Validating the Collecting Efficiency Factors of Wet Chemical Method for determination of Sulphur Dioxide and Nitrogen Dioxide in ambient air under Sri Lankan situation

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Abstract— Air pollution has drawn worldwide concern as it has adverse effects on the health and welfare of all humans, on plants and on materials. Increase in level of Sulfur Dioxide (SO2) and Nitrogen Dioxide (NO2) has become a global threat and affects on the environment causing many issues to human health and quality of life. Thus, monitoring of these gases is a prime requirement to decide on the quality of ambient air as well as for formulation of air pollution management mechanisms. To monitor these two primary pollutants, high cost analytical methods are available. However, monitoring programs need to be cost-effective, sustainable and applicable to national and local priority needs and conditions. Therefore simplest technologies and procedures that are consistent with fulfilling overall monitoring objectives should be used. Even though the wet chemical methods (low cost) are available in the world wide, accuracy of these methods is depending on the local climatic conditions like temperature and humidity of atmosphere and the level of pollution in the region. Based on above factors, collection efficiency can be varied from region to region. Presently wet chemical methods are used to monitor SO2 and NO2 with use of collecting efficiency factors of gaseous pollutants in absorbing solution as in ASTM method. The main focus of this study was to get suitable collecting efficiency factors to Sri Lanka to measure SO2 and NO2 using wet chemical methods. Both SO2 and NO2 levels were determined by West and Gaeke method and Saltzman method as per the National Ambient Air Quality Standards. These values were also determined at the same location and same time by automated on-line analytical methods; Pulse Fluorescence method and Gas Phase Chemiluminescence method as per National regulations. Linear Regression Analysis was done to determine a suitable collecting efficiency factor in determining both NO2 and SO2. The collecting efficiency factors for both NO2 and SO2 for Sri Lanka was found out to be 0.72 and 0.99 according to this study instead of 0.82 and 1.00 used in ASTM methods respectively

Keywords— Air quality, Chemiluminescence method, Collecting Efficiency, Wet chemical method, Pulse Fluorescence method

I. INTRODUCTION

Air pollution, with its short and long-term impacts on environment and human health, has been a globally recognized problem mainly due to rapid population growth, industrialization and urbanization in the recent decades. Further, it has become a topic of intense researches at all levels because of the increased level anthropogenic activities and climatic changes. As a result, adverse effects of air pollution have been identified and studied in detail with respect to human health and public welfare in the industrialized countries.

However, such effects have not been studied adequately in the developing countries. Among the major obstacles, developing countries have to confront with respect to management and control of air pollution, limited understanding of the subject to design cost effective air pollution management programs and nonavailability of resources for their implementation.

The monitoring of ambient air quality focuses on the concentrations of outdoor air pollutants. The exposure to outdoor pollutants determines the dose to human lungs and later to target body organs. Therefore, the amount of pollutants received by different biological systems along with the toxicity of the pollutant as well as individual susceptibility determines the individual health effects.

Ambient air quality standards were established using guidelines given by World Health Organisation (WHO) by many countries around the world to safeguard the local, regional and global atmosphere [1]. Routine air quality monitoring studies are very vital to identify longterm air quality changes and to assess the effectiveness of air quality monitoring and management efforts. Day by day increase in level of Sulfur Dioxide (SO₂) and Nitrogen Dioxide (NO₂) are becoming a major cause of concern in balancing the quality of life of urban dwellers, maintaining ancient architectural heritage, natural environment, its contributions to the acidification of the ecosystems, its health impacts and the formation of photochemical oxidants by the action of NO_2 [2]. In addition, both NO2 and SO2 can also impact on the visibility as their corresponding oxidation products are able to combine with ambient aerosols. Therefore, continuous monitoring of NO2 and SO2 with suitable measurement methods is needed to investigate both temporal and spatial changes in air quality on local to global scales [3]. To address the problem of air pollution it is important to measure the level of air pollutants in the risk ambient air surrounding. The information of the status of air pollutants are essential in preventing the long term effects.

A wide range of methods are available for the measurement of air pollutants, from the very simple to the highly sophisticated, and with a corresponding variation in costs. Most of the instrumental methods(direct-reading) based on absorption or emission spectroscopic methods are best suited to monitor air pollutants but high in costs. The manual procedures like bubbler systems and passive samplers are low cost and limited information provided.

Bubbler systems (wet chemical method) are one of the most universal approaches for the collection of gaseous pollutants and involve bubble the air through a solution designed to absorb. Most gases and vapours can be collected in this way, followed by an appropriate laboratory analysis of the resulting solutions. But accuracy of these methods is depending on the local climatic conditions like temperature and humidity of atmosphere and the level of pollution in the region [4][5]. Therefore, it is clear that collection efficiency can be varied from region to region.

Air pollution in Sri Lanka is brought by transportation, industrialization and increased urbanization. The transport sector dominates among the air pollutant sources. In Sri Lanka contribution to the air pollution by transport sector is greater than 60% [6].

According to the monitoring result of ambient air quality in Fort monitoring site from 2003 to 2008, it was showed that NO₂ and SO₂ concentrations were within the limits of the national standard stipulated under National Environment Act. However air pollution trends with respect to SO₂ and NO₂ were slowly increasing. Further, air pollution monitoring system is essential for policymaking suited to the primary objective of protecting human health and also can help us to understand how pollutants behave and their relationships with the weather. In the majority of the developed world, legislation has already been introduced to the extent that local authorities are required by law to conduct regular Local Air Quality Reviews of key urban pollutants such as SO₂, NOx or Ozone - produced by industrial activity and/or road transport [5].

Therefore, the main objective of this research is to measure SO_2 and NO_2 in the ambient air using bubbler systems (wet chemical methods) parallel to automated test methods and to validate the above wet chemical methods in order to get the suitable collecting efficiency factors to Sri Lanka.

II. METHODOLOGY

Concentration of SO₂ and NO₂ levels were determined by West and Gaeke method and Saltzman method (wet chemical methods) as per the National Ambient Air Quality Standards. SO₂ and NO₂ levels at the same location at the same time were determined by automated on-line analytical methods; Pulse Fluorescence method and Gas Phase Chemiluminescence method as per National regulations[7] [8].

The data of SO_2 and NO_2 were analysed using Wilcoxon signed rank test to see whether there was a statistically significant difference between concentrations of NO_2 and SO_2 of wet chemical method and automated test method. Calculation of collecting efficiency factors for NO_2 and SO_2 which are suitable for Sri Lankan climatic condition were calculated using Linear Regression Analysis.

III. RESULTS AND DISCUSSION

A. Concentrations of Nitrogen Dioxide (NO₂)

Samples (n = 35) were collected during 8 hours period for the manual determination of Nitrogen Dioxide (NO₂) in the ambient air and were analysed according to the Griess-Saltzman test method. NO₂ concentrations in the ambient air were also measured by Chemiluminescence method in the same period and 8 hour average concentrations were also obtained[11].

Monthly average concentrations of NO₂ by Chemiluminescence test method and Griess-Saltzman test method are shown in Table 1.

TABLE I
MONTHLY AVERAGE CONCENTRATIONS OF NO_2 BY CHEMILUMINESCENCE
TEST METHOD AND GRIESS-SALTZMAN TEST METHOD

Average	NO ₂ -(µg/m3) Automated System (Chemiluminescence)	NO2 -(µg/m3) Wet Chemical System(Griess- Saltzman)	
January	42.097	33.971	
February	49.753	40.182	
March	62.764	51.381	
April	37.178	30.640	
May	34.366	28.382	
June	34.275	28.418	



Fig.1 Monthly Average NO2 Concentration

Wilcoxon signed – rank test was done to these two sets of data to see whether there was a statistically significant difference between these two data sets. The p value (($P \le 0.005$) indicated that there was a statistically significant difference between these two data sets. This could be attributed to either the efficiency of the collector of the wet chemical method or hyper activity of the automated method. However it was reported that the accuracy of the wet chemical methods depends on the local climatic conditions such as temperature and humidity of atmosphere and the level of pollution in the region[10]. Based on above factors, collecting efficiency can be varied from region to region[11].

Collecting efficiency factor for NO₂ which is suitable for Sri Lankan climatic condition was calculated using the following formula [9].

$$C (NO_2 \mu gm^{-3}) = \frac{S (NO_2 mg) \times 10^3}{V (m^3) \times CEF}$$

C = concentration, S = spectrometer reading (wet chemical method), V = volume of air sampled, CEF = Collecting efficiency factor

To determine the suitable Collecting efficiency factor, Linear Regression Analysis was done and calculated[12]. Y = BX

 $Y = NO_2$ Auto – Automated Instrument reading equal to C in the above formula.

$$X = NO_2Cal$$

- $\frac{S(NO_2mg) \times 10^3}{V}$ from the above formula
$$B = \frac{1}{CEF}$$

S = spectrometer reading (wet chemical method), V = volume of air sampled,

CEF = Collecting efficiency factor

Value of B was taken from regression analysis and Collecting Efficiency factor was calculated from B.

Figure 3 showed that there was a linear relation between NO_2 Cal and NO_2 Auto.



Fig. 2 Regression Analysis between $Auto_NO_2$ and NO_2 Vol.

Therefore, Coefficient B = 1.386 (as per Figure 2) However, B = 1.386 = 1/ Collecting Efficiency factor

Therefore, collecting efficiency factor for NO_2 is 0.72 for this location.

B. Concentration of Sulphur Dioxide (SO₂)

Samples (n=35) were collected during 8 hours period to manual determination of Sulphur Dioxide (SO₂) in the ambient air and were analysed according to the West and Gaeke method. SO₂ concentrations in the ambient air were also measured by Ultraviolet Fluorescence method during the same period and 8 hour average concentrations were also obtained.

Monthly average concentrations of SO₂ measured by Ultraviolet Fluorescence test method and West and Gaeke test method are shown in Table 2.

 TABLE 2

 MONTHLY AVERAGE CONCENTRATIONS OF SO2 BY

 CHEMILUMINESCENCE TEST METHOD AND GRIESS-SALTZMAN

 TEST METHOD

 TEST METHOD

 Average

 SO2 -(µg/m3) Automated

Average	SO_2 -($\mu g/m3$) Automated	SO_2 -($\mu g/m3$)
	System (Ultraviolet	Wet Chemical
	Fluorescence)	System
January	27.740	27.655
February	40.210	40.029
March	46.898	46.825
April	20.266	20.200
May	19.736	19.688
June	23.755	23.683



Fig. 3 Monthly Average SO₂ Concentration

Wilcoxon signed – rank test was done to these two sets of data to see whether there was a statistically significant difference between these two data sets. The P value(P \leq 0.005) indicated that there was a statistically significant difference between these two data sets.

Collecting efficiency factor which is suitable for Sri Lankan climatic condition for SO₂ was calculated using the following formula with linear regression analysis.

$$C(SO_2 gm^{-3}) = \frac{S(SO_2 mg) \times 10^3}{V(m^3) \times CEF}$$

C = concentration, S = spectrometer reading (wet chemical method), V = volume of air sampled, CEF =Collecting efficiency factor

Value of B was taken from regression analysis and Collecting Efficiency factor was calculated from B.

To determine a suitable Collecting efficiency factor, Linear Regression Analysis was done as follows.

Y = BX

 $Y = Auto_SO_2 - Automated Instrument reading equal to C in the above formula.$

$$X = SO_2 vol (mg) - \frac{S(SO_2 mg) \times 10^3}{V}$$
 in the above formula

$$B = \frac{1}{CEE}$$

S = spectrometer reading (wet chemical method), V= volume of air sampled, CEF = Collecting efficiency factor



Fig. 4 Regression Analysis between Auto_SO2 and SO2_ Vol.

Therefore, regression analysis was done to get the value for Coefficient B which is 1.002 as per Figure 4.

B = 1.002 = 1/ Collecting Efficiency factor

Therefore, collecting efficiency factor for NO_2 is 0.99 for this location.

IV. DISCUSSION

It is clear from this study that collecting emission factors are not constant and varying with different regions. Wilcoxon signed – rank test done in this study further proved that there was a statistically significant difference between these two data sets for SO_2 and NO_2 .

To generate a reliable database for NO_2 and SO_2 in ambient air, flow rate of sampling assembly was maintained at a constant flow rate during each eight hour period. Therefore, the efficiency of SO_2 and NO_2 absorption was almost the same.

Collection efficiency factor for NO_2 for Sri Lanka was determined by regression analysis and it was 0.72 according to this study instead of 0.82 which was used in ASTM methods.

Collection efficiency factor for SO_2 for Sri Lanka was determined by regression analysis and it was 0.99 according to this study instead of 1.00 which was used in

ASTM methods.

V. CONCLUSION

Validated collection efficiency factors for wet chemical methods of determining NO_2 and SO_2 in ambient air under Sri Lankan climate are 0.72 and 0.99 respectively. However, this low cost monitoring method should apply to monitor and conduct regular measurements of SO_2 and NO_2 at more locations to identify the levels of SO_2 and NO_2 concentrations in different areas. Accuracy of the new collection efficiency factors under local climate could be further validated by conducting the same procedure with more number of samples.

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