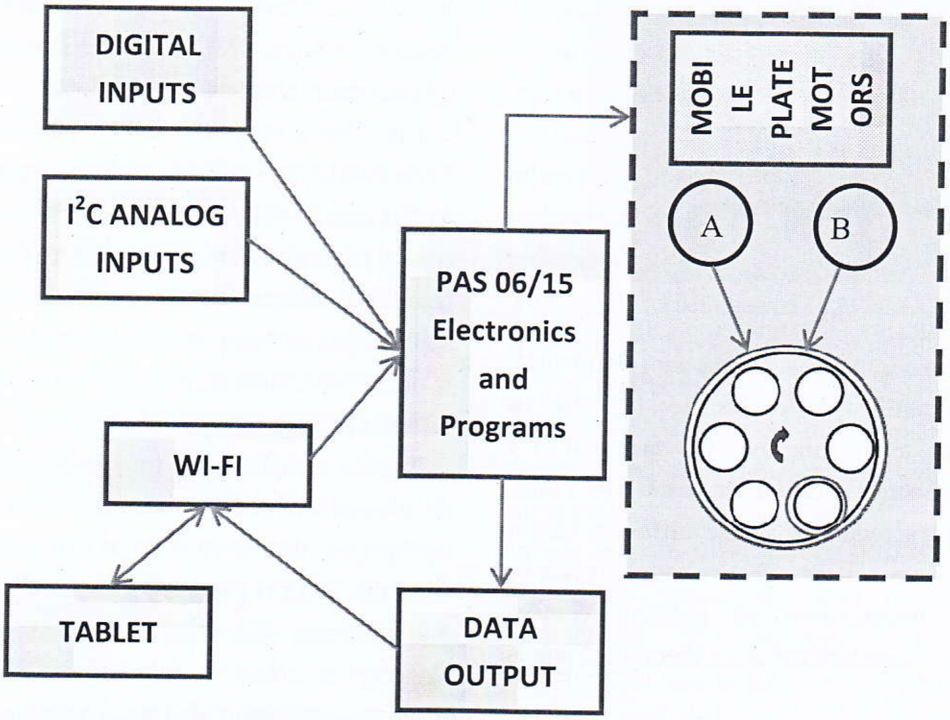

Fig. 3 Electronics and interfaces of the sampler.

Digital inputs (dry contacts) may be used for activating different sampling programs. The instruments may accept up to 8 different sampling programs which can be automatically selected by time or by the status of digital input. Since the number of digital inputs are three, the instrument may run up to eight different programs. This feature is very useful when sampling on different passive samplers are needed according to external parameters. This is for instance the case of some meteorological parameters such as wind speed and direction allowing a sort of "source apportionment" of the pollutants under investigation. This approach may easily complement investigations on diffuse pollution from sources [7].

In addition to the above "on board equipment", the instrument is able to monitor external analog data through I^2C interface which may be very useful in controlling additional environmental parameters. They are read by the microprocessor and output according to the output file programme by the user. This feature turns PAS 06/15 into a very effective environmental data logger.

Finally, the instrument is powered by a 12 VDC rechargeable battery which allows unattended and continuous operation for typically 45 days.

Fig. 4 shows the picture of the instrument with a wind shield at the bottom. Dimensions are 20 cm diameter and 20 cm height. The wind shield is used to

Fig. 4 Picture of PAS 06/15 with wind shield.

limit air turbulences, still allowing air circulation. Several studies confirmed (for instance [8]) that in windy conditions, air moving over the open end of a diffusion tube generates turbulence inside the tubes. This can lead to a reduction in the diffusion length resulting in an increase in the effective sampling rate so that the air concentration of pollutants under investigations is overestimated if the theoretical rate is used.

2.3 Analytical Procedures for the Field Tests

Analyst type passive samplers were used during the preliminary field tests. The passive samplers used were addressed to the measurement of Ozone and Hydrogen Sulphide.

The measurement of Hydrogen Sulphide is based upon an original paper based upon the use of a passive sampler with an active surface of a paper filter coated with a silver ion solution followed by optical (reflectance) determination of the metal sulphide. Laboratory tests were conducted in controlled atmosphere to evaluate linearity, uptake rate, face velocity effects, sample stability, precision, accuracy, and influence of relative humidity, as well as interfering species [9].

Characteristics of this diffusive sampler are:

- Uptake rate (ml/min) 7.5±1.2 Standard Deviation
- Precision 3.8-6.2%
- Limit of detection 400 μg m-3 h corresponding to about 0.5 μg m-3 for a monthly sampling.

The limit of detection is calculated taking into account the blank value plus three time the standard deviation so that, even at low concentration range, the measurement is very sensitive.

The original paper and subsequent tests demonstrate that other species commonly found in the atmosphere do not interfere significantly with the measurement. A critical aspect is related to the effect of solar radiations, thus the analyst passive sampler used for this application, has been modified from the original design in order to avoid the direct exposure of active surface to diffuse sunlight.

Passive sampler used for Ozone passive was also developed in order to provide a simple a reliable method for the monitoring of this pollutant starting from the original paper by Koutrakis [10]. The use of Nitrite coated filter was adapted to Analyst passive sampler in order to monitoring Ozone in remote environments resulting into a reliable, accurate and sensitive device [11].

2.4 Details of Field Test Site

Field tests have been done in Montopoli di Sabina, a small city north of Rome, Italy. The site is not affected by local emissions air pollution, with the exclusion of a very limited amount of local traffic, thus the only significant polluting species are those related to background pollution and long range transport such as Ozone. No previous air pollution data are available for this site. Geographical data for the site are:

- Latitude: 42°15′37.40″
- Longitude: 12°41′26.08″
- Elevation: 276 m a.s.l.

Measurements were carried out during July 2017 by exposing two sets of PAS 06/15. One of them was addressed to the measurement of ambient Ozone and was operated outdoor. Two Ozone Analyst passive samplers were used. The instrument was programmed in order to operate the first passive sampler between 10:00 AM and 6:00 PM, while the second passive sampler was active between 6:00 PM to 10:00 AM of the following day. It should be stressed that data relevant to time interval 10:00 AM–6:00 PM corresponds to the 8 hours of the day in which Ozone concentration reaches the highest concentration levels. This data is related to the Ozone target value for the protection of human health [12]. The target value is set to 120 μg/m^3 not to be exceeded on more than 25 days per calendar year averaged over three (3) years. Although the evaluation of this parameter needs the knowledge of hourly Ozone concentrations, the average 8 hours concentration by passive samplers is a valuable data to recognize if Ozone is a problem for the site under investigation.

The Ozone passive samplers were collected after 30 days of exposure and the active substrate analysed by ion chromatography as its Nitrate ion content.

The second set of PAS 06/15 was used for the evaluation of Hydrogen Sulphide and was operated indoor. In this case, two Analyst passive samplers intended for the measurement of Hydrogen Sulphide were used. PAS 06/15 was programmed in order to expose the first sampler between about 08:00 AM and 08:00. Modulation of ambient concentrations of Hydrogen Sulphide was ensured by opening windows during the day and closing them over night. Even in this case, passive samplers were removed after 30 days and analysed by photometry.

3. Results and Discussion

This paper, as said before, is addressed to preliminary measurements only in order to show how an automatic sampler may extend the applications of passive samplers. However, even though the number of experimental data are relatively small, the results are still quite interesting.

Hydrogen Sulphide average indoor concentrations during the day (most of the time with open windows) is about 0.6 μg/m^3, i.e., not far from the lowest detection limit. On the contrary, when windows are closed, the average concentration is 1.6 μg/m^3. The concentration levels gathered in this test, although much lower than that assumed to be significant for the protection of human health, offer useful information about the occurrence of human exposition to this species and to indoor pollutants in general [13].

Specific sources of Hydrogen Sulphide are usually related to nearby industries or to re-entrainment of underground gases into building. None of these potential sources are present in the area of test, thus the only significant source may be the non-perfect isolation of sewage systems which causes higher indoor concentrations when air is not diluted by external air. Also the use of low quality drywall may cause undesirable emission of Hydrogen Sulphide. However, this source also should be excluded for the present case.

Data for Ozone are also interesting for the environment. The average 8 hours (daytime) concentration was found to be 105 μg/m^3. This figure, compared with the target value of 120 indicates that that exceedance occurred for several days. This is not surprising since the period of the test was in full summer season when Ozone concentration is high. Very high hourly concentration of Ozone were indeed recorded in automatic monitoring stations near Rome. However, significant comparison cannot be attempted with official data since location and elevation of the stations are completely different from the test site.

Average night time concentrations was 45 μg/m^3 which is 43% of daily data. This ratio is higher than that observed for other air quality monitoring stations in the region of Rome [14]. However, most of monitoring stations are at relatively low elevation, thus below the average top of the nocturnal mixed layer. In fact, data relevant to stations at high elevation do not show significant changes between daily an night time concentration data.

4. Conclusions

The automatic sampler PAS 06/15 described in this paper is very useful when conditional sampling needs to be performed with passive samplers. The flexibility of the apparatus is such that it is able to solve several practical problems at a relatively low cost and efforts. Indoor and outdoor measurements are obvious applications. However, other environmental applications can be sought. For instance, conditional monitoring for source apportionment as well as sampling in working sites during periods of time where the risk of exposure to toxic pollutants is relevant are just examples of possible applications.

Tests presented in this paper, although limited in number, is more than enough to demonstrate that coupling of Analyst passive samplers and PAS 06/15 may become a new tool for applications of passive monitoring in fields not attempted before.

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