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Project Summary

Construction and Testing of Electrochemical NO_2 PSDs

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The objective of this project was to develop, test and deliver a prototype electrochemical instrument capable of real-time measurement of low-ppb levels of NO_2. The unit must be small enough for use as a personal monitor.

The work was conducted in two distinct tasks that were performed concurrently: (1) improvement of the currently available NO_2 sensing technology to provide a sensor with sufficiently high signal/noise ratio and stable background signal for continuous low-ppb level measurements, and (2) the design, assembly, testing, and delivery of a portable instrument incorporating this sensor technology to provide capability for monitoring personal exposure to ambient NO_2 concentrations.

During this project, the following work was completed:

A very low background, low noise, attitude-insensitive sensor was developed and tested to provide detection of NO_2 at levels as low as 5 ppb. A portable, modular prototype NO_2 monitor was developed and tested. The instrument was interfaced to a commercial data logger to allow collection and storage of real-time concentration data, as well as a continuous display of ambient NO_2 levels. Three of these units were constructed for evaluation. In addition, preliminary design of a second generation data logger/controller that can provide optimum ease of use and maximum accuracy was completed.

Future work will address further improvement in the NO_2 sensor stability, reduction in NO_2 instrument size, development of the optimum data logger/controller, expansion of the monitor to measure other compounds, and the investigation of multiple-function, multiple-compound, sensor-array based real-time monitors.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back.)

Introduction

The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The monitoring of pollutant gases at sub-ppm and low-ppb levels is of primary concern in indoor air and non-industrial locations such as the home. The trend toward more airtight homes, which began during the energy crisis of the early 1970's, has caused concern among health experts about increased levels of indoor pollutants such as the sulfur and nitrogen oxides. It is the objective of this work to develop a personal sampling device (PSD) which will allow real-time monitoring of low concentrations of NO_2 in the presence of ambient levels of potential interferents such as NH_3, CO, H_2S, common hydrocarbons, and SO_2.

Amperometric electrochemical sensors provide portable real-time analysis capability and have been used for ppm level measurement of NO_2. These sensor systems do not suffer interferences from NO, N_2O, or nitrous acid but often possess too much noise and drift to provide accurate data at ppb levels. Major sources of drift have been tentatively identified as temperature and relative humidity fluctuations.

The work discussed in the full report has focused upon improvement of the existing electrochemical technique so that it can be used at ppb levels. This requires gaining an understanding of the reactions of NO_2 in the sensor system. This knowledge is required to design and build an improved real-time portable instrument for the measurement of NO_2 in the field.

Procedure

All gases and gas mixtures were supplied by Scott Specialty gases in pressurized cylinders at a concentration of 49-400 ppmv in zero air. Working standard mixtures of NO_2/air were prepared fresh several times daily by dilution of the stock gas mixture. Low levels of NO_2 in air were prepared using a calibrated permeation device (KinTek Laboratories, Houston, TX).

Gas flow through the sensors was controlled using Spectrex AS-400 pumps and Matheson Model 602 (0-1L) and 603 (0-5L) flow meters fitted with Clippard needle valves. Elevated temperature experiments were conducted in a GCA/Precision Scientific Model 18 oven. Low temperature experiments were performed in a modified GE TA242TH refrigerator. Temperature was monitored with a 0-110°C mercury thermometer.

Commercial sensors were obtained from the Energetics Sciences Division of National Dräger (ND or ESI). Solid electrolyte sensors using Nafion (El DuPont TM) cation exchange material and aqueous electrolyte sensors with low surface area (LSA) and high surface area (HSA) sensing electrodes were designed and built by TRI under carefully controlled conditions.

Sensors were tested in the drawn-air ("pump-after-sensor") flow configuration recommended in earlier work. A low volume exposure chamber was used to test the ND sensors. The volume of the chamber used with the TRI sensors was decreased by 50% from the prior work in order to increase the linear flow rate of analyte past the working electrode. This design change should improve response time and signal magnitude.

All of the bench-top experiments were performed at room temperature (approximately 22°C) and the potential of the NO_2 gold sensing electrode was maintained constant at +800 mV vs. SHE (-200 mV vs. Pt/air reference electrode) throughout the tests. The sample (analyte) flow was 100 cc/min through the sensor and, since the gas mixtures were prepared from laboratory air, most tests were performed at 30-60% RH. Only tests of the 49 ppm NO_2/air commercial mixture were dry ("approximately" 0% RH).

Results and Discussion

The Proposed Instrument

After discussion of the specifications of the "ideal" instrument, the hardware designs for the NO_2 instrument were prepared. A block diagram of the NO_2 unit is as shown in Figure 1. The components of the instrument were identified as:

1. Pump/sensor - module 1: This component is the center of the unit. It contains the sensor, pump, potentiostat circuit, pump motor control circuit, circuit to provide a stable power supply, temperature circuit, and all signal measurement circuits. There are also provisions for an alarm circuit and LED display for continuous readout, but these were not be included in the prototype instruments.
2. Data logger/controller - module 2: This component of the unit will contain the A/D channels for signal input and digital input/output channels for instrument control. The input channels will monitor the sensor output, temperature, battery voltages, sensor bias, and other pertinent parameters. The output channels will allow control of the pump motor circuit and analog switch for auto-gain set and auto-zero measurements. An evaluation of existing and possible data loggers relative to these specifications was completed as a part of this work.
3. Battery pack - module 3: This module contains the rechargeable Ni-Cad batteries used for pump power. To provide the voltage to operate the pump motor circuit as well as power the pump, a 7.2 V pack was originally specified. A 9V battery will be included in module 1 to keep the sensor on standby and ready for use even when the instrument was not deployed.

Sensor Development

TRI has obtained excellent response from catalyst films vapor deposited onto porous membranes. By controlling the nature of this film, the signal can be optimized. Commercially available high surface area (HSA) sensors and the TRI Nafion sensor were used as "performance standards" for evaluation of the "improved" responses from the TRI LSA sensors tested in this work.

Figure 2 compares the response of a commercial NO_2 sensor to that of the TRI Nafion sensor and the acid electrolyte low surface area working electrode sensor. The work outlined briefly below was focused on optimizing the sensor performance further, and characterizing its response and lifetime behavior.

Membrane Selection:

Choice of a membrane for the sensing electrode is critical and the membrane can have a profound effect upon analytical performance. For use in a personal monitor, it is necessary that the membrane be rugged and possess a very high resistance to water flow through the pores. A series of tests were performed to compare the properties of several porous membranes to determine the one most suited for the NO_2 monitor.

The membrane properties evaluated included tensile, or tear, strength, porosity, weeping pressure (the pressure required to force electrolyte through the membrane), and response characteristics. Several of the membranes tested provide suitable substrates. The Gortex (0.45 μm and 1.0 μm pore size), Celgard (0.02 and 0.04 μm) as well as the Zitex material (E606122 and E606-223) were tested in TRI sensor designs.

Catalyst Loading:

The magnitude of the signal from a given concentration of analyte gas is proportional to the catalyst loading on the membrane until the reaction in the sensor (at the working electrode) is no longer catalyst limited. The optimum loading for a sensor is the one that produces constant response and for which slight variations in catalyst activity (due to small changes in temperature or specific surface area) do not substantially affect the sensor signal.

A series of tests were performed to establish the relationship between catalyst

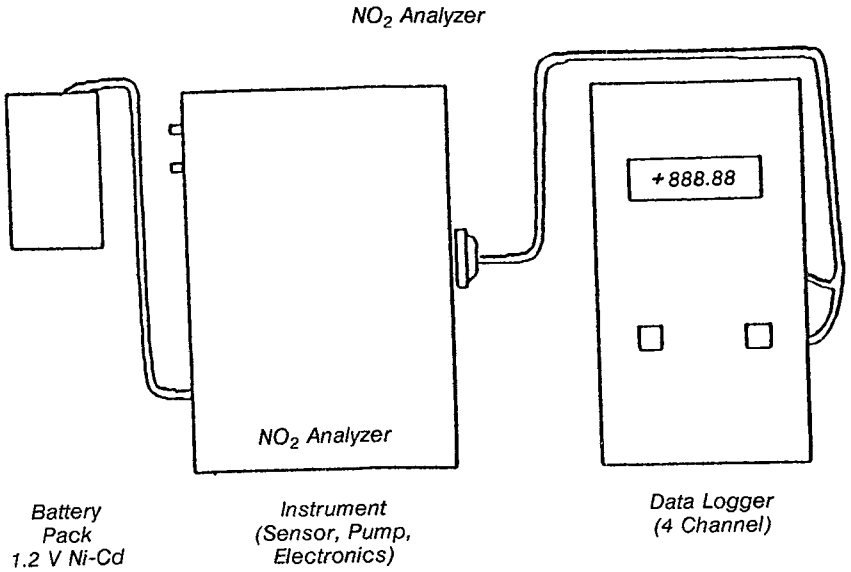

Figure 1. *NO_2 Instrument at the end of this phase of the project, showing the three modules and connectors.*

loading and sensor response to NO_2 for each of the potential membrane materials. These included the three different porous membrane materials and several catalyst loadings for each membrane: 600, 900, 1200, 2100, and 3000 Angstroms. The array of sensors constructed from the different electrode and membranes were evaluated for signal magnitude (μA/ppm), background current (ppm), noise level (ppb), and response time.

Based upon signal magnitude and physical properties, the G-1.0 membrane, was chosen as the most suitable membrane for the sensor. Initial tests of the precision and stability of sensors using this material were encouraging. Precision of the sensor response was typically within ± 5%, and baseline drift less than 20 μA,(> 100 ppb) over 4 hrs of testing at 1-5 ppm NO_2 levels. The data indicate that the performance of the sensor could be improved even further with a higher loading of electro-catalyst.

Attitude Sensitivity:

In order to use the sensor for a portable monitor, it is necessary to make it position and attitude insensitive. An hydrophilic polypropylene wick material was packed behind the sensing electrode membrane so that it extended down into the electrolyte. This wick insures continuous contact between the sensing electrode and the electrolyte; even if the sensor were turned upside down.

Characterization of TRI NO_2 Sensor

Based upon the data from the optimization study described above, several sensors were constructed for testing in the personal modular prototype monitors that were built. A series of tests were performed to characterize the response of the new TRI sensor described above. These tests included evaluation of the following characteristics:

Signal Magnitude:

The signal for NO_2 from the low surface area sensor is typically 0.2-0.5 μA/ppm. Signal noise is less than 5 nA, allowing the detection of about 5 ppb NO_2. The improvements realized in the signal to background ratio with the LSA sensor should allow the optimum monitoring for NO_2 at the lowest levels. However, the versatility of the monitor will allow use of many different sensors in the unit. The HSA sensors may provide a better response at extremely high levels of pollutant while the LSA sensors are optimized for performance at low NO_2 concentrations.

Response of Potential Interferents:

Several compounds may be present in significant concentrations in ambient air. Table 1 lists a number of compounds likely to be encountered during the use of the instrument. Of the compounds tested, only H_2S yielded a signal large enough to be of concern.

The use of a selective filter to remove the H_2S from the sample was studied. Initial tests of the filter at NO_2 levels of 1 ppm indicate little scrubbing NO_2 by the H_2S filter. This filter needs to be studied in detail at low concentrations of NO_2, to determine the effect on response time and calibration of the NO_2 personal monitor.

Effects of Flow Rate:

For a sensor operated in a flowing air stream, it is necessary to determine the effect of the rate of air flow upon the response of the sensor. The LSA sensor is independent of flow rate in the range 45-300 cc/min. Since the air flow in the instrument is set at 100 cc/min, any fluctuations in pump speed will not greatly

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James D. Mulik is the EPA Project Officer (see below).
The complete report, entitled "Construction and Testing of Electrochemical NO_2 PSDs," (Order No. PB 89-169 874/AS; Cost: $15.95, subject to change) will be available only from:
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