

Application of Ion Chromatographic Method for the Simultaneous Measurement of NO₂ and SO₂ by Passive Sampling Method in Eskisehir, Turkey

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Abstract: The applicability of a passive sampling method for the simultaneous determination of atmospheric NO₂ and SO₂ concentrations in Eskisehir, Turkey was presented in this study. Measurements of two-week average concentrations of NO₂ and SO₂ were carried out in the period of January-August 2006 at two sampling sites in the city. Pollutants were collected by TEA solution in the passive sampler that was developed with the modification of Analyst and Palmes tube type samplers in our laboratory and determined as nitrite (NO₂⁻) and sulphate (SO₄²⁻) with suppressed ion chromatography in a single run. Also, colorimetric (Griess-Saltzman) analysis method was applied as an alternative method for the determination of NO₂ and high degree of correlation (correlation coefficient > 0.90) was found between the two different analysis methods. For the accuracy test, NO₂ passive samplers were compared with the chemiluminescence method and the error level was found 12.50 and 16.70% using ion chromatographic and Saltzman methods, respectively, for the passive samplers. SO₂ concentrations were also compared with a reference acidimetric (H₂O₂) method and the error level was 25.68% (below 30%). Precision of the method as RSD was 5.01 and 6.59% for NO₂ and SO₂, respectively, analyzed with ion chromatography while it was 6.68% for NO₂ analyzed by colorimetric method.

Key-Words: Nitrogen dioxide, sulphur dioxide, passive sampling, simultaneous measurement.

1 Introduction

Air pollution is an important global issue because much of the air pollutants travel long distances into areas far from the emission sources and also affects human health and damages ecosystems. Among these, NO₂ and SO₂ are important and the most frequently monitored air pollutants because of being main precursors of acid deposition, having effects on the human respiratory system and roles in the photochemical reactions. They are commonly present especially in the urban areas and emitted from the various sources including vehicles, fossil fuel combustion activities, industries, etc. Also, they are subject to mixing, transport and transformation processes in the urban atmosphere.

The general situation of the air quality in the world indicates that SO₂ maintains a downward trend while NO₂ maintains levels very close to those of World Health Organization (WHO) [1]. Scientific researches have shown that long-term exposure to these pollutants above a specific level

may cause effects which may differ from those mentioned above. Therefore, most of the countries in the world such as United Kingdom, United States, China, Japan, Germany, India, etc. have established national air quality regulations for these pollutants and also there are many different international organizations such as World Health Organization (WHO), the European Union Air Quality Framework and Daughter Directives, World Bank, etc. published their own standards [2]. Turkey is also among these countries established its national air quality standards for different atmospheric pollutants including NO₂ and SO₂ [3]. In this case, monitoring studies gain more importance in order to observe the effectiveness of air quality control regulations, improve air quality management efforts and detect long-term air quality trends.

Standard NO₂ and SO₂ monitoring methods are complicated, expensive and require highly skilled operators. Therefore, there is an urgent need of adopting inexpensive, simple and reliable methods for air quality monitoring studies. This

need can be fulfilled by such methods as passive sampling which is simple, light, inexpensive, easy to use, do not need maintenance and pumping of air and also provide possibility for the determination of pollutant distribution over a large area.

The principle of the passive sampling method is based on Fick's law of diffusion that includes the passive diffusion of a pollutant into the sampler where it is collected on an impregnated filter or an absorbent material. Thus passive samplers achieve a time-integrated (or average) concentration. The sampling rate is controlled by the diffusion rate of the pollutants through the inside of the sampler. The quantity of absorption products in the sampler is proportional to the concentration in the air outside the sampler, the sampling time, the diffusion coefficient and the dimensions of the sampler. Concentrations are calculated from the quantity of the pollutant captured in the sampler using the following formula:

$$C = \frac{Q * z}{A * t * D} \quad (1)$$

where, C represents the ambient air pollutant concentration measured by passive sampler ($\mu\text{g}/\text{m}^3$), Q is the quantity of pollutant captured in the sampler (μg) and z, A, t and D denote the diffusion length (m), cross-sectional area (m^2), sampling time (s) and diffusion coefficient (m^2/s), respectively.

The classical passive sampler is the tube-type sampler first introduced by Palmes and Gunnison (1973) in the field of the occupational hygiene for SO_2 . After then, application of the passive sampling method in the determination of pollutants including NO_2 and SO_2 in ambient air was started to be used in a wide range [5-12] and also some studies were conducted for the simultaneous determination of atmospheric NO_2 and SO_2 [13-16]. Ion chromatography is a useful method for the simultaneous determination of such inorganic substances in air samples with high sensitivity.

Even if urban air concentrations of SO_2 have been measured in Turkey for the last 20 years, NO_2 concentrations have not been measured widely, except in a couple of cities. So, this study provides an advantage of measurement of both pollutants simultaneously in the urban air and also in the background levels. In the study; (1) simultaneous determination of NO_2 and SO_2 in the ambient air as nitrite and sulphate with ion chromatography was carried out by using the passive sampler developed in our laboratory with the modification of Analyst

and Palmes tube type passive samplers, (2) colorimetric (Griess-Saltzman) analysis method was also applied as an alternative method for the determination of NO_2 and the results of the ion chromatographic and colorimetric methods were compared, (3) some performance data such as accuracy and precision was evaluated for the passive samplers using with the field measurements in two different sites.

2 Experimental Section

2.1 Description and preparation of the passive sampler

Few types of passive samplers for the simultaneous measurement of NO_2 and SO_2 have been described with various dimensions (tube or badge) and absorbing reagents (TEA, TEA+KOH, etc.), but all of them uses ion chromatographic method for the analysis [13-16].

The passive sampler used in this study for the measurement of ambient NO_2 and SO_2 concentrations is a tailor made sampler and it is a modification of the open-tube design Palmes [17,18] and Analyst [19,20] type passive samplers. The sampler comprises a plastic (delrin) body with the dimensions of 2.5 cm length and 2.0 cm inner diameter, close plastic cap and stainless steel mesh barrier, the collecting medium: triethanolemine (TEA) on fibre glass filter paper and a 5 mm-thickness ring to fix the collecting medium to the bottom of the sampler (Fig. 1). Since NO_2 and SO_2 can be collected simultaneously by TEA solution in the same sampler during the same exposure period, Whatman GF/A fibre glass filter paper was impregnated with 20 % TEA aqueous solution and dried for a few minutes. Then, the filter paper was placed to the bottom of the sampler and fixed with the ring. The inlet end was then closed with a plastic cap.



Fig.1. Plastic passive sampler and its parts

2.2 Sampler exposure

Simultaneous NO₂ and SO₂ measurements were carried out at two sampling sites with the different pollutant levels in Eskisehir city in Turkey during two-week exposure period to guarantee a sufficient collection of the pollutants. For each pollutant, two samplers were exposed with one unopened sampler being used as field blank. These samples were analysed by ion chromatography. Also, for the analysis method comparison, another set of passive samplers for NO₂ (2 samplers + 1 blank) was placed at the same sampling sites during the same sampling period and they were analysed by colorimetric (Griess-Saltzman) method.

Figure 2 shows the study area and sampling sites for NO₂ and SO₂ on the map given for Eskisehir. Site 1 is a traffic dense region when compared to Site 2, which is a university campus in the north of the city that is nearly 8 km far away from the city centre. Also, Site 1 can be defined as a residential area where the heating activities are mostly done by coal burning while the other site (Site 2) use natural gas for the heating demand.

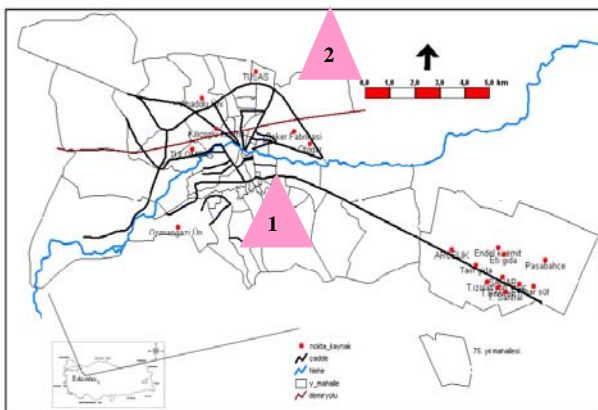


Fig.2. Study area and sampling sites

An automatic NO_x analyser (chemiluminescence method) was available at one sampling site (Site 2) for the last two months to monitor daily and hourly NO₂ concentrations. The results from the passive sampling method analysed by both Saltzman and ion chromatographic methods were compared with the chemiluminescence method for the accuracy control. Also, SO₂ concentrations were compared with the results of the reference acidimetric (H₂O₂) method which was included in the Turkish ambient air monitoring network belongs to the Ministry of Health at one point in the city which is on the same street with Site 1.

The ion chromatographic determination of NO₂ and SO₂ may be subject to effects of the

corresponding NO₃⁻ and SO₄²⁻ compounds on PM trapped in the filter inside of the passive samplers. To move these effects, the samplers were mounted vertically with the open end downward in a shelter and also protected from wind and rain during the sampling period at both sampling sites. Also, to minimize turbulence effect of wind inside the sampler, stainless steel mesh barrier was placed at the open end, and during transportation of the sampler, the barrier was replaced with a plastic cap.

2.3 Extraction and analyses of the samples

For the simultaneous determination of NO₂ and SO₂, analysis was carried out using ion chromatography. After every sampling period, filter papers (for both blanks and exposed samplers) were transferred to the extraction vials and then extracted with 10 mL ultra pure distilled water and 0.3 mL 30% H₂O₂ for 10 min; in the meantime the extraction was shaken 2-3 times. H₂O₂ solution was used to oxidize products of absorption of SO₂ to sulphates. The alkaline pH of this extract (about 10) due to the presence of TEA prevents oxidation of nitrites to nitrates [15].

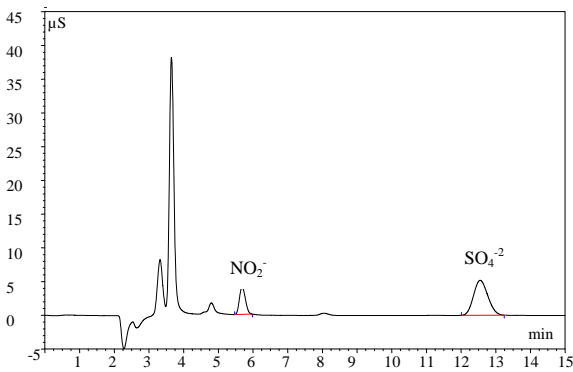
NO₂ and SO₂ were respectively determined as NO₂⁻ and SO₄²⁻ with the analyses of extract by ion chromatography in a same run. A DIONEX 2500 ion chromatography with GP 50 gradient pump, LC 25 column oven and a conductivity detector was used for the analysis. Some technical properties and analytical conditions for the ion chromatography were given in Table 1.

Table 1. Technical properties and analytical conditions of ion chromatography

	Property
Anion analytical column	AS9-HC (250 x 4 mm)
Anion guard column	AG9-HC (50 x 4 mm)
Suppressor	ASRS-ULTRA II, "Water Cycle"
Suppressor current	60 mA
Eluent	10 mM Na ₂ CO ₃
Flow rate	1.2 mL/min
Sample size	500 µL
Oven temperature	30 °C

Example chromatographs of an exposed and blank sampler were presented in Figure 3. A low concentration of NO₂⁻ and SO₄²⁻ could be found in some unexposed samplers due to the trace of NO₂ and SO₂ contamination.

a) exposed sampler



b) unexposed (blank) sampler

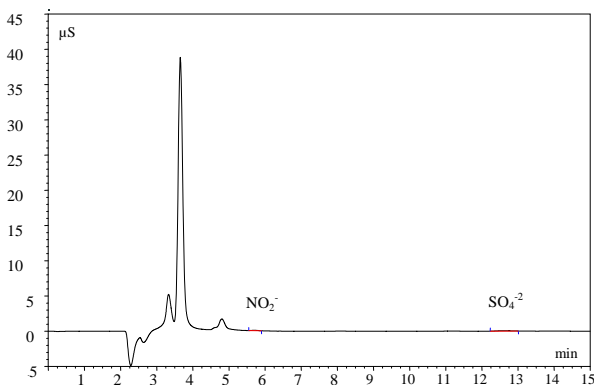


Fig.3. Example chromatograms of NO₂ and SO₂ from exposed and unexposed passive samplers

The quantity of the collected NO₂ and SO₂ were calculated as follows:

$$Q_{NO_2} = m_{NO_2^-} \text{ and } Q_{SO_2} = (64/96) \times m_{SO_4^{2-}} \quad (2)$$

Another set of NO₂ samples that were exposed at the same sampling sites during the same sampling period with the NO₂-SO₂ samples was analyzed by the colorimetric method (Griess-Saltzman) for the comparison with the results of ion chromatography. After every sampling period, the concentration of NO₂ absorbed was determined colorimetrically as NO₂⁻. For the analysis, filter papers (for both blanks and exposed samplers) were extracted with 5 mL (for 0-40 μg/m³ NO₂ concentrations) and 8 mL (for > 40 μg/m³ NO₂ concentrations) Saltzman reagent during 40 minutes. After extraction, the absorbance was measured at 550 nm wavelength [21]. A Shimadzu 2450 UV Spectrophotometer was used for the analysis. Due to impurities in the reagents, the spectrophotometer was zeroed against a blank reagent solution. The amount of NO₂⁻ collected on

the filter paper was determined from the calibration curve by the Saltzman method [21].

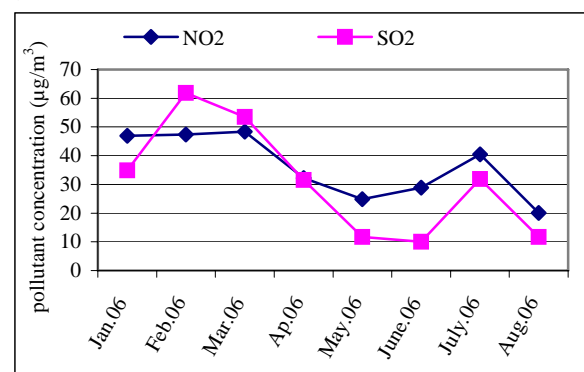
Then, the concentrations of NO₂ and SO₂ in μg/m³ were determined by the Equation (1). The difference between the measured and blank values was used to calculate the pollutant concentrations. The diffusion coefficient of 0.154 cm²/s for NO₂ and 0.127 cm²/s for SO₂ was used in the calculations.

Although most of the commercially available passive samplers are not designed for reuse, all the individual components of our sampler were reused by cleaning with high purity water (Milli-Q) after each analysis.

3 Results

The concentrations of atmospheric NO₂ and SO₂ at two different sites having different characteristics were measured simultaneously by the passive sampling method between January-August 2006. The spatial and temporal changes in the concentrations are shown in Fig. 4. The reason of higher NO₂ concentrations in winter may be the higher traffic density in general and also the formation of a temperature-inversion layer, while the lower NO₂ levels in summer can be due to the destruction by photochemical reactions. Also, higher NO₂ levels were obtained in Site 1 because of having higher traffic density. Atmospheric SO₂ levels were higher in winter due to the heating activities especially in Site 1 where coal is mostly used for domestic heating.

a) Site 1



b) Site 2

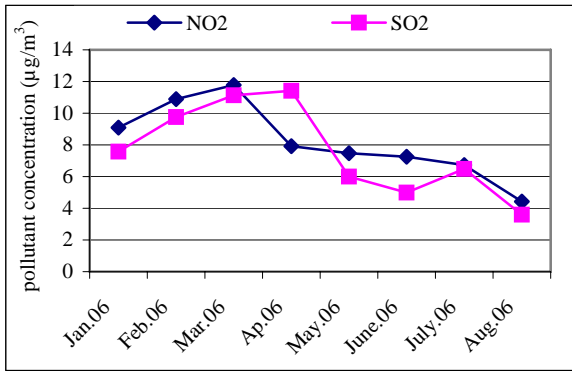


Fig.4. Temporal variations of NO₂ and SO₂ in two different sites in Eskisehir, Turkey

Colorimetric (Saltzman) and ion chromatographic methods carried out for the analysis of NO₂ concentrations were compared. There was a very good agreement between the results of the two different analysis methods with the correlation coefficient of higher than 0.90 (Fig.5).

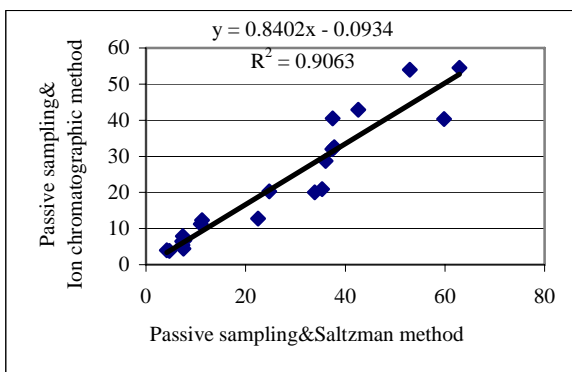


Fig.5. Comparison of Saltzman and ion chromatographic methods for NO₂ concentrations (µg/m³) by using passive samplers

The results of the two analysis methods for NO₂ were also compared with the results of chemiluminescence method for the accuracy test (Fig.6). The error level was obtained 16.7 and 12.5% for Saltzman and ion chromatographic methods, respectively.

Two-week SO₂ concentrations obtained by the passive sampling method at Site 1 were compared with the SO₂ values obtained from the reference acidimetric method. The comparison results are presented in Fig. 7. When the results of the passive sampling method were compared with the reference method results, the error level was found 25.68%.

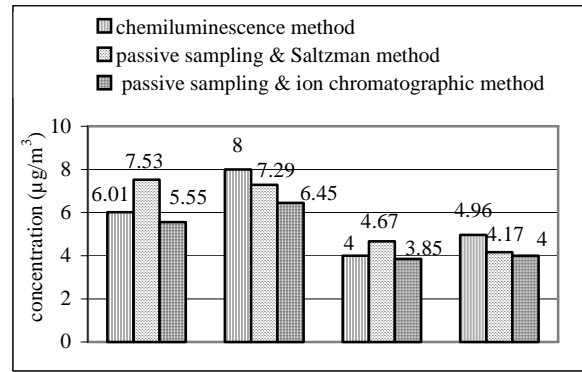


Fig.6. Comparison of NO₂ passive samplers to the chemiluminescence method

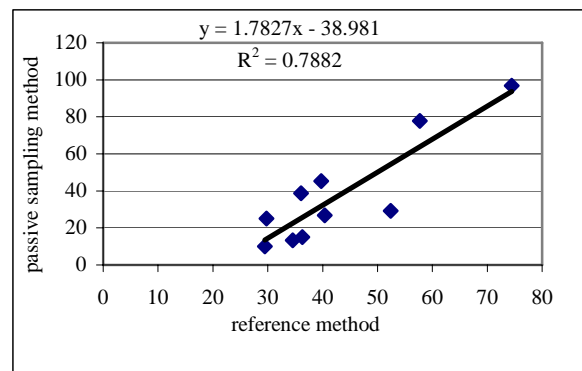


Fig.7. SO₂ concentrations (µg/m³) by passive sampling method compared with the reference method

The precision of the duplicate passive samplers for the simultaneous measurements of NO₂ and SO₂ that were analyzed by ion chromatography was 5.01 and 6.59%, respectively, in terms of relative standard deviation (RSD). The precision of NO₂ passive samplers analyzed by colorimetric method was obtained 6.68% as RSD.

4 Conclusion

Passive sampling method is a good alternative to conventional, manual methods for the determination of NO₂ and SO₂. By using a passive sampler developed in our laboratory, simultaneous NO₂ and SO₂ determination was carried out at two sampling sites, one of the sampling sites is in the city centre while the other one is far from the city centre.

Ion chromatographic method was used for the analysis and when compared to the colorimetric method for NO₂, it seems a good alternative. Also, it has an advantage of the possibility for the collecting of NO₂ and SO₂ by the same absorbent in the same sampler. The accuracy and the precision

values also showed the applicability of the method for the simultaneous determination of NO₂ and SO₂.

When we compared our results in case of the performance data to the available passive samplers for the simultaneous determination of NO₂ and SO₂ in the previous studies [13-16], our sampler had much more lower precision values and the accuracy was also in comparable levels.

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