# SnO<sub>2</sub> gas sensors and geo-informatics for air pollution monitoring

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Increased consumption of fossil fuels arising from population growth has resulted in increase in air population. The Bangkok metropolitan area is cited as one of the most polluted cities in Southeast Asia, thus necessitating air quality monitoring that provides assessment and situational awareness in real-time. Conventional air pollution monitoring methods are expensive, bulky, rarely used in real-time, and require costly maintenance by trained personnel. The objective of this investigation is to develop a simple, reliable, low-cost, portable and real-time air pollution monitoring system for use in central Bangkok areas. In this investigation, nanotechnology based SnO<sub>2</sub> semiconducting gas sensors were used to measure NO<sub>2</sub> gas concentrations. The sensors show good performance characteristics, including high selectivity and sensitivity to NO<sub>2</sub> gas (< 0.05 - 5 ppm) with 82% accuracy, calibrated *in-situ* with data measured from the Bangkok Pollution Control Department. The operation of the device is practically maintenance free. In addition, Aerosol Optical Thickness data were evaluated from MODIS to identify the correlation with PM<sub>10</sub> data acquired from field measurements. The correlation and distribution of air pollutants are transferred to a Pocket PC linked via Bluetooth communication tools and a Global Positioning System for rapid and simultaneous dissemination of information on pollution levels at multiple sites so that air quality in Bangkok areas can be retrieved and disseminated to concerned citizens and decision makers. Eventually, public awareness and involvement in detecting and responding to unhealthy air quality readings can be enhanced for policy guidance by using this air quality monitoring system.

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## 1. Introduction

Rapidly increasing economic growth, urbanization, and industrialization are negatively affecting the environment and natural resources, and perhaps may be linked to observed climate change. Many opinions link effects arising from enhanced industrialization, traffic density, and human activities to the Earth's rapidly vanishing ozone layer, melting Arctic ice cap, and increasing global temperatures. Since a large segment of the population, economy base, and industrialization growth are centered in Asia, large cities such as Bangkok, Beijing, Jakarta, Manila and New Delhi are facing major air pollution crisis. Air quality monitoring stations in Bangkok, Thailand report high levels of particulate matter and Nitrogen dioxide (NO<sub>2</sub>), especially in areas with high traffic and populated densities. Suspended aerosols also have become one of major air pollution problems affecting index of quality of life, air quality, and health of citizens.

Normally, Alert Response Systems (ARS) have helped citizens to adapt to rapid changes in climate and environment. Unfortunately, conventional air quality monitoring systems (AQMS) are not capable of monitoring air quality in real-time beyond a fixed installation and area of operation. Furthermore, conventional systems sample a limited region, expensive

to install and maintain, and require weekly calibration and maintenance. Furthermore, effective assessment of human exposure to air pollution requires measurement of pollution at the microclimate level. In turn, measurement of pollution at the microclimate level calls for inexpensive, geographically dispersed air quality sensing systems. The present investigation pertains to the measurement of air pollution using inexpensive sensors dispersed geographically in metropolitan Bangkok area. It should further be noted that traditional air quality monitoring systems are not scalable due to expense and fixed operations, therefore new techniques employing novel development and applications of technology are investigated to prove their efficacy in monitoring air quality with an ultimate goal for mitigating causes of air pollution at the point-of-source.

This research aims to deploy nanomaterials of  $\text{SnO}_2$ gas sensors for NO<sub>2</sub> detection in conjunction with an Internet GIS (Geographic Information System) for realtime detection and monitoring of contaminants in air. Additionally, the proposed research describes the efficacy of AQMS that is real-time, low-cost, portable, and usable in terms of operation and maintenance. A Minnesota mapserver and PostGIS/PostgreSQL database is used to store NO<sub>2</sub> levels data which can be retrieved and reported via the http protocol. Web users are able to view real-time NO<sub>2</sub> data which is overlaid with base maps including attributed data. A MODIS (or Moderate Resolution Imaging Spectroradiometer) sensor onboard a Terra/Aqua satellite is also used to identify Aerosol Optical Thickness (AOT) correlated with in-situ PM<sup>10</sup> measurements over the area under investigation. Eventually, it is expected that such emerging and potentially transformative technologies for air pollution monitoring will make a major contribution to improving the quality of the life index for Bangkok citizens by way of public awareness and guidance for policymakers. Figure 1 illustrates a conceptual framework of this study.

#### 2. Methodology

Bangkok was chosen as an area of study, primarily due to tremendous increase in traffic density and also with a population density exceeding 8 million people. The experimental methods are threefold. First, we perform a calibration experiment of SnO<sub>2</sub> semiconducting gas sensor to different known NO<sub>2</sub> concentrations to receive accurate sensor responses  $(R_s/R_o)$  prior to their use for field work. Second, we implement real-time AQMS based on an internet GIS. The in-situ sensor responses of NO<sub>2</sub> gas is converted to digital format using an analog to digital (A/D) converter with Bluetooth connection and stored in PostGIS/PostgreSQL database. The air quality of NO2 gas is published using Mapserver software. Third, we detect aerosol optical thickens (AOT) using MODIS. PM<sub>10</sub> ground measurements of the Pollution Control Department (PCD) were used to identify the correlation between insitu PM<sub>10</sub> concentrations and AOT data. The following sections provide further elaboration of the above described methodology.

#### 2.1 SnO<sub>2</sub> gas sensor calibration

The semiconducting NO<sub>2</sub> sensor is prepared on a  $SnO_2$  thick film (Alumina substrate) material acquired from E2V Technologies. Platinum electrodes were used to measure conductivity changes of the sensor at recommended sensor working temperature of ~ 220 °C. The SnO<sub>2</sub> semiconducting film is an n-type oxide which increases the resistance in presence of an oxidizing atmosphere of NO<sub>2</sub> due to its electrochemical property.

Sensor response due to NO<sub>2</sub> is caused by adsorbed species which capture electrons, thus increasing sensor resistance and voltage drop ( $R_s$  and  $V_s$ ) (Gurlo et al.1998). A possible interaction mechanism between NO<sub>2</sub> and SnO<sub>2</sub> may be through superficial Sn<sup>4+</sup> state.

$$NO_2 + Sn^{4+} \rightarrow (Sn^{5+}) - NO_2^{-1}$$
(1)

The sensor response is indicated by a ratio of  $R_s$  in presence of NO<sub>2</sub> gas to resistance of sensor in air (i.e. without NO<sub>2</sub> gas) ( $R_o$ ). The Sensor Supply Voltage ( $V_{cc}$ ) is set at 5 volts. The heater voltage ( $V_H$ ) is applied to the sensor to control temperature and humidity. The load resistor ( $R_L$ ) is attached to  $R_s$  so as to observe  $V_s$  across  $R_s$ , as seen in figure 1. The  $R_s$  value can determined using the following equation;

$$R_{s} = R_{L} * V_{s} / (V_{cc} - V_{s})$$
(2)

The calibration experiment was conducted by Petro-Instruments Corp. ltd., and implemented prior to its use in the field. The sensor itself shows high sensitivity to NO<sub>2</sub> gas (< 0.05 - 5 ppm) however the concentrations of NO<sub>2</sub> in ambient environment are usually found less than 1000 ppb. Thus, in this investigation, the sensor was tested and calibrated to known NO2 gas concentrations in 0-1000 ppb range. Programmable multi-gas calibrator, model 5008, Dasibi Environment Corp. was used to produce gas mixtures of  $O_3$  and  $NO_x$  (1:1 ratio) to receive  $NO_2$  gas concentrations in 0-1000 ppb range. To achieve accurate calibration results, NO<sub>x</sub> analyzer, Dual Chamber Chemilunescense Nitrogen Oxides monitor, Environment S.A., was connected to multi-gas calibrator. Air and gas flow rate were controlled precisely at 35 ml/min using DC-lite flow meter. The sensor was installed inside a manifold chamber to maintain steady air and gas flow rates. The sensor typically must be stabilized for several hours at room temperature prior to measuring NO<sub>2</sub> gas. NO<sub>2</sub> gas concentrations in 0-1000 ppb range were exposed to SnO<sub>2</sub> connected to evaluation circuit board and values of V<sub>s</sub> were recorded every one minute to investigate sensor responses. Moreover, selectivity of the sensor was also studied by exposing NO and O3 gases concentrations in 0-1000 ppb.



#### 2.2 AQMS based SnO<sub>2</sub> sensor and Internet GIS

An analog to digital converter was employed to connect the  $SnO_2$  sensor to convert sensor responses (V<sub>s</sub>) into digital format (NCD, 2008). The converter is a Bluetooth relay board including 8-channels and 8 bit and requires internal or external power supply of 12 VDC. This Bluetooth converter is also linked to a Pocket PC via communication port and Bluetooth connection. Using the configuration of Microsoft Visual Studio .NET 2008, the sensor transferred responses can be to PostGIS/PostgreSQL database through http protocol. Prior to transfer the sensor responses, V<sub>s</sub> signal must be altered into NO<sub>2</sub> concentration retrieved from calibration experiment. The Minnesota Mapserver 2009 was used so that NO<sub>2</sub> concentration quality levels can be monitored, retrieved and viewed in real-time together with GIS base maps (transportation, administrative boundary, residence) and satellite image of Bangkok.



Fig. 2a. The characteristic of sensor response illustrated in the relation of log-log scheme, b. characteristic of sensor response illustrated in the third order equation

#### 2.3 AOT MODIS and In-situ PM<sub>10</sub>

The Bangkok PCD reported recently that  $PM_{10}$  concentration levels around populated and crowded traffic are above the national air quality standard (The Pollution

Control Department, 2008). Several datasets of the MODIS instrument (on board Terra/Aqua satellite) were retrieved from ground station at Geoinformatics Center (MODIS, 2008). The MODIS aerosol products (MOD04) in HDF-EOS format were acquired and modeled using MODIS data of Level 1B containing the AOT physical parameter (Remer et al. 2006). Geometric correction is thus required. Afterwards, scientific data set of 'Image Optical Depth Land and Ocean' (AOT at 0.55  $\mu$ m) was extracted and eventually AOT imagery in binary format are retrieved. Digital number (DN) of the AOT imagery varies from -100 to 5000 which must be converted to AOT using linear equation,

$$AOT = \alpha * DN + \beta \tag{3}$$

Where  $\alpha$  – the scale factor and  $\beta$  is the offset, which equal to 0.001 and 0.0, respectively (Remer et al. 2006). Hourly data of PM<sub>10</sub> from 13 ground stations were collected and used to correlate with multi-temporal time series of MODIS imagery indicating AOT values.

#### 3. Results and discussion

#### 3.1 SnO<sub>2</sub> gas sensor sensitivity and selectivity

The SnO<sub>2</sub> semiconducting gas sensor was tested to different NO<sub>2</sub> gas concentrations in 0-1000 ppb and shows sturdy and reproducible responses. The sensor was exposed to NO<sub>2</sub> gas of 0, 50, 75, 100, 200, 300, 400, 500, 600, 700 and 1000 ppb presenting V<sub>s</sub> as 0.304, 1.430, 1.782, 2.091, 2.650, 3.000, 3.230, 3.400, 3.520, 3.620, and 3.760 respectively. This sensor response is non linear type (E2V, 2007) varied from the study of Vaseashta et al., 2007. The relation of  $R_s/R_0$  to sensor response was calculated and plotted in log-log scheme as seen in figure 2 (a). Afterwards, a scatter diagram was applied to investigate the correlation between  $R_s/R_0$  and NO<sub>2</sub> gas concentration. It is found that the characteristic of sensor response is shown the best correlation in the third order equation,

$$y = 2E - 08x^3 - 6E - 05x^2 + 0.0896x + 1.8298$$
(4)

y,  $R_s/R_0$  or sensor response, and x or NO<sub>2</sub> concentration are as shown in figure 2(b). Regression square value of 0.9984 indicates high accuracy of this correlation.

Reproducibility of sensor was investigated by exposing NO<sub>2</sub> gas concentration tested (0-1000 ppb) as explained above. It is discovered that the time sensor requires to reach 90% of maximum response ( $T_{90}$ ) is approximately within 1-2 minutes; conversely the time sensor needs to reverse to 10% of baseline is around 30 seconds. Nevertheless the sensor was tested selectively to NO and O<sub>3</sub>, both in 0-1000 ppb range and the results show that this SnO<sub>2</sub> semiconducting gas sensor demonstrates excellent selectivity to both gases.



Fig. 3. Scatter diagram of NO2 concentrations (ppb) monitored from SnO2 sensor and conventional method.

In order to examine the accuracy of  $SnO_2$  sensor responses, the PCD's conventional ground  $NO_2$ monitoring method was implemented at Dindang station (Central Bangkok). The hourly data of  $NO_2$  gas concentrations attained from the  $SnO_2$  sensor were monitored and compared to hourly data received from the PCD's monitoring station at average 27.5 °C and 60 % of ambient temperature and humidity, respectively. The comparison is identified by the coefficient of Determination at 0.82 (82% accuracy). Fig. 3 shows a scatter diagram of both mentioned monitoring data.

## 3.2 Ground measurements using SnO<sub>2</sub> semiconducting gas sensor

The SnO<sub>2</sub> semiconducting gas sensor was used to measure ground NO<sub>2</sub> quality levels on two observation sites. The sensor was placed at a car park area of the Future Park shopping mall and Thammasart hospital in order to monitor NO<sub>2</sub> concentrations from road side during 0800 to 2100. The results of NO<sub>2</sub> hourly average data monitored from both sites are demonstrated in figure 4(a)-(b). It can be explained that NO<sub>2</sub> quality levels are dependent on the time. During rush hours from 0800-0900 and 1900-2100, NO<sub>2</sub> levels are higher than non-rush hours.



Fig. 4. Sensor signal (Vs) and NO2 gas concentration monitored from (a): Future park Rangsit and (b): Thammasart Hospital.

# 3.3 Real-time AQMS

The AQMS was developed comprising 4 components including (1) sensing node, (2) transferring node, (3) receiving node, (4) server node, and (5) visualization node as shown in figure 1. Integrating SnO<sub>2</sub> semiconducting gas sensor linked to an analog to digital converter via Bluetooth is to transfer sensor responses dependent to NO<sub>2</sub> gas concentrations into a Pocket PC at the receiving node. In order to acquire  $NO_2$  gas concentration data, the correlation of sensor responses and NO2 gas concentration (See equation 2) acquired from calibration experiment was configured using Microsoft Visual Studio .NET application. A PostGIS/PostGreSQL database is employed to store NO<sub>2</sub> gas concentration data obtained from the Pocket PC which NO<sub>2</sub> data uploading is every 5 minutes. The NO<sub>2</sub> data uploaded must be converted to one hour average according to the national ambient air quality standard (The Pollution Control Department, 2009). Furthermore geographical coordinates of current ground monitoring site can be also captured and stored. At server node, Mapserver is configured with PostGIS/PostGreSQL database and PHP using map file (.map) to ensure Web Map Service (WMS), which is a Common Gateway Interface (CGI) based development environment for building spatially enabled Internet applications. The above configuration allows execution of the user's request and management of the database in real-time. The only requirement on the client side to retrieve and view NO<sub>2</sub> gas concentration data is available Internet access using Web-browsers. In addition to observing the NO<sub>2</sub> gas concentration, GIS base maps and IKONOS satellite image are also established so that NO<sub>2</sub> quality levels can be monitored and interpreted based on relevant geographical information.

# 3.4 AOT MODIS and in-situ PM<sub>10</sub> ground measurements

The data in January 1 - December 31, 2008 range of hourly average  $PM_{10}$  concentration data obtained from 13 PCD's *in-situ* monitoring sites and AOT detected from MODIS sensor were correlated. The results show that correlation between  $PM_{10}$  and AOT are from 0.065 to 0.555. A meteorological station data shows maximum correlation with 0.555 R<sup>2</sup> as illustrated in figure 5. The

correlation investigated is not quite high which can be explained by following reasons: (1) some missing hourly average  $PM_{10}$  data discovered from a few PCD's *in-situ* stations, and (2) MODIS product is consistent with the time pass covering Bangkok area. Thus, it is difficult to receive MODIS AOT image at the same time as hourly average  $PM_{10}$  concentration data monitored from the PCD., and (3) large standard residual during statistical analysis of each station contributes massive influence. In order to demonstrate better correlation,  $PM_{10}$  data from each ground monitoring site mustt to be measured at the same time as MODIS sensor passes by the current station.



Fig. 5. The correlation between hourly average PM10 concentration data obtained from 13 PCD's in-situ monitoring sites and AOT detected from MODIS sensor at Meteorological department station.

# 4. Conclusion and way forward

Use of nanotechnology and wireless GIS has made it possible to design low cost gas sensors and portable devices for air quality monitoring. The  $SnO_2$ semiconducting sensor shows strong performance on selectivity, reproducibility and sensitivity of NO<sub>2</sub> gas in 0.05-1000 ppb range. The conventional AQMS of the PCD can be enhanced by employing the AQMS developed from this study. Due to its real-time NO2 quality data dissemination, the developed AQMS can be used as an Alert Response System in Bangkok area. To make the ARS complete, other kinds of gas sensor (O<sub>3</sub>, NO, CO, SO<sub>2</sub>) should be implemented. The AOT derived from MODIS sensor can be used to monitor PM<sub>10</sub> in near-real time due to its multi-temporal characteristic. Detecting other gases from MODIS imagery needs further investigation.

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