FINAL REPORT

to J&N Associates, Inc

from

Illinois Institute of Technology

Re: Department of Energy
Phase I STTR Project
DOE No. DE-FG02-99ER86090

**"ELECTROCHEMICAL SENSORS FOR VOLATILE
NITROGEN COMPOUNDS IN AIR"**

DOE Patent Clearance Granted

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CHAPTER 1 PROJECT SUMMARY

Task 1: Establishing Reliable Sources of HONO and Peroxyacetyl Nitrate

Nitrous acid vapor sources using solid oxalic acid and sodium nitrite were constructed according to literature descriptions, but these never performed as reported. Nitrous acid vapor concentrations produced were in the low ppb range, and some tests were performed. The exact concentration of nitrous acid was difficult to analyze by the colorimetric method available because of the very low concentrations.

Peroxyacetyl nitrate (PAN) was not made or used. Resources were directed to Tasks 2 and 3, which had to be accomplished before the PAN could be used at realistic atmospheric concentrations.

Task 2: Responses of Commercially Available Sensors to Nitrogen Compounds

Responses of a series of commercial Pt and Au electrode sensors to nitric oxide and nitrogen dioxide were measured. We also made preliminary measurements on an iridium electrode sensor intended for measurement of NO.

Task 3: Building Sensors With Alternative Catalysts

Sensors with sputtered gold electrodes were built in order to reduce the noise and hence to improve the lower detection limit of the sensors.

Task 4: Controlled-Potential Voltammetry of Nitrogen Compounds on Gas Sensors

This task was deferred at the request of our collaborators so that additional NO sensors could be fabricated and tested.

Task 5: Comparative Survey of All Sensors Tested in This Project

A sensor made from gold sputtered onto Zitex with platinum black counter electrodes seems to have performance equal to the best available commercial sensor, with respect to NO and NO₂. The TSI, Inc. Type 106 sensor has been used for low concentration measurements down to 3 ppb NO₂ in the past, but supply of this part is no longer assured in the future.

Task 6: Final Report

This document is the final report and sole deliverable for this project.

CHAPTER 2

APPROACH AND ORGANIZATION

The Department of Energy requires methods of measuring energy-related air pollutants, specifically gases and particulate materials. Among these are a number of nitrogen compounds, including nitrogen dioxide, nitric oxide, nitrous acid (HONO), and peroxyacetyl nitrate (PAN). Each of these compounds has distinct environmental behavior and toxic effects, but measuring the gases individually continues to be a difficult task. Measuring them in real time, accurately, and economically is even more difficult.

Amperometric gas sensors (AGS; also called electrochemical gas sensors and fuel cell sensors) have properties that make them attractive for long-term monitoring applications [Cao et al., 1992]. They are simple in structure, reliable and rugged in use, and modest in cost. They are stable in operation, resistant to contamination, and have long operating lifetimes. Power consumption is low -- in fact, because it is also a fuel cell, an AGS is actually an electric *generator*, oxidizing or reducing traces of electroactive gases to produce a measurable electric current. Furthermore, they have been proven in use: AGS have been used in gas measurement systems for oxygen, carbon monoxide, hydrogen sulfide, and other toxic gases for three decades. The sensitivity limit of a commercially available, unadorned AGS is in the low parts per million by volume (ppmv, or just PPM) for most gases. This has been sufficient to make these sensors irreplaceable in toxic gas alarms for personal and industrial use.

There are three major barriers to the wider use of AGS: cost, sensitivity, and selectivity. Many large markets would become available if either or both of these difficulties can be overcome. This proposal will address ways to improve the selectivity of AGS, in order to take advantage of some of the recent, spectacular improvements in sensitivity of sensors of this class. Selectivity is defined as the ability of a sensor to respond only to the gas or gases of interest. With few exceptions, gas sensors are not very selective. A typical carbon monoxide sensor will respond to vapors of alcohols, carbonyl compounds, ethers, epoxides, and many nitrogen and sulfur compounds. The sensor remains nevertheless useful because the hazardous levels of carbon monoxide are so much greater than those of most other toxic gases.

Selectivity (the ability to respond to only one gas) has been a continuing concern with the AGS. They are dependent on a catalytic electrode for operation, and only two electrode materials have proven satisfactory for most commercial sensors: platinum and gold. Gold-based sensors respond to ozone and to nitrogen and sulfur compounds (e.g., NO₂, NO, HONO, HNO₃, O₃, H₂S, SO₂, HCN); platinum-based sensors respond to all of those gases plus carbon-oxygen compounds (CO, formaldehyde, alcohols, etc.).

We have recognized for a long time that improving the sensitivity and selectivity of AGS would open up many new applications. Over the past ten years, we have made real advances in these areas. Most relevant here has been our work with atmospheric oxidants [Penrose et al., 1990a,b,c, 1994, 1995]. In brief, we have achieved reliable detection limits for environmental NO₂ of 0.010 PPM and eliminated interference from NO, ozone, and sulfur dioxide. The strategies we used to achieve this performance were:

- A proprietary form of the gold electrode (so-called low-surface area, or LSA-Au) with a signal/noise that is 100-fold better than alternate electrodes.
- Periodic correction to compensate for baseline drift (span drift is not a problem).
- Electrode operating conditions that eliminate interference from nitric oxide.

- Chemical filters that eliminate all or nearly all interference from ozone and acid gases (assumed to be nitrous acid, nitric acid and sulfur dioxide).

The LSA-Au sensor has become a product of TSI, Inc., which employs it in applications requiring sensitivity at the low-part per billion levels.

In this work, we addressed the issue of selectivity in three ways: (a) a thorough evaluation of the responses of existing sensors to a selection of nitrogen compounds (NO_2 and NO) over the maximum range of bias potentials and (b) the examination of unconventional electrode materials.

The work, as originally conceived, divided the effort on this project into six Tasks:

Task 1: Establishing Reliable Sources of HONO and Peroxyacetyl Nitrate

Task 2: Responses of Platinum and Gold Electrode Sensors to Nitrogen Compounds

Task 3: Building Sensors With Alternative Catalysts

Task 4: Controlled-Potential Voltammetry of Nitrogen Compounds on Gas Sensors

Task 5: Comparative Survey of All Sensors Built in This Project

Task 6: Final Report

CHAPTER 3

TASK 1: APPARATUS AND SOURCES OF TEST GASES

Sensors

Sensors were obtained from Sensor Tek, Inc. (Valparaiso, IN), TSI, Inc. (Shoreview, MN) and from International Technologies (Wismar, Germany). Because of a regular collaborative arrangement with J&N Associates, Sensor Tek parts were obtained for assembling sensors from membranes constructed in the laboratory. A disassembled set of sensor parts is shown in Figure 3-5.

The electrodes, however prepared, were packaged into the standard sensor housings. In this way, they could be tested in a familiar geometry without dramatic changes in the equipment available. The standard 30% sulfuric acid electrolyte was used to fill the sensors. Finished sensors were exposed to temperature soaking in an insulated chamber at 68°C to pre-empt leaks.

Sensor Manifolds

For testing, sensors were mounted in an apparatus that controlled the access of test gases to the sensitive membrane. It is necessary that the concentration, flow rate, and flow geometry of the test gases be rigidly controlled, in order to get reproducible results.

Because sensors of different shapes and dimensions were to be tested in this work, a manifold design was developed that could be adjusted to work with several types of sensors (Figure 3-1). It was made from stock ultra-high molecular weight polyethylene (UHMW-PE) bar stock 2 inches wide and 0.5" and 0.125" thick. The manifold consists of three plates held together by stainless steel bolts (Figure 3-1). The bottom plate contains ports for inflow and outflow of gas, and a pocket 1 cm diam x 5 mm deep which is directly under the sensor membrane. The guide plate serves only to prevent lateral movement of the sensor; the holes are slightly larger than the diameter of the sensor. Between the bottom plate and the guide plate is a thin gasket of polyethylene or clear silicone to seal the sensor against the bottom plate. The bottom plate, gasket, and guide plate are bolted together before the sensors are inserted.

The top plate serves to press the sensors against the bottom plate to form the gastight seal. There is one top plate for each sensor, to account for slight differences in dimensions of a sensor. Holes are drilled above each sensor to allow connection of the electrical leads. The same bolts that hold the bottom assembly together provide the pressure to hold the top plate against the sensor.

Potentiostats

A potentiostat circuit has two basic functions: (a) to apply a known and controlled potential to the working electrode, relative to the reference electrode, and (b) to measure the current flowing to or from the working electrode. The first function is performed by a simple control loop in which a voltage is applied to the third (counter) electrode which is just sufficient to bring the working-reference potential to the expected value. A simple potentiostat is shown in Figure 3-2.

Potentiostats were constructed using circuit boards designed for the TSI, Inc. (Shoreview, MN) sensor or assembled from circuit boards from Custom Sensor Solutions, Inc. (Naperville, IL). Power was provided by a wall transformer.

Figure 3-1. The gas manifold used in this project, shown in front of a rack of potentiostats.

Figure 3-2. A simple potentiostat.

Potentiostat
P/N 1501
or 1501Kit

The potentiostats were calibrated according to the method recommended by the manufacturer. The voltage signal from the potentiostat was converted to current output with a simple conversion factor; for example, if calibrated at $10 \mu\text{A/V}$, the current in amperes could be obtained by multiplying the signal by 10^{-5} .

Gas Concentration Control

Test gases were supplied from 4 L and 40 L 2 mil Tedlar sample bags (Bag Man, Palatine, IL) connected to the inlet of a dynamically controlled diluter (Model 1010P, Custom Sensor Solutions, Inc., Naperville, IL). Concentrations from 0% to 100% of the inlet value could be generated either by front panel selection or by a computer-controlled analog output.

Test Gas Sources

Zero grade air, zero grade nitrogen, and nitrogen dioxide in air (1000 ppm) were obtained from Praxair, Inc. (Hillside, IL). Nitric oxide in nitrogen (1000 ppm) was obtained from Scott Air Products, Inc. (Pittsburgh, PA). We have observed earlier that nitric oxide was slowly oxidized in the sample bag even in a nitrogen atmosphere. Therefore, nitric oxide was preprocessed immediately before use by passage through a triethanolamine filter [Lodge, 1989]; this frequently removed up to 40% of the signal, which was apparently due to formed NO_2 . Further evidence of contamination by NO_2 was the reduction signal seen at bias settings below 0 mV; this signal is absent for pure NO.

Nitrous acid vapor was made using a generator described by Braman et al. [1986]. In our hands, a generator made by this method produced very low concentrations of nitrous acid vapor. Nitrous acid was absorbed and measured according to the diazonium coupling method described in Lodge [1989].

Data Acquisition and Experimental Control

Potentiostat output signals were connected through shielded cables to the breakout box of a multipurpose data acquisition card installed in a Windows 98 computer. All data acquisition equipment was supplied by National Instruments Corporation. The card used had two analog output channels, of which one was used to control the dynamically controlled diluter.

A program written in the LabVIEW graphical programming language (National Instruments Corp.) was used to acquire data as well as control the gas concentration. A LabVIEW program (VoltammetryA.vi) was written which was used for all experiments. The program used a text file generated in Microsoft Excel to control the gas concentration supplied to the sensors. In each run, the sensor outputs were recorded in a text file which could be imported into Excel for processing, plotting, and archiving. The output file also included an echo of the concentration control data contained in the input file.

The entire experimental apparatus is shown in Figure 3-1.

A typical view of the LabVIEW program is shown in Figure 3-3. The LabVIEW program itself is shown in Figure 3-4.

The screenshot displays the Voltammetry-A.vi LabVIEW interface. The top menu bar includes File, Edit, Operate, Project, Windows, and Help. The toolbar contains icons for file operations and execution. The main display area features a 'LOGGED DATA' plot with a grid. The plot shows four data series, each with a step-like transition. The y-axis ranges from -2.000 to 0.000. The x-axis is labeled with '00:12:40 AM' and '00:14:21 AM'. On the left, there are control panels for 'Time Incr' (set to 1560.00), 'Current Control Value' (set to 1.30), 'Start/Stop Legend' (a dropdown menu), 'Channels to Log' (set to 0, 1, 2, 3), 'Time Between Points' (set to 1), and 'Control Path File' (set to 'H0.50% b4'). Below the plot, there are controls for 'File Header Text' (a text box) and 'Digits of Precision' (a numeric control set to 4). The status bar at the bottom shows the file path 'C:\WINDOWS\Desktop\veewmon\Nathan\bog-hole\5.2.WO-2000.A\...'.

The screenshot shows a LabVIEW block diagram titled "Vollammetry-A.vi Diagram". The diagram is organized into several functional areas:

- File Handling:** Includes a "Prompt for control file" control, an "Open File.vi" block, and a "Save File.vi" block. A "File Header" string is also present.
- Data Processing:** Features a "Read File (control.vi)" block that reads data from a file. The data is then processed by a "Split Control String" block, which outputs a "Control Value" and a "Time" value. The "Control Value" is further processed by a "Match Pattern" block and a "Current Control Value (99.1)" block. The "Time" value is processed by a "Time in sec" block and a "Time in min" block.
- Data Storage:** Includes a "Write to Spreadsheet String" block and a "Save time to data string" block. The "Write to Spreadsheet String" block outputs a "String to Spreadsheet String" value, which is then processed by a "Join time to data string" block.
- Control and Timing:** Features a "Rate of Data Collection" control, a "No of samples" control, and a "Delay" block. A "Rate of Data Collection" control is also present at the bottom of the diagram.
- Output:** The final output is a "LOGGED DATA" string, which is displayed in a text box.

Sputtered Electrode Materials

Gold sputtered electrode materials were made at the Microfabrication Applications Laboratory of the University of Illinois at Chicago (MAL/UIC). A subscription was purchased to join the user group of the MAL/UIC. This gave access to the facility for a four month period.

To assemble the sensors for testing, we made use of a platform designed for carbon monoxide sensors. This consisted of a sensor case made of a nonconducting polypropylene and a carbon-filled conductive polypropylene (Figure 3-5). The conductive PP was used to apply potentials and carry signal current to and from the electrodes. The conductive PP Metal masks were made by a machine shop to provide for sensor electrodes in specific geometric configurations. The shape of the electrodes is shown in Figure 3-5. In some cases, all three electrodes were open to gold sputtering; in most cases, only the working electrode was formed by sputtering and the counter and reference electrodes formed by filtration of a platinum black-PTFE mixture.

The platinum black -PTFE mixture was made and filtered onto Zitex disks by a proprietary process which predates this work. Each of these electrodes contained about 10 mg of a selected Pt black fuel cell catalyst. With these electrodes in place, the Zitex disk was clamped in place under the metal mask and inserted in the vacuum chamber of the vacuum sputtering apparatus.

The initial vacuum was 5×10^{-7} Torr. The masks were rotated on a planetary holder at 25rpm. The electron beam operated at 10.13KV and 60mA. The coating rate under these conditions was 0.7 Å per second. Electrodes were made of thickness 2000, 5000, and 7000 Angstroms. The resulting surface resistivity was close to 1.1Ω for all materials.

These coatings were inspected under a microscope. They were not uniform, showing clumps and fine lines connecting the clumps.

Figure 3-5. Sensor parts set showing electrode assembly.

CHAPTER 4

TASK 2: RESPONSES OF AVAILABLE SENSORS TO NITROGEN COMPOUNDS

Two types of commercially-available sensors are available to us. One is the series of sensors produced by TSI, Inc. (Shoreview, MN). The other is a sensor made by Sensor Tek, Inc. (Valparaiso, IN).

The TSI sensors come in three types. Type 102 (CO Sensor) has a working electrode of platinum black and responds to carbon monoxide, ethanol, and most permanent electroactive inorganic gases. Type 104 (H₂S Sensor) has a working electrode of powdered gold and responds to most electroactive inorganic gases, such as nitrogen dioxide, nitric oxide, and hydrogen sulfide. Type 106 (NO₂ Sensor) has a vapor-deposited gold electrode. It responds to the same range of gases as Type 104, but has a much better detection limit due to the lower noise of the working electrode.

A set of Type 106 sensors was installed in the test manifold and allowed to come to equilibrium. The bias potential was adjusted over the range -250 mV to +225 mV. At each bias setting, the baseline current was measured, then the sensors were exposed to 10 minute pulses of 10 ppm nitric oxide or nitrogen dioxide. The plot of sensitivity ($\mu\text{A/ppm}$, signal in microamps per part per million) vs. bias potential is shown in Figure 4-1. All four sensors respond similarly to the NO₂ exposure. Optimum sensitivity of the TSI NO₂ sensor occurred at an applied bias potential of -180 to -200 mV.

Once sensitivity was determined at each bias level, the noise in the signal was determined as the standard deviation of 20 time points of the equilibrium signal. The sensitivity was used to convert the noise (in volts) to equivalents of ppm gas (Figure 4-2). Three times this value would represent the conventional Lower Detection Limit. At -200 mV, the noise was 0.007 to 0.014 ppm NO₂.

Interestingly, at the bias potential recommended by the manufacturer of the sensor, -100 mV, the sensitivity was only half as high, 0.025 to 0.062 $\mu\text{A/ppm}$, as at the maximum sensitivity. The LDL was dramatically worse, however, to three times the noise level of 0.1 to 0.8 ppm, or 0.3 to 2.4 ppm.

A unique Nitric Oxide sensor using a sputtered iridium electrode (International Technology) was tested in our laboratory. Its sensitivity was limited, but testing was not completed because each of the three sensors supplied to us became noisy upon testing. Disassembly revealed advanced corrosion inside the cell. The only data we were able to recover showed a relatively low sensitivity of 0.031 $\mu\text{A/ppm}$ and a noise level of 0.84 ppm (LDL 2.5 ppm).

Figure 4-1. Sensitivity of TSI sensors to nitrogen dioxide as a function of bias potential.

Figure 4-2. Noise of TSI sensor expressed as ppm of nitrogen dioxide.

CHAPTER 5

TASK 3: SENSORS WITH ALTERNATIVE CATALYSTS

Most of the work done in this Chapter used the gold-sputtered electrodes (Chapter 2), because these were known from previous work to have high sensitivity for both oxidizing gases such as ozone and nitrogen dioxide, and reducing gases such as hydrogen sulfide. These could be made to deliver lower detection limits under 3 ppb for all three gases.

Sensors with three gold electrodes operated poorly, most likely because the gold/sulfuric acid reference electrode could not be depended on to operate with a stable potential over long time periods. The second type of sensor, where the gold working electrode was deposited with the conventional platinum black counter and reference electrodes, gave very encouraging results.

The sensors were tested in the same fashion as in Chapter 4. The sensitivity of the sensors to nitric oxide is shown in Figure 5-1. The sensitivity was used to calculate the noise level of the sensors, expressed in concentration units (Figure 5-2). Optimum sensitivity to NO was achieved at a bias potential of +200 mV to +400 mV (0.017 to 0.040 $\mu\text{A/ppm}$). The LDL was three times 0.02 to 0.05 ppm, or 0.06 to 0.15 ppm. This is an extremely good LDL for NO, which is typically difficult to detect by this or any other means.

The sensitivity to NO₂ was lower than the TSI sensors, about 0.02 to 0.035 $\mu\text{A/ppm}$ at the optimum bias of -100 mV bias (Figure 5-3). On the other hand, the noise level was dramatically better than the TSI units, 0.001 to 0.005, yielding an LDL for NO₂ of 0.003 to 0.015 ppm (Figure 5-4).

Figure 5-1. Sensitivity of the SG sensors to nitric oxide.

Figure 5-2. Noise level of the SG sensors expressed as ppm of nitric oxide.

Figure 5-3. Sensitivity of the SG sensors to nitrogen dioxide.

Figure 5-4. Noise level of the SG sensors expressed as ppm of nitrogen dioxide.

CHAPTER 6
TASK 4: VOLTAMMETRY OF NITROGEN COMPOUNDS ON GAS SENSORS

This task was deferred due to the inability to get sputtered electrodes early in the project. Also we evaluated iridium-catalyzed sensors for NO and NO₂, which was not in the original plan.

CHAPTER 7
TASK 5: COMPARISON OF ALL SENSORS

The summary of all sensor data is shown in Table 7-1.

Table 7-1. Summary data on experiments done in this proposal.

Sensor & Mfr	Serial No.	Gas	Optimum Bias (mV)	Sensitivity (μA/ppm)	LDL (ppm) (3X noise)
TSI	1	NO ₂	-200	-0.050	0.041
	2			-0.133	0.020
	3			-0.096	0.021
	4			-0.133	0.011
Int. Technol.	1	NO	+300	0.031	2.5
Lab *sputtered Au	D2	NO ₂	-100	-0.020	0.0050
	D3			-0.035	0.0075
	D5			-0.022	0.0021
	D6			-0.022	0.0025
Lab *sputtered Au	D2	NO	+200	0.040	0.030
	D3			0.031	0.020
	D5			0.022	0.08
	D6			0.017	0.06

CHAPTER 8

TASK 6: FINAL REPORT

This document is the final report.

CHAPTER 9

CONCLUSIONS

Nitrogen oxides were detected at low concentrations using porous-electrode amperometric gas sensors. The best sensors tested were those made with sputtered gold (SG) electrodes. The sensitivities demonstrated are sufficient to detect both nitric oxide and nitrogen dioxide at environmentally-significant concentrations. These sensors show promise for immediate commercial implementation.

Based on these data, the same sensors could be used for many other gases, including HCN, H₂S, HONO, and peroxyacetyl nitrate. We recommend measurement of SG sensor responses to these gases in the future.

Carbon monoxide signals were also obtained on the SG sensors. Although the sensors respond to CO, the signals are low, implying a strong selectivity for nitrogen gases.

The nitrous acid (HONO) source as reported in the literature [Braman et al., 1986] could not be reconstructed in our laboratory. Trace amounts of oxidizing gases were produced. Nitrous acid has been reported to have 10 X the response of nitrogen dioxide [Spicer et al., 1991, 1994], but we were unable to confirm this result.

Future investigations should include:

- repeatability of the SG electrodes
- the effect on sensitivity of increasing electrode size
- the cost and fabrication implications of the SG electrode

CHAPTER 10

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