The Relationship between Nitrogen Dioxide Concentrations in the Atmosphere Measured by the Sodium Arsenite Method and the Chemiluminescence Method

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Abstract: The relationship between the nitrogen dioxide concentration measured by the Sodium Arsenite method and the Chemiluminescence method, aimed at developing a device for measuring nitrogen dioxide in the atmosphere by means of the Sodium Arsenite method and studying the correlation between the concentration of nitrogen dioxide in the atmosphere which was measured by Sodium Arsenite method and the Chemiluminescense method done by the Pollution Control Department, Thailand. In this research sampling collection of nitrogen dioxide concentration in various conditions by the Sodium Arsenite method was compared with that by the Chemiluminescence method done by the pollution control Department at the Air Quality Measurement Station at the Din Dang district, Bangkok. It was done by one-hour average value totaling of thirty data. The research result found that the sampling collection with the flowing rate of 160 ml/min and the absorption reagent with mixture of 0.2 M sodium hydroxide and 0.015 M sodium arsenite had the highest relationship to the measurement result done by the Pollution Control Department at a statistical significance level of 0.05 with the value of correlation coefficient at 0.658 which had a high relation.

Keywords: Air pollution sampling, Chemiluminescense, Nitrogen dioxide, Sodium arsenite.

Introduction

The air pollution problem in Bangkok Metropolitan has been an important concern and has become more violent especially concerning problems of fine particulate matter (PM – 10 and PM - 2.5), carbon monoxide (CO), nitrogen dioxide (NO_2), etc. Nitrogen Dioxide was the same type as the gas in a high reaction called "oxides of nitrogen or NOx". This gas occurs when there is fuel combustion with high temperature. Nitrogen dioxide is one of the most common air pollutants in ambient air (Hanninen et al., 2004; Lai et al., 2006).

Oxide of Nitrogen's important source was from combustion with a high temperature as in Table 1, both from natural existence and man-made occurrences. The Oxides of Nitrogen by combustion was categorized into three types (De Nevers, 2000).

• Oxide of the Nitrogen caused from the combustion at the temperature of higher than 1,300 degrees Celsius is called "thermal NO_x".

• Oxide of the Nitrogen caused from nitrogenous substances in fuel combustion is called "fuel NO_x"

• Oxide from Nitrogen that occurs from the reaction between molecules of nitrogen and the free oxidants of HCN, NH, and N in the flame is called "prompt NO_x" which occurs at a low temperature.

The major outdoor source of NO_2 concentrations are mobile and stationary combustion sources (Lewne et al., 2004; Kampa & Castanas, 2008). Oxides of nitrogen were emitted from vehicles and factories of many kinds such as power plants, cement plants, electronic plants, etc.

Nitrogen dioxide is mainly formed from the oxidation of Nitric oxide (NO) emitted from fuel combustion. Long-term exposure to NO_2 can

lower a person's resistance to respiratory infections and aggravate existing chronic respire- tory diseases. (Air Science Group, 2012). Nitro- gen dioxide is a toxic gas and is thus a regulated in Thailand. Nitrogen dioxide with high concentration will directly jeopardize the lungs; for example, it irritates the lungs, irritates alveoli and results in decreasing the function of the body's immune system which causes pneumonia and lung cancer, causing constricted emphysema, and finally respiratory system infections such as the Asian flu. If the nitrogen dioxide reaches 300-500 ppm, it causes life threating conditions, coma, or even death, because the brain lacks oxygen. This is because Nitric Oxide merges with hemoglobin in the same way as Carbon Monoxide which causes a decrease of oxygen in the blood. However, in the atmosphere, there is less of a nitric oxide concentration; it is less than 1.22 mg/M^3 (1 ppm). Thus, it is not dangerous to a human being's health. However if Nitric Oxide is at the concentration level of 0.7 - 20 ppm in 10 min, a human being will not be able to breathe and if it is at the level of 0.11-0.22 ppm, a human being will be able to smell it. Nitrogen dioxide affects a human being's health more than nitric oxide does at the same concentration level.

Table 1. The concentration of nitric oxide occurring at different temperatures.

Temperature (°C)	Concentration (ppm)
20	0.001
427	0.30
527	2.00
1,538	3,700.00
2,200	25,000.00

Source: Suadee, 2003.

The present measurement method used in various countries and also Thailand is the standard measurement and that is equivalent to the measurement method used in the U.S. EPA, which defines the nitrogen dioxide measurement method by the Chemiluminescence method as a standard method, and with the Sodium arsenite method as well as TGS-ANSA as equivalent methods. (Choo-in, 2013)

The samplings and the measurement by the Sodium Arsenite method is used mainly by passing air sampling through sodium hydroxide (NaOH) with sodium arsenite ($NaAsO_2$) becoming a nitrite ion (NO_2). The nitrite ion quantity occurring can be measured by the colorimetric method or spectrophotometric analysis at 540 nanometers after reaction with phosphoric acid, sulfanilamide and 1 - napthyl ethylene diamine dichydrochloride or NED respectively (Choo-in, 2013). A purple-red azo dye is produced. Ultra Violet–Visible spectrophotometer was used for analysis. The spectrophotometer is calibrated against different concentrations of standard solutions of sodium nitrite ($NaNO_2$) at a wavelength of 540 nm. (Lodhi, 2006).

The principle of the Chemiluminescence method is the measurement method or the spectrum analysis occurring from the chemical reaction for the measurement of all oxides of nitrogen (NO_x), nitric oxide concentration first, and finding the balance from the nitrogen dioxide concentration. In the first step, the nitric oxide has to be measured before by the principle that nitric oxide will react with the ozone and produce nitrogen dioxide and oxygen. A part of the occurring nitrogen dioxide will be in the stimulating status and back down immediately together with the release of spectrum energy (photon) as in the equation (1) - (3). This spectrum energy produced is the direct property to nitric oxide quantity which can be measured. The oxide measurement of all the nitrogen can be done by transforming oxide of other nitrogen to be nitric oxide and measuring all nitric oxide quantity which will equal to the value of all the oxide of all nitrogen. Then the electronic circuit in the measurement device will calculate the concentration value of nitrogen dioxide that was found firstly to be deducted from the oxide concentration value of all nitrogen after being transformed as a form of nitric oxide from the various oxide forms.

$$NO + O_3 \text{ -----> } NO_2 + O_2 \quad \ldots\ldots \quad (1)$$

$$NO + O_3 \text{ -----> } NO_2^* + O_2 \quad \ldots\ldots \quad (2)$$

$$NO_2^* \text{ -----> } NO_2 + h\upsilon \quad \ldots\ldots \quad (3)$$

Because the measurement device which uses the Chemiluminescence method is very expensive, this research aimed at the study of the relationship between the nitrogen dioxide concentration measured by the Sodium Arsenite method and by the Chemiluminescence method of the Pollution Control Department of Thailand in order to apply it in the measurement of nitrogen dioxide in the future.

Materials and Methods

I. Instrument

Instrument for the sampling collecting (Fig. 1) comprises:

- Impinge
- Pump for air sucking
- Air flowing rate calibrator of dry type
- A thermometer and barometer
- Spectrophotometer: at 540 nanometer

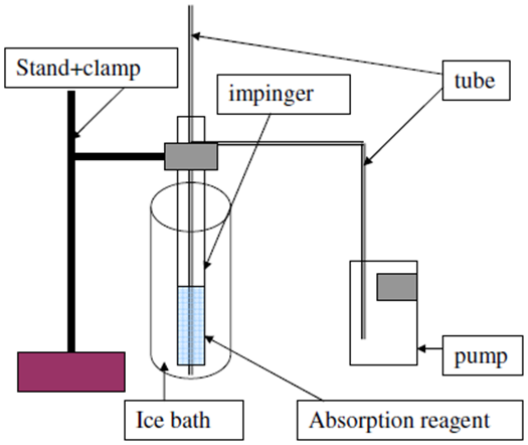

Figure 1. Equipment for collecting samplings.

II. Chemical substances

- Absorbing reagent was 0.05M sodium hydroxide, (NaOH) and 0.004M sodium arsenite ($NaAsO_2$). Preparation was done by dissolving 0.5 g. of sodium arsenite and 2 g. of sodium hydroxide in deionize water and diluting to 250 m. in the volume metric flask. It should be kept in a light brown bottle.
- Sulfanilamide solution can be prepared by dissolving 20 g. of sulfanilamide in 700 ml. of deionize water. Slowly add 50 ml. of phosphoric acid (85% H_3PO_4) and dilute it with the deionize water to 1,000 ml. in the volumetric flask. This reagent will remain unchanged for one month if chilled.
- Hydrogen Peroxide (H_2O_2) solution can be prepared by dissolving 0.2 ml. of 30 % Hydrogen Peroxide solution and diluting it with deionize water to 250 ml. in the volume metric flask. This solution will remain unchanged for a month if chilled in the dark.
- N-(1-napthyl) ethylene diaminedichydrochloride (NED) is prepared by dissolving 0.5 g. of N-(-1napthyl) ethylene diaminedichydrochloride in deionize water and diluting it to 1,000 ml. in the volumetric flask. This solution will remain unchanged for a month if chilled in the dark.
- Nitrogen dioxide standard solution. The preparation used sodium nitrite ($NaNO_2$) at the purity level of at least 97% $NaNO_2$. Sodium Nitrite Stock Solution can be prepared as follows: precisely weigh $NaNO_2$ at the amount of 0.1 mg. and the weight of the substance as follows in equation (4)

$$G = \frac{1.5 \times 50}{A} \quad \ldots\ldots (4)$$

Definitions:

G is the weight of $NaNO_2$ (g)
1.5 is the gravimetric conversion factor
A is $NaNO_2$ in the chemical substance (%)

Sodium nitrite was diluted with deionize water to 1,000 ml. in the volume metric flask. This solution will contain the concentration of 500 mg of NO_2 per ml.

- Sodium nitrite working standard (10 mg/ml. of NO_2 (can be prepared by pipette 5 ml. of stock solution NO_2 and dilute it with deionize water to the 1,000 ml. in the volume metric flask. Freshly prepare it when it is to be used.

III. Research Methodology

- Sampling implementing by studying of the flowing rate of air samplings (140, 150, and 160 ml/min) and the appropriate concentration of the absorption solution by the Sodium Arsenite method with 9 experimenting sets are in Table 2.
- Collection of nitrogen dioxide according to the components in each experimenting set as an average value of each hour with the amount of 30 samples. The study was done at the Air Quality Measurement Station (Din Dang Station) of the Pollution Control Department (PCD), Bangkok. This station used the Chemiluminescence method.
- The study of the correlation between nitrogen dioxide concentration value measured by the Sodium Arsenite method and the Chemiluminescence method by using the principle of correlation statistics was at the confidence level of 95%.

Table 2. The experimental set to find the appropriate factors in the measurement of Nitrogen dioxide by the Sodium Arsenite method.

Set	Air flow rate (mL/min)	Absorption substance	Concentration of absorption substance (M)
1	140	Sodium hydroxide Sodium arsenite	0.05 0.004
2	140	Sodium hydroxide Sodium arsenite	0.1 0.008
3	140	Sodium hydroxide Sodium arsenite	0.2 0.015
4	150	Sodium hydroxide Sodium arsenite	0.05 0.004
5	150	Sodium hydroxide Sodium arsenite	0.1 0.008
6	150	Sodium hydroxide Sodium arsenite	0.2 0.015
7	160	Sodium hydroxide Sodium arsenite	0.05 0.004
8	160	Sodium hydroxide Sodium arsenite	0.1 0.008
9	160	Sodium hydroxide Sodium arsenite	0.2 0.015

Result

The result of the correlation of appropriate experimental set 0.2 M sodium hydroxide mixed with 0.015 M sodium arsenite at concentration level of to test the correlation between concentration value measured by the Sodium Arsenite method and the Cheiluminescence method by using the correlation statistics. It was found that they had correlation and the highest correlation coefficient value was 0.658 and it was at the statistical significance level at 0.01 as in Table 3 and Figure 2.

Table 3. The result on the relationship between nitrogen dioxide concentration measured by the Sodium Arsenite method in each experimental set.

Set	N	Sig value	R
1	30	0.140	0.267
2	30	0.005*	0.504
3	30	0.945	0.013
4	30	0.417	0.154
5	30	0.034	0.389
6	30	0.069	0.337
7	30	0.226	0.337
8	30	0.002*	0.538
9	30	0.000*	0.658

Remarks: * means there was a relationship at statistical significance at the level of 0.01.

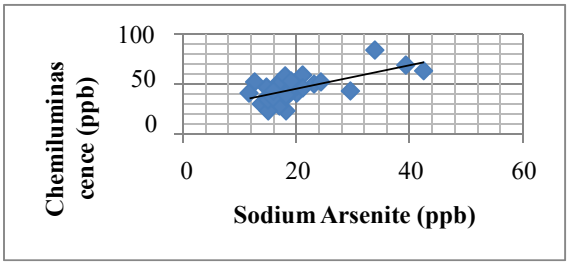

Figure 2. Correlation of the nitrogen dioxide concentration measured by the Sodium Arsenite method (in experimental set 9) and the Chemiluminescence method.

The regression result between nitrogen dioxide concentrations measured by the Sodium Arsenite method in each experimental set is shown in Table 4.

Table 4. The regression result between nitrogen dioxide concentrations measured by the Sodium Arsenite method in each experimental set.

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	Constant	21.962	5.460		4.023	.000
	set 9	.012	.003	.658	4.626	.000

a Dependent Variable: CHEMI2

The regression equation can be written as in equation (4):

$$(NO_{2(chem)}) = [0.012 \times (NO_{2(So)})] + 21.962 \quad \ldots(4)$$

When

$NO_{2(So)}$ is the concentration of nitrogen dioxide measured by the Sodium Arsenite method (ppb).

$NO_{2(chem)}$ is concentration level of nitrogen dioxide measured by the Chemiluminescence method (ppb).

0.012, 21.962 are constant values.

Conclusions

The research result found that the sampling collection with the Sodium Arsenite method which used the air flowing rate at 160 mL/min and used the absorption substance that was a mixture of 0.2 M sodium hydroxide at the concentration level and 0.015 M sodium arsenite at the concentration level of for one hour will showed the highest relation value and concentration value measured by the Pollution

Control Department with an r value was 0.658 which showed a rather high relationship.

The regression study result was utilized in adjusting the concentration value of nitrogen dioxide measured by the Sodium Arsenite method to be approximate to the measurement result gotten from the Chemiluminescence method of Pollution Control Department. The regression equation can be written as equation (5) as follows.

$$NO_{2(chem)}) = [0.012 \times (NO_{2(So)})] + 21.962 \quad \ldots.(5)$$

When

$NO_{2(So)}$ is the concentration level of nitrogen dioxide measured by the Sodium Arsenite method in (ppb).

$NO_{2(chem)}$ is the concentration level of nitrogen dioxide measured by the Chemiluminescence (ppb).

0.012, 21.962 are constant values.

Acknowledgements

I would like to thank the Research and Development Institute of Suan Sunandha Rajabhat University for supporting the funding for this research implementation.

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