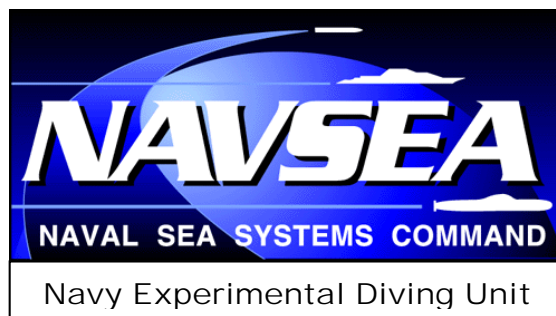


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DEVELOPMENT AND EVALUATION OF A HYPERBARIC TOXIC GAS MONITOR (SUBTOX) FOR DISABLED SUBMARINES



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14. ABSTRACT: Current procedures for monitoring toxic gases on disabled submarines (DISSUBs) rely on chemical detector tubes to determine when submarine escape action levels (SEALs) of such gases are reached, so that specific steps can be taken to protect the survivors. However, detector tubes are known to have limited storage times; to degrade quickly under adverse storage conditions such as high temperatures; and to be inaccurate, costly, time consuming, and cumbersome to use. In addition, pressures aboard a DISSUB may become elevated and produce currently unknown effects on detector tube performance. Over an eight-year period (2004–2012), Navy Experimental Diving Unit (NEDU) helped ENMET Corp. to develop the first hyperbaric toxic gas analyzer (SubTox) to monitor, under pressure, the eight gases — ammonia, carbon monoxide, chlorine, hydrogen chloride, hydrogen cyanide, hydrogen sulfide, nitrogen dioxide, and sulfur dioxide — for which SEALs have been defined. With results from laboratory and field testing, and with positive feedback from many Fleet personnel — including an endorsement by U.S. Navy Board of Inspection and Survey (for submarines; INSURV) and overwhelming enthusiasm among submariners who have seen SubTox during NEDU field testing, NEDU and Naval Sea Systems Command (NAVSEA) agree that SubTox is ready for a proposed 18-month transition plan that NEDU and ENMET have developed. This plan, if successful, would result in the Fleet procuring a limited number of first-production SubTox monitors. NEDU believes that SubTox, by replacing the detector tubes now used, should improve the Navy's ability to monitor DISSUB atmospheres. To date, however, Navy support has not yet been obtained for the proposed transition plan.					
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INTRODUCTION

So that specific steps can be taken to protect survivors, current procedures for monitoring toxic gases on disabled submarines (DISSUBs) rely on chemical detector tubes to determine when submarine escape action levels (SEALs) are reached. However, detector tubes are known to be inaccurate: Even the *Nuclear Powered Submarine Atmosphere Control Manual* states that these tubes provide only “a qualitative measurement of atmospheric limits.”¹ Furthermore, such tubes are costly, cumbersome, and time consuming to use, and — since they degrade quickly under adverse storage conditions such as high temperature — their storage times are limited. In addition, onboard DISSUB pressures may become elevated and produce unknown effects on detector tube performance: Although a few toxic gas analyzers have been evaluated for possible submarine use,^{2,3} no tests have been performed under pressure. A later section (**DETECTOR TUBE COMMENTS**) of this report provides additional, and somewhat surprising, information about detector tubes that we have learned during this project.

In view of the reliability problems with using detector tubes, the U.S. Navy’s Submarine Escape and Rescue Review Group (SERRG), the Chief of Naval Operations (CNO), and the Deep Submergence Unit (DSU; responsible for providing DISSUB rescue capability) at Submarine Development Squadron 5 have formally recognized the need for improved monitoring of DISSUB contaminants as a Navy priority requirement in the following references:

1. CNO letter 9594 Ser N873/9U657072 of 15 July 99. Includes atmospheric monitoring for O₂, CO₂, and toxic gases during a DISSUB in the Integrated Priority List.
2. CNO 3900 Ser 912D3/9U544572 of 23 Nov 99. Includes guidance on contaminant exposure in a DISSUB atmosphere as a desired deliverable.
3. COMSUBDEVRON FIVE 9594 Ser 00-007/126 of 21 Feb 2003. SERRG Consolidated Requirements. Endorses a requirement to provide a senior survivor with monitors to accurately sample DISSUB atmospheres under pressurized conditions.

Furthermore, in 2002 the Committee on Toxicology, National Research Council (NRC), National Academy of Sciences, acknowledged the shortcomings of detector tubes during its review of proposed U.S. Navy SEALs by *recommending that the Navy give high priority* to developing battery-operated instruments as an increasingly accurate way to measure DISSUB contaminants.⁴ This followed a similar, though less forceful, 1988 NRC recommendation during its review of submarine air quality.⁵

OBJECTIVE

The objective of this work was to develop procedures using portable analyzers to monitor, under pressure, the eight DISSUB gases for which SEALs have been defined: ammonia (NH₃), carbon monoxide (CO), chlorine (Cl₂), hydrogen chloride (HCl), hydrogen cyanide (HCN), hydrogen sulfide (H₂S), nitrogen dioxide (NO₂), and sulfur dioxide (SO₂). These procedures would replace the currently used detector tubes.

We believe that delivering a hyperbaric toxic gas analyzer to the Navy would be *an important breakthrough* for ensuring chemically safe atmospheres on DISSUBs. Such a gas monitor would be useful for both the weekly atmospheric monitoring now required on all U.S. Navy submarines under normal (nondistress) conditions¹ and ensuring safe gas supplies and atmospheres in other Navy applications such as diving facilities, treatment chambers, and the closed living spaces on other Fleet vessels.

This work thus responds directly to the National Academy of Sciences recommendation that the Navy give high priority to developing improved procedures to measure DISSUB contaminants.

SUMMARY OF PROJECT

Over an eight-year period (2004–2012), Navy Experimental Diving Unit (NEDU) helped ENMET Corp. to develop SubTox — the first hyperbaric toxic gas analyzer designed to monitor, under pressure, the eight DISSUB gases for which SEALs have been defined. SubTox, which was designed specially for the U.S. Navy, also monitors the concentration of hydrogen (H₂) gas and displays other variables including ambient pressure. To the best of our knowledge, SubTox contains the first toxic gas sensors modified to work more reliably at pressure than conventional sensors work. Through an iterative process of repeated laboratory testing followed by manufacturer modifications in response to NEDU test results, SubTox has been refined over a multiyear period to better meet requirements for monitoring DISSUB atmospheric contaminants. This report describes the development and evaluation of the SubTox monitor, with the final goal of delivering a reliable DISSUB toxic gas monitor to the Navy.

APPROACH

The tremendous advances in portable instruments and sensors for analyzing gases during the past 20 years have made using portable analyzers to reliably monitor contaminants in submarine atmospheres a real possibility. Initially we expected that existing technologies could be adapted for monitoring at least some of the eight DISSUB gases for which SEALs have been defined, although we were unaware of any

commercial, off-the-shelf (COTS) toxic gas monitors that were advertised to work at pressure. The approach we planned to use — that of reviewing COTS instruments, followed by in-house testing and collaborating with the manufacturer to improve performance where possible — has proven successful in previous projects that we have delivered: for example, a working hyperbaric CO₂ analyzer for Fleet DDS operations in less than three years (an analyzer that was subsequently upgraded to include O₂ monitoring capability⁶), and a real-time, online air quality monitor to ensure safe diving air, a monitor now under consideration for transition to Navy divers.^{7,8}

REPORTING OF THE RESULTS

During the more than seven years of developing and evaluating the SubTox monitor, we conducted countless hours of laboratory testing. Much of the data and discussion in this report is based on the many data summaries provided to, and E-mail discussions with, ENMET over the life of this project, as well as on many PowerPoint presentations and text documents prepared by NEDU and the U.S. Navy Board of Inspection and Survey (INSURV) in support of SubTox for submarines. Rather than presenting all the data we collected during these years (a daunting task that would result in an excessively long document), this report presents a limited amount of data that we believe suffices to document our effort to deliver a reliable DISSUB toxic gas monitor to the Navy.

MONITOR REQUIREMENTS

The first steps of this project were to (1) draft an initial version of the operational requirements for any toxic gas analyzer to be used on a DISSUB, (2) circulate these requirements to the DISSUB community for review and comment, (3) modify the requirements to incorporate Navy input, and (4) adopt the modified version for this project. The adopted monitor requirements are listed below as either “essential” or “desired but not essential.” However, since the feasibility of some of the essential requirements for any prototype monitor was difficult to predict in advance of testing, we anticipated that our early testing of prototype monitors might suggest which requirements could be easily met, which could possibly be met only with some effort, and which could not easily be met. The comments included below in the **Essential requirements** and **Desired but not essential requirements** subsections indicate our initial levels of expectation for meeting a particular requirement — or some of the rationales for these requirements.

Summary of monitor requirements

The desired analyzers were to be portable instruments for measuring one or more of the following eight SEAL gases of concern: NH₃, CO, Cl₂, HCl, HCN, H₂S, NO₂, and SO₂. In general, analyzers were to be rugged, reliable, user friendly, and field compatible. The

important criteria for analyzers in operation included the capabilities of (1) performing under hyperbaric conditions; (2) compensating, if necessary, for changes in ambient temperature; and (3) minimizing, where possible, sensor cross sensitivity to other gases — particularly the cross sensitivities among those eight SEAL gases. We expected that any existing COTS analyzers thought to be potential candidate monitors would probably need to be modified to satisfactorily meet these three requirements.

Essential requirements

1. Eight SEAL gases measured, measurement ranges, and units (where ppm = parts per million):

NH₃: 0 to 250 ppm
CO: 0 to 300 ppm
Cl₂: 0 to 5 ppm
HCl: 0 to 70 ppm
HCN: 0 to 30 ppm
H₂S: 0 to 60 ppm
NO₂: 0 to 20 ppm
SO₂: 0 to 60 ppm

All eight gases in balance air are displayed simultaneously in ppm with one or more monitors.

These concentration ranges are based on the NRC's proposed 2002 SEAL levels⁴, which are defined at two exposure levels (SEAL 1 and SEAL 2) for each gas and relate to 10-day and 24-hour exposures, respectively. To accommodate possible future changes in these SEAL ranges, our requirements defined the upper measurement limits of all eight gases to be twice those of the NRC SEAL 2 values. More about the SEALs and their influence on our selection of test gases is discussed in the **GENERAL TESTING METHODS** section.

2. Display resolution (minimal): 5 ppm for NH₃ and CO; 1 ppm for each of the other six gases.

3. Minimal number of units: To minimize the total number of analyzers, maximize the number of sensors within a given instrument.

4. Operating and storage conditions:

Pressure: 0.8 to 5 atmospheres absolute (ATA)
Temperature: 4 to 50 °C
Relative humidity (RH): dry to 99% (noncondensing)

The pressure requirement represents the deepest submarine rescue depth for which the U.S. Navy had planned at the time the requirements were defined. The temperature

requirement is expected to bracket the range of ambient air temperatures within most, if not all, DISSUBs. However, our experience suggests that, in compensating for changes in ambient temperatures, portable gas analyzers commonly have problems. Thus, when used at ambient temperature extremes, they may be less accurate than they otherwise are. The relative humidity requirement is based on the need for water resistance, as discussed in item #6 below.

5. Gas sampling pump: If this device is needed, a brushless pump is required — to eliminate explosion risks at pressure.

6. Water resistance: Since analyzers could be exposed to high humidity (and may have some water contact, including being dropped into the water) during use, they need some water resistance capability.

7. Portability: To monitor the atmosphere, users need to be able to easily carry analyzers throughout the spaces of a submarine.

8. Electrical power: Powered by nonrechargeable batteries, analyzers are to be capable of operating for seven days at 20% duty cycle, or three days of continuous operation.

9. Alarms: Visual and audible, with selectable limits.

To alert the operator to a possible problem, a visual alarm needs to be easily discernible at close range. An audio alarm was initially also desired, but such an alarm was determined to be difficult, if not impossible, for users to reliably hear in a submarine's noisy environment.

10. Backlighting for the analyzer's display: This requirement was made to allow displayed readings to be discerned in low-light areas.

11. Simplicity of operation: The analyzer was to be a stand-alone unit (i.e., one that does not require a computer or other type of controller) that Navy submarine personnel could operate. The only exception to this requirement was that, during NEDU testing, any data logging capability was presumed to require a computer for downloading data.

12. Ruggedness: The analyzer was to be stable electronically and mechanically under field conditions expected on a submarine during both routine and accident conditions.

Desired but not essential requirements

1. Calibration: This procedure was to be performed at the factory and possibly also at Navy facilities.

Although challenge testing using gas standards in the field may be useful for confirming monitor stability between calibrations, field calibration is not expected to be possible.

2. Precision (defined as repeatability of short-term [≤ 10 -minute] gas readings): This requirement was determined by individually sampling each of the eight gases at 1 ATA in the laboratory at their SEAL2 concentrations: $\pm 5\%$ relative to each of the gases.

A well-designed analyzer was expected to meet these levels of precision.

3. Accuracy (within 90 days of calibration) over pressure and temperature ranges: This requirement was determined in the laboratory by individually sampling each of the eight gases at their SEAL2 concentrations: $\pm 30\%$ relative to each of the gases.

Until laboratory testing was done, whether this level of accuracy could be achieved and what degrees of mathematical compensation for pressure and temperature readings might be needed and possible were unknown. However, even if we assume that some increase in error occurs in the field, this $\pm 30\%$ level of accuracy — particularly at pressure — represents a significant improvement in DISSUB toxic gas monitoring from that currently provided by detector tubes.

4. Chemical interferences: Each gas sensor's cross sensitivity to the other seven gases at their SEAL2 concentrations — as well as H_2 up to 1%, CO_2 up to 6%, and volatile organic compounds (VOCs) at expected levels in the submarine atmosphere — was minimized.

Cross sensitivity to other gases is a major weakness of many chemical sensors, and therefore laboratory testing was to determine how well this requirement could be met.

5. Sensor life: longer than one year for all sensors.

6. Response time: < 60 seconds to reach 90% of each sensor's reading.

This response time should be more than adequate — even during casualties such as a fire or flooding, when gas concentrations in a submarine's atmosphere might be expected to change rapidly.

7. Weight: ≤ 10 lb.

Some flexibility exists with the weight requirement — although the lighter the monitor, the better.

8. Maximum dimensions: 30 cm x 30 cm x 30 cm (1 ft x 1 ft x 1 ft).

Although a large, bulky monitor is undesirable (regardless of the number of constituents it can measure), some flexibility exists for this requirement.

IDENTIFICATION OF CANDIDATE MONITORS

To help us initially identify potentially useful instruments for our hyperbaric application, we reviewed and discussed with the Naval Research Laboratory its testing of nonhyperbaric gas monitors for submarine atmospheres.^{2,3} We also completed a market survey and put a “sources-sought notice” on the Federal Business Opportunities (Fed Bus Ops) Web site to solicit manufacturers of gas analyzers to respond to our requirements. This solicitation generated responses from many vendors, with whom we discussed in detail our requirements and their abilities to meet them. As we expected, no COTS toxic gas analyzers designed for use or tested at pressure were found. However, from our contacts, market survey, and solicitation on the Fed Bus Ops site, we identified six vendors with possible interests in participating in this project with us.

From these six, we selected for preliminary testing several COTS monitors that we thought might be potentially useful for the DISSUB application. However, this limited testing revealed that none of these toxic gas monitors operated reliably at pressure, a finding that suggested that we probably needed to collaborate with one or more manufacturers to try to develop an analyzer that might be useful for the DISSUB scenario. So in 2004 we invited two interested manufacturers (ENMET Corp., Ann Arbor, MI, with its commercially available “Target” toxic gas monitor; and one other company) to assist us in developing a toxic gas monitor for use under hyperbaric conditions. After having spent considerable time and achieving only unsuccessful results from attempts to solve some of the performance problems we found during testing with the second manufacturer’s monitor, however, that second participating manufacturer withdrew from the project in 2006. We therefore continued to collaborate with ENMET, the remaining manufacturer.

GENERAL TESTING METHODS

INTRODUCTION

The laboratory testing procedures presented in this section were used throughout this project. Details about additional laboratory testing, where such details are needed, are provided later in this report within the **METHODS** sections of each of the three individual instruments tested. Procedures used during field testing are presented separately in the **FIELD TESTING OF SUBTOX** section.

It is also important to emphasize that all pressure testing was done at NEDU: At the time this work was done, ENMET had no hyperbaric testing capability or experience. Consequently, this project employed an iterative modification and testing process, with ENMET making software and hardware changes guided by results from NEDU’s laboratory testing.

SUMMARY OF TESTING

During this project we tested three different ENMET instruments: initially, the Target; then a testing platform that we refer to as a “Sensor Test System;” and finally the SubTox. All three instruments were tested both on the laboratory bench at 1 ATA and inside a hyperbaric chamber at pressures ≤ 5 ATA. The following summarizes the testing of these three instruments:

1. Target. We used the Target first to evaluate this monitor, with its commercially available toxic gas sensors, for possible use under hyperbaric conditions. We then worked with ENMET and its suppliers to develop new sensors that operated more reliably at pressure. However, we realized from the start that, for reasons to be discussed in the **TESTING OF SENSOR TEST SYSTEM** section further down in this report, the Target would be inappropriate for monitoring the DISSUB atmosphere.
2. Sensor Test System. Once we had sensors that worked reliably at pressure, ENMET built one Sensor Test System, as a precursor to any future prototype DISSUB analyzer, for NEDU. This System allowed us to test up to eight gas sensors together, a procedure which sped up the overall testing process and facilitated our examination of performance questions that were important to understand before the initial prototype monitor was built.
3. SubTox. As our testing of the Sensor Test System was proceeding in 2007, ENMET began to design and build a prototype DISSUB toxic gas monitor (named “SubTox,” per NEDU’s decision) based on Navy requirements and the configuration for the antecedent Sensor Test System. Once NEDU had received the first SubTox prototypes, we began an iterative process of repeated testing followed by modifications that such testing found to be necessary.

SEALS AND SELECTION OF TEST GASES

We chose to use SEAL1 and SEAL2 concentrations of gases for much of our testing, since data on SubTox’s accuracy at these concentrations would be most useful in evaluating it for DISSUB scenarios. However, after having completed the Target testing based on the NRC’s 2002 recommended SEAL values,⁴ we changed our subsequent testing of CO test gas concentrations from 125 and 150 ppm (NRC’s values for SEAL1 and SEAL2, respectively) to those lower values of 75 and 85 ppm that the Navy had initially proposed in 1998.⁹ We made this change in CO concentrations because, by the time the Target testing had been completed, the Navy medical community had begun to reconsider which SEAL levels were most appropriate for CO. Since the eventual SEALs to be adopted by the Navy for CO were uncertain, we chose to test at the lower CO concentrations. Although testing the gas monitoring at these levels would potentially be technically more difficult than that done at higher concentrations, our results from testing at these lower concentrations should be relevant to any recommendation to be made about SubTox — regardless of what SEAL values for CO were eventually adopted.

The NRC SEALs, except for those for H₂S, were eventually adopted in place of the Navy's originally proposed SEALs in the 2003–2004 SSN 688, SSN 21, and SSN 774 Class *Guard Books*,¹⁰ the U.S. Navy DISSUB survival guide. Although H₂S was not listed in the 2003–2004 *Guard Books*, we left H₂S in our monitoring requirement on the basis of the NRC's original recommendation. To the best of our knowledge, the SEALs listed in the revised 2011 *Guard Books*, pending publication,¹¹ remain identical to those in the 2003–2004 books.

In summary, Table 1 presents the SEAL values on which SubTox testing was based, values used to define the SEAL1 and SEAL2 gas concentrations to test the Sensor Test System and the SubTox. However, we emphasize that the gas sensors used in the SubTox should allow an increase in the measurement ranges of any of the SEAL gases — if such increases become desirable.

TESTING

Other than inside a hyperbaric chamber, all three ENMET instruments we tested were stored, calibrated, and tested on the bench at laboratory temperatures between 22 and 26 °C. During periods when instruments were not being tested, the analyzers were turned off and stored on the bench — with the Targets connected to their battery chargers, and the battery used to run the sample pump of the Sensor Test System also connected to its battery charger. SubTox monitors, with their six replaceable D-size alkaline batteries, did not use battery chargers.

At the beginning of each test day, battery chargers were disconnected from the instrument batteries. As described in the **TESTING OF SENSOR TEST SYSTEM** section, however, for that System a standard Target battery charger was connected at the start of each test day to power its circuit board and liquid crystal display (LCD). Instruments were then turned on and allowed to warm up for at least 20 minutes before testing began, a period conservatively chosen to ensure instrument stabilization for our testing, since a review of test data suggested that all the instruments were stable after this period. However, in defining a minimum required warm-up period, we did not conduct any testing to evaluate stabilization time following initial startups for any of the three ENMET instruments.

The status of the Target and SubTox batteries was recorded at the beginning of each test day, as well as at other times throughout the day. We replaced the SubTox batteries, which normally lasted for at least a week of daily testing, when such replacement was needed (i.e., when the battery reading was <20%). At the beginning of and at frequent intervals throughout each test day, ambient temperatures were recorded with a digital thermometer (model Thermapen 5, Electronic Temperature Instruments; West Sussex, UK) within one foot of the analyzers while they were on the laboratory bench. Barometric pressures in the laboratory were recorded with a digital barometer (model AG400, Honeywell Sensotec Sensors; Columbus, OH) that the manufacturer had calibrated within the year.

High purity air and primary standards of the eight SEAL gases at the SEAL1 and SEAL2 concentration levels (balance air) were used for testing; all gases were obtained commercially, with primary standards certified to $\pm 1\%$ relative or better. In addition, primary standards of H_2 , CO_2 , and isobutylene (all of which were also certified to $\pm 1\%$ relative or better, and all balance air) were used for testing cross-sensitivity responses of the toxic gas sensors.

All instruments were tested in two laboratory locations: on the laboratory bench at ambient pressure, and inside a temperature-controlled hyperbaric chamber at pressures up to 5 ATA. Rated well beyond the maximum test pressure, the chamber was equipped with separate air supply and decompression circuits so that it could be compressed with air or decompressed at precise rates. The travel rate for testing in this study was 0.03 ATA/sec (1 foot of seawater [fsw] per second) during both compression and decompression. Chamber pressure was monitored from a digital pressure gauge (model DPG 2101, Mensor Corp.; San Marcos, TX) that the manufacturer had calibrated within the year. The chamber temperature was maintained within 1 °C of that set by a temperature controller (model 89000-10, Cole-Parmer Instrument Co.; Barrington, IL). For most chamber testing, the temperature was set at 25 °C, although some testing was done with the chamber set at colder or warmer temperatures to examine how those levels affected the performance of the gas sensors.

For all testing, high-purity regulators were used to deliver individual test gases from the cylinders. For chamber testing, an ~10 ft, high-pressure Teflon-lined whip was used to attach the high-purity regulator on each of the test gas cylinders outside the chamber to a stainless steel penetrator on the exterior of the chamber wall. Inside the chamber, gas flowed from the penetrator and was delivered to the instruments. Generally for both bench and chamber testing, the final leg of the gas delivery pathway used various Teflon tubing arrangements (tubing with 1/8-inch outer diameter, 1/16-inch inner diameter [ID]) described later in this report within the **METHODS** sections of each of the three individual instruments tested. Since the test gases, many of which are highly reactive, could be affected by the hardware used to deliver them during chamber testing, all that testing of each of the three instruments was initially accompanied by some daily preliminary checks of gas readings with the instruments on the bench.

Some bench testing delivered the gas through a branching circuit of Teflon tubing with a precision gas divider (STEC model SGD-710, Horiba/Stec Inc.; Austin, TX). This STEC device allowed one of the SEAL gas standards to be blended with a diluent gas (here, high purity air) in ten equal steps of 10% each, from 0 to 100% of the standard concentrations. This divider thus allowed us to generate instrument response curves from up to 10 concentrations from a single gas standard.

By using low ppm levels of VOCs and up to 25% of fixed gases (e.g., O_2 , CO_2), we have shown the STEC gas divider's results to be linear to within the manufacturer's specification of $\pm 0.5\%$ of full scale.⁷ However, with some of the more reactive SEAL gas mixtures, we were unsure how well the STEC could work.

For our testing, we normally started at a STEC setting of 30%, then went to 70%, 100%, and then down to 50% — a procedure reducing the test time but covering the entire range from 0% to 100%. After each step change in the STEC, normally 10 min or more were allowed until readings were stable; the STEC was then adjusted to the next concentration. As described, this complete test procedure is hereafter referred to as a “STEC test” in this report.

For chamber testing, individual gases — starting at surface pressure — were delivered to the instruments; generally, pressure was then increased in 1 ATA steps up to a maximum of 5 ATA and then back to 1 ATA, with delays at time intervals ranging from ~5 to 20 min at each new pressure. However, other testing involved somewhat different pressure profiles that this report describes at those relevant places. Following pressure stabilization that occurred within 1–2 min of reaching a specific depth, the test depth was normally controlled to a level within 0.03 ATA of the desired value.

To collect sensor and other data during testing, data logging was normally used — typically at intervals of 10 sec, although longer logging times were used for some testing such as that of determining battery viability during use of the instruments. During some testing on the laboratory bench, instrument readings were also recorded manually on a data sheet. However, data logging was essential when instruments were being tested inside the hyperbaric chamber, since poor visibility through the chamber ports prevented reliable viewing of instrument displays.

Data analysis

1. Precision.

With precision defined as the range in readings over time periods up to 10 min, the short-term repeatability of test measurements using samples of SEAL2 levels of test gases at the surface and at pressure was determined from logged data taken at 10 sec intervals. Since the data logged at these intervals were recorded directly from the displayed values (with the displayed data updated several times each second), our precision values should reliably estimate the precision for the displayed data.

2. Accuracy.

Accuracy data were used to calculate the relative percent error:

$$\text{Relative percent error} = \frac{(\text{Observed reading} - \text{Expected reading})}{\text{Expected reading}} \cdot 100.$$

Expected readings were equal to the values on the certificates of the gas standards used for testing. For STEC testing, the certificate values were multiplied by the dilution factor at the specific STEC setting: e.g., for a STEC setting of 30, the expected value = the certificate value • 0.3.

3. Error in Gas Standards.

Measurement results from our testing will reflect the relative percent error of $\pm 1\%$ associated with the certified concentrations of the gas standards.

TESTING OF TARGET MONITORS

For our testing, ENMET provided six Target multigas monitors (with sensors for some, but not all, of the SEAL gases) during the first several years of this project — monitors which included some nonstandard modifications specific to our testing. The Target testing was designed to evaluate its COTS toxic gas sensors, and later the specially developed pressure-adapted sensors, for use at pressures up to 5 ATA. Figure 1 presents a typical Target monitor and one of its gas sensors. All display and data logging values were measured in ppm which were used to evaluate the monitors' performance,

ENMET expanded the measurement ranges of the gas sensors in these monitors to enable gas measurements within the ranges defined in the **MONITOR REQUIREMENTS** section, measurements typically greater than the workplace limits for which toxic gas monitors are designed. The data logging function was also modified to facilitate our testing. Although each Target monitor could be equipped with up to five different gas sensors, only two of these sensor positions could accommodate the type of sensors required for detecting any of the eight toxic gases our project was studying. Thus, we required a greater number of Target monitors for our evaluation than might otherwise have been needed.

METHODS

Up to two Target monitors were tested simultaneously. During their calibration and initial testing, the internal gas sampling pump was off, and the calibration shield supplied by ENMET was attached. Gas was delivered to the calibration shield with a branching circuit made of Teflon tubing downstream from the high-purity regulator on each test gas cylinder. The gas flowed into the calibration shield, over the top of each of the chemical sensors, and then out of the calibration shield into the surrounding atmosphere. A slight overflow of ~ 400 mL/min, as measured with a rotameter flowmeter off a side branch of the gas delivery line upstream from the instruments, was maintained to ensure that gas was delivered, but with minimal back pressure (<1 psi). The rotameter in this case was simply used as a rough indicator of flow, for readings from rotameters used at pressure normally need to be corrected.¹² When the overflow was varied up to ~ 800 mL/min during testing on the bench and inside the hyperbaric chamber, some instrument readings showed minor effects.

The Targets were commonly calibrated weekly by first zeroing the instruments with the high purity N_2 and then spanning them with one of the SEAL2 primary standards, per

the procedures in the Target operating manual.¹³ These instruments often failed to read the span gas with exact accuracy following calibration, or during the testing between calibrations. However, recalibrations were not normally made to correct minor discrepancies in gas readings, for such discrepancies did not affect our ability to evaluate how pressure was affecting sensor performance.

Later Target testing was done without the calibration shield attached (and again with the sampling pump turned off), with the Targets placed inside a small Plexiglas box with a removable lid (internally ~8" wide x 11" long x 3" high), a box that we specially fabricated to accommodate up to two of these monitors. Test gas was delivered from the high-purity regulator through Teflon tubing in series with a rotameter to one end of the box via a 2 mm ID fitting opening at rotameter flows of ~800 mL/min; it was then allowed to exit through two additional 2 mm ID fittings at the opposite end of the Plexiglas box. The single gas inlet fitting was centered on one end of the Plexiglas box, while the two gas outlet fittings — to ensure efficient flushing of the box with the test gas — were spaced apart at the box's other end.

The use of the Plexiglas box, a method closer to actual sampling of an atmosphere by the Target, avoided potential artifactual effects, especially at pressure, on instrument readings that might have been caused by flowing gas through the calibration shield. However, as judged by gas readings from the Sensor Test System, this method required increased gas flows to maintain inside-box concentrations of the test gas. Similar testing was also made after one or two Targets were placed inside a 10 L Tedlar bag (SKC Inc.; Eighty Four, PA) that was also purged with test gas: The Tedlar bag provided a relatively inert gas reservoir surrounding the monitors.

Dives typically started with the Targets being supplied with test gas in the pressure chamber for 20–30 min at the surface. Pressure was increased in 1 ATA steps up to a maximum of 5 ATA, and the monitors — waiting at each new pressure level usually from 6 to 15 min, but depending on the specific test — were then returned to the surface.

RESULTS AND DISCUSSION

Considerable testing of the modified Target monitors at pressures up to 5 ATA showed that the output signal of many of the gas sensors often declined as pressure was increased, frequently resulting in very unstable sensor signals. Sensor responses to pressure generally were irreproducible and hard to predict, the responses varying not only with the type of sensor (e.g., CO, H₂S, etc.) but also with the specific sensor when sensors for the same gas were compared. Examples of the standard sensor responses to pressure during two repeat tests (one in the morning and the second in the afternoon of the same day) with the same Target and calibration shield are given in Figures 2A–2D for four of the SEAL gases (CO, H₂S, SO₂, and Cl₂). The transient spikes in sensor outputs to each change in pressure, spikes most easily observed on the graphs at the low pressures before the signals become erratic, are unimportant to our work and can be ignored.

To try to improve the Target sensors' performance at pressure, we worked with ENMET and its sensor supplier from 2005 to 2006 to develop sensors with pressure responses that were both more reproducible as well as reduced in magnitude. Four sensors for five different SEAL gases (CO, H₂S, SO₂, and NO₂/Cl₂ — that fourth sensor was used for both of the last two gases identified) were modified in various ways by the sensor supplier and tested at pressure at NEDU to determine which modifications best improved performance. Since this supplier did not manufacture COTS sensors for the other three gases (HCN, HCl, and NH₃) at this time, no pressure-adapted or "hyperbaric" sensors were developed for these three.

Candidate sensors with the best performance at pressure were selected for continued use in developing a DISSUB monitor. From our discussions with ENMET, we believe that the effective modification adopted for the new hyperbaric sensors entailed applying epoxy to the bases of these sensors to stiffen these parts and prevent pores in the sensor membranes from collapsing when ambient pressure is increased. Such collapse of the pores under pressure was thought to have caused the problems with the original sensors.

Examples of the responses with each of four prototype hyperbaric sensors during one pressure test are given in Figures 3A–3B, with the calibration shield used for the first three tests (CO, H₂S, Cl₂) and the small Plexiglas box for SO₂. As these figures reveal, all the hyperbaric sensors still show at least some response to pressure. However, based on additional tests not shown here with replicate sensors for each gas, the magnitude and pattern of the pressure responses appeared similar for the same type of gas sensor. In addition, the responses for replicate tests with the same individual sensor were much more reproducible than those we had observed with the standard sensors, a finding suggesting that mathematically correcting the sensor signal for pressure might be possible.

Again, the sensor output's transient spikes to each change in pressure can be ignored. In addition, the noise in the signal from the CO sensor at pressure in Figure 3A's top graph is from the test chamber's cooling and heating cycles, noise seen with some of the sensors and presumably due to chamber pressure fluctuations. This artifact was eliminated in later testing with the Target as well as with the Sensor Test System and SubTox: The chamber's temperature control system was modified to allow either heating or cooling only, rather than a back-and-forth heating and cooling around the temperature set point.

From initial testing results with the prototype gas sensors, our tentative plan became to develop mathematical corrections for any final monitor and thereby minimize, as much as possible, the remaining pressure effects on the mV output from each of the sensors. We hoped that these pressure corrections would result in relatively stable gas readings directly derived from the sensor output. Maintaining relatively constant gas readings as pressure varies would be useful, for readings from instruments previously calibrated at the surface can then simply be multiplied by the ambient pressure to convert such

readings into surface equivalent values (SEVs) before they are compared to the SEAL values. This correction would be identical, in effect, to following the National Academy of Science's recommendation that SEAL values be reduced in inverse proportion to any atmospheric pressure increase in the DISSUB.⁴

TESTING OF SENSOR TEST SYSTEM

From the start, we had realized that the Target analyzer we had been using for testing standard and modified sensors would be inappropriate for monitoring the DISSUB atmosphere, because

1. Each Target can be equipped with only two toxic gas sensors.
2. The size of the text displayed by the Target is so small that it is difficult to read quickly the gas names and concentrations, as well as the menu items when selecting various Target functions.
3. Air can be sampled with the Target in either of two different ways — passively, or actively with its optional internal sampling pump. Passive sampling relies on diffusion and air currents to bring air into contact with the sensors, which are located in the back of the analyzer with their sensing areas facing outward and exposed to the atmosphere. Alternatively, the pump can be used with a special sampling shield to draw gas perpendicularly across the top of the sensors' sensing areas. However, neither passive nor active sampling directs a gas stream straight at the sensor head, a design that ENMET recommends using to get the best sensor performance with some of the more reactive gases such as Cl₂.

Although these (and other) Target shortcomings did not prevent us from using this analyzer as an initial test platform for evaluating sensors, once we had sensors that worked reliably at pressure, we were ready to advance with designing and building an instrument better suited for our application. In 2006, ENMET proposed that, as a first step, it would build NEDU a Sensor Test System that would include: (1) a specially designed printed circuit board capable of holding up to 12 toxic gas sensors, (2) electronic mass flow and pressure sensors, (3) an LCD, (4) a gas manifold to deliver sample gas directly to the heads of the sensors, and (5) a gas sample pump. This Sensor Test System was to allow us to test multiple sensors simultaneously (and thereby speed up the testing process) and to examine some important questions before the initial prototype monitor was built. These questions included the following:

1. How changes in gas flow delivered to the gas sensors might affect sensor output. The concern was that, with increasing ambient pressures, the increase in gas density might increase the gas flow to the sensor — although

the exact changes in flow would depend partly on how the sample pump's stroke volume or cycle frequency might vary with increasing pressure.

2. How changes in ambient temperature might affect gas sensor output, since most, if not all, COTS gas sensors are affected to some extent by temperature.
3. What degree of cross sensitivity the gas sensors have to different gases, particularly to the other SEAL gases and H₂, since most COTS gas sensors are known to respond to at least some gases other than the specific ones they are used to measure.

In addition to the Sensor Test System hardware, ENMET developed specially written software to control data logging and various other functions related to the System. At the time, ENMET considered this System to be the “guts” of any future prototype DISSUB analyzer. Thus, test results from it would help determine the need for significant changes in any of the components or the design configuration before the prototype analyzer was built.

METHODS

Late in 2006, ENMET provided NEDU with the components of the Sensor Test System, and — with Teflon and stainless steel tubing, and chrome-plated connectors — NEDU assembled the System inside in a clear Plexiglas box. The box was vented to the surrounding atmosphere via a number of ~1½ -inch holes cut in two of its sides to equilibrate with the ambient pressure and temperature outside the box. The Test System configuration shown in Figures 4A–4D allowed test gas to be drawn from a 10 L Tedlar bag, with the gas flowing sequentially from the bag through the manifold containing the gas sensors; through the electronic mass flowmeter and a section of capillary tubing; and finally to the small brushless pump, where the gas was exhausted into the atmosphere. To allow faster purging of the Tedlar bag before testing, and to reduce its overall size during testing, this bag's gas capacity was reduced ~50% by having one end of it carefully folded up and taped securely, as can be seen in the upper right of Figure 4D.

The capillary coil of tubing shown in Figures 4C–4D was used to reduce the pump artifact that had been observed in the sensor output during preliminary testing. The exact ID and length of the capillary tubing chosen for final use was based on initial laboratory testing. During all testing, the sample pump was powered by the Target monitor's 4.8-volt nickel hydride battery pack. At first, the circuit board and LCD were powered by six D-cell alkaline batteries, but later a standard Target battery charger was used.

Installing the Sensor Test System in the Plexiglas box allowed us to easily move the System from the laboratory bench into the hyperbaric chamber, and then back to the bench, during testing. For both bench and chamber testing, gas was delivered to the

Tedlar bag from each test gas cylinder via a pathway of Teflon tubing in series with a rotameter. This bag, which served as a relatively inert gas reservoir for the System, had dual stainless steel fittings that allowed gas to be delivered to it through one fitting, while the System's sample pump (which was always turned on throughout testing) simultaneously drew gas from the bag through the other fitting via Teflon tubing. Sampling gas in this manner was thought to be similar to drawing it directly from the atmosphere, as it would be drawn during actual monitoring of the submarine atmosphere. Using this gas delivery procedure avoided potential concerns with alternative delivery methods that might introduce artifacts into sensor responses.

Before each test with the Tedlar bag was done, we always purged the bag with the test gas by completing two cycles of filling it to ~50% of its already reduced capacity (as discussed three paragraphs above) and then emptying it. We then filled the bag to ~50% for a third time, attached the SubTox to it, and began to collect data. During testing, we adjusted the delivery flow rate — as read from a rotameter either on the bench for surface testing or inside the chamber for pressure testing — from ~250 mL/min at the surface to ~500 mL/min at 5 ATA, an adjustment made to approximately match the withdrawal flow rate to maintain the bag at a level approximately 50% full. Again, the rotameter was used simply as a rough indicator to adjust the flow to the bag, rather than to provide a precise flow measurement. We note, however, that the need to increase the flow to maintain the bag at ~50% as depth was increased acknowledges the bag's compression by increased pressure as well as by any change in mass flow from the sampling pump: Pump flow is discussed further in the next section, **RESULTS AND DISCUSSION**.

Although gas readings could be displayed and logged in either ppm or mV, we chose to primarily use mV — to eliminate any confounding issues that might relate to calibration in our evaluation of the Sensor Test System.

RESULTS AND DISCUSSION

Initial testing of the Sensor Test System showed that as pressure was increased, the sample gas flow measured by the mass flowmeter decreased in an often nonreproducible manner — rather than being increased, as might be expected with the greater density of the test gas at pressure. Following inspection of the ENMET gas manifold that delivers sample gas to all the sensors, we thought that the most likely reason for the decreasing flow with the increase in pressure was a gas leakage through the mating surfaces of the manifold, a leakage resulting from compression of the “spongy” O-rings used to seal those surfaces.

Consequently, NEDU redesigned and fabricated, through a three-month trial-and-error procedure, a replacement manifold that, when tested, resulted in reproducible increases in gas flow as pressure was increased to 5 ATA. We interpreted this as evidence that the new gas manifold was not leaking at pressure and that an increase in sample pump mass flow was occurring as the ambient pressure was increased — a pressure increase requiring a corresponding gas flow increase to maintain the Tedlar bag at a level ~50%

full. ENMET subsequently adopted the NEDU manifold for the Sensor Test System as well as for the anticipated prototype DISSUB monitor.

Once the manifold problem was resolved, we proceeded to examine the performance of the System for the five different gases for which we had working hyperbaric sensors: CO, H₂S, SO₂, NO₂, and Cl₂. For these tests, we recorded mV readings as the responses for the gas, flow, and pressure sensors, while noting that the normal “offset” for all gas sensors when clean air is being sampled is ~2500 mV, so that the sensor response in mV is always defined relative to ~2500 mV. We also point out that the NO₂/Cl₂ sensor’s response to both gases is “negative” and reduces the sensor output to a level less than that of the ~2500 mV offset. This negative response contrasts with the more usual “positive” one that the other test gases show — a response that *increases* sensor output to a level greater than that of the ~2500 mV offset. Thus, where it is useful to facilitate a comparison among gases, we have sometimes plotted the NO₂ and Cl₂ test results on graphs that reverse the y-axis.

Representative test results are presented in Figures 5A–5E, with the top graphs in each case plotting gas sensor, gas flow, and pressure responses from one test, and the bottom graphs plotting only the gas sensor response from two replicate tests made on the same day (one of these replicate tests being the same as that in the top graph). Again, the transient spikes in gas sensor output to each pressure change should be ignored. The additional rare spikes in sensor plots, spikes not associated with a change in pressure, result from a software bug in the Test System’s data logging function. This bug resulted in missing data, so these resulting spikes should also be ignored.

As the results indicate, all sensors still show responses to pressure, the greatest response for all sensors occurring during that change from 1 to 2 ATA. Also, gas flow substantially increased as pressure was increased to 5 ATA, a flow increase followed by a reduction to pre-dive rates when pressure was subsequently returned to 1 ATA. With the calibration factors ENMET provided for the flow sensors to enable us to convert the flow mV readings to mL/min, we estimate that the initial gas sample flow of ~200 mL/min at the surface was increased to ~1000 mL/min at 5 ATA. This fivefold increase is exactly what would be expected from the increased density of the gas at 5 ATA, if the stroke volume and cycle frequency of the sample pump has experienced little or no change with depth.

When we compare sensor responses, we find that, relative to the mV levels at 1 ATA (Figures 5C–5E), the SO₂ and NO₂/Cl₂ sensors show the greatest changes in mV during each 1 ATA step, while the CO₂ and H₂S sensors show changes much smaller in response to pressure changes (Figures 5A–5B). However, except for the testing with Cl₂ gas, the two replicate tests for each gas appear to agree well (within 5% relative), and during both compression and decompression, the sensors appear to have equilibrated, or nearly equilibrated, by the end of each of the 10- or 15-minute stops. The response to Cl₂ was slower to equilibrate, and, on the basis of additional testing not shown here, the first test with Cl₂ done a week or more after the last testing showed a response ~5–10% smaller than those from subsequent tests on the same or following

days. However, we conducted no special testing to investigate these observations with Cl_2 .

We assume that the slow increase in the mV trace commonly seen for the gas sensors during each of the dive stops results from the slow chamber pressure increase caused by the test gas exhausting from the System (i.e., from the outlet of the sample pump) into the chamber atmosphere. This assumption was subsequently supported once a pressure compensation method was developed and applied to the SubTox data (data which showed similar rising sensor plots during each dive stop) producing relatively stable gas sensor mV readings at depth (as is discussed in the **DEVELOPMENT OF SUBTOX** section).

Initially we thought that many, if not all, of the sensor responses to pressure might have resulted from the increase in gas sample flows caused by increasing depths. Furthermore, since replicate tests (at least over a several-day period) generally agreed closely, a correction for this pressure effect seemed feasible. One possible option involved nulling the pressure response by electronically adjusting the pump flow back to surface values. Another approach we considered was to mathematically correct the sensor responses to pressure in the algorithm for calculating ppm. Although we expected that other possible options might also be effective, we first needed to experimentally test whether there was any effect of changes in gas flow on sensor output.

We tested how gas flow affects sensor output by varying the voltage delivered to the sample pump at the surface and at 2 ATA while test gas was delivered to the sensors, and we observed mV outputs from the mass flowmeter (as indices of gas flow) and from the gas sensors. At both test pressures, voltage delivered to the sample pump from a variable voltage source was initially set at 5.9 VDC (“normal” voltage) before being decreased to 3.1 VDC (near pump stall) and held there for ~10 min. Pump voltage was then increased back to 5.9 VDC.

This procedure produced flow sensor readings varying from ~2600 mV (close to the flow sensor’s “no-flow” calibration offset reading) to ~2900 mV (similar to that seen during normal pump operation on the surface) and even to ~4000 mV (compared to the ~4900 mV normally seen at 5 ATA). Figures 6A–6E, showing one graph for each test gas (although two complete tests were made with each gas), suggest that although this procedure produced large changes in gas flow, the output from any of the sensors showed little effect for those gases tested. In our opinion, this was good news as compensating for the effects of gas flow, especially as pressure changed, might not have been easy to accomplish.

By comparing pressure tests at 25, 40, and 10 °C, we next examined how changes in ambient temperature affect sensor output. Following equilibration of the hyperbaric chamber at the test temperature, the Sensor Test System was placed inside the chamber and allowed a 30 min equilibration at the surface while SEAL2-level test gas

was sampled. The chamber was then compressed to 3 ATA before being returned to the surface in 1 ATA increments.

On the first day, the 25 °C test was made in the morning, followed by a second test with the same test gas several hours later in the afternoon at 40 °C. On the next or a later day, additional tests with the same test gas were repeated at 25 °C in the morning and followed by afternoon testing at 10 °C. Results (Figures 7A–7C) demonstrate that the effect of temperature was variable for these five gases, with the mV response increasing, decreasing, or not changing at 40 or at 10 °C, relative to our standard testing temperature of 25 °C. However, any effect of these warm and cold temperatures was small: changes less than $\pm 5\%$ in the 25 °C responses for four of the sensors, and a change less than $\pm 10\%$ for the Cl₂ sensor.

The results from these temperature tests with the System provided data to examine how the sensors might have cross sensitivity to different SEAL gases. Because the results agreed closely with those from the subsequent SubTox testing, and because we wanted to reduce the total number of figures in this document, these System results are not being reported here. However, as will be discussed when the results from SubTox testing are provided, some of the sensors respond weakly or strongly to other gases. Nevertheless, we will present our results from the cross-sensitivity testing of the System's sensors to H₂.

We tested the response to H₂ by Sensor Test System at the surface on the bench by sampling 1% H₂ with a Tedlar bag for ~7 min. This H₂ concentration was chosen for initial testing because 1% H₂ is currently defined as the 90-day, 24-hour, and one-hour limit for U.S. Navy submarine atmospheres¹ and therefore might be expected to occur during submarine operations. The first graphs in Figures 8A–8B show the responses by the four working sensors (for CO, H₂S, SO₂, and NO₂/Cl₂) to the H₂ exposure. As shown in Figure 8A, exposure times were limited because the CO and H₂S sensors became saturated. Although we had expected the CO sensor to respond to H₂, we had not realized in advance that both the CO and the H₂S sensors would become saturated, and that this saturation would last so long and thereby indicate such a strong response to H₂ by these two sensors. Following the 7 min exposure, it took ~1 hour for the CO sensor to return to baseline, and ~15 min for a similar recovery by the H₂S sensor.

At the time of this testing, we were also unsure how significant the on and off responses by the SO₂ and the NO₂/Cl₂ sensors (Figure 8B) were. However, the graphs in Figures 9A–9C compare the magnitude of each sensor's H₂ responses to that for the respective test gas at SEAL2 levels during previous dives from other testing. These graphs therefore document whether H₂ interference might significantly affect the accuracy of readings for the five test gases during a DISSUB scenario: The data suggest that H₂ at levels up to 1% would interfere with accurately measuring CO and H₂S — but may not significantly interfere with Sensor Test System readings for SO₂, NO₂, and Cl₂.

DEVELOPMENT OF SUBTOX

As our testing of the Sensor Test System was proceeding in 2007, ENMET and NEDU agreed that ENMET should start designing a prototype DISSUB toxic gas monitor that NEDU decided to name “SubTox,” a monitor based on both Navy requirements and knowledge gained from NEDU’s testing of the Sensor Test System. Although this monitor would be “built from the ground up,” ENMET planned to use some components from that System in the SubTox prototype, and to base its SubTox design on the configuration of that System. During the SubTox planning, NEDU was able to suggest some additional capabilities and features so that the final analyzer, when produced, could better meet Navy needs. This opportunity was rather unusual, since most of NEDU’s projects in developing gas screening procedures for the Fleet have relied on manufacturers to modify existing COTS instruments to meet Navy requirements, rather than to produce completely new instruments.

Following the agreement between NEDU and ENMET on the design and capabilities of the initial SubTox prototype, ENMET began building those first monitors. NEDU received the first two of six prototypes in April 2008, and the remaining four units were delivered over the next six months. The configuration of these monitors was based on, and the units actually turned out to be, very similar to that antecedent Sensor Test System. Where needed, this report identifies those first six monitors, with serial numbers 140-0001 through 140-0006, as ST-1 through ST-6.

To draw a gas sample into the SubTox, the unit used a small internal brushless pump, with the gas flowing first through the inlet port (containing a hydrophobic filter to prevent water ingress) in the wall of the Pelican-like case, then through the manifold containing the hyperbaric gas sensors, then through the electronic mass flowmeter (which was eventually moved upstream from the manifold to improve the ability to detect leaks in this manifold), then through a small resistive fitting (rather than the capillary tubing used in the Sensor Test System, to reduce the artifact from the pump), and finally to the pump, where the gas was exhausted into the SubTox’s internal gas space. Teflon-lined Tygon tubing was used to connect all the components together allowing gas to flow through the unit while minimizing any effects from the surfaces that the eight SEAL gases contacted. A small vented fitting equipped with a hydrophobic filter in the wall of the SubTox ensured equilibration between the outside ambient pressure and the unit’s internal pressure. (See Figures 10A–10D for SubTox photos.)

INITIAL FEATURES OF SUBTOX

As SubTox testing proceeded and discussions between NEDU and ENMET continued, additional features, functions, and capabilities based on those discussions were introduced. However, the initial features of SubTox included the following:

1. Seven of the eight SEAL gases (CO, Cl₂, HCl, HCN, H₂S, N₂O, and SO₂) and their concentrations (ppm), with all gas readings updated several times a second, were

displayed. (ENMET believed that a reliable hyperbaric NH_3 sensor was not available at that time, but expected that such a sensor was likely to be developed soon.)

2. A sensor for measuring H_2 was not included, but it was later added to evaluate the feasibility of reducing H_2 's effect on the CO sensor.

3. The upper display limit for concentrations was two times the SEAL2 levels for all SEAL gases. (After an H_2 measuring capability has been added, the upper display concentration limit for H_2 has become 10,000 ppm [1%].)

4. Display and logging resolutions of 1 ppm were established for the SEAL gases (for Cl_2 , these have subsequently been changed to 0.1 ppm), and the resolution for H_2 was also established at 1 ppm when a H_2 sensor was added.

5. The design incorporated a capability for a total of at least 12 (and possibly more) gas sensors.

6. Gas was delivered to the sensors via the NEDU-designed sensor manifold that had been developed with the Sensor Test System.

7. The pressure range for the unit was from 1 to 5 ATA.

8. The unit was powered by a set of six D-cell alkaline batteries with the goal of providing over three days of continuous operation per battery set.

9. The custom circuit board was designed by ENMET.

10. The unit included a waterproof gas sampling inlet, mass flow and pressure sensors, a data logger, an LCD with backlighting, a computer interface, and a brushless sample pump with an adjustable duty cycle. (The data logging function allows readings to be recorded at intervals down to every second. After the unit is connected to an RS232 serial port of a personal computer with the supplied lead, the data can then be downloaded via ENMET's SubTox Visual Basic [VB] software.)

11. The unit's LCD displayed:

Uncorrected and SEV concentrations of all SEAL gases.

Sample gas flow (L/min), ambient pressure (ATA), gas sample temperature ($^{\circ}\text{F}$), and battery voltage (VDC).

Status screen readings for battery percentage remaining, date, time, and pump mode.

mV readings from the SEAL gas sensors; for laboratory and diagnostic use, but this display could be disabled.

mV readings from the sensors for sample gas flow, ambient pressure, gas sample temperature, and battery voltage; for laboratory and diagnostic use, but this display could be disabled.

12. Software specifically for the Navy DISSUB application, with passcode protections, was written and included. (These VB and SubTox codes establish many capabilities — e.g., those for calibration and for compensations for pressure, temperature, and cross sensitivities among gases.)

13. Visual/audio alarms were included.

METHODS

Once NEDU had received the first SubTox monitors, the initial testing goal was to compare its performance to that of its simplified predecessor, the Sensor Test System. Any significant performance differences between the two monitor systems would need to be resolved before we proceeded with any further SubTox testing, which would then concentrate on developing techniques to mathematically correct the effects of pressure on the gas sensors and on addressing other performance features of the SubTox. Results would be used to judge its suitability for monitoring DISSUB atmospheres and to make a recommendation on transitioning it to the submarine fleet.

Each SubTox monitor was tested one at a time, with its internal gas sampling pump operating continuously. Test gas was delivered in ways similar to those used by the Sensor Test System, both on the bench and inside the hyperbaric chamber: The SubTox drew gas from a 10 L Tedlar bag (its overall capacity reduced by ~50%, as in the Sensor Test System) maintained at a volume of ~50% full by adjustments to the gas flowing into the bag from ~400 to 500 mL/min at the surface, and up to ~900 mL/min at 5 ATA, as displayed by a rotameter in series with the delivery gas circuit. After we completed our standard two-cycle bag purge procedure, the SubTox was attached to the bag and data collection was started. (See Figures 11A–11D to view the testing setup.)

SubTox gas readings could be displayed and logged in ppm or mV, and our testing used both of these measurement units to evaluate the monitor's performance.

Battery duration

To determine how long monitors would last on a single charge of six D-cell alkaline batteries and to address specific operating problems that had been observed when the voltage levels became low, battery duration was tested during various phases of this project. To allow sufficient logging memory for >10 days of continuous logging (a length of time much greater than the expected battery duration), we initially tested to determine battery duration by setting the data logging interval to every 5 min. We then installed new batteries, turned on the monitors with the pump sampling the laboratory

atmosphere in a continuous mode, and allowed the monitors to run on the laboratory bench until low battery voltage caused them to shut off. Operating time until such a shutoff could then be easily determined to the nearest 5 min from the time (and date) of the last logged entry. During battery testing, periodically we also manually recorded both displayed readings from the monitor and details of procedures related to the tests at the time.

Relative humidity

The effect of water vapor (i.e., RH) on SubTox readings was examined by comparing dry (~0% RH) to wet (~95%) gas standards. Water vapor was added to the test gases by using two water bubblers connected in series and held at 35–45 °C in a water bath. We used a hand-held humidity and temperature meter (model HM70; Vaisala Oyj, Finland), with its calibration traceable to the National Institute of Standards and Technology, to initially monitor gas leaving the humidification setup from an overflow site on the gas delivery circuit just upstream from the Tedlar bag. When temperature and humidity readings were stable and RH was confirmed to be at least 95%, a valve was turned to begin purging the Tedlar bag in the normal manner. After having been purged, the SubTox was attached and readings were recorded manually and logged for at least 10 min.

Since humidification could potentially affect the concentration of the SEAL gases delivered to the SubTox if the gases were to go into solution or react with the water in the bubbler, gas chromatography (GC; as performed by Lillo, Caldwell, and Porter¹⁴) was used to determine the actual gas concentration delivered to the analyzer. To allow a sample to be introduced into the GC, several feet of Teflon tubing was used to divert gas leaving the overflow site on the delivery circuit into the introduction line of the GC gas sample valve. This GC analysis was made only when CO was being tested, however, because we had no established method to reliably check the concentrations of the other SEAL gases.

RESULTS AND DISCUSSION

Initial testing of the SubTox prototype monitors at pressures up to 5 ATA was completed with seven of the eight SEAL gases, since at that time we were still waiting for a hyperbaric NH₃ sensor to be supplied. Results from this initial testing (top graphs in Figures 12A–12G) suggest that SubTox's sensor performance was similar to that of the Sensor Test System (top graphs in Figures 5A–5E). However, one obvious difference with the SubTox was that its sample gas flow changed little, if at all, as test pressure was increased and then decreased — whereas we had observed the Sensor Test System gas flow to undergo an apparent fivefold increase in flow while that unit went from the surface to 5 ATA.

Over a series of dives with two SubTox monitors, further review of logged sample flows (expressed in mL/min per ENMET's flow calibration factors) showed that flows varied from 0.4 to 0.6 L/min during the testing from 1 to 5 ATA — although the greatest flow

was not always at the greatest pressure. Though we did not investigate further, we presumed that this difference in flow response to pressure resulted somehow from the different gas flow configurations in the SubTox and the Sensor Test System, with the small resistive fitting just upstream from the SubTox sampling pump possibly limiting the mass flow through the gas sampling pathway. Nevertheless, the prototype analyzers appeared overall to work reliably in the laboratory, and a few initial minor problems were resolved with ENMET's help.

We presume that the variability in sensor responses among three SubTox monitors (bottom graphs, Figures 12A–12G) resulted from differences in sensors and in the SubTox electronics. Although this variability was relatively small for some of the sensors (CO, H₂S, and SO₂) among the SubTox monitors, it is larger for the other sensors.

In addition, as with the Sensor Test System, the two replicate tests with each SubTox (done in the morning and afternoon on the same day) appear to agree well (within 5% relative) for all the sensors except the NO₂/Cl₂ sensor (with Cl₂ test gas) — and for the HCN and HCl sensors, which had not been tested with the System. As with that Sensor Test System, we observed that the first SubTox test with Cl₂ gas, after the SubTox had not been exposed to Cl₂ for at least several days, typically produced responses ~5–10% smaller than those from subsequent tests on the same or following days. Such subsequent tests with Cl₂ then exhibited the ~5% variability between morning and afternoon responses, as the other sensors had. For this reason, we chose to omit the data from those “first day” tests with Cl₂ in our evaluation of the correction discussed in the **Mathematical pressure correction and calibration** subsection below.

For the HCN and HCl gas tests, we suspect that the increased variability among monitors and between replicates suggests some deterioration in these sensors, since their operating lives are shorter than those of some of the others: HCN and HCl sensors are warranted for six months; the others, for twelve months. Unfortunately, throughout the course of the SubTox project, it was not always practical to ship SubTox monitors back to ENMET to replace these sensors, even when such replacements seemed necessary. More about some of the poorly performing sensors will be discussed as we continue to present results from our testing of SubTox.

The similarity between the performance of the prototype SubTox monitor and that of the Sensor Test System suggested that the SubTox's hardware configuration — including its electronic boards, sensor manifold, pump, and flow pathways — did not significantly alter its sensors' performance from that of the Test System. Therefore, we could then begin formal testing to address those specific SubTox issues discussed in the preceding **METHODS** section. However, we emphasize that as formal testing proceeded, many modifications, both major and minor, were made to the SubTox hardware and software to correct emergent problems or address specific questions. Other changes were also made to improve performance and expand capabilities that NEDU and ENMET had agreed to pursue or implement.

Usually the approach was to modify only one or more of the SubTox monitors, rather than all of them, at a time — until the specific modification could be verified as acceptable or as needing additional work. Many of these changes necessitated the return of one or more monitors to ENMET. In addition, when field testing began and one or more of the monitors were sent into the field, some of them were therefore unavailable for laboratory testing. Consequently, the population of SubTox monitors available for laboratory testing, as well as the hardware and software status of individual monitors, varied over time. Our ability to perform replicate testing with more than one or two SubTox monitors, which were in identical, or similar, hardware and software states at the time of testing, was therefore often limited.

Surface linearity (1 ATA)

For SubTox, one important assessment in determining its overall accuracy is that of the linearity of its response across a specified test gas concentration. Such linearity tests using the STEC allowed the relative percent error at the surface to be determined at normal laboratory temperatures (22 to 26 °C). In Figures 13A–13F, the top graphs plot the observed vs. the expected readings, and the bottom graphs plot the relative percent error vs. the expected readings. To facilitate our combining of data from the six SubTox monitors that were not all in calibration, we normalized responses by setting the response to SEAL2 concentrations to 100%. Using the mean ± 2 standard deviation of the relative percent error as an index of linearity, we estimated the linearity for the sensors tested down to the SEAL1 concentrations to be

$0 \pm 4\%$ for CO,

$-2 \pm 8\%$ for H₂S,

$0 \pm 2\%$ for SO₂,

$1 \pm 15\%$ for NO₂,

$0 \pm 13\%$ for Cl₂, and

$5 \pm 4\%$ for HCN.

We chose to limit our definition of surface linearity only down to SEAL1 levels, since these are the lowest points of major concern. Results for concentrations less than those of SEAL1 levels generally have larger percentage errors — in part, simply because of the definition of percentage error, where the difference between the observed and the expected readings is divided by a decreasing denominator (the expected reading):

$$\text{Relative percent error} = \frac{(\text{Observed reading} - \text{Expected reading})}{\text{Expected reading}} \cdot 100.$$

We also expected that our testing with low concentrations of some of the more reactive gases introduced additional, although hard-to-define, error into the linearity estimates.

Unfortunately, most of the results for HCl show poor linearity, presumably because of sensor deterioration: All of the tested HCl sensors had been used for periods much longer than six months, their expected and warranted lifetime. Therefore, we are omitting these HCl data.

Air sampling dives

Three SubTox monitors were tested from 1 ATA to 5 ATA, while the monitors were directly sampling the air atmosphere within the hyperbaric chamber and unconnected to test gas or Tedlar bag, to discover whether any pressure artifacts on the sensors might significantly interfere the ability to measure toxic gases at pressure. Representative results (Figures 14A–14C) from one SubTox revealed only small effects on the sensors during the dive. The greatest response to pressure was seen with the NO₂/Cl₂ sensor — a response we expected, because this sensor’s signal had to be amplified more than the signal of any other sensor, due to these two gases having the lowest SEAL1 and SEAL2 concentrations. However, relative to the sensor signals when sampling any of the test gases at SEAL2 concentrations (FIGURES 12A-G), the responses during the air sampling dives suggest little concern about pressure artifacts with SubTox.

Stability of response over time (months): mV

After testing long-term stability of sensor output from two SubTox monitors, we provide representative results in Figures 15A–15D, where sensor mV signals are plotted from two replicate tests performed at 1 to 5 ATA on one day and repeated six to eight months later. These results show that the percentage variation between the two test days was <5% for CO, H₂S, and NO₂, and <10% for SO₂ and Cl₂. Much greater variation was seen for HCN and HCl — again, probably, because of suspected deterioration in these last two sensors, with their shorter operating lives.

Mathematical pressure correction and calibration

The reproducibility of the hyperbaric sensors’ responses to pressure suggested that their signals could be mathematically corrected for changes in pressure. Our goal was to minimize, as much as possible, the pressure effect remaining on the mV output from each of the gas sensors — so that relatively stable gas readings could be derived from their output, regardless of the SubTox’s current pressure level. NEDU therefore developed a mathematical approach implemented by ENMET: a specially designed EXCEL spreadsheet file (the calibration and pressure correction “tool file”) to be used with the collected data during what is hereafter identified as a “calibration dive.”

The tool file not only allowed correction of the raw mV readings for pressure, but also calculated calibration factors (slope and offset) to convert (1) gas mV readings to ppm (based on SubTox mV readings while sampling air and test gas at the surface) and (2)

pressure mV readings to ATA (based on mV readings from the pressure transducer inside the SubTox at the surface and 5 ATA). The approach used for correcting gas mV readings for pressure was to calculate using the data from the calibration dive correction factors we termed “slope multipliers” by dividing the stabilized gas mV reading at each pressure stop (i.e., 2, 3, 4, 5 ATA) by the gas mV reading at 1 ATA.

Once these slope multipliers were defined, we could then correct all gas mV readings from any data set (either the calibration dive or a subsequent test dive) for pressure by dividing by the slope multiplier for that pressure if it were exactly 2, 3, 4, or 5 ATA. For the more likely situation when the pressure was between two pressure stops of the calibration dive, the correction could be made by dividing with a slope multiplier calculated by linear interpolation between the relevant pair of slope multipliers. Finally, we converted these pressure-corrected gas mV readings to ppm, and the pressure mV readings to ATA, by using the tool file’s calculations of calibration slopes and offsets.

When we compared this approach with that using a longer dive profile with pressure steps of 0.5 ATA (i.e., 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 ATA — a profile providing additional data and thus shortened pressure stop interpolations on which to base the correction), we saw no obvious benefit in using the longer dive profile in terms of holding gas readings stable over pressures from 1 to 5 ATA. In addition, although normal submarine pressures may at times be <1 ATA, the pressure correction as developed and tested with SubTox “clamped” all subatmospheric pressures at 1 ATA in mathematically correcting gas readings. Whether this approach needs to be changed in the future is unknown.

We now explain in more detail the steps required to use the tool file both to derive the pressure correction and calibration factors and to apply these factors to a set of data to evaluate its effectiveness. With the SubTox inside the hyperbaric chamber while one of the SEAL gases was being sampled and data were being logged to collect mV readings every 10 sec, the first step was to conduct a calibration dive using the following profile:

1. Start at the surface sampling air for 5+ min.
2. Switch to sampling SEAL2 test gas at the surface for 15+ min, then compress to 2 ATA.
3. Remain for 15 min at 2 ATA while sampling SEAL2 test gas, then compress to 3 ATA.
4. Remain for 10 min at 3 ATA while sampling SEAL2 test gas, then compress to 4 ATA.
5. Remain for 10 min at 4 ATA while sampling SEAL2 test gas, then compress to 5 ATA.
6. Remain for 10 min at 5 ATA while sampling SEAL2 test gas.

7. Finally, decompress the chamber directly to 1 ATA following the 10 min spent at 5 ATA. (To minimize the length of the calibration dive, no stops are included.)

All pressure changes were made at the rate of 0.03 ATA/sec (1 fsw/sec) during both compression and decompression. At Step #2, the time allowed for surface sampling of the test gas was sometimes lengthened — particularly for Cl_2 and HCl , both of which normally showed responses slower than those of the other sensors. Since the sensor signal generally required additional time to equilibrate following the first compression step to 2 ATA, during that Step #3 compression phase we also allowed a longer time (15 min) than that at the other pressures (10 min). Following the first calibration dive, additional calibration dives were made with one or more of the remaining SEAL gases — depending on what sensors were to be recalibrated at the time.

After the calibration dives and data downloading were completed, a separate tool file was produced for each of the gases: For each of these tool files, stabilized gas mV values for the specific sensor being tested, at the surface and at each pressure stop (i.e., 2, 3, 4, 5 ATA), were selected from the logged data file. These gas mV values — along with the sensor number (as defined for each gas by the SubTox configuration: e.g., $\text{CO} = 1$), the pressure stop values (in ATA), and the test gas concentration (in ppm) — were entered into the green-colored cells of the tool file (see sample tool file, Figure 16). In addition, to allow the pressure transducer to be calibrated, its mV values at 1 and 5 ATA were also entered — although these pressure values were entered in only one of the tool files being compiled for each SubTox monitor, since only one pressure sensor calibration, overall, is used for each SubTox.

As the mV data was entered into the tool file's green cells, the yellow-colored cells were automatically populated with not only the calibration offsets and slopes for the specific gas and pressure transducer (if data were to be entered for the pressure transducer), but also the slope multipliers, which would be used to correct the gas mV readings for pressure. After all the yellow cells were populated with the calculated calibration and pressure correction factors, data from part or all of the calibration dive (or an actual test dive) could then be pasted into a specified tool file location to automatically generate a listing alongside each line of mV data of (1) pressure (ATA), (2) slope multiplier, and (3) pressure-compensated gas readings (in both ppm and mV). For the calibration dive data (or for a subsequent test dive or one with a much different dive profile), these results were used to judge both the effectiveness of the calibration and pressure compensation procedure just described and the accuracy with which those calibration and pressure correction factors worked during such a dive.

After the tool file was completed, both these pressure correction and calibration factors could be loaded into the SubTox so that it could display and log pressure readings (ATA) and pressure-corrected gas readings (ppm). For flexibility in our testing, the VB software allowed the pressure correction to be turned on or off, and mV or ppm to be logged by the data logger. For the duration of this project, keyboard entry using the VB

software loaded the pressure correction and calibration factors. However, we expect that an automated procedure can be developed — if the SubTox is transitioned to the Fleet.

Pressure correction of mV response

Using data from four SubTox monitors, Figures 17A–17G provide representative results documenting the effectiveness of our pressure correction technique. In all the graphs in this series, the top ones plot the sensor and pressure responses (mV) from one calibration dive, while the bottom graphs replot the uncorrected sensor responses from the top graph alongside the pressure-corrected responses produced when the tool file is used. Since the pressure correction is applied to the same sensor data used to derive those correction factors with the tool file, this evaluation of our approach should illustrate the best results possible from using those factors to subsequently correct SubTox performance data.

Although the calibration dive profile has no stops during decompression to the surface, all the top graphs show the typical sensor responses. Except for HCl, those responses to the test gas at pressure are corrected to values within 2% relative to the pre-dive mV value, and the graphs illustrate relatively stable mV readings over the 1 to 5 ATA pressure range. We presume that the reduced signal-to-noise levels and more erratic nature — associated with the HCl sensor in Figure 17G as well as with some other HCl sensors tested — are at least partly due to sensor deterioration. If so, such deterioration could thus lead to greater deviation in the pressure corrections.

Pressure correction and conversion to ppm

Figures 18A–18D illustrate representative results (again, from four SubTox monitors) from using the tool file to correct the data from the calibration dive for pressure and then to convert the gas readings to ppm. These graphs show how gas readings at the surface and during the compression phase were within 1 ppm of expected levels — for all the gases except Cl₂ and HCl. This level of deviation in gas readings agrees with the 1 ppm of resolution for both displayed and logged data for these gases.

The variability in the pressure-corrected readings for the Cl₂ also agrees with its displayed and logged resolution of 0.1 ppm. HCl again had considerably more deviation than the other SEAL gases from the expected concentrations. Pressure readings (not shown in the graph) from the tool file agreed to values within 0.03 ATA of expected pressures, an agreement level equivalent to 1 fsw — the target tolerance for each pressure stop made during the testing. However, the practical accuracy of the pressure sensor would be limited by the 0.1 ATA resolution of the SubTox pressure sensor's displayed and logged pressure readings.

Again, these results comprise the “best case,” since the pressure correction and calibration factors are based on the same data (i.e., calibration dive data) that are being converted to pressure-corrected ppm and pressure in ATA.

Evaluation of pressure correction and calibration with test dives

These tests examined the accuracy of using the pressure correction and calibration factors with test dives, rather than with the calibration dives that had been used to derive these factors. As with a standard calibration dive, a morning dive was performed with stops at 2, 3, 4, and 5 ATA during compression, but this dive was then followed during decompression with stops at 4, 3, and 2 ATA on the way to the surface (rather than with decompression directly to the surface for the calibration dive). Both dives used SEAL2 levels of the test gases.

For this exercise, the compression phase of the morning dive was used as the “calibration dive phase” to generate pressure and calibration factors via the tool file. The afternoon test dive performed stops midway between those of the morning dive (i.e., at 1.5, 2.5, 3.5, and 4.5 ATA) during compression, and it repeated these stops (at 3.5, 2.5, and 1.5 ATA) during decompression to the surface, levels requiring the tool file to be used to interpolate between those pressures in the morning profile so that the afternoon dive readings could be corrected for pressure.

After the tool file had been used to correct gas mV values for pressure and convert the logged mV readings to ppm, data from two SubTox monitors tested in morning and afternoon dives were plotted in representative results shown in Figures 19A–19C. As these results indicate, gas readings at the surface, and during both the compression and decompression phases, were within 2 ppm of expected levels for both the morning and afternoon dives with CO, H₂S, SO₂, and NO₂. Both at the surface and during compression, a similar degree of deviation from the expected was observed with HCN, while a deviation within 0.2 ppm was associated with Cl₂ (the one SEAL gas with a displayed and logged resolution of 0.1 ppm). However, during decompression, both Cl₂ and HCN had much larger deviations than those at the surface and during compression, an observation that may be related to sensor aging (as the forthcoming **Stability of pressure correction over time** subsection suggests). Again, pressure readings (not shown) agreed to levels within 0.03 ATA of those expected.

Subsequent further testing, with pressure profiles similar to those used for the preceding dives, was then done to evaluate the tool file’s ability to address the combined factors of different pressures and test gas concentrations from those of the calibration dive profile. While the morning dives in these additional tests used SEAL2 levels of the test gases, the afternoon dives used SEAL1 levels. For these dives, we used one of the two SubTox monitors used in the preceding experiments.

The top graphs of Figures 20A–20E show the mV plots from both the morning and afternoon dives with SEAL2 and SEAL1 gases, respectively. The bottom graphs show the ppm plots following pressure corrections and conversions to ppm; these plots for the SEAL2 tests demonstrate that gas readings at the surface, and during both the compression and decompression phases, are again within 2 ppm of the levels expected for H₂S and SO₂. (We saw no benefit in testing CO, since its SEAL2 and SEAL1

concentrations of 85 and 75 ppm, respectively, are very close.) Although deviations from the expected levels observed for NO₂, Cl₂, and HCN at the surface and during compression were similar to those for H₂S and SO₂, those three gases showed much larger deviations during decompression — presumably due to sensor deterioration.

Because only one monitor was used during the SEAL2 vs. SEAL1 gas testing, both NO₂ and Cl₂ results are based on the same sensor, the combined NO₂/Cl₂ sensor. Thus, we presume that this aging sensor is responsible for the poor performance seen with both NO₂ and Cl₂ during decompression (Figures 20C–20D). Since different monitors (and thus different NO₂/Cl₂ sensors) had been used for these two gases during the preceding testing with only SEAL2 gas, the differences in decompression performance (i.e., a relatively stable NO₂ signal alongside an erratic Cl₂ signal; see Figures 19B–19C) between these NO₂ and Cl₂ tests could be explained by differences in the condition of these NO₂/Cl₂ sensors: The monitor with the poor Cl₂ response in Figure 19C is the same as that with the poor NO₂ and Cl₂ responses in Figures 20C–20D.

The bottom graphs in Figures 20A–20E also show the afternoon ppm plots of the SEAL1 tests. Since these plots closely track the SEAL2 plots in terms of the monitor's ability to hold gas readings at surface values across the dive pressure profile, the pressure correction factors derived from the calibration dives may also work well for the lower-concentration gases. Where problems exist during decompression (e.g., with NO₂, Cl₂, and HCN), these problems are also seen with both SEAL2 and SEAL1 tests. As the surface linearity was previously shown to be good, we expect that any significant deviation from the levels expected in surface readings of SEAL1 gases may be at least partly due to disagreements between the certified values of SEAL2 and SEAL1 gases. In our experience, such discrepancies with low-level gas standards, particularly those involving relatively reactive gases such as many of the eight SEAL gases, are common.

Stability of pressure correction over time

Additional long-term testing evaluated the stability of the pressure correction and calibration factors. After ENMET had installed new sensors into two SubTox monitors just before the initial calibration dives, the pressure correction and calibration factors derived from those initial calibration dives were first loaded into these monitors for this evaluation, and test dives were then performed approximately one-half and 1½ years after those calibration dives. Although the intent of this testing was to make no changes during the entire 1½-year test period to any of the initial calibration slopes and offsets, or to any of the slope multipliers used to correct the gas mV readings for pressure, this intention proved not to be feasible.

Since the HCN and HCl sensors are warranted for six months and the others for twelve, we realized that this testing was pushing beyond what might be expected in terms of long-term sensor performance. However, the goal was to gather data to assist in making decisions about the frequency of calibration and of sensor replacement in the SubTox — when, or if, it is to be transitioned to the Fleet.

For both the ½- and 1½-year tests, dives were made in pairs: one dive with one monitor (with the pressure correction turned off via the VB software) in the morning, and a second dive with the same monitor (with the pressure correction turned on) in the afternoon. We chose to present the results from the best-performing monitor for each test gas in Figures 21A–21G — as well as to discuss the other data.

The top graphs, each plotting the ppm data from one monitor or the other, show that the ½-year data produced pressure-corrected gas readings within 2 ppm of those expected for H₂S and SO₂, 3 ppm for NO₂, 5 ppm for CO, and 0.2 ppm for Cl₂, both at the surface and during the compression and decompression phases. Deviations from expected pressure-corrected readings were within 2 ppm for HCN except during decompression — when this deviation was somewhat >2 ppm. HCl produced very poor results. No changes in the calibration slopes and offsets, or in the slope multipliers, were made from those derived from the original calibration dive at the start of testing. Logged pressure readings (not shown) agreed to values within 0.1 ATA of those expected for both monitors.

Unfortunately before the 1½-year stability testing began, other unrelated testing necessitated the surface recalibration of the sensors in the two monitors to be used for this testing. As a result, calibration offsets for all seven gases, and calibration slopes for three of the gases, were changed before testing began. However, we did not change any of the slope multipliers to correct gas mV readings for pressure from those initial slope multipliers that had been loaded into the monitors at the start of this testing. Our need to recalibrate these two monitors before the 1½-year testing could begin was expected: We had a limited population of SubTox monitors available, a population for which each monitor's hardware and software status varied in time. Since this situation often restricted which monitors were available for specific testing, we normally did not have the option of dedicating any monitors to long-term testing schedules (such as that of the stability testing) that might prohibit recalibration.

We have used the 1½-year results plotted in the bottom graphs of Figures 21A–21G to judge the stability of the pressure correction but not to judge the accuracy of gas readings, since the times of the last calibration (producing new sensor offsets and some new slopes) were not uniform and sometimes had occurred months before the 1½-year testing. As these graphs show, in some cases the gas concentrations (nominally equal to SEAL2 concentrations) had also changed slightly from those used for the 1½-year testing because of the need to switch to a new gas cylinder when the original one had become depleted.

To examine the 1½-year results, therefore, we have compared how effectively the pressure-corrected plots in the top and bottom graphs of each of the Figures 21A–21G manage to maintain the stability of the observed gas readings at the surface (before the dive begins), across the dive profile, and back to the surface (independent of the exact ppm level of the plots). Based on that criterion, the effectiveness of the pressure corrections for the 1½-year data appears similar to that for the ½-year data for CO, H₂S, NO₂, and HCN. However, the pressure corrections for the 1½-year data with SO₂ and

Cl₂ appear worse (than for the ½-year data), although the particularly erratic Cl₂ plots probably signal the sensors' advanced aging. HCl produced very poor results that were also presumably due to sensor deterioration. Logged pressure readings (not shown) again agreed to values within 0.1 ATA of the pressures expected for both monitors, except that one of the monitors read 4.8 ATA at 5.0 ATA. All pressure readings were based on the original pressure calibration factors loaded into the monitors at the start of stability testing,

Since the graphic pairs for each gas test in Figures 21A–21G are derived from one or the other of the two monitors used for the stability testing, the following summary of the results from the alternate monitor (*not* included throughout this Figure 21 series) completes the reporting on this testing and compares, where appropriate, these alternate monitor results to those illustrated in our figures (and noted below as those of the “first monitor”):

CO tests: Both ½- and 1½-year data are omitted, due to an apparent SubTox manifold leak affecting the CO responses during both sets of testing.

H₂S tests: For the ½-year tests, deviations from the expected readings were similar to those for the first monitor. The effectiveness of the pressure corrections agreed between the ½- and the 1½-year testing.

SO₂ tests: Since a temporary short-term change in this sensor's sensitivity (a change sometimes observed in some of the monitors following testing with other gases) confounded the stability testing with the alternate monitor, no results are reported.

NO₂ tests: For the ½-year tests, surface readings agreed within 1 ppm of the expected levels, but readings at pressure were ≤5 ppm higher than those expected. The effectiveness of the pressure correction differed between the ½- and the 1½-year testing.

Cl₂ tests: Deviations from expected levels were ≤0.5 ppm for the ½-year testing. The effectiveness of the pressure corrections agreed between the ½- and the 1½-year testing.

HCN tests: Because of erratic responses (presumably due to sensor deterioration), results are omitted.

HCl tests: Because of poor responses (presumably due to sensor deterioration), results are omitted.

Although results from stability testing of the SubTox prototypes that have been based on two monitors cannot be used to estimate the average in-field performance of either these prototypes or actual production monitors, these results suggest that ENMET's proposals for six-month recalibrations and sensor checks (with replacements of these

sensors, if needed) appear to be a realistic initial approach for using SubTox monitors in the Fleet. The 1½-year data also provide information about the feasibility of performing only surface recalibrations (without conducting a calibration dive) for each sensor, instead of making a more time-consuming calibration dive with each SEAL gas. Results suggest that, at least for some gases and perhaps over short time periods such as a single year, performing surface recalibrations only might be a feasible strategy.

Precision

Since monitor accuracy is affected by short-term changes in measurements, SubTox's precision is important to know. As estimated from logged data at the surface (1 ATA) and at depths ≤5 ATA from the various testing we have described, the short-term repeatability of SubTox measurements over a 10 min period for each gas was

- ±1 ppm, for CO;
- ±1 ppm, for H₂S;
- ±1 ppm, for SO₂;
- ±1 ppm, for NO₂;
- ±0.2 ppm, for Cl₂; and
- ±1 ppm, for HCN.

Due to the instability we routinely observed in readings for HCl, we made no estimate of precision for that gas. We ignored the data from aging sensors (e.g., in the bottom graph for Cl₂, Figure 21E) in making all estimates of precision.

Temperature testing

Using procedures similar to those followed with the Sensor Test System, we tested two SubTox monitors to discover the effects of ambient temperatures at 5 °C and 42 °C vs. the normal test temperature of 25 °C. Following equilibration of the hyperbaric chamber at the test temperature, the monitors were placed inside it and allowed a 30 min equilibration at the surface while they sampled SEAL2 level test gas. The chamber was then compressed to 3 ATA before being returned to the surface in 1 ATA increments. On the first day, the 25 °C test was made in the morning, followed by a second test with the same test gas several hours later in the afternoon at 42 °C. On the next or a later day, morning tests with the same test gas were repeated at 25 °C and then followed by afternoon testing at 5 °C.

With most gases, the effects on the sensor signal were small (±5% relative; see Figures 22A–22C), similar those seen with the Sensor Test System, so we did not evaluate the software that ENMET had provided to correct for temperature. Although our lower and upper test temperatures do not fully span the range in desired operating temperatures (0 to 50 °C), the range of temperatures tested represents those extremes at which our chamber could be reliably maintained during our test procedures.

Cross sensitivity of sensors to SEAL gases: mV

Data from SubTox temperature testing was subsequently used to evaluate the magnitude of the cross-sensitivity response to the SEAL gases by the SubTox electrochemical sensors. Such testing examined the sensor responses only in terms of mV; the **Compensation for cross sensitivity of sensors to SEAL gases: ppm** subsection examines the magnitude of these responses further by investigating them in terms of ppm and evaluating ENMET's initial software approach to mathematically minimizing these responses.

Figures 23–29 provide representative results from the data for three SubTox monitors, data showing the responses by all six gas sensors to each of the seven SEAL gases tested. In each series of graphs for each test gas (e.g., Figures 23A–23C present the series of graphs for CO; Figures 24A–24C present the series of graphs for H₂S; etc.), each graph contains two plots: (1) the mV plot from the sensor specific to the test gas, and (2) the mV plot from one of the other sensors. Such dual plotting allows us to easily compare the mV response by the “nontest” gas sensor to that by the sensor for the test gas — and to determine cross-sensitivity effects in terms of mV. Although the actual influence of any mV response depends on the calibration factors that translate mV to ppm, the following summary of significant cross-sensitivity effects we observed is the first step in understanding this problem:

- 85 ppm CO gas: small effect on the HCN sensor;
- 30 ppm H₂S gas: large effects on the NO₂/Cl₂, HCN, and HCl sensors;
- 30 ppm SO₂ gas: small effects on the H₂S, HCN, and HCl sensors;
- 10 ppm NO₂ gas: small effects on the H₂S, SO₂, and HCN sensors;
- 2.4 ppm Cl₂ gas: small effects on the H₂S and HCN sensors;
- 15 ppm HCN gas: small effects on the SO₂ and NO₂/Cl₂ sensors; and
- 35 ppm HCl: large effect on the HCN sensor.

The responses to the test gas were arbitrarily defined as “small” if they were observable from the plot on the graph but were <10% of the responses by the sensor specific to the test gas. They were defined as “large” if they were >10% of those responses by the sensor specific to the test gas. These results thus show that only two of the seven SEAL gases tested (H₂S and HCl; Figures 24 and 29, respectively) had large effects on one or more of the sensors not specific to those gases, with H₂S potentially causing the most problems because of its great effect on three other sensors.

Cross sensitivity of sensors to H₂: mV

Testing comparing the sensor mV responses to H₂ vs. the SEAL gases was performed with two SubTox monitors by sampling these gases at the surface for up to 6 min. On the basis of results from the Sensor Test System (with which 1% H₂ had appeared to saturate the CO and H₂S sensors), we reduced the 1% H₂ test gas to a 0.1% concentration by using the STEC at a setting of 10% to deliver the gas to the Tedlar bag. Results from the two monitors in the top graphs of Figures 30A–30B show that the mV responses from the CO sensors were similar for both 85 ppm CO (SEAL2 level) and 0.1% H₂. However, in the bottom two graphs of these same figures, the H₂S sensor displays only a small response to 0.1% H₂, in comparison to its response to 30 ppm H₂S (SEAL2 level).

The other tested sensors (for SO₂, NO₂/Cl₂, HCN, and HCl) all show little, if any, response to 0.1% H₂ (Figures 30C–30D), with all graphs plotting the responses to H₂ by both the individual sensor and the CO sensor so that the H₂ exposure period can be seen. This minimal response contrasts with that in some earlier results from the 1% H₂ testing with the Sensor Test System, where we observed on-and-off responses by the SO₂ and NO₂/Cl₂ sensors (cf, Figure 8B). Thus, the results in Figures 30C–30D suggest that H₂ at levels up to at ~0.1% may interfere with accurately measuring CO and H₂S but may not interfere significantly with reading SO₂, NO₂, and Cl₂.

Cross sensitivity of sensors to CO₂ and isobutylene: mV

During testing with three final-version prototype monitors, we observed that two of the six electrochemical sensors (CO, H₂S, SO₂, NO₂/Cl₂, HCN, and HCl — with all sensors in operation for <1 year) showed responses greater than their ±5 mV noise level after a 10 min exposure to ~2500 ppm CO₂: the HCl sensor, with an ~20 to ~40 mV response, and the HCN sensor, with an ~20 to ~30 mV response. Those HCl and HCN sensors were also the only ones to respond significantly to the ~20 ppm isobutylene used as one example of a common hydrocarbon species: the former, with an ~30 to ~50 mV response; the latter, with an ~20 mV response. Such relatively small responses suggest that CO₂ and isobutylene at the levels tested, and probably at levels several times those, are not expected to interfere with accurately measuring HCl and HCN at their SEAL2 levels.

Hydrogen testing

The rationale for having ENMET add a H₂ sensor to SubTox was to determine whether H₂'s effect on the CO sensor could be reduced or eliminated by mathematically “subtracting” its influence on the CO reading. Such a correction requires knowing both the concentration of H₂ and the ppm CO response that the CO sensor showed per ppm H₂; thus, our testing needed a H₂ sensor. But although we found that the CO sensor's mV responses to both 85 ppm CO (SEAL2 level) and 0.1% H₂ were very similar (as reported earlier in the **Cross sensitivity of sensors to H₂: mV** subsection), additional testing revealed that CO also affected the H₂ sensor: 85 ppm CO produced a reading of

~100 ppm H₂ in two H₂ sensors calibrated by ENMET. Therefore, the goal of mathematically correcting for H₂ seemed unfeasible, and we conducted no additional testing specific to that sensor — and did not attempt any testing at pressure — and relied on ENMET to perform all H₂ sensor calibrations.

Battery duration and related problems

With the SubTox pump running continuously on its single set of six D-cell alkaline batteries, we spent considerable time testing battery duration and working with ENMET to increase that duration to the desired three-day minimum. To eliminate concerns about defining adequate warm-up and equilibration times for the sensors and other electrical components every time the SubTox was turned off and then back on, we assumed that during operation of the SubTox in the Fleet, the monitor and pump would be kept continuously on. In addition, having the pump run continuously would allow users to observe up-to-date gas readings at all times.

We also worked with ENMET to correct specific operating problems observed when battery voltage levels became low or when monitors were stored with batteries in place. Since percentage battery readings for many electrical instruments are generally acknowledged only to approximate remaining battery life, we relied on battery VDCs to evaluate battery performance, rather than on any displayed battery “readings” that, for SubTox, are in a format of XXX.X%. Furthermore, such percentage battery readings do not appear to be very linear and depend on the precise battery VDC defined by the manufacturer to represent 0% remaining battery life.

Initial testing showed that, after a fresh set of batteries had been installed, SubTox usually operated for a little more than one day (~27–28 hours) with its pump and backlight continuously on. Although these were significant power drains (of 75 and 50 mA, respectively, as ENMET reported), other SubTox components also required much power: ENMET reported that, when the monitor was operating with the pump on, the total measured current draw was 220 mA. Furthermore, our testing during a duty cycle, with the pump on for 2 min of every 10 min cycle, extended the run times only to ~44–46 hours in the two SubTox units we evaluated.

Besides battery duration, a related problem was that, when battery voltages decreased to 7.2–7.3 VDC (levels only slightly higher than the ~7.1–7.2 VDC at which SubTox had automatically shut off during initial testing), the sensors’ offset voltages increased from their normal ~2500 mV. As we expected, these changes in sensor offset voltage produced changes in gas readings, while the sensors were sampling contaminant-free air, from the normally observed ~0 ppm to several ppm or greater (e.g., 10+ ppm CO).

Still another problem was that of the sampling pump’s failure to start up when the SubTox was turned on at battery voltages of ~7 VDC. And a third problem was that batteries slowly discharged during monitor storage (with the monitor turned off), due to an ENMET-measured 17 mA current draw by some of the electrical components. After

several months of storage, in fact, batteries were estimated to have lost up to one-half of their expected operating duration.

One solution might have been to remove the batteries during storage. However, following complete drawdown of the batteries during storage, or battery removal prior to storage, we observed that some sensors showed noisy signals for at least several hours when new batteries were reinstalled. ENMET reported that this problem resulted from a bias voltage having been removed from these sensors.

To extend the operating time from a single set of batteries and to correct those battery-related problems, ENMET invested much time and effort in changing the electrical components on the printed circuit board. As a result, the final-version prototypes were demonstrated to operate, with their sample pumps and backlights continuously on, for more than three days on a single set of batteries. Sensor voltages remained normal until battery voltages diminished to ~6 VDC, whereas the LCDs completely faded out at ~5 VDC. The SubTox monitors then shut down at ~4 VDC. Limited testing showed that the sampling pumps started when monitors were turned on with batteries at ~6 VDC.

On the basis of these results, ENMET reset the “low battery warning” to be displayed at 6.45 VDC, a level that produced a battery reading of ~15%. When such modified monitors were turned off, ENMET estimated their power draws to be close to 0 amps, and our experience indicates that these monitors can then be stored for weeks at a time with no observed decline from 100% in their displayed “battery readings.” Furthermore, subsequent testing suggested that the noisy sensor response no longer occurred upon restart of the SubTox, following complete drawdown of the batteries or removal of the batteries.

When one particular brand of alkaline batteries was being used during testing, an additional battery problem unrelated to duration or low voltage arose: The monitors often turned off during the compression phase of a dive, a problem never seen before and not observed with other batteries. By trial and error, we concluded that the ends of these batteries were being compressed inward as ambient pressure was increased, and that one or more of such batteries lost contact with the circuit contacts in the battery holder — a lost contact that thus shut off the SubTox. Our solution to this problem was simply to avoid using this particular brand of battery. To what degree this problem might result with other brands of batteries that might be used in SubTox is unknown.

Relative humidity

Although sensors can lose or gain water over long-term use (e.g., days) in low- or high-humidity environments, the sensor industry generally accepts the fact that electrochemical sensors of the type used in SubTox are little affected by humidity.^{15,16} During our testing, SEAL2 levels of CO (85 ppm), as measured by three SubTox monitors at high (>95%) vs. low (<1%) RHs, were similar and within the monitor’s level of precision (± 1 ppm). Furthermore, GC analysis showed that the “wet” gas measurements were lower than those of the dry gas by only 2 ppm CO — a reduction

explained by the estimated water vapor pressure in the sample gas (assuming the water in the humidifying system's bubbler to be saturated with the test gas), based on the RH and the temperature measured in the overflow gas during the GC analysis. Thus, we conclude that at the tested humidity levels, RH has little, if any, effect on CO readings.

For humidified readings of SEAL2 levels of two other gases (H_2S and NO_2) in the same three SubTox monitors, levels of humidified test gas were more than 50% lower than those of dry gas — but we had no way to verify the actual concentrations of the humidified gases. Because of the reactive nature of these two gases, we suspect that the bubbler absorbed a large fraction of each. Thus, having no independent method to measure the humidified gas concentrations, we did not test any other gases.

Compensation for cross sensitivity of sensors to SEAL gases: ppm

Before the final phase of testing (evaluation of ENMET's software designed to compensate for any sensor cross sensitivities among the eight SEAL gases), ENMET recalibrated the SEAL gas sensors in two SubTox monitors after several new sensors (including a new candidate NH_3 sensor) had been installed. Unfortunately, the several previous candidate NH_3 sensors we had tested had proven unsatisfactory due to sensor leakage following one or more test dives. Since the compensation software was not designed to correct for any H_2 effects on the other gas sensors and ENMET had not recalibrated the H_2 sensors before our testing, no data from the H_2 sensors are reported.

Using the first software version during the first two days on the bench, two SubTox monitors were tested with a 10 min exposure to SEAL2 levels of each of the following gases: on the first day, testing of CO, H_2S , SO_2 , NO_2 , and HCN (in this order); and on the next day, testing of Cl_2 , HCl, SO_2 , Cl_2 , and NH_3 (again, in this order). On the basis of previous test data suggesting possible changes in the responses of SO_2 sensors after they had been exposed to other gases, two SO_2 tests were made. And, following observations that initial Cl_2 exposures after several days of nontesting often produced smaller sensor responses than those of subsequent tests, two tests with Cl_2 were also made. During the first two test days with all gases, the compensation software was turned off via the VB software. Testing was then repeated on the next two consecutive days, but with the compensation software turned on. This four-day test cycle was repeated three times over a three-week period during which SubTox gas readings were both recorded and logged in ppm. All testing was done at surface pressure (1 ATA) on the laboratory bench.

For our data evaluation, we chose to use gas readings at the end of the 10 min exposures (i.e., the "10 min readings") to judge the cross-sensitivity responses and the effectiveness of the correction software. Except for the NH_3 sensor responses, all the target gas responses (e.g., that of the CO sensor response to CO test gas) appeared to be equilibrated, or at least to be close to equilibration, before 10 min. Once we tabulated the data, we arbitrarily defined sensor cross-sensitivity responses to nontarget gases (e.g., CO sensor responses to non-CO gases) as significant — and thus warranting

correction — *if* the sensor response to the nontarget gas were at least 10% of same sensor response to the SEAL2 level of its target gas. This approach, while it ignored effects we regarded as less significant, both identified the cross-sensitivity responses thought to be potentially important in shaping the accuracy of the target gas readings and accommodated the common situation in which sensor readings of the target gas did not always match those certified gas concentrations. We believe that the latter situation resulted partly because gas standards from different vendors are often disparate — especially for *reactive* gases, a term that characterizes most of the SEAL gases — as we previously discussed in the **Evaluation of pressure correction and calibration with test dives** subsection.

As expected, some significant cross-sensitivity responses were found during the three cycles of four-day testing. However, the initial version of the software was only partly successful in reducing these cross-sensitivity effects. Therefore, ENMET subsequently developed a second version of software to improve and facilitate the difficult process of eliminating, or at least reducing, these cross-sensitivity effects. Testing, in the same fashion as before, was then repeated. Unfortunately, results with the second version of software were similar to those from the first; thus, we have reported only those results from the second software version — with which, again, compensation for the unwanted effects from other gases is still incomplete.

When we initially examined the results from the second software version (Table 2), we found it encouraging that the uncorrected and corrected readings for each of the eight target gases (e.g., the CO sensors' responses to CO test gases) are approximately the same. (Note that the uncorrected readings of each target gas are marked with a "T" ["target gas"] to ensure easy identification.) This finding suggests that the compensation software did not significantly affect the target gas readings, an outcome which should be the first requirement that any compensation software must meet.

We also combined the two sets of three SO₂ tests for a total of six tests in Table 2, since no difference in the range of SO₂ readings, or in the range of the nontarget gas readings, was apparent between these sets. For the Cl₂, although we did observe that the first test during each of the three weeks of testing tended to produce a lower range of Cl₂ readings than those from the subsequent tests, the nontarget gas readings (i.e., the cross-sensitivity responses) were similar among them. Thus, when we also combined the two sets of tests each week with Cl₂, those lower Cl₂ readings from the first tests produced a range in Cl₂ readings wider than that shown by the second set of Cl₂ readings alone.

With the 10% target gas criterion we defined four paragraphs above and the "significant" cross-sensitivity responses set in boldface in Table 2, the data show three SEAL gases (H₂S, SO₂, and HCN) that each significantly affect three other nontarget gas sensors. Four other gases (CO, Cl₂, HCl, and NH₃) each significantly affect one or two nontarget sensors — while NO₂ affects no other nontarget sensors. (We ignore the effects of the NO₂ and Cl₂ test gases on NO₂ and Cl₂ readings: These effects are expected, since the same NO₂/Cl₂ sensor is used for both gases.) The cross-sensitivity responses found

during the three cycles of four-day testing compare well, although not completely, with the cross-sensitivity results (Figures 23–29) based on the mV responses from the SubTox — especially if the comparison is directed toward the “large” effects reported in the **Cross sensitivity of sensors to SEAL gases: mV** subsection above.

To consider cross sensitivity in another way, we found that two sensors (CO and NH₃) were not significantly affected by the other SEAL gases, while the other five sensors (including the one NO₂/Cl₂ sensor used both NO₂ and Cl₂ readings) were affected by from one to six other SEAL gases. However, since the HCl sensors performed so poorly throughout the entire testing — and since the NH₃ sensors were new candidates that underwent only limited, and no hyperbaric, testing — we urge caution in drawing conclusions about the cross-sensitivity effects given in the data from these two sensors.

So, from a total of 15 significant cross-sensitivity responses with the compensation software turned off (boldface responses, Table 2), four of these responses appear to have been fully corrected to ~0 ppm (Table 2 responses noted by a “C” and the “unbolding” of the readings). Three other responses (noted by a “PC”) were partially corrected, five responses (noted “NC”) seem not to have been corrected much at all, and in three cases, the correction was noted as questionable (“?”) because its effectiveness was difficult to judge. These mixed results were expected, because we had always assumed that an acceptable solution to cross-sensitivity effects would probably require multiple iterations of software refinements followed by retesting. Unfortunately, we ran out of time on this project and had to end this testing.

Ammonia sensor

As the SubTox was being developed and evaluated, ENMET was attempting to identify (through discussions with various sensor manufacturers) a reliable hyperbaric NH₃ sensor that the monitor could use. The first two NH₃ candidate sensors provided for our testing were found to leak following hyperbaric exposure at NEDU. The last candidate sensor, installed in two SubTox monitors near the end of this project, was used only for our cross-sensitivity testing at 1 ATA and was never tested at pressure. Consequently, the limited testing results from this last NH₃ candidate sensor prohibit any decision about its suitability for use in the SubTox.

Water tolerance

NEDU did not perform any testing of SubTox’s ability to tolerate water immersion. Instead, to initially evaluate the prototype’s watertightness, we relied on ENMET to water-test two of the monitors. The first testing showed that after 5 min of immersion with ~1 foot of water covering the case, a few water drops were found inside one monitor’s case after it had been removed from the “dunk” tank. A second monitor, following a 15 min immersion, allowed considerably more water inside. In both cases, the source of the leak appeared to be at least one of the three push-button switches on the front of the SubTox case.

ENMET therefore located and installed new switches that did not leak, but limited testing by NEDU found that pressure during hyperbaric exposure actuated these new switches — a result apparently due to their not being vented to the atmosphere. Venting these new switches by drilling a small hole in their sides was subsequently shown to prevent them from actuating under pressure. ENMET, however, decided to return to using the original switches — and to install rubber “boots” on their outsides. When these booted original switches were tested, they prevented water entry and proved to be unaffected by pressure. Future plans for any first-production monitors are to use a vented switch designed with protection from liquid ingress, and ENMET has identified such a switch for the SubTox application.

ENMET also tested the ability to restore SubTox to operation following a dunking. When one SubTox was dunked under the water, the increased flow resistance actuated its automatic pump shutoff, which shut off the monitor in ~15 sec. Upon inspection, no water was found to have passed the hydrophobic filter on the inlet. When the filter was then removed by unscrewing the inlet port nut, it was easily cleared by a mouth blowing air through it. Following filter reinsertion, the monitor was restarted with no further problems.

Such limited testing suggested that the SubTox prototypes could be safely immersed and subsequently restored to operation. Improved switches would also make their rubber booties unnecessary.

Alarms

To prevent the alarms from being triggered under most testing situations, laboratory testing was conducted with the monitor’s visual and audio alarm limits set at the upper ranges of each of the SEAL gases (two times the SEAL2 values of each gas). We did not purposely test any of the alarms, but we did occasionally observe that, under over-range conditions, the LED alarm light flashed and the upper range gas value displayed on the LCD blinked. Early in our testing, we disconnected the internal lead of the audio alarm to prevent it from going off. However, we did confirm a few times that the audio alarm would shut off after the mute function had been activated by touching the mute button on the front of the SubTox case.

GENERAL PERFORMANCE

During the development and evaluation of SubTox, the six prototype monitors were tested for hundreds of hours in the laboratory. Analyzers generally worked well, without incident, during most of the testing. The display menu was easy to follow and simple to use, even with little training; data logging and downloading were easy to accomplish and invaluable for our laboratory evaluation.

However, as with any electrical instrument (especially with the unproven SubTox prototypes regularly undergoing various hardware and software modifications during this project), occasional problems resulted. In addition to addressing such hardware and

software problems and making the modifications discussed seriatim in the preceding subsections, some of the miscellaneous laboratory problems we encountered include the following.

1. Pump shutoff occurred in two units. ENMET diagnosed one incident as resulting from small amounts of particulate matter collecting inside the pump; ENMET corrected this simply by cleaning the pump. Another shutoff seemed related to an unexplained change in pump settings that had been stored in SubTox's memory and had caused the shutoff. A resetting of pump settings corrected this latter problem.

2. During compression, one simultaneous implosion of a Cl_2 sensor and an adjacent "dummy" sensor occurred in one monitor, with two results: The top of the dummy sensor (used to fill the empty space in the manifold where an NH_3 sensor would eventually be located when this sensor became available) was broken, and a considerable amount of electrolyte leaked from the cracked Cl_2 sensor, with this electrolyte spilling onto an adjacent HCN sensor.

This incident occurred when we were trying to improve the water resistance of the submerged SubTox case, and, as discussed in the **Water tolerance** subsection, the case had been fitted with three externally vented switches, with rubber boots attached to each. At the time, we wondered whether the switch modifications influenced the sensor implosion. However, no other sensor implosion resulted, so we conclude that this incident was merely a random failure.

3. When standing upright, the initial SubTox monitor was rather unstable and susceptible to tipping. Mechanical extension "feet" were subsequently added to the monitor case to enhance the monitor's stability and its support when it was positioned upright.

FIELD TESTING OF SUBTOX

Though some of the SubTox software was still undergoing modifications, we began field testing the monitor near the end of its development period, when we had a working version that was expected to function similarly to the final-version prototype.

METHODS

Field testing consisted of both (1) making dockside comparisons (indoors, *not on submarines*) between using the SubTox and using detector tubes to measure SEAL2 or SEAL1 levels of test gases from commercially obtained cylinders, and (2) monitoring, without test gases, the atmospheres of different spaces aboard submarines. Because of concerns about using toxic gas mixtures on submarines, no such gases were used aboard submarines. During all testing, a major consideration was to involve submarine

corpsmen in the testing — so that they could gain SubTox experience and an understanding of the new monitor's capabilities.

Initially all field testing was coordinated by NEDU's Diving Medical Officers (DMOs) who, desiring "ride time" toward certification as Undersea Medical Officers (UMOs), arranged trips on submarines as opportunities arose. After being trained at NEDU, these participating DMOs arranged scheduling with submarine personnel, brought all testing gear (including gases) to the test site, trained submarine personnel on site to assist with field testing, and ensured that testing was completed correctly. For convenience, all DMO trips (with one DMO going on each trip) were on submarines operating from King's Bay, GA, so that they could easily travel from NEDU by private vehicle and transport all the gear to the site where the submarine was accessed. (Driving to the test site was also important because it eliminated the need to transport the gas cylinders by air.)

As field testing progressed, INSURV personnel also volunteered to carry a SubTox monitor with them during their inspection trips, to demonstrate its use, and to gather submarine atmosphere data. Before these INSURV personnel participated in any testing, telephone conversations were held to talk them through the use of the SubTox monitor.

All field testing by the DMOs and INSURV personnel was done per an NEDU test plan, with test results recorded on the data sheet provided therein, the SubTox readings collected via the SubTox data logging function, and the logged data subsequently downloaded upon the return of the DMOs to NEDU. That the results from this testing were considered to be research data and *not data to determine the status of the submarine atmosphere* was made clear to all involved.

For each field test, NEDU supplied one or two SubTox monitors, spare batteries for them, digital thermometers for measuring ambient temperature, and all other equipment required for testing. Before the equipment was transferred from NEDU to the test site, the SubTox monitors were set up to automatically log data at 2 min intervals (for the first two field tests) or at 5 min intervals. (The 5 min logging intervals allowed data to be logged over a longer time, until the logging memory was full.)

If dockside testing were planned, test gases, detector tubes, and detector tube sampling apparatus were also provided. All of the four gases selected for field testing (CO, H₂S, SO₂, and NO₂) at SEAL1 or SEAL2 levels were in 33A-size aluminum cylinders containing ~900 L each: more gas than was needed, but available in the minimum cylinder size that the vendor was willing to supply for some of these gas mixtures. For initial testing, we planned to use two of the four test gases at their SEAL2 concentrations, since two cylinders were expected to be practical for NEDU participants to haul to the test site. The additional gases and concentrations less than those SEAL2 levels that were procured allowed changes to be made in testing procedures, if such changes became desirable.

Dockside testing

Dockside testing involved NEDU DMOs and submarine corpsmen challenging the SubTox with different test gases before or after submarine deployment. Detector tubes were also used to test the same gases and to compare the relative time and effort required by the two methods. However, with such limited testing and with prototype SubTox monitors still being refined in the laboratory, we emphasize caution in drawing conclusions — from dockside results — about the relative accuracy of the two methods.

Gas was sampled by the SubTox and by detector tubes via Tedlar gas sample bags, after these bags had been purged with the test gases. This method was identical to that used during the SubTox laboratory testing, and it contained the gas during delivery, a method limiting both the gas usage and the potential gas exposures for personnel involved in the testing. Using SEAL1 and SEAL2 levels of individual gases in this way minimized exposure risk, especially since test procedures called for adequately ventilating the dockside test site during gas usage.

Submarine testing

Following any initial dockside gas challenge testing, test gas cylinders and other items were stored dockside, and the two SubTox monitors and some limited testing gear were moved aboard. Corpsmen were then given some additional training before onboard testing began. Once underway, testing consisted of NEDU or INSURV personnel, with submarine corpsmen, using the SubTox to monitor selected spaces on the submarine. We preferred to perform this testing daily, although its frequency depended on the availability of the testers and the permission needed to move throughout various spaces aboard the submarine.

As the atmosphere within the submarine spaces tested with SubTox was expected to be relatively free of the toxic gases the monitor measured, this SubTox screening was expected to be uneventful and primarily an exercise in using the monitor to acquire user input about its procedures and features as well as to confirm that it worked correctly in the submarine atmospheric environments of low-level contaminants. However, we thought that, due to interfering species such as H_2 , which significantly affects responses in currently available CO sensors, testing might show some elevated SubTox gas readings. When it was possible, we obtained records from the Central Atmosphere Monitoring System (CAMS) to assist with evaluating SubTox H_2 and CO readings, although these records were of questionable value for interpreting other gas readings not directly reported by CAMS.

Between submarine inspections, INSURV personnel kept possession of the one SubTox they held, and they updated NEDU via E-mail or telephone on testing progress. When needed, NEDU assisted INSURV in answering any questions and in correcting any problems that arose during testing.

Completion of testing

After all testing had been completed, participating NEDU and non-NEDU personnel completed questionnaires on the SubTox and its testing. NEDU's DMOs returned the gear and the completed data sheets to NEDU, the logged SubTox data was downloaded, and the trip was discussed with the DMOs.

RESULTS AND DISCUSSION

NEDU DMOs and INSURV personnel tested the SubTox on more than nine Los Angeles Class, SSGN, or Ohio Class submarines between May 2010 and December 2011. Three NEDU DMOs completed four trips to submarines to coordinate the onboard field testing: two trips on SSGN submarines and two on Ohio Class submarines. Other trips were planned or anticipated, but last-minute changes in deployment schedules cancelled these additional trips. Dockside tests involving SubTox and detector tube comparisons were made on only the second NEDU trip; however, testing aboard submarines was done during all four of the NEDU trips. On all the other trips, INSURV personnel demonstrated and tested SubTox during their official submarine inspections.

To avoid making this report excessively long, results are summarized below. In addition, some anecdotal impressions from the DMOs (in some cases, with minimal changes in wording from those DMOs' written comments provided to NEDU) and from the submarine crews — where these crews' impressions are thought to usefully convey their responses to SubTox — are included.

Dockside testing reported by NEDU DMOs

Dockside testing went smoothly during the second field test trip in August 2010, with four Navy enlisted personnel participating with the DMO. Two challenge gases were tested — first, with two SubTox monitors, and then with two detector tubes, each of which was designed for one of the two gases: 85 ppm CO and 30 ppm SO₂ (both of these gases at SEAL2 levels and certified by the supplier to 1% of their stated concentrations). After a 10 min exposure, SubTox readings were 91 and 79 ppm for the CO, and 29 and 26 ppm for the SO₂. Detector tube readings were 27 ppm for the CO, and 15 ppm for the SO₂. Each SubTox had been calibrated in the lab three to four months earlier, and the detector tubes had been purchased within several months of their use and were well within their time limits for recommended use with an expiration date of April 2012,. Although we again caution against drawing conclusions from such limited data, the disparity in results between the SubTox readings and those of the detector tubes was surprising to us and points out the potential for large errors when detector tubes are being used.

Submarine testing reported by NEDU DMOs

Three DMOs completed four trips, during which they had good access to various areas on the submarines they were aboard. Each field trip is separately summarized below:

Field testing trip #1.

The following areas on the submarine were monitored during three days of testing with one SubTox monitor: the engineering compartment, the missile compartment, and the forward compartment (crew's mess, control room, refrigeration area, and torpedo room). During testing, the CAMS data for the fan room was recorded, as well as the CAMS CO readings for each area. Except for CO, all SubTox readings of the SEAL gases were low (0–1 ppm), while those for CO ranged up to 8 ppm (~6 mTorr). In all cases, CO and H₂ levels from the CAMS were 0–1 mTorr and 0.0 Torr, respectively. Sampling was done at ambient pressures after a variety of procedures (i.e., ventilating and snorkeling). The snorkeling sampling with SubTox was made in conjunction with the independent duty corpsman (IDC) conducting detector tube testing for NO₂ per requirements other than those for our testing. Snorkeling sampling showed that NO₂ levels for all but one area was 0 ppm by tube and SubTox; the exception was an area that had a 0.5 ppm tube reading for NO₂ and a 1 ppm SubTox reading (with SubTox readings displayed to the nearest 1 ppm) for NO₂.

The DMO reported the SubTox monitor to have performed “perfectly” during the entire field test; it stabilized very quickly (within a minute or so) once it was started up in preparation for testing. Only one set of batteries was used for all testing, and these batteries were still at 58% at the time of disembarking.

Field testing trip #2.

The DMO completed four days of testing on various areas of the submarine while it was underway during a short mission that included an inspection by the INSURV team. With the exception of CO and HCl, most SubTox readings of the SEAL gases were generally low (0–1 ppm), while CO ranged up to 6 ppm and HCl up to 9 ppm. However, the DMO had the opportunity to sample a loaded Tomahawk missile tube when the IDC was gas freeing the space for an inspection: A smell similar to that of wet paint or lacquer was in the area, and the IDC felt light-headed. However, the detector tubes used to sample the missile tube showed 0.2% CO₂, 0 ppm CO, and 0 ppm toluene; as measured with an explosimeter, H₂ also displayed 0% of its lower explosive limit. On the other hand, one SubTox registered up to ~130 ppm CO, 6 ppm H₂S, and 6 ppm SO₂. Due to this space's smell and the wooziness it caused, access to the space was declared limited to those personnel breathing via the Emergency Air Breathing (EAB) System. The DMO did not know whether the SubTox was registering CO, but he thought it likely that the monitor was registering some contaminant at high levels. Members of the INSURV team were present during this test, and all were impressed. The logged data subsequently downloaded at NEDU confirmed the high gas levels that the SubTox had recorded at the missile tube.

Field testing trips #3 and #4.

The same DMO went on both these trips. SubTox readings were generally low (0–1 ppm) for most of the testing. However, CO readings ranged up to ~130 ppm a few times, with corresponding CAMS data showing 0.3 Torr H₂ — the latter reading possibly accounting for some, if not most, of the CO response. During another period of testing, elevated Cl₂ and NO₂ readings were also observed up to the maximum displayed value of 5 ppm for Cl₂ and up to 8 ppm for NO₂. Since Cl₂ and NO₂ readings were measured by the same sensor, it is impossible to tell whether the contaminant was Cl₂, NO₂, or some other species. Furthermore, CAMS data were unavailable for this time, and Draeger tube readings showed undetectable levels of Cl₂.

After the batteries had been removed for several days during transport of the SubTox equipment to the field testing site, reinstalling the batteries and restarting the monitor were observed to produce very high short-term readings for some of the gases (e.g., 60 ppm of H₂S, the maximum reading displayed by SubTox). These elevated readings subsequently diminished and stabilized. As discussed earlier in the **Battery duration and related problems** subsection, this phenomenon had been observed in the laboratory with an early hardware version of SubTox (which was being used during trips #3 and 4), and it was attributed to voltage having been removed from some of the sensors during storage. This undesirable response was corrected in later versions of SubTox.

Summary of comments from trips #1 through #4.

While aboard the submarines, the DMOs were able to demonstrate SubTox to the COs, XO's, chiefs of the boats (COBs), IDCs, and other crew members. The Squadron Deputy Commodore, who was aboard during one trip, was also able to see the monitor. The SubTox was well received, and many pleas were made to leave it behind.

From the cost and complexity of using the detector tubes, as well as the burden of maintaining in stock the required inventory of in-date tubes, all personnel aboard saw the value of replacing them with the SubTox. Another advantage that the Deputy Commodore saw for the DISSUB monitor was in using it during a fire situation, regardless of whether or not the situation was related to a DISSUB. Finally, the DMO wrote that the positive response to SubTox further emphasized the importance of completing the development and testing of the prototypes so that it could be transitioned to the Fleet as soon as possible. Once it had been initially transitioned, further consideration could then be given to increasing its capabilities to cover additional gases (e.g., O₂ and CO₂, now monitored on submarines with the Analox hyperbaric O₂/CO₂ monitor) as well as total hydrocarbons, since these gases were “wish-list” items mentioned by various crew members who had been involved in the testing.

While everyone was excited to see the SubTox, both the CO and the head of INSURV had anticipated that it would replace the portable Analox O₂/CO₂ monitor. In response, the DMO explained to everyone that the SubTox was designed for the specific task of monitoring the eight SEAL gases, not the normal atmospheric O₂ and CO₂ gases. However, the CO, the head of INSURV, and all IDCs expressed strong interest in

adding O₂ and CO₂ sensor capabilities to the SubTox, so that it could monitor the complete atmosphere. In addition to O₂ and CO₂ sensors, the IDCs stated that they would like to be able to monitor toluene (or an equivalent indicator of hydrocarbon contamination) and Freon.

"This thing [SubTox] is awesome!" was one of the many comments provided by onboard personnel who were overwhelmingly positive about the SubTox. Another voiced his appreciation of its capabilities by stating, "I hate Draeger tubes" — an implicit expression of his approval of the monitor's capabilities, since the onboard personnel who routinely use the Draeger tubes were, overall, extremely hopeful that the SubTox would be available to the Fleet. Everyone on board — including the XO's and CO's — showed great interest and enthusiasm for replacing the Draeger tubes with the SubTox. Since Otto Fuel is the propellant used in torpedoes, the torpedo personnel also were especially excited: Spills of Otto Fuel release HCN, and therefore considerable expenditures routinely must be made to obtain Draeger tubes for Otto Fuel spills, drills, and training.

INSURV testing

As of June 2011, INSURV personnel had demonstrated and tested SubTox on three Los Angeles Class submarines. Since then, INSURV has demonstrated the SubTox on some additional submarines. Although SubTox readings were normally low, testing did occasionally produce elevated readings, as seen in some of these results:

1. The diffuser outlet for an O₂ candle furnace was sampled at light-off. CO peaked at 29 ppm and then, after a couple minutes, leveled off at 10 ppm. NO₂ peaked at 10 ppm and then, in a couple minutes, returned to 0 ppm. Cl₂ alarmed at 2.5 ppm, peaked at 2.8 ppm, and leveled off at 0.2 ppm in a couple minutes. The short burst of salt smoke had no apparent ill effect on the monitor.
2. During another test, the candle furnace light-off showed that diffuser outlet CO peaked at 131 ppm, then leveled off at 22 ppm. The Cl₂ peak was >5.0 ppm (over the SubTox's range) before that gas then leveled off at 0.8 ppm.
3. The air 1 foot away from an O₂ candle furnace was sampled at light-off. CO peaked at 13 ppm and leveled off at 4 ppm. NO₂ and Cl₂ were not detected.
4. The air in the Auxiliary Machinery Room (where the diesel engines are located) was sampled during diesel operation. Although a strong smell of hot oil was in this space, SubTox showed no response in its SEAL gas readings.
5. When the air near the CO₂ scrubbers was sampled, the common amine/ammonia smell was present. And while no NH₃ sensor was installed in the SubTox, no monitored gases were detected.

One notable result occurred following the INSURV tester's commercial plane flight to a site with the testing gear, including one SubTox, transported as checked baggage. After the batteries had been installed and the monitor turned on, the SubTox showed the initial startup display screen but did not advance to the normal operating screens. ENMET's subsequent evaluation of the problem monitor revealed a blown transistor, which ENMET believes had resulted from a voltage spike traveling to the transistor from the battery compartment. Although NEDU had changed batteries in all six SubTox units many times, this incident was the first sign of such a problem, and it was thought possibly to result from a static discharge in the dry submarine atmosphere during battery installation. ENMET concluded that, to prevent this transistor from being so blown, a resistor in this circuit should have been protecting it — but somehow such a resistor had been omitted from the original design. ENMET added a resistor to correct this problem.

Summary of comments by INSURV personnel:

1. Underway, corpsmen use Draeger tubes for weekly monitoring, gas free engineering for tank and void entries (usually unplanned), four-hour monitoring when CAMS is inoperative (unplanned but common situations) at sea, and atmosphere monitoring following fires (unplanned). The Guard Book tells the senior survivor to inventory the Draeger tubes in the compartment and create a toxic gas monitoring plan based on the available inventory. Thus, the Draeger tube inventory defines what toxic gases are monitored. However, possibly no survivor in the compartment may know where to find the Draeger tubes or how to use them properly, even under ideal conditions.

2. The interviewed corpsmen indicated that SubTox would be very useful as part of the normal atmosphere monitoring program, since the monitor detects many of the same gases that the corpsmen use Draeger tubes to monitor.

3. The submarine electrical technicians (ETs) indicated that the SubTox could also supplement or even replace their current atmosphere monitoring equipment. Since the SubTox case can hold more than 12 gas sensors, this capacity would allow the list of monitored gases to be expanded. If O₂ and CO₂ sensors were added, for example, SubTox could replace the Analox O₂/CO₂ monitor. With the H₂ monitoring, if a refrigerant sensor and a plug-in power supply were added, the SubTox could also replace CAMS — a big, heavy, and expensive piece of equipment. One submarine provided its repair cost data for CAMS: Since May 2008, the submarine — one that had spent most of its past three years in port or in the shipyard with CAMS secured — had spent \$131K on three CAMS A5 module replacements. And this submarine is not exceptional: The A5 module is a common-failure item in the Fleet. The submarine community should consider the potential cost savings from eliminating Draeger tubes, Analox, and eventually CAMS.

4. The disadvantages of Draeger tubes include the following:

A. Tubes are one-time-use items with a limited shelf-life.

- B. Each type of tube can monitor only a single gas.
- C. Special training is required to use the tubes.
- D. Each tube has a different color code, and using the wrong tube is a concern.
- E. Tubes are difficult to use while gloves are being worn (a situation common during damage control).
- F. Tubes are known to be inaccurate.
- G. Tubes are not rated for hyperbaric use (and are thus dubiously useful in DISSUB situations).
- H. Tubes are difficult to use in low light (a familiar occurrence in DISSUB situations).
- I. Pre-deployment planning for adequate tube supplies is difficult because tube usage is highly variable, and leftover tubes are used for DISSUB monitoring.

FEATURES OF FINAL-VERSION SUBTOX PROTOTYPES

As laboratory testing proceeded, the initial SubTox prototypes were refined, through an iterative process of repeated testing followed by manufacturer modifications, to better meet NEDU requirements. However, not all the modifications that have been made to the final-version prototypes have been fully tested or herein discussed in detail. Yet we believe that all the features of the final-version SubTox prototypes that this section describes have been developed and tested sufficiently to allow them to be incorporated into any first-production monitors. Subsequent review and testing of the first-production monitors will indicate needs for further improvements in performance.

FEATURES

The final version of the SubTox prototype has the following features:

1. It monitors the eight SEAL gases — NH_3 , CO , Cl_2 , HCl , HCN , H_2S , N_2O , and SO_2 — as well as H_2 , with all gas readings updated several times a second.
2. It measures concentration ranges from 0 to 2 times SEAL2 levels (see Table 1) for the eight SEAL gases, and from 0 to 1% for H_2 .
3. Its electrical power is supplied by six D-cell alkaline batteries, with an expected battery life of >3 days of continuous operation with its gas sample pump on.
4. Its operating conditions include the following parameters:

Pressure: up to 5 ATA.

Temperature: 0 to 50 °C (32 to 122 °F).

Relative humidity: dry to 99% (noncondensing).

5. It includes a waterproof gas sampling inlet, mass flow and pressure sensors, a data logger, an LCD display with adjustable backlighting, a computer interface, and a brushless sample pump (with an adjustable duty cycle).

6. Its LCD (see Figures 31A–31B) displays values or coordinates operations for the following:

Uncorrected and SEV values of all SEAL gases.

Sample pump flows, pressure (ATA), inlet temperatures, battery voltage, and H₂.

Battery life, date, time, and pump mode — per a status screen.

Information screen.

Logger menu.

7. Software with passcode protections and compensation of gas readings for ambient pressures, ambient temperatures, and cross sensitivities among gases are provided via its

VB and SubTox codes, which have many capabilities (see Figure 31C);

final-version VB code = 1.2.2, and final-version SubTox code = 10.10; and

ability to load test data for calibration and compensation of gas readings.

8. Two user-selectable alarm modes are provided: one visual (LED, and a blinking display on LCD), and the other audio (with a mute capability). In addition to the original “nonlatching” mode (in which the audio and visual alarms cease as soon as the gas concentrations become acceptable), the user can select an alternative “latching” mode so that, once triggered, the alarms will continue — even if the gas concentrations return to acceptable levels. This latter mode ensures that even when test personnel are briefly away from the immediate area, they do not miss a transient alarm.

9. Its data log reviewer allows users to scroll down the display screen to view gas readings already logged.

10. Its peak display function allows users to display maximum gas readings during a recorded time period.

11. It includes additional passcode-protected functions.

Suggested improvements to SubTox

We expect the most promising improvement for SubTox’s performance to be that of better gas sensors, which would have the following requirements:

1. Sensors that show reduced response to pressure, and thus require less compensation for pressure — improvements presumably resulting in greater accuracy and reproducibility in recorded data.

2. A CO sensor with much-reduced sensitivity to H₂ — although until a market demand develops for such sensors (i.e., until SubTox is transitioned to the submarine Fleet, since the submarine atmosphere is the only apparent place where CO would be monitored alongside significant H₂ levels), we expect no company will invest the time and money to develop such sensors.
3. An improved HCl sensor — with improvements both in its gas responsiveness and in the repeatability of its recorded data, since our limited testing suggests that the current sensor does not seem to work well.
4. An NH₃ sensor that has been shown to work reliably at pressures up to 5 ATA. (This may be the current candidate NH₃ sensor, which has not yet been fully tested.)

Unfortunately, without transition of SubTox to the Fleet, we do not expect a large commercial interest in pursuing any of these four objectives — except, perhaps, that of improving the HCl sensors, since these should have many other applications besides those in submarines.

Beyond H₂'s effects on CO sensors (and, to a lesser extent, on H₂S sensors), we see little possibility in the immediate future that any sensor manufacturer will reduce the wide range of cross-sensitivity responses commonly seen (and acknowledged) with most electrochemical sensors. Our attempt to address the problems generated by the cross sensitivity of toxic gas sensors in SubTox is the first such attempt we know of and, as expected, it has been only partly successful. Thus, improved software to minimize how the gas sensors used in SubTox (and in other applications) affect nontarget gases is a real need.

SUBTOX VS. PROJECT SPECIFICATIONS

If we attempt to compare how well the final-version SubTox meets the monitor requirements adopted for this project, several considerations complicate such a comparison. Since the feasibility of some of the essential requirements for any prototype monitor was difficult to predict in advance, we expected our early testing of prototype monitors to help refine these requirements by suggesting which of them could be easily met, which could be possibly met only with some effort, and which could not easily be met.

The following list reviews each of the requirements identified in the **MONITOR REQUIREMENTS** section and, directly below each, assesses how well the final-version SubTox meets that requirement.

1. Capability to effectively measure one or more of the following eight SEAL gases of concern: NH₃, CO, Cl₂, HCl, HCN, H₂S, NO₂, and SO₂.

SubTox: SubTox meets these requirements — except for monitoring NH_3 , since an acceptable hyperbaric sensor for that gas remains to be identified. In addition, a sensor for monitoring H_2 was added to SubTox.

2. In general, ruggedness, reliability, user-friendliness, and field compatibility. The important operating criteria are that the analyzer operate under hyperbaric conditions; compensate, if necessary, for changes in ambient temperatures; and minimize, where possible, sensor cross sensitivity to other gases — particularly any cross sensitivities among the eight SEAL gases.

SubTox: SubTox meets most of these requirements — although its capability to compensate for ambient temperatures was deemed unnecessary (and was therefore not implemented), and the software used to compensate for sensor cross sensitivities to other gases was only partially successful.

Essential requirements

1. Eight gases measured, in the following measurement ranges and units:

NH_3 : 0 to 250 ppm
 CO : 0 to 300 ppm
 Cl_2 : 0 to 5 ppm
 HCl : 0 to 70 ppm
 HCN : 0 to 30 ppm
 H_2S : 0 to 60 ppm
 NO_2 : 0 to 20 ppm
 SO_2 : 0 to 60 ppm

where ppm = parts per million. All eight gases in balance air were to be displayed simultaneously in ppm with one or more monitors.

SubTox: SubTox meets these requirements, although all concentration ranges are from 0 to SEAL2 levels of the gases — so CO is presently measured from 0 to 170 ppm. But this range could be easily expanded to one of 0 to 300 ppm.

2. Minimal display resolution for concentrations: no less than 5 ppm for NH_3 and CO , and 1 ppm for the other six gases.

SubTox: All gases are displayed and logged ± 1 ppm, except for Cl_2 — which is displayed and logged ± 0.1 ppm.

3. To minimize the total number of analyzers incorporated in the monitor, the number of sensors within it should be maximized.

SubTox: A single monitor allows measurement of all SEAL gases.

4. Operating and storage conditions:

Pressure levels: from 0.8 to 5 ATA.

Temperatures: from 4 to 50 °C.

Relative humidity: dry to 99% (noncondensing).

SubTox: Per the manufacturer's specifications, SubTox meets these operating conditions — although it was not tested at pressures <1 ATA or at the extreme cold and hot temperatures. And although only limited humidity testing was done (for reasons discussed in the earlier **Relative humidity** subsection), the testing of the sensor manufacturers provided bases for expecting that humidity was not to significantly affect any of the SubTox's electrochemical sensors.

5. To eliminate the risk of explosions at pressure, if a gas sampling pump is needed, then a *brushless* pump is required.

SubTox: The SubTox uses a brushless pump.

6. Since analyzers will be exposed to high humidity and may have some water contact (including that from being potentially dropped into the water) during use, the device should be water resistant.

SubTox: ENMET testing suggested that the SubTox prototypes could be safely immersed and subsequently restored to operation.

7. The device should be capable of being easily carried throughout the various spaces of a submarine to monitor the atmosphere.

SubTox: The SubTox monitor is portable.

8. The device should be powered by nonrechargeable batteries capable of operating for seven days at 20% duty cycle, or three days of continuous operation.

SubTox: The monitor meets the required power specification for being capable of three days of continuous operation.

9. The monitor should have both visual and audible alarms, with selectable limits.

SubTox: The SubTox has both visual and audible alarms, but these have not been fully tested.

10. The monitor's displayed readings need to be readable in low-light areas.

SubTox: The SubTox's backlighting includes a variable control to allow "night vision" to be maintained.

11. The monitor needs to be simple to operate — to be a standalone unit (e.g., one not requiring a computer or other type of controller) capable of being easily operated by Navy submarine personnel. (The only qualification to this requirement is that any data logging capability would presumably require a computer for downloading data.)

SubTox: The SubTox meets this “simplicity” requirement.

12. The monitor needs to be rugged — stable, electronically and mechanically, under field conditions expected on a submarine under both nonaccident and accident conditions.

SubTox: Field testing shows that SubTox meets this ruggedness requirement.

Desired but not essential requirements

1. Calibration: performed at the factory and possibly also at Navy facilities.

SubTox: The SubTox transition plan includes this required procedure.

2. Precision, a requirement defined as the repeatability of short-term (≤ 10 min) gas readings, as determined by individually sampling in the laboratory at 1 ATA each of the eight gases at their SEAL2 concentrations: $\pm 5\%$ relative for each of the eight gases.

SubTox: Expressing our precision (now in \pm ppm) in relative percent, SubTox meets this requirement — except for HCl, the sensor for which was so unstable that its degree of precision could not be estimated; and for NH_3 , since the current NH_3 candidate sensor was not fully tested.

3. Accuracy (within 90 days of calibration) over pressure and temperature ranges, a requirement determined by individually sampling in the laboratory each of the eight gases at their SEAL2 concentrations: $\pm 30\%$ relative to each of the eight gases.

SubTox: Expressing our accuracy (now in \pm ppm) in relative percent, and incorporating the $\pm 5\%$ relative variation we estimated that temperature might add, SubTox meets this requirement (in the laboratory through its half-year of testing) for all gases — except for HCl and NH_3 (for the reasons briefly explained under the preceding “Precision” requirement). With the 1½-year data for many of the gases, SubTox also meets this Accuracy requirement. How the SubTox’s accuracy will be affected by its use in the field is unknown. However, even if we assume that some increase in error will result in the field, SubTox’s degrees of accuracy — particularly at pressure — should represent significant improvements in monitoring DISSUB toxic gases from those accuracy levels that detector tubes currently afford (see the **DETECTOR TUBE COMMENTS** section).

4. Chemical interferences: Each gas sensor's cross sensitivities to the other gases are to be minimized to meet accuracy limits with the other seven gases at their SEAL2 concentrations; H₂, up to 1%; CO₂, up to 6%, and VOCs at levels expected in the submarine atmosphere.

SubTox: Our two initial versions of compensation software were only partly successful in reducing the cross-sensitivity effects among the SEAL gases. Unfortunately, we ran out of time on this project and therefore had to end testing. CO₂ (~2500 ppm) and isobutylene (~20 ppm) at the levels tested did not appear to affect the readings of the SEAL gases. However, even at the relatively low levels of ~0.1% that we tested, H₂ significantly affected CO and, to a lesser extent, H₂S.

5. Sensor life: >1 year for all sensors.

SubTox: HCN and HCl sensors are warranted for six months, in contrast to the 12 months for which the other sensors are warranted. However, results from limited testing of sensor stability suggest that ENMET's six-month recalibration and sensor checks (with any replacements, if such are needed) appear to be a realistic initial approach. Until field experience suggests otherwise, useful sensor lifetimes should thus probably be viewed as six months, a period that we expect should still be practical for the Navy.

6. Response time: <60 seconds to 90% of the readings.

SubTox: Except for the HCl sensor (the poor performance of which has shown it to be unacceptable), the other sensors appear to meet this response requirement. However, full equilibration of gas readings takes several minutes for most sensors, and often >20 min for the Cl₂ sensor. The long Cl₂ response time may result at least partly from Cl₂'s interaction with the gas delivery system used for our testing as well as from SubTox internal hardware.

7. Weight: ≤10 lb.

SubTox: The SubTox monitor meets this requirement.

8. Maximum dimensions: 30 cm x 30 cm x 30 cm (1 ft x 1 ft x 1 ft).

SubTox: The SubTox monitor also meets this requirement.

DETECTOR TUBE COMMENTS

To compare the performance of detector tubes to that of SubTox requires both knowing how detector tubes perform under various conditions and understanding how procedures for using them can affect gas measurements. In our attempts to learn more

about detector tubes, we unfortunately found some surprising information (or a surprising lack of information) about such tubes — information that we share here.

At least several detector tube manufacturers list in their product information the standard deviation value for each of their tubes.^{17,18} Such standard deviations define the precision, or repeatability, of their multiple measurements — not the accuracy of those measurements, or how well those measurements agree with the actual concentrations of the target gases. Such standard deviations are commonly less than the $\pm 25\%$ level that users frequently, but in our view incorrectly, associate with the accuracy of these tubes.

The Safety Equipment Institute (SEI) — a private, nonprofit organization — administers an independent third-party testing and certification program (one which replaces that of the National Institute for Occupational Safety and Health) for a limited number of detector tubes.¹⁹ For SEI certification, detector tubes must meet, among other test criteria, accuracy levels of $\pm 25\%$ at 1.0 to 5.0 times the threshold limit value (TLV) concentration of the target gas, and $\pm 35\%$ at 0.5 times the TLV.²⁰ Unfortunately only a few types of tubes (currently 21, to the best of our knowledge) are eligible for the certification program. Although a recent (January 2013) online search suggested that detector tubes might be produced by at least seven different manufacturers, only 3, 19, and 21 tubes from three different manufacturers were listed on the SEI certified list.²¹

This limited listing, particularly the presence of only three tubes that are certified from a major supplier of detector tubes to the U.S. Navy, suggests that we really know little about the accuracy of many of those that the Navy uses. Furthermore, our recent repeated requests to one of these large manufacturers were unsuccessful in getting much useful information about the performance of its tubes — and no information about their accuracy either at the surface or at depth. In fact, the only study to have evaluated detector tube accuracy at depth (a study of CO₂ detector tubes, and the only one that we are aware of) concluded that the tubes did not work reliably under pressure.²²

Finally, the use of the detector tubes entails many concerns related to either the procedures for using them or their characteristics. Such concerns include the following:

1. The detector tubes are fragile and can be used only once.
2. The tubes are designed for a particular gas or gases, so multiple tubes may be needed to sample more than one gas.
3. Many tubes react to gases other than the one(s) for which they are designed to react (i.e., they react with cross sensitivity).
4. The tubes have a limited shelf life (often of one to three years), which can be shortened by storage at cold or hot temperatures.

5. Personnel who are to use detector tubes require special training, and preferably experience, in using them.
6. Measurements can be affected by how gas sampling is done and how the tubes are read (i.e., the tester[s] can subjectively influence the testing).
7. To ensure the reliability of the tubes, the sampling hardware for using them needs to be routinely checked.
8. Tube measurements may be affected by temperature and humidity.
9. Tube measurements may be affected by pressure — but little, if any, data are available about possible pressure effects on such measurements.
10. After sampling has been done, reading the length of a tube's color stain can be confusing, particularly if that stain is oblique, diffuse, or indistinct.
11. Using a detector tube requires good lighting both for sampling (e.g., to avoid being cut) a gas and for subsequently reading the tube measurement.
12. Tubes are expensive (and particularly so for the Navy and the Fleet, which uses large numbers and types of tubes routinely for various kinds of testing), and, since they often reach their expiration dates before being used, they must often be discarded.

In view of the features of SubTox and the concerns associated with the performance and use of detector tubes, using the SubTox monitor appears to offer significant advantages over using detector tubes.

CONCLUSIONS

1. Development of hyperbaric sensors for the SEAL gases, sensors that work reliably at pressure, occupied the initial phase of this project and was essential to the development of SubTox — to our knowledge, the first hyperbaric monitor of toxic gases.
2. Our extensive testing showed that the SubTox monitors generally worked well, were easy to use, and had many useful features including multiple display screens as well as data logging and data log review functions.
3. Laboratory testing demonstrated that the final-version prototypes met, or came close to meeting, most of the essential and the desired requirements identified in the **MONITOR REQUIREMENTS** section.

4. Immediately following sensor calibration, the accuracy of the pressure-corrected readings for most of the SEAL gases, as tested up to 5 ATA at 25 °C, was acceptable — and remained so for up to ~6 months (for a few gases, it remained so for up to ~18 months). Unfortunately, all HCl sensors we tested performed poorly, and we never identified an acceptable hyperbaric NH₃ sensor before the SubTox project ended.
5. Developing a mathematical technique to compensate SubTox gas readings for the effects of pressure required considerable work, but the compensation tool adopted for the final-version prototypes appears to work well.
6. The last version of cross-sensitivity software we tested was only partly successful in reducing or eliminating the effects of other gases on displayed gas readings. In our attempts to improve the software, we unfortunately ran out of time on this project.
7. The effect of ambient temperature on sensor signal was generally small ($\pm 5\%$ relative), so we did not evaluate the software that ENMET provided to correct for temperature.
8. Humidity was shown to have negligible effects on CO readings, and, although technical reasons kept us from evaluating how humidity affected the other gas readings, results from testing by sensor manufacturers have suggested that humidity is not expected to significantly affect any of SubTox's electrochemical sensors.
9. Results from our limited testing of sensor stability suggest that ENMET's proposed 6-month recalibration and sensor checks (with any sensor replacements that may be necessary) appear to be a realistic initial procedure for using SubTox monitors in the Fleet.
10. We expect that the one general change that would improve SubTox performance the most would be better sensors. Some desired advances in sensor performance would include (1) gas sensors that are less responsive to pressure than the current ones are, (2) CO sensors with much reduced sensitivity to H₂, (3) HCl sensors with improved responses and performance repeatability, and (4) NH₃ sensors that have been confirmed to work reliably at pressure.
11. Manufacturer recommendations have provided the basis for operating procedures to direct the general use of SubTox in monitoring the atmosphere for SEAL gases and H₂. Using Navy SEAL limits, we have developed these procedures and presented them in **APPENDIX A**.
12. On the bases of results from laboratory and field testing, as well as positive feedback from many in the Fleet — including INSURV endorsement and overwhelming enthusiasm among submariners who have seen SubTox during our field testing, NEDU and Naval Sea Systems Command agree that SubTox is ready for the proposed 18-month transition plan discussed in the following **TRANSITION OF SUBTOX** section. If implemented, this plan will result in Fleet procurement of a limited number of first-

production SubTox monitors. Once SubTox has been transitioned to the Fleet, we believe that the Navy's ability to monitor DISSUB atmospheres will be improved by allowing the currently used detector tubes to be replaced.

TRANSITION OF SUBTOX

Transition plan

The proposed 18-month transition plan developed by NEDU and ENMET includes the following:

1. The Navy ordering a limited number (e.g., 15 to 20) of first-production SubTox monitors.
2. NEDU then working with ENMET to (1) assist ENMET in acquiring a pressure-testing capability to produce, calibrate, and service SubTox monitors, and (2) define monitor-supporting needs including calibration and servicing.
3. The first-production SubTox monitors then being given qualification testing by NEDU (or another Navy-authorized laboratory) to ensure that their performance is similar to that of the prototype monitors and meets the requirements identified in the **MONITOR REQUIREMENTS** section of this report.
4. These first-production monitors then being issued to selected submarines — with the Navy maintaining a database on their performance, problems, repairs, servicing, and calibration history (if and when the Navy determines that these first-production monitors are acceptable for use on submarines).
5. Results from the first-production monitors being used to guide decisions about additional procurement.
6. ENMET overseeing the entire manufacturing and support process at the end of the transition — although an in-house Navy servicing capability is desirable.

Premise behind transition plan

The premise behind this plan is that testing results for the final-version SubTox prototypes suggest that the first-production monitors can potentially meet the requirements defined in this report. However, before any first-production monitors are delivered to the Fleet, qualification testing is needed to confirm that they (manufactured and calibrated solely by ENMET) meet these requirements.

Status of transition plan

To date, we have yet to receive Navy support for our proposed transition plan. We have briefed the SERRG (February 2011), the Submarine Atmosphere group in Washington DC (April 2011), and the SUBMOD 2011 Conference (September 2011; given by LCDR Walsh from INSURV, a presentation that included a cost breakdown and a supporting business case for SubTox). Also, as requested by CDR McClellan (August 2012), we have assisted LCDR Walsh in preparing a PowerPoint brief on the benefits of SubTox for the Submarine Force, U.S. Atlantic Fleet (SUBLANT).

However, despite the Navy DISSUB community's initial letters of support (2003) recommending that the SubTox project be funded, and the apparently overwhelming enthusiasm among submariners who have seen SubTox during our field testing, our plan to transition SubTox to the Fleet has not been endorsed. Unfortunately, from our experience with similar projects, the reality has been that any halt in the SubTox project may make restarting SubTox work very difficult, if not impossible.

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Table 1. SEAL Values: The Basis for SubTox

GAS	SEAL1 (ppm)	SEAL2 (ppm)
CO	75	85
H2S	15	30
SO2	20	30
NO2	5	10
Cl2	1	2.5
HCN	10	15
HCl	20	35
NH3	75	125

NOTES:

1. Except for the CO values, these agree with the recommendations by the NRC in 2002.⁴
2. The NRC recommended that CO be 125 and 150 ppm for SEAL1 and SEAL2 respectively, but the Navy disputed these values at the time we began the SubTox project in 2004. For our work, we therefore adopted the lower CO values of 75 and 85 ppm that the Navy had proposed in 1998.⁹

Table 2. Cross-Sensitivity Testing Results: Ranges in Uncorrected and Corrected Gas Readings, with Values in BOLD Indicating Significant Cross Sensitivity

TEST PROCEDURE	SENSOR READINGS								#TESTS
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
85 ppm CO									
Uncorrected									
ST-1	78–80T	1	3–5	0	0.1–0.2	0	0	0	3
ST-2	83–84T	0–1	6–9	0	0.0–0.1	0–1	0	0	
Corrected									
ST-1	78–79	0–1	0	0	0.1–0.3	0	0	0	
ST-2	84	0	0	0	0.0–0.1	0–1	0	0	
			C						
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
32 ppm H ₂ S									
Uncorrected									
ST-1	0	19T	38–42	1–2	0.0	30	1	0	3
ST-2	0	19–20T	53–60	1–7	0.0	30	0	0	
Corrected									
ST-1	0	19	0	1	0.0	0–4	0–1	0	
ST-2	0	19–20	3–10	4–8	0.0	0	0	0	
			PC	NC		C			

Notes: ST-1 and ST-2 are two SubTox monitors. T = Uncorrected SEAL2 target gas readings, **C** = corrected, **PC** = partially corrected, **NC** = not corrected. ? = questionable correction. M = maximum reading displayed by SubTox. All readings were taken at 10 min.

Table 2 (cont). Cross-Sensitivity Testing Results. Ranges in Uncorrected and Corrected Gas Readings, with Values in BOLD Indicating Significant Cross Sensitivity

TEST PROCEDURE	SENSOR READINGS								#TESTS
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
30 ppm SO₂									
Uncorrected									
ST-1	0	3-4	3-4	34-37T	1.5-2.2	0-1	2-3	1	6
ST-2	0	3	4-8	29-36T	1.6-1.9	0-1	4-5	1	
Corrected									
ST-1	0	3-4	0	35-38	1.5-2.1	0	0-3	1	
ST-2	0-1	3	0	32-35	1.7-12.0	0	2-5	1	
		NC	C		NC				
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
11 ppm NO₂									
Uncorrected									
ST-1	0	0	0	0	5.0M	0	0	5T	3
ST-2	0	0	0	0	5.0M	0	0	6T	
Corrected									
ST-1	0	0	0	0	5.0M	0	0	5	
ST-2	0	0	0	0	5.0M	0	0	6	

Notes: ST-1 and ST-2 are two SubTox monitors. T = Uncorrected SEAL2 target gas readings, **C** = corrected, **PC** = partially corrected, **NC** = not corrected. ? = questionable correction. M = maximum reading displayed by SubTox. All readings were taken at 10 min.

Table 2 (cont). Cross-Sensitivity Testing Results. Ranges in Uncorrected and Corrected Gas Readings, with Values in BOLD Indicating Significant Cross Sensitivity

TEST PROCEDURE	SENSOR READINGS								#TESTS
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
2.5 ppm Cl₂									
Uncorrected									
ST-1	0	0	4–5	0	1.3–3.4T	0	0	1–2	6
ST-2	0	0	5–8	0–2	1.9–3.3T	0–1	0	0–2	
Corrected									
ST-1	0	0	0–1	0	2.2–3.5	0–1	0	1–2	
ST-2	0	0	0–5	0–1	2.7–3.3	0–1	0	1–2	
			PC						
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
16 ppm HCN									
Uncorrected									
ST-1	0	0	3–13	6–7	0.2–0.4	15T	0	0	3
ST-2	1–2	0	11–33	5–7	0.1	12–13T	0	0	
Corrected									
ST-1	0	0	0	2–3	0.3	15–16	0	0	
ST-2	1	0	0	0–3	0.1	12–13	0	0	
			C	PC	?				

Notes: ST-1 and ST-2 are two SubTox monitors. T = Uncorrected SEAL2 target gas readings, **C** = corrected, **PC** = partially corrected, **NC** = not corrected. ? = questionable correction. M = maximum reading displayed by SubTox. All readings were taken at 10 min.

Table 2 (cont). Cross-Sensitivity Testing Results. Ranges in Uncorrected and Corrected Gas Readings, with Values in BOLD Indicating Significant Cross Sensitivity

TEST PROCEDURE	SENSOR READINGS								#TESTS
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
35 ppm HCl									
Uncorrected									
ST-1	0	0	10–14T	0	0.3–0.4	0–1	0	0	3
ST-2	0	0	16–21T	0–1	0.0–0.1	2–4	0	0	
Corrected									
ST-1	0	0	13–18	0	0.0–0.5	0	0	0	
ST-2	0	0	7–23	0–2	0.1	0–7	0	0	
					?	NC			
	CO	H ₂ S	HCl	SO ₂	Cl ₂	HCN	NH ₃	NO ₂	
125 ppm NH₃									
Uncorrected									
ST-1	0	0	4–5	0	0.3–0.4	0	178–181T	0	3
ST-2	0	0	4–8	0–1	0.1–0.2	0–1	177–184T	0	
Corrected									
ST-1	0	0	3–5	0	0.1–0.4	0	179–186	0	
ST-2	0	0	1–8	0–1	0.1–0.2	0–1	182–185	0	
			NC		?				

Notes: ST-1 and ST-2 are two SubTox monitors. T = Uncorrected SEAL2 target gas readings, **C** = corrected, **PC** = partially corrected, **NC** = not corrected. ? = questionable correction. M = maximum reading displayed by SubTox. All readings were taken at 10 min.

FIGURE 1. Target toxic gas monitor (top) — with one of its electrochemical sensors (bottom) about the diameter of a thumbnail.

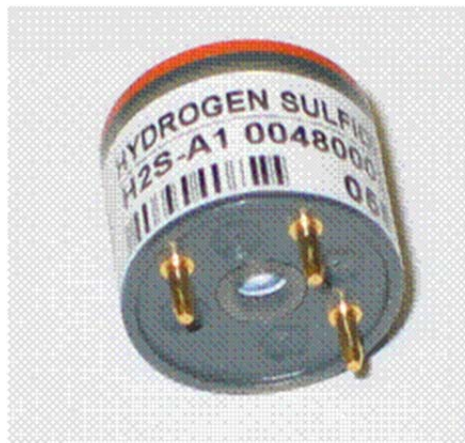
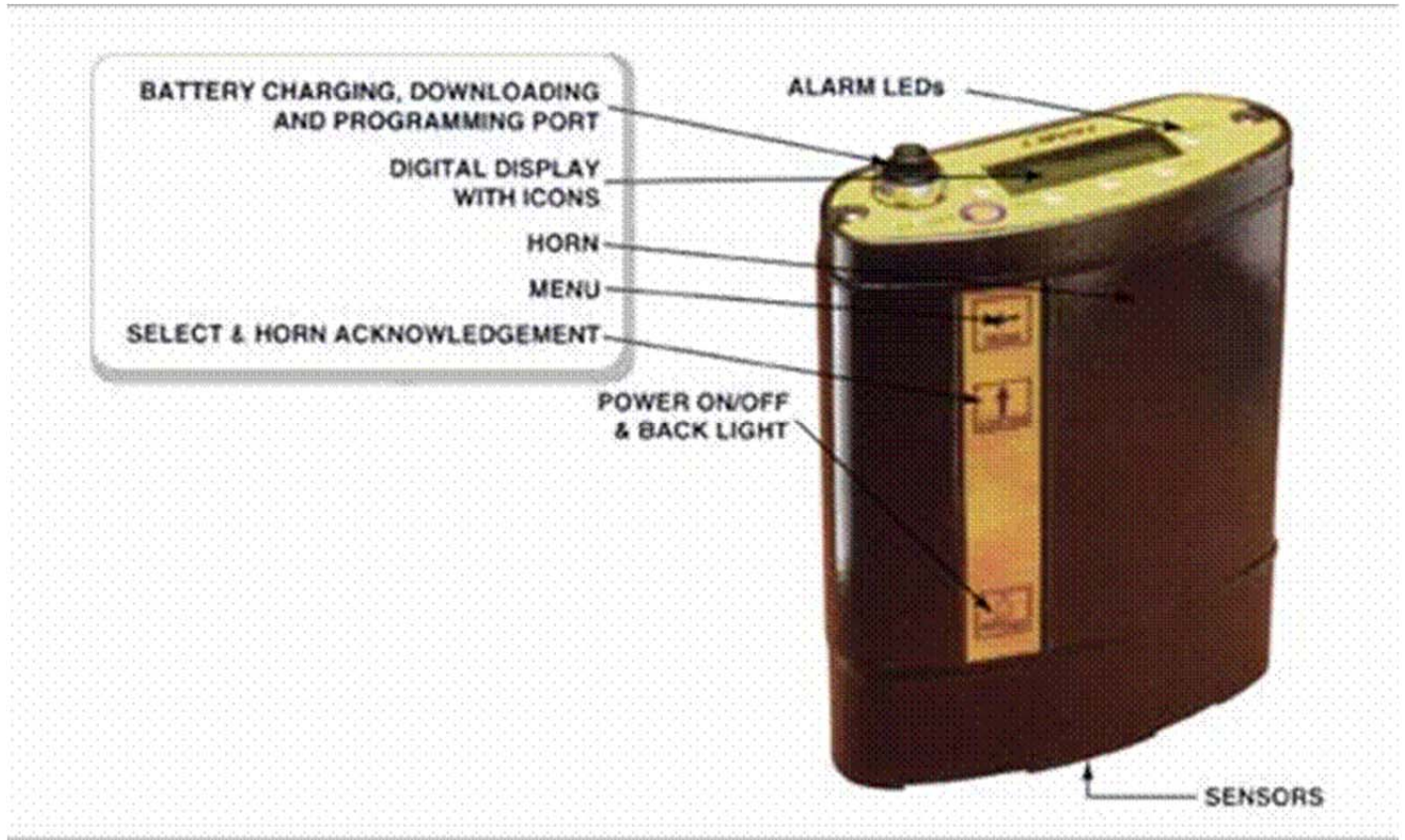


FIGURE 2A. Target response to 5 ATA pressure test: CO.

With ppm plotted
Top Graph: AM test
Bottom Graph: Repeat PM test

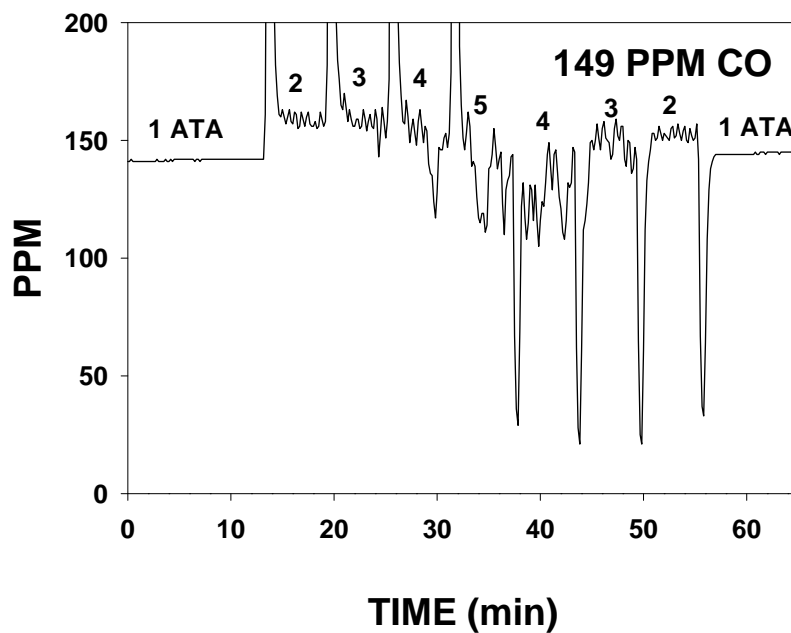
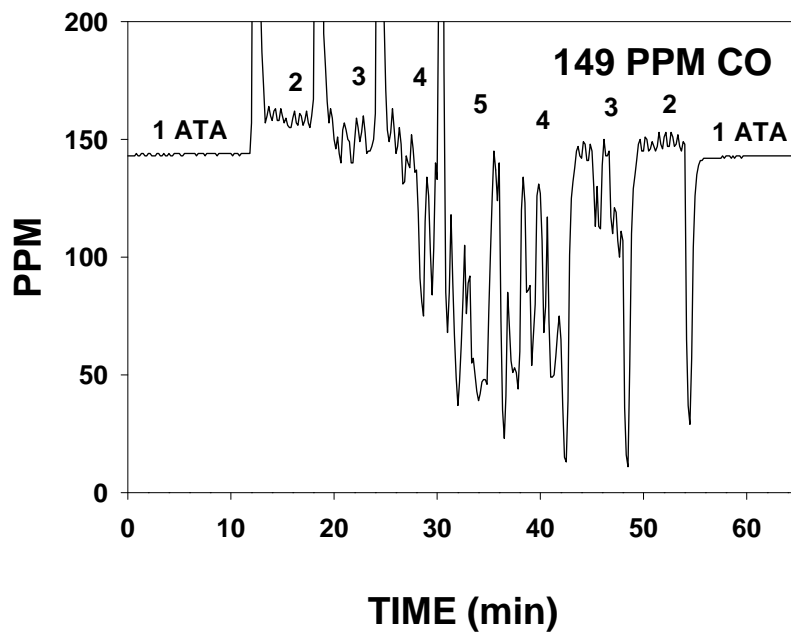


FIGURE 2B. Target response to 5 ATA pressure test: H₂S.

With ppm plotted
Top Graph: AM test
Bottom Graph: Repeat PM test

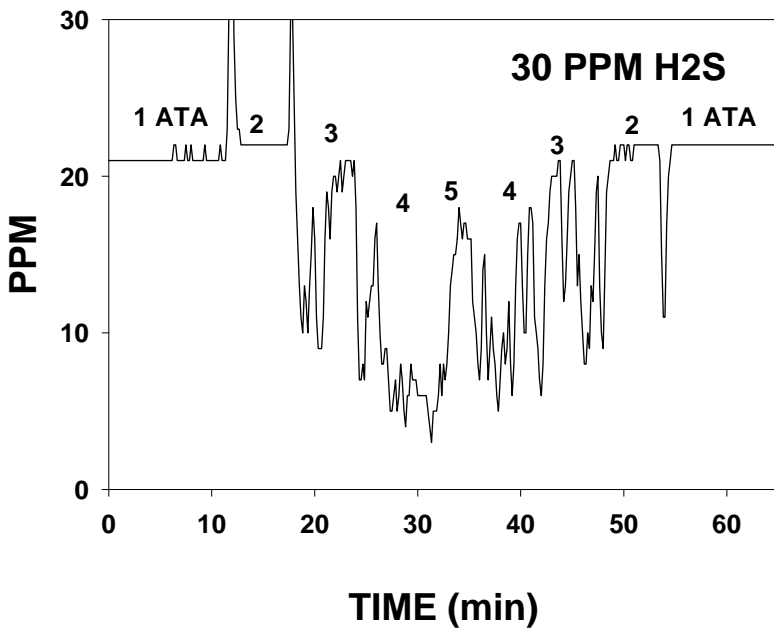
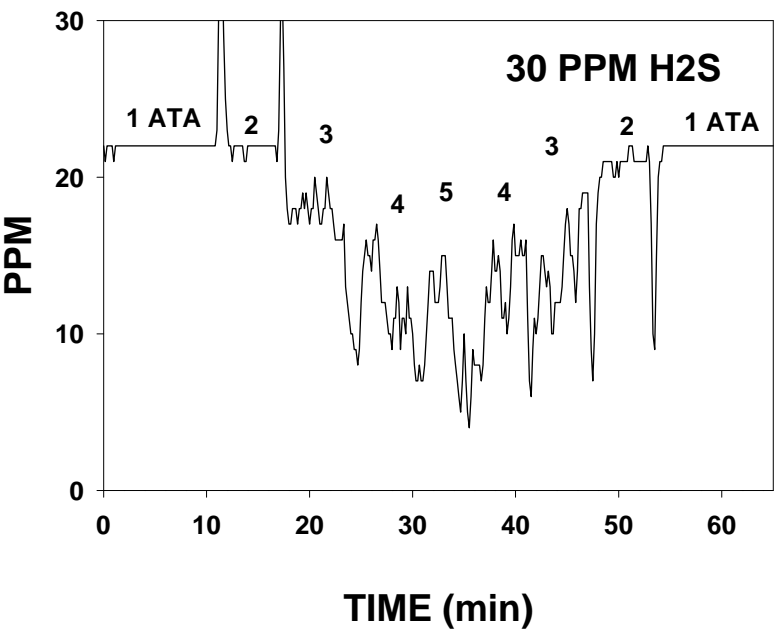


FIGURE 2C. Target response to 5 ATA pressure test: SO₂.

With ppm plotted
Top Graph: AM test
Bottom Graph: Repeat PM test

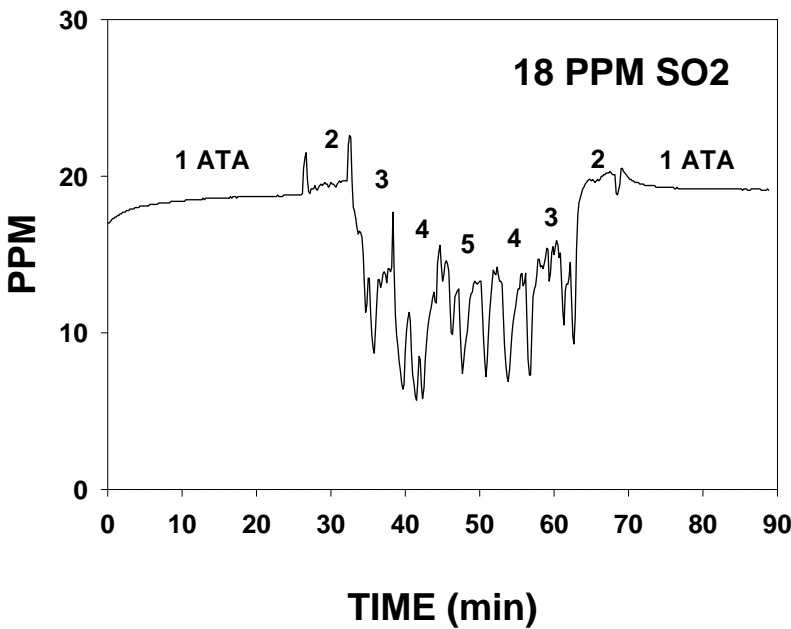
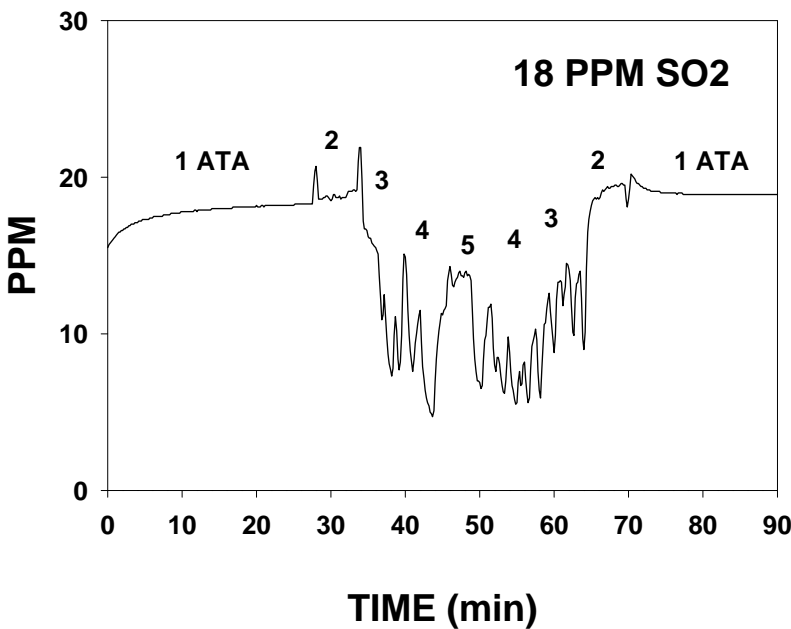


FIGURE 2D. Target response to 5 ATA pressure test: Cl₂.

With ppm plotted
Top Graph: AM test
Bottom Graph: Repeat PM test

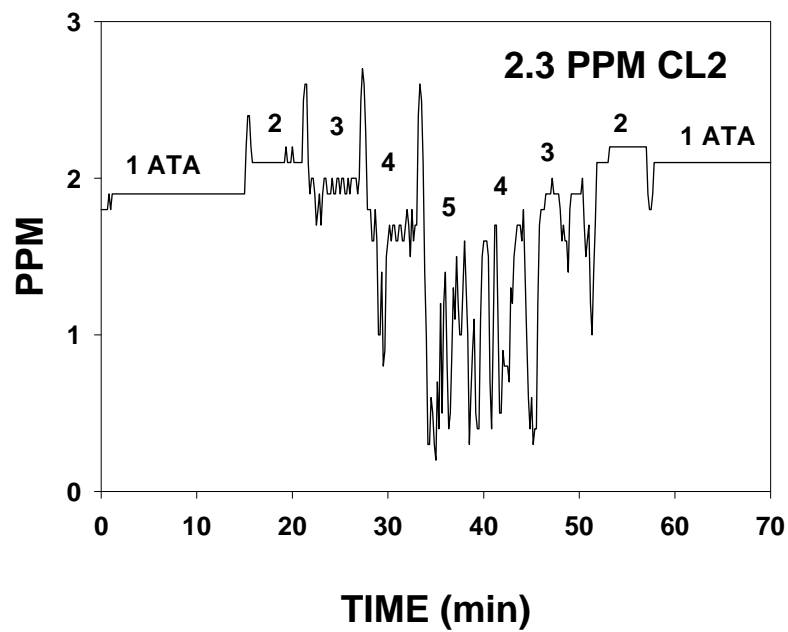
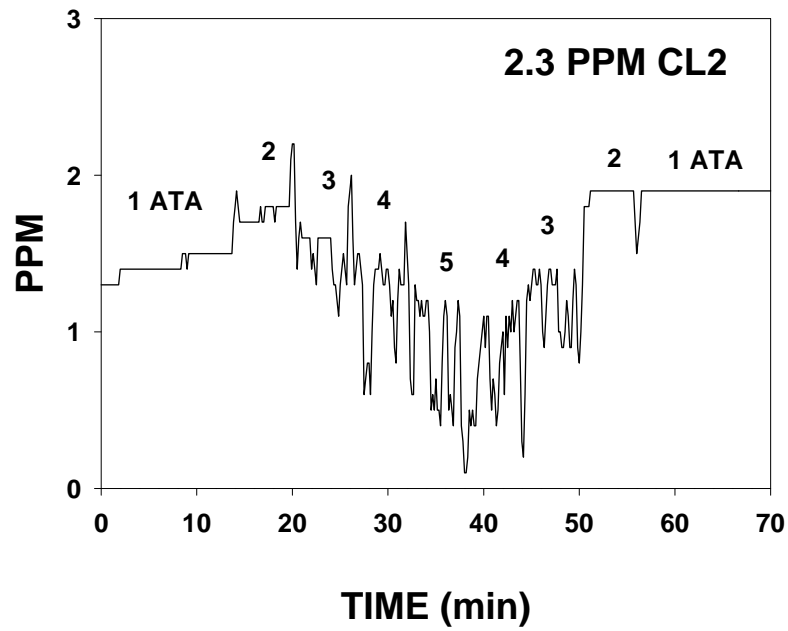


FIGURE 3A. Target prototype hyperbaric sensors' responses to 5 ATA pressure test: CO and H₂S.

With ppm plotted for one test

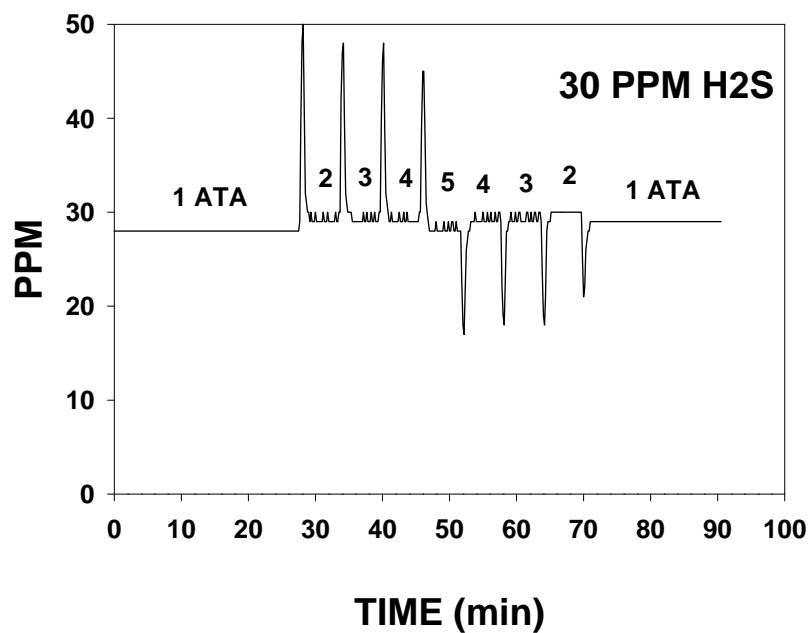
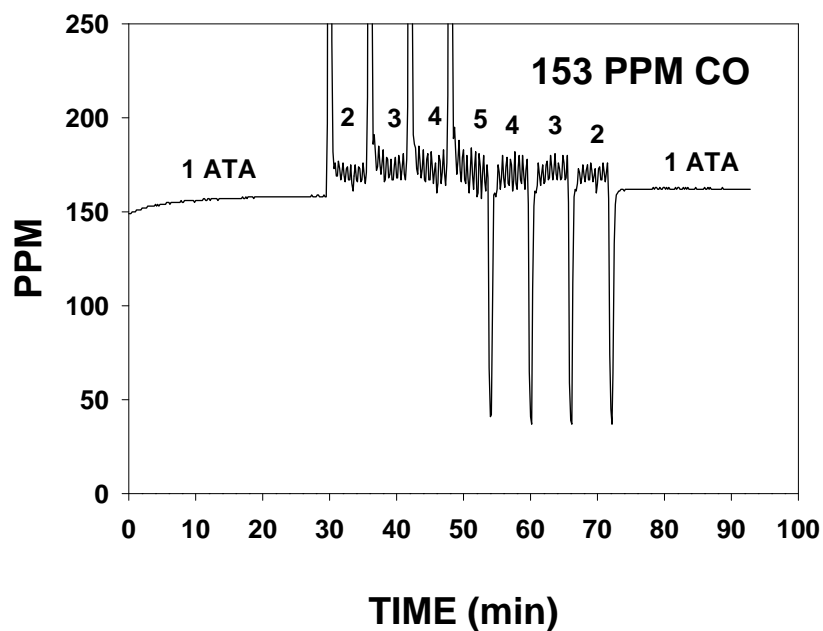


FIGURE 3B. Target prototype hyperbaric sensors' responses to 4 or 5 ATA pressure test: Cl_2 and SO_2 .

With ppm plotted for one test

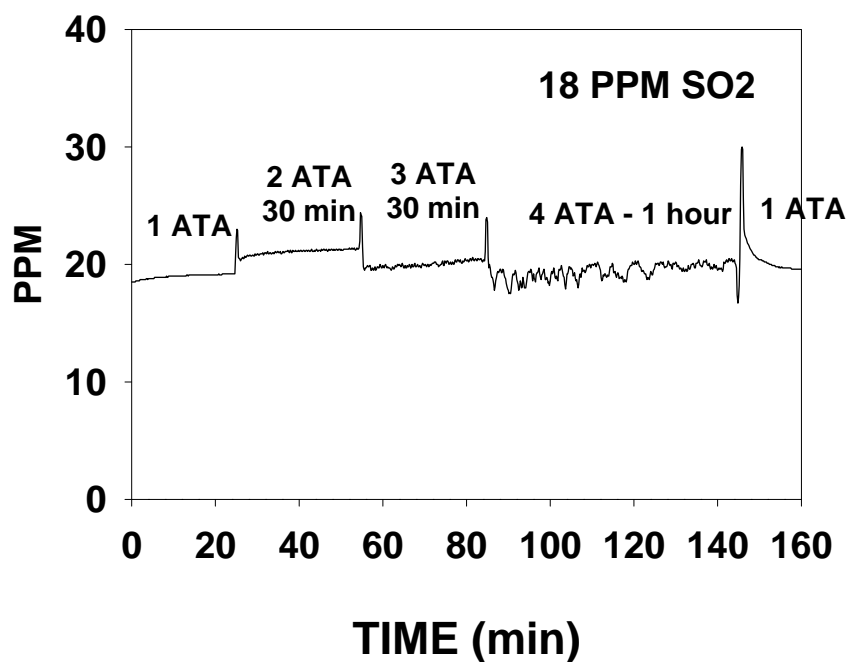
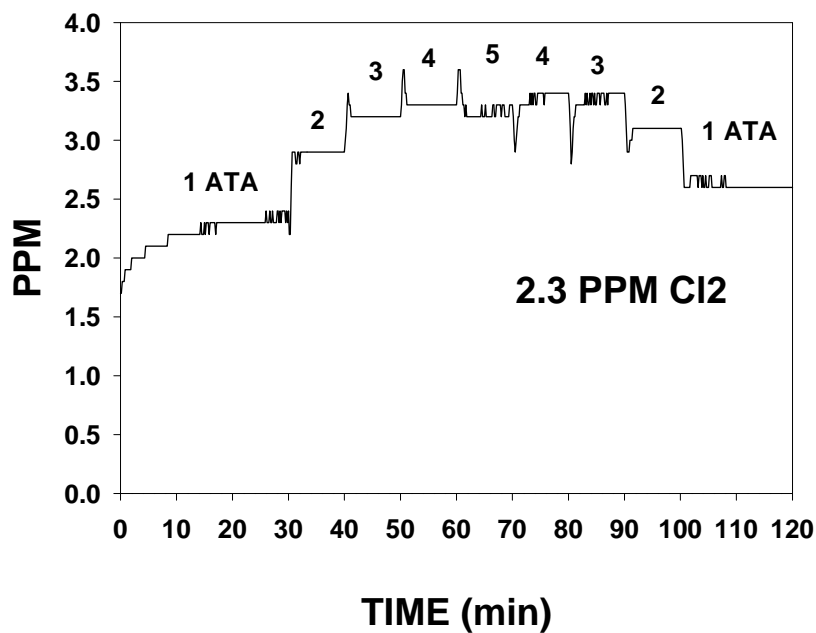


FIGURE 4A. Sensor Test System's printed circuit board with two sections of gas manifold, each holding four sensors.

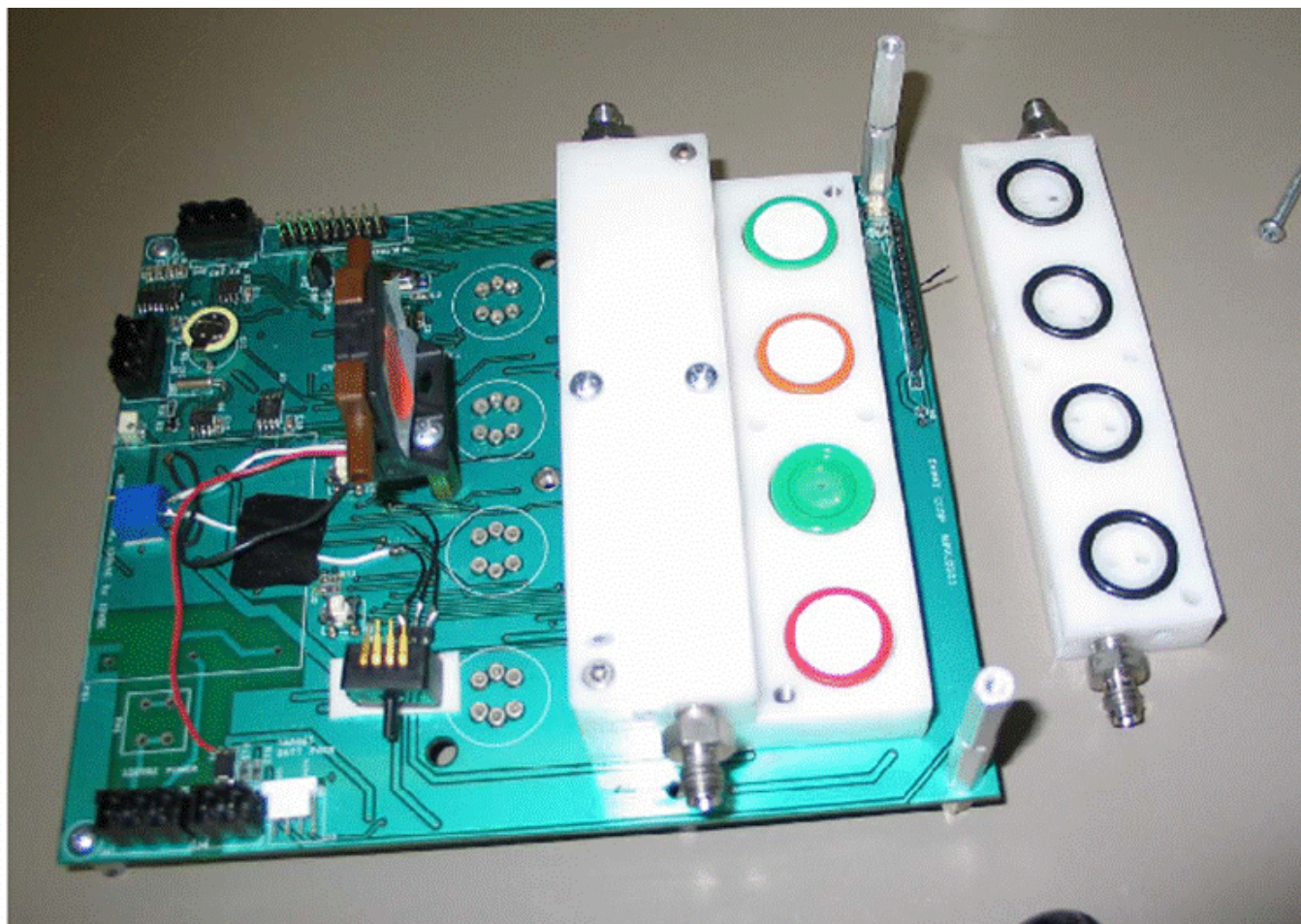


FIGURE 4B. Sensor Test System's printed circuit board, with intact gas manifold and LCD mounted atop manifold.

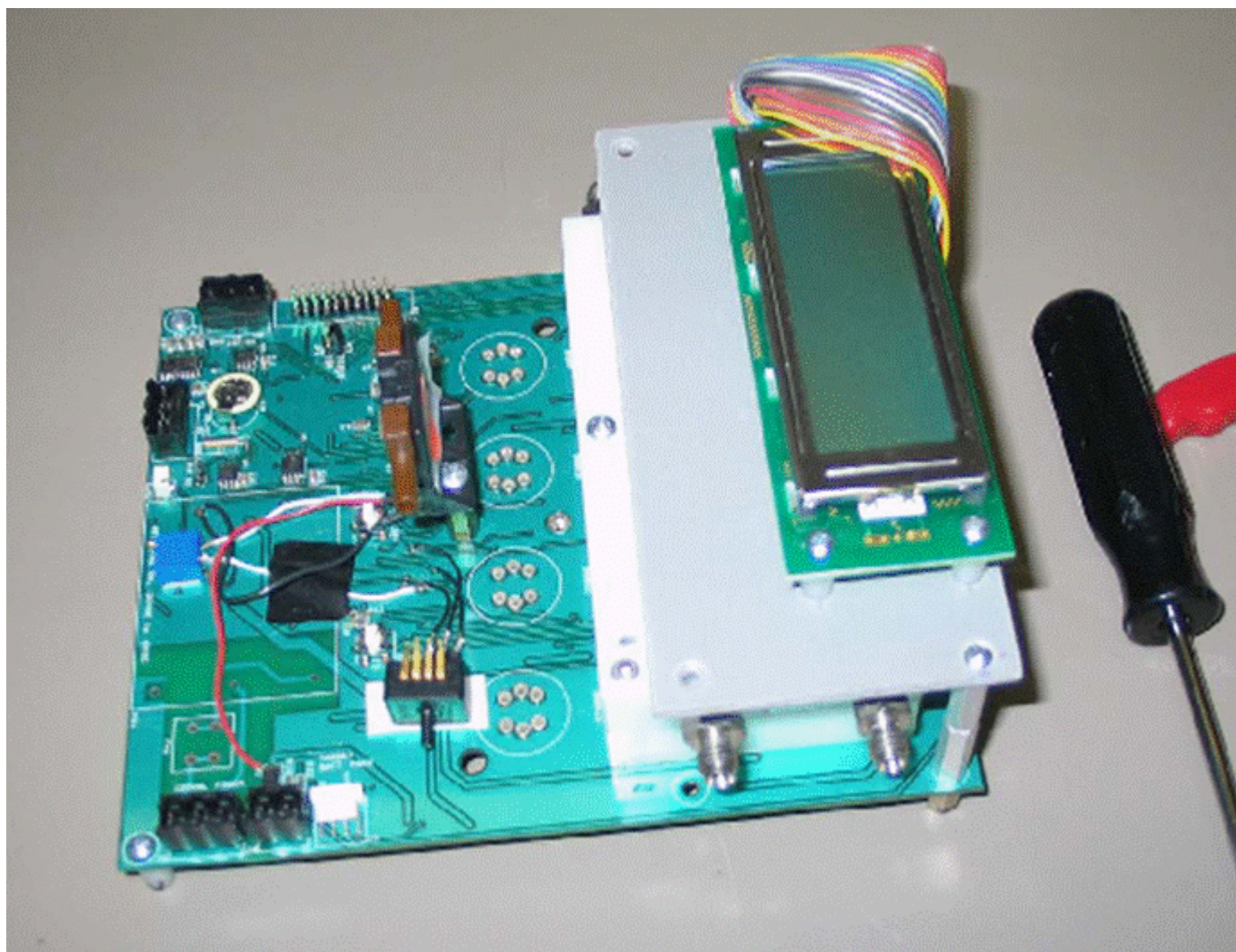
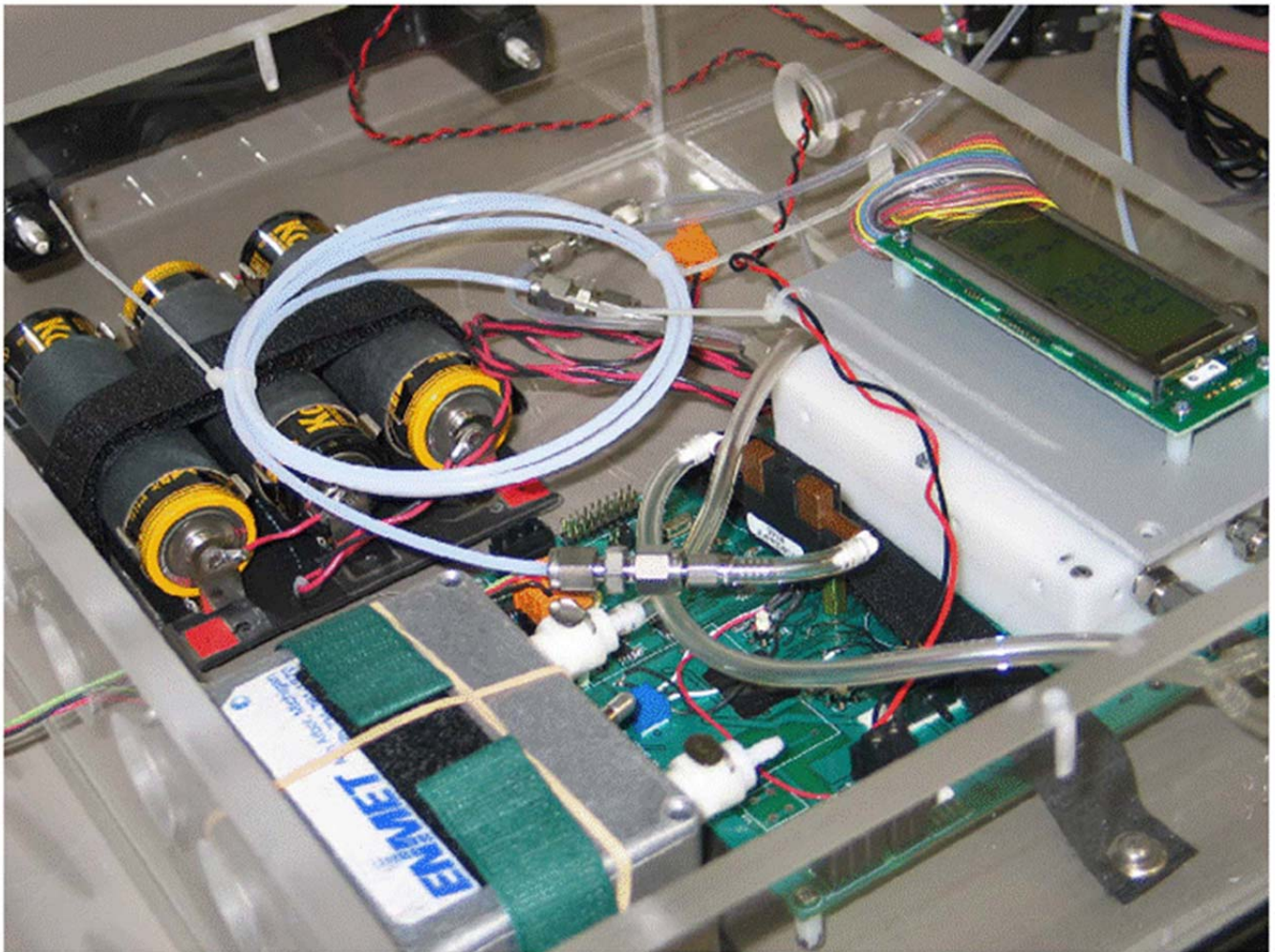
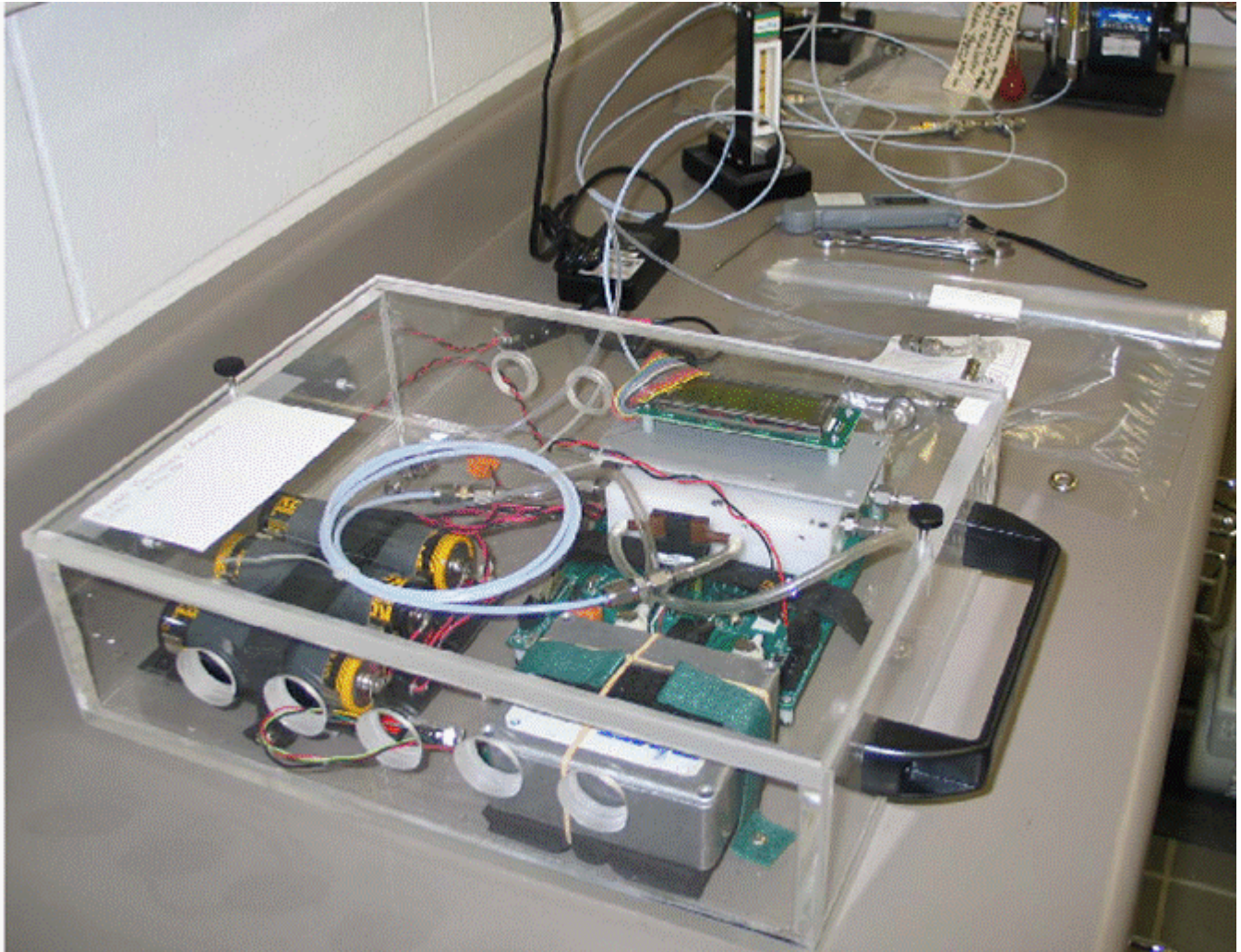


FIGURE 4C. Sensor Test System's inside its Plexiglas box:

Pump (lead gray box) draws gas into gas manifold, with Test System powered by either six D-cell alkaline batteries (shown) or standard Target battery charger.

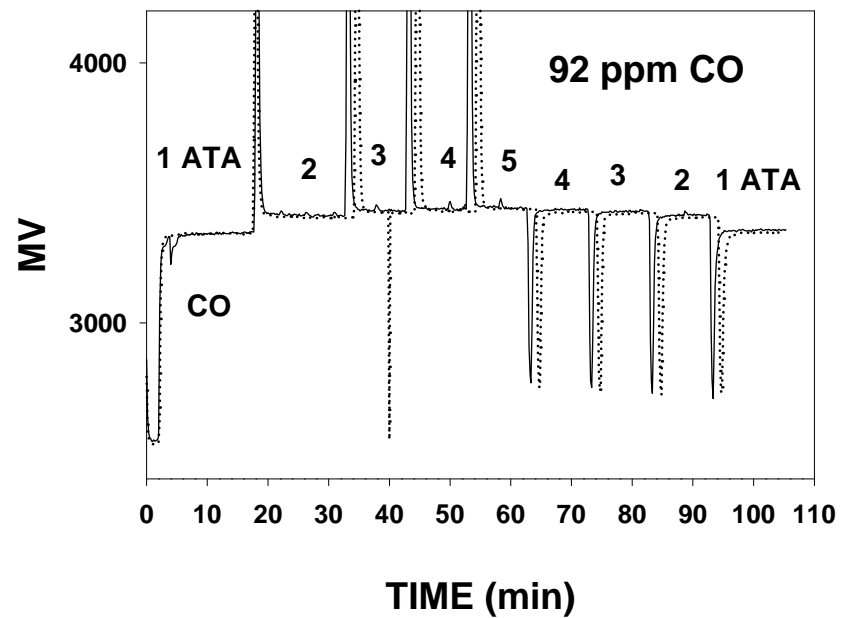
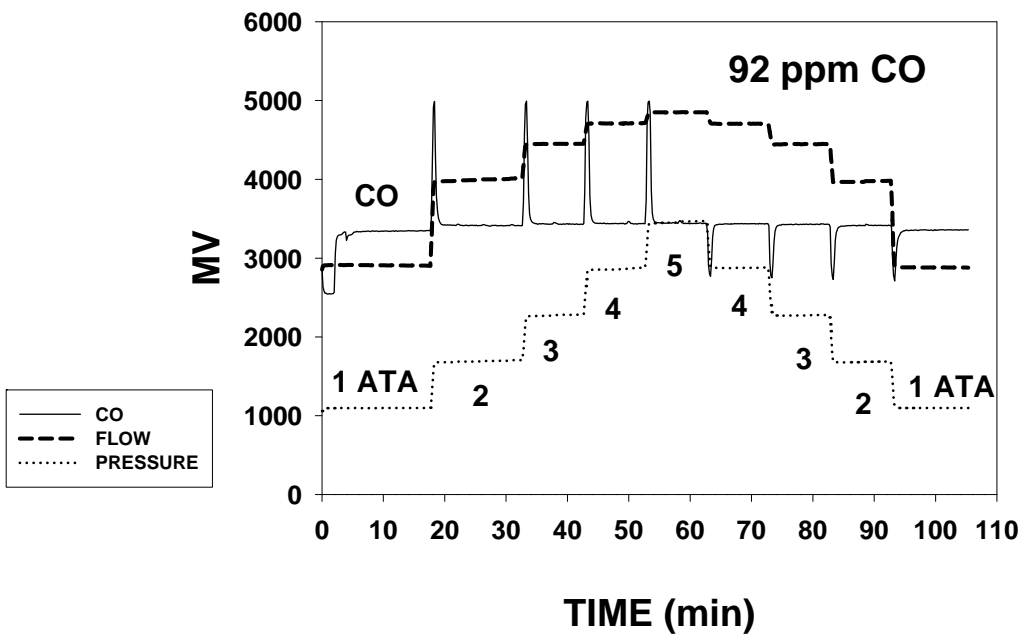


**FIGURE 4D. Sensor Test System's inside its Plexiglas box:
Gas is sampled from Tedlar bag, after bag has been
connected to tubing from upstream side of
gas manifold.**



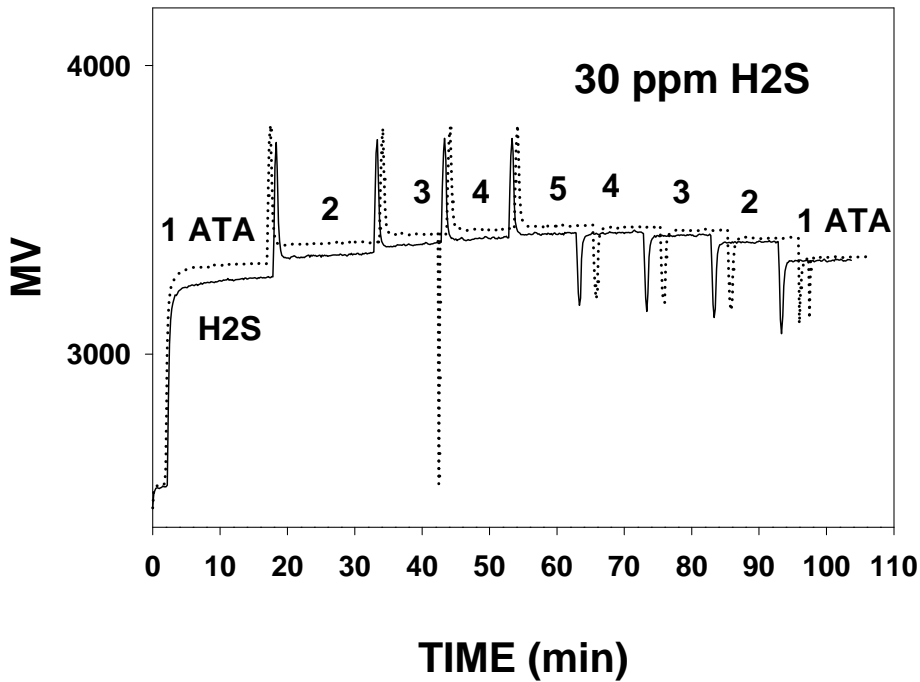
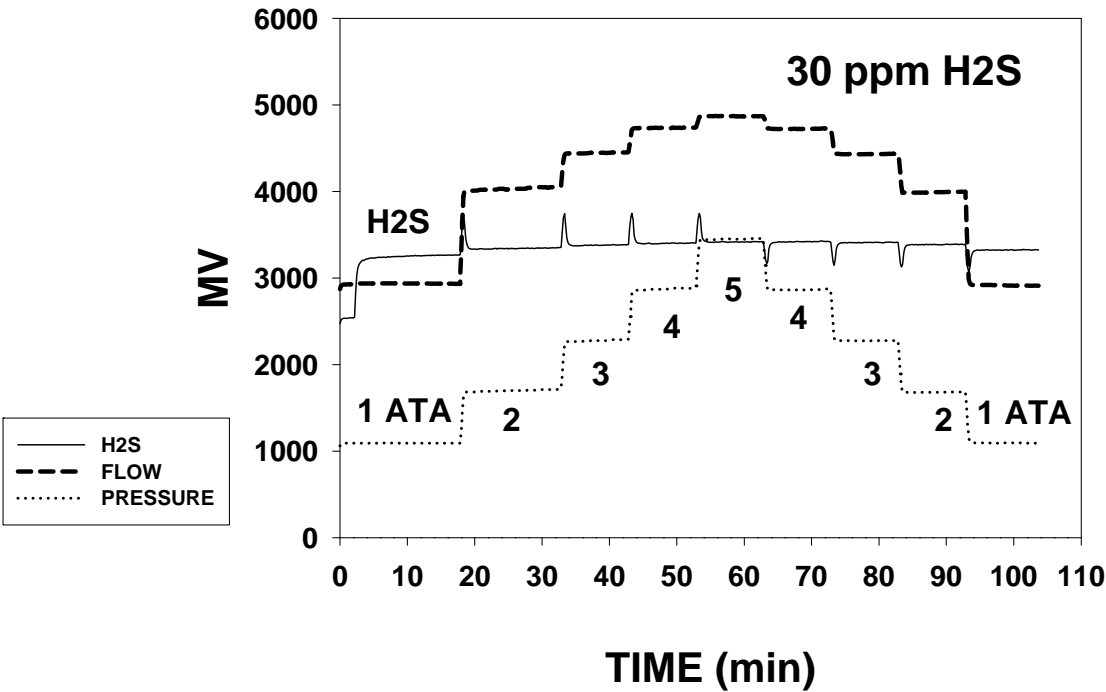
**FIGURE 5A. Test System's prototype hyperbaric sensor:
CO.**

With mV plotted
Top Graph: One test
Bottom Graph: One AM and one PM test



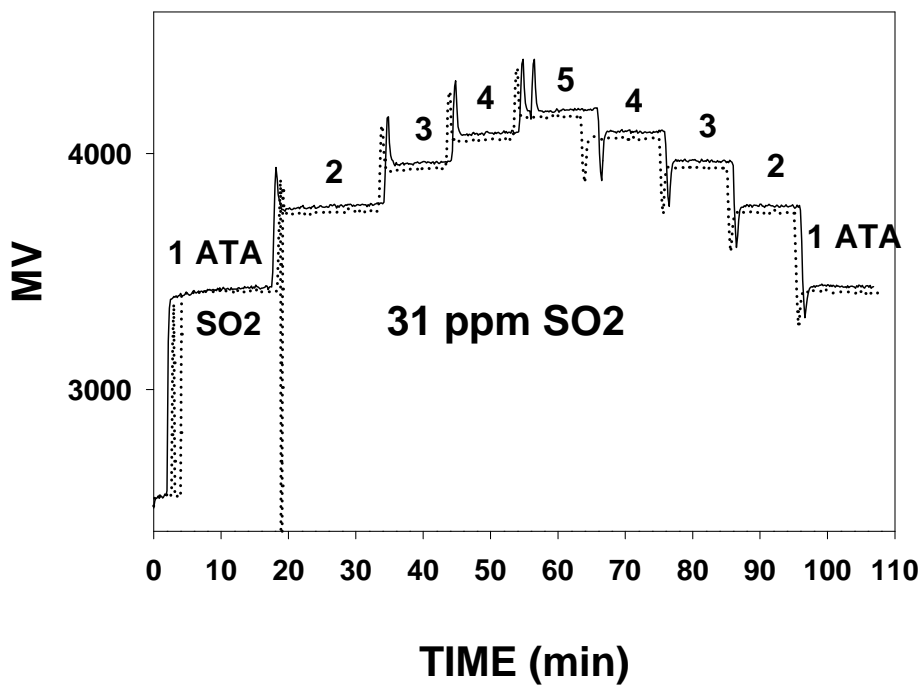
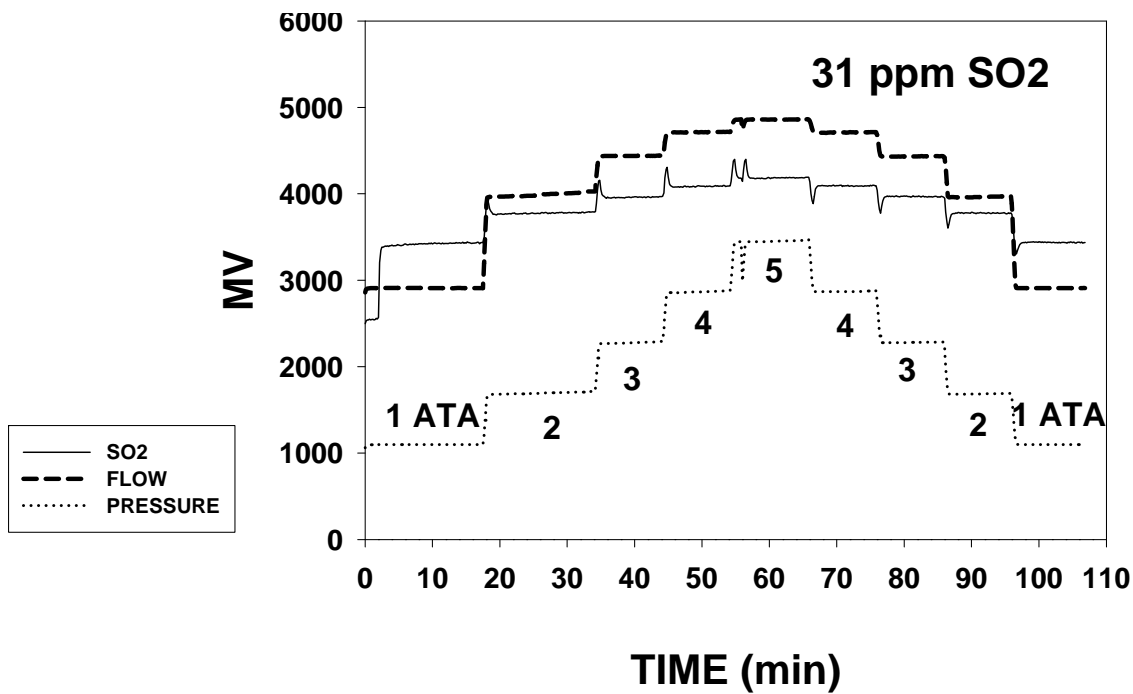
**FIGURE 5B. Test System's prototype hyperbaric sensor:
H₂S.**

With mV plotted
Top Graph: One test
Bottom Graph: One AM and one PM test



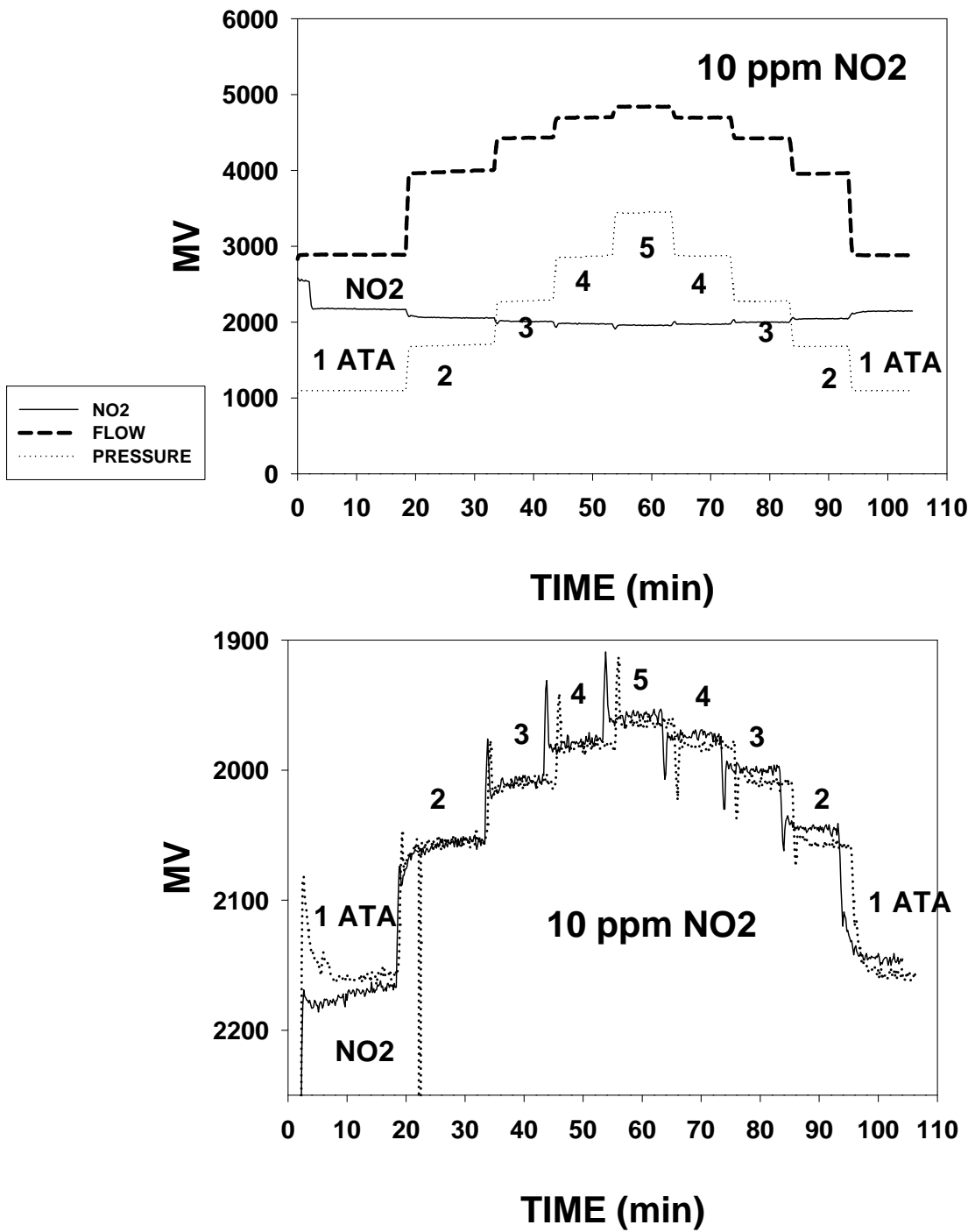
**FIGURE 5C. Test System's prototype hyperbaric sensor:
SO₂.**

With mV plotted
Top Graph: One test
Bottom Graph: One AM and one PM test



**FIGURE 5D. Test System's prototype hyperbaric sensor:
NO₂/Cl₂.**

With mV plotted
Top Graph: One test
Bottom Graph: One AM and one PM test



**FIGURE 5E. Test System's prototype hyperbaric sensor:
NO₂/Cl₂.**

With mV plotted
Top Graph: One test
Bottom Graph: One AM and one PM test

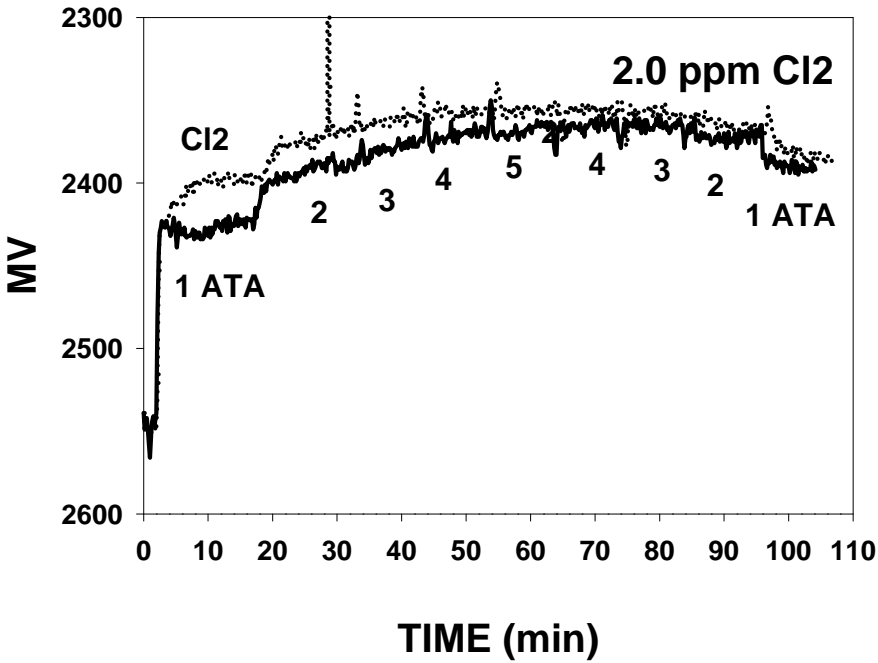
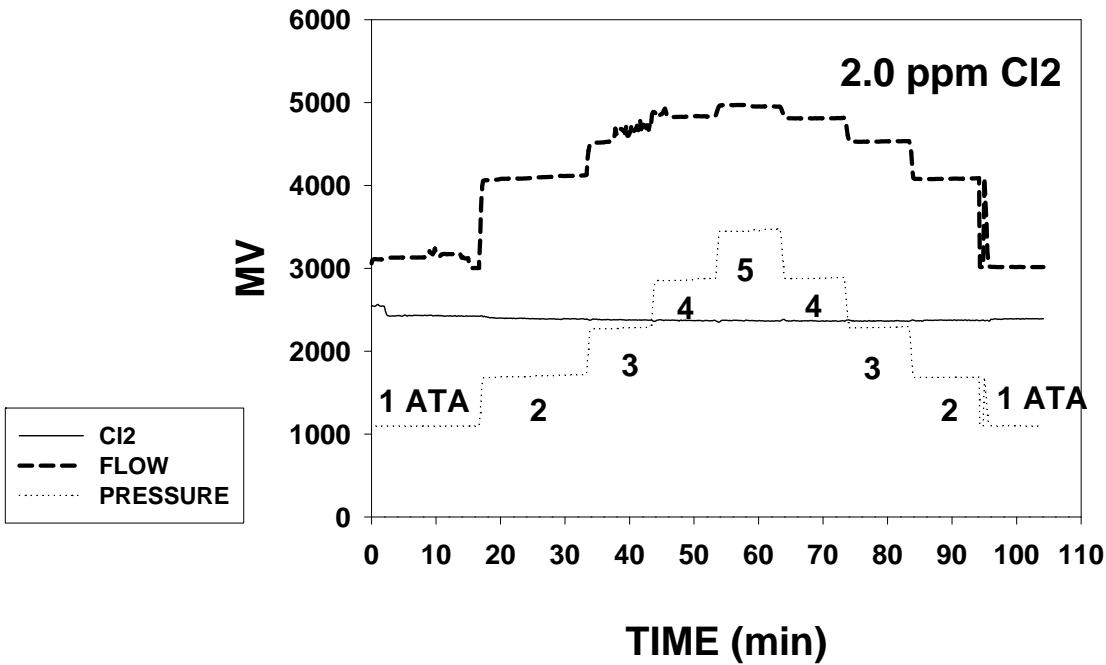


FIGURE 6A. Test System's varying pump flow, which does not affect CO sensor output.

Top Graph: With mV plotted from one test
Bottom Graph: Same graph expanded

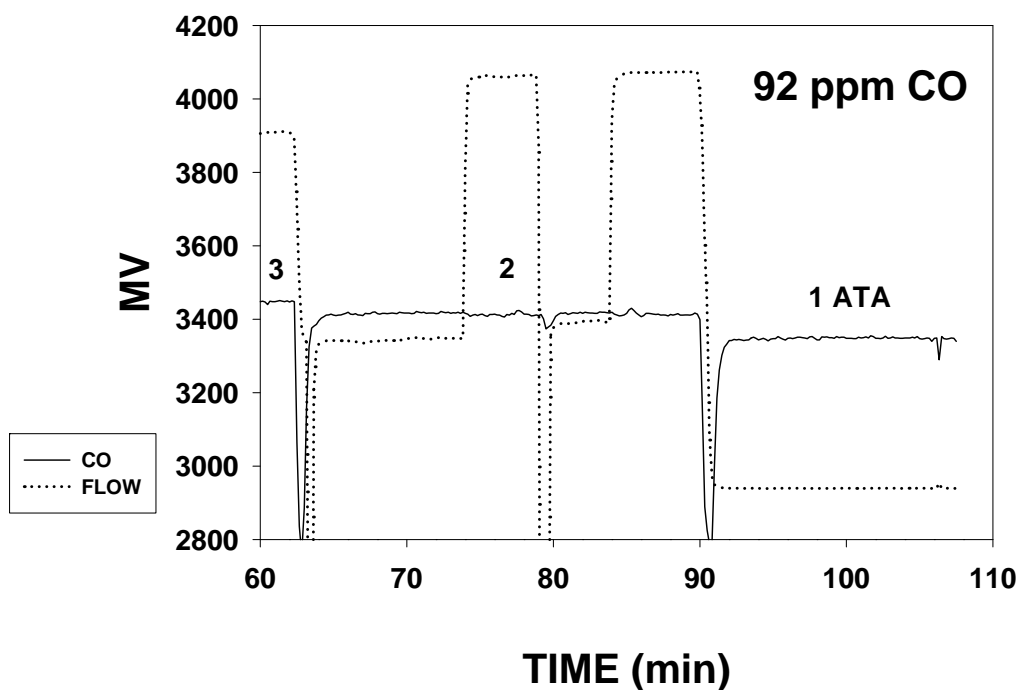
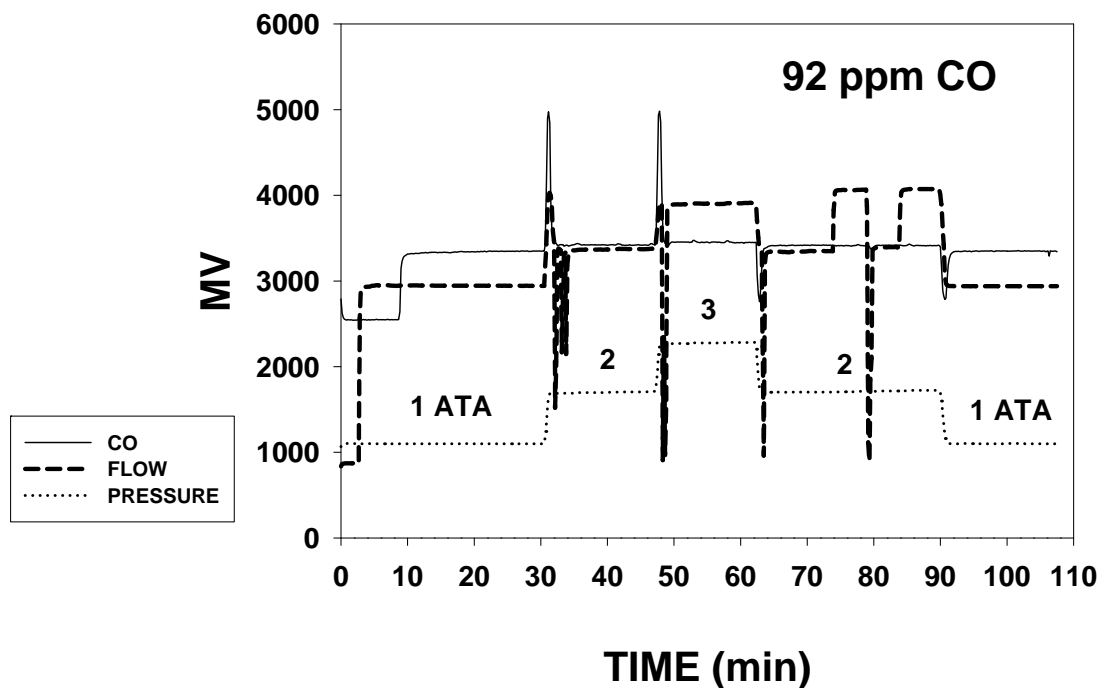


FIGURE 6B. Test System's varying pump flow, which does not affect H₂S sensor output.

Top Graph: With mV plotted from one test

Bottom Graph: Same graph expanded

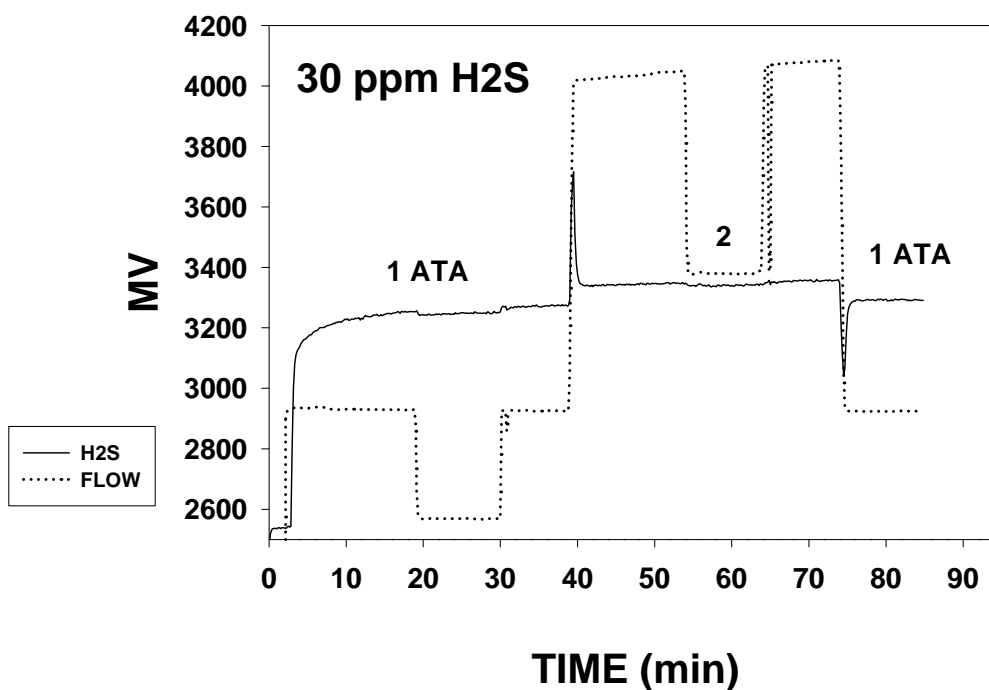
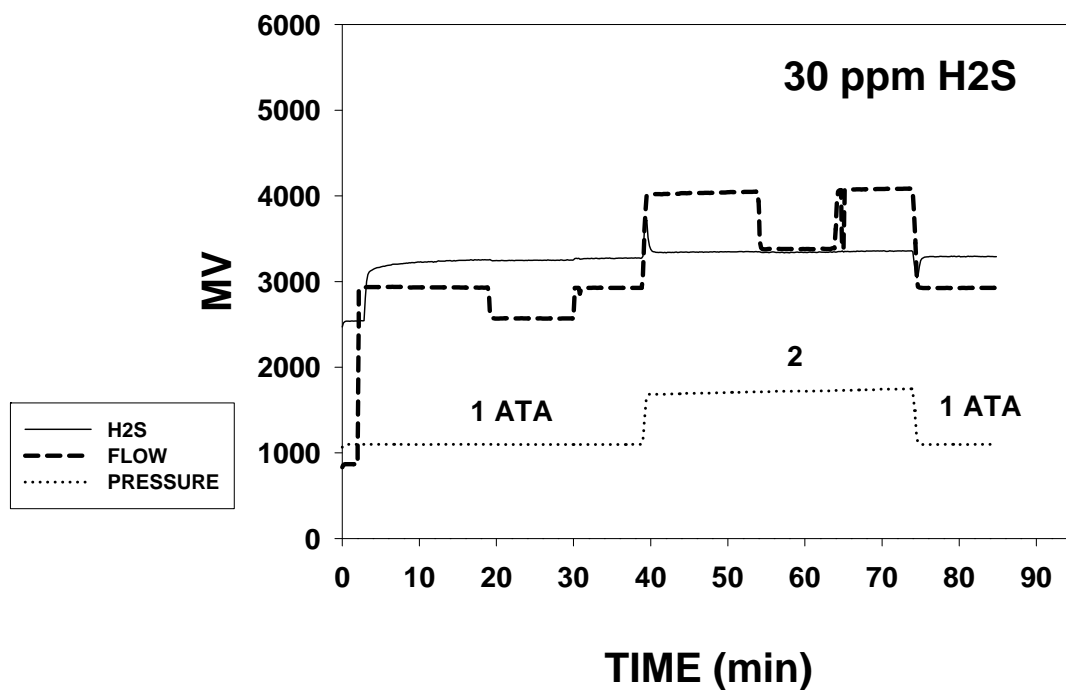


FIGURE 6C. Test System's varying pump flow, which does not affect SO₂ sensor output.

Top Graph: With mV plotted from one test

Bottom Graph: Same graph expanded

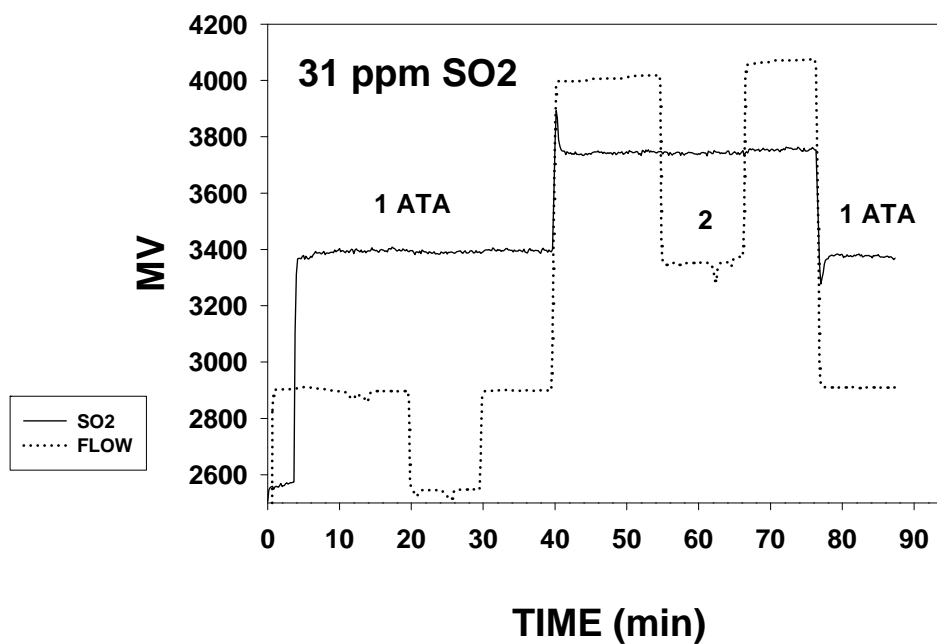
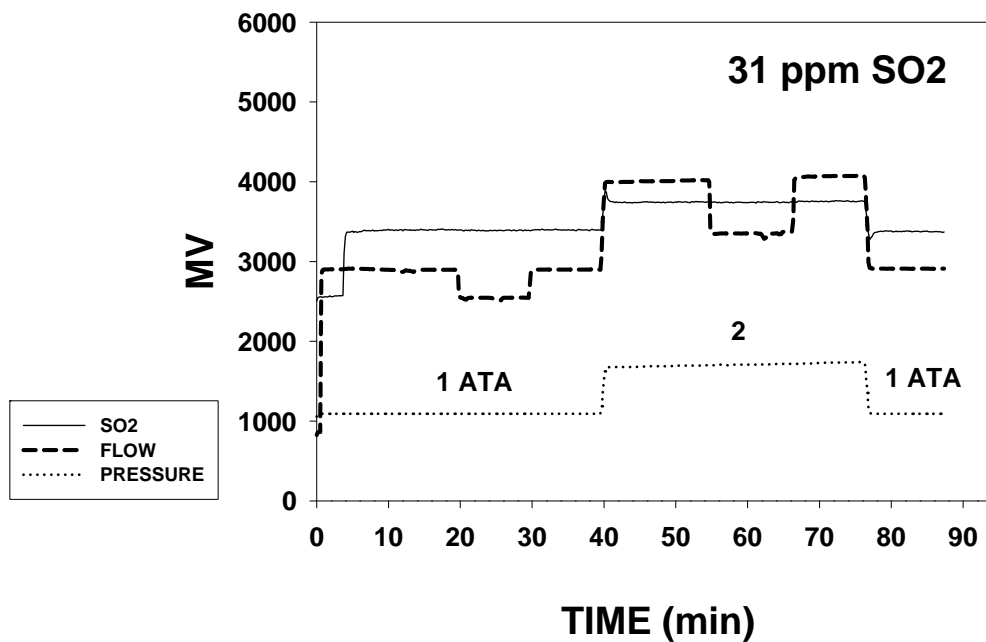


FIGURE 6D. Test System's varying pump flow, which does not affect NO₂/Cl₂ sensor output.

Top Graph: With mV plotted from one test

Bottom Graph: Same graph expanded

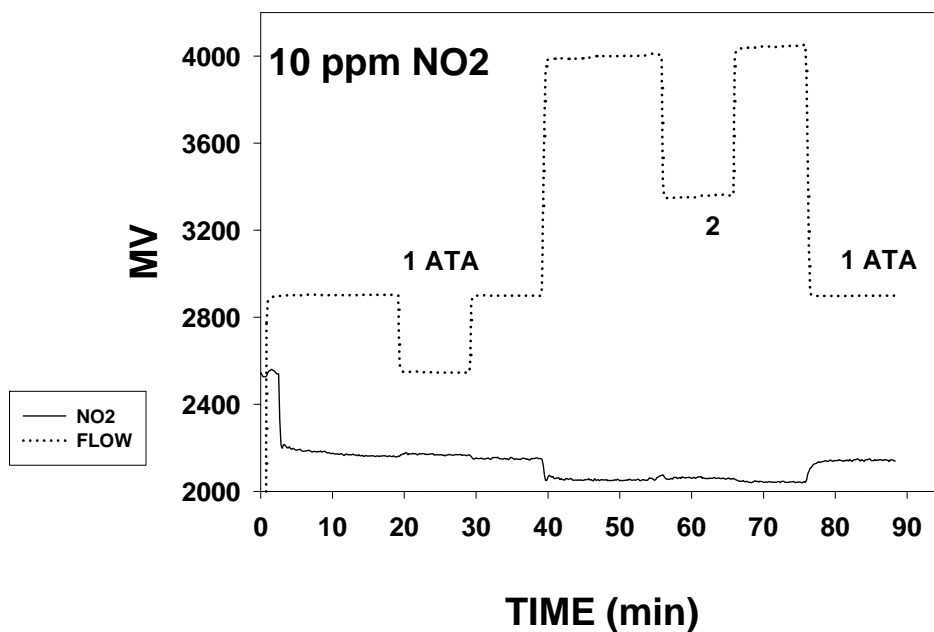
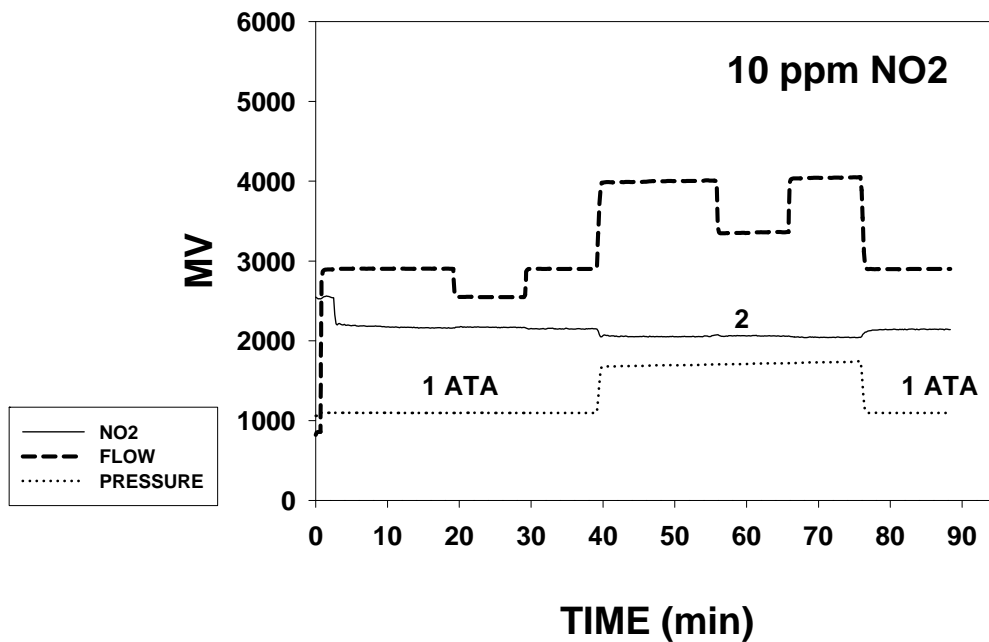


FIGURE 6E. Test System's varying pump flow, which does not affect NO₂/Cl₂ sensor output.

Top Graph: With mV plotted from one test

Bottom Graph: Same graph expanded

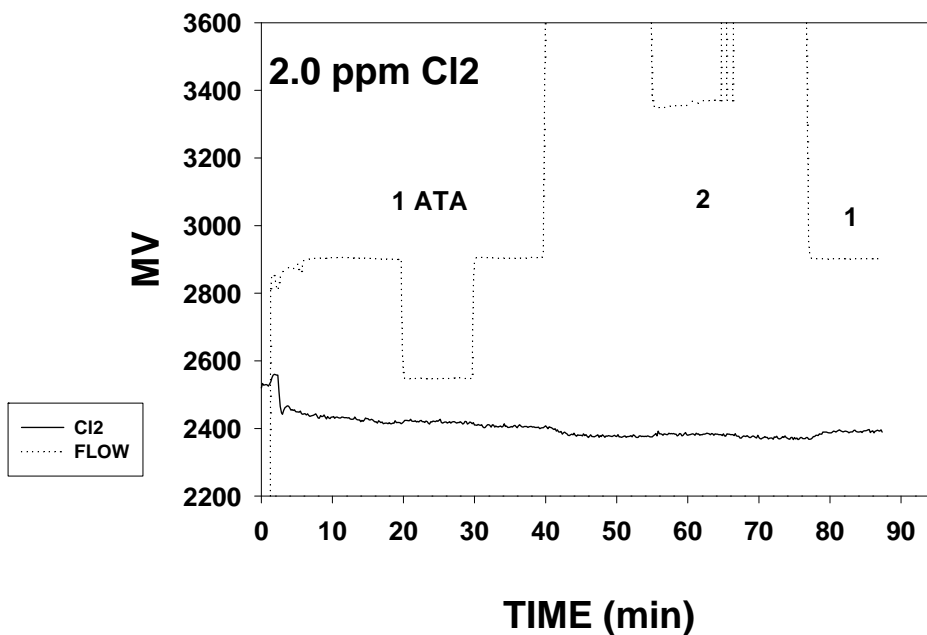
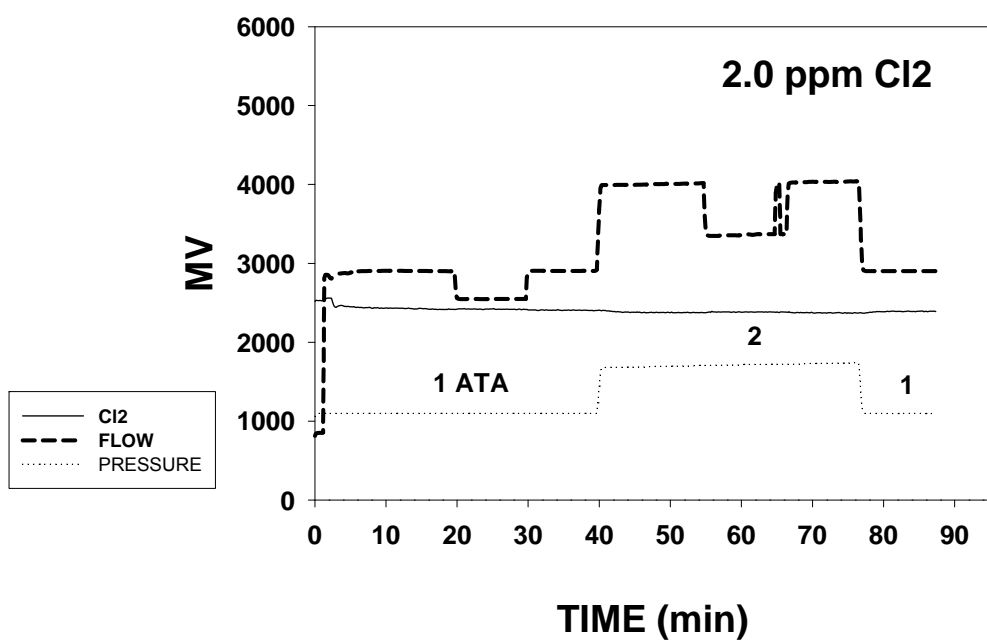


FIGURE 7A. Test System: Temperature effects on CO (top graph) and H₂S (bottom graph) sensors.

With mV plotted from AM (25 °C) and PM (10 °C or 40 °C) tests

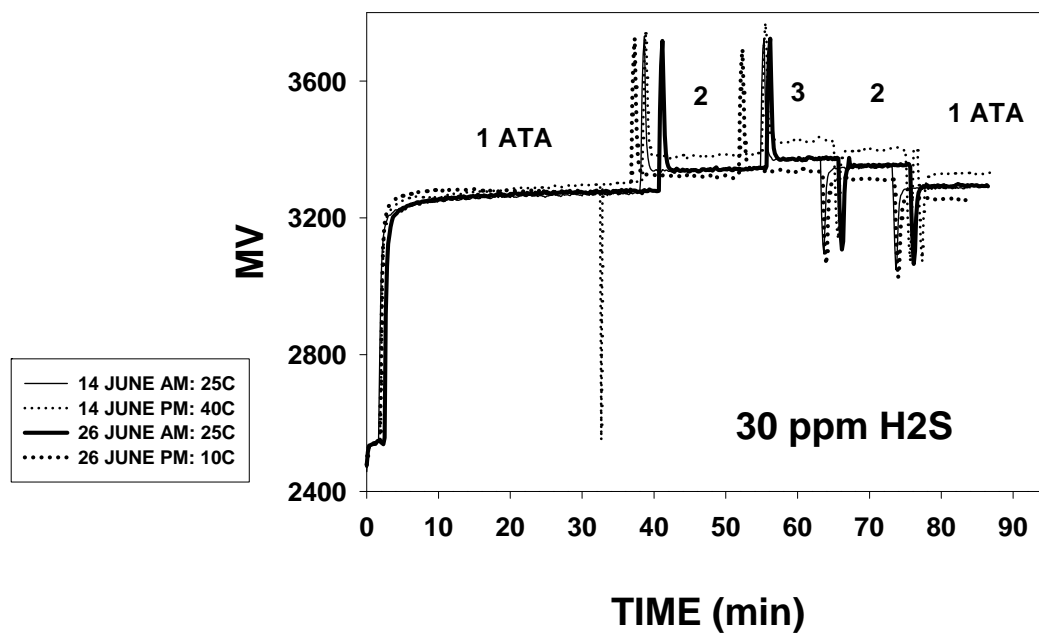
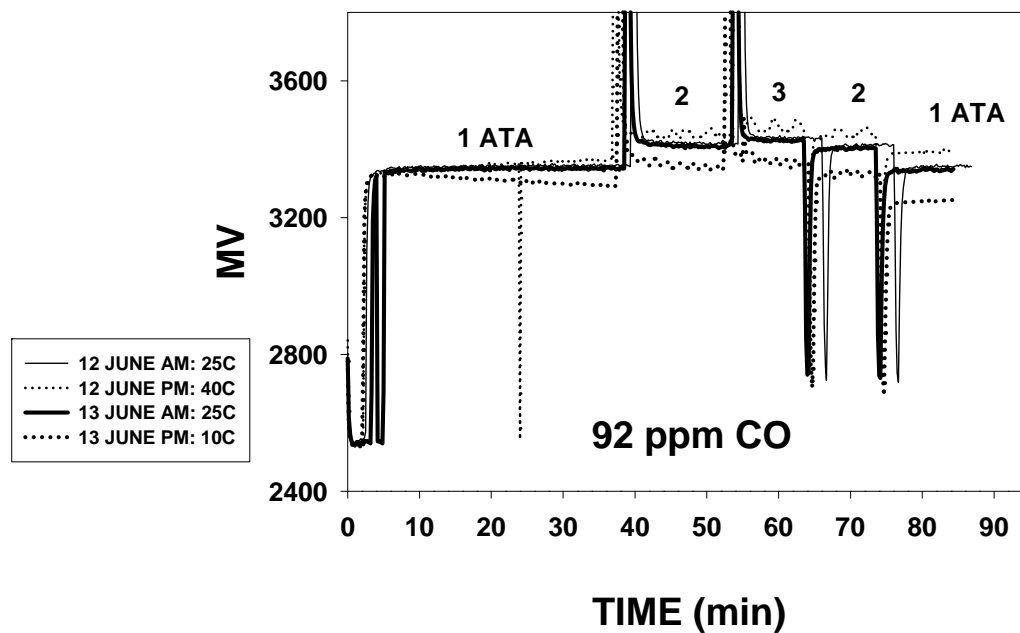


FIGURE 7B. Test System: Temperature effects on SO₂ (top graph) and NO₂/Cl₂ (bottom graph) sensors.

With mV plotted from AM (25 °C) and PM (10 °C or 40 °C) tests

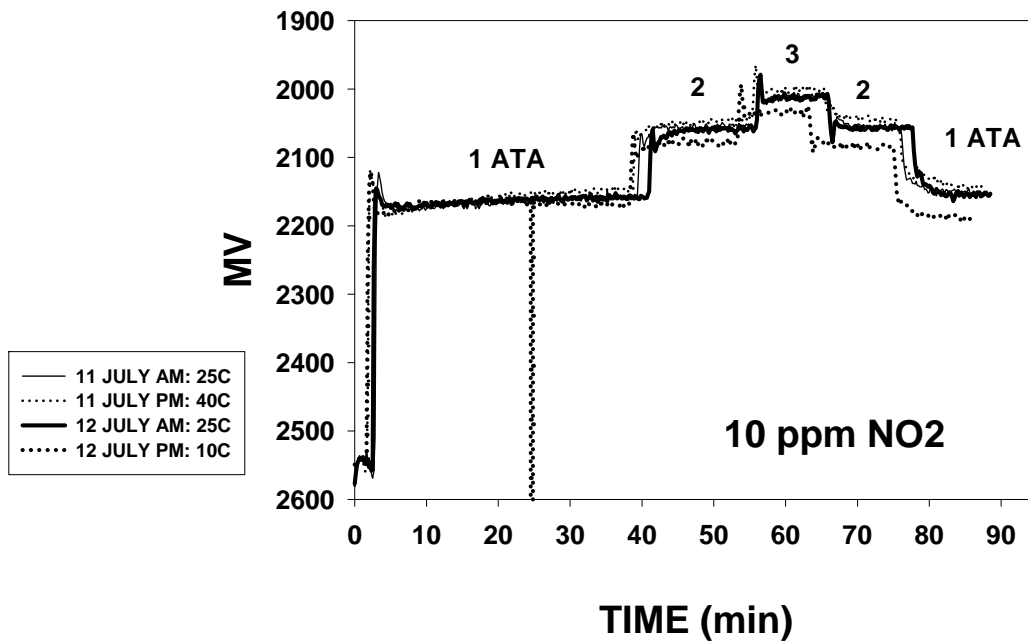
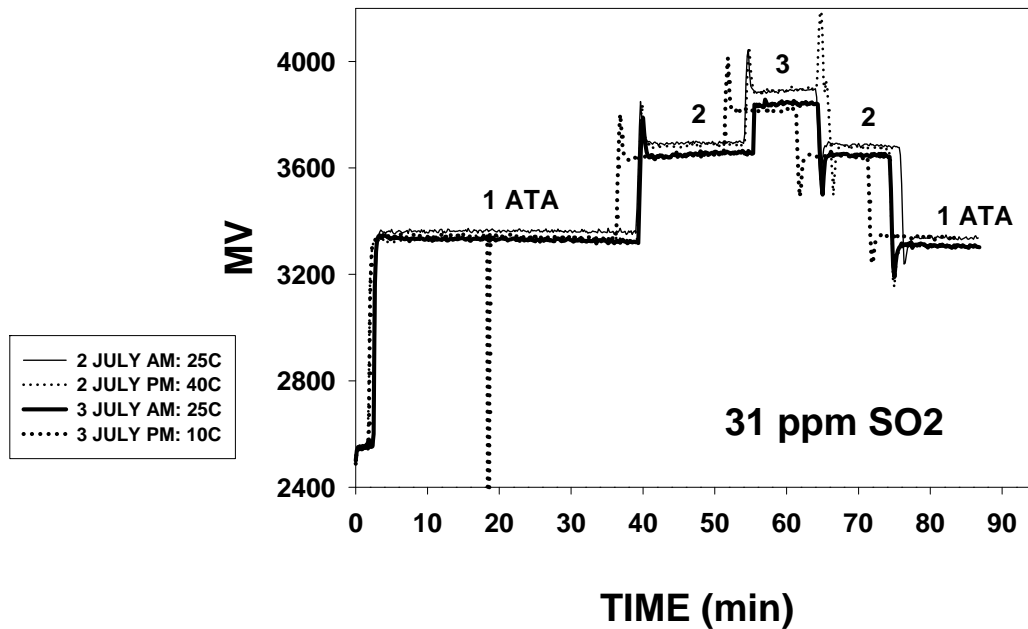


FIGURE 7C. Test System: Temperature effects on NO₂/Cl₂ sensor.

With mV plotted from AM (25 °C) and PM (10 °C or 40 °C) tests

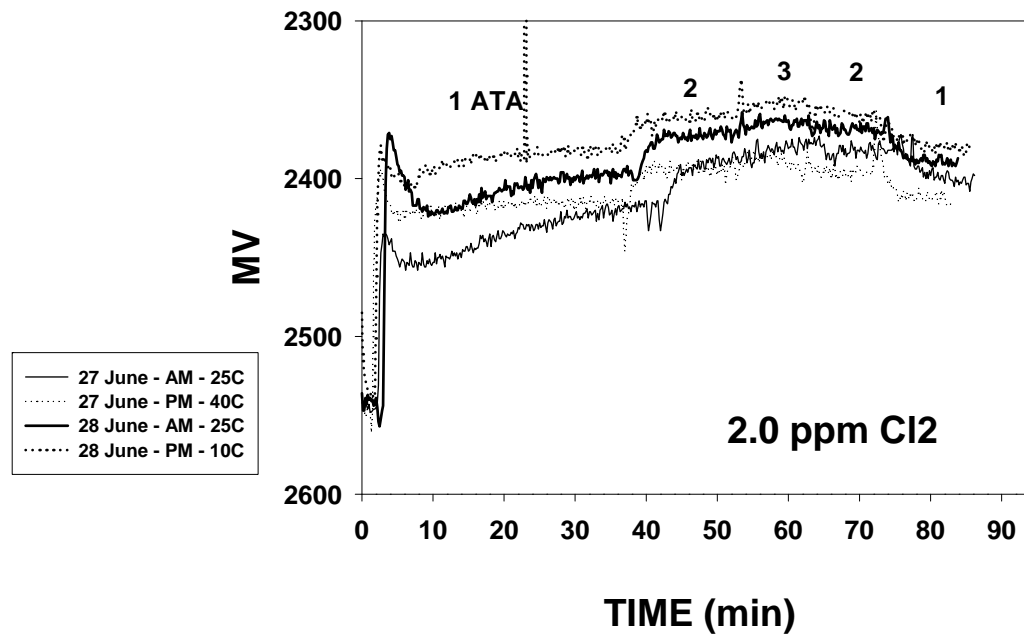


FIGURE 8A. Test System: Cross sensitivities for H₂ in CO and H₂S sensors.

With mV plotted for one test with 1% H₂ at 1 ATA

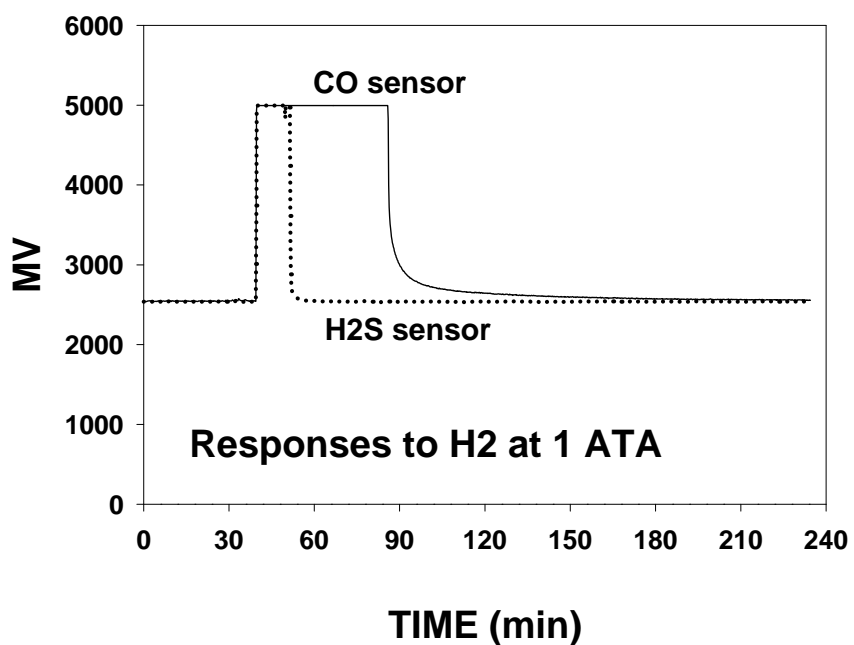


FIGURE 8B. Test System: Cross sensitivities for H₂ in SO₂ (top graph) and NO₂/Cl₂ (bottom graph) sensors.

With mV plotted for one test with 1% H₂ at 1 ATA

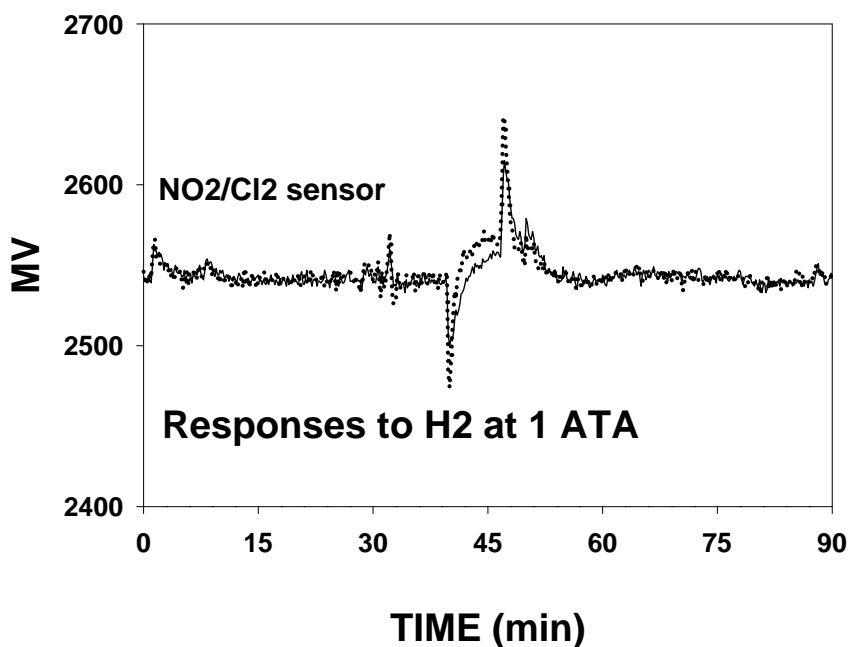
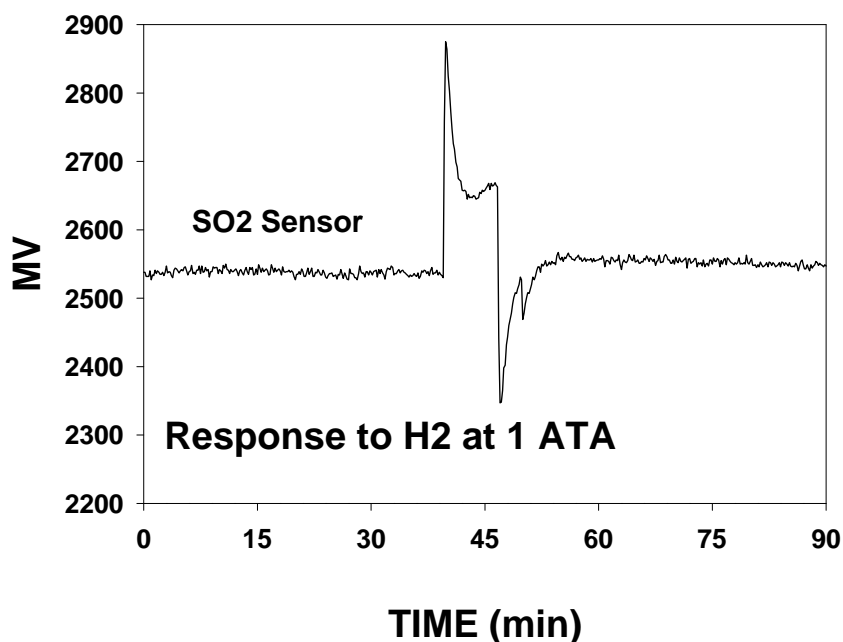


FIGURE 9A. Test System: Cross sensitivity of sensors to H₂ — comparing responses to 1% H₂ vs. 92 ppm CO and 30 ppm H₂S.

With mV plotted for one test each, at 1 ATA and 3 ATA dives

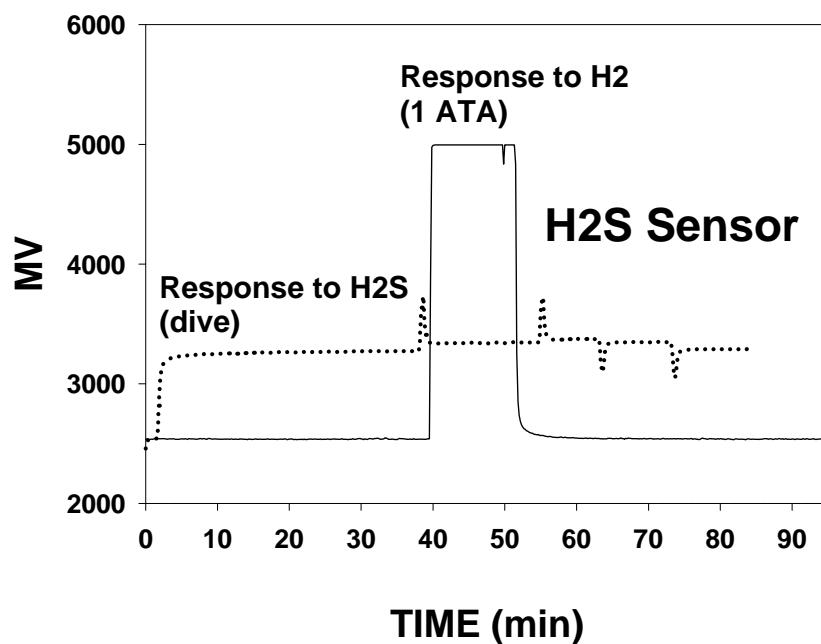
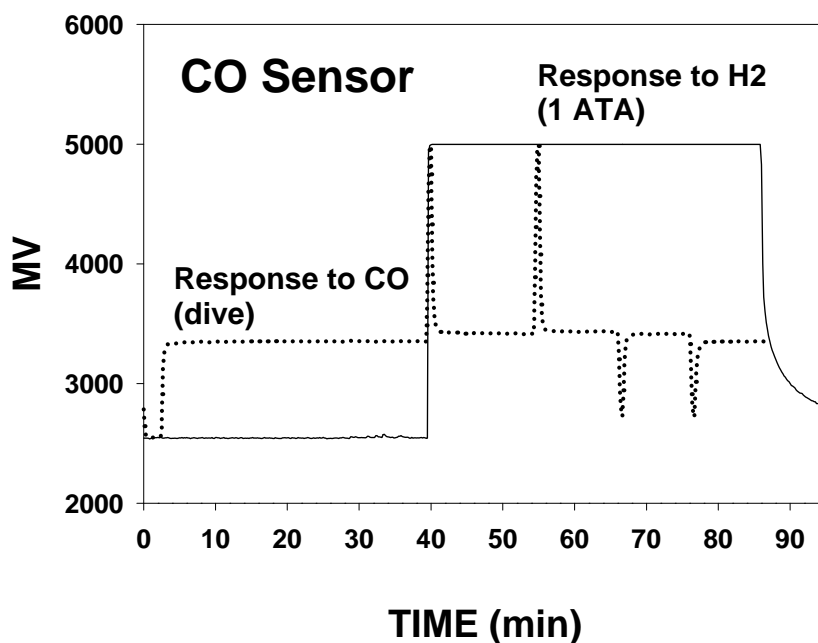


FIGURE 9B. Test System: Cross sensitivity of sensors to H₂ — comparing responses to 1% H₂ vs. 31 ppm SO₂ (top graph) and 10 ppm NO₂ (bottom graph).

With mV plotted for one test each, at 1 ATA and at 3 ATA dives

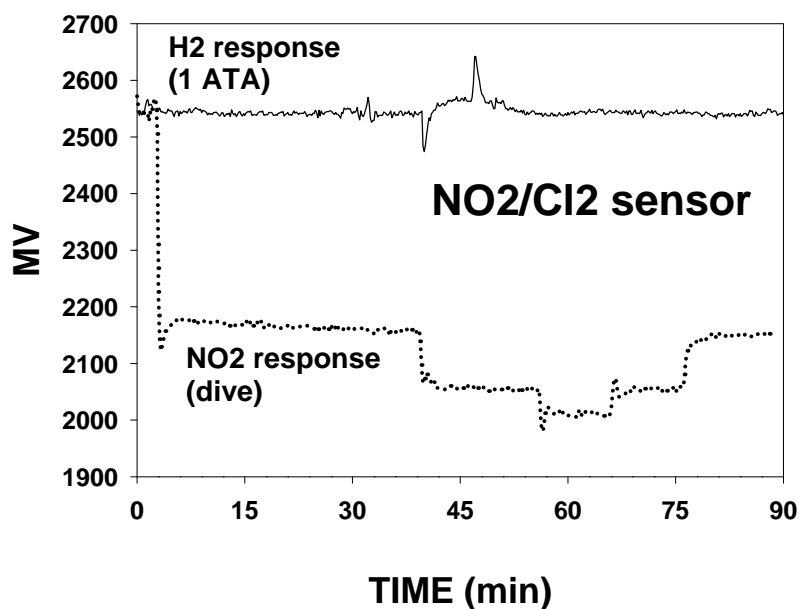
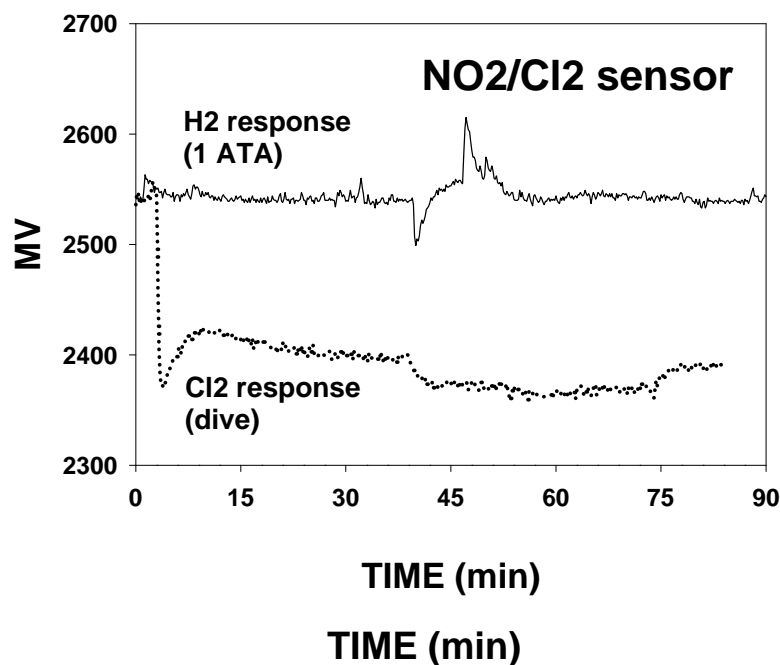
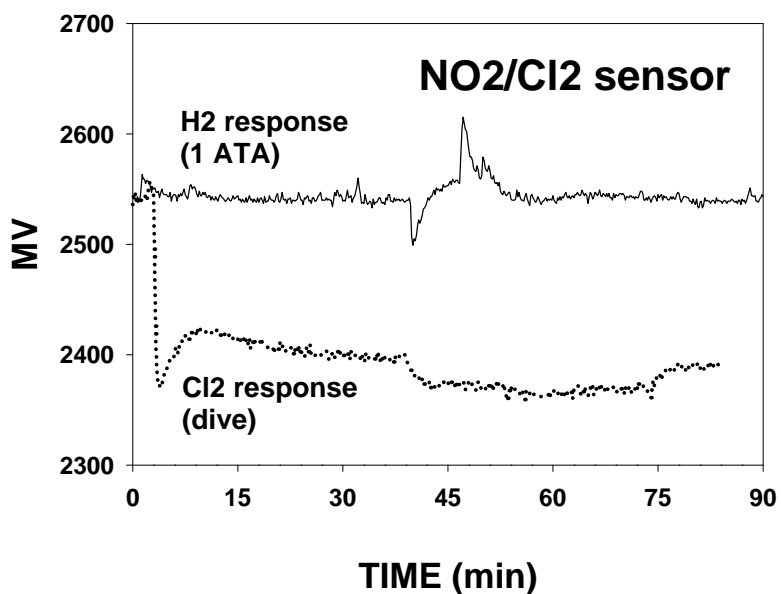


FIGURE 9C. Test System: Cross sensitivity of sensor to H₂ — comparing responses of 2.0 ppm Cl₂ to 1% H₂.

With mV plotted for one test each, at 1 ATA and at 3 ATA dives



**FIGURE 10A. SubTox hyperbaric toxic gas monitor,
one of six tested at NEDU.**

**LCD display as shown is from an early version SubTox and
different from that in the final-version SubTox.**



FIGURE 10B. SubTox hyperbaric toxic gas monitor with LCD.

On left: gas inlet with hydrophobic filter and LED alarm

On right: audio alarm and menu/select buttons

Again, the LCD display as shown is from an early version SubTox.



FIGURE 10C. SubTox hyperbaric toxic gas monitor.

Inside view, bottom half of case: custom circuit board, batteries, gas manifold (two “white blocks”), and sampling pump (mounted atop gas manifold)

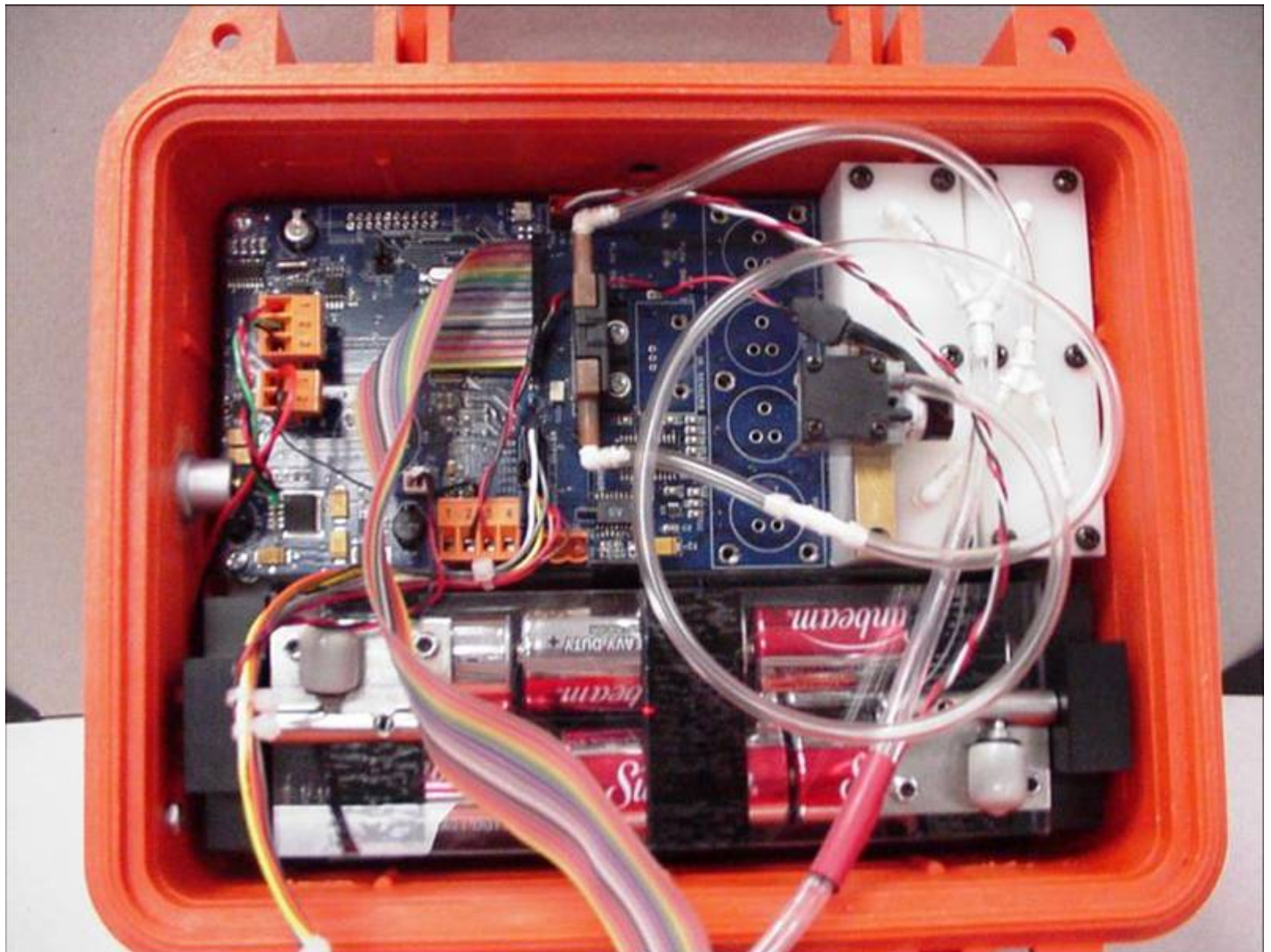


FIGURE 10D. SubTox hyperbaric toxic gas monitor.

Inside view, top half of case: back of LCD, gas inlet block with attached tubing, and several switches and audio alarm

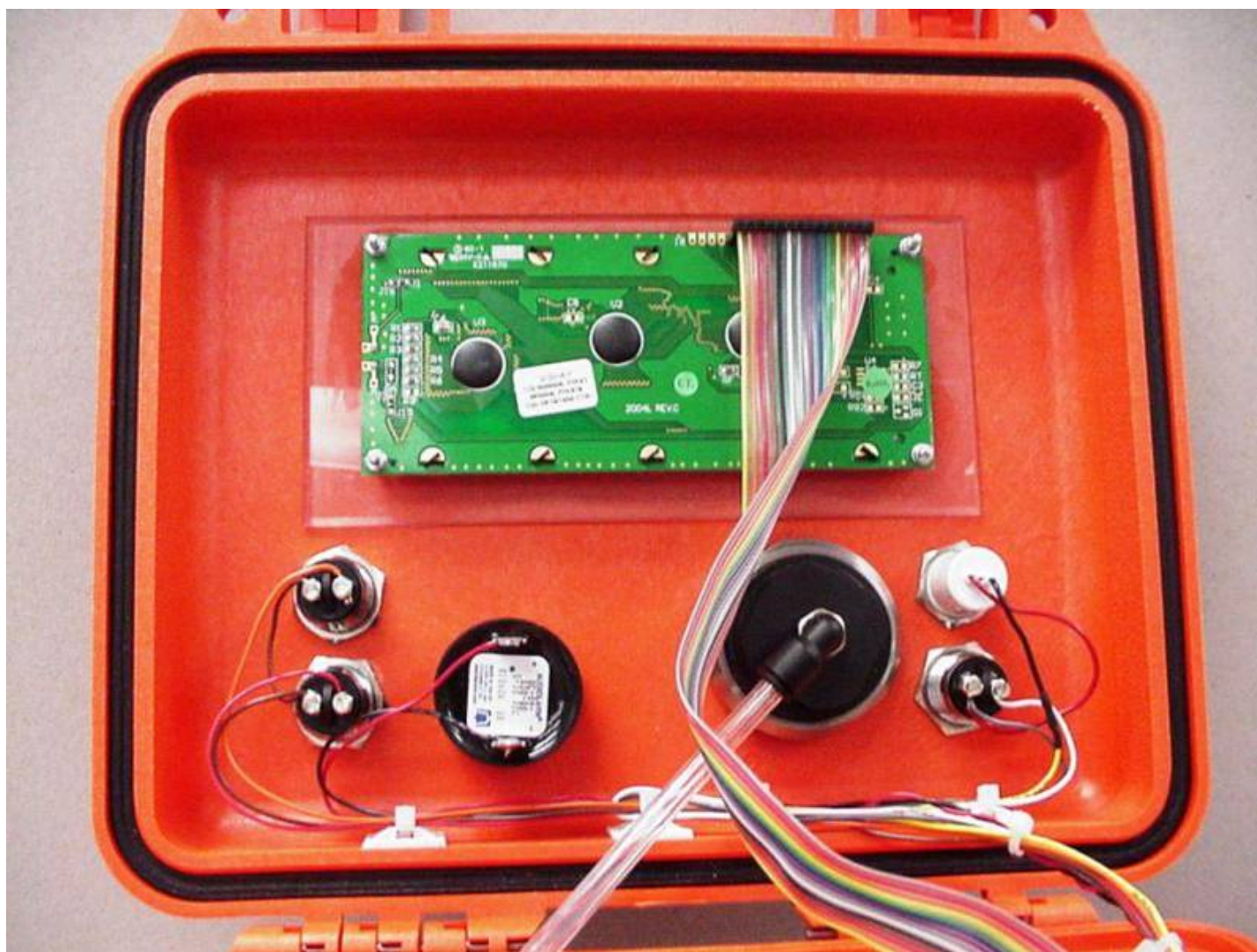


FIGURE 11A. SubTox bench testing setup.

Test gas is drawn from Tedlar bag, which is kept ~50% full by flowing ~400 to 600 mL/min into it from the rotameter. Rotameter's gas flow is adjusted via low-pressure delivery regulator installed on test gas cylinder (not shown).



FIGURE 11B. Hyperbaric chamber used to test SubTox at pressure.

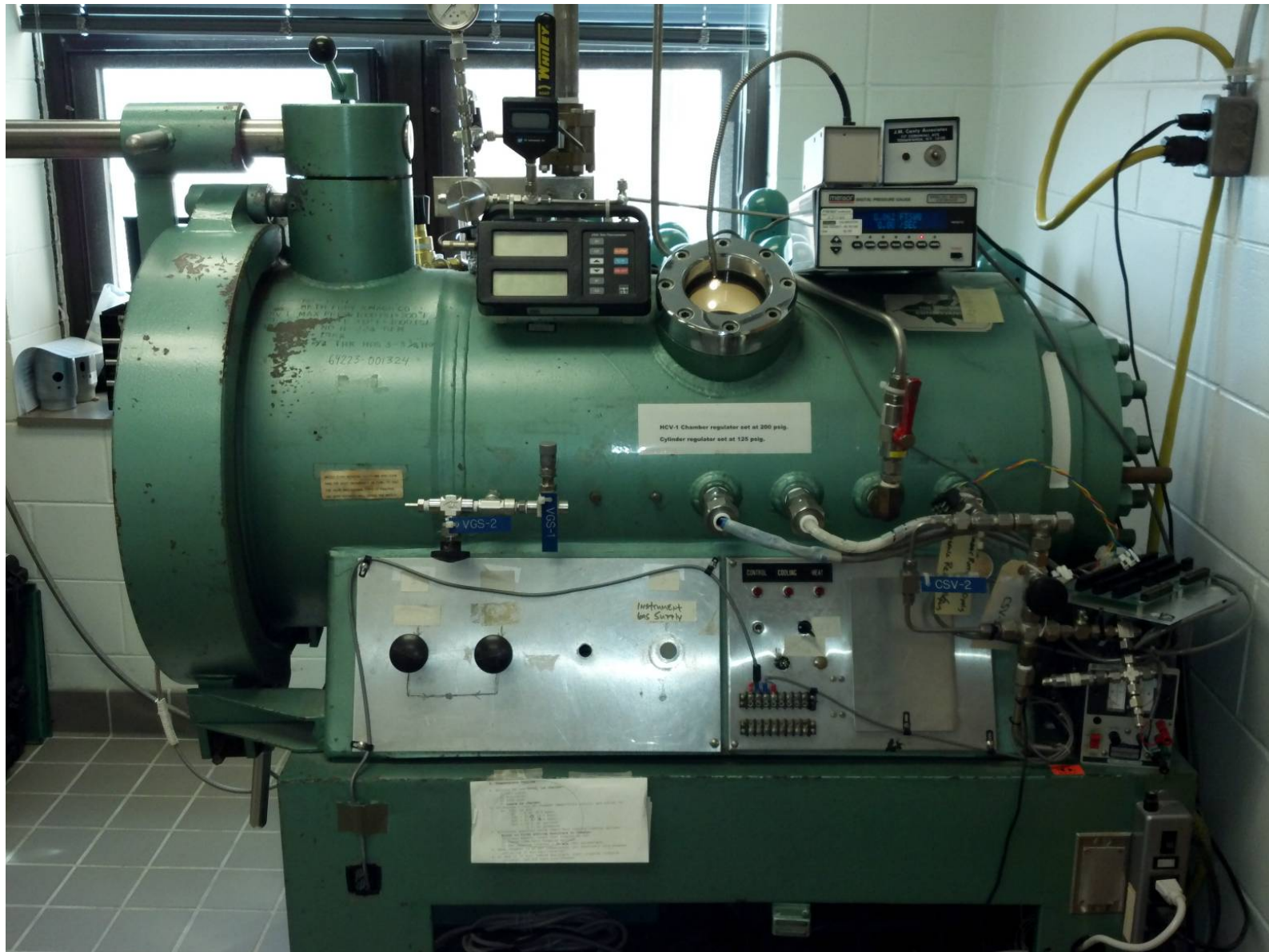


FIGURE 11C. Front view, hyperbaric chamber used to test SubTox.

Test gas cylinder delivers gas to inside of chamber via high-pressure whip connected to hardware “penetrator” on exterior of chamber wall.

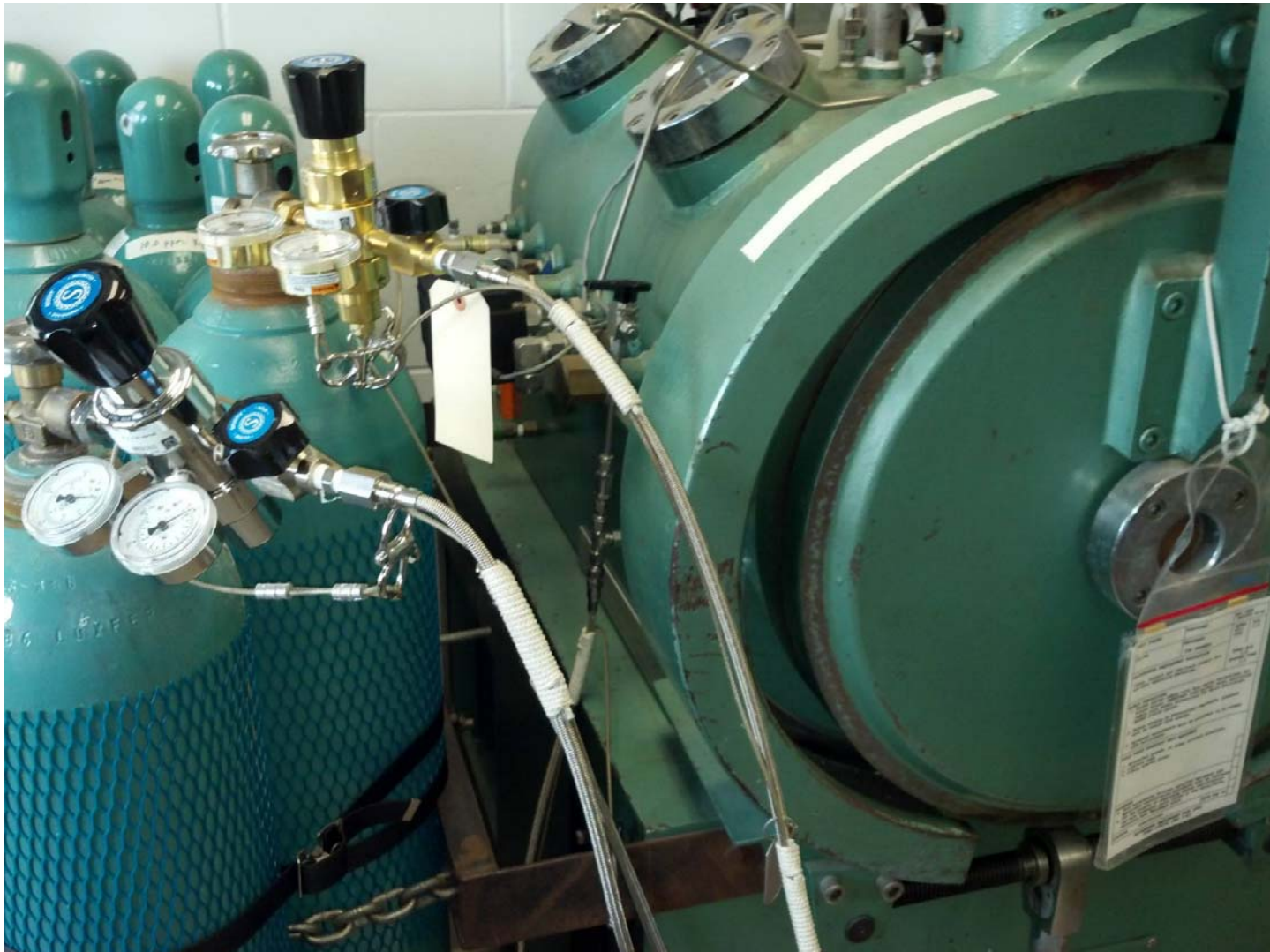


FIGURE 11D. Inside view, hyperbaric chamber containing SubTox.

Using procedure identical to that for bench testing, rotameter delivers test gas from chamber penetrator to Tedlar bag, from which SubTox draws gas. Gas flow to rotameter is adjusted via valve on outside of chamber.



FIGURE 12A. Variability among three SubTox monitors.

CO: mV plotted

Top Graph: One test with one SubTox

Bottom Graph: One AM and one PM Test with each SubTox

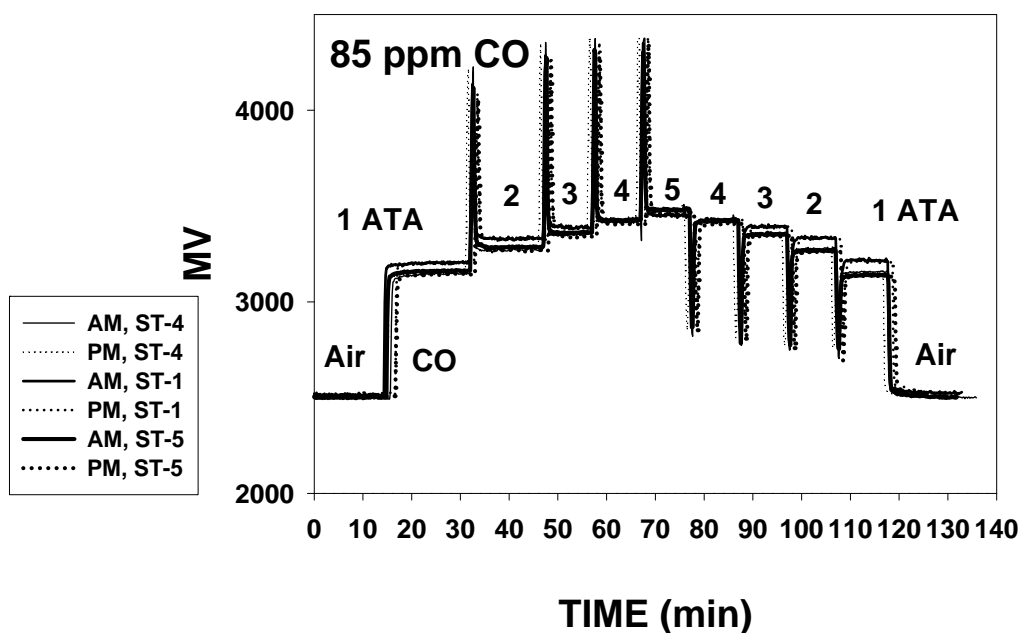
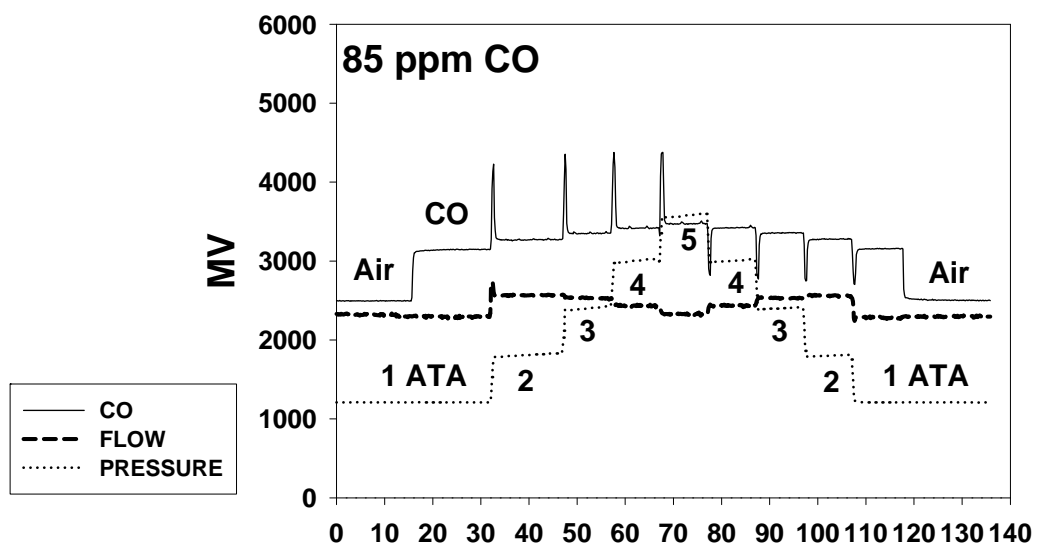


FIGURE 12B. Variability among three SubTox monitors.

H₂S: mV plotted

Top Graph: One test with one SubTox

Bottom Graph: One AM and one PM test with each SubTox

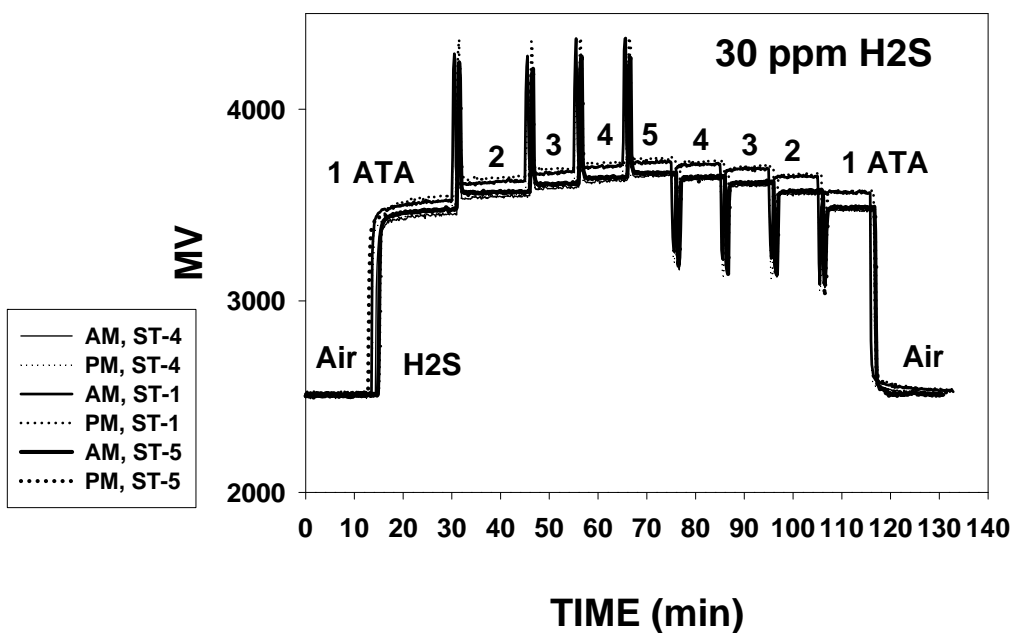
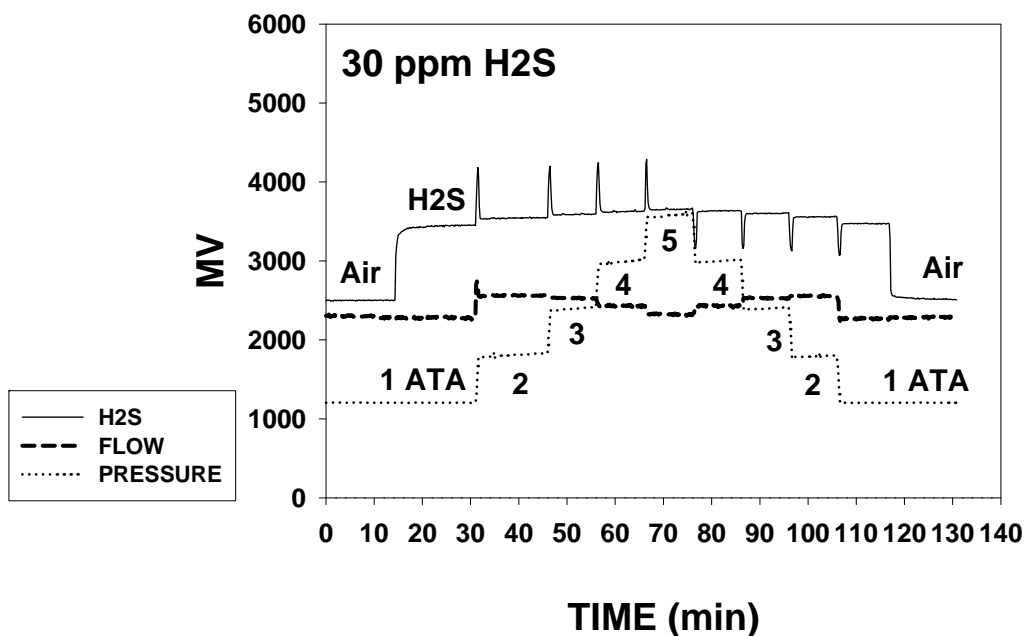


FIGURE 12C. Variability among three SubTox monitors.

SO₂: mV plotted
Top Graph: One test with one SubTox
Bottom Graph: One AM and one PM test with each SubTox

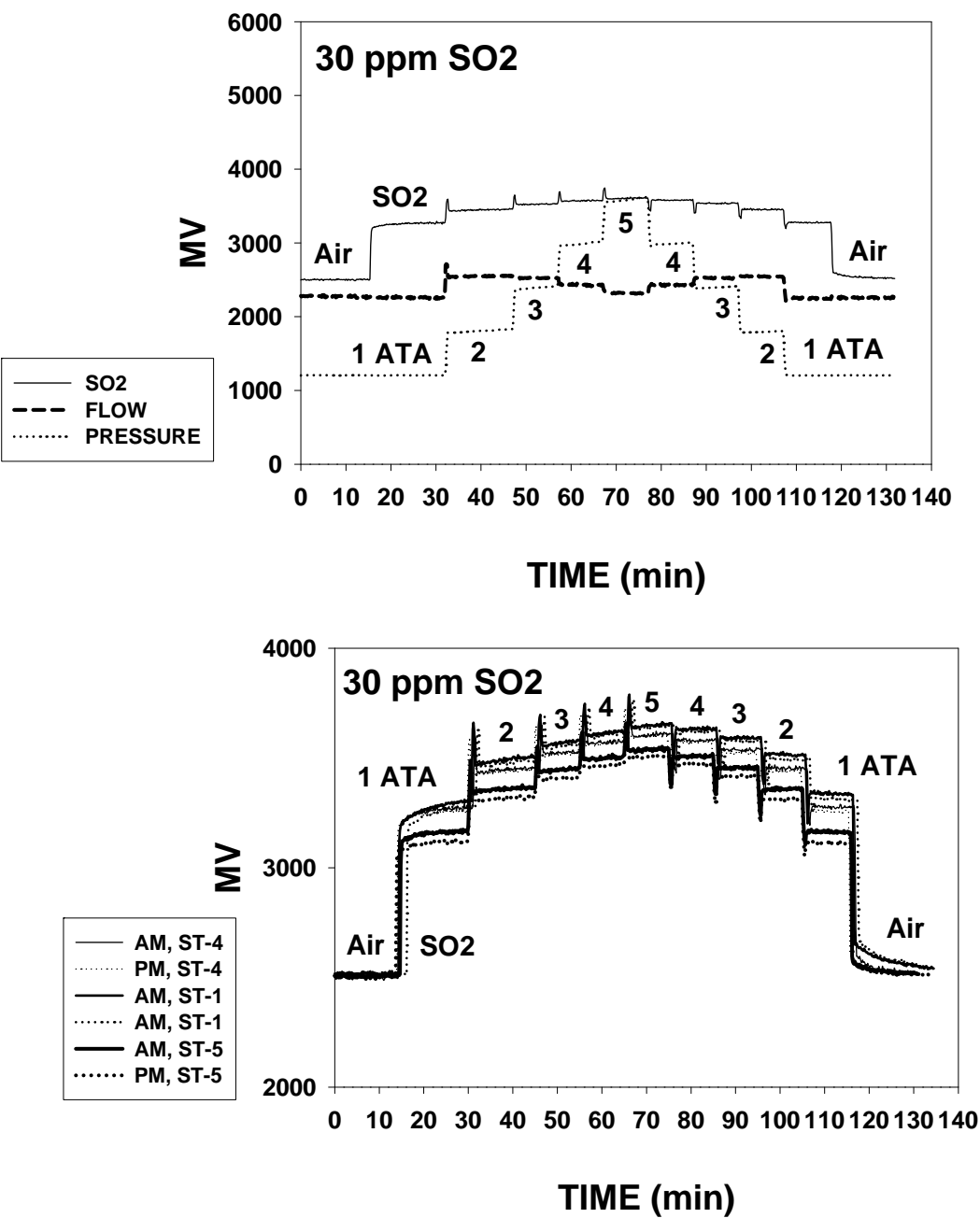


FIGURE 12D. Variability among three SubTox monitors.

NO₂: mV plotted

Top Graph: One test with one SubTox

Bottom Graph: One AM and one PM test with each SubTox

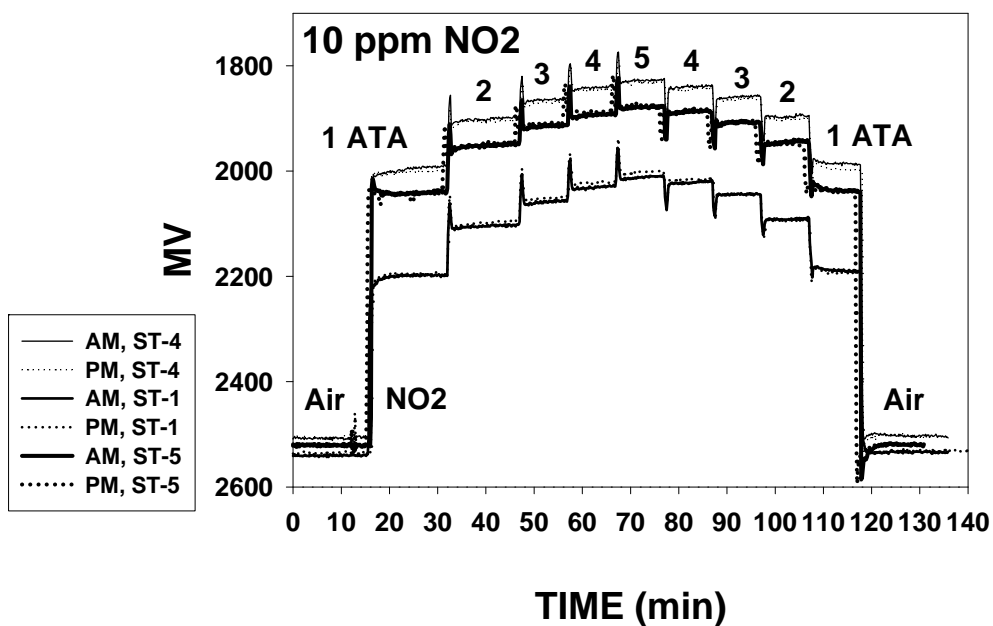
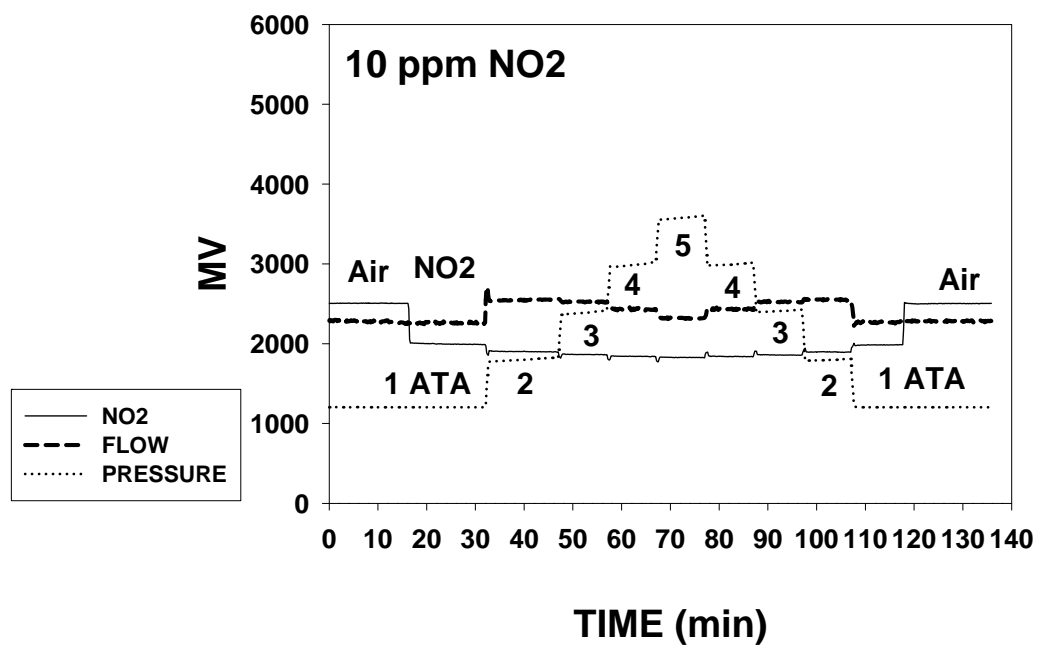


FIGURE 12E. Variability among three SubTox monitors.

Cl₂: mV plotted

Top Graph: One test with one SubTox

Bottom Graph: One AM and one PM test with each SubTox

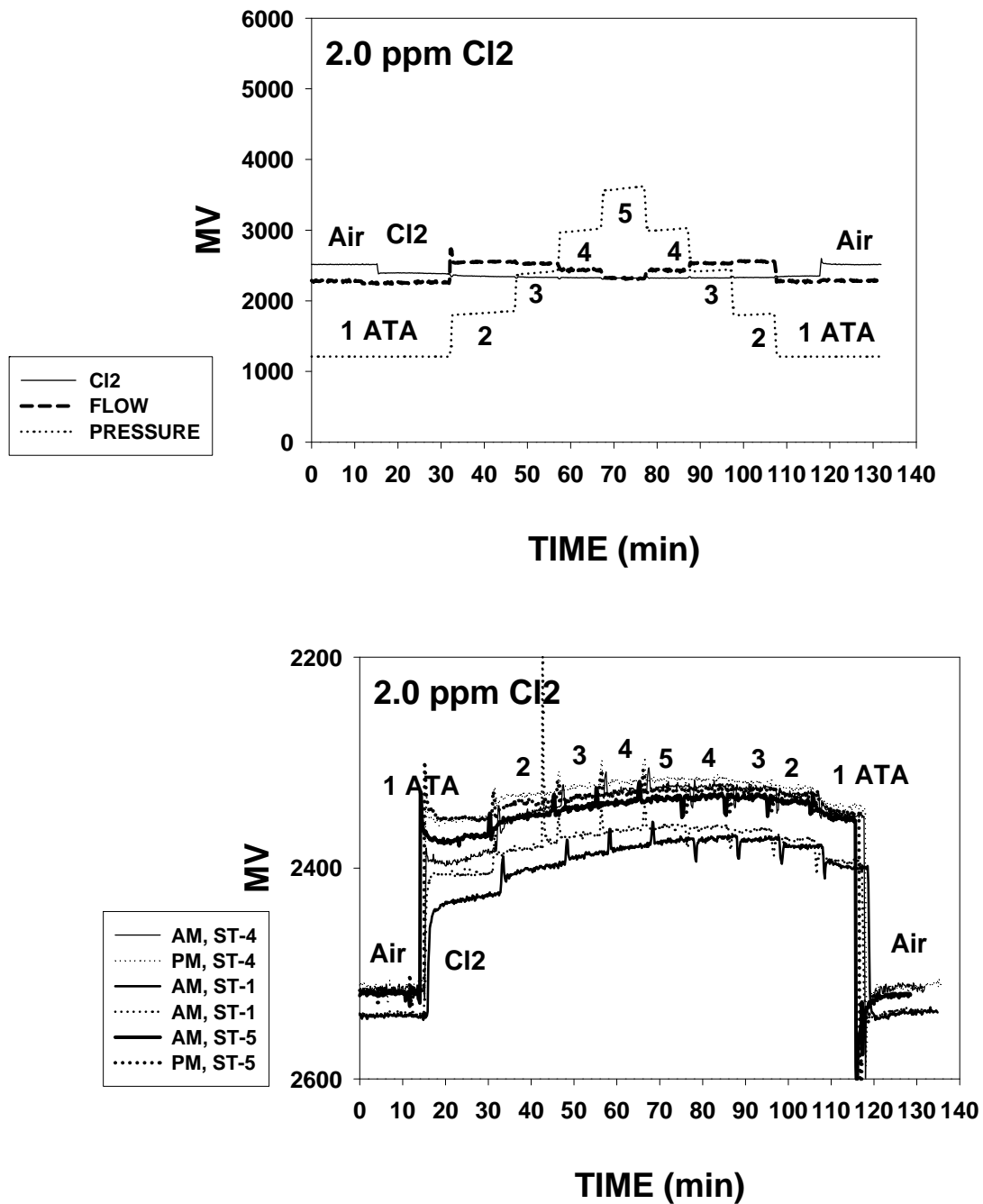


FIGURE 12F. Variability among three SubTox monitors.

HCN: mV plotted
Top Graph: One test with one SubTox
Bottom Graph: One AM and one PM test with each SubTox

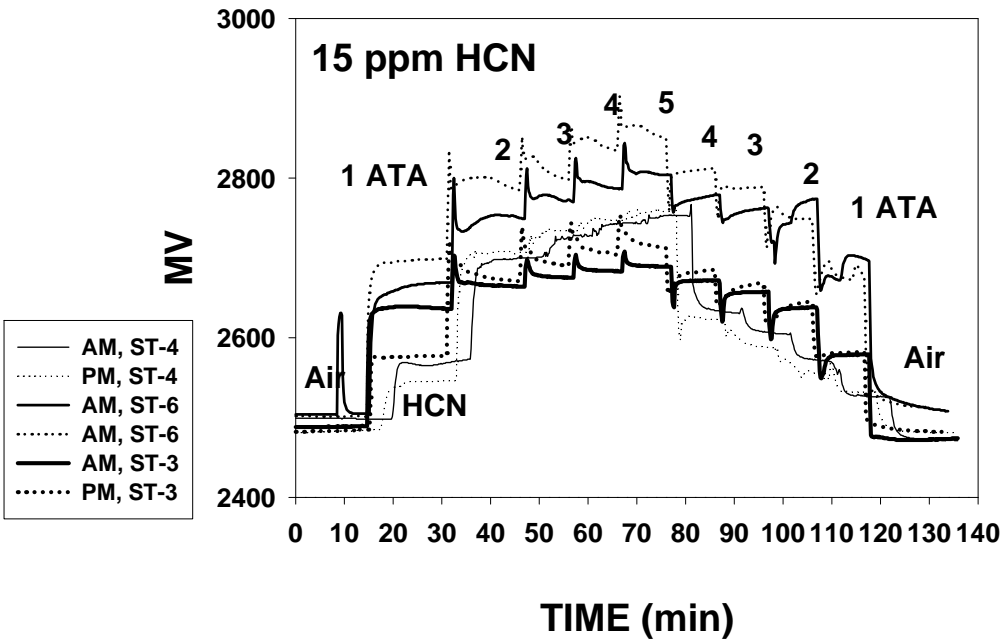
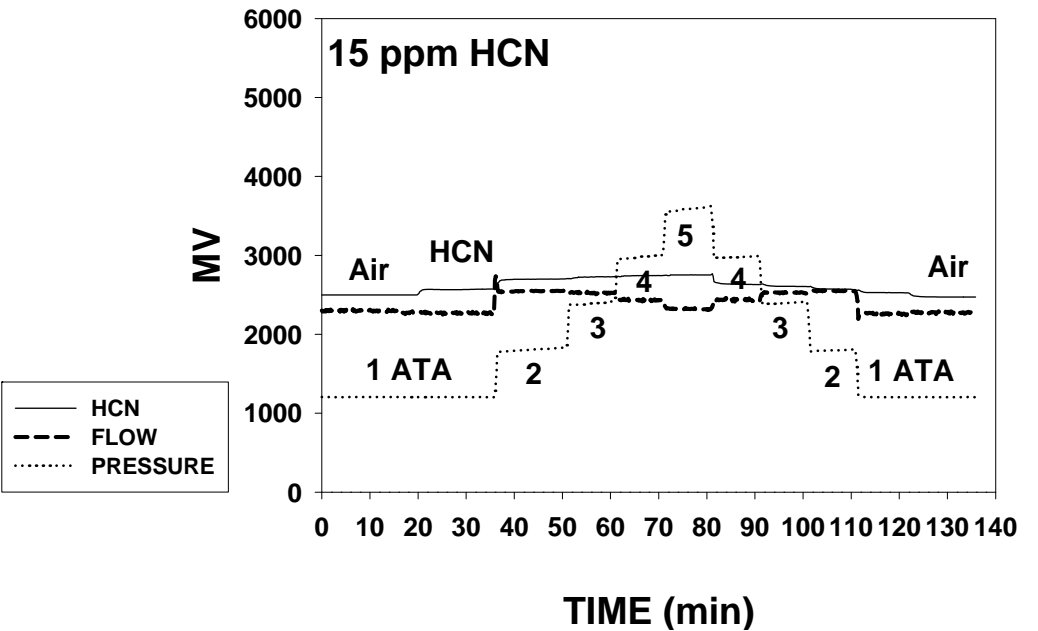


FIGURE 12G. Variability among three SubTox monitors.

HCl: mV plotted

Top Graph: One test with one SubTox

Bottom Graph: One AM and one PM test with each SubTox

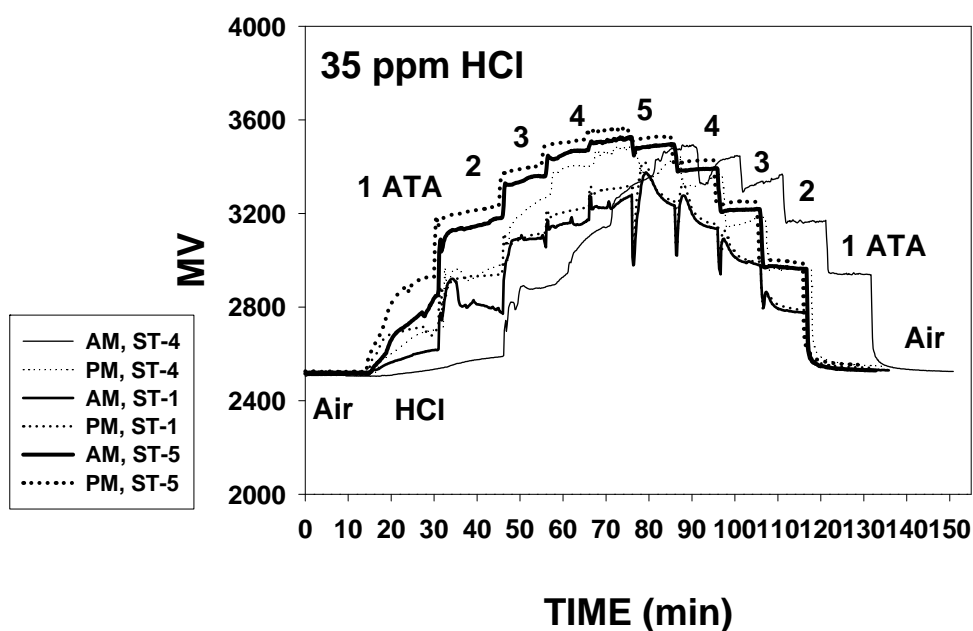
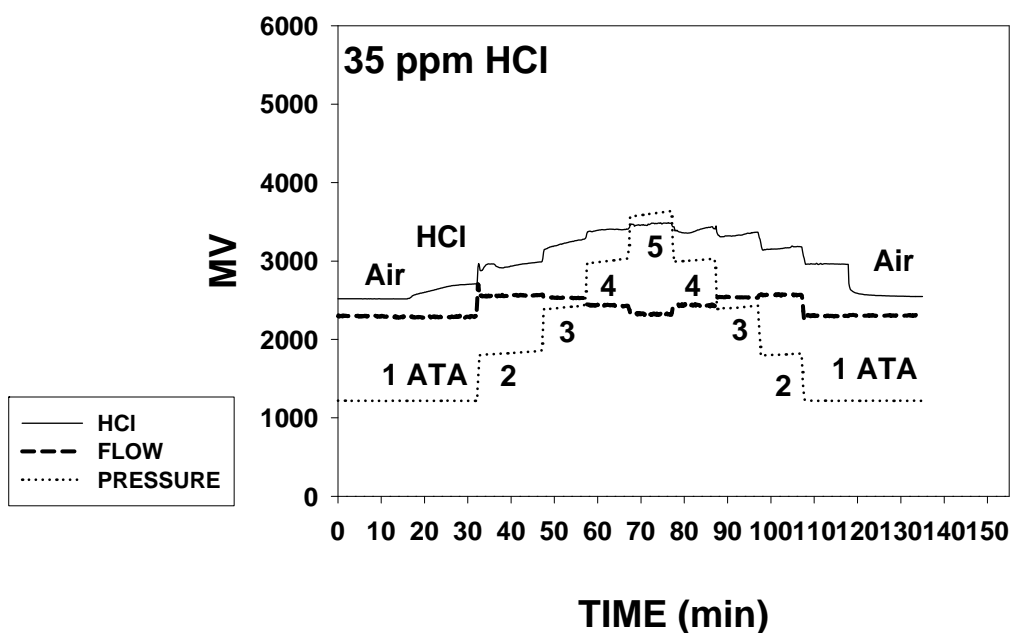


FIGURE 13A. SubTox linearity at 1 ATA: CO.

Means and SDs from one test with each of six SubTox monitors
100% = SEAL2 response = 85 ppm CO

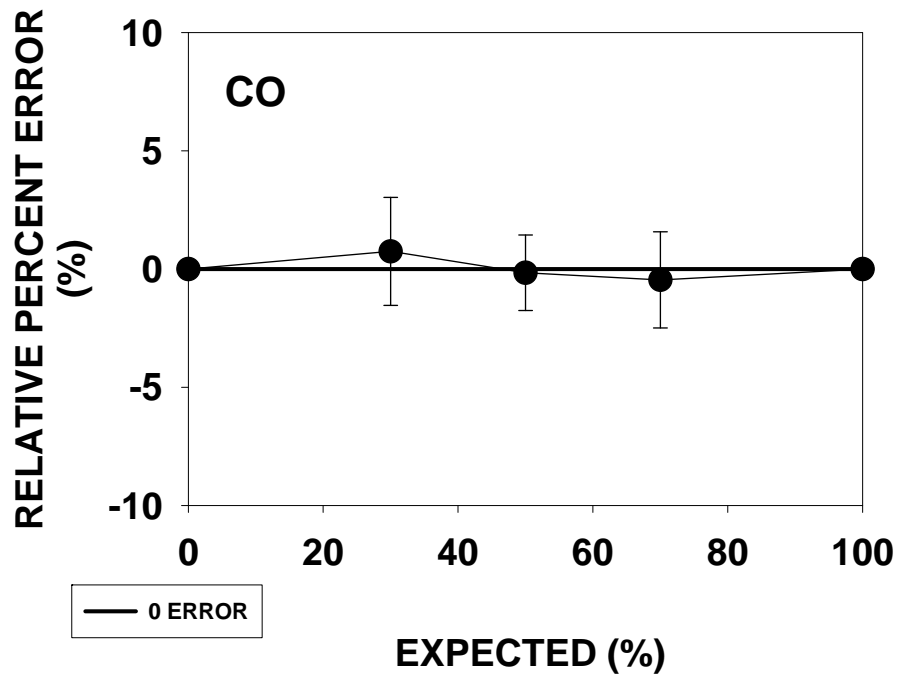
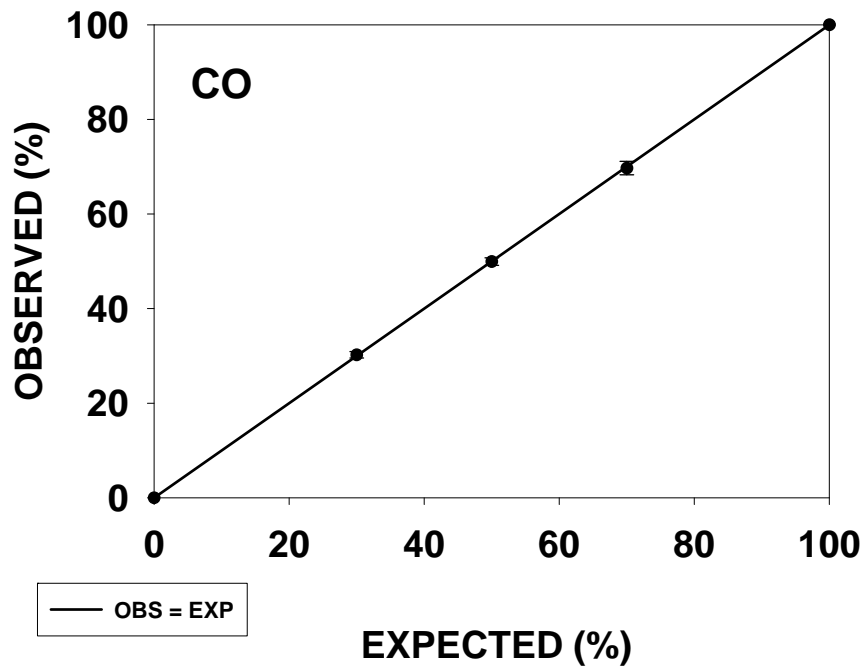


FIGURE 13B. SubTox linearity at 1 ATA: H₂S.

Means and SDs from one test with each of six SubTox monitors
100% = SEAL2 response = 30 ppm H₂S

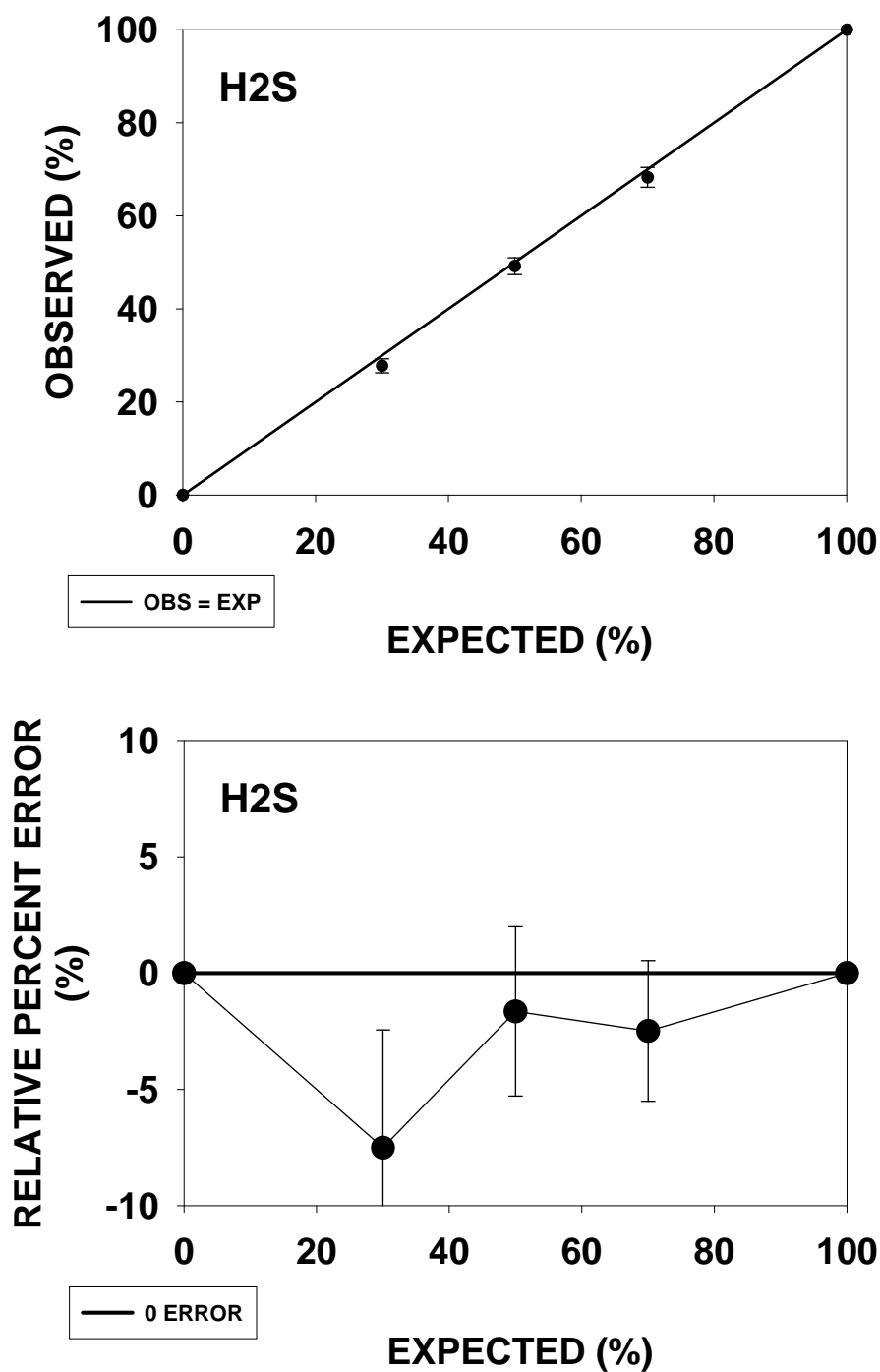


FIGURE 13C. SubTox linearity at 1 ATA: SO₂.

Means and SDs from one test with each of six SubTox monitors
100% = SEAL2 response = 30 ppm SO₂

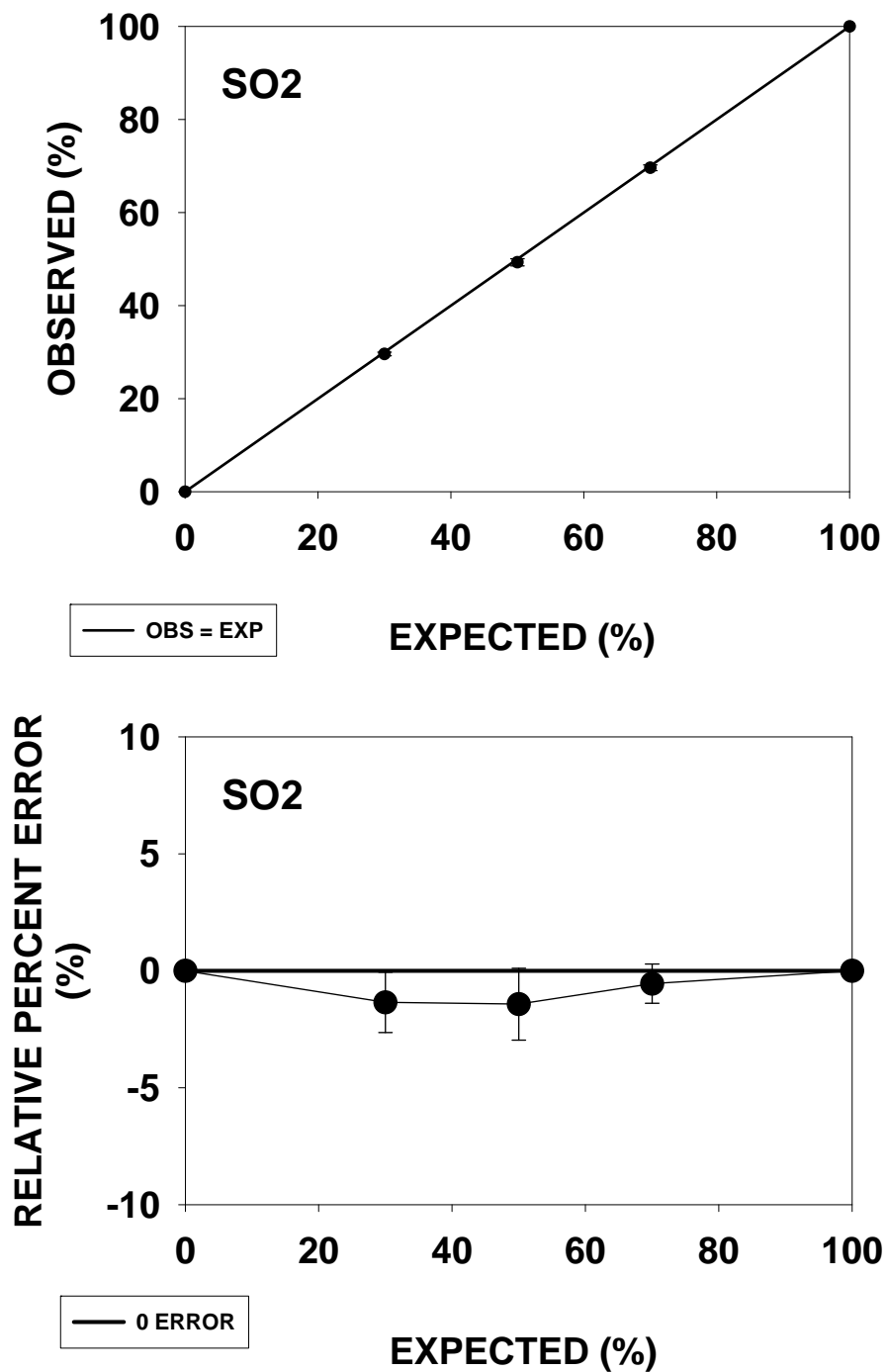


FIGURE 13D. SubTox linearity at 1 ATA: NO₂.

Means and SDs from one test with each of six SubTox monitors
100% = SEAL2 response = 10 ppm NO₂

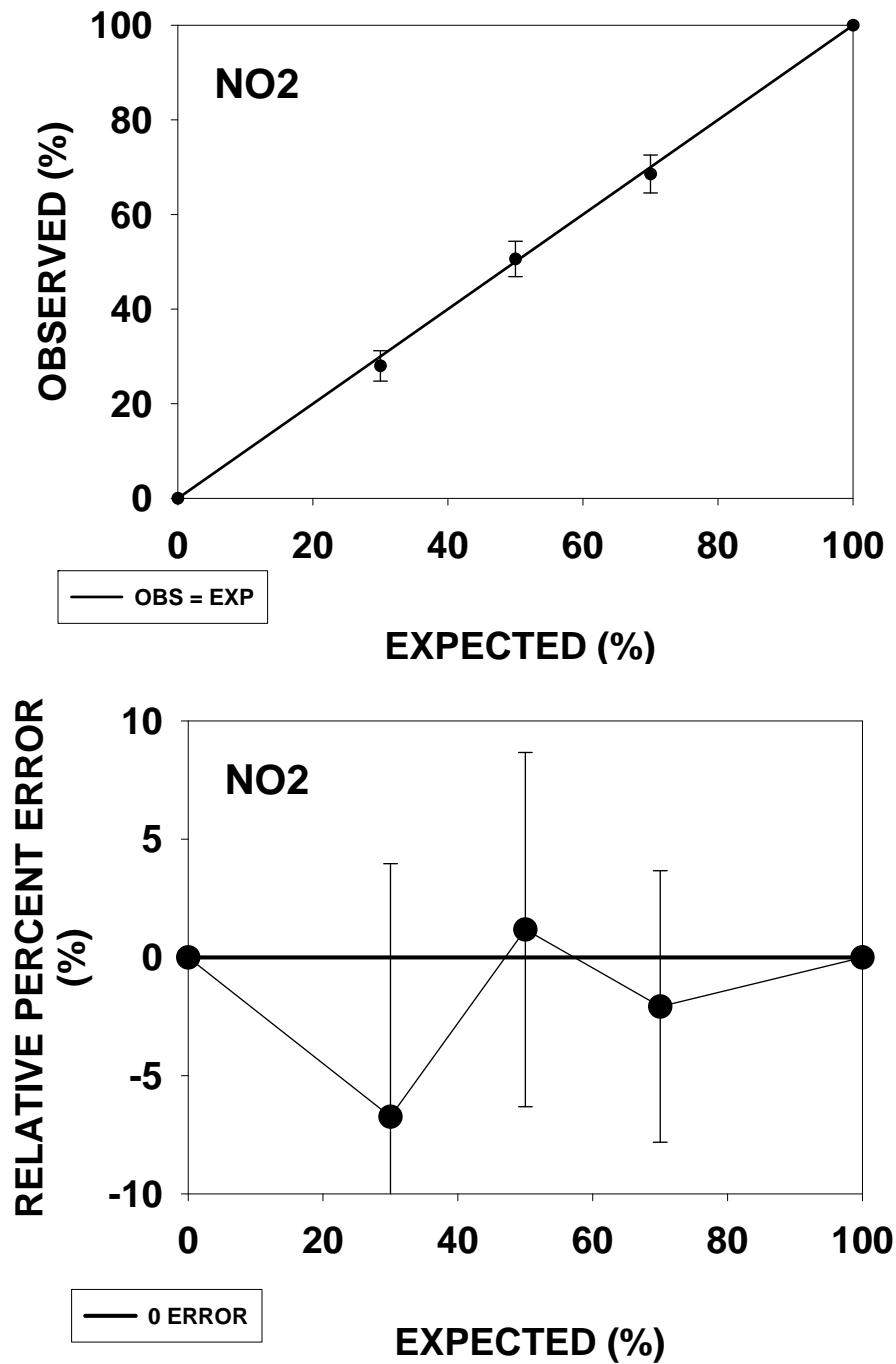


FIGURE 13E. SubTox linearity at 1 ATA: Cl₂.

Means and SDs from one test with each of six SubTox monitors
100% = SEAL2 response = 2.5 ppm Cl₂

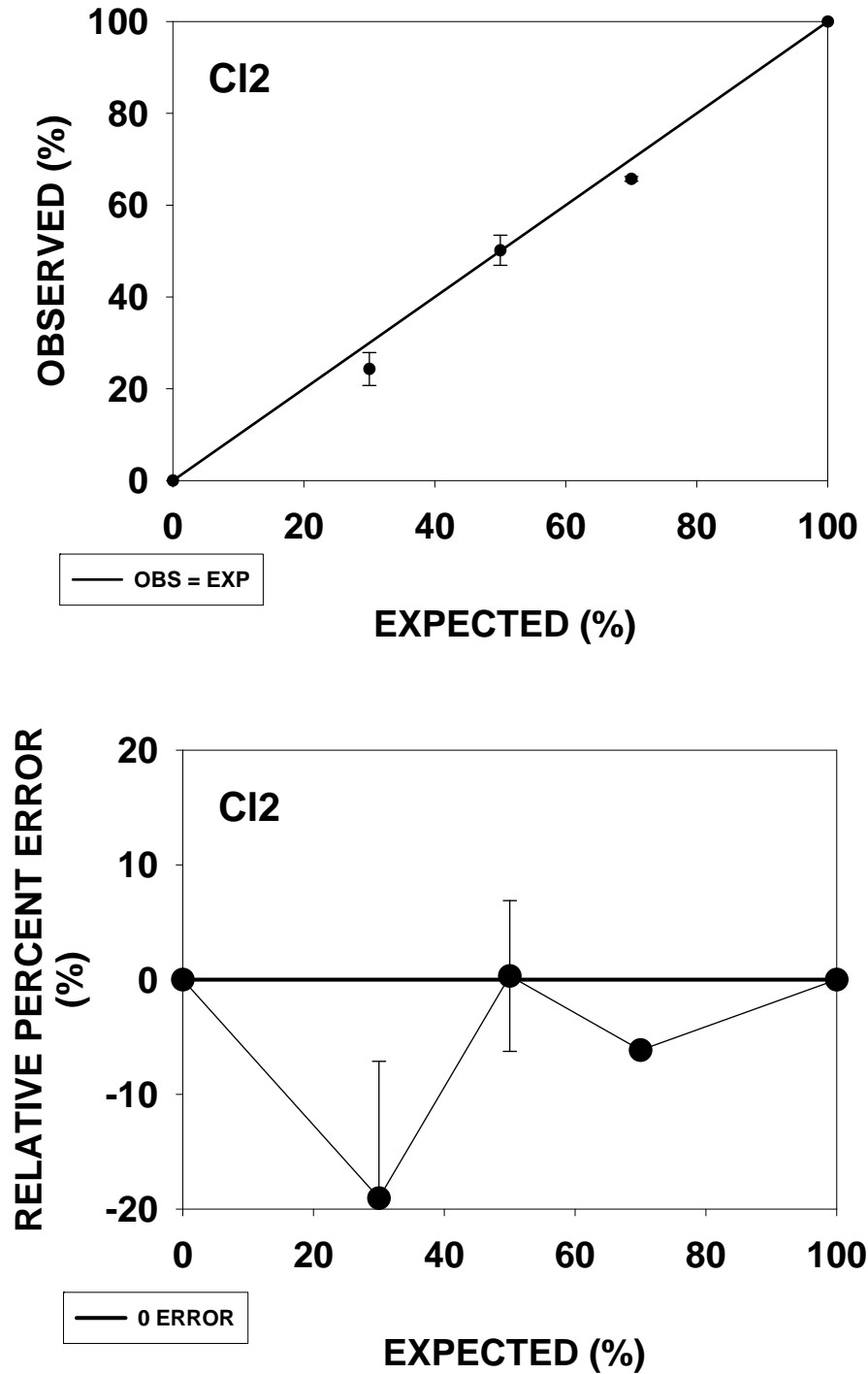
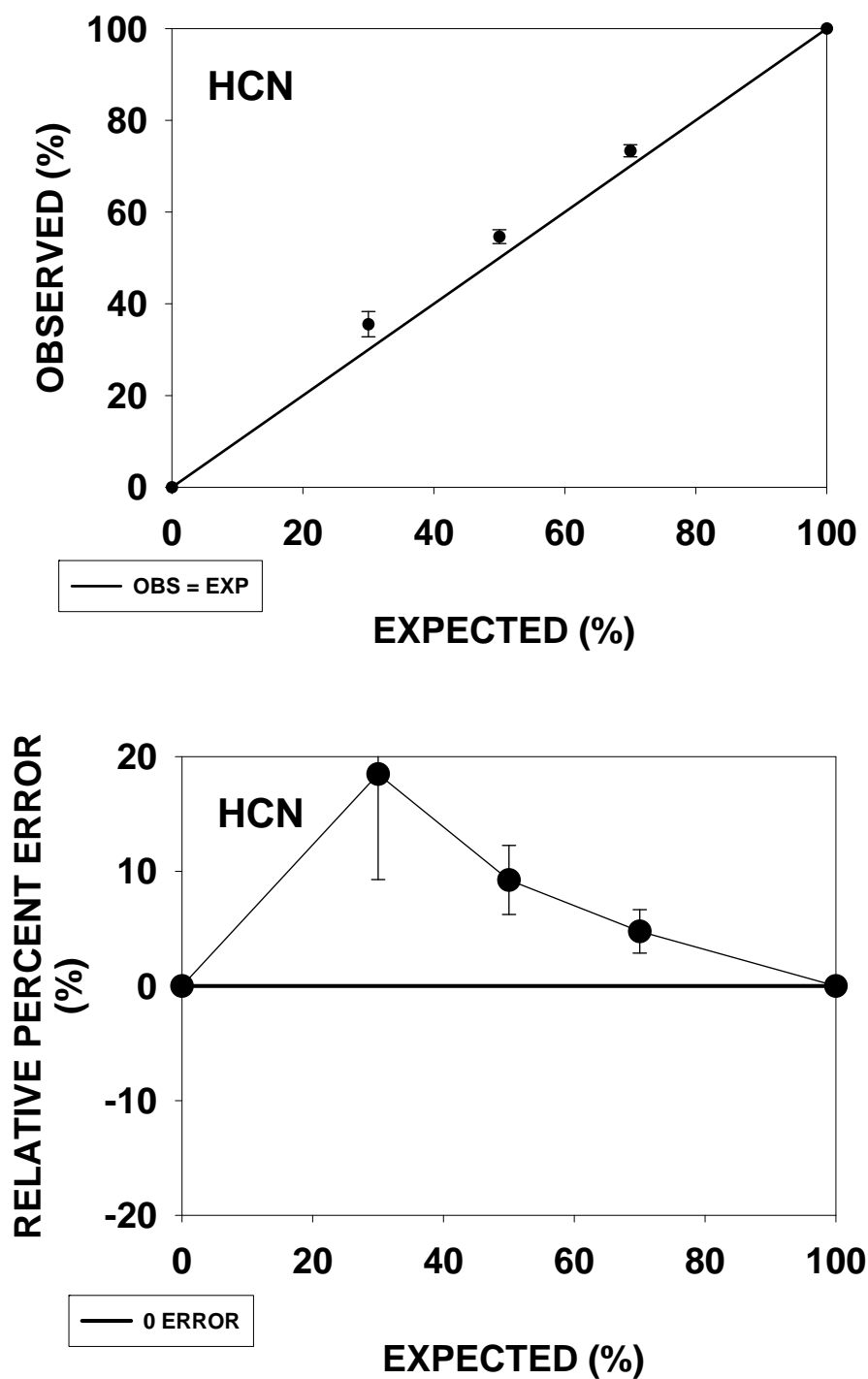


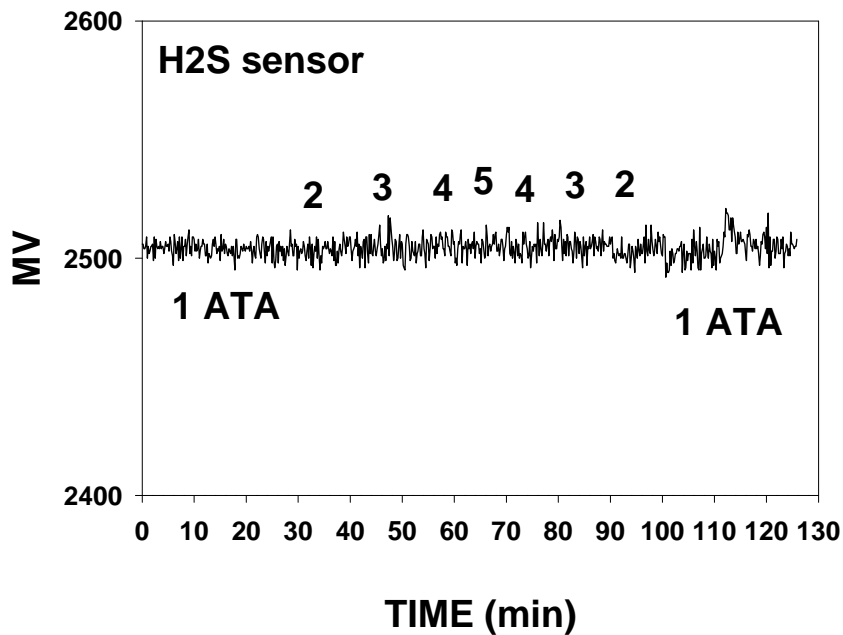
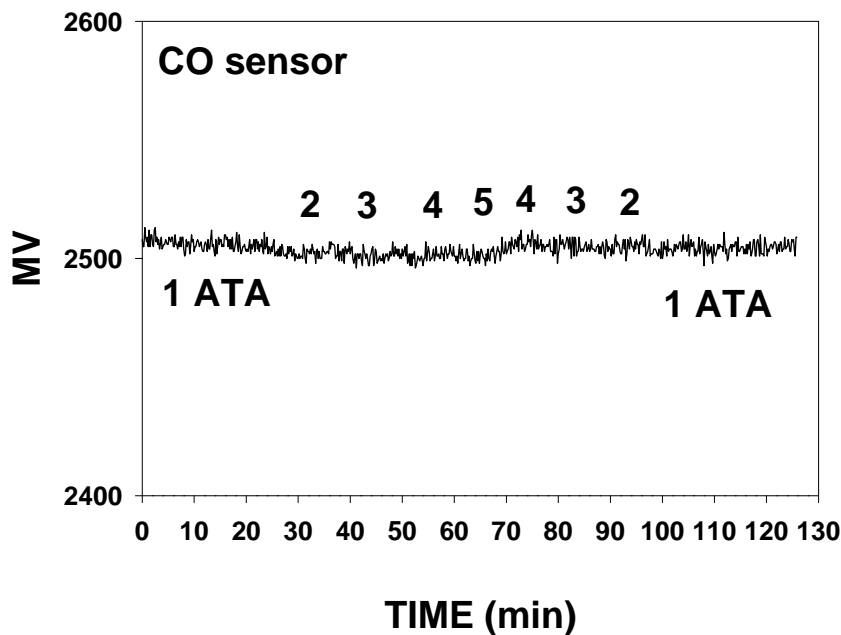
FIGURE 13F. SubTox linearity at 1 ATA: HCN.

Means and SDs from one test with each of six SubTox monitors
100% = SEAL2 response = 15 ppm HCN



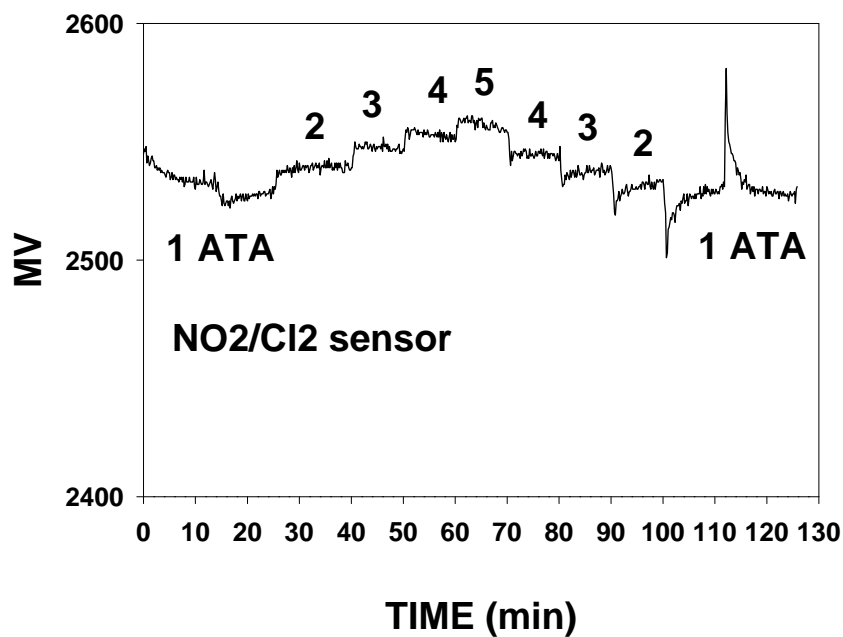
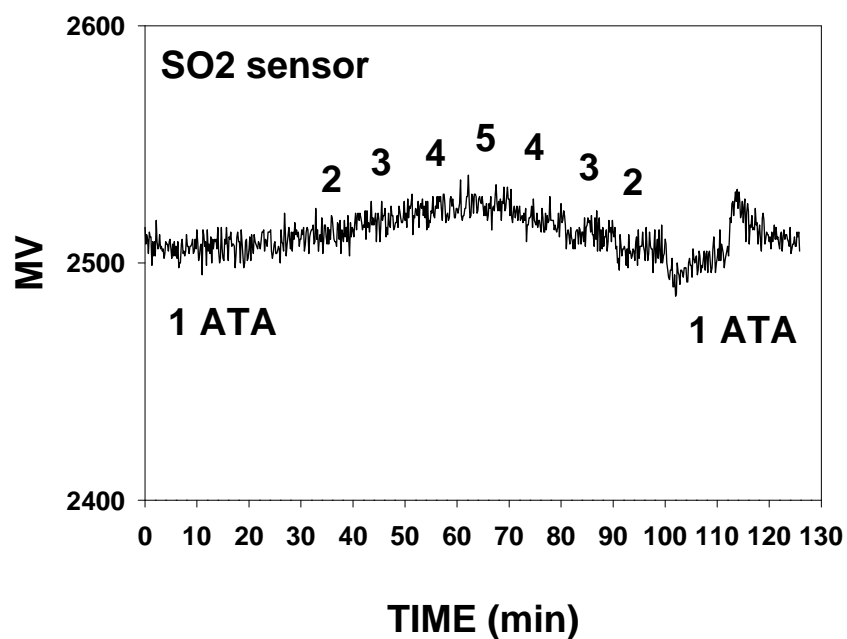
**FIGURE 14A. SubTox responses to air dives to 5 ATA:
CO (top graph) and H₂S (bottom graph) sensors.**

With mV plotted from one test



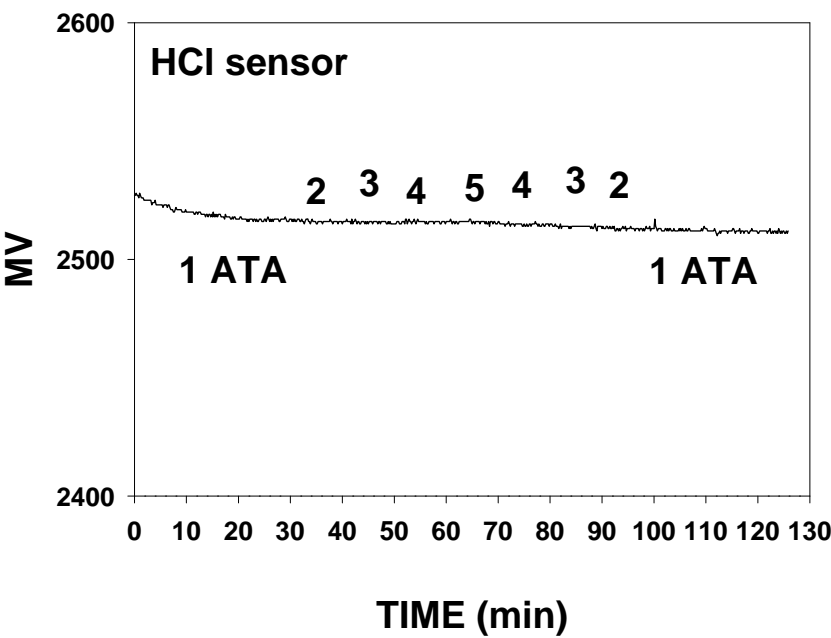
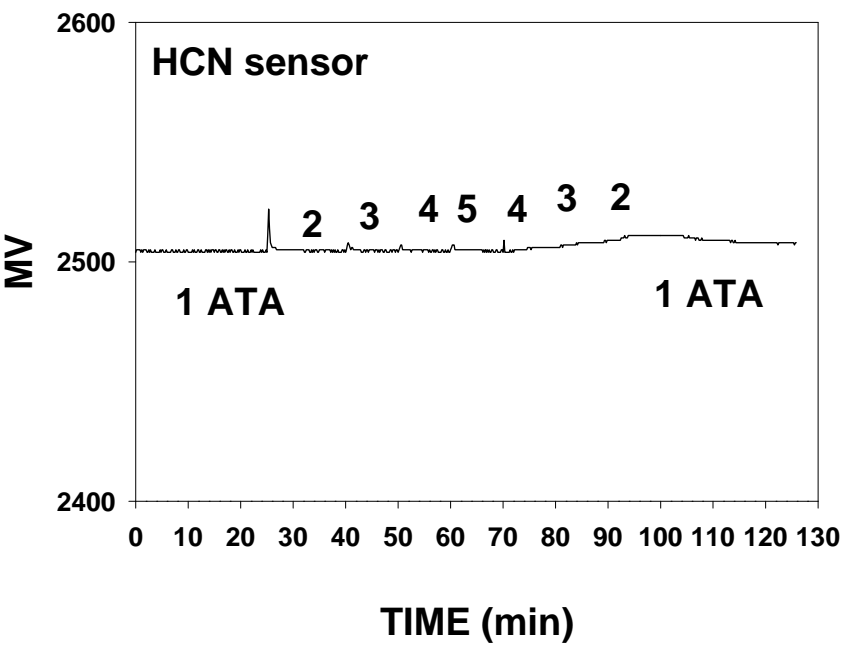
**FIGURE 14B. SubTox responses to air dives to 5 ATA:
SO₂ (top graph) and NO₂/Cl₂ (bottom graph) sensors.**

With mV plotted from one test



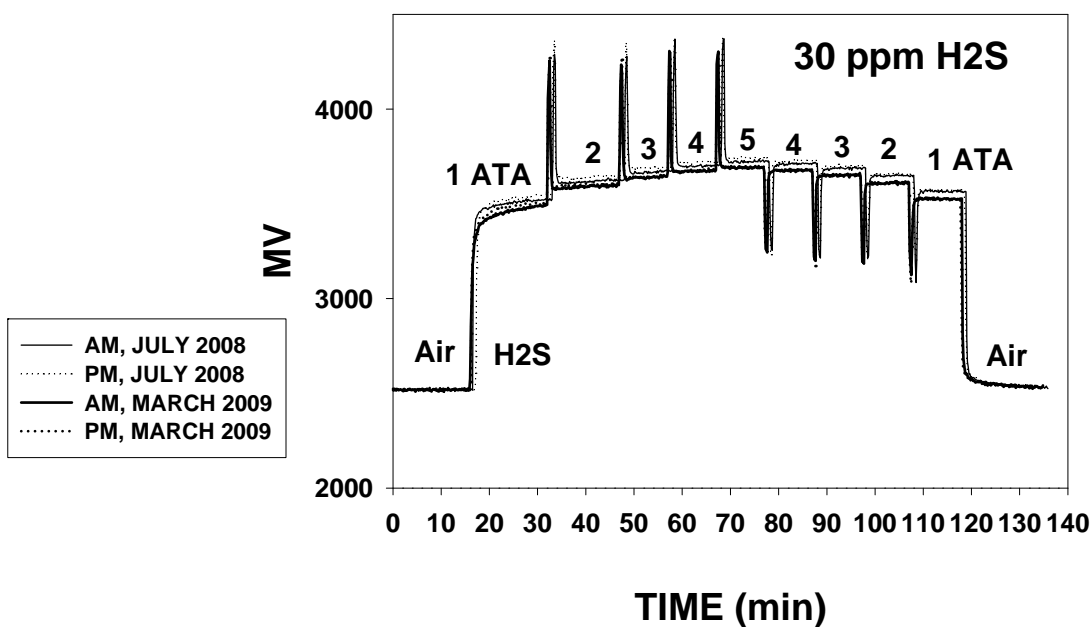
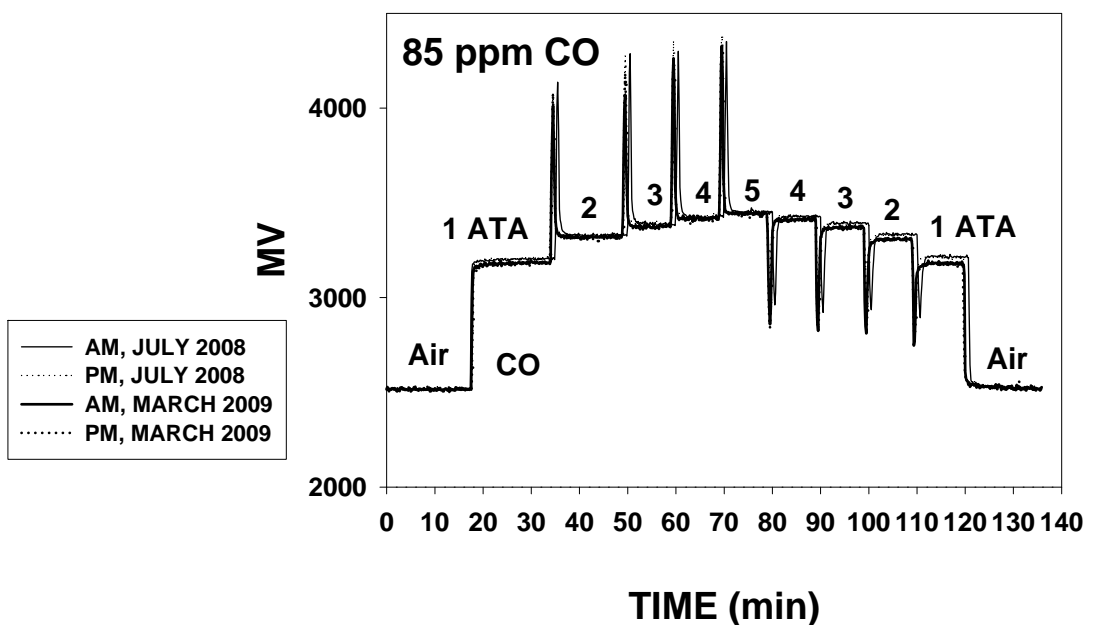
**FIGURE 14C. SubTox responses to air dives to 5 ATA:
HCN (top graph) and HCl (bottom graph) sensors.**

With mV plotted from one test



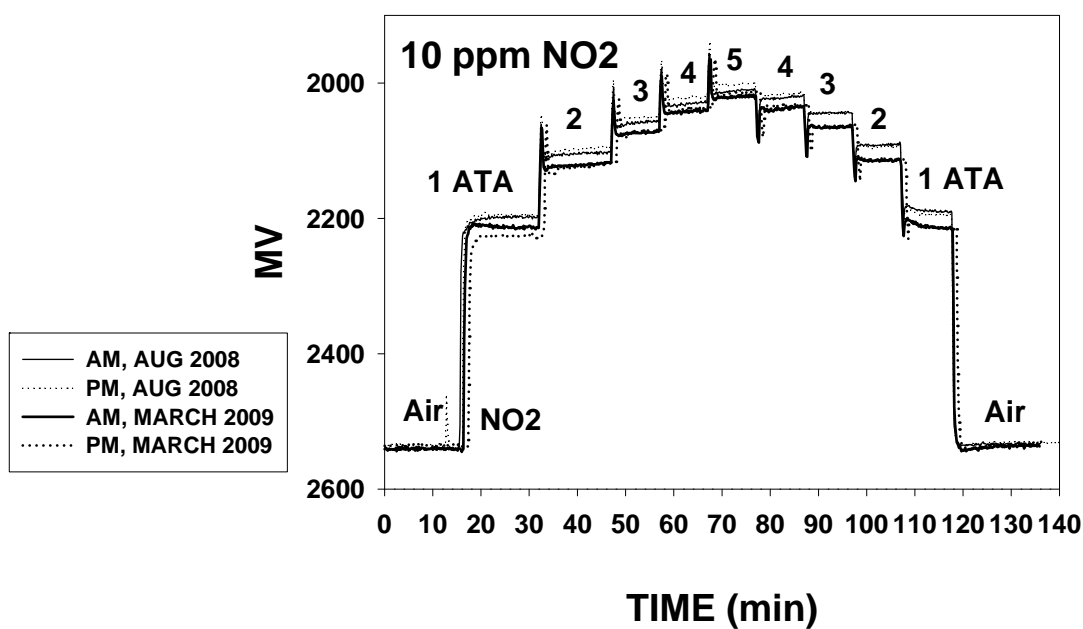
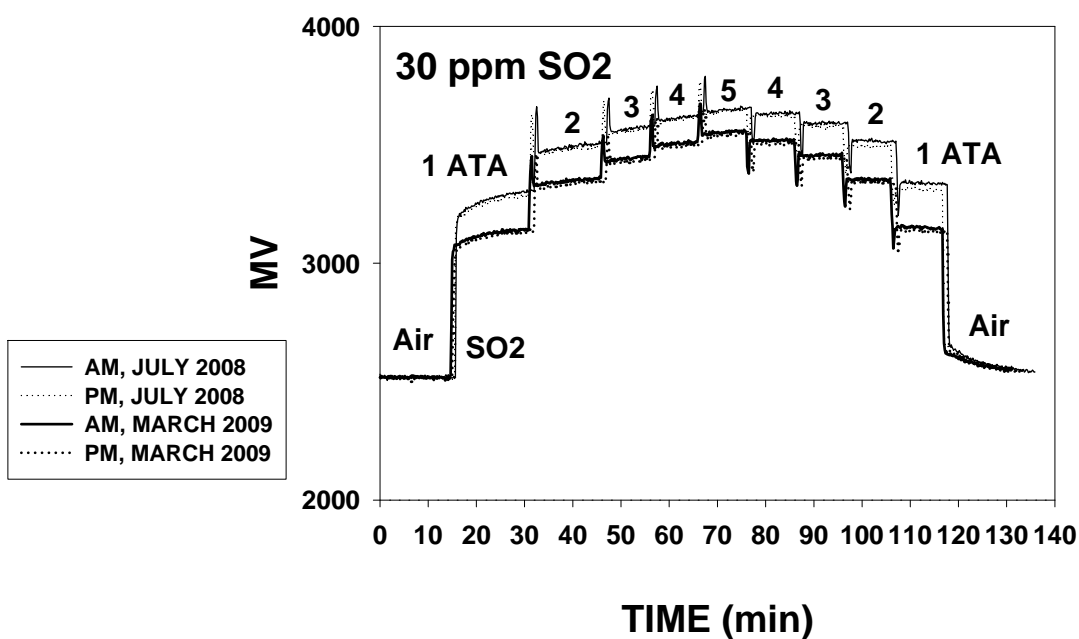
**FIGURE 15A. SubTox variability over time:
CO (top graph) and H₂S (bottom graph).**

**With mV plotted from same SubTox,
AM and PM tests eight months apart**



**FIGURE 15B. SubTox variability over time:
SO₂ (top graph) and NO₂ (bottom graph).**

With mV plotted from same SubTox,
AM and PM tests seven to eight months apart



**FIGURE 15C. SubTox variability over time:
Cl₂ (top graph) and HCN (bottom graph).**

**With mV plotted from same SubTox,
AM and PM tests six months apart**

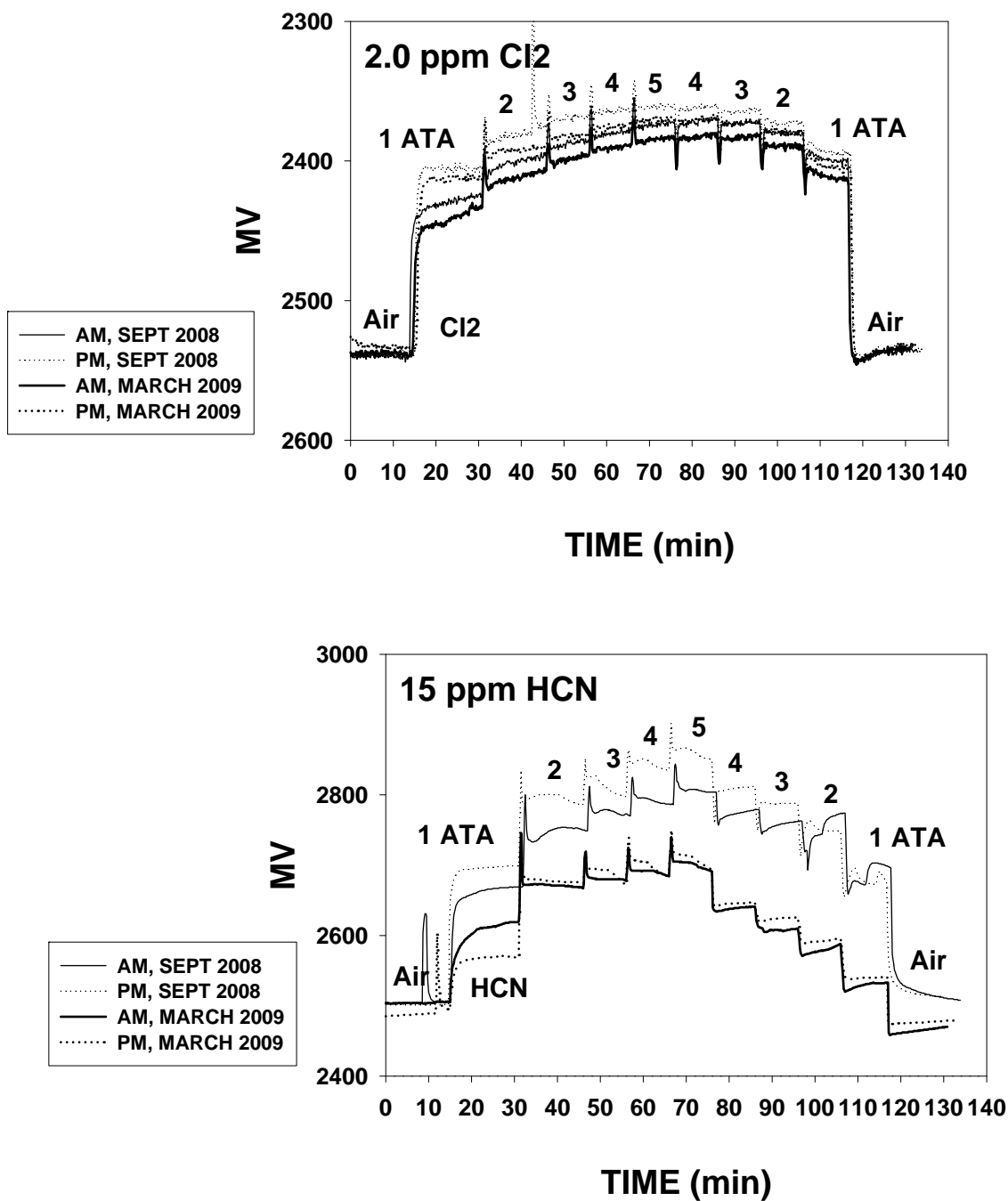
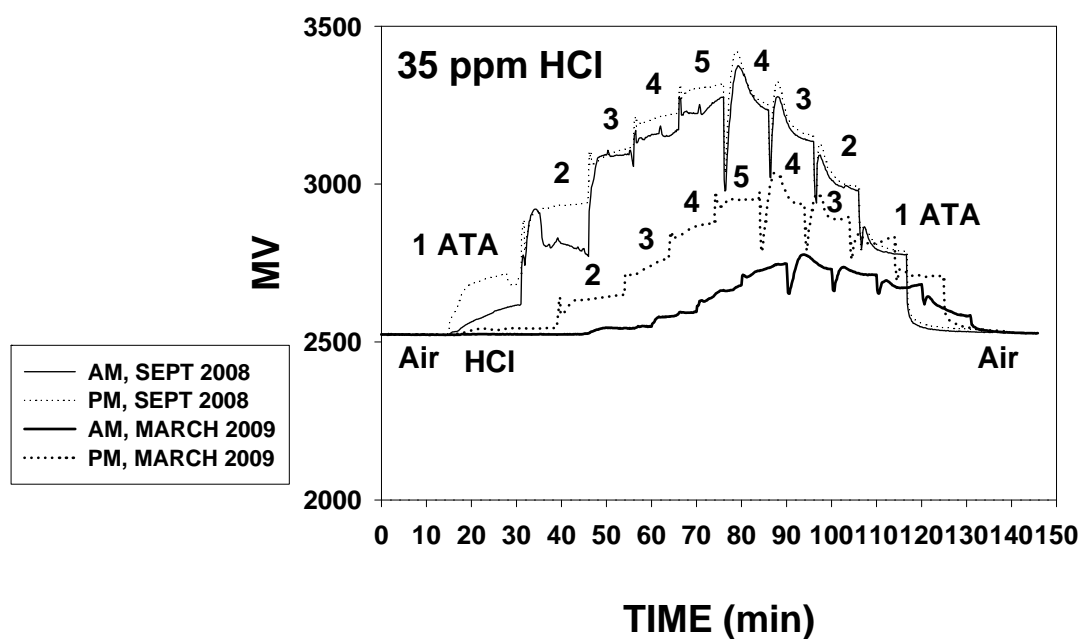


FIGURE 15D. SubTox variability over time: HCl.

With mV plotted from same SubTox,
AM and PM tests six months apart



**FIGURE 16. SubTox pressure correction tool:
EXCEL spreadsheet, as viewed on computer screen.**

VALUES ENTERED DURING A PRESSURE RESPONSE TEST			
Color Legend:			
<i>User Entered Values from test data</i>			
<i>Calculated values sent to the Subtox via Modbus</i>			
<i>Fixed Values</i>			
Gas sensor #	1		
PRESSURE	Gas Value	Gas Sensor	PRS Sensor
ATM	ppm	mV	mV
1	0 [Air]	2499	1287
1	85	3176	
2		3290	
3		3354	
4		3413	
5		3460	
5		3460	3646
Pcomp data is extracted from the above entries for uploading to			
Item	Description	Value	Register Add
Gas Sensor	Offset	2499	40177
	Slope	7.965	40179
PRS Sensor	Offset	697.25	40463
	Slope	589.75	40465
Pcomp Table	ATM #1	1	40705
	#2	2	40707
	#3	3	40709
	#4	4	40711
	#5	5	40713
	#6	5	40715
	Slope Mult #1	1.000	40717
	#2	1.168	40719
	#3	1.263	40721
	#4	1.350	40723
	#5	1.419	40725
	#6	1.419	40727

FIGURE 17A. SubTox pressure correction: CO (mV plotted).

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots

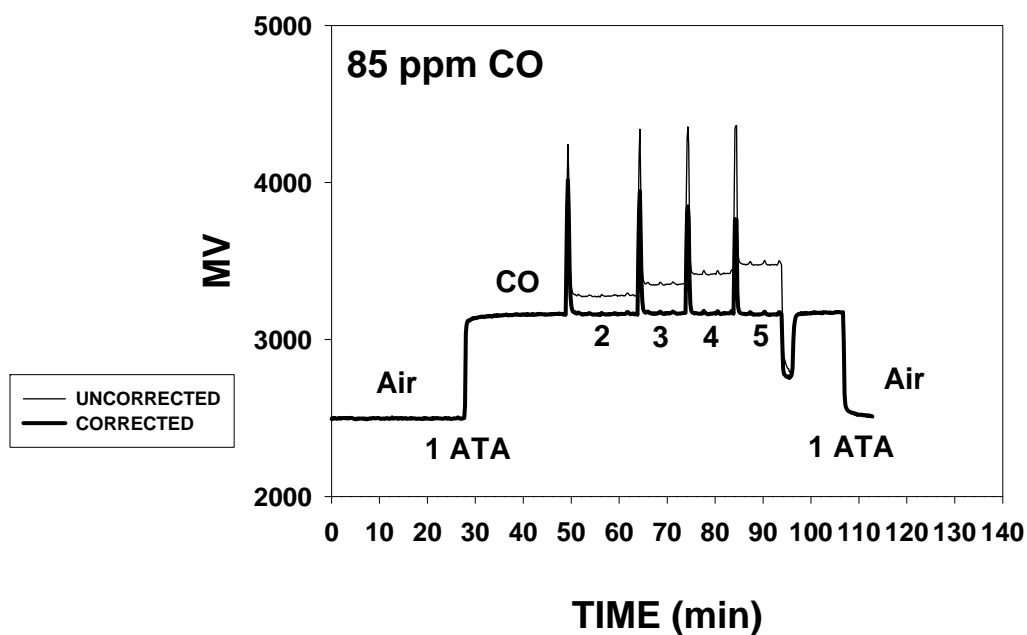
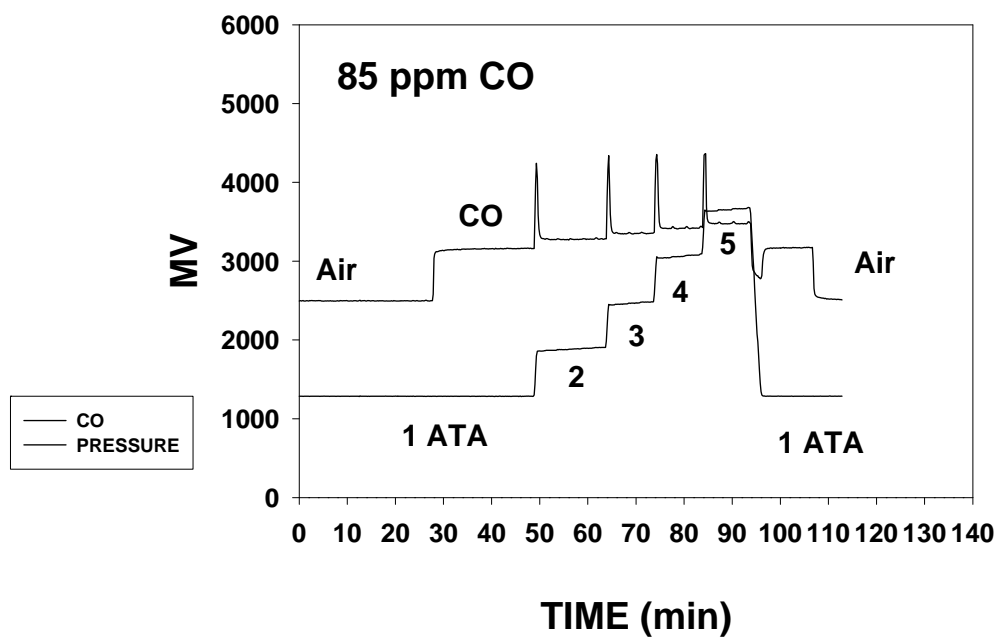


FIGURE 17B. SubTox pressure correction: H₂S (mV plotted).

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots

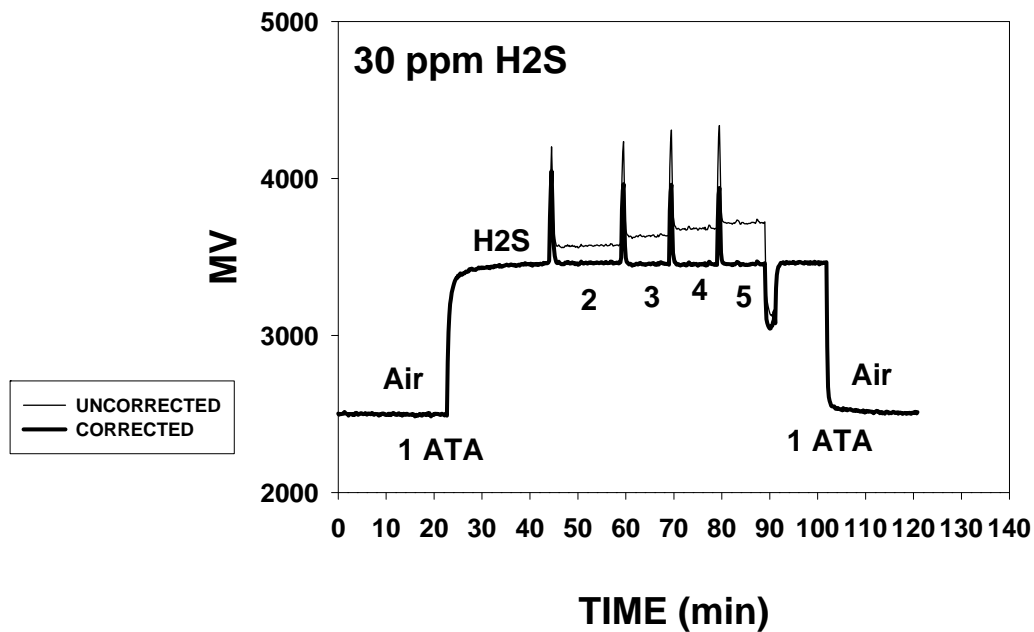
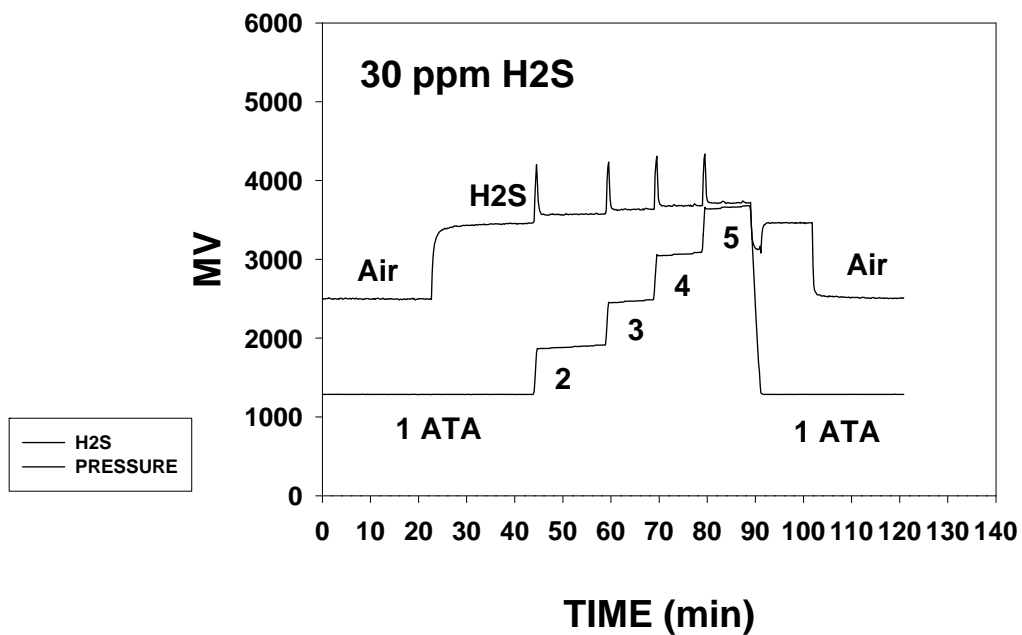


FIGURE 17C. SubTox pressure correction: SO₂ (mV plotted).

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots

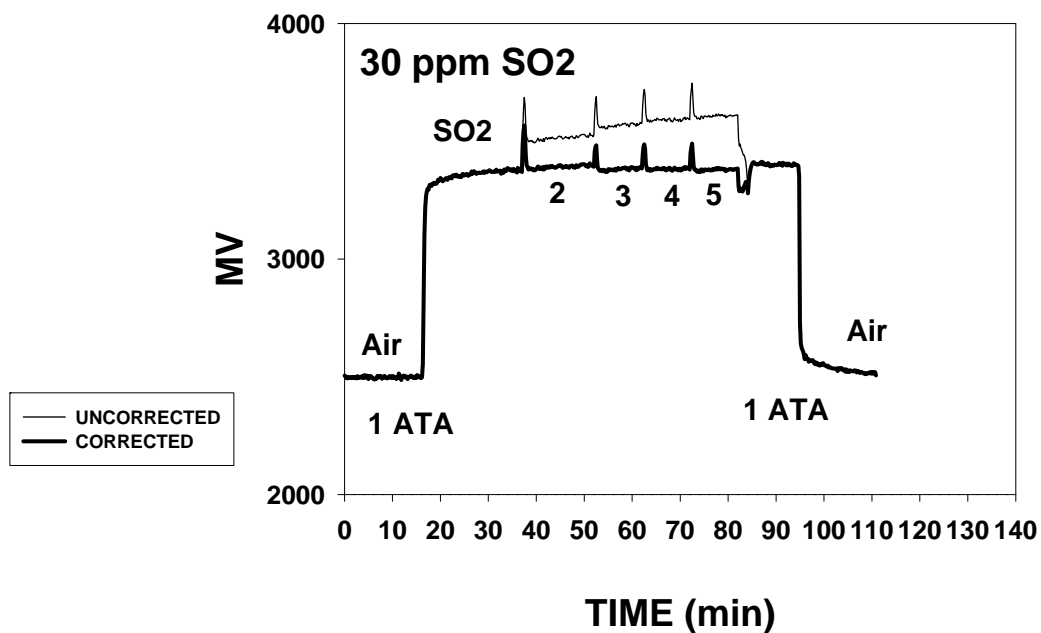
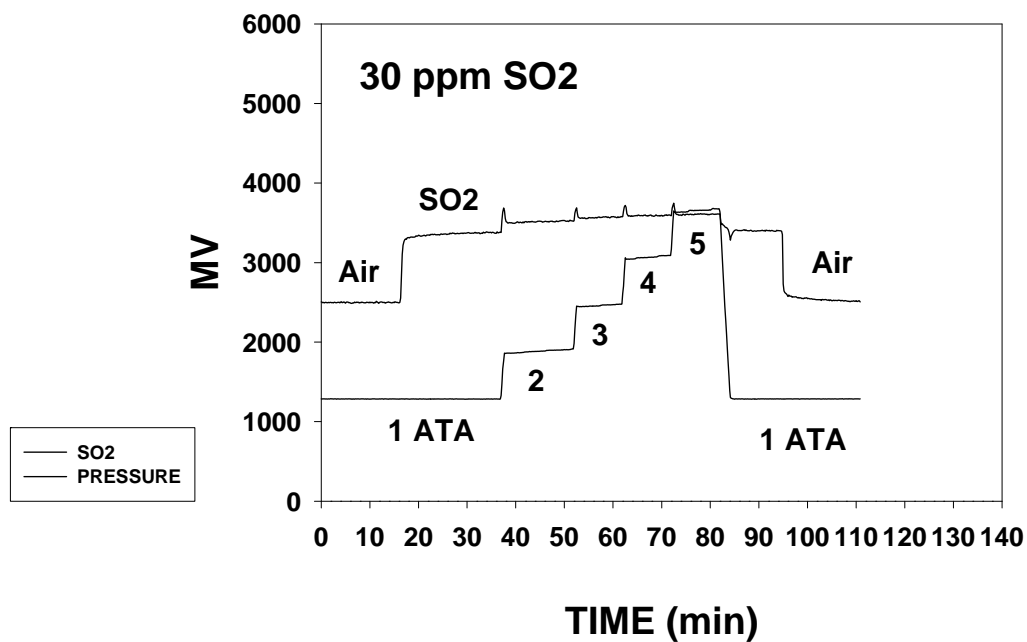


FIGURE 17D. SubTox pressure correction: NO₂ (mV plotted).

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots

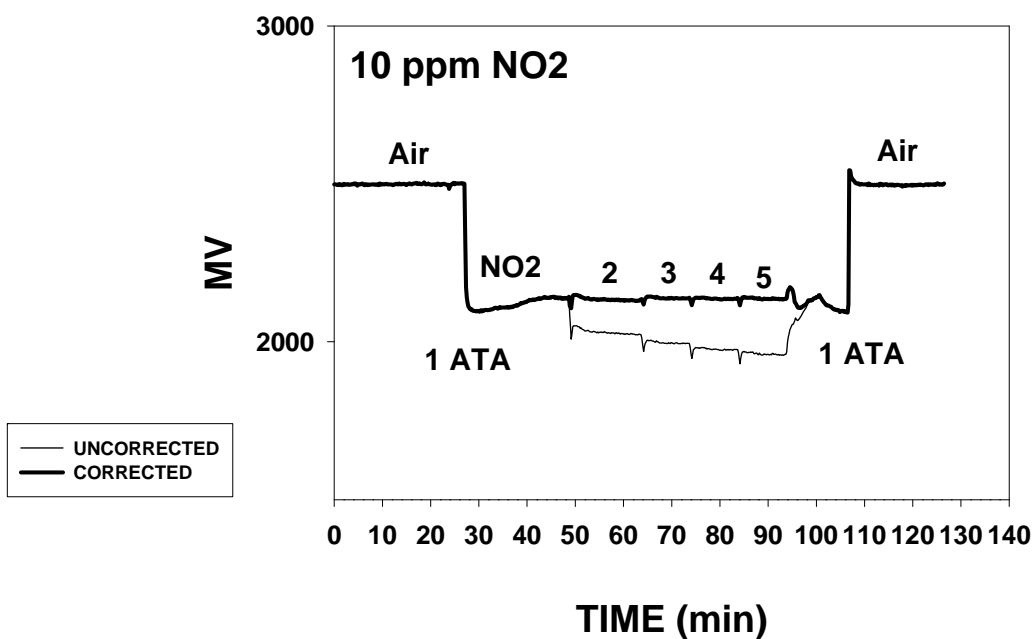
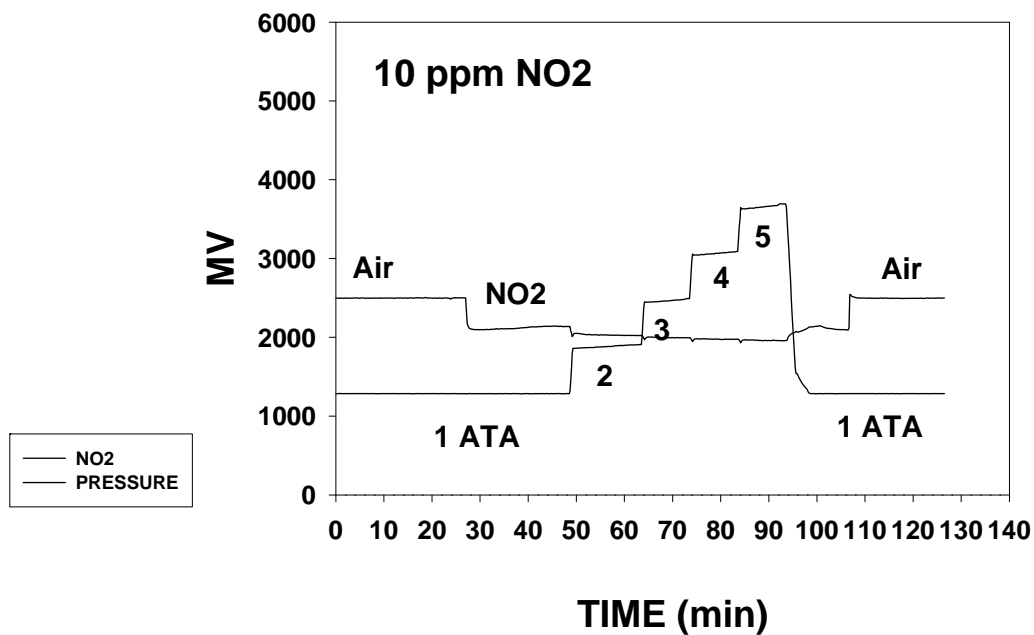
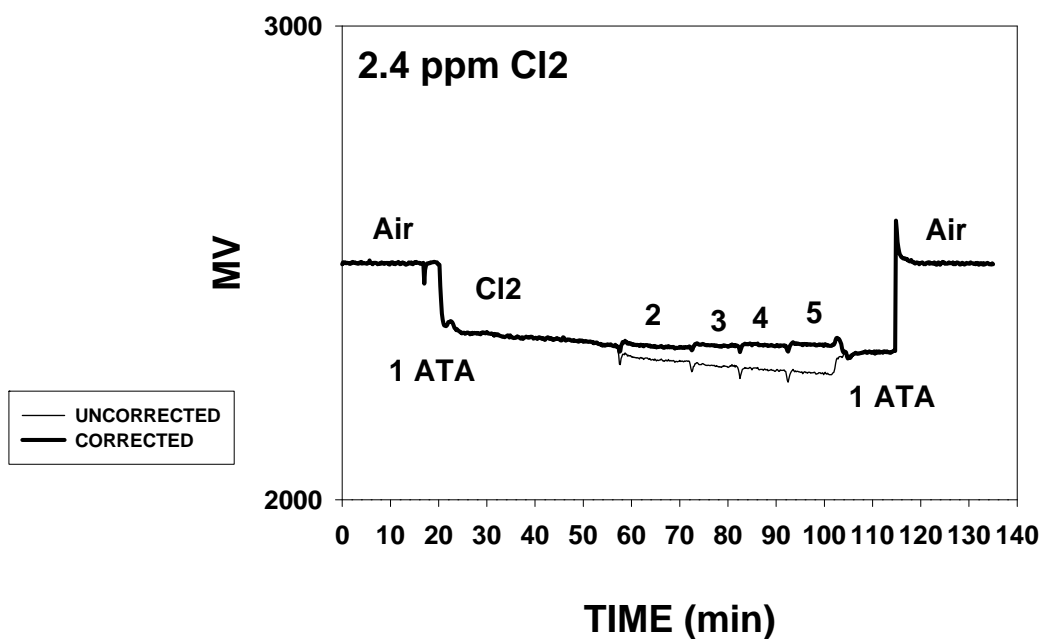
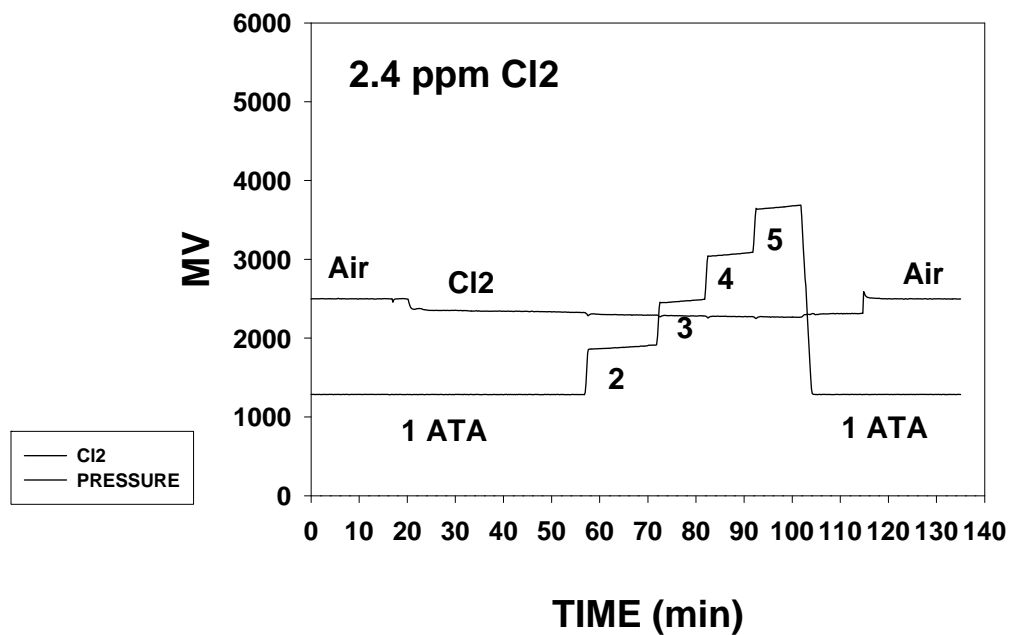


FIGURE 17E. SubTox pressure correction: Cl_2 (mV plotted).

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots



**FIGURE 17F. SubTox pressure correction:
HCN (mV plotted).**

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots

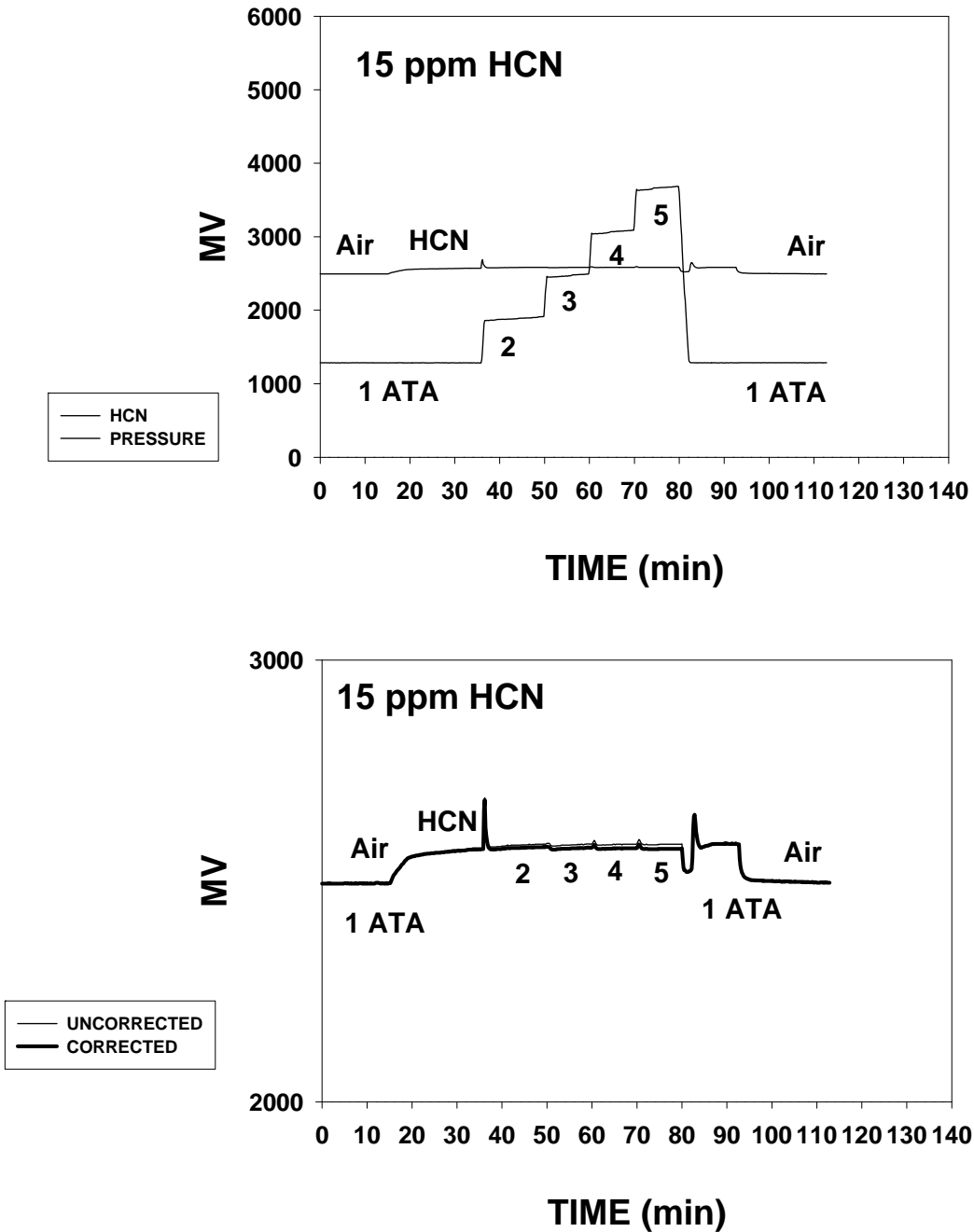


FIGURE 17G. SubTox pressure correction: HCl (mV plotted).

Top Graph: Pressure correction calibration
Bottom Graph: Corrected and uncorrected plots

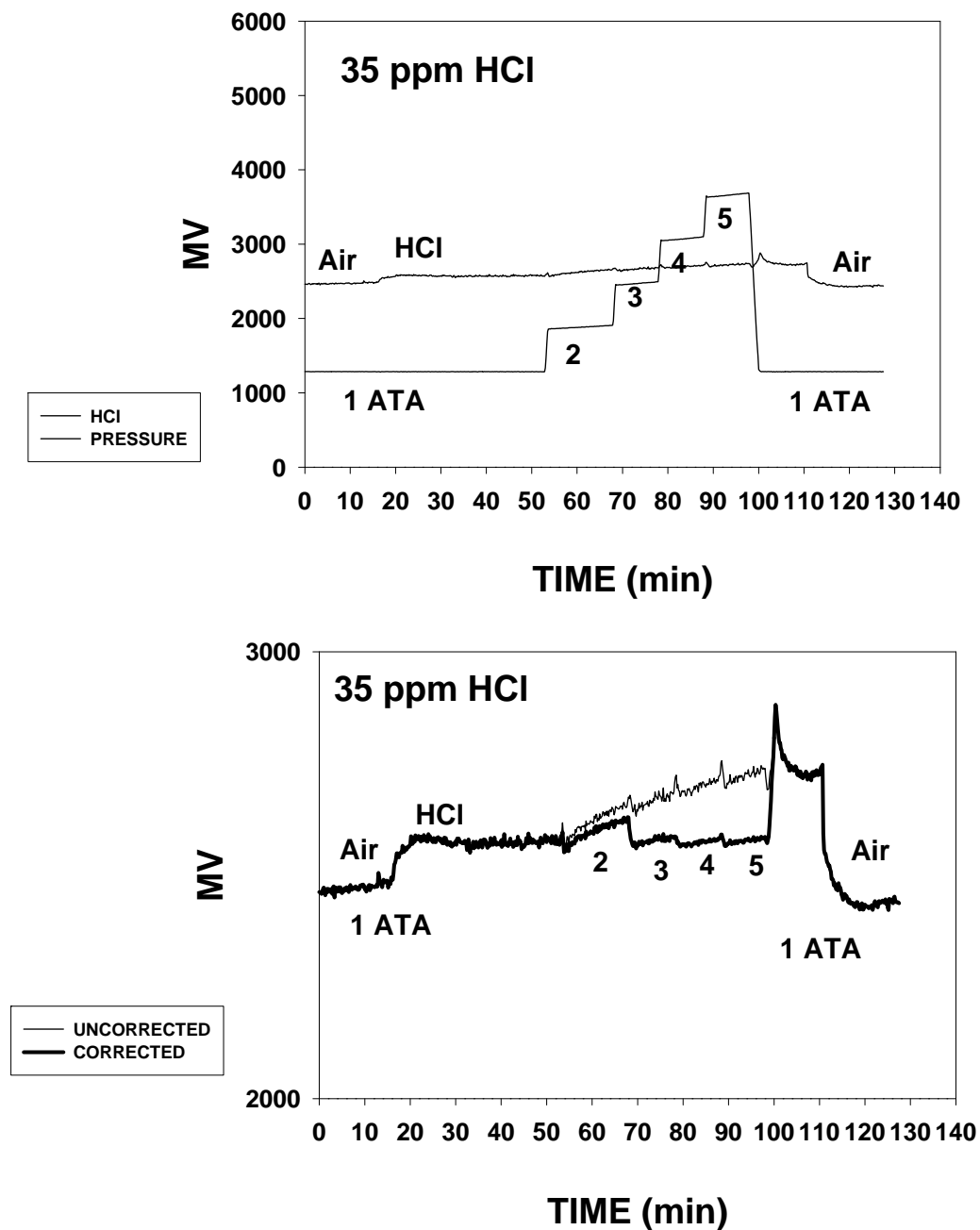


FIGURE 18A. SubTox pressure-corrected plots for CO (ppm; top graph) and H₂S (ppm; bottom graph).

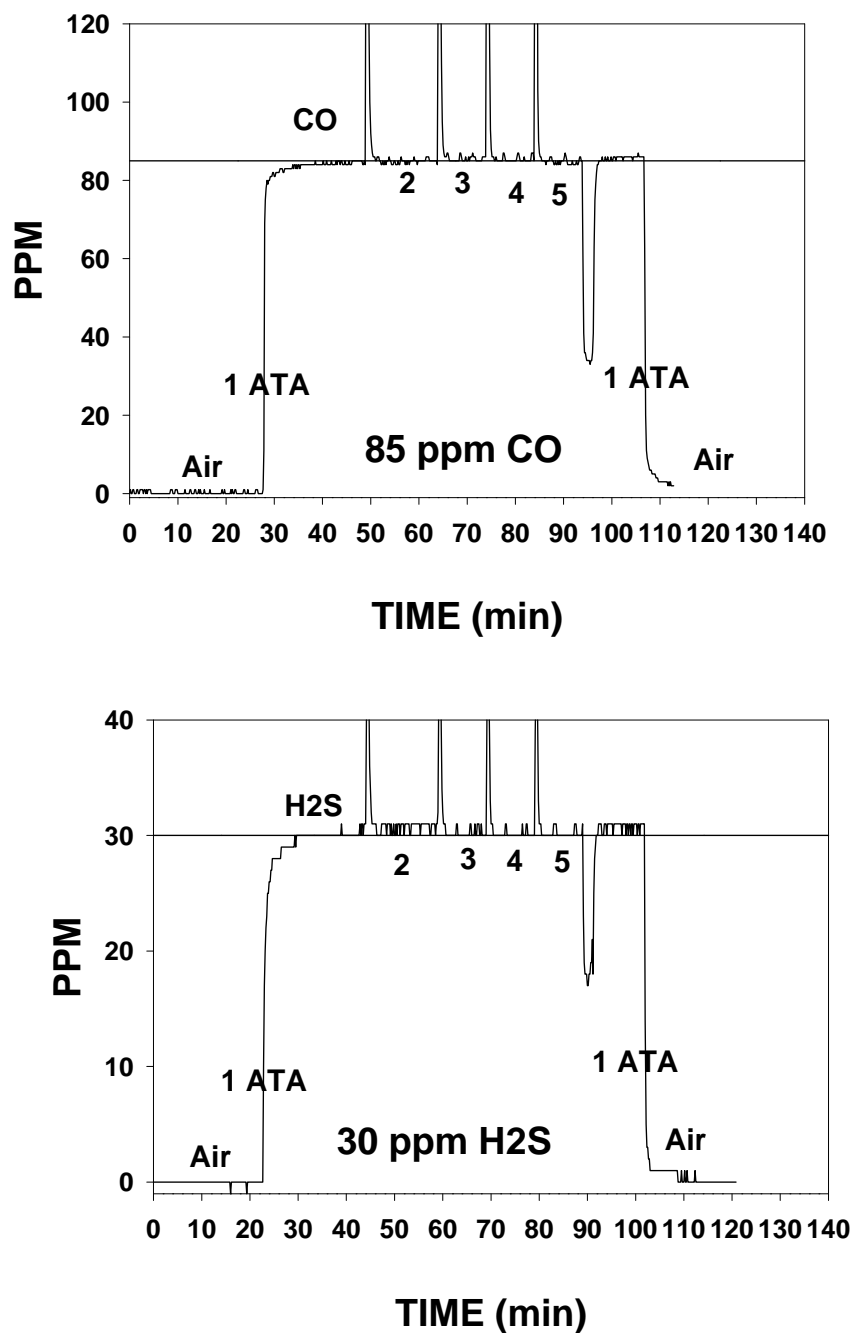


FIGURE 18B. SubTox pressure-corrected plots for SO₂ (ppm; top graph) and NO₂ (ppm; bottom graph).

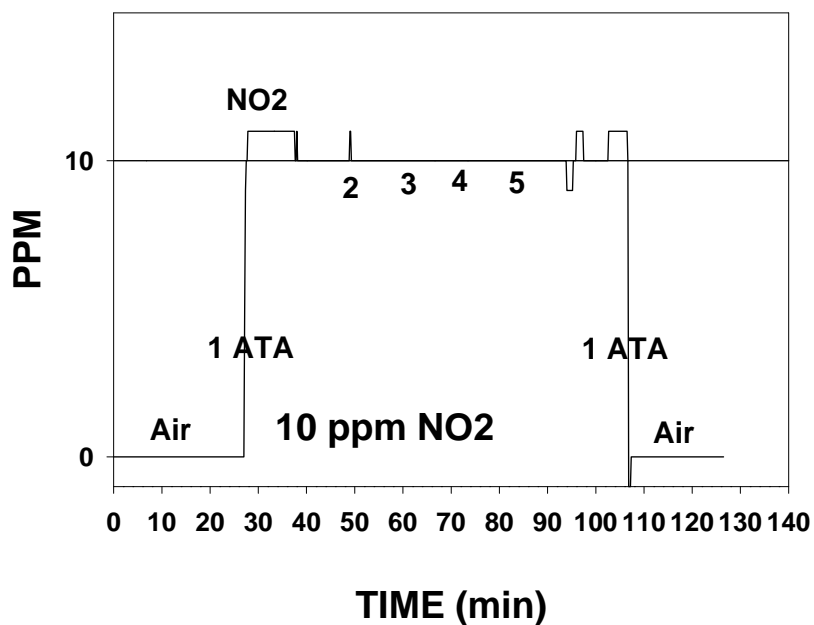
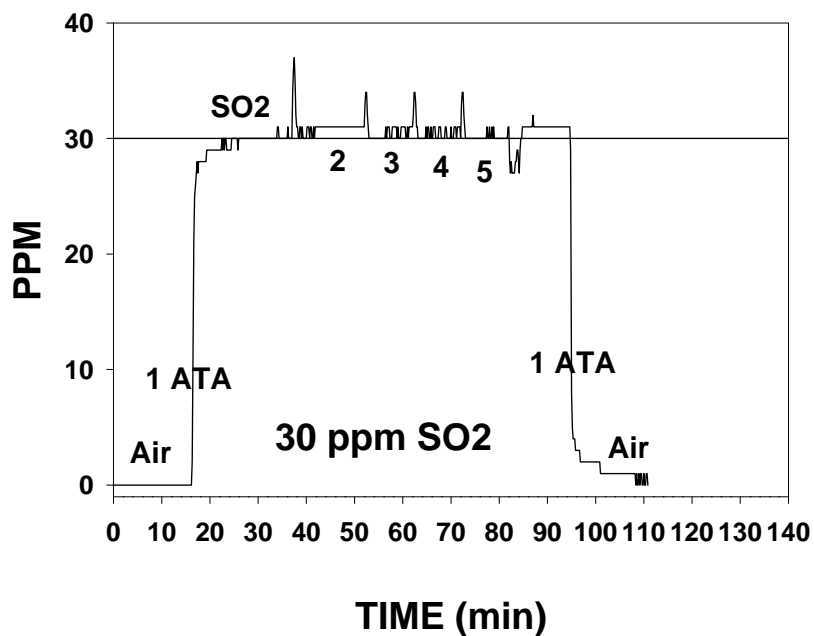


FIGURE 18C. SubTox pressure-corrected plots for Cl₂ (ppm; top graph) and HCN (ppm; bottom graph).

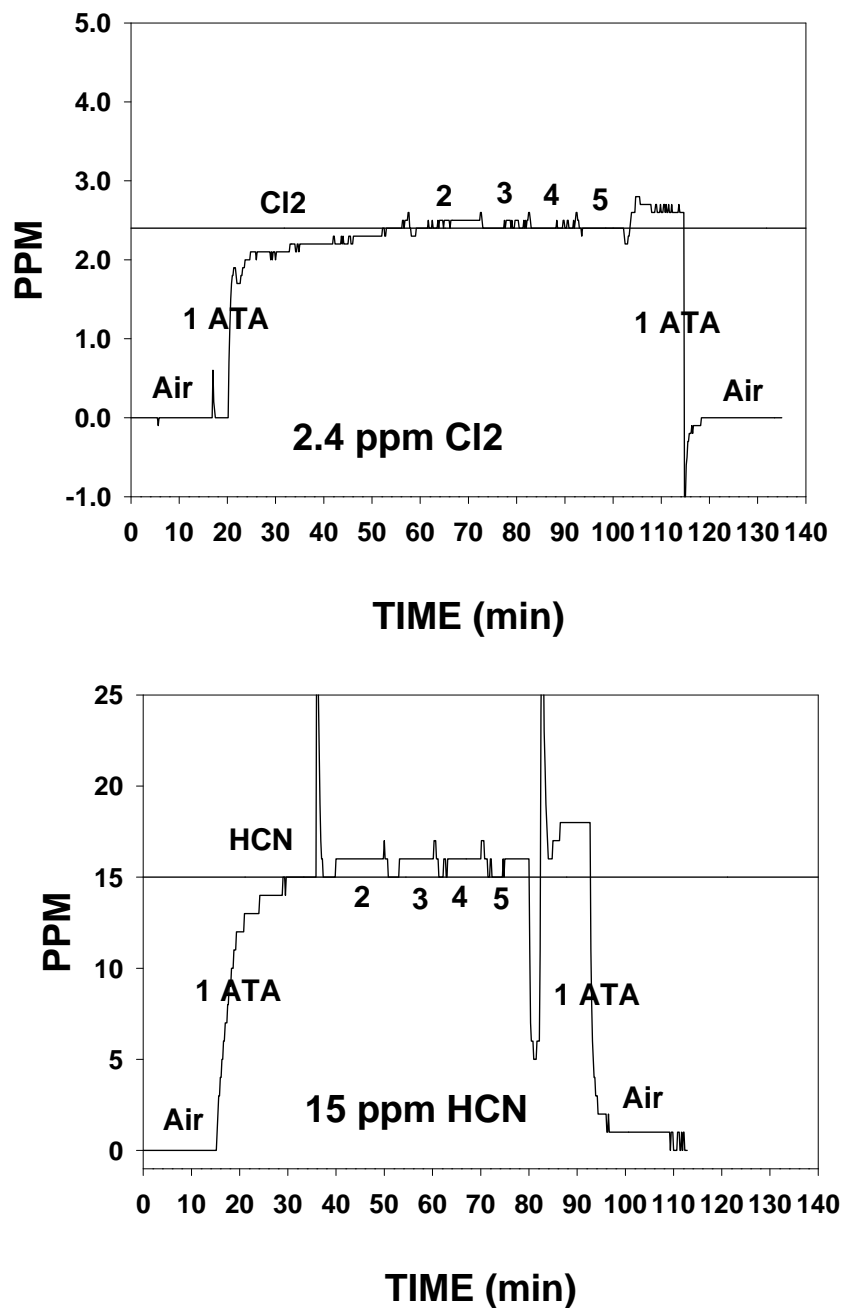
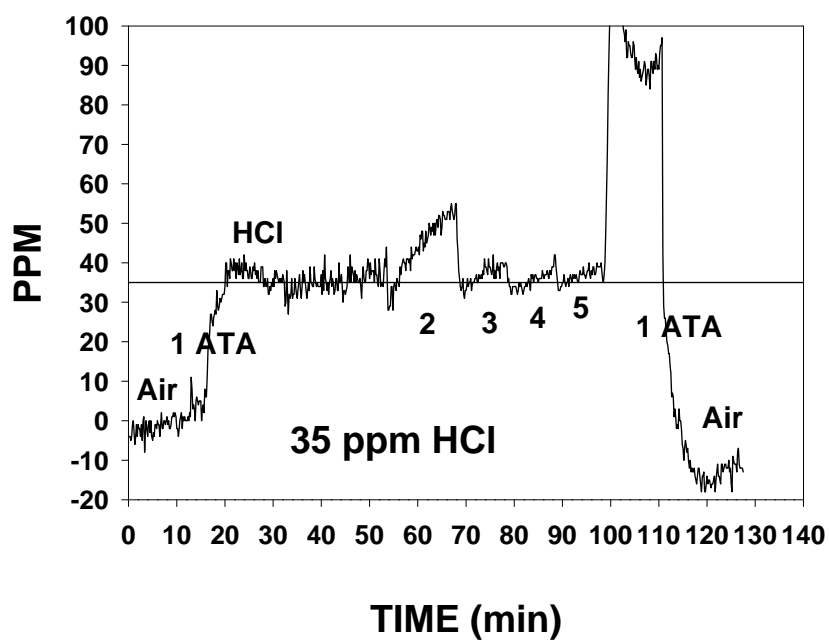
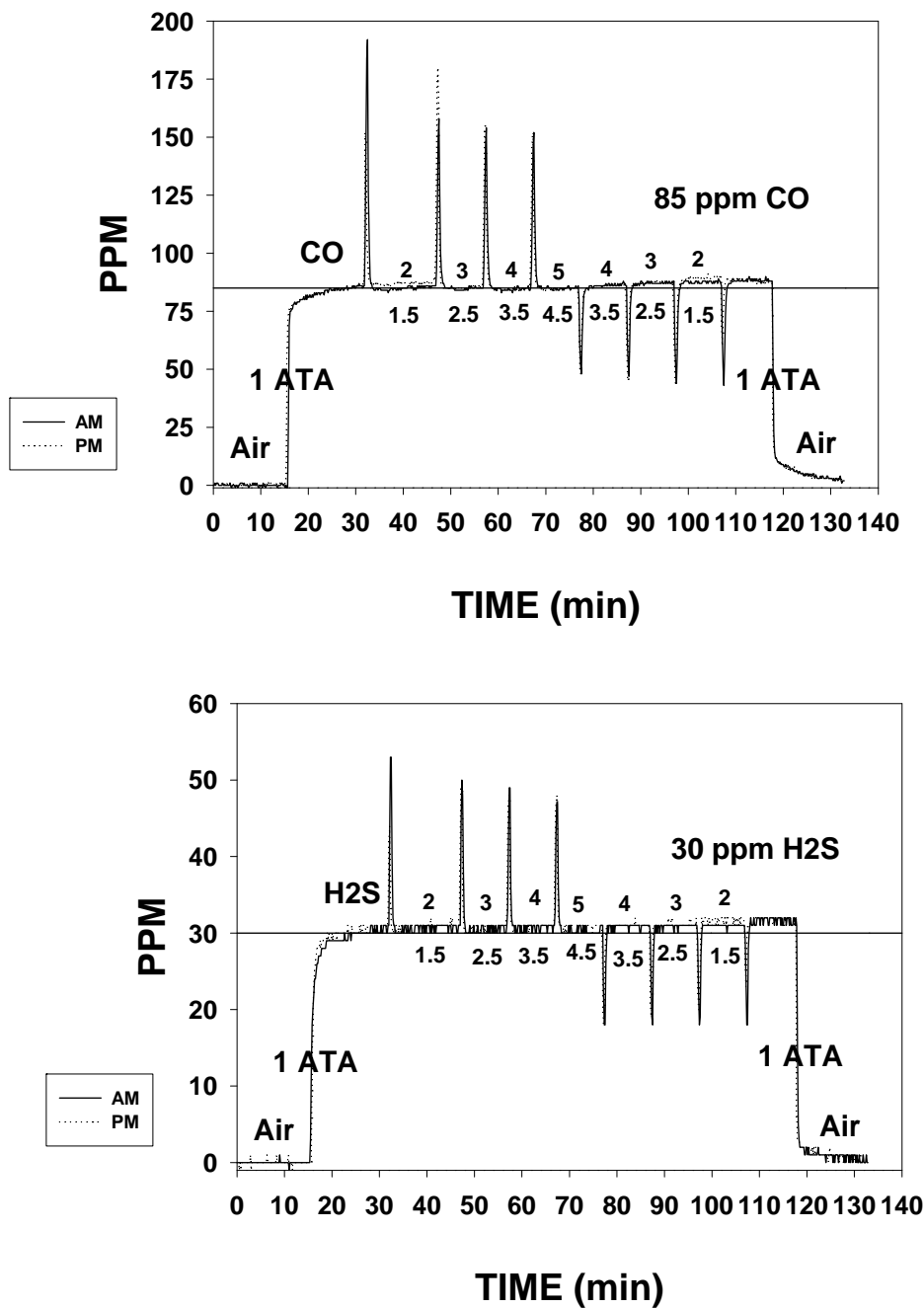


FIGURE 18D. SubTox pressure-corrected plot for HCl (ppm).



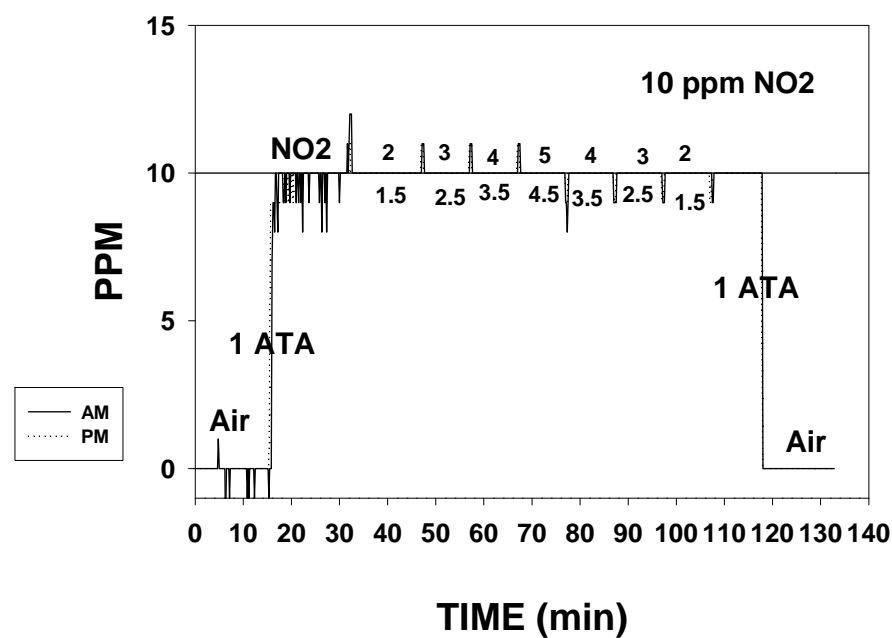
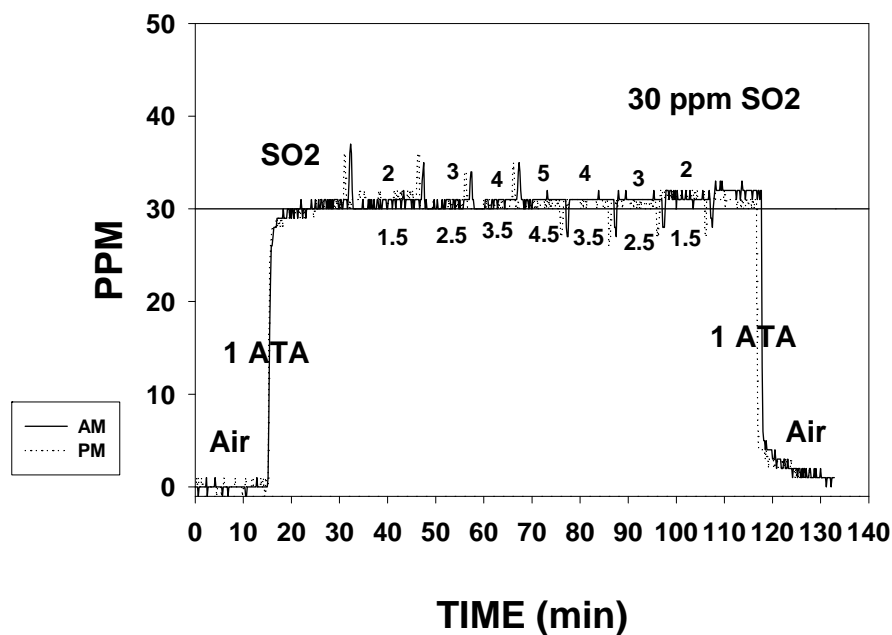
**FIGURE 19A. Interpolation of pressure corrections:
CO (ppm; top graph) and H₂S (ppm; bottom graph).**

**AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA**



**FIGURE 19B. Interpolation of pressure corrections:
SO₂ (ppm; top graph) and NO₂ (ppm; bottom graph).**

**AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA**



**FIGURE 19C. Interpolation of pressure corrections:
Cl₂ (ppm; top graph) and HCN (ppm; bottom graph).**

**AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA**

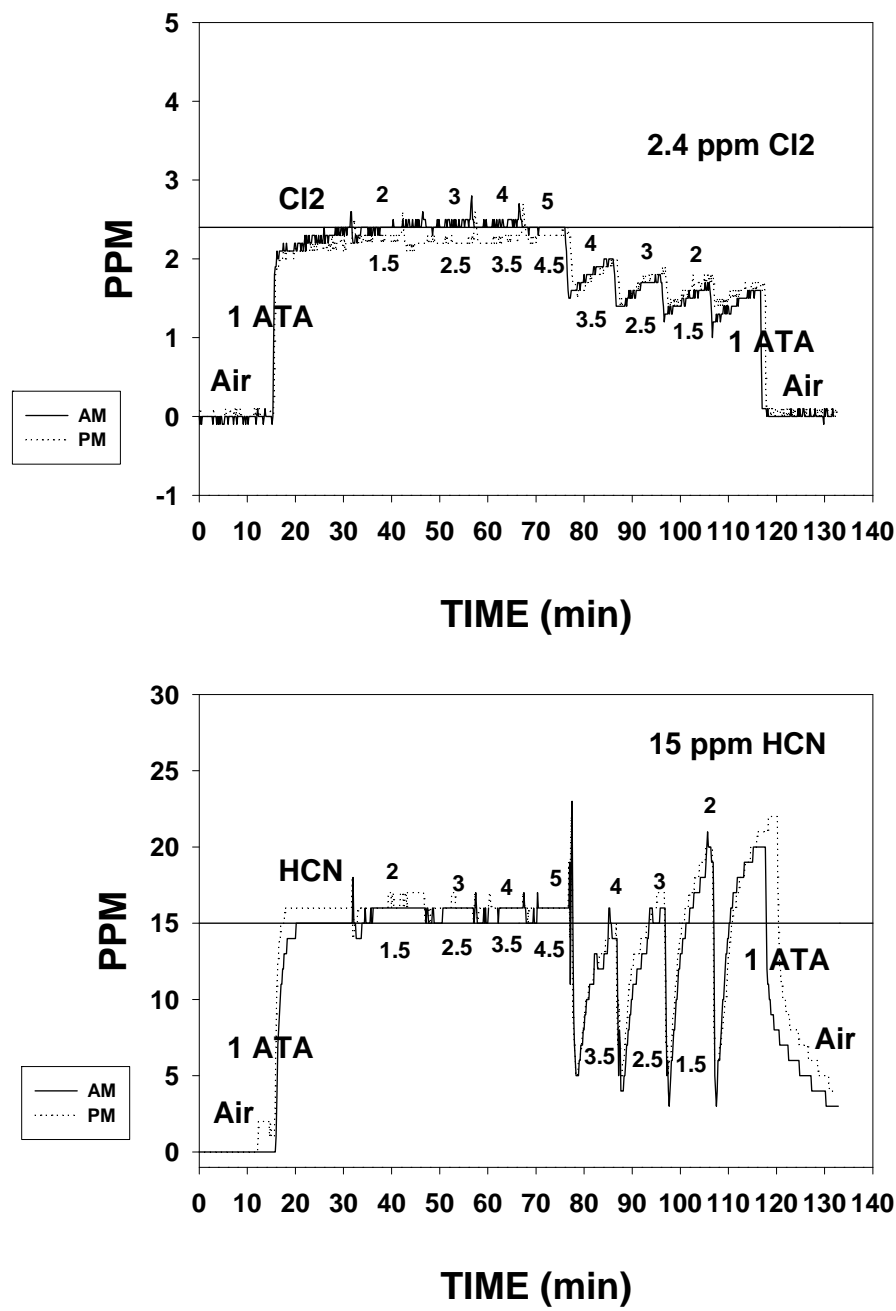


FIGURE 20A. Interpolation of pressure corrections and SEAL2 vs. SEAL1 gases: H₂S (mV and ppm plotted).

AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA with SEAL2 gas
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA with SEAL1 gas

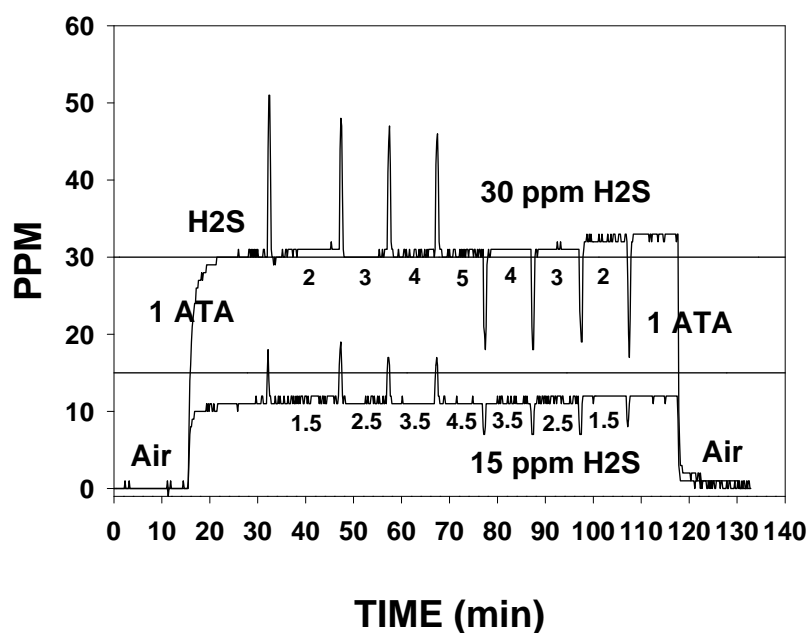
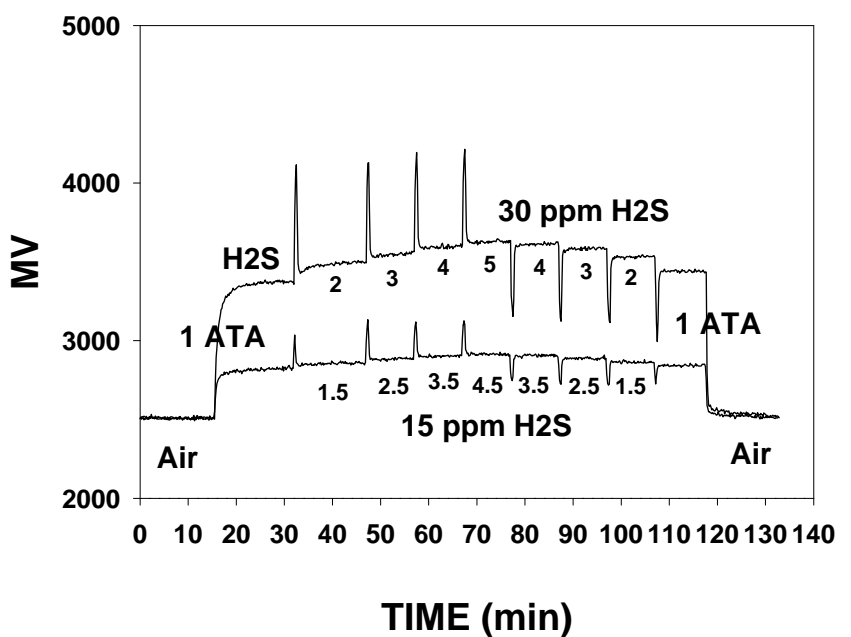


FIGURE 20B. Interpolation of pressure corrections and SEAL2 vs. SEAL1 gases: SO₂ (mV and ppm plotted).

AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA with SEAL2 gas
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA with SEAL1 gas

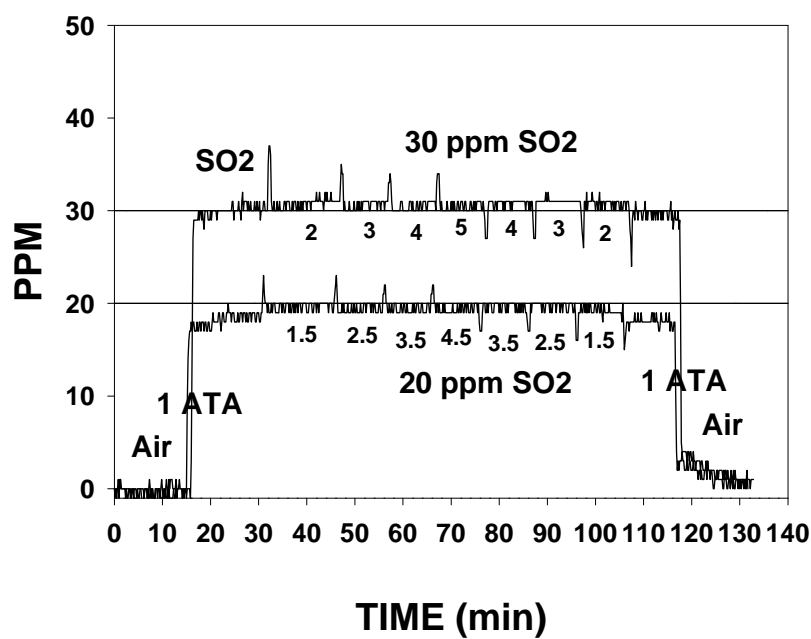
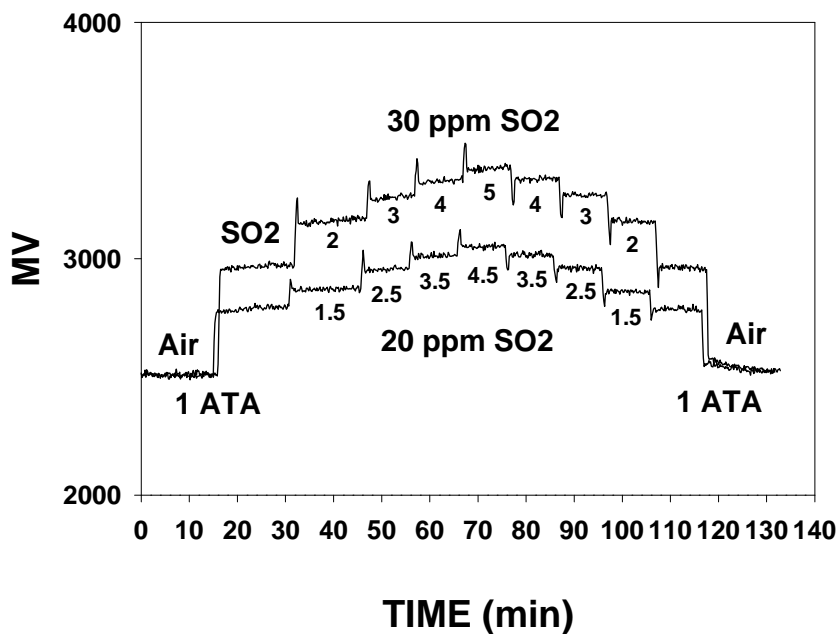


FIGURE 20C. Interpolation of pressure corrections and SEAL2 vs. SEAL1 gases: NO₂ (mV and ppm plotted).

AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA with SEAL2 gas
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA with SEAL1 gas

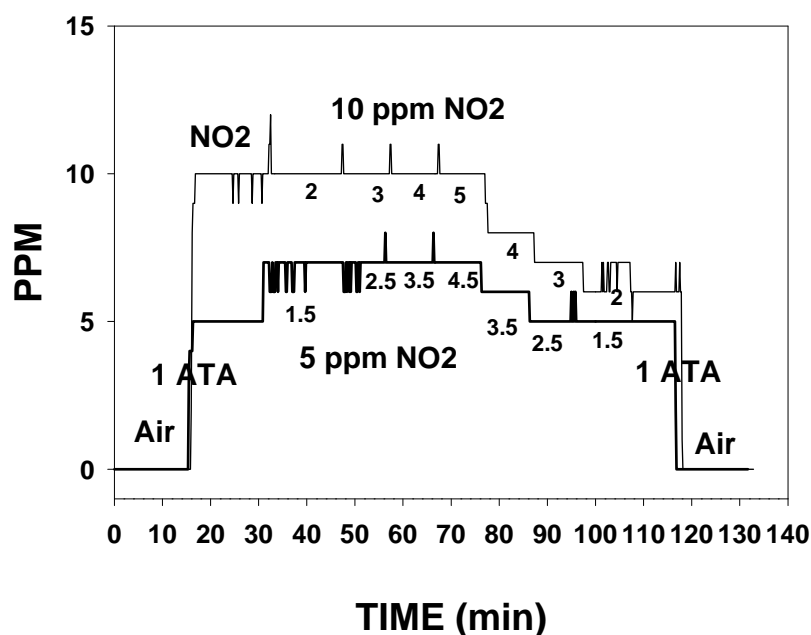
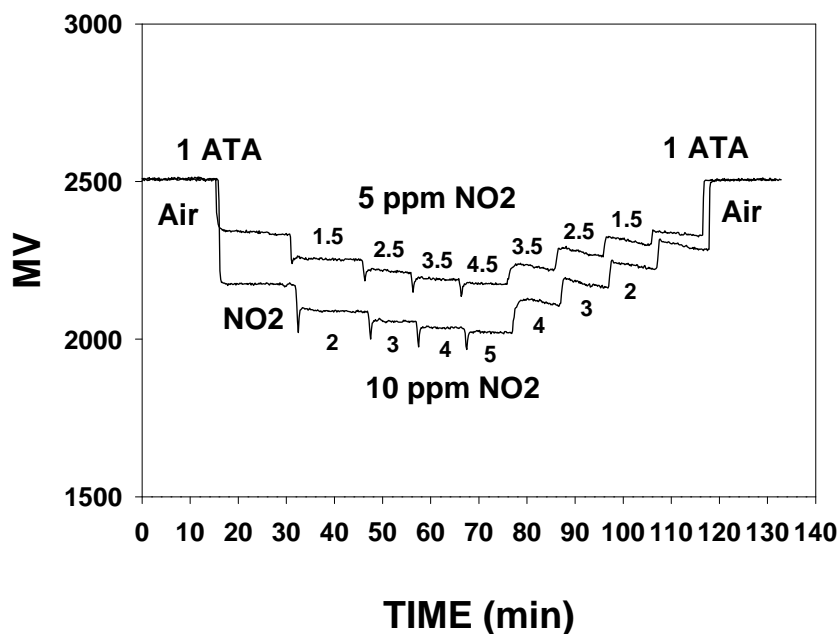


FIGURE 20D. Interpolation of pressure corrections and SEAL2 vs. SEAL1 gases: Cl₂ (mV and ppm plotted).

AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5 ATA with SEAL2 gas
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA with SEAL1 gas

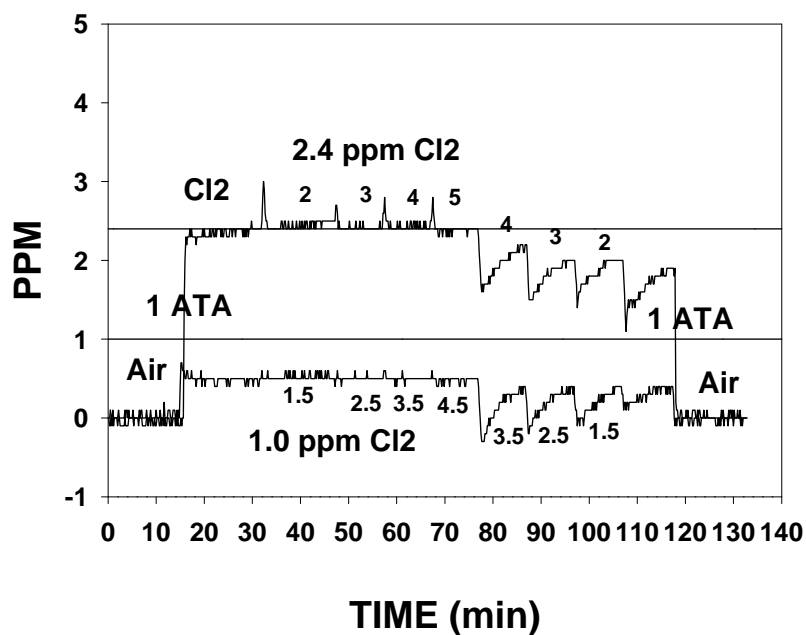
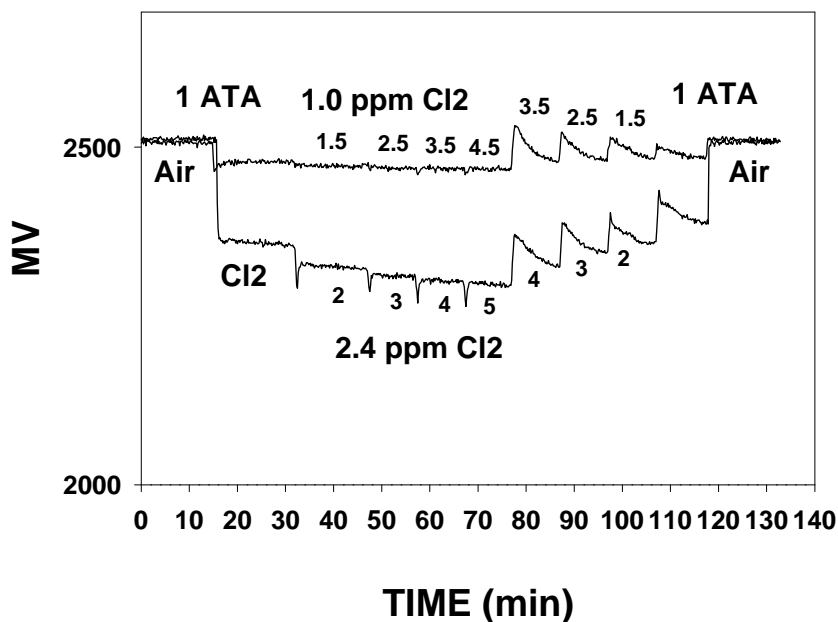


FIGURE 20E. Interpolation of pressure corrections and SEAL2 vs. SEAL1 gases: HCN (mV and ppm plotted).

AM calibrations at 1.0, 2.0, 3.0, 4.0, and 5.0 ATA with SEAL2 gas
PM tests at 1.0, 1.5, 2.5, 3.5, and 4.5 ATA with SEAL1 gas

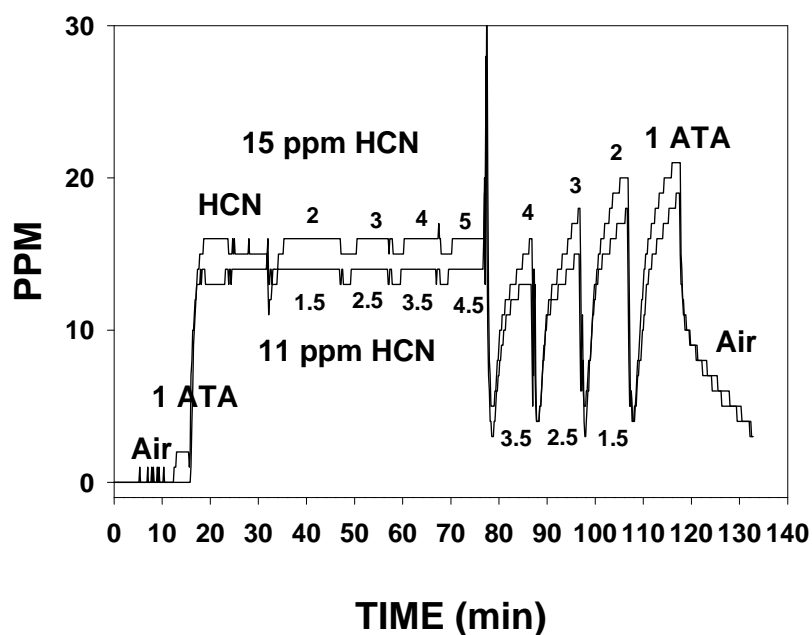
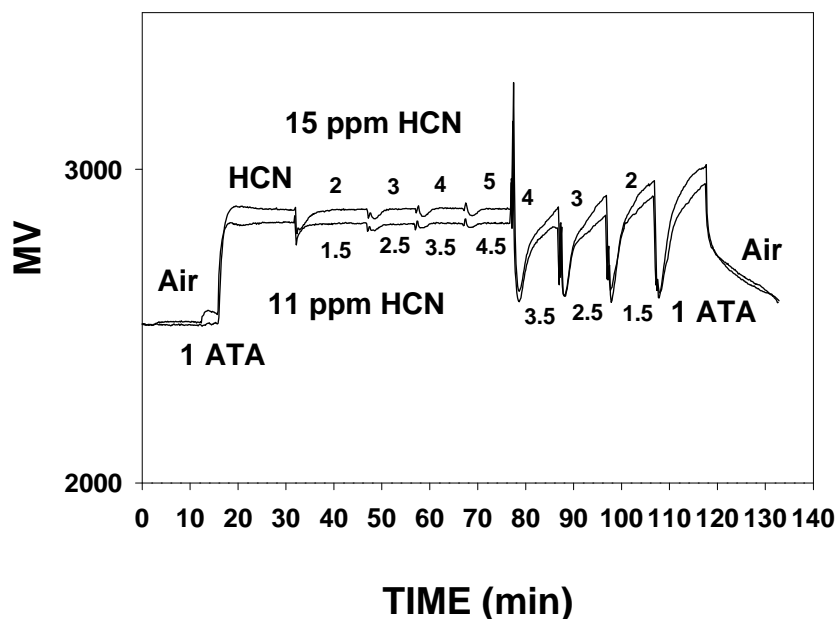


FIGURE 21A. Stability of pressure corrections: CO (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations
Bottom Graph: ~1.5 yr following pressure correction calibrations

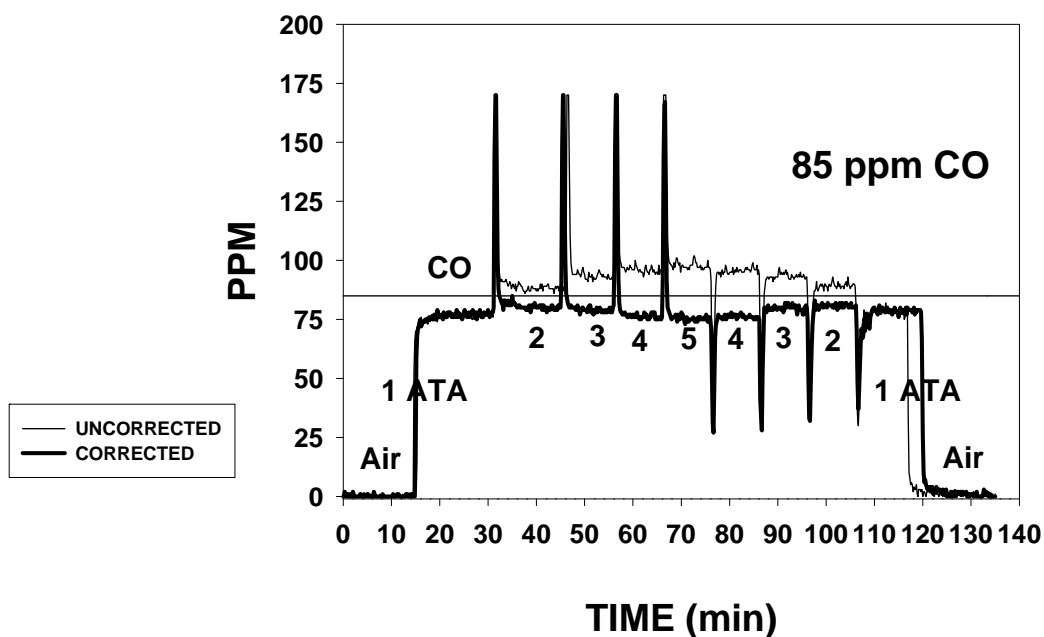
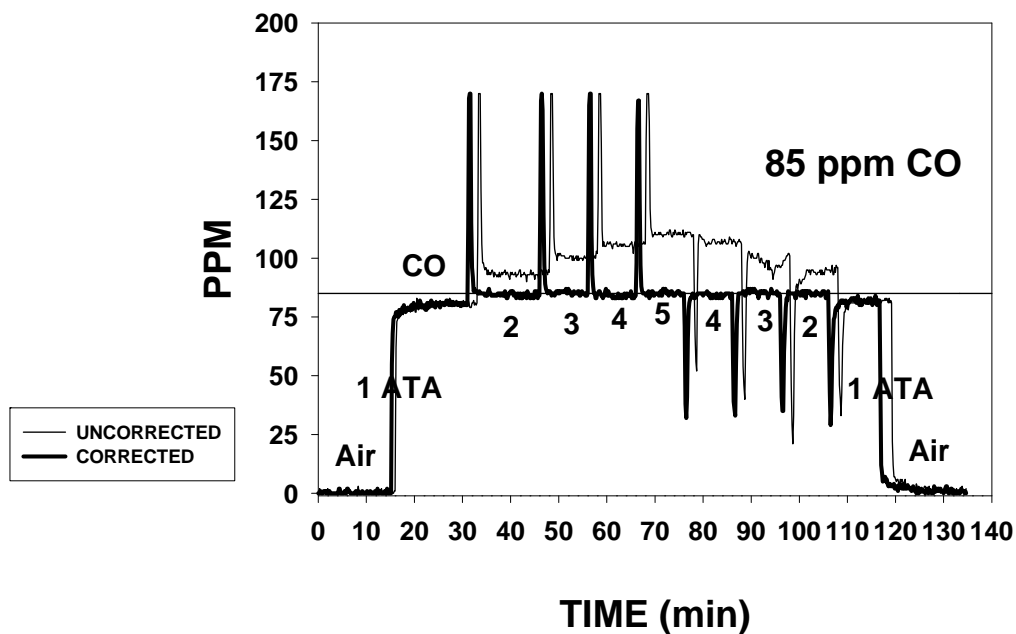


FIGURE 21B. Stability of pressure corrections: H₂S (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations
Bottom Graph: ~1.5 yr following pressure correction calibrations

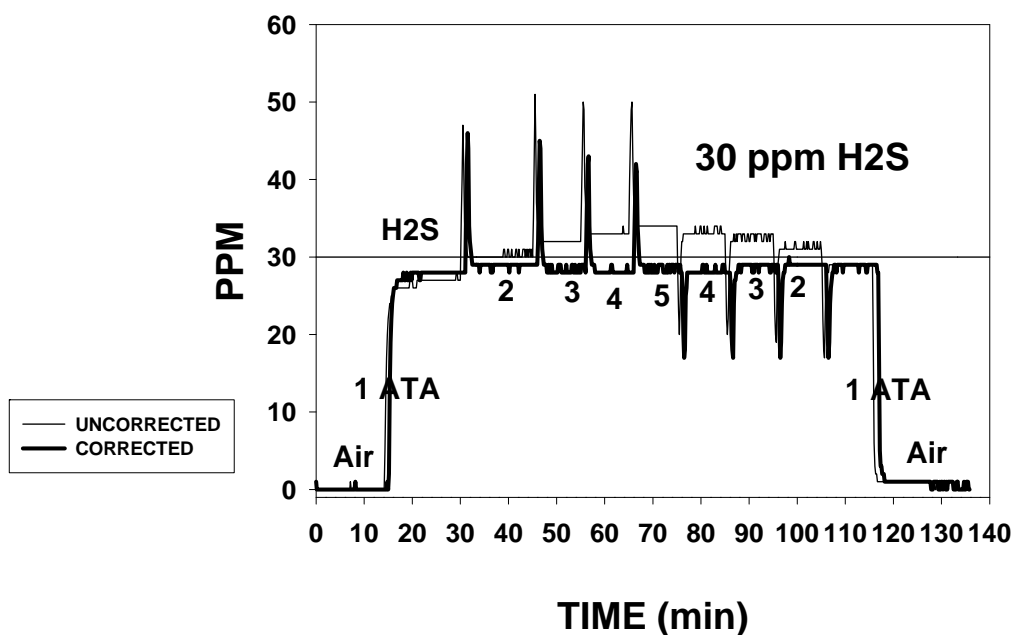
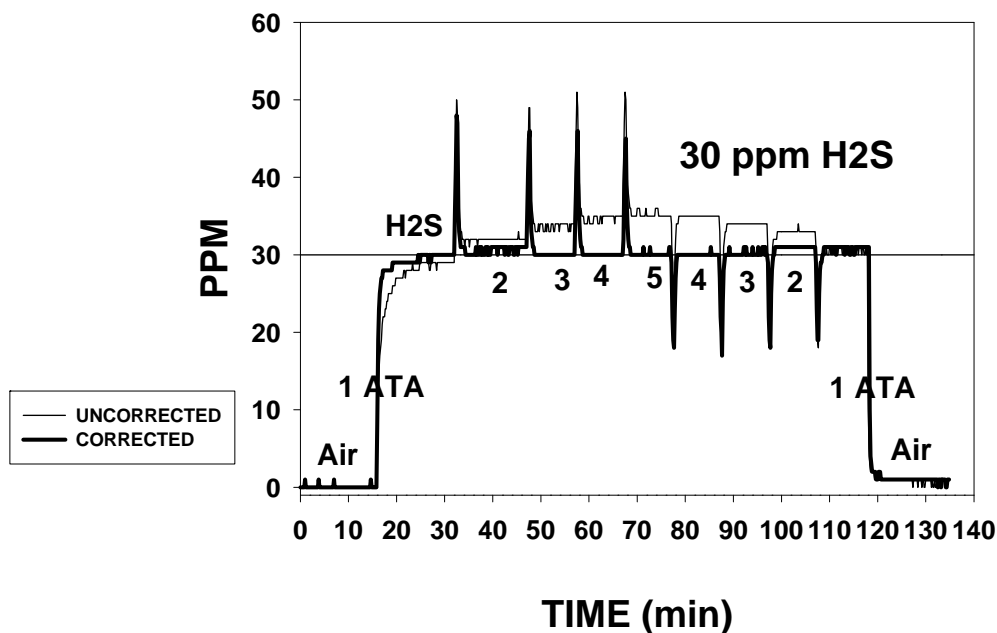


FIGURE 21C. Stability of pressure corrections: SO₂ (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations

Bottom Graph: ~1.5 yr following pressure correction calibrations

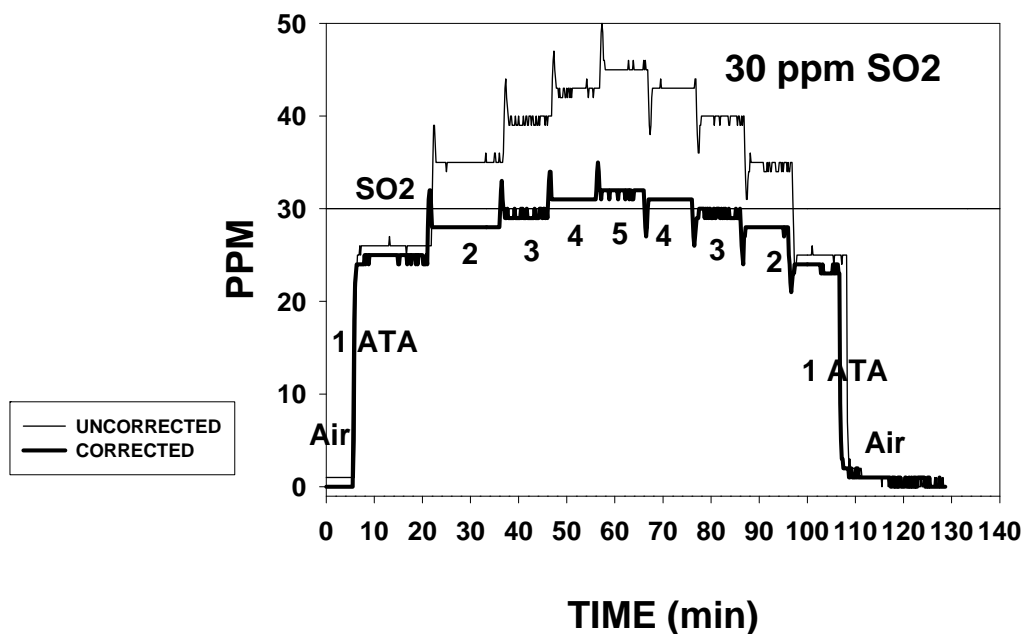
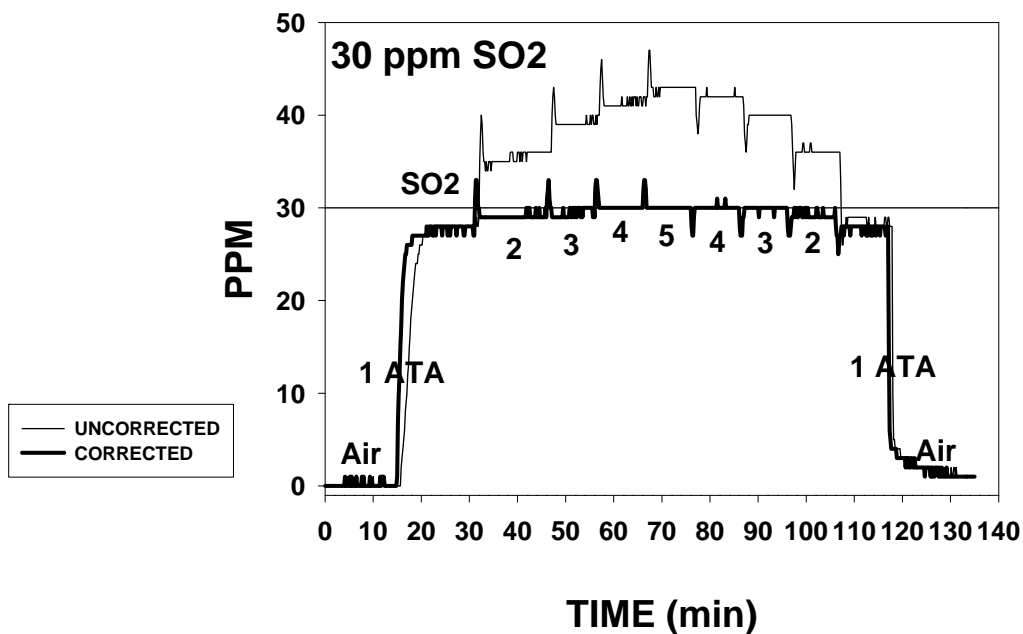


FIGURE 21D. Stability of pressure corrections: NO₂ (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations
Bottom Graph: ~1.5 yr following pressure correction calibrations

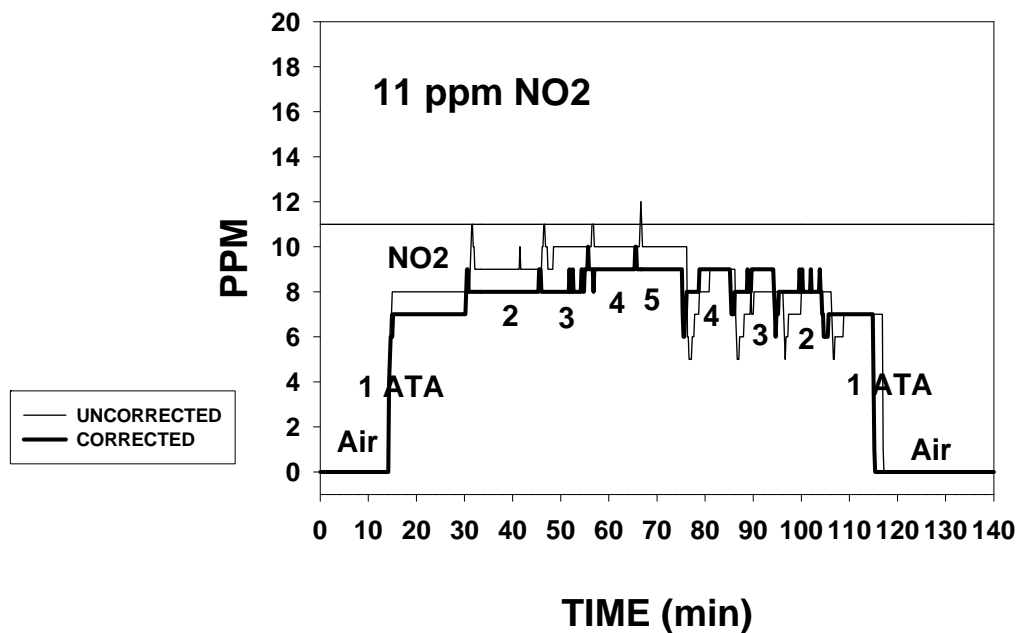
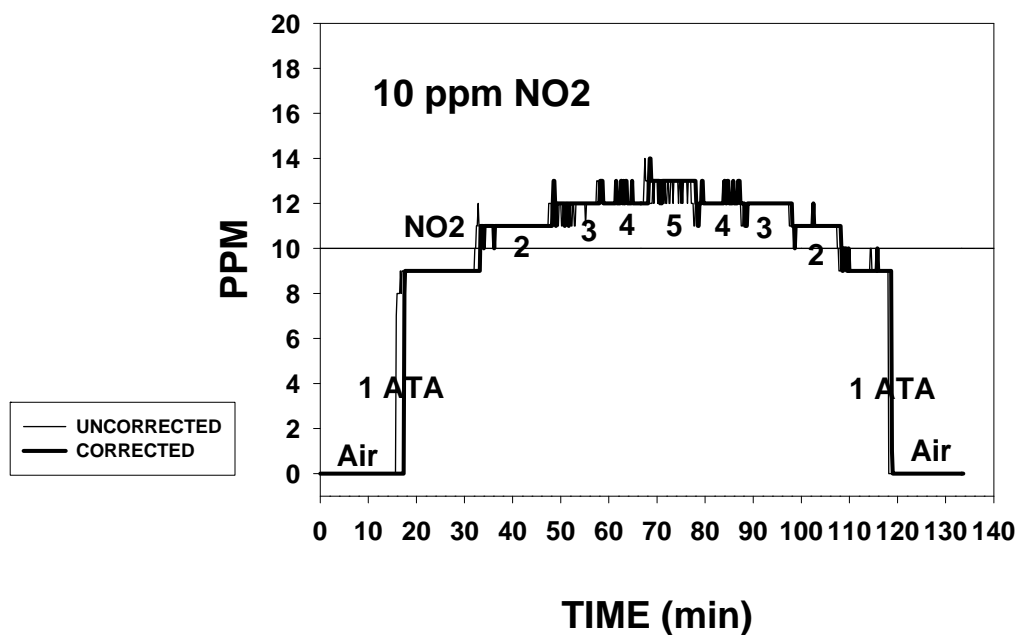


FIGURE 21E. Stability of pressure corrections: Cl₂ (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations
Bottom Graph: ~1.5 yr following pressure correction calibrations

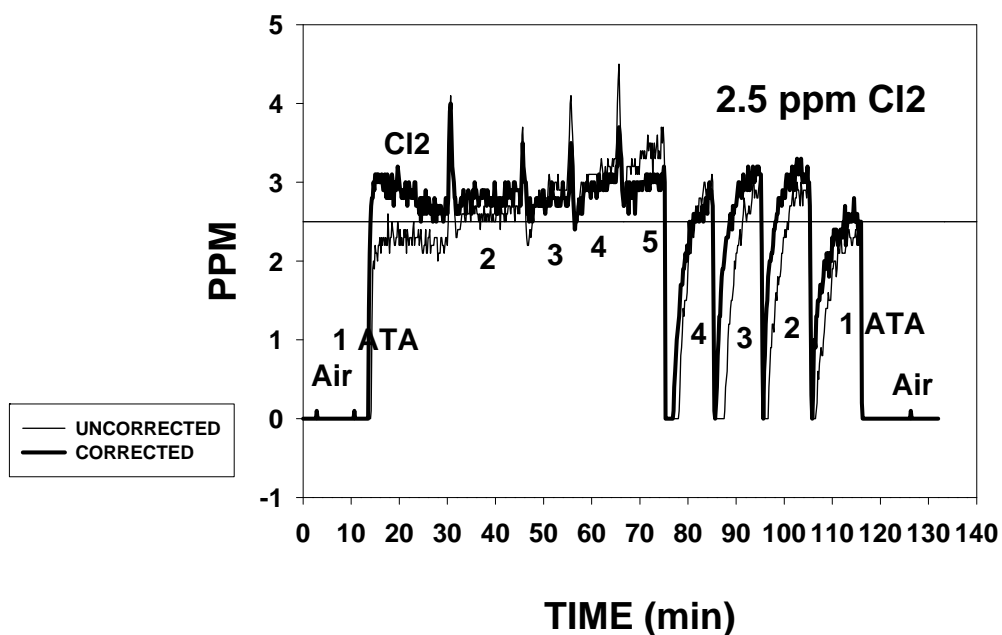
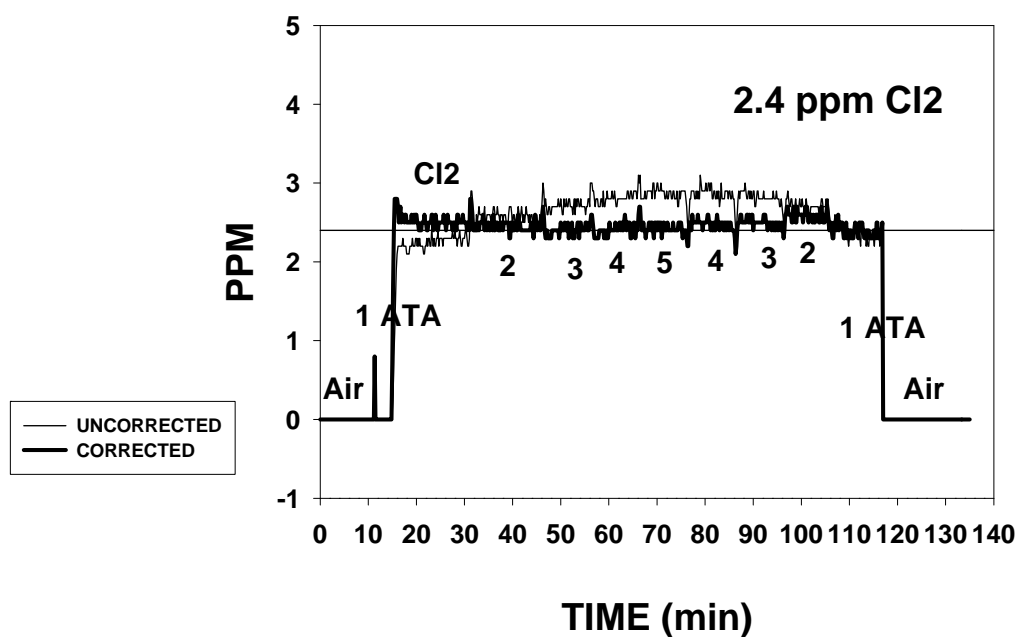


FIGURE 21F. Stability of pressure corrections: HCN (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations
Bottom Graph: ~1.5 yr following pressure correction calibrations

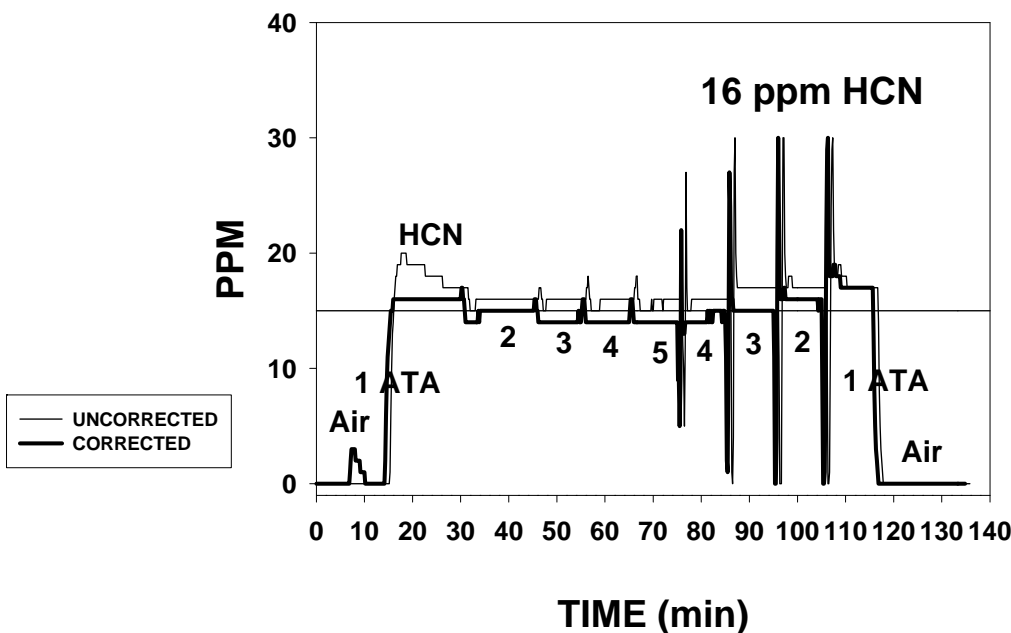
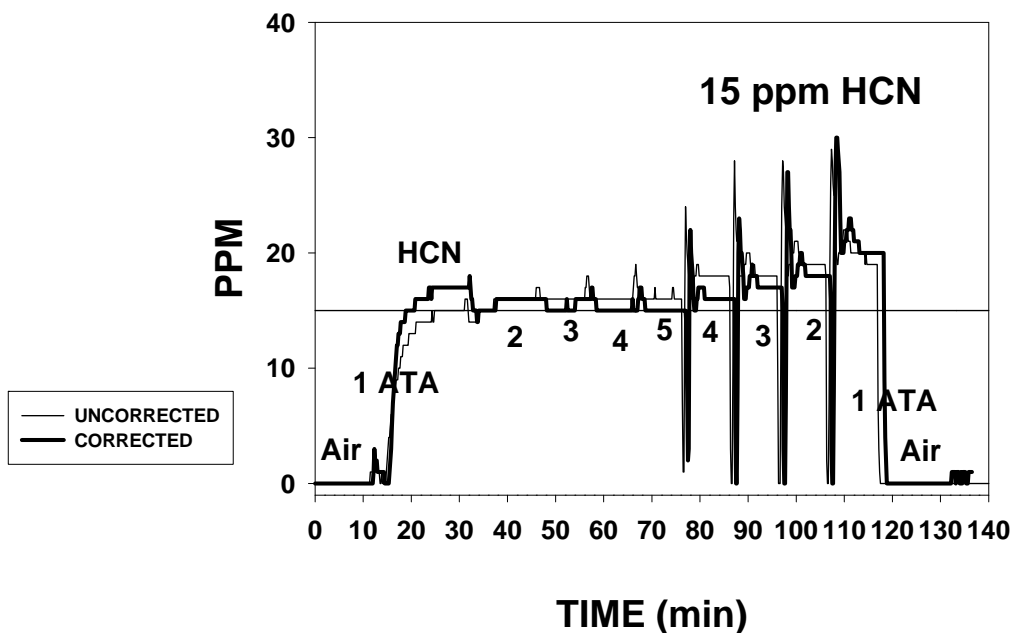


FIGURE 21G. Stability of pressure corrections: HCl (ppm; uncorrected vs. corrected plots).

Top Graph: ~0.5 yr following pressure correction calibrations
Bottom Graph: ~1.5 yr following pressure correction calibrations

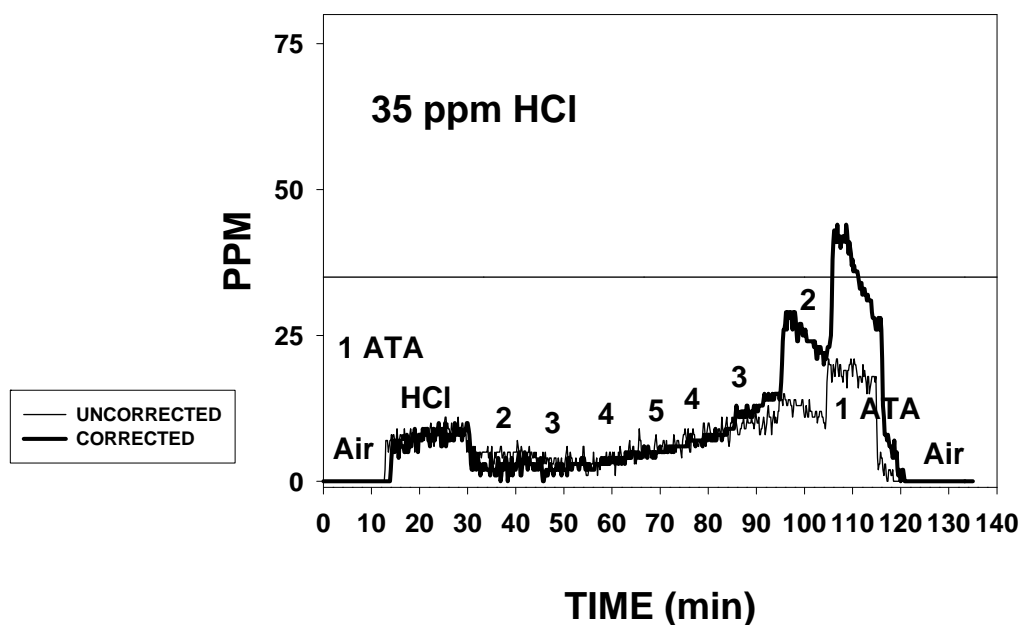
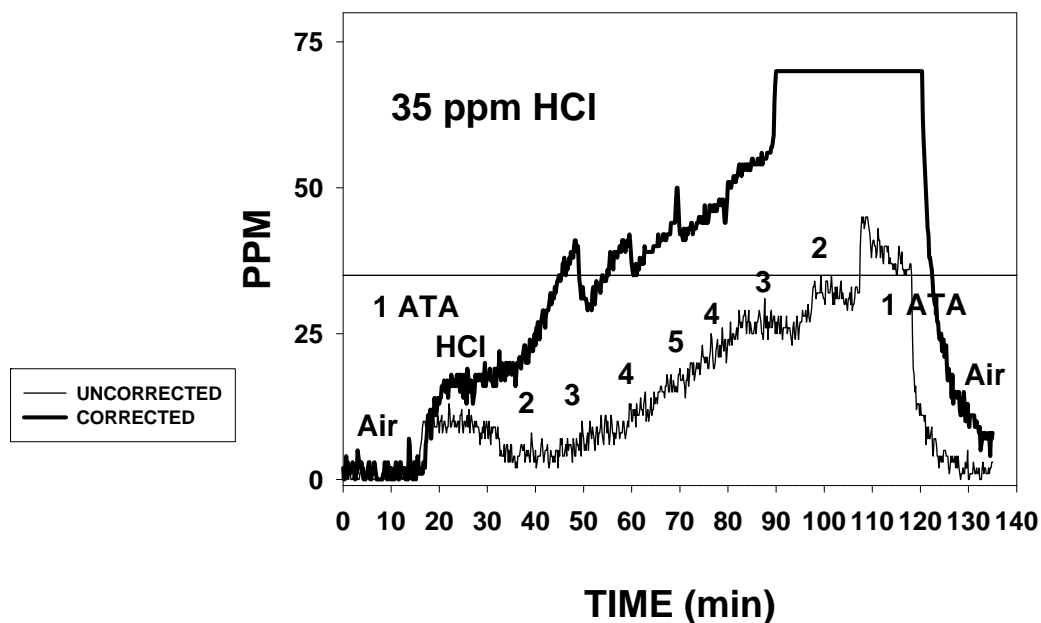


FIGURE 22A. Temperature effect on sensors: CO (top graph) and H₂S (bottom graph).

With mV plotted from AM (25 °C) and PM (5 °C or 42 °C) tests

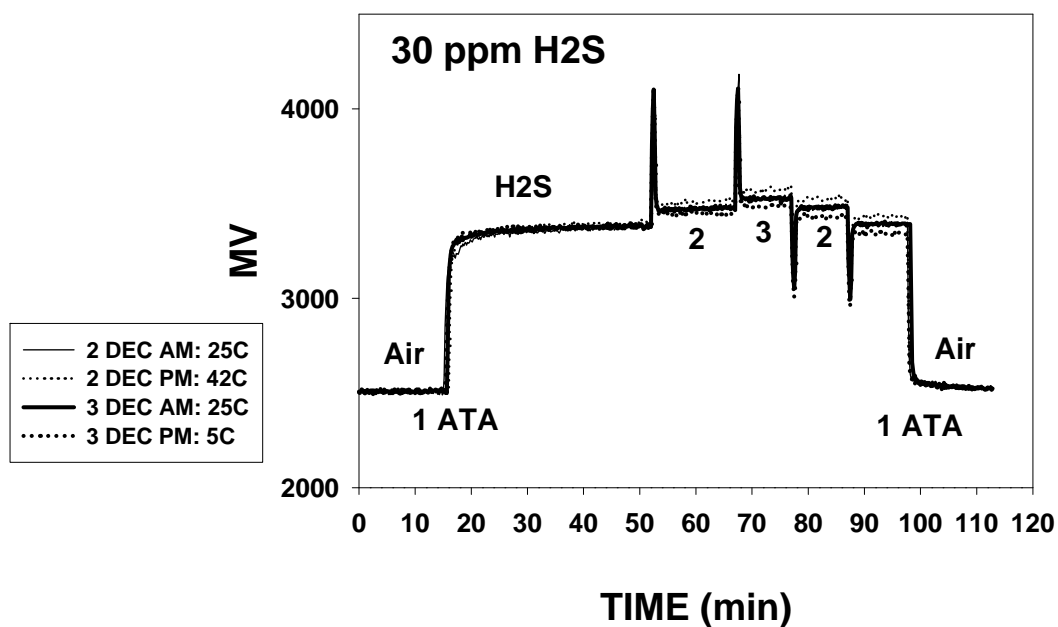
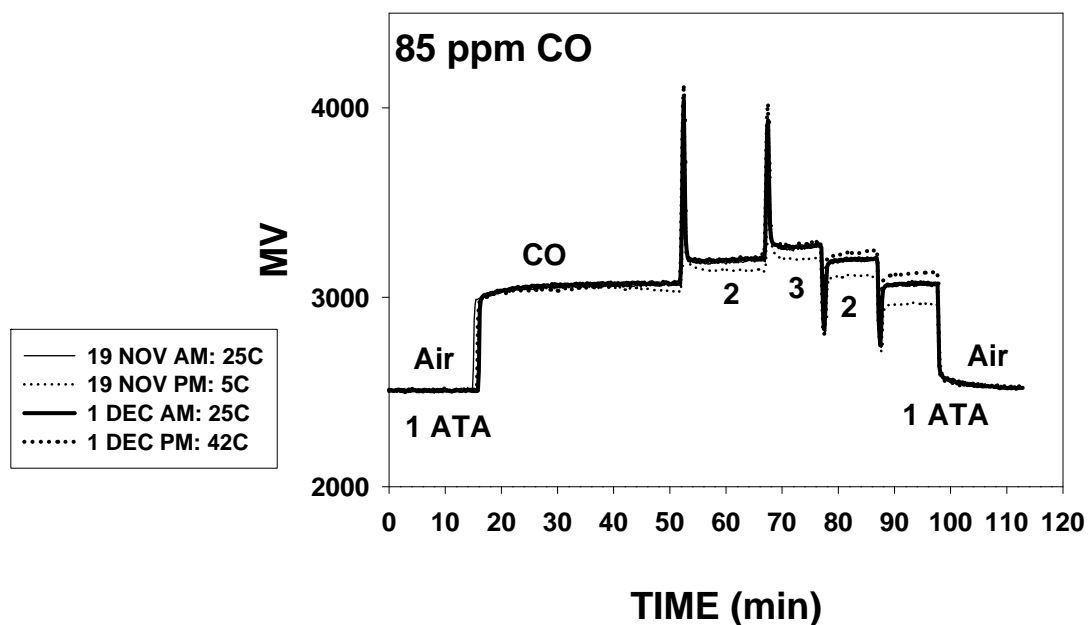


FIGURE 22B. Temperature effect on sensors: SO₂ (top graph) and NO₂/Cl₂ (bottom graph).

With mV plotted from AM (25 °C) and PM (5 °C or 42 °C) tests

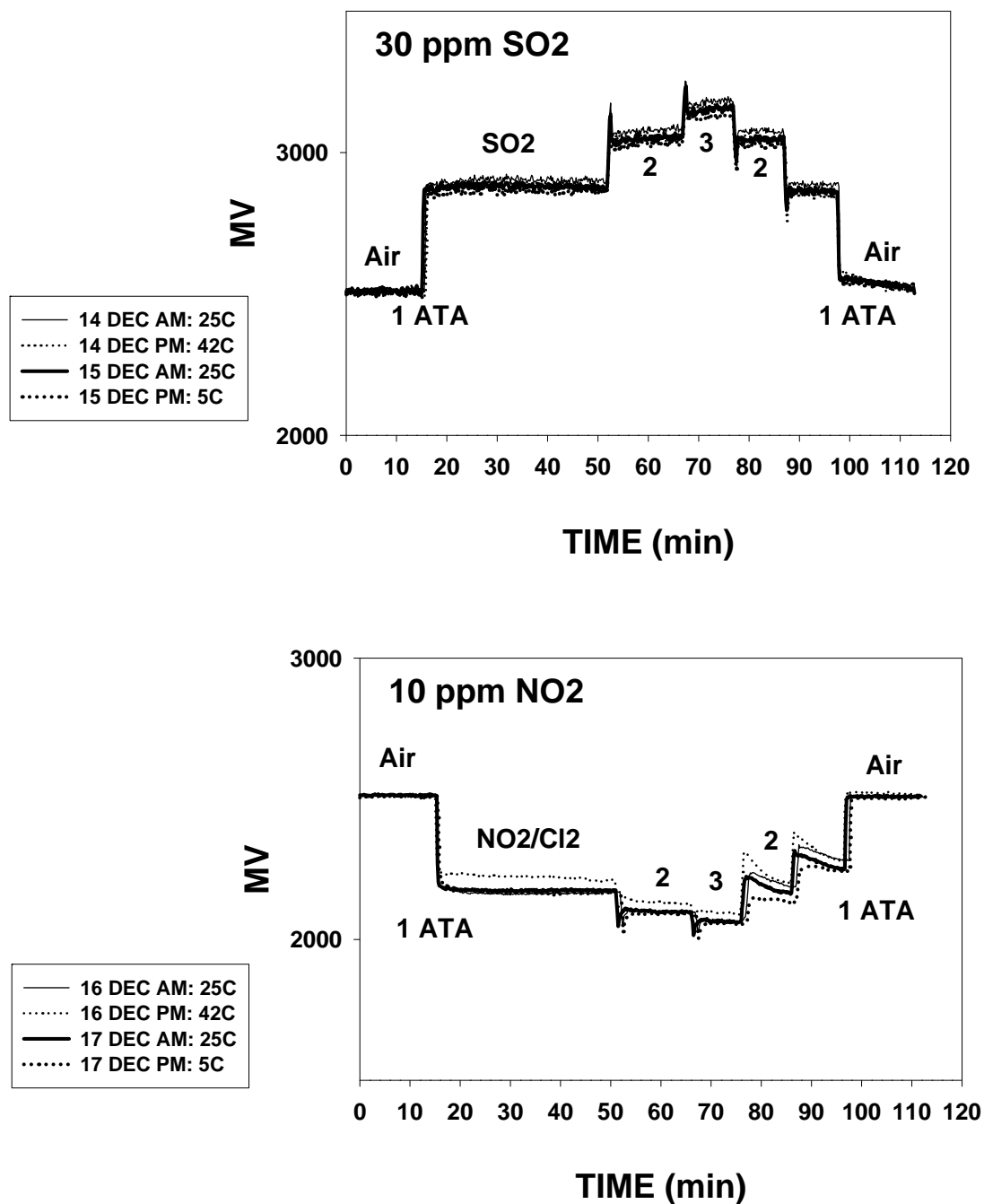
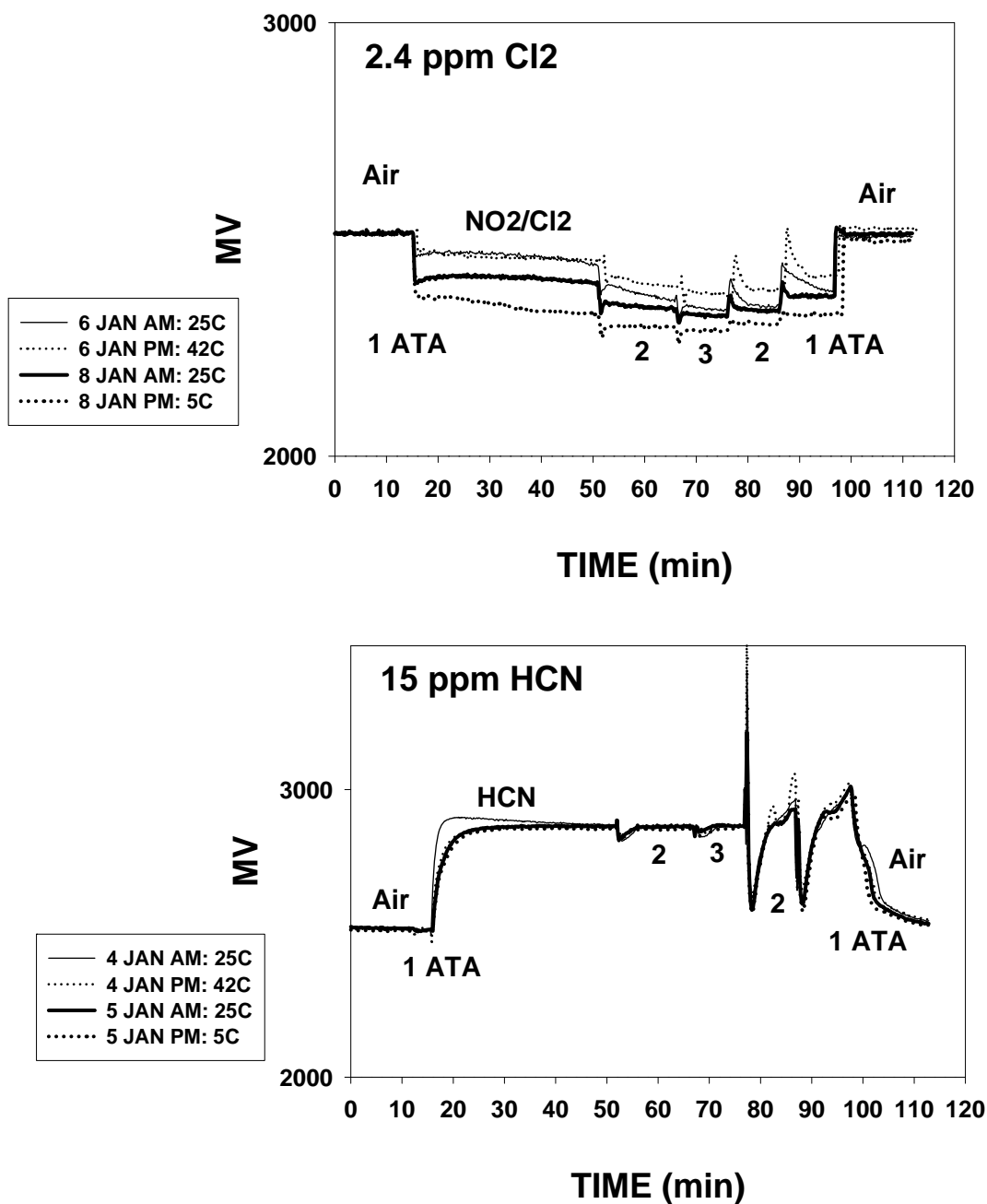


FIGURE 22C. Temperature effect on sensors: NO₂/Cl₂ (top graph) and HCN (bottom graph).

With mV plotted from AM (25 °C) and PM (5 °C or 42 °C) tests



**FIGURE 23A. Sensor cross sensitivities to other gases:
CO test gas vs. H₂S and SO₂ sensors.**

With mV plotted for TWO repeat tests on different days

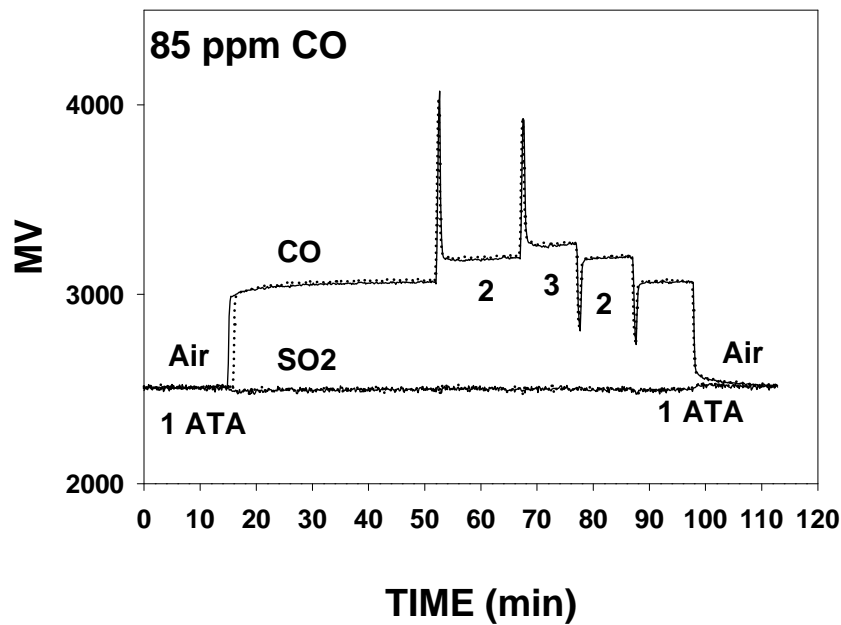
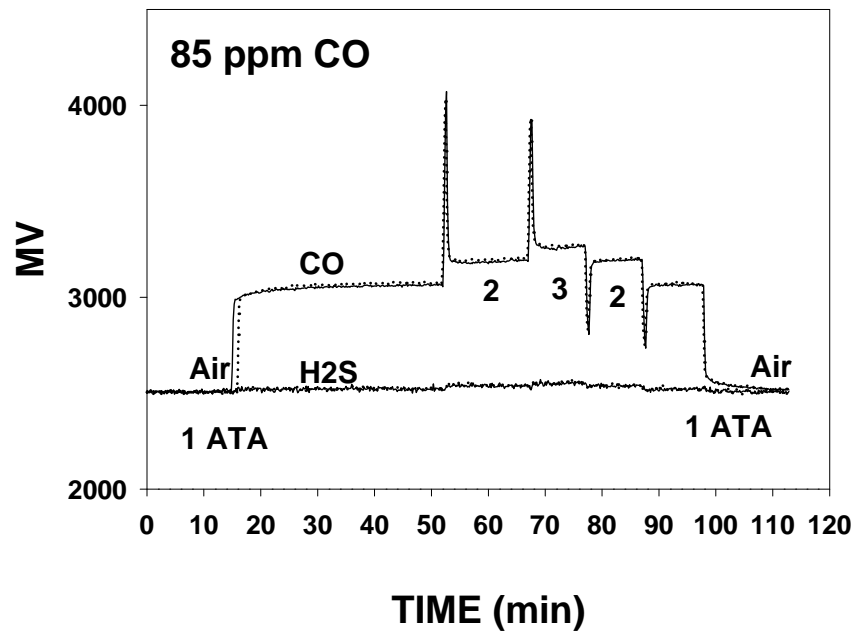


FIGURE 23B. Sensor cross sensitivities to other gases: CO test gas vs. NO₂/Cl₂ and HCN sensors.

With mV plotted for TWO repeat tests on different days

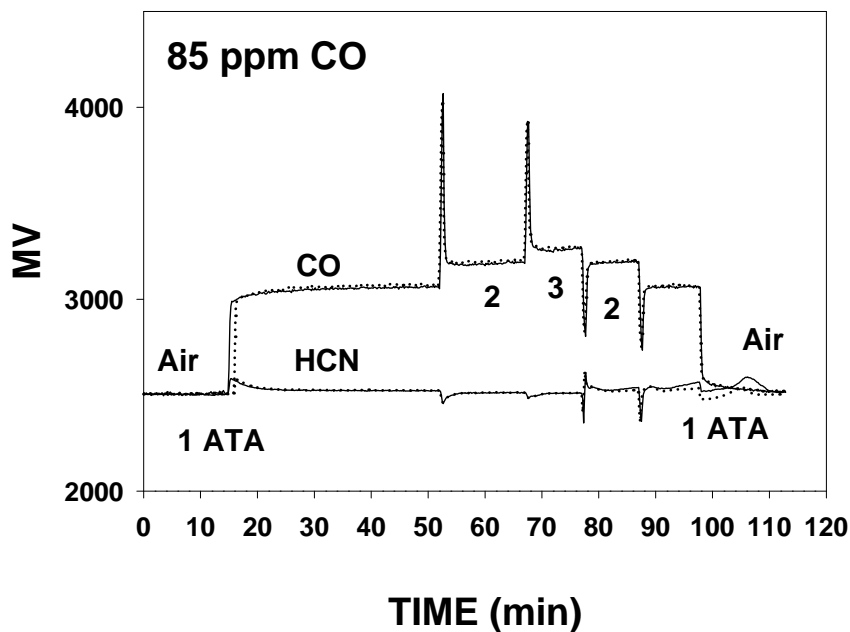
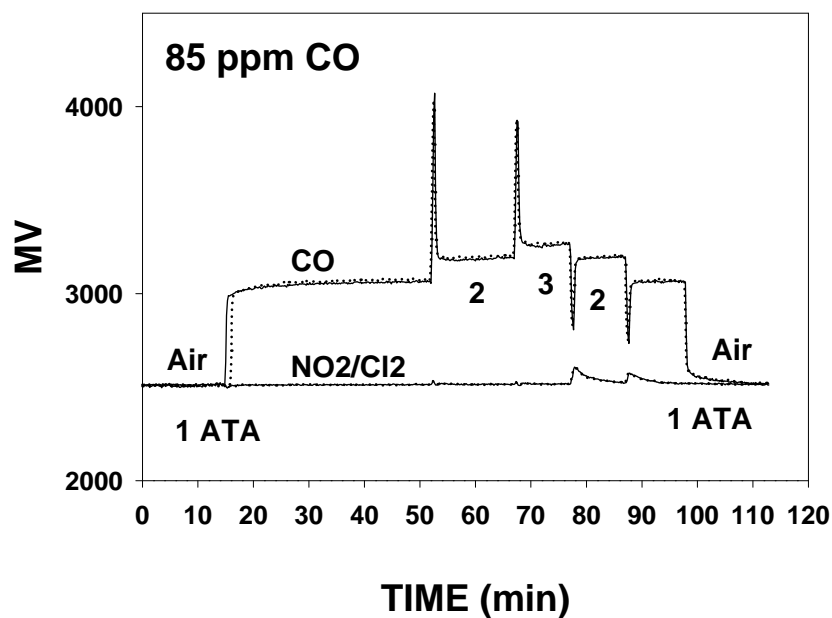
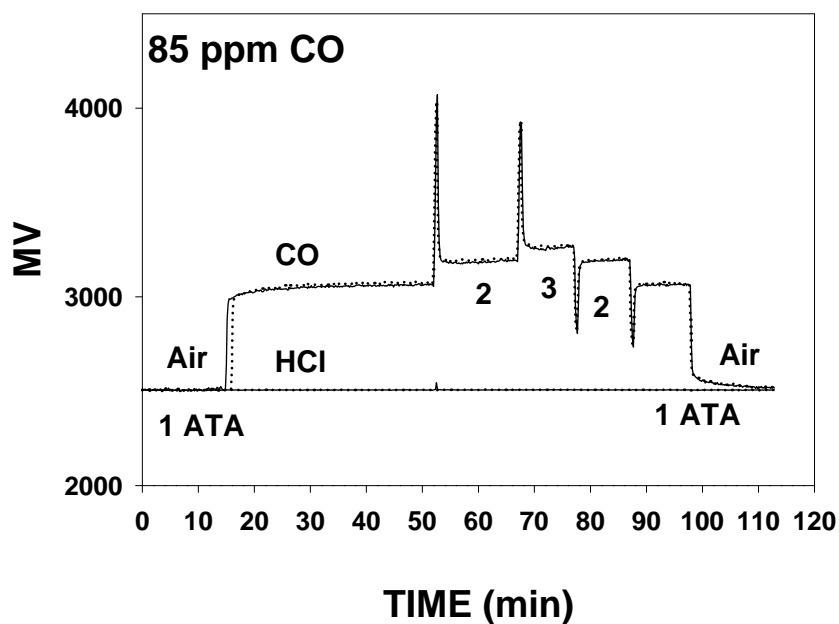


FIGURE 23C. Sensor cross sensitivities to other gases: CO test gas vs. HCl sensor.

With mV plotted for TWO repeat tests on different days



**FIGURE 24A. Sensor cross sensitivities to other gases:
H₂S test gas vs. CO and SO₂ sensors.**

With mV plotted for TWO repeat tests on different days

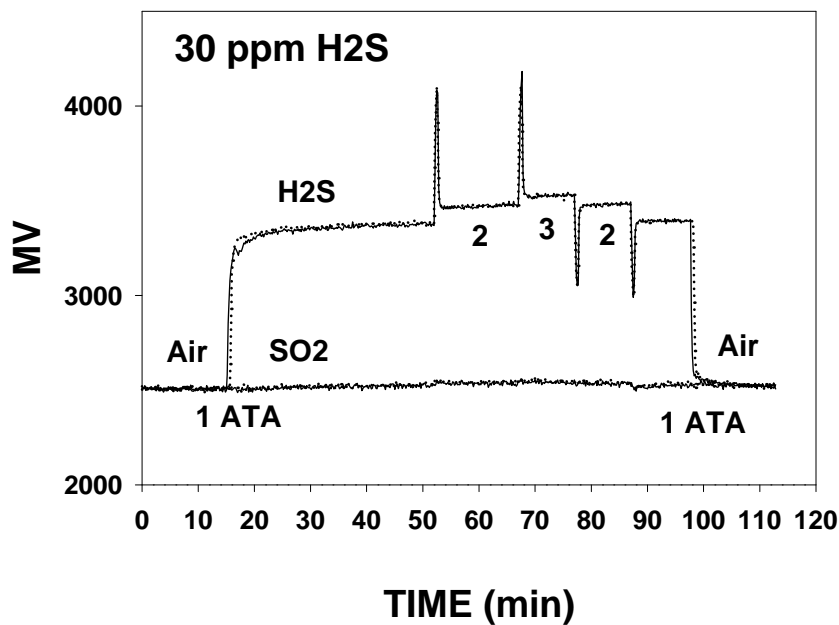
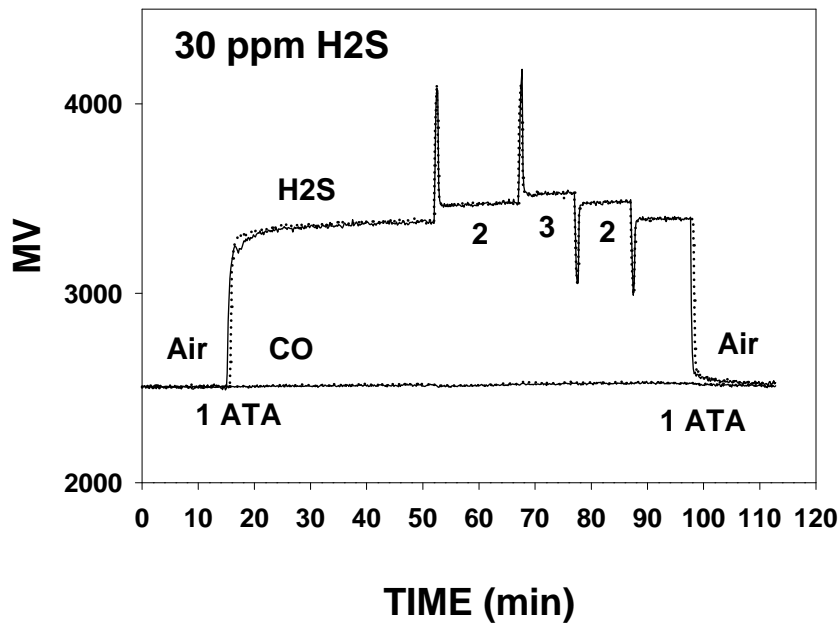


FIGURE 24B. Sensor cross sensitivities to other gases: H₂S test gas vs. NO₂/Cl₂ and HCN sensors.

With mV plotted for TWO repeat tests on different days

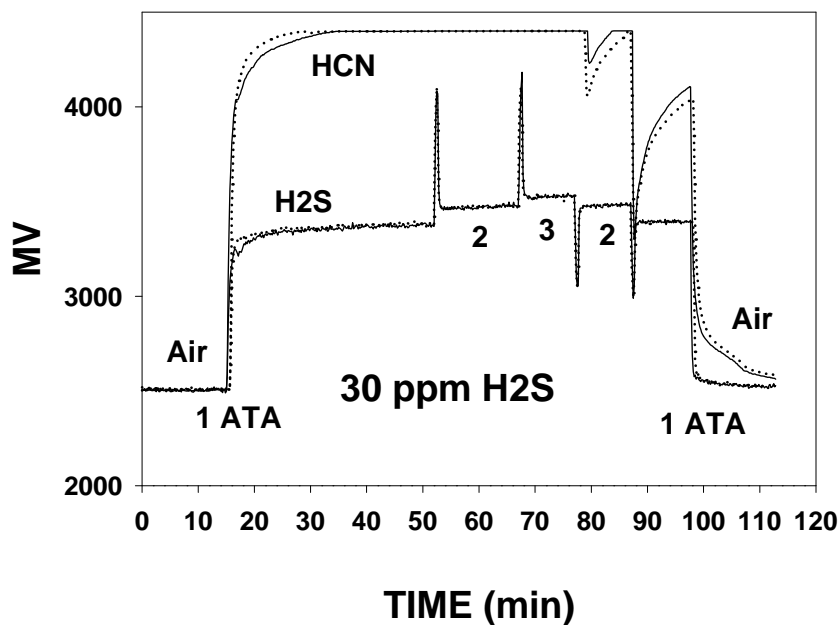
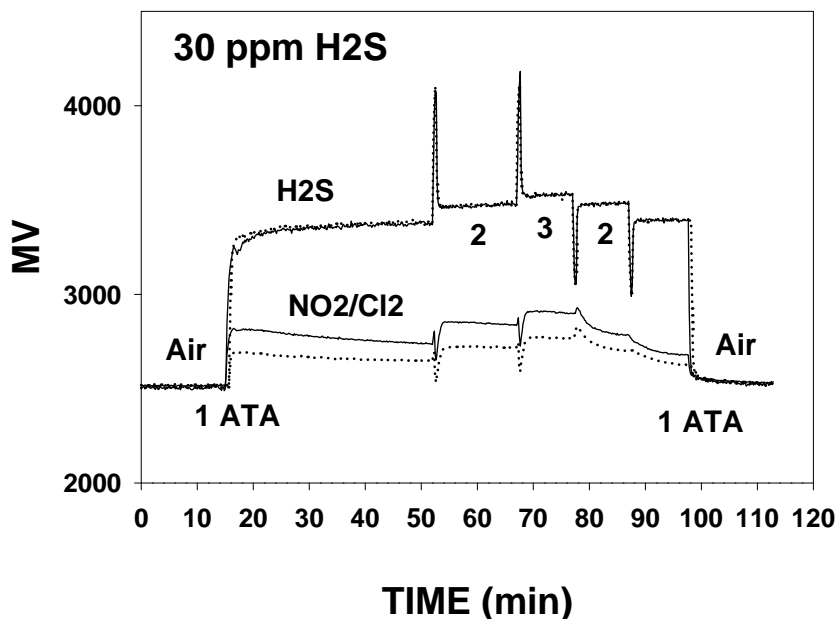


FIGURE 24C. Sensor cross sensitivities to other gases: H₂S test gas vs. HCl sensor.

With mV plotted for TWO repeat tests on different days

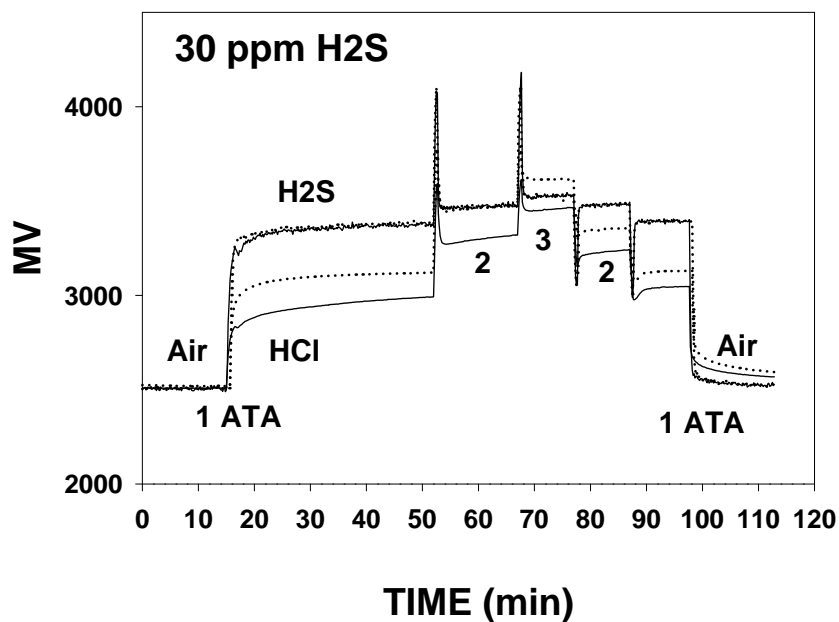


FIGURE 25A. Sensor cross sensitivities to other gases: SO₂ test gas vs. CO and H₂S sensors.

With mV plotted for TWO repeat tests on different days

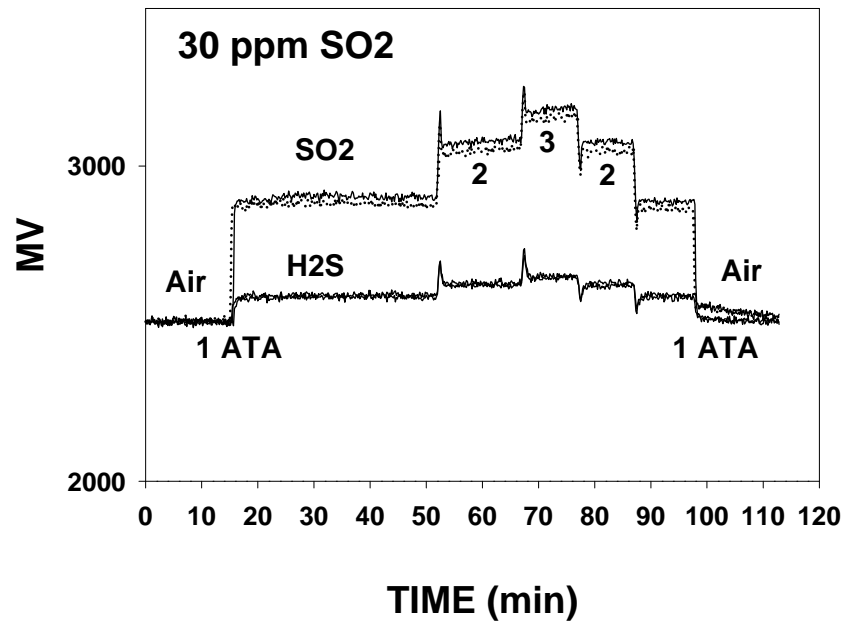
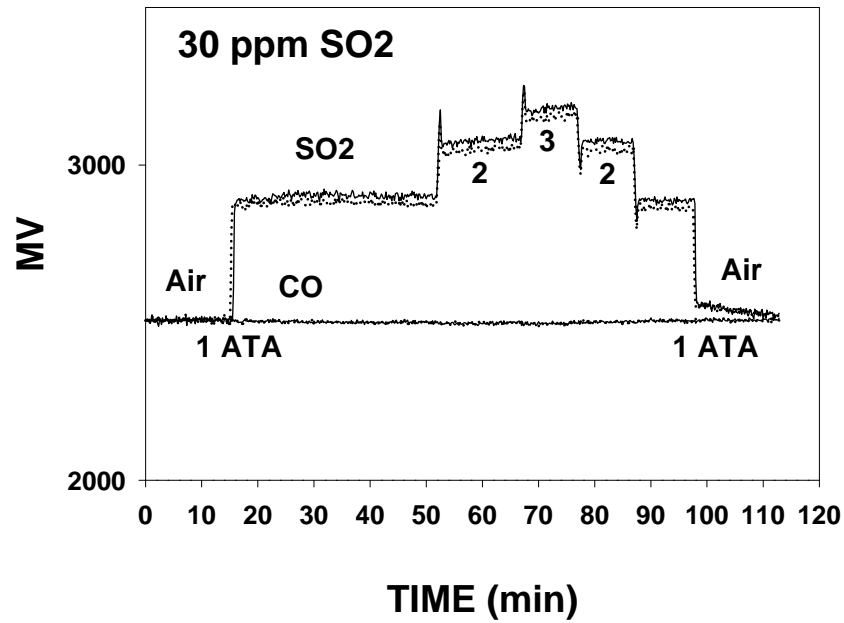


FIGURE 25B. Sensor cross sensitivities to other gases: SO₂ test gas vs. NO₂/Cl₂ and HCN sensors.

With mV plotted for TWO repeat tests on different days

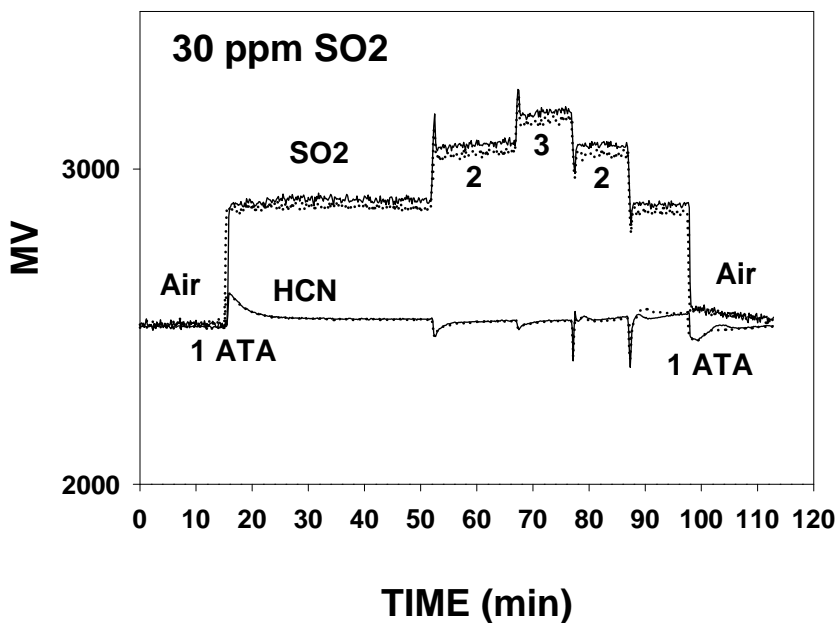
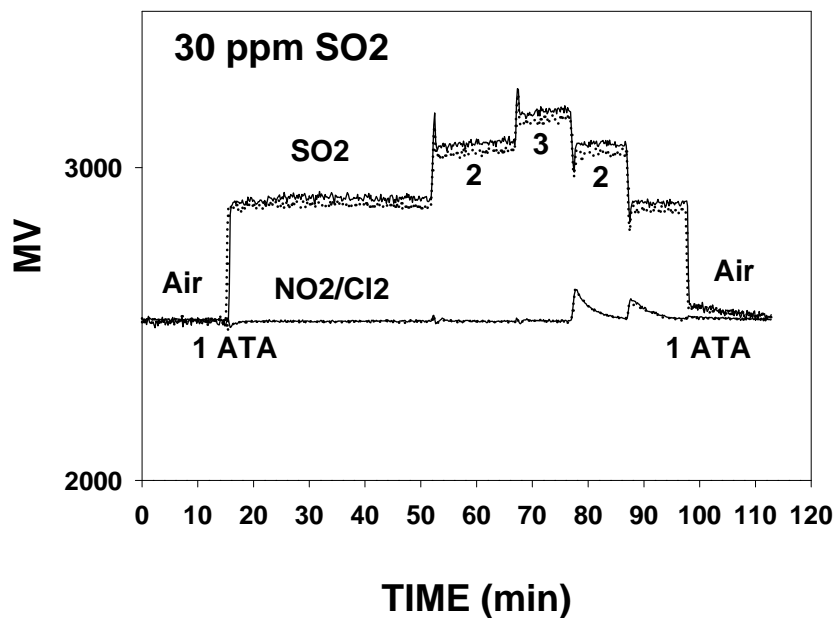


FIGURE 25C. Sensor cross sensitivities to other gases: SO₂ test gas vs. HCl sensor

With mV plotted for TWO repeat tests on different days

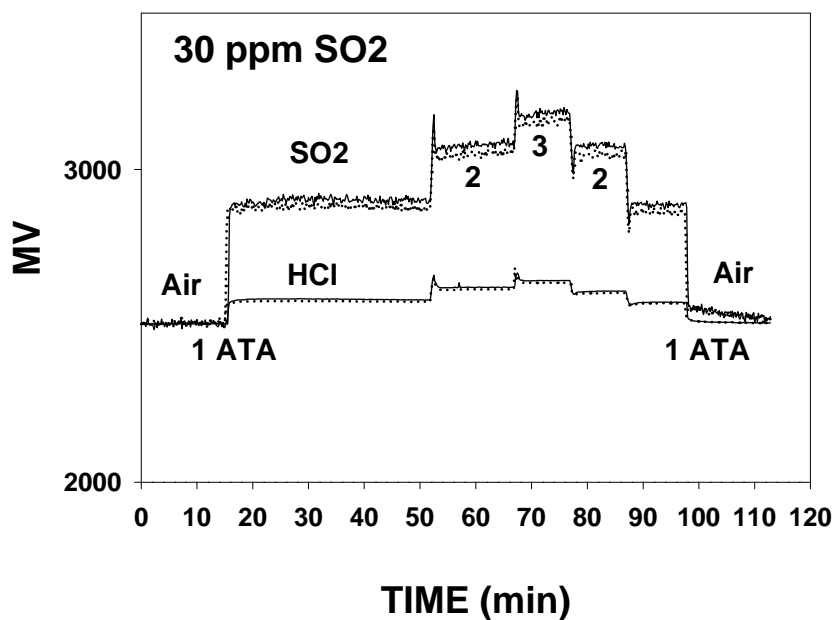


FIGURE 26A. Sensor cross sensitivities to other gases: NO₂ test gas vs. CO and H₂S sensors.

With mV plotted for TWO repeat tests on different days

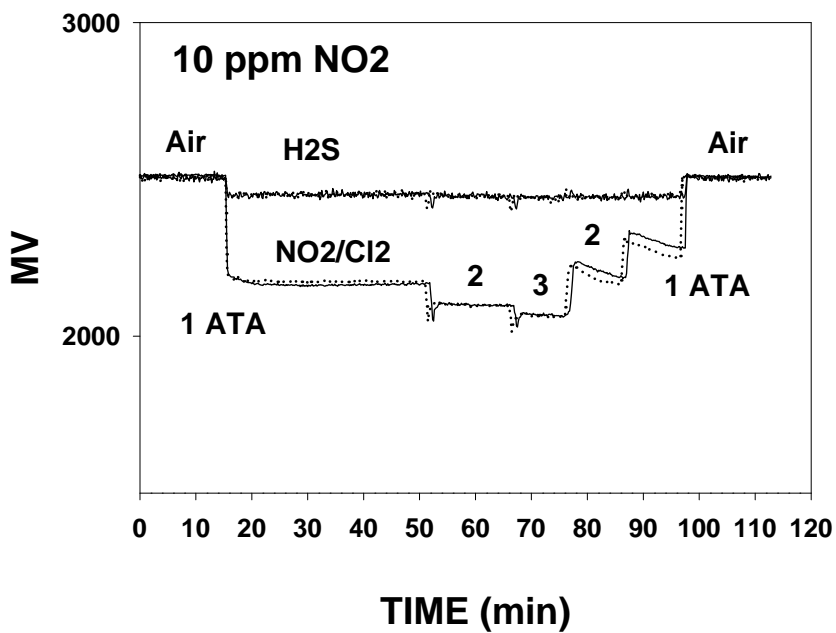
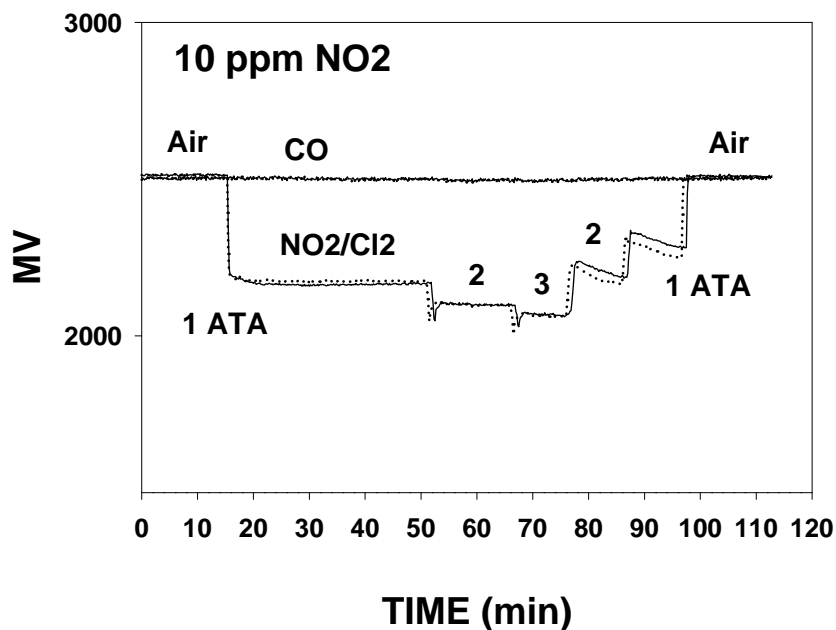


FIGURE 26B. Sensor cross sensitivities to other gases: NO₂ test gas vs. SO₂ and HCN sensors.

With mV plotted for TWO repeat tests on different days

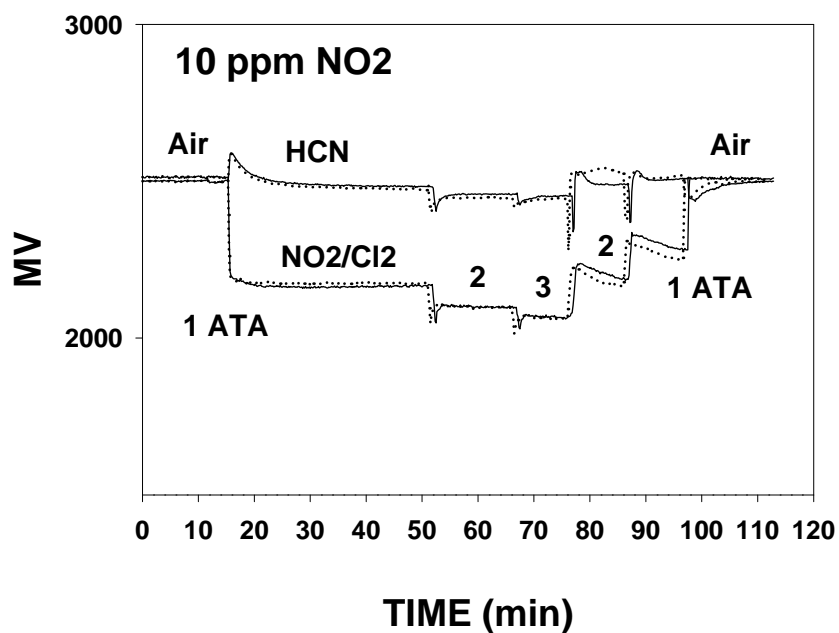
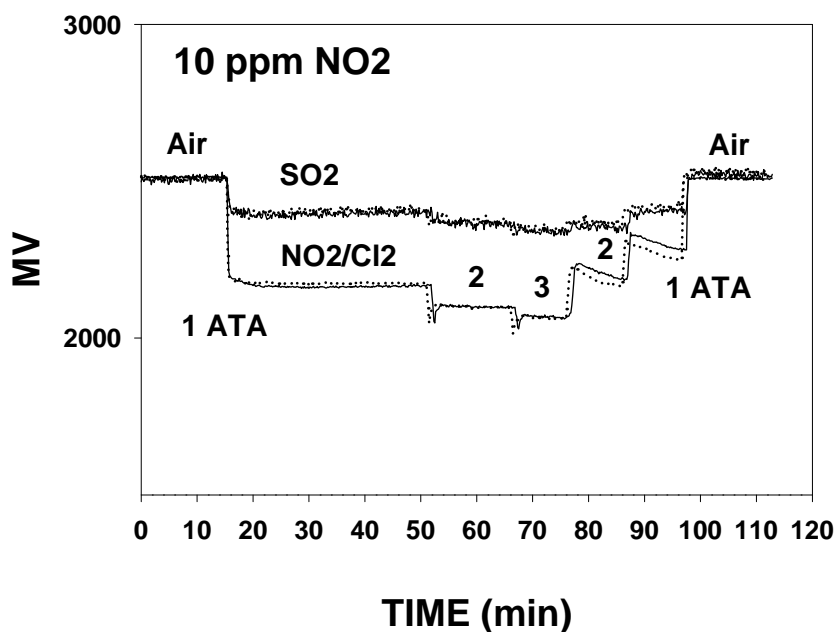


FIGURE 26C. Sensor cross sensitivities to other gases: NO₂ test gas vs. HCl sensor

With mV plotted for TWO repeat tests on different days

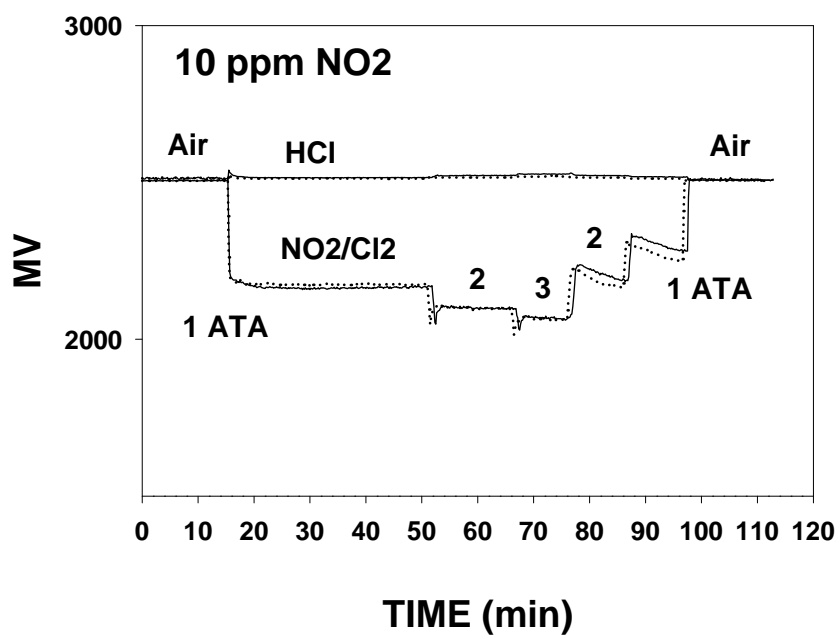


FIGURE 27A. Sensor cross sensitivities to other gases: Cl₂ test gas vs. CO and H₂S sensors:

With mV plotted for TWO repeat tests on different days

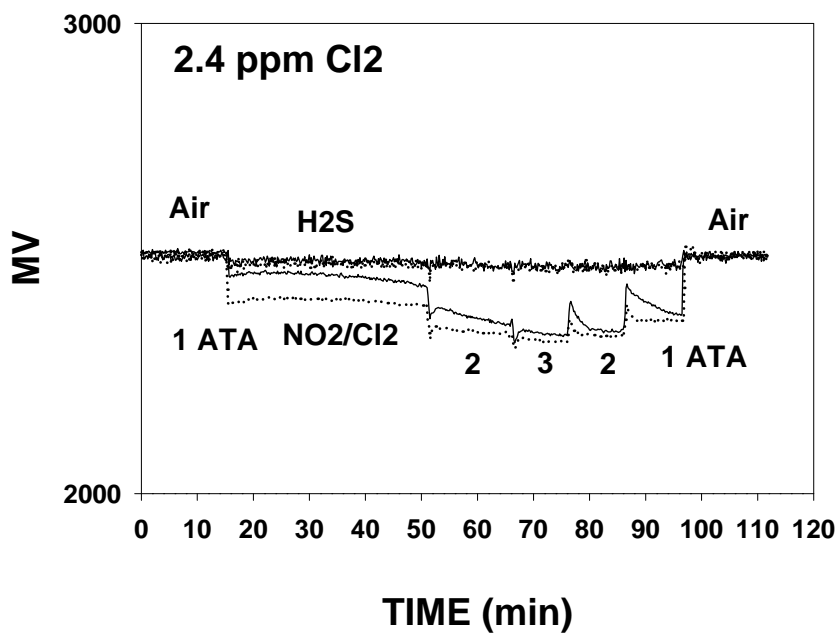
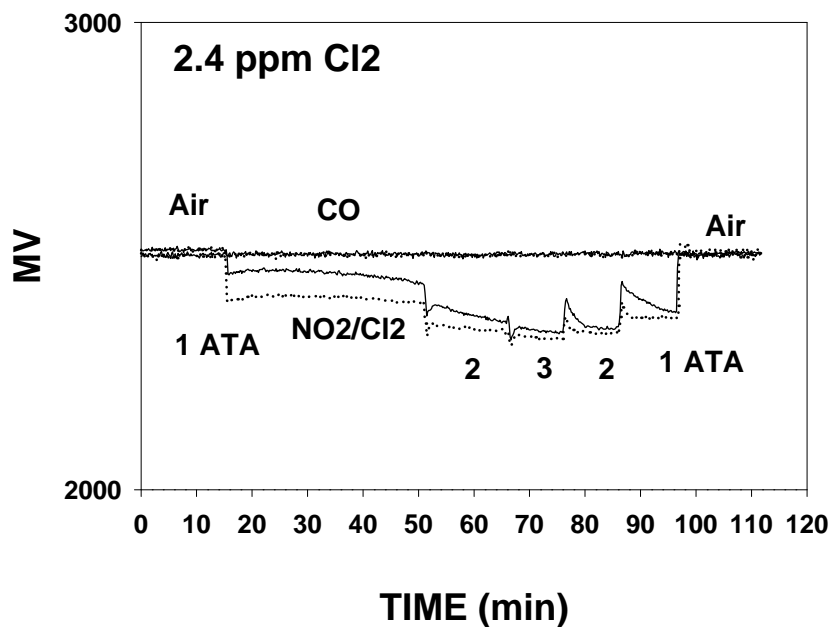


FIGURE 27B. Sensor cross sensitivities to other gases: Cl₂ test gas vs. SO₂ and HCN sensors:

With mV plotted for TWO repeat tests on different days

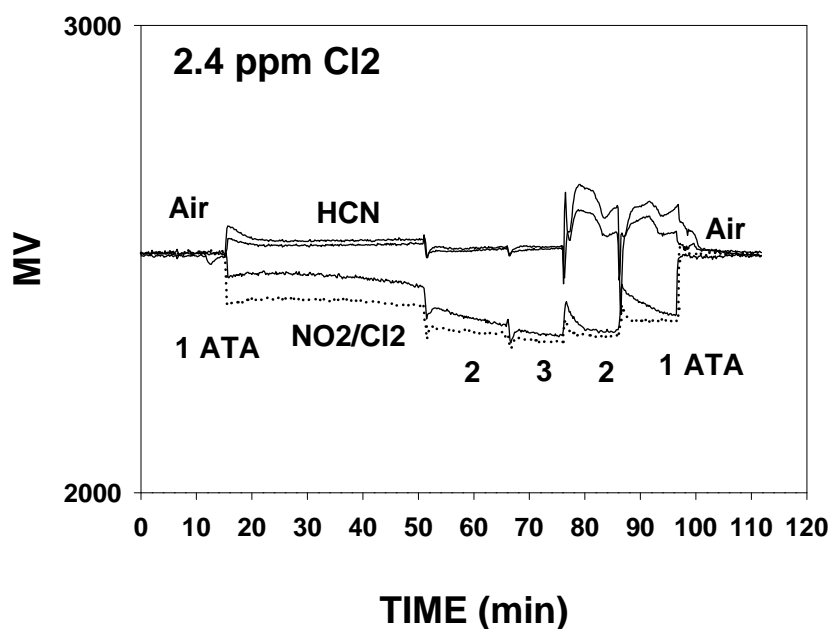
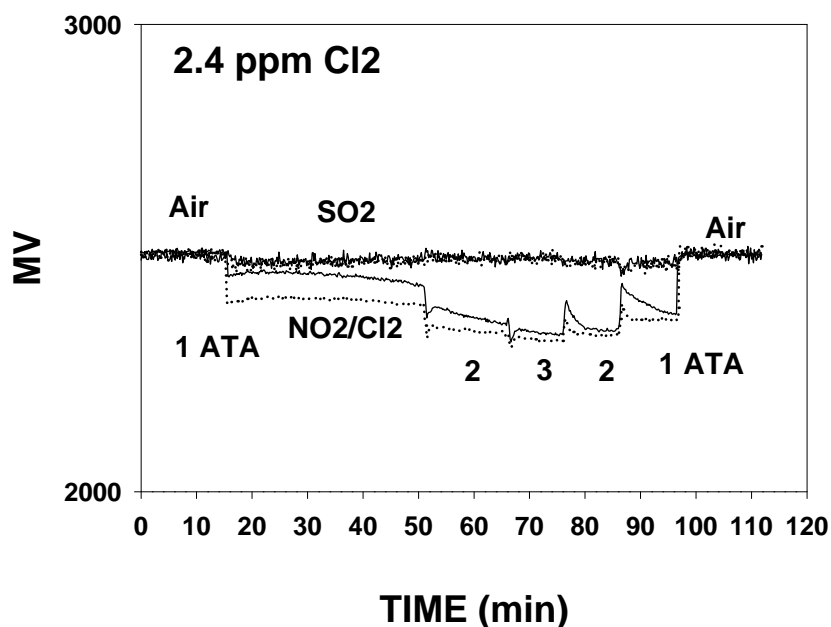


FIGURE 27C. Sensor cross sensitivities to other gases: Cl_2 test gas vs. HCl sensor.

With mV plotted for TWO repeat tests on different days

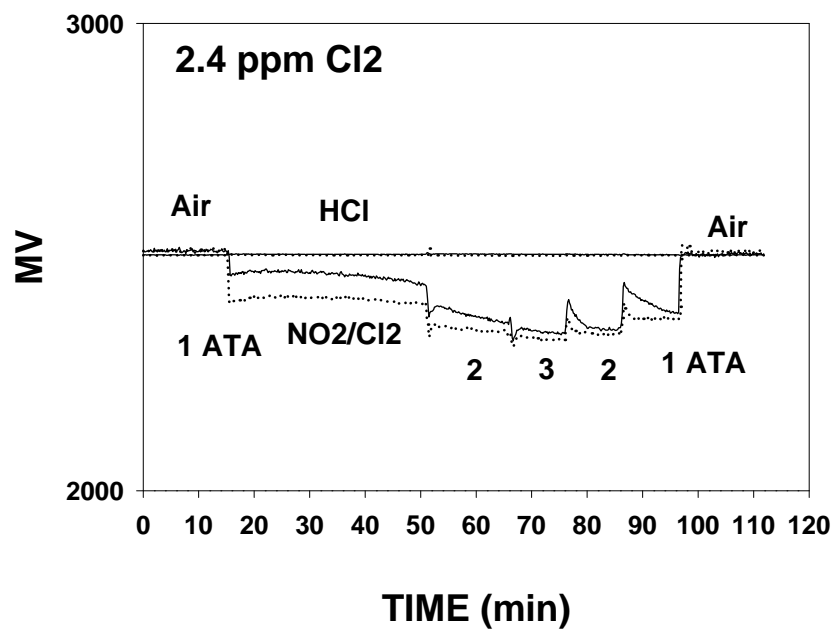


FIGURE 28A. Sensor cross sensitivities to other gases: HCN test gas vs. CO and H₂S sensors.

With mV plotted for TWO repeat tests on different days

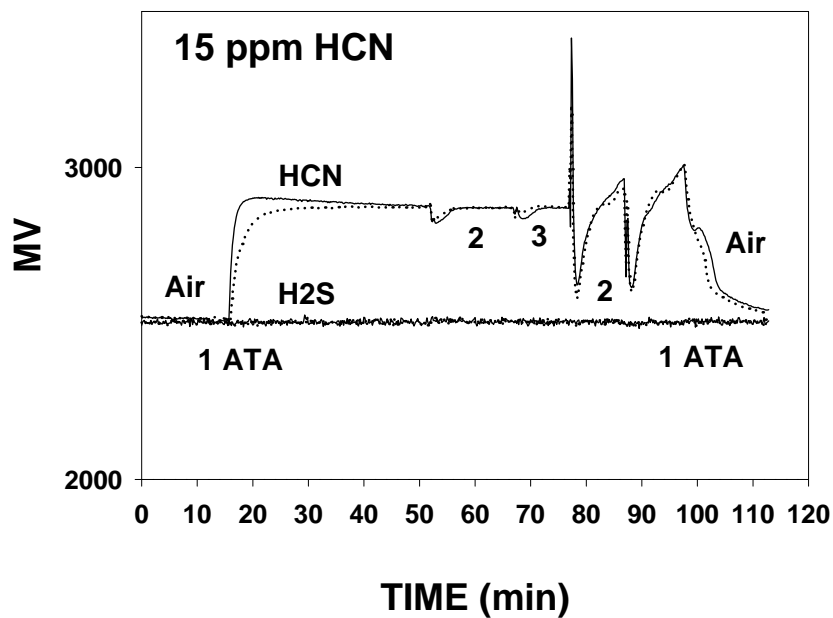
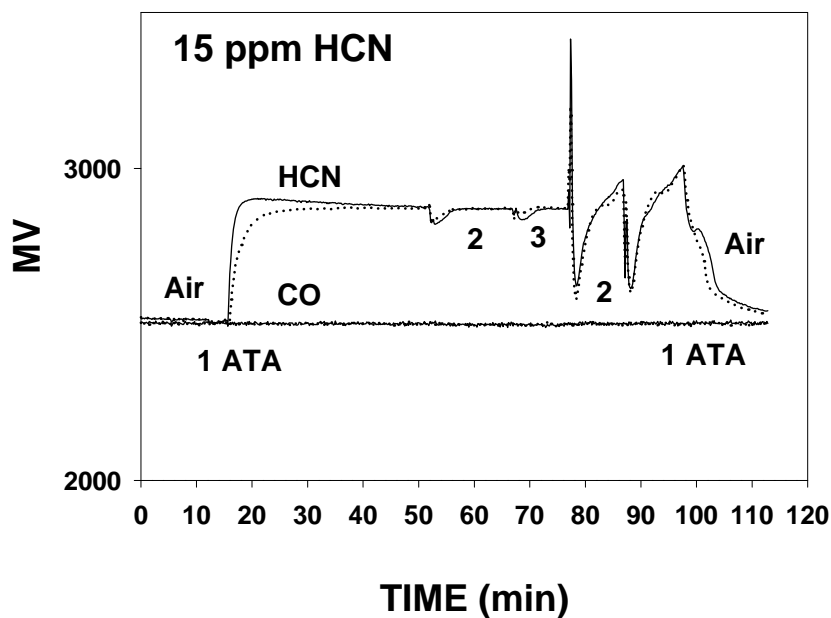


FIGURE 28B. Sensor cross sensitivities to other gases: HCN test gas vs. SO₂ and NO₂/Cl₂ sensors.

With mV plotted for TWO repeat tests on different days

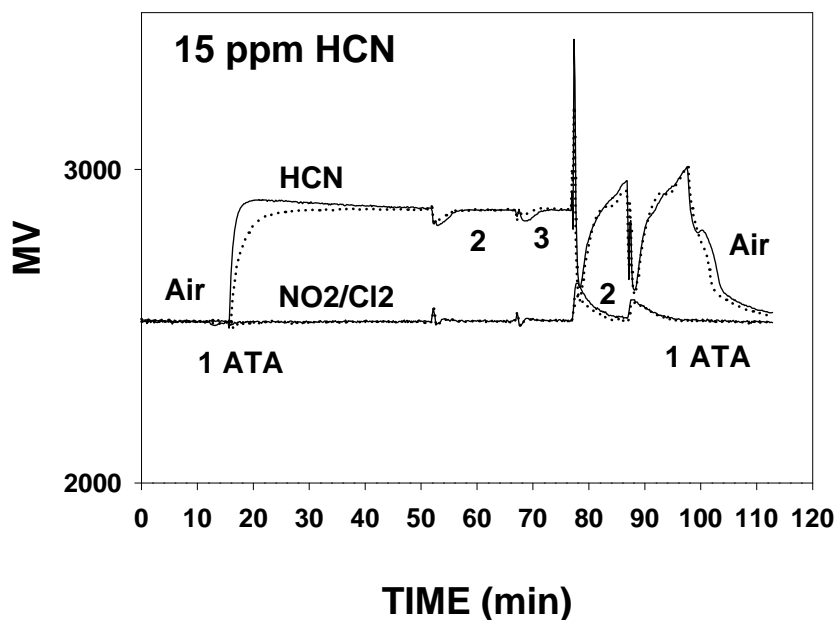
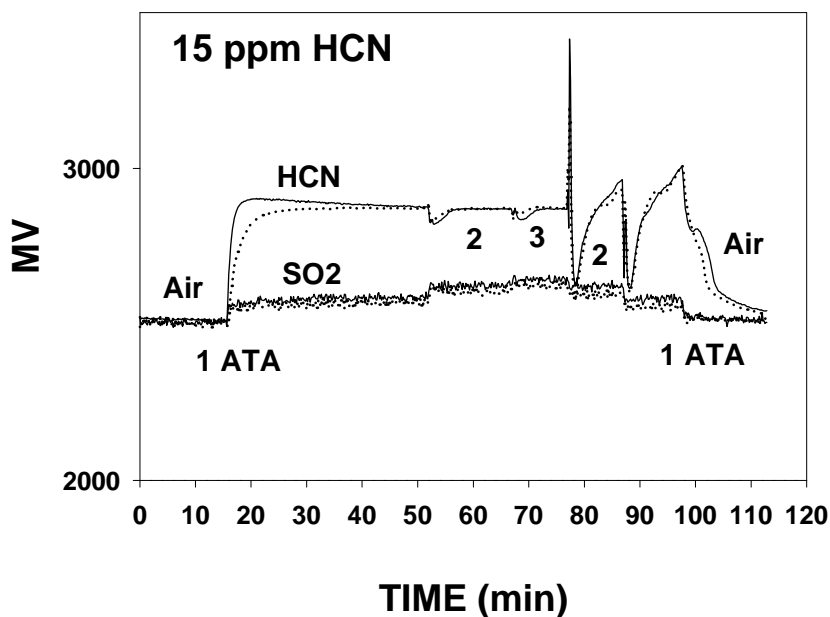


FIGURE 28C. Sensor cross sensitivities to other gases: HCN test gas vs. HCl sensor.

With mV plotted for TWO repeat tests on different days

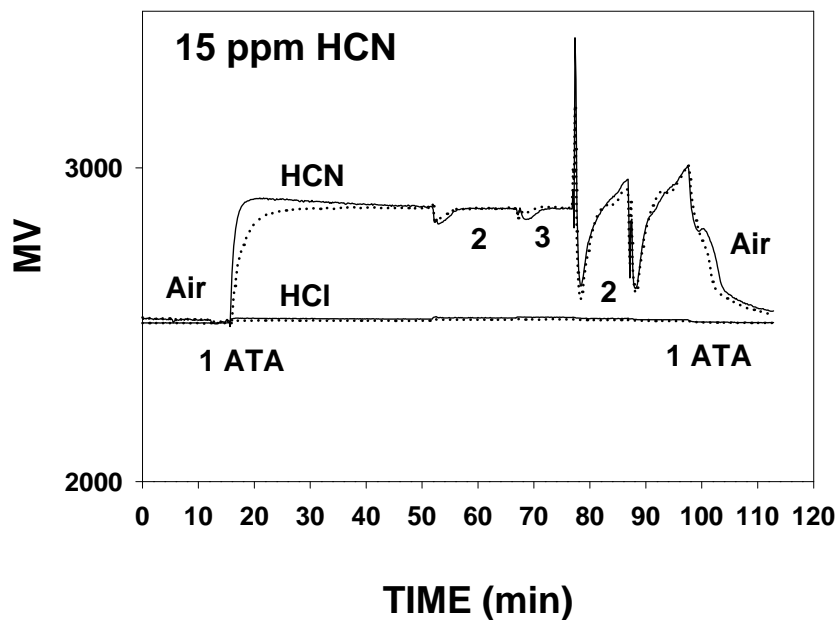


FIGURE 29A. Sensor cross sensitivities to other gases: HCl test gas vs. CO and H₂S sensors.

With mV plotted for TWO repeat tests on different days

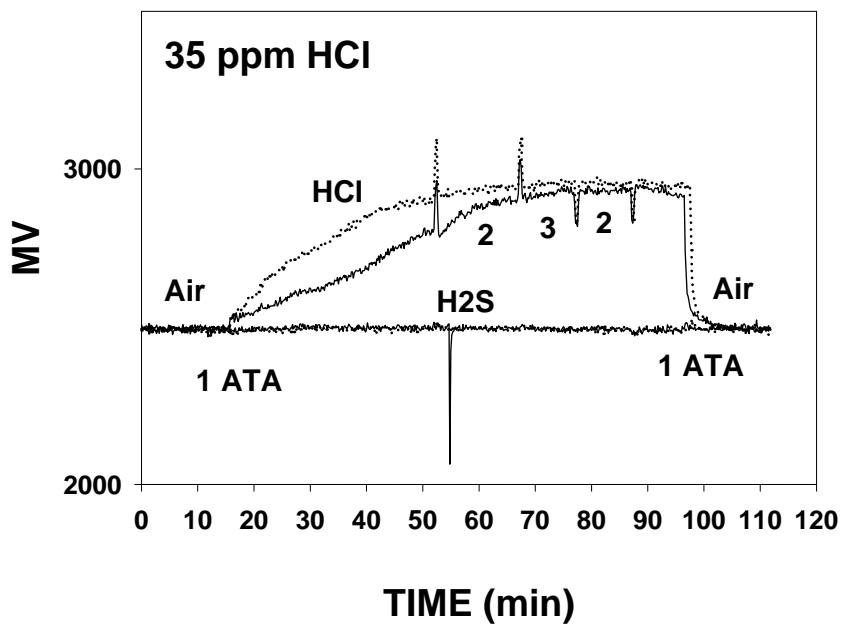
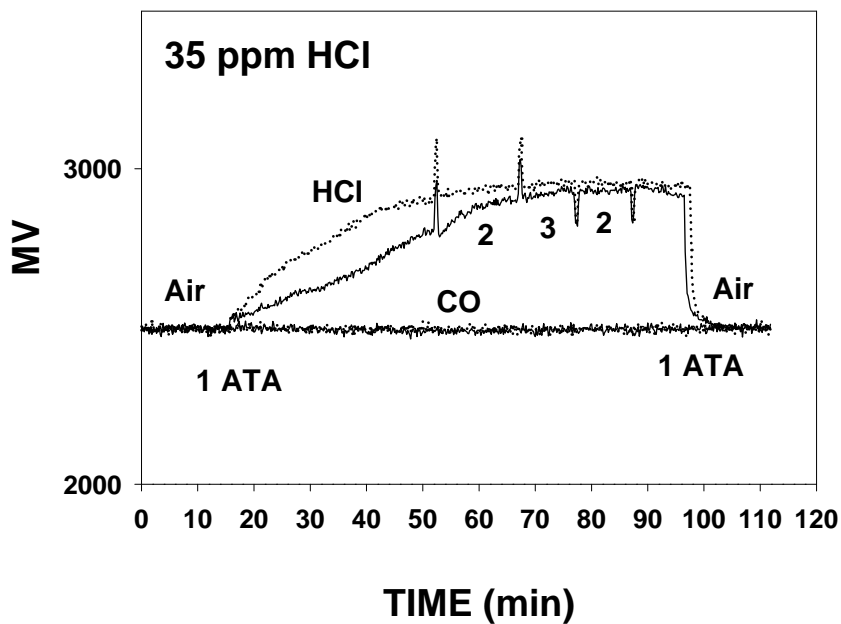


FIGURE 29B. Sensor cross sensitivities to other gases: HCl test gas vs. SO₂ and NO₂/Cl₂ sensors.

With mV plotted for TWO repeat tests on different days

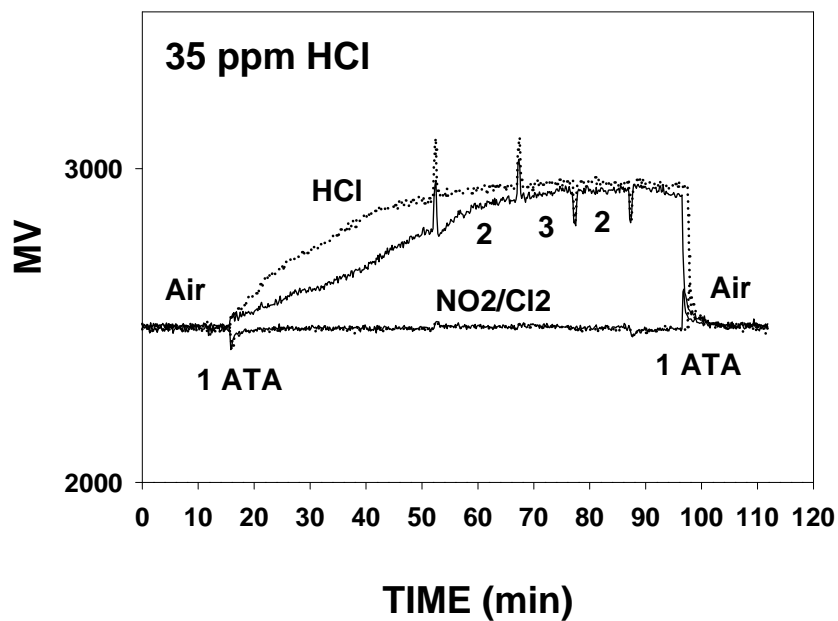
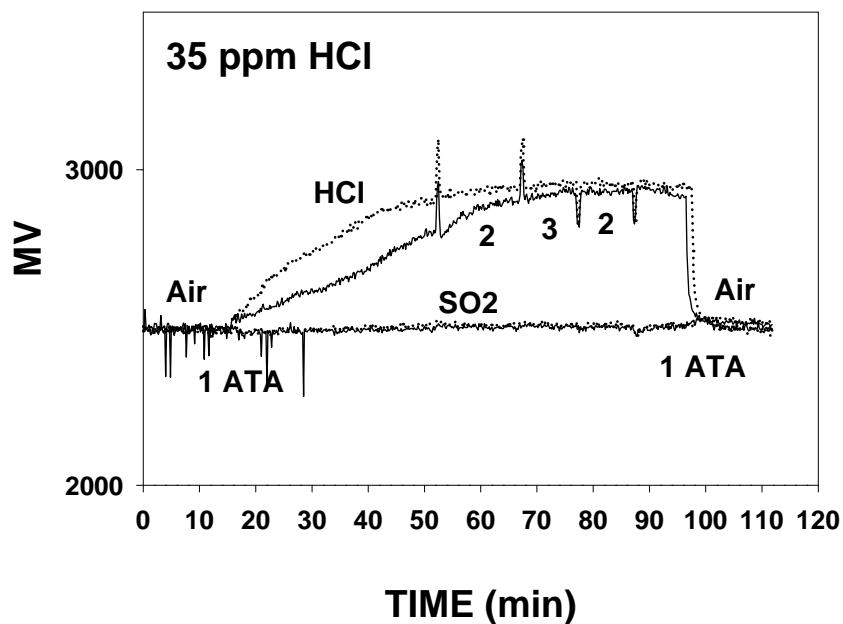
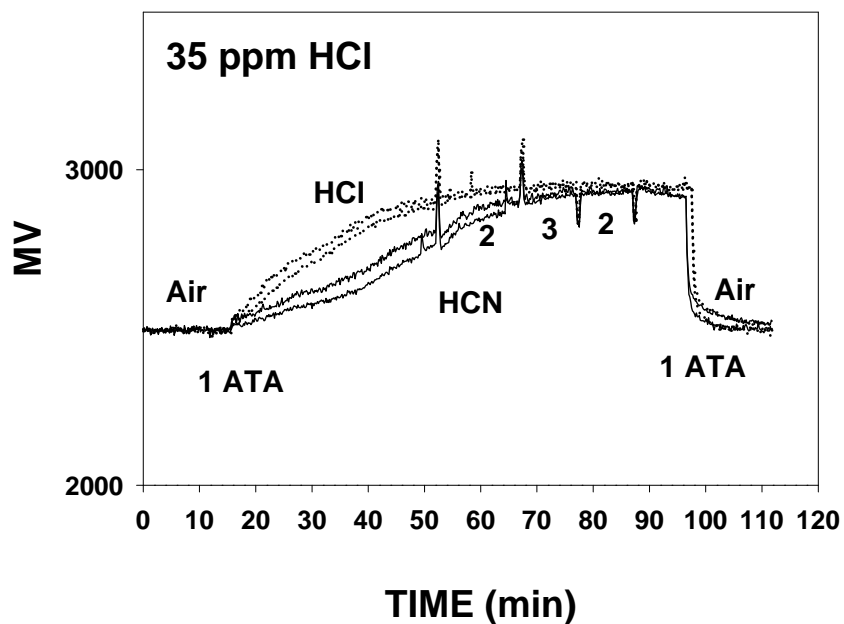


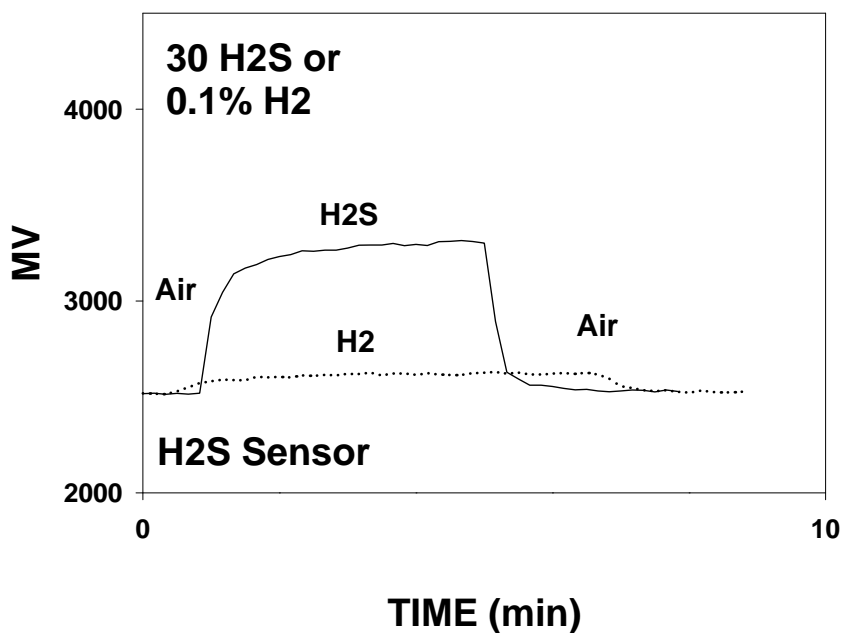
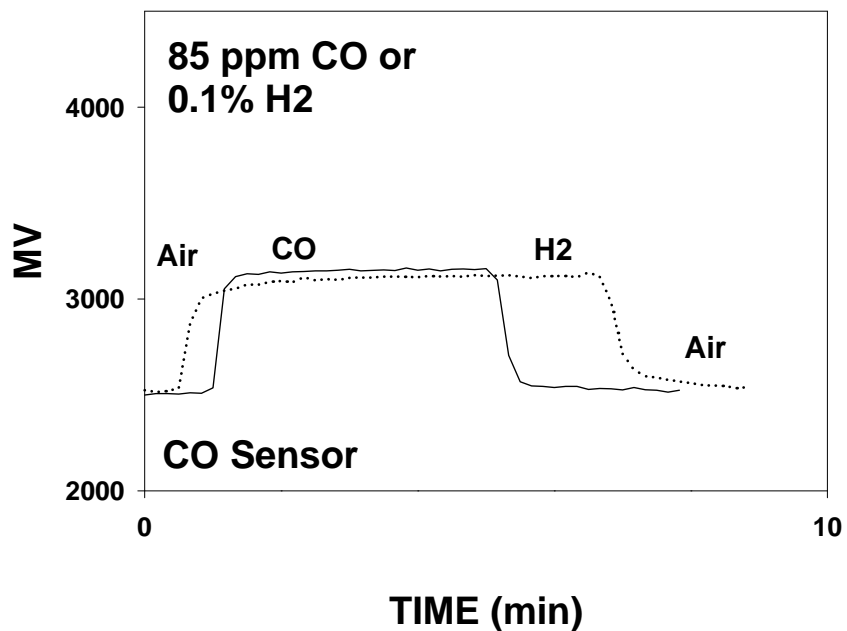
FIGURE 29C. Sensor cross sensitivities to other gases: HCl test gas vs. HCN sensor.

With mV plotted for TWO repeat tests on different days



**FIGURE 30A. Sensor cross sensitivities to H₂:
H₂ and CO test gases vs. CO and H₂S sensors, ST-1.**

With mV plotted for ONE test at 1 ATA



**FIGURE 30B. Sensor cross sensitivities to H₂:
H₂ and CO test gases vs. CO and H₂S sensors, ST-2.**

With mV plotted for ONE test at 1 ATA

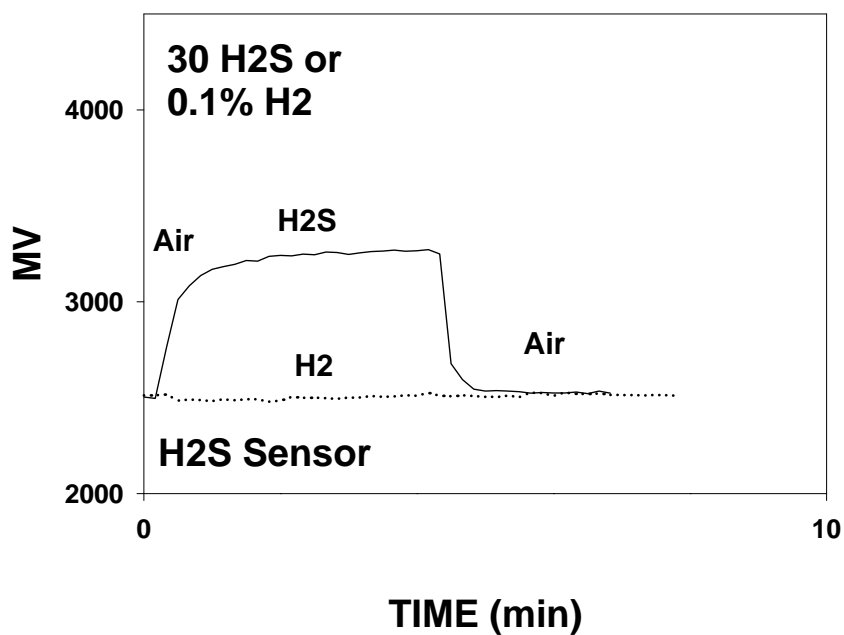
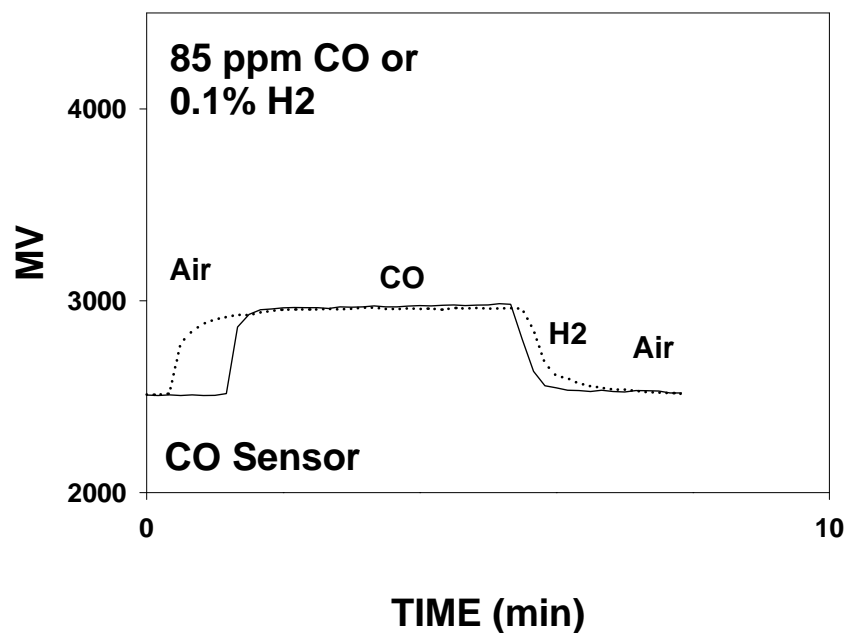


FIGURE 30C. Sensor cross sensitivities to H₂: H₂ test gas vs. SO₂ and NO₂/Cl₂ sensors.

With mV plotted for ONE test at 1 ATA,
CO sensor plotted for reference

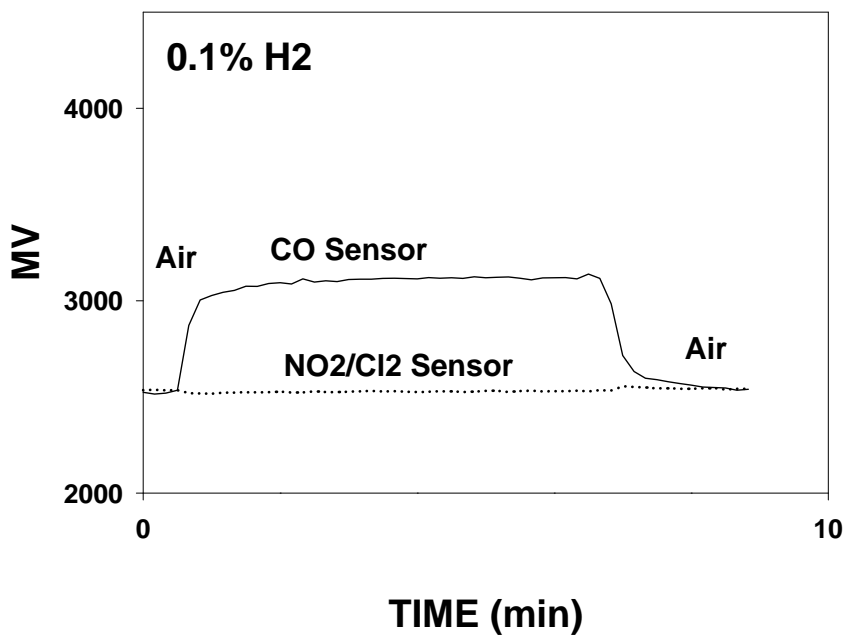
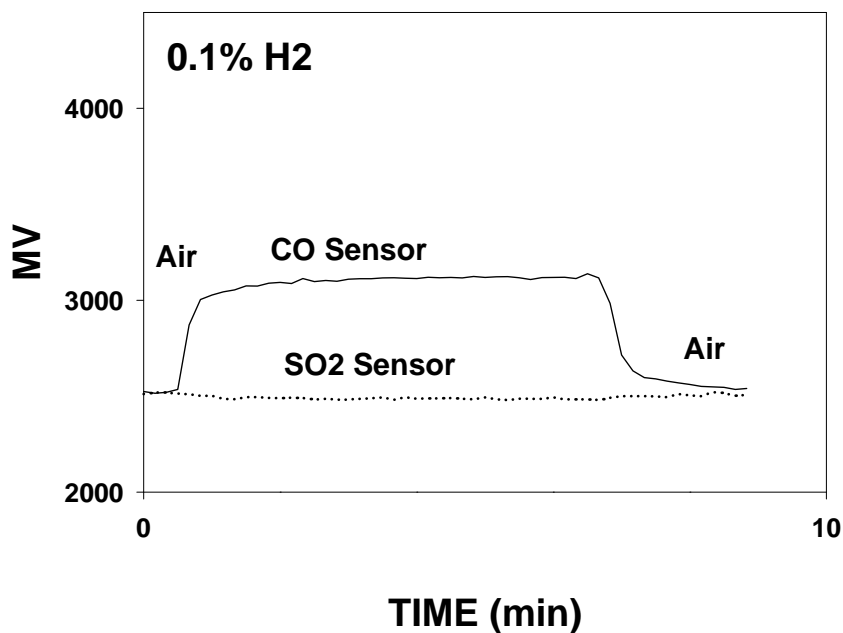


FIGURE 30D. Sensor cross sensitivities to H₂: H₂ test gas vs. HCN and HCl sensors.

With mV plotted for ONE test at 1 ATA,
CO sensor plotted for reference

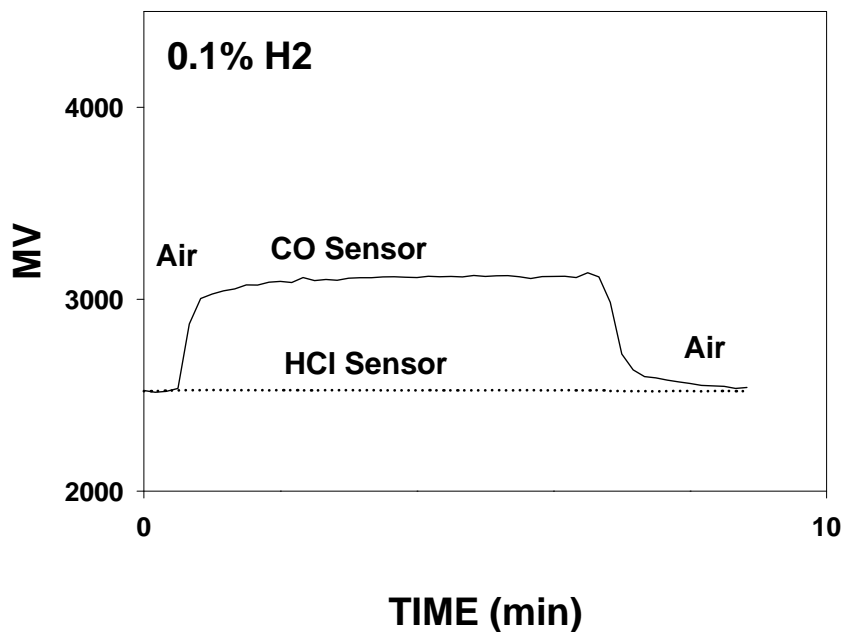
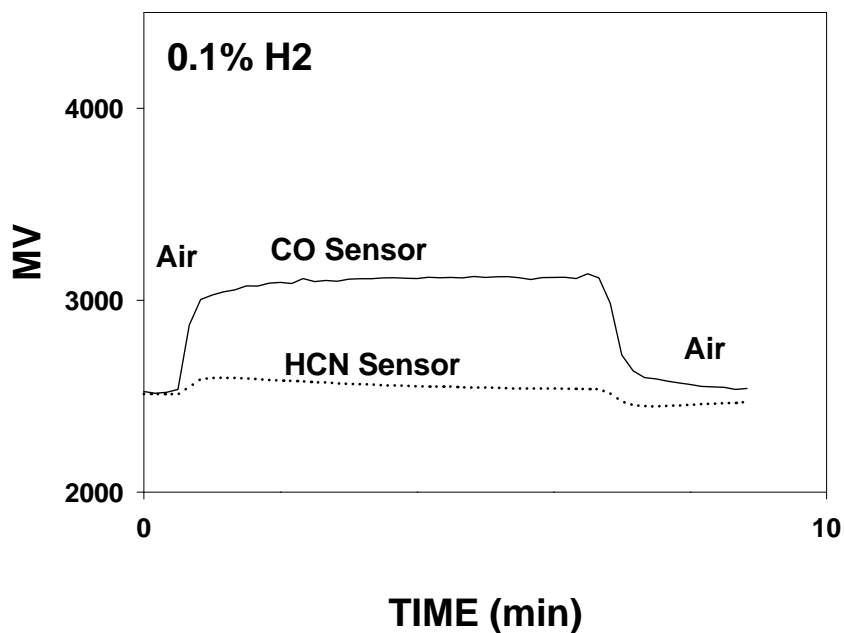
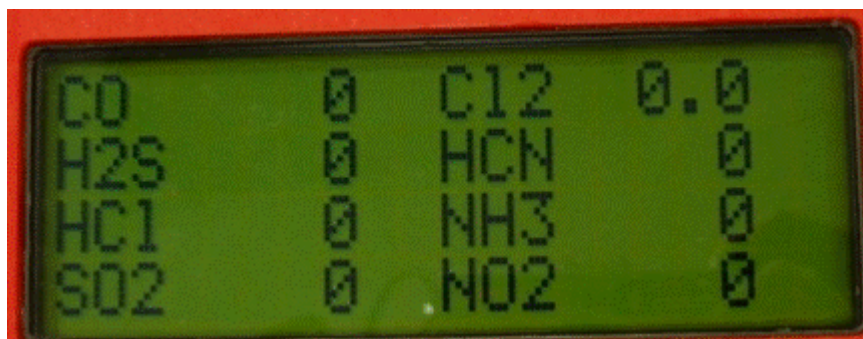


FIGURE 31A. SubTox main display screens.



A green monochrome LCD screen with a black border. It displays gas concentration readings in a two-column format. The left column lists CO, H2S, HCl, and SO2. The right column lists C12, HCN, NH3, and NO2. Each reading is followed by a numerical value, mostly zeros or 0.0.

Gas	Value	Gas	Value
CO	0	C12	0.0
H2S	0	HCN	0
HCl	0	NH3	0
SO2	0	NO2	0



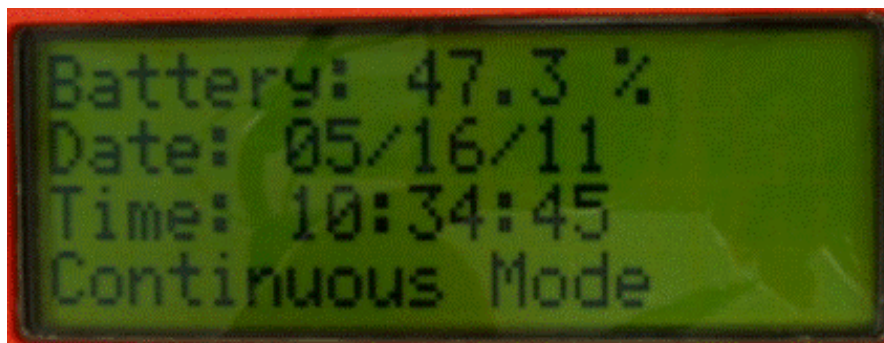
A green monochrome LCD screen with a black border. It displays various sensor readings in a two-column format. The left column lists FLO, PRS, TMP, and VBT. The right column lists H2. Numerical values are shown next to each reading.

Parameter	Value	Parameter	Value
FLO	0.5	H2	0
PRS	1.0		
TMP	68		
VBT	7.3		



A green monochrome LCD screen with a black border. It displays gas concentration readings in a two-column format, similar to the first screen. The left column lists CO, H2S, HCl, and SO2. The right column lists S C12, E HCN, U NH3, and NO2. Numerical values are shown next to each reading.

Gas	Value	Gas	Value
CO	0	S C12	0.0
H2S	0	E HCN	0
HCl	0	U NH3	0
SO2	0	NO2	0



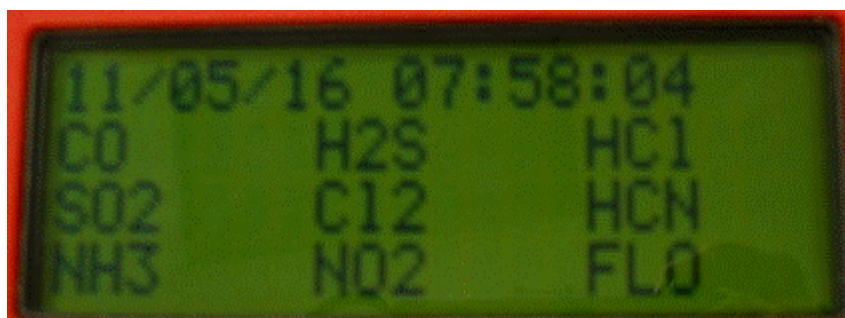
A green monochrome LCD screen with a black border. It displays system status information in a single column. The text includes battery percentage, date, time, and mode.

Battery: 47.3 %
Date: 05/16/11
Time: 10:34:45
Continuous Mode

FIGURE 31B. SubTox data logger screens.



ENTER LOGGER MENU
Menu = Exit
Select = Enter

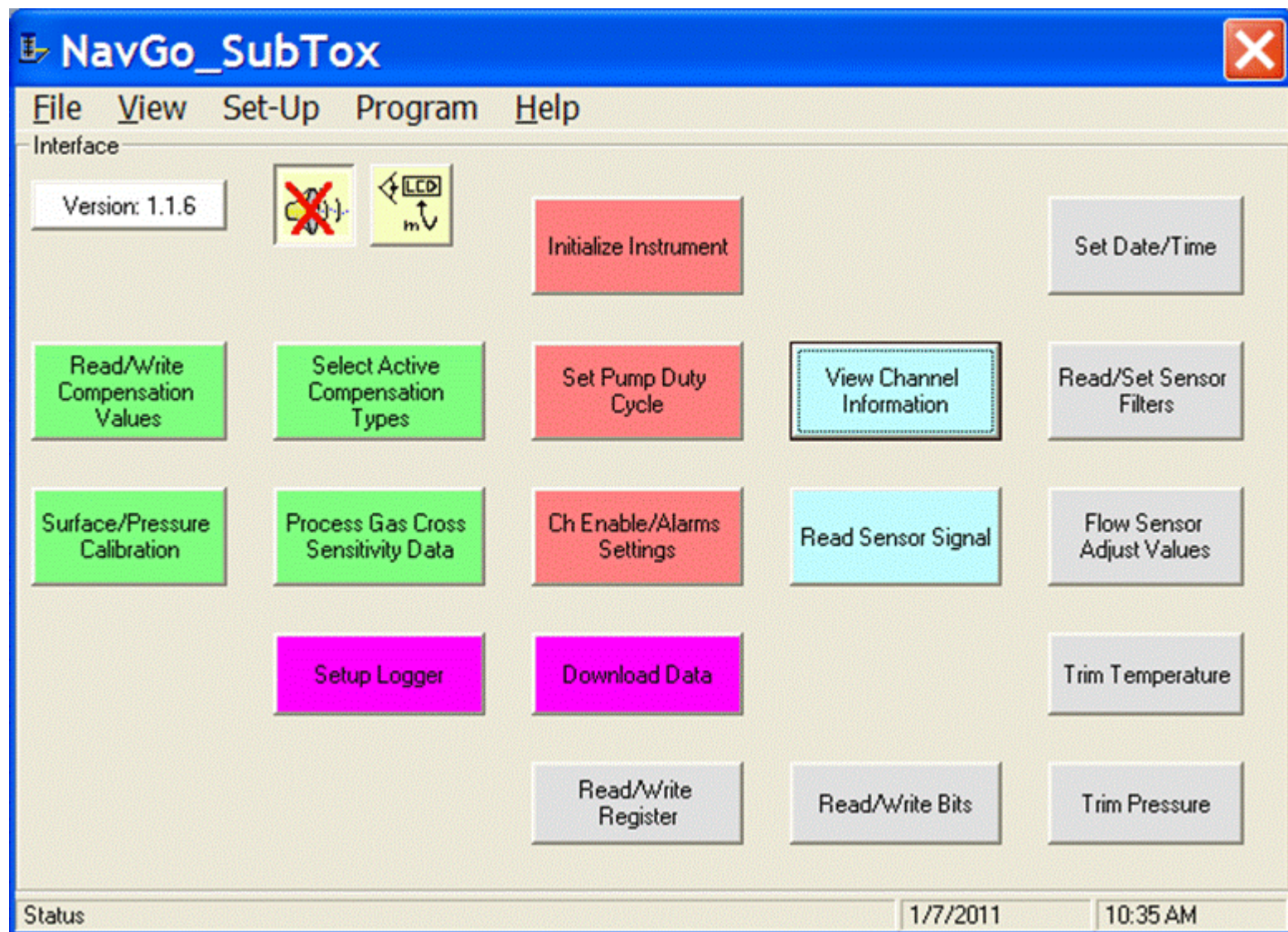


11/05/16 07:58:04
CO H2S HCl
SO2 Cl2 HCN
NH3 NO2 FLO



11/05/16 07:58:04
0 0 0
0 0.0 0
0 0 0.5

FIGURE 31C. SubTox VB's main menu, as viewed on computer screen.



APPENDIX A — OPERATING PROCEDURES FOR THE FINAL-VERSION SUBTOX PROTOTYPE

BACKGROUND

This Appendix provides limited information for operating the final-version SubTox prototype (the final version as of September 2012, with SubTox software version 1.2.2) and for using the monitor to screen the atmosphere for the eight SEAL gases and H₂. However, we caution that the SubTox, as well as these procedures for using it, *have not been officially approved by the U.S. Navy*.

Our description of procedures here primarily addresses how to operate the SubTox in stepping through the display screens (discussed below) and in viewing gas readings as well as other variables. We emphasize that many display screens, accessed through the “Maintenance Menu” by using passcodes, are used to adjust various operating settings for SubTox and to perform other functions.

In the recommended **Procedures** subsection below, we discuss the two passcode-protected screens (“Set Duty Cycle” and “Set Date/Time”) that may be initially needed to operate SubTox. Although some of the other passcode-protected functions may prove useful in the field, we expect that most of those functions will be performed in any first-production SubTox using the VB software that NEDU and ENMET developed to assist in their evaluation of the monitor.

We also expect that SubTox’s recalibration will be not done in the field; rather, recalibration and periodic servicing will most likely be performed at a shore-based facility, presumably by Navy personnel who have been trained and certified by ENMET.

Lastly, we assume that the SubTox will be operated with the sampling pump always ON, although both the monitor and the VB software allow other options to be selected.

FEATURES

1. Monitor the eight SEAL gases — NH₃, CO, Cl₂, HCl, HCN, H₂S, NO₂, and SO₂ — as well as H₂, with all gas readings updated several times a second.
2. Measure gas concentration ranges from 0 to 2 times SEAL2 levels for the eight SEAL gases, and 0 to 1% for hydrogen.
3. Use six D-cell alkaline batteries, with an expected battery life of >3 days of continuous operation with the gas sampling pump on, as the electrical power source.
4. Operate under the following conditions:

Pressure: up to 5 ATA.

Temperature: 0 to 50 °C (32 to 122 °F).

Relative humidity: dry to 99% (noncondensing).

5. Consist of a waterproof gas sampling inlet, mass flow and pressure sensors, a data logger, an LCD display with adjustable backlighting, a computer interface, and a brushless sample pump (with an adjustable duty cycle).

6. Display, via the LCD:

Uncorrected and SEV values of all SEAL gases.

Sample pump flow, pressure (ATA), inlet temperature, battery voltage, and H₂ levels.

Status screen: battery life, date, time, and pump mode.

Information screen.

Logger menu.

7. Incorporate software with passcode protections and compensation of gas readings for ambient pressures, ambient temperatures, and cross sensitivities among gases.

8. Provide both visual (via LED, and blinking display on LCD) and auditory (with a mute function) alarms — with optional “nonlatching” and “latching” modes.

9. Allow users to review logged data by scrolling down the display screen to view past gas readings.

10. Allow users to display maximum gas readings logged during previous time periods via its peak display function.

11. Provide additional passcode-protected functions.

OPERATION

Description

1. The small internal pump draws a gas sample into the monitor, where separate electrochemical sensors measure the concentrations of the eight SEAL gases and H₂.

2. Gas leaving the sensor manifold is routed into the interior of the SubTox case. A small vented fitting, located in the wall of the monitor and equipped with a hydrophobic filter, ensures equilibration between the SubTox's internal and external ambient pressures.

3. Powered by six D-cell alkaline batteries providing more than three days of continuous operation per set of batteries, the SubTox's LCD displays warnings — and its LED flashes — when those batteries are running low and need to be replaced. Upon startup, the monitor displays the batteries' power status (in terms of percentage

remaining, which is only a rough estimate) on its initial screen — and on the “Status” screen (Screen 6, discussed below) that the user can select.

4. The SubTox’s data logging function allows the user to define intervals (in seconds) at which readings are recorded. After data have been logged, the SubTox’s supplied lead can be connected to the serial port of a personal computer so that the VB software can then download this data. After the user has entered the Logger Menu (Screen 8, discussed below), data can also be viewed on the LCD.

5. The audio and visual alarms can be set to trigger at specific concentration levels of the individual gases. The audio alarm can also be muted by touching the “Mute” button on the front of the SubTox. An alarm latching function causes these alarms, once triggered, to stay on even when the gas concentrations have eventually become acceptable. But when this latching function is turned off, the alarms stop as soon as the gas concentrations have become acceptable.

6. The following switches and displays, relevant to operating the SubTox, are located on the front of its case:

- a. **LCD** display.
- b. **Alarm** LED light (for various alarm conditions), on the lower left.
- c. **Power** button, to turn the SubTox on and off, on the lower left — below the LED.
- d. **Menu** button on the lower right, to allow the user to advance to the next display screen — and to enter the Maintenance Menu, where passcode-protected functions are accessible.
- e. **Select** button on the lower right (below the Menu button), to select items on the passcode-protected and other menus.
- f. **Mute** “button” (actually, an opening in the audio alarm) to the left of the Menu and Select buttons, to mute the audio alarm.

7. After the SubTox has been turned on and allowed to warm up for one minute, the user can step through the series of display screens (in the following order of appearance) by repeatedly pushing the **Menu** button:

Screen 1: the eight SEAL gases and their concentrations in ppm.

Screen 2: readings for sample gas flow (L/min), ambient pressure (ATA), gas sample temperature (°F), battery voltage (VDC), and H₂ concentration (ppm).

Screen 3: the eight SEAL gases, their concentrations in ppm surface equivalent value (ppm SEV), with ppm SEV calculated by multiplying those concentrations in Screen 1 by the ambient pressure.

Screen 4: mV readings (which can be disabled) for laboratory and diagnostic uses, from the eight gas sensors (per Screen 1).

Screen 5: sensor mV readings (which can be disabled) for laboratory and diagnostic uses, for sample gas flow, ambient pressure, gas sample temperature, battery voltage, and H₂ concentration (all from Screen 2).

Screen 6: Status Screen showing battery power percentage remaining, date, time, and pump mode (continuous or duty cycle).

Screen 7: "Information Screen" to inform users of particular issues (only one message is currently available on this screen).

Screen 8: "Enter Logger Menu" to access functions to (1) set logging intervals, (2) reset the logger, (3) show the maximum value logged during a previous time period for each of the eight SEAL gases, along with the date and time when the maximum value occurred, (4) view all logged records on the LCD, with an ability to "jump" quickly through these records, and (5) print logged data (although this print function has not been tested).

8. Maintenance Menu functions can be accessed by holding down the **Menu** button for several seconds, until the "Maintenance Menu" prompt appears. To continue, the user can then press the **Select** button and enter the passcode _1270 (the **Menu** button is used to adjust each digit, with each adjustment then followed by pressing the **Select** button to confirm it). The following functions are available under the Maintenance Menu:

- Calibration: Zero All
- Calibration: Span
- View Sensor Range
- Set Alarm1
- Audible Alarm Option: Enable, or Disable
- Set New Password
- Set Duty Cycle: Continuous, or Timed
- Backlight Settings
- Enable mV Display
- Unlatch Alarms
- Set Date/Time
- Exit

Two of these functions, "Set Duty Cycle" and "Set Date/Time," are discussed below under **Procedures**; the other passcode-protected functions will not be discussed in detail.

Procedures

Although the air monitor has a data logging capability that was used extensively during its laboratory testing and evaluation, procedures for logging data are not addressed in this subsection. Personnel operating the SubTox are responsible for producing a data sheet that is appropriate for their use.

1. Whenever possible, SubTox monitors should be stored indoors at “normal room temperatures” (those ranging between 19 and 25 °C [66–77 °F]), where they can be thus protected from inclement weather. SubTox can be stored with batteries in place, since little, if any, current draw results when SubTox is OFF.
2. The acceptable range in ambient temperatures for operating the air monitor is from 0 to 50 °C (32 to 122 °F). However, if the SubTox is moved to a significantly warmer or colder area, we recommend *waiting at least two hours* for the monitor to equilibrate with the ambient temperature before it is turned on and restarted.
3. After any temperature equilibration time has passed, install batteries (if such installation is needed), push the **Power** button to start the monitor, and observe the initial startup screen that displays (for ~3 sec) the software revision, the SubTox serial number, and the remaining battery percentage.
4. After the one-minute warm-up period, push the **Menu** button five times to advance to the Status Screen and read the battery percentage. If the batteries’ power capacity is <40%, push the **Power** button to turn off SubTox and replace the batteries. Restart the monitor and confirm that the replacement batteries’ capacity is ~100%.
5. Then confirm on the Status Screen that the date and time are correct, and that the pump is in the “Continuous Mode.” If any of these settings need to be changed, hold down the **Menu** button several seconds, until the “Maintenance Menu” prompt appears. Then press the **Select** button to continue, and enter the passcode _1270 (the **Menu** button is used to adjust each digit, with each adjustment then followed by pressing the **Select** button to confirm it) to enter the Maintenance Menu.
6. Once in the Maintenance Menu, repeatedly press the **Menu** button until the “Set Duty Cycle” screen appears, and then (if needed) press the **Select** button to enter the Menu and set the pump to “Continuous.” Then advance the LCD to the “Set Date/Time” screen, where the corrected information (if needed) can be entered, adjusted, and selected. Once all these changes have been made, exit the Maintenance Menu and confirm them on the Status Screen.
7. Advance to Screen 2, displaying flow and pressure, and confirm that the flow is ~0.5 L/min (0.4 to 0.6 L/min) and that the pressure is ~1 ATA. Flow and pressure readings much different from these may suggest that the SubTox has problems that need to be fixed.

8. Ensure that the SubTox is given *at least 30 min to warm up*.
9. Following warm-up, the SubTox can be moved about to sample the ambient air. But to avoid contaminating the air that the pump draws into the monitor, avoid breathing near the monitor's inlet. Leave the monitor ON as it is moved from location to location during the testing.
10. To produce reliable gas readings as the monitor is moved from one location to the next, wait at each sampling location to *allow the readings to stabilize for at least 10 min*. Such stabilized readings are best achieved by setting the monitor down at each location where the atmosphere is to be monitored and, while waiting for equilibration, observing the gas readings at a distance: This procedure prevents the user's breathing from influencing the monitor's readings.
11. Continue to monitor the atmosphere and, on the data sheet, **record** all needed gas readings, locations, and times — as well as any procedures performed during the testing. Also **record** any information relevant to the test: e.g., triggered alarms (SubTox or others in the area), problems such as instrument malfunctions, or the presence of any objectionable odor in the sampled gas.
12. At the end of testing, **record** the battery power percentage, flow, and pressure.
13. Turn OFF the SubTox with the **Power** button, and store it.