CHAPTER 4

CONCLUSION

The passive sampling of air was found to be good alternative conventional, manual method for determination of NO_2, SO_2 and O_3 in ambient air. In this work NO_2, SO_2 and O_3 were collected by passive sampling technique and then determined by both ion chromatography (IC) and spectrophotometry under the optimized conditions. The focus was on the development of the passive sampler to achieve the appropriate device by testing the efficiency of materials including type of diffusion tube, sorbent and absorbing chemical. The accuracy of the method was compared with active analyzer expressed as the percentage difference.

Two types of diffusion tube (PE and PS tube) with the similar shape and size were tested in the same environment. It was found that PE tube showed the higher gas concentration. One important reason was that the PE tube was less transparent than PS tube and therefore less effect from light and temperature.

Four types of sorbent including three types of cellulose filter (Whatman no.1, no.6 and no.40) and glass fiber filter (Whatman GF/A) were examined. It was found that the glass fiber filter GF/A gave the highest value of absorptivity.

There was a good correlation between active and passive samplers for NO_2 measurement. The correlations were 0.7820 and 0.7310 for NO_2 determination by IC and spectrophotometry, respectively. All tested absorbing chemicals showed no significantly different at $P \leq 0.01$. Determination of NO_2 by both IC and spectrophotometry also showed no significantly difference ($P \leq 0.01$). However, a mix solution of KI/$NaAsO_2$/ethylene-glycol/NaOH in methanol and methanolic NaI/NaOH contributed a large interference peak in IC chromatogram, but they had no effect on NO_2 determination by spectrophotometry.

Determination of NO_2 by spectrophotometry was done by mixing extractant and Saltzmann reagent (1:2) for 10 min and measured at 542 nm. The trapped-NO_2 was extracted by adding 4 ml of milli-Q water into the diffusion tube and then sonicated for 15 min. The recovery of NO_2^- was 92.6%.

Using of the glycerin added in TEA solution as an absorbing solution for trapping NO_2 in ambient air for IC and spectrophotometry determination was found to be appropriate. It gave the closed absorption to the active analyzer with low variation when comparing to the TEA solution without glycerin. The reason was the viscous property of glycerin, which helped to stabilize target gases in low humidity. However, the amount of added glycerin, which was varied from 2-10%, was not directly affected the amount of gas intake.

The NO_2 concentrations obtained from passive sampling (analysed by IC and spectrophotometry) were relatively closed to those from active analyzer with the difference less than 5.2%. However, the variation (%RSD) of spectrophotometry measurement was higher than that of IC.

SO_2 can be determined by IC in from of SO_4^{2-}. Determination of SO_2 by IC was done by using the same absorbing chemical as NO_2 determination. Trapped SO_2 was extracted in milli-Q water for 15 min with ultrasonication. The extraction efficiency was expressed as %recovery. The recovery of SO_2 extraction was 106.8%.

The absorbing chemical for determination of SO_2 by spectrophotometry was 2 ml of 4M TCM. It was directly filled in the diffusion tube without the sorbent. After exposure, this solution was measured at 550 nm using the pararosaniline method.

Study of exposure duration for SO_2 determination by developed passive sampler was conducted. It was found that the sampler have to be exposed longer than 24 hr. This might be due to rather low concentration of SO_2 in ambient air. Results of 3 days exposure showed minimum duration for SO_2 determination.

The correlation of SO_2 concentrations between the values obtained from active analyzer and passive sampling technique were quite good in case of IC ($r^2 = 0.7897$) and moderate in case of spectrophotometry ($r^2 = 0.5458$). Concentrations of SO_2 obtained from passive sampler, which determined by IC, was much higher than active monitoring (>79.8%). However, IC technique gave higher precision (%RSD) than spectrophotometry. From this point of view, the overestimated SO_2 values got from IC could be caused by interferences from wall deposition of SO_4^{2-} aerosols (Kasper-Giebl and Puxbau, 1999). The dusts might contain SO_4^{2-} ion leading to overestimation of SO_2 concentrations as far as expose for long time. This reason could be affected to the extraction technique for IC determination, which illustrated almost 2 times overestimated SO_2 values comparing with active analyzer. The error could be minimized by using the porous membrane at the mouth of tube to avoid the interference from SO_4^{2-} aerosol. Noticeably, SO_2 concentration obtained from spectrophotometry were relatively close to those of active analyzer with the difference less than 29.2%, even the precision of spectrophotometry was not so good due to low sensitivity, which can be seen from the low value of slope of calibration curve.

O_3 in ambient air can be measured by either IC or spectrophotometry. The applied technique depended on final product after the reaction of ozone and absorbing chemical. The correlations of O_3 concentrations from active analyzer and passive sampling were 0.6331 and 0.4636 for IC and spectrophotometry, respectively.

O_3 determination by IC was done by using a mix solution of 0.1% $NaNO_2$, 0.1% Na_2CO_3 and ethylene glycol impregnated onto the sorbent fixed in diffusion tube. Then O_3 was extracted by 15 min sonication in milli-Q water. The good recovery was obtained (98.8%).

O_3 determination by spectrophotometry was done by using 2 ml of 0.1% DPE in methanol as the absorbing solution. The solution was filled in a diffusion tube without any sorbent. After exposure, this solution was mixed with MBTH solution (1:1) for 20 min before measured at 432 nm.

The exposure period for O_3 trapping in both determination of O_3 by IC and spectrophotometry was 24 hr. It should be noted that the diffusion tube must be wrapped with aluminium foil to protect them from radiation, which was the main factor affect amount of O_3 inside the tube.

The O_3 concentrations obtained from passive sampling was relatively closed to those from active monitoring. IC determination showed both over- and underestimate values with the difference less than 21.1% from active analyzer. Whereas O_3 concentration from spectrophotometry showed only the underestimate values with the difference of 13.0-40.0%. However, the variation of O_3 concentration determination by spectrophotometry was relatively high in comparison with IC determination, which can be observed by %RSD.

Recommendation

The developed passive samplers still has some limitation that sometime difficult to overcome. The most important of which is effect of environmental conditions including temperature, air movement and humidity on the analyte uptake. The accuracy might be better if the calculation was done with consideration of the real environmental conditions. The diffusion coefficient was one parameter, which actually depended on the environmental conditions especially air temperature and site specification. Therefore, more researches should be conducted.

SO_2 concentration from passive sampler, which determined by IC indicated rather high difference from PCD data. There is a limitation of SO_2 detection by UV-fluorescence detector used as analyzer at PCD station. Its detection limit was 1 ppbv. Therefore, low concentration of SO_2 (< 1 ppbv) in ambient air can not be detected. Thus, the SO_2 was reported as ND or 0 pbbv, which lead lower value of 24 hr average concentration than the actual value. When the values were compared with our developed passive samplers, the difference was rather high.

Passive sampling has long history and still developing to obtain the best condition and high precision. However, it has many significant advantages, including simplicity, low cost, no need for expensive and sometimes complicated equipment, no power requirements and unattended operation.