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Air pollution monitoring using semiconducting gas sensors and Internet GIS

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Abstract

Recently, air pollution has become a serious problem in thickly populated and industrialized areas in Thailand, especially in Bangkok. The air pollution in Bangkok is abundant, especially in areas where pollution sources and the human population are concentrated. Economic growth and industrialization are proceeding at a rapid pace, accompanied by increasing emissions of air polluting sources. Furthermore, the development of a suitable method for monitoring the pollution causing sources has not followed at the same pace. Recently the main pollutants causing such critical air pollution problem are Ozone (O_3) and particulate matter i. e., total suspended particulate (TSP) and particulate matter lesser than 10 µm (PM_{10}) as reported by the Pollution Control Department, Thailand (PCD). To prevent or minimize the damage caused by atmospheric pollution, suitable monitoring systems are urgently needed that can rapidly and reliably detect and quantify polluting sources for monitoring by regulating authorities in order to prevent further deterioration of the current pollution levels. Consequently, it is important that the current air quality monitoring system, controlled by the PCD**,** should be adapted or extended to aid in alleviating this problem. So as to carry out air pollution monitoring over an extensive area, a combination of ground measurements through inexpensive sensors and Internet GIS are employed for this purpose. This portable device, comprising commercial tungsten oxide (WO_3) semiconducting gas sensor integrated to a Personal Digital Assistant (PDA) linked through Bluetooth communication tools and Global Positioning System (GPS), will allow rapid dissemination of information on pollution levels at multiple sites simultaneously. To provide air quality report can be then published using Internet GIS in order to contribute a real-time information service for the PCD, for increased public awareness and enhanced public participation. The investigations of this new sensor technology are discussed in detail as well as a summary of the advantages and disadvantages of using this portable device will is concluded in the paper.

Key-words: air pollution, tungsten oxide semiconducting sensor, Internet GIS, real time monitoring system

1 Introduction

In Bangkok, where the air is thick with adverse air pollutants, increasing emissions are unavoidable due to excessively rapid economic and industrial growth. The cost of establishing and implementing ordinary monitoring systems is extremely high; use of analytical instruments is time-consuming, expensive, and can rarely be applied for real-time monitoring in the field, even though these can give a precise analysis. Hence, a new generation of detector, WO_3 semiconducting gas sensor, offers an excellent alternative for environmental monitoring due to low cost, light weight, extremely small size and also because of the reason that they can be deployed anywhere so as to receive data that can eventually be transmitted through a Internet GIS network system as a rapid monitoring tool to the general public. Because of cost consuming to retrieve satellite imagery, the central parts of Bangkok were chosen to determine the air quality levels. The satellite image from IKONOS, contributed by the Department of City Planning, Thailand, was included to the air quality monitoring (AQM) mapserver and overlaid with relevant maps. The air pollutants monitored include NO_2, O_3, CO, and PM_{10}. These pollutants were uploaded in real time to the AQM server as concentration levels using data logging technique. The current and daily historical air quality (AQ) data were captured from each *in-situ* AQ station through the telephone modem line using Hyper Terminal program and the data were kept in the mapserver. Users can simply browse and view the graphical AQ data in real time. Sampling time of each day comprises rush hours in the early morning and in the evening, Additionally, other sampling time is also carried out when the traffic flow is normal, so as to compare the air quality levels between dense and less traffic conditions.

In laboratory, computer based simulations between air pollutant concentration in 0-7.50 ppm range, obtained from WO_3 semiconducting gas sensor, and Internet GIS are integrated in order to test the Air Quality Monitoring System (AQMS) and contribute as easy portable device for real-time air quality monitoring as well as it can initiate other researchers in different fields of applications. The model as developed will then be used for acquiring and monitoring real time AQ levels and also updating information through Internet GIS using Web Map Service (WMS). The results are illustrated information of which AQ levels are monitored and demonstrated in the form of GIS database. The air pollutant concentration levels will be categorized into 3 classes including good, moderate and high relied on the Ambient Air Quality Standard (AAQS) of the PCD [1]. This illustration, therefore, can be used to enhance public awareness and participation. After all this simulation can be referred to as an air pollution monitoring system, which will be able to support the PCD to establish priorities and measures air pollution and also facilitate the problem analyzing and monitoring air pollution in Bangkok area.

2 Objectives

Objectives of the study are:

1) to apply a gas sensing device coupled to a PDA for monitoring of air pollution in urban area and disseminate the information in real time through wireless GIS.
2) to assist in establishing priorities, measurements of air pollution in Bangkok and increasing public awareness and enhanced public participation.

3 Semiconducting tungsten oxide thick film gas sensors for air pollution

The semiconducting NO_x sensor applied in this present work is packaged in a commercial electronic package referred to as a TO-39-4 header and cap, developed by the Synkera Technologies Inc. [2]. The deposition of the sensing layer is WO_3 thick film (Alumina substrate) materials, sputtered by screen printing technique. Platinum is used as electrodes to measure conductivity changes of the sensor and the necessary sensor working temperature is about 250 ºC , achieved by ruthenium oxide heater [3]. Fundamentally, the resistance change is caused by a loss or a gain of surface electrons as a result of adsorbed oxygen reacting with the target gas. The WO_3 semiconducting used in this research is an n-type, there is, hence, either a donation (reducing gas) or subtraction (oxidizing gas) of electrons from the conduction band. The result is shown that n-type oxides increase their resistance when oxidizing gases such as NO_2 or O_3 are present while reducing gases such as CO or CH_4, lead to a reduction in resistance. This then translates into corresponding changes in electrical resistance. The basic adsorption of NO_2 to the WO_3 film surface is a reversible chemisorption reaction as shown below.

$$NO_2 + e^- \leftrightarrow NO_2^- \qquad (1)$$

Sensor response of metal oxide based gas sensors to NO_2 is caused by adsorbed species which capture electrons and hence make sensor resistance (voltage out) increase [4]. The different adsorbed species can be NO_2^- as seen in equation (1), O^- and $2O^-$, dependent on the operating temperature. In any case, these species must adsorb on surface defects-reducing states, such as metal cations in low oxidation states or oxygen vacancies. Accordingly, a possible interaction mechanism between nitrogen dioxide and WO_3 may be through superficial W^{5+} states:

$$NO_2 + W^{5+} \leftrightarrow (W^{6+} \text{-} NO_2^-) \qquad (2)$$

The electron depletion at the WO_3 gas sensing surface is proposed in the Fig.1. The adsorption of atmospheric oxygen is due to O_2^- specie (equation 2) which ties up electron carriers. When WO_3 sensor is sensed to NO_2, the depletion region is increased which changes the microscopic structure as well. Hence the electric properties are totally influenced by the depletion layer. On the top of that the detection of electric conductivity promisingly contributes sensor signals.

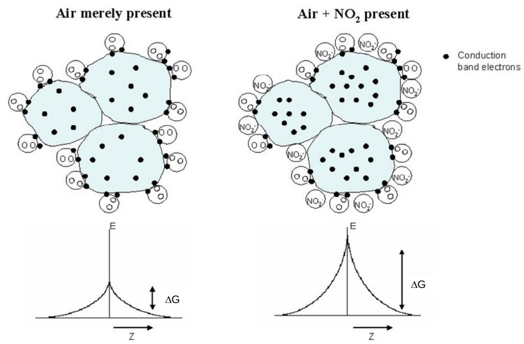

Fig.1 The chemisorption of oxygen atoms at semiconducting surface and the associated potential barrier formed at each interparticle contact

4 Methods and experimental setup

4.1 Sensor calibration and gas sensitivity test

The schematic diagram of the calibration system is shown in Fig.2.

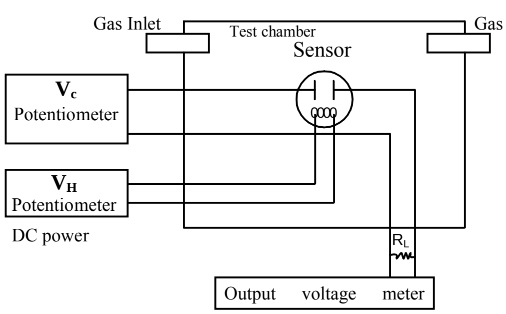

Fig.2 Schematic diagram of the measurement system. V_c: circuit voltage; V_h: heater voltage; R_L: load resistance; V_{RL}: output voltage

4.1.1 Adjustments

Heater voltage was adjusted to a target voltage at 4.5V, supplied by the Synkera technology Inc [2]. Sensor zero adjustment is capable of adjusting potentiometer with no gas applied (0 ppm NO_2). With a voltmeter it ought to be turned counter-clockwise until a minimum signal (approximately 6mV) is reached. Sensor gain was adjusted to 5VDC using potentiometer as well with full-scale gas (7.37 ppm of NO_2).

4.1.2 Typical response of WO_3 semiconducting sensor to NO_2 gas

This calibration experiment was collaborated with Petro-Instruments Corp., Ltd. 0-7.34 ppm of NO_2 gas was produced by gas mixtures between O_3 and NO_x using the instrument "Programmable multi-gas calibrator, model 5008. This gas calibrator is connected parallel to NO_x analyzer "Dual chamber chemilunescense nitrogen oxides monitor, Environment S.A., which is purposed to obtain accurately NO_2 concentrations produced from the multi-gas calibrator. The ratio used for mixing gases was the gas volume of NO_x: O_3 (1:1). Flow meter "DC-lite" was employed to control the flow rate of air and gas. Flow rate of air and gas was 70 ml min^{-1}. Power supply was provided by adapter of 9V and 1.2 mAH. The sensor was housed inside a plastic chamber of 10 ml volume under continuous flowing of testing gas mixtures at a constant flow rate. The sensor was stabilized for 16 hrs at least at room temperature before measuring NO_2 gas in the chamber**.** At each investigation of sensor response, the sensor was exposed to NO_2 gas for 5 min and exposed to zero air in between each sensor response test for 2 min.

4.1.3 Sensor response to NO gas (10 ppm)

This WO_3 sensor was tested to pure NO gas of 10 ppm for 5 minutes to investigate the selectivity of sensor as explained the results in section 5.1.5.

4.1.4 Sensor response to O_3 gas

As investigated in previous experiments, it was found that this WO_3 semiconducting gas sensor has detection in 0.54-7.5 ppm range of NO_2 gas. This discovery causes a difficulty to deploy the sensor in urban environment, polluted low concentration of NO_2 (<0.50 ppm). According to the study of Lee D. D. [5], the experiment of sensor response to O_3, hence, was interested to carry out. To expose pure O_3 to the sensor was applied by the instrument "Programmable multi-gas calibrator, model 5008. Gas and air flow rate was 70 ml min^{-1} and exposed with concentrations of O_3 in 75-500 ppb range. Additionally the heater was adjusted varying from 3.0 to 4.2 V to investigate the characteristics of sensor response as well.

4.2 Real time air quality report using the Internet GIS setup

4.2.1 Internet GIS mapserver setup

Internet GIS is a linkage between GIS and Internet. Users will be able to access GIS applications without purchasing GIS software by using a web browser. Detailed maps can be generated from huge databases of spatial information and distributed all over the world [6]. The Web is a cost effective way to share or provide public access to data worldwide on the Internet. As shown in Fig.3, the wireless GIS Data Logging System being developed in this study is composed of two parts, i.e. hardware and software. On the hardware side, a Mandrake server version 10.0 provides the back-end support. On the front-end, a user has a PDA (Pocket PC) or ordinary personal computer. So as to be complete, a Global Position Receiver (GPS) and Digital camera can be also integrated through proper extensions. On the software side, a Minnesota Map server 4.4.0 ensures Web Map Service (WMS), which is an Open Source Common Gateway Interface (CGI) based development environment for building spatially enabled Internet applications. The server setup is made up of PostgreSQL, PostGIS and PHP, configured with each other to execute the client's request and manage the database. The client setup is composed of interfaces, developed using JavaScript and Hyper Text Markup Language (HTML) [7]. For wireless Data Updating System, it is composed of three tiers, including Front-End Tier, Middle-Tier and Back-End Tier. On the Front-Tier is the client, making a request, Minnesota Map Server in the Middle Tier passes the CGI-request over to the Back-End Tier where PHP and PostgreSQL with PostGIS read the data and execute the request.

This WMS for AQ monitoring provides functions for users to be able to simply browse, zoom in-out the map objects and query historical and daily AQ data graphically. PostgreSQL RDBMS has been used for managing attribute data of historical AQ levels. The front-end for the RDBMS is coded using the PHP scripting language running on Linux. The only requirement on the client's side is the ability to access the Internet using the Web-browser. In brief the developed AQ monitoring system in this study comprises spatial and database query, data management, relevant information links and general information regarding air pollution monitoring issues.

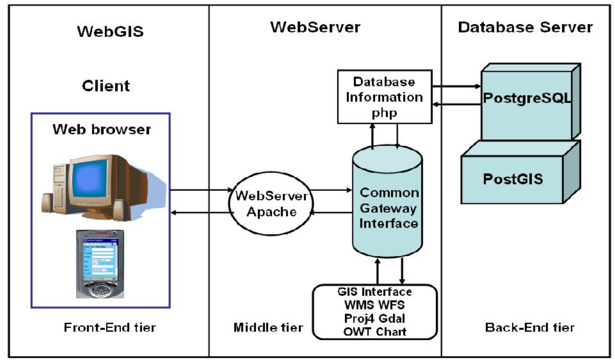

Fig.3 Web mapserver composition

4.2.2 Real time air quality monitoring in urban environment using GIS modeling

The input data used for this study comprise measured NO_2 levels from WO_3 sensor, the real-time AQ logged from the PCD's AQM sites, and historical AQ database acquired from the PCD. A limited number of observation sites were taken to test the method at locations which are critical for automobile pollution. The data were collected every hour, which were fed to the GIS for further processing. In Fig.4, the WO_3 semiconducting sensor gives out electric signals, dependent on NO_2 concentration. An A/D circuit converter is employed so as to convert the NO_2 concentration values from an analog signal to digital one. The digital pollutant concentration data are stored in Postgresql, besides historical and daily CO and O_3 are uploaded to the database as well. For real-time AQ logged from AQM sites and historical AQ of the PCD, both of them are kept in Open database Connectivity (ODBC). Pollutants data, GIS base maps, satellite image and attributes were uploaded to the mapserver as a map file. The results are utilized for AQ level modeling of the study area. The model developed can be applied for acquiring and monitoring real time AQ levels and also updating information through the Internet GIS using WMS. The information of AQ levels can be operated as a monitoring approach and displayed in the form of GIS database.

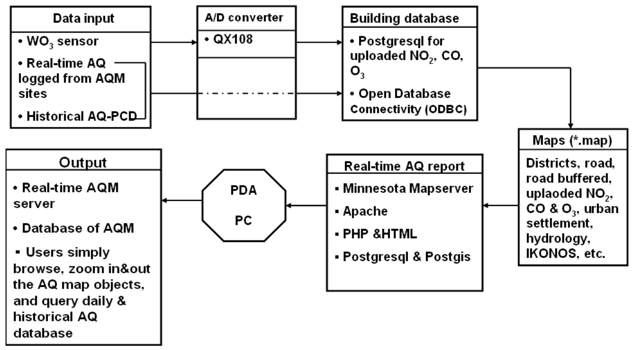

Fig.4 Conceptual framework for real time air quality monitoring using GIS modeling

4.2.3 The real time data logging of current and daily AQ data from the PCD station

The current and daily historical AQ data monitored by the PCD are logged as well using Hyper Terminal program through the modem of telephone line. The AQ data from Ladphrow station (Bangkok) are chosen to capture and stored in the mapserver in the database as an excel file format. Users can simply browse and query to view the current and daily historical AQ data as well.

4.2.4 The integration of nanosensor, A/D converter and Internet GIS

The voltage output retrieved from the sensor will perform as input analog signal to the A/D converter. Hence the analog signal will be converted to digital output as ASCII format (10 bits) by the A/D converter "QX108". U-ART will receive (Rx) and transmit (Tx) the output signal to PDA through serial port (comport). To transmit and receive the data through comport, RS232 or EIA232 will adjust the proper pressure as comport required before transferring the data. The period of data reading from the A/D is every 5 minutes. Before transferring the data to the server, voltage output values acquired from this A/D are needed to convert to be concentration values of NO_2, following the calibration curve (see Fig.6). Later on the NO_2 data are averaged as an hourly value using Visual Basic language programming and using SQL to query the hourly averaging data and upload them to PostgreSQL database through http protocol.

5 Results and discussion

5.1 Sensor calibration and sensitivity

Sensitivity [8] is one of the most important issues in gas sensing devices applying in AQ monitoring field. In the term of gas sensor, sensitivity can be identified that the detection of gas concentration is measured in part per million (ppm). For Selectivity, it can be referred to as the detection of specific gases in mixed gas environment [8, 9]. Sensitivity can be sensitized differently to each gas [10] depending on operating temperature, microstructural modification, dopant utilities, catalysts [11] and so forth.

5.1.1 Adjustments

After exposing zero air to the sensor and the sensor responds minimum voltage out (V_{out}) for 90s, sensor zero was adjusted to 6 mV**.** Later on full scale of gas (7.37 ppm of NO_2) was applied, the V_{out} increases from 0.006V to 4.870 V and was stable for 60s. The sensor gain sensitivity was adjusted to maximal 4.880V. The heater was adjusted to target voltage of 4.2V, according to sensor specification.

There are several factors which can improve the sensor sensitivity. The sensitivity of WO_3 sensor is highly dependent on the roughness of substrate which can be adjusted by increasing the surface area and porosity of film surface regarding modifications in the film surface morphology [5]. Moreover the sensitivity can be improved by decreasing the particle grain size as well as using nanocrystalline materials [4], increasing surface area and incorporating additives, such as Au, Pd, and TiO2 [12, 13]. The humidity factor (high level) is also one of the significant limitations of the semiconducting sensor, which can be decreased by adding specific catalyst [14]. Increasing operating temperature is able to improve sensor sensitivity as well [15].

5.1.2 Typical response of WO_3 semiconducting sensor to NO_2 gas

The sensor was exposed to the gas of NO_2 in 0-7.54 ppm range to investigate the characteristics of sensor response with different gas concentrations as shown in Fig.5. Across this range of exposed concentrations, the sensor illustrates a strong, reproducible response and this type of sensor is a linear device as seen in Fig.6 as similar as the study of Wang et al [16], which the sensitivity of WO_3 film calcined at 500 °C as correlated with NO_2 concentrations shows strongly linearity. When viewed on a curve of voltage output versus concentration plot, the characteristic of sensor response can be considered as a linear correlation between NO_2 gas concentration and voltage output measured from the sensor. It can be explained by the equation of $Y = 0.219+1.194X$ which X is referred to as voltage output and Y is called NO_2 concentration. Regression square value of 0.934 shows the accuracy of this correlation with high accuracy. The statistic results explain this calibration curve that voltage output as a constant value predicts NO_2 gas concentration with 93 percentage of accuracy. The standard deviation of predictors and predicted values are 2.411 and 1.958 respectively.

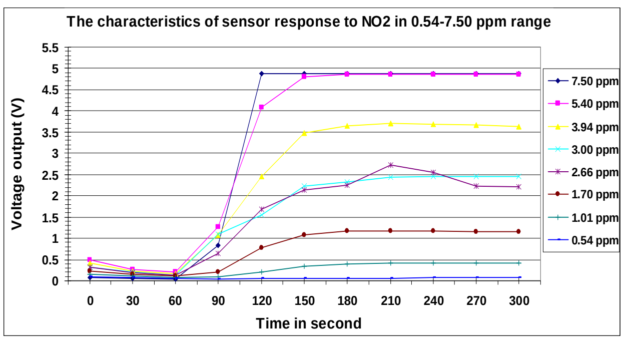

Fig.5 The characteristics of sensor response of NO_2 in 0.54-7.50 PPM range

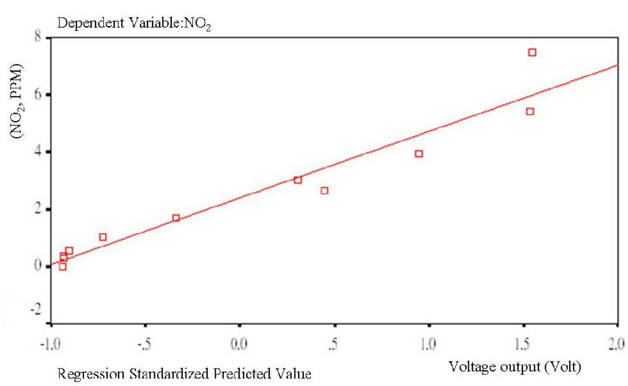

Fig.6 Sensor response (V_{out}) in linearity to different concentrations of NO_2 challenge

5.1.3 The sensitivity and selectivity of sensor

The voltage detecting method is used to calculate the sensitivity of the sensor which is identified as V_{gas}/V_{air}, where V_{gas} and V_{air} is the electric voltage out in NO_2 gas and clean air, respectively. The sensitivity of this sensor is between 0.54-7.50 ppm of NO_2 as explained by Fig.7. Additionally, it can be referred that the higher concentration of NO_2 gas, the more sensitivity of the sensor. Due to the sensitivity of the sensor is nearly none ($V_{gas}/V_{air}=1$) at low concentration (0-0.54 ppm), it is identified that this WO_3 sensor has detection limit at low concentration of NO_2 (below 0.54 ppm).

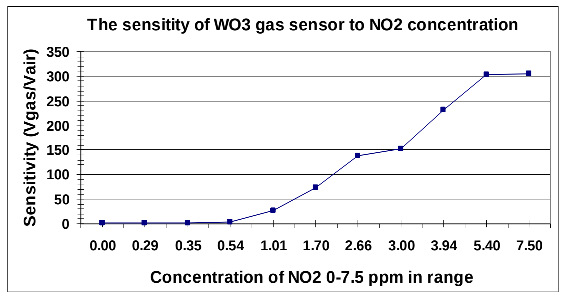

Fig.7 The sensitivity of WO_3 gas sensor to NO_2

5.1.4 Reproducibility of sensor response

The sensor was again held in air with challenge gas applied gradually for 5 min and exposed to zero air in between each sensor response test for 2 min. Response time (T_{90}) is identified as the time required for the sensor to reach 90% of its full response, while recovery time (T_{10}) is the time required returning to within 10% of the original baseline [3]. As illustrated in Fig.8, the sensor response is very reproducible. 7.24 ppm of NO_2 was exposed for 240s into a background dry air, which response time of the sensor is approximate 120s (T_{90}). Zero air was introduced for two minutes (240-300s) and 5.64 ppm of NO_2 was exposed for 300s afterwards. It was found that recovery time (T_{10}) is around 2 minutes. From the experiment, it can be identified that typical response time is 1.5-2.5 minutes, depending on the concentration of challenge gas applied, while recovery time is generally lesser than 2 minutes. These sensor responses are nearly identical in terms of baseline, sensitivity and response time. The sensor comprises a complete recovery after gas exposure.

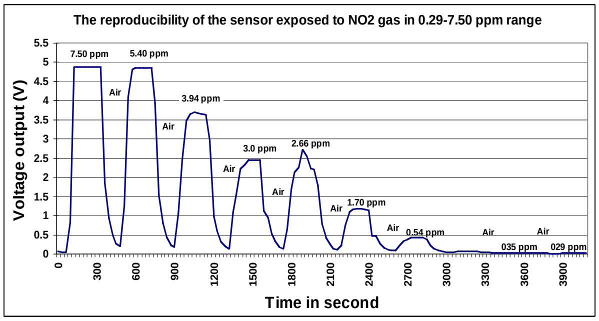

Fig.8 The reproducibility of the sensor exposed to NO_2 gas in 0.54-7.50 ppm range

5.1.5 Sensor response to NO gas (10 ppm)

It was found that the WO_3 sensor has no response to NO (V_{gas}/V_{air} equal to 1). The results are similar as studied by Deininger et al. [3]. The reason due to the sensor more sensitive to NO_2 than NO is because NO_2 is a stronger oxidizing agent to interact with W^{5+} as explained earlier. Basically, when the sensing material is exposed to NO_x, it is oxidized and the sensor resistance increases indicating the presence of gas. Conclusively, the sensitivity of this sensor is high, and the selectivity is less.

5.1.6 Sensor response to O_3 gas

The sensor was exposed to different concentrations of gas in 0-500 ppb range. The results show that this WO_3 semiconducting gas sensor has no typical response to Ozone, even when the heater was adjusted. When the sensor was exposed to different concentrations of gas, the voltage output was not changed much relatively and absolutely, compared to the sensor exposed to zero air (Fig.9).

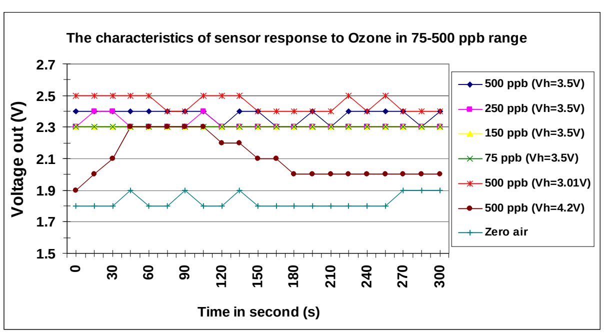

Fig.9 The sensitivity of WO_3 gas sensor to O_3

5.2 Real time air quality report using the Internet GIS

5.2.1 Real time air quality monitoring in urban environment using GIS modeling

NO_2 concentration levels, acquired from monitoring sites, GIS base maps, satellite image from IKONOS and attributes were input into PDA linked with GPS. The results were utilized for AQ level modeling of the study area. The model developed can be used for acquiring and monitoring real time AQ levels and also updating information through wireless GIS using WMS to be displayed in the form of GIS database. The AQ levels were overlaid with Bangkok base maps and IKONOS's (4 m multispectral, visible bands) image. The three classes of AQ levels reported include low, moderate, and high related to the ambient AQ standard of the PCD. Hence, Internet users can browse and query air quality based maps, relating to geographic information, including districts, urban settlement (education, offices, villages, temple, and so forth.), roads, railways, hydrology, and IKONOS image as a background. Furthermore buffer lines from each AQM site to report AQ levels, two days earlier and current AQ situation of NO_2, O_3 and PM_{10} can be queried. The Internet based GIS is useful real time interaction on AQ levels and increases public awareness and participation. The fundamental functions are developed for both PDA and PC users including the buttons of browse, refresh map, query, zoom in, pan, and zoom out to retrieve GIS layers and IKONOS as background. Fig.10 illustrates an example of the AQ report underlaid with IKONOS and road layer. The AQM site is Dindang station showing the current AQ situation under low concentration of NO_2 covering 70-100 meter around the station. Additionally, users can query the current and daily AQ level in graph formats as seen in Fig.11. This query information was carried out by using OWT Chart open source software.

Fig.10 The current NO_2 level from Dindang station

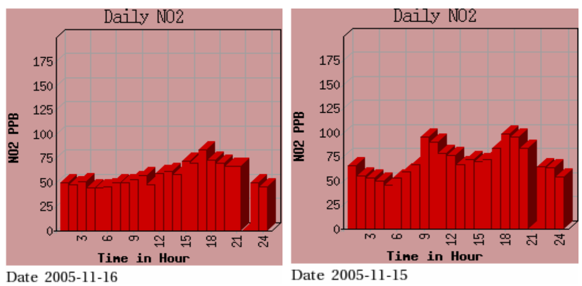

Fig.11 The daily NO_2 level in graph format

5.2.2 The real time data logging of daily and historical AQ data from the PCD station

To capture real time AQ data, monitored by the PCD was implemented by using Hyper Terminal program. The AQ data were logged through the telephone line. The configuration of modem connection preferences is required to carry out prior to capturing the real time AQ data from each AQM station. The captured data are exactly the same as shown on the monitor of *in-situ* AQ monitoring instruments. Hence it can be concluded that using the Hyper Terminal program enables to log the AQ data as real time.

5.2.3 The integration of nanosensor, A/D converter and Internet GIS

The A/D converter applied for PDA users receives and transmits the data of NO_2 levels through serial port as seen in the Fig.4. Visual Studio .Net is used to create the emulator of the nanosensor, A/D converter and PDA interface which is able to process on PC. All the functions required for the integration are created by Visual Basic Language. The data logging interface has several functions for data source setting and for timer setting. Using the timer setting function, the data of voltage output values acquired from the sensor can be set to log every 5 minutes and then will be averaged continuously every 60 minutes. The AQ level of NO_2 is reported as averaging hourly value according to the ambient AQ standard of Thailand. The averaged data, hence, will be sent to the database server "PostgreSQL" through http protocol in 'GET' method. Besides the data of voltage output will be converted into NO_2 concentration value based the relation of voltage output (X) vs. NO_2 concentration value (Y) as shown in Fig.6. Finally the AQ data of NO_2 will be uploaded to the database and shown as map objects as well.

6 Conclusion

The current AQ situation of Bangkok is critical caused by air pollutants, therefore the quick, easy, low cost, and real-time portable AQ monitoring devices are tremendously necessary to carry out and support AQ problems. This work has successfully resulted in offering a suitable monitoring system using low cost portable gas sensing system based on "WO_3 semiconducting gas sensor" so as to carry out air pollution monitoring over an extensive area and to be able to report real time AQ data through Wireless Internet GIS. Later on this modeling can be referred to as an real-time portable air pollution monitoring system, which will be able to support the PCD to adapt or extend the current the PCD's air quality monitoring systems, to facilitate the problem of analyzing and monitoring air pollution, and also to assist in establishing priorities and measurements of air pollution in the Bangkok area. Finally public participation and awareness can be enhanced by contributing this real time AQ monitoring system.

Nevertheless, the NO_2 levels monitored generally from the PCD are under low concentration (0-0.2 ppm), the sensor applied in this study needs further investigation to obtain more sensitivity for low concentration detection (<0.5 ppm). The improvement of sensor sensitivity can be carried out by (1) decreasing grain size which affects to the increase of surface area and porosity of film surface, (2) increasing operating temperature and (3) adding incorporating additives or specific catalyst. As reviewed In_2O_3 nanowires gas sensor can be a good alternative in terms of high sensitivity with detection limit of ~20 ppb and 5 ppb, respectively, great reliability, and simple fabrication [4]. Furthermore different kinds of gas sensors may be suitable to monitor other air pollutants such as NO, CO, O_3, SO_2 as well as the sensor to detect particulate matter.

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