PERFORMANCE COMPARISON OF DIFFERENT BRANDS OF PASSIVE SAMPLING TUBES FOR THE DETERMINATION NO_2 AND O_3 IN URBAN ATMOSPHERE

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ABSTRACT

The efficiency of passive sampling tubes for simultaneous measurements NO_2 and O_3 in ambient air were evaluated. Results obtained from passive sampling tubes were compared with continuous monitoring device results. NO_2 is chemiadsorbed onto TEA as nitrite ions and determined with UV-VIS spectrophotometry. For Brand I and Brand II passive sampling, ozone reacts with DPE to form 4-pyridylaldehyde and measured with UV-VIS spectrophotometry. Brand III diffusion tubes contain stainless steel wire coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography. Precisions of the method as Standard Deviation are between 4- 20 $\mu g/m^3$ for NO_2 and 0.35 – 19 $\mu g/m^3$ for O_3. When results were compared with continuous monitors, deviations were ranged from +26% to -28% for NO_2. For O_3 differences between passive samplers and active monitors ranged between -50% and +30%. Some brands did produce results that are fairly comparable with the average concentrations obtained from continuous monitoring instruments. Further tests, such as effect of exposure periods on accuracy and reproducibility, reproducibility and accuracy tests at successive periods, effect of storage time will be performed using these brands.

Key Words: passive sampling, nitrogen dioxide, ozone

1. INTRODUCTION

Nitrogen dioxide is secondary pollutant in the atmosphere which converted from NO. As a result of reaction nitrogen dioxide with the VOCs which are abundantly present in the urban atmosphere, it contributes ozone formation and other photochemical oxidants. It has direct impact on the environment and human health through the formation of ozone, other photochemical oxidants and the deposition of acidity. Ozone is a strong oxidant and has adverse effects on human health and on materials.

Some 100 years after the first deployment of a 300- station passive monitoring network to determine relative atmospheric ozone concentrations (Fox, 1873), during some past two decades, there has been increasing interest to improve and use passive samplers to collect a number of gaseous air pollutants (Namiesnik et al., 1984; Cao and Hewitt, 1991). Today a number of passive samplers are commercially available and have been used to determine air quality in workplace, indoor living environment

and ambient air. Passive samplers have found wide use for routine monitoring of air pollutants, because they are cheap, small in size, light, silent and do not require power and skilled people. However, passive samplers may be subject to biases caused by alteration in sampling rate due to variation in atmosphere turbulence, or caused by chemical interference (Ayers et al., 1998). So some evaluations are required by performing the tubes under real condition, before passive absorption samplers can be used to collect data on ambient pollutant concentrations.

A number of studies which has compared measurements of NO_2 and O_3 in parallel trials between passive samplers and real-time continues techniques. For example Atkins et al., 1986; Moscheandras et al., 1990; Campbell et al., 1994 used chemiluminescence techniques and Bernard et al., 1999 and Manning et al., 1996 used UV ozone monitors to compare results. Unfortunately results show variation. Campbell et al. (1994) found that NO_2 concentrations were overestimated, by up to 40%, by diffusion tubes in exposed positions. Atkins et al. (1986) observed no significant difference for NO_2 concentrations measured during validation trials in the field. Moschandreas et al. (1990) reported that low temperatures in the range 251-283 K resulted in underestimation of NO_2. Bernard et al. (1999) found satisfactory reproducibility and precision results for O_3 measurements. The correlation coefficient for forty measurements was r= 0.9, p <10-3, and the regression coefficient was close to 1. Manning et al. (1996) found that monitor/sampler ratios were between 0.78- 1.17. The authors concluded that any differences in the results between ozone passive sampling and continuous monitoring were solely due to their experimental error.

In the present work, three different commercially available passive sampling tubes were used to measure NO_2 and O_3 at point where close to cross section of the crowded roads in urban area (Sıhhiye) and results were evaluated with continuous monitoring system. The passive tubes used in this study have been widely in scientific researches and monitoring studies through the world.

We are planning to use passive samplers to determine spatial distribution of organic and inorganic pollutants at Bursa, to be able to evaluate distribution of health risk caused by these pollutants. Variety of passive samplers is available in the market. A small experiment was performed to test their performances and select the brand that will be used at Bursa. The experiment involved comparison of NO_2 and O_3 passive samplers. Although SO_2 was also initially included in the exercise, it is later not included in the experiment because some of the SO_2 samplers were contaminated in our laboratory.

Since sampling duration was very short and considerable small amount of sample was collected during this period of time, it is difficult to interpret the possible interferences arising from chemicals used to coat the filters. Hence aim of the study is compare efficiency of commercially available passive sampling tubes in real condition with the continuously monitoring devices.

2. EXPERIMENTAL

Three different commercially available passive sampling tubes were evaluated after one week sampling period. Since we don't want to declare brands of passive tubes used in the present work when evaluating the performance of tubes with continuous monitoring devices, cylindrical badge tube with tubular diffusion membrane was called as Brand I, open ended diffusion tube with protective shelter and without protective shelter were called as Brand II and Brand III, respectively. In Brand I cylindrical badge tube within microporous sintered polyethylene diffusive barrier; NO_2 is collected onto triethanolamine (TEA) mycroporous polyethylene cartridge. Brand II passive samplers comprise 7.4 cm long polypropylene tubes with 9.5 mm internal diameter, which contains glass fiber filter coated with TEA. Brand III passive samplers consist of a 7.1 cm length acrylic tube with 1.1 cm internal diameter which have stainless steel wire impregnated with TEA. And 7.4 cm long and 9.5 mm diameter polypropylene tubes, which contain glass fiber filter coated with TEA, were designed and improved extraction and analyzing procedure for determination NO_2, which was called as custom-made. For all passive sampling brands, nitrogen dioxide is chemiadsorbed onto TEA as nitrite ions.

For ozone measurement, Brand I badge cartridge is formed by a micropore olyethylene tube filled with slica gel coated with 4, 4'dipyridylrhylene (DPE). Brand II diffusion tubes consist of 4.9 cm long polypropylene tube with 9.5 mm diameter which contain glass fiber filter soaked in an acetic acid DPE solutions. For Brand I and Brand II passive sampling, ozone reacts with DPE to form 4-pyridylaldehyde. Brand III diffusion tube is acrylic tube which contain stainless steel wire coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography.

On site, Brand I and Brand II passive samplers were used with protective shelter to eliminate sun light and bad weather conditions. In addition, for Brand II and III tubes was opened on one end placed vertically inside a shed, with the opened side downwards, in order to avoid possible influence of meteorological parameters such as insolation, rainfall on the sampling. Since Brand cylindrical adsorbing cartridge is housed inside in a cylindrical diffusion body, there is no need to protect the cartridge from bad condition by placing vertically. These cartridges were placed parallel during sampling. All the samplers were hanged onto the bodies of trees, which were < 2m away from the inlets of continuous monitors. Three unused tubes were analyzed as blanks for each brand and. To evaluate precise of the tubes, more than three tubes were used for each brand. After 1 week sampling period, tubes were taken from the field and brought to the laboratory. After exposure the samplers were stored dark and cold condition. And they were analyzed within a week. Exposed and unexposed sample filters and cartridge were extracted in deionized water in sealed plastic bags.

Nitrite ions were determined calorimetrically with Griess Saltzman method. Extracted solutions for each brand were colored with NEDA (N- (1 naphtyl) ethylendiamine dihydrochloride) and sulphanilamide solution. PH of the colored

solutions were adjusted with phosphoric acid for Brand II and Brand II and hydrochloric acid for Brand I and Hand-made sample. To determine concentration of colored sample solution, five point calibration curve was prepared from stock sodium nitrite solution (250 mg/L expressed as NO_2^{2-}). Nitrite ions were quantified by The Bausch&Lomb U.V. Visible Spectronic 20 D Spectrophotometry at 537 nm for Brand I and hand-made and 540 nm for Brand II and Brand III, respectively.

To quantify ozone ions, extracted solutions were colored with MBTH (3-methyl-2-benzothiazolinone hydrazone hydrochloride) solution to obtain the corresponding azide, yellow coloured for Brand I&II and hand made tubes. Standard stock solution was prepared from 4-pyridyaldehyde by using of the relationship between O_3 and pyridyaldehyde (1µg pyridyaldehyde=0.224 µg ozone) and colored with MBTH. Colored extraction solutions and standards were measured with spectrophotometry Brand III diffusion tube is acrylic tube which contain stainless steel wire coated with sodium nitrite. Nitrate ions formed as a result of oxidation of nitrite with ozone were analyzed with ion chromatography Varian Model 2010 HPLC coupled with VYDAC 302 IC anion exchange column. Standard solutions were prepared from stock sodium nitrate solution.

The atmospheric concentrations of NO_2 and O_3 in the measuring period were calculated by using the equation which based on Fick's First Law and obtained from manufactures. Although theory of the equations is same, each manufacture improved the equation by taking their tube shapes and meteorological conditions into consideration. Specific equations improved by manufactures were corrected with respect to temperature values daily recorded by Turkish State Meteorological Service. Hence, atmospheric concentrations of O_3 and NO_2 were calculated via these equations.

3. RESULTS AND DISCUSSION

Results were compared with the average concentrations measured by the automated monitors. Mean concentrations and percent error values for all NO_2 and O_3 passive sampling tubes are depicted in Table 1 and Table 2, respectively.

Table 1. Mean NO2 concentration results for all Brand passive sampling after 1 week period

Analyzing Brand	Mean NO_2 concentration ($\mu g/m^3$)	Percent Relative Error
Chemiluminescence Analyzer	53.6	
Brand 1 Passive Sampling	38.0 ± 4.0 (n=3)	- 27.8
Brand 2 Passive Sampling	67.0 ± 7.9 (n=4)	+25.7
Brand 3 Passive Sampling	59.2 ± 2.4 (n=6)	+10.4
Brand 4 Custom- made	39.7 ± 20.0 (n=7)	-25.9

Table 2. Mean O3 concentration results for all Brand passive sampling at 1 week periods

Analyzing Brand	Mean O_3 concentration ($\mu g/m^3$)	Percent Relative Error
UV Fluorescence Analyzer	19,75	
Brand 1 Passive Sampling	9.6 ± 0.35 (n=3)	-51.1
Brand 2 Passive Sampling	16.6 ± 1.80 (n=4)	-15.8
Brand 3 Passive Sampling	26.2 ± 19.0 (n=5)	+32.7

The limited exercise performed in this study demonstrated that there are differences in performances of different brands of passive samplers in the field for NO_2 and O_3 sampling. Generally, parallel samplers used from each brand generated comparable data indicating that reproducibility of are reasonably good for all brands tested. However, data generated from each brand deviated from average concentrations obtained from freshly calibrated continuous monitors for the same time period. For NO_2, deviations ranged from +26% to -28%. For O_3 differences between passive samplers and active monitors ranged between -50% and +30%.

Results showed that a general feeling for the levels of pollutants can be obtained with all brands of passive samplers. However, use of passive samplers beyond this, such as compliance with regulations, is not warranted.

Some brands did produce results that are fairly comparable with the average concentrations obtained from continuous monitoring instruments. Further tests, such as effect of exposure periods on accuracy and reproducibility, reproducibility and

accuracy tests at successive periods, effect of storage time will be performed using these brands. They will be deployed to the field if satisfactory results are obtained from all those tests.

4. ACKNOWLEDGEMENTS

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